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Material & Energy Recovery and Sustainable Development
ECOMONDO 2014

"Gheorghe Asachi" Technical University of Iasi

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Editorial

Special issue selected papers

ICEEM 08

www.iceem.eu

9 - 12 September 2015
Iasi, Romania

Location

The ICEEM 08 Conference will be hosted by the "Gheorghe Asachi" Technical University of Iasi

Abstract Submission

The **extended abstract submission** should be done **no later than March 30, 2015,** via www.iceem.eu. After the review process, the accepted abstracts (2 pages) will be published electronically in a Book of Abstracts.

The 2nd Conference Call and decisions on **abstract acceptance will be available after May 1st 2015.**

Selected papers by the International Scientific Committee will be published in special issues of the journals:

- **Process Safety and Environmental Protection**

(ISI impact factor: 1.829) will publish papers with the topics:

  - *Environmental pollution and monitoring*
  - *Water and wastewater treatment and management*
  - *Air pollution, prevention and treatment*
  - *Waste management for resources and energy recovery*

- **Environmental Engineering and Management Journal**

(ISI impact factor 1.258) will publish papers with the topics:

  - *Sustainable production and consumption*
  - *Environmental management and sustainability assessments*
  - *Environmental education*

- **New Biotechnology** (ISI impact factor 2.106) will publish papers in :
  - *Environmental biotechnology*

The Conference language is English.

Fees

The fees for the ICEEM 08 Conference will include the conference materials (Program, Abstracts book), coffee breaks, lunches and conference dinner.

- Full fee: **300 EUR**,
- M.Sc. and PhD students fee: **150 EUR**. More details on www.iceem.eu

Contacts

For details please visit the conference site: www.iceem.eu, or contact the Conference Organizing Committee: iceem08@gmail.com

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The "Gheorghe Asachi" Technical University of Iasi
Faculty of Chemical Engineering and Environmental Protection
Department of Environmental Engineering and Management

8th INTERNATIONAL CONFERENCE ON ENVIRONMENTAL ENGINEERING AND MANAGEMENT

1st Call for Papers

ICEEM / 08

9 - 12 September 2015
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ICEEM 08

9 - 12 September 2015
Iasi, Romania

www.iceem.eu

ICEEM / 08

Foreword

After two editions abroad, in Hungary and Austria, the 8th edition of ICEEM will be organized in Iasi, Romania between 9 and 12 September 2015 by the "Gheorghe Asachi" Technical University of Iasi.

This ICEEM edition aims to bring together international researchers, academics, professionals and students activating in the fields of environmental engineering and management and to support knowledge exchange and dissemination of specific research and educational programmes.

Like before, ICEEM 08 strongly encourages contributions that focus on innovation, multidisciplinarity and cross-sectorial approaches related to environmental issues and sustainability.

Furthermore, the ICEEM conference welcomes contributions of young and senior scientists, and at the same time it encourages practitioners and specialists in various environmental fields to add a more practical-oriented approach to the conference sessions.

We hope that the plenary sessions, oral and poster presentations, workshops and side-events of ICEEM 08 will enhance multidisciplinarity, international cooperation and effective communication of scientists, engineers and managers.

Conference chairperson

Prof.dr.,dr.h.c. Carmen Teodosiu
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Topics

I. Environmental pollution and monitoring
II. Water & wastewater treatment and management
III. Air pollution, prevention and treatment
IV. Environmental biotechnology
V. Environmental management and sustainability assessments
VI. Sustainable production & consumption
VII. Waste management for resources and energy recovery
VIII. Environmental education, Workshops and Exhibitions

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Key note lectures
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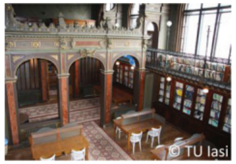
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EDITORIAL

Material & Energy Recovery and Sustainable Development ECOMONDO 2014

18th International Trade Fair of Material & Energy Recovery and Sustainable Development

The contributions in the form of Full papers collected in this Special Supplement of *Environmental Engineering and Management Journal* were selected from lectures and posters of the scientific and technical conferences hosted by *Ecomondo 2014* held in Rimini, Italy, 5–8 November, 2014 (http://en.ecomondo.com).

Ecomondo is the most recognized platform for the Mediterranean basin, in terms of materials exploitation and recycling for the large industry of the future, which will be part of *Green Economy*, ensuring a weighted and rewarding balance between sales dimension and technical-scientific dimension, with extensive room dedicated to innovation.

As with the previous editions, the aim of Ecomondo 2014 was to explore recent industrial advances and opportunities in waste production reduction, waste collection, fractionation, recycling, exploitation; biomass and biowaste exploitation via integrated biorefinery scheme, bioplastics, biobased products and biomethane; green and sustainable chemistry; water resources monitoring and protection; wastewater treatment and valorization with nutrients recovery and marine resources protection; sustainable remediation of contaminated sites and marine ecosystems; and indoor and outdoor air monitoring and clean up.

A special emphasis was given to European Eco Innovation in the broad field of green economy. Horizon2020 priorities and relevant innovation funding opportunities have been presented by delegates of the EU commission. Other initiatives were dedicated to the promotion of industrial symbiosis and networking i.e. the creation of partnerships between industries working in the complementary sectors or different countries and to the presentation of the most prominent international and EU RTD and industrial projects.

The areas of particular interest addressed within *Ecomondo 2014* are:

- waste characterization, management, recycling and exploitation (*Waste)*,
- monitoring, management and treatment/ exploitation of industrial and civil wastewaters *(blue gold)*
- the sustainable and biomass-based chemical industry, with a special focus on the Join Technology Initiative Bio Based Industry (JTI BBI) and biomethane production (*Biobased Industry*)
- the monitoring and clean-up of contaminated sites, soils and sediments (*Reclaim Expo*)
- monitoring and treatment of air pollution (*Air*)
- smart cities and communities (*Sustainable City*)

Ecomondo 2014 hosted over than 100 conferences, more than 500 oral communications and over than 150 papers. This special issue provides some of the key information presented and discussed in the frame of some of such conferences. Over 100,000 delegates from 80 different nations were participating in the event.

We believe that this collection of papers will be useful to people who could not able to participate directly. It is primarily towards those individuals that it is directed, but it also aspires to provide permanent records in process of turning environmental problems and challenges into new opportunities for a green economy with a bright future.

Guest editors:

Prof. Fabio Fava
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Dr. Grazia Totaro
Alma Mater Studiorum - Università di Bologna
(University of Bologna), Bologna, Italy
Prof. Maria Gavrilescu
„Gheorghe Asachi" Technical University of Iasi, Romania

Fabio Fava, born in 1963, is Full Professor of "Industrial & Environmental Biotechnology" at the School of Engineering of University of Bologna since 2005.

Dr. Fava is the coordinator of the FP7 projects NAMASTE (on the integrated exploitation of citrus and cereal processing by-products with the production of ingredients and new food products) and BIOCLEAN (aiming at developing biotechnological processes and strategies for the bioremediation and the tailored depolymerization of major oil-deriving plastics). He also coordinates the Unit of the University of Bologna participating in the FP7 projects ECOBIOCAP and ROUTES (on the production of microbial polymers from different organic waste and food processing effluents), MINOTAURUS and WATER4CROPS (on the intensified bioremediation of contaminated waste- and ground-water and the integrated decontamination and valorization of wastewater of the food processing industry and of biorefineries), and ULIXES and KILL-SPILL (on the development of strategies for intensifying the in situ bioremediation of marine sediments polluted by (chlorinated)hydrocarbons and for the isolation and industrial exploitation of microbes from those matrices). He is vice-chairman of the "Environmental Biotechnology" section of the European Federation of Biotechnology (EFB). He is member of the "Task Force on Industrial Biotechnology" of the Working Party on Biotechnology of the Organisation for Economic Co-operation and Development (OECD, Paris). Further, he is joining the "High Level Group on Key Enabling Technologies" and the "Expert Group on biobased products" of the DG-GROW of European Commission (Brussels), as well as the "Expert Group on eco-industries" of the JRC Directorate at the European Commission. Finally, he is the Italian Representative for Bioeconomy in the Horizon2020 Programme Committees (DG RTD, EU commission).

Grazia Totaro, born in 1976, has a degree in Chemistry (University of Ferrara), a Master's Degree in Science, Technology & Management with a specialization in Environmental Chemistry (University of Ferrara) and a PhD in Materials Engineering, about modification, characterization and applications of technopolymers (University of Bologna).

She worked at the R&D Centre of Basell Polyolefins in Ferrara for 2 years in the frame of a project addressed to the development of a novel methodology for qualitative and quantitative analysis of additives in polymers. She also worked at ARPA, Regional Agency for Environment in Ferrara, division Water Analysis. Then she started working at the school of Engineering of the University of Bologna for a Ph.D. in Materials Engineering (2007-2010). After that she had a scholarship "Spinner 2013" in cooperation with Reagens spa (San Giorgio di Piano) on novel PVC nanocomposites. Now she is post doc fellow at the same school on new polymer-based nanocomposites from renewable sources and inorganic fillers. She also worked at the laboratoire de Chimie et Biochimie Pharmacologique et Toxicologique (Université Réné Descartes) in Paris in 2001 and was visiting professor at the Ecole Nationale Superieure de Chimie (Université Blaise Pascal, Clermont Ferrand, FR) in 2012.

Dr. Totaro has about 13 scientific papers and several participations at conferences and scientific schools.

Maria Gavrilescu (born in 1956) is professor at the Department of Environmental Engineering and Management–Faculty of Chemical Engineering and Environmental Protection of the „*Gheorghe Asachi*" Technical University of Iasi, Romania, where she teaches courses in Chemical and Biological Process Engineering, Process Synthesis and Analysis, Integrated Pollution Prevention and Control, Sustainable Industrial Production, Environmental Risk Assessment and Management. She supervises doctoral programs in the fields of Chemical and Environmental Engineering. Prof. Gavrilescu has authored more than 350 books and articles in the fields of chemical and environmental engineering, pharmaceutical and environmental biotechnology, pollution prevention and cleaner production, and risk assessment and management. Prof. Gavrilescu has also managed or participated in 18 national and 7 international research projects and 25 research projects with industrial companies. The scientific visibility is illustrated by over 2000 citations (WOS h-index 22, Scopus h-index 22).

The professional memberships includes the followings: 2012-Founder of the *Romanian Society of Environmental Science and Engineering*; Member of: the Editorial Advisory Board of six international journals; Romanian Society of Chemistry; European Federation of Biotechnology-*member of Experts Board* of the Environmental Biotechnology Section.

Prof. Gavrilescu is the Editor-in-Chief of the *Environmental Engineering and Management Journal* edited by the *Gheorghe Asachi* Technical University of Iasi, Romania; Editor-in-Chief of *Procedia-Environmental Science, Engineering and Management,* edited by the *National Society of Environmental Science and Engineering,* Romania; Series Editor of *Annals of the Academy of Romanian Scientists* – Series of *Chemistry Sciences*.

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RECOVERY OF SEWAGE SLUDGE ON AGRICULTURAL LAND IN LOMBARDY: CURRENT ISSUES AND REGULATORY SCENARIOS

Maria Cristina Collivignarelli[1], Alessandro Abbà[1*], Sergio Padovani[2], Maurizio Frascarolo[3], Dario Sciunnach[3], Maurizio Turconi[3], Marina Orlando[4]

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Abstract

Issues concerning the treatment and the recovery/disposal of sludge derived from the municipal WWTPs (Wastewater Treatment Plants) are gaining importance both in Italy and abroad. In Lombardy Region this aspect is particularly relevant due to both the amount of sludge produced and its remarkable reuse in agricultural soils. This paper discusses different strategies for land application of sludge in order to provide technical and regulatory guidance at regional level. The work is based on a survey concerning qualitative and quantitative characteristics of sewage sludge (derived from WWTPs and sent to Sludge Treatment Plants – STPs – authorized for the treatment on behalf of third parties) reused for agricultural application. Then, the effects of six different regulatory scenarios (considering the rules of the European Commission, national legislation and the laws of regions neighbouring to Lombardy) on the qualitative characteristics of sludge reused in agricultural soils have been evaluated. The results of this work have been incorporated into regional guidelines that were approved with Decree of Regional Government (DGR) n. X/2031 dated 1 July 2014. On the basis of this work, the principles of the regional guidelines are: 1) improvement in the quality of the sludge spread on agricultural land; 2) protection of the high-quality sludge (ingoing to the STPs), avoiding its mixing with other sludge suitable for agricultural reuse, but with qualitative characteristics closer to the regulatory limits; 3) minimization of the problems concerning the odour emissions (one of the main critical issue).

Key words: agricultural use, heavy metals, Regional Guidelines, sewage sludge

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1. Introduction

In Europe, the yearly production of sewage sludge is estimated at 10.13 million tons of dry matter; about the 40% is reused in agricultural soils (European Commission, 2010). The situation varies a lot among Member States: in some countries such as Denmark, France, Ireland, Spain and United Kingdom, over 50% of the sludge produced is spread on agricultural land, while in Belgium, Romania, the Netherlands and Greece this percentage equals zero. The incineration is the main alternative for sludge management in the EU15 States (Member State that joined the EU before 2004), while in the remaining countries the landfill is still the main destination for these wastes. The choice of recovery/disposal routes is influenced by the costs of different options; at European level the reuse in agriculture is around an average value of 44€/$t_{wet\ sludge}$ (transport included), while landfilling and incineration costs (always considering the transport) are 88 and 91€/$t_{wet\ sludge}$ respectively (Foladori et al., 2010).

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The issue of sludge management should be solved with several actions in different directions: the basic principles of European legislation on waste (EC Directive, 2008) transposed in Italy (Italian Decree, 2006, and subsequent modifications) provide, on priority scale, interventions aimed at waste prevention (e.g. reducing production at source), recovery (of matter and energy) and safe disposal.

As concerns the *sludge prevention*, several innovative technologies are available (Fytili and Zabaniotou, 2008): some processes are already present in the market and many treatments are being tested (Chu et al., 2009; Feng et al., 2009; Liu, 2003; Montusiewicz et al., 2010; Saby et al., 2003; Song and Hu, 2006; Tokumura et al., 2009; Wan et al., 2014; Zábranská et al., 2006). In particular, the minimization technologies applied on the sludge line of Wastewater Treatment Plants (WWTPs) are promising and could be used due to the high level of reliability with respect to technologies applied in the water line of WWTPs. Moreover, the biological treatments with very low sludge production (e.g. thermophilic aerobic membrane reactor, anaerobic biological processes etc.) seem to be very interesting (Bertanza et al., 2010; Collivignarelli et al., 2014).

Regarding *matter recovery*, the sludge can be reused in agricultural soils both with preventive hygienization treatment (with the use of alkaline reagents) and after a composting process (Zaha et al., 2011). There are many actions, mainly proposed by Control Bodies and Standardization Organizations, aimed at assessing the effects of this practice and at “renewing” the existing legislation, to ensure that the sludge recovery can be carried out with minimal risks for human beings and the environment (Piccinini and Centemero, 2007).

In terms of *energy recovery*, the innovative technologies (gasification, pyrolysis etc.) with important industrial applications (Dominguez et al., 2006; Nipattummakul et al., 2010; Sanin et al., 2008) are added to the conventional processes of incineration and the use of dried sludge as an alternative fuel in industrial kilns (e.g. for cement production).

Finally, as far as *landfill disposal* is concerned, it will be foreseen only for residues derived from the treatment for sludge recovery.

The *agricultural reuse* of sludge (directly or after composting) is an efficient solution to the problem of landfill disposal and becomes more interesting in terms of agronomic and economic effectiveness. The use of good-quality sludge has positive effects such as the supply of partially stabilized organic matter and the addition of macro-nutrients present mainly in organic form (and therefore with a slow release). However, the sludge contains heavy metals and poorly biodegradable trace organic compounds (Manea et al., 2013; Suciu et al., 2014) that can accumulate in the soils, even if some of them (such as copper and zinc), in small doses, could improve the biological cycle of the crops.

The spreading of sludge in agricultural soils has to be carried out in compliance with the legislation: (Directive 86/278/CEE at European level, transposed in Italy with Legislative Decree 99/92) in order to avoid any risk for the environment and the health of the population (EC Directive, 1986; Italian Decree, 1992). Many experiments carried out in Italy by Control Bodies have shown, after several years of sewage sludge application on agricultural soils with different crops (especially rice), an excellent nutrient effect (Gaskin et al., 2012; Najafi and Abbasi, 2013; Romani et al., 2013); nitrogen is also available throughout the crop cycle. The contribution of sewage sludge on agricultural land reduced the effect of organic matter loss in the soil (Mantovi et al., 2005), that, especially in southern Europe, is becoming a problem (Rusco et al., 2001), with the consequent increase in soil fertility.

In 2010, the sludge production in Italy was equal to 1.1 million tons of dry matter; the percentage of the sludge reused for agricultural applications has reached about 30% of total production (data reported in “Sewage sludge production and disposal from urban wastewater (in dry substance (d.s.))” Eurostat table – (Eurostat, 2015).

At regional level, the situation varies considerably: there are some regions, such as Liguria, Valle d'Aosta, Calabria and Marche, where the agricultural reuse of sludge is not implemented, while in other regions, such as Lombardy, Emilia Romagna, Puglia, Tuscany and Veneto where this practice is highly developed: these five regions spread in agricultural soils more than 90% of the total quantity reused in Italy for agricultural applications (ISPRA, 2013).

As concerns the Lombardy Region, the sludge produced was approximately equal to 800000 t/year “as it is”. About 50% derives from WWTPs that treat municipal wastewater, 30% from WWTPs for industrial wastewater treatment and 20% from WWTPs of industry (especially food companies). Fig. 1 shows that over 50% of sewage sludge produced in Lombardy was reused in agricultural soils (R10): overall, the amount of sludge spread in agricultural land in Lombardy, between 2007 and 2010, is equal to an average value of 700000 t/year “as it is”, corresponding to 116000 t/year of dry matter (about 330000 t/year “as it is” equal to 63000 t/year of dry matter in Pavia province). It is important to note that the plants on behalf of third parties (called Sludge Treatment Plants – STPs) located in Lombardy (that receive sludge from WWTPs for spreading in agricultural soils after suitable treatments), in addition to sewage sludge produced in the region, receive an additional quantity from other regions (mainly in the Po Valley); this value represents 50% of the total sludge for agricultural reuse in Lombardy.

As sludge is classified as a non-hazardous special waste, there is no legal ground to regulate such dynamics in the EU.

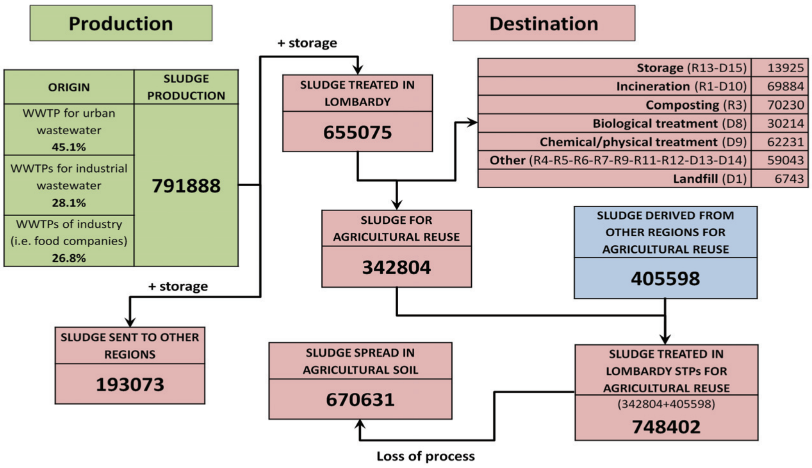


Fig. 1. Management of sewage sludge in Lombardy (2010) (all values are expressed in tons of raw sludge per year)

The Lombardy Regulation on the public utilities is the Regional Law 26/2003, that concerns the agricultural reuse of sewage sludge, has undergone two changes, through the Regional Laws 12/2007 and 7/2012. According to these regulations, the Regional Departments for the Environment, Territory and Agriculture began a process for the drafting of technical guidelines reported in DGR n. X/2031 (1 July 2014), replacing the previous DGR n. 7/15944/2003 (Lombardy Region, 2003; Lombardy Region, 2014).

The aim of the present work is to study the issues concerning agricultural reuse of sludge with the proposal of different intervention strategies. First, the qualitative and quantitative characteristics of sewage sludge reused in the Lombardy agricultural soils were analyzed (in particular, the concentrations of pollutants were compared with the limit values provided in DGR n. 7/15944/2003, in force before the publication of DGR X/2031/2014) (Lombardy Region, 2003; Lombardy Region, 2014). This phase was aimed to identify the issues regarding the recovery of sludge on agricultural land in Lombardy. Then, in order to identify the correct environmental strategies, six different regulatory scenarios were studied: the scenario effects on the qualitative characteristics of sludge reused in agricultural soils has been evaluated; particular attention has been paid to the odour emissions.

This work has highlighted some critical aspects related to reuse of sewage sludge, especially in Lombardy; moreover, it has been used as support for the drafting of DGR n. X/2031 (1 July 2014) (Lombardy Region, 2014).

2. Case study

2.1. Data collection

In order to analyze the characteristics of sewage sludge reused in agricultural land, a survey was performed; this investigation was carried out involving nine STPs (located in Lombardy) authorized for the treatment of sludge derived from WWTPs (public and/or private). In particular, we have elaborated over 2000 chemical analyses (ingoing and outgoing from STPs) obtained from Lombardian plants operating on behalf of third parties; these data regards the last five years. The considered STPs have treated an amount of sludge up to over 80% of the total sludge spread on agricultural land in Lombardy: so, the elaborations carried out are certainly representative of the regional situation.

2.2. Criteria for data elaboration

The data obtained during the survey regard heavy metals (arsenic, cadmium, hexavalent chromium, total chromium, mercury, nickel, lead, copper and zinc), microbiological parameters (fecal coliforms, Salmonella and viable helminth ova) and agronomic characteristics of the sludge (organic carbon – C_{org}, Total Phosphorus – TP and Total Nitrogen – TN). For each parameter, we calculated the percentiles (10th, 25th, 50th, 75th, and 90th) and the mean; the standard deviation (σ) and the coefficient of variation (σ*) were also calculated in order to evaluate the scattering of the results.

The results (concerning the sludge ingoing and outgoing from STPs) were compared with the regulatory limits reported in DGR n. 7/15944/2003 (in force, in Lombardy, before the publication of DGR X/2031/2014), in order to show any excesses (Lombardy Region, 2003; Lombardy Region, 2014).

3. Results and discussion

3.1. Survey results

3.1.1. Heavy metals, agronomic and microbiological parameters

In Table 1 the characteristics of sewage sludge ingoing and outgoing from STPs are shown. In particular, the content of heavy metals, the values of agronomic and microbiological parameters are reported; for each parameter minimum, mean, maximum and coefficient of variation (σ*) are shown.

Heavy metal concentrations that concern the sludge ingoing and outgoing from STPs are reported in the box plots shown in Figs. 2 and 3. In particular, for each parameter, the gray box represents the concentrations between the 10th and 90th percentiles; the spacing between the different parts of the box indicates the degree of dispersion (scattering); the lower and upper values outside the box represent minimum and maximum concentrations respectively. Furthermore, for each parameter, the regulatory limit (according to DGR n. 7/15944/2003) is reported (Lombardy Region, 2003).

The sludge ingoing to STPs showed average qualitative characteristics (in terms of heavy metals content) suitable for spreading in agricultural soils; nevertheless, some samples present remarkable excesses over threshold limit for arsenic, nickel, zinc and total chromium (as defined by Lombardy DGR n. 7/15944/2003). Furthermore, the STPs and their equipments do not allow the removal of heavy metals. The results of coefficients of variation (σ*) show that the variability of metal concentrations in the input sludge is very high; in the sludge reused in agricultural soils (outgoing from STPs) the scattering is generally reduced, in some cases significantly (Table 1).

The sludge derived from the WWTPs that treat municipal wastewater (classified with European Waste Code – EWC – 19 08 05) has concentrations of arsenic, nickel, mercury and cadmium significantly higher than other kinds of sludge (derived from biological treatment of industrial wastewater – EWC 19 08 12 – and from the treatment of textile industries, processing of paper and paperboard effluents).

As concerns the *agronomic parameters*, 5% of the samples ingoing to STPs do not meet the minimum content of organic carbon required by the regulation for reuse in agriculture. Moreover, the sludge outgoing from STPs shows concentrations of organic carbon and total nitrogen slightly lower than the sludge ingoing due to the effect of hygienization by means the use of alkaline reagents (Fig. 4). As regards the content of TP minor differences were observed between the ingoing and outgoing sludge treated by STPs.

As regards the *microbiological parameters* in the sludge ingoing to STPs the contents of Salmonella and especially of fecal coliforms usually exceed the regulatory limits; so the treatment of hygienization is needed.

The values obtained in the inactivation of microorganisms varied from 3 to 4 log for fecal coliforms and between 1.9 and 2.6 log for Salmonella.

Table 1. Characteristics of sludge ingoing and outgoing from STPs: results of survey (the bold values do not comply with DGR 7/15944/2003) (Lombardy Region, 2003)

	Parameter	*DGR* 7/15944/2003 limit values*	*Sludge ingoing to STPs*					*Sludge outgoing from STPs*				
HEAVY METALS			*Minimum [mg kg$_{ss}^{-1}$]*	*Mean [mg kg$_{ss}^{-1}$]*	*Maximum [mg kg$_{ss}^{-1}$]*	*σ**	*Number of exceeding/ number of analysis*	*Minimum [mg kg$_{ss}^{-1}$]*	*Mean [mg kg$_{ss}^{-1}$]*	*Maximum [mg kg$_{ss}^{-1}$]*	*σ**	*Number of exceeding/ number of analysis*
	As	10	0.01	5.9	**50**	2.7	166/1452	0.02	3.9	10	0.7	0/526
	Cd	20	0.01	1.2	17	1.4	0/1451	0.01	1.4	11	1	0/664
	Cr_{tot}	750	0.05	104	**1574**	1.3	7/1453	0.05	89	469	0.9	0/660
	Cr(VI)	10	0.01	0.3	5	1	0/612	0.01	0.5	5	1.2	0/564
	Hg	10	0.01	1.3	**14**	1.3	8/1096	0.01	1	10	1.3	0/663
	Ni	300	0.05	61	**1430**	1.5	33/1455	0.04	58	245	0.7	0/667
	Pb	750	0.05	78	**1163**	1.2	2/1454	0.10	62	432	0.9	0/668
	Cu	1000	2	317	**1350**	0.6	9/1456	1	282	908	0.7	0/668
	Zn	2500	5	757	**4718**	0.7	12/1459	19	675	2490	0.7	0/667
AGRONOMIC PARAMETERS	*Parameter*	*DGR* 7/15944/2003 limit values*	*Sludge ingoing to STPs*					*Sludge outgoing from STPs*				
			Minimum [%ss]	*Mean [%ss]*	*Maximum [%ss]*	*σ**	*Number of exceeding/ number of analysis*	*Minimum [%ss]*	*Mean [%ss]*	*Maximum [%ss]*	*σ**	*Number of exceeding/ number of analysis*
	C_{org}	20^	**2.2**	33	82	0.3	35/680	20	30	54	0.2	0/571
	TN	1.5^	**0.3**	5.2	45	0.5	6/684	**0.4**	4.4	30	0.6	3/571
	TP	0.4^	**0.01**	1.8	10	0.7	16/689	**0.3**	2.4	27	1.1	1/571
MICROBIOLOGICAL PARAMETERS	*Parameter*	*DGR* 7/15944/2003 limit values*	*Sludge ingoing to STPs*					*Sludge outgoing from STPs*				
			Minimum [MPN g$_{ss}^{-1}$]	*Mean [MPN g$_{ss}^{-1}$]*	*Maximum [MPN g$_{ss}^{-1}$]*	*σ**	*Number of exceeding/ number of analysis*	*Minimum [MPN g$_{ss}^{-1}$]*	*Mean [MPN g$_{ss}^{-1}$]*	*Maximum [MPN g$_{ss}^{-1}$]*	*σ**	*Number of exceeding/ number of analysis*
	Fecal coliforms	10000	0	**$4\cdot10^6$**	**$1500\cdot10^6$**	14.4	429/683	2	4200	**150000**	2	4/496
	Salmonella	100	0	**531**	**46000**	6.6	81/687	0	7	100	3.1	0/567

^ as lower limit; σ means "coefficient of variation"; "MPN" means "Most Probable Number"(DGR*: Lombardy Region, 2003)*

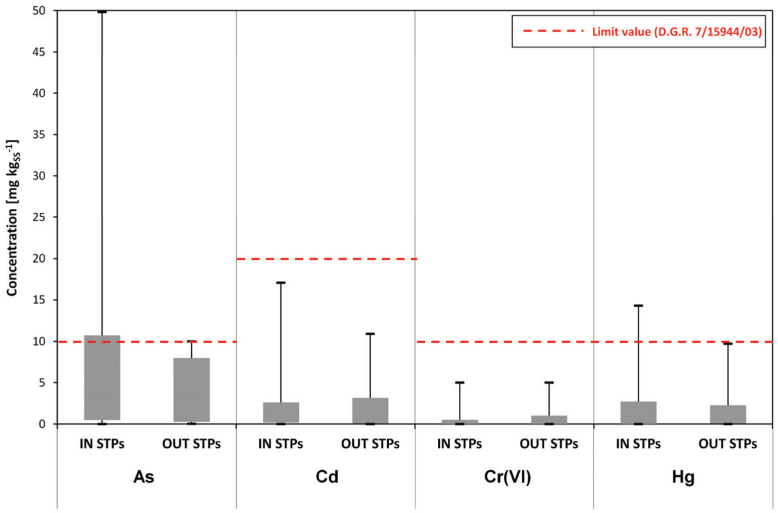


Fig. 2. Sludge ingoing (IN STPs) and outgoing (OUT STPs) from STPs: concentrations of As, Cd, Cr(VI), Hg

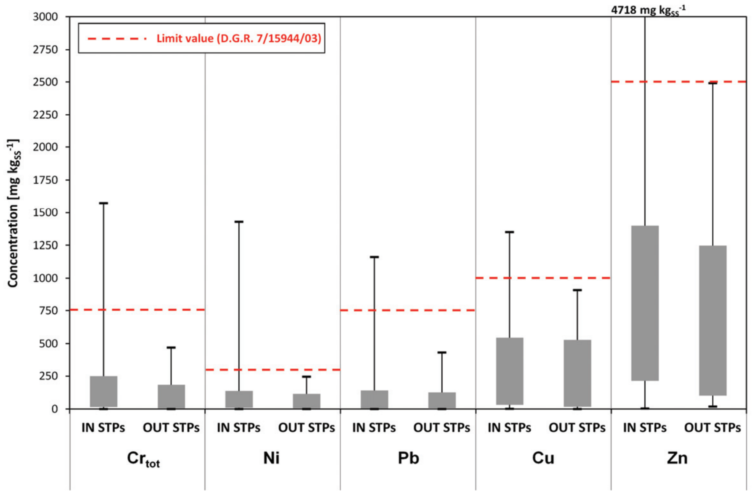


Fig. 3. Sludge ingoing (IN STPs) and outgoing (OUT STPs) from STPs: concentrations of Cr_{tot}, Ni, Pb, Cu, Zn

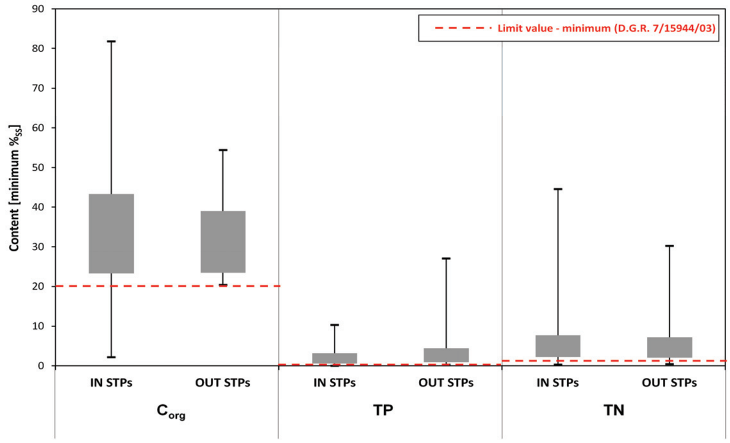


Fig. 4. Sludge ingoing (IN STPs) and outgoing (OUT STPs) from STPs: content of C_{org}, TP and TN

3.1.2. Sludge stabilization

In order to assess the *degree of sludge stabilization*, the percentage of volatile suspended solid (VSS) with respect to the total suspended solid (TSS) was calculated; this ratio (indicated by VSS/TSS) provides an evaluation of the sludge stabilization. The sludge is defined "stabilized" when it does not cause harmful effects on the environment due to biological transformation that occur in itself. The stabilization procedures commonly reduce putrescibility and odour, pathogenic microorganisms and VSS content.

In Fig. 5 the comparison between the VSS/TSS of sludge ingoing and outgoing from STPs is shown. It may be noted that the sludge ingoing to STPs is slightly stabilized (with a mean value of VSS/TSS equal to 68%); after the mixing/hygienization operation carried out into STPs, an average value of VSS/TSS equal to 58% is achieved. It is important to note that about 35% of sludge spread in agricultural soils has a ratio VSS/TSS higher than 60%.

As concerns the "weighted average" (calculated considering the amounts of sludge ingoing to STPs and their VSS/TSS values) a value of about 61% is obtained: in fact, the high quantities of sludge derived from medium-large size WWTPs are generally well-stabilized (low VSS/TSS), while the sludge with high values of VSS/TSS derives from small size WWTPs, that generally are equipped with sludge treatments (when present) poorly or not effective in terms of putrescibility reduction.

The control of this parameter is more important in order to reduce odour emissions: therefore, it is essential to provide stabilization treatments aimed at reducing the original characteristics of putrescibility and the odour issue. From technical point of view, several conventional and advanced treatments are available: they are based both on biological and chemical processes (Working Document on Sludge – 3rd Draft, 2000). In the biological stabilization processes, reduction of sludge putrescibility is achieved by means the removal of volatile solids; chemical stabilization, however, reduces the putrescibility through the inhibition of biological reactions by raising the pH up to 12 (for example with the use of lime). In this case, the effects of stabilization are temporary, because the carbonation of the lime by atmospheric CO_2 causes the progressive pH reduction, with a possible reactivation of the bacteria. In addition, the odours can be significantly reduced with appropriate management practices; for example, injection or incorporation of sewage sludge within 24 hours is recommended (Krogmann et al., 2001).

3.1.3. Critical issues obtained from survey

In summary, the results of the survey suggest the issues discussed below.

A. As concerns the sludge ingoing to STPs, acceptance criteria were not provided. Moreover, the equipments currently available in STPs are not able to remove heavy metals; in this case, the most critical pollutants are zinc and nickel.

B. The sludge ingoing to STPs has high variability in terms of qualitative characteristics. Moreover, an amount of high-quality sludge (especially in terms of low metal content) was sent to STPs. However, the mixing/hygienization operations carried out in STPs led to a "dilution" of high-quality sludge with the other sludge suitable for agricultural recovery, but with a worst quality.

C. The issue concerning the odour emissions is very relevant: more than one-third of sludge spread in agricultural land showed a VSS/TSS ratio higher than 60%. So, the reduction of VSS should be improved both for the WWTPs and for STPs.

D. As concerns the organic pollutants, no limit values were provided.

3.2. Analysis of different strategies and actions proposed

In order to contain the exceeding of regulatory limits for some heavy metals (issue A), it is appropriate to introduce *controls on sludge ingoing to STPs*. The acceptance criteria proposed (see Table 2) are based on thresholds for heavy metals in sludge provided by Legislative Decree 99/92 (Italian Decree, 1992), but taking into account tolerances of 10 or 20%, depending on pollutants. The tolerance values are related to: bioaccumulation, carcinogenicity of pollutants and quality of agricultural soils in Lombardy available for sludge application (Vitali et al., 2011).

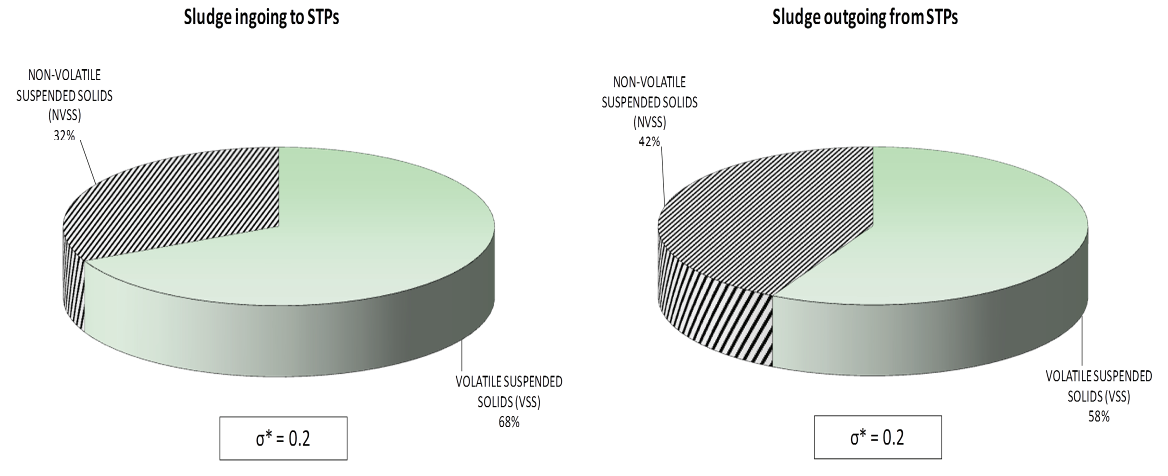


Fig. 5. Sludge ingoing and outgoing from STPs: VSS average content

The application of this criteria shows that almost all the sludge ingoing to STPs complies with the limit values proposed (Table 2).

As concerns the protection of high quality sludge ingoing to STPs (issue B), the different kinds of sludge should be diversified: this operation is provided in order to avoid the "dilution" of *high-quality sludge* with the *sludge with worst qualitative characteristics* but suitable for agricultural recovery. Thus, six policy strategies, based on different regulatory scenarios, were studied; their limits (regarding heavy metals and organic pollutants) are reported in Table 3.

Scenario 1 shows the limit values (for heavy metals only), equal to 1/5 of those considered in the Lombardy Region (2003): this option was provided by the legislation in case of sludge reuse (only for biological sludge derived from food industry) with a specific amount (per hectare of soil) three times higher than allowed. As concerns scenarios 2 and 3 two different options were evaluated (option 2 "moderate changes" and option 3 "more significant changes") provided by Working Document Sludge and Biowaste (European Commission, 2010); scenario 4 is based on Working Document on Sludge – 3rd Draft (European Commission, 2000).

Finally, two last scenarios are referred to the limit values of two regions near to Lombardy (Veneto and Emilia Romagna) in which the sludge recovery in agriculture is a common practice (ARPA Veneto, 2006). Based on the sludge quality survey carried out, the policy strategies were applied on the sludge outgoing from STPs. The results obtained are shown in Table 4; in particular, the percentages of sludge within the limit values provided by the different scenarios (only for heavy metals) are reported. The percentages values lower than 50% are highlighted.

In order to improve the quality of sludge in agricultural soils, "high-quality sludge" should be separate from "sludge suitable for spreading". This important aspect was adopted in DGR n. X/2031/2014 (Lombardy Region, 2014). As concerns the limit values of heavy metals, for high-quality sludge, scenario 3 (with the addition of arsenic reported in DGR n. 7/15944) was chosen (Lombardy Region, 2003). For other sludge suitable for reuse in agriculture, the limit values were provided in DGR n. 7/15944/2003 with the exception of As and Cr(VI) (that were deleted) (Lombardy Region, 2003).

Furthermore, in order to *contain the odour emissions* (issue C), limit values of VSS/TSS ratio were provided, both in high-quality sludge and in other sludge suitable for agricultural reuse; the limit thresholds are 60% and 65% respectively. According to the European disposition, the limit values of *organic pollutants* (issue D) were introduced. For all sludge spread in agricultural soil, scenario 2 was chosen; moreover, for PCDD/F, the limit value chosen is reported in DGR n. 2241/2005 of Veneto.

Summary, in Fig. 6 a flow diagram (*considering heavy metals only*) based on the evaluation carried out in the present work are shown. Heavy metals were considered because they represent the most critical parameters and cannot be controlled with the current equipments of STPs. According to DGR n. X/2031/2014, the acceptance criteria involve an amount of 1% of sludge that could not be sent to STPs for land application (Lombardy Region, 2014). Moreover, only considering heavy metals, the sludge reused in agricultural soils is divided into "high-quality sludge" and "sludge suitable for spreading": the partitioning is shown in Fig. 6. The critical parameters are nickel and zinc (Table 4).

4. Conclusions

In this study a methodological approach for regulatory planning concerning the use of sewage sludge for land application is reported. The case study is Lombardy, where sewage sludge reused in agriculture is very relevant. In fact, about 40% of sewage sludge (corresponding to 116000 t/year of dry matter) reused in Italy for land application is spread in the agricultural soils of Lombardy. The survey concerning the qualitative and quantitative characteristics of sludge reused in agriculture allowed the identification of several issues that were faced as follow:

Table 2. Acceptance criteria for sludge ingoing to STPs and percentages (by weight) of sludge within the limit values proposed

Parameter	*Measurement unit*	*Limit value for sludge ingoing to STPs*	*Sludge ingoing to STPs within the limit values [weight %]*
HEAVY METALS			
Cd	[mg kg_{SS}^{-1}]	≤22	100
Hg	[mg kg_{SS}^{-1}]	≤11	99.4
Cr_{tot}	[mg kg_{SS}^{-1}]	≤900	99.7
Ni	[mg kg_{SS}^{-1}]	≤330	98.9
Pb	[mg kg_{SS}^{-1}]	≤900	99.7
Cu	[mg kg_{SS}^{-1}]	≤1200	100
Zn	[mg kg_{SS}^{-1}]	≤3000	99.1
AGRONOMIC PARAMETERS			
C_{org}	[$\%_{SS}$]	>10	98.7
TN	[$\%_{SS}$]	>1	99.6

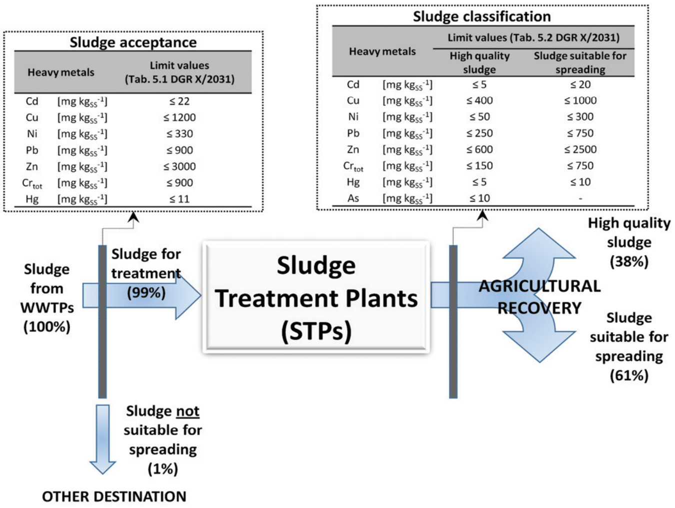
Table 3. Policy strategies evaluated in the present work

Parameter		***Measurement unit***	***Limit values***		***SCENARIO1***	***SCENARIO 2***	***SCENARIO 3***	***SCENARIO 4***	***SCENARIO 5***	***SCENARIO 6***
			Legislative Decree 99/92	***DGR 7/15944/ 2003***	***(1/5 of DGR 7/15944/2003 limit values)***	***(Option 2 Working Document Sludge and Biowaste)***	***(Option 3 Working Document Sludge and Biowaste)***	***(Working Document on Sludge 3rd Draft)***	***(DGR 285/2005 Emilia Romagna)***	***(DGR 2241/2005 Veneto)***
Heavy metals	As	[mg kg$_{SS}^{-1}$]	-	≤10	≤2	-	-	-	<10	-
	Cd	[mg kg$_{SS}^{-1}$]	≤20	≤20	≤4	≤10	≤5	≤5	<20	<20
	Cr(VI)	[mg kg$_{SS}^{-1}$]	-	≤10	≤2	-	-	-	-	-
	Hg	[mg kg$_{SS}^{-1}$]	≤10	≤10	≤2	≤10	≤5	≤5	<10	<10
	Cr_{tot}	[mg kg$_{SS}^{-1}$]	-	≤750	≤150	≤1000	≤150	≤800	<1000	<750
	Ni	[mg kg$_{SS}^{-1}$]	≤300	≤300	≤60	≤300	≤50	≤200	<300	<300
	Pb	[mg kg$_{SS}^{-1}$]	≤750	≤750	≤150	≤750	≤250	≤500	<750	<750
	Cu	[mg kg$_{SS}^{-1}$]	≤1000	≤1000	≤200	≤1000	≤400	≤800	<1000	<1000
	Zn	[mg kg$_{SS}^{-1}$]	≤2500	≤2500	≤500	≤2500	≤600	≤2000	<2500	<2500
	Se	[mg kg$_{SS}^{-1}$]	-	-	-	-	-	-	-	<5
Organic pollutants	AOX[1]	[mg kg$_{SS}^{-1}$]	-	-	-	-	-	≤500	≤1500	-
	LAS[2]	[mg kg$_{SS}^{-1}$]	-	-	-	-	<5000	<2600	-	-
	DEHP[3]	[mg kg$_{SS}^{-1}$]	-	-	-	-	-	<100	<100	-
	NPE[4]	[mg kg$_{SS}^{-1}$]	-	-	-	-	<450	<50	<50	-
	PAH[5]	[mg kg$_{SS}^{-1}$]	-	-	-	<6	<6	<6	<6	<6
	PCB[6]	[mg kg$_{SS}^{-1}$]	-	-	-	<0.8	<0.8	<0.8	<0.8	<0.8
	PCDD/F[7]	[ngI-TE kg$_{SS}^{-1}$]	-	-	-	-	<100	<100	<100	<50

[1] Sum of adsorbable organic halogen compounds; [2] Linear alkylbenzene sulfonate; [3] Di(2-ethylhexyl) phthalate; [4] Nonylphenol and nonylphenolethoxylates; [5] Polynuclear aromatic hydrocarbons; [6] Chlorinated biphenyle; [7] Polychlorinated dibenzo-p-dioxins and -furans

Table 4. Percentages (by weight) of sludge within the limit values of different scenarios

Parameter	***SLUDGE OUTGOING FROM STPs WITHIN THE LIMIT VALUES [weight %]***					
	SCENARIO 1	***SCENARIO 2***	***SCENARIO 3***	***SCENARIO 4***	***SCENARIO 5***	***SCENARIO 6***
	(1/5 of DGR 7/15944/2003 limit values)	***(Option 2 Working Document Sludge and Biowaste)***	***(Option 3 Working Document Sludge and Biowaste)***	***(Working Document on Sludge 3rd Draft)***	***(DGR 285/2005 Emilia Romagna)***	***(DGR 2241/2005 Veneto)***
As	**31**	-	-	-	100	-
Cd	95	100	98	98	100	100
Cr(VI)	100	-	-	-	-	-
Hg	86	100	98	98	100	100
Cr_{tot}	67	100	67	100	100	100
Ni	**48**	100	**39**	99	100	100
Pb	95	100	97	100	100	100
Cu	**23**	100	65	99	100	100
Zn	**31**	100	**38**	98	100	100



Sludge acceptance

Heavy metals		Limit values (Tab. 5.1 DGR X/2031)
Cd	[mg kg_{SS}^{-1}]	≤ 22
Cu	[mg kg_{SS}^{-1}]	≤ 1200
Ni	[mg kg_{SS}^{-1}]	≤ 330
Pb	[mg kg_{SS}^{-1}]	≤ 900
Zn	[mg kg_{SS}^{-1}]	≤ 3000
Cr_{tot}	[mg kg_{SS}^{-1}]	≤ 900
Hg	[mg kg_{SS}^{-1}]	≤ 11

Sludge classification

Heavy metals		Limit values (Tab. 5.2 DGR X/2031)	
		High quality sludge	Sludge suitable for spreading
Cd	[mg kg_{SS}^{-1}]	≤ 5	≤ 20
Cu	[mg kg_{SS}^{-1}]	≤ 400	≤ 1000
Ni	[mg kg_{SS}^{-1}]	≤ 50	≤ 300
Pb	[mg kg_{SS}^{-1}]	≤ 250	≤ 750
Zn	[mg kg_{SS}^{-1}]	≤ 600	≤ 2500
Cr_{tot}	[mg kg_{SS}^{-1}]	≤ 150	≤ 750
Hg	[mg kg_{SS}^{-1}]	≤ 5	≤ 10
As	[mg kg_{SS}^{-1}]	≤ 10	-

Fig. 6. Flow diagram of sludge ingoing and outgoing from STPs, according to DGR n. X/2031/2014 (considering heavy metals only) (Lombardy Region, 2014).

- introducing criteria for limiting the content of heavy metals in the sludge ingoing to STPs;
- defining two different sludge quality classes ("high-quality sludge" and "sludge suitable for spreading") in order to avoid the mixing of sludge with different quality in the STPs;
- controlling odour emissions due to poor sludge stabilization by means of restriction for VSS/TSS ratio;
- introducing limit values for organic pollutants, in compliance with European disposition.

The results of this study have been incorporated in regional guidelines.

Acknowledgments

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COST-EFFECTIVE TECHNOLOGIES TO CONTROL INDOOR AIR QUALITY AND COMFORT IN ENERGY EFFICIENT BUILDING RETROFITTING

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Abstract

This paper presents a toolset for the efficient control of the indoor air quality and thermal comfort in retrofitted buildings. The refurbishment of existing buildings, compliant to actual regulations, often leads to airtightness and the consequent poor conditions for the occupants that could cause low productivity and even sickness. For this reason, the CETIEB (Cost Effective Tools for Better Indoor Environment in Retrofitted Energy Efficient Buildings) project developed innovative low-cost solutions to monitor and control the indoor air quality and thermal comfort. Among the technologies developed, this paper presents ad-hoc sensors for the monitoring of Total Volatile Organic Components (TVOC), CO_2 and thermal comfort together with a control logic that, using measured data, provides the optimal rules to actuate the control devices (ventilation, heating/cooling, windows opening, shutters operation and so on). The application and validation of the integrated solution, monitoring plus control logic, was performed in a laboratory building to compare the performance of the proposed solution with the traditional system employed in buildings. The results turned out to show sensors performances comparable with commercial solutions but with a significant reduction of costs. Moreover, the application of the integrated solution showed an improvement of the indoor air quality and comfort with a 15% of energy saving, compared to the traditional thermostatic control.

Key words: energy efficiency, gas sensor, HVAC control, indoor air quality, thermal comfort

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1. Introduction

The built environment is the place where people spend 60-90% of their life (European Commission, 2011) and where about the 40% of the European energy is consumed (European Commission, 2009), also to maintain and guarantee the required living quality. It is estimated that HVAC (Heating, Ventilation and Air Conditioning) energy consumption accounts for 10 ÷ 20% of total energy consumption in developed countries (Pérez-Lombard et al., 2008). The problem of achieving healthy and comfortable buildings is well recognized by scientific community (Ioan and Ursu, 2012) and, for example, Mendell (2007) demonstrated that improving the indoor air quality could bring to increased productivity, reduced sick leave and medical costs and prevention of potential liabilities. Thus, buildings

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have to provide the best indoor living conditions but with the minimum energy use (Kalmár and Zöld, 2011). It is clear how the two objectives could easily go in opposite directions. In fact, the reduction of the energy consumption requires a high level of air tightness to ensure low outward leakage and this could lead to health problems as described in (Sharpe et al., 2015). Given this background, one of the main possibilities to face the issue of maintaining indoor air quality in compliance with the energy regulations is the inclusion of advanced monitoring and control methodologies to be entailed in the traditional HVAC systems together with the adoption of ad-hoc materials, e.g. exterior walls (Giuşcă et al., 2009), as replacement of the traditional ones. To this aim some studies investigate procedures for the indoor building assessment, as the one presented by (Capolongo et al., 2013) or developed monitoring methodologies and tools to improve the efficiency of HVAC management (Revel and Arnesano, 2014a, 2014b) and the overall building management (Grindvoll et al., 2012). However, even if procedures and methodologies are well-known, actual commercial solutions for the real-time monitoring and control of the indoor air quality are not able to take into account the full spectrum of parameters required to assess the air quality or, if able, they are too expensive especially in the case of building retrofitting.

The FP7 European project CETIEB (Cost Effective Tools for Better Indoor Environment in Retrofitted Energy Efficient Buildings) replied to this requirement with the development of a toolset specific for the improvement of the Indoor Air Quality (IAQ) in energy efficient refurbishment projects. The toolset includes ad-hoc sensor networks, innovative sensors and active/passive control systems. Each component was developed with the aim of overcoming limits of the actual solutions or to provide improved functionalities with a cost reduction. The resulting toolset entails sensors for the continuous monitoring of VOCs (Volatile Organic Compound), CO_2, light and thermal comfort sensors, HVAC control systems and biofilters for the active air cleaning, new materials for the passive control of the environment, such as photo-catalytic plasters and light materials with low thermal conductivity.

The overall approach of the technologies developed in the CETIEB project was presented in a previous paper (Revel et al., 2013). This paper presents the results achieved with the monitoring tools and active HVAC control. A test building was used to compare the cost-effective environmental control developed with respect to the traditional systems.

The paper illustrates the comparison of the indoor air quality and energy consumption of two identical rooms, the reference one equipped with traditional thermostat and ventilation control, the test one equipped with the monitoring and control tools developed in the project. The aim of this paper is to demonstrate how the environment can be better controlled to achieve the required indoor air quality with the lower energy consumption.

2. Materials and methods

In the following sections, the innovative sensors (VOC, CO_2 and thermal comfort) and the environmental control logic developed within CETIEB are presented, together with information about their performances, obtained with ad-hoc laboratory tests conducted.

2.1. Detection of VOC

Within CETIEB, innovative sensor technologies have been developed to monitor indoor air quality. In particular, the focus has been on volatile organic compounds as indicator for health status of the subject in a room. The objectives of the VOCs sensors development have been their qualitative and quantitative assessment, while providing affordable and small-sized systems for integration in smart sensor networks. According to the state of the art for VOC monitoring, mainly metal-oxide gas sensors are used. They offer low-cost, small-sized solutions and are able to detect VOC levels with enough accuracy. However, the referred output of such sensors is the total volatile organic compound level, as they cannot distinguish different VOCs (e.g. alcohols, ketones, aldehydes). The detection of such single compounds can be performed through optical sensors, by performing analysis in the infrared wavelength range. For these devices, the resolution is generally low, because of the not sufficient optical power. In fact, the infrared light sources power decreases with wavelength and is generally not adequate in the range 8÷12μm, where there is the maximum absorption of most of the VOCs. For this reason, two low-cost solutions have been developed for the monitoring of VOCs: a gas sensor array consisting of four metal-oxide (MOX) sensors and a spectroscopy-based VOC sensor to monitor selectively the typical indoor contaminants absorbing in the mid-IR range. The MOX sensors (Fig. 1a) are commercially available low-cost products (< 100 €), which are combined to a sensor node: the combination of the measured gas signal can be used to gain additional benefit by pattern recognition. The other device (as shown in Fig. 1b) is a miniaturized and compact spectrometer for the IR-range. Compared to huge and cost-intensive laboratory IR spectrometers, this sensor delivers an absorption spectrum of the target gas in a reduced IR-range, but is much more effective concerning size and costs. Broadband emitter, pyroelectric detector, tunable filter and long path cell are components which can reach prices in the range of several tens of Euros in higher quantities, while a single sensor is estimated to be near the thousands Euros.

Methane and acetaldehyde have been used as test gases for indoor air quality assessment with the spectroscopic system.

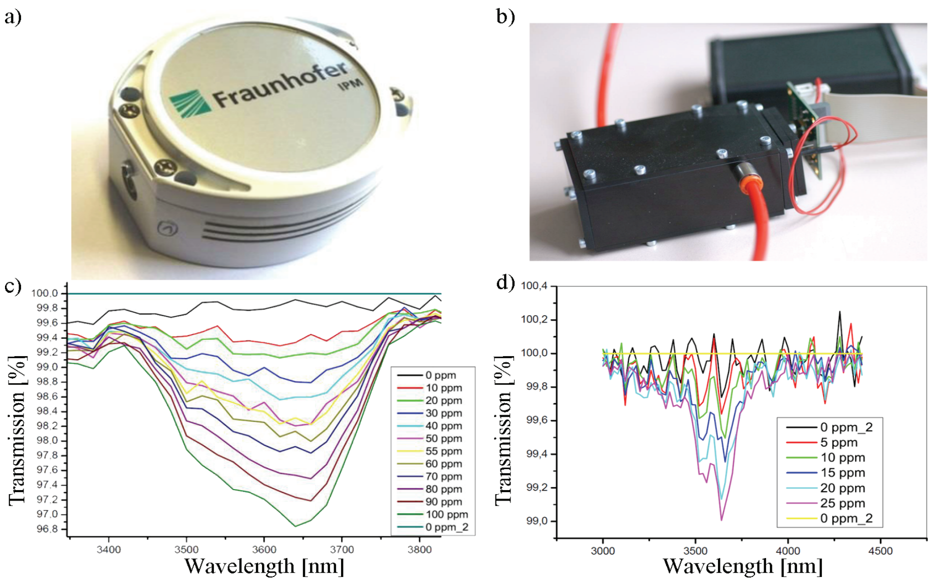

Fig. 1. (a) Gas array sensor; (b) spectroscopic sensor; (c) Measurement of acetaldehyde in N_2 from 0÷100 ppm in 10 ppm steps; (d) Measurement of acetaldehyde in N_2 from 0÷25 ppm in 5 ppm steps

Acetaldehyde (peak absorption at 3.65 µm) was measured from 0-100 ppm in N_2 in 10 ppm steps. The Maximum Allowable Concentration (MAC) for acetaldehyde is 50 ppm, so that this concentration needs to be reliably detected (Figs. 1c and 1d). The Limit of Detection (LOD) for acetaldehyde has been determined to be lower than 10 ppm.

2.2. CO_2 measurement

The CO_2 is one of the crucial parameters to assess the indoor air quality and it is directly linked with the occupancy. For indoor environments, concentrations above 1000 ppm are known to cause fatigue, headache and dizziness in people, while from 1500 ppm, usually, people begin to feel sick (Myhrvold et al., 1996). To maintain the well-being of occupants, the CO_2 level should be monitored constantly (with enough accuracy) and maintained at a level close to the atmosphere (around 390 ppm). The solution developed within CETIEB is based on the working principle of filterphotometry that makes use of the specific absorption of infrared (IR) radiation of molecules. A basic filterphotometer comprises an emitter and a detector with IR-filters. The absorption path between these two optical elements defines the measurement range. A longer path enhances the statistical possibility of a molecule to absorb a photon and results in a higher accuracy. A 2-channel filter photometer based on two commercial detectors and two different filters has been adopted. The first filter has a high transmission at 3.95 µm and serves as reference. In fact, no specific molecule absorbs in this band. With this filter, signal drifts of the optical components can be detected and compensated. The transmission peak for the second filter is at 4.25 µm, where CO_2 has its main absorption band. The absorption path has been chosen equal to 3 cm, in order to cover the relevant concentration range for indoor air quality measurements. The IR filters have been placed in front of the detector to define the molecule-specific wavelength bands of interest. Both the thermal emitter and detector have been placed within an aluminum tube-shaped housing that defines the absorption path and at the same time serves as mechanical protection for the sensor element. An electronic control unit (Fig. 2a) has been developed to control all the optical components and to process the detector signals. The combination of both filters and absorption path, as described previously, allows a measurement range from 0÷20.000 ppm.

The sensor performance was assessed with a dedicated calibration conducted in laboratory, using different CO_2 concentrations in a standard gas (N_2). Figs. 2c and 2d show an example of the sensor response (0÷20000 ppm) during a test conducted in laboratory. The system was placed into a large chamber of about 1 dm^3 volume to simulate a real situation as in indoor environments. The CO_2 concentration was varied at fixed time intervals, covering a range from 0÷20000 ppm. The test showed a limit of detection of 20ppm with an accuracy of about ±50ppm.

2.3. Continuous thermal comfort monitoring

A low-cost infrared-based system for the real-time monitoring of human thermal comfort has been developed to provide the same information of traditional microclimate stations (assumed as the gold standard for short-term monitoring), but with a decrease of costs in the order of 1/10 of the station and with potentials for real-time and spatial measurements. The system (prototype version in the range of 200 ÷ 240 €) is based on a microcontroller, sensors and embedded algorithms to derive the thermal comfort index PMV (Predictive Mean Vote) for multiple positions in the room. PMV is a standard index (according to ISO 7730), which predicts the mean votes of a large group of people on a seven-point thermal sensation scale, from -3.0 (“Cold”) to +3.0 (“Hot”).

Four environmental parameters (air temperature, relative humidity, air velocity and mean radiant temperature) and two personal parameters (metabolic activity and clothing level of the subject) need to be measured or provided in order to apply the methodology and calculate accurately the PMV value.

The working principle and measuring performances have been described in (Revel et al., 2012, 2014a). The solution consists of three main parts (as shown in Fig. 3):

- The IR scanning system, fixed on the ceiling of the room so to allow the continuous measurement of surfaces temperature and calculation of mean radiant temperature maps (in agreement with the methodology proposed in the ISO 7726 standard);
- The control unit, managing the data flow between integrated sensors (indoor temperature, relative humidity and air velocity) and from/to the user interface where the thermal comfort for multiple positions is calculated;
- A dedicated user interface (e.g. for Android devices), for setting data input and data storage for further analysis.

Each sensor is able to provide accurate measurement of indoor thermal comfort in medium spaces (< 100 m^2, maximum distance of about 5 m from the surface to monitor). More than one sensor should be installed in the case of larger environments (i.e. open spaces), eventually with optimized positioning so to reduce the sensors number.

Several tests were conducted to provide the metrological characterization of the system developed (e.g. tests in controlled environments as in Revel et al., 2014b). The final performances of the system are summarized in Table 1.

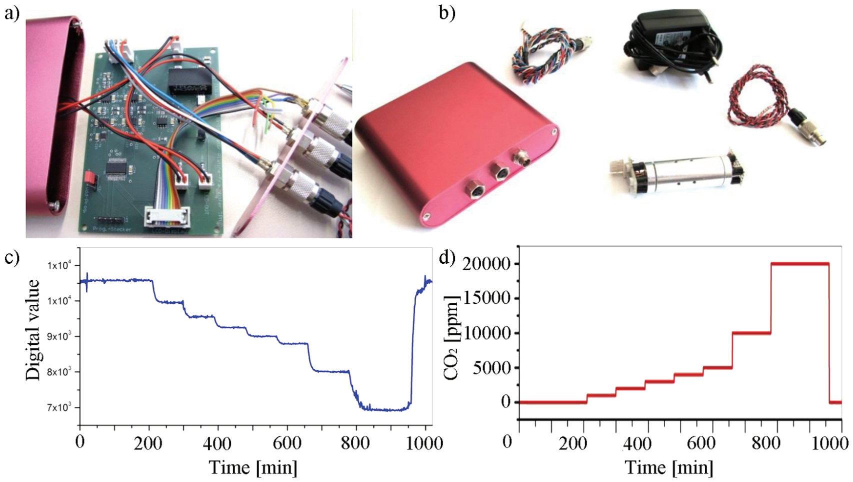

Fig. 2. (a) Assembled circuit board of CO$_2$ sensor; b) The final prototype developed; (c) sensor raw reading during the laboratory test; (d) resulting CO$_2$ concentration during the laboratory test

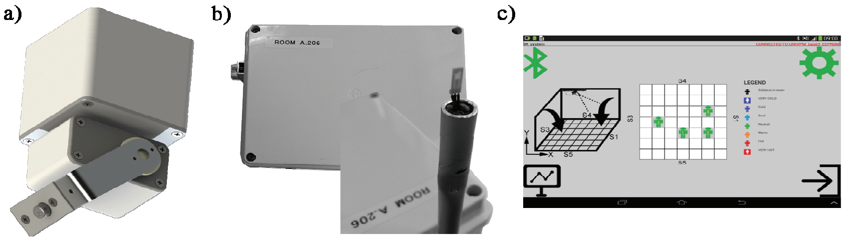

Fig. 3. Thermal comfort measuring tool. (a) IR scanning system; (b) Control unit and integrated sensors; (c) User interface for smart devices

Table 1. Performances of the system developed for the environmental parameters measurements

Parameter	***Methodology***	***Accuracy***
Air temperature	Direct measurement	±0.3°C
Relative humidity	Direct measurement	±2%
Air velocity	Direct measurement	±0.1m/s
Surface temperatures	Direct measurement	±0.9°C
Mean radiant temperature	ISO 7726 methodology from surface temperatures measurement	±0.5°C
Predicted Mean Vote	ISO 7730 methodology	±0.2

The system is able to provide the continuous measurement of PMV index with an accuracy of ±0.2 units. Several tests conducted in real spaces (offices, classrooms) demonstrated the potentials of using the thermal comfort system to provide continuous information about the real thermal perception of the users. For example, Fig. 4 shows results from two measurement campaigns (summer season in a) and winter season in b)) conducted in an office room. The PMV profile measured by the system presents little deviations (0.1±0.1 and 0±0.2 respectively) with respect to the traditional microclimate station (HD32.1 from DeltaOhm).

These results confirm the performance of the device for the continuous measurement of thermal comfort and the potentials of using such measurement to apply an optimized HVAC control by means of this index.

2.4. Development of optimized IAQ and PMV-based control algorithms

The HVAC systems are designed to maintain good indoor air quality through adequate ventilation and provide thermal comfort. HVAC systems are among the largest energy consumers in buildings (i.e. they account for 39% of the energy used in commercial buildings). Consequently, almost any business or government agency has the potential to realize significant savings by improving its control of HVAC operations and improving the efficiency of the system it uses. Moreover, a correct indoor ventilation is necessary to allow carbon dioxide to go out and oxygen to get in, making sure that people are inhaling fresh air. Indoor air quality is a major challenge in energy efficiency as enhanced air tightness improves the comfort with direct impact on medical costs, as well as improvement in both people's productivity and concentration level. Control strategies and algorithms have been developed within the project to control both IAQ and thermal comfort. The main scope is to ensure IAQ staying within acceptable limits, improving the global comfort of the room and energy efficiency.

The control system developed is rule-based and is composed of two main modules: the first one focused on IAQ, the second one on thermal comfort, making use of the PMV index.

IAQ is satisfied when the concentration of the pollutant considered (CO_2, TVOC) is under the acceptable limits, while thermal comfort is satisfied when the PMV is between ±0.5. The priority has been given to IAQ, meaning that the thermal comfort would be ensured only once the pollutants concentration is under the limits. The control structure developed is potentially applicable to any kind of indoor environment and monitoring system, e.g. taking advantage of the IR-based thermal comfort system developed within CETIEB (an example of the routine implemented is shown in Fig. 5).

2.5. Experimental

An experimental test was performed in a real building (Fig. 6.) of the INES (*Institut National de l'Energie Solaire*, France) platform in order to test the potential of using the thermal comfort system (in combination with a dedicated PMV-based HVAC control algorithm) to improve the indoor comfort. The demo site was modified in order to provide two identical rooms (geometry, orientation, HVAC system and monitoring devices) and to monitor continuously their behavior with and without the control algorithms. In particular, a test similar to the one described in (Yang et al., 1997) was conducted. In the first room (referred as Test Room) the microclimate was controlled with the PMV-based approach, i.e. the continuous measurement provided by the thermal comfort system and the rule-based architecture developed in the project. In the other room (referred as Reference Room) a constant temperature set point of 24°C was maintained so to replicate the traditional thermostatic control.

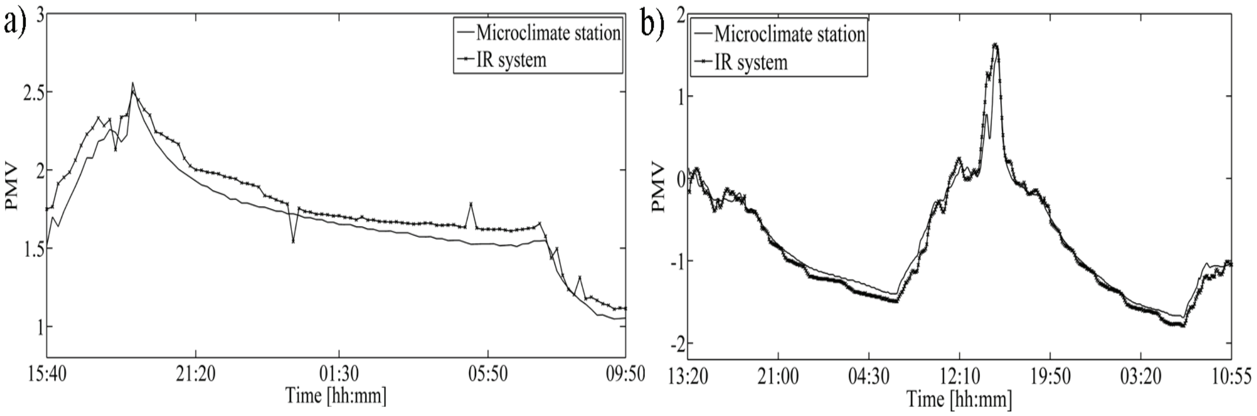

Fig. 4. Comparison of the thermal comfort measurement performed by the system developed with respect to the microclimate station

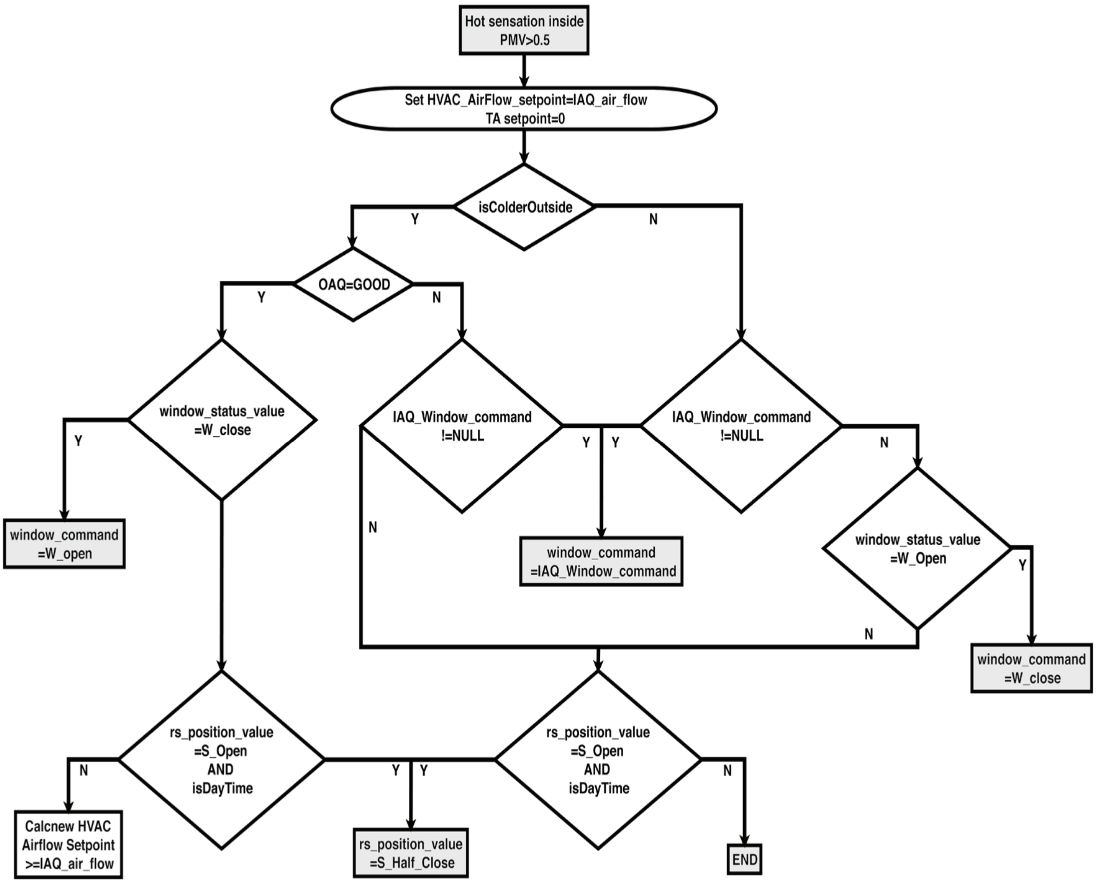

Fig. 5. Rules architecture to control IAQ and thermal comfort

(a) **(b)**

Fig. 6. (a) Building in the INES platform for the test conducted; (b) Thermal comfort system placed on the ceiling of Test Room for the test

According to the sensors and actuators available in the rooms, the control algorithm was able to regulate the room ventilation, air temperature and incoming solar radiation (window opening, rolling shutter, inlet/outlet fans, electrical heating system). A LabView software was implemented to manage the devices used to control the systems and to monitor the environmental parameters. Therefore, IAQ (CO_2 and TVOC) was also monitored in this test through commercial sensors. A standard TCP/IP communication protocol was implemented for the thermal comfort system in order to provide the continuous measurement (environmental parameters and PMV) to the HVAC control algorithms, with a sampling frequency of one measurement each 5 minutes. Then, the control algorithm made use of those data to identify the best actions to perform and sent them as input to LabView platform through a web-service. Both rooms were also equipped with energy meters to measure the electrical consumption and compare the results after the application of the proposed approach.

3. Results and discussion

The test lasted one week, during which the Reference and Test rooms ran with the traditional and innovative control system respectively. The

PMV computed in the rooms by the thermal comfort systems was compared to the one calculated from the environmental sensors installed and the results are shown in Figs. 7 a) and 7 b). Both the systems measured similar profiles (deviations of -0.1±0.1 and -0.1±0.2 in test room and reference room respectively), validating the performance of the low-cost solution developed. It can be noticed that an improvement of the thermal comfort (around one unit during the hot hours and mitigated variations) was achieved in the Test Room after the application of the PMV-based algorithm. Again, similar improvements can be observed for the indoor CO_2 concentration (Fig. 7c), where an average reduction of around 100 ppm was obtained in the Test Room.

The control system was able to actuate the window shutter and the inlet/outlet airflow (no heating or cooling, only mechanical ventilation). The strongest improvement in the thermal comfort was obtained by the control of the shutter. In fact, the indoor total solar radiation measured in the test room was strongly reduced (Fig. 8a) and this turned out to provide an improvement in the comfort conditions (a deviation with respect to the reference room from 0.5 up to 1.0 unit when the solar radiation contribution is maximum). The highest improvement in the thermal comfort was reached when the solar contribution was maximum, central zone of maps reported in Figs. 8 a) and b).

In fact, the strong contribution to the mean radiant temperature due to direct and diffuse solar radiation was reduced in the test room with an adequate control of the shutter. Because of this, a significant improvement in the thermal comfort (denoted by a higher deviation with respect to the reference room) was obtained as shown in Fig. 8b) where the central zone becomes colder from the 04/13/2014 when the optimal control is actuated.

The test conducted highlighted the efficiency of the system in improving both the IAQ and the thermal comfort with an energy saving. In fact, the proposed control system allowed an energy saving of the 15% (2804 Wh in the test room, 3293 Wh in the reference room) during the week of testing.

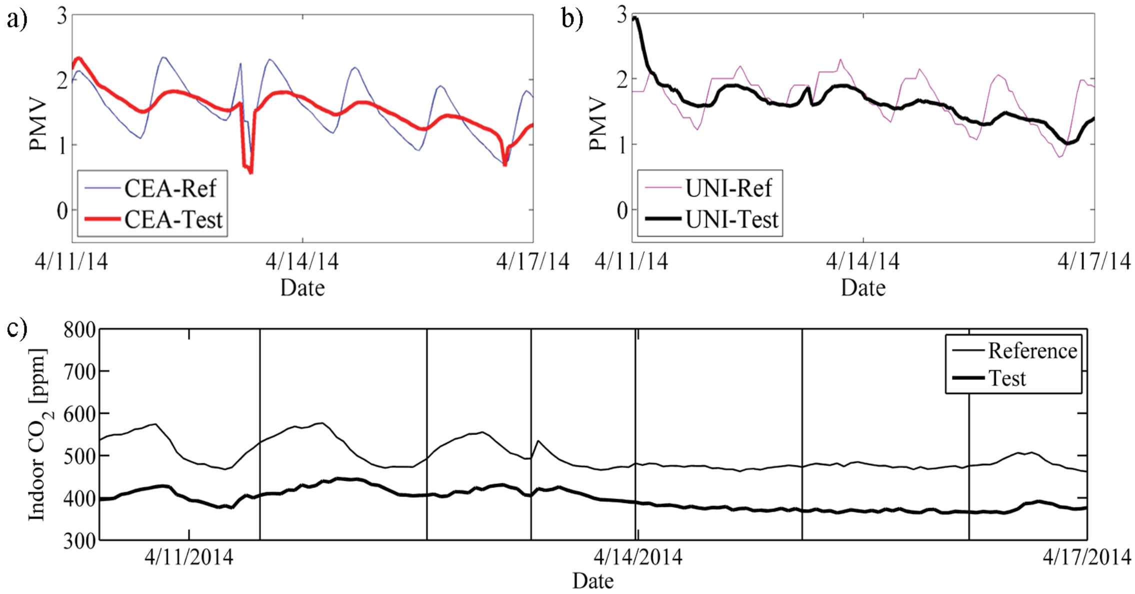

Fig. 7. (a) PMV calculated in post processing from the environmental sensors installed; (b) Continuous measurement provided by the thermal comfort systems developed; (c) Improvement in the indoor CO_2 concentration in Test Room after the application of the PMV-based approach

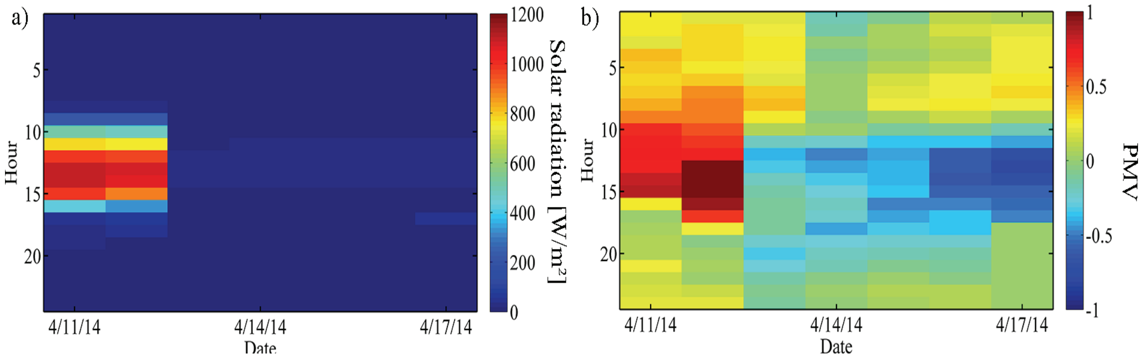

Fig. 8. (a) Indoor total solar radiation measured in test room during the measurement campaign; (b) PMV deviation between Test Room and Reference Room

4. Conclusions

The innovative solutions developed within the CETIEB project and discussed in the paper allow the cost-effective monitoring and control of the indoor environment for optimal living conditions with the lower energy consumption. The results obtained from the laboratory testing of the sensing devices presented are comparable: in fact, they are all able to reproduce the performance of typical solutions currently used, but with reduced cost and high integration capability, overcoming the limits in the market. For example, the solution developed for the thermal comfort allows measurements of the PMV for all the occupants in the operational phase with IR-based sensor, which is not feasible up to now with the commercial instrumentation available.

The potential of integrating the information provided by these sensors in an optimized HVAC control algorithm leads to an improvement of the perceived thermal comfort and energy efficiency. This has been initially demonstrated with the test conducted in the test building, as reported in the paper, where an improvement of the IAQ and thermal comfort was obtained with the reduction of about the 15% of energy consumption. Thus, the complete solution developed in CETIEB is able to improve significantly the indoor air and environmental quality by means of a cost-effective monitoring, with cheap tools embedded in a modular sensor network and optimized control actions.

Further tests could be useful to demonstrate the potential of such technologies in the improvement of the indoor air quality.

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CARBON FOOTPRINT OF ELECTRICITY FROM ANAEROBIC DIGESTION PLANTS IN ITALY

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Abstract

In the context of biogas sustainability assessment, a promising way to reach greenhouse gases (GHG) reduction and fossil energy savings is the anaerobic digestion (AD) of both animal manure and energy crops.

Nowadays, more than 1,100 AD plants are working in Italy, mostly located in Northern Regions. To those plants with an electrical power lower than 1 MW, strong public incentives were given, therefore, several of them have been put into operation; this entailed increasing cereal silage prices, feedstock transportation distance and issues about digestate management and heat valorization.

In this study the Carbon Footprint (CF) of electricity production from biogas has been evaluated considering five AD plants located in Lombardy and Piedmont. A Life Cycle Assessment (LCA) approach and a cradle-to-grave perspective have been considered. Different plant sizes (100, 250, 300, 300 and 998 kW) and feeding rate (maize and pig slurry, only maize, only pig slurry and only cow slurry) have been studied.

The CF was calculated for a 100-year time frame based on GHG emissions, indicated as mass of CO_2 equivalents (kg CO_2eq), according to IPCC. The Functional Unit (FU) is 1 kWh of electricity fed into the electric grid. The CF saving for electricity produced by the AD plants ranges from -0.208 to -1.07 kgCO_2eq/kWh, being mainly related to the substitution of energy production from fossil fuel. Electricity from biogas has a big potential to reduce GHG emissions: valorization of surplus heat and reduction of transport distance can support the lower GHG emissions achievement of this bioenergy system.

Key words: anaerobic digestion, climate change, Greenhouse Gases, renewable energy, LCA

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1. Introduction

The interest in Renewable Energy Sources (RES) has strongly increased due to the need of reducing fossil energy consumption and Green Houses Gases (GHG) emissions. Considering that the profitability of food crops is generally decreasing (Bacenetti et al., 2015a), RES represent a good opportunity for the agricultural sector. Within the "Green Economy" context, Common Agricultural Policy (CAP) highlights both the need to contrast environment alteration and the RES development as the main challenges for the agricultural sector (De Cara et al., 2005, Mateescu et al., 2008). In particular, the micro-energy generation model (small-size and widespread plants) is suggested to achieve the "multi-functionality" of the modern agriculture as well as to improve the farmer's income (Bacenetti et al., 2013b; Duan et al., 2014; Li et al., 2012; Wu et al., 2014). At the moment, in Italy, biogas production from agricultural biomass is having a strong appeal on farmers who are looking for diversifying their income sources. In fact, to the electricity generated through Anaerobic Digestion (AD) of biomass, strong public subsidies are applied.

In this context, the production of energy from biomass represents an interesting business-opportunity for many livestock farms; actually, they

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can: (i) directly manage the whole add-value coming from energy production, and (ii) sell their whole production (electricity) to a single customer (grid company), at a fixed rate, for a long-period (15 years), which explains the, significant agricultural biogas production increase in the last two decades. At present, more than 1,100 agricultural biogas plants are operating, mainly located in northern regions of Italy. At the end of 2012, the installed power was 756 MW: nearly 1.65% of Italian electricity consumption was generated in agricultural biogas plants (Bacenetti and Fiala, 2014; Negri et al., 2014).

However, biogas production can generate significant impacts to the environment, especially focusing on global warming, acidification, eutrophication, etc. For this reason, environmental sustainability and performance of biogas production systems were object of numerous studies and researches (Hoppe and Sanders, 2014; Li et al., 2012; Wu et al., 2015). In particular, special attention has been paid on Carbon Footprint (CF) related to the electricity (EE) produced by AD plants (Dressler et al., 2012; Lijó et al., 2014a, 2014b; Meyer-Aurich et al., 2012; Rehl and Muller, 2013; Tricase and Lombardi, 2012).

The goal of this study is to estimate, using a Life Cycle Assessment approach, the CF of EE co-generated in 5 CHP (Combine Heat and Power) systems fuelled with biogas produced in AD agricultural plants fed with different agricultural feedstock. The AD plants have been selected considering feeding: in more details, to better highlight the impact of the different feedstock, four of the five selected AD plants are mainly fed with animal wastes (pig and cow slurry). The CF of these plants, characterized by low electrical power (maximum 300 kW), is compared to that of the electricity produced from fossil fuel but also to the CF of the 5th AD plant fed only with maize silage. Although several studies highlighted that environmental benefits are achieved from AD, only few researches in Italy have focused the attention on AD plants fed with by-products (Bacenetti et al., 2015b; Battini et al., 2014). In fact, given the subsidy framework, the major part of AD plants are fed with cereal silages and have an electrical power close to 1 MW. Although in Italy there are several natural gas fuelled cars, the attention of this study was paid on electricity generation because this is by far the most widespread utilization pathway for the biogas produced by agricultural AD plants. Due to the lack of a proper and clear legislation, the development of the “bio-methane sectors” is limited to few pilot plants.

2. Case studies

2.1. Process description

The analysis considers a cradle-to-grave system boundary; therefore, all the processes (and the related inputs) involved throughout the life cycle have been taken into account: (i) energy crops production, (ii) feedstock transport to the biogas plant, (iii) anaerobic digestion and biogas use, and (iv) digestate storage and management. Information concerning the agricultural biogas plants and the feedstock digested are reported in Table 1.

In more details:

i) **Plant A** – **Pavia 1** has an electrical power of 300 kW; it is located in Pavia district (Lombardy), has 2 digesters (1 for the storage of digestate) and is fed with maize silage produced on farm and pig slurry coming from nearby breeding farms.

ii) **Plant B – Lodi** has an electrical power of 250 kW; it is located in Lodi district (Lombardy), has 2 digesters (1 for digestate storage) and digests pig slurry only, produced on farm.

iii) **Plant C** – **Pavia 2** has an electrical power of 300 kW; it is located in Pavia district (Lombardy), has 2 digesters (1 for digestate storage) and is fed with pig slurry and maize silage.

iv) **Plant D** – **Cremona** has an electrical power of 100 kW, is located in Cremona district (Lombardy Region), has 2 digesters (1 for digestate storage) and is only fed with cow slurry.

v) **Plant E** – **Novara** has an electrical power of 998 kW, is located in Novara district (Piedmont), has 4 digesters (2 for digestate storage) and digests only maize silage.

The biogas-to-electricity process can be divided into:

i) Subsystem 1 - Feedstock: it includes maize cultivation and harvest as well as pig slurry transport. Table 2 reports details about maize cultivation.

ii) Subsystem 2 - Transport and storage: it includes maize transport and ensiling and slurry transport and storage at the biogas plant. Both pig and cow slurries are transported by means of slurry tanks; distances between the breeding farm and the digesters are 0.8, 2.2, 3.0 and 0.3 km for Plant A, B, C and D, respectively, whereas in Plant E no slurry was transported.

iii) Subsystem 3 – Energy production: the conversion of feedstock into biogas and of biogas in energy (electric energy - EE- and thermal energy - ET) has been considered. Table 3 reports further details concerning the microbiological biogas production inside digesters. Among the different feedstock, maize silage shows the highest dry matter content and, consequently, the highest biogas production. Between the animal wastes, cow slurry has a dry matter content 2.5 times higher than pig slurry and, approximately, a 2 times higher methane production.

Fig. 1 shows the system boundaries for the five biomass-to-energy processes. The animal slurry production has been excluded from the system boundaries due to the fact that it is a waste belonging to the pig meat and cow milk production processes.

2.2. Data collection

Background data for the production of seeds, diesel fuel, fertilizers and pesticides were obtained from the Ecoinvent Database (Ecoinvent Database, 2015; Frischknecht et al., 2007; Nemecek and Käggi, 2007; Spielmann et al., 2007).

Data concerning the agricultural AD plants running parameters (e.g. biomass consumption, biogas production, EE and ET self-consumptions), were obtained through daily direct monitoring over 12 months (from September 2012 to August 2013), gathering the following information:

i) feedstock consumptions (t/day);
ii) temperature inside the digester (°C);
iii) organic loading rate ($kg_{VS}/m^3 \cdot day$);
iv) biogas production and composition (m^3/day; CH_4 % vol.);
v) gross EE production, EE self-consumption and net EE production (kWh per day).

In the five AD plants assessed, biogas losses were considered, both from digesters and biogas treatment devices (1.0%) and from the CHP (0.5%) (Dressler et al., 2012).

Emissions data from biogas combustion in Combined Heat and Power (CHP) devices are assumed from National Environmental Research Institute (NERI, 2010).

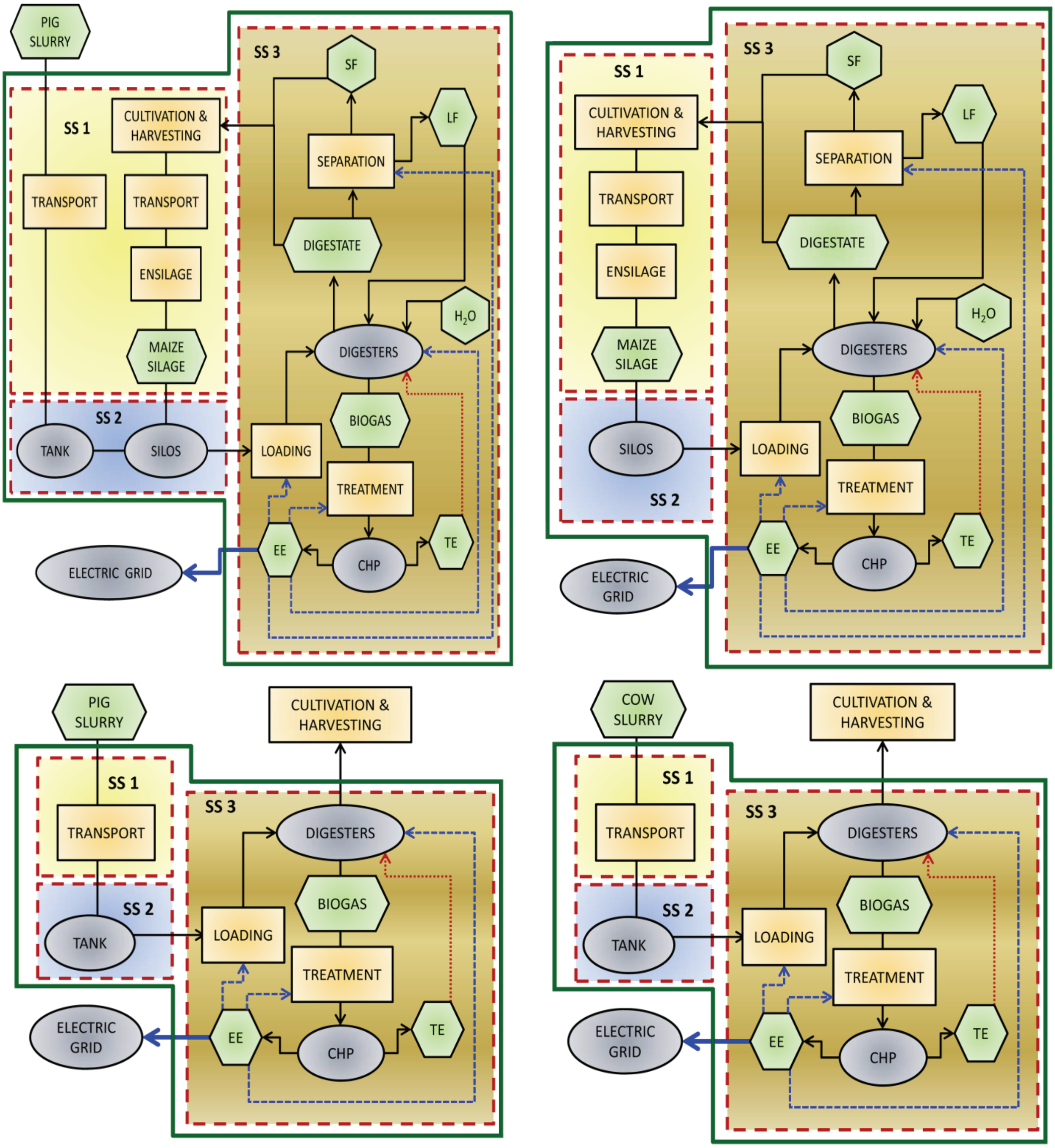

Fig. 1. Biomass-to-electricity process for the five agricultural biogas plants: on the top: plant A&C (left) and plant E (right); on the bottom plant B (left) and plant D (right). Green lines are the system boundary; red lines are the sub-subsystems boundary. (SS1 = Feedstock production and recovery; SS2 = transport and storage; SS3 = Conversion; EE = electricity; TE = heat)

Table 1. Main technical data for the five biogas plants

Biogas plant	***Engine power***	***Electric efficiency***	***Thermal efficiency***	***Maize silage***	***Pig slurry***	***Cow slurry***
	kW	***%***	***%***	***t/day***	***t/day***	***t/day***
A - Pavia 1	300	39.0	50.8	14	45.0	0
B – Lodi	250	36.0	50.5	0	175	0
C – Pavia 2	300	38.6	49.5	13	35	0
D - Cremona	100	35.0	48.0	0	0	33.0
E – Novara	998	40.9	44.0	55	0	0

Table 2. Maize cultivation: field operations and the production factors

Field operation	***Means***	***MECHANIZATION***						
		Tractor 4WD + Machines	***Mechanical Power***		***Field Capacity***	***Diesel Consumpt.***	***APP. rate***	***Times***
			TR[a]	***OM***[a]				
			(kW)		***(ha/h)***	***(kg/ha)***		
Cutting up field sides	-	Rotary tiller	74	35	2.0	4.18	-	1
Organic fertilization	Solid Fraction (SF) of digested matter	Front loader, 2 m^3	100	25	0.1	3.65	-	1
		Manure spreader 20 m^3	132	55	0.5	27.21	15 t/ha (N slurry content = 8.60 kg/t)	1
Ploughing	-	Four-furrow plough	180	110	1.3	22.61	-	1
Harrowing	-	Rotary harrow 4 m	130	85	0.8	23.69	-	1
Precision seeding	Seed	Precision seeder (8 lines)	100	70	1.0	13.4	11 kg/ha	1
Soil sanification	Chemical						12 kg/ha	
Local fertilization	Diammonium phosphate [b]						200 kg/ha	
Pre-emergence weed control	Herbicide	Sprayer 3 m^3	74	40	2.5	3.52	4 kg/ha	1
Post-emergence weed control	Herbicide (mix)	Sprayer 3 m^3	74	40	2.5	3.52	1.6 kg/ha	1
Top fertilization	Urea	Fertilizer spreader 1 m^3	74	50	2.0	6.06	210 kg/ha	1
Irrigation	Water	Pump + sprinkler system	100	70	0.5	22.4	400-500 m^3/ha	3
Harvest	-	Self-propelled forager	-	300	1.0	76	-	1

[a]TR = tractors, OM = operative machines; [b]= Typical formulation is 18-46-0 NPK

Table 3. Feedstock characteristics

Feedstock	***Total Solid Content (TS)***	***Volatile Solid Content (VS)***	***Specific biogas production***	***Methane content***
	% of fresh matter	***% of total solid***	***m^3/t of VS***	***%***
Maize silage	33.0	90.0	650	60.0
Pig slurry	3.5	85.0	450	53.0
Cow slurry	9.0	83.0	325	58.0

3. Methodology

The Carbon Footprint of EE produced from the different agricultural biogas plants was calculated for a 100-year time frame based on GHG emissions indicated as CO_2 equivalents (eq) (IPCC, 2006). The Functional Unit (FU) is 1 kWh of electricity fed into the electric grid.

The software Simapro® was used to organize and process data. GHG emissions were calculated according to the following 100-years factors expressed in kg CO_2 equivalents, CO_2: 1; CH_4: 25; N_2O: 298 (IPCC, 2007). The GHG emissions (EM_{GHG}; (kg CO_2eq/kWh electrical) derived from the proposed bioenergy processes have been calculated considering that - in accordance with the guidelines of IPCC (2006) - the CO_2 removed from the atmosphere through photosynthesis offsets the CO_2 released during Anaerobic Digestion and biogas combustion. The Carbon Footprint of EE generated from biogas derives from a balance between GHG emissions that occur during the bioenergy process and credits that can be attributed to it (e.g., for the substitution of energy production from fossil fuels, avoided GHG emissions from the storage of animal slurry in open tanks, etc.).

The considered GHG emissions are connected to:

i) maize silage production (Plants C and E) and animal slurry recovery (Plants A, B, C and D);

ii) energy and materials consumption -in addition to feedstock- that occurs in Subsystem 3 (diesel fuel for maize silage loading, lubricants for CHP, additive substances for digesters, EE for plant self-consumption). Considering that the ET self-consumption of plants are met by CHP, no emissions have been considered for heat generation;

iii) methane losses from digesters, pipes, biogas treatments devices and CHP utilization. Due to high GWP of CH_4, these losses -although small- have a strong impact on environmental performances of the process.

Emissions of GHG due to the production of both farm equipment (e.g., tractors, machines) and biogas plant and infrastructure (e.g., roads and trucks) were not included in the system boundaries. For these production factors, Hartmann (2006) reported a small contribution (4% approximately of the total GHG emission).

Background data for the production of seed, diesel fuel, fertilizers, pesticides as well as for transport were obtained from the Ecoinvent database v.3 (Ecoinvent, 2015).

Emissions from digestate were not considered because of the use of covered tanks.

To the biogas system are attributed credits for:

i) the substitution of the EE otherwise produced mainly using fossil fuels. In more details, the EE from biogas replaces the production of the same amount of electricity produced with the Italian mix of energy sources. Therefore this EE has been credited with the GHG emissions that characterize the actual Italian electricity production (currently, 541.7 g CO_2eq/kWh);

ii) the substitution of ET otherwise produced using fossil fuels. In more details, considering that plant self-consumption is covered by CHP, these credits are granted only for the net thermal energy cogenerated;

iii) the avoided GHG emissions due to anaerobic digestion of animal wastes. AD of slurry reduces CH_4 emissions compared with an uncovered storage tank (IPCC, 2006); in accordance with Lansche and Müller (2012), it has been assumed that these avoided emissions from animal slurry are equivalent to 16% of the potential biogas production. More details about the calculations of these credits are reported by Bacenetti et al. (2013a). With regard to the effect of AD credits on the CF, a sensitivity analysis has been carried out (alternative scenario 2).

Credits due to the mineral fertilizers replacement - the digestate is used as organic fertilizer at the end of the process - have not been considered because: (i) in biogas Plants A and B the digestate is completely spread on maize fields and, (ii) in biogas Plants C and D, the amount produced by the animal slurry is used as fertilizer in fodder production and, hence, is excluded from the analysis because it would be spread also in absence of the biomass-to-energy process.

3.1. Alternative scenarios

In addition to Base Scenario (BS), three Alternative Scenarios (AS1 and AS2) have been proposed and evaluated in this report. In AS1, the impact of heat valorization has been assessed using the credit approach; the credits were attributed to the biomass-to-energy process, assuming the full valorization of ET produced by CHP net thermal energy (Tashima et al., 2014).

The heat is credited considering the GHG emissions entailed in a fossil-based energy generation plant (0.226 $kgCO_2eq/kWh$ thermal) (Capponi et al., 2012). In AS2 no credits for AD have been taken into account in order to assess their impact on CF.

4. Results and discussion

Fig. 2 shows the results for the five agricultural AD plants and for BS, AS1 and AS2. In baseline scenario (BS) the CF of electricity produced from biogas ranges between -0.208 $kgCO_2eq/kWh$ to -0.930 $kgCO_2eq/kWh$. The differences are mainly due to the credits attribution and, secondarily, to feedstock production and recovery. The lower values of CF are achieved in the AD plants fed with animal slurries (Plants A, B, C and D) and, consequently, credited with high credits for AD of animal slurry. Without the accounting of credits for AD (AS2), the CF varies from -0.263 $kgCO_2eq/kWh$ for the Plant C (Lodi, fed with pig slurry) to -0.476 $kgCO_2eq/kWh$ for the Plant E (Novara fed only with maize).

The considerable differences between the two AD plants fed only with slurry (B and D) are due to the transport distance: in Plant D the slurry is available on the farm, while in Plant B it must be transported for 3.0 km. With regard to GHG emissions, it must be underlined that in all the AD plants about 20% of the total is due to methane losses. The comparison among the different scenarios highlights that, with respect to the BS:

i) the attribution of credits for heat valorization entails a reduction of CF. This reduction is lower for Plants B and D that are fed only with animal slurry and, consequently, characterized by a higher heat self-consumption. On the contrary, Plants C and E -mainly fed with energy crops- digest feedstock with a high energy density, have a lower heat consumption and, consequently, more credits for heat valorization;

ii) the credits for AD of animal slurry have a strong impact on the CF for the Plants (A, B and D) where the digesters are fed with a high amount of these feedstock. In BS, these credits represent 66%, 75%, 47% and 51% of GHG savings, respectively for biogas plant A, B, C and D.

The CF differs considerably between the biogas plants fed with maize silage (C and E) and the ones in which slurries are utilized (A, B and D). The feeding of the digesters with slurries involves high thermal self consumption and, therefore, low credits for heat valorization; furthermore, when these feedstock are transported high GHG emissions occur.

The results are similar for the ones recorded by previous studies (Bacenetti et al., 2012; Bacenetti et al., 2013b; Bachmaier, 2010; Lijó et al, 2014a, 2014b; Meyer-Aurich et al., 2012; Pöschl et al., 2010; Poeschl et al., 2012; Szabó et al., 2014; Schumacher et al., 2010), which show that EE from biogas is an effective solution to reduce GHG emissions. Moreover, the utilization of the cogenerated heat can substantially improve the CF of electricity production from biogas. Further improvements can be achieved by using animal waste as feedstock. Animal slurry as feedstock can partially substitute energy crops and avoids GHG emissions from undigested manure. However, compared with cereal silages, the use of animal slurry involves higher thermal energy self-consumption for heating the digesters and, consequently, lower credits are available for heat valorization.

4.1. Sensitivity analysis

Considering that the credit granted for the substitution of EE produced from fossil fuels has a deep impact on CF of EE produced in the 5 agricultural biogas plants, a sensitivity analysis was carried to this regard. In more details, CF has been assessed considering the possibility that, in addition to the Italian electric mix, the EE from biogas replaces the electricity produced from different fossil sources (coal, natural gas and oil) and from different technologies (e.g., combined cycle plant). The CF of electricity from coal, natural gas and oil have been taken from the Ecoinvent database (Ecoinvent, 2015). Table 4 shows the results of the sensitivity analysis.

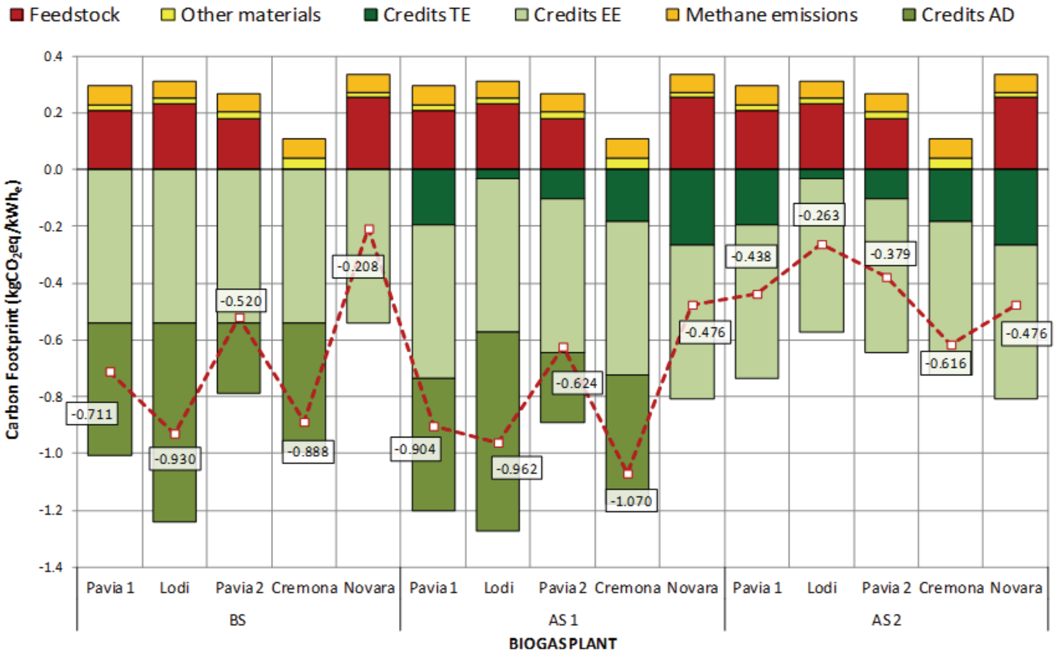

Fig. 2. Carbon Footprint for the five considered agricultural biogas plants, under different scenarios (BS, AS1 – credits for thermal energy valorization and AS2 – no credits for anaerobic digestion of animal slurries)

Table 4. Results of the sensitivity analysis: absolute and comparative (with respect to Baseline Scenario – BS) values

CASE	***Unit***	***BIOGAS PLANT***				
		Pavia 1	***Lodi***	***Pavia 2***	***Cremona***	***Novara***
Electricity mix ITA (BS)	kg CO_2eq/kWh	-0.711	-0.930	-0.520	-0.513	-0.208
Coal	kg CO_2eq/kWh	-1.204	-1.418	-0.921	-0.819	-0.696
	% respect BS	169%	152%	177%	160%	335%
Natural gas “combined cycle plant”	kg CO_2eq/kWh	-0.421	-0.813	-0.316	-0.214	-0.091
	% respect BS	59%	87%	61%	42%	44%
Oil	kg CO_2eq/kWh	-1.054	-1.268	-0.771	-0.669	-0.546
	% respect BS	148%	136%	148%	130%	263%
Natural gas “old technology”	kg CO_2eq/kWh	-0.833	-1.047	-0.550	-0.448	-0.325
	% respect BS	117%	113%	106%	87%	156%

As expected, the replacement of EE produced from different fossil fuels affects the CF of EE from biogas: the more the GHG emissions of the replaced EE are high, the more the CF of electricity from biogas is interesting (higher GHG savings). The highest benefits are achieved when EE from biogas replaces electricity from coal and oil. As regard to electricity from natural gas, it is interesting to underline that, when electricity produced from natural gas in combined cycle plants is substituted, the CF of EE from biogas shows lower GHG savings with respect to the baseline scenario.

5. Conclusions

In this study, we evaluated the carbon footprint (CF) of five agricultural biogas plants characterized by different electrical power and fed with different feedstock. The results showed that electricity production from biogas has huge potential to reduce GHG emissions.

The results highlight the environmental sustainability of anaerobic digestion based on agricultural feedstock as a bearable solution to produce electricity: for all biogas plants evaluated, the CF of EE is negative. Nevertheless, it should be underlined that the favorable CF of biogas bioenergy process is mainly related to the credits obtained from the substitution of electricity generation from fossil fuels. In fact, the biogas process does not sequestrate GHG but it just produces EE substituting the current technology characterized by high GHG emissions. To further improve the environmental sustainability of this bioenergy production process, slurry transport must be minimized and as much as possible of the surplus heat should be valorized substituting heat generation from fossil sources. If possible, instead of feeding the AD plants with cereals silage, they should be fed with animal slurries and agro-food industry by-products. Actually, considering that intensive livestock activities are carried out in some Italian areas (e.g., Lombardy, Emilia Romagna, etc.), there is still availability of animal slurries for biogas production scopes. Therefore, in order to improve the CF of EE from biogas, until this last condition occurs, the feeding with cereals silage and other feedstock from energy crops should not be subsidized, above all in case of new agricultural AD plants.

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CATHODE RAY TUBE (CRT) LEAD GLASS: LEAD LEACHING STUDY AFTER A CHELATING AGENT TREATMENT

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Abstract

This study is focused on the removal of leachable lead present in CRT (cathode ray tube) glass employing different chelating agents, NTA (nitrilotriacetic acid) and ATMP (amino trimetilen phosphonic acid), and then on the evaluation of their extractive capability. The operating conditions are the following: T=80°C, t=1h, pH=10, solid/liquid weight ratio=1/10, reagent concentration= 0.1 M. Afterwards a number of leaching tests at controlled pH were performed in the 5-9 range for 48h at room temperature to define the lead leaching curves for CRT glass matrix and to evaluate the chelating process efficiency.
Experimental leaching curves showed a semi-U-shaped pattern, with maximum lead release at acid pH. Results demonstrated that NTA is able to remove the 66-80% of lead leachable at pH 5.

Key words: chelating agents, leaching tests, lead extractive method, WEEE lead-glass

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1. Introduction

Since the end of the 90s, the re-use of waste electrical and electronic equipment (WEEE) generated over the world has been of great interest. In recent years the replacement of TVs with Cathode Ray Tube (CRT) glass by flat-panel displays caused a drastic increase of WEEE characterized by a high lead content. Discarded computer monitors and television sets are identified as hazardous materials due to the high content of lead in their cathode ray tubes (CRTs). In particular, over 98% of lead is found in CRT glass. Directive 2002/95/EC, on the restriction of the use of certain hazardous substances in electrical and electronic equipment, is not applicable to every product, in fact there are some applications which are exempted from these requirements. An example is the glass from cathode ray tubes which contains PbO ranging from 12 to 25 wt% as protection from X-ray radiation (ICER, 2004).

Today, the disposal of lead-containing glass has become a serious environmental issue. High amount of obsolete electronics including TV and CRT monitors are in storage because appropriate e-waste management and remediation technologies are insufficient. Since leaching is of concern, heavy metals need to be removed before the residual inorganic materials can be disposed of in landfills or otherwise used.

Many approaches for the treatment of CRT glass have been performed mainly from 2009 up to now. Hydrothermal conditions have been applied (Miyoshi et al., 2004), C and CO (Chen et al., 2009; Nakada et al., 2008) and TiC and SiC are exploited to reduced lead to its elemental form (Yot and Méar, 2009). Leaching under acidic conditions was also used for lead recovery by removing lead from

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crushed funnel glass surface by means of nitric acid at 3–5% concentration (Ling and Poon, 2012).

Yuan et al. (2012, 2013) treated CRT glass mechano-chemically by ball milling and removed 92.5% of the lead by diluted nitric acid leaching. Wang and Zhua (2012) extracted lead oxide nanoparticles from cathode-ray tube (CRT) funnel glass using self-propagating high-temperature synthesis method.

Okada et al. (2012) removed most of the lead as metal by reductive melting and immobilized the remaining lead by oxidative melting in such a way that the treated glass passed Japanese legal criteria for recycling. Carboxylates and phosfonates as chelating agents can be used to extract lead from funnel glass (Barbieri et al., 2014; Sasai et al., 2008) and also methods of chlorides volatilization (Grause et al., 2014a, 2014b).

In this paper the effectiveness of two different chelating agents with different functional groups such as the phosphonate group amino trimetilen phosphonic acid (ATMP) and the carboxylate group nitrilotriacetic acid (NTA) was further investigated in order to develop an extraction process efficient and with low environmental impact with regard to both the procedure to be followed (temperature, time, cycles) and the reagents/solvents used.

In particular the study focuses on the definition of the lead leaching curves for treated and untreated CRT glass matrix at different pH. This was achieved by means of leaching tests at controlled pH in the 5-9 range, useful to simulate the real environmental leaching conditions. Lead concentration in eluates was determined through FA-AAS analysis.

The metal-sequestering properties of carboxylates and phosphonates are commonly employed in different products and applications, such as in household detergents, to prevent precipitation of bivalent ions from washing suds and thus avoiding scale deposition on both textiles and washing machine parts; but also in the water treatment, descaling of boilers, in the photography industry, in agricultural fertilizers, during pulp and paper production, for metal finishing and rubber processing, or in food, pharmaceuticals and cosmetics (Egli, 1994).

The development of a novel recycling process for spent lead glass is essential in order to increase the recycling rate with higher efficiency. Pb powder or Pb salts can be obtained from the leaching solution and the Pb-depleted solution reused into the leaching step (Zhang et al., 2013). At the end of the paper a regeneration process of spent chelating agent solution with formation of lead sulphide precipitate was further proposed.

2. Experimental

2.1. Materials preparation

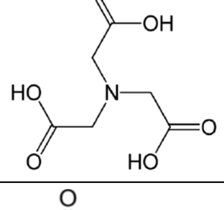
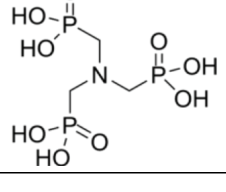
Waste funnel glasses of TVs and PCs monitors were provided by a treatment plant in North of Italy already cleaned from the coating and ground below 2 cm. The glass was firstly dry-ball milled and sieved in order to separate 0.5-1 mm and 1-4 mm particle sizes.

The chelating agents employed, 2,2’,2’’-Nitrilotriacetic acid NTA (≥99% purity) and Amino tris(methylene-phosphonic acid) ATMP (≥99% purity), were used as sodium salts. Their structures are reported in Table 1. For both the chelating agents a solution of 0.1 M was prepared keeping pH fixed around 10 with a buffer solution.

2.2. Total lead concentration of untreated funnel glass

The total lead concentration in funnel glass was determined by a strong acid digestion method. The digestion procedure followed is that indicated by Test Method CPSC-CH-E1002-08 “Standard Operating Procedure for Determining Total Lead (Pb) in Non-Metal Children’s Products” (2009), that for the determination of lead in ceramic, glass, crystal and other siliceous materials refers to EPA Method 3052, “Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices” (1996). For the digestion of the funnel glass an Ethos Touch Control Advanced Microwave LabStation was used.

Table 1. Used chelating agents

Abbreviation	***Name***	***Structure***
NTA	2-[Bis(carboxymethyl)amino]acetic acid; 2,2’,2’’-Nitrilotriacetic acid	
ATMP	Amino tris(methylene-phosphonic acid)	

Lead concentration in digested funnel glass was determined by FA-AAS analysis (Perkin Elmer AAnalyst 400). The result is 186.02 ± 5.34 (mg/g), which is the mean values of three sample digestions. Considering that the PbO concentration in CRT glass shows a wide range of concentration which depends on the lot of sample (from 12 to 25%), this value could not be considered representative of the average lead content in CRT glasses from a treatment plant.

Total lead content in treated glass was not determined since, acting only on the surface lead content, and working with granular and not powdery samples, this was assumed remaining almost constant before and after the chelating agent treatment.

2.3. Chelating agent treatment at T=80°C

For each of the two lead glass particle sizes (0.5-1 mm and 1-4 mm) a treatment with NTA or ATMP chelating agent solutions (0.1 M at pH 10, conditions chosen by a previous work (Barbieri et al., 2014), which demonstrated that alkaline environment favors the reaction) was performed. The lead glass characterized by a specific particle size was sealed in container with chelating agent solution, employing a solid/liquid weight ratio of 1/10. The system was heated at 80°C for 1 h. The treated glass was separated from the chelating agent solutions by settling and washed with distilled water in order to remove any chelating agent traces. The cleaned glass was collected and dried in oven at 110°C overnight.

2.4. Lead leaching tests

A number of leaching tests at controlled pH were performed to evaluate the lead leaching properties of CRT funnel glass and the effectiveness of the chelating agent treatments. In order to simulate the leaching conditions to which CRT lead glass may be exposed to environmental scenarios, a pH range between 5 and 9 was considered.

Leaching tests were performed on both untreated and treated glass. Regarding untreated glass, only 1-4 mm particle size was employed in the tests. The samples were sealed in suitable polypropylene vessels with a solid/liquid weight ratio of 1/10. The system was kept in stirring for 48 h at room-temperature. Set a pH value, the instrument kept it within a narrow range (+/- 0.2). Control was achieved automatically by adding appropriate volumes of acid or base (HNO_3 0.1 M and NaOH 0.1 M) varying from 0.05 mL to over 1 mL. Leaching procedure is in compliance with CEN/TS 14997:2006. Lead concentration in eluates from leaching tests was determined by FA-AAS analysis (Perkin Elmer AAnalyst 400).

2.5. Microstuctural and semiquantitative analyses

The microstructural analysis before and after all the funnel glass treatments was performed by scanning electron microscopy (ESEM, Quanta-200 Fei, Oxford Instruments) equipped with EDS (microanalyzer Inca-350, Oxford Instruments) for the semiquantitative element analysis in particle surface.

In Fig. 1 a flow chart of the overall process is reported.

3. Results and discussion

3.1. Leaching test at controlled pH

The leaching tests results are reported in Fig. 2. Curves represent the lead release trends for different samples. The lead leachable was investigated in different pH in order to simulate the leaching conditions to which CRT lead glass may be exposed to environmental scenarios. For the treated glasses, the determination was performed at pH 5, 6, 8, 9, and the natural pH of water/glass equilibrium (about 7), whereas for untreated glass only pH 5, 9 and system equilibrium one were investigated.

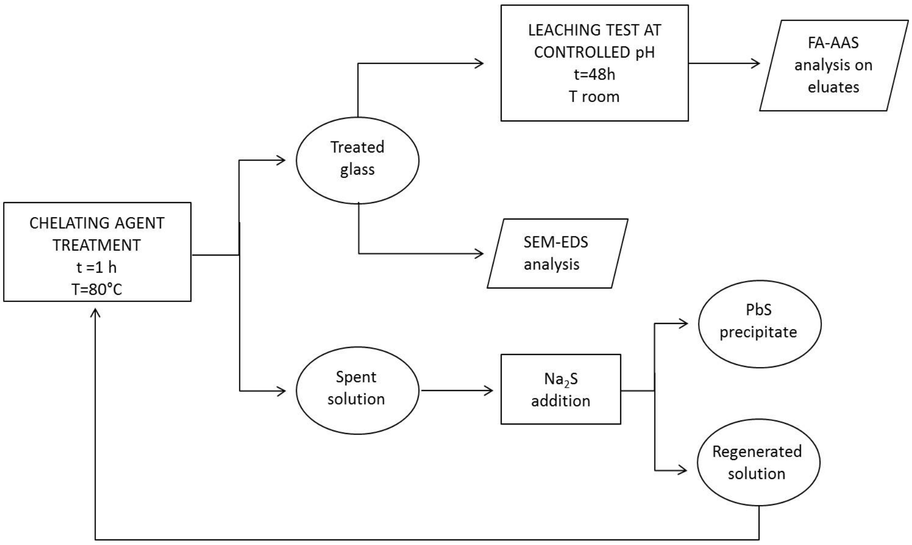


Fig. 1. Flow chart of the process

The experimental leaching curves obtained for glass matrices (Fig. 2) well retrace the theoretical characteristic curves for lead leaching at different pH reported in literature for other matrices. This trend shows a semi-U-shaped pattern, with maximum lead release at acid pH (Centioli et al., 2008, Popovici et al., 2013).

Fig. 2 shows that at pH 5, the pH of interest in the lead extraction as it promotes the higher release, the treatment with NTA produces a Pb leachable reduction of 66-80% depending on particle size (0.29 mg/g released by 1-4 mm treated glass and 0.53 mg/g by 0.5–1 mm treated glass against 1.56 mg/g of untreated glass).

This significant result, obtained using NTA as chelating agent, has not been achieved employing ATMP. In fact the Pb release values for samples treated with ATMP solution were comparable with those obtained for untreated glasses for the same particle sizes. This data suggest that, compared to ATMP, NTA presents a higher chelating capability towards lead in the considered matrix.

As regards the effect of the particle size some consideration should be made. It is noted that glass particle size is a significant factor affecting lead extraction, as the smaller is the particle size the forceful is the leaching, as observed for the glass treated with NTA.

For ATMP an anomalous trend is observable due to the ineffectiveness of the treatment with ATMP especially on the high particle size, so all the surface Pb amount was available from 1-4 mm glass matrix to be leached by the leaching test. On the opposite NTA appears to have been effective on both the particle sizes, and so with equal effectiveness of the treatment the fine particle size is that which released more.

3.2. Microstuctural and semiquantitative analyses

The results of SEM-EDS analyses on 0.5-1 mm treated glasses and untreated glass are reported in Fig. 3. Different areas of the funnel glass were analyzed to obtain the average percentage of surface lead content before and after the treatments. Results are consistent with those obtained from leaching tests. In fact starting from a lead content of 20% average in untreated glass, NTA treatment reduced it to 14.37% (with an extraction percentage of about 28%), where as ATMP did not go below 18.30%.

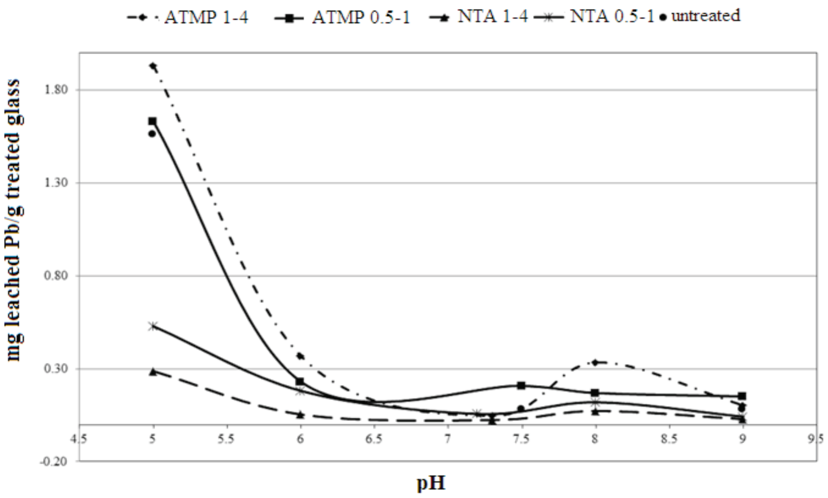


Fig. 2. Quantity of leached lead (mg) for unit of mass (g) of treated lead-glass at controlled pH after 48h

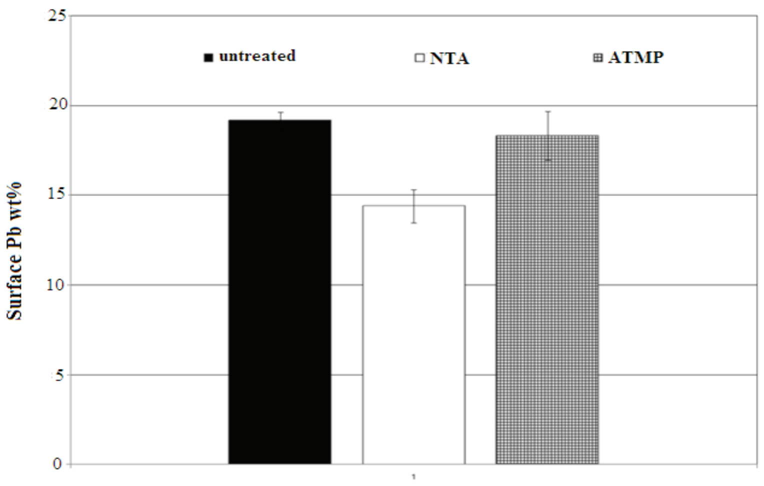


Fig. 3. Average percentage of surface lead content before and after the treatment for 0.5-1 mm particle size glasses

Furthermore, a single 1-4 mm glass grain that was previously treated with NTA (as it proved to be the best chelating agent) was lapped with sandpaper in order to remove the first superficial layers of the glass. SEM-EDS analyses were carried out on both the lapped area not exposed to the treatment and on the surface area directly exposed to the chelating agent solution. As expected, in the lapped area the lead concentration was higher than the un-lapped area (Fig. 4). In the SEM-EDS image reported in Fig. 4 the dividing line between the lapped area (on the right) and the un-lapped area (on the left) is clearly visible.

3.3. Chelating agent solution regeneration

At the end of the lead removal process a treatment of the spent chelating agent solution, the new waste obtained was developed. It allows both the exhausted solution regeneration and the recovery of extracted lead as lead sulphide precipitate. The study of the regeneration process was developed only for NTA solution, since it proved to be more effective in the removal of lead from the funnel glass than ATMP.

Lead was precipitated by adding to the solution an appropriate quantitative of sodium sulphide (Na_2S), a highly water-soluble salt (470 g/l at 10 °C). The reaction that occurs is the following (Eq. 1).

$$NTA\text{-}Pb + Na_2S \rightarrow NTA\text{-}Na + PbS_{(s)} \quad (1)$$

Lead sulphide gradually settles and its high insolubility ($K_{ps}=3.4*10^{-28}$) favours the reaction proceeding. PbS was separated from NTA solution by filtration. In Fig. 5 the XRD spectrum of lead sulphide precipitate is reported.

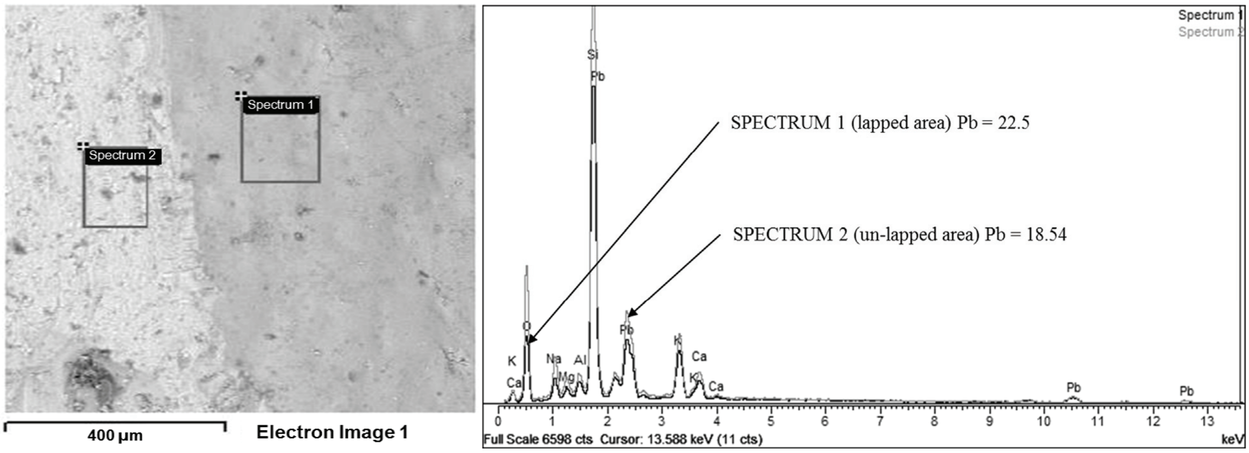


Fig. 4. SEM image and EDS spectra of a 1-4 mm glass grain treated with NTA and lapped with sandpaper

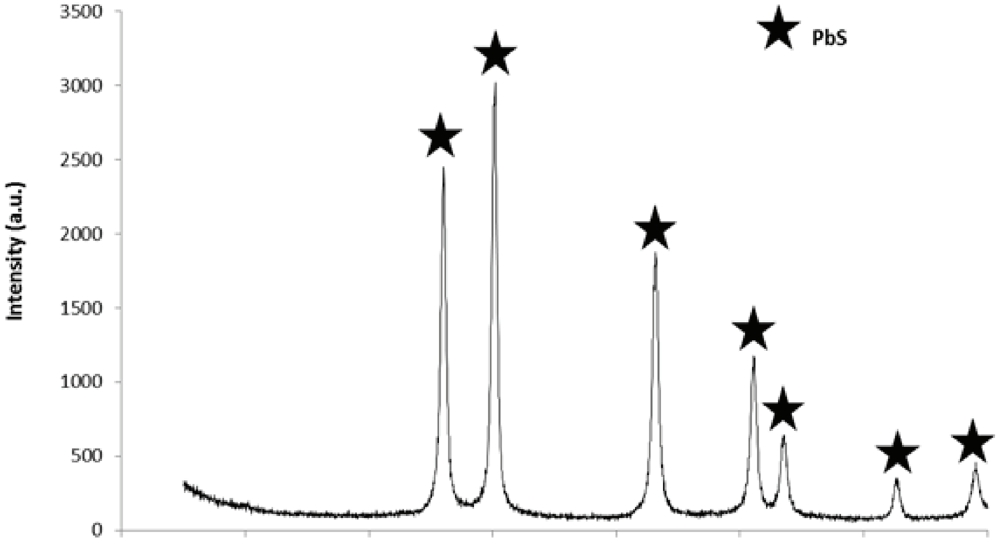


Fig. 5. XRD spectrum of PbS precipitate

4. Conclusions

In the present study the lead leaching from CRT glass was investigated before and after a chelating agent treatment by means of leaching tests at controlled pH for 48h at room temperature. In particular, the 5-9 pH range was considered in order to simulate different environmental scenarios. In accordance with the theoretical characteristic curves for lead leaching at different pH reported in literature for other matrices, the experimental leaching curves obtained for CRT glass showed the higher release at acid pH. Through a comparison of the results obtained for treated and untreated glass, it was found that NTA is an efficient chelating agent in the removal of lead from funnel glass network, since after the treatment at 80°C for 1h at pH 10 lead leachable at pH 5 was reduced for 66-80% depending on particle size (0.29 mg/g released by 1-4 mm treated glass and 0.53 mg/g by 0.5-1 mm treated glass against 1.56 mg/g of untreated glass). On the other hand, ATMP proved to be ineffective in lead removal from WEEE glass.

In terms of benefits, it should be noted that the chelating agent treatment developed is eco-friendly, since the process doesn't need high temperatures (T=80°C) or long time of reaction (t=1h); the solvent utilized is water; NTA is easily biodegradable by various groups of bacteria; considering that the chelating technique maintains the glass natura of the powder, the solid leaching glass residues obtained after Pb removal could be used for the preparation of building materials such as foam glass, glaze, ceramic tiles, cement.

Further aspect of sustainability, the regeneration of the solution by means of Na_2S allows the obtainment of PbS precipitate as secondary product and the solution can be used for new treatment of the glass.

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PARTITIONING DYNAMICS AND FATE OF METALS IN AN URBAN WASTEWATER TREATMENT PLANT

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Abstract

This study focused on the fate of the most representative metals in urban wastewater treatment by the conventional activated sludge process. The research analyzed: distribution between soluble and particulate fraction in the different treatment stages, removal efficiencies as related to partitioning, and metal behavior during rainfall events. A mass balance approach allowed evaluating the behavior of the metals, migration between phases and final fate, in order to investigate metal dynamics during the treatment cycle. Metal distribution between phases in outflow fluxes (treated effluent and sludge) resulted consistent with their partitioning between soluble and particulate fraction in the influent and significant migration between phases was not observed. Arsenic was found to be the most critical element for sludge reuse, despite being mostly partitioned into the soluble fraction.

Key words: activated sludge, arsenic, metals, sludge reuse, wastewater treatment

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1. Introduction

Over the last thirty years, the approach to wastewater treatment has been aimed at improving treated effluent quality, according to regulatory developments and given the increased sensitivity to environmental issues and to the protection of water resources.

Numerous studies have focused on the enhancement of secondary treatment efficiency and the implementation of tertiary processes, such as disinfection and/or refinement of treated water for reuse purposes. As a secondary effect, these innovations have inevitably led to an increase of sludge production per population equivalent (Fytili and Zabaniotou, 2008; Kelessidis and Stasinakis, 2012).

More recently, also by reason of tightening of regulations on landfill disposal and more stringent requirements for agricultural and energetic reuse, technologies aimed at reducing sludge production and improving its quality, in order to promote recovery/reuse are gaining increasing interest.

In this sense, it is essential a better understanding of partitioning dynamics and removal processes of potential pollutants, such as metals, and to investigate on the possibility of adopting targeted measures, aimed at reducing their concentrations in sludge. However, given the conservative behavior of metals, migration between phases does not result in removal but simply in a transfer of the impacted area from the solid matrix to the receiving water body, which should therefore be assessed in relation to the overall environmental benefits.

2. Outline of the work

On the basis of European and Italian regulations, wastewater sludge is classified according to the European Waste Catalogue (EWC, 2002) with the Code 19 08 05 ("Sludge from treatment of urban waste water").

In Italy, landfilling has been the most widely used method for wastewater sludge disposal (EC,

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2010), until recent regulations (Decree, 2005) introduced more stringent measures. In light of the new standards, landfill disposal of urban wastewater sludge is expected to cease, because of Total Organic Carbon (TOC) content in sludge and of Dissolved Organic Carbon (DOC) concentration in the eluate; anyway, the impossibility to apply the new rules immediately has led to grant extensions in order to implement interventions and organize alternative reuse systems and strategies.

Wastewater sludge management is thus a highly relevant and important issue, also because of the energetic and agronomic properties of the sludge itself. Sludge reuse in agriculture as a soil conditioner is viewed positive because of the organic matter and nutrient contents, and it can be carried out by two different techniques: a) direct spreading on the soil, after stabilization processes and if complying with chemical-physical requirements set by EC Directive (1986) and its national transposition, the Italian Legislative Decree n. 99/1992 (Decree, 1992). Similarly, the calorific value of the organic matter makes wastewater sludge suitable for energy recovery and therefore to be treated by dedicated waste to energy plants, or in co-combustion with other fuels.

In this case, in systems operating according to the simplified procedure, sludge combustion is allowed after compliance with the requirements set by the technical standards of the Decree of the Italian Environment Ministry 05/02/1998 (Decree, 1998). Both for agricultural reuse and energy recovery purposes some issues are posed, on one hand concerning the safety of agricultural products and of the workers employed in spreading operations and the other hand related to the potential environmental impacts. EC Directive (1986) on agricultural land treatment is currently under revision, and a tightening of limits and a review of the parameters could be introduced; moreover, some Italian regions (Emilia Romagna, Lombardia) have already issued supplementary regulations to the national laws, by introducing additional inorganic and organic parameters and restricting some of the quality standards.

Heavy metals represent the category of parameters more involved in the above revision processes, as a consequence of their characteristic tendency to accumulate; gaining a better understanding of their presence and behavior is therefore essential, in order to address sludge management strategies, also in relation to the evolution of the regulatory framework concerning the different reuse systems.

3. Case study

The main object of the current study was to investigate dynamics and final fate of the most representative metals in conventional wastewater processes, such as the activated sludge systems. Based on a mass balance approach, partitioning between soluble and particulate fraction and distribution in the different treatment stages were considered, in order to evaluate removal efficiency, behavior, migration between phases and final fate in the output flows of the systems.

Behavior during rainfall events has also been studied. The study was carried out at a wastewater treatment plant (WWTP) located in Rome metropolitan area, with average input flow-rate 3.0 m^3/sec; treated effluent is discharged into the Tiber river.

The water line is made of a pretreatment stage and two identical process trains, each including two parallel primary clarifiers, an activated sludge unit and two parallel secondary clarifiers. The sludge line includes pre-thickening, anaerobic digestion (not operating during the study), post-thickening and dehydration with centrifuges. Fig. 1 describes the process diagram of the WWTP showing the location of the sampling points.

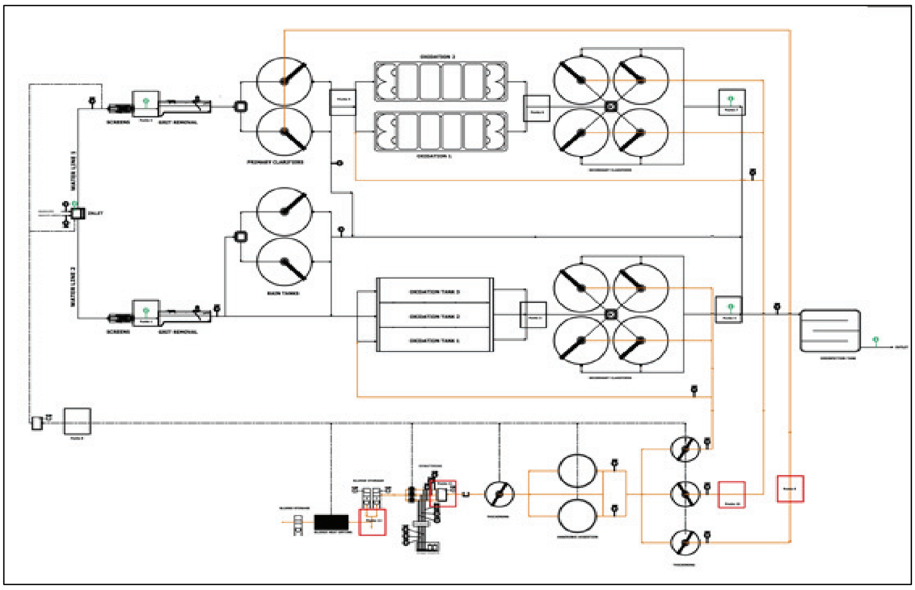


Fig. 1. Process diagram of the wastewater treatment plant

4. Material and methods

Monitoring campaigns based on regular and systematic sampling of influent, treated effluent and sludge were carried out, weekly/fortnightly, for a period of 15 months. Composite samples were taken, constituted by the assembling of subsamples collected on a hourly basis by means of automatic samplers. At the same time, discrete samples were also drawn, in order to assess comparability between the average data collected through composite and discrete sampling. Discrete sampling on the water treatment line and sludge was carried out according to international methods (APHA-AWWA-EF, 2005).

Wastewater samples were taken at 8 monitoring points: influent; effluent from primary sedimentation (first and second train); effluent from activated sludge unit (first and second train); effluent from secondary sedimentation (first and second train); treated effluent.

Sludge samples were collected at 4 locations: secondary sludge from first and second train; inlet and outlet of dehydration. Supernatants from the sludge treatment line were also sampled. Altogether for each sampling campaign 13 treatment stages were monitored; a total of 28 campaigns were carried out. Analyses were performed with methods accredited by the Italian accreditation body Accredia under UNI CEI EN ISO/IEC 17025 Quality Procedures.

Table 1 lists analytes, methods and related quantification limits (LOQ), both for water and sludge samples. Dissolved metals were determined after filtration of the sample through 0.45 um filters.

During monitoring campaigns, flow-rate data of the main fluxes of both the water and the sludge treatment lines were collected.

5. Results and discussion

5.1. Influent

Table 2 shows metal concentrations in the influent both for discrete and composite samples. For statistical purposes, concentrations below the detection limits were taken as equal to the detection limit itself.

Comparison of analytical results from composite and discrete samples shows that concentrations found are in a strictly close agreement, which is consistent with what might be expected for an urban wastewater treatment plant receiving no anthropogenic inputs from industrial activities. Metal concentrations in the influent were extremely low, such as to comply or at least be comparable with quality standards set for drinking water (EC Directive, 1998). The graph below (Fig. 2), in logarithmic scale to allow visualization of the trends for all parameters, compares statistical figures (minimum, maximum, average, median) of influent composite samples with quality standards for drinking water.

5.2. Treated effluent and metal removals efficiency

Table 3 shows treated effluent concentrations of metals both for discrete and composite samples.

Table 1. Parameters, analytical methods and instrumental detection limits

	WATER SAMPLES		***SLUDGE SAMPLES***	
	LOQ µg/L	***Method***	***LOQ mg/kdDW***	***Method***
Cu	1.0	APHA SM2005 3030K+3125	1.0	EPA 3052 1996+EPA 6010 C 2007
Pb	0.2	APHA SM2005 3030K+3125	1.0	EPA 3052 1996+EPA 6010 C 2007
Ni	2.0	APHA SM2005 3030K+3125	1.0	EPA 3052 1996+EPA 6010 C 2007
Zn	1.0	APHA SM2005 3030K+3125	1.0	EPA 3052 1996+EPA 6010 C 2007
Cd	0.2	APHA SM2005 3030K+3125	1.0	EPA 3052 1996+EPA 6010 C 2007
Cr	5.0	APHA SM2005 3030K+3125	1.0	EPA 3052 1996+EPA 6010 C 2007
As	1.0	APHA SM2005 3030K+3125	4.0	EPA 3052 1996+EPA 6010 C 2007
Hg	0.2	EPA 7473 2007	0.001	EPA 7473 2007
Mn	0.2	APHA SM2005 3030K+3125	1.0	EPA 3052 1996+EPA 6010 C 2007

Table 2. Metal concentrations in WWTP influent

Concentration (µg/L)		Cu	Pb	Ni	Zn	Cd	Cr	As	Hg	Mn
WWTP INFLUENT Discrete Samples	***Minimum***	9.1	2.9	1.4	44.7	0.2	5.0	3.3	0.2	34.4
	Average	26.4	12.5	3.5	105.2	0.2	5.5	5.0	0.2	90.4
	Maximum	63.4	32.9	7.6	216.2	0.3	10.5	8.8	0.5	213.4
	Median	23.5	11.8	2.8	95.4	0.2	5.0	4.8	0.2	83.7
WWTP INFLUENT Composite Samples	***Minimum***	5.9	2.2	1.3	31.1	0.2	5.0	3.0	0.2	29.9
	Average	31.4	12.8	4.4	195.2	0.2	5.8	4.9	0.5	90.8
	Maximum	98.6	41.5	8.6	841.6	0.6	11.1	10.2	6.1	159.2
	Median	23.4	9.0	3.8	109.0	0.2	5.0	4.8	0.2	88.0

Table 3. Metal concentrations in WWTP effluent

Concentration (µg/L)		Cu	Pb	Ni	Zn	Cd	Cr	As	Hg	Mn
WWTP EFFLUENT Discrete Samples	***Minimum***	1.0	0.3	1.0	7.9	0.2	5.0	2.7	0.2	14.8
	Average	5.8	2.6	2.6	37.3	0.2	5.0	3.7	0.2	61.6
	Maximum	14.7	6.0	10.0	68.6	0.2	5.5	5.2	0.4	110.8
	Median	5.1	2.5	2.2	34.0	0.2	5.0	3.6	0.2	62.4
WWTP EFFLUENT Composite Samples	***Minimum***	1.0	0.2	1.0	2.2	0.2	5.0	1.0	0.2	1.9
	Average	5.9	2.8	3.6	37.1	0.2	5.0	3.6	0.2	63.6
	Maximum	15.8	6.2	39.6	71.8	0.2	6.3	4.9	0.5	97.3
	Median	5.7	2.8	2.3	36.9	0.2	5.0	3.4	0.2	61.9
EFFLUENT LIMITS (discharge in surface water)	***Parametric value***	400	300	4,000	1,000	20	4,000	500	5.0	4,000

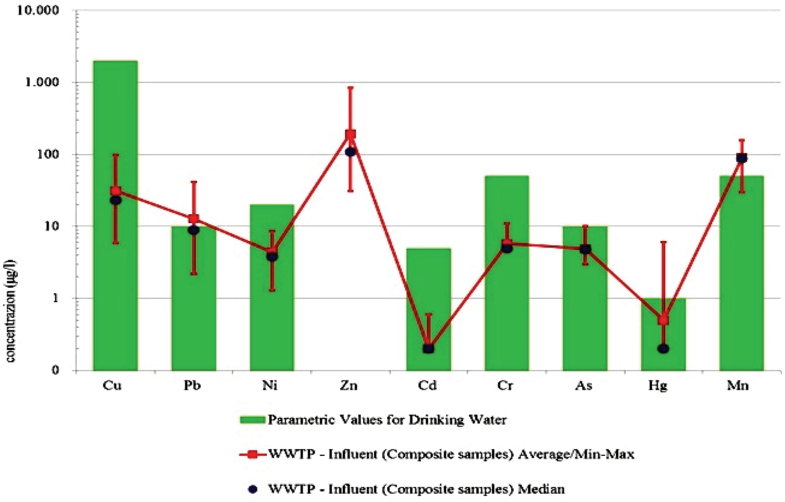


Fig. 2. Comparison between drinking water quality standards (EC Directive, 1998) and values in WWTP influent

Treated effluent concentrations were low, with values significantly below the standards for discharge into surface water (EC Directive, 1998). Average concentrations were lower than the limits by a factor, dependent on the metal, ranging from 15 for Zinc and 1,000 for Nickel.

Fig. 3 shows overall removal efficiency in the liquid stream, based on composite sample results, for all metals except for cadmium and mercury, whose concentrations both in influent and treated effluent samples often resulted lower than the instrumental detection limit.

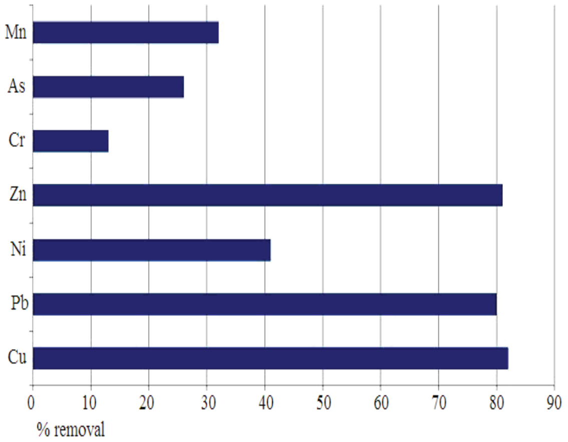


Fig. 3. Overall removal efficiencies of WWTP

Removal computed from discrete samples exhibited a similar trend. The chart shows that, despite urban wastewater treatment plants are not designed for removing metals, significant removal efficiencies are obtained, especially for lead, zinc, and copper.

5.3. Dewatered sludge

The analysis of the residual solid fraction shows that, contrary to results for the treated effluent, in which concentrations were significantly below discharge standards, in sludge average values were close to the levels allowed for reuse (Table 4). Concentrations found are in good agreement with other studies (Chipasa, 2003; Hoss et al., 2001; Mayr, 2005).

Data show as many parameters can often reach critical concentrations, especially arsenic, which was found to constantly exceed the standards for energy reuse and specific standards set by some Italian regions for agronomic use.

To verify the representativeness of the data acquired from the treatment plant considered by the present study, they were also compared to the average values obtained from WWTPs of the same territorial context and similar capacity and process diagrams (Fig. 4); the graph shows that the values taken from different treatment facilities were fully comparable.

Table 4. Results in dewatered sludge

Concentration (mg/kgDW)	*Cu*	*Pb*	*Ni*	*Zn*	*Cd*	*Cr*	*As*	*Hg*	*Mn*
Average	279	128	29	758	1.3	34	12	1.2	203
Median	250	124	25	722	1.3	33	13	1.2	177
Land Application, EU; Directive 1986/278/EEC	1,000÷1,750	750÷1,200	300÷400	2,500÷4,000	20÷40	-	-	16÷25	-
Land Application, Italy; Legislative Decree 99/1992	1,000	750	300	2500	20	-	10(1)	10	-
Incineration, Italy; Environment Decree 05/02/98	300	200	40	-	7(2)	100	9	7(2)	400
Secondary solid fuels; CTI (2012) – Recommendation 8/2012	2,000	600	200	-	10	500	15		600

(1) Regional limits Emilia Romagna (DRG 285, 2005); (2) Sum Cd + Hg

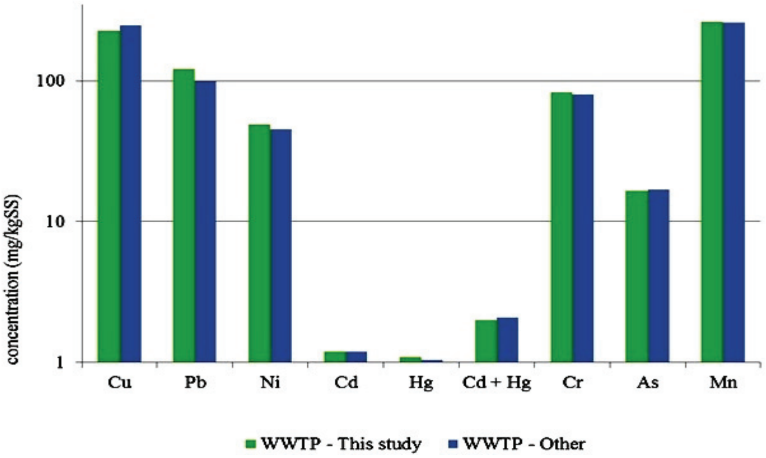


Fig. 4. Metal concentrations in sludge from this study compared with results from another WWTP

5.4. Influence of polyelectrolyte

In order to investigate on possible contribution to the concentration of metals in sludge from polyelectrolyte used in sludge treatment, a sample of polyelectrolyte was analyzed. Table 5 shows obtained results in the polyelectrolyte and its relative contribution to the metal content in sludge, computed based on quantities used daily. As shown, the contribution of polyelectrolyte can be considered negligible in comparison to the average concentrations in sludge.

Table 5. Metal contributions from polyelectrolyte

Metal	*POLYELECROLYTE Concentration (mg/kg)*	*DEWATERED SLUDGE Contribution from polyelecrolyte (mg/kgDW)*
As	<1	0.005
Cd	<0.25	0.001
CR	0.528	0.003
Cu	11.3	0.061
Pb	3.92	0.021
Mn	0.5	0.003
Ni	<0.25	0.001
Zn	16	0.086
Fe	13.5	0.073

5.5. Metal concentrations during rainfall events

In order to investigated metal behavior during rainfall events, a collector-sewer to the treatment plant was monitored during a forecasted intense rainfall, following a dry weather period. Monitoring was carried out between 6.30 - 13.30, sampling wastewater with an automatic device every 20 minutes. During the event there was a peak of 100 mm rainfall at 8.30. Trends resulted for the various metals are shown in Fig. 5.

All metals showed a significant increase in concentration during the monitored period; maximum values were observed two hours after the rainfall peak, and levels higher than reference value recorded during dry weather conditions continued for a few hours.

By analyzing the concentrations of individual metals in the observation period the following trends were found:

- zinc and copper showed a concentration peak 20 times higher than the average value during dry weather;
- arsenic, nickel, manganese and lead peaks exceeded by more than 100 times the average influent concentration during dry weather.

The survey found that intense rainfall events after dry weather periods cause, for limited periods, significant increases of metal contents in WWTP influents.

These increases, anyway, were not reflected on metal concentrations of treated effluent composite sample and sludge, for two reasons:

- by reason of the hydraulic residence time of the system and of the production time span of dehydrated sludge;
- because of the dilution determined by rain events in the medium term.

5.6. Metal partitioning between soluble and particulate fraction

In order to understand removal mechanisms, partitioning of each metal between soluble and particulate fraction in influent and effluent was determined. Average values on composite samples are shown in Fig. 6.

Fig. 7 compares, for each metal, the percent fraction of soluble and particulate metals in the raw influent with the overall percent removal efficiency of the treatment plant.

Cadmium and mercury are not represented, as their concentrations in the influent were lower than instrumental detection limits. Removal efficiencies are evidently linked to the removal of the particulate fraction, in it self associated with the reduction of Total Suspended Solids (TSS); the amount not removed is clearly connected with the dissolved fraction, which remains in the treated effluent.

Keeping into account metal partitioning between soluble and particulate fraction in both influent and treated effluent, the Figs. 6 - 7 show that the dissolved fraction, indeed, for all metals considered by this study does not undergo significant changes with treatment. Manganese represents the only significant or most marked exception, since a part of its dissolved fraction is removed.

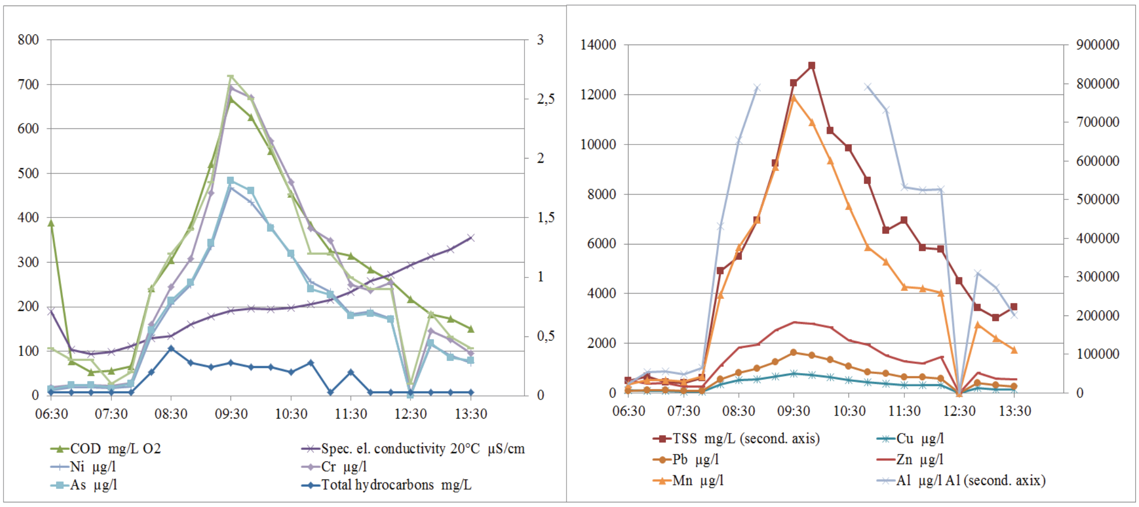
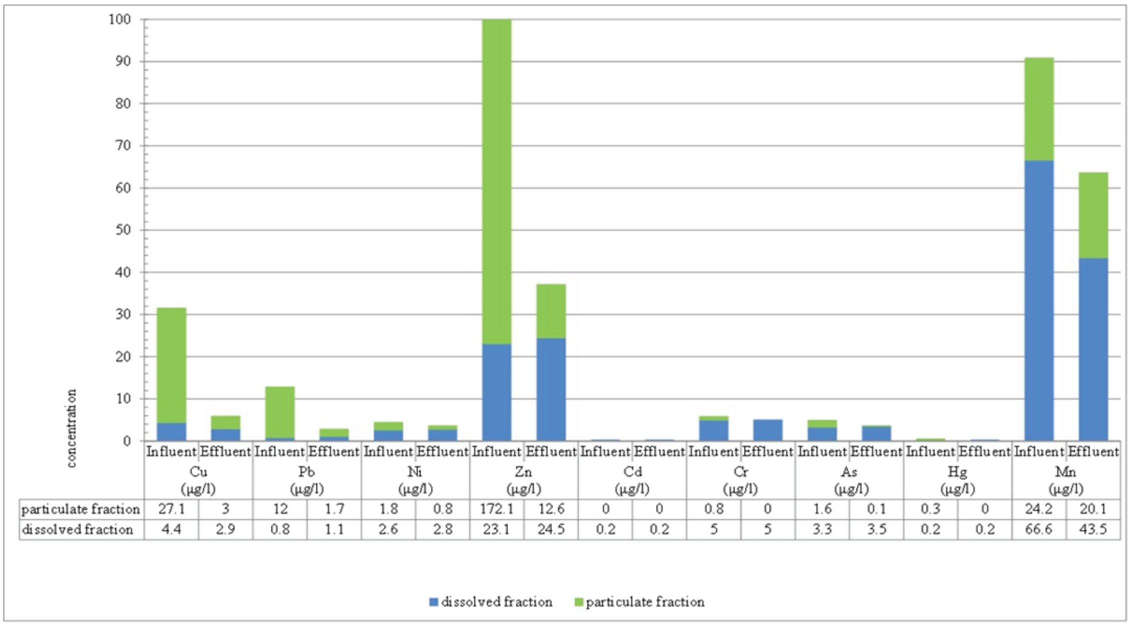


Fig. 5. Metal concentrations in WWTP influent during intense rainfall



	Influent Cu (µg/l)	Effluent Cu (µg/l)	Influent Pb (µg/l)	Effluent Pb (µg/l)	Influent Ni (µg/l)	Effluent Ni (µg/l)	Influent Zn (µg/l)	Effluent Zn (µg/l)	Influent Cd (µg/l)	Effluent Cd (µg/l)	Influent Cr (µg/l)	Effluent Cr (µg/l)	Influent As (µg/l)	Effluent As (µg/l)	Influent Hg (µg/l)	Effluent Hg (µg/l)	Influent Mn (µg/l)	Effluent Mn (µg/l)
particulate fraction	27.1	3	12	1.7	1.8	0.8	172.1	12.6	0	0	0.8	0	1.6	0.1	0.3	0	24.2	20.1
dissolved fraction	4.4	2.9	0.8	1.1	2.6	2.8	23.1	24.5	0.2	0.2	5	5	3.3	3.5	0.2	0.2	66.6	43.5

Fig. 6. Metal partitioning in WWTP influent and effluent

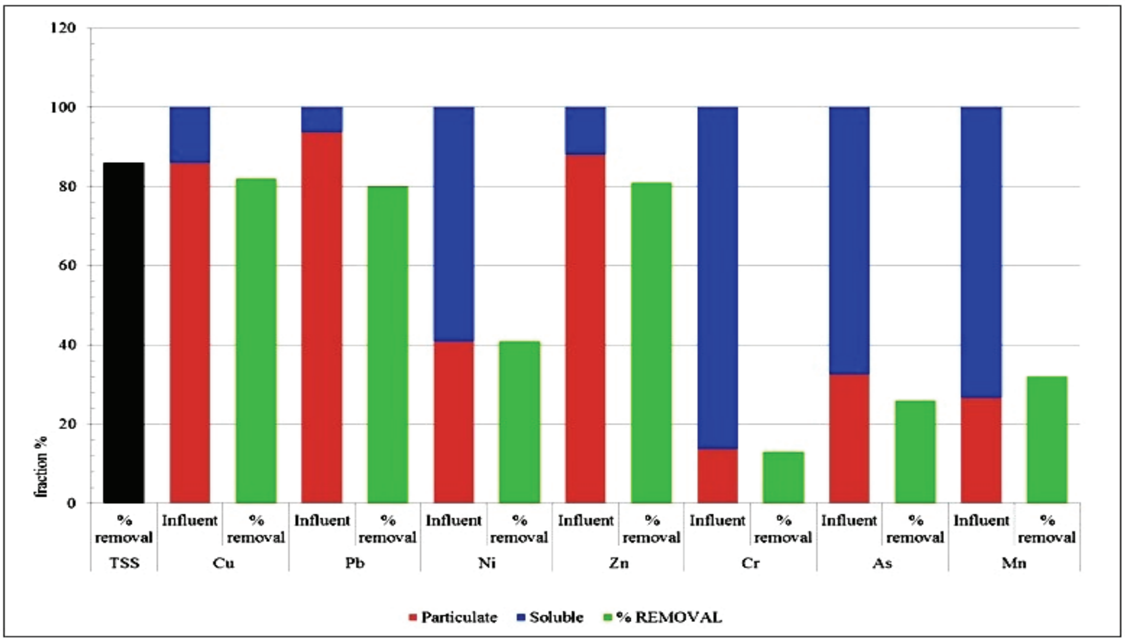


Fig. 7. Metal partitioning in WWTP influent and removal efficiency

5.7. Mass balances

Given the close agreement between data from composite and discrete samples, the discussion of the results of mass balances and partitioning between dissolved and particulate phase will be presented by analyzing the results from the composite samples only. Mass balances were drawn for each metal, based on the average flow-rate values taken at the different plant units, and on the average concentrations detected over the course of monitoring. Overall results are summarizes hereafter (Table 6).

Table 7 shows, for each metal, influent and effluent loads of the WWTP, partitioned between dissolved and particulate phases, both as kg/d and percentage. Influent and treated effluent loads are computed based on the results of composite samples.

With reference to the mass balances, percentage distributions of the metals in the output flows (treated effluent and dewatered sludge) were found, as shown in Fig. 8.

Metal behavior was found consistent with their partitioning between the soluble and particulate fractions in influent wastewater; this allowed defining four different clusters:

- CLUSTER 1 - copper, lead and zinc: these metals showing a predominant distribution in the particulate phase (around 70-80%) and high tendency to accumulate in sludge;
- CLUSTER 2 - arsenic, manganese and chromium: characterized by being partitioned mostly in the soluble phase (about 70-90%), were mainly found in the effluent;
- CLUSTER 3 - nickel: exhibited an intermediate behavior, being equipartitioned between particulate and soluble fraction;
- CLUSTER 4 – mercury and cadmium: they cannot be classified, as generally present at concentrations below the detection limits.

With reference to the process chain considered in this work and based on mass balances and removal efficiencies, the data below (Table 8) show how influent concentrations of metals are distributed in the two output flows. Besides, it also allows highlighting the influent concentrations that produce metal concentrations found in dewatered sludge.

Arsenic was found mostly partitioned in the soluble phase of plant influent (74%) and its contribution to the sludge content was only 26% of the input loading. Despite this, because of the stringent quality standards set by some Regional authorities, mass balances indicate that with average influent values around 6 μg/L, a transfer of 1-2 μg/L to the sludge is enough produce non-conformity with quality standards set for agronomic or energy reuse.

6. Discussion

Ziolko et al. (2011), in their extensive review, highlighted the scarcity of recent studies on metal removal efficiency in the activated sludge process, and that both metal concentrations and their partitioning between soluble and particulate phases in influent wastewater have been found to be rather variable in different locations. Some recent data on metal concentration in dewatered sludge from urban wastewater treatment plants are reported in Table 9.

Concentrations appear highly variable especially for copper, nickel and chromium; data from this study are mostly in the low-middle range, except for arsenic, whose average value is very close to that found by Van der Velden et al. (2008).

Table 6. Metal mass loadings in WWTP influent and effluent

	Cu (kg/d)	***Pb (kg/d)***	***Ni (kg/d)***	***Zn (kg/d)***	***Cr (kg/d)***	***As (kg/d)***	***Mn (kg/d)***
WWTP influent (Avg composite sample)	8.14	3.33	1.14	50.60	1.49	1.28	23.54
WWTP effluent (Avg composite sample)	1.54	0.72	0.94	9.61	1.31	0.93	16.48
Dewatered sludge	7.40	3.38	0.76	20.09	0.90	0.33	5.39

Table 7. Metal loading and partitioning in influent and effluent (composite samples)

	Cu	***Pb***	***Ni***	***Zn***	***Cr***	***As***	***Mn***
Partitioning							
Influent - particulate (kg/d)	7.01	3.12	0.48	44.61	0.20	0.42	6.27
Influent – soluble (kg/d)	1.13	0.21	0.66	5.99	1.30	0.85	17.26
Effluent - particulate (kg/d)	0.79	0.44	0.21	3.25	0.01	0.02	5.19
Effluent – soluble (kg/d)	0.75	0.28	0.74	6.36	1.30	0.91	11.29
Percent partitioning							
Influent - particulate %	86%	94%	42%	88%	13%	33%	27%
Influent – soluble %	14%	6%	58%	12%	87%	67%	73%
Effluent – particulate %	51%	61%	22%	34%	1%	2%	32%
Effluent – soluble %	49%	39%	78%	66%	99%	98%	68%

Table 8. Concentration and daily loads in WWTP input and output flows

			Cu	Pb	Ni	Zn	Cr	As	Mn
INPUT	***WWTP Influent***	Avg conc. comp. sample (µg/L)	31.4	12.8	4.4	195.2	5.8	4.9	90.8
		Daily load (kg/d)	8.14	3.33	1.14	50.60	1.49	1.28	23.54
OUTPUT	***WWTP Effluent***	Avg conc. comp. sample (µg/L)	5.9	2.8	3.6	37.1	5.0	3.6	63.6
		Daily load (kg/d)	1.54	0.72	0.94	9.61	1.31	0.93	16.48
	Dewatered sludge	Avg conc. (mg/kg DW)	279	128	29	758	34	12	203
		Daily load (kg/d)	7.40	3.38	0.76	20.09	0.90	0.33	5.39

Table 9. Metal concentration in dewatered sludge (mg/kgDW)

	Cu	***Pb***	***Ni***	***Zn***	***Cd***	***Cr***	***As***	***Hg***	***Mn***
This study	279	128	29	758	1.3	34	12	1.2	203
Van der Velden et al. (2008)	300	162	38.7	1581	4.5	85	10.5	1.1	-
Zorpas et al. (2011)	141.9	82.0	15.55	287.6	0.775	11.01	-	-	177.3
Guillemet et al. (2009)	238.9	81.2	22.5	934.6	3.0	47.8	3.5	1.2	-
Bright and Healy (2003)	1300	96	68	760	5.7	91	6.1	-	-
da Silva Oliveira et al. (2007)	391.7	132.1	239.4	864.4	1.34	195.0	1.14	0.31	208.1
Höss et al. (2001)	278.89	96.61	61.59	1320.60	2.88	88.27	-	-	-
Dimitriou et al. (2006)	770	36	21	875	1.8	27	-	-	-
Hernández-Sánchez et al. (2013)	37.05	26.44	8.04	544.01	-	24.10	-	-	-

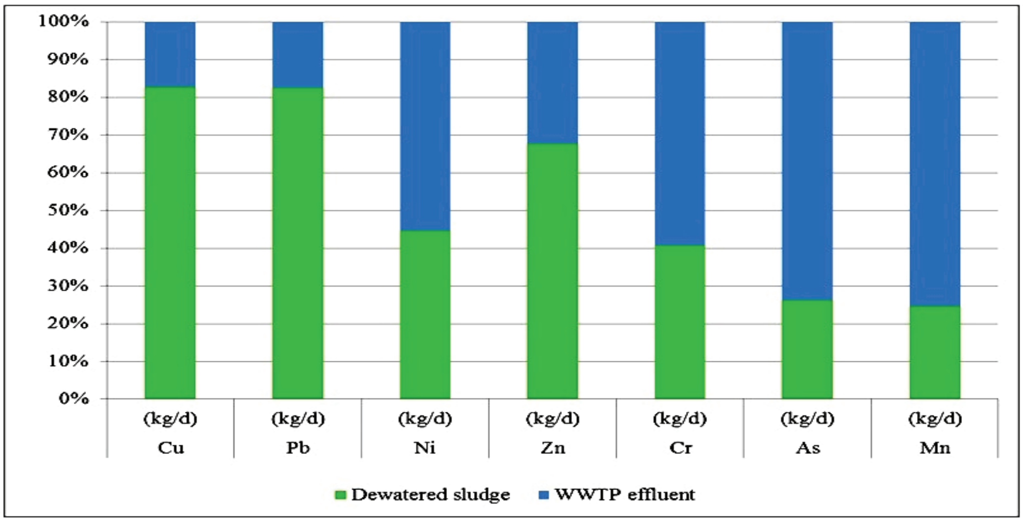


Fig. 8. Metal distribution in WWTP effluent and dewatered sludge

Buzier et al. (2006), on a large size activated sludge plant, found that after secondary treatment lead and copper, mostly distributed in the particulate phase, were removed with efficiencies around 70%, whilst nickel removal efficiency was found to be about 25%. These removal efficiencies are slightly lower than the ones in the present study, in which, anyway, percent particulate fractions were found higher.

Petrie et al. (2014) on a pilot scale activated sludge plant found zinc, copper and lead removal efficiency up to 70-80%, depending on both hydraulic and sludge retention time.

Manganese removal efficiency is highly variable and recent literature reports values in the range 10÷50% (Gulyás et al., 2014; Silva Oliveira et al., 2007). In this study manganese was the only metal with the soluble fraction significantly affected by treatment, as shown in Fig. 6; dissolved manganese is indeed subjected to change in oxidation state from soluble Mn(II) to insoluble Mn(IV) during aerobic treatment, this allowing to improve removal (Karvelas et al., 2003).

7. Conclusions

Average metal concentrations in plant influent and treated effluent were found extremely low. The study confirms previous findings that metal partitioning between soluble and particulate phases plays a key role on their removal efficiency in activated sludge process. Mass balances based on partitioning show that output fluxes respectively to receiving waters (liquid stream) and sludge are in most cases consistent with metal distribution between the soluble and particulate phases in raw wastewater. Migration between phases was not observed for any metal, with the exception of manganese, whose dissolved fraction was significantly removed (about 35%) from the liquid stream.

Results on dewatered sludge highlight possible critical situations, particularly with respect to the concentrations of arsenic, although the concentration of arsenic removed from the influent and transferred to the sludge was only 1-2 μg/L.

Alternative treatment chains or dedicated units could transfer critical metals from the solid to the liquid phase; anyway, these options should be assessed in relation to the overall environmental benefit.

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THE EXPERIENCE OF THE FIRST INDUSTRIAL SYMBIOSIS PLATFORM IN ITALY

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Abstract

This paper reports the activity, promoted by the Italian agency for new technologies, energy and sustainable economic development (ENEA), in the framework of the project for the development and implementation of the first Italian Platform for Industrial Symbiosis implemented in Sicily (2011-2015). The goals of the project were: to provide a methodology and an instrument for industrial symbiosis implementation at regional scale, to implement a IS Platform as a support to SMEs to individuate symbiosis opportunities in the region.

The whole approach includes: network activation, platform architecture design and implementation, analysis of the productive sector in Sicily, data collection and companies involvement. In particular the paper focuses on the activities developed for companies' network creation trough a preliminary analysis of the predominant productive sectors followed by the organization of operative meetings in Sicily for companies' involvement, analysis of potential synergies and resources sharing, and finally platform population. During the first two meetings more than 80 SME were linked giving rise to almost 400 output resources and almost 180 input resources. More than 690 potential matches were found between the participating enterprises showing interesting opportunities both for substituting resources with waste products in real and virtual cases and for sharing waste management services and infrastructures. The discussion occurred during the meeting has remarked the significance and the consequences of the regulatory and control system on IS application, underlining the necessary participation of local stakeholders and control authorities. It has also emerged the need to identify predominant productive activities in well-defined territorial contexts where to investigate the specific/local tangles taking into account legislative and technical-economic feasibility. Technical dossiers on three main resource streams (wastes from processing stone materials; plastics and agro-industrial wastes), which may generate the more interesting potential synergies, are being processed. These dossiers include European, Italian and regional regulations, guidelines, technical standards, logistic and economical aspects useful for supporting companies in synergies implementation. Results of this activity will also be used to improve the algorithm in the platform to find synergies.

Key words: industrial symbiosis, platform, resources, synergies, waste

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1. Introduction

In industrial ecosystems efficiency and optimization of resources and energy, waste minimization and enhancement of the products represent an important strategy in a perspective of circular economy (Atasu et al., 2008). Industrial ecology is aimed at closing and optimizing cycles of matter and energy (Bringezu, 2003; den Hond, 2000; Korhonen, 2007), developing a systemic approach of the industrials systems (Graedel and Allenby, 2003).

Industrial symbiosis (IS), which represents one of the main features of industrial ecology, aims to increase the efficiency in the use of materials and

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energy (Chertow, 2004). It examines cooperative management and exchange of resource flows—particularly materials, water, and energy—through clusters of companies (Chertow and Ehrenfeld, 2012).

IS approach reflects the recent European strategies of decoupling economic growth, environmental impacts and natural resource consumption through the promotion of a more sustainable circular economy as clearly identified in different programming and financing documents of the European Commission (EU COM, 2011, 2012, 2014a, 2014b).

IS application at local scale can contribute to the systematic reuse of waste and by-products, which minimizes the need to extract natural resources and the depletion of environment, according to the internationally recognized waste hierarchy (EU, 2008). Within this framework, a market of secondary resources and services arises, which should be promoted and accelerated within companies. Each member state of the EU must internally adopt and adapt the European policy to overcome the legal and administrative hurdles pertaining to the condition of by-products and the end of a waste product's life (Costa et al., 2010).

In this regard huge efforts are being made to define the criteria that waste flows must meet in order to no longer be considered as waste. These include criteria for aggregates, paper, glass, metal, tires and textiles. Criteria have already been approved for scrap metal, glass and copper. A waste declassification would help companies reduce the uncertainty of trade-off and realize the value from wastes with a risk that can be accepted by them in the direct marketing of the secondary products. Therefore the whole process for IS application pass through a sensitization of public authorities, political actors and stakeholders on IS benefit waste declassification needs. For this reason in recent years ENEA promoted several activities at both regional and national scale for enterprises, stockholders sensitization on IS environmental and economic benefit and for authorities and public actors involvement in the process of waste declassification.

With specific regard to existing models of industrial symbiosis it is possible to differentiate a first model of a cluster of companies in a geographically confined space which exchange resources often called an eco-industrial park. The second model is a network of companies that has no strict requirement of geographical proximity, often spread over large areas (Agarwal and Strachan, 2006). The spatial scale most suitable for cycling has been largely investigated by many authors (Lambert and Boons, 2002; Lyons, 2005; Sterr and Ott, 2004; Yang and Lay, 2004). Lombardi and Laybourn (2012) state that the possibility for IS application is no longer limited in geographical proximity.

There is no preferable spatial scale at which loop closing should be organized: loop closing is dominated by the spatial economic logic of the transactions of the involved firms (Lyons, 2007). Larger regional areas, in fact, may be more suitable for closing material loops and creating sustainable industrial ecosystems. Larger areas may provide the necessary volumes to achieve the economies of scale required to ensure profitability, especially because heterogeneous wastes are generally dispersed widely across space and have often low economic value. Larger areas provide a greater variety of potential customers to consume the newly reconstituted items and solve problems of redundancy by providing alternative customers if or when a particular cycling transaction fails (Posch, 2004; Sterr and Ott, 2004).

Location may be useful to create possibilities for firms to work collaboratively towards more environmentally friendly designs, more effective waste management, and beyond (Chertow and Ehrenfeld, 2012). Jensen et al. (2011) conducted an interesting statistical analysis of synergies facilitated by the United Kingdom's National Industrial Symbiosis Programme (NISP), which represents the first national facilitated industrial symbiosis pilot programme. This article attempts to quantify geographic proximity and in the process provide practitioners with an insight into the movement trends of different waste streams.

However, the most important factor for developing IS relationships is collaboration amongst organizations (Bansal and McKnight, 2009; Chertow, 2000; Chertow and Ehrenfeld, 2012; Sakr et al., 2011). For this reason the presented project applied in Sicily, aimed at creating a symbiosis platform with the idea of the active participation of both SMEs and local stakeholders. The goals were: provide a methodology and a tool for industrial symbiosis implementation in this case at regional scale, implement a IS Platform as a support to SMEs to individuate symbiosis opportunities in the region. Facilitation of IS development using ICT tools together with identification of different tools and their application is investigated by Grant et al. (2010). The authors argued that, since ICT tools have been developed over time from an optimization and data sharing application toward a “community-building” tool, it has become more helpful to IS.

The goals were achieved through different steps: first of all the design of the architecture, then the analysis of the productive system in the region, data collection and companies’ involvement in operative meetings. Collected data were used for potential matches individuation, through a collaborative approach with the companies who participated in the meetings, and then they were analyzed in technical and regulatory terms to individuate potential synergies.

Technical dossiers on three main resource streams (wastes from processing stone materials; plastics and agro-industrial wastes), which may generate the more interesting potential synergies, were implemented to support companies in synergies actual realization.

2. Materials and methods

The Industrial Symbiosis Platform has been addressed in particular to small medium enterprises (SMEs) and other local operators to enable the transfer of resources (materials, energy products, water, services and expertise) and to offer other operational instruments (legal database, tools LCA and Ecodesign, Best practices database, etc.) The methodology for the realization and operation of the platform involved different steps from the beginning of the project (2011) till the programmed end (2015):

- design and the implementation of the platform architecture, ICT and database tools (the implementation is in training phase);
- network activation and promotion activities by means of stakeholders involvement at regional level (in Sicily) and at national and international level;
- analysis of productive sectors in the Region and realization of a broad database (DB) of companies in Sicily;
- operative meetings finalized to involve companies in the project, to have from them input-output related information, looking for potential synergies.

2.1. Matching between outputs and inputs in the ENEA's industrial symbiosis platform

The platform architecture, previously described in Cutaia et al. (2014a, 2014b), works on a GIS system where many different databases have been uploaded. One of these databases is that of the registered companies, that, through the www.industrialsymbiosis.it portal can provide their general information (name, address, activity sector by mean of Italian and European codes - Istat 2009; EUROSTAT, 2008 - and so on). Doing this the GIS system can localize registered companies in the map. Then, companies can go further and look for "cooperation" in terms of industrial symbiosis potential. In order to look for industrial symbiosis potential, registered companies can become "associated companies", providing their own information about inputs and outputs they want to share within the industrial symbiosis network.

Users are in this way encouraged to go from the "registered company" level to the "associated" one, also because in this way they can use all the functions provided by the platform (queries, DBs, industrial symbiosis matching). Another database contains the information about resources (input-output) which are geo-referred together with related companies. The information about resources is collected using Input-output tables (Fig. 1). ENEA input-output table foresees taxonomy for the inventory of input-output data of companies, taking into account as resources "materials, energy, services, skills" and using code systems officially used in Italy (according EU regulation) for different kind of inventories. Information asked in the input-output tables for collecting data are the more simplified available in order to allow companies to fill the tables with the less possible effort, since information asked are those already used by the companies for their normal management.

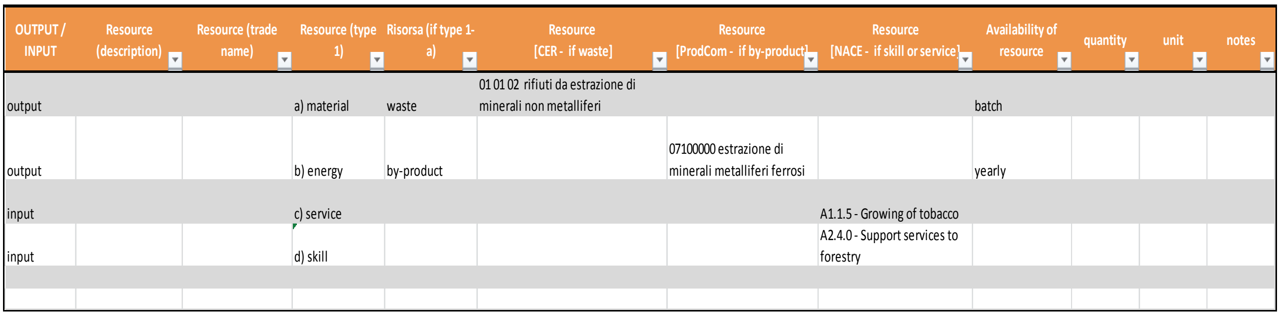
The first column specifies if the resource is an input (requested resource) or an output (generated resource). Second and third columns are two free text fields in which the company can specify the characteristics and a brief description of the resource. The fourth column reports the category of the resource:

a) materials,
b) energy,
c) services,
d) skills.

"Services" means every kind of support resources such as transportation, available storage space, etc. that are not used entirely by the company and which can be shared with other participants, after proper agreements. The same applies to "skills", but in this case it refers to the skills and competences that can be shared if not fully used. The fifth column ask if the resource, if materials, can be defined as waste or as by-product. Sixth seventh and eighth columns presents drop-down boxes with specific codes that describe the resource using the codes normally used by companies:

- ERC (European Waste Catalogue) is the classification of waste types according to Directive 75/442 / EEC. It is used if the resource is waste.
- PRODCOM Community Production): is the code that the European Union has adopted to harmonize statistical observations about industrial production, and consists of a list of products (these are generally "goods", but also including some industrial services) grouped according to the economic sector of the manufacturer. It is used if the resource is a sub-product.
- NACE or ATECO are classifications of economic activities. ATECO is a type of classification adopted by the Italian National Statistics Institute (ISTAT), whereas NACE is a taxonomy developed by Eurostat, the statistical body of the European Commission. It is used if the resource is a skill or service.

The last three columns require to specify quantities, unit of measure and if the quantity is batch (available only at specific intervals) or if it distribution during the year is continuous (yearly). An important aspect in collaborative IS platforms is the ontological issue (Cecelja et al., 2015; Raafat et al., 2013). The Platform allows for automatic input-output matching. In this way, associated companies can find matches and potential synergies. This characteristic represent the core and the novelty of the platform making it a valuable tool, not only for the IS practitioners, but also a as a service directly usable by companies. By now the Platform is in its test phase that will end in December 2015. The connection between an available resource and its possible destinations as input pass through an <origin, destination> string (Fig. 2).



OUTPUT / INPUT	Resource (description)	Resource (trade name)	Resource (type 1)	Risorsa (if type 1-a)	Resource [CER - if waste]	Resource [ProdCom - if by-product]	Resource [NACE - if skill or service]	Availability of resource	quantity	unit	notes
output			a) material	waste	01 01 02 rifiuti da estrazione di minerali non metalliferi			batch			
output			b) energy	by-product		07100000 estrazione di minerali metalliferi ferrosi		yearly			
input			c) service				A1.1.5 - Growing of tobacco				
input			d) skill				A2.4.0 - Support services to forestry				

Fig. 1. Input-output data collection table

The connection algorithm uses the logic "one-to-many" to find relations between the main characteristics of a waste/by-product from one company and its potential as an input resource for another company. Following the opposite direction the same algorithm allows verifying which resource, from different companies, can satisfy the quality specifications to allow the use, as an input resource, for a given company.

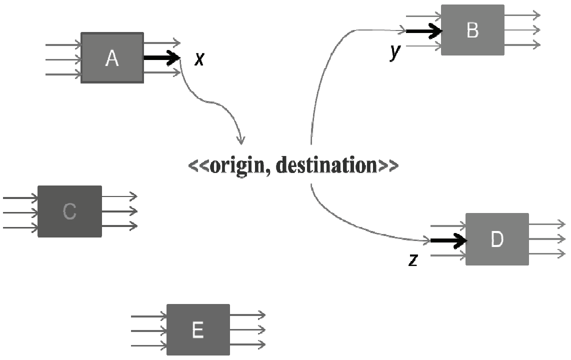


Fig. 2. Matching between outputs and inputs according with the <origin-destination> strings logic

One empty <origin, destination> string is shown in Fig. 3, showing information in this case for the connection of one output to its possible productive destinations. There is a similar, but inverted table, for the opposite direction (one input and its possible alternative supply). In other terms, searching for possible matches for output *x* of company A, the software finds two or more possible destinations as inputs for companies B or D as inputs *y* or *z*. The <origin-destination> string mainly contains:

- Resource's information: resource's description by means of EWC Code (or other appropriate code (ATECO/NACE or PRODCOM if the resource is not a waste); Resource's origin and composition;
- Possible resource's destinations using ATECO/NACE codes and information about its properties;
- Applicable regulations and technical norms;
- Others useful information (e.g. collecting managing systems).

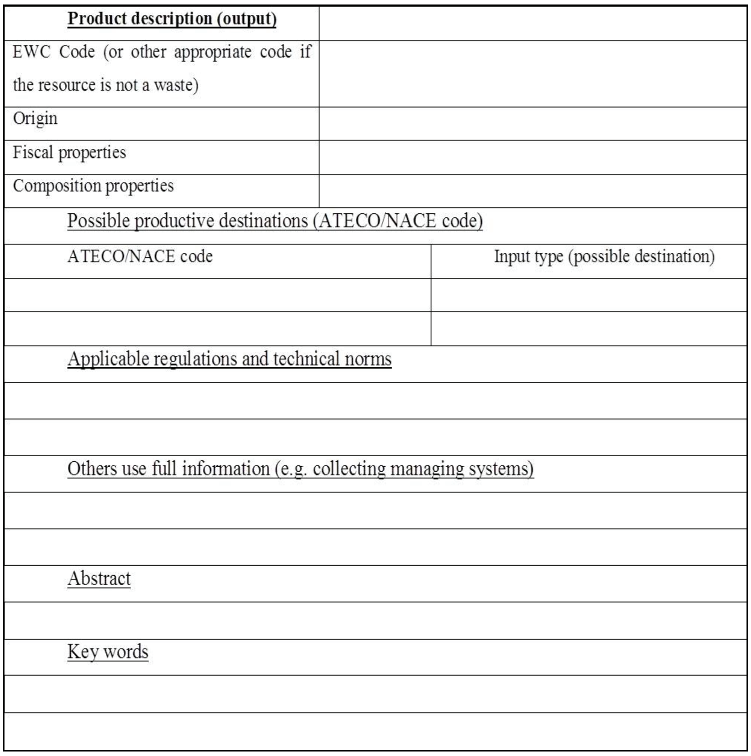
The platform actually contains several filled <origin destination> strings covering all possible use of many resources, allowing for potential matches, some of them need to be verified in regulatory, logistic and economical terms. Then actually these strings represent potential synergies which will become effective once all the terms will be verified. The platform will be continuously updated and enriched with new filled strings enhancing in this way the possibilities of finding synergies between associated companies and their shared resources.

The <origin destination> strings and the relation between different databases (resources database and origin destination string database) allow addressing ontological issue, which is one of the most important arguments of debate (Cecelja et al., 2015; Raafat et al., 2013).

2.2. Network activation and promotion activities

Starting from the consideration that the first success factor in IS development is the establishment of network between companies and stakeholders and maintaining their continuous interest, mutual trust, and involvement (Sakr et al., 2011), several activities were continuously promoted at both regional and national scale for companies, authorities and stakeholders sensitization on IS environmental and economic benefit. For sensitization and dissemination purposes in 2011 ENEA registered the domain www.industrialsymbiosis.it and other equivalents and more in general, the reference website for the promoted activities (Cutaia et al., 2014a, 2014b). Starting from 2012 onwards ENEA promoted at Ecomondo Exhibition (the main Italian fair trade on environment held, yearly, in Rimini in November) a series of national Conferences on industrial symbiosis aimed at collecting experiences made on this topics and sensitizing political and institutional stakeholders in order to allow applications overcoming regulatory procedural barriers and promote industrial symbiosis strategy.

Local stakeholder's involvement was carried out through contacts with Sicilia Region (Regional waste Agency), meetings and specific framework agreement signed between ENEA and Confindustria Sicilia (Sicilian association of Industrials) and ENEA and University of Catania.



Product description (output)	
EWC Code (or other appropriate code if the resource is not a waste)	
Origin	
Fiscal properties	
Composition properties	
Possible productive destinations (ATECO/NACE code)	
ATECO/NACE code	Input type (possible destination)
Applicable regulations and technical norms	
Others use full information (e.g. collecting managing systems)	
Abstract	
Key words	

Fig. 3. Example of <origin, destination> string (output to inputs direction)

In 2015 ENEA established the first Italian Industrial Symbiosis Network (SUN: Symbiosis Users Network). This network aims at being the Italian reference point in the field of Industrial Symbiosis through the support of scientific/research bodies as well as the participation of operative stakeholders (companies and institutions).

2.3. Research and analysis of companies to be involved

The Platform operates with the cooperation of companies (associated users) who have the core information needed for implementing the industrial symbiosis: data on outputs they want to share or inputs they want to have. Companies can share their input-output data on-line, as associated users through the website, or on-site, during operative meetings. In this stage, in which the platform is populated and tested, the engagement of companies requires to have private information (e.g. for each company the name of the responsible person, email and phone number). This information is not normally available from the data provided by Italian Institute of Statistic (ISTAT) or by other institution, which provides only information on sectors and size of companies at macro and meso level.

For this reason, in order to have a consistent number of companies to try to involve in the project, a database containing information on more than 2000 companies was developed collecting data from regional productive districts, chambers of commerce, universities, industrial associations and companies' web sites. The main information collected into the database was: geographic localization, name of the company, name of the owner, productive sector, number of employees and contact details (email and phone). The productive sectors were represented by the classification of economic activities ATECO (Istat, 2009) or NACE (EUROSTAT, 2008) codes. Companies listed in the compiled database are representative of part of the overall companies operating in Sicily, with a particular focus for the provinces of Catania, Siracusa (where operative meetings were held).

Starting from this DB an analysis of productive sectors and an evaluation of quantity and dimension of companies were made to identify the most productive areas in the region with a sectors diversification more suitable for the organization of operative meetings to begin symbiosis paths according to Jensen et al. (2012) that states that the key to successful industrial symbiosis programs is to build on existing opportunities in brownfield industrial systems since the level of diversification in these mature industrial systems create an environment where opportunities can be identified and facilitated more easily.

Then, considering sectors, employees and location, groups of heterogeneous companies were selected and invited to take part to operative meetings aimed at sharing information about resources flows and wastes and looking for potential synergies. All the sectors were considered to contact companies in order to have a diversified composition. A threshold value on the number of employees has been fixed. This value varies according to the business sector.

2.4. Operative meetings

Two operative meetings, for a maximum of 50 delegates each one, were organized in most productive area of Sicily (East Sicily) with the main goal of involving companies in the project, get from them data, and at looking for potential synergies. The first meeting (Cutaia et al., 2014b) held in Siracusa in on March 28th 2014 with the support of the Chamber of Commerce. Sicilia Region gave their patronage to the workshop as Confindustria Sicilia did. The province of Siracusa was represented and did an oral presentation in the opening session as ENEA and the Chamber of Commerce did. The second operative meeting was held in Catania on October 24th 2014 with the support of Confindustria Catania and the collaboration of University of Catania (Department of Industrial Engineering).

For meeting organization, invitation emails were sent to a selected number of companies present in our database (almost 800 for Siracusa meeting and almost 1100 for Catania meeting). For a more capillary diffusion, invitations were made also by our local partners (Confindustria Catania, Chambers of Commerce of Siracusa and the Department of Industrial Engineering of the University of Catania).

A more restricted group of companies was directly contacted by phone, apart from emails they already received (200 for Siracusa Siracusaand 300 for Catania meeting) in order to better explain the goal of the meeting.

According to ENEA methodology before the meeting companies have been asked to fill in input-output tables with resources intended to be shared within the project. Those resources could be eventually be updated and improved during the meeting (with the specific work of sharing and matching between companies) and after the meeting (when ENEA sent back to the companies the list of shared resources by each company for their final control). Information shared by companies was included in the input-output database, checked and loaded on the ENEA platform in order to search for synergies using the “origin-destination” strings, in addition to those find during the meetings.

3. Results and discussion

3.1. Analysis of companies to be involved

The most productive areas in Sicily, on the basis of collected data, are represented by Catania and Siracusa provinces were the greatest number of companies (33%) with a greater number of employees is concentrated (52%) (Fig. 4). Theses areas were selected for the organization of operative meetings also because of a major interest and collaboration of local stakeholders (University of Catania and local industrial associations). The main sectors of activities for the companies listed in the database (Fig. 5), are represented by agriculture (32%) and manufacturing (27%).

The central zones of Sicily (Enna and Caltanissetta) are characterized by a productive sector prevalently rural based on agriculture activities (66%). Agriculture and particularly fishing are also well developed in the northern part of the island (Palermo and Messina (47%), Trapani and Agrigento (26%). In the south east (Ragusa) the manufacturing sector represents an important percentage (33%) together with agriculture (43%). Numerous farms for breeding livestock are present in this area.

Industrial production in this region is characterized by a few but important industrial centers. Industrial poles, in particular petroleum and chemical industries, are concentrated in eastern Sicily (Catania and Siracusa) (Fig. 5) where the manufacturing sector represents an important percentage (35%) subdivided prevalently, as reported in Table 1, in manufacture of food products (20%) manufacture of other non-metallic mineral products (16%) and manufacture of fabricated metal (13%).

3.2. Operative meetings results

A number of 44 delegates attended the Siracusa workshop, coming from 36 different companies prevalently from manufacturing and agriculture sectors (A) (37.1%) followed by water supply, sewerage waste management and remediation activities (E) (14.3%) and professional, scientific and technical activities (M) (14.3%). Also in Catania meeting, where 37 companies with 42 delegates participated, the main sector was manufacturing with a higher percentage respect to Siracusa meeting (47.2%), followed by electricity sector (13.9%) and professional, scientific and technical activities (13.9%) (Table 2).

The most represented manufacturing sector in Catania meeting (Table 3) was manufacture of food products (28%) followed by manufacture of other non-metallic mineral products (17%), manufacture of fabricated metal products (17%), manufacture of rubber and plastic products (11%), manufacture of electrical equipment (11%), manufacture of beverages (6%) and manufacture of chemicals and chemical products (6%).

During Siracusa meeting the main sector of participating companies was manufacture of computer (36%) followed by manufacture of food products (14%) manufacture of machinery and equipment (14%), repair and installation of machinery and equipment (14%), manufacture of rubber and plastic products (7%), manufacture of basic metals (7%), manufacture of fabricated metal products (7%).

The lower participation in Catania meeting of delegates from administrative and support service activities (N), human health and social work activities (Q), service activities and water supply, sewerage, waste management and remediation activities (E), resulted in a greater number of potential matches with almost the same number of declared resources (Table 4).

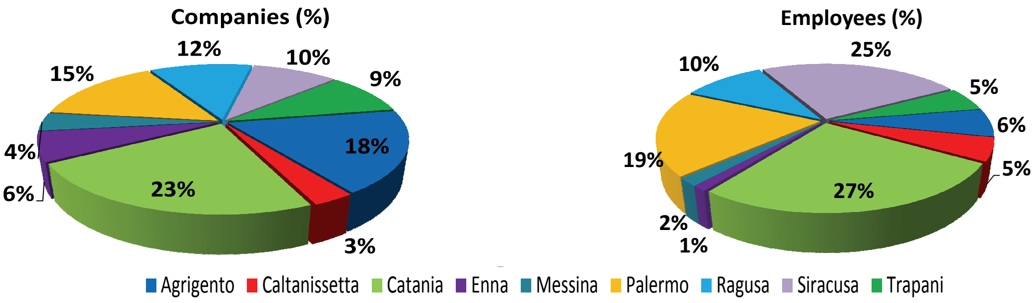


Fig. 4. Companies and employees (data from ENEA database)

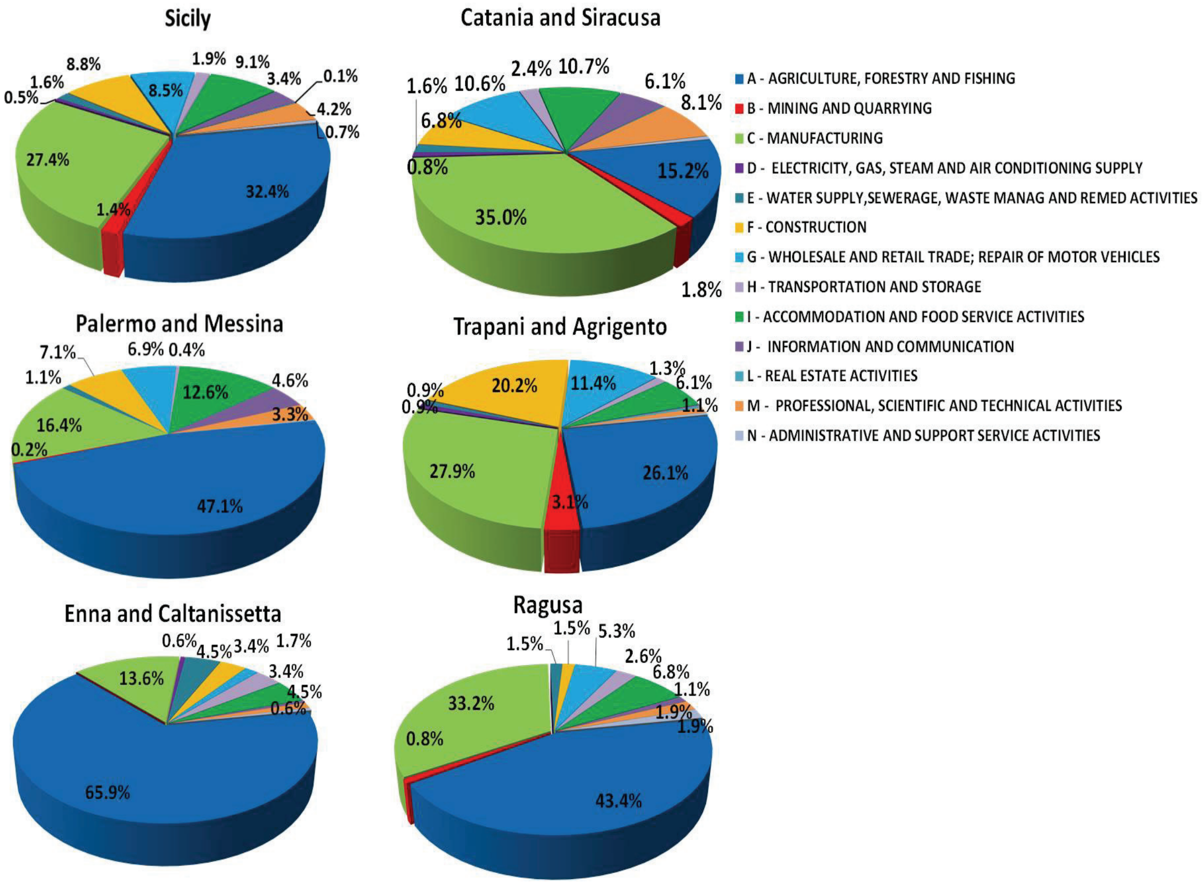


Fig. 5. Industrial sectors in Sicily (on the basis of ENEA database)

Table 1. Manufacturing Sector in Sicily and in Catania and Syracuse districts (on the basis of ENEA database)

	Sicily		*Catania and Siracusa districts*	
C- Manufacturing	*Companies (n.)*	*Companies%*	*Companies (n.)*	*Companies%*
C10 - Manufacture of food products	136	24%	51	20%
C11 - Manufacture of beverages	6	1%	3	1%
C13 - Manufacture of textiles	1	0%	0	0%
C15 - Manufacture of leather and related products	21	4%	1	0%
C16 - Manufacture of wood and of products of wood and cork	25	4%	18	7%
C17 - Manufacture of paper and paper products	2	0%	1	0%
C19 - Manufacture of coke and refined petroleum products	2	0%	2	1%
C20 - Manufacture of chemicals and chemical products	10	2%	3	1%
C22 - Manufacture of rubber and plastic products	11	2%	5	2%
C23 - Manufacture of other non-metallic mineral	99	17%	42	16%

products				
C24 - Manufacture of basic metals	6	1%	2	1%
C25 - Manufacture of fabricated metal products	75	13%	33	13%
C26 - Manufacture of computer	17	3%	11	4%
C27 - Manufacture of electrical equipment	13	2%	5	2%
C28 - Manufacture of machinery and equipment n.e.c.	29	5%	7	3%
C29 - Manufacture of motor vehicles	10	2%	1	0%
C30 - Manufacture of other transport equipment	11	2%	4	2%
C31 - Manufacture of furniture	23	4%	19	7%
C32 - Other manufacturing	4	1%	3	1%
C33 - Repair and installation of machinery and equipment	14	2%	11	4%
unknown	53	9%	36	14%
Total C- Manufacturing	568	100%	258	100%

Table 2. Delegates at the meetings for each industrial sector

	Siracusa meeting		***Catania meeting***	
NACE CODES	***Registered delegates (%)***	***Delegates to the meeting (%)***	***Registered delegates (%)***	***Delegates to the meeting (%)***
A - Agriculture, forestry and fishing	3.3	5.7	9.1	8.3
C - Manufacturing	36.1	37.1	37.9	47.2
D - Electricity, gas, steam and air conditioning supply	1.6	2.9	7.6	13.9
E - Water supply; sewerage; waste management and remediation activities	13.1	14.3	6.1	2.8
F - Construction	4.9	2.9	6.1	5.6
G - Wholesale and retail trade; repair of motor vehicles and motorcycles	1.6	0.0	9.1	8.3
H - Transporting and storage	6.6	8.6	6.1	8.3
J - Information and communication	6.6	2.9	1.5	0.0
M - Professional, scientific and technical activities	13.1	14.3	16.7	13.9
N - Administrative and support service activities	3.3	2.9	0.0	0.0
O - Public administration and defense; compulsory social security	0.0	0.0	1.5	0.0
P - Education	0.0	0.0	1.5	0.0
Q - Human health and social work activities	1.6	2.9	0.0	0.0
S - Other services activities	8.2	5.7	6.1	0.0

Table 3. Delegates at the meetings for manufacturing sector

	Siracusa meeting		***Catania meeting***	
C- Manufacturing	***Registered delegates (%)***	***Delegates to the meeting (%)***	***Registered delegates (%)***	***Delegates to the meeting (%)***
C10 - Manufacture of food products	17	14	26	28
C11 - Manufacture of beverages	4	0	9	6
C13 - Manufacture of textiles	0	0	0	0
C15 - Manufacture of leather and related products	0	0	0	0
C16 - Manufacture of wood and of products of wood and cork	0	0	0	0
C17 - Manufacture of paper and paper products	0	0	4	6
C19 - Manufacture of coke and refined petroleum products	0	0	0	0
C20 - Manufacture of chemicals and chemical products	0	0	4	6
C22 - Manufacture of rubber and plastic products	17	7	4	11
C23 - Manufacture of other non-metallic mineral products	0	0	17	17
C24 - Manufacture of basic metals	4	7	0	0
C25 - Manufacture of fabricated metal products	8	7	17	17
C26 - Manufacture of computer	21	36	0	0
C27 - Manufacture of electrical equipment	0	0	9	11
C28 - Manufacture of machinery and equipment n.e.c.	13	14	4	0
C29 - Manufacture of motor vehicles	0	0	0	0
C30 - Manufacture of other transport equipment	0	0	0	0
C31 - Manufacture of furniture	0	0	4	0
C32 - Other manufacturing	4	0	0	0
C33 - Repair and installation of machinery and equipment	13	14	0	0

Thanks to Siracusa meeting 109 output resources and 88 input resources of different categories were shared (Table 4). The resources shared by the companies were mainly "materials" (59% of the output resources and 59% of the input resources) and expertise, consultancy and services (34% of the output resources and 32% of the input resources). In the category "materials", companies were interested to share (Table 5) as output prevalently packaging (19%), plastics and plastic products (15%), metals and metal products (11%), organic chemicals (10%), water (8%), materials from agriculture (8%), construction and demolition wastes (6%).

As input the resources more requested were: foodstuffs (31%), organic chemicals (21%) and fuels, products from livestock and fisheries, construction and demolition wastes (6%).

A total of 165 potential matches were found, involving prevalently materials (53%) and expertise, consultancy and services (37%). Matches were mainly related to plastics and plastic products (16%), metals and metal products (16), municipal wastewater treatment sludge (11%), construction and demolition wastes (10%). From the workshop held in Catania good results have been achieved (Table 4): 529 potential matches were found starting from 187 outputs (37% materials, 35% expertise, 16% equipment) and 91 input resources (66% materials, 23% expertise, consultancy and services). The sharing was more balanced for output resources.

In the category "materials" (Table 5), companies were interested in sharing as output mainly electrical and electronic (14%), paper and paperboard (12%) and plastics and plastic products (8%). Potential matches were related prevalently to materials (50%) and expertise, consultancy, services (31%). In "materials" category, potential matches were individuated (Table 5) in paper and paperboard (25%), plastics and plastic products (13%) and electrical and electronic (8%).

In both meetings, companies involved in the most part of matches were those from manufacturing of food products; agriculture, manufacture of fabricated metal and non-metals products, and construction sectors.

Table 4. Resources shared during the meetings and potential matches

Resources	***Siracusa meeting (%)***			***Catania meeting (%)***		
	input	***output***	***matches***	***input***	***output***	***matches***
Materials	52	129	88	34	124	267
Energy	6	4	7	5	4	36
Expertise, consultancy, services	28	74	61	32	43	164
Logistic, transportations	1	9	6	3	3	5
Land, capacity	1	2	2	2	5	13
Equipment		1	1	15	8	44
Total	88	219	165	91	187	529

Table 5. Materials shared during the meetings and potential matches

Resources (materials)	***Siracusa meeting (%)***			***Catania meeting (%)***		
	input	***output***	***matches***	***input***	***output***	***matches***
water	2	8	7	3	4	6
fuels	6	2	1	9	1	0
materials from agriculture	2	7	6	9	7	6
electrical and electronic	6	6	9	0	14	8
municipal wastewater treatment sludge	0	0	11	0	2	2
industrial sludge	0	0	0	0	8	6
packaging	4	19	0	3	6	5
wood and wood products	2	1	0	0	2	2
metals and metal products	4	11	16	3	5	4
construction minerals	0	2	0	6	2	2
industrial minerals	4	0	8	3	4	3
Mineral waste oils	0	0	0	9	2	3
Plastics and plastic products	0	15	16	12	8	13
foodstuffs	31	5	2	3	6	5
inorganic chemicals	2	10	5	6	2	0
organic chemicals	21	2	3	6	4	2
products from livestock and fisheries	6	0	1	3	0	1
construction, demolition, excavation materials	6	6	10	6	4	4
paper and paperboard	2	5	1	15	12	25
sands from separation processes	0	0	0	0	1	0
textile	0	0	0	0	1	0
glass and glass products	4	2	3	6	4	5

3.3. Potential matches verification and potential synergies implementation

Because of the scale of the project, after the meetings a selection of the most interesting potential synergies, or group of synergies, was made, based on the number and amount of shared resources. For each one of these selected synergies specific operative handbooks are being prepared, collecting, analyzing and systematizing information on technical, regulatory, logistic, economic and other issues influencing the possibility to actually realize the proposed synergy, as well as quantities of materials or other resources involved.

Two categories of resources involved in potential synergies were selected:

- agro-industrial waste;
- construction and demolition wastes, residues of ornamental stone processing and other residue to be utilized in construction field.

In Fig. 6 an example of potential matches verification stage for the third category is reported, according with shared resources and involved companies (represented by a code). Similar flow diagrams were elaborated for the other categories. Continues lines represents matches find during the meetings, while dashed lines represent further synergies proposed by the authors. Faces synthetize the actual state in terms of existing barrier or state of the process (green=no barrier, yellow=some aspect to be further investigated, red=synergy cannot be implemented).

Basalt and mixed sawing silt, shot blasting residues and broken slabs can be re-used by a road construction company as aggregates and by others companies in bricks and ceramics production, after the verification of their physical-chemical characteristics (yellow face indicate only that companies need to provide more details on the physical and chemical characteristics). For these flows no legislative barriers were encountered, because such materials have been recently regulated by Italian law that has assimilated them to excavation materials that can be considered as byproducts. Reuse milled road, however, is a matter still debated. The verification of the possibility of using bottom ashes from special waste incineration in road construction is still on going. Similar destinations are actually implemented in other Italian region as well as the issue of bottom ashes, coming from different feed, and their reuse, were already investigated (Cossu et al., 2014). For these types of residues the most important issue to be addressed is related to the residues characteristics (Mancini et al., 2014a, 2014b).

Various metals can however be removed and recovered from bottom ashes by a combination of mechanical (e.g. crushing, sorting) and physical (e.g. magnetic and eddy-current separation) unit operations. Reducing the metal contents, the process could make these wastes comply with building material standards, thus increasing their recycling potential in the construction industry in compliance with the standard fixed by European (UE N. 305/2011) and Italian regulations.

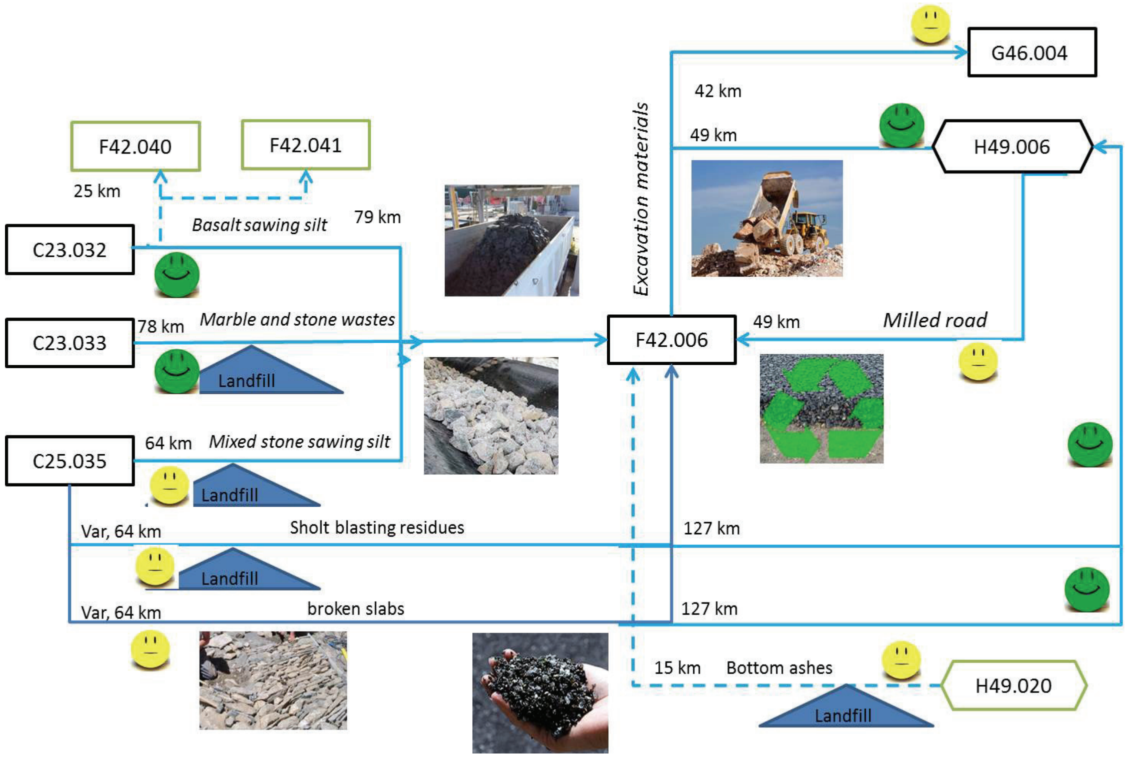


Fig. 6. Synergies verification in the field of construction/demolition and stone processing sectors

Interesting possibilities were encountered for agro-industrial by-products valorization in the region, both for sector size and its importance, and both for the possibilities of new plants development.

Biomass, and in particular agro-industrial wastes, provides a clean, renewable energy source, which could improve economic, energetic and environmental sectors (Gavrilescu, 2008; Lako et al., 2008). However technical aspects, concerning the methane production from codigestion of different sources, should be deepened, as well as the effect of several pretreatments (Battista et al 2015; Ruggeri et al., 2015) and the sulphur removal from biogas (Callegari et al., 2013).

Three different paths were identified for these flows: feed production, energy production (Gavrilescu, 2008) and compost production and the barriers were analyzed (Mateescu et al., 2008).No barriers were encountered in defining these synergies; the main issue is represented by quantitative and temporal distribution needed to ensure a suitable supply for the plants related to the requirements of the productions. Results of the activities above mentioned were used to develop technical dossier, in form of operative handbooks, helping companies in all steps for synergies' implementation.

These operative handbooks include European, Italian and regional regulations, guidelines, technical standards, logistic and economical aspects useful for supporting companies in synergies implementation. Additional meetings with companies and local stakeholders (such as local authorities), are scheduled by July 2015 to discuss all aspects contained in these operative handbooks. Results of this activity will also be used to update, with more information, the <origin-destination> strings, which represent the core of the platform for checking for matches between uploaded and available inputs and outputs.

4. Discussion

Many technical solutions for waste and by-product materials, water, and energy reuse between neighboring industries have been discovered and applied in the IS examples from all over the world. However, from the analysis of IS application (Jensen et al., 2011; Laybourn and Morrissey, 2009; Lombardi and Laybourn, 2012; Schiller et al., 2014) the potential for uptake of new synergies in the regions is often limited by a range of nontechnical barriers. These barriers include environmental regulation, lack of cooperation and trust between industries in the area, economic barriers, and lack of information sharing.

One of the main results of the discussion occurred during the meetings held in Sicily was the significance and the consequences of the regulatory and control systems. For this reason it was particularly important the presence and participation of local stakeholders and control authorities in all the phases of the project for industrial symbiosis implementation. The last part of the project is addressed (from July 2015 to the end of the year) in overcome barriers and obstacles to the actual implementation of synergies, specifically deeply investigated by means the realization of the two cited operative handbooks, addressed at involved companies as well as local authorities. Discussion and consultation meetings are foreseen for the month of July 2015 to be held in Catania with ENEA, companies and interested local authorities.

In some instances, regulatory actions encourage industrial symbiosis. Landfill bans in key European countries have driven symbiotic practices such as the reuse of organic wastes prohibited from land disposal in Denmark and the Netherlands. Very high tipping fees for waste disposal in Canada and climate change levies in the United Kingdom have been cited as stimulating innovation and action in by-product reuse. Although also in Italy there is a tax on waste disposal on landfill, since 1995, it has not had the desired results, because of low disposal costs. More efforts should be made by the political system to discourage disposal and encourage virtuous policies of reuse and recycling of waste and byproducts.

Another issue raised during the experience in Sicily is the difficulty in overcoming the distrust of companies approach. Policy makers and regulators are critical to creating the market conditions that incentivize IS and resource efficient behavior as well as policies and regulations that clarify definitions and responsibilities. Responsibilities, predictability and reliability are the key to overcome companies' distrust in in pursuing paths of symbiosis.

5. Conclusions

ENEA developed the first Industrial Symbiosis Platform in Italy implemented in Sicily. The platform, whose main objective launching Industrial Symbiosis through a geo-referred information system support, acts as a tool in the service of business and territory and also offers a range of tools that may be of interest especially for SMEs.

The core and the novelty of the platform are represented by the possibility to find matches by using an algorithm that links output with inputs (with a logic one-to-many) or vice versa, by means of <origin, destination> strings, linking one type of output with its potential productive destinations (or vice versa).

A methodology was followed for industrial symbiosis implementation at regional scale; some activities were addressed at the consultation with stakeholders, in Sicily and at national level; the Sicilian productive system was investigated and then companies were involved in operative meetings for resources sharing, potential synergies individuation and finally for platform population and validation.

During the meetings 80 SME were involved and almost 400 output resources and almost 180 input resources were shared by companies. More than 690 potential matches were found between the participating companies. Results also highlighted the needs of identify predominant productive activities in well-defined territorial contexts where to investigate the specific/local tangles involving legislative and technical-economic feasibility. So, potential synergies verification from a technical, regulatory, logistic and economic point of view was performed for a selected group of categories (agro-industrial waste; construction and demolition wastes, residues of ornamental stone processing and other residue to be utilized in construction field).

Operative handbooks on the cited two main resource flows, which may generate the more interesting potential synergies, will be developed. These handbooks include European, Italian and regional regulations, guidelines, technical regulations, standards, logistic and economical aspects and more in general describe the pathways to be done in order to go from the idea till the actual implementation of the match. Aim of those dossiers is support companies in implementing matches. On these operative handbooks specific discussion and consultation meetings are foreseen for the month of July 2015 to be held in Catania with ENEA, companies and interested local authorities.

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OPTIMIZATION OF THERMOPHILIC ANAEROBIC DIGESTION OF WINERY BIO-WASTE BY MICRO-NUTRIENTS AUGMENTATION

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Abstract

Thermophilic anaerobic digestion is a suitable technology to treat agricultural waste because of its higher biogas production, hygienisation effect and solids removal efficiency. Although these benefits, poor effluent quality and instability are encountered in some cases. The anaerobic co-digestion of winery waste and waste activated sludge at 55°C, operating at 23 days HRT and with an organic loading rate of 3.2 kg COD/m^3d, was characterized by accumulation of volatile fatty acids, pH fall and reduction of biogas production, while mesophilic process was steady at long term. The study evaluated the effect of trace elements (iron, cobalt and nickel) augmentation in the thermophilic reactor at different concentration of micro-nutrients. The addition improved the process stability: pH became constant and average volatile fatty acids concentration was below 1,000 mg COD/L. The biogas production increased from 0.38 to 0.45 m^3/kg COD, corresponding to 90% of COD removal, while mesophilic reactor removed the 78% of total COD. Digestate had interesting characteristics as fertilizer in fact the higher solids removal (28%) allowed to concentrate the phosphorus in the particulate fraction and nitrogen was transformed into more available form for plants growth.

Key words: mesophilic anaerobic digestion, micro-nutrients, minimum requirement, thermophilic anaerobic digestion, winery waste

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1. Introduction

Agro-industrial activities represent important sources of environmental impact because fruit and vegetable processing generates high amount of organic wastes. Among these bio-wastes, the winery residues have great relevance in terms of quantity and of potential pollution. In fact their uncontrolled field spreading could cause relevant environmental problems due to their high biodegradability, expressed by high level of chemical oxygen demand (COD). The raw wastes disposal on soils can consume large quantity of oxygen consequently they create anoxic conditions, reducing soil fertility. Moreover winery residues content antibacterial compounds produced by plants such as polyphenolic compounds, and toxic compounds like pesticides and heavy metals that can reduce crops growth (Moldes et al., 2008).

For these reasons winery wastes need a treatment before the disposal, the most diffused process is composting but it is economically and energetically expensive. Considering the costs of the composting and of disposal, the production companies are seeking alternative biological treatments with a low environmental impact and economically sustainable for winery residues valorisation, consisting in the recovery or transformation of the present components into high value-added resources.

Anaerobic digestion represents a suitable technology to reduce pollutant load of winery residues and to produce biogas, a renewable energy source. This technology is commercially proven and

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is widely used for treating high moisture content organic wastes (Ciubota-Rosie et al., 2008).

Mesophilic processes, with a working temperature of 35-37°C, are the most applied conditions but the interest for thermophilic condition (55°C) is increasing for its several advantages. Kafle et al. (2014) demonstrated, in terms of digestate characteristics and kinetic constant, that VS removal was significantly higher under thermophilic temperature conditions than under mesophilic temperature conditions. Since reaction rates increase with temperature, significantly higher organic loads and considerably shorter hydrolysis retention times are expected at 55°C (Van Lier et al., 1997). Therefore, a smaller reactor volume will be sufficient at thermophilic temperatures compared to mesophilic conditions (Lens and Verstraete, 2001). Usually higher temperature improves solid and organic matter removals due to faster hydrolysis rates, and consequently biogas productions increased and effluent stream quantity reduced. Pathogens removal is guaranteed by maintaining 55°C for few days (Sahlström et al., 2004) and also the phytotoxicity of thermophilic digestate seems lower than mesophilic one (Vallini et al., 1993).

Although these benefits few full scale plants operate in thermophilic range, this is due to the higher heating costs and less stable operation (De Baere, 2000). The causes of instability are several: with regard to manure digestion, high ammonia concentrations may limit the thermophilic anaerobic treatability, owing to toxicity problems (Angelidaki and Ahring, 1993; Zeeman et al., 1985). As the free ammonia fraction increases with temperature and pH, the ammonia concentration tolerated at high pH and at thermophilic temperatures would be expected to be low (Ahring, 1994). Another drawback is the often-found high effluent volatile fatty acids concentration but the etiology is not clear. Variation of temperature determined a change in methanogenic population (Van Lier et al., 1992) explained by a rapid die-off of mesophilic organisms at temperature exceeding the maximum growth temperature of these bacteria. Thermophilic anaerobic population is composed by a lower numbers of species and probably has different nutrients requirements.

The treatment of industrial substrates emphasizes these aspects because usually these wastes have low concentration of micro-nutrients and an inadequate amounts of bio-available trace elements, metals in particular (Rittmann and McCarty, 2001; Speece, 1983; Zandvoort et al., 2006). In fact some metals are involved into biochemistry of anaerobic microorganisms and play important roles as co-factors of various enzymes involved in anaerobic reactions and transformations as reported by Fermoso et al. (2009).

Depending on the pathway, metal requirements may differ, but the general trends remain the same: Fe is the most abundant metal, followed by Ni and Co, and smaller amounts of Mo (and/or W) and Zn. The function of these metals on the growth and metabolism of anaerobic bacteria is well documented in the literature (Agler et al., 2008; Fermoso et al., 2009; Oleszkiewicz et al., 1990) but the effect of missing nutrients occasionally could be not evident. In fact the anaerobic microorganisms respond quite slowly and have long lag phase time after the supplementation of micronutrients, therefore batch tests results usually are not sufficient to understand the real nutrients necessity.

The experiments have to be carried out in continuous mode for quite long period as made by Takashima et al. (2011). That work reported a complete study on continuous reactor working at 55-57°C with metals supply and demonstrated that trace elements requirements in thermophilic digestion is greater than in mesophilic one, implying more requirements for biomass growth and activity and/or less bioavailability of those trace metals at higher temperature. The experiment was carried out using a solution of sole glucose as feed, then the effect of the substrate was not considered in that study. In general the variations in optimal concentration of trace elements at mesophilic and thermophilic temperature ranges are explained by the variety of methanogens, each having a unique trace metal requirement, which also depends on the type of substrate utilized (Paulo et al., 2004). For example Qiang et al. (2013) determined the metals requirements in thermophilic digestion of solid food waste and the values were lower than ones reported by Takashima et al. (2011).

In present study the anaerobic digestion of winery wastes, originated from wine making process, was carried out in thermophilic condition with different supplementation of trace elements. In order to evaluate the process, the stability parameters and the specific biogas production were compared with the same parameters of stable mesophilic reactor working with the same operational conditions but without necessity of metals supply. Two parallel experiments, with different temperature conditions, were carried out in order to verify that the operational conditions were not extreme and that inhibition of thermophilic reactor was not due to overloading of the reactor.

2. Materials and methods

2.1. Analytical methods

Substrates and effluents were monitored once a week in terms of total and volatile solids content (TS and VS), COD on particulate and soluble fraction (pCOD and sCOD respectively), total Kjeldahl nitrogen (TKN) and total phosphorus (P_{tot}). The process stability parameters, namely pH, volatile fatty acids (VFAs) content and speciation, total and partial alkalinity (TA and PA) and ammonium ion, were checked twice a week. All the analyses, except for VFAs, were carried out in accordance with the Standard Methods (APHA–AWWA–WEF, 2011). Volatile fatty acids content was monitored using a gas chromatograph (Carlo Erba instruments) with hydrogen as gas carrier, equipped with a Fused Silica Capillary Column (Supelco NUKOLTM, 15m×0.53mm×0.5 µm film thickness) and with a flame ionization detector (200°C). The temperature during the analysis started from 80°C and reaches 200°C trough two other steps at 140 and 160°C, with a rate of 10°C/min. The analyzed samples were centrifuged and filtrated on a 0.45 µm membrane. The concentration of total polyphenols was measured using a modified version of the Folin–Ciocalteu reaction as reported in Laftka et al. (2007) and converted into Gallic acid equivalent (mg HGal/L).

Gas productions were monitored continuously by two gas flow meters (Ritter Company, drum-type wet-test volumetric gas meters), and their composition (CH_4, CO_2 and O_2) were monitored by portable biogas analyzer (Geotechnical Instruments, GA 2000). This instrument was calibrated using air with content of oxygen of 21%, and a certificated mixture of CH_4 and CO_2 (60% and 40% respectively).

2.2. Experimental setup

The experimental trial was carried out by two identical continuous stirred pilot-scale bioreactors each with working volume of 230 L. The reactors included a water jacket connected to a heating recirculation system to maintain a constant temperature of 37°C and 55°C. The digesters were fed once a day with a mixture of waste activated sludge and wine lee to reach HRT of 23 d and organic loading rate (OLR) of 3.2 kg COD/m^{3}d. The organic loading rate was chosen considering the results obtained by Da Ros et al. (2014), that demonstrate this OLR could inhibit the thermophilic process. The composition of feeding mixture derived from the real availability of winery wastes in a cellar able to receive about 300 thousand liters of wine per year: the mixture was composed by 0.6 kg COD/m^{3}d of waste activated sludge (WAS), and the remaining fraction (2.6 kg COD/m^{3}d) of wine lees (WL). Both the reactors started without metal elements addition, but after the failure of thermophilic process, a solution of Iron, Cobalt and Nickel was added to the reactor working at 55°C to reach the concentration suggested by Takashima et al. (2011) of 4.3 mg Fe-$FeCl_3$/L, 0.46 mg Ni-$NiCl_2$ $6H_2O$/L and 0.51 mg Co-$CoCl_2$ $6H_2O$. In order to evaluate the best concentration of metals, the doses were lowered step-by-step and maintained for at least a HRT for each dosage. In Table 1 tested doses in thermophilic reactor were reported, while the stable mesophilic system worked without metals addition and was used as control.

2.3. Inoculum and substrates characteristics

The reactors were initially filled-up with mesophilic and thermophilic digestates deriving from previous experimentation. The inocula were well stabilized, solids content was lower than 10 gTS/kg and stability parameters were in the optimum ranges of anaerobic digestion (Table 2).

Biowastes from wine-making process were used as feeding in this experimentation because of their low concentration of trace elements. Waste activated sludge (WAS) derived from a wastewater treatment plant working mainly with winery wastewater; the plant treated about 170 m^3/d of wastewater with average concentration of 3,747 mg COD/L. The treatment process was characterized by food to microorganisms ratio of 0.26 g COD/g MLVSS and long sludge retention time (35 d).

The WAS had high VS/TS ratio (88%) probably due to characteristics of raw wastewater, and well balanced nutrients ratio for biological treatment (Table 3). The wine lees were collected in same cellar that produced the WAS and it was formed by wine decanting after addition of bentonite.

Table 1. Tested metals doses in thermophilic reactor

	RUN 0	*RUN 1*	*RUN 2*	*RUN 3*	*RUN 4*
Fe (mg/L)	0	4.3	3.01	2.15	0.86
Ni (mg/L)	0	0.46	0.32	0.23	0.09
Co (mg/L)	0	0.51	0.36	0.25	0.10

Table 2. Mesophilic and thermophilic seed digestates characteristics (TS: total solids, VS: volatile solids on wet and dry weight, pCOD: COD on particulate fraction, sCOD: COD on soluble fraction, pH, TKN: total Kjeldahl nitrogen on particulate fraction, NH_4^+: ammonium concentration in soluble fraction; P_{tot}: total phosphorus, Polyphenols)

Parameter	*Unit*	*37°C*	*55°C*
TS	gTS/kg$_{ww}$	8.84	9.37
VS	gVS/kg$_{ww}$	5.92	4.69
VS	% TS	67%	50%
pCOD	mg/g TS	552	751
sCOD	g/L	910.7	1072.5
pH	-	7.53	8.33
TKN	mg N-NH_4^+/g TS	41.63	33.09
NH_4^+	mg N NH_4^+/L	193.4	539.4
P_{tot}	mg P-PO_4^{3-}/g TS	47.0	26.8
Polyphenols	mg HGal/L	83.75	58.35

The presence of this inert material determined low content of volatile solids (57% of total solids) and the COD was concentrated in the soluble form (sCOD was the 83% of total COD). The levels of nitrogen and phosphorus were limiting for bacterial growth if compared with pCOD concentration. Considering WL (Table 3), variability ranges of total and volatile solids were larger than ones of WAS, because of the variability of produced wine. Both substrates were poor in micro-nutrients because of their origin.

3. Results and discussion

The initial start-up period, in both reactors, consisted with stepwise increases of organic load maintaining constant the contribution of WAS (0.6 kg COD/m^3d) and increasing the amount of WL. In the same time the HRT was lowered from 46 d to 23d. During this period the specific gas production increased agree with OLR (Fig. 1), in fact supplied sCOD from WL, which was easily biodegradable COD, was completely converted to biogas. This transient period lasted 114 days.

3.1. Comparison of mesophilic and thermophilic processes without trace-elements

Mesophilic process reached steady state after two HRTs at constant conditions and was characterized by good stability parameters for the monitored period (9 HRTs). In particular pH ranged from 7.2 to 8.1, the soluble COD concentration was around 360 mg/L with less than half due to VFAs, and the ammonium content was about 400 mg/L. The process guaranteed the complete soluble COD removal but only a part of the particulate COD was converted into biogas. The 81% of COD was converted into biogas while solids were reduced of 19%. The average biogas production was 0.386 $m^3/kgCOD_{fed}$ with 78% of methane.

On the other hand thermophilic process did not show instability problems during the start-up period but started to accumulate VFAs after reaching the fixed conditions. In particular the VFAs concentration ranged from 476 mgCOD/L, at the end of start-up, to 6,825 mgCOD/L after 23 days of regular feeding.

The dominant volatile fatty acids were acetic and propionic acids, corresponding to the 66 and 15% of total COD, respectively. Consequently partial alkalinity was consumed, pH dropped down to 5 and methanogenesis was totally inhibited. The biogas production was reduced in this period from 0.39 to 0.25 $m^3/kgCOD_{fed}$, and later stopped.

Fig. 1 highlights the process instability in RUN0, detected by VFAs increase, and consequently specific biogas production (SGP) reduction. After feed suspension the hydrolysis of organic matter continued, in fact the VFAs concentration increased and degradation of proteins enhanced ammonium content.

The possible inhibitors were examined (free ammonia, polyphenols, sulphide). The free ammonia (FA) at 55°C was about 177 mg $N\text{-}NH_3/L$ and concentrations below 200 mg $N\text{-}NH_3/L$ are generally believed beneficial to anaerobic process since nitrogen is an essential nutrient for anaerobic microorganisms (Liu and Sung, 2002). Polyphenols were present in the winery waste at concentration of 1,496 mg HGal/L and, although their degradation was more difficult at thermophilic temperature than at mesophilic one (Levén and Schnürer, 2005), the measured concentration in the thermophilic effluent was 152.8 mg HGal/L, far lower than inhibiting level (Melamane et al., 2007). Utilization of $CuSO_4$ and SO_2 during winemaking process can cause high concentration of sulphates in WL. During the anaerobic digestion the sulphates were reduced to sulphides and H_2S was formed.

The H_2S is the most toxic sulphide form for the microorganisms involved into methanisation, and the inhibiting concentration range was 50–400 mg H_2S /L (Parkin et al., 1990). The content of H_2S was monitored in the biogas of both the reactors and resulted similar at different temperature (800 ppm). Considering the Henry's law the concentration in liquid phase of H_2S was lower at 55°C than at 37°C, and mesophilic reactor did not show inhibition effects. Moreover the pH > 7 determined the dominance of HS^- specie, less toxic than unionized sulphide.

Table 3. Waste activated sludge and wine lees characteristics (TS: total solids, VS: volatile solids on wet and dry weight, pCOD: COD on particulate fraction, sCOD: COD on soluble fraction, pH, TKN: total Kjeldahl nitrogen on particulate fraction, NH_4^+: ammonium concentration in soluble fraction; P_{tot}: total phosphorus)

Parameter	***Unit***	***Waste Activated Sludge***				***Wine Lees***			
		average	CV %	min	max	average	CV %	min	max
TS	gTS/kg_{ww}	158.9	31%	22.7	267.8	62.0	45%	12.3	120.0
VS	gVS/kg_{ww}	143.5	29%	20.7	237.3	33.6	45%	10.3	73.0
VS/TS	%	88%	3%	79%	93%	57%	23%	29%	86%
pCOD	mg/g TS	868	8%	749	1008	559	27%	312	919
sCOD	g/L	-				167	27%	111	204
TKN	mg $N\text{-}NH_4^+$/g TS	52.7	31%	14.5	80.3	30.3	42%	9.7	68.7
NH_4^+	mg N NH_4^+/L	-				33.9	67%	6.7	95.3
P_{tot}	mg $P\text{-}PO_4^{3-}$/g TS	7.3	27%	2.5	10.7	6.2	46%	2.6	14.3

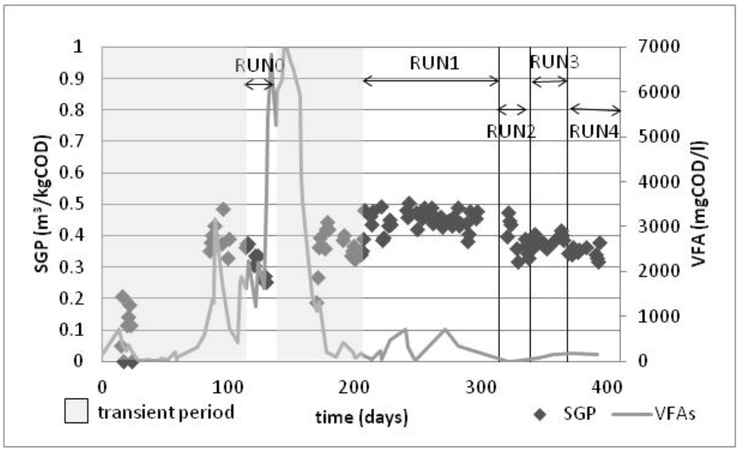

Fig. 1. Trend of biogas production in thermophilic reactor, comparison with mesophilic process (continuous line)

3.2. Thermophilic anaerobic digestion with trace-elements augmentation

High concentrations of VFAs and mainly of propionate were indicative of less bioavailability of trace elements at thermophilic operating temperature as suggested by Takashima et al. (2011). In order to verify the effect of trace elements supply, the thermophilic reactor was recovered and the second start-up was designed with trace elements addition to obtain concentration of 4.3 mg Fe /L, 0.46 mg Ni/L and 0.51 mg Co/L. The same metals augmentation was tested in the feed during RUN1 from day 205. The thermophilic process with these dosages was carried out for 4 HRT and it appeared steady in terms of stability parameters, effluents characteristics and biogas production. The pH ranged from 7.7 to 8.0, average ammonium concentration was 664 mg N-NH_4^+/L and the corresponding free ammonia value was 158 mg N-NH_3/L. Comparing VFAs in RUN0 and RUN1 (Fig. 1), it is clear the VFA concentration reduction and the corresponding increase of biogas production to 0.45 m^3/kgCOD$_{fed}$ with 77% of methane. On the other hand, comparison of mesophilic and thermophilic process (RUN1) showed an improved biogas production of 18% and increase of solid removal from 17% to 28%. In fact the average solid concentration was 20.6 g TS/kg$_{ww}$ because of greater hydrolysis of particulate matter at this temperature. The higher hydrolysis rate explained also the value of sCOD (995 mg COD/L) that was higher than in mesophilic effluent. Just the 30% of soluble COD was due to VFA, but they did not accumulate and the buffer capacity (total alkalinity 3,390 mg $CaCO_3$/L) was enough to maintain optimum pH value for anaerobic digestion.

The addition of trace elements also improved polyphenols degradation, in fact the concentration has been reduced to 66 mg HGal/L, slightly higher than in mesophilic effluents. The difference in degradation efficiencies between the operational temperatures were due to presence of the different microbial populations in the two environments and to partial inactivation of enzyme involved into phthalate-degrading pathways at 55°C (Levén and Schnürer, 2005).

In order to evaluate the best dosage, the amount of added metals were reduced to 70% of initial quantities (3.01 mgFe/L, 0.32 mgNi/L and 0.36 mgCo/L) in the RUN2. The stability parameters remained in the suggested range for anaerobic digestion during whole HRT. The monitoring results showed a slightly reduction of ammonium concentration (590 mg/L), alkalinity and pH, also the solid concentration was lower. These changes were not due to process but to wine lees variability. In fact the WL at the beginning of this period had low solid concentration (20.6 mg/g) and consequently the inlet nitrogen into reactor has been reduced. The results showed that the process could support nitrogen load variation and macro-nutrients were not limiting. During RUN2 the biogas production reduced of 14% and reached values equal of mesophilic process (0.39 m^3/kgCOD) with 71% of methane. Also the COD removal (73%) was quite similar to process at 37°C. Beside the reduction of biogas production the process remained stable and metabolites remains at low concentration, in fact average soluble COD was 740 mg/L. Instead, in terms of energetic and economical balance, thermophilic process became not advantageous compared with mesophilic one, even considering the major cost of metals supplementation.

In RUN3 metals addition had been reduced again to 50% of initial dose (2.15 mgFe/L, 0.23 mgNi/L and 0.25 mgCo/L) and the process did not change significantly its performances if compared with RUN2. The soluble fraction in the effluent remained below than 900 mgCOD/L, pH values ranged from 7.6 to 8 and ammonium stabilized around 650 mgN/L, corresponding to about 150 mgN/L of free ammonia. Total alkalinity was strongly affected by ammonium and increased from 2,440 mg$CaCO_3$/L, of previous condition, to about 3,160 mg$CaCO_3$/L in RUN3. The biogas production slightly reduced to 0.381 m^3/kgCOD with 69% of methane. Considering these results, significant differences between RUN2 and RUN3 were not detected, but anaerobic digestion is really complex process and is affected by many factors such as variability of substrates.

Finally trials with 20% of initial dose were carried out (RUN4) and the main variation was in terms of biogas production that reduced to 0.347 m^3/kgCOD, but the methane percentage remained good (70%). Although the decrease in biogas production was a sign of instability, the other parameters were consistent with anaerobic digestion range. pH was 7.9, total alkalinity stayed around 3,023 mg$CaCO_3$/L and ammonium concentration was 644 mg/L. Soluble COD was similar to the value obtained in RUN3 and indicated that methanogenic bacteria were not inhibited but probably the biological activity slowed with low metals addition. Considering performances of this condition the failure of process was expected with further reduction in metals dose.

3.3. Comparison of anaerobic digestion operational conditions

Monitored parameters of all tested conditions were reported in Table 4. Thermophilic process with metals augmentation had suitable stability parameters for anaerobic digestion without any significant differences among the tested dosages. Comparing with mesophilic process, ammonium concentration was higher, because of greater hydrolysis rate, and the free ammonia was one magnitude order different. Ammonium and volatile fatty acid concentration determined values of alkalinity greater than 3,000 mg $CaCO_3$/L and pH around of 7.9. The degradation of solid particles also affected the solid content in the digestates, which reduced at least of 10% respect to mesophilic effluent, and the nitrogen distribution. In fact the nitrogen is for 39-49% in soluble form at 55°C, while at 37°C less than 30% was ammonium nitrogen.

Greater solids removal efficiency also determined concentration of phosphorus into digestate, in fact the content in thermophilic effluent was always higher than in mesophilic one. The nutrients concentration in thermophilic digestate became it more interesting in terms of fertilization capacity.

Comparing metals requirement obtained by linear correlation between removed COD and metals addition, reported in Fig. 2 (0.352 $mgFe_{added}/gCOD_{rem}$, 0.042 $mgCo_{added}/gCOD_{rem}$ and 0.038 $mgNi_{added}/gCOD_{rem}$), with those reported by Takashima et al. (2011), they were in the same magnitude order but slightly lower probably because the metals content of the substrates increased the available metals concentration in the reactor feed.

The addition of metals, also in low concentration, allowed better degradation of polyphenols probably because trace elements were involved into polyphenolic degradation pathway. The process yields were the most interesting results of this study, the specific gas production and COD removed at 55°C went over mesophilic yields only with maximum tested dose, while in the other cases the productions were comparable or minor. Relationships between metals addition and COD removal were showed in Fig. 2. Considering the trials with lower additions of metals (RUN2, RUN3 and RUN4), micro-nutrients augmentation was well correlated with COD removal (R^2 99%), while in RUN1 the COD removal was higher than expected value from linear correlation.

Table 4. Comparison of stability parameters, digestate characteristics and yield at different operational conditions (pH, PA: partial alkalinity, TA: total alkalinity, NH_4^+: ammonium concentration in soluble fraction, FA: free ammonia, TS: total solids, VS: volatile solids on wet and dry weight, VS/TS percentage, pCOD: COD on particulate fraction, sCOD: COD on soluble fraction, TKN: total Kjeldahl nitrogen on particulate fraction, P_{tot}: total phosphorus, Polyphenols, SGP: specific gas prouction, percentage of CH_4, COD removal)

Parameter	*Unit*	*37°C*	*55°C*				
			RUN0	*RUN1*	*RUN2*	*RUN3*	*RUN4*
			Stability parameters				
pH	-	7.38	6.7	7.91	7.78	7.82	7.9
PA	mg $CaCO_3$/L	1370	1688	2043	1678	1941	1944
TA	mg $CaCO_3$/L	2287	3673	3390	2439	3062	3023
$N\text{-}NH_4^+$	mg $N\text{-}NH_4^+$/L	373	820	630	455	665	644
FA	mg $N\text{-}NH_3$/L	11.8	110	154	90	145	155
			Digestate characteristics				
TS	gTS/kg_{ww}	24.7	31.9	20.6	19.8	22.1	20.3
VS	gVS/kg_{ww}	14.3	19.5	12.1	13.3	11.6	11.5
VS/TS	%	58	61	59	67	52	61
pCOD	mg COD/gTS	614	671	615	680	602	556
sCOD	mg COD/L	391	5394	995	740	870	882
TKN	mg $N\text{-}NH_4^+$/gTS	37.9	40.4	33.1	35.9	37.6	33.1
P_{tot}	mg $P\text{-}PO_4^{3-}$/gTS	8	11.1	10.6	11.3	9.8	8.5
Polyphenols	mg HGal/L	26	153	66	61	57	-
			Yields				
SGP	m^3/kgCOD	0.386	0.390	0.450	0.386	0.381	0.347
CH_4	%	78%	72%	77%	71%	69%	70%
COD removal	%	79%	-	92%	73%	70%	65%

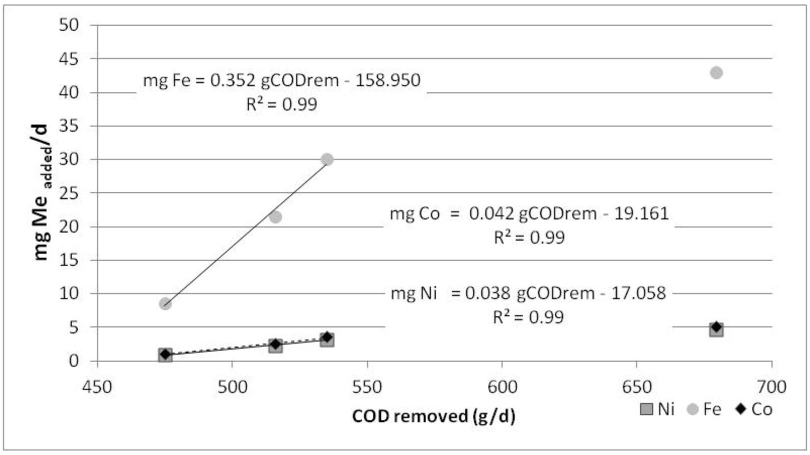

Fig. 2. Metals requirements in different tested conditions

It is clear that micro-nutrients have positive effect on anaerobic degradation of organic matter but they were also involved in complex chemical reaction in the reactor. Probably the metals at high concentration react with potential inhibiting agents as reported by Gustavsson et al. (2013) and have synergic effect on anaerobic process.

Naturally the metals dosages and the consume of energy to maintain a higher operational temperature should increase management cost, then the economical aspect has to be evaluated deeply in order to apply thermophilic process at full-scale. Metal salts costs depend on location of the treatment plant and transportation cost, quality of salts and quantity purchase. Quoted prizes range from 0.29 to 7.10 \$/kg $FeCl_3$ (Schafer, 2001) and are 147 \$/kg $NiCl_2$ $6H_2O$ and 1440 \$/kg $CoCl_2$ $6H_2O$ (Pfluger, 2010). More attractive nutrient sources could be some wastes with good content of metals such as livestock effluents or waste activated sludge from civil or industrial wastewater treatment. In fact sludge, deriving from wastewater treatment of fruit and vegetable processing, has low concentrations of metals. It is important to note that both sludge and manure have characteristics other than nutrients which may aid digestion: they increase bacteria population by continuous system inoculum, add alkalinity to the system and are a source of degradable organic matter. It is more effective to mix two or three organic wastes to prepare a nutrient sufficient feed-stock for a high-solids anaerobic digestion process (Kayhanian et al., 1995). Hinken et al. (2008) reported that anaerobic digestion of silage failed after the removal of manure in the feeding of reactor and demonstrated that trace elements concentration in biomasses depends on amount of manure in the substrate for digestion plants.

On the other hand thermophilic process could reduce effluent disposal costs because of better hygienisation effect. Several studies reported the greater pathogens depletion were reached at 55°C because the *E.coli* and *Salmonellae spp.* were significantly removed (Da Ros et al., 2014; Sahlstrom et al., 2004).

4. Conclusions

Mesophilic anaerobic digestion fed with winery wastes was steady and SGP reached 0.386 m^3/kgCOD, while thermophilic one failed because VFAs accumulated. The cause of instability was the different requirement of thermophilic bacteria. The augmentation of iron, cobalt and nickel in thermophilic process at different concentrations was carried out. Higher trace-elements augmentation (4.3 mg Fe /L, 0.46 mg Ni/L and 0.51 mg Co/L) increased biogas production to 0.450 $m^3/kgCOD_{fed}$ and COD removal reached 92%. While reducing metals addition, stability process remained in the optimum ranges for anaerobic digestion but yield reduced to value equal or lower than mesophilic one.

Relationship between metals addition and COD removal was linear only for the lowest three doses: 0.352 $mgFe_{added}/gCOD_{rem}$, 0.042 $mgCo_{added}/gCOD_{rem}$ and 0.038 $mgNi_{added}/gCOD_{rem}$. In the case of highest addition maybe other chemical equilibria, not considered in this study, interact with trace-elements availability.

Thermophilic anaerobic digestion had several benefits, but metals and heat costs should be kept into account.

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INVESTIGATION OF STRESS - STRAIN BEHAVIOUR OF RECYCLED AGGREGATE CONCRETE UNDER CYCLIC LOADS

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Abstract

The recent awareness about recycling also involves the resources used in civil engineering. The use of Recycled Aggregate Concrete (RAC) has several advantages in terms of conservation of natural resources and of reduction of pollution. Although the interest on the use of structural concrete with recycled aggregates is increasing, extensive studies on the mechanical behaviour of such materials that can allow their use in alternative to standard concrete are still lacking. As a consequence most of the structural codes do not provide any information on the mechanical characteristics of RAC while other codes just provide very basic information. This paper presents the results of an experimental investigation about the mechanical behaviour of recycled aggregate concrete under uniaxial and cyclical compressive loads. Both monotonic complete stress–strain curves and cyclic behaviour under high-level compressive loads were analysed. Stress – strain behaviour of RAC is particularly significant for a subsequent analytical investigation of the mechanical behaviour of the material. Indeed, the envelope diagram provides the modulus of elasticity, the elastic deformation, the proportional limit, the peak resistance and the total elongation, useful to understand the mechanical capabilities of the material and to plan further experimental tests. The cyclic tests were made with repeated loads with values varying between 25% and 75% and between 25% and 80% of the peak load. The aim of the tests was to evaluate the decay of the mechanical properties over time due to fatigue-induced damage. Three different percentages of recycled coarse aggregate, namely 0%, 50% and 100%, have been investigated in each test. The objective of the experimentation is to provide more information on the mechanical properties of concrete with recycled aggregates in order to better model their behaviour and to enhance their use in civil engineering.

Key words: compressive test, cyclic loads test, recycled aggregate concrete, stress-strain curve

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1. Introduction

Environmental sustainability is an important issue concerning the protection of the natural world, with particular accent on preserving the environment from the dangerous impact that human activities can have on it (Nicuţă et al., 2013). In this contest, the research of alternative solutions to reduce demolition and construction waste is becoming an increasingly popular issue (Muscalu et al., 2013; Simion et al., 2013). The reuse of recycled aggregates (RA) or recycled concrete aggregates (RCA) has several advantages: the conservation of the natural sources, the reduction of the environmental costs of exploitation and transportation of virgin materials and the reduction of landfills where the C&D waste material is disposed.

Nevertheless, the use of recycled material meets many barriers and obstacles due to lack of confidence with this material and to the lack of laws and standards for its use as aggregate for structural concrete. However in the recent years the interest to perform research on these materials grew up. The most common technologies for concrete recycling utilize RCA as road sub-base material and in non-structural concrete. The reuse of hardened concrete as

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new aggregate could also allows structural uses. The old concrete can be crushed and reused as a partial replacement for natural aggregate in new concrete constructions. The hardened concrete can be sourced either from the demolition of concrete structures at the end of their life or from leftover or surplus fresh concrete. Generally, performances of recycled aggregate concrete are comparable with those of concrete made with natural aggregates. However, before its extensive use in civil engineering, it is essential to understand the mechanical behaviour of recycled aggregate concrete. This paper is aimed at improving the knowledge of the mechanical properties of concrete realized with recycled concrete aggregates. In particular complete stress – strain curves and low-level cyclic tests has been performed on specimens with different RCA contents in order to evaluate the decay of the mechanical properties over time due to fatigue-induced damage.

The paper is organized as follows: Section 2 gives a background about research on the recycled aggregate concrete, with focus on fatigue behaviour; Section 3 presents the materials' properties and the experimental methodology; Section 4 presents the experimental results of displacement-controlled tests and cyclic tests; Section 5 concludes the paper.

2. Background

The use of recycled aggregates concrete has several advantages in terms of conservation of natural resources and reduction of pollution. Although the interest on the use of this new material is increasing, studies on several mechanical properties that could facilitate its use in alternative to standard concrete, such those on its fatigue strength, are still lacking.

Among all recycled aggregates, the most suitable ones for the production of new structural concrete are the recycled aggregates coming from concrete crushing (Recycled Concrete Aggregates - RCA). Nevertheless, even if it is generally agreed that there is a loss in the physical and mechanical properties of RAC if compared to natural aggregate concrete (Breccolotti and Materazzi, 2010, 2013), their fatigue behaviour has not been extensively analysed.

Fatigue studies on Natural Aggregate Concretes (NAC) have been undertaken since the beginning of the twentieth century (Van Ornum, 1907) reaching a consolidated state of knowledge. As far as NAC are concerned, Holmen (1979) and other authors observed the same behavioural pattern with regards to the strain increase during the fatigue life of a specimen subject to constant stress levels. This pattern can be described as follows. In a first stage a quasi-logarithmic increase in the maximum and minimum strain is achieved, with the increase rate of the maximum strain being slightly higher than that of the minimum. This stage corresponds to the initial formation of micro-cracks. During the second stage, associated with the growth and stabilization of the formed cracks, these strains grow following a linear trend until the third stage is reached. In this latter the interconnections of cracks cause the collapse of the concrete under fatigue loading. The increase in deformation, unlike the previous stages, is exponential. In the research of Petryna et al. (2002) a constitutive model for concrete subjected to cyclic loadings in both compression and tension is presented. This model was intended to provide improvements on modelling the cyclic behaviour of concrete structures in the context of computational programs based on a smeared crack approach. Particular emphasis has been paid to the description of the strength and stiffness degradation produced by the load cycling both in tension and in compression, the shape of unloading and reloading curves and the transition between opening and closing of cracks.

As far as lightweight aggregate concretes are concerned, the first studies about their fatigue strength, in particular on mix-design with different typologies of aggregate, were carried out during the sixties of the last century by Gray et al. (1961). The Authors performed fatigue tests on two different lightweight aggregate concretes, one with a high design strength and the other with low design strength. Specimens of approximately the same age were tested at different stress levels ranging from 40% to 80% of the ultimate static compressive strength of the respective mix-designs. Within the limits of the investigation, the fatigue behaviour of high strength lightweight concrete was similar to that of low strength lightweight concrete.

Only limited studies on the fatigue strength of RAC have been performed up to now and the results of experimental tests are not always in good agreement.

Xiao et al. (2013) carried out a research on the fatigue behaviour of RAC under uniaxial compression, in particular for the typology with 100% of recycled coarse aggregate. The main factors such as the residual strain variation, the fatigue strain variation and the fatigue modulus of RAC, were evaluated to find the relation between strain response and fatigue damage behaviour in RAC. The analyses didn't show significant differences between the fatigue compressive behaviour of RAC and NAC. Nevertheless, they observed by experimental tests two opposite trends in RAC's fatigue strength under uniaxial compression and bending cyclic loading: the fatigue life of RAC for the same stress level is higher than that of NAC under cyclic compression loading while the contrary is true under bending loading.

Yan et al. (2011) analysed the fatigue behaviour of RAC specimens subjected to axial and eccentric compression finding differences respect to non-recycled concrete. In fact, the Authors showed that, for the same water/cement ratio, the use of recycled aggregate in concrete implies a reduction of the fatigue life. There reduction is enhanced with smaller water/cement ratios due to the lower strength capacity of the recycled aggregates.

Luo and Yao (2011) analyzed the deformation curves and the response to ultrasonic pulses of recycled plain concrete subjected to low frequency fatigue. Their findings confirmed the presence of a damage accumulation similar to that observed by Holmen (1979) with amplitude of the three stages equal to 10%, 80% and 10% of the fatigue life, respectively.

Similarly, Thomas et al. (2014) observed that the three stages represent approximately 15%, 70% and 15% of the total life time respectively. The Authors also noticed that, for the same water/cement ratio, the use of recycled aggregate in concrete implies a reduction of the fatigue life in compression. This reduction is more evident for low water/cement ratios and the Authors suggest that such behavior is caused by the lower strength of the recycled aggregate in comparison to the natural ones.

Low cycle fatigue strength of RAC has been investigated by Gordon (2011) who carried out tests with three different w/c ratios and five natural aggregate replacements for a total of 224 concrete samples. The Author found that RAC concrete is virtually indistinguishable from a natural concrete up to a recycled coarse aggregates replacement of 25%. For higher values of replacement, RAC exhibits reduced resistance to degradation, increased stiffness degradation and a reduction in the energy dissipated during cycling.

3. Experimental program

To investigate the stress-strain behaviour of RAC under cyclic loads a two phases experimental program has been established. In the first phase tests have been carried out to evaluate the basic mechanical properties (compressive strength, elastic modulus and stress-strain envelope) of RAC. In the second phase tests with compressive and cycling load have been performed.

3.1. Materials

The recycled aggregates used in the experimental tests have been taken from 63 cubic specimens crushed in compression tests in a concrete testing laboratory (Fig. 1). Their compressive strength was between 30.1 and 32.1 MPa, with an average resistance of 32.5 MPa and a standard deviation σ of 0.716 MPa (Table 1). The concrete cubes were subjected to crushing to obtain recycled concrete aggregates (Fig. 2).

The aggregates used in the experimentation were investigated through the determination of the particle size distribution, the density in conditions of saturated surface dry (SSD), the absorption and the water content.

Through the particle size distribution, the percentage of different grain sizes contained within the aggregates has been achieved, according to Italian Standard Specificarions.

A representative dried sample of material was previously weighed and then sieved, following UNI EN 933-1 (UNI, 2012). The aggregates were analyzed by using a set of ASTM sieves with progressive smaller screen openings with dimension 40, 31, 5, 25, 20, 16, 12.5, 8, 4, 2, 1, 0.5, 0.25, 0.125 and 0.075 mm. Cumulative weight passing through each sieve is calculated as a percentage of the total sample weight. The results of the measurements and the particle size distributions of the natural aggregates are shown in Fig. 3. Differently from NA, it can be observed that RAC posses a continuous grain size distribution in the range 0.4 – 30 mm.

Fig. 1. Concrete specimens after compression test going to be recycled for new aggregates

Fig. 2. Recycled concrete aggregates after crushing

The estimation of the absorption and of the saturated surface dry (SSD) density of the aggregates have been carried out following the procedure of UNI EN 1097-6 (UNI, 2013) for fine materials, passing through the sieve with mesh size of 4 mm and for coarse aggregate, over 4 mm.

Table 1. Mechanical properties of concretes samples used for the recycled aggregates.

Concrete strength	*n. samples*	$R_{c,min}$ *[MPa]*	$R_{c,max}$ *[MPa]*	R_{cm} *[MPa]*	σ *[MPa]*	*COV*
C25/30	63	30.1	32.5	31.4	0.716	0.023

Table 2. Water absorption and SSD density of natural (sand and gravel) and recycled aggregates

Aggregate	*Water absorption [%]*	*Saturated Surface Dry particle density [kg/m^3]*
Sand	1.70%	2650
Gravel 4/8 mm	1.70%	2657
Gravel 8/12 mm	1.70%	2662
RCA	5.24%	2340

Table 3. Water absorption and SSD density of fine and coarse recycled aggregates

Recycled aggregates	*Water absorption [%]*	*Saturated Surface Dry particle density [kg/m^3]*	*Weight fraction*
Fine (< 4 mm)	7.70%	2222	25.6%
Coarse (> 4 mm)	4.40%	2381	74.4%

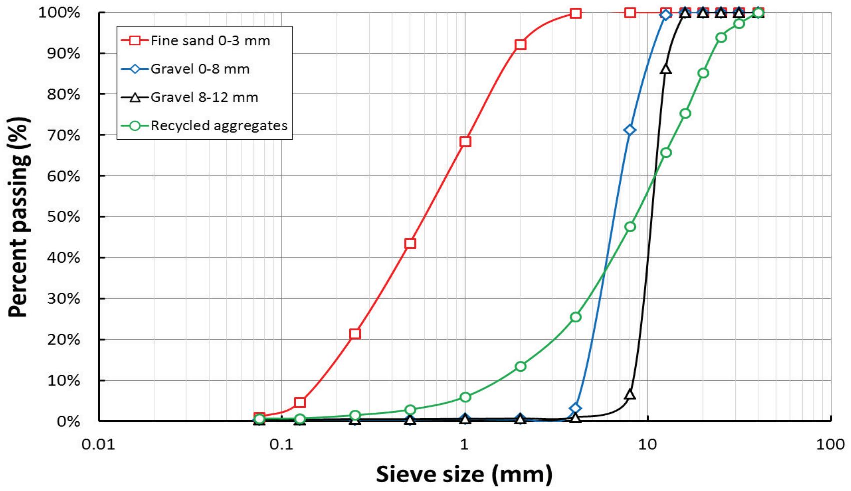

Fig. 3. Grading of natural (sand and gravels) and recycled aggregates

The representative values of the total recycled aggregates were obtained as a weighted average of the amounts of fine and coarse aggregate. For fine aggregate, water absorption and SSD density was calculated using Eqs. (1-2), where m_{ssd} is the saturated surface dry mass of 1 kg of aggregate, m_d is its dry mass, ρ_w is the water density, m_{p1} and m_{p2} are the pycnometer mass full of water and, respectively, with and ithout the original aggregate.

$$A = 100\frac{m_{ssd} - m_d}{m_d} \tag{1}$$

$$\rho_{ssd} = \rho_w \frac{m_{ssd}}{m_{ssd} - (m_{p1} - m_{p2})} \tag{2}$$

In the case of coarse aggregates water absorption and SSD density have been obtained as given by Eqs. (3-4), where V_{ssd} is volume of the saturated surface dry aggregate obtained by inserting the material into a graduated burette partly filled with a known quantity of water.

$$A = 100\frac{m_{ssd} - m_d}{m_d} \tag{3}$$

$$\rho_{ssd} = \rho_w \frac{m_{ssd}}{V_{ssd}} \tag{4}$$

Water absorptions and SSD densities are shown in Tables 2 and 3 for the natural and the recycled aggregates, respectively.

3.2. Specimens

The specimens for the investigation on the compressive strength and the complete stress-strain curve were cubes of 15 cm sides. For fatigue tests cylindrical samples with diameter of 10 cm and height of 20 cm has been investigated. A total of 48 cubic samples and 6 cylindrical samples were manufactured for those purposes. Cement type Portland 52.5 R was utilized. The water/cement ratio of the mixtures was 0.45.

To improve workability, a plasticizer was added in the amount of 0.8% by weight of cement. Table 4 summarizes the mix design of the different typologies of concrete realized for the experimentation. Table 4 lists the components by weight for a cubic meter of the realized concretes. The second column reports the mix design of the reference concrete. The third and the fourth columns describe the mix design of the recycled concretes where the natural coarse aggregate was substituted with respectively 50% and 100% of recycled coarse aggregate. For each mix-design, twin samples were realized. After the mixing and the cast, the samples of both natural and recycled concretes have been cured for 28 days in water at a controlled temperature of 20 °C.

Table 4. Mix design of recycled concretes

Component	Content (kg/m^3)		
	0% RCA	50% RCA	100% RCA
Cement 52.5 R	400	400	400
Water	180	180	180
Plasticizer	3.2 L	3.2 L	3.2 L
Sand	996	978	1067
Gravel 4/8	373	302	-
Gravel 8/12	409	89	-
Recycled coarse aggregates	-	369	641
Water/cement ratio	0.45	0.45	0.45

a) b)

Fig. 4. a) Experimental setup; b) Sample during complete stress-strain test

Before carrying out the experimental tests the cylindrical samples were superficially leveled by diamond grinding to ensure the flatness of the surface of the bases.

3.3. Experimental set up and test procedure

Three different test typologies were performed. The first one was about the compressive strength evaluated by means of a force controlled test. The second one was about the assessment of the complete stress-strain curve by means of a displacement controlled test. It also allowed determining the highest peak strength of the different mix designs. The third test was a cyclic fatigue test between two specific loads. In particular two ranges of values have been used: from 25% to 75% of the peak strength and from 25% to 80% of the peak strength, in order to evaluate the fatigue behavior under low-cycle fatigue. Thus the maximum loads (75% and 80%) used in fatigue tests were relatively high and close to the peak compressive strength.

The lower limit of 25% has been chosen to represent the service load that concrete is expected to experience during its life in typical structures. According to the envelope theory (Sinha et al., 1964), the failure in the fatigue tests arises when the cyclic curve reaches the stress-strain curve. Since concrete is a rate dependent material, it has been necessary to study the rate of the applied load. At the end of the stress-strain test, the Young's module has been calculated in order to calibrate the loading rate of the fatigue test.

Both typologies of test were performed with a Controls Advantest machine with a maximum capacity force of 5000 kN, instrumented with three linear displacement transducers arranged at 120 degrees (Fig. 4). Specific software allowed the test performances under displacement control for the envelope curves and under load control for the cyclic tests. The stress-strain tests performed on cubic specimens have been carried out with a strain rate of 1 µm/s. For the stress-strain tests on cylindrical specimens, the displacement rate was set equal to 26.4 µm/s. The loading rate of the fatigue test has been estimated in order to ensure that the behaviour of the material was similar to that of the envelope test in terms of strength and stiffness, with an upper limit of 3.5 MPa/s.

4. Experimental results

4.1. Fresh concrete properties

During the realization of the mixes of normal and recycled concrete fresh density and workability has been investigated. Fresh concrete workability was estimate through slump and flow tests by Abrams cone. Slump test concerns the measure of the subsidence of a standard cone of fresh concrete, while the flow is the average of two diameters in orthogonal direction after spreading of the concrete.

The results show (Table 5) that the realized concretes belong to the class of consistency S5, super fluid. Table 5 shows also comparable values of the density of fresh concrete for the three types of concretes with a slight decrease of the density for higher content of RA.

Table 5. Results of the slump and flow tests

Concrete type	*Slump [cm]*	*Flow [cm]*	*Density [kg/m^3]*
0% RCA	25.5	55.5	2368
50% RCA	26.2	67.7	2340
100% RCA	25.3	61.7	2278

4.2. Uniaxial compressive tests

After the proper curing period, cubic samples made of normal and recycled concrete were tested to investigate their compressive strength with a statistic approach. Resistance after 24 hours, 7 and 28 days has been evaluated. For each mix design two samples were tested after 24 hours and two samples after 7 days, while 9 specimens has been tested after 28 days of curing, in order to calculate the standard deviation and the coefficient of variation.

Before proceeding to the positioning of the specimens in the press, their mass has been evaluated, so to estimate the density of hardened concretes. The compressive tests on concrete cubes were performed following the UNI EN 12390-3 specifications (UNI, 2009). Tables 6 and 7 show the results of uniaxial compressive tests and the measurements of the average mass and the density during the curing time.

Since its early curing, the concrete with natural aggregate demonstrates higher compressive strength than those with recycled aggregates. Moreover, higher values of the coefficients of variation have been evidenced in recycled concretes in comparison with the normal one, highlighting a greater variability of their resistance.

4.3. Stress-strain curve tests

The stress-strain compressive behaviour with increasing strain of both normal and recycled aggregate concrete has been investigated by means of displacement-controlled tests described in the previous section. Figs. 5 and 6 show the complete stress-strain curves for the normal specimen and for the samples with 50% and 100% of recycled aggregates. In particular Fig. 5 is relative to cubic specimens, while Fig. 6 reports the results of the representative twin cylindrical specimens of that subjected to fatigue stress test.

The results appear consistent with the literature. Indeed, Xiao et al. (2005) found that RAC showed significant ductility decrease in the post peak region of the stress-strain curves. González-Fonteboa et al. (2010) observed opposite behaviour with a shift to the right in the stress–strain curves of the recycled concretes that becomes of considerable importance when the percentage of replacement is high. Such behavior is more visible in the results of the cylindrical samples. As observed by Dilger et al. (1984) this can probably be ascribed to the smaller confinement to which cylindrical samples are subjected that significantly reduces their ductility. The Authors also believe that the different speed of load application did not produce pronounced effects on the shape of the stress-strain curves.

Regard to the stress-strain tests on cylindrical samples, the peak compressive strength for the concrete with traditional aggregates is about 62 MPa, while the strength of concrete with 50% of recycled aggregates is 54 MPa and the compressive strength of the concrete with 100% of recycled aggregates is significantly lower and equal to 37 MPa. These results suggest that, given a certain concrete mix design, the replacement of standard quarry aggregates from recycled ones produces a lowering of concrete compressive strength. The Young's modulus, evaluated in correspondence of 0.4 times the peak strength according to the Italian standard NTC 2008, follows the same trend: concrete stiffness is higher for standard aggregate concretes, while it is lower for RAC.A summary of these data is reported in Table 8. As far as ductility is concerned, the lower the recycled aggregates content, the steeper the softening branch is. This observed behaviour allows authors to conclude that the use of recycled aggregate concrete produces an increase in ductility, partially due to the lower compressive strength.

Table 6. Results of compressive tests on samples of normal and recycled concrete after 24 hours and after 7 days of curing

Concrete type	*After 24 hours*			*After 7 days*		
	R_{cm} [MPa]	*M_m [kg]*	*Density [kg/m^3]*	*R_{cm} [MPa]*	*M_m [kg]*	*Density [kg/m^3]*
0% RCA	37.8	8.096	2399	55.5	8.176	2423
50% RCA	32.6	7.839	2323	53.1	7.959	2358
100% RCA	33.2	7.667	2272	46.1	7.676	2274

Table 7. Results of compressive tests on samples of normal and recycled concrete after 28 days of curing

Concrete type	*R_{cm} [MPa]*	*M_m [kg]*	*Density [kg/m^3]*	*σ [MPa]*	*COV*
0% RCA	64.0	8.088	2396	2.42	0.038
50% RCA	61.0	7.911	2344	2.81	0.046
100% RCA	54.3	7.782	2306	2.31	0.043

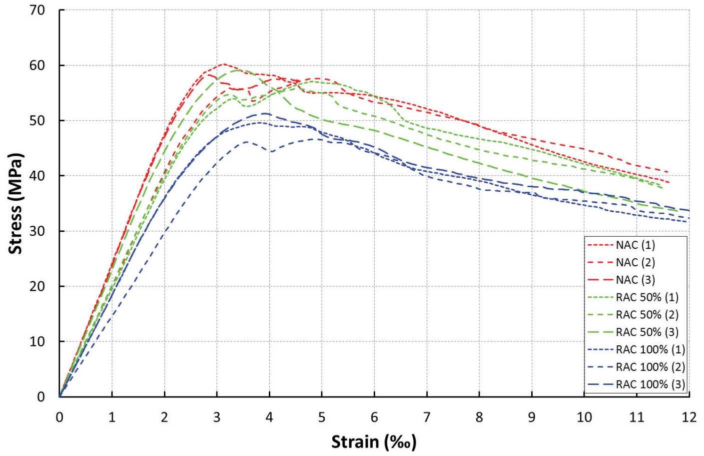

Fig. 5. Stress-strain curves for cubic specimens with different percentages of recycled aggregates content

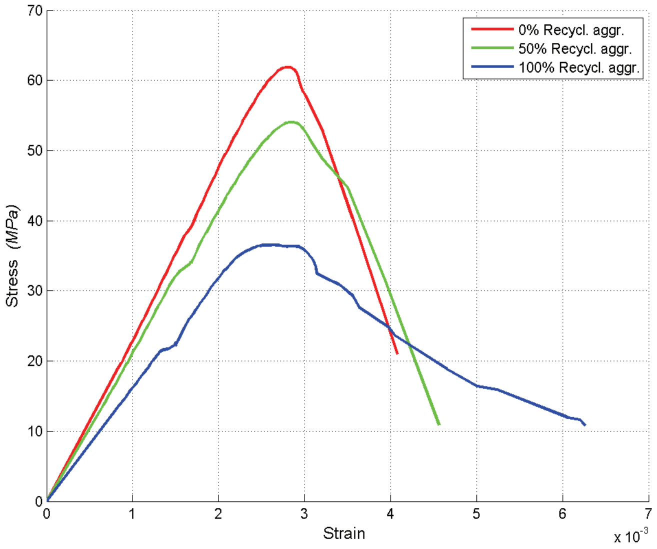

Fig. 6. Stress-strain curves for cylindrical specimens with different percentages of recycled aggregates content

Table 8. Mechanical properties of concretes with different content of recycled aggregates

Concrete type	***Compressive strength*** *[MPa]*	***Elastic modulus*** *[MPa]*
0% RCA	62	23053
50% RCA	54	21433
100% RCA	37	16301

4.4. Cyclic tests

In this section the results of fatigue tests on recycled aggregate concrete are presented. Authors studied how the variation of the recycled aggregates content influences the fatigue behaviour of concrete. These investigations have been performed using force-controlled tests having the lower bound equals to 25% of the concrete strength and the upper bound equals to 75% and 80% of concrete strength.

Table 9 summarizes the results of fatigue tests between 25% and 80% of concrete strength. In Figs. 7-9 the experimental stress-strain behaviour of, respectively, 0% (NAC), 50% and 100% recycled aggregate concrete is depicted side by side with the strain development with cycle progression.

Table 9. Fatigue behaviour of concretes with different content of recycled aggregates for loading cycles between 25% and 80% of peak compressive strength

Concrete type	***Strain at failure***	***Fatigue life*** *(n° cycles)*	***Load frequency*** *(cycles/min)*
NAC	$3.47 \cdot 10^{-3}$	400	3.20
50% RCA	$3.16 \cdot 10^{-3}$	236	2.99
100% RCA	$3.50 \cdot 10^{-3}$	271	3.35

The analysis of these results allows inferring the following facts. First of all fatigue induced failure occurs approximately when the fatigue stress-strain curve reaches the softening branch of the compressive envelope curve, as many authors have observed to happen for standard concrete. So no difference between this latter and RAC is observed in regards with this behaviour. As far as it concerns fatigue life no significant differences were observed by increasing recycled aggregates content from 50% to 100%. Strain development seems to resemble the trend described in literature according to which strain increases following a quasi-logarithmic rule during the first 15% of fatigue life, followed by a linear increase until about 85% of fatigue life, and finally failure is achieved with an exponentially increasing strain during the last 15% of specimen life.

In Table 10 results for fatigue tests between 25% and 75% of concrete strength are summarized. It should be noticed that for concrete with 50% of recycled aggregates content fatigue life was not observed during low cycles tests. In Figs. 10 and 11 the stress-strain curves for both 50% RAC and 100% RAC are depicted. By comparing these results with the previous ones it is clear how just a slightly lower upper bound on the applied load produces a significant increase in concrete fatigue life. Moreover, even if 50% RAC failure did not reached failure, the 100% sample illustrates how failure still occurs approximately when the stress strain path meets the softening branch of the envelope curve, regardless of the applied loading level. As a consequence, it can be concluded that a higher load level increases the plastic strain developed at each cycle but does not modify the failure mechanism.

Table 10. Fatigue behaviour of concretes with different content of recycled aggregates for loading cycles between 25% and 75% of peak compressive strength

Concrete type	***Strain at failure***	***Fatigue life*** *(n° cycles)*	***Load frequency*** *(cycles/min)*
NAC	n.a.	10117[a]	n.a.
50% RCA	$> 2.59 \cdot 10^{-3}$	> 1838	3.14
100% RCA	$3.23 \cdot 10^{-3}$	1122	3.70

[a] *experimental data according to Kim and Kim (1996)*

5. Conclusions

The present work presents the first results of a study on constitutive laws and on fatigue behaviour of RAC. Compressive strength decreases with the RAC percentage increase in the mixtures. Indeed the peak resistances of concretes with 50% and 100% of recycled aggregates are respectively 13% and 40% lower than that of normal concrete.

Moreover, the tests show a decrease in the stiffness of RAC with respect to normal concrete, especially for the mix with higher percentages of recycled aggregates.

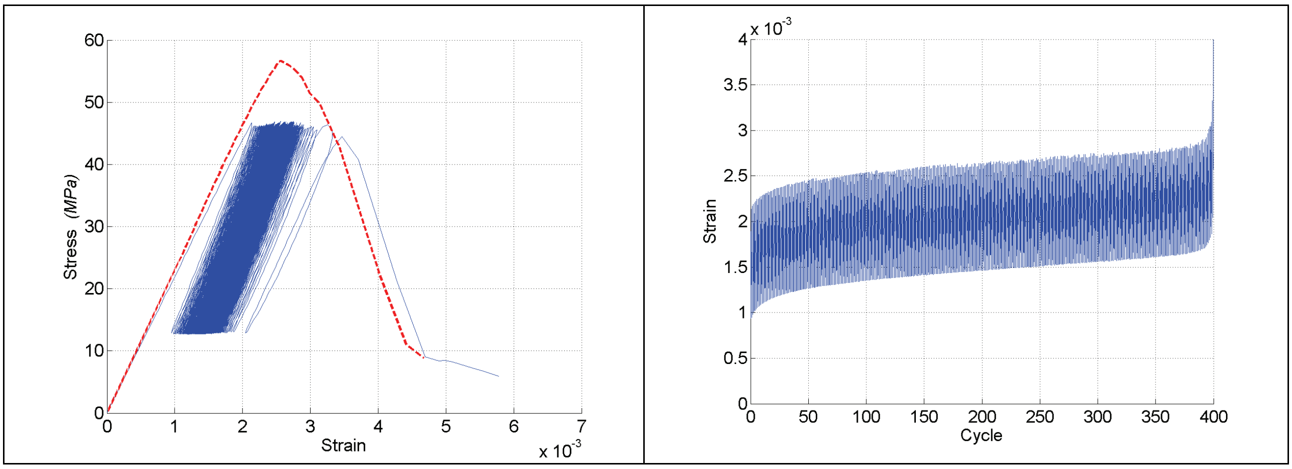

Fig. 7. On the left: fatigue stress strain behaviour of NAC loaded between 25% and 80% of peak strength. On the right: strain development with increasing cycles

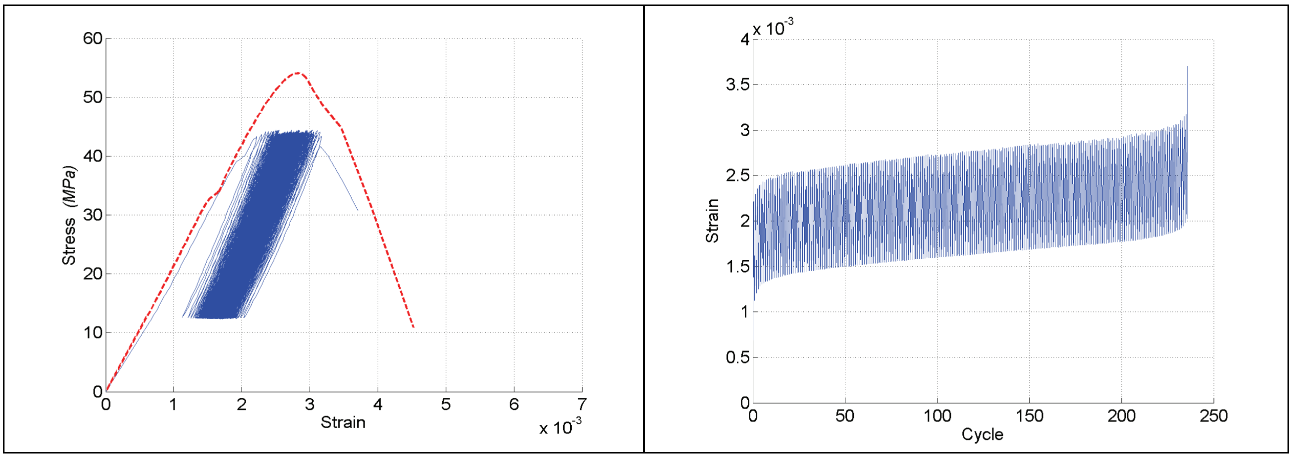

Fig. 8. On the left: fatigue stress strain behaviour of 50% RAC loaded between 25% and 80% of peak strength. On the right: strain development with increasing cycles

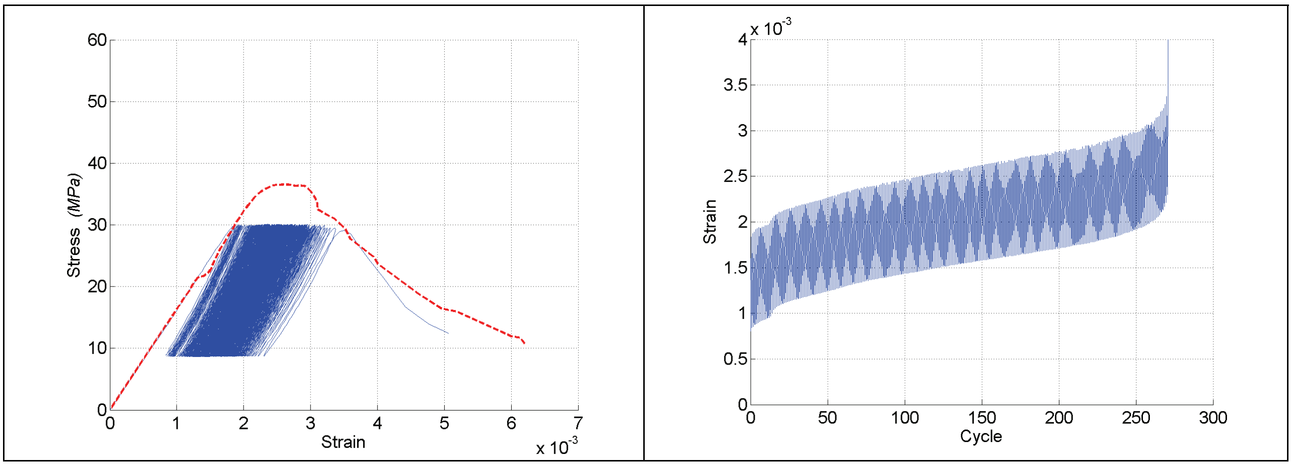

Fig. 9. On the left: fatigue stress strain behaviour of 100% RAC loaded between 25% and 80% of peak strength.
On the right: strain development with increasing cycles

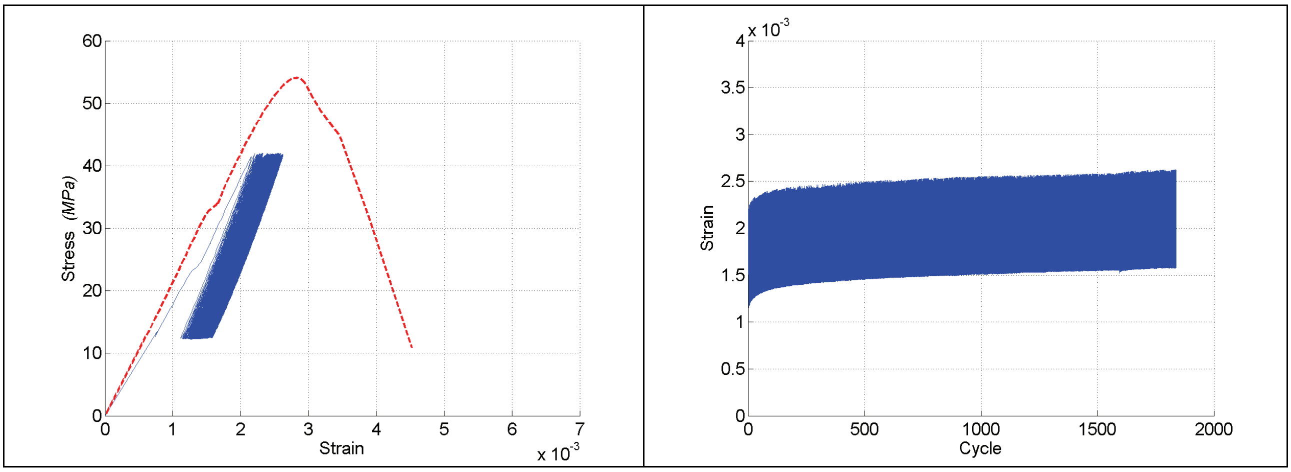

Fig. 10. On the left: fatigue stress strain behaviour of 50% RAC loaded between 25% and 75% of peak strength.
On the right: strain development with increasing cycles

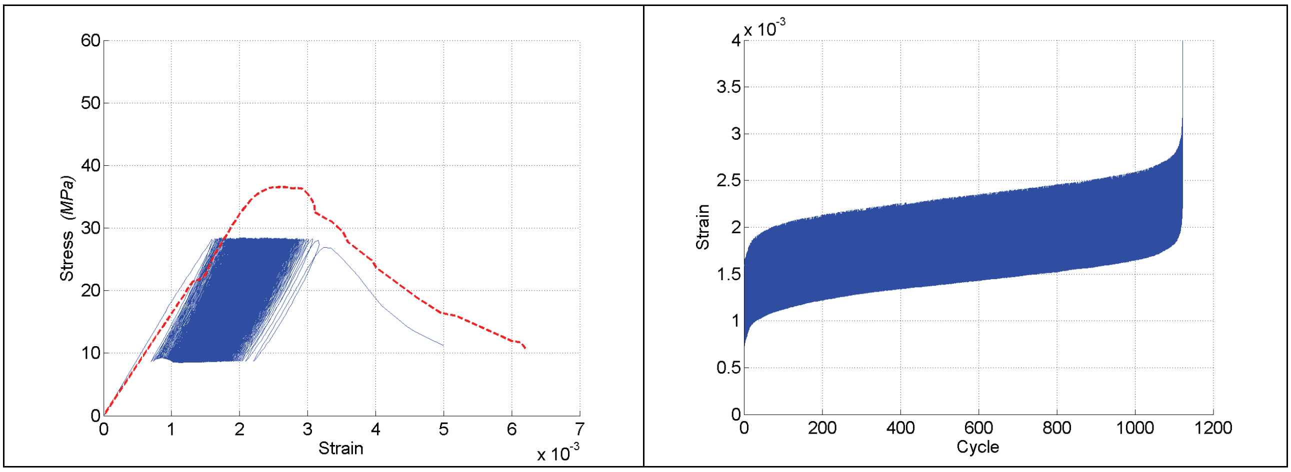

Fig. 11. On the left: fatigue stress strain behaviour of 100% RAC loaded between 25% and 75% of peak strength.
On the right: strain development with increasing cycles

The fatigue behaviour of RAC exhibits characteristics and damage accumulation pattern similar to those available in literature for normal aggregate concrete. Nevertheless, as observed by other Authors the use of recycled aggregate as replacement of natural coarse aggregates in concrete seems be responsible of a reduction of the concrete fatigue life.

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INNOVATIVE TECHNOLOGIES FOR METALS RECOVERY AND PLASTIC VALORIZATION FROM ELECTRIC AND ELECTRONIC WASTE: AN INTEGRATED APPROACH

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Abstract

The increasing diffusion of Hi-tech complex products has raised the attention of scientific community towards their End of Life (EoL) treatment, both in terms of assuring an appropriate disposal, to avoid the dispersion of harmful substances, and at the aim of their exploitation as valuable sources of raw materials. Within this study an integrated approach for waste electrical and electronic equipment (WEEE) end of life treatment is proposed based on the integration of hydrometallurgy for metal recovery and pyrolysis for plastic fraction valorization, with a particular focus on EoL personal computers. An innovative hydrometallurgical process with limited environmental impact for the recycling of added value metals (Au, Ag, Cu, Sn, Pb) from printed circuit boards was developed and thermal technologies were investigated for the valorization of mixed plastic components. The results show metal recovery rates up to 99% and purity grade up to 99%. With reference to plastic valorization, the maximized production up to 95% w/w of both a liquid and gaseous hydrocarbon-based stream to be exploited as a fuel or as source of chemicals was achieved from WEEE plastic fractions.

Key words: hydrometallurgy, mixed plastic, personal computers, printed circuit boards, raw materials, recycling, recovery, thermal technologies, WEEE

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1. Introduction

Technological advancements of these last decades have led to high demand for strategic raw materials, essential for the manufacturing of electrical and electronic devices and to an increase of e-waste generation. Modern electronic equipment can contain more than 60 elements (Circular Economy & Resource Efficiency Experts, 2012) some of which contain harmful substances that require adequate treatment before disposal. On the other hand e-waste could represent a highly valuable source of raw material, while this opportunity is nowadays being lost, since just 15-20% of the world e-waste results to be recycled annually (US Environmental Protection Agency, 2012). This is particularly due to the metal centric approach which is mainly focusing on the recycling precious and high content added value metals, discarding all the rest. As stated also in the UNEP report (UNEP, 2013) a shift from metal centric towards a product centric approach is mandatory in order to achieve higher recycling rates of raw materials and lower production of discarded waste.

In the last years the issue of raw materials supply has emerged worldwide, and especially in

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Europe. Indeed raw materials availability for European industry system is becoming more problematic as shown by a recent report published by the European Commission (European Commission, 2014), identifying a periodically updated list of critical raw materials (20 CRM identified in 2014), most of which are contained in waste electrical and electronic equipment (WEEE).

To solve the issue, EC strategy is based on three main pillars: sustainable mining, recycling and substitution with alternative (not critical) materials. Furthermore, there is a need to address compliance with the EU WEEE Directive (European Commission, 2012), fixing a collection target of 4 kg/capita/year until December 31st 2015, with progressive increments since 2016, and with the EU Landfill Directive (Official Journal, 2003), forbidding the landfilling of waste with a Lower Heating Value (LHV) exceeding 13 MJ kg^{-1}, including in particular plastics which, as a petroleum derived product, show a LHV ranging between 35 and 45 MJ/kg (Green and Perry, 2007).

Within this frame, an integrated approach for the recycling of added value metals and plastic from WEEE is presented, as a part of a wide project named ‘Ecoinnovation for Sicily’, funded by Italian Government (2011-2015). In particular, the work is focused on the exploitation of WEEE as special source of raw materials. The main objective of this study was to develop and test eco-innovative integrated technology solutions for raw materials recycling and plastic valorization from WEEE, with a special focus on personal computers (PC) external cases and printed circuit boards (PCBs).

Many authors studied recovery of valuable materials from WEEE (Waste Electrical and Electronic Equipment) (Kumar et al., 2014). The novelty of this study consists in the definition of integrated solutions allowing the maximization of materials recovery from end of life complex products and the minimization of discarded waste.

The complexity of WEEE matrices requires the application of an all-round strategy involving the integration of different technologies (De Marco et al., 2008; Ficeriová et al., 2005; Heerman et al., 2001, Hidalgo et al., 2014). With regard to added value metals recycling, an eco-innovative technology was developed and tested, based on hydrometallurgy. Hydrometallurgical techniques were chosen as an alternative to the pyrometallurgy (heat treatment) since they present a series of advantages. Hydrometallurgy, being operative at room temperature, compared to pyrometallurgy has lower requirements in terms of energy consumption and atmospheric emissions; in addition, being based on a sequel of chemical and physical-chemical steps it allows the recovery of low content metals, combined to high selectivity, modularity and flexibility of the operating plants.

With reference to WEEE mixed plastic components valorization, mechanical recycling is generally problematic both for the great heterogeneous composition and for the presence of hazardous substances. Currently mechanical treatments cannot be used on mixed plastics waste with a consistent content in inert and metal fraction, as it frequently happens in WEEE recycled mixed plastics unfortunately has poor mechanical properties and short lifetime, and, therefore it is only exploitable in lower grade applications (Riess et al., 2000). Although plastic reprocessing is technically feasible, ecological-impact studies in the Netherlands and Germany (Brandrup, 1996) have demonstrated that there is a limit of 15%–18% to the amount of thermoplastic waste that can be mechanically recycled with environmental convenience; thus the majority of remaining waste must be recycled by other techniques. For this reason in this study it was decided to focus on the recovery of valuable aliphatic and aromatic fragments (liquid fraction) and valuable gas from PCs mixed plastic components by application of pyrolytic processes.

Following a product-centric approach, an integrated process to recover added value metals and valorize plastic components has been developed: added value metals (i.e. Au, Ag, Cu) were recovered by hydrometallurgical techniques and plastic components were treated by pyrolysis to produce liquid and gaseous hydrocarbon-based streams to be exploited as a fuel or as possible source of chemicals, after an adequate further refining treatment.

2. Experimental

2.1. WEEE materials

The PCs and PCBs were obtained from an authorized Italian WEEE collector after manual dismantling/disassembly of end of life (EoL) household computers.

PCBs wastes are characterized by significant heterogeneity and high complexity with a relatively low metal content: metals are present as a coating of various thickness, and as component of solders, capacitors, resistors etc. The PCBs were checked to manually remove connecting devices when present before undergoing leaching processes. The plastic fraction from PCBs was mixed with that from external housing of PCs.

2.2. Recovery of added value metals from PCBs

All solutions for leaching experiments and metals content evaluation were prepared with analytical grade reagents and de-ionized water. The acids, standards and salts were purchased from Sigma Aldrich, metal ions were determined by Microwave Plasma Atomic Emission Spectrometery (4100 MP-AES, Agilent Technologies); powder composition was determined by X-ray fluorescence spectrometer (Spectro X-LAB 2000 spectrometer). Calibration was carried out for each analysed metal by analyzing at least 5 concentration level standard solutions. Internal quality control checks were carried out, including procedural blank evaluation. All experiments were performed at 25°C.

Leaching experiments and total content evaluation were performed on 10 whole PCBs samples (ranging from 1 to 3 kg).

The total metal content was evaluated as sum of two successive leachates content (1st leaching on whole PCBs, 2nd leaching on triturated remaining PCBs) and solid residue content, after dissolution in aqua regia.

Comparative leaching experiments were carried out using different acidic media: HNO_3, H_2SO_4, HCl, HNO_3 + H_2O_2 with at least 20% w/w acid concentration. Kinetic studies were performed from 0.5 h up to 24 h.

The leached PCBs deriving from leaching treatment were grinded and subject to further leaching experiments with HNO_3, in order to recover the Cu contained inside the plastic/resin slices. A comparison among different operation conditions was carried out, in terms of acid concentration.

The recovery of Cu, Ag, Pb and Fe from leachates was performed using a fractioned precipitation process, varying pH and solubility conditions. The products (salt and/or hydroxides) were purified through a further dissolution and precipitation processes. Ag and Cu were recovered by chemical and/or electrochemical reduction (Donati et al., 2009). The precipitates were washed, dried and weighted, then dissolved again by acidic media to be analyzed.

2.3. Thermo-valorization of plastics from PCBs and small appliances

A pyrolysis process aimed at fuel and/or feedstock production from WEEE mixed plastic fractions was developed. The fixed bed pyrolysis system consisted of a quartz tube reactor, electrically heated, 450 mm in length and 14 mm of inner diameter. Batch runs employed 10-50 g of sample, under N_2 flow at the rate of 2 mL/min to ensure an inert atmosphere. Identification of the type of polymers was carried out using Fourier Transform Infrared Spectroscopy (FT-IR). The oil recovery was assured by a water-cool condenser located downstream the pyrolysis reactor. The gaseous product was sampled by proper gas bags whose content was qualitatively analysed by a Thermofisher Ultra Gas Chromatograph, utilizing a 30 m long and 0.5 mm of inner diameter column, based on synthetic spherical carbon molecular sieves. The char fraction was mechanically collected after each run; moreover, any tar residue stuck to the inner walls of the quartz tube was thermally removed. Both oil and char weight composition were analysed, in terms of %C, %H, %N, %S by an Elemental Vario Macro Cube Instrument. The gas yield was estimated as a difference between the input material and the sum of the oil, char and ash collected from each run. Chemical species in the oil fraction were identified by a FT-IR Thermofisher Nicolet spectroscope on-line connected. The establishment of the pyrolysis operating conditions has required a preliminary kinetic study which allowed predicting the decomposition reaction time with temperature and conversion.

Thermal analysis experiments were performed on about 10 mg of sample (in a powder form) with a SETARAM 92-16.18 Thermogravimetric Analyser coupled with a Thermofisher Omnic FTIR spectrometer (TGA-FTIR) between 298 and 973 K using four heating rates (2, 5, 10 and 15 K min^{-1}), under an argon carrier gas of 30 mL min^{-1} flow rate. The instrument was calibrated by melting some standard metals in the temperature range of 430 K (Indium) and 1235 K (Silver) and heating rates between 2 and 15 K min^{-1}; the temperature uncertainty was 0.5 K. Because of the buoyancy effect, a preliminary "blank experiment" was carried out before each run.

3. Results and discussion

3.1 Hydrometallurgical process for the recovery of added value elements from PCBs

In Table 1 the average material content distribution in PCBs is shown: data has been evaluated out of three different samples (ranging from 0.5 to 3 Kg) and reported as percentage in weight with a standard deviation below 5%.

Table 1. Average PCBs materials composition

Materials	***% w/w***
Plastic	18.30
Au	0.02
Cu	12.90
Pb	1.54
Sn	4.30
Ag	0.03
Fe	0.96
Ni	0.53
Zn	0.09
Al	1.45
Mn	0.02
Cr	0.02
Solid residue (resin, glass fiber, etc.)	59.84

It was found that HNO_3 (at least 20%) is the best leaching agent, gold not being dissolved: two consecutive leaching steps were carried out using the selected leaching agent and the solid residue was leached with aqua regia in order to verify mass balances.

In Table 2, as an example, the results using liquid/solid (L/S) ratio equal to 3:1, HNO_3 20% in 24 h are reported. During the treatment tin precipitates as oxide/acid metastannic. This precipitate was separated, then gravimetric and XRF analyses were performed, thus confirming this hypothesis. Applying this leaching conditions, both Au and $SnO_2/Sn(H_2O)_n$ can be recovered from the residue by a physical-mechanical process with a yield of 99%.

Finally the remaining depopulated PCBs, were shredded and leached by nitric acid to recover the remaining 48% of Cu present in the inner layers, to reach an overall yield of 98%, thus demonstrating the process effectiveness.

Table 2. PCBs leaching efficiency of two sequential steps (HNO_3 20%, L/S = 3:1, 24 h). Standard deviation associated to all data is below 5%

Metal	*1st leaching on whole PCBs (%)*	*2nd leaching on triturated remaining PCBs (%)*	*Leaching solid residue (%)*
Cu	45	7	48
Pb	91	3	6
Sn	31	5	64
Ag	99	1	0
Fe	18	37	45
Ni	82	6	12

In Fig. 1 the results of a leaching test performed using HNO_3 20%, L/S ratio 3:1, are reported as function of the time. As confirmed by kinetic curves, Au is not solubilized under this leaching conditions and Sn content decreases over time, due to precipitate formation $SnO_2/Sn(H_2O)_n$. As shown in Fig. 1, 90% of leached metals can be already recovered after 6 hours leaching.

The leachate coming from the first leaching step contains Ag, Pb, Fe and Cu which can be separated through a fractioned precipitation process. After their recovery, Ag and Cu are treated to obtain the elements as metals via electrowinning and/or chemical reductive processes.

Finally the leached boards resulting completely cleaned from metals on the surface, but still containing significant amounts of Cu inside, were triturated and subjected to new leaching treatment to recover remaining Cu.

As a results of this hydrometallurgical process, a metal recovery up to 99% as yield and purity grade was achieved. Furthermore this process allows treating the whole PCBs, avoiding any preliminary trituration step. The developed hydrometallurgical process is reported in Fig. 2.

3.2. The recovery of mixed plastics from small appliances

3.2.1. Plastic components FT-IR analysis

As it has been previously stated, WEEE plastic fractions enclose a large number of different polymers.

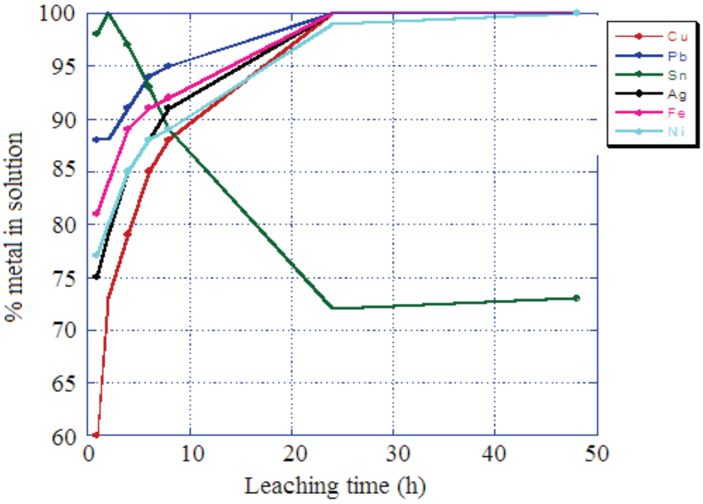

Fig. 1. Leaching kinetic test (HNO_3 20%, L/S = 3:1)

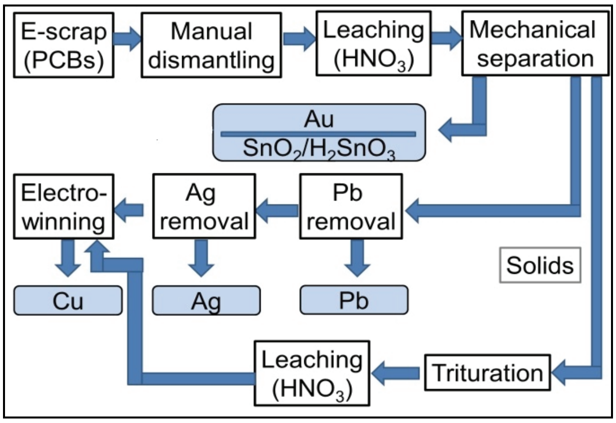

Fig. 2. Hydrometallurgical process for the recycling of gold, silver, tin, copper and lead from waste printed circuit boards (Fontana et al., 2013)

Polymer identification in mixed plastic components from personal computers (external cases and PCBs) by FTIR analysis revealed the presence of high-impact-polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) as main components for external cases (Fig. 3 sample A); conversely, as far as the PCB is concerned, polybutadientherephtalate (PBT), polyamide 66 (Nylon 66) and polyphenylene sulfide (PPS) were mainly found (Fig. 3 sample B).

Taking into account the results of a field investigation carried out through WEEE sampling and IR analysis and interviews to managers and technicians of some waste treatment plants located in center Italy, a simplified ternary mixture of the three main polymeric constituents (ABS, HIPS and PBT) was defined to be used as representative of personal computers plastic composition.

A simulated PC sample was prepared for process development purposes by mixing defined triturated fractions of the three above mentioned polymeric components.

This sample was defined as "simulated PC" having the following composition: ABS, 64%, HIPS, 33%, PBT, 3%, being considered as representative of plastic composition in personal computers. The work proceeded by investigating a pyrolysis process applied to the sole thermoplastic fraction inside the PCBs, defined as "black slot", which makes up the inner electronic connectors. Finally, pyrolysis was applied to "simulated PC" samples.

3.2.2 Thermal and spectroscopic (TG–FTIR) characterization under pyrolytic conditions

TGA-FTIR results related to the thermal decomposition of black slot samples are showed in Fig. 4. The plot of the Gram-Schmidt curve along with the TG diagram allows describing the reaction trend.

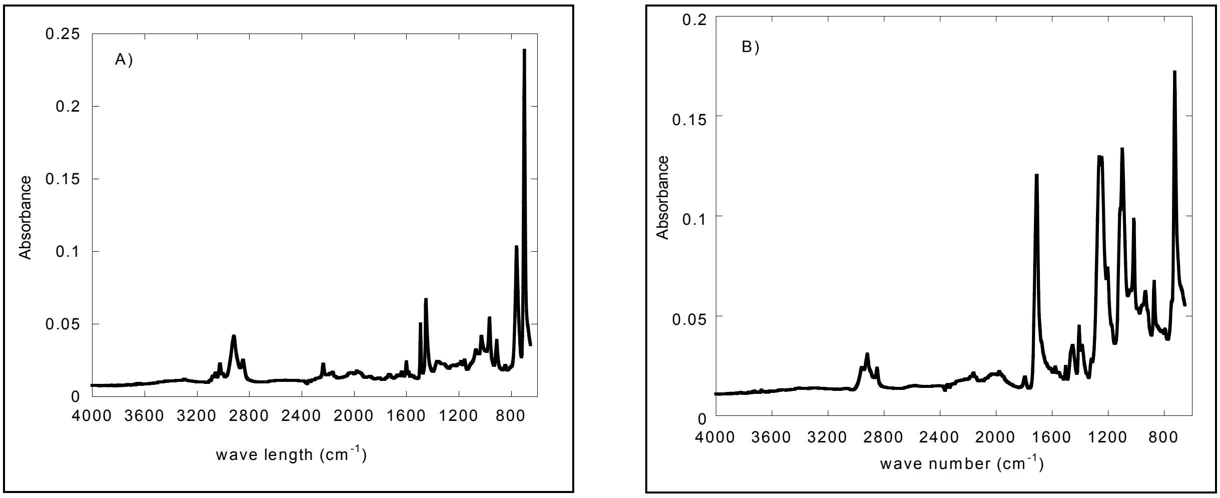

Fig. 3. FT-IR analysis of mixed plastic from PC external case (sample A) and PCBs (sample B)

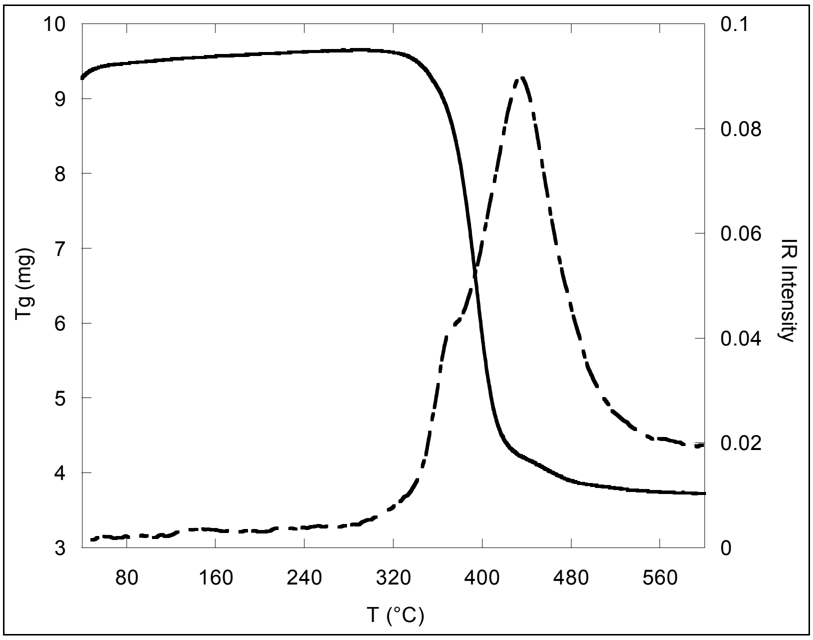

Fig. 4. TG/Gram-Schmidt plot for thermal decomposition of black slot

By examining the TG curve, a sharp mass decrease can be observed at 390°C, corresponding to the thermal degradation, as it is confirmed by the appearance of the Gram Schmidt plot which sums the IR signal intensities of the gaseous products; the TG/FT-IR diagram puts in evidence that thermal degradation occurs in a single step. Besides, the TG curve shows a remarkable residue amount around 22% w/w, which can be attributed to the production of conjugated aromatic rings and the high concentration of flame retardants used in the slots of PCBs (Cafiero et al., 2014). Fig. 5 shows the results of simulated PC sample which is mainly made up with styrene-based polymers. Thermal degradation occurs at 422°C leaving a low residue amount (less than 2% w/w).

IR spectrum of evolved gases from black slot sample pyrolysis is reported in Fig. 6. The bands around 2870 and 2981 cm^{-1} are characteristic of the presence of aromatic ring or substituted phenyl ring. Absorption bands at about 900 cm^{-1} are related to pulsation vibrations and those at about 1080 cm^{-1} to asymmetric skeletal vibrations of the Tetrahydrofuran (THF) ring (stretch C-O ether). Asymmetrical stretching vibrations of the CH_2 groups at 2981 cm^{-1}, and CH stretching at 2870 cm^{-1} are observed and attributed to butadiene fragment-units. Peaks of carbon anhydride are also visible. These findings are confirmed by literature (Samperi et al., 2004), where PBT degradation is described as occurring in the following steps: the primary formation of cyclic oligomers, their further decomposition to generate unsaturated oligomers (butadiene) plus terephtalic anhydride containing oligomers; besides, THF results to be a secondary product of the polycondensation of PBT from 1,4 polybutanediol and terephthalic acid (Buyle et al., 1981). THF is a cyclic ether used as a solvent in the manufacture of paint, adhesives, impression ink, pharmaceutical products, etc.

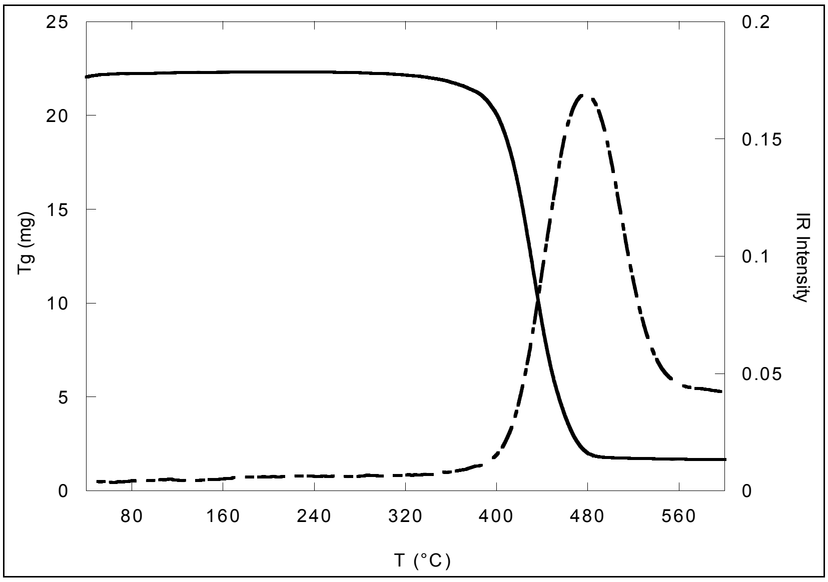

Fig. 5. TG/Gram-Schmidt plot for thermal decomposition of simulated PC

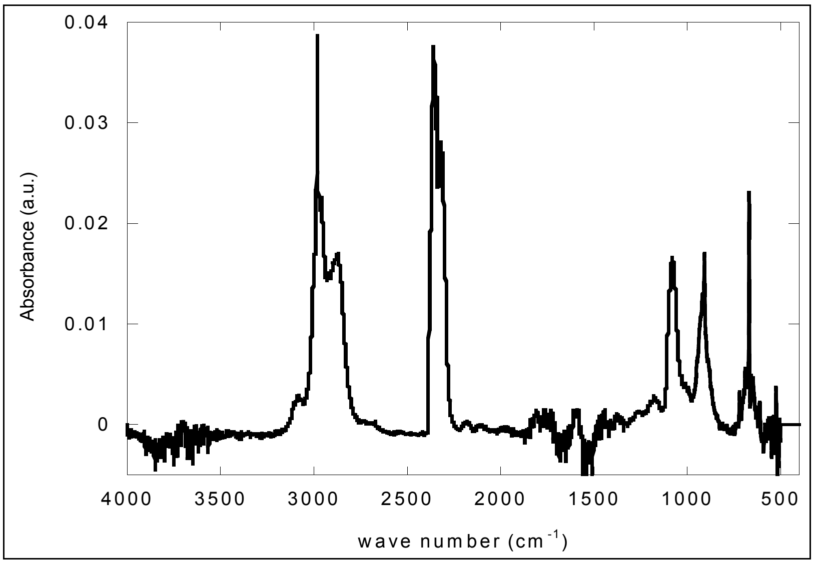

Fig. 6. FTIR spectrum of black slot sample pyrolysis evolved gases

THF most important industrial application is the production of politetramethylene-glycol (PTMEG), necessary in the elaboration of Spandex Fibres, polyurethane and polyester ether (Nexant, 2004). The other obtained product is the butadiene, the largest use of which is the production of synthetic elastomers including styrene-butadiene rubber (SBR) and polybutadiene rubber, employed in the manufacture of tires. Butadiene is also copolymerized into plastics, such as ABS. The FT-IR spectrum of the gas generated by the pyrolysis of simulated PC sample is represented in Fig. 7.

The substance which matches the highest numbers of peaks corresponds to styrene. In addition to the characteristic peaks of styrene, the alchilic peak at 2850 – 2920 cm_{-1} (ν $–CH_2$) probably related to a butadiene fragment and the peak 2200 – 2300 cm^{-1} characteristic of CO_2, coming from the break of the esteric group of PBT can be observed. The fact that styrene appears to be the largest pyrolysis product is also confirmed by the trend of the Gram Schmidt curve reported beside the TG diagram in Fig. 5. This curve is the expression of the sum of intensities associated to the IR signals; its symmetric bell-shape is the sign that a prevalent compound is generated by the personal computer plastic decomposition, without any apparent interference from the evolution of other decomposition compounds. Styrene is a typical petroleum derived chemical with a LHV of 44 MJ/kg (Prosen at al., 1945) and a very important commodity, used mostly in polymer production for PS, ABS and styrene-acrylonitrile (SAN) resins, styrene-butadiene elastomers and latexes, and unsaturated polyester resins.

3.2.3. Kinetic studies

The next step to set up the pyrolysis process is the kinetic study. The determination of the reaction time needed to achieve a given pyrolysis conversion is described by Eq. (1) according to Vyazovkin et al. (2011).

$$t_\alpha = \frac{g(\alpha)}{A\,exp\left(\frac{-E}{RT}\right)} \tag{1}$$

where α is the mass conversion, E the activation energy (kJ/mol), A the pre-exponential factor (sec^{-1}), $g(\alpha)$ the reaction model, R the gas constant (8.3441 $Jmol^{-1}$ K^{-1}) and T the temperature (K).

The adopted procedure has been carried out following the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee Recommendations (Vyazovkin et al., 2011). The E, A and $g(\alpha)$ of the most representative polymers in WEEE and of a real plastic sample have been estimated from non-isothermal kinetic results by TGA.

As far as the interpretation of kinetic results is concerned, Simon suggested that kinetic parameters represent apparent quantities without a mechanistic interpretation (Simon, 2004): the parameters cannot be used for any theoretical considerations, but they enable modeling the processes for other temperature regimes than those applied in the measurements. Conventional reaction times are taken in correspondence of the 1st derivative TG peak at the thermal degradation step, which occurs with a conversion of 0.6.

Times for black slot and simulated PC samples were 19 min and 3 min respectively. The difference is probably due to the presence of flame retardants in black slot which increases the thermal resistance of the polymer.

In the past, many authors examined the pyrolysis of WEEE plastic as a whole (De Marco et al., 2008; Donati et al., 2009; Guo et al., 2010), but they did not consider the process occurring in each component.

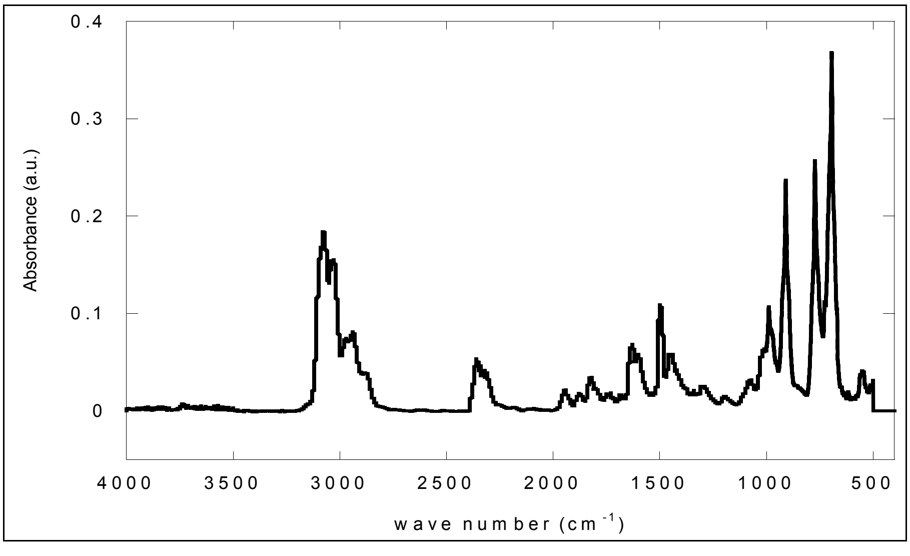

Fig. 7. FTIR spectrum of real WEEE sample pyrolysis evolved gases

On the other hand, a great deal of data on pyrolysis kinetics comes from studies applied to single polymers (Blom et al., 2006; Montaudo et al., 1993; Pramoda et al., 2003), but less to plastic components extracted from WEEE.

3.2.4. Pyrolysis with the bed reactor

Table 3 represents mass balance results for two pyrolysis runs performed on "simulated PC" samples at 400 and 600 °C; these temperatures were chosen on the basis of the results obtained in the previous thermal and spectroscopic (TG–FTIR) characterization experiments carried out under pyrolytic conditions. Besides, high heating value of the oil output, elemental composition of both the oil and the char are also reported.

It can be observed from Table 3 that pyrolysis brings about a strong plastics conversion (over 85% w/w production) into oil at the two temperatures, achieving a yield of 94.1 % w/w at 600 °C; elemental composition as well as the High Heating Value appear unchanged and resemble the one of a typical petrol derived product (Green and Perry, 2007). Gas yield appears not dependent from temperature and contains low chain hydrocarbons such as methane, ethane, ethylene. At higher temperature, char output diminishes from 10.8 % to 2.4 %, mostly at the expenses of oil; at 600 °C its ash content strongly increases, going close to 40 % w/w; at the same time the % C decreases from 70 % to 53 %.

These first tests allow concluding that pyrolysis appears to succeed to treat a heterogeneous plastics charge made up of tecnopolymers, converting it into an energy enriched hydrocarbons mixture from which specific fractions may be subsequently extracted for further valuable uses.

The process tested on the simulated PC sample, which includes both external cases and PCBs plastics, is reported in the sketch shown in Fig. 8, indicating best results obtained carrying out the pyrolysis at 600 °C. The process developed for personal computers plastic components can be extended to other small household appliances as well since they have similar plastic composition.

3.2.5. Economic and environmental considerations

This work has demonstrated the possibility to deliver an integrated approach allowing the recovery of more than 40% weight of PCBs. In Fig. 9 a pie chart evidences the materials that can be recovered by using the developed integrated technology solution presented, as well as future perspectives based on ongoing studies. Furthermore, the overall process includes gas emission treatment, thus matching atmosphere emission reduction and possibility to have product with potential market, and liquid re-use into the overall process is under evaluation. On the basis of these results we can conclude that this approach focuses environmental sustainability.

In order to assess the economic sustainability of the proposed process, we evaluated the average amount of materials recoverable from a ton of PCBs and taking into account the market value of the individual elements (values in September 2014), it is possible to assess a potential value of approximately 9700 euros per ton (Table 4).

Table 3. Mass balance for pyrolysis runs and products elemental composition (C, H, N)

T (°C)	*Oil*				*Char*				*Gas*
400	Mass balance (%)								
	85.3				10.8				3.9
	Elemental analysis (%)			HHV, MJkg	Elemental analysis (%)			Ash (%)	Detected substances: Methane, Ethane, Ethylene
	C	H	N		C	H	N		
	85.0	7.3	4.2	40.01	70.2	2.2	2.6	13.5	
600	Mass balance (%)								
	94.1				2.4				3.5
	Elemental analysis (%)			HHV, MJkg	Elemental analysis (%)			Ash (%)	Detected substances: Methane, Ethane, Ethylene
	C	H	N		C	H	N		
	87.8	7.5	3.4	40.40	52.6	1.4	1.7	38.0	

Table 4. Economic potential of developed integrated technology solution applied to PCBs

Material	*Process recovery kg/ton*	*Material value (KITCO Market Data - London Metal Exchange – September 2014) €/kg*	*Estimated value €/ton*
Ag	0.350	464	162
Au	0.240	33551	8052
Cu	129	5.30	684
Pb	15	1.62	24
Sn	43	16.53	711
plastic	200	0.37 €/kg oil for electrics	74 €/ton 100% oil for electrics
		0.58 €/kg fuel oil	116 €/ton 100% fuel oil
		Total: 9707	

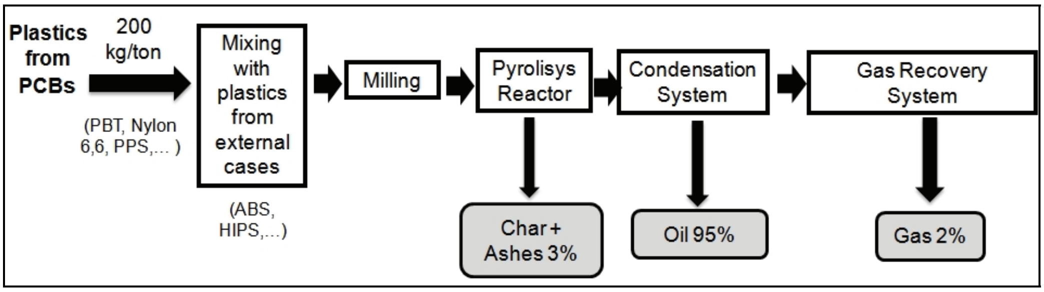

Fig. 8. Plastic valorization process

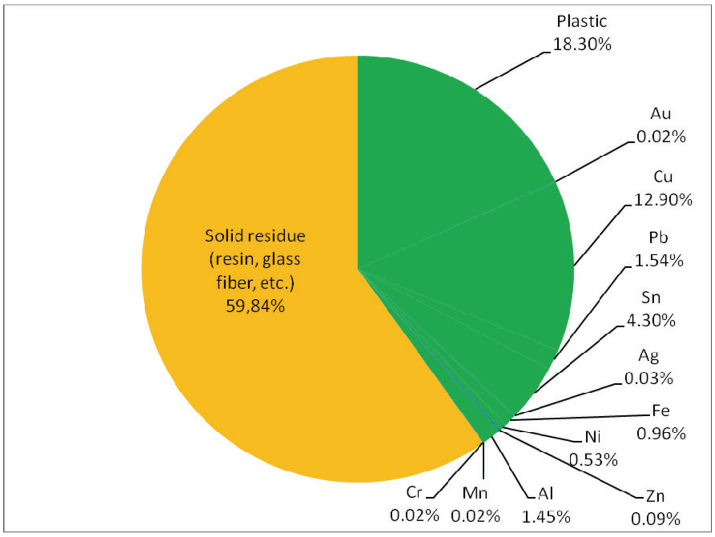

Fig. 9. Recovered material distribution following proposed integrated recovery/valorization approach (green) and considering future perspectives (orange)

Considering the End-of-Life pc sold in Italy in 2014, we can assess a potential market of End of Life domestic PCBs at about 19 milion of euros. This evaluation takes into account only domestic PCs, containing PCBs that have on average higher content of added value metals if compared to other small household appliances and lower content if compared professional computers. Overall, it can be concluded that integrated approach, based on the holistic view of all elements contained in an End of Life complex product, supports economic feasibility of process recovery.

Unfortunately not all the hi-tech products on the market become recoverable waste, since about 75% of end-of-life Hi tech products are not currently collected in legal and traceable way (Ecodom, 2013). However, this work could support business plan building in this field and policy makers awareness about economic opportunity in waste management field.

4. Conclusions

The increasing diffusion of Hi-tech complex products has raised the attention of scientific community towards their End of Life treatment, both in terms of assuring an appropriate disposal, to avoid the dispersion of harmful substances, and with the aim of their exploitation as valuable sources of raw materials. PCBs were subjected to an innovative integrated process based on product centric approach to recover all valuable materials, and mixed plastic associated is also treated to maximize the production of valuable liquids and gas, reaching percentages at the highest equal to 95%.

The results obtained with the hydrometallurgical process show recovery rates for gold, tin, silver, lead and copper and purity grade up to 99%. The experiments carried out on personal computers plastic fraction (including PCBs and external cases) allow to conclude that pyrolysis appears to succeed to treat a heterogeneous plastics charge made up of engineered polymers, converting it into an enriched hydrocarbons mixture with yields around 95 % w/w, to be exploited as a fuel, or as possible source of chemicals after an adequate further refining treatment. The process developed for personal computers plastic components can be extended to other small household appliances that have similar plastic composition.

The integration of the developed technological solutions allows the recovery of over 40% weight of materials. The results of this work indicate that the proposed integrated approach, based on the holistic view of all elements contained in an End-of-Life complex product, focuses environmental sustainability and supports economic feasibility of process recovery.

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INDOOR AND OUTDOOR VOLATILE ORGANIC COMPOUNDS MONITORING IN A MULTI-STOREY CAR PARK

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Abstract

A VOC monitoring was carried out inside and outside a multi-storey car park in order to characterize the emission profile of vehicular traffic source in an indoor environment. BTEX, and in particular toluene, were the most abundant compounds in all monitored sites, with different compositions between indoor parking areas and outdoor sites. The motor vehicle exhaust and gasoline vapor emission in these enclosed parking garages were characterized by diffusion or degradation phenomena different from those that occur in urban areas as the BTEX compositions, their ratios and their reactivity with OH and with NO_3 radicals demonstrate. In detail, xylenes/BTEX and ethylbenzene/BTEX ratios in indoor environments were twice than those in outdoor ones, while toluene/BTEX ratio resulted half than that obtained in outdoor sites. In this work, BTEX concentrations depend both on number of vehicles, on vehicular characteristics (age, emission control technology, fuel quality etc.) and on factors related to the characteristics of parking facilities (volume of the monitored areas, indoor or open facilities, ventilation systems, size and maintenance). However, it was found that the external contribution (intrusion of pollutants from outdoor and from the other floors) and the influence of mixing air (removal of pollutants by ventilation and air exchange) on BTEX concentrations were not significant if inside the multi-storey car park there was a strong source (due to the number of vehicles) such happened in the first and second floors and along the ramp that connected them.

Key words: BTEX ratios, garage, indoor environment, number of vehicles, VOC

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1. Introduction

Volatile Organic Compounds (VOC) are considered ubiquitous pollutants and so they are used as important compounds to evaluate indoor and outdoor air quality as discussed in different studies (Amodio et al., 2011; Bruno et al., 2006, 2008a; Caselli et al., 2010; Postolache et al., 2013; Revel et al., 2014).

The most important sources of these compounds in urban areas are represented by vehicles emissions, filling stations, chemical plants and petroleum refineries. In particular BTEX compounds (benzene, toluene, ethylbenzene and xylenes) and methyltertbutylether (MTBE) are pollutants related to traffic emissions (Hun et al., 2011). In and around urban areas, anthropogenic emissions of these VOCs are usually more significant, in fact for this reason they are considered ideal tracers for gasoline-related exposures. The vehicular emissions of BTEX come from different contributions: exhaust emissions (cold and hot), evaporative emissions, and emissions from brake and tyre wear (Franco et al., 2013). Transport-related emissions are important factors in determining air quality in many urban regions, depending on the altitude and thus the dispersion pattern of emissions. In most urban areas, air pollution is now badly affecting the quality of life and the improvement of air quality has become a priority for most cities in

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developed countries. Therefore, many public administrations adopted different strategies to reduce the number of vehicles operating in urban areas, to improve road traffic conditions and to promote the use of public transport. These actions caused the creation of many multi-storey car park well as in urban areas, even in the peripheral areas of a large number of city. In these environments high VOC concentrations can be due to the number of cars that daily attend them (Graham et al., 1999, 2004; Lansari et al., 1996; Murphy et al., 1997; Noseworthy and Graham, 1999; Thomas et al., 1993; Tsai and Weisel, 2000). Exhaust emissions and evaporative emissions produced by vehicles, powered by gasoline or diesel, are the main sources of VOCs in enclosed parking garages (Rakha and Ding, 2003). The exhaust emissions are commonly referred to as "tail-pipe" emissions and are the results of the combustion of fuels within the vehicle's engine.

The operation mode of the vehicle affects the rate of VOCs emissions: in general, they are less during hot starts than cold starts and are lowest for hot stabilized operation mode (Singer et al., 1999). Instead the escape of hydrocarbons from the fuel storage and delivery system represents the evaporative emission. In general very important in the definition of the motor vehicle emission rate of VOCs are parameters such as vehicle characteristics and fuel properties (Krarti and Ayari, 1999).

Air quality in indoor environments also depends on factors related to the characteristics of parking facilities (indoor or open facilities, ventilation systems, size and maintenance).

In this work, a monitoring campaign was carried out inside and outside a multi-storey car park in order to assess VOC concentrations in a confined environment. Moreover the main factors related to the structural characteristics of the parking facility (ventilation rate, climatic conditions, air mixing, size of the environments, number and size of the openings) and number and strength of the sources (number of cars) were evaluated. In detail, an equation was provided and applied to describe how and which factors contribute to indoor VOC concentrations in different investigated environments (parking areas and ramps).

2. Material and method

2.1. Sampling sites

The monitoring campaign was carried out inside and outside a multi-storey car park from 06 to 21 September 2013. Forty 3-day samples were collected in six indoor and four outdoor sites. The multi-storey car park is situated inside of a stone rock mountain located on the Amalfi coast highway (province of Salerno, southern Italy) (Fig. 1). The entrance to the garage is located near a road tunnel and on the side of the Amalfi coast highway, a very busy street that connects two resort towns of the south of Italy as Atrani and Amalfi (on the right and on the left in Fig. 1, respectively). The structure has two exits; the exit for the vehicles is on the opposite site to the entrance, while the second one connects the parking area with the central square behind the garage that can be reached on foot from the garage itself. Inside the parking area, there were 204 car parking spaces and 30 motorcycle spaces spread over four floor. The ground floor has an area of approximately 2150 m^2 and a height of 2.70 m. The first and the second floor have an area of about 2100 m^2 and a height of about 2.60 m, and the third floor, at the top of the building, has an area of 1750 m^2 and a height of about 4.00 m. The entire parking structure is equipped with a ventilation system that draws air from the outside and distributes it within the structure. An additional system directs indoor air outside the building through a pipe located at about one meter below the road surface.

Fig. 1. Position of monitored structure on the Amalfi coast highway

Four monitored sites were selected in outdoor (Site 1 - 4). In detail, site 1 was located next to the vehicles access, adjacent to the road tunnel, on the Amalfi coast highway. Site 2 was positioned next to the exit of vehicles from the parking area on the Amalfi coast highway as well. Site 3 was located in proximity of the aeration system pipe of the parking area. Furthermore, an outdoor site (Site 4) was positioned in the square behind the parking structure.

Six indoor sites were selected inside the rock multi-storey car park. In particular, four indoor sites (Site 5 - 8) were positioned in the center of each level at about 2 m above the floor. Sites 9 and 10 were located instead on the two ramps that respectively connect the third with the second floor and the second with the first floor. The choose of indoor and outdoor sampling sites was performed in order to consider the dimensions of monitored area and so that each of them could sample a homogeneous area.

2.2. Sampling and analytical method

VOC monitoring was performed according to the previously validated procedure (Bruno et al., 2005, 2008a). VOC were sampled exposing Radiello® diffusive samplers containing graphitised charcoal (Carbograph 4) as adsorbent beds. Then, collected cartridges were thermally desorbed (Markes International, Llantrisant, UK) and a gas chromatography-mass spectrometry analysis of VOCs (GC-6890 PLUS, MS- 5973 N; Agilent Technologies, Santa Clara, California, USA) was carried out (UNI EN ISO 16017-2, 2007). For quantitative analysis, standard solutions were prepared by injecting into cartridges successive dilution in methanol of a VOC standard mixture at 2,000 µg/mL (Cus-5997 Ultra Scientific, Bologna, Italy). Atmospheric concentration of each detected VOC was calculated in accordance with Bruno et al. (2005, 2008b).

3. Results and discussion

Twenty-two volatile organic compounds were detected in indoor and outdoor sites during the monitoring campaign. Average VOC concentrations and variability over the sampling period are listed in Table 1.

Data analysis showed that indoor concentrations were higher than outdoors one for all monitored sites, with the exception of the parking area on the third floor. The indoor concentrations in this area were comparable to those detected in outdoor sites. BTEX were the most abundant compounds among detected VOCs both in indoor and outdoor sites. In addition, a significant contribution of alkanes (on average 16% compared to the sum of VOCs detected) was observed. In detail, the ratios BTEX/VOCs were on average equal to 68% both in indoor sites (ranging from 67% to 69%) and outside (ranging from 65% to 76%). However, VOC percent compositions observed in indoor parking areas and outdoor sites were different. This result confirmed that a different pattern of VOCs characterized traffic emission source in indoor environments.

Toluene was the most abundant compound in all monitored sites, but difference in percentage composition was observed among the investigated sites. In fact in outdoor sites, Toluene accounted on average for 56% and 38% of the composition of BTEX and detected VOCs, respectively. These percentages were higher than those observed in parking areas (35% and 24%) and long ramps (26% and 19%) of the multy-storey car park. On the contrary, higher percentage composition of xylenes were found (X/BTEX percentage = 37%; X/VOCs percentage = 25%) in indoor air. Same finding was found for ethylbenzene: its indoor percentage compositions (E/BTEX percentage = 11%; E/VOCs percentage = 10%) were double than those for outdoor sites.

These evidences suggested that vehicle exhaust emissions (when the vehicles are moving) and evaporative emissions (when the vehicles are parked) in a confined environments can be affected by diffusion or degradation phenomena different from those that occur in urban areas or in general in outdoor sites.

This evidence was further confirmed from the higher variability over the sampling periods obtained for indoor concentrations, as showed in Fig. 2 for benzene concentrations.

Several studies conducted in urban areas demonstrated that the ratios among BTEX are diagnostic to indicate that emissions are predominantly from vehicles (Amodio et al., 2011; Bruno et al., 2006, 2008a; Caselli et al., 2010). In detail, Benzene/Toluene (B/T) (values between 0.26 and 0.50) ratios are commonly used as indicators of the predominance of the vehicular traffic emission, while xylenes/ethylbenzene (X/E) ratios give an indication of the photochemical aging of the emission and thus of the proximity of the emission source. Average indoor and outdoor diagnostic ratios obtained for the monitoring campaign are listed in Table 2.

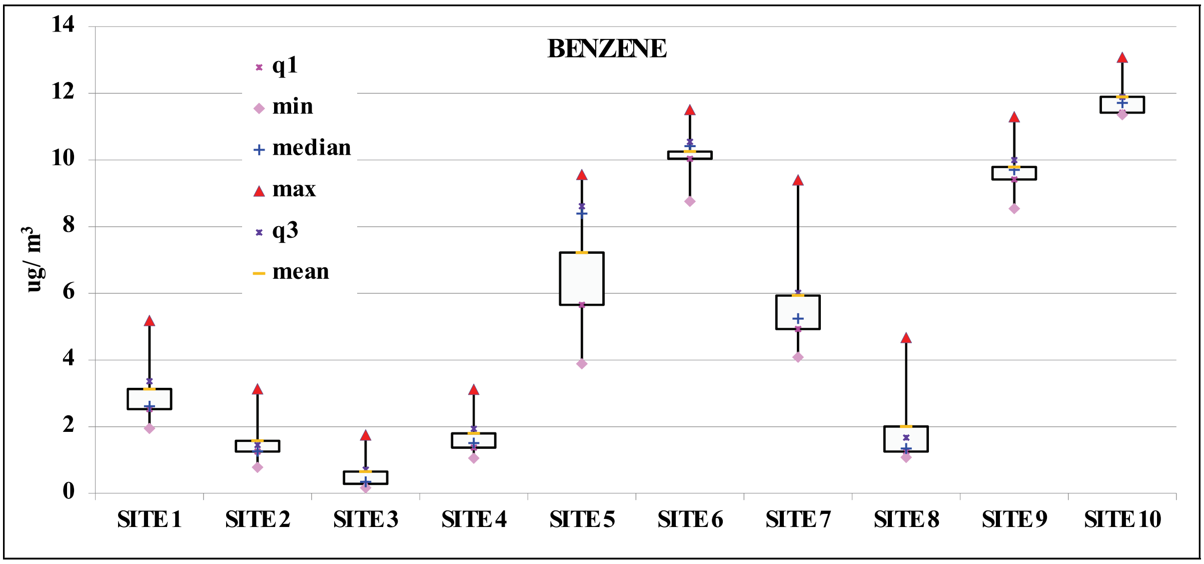

Fig. 2. Trend of the levels of benzene during the monitoring campaign in outdoor sites (1-4) and indoor sites (5-10)

Table 1. Average VOC concentrations and variability over the sampling periods

	Site 1		***Site 2***		***Site 3***		***Site 4***		***Site 5***		***Site 6***		***Site 7***		***Site 8***		***Site 9***		***Site 10***	
	Outdoor		***Outdoor***		***Outdoor***		***Outdoor***		***Ground floor***		***First floor***		***Second floor***		***Third floor***		***Ramp***		***Ramp***	
	ug/m^3	SD	ug/m^3	SD	ug/m^3	SD	ug/m^3	SD	ug/m^3	SD	ug/m^3	SD	ug/m^3	SD	ug/m^3	SD	ug/m^3	SD	ug/m^3	SD
MTBE	0.2	0.1	0.21	0.12	0.12	0.03	0.27	0.08	2.24	2.95	0.9	0.2	0.77	0.37	0.3	0.23	0.93	0.25	1.61	1.66
ETBE	1.56	1.34	0.66	0.61	0.44	0.06	1.66	1.07	2.62	2.55	3.51	1.12	1.82	1.19	0.71	0.78	3.03	1.07	5.18	1.36
1,1,1-trichloroethane	0.04	0.02	0.04	0.02	0.05	0	0.054	0	0.03	0.04	0.05	0.03	0.04	0.02	0.04	0.03	0.053	0	0.056	0
Benzene	3.13	1.26	1.58	0.9	0.54	0.68	1.8	0.91	7.22	2.37	10.25	1	5.94	2.06	2	1.51	9.79	1	11.89	0.7
Heptane	5.25	2.17	1.78	0.84	0.83	0.67	2.84	1.58	9.94	8.3	13.22	9.66	6.01	2.55	1.82	0.71	10.8	3.7	15.53	4.61
1,1,2-trichloroethane	0.033	0	0.033	0	0.03	0.01	0.033	0	0.04	0.02	0.06	0.06	0.07	0.09	0.04	0.02	0.09	0.12	0.1	0.12
Toluene	9.57	1.19	6.54	1.51	3.71	1.56	8.22	1.27	13.79	2.1	16.51	1.43	13.72	2.3	8.48	2.04	15.8	1.61	18.86	2.16
Octane	0.24	0.05	0.17	0.06	0.1	0.05	0.2	0.04	0.55	0.24	0.91	0.46	0.58	0.54	0.2	0.12	0.84	0.54	1.08	0.67
Tetrachloroethylene	0.08	0.06	0.09	0.05	0.08	0.04	0.13	0.06	0.08	0.06	0.11	0.1	0.12	0.14	0.08	0.06	0.15	0.17	0.21	0.21
N-butyl acetate	0.06	0.08	0.06	0.08	0.01	0.01	0.04	0.04	0.09	0.15	1.04	2.17	1.96	4.34	0.1	0.16	2.45	5.33	8.41	10.7
Ethylbenzene	1.5	0.49	0.67	0.4	0.19	0.25	0.96	0.37	3.71	1.67	7.08	2.63	4.21	3.37	1.18	0.96	6.82	3.5	11	5.2
M/p-xylene	3.79	0.96	1.93	1.26	0.62	0.83	3.09	1.02	8.66	2.83	12.78	2.6	8.21	4.6	2.93	2.28	12.46	3.12	15.6	3.48
Styrene	0.14	0.03	0.14	0.05	0.09	0.04	0.14	0.03	0.46	0.13	0.6	0.2	0.36	0.17	0.32	0.09	0.54	0.11	0.63	0.16
O-xylene	2.07	0.53	1.03	0.74	0.3	0.45	1.67	0.55	5.81	2.69	9.82	3.02	5.54	4.35	1.51	1.24	9.5	3.28	12.42	3.77
Nonane	0.14	0.03	0.14	0.05	0.11	0.02	0.13	0.03	0.43	0.33	0.69	0.74	0.41	0.47	0.14	0.04	0.38	0.22	0.33	0.14
Alpha-pynene	0.24	0.08	0.26	0.13	0.22	0.03	0.3	0.09	0.24	0.09	0.32	0.11	0.26	0.09	0.23	0.09	0.24	0.05	0.36	0.09
Camphene	0.15	0.14	0.16	0.17	0.15	0.16	0.24	0.18	0.19	0.22	0.19	0.18	0.22	0.2	0.17	0.19	0.19	0.2	0.18	0.17
1,2,4-trimethylbenzene	0.89	0.62	0.98	1.3	< LOD	-	0.94	0.97	3.73	2.71	3.58	4.17	7.03	3.02	0.47	0.19	4.78	2.6	2.8	1.62
Decane	0.12	0.01	0.14	0.06	0.12	0.03	0.12	0.03	0.22	0.15	0.49	0.62	0.27	0.29	0.13	0.03	0.2	0.1	0.18	0.06
1,4-dichlorobenzene	0.024	0	0.026	0	0.025	0	0.028	0	0.025	0	0.025	0.01	0.025	0	0.024	0	0.025	0	0.025	0
Limonene	0.16	0.01	0.19	0.07	0.16	0.02	0.26	0.07	0.18	0.04	0.24	0.14	0.22	0.09	0.15	0	0.16	0.01	0.51	0.09
Undecane	0.17	0.01	0.19	0.06	0.18	0.04	0.19	0.03	0.2	0.04	0.37	0.3	0.27	0.19	0.18	0.02	0.22	0.04	0.23	0.04
ΣVOCs	29.57	9.19	17.01	8.51	8.08	4.98	23.34	8.42	60.46	29.7	82.72	30.9	58.06	30.5	21.19	10.8	79.45	27	107.19	37
Σ BTEX	20.07	4.43	11.75	4.82	5.37	3.77	15.75	4.13	39.19	11.7	56.44	10.7	37.62	16.7	16.1	8.02	54.38	12.5	69.77	15.3
Σ Alifatics	5.93	2.27	2.42	1.07	1.35	0.81	3.49	1.7	11.35	9.06	15.69	11.8	7.55	4.04	2.47	0.92	12.44	4.6	17.35	5.51
Others	3.57	2.49	2.84	2.63	1.37	0.39	4.1	2.59	9.93	8.96	10.59	8.49	12.9	9.74	2.62	1.83	12.63	9.91	20.07	16.2

Table 2. Average indoor and outdoor diagnostic ratios

Diagnostic ratios	***Outdoor sites***	***Parking area***	***Ramps***
B/T	0.23	0.54	0.63
X/T	0.47	0.99	1.44
MTBE/B	0.14	0.17	0.12

B/T ratios confirmed that exhaust vehicle emissions affected mainly indoor and outdoor air quality. This evidence was further highlighted plotting benzene versus toluene concentrations (Fig. 3): the high linearity confirms the presence of a common source of two pollutants, while the different slope of the straight lines indicates that pollutants may have suffered different degradation or diffusion phenomena in outdoor sites and in indoor sites.

BTEX compounds were characterized by a reactivity that consists in two main depletion reactions: with OH radicals in presence of light and with NO_3 radicals in the absence of light. The rate constants for the reactions of BTEX with OH radicals are so higher than those with NO_3 that with OH can be considered as predominant. Xylenes are the most reactive compounds with respect to the OH reaction, followed by ethylbenzene, toluene, and benzene. In indoor environments, and in particular on the ramps characterized by lower lighting, this reaction can result lower with respect to that expected in open atmosphere. This phenomenon can explain the higher X/T ratios obtained in parking areas and long the ramps. In addition, the ratio of methyltertbutylether (MTBE) (used as an additive in gasoline) to benzene indoor concentrations can be used to examine if these compounds originated from gasoline vapors or car exhaust. Low MTBE/benzene ratios (0.40) indicate that tailpipe emissions are dominant because during combustion the amount of MTBE decreases while benzene is enriched due to toluene and xylene dealkylation (Zielinska et al., 2006).

Alternatively, high MTBE/benzene ratios (up to 50) suggest a significant contribution from evaporative emissions from hot soak and/or fuel system leakage. MTBE/B ratio obtained in this study (0.15) confirmed car exhaust emissions as main source of VOCs both in indoors and outdoors.

Data analysis showed that different levels of BTEX were detected in monitored environments of the multi-storey car park. Several studies showed that pollutant concentrations in an indoor environment depend not only on chemical degradation, but on several factors such as number and strength of the sources, ventilation rate, climatic conditions, air mixing, building characteristics, and possible sinks (e.g. sorption by surfaces and furnishings) (Graham et al., 2004; Spengler and Chen, 2000).

To study the impact of these factors on detected VOC concentrations, Eq. (1) describing the relationship among them in the multi-storey car park is reported.

$$C = \left(\frac{K_1 \times N}{V}\right) + K_2 - K_3 \qquad (1)$$

where: $K_1 \times N$ represents the contribution due to the number of vehicles that entered inside the parking area during each monitoring period; V is the volume of the parking area in each floor, expressed in m^3; K_2 represents the external contribution due to intrusion of pollutants from outdoor and from the other floors; K_3 represents the contribution due to removal of pollutants by ventilation and air exchange.

In detail, the first term of the equation in brackets describes both the increase in the concentration linked to the number of vehicles and the possible decrease due to the dilution of pollutants in the volume of the environment. In order to immediately display which factors had a greater effect in the different environments monitored, benzene concentrations per site versus the number of vehicles are showed in Fig. 4.

The lack of correlation between benzene concentration and number of vehicles on the ground floor (Site 5) can be explained by considering the characteristics of the environment.

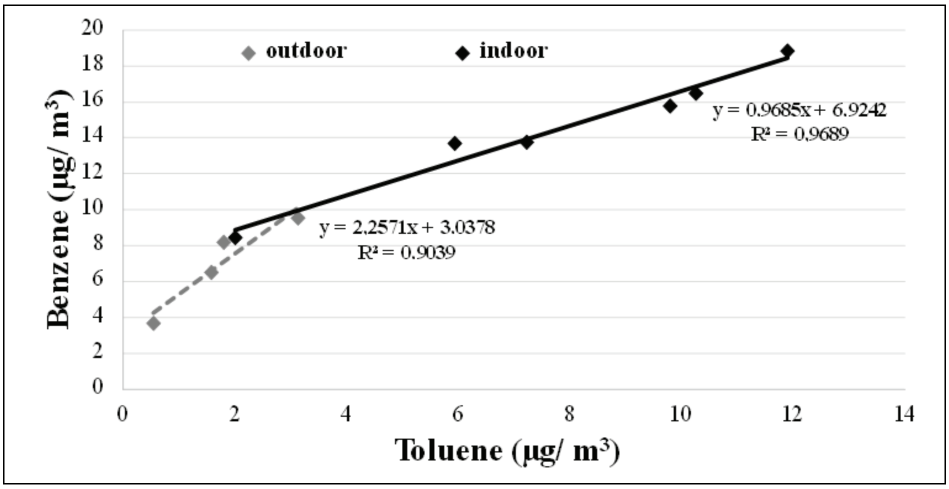

Fig. 3. Benzene concentrations versus toluene concentrations in indoor and outdoor sites

The presence of wide openings for access and exit of vehicles produced a dispersion of pollutants variable in time (high contribution of K_3). High correlation was found at first and second floor (Site 6 and Site 7), respectively. A higher correlation revealed in Site 6 (R^2 = 0.965) can be explained considering the greater number of vehicles that reached the first floor than the second one. Therefore, in this case K_2 and K_3 can be considered negligible. The third floor (Site 8) was characterized by a volume greater than the other floors and it was reached by a lower number of vehicles. These factors explain the lower correlation found in this parking area (R^2 = 0.853).

The highest benzene and VOC concentrations were detected along the two ramps (Site 9 and Site 10) that connect the third with the second floor and the second with the first floor, respectively. In detail, the highest correlation (R^2 = 0.962) was obtained in Site 10 as it was crossed by cars that reached the second and third floors. Therefore, the concentrations detected in this environment were mainly due to the number of cars (high contribution of K_3). However, the small size of the environment (small volume) and the absence of openings (low contribution of K_2) may have contributed to detected levels.

To evaluate indoor air quality (IAQ) in the multy-storey car park, indoor VOC concentrations were compared with others monitored in non-residential indoor environments by using the same methodology (Amodio et al., 2014; Bruno et al., 2008b, 2009; de Gennaro et al., 2013).

It was found that, although in the multi-storey car park there was a continuous source of volatile compounds, the levels of BTEX and in particular of benzene obtained in this study were comparable and, in many cases, lower than those monitored in businesses, schools and offices, environments characterized by the small size and reduced air exchange (Table 3).

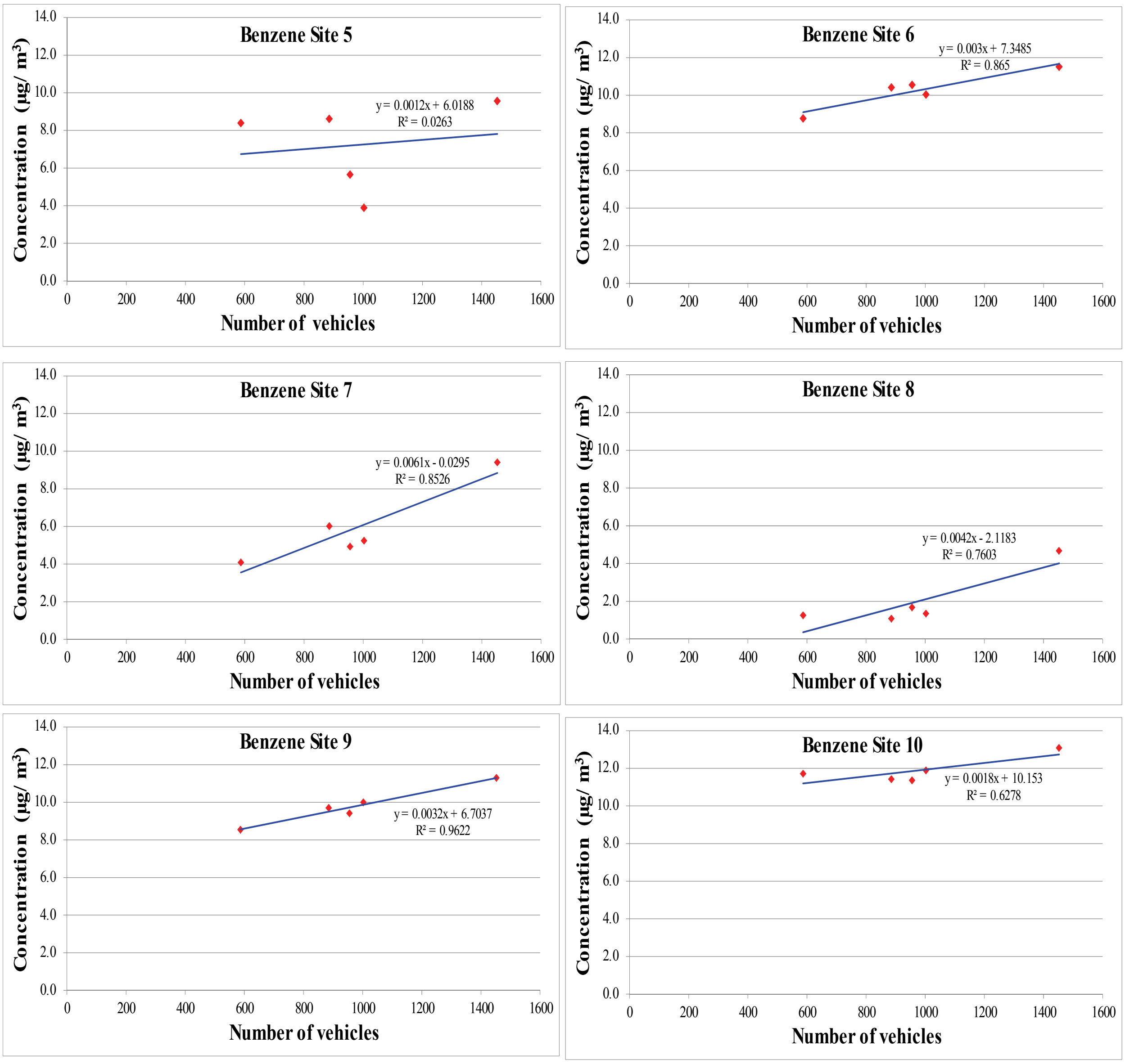

Fig. 4. Benzene concentration in indoor sites vs the average number of vehicles in each monitoring periods

Table 3. Indoor concentration of BTEX and benzene in several not-residential indoor environments

	BTEX (µg/m^3)	*Benzene (µg/m^3)*	*References*
Coffee shops	271	5	Bruno et al. (2008)
Libraries	38	2	Bruno et al. (2008)
Copy centers	545	10	Bruno et al. (2008)
Pharmacies	834	7.5	Bruno et al. (2008)
Newspaper stands	690	3	Bruno et al. (2008)
Offices	26	3.3	Bruno et al. (2008)
Gymnasiums	69	1.7	Bruno et al. (2008)
Hairdressing salons	150	2.7	Bruno et al. (2008)
Restaurants	79	2.5	Bruno et al. (2008)
Supermarkets	90	2.2	Bruno et al. (2008)
School Buildings	4.2	0.04-6	de Gennaro et al. (2013)
Multi-storey shopping mall	18	0.7-9	Amodio et al. (2014)
Multi-storey car park	45.6	7.9	This study

4. Conclusions

The study of VOC concentrations, the reactivity of BTEX, the main structural parameters and the number of cars that characterized the multi-storey car park highlighted that, in an indoor environment, diffusion or degradation phenomena are different from those that commonly occur in urban areas. Furthermore, a comparison with other non-residential indoor environments showed that the structural characteristics of the buildings, such as air exchange systems and the high volumes of the environments could have a considerable impact on the indoor air quality even when a strong emission source is present.

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MULTIDISCIPLINARY AND INNOVATIVE METHODOLOGIES FOR SUSTAINABLE MANAGEMENT IN AGRICULTURAL SYSTEMS

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Abstract

Sustainability issues have driven academic researchers towards the definition of methodological tools to assess the impacts derived from products and services and to make them more ecologically friendly, economically profitable and socially suitable, and whose results have to be clear and understandable to a broad public. In the evaluation of complex socio-environmental systems, like agricultural ones, uncertainty often arises and the quality of decision processes can be a high concern. This paper presents the conceptual and methodological framework of an Italian research project entitled "MIMeSMAS", i.e. Multidisciplinary and Innovative Methodologies for Sustainable Management in Agricultural Systems. Through a multi-disciplinary, multi-methodological, systemic and participatory approach, the project attempts to define an integrated approach for the assessment of environmental, economic and social sustainability of innovative agricultural practices in Mediterranean areas. The project activities are carried out by four Italian research institutions in order to bring together agronomic, hydraulic and mechanical expertise and to conduct a combined implementation of Life Cycle methodologies (LCA, LCC and s-LCA) and multi-criteria analysis tools. The approach is applied to assess and rank alternative cropping systems scenarios; results are expected to help optimising the management of soil, water and energy macro-systems of perennial crops (olive), horticultural crops (artichoke) and dedicated energy crops (giant reed). In this paper the theoretical concept of the project, the preliminary results of project's activities linked to the identification of experimental trials scenarios and to the definition of specific indicators are presented.

Key words: agricultural sustainability, life cycle methodologies, multidisciplinary approach, multi-criteria decision analysis, participatory approaches

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1. Introduction

Since long time now, researchers from different scientific fields debate extensively about agricultural sustainability by considering, from several points of view, all multifarious aspects and implications. Although the early idea of sustainability is backdated to the German forestry studies of the 18th century (Caradonna, 2014; Spindler, 2013), as it is known, the Brundtland Commission's definition represents the undisputed milestone on this subject (WCED, 1987).

Nevertheless, only two years later the American Agronomy Society coined a less known definition of sustainable agriculture as an activity "that, over the long term, enhances environmental

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quality and the resource base on which agriculture depends; provides for basic human food and fiber needs; is economically viable; and enhances the quality of life for farmers and society as a whole" (Weil, 1990).

It is now well recognised that achieving sustainable agricultural production needs a special effort to overcome the sector-based perspective and to provide solutions to real-world problems through scientific and socially robust knowledge (Brandt et al., 2013). In this sense, it is possible to frame the research on sustainable agriculture within the umbrella of the so-called "Sustainability Science" (SS): "a solution-oriented discipline that studies the complex relationship between nature and humankind, conciliating the scientific and social reference paradigms which are mutually influenced- and covering multi temporal and spatial scales. The discipline implies a holistic approach, able to capitalize and integrate sectorial knowledge as well as a variety of epistemic and normative stances and methodologies towards solutions' definition" (Sala et al., 2013a).

By examining the latest scientific literature on sustainability discourses, Kajikawa et al. (2014) argued that agricultural sustainability is the more representative disciplines-focus issue that provides also the most numerous links with other fields within the overall landscape of the sustainability research. In the last years, several scholars stressed the importance of a comprehensive framework approach in sustainability studies that increasingly recognize the urgency to adopt *multi-inter-trans-disciplinary approaches* to deepen the complexity of sustainability issues (Brandt et al., 2013; Lang et al., 2012; Mattor et al., 2014; Mobjörk, 2010; Polk, 2014; Serrao-Neumann et al., 2015). Especially in terms of transdisciplinary approaches, several, but not univocal, definitions linked to agricultural sustainability research have been proposed. However, as well summarised by Darnhofer (2014), the most important and frequent characteristics of a transdisciplinary research are the follows: the integration of disciplinary paradigms; the co-production of knowledge with non-academics actors; the use of participatory methods and the application to real-life problems.

In this sense, it is possible to affirm that the aim of transdisciplinary approaches in sustainable agriculture studies is to go further the limits of multidisciplinary and interdisciplinary research (Nagabhatla et al., 2015; Vandermeulen and Van Huylenbroeck, 2008) to get toward a combined approach inspired by both the so-called hard sciences and the soft ones. Such mixed methodological procedures can borrow different methods moving from opposite paradigms, like positivism-oriented approaches and constructivist-oriented ones (Iofrida et al., 2014), to work together in an integrated conceptual framework. Furthermore, an integrated assessment of complex issues - like sustainability concerns - requires "a mutual interdependence of participatory and modelling approaches in assisting policy-making" (Hisschemöller et al., 2001).

In the light of these considerations, this paper presents the conceptual and methodological framework, as well as the preliminary results, of a national research project entitled "MIMeSMAS" (Multidisciplinary and Innovative Methodologies for Sustainable Management in Agricultural Systems). Starting from a multi-disciplinary and systemic approach, the project attempts to pursue a twofold purpose. The first one is the definition of an unprecedented methodological framework that, with an innovative and integrated approach, can contribute to increasing the knowledge about agricultural sustainability assessment. Secondly, the implementation at experimental and farm scale is functional to achieve solutions in real-world scenarios of different agricultural systems by highlighting the potential effects in terms of environmental, economic and social impacts, examined individually through specific analysis tools and finally combined in a holistic approach. Furthermore, from a trans-disciplinary point of view, the project aims to test participative models to conduct the sustainability assessment in co-learning pathways with non-academic stakeholders. The project involves four Italian research institutions that will assess alternative scenarios useful to optimizing agricultural practices for permanent crops (olive), horticultural crops (artichoke) and dedicated energy crops (giant reed).

In the next paragraph a description of project is fulfilled by distinguishing in sub-paragraphs the general framework, the experimental activities and the cross-cutting analysis (common for each scenario) related to life cycle evaluations and participatory activities. Finally, in the last paragraph, some preliminary results, at this stage of the project, are reported.

2. Material and method

2.1. General research framework

The research project takes into account the complexity of the sustainability issues, by articulating operative activities at different levels (experimental and farm-based), according to three general research questions: which are the possible innovative experimental protocols for sustainable management of resources (in terms of soil, water and energy)? Which are the environmental, economic and social effects of the implementation of these innovative systems? How implement jointly different methodological tools and how create new pathways to transfer scientific knowledge from scientists to actors involved in the validation and interpretation of results?

Answering to similar questions on sustainability implies for scientists to take some challenges, as argued by Brandt et al. (2013), like as, for example, that to talk a common language starting from different "[…] ontological assumptions, epistemological commitments and methodological choices" (Darnhofer et al., 2015). The project starts from a multifaceted theoretical setting (Fig. 1). In particular, a *systemic* approach is obtained by including specific research activities focused on three main components (named generically "macro-systems") that considered simultaneously and in all their specific features contribute to explain the most part of sustainability in agricultural systems. The complexity due to the *multi-disciplinary* feature of the research project is tackled through the involvement of an experts' team in agricultural hydrological models, agronomic methods, mechanical engineering and agricultural economic and policy analysis. Finally, a *multi-methodological* approach is followed by using different analysis tools useful to evaluate from different point of view the overall sustainability of the processes under study.

In operational terms, the project is structured in four main work packages (WP) articulated in specific sub-activities (tasks) each of which represents an input for the following phase (Fig. 2).

In particular, the project's research activities consist in the following principal steps: (i) characterisation of crop production systems in relation to the main issues linked to the efficiency utilisation of soil, water and energy resources; (ii) definition of a common methodological protocol and of a structured set of biophysical and socio-economic indicators; (iii) implementation of the methodological protocol for the experimental activities and farm case studies; (iv) development of sustainable management options.

The multi-methodological character of the project is pursued through a joint application of agronomic, hydraulic and mechanic models for cropping systems and through a combined implementation of Life Cycle methodologies (LCA, LCC and s-LCA) that are cross-cutting for each scenario analysed.

The multi-dimensional indicators obtained from the experimental activities and life cycle analysis are integrated through Multi-Criteria Decision Analysis (MCDA) in order to rank the alternative scenarios and mixed (quali-quantitative) participatory techniques are used to involve local actors in a knowledge pathway able to identify, as main upshot, a real-world support for private decision and policies making.

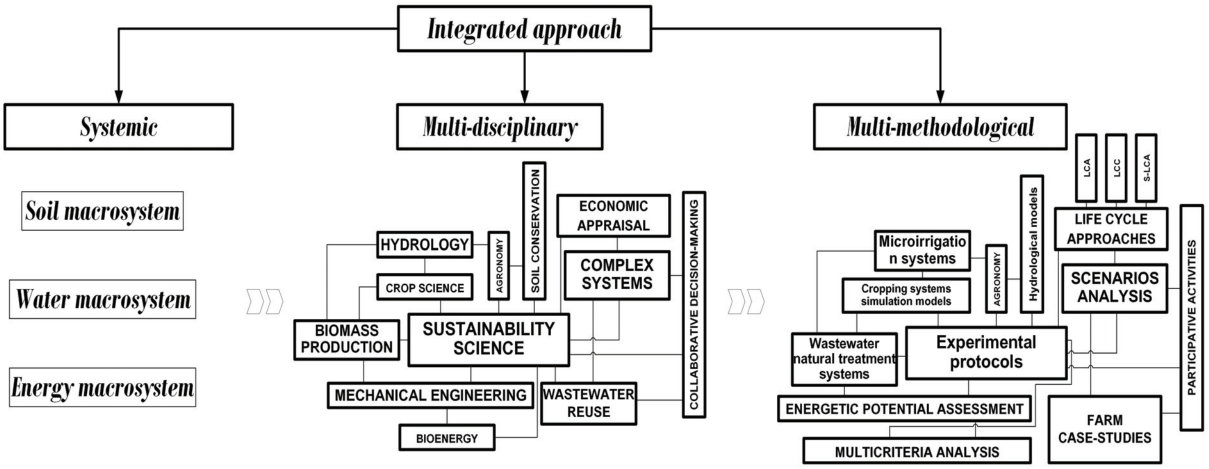

Fig. 1. Theoretical concept of MIMeSMAS project

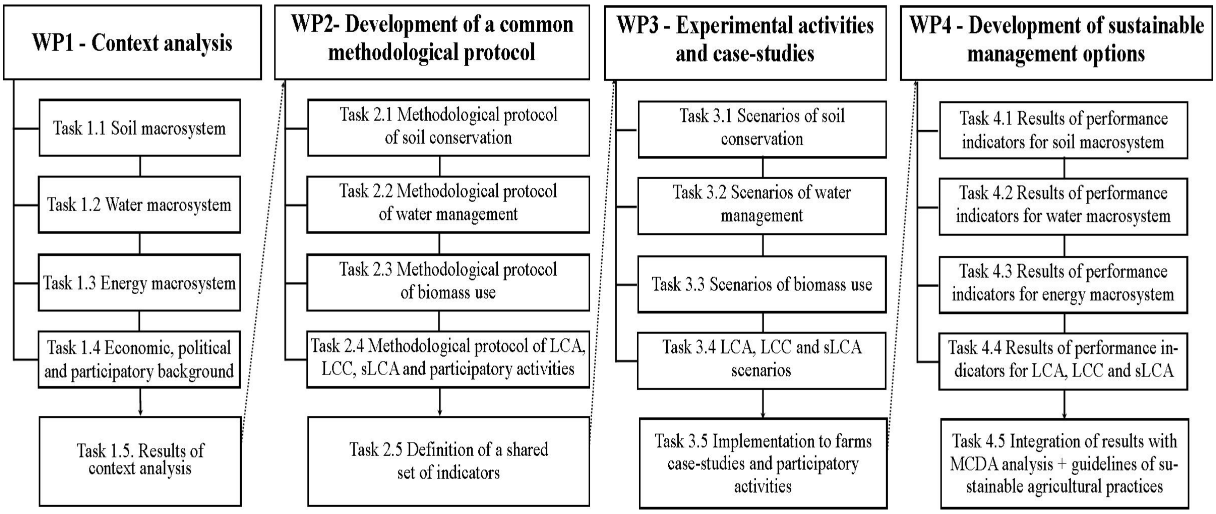

Fig. 2. Operational framework of MIMeSMAS project

2.2. Experimental activities and case studies

By detailing the second work package related to the common methodological protocol, an overview of the experimental activities on each so-called "macro-systems" considered is provided below. It is necessary to clarify that the following explanation considers separately the experimental activities merely in order to a greater understanding of different case studies. However, coherently with the project framework design, all resource typologies (soil, water, and energy) are included and analysed, simultaneously, within each scenario studied. In terms of "soil macro-system", the research activities are aimed to assess the effects in terms of hydrological runoff and erosion and provide guidance on the efficiency to forecast runoff and erosion of widespread hydrological models and to assess the impacts of different growing techniques on soil quality.

The experimental analysis on hydrological effects are conducted in olive growing contexts typical of semi-arid Mediterranean areas and particularly significant in terms of agronomic and ecological impact on soil, especially in Calabria region where olive crops play an essential role in landscape enhancement and hydrological defence. Indeed, while in the past the careful and constant work of farmers allowed to maintain a dynamic balance between farming and the environment, since several decades high levels of mechanization and the increasingly abandonment of traditional techniques of soil management have occurred. This resulted the increased processes of runoff and erosion due to both the soil compaction and the removal of vegetation cover. The European agricultural policies have been geared, by European Regulation No 1782/2003, to promote soil conservation practices through by maintaining the land in "Good Agricultural and Environmental Condition" (GAEC) defined in the context of cross-compliance mechanism (EC, 2003). However, according to Bombino et al. (2011) "the information about the impacts of different management practices on soil losses is still insufficient and does not allow a proper evaluation of the erosive risks in hilly olive groves across the different local conditions".

Soil management issues in the Mediterranean cultivated areas, like in Calabria, concerns the identification of crop models environmental friendly and with low hydrological and energetic impacts, able to combine conflicting objectives, i.e. to maintain an adequate level of soil coverage during the rainy period and, on the contrary, to contain it during the period of drought. Some authors suggest the use of specific mathematical models to predict the effects of plant cover on soil loss (Bombino et al., 2002, 2004, 2011; Zema et al., 2012a).

In particular, the experimental activities on "soil macro-system" are arranged in cultivated areas, typical of semi-arid environment, in which will be hydraulically isolated plots (Wischmeier and Smith type) equipped with devices for measuring variables and hydrological adopted different methods of soil management in terms of weed control. To this end, in experimental plots, three weed control practices commonly adopted in Mediterranean olive growing are simulated and their hydrological effects are measured.

Conventional chemical weed control is compared with conservative practices, i.e. minimum chemical weed, mechanical weed and total removing of herbaceous cover.

Referring to "water macro-system", the activities research includes the construction of an experimental irrigation field using micro-irrigation systems. In Mediterranean regions, characterized by water scarcity, climate changes and increasing water demand, the sustainable management of water resources is now an urgent need especially for the agricultural sector that is by far the biggest user of freshwater. However, especially in the Mediterranean area, the use of high irrigation water volumes and fertilizers are considered as essential elements to achieve high crop productivity.

Therefore, the use of treated wastewater for irrigation can play an important role in water resource management in order to increase environmental and economic sustainability of the entire production process (Barbagallo et al., 2012, 2014; Molari et al., 2014; Zema et al., 2012b). Indeed, the agronomic reuse of non-conventional water can produces many advantages, among which the improvement of soil fertility by delivering nutrient compounds held in wastewaters, the reduction of conventional water use and the reduction of the damage caused to the environment by dumping untreated or poorly treated wastewater into water bodies.

Furthermore, some benefits can be attributed to the reduction of technical and economic difficulties arising from the management of wastewater treatment plants as well as to the saving for farmers due to the reduction of the amount of fertilizers to add in the irrigation water.

Improving the sustainability of irrigation practice also means to use deficit irrigation techniques in order to obtain satisfactory yields and economical cost-effectiveness. The use of irrigation techniques, such as the micro-irrigation, combined to the fertilizing properties of the wastewater, can produce environmental, social and economic benefits, if wastewater is treated with efficient and cheap treatments.

Among the available wastewater treatment techniques, natural treatment systems such as constructed wetland (Toscano et al., 2013, 2015) has low operational and management costs and it is able to improve water quality through efficient pollutant removal.

Within the project's activities, wastewaters treated with natural systems are used to irrigate horticultural crops and "no food" biomasses. Constructed wetland systems (phytoremediation systems) are analysed in order to evaluate their efficiency in terms of possible reuse of treated wastewater for crop irrigation. The experimental irrigation field, constituted by several parcels, are located near the constructed wetland treatment plant. Wastewater effluents from constructed wetland are used for crop irrigation. Reservoir effluents are also used for crop irrigation in order to compare the performance of various natural wastewater treatment systems.

Different restitutions of crop evapotranspiration are considered during the irrigations. In order to evaluate the efficiency of the treatment systems - taking into account the regulatory limits for wastewater irrigation reuse - physical, chemical and microbiological analyses are carried out on wastewater samples collected at the influents and effluents of wastewater treatment systems. In order to evaluate the effects of irrigation using treated wastewater on soil and plants, physical, chemical and microbiological analyses are carried out on wastewater samples collected at the end of filtration unit of the micro-irrigation system. The applicability and sustainability of the irrigation methods are evaluated, in terms of efficiency, water requirements of crop, yield and health hazards linked with the use of treated wastewater for crops irrigation.

In particular, the following measures are monitored to determine micro-irrigation system performance: rate of pressure loss, time and effort required by a skilled operator to clean filters. In order to rank emitter clogging, drip lines discharge rate are computed. In order to evaluate the effects of different amount of irrigation volumes, physical, chemical and hydraulic analyses are carried out on soil samples. In particular, undisturbed soil samples are collected at the beginning of experimental activity and ant the end of each crop life cycle. According to the standard method, the soil texture (percentage of fine soil, sand, silt and clay) and chemical characteristics will be determinate for each soil sample.

Finally, to ascertain the changes induced in soil hydraulic and transport properties at the end of wastewater application cycle, hydraulic conductivity curve is determined. Microbiological parameters are analysed on soil, water and plants in order to evaluate the health risk associated with the use of wastewaters for irrigation.

The experimental activities on "energy macro-system" provide a technical assessment of energy systems based on the use of biomass from agricultural by-products and dedicated crops.

This is achieved through the analysis of chemical and energy-related characteristics of different biomass, the storage properties, and the dimensional optimization of the energy system in relation to the local potential supply (de Menna et al., 2015). The main energy-related characteristics of biomass are identified from collected samples, where the experimental tests are conducted. For these samples, the energy yields of the fuel conversion in a small-scale pilot boiler, the storage properties and the environmental impacts in terms of emissions from the combustion of biomass are evaluated.

For the crop systems analysed in the previous experimental activities (i.e. olive growing and dedicated energy crops), the "energy macro-system" is analysed through the development of management options for the crops residuals valorisation finalized to energy production.

Furthermore, the same analysis are carried out with specific reference to the artichoke grown as horticultural system particularly interesting (in Sardinia and Sicily regions) also in terms of biomass energetic potential (Ledda et al., 2013).

The agronomical activities are organized into several phases: development of dataset on the artichoke crop residuals yields and their energy conversion at regional scale; identification of experimental protocols; agronomic characterization of artichoke crop residuals; application of a cropping system simulation model in order to evaluate the effect of different agricultural practices on the production of the artichoke crop residuals; assessment of the energy productivity of the artichoke crop residuals.

2.3 Cross-cutting analysis: life cycle approaches and participatory activities

As indicated in Fig. 2, a cross-cutting methodological approach used in this project is represented by Life Cycle Thinking (LCT), a conceptual model born, since the early '90, to deepen the knowledge about all impacts generated by products and services during their life cycles, taking into account all inputs and outputs used (Guinée et al., 2002).

From this vision, it derived the "life cycle toolbox" that includes Life Cycle Assessment (LCA), Life Cycle Costing (LCC) useful for respectively environmental and economic assessment, as well as Social LCA - still to be defined - to evaluate the social consequences of production processes. According to the definition of SETAC (Fava et al., 1991), when LCA is applied to crop scenarios, the aim is to measure resources usage and environmental releases and to evaluate opportunities to achieve sustainability improvements.

Commonly, LCA methodology is implemented taking into account the same assumptions in the choice of system boundaries and procedures of allocation, the choice of environmental impact categories and the models for their interpretation, data requirements and quality criteria (Comandaru et al., 2012; Ghinea et al., 2014). In particular, for each crop studied in the project, the environmental impacts related to agricultural phase, transportation of agricultural products or by-products and industrial conversion for power generation, are considered.

In terms of system boundaries, the project's LCA analysis consider a cycle "from cradle to grave" in the case of dedicated energy crops, while "from cradle to gate" with an extension of the system related to the biomass conversion process for perennial and horticultural crops for which only residuals are destined to energy purposes.

From experimental activities on crops scenarios, primary data, linked to input and outputs used in the production systems are used to realize the LCA inventory. Similarly, through the same data detection mode and also by adapting experimental results to farm realities, a costs inventory is realized to conduct a LCC analysis by taking into account all cash flows (i.e. all the costs and revenues) associated to all phases, according to other applications of several scholars (De Gennaro et al., 2012; De Luca et al., 2014; Falcone et al., 2015; Iotti and Bonazzi, 2014; Mohamad et al., 2014; Pergola et al., 2013; Strano et al., 2013).

In particular, each input and output considered in LCA analysis is transformed in monetary values and all other costs associated to them (e.g. variable costs of labour, disposal, etc. and fixed costs as shares of insurance, taxes etc.) are included, in order to calculate the total cost of every single process within the entire production system. Obtained data are used to perform also profitability analysis of investments by assessing the overall life cycle cost through appropriate financial indices as the Net Present Value (NPV) and the Internal Rate of Return (IRR) to assess the economic and financial trend of investments during the whole life cycle.

Therefore, a unique inventory of data is utilised to obtain complementarity between LCA and LCC analyses - that are conducted using the same functional unit and system boundary - in order to interpret jointly environmental and economic results of sustainability (De Luca et al., 2014; Falcone et al. 2015; Strano et al., 2013;).

Concerning the social dimension sustainability, the project's methodological choice starts by the assumption that a sustainability assessment have, necessarily, contemplate the inclusion of social aspects, whether included as a one of the "three pillar", albeit connected with the others, or as general umbrella within which to consider the other aspects. It is increasingly recognised the need of further research development to integrate, with more scientifically robust methods, the results of sustainability assessment, especially when coming, at the same time, from different issues (environmental, economic and social), strictly interconnected among them.

From a life cycle perspective, a promising but still new concept, is the so-called Life Cycle Sustainability Assessment (LCSA) (Kloepffer, 2008; Sala et al., 2013a, 2013b) in which the three well-known dimensions of sustainability (environmental, economic, and social) are integrated by using the three independent methodologies (LCA, LCC and s-LCA). However, according to Onat et al. (2014), despite the studies on methodological aspects are in expansion, the real cases of applications of LCSA are highly limited. Furthermore, if the integration of methods appears to be a critical challenge, the definition of appropriate indicators from environmental, economic and social points of view, when related to the stakeholder's *desiderata*, is a more critical point. This is particularly true especially for local-based assessments, because social indicators that are necessarily context-dependent.

This is the reason why the evaluation approaches have to take into account not only the expert's opinions on the choice of impact indicators but also the viewpoints of other subjects, both those directly or indirectly affected (i.e. public stakeholders through regulatory measures and privates with managerial behaviours) (De Luca et al., 2015). Participation, in this sense, can play a key role to make the assessment legitimate and adherent to reality (Iofrida et al., 2014).

An increasing literature deepens these topics in life cycle studies, but several scholar affirm that only few explicit analyses has been made until now, both in terms of integration of results and of participatory approaches into life cycle methodologies (Jørgensen, 2013; Mathé, 2014; Sala et al., 2013a, 2013b). An integrated assessment of complex issues - like sustainability concerns - requires "a mutual interdependence of participatory and modelling approaches in assisting policy-making" (Hisschemöller et al., 2001). In this sense, the Multi-Criteria Decision Analysis (MCDA) serves a two-fold purpose. Firstly, it allows conducting a joint assessment moving from analyses methodologically different and integrating their results. Secondly, it permit to directly incorporate the preferences of different interest groups or stakeholders (Banville et al., 1998; Estévez et al., 2013; Macharis et al., 2012), providing useful information to be spent, for example, in the improvement of political actions based on new contextual knowledge. Recently, MCDA and participatory approaches have been applied to LCA studies (Bachmann, 2012; Castellini et al., 2012; De Felice et al., 2013; Malloy et al., 2013; Mathé, 2014; Recchia et al., 2011; Yue et al., 2014). However, the use of these methodologies for integrating different life cycle results remains a little explored field.

Starting from these assumptions, the MIMeSMAS project attempts to conduct an integrated assessment of agricultural systems sustainability setting up the most suitable environmental, technical and economic indicators with the contribution of different expertise from the project's team.

These indicators are measured through experimental activities conducted at both pilot-scale (one for each site and scenario considered) and specific evaluation analysis at farm-scale selected in the study areas. For the same contexts, social indicators are selected by researchers starting from the context analysis carried out in the first phase of the project and, in a second phase, are validated through inclusive participatory activities.

The analysis is based on literature review and focus groups with regional officials and experts in the sector. Participatory activities are carried out through a joint use of qualitative procedures, starting from the "stakeholder theory" (Mitchell et al., 1997), the "Q-methodology" application (Stephenson, 1953) and Delphi analysis, in order to define the stakeholder's sample to be involved and the social sustainability dimensions to be assessed (Iofrida et al., 2014). Direct and proxy indicators measurement are developed to elaborate the data gathered from secondary sources (official statistics and literature) and primary ones (with semi-structured questionnaires and direct interviews conducted at farm level) according to De Luca et al. (2015).

Participative activities among stakeholders are carried out in order to facilitate reflection and promote social learning processes (Toderi et al., 2007) and by sharing the research results to create new knowledge and new learning spaces between researchers and local stakeholders (Allan et al., 2013).

Finally, once the indicators are defined and measured, for each agricultural system studied, multi-criteria tools are used to integrate environmental, economic and social sustainability results derived from the application of the others methodologies. MCDA are also used to weight each indicator according to the preferences of the actors involved, in particular through the application of the Analytic Hierarchy Process (AHP) by Saaty (1990). This weighting process will permit to compare different categories, to rank the scenarios, and to quantify the sustainability of the agricultural systems in a comparative way between scenarios of analysis.

3. Preliminary results

Summarising the results of the first year of MIMeSMAS project, a twofold direction of research activities can be distinguished. Firstly, the characterization of analysing contexts and of the identification of crops systems is significant for agricultural sustainability issues. Subsequently, the definition of methodological protocols has been carried out, in an integrated approach, to pursue the objective of a holistic assessment of alternative agricultural management options.

As already mentioned, the project aims to define a multidisciplinary methodological framework to assess the agricultural sustainability through an all-embracing way. At the same time, the project aspires to implement this methodology in different cultivated areas by choosing different crops systems as representative for each area in terms both of agronomic and economic relevance, and also for potential benefits of alternative management options in real farm contexts.

At this stage of the project three outcomes derived from the first year of projects' activities can be outlined: first, the identification of crops variety to be studied derived from an in-depth analysis of the territorial contexts and their sustainability issues. Secondly, the definition of alternative management scenarios evaluated through experimental-based and farm-based analysis (Table 1).

Finally, the selection of specific indicators derived from the hydraulic, agronomic and mechanical model used in experimental activities as well as the life cycle indicators related to the assessment of environmental, economic and social impacts (Tables 2 and 3).

Table 1. Crops systems identified and related experimental scenarios

Local-based case-studies in Mediterranean areas	***Experimental scenarios***	
Giant reed plantations (Sicily/Emilia Romagna)	Sicily: - Treated wastewater (TWW) with phytoremediation systems; - Micro-irrigation with different TWW levels and conventional water (CW) - Energetic Potential assessment of biomass.	Emilia Romagna: - Different levels of irrigation; - Energetic Potential assessment of biomass.
Artichoke plantations (Sicily/Sardinia)	Sicily: - Treated wastewater (TWW) with phytoremediation systems; - Microirrigation with different levels of TWW and conventional water (CW); - Energetic Potential assessment of by-product biomass.	Sardinia: - # 5 Artichoke botanical varieties; - Water and nitrogen in late spring; - Energetic Potential assessment of by-product biomass.
Olive orchards (Calabria)	Calabria: - Chemical weed control; - Minimum chemical weed; - Mechanical weed; - Total moving of herbaceous cover control. - Energetic Potential assessment of by-product biomass and herbaceous cover biomass.	

Table 2. Indicators measured with experimental activities on soil, water and energy macro-systems

Soil macro-system indicators	Chemical	L_{TOC} (Total Organic Carbon)		g C kg^{-1} soil
		Macronutrients		g N P K
	Physical	$I_{TEXTURE}$ (Soil texture)		mm
		IK_{sat} (Saturated hydraulic conductivity)		cm s^{-1}
		pH		-
	Agronomic	I_{TotSur} (Total Parcel Surface)		ha
		I_{Var} (Varietal type)		Qualitative var.
		I_{bCyc} (Cycle starting date)		DOY
		I_{dCyc} (Cycle duration)		DAP
		I_{Den} (Density)		n. plants m^{-2}
		I_N (Input N and other fertilizers)		kg ha^{-1} year^{-1}
		I_{nPest} (Pesticides input)		n. interventions and dosage (kg ha^{-1} year^{-1})
		I_{Till} (Tillage typology)		Qualitative var.
		I_{Depth} (Principal Tillage Depth)		cm
		I_{nTill} (N. of tillages)		n.
		I_{yield} (Principal Product Yield)		Kg ha^{-1}
		I_{HI} (Harvest Index)		%
Water macro-system indicators	Meteorological	R (Precipitations)		mm
		T (Temperature)		°C
		RH (Air moisture)		%
		WS (Wind speed at 2 m)		m s^{-1}
		SR (Net solar radiation)		MJ m^{-2} d^{-1}
	Water quality	pH		-
		CE (Electrical conductivity)		µS/cm
		SST (Total suspended solids)		(mg L^{-1})
		SAR (Sodium Adsorption Ratio)		-
		N_{TOT} (Total Nitrogen)		(mg L^{-1})
		P_{TOT} (Total Phosphor)		(mg L^{-1})
		BOD_5 Organic matter		(mg L^{-1})
		E. coli (Escherichia coli)		(UFC 100 ml^{-1})
	Irrigation	I_{nIrr} (Irrigations during irrigation season)		Number
		I_{Irr} (Distributed irrigation volumes)		(m^3 ha^{-1})
		UE (Distribution uniformity)		(%)
		R_d (Average flow reduction coefficient)		(%)
		Duration of irrigation season		start and end dates
		ET_0 (Reference evapotranspiration)		mm day^{-1}
		ET (Evapotranspiration)		mm day^{-1}
Energy macro-system indicators	Characterization	I_{resid} (management of residual biomass)		Qualitative var.
		Fresh weight		t ha^{-1} year^{-1}
		Water content		%
		Dry weight		t ha^{-1} year^{-1}
		Higher heating value		MJ kg^{-1} (x%DW)
		Bulk density		kg m^{-3}
		Prox Analysis (Ashes)		% DW
		Biogas (Extractives, Total lignin, Polysaccharides, Methane yield, CH_4)		% DW; m^3 kg^{-1} VM; %
	Conversion	Feedstock collection and treatment; Energy conversion; Energy production	Electricity and Heat consumption	kWh ha^{-1} year^{-1}
			Fuel consumption	l ha^{-1} year^{-1}
			Machinery	kg ha^{-1} year^{-1}
			Electricity yield	kWh ha^{-1} year^{-1}
			Heat yield	kWh ha^{-1} year^{-1}
			Biochemical methane potential	m^3 ha^{-1} year^{-1}
		Ashes	Amount	t ha^{-1} year^{-1}
			Disposal	t ha^{-1} year^{-1}
		Digestate	Amount	t ha^{-1} year^{-1}
			Disposal	t ha^{-1} year^{-1}

Table 3. Selection (not exhaustive) of indicators used for Life Cycle analysis (LCA, LCC, sLCA)

Life Cycle Indicators	*LCA*	Climate change (Global Warming Potential)	Kg CO_2 eq.
		Ozone Depletion (ODP)	Kg CFC-11 eq.
		Marine eutrophication (MEP)	Kg N eq.
		Freshwater eutrophication (FEP)	Kg P eq.
		Urban Land Occupation (ULOP)	m^2 a
	LCC	Total costs of production	€ ha^{-1}
		Net Cash Flows	€ ha^{-1}
		Net Present Value (NPV)	€ ha^{-1}
		Internal Rate of Return (IRR)	%
	sLCA	Health and safety working conditions	Direct or proxy indicators (quali/quantitative)
		Fair working conditions /Equal opportunities	Direct or proxy indicators (quali/quantitative)
		Area reputation /Contribution to economic development	Direct or proxy indicators (quali/quantitative)

3. Conclusions

The project presented in this paper is currently ongoing; therefore, some research activities are still in working progress. The focus of the project is the analysis of several agricultural ecosystems (giant reed, artichoke and olive) from a holistic and multi-disciplinary approach aimed to define management systems to optimize the use of soil, water and energy resources. The activities involve experimental trials and farm case studies to test and validate sustainable agricultural techniques that are analysed through LCA, LCC and sLCA tools, multi-criteria methodologies - to integrate environmental, economic and social results - and participatory approaches to legitimate the research activities.

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AROMATIC HYDROCARBON LEVELS AND $PM_{2.5}$ CHARACTERIZATION IN ROME URBAN AREA: PRELIMINARY RESULTS

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Abstract

The preliminary results of aromatic hydrocarbon (AR) levels and $PM_{2.5}$ physico-chemical characterization in Rome urban air throughout the 2014 are reported. A gas chromatograph was used for continuous measurements of AR concentrations with 30 minute time intervals. $PM_{2.5}$ was collected by PM swam Dual Channel. Metal content was determined by ICP-MS. Single particle characterization was performed by Scanning Electron Microscopy equipped with a thin window system for X-ray microanalysis by energy dispersion spectrometry. X-ray microanalysis data were used to classify the particles into clusters of similar chemical composition. Results showed variations in seasonal AR levels, higher concentrations in winter and lower in summer. Toluene was the most abundant compound, followed by *m,p*–xylene and benzene. The compounds showed similar correlations in winter and summer. According to T/B ratio and meteorological analysis, AR levels were under the influence of vehicular sources. Seasonal variation of different inter-species ratios showed a decreasing trend from winter to summer and an increase from August to December. ICP-MS analysis revealed Fe, Al and Zn as the most abundant elements, decreasing from March to July (except Zn). $PM_{2.5}$ single particle characterization detected four particle clusters: C-rich particles, metal particles, sulphates and soil dust. C-rich particles were constituted of a large number of spherule aggregates carrying trace of S, Na and K. Metal particles are the second significant component, including Fe, Pb, Cu, Zn, Ni and Ti.
Further studies must be performed to better understand the processes of transformation that undergo the carbonaceous particles in the atmosphere.

Key words: analytical electron microscopy, aromatic hydrocarbons, physico-chemical characterization, $PM_{2.5}$

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1. Introduction

Volatile organic compounds (VOCs) attracted much attention due to their wide occurrence and health impacts, especially in urban area. Quantification of VOCs in the ambient air is important for air quality assessment and for understanding the photochemical formation of smog. Aromatic hydrocarbons (ARs) usually represent a significant fraction of total VOCs, and they are emitted by fuel combustion and evaporation of fuels and solvents. Among ARs, benzene, toluene and xylene are well known as major components with a potential health risk (Lawryk and Weisel, 1996; Leung and Harrison, 1999). Atmospheric ARs participate in complex chemical reaction to form secondary pollutants. Several studies suggest that 10%-60% of fine particulate matter ($PM_{2.5}$) is

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composed of organic compounds (Pandis et al., 1992; Seinfeld and Pandis, 1998; Zhang et al., 2011). $PM_{2.5}$ is composed of a wide variety of organic and inorganic components of primary and secondary origin. Atmospheric hydrocarbons may contribute to particulate matter generation via semi-volatile reaction products that undergo gas-to-particle conversion.

In particular, aromatics typically contribute with 0.1 to 0.45 μg/m^3 to the observed $PM_{2.5}$ concentrations as shown in several studies (Kleindienst et al., 2010; Lewandowski et al., 2008; Offenberg et al., 2011; Stone et al., 2009).

Epidemiological studies have linked ambient particulate matter (PM) levels to an increased incidence of adverse cardiovascular events. Numerous epidemiological studies have associated short-term and long-term PM exposures to increased mortality (Dockery et al., 1993; Hart et al., 2015; Kloog et al., 2013; Peters et al., 2005; Pope et al., 2006; Samet et al., 2000). Moreover, several studies have shown that iron and other transition metals leaching from particles or by their presence on particle surfaces play a role in the generation of reactive oxygen species (ROS) in biological systems (Ghio et al., 2000) and ROS production activate cellular inflammatory response pathways (Heal et al., 2005).

Rome has a surface area of 1300 km^2, 2.5 million inhabitants and the highest number of vehicles (~1.8 millions in 2013) among Italian cities.

In the present work are reported the preliminary results of a collaboration, started in January 2014, between the Italian National Institute of Health (ISS, Department of Environmental Health and Primary Prevention) and National Institute for Insurance against Accidents at Work (INAIL, Department of Technological Innovations and Safety of Plants, Products and Anthropic Settlements) whose main purpose is to undertake very in-depth studies on fine particulate matter through the physical-chemical characterization of individual particles and the study of the processes of transformation that undergo the particles in the atmosphere. For these reasons the AR levels, the concentration of several trace metals in $PM_{2.5}$ and single particle characterization of $PM_{2.5}$ have been evaluated in the urban air of Rome.

Moreover, natural radioactivity has been used as a reliable tracer of the dilution properties of the lower atmosphere.

2. Experimental

2.1. Sampling site description

The measurements presented in this work were carried out at the monitoring station located in the front yard of the Italian National Institute of Health (ISS) (2 km east of the city center) on the right side of the ISS main building central entrance. The station is about 8 m from the curb of the street, a large road with medium-high traffic intensity.

2.2. AR monitoring and analytical method

Continuous measurements of AR concentrations were carried out between January 1 and December 10, 2014. The January data were not taken into account because the measurements for most of the days did not cover more than 90% of the daily hours. A Syntech Spectras 955 gas chromatograph (GC) was used for continuous measurements of 7 aromatic hydrocarbon concentrations with 30 minute time intervals, in 2014. A detailed description of the analytical system can be found elsewhere (Fanizza et al., 2014; Xie et al., 2008; Wang et al., 2004). The GC was calibrated according to Syntech recommendations; one complete full dynamic calibration was performed before each seasonal campaign by using a standard certified calibration gas mixture, containing 28 target species with mixing ratios of 1 ppm in nitrogen (Sapio, Italy), prepared by the gravimetric method (SR ISO 6142/2001). The calibration gas was diluted with zero air (quality 5.0) to prepare six calibration spans; the dilutions were prepared using a calibration system (Calibration System CMK5, MCZ, Umwelttechnik, DE). For every concentration (3, 5, 10, 15, 30, 50 ppbV) at least 6 samples was analyzed.

For each analysis, an air sample with a volume of 250 mL was sampled. The height of air intake was at road level. The daily averages were taken into account when the measurements covered more than 90% of the daily hours. The detection limits are estimated to be 0.03 to 0.05 μg/m^3, and the uncertainty is estimated to be 5%.

2.3. Natural radioactivity

The knowledge of the low atmosphere dilution properties layers makes possible to understand the accumulation of pollutants as well as the temporal evolution of all air pollution processes. We applied the technique based on the monitoring of a chemically stable compound (Radon) with an emission flow in order to get information about dilution potential of the Planetary Boundary Layer that can be considered constant in the space-time scale of interest.

The Radon gas is produced in the ground by the 222Rn and the 220Rn isotope (Thoron) radioactive decay and it is released in atmosphere where it disperses prevalently by turbulent scattering. Therefore, the concentration of Radon in atmosphere is mostly dependent on the vertical dilution factor, while the Radon products could be seen as natural tracers of mixing properties for low PBL layers. In case of convective mixing or advection, the natural Radon accumulation is allowed the in the low PBL layers (Perrino et al., 2009). A sequential automatic system, namely PBL Mixing Monitor (FAI

Instruments, Fontenuova, Italy) was used to assess the mixing ratio of low PBL layers.

The instrument samples on hourly basis the atmospheric particulate matter where Radon progeny fixes and, by a Geiger-Muller counter, determines the sample radioactivity level. The instrument manufacturing characteristics allow getting 24 averages per hour of the natural radioactivity values per every sampling day.

2.4. $PM_{2.5}$ sample collection and metal content determination

$PM_{2.5}$ was collected by PM swam Dual Channel FAI Instruments, operating at 2.3 m^3/h flow rate. Six particulate sampling for metal content determination and single particle physico-chemical characterization by analytical electron microscopy, were conducted from March 2014 to July 2014.

For the determination of metal content $PM_{2.5}$ was collected on mixed cellulose ester membrane (pore size 1.2 µm) during 24 h; for single particle characterization by electron microscopy particulate matter was collected on polycarbonate membranes (pore size 0.8 µm) during 8 h. In a quartz tube sampled cellulose filters were added with 3 ml HNO_3 (67-69% Romil, ICP grade, metallic impurities less than 5 ppb), put in a closed vessel and mineralized by Microwave Digestion System (START D - Milestone). The obtained solutions were diluted with purified water (MilliQ Integral A10 System – Millipore) and analyzed using ICP-MS (Elan 9000 - Perkin Elmer) for 9 elements. The elemental concentrations were obtained by external calibration (3 points each element) using indium as internal standard.

A blank's elemental concentration has been subtracted in order to obtain the final values. The analytical uncertainty for each elemental concentration was determined. The minimum detection limit (MDL) for each element was defined as 3 times the blank's standard deviation.

2.5. Physico-chemical characterization of $PM_{2.5}$

Single particle characterization of $PM_{2.5}$ was performed by SEM equipped with a thin –window system for X-ray microanalysis by energy dispersion spectrometry. A semi-automatic analysis system (Particle Analysis, EDAX) was used.

For each particle morphological parameter (mean diameter, Feret Diameter, Aspect ratio, shape factor) and chemical composition were determined (De Berardis et al., 2007). The intensities of the characteristic X-ray lines, collected from each particle and converted to the corresponding atomic concentration by standardless ZAF correction method, were analyzed by hierarchical cluster analysis (HCA) to determine the principal components of $PM_{2.5}$ (Paoletti et al., 2003).

2.6. Data analysis

Pearson correlation test was carried out to study the relationship between compounds. $p<0.05$ was considered significant, $p<0.001$ highly significant.

3. Results and discussion

3.1. AR monitoring

The seasonal mean concentrations of ARs are given in Table 1. AR levels ranged from 19 µg/m^3 in the winter period to 4.4 µg/m^3 in the summer. The fall AR concentrations (7.3 µg/m^3) were lower than spring levels (8.6 µg/m^3), which can be linked to atmospheric conditions. Generally, VOC concentrations were higher in winter and autumn than in spring and summer, as found in many other cities (Batterman et al., 2002; Fanizza et al., 2014; Kourtidis et al., 2002; Pankow et al., 2003; Zou et al., 2015). Because November 2014 has been the hottest since 1800 and the wettest from 1926 (Brunetti, 2014), the correlations (hourly averages) between concentrations and temperature during spring, summer and fall were carried out to verify the influence of temperatures on AR levels. The AR/T winter correlations were not developed because of the lack of data related to hourly average temperature.

All ARs had highly significant ($p<0.01$) negative correlations with temperature during the periods taken into account. These results are consistent with the effects of photochemical reactions, in summer these reactions must proceed faster than in winter. The average temperature during spring and fall period was 20°C and 18°C, respectively.

Table 1. Seasonal and annual AR concentrations (µg/m^3)

Aromatic hydrocarbons	*WINTER*		*SPRING*		*SUMMER*		*FALL*		*2014*	
	Avg	*Max-Min*	*Avg*	*Max-Min*	*Avg*	*Max-Min*	*Avg*	*Max-Min*	*Avg*	*Max-Min*
Benzene	1.95	4.55-0.83	1.39	3.66-0.34	1.16	2.52-0.37	1.06	10.28-0.46	1.28	10.28-0.34
Toluene	6.86	23.49-1.34	2.58	14.03-0.32	1.39	9.47-0.15	2.27	22.41-0.17	2.57	23.49-0.15
Ethylbenzene	1.15	6.95-0.21	0.46	5.21-0.04	0.16	1.08-0.04	0.36	4.53-0.04	0.40	6.95-0.04
m, p-xylene	6.04	23.86-1.09	2.47	19.40-0.28	1.04	6.94-0.04	2.22	24.63-0.15	2.32	24.63-0.04
o-xylene	1.68	7.41-LOD[a]	0.70	6.33-0.07	0.31	2.13-0.04	0.66	7.62-0.04	0.67	7.62-LOD[a]
1,3,5 -TMB[b]	0.60	3.49-0.06	0.26	10.35-0.02	0.12	2.80-0.05	0.22	3.17-0.05	0.25	10.35-LOD[a]
1,2,4 -TMB[b]	1.24	7.70-0.16	0.72	16.01-0.07	0.28	4.27-0.05	0.59	8.65-0.05	0.60	16.01-0.05
Total	18.97	69.23-4.27	8.55	64.09-1.37	4.39	20.36-0.67	7.25	69.88-0.78	7.87	69.88-0.67

[a]LOD = below the limit of detection, estimated to be 0.03 to 0.05 µg/m^3; [b]TMB = trimethylbenzene

However, other atmospheric parameters have probably contributed to the low AR concentrations in fall as rain and relative humidity. During summertime the AR total concentration reduced of 77%. The minimum concentrations during summer months are probably due to the seasonal variation in the reactivities of ARs and to the higher mixing height in summer period.

Fig. 1 shows variations of all measured AR seasonal averages (mean, minimum and maximum values, standard deviation). All AR showed the same seasonal variation (Fig. 1), registering the highest concentration during winter and the lowest concentration during summer. Toluene was the most abundant ARs with an annual mean concentration of 2.57 μg/m^3, the second and third ARs measured were m,p–xylene (2.32 μg/m^3) and benzene (1.28 μg/m^3) (Table 1). Toluene was found the most abundant AR in other cities around the world, such as Rome (Fanizza et al., 2014; Fuselli et al., 2010), Weldgegund (South Africa) (Jaars et al., 2014), and Pamplona (Parra et al., 2009).

AR concentrations measured in this study are smaller than levels reported for Asiatic urban areas (Ran et al., 2009; Song et al., 2007), Pamplona, Spain, (except for m,p–xylene) (Parra et al., 2009), Kocaely, Turkey, (Pekey et al., 2011), Mexico City (Sosa et al., 2009) and for an urban area located in a relatively medium-size town from Mures County, Romania (Roba et al., 2014). On the contrary AR concentrations were higher than London levels (Russo et al., 2010) and tend to follow within the range of the Los Angeles measurements (Warneke et al., 2012). These differences can be attributed to particular characteristics of the studied cities.

The Pearson's correlations among AR measured, during winter and summer period, are reported in Table 2.

The evaluated correlations resulted to be highly significant (p<0.01) and positive and remained quite similar in both periods, even if the correlations were slightly higher in summer than in winter, which could be due to range of atmospheric and traffic conditions. Most AR concentrations were very strongly correlated (r≥0.61) in both seasons, suggesting that they came from the same sources during both periods, like vehicular traffic (Khoder, 2007).

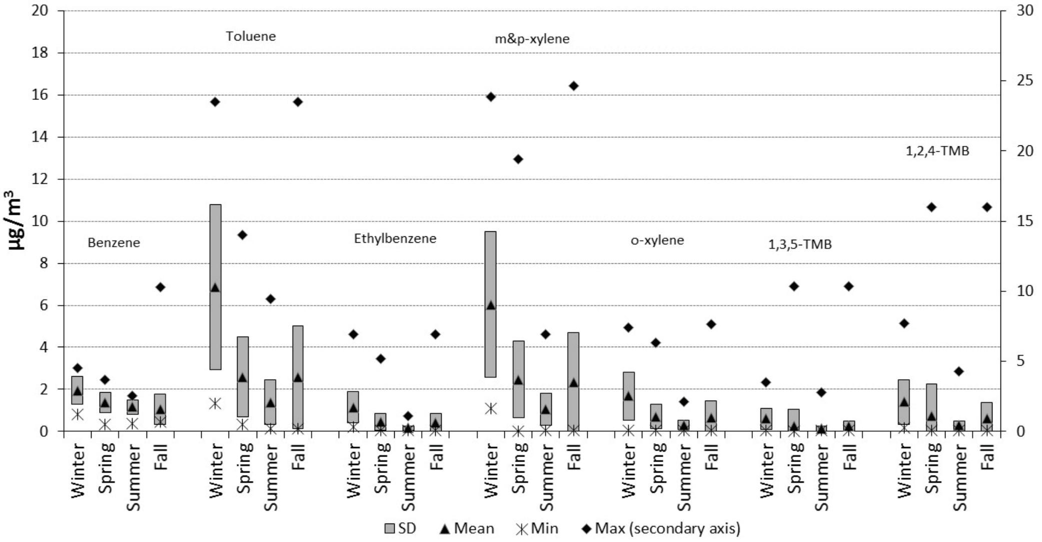

Fig. 1. AR seasonal variations during this study

Table 2. Pearson Correlation Coefficients

	WINTER					
	toluene	***ethylbenzene***	***m, p-xylene***	***o-xylene***	***1,3,5-TMB***	***1,2,4-TMB***
Benzene	0.58	0.48	0.53	0.53	0.35	0.35
Toluene		0.87	0.95	0.94	0.69	0.66
Ethylbenzene			0.93	0.96	0.84	0.83
m, p-xylene				0.99	0.85	0.83
o-xylene					0.85	0.83
1,3,5-TMB						0.96
	SUMMER					
Benzene	0.61	0.61	0.67	0.64	0.30	0.45
Toluene		0.76	0.85	0.81	0.40	0.54
Ethylbenzene			0.92	0.90	0.57	0.69
m, p-xylene				0.97	0.67	0.79
o-xylene					0.68	0.79
1,3,5-TMB						0.91

The inter-compound ratios can also be used to determine possible sources for ARs and the age of the air masses (Hoque et al., 2008). The T/B ratio is usually high close to anthropogenic emissions and decreases with an increase of distance from the sources and, based on T/B ratio, several studies individuate the possible sources (Lan and Minh, 2013). A T/B<3 was characteristic of fresh emissions originating from traffic. In our study the T/B ratio was 2 highlighting that vehicular emissions are the main source of VOCs in Rome urban air. Seasonal variation of different inter-species ratios is graphed in Fig. 2. AR concentrations in ambient air are higher in winter than in summer period.

The inter-species ratios showed a decreasing trend from winter to summer, with the lowest value in August, and an increase from August to December.

The lowest values observed during the hottest months were due to enhanced photochemical reactions: the abundance of more reactive species decreased leading to reduction in inter-species ratios. Diurnal variations of all sampling days, monitored throughout the four seasons, showing the evolution of aromatics are presented in Fig. 3. AR levels followed every week day a similar pattern that changed during the weekends, e.g., Fig. 4 shows a typical week for each season.

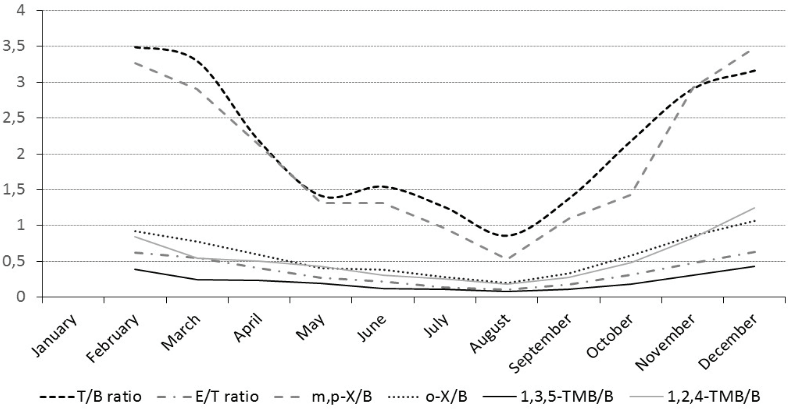

Fig. 2. Seasonal variations of AR inter-species

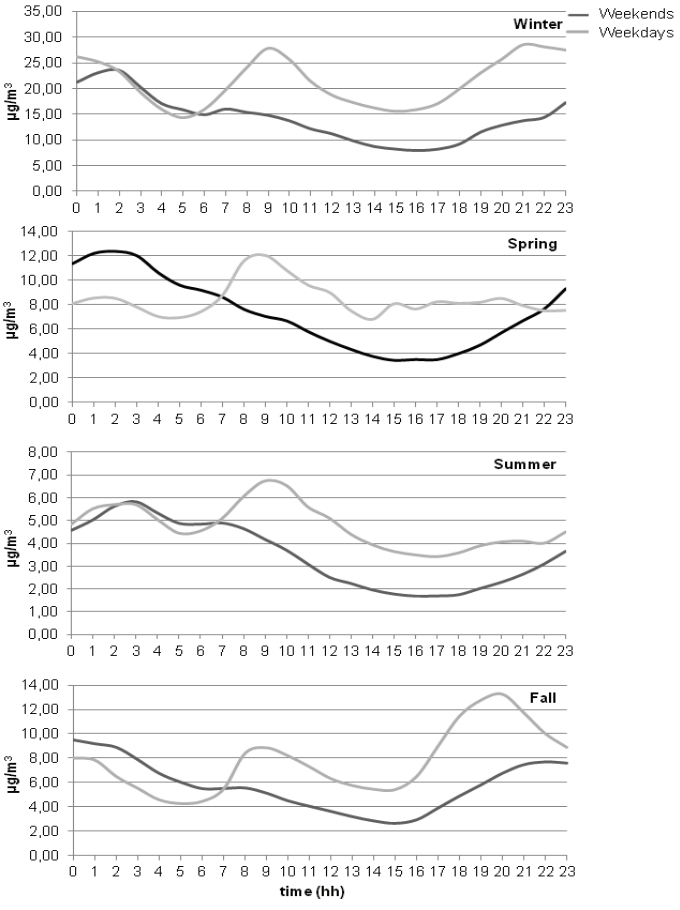

Fig. 3. AR diurnal variations during the monitored days

The AR concentrations were not the same throughout the day. Higher concentrations were recorded in the morning and in the evening and lower ones during the first afternoon on working days. The AR concentrations were cyclically lower during weekends than on working days in all four season, reflecting reduced levels of vehicular emissions on weekends, as it can be observed in Figs. 3-4. At weekends, there were slight increases in concentrations on evening.

These increases in concentrations coincided with traffic rush hours usually registered in the morning and in the evening on working days. A similar trend was found in previous studies developed in Rome urban air (Brocco et al., 1997; Fanizza et al., 2014).

Observed seasonal variations in AR concentrations are probably due to two different reasons: the seasonal variation in the reactivities of ARs and the height of the mixing layer that influences the dilution or the concentration of volatiles. In cold seasons (winter and fall) the thinning of the mixing layer and the occurrence of temperature inversion layers near the ground inhibits the vertical dilution of pollutants at night causing an increase of pollutants.

Consequently, AR trend follows mainly traffic emissions. In winter the second peak was slightly higher than the first, while in fall the peak in the late afternoon was considerable higher. In these periods the lowest values are found in the early morning around 5 a.m. During spring and summer, photochemical reactions are more rapid during the day and in the afternoon than in the morning, then the first concentration peak in the morning is higher than that in the late afternoon. Moreover the increase of mixing layer in the warmest hours of the day lead to a pollution dilution and a decrease of pollutant level in late afternoon.

The monthly variations of AR concentrations expressed as media, median, minimum and maximum values are graphically presented in Fig. 5a.

The AR concentration decrease, registered during the hottest months (July-September), was due to photochemical activity resulting from enhanced solar flux, temperature and higher OH radical concentrations in summer period. Traffic activity also contribute to observed seasonal variation in AR concentration, indeed a decrease in vehicular traffic volume was generally observed during the warmest months (July-August) compared to other months of the year in the center of Rome.

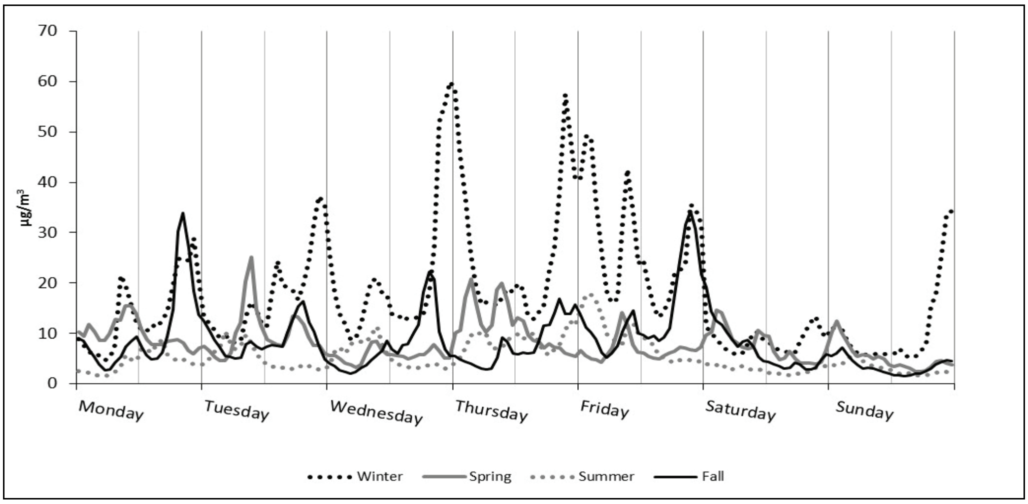

Fig. 4. Weekly averages of AR concentrations

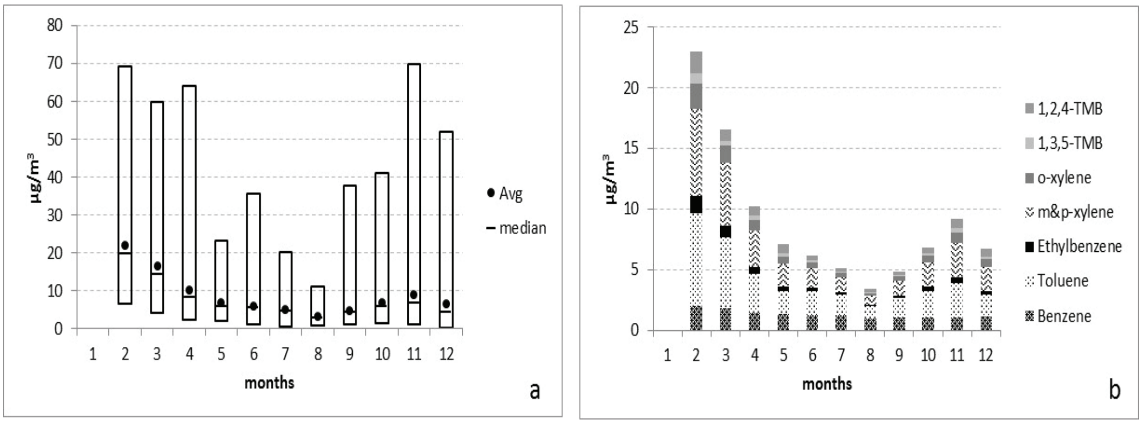

Fig. 5. (a) Monthly variations in AR concentrations during the period of study; (b) the contribution of individual compounds in the different months of the year

The highest concentrations of ARs were found in February and March. In November, AR concentration was lower than April, this was probably due to abnormal weather condition registered in this month. As above mentioned, in November temperatures higher as the seasonal averages were recorded and this month was particularly rainy.

The contribution of individual compounds in the different months of the year is shown in Fig. 5b. The maximum monthly average concentrations of all measured compounds were found in February, whereas the minimum were observed in August. Monthly average concentrations varied from 2.03 μg/m^3 to 1.00 μg/m^3 for benzene, from 7.64 μg/m^3 to 1.76 μg/m^3 for toluene, from 1.45 μg/m^3 to 0.35 μg/m^3 for ethylbenzene, from 7.15 μg/m^3 to 1.99 μg/m^3 for *m,p*–xylene, from 2.05 μg/m^3 to 0.61 μg/m^3 for *o*–xylene, from 0.85 μg/m^3 to 0.23 μg/m^3 for 1,3,5-TMB and from 1.84 μg/m^3 to 0.69 μg/m^3 for 1,2,4-TMB.

Moreover, Fig. 6 shows examples of typical sequences for summer and winter periods of natural radioactivity, which can be considered a good natural tracer of the mixing properties of the lower atmosphere. The variation with time of the radon concentration provides immediate information on current atmospheric conditions and on their changes. During summer the pattern indicated high nocturnal stability and low values from early morning to late evening (Fig. 6). The mixing period typically starts early in the morning and lasts until the late evening. During wintertime the pattern indicated an alternation between atmospheric stability (high night-time radon values and daytime minima) and advection (steady low radon values) (Fig. 6).

To estimate the potential health risk of benzene in our monitoring site, formulas recently reported by Zhang et al. (2015) were used. Based on our collected data, benzene concentrations was 1.28E-03mg/m^3, the average daily exposure was 3.92E-04 mg/kg per day, the lifetime cancer risk (LTCR) resulted 1.13E-05, while the non-cancer risk of benzene (HQ) was estimated to be 0.04. According to USEPA, the acceptable LTCR for adults is 1E-06, and the HQ should be lower than 1 (USEPA, 2009). In our case, LCTR exceed the limit, implying that the potential cancer risk due to ambient benzene exposure should be a health concern in the urban Rome area. Moreover, calculated HQ indicated that non-cancer risk of benzene is not as distinctive as its cancer risk, as already reported also for four background sites in China (Zhang et al., 2015).

3.2. $PM_{2.5}$ metal content analysis

Table 3 shows the concentration's mean value, expressed in ng/m^3, for the six campaigns of $PM_{2.5}$ sampling. Fe was the most abundant element, followed by Al and Zn in agreement to chemical composition of fine particulate particles collected in areas heavily impacted by traffics, as Milan and New York (Perrone et al., 2010; Song and Gao, 2011).

Table 3. Mean value (SD) of elemental concentration expressed in ng/m^3

Analyzed Metal	*Mean value (SD)*
Al	2.671 (2.704)
Cd	0.006 (0.005)
Cu	0.450 (0.162)
Fe	6.589 (3.172)
Ni	0.093 (0.042)
Pb	0.241 (0.141)
Ti	0.098 (0.069)
V	0.103 (0.056)
Zn	0.615 (0.123)

As in sampling site industrial plants or thermo electrical sites were absent and vehicular traffic was the main source of pollution the metals were attributed to fuel combustion, tyre and brake wear (Kumar et al., 2013; Pant and Harrison, 2013). Many study showed that abrasion particles contribute significantly to fine particulate (Lin et al., 2005; Narvaez et al., 2008; Song and Gao, 2011). In Fig. 7 the concentrations of metals in $PM_{2.5}$ collected from March 2014 to July 2014 are displayed. Generally, metal's concentrations decreased from March to July; Zn, instead, remained mostly constant during the sampling period.

3.3. $PM_{2.5}$ characterization by SEM/EDX

HCA allow us to classify the $PM_{2.5}$ into four principal components or cluster with similar chemical composition: C-rich particles, sulphates, soil dust and metals (Fig. 8). C-rich particles were the most important component of $PM_{2.5}$ making up 90% of $PM_{2.5}$. Many authors showed the prevalence of C-rich particles in $PM_{2.5}$ in different urban environments (Baulig et al., 2004; He et al., 2001; Longhin et al., 2013; Pipal et al., 2011).

This kind of particles were mainly spherules with size ranging from 40 to 70 nm showing two different morphologies: chains of spherules with dimensions up 2 μm and aggregates of large number of spherules ranging from 360 nm to 4 μm. Our data on morphological characteristics of this type of particles are in agreement with Longhin et al. (2013). These authors showed that carbon soot particles were mainly aggregates constitute by round-shaped nanoparticles of 40 nm in diameter.

Moreover analytical electron microscopy characterization showed that C-rich aggregates act as carrier, on their surface, of different elements. X ray microanalysis data showed traces of S, Na, and K on 12% of aggregates, suggesting that carbonaceous particles act as vehicles of alkaline metal sulphates, produced by SO_2 photochemical oxidation catalysed by C-rich particles themselves. 18 % of C-rich aggregates showed traces of S and heavy metals, as Fe, V, Zn and Pb.

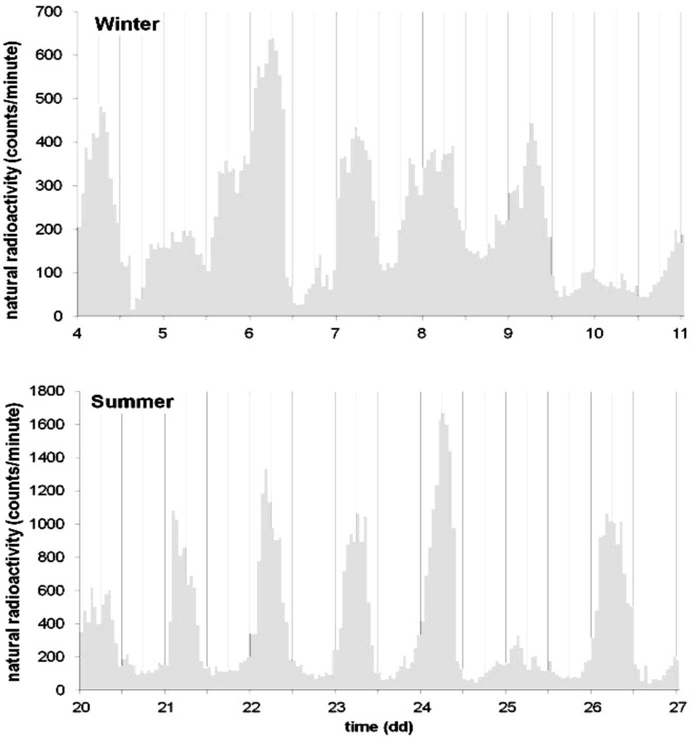

Fig. 6. Natural radioactivity trends in winter and summer periods

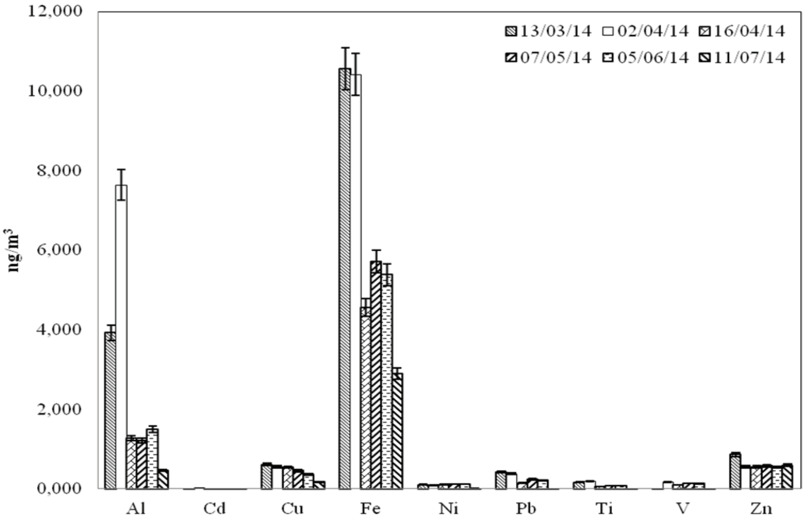

Fig. 7. Metal concentration (ng/m^3) for each sampling day

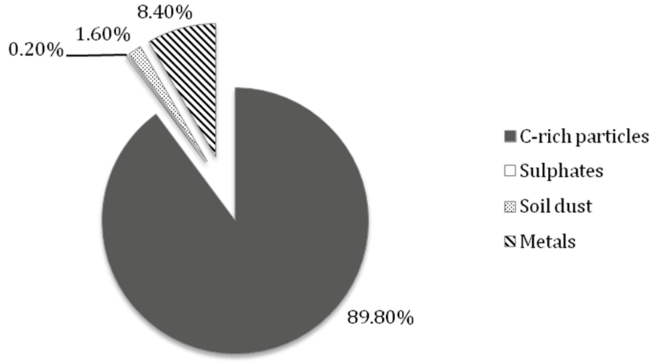

Fig. 8. Abundance of principal component identified in PM$_{2.5}$ by HCA on SEM/EDX physico-chemical characterization data

These carbonaceous particles, coming from fuel oil combustion (Chen et al., 2005, Moldanova et al., 2009), showed an average size of 512 nm. In addition, larger and pure spherical carbonaceous particles (in the size range 200-600 nm), deriving from incomplete fuel oil combustion, were rarely observed.

Metal particles are the second more important cluster of $PM_{2.5}$. They showed a size distribution ranging from 670 nm to 200 nm. This component includes oxides and metal compounds of Fe, Pb, Cu, Zn, Ni, Ti. Iron oxides are the most abundant particles in this cluster. The cluster of soil dust consists of silica and clay (Si, Al or Si, Al, Fe) particles. This component made up only 1.6% of $PM_{2.5}$.

4. Conclusions

AR concentrations in this work showed values comparable to those reported for Los Angeles, while resulted lower than other cities like Pamplona and Mexico City. AR seasonal variations showed the highest concentrations during winter, decreasing during warmer seasons and registering the lowest value during summer. Moreover, AR fall concentrations were lower than spring levels due to the particular meteorological conditions during this period. According to T/B ratio and the meteorological analysis, AR levels were under the influence of vehicular sources.

Vehicular traffic was the most important source of $PM_{2.5}$ as shown by the main components (C-rich particles and metals) identified in the particulate by physico-chemical characterization. Moreover X-ray microanalysis data focused out a coating of alkaline metal sulphates on the carbonaceous particle surfaces, due to the catalytic action of particles themselves. However, it is necessary to carry out further studies in this site on ozone, nitrogen oxides, carbon monoxide and sulphur dioxide analysis in order to better understand the processes of transformation that undergo the carbonaceous particles in the atmosphere.

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WHY MANUFACTURERS OF ELECTRICAL AND ELECTRONIC EQUIPMENT (EEE) CREATE PRODUCER RESPONSIBILITY ORGANIZATIONS (PROS) TO COMPLY WITH THE WEEE DIRECTIVE? THE CASE OF ERP ITALIA SRL WITH FOCUS ON COSTS

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Abstract

This paper investigates the role of collective organizations created by producers to comply with the WEEE Directive. There are limited case studies on these producer responsibility organizations (PROs) despite the crucial role that they play in Extended Producer Responsibility (EPR) schemes. An important aspect in order to evaluate the efficiency of these compliance schemes is the analysis of their internal costs including transaction costs. First of all, this research provides an understanding of the Italian WEEE system for households WEEE. Then, it focuses on one compliance organization and how it deals with physical, informative and financial responsibility that are different aspects of the EPR principle. We provide evidence on the costs incurred by the compliance organizations. We briefly describe the transaction costs involved in operating a collective PRO in comparison to individual scheme. We investigate the issue with the "ERP ITALIA S.R.L." case study. This is one of the producer responsibility organisations (PROs) operating in Italy and the only pan-European compliance scheme. This will allow future comparative studies with the other branches of ERP across Europe.

Key words: compliance organization, Extended Producer Responsibility, e-waste, PRO, WEEE

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1. Introduction

Extended Producer Responsibility (EPR) is a policy principle which is the basis of the European legislation regulating packaging, end-of-life vehicles, batteries and waste of electrical and electronic equipment (WEEE). The WEEE Directive is the result of a long developing process started in April 1998 as a part of the shift in the European environmental legislation from process to product (Castell et al., 2004). Eventually, the first issue of the Directive was published in January 2003 and it was recast in 2012. After more than 10 years, several scholars advocate that a great amount of work on the topic is still needed. We can assert that the green design goal and waste prevention have not proven to deliver what expected. If the design for recyclability in plastic products has been somehow introduced (Corabieru et al., 2014) this is not always the case for electric and electronic products (Atasu and Van Wassenhove, 2012; Castell et al., 2004; Gottberg et al., 2006; Khetriwal et al., 2009; Rotter, 2011; Yu et al., 2008).

The "public good" aspect of recyclability prevents the incentive for the producer to design devices easy to recycle (Palmer and Walls, 1999). Moreover, EEE producers argue that it is difficult to design recyclable products when their lifespan is long and the recycling technology is unknown (Wagner, 2009). Therefore, several scholars share the idea that the drive for eco-design is effective only if producers are responsible for their own end-of-life products. This is also defined as individual producer responsibility (Castell et al., 2004; Lifset et al., 2013). However, this solution would carry important transaction costs. The view that the green design is a missing achievement is shared by several authors (Lifset et al., 2013; Mayers et al., 2011, Mayers and Butler, 2013; Özdemir et al., 2012; Smith in OECD, 2005; Toffel, 2003; Webster and Mitra, 2007). On the other hand, the shifting of responsibility for recycling targets on producers facilitated recycling in all European countries (Massarutto, 2007). Moreover, the WEEE collected in Europe has been recycled at rates between 80% and 95% (Rotter, 2011).

Finally, the overall efficiency of the solutions adopted within the EPR scheme is still an open question (Lifset et al., 2013; Mayers, 2007; Massarutto, 2007, 2014; Palmer and Walls, 1999). Any form of intervention by government or non-government to address market failure must be efficient i.e. the benefits must be greater than the costs. It is widely recognized that PROs are one of the key players of the network design of EPR. However, their role is still controversial (Lifset et al., 2013; Mayers, 2007; Massarutto, 2007; Palmer and Walls, 1999). First, there is no clear agreement on the outcome they could reach (Massarutto, 2007; Mayers, 2007). Second, previous research on detailed operations of PROs is quite limited (Lifset et al., 2013; Mayers and and Butler, 2013). We follow this call for a more fine-grained understanding on the efficiency of the solutions adopted within EPR schemes and for empirical research on compliance organisations (Atasu and Van Wassenhove, 2012; Khetriwal et al., 2009; Mayers and Butler, 2013; Walls, 2011). We focus in this paper on a producer responsibility organization (PRO), its responsibilities as well as its efficiency issues.

According to Mayers (2007) in Europe there were 10,000 producers and more than 80,000 European municipal authorities at the time when the author wrote the article. A new subject (PRO) was created in order to deal with the potential complexity of the numerous entities in the field. In fact, as early as 2007, in Europe there were 130 PROs established to deal with WEEE. On this basis, this research has three main objectives. First it explains how the Italian WEEE system for households works. Then it investigates the critical aspects of one producer responsibility organization operating in Italy: ERP ITALIA S.R.L. This is performed analyzing the physical responsibility, the economic/financial responsibility and the informative responsibility. Finally, it underlines the internal costs and transaction costs involved in operating a PRO using the ERP case study. The paper is organized as follows. After this introduction, we provide a theoretical background followed, in section three, by the method that was used. In this section we briefly present the case study and the data collection method. The results and discussion part contains the analysis of ERP case study divided in the physical responsibility, informative responsibility and economic/financial responsibility. The conclusion section provides an overview of the results as well as it limitation and the need for future studies.

2. Theoretical background

According to Goulder and Parry (2008) the inability of the market to address externalities from pollution is the market failure that seems more central to environmental issues. Coase (1960) within the New Institutional Economics considers externalities a problem of insufficient defined property rights. The theory of New Institutional Economics (NIE) asserts that the change of property rights could force actors to internalize externalities (Demsetz, 1967).

There are several environmental policies that address the externality issue. One of these is the Extended Producer Responsibility principle, a general concept that gradually replaced the product take-back approach (Walls, 2011). The WEEE Directive includes the EPR principle. The European directive changed the property rights among actors by shifting of responsibility toward producers and away from municipalities. According to Buitelaar and Needham (2007), property rights are rules and the rules are institutions. When the property rights are changed to achieve certain results, these are purposeful institutional changes. Property rights and transaction costs are fundamentally interlinked, and they can be considered as two sides of the same coin (Allen, 1991). In his definition property rights are the capability to exercise a choice over a good or service while the transaction costs are the costs to establish and maintain such property rights.

Changing property rights and appointing producers responsible for the end of life products have created several positive aspects. Massarutto, (2014) points out that the implementation of the EPR principle managed to collect and allocate financial resources necessary to fuel the waste management system for WEEE. One interesting question is why producers have created collective systems to comply with the directive. According to Fleckinger and Glachant (2010) producers created associations because bearing the responsibility may be very costly for individual producers. In fact, according to Sachs (2006), individual schemes are affected by substantial transaction costs.

On this basis, it is quite natural to investigate the PRO approach to ERP requirements in terms of responsibilities, production and transaction costs. However, empirical measurement of transaction costs is problematic (Musole, 2009). In fact, according to Buckley and Chapman (1997) it is difficult to measure and assess transaction costs as the most important of them are the avoided costs that would have existed in situations that did not happen. In this respect, producers could choose between manage their responsibilities individually or by creating organizations.

In general terms, the management of take-back schemes can be carried out by third party organization (TPO) also known as "compliance schemes" (Gregory et al., 2009). The StEP report presents two different approaches to TPOs: own-branded TPOs and non-own-branded TPOs. The solution adopted in most cases (like in Italy) by producers is the second approach, where the compliance schemes collect and treat a share of e-waste arising in the country regardless of their brand. As reported before, according to Atasu and Van Wassenhove (2012), there are no individual producer operated systems in Europe because they may not be cost effective.

The few cases of producers taking care of their own-branded waste products (or individual producer responsibility) are developed only in the business to business (B2B) sector. Regarding the individual producer responsibility in the B2C (business to consumer) sector, there are limited cases such as HP and DELL Computer who encourage the take-back of their products (Van Rossem et al., 2006). However, this solution applies only to a portion of their products and therefore these producers also adhere to a PRO to fulfill their obligations.

To summarize, WEEE PROs are a central as well as controversial players in the EPR scheme. Nevertheless, they have been studied and compared only in few works. In this current paper we analyze one of the operating collection systems and we give some evidence of the structure of the WEEE system in Italy. We draw attention on how it fulfils its responsibilities, it internal costs including a description of transaction costs in comparison to a potential individual solution. We present how the ERP ITALIA S.R.L. complies with the economic responsibility, physical responsibility and informative responsibility as described by Linqhqvist (1992, 1998). Furthermore, we analyze how ERP ITALIA compliance scheme charges its consortium's member.

3. Method

3.1. Case study presentation

The ERP S.R.L. company is part of a broader organization named ERP (European Recycling Platform) established in 2002 by four producers of EEE. It developed the idea of setting the first pan-European compliance scheme in response to the European Union's groundbreaking directive to promote e-waste collection and recycling (Shao, 2009). ERP works in 16 states and has 2403 members in the world. So far, it has collected 2 million tons of e-waste (ERP, 2013). ERP ITALIA S.R.L. was established in 2006 and has one shareholder i.e. ERP SAS France. Also, ERP ITALIA S.R.L has four "founding members" who make up the board in charge of the decisions; 35 "European members" and 2300 "local members" and it employs 12 people. In 2012, ERP ITALIA S.R.L. collected 12.63% of national e-waste.

The goals set at heart of the new organization in 2002 were (ERP ITALIA S.R.L. – corporate profile, March 2013): to stimulate market forces and competition; to achieve scale economies to ensure competition and efficiency in recycling; to keep low overheads; to reduce market price for the highest quality available on the market and to support IPR (Individual Producer Responsibility).

ERP ITALIA S.R.L. operates in Italy where a national clearing house (CdC RAEE) was created in accordance to the Italian regulation. It is owned by the 17 Italian WEEE PROs. In 2012 ERP owned 1/9 of the national clearing house. The primary role of the CdC RAEE is to ensure the same market conditions to all members. It defines annually the market share of each producer and it determines which collection sites are assigned to each PRO, on the basis of an algorithm. The Italian branch of ERP has never been analyzed while the UK branch has recently been studied (Butler, 2009; Lee and Shao, 2009; Mayers, 2007; Mayers and Butler, 2013).

3.2. Data collection

In this section we present the case study of ERP ITALIA S.R.L. Following the idea that one of the major strengths of case study is the opportunity to use different sources of evidence (Yin, 2003), our study is based on qualitative and quantitative primary and secondary data. We used a wide range of sources: reports, studies, company presentations, on line publications, company web site, brochures, as well as balance sheets (including "explanation notes"). We accessed the national clearing house data to have useful information on the compliance system. We also analyzed the research papers on the corporate headquarters and on the English branch of ERP. Furthermore, a semi-structured interview was utilized in the meeting in order to gain a deep knowledge and to attain specific details. The content of the interview was disclosed to the company before the meeting. One semi-structured long interview was held at the company premises in July 2013 and it involved two key employees: the head of operations and the head of marketing. The draft document of this paper was submitted for checks and approval to the financial officer of ERP. Inputs, clarifications and corrections were used to review and improve the paper. Additionally, we carried out several interviews to different players of the system. The first and most important one, was a long interview with the head of operations of the national clearing house. Four additional interviews were carried out: two with different recyclers of WEEE, one with an Italian municipality and the last one with the regional director of ERP UK. All of these meeting were executed at their premises and were very important to understand the Italian WEEE system where ERP is included as well as underline the key differences with the British WEEE system. Data triangulation was used to address the potential problem of construct validity (Yin, 2003). The Italian regulation that implements the WEEE Directive was also studied (Decree n. 151/2005 and following application decrees) in order to frame the case study.

4. Results and discussion

The case study is presented in accordance with the theoretical approach of EPR carried out by Lindhqvist (1992 and 1998) which distinguishes different forms of responsibility: physical responsibility, economic responsibility and informative responsibility. The physical responsibility characterizes the systems when the producers have to deal with the physical management of the end-of-life products.

The economic responsibility means that the manufacturers bear the full or partial cost for the collection, recycling or disposal of the product manufactured. The informative responsibility requires producer to supply information on the environmental property of the products. In the next section we present ERP case study within the Italian system for WEEE. We distinguish the physical responsibility, the financial/economic responsibility and the informative responsibility of the compliance organization.

4.1. Physical responsibility

In Italy producers can fulfill their physical obligations (collection, treatment and recovery) either individually or joining a collection system according to the national regulation that implement the WEEE directive (Decree no. 151/2005). The solution adopted by all Italian producers is to join a PRO. More precisely, all the 17 existing PROs are collective organizations. ERP ITALIA S.R.L is one of these. In Italy the national clearing house (CdC RAEE) is established by law together with other institutes that manage the system (Ministerial decree n. 185/2007). Each collection system has to register to the CdC RAEE and its main task is to ensure uniform and homogeneous conditions to the collective systems. Having a national clearing house reduces transaction costs related to support and administer the program as well as it reduces costs for the monitoring operations. CdC RAEE determines the market share of each collective system which is proportionate to the amount of EEE put on the market in the previous year by the producers associated to that specific PRO.

Compliance organizations have to collect e-waste from the assigned collection points. These municipal and the retailers collection points contact the national clearing house when the quantity of WEEE collected needs to be picked up by the compliance organizations. The national clearing house assigns the collection sites in the national territory to the compliance organizations based on a complex algorithm, which incorporates several variables. The variables taken in consideration are: the quantity of WEEE collected in each collection point, the physical allocation of the collection point, the ease to reach the collection point and so on. Compensations on quantities collected are made the year after by reassigning the collecting points to the producers. In this way there are not fee compensations between producers. Therefore, ERP ITALIA S.R.L states that PROs do not compete on e-waste collection, since the collection activity is decided by CdC RAEE but they compete on the services provided to the customers.

Transaction costs related to research and information gathering are reduced during the collection phase. This is quite different from the situation in the UK, for example, where ERP- UK (like the other British PROs) has to sign agreements with a sufficient number of collection points in order to reach the amount of e-waste collected that fulfil the responsibility of the members of the system (Mayer et al., 2013). In this respect, for producers enrolled in Italian collective PROs, transaction costs related to e-waste procurement is significantly reduced thanks to the role played by the national clearing house. Moreover, if we consider that an individual responsibility organization should collect and treat a share of its own e-waste by setting a separate collection and treatment route, this would create considerable transaction costs such as research costs, information gathering costs; contracting costs; monitoring/detection costs and prosecution/inducement/conflict resolution costs.

In Italy there are two different types of collection points: retailers collection points ("Luoghi di raggruppamento – LdR") and municipal collection points ("centri di raccolta – CdR" or "ecopiazzole comunali"). By law CdR must accept the e-waste from the local LdR. However, if the LdR is too big for the local CdR then PRO collects e-waste directly from the retailer collection point and sent to the treatment facility. The compliance organizations through the CdC RAEE recognize incentives to the collection sites which reach some defined threshold. These compensation fees are regulated by deals signed by CdC RAEE, the national association of municipalities and the retailer organization.

Producers do not have property rights on e-waste, nor PRO. The property of the e-waste belongs to the CdR or LdR when is discharged by end users and it is then owned by recyclers when it reaches their premises. PROs don't have the property on e-waste: they offer a service to pass them from the collection points to the recycler points. When the CdR or LdR collect enough e-waste, they contact the CDC RAEE. Then CDC RAEE contacts the collection scheme that has in charge that specific collection point. In this way, possible changes due to the reassignment of collection point to another PRO do not create a disservice to third parties. Typical transaction costs due to research and information gathering are reduced. CDC RAEE established a "maximum time of intervention" i.e. the maximum time from the moment in which the subscriber (either CdR or LdR) requires the intervention and the moment in which the PRO withdraws the WEEE from the collection point. In 2012 ERP ITALIA S.R.L reached on average 98.38% of the target. Then each PRO establishes a deal with transporters and recyclers to perform the operations. ERP ITALIA S.R.L has few contracts with companies that transport and recycle the e-waste. These agreements reduce transaction costs if compared to an individual producer organization which has to find, collect and treat its own products. Several transaction costs are reduces such as research and information gathering costs, contracting costs; monitoring/detection costs and prosecution/inducement conflict resolution costs. On the other hand, compliance organizations can provide a stable flow of e-waste to the contractors (logistic and treatment operators) with contractual conditions fixed for few years. This situation reduces the problem of hold-up especially for the recyclers and it allows long term investments.

The recyclers have to be accredited as enterprises of the treatment of WEEE by the CdC RAEE in accordance with its technical specification. The accreditation is based on a specific audit conducted by third-party certifiers which are selected and approved by the CdC RAEE. In 2013 (CdC RAEE web site) there are 113 waste treatment plants. Each of them is accredited for one or more of the five groups of WEEE (R1-R5 following in the Italian legislation). According to the data provided by ERP ITALIA S.R.L, the recycling performance (including energy recovery) reached 90% in 2012.

4.2. Financial/economic responsibility

Producers are responsible for financing of collection, treatment, recovery and environmentally sound disposal of WEEE. As for the physical responsibility, the legislation allows to fulfil this obligation either individually or by joining a collective scheme (WEEE Directive). The Italian regulation (Decree no 151/2005) concedes the same options to producers. ERP founders claim that they contributed in changing the paradigm in European e-waste recycling by breaking with the monopolistic mentality and introducing competition among PROs (Shao, 2009). This allowed ERP to reduce average take-back costs significantly (Atasu and Van Wassenhove, 2012). According to Mayers and Butler (2013), EPR was founded by producers in order to have more control and lower costs in the delivery of take-back services for WEEE. In order to investigate the reduction of average take-back costs and therefore the improved efficiency, we analyze the internal costs of the PRO. We assess the cost structure of ERP ITALIA S.R.L. in the last three year (2010-2012) (Table 1). Following the Remedia's scheme (2012), we classify the costs in the following categories: treatment costs, logistic costs, performance bonuses (provided to collection points), communication costs and structure costs (including national clearing house).

The break-down information on treatment and logistic costs in 2010 and 2012 have been provided directly from the ERP. Total treatment and logistic costs decreased over time for two main reasons: the company became more efficient and the value of the metal recovered from e-waste increased. More specifically, in 2012, ERP managed to reduce these costs thanks to the new business model that allows ERP to select contractors in the market instead of having one single dealer as in year 2010. In fact, while up to the first part of 2011, the general contractor was in charge of the selection of suppliers and the pick-up activities, from the second part of 2011 ERP internalized these activities with an appropriate internal structure. This new business model explains the increase of the structural costs and, more important, it clarifies the decrease in the cost per ton of e-waste managed by the consortium.

On the other hand, the cost allocation under collective systems is a crucial aspect of EPR design (Atasu and Van Wassenhove, 2012; Fleckinger and Glachant, 2010; Lifset et al., 2013). It can influence its efficiency as well as the incentives to waste prevention. Therefore, we analyze in detail how this compliance scheme works out the cost allocation among its members.

According to Forslind (2009), the EPR program can be implemented with two different financial schemes: "pay-as-you-go system" (PAYG) or "insurance system".

Table 1. Cost classification for ERP ITALIA S.R.L. during years 2010, 2011 and 2012

	YEAR 2012	***%***	***PER TON***	***YEAR 2011***	***%***	***PER TON***	***YEAR 2010***	***%***	***PER TON***
Treatment costs	€ 1,887,389	23.59	€ 62.76	€ 3,158,423	26.79	€ 85.42	€ 3,241,142	30.98	€96.77
Logistic costs	€ 3,505,152	43.81	€ 116.55	€ 5,865,642	49.76	€158.64	€6,019,265	57.53	€179.72
Performance bonuses	€860,421	10.76	€28.61	€ 1,052,545	8.93	€ 28.47	€799,386	7.64	€23.87
Communication costs	€56,987	0.71	1.89	€ 0	0	€ 0	€0	0	0
Structure costs	€1,690,087	21.13	56.20	€ 1,712,107	14.52	€ 46.30	€ 402,493	3.85	12.02
Total costs	€8,000,036	100	€266.02	€ 11,788,717	100	€ 318.83	€10,462,286	100	€ 312.38

Structure costs= tot WEEE production costs – (treatment costs + logistic costs + performance bonuses + communication costs). 2010: 33,492,450 kg collected by ERP; 13.65% ERP share of national collection rate; 2011: 36,975,227 kg collected by ERP; 14.22% ERP share of national collection rate; 2012: 30.073.569 kg collected by ERP; 12.63% ERP share of national collection rate

The PAYG is based on the costs incurred when the products reach their End-of-Life. With the insurance system, producers pay one contribution per product sold (Put on Market - PoM) and this will cover the costs of the end-of-life management when the product is dismissed.

ERP ITALIA charges the operation costs to its members according to one of the following option: the "collected and treated" (same as PAYG system) and PoM tariff (same as the insurance system). ERP promotes the first option. According to the managers of ERP ITALIA S.R.L., the costs paid by their members are as low as possible and they charge producers only the actual costs. These costs are classified by ERP ITALIA S.R.L. in: 1) membership fee (i.e. general costs); 2) registration fee (i.e. cost for the local government); 3) operation costs (i.e. compliance costs). There are two options for the "membership fee": "local membership" and "European membership". On one hand, the "local membership" is defined in each Member State and in Italy it is about €200 for customers that have to treat up to 5 tons of EEE. For the customers that have more than 5 tons of EEE, the membership fee is proportionate to the quantity of EEE put on the market (PoM). This fee covers the functionality and fixed costs. On the other hand, the "European membership" works in the same way but the agreement covers at least three European Countries.

Moreover, the "Registration fee" is used to register the producer to the national system. In Italy for example these fees include: €16 for the stamp duty; € 168 for the government and revenue agency tax; €30 for the Chamber of Commerce. The "operation costs" i.e. the compliance costs can be computed in two ways: a) PoM put on market and b) collected and treated. The PoM tariff is set either by units or by kg of product put on the market. The "collected and treated option", charges the costumers for what it is really collected that year and it is computed by multiplying the quantity times the unit costs. The advantage of PoM is that the customer pays a predefined amount of money. The disadvantage of such system is that members have to pay in advance.

The problem for the compliance scheme using this system is to fix the appropriate fee which covers all the costs without accumulating financial reserves. Of course, the compliance solution in place of many single producers solutions reduces the transactions costs related to research and information gathering; support and administration of the ongoing program; contracting; monitoring/detection and prosecution/inducement/ conflict resolution. ERP ITALIA S.R.L. prefers to charge members according to the "collected and treated" way. In order to compute the "collected and treated" tariff, ERP ITALIA S.R.L. multiplies the PoM tariff (fee per ton) by the expected rate of return. The PoM tariff is a fixed tariff computed per ton per each of the five WEEE groups (R1-R5). The expected rate of return is: tons of WEEE collected in year t+1 divided by tons of EEE sold in year t. Example tons of EEE sold in 2012 = 10,000; tons of WEEE collected in 2013 = 12,500; expected rate of return 125%. Then ERP ITALIA S.R.L. shares the costs between producers based on their market share of the previous year. For ERP ITALIA S.R.L. this is the correct application of art 10 and 11 of DM 151/2005 as producers pay in function of their market share of the year before. ERP ITALIA S.R.L. points out the problem of setting the right tariff and gets the financial sheet balance. This was especially difficult when the systems were set up. According to ERP ITALIA S.R.L., the tariffs applied to its members are the lowest possible and there are no reserves set aside.

It is very important to point out that these two ways that PRP uses to compute the fee and charge the consortium's members do not include any incentive to eco-design. Design incentives come from the fees differentiation paid for EoL management (Sander, 2007). ERP ITALIA S.R.L. does not apply any individual producer responsibility as there is any cost sharing system based on the actual cost contribution of the EoL product.

In fact, the ERP and other major EE producers say that in order to invest in product recoverability producers need control over final treatment of their products. For Özdemir et al. (2012) collective responsibility does not give any incentive to producers for product recoverability improvement. This vision is supported by other studies (Castell et al., 2004; Mayers et al., 2011; Mayers and Butler, 2013; Smith in OECD, 2005; Webster and Mitra, 2007). Nowadays, individual operating systems can be very expensive and brand sorting activities too costly.

4.3. Informative responsibility

When responsibilities and costs are shifted to collective actors like PROs, which are easier to control, the incentive to comply is strengthened (Massarutto, 2014) and transaction costs are reduced. As reported by Atasu and Van Wassenhove, (2012) regulators need to take into account costs of monitoring and controlling take-back systems. In this respect, the Italian law delegated this duty to the CdC Raee that must collect and process the information provided by the 17 PROs. This reduces the transaction costs, if we compare a solution that involves a myriad of individual PROs established by individual producers. It reduces research and information gathering; lobbying and public participation costs; support and administration of the ongoing program; monitoring/detection.

CdC RAEE has a national call centre where municipal and retailer collection points can submit requests for waste collection and citizens can address general information. In this way any change in the allocation of collection point to a PRO does not create disservices to the users. This reduces transaction costs for the actors involved such as research and information gathering costs. On the other hand, the national clearing house gets information and controls the system as well as provides equal possibilities to all parties involved. As reported before, producers pay a fee to the chamber of commerce which keeps the public registers of producers (www.registroaee.it). Each producer and PRO has to enroll in this public register. Moreover, producers have several declarations to fulfill such as PoM (quantity of EEE put on market) during the previous year, by the 30th of May; the quantity of e-waste collected by PRO on behalf of its members and the percentage of e-waste recovered (using a form called MUD "single model statement"). Usually ERP is also in charge of declaring the PoM on behalf of its members and it provides additional service. In this way ERP can also check the volumes of the PoM by its members reducing the monitoring/detection cost. In case of differences in volumes, ERP can conduct an audit to the producer.

ERP ITALIA S.R.L. declares a complexity of documentation required by the Italian central government. Moreover, the requirements are different in each member state. A statement by the European commission acknowledges that improvements under the Directive are necessary in order to harmonize the national registration and reporting requirements. Member States' registers for producers of EEE will be integrated more closely. Moreover, the Commission will adopt a harmonized format to be used for the supply of information. Consequently, administrative burdens are expected to decrease (European Commission, 2012).

5. Conclusions

After 10 years from the WEEE Directive publication it is widely recognized that PROs (producer responsibility organizations) play a central role in EPR schemes. Despite this fact, empirical investigations on EPR implementation and on compliance scheme solutions are still limited. This fact has raised several calls to investigate these aspects. This paper provides an overview of the Italian WEEE system for households. It then studies one of the compliance organizations with attention on how it complies with the physical responsibility, economic/financial responsibility and informative responsibility.

The paper provides evidence of the costs incurred by the collective system including the transaction costs. The research also explains how the operations of the ERP ITALY srl are carried out as the previous research on this aspect is limited. Indeed, PROs play a pivotal role in the implementation of EPR scheme as they represent an important interface to organize the financial transactions, collection activities, and communications among governments, producers, waste companies, retailers, and municipal authorities. Furthermore, this centralized organization offers long term agreements, a more stable market, a reduced hold-up risk. Finally, it encourages specific investments in the recycling industry as well as it counterbalances its market power. Such centralization of activities coordinated by a collective system reduces transaction costs if compared to a multitude of individual producer organizations. The results show that, as pointed out by the previous literature, producers create these organizations because they reduce transaction costs if compared to individual compliance organizations. Furthermore, this paper discloses how compliance organizations, such as ERP, allocate costs among its members.

The research demonstrates the composition of internal costs of ERP S.R.L. ITALIA over time. In this respect, the paper fills a gap in the literature as only important but few case studies on WEEE collective systems are carry out so far. The paper has some limitations. First of all, we investigated only one compliance organization and its internal costs over a limited period of time. Second, the analysis of the revenues aspects of the collective system would have provided a better understanding of the scheme. Future research is needed in order to provide insight of the functioning of other PROs in Italy and in other member states. Additional investigation on other collective systems will allow interesting comparisons on the adopted solutions. Research on best practices solutions for the WEEE system would be also interesting for the business sector.

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A HYDROMETALLURGICAL PROCESS FOR RECOVERING RARE EARTHS AND METALS FROM SPENT FLUORESCENT LAMPS

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Abstract

The recovery of raw materials from waste represents a sustainable growth opportunity for those countries with limited mineral resources availability. A case study for an integrated approach to recover raw materials from spent fluorescent lamps is presented, with the aim of improving the current treatments which are only able to recover the glass fraction. In particular a hydrometallurgical process was developed to obtain valuable metals such antimony, copper, and rare earths (yttrium and europium). Grinded powders were leached with several inorganic acids, then antimony and copper were recovered by electrodeposition; Y and Eu were finally precipitated as oxalates. The precipitate was dissolved and the rare earths were separated by solvent extraction. This approach, based on the holistic view of all elements contained in an End–of–Life complex product, ensures both environmental and economic sustainability since it allows waste reduction and materials recovery.

Key words: fluorescent lamps, hydrometallurgy, rare earths, WEEE

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1. Introduction

The availability of raw materials (not-energetic and not coming from agricultural activities) for European industry is becoming problematic as shown in a recent report published by the European Commission (European Commission, 2014) and reported in Fig. 1. Great relevance was given to Rare earth elements (REEs), due to their economic importance and very high supply risk, becoming increasingly important in the transition to a green economy. In the next future demand for some of the rare earths is, in fact, expected to exceed supply. The substitution is the object of ongoing research, but REEs replacement by more common metals is still far from solution, due to their specific properties.

Many authors studied recovery of valuable materials from WEEE (Waste Electrical and Electronic Equipment) (Kumar et al., 2014). Also rare earths are potentially recoverable from WEEE, but their recycling rates are still low (below 1%) (Graedel et al., 2011a, 2011b; Reck and Graedel, 2012), due to technological difficulties, low toxicities of the REEs, and, until recently, low prices and lack of incentives. Unfortunately, the REEs are often minor components of complex materials in consumer goods (Schüler et al., 2011), but they are still essential in a lot of complex products, i.e. permanent magnets, due to special electronic, magnetic, optical, and catalytic properties, but also in tyre industry (i.e. neodymium based catalyst for cis-1,4-polybutadiene synthesis). Their low content makes the recovery process often unsustainable, especially with focused-strategy only aimed at REEs recovering and considering the rest of materials as a waste. The current treatment technologies are only focused on glass recovery (Andreola et al., 2010; Taurino et al., 2012).

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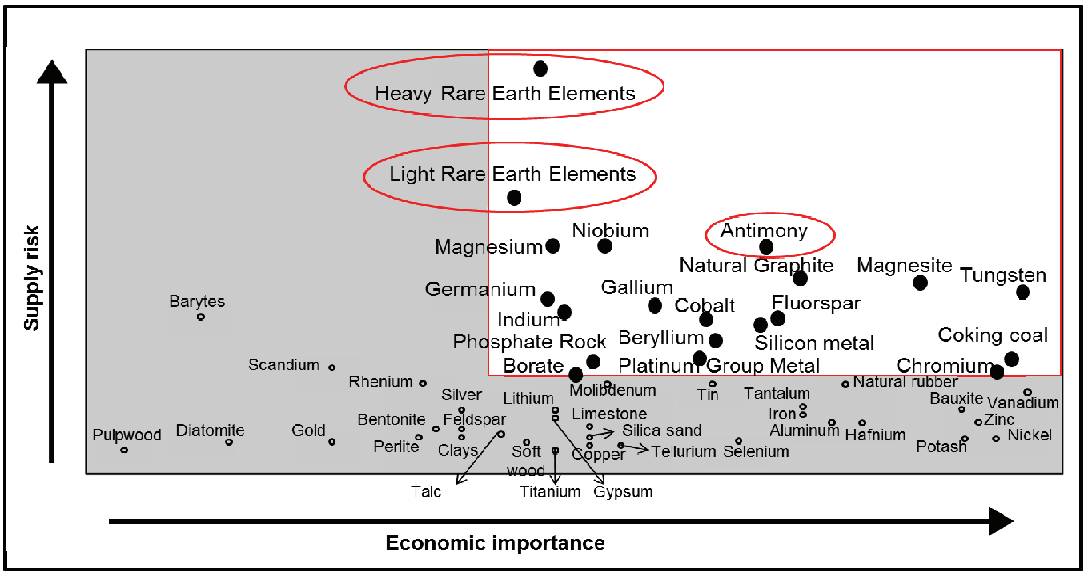


Fig. 1. Critical raw materials stated by the European Commission (May 2014)

In this work a product-centric approach is presented, aimed at recovering all the valuable components contained in an End-of-Life (EoL) product, i.e. REEs and other valuable metals.

A fluorescent lamp (Tan et al., 2014) is a sealed tube under vacuum conditions and works by exciting gaseous vapour, usually mercury, with electricity. Its inner surface is coated by a fluorescent film. In Fig. 2 a scheme of the fluorescent lamp is given.

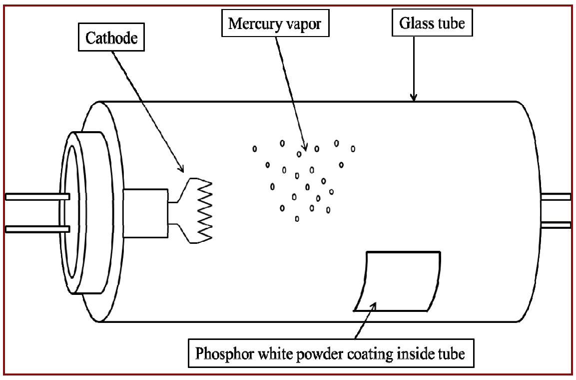


Fig. 2. Fluorescent lamp scheme

2. Experimental

2.1. Materials

Grinded powder without mercury was supplied by a recycling WEEE.

All solutions were prepared with analytical grade reagents and deionized water. The acids, standards and salts were purchased from Sigma Aldrich, the acidic organophosphorous extractant PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) was supplied from Daihachi, Chemical Industry co.

Metal ions concentration was determined by Microwave Plasma – Atomic Emission Spectrometer (4100 MP-AES, Agilent Technologies). Powder composition was determined by X-ray fluorescence spectrometer (Spectro X-LAB 2000 spectrometer).

The electrolysis device was supplied by Bicasa (mod. BE-47D, cathode surface: 55 cm^2).

2.2. Methods

2.2.1. Leaching

Samples were manually homogenized using a mortar. A 50 mL glass beaker was used for all the leaching experiments. Sample weight was fixed at 2.0 g; leaching was conducted at 25°C and under continuous agitation by a magnetic stirrer for 24 h. Leaching tests using different mineral acids at different concentrations and with a solid/liquid (S/L) ratio equal to 1/10 were carried out. The following conditions were evaluated: 15M, 7.5M and 1.5M HNO_3; 12M, 6M and 1.2M HCl; 1.8M and 9M H_2SO_4. After the leaching, the solid residue was separated from the leachate by a centrifuge, washed by distilled water and dried to assess the mass balance.

2.2.2. Electrodeposition

Electrodeposition of antimony on net platinum cathode at constant current intensity of 1A with magnetic stirring was performed, (t=2.5 h, T= 25°C). Metal ions in the liquid phase were then analyzed to check the process efficiency which was calculated according to Eq. (1), where C(fin) is the concentration after the treatment and C(0) is the initial one.

$$E\% = \frac{C(fin)}{C(0)} \times 100 \qquad (1)$$

After the electrodeposition process, the cathode, coated by an antimony black layer, was washed, dried and weighed in order to verify the mass balance. Finally this layer was dissolved in HNO_3 to characterize the solution by MP-AES. In Fig. 3, the electrodeposition cathode is shown.

Fig. 3. Black layer of antimony on net platinum cathode

2.2.3. Precipitation and solvent extraction

After antimony electrodeposition, the solution was partially evaporated to increase yttrium and europium concentration, then a 1M $H_2C_2O_4$ solution was added in order to precipitate Y and Eu as oxalates. The RE oxalates were separated by filtration and treated with $KMnO_4$ 0.1N in acidic medium (HCl, pH 0.5-1) to oxidize the oxalates and completely remove them from the solution; this was done in order to avoid a calcination process that involves energy consumption to produce a mixed RE oxide and a further acidic dissolution step. The pH was raised to 2.0 by NH_4OH, then samples were filtered to separate manganese oxide.

Solvent extraction tests were carried out in order to selectively separate yttrium and europium from the leachate obtained as above described: preliminary extraction tests on simulated hydrochloric solutions were performed to find the optimal conditions for yttrium and europium extraction. 0.01M Y and Eu solutions were treated with 0.05M and 0.1M PC-88A in kerosene (aqueous phase/organic phase ratio (A/O): 1/1), then shaken for 1 h in stoppered glass tube at room temperature and allowed to settle for at least 30 min. Organic phase was stripped with HCl 2M with organic/aqueous volume ratio 1:1. Extraction efficiency was calculated according to Eq. (2), where *C(eq)* is the equilibrium ion concentration in the aqueous phase and C(0) is the initial one.

$$E\% = \frac{C(eq) - C(0)}{C(0)} \times 100 \qquad (2)$$

All tests were repeated on four samples; the error percentage was <5%.

3. Results and discussion

3.1. Characterization of spent fluorescent lamp powder

The metal content of spent fluorescent lamp powder is reported in Table 1.

Table 1. Spent fluorescent lamp chemical characterization by XRF analysis

Element	*Mass of powder g/kg*	*Element*	*Mass of powder g/kg*
Glass	820.0	Sb	1.4
Ca	135.1	Eu	1.2
Y	10.8	La	0.8
Ba	7.7	Tb	0.7
Pb	7.5	Ce	0.5
Al	6.3	Cu	0.4
Fe	2.7	Zn	0.2
Sr	2.6	Cd	<0.1
Mn	2.2	Ni	<0.1

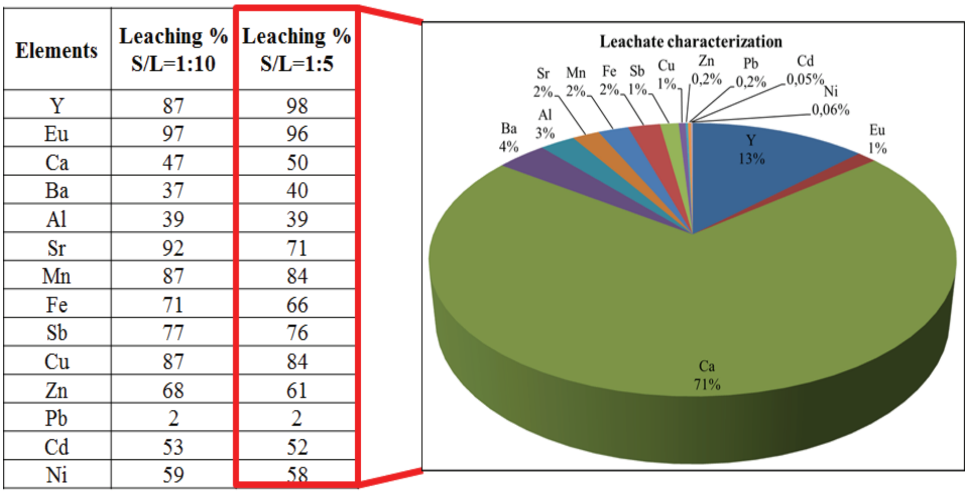
3.2. Leaching

In Table 2 the results of the leaching tests are reported: the best leaching acid is HCl 6M, since it allows the highest recovery rates for the elements of interest. Lead is not leached out, suggesting that this element is not present into the coating but in the glass. It can be observed that Eu leaching efficiency is higher than Y: this different chemical behavior might be due to the fact that Eu is present not only as trivalent europium mixed with Y oxide (Y_2O_3:Eu^{3+}) but also in divalent form as an activator, while Y is only present as oxide (Tan et al., 2014). Furthermore a solid/liquid ratio equal 1:5 was tested on HCl 6M in order to verify the possibility of using a lower amount of reagents. In Fig. 4, a comparison between the leaching efficiency with S/L=1:10 and S/L=1:5 was reported, with leachate characterization obtained using S/L 1:5. The experimental data showed that S/L 1:5 allows comparable efficiency, then better conditions are obtained by leaching the powder by HCl 6M at S/L 1:5.

The pie chart on the right side of Fig. 4 shows the relative amount of each element compared to the total cation content in the leachate using S/L 1:5: it can be observed that calcium, probably present in the coating as $Ca_5(PO_4)_3(OH)$, $Ca_5(PO_4)_2(SiO_4)_6$, $Ca_4P_2O_9$ (De Michelis et al., 2011), represents a large part of the ions in solution despite its dissolution yield is only 50%. It was observed that lanthanum, terbium and cerium were not leached: these results agree with those found by Eduafo (2013). Moreover, Eduafo (2013) and Wang et al. (2011), testing different leaching agents, found hydrochloric acid as the best leaching agent, with europium and yttrium extraction efficiency equal to 90%.

Table 2. Spent fluorescent lamps leaching tests (t=24 h, S/L= 1:10, T=25°C; – Best leaching acid marked; data reported with reference to XRF value)

Metal	***Leaching tests***							
	HCl 1.2 M	***HCl 6 M***	***HCl 12 M***	***HNO_3 1.5 M***	***HNO_3 7.5 M***	***HNO_3 15 M***	***H_2SO_4 1.8 M***	***H_2SO_4 9 M***
	Leaching %							
Y	75.9	87.4	82.6	71.4	72.4	73.0	62.8	53.5
Eu	92.7	97.0	98.3	92.1	90.7	96.9	54.1	42.2
Ca	47.1	47.0	46.4	38.9	46.4	47.7	15.0	15.1
Ba	34.0	36.9	37.6	30.6	35.8	38.4	<0.01	<0.01
Al	38.8	39.4	38.9	32.1	39.7	38.3	27.2	27.0
Sr	94.4	91.6	84.9	72.2	84.5	82.0	17.1	14.3
Mn	94.8	87.3	86.5	70.3	80.9	80.1	64.4	62.5
Fe	68.3	70.7	68.4	49.8	59.4	60.5	56.4	56.9
Sb	71.5	76.9	72.9	51.1	60.4	68.4	68.2	56.4
Cu	85.8	87.2	92.2	66.9	84.0	86.9	67.6	68.1
Zn	61.1	68.2	73.3	47.7	56.8	64.5	27.0	34.7
Pb	2.1	2.2	2.1	1.8	1.9	2.0	<0.01	<0.01
Cd	56.9	53.1	51.8	38.0	48.8	49.0	<0.01	<0.01
Ni	64.0	59.1	62.8	48.6	57.1	57.4	<0.01	<0.01



Elements	Leaching % S/L=1:10	Leaching % S/L=1:5
Y	87	98
Eu	97	96
Ca	47	50
Ba	37	40
Al	39	39
Sr	92	71
Mn	87	84
Fe	71	66
Sb	77	76
Cu	87	84
Zn	68	61
Pb	2	2
Cd	53	52
Ni	59	58

Fig. 4. HCl 6N leaching efficiency: comparison between S/L=1:10 and S/L=1:5, leachate elements being compared to the total cation content

3.3. Antimony recovery

Electrolytic recovery of antimony from waste fluorescent lamp is not currently available in literature, but it can be found in metallurgic processes (Gupta and Krishnamurthy, 2004; Madkour and Salem, 1996) or in copper electrorefining (Ando and Tsuchida, 1997; Lin et al., 1994; Koparal et al., 2004).

The electrodeposition process only occurs for copper and antimony that are reduced in two distinct layers because of their Standard Electrode Potential:

$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^0 = +0.34V$

$SbCl_4^- + 3e^- \rightarrow Sb + 4Cl^- \qquad E^0 = +0.17V$

The layering of metals was verified by leaching them through HNO_3: copper was detected as an inner layer, while antimony was the outer: each layer was of purity grade > 98%. Sb and Cu are obtained respectively with a recovery rate of 81% and 31%. It is possible to separately reduce the two elements using two different cathodes and controlling the electrode potential.

3.4. Rare earths recovery

3.4.1. Precipitation

The rare earths oxalates Kps is equal to 5.1×10^{-30} and 4.2×10^{-32} for yttrium and europium respectively (Chung et al., 1998). Oxalic acid is commonly used as a precipitating agent for rare earths in fluorescent lamps, cathode ray tubes and spent nickel-metal hydride batteries (De Michelis et al., 2011; Innocenzi et al., 2013; Tan et al., 2014; Wang et al., 2011; Zhang et al., 1999).

Precipitation efficiency as oxalate was determined according to Eq. (1), showing 90% for Y and 80% for Eu (Fig. 5).

3.4.2. Solvent extraction

In this work PC-88A has been used as an extractant because of its selectivity for rare earths: it is a liquid cation-exchanger, the extracted metal being exchanged by the hydrogen ion of its hydroxyl group (Fernandes et al., 2013; Fontana et al., 2009; Wu et al., 2009).

The PC-88A solvent extraction efficiency, calculated according to Eq. (2), is shown in Fig. 6. It can be observed that the best condition to extract Y from Eu is pHeq = 1.45. At this pH rare earths extraction by PC-88A from solutions containing oxalates as anions is not feasible, due to their precipitation. For this reason oxalate oxidation is required, as explained in 2.2.3. The other elements in solution, except for iron, in these conditions are not extracted.

Using a 0.1M PC-88A solution, an organic phase loaded by 91.6 % of Y and 8.5 % of Eu is obtained, the aqueous phase still containing 76.8 % of the initial Eu. Stripping treatment with 2M HCl is not selective since both Y and Eu are stripped with an efficiency of 95.0%: taking into account the efficiency of the previous processes, the stripping liquor solution contains 76.7% and 6.2% respectively of the initial Y and Eu.

By increasing the number of extraction/stripping steps, it is possible to achieve further purification.

3.5. Proposed flowsheet

According to the experimental data, a block diagram for the hydrometallurgical recovery of Sb, Y, Eu and glass is shown in Fig. 7, starting from an electromagnetic separation of the crushed lamps to recover ferrous and ferromagnetic materials.

After a milling process, the powder is leached by HCl, then is filtrated to recover the glass; the leaching liquor is treated by electrodeposition to recover metallic Sb and Cu. Rare earths are precipitated as oxalates from the residue solution and extracted by PC-88A after oxidizing reaction by $KMnO_4$.

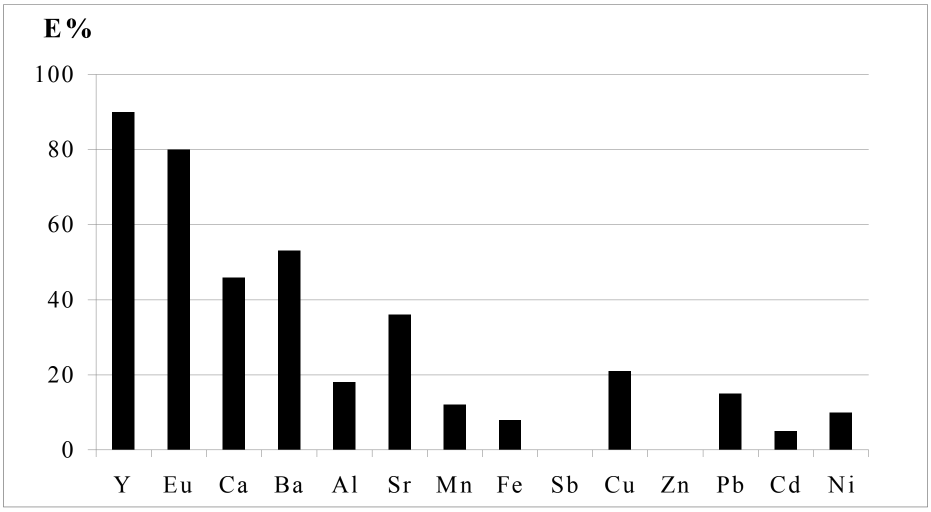


Fig. 5. Element precipitation efficiency by oxalic acid at 25°C

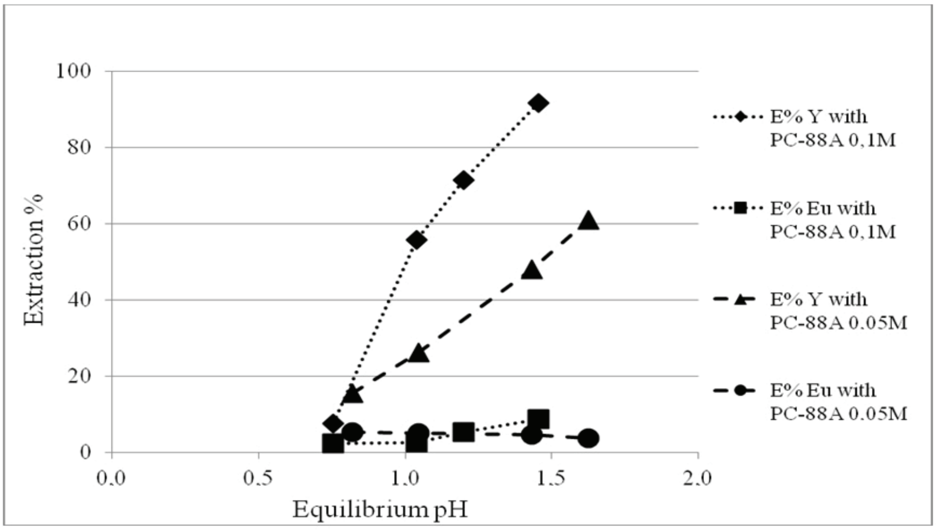


Fig. 6. Solvent extraction efficiency ([Y] = 0.01M; [Eu]=0.01M; extractant: PC-88A)

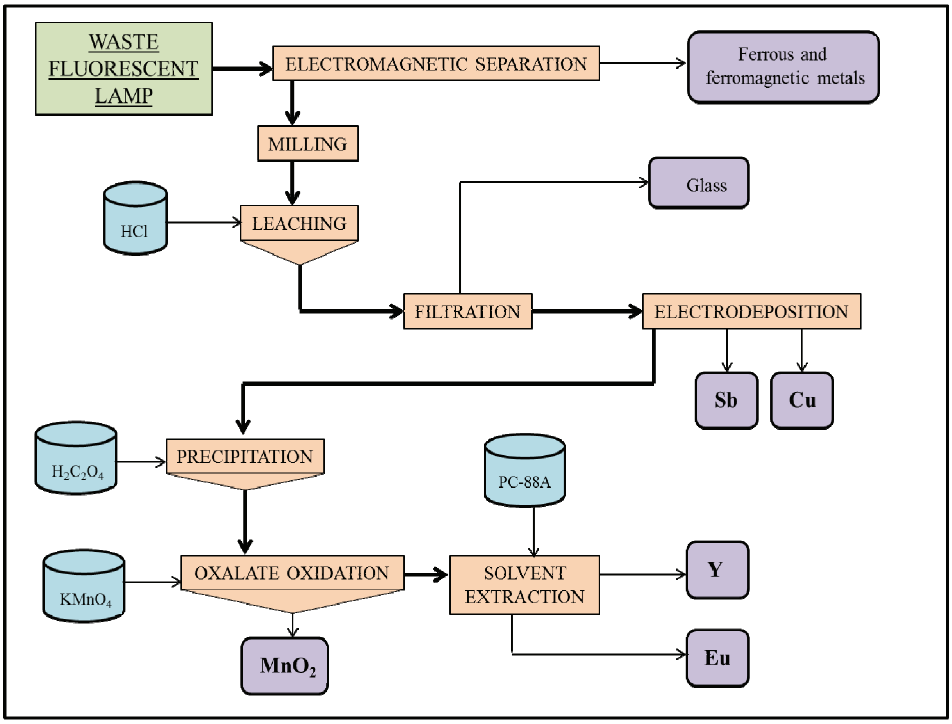


Fig. 7. Proposed process flowsheet

4. Conclusions

A hydrometallurgical process was developed to recover valuable metals from spent fluorescent lamps. Antimony is recovered by electrodeposition with recovery rates up to 80% and purity grade up to 98%; yttrium and europium, after a precipitation process as oxalates and a subsequent dissolution step by $KMnO_4$, are recovered and separated by one stage solvent extraction/stripping process with an efficiency up to 78% for yttrium and 76% for europium. The product-centric approach focuses environmental sustainability by reducing the waste, and supports economic sustainability of strategic materials process recovery.

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EFFICIENT RECOVERY OF NON-SHREDDED TIRES VIA PYROLYSIS IN AN INNOVATIVE PILOT PLANT

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Abstract

New and end of life tires have been pyrolyzed in an innovative pilot plant that processes whole tires, thus saving the energy costs of shredding while allowing energy and materials recovery. Furthermore, the presence of a hydraulic guard guarantees high process safety. Several tests at different temperatures have been performed and the collected solid, liquid and gaseous products have been quantified and characterized. The influence of the maximum process temperature on yields and chemical-physical properties of pyrolysis products has also been evaluated. In view of a plant scale-up to continuous mode, we have studied the influence of variation of tires type and wear and the effects of the final products aging.

Key words: char, pyrolysis, pyrolysis gas, tires recovery, waste management.

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1. Introduction

The management of end-of-life tires (ELTs) is becoming increasingly worrying owing to a number of concurrent factors such as the massive, and still growing, amount of exhausted tires involved (estimated annual world production of tires at 23.3 million tonnes (ETRma, 2014)), the almost complete lack of biodegradability of such a kind of waste and the tendency to get rid of them wildly, with no concern at all of their destiny.

Presently, several disposal techniques are available though they all present some drawbacks: for example re-treading can only be performed on undamaged carcasses while material recovery involves necessarily some preliminary shredding with a significant energy consumption. On the other hand, energy recovery, which mainly consists of incineration treatments of mixed waste streams, leads to the loss of valuable materials and the production of polluting emissions, thus imposing expensive gas cleaning devices (Kandasamy et al., 2015).

Pyrolysis is a process in which organic materials are thermally decomposed into simpler components when subjected to high heat, under an oxygen free atmosphere (Fig. 1). The pyrolysis of ELTs involves the thermal cracking of the rubber and other ingredients generating a volatile fraction composed of condensable (pyrolysis oil) and non-condensable (pyrolysis gas) fractions (Quek and Balasubramanian, 2013). The solid residue consists of steel wires and char. Steel, char, oil and gas are all highly valuable products. Char is a carbonaceous residue with a Gross Calorific Value (GCV) of about 28.8 MJ/kg (de Marco Rodriguez et al., 2001) which makes it suitable as fuel. Moreover, some activation studies were conducted to increase its surface area and improve its attractiveness as carbon black or

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active carbon (Zabaniotou and Stavropoulos, 2003). Pyrolysis oil is a complex mixture of organic compounds with a high fraction of aromatics (Laresgoiti et al., 2000) which can be used either as a fuel or as chemical feedstock. Finally, pyrolysis gas is a combustible gas (GCV of about 68-84 MJ/m^3) composed of CH_4, aliphatic C_2-C_6 compounds, H_2, CO, CO_2 and H_2S which can fuel internal combustion engines to generate electricity and heat, thus reducing greenhouse gas emissions (de Marco Rodriguez et al., 2001).

Different technologies have been applied to tires pyrolysis: the process can be performed with or without a catalyst in order to maximize the yields of valuable volatile products (Williams and Brindle, 2003). A number of different reactors can be used, such as conical spouted bed reactor (Lopez et al., 2009), autoclave (de Marco Rodriguez et al., 2001; Laresgoiti et al., 2000), circulating fluid bed reactor (Dai et al., 2001), rotatory oven reactor (Acevedo et al., 2014a 2014b), fixed bed reactor (Aydin and Ilklic, 2012; Rofiqul Islam et al., 2008) and high vacuum process (Roy et al., 1999).

In this context, Curti S.p.A. has recently built an innovative static bed batch pilot reactor (Bortolani et al., 2014; Giorgini et al., 2015) that combines in one single process, the main advantages of different disposal techniques: in particular pyrolysis can be performed on whole tires to save the shredding costs while recovering energy and materials as previously discussed, and thanks to an innovative hydraulic guard, the plant guarantees a high process safety. The pilot plant has been used to pyrolyze new tires (NTs) and end-of-life tires (ELTs) at different temperatures, namely 400, 450, 500, 550 and 600°C in presence of steam due to water evaporation from the hydraulic guard.

The main objective of this research is to evaluate the influence of the maximum process temperature on yields and on chemical-physical properties of pyrolysis products. In addition, in view of a scale-up of the plant to continuous mode, we have studied the influence of the variation of the feedstock on the pyrolysis output and the effects of the final products aging.

2. Experimental

2.1. Pilot plant

A scheme of the pilot plant is shown in Fig. 2. The system is easily controllable and safe owing to a hydraulic seal that prevents air infiltration into the treatment chamber. The batch reactor has an internal volume of 5.5 m^3 and can treat up to 70 kilograms of tires. It is composed of two parts, the lower being a tank containing water, which acts as hydraulic guard, the upper a mobile bell whose lifting allows the sample insertion and the removal of the solid residue at the end of the process. The latter element is double walled hosting electric resistances with a total power of 21000 W.

The pyrolysis batches have been performed isothermally at different temperatures, namely 400, 450, 500, 550 and 600°C, as defined upon preliminary TGA investigation. All the gases generated in the process are conveyed outside the reactor and partially condensed in a water cooled coil (2). The obtained oil (and water) is collected through a demister, picked up at point B and subsequently characterized.

The uncondensed gas proceeds encountering a H_2S scrubber (3) and a fan (4), required to adjust the pressure of the gaseous stream. Along the line connecting the fan to the burners there is a bleed point for the gas analysis (C). Different indicators and monitoring points for the operating variables are distributed along the system and everything is supervised through a centralized electronic control panel.

In a typical run, tires are placed into the reactor. After closing the lid, the reaction chamber is initially flushed with nitrogen in order to remove air, then the system is heated at 8°C/min up to the set point, and kept at the desired temperature up to 150 min total residence time. During heating the water from the hydraulic guard facing the inner chamber evaporates, forming steam that adds up to the pyrolysis products flow, hence requiring a separation step of the vaporized water from the oily products in the demister.

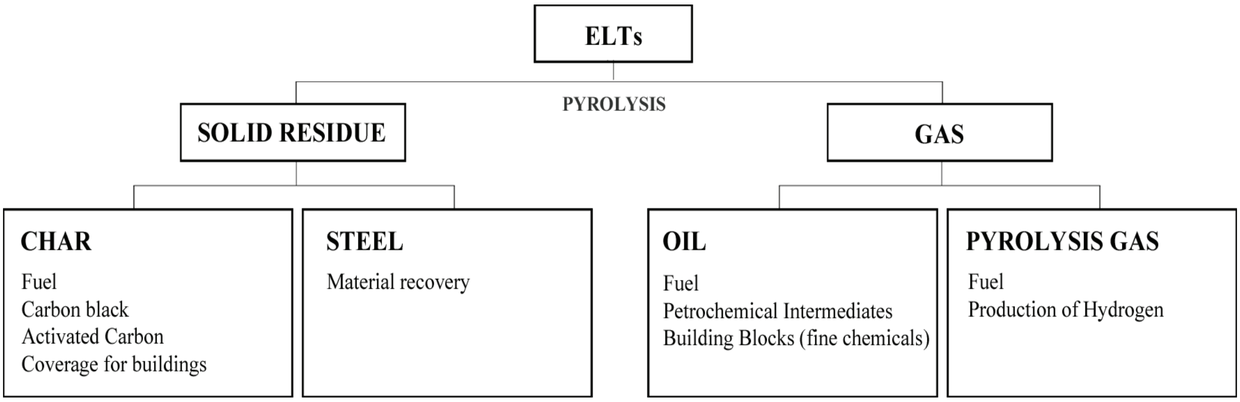

Fig. 1. Schematic plot of ELTs pyrolysis products evolution

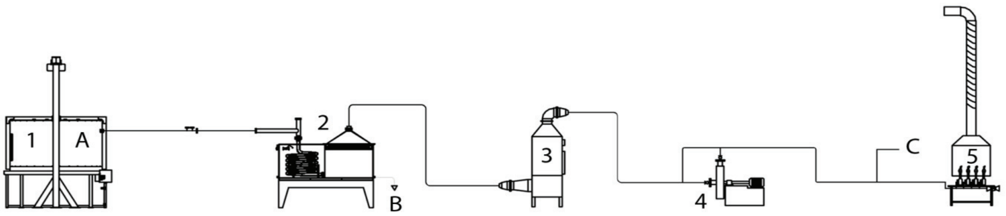

Fig. 2. Schematic layout of the experimental pyrolysis pilot plant: 1, pyrolysis chamber; 2, demister; 3, H_2S scrubber; 4, fan; 5, burners; A, collection point of solid residue; B, collection point of pyrolysis oil; C, bleed point of gas

After 150 min the resistances are switched off and the reactor begins to cool down; this is considered the end-point of the test. When the temperature goes down below 100°C, the upper bell of the reactor is opened for removal of the solid residue (char and steel) and the liquid (oil and water) is removed through the demister sampling point.

2.2. Feed materials

The tests with ELTs have been performed on tire sets in different state of wear and with a random mix of brands and models (the details are reported in Table 1 with respect to each run) while, for all the NT experiments, Lassa model Atracta has been used. For each set of tires, at least two tests have been carried out at each selected temperature with a 150 min overall residence time, while at 400°C tentative longer runs were also carried out. Several further tests have been carried out at 500°C that appears the optimal process temperature, sufficient to guarantee complete thermal degradation of whole tires, while leading to a considerable energy saving in terms of heating. The yields data of the pyrolysis products and composition of the gas have been averaged for analogous runs.

The different tires wear status implies the variation, from set to set, of the degradable/non-degradable components weight ratio. In particular, NTs are characterized by steel fraction in the 9-10wt% range while the ELTs are richer in steel ranging from 11 to 13wt%.

2.3. Analysis of the final products

At the end of each test, the pyrolysis solid and liquid products have been recovered, the char has been manually separated from the steel wires, then steel, oil, and char weighed. The gas fraction has been obtained by difference. The char produced through similar tests has been collected and then sampled and characterized to evaluate its possible use as fuel or as raw material. Ashes, water and volatile materials contents have been determined by TA instruments SDT Q600 according to the ASTM D 7582. The elemental composition CHN-O/S has been used to calculate the higher heating value (Gross Heating Value, GHV) and lower heating value (Net Heating Value, NHV). X-Ray Fluorescence spectra have been recorded on a PANalytical AxiosMAX Advanced XRF Spectrometer, equipped with a rhodium X-ray tube target, set to a power of 2.4 kW in order to quantify the sulfur and zinc contents and detect the presence of heavy metals. Finally, the determination of the total surface area has been carried out by nitrogen adsorption at −196°C using Carlo Erba SORPTY 1750 equipment which uses the simplified BET model.

The particular characteristic engineering plant involves co-condensation of oil and process water. For this reason, after draining the demister, the two fractions have been separated with a centrifuge operating at 4200 rpm for 6 minutes. The oil fraction has been characterized by GC-MS analysis using a Thermo FOCUS GC, coupled to a DSQ mass spectrometer as detector and equipped with a Supelco SPB™ fused silica capillary column. This analysis allows the identification of compounds in the lighter oil fraction. The dynamic viscosity has been determined at 25°C using a digital Brookfield viscometer – Model DV-II +, spindle "I" with a rotational speed of 100 rpm. The values have been compared with those obtained for a common commercial diesel fuel. To assess the effect of shelf life on the physical properties of the oil, the density and dynamic viscosity of some significant samples has been re-measured after 6 and 12 months. Simulated distillation using the thermogravimetric method (SimDis TGA) has been performed on oil samples of about 15 mg in platinum pans suitable for liquids (heating rate of 5°C/min from room temperature (RT) to 500°C in a 100 mL/min nitrogen flow).

The gaseous phase has been analyzed *in situ* with a Micro-Gas Chromatograph Agilent 490 Micro-GC placed on-line in the pilot plant so no active sampling is required. Two columns have been used for analysis: a Molsieve 5 Å (MS, 20 m) with molecular sieves made with zeolites as stationary phase and argon as carrier gas. The MS column has been held at 80°C throughout the experiment. This apparatus has been designed for separating H_2, O_2, N_2, CO and CH_4. The second column is a PoraPLOT U (PPU, 10 m) with divinylbenzene-ethylene glycol/dimethylacrylate as stationary phase and helium as carrier gas. The PPU column has been maintained at 90°C throughout the experiment. This apparatus has been designed to separate H_2S, CO_2, C_2H_4, C_2H_6 and hydrocarbons up to C_3, with the possibility of detecting even the C_4. The detector used by the device is a Thermal Conductivity Detector (TCD).

Table 1. List of experimental runs

Test Code	*T (°C)*	*Brand and model of tires*	*Number of tires*	*Weight (kg)*
NT400.01	400	Atracta 155/70R13 79T	2	12.92
NT400.02	400	Atracta 155/70R13 84T	3	18.75
ELT400.01	400	Driver couvier 185/65 R15 88H, Firestone Firehawk 185/65 R15 88H, Driver Couvier 185/65 R15 88H	1+1+1	19.69
ELT400.02	400	Dunlop Sport 205/55 R16 91V, Firestone Firehawk 185/65 R15 88H	1+2	19.12
NT450.01	450	Atracta 155/70R13 79T	2	12.96
NT450.02	450	Atracta 165/70R13 84T	3	20.91
ELT450.01	450	Dunlop Sport 205/55 R16 91V, Bridgestone turaz 195/55 R15 87 H, Firestone fire hawk Tz 88H	1+1+1	22.84
ELT450.02	450	Bridgestone turaz 195/55 R15 87 H, Michelin energy 175/65 R13 82T, Dunlop SP sport 205/60 R13 91H	1+1+1	18.94
NT500.01	500	Atracta 155/70R13 79T	2	12.24
NT500.02	500	Atracta 165/70R13 79T	2	12.32
NT500.03	500	Atracta 155/70R13 79T	2	12.65
NT500.04	500	Atracta 155/70R13 79T	2	12.71
NT500.05	500	Atracta 155/70R13 79T	2	12.82
NT500.06	500	Atracta 165/70R13 79T	2	12.82
NT500.07	500	Atracta 165/70R13 79T	2	12.89
NT500.08	500	Atracta 165/70R13 79T	2	12.95
NT500.09	500	Atracta 155/70R13 79T	2	12.96
NT500.10	500	Atracta 155/70R13 79T	2	13.02
NT500.11	500	Atracta 155/70R13 79T	2	13.16
NT500.12	500	Atracta 155/70R13 79T	2	13.77
ELT500.01	500	Matador Stella 195/65 R14 79T, Continental ContiWinterContact 205/55 R16 91H, Pirelli P3000 175/65 R15 84T	1+1+1	19.66
ELT500.02	500	Michelin Energy 165/70 R14 81T, Pirelli P7 205/55 R16 91V	1+2	20.53
ELT500.03	500	Michelin Energy 175/65 R13 82T, Pirelli P7 215/55R16 93V, Firestone CV 2000 195 R14C 102/110 N6 P.R.	1+1+1	22.4
ELT500.04	500	Miratta Lassa 175/70 R14 88H, Pirelli P6000 195/60 R15 88H, Toyo Proxer R32, 205/50 R17 89W	1+1+1	24.24
ELT500.05	500	Bridgestone Turanza ER 300 205/55 R16 91H, Dunlop SP sport 205/60 R13 91H	2+1	25.65
ELT500.06	500	Pirelli P7 205/55 R16 91V, Lassa Impetus revo 205/65 R16 99H, Michelin Primacy HP 225/55 R1797W	1+1+1	26.96
NT550.01	550	Atracta 165/70R13 79T	2	12.93
NT550.02	550	Atracta 175/70R13 84T	2	13.97
ELT550.01	550	Atracta 165/65R13 77T, Atracta 155/70R13 75T, Atracta 165/70R13 79T	1+1+1	19.37
ELT550.02	550	Pirelli P3000 175/65 R15 84T; Pirelli Pzero 205/50 ZR17 93W, Pirelli P3000 165/65 R13 77T	1+1+1	19.63
NT600.01	600	Atracta 155/65R13 73T	3	17.59
NT600.02	600	Atracta 175/70R13 84T	2	13.94
ELT600.01	600	Pirelli Pzero 205/50 ZR17 93W, Michelin Classic 185/75 R14 PR8	2+1	18.65
ELT600.02	600	Michelin Energy 185/60 R15 84H, Michelin Classic 185/75 R14 PR8	1+2	20.54

Quantification has been performed by comparison with a blend of gases of known composition. The calorific value of the gas (GCV) has been calculated, according to the UNI 7839, based on the obtained composition.

3. Results and discussion

3.1. Pyrolysis yields

The aim of this research is to study the influence of the maximum reached temperature and of the state of wear on tires pyrolysis products in presence of steam. Since the steel content in each set of tires is variable, as discussed in the Experimental, the products yields (Fig. 3) are net of steel. The obtained trends reported in Fig. 3 are similar for both tire series in the studied temperature range. It is worth noting that the highest carbonaceous residue (char) has been achieved in tests carried out at 400°C for both NT (49.6 wt%) and ELT (49.5 wt%). Such a behaviour suggests that at this temperature, even for protracted times, it is not possible to achieve a complete thermal degradation of the polymeric fraction. Furthermore, the composition of the pyrolyzed gaseous fraction is rich in light compounds (pyrolysis gas) due to the cracking of the long molecular chains (oil) which is favoured at long residence time. In other words, at 400°C, the low amount of degraded rubber forms heavy products and longer residence time involves additional molecular cracking (Leung et al., 2002). Between 450 and 600°C, the thermal degradation of tires increases, as demonstrated by the decrease of the char fraction that reaches a constant value around 40 wt%.

At these temperatures, the produced volatile fraction tends to spontaneously flow out the reaction dome, favoured also by the increase of the thermal expansion of the gases, thus cooling down and interrupting the subsequent cracking reactions that might occur at higher temperatures. This effect results in an important increase of the oil fraction between 400 and 450°C for both series (from 14.0 to 29.9 wt% for NT and from 12.1 to 26.0 wt% for ELT) and a slight decrease of the incondensable fraction. Between 450 and 600°C, a further slight enhancement of the oil fraction with a corresponding decrease of gas takes place. It is important to note that for both sets of experiments, between 500 and 550°C, the oil/gas weight ratio reaches the value of 1.

Many scientific investigations on pyrolysis of shredded tires are reported in the literature. In Table 2 we have collected the results of some of them, thus showing how different technologies (i.e. type of reactor) and process parameters (i.e. temperature, pressure, heating rate, residence time) can lead to very different products yields. The oil fraction, for example, covers an extremely wide range of percentage and its trend with the increase in temperature is not constant. In the tests carried out with experimental conditions similar to those presently reported, the oil yield has a stable/slow increasing trend with the increase in temperature (Aydin and Ilklic, 2012; Berrueco et al., 2005; Dai et al., 2001; de Marco Rodriguez et al., 2001; Fernandez et al., 2012; Laresgoiti et al., 2000). In these tests, the yield in gas, also at low temperatures, is noticeably higher than what reported by other authors (Table 2). In particular, pyrolysing non-shredded tires at 500°C, Roy et al. (1999) obtained a smaller amount of incondensable gas and a bigger oil fraction. Furthermore, according to Kaminsky and Mennerich (2001) that evaluated the effects of the presence of steam on the pyrolysis process of tires at 500°C in a fluidized bed reactor, the yield of pyrolysis products results not significantly influenced by this process parameter.

3.2. Char characterization

The solid residue is the product most influenced by the compositional variability of the processed tires, because in the char are concentrated, among others, sulfur and metals introduced as fillers and adjuvants in the process of vulcanization. The proximate and elemental analysis, conducted on char samples produced by pyrolysis at 500°C compared to previously reported data of char obtained in similar conditions, are reported in Table 3. Proximate analysis shows no significant differences between the char obtained by ELT and NT at the same temperature. The values obtained for moisture and ashes are in line with the values reported by other authors. The content of volatile compounds, which in literature covers a wider range, is similar to that reported by Diez et al. (2004).

Zinc is originally present in the rubber as vulcanization activator, as inorganic filler in replacing the silica and/or as resulting from the galvanizing of steel reinforcing mesh which produces the iron. This element has been found in the range 3.73-4.06 wt% similarly to the values reported by Helleur (4.2±0.3 wt%) and below those reported by Conesa (6.68 wt%). Silicon is more than five times lower than what reported in the literature (Conesa et al., 2004; Helleur et al., 2001). Heavy metals, such as nickel, vanadium, chromium, lead, detected in low concentrations in some reported testing (Galvagno et al., 2002), are not detectable in the obtained chars (<5 ppm).

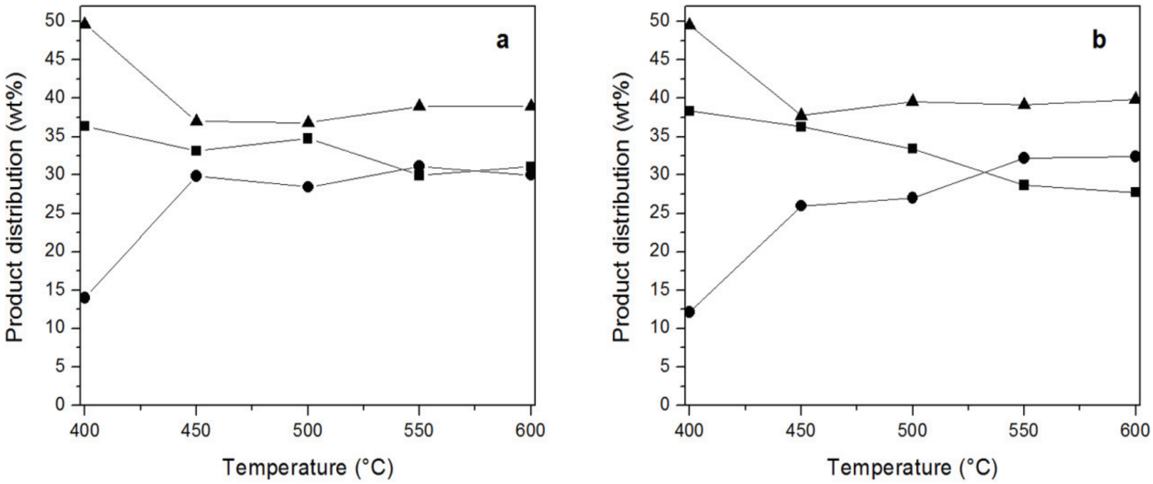

Fig. 3. Effect of temperature on the yield of the different pyrolysis products: a) NT and b) ELT: (▲) Solid residue; (■) Gas; (●) Oil

Table 2. Literature survey of results of the waste tires pyrolysis

Experimental system	***Reference***	***Process (°C)***	***Note***	***Yields (wt%)***		
				Char	***Oil***	***Gas***
Conical spouted bed reactor	Lopez et al. (2009)	425-600	feedstock size <1mm	34-36	64-56	2-8
Fluidized bed reactor	Dai et al. (2001)	360-810	feedstock size 0.32mm	40-30	50-30	10-40
	Kaminsky and Mennerich (2001)	500-600	feedstock size 1-2mm	30-40	65-51	5-9
		500	feedstock size 1-2mm presence of steam	31	65	3.5
Pyrocycling process	Roy et al. (1999)	500	under vacuum (7 kPa), whole tires, 10% steel	37	47	5
Fixed bed reactor	Aydin and Ilklic (2012)	400-700	shredder sample	62-41	31-40	7-19
	Choi et al. (2014)	500-800	feedstock size 1-2mm heating rate 10°C/min	37-37	38-30	23-30
Static-bed batch reactor	Cunliffe and Williams (1998)	450-600	feedstock size 4.5cm^3, including metallic and textile part	37-38	58-53	4-9
	Berrueco et al. (2005)	400-700	feedstock size 2cm, including metallic and textile part	64-51	30-43	2-4
Rotary kiln	Galvagno et al. (2002)	550-680	feedstock size <2cm	49-49	38-32	2-11
Horizontal oven	Fernandez et al. (2012)	400-900	feedstock size <2cm	68-38	31-57	1-5
Autoclave	de Marco Rodriguez et al. (2001)	300-700	feedstock size ≈3cm^2; heating rate 15°C/min	88-44	5-38	7-18
	Laresgoiti et al. (2000)	400-700	Radial portion (175g) heating rate 15°C/min	53-43	28-40	7-9

Table 3. Proximate average and elemental analysis of char produced at 500°C for NT and ELT compared with literature data

	NT	ELT	Conesa et al. (2004)	Helleur et al. (2001)	Galvagno et al. (2002)	Diez et al. (2005)	Diez et al. (2004)	
Process (°C)	500	500	450	550	550	550	450	550
Proximate analysis (wt%)								
Moisture	2.1	1.0	0.37		3.57	0.9-1.14	1.5	1
Volatile Matter	0.0	1.5	7.78		12.78	2.9-3.5	3.1	1.2
Ash	9.9	9.5	8.27	15.2±0.2	15.33	14.3-13.6	16.0	16.5
Char Composition (wt%)								
Zn	4.06	3.73	6.68	4.2±0.3				
S	2.51	2.67	1.9	2.0±0.1				
Mg	0.06	0.07	0.147	0.1±0.02				
Al	0.04	0.05	-	1.0±0.3				
Si	0.29	0.31	1.69	1.6±0.2				
K	0.12	0.08	0.0969	-				
Ca	0.18	0.16	0.127	-				
Ti	0.00	0.02	0.0171	1.3±0.2				
Fe	0.03	0.03	0.0393	0.3±0.1				

The specific surface area, the elemental analysis and the calorific values (Gil-Lalaguna et al., 2014), essential parameters for assessing the quality of the char, are reported in Table 4. In the solid samples produced by pyrolysis at 500°C 0.84 wt% (NTs) and 0.87 wt% (ELTs) sulfur content with respect to the total weight of the pyrolyzed tires is found. The sulfur content, reported as weight fraction of the char (2.51 wt% for NTs and 2.50 wt% for ELTs), is similar to the average values reported by analogous processes (Table 4).

The Gross Calorific Value (GHV) is over 32000 kJ/kg, higher than other char residues and this is mainly due to its higher hydrogen content. The specific surface area (SSA), about 63 m^2/g, is in line with literature data and could be increased considerably through specific activation processes to obtain active carbon (Zabaniotou and Stavropoilos, 2003).

3.3. Oil characterization

To evaluate the influence of the process parameters, the oils obtained from different pyrolysis tests have been analyzed in terms of both fuel characteristics and chemical composition. The influence of the pyrolysis temperature on the oil density and dynamic viscosity is reported in Fig. 4. The density values tend to slightly increase with increasing pyrolysis temperature and are quite narrowly distributed (0.93-0.97 kg/m^3), in line with the value (0.95 kg/m^3) reported in the literature (Lopez et al., 2009; Roy et al., 1999) and higher than those measured on a commercial diesel (Eni-Blue diesel+, 0.84 kg/m^3). The dynamic viscosity of the oils tends to decrease rapidly between 400 and 550°C (from 36.73 to 18.20 cPs) where it reaches its minimum. The viscosity of oils produced between 500 and 600°C is similar to the one of commercial diesel fuel. In order to evaluate the possible effects of the oils aging, the samples have been analyzed immediately after the process and after further 6 and 12 months (Fig. 4). The density and the viscosity of the oils do not show substantial variations with aging and with the wear status of the tires. These results are in good agreement with previous reports (Rofiqul Islam et al., 2008).

Elemental composition of the presently investigated samples is similar to that of previously reported pyrolytic oils (Table 5).

However, the determined sulfur content (about 1.0-1.1 wt%) is lower than that reported in the literature and it is interestingly close to the threshold for the potential marketing of this product as a low sulfur containing fuel.

From these data it is possible to calculate (Koo et al., 2014) the relative calorific values (around 10300 kcal/kg) which, as expected, are similar or slightly higher than what reported in the literature for similar processes.

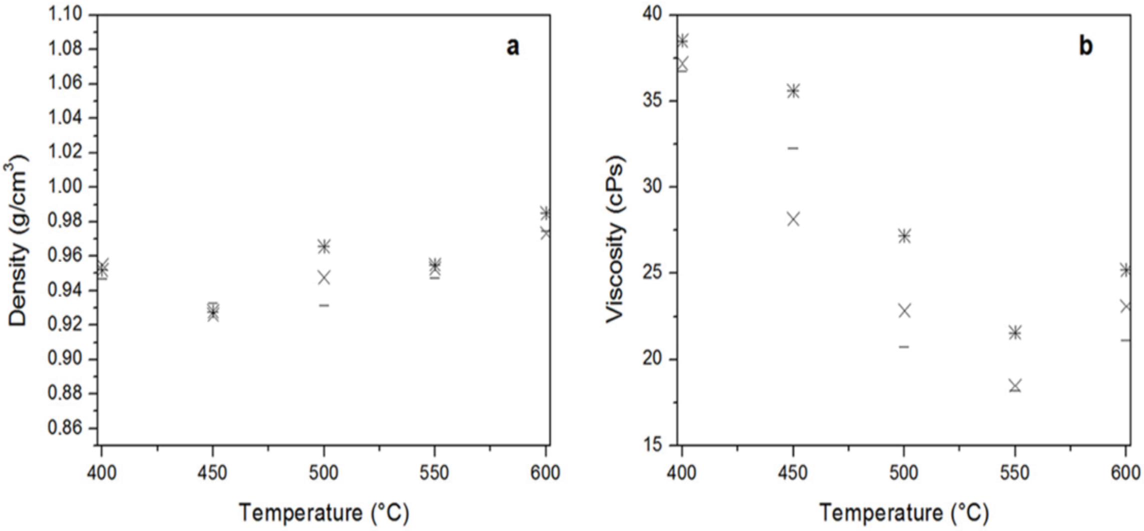

Fig. 4. Density (a) and dynamic viscosity (b) at 25°C of investigated pyrolysis oils at three different aging times: immediately after the process (-), at 6 (x) and 12 (*) months

Table 4. Specific surface area (SSA), CHN-O/S analysis and calorific values of the chars produced at 500°C compared with literature data

Sample	*Process (°C)*	*Elemental composition (wt%)*					*SSA (m^2/g)*	*GHV (kcal/kg)*	*NHV (kcal/kg)*
		C	*H*	*N*	*O*	*S*			
NT	500	86.40	3.10	0.30	4.43	2.51	63.1	7900	7800
ELT	500	85.50	3.30	0.40	4.90	2.50	63.7	7900	7700
Conesa et al. (2004)	450	88.19	0.60	0.10	-	1.90	93	-	7367
Lopez et al. (2009)	500	86.62	1.39	0.75	-	2.24	65.2	-	-
Diez et al. (2005)	550	95.9	0.5	0.2	<0.1	3.3	-	6831	-
de Marco Rodriguez et al. (2001)	500	83.5	0.6	0.3	1.1	2.4	-	6979	-
Galvagno et al. (2002)	550	85.31	1.77	0.34	-	2.13	-	7336	-
Ucar et al. (2005)	550	-	-	-	-	-	55.5	-	-

Table 5. CHN-O/S analysis and calorific values for the investigated oils compared with literature data

Sample	*Process (°C)*	*Elemental composition (wt%)*					*GHV (kcal/kg)*	*NHV (kcal/kg)*
		C	*H*	*N*	*O*	*S*		
NT	400	86.0	11.1	0.6	1.2	1.1	10300	9700
	450	85.9	11.2	0.5	1.4	1.0	10300	9700
	500	85.8	11.3	0.6	1.3	1.0	10300	9700
	550	85.7	11.3	0.6	1.4	1.0	10300	9700
	600	85.7	11.5	0.5	1.3	1.0	10400	9800
ELT	500	85.9	11.2	0.5	1.3	1.1	10300	9700
Diez et al. (2004)	450	78.2	10.0	0.4	-	1.4	9268	8696
Cunliffe and Williams (1998)	500	84.9	10.2	0.5	3.1	1.3	10071	-
de Marco Rodrigez et al. (2001)	500	85.6	10.1	0.4	-	1.4	10055	-
Ucar et al. (2005)	650	87.57	10.35	<1	-	1.35	9952	-

GC-MS allows identifying and quantifying the chemical composition of the lighter fractions of the oil. Significant amount of benzene, toluene, ethylbenzene, xylene and styrene derived by Styrene-Butadiene rubber component are produced (Table 6). These species, due to thermal decomposition of styrenic rubbers and to cyclization of olefin structures followed by dehydrogenation and Diels Alder reactions, tend to increase with the temperature process, as reported by other authors (Cunliffe and Williams, 1998; Lopez et al., 2009).

High concentration of these compounds suggests a potential recovery of high value products as chemicals: xylenes can be employed in the plastics industries; toluene in the production of pesticides, dyestuffs, surfactants and solvents; styrene is one of the most utilized building blocks in the production of polymeric materials. The increase in temperature causes the formation of lower molecular weight species. The sum of the identified $C_{\leq 12}$ fractions shows a considerable increase with temperature: at 400°C, only 3% of the oil is composed of light fraction while at 600°C this value rises up to 25%. Moreover, the analysis of the $C_{5\text{-}12}$ components shows that this is mainly made up of lighter compounds ($C_{<9}$). This trend can be attributed to the increase of thermal cracking due to the increasing temperature (Cunliffe and Williams, 1998; Lopez et al., 2009). For comparison, the same analysis has been carried out on the oil produced at 500°C by ELTs pyrolysis. The obtained data highlight that there are no significant differences with the NT 500 sample. Furthermore, the oil composition confirms the similarity found between the oil fractions for both density and viscosity and the limited aging changes, as confirmed by GC-MS analysis repeated on the same samples after 12 months.

In order to evaluate possible destinations for the pyrolysis oils, a simulated distillation using thermogravimetric method (SimDis TGA) in inert atmosphere has been performed. The obtained results are shown in Table 7 and Fig. 5. As reported in Fig. 5, the trend of the obtained curves is almost linear until the distilled masses reach 85–90 wt%. It is worth noting that oils produced at lower pyrolysis temperatures (400 and 450°C) show higher distillation temperature and dynamic viscosity, due to the greater content of heavier molecules.

Table 6. Yields (wt% on total oil) of the identified major compounds in C_5-C_{12} fraction oil

	NT					***ELT***
Process temperature (°C)	400	450	500	550	600	500
TOT C_5	0.05	0.05	0.02	0.03	0.02	0.04
Aliphatic acyclic hydrocarbons	0.05	0.04	0.02	0.02	0.02	0.03
3-methylthiophene	0.00	0.01	0.00	0.01	0.00	0.01
TOT C_6	0.04	0.24	2.16	1.98	2.16	1.00
Benzene	0.02	0.23	2.15	1.97	2.15	0.99
Phenol	0.02	0.01	0.01	0.01	0.01	0.01
TOT C_7	0.37	2.69	9.30	9.79	9.98	7.23
Substituted cyclopentenes	0.00	0.02	0.01	0.01	0.01	0.02
Benzothiazole	0.02	0.02	0.01	0.01	0.01	0.02
Methyl phenols	0.03	0.02	0.01	0.01	0.01	0.01
Toluene	0.32	2.63	9.27	9.76	9.95	7.18
TOT C_8	1.49	5.28	11.15	11.93	12.19	10.26
Ethylbenzene	0.56	2.06	2.70	3.67	3.00	2.70
p-xylene	0.72	2.56	6.67	6.50	7.20	6.33
Styrene	0.21	0.66	1.78	1.76	1.99	1.23
TOT C_9	0.22	0.21	0.21	0.22	0.21	0.21
Indene	0.01	0.00	0.03	0.02	0.03	0.01
Methylstyrenes	0.04	0.04	0.02	0.03	0.02	0.03
Substituted benzenes	0.17	0.17	0.16	0.17	0.16	0.17
TOT C_{10}	0.35	0.32	0.26	0.22	0.24	0.33
1,4-Dihydronaphthalene	0.02	0.01	0.04	0.03	0.03	0.02
D,L- Limonene	0.03	0.06	0.02	0.02	0.02	0.04
Naphtalene	0.03	0.01	0.05	0.03	0.06	0.01
Substituted benzenes	0.27	0.24	0.15	0.14	0.13	0.26
TOT C_{11}	0.11	0.05	0.08	0.09	0.09	0.08
Methyl dihydronaphtalenes	0.02	0.01	0.02	0.02	0.02	0.02
Methyl naphtalenes	0.05	0.02	0.04	0.04	0.05	0.03
Substituted indenes	0.04	0.02	0.02	0.03	0.02	0.03
TOT C_{12}	0.05	0.01	0.05	0.04	0.05	0.03
Substituted benzenes	0.05	0.01	0.05	0.04	0.05	0.03
$C_{>12}$ Others	0.03	0.09	0.01	0.01	0.01	0.01
$C\leq 12$ NOT ATTRIBUTED	0.36	0.37	0.14	0.17	0.19	0.24
TOTAL DETECTED	2.68	8.85	23.23	24.30	24.94	19.18

The increase of the pyrolysis temperature, instead, leads to a progressive lowering of distillation temperatures and viscosities, due to the presence of lighter compounds.

This fact is also detectable observing the distillate masses in typical temperature ranges for commercial petrol and diesel (de Marco Rodriguez et al., 2001), as reported in Table 8.The amount of distillate in the lowest temperature range (petrol, 70–210°C) increases with pyrolysis temperature process whereas for the highest temperature range (diesel, 150–370°C) the trend is opposite. These data demonstrate that the composition of the pyrolysis oils, in terms of distillable fractions, is intermediate between the composition of petrol and diesel, as also reported by Ucar et al. (2005). The pyrolysis oil produced at 500°C from ELTs is richer in light compounds and more similar to petrol than other reported oils obtained in similar conditions (Table 7).

3.4. Pyrolysis gas characterization

The gas mixture produced by pyrolysis of both NTs and ELTs samples has been analyzed online on the plant, in order to correlate the volatile composition with the applied pyrolysis conditions. A typical trend recorded during a run is shown in Fig. 6.

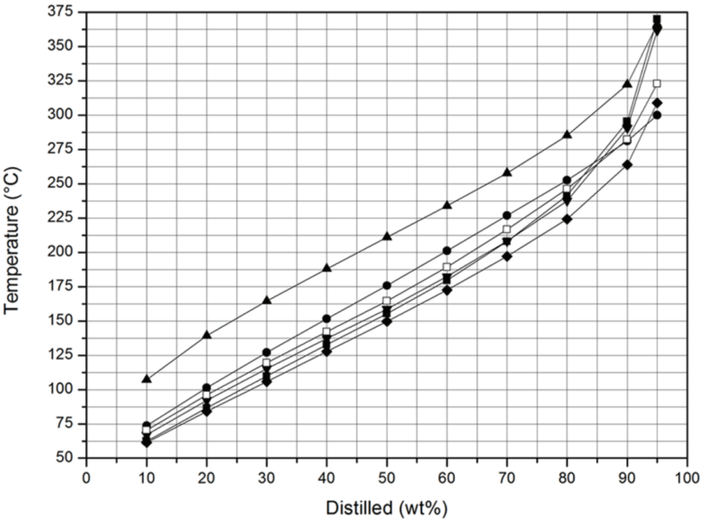

Fig. 5. Simulated distillation curves of pyrolytic oils obtained by means of SimDis TGA: (▲) NT, 400°C; (●) NT, 450°C; (■) NT, 500°C; (♦) NT, 550°C; (▼) NT, 600°C; (□) ELT, 500°C

Table 7. Distillation temperatures of investigated oils and other reported pyrolysis oils

	NT					ELT	Aydin and Ilklic (2012)	Ucar et al. (2005)	de Marco Rodriguez et al. (2001)
Process (°C)	400	450	500	550	600	500	Diesel Fuel	500	500
Distilled (wt%)	***Distillation temperature (°C)***								
10	109.1	81.0	62.5	60.5	67.22	65.6	175	150	114.5
20	141.3	110.2	87.5	83.3	93.3	91.4	185	177	168.8
30	166.0	135.7	110.8	104.9	116.7	114.8	195	185	198.2
40	189.1	159.4	133.9	126.9	138.9	137.8	-	-	249.3
50	211.8	182.6	156.6	148.9	160.8	160.3	214	234	296.1
60	234.0	206.4	181.1	171.5	184.9	184.7	-	-	333.8
70	257.1	230.7	210.0	196.3	212.3	211.8	250	293	359.8
80	283.2	257.0	244.9	224.1	245.6	240.8	-	-	373.9
90	319.0	288.4	303.9	265.4	306.7	276.4	310	359	386.4
95	371.4	310.6	392.2	312.6	405.9	309.6	334	402	388.7

Table 8. Distillate mass of investigated pyrolytic oils in the typical temperature ranges for diesel and petrol

	NT					ELT
Pyrolysis temperature (°C)	400	450	500	550	600	500
Temperature range (°C)	***Distillate (wt%)***					
70-210 (petrol)	46.6	54.1	57.2	61.1	58.3	57.8
150-370 (diesel)	71.7	62.8	47.2	46.6	49.0	52.0

The average compositions of the gas produced during the different pyrolytic experiments are reported in Table 9 and Fig. 7. The measured gases are H_2, CH_4, CO, CO_2, ethylene, ethane and H_2S. C_3 is the sum of propane and propylene while C_4 is the sum of 1-butene, n-butane, 1,3-butadiene and iso-butylene. The sum of other indeterminate incondensable species is labelled as "Others".

It is worth noting that gas produced by pyrolysis of NTs or ELTs at the same temperature are composed of comparable amounts of different species. By increasing the batch temperature, a decrease in concentration of heavier molecular weight compounds (C_3 and C_4) and a simultaneous increase of lighter species, in particular methane and hydrogen, are observed. The main compound, at process temperature ≤450°C, for both series, is the sum of the C_4 (between 27.2 and 39.2 mol%). Starting from 500°C the formation of hydrogen and methane increases, and at 600°C, the latter reaches almost 40 mol%. This trend, observed for both NTs and ELTs and reported also by other authors (Berrueco et al., 2005; de Marco Rodriguez et al., 2001), can be related to further cracking of evolved volatile matter at elevated temperatures. At the same time a reduction in CO_2 and CO content is registered (Fig. 7).

Kaminsky and Mennerich (2001) reported that the use of steam as fluidizing medium at 500°C did not significantly affect neither yield, nor the compositions of the reaction products. However, they reported that when the experiment is carried out in the presence of steam, there are high yields of CO_2 and CO which increase with the process temperatures, and lower yields of C_3 and C_4 compounds. Such a behavior has been attributed to the reaction with water.

In our case, the amount of carbon oxides decreases with the temperature, showing that in this experimental pilot batch pyrolyzer, the presence of steam at low temperature ≤ 600°C did not affect the composition of the pyrolysis gas. Thus the trend of production of H_2, CH_4 and hydrocarbons C_3-C_4 can be justified by the thermal cracking reactions only.

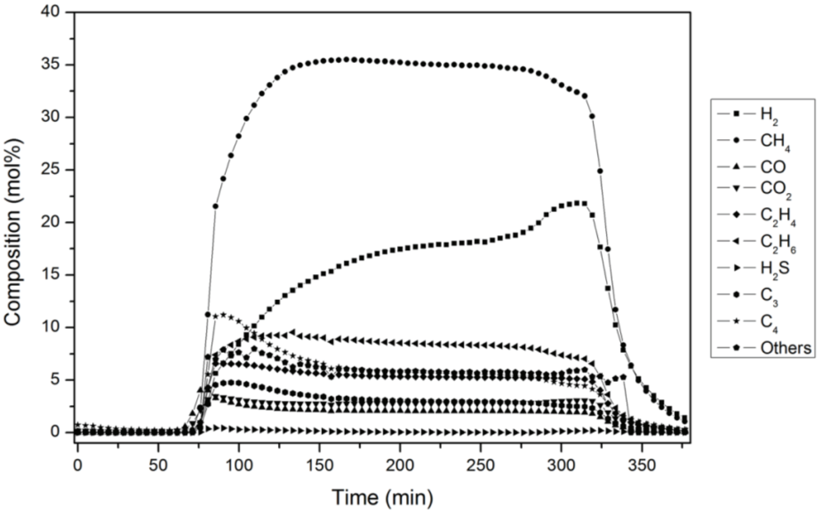

Fig. 6. Composition of the gas during a run, at 600°C with NT

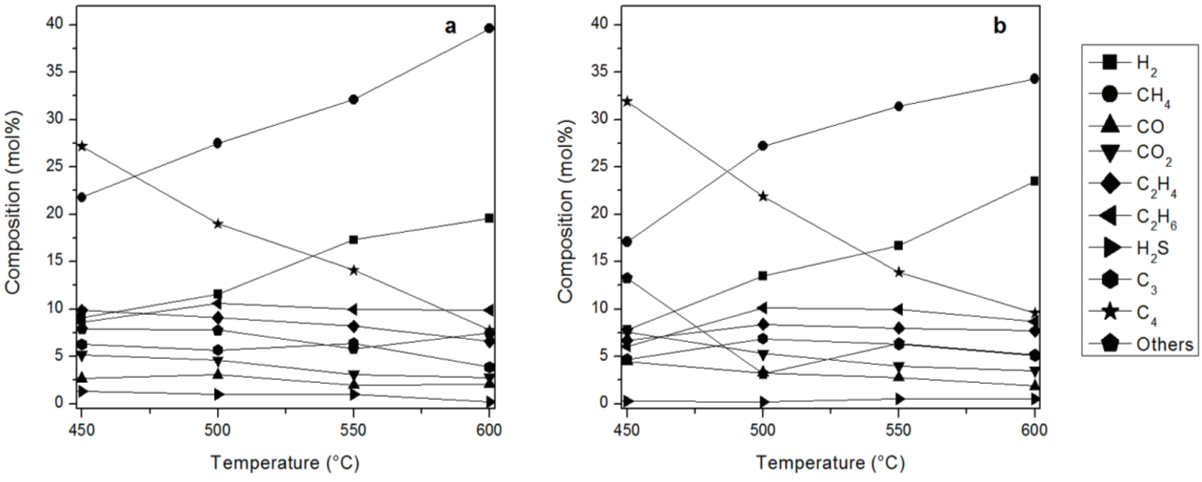

Fig. 7. Trend of the chemical species of the pyrolysis gas as a function of temperature: (a) NTs and (b) ELTs

Table 9. Chemical composition (mol %) and GCV (MJ/Nm^3) of the pyrolysis gas produced at different process temperatures

	NT					***ELT***				
	Process Temperature (°C)					***Process Temperature (°C)***				
	400	***450***	***500***	***550***	***600***	***400***	***450***	***500***	***550***	***600***
H_2	8.0	9.1	11.6	17.3	19.6	5.3	7.8	13.5	16.7	23.5
CH_4	20.3	21.8	27.5	32.1	39.6	17.0	17.1	27.2	31.4	34.3
CO	4.5	2.7	3.1	2.0	2.1	3.4	4.5	3.3	2.8	1.9
CO_2	5.8	5.2	4.6	3.1	2.8	6.0	7.6	5.3	4.0	3.5
C_2H_4	9.2	9.9	9.1	8.2	6.6	11.6	6.7	8.4	8.0	7.7
C_2H_6	6.6	8.6	10.6	10.0	9.9	5.9	6.1	10.1	10.0	8.7
H_2S	0.9	1.3	1.0	1.0	0.2	0.3	0.3	0.2	0.5	0.5
C_3	6.5	6.3	5.7	6.4	3.9	7.3	4.7	6.9	6.3	5.1
C_4	31.8	27.2	19.0	14.1	7.8	39.2	31.9	21.9	13.9	9.6
Others	6.4	7.9	7.8	5.8	7.5	4.0	13.3	3.2	6.4	5.2
GCV (MJ/Nm^3)	62.5	61.9	57.0	52.6	47.9	67.0	63.9	55.7	52.4	46.9

Finally, as reported in Table 9, the GCV values calculated according to UNI 7839, in the range 47-67 MJ/m^3, decrease with process temperature for both series. This trend is mainly due to the reduction of C_3 and C_4 molar fractions in the pyrolysis gas mixture caused by the increase of the process temperature. In agreement with the very similar compositions of gas obtained at the same temperature, the calorific values of the two series are also almost coincident. These values are intermediate between those previously reported: 75.3-84 MJ/m^3 (de Marco Rodriguez et al., 2001) and 47.7-39.6 MJ/m^3 (Diez et al., 2004).

4. Conclusions

New and end of life tires have been pyrolyzed in an innovative pilot plant able to process whole tires, saving the energy costs of shredding, and allowing energy and materials recovery. By performing pyrolysis above 450°C, the process leads to:

- a char fraction (40wt%) with high GHV and promising specific surface area;
- an oil fraction rich in high commercial value compounds, with high GHV and low sulphur content (1wt%);
- a gas fraction enriched with hydrogen and methane.

The characterization of the oil fraction, repeated after one year, shows negligible changes during this period.

Acknowledgments

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LIQUID INJECTION TO ENHANCE BIOGAS PRODUCTION IN LANDFILLS FOR PRETREATED MUNICIPAL SOLID WASTES - BIO.LEA.R. PROJECT (LIFE+ PROGRAM)

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Abstract

The Bio.Lea.R project aims to demonstrate the performance of a landfill for less reactive, biologically treated waste (pretreated organic wastes) compared to a conventionally managed landfill, with regard to both environmental (biogas and leachate production) and economic aspects. The objective is to control the pretreated biodegradable waste through a liquid injection in order to achieve the same biogas quantity in a shorter time than in conventional landfill.

Laboratory and full scale monitoring were performed in order to check the efficiency of the landfill acting as bioreactor. A small-scale lysimeter was set up to simulate in laboratory the biological processes that happen at a bioreactor landfill. The lysimeter consists of a cylindrical reactor filled with waste. The monitoring activity of the geophysical parameters of the landfill is based on network of geophysical sensors to detect the changes in time and space of the electrical conductivity at different depth in the landfill. Electrical conductivity is potentially a good indicator of spatial and temporal changes of liquid content of the waste within, as results of the infiltration process.

Results of the lysimeter experiment have proved the faster production of biogas, with the Methane Potential Yield at 900 days. The current modeling of leachate infiltration is influenced by availability of experimental data which in this case are provided by time lapse monitoring of geophysical parameters. The combination of time-lapse geophysical monitoring, advanced inversion technique and traditional waste sampling techniques provides robust data to evaluate the infiltration process and degradation of waste.

Key words: bioreactor, biogas, geophysical monitoring, sanitary landfill

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1. Introduction

Management of landfills as bioreactors (indicated as "bioreactor landfills" in the following) has been studied and tested since 1970 in the US and has increasingly been spreading world-wide in the last decades (Sanphoti et al., 2006). Bioreactor landfill method aims to speed up the waste biodegradation in Municipal Solid Waste (MSW) landfills by constantly maintaining appropriate waste moisture and, depending on the management configuration, aerobic or anaerobic condition. With respect to the conventional landfill management approach, the following benefits of bioreactor landfills must be considered: i) a quicker stabilisation (10 to 15 years compared to 30 to 100 years with a classical landfilling operation) of biodegradable content can be achieved (Pacey et al., 1999); ii) the

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biogas production period can be shortened and the biogas quality increased, thus providing a significant improvement of energy recovery; iii) when a leachate recirculation system is used, the environmental hazard is reduced because the volume of leachate to be treated is reduced, thanks to the liquid retention by the waste matrix (Pohland, 1980; Warith, 2002).

However, *in situ* operations at a bioreactor landfill require careful monitoring and control of the operative parameters due to the great influence of the moisture content on the efficiency of the methanogenic bacteria (Reinhart and Townsend, 1998; Reinhart et al., 2002). The methanogenesis is enhanced by a high moisture content that can be reached by adding water/leachate to the waste. The threshold value of water content, under which no biodegradation activity is observed, ranges from 0.15 to 0.50 kg H_2O per kg of dry waste (DM), while fresh refuse moisture content ranges from 0.25 to 0.65 kg $H_2O\cdot$kg DM^{-1} (Pommier and Lefebvre, 2009). The waste must be maintained at nearly constant water content, especially under temperate climate, where waste disposed in landfill is generally too dry to guarantee the optimal biodegradation. The fluid necessary for obtaining optimal condition can be supplied either by the leachate recirculation or from rain water infiltration (Morris et al., 2003). Moreover, the leachate recirculation tends to uniform the spatial distribution of adapted microflora. As far as an efficient monitoring of the bioreactor is concerned, measuring the liquid distribution all over the landfill is a key issue (Imhoff et al., 2007): the optimisation of leachate injection systems remains a challenging and open problem for bioreactor landfill operators. Laboratory experiments demonstrated the relevancy of a proper calibration of the rate of leachate re-circulation to enhance the waste degradation and increase the biogas production (Hernández-Berriel et al., 2014). Moreover, innovative wells could be adopted to enhance the recovery efficiency of methane, as suggested by Xue et al. (2014).

In such a context, the project Bio.Lea.R. (within the frame of Life+ Program) aims to study a landfill managed as bioreactor, in order to exploit the biodegradable matter at its maximum extent and give the best yields of biogas.

Bio.Lea.R. project has a demonstrative character on full scale, and focuses on two parallel and mutually useful studies:

- ➢ at laboratory scale, with a lysimeter filled with waste coming from the landfill under study and managed as bioreactor;
- ➢ at landfill scale, with monitoring of the bioreactor activities, in terms of biogas production, and leachate recirculation efficiency and management (recirculation started in January 2014).

Herein we focus on the laboratory results and the main characterisation of the landfill. Particularly, we have designed and installed a network of geophysical sensors capable to explore the changes of electrical conductivity (or resistivity ρ, to say the reciprocal of electrical conductivity) and waste temperature at different depth of the landfill. These parameters can be a good indicator of spatial and temporal changes of liquid content within the bioreactor, as results of the infiltration process. Relationships between resistivity and temperature of leachate, and between resistivity and volumetric water content of waste, can be established by laboratory experiments (Grellier et al., 2005). In such a way, the results of geophysical monitoring collected in the landfill can be converted into water content.

The up-scaling from the laboratory results to the *in situ* properties is based upon the assumption that the properties of the solid waste tested in the laboratory are similar to those of solid waste in the field and that the leachate has the same properties of the leachate within the landfill. Both the assumptions do not have general validity because of the different scale of heterogeneity of the mass of waste and because of the spatial and temporal changes of the leachate properties in the landfill that cannot be controlled (Imhoff et al., 2007).

Electrical Resistivity Tomography (ERT) is suitable to study the complex resistivity distribution (2D and 3D) at large scale (ten to hundreds of meters wide and down to 30 meters deep) and small scale to characterize the waste landfill structure (Bernstone et al., 2000; Meju, 2000). Moreover, ERT is becoming a common tool for studying recirculation experiments in landfills (Acworth and Jorstad, 2006; Guérin et al., 2004; Mondelli et al., 2007; Moreau et al., 2003; Olofsson et al., 2006; Rosqvist et al., 2005). During recirculation process, if leachate content or gas migration creates resistivity changes, ERT can be considered using a time-lapse approach (i.e. repeating ERT survey several times during the injection). On the basis of this background, we designed a monitoring geophysical system, sensitive to the spatial and temporal changes of the liquid within the cell.

In Bio.Lea.R. project, ERT is one of the tools used to study the effects of leachate recirculation, and at the same time its methodological value is evident.

2. Materials and methods

2.1. The landfill

Cerro Tanaro landfill is located in Northern Italy (Fig. 1) and contains wastes treated with a Mechanical Biological Treatment (MBT), according to the EU Landfill Directive (Directive 1999/31/EC).

MBT reduces the environmental impact of the treated waste, also thanks to the reduction of its moisture and biodegradable fraction; however, the mean waste moisture content is in the order of 20-30% by weight, values unsuitable for the biological processes. In addition, the content of rapidly biodegradable matter is lower since a huge part has been already consumed during the biological treatment itself.

Fig. 1. Plan view of the landfill and position of geophysical profiles for waste characterization (the three images are the location of the vertical boreholes equipped with electrodes for geophysical monitoring)

Thus, low contents of water and rapidly biodegradable matter induce slow biogas production, which implies a longer post-management period.

The landfill is built with two hydraulically independent cells, filled with pretreated wastes. One cell is managed as independent anaerobic bioreactor landfill, in order to shorten and maximize the biogas production. The other cell, managed as conventional landfill, constitutes the comparison term. Each cell is equipped with biogas, leachate and moisture monitoring systems, liquid distribution plant, data transmission system.

2.2. Waste characterization

To characterize the material conveyed to the landfill, at the project starting point, undisturbed waste samples coming from *in situ* well drilling cores and output samples directly after the MBT were collected and analyzed.

The on-site characterization of the waste heterogeneity focused on evaluating the infiltration rate and the liquid distribution within the landfill by integrating drilling and geophysical survey.

2.3. Leachate recirculation and biogas extraction systems

In Cerro Tanaro landfill the leachate recirculation system mainly consists of 8 sub-irrigation rings of 20 m diameter, located at the top of 8 gas extraction wells, below the final waste capping. In addition, 8 horizontal pipes of 10 m length are placed in the zones not reached by the influence areas of the rings, at 0.5 m depth, as well as 4 vertical injection wells where three HDPE pipes reach different depths.

A manually-controlled pumping plant, located at the leachate storage tanks, supports the whole sub-irrigation system. Details on the technologies adopted to inject the leachate in bioreactor landfills are well documented in literature, using vertical wells (Khire and Mukherjee, 2007) or horizontal trenches (Haydar and Khire, 2005). The biogas extraction system consists in 26 vertical biogas wells, perimetral horizontal pipe lines, 8 horizontal rings (10 meters diameter) laid around 8 biogas wells on the top of the landfill and under the capping system.

Through three regulation stations, each well is connected to an energy recovery station where biogas is burnt in order to produce electricity.

2.4. Monitoring of biogas and leachate

Both landfill cells are equipped with the same system for biogas extraction and monitoring (temperature, flow rate, composition by methane, carbon dioxide, oxygen, hydrogen sulphide).

In-line analysis of biogas composition constitutes evidence of the cell response to the leachate recirculation, to verify the effectiveness of the process in enhancing biodegradation. The recirculated leachate is analysed weekly by temperature, pH, electrical conductivity, oxidation-reduction potential (ORP). At the same time, ammonium content and Chemical Oxygen Demand (COD) are analyzed on samples.

In addition, the cell managed as bioreactor is equipped with the system to monitor the leachate recirculation and collect the data about temperature and electrical conductivity measured by the geophysical sensors.

2.5. Laboratory scale tests

In order to simulate the biological processes that happen at a bioreactor landfill, a small-scale lysimeter was set up. The lysimeter consists of a cylindrical reactor (diameter = 0.18 m; height = 0.35 m) filled with waste coming from Cerro Tanaro landfill (Fig. 2).

When the lysimeter was set up, the waste was already 5-years-old (averaged among the different samples), with a mean dry matter content (DM) around 59 % by weight. To completely fill the lysimeter, 3.12 kg of waste were necessary. Given the waste age, just the slowly biodegradable carbon was present, with expected slow degradation kinetics.

The operating conditions in the reactor were optimized to increase the biodegradation:

1) the waste was shredded and the reactor was placed in a thermostatic room (30°C ± 1°C);

2) leachate was recirculated at adequate flow rate (0.1 – 0.7 L min^{-1}) in order to reach the maximum water retention capacity of the waste itself.

To study the degradation process, the following parameters were analyzed:

- *in leachate*: pH, oxidation-reduction potential (ORP), ammonium concentration;
- *in biogas*: flow rate, composition.

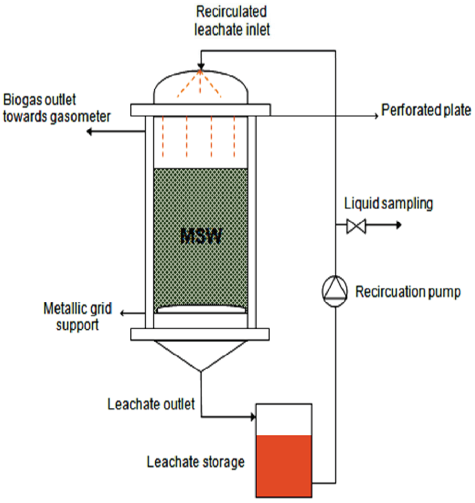

Fig. 2. Lysimeter scheme

2.6. Geophysical characterization

We characterised the electrical behaviour of the landfill by Electrical Resistivity Tomography, along 6 vertical sections. The ERT method is widely applied in environmental study both for monitoring the water infiltration process in landfill (Grellier et al., 2008) and to outline hydrological parameters of the subsoil (Godio and Ferraris, 2005), and to characterise contaminated sites (Godio and Naldi, 2003; Godio et al., 2010). The geophysical investigation has been performed from the surface, with electrodes placed directly on the waste material before the disposal of the final capping. The survey focused on mapping the inner heterogeneity of the landfill, to a depth of about 15 meters and checking the most promising zones for a subsequent hydraulic characterization. We performed 6 ERT profiles aligned as indicated in Fig. 1.

Each profile consisted of 48 in-line electrodes, spaced 2 m, covering a total length of 94 m. Five profiles were parallel between each other, and they were traced with an approximate profile separation of 10 meters.Besides the preliminary geo-electrical characterization of the waste, an infiltration test was carried out in order to estimate the infiltration rate in the uppermost part of the cell. The experiment was carried out on the cell top, before the complete capping of the cell itself, by infiltrating a controlled volume of water from the surface and monitoring the infiltration process, using two cross-profiles of electrical tomography in time-lapse fashion (Arato et al., 2014a).

The test was intended to simulate a rainfall event, as the water was supplied over a 3x5m area through a set of gardening sprinklers. A total volume of 6 m^3 was infiltrated during an infiltration time of about 2 hours. Water resistivity, measured before the test, was 16 Ω·m. The ERT lines, each one set up with 48 electrodes 1 m spaced, were both centered in correspondence of the infiltration area (Fig. 3).

2.7. Geophysical monitoring

The full scale monitoring in the selected landfill was designed to check temperature and humidity evolution at different depths, to be related to leachate infiltration and circulation.

Vertical temperature sensor strings were installed within the landfill along five biogas extraction boreholes. Each string had 5 temperature sensors, with a spacing of 3 m, in order to measure a vertical temperature profile in the depth range between 3 to 15 m from the top of the landfill.

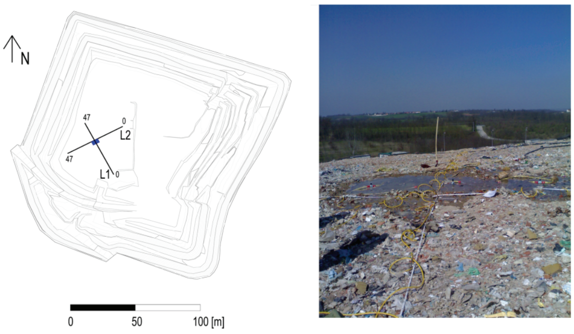

Fig. 3. Position of the two perpendicular profiles (ERT) for the monitoring of the infiltration test from the surface of the landfill

Ten boreholes were specifically installed for geo-electrical monitoring. Each borehole consists of a PVC pipe, with a multi-electrode cable attached along the pipe itself. Each multi-electrode cable has 24 graphite electrodes, 0.6 m spaced, and covers a depth of 13.8 m between the top and the bottom of the landfill, depending on the criticisms occurred during the drilling and completion of the boreholes. All the electrodes were connected by specific electrical cables to a control unit for remote monitoring controlled in real time.

As described in Fig. 4, the geophysical monitoring system was designed to perform cross-hole ERT surveys between three pairs of boreholes near three leachate injection-biogas collection stations, plus two isolated vertical boreholes for periodic controls. Since August 2012, monthly we have measured the electrical resistivity along the depth of each borehole. Cross-hole ERT data acquisition was performed in 3 different panels between pairs of boreholes, and the temperature effect on electrical parameters was also checked according to the values measured by the temperature sensor strings.

The permanent system for remote monitoring of the injection has been installed in October 2013, after the complete capping of the cell (Fig. 4). Since then, the switching unit and the control unit were located in a wooden hut; the cabling was performed and controlled to ensure perfect correspondence between electrodes and connectors to the control unit. Preliminary tests were focused to fix some bugs in the electrical connection of the system. In the period November 2013-January 2014, measurements were carried out more frequently (bi-weekly) in order to define a background resistivity model for the stations A, B and C (corresponding to biogas extraction wells CTB107, CTB110 and CTB111, respectively).

The monitoring system has been subjected to an initial step of calibration and start-up, which was based on repeating the electrical surveys at different time periods before starting the leachate recirculation, in order to evaluate the repeatability of the measurements and the stability of the monitoring system. The start-up step referred to the initial monitoring in time-lapse modality of a well-controlled infiltration, limited to injection-extraction station CTB107. A total volume of about 250 m^3 of leachate was supplied to the landfill, with a flow rate of 5 m^3/h. The test began in January 2014 and lasted 5 days.

The leachate had been infiltrated discontinuously for 6-10 hours/day, while cross-hole ERT acquisition had been carried out every 6 hour, to evaluate the sensitivity of the monitoring devices to the humidity changes. The time-lapse ERT inversion (Arato et al., 2014b) was carried out by using R2 finite-element inversion software, (Binley, 2013) which also features the difference inversion algorithm developed by La Brecque and Yang (2001).

The conceptual model of the geo-electrical behavior takes into account that during the subsequent monitoring of the fluid distribution within the bioreactor, the cell is covered by a low permeability capping. The uppermost part of the cell is composed by clay material layer, above a thin layer of drainage material (coarse pebble). These layers form the overburden of the cell with an average thickness of about 0.8 meters; the HDPE liner is disposed above the clay, and hydraulically insulates the cell from the superficial runoff.

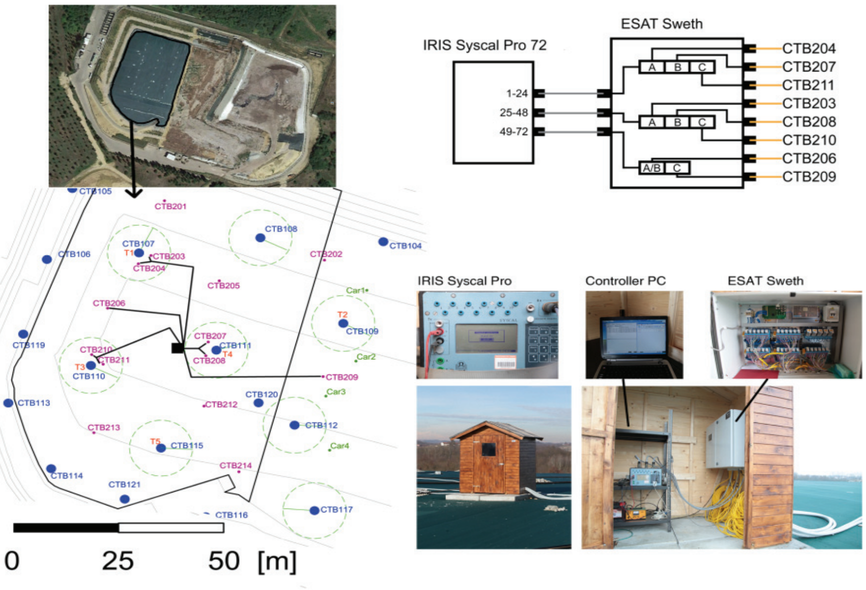

Fig. 4. Map of the cell after the disposal of the final coverage; the black lines on the map refer to the electrical connection between the boreholes (equipped with geophysical sensors) and the remote monitoring system (in the centre of the cell). The acquisition unit (Iris Syscal Pro) is connected to the boreholes through a multiplexer (Esat Sweth); an external PC guarantees the remote control of the unit)

3. Results

3.1. Laboratory tests

3.1.1. Leachate

The chemico-physical parameters measured on leachate samples show values commonly achieved in anaerobic digestion. Among the others, pH, ORP and ammonium concentration are plotted in Fig. 5. pH values are rather constant and around neutrality (except the starting period when the biological system must still adapt), to say suitable for microbial activity, as a whole. ORP shows negative values, typical of the anaerobic systems, even if not so evident.

The ammonium concentration decreases with time, to say it is consumed and after about 60 days its value is negligible.

3.1.2. Biogas

Despite the difficulty in degrading this type of waste, the time needed to reach methanogenesis was reduced and methane production occurred from the 57th day of monitoring. The kinetic model of Gompertz growth equation was used to predict the production of methane which could be obtained in lysimeter (Eq. 1) (Zhu et al., 2009), where: *BM* = cumulative methane yield (NL·kg DM^{-1}); *t* = digestion time (d); *BMP* = methane yield potential (NL·kg DM^{-1}); R_m = maximal daily methane yield (NL·kg DM^{-1} d^{-1}); λ = bacteria growth lag time (d).

$$BM = BMP\,exp\left[-exp(\frac{e\,R_m}{BMP}\left(\lambda - t\right) + 1)\right] \qquad (1)$$

The experimental data (Fig. 6) allow estimating kinetic parameters and evaluating the degradation trends; the half transformation time ($t_{1/2}$) is 319 days.

The Methane Yield Potential (BMP) can be reached approximately after 900 days; thus, the overall biodegradation kinetics, which is the derivative of the curve, shows higher methane production rate compared to landfill behaviour. It was possible to compare it with values present in the literature. The estimation of BMP equal to 71 NL·kg DM^{-1} agrees with the results of other experimental studies (Mali et al., 2012; Bayard et al., 2009; Sanphoti et al., 2006), that present a rather large range of results (36-185 NL·kg DM^{-1}).

The prediction of biogas production in the landfill is more complex than in lysimeter since there are many different phenomena to take into account, such as waste physical interactions as well as environmental and hydrological ones which can modify the physical and chemical parameters. In addition, the landfill management options and some unpredictable inhibitory phenomena and/or some synergic ones affect the biogas production. The predictive model used in this study was BIO-5 model, which allows getting the biogas production trend for a given landfill (Magnano, 2010). Two cases were simulated with BIO-5 model: conventionally managed landfill (assuming waste moisture equal to 41 % by weight) and the same landfill with leachate recirculation (assuming waste moisture equal to 55 % by weight). Fig. 7 reports the data obtained with these simulations and lysimeter: the positive influence of leachate recirculation is evident.

Considering the biodegradation kinetics, the half-transformation times are approximately 7 years for the traditional landfill, 5 years for the enhanced moisture landfill and 319 days for the lysimeter operation at its maximum water content.

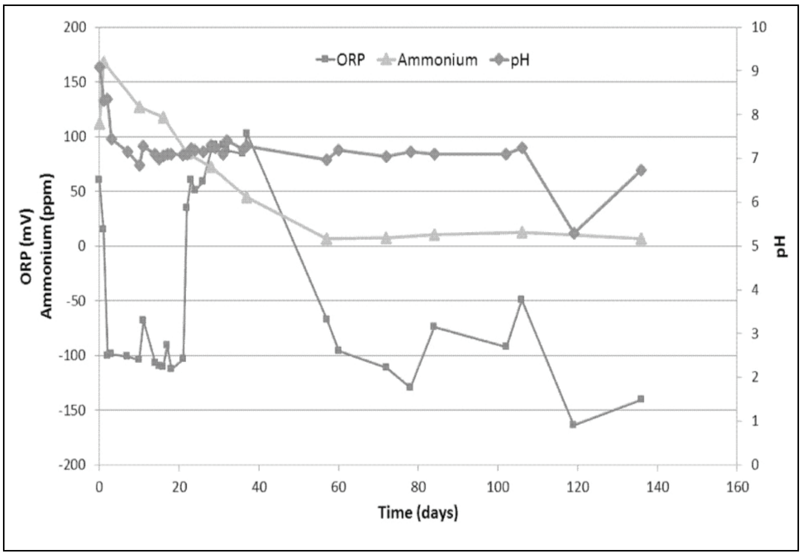

Fig. 5. pH, ORP and ammonium concentration in leachate recirculated in the lysimeter

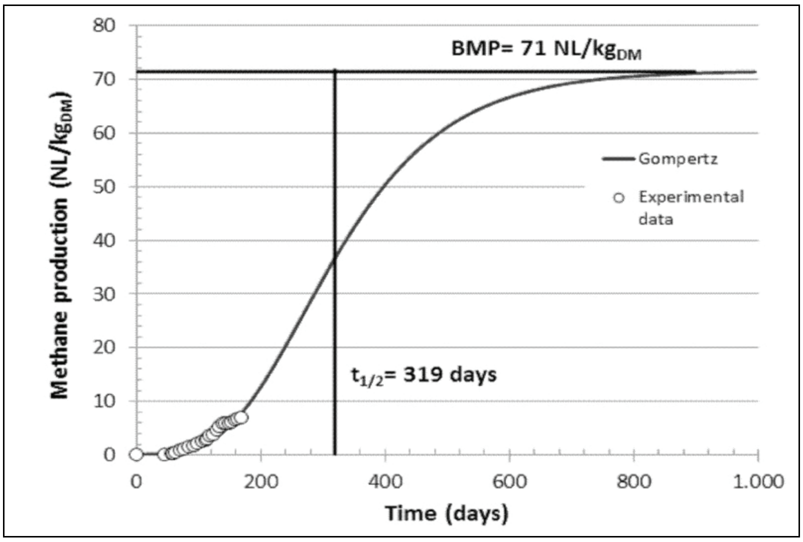

Fig. 6. Cumulative methane yield in the tested lysimeter

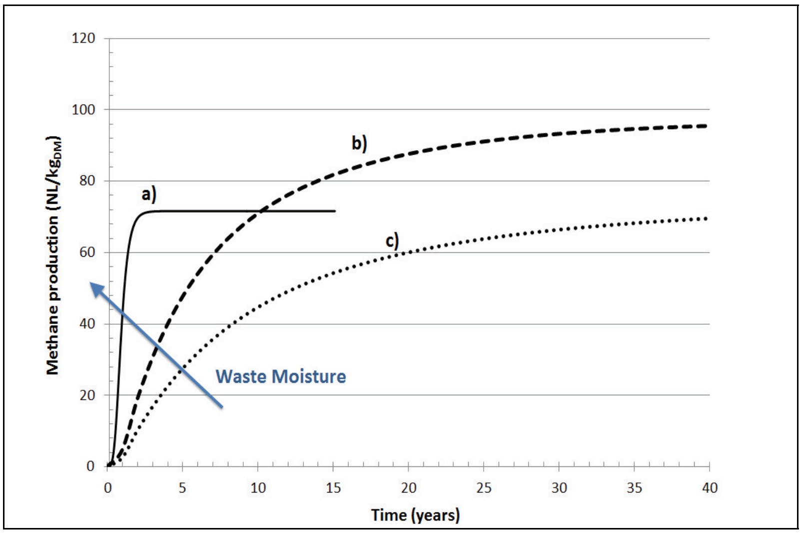

Fig. 7. Comparison of cumulative methane yield in: a) the tested lysimeter; b) landfill with leachate recirculation; c) landfill without leachate recirculation

3.2. Recirculated leachate

The weekly analyses done on landfill leachate have evidenced the wide range of the measured parameters, namely:

- temperature: 10-30 °C;
- pH = 7.8-8.7
- ORP = (-252)-(-52) mV
- electrical conductivity = 7825-32890 $\mu S \cdot cm^{-1}$
- COD = 5280-18380 $mg \cdot L^{-1}$
- ammonium concentration = 737-3730 $mg \cdot L^{-1}$.

The wide spectrum of each parameter demonstrates the huge heterogeneity of the leachate, which can be influenced by season, and weather.

3.3. Small scale test

A "cube-scale" controlled infiltration test has been carried out in October 2014, in order to analyze the small-scale behavior of the waste under re-circulation and to try to understand the dependence of the resistivity on the waste moisture content. A single cube of pretreated waste (1.5 m^3 in volume and mass around 1400 kg) has been equipped with 24 electrodes for apparent resistivity measurements, to follow the evolution of geo-electrical properties of a cycled infiltration experiments. The test started infiltrating 600 L of tap water (conductivity = 800 $\mu S \cdot cm^{-1}$), in 3 hours. From the bottom of the cube, 300 L of liquid were collected into two PVC containers. Water was supplied from the top of the cube, through a regular grid of holes, as shown in Fig. 8. In-flow liquid volume has been measured with a flowmeter, while out-flow volume has been measured by taking manual measurements of liquid height in the containers. The filtrated liquid has been progressively recirculated for 5 days, with the aim of following the evolution of electrical resistivity under this wetting process. Water conductivity has been measured with a multi-sensor probe.

The out-flow volume of leachate at the end of the test (after 5 days), was around 150 L, meaning that more than 400 L had been retained by the waste. The results of the small scale experiment are shown in Fig. 9: the in-flow and out-flow volumes versus time are reported at the top; the specific fluid conductivity values are reported over the same time-scale (in the central plot); the evolution of apparent resistivity measured between electrodes at the top face of the cube is plotted on the bottom plot.

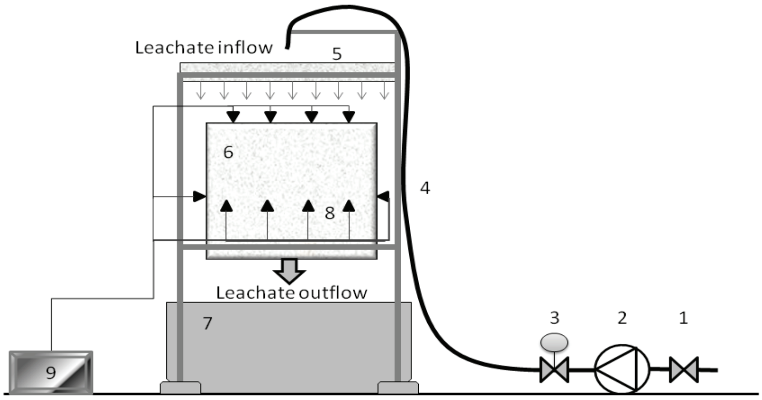

Fig. 8. Experimental set up of a single cube of pretreated waste for the small-scale re-circulation test and resistivity monitoring: 1) closure valve, 2) pump, 3) regulator valve, 4) delivery pipe, 5) distribution grid, 6) waste, 7) collecting tank (discharge), 8) electrodes, 9) acquisition unit for resistivity monitoring

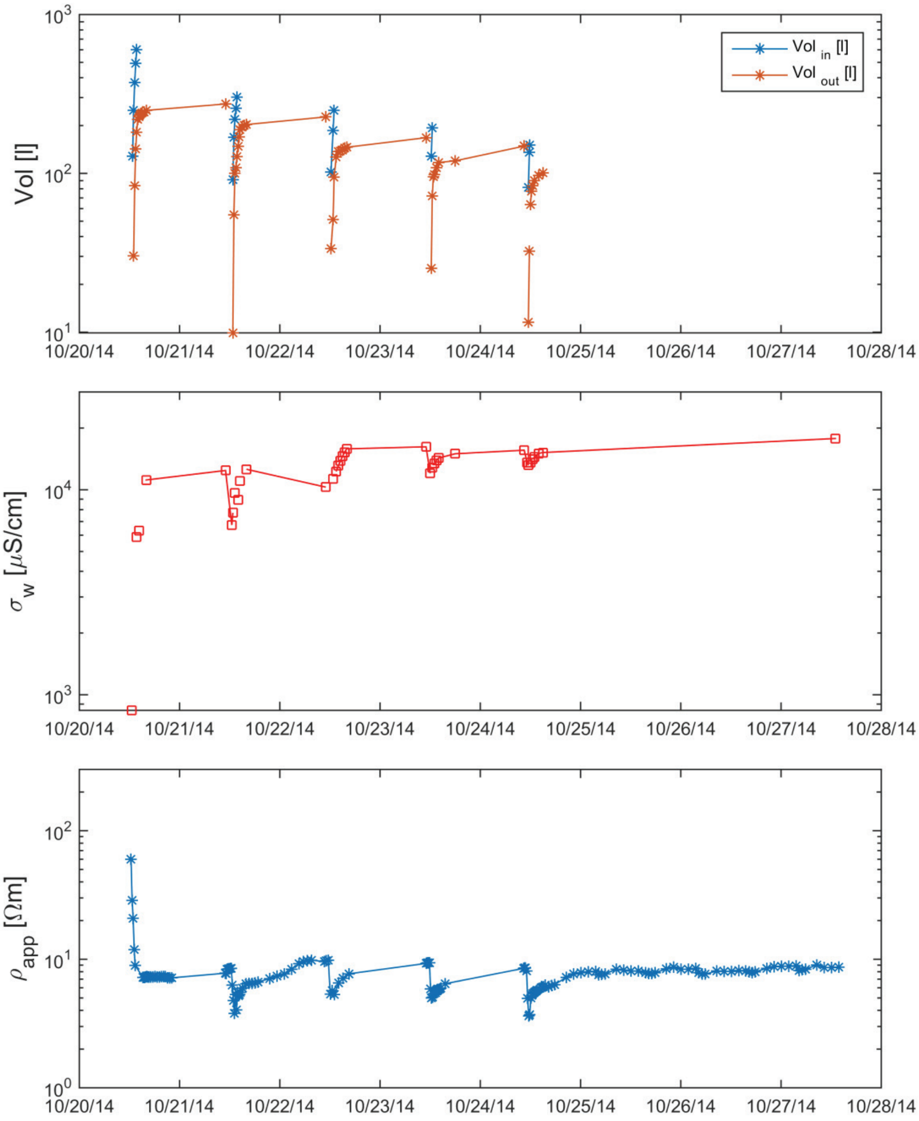

Fig. 9. "Cube-scale" test: in-flow and out-flow volumes (top); fluid conductivity of the recirculated fluid (center); apparent resistivity measured with the quadripole at the top of the cube (bottom)

3.4. Geophysical characterization

The electrical resistivity characterization refers to five parallel vertical sections in the Western sector of the landfill, along SW-NE direction, plus one diagonal section along SE-NW direction. According to the electrical characteristics of the landfill and the electrode spacing, a maximum depth of investigation of about 10-12 meters was reached. This is enough to characterise the waste material down to the bottom of the cell.

The results of the electrical characterisation points out a portion of the landfill of with a rather homogeneous electrical response (Fig. 10). Particularly, we observe:

- the presence of upper layers of waste material up to a depth of about 3-5 meters characterized by resistivity values in the range 20-50 Ω·m;
- at greater depth a slight decrease of the resistivity values, that are in the range 2-5 Ω·m.

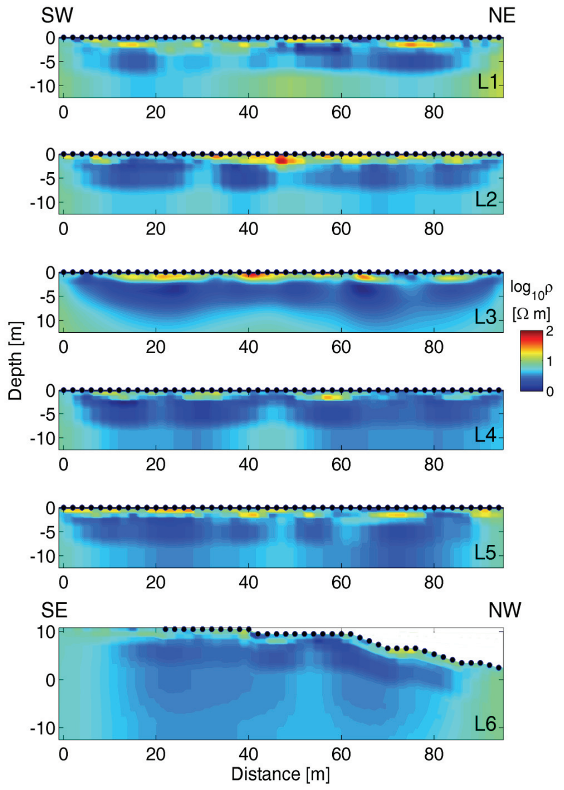

Fig. 10. Electrical resistivity distribution along several transects of the landfill (see Fig. 1 for positioning)

The results of the surface infiltration test, monitored by using time-lapse ERT, are shown in Fig. 11. The panels on the left are referred to Line 1, while the panels on the right are referred to Line 2. The top row reports the background resistivity distribution while the other panels are related to subsequent relative resistivity differences, with respect to the background values, at five time steps (t_0=background; t_1=0-0.5 hours; t_2=1-1.5 hours; t_3=2-2-5 hours; t_4= 4-4.5 hours; t_5=24-24.5 hours. Times are referred to the start of the irrigation).

Based on the results of the time-lapse monitoring of the infiltration test, we pointed out that:

- the infiltration proceeded very fast, according to an initial horizontal spreading in the upper surface layer (1-2 meters) and then moving downwards;
- the vertical movement of the flow follows some preferential pathways, due to the high waste anisotropy; indeed the water creates an elongated plume along Line 1 direction, as it is clear from the negative difference anomalies in correspondence with the infiltration area;
- a preferential zone of fluid accumulation (low electrical resistivity) is observed at the depth of about 4-6 meters; this means that a relevant substrate at low permeability has been reached by the vertical flow and the infiltration will proceed downward very slowly.

An example of monitoring of electrical resistivity in cross hole configuration is plotted in Fig. 12. The left panel refers to the vertical resistivity section between the wells CTB203-CTB204 (monitoring station A) and, on the right, the vertical section between the wells CTB210-CTB211 (monitoring station C). In the uppermost part of the sections, we pointed out resistivity values around 50-60 Ω·m, which are in accordance with the preliminary measurements shown in Fig. 10: resistivity tends to gradually decrease with depth, and at 6-8 meter depth, a very conductive zone is detected (resistivity less than 1 Ω·m).

These values are in good agreement with the stratigraphic column of the boreholes, indicating the presence of dry waste up to 4-6 meters in depth and wet waste at greater depth. The resistivity heterogeneities around the electrodes come from the extremely complex material which is in place, and could even be caused by the presence of organic material and inert separating the pretreated wastes. Moreover, the resistivity gradient with depth is strongly affected by temperature effect: it should be noted that a decrease of about 2 % of resistivity values is expected for an increase of 1 Kelvin degree. We observe an average temperature of about 45 °C, starting from a depth of 4-6 meters from the top of the landfill, which could be partially responsible of the very low resistivity values pointed out at greater depth in the landfill.

The results of the time-lapse monitoring of the first recirculation test are shown in Fig. 13a, 13b. The Figures are organized in rows of resistivity difference panels, covering four days of the test, each day is described in a single row. Following the background resistivity, it is clear how the leachate recirculation affects the resistivity measurements. The most influenced zone is the shallow layer, down to 4 m depth. As the volume of infiltrated leachate increases, the resistivity differences with respect to the background increase, because of the wetting induced by the leachate migration. Furthermore, the resistivity contrasts between the different waste layers are enhanced too. The last panels of the bottom row refer to the fifth day of the test, when recirculation had been stopped. Resistivity contrasts tend to reduce, as the system starts to return to background conditions.

4. Discussions

Experimental simulation of bioreactor landfill showed that leachate recirculation gives its benefits even in the case of waste with low biodegradable content. Despite the difficulty in degrading this type of waste, thanks to the increase of moisture content, it is possible to reduce the time needed to reach methanogenesis. Gompertz equation allowed us to build a predictive curve of methane evolution for the experimental conditions.

By comparing the experimental ones, it can be noted that the biodegradation is strongly affected by the moisture content: the quantity of retained water in the refuses affects positively the Methane Yield Potential as well as its rate. Modeling of biogas production is fundamental in such a context, because it allows predicting the biogas production in a long term (decades of years), necessary to mineralize the waste.

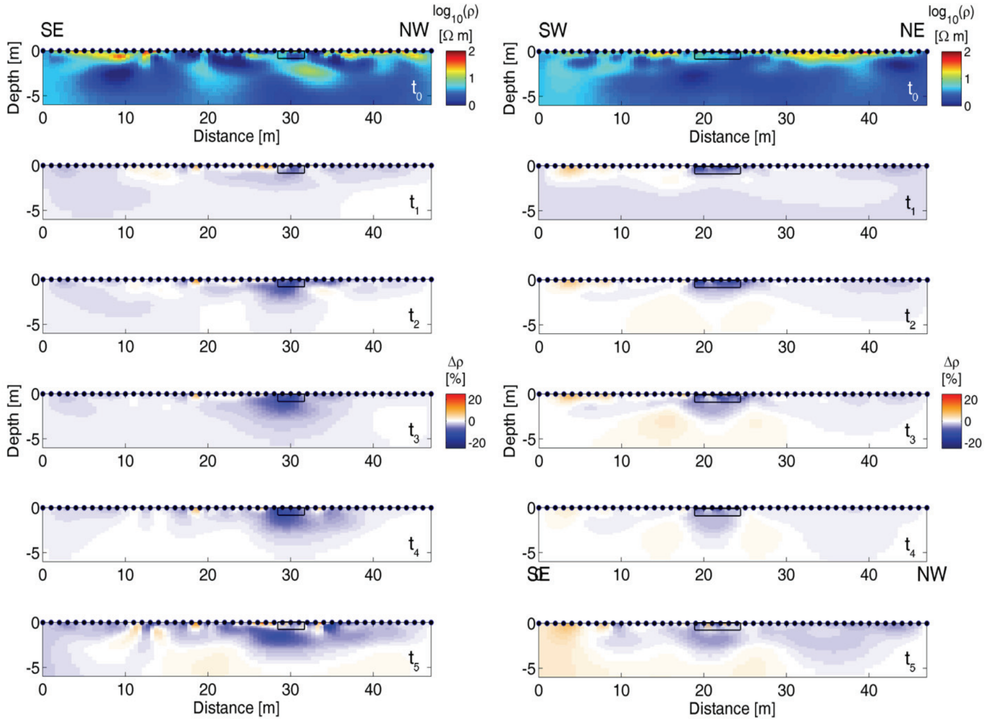

Fig. 11. Relative differences obtained by inversion of resistance data at time-lapse steps (compared to the corresponding background data); the experiment refers to an infiltration test of 6 m^3 of water, infiltrated from the top of the landfill

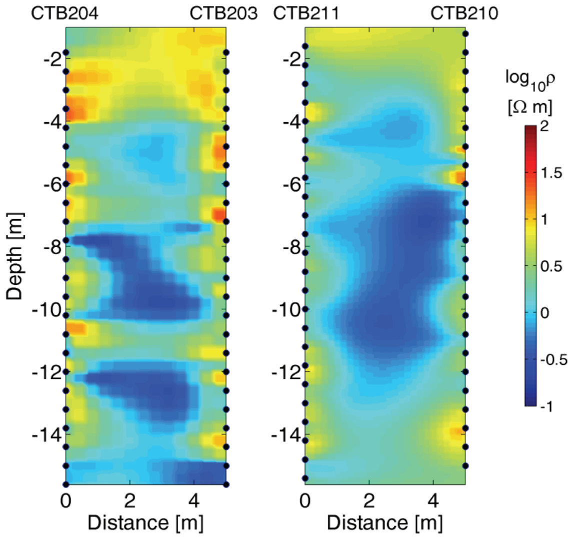

Fig. 12. Background resistivity distribution along two vertical sections of the landfill; section A (left) and C (right)

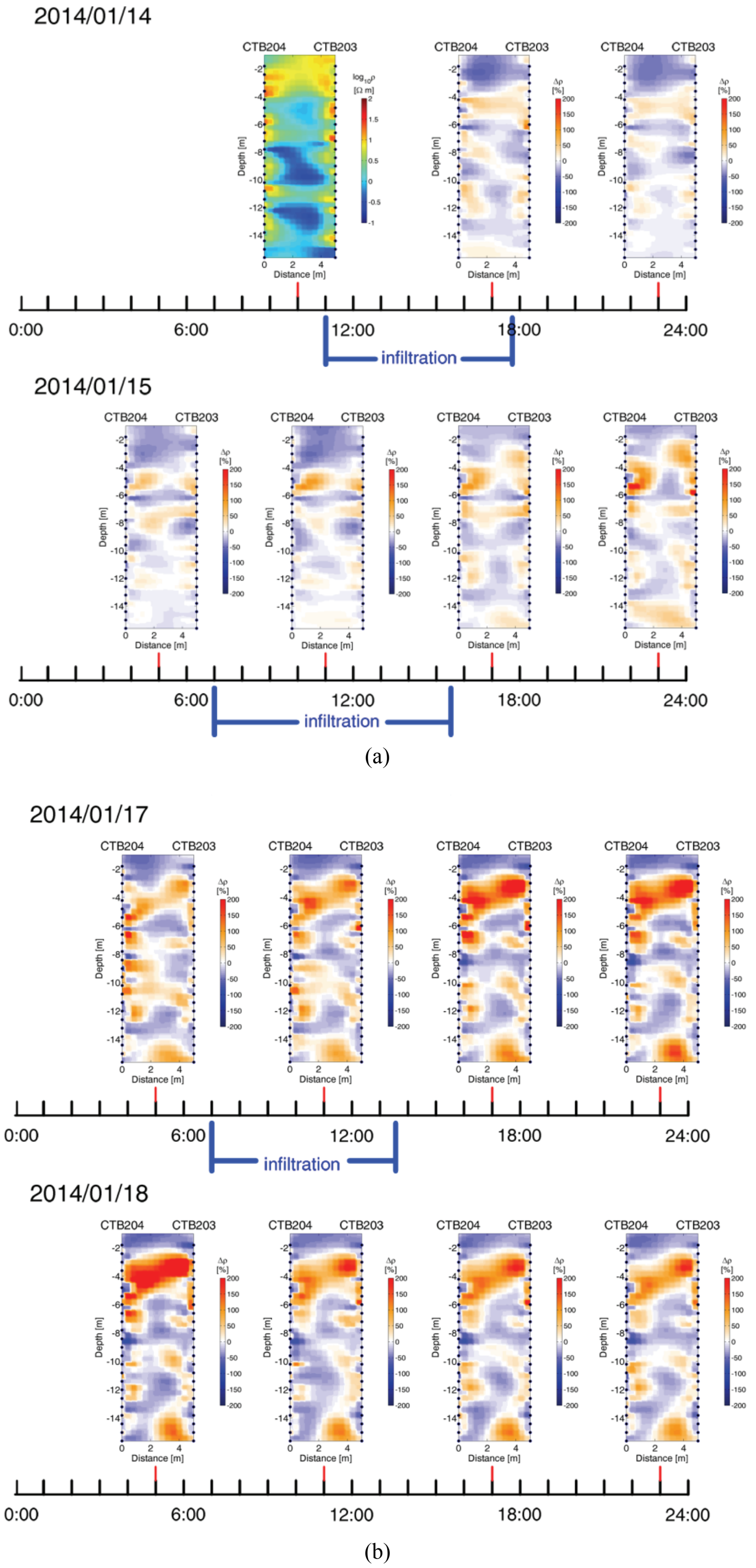

Fig. 13. Time-lapse geo-electrical monitoring of a pilot re-circulation test, at boreholes CTB203-CTB204: (a) background resistivity image and first two days of infiltration; (b) end of the infiltration and redistribution phase

The preliminary characterisation and the set up of the monitoring system were focused to check the sensitivity of geophysical methods to monitor dynamic processes in a heterogeneous medium and assess the efficiency of the landfill working as bioreactor. The geophysical characterisation aimed to point out the electrical response of the landfill and the sensitivity of electrical tomography to detect the infiltration and the volume affected by leachate recirculation. According to our experience, this is the first attempt of monitoring long-term behaviour of the bioreactor landfill by using geophysical sensors permanently installed within the wastes. This required great care in designing the monitoring devices in order to warrant long life to the monitoring system: high temperature resistant cables and graphite electrodes were installed to preserve the devices against effect of high temperature and corrosive environment.

In the cube-scale test, the dependence of the observed resistivity on the fluid content in the waste is well demonstrated: the resistivity dramatically drops down when the wastes are being hydrated, as the fluid is supplied and filtrates through the solid mass. The fluid specific conductivity (observed at the leachate outflow) follows an opposite trend, as it increases due to increasing of dissolved solid content. It is therefore realistic to observe a sharp changes of electrical resistivity during the infiltration (after few hours or days), while the prediction of electrical behavior at long term still remains a challenge.

In the mature waste mass throughout the landfill, the geo-electrical response is related to changes in the chemistry of the pore fluids. Particularly, in porous material the electrical resistivity is mostly affected by temperature (Campbell et al., 1948) and volumetric fluid content (Archie, 1942). In such a context, we observe low resistivity values all around the cell, with an abrupt decrease at deeper level; this agrees with an increase of temperature and moisture content with depth.

In steady-state condition, without infiltration, the surface layers of landfill waste (just below the capping) are the part of the landfill waste where oxygen and bacterial supply are abundant, with quicker decomposition than in the deeper parts: the bulk resistivity of this oxidized zone points out a relative increase with time, because of the organics for microbial degradation become depleted in supply and much of the soluble elements have been removed.

It may thus be relatively more resistive in comparison with the clay cap and the underlying zone of incomplete waste decomposition. The bulk resistivity of the waste at deeper level may have only been partially decomposed under anaerobic conditions thus leading to different physical properties. The lower part of the waste deposit contains a zone dominated by relatively incomplete leaching and therefore exhibits relatively low bulk resistivity.

During infiltration, the time-lapse electrical resistivity panels point out relevant changes of the electrical properties with time up to a depth of about 6-8 meters, with changes of increase and decrease of bulk resistivity. The water flux through the top of the landfill affects its resistivity characteristics: a highly conductive fluid like leachate can influence the electrical behavior of a medium in different ways. Theoretically, higher fluid content implies a reduction of resistivity, but anomalous electrode polarization phenomena can arise in such conditions. Electrodes can be themselves a source of polarization effect; this effect can be difficultly removed from the measurements and produces artifact in resistivity distribution. Thus, in such a harsh environment, only qualitative explanation of the infiltration processes can be given but, nevertheless, the zone impacted by the leachate flow can be delineated.

A fast vertical infiltration rate is expected in the uppermost zone, because of the high permeability of the detritus coverage mixed with low-compacted wastes. At deeper levels, a decrease of waste permeability is expected. On the other hands, the main drawbacks related to an efficient infiltration from the top of the cell are related to the relevant lateral spreading of the infiltrated water, as pointed out by the infiltration tests. This could lead to a non-uniform distribution at deeper level of leachate within the waste, partially reducing the efficiency of the enhancement of biogas production.

5. Conclusions and future activities

Leachate infiltration in landfills is a complex process and detailed information on the flow characteristics are needed to provide fundamental understanding of the processes involved for prediction of biogas production. We are analyzing the complexity of processes by integration of laboratory tests on waste samples and geophysical characterization and monitoring in the landfill: the final goal of Bio.Lea.R. project (Life+ Program) is to demonstrate the improvement of biogas production by leachate recirculation in a landfill for MBT wastes.

First results at laboratory scale have proved the faster production of biogas, with the Methane Potential Yield at 900 days. The current modeling of leachate infiltration is influenced by availability of experimental data which in this case will be provided by time lapse monitoring of geophysical parameters.

The combination of time-lapse geophysical monitoring, advanced inversion technique and traditional waste sampling techniques provide robust data to generate a consistent structural framework of the landfill as well as experimental results on the infiltration process and degradation of waste. Experiments at different scales and environmental conditions, to say lysimeter and landfill, point out the processes that are involved in biodegradation. This leads to advanced characterization of biodegradation and prognosis of local process development. The data of biogas production and emission of the two cells (with and without re-circulation of leachate) will be compared to define optimal conditions of liquid recirculation/distribution to reduce and concentrate the biogas production period. In this way, the project is useful for future implementations of non-hazardous landfills managed as bioreactors. The re-circulation of leachate is another positive solution to reduce the environmental impact of effluents of waste landfilling (Şchiopu et al., 2012; Şchiopu and Ghinea, 2013)

The project can warrant a more efficient biogas extraction and consequently lower methane losses in the environment.The methane exploitation to produce electricity is another positive aspect, in view of fossil fuel substitution.

Acknowledgements

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PYROLYSIS OF WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE) FOR RECOVERING METALS AND ENERGY: PREVIOUS ACHIEVEMENTS AND CURRENT APPROACHES

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Abstract

The amount of collected Waste Electrical and Electronic Equipment (WEEE) in Europe is growing about 7 wt.-% per year (2007-2012). It contains a number of economically relevant base, precious and high-tech metals. However, only a limited number of these metals can be recovered by currently applied recycling processes. Especially high-tech metals like gallium, germanium and tantalum get lost during the treatment of WEEE. The pyrolysis technology allows an accumulation of these metals from WEEE-fractions without oxidation as well as the generation of high calorific gases and liquids for energetic utilization. This paper provides a literature based review of lab and medium-scale investigations on pyrolysis processes of different WEEE-fractions like printed wiring boards (PWB) or plastics to outline opportunities and challenges for recovering critical metals from WEEE via pyrolysis. The key procedural challenges are dehalogenation, avoidance of highly-toxic emissions (mainly PBDD/F) as well as preparation and accumulation of metals for recycling processes.

Key words: critical metals, metal recycling, pyrolysis, WEEE

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1. Introduction

The raw material supply of many industrial nations e.g. in the European Union is vulnerable due to fading geogenic reserves or export restrictions and political conflicts in countries of exploration. To enable a continuous and sustainable supply, the recovery of raw materials from secondary resources offers promising potential. Waste Electrical and Electronic Equipment (WEEE) is a source of various metals and polymers but also hazardous substances. WEEE became one of the fastest growing waste streams in the world, especially in industrial nations (Ciocoiu et al., 2013). The amount of collected WEEE in the EU-27 increased about 7 wt.-% per year (2007-2012) (Eurostat, 2015). Relating to this, the WEEE-directive (2012/19/EU) defines recycling targets referring to a minimum weight of recovered materials, regardless the type of recovered material (EC Directive, 2012). However, WEEE contains a number of different critical elements, whereof many are not recovered yet (Bakas et al., 2014; Buchert et al., 2012; European Commission, 2013).

Against this background, pyrolysis offers the opportunity to enable both, a recovery of these critical elements and an energetic utilization of organic materials. The purpose of this work is to outline the state-of-the-art and challenges of this

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thermo-chemical technology as part of a process chain, to recover metals and energy. The findings of the review will be used to design a pyrolysis process, which is focused on the recovery of critical metals, whose end-of-life recycling rates from WEEE are less than one percent.

2. Waste Electrical and Electronic Equipment – WEEE

2.1. Amount and composition of WEEE

In the year 2012 the total amount of WEEE collected in the EU 27 was about more than 3.5 Mio. tons (Eurostat, 2015). An average composition of WEEE is shown in Fig. 1 (Eurostat, 2015; Haig et al., 2012; Reuter et al., 2013). Beside base metals like Fe, Al and Cu, WEEE mainly consists of different plastics like acrylonitrile-butadiene-styrene (ABS), polystyrene (PS), polycarbonate-ABS (PCABS), polyethylene (PE), polyvinyl chloride (PVC), styrene acrylonitrile (SAN) or ethylene-propylene-diene monomer (EPDM). In addition to these main components, WEEE contains a number of precious and critical metals. Bakas et al. (2014) reported the amount of critical metals contained in waste mobile phones, laptops (both including batteries), computers and flat-screens in the EU for 2010.

Fig. 2 shows that the amount of some critical metals contained in these WEEE holds the potential for covering a considerable part of the demand of these metals in the EU: The percentages indicate that between 0.5 wt.-% (W) and up to 17.5 wt.-% (Co) of the total metal-demand in the EU could be supplied by WEEE. This quantity amounts to about 2,000 tons per year. According to current market data, the amount of Pd and Co in WEEE equals a value of 215 Mio. € (Bakas et al., 2014; European Commission, 2013; Johnson Matthey, 2012; Mineralprices.com, 2014).

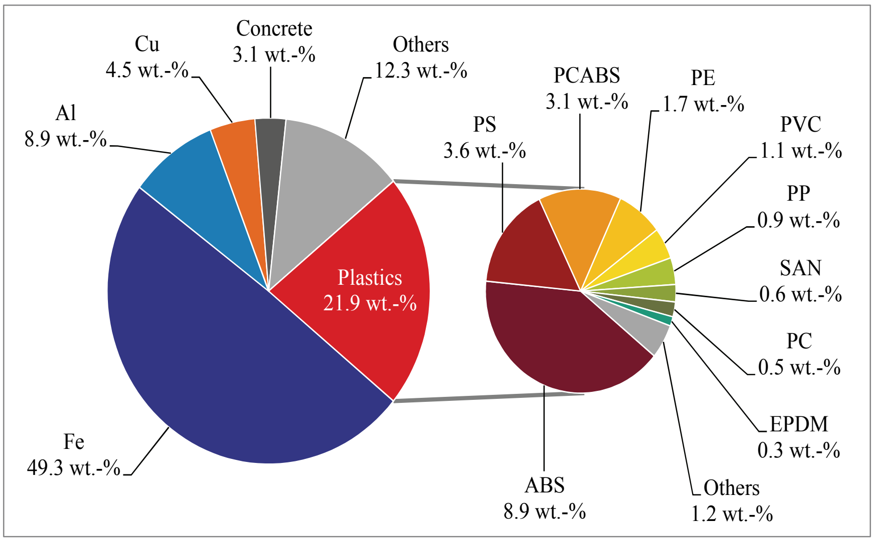

Fig. 1. Average composition of collected WEEE in the European Union for 2012 (without categories 5, 8, 9, 10; composition stands for 98.6 wt.-% of all WEEE collected) (Eurostat, 2015; Haig et al., 2012; Reuter et al., 2013)

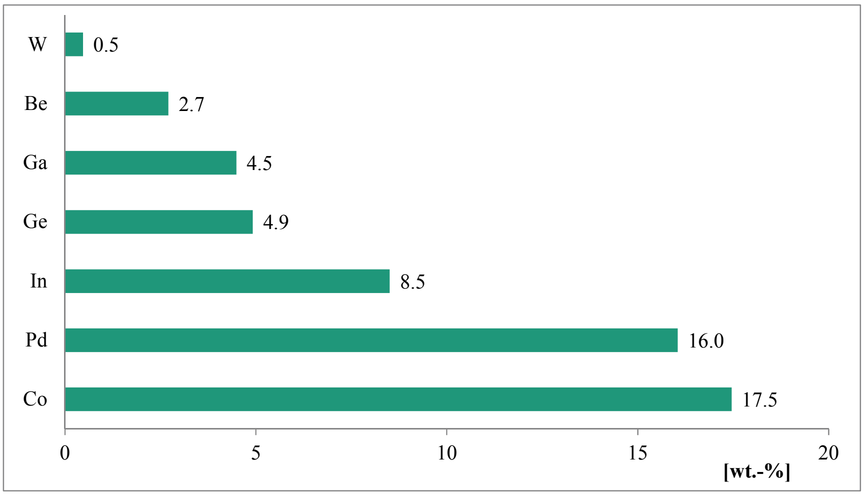

Fig. 2. Ratio of critical metals contained in waste mobile phones, laptops (both including batteries), desktop computers, and flat screens and the total demand for these metals in the EU (2010) (Bakas et al., 2014; European Commission, 2013; Johnson Matthey, 2012)

Next to plastics and metals, there are also components that cause problems in recycling processes. Generally, about one quarter of plastics from WEEE contain flame retardants (Eionet, 2013), of which one third are based on halogens (EFRA, 2007). However, the amount of halogens in plastic fractions from WEEE could reach up to 10.9 wt.-% Br (Hall et al., 2008) and 57.8 wt.-% Cl (Ma et al., 2002). Since the use of selected brominated substances as flame retardants, namely poly-brominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE), is limited in EU countries by Directive 2011/65/EU on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) (EC Directive, 2011), alternative materials, mainly phosphorous- or nitrogen-based, were developed. However, the production of halogenated flame retardants still increases. Most are combined with inorganic compounds like aluminum or magnesium hydroxide ($Al(OH)_3$, $Mg(OH)_2$) and antimony trioxide (Sb_2O_3). For example, the amount of Sb in brominated ABS and high-impact polystyrene (HIPS) is in between 3.2 wt.-% and 4.6 wt.-%, respectively. Sb_2O_3 acts as synergist in the condensed as well as the gaseous phase of a flame (EFRA, 2007). In addition, decomposition products of Sb_2O_3 are catalysts for recombination of hydrogen, hydroxyl and oxygen radicals (Lewin, 2001; Dettmer, 2001).

Thermal decomposition on halogenated flame retardants can cause the formation of highly toxic and persistent polycyclic aromatic hydrocarbons (PAH), polyhalogenated aromatic hydrocarbons (PHAH) as well as dioxins and furans like polybrominated dibenzo-p-dioxins and furans (PBDD/F) (Reuter et al., 2013). The formation starts under presence of oxygen and is catalytically increased by presence of heavy metals, mainly copper and its oxides (Dettmer, 2001; Sakai et al., 2001). Dibenzo-p-dioxins and furans (PCDD/F) and PBDD/F are mainly formed in a temperature range between 260 °C and 430 °C (heating phase) and between 250 °C and 450 °C (cooling phase) (Dettwiler et al., 1997). Therefore, these temperature ranges should be skipped as fast as possible to prevent the formation of these toxic substances. Applying a pyrolysis temperature above 850 °C leads to decreased total yield of PCDD/F and PBDD/F (Lai et al., 2007). In general, most of these substances are absorbed by solid residues like char and just a small amount can be found in flue gas (Lai et al., 2007). This may be related to the high molecular weights and low vapor pressure of PCDD/F and PBDD/F (Birnbaum et al., 2003).

2.2. Status Quo of WEEE-treatment

In most industrialized countries, state-of-the-art initial treatment of WEEE is a combination of different mechanical processes and physical and / or optoelectronic separation systems. Usually, this treatment starts with a manual dismantling, followed by shredding and separation, for example with magnetic, eddy-current or infrared systems. Heterogeneous fractions like mixed plastics can be further split into halogenated and non-halogenated plastics with optoelectronic systems (Husemann et al., 2010). Recovered fractions like non-halogenated plastics or metals are handed over to recycling processes to recover secondary raw materials, while hazardous materials like halogenated plastics are usually landfilled or incinerated. Metal-rich WEEE like mobile phones or components like printed wiring boards (PWB) are given to pyrometallurgical plants to recover metals and to use the plastics as energy source and reduction agent. Modern processes in the copper industry are able to recycle up to 17 metals (Hagelüken and Corti, 2010), however limited to base and precious metals. The recycling usually starts with a smelter process, in which critical metals like Be, Ga, Ge, Nb, W and a number of Rare Earth Elements (REE) contained in WEEE oxidize and become slagged due to their ignoble character (Bakas et al., 2014; Kumar et al., 2014). Due to this, the end-of-life recycling rates of most critical metals from WEEE are less than one percent (Bakas et al., 2014; Buchert et al., 2012; Graedel et al., 2011).

3. Pyrolysis of WEEE: Review of previous achievements and current approaches

In pyrolysis processes, organic compounds are degraded in an inert atmosphere. Due to this, contained metals are not oxidized during the thermo-chemical process. Pyrolysis can be operated under different conditions mainly based on temperature, heating rate or dwell time, depending on the input material and desired product quantities and qualities.

Some of the previous achievements in the pyrolysis of WEEE are successfully handled already by mechanical or pyrometallurgical treatment of WEEE; that is why they are not further pursued in this paper. For example, an issue of achievements was pyrolysis of PWB (Williams, 2010). However, as mentioned above, PWB could efficiently be recycled in copper smelting processes, as far as the recycling of base and precious metals is concerned (Hagelüken and Corti, 2010).

Due to the described increasing demand for critical elements (chapter 1) a promising future application of pyrolysis can be the separation and recovery of critical metals, which are not recycled, yet. A pyrolysis process could become part of a process chain to separate critical metals and to generate fuels with low yields of halogens for an energetic utilization. Products of this thermo-chemical process would be (1) a mixture of certain metals, (2) a char-metal mixture, which could be treated in copper processes, as well as (3) calorific gas and oil for an energetic utilization, e.g. in a combined heat and power (CHP) plant. This energetic utilization of pyrolysis oil and gas is an appropriate option, because these products can present fuels with heating values, which are often comparable to conventional fuels like diesel fuel (41.8 $MJ\cdot kg^{-1}$) or natural gas (CH_4: 35.9 $MJ\cdot m^{-3}$) (Bauforumstahl, 2015).

Results from a review of different papers, which present heating values of pyrolysis oils and gases from WEEE plastics, PWB or other materials from WEEE, are shown in Table 1. From the results it can be seen that the ranges of this values are between 26.5 and 44.8 $MJ\cdot kg^{-1}$ for liquid products and between 12.3 and 48.6 $MJ\cdot m^{-3}$ for gaseous products. However, there is currently no paper presenting a closed energy balance for all pyrolysis products (solids, liquids and gases) from WEEE or WEEE plastics.

The following sections of this chapter give an overview on how pyrolysis processes are influenced by the main parameters temperature, heating rate, residence time, operation mode (one- vs. two-stage), and additives as well as the influence of these parameters on quality and quantity of pyrolysis products and emissions. The first section (3.1) describes current achievements in thermal decomposition of halogenated plastics from WEEE with and without additives. Section 3.2 shows different approaches to dehalogenate pyrolysis products. The last part (3.3) focuses on those reactions between bromines and metals, which are relevant for a recycling of mainly ignoble critical metals, to achieve optimal results regarding the enrichment of these high-tech-metals.

Table 1. Pyrolysis product yields and corresponding heating values for different input materials at given pyrolysis temperatures

Input material	***Pyrolysis temperature***	***Pyrolysis product yields[1]***		***Heating values (*LHV; **HHV)***		***Reference***
	[°C]	[wt.-%]		[$MJ\cdot kg^{-1}$]	[$MJ\cdot m^{-3}$][2]	
Plastics						
from WEEE containing Cathode Ray Tubes	600	S:	14.5	---	---	Hall and Williams (2007a)
		L:	83.9	---	---	
		G:	1.4	37.4*	48.6*	
from refrigeration equipment	600	S:	20.4	---	---	Hall and Williams (2007a)
		L:	76.5	---	---	
		G:	3.0	29.5*	28.2*	
from mixed WEEE	600	S:	21.1	---	---	Hall and Williams (2007a)
		L:	70.6	---	---	
		G:	7.8	11.9*	18.2*	
PWB						
from Computers	500	S:	78.0	---	---	Jie et al. (2008)
		L:	9.1	---	---	
		G:	12.9	58.8*	21.2*	
from Computers	800	S:	68.9	---	---	Hall and Williams (2007b)
		L:	22.7	---	---	
		G:	4.7	16.6*	13.4*	
from Televisions	800	S:	60.0	---	---	Hall and Williams (2007b)
		L:	28.5	---	---	
		G:	6.5	17.5*	16.6*	
from Mobile Phones	800	S:	82.2	---	---	Hall and Williams (2007b)
		L:	15.2	---	---	
		G:	2.3	16.2*	12.3*	
Mixture	500	S:	76.5	---	---	de Marco et al. (2008)
		L:	16.2	26.5**	---	
		G:	7.3	---	---	
Mixture	500	S:	37.0	---	---	Chiang et al. (2010)
		L:	39.0	35.6 - 39.8*	---	
		G:	24.0	---	---	
Others						
PE-Wires[3]	500	S:	32.9	---	---	de Marco et al. (2008)
		L:	44.1	44.8**	---	
		G:	23.0	---	---	
Table Phones[4]	500	S:	34.4	---	---	de Marco et al. (2008)
		L:	53.5	37.9**	---	
		G:	12.2	---	---	
Mobile Phones[4]	500	S:	30.3	---	---	de Marco et al. (2008)
		L:	57.4	34.2**	---	
		G:	12.3	---	---	

[1]S: Solid products, L: Liquid products, G: Gaseous products; [2]Heating values in $MJ\cdot m^{-3}$ were calculated under standard conditions (0 °C and 1,01325 bar); [3]PE-rich fraction after conventional removing of Al und Cu by Flotation; [4]Waste streams after grinding and separation of magnetic parts from table and mobiles phones, respectively

3.1. Behavior of halogenated compounds in pyrolysis processes

In order to reach the aims of metal accumulation and fuel generation from WEEE, a fundamental understanding of chemical reactions in pyrolysis processes is necessary. The following part of this chapter describes these reactions for plastics and polymers with additives like halogenated compounds, mainly tetrabromobisphenol A (TBBPA), and Sb_2O_3. The reaction behavior of halogens and Sb_2O_3 is important for both metal accumulation and fuel generation, because due to the reactions, metals can be lost and fuels can contain Sb or halogens, which could cause problems in an energetic utilization.

To understand different decomposition ways of BFR, Marongiu et al. (2007) developed a detailed kinetic model for the decomposition of TBBPA in a pyrolysis process. They showed four representative reaction classes: initiation, propagation, molecular and termination reactions. An increase of process temperature or duration time let debromination start with a release of Bisphenol A as well as HBr and later phenol. By a further increase of temperature or time, larger organic compounds and later char are produced, while CH_4 and CO are emitted.

Similar, but quantitative results were published by Grause et al. (2008). They investigated the pyrolysis behavior of TBBPA containing paper-phenol resin laminated PWB. Thermal gravimetric analyzes (TGA) in a temperature range between 40 and 1000 °C and degradation experiments in a temperature range between 50 and 800 °C were performed. It was possible to characterize the Br-products generated during different temperature levels. Three levels in which the samples degraded where found. In a first step, with a maximum at 272 - 280 °C, H_2O and CO_2 evaporated from decomposition of cellulose. During the second step (270 - 370 °C) the contained fire retardants degraded by forming Br-products. The production of HBr, as main product from decomposition of BFRs, proceeded in a temperature range between 270 and 500 °C and was characterized by two single peaks, located at 305 °C and 398 °C. During the third step, beginning with a temperature of 370 °C, phenol resins were decomposed and char was formed. The generation of brominated aromatic compounds took place just in a temperature range between 270 and 400 °C. Above 400 °C, Br-products were formed primarily as HBr, so that phenol products generated at 450 °C showed a low concentration of Br. Therefore it was concluded, that a pyrolysis at 450 °C produces mainly HBr, which is easily separable in a water trap, and just a small yield of brominated aromatic compounds, which could act as precursors for the generation of PBDD/F (Marongiu et al., 2007).

As mentioned above, BFR are often applied in combination with metal oxides like Sb_2O_3, which act as synergist. Depending on the temperature during thermal treatment of fractions of WEEE, various Me_x-X_y-Br_z-compounds are formed. These reactions are an interesting aspect concerning pyrolysis processes as part of a recycling chain for recovering metals from WEEE. On the one hand, due to Br-fixation reactions, metals could vaporize as Me_x-X_y-Br_z-compounds and become enriched in the liquid or gaseous phase. On the other hand, the presence of metals and metal oxides could influence the production of brominated compounds which could act as precursors for the generation of PBDD/F (Marongiu et al., 2007). As an example Bhaskar et al. (2002) revealed that HIPS containing both Sb_2O_3 and decabromodiphenylene ethers (deca-BDE) produces dioxins at a temperature of 275 °C. To figure out the reaction behavior of Sb-oxides, mainly Sb_2O_3, Jakab et al. (2003) investigated the thermal decomposition of HIPS with BFR, whereat selected samples contained Sb_2O_3. They presented~~,~~ that the thermal decomposition of PS was not affected by presence of BFR. PS decomposed mainly in one single peak at about 440 °C. In contrast, the thermal decomposition of PS with addition of 5 wt.-% Sb_2O_3 took place in two single peaks at approximately 370 °C and 440 °C. As suggested by Luijk et al. (1991), pyrolysis tests at 420 °C confirmed that Br vaporized during the first stage of decomposition in form of $SbBr_3$ and different brominated organic compounds. Rzyman et al. (2010) pyrolysed TBBPA and Sb_2O_3 up to a temperature of 650 °C and quantified the yield of $SbBr_3$. Between 440 and 650 °C the maximum yield of $SbBr_3$ (above 60 wt.-%) vaporized. Due to a further increase of temperature above 650 °C, the reduction of Sb_2O_3 started with the result that Sb remained in the solid residue as elementary Sb. Bhaskar et al. (2007) and Mitan et al. (2008) treated samples of mixed brominated plastics, with and without adding Sb_2O_3 in a two-stage pyrolysis at 330 °C, for two hours, and 430 °C, till the end of the experiment. Sb_2O_3 mainly reacted with Br by forming $SbBr_3$, which was identified just in oils from the first pyrolysis stage but not in those from stage two. A small yield of Sb was found in the residue. By adding Sb_2O_3, the yield of oil from stage one was highly increased, whereas the yield of step two oils decreased slightly. Also, there was a slight increase of gas yield and a high increase of solid residues. The results revealed that in a pyrolysis of brominated plastics degradation takes place in three steps while at 450 °C mainly HBr and just a small amount of brominated aromatic compounds are formed. However, due to the presence of metal oxides both levels of degradation and Br containing products as well as the yield of solid, liquid and gaseous products can vary.

3.2. Dehalogenation

Dehalogenation of pyrolysis products is one of the main topics concerning thermo-chemical treatment of WEEE. The subject summarizes methods and techniques to gain pyrolysis products with low yields of halogens and to reduce toxic emissions as much as possible. Only if the pyrolysis products have low yields of halogens, they can be utilized appropriate. For example, in order to apply produced liquid fuels in a CHP for the production of power and heat, a considerably low content of halogens has to be ensured.

There are several ways for dehalogenation, which could be classified as (1) separation of pyrolysis and dehalogenation, (2) the use of additives in a co-pyrolysis, and (3) procedural approaches as well as combinations of these three ways. In a co-pyrolysis not only WEEE is thermally treated but also other waste materials or additives. An example for the first mentioned approach is the "Pyromaat" process, which was developed to recover Br from WEEE in a process combination of pyrolysis and gasification. The pyrolysis runs at 550 °C for a minimum of 15 minutes. The produced char-metal mix was used as feedstock for pyrometallurgical processes. The uncondensed gas fraction was lead through a high temperature gasifier at 1230 °C to crack tars and to produce a syngas. The syngas is cleaned by a NaOH-scrubber to remove and recover halogens as NaBr / NaCl. The remaining syngas is used in a combustion chamber, where NH_3 is injected as neutralization agent for remaining halogenated compounds. Halogens from the input material volatilized as HBr / HCl, Br_2 / Cl_2 and, in connection with Sb_2O_3, as different halogenated Sb-compounds, which hydrolyze to Sb_2O_3 in the scrubber. The described process was able to recover up to 96 wt.-% of Br and 97 wt.-% of Cl (Boerrigter et al., 2002).

The use of biomass as an additive is another approach for dehalogenation and prevention of PBDD/F. Liu et al. (2013) performed a co-pyrolysis of plastics from WEEE and biomass. Adding biomass to the pyrolysis of WEEE seems to prevent the formation of PBDD/F due to a high amount of hydrogen, which leads to a formation of HBr / HCl. However, to increase the amount of hydrogen in the feedstock, hydrogen-rich waste plastics like PP could be added to receive the same results (Hornung et al., 2005).

A two-stage pyrolysis, with or without additives, is the third option to reduce the amount of halogens, mainly in the pyrolysis oil. It is based on the different temperature dependencies of thermal degradation of polymers and flame retardants. Bockhorn et al. (1998) and Ma et al. (2002) described this degradation behavior for chlorinated, Hornung et al. (2003) and Jakab et al. (2003) for brominated polymers. However, due to the composition of the feedstock and the use of additives, there could be different levels of thermal degradation. The following sections will give a brief overview at which temperatures thermal degradation of BFR containing plastics takes place and how thermal decomposition is affected by additives like calcium compounds or BFR synergists like Sb_2O_3.

Bockhorn et al. (1999) investigated the thermal degradation behavior of halogenated plastics, mainly PVC, and showed that dehydrohalogenation takes place at lower temperatures than the degradation of thermoplastics. Due to this, they estimated that a separation of pyrolysis products in fractions containing halogens and halogen free fractions could be possible, corresponding to the two degradation stages. They developed a two-stage process, called Haloclean®, that was operated at 350 (first stage) and 450 °C (second stage) under nitrogen atmosphere. However, it could not be shown that the process is able to produce halogen-free oil, but in comparison to other process parameters, with the two-stage pyrolysis at 350 and 450 °C for two hours each, the lowest yields of PBDD/F in the solid residues could be achieved (Koch, 2007). Later the process chain was successfully upgraded with a downstream polypropylene-reactor, to clean the oil from halogens and to produce HBr (Hornung et al., 2007).

Zhu et al. (2008) examined the decomposition of PVC samples with different Ca-based additives ($CaCO_3$, CaO, $Ca(OH)_2$) by TGA. Ca is an effective additive to capture hydrogen-halogen compounds, mainly HCl and HBr, in the solid residue as $CaCl_2$ / $CaBr_2$. The degradation of PVC took place between 280 and 400 °C with a maximum at 320 °C as well as between 400 and 560 °C with a maximum at 482 °C. HCl was released in the first stage, hydrocarbons in the second one. Without additives, Cl was completely found as HCl after degradation. By adding Ca-based additives, the yield of HCl decreased while the yield of $CaCl_2$ increased. To use the tested Ca-based additives as agents to achieve less HCl in the pyrolysis products, Ca/Cl molar ratios of 1.5 for $Ca(OH)_2$, 1.5-2.5 for CaO and 2.6 for $CaCO_3$ were recommended. To enhance the efficiency of dehalogenation by a Ca-based additive, Bhaskar et al. (2002, 2004) formed a Ca-C catalyst by kneading, molding and calcination of a mixture of $CaCO_3$ and phenol resin. Pyrolysis tests of a plastic-mixture containing Cl and Br were performed at 430 °C and revealed that the tested catalyst seemed to be very effective: without catalyst, pyrolysis oils contained a minimum of 0.49 wt.-% of Br and 0.12 wt.-% of Cl. In contrast, oils from a pyrolysis test with 20 - 80 wt.-% of Ca-C catalyst contained a maximum of 0.07 wt.-% of Br and 0.01 wt.-% of Cl. Due to the addition of the catalyst, the yield of liquids and solid residues decreased while those of gaseous products increased. In addition, the composition of the liquid products changed: the yield of C_6-C_{10} hydrocarbons increased highly by 50 wt.-% and the yield of C_{11}-C_{15} hydrocarbons slightly, but higher hydrocarbons (C_{16}-C_{20}) decreased significantly. Similar results were published by Mitan et al. (2007), who tested different catalysts during thermal degradation of HIPS-Br and ABS-Br at 450 °C. It was concluded that a combined catalytic system based on folded sheet mesoporous silica (FSM) and a "calcium to carbon composite" offers low concentrations of Br, N and O in the oil and the highest quantities of oil and gas with mainly short-chained hydrocarbons. These results, obtained by Bhaskar et al. (2002, 2004) and Mitan et al. (2007), reveal that a process with an effective dehalogenation by additives is able to produce fuels with good quality concerning energetic utilization (low amounts of metals, halogens, N, O and higher hydrocarbons (>C_{16})). Using other additives like red mud or calcined limestone can present another option to decrease the parameters of Br- and Sb-yields. Wu et al. (2014) conducted pyrolysis tests at 500 °C with HIPS containing BFR and Sb_2O_3 in addition with red mud, calcined limestone or natural zeolite at a ratio of 5 to 1. Mainly by adding red mud or limestone, the content of Sb and Br in pyrolysis oils decreased significantly between 72 and 81 wt.-% for Sb and between 88 and 90 wt.-% for Br, respectively.

The effectiveness of two-stage pyrolysis processes for dehalogenation is strongly affected by the composition of the input material. Tests by Blaszo et al. (2002) revealed that the effectiveness decreases e.g. for PWB. Experiments with PWB-samples consisting of brominated phthalic polyester and ceramic fibers were conducted at 450 and 600 °C for 20 seconds each. The authors recommended that the decomposition of the contained flame retardant bisphenol A was not successful by two-stage pyrolysis. Furthermore, pyrolysis tests with different additives (CaO, ZnO, Na_2CO_3, Na_2SiO_3, NaOH and two kinds of molecular sieves (5A and 13X)) were performed to identify relative amounts of CH_3Br as well as Br- and Br_2-phenols. Concerning matters of health, safety and product utilization, the quantity of these products is crucial. For instance, CH_3Br is hardly inflammable, potentially explosive and toxic (Sigma Aldrich, 2014). An increased yield of CH_3Br occurred after the addition of molecular sieve 5A, ZnO and NaOH. The addition of CaO or ZnO resulted in an increased yield of Br- and Br_2-phenols, whereas all other kinds of additives, mainly NaOH and Na_2SiO_3, caused a decreased yield.

The most significant reduction of CH_3Br, Br- and Br_2-phenols was observed after the addition of molecular sieve 13X as well as after the addition of Na_2SiO_3 (Fig. 3). These results revealed that the use of molecular sieve 5A, ZnO or NaOH is disadvantageous while that of molecular sieve 13X or Na_2SiO_3 seems to be advantageous. Further analyses on the formation of other brominated compounds, mainly HBr, molecular bromine (Br_2) and brominated metals, are necessary to figure out which additives have the most promising effects.

3.3. Halogen fixation with metals and metal oxides

As shown in the previous part 3.2, a number of scientific papers deal with the co-pyrolysis of plastics from WEEE with metal oxides or silicates. One of the main reasons for the application of additives is to bind halogens as Me_xX_z or $Me_xO_yX_z$. Concerning the recycling of mainly ignoble critical metals, the reactions are relevant to understand vaporization of these metals from the solid residue into the condensable phase. The following section focuses on the halogen fixation with metals and metal oxides in pyrolysis processes.

Alston and Arnold (2011) operated pyrolysis tests at 800 °C with two different mixtures of plastics, both typically used in EEE. One of these samples contained an amount of 11.4 wt.-% Cl, mainly from PVC and 6.7 wt.-% Ca, mainly in form of $CaCO_3$, which serves as a filler material in PVC-plastics. The yield of potential fuels was about 72.0 wt.-% (45.5 wt.-% permanent gases and 27.8 wt.-% oils including tars). The authors presented an interesting aspect on bromine fixation: the amount of Cl and Ca in the solid residue was much lower than in the input material. In addition, only a small amount of Cl and no Br was detected in the liquid phase. The authors suggested that Cl reacted with $CaCO_3$ by forming water-soluble $CaCl_2$, which could be removed in a water-trap.

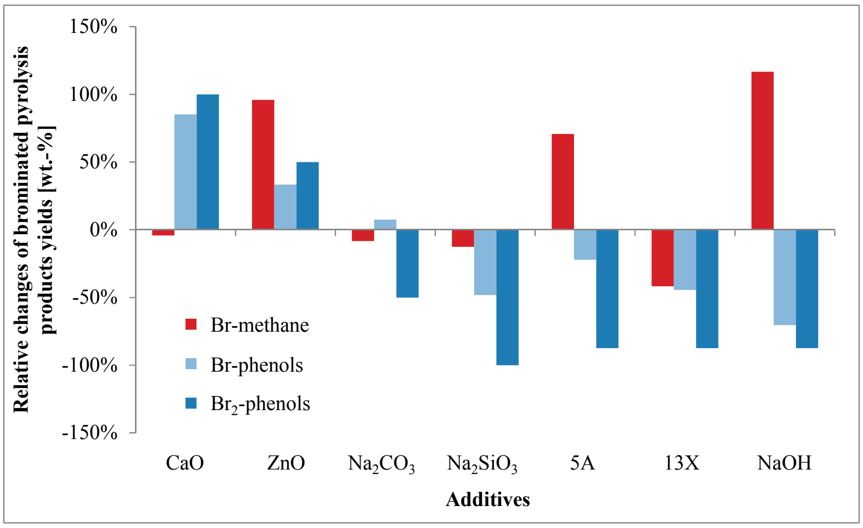

Fig. 3. Relative changes of brominated pyrolysis products yields (Br-methane, Br-phenols and Br_2-phenols) in relation to the yields without additives (Blazsó et al., 2002)

Grabda et al. (2009, 2011) investigated a stoichiometric mixture of ZnO and TBBPA (3.34:1). The impact of temperature and process duration on the formation and vaporization of $ZnBr_2$ has been examined. The tests clearly revealed that the diffusion of $ZnBr_2$ significantly depends on dwell time. At even higher temperatures of 850 °C and above, a deoxidation process of $ZnBr_2$ into elementary Zn took place with char reacting as reductive while CO and CO_2 were formed.

Further studies on Br-fixation reactions by metal oxides are published by Terakado et al. (2011, 2013). In the first examination they compared the Br-fixation ability of ZnO, Fe_2O_3, La_2O_3, CaO und CuO during the thermal degradation of TBBPA. Both TGA and pyrolysis experiments were carried out at 400 °C and 800 °C under He-atmosphere with mixtures of 1:1 for Fe_2O_3 and 1:2 (TBBPA : metal oxide) for all other oxides. Similar to those results of Grause et al. (2008) (chapter 3.1), the amount of HBr strongly increased at higher temperatures, regardless the presence of metal oxides. In case of pure TBBPA, about 90 wt.-% of Br was formed as HBr at a process temperature of 800 °C. The addition of metal oxides decreased the amount of HBr by minimum 30 wt.-% (CuO) and maximum 99 wt.-% (La_2O_3). To take a look at other WEEE fractions, Terakado et al. (2013) examined the Br-fixation ability of metal oxides using PWB as feedstock material. Fe_2O_3 showed similar suppressive effects on HBr formation like with the TBBPA as a feedstock. However, the impact of CaO and La_2O_3 decreased while the impact of CuO and ZnO increased. The authors explained the reduced effect of CaO by deactivation reactions with glass fibers contained in PWB, e.g. due to the formation of Ca-silicates. With respect to the yield of precursor compounds of PBDD/F, due to the addition of ZnO no bromophenols were formed. Furthermore, the addition of metal oxides led to an enhanced yield of CO_2 in the pyrolysis gas and of heavy metals in the solid residue. Heavy metals, especially Cu, act as catalyst during the formation of PBDD/F (Dettmer, 2001; Sakai et al., 2001).

Oleszek et al. (2013a) investigated the distribution of Cu, Ag and Au in a mixture with TBBPA and TTBPA-TBBPA-diglycidyl ether copolymer (TTDE) at different temperatures between 320 and 1000 °C. Pyrolysis of mixtures with TTDE delivered the following results: at 370 °C, about one quarter of Cu was brominated. At 600 °C, more or less half of the present Cu and Ag was brominated and, in case of Cu, a very small amount of CuBr / $CuBr_2$ was vaporized (0.4 wt.-%). Due to a further increase of temperature up to 1000 °C, more than one third of Cu and Ag was vaporized as MeBr, whereas Au did not react with Br. The study points towards fixation of Br in form of metal bromides, which explains the translocations of metals in WEEE pyrolysis. Two further studies by Oleszek et al. (2013b, 2013c), dealing with pyrolysis of TBBPA-Fe_2O_3 and TBBA-PbO mixtures, delivered similar results concerning metal bromination. The results from the different tests concerning reactions of metals and metal oxides with brominated compounds TTDE (Cu, Ag) and TBBPA (PbO, Sb_2O_3, ZnO) are shown in Fig. 4.

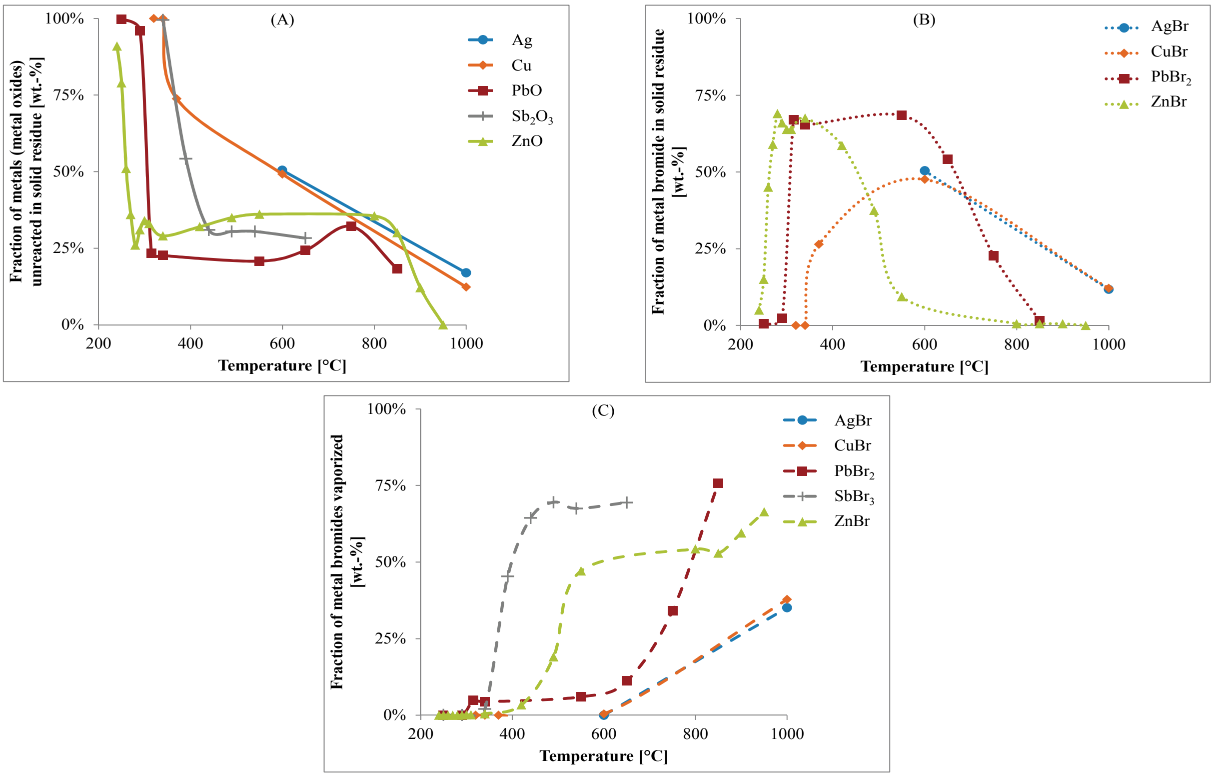

Fig. 4. Fractions of metals (metal oxides) unreacted in solid residues (A), metal bromides in solid residues (B) and metal bromides vaporized (C) (Grabda et al., 2009, 2011; Oleszek et al., 2013a, 2013c; Rzyman et al., 2010)

The available results from literature so far suggest that pyrolysis temperatures below 600 °C do not affect vaporization of (brominated) copper and precious metals. However, less noble metals like Sb, Pb or Zn become brominated, and increasingly vaporize with a rise of temperature and dwell time. After being separated, either from the liquid and gaseous phase or from the fly ash, these metals can be subjected to special electrochemical recycling processes for further treatment. However, the investigations also revealed that the better part of metals does not vaporize in pyrolysis processes. Due to char in the solid residual fraction, metal oxides usually become deoxidized, so that remaining metals may easily be separated by density slicing. Further analyses on different metals to identify their reaction behavior with halogens in a pyrolysis process are necessary.

4. Conclusions and outlook

WEEE contains a number of economically relevant metals like Cu and precious metals, and also critical metals such as Ga, Ge and a number of REE. However, the end-of-life recycling rates from WEEE are low and sometimes even less than one percent. Pyrolysis of WEEE-fractions offers the opportunity to separate valuable metals from plastic matrixes and to produce liquid and gaseous fuels at the same time. The process could represent a main part in a more comprehensive process chain to separate organic matter on the one hand and different fractions enriched with metals on the other hand. These metal fractions can be further sorted and subjected to specialized electro- and pyrometallurgical post treatment. The key procedural challenges for such a process chain are dehalogenation, avoidance of highly-toxic emissions (mainly PBDD/F) as well as preparation and accumulation of metals for the specialized recycling processes.

To design this process chain, temperatures between 250 °C and 450 °C should be avoided to prevent the formation of PBDD/F. Br has to be captured either as evaporating compound, mainly in the form of HBr or $SbBr_3$, or in the solid phase in the form of metals as metal bromines. To achieve a translocation of Br as HBr with only low amounts of brominated aromatic compounds, pyrolysis should be operated in a temperature range between 450 and 500 °C. The water-soluble brominated products HBr and $SbBr_3$ could easily be captured by downstream H_2O- or NaOH-filters. At lower temperatures, predominantly brominated organic compounds, with mainly brominated phenols, are formed. They could act as precursor substances for the formation of PBDD/F. Other options for dehalogenation were presented, which could be advantageous for dehalogenation of remained Br and Cl. Two-stage pyrolysis shows a good way in case of selected Cl or Br containing plastics. However, in a mixture consisting of plastics and other compounds like PWB, metals and ceramics, dehalogenation by two-stage pyrolysis did not show the desired success. In this case, thermal decomposition of plastics took place in two or more peaks with the negative effect that not only oil from the first pyrolysis stage contained halogens but also that oil from the second stage. Another option for dehalogenation is to capture halogens as part of the solid residue, e.g. by Na- or Ca-based additives. Mainly Na_2SiO_3, $CaCO_3$ and Ca-C composites seem to be very effective to fixate Br as NaBr or $CaBr_2$, respectively.

Furthermore, investigation of the quality of pyrolysis oils is necessary in respect to energetic utilization. Due to the addition of a Ca-C catalyst, for example parameters characterizing the quality of produced oil were optimized, mainly because the amount of higher hydrocarbons strongly decreased while the amount of smaller ones ($<C_{10}$) increased. In addition, more analyses has to be conducted concerning the quantity of all remaining Br-compounds HBr, Br_2, Br-phenols, brominated metals and toxic compounds like CH_3Br, since the process configuration loses its merit, if on the one hand most Br is captured as $CaBr_2$, but on the other hand the yields of hazards like CH_3-Br increases.

From a practical point of view, the obtained findings suggest that the pyrolysis technology offers an opportunity for recovering metals and energy from WEEE. Actually an accumulation of base and precious metals is still possible without using additives. However, concerning the recovery of critical metals a co-pyrolysis with different additives should be tested, in order to capture halogens before they could react with this kind of metals. In this context especially further analyses on different metals are necessary to identify their reaction behavior with halogens in a pyrolysis process. Additionally, there are several additives which modify the quality and quantity of produced oil and gas. These are potential fuels for a decentralized, energetically self-sufficient process chain for treating different fractions from the WEEE treatment.

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DEVELOPMENT OF A MULTRICRITERIA INDICATOR OF VIRTUOSITY IN WASTE MANAGEMENT ADDRESSED TO LOCAL AUTHORITIES

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Abstract

As the percentage of segregated waste, taken as individual indicator, is insufficient to measure the virtuosity of a Municipality waste management, a multicriteria indicator has been developed to broaden the horizon of the analysis of waste management performance. The aim of this study is to experiment a new and easy–to-use methodology for the evaluation of Municipalities virtuosity in waste management, built from Public Administrators to verify the responsiveness between their ideal guidelines and their real applications. The identified criteria are eight: percentage of segregated waste collection, production of unsorted waste per capita, total production of waste per capita, service costs, environmental impact of the waste collection and treatment system, traceability of Municipal Solid Waste's fate, involvement of population, citizen's convenience. Scores given to each criterion were assigned by experts in each field and then normalized [0-1]; weights were determined applying Pairwise Comparison method to Public Administrators of municipalities selected as a case study. For each Municipality, a score for each criterion is assigned and, subsequently, multiplied by the weight given to the criterion itself. The indicator provides a wide spectrum analysis, marking the state of the art, the scope for improvement and deficiencies of each area of analysis; thus to become an effective decision support tool for Administrations. This tool was, applied to a case study, returning results in terms of virtuosity far different from those obtained in terms of percentage of recycled waste alone, thus highlighting the importance of a multidisciplinary approach to the issue.

Key words: Analitic Hierarcy Process, involvement of population, Multi-Criteria Decision Analysis, Municipal Solid Waste Management, Pairwise Comparison

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1. Introduction

The percentage of segregated collection is the only indicator of virtuosity in waste management applied to municipalities so far in order to check their performance. This measurement, however, is incomplete (Matei and Ungureanu, 2014; Simion, 2013): it is now known that, beyond the percentage of segregated collection, other conditions could define the virtuosity of a waste collection system (Simion et al., 2014), for example the amount of waste products, the cost applied for the service or the environmental impact generated by the waste collection and treatment. In the present study were collected these and other criteria relevant to the overall performance assessment of a municipality with respect to the production, collection and treatment of waste, in order to build a more complete analysis of virtuosity of local authorities in waste management. The indicator is proposed with two objectives: first, being a multi criteria indicator, overcoming the contradictions and partiality of the measure of the percentage of segregated collection alone; secondly, providing municipal government

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with a tool to address their investments in the improvement of the waste management system more effectively, in order to reach the European strategic objectives in waste management (Sarkady et al., 2013a, 2013b).

The methodology selected was the Analytic Hierarchy Process, a multi criteria decision analysis method already used in waste management field (Kim et al., 2013; Pires et al., 2011; Soltani et al., 2015). In this study a different perspective is outlined: the target of the Analytic Hierarchy Process is not finding the best alternative, but only giving an evaluation to the Municipalities involved, in order to put in evidence their strengths and weaknesses compared to the theoretical guidelines they give themselves.

Thus resulting in a decision support tool built on the results of the analysis. Another novelty is that the case study Municipalities were directly involved in building the scores and weights system to be applied to the criteria: they were asked to express their point of view on the basis of their decision criteria on which they base their policies. This indicator is built by Municipalities for Municipalities.

The aim of this study is to develop a new methodology for the evaluation of Municipalities virtuosity in waste management: for this reason the focus of the paper is on the building of the indicator, while its application on the case study is summarized as an example, in order to give an idea of the potentiality of this methodology.

The Analytic Hierarchy Process is defined as follows: the goal is the numeric evaluation of the virtuosity of a Municipality; the criteria of evaluation are eight and they were chosen from a pre-selection performed by the authors, in order to evaluate all the main issues connected with waste management, and then they were re-defined by the Municipalities in order to meet the needs of verification of local authorities; finally the alternatives are eight Municipalities of the case study. They were chosen because of their organisation: not only they form a formal Union, but also they organized Municipal Waste collection as a “Smart Area”, with the same management and different options of application for all the eight Municipalities.

The indicator of virtuosity was built in relation to the case study of the territory of the Unione Terre di Castelli, a union of eight municipalities of small and medium size, with a total population of about 82 000 inhabitants in a territory extended over an area total of 312.15 km² in the Province of Modena, Emilia-Romagna, in Italy. The involvement of local stakeholders in the definition (including mathematics) of the evaluation model represents a strong element of novelty: service managers, mayors and local administrators, municipal technicians, universities, experts from the sectors involved, associations, and citizens contributed to define the structure of this indicator of virtuosity. These subjects and mayors in particular, were chosen for their public role of decision-makers and they were asked to assess the weights to be assigned to different criteria.

The proposed methodology for the allocation of weights is the Pairwise Comparison (Saaty, 1980), which allows decomposing a multi-dimensional problem in a number of two-dimensional problems and, through a simple matrix calculation, to obtain the weights attributed to each indicator.

Therefore, the virtuosity indicator was applied to the eight municipalities of the case study, showing for each performance for each criterion, and the overall result, how the various management decisions affect the virtuosity of waste management. Finally, the virtuosity indicator proved to be an effective decision support tool, able to mark the state of the art, as well as the scope for improvement and deficiencies in each area of analysis.

2. Materials and methods

The study started with the identification of eight criteria constituting the virtuosity indicator: percentage of waste collection, production of mixed waste per capita, production per capita of total waste, service costs, and environmental impact of the system of waste collection and treatment, traceability of municipal waste fate, involvement of population, citizen's convenience. They were chosen in reference to the environmental, economic and social aspects to promote a systemic approach to the issue of waste

The creation of an indicator of virtuosity has gone through three main phases: deepening of environmental and management aspects associated with waste management and criteria selection; construction of the indicator of virtuosity, with criteria scoring and weighting; application of the virtuosity indicator to the case study.

The evaluation of virtuosity for Municipalities is performed by adding the scores obtained for each criterion, multiplied by the weights assigned to the criteria themselves. The development of the indicator continues with the normalization of the scores given to the criteria, carried out through interviews with key figures in each field, in order to turn these indicators making them dimensionless variables, with values in the range [0-1]. The 0-1 scale was selected because it allows a very simple normalization and convenient calculation of the scores, both in the phase of score definition and in the phase of calculation of the score reached by each Municipality for each criterion.

For the first four criteria, which were not dimensionless, an appropriate utility function was established, requiring interviewed people to assign a score from 0 to 1 to several possible values for each criterion. Through a regression curve were, then, built utility functions that associate univocally a score between 0 and 1 to each value of the criterion. The weighting of the criteria concludes the construction of the indicator. Mayors and directors of the eight municipalities of the case study were interviewed, chosen for their public role of decision-makers and proficiency in multi-disciplinary analysis. They were then asked to assess the weights to be assigned not just referring to their town, but providing a universal perspective, representative of their ideal priority scale. The proposed methodology for the allocation of weights is the Pairwise Comparison (Saaty, 1980), which allows to decompose a multi-dimensional problem in a number of two-dimensional problems and, through a simple matrix calculation, to obtain the weights attributed by interviewees to each indicator.

The method consists in comparing all possible pairs of criteria by assigning a numerical judgment of relative virtuosity among the criteria considered, according to the scale proposed in “Analytic Hierarcy Fundamental Process Scale for Pairwise Comparison”, and then on through a matrix calculation to the exact definition of the weights assigned. Pairwise Comparison was chosen instead of other methodologies (such as Ranking or Rating Analysis), because it ensures a more consistent weight distribution related to interviewee’s response, thanks to its mathematical approach. It also allows to measure distance between subsequent choices and the difficulty of responding to the interview does not increase with increasing choices.

In conclusion, the virtuosity indicator was applied to the eight municipalities of the case study, showing for each community, the performance for each criterion and the overall result. In this way, it becomes evident how the various management decisions affect the virtuosity performance of waste management and finally making it an effective decision support tool for waste management, being able to mark the state of the art, as well as the scope for improvement and deficiencies in each area of analysis. The criteria included into virtuosity indicator were:

1) Percentage of segregated waste collected [%SC]: it is obtained, following EU regulation, as the ratio of the sum of the weights of the fractions collected separately, considering both those intended to recovered and those to be disposed, and the total amount of municipal solid waste produced.

*2) Unsorted waste [kg/(ab*y)]:* it provides an indication of the ability of citizens in reducing the more impactful fraction of waste (to be disposed of in landfills or by incineration).

*3) Total waste produced per citizen [kg/(ab*y)]:* used to measure the virtuosity in reducing the overall quantity of waste.

4) Service costs [€ per capita]: it is intended as an administrative indicator, since, with the same environmental performance, the Municipality that uses less economic resource for waste management, freeing cash for other interventions, should be considered the most virtuous. It has been frequently shown that once reached percentages of segregated collection close to 65-70%, reaching higher goals involves a considerable economic effort.

It is believed that a careful administrator should ask what environmental benefit could be gained from further investments in other areas of prevention from environmental damage, such as water management, the insulation of buildings, energy production from renewable sources, the mitigation of the effects of climate change, sustainable mobility etc.

5) Environmental impact of the service: several studies show how different waste management systems produce different impacts in terms of different pollutant emissions (Marini, 2010), or of ecological footprint (Simion et al., 2013). In addition to this, the intended final fate of the waste produces different impacts on the ecosystem: to dispose a waste in landfill, incinerator or recycle it evidently produces significantly different impacts. This indicator has to be taken into account as part of an integrated environmental approach.

6) Waste fate traceability: The presence of a system of traceability of waste allows precise control of the waste fate, promoting proper disposal of waste, checking for any areas of inefficiency and making punctual communications for any difficulties in service. A traceability system allows also making the whole chain of waste management transparent.

7) Involvement of population: it takes into consideration the participation of users and the stimulus that the local administration can give in terms of political awareness and prevention of waste. National experience shows how some governments, while providing citizens with an integrated waste management service and information on how to use it, they do not share with citizens the reasons behind the legislator's requirements.

Thus leaving behind the information related to the environmental issues and the benefits that may result from a more virtuous and effective segregated collection and waste reduction. This criterion therefore takes into account the training proposed to citizens on waste and more generally on environmental issues; then consider actions taken for the prevention of waste and the ability of public administrator in engaging their citizens in the strategic choices of waste management.

8) Convenience for the citizen: the possibility to dispose of waste with the maximum flexibility during the week is a criterion which many citizens take into account. This criterion, however, evaluates even the maximum predicted distance for waste disposal, with the awareness that in most unfavorable territories (such as mountains, or in the presence of a widespread urbanization) the distance to travel to get rid of the waste produced can be crucial in participation of the population to the segregated collection.

The administration that mostly meets the proximity request was accounted to deserve the highest score in this criterion.

3. Experimental

The construction of the indicator was performed in two stages: normalization of scores and weighting of criteria.

Normalization of scores: in order to compare the above criteria, which are mutually independent and characterized by different units of measure, it is necessary the introduction of the utility functions (FU) to transform these indicators so that the dimensionless variables take values in the interval [0-1].

The definition of the utility functions is independent from the alternative collection systems commonly applied (dumpsters or curbside collection). In order to achieve this goal, the first step taken was an interview with different specialists of the issues involved by different criteria, asked to attach a judgment with respect to certain values verified or verifiable for that indicator. The opinion was expressed in numerical form by an assignment of utilities between 0 and 1, depending on the sensitivity of each respondent. With regression mathematic methods was then assigned an analytic function to each criterion that matches utility values with opinions expressed. For dimensionless criteria, experts were asked to assign scores between 0 and 1 to identified actions replicable by municipality and the sum is always equal to 1.

Identified "countable criteria", i.e. criteria with unambiguous units, are the percentage of segregated waste collected, the amount of unsorted waste, total amount of municipal solid waste and service costs. One-to-one relationships between value and judgment of utility were obtained asking interviewee judgments relating only to small number (4-7) values of all different.

The possible results for each criterion were previously divided into ranges such that the set of values presented a wider step to the extreme values and a denser one for the central values, where often even moving very little can significantly change the information provided.

All respondents were asked to judge the values present in all range, so that the interviewee sensitivity could not determine an excessive subjectivity factor.

In this way a regression curve more faithful to the data was obtained, having a sufficiently dense distribution of points on the ordinate where the opinions expressed were, and having judgments values that, while not the same, are still very close together.

They have always been respected the three axioms of utility functions:

1. U = 0 minimum utilities
2. U = 1 maximum utilities
3. (dU/dNB) ≥ 0 Utilities non decreasing

3.1. Countable Criteria

3.1.1. Criterion n°1: percentage of segregated waste collected (%SC)

Respondents were required to express judgments related to fixed values of percentage of segregated waste collected. Subject involved were Technical Support Manager Administrative Area Ferrara - Modena, Environmental Services Directorate - Hera SpA (waste management company - interview N°1); head of the environmental services of the Unione Terre di Castelli (case study - interview N°2); head of environmental services of Ferrara - Hera Spa (waste management company - interview N°3).

Following the same principle, the same respondents were asked to express an opinion on the criteria of annual per capita production of unsorted waste (criterion n.2) and the annual production per capita of total waste (criterion n.3); the obtained results are stated in Table 1, while the Fig. 1 shows the scores assigned in %SC, kg UW; Kg MSW criteria, and relative regression curves.

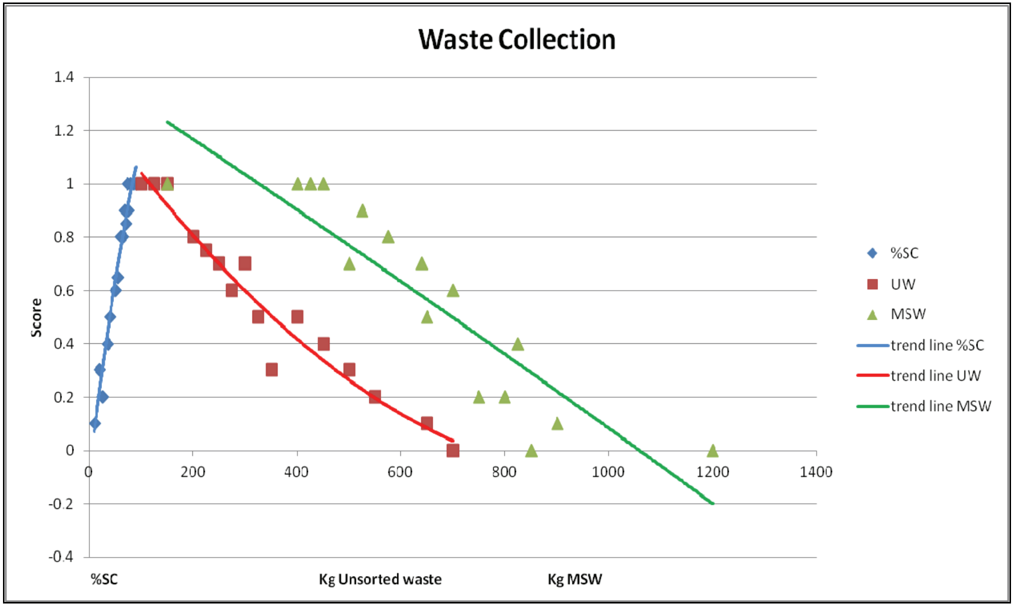

Fig. 1. Graph of the scores assigned in %SC, kg UW; Kg MSW criteria,and relative regression curves

Table 1. Results of the interview about the %SC, UW and MSW Criteria

Performance sector	***% SC***	***Interview n°***	***Score assigned***	***kg UW***	***Interview n°***	***Score assigned***	***kg MSW***	***Interview n°***	***Score assigned***
High	90	1	1	100	3	1	400	1	1
High	85	2	1	125	2	1	425	3	1
High	80	1	1	150	1	1	450	2	1
Middle-High	75	1	0.9	200	2	0.8	500	1	0.7
Middle-High	74	2	0.9	225	3	0.75	525	3	0.9
Middle-High	73	3	1	250	2	0.7	575	2	0.8
Middle-High	70	2	0.85	275	2	0.6	640	2	0.7
Middle-High	67	3	0.9	300	1	0.7			
Middle-High	65	1	0.8						
Lower-Middle	64	2	0.8	325	2	0.5	650	1	0.5
Lower-Middle	60	3	0.8	350	2	0.3	700	2	0.6
Lower-Middle	55	2	0.65	400	3	0.5	750	1	0.2
Lower-Middle	50	1	0.6	450	1	0.4			
Low	40	3	0.5	500	3	0.3	800	3	0.2
Low	35	2	0.4	550	1	0.2	825	2	0.4
Low	25	1	0.2	650	3	0.1	850	1	0
Low	20	2	0.3	700	1	0	900	3	0.1
Low	10	3	0.1						

The utility function for %SC becomes (Eq. 1):

$$y = -4^{0.5}x^2 + 0.0165x - 0.0897 \qquad (1)$$

The regression curve choice is a polynomial of the second order, with a value of $R^2 = 0.9695$

3.1.2. Criterion n°2: annual production of unsorted waste per capita (UW)

The regression curve choice is a polynomial of the second order, with a value of $R^2 = 0.9485$. The utility function thus becomes (Eq. 2):

$$y = 1^{-0.6}x^2 + 0.0027x + 1.3028 \qquad (2)$$

3.1.3. Criterion n° 3: annual production of municipal solid waste per capita (MSW)

The regression curve choice is a polynomial of the second order, with a value of $R^2 = 0.8932$. The utility function thus becomes (Eq. 3):

$$y = -9^{-0.7}x^2 + 0.0008x + 1.4834 \qquad (3)$$

3.1.4. Criterion n°4: service costs

The cost items included in the Economic Financial Plans of Municipalities were considered. To build the utility function for this criterion, all Budget Offices of case study municipalities were surveyed, and as before, were asked to formulate judgments related to specific cost values of service per inhabitant, capable of covering all the cost items related to waste management. The regression curve choice is a polynomial of the second order, with a value of $R^2 = 0.6524$. The value of R^2 is significantly lower than in the previous cases. In particular, as stated in Table 2 and in Fig. 2, one of the interviews reported values significantly distant from other experts involved, and it has significantly influenced the result because of the choice of the boundaries of the system, which provided a limited number of opinions.

It was decided, nevertheless, not to exclude the results provided the above interview because it reflect the qualified opinion of the interviewee. The utility function thus becomes (Eq. 4):

$$y = -4^{-0.6}x^2 + 0.0039x + 1.1773 \qquad (4)$$

3.2. Uncountable criteria

The “uncountable criteria” category includes the environmental impact of the service, the traceability of the waste fate, involvement of the population and the convenience of the service. Since the very nature of these criteria substantially differs from the previous ones, experts involved were required to identify some standard actions reproducible by administrations and citizens, and to assign them a score between 0 and 1 according to the importance of each action, the commitment required, the expected results and, in essence, the virtuosity assigned to a specific action.

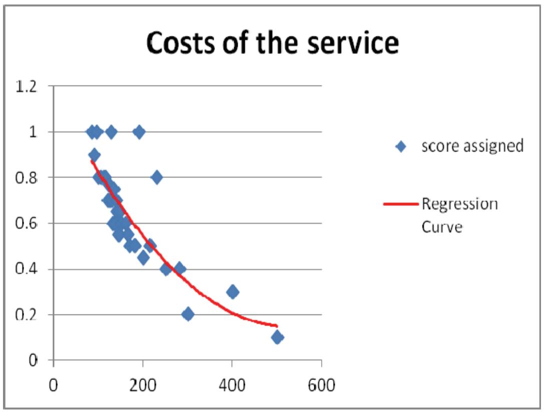

Fig. 2. Graph of the scores assigned and regression curve

Table 2. Reports of interviews with experts on service costs

Performance sector	*cost (€/yr) for inhabitant*	*Interview n°*	*score assigned*
High	80	2	1
High	85	6	1
High	90	1	0.9
High	95	5	1
High	100	2	0.8
High	105	4	0.8
High	110	3	0.8
High	115	1	0.8
High	120	2	0.7
High	122	7	0.77
Middle-High	124	4	0.7
Middle-High	126	3	0.7
Middle-High	128	5	1
Middle-High	130	1	0.7
Middle-High	132	2	0.6
Middle-High	134	6	0.75
Middle-High	136	4	0.6
Middle-High	140	3	0.7
Middle-High	142	7	0.65
Middle-High	144	2	0.55
Lower-Middle	146	6	0.65
Lower-Middle	148	4	0.6
Lower-Middle	150	1	0.6
Lower-Middle	160	3	0.6
Lower-Middle	165	7	0.55
Lower-Middle	170	6	0.5
Lower-Middle	180	1	0.5
Lower-Middle	190	5	1
Lower-Middle	200	2	0.45
Lower-Middle	215	4	0.5
Lower-Middle	230	5	0.8
Low	250	7	0.4
Low	280	6	0.4
Low	300	4	0.2
Low	400	6	0.2
Low	500	5	0.2

This procedure does not necessarily entail the presence of an analytic function representative of the opinions of respondents, but the results are divided into score ranges attributed to the actions taken by the local administrations evaluated.

3.2.1. Criterion n°5: environmental impact of the service (LCA)

The criterion of environmental impact of the service is designed to estimate the virtuosity of Municipalities in the choice of the collection system to reduce its impact on the ecosystem, in terms of pollution and use of natural resources. In building this criterion it is taken into account that very rarely Municipalities submit its waste management system to a comprehensive Life Cycle Assessment. Therefore, this criterion is built by allocating points to some important aspects of waste management, in particular:

1. Type of collection (dumpster, curbside or mixed): on the basis of Life Cycle Assessment provided by literature in waste collection systems (Marini, 2010), a higher score is assigned to the dumpster collection, rather than curbside one.

<u>TYPE OF COLLECTION</u> [MAX 0:25]

- Dumpster points 0.25
- Curbside collection points 0.15

2. Ratio users/inhabitants: a greater number of users means a higher number of stops of the vehicles employed for the collection, and consequent greater pollution. In order to avoid disadvantaging excessively the most populous municipalities, the number of users is normalized the number of inhabitants.

<u>REPORT USERS/POPULATION</u> [MAX 0:25]

- *(Utilities/Inhabitants)< 0.35*	0.25 points
- 0.35<*(Utilities/Inhabitants) <0.45*	0.20 points
- 0.45<*(Utilities/Inhabitants)<0.60*	0.15 points
- 0.60< *(Utilities/Inhabitants)<0.75*	0.10 points
- *(Utilities/Inhabitants)>0.75*	0.05 points

3. Distance traveled: it is the distance of Municipality from the landfill or treatment center used and points assigned are divided into distance bands.

DISTANCE (average distance of landfills and treatment plants) [MAX 0:25]

1. d ≤ 50 km	0.25 points
2. 50km ≤ d ≤ 100km	0.10 points
3. 100km ≤ d ≤ 300km	0.05 points
4. 300km ≤ d	0 points

4. Waste destination: as stated in Table 3, for each sorted waste fraction, it is awarded the highest score in relation to the recycling (or quality composting for organic) and a lower one if the waste is destined to incineration or landfill. For unsorted waste, the highest rating is assigned to the incineration for energy recovery and lower to landfill in accordance with the European Community instructions.

DESTINATION OF WASTE (to be weighted on quantities of each fraction) [MAX 0:25].

The allocation of scores, however, ignores the fact that the local administration can not decide the final destination of the waste, which remains exclusive prerogative of the waste manager. For this reason it was decided to give all municipalities a fixed score amounted to 0.3 by the sum of points 3 and 4. The scores due to the type of collection and ratio users/residents are assigned on the basis of strategic choices of each Administration.

3.2.2. Criterion n°6: waste fate traceability

A Councilor for environmental policies of one of the case study Municipalities was interviewed on this issue as carrier of one of the most advanced traceability methods applied in Italy for segregated collection through dumpster along the roads.

An effective traceability system of municipal waste fate associates each user with the amount of waste produced for each waste fraction and it works mainly on two fronts: on one hand, the ability to sanction users who deliberately or carelessly performs an incorrect waste disposal, on the other the opportunity to reward the most virtuous citizens through tax cost discharging. Another significant advantage is the ability to introduce a punctual communication to the users who misapply - or not apply - some or all of segregation fractions for recycling. It is possible, in fact, that these people have not understood how to profit of the waste management system and, verifying this through the traceability system, the administration is, then, able to intervene in time to provide correct information and solve the problem.

From the management point of view, the Municipality and the Managers are also facilitated by the presence of a monitoring system in the definition of strategic choices. Being able to know the usage rate of the service by all users, in fact, they would be better able to develop studies on trends of use, in order to improve the efficiency of the system.

From the citizen's point of view, it is commonly believed that the ability to easily access data about their own contributions as well as aggregates information on the overall management of waste in the municipal area and to their destinations, can be an incentive to users to improve their segregated collection. The awareness of no longer being an anonymous user, but a verified citizen would improve user empowerment.

A disadvantage of traceability systems is clearly the high costs of installation and management, due to the increased complexity in the system and the possible adversity of the users, who do not perceive the benefits and complain about increased discomfort of the system.

The respondent has identified four actions that mark the different degrees of virtuosity of a municipal administration traceability system of waste:

1. The presence of an agreement with Voluntary Ecological Guards or other agencies or organizations for the control and sanction of improper waste disposal.
2. The existence of a traceability system for household waste though which the Municipality is able to recognize precisely the disposal of different users.
3. The transparency of information with the possibility for citizens to access the data of their own contributions and the overall management information of waste in the municipal area.
4. The presence of economic incentives and rebates on the tax for more virtuous citizens.

Each action is assigned a score of 0.25, as it is believed that each of these procedures can produce a benefit of the same order of magnitude. Note that this procedure will only set goals that can be achieved with different instrumentation and perfectly adaptable to any waste management system (curbside or dumpster collection or mixed). It is even not necessary that a municipality implements the action number one to activate subsequent actions and accessing to its benefit, leaving every administration free to implement whatever action it deems most effective or viable, being, nevertheless, able to be rewarded by an improvement in the indicator of virtuosity.

Table 3. Scores assigned for each type of waste according to the destination

UNSORTED WASTE		***PLASTIC***		***GLASS***	
landfill	0.02 points	landfill	0.00 points	landfill	0.00 points
incinerator	0.05 points	incinerator	0.04 points	incinerator	0.00 points
		recycling	0.05 points	recycling	0.05 points
		PAPER		***ORGANIC***	
		landfill	0.00 points	compost quality	0.05 points
		incinerator	0.03 points	landfill	0.03 points
		recycling	0.05 points	anaerobic digestion	0.04 points

3.2.3 Criterion n°7: involvement of population

This criterion was created with the aim of measuring the ability of Municipalities to form their own citizens on the importance and proper use of the waste collection, to reward the strategies put in place by the Administration, by individual citizens or by entrepreneurs, on waste prevention, and, finally to build the real possibility for the users to intervene in the strategic choices regarding waste management.

The significant initiatives in the field of information and waste prevention are evaluated, being taken by individuals or groups of citizens, as the virtuosity of the Municipality is not only meant as a management skill of the Administration, but also and above all as the answer provided by the community to the waste issue. It remains true that, despite the scarcity of resources available, the City Council may provide significant results, creating the network between those who must get rid of a product and others possibly searching it for their own purposes.

This policy aims to support the leading role of citizens in the management of this important environmental issues, seen as a concrete tool of democracy, a facilitating factor and sometimes a prerequisite to the achievement of the expected results, whereas policies and actions widely shared with the users of the service can produce significant improvements.

To develop this criterion, two founders of the Transition Movement in Monteveglio (BO) were interviewed, which is a cultural and environmental movement engaged in “a dedication to the creation of tangible, clearly expressed and practical visions of the community beyond its present-day dependence on fossil fuels. The primary focus is not campaigning *against* things, but rather on positive, empowering possibilities and opportunities” (Hopkins and Lipman, 2009). One of the cardinal principles of the Transition is openness and involvement "bottom-up" of the larger part of the community as possible.

From the interview conducted emerge some pivotal actions, such as systematic information of the population (underlining the ineffectiveness of meetings and conferences organized from time to time), or the creation of a cultural density in which a continuous and pervasive signal would be able to change bad habits. This is not always possible at all levels of society, but in the experience of the respondents, the widespread presence of target educational activity in schools is very effective, which in many cases has led the boys to involve their own families in the activation of virtuous behavior. Another level of strategic actions emerged from the interview covers all initiatives aimed to waste prevention, considered the priority solution rather than the mere segregated collection of waste. It is considered in fact much more virtuous a reduction policy applied in "upstream", capable of greatly reducing the problem of costs and disposal and which can also be made by individuals, rather than a management “downstream” which is not always effective.

Finally, the participation of the population can have a very positive impact if citizens are really involved in management decisions: the involvement can be defined accordingly to the scale of participation provided by Lewanski (2009). It is emphasized that the actions of involvement of the population often have not an immediate a return, but the investment in the formation of a widespread civic and environmental consciousness can bring very convincing results over time, if handled properly. The proposed actions and their scores are as follows:

1) Information:

- Leaflets, illustrating how to differentiate waste;
- Activities in schools, continuous and constant (for example, every year turn of training with all children of a certain class, so in time to meet all the students of the city).

2) Waste prevention:

- Promotion of home composting, while decreasing the percentage of segregated waste of the organic fraction, this initiative produces a significant economic and environmental benefits, producing a local compost to be entirely reused, preventing issue related to transport, treatment and possible rejection by the market.
- Re-use markets.
- Actions for the prevention of disposable items use:
    - agreements with the mass distribution to apply a tax reduction on municipal tax for shops proportional to the area for the distribution of products “on tap”;
    - introduction of cloth diapers in kindergartens: in addition to reducing waste from school often produces an effective conviction to families, so that they start to use cloth diapers even in their homes.

Any of these actions or other similar left to the free initiative of citizens are attributed the score shown in Table 4, the presence of more than one action, however, does not increase further the score indicator. Possible agreement between Municipality and a laboratory to perform analysis on tap water with reduced cost to the citizens, encouraging the use of public water instead of mineral water. Always with the goal of increasing the use of public water to the detriment of that bottle, the introduction of tap water distributors, to be placed in areas of passage on the streets normally traveled by users, in order not to improve traffic.

3) Mitigation:

The temporary subscription of the Last Minute Market (www.lastminutemarket.it), born from a Spin off initiative of University of Bologna or similar initiatives (such as the permanent Food Bank) is considered by respondents as an effective reuse of potential food waste, a sort of emergency management. A systematic use of this practice however, it is feared may adversely affect management practices in the food chain, considering the presence of a significant food waste as a meritorious work to the most disadvantaged population. Coupling, instead, these practices with the actions of waste reduction would close the circle of the food chain in the most virtuous way.

4) Management service:

What makes a Municipality an efficient recycler of their own waste is undoubtedly the willingness of users to participate in the collection. It is believed that the establishment of virtuous solutions for training, feedback collection and involvement of the population in the decisions about waste management practices can greatly increase the susceptibility of the users to the best use of the waste collection service.

The commitment of an administration can be declined on different levels, making citizenship more or less active participant of the decisions, to bring the "ordinary citizens" to contribute with overt behaviors to at least a part of public decisions through processes of participatory politics.

To identify the possible variations of the commitment of an administration towards public participation to decisions, interviewees suggested the use of the Participation Scale (Lewanski, 2009), which identifies five degrees in the actions that the Municipality can activate.

Into virtuosity indicator a score for each level of scale achieved has be assigned and, for simplicity, the different steps of the participation scale have been developed this way:

1. INFORM: it includes, in addition to the normal routine information on how to dispose the waste, the information on the importance of waste reduction and segregation, in a cultural and educational approach to environmental issues.
2. CONSULT: it is the ability to listen to citizens' feedback, to gather information and opinions from the users, such as in public meetings or through devoted offices.
3. INVOLVE: it requires action by the administration in research and involvement, proposing the collection of qualified opinions, so that those who present grievances or new proposals must identify themselves. This is to encourage the user empowerment that can no longer hide behind the anonymity guaranteed by the response to a questionnaire or intervention during a meeting or conference open to the public. In this phase, the Administration is not, however, obliged to answer.
4. COOPERATE: the gathering of opinions qualified is not regarded to be sufficient and it becomes necessary that the public administration fulfills its obligation to reply to all users bringing considerations and evaluations.
5. EMPOWERMENT: the final step in which the public administration decision leaves a window open to the public, which can take any decision in that space.

Score attribution: given the difficulty of assigning scores to actions so different and with so different and uncertain results remaining in a 0-1 scale, a value of 10 was attributed to the first initiative taken into consideration (the presence of leaflets), and then score were assigned for all other actions.

All scores were then rescaled to bring their sum to 1. Below there is a summary table of the scores assigned to different actions, which shows, in line with the previously stated, how waste prevention is the action deemed as the most important.

3.2.4. Criterion n° 8: citizens' convenience

Here are presented the scores assigned on the basis of the distance in the case of dumpster collection and collection frequency in the case of curbside collection. For Municipalities that have both types (in a mixed collection system), an average value weighted on the number of users served is provided, so that the maximum score is always equal to 1.

Table 4. Summary scores for the criterion "Involvement of Population"

Criterion	*Actions*	*Scores*	*Scores in 0-1 scale*	*Relative impact*
Information	Flyers information	10	0.07	28%
	School activity	30	0.21	
Waste prevention	Home composting	20	0.14	38%
	Re-use market	15	0.10	
	Water quality test	3	0.02	
	Prevention of disposable goods	10	0.07	
	Water distribution point	7	0.05	
Mitigation	Last Minute Market or Food Bank	10	0.07	7%
Participatory management of decisions	Inform	8	0.06	28%
	Consult	8	0.06	
	Involve	8	0.06	
	Cooperate	8	0.06	
	Empower	8	0.06	
SUM		145	1	100%

Dumpster collection: Presence of complete dumpster set (for all segregated fraction): 0.5 points to be added to the maximum distance between dumpsters and homes

$d_{max} \leq 100$ 0.5 points
$d_{max} \leq 150$ 0.4 points
$d_{max} \leq 200$ 0.3 points
$d_{max} \leq 300$ 0.2 points
$d_{max} > 300$ 0.1 points

It was then decided, in case of opening of the box through magnetic card, to multiply the result by 0.9, since it could represent an increased discomfort in the waste disposal operation.

Curbside collection: This is calculated on the basis of frequency of collection of each fraction and then applying an average calculation. Scores are estimated on the basis of discomfort experienced keeping waste at home for different intervals (one or two collection shifts, in case unable to deliver it at the first occasion), and presented in Table 5.

3.3. Weighting of criteria

For the delicate process of allocating weights the Mayors of Terre di Castelli Municipalities were involved. They had been chosen for their key role of public decision-makers and because they are considered the figures better able to compare criteria belonging to different policies and disciplines, something that an expert specializing in one area would find more difficult to perform. They were asked to rate the criteria providing a universal judgment as representative of their priority ideal scale.

The methodology chosen is the pairwise comparison as proposed by Saaty in the study of Analytic Hierarcy Process (Saaty, 1980), which allows decomposing a multidimensional problem in a number of two-dimensional problems. The interviewee have been proposed all possible combinations between the criteria and, attributed a score of 1 to one of the two criteria, they were asked to assign a rating of greater or lesser importance to each other on a scale from 1 to 9 if best match or from 1 to 1/9 if lower.

1: EQUAL IMPORTANCE: two elements contribute equally to the objective.

3: MODERATE IMPORTANCE: experience and evaluation moderately favor one element over another.

5: STRONG IMPORTANCE: experience and evaluation strongly favor one element over another.

7: IMPORTANCE VERY STRONG: an element is very strongly favored over the other. His domain is shown in practice

9: EXTREME IMPORTANCE: The evidence that favors an element on the other is of the highest possible order of affirmation.

Scores 2, 4, 6, 8 can be used for intermediate values. The opinions so expressed were placed in a 8x8 square matrix, whose rows and columns represent the criteria considered. The main diagonal is entirely occupied by the value 1, while the other positions host numerical assessments for the various pairs evaluated, according to the table. A weight matrix has been, therefore, produced for each auditor interviewed.

Then, calculating the right eigenvector of the matrix the weight vector is obtained, which provides the weight of each criterion. All the scores are normalized between 0-1: in order to normalize the 1-9 Saaty scale is calculated the right eigenvector of the weights matrix, that automatically normalize the scores from 1-9 scale to 0-1, reporting the weighted scores assigned from each person interviewed. The right eigenvector is defined by Eq. (5), where A is a symmetric matrix, x is the eigenvector right, λ the eigenvalue.

$$A * x = \lambda * x \quad (5)$$

Built the matrix, a verification of its consistency was needed, as the consistency of judgments provided by interviewees: the matrix is perfectly consistent if $\lambda = N$ (number of criteria) and is much more inconsistent, as $\lambda > N$. However, there is a tolerance on the number of criteria analyzed that, starting from the calculation of the coefficient of inconsistency (CI) given by Eq. (6) divided by the Random Consistency Index (RI) provides the Consistency Rate (CR) (Eq. 7).

$$CI(A) = ((\lambda max - N) / N) \quad (6)$$

$$CR(A) = CI(A) / RI(N) \quad (7)$$

The Random Consistency Index represents the consistency of a matrix of pairwise comparison randomly generated. It is derived as the average index of consistency calculated from a sample of 500 randomly generated matrices based on the scale AHP seen previously. The value of RI depends on the number of criteria, as expressed by Saaty (Saaty, 1980).

Table 5. Scores assigned to every type of waste, according to collection frequency

Scores assigned for collection frequency	*Organic Fraction*	*Unsorted fraction*	*Dry fractions (for each fraction)*
1 time / week	0.2 points	0.3 points	0.4 points
2 times / week	0.5 points	0.7 points	0.8 points
3 times / week	0.8 points	0.8 points	1 point
4 times / week	1 point	1 point	1 point

If CR (A) ≤0.1, the pairwise comparison matrix is considered significant enough. In the case where CR (A) > 0.1 the pairwise comparison matrix must be improved by modifying certain ratings. For the pairwise comparison, it was made use of the software tool MakeItRational Decision Tool, which, thanks to a graphical interface easy to understand and the real-time reporting of any inconsistent judgments, allowed to go directly to the definition of the weights that each auditor has determined, immediately creating matrices sufficiently consistent.

Finally, even if the sensitivity analysis is usually used as the confirmation of weighting strength of criteria due to pairwise comparison (Cabala, 2010; Chen and Kocaoglu, 2008; Dalalah et al., 2010), in this study it is considered unnecessary. The reason is that the aim of this paper is not to make a choice among alternatives, but to experiment a complete tool for the Local Administrations to decide how to manage their urban waste, with respect to the their policy's goals.

This function is completely performed by the indicator as described heretofore. In fact in the construction of this indicator the mayors were asked what their guidelines are. Subsequently, the application of the indicator will tell if the Municipalities are following these steps that they have set themselves.

Furthermore, weights given to the criteria would change choosing a different case study providing a serviceable ranking of Municipalities if performed on an extended case study (like a Region). In a broader framework, a sensitivity analysis would be useful as the statistical basis for interview would increase and this new setting would be particularly interesting, as the Italian Region is the competent authority in waste management.

4. Results and discussion

After interviewing the sector managers of all the Municipalities of the Unione Terre di Castelli and having collected weights assigned to each respondent to the eight criteria with the method of Pairwise Comparison, before performing the definitive allocation of weights to the criteria selected to form indicator virtuosity, the results of calculation of Random Consistency Index have been checked. In Table 6 it is shown that every matrix performed with Pairwise Comparison methodology was consistent enough. It was therefore calculated the arithmetic mean of the values obtained from the interviews; it is not a weighted average and no other correction factor is applied, since the results are the fruit of thought and sensibility of administrators, and not necessarily the synthesis of the will or the priorities of residents of the Municipality.

The results thus obtained are shown below in Table 7, "Weight" column, and in Fig. 3.

A substantial lack of a single view of the priorities related to waste management emerges from results presented, although some judgments are common to all respondents. The case of the environmental impact of waste collection and treatment is considered a strategic indicator of a virtuous waste management, while the percentage of recycling has never reached the 10% of the total weight because of the many flaws identified by the respondents on this indicator. No doubt the criterion subject to major contradictions is the traceability of waste fate, sometimes considered a good strategy to improve service and considered a waste of effort and money by other respondents.

Different levels of interest, but still significant, were provoked by the criteria related to costs (essential for a municipal administration) and involvement of the population. Among criteria for waste collection stands out the importance attributed to the amount of unsorted waste, recognized as the component of major concern for the impact it produces both on ecosystem and on municipal budget. To clarify the subject, the graph reporting weights assigned by administrators interviewed is shown below.

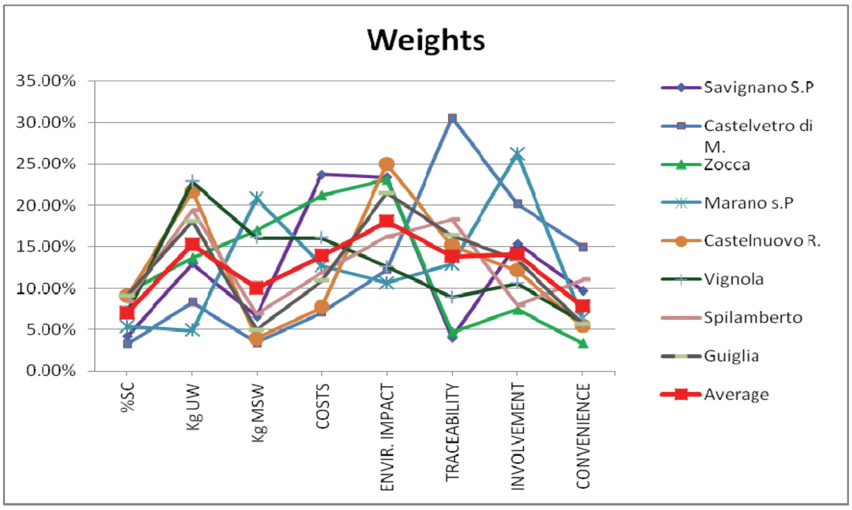

Fig. 3. Chart of weights assigned by the respondents and the average value

Table 6. Random Consistency Index calculated for the weights matrix proposed by each Municipality interviewed

MUNICIPALITY	*CR(A) calculated*	*CR(A) limit*	*RESULT*
Savignano S.P.	0.04	≤0.1	Consistent
Castelvetro	0.1	≤0.1	Consistent
Zocca	0.07	≤0.1	Consistent
Marano S.P.	0.05	≤0.1	Consistent
Castelnuovo R.	0.06	≤0.1	Consistent
Vignola	0.03	≤0.1	Consistent
Spilamberto	0.05	≤0.1	Consistent
Guiglia	0.03	≤0.1	Consistent

Table 7. Weights attributed by respondents and the scores obtained by each Municipality, for each Criterion at the end of the analysis

Municipality	*% SC*		*Kg UW*		*Kg MSW*		*COSTS*	
	Weight %	*Score*	*Weight %*	*Score*	*Weight %*	*Score*	*Weight %*	*Score*
Savignano S.P.	4.17	0.1078	12.97	0.0805	6.59	0.0648	23.74	0.1102
Castelvetro	3.26	0.0578	8.33	0.13	3.43	0.0776	7.08	0.1164
Zocca	9.53	0.0284	13.67	0.0533	16.97	0.0640	21.22	0.1067
Marano S.P.	5.38	0.0451	4.92	0.1169	20.86	0.0955	12.71	0.1107
Castelnuovo R.	9.05	0.0565	21.69	0.1028	3.93	0.0428	7.71	0.1032
Vignola	7.04	0.0449	22.85	0.0790	16.06	0.0541	16.06	0.1039
Spilamberto	8.37	0.0536	19.44	0.1120	6.87	0.0700	11.89	0.1132
Guiglia	9.12	0.0537	18.09	0.1175	4.94	0.0768	10.88	0.1130

Municipality	*Environmental Impact*		*Traceability*		*Involvement*		*Convenience*		*Total score*
	Weight %	*Score*	*Weight %*	*Score*	*Weight %*	*Score*	*Weight %*	*Score*	
Savignano SP	23.37	0.1262	4.04	0.0693	15.39	0.0906	9.72	0.0544	0.7039
Castelvetro	12.23	0.1356	30.54	0.0693	20.18	0.0864	14.95	0.0546	0.7255
Zocca	23.11	0.1085	4.73	0.0693	7.42	0.0765	3.36	0.0546	0.5612
Marano s. P.	10.64	0.1265	12.92	0.0693	26.22	0.0765	6.37	0.0546	0.6953
Castelnuovo R.	24.96	0.1260	15.12	0.0693	12.12	0.1076	5.42	0.0544	0.6626
Vignola	12.61	0.1257	8.88	0.0693	10.58	0.0935	5.91	0.0609	0.6313
Spilamberto	16.20	0.1263	18.26	0.1386	7.99	0.1076	10.99	0.0632	0.7845
Guiglia	21.48	0.1175	16.39	0.0693	13.40	0.0765	5.71	0.0546	0.6789

The mean value obtained is then shown in the following pie chart (Fig. 4).

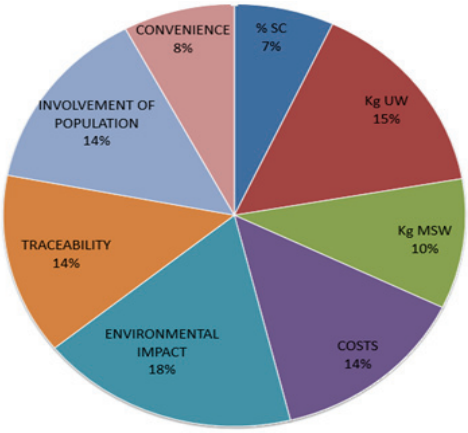

Fig. 4. Average distribution of weights

In summary, the weights assigned by the administrators of the Union of Terre di Castelli, presented in order of importance are given in Table 8.

The results presented in Table 7, "Score" column, derived from the application of the indicator of virtuosity and scores obtained by the Municipalities belonging to the case study, with the aggregated performance data of the Unione Terre di Castelli Municipalities in relation to each of the eight criteria taken into examination. It was decided to use a time interval of 12 months of analysis, covering the period from July 2012 to June 2013.

For each criterion, each municipality received a score as explained above, multiplied by the weight assigned by the mayors interviewed (Table 9, Fig. 5).

As demonstrated by Fig. 5, one of the most interesting potential applications for the method proposed is the support to strategic choices about waste management: reporting for each municipality performance measured by each criterion, the indicator shows clearly the areas where it may be more effective to invest for the overall improvement of the waste management system. The indicator can also be used as a simulator for the actions that the Administration of Spilamberto plans to take, for example viewing if the investments to improve some criteria are sustainable or if their economic impact can reduce the overall virtuosity. In conclusion, the overall scores are shown in the summary chart below, marking how this ranking differs from a judgment based solely on the percentage of segregated waste collected. This means extending the horizon of the investigation into all areas pertaining to the management of waste, obtaining a measurement of virtuosity that moves beyond from the Italian legislator's present requirement.

All this underlines the importance of a multi criteria approach to the delicate issue of waste management in order to achieve a more accurate estimation of the real virtuosity of Local Authorities and the actions to be taken in order to improve the approach to discipline and to reduce the impact environmental product from municipal waste. Table 10 shows a comparison of the rankings obtained by the exclusive evaluation of the percentage of segregated collection against the indicator proposed. Examples of Savignano and Spilamberto show how this indicator awards the attention to different aspects of waste management and the various actions that can be implemented, increasing the Municipality score of virtuosity.

Fig. 6 shows the overall results, to provide a visual clue to easier and more immediate understanding.

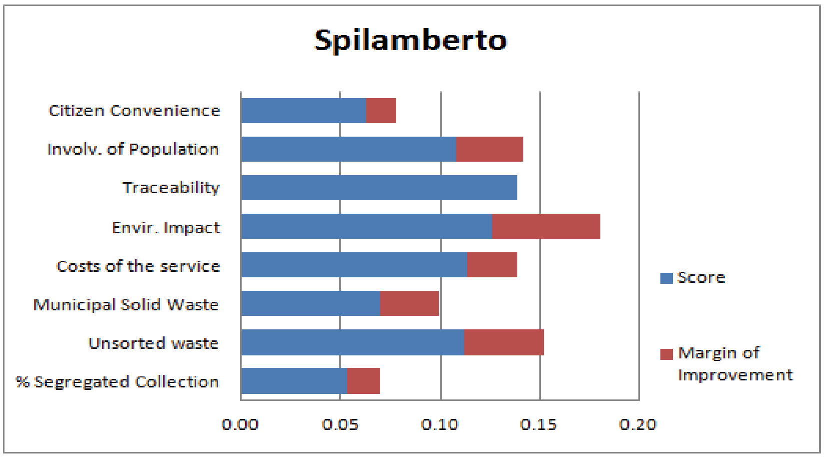

Fig. 5. Performance of Spilamberto

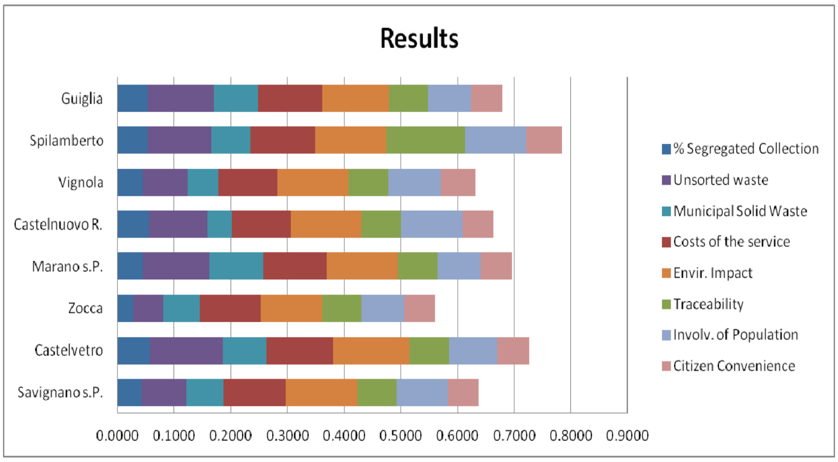

Fig. 6. View of the sums of the partial results obtained by the municipalities with the application of the indicator of virtuosity

Table 8. Weights distribution

Criterion	*Value%*	*Weights*
Environmental impact of the service	18:08%	0.1808
Unsorted waste produced	15:24%	0.1524
Involvementnt of population	14:16%	0.1416
Costs	13.91%	0.1391
Traceability	13.86%	0.1386
Municipal Solid Waste	9.96%	0.0996
Convenience for users	7.80%	0.0780
% Segregated Collection	6.99%	0.0699
SUM		**1.0000**

Correctly the sum of the weights is 1

Table 9. Performance of Spilamberto

% SEGREGATED COLLECTION		***UNSORTED WASTE***	
Segregated Collection [%]	60.86%	UW per capita [kg]	229.92
Score assigned	0.77	Score assigned	0.73
Weight attribuited	0.0699	Weight attribuited	0.1524
Result %RD	0.0536	Result UW	0.1120
Margin of improvement	0.0163	Margin of improvement	0.0404
MUNICIPAL SOLID WASTE		***COSTS OF SERVICE***	1458769
MSW per capita [kg]	587.42	Cost per capita [€]	108.06
Score assigned	0.70	Score assigned	0.81
Weight attribuited	0.0996	Weight attribuited	0.1391
Result MSW	0.0700	Result COSTS	0.1132
Margin of improvement	0.0296	Margin of improvement	0.0259
ENVIRONMENTAL IMPACT OF SERVICE		***WASTE FATE TRACEABILITY***	
Score assigned	0.70	Score assigned	1
Weight attribuited	0.1808	Weight attribuited	0.1386
Result ENV. IMPACT	0.1263	Result TRACEABILITY	0.1386
Margin of improvement	0.0545	Margin of improvement	0.0000
INVOLVEMENT OF POPULATION		***CITIZEN CONVENIENCE***	
Score assigned	0.76	Score assigned	0.81
Weight attribuited	0.1416	Weight attribuited	0.0780
Result INVOLV. POPULATION	0.1076	Result CITIZEN CONVENIENCE	0.0632
Margin of improvement	0.0340	Margin of improvement	0.0148

Table 10. Different classifications of virtuousness of Municipalities examined

RANKING FOR RD%		***RANKING FOR INDICATOR VIRTUOSITY***	
Municipalities	***% RD***	***Municipalities***	***Total scores***
Castelvetro	66.19%	Spilamberto	0.7845
Castelnuovo R.	64.51%	Castelvetro	0.7255
Guiglia	61.07%	Savignano s.P.	0.7039
Spilamberto	60.86%	Marano s.P.	0.6953
Marano s.P.	50.85%	Guiglia	0.6789
Vignola	50.59%	Castelnuovo R.	0.6626
Savignano s.P.	46.92%	Vignola	0.6313
Zocca	32.59%	Zocca	0.5612

5. Conclusions

This application has proved a valid and complete tool for local governments to evaluate the consistency between their own ideals guidelines and the actions they intend to apply. This work has proved a valuable decision support tool for local administrators, showing for each criterion not only state of the art but also the scope for improvement.

The indicator can also be used as a simulator for actions planned by administration, for example verifying sustainability of investments needed to improve performance in specific criteria or if their impact does not affect the overall virtuosity, with a simple and user-friendly tool.

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REUSE OF TREATED MUNICIPAL WASTEWATER FOR IRRIGATION IN APULIA REGION: THE "IN.TE.R.R.A." PROJECT

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Abstract

The use of non-conventional water resources including treated municipal wastewater has been increasing in the Mediterranean regions over the last decades to cope with water shortages and uneven rainfalls due to climate change.

The aim of this paper is to present the first results from two years of experimental field activities carried out in two different demo-places in Southern Italy: the municipal wastewater treatment plants of Noci and Castellana Grotte (Apulia region). In these sites different vegetable crops (cucumber, lettuce, melon, endive in Noci and fennel, lettuce, fennel in Castellana Grotte) were grown in succession and irrigated in parallel with treated wastewater and conventional water pumped from wells, for comparing the effects of the different water sources on soil and vegetables. Reclaimed water quality was monitored for chemical and microbial parameters and compared with conventional water. At harvesting time, microbial indicators were measured on edible part of crops and in soil.

Results show that the effluents produced by a full scale membrane bioreactor (MBR) treatment plant (Noci) comply with the stringent Italian standards for reuse in agriculture, and its microbiological quality is higher than the conventional well water. In Castellana Grotte the effluent quality of the two pilot plants was different according to the adopted technologies (MBR and tertiary cloth filtration), and sometimes depended on the quality of incoming wastewater.

As for the agronomic results, in both sites crop yields were higher in the plots irrigated with treated wastewater, and the microbial indicators *Escherichia coli* and *Salmonella* were never found, at harvesting time, on edible parts of crops and in the soil.

Key words: agricultural reuse, drip irrigation, treated wastewater, vegetable crops

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1. Introduction

Water stress in Mediterranean countries calls for solutions that should promptly provide responses to the effects of climate change and consequent decrease of available resources. Two approaches that should be combined to properly tackle the current water scarcity refer to (i) the improvement of resource management practices by balancing demand and supply, and (ii) the adoption of alternative water resources (e.g. desalination, wastewater reuse, rainwater harvesting, etc.)(GWP, 2012). Countries facing the Mediterranean have different priorities and constraints with respect to the improvement of freshwater availability, and strong differences exist among the regulations governing, for instance, treated wastewater reuse (Carp and Barbu, 2014; Kellis et al., 2013). In this context, several activities were carried out over the last decades to test and demonstrate the feasibility of wastewater recycling for producing a dedicated resource to activities requiring continuous water availability during the dry season (e.g. agriculture) (Bixio et al., 2006; Valipour et al., 2014). The concept of water production from wastewater treatment is implemented in Apulia (South East Italy), a region whose economy is based on agriculture despite its strong lack of water availability (Lopez et al., 2006). Here, the combination of dry weather conditions, absence of permanent rivers and natural lakes, and progressive

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groundwater salinization due to overexploitation requires the adoption of non-conventional resources. Previous experimental activities have shown the long term feasibility of adopting tertiary membrane filtration as a suitable tool for the upgrade of municipal effluents to comply with the stringent local standards for reuse (Lopez et al., 2010; Pollice et al., 2004). Different combinations of biological process and surface filtration were tested for the treatment of municipal sewage aimed at producing effluents suitable for agricultural reuse. The activity included the test of wastewater treatment process technologies, and the comparison of the produced effluents with conventionally treated tertiary effluents and with the well water normally used for irrigation by local farmers. This comparison was performed through agronomic experiments where test fields were cultivated and different types of vegetable crops were grown in succession.

In particular some relevant aspects were studied at the field scale, such as partial preservation of nutrients and "on-demand" disinfection. Moreover non-conventional water purification technologies were tested and compared to conventional treatments in terms of effluent quality and suitability for reuse practices. The innovative features of the proposed technologies will be briefly described here and evaluated with particular reference to effluent quality and suitability for reuse in irrigation of vegetable crops.

The results discussed in this paper refer to the activities performed at two demo sites: The municipal wastewater treatment plants of Noci and Castellana Grotte (Apulia region). At the first one, the effluent of a full scale membrane bioreactor (MBR) was monitored for chemical and microbiological quality and used for irrigation of a test field in comparison with local well water. At the second one, two demo-scale treatment plants were installed and operated for testing their potential. These were based on two non-conventional technologies: the IFAS-MBR, Integrated Fixed Film Activated Sludge - Membrane Bioreactor, and the GDF, Gravity Disk Filtration, respectively. Both plants were followed by UV disinfection systems operated "on demand".

The present paper reports some results of the experimental activities carried out within the projects In.Te.R.R.A. (funded by the Italian Ministry of Education and Research, PON 2007/2013). Goals of this project are to study, test and suggest innovative and sustainable technological and process strategies to promote reuse of treated municipal wastewater for irrigation.

2. Case study 1: The site of Noci

The full scale MBR wastewater treatment plant was monitored in terms of the chemical and microbiological suitability of its effluent for agricultural reuse and compliance with the local and national standards. The results reported in this paper refer the first two years of irrigation on four vegetable crops in succession.

2.1. The MBR treatment plant

The municipal MBR treatment plant of Noci (Apulia region, South Eastern Italy) is equipped with submerged hollow fiber membrane ultrafiltration modules (GE Water) providing solid/liquid separation and the desired biomass concentration in the final sections of the treatment train. Ultrafiltration is operated with the out-in mode and the modules are equipped with an air scouring cleaning system that prevents biomass accumulation on the membrane surface, limiting the effects of fouling and ensuring a membrane life of several years. The purifying performance is very high since it is possible to work with high concentration of biomass, and this promotes biological removal of COD and nutrients (the plant is operated for pre-denitrification). Moreover, according to the membrane pore size (0.04μm) the effluent quality is bacterial-free guaranteed.

2.2. The experimental field

The experimental field was located near the municipal wastewater treatment plant of Noci (40°47'56"N 17°04'63"E; altitude 360 m a.s.l.). The trial was carried out in a silt-loam soil (USDA classification) with a field capacity (-0.02MPa) of 25.2% dry weight (dw), a wilting point (-1.5 MPa) of 7.1% dw and a bulk density of 1.88 t m^{-3}. The main characteristics of the soil layer of the experimental site (0-0.4 m) characterized once before trial were the following: sand 35.7%; loam 60.0%; clay 4.3%; organic matter 1.67%; Olsen P_2O_5 15 mg kg^{-1}; Ac-extractable K_2O 80 mg kg^{-1}; total N 0.63‰ (Kjeldahl); pH 7.7; electrical conductivity 0.40 dS m^{-1}.

Four vegetable crops were grown in succession during two years of trials: cucumber, lettuce, melon and endive. The cucumber (*Cucumis sativus* L.), was transplanted on May 31st, 2012 in single rows, spaced at 1 m with plants 0.5 m apart from each other, realizing a plant density of 2 plants m^{-2}, and was harvested in 7 times, between July 10th and August 17th, 2012. Lettuce (*Lactuca sativa* L.) was transplanted on the same plots on September 26th 2012 in single rows, spaced 0.5 m with plants 0.3 apart from each other, realizing a plant density of 6.7 plants m^{-2}, and was harvested on January 22nd 2013. Melon (*Cucumis melo* L.) was transplanted on April 18th 2013 in single rows, spaced 2.0 m with plants 0.7 apart from each other, realizing a plant density of 0.7 plants m^{-2}, and was harvested in 7 times, between July 15th and August 28th 2013. Endive (*Cichorium endivia* L.) was transplanted on September 12th 2013 on the same plots, in single rows, spaced 0.5 m with plants 0.3 apart from each other, realizing a plant density of 6.7 plants m^{-2}, and was harvested on November 29th 2013.

Two types of water were compared for irrigation: MBR municipal effluent (MBReff) and conventional water pumped from phreatic well (Well1).

The experimental design used for all crops was a randomized block design with 4 replications, obtaining 8 plots of size 8 x 15 m (Fig. 1). For all crops, drip irrigation was used placing the dripping lines every other row.

The four crops were irrigated when the soil water deficit (SWD) in the root zone was 35% of the total available water (TAW). Irrigation was scheduled based on the evapotranspiration criterion, providing water to the crops when the following conditions were met (Eq. 1):

$$\sum_{1}^{n}\left(E_{tc}-R_{e}\right)=RAW \qquad (1)$$

where: *RAW* (Readily Available Water) = 30 mm for cucumber and melon; 25 mm for lettuce and endive, worked out for the soil in which researches were carried out ; *n* = number of days required to reach the SWDlim starting from the last watering; *Etc* = crop evapotranspiration (mm); *Re* = rainfall (mm). Evapotranspiration can be expressed by Eq. (2), where *E* is "class A" pan evaporation (mm); *Kc* is the crop coefficient; *Kp* is pan coefficient (0.8).

The experimental field was cultivated according to the agronomical practices (fertilization, pest and weed control) commonly adopted by the local farmers. The mean monthly main climate parameters recorded during the trial are reported in Table 1. These data were measured by a weather station located near the experimental area (http://www.agrometeopuglia.it).

$$E_{tc} = E*K_p*K_c \qquad (2)$$

2.3. Sampling and analyses

The irrigation water samples (treated effluent and conventional well water) were collected, under the dripper, on every watering and analyzed for chemical parameters according to standard methods (APHA et al., 2012). The measures parameters were: pH, electrical conductivity (EC), BOD_5, COD, $N\text{-}NH_4$, $P\text{-}PO_4^-$, Cl^-, SO_4^-, NO_3^-, F^-, Sodium Adsorption Ratio (SAR), Escherichia coli and Salmonella spp by the membrane filtration method. Soil samples were taken from each plot before and after every crop cycle at depths decreasing from 0 to 0.4 m, every 0.2 m.

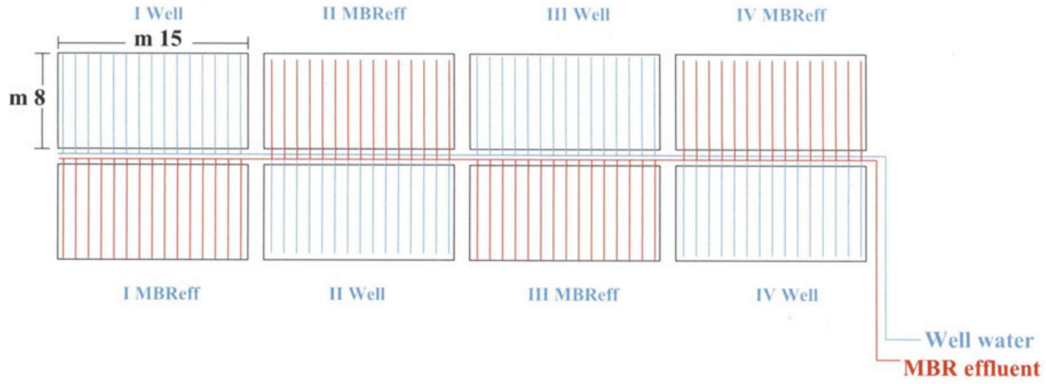

Fig. 1. The experimental randomized block design used for all crops with 4 replications

Table 1. Main climatic parameters recorded in Noci during the growing season of the four vegetable crops

Month	*^{a}Climatic Parameters*							*T_{max} Long term average (°C)*	*T_{min} Long term average (°C)*	*P Long term average (mm)*
	T_{max} (°C)	*T_{min} (°C)*	*RH_{max} (%)*	*RH_{min} (%)*	*Ev (mm)*	*Ws ($m\ s^{-1}$)*	*P (mm)*			
Growing season Cucumber (april - august 2012)	28.07	12.93	93.28	35.53	5.44	1.99	129.20	23.55	14.91	180.30
Growing season Lettuce (september 2012 - january 2013)	17.76	7.56	99.38	63.40	1.89	2.11	436.80	15.70	9.51	362.10
Growing season Melon (april-august 2013)	24.42	10.59	89.49	38.81	4.72	2.11	162.40	23.55	14.91	180.30
Growing season Endive (september -december 2013	21.65	10.27	91.84	49.36	3.05	1.56	248.90	19.16	12.33	207.60

^{a} T_{min}, T_{max}, monthly minimum, maximum air temperature; RH_{min}, RH_{max}, monthly minimum, maximum relative air umidity; P, total precipitation; W_s, monthly mean wind speed; E_v, total "class A" pan evaporation.

They were analyzed for Kjeldahl nitrogen (N), phosphorus (P_2O_5), organic matter (O.M.), pH and electrical conductivity according to standard procedures (Spark, 1996). Microbiological analyses (*E. coli* and *Salmonella spp*) were also carried out on soil samples at depth of 0-0.1 m according to standard methods (Woomer, 1994).

At harvesting time, the number of plants from each plot was counted and weighted to estimate total yield (TY, t ha^{-1}), marketable yield (MY, t ha^{-1}), and nonmarketable yield (NMY, t ha^{-1}). On 6 marketable samples from each plot, cucumber and melon fruits were also measured for: dry matter content (DM, % fresh matter) (AOAC 1990), average fruit weight, mean diameter (equatorial and longitudinal diameter) (D, cm), soluble solids content of the fresh (SSC; °Brix), titratable acidity (TA; g citric acid 100 mL^{-1} fresh juice) (AOAC, 1995) and texture. For lettuce and endive: number of plants and average clumps weight.

Microbiological analyses (*E. coli* and *Salmonella spp*) were also carried out on washing water of clumps and fruits according to standard methods (Sharf, 1966).

The measured data from each of the continuum variables relating to the qualitative/quantitative traits were processed statistically using analysis of variance (ANOVA). When significant effects were detected ($P \leq 0.05$), mean multiple comparisons were performed according to Tukey's tests. With reference to the analyzed qualitative parameters, the Bartlett test confirmed the homogeneity of the variance among the harvest data, so a combined statistical analysis was performed later. When the normality and the homogeneity of standard deviations about the distribution of the population from which the samples were drawn were not respected, Kruskall-Wallis non parametric test was performed.

2.4. Results

As reported in Table 1, during the growing season of four vegetable crops in succession the maximum temperature recorded, on average, was always higher respect to the long-term average and minimum temperature (always lower by about 2°C). Table 2 shows the average values of the main chemical and physical characteristics of the well water and the MBR effluent, as measured during the experimental trials. The overall quality of the two water sources was comparable, and complied with the Italian national standards (D.M. 185, 2003) and the Regional regulation for treated wastewater reuse (R.R. 8, 2012). MBReff was characterized by higher values of NH_4, PO_4^{3-}, SO_4^- and K^+ than Well1, which represent important nutrients to increase soil fertility, plant growth and crop yield.

As observed along the soil profile (0-0.40 m) over the research period, the use of MBReff for irrigation contributed to increase the values of O.M., N, and K_2O , if compared with the use of Well1 (Table 3).

The data about the influence of the type of water on the qualitative and quantitative crop parameters are shown in Table 4.

Table 2. Average values of the main chemical, physical and microbiological parameters measured during the experimental period of trials in Noci, for the well water (Well1) and the effluent of the full scale municipal MBR (MBReff), used for vegetable crops irrigation

Water parameters	***Irrigation treatment***		***Significance***	***Italian/Regional limit values (R.R. 8/2012)***
	Well 1	***MBR_{eff}***		
EC (dS m^{-1})	0.77 ± 0.05	0.98 ± 0.02	**	3.00
pH	7.75 ± 0.07	7.48 ± 0.06	**	6.0 – 9.5
BOD_5 (mgO_2 L^{-1})	4.10 ± 1.2	9.69 ± 2.4	n.s.	20
COD (mgO_2 L^{-1})	17.8 ± 8.4	28.4 ± 6.3	n.s.	100
$NH_4^+ - N$ (mg L^{-1})	0 ± 0	5.1 ± 2.0	*	2 (15)[a]
$NO_3^- - N$ (mg L^{-1})	7.2 ± 3.0	8.6 ± 3.4	n.s.	35 (15)[b]
$PO_4^{3-} - P$ (mg L^{-1})	2.0 ± 4.2	4.6 ± 6.2	n.s.	10 (2)[b]
SO_4^- (mg L^{-1})	12.2 ± 3.3	38.9 ± 7.2	**	500
F^- (mg L^{-1})	0.28 ± 0.09	1.18 ± 0.37	*	1.5
Cl^- (mg L^{-1})	62.6 ± 12.5	129.3 ± 10.6	**	250
Na^+ (mg L^{-1})	36 ± 7	81 ± 6	**	
K^+ (mg L^{-1})	2 ± 0	12 ± 2	**	
Ca^{2+} (mg L^{-1})	71 ± 10	65 ± 7	n.s.	
Mg^{2+} (mg L^{-1})	19 ± 4	16 ± 3	n.s.	
SAR	1 ± 0	2 ± 0	n.s.	10
E. coli (CFU 100 mL^{-1})	0 ± 0	6 ± 4	n.s.	10
Salmonella (CFU 100 mL^{-1})	Absent	Absent		Absent

*Data are average ± standard error for each water sample analyzed between April 2012 and November 2013. **: Statistically significant at $P \leq 0.01$;*: Statistically significant at $P \leq 0.05$; n.s.: not significant. [a] Limit concentration for ammonium can be raised to the value in brackets upon special permission (R.R. 8/2012). [b] Limit concentrations for total nitrogen and total phosphorus (in brackets the limit concentrations for areas declared vulnerable to nitrate and phosphate pollution).*

Table 3. Average values of the main soil chemical parameters measured over the research period along the soil profile in Noci. EC and pH were measured on 1:2 (w/v) and 1:2.5 (w/v) aqueous soil extract, respectively

	Cucumber		***Lettuce***		***Melon***		***Endive***	
Soil parameters	***Well1***	***MBR_{eff}***	***Well1***	***MBR_{eff}***	***Well1***	***MBR_{eff}***	***Well1***	***MBR_{eff}***
EC	0.40	0.28	0.21	0.21	0.33	0.56	0.30	0.34
pH	7.68	7.68	8.02	8.04	8.13	8.15	8.28	8.21
OM (%)	1.7	1.8	1.5	1.6	1.9	2.2	1.3	1.7
N (g kg^{-1})	0.6	0.7	1.1	1.2	1.1	1.2	0.9	1.3
P_2O_5 (mg kg^{-1})	15	21	43	37	44	30	11	13
K_2O (mg kg^{-1})	77	89	84	91	82	88	83	92

Table 4. Average values of main quantity and quality crop parameters measured over the research period, at harvesting time in Noci

	Cucumber		***Lettuce***		***Melon***		***Endive***	
Crop parameters	***Well1***	***MBR_{eff}***	***Well1***	***MBR_{eff}***	***Well1***	***MBR_{eff}***	***Well1***	***MBR_{eff}***
Total Yield (t ha^{-1})	7.6 b	23.9 a	16.8 a	18.9 a	25.6b	35.2a	29.8a	35.2 a
Marketable Yield (t ha^{-1})	7.6 b	23.9 a	12.2a	13.7 a	25.48b	35.12a	29.8a	35.2a
Non Marketable Yield (t ha-1)			4.6a	5.2a	0.12a	0.08a		
Dry Matter (%FM)	3.4b	6.2a	4.9a	4.3a	11.2a	12.9a	5.9a	6.2a
SSC (°Brix)	3.2b	5.1a			9.9b	12.7a		
pH					6.36a	6.37a		
TA (g 100 mL^{-1})	0.1b	0.3a			1.10b	1.33a		
N of plant (m^{-2})	1	1	5.5	5.3	1.48	1.50	6.3	6.2
N. of fruits per plant	80b	229a			10.0a	12.4 a		
Average clumps weight (g)	294a	326a	221a	258a	411b	556a	477aa	556a

Letters represent significant differences between treatments ($p < 0.05$)

They show that the yield of different crops were significantly higher in plots irrigated with MBReff than in plots irrigated with Well1. Also, some quality crop parameters showed significant differences between MBReff and Well1 (D.M., SSC, pH and n. of fruits for cucumber crop and SSC for melon crops).

The microbiological analyses carried out on water show that faecal pollution indicator (*E. coli*) was never present in well water, while in MBR effluent, if present, was in very low concentration.

In soil and on crop samples *Escherichia coli* and *Salmonella* were never found.

3. Case Study 2: The site of Castellana Grotte

Another experimental investigation was carried out at Castellana Grotte (Apulia region, South Eastern Italy) to evaluate the feasibility of adopting the effluent of the local municipal wastewater treatment plant for agricultural reuse (irrigation of vegetable crops). Two non-conventional pilot-scale treatment plants were also installed and operated at the same site to test alternative treatment technologies based on surface filtration (membrane and cloth filtration, respectively). The demo-site includes a test field located immediately outside the treatment plant where vegetables can be grown for testing irrigation with different water sources. The results reported in this paper refer the first two years of irrigation on three vegetable crops in succession.

3.1. The municipal wastewater treatment plant

The full scale municipal wastewater treatment plant of Castellana Grotte is based on a pre-denitrification process scheme. The sewage, after pre-screening and primary settling, is sent to the first anoxic reactor where the nitrate recirculated from the following aerobic tank is removed from the liquid phase through biological denitrification. In the subsequent aerated reactor, oxidation of the organic fractions and nitrification occur. The produced sludge is separated from the liquid phase in the final settling tank and partly recirculated to maintain the required biomass concentration. The secondary effluent is further treated through granular media filtration and disinfection (chlorination), before being discharged on soil. During the experimental activities described here, a fraction of this effluent was diverted and used for irrigation at the test field located immediately out of the treatment plant.

3.2. The IFAS-MBR pilot plant

The first pilot plant was based on the IFAS-MBR technology (Integrated Fixed film Activated Sludge – Membrane BioReactor), and treated sewage after preliminary screening. The IFAS technology is based on the presence of plastic carriers in the aerobic bioreactor. These carriers promote biomass accumulation in the form of biofilm, and biological processes are carried out synergistically by the suspended biomass and the biofilm, resulting in limited biomass growth. Coupling the IFAS with an MBR has further potential benefits, since the membrane bioreactor allows optimal control of suspended biomass in terms of sludge retention time, possibly resulting in reduced production of partially stabilized sludge. This plant was operated to promote the nitrification of ammonia, in order maintain the nitrogen concentration of treated wastewater and evaluate the nutrient contribution to the growth of vegetables. Moreover membrane separation results in high quality effluent in terms of suspended solids, favoring the adoption of UV disinfection technologies. In fact the outlet of this plant was connected to a UV disinfection system that was activated when the irrigation line was switched on ("on demand" disinfection).

3.3. The GDF pilot plant

The second pilot plant was based on the GDF technology (Gravity Disk Filter). It treated a fraction of the secondary effluent taken downstream to the secondary settling tank of the main wastewater treatment plant. Therefore, the GDF provided a tertiary physical treatment allowing for improved removal of residual suspended solids. The system was based on a cloth filtration process that was operated through a set of disks submerged into the tank. Also in this case a UV system was placed downstream and treated the effluent "on demand", i.e. when irrigation was performed.

3.4. Experimental trials

The experimental field was located near the wastewater treatment plant of Castellana Grotte (40°53'20"N 17°11'51"E; altitude 305 m a.s.l.). The trials were carried out in a loam loose soil (USDA classification) with a field capacity (- 0.02MPa) of 24.4% dry weight (dw), a wilting point (-1.5 MPa) of 6.7% dw and a bulk density of 1.7 t m^{-3}. The main characteristics of the soil layer of the experimental site (0-0.4 m) characterized once before trial are as follow: sand 44.4%; loam 54.1%; clay 1.6%; organic matter 1.50%; Olsen P_2O_5 19 mg kg^{-1}; $BaCl_2$ extractable K_2O 70 mg kg^{-1}; total N 1.11‰ (Kjeldahl); pH 8.1; electrical conductivity 0.22 dS m^{-1}.

Four types of irrigation water were compared: the effluent from the full scale plant (EFF), the effluent from the pilot IFAS-MBR plant (IMBR), the effluent from the GDF pilot plant (GDF), and the water pumped from a local phreatic well (Well2). For all crops, drip irrigation was used placing the dripping lines every other row. During two years of trials three vegetable crops were alternated: fennel, lettuce and fennel.

Fennel (*Foeniculum vulgare* Mill) was transplanted on September 29th, 2012 in single rows, spaced 0.2 m with plants 0.5 apart from each other, realizing a plant density of 10 plants m^{-2}, and was harvested on March 19th, 2013.

Lettuce (*Lactuca sativa* L.) was transplanted on the same plots on April 18th 2013 in single rows, spaced 0.5 m with plants 0.3 apart from each other, realizing a plant density of 6.7 plants m^{-2}, and was harvested on June 17th 2013 in plots irrigated with IMBR water; after three days (June 20th) in plots irrigated with EFF and GDF, and after eight days in plots irrigated with Well2.

Fennel (*Foeniculum vulgare* Mill) was transplanted on the same plots on August 30th 2013 in single rows, spaced 0.2 m with plants 0.5 apart from each other, realizing a plant density of 10 plants m^{-2} and was harvested on .

Marketable yields data (t ha^{-1}), average weight (g), and clumps dry matter (%) were measured at harvesting time, i.e. after 102 (December 10th 2013) , 109 (December 17th 2013), 127 and 137 days (January 14th 2014) from transplanting in plots irrigated with IMBR water, EFF water, GDF and Well2, respectively. The experimental design used for all crops was a latin square design obtaining 16 plot of size 20 x 20 m (Fig. 2).

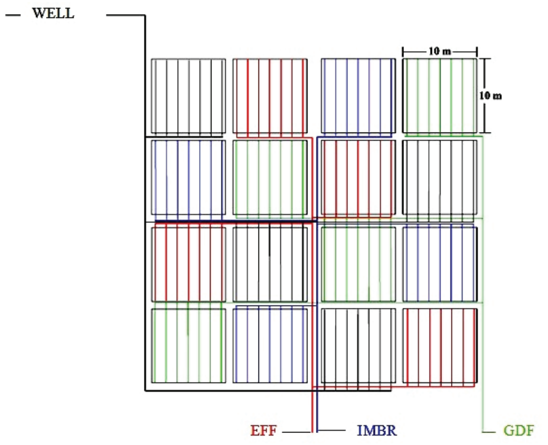

Fig. 2. Latin square experimental design used for all crops

The three crops were irrigated when the soil water deficit (SWD) in the root zone was 35% of the total available water (TAW). Irrigation was scheduled based on evapotraspiration criterion providing water to the crops when the following conditions were met (Eq. 3):

$$\sum_{1}^{n}\left(E_{tc}-R_e\right)=30 \text{ mm for lettuce; 25 mm for fennel} \qquad (3)$$

The experimental field was cultivated according to the agronomical practices (fertilization, pest and weed control) commonly adopted by the local farmers.

The mean monthly main climate parameters recorded during the trial are reported in Table 6. These data were measured by a weather station located near the experimental area (ASSOCODIPUGLIA).

3.5. Sampling and analyses

Irrigation water samples of the different types (EFF, IMBR, GDF and Well2) were collected under the dripper on every watering and analyzed for chemical parameters according to standard methods (APHA et al., 2012). The measured parameters were: pH, electrical conductivity (EC), BOD_5, COD, N-

NH_4, $P\text{-}PO_4^-$, Cl^-, SO_4^-, NO_3^-, F^-, Sodium Adsorption Ratio (SAR), *Escherichia coli* and *Salmonella spp* by the membrane filtration method (Table 5).

Soil samples were taken from each plot before and after every crop cycle at depths decreasing from 0 to 0.4 m, every 0.2 m. They were analyzed for nitrogen Kjeldahl (N), phosphorus (P_2O_5), organic matter (O.M.), pH and electrical conductivity according to standard procedures (Spark, 1996). Microbiological analyses (*E. coli* and *Salmonella spp*) were also carried out on soil samples at depth of 0-0.1 m according to standard methods (Woomer, 1994). At harvesting time, the marketable edible parts of vegetable crops were counted and weighted to estimate total yield (TY, t ha^{-1}), marketable yield (MY, t ha^{-1}) nonmarketable yield (NMY, t ha^{-1}). On 6 marketable samples from each plot, were also measured dry matter content (DM, % fresh matter) (AOAC, 1990), average fruit weight and number of plants. Microbiological analyses (*E. coli* and *Salmonella spp*) were also carried out on washing water of clumps and fruits according to standard methods (Sharf, 1966). Statistical analysis was performed just as for the site of Noci (see paragraph 2.3).

3.6. Results

Climatic conditions in the experimental period September 2012 - January 2014 (Table 5) show that the maximum temperatures were higher than the long-term average, while minimum temperatures have been in accordance with the long-term average. The average values of the main chemical and physical characteristics of the irrigation waters during the experimental trials are reported in Table 6. COD, NO_3, K^+, Na^+ and Cl^- are the only parameters significantly different between the various types of water. However, if compared with Well2, all treated wastewaters (IMBR, EFF and GDF) were also characterized by higher average values of NH_4, PO_4^{3-}, SO_4^- and Ca^{2+}, which represent important nutrients to increase soil fertility, plant growth and crop yield.

Data observed along the soil profile (0-0.40 m) over the research period, show no differences in terms of soil fertility (Table 7). About the influence of the different types of water on the qualitative and quantitative crop parameters, results are shown in Table 8. They show that the yield of different crops are significantly higher in plots irrigated with IMBR than Well2.

The microbiological analyses conducted on water, reported in Table 6, show that faecal pollution indicator (*E. coli*) was never present in well water; in IMBR, when present, was in very low concentration and not significantly different from the well water, while in EFF and GDF, *E. coli* values exceeded respect to the Italian law value and result significantly different respect to Well2. *Salmonella* was never found in waters. In soil and on crop samples *Escherichia coli* and *Salmonella* were never found.

4. Discussion

The MBR technology (full-scale MBR at Noci, pilot scale IFAS-MBR at Castellana Grotte) showed the potential to produce an effluent that complies with the local limits for reuse in agriculture. On the contrary GDF and EFF did not allow to respect the limit related to the faecal indicator *E. coli*. All types of treated wastewater had on average higher values of important nutrients for the crops, such as NO_3, NH_4, PO_4^{3-}, SO_4^-, K^+ and Ca^{2+}. This resulted, in most of the cases and for different type of crops, in a significant increase of crop yields.

The pilot scale IFAS-MBR was operated only for nitrification to supply nutrients to plants. The higher content of nitrates in IMBR, if compared with all the other sources of water used in this study, not only increased crop yields, but also resulted in a early ripeness. In fact for all crops grown there was a maturity advance variable from 8 to 30 days between IMBR and Well2 plots, respectively. The IMBR provided, constantly at each watering, small but still significant amounts of nutrients to a soil, not very fertile, as that of Castellana Grotte.

The soil fertility and the quality of the crops was not systematically improved by the use of treated wastewater for irrigation.

Table 5. Main climatic parameters recorded in Castellana Grotte during the growing season of the three vegetable crops

Month	***^{a} Climatic Parameters***							***T_{max} Long term average (°C)***	***T_{min} Long term average (°C)***	***P Long term average (mm)***
	T_{max} (°C)	***T_{min} (°C)***	***RH_{max} (%)***	***RH_{min} (%)***	***Ev (mm)***	***Ws ($m\ s^{-1}$)***	***P (mm)***			
Growing season Fennel (september 2012- march 2013)	15.97	7.52	98.70	56.17	1.72	3.22	528.4	14.49	7.26	68.93
Growing season Lettuce (april – june 2013)	23.02	11.44	87.98	32.38	4.29	2.89	39.2	21.22	11.50	37.73
Growing season Fennel (august 2013 - march 2014)	17.88	8.71	95.49	55.19	2.16	2.67	559.1	16.22	8.58	63.40

$^a T_{min}$, T_{max}, monthly minimum, maximum air temperature; RH_{min}, RH_{max}, monthly minimum, maximum relative air humidity; P, total precipitation; W_s, monthly mean wind speed; E_v, total "class A" pan evaporation

Table 6. Means of the main chemical-physical and microbiological parameters measured during the experimental period of trials in Castellana Grotte, for the well water (Well2), the full scale municipal wastewater treatment plant effluent (EFF), the IFAS-MBR pilot plant effluent (IMBR) and the GDF pilot plant effluent (GDF), used for vegetable crops irrigation

Water parameters	***Irrigation treatmen***					***Italian Law Limit value (DM 185/2003) (R.R. 8, 2012)***
	Well2	***EFF***	***IMBR***	***GDF***	***p-value***	
EC (dS m^{-1})	0.87 ± 0.01	1.02 ± 0.09	0.95 ± 0.03	0.88 ± 0.01	0.103	3.00
pH	7.53 ± 0.10	7.62 ± 0.06	7.59 ± 0.09	7.62 ± 0.08	0.949	6.0 – 9.5
BOD$_5$ (mgO$_2$ L^{-1})	2.64 ± 1.05	9.55 ± 1.73	9.60 ± 2.71	5.28 ± 0.71	0.075	20
COD (mgO$_2$ L^{-1})	4.40 ± 1.53 B	49.71 ± 12.45 A	24.20 ± 2.21 A	20.22 ± 2.43 A	0.004	100
NH_4^+-N (mg L^{-1})	0.78 ± 0.72	9.89 ± 4.01	10.11 ± 3.53	2.09 ± 2.09	0.057	2 (15)^a
NO_3^--N (mg L^{-1})	1.50 ± 0.46 B	5.68 ± 1.14 B	22.17 ± 3.72 A	9.68 ± 3.06 B	0.0001	35 (15)^b
PO_4^{3-}-P (mg L^{-1})	5.71 ± 5.23	8.76 ± 3.03	11.64 ± 4.17	9.13 ± 4.21	0.427	10 (2)^b
SO_4^- (mg L^{-1})	18.19 ± 12.40	35.59 ± 9.71	45.75 ± 11.52	32.02 ± 8.08	0.407	500
F^- (mg L^{-1})	0.69 ± 0.36	0.59 ± 0.25	1.43 ± 0.52	0.71 ± 0.31	0.285	1.5
Cl^- (mg L^{-1})	56.34 ± 25.24 B	135.03 ± 31.72 A	102.41 ± 5.99 A	87.37 ± 5.32 AB	0.018	250
Na^+ (mg L^{-1})	31.52 ± 12.6 B	87.58 ± 13.26 A	94.13 ± 17.15 A	82.51 ± 6.48 A	0.015	
K^+ (mg L^{-1})	0.71 ± 0.42 B	20.69 ± 3.93 A	21.14 ± 3.26 A	17.74 ± 1.99 A	0.001	
Ca^{2+} (mg L^{-1})	63.66 ± 10.8	59.56 ± 5.58	112.96 ± 42.14	70.78 ± 9.73	0.932	
Mg^{2+} (mg L^{-1})	23.86 ± 6.73	9.41 ± 2.32	18.07 ± 6.71	6.92 ± 1.88	0.208	
SAR	0.71 ± 0.42 B	2.94 ± 0.32 A	2.57 ± 0.20 AB	2.77 ± 0.23 A	0.0023	10
E. coli (CFU 100 mL^{-1})	2 ± 2 B	1389 ± 477A	9 ± 4 B	431 ± 189 A	3.183 E^{-6}	10
Salmonella (CFU 100 mL^{-1})	Absent	Absent	Absent	Absent		Absent

Data are means ± standard error for each water analyzed between September 2012 and January 2014. Capital letters represent significant differences between treatments ($p < 0.01$); ^{a} Limit concentration for ammonium can be raised to the value in brackets upon special permission (R.R. 8, 2012); ^{b} Limit concentrations for total nitrogen and total phosphorus (in brackets the limit concentrations for areas declared vulnerable to nitrate and phosphate pollution)

Table 7. Average values of main soil chemical parameters measured over the research period along the soil profile in Castellana Grotte. EC and pH were measured on 1:2 (w/v) and 1:2.5 (w/v) aqueous soil extract, respectively

Soil parameters	***Cucumber***				***Lettuce***				***Fennel***			
	Well2	***IMBR***	***GDF***	***EFF***	***Well2***	***IMBR***	***GDF***	***EFF***	***Well2***	***IMBR***	***GDF***	***EFF***
EC	022	0.21	0.20	0.20	0.38	0.43	0.40	0.35	0.16	0.26	0.23	0.25
pH	8.10	8.04	8.14	8.07	8.03	8.05	8.16	8.15	7.88	8.02	8.09	8.09
OM (%)	1.77	1.61	1.52	2.02	1.84	2.03	1.74	1.72	1.69	1.91	1.76	1.76
N (g kg^{-1})	1.11	1.14	1.04	1.11	1.21	1.08	1.12	1.39	1.40	1.25	1.08	1.11
P_2O_5 (mg kg^{-1})	87	133	19	32	43	77	48	47	14	13	12	8
K_2O (mg kg^{-1})	132	148	96	134	120	116	108	111	73	82	79	84

Table 8. Average values of main quantity and quality crop parameters measured over the research period, at harvesting time in Castellana Grotte

Crop parameters	***Cucumber***				***Lettuce***				***Fennel***			
	Well2	***IMBR***	***GDF***	***EFF***	***Well2***	***IMBR***	***GDF***	***EFF***	***Well2***	***IMBR***	***GDF***	***EFF***
Total Yield (t ha^{-1})	32.2b	47.8a	31.1b	46.1a	34.2b	53.6a	34.9b	38.5b	31.6a	38.7a	35.7a	29.8a
Marketable Yield (t ha^{-1})	32.2b	47.8a	31.1b	46.1a	34.2b	53.6a	34.9b	38.5b	31.6a	38.7a	35.7a	29.8a
Dry Matter (%FM)	7.85a	7.37a	7.87a	7.42a	4.93a	4.01a	4.66a	4.79a	8.98a	7.67a	8.18a	8.70a
N. of plant m^2	140.5	139	127	138	154	163	158	163	144	159.2	160.3	175
Average clumps weight (g)	441.2b	667.7a	477.6b	656.1a	556.4b	826.0a	553.3b	591.8b	373.8a	487.0a	442.6a	403.0a

Letters represent significant differences between treatments ($p < 0.05$)

This occurred in the experimental site of Noci, whereas not relevant differences in terms of soil fertility and quality crop parameters were observed in the site of Castellana Grotte.

In both the experimental sites, in soil and on crop samples *Escherichia coli* and *Salmonella* were never found. These results are in agreement with Lonigro et al. (2007), Benami et al. (2013), which assessed soil irrigated with treated wastewater and with fresh water. Other studies have reported that the level of other faecal indicators in soil irrigated with raw or treated wastewater can significantly differ from that with freshwater application (Malkawi and Mohamad, 2003; Travis et al., 2010). It also needs to be considered that in the study of Malkawi and Mohamad (2003) there were no fecal coliforms recorded in the soil before the irrigation with fresh water, and thus sources other than water can affect this indicator. With Travis et al. (2010), the levels of *Faecal Coliforms* in soil irrigated with untreated or treated gray water was always below 100 CFU g^{-1}.

Considering that *E. coli* was not isolated from any of the soil samples in the present study, it is possible that the die-off, or at least the loss of cultivability, of this important indicator in the present field study occurred faster than previously reported (Lang et al., 2007; Van Elsas et al., 2011). Analogous data were obtained for the edible portion of plants, in which no *E. coli* was isolated from every plots. These data are in agreement with other studies (Cirelli et al., 2012; Lonigro and Rubino, 2005), in which only fruit samples (tomato and eggplant) directly in contact with the soil where contaminated by faecal bacteria. Wood et al. (2010) showed that the decline in *E. coli* on the surface of spray-irrigated spinach was considerably rapid (3–5 log reduction in 72 h, and no isolation after 6 days). Another study reported that in the summer months, which are characterized by higher sunlight exposure of the crops, there was a more rapid decay of both the indicator and pathogenic microorganisms (Sidhu et al., 2008). In the present study, irrigating with treated wastewater (EFF) with an average value of 600 CFU 100 mL^{-1} of *Escherichia coli*, at harvesting time was not registered any presence of fecal contamination on lettuce crop.

We would thus argue that the good microbial quality of vegetable crops, (no *E. coli*, no *Salmonella spp.*), can be seen as the positive consequence of several factors: among the principal ones, drip irrigation method, that does not dirty the leaves, the summer period with increased UV radiation exposure of lettuce leaves surfaces. Also, the interval time between irrigation and harvesting may have contributed to reduce the effect of treated wastewater on the microbial load of vegetables.

5. Conclusions

Demo-scale research activities were conducted in Southern Italy for studying the effects of irrigation with treated municipal wastewater on vegetable crops, in terms of their quality and safety. The different wastewater treatment technologies tested produced effluent quality mostly within the stringent local standards and suitable for irrigation. Crop yields obtained with treated wastewater were higher than those of well water, due to the positive effect of higher water-borne nutrient concentrations.

Microbial indicators *E. coli* and *Salmonella* were never found in soil and on plants. Treated wastewater reuse in semiarid areas allows relevant fresh water savings and limits pollution due to fertilizers.

Acknowledgments

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INTERSECTORIAL REUSE OF WASTE AND SCRAPS FOR THE PRODUCTION OF BUILDING PRODUCTS: STRATEGIES AND VALORIZATION OF WASTE

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Abstract

The European Commission has introduced a whole range of policies and initiatives to promote the product eco-innovation and the environmental impacts reductions. One of the key topic for the reduction of the environmental impacts is the waste recycling and reuse (turning waste into useful resources). A teamwork of Politecnico di Milano has developed a research work, still ongoing and continuously updated, called *"The usefulness of the useless. Cross-sectorial evaluation of waste in construction"* which regards the possible reuse of pre-consumer scrapes/waste, deriving from various sectors, as secondary raw materials for the supply chains of the building sector. The goals of research work are the identification of the chains with high production of pre-consumer waste and scraps, the classification of these wastes by typology, the definition of scenarios for the reuse/valorization of the identified waste and the improvement of the environmental profile of products through an integration of recycled content. The research starts from the study of the most significant supply chains inside various sectors, analyzing the input/output and defining typologies and characteristics of waste/scrapes. To simplify the identification of recycling scenarios, the supply chains and related typologies of scraps have been classified according to a typical Italian filing system code. Then the data have been collected in a matrix used to identify feasible strategies and scenarios for the valorization of waste (this represent the first result of the work). The same matrix is also useful for public and private stakeholders for pursuing strategies aiming to the generation of positive externalities, at local and at global level. The next step is the proposal of new products deriving from the waste/scraps collected during the first phase.

Key words: eco-innovative supply chain scenarios, intersectorial analysis, pre-consumer recycling, product eco-innovation, waste valorization

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1. Introduction

Heavy metals can pose health hazards to man and during the last decades, one of the effects of a power-intensive industrial development, with the progress of the consumer culture, is the increasingly indiscriminate use of natural resources (OECD, 2012). In the last years, the inclination to consider the environment as an inexhaustible resource from which to draw benefits without any regulation and control, has generated several problems (availability of resources, social equity, etc). Every year, the Global Footprint Network, an international think tank that provides Ecological Footprint accounting tools to drive informed policy decisions, communicates the official date of the "Earth Overshoot Day" (the date on which natural resources consumption exceeds the Earth Planet capacity production for that year). In

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2014 (Global Footprint Network, 2014), this date has been in August: in just eight months, humankind has used the same quantity of resources which the planet Earth regenerates in a year. It represents a dramatic situation that we should not underestimate and we should monitor.

The interest of European Commission in this topic emerges from many initiatives which have been put in place recently. The most representative are:

- the "Thematic Strategy on the Sustainable Use of Natural Resources", to reduce the environmental impacts associated to resources use, and the "Thematic Strategy on the prevention and recycling of waste" (European Commission, 2005);
- the "Waste Framework Directive", that includes two new recycling and recovery targets to be achieved by 2020: 50% preparing for re-use and recycling of certain waste materials from households and other origins similar to households, and 70% preparing for re-use, recycling and other recovery of construction and demolition waste (European Commission, 2008a);
- the "Sustainable Consumption and Production Action Plan", SPC (European Commission, 2008b), that is contributing to improve the environmental performance of products and increase the demand for more sustainable goods and production technologies;
- the "Eco-innovation Action Plan", EcoAP (European Commission, 2011c), that started from the success of the experimentations conducted within the ETAP plan and, on the basis of the obtained results became its natural succession for development and promotion of eco-innovation in EU member countries;
- the ten-year strategy plan for growth and jobs, called "Europe 2020" (European Commission 2010), that has been launched to overcome economic crisis through the improvement of current growth models and to create favourable conditions toward a circular economy, supporting initiative as "The resource-efficient Europe flagship" and "The Roadmap to a resource efficient Europe";
- the long period strategy, called "Roadmap 2050" (European Commission, 2011b), that aims to reducing greenhouse gas emissions by at least 80% below 1990 levels by 2050 and to promote and developing a low carbon economy.

Nowadays the European scenarios confirm that there is a favourable climate to change the typical industrial production, oriented to unlimited waste production (Fig. 1), into a more sustainable system. Indeed, results from the 365th Eurobarometer (European Commission, 2013; Luca and Ioan, 2014; Martinez et al., 2014) estimate that the 95% of the European population believe that buying "green products" is the right thing to do for satisfying new environmental requirements (there are many people who are careful to the products information and in particular to their composition/production).

The environmental awareness has set the conditions for the research of alternative ways to produce new materials and to design new products, not only from virgin raw materials. So, a research group of the ABC Dept. (Architecture, Construction Engineering and Built Environment) of Politecnico di Milano, has been working for several years about the topic of pre-consumer waste/scraps intersectorial reuse for the production of new products.

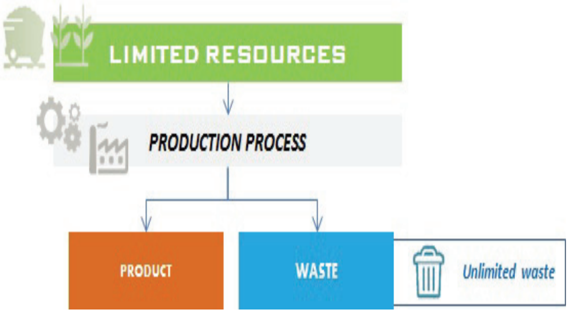


Fig. 1. Linear cycle – typical production model of industrial supply chain

The research focuses on the building sector supply chains investigating waste that are output of various production sectors and that potentially could be introduced in the building sector creating new products and improving the environmental quality of existing products and the process. Currently the sectors examined are the production of: wood, ceramics, stone, aluminum, concrete, paper, glass, mais, textiles and steel. Obviously, many are the sectors which could be integrated in this study, but this first phase is oriented to provide a methodology that, if pursued, could be able to involve interest at a larger scale.

The topic of the reduction of raw materials consumption is also being considered by an increasing number of companies, which are working on the optimization of the supply chains, through the contributions of new topics, such as the blue economy (Pauli, 2010) and the systemic design (Bistagnino, 2011). Stakeholders' involvement addresses the achievement of several important results in a short period. Moreover, European Commission initiatives simplifies those actions oriented to the eco-innovation (European Commission, 2011b), with active contributions and resource sharing.

The main contribute of this research work is the setting up of a material flows management system. The goals of the research are: the improvement of the environmental profile of products through an integration of recycled content (Bilgin et al., 2012; Pacheco-Torgal and Jalali, 2010; Rajput et al., 2012; Ulsen at al., 2013) and the set-up of an information system that supports the identification of opportunities of reuse/valorization of the waste coming from various productive sectors destined for disposal in landfill (Borsellino et al., 2009; El-Mahllawy, 2008; Silvestre et al., 2013). The research starts from the study of the most significant supply chains inside various sectors, analyzing the input/output and defining typologies and characteristics of waste/scrapes (Jin Choi et al., 2013; Kizinievic et al., 2013; Madurwar et al., 2013).

The data obtained from analysis phase have been collected in a matrix useful to identify feasible strategies and scenarios for the valorization of waste by using them in the construction sector as secondary raw materials.

2. Material and methods

One of the best strategies to promote product and process innovation is to create synergies and connections among companies (also operating in different sectors); moreover sharing information (Verganti, 2009) and knowledge is a basic step to ensure a project success. The contribution of the research "*The usefulness of useless. Cross-sectorial evaluation of waste in construction*" is to support the sharing of information between industrial sectors for a better use of waste as secondary raw material. The goal is to outline how it is simple to create industrial scenarios (not only at local level) aiming at mutual and global environmental performance improvement (Buenrostro et al., 2014; Hidalgo et al., 2014; Popescu et al., 2012). If we consider the geographical area interested by growth or extraction (for example: natural stone, wood, clay, and so on), it is clear that in a specific region there could be a significant concentration of environmental impacts (waste, dump, pollution). If we consider waste, if local decision makers collaborate among each other, they can decide to improve their processes, for example establishing a presence on the territory of a supply chain which uses, as raw material, waste and scraps of an other sectors. In this way individual and collective benefits could beincreased exponentially through a system based on intersectorial exchange of waste that within new processes can became secondary raw material (positive externalities overcome the negative ones, creating a balance).

The ideal supply chain scheme (Fig. 2) represents the cycle that materials should follow in order to enhance the proposed system. Starting from a typical situation of extraction or growing, the raw material follows its life cycle, passing through each stages and creating: a product, a pre-consumer scrap (object of interest in this work) and a post-consumer scrap (not the subject of this study, but it could be implemented in the matrix).

In order to enhance the environmental profile of the product the hypothesis is that the last two ones (pre and post consumer scraps) have to be reused or in the same supply chain or to other sectors. It is clear that decision about this reuse should be evaluated with appropriate tools; at this aim, Life Cycle Assessment could be assumed, as it is an internationally recognized and reliable method for assessing the environmental performance. LCA analysis allows to compare different scenarios/strategies, using for the inventory the quantitative data collected in the matrix; the results can support the decision-making process of different stakeholders (manufacturers, local public institution, etc.). LCA (Bribiàn Zabalza et al., 2011; Lavagna, 2008) provides a real assessment of the impacts at local (e.g. land use) and global scale (e.g. GWP). In this way, the result can support the choice of the strategies that can improve local realities giving results on a global scale (ERVET, 2005, 2009).

2.1. The reuse of waste/scraps to reduce environmental impacts

One of the key topics to reduce environmental impacts is represented by the recycling of waste/scraps derived from industrial productions and raw materials supply chain (pre-consumer waste). This type of waste/scraps is more easily to be mapped, tends to be produced with an annual fairly constant quantity and be uniform in its composition, unlike the post-consumer waste. Starting from considering waste and scraps as a resource it is possible to outline some alternative ways to encourage products sustainability and then to promote eco-innovative initiatives, in line with new environmental requirements (European Commission, 2005, 2011a).

The first phase of the research work concerns the study of different supply chains (not only related to the building sector), and the definition of waste and scraps typologies by analysing their material flows (input/output). One of the most important steps is the production processes mapping. Indeed, through the division of supply chain in "manufacturing steps", it is possible to outline the less efficient stages of the process (for example which are the steps that generate more scraps or waste) and to identify the specific type of waste/scraps which have been generated (for the individuation of the best reuse).

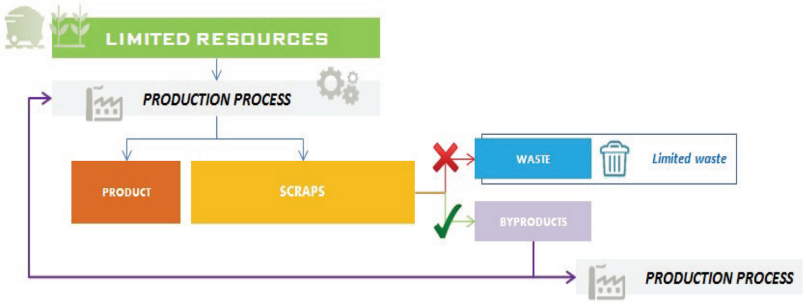


Fig. 2. The ideal supply chain

For example, considering the stone sector, the major quantity of scraps derives from the extraction and blocks squaring phases, and it is realistically quantifiable between 30 and 70% of the extracted material (the percentage depends on the extraction tipology, the lithotype and quarry characteristics). The consciousness of this situation allows to identify strategies and reuse scenarios, especially preferring upcycling processes (in this case it is possible to reuse the scraps as raw material for the artificial stone production, a new material with better performance than the natural stone).

The main contribution of the research is a matrix, which is going to be gradually implemented with new information, intended as a support to make preliminary assessments and to motivate strategic policies (at local and global level). The matrix contains information related to various production sectors and can be implemented with new chains and the related information. Actually the matrix is based on specific data reporting quantities and characteristics of scraps/waste coming out from specific manufacturing steps.

The matrix is structured in five different information levels (Fig. 3). At the first level of the matrix (Fig. 4) are listed the supply chain and the corresponding manufacturing steps. They are classified with a code which derives from a typical italian filing system (Ateco 2007 created by ISTAT, the national statistic centre accordingly to the European classification "NACE Rev. 2 – Statistical classification of economic activities").

For each manufacturing step waste and scraps typologies are classified with a code, which derives from CER catalogue (a European method to classify the typology of waste), and with an additional code for a better definition. The definition of materials potentially available (considering waste as resource) enables decision-makers to understand how and where they could develop new manufacturing process.

In the second level (Fig. 5), it is possible to split the production into different main steps (before use); each step generates some scraps, which can be reused as a secondary raw material in other industry sectors. For example, in the case of the stone production, the scraps deriving from the cutting (identified in the matrix with the code 01.04.13 CUT) can be reused for the realization of products assembled on supports, such as mosaics or precast facedes. In this case the reuse of the scrap, in addition to the environmental benefits involves a process of upcycling.

The third level of the matrix provides information on the locationing of the scraps. For example, if in an industrial district(Fig. 6), the amount of waste/scraps is considerable (both for quantities and availability), it is possible to:

- activate new supply chains (deriving from the studies about possible reuse);
- improve current industrial strategies (with the aim of reducing the amount of waste/scraps);
- evaluate those materials which can be transferred in another supply chains.

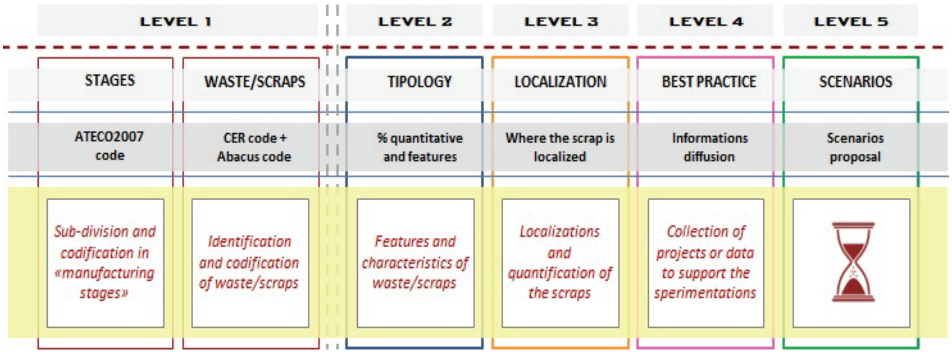


Fig. 3. The conceptual scheme of the matrix and the subdision into level of detail

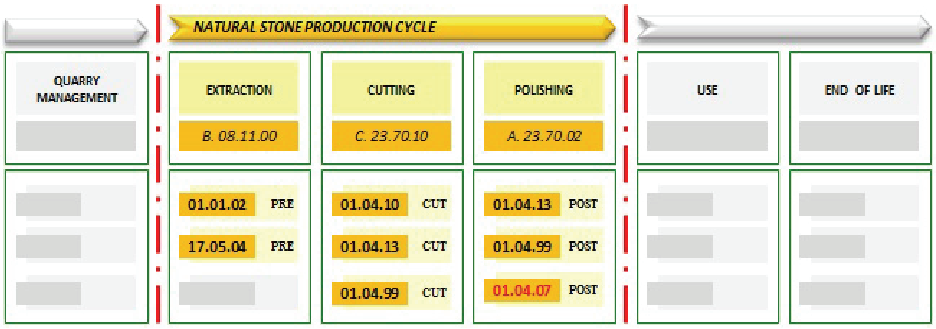
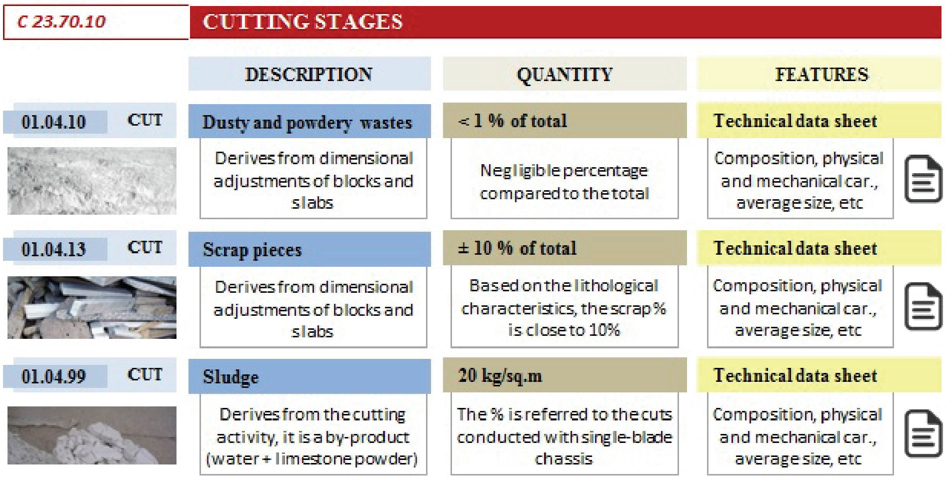


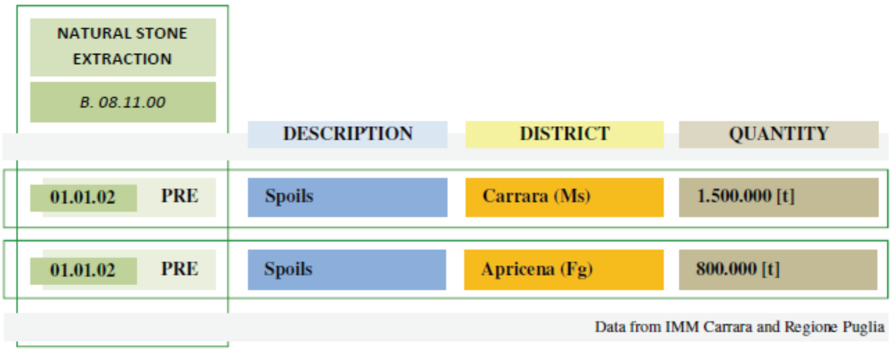
Fig. 4. Natural stone production cycle (level 1) - subdivision of a typical supply chain in "manufacturing stages"



C 23.70.10 **CUTTING STAGES**

		DESCRIPTION	QUANTITY	FEATURES
01.04.10	CUT	**Dusty and powdery wastes** Derives from dimensional adjustments of blocks and slabs	**< 1 % of total** Negligible percentage compared to the total	**Technical data sheet** Composition, physical and mechanical car., average size, etc
01.04.13	CUT	**Scrap pieces** Derives from dimensional adjustments of blocks and slabs	**± 10 % of total** Based on the lithological characteristics, the scrap % is close to 10%	**Technical data sheet** Composition, physical and mechanical car., average size, etc
01.04.99	CUT	**Sludge** Derives from the cutting activity, it is a by-product (water + limestone powder)	**20 kg/sq.m** The % is referred to the cuts conducted with single-blade chassis	**Technical data sheet** Composition, physical and mechanical car., average size, etc

Fig. 5. Natural stone production (level 2) - definition of type of scraps and characteristics



NATURAL STONE EXTRACTION

B. 08.11.00

		DESCRIPTION	DISTRICT	QUANTITY
01.01.02	PRE	Spoils	Carrara (Ms)	1.500.000 [t]
01.01.02	PRE	Spoils	Apricena (Fg)	800.000 [t]

Data from IMM Carrara and Regione Puglia

Fig. 6. Natural stone production (level 3) - geographical location and definition of quantity

The third level of the matrix is very important for the activation of strategic scenarios because it allows to quantificate the amount of waste that might became second raw materials, in a specific area. An hypotethical artificial stone producer, for example, may need natural stone scrap for his production and so he may decide to establish synergies with some companies operating in the stone sector. With this matrix, he could identify both the area of higher concentration of stone industries and the byproduct more responding to his needs and especially the quantity of available material. In this way it is possible to create a strong collaborations among companies achievable the entire production chain, in order to set conditions for the institution of an "Eco Industrial Park" (Biali et al., 2014; Chertow et al., 2000; Lowe, 2011; Lowe et al., 1997, 1996).

The fouth level of the matrix, pursuing the aims of activations of new productions, collect contributions and original experiments conducted starting from a specific waste/scraps in other productive contexts. An Eco-industrial Park (Pauli, 1997) could promote the reuse of all by-products obtained from production activities. The goal is the reduction of the waste production and especially the environmental improvement of production processes and products profile. The achievement of this goal is possible only through a radical innovation process starting from the proposal of new industrial scenarios, the development of new products design and the acquisition of new markets. Another key strength of this research work is the focus on recycling methods which move toward the so called "upcycling" process (waste or scraps should not be considered as second-rate materials but as a resource similar to virgin raw materials). Indeed, by identifying similar characteristics between scraps and raw materials, it is easier for the decision maker to assess the replacement of virgin raw materials with secondary raw materials. Thinking so, the positive externalities generated may allow to overcome negative externalities and the environmental improvement obtained could be available for everybody (the raw material is more, the landfills are not feeded, the product environmental profile is improved, the final product can be considered as a sustainable material, etc).

3. Results and discussion

The results of this research work are:

- definition of the matrix and structuring into five divided levels, four of which are already implemented at the experimental level
- application of the matrix to ten manifacturing sectors;
- implementation of information relating to the ten sectors on the quantity and on the characteristics

of the scraps

- test of the application of matrix on the stone supply chain, with geographical mapping of waste
- elaboration of data and construction of hypothetical scenarios of reuse
- proposal of use of LCA method for the evaluation of the data collected in the matrix
- testing of the LCA on the stone supply chain and definition of reusing scenarios

Below are some examples of the possibility to reuse scraps with profitable results, encouraging processes of upciclyng, and environmental improvements: the reuse of scraps deriving from ceramics sector in the same production process or as raw material for the production of other ceramic products (bricks, panels, etc), or self compacting concrete; the reuse of scraps deriving from wood sector for the production of remineralized wood useful for the production of insulation panel or floor surface, this use is better than the use as fuel for heating system (case of downciclyng).

4. Conclusions

The study has showed that the waste production is a common practice in almost all industry sectors; in some cases the amount produced is very important (this trend can be identified mainly in the sectors involved by the extraction or coltivation of raw material) and the scraps percentage can be rise even up to 70% of the amount extracted/coltivated (tipically in the stone or wood sector). Currently, in many companies, the waste/scraps are landfilled and this praxis is not profitable for the companies. If they decide to reuse the scraps in the same or other supply chain (with a strategy that could be oriented and supported by the contribute of this research work), they could have a significant economic gain (optimization of the raw material, reduction in cost of waste disposal, improvement of the environmental profile of the product, etc).

The research aims at creating a platform from which to get information suitable to support the development of forms of industrial ecology. Pursuing this goal, the creation of new production cycles (in symbiosis with the existing ones) becomes easier, and this result is the starting point for an efficient contribution to the environmental impacts reduction.

The next step of the research is the implementation of the matrix with new information and data, together with the elaborations of the design guideline for products made by using waste or scraps. The definition of new products, made by waste/scraps, (more simply the identification of sectors where is possible the waste/scraps reuse) could steer the producers towards new more sustainable company policies, from a small scale to all production scales. Another important aspect, in this research work, is the possibility to quantify and contextualize the information about the amount of waste/scraps available on the territory. This allows to set up a continuative scenarios of reuse and valorization of waste/scraps (in the logic of the opening of new production chains, based on the material recovered, have to consider the constant presence of the recovery materials, otherwise it becomes difficult to establish efficient synergies). To achieve this result, the research group is developing a GIS mapping system, which takes official data and becomes a local management instrument, supporting decision-makers who have the task of establishing strategic plans for environmental development.

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EFFECT OF NICKEL CONTAMINATION ON THE GROWTH OF OLEAGINOUS YEASTS IN HYDROLISATES OF *Arundo donax*

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Abstract

Hydrolysates of *Arundo donax*, a crop offering high productivity in contaminated or salinized soils with no inputs of irrigation and agrochemicals, were used in a discontinuous fermenter to grow the oleaginous yeast *Lipomyces starkey*, to obtain microbial oils potentially useful for the production of 2nd-generation biodiesel.

A mixture of fermentable sugars was obtained by steam-explosion and subsequent enzymatic hydrolysis of the lignocellulosic materials. The concentration of Ni^{2+} ions and of inhibitors of the microbial growth significantly affected both the biomass and the triglyceride yields. The microbial lipids produced were compatible with the synthesis of an automotive-grade biodiesel.

A physico-mathematical model, developed to describe the biomass growth, demonstrated that the concentration of heavy metals affected the maximum biomass concentration, though its influence on the specific growth rate of the yeasts was not significant.

Key words: Arundo donax, heavy metals, microbial oils, oleaginous yeasts.

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1. Introduction

The application of the first-generation biodiesel, mainly obtained from vegetable oils or animal fats, is critically limited by the relatively high costs of the feedstocks, that make the biodiesel still more expensive than mineral diesel (Huang et al., 2009; Yu et al., 2011), and by the insufficient availability of fertile land. In addition, the use of edible oils to produce biodiesel is threatening food supplies and biodiversity, causing social and environmental problems in developing countries.

New perspectives are offered by the recent development of new preparations of cellulolytic enzymes, that are able to efficiently hydrolyze lignocellulosic materials (Hendriks and Zeeman, 2009; Jorgensen et al., 2007), such as non-food parts of crops, forest products, and industry wastes, that can be recycled to obtain fermentable sugars. Though so far the hydrolysates of lignocellulose have been mainly used for the production of bioethanol, they can be alternatively employed for culturing oleaginous microorganisms, that are able to produce more than 20% of their weight in the form of lipids (Huang et al., 2012a; Pirozzi et al., 2013; Yu et al., 2011; Zhao et al., 2012). These lipids are mainly triglycerides, potentially exploitable as feedstock for the synthesis of the so-called *2nd generation biodiesel*. Among oleaginous microorganisms, oleaginous yeasts are particularly attractive due to their simpler cultural requirements (aerobic condition and a C/N ratio > 50), as well as to their ability to metabolize low-cost industrial wastes (Angerbauer et al., 2008; Fakas et al., 2008; Papanikolau et al.,

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2009). They are able to metabolize a wide range of wastes (Huang et al., 2012a; Liang et al., 2012; Meng et al., 2009; Papanikolaou et al., 2009; Pirozzi et al., 2013; Wang et al., 2012; Yu et al., 2011; Zhao et al., 2012), and have very simple cultural requirements, as the lipid accumulation occurs under nitrogen limiting conditions and excess of the carbon sources (Papanikolaou et al., 2011a, 2011b). In addition, the microbial oils obtained from yeasts have a composition quite similar to that of vegetable oils (Angerbauer et al., 2008), and are consequently suitable for the production of a biodiesel offering satisfactory performances as automotive fuel (Pirozzi et al., 2012).

The *Arundo donax* is a perennial crop known for its adaptability to different climatic and soil conditions, offering good yields in marginal lands and with low input cropping systems. *A. donax* is able to grow in soils polluted (Fiorentino et al., 2013) and salinized, and guarantee efficient protection to soils subjected to accelerated erosion (Fagnano et al., 2015).

In order to exploit the plant biomasses obtained from the polluted soils for the production of 2nd-generation biofuels, it is of crucial importance to analyse the effect of the pollutants in each stage of the process.

Heavy metals, apart from affecting the plant growth (Jamali et al., 2014; Malschi et al., 2013; Rashid et al., 2014), may significantly affect the performance of cellulolytic enzymes. In some cases, heavy metals at low concentrations may act as co-factors and activators to enhance the enzyme activity (Nanda and Abraham, 2013). Yet, in many cases they cause the inhibition of the cellular enzymes (Liu et al., 2010), forming complexes with the substrates, or interacting with specific functional groups, with enzyme-substrate complexes (Mikanova, 2006) and with sulphydryl groups (Shaw and Raval, 1961). They can also displace essential metal ions in metalloenzymes (Tamás et al., 2014), and affect the enzyme transcription (Baldiran, 2003). Obviously, different metals have a different effect on the enzyme performance.

Heavy metals can also affect the growth of the yeasts. Some heavy metals (e.g. Cu, Fe, Mn, Ni and Zn) may act as micronutrients contributing to the yeast's growth, whereas others (e.g., Cd and Pb) are not necessary for biological functions and produce only toxic effects (Bayoumi Hamuda and Toth, 2012). The toxic effect of heavy metals is often due to their affinity for cellular ligands (phosphates, purines, pteridines, porphyrins, or cysteinyl and histidyl side chains of proteins), that may cause the formation of complexes and clusters (Gadd, 1993). As a consequence, heavy metals can bind on the cell surface and alter the net charge of the cell, leading to the alteration of different physiological functions of the yeasts (Collins and Stotzky, 1992). They can also disrupt the integrity of the yeast's membranes (Avery et al., 1996).

Another potential problem for the production of the 2nd generation biofuels stems from the phenomenon of biosorption, i.e. the ability of the yeasts to adsorb or bind heavy metals. Obviously, biosorption may increase the chance of contamination of the final product (i.e. the biofuel).

In this study, we have characterized the effect of a heavy metal, namely the Ni^{2+} ions, on the growth of the oleaginous yeast *Lipomyces starkeyi* in the presence of hydrolysates of *Arundo donax*, and on the lipid accumulation within their cells. We have analysed the implications of the sorption treatment of the polluted hydrolysate, by evaluating the changes in the concentrations of both the Ni^{2+} ions and the inhibitors of the microbial growth.

Though the detoxification of the heavy-metal-contaminated wastes has been widely studied, very few studies have been so far focused on the removal of heavy metals from lignocellulosic hydrolysates (Lee et al., 2011; Mussatto et al., 2010; Silveira Chaud et al., 2012). In particular, no attempts have been made to evaluate separately the effects of the heavy metals and of other inhibitors on the oleaginous yeast's growth.

Lipomyces starkeyi have been so far grown using different waste materials as culture media, such as sewage sludge (Angerbauer et al., 2008), olive mill wastewaters (Yousuf et al., 2010), *A. donax* hydrolysates (Pirozzi et al., 2012), potato starch (Wild et al., 2010).

2. Materials and methods

2.1. Lignocellulosic biomass and microorganisms

A. donax was grown in open field conditions in hilly areas in Piana di Monte Verna (Campania, Italy). The transplanting of *A. donax* was made from rhizomes with a plant density of 1 x 1 m, and nitrogen fertilization was made at the end of rainy period (April) using a low dose (100 kg N ha^{-1} from urea). A strain of the oleaginous yeast *Lipomyces Starkeyi DBVPG 6193* (Culture Collection of the Dipartimento di Biologia Vegetale of the Perugia University, Italy) was used in the experiments. The yeast was maintained at 5 °C on YPD agar plate containing 20 g/L agar (Sigma), 20 g/L D-glucose (Sigma), 10 g/L yeast extract (Sigma) and 20 g/L peptone (Fluka). Prior to fermentation, 100 mL preculture in YPD medium containing 20 g/L D-glucose, 20 g/L peptone and 10 g/L yeast extract in 250 mL flask was carried out at 161 rpm and 30 °C for 24 h (Minitron, Infors HT, Switzerland).

2.2. Hydrolysis of lignocellulosic biomasses

The hydrolysis of the *A. donax* biomass was carried out following a two-step protocol, based on a steam-explosion followed by enzymatic hydrolysis. The steam explosion was carried out loading a 100 g batch of biomass in a pressurized vessel (5 L), and supplying saturated steam, heating the material at 205°C for 10 min.

Subsequently, the enzymatic hydrolysis was carried out using cellulase from *Trichoderma reseei ATCC 26921* (Sigma-Aldrich) and cellobiase from *Aspergillus niger* (Sigma-Aldrich). The activity of cellulase was determined as 161 filter paper units (FPU)/mL and 20.3 cellobiase units (CBU)/mL (Adney and Baker, 1996; Ghose, 1987).

2.3. Fermentation of yeasts in hydrolysates of A. donax

The growth tests were carried out using a fixed volume (150 mL) of hydrolysate without external organic supplement, contained in conical flask of 500 mL. The liquid medium was inoculated by 2 mL of microorganism suspension (optical density = 0.12 at 600 nm, which corresponds to ca. $2 \cdot 10^6$ CFU/mL). The flasks were incubated in a rotary shaker at an agitation rate of 160 ± 5 rpm and an incubation temperature $T = 30 \pm 1°C$. The effect of Ni^{2+} ions on the growth of oleaginous yeasts was analyzed by addition of $NiSO_4$ in three different concentrations (0, 50, 100 μM).

2.4. Removal of heavy metals

Ni^{2+} ions were removed by adsorption. The hydrolysate was first neutralized with NaOH to pH 6.5, and then treated with activated charcoal at different weight ratios. The hydrolysates were then incubated 8 h at 30°C and 160 rpm, then filtrated to remove the adsorbent. Finally, pH was adjusted to 6.5 with $Ca(OH)_2$ or 5 M H_2SO_4.

2.5. Lipid extraction and measurement

Methanol (5.0 mL) and chloroform (2.5 mL) were added to 200mg of dry biomass and vortexed 5 sec. Subsequently, the cells were disrupted for 12 min in an Ultrasonic Homogenizer (Omni Ruptor 250, USA) at 50% power and 90% pulser. The cells were then filtered off with Whatman no.1 filter paper and the solvent-lipid mixture was placed in a 50 mL tube fitting with centrifuge racks. The layers were separated by centrifugation for 10 min at 2000 rpm in a thermostatic centrifuge (Rotanta 460R, Hettich, USA) at 20°C. The lower layer was then transferred to a pear-shape flask with Pasteur pipette. Again, 10 mL of 10% (v/v) methanol in chloroform were added to the residue, a new centrifugation was carried out, and the lower phase was added to that from the first extraction. The solvent in the pear-shape flask was evaporated to dryness (BÜCHI Rotavapor R-200, Switzerland). After the extraction, the lipid amount was determined by weighting the extracted lipids after drying at 105°C for 1 h (Fontanille et al., 2012; Gong et al., 2013; Huang et al., 2012a; Liang et al., 2012; Tapia et al., 2012; Wang et al., 2012; Zhao et al., 2012).

2.6. Biomass and chemical analyses

The biomass growth was evaluated in terms of dry biomass weight. To this scope, the biomass was collected by centrifugation at 6000 rpm for 10 min and dried at 105°C until constant mass was achieved.

The concentration of Ni was measured following a modified method of Demirci et al. (1999) to prepare the samples. Briefly, the yeasts were precipitated by centrifugation (10,000 rpm and 4ºC for 15 min), collected, washed three times (with 0.9% saline water) to remove the compounds adsorbed on the cell surface, and dried. Concentrated nitric acid (2.5 ml) was added to dried yeasts (0.05 g) in a kjeldahl flask, and heated at 160ºC. Concentrated sulfuric acid (1 ml) was then added under constant heating.

Small amounts of concentrated nitric acid were added until the solution was colorless, to keep oxidizing conditions. The sample was heated until a fume of sulfuric acid was observed, then cooled, diluted with distilled water (10 ml), filtered and diluted again with distilled water. The concentration of Ni was measured by an atomic absorption spectrophotometer at 213.9 nm.

Potential inhibitor compounds were analyzed by HPLC (LC2010c), equipped with a refractive index detector (RID-10A, Shimadzu, Japan), following the method adopted by Chen and co-workers (2009). The reducing sugars were measured by the Nelson-Somogyi method (Sadarivam et al., 1996).

2.7. Statistical analysis

All experiments were carried out adopting a minimum of three replicate tests. All values are means of three separate experiments. Differences were considered statistically significant for $P < 0.05$.

3. Results and discussion

3.1. Hydrolysis of A. donax biomass

In a first series of experiments, samples of *A. donax* were hydrolyzed by a two-step procedure, based on a steam-explosion followed by enzymatic hydrolysis, obtaining a final concentration of reducing sugars of 15.6 g/L in the hydrolysate. The pH of the hydrolysate was 5.2. The hydrolysate was characterized as regards the inhibitors of the microbial growth produced in the course of the hydrolysis (Papanikolaou et al., 2009; Yousuf et al., 2010) due to the degradation of sugars (e.g. furfural from xylose and 5-hydroxymethylfurfural), of lignin (e.g. vanillin, syringaldehyde, and 4-hydroxybenzaldehyde) and of other components of the lignocelluloses (e.g. acetic acid from acetyl groups, formic acid from xylose oxidation, and levulinic acid from glucose oxidation) (Palmqvist and Hahn-Hägerdal, 2000).

The concentrations of some potential inhibitors in the hydrolysate of *A.donax* are reported in the Table 1.

Table 1. Concentrations (g/L) of the main inhibitors of the microbial growth in the raw hydrolysate of *A. donax*

Inhibitors	*Concentrations (g/L)*
Acetic acid	5.6
Levulinic acid	1.6
Formic acid	1.8
Furfural	0.091
5-HMF	0.82

3.2. Effect of Ni^{2+} ions on the growth of L- starkeyi and growth model

The subsequent tests were aimed at analysing the growth of *L. starkeyi* in the hydrolysates of *A. donax*. A typical growth profile is reported in Figure 1 (square symbols).

The effect of the addition of $NiSO_4$ on the yeast's growth is also described in the Fig. 1. Significant decreases in the final biomass concentration were observed in the presence of $NiSO_4$: 22% with 50 μM $NiSO_4$, 30% with 100 μM $NiSO_4$. The addition of $NiSO_4$ also reduced the growth rate of *L. starkeyi* (Table 2).

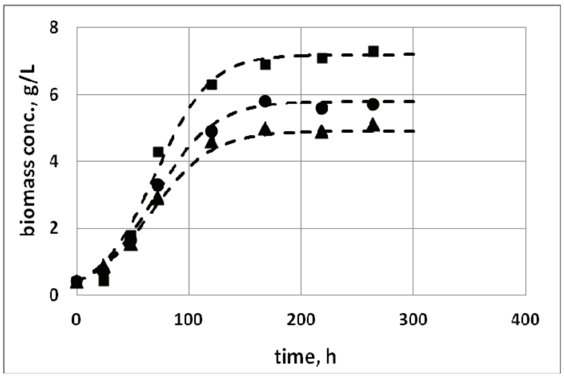

Fig. 1. Effect of the $NiSO_4$ concentration on the growth profiles. L. starkeyi cultured in batch reactors, in the presence of *A. donax* hydrolysate, T = 30°C. The dashed curves represent the theoretical data obtained with the logistic model. $NiSO_4$ concentrations: 0 μM (■), 50 μM (●), 100 μM (▲)

These results can be explained taking into account that, in the presence of 100 μM nickel, the absorption of Ni^{2+} ions in the yeast's cells may occur (Mariano da Silva et al., 2007). The nickelous ions absorbed may inhibit both the growth and the cellular metabolism of the yeasts (Joho et al., 1995), due to their interaction with enzymes (Hausinger, 1987), or other cellular components (Martin, 1988; Van Steveninck, 1966).

The pH value may affect the toxicity of the nickel. At lower values of the pH, nickel free ions are more available for interaction with the yeast, as their tendency to form nickel oxide and hydroxide is reduced (Hahne and Kroontje, 1973). As a matter of facts, the toxicity of nickel at pH 6.0 has been found very low (Soares et al., 2003), whereas the growth rate of yeasts is significantly reduced at pH 3,5 (Mariano da Silva et al., 2007). In our experiments, during the oleaginous fermentations, the pH dropped from an initial value of 5.2 to final values in the range 3.5-3.8. This may explain the observed reduction in the growth rate and in the final biomass concentration of *L. starkeyi*.

The profiles of biomass concentration obtained under different experimental conditions were described by a logistic growth model. The model includes a biomass balance (Eq. 1), where μ is the specific growth rate, defined by the logistic Eq. (2).

$$\frac{dX}{dt} = \mu X \tag{1}$$

$$\mu = \mu_{max}\left(1 - \frac{X}{X_{max}}\right) \tag{2}$$

In order to obtain the *X(t)* profiles, Eqs. (1-2) were integrated using a fourth-order Runge-Kutta integration method. The least-square method was used to obtain the parameter estimates. The model fitted the experimental data with a satisfactory R-squared value (R^2 = 0.95). In the Fig. 1 a graphic comparison is made between the model predictions (dashed curves) and the experimental results obtained at different concentrations of $NiSO_4$.

The results reported in Table 2 demonstrate a good correspondence between the experimental and theoretical data. The experimental data indicate that the final biomass concentration (X_{max}) decreases as higher concentrations of $NiSO_4$ are adopted, confirming the results shown in the Fig. 1. On the contrary, the specific growth rate (μ_{max}) appears not to be significantly affected by the $NiSO_4$ concentration.

3.3. Effect of the preliminary sorption of Ni^{2+} ions

The Fig. 2 summarizes the results obtained in the tests for the removal of Ni^{2+} ions from the hydrolysate at pH 6.5. The removal fraction increased with the amount of charcoal added.

Table 2. Comparison of experimental measurements of growth parameters with the theoretical data obtained with the logistic model, at different concentrations $NiSO_4$. Values are significantly different ($P < 0.05$, n = 3)

Concentration of $NiSO_4$, μM	*Xo*	*μ_{max}, h^{-1} (exp)*	*μ_{max}, h^{-1} (pred)*	*X_{max}, g/L (exp)*	*X_{max}, g/L (pred)*
0	0.4	$4.33 \cdot 10^{-2}$	$4.12 \cdot 10^{-2}$	7.12	7.21
50	0.4	$3.70 \cdot 10^{-2}$	$3.81 \cdot 10^{-2}$	5.88	5.86
100	0.4	$3.66 \cdot 10^{-2}$	$3.70 \cdot 10^{-2}$	5.01	4.96

A maximum removal fraction of 82% was obtained adopting charcoal concentrations above 0.06 g/(100 mL). Subsequently, the effect of the sorption treatment on the oleaginous fermentation was evaluated. To this scope, we carried out a growth test of *L. starkeyi* in a medium obtained from an *A. donax* hydrolysate with an initial Ni^{2+} ion concentration of 100 μM, after sorption treatment with 0.08 g/(100 mL) of charcoal (indicated as **sample A** in the Fig. 2). The residual concentration of Ni^{2+} ion concentration in the sample A was 25 μM. The sorption treatment did not cause appreciable changes in the concentration of reducing sugars (15.3 g/L in the sample A).

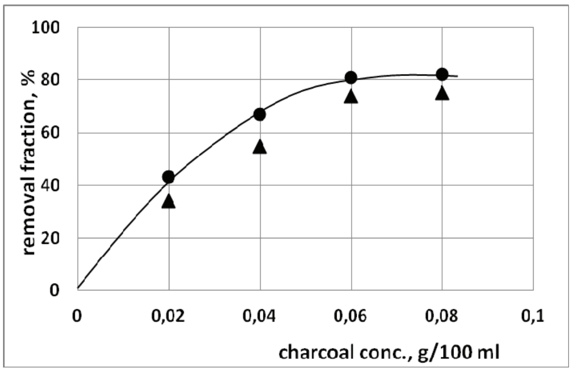

Fig. 2. Removal fraction of Ni^{2+} ions from the *A. donax* hydrolysate as a function of the charcoal concentration adopted. T = 30°C, pH 6.5, incubation time: 8 h. Initial concentration of Ni^{2+} ions: 50 μM (●), 100 μM (▲)

In order to achieve a clearer evaluation of the effect of the sorption treatment, we prepared a reference growth medium (**sample B**) from the raw hydrolysate of *A. donax*, adding a similar concentration of Ni^{2+} ion as in the sample A (25 μM). The Fig. 3 describes the effect of the Ni^{2+} ion concentration and the sorption treatment on the growth profiles of *L. Starkeyi*.

The experimental results showed a significant difference between the maximum biomass concentrations obtained using samples A and B as growth media, though the Ni^{2+} ion concentrations in these media was the same. The higher biomass production observed in the presence of sample A could be explained taking into account that the sorption treatment of the hydrolysate removes not only the Ni^{2+} ion, but also the inhibitors of the microbial growth contained in the raw hydrolysate (see Table 1).

Therefore, the growth of *L. Starkeyi* in the presence of sample B was slower as compared to that in the presence of sample A, due to the lower concentration of inhibitors in the sample A caused by the sorption treatment. In order to confirm this hypothesis, we measured the concentration of some inhibitors in the sample A. The data shown in Table 3 demonstrate that the content of all the measured inhibitors in the sample A is lower as compared to their content in the raw hydrolysate of *A. donax*. The pH values of samples A and B were very similar to the pH of the *A. donax* hydrolysate (i.e. 5.2). Therefore, these results were not affected by changes in the availability of nickel free ions for interaction with the yeast, as discussed in Paragraph 3.2.

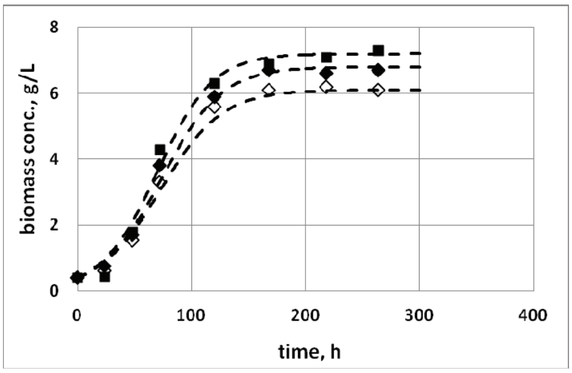

Fig. 3. Effect of Ni^{2+} ions and sorption treatment on the growth profiles. L. starkeyi cultured in batch reactors, in the presence of *A. donax* hydrolysate, T = 30°C. The dashed curves represent the theoretical data obtained with the logistic model. Growth media used:- raw hydrolysate of *A. donax* (■);- sample A (◆): raw hydrolysate of *A. donax,* after addition of $NiSO_4$ (100 μM) and sorption treatment with 0.06 g/(100 mL) of charcoal, to obtain a final Ni^{2+} ion concentration of 25 μM;- sample B (◇): raw hydrolysate of *A. donax,* after addition of $NiSO_4$ (25 μM)

Table 3. Concentrations (g/L) of the main inhibitors of the microbial growth. Values are significantly different ($P < 0.05$, n = 3)

	raw hydrolysate of A. donax	*sample A*[1]
Acetic acid	5.6	4.4
Levulinic acid	1.6	1.4
Formic acid	1.8	1.3
Furfural	0.091	0.073
5-HMF	0.82	0.24

[1] *sample A has been obtained as described in the paragraph 3.3*

3.4. Production of the microbial triglycerides

Table 4 reports the final biomass concentration and the lipid fraction within the yeast's biomass (%) obtained under different experimental conditions. The experimental results indicate that, when using the raw hydrolysate of *A. Donax* as growth medium, the lipid fraction was not significantly affected by the Ni^{2+} ion concentration.

Yet, the lipid fraction obtained when growing the yeasts in the presence of sample A was significantly higher, showing that the accumulation of lipids is more significantly affected by the inhibitors contained in the growth medium than by Ni^{2+} ions. However, when using the sample A the biomass fraction was lower. Consequently, the maximum lipid concentration (g/L) was obtained when using the raw hydrolysate with no $NiSO_4$ addition.

Table 4. Biomass and lipid concentrations of *L. starkey* grown under different conditions. Values are significantly different ($P < 0.05$, $n = 3$), unless they have a common superscript

$NiSO_4$ conc., μM	*Biomass conc., g/L*	*Lipid fraction, %*	*Lipid conc., g/L*
0	7.2	19.9^a	1.43
25	6.8	20.1^a	1.37
50	5.8	19.9^a	1.15
100	4.9	19.8^a	0.97
sample A[1]	6.1	22.5	1.37

[1] sample A: raw hydrolysate of A. donax, after addition of $NiSO_4$ (100 μM) and sorption treatment with 0.06 g/(100 mL) of charcoal, to obtain a final Ni^{2+} ion concentration of 25 μM.

The increase in lipid accumulation at lower concentrations of the inhibitors produced in the course of the hydrolysis is in agreement with previous studies In particular, it has been shown (Huang et al., 2012b; Zhao et al., 2012), that furfural is a strong inhibitor of the lipid accumulation of the yeasts.

As regards the effect of the heavy metals on the lipid accumulation, some conflicting indications are given by the studies available on this topic. Redox-active metals, such as Nickel, can induce free-radical production and promote oxidative stress (Hosiner et al., 2014). As a consequence, lipid peroxidation can be induced, causing a reduction of the lipid yield in the oleaginous yeasts. On the other hand, recent studies on fungi have shown (Yilancioglu et al., 2014) that oxidative stress can promote the lipid accumulation. In any case, our results demonstrate that Ni^{2+} ions, under the conditions adopted, do not affect significantly these mechanisms.

4. Conclusions

In spite of the presence of inhibitors of the microbial growth and of Ni^{2+} ions, *A. donax* hydrolysates could be used to produce microbial triglycerides potentially useful for the synthesis of II-generation biodiesel.

In all instances, the growth profiles of L. starkeyi in the *A. donax* hydrolysates could be described adopting the logistic curve model, obtaining a satisfactory correspondence between the experimental and theoretical data. Increases in the $NiSO_4$ concentration resulted in the reduction of the biomass yield and of the specific growth rate of the yeasts.

We demonstrated that the treatment with charcoal of *A. donax* hydrolysates containing heavy metals can significantly increase the yields in biomass and in lipids, due to the simultaneous removal of Ni^{2+} ions and of inhibitors of the microbial growth.

The lipid fraction within the biomass was increased by the removal of inhibitors. On the contrary, the lipid fraction was not significantly influenced by the concentration of Ni^{2+} ions.

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DEALING WITH LCA MODELING FOR THE END OF LIFE OF MECHATRONIC PRODUCTS

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Abstract

This paper discusses end-of-life (EoL) modeling issues in Life Cycle Assessment (LCA), through the application to a domestic cooker hood. Two EoL approaches are applied and discussed, namely the avoided burden and the one recommended by the Product Environmental Footprint (PEF) Guide, presently under testing. While no case studies on PEF application have been published yet, to the best of our knowledge, the scientific community is questioning the robustness and relevance of some methodological aspects, especially the EoL formula.

The objective of the work is to provide a case study for supporting the scientific discussion on EoL modeling by: applying the avoided burden approach to the cooker hood EoL; testing the PEF EoL approach on a cooker hood component, the aluminum filter, and compare the results with those obtained from the avoided burden approach; evaluating how both the approaches affect the allocation of burdens/credits associated to recycling. The Global Warming Potential (GWP) and the Abiotic Depletion Potential (ADP) impact categories are investigated.

The study points out that the PEF EoL approach delivers higher environmental impacts than the avoided burden one, due to a reduced contribution from the avoided impacts.

Overall, the application of the PEF EoL approach is more complex, due to the additional and often not available information needed, such as the recycled content of the materials and the disposal treatments that are avoided when recycled materials are used in the product. Also the structure of the LCA datasets may limit the application of the PEF EoL.

Key words: avoided burden, EoL recycling, Life Cycle Assessment, Product Environmental Footprint, recyclability rate

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1. Introduction

The Life Cycle Assessment (LCA) is widely recognized as the best framework for assessing the potential environmental impacts of products, systems and services (EC Communication, 2003). By accounting for inputs (materials, energy) and outputs (emissions, waste) at each step of the product life cycle, it enables options for environmental improvements to be identified. Though the methodology is standardized by the ISO 14040 series (ISO, 2006a, 2006b), subjectivity exists on how to deal with some methodological issues. End-of-Life (EoL) modeling has been discussed for years (Allacker et al., 2014; Ardente and Cellura, 2011; Ekvall, 2000; Frischknecht, 2010; Liu and Muller, 2012), mainly in relation to the topic of multi-functionality in recycling situations. Multi-functionality arises as recycling fulfils the dual functions of waste management and secondary material production (Nakatani, 2014), and thus an allocation has to be performed. There is currently no single, generally accepted approach to modelling EoL, and this is partly justified by the fact that it is

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not merely a scientific issue but a normative one in defining who gets the credits and the burdens of the recycling process. In addition, the reference standard (ISO 14044:2006) only distinguishes between open-loop product systems and closed-loop product systems.

Different approaches have been developed to deal with multi-functionality in recycling, such as the EoL recycling (also known as the avoided burden approach), the recycled content and the 50/50, to mention just a few. Each approach is characterized by different rationales of accounting for burdens and credits associated to the recycling process (Atherton, 2007; Dubreuil et al., 2010; Ekvall and Tillman, 1997; Frischknecht, 2010; Harper et al., 2006; Johnson et al., 2013). Since no agreement exists and ISO standards also leave room for interpretation, stakeholders usually support the use of the EoL approach that better promotes the environmental sustainability of their products on the market.

Modeling the EoL is a challenging aspect in sectors/product groups in which the EoL chain is fragmented and/or not yet fully developed from the technology point of view, like the electric and electronic equipment (EEE). The European Directive 2012/19/EC on Waste Electric and Electronic Equipment (WEEE) (EU Directive, 2012) has set a group of rules and procedures to ensure that each electronic component undergoes the most sustainable EoL treatment, with the general objective to improve the quality of the environment, and at the same time, to protect human health and to use natural resources prudently and rationally. Moreover, this product group is extremely significant from the point of view of the resources as strategic raw materials (significant amounts of base metals and copper, but also small content of precious metals) are used, high rate of EEE are produced and growing of WEEE is expected (Ciocoiu et al., 2013; Cui and Forssberg, 2003).

In fact, resources efficiency has been identified by the "Europe 2020 strategy" as a key element of the progress toward a low carbon economy and sustainable growth (EC Communication, 2010). "Sustainable consumption and production" and "Turning waste into a resource" are two interconnected policies that the "Roadmap to Resources Efficient Europe" (EC Communication, 2011) has identified to transform the economy into a resource-efficient one, which means improved efficiency, commercialization of innovations and better management of resources over their whole life cycle. Several actions are being adopted among which: "*a) the development of a common methodological approach to enable Member States and the private sector to assess, display and benchmark the environmental performance of products, services and companies based on a comprehensive assessment of environmental impacts over the life cycle, b) encouraging a secondary products market as well as the demand for recycled materials through economic incentives and developing of end-of-waste criteria, b) reviewing existing prevention, reuse, recycling, recovery and landfill diversion rate in order to move toward an economy based on reuse and recycling-based, with residual waste close to zero"* (EC Communication, 2011).

In this context, the European Commission has recently proposed a harmonized LCA methodology, the Product Environmental Footprint (PEF) (EC Recommendation, 2013) with the aim to create a single market for green products and to foster both supply of recyclable materials and demand for recycled materials. Moreover the Communication "Towards a circular economy: A zero waste program for Europe" pushes for materials such as metals, plastic, glass to re-enter the economy as secondary raw materials at competitive prices (EC Communication, 2014). In particular, for priority waste streams, such as metals, criteria have already been developed (Council Regulation, 2011).

The PEF Guide introduces an analytical approach to deal with multi-functionality in recycling (Pelletier et al., 2014), and it is currently under tests in several pilots in Europe. Criticisms have been raised, mainly related to the applicability of the approach (Lehmann et al., 2015) and to the fact that it is neither extensively tested nor extensively used, besides not being used in "*real-word decision making in either private or public organizations*" (Finkbeiner 2014).

In the framework of the current initiatives on EEE and PEF, the study here proposed is intended to contribute to the discussion about reliable scenarios for end-of-life of EEE, in particular of a product group presently not covered by the ongoing PEF pilot tests (http://ec.europa.eu/environment/eussd/smgp/pef_pilots.htm. The case study concerns the modeling of the EoL of a household appliance, namely a domestic cooker hood. Household appliances are characterized by considerable energy consumption during the use phase, which usually – in a life cycle perspective - overcomes the environmental impacts of the other phases. However, most of the household appliances, including cooker hoods, are equipped with basic or advanced electronic parts such as electronic boards and, capacitor; moreover, they are characterized by high content of metals (steel, aluminum and copper). Thus, management and optimization of the EoL processes play an important role when dealing with resource efficiency.

More in detail, the aims of the study are: a) to evaluate the EoL of the cooker hood, with the avoided burden approach; b) to test on the aluminum filter component the PEF EoL approach, as the one supported by the EU Commission, and compare the applicability and results to the avoided burden approach, as the one endorsed by the Metal Industry (Atherton, 2007). It is out of the scope of the paper the discussion on end of life treatments for WEEE.

The section "Materials and Methods" introduces i) the studied product, i.e. the cooker hood, ii) the EoL scenario defined for the product, iii) the description of the avoided burden approach application to the cooker hood, iv) the description of the application of avoided burden and PEF EoL approaches to the aluminum filter, which is a product component v) the Life Cycle Inventories (LCIs) arising from the application of the EoL formulas. The environmental impact results are shown in "Result" and, in the last section, main conclusions are discussed in relation to the stated objectives.

2. Material and methods

2.1. Description of the cooker hood and of the EoL scenario

The product under analysis is a domestic cooker hood (Fig. 1) manufactured by an Italian company. The studied model belongs to the T-shape product family and it is installed on the wall. It has both ventilation and filtration functions and can work at four different speed levels with a suction capacity of 660 m^3/h and a 68 dB noise level (at maximum speed). It is equipped with an electric motor (power rate of 250 W), two halogen lamps (20 W each), three aluminum-made filters, dishwasher safe, a filter alarm and a touch screen control panel.

Fig. 1. Cooker hood model

The cooker hood includes different components and materials (Table 1).

Table 1. Cooker hood materials and mass

Materials/components and mass	*(kg)*
Steel	11.9
Copper	0.638
Aluminum	0.546
Plastic	1.428
Glass	0.65
Electric and electronic devices	0.24
Capacitor	0.065

The primary function of the cooker hood is to remove cooking exhaust fumes from the cooking area.

The **functional unit** (FU) is defined as the capacity to draw air from the cooking area with a suction rate of 660m^3/h for one hour per day, to light the cooking area for 2 hours per day (EC Regulation, 2014) and to work for nine years (including all the ordinary and maintenance operations). The considered cooker hood does not include active carbon filtering. The reference flow of this study is one cooker hood working for 9 years.

Though an LCA study has been carried out from cradle to grave (ENEA, 2015), in this paper only the EoL phase is discussed. Thus, the boundary of the system includes the different processes occurring in the EoL stage, namely: collection of the cooker hood at its EoL, sorting (through manual or mechanical disassembly), transport between the different plants, and final treatment. The final treatment may include either secondary material production incineration or landfill.

The impact assessment method is CML 2001 (update Apr. 2013). In this paper those impact categories identified as relevant for resource efficiency (EU Communication, 2011) and the achievement of Kyoto Protocol goals (EU Progress Report, 2003) are analyzed, namely: Abiotic Depletion Potential Elements (ADP Elements), ADP Fossil and Global Warming Potential (GWP). The software Gabi 6 is used for the study.

As far as the EoL scenario is concerned, information currently available is scarce and country-related.

It is widely known that just a share of EEE at EoL is collected to be properly managed as WEEE. In order to raise the collection rate, the directive on WEEE has established that no costs have to be charged to consumers for WEEE management (EU Directive, 2012). The available studies on WEEE report data concerning production rate (UNEP, 2005; Huisman et al., 2007); typical compositions (ETCSCP, 2009); and/or metals/elements included (UNEP, 2013), and highlight the recycling potential. These studies usually concern office equipment, high-tech devices such as mobile phones and domestic appliances different from the cooker hood. Moreover, they do not include information on how the WEEE is effectively managed once collected and transported to the disposal/recycling plants. Therefore, in order to build a reliable EoL scenario, information was needed on a) the available technologies for household appliances dismantling as well as the ones generally adopted at disposal plants, b) the value and amount of scrap flows coming out from dismantling process of household appliances, c) current barriers to more resources efficient management of EEE EoL. To acquire this information the following approach has been adopted:

- visit to disposal plants, collection of technical data (disassembly sequence and time) concerning the actual dismantling process for household appliances and consultation with experienced operators;
- scientific and grey literature survey;
- interviews with experts;
- analysis of technical literature, in particular the Joint Research Center (JRC) report concerning the method for the measurement of recyclability, reusability and recoverability (Ardente et al., 2011).

The cooker hood EoL scenario analyzed consists in the collection and transport to the plant where dismantling is carried out in two stages, i.e. manual and mechanical. It takes into account the value of materials contained in the product and the cost and time for disassembling (Fig. 2).

The manual disassembly enables the following components to be removed: electric motor (including the capacitor), halogen lamps, printed circuited boards (PCBs) and the external cables. The capacitor is classified as hazardous waste. The other parts of the motor are made of valuable materials such as copper, steel and aluminum, which will be processed for recycling. The copper cables are removed manually mainly to increase the recyclability rate of copper. Based on information acquired at the visited disposal plant, halogen lamps can be easily removed, in order to avoid further contamination of the streams of material coming out from the shredder (Buttol et al., 2015). Though in this study the recovery of rare elements from PCBs has not been investigated, and the PCBs have been assumed to be sent to incineration, a scenario of manual dismantling of the PCBs has been assumed. Indeed, in presence of adequate treatment plants, their manual dismantling would allow the recovery of higher amount of precious metals (mainly copper, for low-value PCBs) (Stefănuţ et al., 2013) if compared with shredding together with other components (Ardente et al., 2012). Overall, the manual disassembly provides metals scrap for recycling and materials for energy recovery.

After the manual disassembly, all the remaining components are mechanically disassembled. The cooker hood is inserted into a shredding machine, which is equipped with separators able to sort ferrous and non-ferrous metals, while the fraction of materials containing plastic, rubber, glass and metals are not further separated.

The energy consumption for the shredding process has been estimated on the basis of data coming from the Ecoinvent 2.2 database. A standard distance of 100 km covered by a diesel truck has been assumed for all transport. For all electricity consumption in this study the EU 27 Electricity Mix 2002 from ELCD was used.

2.2. Recycling process for the involved material supply chains

Based on the described scenario, the materials sent to recycling are steel, aluminum and copper. Both the avoided burden approach and the PEF EoL approach account for burdens and credits of recycling, but with different rationales (see next two paragraphs for details), and require the identification of the following aspects:

- the recycling process, and related efficiency, of each material intended to be recycled;
- the virgin material, whose production will be potentially avoided, for each material addressed to recycling.

The recycling efficiency has been calculated by considering the efficiency of each step along the whole process: collection, sorting, transportation and treatment (here intended as secondary production). No material loss occurs during collection and transport stages, as it has been assumed that all private households, encouraged by the WEEE Directive (EU, 2012), return the cooker hood for proper dismantling. On the contrary, material loss occurs in sorting and treatment and it has been accounted for.

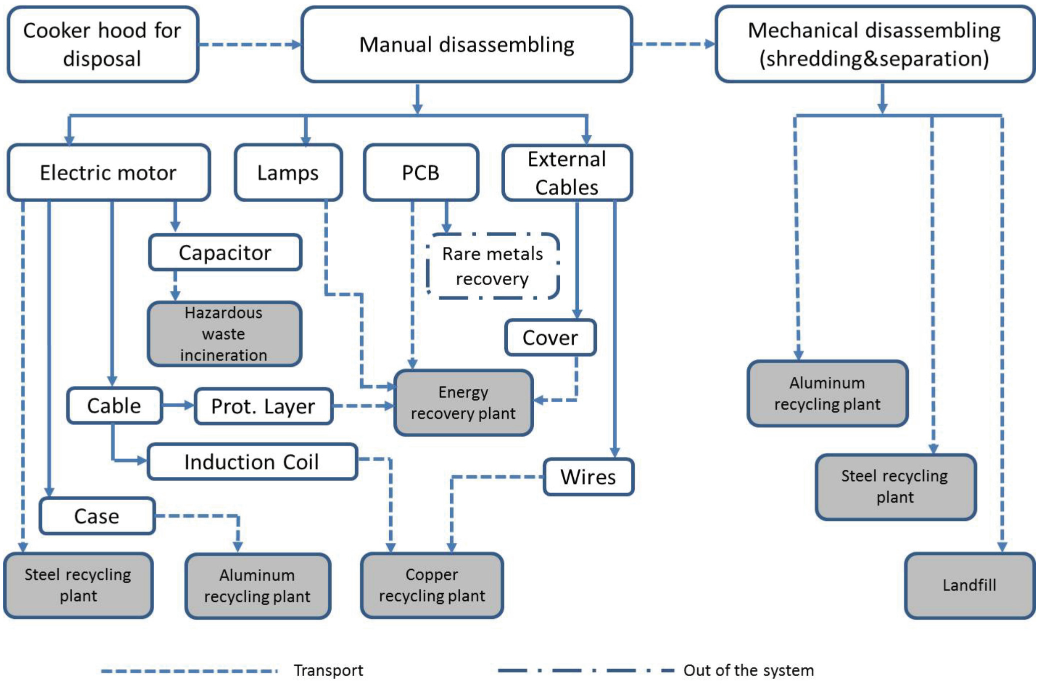


Fig. 2. Cooker hood End-of-life scenario

The sorting efficiency has been identified with the Recyclability rate defined by the JRC-IES methodology (Ardente et al., 2011). This index indicates a potential Recyclability rate of a product on the basis of measurable characteristics and specific assumptions, and considers each component and material used in the product.

The index takes into consideration 1) the disassemblability of the product (*D*) in both manual and mechanical disassembly; 2) the contamination of the material (*C'*) when incompatible materials can be found after disassembly, 3) the degradation of the material (M_D) as a measure of quality loss after use and recycling treatment. The Recyclability rate does not take into account the material lost in the treatment.

The Recyclability of each material (R_m) is considered as a sub-task of the assessment (Eq. 1):

$$R_m = D_m * C'_m * M_{Dm} \qquad (1)$$

Table 2 shows values D_m, C'_m, M_{Dm} for both manual and mechanical sorting, taken from Tables 6, 8, 11 and 13 in Ardente at al. (2011).

Data on the efficiency of the treatment come from industrial associations or from Best Available Techniques (BAT) documentation.

The Table 3 shows the recycling process efficiency for steel, aluminum and copper. Details on sorting efficiency (Recyclability rates), treatment efficiency and avoided virgin materials are described here below for steel, aluminum and copper.

2.2.1. Steel

Steel is used for many components of the cooker hood and is managed to be recycled. Recyclability rates have been defined for steel coming out from both manual and mechanical sorting. For manual sorting, we have considered disassembly efficiency equal to 100%, no contamination as well as no material degradation, according to the values and information reported in Ardente et al. (2011). For mechanical sorting, the indexes of disassembling, contamination and degradation consider the losses due to shredding, according to the values reported in Ardente et al. (2011). The Recyclability rates are shown in Table 2.

The efficiency value of the treatment has been estimated on the basis of the Input/Output value reported in the BAT (Remus et al., 2013) for the production of steel from Electric Arc Furnace Route, where we considered that only scraps are processed.

The steel slab from basic oxygen furnace has been identified as the avoided virgin material, and the steel slab from electric arc furnace as secondary steel. The choices of primary and secondary steel production are consistent with the position of the World Steel Association (World Steel Association, 2011). On the basis of the Declaration by the Metals Industry on Recycling Principles (Atherton, 2007), they recognize that a closed-loop (as defined by ISO 14044, part 4.3.4.3.3.) can be applied for steel recycling, thus scrap is considered as an alternative source of equivalent (virgin) ferrous metal.

2.2.2. Aluminum

Aluminum is used for the filter and, in small amount, for the electric motor, namely the aluminum case and the squirrel cage of the electric motor. In the electric motor, only the case can be manually separated and addressed to aluminum recycling plant, while the aluminum of the cage cannot be separated and is sent to the recycling process together with the other steel components. Aluminum that makes up the filter is sorted after shredding to be sent to aluminum recycling plant. Therefore, two Recyclability rates have been defined, for manual and mechanical separation. The same assumptions adopted for steel have been considered. The calculated values are shown in Table 2.

The efficiency value of the treatment comes from data of the European Aluminum Association (2013a) for the production of secondary aluminum ingot.

The avoided virgin material is the aluminum ingot (primary production). This choice is consistent with the position of the European Aluminum Association (2013b) and with the Declaration by the Metals Industry on Recycling Principles too (Atherton, 2007), endorsed by the International Aluminum Institute. According to them aluminum can be recycled to produce wrought or cast aluminum alloys without any downgrading.

2.2.3. Copper

Copper is used for the coil of the electric motor, and for the external cables. All copper is manually separated and sent directly to copper recycling plant. A Recyclability rate equal to 100% has been calculated (Table 2), considering the same assumptions and references specified for steel.

As far as the treatment efficiency and the avoided impacts are concerned, the available inventory dataset on copper wire production is aggregated and already includes burdens and credits associated to treatment (secondary copper production) considering that 95% of copper waste feeds back into production with a recycling rate of 95%. Thus, conservatively, burdens and credits associated to copper wire treatment have not been accounted for in the EoL.

2.3. The application of the avoided impact approach to the EoL of the cooker hood

The avoided burden approach has been used to model the EoL of the whole cooker hood. According to this method the whole burdens and credits associated to recycling (as well as to recovery) are allocated to the studied system and the use of secondary material displaces the use of virgin (primary) materials (ISO 14044).

Table 2. Sorting efficiency for the recyclable materials. The sorting efficiency is identified by the Recyclability rate

MATERIAL	***Recyclability rate ($D * C' * M_D$)***	***Disassembling index - D***	***Contamination index – C'***	***Material degradation index M_D***
Steel - mechanical sorting	47.5%	95%	50%	100%
Steel - manual sorting	100%	100%	100%	100%
Aluminum - mechanical sorting	45%	90%	50%	100%
Aluminum - manual sorting	100%	100%	100%	100%
Copper – manual sorting	100%	100%	100%	100%

Table 3. Recycling efficiency for recyclable materials. The overall recycling efficiency results by the product of the collection, sorting, transport and treatment efficiencies

	Step efficiency				
	Collection	***Sorting (Recyclability rate)***	***Transport***	***Treatment***	***Overall recycling***
Steel	1	1 (manual) 0.475 (mechanical)	1	0.95	0.95 (manual) 0.45 (mechanical)
Aluminum	1	1 (manual) 0.45 (mechanical)	1	0.96	0.96 (manual) 0.432 (mechanical)
Copper	1	1	1	Not available	Not available

This approach focuses on the fate of the product after the use stage and on the consequent material output flows, based on the premise that supply of secondary material is constrained (Johnson et al., 2013).

The application of the approach needs information on:

- recyclability rates and avoided virgin materials on steel, copper and aluminum, described in section 2.2;
- plastic. The plastic of the cooker hood cannot be recycled because of the brominated flame retardants (BFRs) content. Plastic comes partly from manual disassembling (as residual of cables separation for copper recycling, see Fig. 2), and partly from shredding. The plastic rate that is mechanically disassembled cannot be sorted and is sent to landfill. The plastic coming out from manual disassembly, as well as the PCBs and the lamps, is sent to incineration for energy recovery;
- capacitor. Two options were available for the disposal of the capacitor: landfill of hazardous waste and incineration of hazardous waste. Incineration has been assumed as it is more impacting, thus adopting a conservative perspective.
- all materials that cannot be fully separated after shredding are not suitable for recycling because contaminated and are sent to landfill.

The energy consumption due to the shredding and separation processes of the total mass entering in the shredder is included. No environmental impacts occur in the manual disassembly step. In agreement with the Recyclability rates calculated, the mass entering in the treatment plants is 6.34 kg for the steel and 0.295 kg for the aluminum. The whole burdens associated to the treatment of these amounts in the respective plants are accounted for. The treatment delivers 6.02 kg of secondary steel (slab) and 0.285 kg of secondary aluminum (ingot): credits associated to the avoided production of an equal amount of primary steel and aluminum, respectively, are accounted for. The treatment process for aluminum and steel (respectively, secondary aluminum production and secondary steel production) come from the PE database.

The quantity of copper sent to recycling is 0.638 kg.

The cooker hood rate sent to incineration for energy recovery is 0.43 kg, including plastic (cover 0.04 kg, protection layer 0.089 kg, PCBs 0.24) and glass (lamps 0.06 kg). The datasets of life cycle inventory (LCI) for incineration of plastic and glass come from PE/ELCD. The LCIs represent the share of environmental burdens (and credits for energy and metal scrap export, through system expansion) associated to the specific fraction in a European average Waste-to-Energy (WtE) plant treating European average Municipal Solid Waste (MSW). The datasets include the production of 1.09 GJ electricity and 3.2 GJ thermal energy per ton of treated MSW and a European average grid loss of about 7%. The EU 27 District Heating Mix 2002 and EU Electricity Mix 2002 are used for the credit calculation. Credits for the metal recovery are included by considering the standard metal production. Burdens of remelting and re-processing of scraps are considered.

A hazardous solid waste incineration process (HWI) from Ecoinvent 2.2, with a technology representing modern incineration practices in Europe, has been used to model the incineration of capacitor (0.065 kg). The whole burden (100%) is allocated to the waste disposal function of HWI; no credit is included for energy production.

The remaining mixed mass coming from the shredding process is 7.69 kg (steel 5.61 kg, glass 0.59 kg, plastic 1.3 kg, aluminum 0.198 kg) and is sent to landfill. To model the process, the following PE datasets have been used:

- Landfill of ferro metals, for steel and aluminum;

- Landfill of glass/inert waste;
- Landfill of plastic waste.

2.4. Application of the PEF EoL approach to the EoL of the aluminum filter and comparison with the avoided impact approach

The avoided impact approach has been used to modeling the EoL of the whole cooker hood, but for testing and comparison purposes with the PEF EoL approach (EC, 2013), the application to the end-of-life of a component, the aluminum filter, is here presented and discussed. The PEF EoL approach is based on the general idea that both demand and supply are needed to promote material recycling. The recycled material substitutes primary raw material for 50% and other secondary material for the remaining percentage (Ekvall, 2000). According to the PEF EoL approach, 50% of burden and credits associated to recycling (output) are allocated to the system under study. The same percentage is considered for the allocation of burdens and credits due to the use of recycled material in the manufacturing stage (input). Concerning the energy recovery, the whole burdens and credits are included, as in the avoided impact approach. The Eq. (2) represents the PEF EoL formula, as indicated in the Annex V of PEF methodology (EU Recommendation, 2013):

$$\begin{aligned}&\left(1-\frac{R_1}{2}\right)*E_V+\frac{R_1}{2}*E_{recycled}+\frac{R_2}{2}*\left(E_{recycling}-E^*{}_V*\frac{Q_S}{Q_P}\right)+\\&R_a*(E_{ER}-LHV*X_{ER,heat}*E_{SE,heat}-LHV*X_{ER,elec}*E_{SE,elec})+\\&\left(1-\frac{R_2}{2}-R_a\right)*E_D-\frac{R_1}{2}*E^*{}_D\end{aligned}\tag{2}$$

where,

- R_1, is the "recycled (or re-used) content of material". It is the proportion of material in the input to the production that has been recycled in a previous system ($0 \le R_1 \le 1$).

- R_2 is the "recycling (or reuse) fraction of material". It is the proportion of the material in the product that will be recycled (or re-used) in a subsequent system. R_2 shall therefore take into account the inefficiencies all over the recycling (or re-use) processes ($0 \le R_2 \le 1$). The R_2 index corresponds to the overall recycling efficiency in Table 3.

- R_3 is the proportion of material in the product that is used for energy recovery (e.g. incineration with energy recovery) at EoL ($0 \le R3 \le 1$).

- E_V is the specific emissions and resources consumed (per unit of analysis) arising from virgin material (i.e. virgin material acquisition and pre-processing.

- $E_{recycled}$ is the specific emissions and resources consumed (per unit of analysis) arising from the recycling (or re-use) process of the recycled (or re-used) material, including collection, sorting and transport processes.

- $E_{recyclingEoL}$ is the specific emissions and resources consumed (per unit of analysis) arising from the recycling process at the End-of-Life stage, including collection, sorting and transportation processes. In closed loop $E_{recyclingEoL} = E_{recycled}$

- $E^*{}_V$ is the specific emissions and resources consumed (per unit of analysis) arising from virgin material (acquisition and pre-processing) assumed to be substituted by recyclable materials. In closed loop $E^*{}_V = E_V$.

- E_D is the specific emissions and resources consumed (per unit of analysis) arising from disposal of waste material at the EoL of the analyzed product (e.g. landfill, incineration, pyrolysis).

- $E^*{}_D$ specific emissions and resources consumed (per unit of analysis) arising from disposal of waste material (e.g. landfilling, incineration, pyrolysis) at the EoL of the material where the recycled content is taken from. In closed loop $E^*{}_D = E_D$.

- E_{ER}, are specific emissions and resources consumed (per unit of analysis) from the energy recovery process.

- $E_{SE,heat}$ and $E_{SE,elec}$ are specific emissions and resources consumed (per unit of analysis) that would have arisen from the specific substituted energy source, heat and electricity, respectively.

- $X_{ER,heat}$ and $X_{ER,elec}$ are the efficiency of energy recovery process for heat and electricity;

- LHV is the Low Heating Value of the material in the product that is used for energy recovery.

- Q_S/Q_P is the ratio between the quality of secondary material (recycled) and the quality of primary material.

The Recyclability rate and the avoided virgin material defined in section 2.2 for aluminum have been considered. The R_2 index calculated for the filter, which represents the efficiency of the overall recycling process (Table 3), is equal to 0.432 and lower than the Recyclability rate. The R_3 index is zero because no filter fraction is sent to energy recovery. The application of the PEF EoL formula requires also the following information:

- for each material included in the product under study, the percentage of recycled as well as the process for the production of recycled itself (related recycling process);

- for each recycled material used in the product under study, the disposal (e.g. landfilling, incineration) from which material has been diverted.

In this case study, we assumed that the aluminum used in the manufacturing of the product is from primary production (R_1=0).

Considering the Recyclability rate, 0.162 kg (45% of the aluminum) are sent to treatment (aluminum recycling plant), while 0.198 kg are sent to landfill. Unlike the avoided impact approach, in the PEF EoL approach, burdens and credits associated to the whole recycling process (from collection to the treatment) are accounted for an $R_2/2$ proportion of filter mass, that means, in our case, a factor equal to 0.216. According to the formula, a landfill process is associated to the remaining mass proportion and the related impacts. Being zero R_1 and R_3, the impacts associated to the filter EoL depends just on the production, recycling (including avoided burden) and disposal. Fig. 3 shows the schema of the PEF EoL and avoided burden approaches application to the aluminum filter, in order to highlight the differences.

The Table 4 summarizes final quantity of aluminum associated to each process occurring within the aluminum filter EoL.

3. Results

3.1. The EoL of the cooker hood, according the avoided burden approach

The environmental impacts associated to the EoL of the cooker hood are here reported for ADP Elements, ADP Fossil and GWP. Figs. 4 - 6 show the total values and process contributions.

The recycling treatment includes the re-processing of steel and aluminum scrap in the recycling plant for the production of secondary materials and the avoided impact includes the avoided primary production of steel and aluminum. The environmental impacts due to landfill of glass and plastic, electricity consumption for shredding and transport are grouped into other contributions.

For all the reported impact categories the most important contributions are from either incineration or treatment. The benefits of material recycling (avoided impact) are evident. The steel avoided production gives the main contribution to ADP fossil and GWP (about 82% of the total avoided impact), while in ADP element the main contribution comes from the aluminum avoided production (about 58%). For both ADP Fossil and GWP the avoided burden is the key factor driving the final results of the EoL. This is due to high energy consumption associated to primary steel and aluminum that will not be produced thanks to the recycling.

Table 5 shows that major contributions to all the impact categories come from the capacitor incineration and the steel treatment. The contribution of landfill is always negligible. The avoided impact of glass and plastic incineration in the ADP elements and fossil is due to energy recovery. Regarding the GWP, the emissions from plastic and glass incineration are higher than those related to the energy recovery, so the results show positive values of the impacts.

3.2. The end of life of the aluminum filter – comparison between the PEF EoL approach and the avoided burden approach

Here below the results are given of the EoL of the aluminum filter in agreement with the two approaches considered. The environmental advantages generated by the EoL and calculated with the PEF EoL approach are lower than those resulting from the avoided impact approach. This applies to all the analyzed impact categories, as shown in Figs. 7 - 9. Differences between the approaches are about 80% and are mainly due to two aspects: i) the amount of material sent to recycling is about five times higher in the avoided burden approach than in the PEF EoL; ii) the environmental impacts due to the production of primary aluminum are much higher if compared to the impacts of the recycling process. Data of literature report that recovering aluminum from scrap to produce secondary aluminum ingot consumes about 6 percent of the energy required to produce primary aluminum (approximately 23.8 kWh/kg of aluminum produced from bauxite ore) (U.S. Department of Energy, 2007).

Table 4. Comparison of mass accounted for in each EoL process of the aluminum filter, according to the avoided burden approach and the PEF EoL approach

	Avoided burden approach (kg)	***PEF EoL approach (kg)***
Aluminum production	0.36	0.36
Shredding	0.36	0.078
Treatment (aluminum secondary production)	0.162	0.035
Avoided impact (aluminum primary production)	0.155	0.033
Landfill	0.198	0.32

Table 5. Detailed analysis on process contributions (burdens) to the environmental impacts of cooker hood EoL. Percentages are calculated on the total positive values of the potential impacts

Contributions	***Environmental burden associated to EoL – ADP Element***	***Environmental burden associated to EoL – ADP Fossil***	***Environmental burden associated to EoL – GWP***
Capacitor incineration	51%	28%	35%
Plastic and glass incineration	-2%	-10%	5%
Steel treatment	32%	43%	37%
Aluminum treatment	12%	3%	2 %
Transport	1%	12%	9%
Electricity	2%	11%	10%
Landfill	2%	3%	2%

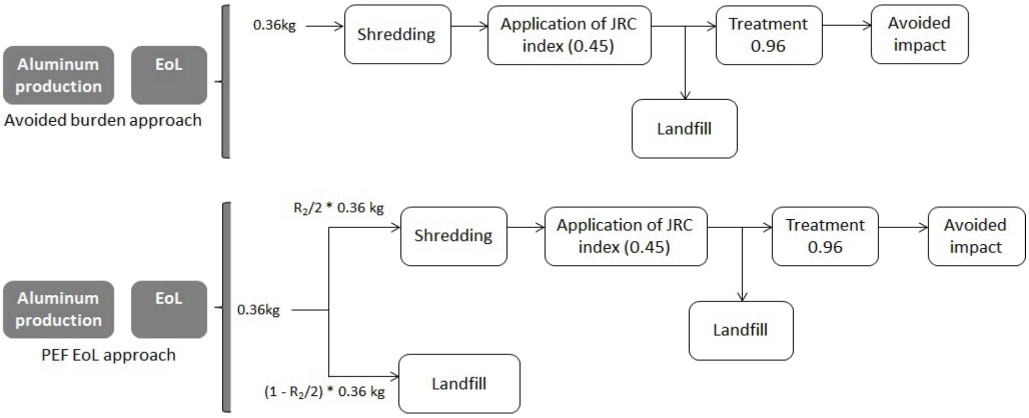
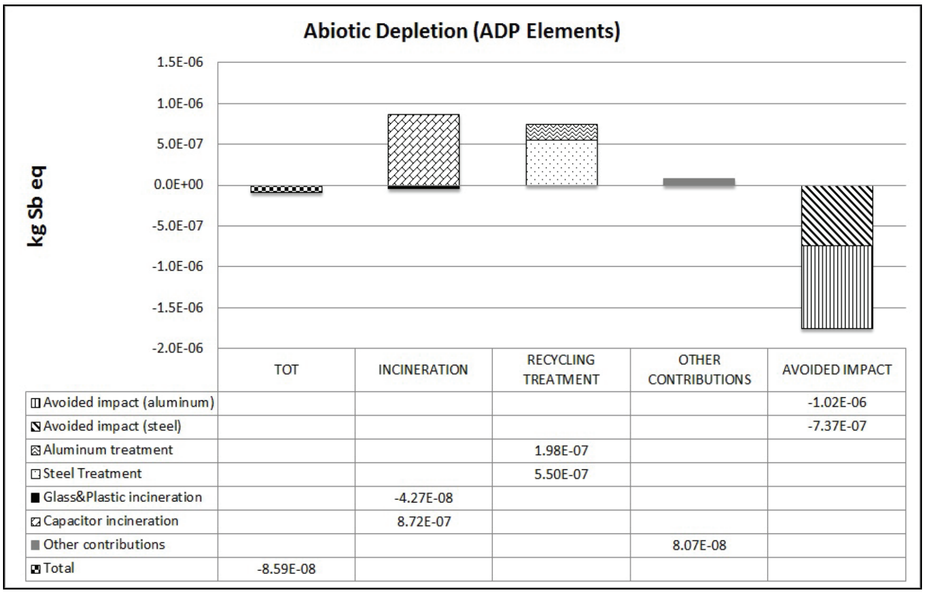
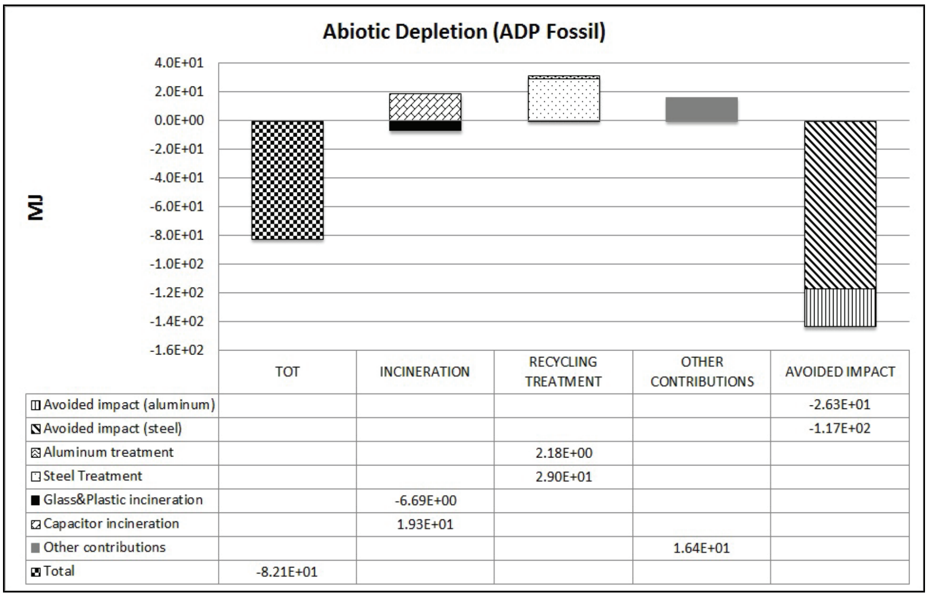


Fig. 3. PEF EoL and avoided burden approaches application to the aluminum filter



	TOT	INCINERATION	RECYCLING TREATMENT	OTHER CONTRIBUTIONS	AVOIDED IMPACT
▥ Avoided impact (aluminum)					-1.02E-06
▧ Avoided impact (steel)					-7.37E-07
▩ Aluminum treatment			1.98E-07		
☐ Steel Treatment			5.50E-07		
■ Glass&Plastic incineration		-4.27E-08			
▨ Capacitor incineration		8.72E-07			
■ Other contributions				8.07E-08	
▩ Total	-8.59E-08				

Fig. 4. Avoided burden approach - Process contributions to the total environmental impacts (burdens and credits) associated to the EoL of the cooker hood – ADP Elements [kg Sb-Equiv.]



	TOT	INCINERATION	RECYCLING TREATMENT	OTHER CONTRIBUTIONS	AVOIDED IMPACT
▥ Avoided impact (aluminum)					-2.63E+01
▧ Avoided impact (steel)					-1.17E+02
▩ Aluminum treatment			2.18E+00		
☐ Steel Treatment			2.90E+01		
■ Glass&Plastic incineration		-6.69E+00			
▨ Capacitor incineration		1.93E+01			
■ Other contributions				1.64E+01	
▩ Total	-8.21E+01				

Fig. 5. Avoided burden approach - Process contributions to the total environmental impacts (burdens and credits) associated to the EoL of the cooker hood – ADP Fossil [MJ]

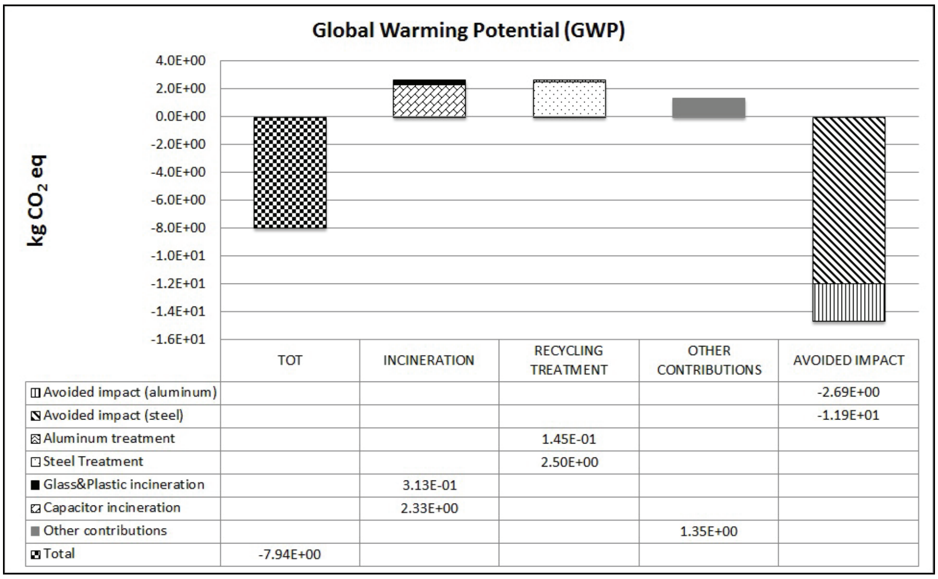


Fig. 6. Avoided burden approach - Process contributions to the total environmental impacts (burdens and credits) associated to the EoL of the cooker hood – GWP [kg CO2-Equiv.]

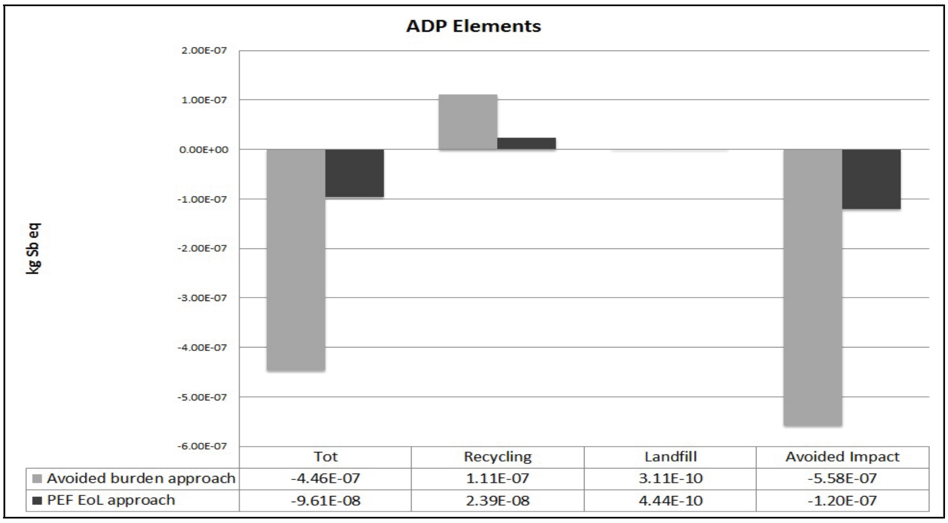


Fig. 7. Comparison between process contributions to the environmental impact (ADP Elements – kg Sb eq) associated to the EoL of the aluminum used in the filter

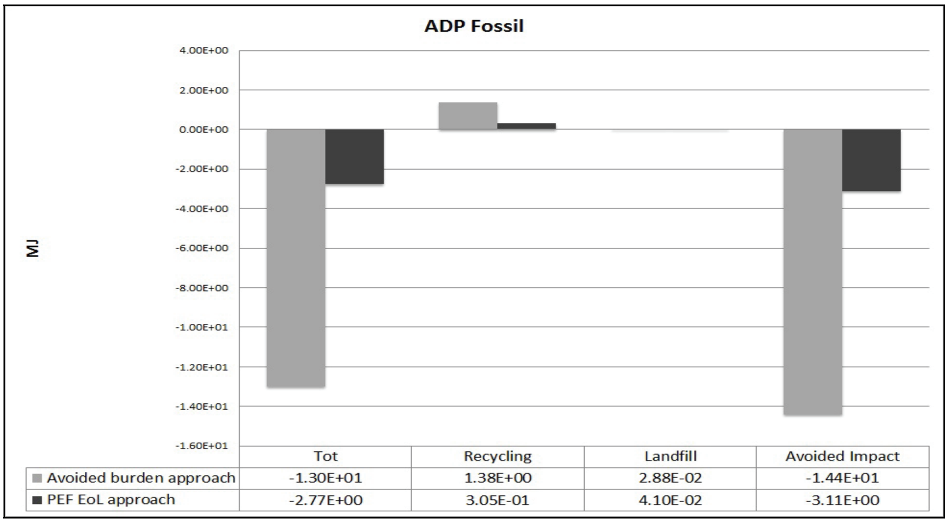


Fig. 8. Comparison between process contributions to the environmental impact (ADP Fossil - MJ) associated to the EoL of the aluminum used in the filter

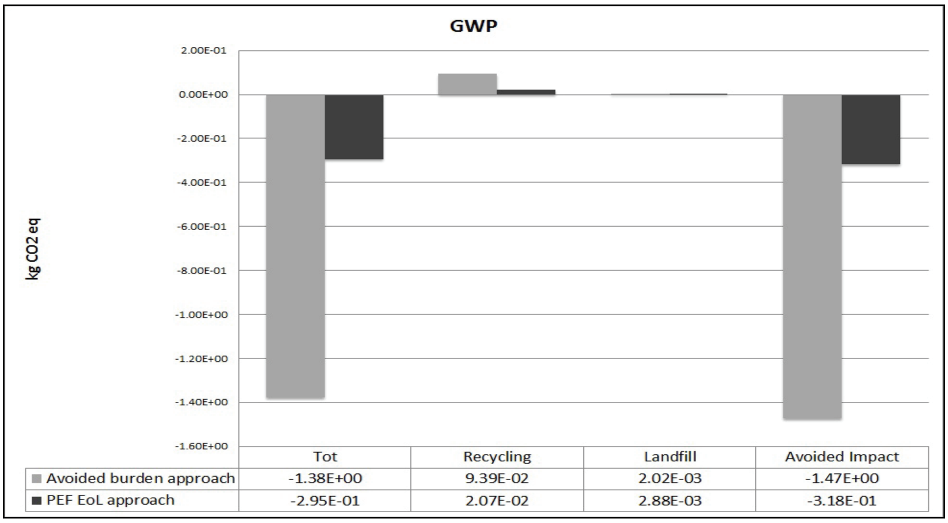


Fig. 9. Comparison between process contributions to the environmental impact (GWP - kg CO_2 eq) associated to the EoL of the aluminum used in the filter

4. Discussion

WEEE contains substantial quantities of valuable materials, in particular base metals such as copper, gold and palladium (Robinson, 2009), which are interesting for recovery purposes. Besides the WEEE Directive (EU Directive, 2012), this is the reason why WEEE collection and recovery have significantly grown in importance all over Europe (Sinha Khetriwal, 2009). Several studies have been conducted assessing environmental loads and advantages of WEEE well established collection and recovery systems at a local scale (Wäger et al., 2011). They highlight that, if the complete recycling chain is considered, the main impacts are associated to the final treatment applied to turn waste into secondary materials (Hischier et al., 2005), and sorting (and dismantling) activities give a small contribution to the total impacts.

Few studies have been conducted on single classes of WEEE, such as household appliances, mainly addressing the economic evaluation of optional recycling processes (Liu et al., 2009) or the environmental impacts all over the life cycle of the products (Bevilacqua et al., 2010).

Instead, critical aspects arise in LCA when modeling the EoL phase, in particular the definition of reference EoL scenario, the EoL treatment of trace elements and the methodological approach to account for burden and credits.

This study aims to add some elements to the discussion of these aspects.

The analysis of the defined scenario of cooker hood EoL shows how the manual disassembly procedure allows higher recyclability rates if compared to mechanical disassembly. However, components design often hampers fast and economic manual separation of materials, thus lowering their recyclability rate. In this scenario the copper is totally recovered for recycling, while the recyclability rates of other valuable materials such as steel and aluminum are strongly reduced by the use of a mechanical disassembly procedure. Nevertheless, the environmental advantages of the recycling are evident in the LCA results for all the three selected impact categories.

A point that should be analyzed more in detail is the potential of recovery and recycling of precious metals, whose primary production significantly affects the impact category ADP (elements). In this study, although PCBs are manually dismantled they have been assumed to be sent to incineration. In fact, as Chancerel et al. (2009) highlight, pre-processing facilities are optimized for recovering mass-relevant materials (steel, copper), while precious and special metals, which are contained at very small concentration in complex components (e.g., PCBs), are often lost.

On one side this calls for the implementation of specialized recovery systems. On the other side, a correct assessment of the potential benefits/disadvantages arising from precious metals recovery requires the definition of detailed technology and management scenarios and the availability of reliable data on resources and energy consumption, waste and emissions related to the recovery processes (Bigum et al., 2012).

As far as the methodological approach to account for burdens and credits is concerned, the application of both the analyzed EoL approaches presents some critical steps, in particular: the identification of the avoided primary material production and the availability of accurate data along the value chain for the calculation of the recyclability rate and R_2 index. Moreover, the application of PEF EoL approach is more complex than the avoided impact one since it requires additional information for the calculation of the other R indexes and the EoL burdens/credits assessment, i.e. the recycled content and the avoided disposal (e.g. landfill, incineration etc.) for the recycled material used in the product. The availability of such information strongly depends on the EoL management operated in each country as well as on the specificity of each material supply chain involved in the product. Further difficulties to model the EoL according to the PEF approach are due to the LCI datasets available. Two critical points can be highlighted: 1) the lack of clear and transparent documentation to understand whether credits and/or burdens for recycling are already accounted for; 2) the availability of aggregated datasets, often not parameterized, which cannot be adjusted according to the needs of the different EoL approaches.

5. Conclusions

A cooker hood EoL scenario has been defined on the basis of a detailed analysis of scientific and grey literature, visit to disposal plants, interviews with experienced operators and scientific experts. The disassembly steps at the dismantling site have been defined on the basis of the materials value and the time and cost needed for components dismantling. Being the recyclability rates "theoretical" and strongly cautious for the studied product, the definition of a realistic EoL scenario, including actual recyclability (and recoverability) rates, and the quantification of its environmental impacts stood out as urgent issues to plan adequate improvement actions for this waste flow and, more in general, for all WEEE. The analysis of the environmental impacts of the EoL scenario has been performed by using the avoided burden and the PEF EoL approaches. The results have highlighted that the application of both of them presents critical steps, discussed in the previous section. Here two aspects concerning the PEF EoL application deserve to be emphasized. Firstly, further guide would be necessary for the calculation and use of R indexes. In fact, if a well-defined and documented EoL scenario is not available, the PEF EoL formula leaves room for interpretation and subjectivity, thus contrasting with the harmonization objectives it aims to. Secondly, since the PEF has the general aim to promote a recycling-based economy, it is urgent to extend the application to other supply chains and to investigate the extent to which it succeeds in achieving this goal.

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ADSORPTION OF SIMAZINE AND BOSCALID ONTO ACID-ACTIVATED NATURAL CLINOPTILOLITE

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Abstract

It has been recently shown that acid activation enhances the ability of zeolitic tuffs to bind weak organic bases. More specifically, tuff containing acid-resistant zeolites (i.e. clinoptilolite) exhibits higher sorption capacity than chabazite/phillipsite-rich tuff.
Based on the above considerations, we investigated in depth the adsorption behaviour of two pesticides onto acid-activated clinoptilolitic tuff under different experimental conditions. The pesticides simazine and boscalid were chosen based on their different physico-chemical properties, simazine being a very weak organic base (pK_a=1.6) of low hydrophobicity (K_{OW} = 126) whereas boscalid is uncharged in the pH range 2-10 (pK_a=12.1) and has a moderate hydrophobic character (K_{OW} = 912). The acid-activated clinoptilolitic tuff adsorbent was obtained by treating a fixed amount of raw tuff with 0.1M HCl solution for two days.
The results of the experiments indicate that sorption is fast for both pesticides, reaching the equilibrium within hours. The acid treatment significantly improved the sorption capacity of the clinoptilolitic tuff for simazine, increasing the saturation level by over 70 times. In contrast, the sorption of boscalid was barely affected by the treatment. pH, cation exchange type and ionic strength appeared to play a relevant role in the sorption process, whereas the temperature and the specific surface area had no significant influence. Fast kinetics and good sorption capacity suggest that clinoptilolitic tuff, conveniently treated with acids, could be a suitable adsorbent for simazine and similar compounds.

Key words: acid activation, adsorption, boscalid, clinoptilolite, simazine

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1. Introduction

Adsorption is one of the most effective method for water and wastewater treatment (Abdulla et al., 2013; Dabioch et al., 2013; Krishnaiah et al., 2013; Lazar et al., 2015; Ma et al., 2013; Taha et al., 2014). Among adsorbents, activated carbon is very often used for removing organic molecules as well as certain metal and inorganic molecules because of its high internal surface (between 500 - 1500 m^2 g^{-1}) which makes activated carbon ideal for adsorption technique.

However, activated carbon does suffer from a number of limitations mainly related to the risk of fouling, especially when the water stream to be treated has high suspended solids content, and to the high cost of production and regeneration (Salam et al., 2011).

For this reason, over recent years, there has been a growing interest in the development of alternative adsorbents to activated carbon.

Natural zeolites are promising materials for using in water purification technologies because of their high cation exchange capacity and microporosity. They are aluminosilicate minerals which are both environmentally acceptable and easily available all over the world. Among them, clinoptilolite is one of most abundant and frequently

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used material in adsorption studies (Günaya et al., 2007; Leone et al., 2013a; Mihaly-Cozmuta et al., 2014; Qian et al., 2009; Russo et al., 2014). It has been shown that the adsorption efficiency of raw clinoptilolite towards certain compounds can be enhanced by modifying its surface properties. This can be achieved, for example, by grafting (Akgül, 2014), surfactant interaction (de Gennaro et al., 2014) or association with suitable molecules (Leone et al., 2013b; Zaremotlagh et al., 2014).

Other studies have focused on the acid activation of clinoptilolite. In particular, Salvestrini et al. (2010) have found in an exploratory investigation that acid activation of clinoptilolite increases its adsorption capacity for weak organic bases. The higher adsorption efficiency of clinoptilolite with respect to other natural zeolites tested (phillipsite and chabazite) mainly depends on the higher tolerance to the acid treatment, while preserving elevated cation-exchange capacity. Although the positive effect of the acid activation on the adsorption of weak organic bases has been clearly established, some aspects of the process still remain to be elucidated. Based on the above considerations, in order to gain deeper insight into the potential applicability of acid-activated clinoptilolite for water remediation, in the present work we investigated the adsorption properties of this zeolite in different cationic-form and under different conditions of ionic strength, temperature, dissolved organic matter and pH. Two pesticides found in natural water (Ahrens et al., 2015; Lapworth et al., 2015; Reilly et al., 2012; Wilson et al., 2011), namely simazine and boscalid, were selected for the adsorption experiments.

Simazine and boscalid were chosen based on their different physico-chemical properties, simazine being a very weak organic base (pK_a=1.6) of low hydrophobicity (K_{OW} = 126) whereas boscalid is uncharged in the pH range 2-10 (pK_a=12.1) and has a moderate hydrophobic character (K_{OW} = 912).

2. Materials and methods

2.1. Reagents

Simazine, boscalid, humic acids and all the other chemicals used in this study were purchased from Sigma-Aldrich. The main physicochemical properties of simazine and boscalid are reported in Table 1.

2.2. Adsorbent

A tuff sample rich in clinoptilolite (79%) was used for the adsorption experiments. The sample, designated as CPL, came from the sedimentary formation of Eskişehir (Anatolia, Turkey). Non-zeolitic phases included opal (15%), quartz (1%) and feldspar (5%). A detailed description of the chemical composition of CPL is reported elsewhere (Capasso et al., 2007).

Acid activation of CPL was obtained according to the procedure optimized in a previous work (Salvestrini et al., 2010). In short, 5g CPL sample was contacted in glass flasks with 500 mL of 0.1M HCl solution and kept under continuous stirring for 2 days. Afterwards, the acid-activated solid (hereafter referred to as H-CPL) was washed with Milli-Q water until no significant difference was observed in the conductance and pH of two sequential washing steps. Finally, H-CPL was collected by centrifugation and dried at 40 °C.

CPL and H-CPL were converted into their Na-exchanged (Na-CPL and Na-H-CPL, respectively) and Ca-exchanged (Ca-CPL and Ca-H-CPL, respectively) forms by contact with 3M solution of NaCl or $CaCl_2$, respectively, for 1 day (w/w ratio 1:10). The procedure was repeated several times with fresh solutions until pH and conductivity were stabilized.

2.3. Adsorbent characterization

IR analysis of the adsorbent was performed by a Spectrum GX Perkin Elmer FT-IR spectrometer. Suitable specimens for the KBr wafer procedure were obtained by diluting 0.5 mg of sample in 95 mg of finely powdered KBr. Specific surface areas (SSA) of the adsorbents were determined according to the BET method.

The measurements were performed using a Micrometrics ASAP 2010 volumetric adsorption apparatus. Zeta potential of the materials was determined using Zetasizer 2000-Malvern Instruments.

2.4. Adsorption experiments

Adsorption measurements were carried out by batch method at different temperatures (15, 25 and 45 °C). Different amounts of each adsorbent (0.5-10 mg) were contacted with 1 mL of pesticide solution (concentration range 1.5-5 mg L^{-1} and 0.5-3mg L^{-1} for simazine and boscalid, respectively) and kept under stirring on an orbital shaker at 120 rpm for 2 days. At programmed times, the samples were centrifuged for 1 min at 13000 rpm and then, a small aliquot of the supernatant was collected and analyzed by HPLC.

Table 1. Physicochemical properties of simazine and boscalid

	Formula	*MW (g mol^{-1})*	*K_{OW}*	*pK_a*	*Vapor pressure at 25°C (torr)*	*Water solubility at 20°C (mg L^{-1})*	*Stability in water (pH 7)*
Simazine	$C_7H_{12}ClN_5$	201.66	126 [a]	1.6 [a]	6.1×10^{-9} [a]	5.0 [a]	Stable [a]
Boscalid	$C_{18}H_{12}Cl_2N_2O$	343.21	912 [a]	12.1 [b]	1.5×10^{-8} [a]	4.6 [a]	Stable [a]

[a]Obtained from http://www.epa.gov/pesticides/; [b]Obtained from the chemicalize.org database by ChemAxon (http://www.chemicalize.org)

HPLC analyses were performed using a chromatographic Waters system consisting of 515 HPLC pumps and a 2487 dual λ absorbance detector, equipped with a C_{18} reversed-phase column TC-18(2) Agilent (4.6 × 250 mm, 5μm i.d.). Simazine and boscalid were eluted by a $CH_3CN(50\%)/H_2O(50\%)$ isocratic method with a flow rate of 1 mL min^{-1} and detected at wavelengths of 220 and 260 nm, respectively. Pesticide adsorption was estimated by comparing its concentration in solution before and after contact with the adsorbent.

Competitive adsorption between simazine and boscalid was investigated by adding 10 mg of adsorbent to aqueous solutions containing fixed amounts of one pesticide but different amounts of the other pesticide. Samples were analyzed as described above for single-component adsorption experiments.

Desorption experiments were carried out according to the following procedure. For a few samples, after adsorption analysis, one-half volume of solution was replaced by an equal volume of an adsorbate-free solution. Afterwards, the samples were stirred till the attainment of equilibrium (about 5 h) and then analyzed for determining the new adsorption level. The whole procedure was repeated four times.

3. Results and discussion

3.1. Adsorbent characterization

Comparison of FT-IR spectra for raw (CPL) and acid-activated (H-CPL) clinoptilolitic tuff reveals the decrease of the band intensity at 609 cm^{-1} (see Fig. 1) which reflects the dealumination and the loss of crystallinity of the sample after the acid treatment (Salvestrini et al., 2010).

However, in agreement with the high Si/Al ratio of CPL, this decrease is small suggesting that CPL can be effectively acid-activated while preserving to a large extent its structure. Destructuration of zeolite is accompanied by the increase of its specific surface area (SSA, see Table 3).

The negative charge of the adsorbent decreases with pH (see zeta potential data in Table 3) consistently with previously published data on clinoptilolite (Ersoy and Çelik, 2002; Huang et al., 2013).

3.2. Adsorption kinetics

The rate of adsorption of simazine and boscalid onto acid-activated clinoptilolite (H-CPL) is fast for all the experimental conditions tested. The pesticides uptake occurs to a large extent in the early stages of the process and equilibrium is achieved within 5 and 2 hours for simazine and boscalid, respectively.

A typical adsorption kinetic profile for simazine and boscalid is reported in Fig. 2. The ordinate *q* in Figure denotes the adsorption amount of pesticide (mmol) per mass of adsorbent (kg) at any time.

3.3. Adsorption isotherms

Figs. 3a and 3b show the adsorption isotherms of simazine and boscalid at T = 25°C onto H-CPL and, for comparison, onto the untreated tuff (CPL). Adsorption experiments carried out at 15°C and 45°C, gave similar results (data not shown), suggesting that temperature has no significant effects on the adsorption process.

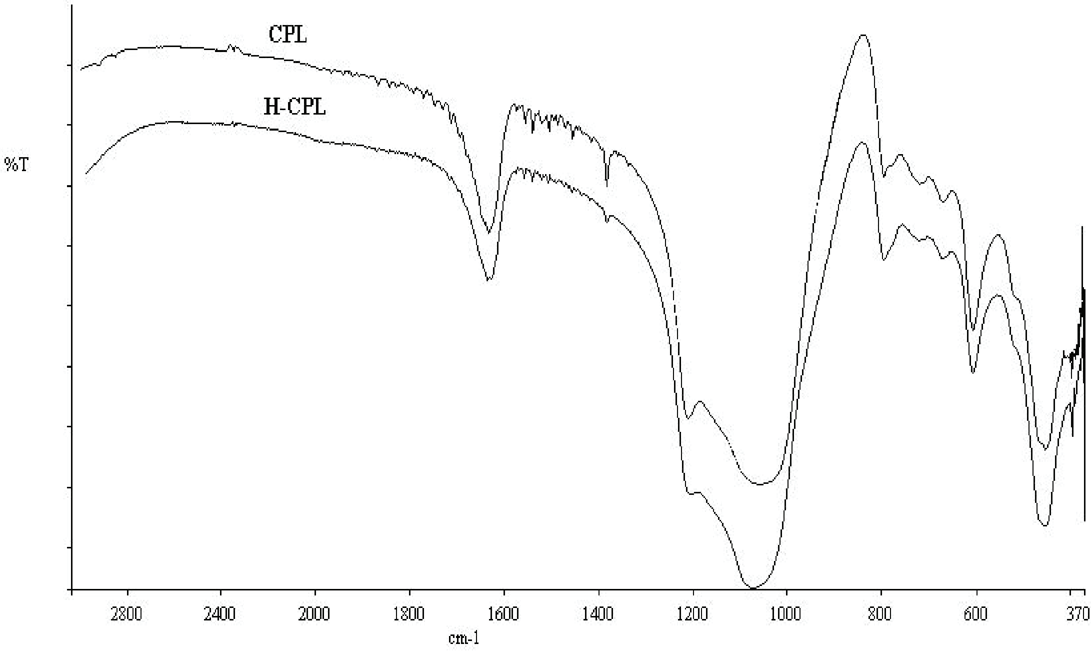

Fig. 1. FT-IR spectra of natural (CPL) and acid-activated (H-CPL) clinoptilolite

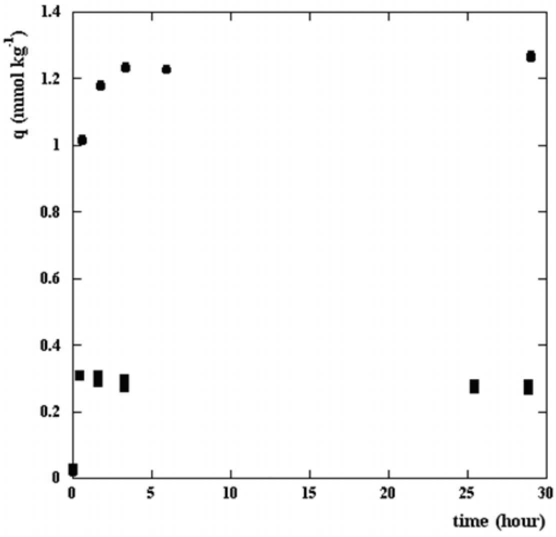

Fig. 2. Adsorption kinetics of simazine (●) and boscalid (■) onto H-CPL. Experimental conditions: T = 25°C; initial simazine concentration = 3.8 mg L^{-1}; initial boscalid concentration = 3.0 mg L^{-1}; mass of adsorbent = 10 mg; volume of solution = 1mL

The curves in Fig. 3a were obtained by fitting the experimental data to the Langmuir model (Eq. 1), where *q* (mmol kg^{-1}) is the adsorption amount per mass of adsorbent at equilibrium, q_m (mmol kg^{-1}) is the maximum adsorption capacity, K_{sim} (L mmol^{-1}) is the Langmuir equilibrium constant and *C* (mmol L^{-1}) is the pesticide aqueous concentration at equilibrium.

$$q_{sim} = q_m K_{sim} C_{sim} /(1 + K_{sim} C_{sim}) \qquad (1)$$

The estimates of K_{sim} and q_m for the adsorption of simazine onto H-CPL are 685 ± 95 L mmol^{-1} and 1.55 ± 0.04 mmol kg^{-1}, respectively. As it can be seen from Fig. 3a, the acid treatment significantly increases the adsorptive capacity of CPL. As a result of the acid activation, the saturation level of CPL increases by over 70 times. As regards boscalid (Fig. 3b), its adsorption onto natural CPL is higher than that of simazine. Moreover, the uptake of boscalid is barely affected by the acid treatment of the adsorbent as the adsorption onto H-CPL is only about 25% higher than that on CPL. Both the isotherms shown in Fig. 3b were found to be linear indicating that H-CPL and CPL exhibit constant affinity toward boscalid in the range of concentration investigated.

Accordingly, experimental data displayed in Figure, were modelled using a partitioning-like model (Eq. 2, linear equation), where *K'* (L kg^{-1}) is the linear partitioning constant.

$$q_{bos} = K'C \qquad (2)$$

The values of *K'* for H-CPL and CPL, determined by using Eq.(2), are 29.2 ± 0.7 L kg^{-1} and 16.9 ± 0.7 L kg^{-1}, respectively.

To examine whether the adsorption process is reversible, adsoption equilibrium data of simazine and boscalid after sequential desorption steps were compared to the adsorption isotherms calculated from Fig. 3.

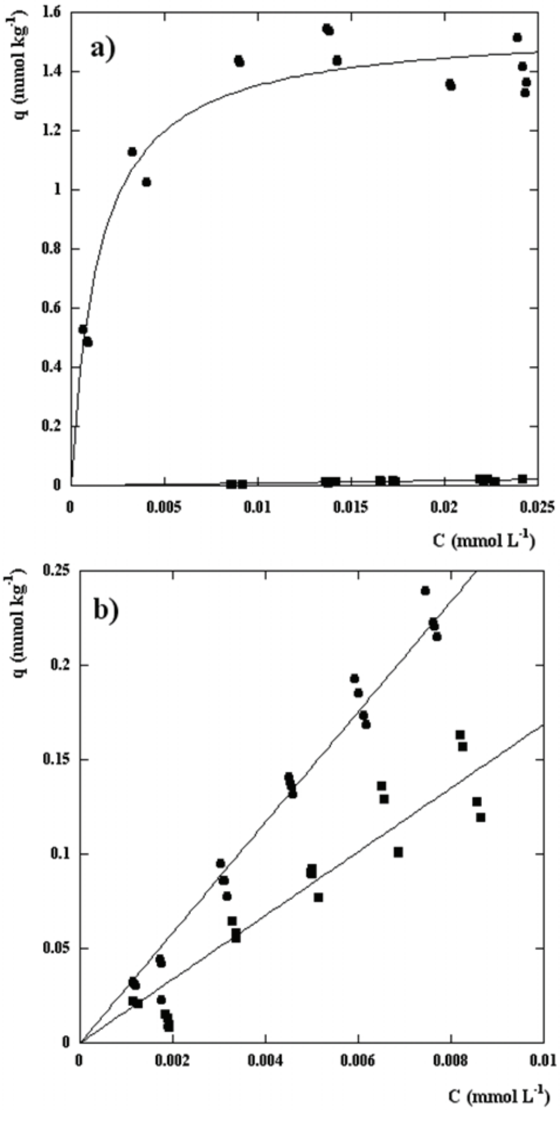

Fig. 3. Adsorption isotherms of simazine (a) and boscalid (b) onto H-CPL (●) and CPL (■) at T = 25°C

The results of these experiments are presented in Figs. 4a and 4b. The good agreement of the isotherms with the data suggests that the adsorption process for both simazine and boscalid is fully reversible. In order to ascertain possible competitive effects on adsorption, binary systems consisting of simazine and boscalid were also investigated. The extended Langmuir equation in the form of Eqs. (3-4) was used for this purpose, where K_{sim} and $q_{m,sim}$ have been already calculated (Eq. 1), whereas K_{bos} and $q_{m,bos}$ denote the boscalid Langmuir parameters (Sismanoglu et al., 2010).

$$q_{sim} = q_{m,sim} K_{sim} C_{sim} /(1 + K_{sim} C_{sim} + K_{bos} C_{bos}) \qquad (3)$$

$$q_{bos} = q_{m,bos} K_{bos} C_{bos} /(1 + K_{bos} C_{bos} + K_{sim} C_{sim}) \qquad (4)$$

Eqs. (3-4) are valid under the assumption that single component adsorption isotherm is described by the Langmuir model, all adsorbent sites are equivalent, each site can hold at most one molecule of simazine or boscalid and there are no interactions between adsorbate molecules.

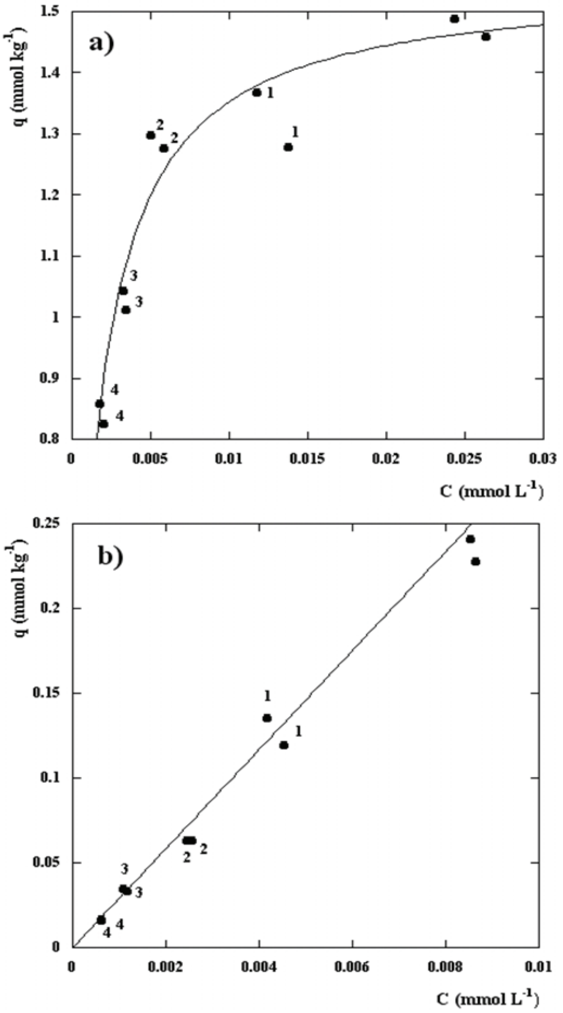

Fig. 4. Comparison between adsorption equilibrium data of simazine (a) and boscalid (b) after desorption and the calculated adsorption isotherm (numbers in Figure refer to four sequential desorption steps)

As discussed above, the boscalid isotherm is far below the saturation level not allowing to experimentally determine K_{bos} and $q_{m,bos}$. However, if simazine and boscalid compete for the same site, we can assume that they would reach at saturation the same surface coverage, thus implying that Eq. (5) can be applied, where A_{sim} and A_{bos} are the surface areas occupied per molecule of simazine and boscalid, respectively.

$$q_{m,bos} = q_{m,sim} A_{sim} / A_{bos} \tag{5}$$

Under this hypothesis, K_{bos} can be evaluated using the relationship (6).

$$K_{bos} = K' q_{m,bos} \tag{6}$$

Eq. (6) can be derived considering that, at low solute concentration, the Langmuir equation reduces to Eq. (7).

$$\begin{aligned} q_{bos} &= q_{m,bos} K_{bos} C_{bos} /(1 + K_{bos} C_{bos}) \\ &\approx q_{m,bos} K_{bos} C_{bos} = K' C_{bos} \end{aligned} \tag{7}$$

It follows that the values of K_{bos} and $q_{m,bos}$ are 31 ± 10 L mmol^{-1} and 1.05 ± 0.09 mmol kg^{-1}, respectively.

Figs. 5a and 5b show the experimental and the calculated adsorption isotherms of simazine and boscalid in binary systems by using Eq. (3) and (4), respectively.

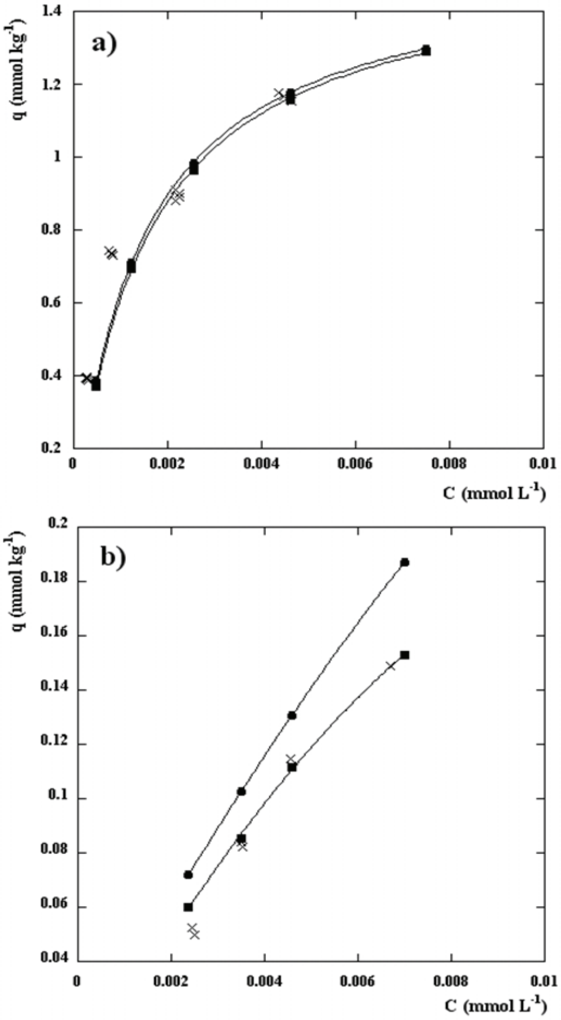

Fig. 5. Adsorption of simazine (a) and boscalid (b) onto H-CPL in binary system; (×) = experimental data; (■) = theoretical dual-component isotherm data; (●) = theoretical mono-component isotherm data

In the same figures, for comparison purposes, the calculated single component isotherms are also reported. Single and simulated dual-component isotherms of simazine (Fig. 5a) are almost coincident because of the much lower adsorption affinity of boscalid with respect to that of simazine (see K_{sim} and K_{bos} values).

For this reason, competitive adsorption can not be excluded a priori but in any case its possible effect is significantly small and negligible.

As regards boscalid (Fig. 5b), it can be observed that the experimental data in binary system are in good agreement with the simulated dual-component model indicating that boscalid adsorption is negatively affected by the presence of simazine.

3.4. Effect of exchangeable cations, ionic strength and dissolved organic matter

The role of the exchangeable cations in the adsorption process was investigated by using in some experiments the Na-exchanged and the Ca-exchanged form of the parent materials. Fig. 6 shows the adsorption isotherms of simazine onto H-CPL in its sodic- (Na-H-CPL) and calcic-form (Ca-H-CPL). The replacement of H^+ with Na^+ significantly decreases the adsorption performance of the adsorbent: the maximum adsorption capacity of Na-H-CPL is about 10 times lower than that of H-CPL. Nonetheless, it is interesting to note that the adsorption efficiency of Na-H-CPL is higher than that of CPL (see Fig. 3a).

In Fig. 6 is also reported the Ca-H-CPL isotherm. As a result of the calcium treatment, the adsorption capacity of Ca-H-CPL for simazine is even slightly lower than that of CPL.

The effect of the exchangeable cations on boscalid isotherms is less marked but follows a similar pattern. For the sake of brevity these results are not displayed.

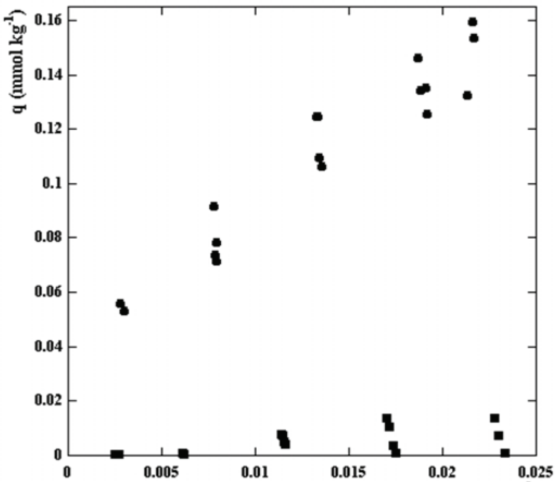

Fig. 6. Adsorption isotherms of simazine onto Na-H-CPL (●), Ca-H-CPL (■)

The effect of the presence of electrolytes was investigated on H-CPL by varying the ionic strength of the solution using NaCl or $CaCl_2$. The ionic strength values selected fall in the range of values commonly found in river waters (Berner and Berner, 1987). The results of these experiments are reported in Table 2. As can be seen from the Table, the presence of salts reduces the simazine uptake for all the experimental conditions tested, while boscalid is not significantly affected. More specifically Ca^{2+} has a greater detrimental impact than Na^+ on simazine adsorption. Adsorption capacity of H-CPL decreases up to 68% in the presence of 0.48 mM $CaCl_2$.

In some adsorption experiments, simulated natural water samples containing humic acids at concentrations normally found in rive water (Salvestrini, 2013; Salvestrini et al., 2008), were used to elucidate the influence of dissolved organic matter on the process. The results (Table 2) reveal that the adsorption of both simazine and boscalid is not influenced by humic acids; the decrease of simazine adsorption with respect to the reference sample (pure water) is mainly ascribable to the presence of salts.

3.5 Effect of pH and SSA

To gain a better understanding of the role of exchangeable cations in the process, we report in Table 3 the adsorption of simazine and boscalid as a function of pH and of the specific surface area (SSA).

As can be seen from Table 3, adsorption of simazine is negligible at pH > 8 whereas it dramatically increases at lower pH up to 1.4 mmol kg^{-1}. It is interesting noting that the effect of pH on the adsorption of simazine onto clinoptilolite differs from that observed with other acid-activated zeolites.

For example, Sannino et al. (2012) found that the adsorption of simazine onto zeolite H-Y is low at acidic pH, increases up to pH 6.5 and then drastically decreases at higher pH. According to the authors, the uptake of simazine likely involves a typical acid-base reaction. Adsorption occurs most favourably at pH where the acid sites of zeolite Y are not neutralized thus promoting acid-base reaction with uncharged simazine.

In order to understand the mechanism by which simazine adsorbs onto clinoptilolite, we examined the SSA of the adsorbents employed in this study. It is expected that the acid treatment positively affects the adsorption properties of clinoptilolite as it leads to destructuration of the zeolite and thus enhances the available surface area for pesticides uptake (Paul et al., 2010). However, in contrast to the above cited work, we found that the increased SSA, subsequent to the acid-activation, plays a marginal role in the simazine uptake. Indeed, as can be seen from Table 3, the adsorption capacity of Ca-H-CPL is lower than that of CPL, although the former material has twice the SSA of the latter. Moreover, when acid-activated clinoptilolite is converted into its sodic- or calcic-form, it loses most of its adsorption capacity while preserving its native SSA. The replacement of H^+ with Na^+ or Ca^{2+} is also accompanied by a raise of pH from 4.3 to 7.5 and 9.7, respectively, suggesting that the type of exchangeable cation is a crucial factor for the adsorption process.

Table 2. Effect of the aqueous phase composition on the adsorption of simazine and boscalid

HCO_3^- (mM)	***NaCl (mM)***	***$CaCl_2$ (mM)***	***Humic acid (mg L^{-1})***	***Simazine uptake (%)^a***	***Boscalid uptake (%)^a***
0.85	1.2	-	-	85	101
-	0.08	-	-	83	99
-	0.7		-	89	101
-	1.3		-	88	108
0.85	0.54	0.04	-	78	99
-	-	0.07	-	79	101
-	-	0.23	-	78	98
-	-	0.48	-	68	96
0.85	0.54	0.04	1	81	100
0.85	0.54	0.04	5	82	100
0.85	0.54	0.04	10	80	101

^{a} *Percentage respect to the adsorbed amounts by H-CPL sample in pure water.*

Table 3. Adsorption of simazine and boscalid as a function of pH

Adsorbent type	***SSA (m^2 g^{-1})***	***pH***	***Zeta potential (mV)***	***Simazine uptake (mmol kg^{-1})***	***Boscalid uptake (mmol kg^{-1})***
H-CPL	42	4.3	-13	1.4	0.22
Na-H-CPL	44	7.5	-32	0.4	0.17
Na-CPL	22	8.2	-38	0.023	0.14
CPL	23	8.7	-37	0.023	0.14
Ca-H-CPL	44	9.7	-41	0.019	0.13

The above considerations lead us to believe that the adsorption behaviour of simazine can be related to its ionizability. The maximum adsorption capacity for simazine is achieved at low pH, where the compound is partially protonated (pK_a = 1.6). At higher pH, uncharged simazine dominates over its protonated form leading to a marked decrement in the solute uptake.

The foregoing considerations suggest that low-energy interactions, i.e. electrostatic interactions, are the most responsible for the adsorption of simazine onto the clinoptilolitic tuff. This hypothesis is further supported by desorption experiments (Fig. 4a) which indicate that the process is fully reversible and by the absence of changes in the adsorption capacity within the range of temperature explored (15 °C - 45 °C, data not shown).

As with simazine, the adsorption of boscalid is not affected by temperature and is reversible (see Fig. 4b). As can be seen form Table 3, the adsorption of boscalid at high pH (>8) is higher than that of simazine. In such conditions, both boscalid and simazine are undissociated (see pKa values), thus suggesting that their adsorption behaviour is mainly related to their different hydrophobicity.

The small but significant increase in the boscalid adsorption at acidic pH, may reflect an increased hydrophobicity of the adsorbent with decreasing pH, as suggested by zeta potential data (see table 3) which indicate a decrease in the negative charge of the adsorbent. The increased hydrophobicty of the adsorbent enhances the hydrophobic interactions between boscalid and clinoptilolite, thus promoting the adsorption of the pesticide.

4. Conclusions

In the present work the effect of the acid-activation of clinoptilolite on the adsorption of simazine and boscalid was studied under different experimental conditions. The results indicate that the acid treatment significantly enhances the adsorption capacity of simazine whereas it has little effect on the adsorption of boscalid.

At higher pH values, boscalid is adsorbed to a greater extent than simazine in line with its higher hydrophobic character. Conversely, at lower pH (i.e. when the surface of clinoptilolite is H^+-enriched) simazine, being a very weak organic base, undergoes appreciable protonation which leads to its enhanced adsorption via electrostatic interactions.

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MYCELIAL GROWTH AND ENZYMATIC ACTIVITIES OF WHITE-ROT FUNGI ON ANAEROBIC DIGESTATES FROM INDUSTRIAL BIOGAS PLANTS

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Abstract

Solid digestate (SD) represents an environmental problem due to the continuous increase of biogas production. In the present study four white-rot fungal strains were screened for their ability to grow on two different SD samples, obtained from industrial biogas plants, using wheat straw (WS) as a control medium. Results show that i) the feedstock used in the biogas plant influences the time required for the colonization of the corresponding SD and ii) different fungal strains have different capabilities to colonize the same digestate. In particular, *Pleurotus ostreatus* SMR 684 reached the maximum proliferation on corn silage digestate (CSD) in the shortest time (12 days). Subsequently, *P. ostreatus* was grown on WS and CSD for 42 days with measurement of lignocellulolytic activities and lignocellulose components (lignin, cellulose and hemicellulose). Enzymatic activities reached a maximum around the 24th day of incubation. Ligninolytic activities showed similar trends on CSD and on WS, while some differences were observed in the levels of cellulolytic and hemicellulolytic activities. Lignin was reduced by 12% on CSD, this suggesting that the fungal treatment can increase polysaccharides accessibility in view of a further utilization of SD for biorefinery purposes.

Key words: biogas, biorefinery, solid digestate, white-rot fungi

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1. Introduction

Anaerobic digestion (AD) for biogas production generates a residue, the anaerobic digestate, which is often still rich in nutrients. When AD takes place in a liquid phase, the solid digestate (SD) is mechanically separated from the liquid fraction, which can be recirculated into the biogas plant. The most widely used feedstocks for biogas production are energy crops, harvest residues, animal manure and food residues. The SD deriving from AD of such substrates is mainly composed by cellulose, hemicellulose and lignin, as these polymers undergo relatively little changes during conventional AD processes because of the esther and ether linkages occurring between the cell wall polymers (Yue et al., 2010). Due to its recalcitrant structure, SD is not generally considered suitable for a further conversion into other useful products (Tambone et al., 2009), and it is currently used by the agricultural industry for soil amendment or animal bedding (Makádi et al., 2012). However, the continuous increase of biogas production poses serious problems in terms of SD disposal, since the high content of N and P in such material might cause environmental pollution if excessive amounts of it should be spread over agricultural soils (Udayasimha and Vijayalakshmi, 2012).

Mushrooms may represent a valid alternative for recycling nutrients contained in SD, since they

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are usually cultivated on lignocellulosic substrates such as wheat straw. Moreover, the ability of some fungi to degrade lignin, which is extensively reported and reviewed as biological pretreatment for second generation bioethanol production (Tian et al., 2012), might help to increase the accessibility of structural polysaccharides in SD, thus making such material susceptible to a further digestion step, with the consequent increase in the final biogas yield.

Some studies report the cultivation of fungi on various substrates supplemented with SD (Banik and Nandi, 2000, 2004; Gangulli and Chanakya, 1994; Isikhuemhen et al., 2009; Udayasimha and Vijayalakshmi, 2012), but there is still lack of knowledge about the ability of ligninolytic fungi to grow on SD as a unique nutrient source.

In the present study four species of edible fungi were screened for their ability to grow on two digestates obtained from AD at commercial scale of corn silage (CSD) and of a mixture of substrates (MSD), using wheat straw (WS) as a control. The best performing strain was then incubated for a longer time (42 days) with sampling approximately twice per week for the determination of proteins, ligninolytic, cellulolytic and hemicellulolytic activities, as well as residual lignin, cellulose and hemicellulose in the substrates used, with the aim of evaluating if fungal growth is able to increase the accessibility of polysaccharides for a further digestion step.

2. Materials and methods

2.1. Substrates

Anaerobic digestate samples were kindly supplied by two industrial biogas plants after removal of the liquid fraction. Corn silage digestate (CSD) was collected at “Fattoria Autonoma Tabacchi” (Città di Castello, PG, Italy); the plant, with nominal power capacity of 1MW per day, operated with 50 Mg of corn silage per day. Digestate from mixed substrates (MSD) was collected at “Azienda Agricola Palombini” (Nepi, VT, Italy); the plant, with nominal power capacity of 0.7 MW per day operated every day with 49.5 Mg of a heterogeneous feedstock composed by cow manure (50%), grass silage (10%), milk whey (21%), poultry litter (10%) and sugar beet-molasses (9%). Wheat straw (WS) was used as a control medium.

2.2. Mycelial growth on anaerobic digestates

Pure fungal cultures (*Agrocybe aegerita* SMR 206, *Pleurotus ostreatus* SMR 684, *Pleurotus columbinus* SMR 688 and *Pleurotus eryngii* SMR 151) were stored in the IBAF International Bank of Edible Saprophytic Mushrooms. Fungal mycelia were grown in sterilized Petri dishes containing 3% malt extract and 1.5% agar. When fungal biomass was abundant, plugs of 9 mm diameter were cut and inoculated in the centre of Petri dishes (11 cm diameter), previously filled with 15 g of the different substrates (WS 100% (control); WS 50%- CSD 50%; WS 50%-MSD 50%; CSD 100%; MSD 100%) with moisture fixed at 75% and sterilized at 121 °C for 30 min. Fungal growth was evaluated by measuring the diameter of the area covered by the mycelium every 24 hours. Radial growth rate (*Kr*) was calculated as $Kr= (R_1 - R_0)/(t_1 - t_0)$ (Trinci, 1971), where R_0 and R_1 are the colony radius at time t_0 and t_1, respectively.

2.3. Enzymatic activities assays

Another set of Petri dishes, filled with WS 100% and CSD 100 %, was made ready to study the enzymatic activities during 42 days of fungal growth. Twice per week the whole content of 3 Petri dishes for each substrate was weighted and extracted with 0.1 M potassium phosphate buffer pH 7.0 in a ratio 1:2 (w/v), filtered through a gauze and centrifuged at 9,000 x *g* for 20 min. In the supernatant, total peroxidases, Mn-independent peroxidase and laccase were assayed spectrophotometrically at 420 nm (ε_{420}=36,000/M cm) by oxidation of 2 mM ABTS (2,2’-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid, diammonium salt) in buffer solution (100 mM sodium acetate pH 4.5). Total peroxidases were assayed in the presence of 0.04 mM H_2O_2 and 0.1 mM $MnSO_4$. In Mn-independent peroxidase test 0.1 mM EDTA substituted $MnSO_4$. Enzyme activity was expressed in U/mg protein (one unit of enzyme activity was defined as the amount of enzyme that oxidized 1μmol of ABTS per min at pH 4.5 and 25°C). Peroxidase activities were obtained by subtracting the laccase activity. Mn-dependent peroxidase activity was obtained by subtracting Mn-independent peroxidase from total peroxidases activity.

In the same supernatants, endoglucanase, cellobiohydrolase and xylanase activities were measured in a buffer solution (sodium acetate 50 mM, pH5) using Avicel (0.5% w/v), carbossimethylcellulose (1% w/v) and xylan from beechwood (0.25% w/v) as substrates, respectively. Reactions were started by incubating the fungal extracts with the substrates for 30 min at 37 °C and subsequently stopped by incubating at 100°C for 3 min (Federici et al., 2012). After the reaction, the reducing sugars produced were determined spectrophotometrically (Miller, 1959). Data are expressed as U/mg protein (one unit of enzyme activity was defined as the amount of enzyme that produced 1μmol of glucose or xylose per min at pH5 and 37°C). Proteins were detected according to Bradford (1976) using bovine serum albumin for calibration.

2.4. Determination of lignin, cellulose and hemicellulose

Residual solids after buffer extraction (see 2.3) were ground (MF 10 miller IKA, Staufen, Germany) to pass a 0.5 mm grid. According to

Sluiter et al. (2008a), samples were deprived of their extractives for the determination of lignin, cellulose and hemicelluloses. The final extractives-free solid residue was hydrolyzed to determine i) acid-soluble lignin (ASL); ii) acid-insoluble lignin (AIL); iii) total monosaccharides content according to the method reported by Sluiter et al. (2008b). Monomeric sugars resulting from the acid hydrolysis of the extractives-free solid residues were analyzed by high-performance anion exchange chromatography, with pulsed amperometric detection (HPAEC-PAD) (Thermo Scientific™ Dionex™ ICS-5000, Sunnyvale, CA U.S.A.), consisting of an isocratic quaternary pump, a pulsed amperometric detector, an injection valve with a 5 µl injection loop and an analytical CarboPac SA10 column (4 mm x 250 mm) with the guard column.

The detection cell contained a gold working electrode (1.0 mm in diameter) and an Ag/AgCl reference electrode. Pulsed amperometric detection was carried out with the following waveform: E_1= +0.10 V (t_1=0.4 sec), E_2= -2.00 V (t_1=0.01 sec), E_3= +0.60 V (t=0.01 s), E4= -0.10 V (t=0.06 s). The electrical signal was integrated in ncoulomb (nC). Runs were carried out at 45°C. NaOH (1 mM) was used as mobile phase at a flow rate 1.0 ml/min with a post-column addition of concentrated NaOH (300mM) using a second pump, at a flow rate of 0.5 ml/min. Samples were filtered through 0.2 µm PPII syringe filters prior to injection. The instrumentation control, data acquisition, and processing was performed by the software Chromeleon Data System (CDS) version 6.8 (Thermo Scientific™, Dionex™).

Cellulose and hemicellulose contents were calculated from the amounts of monomeric sugars according to Ververis et al. (2007).

2.5. Statistical analysis

Experiments were performed twice; each mixture set in triplicate. Data are shown as the means ± standard deviation (SD).

3. Results and discussion

3.1. Mycelial growth on anaerobic digestates

Ligninolytic fungi are able to colonize, degrade and bioconvert lignocellulosic substrates thanks to the concerted and synergistic action of many lignocellulolytic enzymes.

At present, very little is known on the ability of such fungi to grow on SD resulting from biogas production, which is still rich in carbohydrates and might be further exploited through biorefinery.

Fig. 1 shows the trend of mycelial growth on the two digestates obtained from AD of CSD and MSD compared with that in WS, used as a control. It is noteworthy that most of the fungal strains grew faster on the mixture of WS and CSD than on the control medium, this suggesting that anaerobic digestate might improve fungal growth when added to a conventional growth medium.

Among the tested strains, *P. ostreatus* showed the fastest growth on WS 50%-CSD 50%, reaching the full colonization (11 cm) in 8 days, followed by *P. columbinus* and *P. eryngii* (11 cm in 12 and 13 days, respectively). *P. ostreatus* also reached the maximum proliferation on CSD 100% in the shortest time (12 days).

MSD was the harder substrate to colonize for all the tested fungi. In particular, the maximum growth on WS 50%-MSD 50% was reached after 12 days by *P. ostreatus*, and after about 17 days by the other strains.

None of the four fungal species was able to fully colonize the medium composed by MSD 100% in 17 days. These results are confirmed by the growth rate constant (Kr) calculated by linear regression of each colony radius versus time, the highest rate being detected on *P. ostreatus* grown on WS 50%-CSD 50% (Table 1).

These results show that the ability of a certain fungal strain to grow on a digestate can be severely influenced by the feedstock type used in the AD process. Among the tested fungi, *P. ostreatus* resulted to be the most suitable for cultivation on CSD. Pictures reported in Fig. 2 show the mycelial growth of *P. ostreatus* on the 5 tested substrates after 9 days of incubation.

3.2. Long incubation of P. ostreatus on CSD and WS: enzymatic activities and macromolecules content

P. ostreatus was incubated for 42 days on CSD 100% and WS 100% (incubation conditions are described in 2.3) and samples were tested twice per week.

Table 1. K_r*s* of the fungi grown on different substrates

Radial Growth Rate	***K_r (µm h^{-1})***			
Substrate	***Agrocybe aegerita***	***Pleurotus columbinus***	***Pleurotus eryngii***	***Pleurotus ostreatus***
WS 100%	168 ± 2	209 ± 6	157 ± 5	278 ± 18
WS 50%-CSD 50%	175 ± 5	249 ± 12	187 ± 6	316 ± 25
CSD 100%	91 ± 4	199 ± 8	180 ± 4	256 ± 19
WS 50%-MSD 50%	136 ± 2	196 ± 6	167 ± 5	244 ± 21
MSD 100%	25 ± 1	27 ± 3	44 ± 4	93 ± 6

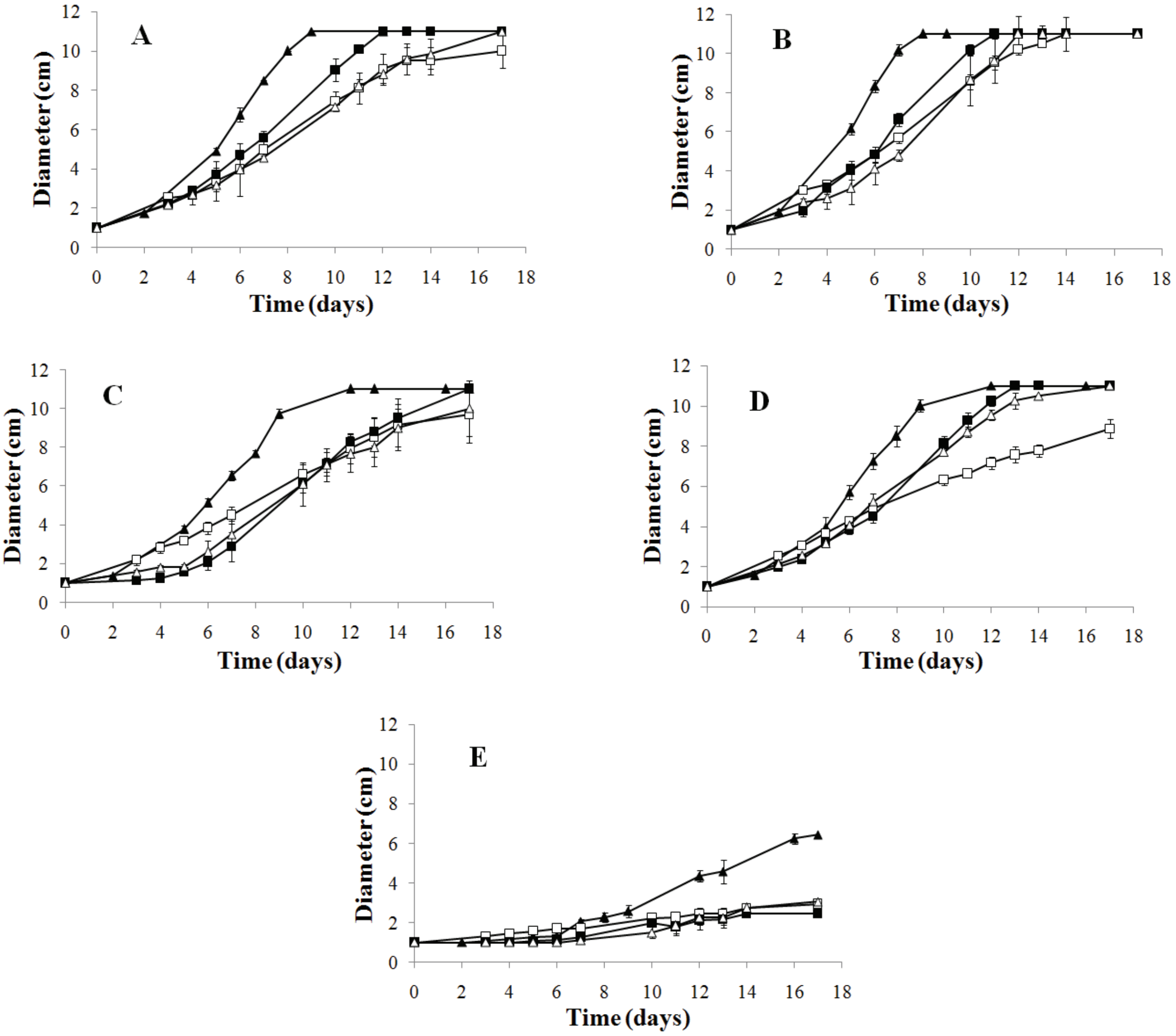

Fig. 1. Mycelial growth of *Agrocybe aegerita* (□), *Pleurotus columbinus* (■), *Pleurotus eryngii* (△) and *Pleurotus ostreatus* (▲) on the different substrates tested: WS 100% (A), WS 50%-CSD 50% (B), WS 50%-MSD 50% (C), CSD 100% (D); MSD 100% (E)

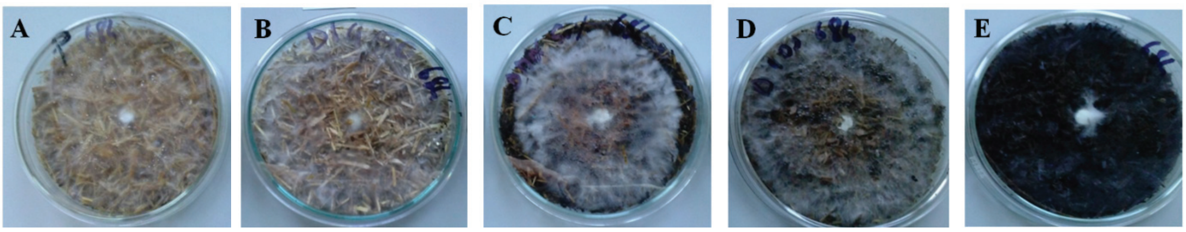

Fig. 2. Mycelial growth of *Pleurotus ostreatus* on the different substrates tested: WS 100% (A), WS 50%-CSD 50% (B), WS 50%-MSD 50% (C), CSD 100% (D); MSD 100% (E) after 9 days of incubation

The mycelium in CSD grew as fast as in the control. Fig. 3 reports ligninolytic activities (laccase, Mn-independent and dependent peroxidase) in CSD and WS during the 42 days of incubation with *P. ostreatus*. The enzymatic activities started to increase with the mycelial growth and continued to increase after the full colonization of the Petri dish (9 days) reaching a maximum around the 24th day of incubation. This trend is characteristic for *P. ostreatus* grown in wheat straw in Petri dishes (Galli et al., 2008). The ligninolytic activities in the plates containing CSD followed the same trend than those in the control medium (WS). Therefore the anaerobic digestate results to be a good material for mycelial growth and it is also able to stimulate the enzymatic activities.

Fig. 4 reports cellulolytic and hemicellulolytic activities (endoglucanase, cellobiohydrolase and xylanase), which were produced simultaneously with the ligninolytic activities during the 42 days incubation with *P. ostreatus*. Endoglucanase and xylanase activities on CSD were higher than on WS in the first period of mycelium growth, reaching the maximum at the 17th day. Cellobiohydrolase activity was higher on WS, with a maximum of activity at 24th day. After 30 days all the activities decreased with similar values in both of the substrates.

Macromolecules content in WS and CSD during mycelial growth is shown in Fig. 5. Insoluble lignin was reduced by 15% in WS and 12% in CSD after 42 days with reference to the initial amount. These results confirmed the expectations based on the enzymatic activities detected during fungal growth and are very interesting if compared to those reported by Isikhuemhen et al. (2009). In their study *A. aegerita* did not degrade lignin when cultivated on anaerobic digestate from broiler litter as unique feedstock. In the present study, part of the lignin was used as organic matter for fungal growth, while a small amount was converted into soluble lignin that was increased from 0.88 to 1.83% (108%) on CSD, and from 0.91 to 1.2% (32%) on WS.

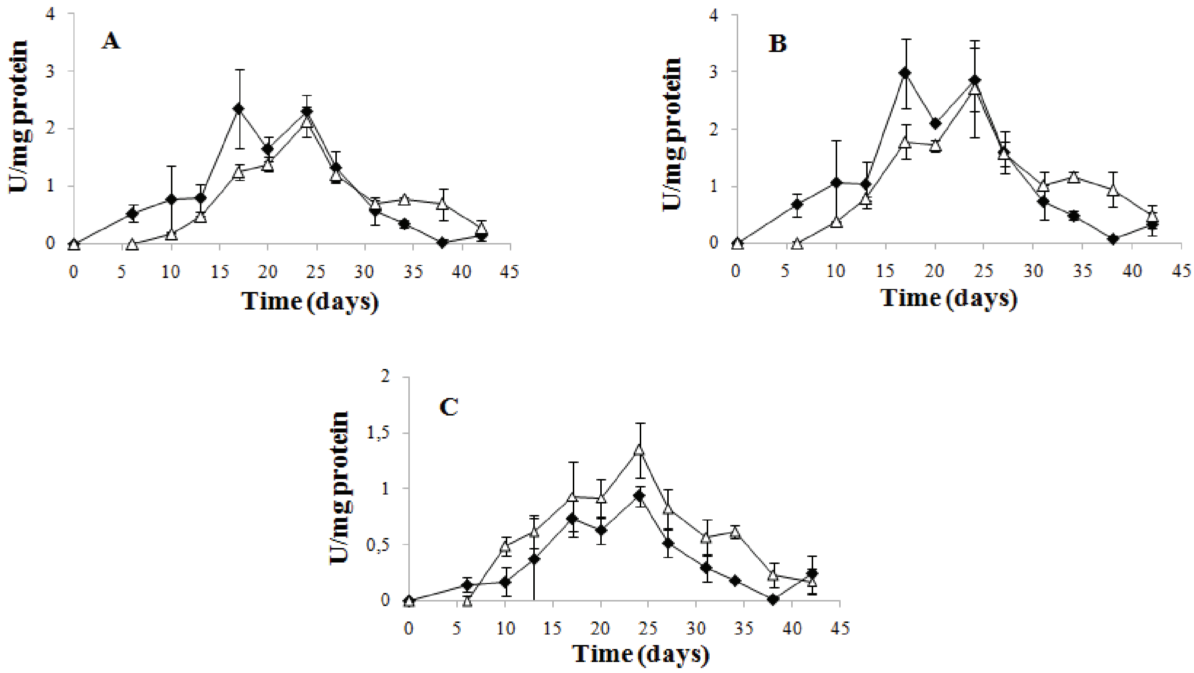

Fig. 3. Ligninolytic activities of *Pleurotus ostreatus* grown on WS (◆) and CSD (△): laccase (A), Mn-independent peroxidase (B), Mn-dependent peroxidase (C)

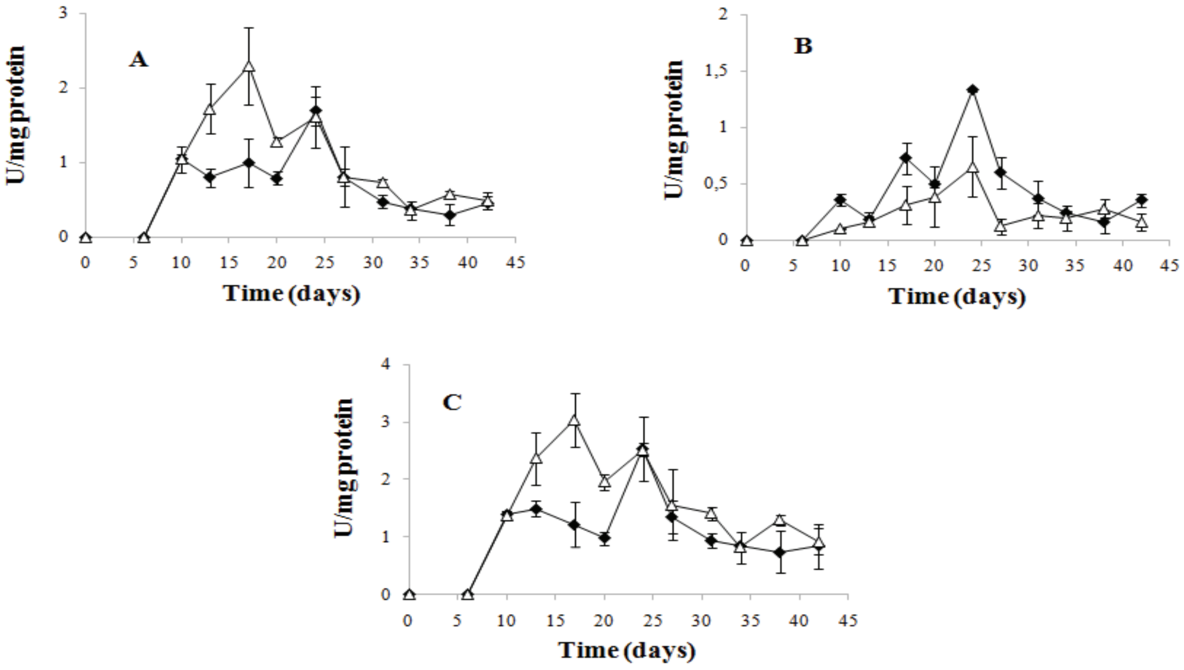

Fig. 4. Cellulolytic and hemicellulolytic activities of *Pleurotus ostreatus* grown on WS (◆) and CSD (△): endoglucanase (A), cellobiohydrolase (B), xylanase (C)

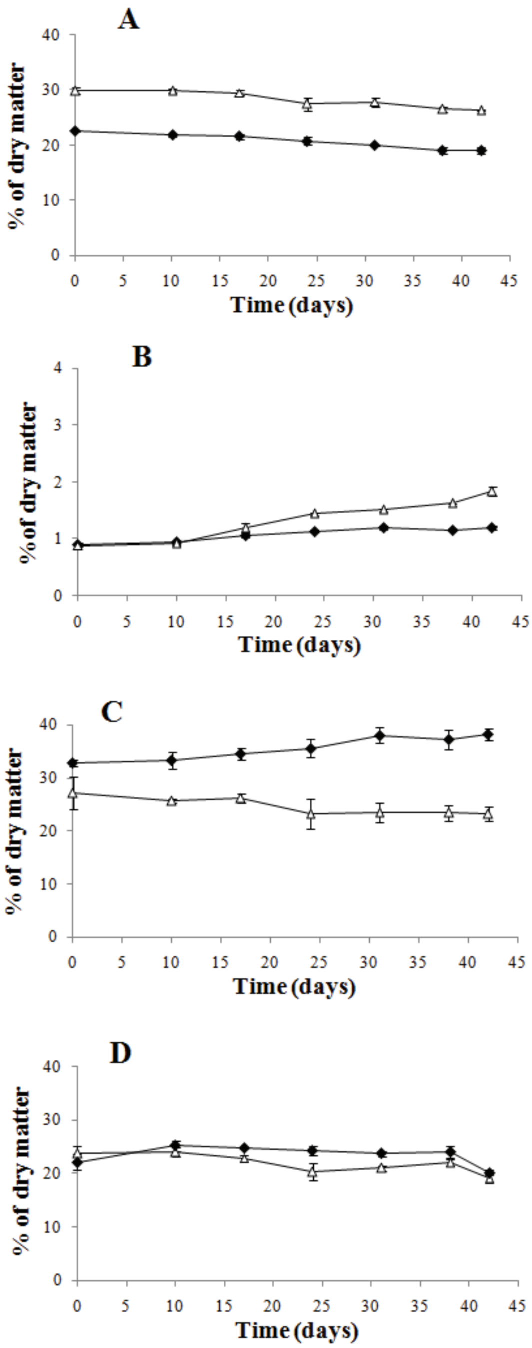

Fig. 5. Acid insoluble lignin (A), acid soluble lignin (B), cellulose (C) and hemicellulose (D) percentages during the growth of *Pleurotus ostreatus* on WS (◆) and CSD (△)

Lignin depletion during fungal growth has been reported to improve biogas production potential. In particular, Müller and Trösch (1986) demonstrated that a partial lignin removal (19% of the initial content) leads to a remarkable increase of biogas yield (30%). Muthangya et al. (2009) report an increase of methane production (about 50%) even after a smaller reduction of lignin (7%). Moreover, the same fungal biomass can also represent a feedstock for biogas production, as reported by Jasko et al. (2012). Thus, reintroducing SD in an anaerobic digester after cultivation of fungi might significantly increase biogas yield.

As for structural polysaccharides, cellulose was reduced by 15% in CSD while, unexpectedly, an increase of cellulose was detected in WS, in spite of the presence of cellulolytic activities during the fungal growth on such substrate. This might be due to the fact that, although a small amount of cellulose was consumed, as suggested by the presence of cellulolytic activities, the fungus found other nutrient sources, the consumption of which influenced the final mass balance more extensively than the utilization of cellulose in WS.

Cellulose increase after fungal growth on WS, in spite of the detection of cellulolytic activities, is also reported in another study (Dias et al., 2010). Moreover, it must be taken into account that endoglucanase activity was higher on CSD than on WS, while the highest level of cellobiohydrolase was measured on WS, but this value was quite low, corresponding to 1.3 U/mg protein. Hemicellulose depletion in CSD (19%) was higher than in WS (8%), this confirming the expectation based on the higher xylanase activity detected on CSD. Cellulose degradation on CSD was much lower than the value (27.7%) reported by Isikhuemhen et al. (2009), while hemicellulose consumption was more extensive in the present study.

In view of a further bioconversion of SD after fungal treatment, *e.g.* through the production of second generation bioethanol, it would be desirable to improve carbohydrate accessibility through the maximization of lignin breakdown. In this sense, the consumption of structural polysaccharides by the fungus might represent a disadvantage, especially with regard to cellulose, representing the main source of fermentable sugars.

Hemicellulose consumption by the fungus, instead, does not reduce the value of SD for bioethanol production, since such polysaccharide is mainly composed by pentose sugars which might pose problems of exploitation during ethanol fermentation, and are often removed through pretreatments (Santi et al., 2014).

4. Conclusions

The present study demonstrates that the feedstock used in anaerobic digestion can affect mycelial growth on the resulting SD, and that different fungal strains show large variation on their ability to grow on SD.

For the first time an anaerobic digestate was used as a unique nutrient source for the growth of *P. ostreatus*, with positive results comparable to the control. Therefore *P. ostreatus* resulted to be suitable for the conversion of CSD into valuable biomass like edible mushrooms. In this sense, further studies might be aimed at producing fruiting bodies.

Moreover, *P. ostreatus* was able to reduce the insoluble lignin contained in CSD by 12%, and partially convert it into soluble lignin. Given the improvement of biogas yield in the presence of low quantity of lignin, the ability of this fungal strain could be exploited as a treatment in order to increase the accessibility of structural polysaccharides in CSD prior to its reintroduction into a digester or, alternatively, for further biorefinery applications such as bioethanol production.

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APPROPRIATE TECHNOLOGIES FOR DRINKING WATER TREATMENT IN MEDITERRANEAN COUNTRIES

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Abstract

This paper aims at analyzing the drinking water issue in the Mediterranean region, highlighting the principal problems and the appropriate technologies applicable in the different countries. The countries of this area are characterized by a huge variety from social, cultural, economic and environmental point of view. In particular, water distribution is inhomogeneous between the North, East, and South; even the type of water sources and the related quantity and quality problems differ country by country.

Potable water comes from brackish and seawater, surface water, groundwater and water reservoirs with each source face different issues. The main problem of brackish and seawater for example is the high salinity and the contamination by disinfection byproducts, in addition to the microbiological and chemical contamination due to human activities that characterize also other surface water sources. Groundwater is also affected by human activity and it is not exempted from salinity because of the water intrusion. Moreover, water reservoirs are often contaminated by seasonal algal blooms.

Technologies applied for drinking water treatment vary country by country. The paper presents the main treatment processes associated with the main water pollutants, according to the Mediterranean region. Case studies of drinking water treatment plants are also analyzed, presenting alternative technologies appropriate for specific contexts, among others. The characteristics of each specific context should be carefully analyzed in order to develop the most appropriate technologies; high-end technologies for drinking water treatment may not be applied equally to all countries or communities of the Mediterranean region.

Key words: drinking water quality, Mediterranean region, water treatment technologies

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1. Introduction

The countries of the Mediterranean region are characterized by a great variety from social, cultural, economic and environmental point of view. Even the water resource has different characteristics in terms of quantity and quality in the various countries due to significant differences in climate, natural resources, development and, therefore, contamination.

The Mediterranean region has a supply of renewable water resources of about 1,500 km^3, which is distributed unevenly between the North (74%), the East (21%), and the South (5%) (Le Nouail, 2013). Precipitation tends to be scarce and concentrated in certain periods of the year and high rates of evapotranspiration cannot assure a sufficient and stable supply of water over time (Le Nouail, 2013). About 5% of the world population lives in the area, but it is among the zones characterized by lower concentration of fresh water in the world, having only 0.9% of global water resources. In the last decades, the situation has been getting worse, as it is possible to note that the number of countries defined in water scarcity were only 3 in 1955, 11 in 1990 and 18 are expected in 2025 (Blinda et al., 2007). Indeed, the change of hydro-climatic and socioeconomic conditions increased regional and global water scarcity problems in the past, as well as the current

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climate change, population growth, and the continuing increase in water demand, are expected to aggravate these water scarcity conditions in the future (Aktaş, 2014; Kiguchi et al., 2015; Navarro-Ortega et al., 2015; Shen et al., 2014; Stefanova et al., 2015; Veldkamp et al., 2015).

In the Southern and Eastern Mediterranean countries, the water issue is quantitative as well as qualitative. There is, in fact, a constant increase in water demand resulting from demographic pressure and from the development of water intensive activities such as in the tourism and manufacturing sectors (Galli et al., 2015; Lelieveld et al., 2012; Milano, 2010). The imbalance between supply and demand can be realized by the reduced availability of water resources on a per capita basis.

A severe water divide in the Mediterranean emerges from the data: the drinking water per capita demand varies from approximately 65 m^3/capita/year (175 liters/day) in the South and East to almost 120 m^3/capita/year (330 liters/day) in the North. In terms of access to improved water sources, the Northern Mediterranean countries and Israel have achieved a 100% rate of access to drinking water, while the remaining areas still stand at 90% with a strong internal imbalance between urban and rural areas (Ferragina, 2010).

The growing water demand creates a strong human pressure over water resources (Barbagallo, 2012; Bixio, 2006; Burnham et al., 2015), as measured by the Water Stress Indicator (WSI), among others.

This indicator represents the total water abstraction per year calculated as a percentage of renewable freshwater resources, thus indicating which countries have a high water demand compared to their available resources. Fig. 1 shows the worldwide WSI: lower values are represented by lighter green colors, whereas the highest values of WSI are characterized by dark green (gray represents countries for which data are missing or unavailable).

The pressure on water is due also to the technological progress and the improvement of pumping techniques that have led to intensive exploitation of aquifers causing their depletion and pollution.

Overuse of non-renewable water resources is one of the challenges in the Mediterranean but, presently, some of the most important water projects in the South and East area of the Mediterranean region are focused on fossil water creating a kind of “pumping race” between the countries that share common aquifers which fuels an unsustainable exploitation of non-renewable water sources. This is why, today, increasing water exploitation is strictly linked to and influenced by political, financial, social (e.g.: social impact of dams) and environmental (e.g.: reduction of new exploitable sources) aspects. However, new prospects are offered by non-conventional water supplies. Currently, desalination of seawater or brackish water in Mediterranean countries has a total installed capacity of over 1,800 Mm^3 per year and the reuse of treated seawater is about 30 Mm^3 per year (Ferragina, 2010).

In the Mediterranean region, the agriculture sector consumes the highest amount of water (64%), followed by the industry sector (22%), and then the domestic sector (14%) (Le Nouail, 2013). In the entire Mediterranean region, the efficiency in water distribution is very low due to poor network maintenance and operation as well as inadequate irrigation techniques: losses, leakages and wastage account for almost 40% of the total water demand (Ferragina, 2010). Because of water scarcity and the high use in the agricultural and industrial sectors, new technologies are being developed for grey and black water re-use (Garrido et al., 2007; Lazarova et al., 2001).

The aim of this work is to analyze the drinking water issue in the Mediterranean region, highlighting the main pollutants affecting water sources and the related technologies appropriate for their removal. Three main contaminants are analyzed: salinity, cyanobacteria and microorganisms. Related characteristics of the treatment technologies, advantages and disadvantages, management procedures and effectiveness are also described. The description of full-scale drinking water treatment plants (located in a country of the Mediterranean region) is also provided for each contaminant taken into consideration.

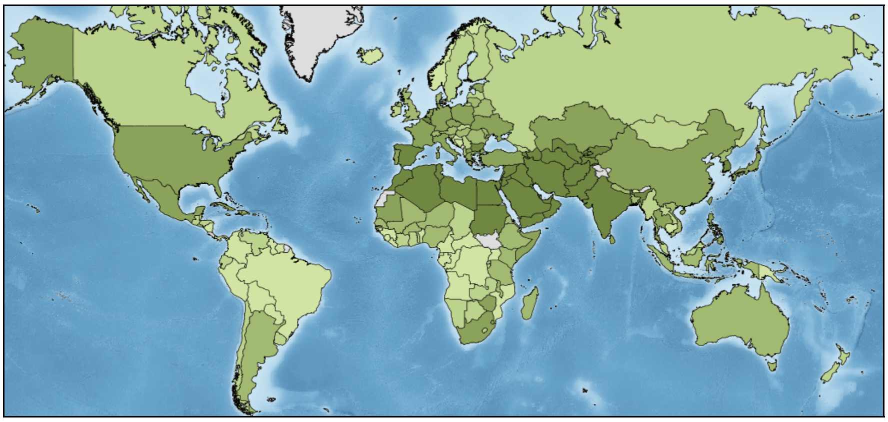

Fig. 1. Water Stress Indicator (FAO, 2015)

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2. A focus on appropriate technology

Currently, the dictionary defines an Appropriate Technology (AT) as *a science or technology considered reasonable and suitable for a particular purpose, that conforms to existing cultural, economic, environmental, and social conditions*.

The first idea about the AT is attributed to Mahatma Gandhi. He advocated for small, local and predominantly village-based technology to support India's villages become self-reliant. He differed with the idea of technology that benefited a minority of people at the expense of the majority or that put people out of work to increase profit (Akubue, 2000).

Despite this, the first definition of AT, in that time named "Intermediate technology", was proposed in the 1970s by the British economist Dr. Fritz Schumacher (Schumacher, 1973). According to him, AT is an approach to technology that builds a strong sense of community and encompasses benefits from a social, environmental, cultural, economic, and spiritual point of view. Other past definitions, still accepted and used, prescribe that AT should be small-scale, requires low capital investment per worker, be energy efficient, environmental friendly and controlled and maintained by the local community. However, Ranis in the 80s, argued that "the appropriate process for a poor labor surplus economy is not always labor intensive and an appropriate good is not always a basic good" (Ranis, 1980). Also UNESCO publications (Ntim, 1988) criticized the standard AT requirements such as "low investment cost per workplace, small scale operation, use of locally available resources, low cost of final product", because this is not always possible or easy to achieve and can be contradictory implying bad results.

Today, we can say that AT not only refers to the tools and techniques used to problem solving in a development setting, but it also includes the less tangible aspects such as knowledge transfer mechanisms and social, cultural, and gender issues. The most important aspect of an AT is its sustainability, which is the balance of technical, social, economic, environmental, cultural and spiritual values in the long-term. AT is not a prerogative of developing countries because it plays a critical role in building sustainable communities in both southern and northern countries.

Effectively an appropriate technology has to be affordable, minimize the environmental impact, involve local people meeting the basic and real needs, be simple in operation and maintenance and use local materials and resources to reduce costs and transport and improve local market. Moreover AT should respect the traditions and values and include gender considerations, develop skills of local people, and reduce economic, social and political dependence between individuals and regions. Above all in the field of water and sanitation, the appropriateness of a technology depends on several factors, mostly related to social and economic aspects. Indeed, a crucial role is played by the willingness to spend money on technologies, the empowerment and the ownership, the educational level and the cultural customs (e.g. the possibility to use bone char as filtration material to remove fluoride in drinking water), among others. Even environmental/natural factors are influencing the design of an appropriate technology, as the type of resource (sea, surface water, groundwater) and the type and concentration of contaminants, among others.

3. Water quality management in the Mediterranean region

3.1. Water quality issues

The Mediterranean region has significant heterogeneity among its countries from a social, demographic, economic and environmental point of view. This impacts the quantity and quality of potable water, in particular the kind of water source where it can be provided. Different water sources present different quality problems according to their nature and sources of contamination to which they are subjected.

Potable water comes from brackish water and seawater, surface water, groundwater and water reservoirs and quality problems that are to be faced in order to have safe water are often very different. The scarcity of water that characterizes the region makes it necessary in many coastal areas to supply from brackish and marine sources whose main problem is certainly the high salinity that can vary between 500 and 30,000 ppm in brackish water and between 30,000 and 50,000 ppm in marine water (Absar and Belhaminiti, 2013; Allal, 2010; Cipollina et al., 2005; DHV Water BV, 2004; Drami et al., 2011; El-Azizi, 2003; El-Sadek, 2010; Lindemann, 2004). Another problem is the microbiological and chemical contamination due to industrial and domestic discharges (Clemente, 2012; Heller-Grossman et al., 2001). Human activities also provide contamination of water disinfection byproducts, such as trihalomethanes, as described in study cases in Egypt (Abdullah and Hussona, 2013; Basiouny et al., 2008).

These problems are also faced in countries that use other kind of surface water other than sea such as rivers or lakes. These sources suffer additional kind of contamination due to anthropogenic and industrial discharges as nitrogen, phosphorus, heavy metals and suspended solids (Masoud, 2014; Golfinopoulos et al., 2005). In addition, groundwater sources are often poorly protected by human activities and thus contaminated with nitrates, heavy metals, arsenic and manganese and the underground sources are not exempted from the above-mentioned problem of salinity as they suffer the salt-water intrusion. Moreover recent studies (El-Aassy et al., 2015) reveal the presence of radioactivity in this kind of water source as new problem.

Finally, water reservoirs are another important water source. In this kind of source, in addition to issues related to microbiological contamination, suspended solids and other contaminants due to anthropogenic discharges, a major problem is the presence of cyanobacteria related to algal bloom (Cook et al., 2004; Dor, 1998; Douma et al., 2010; Nasri et al., 2007; Paerl et al., 2014; Yilmaz and Koç, 2014).

It is very important to control and minimize the release of pollutants from the agricultural and industrial activities because of their impact on water sources. Consequently, research is developing technologies through which it is possible to re-use the gray and black water, at least for the agricultural and industrial activities, due to the water scarcity that characterizes many of the countries of the Mediterranean region.

3.2. Drinking water treatment technologies

3.2.1. General overview of treatment technologies

As already stated, drinking water quality in the Mediterranean region varies widely due to several factors, such as the heterogeneity of the countries characterizing this region, the different climate conditions, available natural, economic and water resources, among others.Strictly related to these factors, technologies applied for drinking water treatment vary country by country. A list of the main specific treatment processes associated with the main water pollutants is shown in Table 1.

Owing to the heterogeneity of the countries of the Mediterranean region, the application and the efficiency of all these processes vary widely. Even regarding the management procedures, specific measures have to be applied for guaranteeing the removal of the different contaminants, such as the continuous supply of electricity, the climate conditions (temperature, humidity, etc.), the availability of resources to apply the treatment, and so on.

The heterogeneity of the technologies applied includes several aspects, which are not deepened in this paper. Indeed, the aim of this work is to focus on three main pollutants characterizing the Mediterranean area, for which specific processes are analyzed.

The first contaminant is the salinity (due to the use of seawater as resource); clearly seawater is a common issue among all the Mediterranean countries, and is becoming increasingly widespread for drinking purposes owing to the increasing water scarcity that threats these countries. The most spread process to desalinate seawater is the membrane filtration, by means of reverse osmosis. The second contaminant analyzed is cyanobacteria (or other algal blooms) due to their presence in artificial reservoirs, which are more and more used for drinking purpose in the Mediterranean region.

Table 1. Main water pollutants versus main treatment technologies

Water pollutant	***Treatment technology***
Salinity	Membrane filtration (nanofiltration, reverse osmosis, electrodialysis)
	Ion exchange
	Thermal processes (e.g. solar still)
	Dilution with rainwater
Settleable solids	Screen filter
	Sedimentation
	Sand filtration
Colloids	Coagulation and flocculation
Fecal bacteria	Disinfection
Iron and manganese	Chemical oxidation (air/oxygen, chlorine etc.)
	Biological filters
Organic compounds	Chemical oxidation (air/oxygen, chlorine, ozone etc.)
	Activated carbon adsorption
Nitrogen compounds (ammonia, nitrates, nitrites)	Stripping (suitable only for ammonia)
	Biological filters
	Membrane filtration (nanofiltration, reverse osmosis, electrodialysis)
	Ion exchange
Arsenic	Chemical precipitation
	Activated carbon adsorption (iron oxide carbon)
	Membrane filtration (nanofiltration, reverse osmosis, electrodialysis)
	Ion exchange
Cyanobacteria (or other algal blooms)	Micro-screen filter
	Chemical oxidation
	Coagulation and flocculation
	Sand filtration
Cyanotoxins	Activated carbon adsorption
Heavy metals	Chemical precipitation

Coagulation and flocculation are considered in the following, since they represent efficient technologies for reducing cyanobacteria (or other algal blooms) and they can be applied by means of alternative and appropriate solutions, such as the use of natural resources instead of chemical reagents.

Moreover, microorganisms are considered since they are typical contaminants characterizing surface water. The traditional process applied for their removal is *disinfection*, which is one of the most important drinking water treatment but poses some constraints for the possible production of Disinfection By Products (DBPs). Even in this case, alternative and appropriate solutions such as the use of sunlight or boiling water can be applied depending on the specific context in which the process is developed.

3.2.2. Reverse Osmosis

Seawater is widely used as drinking water source along the coasts of the Mediterranean countries. The most applied technology for its treatment is represented by reverse osmosis (RO). This is a process in which salts (and in general all the dissolved inorganic solids) are removed by pushing water under pressure (higher than $30*10^5$ Pa) through a semi-permeable membrane. The membrane allows only water to pass through, and not salts or other impurities (with size larger than 0.001 μm).

The main advantages of this technology are the effective salt removal (95-99%), the jointly disinfection action (RO is able to remove almost all the viruses, bacteria and protozoa) and the jointly removal of several ions and metals. Regarding the disadvantages, it has to be underlined that RO requires pre- and post-treatments in order to protect the membrane from obstruction of the pores and to be re-hardened and re-mineralized (for adjusting values of alkalinity and salt content), respectively. Even membrane fouling is a process to take into account as a disadvantage. This phenomenon happens since particles can deposit onto the membrane surface or pores and decrease its performances. For this reason, backwashes or washing by means of chemical reagents need to be applied in order to avoid the pores' occlusion.

Another notable constraint of this technology is represented by the high energy consumption, due to the high pressure that the process needs for guaranteeing the desalination. However, Lindemann (2004) demonstrated by a multicriteria analysis, that RO requires less energy power compared to other desalination technologies like multi-effect desalination and vapor compression.

As already stated and reported in the scientific literature (Fritzmann et al., 2007), and despite these disadvantages, RO is widely spread in the Mediterranean countries, such as Italy (Cipollina et al., 2005), Greece (Manolakos et al., 2008), Israel (Drami et al., 2011), Egypt (El-Sadek, 2010), Libya (El-Azizi, 2003), Algeria (Absar and Belhamiti, 2013), Morocco (El Azhar et al., 2012), Spain (Molina and Casañas, 2010), and so on.

An interesting seawater treatment plant, adopting the reverse osmosis, is located in Larnaca, Cyprus (Fig. 2) (Water Technology, 2014).

The plant is the largest desalination facility in Cyprus, and it is served by a long seawater intake that catches water depth in the sea in order to ensure a clean seawater feed (avoiding algae that are highly present along the coast). The plant treats about 64,000 m³ of seawater on a daily base. As shown in Fig. 2, the plant is composed by the following treatments: rotary screen, coagulation and flocculation, dual-media gravity filtration, microfiltration and finally reverse osmosis. The desalinated water is further treated for re-mineralization and pH adjustment; afterwards, the chlorination treatment completes the process before the supply into the distribution system.

The Larnaca plant has been designed to ensure that power consumption could be reduced. Indeed, frequency converters enable the adjustment of the suction pressure and Pelton turbines are used to recover the energy from the brine stream (Water Technology, 2014).

The heterogeneity of the countries characterizing the Mediterranean region does not permit the application of this treatment technology at all levels. This is mainly due to the high investment and operation costs, as well as for the management practices.

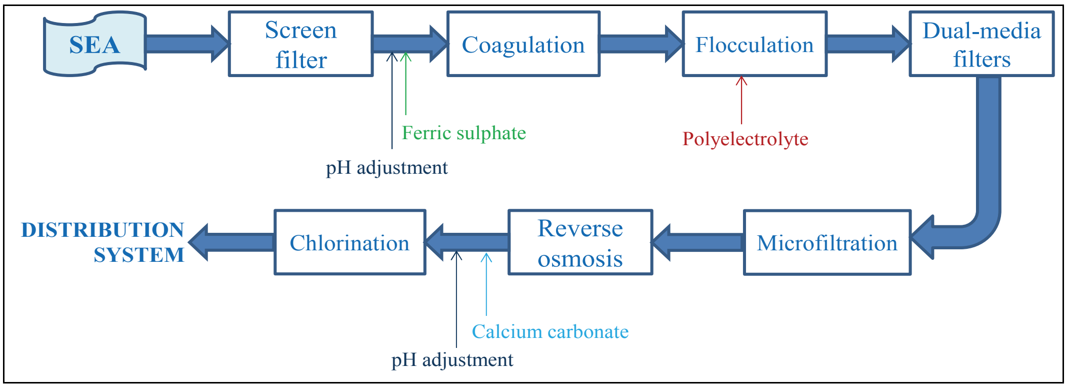


Fig. 2. Scheme of Larnaca seawater treatment plant (Cyprus)

Indeed, in order to control high pressure operations, avoid membrane fouling, apply proper pre- and post-treatments (which require chemical reagents dosage), good technical and management skills would be needed. A technology, for being considered appropriate, should be not only environmental friendly or economic sustainable, but should even guarantee a technical effectiveness (easy to be managed).

Due to the economic and technical conditions that characterize Cyprus (availability of continuous electricity and economic resources), the RO process can be considered appropriate for the specific context. The same technology applied in another country of the Mediterranean region could be inappropriate and unsustainable, depending on the local conditions.

3.2.3. Solar-powered reverse osmosis

An interesting and more sustainable approach, at least from the environmental point of view, for the implementation of the reverse osmosis process, is the RO water desalination using solar technology. The implementation of large-scale concentrating solar-powered desalination systems has been identified as promising solution. Indeed, the high solar energy available above all in the south Mediterranean areas can easily produce the energy required by RO processes to treat water. It has been estimated that, within two decades, solar thermal power plants will become the less expensive technology for electricity and desalted water. Moreover, combining the efficient use of water with large-scale solar desalination systems, overexploitation of groundwater in the Mediterranean region should be ended by 2030 (Allal, 2010).

The city of Guadix (Granada Province, Spain) is provided by a RO drinking water treatment plant, powered by electricity from a Concentrating Solar-Powered (CSP) system. The energy plant produces the maximum electricity during the day for RO operation, in a way that allows the RO system to operate even during night-time. Fig. 3 shows the configuration of the entire Guadix plant, which combines CSP with RO.

3.2.4. Water treatment by coagulation -flocculation

Coagulation and flocculation processes promote the aggregation of small and dispersed particles into larger-size clusters, and they deal with dispersed particles such as mineral turbidity (clay, silt), larger molecular weight natural organic matter, and microorganisms (including cyanobacteria, among others). Chemicals employed for drinking water coagulation include various aluminum and ferric iron salts, while flocculation is usually characterized by the use of polyelectrolytes. For instance, the removal rate of algae by the coagulation-flocculation process is strictly dependent on the optimization of chemical doses and pH (WHO, 1999).

Focusing on the management procedures, which, as previously stated, are one of the factors determining the appropriateness of a technology, it has to be underlined that the main difficulties of these treatment processes arise from the correct dosage of the chemical reagents and the proper mixing speed. These aspects should be carefully controlled in order to guarantee the effectiveness of both coagulation and flocculation. This is the reason why the occurrence of cyanobacteria and their toxins in water bodies used for the production of drinking water poses a technical challenge for water utility managers.

An interesting alternative to the use of chemical reagents is represented by *Moringa oleifera*. *Moringa oleifera* is the best natural coagulant discovered so far that can replace aluminum sulfate (alum), which is used widely for water treatment around the world. *Moringa oleifera* seeds are non-toxic, and their use as coagulant is recommended in water treatment in developing countries (Ali et al., 2010).

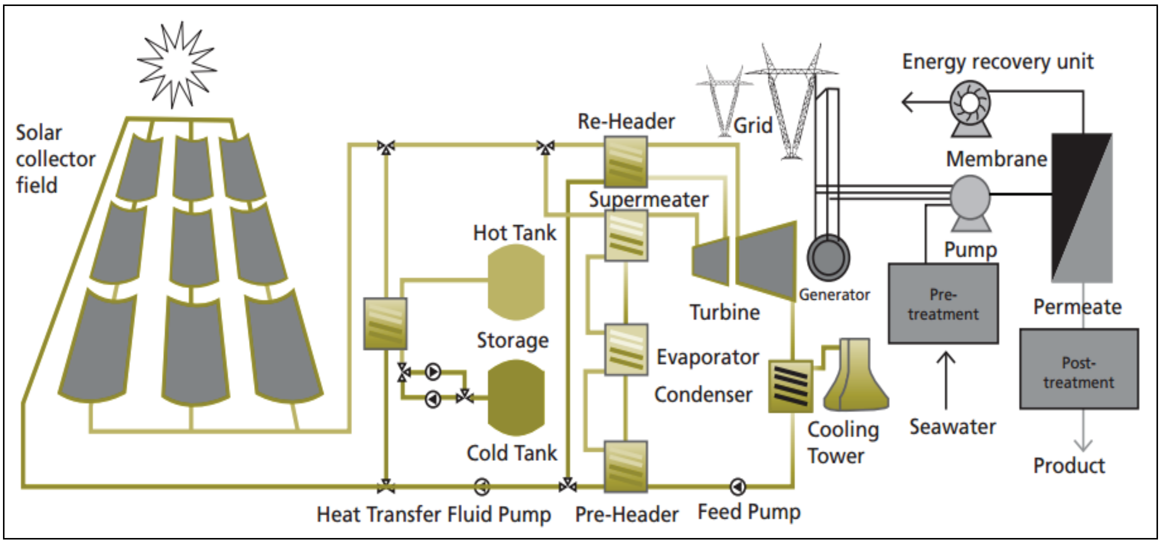


Fig. 3. Scheme of Guadix CSP/RO treatment plant (Allal, 2010)

The seed kernels contain significant quantities of a series of low molecular-weight, water-soluble proteins which, in solution, carry an overall positive charge. When added to raw water these proteins bind to the predominantly negatively charged particles (silt, clay, bacteria, algae, etc.). Under proper mixing, these particles grow in size to form flocs, which are then removed by filtration (Folkard et al., 1994). However, at the moment, *Moringa oleifera* use as natural coagulant is not widely spread in the Mediterranean region owing to the need for warm climates (such as the tropical or sub-tropical) for the plants to grow.

The coagulation-flocculation process is one of the main technologies used for the removal of cyanobacteria; in the international literature, several studies (Bernhardt and Clasen, 1991; Ewerts et al., 2013; Gonzalez-Torres et al., 2014; Lambert et al., 1996; Mouchet and Bonnélye, 1998; Velzeboer et al., 1995) have already investigated roles and removal rates of coagulation and flocculation concerning this contaminant.

Cyanobacteria algal blooms represent one of the most waterborne microbial hazards to human and agricultural water supplies, fisheries production, and freshwater and marine ecosystems (Codd et al., 2005; Paerl et al., 2011). This hazard is mostly due to the production of secondary metabolites, called cyanotoxins, which are a various group of natural toxins, both from chemical and toxicological points of view. Cyanobacteria, and thus cyanotoxins, are contaminants of concern in the Mediterranean countries. In the international literature, several case studies are reported, related to France (Réveillon et al., 2014), Italy (Naselli-Flores et al., 2007), Greece (Cook et al., 2004), Lebanon (Fadel et al., 2014), Israel (Dor, 1998), Egypt (Mohamed et al., 2015), Algeria (Amrani et al., 2014), Morocco (Douma et al., 2010), and so on.

Conventional water treatments involve the combination of coagulation-flocculation with rapid sand filtration, in order to maximize the removal of cyanobacteria. On the contrary, cyanotoxins are usually removed by activated carbon processes, since they arise in dissolved form.

One of the main advantages of coagulation-flocculation processes is the high removal rate of cyanobacteria that guarantees the complete elimination of this algal formation after a sand filtration system. Moreover, this kind of process allows a decrease in the formation of potential precursors of DBPs (Disinfection By Products). On the contrary, the main disadvantages are represented by the need for chemical reagents (as ferric or aluminum salts), which increase the operational costs of the technology.

An interesting drinking water treatment plant, adopting the coagulation-flocculation process (followed by a sand filtration and an activated carbon treatment), is located in Chaiba, Algeria (Fig. 4) (Nasri et al., 2007).

The treatment plant takes its water from the Cheffia dam. The complete treatment chain is composed by pre-chlorination, coagulation and flocculation, slow sand filtration, activated carbon adsorption and chlorination before storage and distribution.

The Cheffia dam contains an unusual morphospecies of *Microcystis* that is the dominant autumn phytoplankton in this reservoir. The cyanobacteria community is also characterized by the presence of a toxin-producing morphospecies of *Microcystis sp*. Cyanobacteria concentration reaches picks up to about 450 µg/L, while cyanotoxins up to about 30 µg/L. Due to the seasonality of these contaminants, removal rates widely vary during the year. Available monitoring data referred to 2004 have underlined values between 20 and 100% of microcystins removal.

Conventional water treatment techniques such as coagulation and flocculation, followed by slow sand filtration and powdered activated carbon at 15 mg/L, are effective and efficient in removing high density cyanobacteria cells and their toxic microcystins from raw water (Nasri et al., 2007).

3.2.5. Water treatment by disinfection

The last pollutant and related technology considered in this work is represented by microorganisms and disinfection. Disinfection is an important step in ensuring that water is safe to be consumed, and its main objective is to control disease-causing microorganisms by killing or inactivating them.

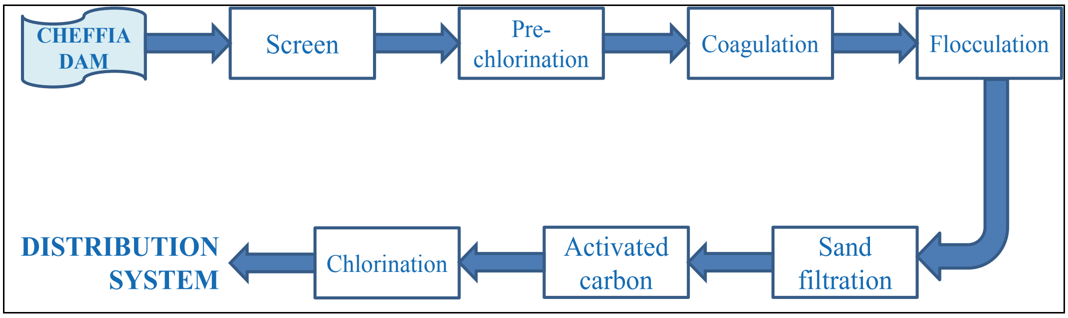


Fig. 4. Scheme of Chaiba treatment plant (Algeria)

However, in the last decades, the strategy is to apply a multi-barrier approach, which consists in minimizing the concentration of fecal bacteria through the action of the different treatments characterizing the drinking water treatment plant. In such a way, final disinfection should, theoretically, only protect the quality of water along the distribution system. Indeed, the most significant and important results are obtained when disinfection is combined with conventional treatments, such as coagulation, flocculation, sedimentation and filtration.

Conventional disinfection treatment methods include chlorination, chlorine dioxide, chloramines, ozone, and ultraviolet light. Table 2 shows the main characteristics, advantages and disadvantages of these methods.

The disinfection methods aforementioned refer above all to chemical disinfection. Due to the heterogeneity of the countries characterizing the Mediterranean region, which includes poor rural parts of the northern Africa states, these methodologies are not always suitable to be carried out.

An interesting alternative for these areas is represented by SODIS (Solar Water Disinfection), developed by EAWAG (Swiss Federal Institute for Aquatic science and Research)/SANDEC (Dept. of Water and Sanitation) and shown in Fig. 5. Solar Water Disinfection (SODIS) is a simple, environmentally sustainable, low-cost solution for drinking water treatment on a household or community level for people consuming biologically contaminated wild water. Raw water is filled in a transparent plastic (PET) or glass bottle and exposed to the sun for 6 hours. During this time, the UV-radiation destroys pathogenic microorganisms, causing water-borne diseases, improving the quality of drinking water. Pathogenic microorganisms are vulnerable to two effects of the sunlight: radiation in the spectrum of UV-A light (wavelength 320-400 nm) and heat (+50 °C).

Table 2. Main characteristics, advantages and disadvantages of disinfection methods (NESC, 1996)

Disinfectant	***Characteristics***	***Advantages***	***Disadvantages***	***Used form***
Chlorine gas	At normal pressure it is a toxic, yellow-green gas, and is liquid at high pressures	It is very effective for removing almost all microbial pathogens and is appropriate as both pre-oxidant and disinfectant	It is a dangerous gas that is lethal at concentrations as low as 0.1 percent air by volume	Chlorine gas is employed as liquid solution
Sodium hypochlorite	It is commercially available as a solution in concentrations of about 5-15 % of active chlorine	It is easier to handle than gaseous chlorine or calcium hypochlorite	It is highly corrosive and its solutions rapidly decompose. It must be stored in a cool, dark, dry area	Sodium hypochlorite solution is readily available
Calcium hypochlorite	It is a white solid that contains some of 60-70 % of active chlorine	It is very stable, allowing a year's supply to be bought at one time.	It is a corrosive material with a strong odor. Reactions between it and organic material can generate enough heat to cause a fire or explosion	Calcium hypochlorite can be purchased in granular, powdered, or tablet form
Chlorine dioxide	It is a yellowish-green gas with a strong odor	It is effective at low concentrations-dosages and is appropriate as both pre-oxidant and disinfectant	It is highly instable, thus, it requires to be produced *in situ*. It is characterized by a low redox potential	Chlorine dioxide is employed as liquid solution
Chloramines	They are formed when water containing ammonia is chlorinated or when ammonia is added to water containing chlorine	They are effective bactericides. Usually, chloramine-forming reactions are 99 % complete within few minutes	They are much less effective against viruses or protozoa than free chlorine. They might be harmful to humans and release a disagreeable taste and odor to water	Chemicals used to generate chloramine from ammonia and chlorine gas depend on the ammonia-based chemical used
Ozone	It is formed by passing dry air through a system of high voltage electrodes	It requires shorter contact time and dosage than chlorine. It has the highest redox potential among all the disinfectants	Ozone gas is highly unstable and must be generated onsite. It does not guarantee adequate residual protection to water along the distribution system	Ozone is employed as gas
UV light	UV radiation penetrates the cell wall of an organism, the cell's genetic material is disrupted and the cell is unable to reproduce	It effectively destroys bacteria and viruses, and requires short contact times	It may not inactivate *Giardia lamblia* or *Cryptosporidium* cysts. It does not guarantee adequate residual protection to water along the distribution system	Radiation

As stated, the heterogeneity of the countries characterizing the Mediterranean region does not permit the application of chemical disinfection at all levels. This is mainly due to the availability of chemical reagents or energy (in the case of ozone or UV radiation), as well as management practices. Indeed, in order to control the proper dosage of disinfectants, good technical and management skills are needed. These are crucial points for considering the appropriateness of a technology. Moreover, while protection against microbial contamination is the top priority, water treatment systems must also control disinfection by-products (DBPs), chemical compounds formed unintentionally when chlorine and other disinfectants are added. A number of factors can affect the formation of DBPs. These include concentrations of organic materials when chlorine is added, dosage of chlorine, concentrations of bromide ion when ozone is added, dosage of ozone, temperature and pH of water, reaction time, among others. The main DBPs that can affect drinking water quality out of a treatment plant (thus post-disinfection process) include trihalomethanes (THMs), chlorite and chlorate (even bromate should be considered if seawater is used as drinking water source and ozone is employed as oxidant/disinfectant). In almost all the countries characterizing the Mediterranean region, the study of DBPs formation (and thus their minimization) has been carried out. Research data have been provided by Greece (Golfinopoulos and Nikolaou, 2005), Cyprus (Pieri et al., 2014), Israel (Heller-Grossman et al., 2001), Egypt (Smith and Kamal, 2009), Algeria (Achour et al., 2014), Morocco (Zidane et al., 2014), and many other states. An interesting drinking water treatment plant, adopting the final disinfection with chlorine and presenting formation of THMs, is located in Casablanca, Morocco (Fig. 6) (Zidane et al., 2014).

Raw water coming from the Bou Regreg dam is treated in a drinking water treatment plant and serves the cities of Casablanca and Mohammedia. Since the distribution system is extremely long (more than 30 km), 36 storage tanks are located along the supply network, in order to provide a security reserve of 24 hours. The drinking water treatment chain is conventional, comprising a physical-chemical treatment of coagulation, flocculation and settling, followed by sand filtration and chlorine disinfection before storage and distribution of water. Pre-oxidation by chlorine (before coagulation and flocculation steps) is even required, owing to the raw water characteristics. Chlorination, in addition to pre-oxidation and disinfection, is also carried out at the inlet and outlet of each storage tank and during the distribution of water at different points of the supply network.

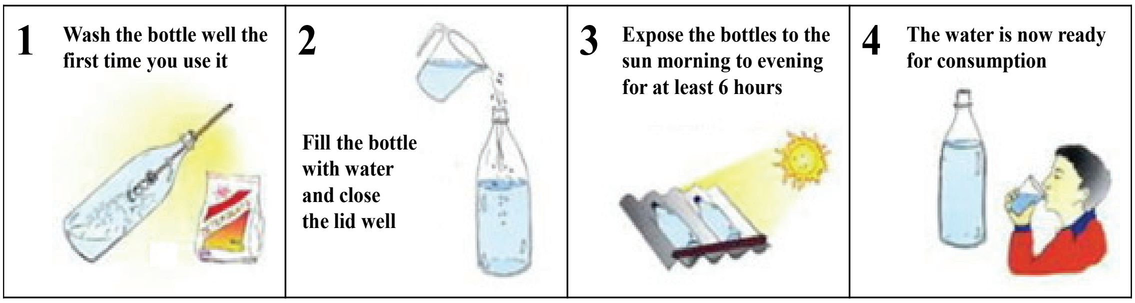
In a research experience, Zidane et al. (2014) have analyzed the presence of the four main THMs (chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHBrCl_2$) and dibromochloromethane ($CHBr_2Cl$)) along the distribution system. Table 3 shows the results of the investigation, indicating the trend of THMs in the water network.

Results indicate that the supplied water contains significant levels of THMs, proving that chlorination has a significant effect. Although water extracted from the Bou Regreg dam is slightly contaminated by organic matter (TOC), it contains important concentrations of benzene and toluene, which are other precursors of THMs formation. Total THMs concentration was high in all the water samples analyzed, with the higher contents corresponding to the water in the outlet tank (89 μg/L) and in the tap water (85 μg/L). Despite this, concentrations remain slightly below the Moroccan limit (100 μg/L).

3.3. Further considerations

Nowadays, advanced drinking water treatments are applied widely and worldwide in order to control the concentration of new specific pollutants. The trend to continuously push for more sophisticated water treatment processes, and thus more expensive and complicated to manage, should be considered together with existing severe economic crisis and the feasibility of implementation of these technologies.

Considering the heterogeneity of countries worldwide (and in this specific context, of the Mediterranean countries), appropriate technologies should be developed, in order to guarantee technology sustainability, and even the protection of the environment.



1 Wash the bottle well the first time you use it

2 Fill the bottle with water and close the lid well

3 Expose the bottles to the sun morning to evening for at least 6 hours

4 The water is now ready for consumption

Fig. 5. SODIS methods for disinfecting drinking water

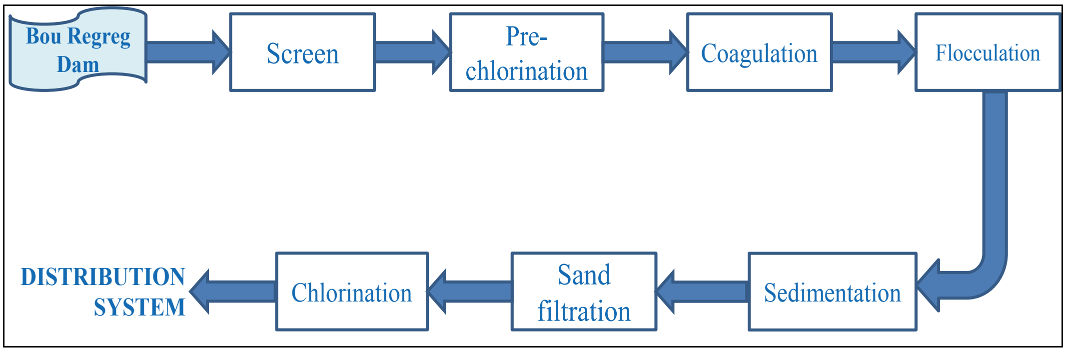


Fig. 6. Scheme of Casablanca treatment plant (Morocco)

Table 3. Trend of THMs concentration along the drinking water supply chain

Parameter	*Raw water*	*Outlet plant*	*Inlet tank*	*Outlet tank*	*Tap water*
$CHCl_3$	0.19	20	27	29	33
$CHBr_3$	< 0.10	2.5	2.6	4.1	2.6
$CHBrCl_2$	0.10	20	24	31	29
$CHBr_2Cl$	< 0.10	16	18	25	21
Total THMs	0.29	59	71	89	85

Consequently, some basic criteria that emphasize the concept of appropriate technology can be summarized as:

- allowing for greater consideration of local needs;
- full respect of the traditions and social values;
- developing technologies that enhance the work and skills of humans rather than mechanical ones;
- developing technologies that can be understood and controlled through easy management procedures;
- enhancing the use of local resources, materials and energy, reducing costs and implementation/process management;
- developing a wealth of experience and expertise within the community from the expertise already available;
- contributing to a local economy that also acts against economic mutations/crises in international markets;
- reducing the dependence on economic, social and political aspects between individuals, regions and nations.

4. Conclusions

The present work aimed at analyzing the drinking water quality issue in the Mediterranean region, highlighting the possible appropriate technologies applicable in the different countries. Case studies of full-scale drinking water treatment plants were proposed in order to report how drinking water quality contaminants are faced in the region, presenting technologies appropriate for specific contaminants and contexts (e.g., solar disinfection by means of SODIS methodology, use of *Moringa oleifera* as natural coagulant, etc.).

High-end technologies for drinking water treatment may not be applied equally to all countries or communities of the Mediterranean region, due to the different characteristics of each specific context. A technology can be appropriate for a context only if can guarantee its efficacy along the time, hence be sustainable.

For these reasons, it is not possible to define *a priori* which technology is more appropriate. Local needs, cultures, traditions, economic conditions, natural resources, technical skills to manage the technology, among others, are aspects that should be carefully considered in order to develop and implement an appropriate technology.

Models of appropriate technologies (e.g., the solar-powered reverse osmosis treatment plant) are already in place in the Mediterranean region, but further efforts should be put in this direction in order to enhance the management of water resources for drinking use.

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PHYSICAL-MECHANICAL PROPERTIES OF NEW GREEN BUILDING MATERIALS BASED ON GLASS WASTE

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Abstract

Recently several innovative suggestions on how industrial wastes can be utilised in new products have been presented in literature, e.g. as filler or additives in concrete, incorporated in ceramic materials to produce glass-ceramics and pavement construction. In this work, metallurgical materials from secondary aluminium scrap processing and glass waste derived from treatments of packaging and fluorescent lamps were considered for fabrication of new ceramic materials using powder technology and sintering process.

The effect of composition and heat treatment temperature, on the sintering process and then final properties, were evaluated. The results showed that, with the proper firing temperature, lightweight ceramic materials containing high amount of glass waste and an innovative product resulting from the processing of secondary aluminum (ArgAlum®) can be produced. The low water absorption (< 1%), low density (< 2 g/cm^3) and the good flexural strength (16-20 MPa) associated to relatively low sintering temperatures obtained with the addition of ArgAlum®-can be considered as promising initial results to obtain new green building materials.

Key words: by-product, ceramic material, low density materials, glass recycling, waste

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1. Introduction

Waste material, defined as any type of material by-product of human and industrial activity, could contribute to increased sustainability of industrial operations by conserving virgin materials and increasing the sustainable use of resources. Categories of waste that the new EC Waste Framework Directive 2008/98/EC (WFD) has recognized as candidate for "end-of-waste" (EoW) criteria can include the waste streams of construction and demolition waste, ashes, slags, scrap metals, aggregates, tyres, textiles, compost, paper and glass (Watkins et al., 2013; Szőke et al., 2014; Li et al., 2014). Three different alternative raw materials can be considered as substituted of traditional ones for the ceramic and building material industries: the glass waste from containers (GWC), glass from fluorescent lamps and products from secondary aluminum scraps processing.

According to data reported by CoReVe, the Italian Consortium for the collection, recycling and reuse of waste from packaging glass in Italy, in 2013 approximately 2,186,300 tons of packaging glass have been put on the market in Italy and the 73% of that it has been collected by separate collection. In other words, around 1,596,000 tons of the packaging glass are recovered mainly (99%) in glassworks and 1% in alternative recovery processes (ceramic industry, building, others glass sectors) (Co.Re.Ve., 2014; Andreola et al., 2013).

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Fluorescent lamps are widely world-wide used due to their long life and energy saving capability. A typical fluorescent lamp is composed by a glass tube coated with different blends of metallic and rare-earth phosphor salts with electrodes located at both ends of the tube (Jansma, 2003). Light tubes are generally made by a soft sodium–calcium glass whereas the materials at the ends, which are connected to the light cap, are made of hard glass with higher lead content. These lamps contain mercury (Hg) as a source of fluorescent radiation, cadmium (Cd) and lead (Pb). Hence, their untreated disposal causes serious health and pollution problems (Andreola et al., 2010)

This work evaluates the potential use of these glass wastes with a product from secondary aluminum process, in the production of new ceramic materials for building sector. The secondary aluminium industry generates a salt-cake waste currently disposed of in a conventional landfill. As much as 50% of the content of this waste is mixed salt (sodium and potassium chlorides). In addition, black dross that is not economical to reprocess in a rotary furnace for aluminium recovery ends up in landfills (Gil, 2005; Gil and Korili, 2010; Wöhlk et al., 1987; Tociu et al., 2014). The composition of the dross is similar to that of salt cake, except that it contains higher concentrations of metallic aluminium (up to 20%) and correspondingly lower amounts of salts. Because of the high solubility of the salts in water, these residues, when put in landfills, represent a potential source of pollution surface-water and groundwater supplies (Tsakiridis, 2012).

Nevertheless, a methodology for salt cake waste from secondary aluminum dross recovery was patented by Intals S.p.A. (Gastaldi and Vedani, 2008). This technique maximizes aluminum recovery, and it also produces a new material, coded, as ArgAlum®, constituted of corundum (Al_2O_3), as main crystalline phase. Specifically, ArgAlum® is an innovative product, with registered trade mark since 24.01.2008 in Class 6 "Common metals and alloys; materials for metal constructions; metallic transportable constructions; metallic materials for railways; non-electric metallic cables and wires; ironmongery, small metal hardware; safes; metal products not included in other classes; raw minerals". It is an eco-friendly material which drastically reduces the need for virgin raw materials mainly in the production of Portland cement and alumina cement with low environmental impact, bricks and brick materials, expanded clay, mineral fibres for thermal insulation (rock wool). ArgAlum® is an inorganic mineral material made from a mixture of oxides, with the appearance of dark sand with a grain size of max 1 mm, sold on the national and international market for almost 10 years.

ArgAlum® contains no substances of very high concern (SVHC) contemplated in the ECHA (European Chemicals Agency) "Candidate List of Substances of Very High Concern for Authorisation" in concentrations over 0.1% in weight (Candiadate List of substances of very high concern for Authorisation). Registering EPD – Environmental Product Declaration - is a further step towards recognising the quality, innovation and sustainability for ArgAlum® (more on PRODUCT INFORMATION data sheet).

The purpose of this work was to test both the compatibility of ArgAlum® with the two different kinds of glass wastes above described and the influence of their different chemical composition on the technological and of processing parameters. The aim was to prepare new green building product based totally on recovery raw material in replacement of traditional feldspar and quartz sand.

2. Experimental procedure

2.1. Materials

In this study glass waste derived from glass containers and fluorescence lamps were chosen. These two wastes were used with refractory clay: K kaolin ceramic grade (Balco, Italy).

In Table 1 is reported the chemical composition of the glass wastes. The highest amount of alkaline oxide, in particular Na_2O combined with the lower amount of silica in the fluorescent lamp composition, underline a higher fluxing action and sintering temperature decrease of fluorescent lamp with respect to packaging glass.

Table 1. Chemical composition of glass wastes

Oxide	*Fluorescence lamp glass waste (wt%)*	*Glass container Waste (wt%)*
SiO_2	68.0	71.7
Al_2O_3	2.27	2.25
Na_2O	17.5	12.5
K_2O	1.59	1.0
MgO	2.96	2.0
CaO	5.1	9.5
SrO	0.07	-
BaO	0.94	-
PbO	0.77	-
Fe_2O_3	0.08	0.43
Sb_2O_3	0.08	-
TiO_2	0.002	0.07
P_2O_5	0.05	-

In Table 2 is reported the chemical composition of ArgAlum®, consisting of corundum (Al_2O_3), quartz (SiO_2), aluminium (Al) and spinel ($MgAl_2O_4$) as main crystalline phases and NaCl.

Table 2. Chemical composition of Argalum

Oxide/element	*wt%*
Al_2O_3	60-80%
Al	1-6%
SiO_2	5-11%
FeO	1-3%
MgO	3-7%
Cl	<0.5%

A series of ceramic batches containing 80 wt% of glass and 20 wt% of a refractory clay were prepared (labeled 80_V20_C for the sample with glass container and $80_{Vfl}20_C$ with fluorescence lamp glass).

In order to investigate the effect of ArgAlum® (Ar) on physical mechanical properties of these new ceramic materials for building sector, a different concentration of Ar was added to the batch replacing glass and/or clay. Thus $X_VY_CXY_A$ composition have been obtained, where X is a digit denoting the concentration of glass, Y the concentration of the clay and moreover XY the presence of Ar in replacement of glass or clay. The list of the prepared samples are reported in Table 3, the batch chemical compositions are completely different with respect to the traditional ceramic products, traditional tiling ceramics, building bricks and roof tiles (EN 14411, 2006).

In order to prepare suitable press-powder, the raw materials were ground and sieved below 500 μm. Each batch composition was prepared by dry-grinding, humidified with 6 wt% of distilled water, and finally the green samples were uniaxial pressed at 40 MPa. Bar samples (50 mm ×5 mm ×4 mm) were sintered in an electric laboratory furnace (Nambertherm) at 10°C/min heating and 1 h soaking step at different temperatures (950-1000-1050-1100°C range). Moreover, parallelepiped samples (100 mm×8 mm×8 mm) were uniaxial pressed at 40 MPa and the obtained specimens were used for flexural strength.

2.2. Characterization of samples

For the fired samples, measurements of linear shrinkage (LS %) and water absorption (WA %) according to ISO 10545-3 were performed. Total porosity (P_T), was evaluated by the difference between absolute density, ρ_{ab} and apparent density, ρ_a, of ceramics (Eq. 1). Apparent density was estimated by a dry flow Pycnometer (Micromeritics GeoPyc 1360) using bulk sample of 1 cm^2 of area, while ρ_{ab} by He displacement Pycnometer (Micromeritics ACCUPYC 1330), after crashing and milling the samples below 45 μm.

$$P\ (\%) = 100\ x\ \rho_{ab} - \rho_a/\rho_{ab} \tag{1}$$

A series of five samples of each composition was used for the evaluation of flexural tests performed according to UNI EN ISO 178. The maximum flexural strength at break (σ_b) and the maximum deformation (ε_{max}) were evaluated for at least five specimens. The microstructure of the fired materials was analyzed by scanning electron microscope (ESEM Quanta 200, FEI Company, USA).

Table 3. List of the prepared samples, including composition and temperature treatment

Sample	***Glass container (wt%)***	***Fluorescence lamp glass (wt%)***	***Clay (wt%)***	***ArgAlum® (wt%)***	***Temperature (°C)***
80_V20_{C950}	80	-	20	0	950
80_V20_{C1000}	80	-	20	0	1000
80_V20_{C1050}	80	-	20	0	1050
80_V20_{C1100}	80	-	20	0	1100
$80_V10_C10_{A950}$	80	-	10	10	950
$80_V10_C10_{A1000}$	80	-	10	10	1000
$80_V10_C10_{A1050}$	80	-	10	10	1050
$80_V10_C10_{A1100}$	80	-	10	10	1100
$70_V20_C10_{A950}$	70	-	20	10	950
$70_V20_C10_{A1000}$	70	-	20	10	1000
$70_V20_C10_{A1050}$	70	-	20	10	1050
$70_V20_C10_{A1100}$	70	-	20	10	1100
$80_{Vfl}20_{C850}$	-	80	20	-	850
$80_{Vfl}20_{C900}$	-	80	20	-	900
$80_{Vfl}20_{C950}$	-	80	20	-	950
$80_{Vfl}20_{C1000}$	-	80	20	-	1000
$80_{Vfl}20_{C1050}$	-	80	20	-	1050
$80_{Vfl}20_{C1100}$	-	80	20	-	1100
$80_{Vfl}10_C10_{A950}$	-	80	10	10	950
$80_{Vfl}10_C10_{A1000}$	-	80	10	10	1000
$80_{Vfl}10_C10_{A1050}$	-	80	10	10	1050
$80_{Vfl}10_C10_{A1100}$	-	80	10	10	1100
$70_{Vfl}20_C10_{A950}$	-	70	20	10	950
$70_{Vfl}20_C10_{A1000}$	-	70	20	10	1000
$70_{Vfl}20_C10_{A1050}$	-	70	20	10	1050
$70_{Vfl}20_C10_{A1100}$	-	70	20	10	1100

The effect of ArgAlum® on the sample color was determined by performing color measurements on both samples before and after the addition of Argalum, by a spectrophotometer (SP60) using the CIELAB method. The method defines a color through three parameters, L^*, a^*, and b^*, measuring brightness, red/green, and yellow/blue color intensities, respectively (Johnston, 1973). The method allows, moreover, to define a color difference as ΔE^*, based on the relationship (2), where ΔL^*, Δa^*, and Δb^* measure the differences in luminosity and in chromaticity between two colors.

$$\Delta E^* = [(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2} \qquad (2)$$

In this way, the variations due to the addition of ArgAlum® were determined.

3. Results and discussion

3.1. Physical properties of final ceramics

Fig. 1 presents the firing shrinkage and water absorption of the ceramic bodies made with 80% of glass waste and 20% of clay. The $80_{Vfl}20_{C}$ sample shows higher shrinkage at low temperature, which can be attributed to the high Na_2O content in the fluorescence glass waste.

In fact, the alkaline oxide rich glass waste, by acting as a fluxing agent, contributed to a decrease of the thermal treatment of about 100°C as can be seen in Fig. 1.

Moreover, a water absorption values within 8-8.3% occurs at 900°C and 1000°C for $80_{Vfl}20_{C}$ and $80_{V}20_{C}$ mixtures respectively.

The sintering behavior changed after the addition of ArgAlum® as confirmed by Figs. 2 and 4. It is evident from Fig. 2a a decreasing trend in the firing shrinkage with Argalum addition at lower firing temperatures (950-1000°C). This was confirmed by the porosity evaluation. The maximum porosity percentage of 28.97% is observed for $80_{V}10_{C}10_{A1000}$, compared to 21.77% for $80_{V}20_{C1050}$ sample (Table 5).

In all of the case, the decrease of linear shrinkage, at lower temperature, could be ascribed to the decreased sintering activity of samples due to the addition of corundum, the main crystalline phase of ArgAlum®. As a consequence of the decreasing of the densification, the water absorption values increase.

Interesting and better results were obtained for the sample $70_{V}20_{C}10_{A1050}$: 1) minor linear shrinkage, 2) minor water absorption, 3) minor apparent density (Table 5), which may be attributed to the expansion phenomena.

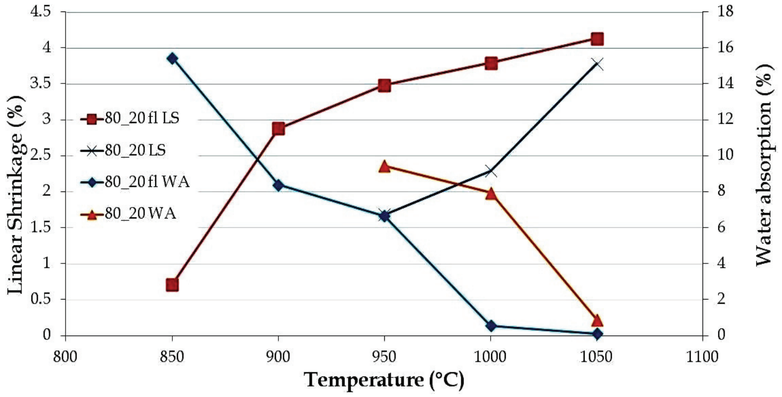
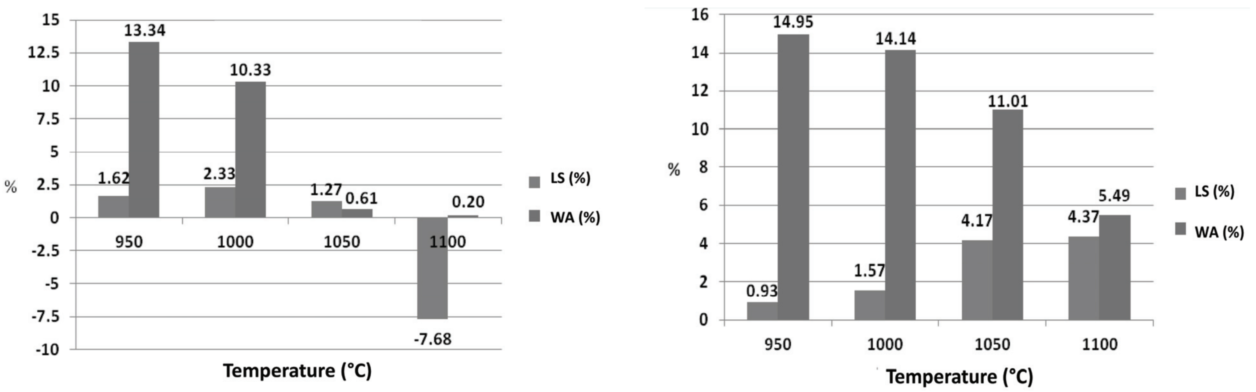


Fig. 1. Linear shrinkage and water absorption of ceramic batch $80_{V}20_{C}$ and $80_{Vfl}20_{C}$ fired at various temperatures



(a) (b)

Fig. 2. Linear shrinkage and water absorption values of sample (a) $80_{V}10_{C}10_{A}$ and (b) $70_{V}20_{C}10_{A}$

The low apparent density and water absorption indicate that closed porosity was formed and that vetrification took place. Fig. 3 reports the image of the sample before and after adding of ArgAlum®. At higher temperature (1100°C) starts overfiring, with WA near 7.16% and about 9.68% of linear expansion. The $80_{Vfl}20c$ composition shows similar behaviour, in agreement with the content of Ar.

As can be seen in Fig 4, in agreement with the content of Ar, the $80_{Vfl}20c$ composition also shows a decreasing trend in the firing shrinkage. Because of the diminution of the densification, the water absorption values increase. The results related to samples obtained at 1100°C are not reported because the samples melt and became deformed at higher temperatures. In addition, in this case, interesting results have been obtained for one composition, the $70_V20_C10_{A1050}$ sample. The addition of ArgAlum® in the mixture with fluorescence lamp glass leads of a decrease in density and water absorption at low thermal temperature resulting advantageous for obtaining porous materials with low water absorption.

Apparent density and total porosity values are listed in Table 5. It can be observed that density ranges from 1.83 g/cm^3 to a minimum of 0.68 g/cm^3 for samples with higher porosity values, while the absolute densities of the these ceramics increase from 2.48 to 2.57 g/cm^3 with ArgAlum®. The absolute densities of these materials are similar to those of the traditional glass-ceramics materials (2.56 g/cm^3), while the apparent density values are lower than those usually measured on some traditional ceramics such as floor (Manfredini and Pellacani, 1992).

Concerning the colour of sintered samples, reported in Table 4, it is pale brown for the 80v20c composition and became green at higher temperature. Finally, the colour of $80_V10_C10_A$ and $70_{Vfl}20_C10_A$ strongly points to grey, due to the presence of metallic aluminum in the Ar powders.

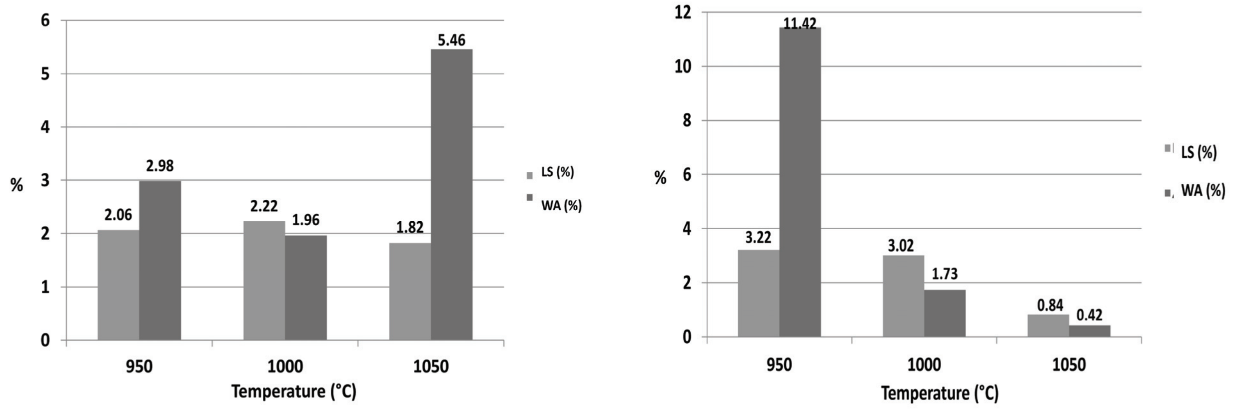
3.2. Structure and mechanical properties of final ceramics

SEM images, taken on the cross section of the fired samples, are reported in Fig. 5a-d. SEM observations confirmed the results of LS% and porosity evaluation and highlight that the microstructure varies with the Ar addition and temperature treatment. It must be observed that sample produced by sintering 80v20c composition at 1000°C shows the presence of distinct grains (Fig. 5a), while the specimen prepared at higher temperature 1050°C (Fig. 5b, 5d) shows the presence of a vitreous phase which is evident in several zones where the microstructure is not perfectly visible since polycrystalline grains are covered by a layer of glass produced by the liquid phase present at high temperature during the sintering process.

The specimen prepared at higher temperature have great amount of heterogeneous porosity that contribute to the decrease of density. The flexural strength, a property that strongly depends on the porosity and microstructural defects of specimen (Alonso-Santurde et al., 2012), has been measured only for some samples, the more interesting for future applications. The flexural strength varied from 4.8 MPa to 28.93 MPa for the composition 80_V20_C, the highest value was obtained for sample 80_V20_{C1050}.

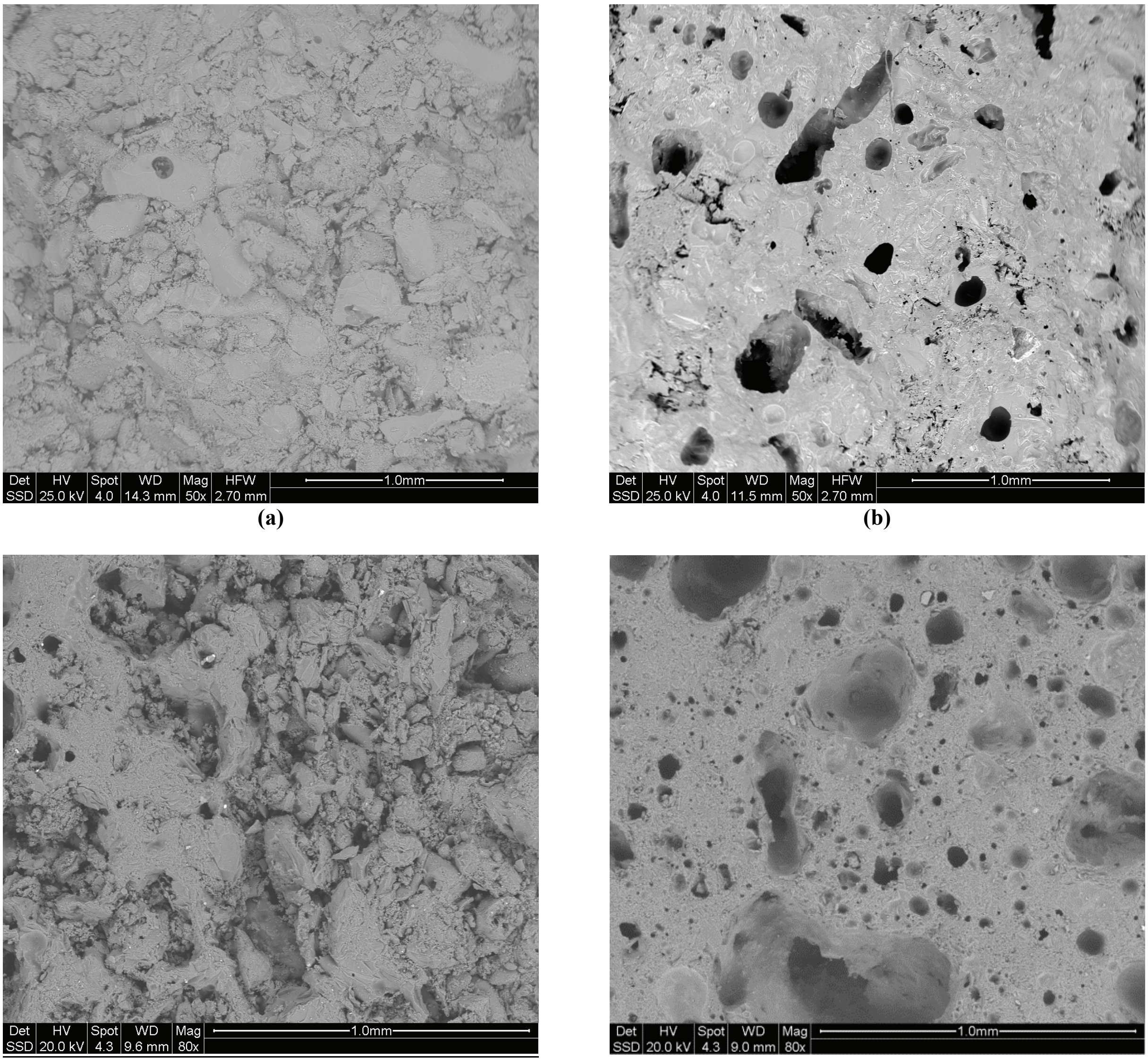

(a) **(b)** **(c)**

Fig. 3. Images of sample (a) $80v20c_{1050}$, (b) $80_V10_C10_{A1050}$ and (c) $70_V20_C10_{1100}$



(a) **(b)**

Fig. 4. Linear shrinkage and water absorption values of sample a) $80_{Vfl}10_C10_A$ and b) $70_{Vfl}20_C10_A$



(a) **(b)**

(c) **(d)**

Fig. 5. SEM micrographs of sample a) $80_{V}20_{C1000}$, b) $80_{V}20_{C1050}$, c) $80_{V}10_{C}10_{A1000}$, d) $80_{V}10_{C}10_{A1050}$

Table 4. Colorimetric measurements

Sample	*L*	*a*	*b*	*ΔE*
$80_{V}20_{C950}$	80.38±0.45	2.8±0.13	13.53±0.51	-
$80_{V}20_{C1000}$	78.86±0.65	1.69±0.14	13.60±0.35	-
$80_{V}20_{C1050}$	67.16±0.84	-1.90±0.22	12.80±0.31	-
$80_{V}10_{C}10_{A950}$	75.84±0.55	0.92±0.06	8.51±0.19	7.07
$80_{V}10_{C}10_{A1000}$	67.37±0.57	-0.08±0.28	7,76±0,26	12.04
$80_{V}10_{C}10_{A1050}$	65.25±0.22	-0.92±0.13	6.35±0.11	7.29
$70_{V}20_{C}10_{A950}$	81.09±0.16	0.79±0.04	6.23±0.11	5.27
$70_{V}20_{C}10_{A1000}$	80.61±0.21	0.68±0.04	5.77±0.12	6.00
$70_{V}20_{C}10_{A1050}$	76.47±0.65	0.32±0.06	5.53±0.25	7.39
$80_{Vfl}20_{C950}$	76.82±0.98	5.63±0.19	12.55±0.41	-
$80_{Vfl}20_{C1000}$	63.06±0.47	5.15±0.20	11.33±0.32	-
$80_{Vfl}20_{C1050}$	60.66±0.44	1.83±0.15	6.93±0.08	-
$80_{Vfl}10_{C}10_{A950}$	58.24±0.97	1.47±0.18	3.84±0.24	6.98
$80_{Vfl}10_{C}10_{A1000}$	62.79±1.19	1.27±0.07	4.25±0.23	8.08
$80_{Vfl}10_{C}10_{A1050}$	60.42±1.36	0.53±0.07	3.62±0.17	3.56
$70_{Vfl}20_{C}10_{A950}$	53.88±0.71	0.88±0.17	2.95±0.24	24.49
$70_{Vfl}20_{C}10_{A1000}$	61.98±0.55	1.51±0.09	5.69±0.27	6.80
$70_{Vfl}20_{C}10_{A1050}$	56.68±1.49	0.24±0.13	3.21±0.32	11.43

Table 5. Physical and mechanical characteristics: apparent density (ρ_{ap}), total porosity (P_T), maximum flexural strength at break (σ_b) and the maximum deformation (ε_{max})

Sample	ρ_{ap} ***(g/cm^3)***	P_T ***(%)***	σ_b ***(MPa)***	ε_{max} ***(%)***
$80_{V}20_{C950}$	2.07	16.53	4.8±1.34	0.435±0.001
$80_{V}20_{C1000}$	1.94	21.77	9.95±2.59	0.022±0.012
$80_{V}20_{C1050}$	2.02	18.55	28.93±2.79	0.016±0.015
$80_{V}10_{C}10_{A950}$	1.79	28.97	2.73±0.82	0.045±0.005
$80_{V}10_{C}10_{A1000}$	1.79	28.97	9.94±3.43	0.022±0.010
$80_{V}10_{C}10_{A1050}$	1.47	41.67	13.82±1.47	0.022±0.020
$80_{V}10_{C}10_{A1100}$	0.95	62.30	-	-
$70_{V}20_{C}10_{A950}$	1.82	27.77	2.07±0.69	0.023±0.004
$70_{V}20_{C}10_{A1000}$	1.90	24.60	6.62±1.05	0.120±0.004
$70_{V}20_{C}10_{A1050}$	1.98	27.70	15.27±0.70	0.094±0.031
$70_{V}20_{C}10_{A1100}$	1.60	36.51	-	-
$80_{Vfl}20_{C950}$	1.98	25.40	18.48±1.18	0.074±0.072
$80_{Vfl}20_{C1000}$	2.04	17.74	-	-
$80_{Vfl}20_{C1050}$	2.15	17.34	-	-
$80_{Vfl}10_{C}10_{A950}$	1.70	32.54	-	-
$80_{Vfl}10_{C}10_{A1000}$	1.83	27.38	-	-
$80_{Vfl}10_{C}10_{A1050}$	1.53	39.28	16.51±4.36	0.026±0.003
$70_{Vfl}20_{C}10_{A950}$	1.89	25.00	-	-
$70_{Vfl}20_{C}10_{A1000}$	1.83	27.38	-	-
$70_{Vfl}20_{C}10_{A1050}$	1.42	39.28	-	-

Due to the poor densification process produced in bodies with Ar, the flexural strength decreases with the Ar addition but increases with the treatment temperature.

Despite the presence of porosity at higher temperature, these materials have sufficient strenght indicating an interesting potential for ArgAlum® recyling to produce new lightweight materials for bulding sector (Barbieri et al., 2013; Dondi et al., 1997).

4. Conclusions

This study has demonstrated the feasibility to use the glass wastes and a material from secondary aluminium scrap processing, in the manufacture of new green materials with composition different from ones of the traditional tiling ceramics, building bricks and roof tiles.

The possibility to obtain new ceramics, with higher waste concentration adopting a very short thermal cycle at relatively low temperatures of 950-1050°C was demonstrated. The results showed that, with the proper firing temperature, lightweight ceramic materials containing high amount of glass waste and a new product (ArgAlum®) can be produced. The low water absorption (< 1%), low density (< 2 g/cm^3) and the good flexural strength (16-20 MPa) were obtained with the addition of 10wt% of Argalum.

However, based on the results of the physical and mechanical properties, glass wastes and metallurgical industrial product are recommended as raw materials in the manufacture of ceramic products, reducing the amounts disposed in landfills, the consumption of raw materials and energy costs.

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FUNGAL LACCASES PRODUCTION USING TOMATO-BASED MEDIUM: A FACTORIAL DESIGN APPROACH

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Abstract

This study was aimed to stimulate laccase production by *Trametes pubescens* MUT 2400 by using a tomato-based medium. Two sequential 2x2 factorial designs were used to determine the effect of carbon (C) and nitrogen (N) source concentration on laccase activity and biomass concentration; copper was used as the sole inducer (0.75 mM). Analysis of the first factorial design showed that N had a strong positive effect on the maximum laccase activity, which occurred at day 12 of cultivation and final biomass concentration. When both C and N concentration (25% v/v, 28.7 g/L) were set at the high level, laccase activity and biomass growth were maximal (9.5 U/mL and 7.15 mg/mL). A second factorial experiment with C and N concentrations in the ranges of 25 - 50 % v/v and 28.7 - 48.7 g/L, respectively, established based on the results of the first one, showed that laccase activity could be further increased by either increasing C or N to their high levels. The enzymatic peak occurred at the 17th day in this second design with a maximum laccase activity of 28.6-32.8 U/mL. Laccase peak occurred when reducing sugars were completely depleted from the medium. The results of this study indicated that laccase activity could be enhanced by acting on nutrient content, and tomato-based medium is a good fermentation substrate.

Key words: factorial design, fungi, laccases, tomato-based medium

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1. Introduction

Agriculture and food industrial chains produce large amount of wastes which represent a constant issue in term of disposal and handling. Common processing strategies foresee landfill storage, animal feeding, composting, burning for energy production, etc. Although some of them are able to manage the huge scale wastes produced, low valuable products are generated. The valorization of wastes as barley bran, sugarcane bagasse, grape, rice and corn wheat straw, vegetables derivates, etc. has indeed become a major research topic. Their organic components may be fruitful for greener technologies, extracting valuable chemicals (polymers, ethanol etc.) or producing fine compounds as enzymes (Arancon et al., 2013; D'Annibale et al., 2014; Gonzalez et al., 2013).

Tomato is one of the most consumed crops worldwide, producing tomato pomace as the major waste. It contains peel, seeds and also a minor fraction of pulp (Del Valle et al., 2006). Tomatoes are rich in sugars (glucose, fructose and sucrose), organic acids (malic and citric acid), phenolic compounds (flavonoids), unsaturated hydrocarbons (carotenoids) and minerals (mainly P, K, Ca and Cu) (Acosta-Quezada et al., 2015). Considering this various chemical composition, tomato derivatives can be used as cultivation medium; proper nourishment content is associated to high economic and environmental sustainability. Laccases (EC 1.10.3.2) are multicopper oxidases, able to catalyze

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the electron transfer from a substrate to a molecule of oxygen, which is thereby reduced to water. They occur in bacteria, insects and plants, but in fungi the highest production yields have been monitored (Rivera-Hoyos et al., 2013). Thanks to the high redox potential, laccases of Basidiomycetes are one of the most promising industrial biocatalysts that can be employed in textile and paper industry, wastewater treatment, chemicals synthesis, beverage clarification etc. (Rivera-Hoyos et al., 2013). Enzymatic treatments are indeed eco-friendly methodologies, displaying low energy requirements and easy process control (Torres et al., 2003), but the availability of large amount of laccases is an essential prerequisite.

Laccases are usually secreted in small amount during secondary metabolisms, but their production can be enhanced by several exogenous stimuli (Desai and Nityanand, 2011; Elisashvili and Kachlishvili, 2009). Metal ions (i.e. Cu), aromatic compounds and nutrient sources are predominant factors, sometimes directly acting at gene transcription level (Piscitelli et al., 2011). Since interactions effects among these factors occur, conventional experimental approaches in which one factor at a time is changed are not only inefficient, but lead to erroneous conclusions and sub-optimal results. Designs of experiment methods are instead able to evaluate the effects of several factors, highlighting combinatorial interactions and identifying optimum range. This approach has been successfully applied for the optimization of fungal laccases production, taking into consideration medium composition and inducers addition (Aghaie-Khouzani et al., 2012; Junghanns et al., 2008; Tinoco et al., 2011).

Obtaining low cost enzymes first passes through a reduction of production costs. To date, most of the researches have used synthetic costly media based on glucose and model inducers as veratryl alcohol, ABTS, dyes etc. (Galhaup et al., 2002; Kanwal and Reddy, 2011) but selected agro-food wastes offer alternative nourishment substrates (Elisashvili and Kachlishvili, 2009). In addition, the high phenolic content as well as the natural occurrence of minerals as Cu makes them (i.e. olive mill wastewaters, coffee husk, soybean pod, apple pomace, etc.) efficient inducers of laccase production (Cambria et al., 2011; Gonzalez et al., 2013: Park et al., 2014). For example, the presence of caffeine and tannins in coffee husk has been univocally associated to laccase production stimulation of *Trametes pubescens* strain (Gonzalez et al., 2013).

In the present study, laccase production by *Trametes pubescens* MUT 2400 was stimulated by medium composition variations. The strain was selected because of its demonstrated capability to transform organic compounds (Anastasi et al., 2012; Spina et al., 2013) making the expressed laccases good candidates for biotechnological uses. To enhance the economic sustainability of the biocatalysts production, complex not-synthetic media were used: previous evidences already demonstrated the capability of this fungal strain to grow and produce the enzyme of interest in presence of agro-industrial wastes (Gonzalez et al., 2013). A tomato-based medium was set up and the concentration of C and N source was varied to define the range where fungal productivity was maximized.

Assuming that these factors may both influence laccase production, the identification of the optimal culture conditions needed to consider single and combinatorial effects. Replicated factorial designs were used to evaluate the behavior of the fungus in response to the medium variations: the production stimulation of relevant enzymes and the biomass growth were both considered as responses.

2. Experimental

2.1. Fungal strain

Trametes pubescens MUT 2400 was selected for its capability to decolorize and detoxify wastewaters producing high concentration of laccases (Anastasi et al., 2011; Spina et al., 2013). The strain is preserved at the *Mycotheca Universitatis Taurinensis* (MUT, University of Turin, Department of Systems Biology and Life Sciences, Torino, Italy).

2.2. Chemicals

All the chemicals were purchased from Sigma Aldrich. The tomato sauce was used as a commercially available formulate (Cirio, San Lazzaro di Savena, Bologna, Italy). The partial chemical composition includes (mass fractions) 5.3 % carbohydrates (including 4.2 % sugars), 1.7 % fibers, 0.1 % fatty acid and 1.2 % proteins. Reducing sugars were analyzed following the method described in 2.4. paragraph: 37 g/L were detected in commercial tomato sauce.

2.3. Production of laccases

The experiments were carried out in 100 mL Erlenmeyer flasks with 40 mL of liquid culture as final volume. Each flask was inoculated with a 0.5 mL fungal suspension, prepared by homogenizing agar squares (1 cm^2) derived from the margins of a grown colony together with sterile water.

A tomato-based medium (TM) was used, using tomato sauce as C source and bactopeptone as N source. After two days from inoculation, laccase production was stimulated by copper addition ($CuSO_4$ 0.75 mM final concentration). A control without Cu was set for a unique cultural composition: 12.5% v/v tomato sauce and 18.7 g/L bactopeptone (corresponding to TM5-center point of *Design I*). Flasks were incubated at 25 °C and 120 rpm for 20 days. Every two days, a sample was collected; enzymatic activity, pH and reducing sugars concentration were measured. At the end of the experiment, biomass growth was also evaluated. The fungal dry weight (mg/L) was calculated after incubation at 60 °C for 24 h.

2.3.1. Description of experimental set up

To evaluate the effects of several parameters on laccase production by *T. pubescens* MUT 2400, a replicated 2^2 factorial design was carried out. Tomato sauce (X_1) and bactopeptone (X_2) were chosen as the independent variables. Tomato sauce was properly diluted with sterile water, and the concentration expressed as volume tomato sauce / total volume (% v/v). Bactopeptone concentration range was fixed considering previous evidences about laccase production by *T. pubescens* MUT 2400 in a synthetic medium (data not shown). The laccase activity and the biomass concentration were taken as response variables. The experimentation was carried out in a sequential fashion by setting up two factorial experiments.

Design I

Table 1 reports the factor levels in both natural and coded values for *Design I*. The low (-1) and high (+1) levels for tomato sauce concentration or bactopeptone concentration were 6.25 and 25% v/v or 8.7 and 28.7 g/L, respectively. An additional medium (TM5) was added with 12.5% v/v tomato sauce and 18.7 g/L bactopeptone and used to estimate response surface curvature. All the experiments were carried out in triplicate with the exception of TM5 medium that was replicated five times.

Design II

A second design was evolved according to the data of *Design I*. One of the experimental points was repeated in the two designs (labeled as TM4 in *Design I* and TM1 in *Design II*). The design factors are tomato sauce concentration (25-50% v/v) and bactopeptone concentration (28.7-48.7 g/L).

As described in Table 2, each parameter was assessed at two levels (-1, +1) and the center point was fixed at 37.5% v/v tomato sauce and 38.7 g/L bactopeptone. All the experiments were carried out in triplicate with the exception of the center point that was replicated five times. Fig. 1 reports the two designs carried out on the X_1-X_2 plane.

2.4. Enzymatic activity assay and glucose consumption analysis

Both enzymatic activity and reducing sugar content were evaluated by colorimetric analysis. A multimode reader spectrophotometer (TECAN Infinite M200, Austria) was used and the protocols were validated to be run in 96-wells microplates.

Table 1. Experimental conditions of the Design I. X_1: tomato sauce (% v/v); X_2: bactopeptone (g/L)

	coded levels		*actual levels*	
	X_1	X_2	X_1	X_2
TM1	-1	-1	6.25	8.70
TM2	+1	-1	25.00	8.70
TM3	-1	+1	6.25	28.70
TM4	+1	+1	25.00	28.70
TM5	-0.333	0	12.50	18.70

Table 2. Experimental conditions of the Design II. X_1: tomato sauce (% v/v); X_2: bactopeptone (g/L)

	coded levels		*actual levels*	
	X_1	X_2	X_1	X_2
TM1	-1	-1	25.0	28.7
TM2	+1	-1	50.0	28.7
TM3	-1	+1	25.0	48.7
TM4	+1	+1	50.0	48.7
TM5	0	0	37.5	38.7

Laccase activities were determined by following the oxidation of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid (ABTS) in sodium-citrate buffer (pH 3.0) at 420 nm (ε_{420} = 36 mM^{-1} cm^{-1}) (Niku-Paavola, 1988). The enzymatic activity was expressed as international units (U), where one unit is the amount of enzyme that oxidizes one µmol of substrate per minute.

Reducing sugars concentration in the culture was determined using the 2,4-dinitrosalicyclic acid (DNS) (λ 540 nm) assay, according to the method of Miller (Miller, 1959). Data were expressed as residual amount (%) in comparison with the initial content before the fungal inoculum.

3. Results and discussion

Enzymes technologies feasibility passes mainly by the maintenance of low costs of fermentation for the production of industrial enzymes.

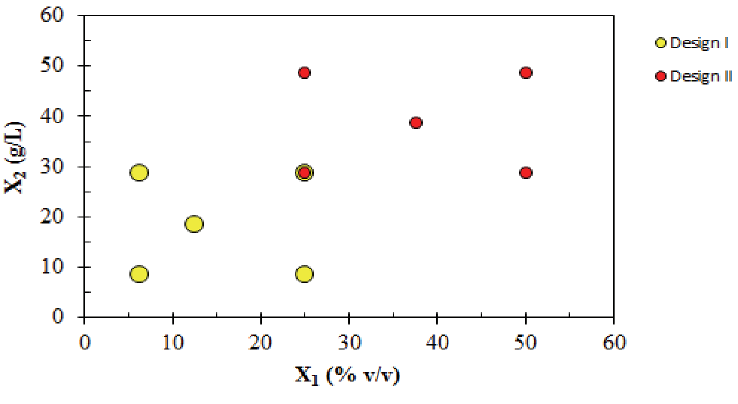

Fig. 1. Design points of *Design I* and *Design II*

Since carbon source in the fermentation medium is of major relevance on the economic balance of the process, pure synthetic sugars can be substituted by cheaper materials as by-products of agro-food industries.

The possibility to use fruits and vegetables derivatives has been recently investigated, taking into consideration for example banana and mandarin peel (Sathishkumar et al., 2010), cedar sawdust (Gonzalez et al., 2013), apricot and pomegranate wastes (Akpinar and Urek, 2014), apple pomace (Park et al., 2014), etc. Among these substrates, tomato based medium have been efficiently used for fungal fermentation by several authors (Carabajal et al., 2014; Freixo et al., 2008; Liers et al., 2007; Junghanns et al., 2008; Ramirez-Cavados et al., 2014).

The addition of inducers as syringaldazide, anthraquinonic dyes, etc. has been often required to achieve high production yields among which copper has often triggered laccase overexpression. In the present study, Cu was the sole added elicitor, taken the assumption that tomato-based medium (TM) already contains a consistent amount of uncharacterized aromatic compounds which could potentially stimulate enzymatic production (Ullrich et al., 2005). In accordance with other reports (Galhaup et al., 2002; Galhaup and Hatrich, 2001; Gonzalez et al., 2013; Hess et al., 2002), in this study *T. pubescens* enzymatic productivity was remarkably influenced by Cu.

The sole addition of 0.75 mM $CuSO_4$ in a culture medium (12.5% v/v tomato sauce and 18.7 g/L bactopeptone) increased laccase production up to 2-fold than the control without Cu (from 3.22 U/mL to 6.43 U/mL). It is indeed essential for the proper folding of laccase active site; it may play as transcriptional inducer of laccase genes due to the present of metal response elements in the promoter (Piscitelli et al., 2011). Moreover, Cu interferes with laccase denaturation catalyzed by proteases (Baldrian and Gabriel, 2002; Palmieri et al., 2001).

3.1. Laccase production by TM: Design I

Laccase production by *T. pubescens* MUT 2400 was stimulated by 5 media (TM1-5) whose composition varied for the tomato sauce and bactopeptone concentration ($CuSO_4$ 0.75 mM). Data concerning the major parameters measured during the experiment are listed in Table 3. In all the media, the maximal laccase activity was reached at the 12th day. The highest laccase activities (8.4 and 8.3 U/mL) and final biomass concentrations (7.1 and 6.1 g/L) were obtained when N source was at its maximum tested concentration (TM4 and TM3, respectively, with 28.7 g/L bactopeptone). Table 4 lists the results obtained from the analysis of variance (ANOVA). Since the p-value of each term was below 0.05 except for the curvature term of biomass, the tested factors significantly influenced laccase productivity and biomass development.

Data on laccase activity show a statistically significant curvature ($p < 0.05$), suggesting that a model with only main effects and interaction is not adequate to describe the system. Since the mean response for the center point (6.43 U/mL) is lower than the mean response at the corners of the experimental design when N is at the high level (8.3-8.4 U/mL) (Fig 2), it could be assumed that the optimum does not belong to the experimental region. A significant interaction between C and N was detected: the effect of each factor depends on the levels of the other factor. Despite this, N played a major role (p = 0.000). As shown in Fig 2, when bactopeptone concentration increased from -1 to +1, laccase activity increased irrespective of the low and high level of tomato sauce.

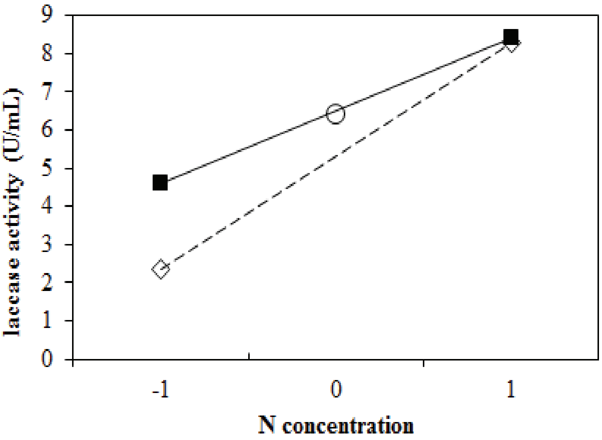

Fig. 2. Interaction plot of C and N for laccase activity: ── high level of C (+1); - - - low level of C (-1)-; ○ internal point

Table 3. Laccase activity (U/mL) at 12th day, dry biomass (g/L), pH and residual reducing sugars content (%) at the end of the experiment for Design I

	laccase activity	*biomass*	*pH*	*residual sugar %*
TM1	2.4 ± 0.1	1.8±0.0	7.6 ± 0.0	3.8
TM2	4.6 ± 1.1	4.5±0.4	8.4 ± 0.9	2.6
TM3	8.3 ± 0.1	6.1±0.4	6.7 ± 0.0	8.4
TM4	8.4 ± 0.5	7.1±1.0	8.3 ± 1.1	2.7
TM5	6.4 ± 1.1	5.0±0.2	7.5 ± 0.0	5.8

Table 4. ANOVA table of Design I data using laccase activity at 12th day (U/mL) and final biomass (g/L). SS: adjusted sum of squares; df: degrees of freedom; MS: adjusted mean sum of squares; F-value: ratio of MS and mean sum of squares for pure error. Data on lack of fit tests (curvature) are not reported

	Laccase activity			***Biomass growth***		
	C	**N**	**C*N**	**C**	**N**	**C*N**
SS	3.10	56.15	2.59	8.25	28.50	1.65
df	1	1	1	1	1	1
MS	3.10	56.15	2.59	8.25	28.50	1.65
F-value	11.16	202.29	9.34	31.15	107.59	6.23
p-value	0.016	0.000	0.022	0.001	0.000	0.047

Biomass development was similarly influenced by nutrients concentration (Table 3), with a strong interaction effect between C and N but no curvature in the system ($p > 0.05$). Within the tested conditions, the analysis of the data suggested that an increase of both N and C levels results in an increase in both laccase activity and final biomass concentration, taking into account the effect of interaction (increase of C at the high level of N does not produce any increase in laccase activity). In fact, maximum laccase activity and final biomass concentration appeared positively correlated (r^2=0.92); greater laccase productions corresponded to greater biomass growth.

pH is an important parameter to take into consideration because its variations have been often correlated with specific fermentation stages, associating this information with laccase production profile. Despite an initial acidification and a further basification of the medium has been often observed (Akpinar and Urek, 2010; Du et al., 2012; Galhaup et al., 2002), the medium composition has a predominant role on pH values fluctuations. When tomato-based media were used for fungal fermentation, the acid initial pH (pH 4-4.5) increased until alkaline values of 7-8.5 (Michniewicz et al., 2006; Ullrich et al., 2005).

Confirming these evidences, in the present study, the pH of TM was barely acidic (pH 5-6) and linearly increased during the following two weeks up to pH 7.6-8.4 (Table 3). The consumption of the C source by *T. pubescens* MUT 2400 was assessed by determining the reducing sugars concentration (Table 3). Despite their initial concentration was not high (2.40 and 7.62 g/L for the -1 and +1 level of tomato sauce concentration), it has to be considered that tomato sauce is a heterogeneous substrate in which both simple and complex carbohydrates are present (Acosta-Quezada et al., 2015), while reducing sugars concentration includes just a fraction of its overall C content.

The fungus was indeed able to develop properly (up to 286 mg dry weight) by using the nutrients provided by TM, consuming most of them. The reducing sugar content at the end of the experiment was almost absent (0.12-0.43 g/L).

3.2. TM development: Design II

Culture conditions assessed in *Design I* allowed to enhance laccase production but the region of the optimum was still far. A second factorial design (referred to as *Design II*) was then set increasing both N and C concentration. Results are listed in Table 5.

The highest laccase activity was obtained at 17th day of cultivation in TM2 (design point +1, -1). As can be seen in Fig. 3, enzymatic production started increasing a lot after 1 week from the induction and the maximal laccase productivity was reached at the 17th day for all the culture media tested.

Biological replicates slightly differed but the error percentage among them was not above 27%. These data (~ 33 U/mL) are among the best ones reported in literature for laccase production in presence of tomato-based medium. The use of media based on agro-industrial sources is indeed becoming more and more actual, as confirmed by the few evidences on complex tomato juice medium.

Table 5. Laccase activity (U/mL) at 17th day, dry biomass concentration (g/L), pH and residual reducing sugars content (%) at the end of the experiment for Design II

	lac activity	*biomass*	*pH*	*residual sugar %*
TM1	21.2 ± 3.0	89 ± 6	7.7 ± 0.1	5.3
TM2	32.8 ± 5.8	156 ± 20	8.1 ± 0.1	7.8
TM3	28.6 ± 7.9	137 ± 10	8.2 ± 0.0	9.8
TM4	19.3 ± 0.7	192 ± 4	8.1 ± 0.0	10.6
TM5	14.6 ± 1.2	174 ± 15	8.3 ± 0.0	9.5

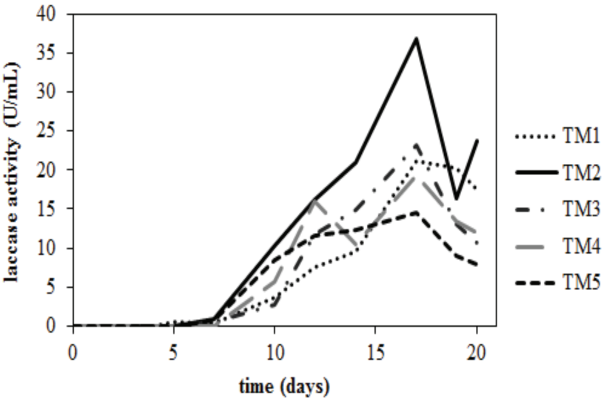

Fig. 3. Time course of laccase activity (U/mL) for the media of *Design II*

However using similar fermentation medium, lower enzymatic concentrations were found in cultures of *Cerrena unicolor* (18.7 U/mL)

(Michniewicz et al., 2006), *Trametes versicolor* (7.9 U/mL) (Carabajal et al., 2014), *Agaricus blazei* (5.0 U/mL) (Ullrich et al., 2005). Higher laccase activity (52.5 U/mL) was instead obtained by *Pycnoporus sanguineus* but, for comparative purpose, it should be mentioned that tomato juice was supplemented with high Cu concentration (3 mM) and soybean oil (1% v/v) as inducers (Ramirez-Cavados et al., 2014).

Table 6 lists the results obtained from the analysis of variance (ANOVA). As regards laccase activity, main effects were not significant upon the response variables ($p > 0.05$). The system was instead dominated by the two-way interaction and the presence of curvature. The effect of C was positive at the low N level and negative at the high N level. Thus increasing tomato sauce concentration from 30 to 50% v/v resulted in an increase in the laccase activity when bactopeptone was at 28.7 g/L (from 21.4 U/mL to 32.8 U/mL), but in a decrease when it was at 48.7 g/L (from 28.6 U/mL to 19.3 U/mL) (Fig. 4). Thus, laccase activity obtained in *Design I* could be increased by either increasing the C level or the N level, while increasing both levels at the same time results in a decrease of the laccase activity. Similarly, the laccase activity determined from the center point did not result in any improvement compared to the (-1, -1) condition (corresponding to the best medium of *Design I*).

Thus, while it was possible to improve laccase activity compared to the results of *Design I*, further experimentation would be necessary to reach optimal conditions for laccase stimulation.

Concerning biomass growth, main effects of C and N appeared statistically significant, and both tomato paste and nitrogen concentration exerted a positive effect on final biomass development. The interaction between the two parameters showed a high p-value ($p > 0.05$), resulting indeed not significant. Furthermore the system exhibited some curvature. As regard the pH and the reducing sugars consumption, *Design I* data were confirmed in *Design II* (Table 6). The pH linearly increased during the fermentation, till alkaline values closed to 8. Besides, most of the available reducing sugars were already consumed after 7-10 days, detecting a final residual amount lower than 10%. Noteworthy, only when the concentration of reducing sugars in the medium decreased to low levels, the laccase activity started to increase (around day 6-7, Fig. 5).

The strict correlation between enzymatic production and depletion of nutrients was already observed by other authors (Du et al., 2002; Hess et al., 2002; Gaitan et al., 2011; Galhaup et al., 2002), and it has been associated to the activation of energy-saving response (Piscitelli et al., 2011).

4. Conclusions

Previous reports have posed the basis for sustainable fermentations: tomato-based medium was here investigated positively stimulating *Trametes pubescens*. Carbon and N concentration exerted an interaction effect on laccase production making a factorial approach essential to screen different media.

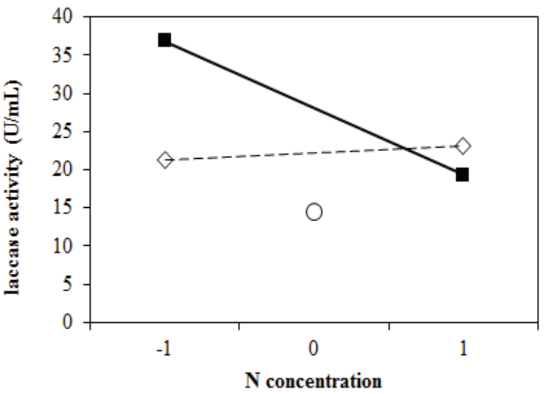

Fig. 4. Interaction plot of C and N for laccase activity: ── high level of C (+1); - - - low level of C (-1); ○ central point

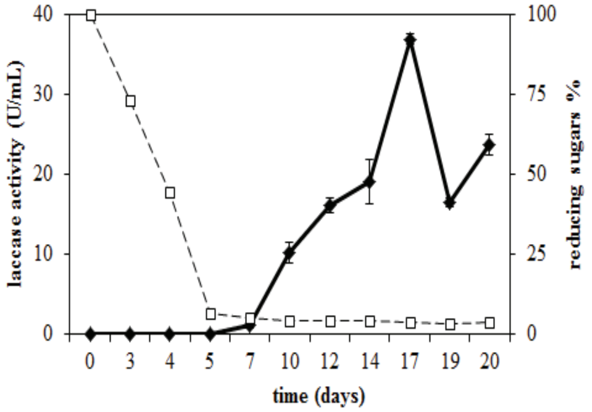

Fig. 5. Time course of *T. pubescens* grown on TM2 medium: ── laccase activity (U/mL); - - - residual reducing sugars %

Table 6. ANOVA table of Design II data using laccase activity at 17th day (U/mL) and final biomass (g/L). SS: adjusted sum of squares; df: degrees of freedom; MS: adjusted mean sum of squares; F-value: ratio of MS and mean sum of squares for pure error

	Laccase activity				***Biomass growth***			
	C	***N***	***C*N***	***curvature***	***C***	***N***	***C*N***	***curvature***
SS	3.80	28.58	324.06	283.87	11342.10	5303.60	99.00	2151.90
df	1	1	1	1	1	1	1	1
MS	3.80	28.58	324.06	283.87	11342.10	5303.60	99.00	2151.90
F-value	0.12	0.90	10.15	8.89	46.75	21.86	0.41	8.87
p-value	0.737	0.366	0.010	0.014	0.000	0.001	0.537	0.014

This method is not yet a common practice in medium engineering but it demonstrated its huge potential to define the optimal growth condition: the final laccase activity (32.8 U/mL) was one the highest reached by similar media. This result can be considered sub-optimal since laccase activity data obtained in *Design II* did not show a peak inside the experimental region investigated.

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BIOGAS PRODUCTION FROM WHEAT STRAW PRE-TREATED WITH LIGNINOLYTIC FUNGI AND CO-DIGESTION WITH PIG SLURRY

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Abstract

This study carried out for the first time a comparison among ligninolytic (white-rot) and cellulosolytic or xylanolytic (*Trichoderma)* pre-treated wheat straw, for biogas production, potential, without or with pig slurry in co-digestion. Methane (CH_4) production from wheat straw pre-treated for 4 and 10 weeks with seven different fungal isolates was preliminarily measured. Then, the effects on biogas yield of the co-digestion with pig slurry were checked on straw pre-treated with 3 selected fungal strains. The maximum production of CH_4 from pre-treated straw with *Ceriporiopsis subvermispora* (SUB) for 4 and 10 weeks was higher than the control (16% and 37%, respectively). The accumulation daily rate was higher than control (42% and 81%, respectively). A positive correlation between CH_4 accumulation daily rate and straw enzymatic digestibility was found. In co-digestion with pig slurry, SUB pre-treated straw for 10 weeks showed an accumulation daily rate of 17.4 mL d^{-1} g^{-1} VS, significantly higher (17%) than that of the control. The time to reach the maximum CH_4 production was shortened on average from 34 to 21 days in co-digestion with pig slurry, in comparison with pre-treated mono-digested wheat straw. The biological pre-treatment with selected white-rot fungi appears a promising technology to increase methane production from wheat straw.

Key words: biogas, *Ceriporiopsis subvermispora*, co-digestion, enzymatic hydrolysis, manure

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1. Introduction

The interest in sustainable biogas production is currently oriented towards the use of agricultural byproducts instead of high-input dedicated crops. These byproducts contain large lignocellulosic fractions that could be exploited to increase methane production. A biomass pre-treatment step could facilitate anaerobic digestion (AD) by partial lignin removal. Biological pre-treatments seem suitable to achieve sustainable biogas production due to low energy requirement, low pollution generation, and simple procedures and equipment (Sun and Cheng, 2002).

Furthermore, this process is expected to avoid the production of inhibitors for the subsequent conversion steps compared to conventional thermo-chemical pre-treatments (Alvira et al., 2010; Gupta et al., 2011; Isroi et al., 2011).

Biological pre-treatment can be carried out by *Basidiomycetes* white-rot fungi which are considered among the most effective biological pre-treatment agents. They produce lignin degrading enzymes, like laccases and peroxidases, which increase the accessibility of holocellulose (cellulose and hemicellulose), for further biochemical transformation (Isroi et al., 2011). *Ceriporiopsis subvermispora*, *Cyathus stercoreus*, *Phanerochaete*

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chrysosporium, *Pleurotus ostreatus*, *Trametes versicolor* and other white-rot fungi have been examined alone or in combination with mild chemicals for the pre-treatment of different lignocellulosic biomasses (Akin et al., 1995; Keller et al., 2003; Salvachúa et al., 2011; Taniguchi et al., 2005). These studies indicate that considerable differences exist among fungal species in terms of the rate of pre-treatment and of mineralization of holocellulose, due to metabolic consumption.

Some authors studied the possibility of producing biogas from lignocellulosic material pre-treated with ligninolytic white-rot fungi. Amirta et al. (2006) tested *C. subvermispora* on cedar wood. Ghosh and Bhattacharyya (1999) studied biogas production from rice straw pre-treated with *P. chrysosporium* and *P. ostreiformis*. Cellulosolytic *Ascomycetes* like *Trichoderma* spp. have also been proposed as pre-treatment agents for biogas production from lignocellulosic materials with positive results (Phutela et al., 2011). These studies considered only a few fungal species and substrate types. There is a need to further investigate fungal isolates with different hydrolytic properties as pretreatments to increase biogas yields from lignocellulosic biomasses.

Wheat straw is the most abundant agricultural residue in Europe, following rice straw in the rest of the world (Kim and Dale, 2004). The use of straw for the production of biogas represents a sustainable option, since it does not compete with human food resources. In particular, wheat straw pre-treated by white-rot fungal isolates has been proposed as feedstock for sustainable biogas production in co-digestion with cow manure (Müller and Trösch, 1986). Co-digestion has received a great deal of attention in academic literature (Hoppe and Sanders, 2014).

Limited amounts of lignocellulosic biomass are commonly used in co-digestion with manure for biogas production in order to enrich manure with volatile solids without excessively enlarging the digester size. However, the frequency of AD using vegetal biomass without manure has recently increased, due to the incentive policies for renewable energies. In fact, biogas producers have reacted by increasing the electrical nominal power of the AD plants and by utilizing mainly high energy content biomass, like amylaceous dedicated crops (Bacenetti et al., 2014). Government incentives have also raised the interest of the agroindustry (such as olive oil mills, cheese factories, breweries) toward the exploitation of agro-industrial waste for biogas production with no connection with livestock.

A critical point of biological pre-treatment of lignocellulosic biomass is represented by the need to minimize the cellulose loss due to fungal metabolism, while increasing the biomass digestibility. In a previous study, the effect of fungal pre-treatment by white-rot and *Trichoderma* spp. isolates on wheat straw enzymatic digestibility was evaluated (Cianchetta et al., 2014).

The results showed that *C. subvermispora* appeared the best performing agent, since it showed the highest digestibility after 4 and 10 weeks of pre-treatment, minimizing weight loss. On the contrary *P. chrysosporium* showed only a moderate increase of digestibility at 4 weeks and a very high mineralization rate, especially after 10 weeks. The other white-rot isolates showed intermediate behaviors, while *Trichoderma* isolates were almost ineffective. Following these findings, the same pre-treated materials were subjected to biomethanation tests. The aim of the study was to compare wheat straw pre-treated with ligninolytic (white-rot) and cellulosolytic or xylanolytic (*Trichoderma)* fungal isolates, for biogas production potential, without or with pig slurry in co-digestion. Wheat straw was chosen since it is considered a low cost residue easily available. Co-digestion of pre-treated wheat straw with pig slurry was also carried out in order to assess any possible synergistic effect of biological pre-treatment and animal manure on biogas production.

A preliminary experiment was carried out in order to evaluate biogas yields and identify the best fungal isolates and pre-treatment time. In a second experiment, possible ameliorative effects of co-digestion with pig slurry were evaluated on selected pre-treated materials.

2. Materials and methods

2.1. Wheat straw, pig slurry and fungal isolates

Naturally dried wheat straw, provided by the CRA-CIN experimental farm at Budrio (BO, Italy), was used as lignocellulosic substrate. Its composition is reported in Table 1. Fresh pig slurry utilized for co-digestion with straw was obtained at CRA-SUI, after biomass mixing with a pumping system, from the farm storage tank collecting the liquid fraction of manure after separation of solids. The values of selected composition parameters are reported in Table 1. Pre-treated wheat straw with 7 fungal strains plus the non-inoculated control were previously obtained (Cianchetta et al., 2014) and samples were used in this study. Briefly, wheat straw had been pre-treated for 4 and 10 weeks with each isolate and aliquots had been stored at -20 °C before being employed in this study for further analysis and biogas experiments.

With regard to the fungal isolates, 5 were ligninolytic white-rot: *C. subvermispora* D-98698 (SUB), *T. versicolor* D-83211 (TRA) and *P. chrysosporium* D-85242T (PHA) from the VTT Technical Research Centre of Finland; *C. stercoreus* CBS 378.80 (CYA) from the CBS-KNAW Fungal Biodiversity Centre, Netherlands; *P. ostreatus* (PLE) from a commercial distributor (Funghi Mara, San Giorgio di Piano (BO), Italy. The remaining 2 isolates, used for comparison, were the hyper-cellulolytic mutant *Trichoderma reesei* Rut-C30 D-86271 (RUT) from VTT, and the xylanolitic wild-type *Trichoderma* sp. IK4 from CRA-CIN.

Table 1. Selected composition parameters for the organic materials used as substrates in the experiment. Standard deviation in parentheses (N=3). FM: fresh matter. TS: total solids

Composition parameter	***Wheat straw***	***Pig slurry***	***Wheat straw + Pig slurry***
Total solids, TS (g kg^{-1} FM)	923 (13)	18.6 (0.3)	24.6
Volatile solids (g kg^{-1} FM)	808 (18)	14.3 (0.2)	20
Volatile solids (g kg^{-1} TS)	875	769	813
Organic carbon (g kg^{-1} TS)	450 (5)	399 (4)	415
Total N (g kg^{-1} TS)	9.1 (1.4)	61.9 (3.4)	46.6
NH_4-N (g kg^{-1} TS)	Nd	35.1 (3.5)	26.54
C/N	49.5	6.45	8.91
pH in water (1.5:50)	7.92 (0.2)	7.04 (0.2)	7.0
Total P (g kg^{-1} TS)	0.10 (0.03)	4.5 (0.01)	3.22
Lignin (g kg^{-1} TS)	125 (4)	57 (1)	77
Hemicellulose (g kg^{-1} TS)	345 (4)	106 (1)	175
Cellulose (g kg^{-1} TS)	371 (11)	61(1)	151

Nd: not determined

2.2. AD inoculum preparation

Digestate prepared in the laboratory from pig slurry was used as the inoculum source. The inoculum was prepared as follows: pig slurry was withdrawn from the farm storage tank collecting the liquid fraction of pig manure after solid separation, at two-thirds depth. Two hundred mL of slurry were mixed with 200 mL definite synthetic medium for methanogens (phosphate buffered basal medium, PBBM, sterilized) without energy sources in 500-mL serum bottles, in an N_2-CO_2 (80:20) atmosphere. This mixture was left to incubate at 35 °C, in strictly anaerobic conditions, and the head space composition was analyzed for CH_4 accumulation.

The aim was to obtain a starving wild methanogenic population. The inoculum was considered as ready for use when CH_4 production had stopped, indicating the complete exhaustion of endogenous energy sources.

2.3. Analytical methods

Total solids (TS), volatile solids (VS), organic C, total N, total P concentrations and pH were determined on straw and pig slurry (APHA, 1992). Total solids were determined gravimetrically by thermal treatment at 105 °C at constant weight. Analyses of the straw were conducted on samples dried at 65 °C at constant weight and milled at 1 mm. Organic C was determined by dichromate oxidation with external heating and reflux condenser. Total N was determined with the Kjeldahl apparatus. Total P was determined on ashes by colorimetry with ammonium molibdate, after solubilization by means of HCl 1N.

The pH was determined after suspension, 2-h stirring and sedimentation of 1.5 g dry matter in 50 mL distilled water. Ammonium N was also determined on pig slurry samples and digestates by distillation. Fiber fractions (neutral detergent fiber, NDF; acid detergent fiber, ADF; and lignin, ADL) were determined on wheat straw, pre-treated wheat straw, pig slurry and AD digestates according to Van Soest et al. (1991).

The hemicellulose content was estimated as the difference between NDF and ADF; cellulose as the difference between ADF and ADL. For each treatment a composite digestate sample, obtained by mixing the digestate of the 3 replicates, was analyzed.

The expected CV for the lignin, hemicelluloses and cellulose measurements was 8.8%, 3.8%, and 1.7%, respectively, as estimated for the same parameters on the basis of measurements done on a 6-sample population of wheat straw, with the same instrument.

3. Experimental

3.1. AD preliminary experiment

AD was carried out using as substrate wheat straw pre-treated for 4 and 10 weeks with the 7 fungal isolates. Non-inoculated controls were also included. The reaction mixture included 1.5 g (fresh weight) of pre-treated wheat straw in 50 mL sterilized PBBM, without energy sources (“hydration medium”), and 5 mL inoculum, in 100-mL reactors (118.5 mL effective volume), in triplicate (48 reactors, in total). Since the comparison was based on the same sample fresh weight, the TS amount in each reactor was different, depending on the different water content of the fresh material utilized.

The biogas production parameters in this experiment were therefore related to the TS content. The initial pH of the mixture was on average equal to 6.3 ± 0.2. The head space of the reactors was gassed with N_2-CO_2 (80:20) throughout the preparation steps before inoculation.

Reactors were plugged with butyl rubber stoppers and aluminum seals and they were incubated at 35 °C for 90 days. During the incubation period they were randomly distributed on the incubator shelves.

3.2. Co-digestion experiment

Selected wheat straw pre-treated for 4 and 10 weeks with 3 different isolates (SUB, PHA and RUT) was utilized for an AD experiment with (PS+) or without (PS-) pig slurry in comparison with an untreated control.

The comparison was based on the same VS content of the reaction mixture: in each PS- reactor, 1g VS of wheat straw was added to 50 mL PBBM (i.e., 2% VS); in each PS+ reactor, instead, 0.29 g VS of wheat straw were added to 50 mL (0.71 g VS) pig slurry, for a total of 1 g VS. Pig slurry alone was inoculated as control. All reactors were in triplicate (51 reactors, in total). Five-mL inoculum was added to all 100-mL reactors (118.5 mL effective volume). The average pH of straw after mixing with PBBM was 6.3 ± 0.4, while in the presence of pig slurry it was 7.0 ± 0.04.

3.3. Biomethanation tests

The biogas production (volume and composition) was measured according to Owen et al. (1979) 2 days after the start of the incubation and then weekly for 3 months. Biogas was collected by means of 100-mL glass syringes. The incubation period was completed when there was no more biogas production in any of the reactors. No methane production was detected in the control reactors, where the inoculum had been suspended in PBBM without energy source.

Methane concentration in the biogas was determined by means of a MicroGC Agilent 3000 gaschromatograph, equipped with 2 columns: Molsieve and Plot U; detector: TCD. Carrier gas: argon.

3.4. Parameters of the cumulative methane production curves (Gompertz parameters)

In this paper *cumulative CH_4 production* means the CH_4 volume accumulated over time, including the amounts of CH_4 released in the syringe at each measurement date as well as the CH_4 volume remaining within the reactor. The comparison of the cumulative CH_4 production curves was based on the parameters: maximum cumulative CH_4 production, *Hmax* (mL CH_4); daily rate of CH_4 accumulation in the linear phase of CH_4 accumulation, *R* (mL CH_4 d^{-1}); and lag time duration (λ, d) that is the time of microbial adaptation before the starting of CH_4 production.

The *R* and *Hmax* values were expressed per weight unit of TS or VS, depending on the experiment. These parameters were estimated by fitting a modified Gompertz equation to measured data (Lay et al., 1997). This function is often utilized for interpolating growth curves, in general, and microbial growth curves, in particular (Zwietering et al., 1990).

Measurements from 3 replicates were merged for the parameter value estimation. Fitting was performed using the PROC NLIN of the SAS package (SAS, 1989); the parameter values were estimated according to the Gauss-Newton method. The time (d) necessary to reach *Hmax* was estimated by calculating the ratio *Hmax / R.*

3.5. Correlation between enzymatic digestibility and AD parameters

The values of enzymatic digestibility of the pre-treated wheat straw were used for a correlation study with the AD parameters described above (*R* and *Hmax*). These values were obtained from data reported in a previous work carried out on aliquots of the same pretreated materials (Cianchetta et al., 2014). The *enzymatic digestibility* is defined here as the amount of sugar released after 48 h of enzymatic hydrolysis by commercial cellulase, using final enzymatic loads of cellulase and xylanase of 10 FPU/g, 110 U/g, respectively and β-glucosidase in excess, on 3.75% straw slurries (w/w).

3.6. Statistical analysis

Analysis of variance (ANOVA) was performed using the PROC MIXED procedure of the SAS statistical package (Littell et al., 1996). Multiple comparisons of the means were carried out using the SAS LSMEANS statement. Factor and factor interaction effects were considered significant at $P < 0.05$. Fisher's LSD test ($P < 0.01$) was used to compare treatment mean values.

4. Results and discussion

4.1. AD preliminary experiment

Biogas production (Fig. 1) started immediately after inoculation, thus the lag phase duration (λ) was equal to 0 for all the treatments, including the controls and with the exception of straw treated with IK4 for 10 weeks (λ = 0.11 d) and with PHA for 4 or 10 weeks (λ = 0.50 and 0.85 d, respectively). These differences between treatments should not be attributed to differences in pH values, since the pH of pre-treated wheat straw, being initially slightly acidic, increased to neutral values after mixing the straw with the hydration medium for all the treatments. This effect could be attributed to an inhibitor released by IK4 and PHA during the straw pre-treatment or to the lack of readily fermentable compounds removed by these fungi.

Larger differences among the materials were found for the 10-weeks pre-treatment than for the 4-week pre-treatment (Fig. 1 a, b). In particular, wheat straw pre-treated with SUB showed the fastest and highest CH_4 accumulation, achieving the maximum CH_4 production in about 30 days. Other pre-treated materials displayed values even lower than that of the untreated control, such as PHA 10-weeks (Fig. 1b).

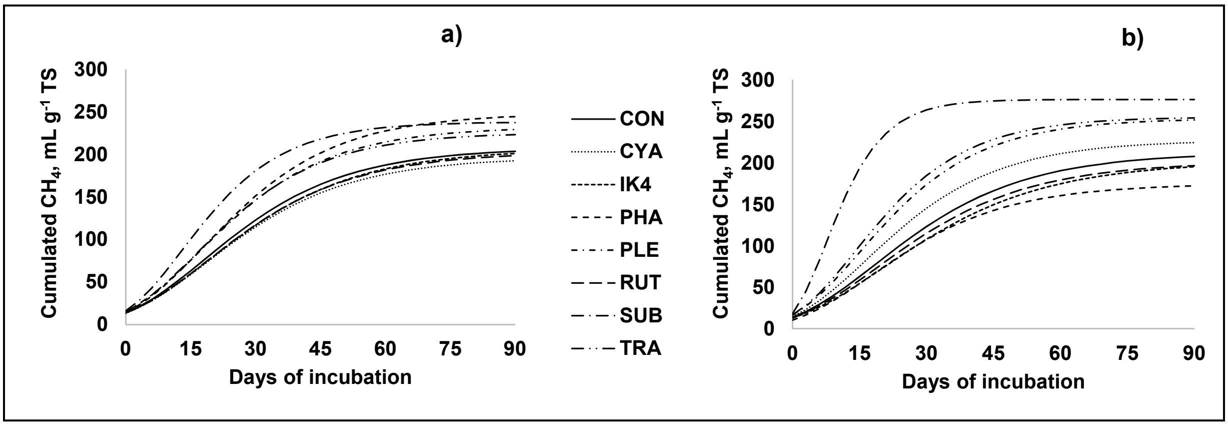

Fig. 1. Gompertz-estimated curves of methane accumulation from wheat straw pre-treated with fungal isolates for a) 4 weeks; b) 10 weeks. CON, untreated wheat straw; CYA, *C. stercoreus*; IK4, *Trichoderma* sp.; PHA, *P. chrysosporium*; PLE, *P. ostreatus*; RUT, *T. reesei*; SUB, *C. subvermispora*; TRA, *T. versicolor*

The daily rate of CH_4 accumulation (*R*) (Table 2) was on average higher for 10-weeks pre-treated straw (5.9 mL CH_4 d^{-1} g^{-1} TS) than for 4-weeks (4.8 mL CH_4 d^{-1} g^{-1} TS).

Four-weeks pre-treated straw with SUB, PHA, TRA and PLE gave *R* values higher than the control; thus, 4 weeks is a sufficient pre-treatment period to appreciate an increased biogas production rate, utilizing these isolates. In particular SUB displayed the highest *R* value (6.7 mL CH_4 d^{-1} g^{-1} TS). With regard to straw pre-treated for 10 weeks, all the white-rot isolates gave *R* values higher than control, except PHA.

This result is not surprising, considering that the straw pre-treated with PHA for 10 weeks showed very low digestibility values (Table 2), due to a high mineralization rate and poor selectivity towards lignin (Cianchetta et al., 2014). The straw pre-treated with SUB for 10 weeks gave *R* values (13.8 mL CH_4 d^{-1} g^{-1} TS) three-fold higher than the control, thus confirming its high performance in increasing biogas production from lignocellulosics, as already reported (Amirta et al., 2006).

Similarly to what was observed for *R* values, 4 weeks pre-treated straw with SUB, PHA, TRA and PLE gave *Hmax* values higher than the control (Table 2); in particular SUB and PHA gave the highest values (16% and 21% higher than control, respectively). Equally, all the straw pre-treated with white-rot isolates for 10 weeks gave *Hmax* values equal to or higher than the control, except the straw types with PHA (13% lower than control). This result confirms the observations about the poor PHA performance at longer pre-treatment times reported by Cianchetta et al. (2014). The straw pre-treated with SUB for 10 weeks gave a 37% higher *Hmax* value than the control. These data show that SUB 10-weeks was the most effective pre-treatment, since it reduced AD duration from 48 to 20 days (58% reduction) in comparison to the control and gave the highest methane yields (276 mL CH_4 g^{-1} TS) (Table 2). The SUB, PHA, PLE and TRA isolates confirmed their suitability to be used for the pre-treatment of lignocellulosic materials for biogas production, in agreement with the findings of other authors. In a screening of white-rot fungi for the pre-treatment of straw, Müller and Trösch (1986) were able to obtain an amount of biogas twice that of the untreated control by using *P. ostreatus*, probably due to the more intense ligninolytic activity of this fungus (Taniguchi et al., 2005).

Ghosh and Bhattacharyya (1999) pre-treated rice straw with the white-rot fungus *P. chrysosporium* (PC) and the brown-rot fungus *P. ostreiformis* (PO). Biogas and CH_4 production were increased by about 35% and 46 % in PC-treated straw and 21% and 31% in PO-treated straw, respectively.

In our study, *Trichoderma* isolates did not show any effectiveness, unlike what was observed by other authors for a similar substrate, like paddy straw (Puthela et al., 2011). This result probably depends on the relatively low N content of wheat straw (Table 1), which can affect ligno-cellulosolytic enzyme production (Mutschlechner et al., 2015).

The improvement in AD performances of straw pre-treated with *C. subvermispora* can be related to its higher cellulose accessibility. A positive correlation was in fact observed between *R* or *Hmax* and the enzymatic digestibility of pre-treated wheat straw (r = 0.91 and 0.79, respectively), measured on the same samples used for the biomethanation tests. This correlation can be interpreted considering that hydrolysis represents the rate-limiting step for the AD of the lignocellulosic materials. In fact the hydrolysis of lignocellulosic materials may be constrained by high lignin content and cellulose crystallization, resulting in low biogas output. Biomass pre-treatments increase digestibility by lignin removal, hemicellulose solubilization, reduction of cellulose crystallization and increased surface for enzymatic attack (Di Girolamo et al., 2013). Analogous effects can be envisaged from biological pre-treatments.

The good correlation observed between *R* and digestibility could indicate that this latter parameter may represent a useful index to evaluate the effectiveness of a fungal pre-treatment in terms of biogas production rate.

4.2. Co-digestion experiment

The co-digestion experiment was carried out on a selection of pre-treated straw including representative isolates in the screening test: SUB and PHA (white-rot fungi), which had shown the best performances, and RUT *(Trichoderma)*, not differing from the untreated control.

The use of pig slurry in co-digestion with straw remarkably increased the rate and amount of biogas production, in comparison with the straw in mono-digestion, for the same amount of added VS (Fig. 2). In particular, no differences were observed for the AD lag-phase duration, except for the substrate effect: λ for straw in co-digestion with pig slurry (0.70 d, on average) was slightly longer than without pig slurry (0.13 d; LSD, at $P<0.01$: 0.48 d). The *R* value for the PS+ reactors was on average 155% and 178% higher than that in the PS- reactors, for 4- and 10-weeks pre-treatment duration, respectively (Fig. 3 a, b).

The *Hmax* value was 61% and 70% higher than that in the PS- reactors, for 4- and 10-weeks pre-treatment duration, respectively (Fig. 3 c, d). When the straw was digested alone (PS-), CH$_4$ production was significantly faster and higher than the control only for the straw treated with SUB, and more pronounced after a 10-weeks pre-treatment. In particular, *R* increased by 42% and 81% and *Hmax* increased by 14% and 31%, for the 4- and 10-weeks pre-treatments, respectively (Fig. 3). RUT and PHA pre-treated straw gave *R* and *Hmax* values not different from the control, or even lower (PHA 10-weeks) (Fig. 3). These results are consistent with those obtained in the preliminary experiment.

When the straw was in co-digestion with pig slurry, differences in AD performances determined by the fungal isolates were reduced, due to the relatively low contribution to VS from the pre-treated straw (29%). Only the straw pre-treated with SUB for 10 weeks had an *R* value (17.4 mL CH$_4$ d^{-1} g^{-1} VS) significantly higher (17%) than that of the control and of the other treatments (included between 14.9 and 15.6 mL CH$_4$ d^{-1} g^{-1} VS) (Fig. 3b). The *Hmax* value obtained by SUB 10-weeks was the highest (350 mL g^{-1} VS) even if not statistically different from the control (Fig. 3d). Besides the straw/pig slurry volume ratio, the straw lignin content could have affected the overall performance. In fact, Pourcher et al. (2013) did not find any significant increase in biogas production from low-lignin straw (6.3%), pre-treated with selected white-rot isolates, in co-digestion with pig slurry. On the contrary, other authors, working with high-lignin straw (16%), found an increase up to 27% of biogas production with *Pleurotus* sp. "florida" pre-treatment in co-digestion with cow manure (Müller and Trösch, 1986). Thus, in co-digestion, biological pre-treatment by selected white-rot isolates would give the best results with relatively high lignin content biomass.

As the maximum production of CH$_4$ from straw was 197 mL g^{-1} VS (Fig. 3c, d), and the maximum production of CH$_4$ from pig slurry alone was 342 mL g^{-1} VS (data not shown), the theoretical production of CH$_4$ from a mixture containing 29% VS from straw and 71% VS from pig slurry should have been 300 mL (197 x 0.29 + 342 x 0.71). Actually, the maximum production of CH$_4$ in the CON PS+ treatment was on average 334 mL (Fig. 3c, d), that is 10% higher than the theoretical one. These results seem to indicate that there was a synergistic effect on methane production when using pig slurry in co-digestion with straw. A synergic effect of co-digestion of animal manure with lignocellulosic materials was already reported (Duong, 2014).

The time to reach the maximum CH$_4$ production was shortened on average from 34 to 21 days, when the straw was in co-digestion with pig slurry, in comparison with mono-digestion, without differences due to the pre-treatment duration.

The improvement in the rate and extent of biogas production when using pig slurry in co-digestion with straw may be attributed to a better composition of the substrate in terms of readily available nutrients for microbial consortia in the anaerobic digester.

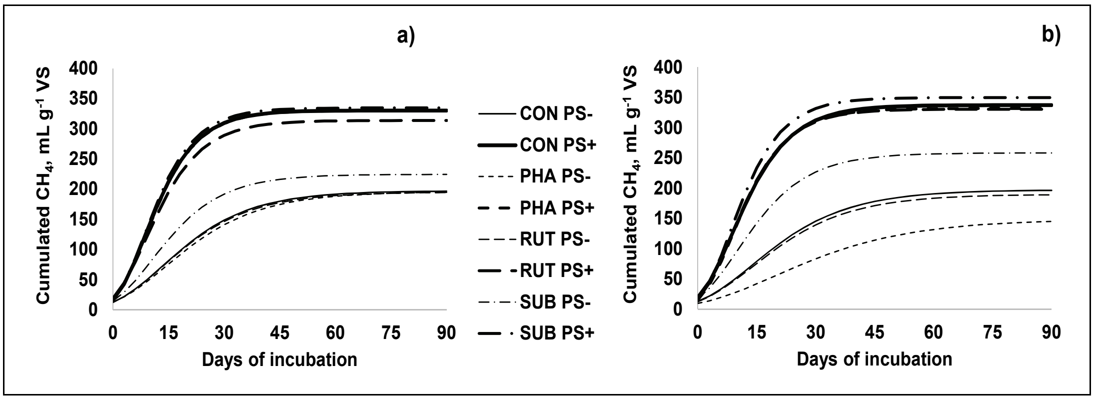

Fig. 2. Gompertz-estimated curves of methane accumulation from pre-treated or untreated wheat straw, digested alone (PS-) or in co-digestion (PS+) with pig slurry. Duration of the pre-treatment a) 4 week; b) 10 week. CON, untreated wheat straw; PHA, *P. chrysosporium*; RUT, *T. reesei*; SUB, *C. subvermispora*

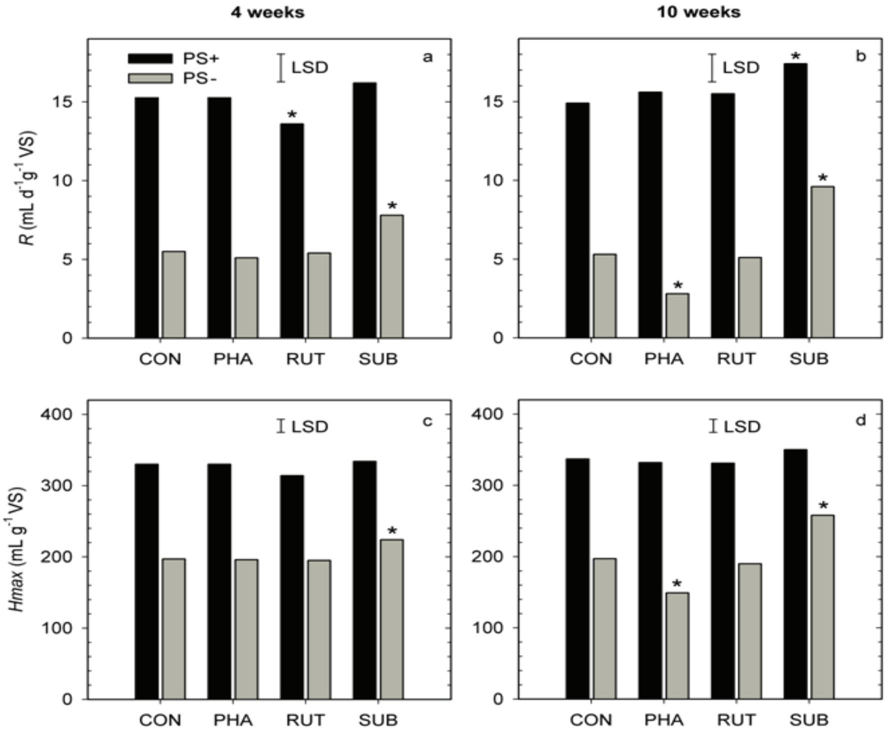

Fig. 3. Daily rate of CH_4 accumulation (*R*) (a, b) and maximum CH_4 cumulative production (*Hmax*) (c, d) for the differently pre-treated straw, as a function of the pre-treatment duration and substrate composition. Columns represent mean values for a 4- (left panels) or 10-weeks (right panels) pre-treatment with PHA, *P. chrysosporium*; RUT, *T. reesei* or SUB, *C. subvermispora* in comparison to CON, untreated wheat straw. Substrate was straw with (PS+) or without (PS-) pig slurry. In each panel, asterisks highlight statistically significant differences from the corresponding control, according to Fisher's LSD test ($P < 0.01$)

In our experiment, the C to N ratio of the untreated wheat straw in co-digestion with pig slurry (8.9) was considerably lower than in mono-digestion (49.5) (Table 1). The reduction of this ratio as well as differences in the prevailing forms of carbon (i.e., lignin) or nitrogen (ammonium or organic) could be the reasons for the improvement in the rate and extent of biogas production in the co-digestion experiments (Wang et al., 2012).

4.3. Input-material and digestate composition

The AD of untreated or pre-treated straw led to a reduction of VS, in comparison with input materials, on average by 46% in mono-digestion and by 56% in co-digestion with pig slurry (Table 3). In particular, the highest and lowest reductions were observed in mono-digestion for SUB 10-weeks (62%) and RUT 10-weeks (36%); the untreated material showed a reduction of 39%.

The hemicellulose content was greatly reduced in mono-digestion (77% reduction on average) with appreciable differences between pre-treatments with the highest reduction displayed by PHA 4-weeks and SUB 10-weeks (89% and 91% respectively). In co-digestion with pig slurry a 76% reduction of hemicellulose was observed, on average, with 86% reduction for SUB 4- and 10-weeks. The untreated material showed a reduction of hemicellulose by 73% in mono-digestion and by 69% in co-digestion.

The cellulose content was almost halved (58% reduction on average for PS- and 48% for PS+). The lowest utilization was observed for RUT 4-weeks in co-digestion (35%) while SUB 10-weeks in mono-digestion showed the highest reduction (83%). In co-digestion PHA 4-weeks displayed the highest reduction of cellulose (68%). The untreated material showed a reduction of cellulose by 49% in mono-digestion and by 45% in co-digestion.

The lignin content, which had been partially reduced during pre-treatment of the straw, remained substantially unchanged after AD. Any fluctuations in the measured valued should be attributed to measurement variability (CV = 8.8%). Actually, no changes were expected for lignin, because the ligninolytic microorganisms, usually aerobic, are not active components of the anaerobic reactor communities.

At the start of the AD, the wheat straw types had different cellulose and hemicellulose contents depending on the fungal pre-treatment (Table 3). However, these available amounts were not equally exploited in AD, given the fact that both the PHA 4-weeks and the SUB 10-weeks treatments permitted a holocellulose consumption during AD higher in percentage than that allowed by the other treatments or by the untreated straw. Therefore the straw treated with these fungi showed a higher accessibility to holocellulose by the AD microorganisms, with higher methane yields.

Table 2. Biomethanation of wheat straw treated with various ligninolytic fungal isolates: daily rate of CH_4 accumulation (*R*) and maximum cumulative CH_4 production (*Hmax*). Enzymatic digestibility (amount of sugar released after 48 h of enzymatic hydrolysis) of pre-treated wheat straw is also reported

	4 weeks						***10 weeks***					
	R ***mL*** CH_4 d^{-1} g^{-1} ***TS***		***Hmax*** ***mL*** $CH_4 g^{-1}$ ***TS***		***Digestibility*** ***mg sugar*** mL^{-1}		***R*** ***mL*** CH_4 d^{-1} g^{-1} ***TS***		***Hmax*** ***mL*** $CH_4 g^{-1}$ ***TS***		***Digestibility*** ***mg sugar*** mL^{-1}	
	mean	***sd***	***mean***	***sd***	***mean***	***sd***	***mean***	***sd***	***mean***	***sd***	***mean***	***sd***
CON	4.2	0.2	205	4	1.2	0.1	4.2	0.5	202	15	1.5	0.1
CYA	3.9	0.2	197	30	3.6	0.1	5.0	0.5	227	14	6.2	0.2
IK4	4	0.1	206	9	0.9	0.1	3.7	0.1	202	3	0.9	0.0
PHA	5.3	0.6	248	9	3.5	0.1	3.8	0.4	175	52	1.3	0.3
PLE	5.0	0.4	233	2	3.6	0.2	6.1	0.2	254	5	7.9	0.2
RUT	4	0.1	203	5	0.6	0.0	3.9	0.1	201	6	0.5	0.1
SUB	6.7	0.1	238	2	7.3	0.2	13.8	1.3	276	1	15.0	0.0
TRA	5.1	0.3	226	7	2.1	0.1	6.7	0.3	255	5	3.1	0.0
Mean	4.8		220				5.9		225			

CON, untreated wheat straw; CYA, C. stercoreus; IK4, Trichoderma sp.; PHA, P. chrysosporium; PLE, P. ostreatus; RUT, T. reesei; SUB, C. subvermispora; TRA, T. versicolor

Table 3. Composition parameters of total and volatile solids**,** lignin, hemicellulose and cellulose of pre-treated or untreated wheat straw with or without pig slurry, before and after anaerobic digestion

		4 weeks									***10 weeks***									
Without pig slurry		***Input material***				***Digestate***					***Input material***					***Digestate***				
Composition parameter	***CON***	***PHA***	***RUT***	***SUB***	***mean***	***CON***	***PHA***	***RUT***	***SUB***	***mean***	***CON***	***PHA***	***RUT***	***SUB***	***mean***	***CON***	***PHA***	***RUT***	***SUB***	***mean***
Total solids (g kg^{-1} FM)	21	21	21	21	21	18	15	19	17	17	21	22	21	19	21	19	15	20	14	17
Volatile solids (g kg^{-1} TS_{Input})	966	957	962	966	963	583	450	571	462	516	966	922	962	966	954	611	507	616	372	527
Lignin (g kg^{-1} TS_{Input})	121	100	122	108	113	123	93	124	115	114	128	75	137	89	107	136	75	138	90	110
Hemicellulose (g kg^{-1} TS_{Input})	341	262	320	263	297	92	28	77	80	69	341	250	333	195	280	95	61	102	17	69
Cellulose (g kg^{-1} TS_{Input})	370	383	359	368	370	192	132	189	106	155	371	308	375	414	367	185	156	204	72	154
With pig slurry	***Input material***					***Digestate***					***Input material***					***Digestate***				
Composition parameter	***CON***	***PHA***	***RUT***	***SUB***	***mean***	***CON***	***PHA***	***RUT***	***SUB***	***mean***	***CON***	***PHA***	***RUT***	***SUB***	***mean***	***CON***	***PHA***	***RUT***	***SUB***	***mean***
Total solids (g kg^{-1} FM)	25	25	25	25	25	15	12	15	16	15	25	25	25	25	25	15	15	15	16	15
Volatile solids (g kg^{-1} TS_{Input})	816	813	813	816	815	367	390	350	394	375	816	806	813	816	813	358	341	362	351	353
Lignin (g kg^{-1} TS_{Input})	75	69	75	71	73	76	61	63	68	67	75	62	80	66	71	71	68	76	55	68
Hemicellulose (g kg^{-1} TS_{Input})	174	151	168	151	161	48	42	54	22	42	176	148	172	132	157	61	26	42	18	37
Cellulose (g kg^{-1} TS_{Input})	151	154	147	150	151	83	50	97	80	77	151	133	152	163	150	83	71	87	75	79

Hemicellulose was degraded to a higher extent in comparison with cellulose probably because it is more accessible to bacteria in mesophilic conditions, as reported by Ghosh et al. (1985).

A positive correlation was observed between *Hmax* and absolute holocellulose loss during AD in mono-digestion (r = 0.84). In the co-digestion experiment a lower correlation was found between holocellulose loss and *Hmax* (r = 0.74). These findings could be interpreted considering that pig slurry contains other digestible compounds which may have acted in competition with holocellulose released by the pre-treatment.

5. Conclusions

Pre-treated wheat straw with *C. subvermispora* for 10 weeks significantly increased the daily rate of CH_4 accumulation, both in mono- and in co-digestion with pig slurry, in comparison with the control (by 81% and 17%, respectively). In addition, the maximum cumulative production of CH_4 increased by 31% in mono-digestion. In co-digestion, a synergistic effect on the rate and extent of CH_4 production was observed, and the time to reach the maximum CH_4 production was shortened in comparison with the straw in mono-digestion.

The biological pre-treatment of wheat straw with selected white-rot fungal strains appears a promising technology to increase methane production from wheat straw because it increases CH_4 production and reduces the time required for AD without any need for energy input, and can thus conveniently be used as a suitable alternative to conventional thermo-chemical pre-treatments.

Acknowledgements

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ASSESSMENT OF INDOOR POLLUTION IN A SCHOOL ENVIRONMENT THROUGH BOTH PASSIVE AND CONTINUOUS SAMPLINGS

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Abstract

The aim of this study is to assess indoor air quality in an educational institute located in a suburban area of the Po plain (Italy). Samplings are carried out in preschool and elementary school classrooms, and also in the garden of the institute, to have information on outdoor levels. The monitoring is performed to determine the most important indoor pollutants (i.e. volatile organic compounds (VOCs), carbonyls and NO_2), by using diffusive passive samplers. Sampling in the classrooms is undertaken only during the lessons, in order to have the evaluation of student exposition to the indoor pollutant burden. To assess seasonal variation, two campaigns are performed, one in winter and the other in spring. Alternatively in the two classrooms, real-time samplers of total VOCs and some chemical-physic parameters, such as CO and CO_2, are employed.

Results show that the classrooms are characterized by low concentration of the pollutants monitored with diffusive samplers, lower than guideline (ex. WHO) and European legislation law limits. Only limonene shows concentrations higher than European schools mean values, and in elementary classroom they are higher.

For the most of the analyzed compounds, there is a contribution of indoor source emissions, especially for aldehydes. Indoor emissions are similar in the monitored classrooms. Daily trends confirm that VOCs have mainly an indoor origin since they are similar to CO_2 ones. However, on same days the contribution of outdoor sources is important. Furthermore, on-line monitored CO_2 concentrations suggest that ventilation in the monitored rooms could be improved.

Key words: children, formaldehyde, indoor air quality, on-line detectors, and volatile organic compounds

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1. Introduction

It is nowadays commonly defined as "indoor" all not industrial life and working environments and in particular dwelling, recreation, work and transport places (Agreement, 2001; Fanger, 2006). Indoor pollutants may produce effects both individually and together with other factors, and cause a decrease in environmental comfort and health risk. Among chemical components usually found in indoor air, some of the most important categories are volatile organic compounds (VOC, i.e. organic compounds with a boiling temperature between 50 °C and 260 °C) and carbonyl compounds (WHO, 1989). For some pollutants, which are present in indoor environment and for which scientific knowledge on effects on human health was judged well-defined, WHO settled *guidelines for indoor air quality* for European region. For carcinogenic pollutants, a unit risk for general population associated to their

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presence in the air is defined. The considered pollutants are: benzene, nitrogen dioxide, polycyclic aromatic hydrocarbons (especially benzo[a]pyrene), naphthalene, carbon monoxide, radon, trichloroethylene and tetrachloroethylene (WHO, 2010).

Priority ranking for indoor air pollutants was identified by European Commission INDEX project. Three groups were defined: group 1 - high priority chemicals, it encompasses formaldehyde, nitrogen dioxide, carbon monoxide, benzene and naphthalene; group 2 -second priority chemicals, acetaldehyde, o-, p- and m-xylene, toluene and styrene are included; group 3 - additional chemicals of interest, encompasses Ammonia, delta-Limonene, and alpha-Pinene (JRC, 2005; Koistinen et al., 2008).

In Europe, urban population spend on average 95-97% of its time in closed environment, 2.4% in means of transport and 1% outdoor (BBW, 1997). Since a great part of population spends its time in closed environment, indoor pollution exposition is prevalent compared to outdoor. For more vulnerable sections of population, such as children that spend the main part of their time at home or at school, indoor air pollutant exposition may lead to the occurrence of specific pathologies or to the worsening of preexisting (Franchi et al., 2006; Oliveira Fernandes et al., 2009).

On 2010, some Italian ministers and WHO representatives responsible for health and the environment declared that, among health challenges of our time, there are the health risks to children and other vulnerable groups posed by poor environmental, working and living conditions (especially the lack of water and sanitation) (WHO and Italian Ministers, 2010).

Usually, indoor VOC monitoring is performed by passive samplers (Geiss et al., 2011; Godoi et al., 2013; Pegas et al., 2011a, 2011b). In some studies, real-time, continuous monitors were also employed. These instruments are useful to understand the temporal changes in actual indoor air quality (Hori et al., 2013). In several studies, they are employed to evaluate the emissions of a specific source (Halios et al., 2005; Su et al., 2007; Zhao et al., 2014), or short-term monitoring, not exceeding four days, were undertaken, in order to have spot information on indoor pollution (Hori et al., 2013; Ramos et al., 2014; Sarkhosh et al., 2012).

In other studies, longer monitoring was performed, but only on-line data were collected (Helmis et al., 2009). In this work, a more comprehensive study was performed.

The aim of this study is to assess indoor air quality in an educational institute. The monitoring was performed during several weeks, both in winter and in spring, to obtain a long-term overview of the indoor air quality in the institute (ISS, 2013). As well as seasonal, outdoor source influence was taken into account, by performing samplings also in the garden of the institute. Besides the common and widespread monitoring by passive samplers, real time monitors were employed.

2. Material and methods

2.1. Site description

The monitored school is located in the suburban area of the province of Bologna, Italy. In this educational institute, preschool and elementary schools are both present. The school is along a highway and close to a polyvinyl chloride (PVC), polypropylene (PP) and polyethylene (PE) tube and connector industry, which is 300 m far (Fig. 1). Thus, the institute was chosen also to assess the influence of these important outdoor sources.

Inside the institute, the sampling was undertaken in two classrooms, one of the preschool and one of the elementary school. At the same time, outdoor samples were collected in the garden of the institute (Fig. 1).

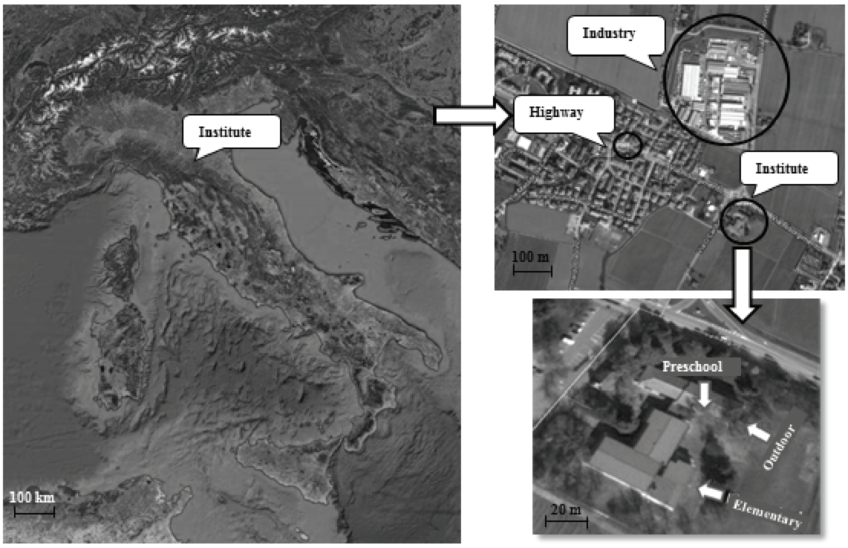

Fig. 1. Studied area and school location (a) on a large-scale map and (b) a local map and (c) sampling points at the school (from Map data © 2014 Google – modified)

Preschool class consists of 21 children, while elementary one of 19 pupils. The furniture of both the classrooms is modern and bought more than two years ago. The rooms were painted more than 2 years ago by water tempera painting. Both the classrooms were used only for didactic scopes. At both the classrooms, windows were opened in the morning for the building ventilation before student arrival.

They were also kept opened when children were not in the classroom during the day, i.e. from 12:30 to 13:30 at the elementary classroom and from 11 to 12 and from 13:30 to 15:30 at the preschool classroom. Moreover, they were opened other times to the discretion of teachers, according to classroom temperature.

2.2. Sampling

Gas samples were collected with diffusion passive samplers (*Radiello*®, Fondazione Salvatore Maugeri, Padova, Italy). Three systems were used, each one with a cartridge specific for different pollutants: one for VOC, another for carbonyl compounds and the last one for NO_2. The samplers were placed in the middle of the room, hanging from a thread 2 m from the floor. In this way, sampling did not interfere with the usual activity of the students and possible sampler tampering was avoided.

In order to obtain the exact assessment of mean weekly exposition, it is necessary to expose samplers not continuously, but only when students are in the classroom. Therefore, sampling in the classrooms was undertaken only during the lessons. Teachers exposed samplers in the morning when children arrived at school and they placed them in hermetically closed glass bins in the evening, at the end of the lessons. Samplers were thus exposed for about 8 hours a day, for five days a week (from Monday to Friday). On Friday evening, at the end of the weekly sampling, cartridges were collected and immediately carried to the laboratory, where they were stored at 4°C until analysis. At the same time as passive samplers and alternatively in the two classrooms, two portable continuous and real-time detectors, which allow obtaining high-resolution data, were employed. The total VOC concentration was measured using Cub (Ion Science Ltd), a photoionization detector (PID), which measures organic compound air concentrations. It employs a 10.6 eV lamp and it detects few hundreds volatile and aromatic organic compounds. It was calibrated by the seller for isobutylene and all response factors are equivalent.

Some chemical-physic parameters, i.e. CO_2, CO, humidity and temperature, were measured using Q-Trak. Sampler characteristics were reported in Table 1. Outdoor air was also monitored, by using the same passive samplers used for indoor air. They were continuously exposed from Monday morning to Friday evening. Two sampling campaigns were performed, the first in the late winter, the second in spring. Winter campaign lasted 4 weeks; it started on the 3rd of March and ended on 28th of March (w1, w2, w3 and w4), 2014. Spring campaign lasted 2 weeks, from 5th to 16th May, 2014 (w5 and w6). For each class, a daily diary was provided. In it, teachers wrote start and end exposition time of passive samplers, pupils in the classroom, particular activities entailed during the day and its time.

2.3. Analysis

For all three systems used, QA/QC was already widely studied and is reported in the web site of the diffusion passive samplers (http://www.radiello.it/ (in Italian)).

2.3.1. Volatile organic compounds (VOC)

In this study, benzene, trichloroethylene, toluene, tetrachloroethylene, p-xylene, ethyl-benzene, m-xylene, o-xylene and limonene were determined. Their sampling was carried out with charcoal based cartridges (530 ± 30 mg, 35-50 mesh) (Radiello code 130, Supelco). Extraction was carried out as indicated by Radiello manufacturer (Pegas et al., 2011a; 2011b). Samples where shacked with 2 mL of carbon disulfide (Sigma Aldrich, low benzene, ≥99.9%) with a rotator drive (Stuart Scientific), for 30 min. Before the extraction, the cartridge was spiked with internal standard 2-Fluorotoluene (Aldrich, ≥99%) (http://www.radiello.it/ (in Italian)).

Analysis was performed by GC-MS (Shimadzu 3400 GCMS-QP2010 Series). Separation was performed with a Zebron, Phenomenex ZB-5MS column (95% arylene dimetil- 5% diphenyl-polysiloxane, 30 m, 0.25 mm i.d., 0.25 µm film thickness) with a temperature program of 40°C for 9 minutes, from 40°C to 200°C at 12°C/min and from 200°C to 250°C at 50°C/min, with helium as carrier gas (purity: 100%). The AOC – 20i, Auto-Inject split/splitless injector was maintained at 250°C and operated under split conditions.

Table 1. Real-time detector characteristics

Sampler	*Parameter*	*Sensor*	*Measure range*	*Resolution*	*Response time (sec)*	*Time resolution (min)*
Cub	VOC	Photoionization detector (PID)	1 ppb-5000 ppm	1 ppb	13	1
Q-Trak	CO_2	Non-dispersive infrared	0-5000 ppm	1 ppm	20	1
Q-Trak	CO	Electrochemical	0-500 ppm	0.1 ppm	<60	1
Q-Trak	Temperature	Thermistor	0-60 °C	0.1 °C	30	1
Q-Trak	Humidity	Capacitive	5-95% rh	0.1% rh	20	1

Data acquisition was performed in the single ion mode (SIM). The SIM programme is reported in Table 2. VOCs were identified by both the mass spectrum and external standard t_r. Quantification was performed by the internal standard method, by preparing solutions containing all the VOC (50 component indoor air standard, Supelco) with different concentrations and the internal standard.

2.3.2. Carbonyl compounds

The carbonyl compounds determined were formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, benzaldehyde, valeraldehyde and heaxaldehyde. Their sampling was done by Florisil® coated with 2,4-dinitrophenyl-hydrazine (2,4-DNPH) based cartridges (Radiello code 165, Supelco). Carbonyls react with 2,4-DNPH and form the corresponding 2,4-dinitrophenyl-hydrazone. Extraction was carried out as indicated by Radiello manufacturer (Pegas et al., 2011a, 2011b). Samples where shacked with 2 mL of acetonitrile (Sigma Aldrich, HPLC grade, ≥99.9%) with a rotator drive, for 30 min. The extract was then filtered by nylon filters (PHENEX, 0.2 µm, 15 mm, Phenomenex) (http://www.radiello.it). 2,4-dinitrophenyl-hydrazones were determined by HPLC with a UV-VIS detector (Agilent 1200 Series). They were separated on a reverse phase column, 4.6 mm x 150 mm, 5 µm, Agilent ZORBAX Eclipse XDB-C18.

The elution program consisted a 60 min gradient from a mixture water and acetonitrile (v/v: 80/20%) to 75% acetonitrile. The separation was performed with a constant flow rate of 1.5 mL min^{-1} at 25˚C. Different species were identified and measured by the external standard method, using solutions of carbonyl compounds (Supelco) with different concentrations. Excitation wavelength was 365 nm.

2.3.3. Nitrogen dioxide

NO_2 sampling was performed by cartridges with steel grids impregnated with moist triethanolamine (TEA) (Radiello code 166, Supelco), which chemiadsorb NO_2 as nitrite. The extraction was performed by adding 5 mL of bidistilled water to cartridge test tube. Samples were stirred for 30 minutes by rotatory stirrer, then the extract was separated. $NO_2^-$was determined by ionic chromatography couplet with a conductibility detector (Metrohom, 761 Compact IC), as reported in Venturini et al. (2013).

3. Results and discussion

3.1. Passive samplers

Results obtained for pollutants monitored with passive samplers are reported in Fig. 2. In general, concentrations are low (Agreement, 2001; Franchi et al., 2006; WHO, 2010). For the most of the analyzed components, there is a contribution of indoor contamination. Nevertheless, except for limonene, all the determined VOCs show lower concentrations than European schools mean values (Geiss at al., 2011).

For high priority chemicals (INDEX definition, see chapter 1), benzene outdoor and indoor concentrations are similar. Spring values are lower, as it is in general found (Franchi et al., 2006; Schneider et al., 2001; WHO, 2010). The concentrations of this study were compared with the values registered by the stations measuring ambient air pollution. The siting of sampling points were located according to specific criteria, as indicated by directive 2008/50/EC (EC, 2008). The values determined in this study are about half of what is found at a Bologna traffic site (http://www.arpa.emr.it).

For formaldehyde, as well as for other aldehydes, there is an increase in indoor exposure compared to outdoor, since indoor concentrations are five times higher. Elementary school values are between 5 and 15% higher than preschool, except for w4 when elementary value is 40% higher than preschool one.

Among second priority chemicals, acetaldehyde outdoor concentration is higher than what is reported for other European sites (Geiss et al., 2011), while toluene and xylene values are particularly low. For additional chemicals of interest, limonene is the only component, as above mentioned, which shows concentrations higher than European schools mean values. Elementary school values are higher than preschool values. Particularly, elementary w4 sample shows high value.

Table 2. Ion programme for SIM determination

Time (min)	*Ions (m/z)*	*Determined pollutant*
2	78	Benzene
2.7	130-132-95	Trichloroethylene
4	91-92-65	Toluene
4.4	109-110-83	2-Fluorotoluene
5	166-164	Tetrachloroethylene
7.5	91-106-105	Ethyl-benzene, p-xylene, m-xylene, o-xylene
13	68-67-93	Limonene
15	43-57	Alkanes

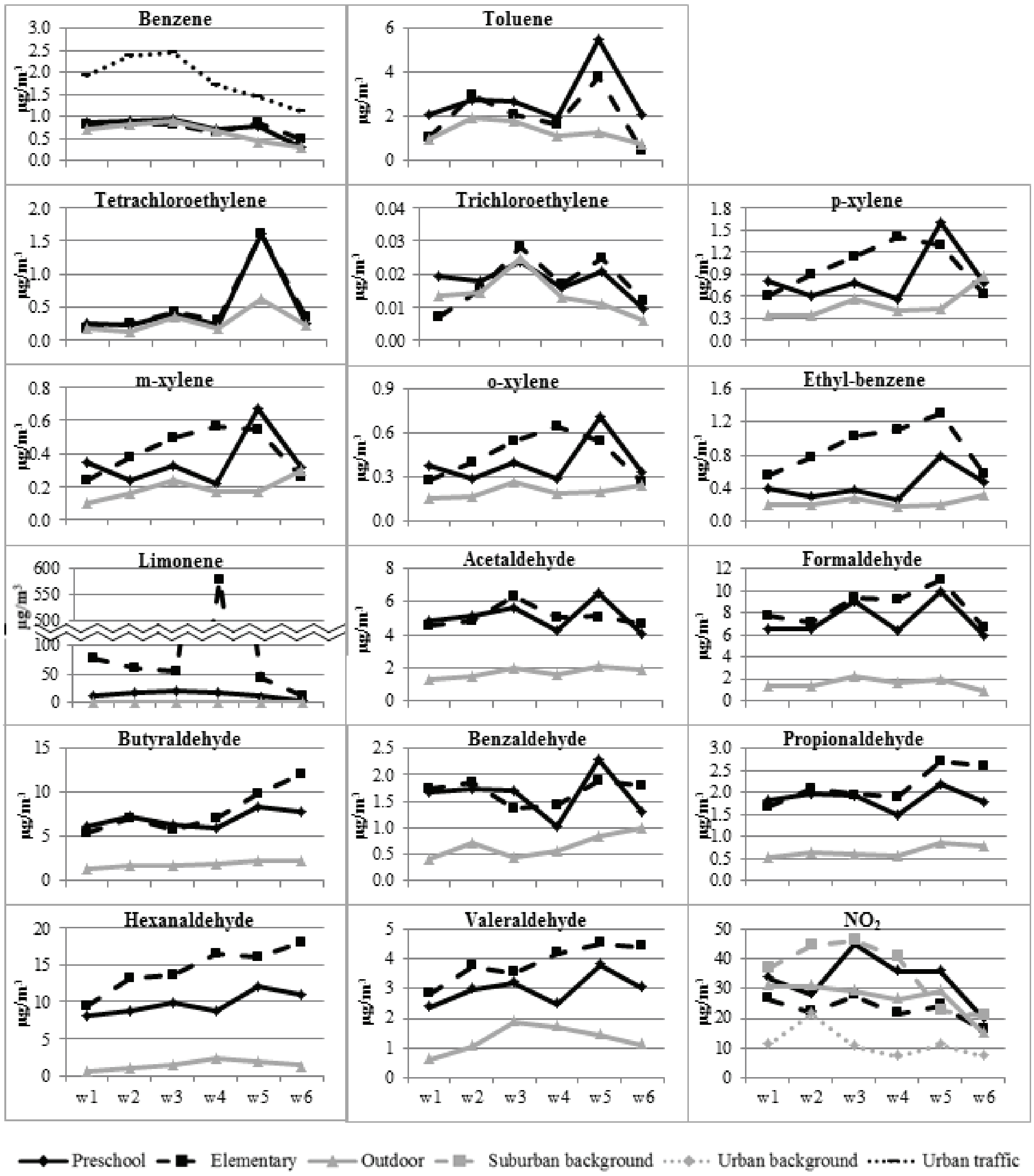

Fig. 2. Concentration trends for pollutants monitored with passive samplers

According to daily diary, no particular activities were performed in the classroom during this week. Spring values, even if still high, are lower than winter ones. Limonene is used as aroma or flavor additive in cleaner products. Its health effects are not of concern, since the most important health effects associated with limonene are irritation of the eyes, nose, throat and skin.

However, it may convert in more dangerous compounds, and thus its concentrations should be reduced (Rohr, 2013; Sarigiannis et al., 2011; Wolkoff, 2013).

NO_2 indoor and outdoor values are similar. The measured values place between rural and suburban background values registered by the stations measuring ambient air pollution (http://www.arpa.emr.it), thus the study area is low contaminated. Elementary school values are lower than preschool values, since elementary classroom is farther away from the highway (WHO, 2010). It is not likely the presence of indoor sources.

Finally, trichloroethylene concentration is lower in spring period and in general this compound values are order of magnitude lower than what it is found in other European sites (Geiss et al., 2011). Hexanaldehyde and Valeraldehyde are between 10 and 90% higher at the elementary classroom than at preschool.

Several determined pollutants were higher at the elementary classroom. Activities reported in the daily diary were checked, to assess if particular activities occurred in this classroom that could justify these results. Nevertheless, special activities did not occur.

The concentrations determined in this study are lower than the guideline values and law limits for indoor pollutants present in some countries (Settimo, 2012; Stranger et al., 2007; WHO, 2000, 2010).

3.2. Pearson correlation coefficients

In Table 3 Pearson correlation coefficients between the pollutants are shown, by considering indoor and outdoor samples separately. For indoor samples, there are some significant correlationse among aldehydes (p-value = 0.01), thus they likely have a common origin or common emission mechanisms. Ethyl-benzene, tetrachloroethylene, xylenes and formaldehyde show also a similar behavior. For outdoor samples, NO_2 and benzene significantly correlate. This is probably due to the common origin of these contaminants, since road traffic is the principal outdoor source of both (WHO, 2010).

3.3. On-line samplers

In Table 4, mean daily values (median, minimum and maximum for CO) of the parameters monitored with continuous samplers are reported. The most of spring values for Q-Trak are missing, due to malfunction. Cub data from a day to another showed high scale variability.

Table 3. Pearson correlation coefficients between the pollutants for indoor samples (a) and outdoor (b). Significant correlations (p=0.01) are reported in bold

(a)	***Trichloroethylene***	***Toluene***	***Tetrachloroethylene***	***Ethylbenzene***	***p-xylene***	***m-xylene***	***o-xylene***	***Limonene***	***Formaldehyde***	***Acetaldehyde***	***Propionaldehyde***	***Butyraldehyde***	***Benzaldehyde***	***Valeraldehyde***	***Hexanaldehyde***	***NO_2***
Benzene	0.56	0.40	0.21	0.04	0.11	0.13	0.17	-0.12	0.40	0.50	-0.01	-0.42	0.42	-0.14	-0.34	0.62
Trichloro-ethylene		0.51	0.49	0.43	0.53	0.56	0.59	-0.04	0.68	**0.76**	0.31	-0.04	0.18	0.26	0.14	0.35
Toluene			**0.79**	0.27	0.64	0.66	0.64	-0.21	0.54	0.57	0.28	0.08	0.59	0.19	-0.10	0.06
Tetrachloro-ethylene				0.56	**0.72**	**0.73**	0.67	-0.14	**0.77**	0.51	0.63	0.46	0.64	0.53	0.30	-0.22
Ethylbenzene					**0.79**	**0.79**	**0.75**	0.48	**0.78**	0.39	0.53	0.28	0.26	**0.78**	**0.75**	-0.50
p-xylene						**1.00**	**0.99**	0.44	**0.81**	0.63	0.37	0.17	0.40	0.59	0.47	-0.25
m-xylene							**0.99**	0.38	**0.81**	0.67	0.40	0.18	0.43	0.59	0.47	-0.24
o-xylene								0.45	**0.81**	0.69	0.30	0.08	0.35	0.53	0.42	-0.13
Limonene									0.27	-0.02	-0.11	-0.12	-0.21	0.34	0.44	-0.17
Formaldehyde										0.70	0.46	0.13	0.44	0.61	0.43	-0.01
Acetaldehyde											0.29	-0.05	0.47	0.30	0.14	0.26
Propion-aldehyde												**0.88**	0.65	**0.84**	**0.72**	-0.51
Butyraldehyde													0.42	**0.72**	0.68	-0.65
Benzaldehyde														0.43	0.18	-0.14
Valeraldehyde															**0.93**	-0.59
Hexanaldehyde																-0.65
(b)	***Trichloroethylene***	***Toluene***	***Tetrachloroethylene***	***Ethylbenzene***	***p-xylene***	***m-xylene***	***o-xylene***	***Limonene***	***Formaldehyde***	***Acetaldehyde***	***Propionaldehyde***	***Butyraldehyde***	***Benzaldehyde***	***Valeraldehyde***	***Hexanaldehyde***	***NO_2***
Benzene	0.87	0.71	-0.35	-0.30	-0.59	-0.43	-0.14	-0.53	0.47	-0.34	-0.78	-0.79	-0.85	0.23	-0.09	**0.94**
Trichloro-ethylene		0.68	0.06	-0.02	-0.33	-0.14	0.27	-0.41	0.75	0.12	-0.50	-0.49	-0.76	0.50	0.06	0.69
Toluene			0.05	-0.24	-0.43	-0.15	-0.01	-0.26	0.51	0.15	-0.14	-0.24	-0.28	0.35	-0.04	0.56
Tetrachloro-ethylene				0.01	0.07	0.14	0.31	0.59	0.63	0.82	0.70	0.60	0.29	0.35	0.20	-0.43
Ethylbenzene					**0.93**	0.90	0.85	-0.38	-0.25	0.44	0.30	0.42	0.35	0.16	-0.00	-0.53
p-xylene						**0.94**	0.78	-0.09	-0.39	0.49	0.50	0.66	0.62	0.14	0.15	-0.78
m-xylene							0.88	-0.06	-0.19	0.64	0.51	0.70	0.59	0.40	0.31	-0.69
o-xylene								-0.08	0.23	0.74	0.32	0.52	0.22	0.64	0.41	-0.45
Limonene									0.25	0.41	0.50	0.58	0.38	0.34	0.63	-0.45
Formaldehyde										0.49	-0.04	-0.06	-0.47	0.65	0.33	0.34
Acetaldehyde											0.74	0.79	0.46	0.64	0.43	-0.59
Propion-aldehyde												0.92	0.88	0.05	0.07	-0.85
Butyraldehyde													0.88	0.32	0.41	**-0.92**
Benzaldehyde														-0.11	0.08	-0.89
Valeraldehyde															0.85	-0.02
Hexanaldehyde																-0.21

Table 4. Mean daily concentrations and standard deviation of CO_2 and VOCs. Median, minimum and maximum concentrations of CO. Mean daily values and standard deviation of temperature and humidity. IDA values used to determine indoor air quality. Pearson correlation coefficient between CO_2 and VOCs for each day (significant correlations (p=0.001) are reported in bold)

	Data	**CO (ppm)**	**CO_2 (ppm)**	**IDA**	**T (°C)**	**H (%rh)**	**VOC (ppb)**	**r^a betweenCO_2 and VOC**
Preschool	03/03/2014	<0.1	800±500	2	21±1	40±2	20±20	0.13
	04/03/2014	<0.1	1100±600	3	22±1	44±3	--	--
	05/03/2014	<0.1	800±300	1	21.4±0.9	42±2	15±7	0.76
	06/03/2014	<0.1 (<0.1;0.1)	700±200	1	21.9±0.6	38±2	20±10	0.75
	07/03/2014	<0.1	800±300	1	22.1±0.7	37±2	--	--
	10/03/2014	<0.1	800±300	2	20±1	37±2	20±10	0.77
	11/03/2014	<0.1	800±300	1	21.2±0.7	35±2	20±20	0.50
	12/03/2014	<0.1	700±300	1	22.9±0.8	25±4	30±20	0.87
	13/03/2014	<0.1	600±200	1	22±1	29±1	8±6	0.59
	14/03/2014	<0.1	600±200	1	22.7±0.5	32±2	16±9	0.89
	05/05/2014	--	--		--	--	20±10	--
	06/05/2014	--	--		--	--	40±40	--
	07/05/2014	--	--		--	--	30±30	--
	07/05/2014	--	--		--	--	20±10	--
	09/05/2014	--	--		--	--	30±20	--
Elementary	17/03/2014	<0.1	1000±500	3	24.2±0.8	43±3	30±40	0.75
	18/03/2014	<0.1 (<0.1;0.1)	1600±800	4	23±1	52±3	--	--
	19/03/2014	<0.1 (<0.1;0.1)	1100±800	3	23.6±0.6	46±4	40±70	0.71
	20/03/2014	<0.1 (<0.1;0.2)	2000±1000	4	24±1	48±3	20±30	0.57
	21/03/2014	<0.1 (<0.1;0.3)	1400±900	3	24.0±0.9	50±3	50±50	0.47
	24/03/2014	0.1 (<0.1;0.3)	2000±1000	4	24±1	37 ±43	50±30	0.90
	25/03/2014	<0.1 (<0.1;0.2)	1400±800	4	24±2	34±5	50±40	0.90
	26/03/2014	0.1 (<0.1;0.7)	2400±800	4	23.9±0.7	45±4	80±60	0.76
	27/03/2014	0.1 (<0.1;0.5)	3000±1000	4	23.7±0.6	48±4	70±50	0.80
	28/03/2014	--	--		--	--	70±50	0.75
	12/05/2014	<0.1 (<0.1;0.1)	1000±600	3	25.1±0.9	41±3	30±10	0.91
	13/05/2014	<0.1	7400±400	1	24±1	42±1	20±20	0.92
	14/05/2014	--	--		--	--	20±20	--
	15/05/2014	--	--		--	--	20±10	--
	16/05/2014	--	--		--	--	41±9	--

The instrument did not always started the scale from zero. Thus, on some days; we had to shift concentrations from instrument relative scale to the scale used on other days. CO values are always lower than 1 ppm; they are lower than values reported in other studies (Franchi et al., 2006; WHO, 2010) guideline values and law limits present in some countries (Settimo, 2012; Stranger et al., 2007). Unlike elementary school values, CO concentration in preschool is in general lower than instrument quantification limit. CO_2 is an indicator of room ventilation (Franchi et al., 2006). Measured values are rather high in comparison with both guidelines and values found in other studies (Franchi et al., 2006; Stranger et al., 2007).

The obtained concentrations were compared with IDA values, which are used to determine indoor air quality (CEN EN, 2007). In the morning, when windows were kept opened for the building ventilation before student arrival, CO_2 concentration values were similar to ambient value (between 400 and 450 ppm). This value was considered as the outdoor concentration. IDA values revealed that in elementary classroom the indoor air quality was usually low (IDA 4). Therefore, ventilation is inadequate. In the spring period concentrations decrease and IDA value as well, probably because windows are kept open longer. At the preschool classroom, indoor air quality is usually high (IDA 1).

Other on-line monitored parameters (temperature, humidity and VOC) show the same trend as CO and CO_2: the measured values are higher in the elementary classroom in winter. On the contrary, in the spring VOC values are similar in the two classrooms and to the winter preschool values. Also the only two values of CO_2 for the elementary classroom are lower than winter ones and similar to winter preschool. Higher VOC concentrations at the elementary classrooms were indicated also by diffusive sampler results. This was mainly due to limonene, since it contributes at list for 40% in indoor samples to the sum of VOCs determined in this study. Nevertheless, for diffusive samplers, VOC concentration was higher at the elementary classroom also in the spring.

3.4. Daily trend

In Figs. 3 and 4, median daily trend and concentration range included between 25th and 75th percentile for CO_2 and VOC at elementary and preschool classrooms are reported.

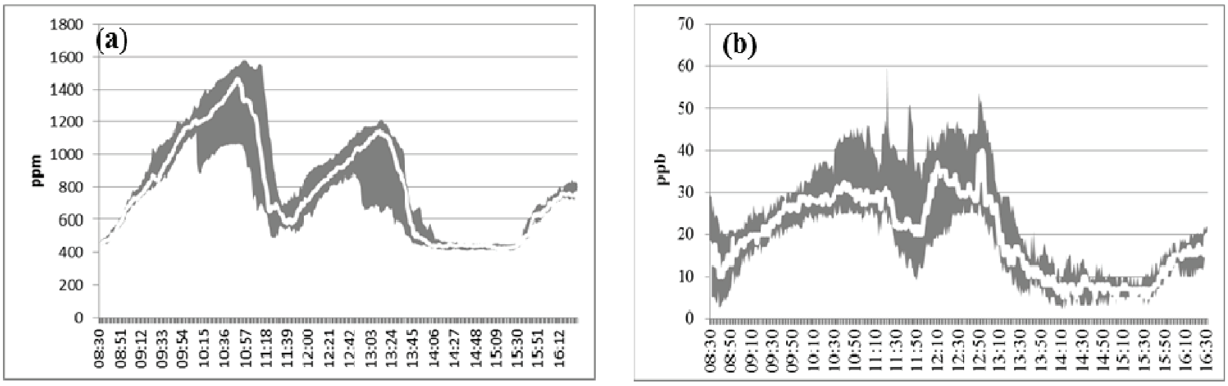

Fig. 3. Daily trends at preschool for CO_2 (a) and VOCs (b): median (white line) and concentration range included between 25th and 75th percentile

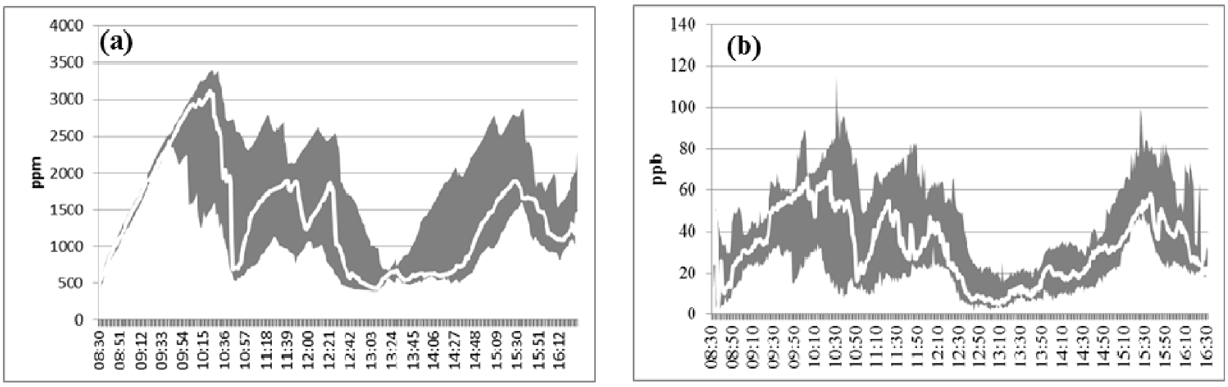

Fig. 4. Daily trends at elementary school for CO_2 (a) and VOCs (b): median (white line) and concentration range included between 25th and 75th percentile

They are clearly the same in the same classroom. CO_2 comes mainly from indoor, and thus also VOCs have mainly indoor sources. In fact, also mean daily value behavior for CO_2 and VOCs is the same, i.e. higher values for the elementary classroom in winter. The main indoor origin for these pollutants is further demonstrated by examining more in details daily trend. In the morning, after window opening for the building ventilation before student arrival, concentrations are low, CO_2 value is similar to ambient value (about 400 ppm). When students arrive, concentrations increase, more markedly at the elementary classroom. In both the classrooms, concentrations decrease when children are not present (between 12:30 and 13:30 at the elementary classroom and between 13:30 and 15:30 at preschool classroom) and air is changed.

The similarity between CO_2 and VOC trends is confirmed by Pearson correlation coefficients (Table 4). All the correlations were significant, except for 3rd March. On this day, VOC concentration peaks are registered when CO_2 concentration decreases. Thus, on 3rd March the contribution of VOC outdoor sources is important. Even though the coefficients are significant, on 13th, 20th and 21st March they are lower. Also on these days, there are VOC concentration peaks when CO_2 concentration is low, and thus the contribution of outdoor sources.

4. Conclusions

Diffusive passive sampler and continuous detector use to evaluate IAQ provides complementary information that together can allow to identify possible critical elements. Passive sampler results of this study demonstrated that the classrooms are characterized by low pollutant concentration even if, for the most of the analyzed components, there is a contribution of indoor contamination. Daily trends confirm that VOCs have mainly an indoor origin.

The method applied demonstrated suitable. IAQ monitoring could be continued only by a PID. However, if an increase in concentration is detected, passive samplers are necessary to go deeper in the causes of the raising.

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SUSTAINABLE DESIGN STRATEGIES AND TECHNOLOGIES FOR A GREEN SPACE FOR STUDENTS AT TERRACINI CAMPUS, UNIBO

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Abstract

To make sustainability transitions happen, it is crucial not only to have strategic planning processes committed by the top management, but also to encourage community engagement, approaching and promoting a bottom-up process. In the specific case of a University Campus, that means the involvement of the students not only as consumers, but with a leading role in the sustainability process. DICAM department of University of Bologna has recently started the implementation of some practical actions to create a sustainability campus Terracini. These activities are parts of the Sustainability Plan of Unibo. A multifunction group, called Terracini Transition Team is managing some of these actions located in Terracini Campus. Moreover, a new model of pedagogy, called flipped classroom, has been experimented. Therefore, Terracini Transition Team has been proposing an innovative and engaging idea that could support sustainability measures: the realization of a space for students designed by themselves with an inclusive and participative approach. To meet environmental performances, the space will be planned with the use of appropriate building technologies, employing low impact and local materials. In addition, the space will be realized in auto-construction, in order to strengthen the involvement of final users, the students. This paper will show an evaluation of appropriate building technologies with an LCA approach. Finally, the reported LCA case-studies has provided the robustness to drive the choices of low impact solutions for the sustainability of Unibo. Finally, the paper demonstrates the efficacy of the adoption of whole-system approach integrating experiential learning with sustainability assessment.

Key words: appropriate technologies, experiential learning, LCA, sustainability transition, sustainability campus

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1. Introduction

Although a high number of international initiatives are promoting campus sustainability (Calder and Clugston, 2003; Wright, 2004), Sustainable Development, SD, still endeavours to become integral part of the whole university system (Bekessy et al., 2007; Lozano et al., 2013; Thaman, 2002). There is the need to overcome the current fragmented approach to SD (Burke, 2000; Cortese, 2003), the adoption of whole-system approach and the creation of proactive processes help to integrate the theory and the practice of sustainability within the campus in order to reconnect education, research and campus operations (Koester et al., 2006; Sharp, 2002). According to UNEP (2013), in this framework, a crucial issue can be played by the students' engagement as co-creators of knowledge, agents and drivers of change (Müller-Christ et al., 2014). According to Kolb (1984), "learning is the process whereby knowledge is created through the transformation of experience". Therefore, the

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learning process can become an experiential learning process by the use of "real world" problems as the context for students to learn critical thinking and problem-solving skills (Bould and Felletti, 1991; Hansman, 2001).

This paper presents the flipped classroom (Foertsch et al., 2002; Lage et al., 2000) as an experiential learning process for sustainability that develop opportunities to teach the theory and the practice of sustainability. The result could be the transformation of the campus into a living-lab of sustainability. In the academic literature, there are numerous examples of the concepts of living-lab of sustainability (UNEP, 2013). Particularly, the case of the Engineering and Architecture School of Bologna University represents a successful case of how to transform campus into a living-lab of sustainability (Cappellaro and Bonoli, 2014). Driven by an experiential learning approach, the Terracini initiative is aimed not only to improve the campus sustainability but also to raise the environmental awareness of the whole university community and especially of Engineering students.

The main instruments adopted for this process are environmental assessment (LCA) and pedagogical methology called Flipped Classroom. This paper presents the realization of a space for students as an innovative and engaging idea that could help to enhance the sustainability process ongoing at Terracini Campus through practical functions of teaching and research with a direct involvement of students. This space can be a driver for enhancing an inclusive and participative approach and provides a significant opportunity to put into practice sustainability concepts. The project will include the sustainability goals in all the life-cycle phases of the students' space realization. Since the design phase, a Life Cycle Assessment study supports the selection of appropriate building technologies with the aim to employ low impact and local materials (Ciutina et al., 2010; Simion et al., 2013; Tundrea et al., 2014; Zhang et al., 2014). Then, the manufacturing phase is meant to realize the space in auto-construction. In this way, the involvement of final users, the students, is constructively strengthened. Furthermore, the use phase is planned to assure energy efficiency target and zero waste and consumptions.

The final aim of this paper is to demonstrate how the adoption of sustainability as whole-system approach can contribute to make sustainability an integral part of the university system. Definitely, the transformation of the campus into place of sustainability can help society to become more sustainable.

2. Materials and methods

2.1. Method and project structure

For the development of the experience in Terracini Campus (Bonoli and Cappellaro, 2013), as a working basis we propose the methodology and results obtained thanks to a recent research project of sustainability, VERSUS "Lesson from Vernacular Heritage to Sustainable Architecture" (Correia et al., 2012, 2014). This way, students propose a project evaluated following the sustainability criteria set by the VERSUS project, in which some authors of this text are directly involved, as following explained. During each classroom session, a rigorous and detailed analysis of the project is carried out from different approaches. Thus, each session is aimed at each of the 15 principles derived from the VERSUS project (Mileto et al., 2015a, 2015b). These principles, in turn, are grouped into three different scopes, so that students are aware of which scope they are working in at all times:

- **Environmental Scope** (5 principles): to respect nature, to be appropriately situated, to reduce pollution and waste materials, to contribute to health quality, to reduce natural hazards effects.
- **Socio-Cultural Scope** (5 principles): to protect cultural landscape, to transfer construction cultures, to enhance creativity, to recognize intangible values, to encourage social cohesion.
- **Socio-Economic Scope** (5 principles): to support autonomy, to promote local activities, to optimise construction efforts, to extend the building's lifetime, to safe resources.

Prior to the session, students are presented with different resources and content (videos, links, examples, web applications) based on principles that are to be treated. Once a classroom session has started, the teaching model follows the following timetable:

- **5 minutes:** Initial open appraisal of the previously proposed resources and content. This way the teacher is aware of the starting level of the students and can adjust the intensity of the session, or identify students with learning issues or deficiencies.
- **5 minutes:** Discussion on the results, so that the students can identify their deficiencies or learning issues.
- **10 minutes:** Questions raised during the previous stage are solved together. Thus, those questions resolved collectively can reach the entire classroom.
- **15 minutes:** Once students have worked on the assignment (apply, understand, remember - Bloom's taxonomy), the next step is for them to create, evaluate and analyse (Bloom's taxonomy) their proposals from any of the aforementioned principles of sustainability.
- **10 minutes:** Joint discussion of the results of the various assignments, and selection of the best approach for the project.
- **10 minutes:** The teacher engages the students in different games, based on the principles discussed so far with the aim of consolidating what has been learned.

After the classroom sessions designed to create, to evaluate and to analyse the project proposal, we turn to the stage of erecting the building, a task carried out by the students themselves. The criteria are obtained by flipped classrooms, considering Versus Project support crossed with LCA analysis. In this frame, as following explained, straw and raw earth plaster applied on a straw bale wall are interesting techniques to be developed. The choice of straw and earth is compatible with auto-construction and low impact design, and assure good energy performances (Fugler and Gonzalez, 2002) and indoor comfort (Fugler, 2000). These solutions could suit socio/ cultural/economical scopes and perfectly adapt to local context of Terracini Campus, involved in "KM0" scenario.

2.2. Life Cycle Assessment of a straw and raw earth plaster

In order to assess the sustainability of a straw and raw earth plaster and identify the environmental hot spots of the system, a Life Cycle Assessment compliant with the ISO norms on LCA (ISO 14040, 2006; ISO 14044, 2006) has been performed. The assessment was carried out using a "from cradle to grave " approach considering as functional unit 1m^2 of plaster with a supposed life span of 100 years. The life cycle has been divided in 4 different phases (Fig. 2):

- the production phase of the plaster
- the installation phase
- the use phase
- the end of life phase (EOL)

The case study belongs to a real experiment located in Todi, Ist. Agrario Ciuffelli, planned by Arch. Eliana Baglioni in collaboration with PantaRei Experimental Center (PG-Italy)(Fig. 1).

Fig. 1. Straw and raw earth plaster applied on a straw bale wall

Several inspections at the construction site and interview to designers have allowed the data collection needed to perform the LCA of straw and raw earth plaster. When primary data have not been available, literature data and the Ecoinvent database have been used.

In the construction of the production and use phase, the extraction and production of all the raw material used have been accounted. Moreover all the transports needed to move the raw material to the construction site and the energy consumed have been inventoried in this phase. In addition, an industrialized production, installation and use of the plaster have been constructed, in order to become more relevant the comparison between a straw and earth plaster with a cement and lime plaster.

For this reason, the use of additional installation has been considered, such as electric sieve and cement mixer. The inventory could be parameterized so that the LCA can be replied for different surfaces in terms of area and plasters.

2.3. Sensitivity analysis

In order to deeply investigate the environmental impact of a straw and earth plaster, a sensitivity analysis, in terms of materials transportation, end of life scenarios and comparison with a conventional cement plaster, has been carried out.

2.3.1. Materials transportation

Different scenarios in terms of materials transportation have been investigated. The first one is based on the hypothesis that the construction materials come from distant locations, as described in Table 1. The case that the raw materials (straw and earth) have been collected very close to the construction site is investigated in the second scenario, called "KM0". This is compatible with the real case (Table 2).

Table 1. Transport for straw and raw earth plaster

Straw and raw earth Plaster	
Component	***Transport from production site to building site (km)***
Earth barbottina	200
Earth 1° layer	200
Earth 2° layer	200
Straw 1° layer	70
Sand 2° layer	200
Sand and lime 3° layer	200

2.3.2. End of Life scenarios

Different end of life scenarios have been studied. The process belongs to the Ecoinvent database, with some modifications, as illustrated in Table 3.

2.3.3. LCA of a cement and lime plaster

A sensibility analysis has been carried out confronting the LCA of the straw and raw earth plaster with cement and lime plaster.

The data of the composition of the cement and lime plaster become from the Pescomaggiore straw bale houses (Bonoli et al., 2014).

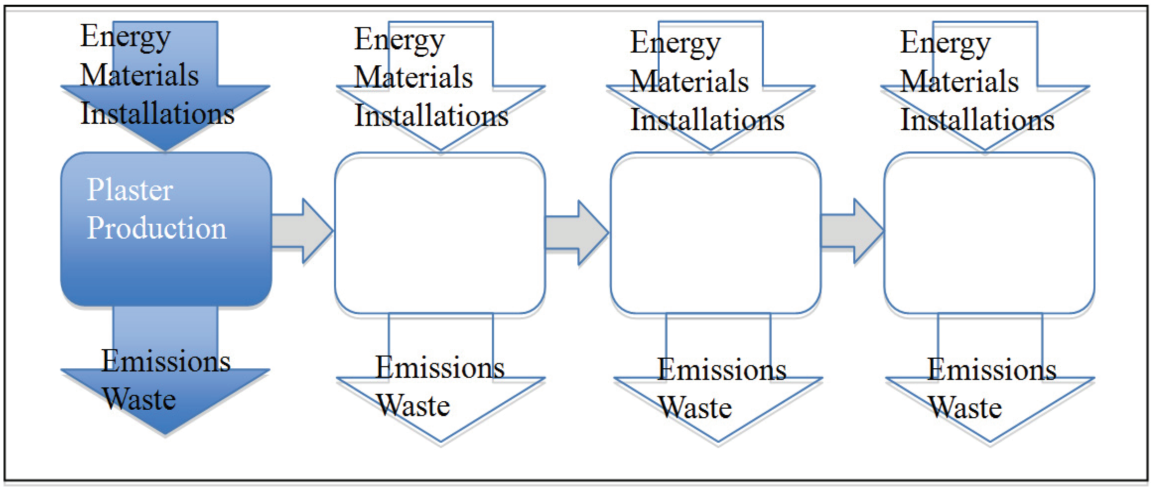


Fig. 2. Process flow chart

Table 2. Transport for straw and raw earth plaster – km0

Straw and raw earth Plaster – km0 case	
Component	***Transport from production site to building site (km)***
Earth barbottina	1
Earth 1° layer	1
Earth 2° layer	5
Straw 1° layer	1
Sand 2° layer	200
Sand and lime 3° layer	200

3. Results and discussion

3.1. LCA of a straw and raw earth plaster.

The use phase shows the highest damage (82.82%), overall due to the particulate emissions in atmosphere from the third layer of plaster in a period of time of 100 years, cause to the atmospheric degradation. A contribution to the damage comes from the emissions in atmosphere during the production of the layers for the maintenance (use phase). The damage is for the 90.41% in the Human Health, due to the emissions in atmosphere. Fig. 3 shows the characterization phase for the straw and raw earth plaster.

3.2. Comparison between straw and raw earth plaster, straw and raw earth plaster-km0 and cement and lime plaster

Fig. 4 the comparison between cement and lime plaster (left), straw and raw earth plaster and straw and raw earth plaster-km0 (right). Fig. 4 shows that the total damage of the cement and lime plaster is a 7.51% greater then the total damage of the straw and raw earth plaster. The damage in Climate Change and Resources is due to the production of cement and lime. The “km0” solution, as a consequence of a reduction of transports, can reduce the damage of a 7.63% less than the straw and raw earth plaster, and a 15.71% less than the cement and lime plaster.

3.3. Comparison between different end of life scenarios

Fig. 5 shows the different EOL scenarios: Incineration (left), Construction and Demolition Waste recycling, Disposal, 85% to Disposal and 15% to C&DW recycling, Restoration of a clay quarry (right). The process of incineration produces the greater damage. The process of restoration of a clay quarry, followed by the process of C&DW recycling, produces the lowest damage.

Table 3. EOL scenarios

EOL scenario	***Process from Ecoinvent***	***Notes***
Incineration	Disposal, building, cement-fibre slab, to final disposal/CH U	
Construction and Demolition Waste recycling	Disposal, building, cement-fibre slab, to recycling/CH U (with transport)	Transport from construction site to disposal has been considered
Disposal	Disposal, building, cement (in concrete) and mortar, to final disposal/CH U	
Disposal and recycling	Disposal, building, cement (in concrete) and mortar, to sorting plant/CH U	85% to Disposal, 15% to C&DW recycling
Restoration of a clay quarry	Fine vita intonaco di terra cruda (da Disposal, building, cement-fibre slab, to final disposal/CH U)	The straw and earth plaster is reused as filler for the restoration of a clay quarry

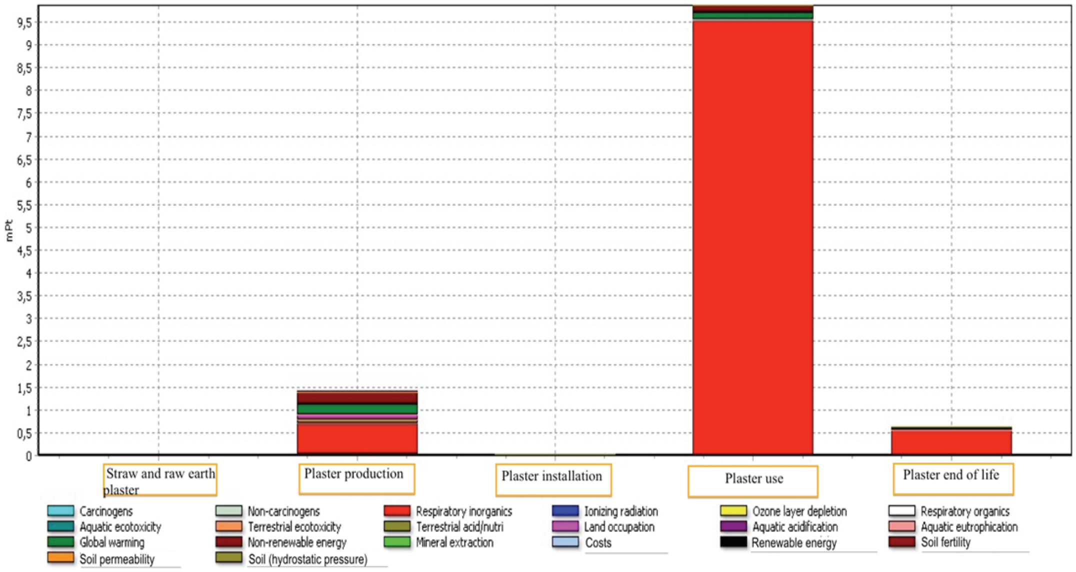


Fig. 3. Characterization phase for the straw and raw earth plaster

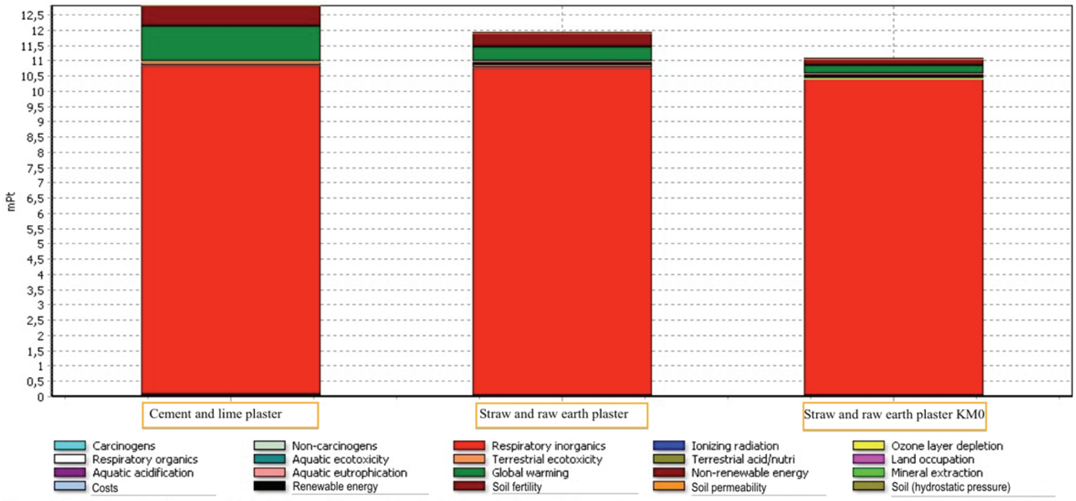
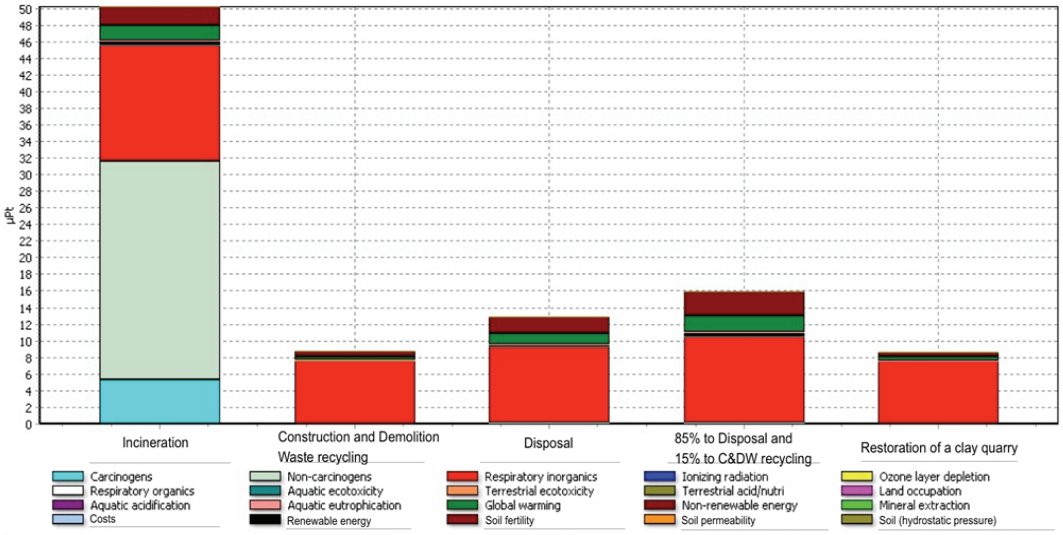


Fig. 4. Comparison between cement and lime plaster (left), straw and raw earth plaster and straw and raw earth plaster-km0 (right)



Comparing processes;
Method: IMPACT 2002 V2.10_141012_suolo_190313 V2.10 / IMPACT 2002+ suolo / Single score

Fig. 5. Comparison between different EOL scenarios

4. Conclusions

The process follows interesting pedagogical steps, replacing the creation/evaluation/analysis stage with another, based on the execution of the auto-construction building at the Terracini Campus of the University of Bologna.

This construction could play an important role as the place where all the initiatives, activities, courses, lectures developed by the Transition Team of the University of Bologna will be centralised. In other words, from an initiative of innovative learning education emerges a space that serves to change the way of devising solutions related to the sustainability or the energy efficiency of the Alma Mater Studiorum Università di Bologna.

In order to assure an eco-design of this space, an LCA approach is fundamentally important, at the same time with the application of sustainable building technologies. These results confirm the choice made during the design phase and allow the students to strength their knowledge in the field of sustainability methodology. The results of the LCA can be useful to guide the realization of the space for students: it will be realized with km0 materials like straw and raw earth at least for plaster and infill wall; it will be designed for an end of life compatible with selective dismissing, so that the raw materials can return to nature; in the manufacturing phase the students will be involved, to improve their skills and sustainability awareness.

Thus, we propose a Transition case study involving both education and sustainability in our universities.

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