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Procedia Environmental Science, Engineering and Management

19th International Trade Fair of Material & Energy Recovery and Sustainable Development, ECOMONDO,
3rd-6th November, 2014, Rimini Fiera, Italy

Selected papers (1)

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Aims and Scope

Procedia Environmental Science, Engineering and Management (P - ESEM) is a journal focusing on publishing papers selected from high quality conference proceedings, with emphasis on relevant topics associated to environmental science and engineering, as well as to specific management issues in the area of environmental protection and monitoring.

P - ESEM facilitates rapid dissemination of knowledge in the interdisciplinary area of environmental science, engineering and management, so conference delegates can publish their papers in a dedicated issue. This journal will cover a wide range of related topics, such as: environmental chemistry; environmental biology; ecology geoscience; environmental physics; treatment processes of drinking water and wastewater; contaminant transport and environmental modeling; remediation technologies and biotechnologies; environmental evaluations, law and management; human health and ecological risk assessment; environmental sampling; pollution prevention; pollution control and monitoring etc.

We aim to carry important efforts based on an integrated approach in publishing papers with strong messages addressed to a broad international audience that advance our understanding of environmental principles. For readers, the journal reports generic, topical and innovative experimental and theoretical research on all environmental problems. The papers accepted for publication in *P – ESEM* are grouped on thematic areas, according to conference topics, and are required to meet certain criteria, in terms of originality and adequacy with journal subject and scope.

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GUEST EDITORS

Fabio Fava, born in 1963, is Full Professor of "Industrial & Environmental Biotechnology" at the School of Engineering of University of Bologna since 2005.
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Other projects are 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 the Past- and the current 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-Enterprise and Industry 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 Horizon2020 Programme Committee.

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.

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COMPARATIVE STUDY IN THE SAFETY ASPECTS OF THE PRODUCTION OF ETHANOL FROM RENEWABLE AND NON-RENEWABLE SOURCES*

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Abstract

Flammable and combustible liquids are present in several workplaces. Fuels and many common products such as solvents, thinners, cleaners, adhesives, paints, waxes and polishes may be flammable or combustible liquids. Everyone, who works with these liquids, must be aware of their hazards and procedures, which allow their safe use. Nowadays, there is a copious amount of lignocellulosic biomass, that can be exploited for fuel ethanol production. Significant advances have been made on industrial scale towards the fuel ethanol generation from lignocellulosics and today there are many industrial plants for the production of bioethanol that are going to be born in the world. Ethanol, which is produced from biomass, provides unique environmental and economic benefits and can be considered as a safe and cleanest liquid fuel, which is alternative to fossil fuels. Ethanol can be generated by renewable sources and has another main advantage, because it can be easily blended with gasoline. When small amounts of ethanol are added to gasoline, there are many advantages; in particular the reduction of carbon monoxide and other toxic pollutants from exhaust gases of vehicles. As we talk about environmental benefits, the safety aspects of these new industrial plants (biorefineries) must be also considered. In order to assess these aspects, in this paper it has been decided to perform a comparative study between two processes for the production of ethanol: traditional process (hydration of ethylene) and fermentation (metabolic process that converts sugars from cellulosic substrates). The goal is to highlight the differences of the flash point along the entire length of these two industrial processes in order to assess their safety level. In fact flash-point is one of the most important physical properties used to determine the potential hazards of flammable and combustible liquids.

Keywords: bioethanol, biorefinery, flash point, safety

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1. The emerging use of bioethanol

During the past decade there has been a substantial increase in biofuels production in the United States as well as an increase of the workforce, which has been employed in this industry. It is estimated that the US biofuels industry could employ up to 94,000 people by 2016 (Demibras, 2009). Although there has been a great deal of research carried out on life-cycle and economic assessments for biofuels production, there is very little published information concerning research or programs, that are dedicated to occupational health and safety in this field. The limited data, that are currently available, suggest that workers in the renewable energy industry may experience reduced rates of occupational injury, illness, and fatality than do traditional fossil fuel energy extraction industries (Sumner and Layde, 2009). The main hazards, which are not infrequent in the traditional fossil industries, are fires, explosions and toxic releases. The most common is fire, but explosion is particularly significant in terms of fatalities and losses. An important safety aspect, which is highlighted in this paper, is the flash point, which is reached during the different processes phases (ethanol production).

Ethanol can be generated in two ways: fermentation of sugars or hydration (adding water) to ethane (Balat et al., 2009). Approximately 95% of the industrial ethanol produced in the world, is generated by the second process (Lyondell Company, 2003), this is because there are large amounts of ethylene low cost, produced by petrochemical refining activities (Limayem et al., 2012). The latest data, which have been shown by the scientific community, demonstrate that this trend is changing. In fact approximately 104 million m^3 of ethanol were produced worldwide in 2013 and over 80% (87.2 million m^3) were used in fuel applications. World leader in the production of bioethanol is the USA with 51.8 million m^3, followed by Brazil with 27.7 million m^3. In the USA, bioethanol is mainly used as a 10% petrol additive. E10 is the standard petrol fuel (Goldemberg, 2007). The USA introduced E15 in January 2011. In Brazil it is not only offered as a pure fuel (E100), but it is also blended with conventional petrol with a content of 20 to 25 %vol. Roughly 90% of the new vehicle registrations in Brazil are Flexible Fuel Vehicles (FFVs), which can use regular petrol, bioethanol or their mixture (Riitonen et al., 2013). In Europe, only in recent years the chemical industry is building new manufacturing sites for the production of second-generation bioethanol (Fig 1).

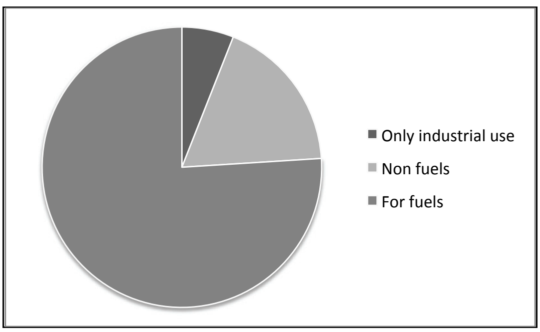


Fig. 1. Installed ethanol production capacity in the EU in 2014
(adapted upon State of the Industry Report 2014)

But it’s not just about fuel! Perhaps the best-known industrial user of ethanol – after transport – is the drinks industry, but it is also used to make perfumes, deodorants, paints, thermometers, cosmetics, medical uses, and can be used as a solvent beyond that it is a precursor of other chemicals derivatives (Martinot, 2013).

From the point of view of the economic aspect, it has been demonstrated in the past such as the construction of these new industrial plants, is economically advantageous, even if simple systems are used (Accardi et al., 2015) and always from preliminary studies comparative between traditional chemical plants and biorefineries, it is clear that the latest, have a low incidental index risk (Accardi et al., 2013).

2. Production of ethanol

Although today synthetic ethanol production is still privileged, in the world several industrial plants for the production of second-generation bioethanol are going to be completed. From a detailed study, that compares the two methods in the production of ethanol, some clear differences, that affect both environmental and process safety are evident (Table 1).

Table 1. Different characteristics between ethanol produced by hydration of ethylene and fermentative method

	Synthetic ethanol	***Bioethanol***
Industrial phases	Storage Ethanol reactor Ethanol production Distillation column	Pre-treatment Hydrolysis Fermentation Distillation column
Type of raw material	Non-renewable	Renewable
Type of process	Continuous	Fed-Batch
Labor	Minimal	High
Rate of reaction	Fast	Slow
Needed conditions	High temperature	Low temperature
	High pressure	Low pressure
Purity of product	Pure	Pure, after treatment
Needed energy	High	Low

From Table 1, it is evident that in the production of synthetic ethanol, kinetics is very fast (equation 1) in consequence of the presence of a large catalyst (H_3PO^4) quantity and the plant operation, which is based on continuous processes. It generates a product with high purity in low time, but with harder operating conditions (Baligia et al., 1965).

$$C_2H_4 + H_2O \rightarrow C_2H_5OH \qquad (1)$$

Fermentative method (Eq. 2) uses a biocatalyst (e.g. *S. cerevisiae*) and is characterized by a slower reaction kinetics due to batch plant solutions but in the face of a lower energy demand and easy operation conditions (Bomberg et al., 2014).

$$\text{Sugars} \rightarrow 2C_2H_5OH + CO_2 \qquad (2)$$

Lignocellulosic biomass consists of three major components: cellulose (50% ± 10), hemicellulose (35% ± 5) and lignin (15% ± 5). Cellulose and hemicellulose constitute the polysaccharides, which can be hydrolyzed to sugars, which could be fermented to ethanol. From cellulose fraction it's possible to extract glucans, which are converted into glucose monomers through enzymatic hydrolysis; it's also possible to obtain xylose monomers starting from hemicellulose fraction of biomass (Less, 1992).

3. Flash point

An important safety aspect, which is highlighted in this paper, is the flash point, which is reached during the different processes phases (ethanol production). Flammability is an important factor of safe practices for handling and storage of liquid mixtures and for evaluation of the precise level of risk. Flash point is an important property, which is used to determine the fire and explosion hazards of a liquid, and it is defined as the minimum temperature at which the vapor over the liquid forms (at equilibrium) a flammable mixture with air (Liaw et al., 2008).

The Occupational Safety & Health Administration (Yodaiken et al., 1986) defines a flammable liquid as having a flash point of not more than 93°C (199.4°F). In most cases, the hazard of a flammable liquid increases as the flashpoint decreases. A typical trend of the flash point of a binary mixture (water-ethanol) is shown in Fig. 2.

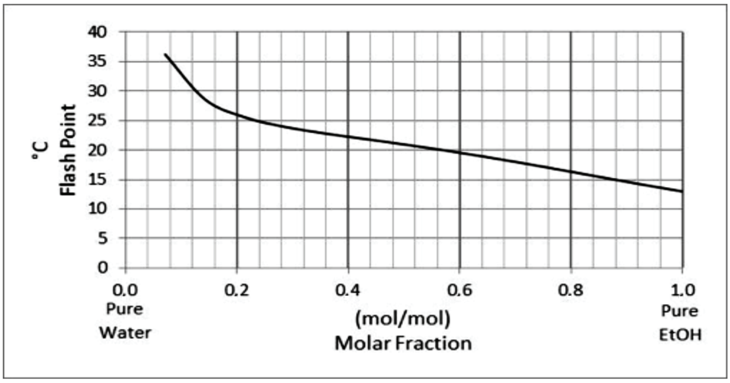


Fig. 2. Flash-point of liquid water/ethanol mixtures

The flash point of mixture can considerably deviate from the flash point values of the individual mixture components (Less, 1992). Prediction methods for evaluation of mixtures flash point are desirable and allow to improve the safety level of the industrial plants, because the flash point estimate can be considered an useful tool in order to mitigate the consequences of accidents. It is also fundamental to know exactly where an event of flash point could occur in an industrial plant in order to apply appropriate safety measures, which prevent a possible accident.

4. Flash point comparison: results

Thanks to the literature data it is possible to compare the main operating parameters for the production of ethanol vs. bioethanol (Cope et al., 1959; Fougret et al., 2001). The flash-points comparison is based on the same amount of produced ethanol (Lin et al., 2006).

For simplicity a binary mixture, which is composed by water and ethanol without the presence of other impurities, that could deflect the prediction calculation of the range of the flash point, is considered. The flash point characteristic, for the two different industrial plants, is determined by following the model, which is shown in Eq. 3. The molar fractions of ethanol (x_j) are calculated by the following equation and literature data (Lichtenstein, 1948; Quintero et al., 2008; Viola et al., 2004) and the results are shown in Fig. 3.

$$x_j = n_j/n \qquad (3)$$

where:
- n_j indicates the ethanol moles;
- n indicates the overall moles (water and ethanol).

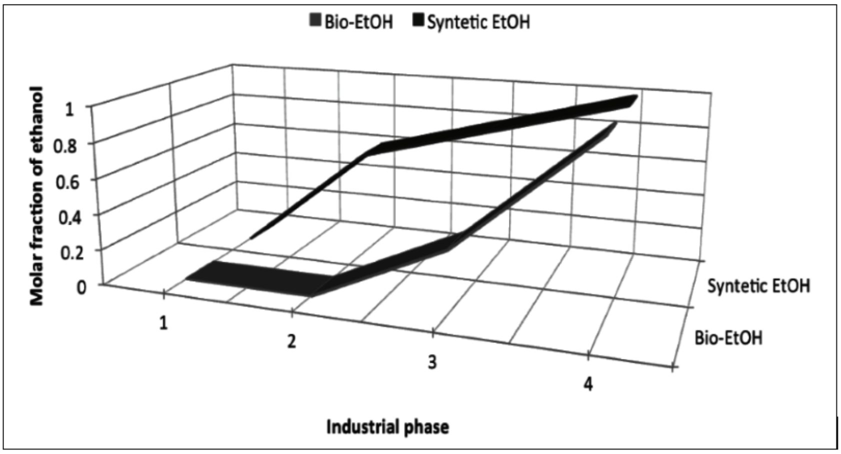
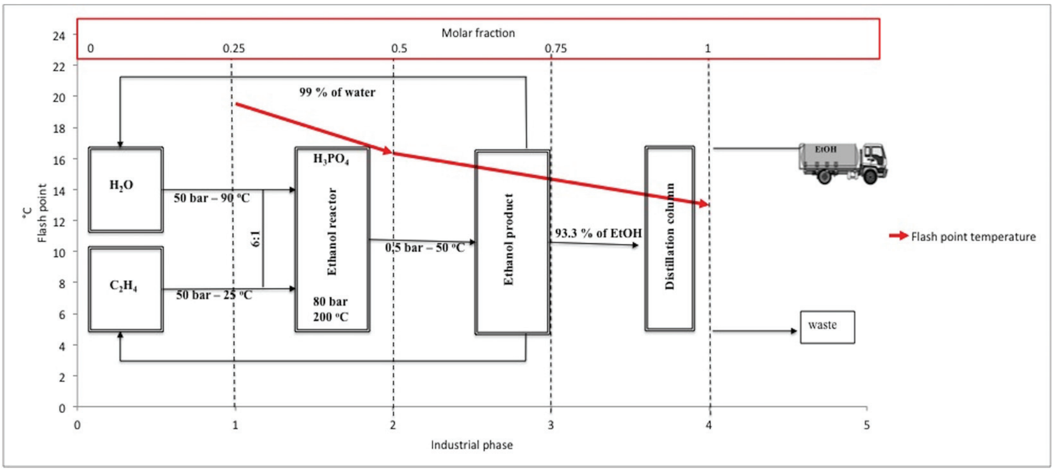


Fig. 3. Ethanol formation during the fermentative method (biorefinery) and hydration of ethylene (traditional process)

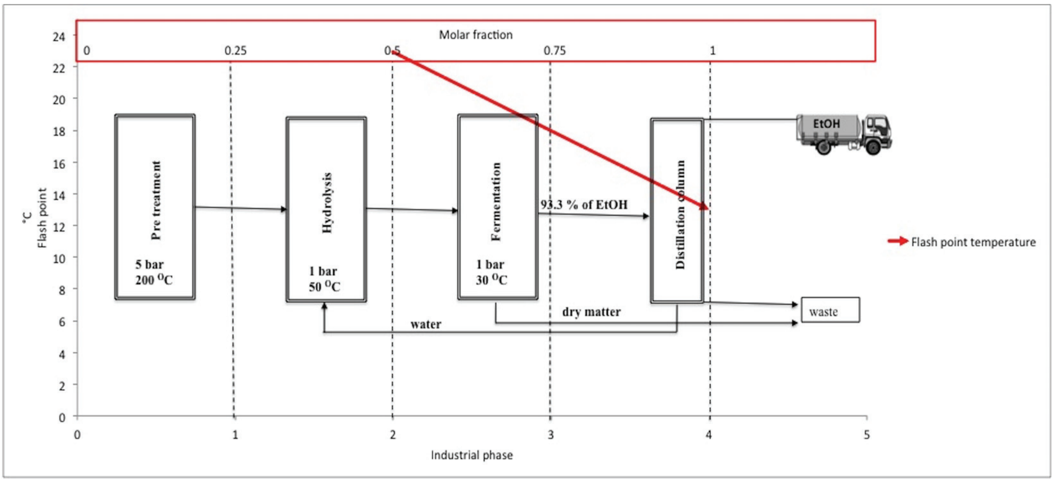
In the production of bioethanol there isn't the presence of ethanol in the first two phases of the process (1. pre-treatment and 2. hydrolysis), but there is subsequently a growing gradient of ethanol in the last phases (3. fermentation $x_j = 0.33$ and 4. distillation $x_j=1$). In the production of synthetic ethanol, its presence begins during the second process phase (2. ethanol reactor $x_j=0.6$) and there is subsequently a growing gradient of ethanol (3. ethanol production $x_j=0.8$) up to pure ethanol (4. distillation $x_j=1$).

In this way it's possible to compare the flash points, which are referred to the different molar fractions and processes phases and therefore we can identify the industrial phases, in which appropriate safety measures must be adopted in order to prevent flash point events (Fig. 4a and Fig. 4b).

From these considerations, it appears that the risk of flash point concerns three blocks of the traditional process (Fig. 4a), while for the production of ethanol by biotechnology, the risk of flash point is limited to the last two process blocks (Fig. 4b). It can be observed that the traditional process is characterized by lower values of flash point than fermentative method and therefore it is more dangerous than the process, which is carried out by the biorefineries. In fact the flash-point is included between 19.8°C and 16.5°C during the second phase (ethanol reactor), 16.5°C and 14.5°C during the third phase (ethanol production) and 14.5°C and 12.3°C during the fourth phase (distillation column), while the flash-point is included between 22.8°C and 17.9°C during the third phase (fermentation) of the fermentative method and 17.9°C and 13.2°C during the fourth phase (distillation column). In this way we can classify the different phases of the process (Table 2) according to the degree of danger (E.C.A., 2009; U.N. 2003).



a.



b.

Fig. 4. a. Trend of flash point during the ethanol production by hydration of ethylene (traditional process); **b.** Trend of flash point during the bioethanol production (biorefinery)

Table 2. Comparison of risk indexes for flash point

Industrial phases	***Synthetic ethanol (Label elements for flammable liquids)***		***Bioethanol (Label elements for flammable liquids)***	
	CLP	*DSD*	*CLP*	*DSD*
From 0 to 1	Absent	Absent	Absent	Absent
From 1 to 2	2	Highly Flammable	Absent	Absent
From 2 to 3	2	Highly Flammable	3	Flammable
From 3 to 4	2	Highly Flammable	2	Highly Flammable

In the two compared methods, the ethanol production from biorefineries only shows highly flammable event throughout the process line, while it can be noticed that these events are three during the traditional process.

5. Conclusion

Although the environmental and health risks, posed by the biorefineries, are expected to be lower than traditional chemical and petrochemical plants, there is still a lack of information about safety aspects of these new plants. However the scenario is changing in these last years. In fact there are various government activities and programs, which are aimed at improving occupational health and safety in the biofuels industry. In Italy, the Italian Workers' Compensation Authority (INAIL) has carrying out a research project, which has been funded by the National Centre for Disease Prevention and Control of the Italian Ministry of Health; this project has been aimed at providing a tool for transparent development of proactive safety standards in order to improve workers health and safety in the biorefineries. A wide variety of potential hazards has been studied in the Italian biofuels industry, including biological, chemical, and physical hazards. The potential exposures to these hazards are quite variable and depend on the specific technology, the stage of development and operation parameters. The INAIL research project involved industry in order to identify occupational health and safety risks and develop best practices.

The flash point is important for the classification of potentially explosive atmospheres. Flammable liquids with a high flash point are less dangerous than those with a flash point at ambient temperature or below. The December 2013 ASTM meeting of the D02 committee marked the turning-point for flash point testing. In this historical meeting, the safer ASTM D7094 flash point standard was officially accepted for the specifications of the following fuels: fuel oils (D396), diesel fuel oils (D975), gas turbine fuel oils (D2880), kerosene (D3699) and ethanol (D4806). This suggests the great attention to which these fuels are subjected, because of their high dangerousness. One of the main practices in the industrial safety is to try to minimize the risks, which could cause an accident. In order to obtain this aim, there are appropriate guidelines and regulations, that impose to train own staff, use mixtures with a higher flash point and improve technologies making improvements, which allow to minimize the risk of accidents. The safety aspects (flash-point), which have been analyzed in this study, give a confirmation that biotechnological processes (new technology) intrinsically have a lower risk factor than the traditional chemical plants. In fact the operating conditions are milder and therefore the direct consequence usually is the restriction of the risk areas in these industrial plants. For all these reasons many ethanol producers or engineering company are today focusing on designing and building-up new biorefineries as rapidly as possible in order to satisfy a growing demand.

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ENVIRONMENTAL IMPACT OF TOMATO PURÉE: ANAEROBIC DIGESTION OF BY-PRODUCTS AS MITIGATION STRATEGY*

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Abstract

Agricultural by-products and wastes usually represent a cost for farmers and agro-food industries. Nevertheless, concerning their use to produce biogas by the anaerobic digestion (AD) there are still unexplored possibilities. In fact, differently than for animal slurries already widely used as feedstock for biogas production, the wastes from agro-food industries are more rarely exploited as feedstock for energy purpose and therefore often represent an economic and environmental issue.
In this study, the environmental benefits arising from the AD of tomato by-products was evaluated, using the Life Cycle Assessment, as strategy to reduce the environmental load of tomato purée production systems. Nine impact categories were evaluated using the Recipe midpoint LCIA method.
Data concerning tomato purée production were collected in an agro-food industry processing each year 200.000 tons of fresh tomato. Laboratory tests were carried out as regard to the methane production of the different tomato by-products. Technical and operative data concerning the operativeness of AD plants were achieved by means of surveys in real AD plants fed with by-products from food industry
The AD of tomato by-products entails an environmental impact reduction for the tomato purée. The achieved results could be up-scaled to all the food industries with high heat demand producing considerable amounts of fermentable by-products employable as feedstock for biogas production.

Keywords: environmental impact, LCA, agricultural wastes

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*Selection and peer-review under responsibility of the ECOMONDO
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1. Introduction

Agricultural by-products (e.g., animal slurries, straw etc.) and wastes from agro-food industry (e.g. olive pomace, skins and peels of tomato, grape marc etc.) usually represent a cost for farmers and agro-food industries. Nevertheless, concerning their use to produce biogas by the anaerobic digestion (AD) there are still unexplored possibilities. In fact, differently than for animal slurries already widely used as feedstock for biogas production, the wastes from agro-food industries are more rarely exploited as feedstock for energy purpose and therefore often represent an economic and environmental issue (Bacenetti and Fiala, 2012; Szabo et al., 2014).

Despite of the agricultural by-products that are available over a wide area in little amounts over the whole year, the agro-food wastes have different characteristics: they are often concentrated in big amounts close to the agro-food industries and are available for a short time over the year. For example, the industry of tomato processing generates large amount of by-products in the harvest seasons during which the tomato fruits are processed. The industrial processing generates residues from water flumes, washing, sorting table, pulper-refiner and cleaning. In addition, some residues are constituted by the discards of the production line, such as immature, defective or damaged tomatoes.

The waste mass can be estimated in about 2-5% of processed product (Bacenetti et al., 2015; Del Borghi et al., 2013; Manfredi and Vignali, 2014). Wet and dry tomato pomace, constituted by skins, seeds and pulp, is the main part of the residual mass that comes from the pulper. In Italy, each year about 4.5 million tons of tomatoes are processed (World Processing Tomato Council, 2014). This activity involves a significant production of residues, mainly constituted by discarded tomatoes, skins, seeds and pulp. These by-products are generally wasted and represent an added cost for manufacturing companies and an environmental issues due to the difficult management, in particular greenhouse gas emissions. The exploitation of these residual materials results complex as their availability is mainly concentrated in the tomato harvest season (June - September). A valuable solution is the anaerobic digestion (AD) of these matrices to produce biogas for energy generation.

In this study, the environmental benefits arising from the AD of tomato by-products was evaluated, using the Life Cycle Assessment, as strategy to support the decision making for reducing the environmental load of tomato purée production system. In more details, the environmental impact of tomato purée production system in which the by-products are not valorized was compared to the system where these matrices are used as feedstock for biogas production.

2. Materials

Tomato purée production system has three steps: (1) crop cultivation, (2) tomato processing and (3) by-products management. Figure 1 shows the two production systems evaluated: the Alternative Scenario (AS) differs from the Baseline one (BS) only for the use tomato by-products for biogas purpose.

Tomato processing can be divided into:

- tomatoes unloading,
- selection and washing,
- chopping,
- blenching,
- concentration and refinement (in which the product is subsequently treated with a series of refiners that extract the juice by eliminating skins and seeds),
- pasteurization.

During section 2 a considerable amount of heat, produced by a natural gas burner, is consumed; in particular during the blanching the high temperature (80-90°C) is applied to inactive the pectolytic enzymes.

The Section 3 involves the management of the by-products arising from Section 2 that are mainly constituted by non-usable tomatoes (about 4000 tons/year) and skins and seeds (about 6000 tons/year). Usually (Baseline Scenario – BS), tomato by-products are sent back to the tomato fields as organic fertilizers (transport carried out by trucks with an average distance of 25 km). In this study, an Alternative Scenario (AS) is evaluated as regard to by-products management: the wasted tomatoes, skins and seeds are used to feed an AD plant located close to the food industry (0.1 km). The AD plant has an electrical power of 300 kW, codigesting tomato by-products, other by-products of the same industry and agricultural waste (cow and pig slurries). As regard to tomato by-products, the feeding of the AD plant is based on the use of tomato skins and seeds (storable as silage) during the whole year and of wasted tomatoes only during the tomato harvest season. When the wasted tomatoes are not available the AD plant is fed with other by-products locally available and a little amount of cow slurry as well.

The biogas produced is burned in a CHP (Combine Heat and Power) engine; the produced EE is fed into the national electric grid, while the ET is partially used to heat the digesters. The surplus heat is recovered and used by the agro-food industry itself during the tomato processing (concentration and pasteurization) substituting thermal energy usually generated by natural gas.

3. Method

In the last decade, Life Cycle Assessment (LCA) has become more and more applied to evaluate the environmental performances of agricultural processes. LCA is a methodology that aims to analyze products, processes or services from an environmental perspective (ISO 14040, 2006), providing a useful and valuable tool for agricultural systems evaluation.

4.1. Functional unit

In this study, 1 kg of tomato purée was selected as functional unit (FU). A gate to-gate perspective was applied: the core system is the tomato processing and the by-products management.

4.2. System boundary

A gate to-gate perspective was applied: the core system is the tomato processing and the by-products management; the cultivation phase as well as the packaging materials and some the downstream processes (e.g., delivery and distribution of the tomato purée) were excluded because equal into BS and AS. For tomato processing, the system boundaries consider the consumption of energy, fuels, and materials (e.g. salt,) as well as the emissions into water and air. In BS, for byproduct management, the system boundary includes only the tomato byproducts transport from the food industry to tomato field; while, for AS, the transport of the tomato by-products to the AD plant, biomass digestion, biogas utilization in a CHP are taken into account.

In AS, regarding the electricity (EE) and the heat (GET) generated by the CHP engine, only the share obtained by the AD of tomato by-products was included in the system boundaries. The digestate stemming from the AD of tomato by-products is used to fertilize the tomato cultivation. Digestate and tomato by-products have the same content of NPK and therefore can substitute the equivalent amount of mineral fertilizer. Therefore only the transport and the spreading on the tomato fields was included in the assessment. Figure 1 shows the system boundary for AS.

4.3. Inventory

Data concerning tomato purée production were collected in a food industry processing each year 200.000 tons of fresh tomato. Laboratory tests were carried out as regard to the methane production of the different tomato by-products (Bacenetti et al., 2015).

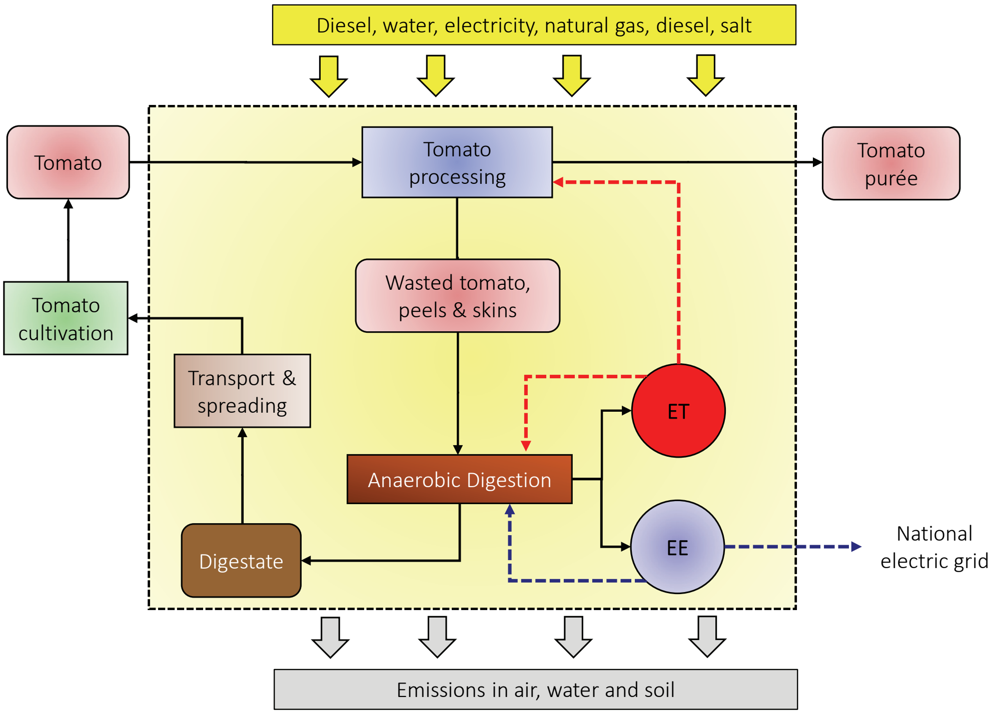

Fig. 1. System boundary for alternative scenario. Note: EE = electricity, ET = thermal energy; dotted lines highlight the energy self-consumptions

Data about chemical characterization of tomato purée by-products as well as about their methane potential were obtained by specific laboratory tests. For 30 samples of by-products (15 for wasted tomato and 15 for skins and seed), the Methane Potential (m3 of CH4 for tonne of byproduct digested) was evaluated in Lab-scale unstirred fermenters placed in thermostatic baths at 40°C (Negri et al., 2014). The inoculums were collected from different full scale AD plants. The achieved results are shown in Table 1. Technical and operative data concerning the operativeness of AD plants were achieved by means of surveys in real AD plants fed with by-products from food industry (Lijò et al., 2014a; Lijò et al., 2014b).

Table 1. Tomato purée by-products laboratory test results.

By-products	*Methane production*
	m^3/t of wet matter
Wasted tomato	20.07±1.57
Skins and seeds	52.33±3.19

4.4. Impact assessment

The characterization factors reported by the Recipe Midpoint method (Goedkopp et al., 2009) were used, the following impact categories were considered: climate change (CC), ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), photochemical oxidant formation (POF), particulate matter (PM), mineral depletion (MD) and fossil depletion (FD).

5. Results and discussion

Table 2 reports the environmental results for the selected FU. Figure 2 shows the environmental hotspots for the processing of tomato purée.

Table 2. Environmental impact for the FU

Impact Category	*Unit*	*Score*
CC	kg CO_2 eq	0.11744
OD	kg CFC-11 eq	$4.34 \cdot 10^{-9}$
TA	kg SO_2 eq	0.00022
FE	kg P eq	$1.26 \cdot 10^{-7}$
ME	kg N eq	$9.12 \cdot 10^{-6}$
POF	kg NMVOC	0.00023
PM	kg PM10 eq	$7.38 \cdot 10^{-5}$
MD	kg Fe eq	0.00067
FD	kg oil eq	0.05260

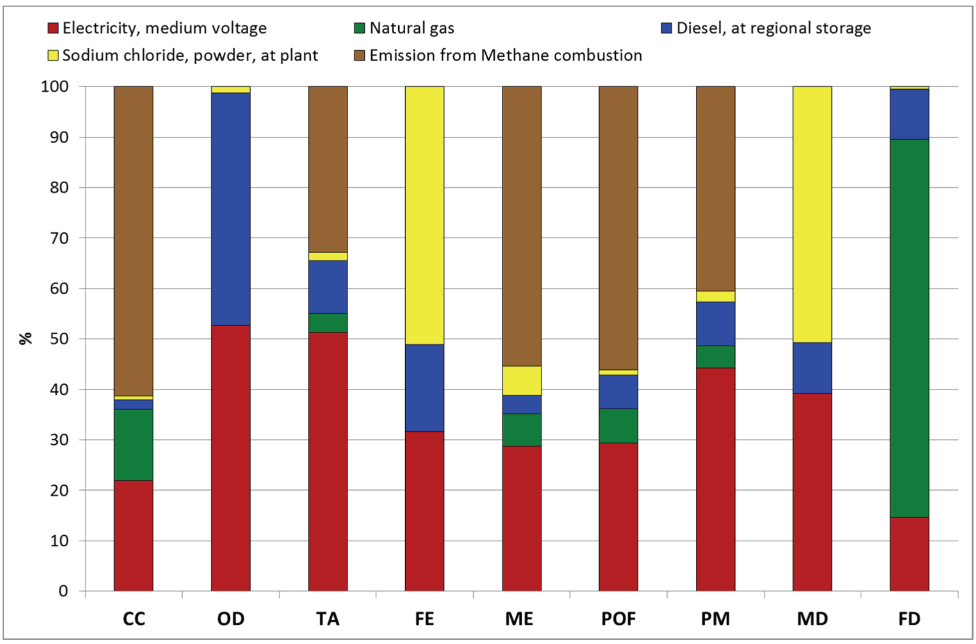

Fig. 2. Hotspot identification for the processing section

For 8 of the 9 evaluated impact categories, the main hotspots of processing step are the consumption of electricity and the fuel combustion emission. These latter are an environmental hotspots for CC (62%); POF (55%) and ME (about 57%). Consumption of diesel fuel and natural gas are hotspots for OD and FD. Figure 3 shows the comparison between BS and AS, as explained in the previous paragraph the differences are related to the different management of by-products.

For all the evaluated impact categories, the AD of byproducts improves the environmental performances of tomato purée (-14% for CC, -43% for OD; -20% for TA; -16% for FE; -12% for ME; -14% for POF, -18% for PM; -19% for MD and – 11% for FD).

Fig. 3. Comparison between BS and AS

6. Concluding remarks

In this study two different by-products management systems in the tomato industry were compared using LCA method. The baseline scenario represents the current situation; the alternative scenario is instead a potential mitigation strategy and it consists in the valorization of the tomato by-products in an AD plant. The achieved results highlighted that the AD of tomato wasted, skins and peels is an effective mitigation solution because it reduced the impact load for all the environmental effects considered.

The environmental benefit arises from the credits related to the production of electricity from biogas that avoid the generation from fossil fuels and, secondarily, from the exploitation (during the tomato processing) of the heat cogenerated by the CHP.

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ARSENIC, CADMIUM, LEAD AND MERCURY IN BIOTA FROM VENICE LAGOON: FROM SOURCES TO HUMAN EXPOSURE*

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Abstract

In this study As, Cd, Pb, and Hg sources and levels in sediments and biota from Venice Lagoon (Italy) are presented and discussed. Estimation of dietary exposure has been calculated in order to assess the human exposure to these harmful pollutants due to the consumption of fishery products.
The Venice Lagoon is diffusely contaminated from point and non-point sources and significant amounts of pollutants are accumulated in sediments, which may constitute a potential source of secondary pollution. Trace elements can be accumulated in marine organisms and transferred to humans through dietary intakes. Estimated weekly intake for Hg indicates that a potential risk cannot be ruled out for younger people.

Keywords: biomonitoring, health risk, trace elements, Venice Lagoon

1. Introduction

The Venice Lagoon is a sensitive area exposed to anthropogenic polluting sources. The watershed of the lagoon is heavily populated supporting approximately 1 million inhabitants and many chemical companies were located on the western shore of the lagoon in Porto Marghera. The municipality of Venice also contributes with urban waste water sewage and

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runoff. Significant amounts of pollutants are accumulated in sediments, which may constitute a potential source of secondary pollution.

The Venice Lagoon is also well known for its shellfish harvesting activity and fish breeding whose extensive production can be an easy target for chemical contamination. As, Cd, Pb, Hg are chemical elements of great concern because of high toxicity and potential accumulation in the food chain. Concentrations of these contaminants in sediments and different species of biota (two bivalve mollusc species: *Mytilus galloprovincialis*, *Tapes philippinarum* and four fish species: *Zosterisessor ophiocephalus*, *Sparus aurata*, *Dicentrarchus labrax*, *Mugil cephalus*) from Venice Lagoon sampled in 2014 are presented and discussed. The results have been used to assess the human exposure to these harmful pollutants due to the consumption of fishery products.

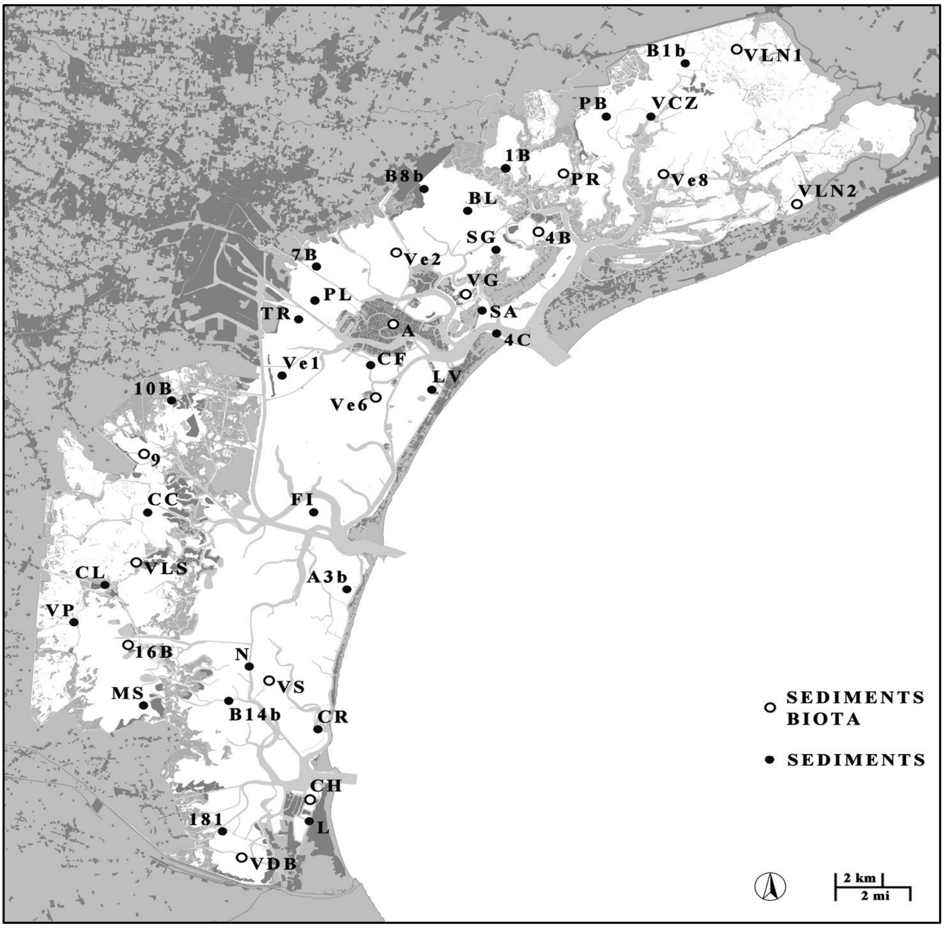

Fig. 1. Sampling sites

2. Materials and methods

Sediments were collected in 42 sampling sites in 2014 (Fig. 1). Samples were freeze-dried, homogenised and mineralised by means of microwave acid digestion (USEPA Method 3051A, 2007). As, Cd, and Pb were analyzed by means of graphite furnace atomic absorption spectrometry (AAnalyst800, Perkin Elmer) (USEPA Method 7010, 2007), Hg was determined using a flow injection mercury system (FIMS400, Perkin Elmer). Accuracy was checked by analysing the RTC standard reference material CRM016 (Trace metals in sediments).

Samples of biota were collected in a restricted number of the same sampling sites (Fig. 1). The bivalves were collected in August 2014 (VG, 4B, Ve8, PR, Ve2, A, Ve6, 9, 16B, VS, VDB, CH for *M. galloprovincialis*; VG, 4B, 9, Ve2, 16B, VS, VDB, CH for *T. philippinarum*). Fish were collected in May 2014 (Ve8, 4B, Ve6, 16B, PR for *Z. ophiocephalus*; VLN2, VLS for *S. aurata*; VLS for *D. labrax*) and October 2014 (Ve6, 4B, PR, Ve8 for *Z. ophiocephalus*; VLS, VLN1 for *S. aurata*; VLN1 for *D. labrax*; VLS for *M. cephalus*).

Bivalve soft tissues and fish dorsal muscle were freeze-dried and homogenised. Concentrations of elements in biota samples were measured by inductively coupled plasma mass spectrometry (ELAN DRC II, Perkin Elmer) after a microwave acid digestion (USFDA, 2013). The accuracy of the measurements was checked by analysing the NIST standard reference materials 1947 (Lake Michigan fish tissue) and the NIST 2976 (mussel tissue).

3. Results and discussion

Boxplots of the measured concentrations of As, Hg, Cd and Pb in sediments are given in Fig. 2. Higher concentrations of Hg were found in sediments at central and northern lagoon. The largest single source of Hg in Venice Lagoon was a chlor-alkali plant operating from 1951 to 2008 located in Porto Marghera. Hg from industrial discharges has contaminated sediments of the central lagoon, facing the industrial area. This contamination has spread to sediments of northern lagoon.

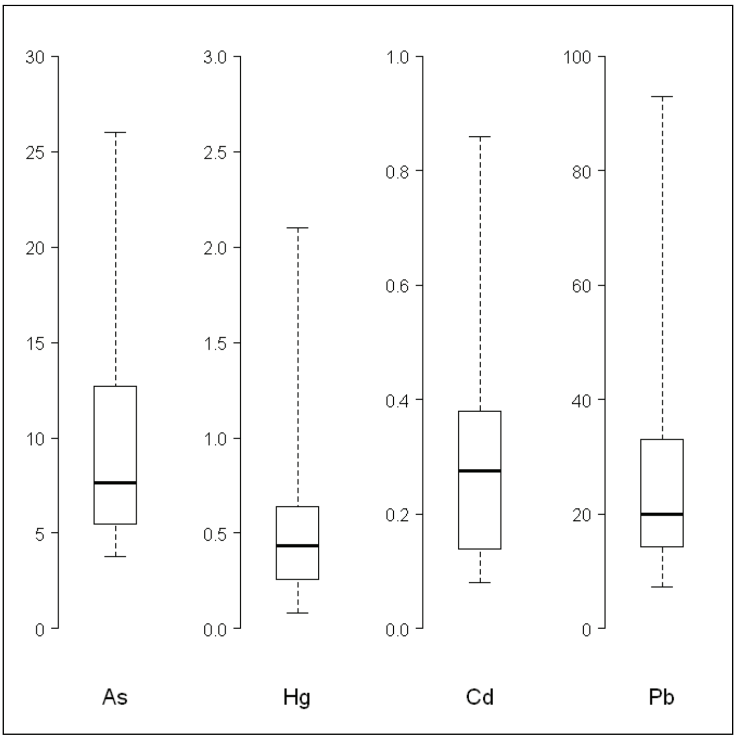

Fig. 2. Concentrations in sediments (mg/kg dw)

The most elevated Hg level was found in the sampling site located in Rialto (2.1 mg/kg) confirming the notion that the city of Venice is a net source of Hg to the lagoon (Bloom et al., 2004). The contamination of Hg is of concern also because Venice Lagoon has been recognised as a source of methylation of Hg (Bloom et al., 2004). Furthermore, tidal flushing seems to play an important rule in the release of both total Hg and methyl-Hg from surface sediments to water column during tidal flooding (Guédron et al., 2012).

Concerning Cd and Pb it is not possible to identify a single important source as for Hg. A wide variety of substances, including many heavy metal oxides are used by glasswork in Murano and the waste products of glassmaking may be a source of Cd, Pb and As. Antifouling and paints used by a number of shipyards located in the lagoon could be another source of heavy metals (Hg and Pb). Pyrite ashes, enriched in As, Cd and other heavy metals, along with other industrial waste were used in the past for marsh land filling for the construction of new embankments inside the industrial area. Moreover a number of landfills are located along the western shore of the lagoon, some of them were used to dispose pyrite ashes. Despite the presence of point sources of anthropogenic As a geochemical origin has been recognised to explain the distribution of As in the Venice Lagoon (Degetto et al., 2003).

Even if the percentage of the available fraction of trace elements is low (less than 1% for Cd and Pb) (Argese et al., 2003), heavy metal concentrations found in the industrial and urban canal sediments are presently the most likely sources of toxic metals to the lagoon. Moreover, positive benthic fluxes for Cd measured in two different sampling sites suggest that Cd may be remobilised from the sediments to the water due to sub-oxygenation condition of water (Turetta et al., 2005).

The concentrations of the investigated elements in bivalve soft tissues and in fish meat are given in the plots of Fig. 3.

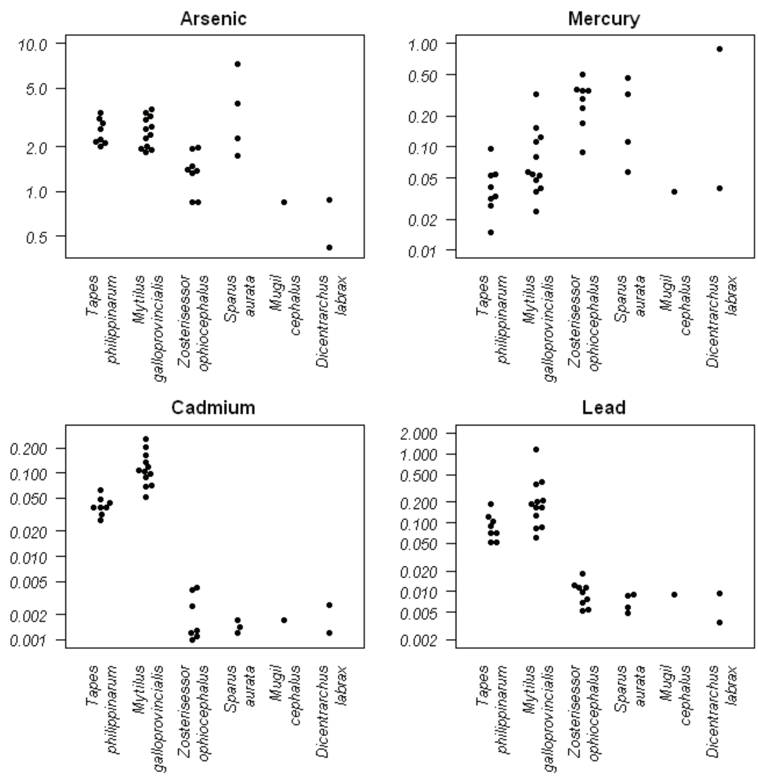

Fig. 3. Concentrations in biota (mg/kg ww, log scale on Y-axis)

The European legislation established permissible limits for certain contaminants in foodstuffs (EC, 2006). In comparison with limits set for bivalve molluscs (Cd: 1.0 mg/kg ww, Pb: 1.5 mg/kg ww, Hg: 0.5 mg/kg ww) and fish muscle meat (Cd: 0.05 mg/kg ww, Pb: 0.3 mg/kg, Hg: 0.5 mg/kg ww) all the values measured were lower than these limits, with the exception of Hg level measured in one sample of *D. labrax* sampled in VLN1 (0.88 mg/kg ww) and in one sample of *Z. ophiocephalus* sampled in Ve8 (0.51 mg/kg ww), both of them in the northern basin. By comparing the mean concentrations measured in bivalves and fish it was found that the more elevated As, Cd, and Pb levels were observed in bivalves rather than in fish (Table 1). On the contrary Hg levels were higher in fish as a consequence of the biomagnification of methyl-Hg along the food chain.

In order to assess the potential hazard of As, Hg, Cd and Pb being transferred to humans the estimation of dietary exposure was calculated using the mean concentrations expressed as wet weight found in this work for bivalves and fish (Table 1). Calculations were performed for different classes of age on the basis of the consumption rates of the Italian population reported by the European Food Safety Authority (EFSA) for the categories molluscs and fish meat (Table 2) (EFSA, 2014).

Table 1. Mean concentrations in bivalves and fish: mg/kg ww (mg/kg dw)

	As	*Hg*	*Cd*	*Pb*
Bivalves	2.6 (15)	0.073 (0.37)	0.089 (0.46)	0.20 (1.08)
Fish	1.8 (7.6)	0.28 (1.3)	0.0017 (0.0074)	0.0087 (0.042)

EFSA has established tolerable weekly intakes (TWI) for inorganic Hg (4 µg/kg bw per week), methyl-Hg (1.3 µg/kg bw per week) (EFSA, 2012) and Cd (2.5 µg/kg bw per week) (EFSA, 2011). There are no tolerable weekly intakes established for As and Pb. EFSA reported that a range of benchmark dose lower confidence limit ($BMDL_{01}$) values between 0.3 and 8 µg/kg bw per day for As was identified for lung, skin and bladder cancer, as well as skin lesions (EFSA, 2009). EFSA identified BMDLs for critical Pb-induced effects: developmental neurotoxicity in young children ($BMDL_{01}$ 0.50 µg/kg bw per day), effects on systolic blood pressure in adults ($BMDL_{01}$ 1.50 µg/kg bw per day) and nephrotoxicity in adults ($BMDL_{10}$ 0.63 µg/kg bw per day) (EFSA, 2010).

Table 2. Classes of age and relative seafood consumption

	Toddlers	*Other Children*	*Adolescents*	*Adults*	*Elderly*	*Very Elderly*
Classes of age (years)	1-3	3-9	10-17	18-64	65-74	>74
Body weight (kg)	12	23.1	52	73.9	76	71.2
Molluscs (g/d)	-	8.8	13.8	9.9	8	4
Fish meat (g/d)	29	21.6	26.7	31.1	35	22.2

The estimated daily intakes of As and Pb and the estimated weekly intakes of Cd and Hg are shown in Fig. 4, expressed respectively as µg/kg bw per day and µg/kg bw per week. The highest dietary exposure to the investigated elements was estimated in the younger population. The maximum calculated percentage contribution to Cd TWI found in the present work was of 9.5% for the class of age “Other children” due to bivalves. The percentage contribution of bivalves to Pb $BMDL_{01}$ for developmental neurotoxicity in young children was of 12%. The highest dietary exposure contribution to As and Hg is due to fish.

The highest amount of As in fish and seafood is in the form of organic As, less toxic than inorganic forms (EFSA, 2009). Argese et al. (2005) investigated the speciation of arsenic in *M. galloprovincialis* collected in Venice Lagoon and found that As appears almost exclusively under organic forms among which arsenobetaine presents the highest percentage.

The highest amount of Hg in fish and seafood is in the form of methyl-Hg, more toxic than inorganic forms. Dominik et al. investigated the biomagnification of Hg and methyl-Hg in the food chain of Venice Lagoon and reported a ratio of methyl-Hg in total Hg of 65% for *M. galloprovincialis*, 97% for juvenile *S. aurata* and 95% for *Z. ophiocephalus* (Dominik et al., 2014). The resulting exposure of the younger population exceeds the established TWI for the methyl-Hg.

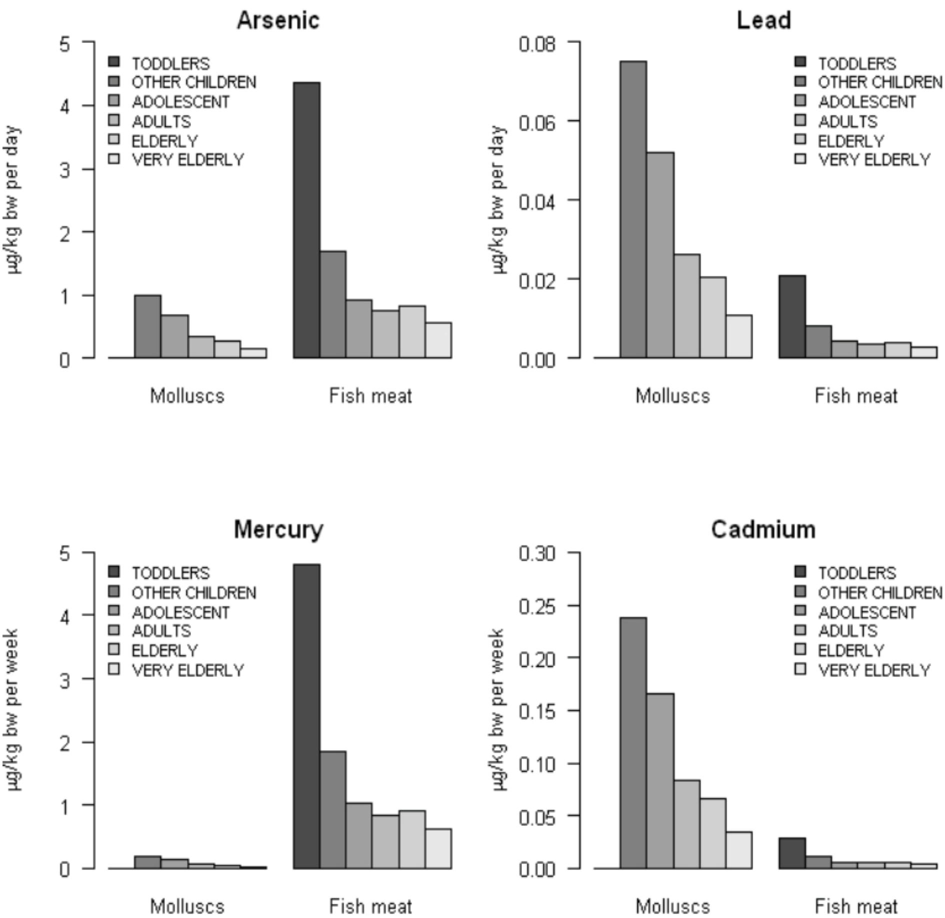

Fig. 4. Estimated intakes for different classes of age

4. Concluding remarks

The Venice Lagoon is diffusely contaminated with As, Hg, Cd, and Pb from a number of point and non-point sources. Biota is an easy target of accumulation for these harmful pollutants which may be transferred to humans through dietary intake of seafood products. An evaluation of the impact on human health of fishery products indicates that a potential risk cannot be ruled out for vulnerable groups.

Indeed an estimated weekly intake exceeding the established TWI has been calculated for methyl-Hg in younger people.

Acknowledgements
Sampling was performed in the framework of the monitoring activity for the classification of chemical status of the Venice Lagoon according to the European Directive n. 60 of 2000 funded by Ministero delle Infrastrutture e dei Trasporti – Provveditorato Interregionale alle Opere Pubbliche del Veneto –Trentino Alto Adige – Friuli Venezia Giulia and his sole concessionaire Consorzio Venezia Nuova. We acknowledge all the people who developed the project and the Thetis team for field activities who carried out sampling.

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IMPROVING INDOOR AIR QUALITY (IAQ) SELF-INSPECTION AND QUALITY CHECK MEASURES TO REDUCE THE GAP BETWEEN BUILDING PREDICTED AND REAL PERFORMANCES*

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Abstract

Built to Specifications (Built2Spec), a new Horizon 2020 EU-funded project in the Energy Efficiency in Buildings domain, seeks to eliminate the gap between a building's designed and as-built performance. Among others, the project focuses on developing instruments and procedures to quickly check and characterize Indoor Air Quality (IAQ) conditions directly on the field during the construction phase, reducing the time and cost needed to obtain the results as well as increasing information transparency. The collected information will be gathered on a virtual management support platform to process the field data and provide recommendations. This paper will briefly present overall project objectives and then focus on the project work on IAQ testing.

Keywords: energy efficiency, on site assessment, construction measurement, predicted vs. real performance gap

1. Introduction

Built2Spec (**B2S**) is an EU Research Project funded within the Horizon 2020 framework addressing the building performance gap between designed and real performances. The project is developing a set of technological advances for self-inspection and quality assurance that will be put into the hands of construction stakeholders (designers, contractors,

*Selection and peer-review under responsibility of the ECOMONDO
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surveyors,…) to help meeting EU energy efficiency targets, new build standards, and related policy ambitions (EC Directive 2010; CEPHEUS 1998; PHPP, 1998).

B2S expands upon a cloud-based construction support platform (VCMP), conceived following the most advanced integrated design and delivery framework for the building sector and hosting applications that facilitate worksite activities and quality compliance by putting knowledge in hands of contractors. This includes shared design specifications, 3D models, installation guidelines, information on regulatory frameworks, and help from construction experts on smartphones and tablets. New self-inspection technologies managed within the platform and developed in the project include:

- portable single device for **Indoor Air Quality** (IAQ) tests;
- portable, innovative low pressure air tightness technique;
- a novel lightweight portable sound source;
- special IR camera in smartphones;
- rapid BIM modelling via instant 3D capture with smartphones;
- smart sensor-embedded construction elements (structural and environmental).

2. IAQ: an overview

Current construction guidelines, procedures and standards for residential buildings usually do not focus much on IAQ - except in special cases; i.e. they are cursory and inadequate for specifying materials and designing ventilation systems to ensure a healthful indoor environment. Inhabitants' awareness as well as the rapid developments and introduction of new building materials and commercial products, pose challenges to systems integration in the design, construction and operation phases of modern buildings (Spengler and Chen, 2000).

As underlined by a study conducted in 2008 in five European cities (Maruo et al., 2008), the choice of building materials strongly influence IAQ (e.g. sources of VOCs and formaldehyde). Particularly, the specific construction procedures implemented can have a major impact on IAQ in the building, thus there is a real need to monitor the IAQ during all the construction stage to conduct self-inspection and quality check measures. For this reason B2S will develop:

- miniaturized and portable analyser (configurable and controlled remotely by a SW) for on-site tests. This device is capable of recording dynamically the most relevant IAQ parameters providing immediate results and feedback to user, reducing costs and times spent on-site;
- proper algorithm to treat and analyse the data relying on big data and data mining techniques;
- integrated IAQ indicator(s) for the end-user interface based on current knowledge, regulatory limits and health risks;
- integration of a proper module regarding IAQ on the VCMP platform. This provides a user friendly visualization of the results (i.e. indicators), requests feedbacks from users and delivers recommendations to the end-user.

3. New device for IAQ monitoring

There are many pollutants indoor, and these pollutants can be very harmful. One example is formaldehyde, confirmed as carcinogenic to humans: many studies show it is present in our living places at concentrations higher than WHO recommended thresholds. Recent studies on dwellings in France, coordinated by CSTB in 2010 and 2011, showed that 80% of homes were above the WHO recommended threshold. The most efficient way to deal with this type of pollution is to eliminate the source.

However it is difficult to measure pollutants in situ: specifically, current measurement methods do not provide real-time results, making it very costly and cumbersome to identify a source of pollution. As a result, indoor pollution is not properly dealt with, causing absenteeism and a risk of penalties or litigation for non-compliance. Thanks to its advanced technology, Blue Industry and Science gives its customers the ability to identify and remove the source of pollution for many pollutants of indoor air. Any organization, conscious of the well-being of its employees or visitors, will benefit from these advances.

Blue Industry and Science develops and markets compact multi-gas analysers, with real-time analysis down to ppb level (part per billion). The analysers (Fig. 1) operate on the principle of infrared laser spectroscopy, and use a proprietary optical source (VHR-TL technology for Very High Resolution Laser Tuneable) which is tuneable in wavelength with a very high resolution (0.01 cm-1). This VHR-TL source can target many gases with very low detection limits: hundreds of gases are quantifiable below 100 ppb, and with a very wide dynamic range. Blue has obtained a first patent of its own and several others are being filed on the various technology blocks included in the analyzer.

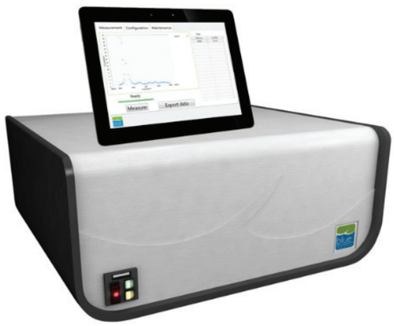

Fig. 1. Blue-X FLR8 MultiGas Monitor (http://www.blueindustryandscience.com)

The Blue-X FLR8 MultiGas Monitor is a portable gas analyser, emitting in the spectral range from 3 to 4.2µm, which is the band where most VOCs absorb IR energy.

Targeted gases include many pollutants of indoor air and species relevant to HSE regulations:

- hydrocarbons;
- amines;
- carbonyl compounds including aldehydes;
- alcohols;
- halogenated compounds;
- esters;
- organochlorines;
- thiols; ...

The technology provides great economy of means in the daily use of the analyser:

- easiness to use, requiring no specialist knowledge to operate the technology;
- no need for frequent calibration;
- no consumables, with the exception of a filter for particulate matters;
- direct reading of the results;
- very fast start (the analyser is operational in a few minutes).

The Blue X-FLR8 MultiGas Monitor has been designed for simple and efficient operation (Fig. 2), allowing up to 90% cost savings on current measurement techniques.

Fig. 2. Blue-X FLR8 MultiGas Monitor on site (http://www.blueindustryandscience.com)

4. New IAQ strategy introduced by B2S: introduction of the evaluation indicators

The indoor air quality is a relatively recent issue. It is now a concern increasingly strong because its health impact is best known and illustrated. Concepts and approaches of sustainable buildings as LEED, BREEAM and HQE approaches integrate since recent years, performance and resources targets on this topic. But generally designers of buildings put very little effort on this topic and focus energy issues, carriers also of good points for these approaches of building certification. However, Attitudes tend to change and policies are also beginning to integrate the issue of IAQ by new regulations. For example, in France, there is now a regulation which obliges the control of IAQ of a certain category of building, those opened to the public (Decret, 2011). These regulatory controls are based on the realization of measurement campaigns using passive metrology solutions that provide information on the average exposure over 5 days (ISO 16000-4, 2011; ISO 16017-2, 2003). They focus on chemical pollutants, especially formaldehyde and benzene. There is a lack of dynamic tool which can give data on in situ chemical pollution. Normative solutions are two-step method which need a laboratory analysis (by chromatography). Developing new real-time metrology solutions which can instantly inform/alert about the indoor air quality is very promising and is the next challenge.

Today's methods for measuring indoor air pollution routinely involve 2 steps, with first on site sampling and then analysis in a lab, a process that takes days or weeks to complete. In spite of the increasing importance of Indoor Air Quality in modern construction requirements, no IAQ test is usually conducted during the construction process: IAQ is measured only after commissioning of the building. In different studies on indoor air quality, despite the variety of outcomes, one fact is consistently found: the importance of indoor sources of VOCs and formaldehyde. Thus, a study conducted in five European cities in public buildings and individual houses in 2008 (Missia et al., 2010) has put forward the importance of building materials on indoor air quality. Indeed, for most of the compounds the main source is within buildings. This is especially true for new buildings or buildings containing new furniture. It has also been proven that building construction materials were the only emission source for some compounds such as acetone or formaldehyde. In parallel, studies to measure both VOC concentrations in indoor air and emission rates of building construction materials also emphasized the link between both (Hodgson et al., 2010).

It was also shown in a study in Finland, that a dwelling designed and furnished with low-VOC materials had better indoor air quality both before and after 5-month occupancy (Tuomainen et al., 2001). Therefore, there is a real need to know, anticipate and control emissions from building materials used to control thereafter the quality of the air inside the building.

The way to implement materials during the construction can have a major impact on indoor air quality in the building. Thus, it is necessary to be able to measure indoor air quality from the worksite to the exploitation of the building, with a portable and fast analyser. B2S project aims to develop this new generation of analyser able to measure on site and in real time different pollutants.

Nevertheless, the development of new sensors of analysers is not enough sufficient in order to give a new solution to survey and control air quality. We need also to develop tools for smart analysis of the data collected by the metrology solutions. Smart analysis of the data means that we need to develop a user-machine interface able to:

- interact with all Metrologic systems/sensors/analysers and collect the data;
- do a smart treatment of the data: need to develop an algorithm;
- provide the results of air quality as a simple indicator or couple of indicators;
- give recommendations for users or workers.

One of the main issues is relative to the construction of a simplified indicator. Define an Air quality indicator is a big challenge but also a real need that B2S is trying to address. Physics parameters (T, HR, CO_2), chemical pollutants, physical pollutants (particles) and bio contaminants (molds, mites, …) are responsible for the good or bad air quality and the variety of the parameters makes the assessment of the air quality very complex. An indicator is clearly needed to facilitate the communication on this issue.

To reach our objective, we need first to investigate the pollutants we must integrate in our final indicator. Are all pollutants relevant in the case of the construction step monitoring? The definition of the parameters we want to monitor will also lead to select the sensors/analysers and then to build the specifications of the final meta-analyser. Our meta-analyser will integrate the Blue industry solution and other relevant sensor/analyser.

The construction of the air quality indicator will start when the measured parameters will be defined. An algorithm will be built in order to take into account the variety of the parameters and their variability over time. Some bricks will be developed, as database of thresholds, database of guideline values, calculation program. The algorithm will permit to make quickly the analysis of all data relative the national and international guidelines and give a final score of air quality. The score will be linked to an air quality ranking, developed using the example of the French ATMO rating (exterior air rating).

To our knowledge, it doesn't exist a unique indicator for indoor air quality assessment. Few connected objects proposed for indoor air quality assessment an interface with a colour grade but the developed ranking and algorithm function like a black box. We need to explore this kind of solutions in parallel with our development.

5. Concluding remarks

In this paper is presented the EU funded Project Built2Spec which intents is to eliminate the gap between a building's designed and as-built performance. An overview of the project and main purposes are presented along with the standard strategy for Indoor Air Quality tests and usual devices for IAQ available on the market.

This paper is focused on describing the tools and procedures will be developed across the life time of the project to check IAQ directly on the field during the construction phase, reducing the time and cost needed to obtain the results as well as increasing information transparency. Finally an alternative way (developments in progress) based on the definition of proper indicators is presented as a future strategy to assess the IAQ.

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USE OF "SEDIMENT QUALITY GUIDELINES" FOR THE ECOTOXICOLOGICAL EVALUATION OF MARINE SEDIMENTS IN THE SIN OF TARANTO*

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Abstract

The SIN area of Taranto It. Act (L. 426/98) is the site of a big commercial port, of the Italian Navy, of the Metallurgy factory "ILVA", of the refinery ENI and of a large urban centre. Consequently, the discharge into the sea of industrial and urban waste products generate a situation of environmental impact very complex in that besides suspension materials waste products contain a "pool" of organic and inorganic toxic contaminants (ammonia, cyanides, fenols, hydrocarbons, heavy metals) very often not degradable and that influence the whole cost area of Taranto. Said compounds released into water undergo dispersion processes and of accumulation in the sediments and in the aquatic organisms. In this case arise the necessity of environmental restoration and requalification also with dredging and following transfer of dredged material towards decontamination plants.

Keywords: environmental impact, remediation, heavy metal, sediment

1. Introduction

In the last few years we have witnessed an increase of the interest in sustainable management of contaminated sediments, especially in Sites of National Interest (SIN). In this context attention has been paid both to the improvement of characterization techniques and to

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the development of "quality" index of sediments, which associates concentration level of different contaminants to ecotoxicological evaluation, in order to define possible remediation necessity. The characterization of contaminated marine sediments is of crucial ecological, toxicological and economical importance (Chapman et al., 2002), as the political decisions about management choices are strongly influenced by the technical evaluation of their quality and risks associated to them.

The transfer of contaminants from sediments to biota is a necessary requirement for the occurrence of toxicity, but the bioaccumulation dynamics of contaminated sediments remain up to now active research fields (McCarty et al., 2002). In fact, chemical data only cannot offer an adequate base for identifying the potential risks associated to the contamination (Chapman, 2007). In this respect, the development and the use of quality guidelines (SQGs) represent a valid instrument to give environmental meaning to the analytical data of concentration. The field of study in this research has been that of Taranto seas (Mar Grande, Mar Piccolo and the Gulf of Taranto) SIN for the remediation due to high concentration of contaminants coming from punctiform and spread sources, Fig. 1. The approach used has been that of "weight of evidence" which define the concentration of contaminants that show evident damaging biological effects. As regards metal contamination different quality index such as TEL, PEL and ERL, ERM, geoaccumulation index and Organic Carbon have been put in comparison in order to obtain risk maps.

Fig. 1. Map of sampling stations in Mar Piccolo (MP), Mar Grande (MG) and in the Gulf of Taranto (GT)

2. Objectives

The aim of the present work has been the evaluation of the kind Weight of Evidence, with the employment of Sediment Quality Guidelines of the quality of marine sediments to the purpose of risk prediction associated with the presence of pollution.

In fact, sediments constitute a step of accumulation of toxic substances, which are not often determinable in the water column. The accumulation and subsequent release can become potential source of contamination. The evaluation of quality sediments provide essential information to evaluate the environmental condition in aquatic ecosystems, especially form the ecotoxicological point of view (Long et al., 1998).

3. Materials and methods

Organic Carbon (%OC) has been estimated in the sediments to the purpose of studying the correlation between organic substance and metals. For the analysis of Organic Carbon has been employed the method published in the Ordinary Supplement of the Official Gazzette (Italian G.U. of 25 May 1992) relating to the description of Organic Carbon within agricultural lands. The principle of this method consists in the oxidation of the organic fraction with dichromate in acid environment due to the presence of concentrated sulfuric acid, at a temperature of 160°C and in the following titration (in presence of 4-diphenylammine sodic sulfate as index) with ferric-ammine sulfate of dichromate with no reaction. To evaluate the extent of metal contamination we have also estimated geoaccumulation index (Igeo). Geoaccumulation index has been calculated by using the following formula:

$$I_{geo} = \log_2 Cn/1.5\ Bn \qquad (1)$$

where *Cn* is the concentration in the sediment for metal *n*. *Bn* is the level of background for the metal *n* and 1.5 is a factor used to eliminate levels' variations of background due to lithological variation. For evaluate sediments quality have been used also ecotoxicological quality index such as TEL (Threshold Effect Level)/PEL (Probable Effect Level) and ERL (Effect Range Low)/ERM (Effect Range Median) (McDonald et al. 1996 and Long et al. (1995).

4. Results and discussion

4.1. Levels of Organic Carbon

In the Table 1 have been entered the values of the Organic Carbon in the sediments of Mar Piccolo, of Mar Grande and of the Gulf of Taranto. The result obtained from the analysis of the Organic Carbon it is possible to deduce important information. In fact, the Organic carbon plays a basic role in the transport and absorption of metals in the sediments. As showed in the table, the levels of Organic Carbon in the sediments of (range 4.81-16.84 % CO) are higher than those of the Gulf (range 2.51- 7.29 % CO) and of Mar Grande (range 0.08- 0.50 % CO). The station with the higher content of Organic Carbon is that located in the first inlet of Mar Piccolo and by of ILVA's water scooping machines (station MP01 with value of 16.84% CO), whereas the station MG04 (0.08 % CO) located in Mar Grande has showed the lower content of Organic Carbon.

Such data mean that urban waste products are discharged in Mar Piccolo, which can be previously purified or not, and coming from the town of Taranto and its province. Further, the Mar Piccolo is a slow renewal sea and has a scarce hydrodynamics with high speed of sedimentation. In fact, the discharging of organic material in the marine ecosystem with scarce hydrodynamic energy has as an immediate consequence the consumption of oxygen dissolved in the waters. This determines the triggering of anoxia phenomena and the production of compounds such as sulfur hydrogen coming from the anaerobic degradation of the organic substance. The sulfur hydrogen produces the decrease of the pH in the interstitial waters with re-dissolution of metals linked to the carbonates, be the precipitation of metallic sulphurs. From the evaluation of the data between the content of Organic Carbon and the levels of metals in the Mar Piccolo, the Mar Grande and the Gulf of Taranto' sediments has resulted that does not exists a correlation between the content of metal and the different station and the Organic Carbon. Therefore the distribution of metals seems to be linked to sources of contamination restricted such as industrial waste in the sea area beyond Punta Rondinella (Gulf of Taranto), to the activity of the Navy Yard and of fuel refuelling station of the Italian Navy (Mar Piccolo).

Table 1. Content of organic carbon (%) in the sediment of the del Mar Piccolo, Mar Grande and Gulf of Taranto

Station Mar Piccolo	*Seno*	*Corg (%)*	*Station Mar Grande*	*Corg (%)*	*Station Gulf of Taranto*	*Corg (%)*
MP01	I	16.84	**MG01**	0.26	**GT01**	6.02
MP02		7.36	**MG02**	0.30	**GT02**	4.58
MP03		9.11	**MG03**	0.30	**GT03**	5.24
MP04		8.48	**MG04**	0.08	**GT04**	3.00
MP05		9.81	**MG05**	0.50	**GT05**	4.24
MP06	II	9.94	**MG06**	0.38	**GT06**	7.04
MP07		4.81	**MG07**	0.13	**GT07**	7.29
MP08		9.23	**MG08**	0.21	**GT08**	3.72
MP09		5.63	**MG09**	0.18	**GT09**	2.51
			MG10	0.38		
			MG11	0.20		

4.2. Meal contamination and geoaccumulation index

Geoaccumulation index is represented by 7 classes, each indicating a different pollution degree (Table 2). From the values obtained from I_{geo}, showed in the Table 3, we deduce that for Hg the sediments of the stations of the first inlet are included in the classes 4, 5 and 6 (from polluted to strongly polluted), whereas the stations MP06, MP08 and MP09 of the second inlet, are included in the classes 2 and 3 (from moderately to polluted).

Table 2. Geoaccumulation index and classes of pollution

I_{geo}	*Classes*	*Pollution*
> 5	6	Strongly polluted
4 - 5	5	From polluted to Strongly polluted
3 - 4	4	Polluted
2 - 3	3	From moderately to polluted
1 - 2	2	moderately polluted
0-1	1	Not polluted to moderately polluted
0	0	Not polluted

Considering that the class 6 of the I_{geo} indicates an enrichment factor 100 times higher than background level, we can affirm that the sediments of the stations of the first inlet are at risk for Hg. Instead, for Pb, Cu e Ni the sediments do not present high concentrations such as to classify the sampled areas as risk areas for such metals (classes 1 and 2 of the I_{geo}). Also the sediments of the Gulf of Taranto do not present such concentrations to arouse troubles. In fact, the sediments for all metal analyzed are included in the classes 0 and 1 of the geoaccumulation index.

This different contamination of Mar Piccolo, Mar Grande and the Gulf of Taranto can be explained by the scarce hydrodynamics and water renewal. This state facilitates the sedimentation of organic material and particulate, and also of metal polluting materials and it plays a basic role in the transport and absorption of metals in the sediments. Is very difficult to establish the value of B_n for the sediments of Mediterranean Sea in that there are many areas with different geochemical variable and different anthropogenic impact. In this work, the geoaccumulation index has therefore been estimated by using background values estimated by Turekian e Wedepohl (1961) for the earth crust and background values determined for some metals in the sediments of the Ionian Sea by Buccolieri et al. (2006) (Table 3). The choice of different background values allows to compare the obtained data considering different areas of the Mediterranean Sea, even if the comparison of background values is often difficult. This because metal concentrations are determined into different fractions of sediments and by using different analytical procedures. The results of geoaccumulation index showed in the Table 4, confirm the difference among the station of Mar Piccolo, Mar Grande and the Gulf of Taranto by using both background values of Turekian and Wedepohl (1961) and Buccolieri et al. (2006), with exemption of Ni and V that show in all stations concentrations classified as no contaminated.

Table 3. Comparison between geochemical values of background (B_n) for Hg, Cd, Pb, Cu, Ni, V and Sn in the marine sediments (μg g^{-1} dry sediment)

Metals	***B_n (Turekian and Wedepohl, 1961)***	***B_n (Buccolieri et al., 2006)***
Hg	0.4	0.07
Cd	0.3	not determined
Pb	20	59
Cu	45	47
Ni	68	57
V	130	not determined
Sn	6	not determined

The stations classified from polluted to strongly polluted have been showed in bold in the Table 4. By using the background values of Turekian and Wedepohl, the station have been classified as not polluted, except those of Mar Piccolo, which result to be classified from not polluted to moderately polluted. For Cd the stations of Mar Piccolo and of the Gulf of Taranto have been classified as not polluted and the stations of Mar Grande have been classified from not polluted to moderately polluted. For Cu, by using both background values all stations have resulted as not polluted, except those GT02, MP03 and MP04, which have been classified from not polluted to moderately polluted and the station MP02, which is moderately polluted. There are also significant differences in the results for Hg and Pb. For Hg all the stations of Mar Piccolo have resulted to be contaminated with the two background levels taken into consideration, in particular the station MP04. By modifying the background levels also the evaluation of the contamination state for some metals is in consequence modified. This demonstrates the importance of the choice of background levels, for the evaluation of contamination by trace elements and the importance implements several information to the purpose to obtain a correct diagnosis of the ecosystem health state.

Table 4. Geoaccumulation index (Igeo) of heavy metals estimated in the sediments of Mar Piccolo, Mar Grande and the Gulf of Taranto

Station	I_{geo}										
	Hg	***Cd***	***Pb***	***Cu***	***Ni***	***V***	***Sn***	***Hg***	***Pb***	***Cu***	***Ni***
MP01	1.53	-0.17	0.99	-0.27	-0.75	-0.93	-0.64	**4.04**	-0.57	-0.33	-0.50
MP02	1.77	-0.79	2.11	1.15	-0.92	-1.19	0.32	**4.28**	0.55	1.09	-0.67
MP03	**3.28**	-1.40	1.50	0.26	-0.72	-1.09	0.12	**5.79**	-0.06	0.20	-0.46
MP04	**4.27**	-0.63	2.20	0.36	-0.82	-0.89	0.70	**6.78**	0.64	0.30	-0.56
MP05	**3.18**	-1.17	1.97	-0.07	-0.68	-0.88	0.27	**5.70**	0.41	-0.13	-0.42
MP06	0.28	-1.32	0.35	-1.07	-0.84	-1.42	-1.62	2.80	-1.21	-1.13	-0.58
MP07	-4.32	n.d.	-1.48	-2.23	-1.24	-1.84	-1.71	-1.81	-3.04	-2.30	-0.99
MP08	1.81	-1.49	0.94	-0.43	-0.79	-1.32	-0.64	**4.32**	-0.62	-0.49	-0.53
MP09	-1.91	-2.68	-0.87	-1.54	-1.08	-1.47	-0.42	0.61	-2.43	-1.60	-0.83
MG01	1.25	2.69	1.08	-1.20	-1.04	-1.93	-0.58	**3.77**	-0.48	-1.26	-0.79
MG02	0.82	1.61	0.54	-1.52	-1.17	-1.34	n.d.	**3.34**	-1.02	-1.58	-0.92
MG03	-0.74	1.94	-0.47	-1.52	-0.68	-1.33	-1.42	1.78	-2.03	-1.58	-0.43
MG04	-3.10	-0.24	-1.24	-4.45	-3.44	-4.12	n.d.	-0.58	-2.80	-4.52	-3.19
MG05	-1.26	1.33	-0.38	-2.37	-2.18	-3.15	n.d.	1.25	-1.94	-2.43	-1.93
MG06	-0.42	0.93	0.12	-2.51	-1.90	-2.44	n.d.	2.10	-1.44	-2.57	-1.64
MG07	-1.82	0.74	-0.90	-2.69	-0.92	-2.08	n.d.	0.70	-2.46	-2.75	-0.66
MG08	-0.51	0.62	-0.37	-2.57	-1.76	-2.04	n.d.	2.00	-1.93	-2.64	-1.51
MG09	-3.58	-1.68	-2.58	-4.58	-3.91	-3.33	n.d.	-1.07	-4.14	-4.64	-3.65
MG10	-0.45	0.42	-0.35	-2.67	-2.40	-2.85	n.d.	2.07	-1.91	-2.73	-2.15
MG11	2.30	1.60	0.48	-2.45	-2.03	-2.00	n.d.	**4.81**	-1.08	-2.51	-1.77
MG12	1.49	2.24	0.52	-1.59	-1.34	-2.06	-2.11	**4.00**	-1.04	-1.66	-1.08
MG13	1.81	2.66	n.d.	-0.60	-1.19	-0.96	-0.37	**4.32**	n.d.	-0.66	-0.93
GT01	-1.32	-1.79	0.15	-1.45	-2.09	-2.34	-1.26	1.19	-1.41	-1.52	-1.84
GT02	-1.96	-2.91	0.23	0.09	-2.62	-2.25	-2.07	0.55	-1.33	0.02	-2.37
GT03	-1.08	-0.97	1.22	-0.60	-1.70	-2.09	-1.36	1.44	-0.34	-0.67	-1.45
GT04	-2.58	-2.49	-0.87	-2.96	-1.62	-1.87	-1.89	-0.07	-2.43	-3.02	-1.36
GT05	-1.49	-1.49	-0.03	-2.28	-2.45	-2.83	-1.14	1.02	-1.59	-2.34	-2.19
GT06	-1.77	-4.49	0.15	-4.86	-1.47	-1.67	-1.16	0.75	-1.41	-4.92	-1.21
GT07	-2.50	-5.49	-1.15	-2.66	-2.03	-2.01	-2.58	0.01	-2.71	-2.72	-1.77
GT08	-3.98	n.d.	-1.93	-3.72	-2.67	-2.76	-2.11	-1.47	-3.49	-3.78	-2.41
GT09	-3.98	n.d.	-2.63	-4.81	-3.56	-2.84	-4.49	-1.47	-4.20	-4.88	-3.31
	Obtained by using the values of B_n by Turekian and Wedepohl, 1961							Obtained by using the values of B_n da Buccolieri et al., 2006			

n.d. not determinated

4.3. Sediment quality index

For the concentrations of Hg, Cd, Pb, Cu and Ni have been used the values of the sediment quality guidelines (Table 5).

Table 5. TEL, PEL, ERL e ERM sediment quality guidelines for Hg, Cd, Pb, Cu, Ni (μg g^{-1} d.w)

	TEL	*PEL*	*ERL*	*ERM*
Hg	0.13	0.70	0.15	0.71
Cd	0.68	4.20	1.2	9.6
Pb	30.2	112.2	46.7	218.0
Cu	18.7	108.2	34	270
Ni	15.9	42.8	20.9	51.6

Table 6. Percentage of the stations that exceed the values of PEL and ERM respect to various basins

		<TEL	*≥TEL and <PEL*	*≥PEL*	*<ERL*	*≥ERL and <ERM*	*≥ERM*
Mar Piccolo	**Hg**	11	11	78	11	11	78
	Cd	100	0	0	100	0	0
	Pb	22	45	33	33	67	0
	Cu	11	78	11	33	67	0
	Ni	0	0	100	0	22	78
Mar Grande	**Hg**	15	46	39	8	53	39
	Cd	23	77	0	54	46	0
	Pb	62	38	0	92	8	0
	Cu	62	38	0	92	8	0
	Ni	15	54	31	23	46	31
Taranto Golfo	**Hg**	44	56	0	67	33	0
	Cd	100	0	0	100	0	0
	Pb	56	44	0	89	11	0
	Cu	67	33	0	78	22	0
	Ni	11	89	0	44	56	0

The aims of ERL TEL and ERM PEL can be compared. Both indexes fix three concentration range (Table 6). Those lower than ERL or TEL identify areas relatively contaminated and therefore with a limited toxicity risk; those included between ERL-ERM and TEL-PEL refers to areas in which the potential toxic effects upon organisms are casual. Concentrations equivalent or higher to ERM-PEL show contaminated sites in which the recurrence of toxic effects is rather high. From the comparison of TEL/PEL we deduced that the Mar Piccolo represents the area at higher ecotoxicological risk: Ni and Hg exceed respectively the limit values of PEL in the 100% and 78% of the examined stations, whereas Pb and Cu respectively in the 33% and 11%. Considering the results of sediments sampled in the Mar Grande, we point out that Hg and Ni only exceed the values of PEL and of ERM. As regards the Gulf of Taranto the major part of the areas taken into consideration is within the lower limits of TEL and in the range TEL-PEL.

None station of the Gulf of Taranto presents a value higher than PEL. When we consider the index ERL-ERM the situation appears to be different, because they put limits less restrictive than TEL-PEL. The Mar Piccolo remains nevertheless the area with higher grade of contamination. Hg and Ni exceed the values of ERM in 78% of the examined stations, whereas for the other metals the concentrations are lower or included within ERL and ERM. As regards the Gulf of Taranto there exist no troubles, considering that the major part of the stations show concentrations lower than ERL.

5. Concluding remarks

From the comparison of the Sediment Quality Guidelines it has been showed that Mar Piccolo represents the area with a major ecotoxicological risk and with a higher degree of contamination. As regards Mar Grande and the Gulf of Taranto the situation is not troubling.

The results obtained with this type of approach on contaminated sediments coming from the industrial coast allows to investigate by integrating data obtained from multidisciplinary methods. This model for the evaluation of weight of evidence is obtained by the integration of different quality index, that are easy to apply and that give an objective evaluation of the sediment quality in different environmental context.

The integration of the chemical analysis with SGQ supply a powerful instrument for the establishment of the danger linked to polluted sediments and to toxicological risks.

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MONITORING PROGRAMME FOR THE CHEMICAL STATUS OF VENICE LAGOON ACCORDING TO THE EUROPEAN WATER FRAMEWORK DIRECTIVE (2000/60/CE)*

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Abstract

The monitoring of the chemical status of the Venice Lagoon according to the European Water Framework Directive (2000/60/CE) has been conducted during the period 2011-2014. Samples of water, sediment, bivalves and fishes of the lagoon have been collected and analysed for priority chemical substances. As for water, the survey revealed the exceeding of the Environmental Quality Standards for 4-nonilphenol in four water bodies and for benzo(g,h,i)-perylene +indeno (c,d)-pyrene in one more water body. Several chemicals exceeded the Quality Standards in the upper layer of sediments.
Mercury is an element of particular concern both for its distribution in sediments both for its bioaccumulation in bivalves and mainly in fish tissues. Tissue residues of mercury are frequently higher than available standard for biota in all the sampled species, with upper levels in fish than molluscs, revealing the process of biomagnification also at low levels of the trophic web. However tissue residues are lower than the limit of 500 µg/kg ww imposed by European Community (Reg. 1881/2006) for the commercialization of fish products.

Keywords: water framework directive, environmental quality standards, priority substances

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1. Introduction

The lagoon of Venice, located in the northern part of the Adriatic Sea (Italy), is the largest Italian Lagoon and the largest wetland in the Mediterranean region. Three inlets connect the lagoon to the Adriatic Sea allowing the water turnover. The drainage basin is densely populated and conveys into the lagoon industrial, agricultural urban and domestic waste waters. However, the establishment of local specific regulations entered into force starting from 15 years ago and the implementation of measures in the field of sewage, wastewater treatment, agriculture and zootechnics in the drainage basin have achieved important targets of lagoon pollution prevention.

Other sources of pollution come from the near industrial area of Porto Marghera (mainly historical pollution, due to the progressive reduction of current industrial activities, land restoration and improvement of waste water treatment) and from the historical center of Venice, located in the middle of the lagoon. Intense boat traffic and clam farming are other diffuse pressures which can affect water and sediment quality through the fuel combustion process, hull boat maintenance and through the physical alteration of the lagoon bottom, increasing sediment resuspension and turbidity.

In the last decades the lagoon environment has been studied in the frame of several monitoring projects, mainly promoted by the Venice Water Authority (Ministry of Infrastructure and Transports), allowing to adequately understand the main ecological processes occurring in the ecosystem and the pollution level of water and sediments.

Recently, after the entry into force of the Italian legislation (DM 260, 2010) implementing the European Water Directive (EC Directive, 2000), the operative monitoring of the chemical and ecological status of the lagoon has been set up according the rules of the Directive. The monitoring has been also recommended by the River Basin Management Plan of the Eastern Alps (first emission in 2010) which includes the territory of the lagoon of Venice, its drainage basin and the coastal area.

In this paper we discuss some of the main outcomes of the chemical monitoring of the lagoon, started in 2011 and currently ongoing, promoted by the Ministry of Infrastructures and Transports –Venice Water Authority - through its concessionary Consorzio Venezia Nuova. The official classification of the lagoon water bodies is performed considering the water concentrations of priority substances, but surveys on sediments and on bioaccumulation were also performed in order to complement the overall picture of lagoon contamination. The water, sediment and tissue residue concentrations of the monitored chemical substances have been evaluated with respect to the Quality Standards established by the EC Directive 105 (2008) and by the transposing Italian Law (DM 260, 2010).

2. Materials and methods

The monitoring of the chemical status of all the 14 water bodies of the water lagoon according to the European Water Directive started in 2011 with a monitoring network (Fig. 1) composed by 20 stations for water monitoring, up to 48 stations for sediment monitoring and 14 stations for bioaccumulation monitoring (Table 1).

As for water, the initial complete list of 46 priority substances monitored in the first monitoring period (2011-2012) was then shorted (38 substances) excluding those chemicals which had previously never been detected and which were not considered as relevant in the water district, as resulted by the inventory of emissions, discharges and losses performed according to the Art. 5 of the EC Directive 105 (2008). The lists of monitored substances are those of DM 260 (2010), with the analytical methods consistent with the law requests.

The monitoring results (chemical concentrations in water, sediment and animal tissues) have been compared to the National Quality Standards established by the Italian Ministerial Decree, DM 260 (2010).

As for water, the standards were transposed by those of the EC Directive 105 (2008), which defined standards both for the annual average (AA-EQS) and for the maximum allowable concentration (MAC-EQS). This directive has been now replaced by the EC Directive 39 (2013), establishing new standards, the Italian transposition process is currently ongoing.

As for sediments, the upper layer of 5 cm was collected and the analysis was performed on the 22 priority substances requested by the national legislation. Finally, for bioaccumulation investigation, different species, belonging to different trophic levels were selected: *Mytilus galloprovincialis* and *Tapes philippinarum* for bivalves, *Zosterisessor ophiocephalus, Dicentrarchus labrax and Sparus Aurata* for fishes. The analysis was performed for mercury, hexachloro-butadiene and hexachloro-benzene.

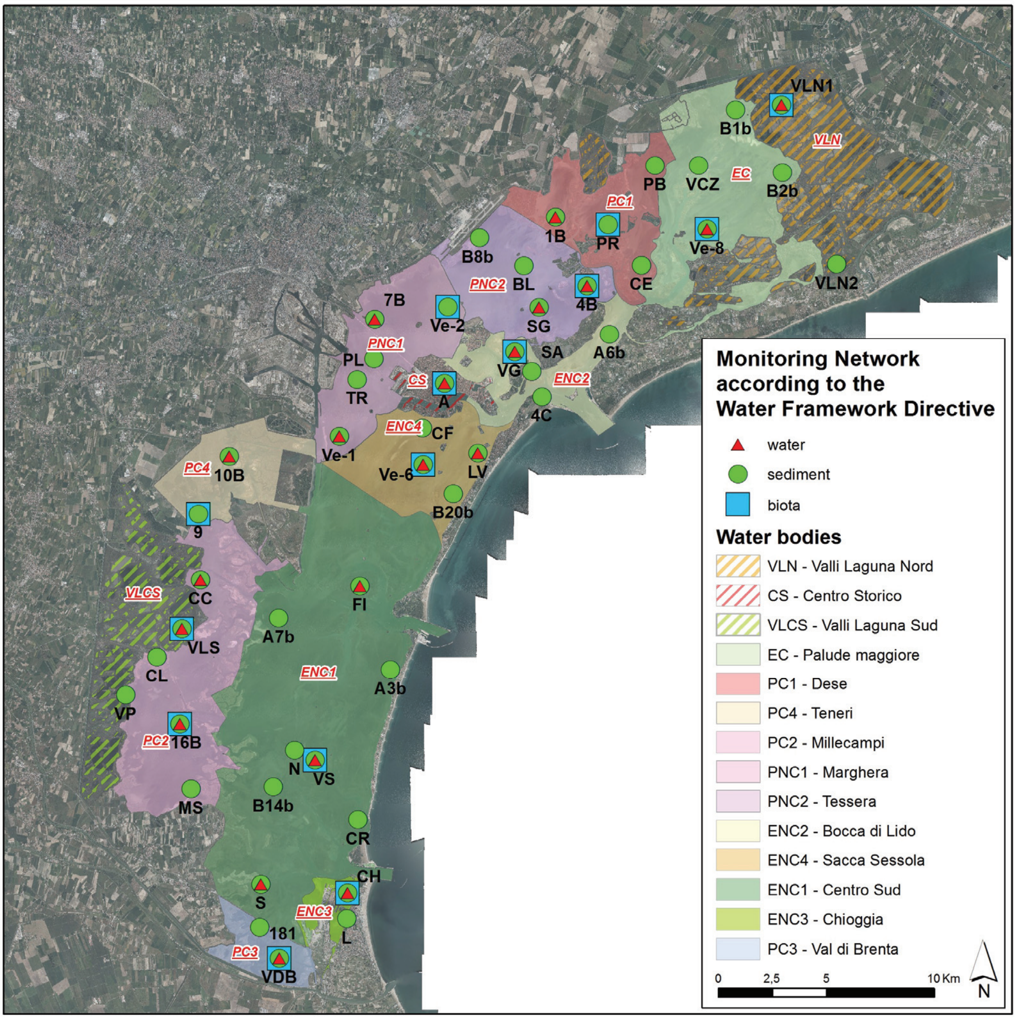

Fig. 1. The monitoring network of the Venice Lagoon for the chemical status of water, sediment and biota

Table 1. Chemical monitoring design of the Venice Lagoon according to EC Directive 60 (2000)

	2011	*2012*	*2013*
Water monitoring	12 monthly campaigns, 20 stations	2 campaigns, 20 stations	12 monthly campaigns from July '13 to June '14, 20 stations
Sediment monitoring	1 campaign, 48 stations	1 campaign, 36 stations	1 campaign, 42 stations
Bioaccumulation monitoring		2 campaigns, summer and autumn, 14 stations, bivalves	1 campaign, 14 stations, bivalves and fishes

3. Results and discussion

3.1. Water monitoring

The overall monitoring of the lagoon waters revealed an high percentage of data below the analytical detection limit for several chemicals, with about an half of the monitored parameters never detected both in the monthly monitoring of 2011, both in the monthly monitoring of 2013-2014. During the monitoring of 2011-2012, all the chemical concentrations complied with the Environmental Quality Standards (AA-EQS, MAC-EQS), leading to provisionally classify all the lagoon water bodies as "good". Otherwise, the monitoring of 2013-2014 revealed the presence of two priority substances with concentration higher than the environmental quality standards: 4-nonyl-phenol in four water bodies of the lagoon and benzo(g,h,i)-perylene +indeno (c,d)-pyrene in one more water body.

The 4-nonylphenol (NP), part of alkylphenols family, is used in several industrial and agricultural applications. In the environment it is also formed mainly by degradation of the respective polyethoxylated (NPE), compounds widely used as surfactants in numerous chemical formulations such as detergents, paints, dispersing agents in pesticides, products for the personal hygiene (Ferrara et al., 2001). The use of NP has been restricted by the European legislation (EC Regulation, 2006): it shall not be placed on the market, or used, as substances or in mixtures in concentrations equal to or greater than 0.1 % by weight for several purposes, such as industrial and domestic cleaning, textile processing, cosmetic products etc. As for pesticides, national authorizations or biocidal products containing nonylphenol ethoxylates as co-formulant, granted before 2003, are not affected by this restriction until their date of expiry. Currently, the European Commission has planned to review this regulation, with a major restriction of NPE in the textile products, in order to limit the release into the aquatic environment mainly through imported textiles being washed.

The spatial distribution of 4-nonylphenol in the lagoon of Venice (Fig. 2) doesn't trace the presence of specific and recognizable sources of pollution, highlighting diffuse sources of this chemical. 4-nonyl-phenol exceeded the Maximum Allowable Concentration (2 μg/L) in three sampling stations, all located in the northern lagoon of Venice: Ve-8 (water body of "Palude Maggiore" – EC), VLN1 (water body of "Fish Farms of the Northern lagoon" and 4B (water body of "Tessera" - PNC2). The Average Annual Concentration exceeded the quality standard (0.3 μg/L) in two of the previous mentioned stations (Ve-8 e 4B) and in another station (LV) located in the water body "Sacca Sessola" – ENC4, located in the central basin of the lagoon, south of the Venice city.

Monthly concentrations of 4-nonylphenol in the 4 stations where the exceeding of the quality standards has been detected, showed a fluctuating behavior, without evidencing a seasonal or a common pattern among the different stations. At the Station of Palude Maggiore a clear anomalous peak of 94 μg/L has been detected in the sample of December 2013, far higher than the maximum allowable concentration and far higher than the other concentrations measured in the same station during the monthly monitoring.

The sum of benzo(g,h,i)-perylene +indeno (c,d)-pyrene (belonging to the priority Polyciclic Aromatic Hydrocarbon identified by the European Community) exceeded the Annual Average Environmental Standard (0.002 µg/L) in the station located in the historical center of Venice in the main inner channel of the city (Canal Grande, Rialto) affected by an intense boat traffic. In this station the concentration of benzo(g,h,i)-perylene +indeno (c,d)-pyrene (Fig. 3) showed one single peak concentration value, corresponding to the sample collected in the month of September 2013 (0.03 µg/L). This concentration value heavily affected the calculation of the annual average and so the comparison with the annual average environmental standard. For this substance the Maximum Allowable Concentration was not established.

The presence of 4-noylphenol and benzo(g,h,i)-perylene +indeno (c,d)-pyrene was already detected in the 2011-2012 monitoring, with concentrations sometimes near to the respective environmental standards but without causing an exceeding.

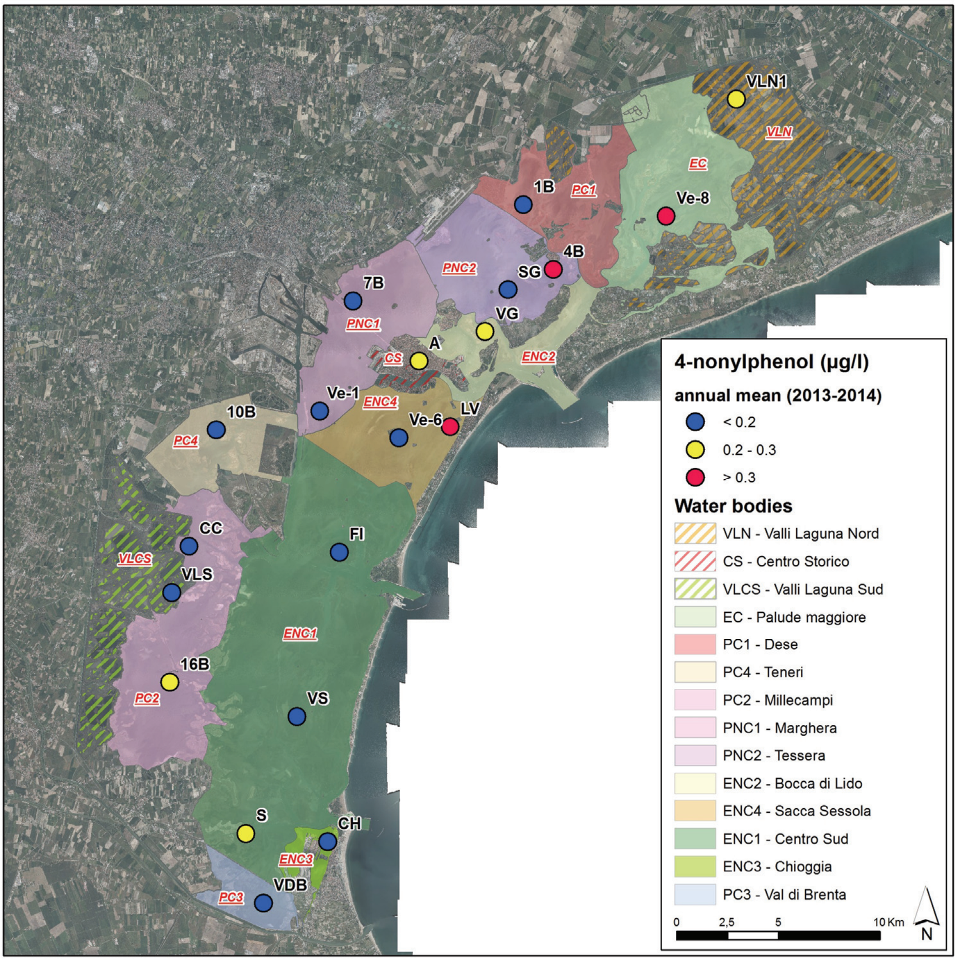

Fig. 2. Spatial distribution of 4-nonylphenol in the Venice Lagoon (annual average of 2013-2014 monthly sampling)

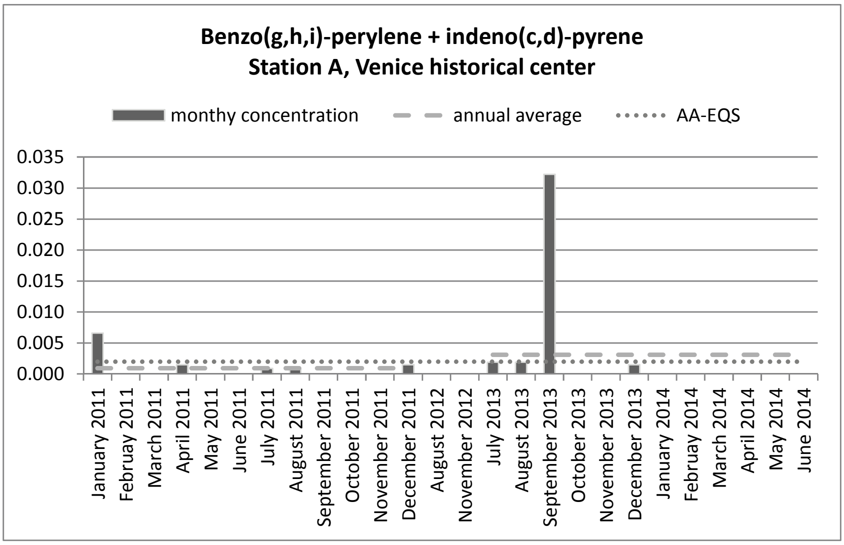

Fig. 3. Monthly concentration of benzo(g,h,i)perilene+indeno(c,d)-pyrene at the station located in the main canal of historical centre of Venice

3.2. Sediment monitoring

The sediment monitoring of the Lagoon revealed the presence of several priority contaminants with concentrations higher than the sediment quality standard established by the Italian Ministerial Decree (DM 260, 2010) (Table 2): mercury, cadmium, lead, PAHs and tributyltin. All water bodies (except for Val di Brenta, the southern edge of the lagoon), are contaminated with at least one chemical exceeding the environmental quality standard, giving a picture of the lagoon very different from that depicted by the water monitoring.

The most polluted site is, as expected, the internal canal of the historical center of Venice, characterized by the presence of several significant pressures (e.g. sewage untreated discharge, intense boat traffic) and by extremely low water exchange. The sediment of this site can be considered as a hot spot of contamination for several chemical substances.

Considering the other stations of the lagoon, mercury is one of the elements of major concern. Average concentrations ranged from 0.02 (stations of the southern lagoon) to 2 mg/kg d.w (city of Venice), exceeding the quality standard (0.3 mg/kg d.w.) in about half of the sampled stations in each year of monitoring, mainly located in six water bodies of the central-northern basin of the lagoon (EC, PC1, PNC1, PNC2, ENC2, ENC4) (Fig. 4). This is a well-established result, coming from all the three years of monitoring (2011-2013) and also substantiating some previous surveys performed in the lagoon since the 80s (Donazzolo et al., 1984) and during more recent monitoring programs, such as QSEV and ICSEL Projects funded by Venice Water Authority (Magistrato alle Acque – CNR ISMAR – SELC, 2011, (Magistrato alle Acque –Thetis, 2004).

It is noteworthy mentioning that mercury was almost never detected during water monitoring (< 0.005 μg/L), i.e. just in two out of 520 samples, with dissolved concentration very close to the analytical detection limit.

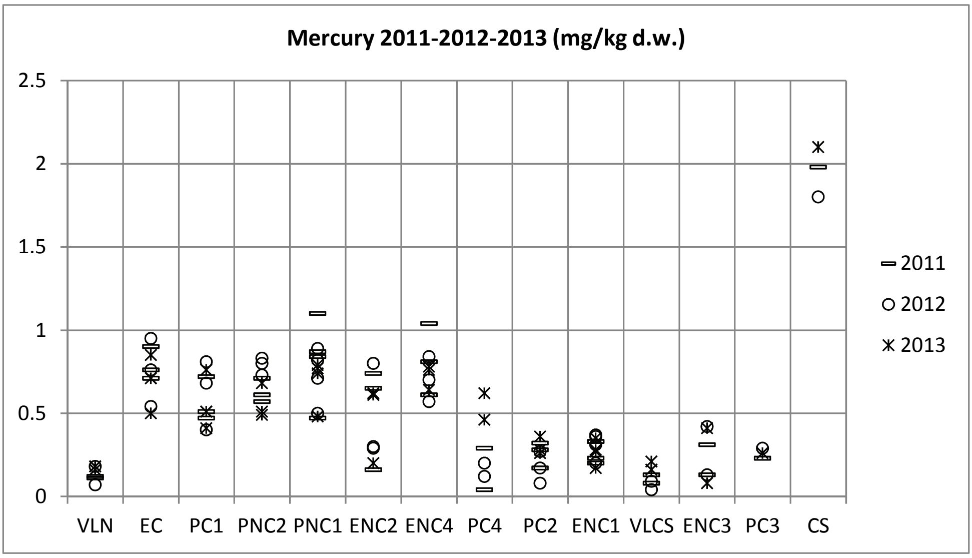

Fig. 4. Mercury concentration in sediments of the lagoon during 2011-2013 monitoring

Other well-established results, are the presence of cadmium in the central part of the lagoon, especially in confined areas influenced by the presence of the industrial area (stations belonging to the water bodies PNC1, PC4, PC2, as well as CS). PAHs are other contaminants of concern, mainly originated by fossil fuel combustion and in particular by the motorboat traffic affecting wide areas of the lagoon. The concentrations of the priority PAHs exceeded the standards in several water bodies, with very high contamination in the inner canal of Venice (peak values up to 61 mg/kg d.w. for the sum of the eight monitored priority PAHs), but also in some other sampling sites, such as the urban center of Chioggia in the southern lagoon.

The overall monitoring finally revealed the absence of all monitored pesticides (Aldrin, Dieldrin, α-β-γ Hexachloro-cyclohexane, Hexachloro-benzene, DDT and its degradation products), which always resulted as non-detectable concentrations.

Average sediment concentrations of the lagoon water bodies are reported in Table 1, together with minimum and maximum concentrations measured in each station during the whole monitoring period.

3.3. Biota monitoring

The investigations on bioaccumulation were performed to complement the survey of the state of chemical contamination of waters and sediments carried out within the same monitoring project. The survey revealed the presence of mercury both in bivalves (*Mytilus galloprovincialis, Tapes philippinarum*) and in fishes (*Zosterisessor ophiocephalus, Dicentrarchus labrax, Sparus aurata*) of the lagoon with almost all concentrations higher than the environmental standard (20 µg/kg w.w) (Fig. 5).

Mercury concentrations in fish are almost everywhere higher than those measured in shellfish, according to the available knowledge on mercury biomagnification process along the food chain, supporting the importance of diet in the transfer of contamination to higher trophic levels. Tissue concentration are however below the European limit for commercialization of fish products (500 µg/kg w.w.), which is far higher than the EQS, suggesting no risk for human consumption of bivalves and fishes of the lagoon.

According the UNEP international review of mercury guidelines in fish for human consumption (UNEP, 2002), the European limit of 500 µg/kg w.w. can be considered of intermediate level (guidelines range from 200 for big consumers to 1500 µg/kg w.w) and it is shared by different countries.

Organic mercury is an important fraction of total mercury, ranging from 33 to 85% of total mercury in clams (average 68%), from 29 to 86% (average 55%) in mussels and from 20 to 100% (average 56%) in fish. These percentages are comparable to metylmercury percentages reported by several authors in the Mediterranean and Adriatic area (Di Leo et al., 2010; Giani et al., 2012; Kljakovic-Gaspic et al., 2006; Wang et al., 2005). They are also consistent with the typical metylmercury percentages in fish reported by the European Food Safety (50-80% of total mercury, EFSA, 2012).

Finally, a positive correlation between mercury bioaccumulation levels and mercury concentrations in sediment has been identified for clams, living more closely with the sediment than mussels and fishes. Bioaccumulation was in fact higher in samples clams collected in the Northern basin of the lagoon, where sediments are more contaminated with mercury.

Table 2. Mean concentrations of priority substances in the sediments of the 14 lagoon water bodies (substances which have experimented concentrations exceeding the standard during the monitoring). Min and max refer to the minimum and maximum concentration achieved in each sampling station of the water body, during the overall monitoring (2011-2013).
(*EQS = Environmental Quality Standard established by the Italian Ministry Decree DM 260 (2010). An exceeding of 20% over the standard is tolerated according to the decree)

	Cd mg/kg d.w.			**Hg mg/kg d.w.**			**Pb mg/kg d.w.**			**Σ priority PAH µg/kg d.w.**		
water body	**average**	***min***	***max***	**average**	***min***	***max***	**average**	***min***	***max***	**average**	***min***	***max***
VLN	0.4	*0.3*	*0.6*	0.1	*0.1*	*0.2*	48	*31*	*57*	103	*42*	*228*
EC	0.2	*0.1*	*0.3*	0.6	*0.2*	*1.0*	16	*12*	*25*	92	*25*	*660*
PC1	0.2	*0.1*	*0.3*	0.6	*0.4*	*0.8*	19	*13*	*24*	434	*25*	*3746*
PNC2	0.2	*0.1*	*0.4*	0.5	*0.5*	*0.8*	14	*11*	*42*	106	*20*	*351*
PNC1	0.6	*0.3*	*1.1*	0.7	*0.2*	*1.1*	26	*10*	*44*	163	*34*	*285*
ENC2	0.2	*0.1*	*0.4*	0.4	*0.2*	*0.8*	11	*6*	*20*	113	*33*	*537*
ENC4	0.4	*0.2*	*0.6*	0.6	*0.04*	*1.0*	16	*10*	*23*	303	*41*	*2345*
PC4	0.9	*0.3*	*1.4*	0.3	*0.04*	*0.6*	31	*22*	*38*	145	*27*	*211*
PC2	0.4	*0.3*	*0.8*	0.2	*0.1*	*0.4*	25	*20*	*39*	357	*82*	*1249*
ENC1	0.3	*0.1*	*0.5*	0.3	*0.02*	*0.5*	16	*8*	*24*	65	*20*	*250*
VLCS	0.4	*0.3*	*0.6*	0.1	*0.04*	*0.2*	38	*31*	*46*	199	*34*	*523*
ENC3	0.3	*0.1*	*0.7*	0.2	*0.1*	*0.4*	21	*9*	*35*	978	*251*	*2475*
PC3	0.2	*0.1*	*0.3*	0.2	*0.1*	*0.3*	20	*11*	*30*	90	*51*	*158*
CS	0.9	*0.8*	*1.0*	2.0	*1.8*	*2.1*	79	*70*	*93*	40027	*13528*	*61573*
*EQS**	*0.3*			*0.3*			*30*					

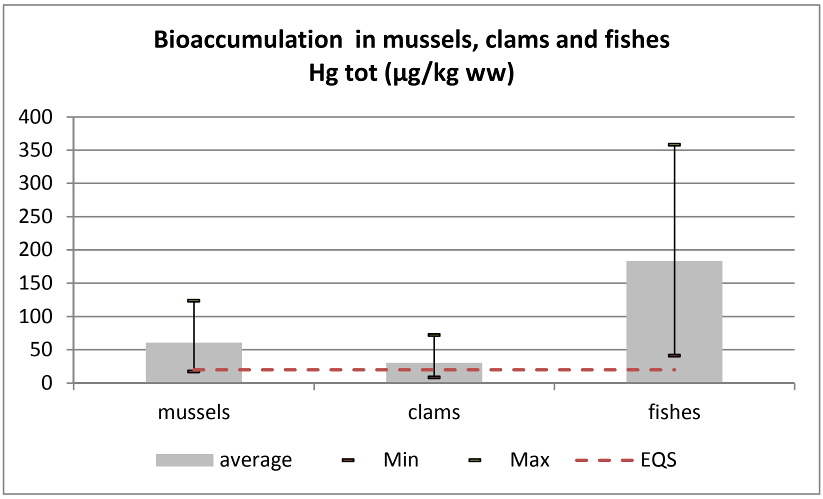

Fig. 5. Bioaccumulation levels of total mercury in mussel, clams and fishes of the Venice Lagoon. EQS (red line) is the environmental quality standard established by the Italian Ministry Decree (DM 260, 2010)

4. Concluding remarks

The chemical monitoring of the Venice lagoon, started in 2011 and currently ongoing, has allowed to produce a wide dataset for priority chemical substances in water, sediment and animal tissues of the lagoon, composing a complex picture of lagoon contamination.

If compared to the EQS, mercury resulted as an element of concern both for sediments and for lagoon bivalves and fishes but not for water where almost all concentrations were below the detection limit. Besides, the exceeding of mercury EQS in lagoon biota seems to pose no risk for human consumption according to the European and other different international limits.

Water monitoring highlighted wide temporal fluctuation in the monthly concentrations of priority substances, so that different evaluations of the lagoon chemical status, based on water, are possible depending on the selected monitoring year. 4-nonylphenol and the sum of benzo(g,h,i)perylene and indeno(c,d)-perylene are chemicals of possible recent concern, which need to be substantiated with the continuation of the survey.

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COMPARISON OF BIOMETHANE GENERATION WITH OTHER OPTIONS FOR ENERGY AND MATERIAL RECOVERY FROM BIO-WASTE: A LIFE CYCLE ANALYSIS*

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Abstract

This study is focused on the analysis and evaluation of environmental impacts generated by different options for managing the bio-waste. The strictly recovery of materials by the generation of an organic fertilizer (i.e. compost) was compared with other integrated options able to allow also the energetic recovery. These options were represented by the anaerobic digestion (AD) aimed to electrical energy generation and to biomethane production. The analysis of this last option was focused on three different uses of biomethane: as fuel in high efficiency co-generators; as fuel for vehicles; as fuel for civil heating. Referring to the single tonne of bio-waste processed, main results confirms the noticeable environmental advantages achievable by the production and use of organic fertilizer. The traditional AD showed impact comparable with the ones of the composting process. The biomethane generation showed in general higher impact with exception of the ozone depletion and photochemical ozone formation. This result was mainly a consequence of the upgrading process considered in the study based on the pressure swing adsorption. Different results were find out referring the impact to the unit of energy recovered. From this point of view environmental performances of the biomethane options resulted increased.

Keywords: biomethane, bio-waste, composting, anaerobic digestion, Life Cycle Analysis

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1. Introduction

Among the different components of municipal solid waste (MSW), if not properly managed, the bio-waste is one of the most relevant, both in terms of quantity and of potential pollutant emissions (Di Maria et al., 2013). On the other side bio-waste can also represent an important source of raw-materials, nutrients, organic carbon and energy (Di Maria et al., 2008; Di Maria and Micale, 2014; Di Maria and Barratta, 2015). In general a widespread solution adopted for recovering material and nutrients is represented by composting. Composting is an aerobic biological process able to stabilize and transform the organic matter in to a valuable product exploitable for agricultural needs. From the other side composting process results in quite high energy consumption per unit of mass of generated fertilizer.

Energetic efficiency of bio-waste treatment can be improved by the introduction of an anaerobic digestion (AD) pretreatment before composting. AD is able to return a gas mainly rich in methane (i.e. 60% v/v) and CO_2 (i.e. 40% v/v) exploitable for energy recovery by the use of co-generators. Starting from December 2013 a new opportunity was introduced also in Italy concerning the energetic utilization of bio-waste. This option was represented by the generation of biomethane exploitable as renewable fuels (Decreto, 2013). Biomethane is a gas rich in methane (>95%v/v) obtained by the upgrading of the biogas generated from the AD of bio-waste and other biodegradable materials. Upgrading process consist mainly in removing the CO_2 together with other contaminants (e.g. H_2S, H_2O…) and can be performed by exploiting chemical and/or physical processes.

Depending on the final use of bio-methane, upgrading process consist of different devices requiring both energy and chemicals consumption. For this reason results of prominence importance analyzing the environmental sustainability of these different options available for the management/recovery of bio-waste.

The main objective of this study is to analyze the environmental sustainability of different options concerning the treatment of bio-waste arising from the source segregated collection of MSW. This work is divided in three main parts:

- generation of the different environmental models to be compared;
- comparison from the energetic point of view of the scenarios reported in Table 1 with the conventional ones based on the exploitation of fossil fuels;
- analysis of results, drawing conclusion and formulation of recommendations for policy and decision makers in the sector of bio-waste.

Upgrading technology exploited in the present work was assumed to be based on the PSA process (Yang et al., 2014) able to return a biomethane with 96% v/v of CH_4 and at a pressure of 5 bar.

2. Materials and methods

Five different scenarios were proposed for the treatment of bio-waste (Table 1): composting; AD followed by composting with direct use of biogas in co-generators; AD followed by composting with biogas upgrading and injection of the bio-methane in the local network of natural gas. After injection, three different biomethane utilization were analyzed: fuel for high efficiency co-generation plants; fuel for transport; fuel for civil heating.

The function unit of the system was considered the treatment of 1 tonne of bio-waste. The functional unit was also assumed as the reference flow. Considering the multi-functionality of the different processes involved in the treatment of the bio-waste the boundaries of the system were expanded (Fig. 1). The results of the study can be exploited for supporting local scale decisions. System background were represented by bio-waste, energy and materials whereas foreground were represented by fertilizer, energy and emissions. Background cannot be influenced by foregrounds and the results of the study can support decisions at micro-level scale. According to Turconi et al. (2011) both avoided and consumed energy was considered the one generated by the natural gas for the Italian scenario.

Table 1. Scenarios for the treatment of bio-waste

Scenario N°	***Treatments***
1	Composting
2	AD+Composting+ Cogeneration
3	AD+Upgrading+Composting+High efficiency cogeneration
4	AD+Upgrading+Composting+Car
5	AD+Upgrading+Composting+Civil heating

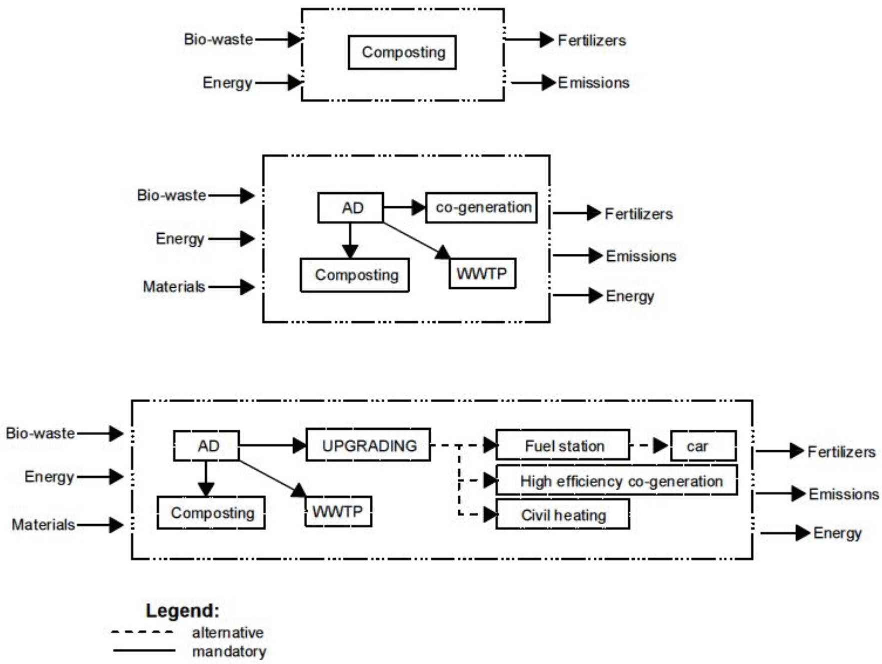


Fig. 1. System boundary for the different scenarios analyzed

Life cycle inventory modelling framework resulted attributional. Experimental data were used for adjusting available environmental models (*i.e.* Ecoinvent 3.0) (Hischier et al., 2010) used for the different components of the system. Simulation were performed by SimaPro 8.0.5.13 program (Prè Consultants, 2013).

Impact categories used in the study were the ones proposed by the ILCD 2011 midpoint method (European Commission, 2012): Global Warming Potential (GWP); Ozone Depletion Layer (ODP); Particulate Matter (PM); Photochemical Ozone Formation (POF); Acidification (A); Eutrophication Terrestrial (ET); Fresh Water Eutrophication (FEW); Resource Depletion (RD) (Table 2). Normalization factor were also utilized for giving an impression of the impact generated by the different systems analyzed. Finally the CO_2 generated from the biological process and from the combustion of the biomethane was assumed biogenic.

5. Results and discussion

Results of the LCA study referred to a single tonne of bio-waste managed (Fig. 2) showed a quite comparable impact for the scenarios concerning biomethane generation (i.e. 3, 4 and 5) and some relevant differences concerning scenarios 1 and 2 depending on the specific impact category. Scenario 1 (i.e. composting) was characterized by the lower value for RD (avoided impact) whereas scenario 2 was characterized by the lower impact for the PM, A and ET with avoided impact concerning POF. Figure 3 represents the contribution of the main activities of each scenario to the values of the impact categories.

A larger contribution to the impact was given by the emissions generated by the biological processes (i.e. composting and AD) (Table 4). Furthermore, in the scenarios 1 and from 3 to 5, the energetic consumption was supplied by the marginal electrical energy assumed in this work (i.e. natural gas Italy). For the scenario with biomethane generation another important contribution to the impact is represented by the upgrading process considered. Impact generated by the emissions due to the exploitation of biomethane and the one due to the fueling of cars resulted in general lower than the other ones with exception of POF. In general avoided impact (i.e. negative values) are represented mainly by the production and use of organic fertilizer, by the substitution of natural gas and by the substitution on electrical energy.

Table 2. Impact categories and normalization factors

Impact category	*Unit*	*Normalization factor EU 27 (2010)*	*Unit*
GWP	kgCO_2 eq.	9.10E+ 03	kgCO_2 eq./a.
ODP	kgCFC-11 eq.	2.16E - 02	kgCFC-11 eq./a.
PM	kgPM2.5 eq.	4.82E +00	kgPM2.5 eq./a.
POF	kgNMVOC eq.	3.18E+ 01	kgNMVOC eq./a.
A	molc H^+ eq.	4.27E+ 01	molc H^+ eq./a.
ET	molc N eq.	1.74E+ 02	molc N eq./a.
FWE	kg P eq.	7.41E+ 08	kg P eq./a.
RD	kg Sb eq.	1.00E - 01	kg Sb eq./a.

Table 3. Compositions of bio-waste

Component	*% on wet basis*
Glass	0.05
Plastics	1.66
Metals	0.16
Organics	96.7
Paper and carboard	1.44
Texiles	0.03
Glass	0.05

AD is of course an effective way for pre-processing bio-waste before composting but its use in the management of bio-waste is finalized to the generation of renewable energy for substituting fossil fuels. On the basis of this consideration in Table 5 were calculated the impact categories related to the specific energy generated/avoided. Impact categories of each scenario, from 2 to 5, were compared to the corresponding scenario based on the exploitation of fossil fuel (i.e. natural gas). For scenario 2 the normalized impact categories were divided by the amount of electrical energy generated; for scenario 3 were divided by the co-generated energy; for scenario 4 were dived by the single km driven by the car; for scenario 5 were dived by the amount of thermal heat.

Table 4. Main data exploited for the Inventory.

Process	***Emission***	***u.m.***
Composting		
air emission per kg of compost		
CH_4, biogenic	0.0101	kg
CO, fossil	0.000128	kg
CO_2, biogenic	0.52	kg
CO_2, fossil	0.00843	kg
NOx	0.000453	kg
NH_3	0.000978	kg
N_2O	0.000281	kg
H_2S	0.000528	kg
AD		
air emission per kg of bio-waste		
CH_4, biogenic	0.005897	kg
N_2O	9.98E-05	kg
H_2S	0.000245	kg
CO_2, biogenic	0.705	kg
NH_3	0.000319	kg
Biogas upgrading process		
air emissions for m^3 *of biomethane*		
CO_2, biogenic	0.86586	kg
CH_4, biogenic	0.022257	kg
H_2S	3.9E-06	kg
SO_2	0.000552	kg

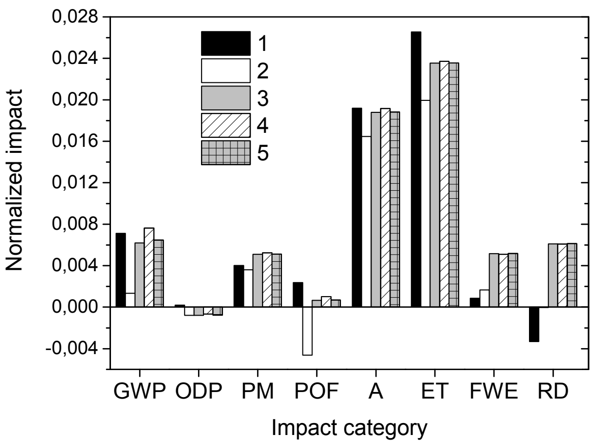
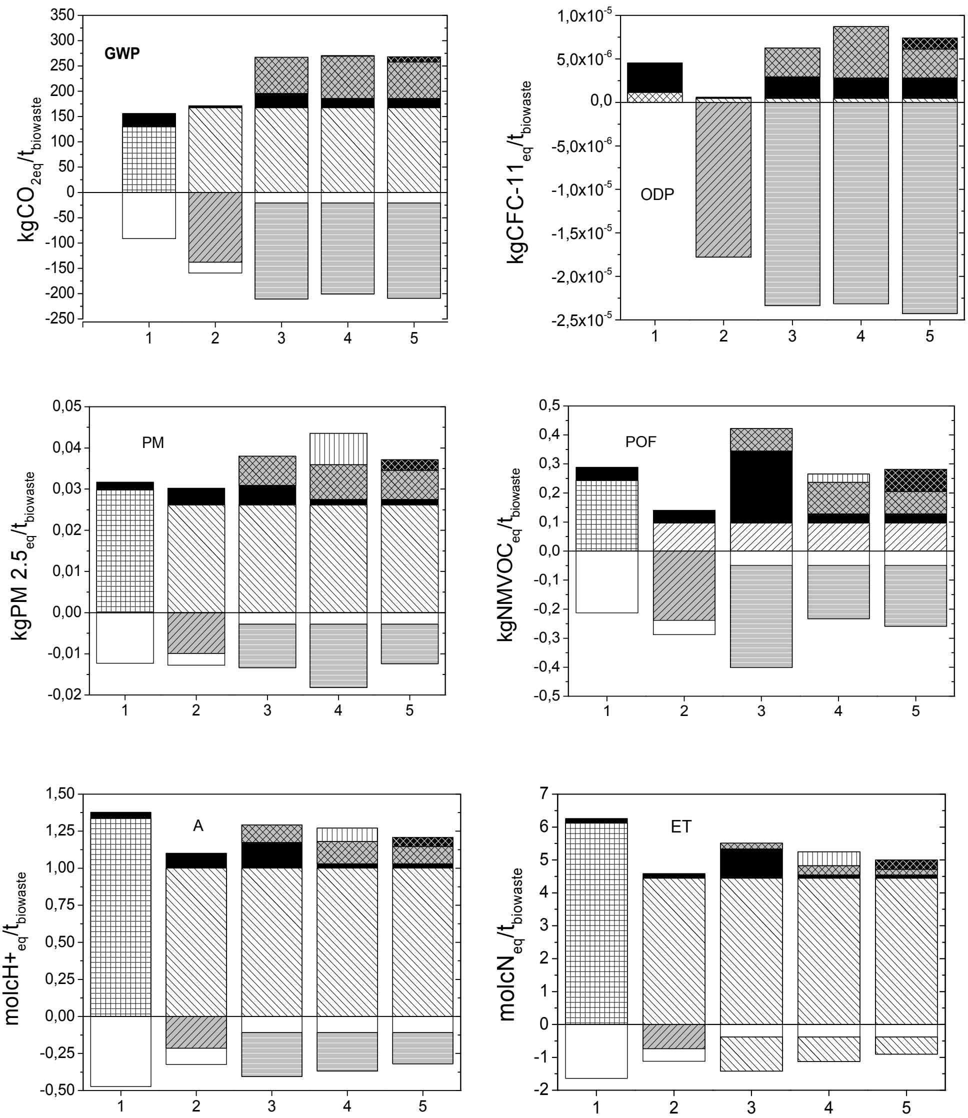


Fig. 2. Comparison of impacts categories for the different scenarios analyzed (Table 1)

Results showed that the impact categories resulting always lower for all the scenario proposed by this study (I) were GWP, ODP and POF. A, ET and FWE resulted generally lower for the conventional scenarios (C), whereas RD resulted lower only for the scenario 2-I.

On the basis of the assumption made this work showed that the composting and AD resulted characterized by a quite similar impact. A main contribution to the impact of AD generating biomethane is given by the upgrading technology chosen in this study. Other technological solutions based on membranes or absorption resulted worthy to be investigated since their adoption could modify the results of this study.

From the energetic point of view the generation of energy and/or fuels from bio-waste resulted always advantageous for the GWP, ODP and POF impact categories. As demonstrated by the values reported in Fig. 3 the most relevant impact categories were represented by GWP, A and ET.



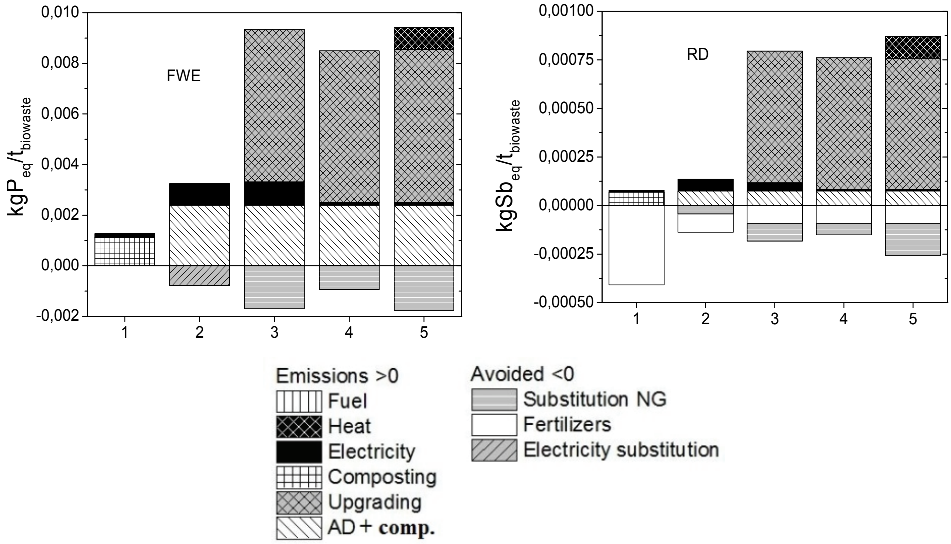


Fig. 3. Contribution of main activities to the values of each impact category per each scenario

Table 5. Normalized impact categories expressed per unit of: electrical energy (kWh_e scenario 2); the co-generated energy (kWh_{tot} scenario 3); the distance driven (km scenario 4); the thermal energy (kWh_e scenario 5) compared with correspondent conventional scenario

Scenario		*Norm. factor*	*GWP*	*ODP*	*PM*	*POF*	*A*	*ET*	*FWE*	*RD*
2	I	kWh_e	6.358E-06	-3.790E-06	1.721E-05	-2.201E-05	7.849E-05	9.498E-05	7.947E-06	-1.265E-07
	C		7.238E-05	3.922E-06	9.792E-06	3.571E-05	2.171E-05	2.029E-05	2.492E-06	2.091E-06
3	I	kWh_{tot}	1.021E-05	-1.306E-06	8.390E-06	1.083E-06	3.097E-05	3.878E-05	8.515E-06	1.008E-05
	C		3.438E-05	1.783E-06	3.604E-06	1.822E-05	1.038E-05	9.864E-06	1.894E-06	1.463E-06
4	I	km	1.002E-05	-8.763E-07	6.895E-06	1.344E-06	2.515E-05	3.113E-05	6.702E-06	7.997E-06
	C		2.597E-05	1.406E-06	4.178E-06	7.579E-06	7.205E-06	5.649E-06	8.350E-07	7.482E-07
5	I	kWh_{th}	8.930E-06	-1.080E-06	7.070E-06	9.693E-07	2.601E-05	3.253E-05	7.147E-06	8.459E-06
	C		2.859E-05	1.552E-06	2.737E-06	9.112E-06	6.186E-06	4.178E-06	1.638E-06	2.272E-06

Legend: I = this study; C= conventional

6. Concluding remarks

The different option for managing the bio-waste analyzed in this study confirms the importance of organic fertilizer production and exploitation. Energy recovery can be a suitable way but single normalized impact categories resulted generally higher than those for composting.

From the energetic point of view the generation/exploitation of energy and of fuels (i.e. biomethane) from the bio-waste by anaerobic digestion resulted environmentally advantageous only for global warming potential, ozone depletion layer and photochemical ozone formation. The other impact categories resulted generally higher compared to the ones of conventional scenario (i.e. using fossil fuels).

On the basis of the results of this study the composting resulted always recommended. Anaerobic digestion with electrical energy generation by direct exploitation of the biogas as pre-treatment before composting, showed environmental impacts comparable with the ones of the composting. Biomethane generation showed often higher environmental impacts. A key factor influencing these results was represented by the processes necessary for biogas upgrading (i.e. chemical/physical adsorption).

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THE INDUSTRIAL SYMBIOSIS APPROACH: A CLASSIFICATION OF BUSINESS MODELS*

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Abstract

Industrial symbiosis is a collaborative approach concerning physical exchange of materials, energy, and services among different firms: accordingly, wastes produced by a given firm are exploited as inputs by other firms. This approach is able to generate remarkable environmental benefits, since it allows to reduce the amount of wastes disposed of in the landfill and the amount of primary inputs used by the industrial sector.

It has been proved that the economic logic is the basis of symbiotic exchanges. Through industrial symbiosis, firms are interested to achieve competitive advantage coming from lower production costs and revenue increase. Therefore, the first requirement for the establishment of a symbiotic relationship is its economic sustainability for all the firms involved.

In this paper, from the analysis of actual cases of industrial symbiosis, we develop a classification of business models oriented to the symbiotic approach. The classification is based on the different ways in which industrial symbiosis is able to generate economic benefits for the firm that implements it. Six different business models oriented to industrial symbiosis have been identified.

The proposed classification could be useful at the company level, in order to promote the implementation of the symbiotic approach, providing a guide about how to integrate it within its current business models.

Keywords: business models, circular economy, competitive advantage, environmental benefits, industrial symbiosis

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1. Introduction

Industrial symbiosis (IS) is a collaborative approach concerning physical exchange of materials, energy, and services among different firms: accordingly, wastes produced by a given firm are exploited as inputs by other firms (Chertow, 2000).

The IS approach allows to achieve environmental, economic, and social advantages (Mirata, 2004; OEDC, 2012). The environmental benefit is the result of the potential reduction of wastes, emissions, primary inputs, and energy (Chertow, 2000). The economic convenience comes from the savings due to minor costs for wastes disposal and for primary inputs purchase (Albino et al., 2015). Finally, about the social benefits, the IS approach may foster the creation of new firms and new jobs (Mirata, 2004). For these reasons, OECD (2012) considers IS as a "sustainable business model", i.e. a "model that creates competitive advantage through superior customer value and contributes to a sustainable development of the company and society" (Lüdeke-Freund, 2010). In addition, the adoption of IS approach has been explicitly recommended by European Commission, in order to boost resource use and production efficiency (European Commission, 2011).

In order to be successfully implemented, each IS project should be feasible from technical, economical, and legal point of view (Garner and Keoleian, 1995). Literature has largely investigated technical aspects about the implementation of IS projects (Yu et al., 2014) but less attention has been devoted to economic and strategic issues, despite the economical convenience is a precondition for the implementation of IS approach. In fact, the first driver that moves firms towards the IS approach is the possibility to obtain economic benefits from it (Lyons, 2007).

In this regard, in order to foster the adoption of IS approach, it is important to better investigate the different strategies through which companies can create value and obtain economic benefits for themselves by IS.

In this paper, we identify business models oriented to the IS approach and classify them based on the different ways in which they are able to provide value for companies. Our aim is to develop a useful tool for companies to better understand how to integrate IS within their business strategies. The paper is organized as follow: Section 2 describes the methodology used and Section 3 shows the classification of business models. Finally, discussion and conclusions are presented in Section 4 and Section 5, respectively.

2. Methodology

Although many specific classifications do exist for business models, each classification can be widely different in terms of research purpose and business context (Dubosson-Torbay et al., 2002; Lambert, 2015). As we did not find in the literature previous classifications about business models specifically oriented to the IS approach, this paper aims to offer a novel contribution. Accordingly, in order to develop the business model classification, we used an inductive approach (Eisenhardt and Graebner, 2007): we reviewed secondary literature about the implementation of IS projects and we analyzed the business model by which each IS project is driven. Three different sources of case studies have been exploited: i) academic literature; ii) professional literature; iii) companies' websites.

For each case, the source of economic benefits for companies involved has been identified. This information has been used for the development of the classification, in which each model is characterized by different source of economic advantage.

3. The classification

In this Section, the classification of business models oriented to the IS approach is presented. In particular, we have identified six different models: *waste exchange, co-product generation, co-product generation destined to the internal consumption, co-product generation from external wastes, online waste exchange platform, IS-based business oriented to product generation.* Fig. 1 shows a graphical scheme of the proposed classification. In the following paragraphs, each depicted model is presented and supported by a short case example.

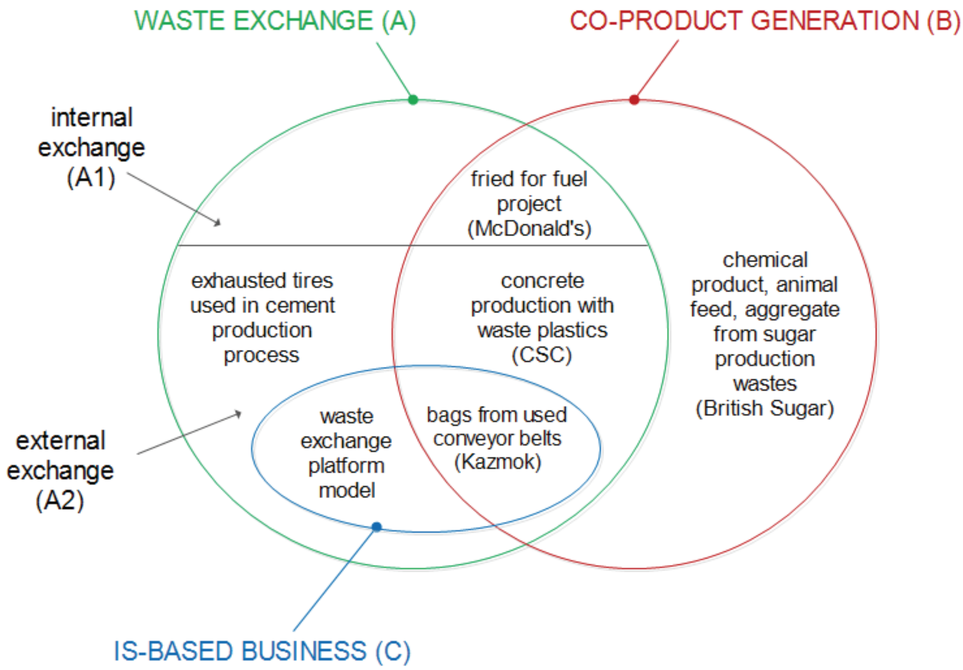

Fig. 1. Graphical classification of business models oriented to the IS approach

3.1. Waste exchange (A)

It is the most common strategy to adopt IS: waste produced by a given production process is used as input by another production process (A in Fig. 1). The involved processes can become to the same firm or conversely can become to different firms: in the first case an internal exchange (A1) is implemented whereas the second one concerns an external exchange (A2). The first sub model is the most simple to implement since it allows to avoid problems arising from inter-firm relationships: non-equal sharing of economic benefits (Fichtner et al., 2005; Paquin and Howard-Grenville, 2009), lack of trust and information sharing (Eilering and Vermeulen, 2004; Gibbs and Deutz, 2007), different bargaining power (Mirata, 2004; Yazan et al., 2012). However, the second sub model has higher potential because the diversity among firms is able to increase the number of symbiotic exchanges technically feasible and then potentially implementable (Korhonen, 2001).

As example of the waste exchange model, we mention a symbiotic exchange involving two companies in the Apulia region (Italy) (Albino and Fraccascia, 2015). Firms belong to different industries: the first firm collects exhausted tires whereas the second one is a cement producer. Exhausted tires are used as substitute of coal in cement production process. Both firms obtain economic benefits from the symbiotic exchange: the firm collecting tires reduces its waste disposal costs whereas the cement producer avoids sustaining the coal purchase costs.

In addition, in the case of external exchanges, firms can obtain additional economic benefits from fee associated with exchange. In fact, each bilateral waste exchange can be characterized by two different contractual schemes (Albino et al., 2015):

- firm producing waste pays firm receiving waste to dispose it: in addition to lower input purchase costs, firm receiving waste increases its revenues by the transaction fee;
- firm producing waste sells it to the firm receiving waste: in addition to lower waste disposal cost, firm producing waste increases its revenues by the transaction fee.

3.2. Co-product generation (B)

Companies value their wastes in the generation of new products that can be sold on the market. Hence, the company implements a business enlargement strategy since new products are added to the ones currently produced by the company. For this reason, this model is strategically more challenging than the previous one, partially because new products can be much different from products belonging to the company main business.

British Sugar, the largest sugar producer in UK, has adopted this model. It uses wastes from sugar production process, in particular residual resin, pulp, and soil stones, for the production of chemical products, animal feed, and aggregate (Short et al., 2014a). All these products are sold on the market. British Sugar obtains two different economic benefits: lower waste disposal costs and the earnings from the sale of new products.

3.3. Co-product generation destined to the internal consumption (A1∩B)

This model arises from the intersection of the internal waste exchange model (A1) and the co-product generation one (B), as graphically shown in Fig. 1. As in the previous model, companies use their wastes to generate new products: however, in this model, co-products are not destined to the external market but to be exploited within the company.

In 2006, McDonald’s launched the “fried for fuel” project, with the goal to produce biodiesel from fried oil generated in its restaurants. The fuel so obtained should have been used to power the company’s trucks. The economic advantages of this business initiative are twofold: lower oil disposal costs and lower fuel purchase costs.

3.4. Co-product generation from external wastes (A2∩B)

This model arises from the intersection of the external waste exchange model and the co-product generation one. Companies produce and sell on the market new products exploiting wastes from other companies. As in the co-product generation model, also this one provides the opportunity for business enlargement, since the new products flank the ones already produced by the company. In this case, the production volume is strictly dependent on the amount of wastes received by the firm (Lee, 2011). Therefore, the risk of supply is a critical issue of this model.

As example, CSC s.r.l., an Italian firm producing concrete, has developed a new concrete product made with waste plastics (Short et al., 2014b). Concrete so produced has 50% less weight than the one produced with aggregate. In addition, research has revealed that the use of plastics has positive impacts on lightweight applications, impact resistance, and noise absorption. In the specific case, the company uses plastics from municipal waste collection. The earnings from the sale of new products make up the economic benefits from the adoption of this model. In order to reduce the supply risk, CSC has implemented a downstream integration strategy creating a joint venture, which directly deals with the collection of plastic wastes.

3.5. IS-based business (C)

The business initiatives belonging to this paragraph are completely based on the IS approach, i.e. the IS approach constitutes the main business of the firms implementing them. Within this category, we can distinguish two different kinds of business, presented in the following sub sections.

3.5.1. Online waste exchange platform [A2∩C-(A2∩C∩B)]

This business model is having a wide dissemination and many new companies are arising to adopt it. Three examples of such platforms are wastetrade.it (Italy), thewastetradecompany.co.za. (South Africa), smileexchange.ie (Ireland). Online waste exchange platforms create an electronic marketplace for wastes allowing the matching between supply and demand. Companies providing such services gain earnings from commissions on transactions.

3.5.2. IS-based business oriented to product generation (A2∩C∩B)

New companies arise with the specific goal to create products from wastes. Kazmok is a Dutch company that produces business bags and accessories made from used conveyor belts, which had a previous life in the flower industry, airports, postal services, in distribution centers, and in the recycling industry. The business of the company is completely based on the IS approach. As for the “co-product generation from external wastes” model, also for this one the risk of supply is a critical issue. In particular, the risk is higher in this case since it can affect the main business of the company. However, in the specific case of Kazmok this risk is very low because the amount of used conveyor belts generated is much higher than the amount required by the firm.

Table 1 summarizes the economic benefits for each identified business model.

Table 1. Economic benefits for each business model.

BUSINESS MODEL	***Lower waste disposal costs***	***Lower input purchase costs***	***Earnings from selling new products***
Waste exchange (A)	X	X	
Co-product generation (B)	X		X
Co-product generation destined to the internal consumption (A1∩B)	X	X	
Co-product generation from external wastes (A2∩B)			X
Online waste exchange platform [A2∩C-(A2∩C∩B)]			X
IS-based business oriented to product generation (A2∩C∩B)			X

4. Discussion

From the analysis, we found that two main models oriented to the IS approach can be implemented: waste exchange and co-product generation. These models are not mutually exclusive since other hybrid models can arise from their combination. IS is not just a strategy oriented to cost reduction but can also be oriented to increase revenues, enter in new markets, and enlarge the corporate business. IS can also be a useful tool able to promote product and process innovation. Finally, new firms can arise exploiting the IS approach, corroborating the claims in the literature about its high economic and social potentialities (Mirata, 2004).

5. Conclusions

This research identifies different business models based on the IS approach and provides a classification of these models based on the different strategies through which they are able to provide economic benefits for companies. Accordingly, six different business models have been identified from reviewing literature about implemented initiatives of IS.

The proposed classification could be useful at the company level, in order to promote the implementation of the IS approach, then contributing to generate environmental benefits for the collectivity as a whole. It provides a guide for existing firms about how to integrate the IS approach within their current business models, reducing risks of implementation through providing examples from practice. Furthermore, our classification could be used to favor new business initiatives or new firms whose business model is completely based on the IS approach.

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REWASTEE:
MANUFACTURING ECO-INNOVATIVE CONSTRUCTION PRODUCTS FROM STEEL MANUFACTURING WASTE*

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Abstract

Europe produces large amount of EAFD, an hazardous, toxic waste with elevated environmental and economic disposal costs. Currently 60-65% of the produce EAFD ends up in authorized landfills and constitute a significant cost for mills and for the society. The current paper presents the progress to date of a research project to incorporate EAFD into insulation material to provide thermal and acoustic properties. The invention arises from the University of Barcelona and the University of Lleida (custodians of the patent) and consists in encapsulating EAFD as inorganic filler in a polymeric matrix to create a dense final "non-hazardous" material with excellent sound insulation for various applications (both alone and coupled to other materials). The addition of Phase Changing Materials (PCM) also provides thermal properties such as thermal inertia. The EU-funded research project aims at the industrial validation, launch and replication of the technology that combines recycling with the production of building multifunctional products bringing benefits in environmental and construction market and introducing a new Eco-Innovative product.

Keywords: acoustic insulation, bioPCM, EAFD recycling, steel waste, thermal insulation, thermal regulation

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1. Introduction

Current statistics shows that Europe is the second largest steel producer in the world with a production of 168 million tons in 2012. The main producers are Germany, Italy, France, Spain, and UK, which account together for 64.7% of EU steel production (Egenhofer et al., 2013). An amount representing 41.6% of EU steel is produced by electric methods, involving the generation of 10-20 kg of Electric Arc Furnace Dust (EAFD) per ton of steel produced (http://www.nobatek.com/downloads/actu/REWASTEE_KoM.pdf). EAFD is a well-known waste of the steelmaking industry, but considered a hazardous waste according to the European Waste Catalogue (EWC) with limited to date recycling alternatives (Barreneche et al., 2013; Fontes Vieira et al., 2014).

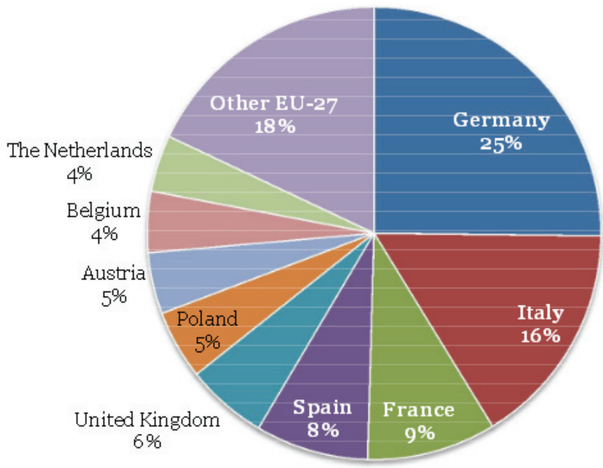

Fig. 1. Share of crude steel production in the EU by member state, 2012 (Egenhofer et al., 2013)

Typically, EAF steel producers currently have two major options: Processing the dust in a metal recovery facility to extract Zinc (the rest is then disposed in landfills) or chemically stabilize it and landfill it (with no metal recovery). The fraction of EAFD recycled varies for every country and region. In Spain, the recycled fraction of EAFD is below 20%, while European average is 50%. Being Europe the 2^{nd} largest EAFD producer (1.3 million tons in 2012), EAFD has become a major waste concern due to the environmental and economic disposal costs. Opposite to the current practices on EAFD stabilization, where EAFD is a cost for EAF steel producers with no possibility of further use, the proposed use offers a way to obtain revenues from the produced EAFD. One very promising route it to incorporate in insulation material providing excellent physical and acoustic properties.

The EU project (REWASTEE, www.rewastee.eu), funded under the Eco-innovation initiative of the European Union (contract number ECO/13/630286), aims to recover Electric Arc Furnace Dust (EAFD) generated during steel making and reincorporate it in the productive cycle, to obtain and bring into the market a multifunctional building insulation material having physical, acoustic properties as well as enhanced thermal inertia (when coupled with PCM) (Barreneche et al., 2013). The project is piloting and manufacturing the innovative insulation material that will be launched into the markets at the beginning of 2017. The project consortium is composed by 8 project partners including research center (EURECAT, Nobatek, BRE), universities (University of Barcelona and University of Lleida) and private companies (R2M Solution, Trimdelson Trade S.L., FCC Construction) ranging the full range of expertise required (Barreneche et al., 2014; Fernández et al., 2010).

2. Materials and methods

The process consists in the incorporation of EAFD into a polymer layer of EPDM and optionally also PCM. During the inertization process EAFD is completely stabilized forming dense sheets/layers by lamination, thus achieving a building multifunctional material.

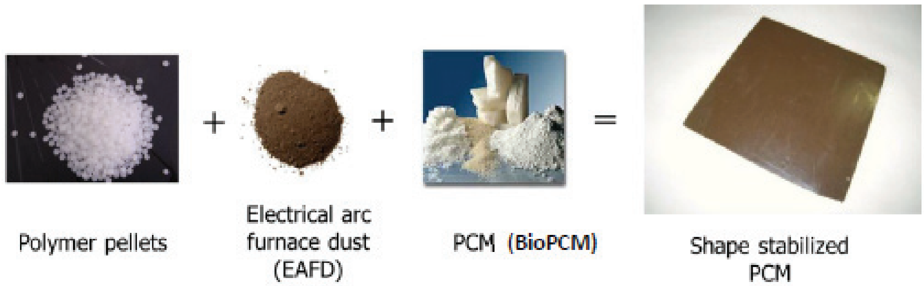

Fig. 2. Pictures of the raw materials and final product

The developed manufacturing process allows the EAFD stabilization and the manufacturing of building material in a single production line at industrial scale (and in the same facility) by using a broadly extended and standardized equipment (typically used for processing and producing rubber sheets), avoiding extra cost derived of transport to the production site, waste treatment (stabilization) or management. It also contributes to the implementation of a multifunctional material in the construction sector that improves energy efficiency of buildings, according to the commitment of the European Directive 2010/31/EC on energy performance of buildings (EC Directive, 2010).

3. Current status and next steps

Several stakeholders (e.g., steel manufacturers, construction companies, insulation product manufacturers) would benefit from the success of the innovative idea to recycle EAFD and incorporate it into insulation material (Fig. 3).

The team's current activities consist of material prototyping, manufacturing process optimization and the initial fabrication of integrated building products. Different manufacturing conditions and material compositions, including different PCM %, were tested to define the preferred one. Mechanical characterization, following UNE ISO-37, as well as apparent dynamic stiffness and damping ratio, following BS EN ISO 9052 -1 1992, have been already performed with the selected products. Steady and transient thermal response of the chosen material compositions will be tested at the University of Lleida to characterize their performance. In parallel, market analysis and business planning activities are identifying which commercial route the consortium should target first. This includes establishing contacts with a number of steel producers and material manufacturers in order to develop potential collaboration opportunities.

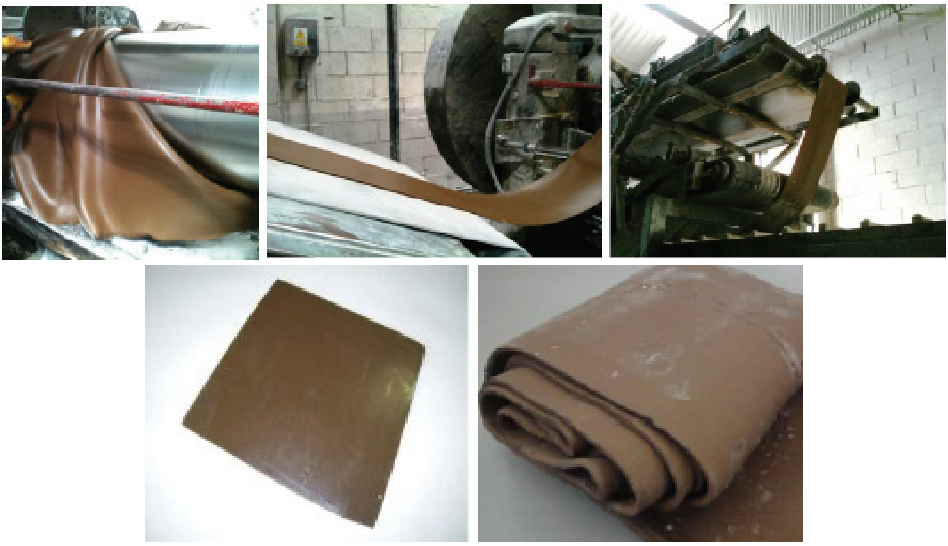

Fig. 3. Pictures of production of final product at Trimdelson Trade S.L. facilities

Fig. 4. Principal stakeholders

4. Concluding remarks

Europe generates significant amount of EAFD, a hazardous material that is currently for its majority landfilled. With the proposed method we provide benefits to several stakeholders and extract value from an otherwise waste with significant economic and environmental benefits. Results to date foster the confidence to be able to develop an interesting insulation material to support the circular economy principles that could enter the construction product market around the beginning of 2017.

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Ensure that each illustration has a caption, placed below the Figure. A caption should comprise a brief title (not on the Figure itself) and a description of the illustration. Keep text in the illustrations themselves to a minimum but explain all symbols and abbreviations used. Multiple Figures can be expressed as one Figure (for e.g. 1a, 1b, 1c etc...), while retaining the maximum limit of 6.

ALL Figures must be submitted in either .jpg or .tiff format with a very good resolution (but do not submit graphics that are disproportionately large for the content).

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