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RECYCLING OPTIONS FOR BIOMASS COMBUSTION ASH

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Abstract

The transition from fossil fuels to renewable energy is one of the pillars of the energy strategies that have been adopted by many governments in the last decades. A key role in the modern energy policies is covered by biomass, whose consumption for heat and power generation, particularly via the combustion technology, is dramatically increasing. This rises an environmental issue related to the wastes produced, the amount of which is rapidly growing and whose management requires to be addressed. At present, biomass ash is usually disposed in landfills, but this residue shows some physical and chemical characteristics that make it worthy to be reintroduced in the natural and production cycles as a valuable material, as the Circular Economy strategy suggests.

The general objective of this work was, therefore, to maximize the potential of this kind of waste and study reuse options that are tailored on its characteristics. The specific objectives of this work were (i) to deeper the understanding of the biomass ash characteristics, and to study two innovative recycling options consisting in reusing ash (ii) as an additive in the composting process and (iii) as a substrate for carbon dioxide sequestration.

To do so, three ash types (bottom, boiler and fly ash) generated from a thermal power plant, fueled entirely with biomass, were characterized and experiments were conducted with two selected ash types (boiler and fly ash).

With the aim of studying ash as an additive for composting, two experiments at pilot- and laboratory-scale were conducted, where a blend of boiler and fly ash was added at several shares to a mixture of organic fraction of municipal solid waste and a bulking material, and then subjected to composting. On the basis of the results obtained, both the composting process and the final product quality were improved by ash addition; in particular, ash resulted to have a potential as a physical conditioner, mineral additive and improver of humification in the composts produced from organic waste. These results also allowed to identify a possible maximum amount of ash that might induce benefits to the compost quality, without being of harm for the health and the environment. In addition, similar process performance and final compost quality were attained even when a significant amount of structuring agent was replaced by a mass of the biomass ash blend, which suggests that ash could give a contribution in the partial replacement of the traditional bulking materials.

As for the ash reuse as a substrate for CO_2 sequestration, the experimental activities were conducted using a reactor for accelerated carbonation and aimed at accelerating and/or maximizing the CO_2 uptake. Fly ash resulted to be effective in the carbon dioxide uptake, and could be a promising substrate in future for reducing the impact generated by the biomass used for energy purposes. Carbonation is also the most representative transformation occurring during the ash ageing process, and this study highlighted that a potential environmental hazard exists in treated/aged ash because of the varied leaching behavior of some heavy metals after the treatment. The directions for further research are many and are summarized at the end of the present work.

Keywords: renewable energy; biomass ash; combustion; composting additive; organic fraction of the municipal solid waste; carbonation; carbon dioxide uptake.

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CHAPTER 1

Introduction

1.1 Background

In the last decades the biomass energy industry experienced a drastic growth, driven by the many environmental issues concerning to fossil fuels and the key-role promoted by the Directive 2009/28/EC on the use of energy from renewable sources. This has generated energetic, economic and environmental benefits, but also impacts that require to be considered as well, among which the wastes produced are of major concern.

At present, combustion and combined heat and power systems based on combustion are the most common biomass technologies, whose residues consist of the ash. The amount of biomass combustion ash produced worldwide has increased in the last years as a consequence of the large diffusion of these energy generation methods, and a growing concern arose about the related management.

The biomass ash properties and composition constitute a complex matter since this waste stream shows variations in their composition in dependence to the feed properties, the combustion technology and operating conditions. In addition, several types of ash are usually produced in biomass thermal power plants depending on their discharging point, whose properties vary significantly. In relation to the latter point, some ash types could be distinguished that are characterized by a high content of macro-elements (such as Ca, K, Mg and P) and micronutrients (including Cu, Fe, Mn and Zn), which could be crucial for maximizing the potential of this waste product. In this respect, reutilization methods are proposed for biomass ash that evolve from the management of other types of residues, like coal combustion ash, and are not tailored on the biomass ash peculiarities. Unfortunately, their application still entails unsolved problems and biomass combustion residues are usually disposed in landfills. Suitable recovery options based on its physical properties and chemical characteristics are rather to be pursued.

Considering that detailed information on the properties variation among the biomass ash types are rarely available, this implies that a wider knowledge on the biomass ash physical and chemical characteristics should be acquired. In particular, if an in-depth analysis of the biomass ash properties and composition is conducted, it will emerge that some ash types show high nutrients content and physical characteristics that make them worthy to be reintroduced in the natural cycles as a valuable material.

A way to maximize the biomass ash value and returning nutrients to the soil could be the use of this kind of residue as an additive to composting. This reuse option converges to the actions included in the framework document recently released by the European Union, named “A zero waste programme for Europe”, where a plan for a more sustainable economic growth is designed in accordance to the Circular Economy strategy.

However, the effects exerted by ash addition are to be examined carefully, so that all the pros and cons on the process itself and the final compost quality are reckoned. Some works on reusing biomass ash as a composting additive have already been made. However, these studies have only partially explored the subject since they do not specify the type of biomass ash involved in the experiments, or use only one single ash type, which is aligned to the existing regulation in some European countries, but does not necessarily correspond to the ash type most enriched in nutrients and with the most suitable physical characteristics.

Another innovative reutilization option consists in reusing ash as a substrate for sequestrating CO_2 by means of the accelerated carbonation technique. This reuse option represents a novelty, due to the fact that this waste stream constitutes an emerging issue and the amounts produced nowadays (though rapidly increasing) have been disregarded if compared to the most common industrial alkaline waste. However, the rapid spread of the biomass combustion plants worldwide suggests that the related residues will cover an increasing importance in the next future, and the evaluation of the potential impact of this reuse option on reducing the carbon dioxide emissions is worthy of investigation.

These two research lines developed during the three-year PhD activity aim at recycling the new waste stream constituted by biomass ash - the return of nutrients to soil and the ash contribution to the CO_2 capture - by addressing some relevant environmental topics.

1.2 Objectives

Based on the context mentioned in Section 1.1, the present work had the scope of contributing to a deeper understanding of the biomass ash characteristics, and studying some suitable recovery options for biomass combustion ash in order to divert it from landfilling and maximize the potential of this waste product. The general objective of my PhD was, therefore, to study the reintroduction of such residues into the natural or industrial cycles, as the Circular Economy strategy suggests.

In particular, the experimental part of my research activity was focused on:

1. The physical and chemical characterization of the three ash types that are generated in a thermal power plant used as a representative example;
2. The recovery of the ash types most-enriched in macro-nutrients, with the highest potential liming effect and most suitable physical properties as an additive to the organic fraction of municipal solid waste composting, and evaluating the effects on the process and the final product quality;
3. The reuse of the most alkaline and reactive ash types as a substrate for sequestrating CO_2, and evaluating their environmental behavior when subjected to carbonation, that is the most representative transformation occurring during the spontaneous ageing process.

1.3 Structure of the work and expected results

The present research work is organized in chapters where single subjects are developed.

In **Chapter 2**, an overview of the current energy scenario is presented. Due to the data provided in this section, it will emerge that biomass ash is a novel waste stream that arises a growing concern and whose peculiarities require an in-depth analysis.

In **Chapter 3,** the typical composition of the fuel biomass and related combustion residues is presented, and the physical and chemical characterization of three ash types (bottom, boiler and fly ash), generated by a model-plant, is described. The analytical results here described will highlighted wide variations among the ash types considered, and each of them deserves a specific recycling path.

In the subsequent chapters, two innovative recycling options for selected ash types (boiler and fly ash) are examined. In particular, in **Chapter 4** the reuse of ash as an additive in the organic waste composting and the results of the experimental tests conducted are discussed. In **Chapter 5,** the possibility of ash reutilization as a substrate for sequestrating CO_2 and the results of the tests performed are presented.

Finally, conclusions are described in **Chapter 6**.

CHAPTER 2

Biomass combustion ash: an emerging issue

2.1 Introduction

In the last decades, many efforts were made by several governments to encourage the transition from fossil fuels to renewable energy sources (RESs). In Europe, the Parliament executed the Directive 2009/28/EC "on the promotion of the use of energy from renewable sources" ("Renewable Energy Directive") as a legal instrument to direct the Member States towards such transition [19]. In this Directive, energy from renewable sources is defined as follows:

"energy from renewable non-fossil sources, namely wind, solar, aerothermal, geothermal, hydrothermal and ocean energy, hydropower, biomass, landfill gas, sewage treatment plant gas and biogases".

What characterizes the renewable energy sources is that they are restored or, anyway, not completely exhausted in the timeline of a human life. Clearly, fossil fuels do not meet this requirement. If the energy needs that currently raise from human activity will be maintained, the natural gas and oil reserves are estimated to be consumed in decades (up to one hundred years, according to some estimates) and only new geological processes will restore those amounts. In addition, the natural gas and oil reserves are located in some specific geographical areas only, and this fact can nurture international political tensions. World coal reserves are equally widespread and more abundant than gas and oil; however, in a few centuries they are expected to be exhausted as well. More importantly, there are many environmental and safety issues concerning the use of fossil fuels. For these reasons, many governments have adopted energy strategies that maximize the recourse to RESs.

Among RESs, biomass has a prominent role. It is defined by the Directive 2009/28/EC as follows [19]:

"the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste".

The Renewable Energy Directive also establishes that biomass should cover a key role in the Member States' national policies, and the related subsequent documents promote the sustainable use of biomass for heating, cooling and electricity production [22-23].

Multiple advantages could be achieved by using biomass:

- *For the society*: increase of employment in the forest and agriculture sectors; more activities aimed at the maintenance of forests; diversification of the income sources in agriculture.
- *For the economic level*: redirection of production in agriculture, valorization of the organic residues and decrease in the expenditure for waste disposal; development and enhancement of forest and wood sectors.
- *For the environment*: positive contribution to the reduction of greenhouse gases emissions, of pollutants typically produced by fossil fuels (SO_x, CO, benzene) and acid rains; energy recovery from waste; control of the erosion and hydrogeological instability thanks to reforestation activities and new crops.

The total energy primary production from renewable sources attained in Europe in 2015 was 205 million tonnes of oil equivalent (Mtoe), of which the share of biomass (including waste) represented 63.5% (Fig. 2.1). Concurrently, among the renewable sources the share of biomass in the total gross inland energy consumption was 64.6% [26].

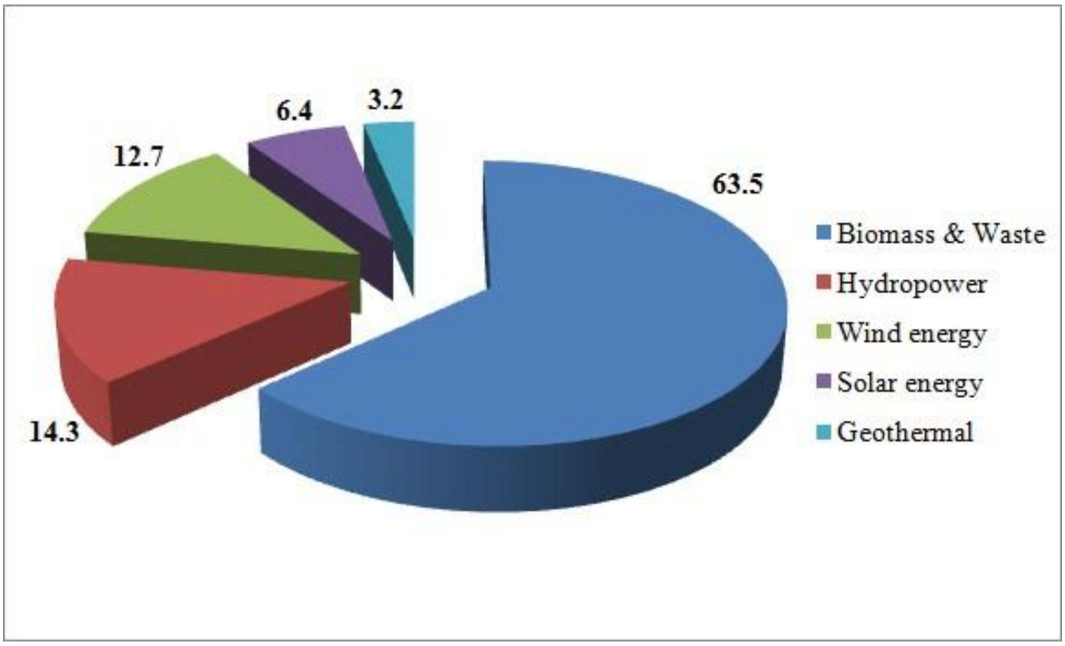

Fig. 2.1. Share of renewable sources in the total primary energy production in EU-28, 2015 [26].

In the same year in Italy, the electricity produced using bioenergy corresponded to 1,668 ktoe of primary energy (541 ktoe from plants treating solid biomass, which included the biodegradable fractions of municipal solid waste, 421 ktoe from biofuels, and 706 ktoe from biogas plants). This amount represented 17.8% of the total electricity produced from renewable sources. Thermal energy generated using bioenergy corresponded to 7,780 ktoe (7,488 ktoe from solid biomass and biodegradable fractions of municipal solid waste, 42 ktoe from biofuels, and 250 ktoe from biogas plants), which represented 73% of the heat produced by the renewable sources. As for the transport sector, biodiesel, bioethanol and ethyl-ter-butyl-ether (ETBE), the latter having a renewable oil share equal to 37%, corresponded to 1,164 ktoe of primary energy [33].

2.2 The use of biomass for energy generation

The clear predominance of bioenergy comparing to the other RESs is due to the fact that biomass is present in every country, in various forms, and constitute a continuous and programmable energy source (which in turn is the greatest disadvantage of wind and solar power). The production of heat and power from biomass increased dramatically in the last years and is expected to grow further. In Europe, according to the National Action Plans for the Renewable Energies of the Member States, the use of biomass to produce heat and power is estimated to grow up to 110.5 million tonnes of oil equivalent (Mtoe) by 2020, which corresponds to an increase of about 22% comparing to the 2012 consumption [23].

A wide range of materials is included in the European biomass definition, having different physical-chemical characteristics and availability in relation to the climatic area and seasonality. The ways to convert biomass into energy are several and, in dependence on the moisture and nutrients content, biomass could be subjected either to biochemical or thermochemical processes; generally:

- biodegradable matter having high moisture and nutrients content is a suitable feedstock for biochemical processes,
- biomass with low moisture and nutrients content is rather converted by means of thermochemical processes.

Given this distinction, any conversion technology leads to the production of specific forms of energy (i.e., power, heat, fuels) and has features that could make it the most preferable in a specific context. However, the thermal conversion technologies are the most practiced since. They are based upon chemical reactions activated by heat, and include combustion, gasification and pyrolysis (Fig. 2.2). Gasification and pyrolysis are mature technologies in some industrial fields such as the chemical and petrochemical sectors, but less practiced in the biomass field. The main differences between the combustion, gasification and pyrolysis processes are listed in Table 2.1. In the combustion process, complete oxidation of the organic matter occurs and heat, flames, gases and light are generated. Theoretically, complete oxidation requires that an amount of air corresponding to the one calculated by stoichiometry (based on the C, H, S content, that are the combustible components of biomass) is provided. In reality, combustion is incomplete because of uneven distribution of oxygen and feedstock in the combustion bed, and limited time of burning, therefore unburned carbon is always present. An excess air of approximately 50-60% is usually provided to overcome such defects. In relation to this aspect, gasification and pyrolysis differ from combustion because they consist in a partial oxidation of the organic matter.

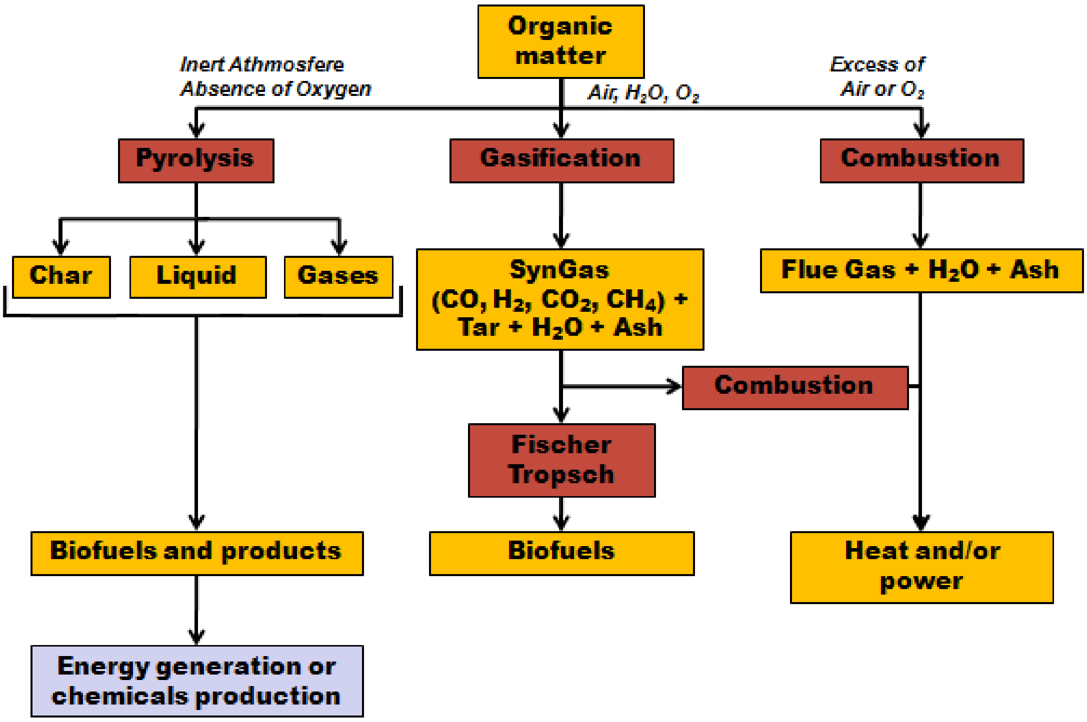

Fig. 2.2. Schematic diagram of the thermal conversion processes.

Tab. 2.1. Main features of the combustion, gasification and pyrolysis processes.

Description	Combustion	Gasification	Pyrolysis
Process temperature	850-1200°C	>800°C	400-800°C
Redox conditions	Highly ossidative (air excess)	Reductive (sub-stoichiometric oxygen)	Absence of oxygen
Energy and product generation	Heat, vapour, hot water, electricity	Fuel gas (CO, H_2, CO_2, H_2O, CH_4)	Fuel gas (CO, H_2, CH_4, C_nH_m), oil
Ash/solid residue	Ash	Ash	Carbonaceous solid residue, inerts

Air is supplied in sub-stoichiometric amounts in gasification and is strongly deficient in pyrolysis. In particular, pyrolysis is typically conducted in an inert atmosphere. The temperature value in gasification is approximately 800°C, while pyrolysis occurs at 400-500°C. The primary scope of gasification is the production of a combustible gas (syngas), composed by H_2, CO, CO_2, H_2O, C_xH_y; a solid residue consisting in carbonaceous matter and ash is also generated. Pyrolysis generates three products, the shares of which depend mainly on the process temperature and residence time of biomass inside the pyrolytic oven: a mixture of non-condensable gases (pyrolysis gas), a liquid consisting in water-soluble compounds (bio-oil), and a carbonaceous residue called biochar. However, among the thermal conversion processes, combustion is still the most common and well-known, and aims at the production of heat and power.

Several biomass types are suitable for thermal conversion, particularly for the purpose of combustion, and could be grouped in categories as follows, according to the supply sectors:

- forest wood
- energy crops
- agricultural herbaceous and residual biomass
- agro-industrial residues.

The most adequate biomass type for energy generation via combustion is forest wood. Similarly to any other industrial sector, energy generation from biomass is based on the supply planning, that should be consistent with the local vegetation and agro-industrial characteristics. Indeed, in order to develop renewable energy systems in a sustainable way, energy generation from biomass should be socially accepted (it should meet the need of local communities and reflect their values), economically affordable (the cost should be accepted by all the stakeholders, i.e. citizens, vendors, public sector, government), environmentally effective (it should generate a low environmental impact in terms of resource depletion, atmospheric emissions, soil and water contamination, and waste production). Therefore, it is essential that the biomass consumption converges to the sustainable use of local resources.

In the Mediterranean region, numerous biomass types exists due to the high favorable exposition to sunlight, mild winters and long summers; in particular, forests exhibit a great biodiversity. As reported by Scarascia-Mugnozza et al. [58], the plant species and forest trees identified in this region are 25,000 and 247, respectively, largely more abundant than the corresponding varieties that could be counted in central Europe (6,000 plant species and 135 forest trees). Data collected in 2010 showed that Italy is the sixth European country for forest area and, in the Mediterranean region, only Spain has a larger forest extension [27,52] (Fig. 2.3).

According to the scientific and technical literature [11,14,27,42,44,52,58], the most common species in the Mediterranean forests are pines, firs, spruces, larches, junipers, oaks, beeches, chestnut trees and birches (that are autochthonous), and eucalyptus, acacia, poplars and plane trees (non-indigenuous species) (Tab. 2.2). In addition, some peculiar vegetation systems are present, such as "macchia", "garigue", "dehesa".

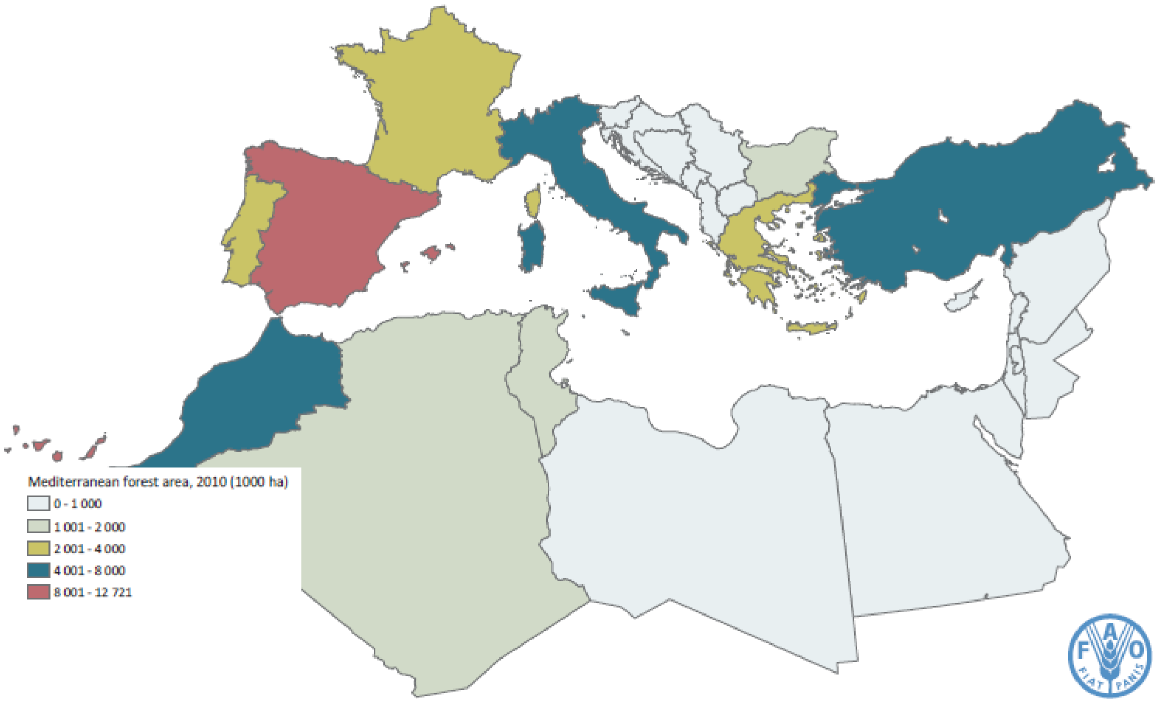

Fig. 2.3. Extension of the Mediterranean forests in 2010 [27].

In the Mediterranean area, summers are dry, and droughts and fires are frequent. The biodiversity conservation and fire protection are of primary importance, and the sustainable management of forests, aimed at maintaining the integrity of the forest heritage, is pursued. For this reason, residual biomass derived from agriculture and agro-industrial activities should be properly collected and destined to energy generation rather than using virgin wood. In Table 2.3, some biomass types eligible for energy purposes are listed.

Tab. 2.2. Typical forestry biomass in the Mediterranean region.

Group	**Biomass**	**Common name**
Conifer	Pinaceae:	
	• *Pinus brutia, P. cembra, P. halepensis, P. heldreichii, P. laricio* Poiret, *P. leucodermis, P. mugo, P. nigra, P. pinaster, P. pinea, P. sylvestris*	Pine
	• *Cedrus brevifolia*	Cedar
	• *Picea abies* Karst, *Abies alba, A. pinsapo, A. marocana, A. numidica, A. cephalonica, A. ciclica, A. equi-trojani, A. nebrodensis*	Fir/Spruce
	• *Larix decidua* Mill	Larch
	Cupressaceae:	
	• *Juniperus oxycedrus, J. phoenicea, J. thurifera*	Juniper
	• *Cupressus sempervirens*	Cypress
Deciduous	Fagaceae:	
	• *Quercus afares, Q. alnifolia, Q. calliprinos, Q. cerris* L., *Q. coccifera, Q. euboica, Q. faginea, Q. frainetto, Q. ilex, Q. ithaburensis, Q. petraea, Q. pubescens, Q. pyrenaica, Q. robur, Q. suber, Q. toza, Q. vallonea, Q. vulcanica*	Oak
	• *Fagus sylvatica* L.	Beech
	• *Castanea sativa*	Chestnut tree
	Anacardiaceae: *Pistacia lentiscus*	Mastic tree
	Betulaceae: *Alnus cordata*	Alder
	Ericaceae: *Arbutus* spp. incl. *A. pavarii, A. unedo*	Strawberry tree
	Fabaceae*: Robinia pseudoacacia* L.	Acacia
	Myrtaceae: *Eucalyptus camaldulensis*	Eucaluptus
	Oleaceae:	
	• *Olea europaea*	Olive tree
	• *Fraxinus angustifolia, F. excelsior, F. ornus*	Ash tree
	• *Phillyrea latifolia*	Green olive tree
	Platanaceae: *Platanus orientalis*	Plane tree
	Salicaceae: Populus nigra	Poplar
	Sapindaceae: *Acer campestre, A. lobelli, A. monspessolanum, A. opalus, A. peronai, A. platanoides, A. pseudolatanus*	Maple
	Sapotacee*: Argania spinosa*	Argan tree
	Ulmaceae*: Celtis aetnensis, Zelkova sicula, Z. abelicea*	Elm
Palm	Arecaceae: *Chamaerops humilis, Phoenix theophrastii*	Palm tree

Tab. 2.3. Biomass suitable for energy production typical of the Mediterranean region.

Supply sector	**Biomass**	**Reference**
Forestry	Pines, Silver fir, Eucalyptus, Holm oak (white oak), Acacia	[11,14,44,52]
Energy crops	*Miscanthus* spp., *Arundo donax, Cynara cardunculus,* maize, triticale, sorghum	[3,38,42]
Agriculture (herbaceous and residues)	Olive tree pruning, cereal straw, wheat, barley, rice husk, artichoke residues, prunings of fruit trees, vine shoot waste	[12,52,59]
Agro-industrial residues	Olive pomace, olive cake, grape marc, fruit shells, hazelnut shells	[12,52]

These biomass types are characterized by great differences in the chemical composition, particularly in terms of macro-nutrients and micro-elements, and ash content (Tab. 2.4-2.6). In relation to the biomass chemical composition, the carbon content ranges from 35 to 54 $\%wt_{d.b.}$ and is the most abundant element, together with oxygen. Prunings and shoots display the lowest carbon content, while the highest is observed in grape marc, olive residues and some forest trees (pines). The hydrogen content ranges from 4.4 $\%wt_{d.b.}$ to 6.9 $\%wt_{d.b.}$. The nitrogen levels display bigger differences, varying from 0.07 $\%wt_{d.b.}$ to 3.42 $\%wt_{d.b.}$, and the highest values could be observed in the acacia tree; alfalfa straw, palm kernel, grape marc and olive pomace have high nitrogen content as well [49]. Sulfur and chlorine are generally low, with some differences between forest trees and other biomass types; in forest trees, the lowest S and Cl content is observed (≤ 0.01 $\%wt_{d.b.}$), while the highest sulfur content could be found in hazelnut shell (0.9 $\%wt_{d.b.}$) and the highest chlorine content is displayed by alfalfa straw (5.3 $\%wt_{d.b.}$).

In general, the most abundant macro-elements in the fuel biomass are Ca, K, Si, Mg, Al, Fe, P and Na, but some differences in dependence to the biomass origin could be observed. Wood biomass is enriched in calcium, magnesium and manganese, while potassium and silica are abundant in agricultural and agro-industrial biomass. The most abundant heavy metals in biomass are zinc, nickel, copper and chromium, as displayed in Table 2.6.

2.3 Biomass combustion ash

The diffusion of biomass as a renewable energy source produces environmental and economical advantages, but also generates increasing amounts of waste, whose reuse is still under investigation. In the next future, the ash amount will predictably grow accordingly to the number of biomass plants. Vassilev et al. [68] estimated that the amount of ash produced annually worldwide from biomass combustion is approximately 480 million ton. Modolo et al. [46] observed that this quantity is becoming comparable to that of coal ash, namely 780 million ton produced per year at present. According to the estimates proposed by James et al. [37], a range of 1.6×10^7 - 3×10^7 tonnes of ash was produced in 2005 in Europe from fuel wood produced domestically (i.e., not imported nor generated from wood industrial residues), and the future trend in the use of biomass for energy generation will potentially lead to a production of 15.5×10^7 tonnes of ash in the EU-27 by 2020.

The ash content varies greatly according to the fuel biomass (Tab. 2.4). Among the woody biomass, it could be observed that the ash content varies greatly according to the section of the tree considered; indeed, prunings contain 3-15 $\%wt_{d.b.}$ of ash, which is largely greater than the corresponding level in the whole plant (0.2-1.5 $\%wt_{d.b}$). The ash content is remarkable higher in the herbaceous and agro-industrial biomass than in trees, and the highest value could be observed in rice husks (19.5 $\%wt_{d.b.}$).

Tab. 2.4. Elemental characteristics and ash content [%wt$_{d.b.}$] of the fuel biomass.

Biomass	**C**	**H**	**O**	**N**	**S**	**Cl^-**	**Ash**	**Reference**
Coniferous wood	51.0	6.3	42.3	0.1	0.02	0.01	0.3	[49]
Deciduous wood	49.0	6.2	44.4	0.1	0.02	0.01	0.3	[49]
Pine	52.8	6.1-6.4	39.8-40.6	0.1-0.5	0.05-0.09	0.01-0.06	0.4	[63-64]
Pine pruning	51.9	6.3	38.6	0.5	0.01	n.d.	2.7	[40]
Eucalyptus	48.5	5.9	44.6	0.3	0.01	0.14	0.8	[63]
Silver fir	52.8	5.5	40.3	0.5	n.d.	n.d.	0.9	[55]
Oak	49.5-50.4	5.4-6.6	41.1-44.5	0.4	0.01	0.04	0.2-1.5	[20]
Acacia	49.2-50.8	5.7-6.0	39.3-40.8	2.3-3.4	0.09-0.18	0.02-0.04	0.3	[20,39,43,63]
Olive tree pruning	37.9	5.9	42.0	0.7	0.21	0.03	13.3	[20,29]
Fruit trees pruning	48.6-51.1	6.2-6.5	26.6-40.6	0.5-1.1	<0.01	0.01-0.04	3.8-15.0	[13]
Vine shoot pruning	34.6-47.6	5.6	40.7-55.3	0.6-1.8	0.08-0.24	0.08	3.8-4.1	[20,29,69]
Cardoon	40.1-43.7	5.5-6.0	36.9-46.8	0.3-1.8	0.05-0.38	1.31-1.82	6.8-11.7	[32,47]
Giant reed	43.0-47.0	6.0	33.8-47.2	0.5-1.6	0.09-0.35	0.29-0.70	3.2-11.3	[47,63]
Miscanthus	47.9-49.2	6.0	40.7-42.6	0.4-0.6	0.15-0.55	0.13-0.33	3.0-3.3	[63,67]
Swichgrass	42.20	5.4	41.2	0.5	0.10	0.10	10.6	[20]
Sorghum	40.8-47.3	4.4-5.8	40.4-48.2	0.4-0.7	0.09-0.27	0.30	4.7-6.9	[29,41,63]
Barley	41.6-46.9	5.3-6.1	39.4-47.0	0.4-1.8	0.06-0.35	0.35-0.98	4.9-6.3	[29,63]
Maize	44.6	5.4	41.0	0.4	0.05	1.48	8.5	[63]
Wheat	46.7-49.2	5.5-6.5	38.9-41.5	0.2-1.2	0.09-0.26	0.33	4.9	[29,63]
Cereal straw	40.2-47.6	5.9-6.9	41.6-49.0	0.4-1.2	0.09-0.32	0.23	3.4	[29,63]
Alfalfa straw	49.9	6.30	40.8	2.8	0.21	5.30	0.5	[67]
Rice straw	50.1	5.7	43.0	1.0	0.16	0.58	20.1	[67]
Rice husk	38.9-49.3	5.0-6.0	24.9-43.8	0.4-0.8	0.02-0.51	0.09-0.12	10.9-19.5	[20,69]
Olive kernel	51.2	6.0	39.3	0.8	0.09	n.d.	2.6	[66]
Palm kernel	48.3	6.2	37.4	2.6	0.26	0.21	5.1	[64]
Almond shell	50.3	6.2	42.5	1.0	0.05	0.06	3.3	[67]
Hazelnut shell	47.1-51.6	5.3-6.2	38.3-46.8	0.1-1.6	0.04-0.86	n.d.	0.7-1.4	[20,29]
Bagasse	45.9	5.7	42.9	1.7	n.d.	n.d.	3.8	[20]
Olive pomace	51.42	6.6	34.3	2.0	0.11	0.39	5.6	[20,45]
Grape marc	54.0	6.1	29.6	2.4	0.15	n.d.	7.8	[40]

Tab. 2.5. Chemical composition [%wt$_{d.b.}$] of the fuel biomass.

Biomass	**SiO_2**	**CaO**	**K_2O**	**P_2O_5**	**MgO**	**Al_2O_3**	**Fe_2O_3**	**Na_2O**	**MnO**	**Reference**
Conifers wood	0.64	0.70	0.24	0.12	0.13	n.d.	n.d.	0.03	0.03	[49]
Deciduous wood	0.03	0.56	0.18	0.07	0.04	n.d.	n.d.	0.01	0.02	[49]
Pine	0.25	0.03	0.02	0.01	0.01	0.03	0.02	0.00	n.d.	[64]
Pine pruning	0.21	1.19	0.60	0.15	0.31	0.07	3.38	0.01	n.d.	[40]
Eucalyptus	0.02	0.73	0.30	0.08	0.08	0.02	0.00	n.d.	0.00	[20]
Silver fir	0.11	0.33	0.15	0.02	0.05	0.03	0.04	0.03	n.d.	[20]
Oak	0.01	0.10-0.99	0.01-0.15	0.02	0.13	0.01	0.01	0.01	0.00	[20]
Acacia	n.d.	0.07-0.56	0.20	0.08-0.26	0.68	0.00	0.00	0.13	0.00	[43,72]
Olive tree pruning	6.66	4.46	0.73	0.25	0.35	0.52	0.21	0.07	0.01	[50]
Vine shoot pruning	0.93	0.29	0.14	0.00	0.03	0.30	0.02	0.00	0.00	[1]
Cardoon	0.19-0.91	1.71-3.89	0.57-0.78	0.31-0.33	0.13-0.31	0.34	0.09	1.73	n.d.	[47]
Giant reed	1.33-3.69	0.14-0.86	0.61-0.68	0.07-0.18	0.17-0.36	0.09	0.04	0.02	n.d.	[47]
Mischantus	0.97-3.57	0.28	0.84	0.16	0.10	0.11	0.01	0.03	n.d.	[5,47]
Switchgrass	6.04-7.42	0.53-1.70	0.11-1.59	0.21-0.58	0.16-0.53	0.05	0.06	0.05	n.d.	[66]
Sorghum	2.55	1.40	0.10	0.04	0.09	0.34	0.16	0.03	0.00	[30]
Barley	0.01	0.36	0.50	0.13	0.07	0.02	0.01	n.d.	0.00	[51]
Maize	5.24	0.34	1.57	0.40	0.05	0.06	0.01	0.02	n.d.	[20]
Wheat	n.d.	0.04	0.42	0.43	0.13	n.d.	0.00	n.d.	0.00	[36]
Cereal straw	1.94	0.23	0.88	0.09	0.06	0.03	0.02	0.02	0.00	[71]
Alfalfa straw	0.42	1.32	2.02	0.55	0.75	0.01	0.02	0.08	n.d.	[67]
Rice straw	15.52	0.49	2.53	0.20	0.54	0.11	0.10	0.36	0.07	[67]
Rice husk	10.31	0.11	0.25	0.06	0.04	0.04	0.04	0.03	0.00	[67]
Olive kernel	1.17	0.60	0.24	0.06	0.10	0.18	0.16	0.02	n.d.	[66]
Palm kernel	0.94	0.48	0.85	1.60	0.47	0.32	0.13	0.01	0.03	[64]
Almond shell	0.56	0.38	1.76	0.16	0.15	0.10	0.09	0.06	0.00	[30,67]
Hazelnut shell	0.23	0.10	0.21	0.02	0.11	0.04	0.05	0.02	0.00	[17,20]
Bagasse	2.04	0.07	0.13	n.d.	0.08	0.58	0.56	0.03	n.d.	[66]
Olive pomace	1.24	0.22	2.44	n.d.	0.26	0.14	0.04	0.05	n.d.	[45]
Grape marc	0.74	2.22	2.87	0.69	0.37	0.21	0.14	0.05	n.d.	[40]

Tab. 2.6. Heavy metal content [mg·kg-1d.b.] in biomass used as fuel.

Biomass	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Reference**
Conifers wood	0.2	n.d.	n.d.	n.d.	3.0	n.d.	[49]
Deciduous wood	0.1	n.d.	n.d.	n.d.	5.0	n.d.	[49]
Pine	6.8	28.2	n.d.	67.4	32.8	n.d.	[48]
Eucalyptus	7.9	56.9	n.d.	43.4	61.1	n.d.	[48]
Oak	10.0	n.d.	120.0	n.d.	220.0	n.d.	[20]
Acacia	n.d.	n.d.	0.7-1.3	n.d.	n.d.	0.4-1.3	[43,72]
Fruit tree pruning	0.2	1.2	2.3-68.9	0.7	1.1	5.1-22.8	[13]
Vine shoot pruning	n.d.	61.8	n.d.	29.4	22.8	45.0	[1]
Miscanthus	0.1	1.0	2.0	2.0	2.0	10.0	[5]
Switchgrass	9.8	49.0	66.0	37.0	3.0	103.0	[69]
Barley	0.6	12.6	90.9	4.8	26.6	181.4	[51]
Wheat	0.1	0.5-10.0	2.0-5.6	0.2-1.0	0.5	10.0-41.2	[5-6,36]
Cereal straw	0.0	4.6	1.9	1.0	0.2	10.6	[9]
Rice husk	8.2	348.0	76.0	107.0	7.4	103.0	[69]

According to the European Waste Catalogue [21], that lists and encodes wastes on the basis of its origin and nature, biomass combustion ash is classified as “wastes from thermal processes” (Chapter 01 of the list of waste and, particularly “wastes from power stations and other combustion plants (except 19)”). Referring particularly to its hazardousness, biomass ash usually consists in non hazardous waste. Depending on its nature, biomass ash could be ascribed to codes 10 01 01 (“bottom ash, slag and boiler dust (excluding boiler dust mentioned in 10 01 04)”) or 10 01 03 (“fly ash from peat and untreated wood”). At present, biomass ash is usually disposed in landfills as a waste, which constitute the least preferable option for the management of waste [18], but reusing these residues should be rather pursued in order to maximize their potential in accordance to the Circular Economy approach.

The economical and environmental strategy called Circular Economy (CE) has been adopted by many countries in the last years, for achieving a more sustainable growth [31,54]. In the European Union, the framework document "A zero waste programme for Europe" and the related action plan were recently released [24-25]. CE, whose roots trace back to ecological economics, is aimed at enhancing the resource productivity and contrasting the open-ended industrial model where resources, products and waste are linearly conceived [2,35]. Economic benefits are expected for all the actors in the society, since the authentic scope of CE is directed at achieving progress in all the socio-economic activities [35,60,70]. In particular, industry competitiveness is expected to increase because the loss of valuable waste and the procurement of new resource are reduced. In relation to the environment, the Circular Economy strategy is based on the efficient use of resources, whereof waste management is a part, and the contrast to natural resources depletion [24-25,31,60]. According to the EU intentions, the adoption of the CE strategy induces the revision of the existing Waste Framework Directive [18] in order to obtain improvements in the Member States' targets related to waste management and promote the residues reuse in the natural and production cycles.

Based on these assumptions, it is compelling to identify possible reuse options for the emerging waste stream constituted by biomass ash, starting from the knowledge of the complex ash composition. Some strategies to reprocess biomass ash have already been proposed. They include the use of ash in many fields [56]:

- construction materials for civil engineering (e.g., for concrete manufacturing, as a component for ceramic bricks and in road construction),
- agriculture and forestry (e.g., soil improvement),

- environmental applications (e.g., neutralization of acid waste, adsorbent preparation),
- general industrial processes (e.g., phosphorus recovery).

The recycling of biomass ash in construction materials meets the recommendations of the European Directive on waste 2008/98/CE and has the significant environmental benefit of minimizing the extraction of natural aggregates from quarries [12]. This category of solutions are the most common and several articles have investigated the ash recycling in concrete, cement and brick production, or as a filling material in embankments. However, these recycling options entail some unsolved problems:

- *Ash as a partial substitute to Portland cement*: The utilization of biomass ash as a cementitious replacement material has not been well received yet as it sometimes needs grinding and only a partial replacement of cement is possible. Moreover, coarse ash usually contains variable amounts of organic matter and is porous; for this reason it increases the mixture water requirement [57].
- *Ash as a filler in concrete manufacturing*: Biomass ash is prone to retain water and could contain unburned organic matter that could impede the reuse as a filler for concrete manufacturing [15]. In addition, the particle size distribution and chlorine content in ash could render it not conformed to the requirements for filler commercialization.
- *Ash as a substitute to sand in concrete manufacturing*: Biomass ash addition may result in a significant decrease of the mechanical and durability properties of concrete. Therefore, it is advisable to use recycled ash at small replacement rates and in non-structural concretes, which do not require high technical needs [5].
- *Ash in road construction*: Coarse biomass ash is composed of particles with rough surface textures which form pores under the road pavement. Previous researches have shown that the water absorbed by ash affects the mechanical properties of road pavement. The manufactured road was found to be susceptible to brittle failure because of ash high porosity and low density [10].
- *Ash in ceramic brick:* The finest type of ash was proposed by Pérez-Villarejo et al. [50] as a component for ceramic bricks, however the high porosity and carbonate content make the ash-containing ceramic products brittle and water retentive.

Controversial aspects characterize also the other reuse options:

- *Phosphorus recovery:* Phosphorus is present in biomass ash and studies to recover it have been conducted. Supercritical extraction resulted to be the most efficient process to release P, that is also the most expensive [62].
- *Glass industry:* Silica is the main chemical species present in the coarsest type of ash. For this reason there are studies aimed at recycling ash in the glass industry, as a source of silica or as an additive for producing silicate glass. However, differences among the ash-derived glass and the one produced from traditional silica source were observed, in relation to glass density, color and absorption spectra [53].
- *Soil improvement:* Ash has high alkaline properties and is subjected to pH changes during its exposure to weathering. These conditions affect the leaching behavior of some of the heavy metals [28,61]. Freire et al. [28] suggested that selenium and chromium could become more leachable at pH values ranging from neutral to alkaline.
- *Neutralization of acid waste:* Due to the alkaline pH and the high acid neutralization capacity, biomass ash was proposed as a neutralization agent for acid mine drainage. This recycling solution could be preferred when high amounts of heavy metals affect the ash quality and hinder the agricultural use [4,65].
- *Adsorbent preparation:* Similarly to the pyrolytic biochar, biomass ash has been proposed as precursors for adsorbent preparation for a wide range of pollutants. However, the ash pore structure, volume and specific surface area could not be suitable for this scope or require an extensive pretreatment before being used to prepare activated carbon, so that this reuse option is not always feasible [16].

In this context, it is interesting to investigate innovative recycling solutions on the basis of the peculiarity of each biomass ash type:

- Some ash types are characterized by high macro- and micro-elements useful for plant growth. It is with the aim of returning nutrients and residual organic carbon to soil, that agriculture and herbaceous residues are often burned at the end of the harvesting operations [8]. The addition of biomass ash as a mineral addition to organic waste composting could be a more adequate option, alternative to burning agricultural residues or spreading ash directly to soil that could generate some issues in terms of environmental pollution and uncontrolled fires.

- These biomass residues are expected to constitute a promising substrate for mineralogical CO_2 uptake because of the high alkali and alkali-earth (hydro)oxides observed by other authors in residues having comparable chemical and mineralogical properties [34]. That said, carbonation naturally occurs when an alkaline residue, such as ash, is subjected to atmospheric CO_2 and moisture conditions. It is part of a wider phenomenon named weathering, which provokes various modifications in the physical, chemical and mineralogical characteristics of ash, the most important of which, under an environmental point of view, is the leaching behavior. For these reasons, biomass ash carbonation deserves a deep investigation, however at present very few studies are available on this issue.

These two research lines are novel and aim at recycling the new waste stream constituted by biomass ash by addressing some relevant topics: the return of nutrients to soil and the enhancement of the compost quality, the need for a major awareness of the evolution of ash leaching behavior, and the ash contribution to the CO_2 capture. For these reasons these recycling solutions were the subjects of the present research, and studied through the analytical determinations and experimental campaigns described in the following Chapters.

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CHAPTER 3

Biomass ash characterization

3.1 Introduction

In a context where the spread of biomass as a renewable source characterize the energy scenario, new environmental concerns become compelling. The recycling of the solid residues generated by biomass combustion is essential to minimize the impact of this kind of activities and offers new opportunities in terms of valorization of waste as a resource.

To this purpose, the knowledge of biomass ash characteristics assumes an essential role. Extremely large variations affect the biomass combustion residues, which impose an in-depth investigation on the ash specificities prior to design any reuse option. Each recycling solution should be developed on the basis of the waste peculiarities, which vary depending on the initial fuel biomass, combustion technology, operating conditions and plant section corresponding to the ash discharging point.

Notwithstanding, information on the ash characteristics are usually scarcely considered and efforts should be made to deepen the understanding of this issue.

3.2 State of the art

The 2008/98/EC Directive on waste [17], known as Waste Framework Directive, is one of the most important environmental policies in the European Union. It sets the fundamental principles of the modern waste management and establishes the Member States' legislation should be conformed to a hierarchy of management options where prevention, reuse, recycling and recovery of waste are to be pursued. Notwithstanding, in many cases suitable reuse options are still under study. The waste generated by the biomass conversion technologies is one such matter, particularly the ones deriving from combustion.

Ash represents the inorganic, mineral fraction of the initial fuel and contains, in concentrated form, all the macro-nutrients and micro-elements originally present in the fuel biomass. In general, biomass ash contains major (Si, Ca, Mg, K, P) and minor elements (Fe, Mn, Zn), and is very alkaline [49,61], but wide variations could be observed among the ash generated from different biomass types. In addition, unburned carbon is usually present in biomass residues at an extent that depends on the combustion conditions and efficiency [63]; indeed, the combustion residues may include amounts of organic matter up to 25 $\%wt_{d.b.}$ due to the inefficiencies in the combustion process [26,66]. Organic matter is composed by carbon, oxygen, hydrogen and, to a lesser extent, nitrogen and sulfur, so that the amount of unburned carbon affects both the quantity and the chemical composition of the ash generated.

In Tables 3.1 and 3.2, the chemical composition of biomass ash, as reported in the literature, is displayed. The wide variability in the ash chemical composition and physical properties reported by several authors depends on the feed heterogeneity (e.g., structure of macro-components in terms of lignin, cellulose and hemicellulose, fertilizers supply, soil characteristics and presence of contaminants), combustion technology and operating conditions. These aspects influence the ash properties at different extent.

Ash deriving from some agricultural biomass varieties, such as rice husk and straws, has high levels of potassium, phosphorus and sodium, eventually present as oxides or silicates, that are low-melting point compounds. This feature affects the ash melting behavior and can cause ash melting on the combustion grate [5,32,37], making forest trees more preferable as a fuel. Interestingly, some ash components could have a role in immobilizing the volatile compounds emitted during the combustion process itself, which are hazardous for the environment.

Tab. 3.1. Chemical composition of ash [%wt$_{d.b.}$] from selected biomass varieties.

Fuel biomass	**Si_2O**	**CaO**	**K_2O**	**P_2O_5**	**MgO**	**Al_2O_3**	**Fe_2O_3**	**Na_2O**	**TiO_2**	**SO_3**	**Cl^-**	**Reference**
Biomass (not specified)	2.8-80.0	4.8-57.7	4.6-31.1	1.2-7.8	0.8-4.8	0.3-18.5	1.7-6.9	0.3-1.9	0.80	0.8-15.0	n.d.	[52]
Wood chips	8.6-23.5	36.4-53.2	5.9-7.6	n.d.	3.7-6.0	n.d.	n.d.	0.4-0.7	n.d.	n.d.	n.d.	[38]
Wood	16.0-45.8	2.4-54.2	0.3-12.2	0.3-4.8	0.4-11.7	0.1-6.3	0.1-5.0	0.1-3.1	0.40	0.7-4.2	0.01	[8,24,37,43,58]
Olive husk, kernel	32.7-67.7	0.5-14.5	0.2-4.3	2.5	0.1-4.2	8.4-20.3	0.1-6.3	11.2	0.30	0.6	0.20	[37]
Rice (husk, straw)	77.2-96.7	0.0-2.7	0.7-12.6	0.2-1.0	2.7	0.1-0.6	0.0-0.5	1.8	0.04	0.1-1.2	0.12	[21,32]
Shells (hazelnut,almond)	23.5-33.7	10.5-15.4	30.4-48.5	3.2-4.5	5.2-7.9	2.7-3.1	2.8-3.8	1.3-1.6	0.10	0.8-1.1	0.2	[32]
Wheat (whole, straw)	8.0-78.9	2.2-14.7	2.0-29.2	0.9-4.0	0.7-4.0	0.1-3.5	0.0-2.0	0.2	0.03	0.1-4.5	3.60	[9,18,32,37,58]
Straw	34.2-64.2	6.3-11.2	12.1-19.3	n.d.	1.8-4.5	n.d.	n.d.	0.2-1.0	n.d.	n.d.	0.54	[38]

Tab. 3.2. Heavy metal content in ash [$mg\cdot kg^{-1}_{d.b.}$] from selected biomass varieties.

Fuel biomass	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mn**	**Mo**	**Ni**	**Pb**	**Se**	**Zn**	**Reference**
Pine	n.d.	10	n.d.	70	210	n.d.	6,631	n.d.	n.d.	330	n.d.	14	[19,24]
Beech wood chips	4.5	4.9	4.2	2	98	n.d.	10,595	2.1	36	39	16.4	213	[62]
Spruce chips	n.d.	3.0-6.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	260-500	[38]
Wood	0.4	0.1	n.d.	51	n.d.	n.d.	5,720	n.d.	37	4	n.d.	48	[8]
Biomass (not specified)	<0.1	n.d.	7.0	61	113	<0.1	1-77	10.0	35	26	<0.1	161	[49,52]
Switchgrass	9.4	9.8	1.3	5	66	n.d.	872	5.4	37	3	37.1	103	[62]
Cereals and cereal straw	n.d.	0.1-6.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	60-90	[4,38]
Rice husk	9.4	8.2	2.1	3	76	n.d.	1,825	4.4	107	7	35.3	103	[62]

Indeed, some ash types having an alkaline composition could be effective in sequestering volatile compounds rich in sulfur and chlorine or having trace elements, and co-firing of biomass and contaminated residues (such as municipal solid waste, sewage sludge, petroleum coke) has been suggested as a strategy for reducing the hazardous gaseous emissions in the incineration plants [60].

The combustion technology and operating conditions affect some of the ash characteristics too. Fernandes et al. [21] conducted a study where rice husk was burned in reactors having different combustion methods: moving grate, fluidized bed, and suspension/entrained combustion chamber. They observed that the residues differed significantly in terms of organic matter content, particle size, specific surface area and silica mineralogy, while the chemical and mineralogical composition was not generally affected by this factor. The process temperature affects the ash composition, because of the decrease in unburned carbon and nitrogen content when temperature values increase [24]; in this case, the amount of some heavy metals increases consequently, as an effect of the inorganic fraction concentration. For some of the heavy metals, available data on the total content are scarce, which is the case of Ba, Sb and Sr.

Finally, several types of ash could be produced in a biomass thermal power plant depending on the distinct discharging point, whose properties vary significantly. Typically, three ash types are produced in a combustion plant, as described by IEA [27]:

- bottom ash,
- boiler or cyclone ash (also named "coarse fly ash"),
- fly ash (also named "fine fly ash").

Each ash type is produced in shares that depend on the combustion technology. In the case of fixed-bed combustion systems, a predominance of bottom ash (60-90 $\%wt_{d.b.}$) and lower amounts of boiler and fly ash (10-40 $\%wt_{d.b.}$) are generated [40]. In Tables 3.3 and 3.4, the typical chemical composition of biomass bottom and fly ash reported by other literature works is displayed; in some cases, the original fuel biomass is not specified, though.

Tab. 3.3. Typical chemical composition [%$wt_{d.b.}$] of bottom and fly ash.

Fuel biomass	**Si_2O**	**CaO**	**K_2O**	**P_2O_5**	**MgO**	**Al_2O_3**	**Fe_2O_3**	**Na_2O**	**TiO_2**	**SO_3**	**Cl^-**	**Reference**
BOTTOM												
Wood chips	n.d.	46	6.1	2.2	7.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	[39]
Wood pellets	n.d.	27	12.8	1.4	7.3	2.0	1.5	1.3	n.d.	0.2	n.d.	[42]
Wood	34-61	11-20	12.7-15.8	n.d.	2.9-4.0	0.6-1.4	1.3-2.2	0.3-0.5	0.1-0.2	0.7-1.2	0.0-0.5	[26]
Straw	n.d.	8	14.3	2.2	4.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	[39]
Biomass	35-40	2-10	0.7-3.0	0.1-0.5	0.3-1.0	0.9-5.0	0.4-2.0	0.2-0.8	0.0-0.2	n.d.	n.d.	[33]
FLY												
Wood (coarse ash)	n.d.	46.8	6.2	2.5	7.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	[39]
Wood (fine ash)	n.d.	18.1	22.0	0.4	2.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	[39]
Wood	n.d.	25.2	2.78	1.6	2.8	3.1	n.d.	n.d.	n.d.	5.7	n.d.	[41]
Wood pellet	n.d.	25.1	12.1	1.5	7.0	1.5	1.1	1.3	n.d.	7.7	n.d.	[42]
Straw (coarse ash)	n.d.	3.7	10.1	1.4	1.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	[39]
Straw (fine ash)	n.d.	1.2	48.2	1.2	0.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	[39]
Biomass	2.6	47.2	20.0	5.0	4.4	0.9	0.5	0.2	0.3	n.d.	n.d.	[58]

Tab. 3.4. Heavy metal content [mg·$kg^{-1}_{d.b.}$] in bottom and fly ash.

Fuel biomass	**As**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mn**	**Mo**	**Ni**	**Pb**	**Se**	**Zn**	**Reference**
BOTTOM														
Wood pellets	1.2	1,590	0.6	8	46	129	0.0	18	7	23	1	0.7	108	[42]
Wood	n.d.	n.d.	0.6	n.d.	15	75	0.0	n.d.	n.d.	16	8	n.d.	200	[10]
Biomass	<0.1	n.d.	n.d.	7	61	113	n.d.	n.d.	n.d.	35	26	<0.1	161	[49]
Biomass	6.4	n.d.	1.8	n.d.	82	125	n.d.	n.d.	n.d.	63	11	n.d.	423	[39]
FLY														
Wood pellet	4	1,470	41	7	120	156	0.1	19	12	21	44	5.9	5,929	[42]
Wood	67	n.d.	11	n.d.	113	192	n.d.	4,340	n.d.	39	553	n.d.	2,600	[41]
Biomass (coarse ash)	11	n.d.	21	n.d.	91	162	n.d.	n.d.	n.d.	66	63	n.d.	3,024	[39]
Biomass (fine ash)	31	n.d.	37	n.d.	87	152	n.d.	n.d.	n.d.	73	219	n.d.	6,828	[39]
Biomass	8	n.d.	5	15	54	127	n.d.	n.d.	n.d.	62	25	n.d.	376	[30]

If the chemical composition of each ash type is analyzed, silica is typically the most abundant element in bottom ash, while calcium is predominant in fly ash. In the finest ash fraction, higher amounts of S and Cl could be observed [64]. The sulfur and chlorine amounts in fly ash depend on the efficiency of the abatement methods adopted to clean the flue gas [5]. Some heavy metals could be found in higher amounts in fly ash than in bottom ash because they vaporize in the combustion chamber and condense in the finest particles when the flue gas temperature decreases; on the contrary, the least volatile metals remain in the bottom ash [5].

Biomass combustion ash is often related to coal ash, being coal the main solid fuel used at global level, whose amount in the fuel (8.5-10.5 $\%wt_{d.b.}$) is usually greater than in the majority of biomass types [57] (Tab. 3.5). However, differences exist between the residues of biomass and fossil fuels combustion, as it could be deduced by observing the characteristics of fossil fuel ash displayed in Tables 3.5-3.6.

Firstly, biomass ash has higher pH values than coal residues. Secondly, biomass ash shows higher macro-nutrients content and lower Al, Fe and S total content than coal residues [23,58,61,65]. On the contrary, some heavy metals such as Cu, Mn, Pb and Zn could be higher in biomass ash than in coal ash, as Tables 3.4 and 3.6 show. Vassilev et al. [62] observed that Cr and Sr are sometimes higher in biomass residues than in coal ash, as well. Indeed, biomass ash could occasionally contain higher amounts of heavy metals than coal residues, that the plants took from soil, fertilizers, water, pesticides with during their lives. For this reason any management option proposed for combustion residues might raise environmental concerns about its impact on water and soil. In relation to heavy metals, the leaching behavior is one essential feature because it defines the hazardousness of a residue. The existing regulation about water-leaching from waste [15] is, therefore, a fundamental reference. Generally, biomass ash does not constitute an environmental issue in terms of the heavy metals leachability because biomass ash leachates are alkaline and the initial concentrations of most of the heavy metals usually low. However, when pH varies the leachate composition changes along with the mobility of a number of chemical species. In fact, the majority of heavy metals are soluble at very pH levels, while Mo, Se, Sb and V oxianions have higher mobility at neutral pH values; nevertheless, chromates are soluble at alkaline conditions, and Pb and Al are amphoters, so that they have higher mobility at high and low pH values than at neutral pH. This suggests that for any step of the ash management and disposal that shall induce pH variations, a potential hazard for the environment arises.

Tab. 3.5. Typical elemental composition [%wt$_{d.b.}$] of ash generated by fossil fuel combustion.

Fuel type	**Si_2O**	**CaO**	**K_2O**	**P_2O_5**	**MgO**	**Al_2O_3**	**Fe_2O_3**	**Na_2O**	**TiO_2**	**SO_3**	**Cl^-**	**Reference**
Peat	38	10.0	1.1	2.8	2.1	20.1	13.8	0.1	0.3	12.1	0.06	[19,61]
Lignite	31-55	7.9-27.2	0.2-1.9	0.0-0.6	2.0-9.0	8.0-29.8	5.0-10.8	0.2-0.7	0.4-1.4	0.8-14.4	0.02	[19,44,57-58,61]
Sub bituminous coal	55	7.1	1.7	0.1	2.1	22.9	5.3	1.1	1.0	4.1	n.d.	[61]
Bituminous coal	48-68	0.4-6	0.3-2.8	0.2	0.3-1.8	22.0-35.0	0.8-10.0	0.1-0.8	1.0-2.2	0.2-3.3	0.07	[19,58,61]
Bituminous/sub bituminous	38-63	0.2-0.8	0.0-0.9	n.d.	0.0-0.5	27.0-44.0	3.3-6.4	0.1-0.4	0.4-1.8	n.d.	n.d.	[44]
Anthracite	52-54	0.3-0.5	2.8-3.0	n.d.	0.9-1.2	21.5-23.8	6.1-7.2	0.2-0.4	n.d.	0.1-0.3	0.08	[19,44]
Coal (ash type not specified)	33-63	0.2-22.8	0.0-3.3	0.3-1.6	0.0-5.2	16.2-44.0	3.3-20.4	0.1-2.3	0.4-1.8	2.2-10.1	0.02	[19,49,57,61,65]
Coal (fly ash)	42-63	0.5-12.4	0.2-3.0	0.2-2.5	0.7-2.7	14.9-59.0	0.4-14.7	0.0-2.0	0.7-1.5	0.0-0.5	n.d.	[3,28,42,46-47,66]

Tab. 3.6. Total heavy metal content [mg·kg$^{-1}_{d.b.}$] in ash generated by fossil fuel combustion.

Fuel type	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mn**	**Mo**	**Ni**	**Pb**	**Se**	**Zn**	**Reference**
Lignite	1	n.d.	77	137	64	<0.1	135	3	140	40	2.4	298	[49]
Coal (ash type not specified)	70-92	2-4	14-16	0-130	46-68	n.d.	0-496	2-5	63-87	39-64	2	0-172	[59,66]
Coal (fly ash)	6-40	0-20	58	4-330	19-82	n.d.	10-111	4-40	2-111	1-199	4-48	6-208	[28,46-47,66]

For this reason, Freire et al. [22] suggested that further investigation, including the acid neutralization capacity curve (ANC) and the study of natural phenomena that changes the ash pH, such as natural carbonation, are needed (See Chapter 5).

Not only the heavy metals should be considered when the harmfulness of ash is discussed; another fundamental category of contaminants are the organic pollutants. These harmful contaminants are generated during the incineration process and can be present in biomass ash as a result of incomplete combustion or slow flue gas cooling:

- polycyclic aromatic hydrocarbons (PAHs),
- benzene, toluene, ethylbenzene, the *ortho*, *para* and *meta*-xylenes (BTEX),
- dioxins and furans.

Nonetheless, their amount and characterization in biomass residues is scarcely studied. Straka and Havelcová [51], Freire et al. [22] and Rey-Salgueiro et al. [45] studied this issue and observed that the presence of organic pollutants in biomass ash was related to the amount of the organic matter (unburned biomass) and, in particular, their concentrations were higher when important levels of aromatization/carbonization and high specific surface areas were found in ash. The biomass residues analyzed in the mentioned studies did not exhibit harmful levels of organic contaminants, if compared to the proposed limits for sludge [20]. However a concern on this issue should be raised and, though not included in the present work, included in the assessment of the ash sustainability for agricultural and industrial uses.

3.3 Materials and Methods

The combustion residues used in this study were generated by an industrial thermal power plant (13 MWe) settled in Sardinia (Italy). The plant is entirely fueled with biomass and is equipped with a reciprocating grate combustion chamber where the temperature value reaches 1040°C.

The fuel biomass consists of a mixture of pine and eucalyptus wood chips, representing 75% of the daily feed, and agro-industrial residues, covering the remaining 25%. The fuel sample was collected from different points of the biomass stockpile.

The combustion residues are discharged from different sections of the plant (Fig. 3.1). The first is set at the bottom end of the combustion bed, the second is placed by the super-heater, and the third is situated in correspondence to the collection plate of the electrostatic filters. Depending on the discharging point, the residues considered in the present study are named bottom (BTA), boiler (BOA) and fly ash (FA), respectively (Fig. 3.2).

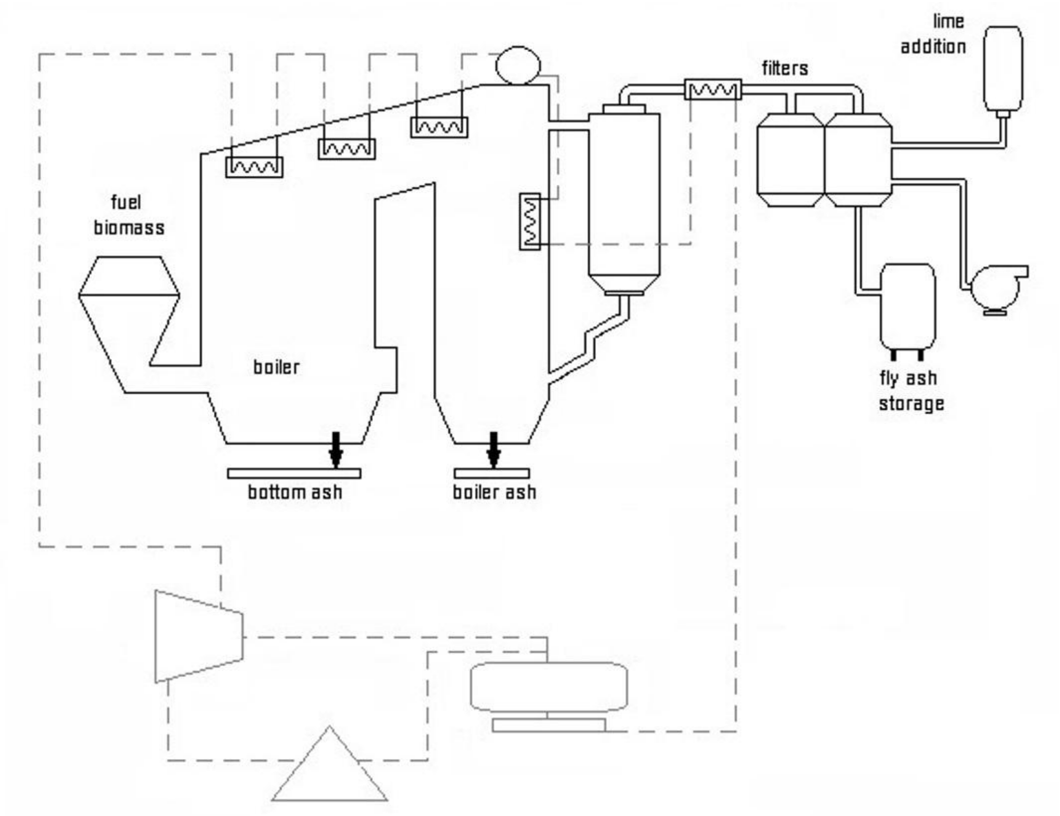

Fig. 3.1. Schematic diagram of the biomass combustion plant where ash were sampled.

Subsamples of biomass and of each of the ash types were collected over a period a 48 hours of usual plant operating conditions, and used to constitute representative samples of approximately 60 kg. The collected samples were air dried and prepared for the subsequent analyses according to UNI 14780:2011. BOA and FA were homogenized and underwent the coning and quartering process, while BTA and the biomass sub-sample were prepared using a riffle box. Biomass, BTA and BOA were ground using cutting and ball mills. Fly ash was constituted by a fine powder, thus did not undergo further preparation.

Fig. 3.2. The biomass combustion residues: BTA (left), BOA (center) and FA (right).

MOISTURE

The moisture content was determined by drying in a thermostatic oven at 105±2°C until mass constancy, i.e. mass did not vary more than 1 mg after a supplementary heating period of 60 min, according to UNI 14774:2009.

Moisture was calculated as follows:

$$M = \frac{(m2 - m3)}{(m2 - m1)} \cdot 100 \qquad (3.1)$$

where

M is the moisture content of the sample, [%wt]

m1 is the mass of the weighting dish, [g]

m2 is the mass of the weighting dish and the sample before drying, [g]

m3 is the mass of the weighting dish and the sample after drying, [g].

LOSS ON IGNITION

Samples were oven-dried at 105±2°C, ground and placed on ceramic crucibles. Loss on ignition (LOI) aimed at determining the volatile solids content was determined by heating the samples in a muffle furnace up to 550±10°C until mass constancy, according to UNI 15169:2007. In this method, chemically bound water and volatile metals are released, thus contributing to the weight loss; while, metals present in the metallic state and sulfides could be oxidized entailing a weight gain. These interferences affect the assumption that LOI at 550°C corresponds to the organic matter present in the sample.

A second ashing step was performed by heating the samples at 950±10°C for 7 minutes according to UNI 15148:2010. Differently from the previous ashing step, carbonates are here decomposed and form CO_2. Thus, the difference between LOI at 950°C and LOI at 550°C is related to the fixed carbon content; however, it should be mentioned that other volatile inorganic compounds are lost or assume a higher oxidation stage, and they could interfere with the results.

Both steps were performed at ambient air and the results are given by the following Equation:

$$LOI = \frac{(m2 - m3)}{(m2 - m1)} \cdot 100 \qquad (3.2)$$

where

LOI is the loss on ignition at 550°C or 950°C, [$\%wt_{d.b.}$]

m1 is the mass of the crucible, [g]

m2 is the mass of the crucible and the sample before heating, [g]

m3 is the mass of the crucible and the sample after heating, [g].

pH AND ELECTRICAL CONDUCTIVITY

The analytical measure was conducted according to UNI EN 15933:2012. The samples were oven-dried at 105±2°C. Amounts of 5.0 g were weighted and placed in Erlenmeyer flasks, where distilled water was added to obtain 100±1 g of solution. The flasks were subjected to shaking for at least 15 minutes, and the obtained solutions were filtered at pore size 0.45 μm membrane filter. The pH and electrical conductivity (EC) values of the filtered solutions were measured using a pH-meter (Orion4 Star, Thermo Fisher Scientific, MA, USA) and a conductivity meter (HQ30d, Hach Company, CO, USA), respectively.

CHN

Samples were dried at 105±2°C and ground. Mass amounts of 0.100 g were weighted using an analytical scale and placed in tin cups. An elemental analyzer (CHN-1000, LECO Corporation, MI, USA) was used to determine the carbon, hydrogen and nitrogen content in biomass and ash in accordance to ASTM D 5373. Certified EDTA (Ethylenediaminetetraacetic Acid) standard was used to calibrate the elemental analyzer.

WATER-SOLUBLE CHLORIDES AND SODIUM

The analytical determination was performed according to the method UNI 15105:2011, aimed at determining the water-soluble chloride. In solid biofuels the Cl-bearing inorganic water-soluble salts (chlorides) and other ion-exchangeable compounds are predominant, so that in this case the results approximate the total chlorine content.

1.0 g of dried and ground sample was weighted and placed into fluoropolymer vessels. After 50.0 g of distilled water was added, the vessels were closed tightly and heated in a thermostatic oven at 120°C for 1 hour. The vessels were allowed to cool down and the solution transferred into 100 ml volumetric flasks with distilled water. Then the solution was filtered at pore size 0.45 μm membrane filter and the chlorides content was determined using an Ion Chromatography System (ICS-90, Dionex, CA, USA).

The sulfur present in the samples as sulfide was completely solubilized as sulfate through a wet digestion, in an acid and highly oxidizing solution. Biomass and ash samples were oven-dried and ground. Biomass and ash amounts of 0.100 g and 0.500 g were weighted using an analytical scale, respectively, and placed in fluoropolymer vessels. 1.35 ml of hydrogen peroxide 30% (vol/vol), 1 ml of nitric acid 65% and 1 ml of hydrochloric acid 37% were added and the covered vessels were placed on a hot plate at approximately 100°C for one hour. After the vessels were uncovered, they were left on the hot plate to continue drying. Distilled water and 0.5 ml of nitric acid were then added and evaporation continued at lower temperature for approximately 15 minutes to ensure complete solubilization of sulfur-bearing salts. The solutions were filtered at pore size 0.45 μm membrane filter and transferred into 50 ml volumetric flasks with distilled water. The total sulfur content in the obtained solutions was analyzed using an Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES, Optima 7000DV, PerkinElmer, MA, USA).

MAJOR AND MINOR ELEMENTS

In the biomass sample, the minor and major elements content was determined by microwave-assisted acid digestion, according to EPA Method 3052.

In the ash samples major elements were determined after alkaline fusion with lithium metaborate ($BLiO_2$) [6], while major elements were determined by microwave-assisted acid digestion.

To perform the microwave-assisted acid digestion, 0.5 g of samples were placed in fluoropolymer vessels with 9 ml of nitric acid 65%, 3 ml of hydrofluoric acid, 3 ml hydrochloric acid 37%. Vessels were closed tight and placed into the microwave. Temperature was increased at 30°C/minute up to 180°C and maintained at 180°C for 9.5 minutes. After digestion, the vessels were cooled down to room temperature, and the solution and the water used to rinse vessels were transferred into fluoropolymer cups. The cups were placed on the hot plate to allow the hydrofluoric acid to evaporate.

Alkaline fusion was conducted by mixing 0.1 g of sample with 1.0 g of $BLiO_2$ at 99% in platinum melting pots. The platinum pots were placed for 1 hour at 1050°C in a muffle furnace. Then the pots were quickly removed from the furnace and placed in glass beakers with 60 ml of distilled water and 5 ml of nitric acid. The beakers were then covered and placed on a magnetic stirrer for 24 hours.

All the obtained solutions were filtered at pore size 0.45 μm membrane filter and transferred into volumetric flasks. The analytical determinations were performed using ICP Spectrometry (ICP-OES, Optima 7000DV, PerkinElmer, MA, USA).

WATER LEACHABLE HEAVY METALS

Samples were pre-treated in order to obtain a grain size suitable for applying the leaching tests. Batch, one-stage leaching tests were performed on ash at a liquid to solid ratio of 10 $L\cdot kg^{-1}$ according to UNI EN 12457-2:2004 for materials with particle size below 4 mm (BOA and FA), and according to UNI EN 12457-4:2004 for materials with particle size below 10 mm (BTA).

Moisture determination was conducted to know the water content in the fresh samples, after which mass samples equivalent to 90±5 g of dried material were weighted and placed in polypropylene bottles. Distilled water was added at the extent of 10 $L\cdot kg^{-1}$ ±2% and the bottles were cupped and placed in a shaker for 24±0.5 hours. The solutions were allowed to settle and filtered at pore size 0.45 μm membrane filter. The eluates were analyzed for the water-soluble fractions of major and minor elements by ICP Spectrometry (ICP-OES, Optima 7000DV, PerkinElmer, MA, USA). The pH and EC values of the eluates were determined as well.

PHYSICAL PROPERTIES

The water holding capacity, bulk density and particle density of the three ash types were determined. Water holding capacity was determined by soaking the samples in water for 24 hours and draining the excess water overnight, according to Ahn et al. [2]. Bulk density was measured according to UNI EN 15103. Particle density was determined using a gas pycnometer (Accupyc II 1340, Micromeritics Instruments Corporation, GA, USA) in accordance to ASTM B 923:2010.

Porosity was determined by means of the formula proposed by Haug [25].

$$n = 1 - \frac{BD_m \cdot TS_m}{G_m \cdot BD_w} \tag{3.3}$$

where

n is the total porosity [%],

BD_m is the wet bulk density of the material [$g \cdot cm^{-3}$],

TS_m is the total solids content of the material [%],

G_m is the specific gravity (unitless), that corresponds to the ratio between particle density of the sample [$g \cdot cm^{-3}$] and particle density of water, corresponding to 1 $g \cdot cm^{-3}$,

BD_w is the bulk density of water, that corresponds to 1 $g \cdot cm^{-3}$.

X-RAY DIFFRACTION

The ash mineralogy was determined using a Rigaku Geigerflex X-ray diffractometer (XRD), with application of Cu-Kα radiation at 30 kV/30 mA and scan speed equal to 2° of (2θ)/min between 4 and 60°.

PARTICLE SIZE DISTRIBUTION

The particle size distribution of BTA and BOA samples was also determined according to UNI 15415-1:2011 and using ASTM and ISO 565 sieves from 8 to 0.063 mm. Loss of ignition at 550°C for each particle size class was determined in accordance to UNI 15169:2007.

3.4 Results and Discussion

3.4.1 Biomass characteristics

The biomass chemical characterization as assessed in the present study is reported in Table 3.7. Moisture content of biomass under concern was 46.6%wt, while LOI at 550°C was 97.3 $\%wt_{d.b.}$. The difference between LOI 950°C and LOI 550°C was very low (0.5 $\%wt_{d.b.}$). According to the ultimate analysis, carbon and hydrogen content were 49.8 $\%wt_{d.b.}$ and 5.8 $\%wt_{d.b.}$, respectively. Sulfur content was 0.02 $\%wt_{d.b.}$, while nitrogen and chloride content were both 0.20 $\%wt_{d.b.}$.

Tab. 3.7. Main properties of the fuel biomass (< d.l.: below detection limit; standard deviation is indicated in brackets).

Parameter	Biomass	Parameter	Biomass
Moisture [%wt]	46.60 (0.43)	Na_2O [$\%wt_{d.b.}$]	< d.l.
LOI 550°C [$\%wt_{d.b.}$]	97.34 (0.10)	MnO_2 [$\%wt_{d.b.}$]	0.01 (0.00)
LOI 950°C [$\%wt_{d.b.}$]	97.84 (0.04)	TiO_2 [$\%wt_{d.b.}$]	0.01 (0.00)
pH [-]	4.5 (0.07)	As [$mg·kg^{-1}_{d.b.}$]	3.05 (1.34)
EC [$mS·cm^{-1}$]	8.67 (0.38)	Cd [$mg·kg^{-1}_{d.b.}$]	0.23 (0.05)
Total C [$\%wt_{d.b.}$]	49.82 (0.50)	Co [$mg·kg^{-1}_{d.b.}$]	0.35 (0.07)
H [$\%wt_{d.b.}$]	5.80 (0.18)	Cr [$mg·kg^{-1}_{d.b.}$]	4.20 (0.57)
N [$\%wt_{d.b.}$]	0.20 (0.05)	Cu [$mg·kg^{-1}_{d.b.}$]	6.62 (0.04)
S [$\%wt_{d.b.}$]	0.02 (0.00)	Mo [$mg·kg^{-1}_{d.b.}$]	0.25 (0.07)
Cl^- [$\%wt_{d.b.}$]	0.20 (0.04)	Ni [$mg·kg^{-1}_{d.b.}$]	2.20 (0.00)
SiO_2 [$\%wt_{d.b.}$]	0.59 (0.07)	Pb [$mg·kg^{-1}_{d.b.}$]	2.70 (0.14)
CaO [$\%wt_{d.b.}$]	0.76 (0.04)	Sb [$mg·kg^{-1}_{d.b.}$]	0.69 (0.01)
K_2O [$\%wt_{d.b.}$]	0.33 (0.02)	Se [$mg·kg^{-1}_{d.b.}$]	0.95 (0.07)
P_2O_5 [$\%wt_{d.b.}$]	< d.l.	Tl [$mg·kg^{-1}_{d.b.}$]	< d.l.
MgO [$\%wt_{d.b.}$]	0.11 (0.01)	V [$mg·kg^{-1}_{d.b.}$]	1.49 (0.10)
Al_2O_3 [$\%wt_{d.b.}$]	0.15 (0.01)	Zn [$mg·kg^{-1}_{d.b.}$]	14.65 (0.36)
Fe_2O_3 [$\%wt_{d.b.}$]	0.05 (0.01)	-	-

The fuel biomass showed an elemental composition, in terms of total carbon, hydrogen and nitrogen content, total solids content and LOI at 550°C, that was aligned with what found in literature [11,54,58,61]. The most abundant major elements were Ca, Si and K (0.76, 0.59 and 0.33 %wt$_{d.b.}$, respectively), while the most significant heavy metals were Zn, Cu and Cr (14.7, 6.6 and 4.2 mg·kg^{-1}$_{d.b.}$, respectively). These features were consistent with recent literature studies [56,58,61] and suggest that the collected biomass sample represented a typical feedstock for the energy production.

3.4.2 Biomass ash chemical characteristics

The ash chemical characterization is reported in Table 3.8. Bottom, boiler and fly ash had moisture content of 37.3 %wt$_{d.b.}$, 1.4 %wt$_{d.b.}$ and 0.7 %wt$_{d.b.}$, respectively. While boiler and fly ash had a negligible water content, BTA showed a significant level of moisture. It is worth to mention that the collecting method affects BTA moisture significantly. The thermal power plant is equipped with a discharging system consisting in a water tank where bottom ash drops and is dragged off (quenching tank). This method allows cooling bottom ash, preventing possible fires and avoiding external air from entering the combustion chamber [14], but provides ash with significant moisture.

Loss on ignition at 550°C is associated to the organic matter remained unburned in the combustion bed, therefore high LOI 550°C values are connected to inefficiencies of the combustion process that depend on plant design and/or operation [26]. Nonetheless, the correlation between LOI and organic matter content may be questioned when non-carbon volatile matter is present [66]. Bottom ash had a high carbon content and a notable LOI value at 550°C, that was consistent with what reported by Hinojosa et al. [26] and could be ascribed to the unburned organic matter. LOI 550°C in BOA was lower than in BTA, while it could not be determined in FA, possibly because of the high content of sulfur which is an interfering element. However, it can be assumed that FA was mainly composed by inorganic matter, as reported in a recent study by Yeboah et al. for similar residues [66].

If the result of the LOI 550°C and LOI 950°C determinations are observed, it could be deduced that BTA had fixed carbon content lower than BOA. As for FA, on the basis of the assumption suggested by Yeboah et al. [66] and previously reported, it could be assumed that this ash type had the highest fixed carbon content.

Consistently, fly and boiler ash had a total carbon content lower than BTA (total C of 2.4 %wt$_{d.b.}$, 5.5 %wt$_{d.b.}$ and 14.8 %wt$_{d.b.}$ in FA, BOA and BTA, respectively). The FA, BOA and BTA hydrogen concentrations were 1.2 %wt$_{d.b.}$, 0.2 %wt$_{d.b.}$ and 1.5 %wt$_{d.b.}$, respectively.

Tab. 3.8. Main properties of biomass and bottom (BTA), boiler (BOA), and fly ash (FA) samples (n.d.: value not detected; < d.l.: below detection limit; standard deviation is indicated in brackets).

Parameter	**BTA**	**BOA**	**FA**
Moisture [%wt]	37.33 (1.35)	1.41 (0.00)	0.66 (0.04)
LOI 550°C [%wt$_{\text{d.b.}}$]	28.12 (0.54)	4.25 (0.04)	n.d.
LOI 950°C [%wt$_{\text{d.b.}}$]	31.03 (0.64)	12.54 (0.29)	23.19 (0.13)
pH [-]	7.5 (0.05)	12.0 (0.03)	13.0 (0.01)
EC [mS·cm^{-1}]	0.88 (0.02)	15.58 (0.33)	33.40 (1.13)
Total C [%wt$_{\text{d.b.}}$]	14.80 (0.21)	5.55 (0.02)	2.44 (0.03)
H [%wt$_{\text{d.b.}}$]	1.48 (0.15)	0.24 (0.07)	1.23 (0.04)
N [%wt$_{\text{d.b.}}$]	< d.l.	< d.l.	< d.l.
S [%wt$_{\text{d.b.}}$]	0.04 (0.00)	0.63 (0.00)	3.67 (0.02)
Cl^- [%wt$_{\text{d.b.}}$]	0.31 (0.10)	0.56 (0.00)	3.41 (0.31)
SiO_2 [%wt$_{\text{d.b.}}$]	38.02 (0.16)	33.94 (0.39)	2.17 (0.11)
CaO [%wt$_{\text{d.b.}}$]	10.79 (0.12)	24.65 (0.12)	41.37 (0.12)
K_2O [%wt$_{\text{d.b.}}$]	4.29 (0.06)	8.14 (0.16)	13.08 (0.08)
P_2O_5 [%wt$_{\text{d.b.}}$]	0.84 (0.02)	3.10 (0.06)	0.78 (0.01)
MgO [%wt$_{\text{d.b.}}$]	3.07 (0.03)	5.50 (0.07)	4.28 (0.08)
Al_2O_3 [%wt$_{\text{d.b.}}$]	7.54 (0.00)	7.80 (0.18)	0.91 (0.03)
Fe_2O_3 [%wt$_{\text{d.b.}}$]	3.39 (0.04)	3.35 (0.11)	0.53 (0.01)
Na_2O [%wt$_{\text{d.b.}}$]	0.75 (0.03)	1.17 (0.01)	1.20 (0.02)
MnO_2 [%wt$_{\text{d.b.}}$]	0.13 (0.00)	0.28 (0.01)	0.09 (0.00)
TiO_2 [%wt$_{\text{d.b.}}$]	0.36 (0.00)	0.41 (0.01)	0.04 (0.00)
As [mg·kg$^{-1}_{\text{d.b.}}$]	2.69 (0.28)	4.18 (0.55)	19.46 (0.33)
Ba [mg·kg$^{-1}_{\text{d.b.}}$]	295.70 (24.02)	350.09 (75.76)	43.65 (0.96)
Cd [mg·kg$^{-1}_{\text{d.b.}}$]	0.60 (0.00)	2.09 (0.10)	4.82 (0.06)
Co [mg·kg$^{-1}_{\text{d.b.}}$]	11.17 (0.39)	12.50 (0.46)	2.26 (0.06)
Cr [mg·kg$^{-1}_{\text{d.b.}}$]	278.06 (0.94)	45.42 (0.71)	21.25 (0.74)
Cu [mg·kg$^{-1}_{\text{d.b.}}$]	68.34 (0.13)	190.96 (0.05)	192.92 (1.19)
Mo [mg·kg$^{-1}_{\text{d.b.}}$]	1.05 (0.21)	0.73 (0.42)	2.56 (0.16)
Ni [mg·kg$^{-1}_{\text{d.b.}}$]	42.58 (3.00)	32.82 (0.26)	12.24 (2.94)
Pb [mg·kg$^{-1}_{\text{d.b.}}$]	7.93 (0.33)	33.44 (0.72)	76.48 (0.74)
Sb [mg·kg$^{-1}_{\text{d.b.}}$]	1.03 (0.15)	0.50 (0.14)	2.56 (0.16)
Se [mg·kg$^{-1}_{\text{d.b.}}$]	0.15 (0.07)	1.00 (0.10)	2.20 (0.14)
Sr [mg·kg$^{-1}_{\text{d.b.}}$]	229.36 (1.99)	553.88 (47.68)	163.87 (1.88)
Tl [mg·kg$^{-1}_{\text{d.b.}}$]	0.75 (0.07)	1.65 (0.21)	1.73 (0.25)
V [mg·kg$^{-1}_{\text{d.b.}}$]	53.87 (0.44)	54.85 (0.52)	8.44 (0.23)
Zn [mg·kg$^{-1}_{\text{d.b.}}$]	142.77 (7.36)	218.05 (1.53)	804.59 (8.38)

Nitrogen content in all the ash types was below the detection limit (< 0.006%). Biomass ash usually has a very low N_{tot} content because during combustion the nitrogen contained in the fuel forms gaseous compounds that are emitted in the atmosphere [50].

The most abundant element in bottom ash was Si (38.0 $\%wt_{d.b.}$), followed by Ca (10.8 $\%wt_{d.b.}$), Al (7.5 $\%wt_{d.b.}$), K (4.3 $\%wt_{d.b.}$), Fe (3.4 $\%wt_{d.b.}$) and Mg (3.1 $\%wt_{d.b.}$) (Fig. 3.3). Fly ash was highly enriched with Ca (41.4 $\%wt_{d.b.}$), K (13.1 $\%wt_{d.b.}$) and Mg (4.3 $\%wt_{d.b.}$). Boiler ash had abundant levels of both Si and Ca (33.9 $\%wt_{d.b.}$ and 24.7 $\%wt_{d.b.}$, respectively) and also contained potassium (8.1 $\%wt_{d.b.}$), aluminum (7.8 $\%wt_{d.b.}$), magnesium (5.5 $\%wt_{d.b.}$) and iron (3.4 $\%wt_{d.b.}$). In addition, BOA had the highest P content (3.1 $\%wt_{d.b.}$). Bottom and boiler ash had low sulfur and chloride content, while FA has the highest concentration of both S (3.7 $\%wt_{d.b.}$) and Cl^- (3.4 $\%wt_{d.b.}$).

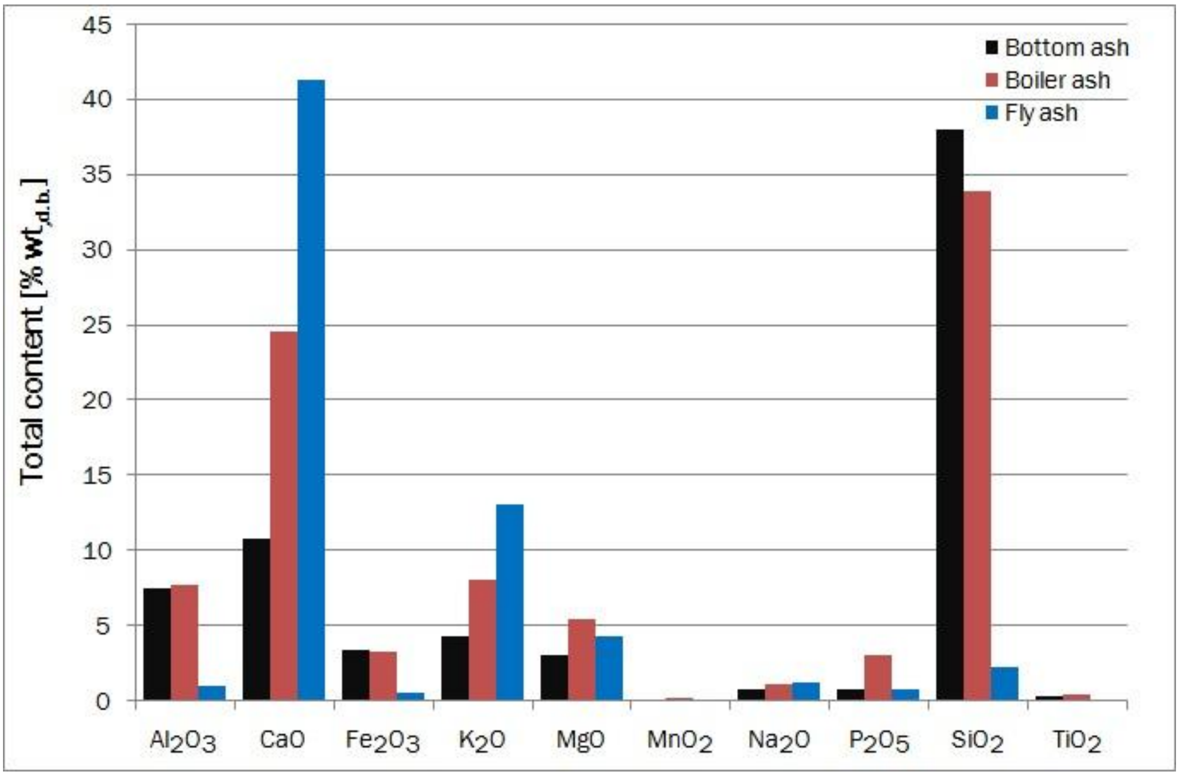

Fig. 3.3. Major elements in biomass combustion ash.

The most abundant minor metals in biomass ash were Zn, Cr and Cu, which reflected the original biomass composition, while Be was not detected (Fig. 3.4). Fly ash was enriched with the most volatile metals (Pb, Zn and Cu), while the least volatile ones (Cr, Ni and V) were abundant in BTA. If compared to the limits set by the current Italian legislation

("*Decreto Legislativo*", in Italian) for the waste classification in the light of its disposal or recycling (the Legislative Decree n. 152/2006 [16], section IV, attachment D), the three ash types constitute non-hazardous waste in relation to the total content of the heavy metals that are included in the regulatory requirements. The analytical results obtained are in accordance to literature studies [26,30,33,38,41,49,52,54,58,66].

As Steenari et al. [50] suggested, most of the elements present in BAsh were taken up by the plants during their lives and retained in the combustion residues. The occurrence and distribution of the elements in the different ash types were due to volatilization during combustion and the particles formation mechanism [49,53]. During combustion, K, S and Cl vaporize and form vapors with low saturation vapor pressure, which are converted into submicron particles by condensation (<1 μm) [12,13,53]; for this reason they were found in fly ash. On the other hand, the high P (and other refractory oxides, such as Mn) content in boiler ash could be explained by the entrainment of these elements in the supermicron particles that constitute this ash type (>1 μm, [50]). The entrainment was due to the combined effect of low temperature values in the convective tubes (lower than in the combustion chamber) and the coarse size of the refractory oxides.

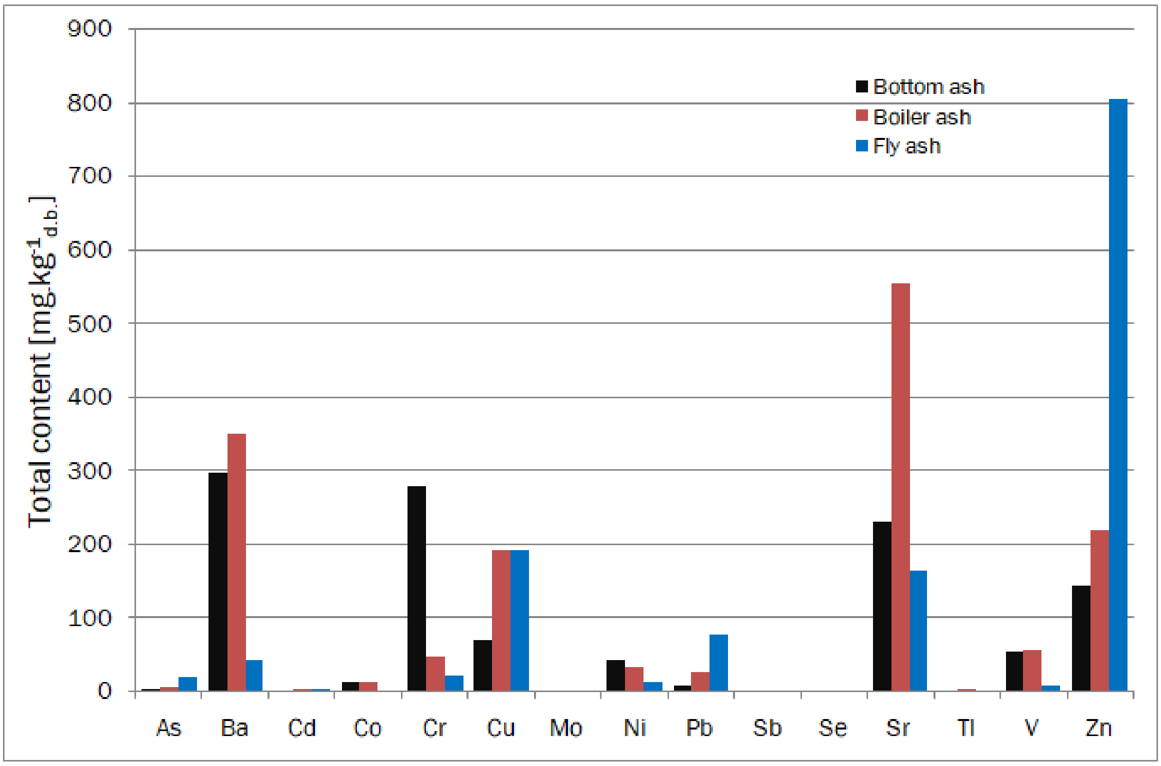

Fig. 3.4. Minor elements in biomass combustion ash.

The mineralogical composition, as described by the X-ray diffraction (Fig. 3.5), confirmed the high Si content in BTA and high Ca level in FA, and also identified different calcium-bearing minerals contained in the three ash types. Calcium was present as a silicate in all the ash types, as a carbonate and sulfate hydrate in BOA, and as a hydroxide in FA. In particular, portlandite ($Ca(OH)_2$) corresponded to one of the most significant minerals in FA, where gehlenite ($Ca_2Al_2SiO_7$) and albite ($(N,Ca)(Si,Al)_4O_8$) were also identified. Beyond deriving from the calcium content in the original biomass, calcium hydroxide in FA could also derive from the lime added to abate the acid gases from the flue gas before fly ash are collected and removed. In BOA, calcite ($CaCO_3$) was the second most abundant peak and gypsum ($CaSO_4{\cdot}2H_2O$) was also present. Quartz (SiO_2) was the most intense peak in both BTA and BOA, while sylvite (KCl) was one of the most significant mineral in FA.

The presence of potassium chloride in fly ash was aligned with the high K and Cl^- content found in this ash type. These results are coherent with the above described chemical composition and consistent with literature studies [22,49,53,55].

All the ash types had an alkaline pH; in particular, BOA and FA displayed the highest pH values (12 and 13, respectively) due to the presence of alkali compounds, such as calcium hydroxides in fly ash. The electrical conductivity in BOA and FA was very high (15.6 and 33.4 $mS{\cdot}cm^{-1}$, respectively). Conductivity was determined by the presence of ionic species deriving from water-soluble compounds, such as portlandite, potassium chloride and gypsum [50].

The metals water extractable fraction is a fundamental information to evaluate the potential environmental risk entailed with the reuse or disposal of residues [22]. Also, it provides information on the easily leachable and bioavailable fraction of macro and micronutrients [48]. Table 3.9 shows the water-soluble concentration of metal constituents in bottom, boiler and fly ash in the eluates after water leaching, as well as the pH and EC values. Calcium and potassium were the most abundant macro-elements in the FA and BOA eluates. Sodium was present in significant amounts in the FA water extractable fraction as well. By comparing the results with the limit values set by the European Union legislation for the acceptance of waste at landfills [15], all the BAsh types fulfilled the criteria established for non-hazardous waste. If each metal constituent is considered, As, Ba, Cu, Ni and Zn complied with the requirements for the acceptance of waste as an inert material in all the ash types analyzed. The limit values for inert materials were also fulfilled for Cr and Se in BTA, Pb in BOA, and Cd and Sb in BOA and FA.

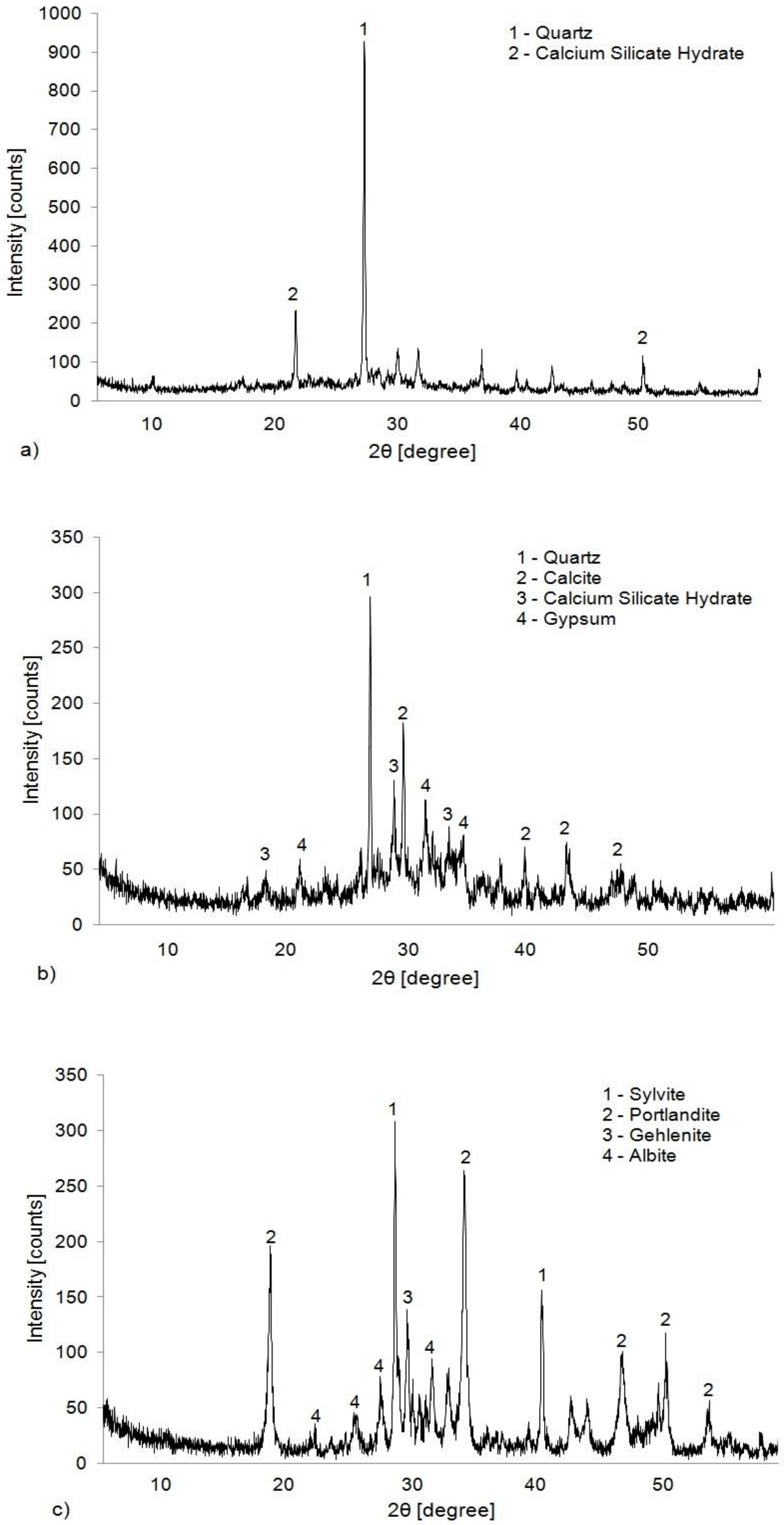

Fig. 3.5. X-ray diffraction of a) BTA, b) BOA and c) FA.

Tab. 3.9. Results of the leaching test performed according to UNI EN 12457-4:2004 (BTA) and UNI EN 12457-2:2004 (BOA and FA) (< d.l.: below detection limit; standard deviation of pH and EC are indicated in brackets).

	BTA	**BOA**	**FA**	**Limit values for non hazardous waste [15]**
pH [-]	7.1 (0.05)	12.7 (0.06)	13.2 (0.03)	-
EC [$mS \cdot cm^{-1}$]	1.22 (0.00)	23.80 (0.10)	39.4 (0.12)	-
CaO [$\%wt_{d.b.}$]	0.07 (0.00)	1.26 (0.00)	1.42 (0.10)	-
K_2O [$\%wt_{d.b.}$]	0.25 (0.02)	2.17 (0.01)	14.53 (0.20)	-
MgO [$mg \cdot kg^{-1}{}_{d.b.}$]	531.67 (0.06)	0.51 (0.00)	0.81 (0.05)	-
Al_2O_3 [$mg \cdot kg^{-1}{}_{d.b.}$]	25.66 (0.99)	26.93 (2.04)	1.62 (0.00)	-
Fe_2O_3 [$mg \cdot kg^{-1}{}_{d.b.}$]	22.00 (1.12)	< d.l.	< d.l.	-
Na_2O [$\%wt_{d.b.}$]	0.04 (0.00)	0.14 (0.01)	1.09 (0.00)	-
MnO_2 [$mg \cdot kg^{-1}{}_{d.b.}$]	13.11 (0.74)	0.06 (0.00)	< d.l.	-
As [$mg \cdot kg^{-1}{}_{d.b.}$]	< d.l.	< d.l.	< d.l.	2
Ba [$mg \cdot kg^{-1}{}_{d.b.}$]	0.40 (0.01)	3.00 (0.03)	4.14 (0.23)	100
Cd [$mg \cdot kg^{-1}{}_{d.b.}$]	0.06 (0.00)	< d.l.	< d.l.	1
Co [$mg \cdot kg^{-1}{}_{d.b.}$]	0.03 (0.00)	< d.l.	< d.l.	-
Cr [$mg \cdot kg^{-1}{}_{d.b.}$]	0.06 (0.00)	1.71 (0.08)	1.29 (0.01)	10
Cu [$mg \cdot kg^{-1}{}_{d.b.}$]	1.06 (0.01)	< d.l.	0.05	50
Mo [$mg \cdot kg^{-1}{}_{d.b.}$]	< d.l.	0.60 (0.00)	2.88 (0.00)	10
Ni [$mg \cdot kg^{-1}{}_{d.b.}$]	0.14 (0.01)	< d.l.	< d.l.	10
Pb [$mg \cdot kg^{-1}{}_{d.b.}$]	1.39 (0.10)	< d.l.	0.83 (0.05)	10
Sb [$mg \cdot kg^{-1}{}_{d.b.}$]	0.07 (0.00)	< d.l.	< d.l.	0.7
Se [$mg \cdot kg^{-1}{}_{d.b.}$]	< d.l.	0.32 (0.01)	0.40 (0.05)	0.5
V [$mg \cdot kg^{-1}{}_{d.b.}$]	0.19 (0.01)	< d.l.	< d.l.	-
Zn [$mg \cdot kg^{-1}{}_{d.b.}$]	1.91 (0.14)	0.166 (0.10)	0.82 (0.00)	50

3.4.3 Biomass ash physical properties

The main physical properties of the different BAsh as assessed in the present study are displayed in Table 3.10.

Tab. 3.10. Physical properties of biomass combustion ash (BD: bulk density; PD: particle density; WHC: water holding capacity; n: total porosity; standard deviation is indicated in brackets).

	BD_{wb} [g·cm^{-3}]	**PD_{wb} [g·cm^{-3}]**	**WHC [g_{water}·$g_{dry\ sample}^{-1}$]**	**n [%]**
BTA	1.170 (0.005)	2.104 (0.005)	0.69 (0.00)	78.15
BOA	0.246 (0.010)	2.620 (0.001)	0.82 (0.00)	91.14
FA	0.137 (0.005)	2.485 (0.002)	1.02 (0.00)	94.77

The values of bulk and particle densities determined for the BAsh considered in this work were consistent with recent literature [7,31,36]. It can be noticed that, while the bulk density varied significantly according to the considered BAsh, the particle density showed smaller variations among the ash types; however, it could be observed that the lowest level of particle density was exhibited by BTA, that is the ash type most enriched in volatile matter (i.e., unburned carbon), whom the particle density is connected to [7,25]. According to Equation 3.3, low BD, high PD and high total solids content are connected to high total porosity [1,25,34]. Boiler and fly ash showed low moisture content and BD, and high PD, thus they exhibit high porosity levels.

The water holding capacity in BOA and FA was higher than in BTA, and consistent with the values reported by Ahn et al. [2] for soil compost blends, and by Karhu et al. [29] for soils. Bodì et al. [7] observed that low BD leads to high water holding capacity.

Since FA consists of a fine powder and is not suitable for sieving, the particle size distribution of only BTA and BOA were determined. The distribution curves displayed in Figure 3.6a show that, as expected, bottom ash was more enriched in coarse particles comparing to boiler ash. The results of LOI determination at 550°C for each of the BTA and BOA particle size classes are shown in Figure 3.6b.

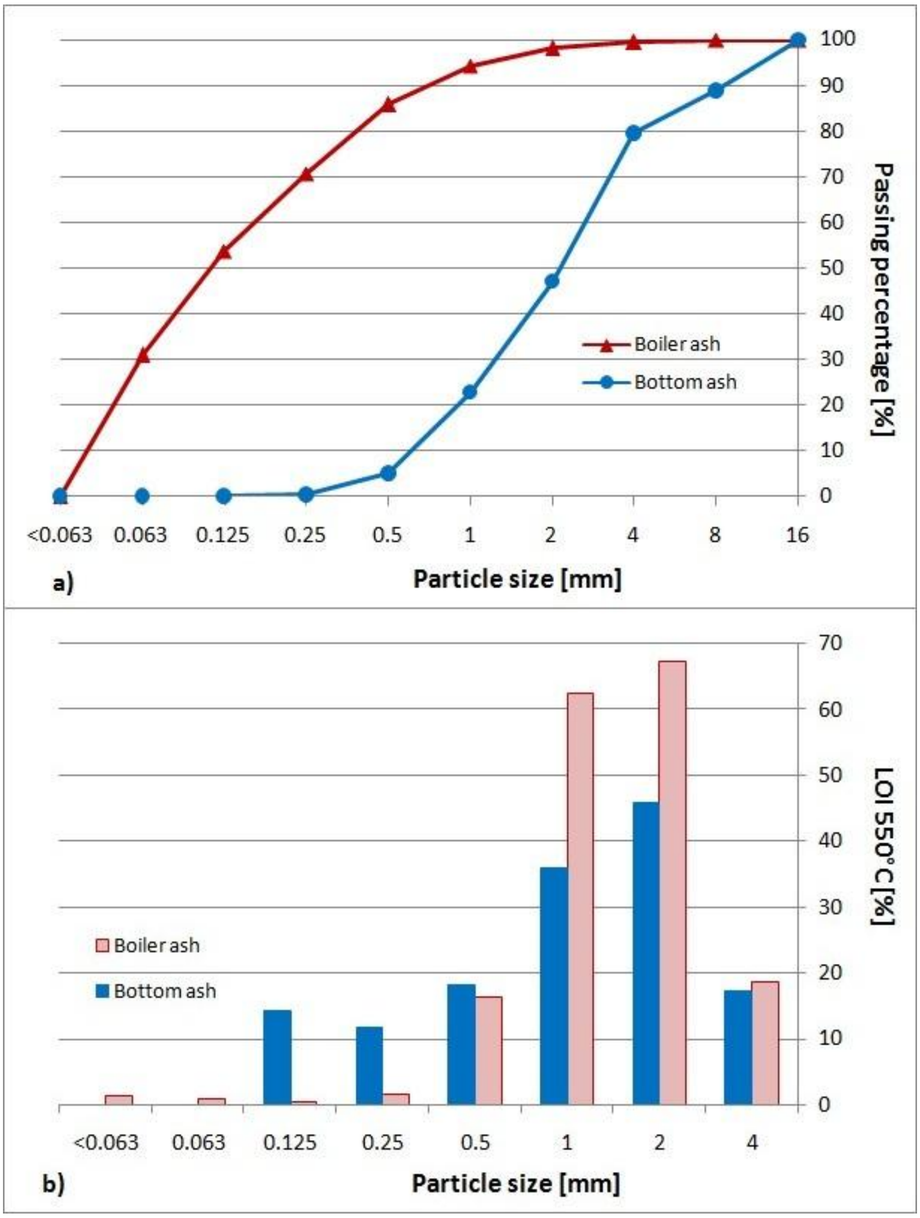

Fig. 3.6. Particle size distribution of bottom and boiler ash (a) and LOI at 550°C for each particle size class (b).

High amounts of unburned organic material constituted the retained fractions at 2 and 1 mm sieves. The LOI values of the BTA fractions retained by the 2 and 1 mm sieves were 46 %wt$_{d.b.}$ and 36 %wt$_{d.b.}$, respectively. This is a relevant result since these two particle size classes corresponded to 56% of the overall bottom ash mass. On the other hand, LOI values of the boiler ash fractions retained by the 2 and 1 mm sieves were 67 %wt$_{d.b.}$ and 63 %wt$_{d.b.}$, respectively. Though higher than what found for bottom ash, this result is less notable since these classes corresponded to 1% and 4% of the total boiler ash mass, respectively. The high overall organic content and the fact that it is concentrated in specific particle size classes, make the BTA worthy of further studies for new possible uses.

3.5 Conclusions

The physical-chemical characterization of the initial biomass showed that the feedstock is representative of a typical renewable fuel used for energy generation.

The physical-chemical characterization of the combustion residues showed that the ash properties were greatly affected by the section of the thermal power plant where the ash was discharged. The results presented in this Chapter are summarized as follows:

- BTA had the highest organic matter content, due to the unburned fuel, and also BOA contained unburned carbon, though at a lesser extent.
- Some of the ash types were enriched in nutrients. Among the samples analyzed, FA was the most enriched in calcium and potassium, and contained high magnesium level, while BOA had also a notable level of calcium and potassium as well as the highest magnesium and phosphorous content. Bottom ash was highly enriched in Si, while nutrients were found in smaller amounts. BOA and FA were also rich in micronutrients, such as Zn and Cu.
- Fly ash has the highest sulfur and chloride content.
- All the biomass residues were very poor in nitrogen, irrespective of the type.
- Biomass ash are alkaline, particularly BOA and FA.
- The ash types had high electrical conductivity, especially BOA and FA.
- As for the metal (total and water-soluble fraction) content, this was not a concern in the ash considered and the three ash types were non-hazardous waste for the Italian current legislation. However, the contamination degree in ash generally depends on the characteristics of soil, water, nutrients and pesticides supply the fuel biomass was in contact with, so that the harmfulness of this kind of residues has to be evaluated for each case study.
- Portlandite was the most representative mineral in FA, while quartz was the most significant mineral in BOA and BTA.
- BOA and FA have high total porosity and water holding capacity.

It could be concluded that a complete characterization of the ash types generated in a thermal power plant fueled with biomass is essential for maximizing the potential of this waste in the light of the 2008/98/EC Directive on waste [17] and the Circular Economy objectives. On the other hand, not considering these aspects does not allow to assess the ash potential, and any proposal for recycling is unsubstantiated.

Because of the variations in biomass ash properties, the establishment of a strict tracking system of the fuel biomass should be recommended, so that the related ash could be identified as a batch having homogeneous characteristics. The technical requirements needed for the selected applications must be assessed. Knowledge of the ash environmental behavior and the possible legal constraints related to its reuse is also essential.

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CHAPTER 4

Biomass ash as an additive in the composting process

4.1 Introduction

One of the innovative reuse options for biomass ash that this work investigates is the addition to organic waste undergoing the composting process so to recycle nutrients-rich materials into soil improvers, that is one of the actions promoted by the European Commission for the implementation of the Circular Economy approach [31].

Composting is a biochemical conversion process aimed at degrading and stabilizing organic substrates that occurs under optimal conditions of moisture, aeration and heat-insulation [15,42]. In particular, moisture, temperature and pH unfavorable conditions, the scarcity of free airspace, and the shortage of nutrients can negatively affect the composting process and the final product quality. Some unfavorable conditions could be contrasted by using mineral additives to the composting mixtures [43], and biomass ash could be used to this purpose. The recycling of biomass ash as an additive in the composting process has already been proposed by some authors [36,53,55-56]. Kurola et al. [56] suggested that biomass ash may enhance the composting process and improve the final compost quality. The favorable effects exerted by ash included higher degradation rates of the organic fraction and the increase of the Ca, K, Mg and P levels in the final composts [36,53,55-56]. In addition, Bougnom et al. [19], who conducted field experiments using the ash-amended compost produced in the experiment described by Kuba et al. [55], observed that the composts enriched with ash had an ameliorating effect on acidic soil due to its liming effect. On the other hand, some possible disadvantages were observed in the final composts produced by using ash, such as the increase of the heavy metals content and salinity, and the dilution of nitrogen, that this kind of residues contains in small amounts or are lacking of [36,56]. However, these studies have only partially explored the subject since they do not specify the type of biomass ash involved in the experiments, or use only one single ash type. As discussed in Chapter 3, different types of ash are generated in a thermal power plant (typically, bottom, boiler and fly ash), whose properties vary significantly. The characterization of each ash type represents an essential information, since the chemical and physical properties of the residues drive the potential effects on the process and the final compost quality. That said, the ash type usually proposed by other authors as a composting additive is bottom ash. This is aligned to the existing regulation in the few European countries (Austria, Belgium, Denmark, Finland, Hungary and Poland) which allow the use of ash as an additive in composting [30]. Indeed, in these countries only bottom and boiler ash are admitted, but it is fly ash that, together with boiler ash, typically displays the highest pH levels, thus acting as a liming agent, and contents of macro- (such as Ca, K, Mg and P) and micro-elements (including Cu, Fe, Mn and Zn). It could be expected that the nutrient intake resulting from the use of fly and boiler ash could confer compost with a higher added value and marketability. In particular, phosphorus is an essential nutrient that often constitutes the limiting factor for plant growth, and potassium is usually low in the composts derived from organic waste [87]. Fly ash also has physical characteristics, such as low bulk density and moisture, that, favouring air diffusion, could have a positive impact on the composting process [11].

In order to provide a wider understanding on the use of biomass ash as an additive in the organic waste composting, in the present work a blend of fly and boiler ash was used that, to the author's knowledge, represents a novelty in this field. Therefore, the general objective of this research line was the study of the effect of increasing amounts of this ash blend on:

- the composting process evolution
- the final products quality.

To achieve these aims, two experimental setups at laboratory and pilot-scale were used, and the organic fraction of municipal solid waste (OFMSW) was subjected to composting with the addition of increasing amounts of selected types of biomass ash. OFMSW is the most common initial substrate for composting, but is also the most challenging for heterogeneity, lack of nutrients and poor marketability. The problem of recycling the organic fraction of municipal solid waste efficiently and obtaining a nutrients-rich final compost is impelling and actions aimed at remedying to these issues are to be undertaken.

First, real source-separated OFMSW and green waste (grass and tree prunings) that served as a bulking agent, collected from a waste treatment facility, underwent composting in pilot-scale reactors. Afterward, a similar experiment was conducted at laboratory-scale using synthetic OFMSW and wood chips in order to assess process evolution and compost quality without the influence raised from real waste heterogeneity and lack of nutrients. The laboratory-scale also allowed to exert a tighter control on the process. In addition, at laboratory-scale two waste/bulking agent ratios were tested, though maintaining the same given ash amount, to investigate whether ash addition could permit, in the light of its physical properties, to act as a physical conditioner and reduce the share of the bulking agent used.

4.2 State of the art

4.2.1 The composting process

Composting is the most common treatment for organic substrates, defined by Haug [42] as:

“the biological decomposition and stabilization of organic substrates, under conditions that allow development of thermophilic temperatures as a result of biologically produced heat, to produce a final product that is stable, free of pathogens and plant seeds, and can be beneficially applied to land”.

The aim of composting is to produce a final product in which organic matter is partially converted into stable humic-like matter, biodegradable volatile solids content is low and pathogenic microorganisms and weed seeds are heat inactivated [58].

The materials suitable for composting are:

- OFMSW,

- Food waste from catering, restaurants, canteens, markets,
- Sewage sludge from the treatment of urban and agro-industrial wastewater,
- Fruit and vegetable residues from the agro-industrial industry,
- Green waste,
- Herbaceous and crops residues,
- Manure.

Among these materials, OFMSW and green waste are predominant [24]. In particular, OFMSW represents the most common substrate for compost production (Fig. 4.1).

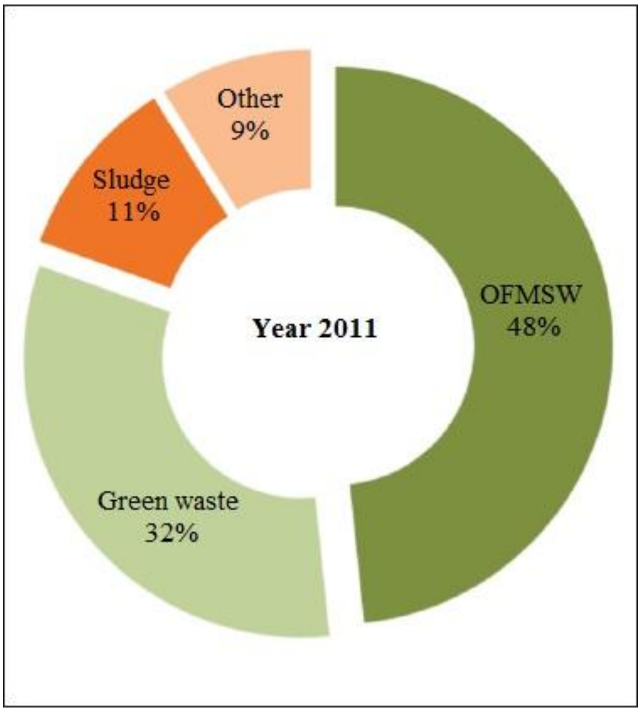

Fig. 4.1. Substrates treated in the composting facilities in Italy [24].

OFMSW consists in the organic matter found in the municipal waste, the latter being defined by the OECD/Eurostat Joint Questionnaire of the European Commission [32] as follows:

"municipal waste covers household waste and waste similar in nature and composition to household waste".

Household waste definition is reported in the Directive 1999/31/EC (Landfill Directive, [28]) as:

"the waste generated by the domestic activity of households and collected by or on the behalf of the municipality".

As IEA specifies [46], "kitchen waste from food preparation, food waste and commercial food waste from food processing, retail outlets, markets and catering activities, and leafy green, waste trimmings and cuttings from households, gardens and urban parks" could be included in the aforementioned household waste definition.

Not only the OFMSW is the most common compost substrate, but it is also the most challenging. Heterogeneity, lack of nutrients and presence of extraneous materials, such as non-degradable plastic, are features that characterize the organic fraction of municipal solid waste. The critical issues associated to compost production from OFMSW could be summed up as follows, and many efforts are made to better its quality as a soil improver.

- Technical problems in conducting the composting process (i.e., moisture and aeration control) or related to the properties of input materials (e.g., moisture content higher than 70%wt) could lead to anaerobic conditions as opposed to aerobic ones, or fail to reduce pathogens because of insufficient temperature raise.
- The nutrient content in the final compost is often scarce, provokes low competitiveness against commercial mineral fertilizers/amendments, and contributes to the low market value of the compost derived from OFMSW.
- Treatment facilities are usually settled close to urban areas, which are the main production sites for OFMSW, and could not cross the demand for soil improvers raised by the agriculture sector in rural areas; moreover, due to the proximity to urban sites, odorous emissions hinder the social acceptance of such plants.

A growth in the number of the composting facilities has been observed in the last decades coherently to the diffusion of the source-separated collection of OFMSW; in Italy, the number of composting facilities having productive capacity higher than 1,000 tonnes per year grew from 10 in 1993 to 256 in 2009 (Fig. 4.2, [24]).

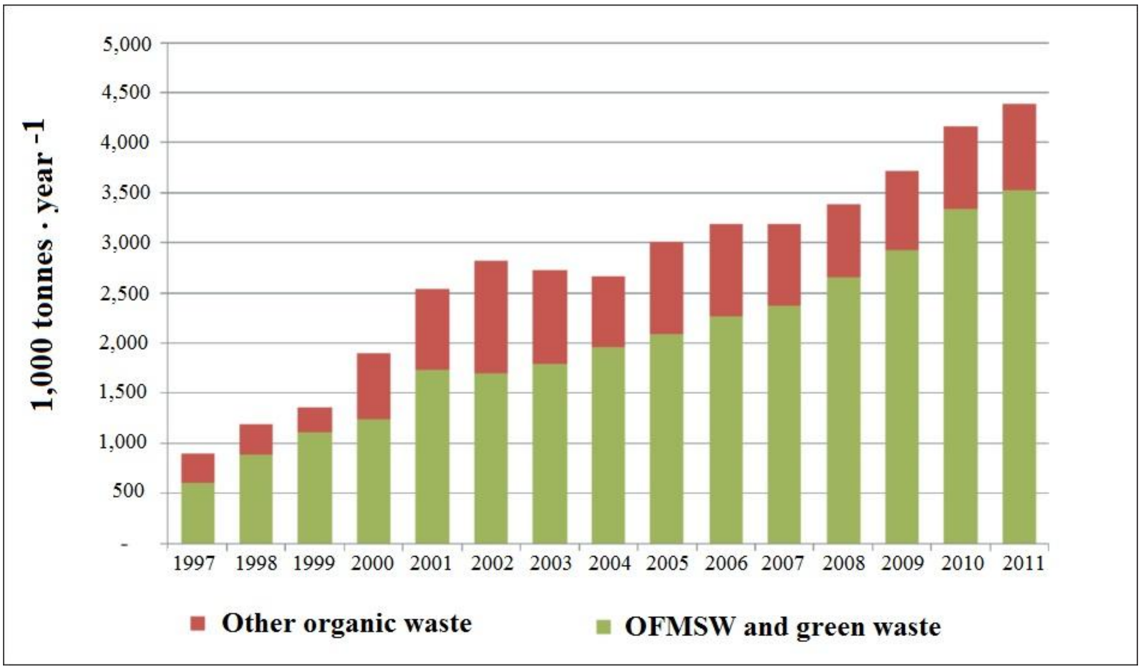

Fig. 4.2. Evolution of the treatment capacity in the composting facilities in Italy and shares of the OFMSW and green waste [24].

Applications to the soil as a conditioner, mulch, top dressing or as a component for organic fertilizers are the main use of the final compost [42]. In Europe there are several national laws concerning compost production, since every Member State has legislated and set requirements for the final compost quality autonomously. In Italy the reference law is the Legislative Decree ("*Decreto Legislativo*", in Italian) no. 75/2010 [26] that regulates quality requirements for fertilizers, amendments and composts. In this decree, two types of composts are defined:

- From OFMSW, carcass, manure, agro-industrial residues, scraps from the textile and wood industry, sewage sludge, green waste, crops and other plant residues ("*Ammendante compostato misto*", in Italian)
- From green waste, crops and other plant residues only ("*Ammendante compostato verde*", in Italian).

The former covers the vast majority of the composts produced. In addition, according to the Italian Decree ("*Decreto*", in Italian) 22 January 2009 no.1601 [25], these compost types are admitted as components of other organic fertilizers such as cultivation substrates and organic-mineral fertilizers, similarly to peat and lignite. Coherently, another product is also defined by the Legislative Decree no. 75/2010 that derives from mixing one of the two previously mentioned categories of composts with peat ("*Ammendante torboso compostato*", in Italian).

The green waste and crop/plant residues used as a substrate contribute to the degradation process at various extent. Grass is easily biodegradable, while leaves are more stable and lignin, which is a major component in wood, is recalcitrant to the biological decomposition [42]. Wood is preferably added to composting as bulking agent, which means that it provides a structural support to the composting substrate. Conditioning by adding physical and/or chemical additives is another action used to exert a control on the composting process. These additives are also defined as "amendments" to the process, and have properties suitable to reduce odor emissions, dry the substrate, and adjust the pH level and the nutrient content. Haug [42] proposed a flow diagram for a generic composting process (Fig. 4.3) where the feedstock is constituted by three inlet streams: initial substrate, bulking agents and amendments. Compost could be recycled to act as a physical amendment; indeed it decreases the bulk density of the substrate with benefit for maintaining a proper aeration. Bulking agent could be recovered after screening to reduce the supply of new bulking material. Compost is depicted as the only final product, however carbon dioxide, water and heat are also produced.

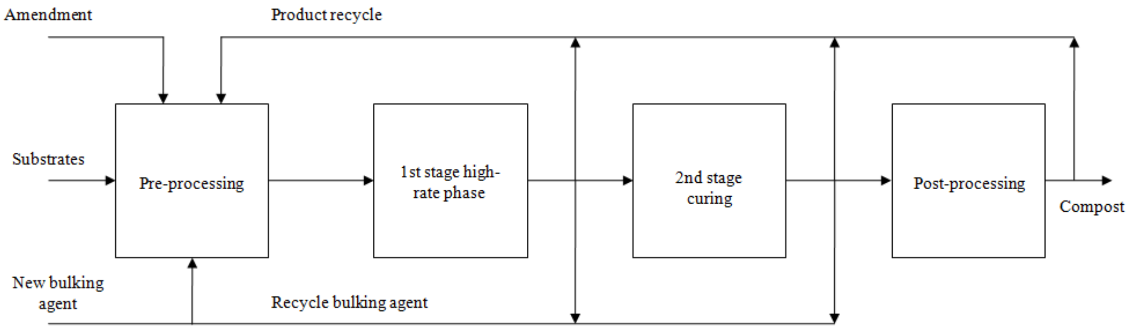

Fig. 4.3. Composting process scheme [42].

Composting is commonly described as a four-phase process. Each phase is characterized by physical, chemical and biochemical conditions, that allow the growth of groups of organisms (microbial consortia) that reach the stationary regime at similar temperature, pH and moisture levels [49]. This is a schematic description; however composting is a more complex process, where continuous changes in the biochemical properties of the mixtures occur.

The four typical stages of composting are:

(i) Starting phase: The primary stage of aerobic decomposition occurs at mesophilic conditions (temperature values range from 25°C to 40°C). In this phase fungi, bacteria and actinobacteria decompose the organic substrate, and their intense microbial activity brings to an increase in the temperature levels.

(ii) Thermophilic phase: As the temperature rises, the species of organisms that could adapt to thermophilic temperature values (35-65°C) continue to reproduce, while the obligate mesophiles are inactivated. The organic matter degradation becomes faster and the substrates, reduced to simpler molecules, are degraded more rapidly than in the starting phase. In this stage, temperature levels of approximately 65°C are reached, which correspond to pasteurization and pathogens suppression conditions. The thermophilic temperature values (higher than 45°C) are essential for weed seeds inactivation as well, and are attained by ensuring adequate moisture and aeration conditions in the substrate. However, a temperature increase beyond 65°C, caused by abiotic exothermic reactions, does not favor the microbial activity. The main disadvantage of excessively high temperature levels seems to be the death of most of mesophiles and the detriment of the subsequent phase. In the starting and thermophilic stages, which constitute the so-called "high-rate phase”, the maximum degradation and stabilization rates are achieved, with the highest heat release and request for stoichiometric oxygen. During this step, composts could contain metabolites toxic for plants, as the biochemical stability is not reached yet.

(iii) Mesophilic phase: The (second) mesophilic phase begins when temperature decreases at the end of the thermophilic stage, i.e. as the degradation of most of the organic matter has occurred; indeed, it is also referred to as “cooling phase”. The microbial activity is less intense and the heat release and oxygen requirement are consequently lower. In this phase, bacteria and fungi able to decompose starch and cellulose proliferate.

(iv) Maturation phase: The maturation phase (also called “curing phase”) is a long-lasting step where the substrate is converted into a final product constituted by the most recalcitrant fractions of the initial substrate (such as lignin) and the stabilized forms of organic matter (humic compounds). This stage is fundamental to achieving advanced humification, and biological stability and maturity in the final product. This stage is dominated by fungi, while bacteria decline.

There are several engineering approaches to conduct the composting process, that correspond to different combinations of factors such as the reactor type, feed flow design and aeration method. There could be distinguished agitated or static, and open or enclosed systems, among which, nowadays, the latter largely prevails.

The high-rate/cooling and curing phases are generally managed as two separate processes with two different approaches. The high-rate and cooling phases are usually performed in enclosed systems, where the degradation process occurs in “in-vessel” mode and a tight control is made possible by the use of sensors for monitoring the main parameters evolution and regulators for supplying air and water. In relation to the aeration mode operated, there are agitated or static piles that consist in turning/tumbling or just force-aerating the substrate, respectively. In particular, these systems are used for treating readily biodegradable substrates and the degradation kinetics are fast. Open systems are typically used to conduct the curing phase or, alternatively, the high-rate phase when slowly biodegradable substrates are treated. Enclosed systems require smaller surface area and are more costly than the open ones. They are used for a limited number of days, while open systems are used the majority of the time. As a whole, composting is a long-lasting process and lasts for several months.

4.2.2 Factors that affect the composting process

Temperature, moisture, aeration rate, pH and presence of nutrients are the main parameters that drive the composting process, and their monitoring and control allow achieving compost stability [58]. Some conditions that can affect negatively the composting process are the excessively low or high temperature and moisture, the scarcity of free airspace, low or high pH, the shortage of nutrients, and the presence of toxic or inhibiting compounds. These issues are hereby discussed.

Temperature

During the composting process heat is released, that is essential to expunge pathogens and inactivate weed seeds. In relation to the pathogens elimination, many countries have established hygiene requirements based on the definition of standard temperature and time. The required conditions range from a minimum temperature value of 55°C maintained for 3 consecutive days, that is the standard for Italy and Australia [22, 67], to temperature values higher than 60°C for at least one week in in-vessel composting, that is a legal requirement in Germany [21].

Though advantageous for the fulfillment of the hygiene requirements, excessively high temperature values might also have a controversial effect for the composting process. Miyatake and Iwabuchi [64] observed that at 70°C the thermophilic bacteria diversity increased, but the organic matter degradation decreased. On the counterpart, Tuomela et al. [89] suggested that lignin solubilization was favored at temperature values higher than 70°C.

Moisture

Moisture is a key parameter in every biochemical process because water is essential for the microbial metabolism and the means that allows nutrients to dissolve in waste [58]. Due to these aspects, the moisture content in the composting mixtures should never be lower than 40-45%wt not to hinder the microorganisms activity [36].

Moisture influences the physical properties of the composting pile as well. Excessively high moisture content is disadvantageous for the composting process because when a great share of pores is occupied by water, it provokes a shortage of space free for air. Consequently, air diffusion is hindered and the composting process is negatively affected [65]. When OFMSW with high water content (usually this value is higher than 80%wt, [50]) is used, this circumstance could occur. The optimal moisture content in the composting mixtures ranges between 50%wt and 70%wt, in dependence to the kind of substrate that is subjected to composting (a compromise between the water required by the biochemical process and the need for space free for air diffusion).

Aeration

Aeration is a key factor for composting because of three reasons. Firstly, it provides the oxygen necessary for the aerobic decomposition of the substrate. Secondly, it removes water vapor and other gaseous products. Thirdly, it removes excess heat from the composting materials in order to maintain the required temperature levels [97]. Air is supplied by forced-aerated circuits or by overturning the composting piles periodically, and is fundamental to avoid that anaerobic degradation takes place instead of the aerobic decomposition.

The portion of the pores free from water could be expressed as the free airspace (FAS), that represents the volume of pores filled with air and constitutes a share of the total porosity. As Annan and White [9] stated, FAS is an efficient way to evaluate the availability of air inside a compost mixture and determines the extent of air diffusion during the process [65]. An initial FAS of 60-65% is considered adequate to maintain the free airspace of 30-40% during the curing phase. On the contrary, low FAS values associated to high moisture contents affect the composting process negatively, because these conditions correspond to low air diffusion [42,65,99]. Usually the optimal free airspace rates are achieved by using an adequate amount of bulking agent in the composting mixtures. Sometimes a physical additive could also be needed, though. Additives with high values of water holding capacity (WHC), that correspond to high water absorbing capacity [5,59], would allow to achieve an optimal degradation.

pH

During composting, pH varies largely, starting from acidic levels to values up to 9. Some authors highlighted that excessively high pH levels could have an inhibitory effect on the biological activity during the composting thermophilic phase [33]. On the other hand, when the pH decrease at the early stage of composting reaches values lower than 5, the microbial activity is hindered (typically, when an acidic substrate, such as food waste, is used [23]). Nakasaki et al. [68] found that optimal pH values for a rapid degradation at the early stage of composting ranged from 6 to 9.

Nutrients

The supply of macro-nutrients (N, P, K) and micro-elements (Ca, Fe, Mg) is needed to support the composting organisms’ microbial activity. They could be limiting factors for the biological degradation and, according to Strom [85], the activity and biodiversity of microorganisms in the substrates subjected to composting are affected by the availability of nutritive compounds as well as by temperature and air supply [94]. However, the materials that undergo the composting treatment typically have enough amounts of nutrients to cope with these requirements (Tab. 4.1, [42]).

The most essential nutrient is nitrogen that is required in amounts higher than the other macro- and micro-elements. The nitrogen amount should balance the carbon content of the substrate, so that the C/N ratio is a key parameter for defining the proneness of a substrate to degradation. Haug [42] reported that C/N ratios from values ≤15 to 30 should ensure that enough nitrogen is provided. During composting, N is partially released as ammonia, which does not correspond necessarily to a N loss, since it could be fixed by the microbes colonies that degrade the low-nitrogen materials, like straw, potentially present. On the contrary, C/N values higher than 30 could limit the degradation process.

Tab. 4.1. Nutrients content [$\%wt_{d.b.}$] in typical composting substrates [42].

Material	**N**	**P_2O_5**	**K**
Eggshells	1.2	0.4	0.1
Fish scraps	2.0-7.5	1.5-6.0	-
Food waste	3.2	-	-
Garbage	2.0-2.9	1.1-1.3	0.8-2.2
Leaves fresh	0.5-1.0	0.1-0.2	0.4-0.7
Mixed grasses	2.4	-	-
Yard waste	1.95	-	-

4.2.3 Factors that affect the final compost quality

Application to the soil as a conditioner, mulch, top dressing or as a component for fertilizers is the main use of the final composts [42]. Currently, there is not a unique European regulation on the characteristics that the final composts should have, and these are defined by each Member State. Generally, the parameters that define compost quality and allow the commercialization are: moisture, pH, nutrients content, presence of toxic or inhibiting compounds, electrical conductivity and the content of total organic carbon. An evaluation of the humification parameters of the final composts is also essential, since humic substances are the most important components of soil organic matter, and they form as the initial substrate evolves to mature composts.

Moisture

The water content in the final composts depends on the initial moisture content in all the materials involved in the composting process, moisture evolution and amount of tap water eventually added. Values lower than 50%wt are optimal moisture content according to other authors [3]. This target corresponds to the limit set by the Italian Legislative Decree 75/2010. The excess water, that is usually present in the initial substrate, is removed in the form of water vapor because of the temperature increase and by the air supplied to the process. Hence, aeration reduces moisture significantly, to an extent that usually requires tap water addition to restore the desired moisture content.

pH

The pH levels in the final composts should be nor excessively low neither too high in order not to induce changes in the soil natural pH. In Italy, the Legislative Decree no. 75/2010 sets the pH target values of 6-8.5 for high quality composts. However, the beneficial effects that each compost would have are to be related to the properties of the soil where the it has to be used.

Nutrients

Though limit values for the heavy metal total content exist, analogous quality benchmark in terms of nutrients content were not set. In spite of this, the nutrient content affects the compost marketability the most [30]. Indeed, compost is a product often characterized by poor market conditions, and it would benefit from an improvement of the macro- and micro-nutrients content [91,93]. In particular, phosphorus is an essential nutrient that often constitutes the limiting factor for plant growth [87]. In Europe, only the Netherlands has included the phosphorus total content among the key parameters for defining compost quality. Potassium should be considered for evaluating compost quality as a fertilizer as well, though it is usually low in the composts derived from OFMSW [87].

Toxic or inhibiting compounds

The EU Member States legislated at national level to set quality standards aimed at avoiding toxicity in the final products, so that in Europe several laws co-exist. Generally, limits are set for the heavy metals total content only; in particular, the metal species regulated in the European countries are: arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc. In some cases, the compliance to the quality requirement standards established for final composts is voluntary. In Austria, Czech Republic, Germany, Ireland, the Netherlands, Slovakia, Spain and the United Kingdom different quality levels for composts are identified by defining two or more classes of products [30]. In Italy, all the composts must comply with the limits set by the Legislative Decree no. 75/2010 on fertilizers (Tab. 4.2).

Tab. 4.2. Limit value for heavy metals [$mg \cdot kg^{-1}_{d.b.}$] set by the Italian Legislative Decree n. 75/2010 [26].

Heavy metal total content	Limit value
Pb	140
Cd	1.5
Ni	100
Zn	500
Cu	230
Hg	1.5
Cr (VI)	0.5

In addition, the Legislative Decree n. 75/2010 imposes a limit value for the thallium concentration (2 $mg \cdot kg^{-1}_{d.b.}$) in composts produced using algae. In relation to compost toxicity, it also sets the limit values for Salmonella (absence in 5 sub-sample of 25 g) and *Escherichia coli* (in 5 sub-sample of 1 g, one sub-sample having bacteria colony-forming units (CFU) between 1000 and 5000 $CFU \cdot g^{-1}$ is admitted), and the minimum germination index (60% at dilution 30%).

However, some other compounds might be present in the final composts that are toxic or inhibiting for plants, such as salts and intermediate compounds (e.g., organic acids). The latter were extensively investigated by some authors [42] and their potentially adverse effect was studied through the germination test performed with cress seeds. In relation to the effect on plants, the acetic acid was reported to provoke the most toxic effect [42].

Salinity

High salinity levels affect the degradation process, since they reduce the enzyme activity (phosphatase, urease and dehydrogenase) when applied to acidic soils [33]. In particular, electrical conductivity (EC) should not be greater than values of 3-4 $mS \cdot cm^{-1}$ in order to avoid osmotic stress on the plant tissues, according to the referenced authors [36,53,55]. There is not a limit set by law for EC, rather the limits vary in relation to the crops that are cultivated. Generally, compost salinity is due to Na^+, K^+, Ca^{2+}, Mg^{2+} and Cl^-.

Stability and maturity of the final compost

Obtaining a stable and mature product useful for plant growth is one of the purpose of the composting treatment. As several authors suggested [16,76], stability and maturity should be assessed on the basis of a set of properties, rather than only one parameter.

Stability is defined as the status of being biologically stable, which means that the microbial activity and the subsequent organic matter degradation tend to be negligible [10,15,80]. Compost stability is assessed by means of a number of direct or indirect methods that include the decline of temperature (when other causes such as lack of oxygen, FAS, moisture content or a previous thermal inactivation of the microbial community are to be excluded), and reduction of the organic content and respiration activity.

The organic content could be measured in terms of volatile solids (VS) or total organic carbon (TOC) content [37]. The carbon to nitrogen ratio (C_{tot}/N_{tot}) decreases with time during composting because of the C_{tot} reduction, due to the organic fraction of the total carbon content decrease. For this reason values lower of 20 are considered indicative of the biological stability. The C_{tot}/N_{tot} ratio is also used to evaluate whether the amount of nitrogen is sufficient to sustain the complete decomposition of the degradable carbon. The evolution of the respiration activity of a substrate (twhich could be expressed in terms of the oxygen consumed by the matter that decomposes) is also used to evaluate the stabilization degree, because the more a substrate is stable the less it consumes oxygen. For this reason, the respiration activity during composting decreases with time until the biological stability is reached [42].

Compost maturity could be related to the absence of phytotoxic effects for plant growth [10,15,80]. Phytotoxicity could be caused by the metabolites generated by the intermediate stages of the organic matter decomposition. Hence, it is strictly related to compost stability. Compost maturity is also generally associated to the formation of humic substances [53]. The achievement of organic waste stabilization and maturation implies an extensive humification, that is a set of complex processes of organic matter conversion into refractory organic compounds that resemble those found in native soils. Humic substances are responsible of several soil processes and properties. Therefore, the extent of humification and the amount and quality of humic substances are of primary importance for the organic amendment in terms of environmental properties and agronomic and economic value. Humic substances are characterized by the presence of functional groups containing oxygen, nitrogen and sulfur, which make possible interacting with ions in a number of ways, such as complexation of metals, precipitation of metals via adsorption, reduction, ion exchange or other sorption processes on insoluble humic substances. Humic substances may also influence the behavior of mineral surfaces and colloidal particles with respect to metal ions, and even the rates of geochemical processes.

4.2.4 The use of additives

The composting feed could be conditioned through the following methods:

- Recycling mature compost to reduce bulk density of the substrate and favor aeration,
- Use of additives (organic or inorganic) aimed at adjusting some specific properties (e.g., pH, moisture content) or enrich the substrate to ameliorate the process and/or the final product quality,
- Add and/or recycle bulking agent to give structure to the substrate,
- A combination of the first three methods.

Additives to the composting mixtures are sometimes used to address some of the most common critical issues concerning the process (i.e., favoring air diffusion, adjusting moisture and pH) and product final quality (i.e., increasing the nutrients and micronutrients content in the final compost) [43]. Additives usually consists of microorganisms, mineral nutrients, readily available forms of carbon, enzymes and/or pH-balancing compounds [43]. Hence, they may influence every aspect of the composting process and the final product quality: the pile volume and mass, water, nutrients and carbon content, and bulk density.

Similarly to additives, bulking agents, which are used to provide more structure to a substrate and ensure a sufficient amount and interconnectivity of voids, could influence the composting process and final compost quality. They have various particle size, water and organic carbon content, and could take part to the degradation process at various extent, depending on the composition (i.e., cellulose is more easily available than lignin).

Temperature

Usually temperature is not directly controlled by additives. It is rather related to moisture and aeration, though. Indeed, temperature increases as a consequence of the aerobic microbial activity, that is favored by maintaining optimal moisture and aeration levels in the whole composting pile. If the moisture content is poor, microbial activity is hindered or even halted, and a massive temperature raise, provoked by the heat released during the aerobic degradation process, is not observed. Similarly, if proper aeration conditions do not occur, anaerobic degradation gradually replaces the aerobic process with a reduction of the heat released (caused by the fact that the anaerobic metabolism generates much less heat than the aerobic one).

Moisture

Since excess water in the initial waste might affect the air diffusion and, consequently, the composting process, additives could be used to adjust the moisture level. To meet a moisture target range of 50-70%wt in the composting mixture, optimal for the biochemical process [50], it is sometimes needed to introduce materials that absorb the excess water. Fibrous and bulky materials, like straw, are usually employed to this aim [58].

Aeration

The shortage of free airspace (typically caused by the high water content in the initial substrate) is one of the factors that affect the composting process the most. Appropriate structuring agents with low bulk density (and low moisture content) should be used to adjust the FAS value and the moisture content, whom the free airspace is correlated to. Bulking materials are used for this purpose, that typically consist of fibrous materials having large particle size, like wood chips [50]. A deficiency of wood chips is observed in some regions, such as Sardinia. They represent a cost for the waste treatment facilities [75], since the supply of wood scraps and prunings competes with the request of feedstock for energy generation or biofuel production.

Alternatives are studied in order to decrease their share in the composting mixtures, still obtaining the same level of process efficiency. Additives with adequate physical properties, such as sawdust, rice husk, peanut shells, and biochar, have been proposed in order to facilitate the fulfillment of aeration requirements [98-99].

pH

For adjusting pH level, several alkaline additives were studied, such as lime, sodium salt solution and coal ash [8,58]. In particular, some authors investigated the use of coal fly ash as an additive in the composting process because of its liming effect and the presence of mineral nutrients [8,13,77,96].

Nutrients

The final product quality could be improved by using nutrients-rich additives. Nutrients could be supplied to lacking substrates by adding jaggery and commercial mineral-based products [38,43]: urea, ammonium sulfate, ammonium chloride and ammonium phosphate, the latter of which provides the mixture with both P and N [42].

Toxic or inhibiting compounds

The presence of toxic or inhibiting compounds could be partially prevented by introducing a systemic control of the input materials characteristics. Several European countries have adopted certification programs aimed at ensuring that the compost has been produced from well-defined starting materials and following appropriate procedures.

Salinity

Similarly to the presence of toxic and inhibiting compounds, excessive salinity should be avoided as well. Caution should be taken in selecting additives with a salinity level not that high to threaten the future use of compost on soils.

Stability and maturity of the final compost

Additives to the composting process often consist in structural or drying amendments and favor air diffusion indirectly. In this sense, they contribute in improving the composting process and obtaining a stable and mature compost more efficiently. However, several variables need to be considered as the effects on the composting process will be multiple and interrelate. For instance, if additives with alkaline properties, such as coal ash, are considered, there will be effects on the C_{tot}/N_{tot} ratio that uncouple it to the compost stability: the C_{tot} content will increase with the fixation of the CO_2 (biologically produced) as $CaCO_3$ after the carbonation reactions, while nitrogen will decrease because of consumption and volatilization in the form of ammonia. As a result, the C_{tot}/N_{tot} ratio, meant as an indicator for compost stability, could provide a misleading information, as Raj et al. [76] affirmed.

4.2.5 The role of biomass ash in composting

The possibility of using residues of the combustion process was originally suggested for coal ash to which forestry wood combustion residues are sometimes related [13,34,95-96]. The recycling of biomass ash as an additive in the composting process was proposed by some authors as a way to enhance the composting process and improve the final compost quality [36,53,55-56]. However, biomass ash differs significantly from coal combustion residues, as reported in Chapter 3.

Kurola et al. [56] suggested that biomass ash may enhance the composting process and improve the final compost quality. In particular, the favorable effects exerted by biomass ash included higher organic fraction degradation rates and the enrichment of final product with minerals essential for plant growth [19,55-56]. In addition, using biomass ash as a composting additive could contribute to controlling the pH decrease at the early stage of the composting process [36]. Bougnom et al. [19], who conducted field experiments using the ash-amended compost produced in the experiment described by Kuba et al. [55], observed that the composts enriched with ash had an ameliorating effect on acidic soil due to its liming effect. Moreover, biomass ash has very low moisture and bulk density, while porosity is high, and these physical properties could help in maintaining air diffusion within the composting mixtures [4,42,65]. On the other hand, some possible disadvantages were observed in the final compost produced by using ash, such as the excessively high pH rise at the early stage of composting, presence of heavy metals, lack of nitrogen [36,55-56] and increase in the final compost salinity [53,74].

Temperature

In some studies on the use of biomass ash in composting, higher temperature values at the early stage of the organic waste composting were observed comparing to the unamended substrate [36,53,55-56]. Some authors suggested that the abiotic heat production deriving from carbonation exothermic reactions could be the prevailing cause of the higher temperature observed in ash-amended mixtures [36,53,55]. Carbonation reactions are expected to occur when mixtures amended with ash (that has high buffering capacity) are exposed to water and aerobic conditions, somehow limiting the emissions of the CO_2 produced during the process.

Moisture

Some ash types can help to maintain the optimal water content in the mixtures undergoing composting because it absorbs the excess water thanks to the high water holding capacity.

Aeration

Additionally to the low moisture content, some biomass ash types have physical characteristics (low bulk density, high water holding capacity) that are suitable for increasing free airspace (FAS) and favoring air diffusion in the composting mixtures [8].

pH

Having alkaline properties, biomass ash could be advantageous for the composting process because it could limit eventual excessive pH decrease at the beginning of the process, that is observed when acid organic substrates are used and could inhibit the microbial activity [2,58]. On the other hand, since an excessive pH rise has an inhibitory effect on the thermophilic microorganisms growth, the amount of ash to add has to be evaluated taking into account this aspect. In the perspective of producing a high quality compost, pH values at 12-13 were considered worth the interest by other authors. Fernández-Delgado Juárez et al. [36], Kuba et al. [55] and Kurola et al. [56] added wood ash to composting mixtures, having pH values of 12.5, 12.3 and 12.8, respectively. According to these authors, the addition of biomass ash constituted a base supply, and resulted in a pH increase during the process and in the final product. As for the final compost quality, ash-enriched composts with pH level of 8.59 have been used as a liming agent for acidic soils because of the alkaline properties [18].

Nutrients

Nitrogen is usually very poor or lacking in biomass ash [55], therefore ash addition to a waste-bulking agent mixture provokes the dilution of the N_{tot}. Ash addition also exerts an effect on the dynamics of the nitrogen forms, as described by Fernández-Delgado Juárez et al. [36] and Himanen and Hänninen [43]. Indeed, the increase of temperature and process pH provoked by ash addition enhances ammonia evaporation, resulting in a earlier reduction of the water-soluble NH_4^+ in the mixtures amended with ash (and any alkaline additives as well) comparing to what happens in the unamended mixtures. Concomitantly, ash addition is reported to increase the nitrate content earlier than what typically occurs during the the maturation phase [43]. For these reasons, if biomass ash is added to a composting mixture, the final compost is expected to be poorer in the total N and an additional N source could be eventually used as a supplementary additive [8].

As for the other macro-nutrients and micro-elements essential for plant growth (such as Ca, Mg, K and P), biomass ash represents a suitable mineral additive to composting mixtures that could influence the final compost quality positively. In their composting experiments with ash addition, Fernández-Delgado Juárez et al. [36] and Koivula et al. [53] reported that the final composts benefited from increasing biomass ash addition in terms of nutrient content. In particular, the K and P total content and availability in ash-enriched compost are aspects of great significance.

Toxic or inhibiting compounds

The heavy metals total content in ash is expected to be the most relevant disadvantage that may affect the final compost quality negatively [36,53,55-56]. Other authors have investigated the use of biomass ash in these terms and found that the harmfulness for the health and environment could be excluded when controlled amounts of ash were added. Few elements were occasionally present at higher concentration though [36,53,55-56], so that the reuse in composting should be conditioned by the assessment of the contamination risk for any specific case. For this reason, in some countries there are quality requirements for each of the materials involved in the compost production, besides of the final product [55-56].

Salinity

Biomass ash has high electrical conductivity (EC) [36,53,55]. As a result, ash addition is expected to increase salinity in the final products to an extent that could be harmful for plant growth [53,74]. An excessively high EC in compost is harmful for the plant growth, since it causes osmotic problems and affects water intake ability [36,53].

Stability and maturity of the final compost

As reported by literature [53-55], biomass ash addition enhances mineralization and humification in terms of a more rapid substrate stabilization and an increased content of humic substances.

4.3 Materials and Methods

4.3.1 Organic waste and bulking agents

The OFMSW used for the pilot-scale test was collected from a waste treatment plant settled in South Sardinia (Province of Cagliari) that have a capacity of 73,000 tonnes·year^{-1} of source-separated OFMSW and green waste. In particular, the OFMSW used in this experiment derived from a medium-sized town having approximately 24,000 inhabitants, where the amount of waste produced daily is sufficient to allow the collection of a representative sample. An amount of OFMSW of a few tonnes was collected and subjected to quartering according to UNI 10802:2004. The OFMSW sampled was highly heterogeneous, reflecting the average quality of the organic waste collected in South Sardinia [75]. It contained 13.7 %wt$_{d.b.}$ of extraneous, non-compostable materials, as displayed in Table 4.3.

Tab. 4.3. Extraneous materials in the real OFMSW used in this study (Source: Tecnocasic S.p.A., May 2014).

	Content in the organic waste [%wt$_{d.b.}$]
Plastic bags	0.6
Plastics	3.0
Glass	0.0
Metals	0.2
Inert waste	9.3
Nappies	0.6
Others	0.0

In order to avoid the interference generated by the waste heterogeneity and impurity on the evolution of the composting process and final compost quality, and to undertake a more detailed study thanks to the tighter control exerted, a laboratory-scale experiment was conducted, where synthetic organic waste was used. It was formulated on the basis of the data provided by Alibardi and Cossu [6] and Cappai et al. [20]. In Table 4.4 the composition of the synthetic waste used in the laboratory-scale experiment is shown.

In the pilot-scale experiment, the bulking material (BM) was constituted by the green waste treated in the above mentioned waste facility, and consisted in grass and tree prunings. In the laboratory-scale tests, wood chips were used that were collected at the thermal power plant where the biomass ash studied in the present work was generated.

Tab. 4.4. Main composition of the synthetic waste used in the laboratory-scale experiment.

	Content in the synthetic waste [%wt$_{d.b.}$]
Vegetables	35.0
Fruits	25.0
Meat, fish, cheese	10.0
Bread and pasta	35.0

Fig. 4.4. The organic fraction of the municipal solid waste (OFMSW) employed in the pilot-scale (left) and laboratory-scale (right) experiments.

Fig. 4.5. The bulking material employed in the pilot-scale (grass and tree prunings, left) and laboratory-scale (wood chips, right) experiments.

4.3.2 Composting mixtures

The choice of the waste:bulking material ratio is strategical for conducting the composting process efficiently. Several OFMSW:BM ratios are proposed in literature works. Schwalb et al. [82] proposed a OFMSW:BM ratio equal to 70:30 w/w, that corresponds to the one often used in full scale composting facilities. Other authors proposed waste:bulking material ratios of 7.1:1 w/w [66], or ranging from 1:1 vol/vol [88] to 3:1 vol/vol [3]. Such variations could be explained by the different physical properties (bulk and particle densities, and moisture content) of the raw materials used.

A predictive study was conducted prior to starting the experiment in order to select the OFMSW:BM ratio that might guarantee the moisture and aeration conditions optimal for the composting process.

The expected moisture and FAS content of a mixture composed by OFMSW and BM, mixed together according to several ratios, were calculated by using Equations 4.1-4.2, the latter being proposed by Mohee and Mudhoo [65], that take into account the organic waste and bulking material physical properties.

$$M_{mix} = \frac{(M_{OFMSW} \cdot x_{OFMSW} + M_{BM} \cdot x_{BM})}{(x_{OFMSW} + x_{BM})} \quad (4.1)$$

$$FAS = 100 - BD_{w.b.} \cdot \left(\frac{M_{mix}}{\rho_{water}} + \frac{100 - M_{mix}}{PD_{mix}}\right) \tag{4.2}$$

where

M_{mix} is the moisture content of the mixture [%wt],

M_{OFMSW} is the moisture content of the organic fraction of municipal solid waste [%wt],

M_{BM} is the moisture content of the bulking material [%wt],

x_{OFMSW} is the share of the organic fraction of municipal solid waste [unitless],

x_{BM} is the share of the bulking material [unitless],

FAS is the free airspace [%$vol_{w.b.}$],

$BD_{w.b.}$ is the wet bulk density of the mixture [$kg{\cdot}m^{-3}$],

ρ_{water} is the density of water, that corresponds to 1000 $kg{\cdot}m^{-3}$,

PD_{mix} is the particle density of the mixture [$kg{\cdot}m^{-3}$].

The bulk and particle densities of the OFMSW:BM mixture, needed to calculate the FAS value, were obtained by using Equations 4.3-4.4.

$$BD_{mix} = \frac{(BD_{OFMSW} \cdot x_{OFMSW} + BD_{BM} \cdot x_{BM})}{(x_{OFMSW} + x_{BM})} \tag{4.3}$$

$$PD_{mix} = \frac{1}{\left(\frac{VS_{w.b.}}{100} + \frac{1 - \frac{VS_{w.b.}}{100}}{2.5}\right)} \tag{4.4}$$

where

BD_{mix} is the wet bulk density of the mixture [$kg{\cdot}m^{-3}$],

BD_{OFMSW} is the wet bulk density of the organic fraction of municipal solid waste [$kg{\cdot}m^{-3}$],

BD_{BM} is the wet bulk density of the bulking material [$kg{\cdot}m^{-3}$],

x_{OFMSW} is the share of organic fraction of municipal solid waste in the mixture [unitless],

x_{BM} is the share of bulking material in the mixture [unitless],

PD_{mix} is the particle density of the mixture [$kg{\cdot}m^{-3}$].

$VS_{w.b.}$ is the volatile solids content on wet basis of the mixture [%$wt_{w.b.}$].

According to literature, moisture content in the organic waste ranges from 65.2%wt [6] to 87.7%wt [3], while the bulk density varies from 280 kg·m^{-3} [6] to 410 kg·m^{-3} [3]. The volatile solids content of the OFMSW reported by Alibardi and Cossu [6] was 91.9 %wt$_{d.b.}$.

Typically, small variations are observed among the bulking materials typically used. Moisture content ranges between 20%wt and 33%wt [3,82], and the corresponding bulk densities are 164-187 kg·m^{-3}. A typical volatile solids content of 97.3 %wt$_{d.b.}$ could be assumed [11].

On the basis of these assumptions, calculations were made to predict the moisture content and FAS level of OFMSW and bulking material mixtures obtained at different OFMSW:BM ratios. Assuming moisture, volatile solids content and bulk densities of OFMSW and BM equal to the ones reported in the literature, in Table 4.5 the predicted characteristics of mixtures having different OFMSW:BM ratios are summarized. A OFMSW:BM ratio equal to 70:30 w/w was definitively selected for the pilot and laboratory scale experimental campaigns, since this ratio was considered the most adequate for assuring conditions of moisture and FAS suitable for composting. Therefore, the initial OFMSW:BM mixtures used in the pilot- and laboratory-scale experiments, eventually added with the ash blend, were constructed complying with the 70:30 w/w ratio.

After the initial mixtures were constituted, the chemical composition of the initial substrates used in the pilot- and laboratory-scale trials was determined, that is summarized in Table 4.6. Because the OFMSW used in the pilot-scale tests was affected by a certain extent of contamination, some of the parameters here listed (e.g., EC, CaO, Ba, Co, Cr and Ni) were considerably higher in the initial mixtures of the 250 L tests than in the corresponding substrates of the laboratory-scale experiment.

Tab. 4.5. Predicted moisture and FAS content of mixtures having different OFMSW:BM ratios and raw materials properties.

Formulation by weight OFMSW:BM	**w/w ratio OFMSW:BM**	**Formulation by volume OFMSW:BM**	**vol/vol ratio OFMSW:BM**	**Moisture OFMSW [%wt]**	**BD$_{w.b.}$ OFMSW [kg·m^{-3}]**	**Moisture BM [%wt]**	**BD$_{w.b.}$ BM [kg·m^{-3}]**	**Moisture mix [%wt]**	**FAS mix [%vol$_{w.b.}$]**
50:50	1:1	37:63	0.6:1	65.2	280	20.0	164	42.6	81.3
55:45	1.22:1	42:58	0.7:1	65.2	280	20.0	164	44.9	80.8
60:40	1.5:1	47:53	0.9:1	65.2	280	20.0	164	47.1	80.3
65:35	1.86:1	52:48	1.1:1	65.2	280	20.0	164	49.4	79.8
70:30	*2.33:1*	*58:42*	*1.4:1*	*65.2*	*280*	*20.0*	*164*	*51.6*	*79.3*
75:25	3:1	64:36	1.8:1	65.2	280	20.0	164	53.9	78.8
50:50	1:1	37:63	0.6:1	87.7	410	33.1	187	60.4	74.5
55:45	1.22:1	42:58	0.7:1	87.7	410	33.1	187	63.1	73.5
60:40	1.5:1	47:53	0.9:1	87.7	410	33.1	187	65.9	72.3
65:35	1.86:1	52:48	1.1:1	87.7	410	33.1	187	68.6	71.2
70:30	*2.33:1*	*58:42*	*1.4:1*	*87.7*	*410*	*33.1*	*187*	*71.3*	*70.0*
75:25	3:1	64:36	1.8:1	87.7	410	33.1	187	74.1	68.7

Tab. 4.6. Chemical characteristics of the initial OFMSW:BM mixtures (n.d.: value not detected; < d.l.: below detection limit; standard deviation is indicated in brackets).

	Pilot-scale OFMSW:BM 70:30 w/w	**Lab-scale OFMSW:BM 70:30 w/w**
Moisture [%wt]	58.30 (0.01)	69.59 (0.01)
VS [%wt$_{d.b.}$]	66.88 (0.03)	96.70 (0.03)
pH	5.09 (0.03)	4.69 (0.03)
EC [mS·cm^{-1}]	4.22 (0.10)	0.46 (0.02)
TOC [%wt$_{d.b.}$]	34.77 (1.97)	49.75 (1.32)
Total N [%wt$_{d.b.}$]	2.05 (0.20)	2.54 (0.13)
C_{tot}/N_{tot}	16.96	19.56
CaO [%wt$_{d.b.}$]	2.37 (0.07)	0.48 (0.01)
K_2O [%wt$_{d.b.}$]	0.61 (0.01)	0.80 (0.02)
P_2O_5 [%wt$_{d.b.}$]	0.44 (0.01)	0.18 (0.01)
MgO [%wt$_{d.b.}$]	0.25 (0.02)	0.12 (0.01)
Al_2O_3 [%wt$_{d.b.}$]	0.29 (0.02)	0.03 (0.00)
Fe_2O_3 [%wt$_{d.b.}$]	0.34 (0.00)	0.03 (0.00)
Na_2O [%wt$_{d.b.}$]	0.35 (0.00)	0.11 (0.01)
MnO_2 [mg·kg$^{-1}_{d.b.}$]	116.93 (3.08)	61.67 (4.69)
Ba [mg·kg$^{-1}_{d.b.}$]	47.19 (1.27)	6.76 (1.16)
Be [mg·kg$^{-1}_{d.b.}$]	0.83 (0.00)	<d.l.
Cd [mg·kg$^{-1}_{d.b.}$]	<d.l.	<d.l.
Co [mg·kg$^{-1}_{d.b.}$]	1.66 (0.00)	<d.l.
Cr [mg·kg$^{-1}_{d.b.}$]	87.38 (1.07)	2.69 (0.69)
Cu [mg·kg$^{-1}_{d.b.}$]	17.76 (0.95)	10.23 (0.43)
Hg [mg·kg$^{-1}_{d.b.}$]	0.02 (0.00)	n.d.
Ni [mg·kg$^{-1}_{d.b.}$]	43.69 (0.54)	2.56 (0.64)
Pb [mg·kg$^{-1}_{d.b.}$]	<d.l.	<d.l.
Sb [mg·kg$^{-1}_{d.b.}$]	1.25 (0.59)	<d.l.
Se [mg·kg$^{-1}_{d.b.}$]	0.83 (0.00)	<d.l.
Sr [mg·kg$^{-1}_{d.b.}$]	79.39 (3.44)	20.88 (0.69)
V [mg·kg$^{-1}_{d.b.}$]	3.61 (0.48)	0.75 (0.03)
Zn [mg·kg$^{-1}_{d.b.}$]	56.64 (2.36)	28.00 (0.41)

4.3.3 Ash blend

In the present research line, the biomass ash types most enriched in macronutrients (boiler and fly ash, BOA and FA, respectively) were mixed together in order to form a blend that was added to the OFMSW:BM mixture. Indeed, among the samples analyzed, FA was the most enriched in calcium and potassium, and contained high magnesium level, while BOA had also a notable level of calcium and potassium as well as the highest magnesium and phosphorous content. Boiler and fly ash had very low moisture and bulk density (BD), while particle density (PD) and water holding capacity (WHC) were high. These physical properties could contrast the excess of moisture in the initial substrate and influence the composting process positively by increasing the free airspace in the composting mixtures [4,42,65]. Lastly, FA and BOA could act as liming agents because of the high pH levels (13 and 12, respectively).

For these reasons, a blend of boiler and fly ash was composed and used as an additive during the composting tests. The two ash types were mixed together according to 71:29% w/w (50:50% vol/vol ratio), which corresponded to the shares that are actually produced in the thermal power plant. The ash blend was then added to the OFMSW+BM mixture at different amounts. The chemical-physical characterization of the biomass ash blend is shown in Table 4.7.

Some ash amounts, suggested by literature studies, were adopted with the aim of pointing out the effects of increasing amounts of ash on the process and the final product quality [55-56]. They were: 0%wt, 2%wt, 4%wt and 8%wt of the composting mixture in the pilot-scale test, and 0%wt, 4%wt, 8%wt and 16%wt in the laboratory-scale experiment. At present, some of the European regulations set the upper limits of 10-15%wt to the share of ash admitted as a composting additive. What is more, these limits are consistent with what Fernández-Delgado Juárez et al. [36] found to be the shares of ash that might entail an excessive heavy metals load and a detriment for the final compost quality. The Austrian Compost Ordinance [12] is more restrictive and sets the limit of 2%wt [53].

Tab. 4.7. Chemical characteristics of the BOA:FA blend (71:29% w/w) blend (n.d.: value not detected; < d.l.: below detection limit; standard deviation is indicated in brackets).

	BOA:FA blend
Moisture [%wt]	1.21 (0.02)
VS [%wt$_{d.b.}$]	2.26 (0.15)
pH	12.77 (0.01)
EC [mS·cm^{-1}]	26.38 (4.5)
TOC [%wt$_{d.b.}$]	4.56 (0.02)
Total N [%wt$_{d.b.}$]	<d.l.
C_{tot}/N_{tot}	n.d.
CaO [%wt$_{d.b.}$]	29.01 (0.12)
K_2O [%wt$_{d.b.}$]	9.43 (0.14)
P_2O_5 [%wt$_{d.b.}$]	2.77 (0.05)
MgO [%wt$_{d.b.}$]	5.18 (0.07)
Al_2O_3 [%wt$_{d.b.}$]	6.00 (0.14)
Fe_2O_3 [%wt$_{d.b.}$]	2.61 (0.08)
Na_2O [%wt$_{d.b.}$]	1.18 (0.01)
MnO_2 [mg·kg$^{-1}_{d.b.}$]	2319.87 (0.01)
Ba [mg·kg$^{-1}_{d.b.}$]	270.15 (0.80)
Be [mg·kg$^{-1}_{d.b.}$]	0.06 (0.00)
Cd [mg·kg$^{-1}_{d.b.}$]	2.80 (0.09)
Co [mg·kg$^{-1}_{d.b.}$]	9.83 (0.36)
Cr [mg·kg$^{-1}_{d.b.}$]	39.11 (0.72)
Cu [mg·kg$^{-1}_{d.b.}$]	191.47 (0.35)
Hg [mg·kg$^{-1}_{d.b.}$]	0.28 (0.02)
Ni [mg·kg$^{-1}_{d.b.}$]	27.45 (0,96)
Pb [mg·kg$^{-1}_{d.b.}$]	44.67 (0.73)
Sb [mg·kg$^{-1}_{d.b.}$]	1.04 (0.15)
Se [mg·kg$^{-1}_{d.b.}$]	1.31 (2.20)
Sr [mg·kg$^{-1}_{d.b.}$]	451.25 (3.62)
V [mg·kg$^{-1}_{d.b.}$]	42.74 (0.44)
Zn [mg·kg$^{-1}_{d.b.}$]	371.06 (3.32)

4.3.4 Varying the OFMSW:BM ratio

In addition to the composting mixtures above described, a supplementary composting mixture was composed and tested at laboratory-scale. In this additional test a smaller amount of bulking agent was used. An ash amount of 8%wt was used to amend the OFMSW+BM mixture so that the moisture and FAS content of the resulting amended mixture has levels comparable to the ones achieved with the OFMSW:BM ratio of 70:30 w/w.

In this case, the ash blend was used to accomplish a saving in the amount of the bulking agent used, still maintaining the moisture and aeration conditions optimal for the process.

The Equations 4.1-4.2 were modified to include the additive contribution, and a simulation of the expected moisture and FAS content in the resulting mixtures was conducted. (Tab. 4.8). Finally, an organic waste and bulking agent ratio equal to 81:19 w/w (74:26 vol/vol) was predicted to have a moisture content and FAS level similar to the ones of the 70:30 w/w unamended mixture.

The chemical composition of the initial OFMSW:BM 81:19 w/w mixture is shown in Table 4.9.

Tab. 4.8. Predicted moisture and FAS content of mixtures amended with 8%wt ash blend (BAsh) having different OFMSW:BM ratios and raw materials properties.

Formulation by weight OFMSW:BM:BAsh	**Moisture OFMSW [%wt]**	**BD$_{w.b.}$ OFMSW [kg·m^{-3}]**	**Moisture BM [%wt]**	**BD$_{w.b.}$ BM [kg·m^{-3}]**	**Moisture BAsh [%wt]**	**BD$_{w.b.}$ BAsh [kg·m^{-3}]**	**Moisture mix [%wt]**	**FAS mix [%vol$_{w.b.}$]**
70:30:0	*65.2*	*280*	*20.0*	*164*	-	-	*51.6*	*79.3*
50:50:8	65.2	280	20.0	164	1.21	201	39.5	81.9
60:40:8	65.2	280	20.0	164	1.21	201	43.7	81.0
70:30:8	65.2	280	20.0	164	1.21	201	47.9	80.2
75:25:8	65.2	280	20.0	164	1.21	201	50.0	79.7
80:20:8	65.2	280	20.0	164	1.21	201	52.1	79.2
81:19:8	*65.2*	*280*	*20.0*	*164*	*1.21*	*201*	*52.5*	*79.1*
85:15:8	65.2	280	20.0	164	1.21	201	54.2	78.7
70:30:0	*87.7*	*410*	*33.1*	*187*	-	-	*71.3*	*70.0*
50:50:8	87.7	410	33.1	187	1.21	201	56.0	75.8
60:40:8	87.7	410	33.1	187	1.21	201	61.1	73.9
70:30:8	87.7	410	33.1	187	1.21	201	66.1	71.8
75:25:8	87.7	410	33.1	187	1.21	201	68.7	70.7
80:20:8	87.7	410	33.1	187	1.21	201	71.2	69.5
81:19:8	*87.7*	*410*	*33.1*	*187*	*1.21*	*201*	*71.7*	*69.3*
85:15:8	87.7	410	33.1	187	1.21	201	73.7	68.3

Tab. 4.9. Chemical characteristics of the initial unamended composting mixture having OFMSW:BM 81:19 w/w (n.d.: value not detected; < d.l.: below detection limit; standard deviation is indicated in brackets).

Parameter	**Value**	**Parameter**	**Value**
Moisture [%wt]	73.20 (0.04)	Ba [$mg\cdot kg^{-1}{}_{d.b.}$]	6.61 (1.09)
VS [$\%wt_{d.b.}$]	96.60 (0.10)	Be [$mg\cdot kg^{-1}{}_{d.b.}$]	<d.l.
pH	4.14 (0.02)	Cd [$mg\cdot kg^{-1}{}_{d.b.}$]	0.04 (0.01)
EC [$mS\cdot cm^{-1}$]	0.47 (0.02)	Co [$mg\cdot kg^{-1}{}_{d.b.}$]	0.07 (0.01)
TOC [$\%wt_{d.b.}$]	50.05 (0.50)	Cr [$mg\cdot kg^{-1}{}_{d.b.}$]	2.45 (0.11)
Total N [$\%wt_{d.b.}$]	2.91 (0.05)	Cu [$mg\cdot kg^{-1}{}_{d.b.}$]	10.80 (0.01)
C_{tot}/N_{tot}	17.11	Hg [$mg\cdot kg^{-1}{}_{d.b.}$]	n.d.
CaO [$\%wt_{d.b.}$]	0.44 (0.01)	Ni [$mg\cdot kg^{-1}{}_{d.b.}$]	2.62 (0.00)
K_2O [$\%wt_{d.b.}$]	0.87 (0.02)	Pb [$mg\cdot kg^{-1}{}_{d.b.}$]	<d.l.
P_2O_5 [$\%wt_{d.b.}$]	0.21 (0.01)	Sb [$mg\cdot kg^{-1}{}_{d.b.}$]	0.15 (0.03)
MgO [$\%wt_{d.b.}$]	0.12 (0.01)	Se [$mg\cdot kg^{-1}{}_{d.b.}$]	0.21 (0.05)
Al_2O_3 [$\%wt_{d.b.}$]	0.01 (0.01)	Sr [$mg\cdot kg^{-1}{}_{d.b.}$]	21.78 (0.40)
Fe_2O_3 [$\%wt_{d.b.}$]	0.03 (0.00)	V [$mg\cdot kg^{-1}{}_{d.b.}$]	0.28 (0.02)
Na_2O [$\%wt_{d.b.}$]	0.13 (0.01)	Zn [$mg\cdot kg^{-1}{}_{d.b.}$]	29.76 (0.25)
MnO_2 [$mg\cdot kg^{-1}{}_{d.b.}$]	59.23 (0.83)	-	-

4.3.5 Experimental set up and layout of the experiment

The composting reactors consisted in static PVC reactors, having a capacity of 250 L or 64 L each, for the pilot- and laboratory-scale tests respectively.

The pilot-scale reactors (Fig. 4.6) were 105 cm tall, had an elliptical base (68 x 84 cm) and were equipped with a movable lid and a bottom, that did not allow the collecting of leachates. The laboratory-scale reactors (Fig. 4.7) were composed by boxes (39.5 x 56 x 29 cm) equipped with lids and bottom chambers, the latter realized by using a rigid plastic grid. The walls and bottom faces of the boxes were insulated with layers of polyurethane foam having a width of 4 cm. According to the study conducted by Wang et al. [93], the size of the laboratory-scale reactors (total volume of 64 L) represented the smallest one for limiting heat losses and simulating the full-scale process adequately.

Fig. 4.6. The pilot-scale experimental setup, with details of the aeration circuit.

Fig. 4.7. The laboratory-scale experimental setup, with details of the aeration circuit.

The pilot-scale experiment was set up at the municipal waste treatment plant settled in South Sardinia, while the lab-scale experiment was conducted at the Sanitary and Environmental Engineering Laboratory of the Faculty of Engineering, University of Cagliari.

In both the experiments, the composting mixtures were forced aerated by means of a compressed air circuit, that supplied an aeration rate calculated according to the air required for moisture and heat removal, in accordance to the formulas proposed by Haug [42]. The aeration rate supplied was set equal to 0.12 $m^3_{air}\cdot m^{-3}_{substrate}\cdot min^{-1}$, and consistent with the air rates provided by Ming et al. [63] and Zhang et al. [99] for similar purposes.

In both the experimental set up, the compressed air was supplied through a PVC tube provided with holes of 3 mm diameter each placed at a distance of 20 cm. The aeration tube was shaped as a spiral, starting from the bottom of each reactor, and climbing up the composting pile to form two (in the laboratory-scale setup) or three (in the pilot-scale one) spiral coils. In addition, in the 64L tests the piles were periodically turned to further favor aeration.

The pilot- and laboratory-scale experiment lasted 96 and 100 days, respectively. In each pilot-scale reactor the total initial wet mass was approximately 133 kg, while in each of the laboratory-scale composters 9 kg of OFMSW+BM mixture was placed.

In the pilot-scale tests, batches of the initial OFMSW:BM 70:30 w/w mixture were added with the following amounts of the boiler and fly ash blend: 2%wt, 4%wt and 8%wt. In the present work, these amended mixtures were called C2, C4 and C8, respectively. In the laboratory-scale tests, batches of the initial mixtures OFMSW:BM 70:30 w/w mixture were added with 4%wt, 8%wt and 16%wt of ash blend, and the corresponding reactors were named C4, C8 and C16, respectively. In each experimental campaign, unamended mixtures constituted by organic waste and bulking agent served as the control and were named C0. The additional test conducted at laboratory-scale, where a composting mixture of OFMSW:BM, mixed together according to 81:19 w/w ratio, was added with 8%wt of ash blend, was named C8*.

An overview of the composting tests conducted and described in the present Chapter is summarized in Table 4.10.

Tab. 4.10. Overview of the trials.

	Pilot-scale	**Laboratory-scale**	**Laboratory-scale**
OFMSW	Source-separated OFMSW	Synthetic OFMSW	Synthetic OFMSW
BM	Grass and tree prunings	Wood chips	Wood chips
OFMSW:BM ratio	70:30 w/w	70:30 w/w	81:19 w/w
Reactors	C0, C2, C4, C8	C0, C4, C8, C16	C8*
Ash addition [%wt]	0, 2, 4, 8	0, 4, 8, 16	8

4.3.6 Analytical methods

In both the experiments, the composting process was monitored by measuring temperature on a daily basis, and determining moisture, pH and the volatile solids (VS) content on samples taken weekly. Temperature values were detected with a thermocouple at the core of the composting mixtures. The bulk and particle densities were measured during the process as well and, together with the moisture content, allowed to calculate the level of free airspace.

In the initial mixtures and final products the total and organic C, total N, P, and major and minor elements content were determined. The respiration activity was assessed in the composting mixtures at the beginning, after 45/46 days and at the end of each test.

Finally, the final composts were characterized in terms of electrical conductivity (EC), water-soluble chlorides and sodium content, water-soluble nutrients and heavy metals, available nutrients, humification parameters and germination index. Some analytical determinations have already been described in Chapter 3, hence they are here recalled briefly.

MOISTURE CONTENT

The moisture content was determined by using a thermostatic oven at 105±2°C according to UNI 14774:2009 (ISO, 2015) until mass constancy.

pH AND ELECTRICAL CONDUCTIVITY

The pH and electrical conductivity (EC) levels were determined using a pH-meter (Orion4 Star, Thermo Fisher Scientific, MA, USA) and a conductivity meter (HQ30d, Hach Company, CO, USA), respectively, according to UNI EN 15933:2012 (EN, 2012).

VOLATILE SOLIDS CONTENT

To determine the volatile solids (VS) content, ceramic crucibles containing ground and dried samples were placed in a muffle furnace and heated at 550±10°C until mass constancy, according to UNI 15169:2007 (EN, 2007) (procedure for the loss of ignition, see Chapter 3).

RESPIRATION ACTIVITY

The respiration activity in the composting mixtures at the beginning, after 46 days and the end of the experiment was assessed by the 4 days respiration activity tests (RA4) performed by using a Sapromat® respirometer (H+P Labortechnik AG, Germany).

Fresh samples were weighed (approximately 50 g) and, then, distilled water was added until the moisture content was 60%wt of the water holding capacity. Then the samples were transferred in glass 500 mL-bottles that were subsequently placed in a temperature-controlled water bath at 20°C. The method is based on the determination of the oxygen amount required by the samples aerobic degradation (biochemical oxygen demand), once the bottles are closed and connected to the Sapromat® oxygen generation and pressure monitoring system. The cumulative oxygen amount supplied during a time period of 96 hours after the beginning of the test is considered. The amount of the oxygen required is referred to the total and volatile solids content in the samples, and expressed as RA4 (respiration activity after 4 days).

PHYSICAL PROPERTIES

The evolution over time of the physical properties of concern (moisture content, bulk and particle density) was monitored during the composting process.

Bulk density (BD) was measured on a weekly basis in accordance to UNI 15103:2010, while particle density (PD) was determined using a gas pycnometer (Accupyc II 1340, Micromeritics Instrument Corporation, GA, USA) in accordance to ASTM B 923:2010. The free airspace (FAS) was calculated by using the formula reported by Mohee and Mudhoo [65] and described in Chapter 3.

TOTAL CARBON AND NITROGEN

An elemental analyzer (CHN-1000, LECO Corporation, MI, USA) was used to determine the total carbon and nitrogen content in the initial mixtures and in the final composts (also see Chapter 3).

TOTAL ORGANIC CARBON

A total organic carbon analyzer (TOC-VCSN and SSM-5000A, Shimadzu Corporation, Japan) was used to determine the total organic carbon (TOC) in the initial substrates and final composts. The TOC determination requires ground and dried samples and consists in a two-step analysis.

Firstly, the total carbon content (TC) is determined. Amounts of approximately 25 mg are weighed in ceramic boats, which are placed in the TC furnace heated at 900°C. Given that the carbon content in the sample is converted to CO_2, the mass of total carbon in the sample is calculated.

Secondly, the inorganic carbon (IC) content is measured. The samples are placed in ceramic boats (approximately 25 mg) and moved to the IC furnace, where phosphoric acid is added. The furnace is heated at 200°C and the inorganic carbon is converted to CO_2, which is purged and detected.

The total organic carbon is then calculated by difference according to Equation 4.5:

$$TOC = TC - IC \tag{4.5}$$

WATER-SOLUBLE CHLORIDES AND SODIUM

The water-soluble chlorides and sodium content was determined according to UNI 15105:2011. The water extract solutions were obtained by heating (120°C for 60 minutes) 1.000±0.001 g of ground and dried samples in 50 mL closed vessels after the addition of 50 mL of deionised water. After filtrating, the Cl^- concentration in the obtained solutions was determined by using an Ion Chromatography System (ICS-90, Dionex, CA, USA).

Water-soluble Na was determined by shaking an amount of dried and ground sample with distilled water at 1:50 w/w for 30 minutes, then filtering and determining by using ion chromatography.

TOTAL CONTENT OF MAJOR AND MINOR ELEMENTS

The total content of major and minor elements in the initial mixtures and final composts were determined by inductively coupled plasma spectrometry (ICP-OES, Optima 7000DV, PerkinElmer, MA, USA) after a microwave-assisted acid digestion, according to EPA Method 3052. The method is described in Chapter 3.

BIOAVAILABLE HEAVY METALS

According to UNI ISO 17402:2008, bioavailability corresponds to:

“the degree to which chemicals present in the soil may be taken up or metabolized by human or ecological receptors or are available for interaction with biological systems”.

It is a broad definition that includes the exposure of plants, soil organisms, higher animals, and humans. These levels of exposure describe the effects of toxic elements on a specific target organism, or represent the steps of a dynamic process where the toxic elements are transferred to human food chain through the plants.

In relation to the specific target organism and type of contaminant, different methods to assess bioavailability could be selected. The amount of toxic elements that could be taken up by plants could be assessed by extracting with water or other extracting/complexing agent. Water extraction allows to assess the amount of contaminants that plants could take up by absorbing through the roots after direct contact with pore water present in the soil. Therefore, it is a method recommended for assessing the heavy metals mobility via the soil-plant pathway [83].

The water extractable heavy metal content was assessed by extracting with distilled water, filtering and analyzing using spectrometry (ICP-OES, Optima 7000DV, PerkinElmer, MA, USA).

WATER-SOLUBLE AND AVAILABLE NUTRIENTS

The water-soluble fractions represent the amount of nutrients present as soluble salts. The NH_4OAc-extractable fraction of Ca, K and Mg provide an information on both the water-soluble fraction and the rapidly exchangeable fractions, which correspond to the one bound to soil surface by weak adsorption [52,57]. Therefore, they correspond to the overall amounts that are readily available for plants [39].

The water-soluble content of major nutrients was determined after extraction with distilled water [83]. To determine the available Ca, K and Mg fraction, 2.0 g of ground and dried samples were weighed and transferred to 125 mL flasks together with 100 mL of ammonium acetate at pH 7.0 [78]. The flasks were placed in a shaker for 30 minutes and the obtained solutions were filtered at pore size 0.45 μm. The filtered liquid was analyzed using spectrometry (ICP-OES, Optima 7000DV, PerkinElmer, MA, USA).

PHOSPHORUS

To determine the total content and available fraction of phosphorus in the initial mixtures and final composts, two extraction procedures were used. Ground and dried samples were weighed (0.5 g) and transferred to fluoropolymer cups, where 5 mL nitric acid and 3 mL perchloric acid were added. The cups were covered and heated on a hot plate to allow a complete evaporation. After the solutions were cooled down, they were filtered at pore size 0.45 μm and transferred to 250 mL volumetric flasks with the deionised water used to wash the cups (APHA, 2005).

To determine the available fraction of phosphorus 1.0 g of dried and ground sample was weighed and transferred to a 125 mL flask, where 40 mL of sodium bicarbonate ($NaHCO_3$) 0.5 M at 8.5 pH was added [70].

The solutions were stirred for 30 minutes and filtered at pore size 0.45 μm. 1 mL of the obtained extracts was measured and transferred in a 50 mL volumetric flask for the colorimetrical determination. A reagent was prepared by weighing and mixing ammonium molybdate + sulfuric acid 8 N+ potassium antimonyl tartrate at 18:80:2 ratio. 1.5 mL of reagent was added to the extracts with 1.5 mL of ascorbic acid, and a time between 5 minutes and two hours was waited to allow the solutions to color.

The P content was determined colorimetrically by using spectrophotometry (U-2000, Hitachi Ltd., Japan).

HUMIFICATION PARAMETERS

The total humic carbon content (Cext) was determined by extracting the humic substances with 0.05 M sodium pyrophosphate, according to Roletto et al. [79].

1.0 g of dried and ground sample was weighed and placed in a 125 mL flask with 100 mL of sodium pyrophosphate. The sample was shook for 14 hours, and it was centrifuged at 3,500 rpm for 20 minutes. The supernatant was collected and stored refrigerated. The residue was washed with the extracting agent and the extraction was repeated twice. At each repetition, the supernatant was collected, and the liquids were finally mixed at the end of the three extraction steps. The obtained extracts were subjected to gravity filtration at pore size 2.0 µm and vacuum filtration at 0.45 µm, and the Cext content was determined by using a total organic carbon analyzer (TOC-VCSN and SSM-5000A, Shimadzu Corporation, Japan).

To determine the fulvic acid carbon content (CFA), 50 mL of the obtained extract and 4 mL of sulfuric acid 96% were placed in a volumetric flask and shook. Humic acids were allowed to precipitate for 2 hours after the H_2SO_4 addition. The solution was filtered at 0.45 µm pore size, and the obtained liquid analyzed using the TOC analyzer. The humic acid carbon content (CHA) was determined by difference.

The humification ratio (HR), humification index (HI) and percentage of humic acids (PHA) were calculated as expressed by Equations 4.6-4.8 [16,79]:

$$HR = \frac{Cext}{TOC} \cdot 100 \tag{4.6}$$

$$HI = \frac{CHA}{TOC} \cdot 100 \tag{4.7}$$

$$PHA = \frac{CHA}{Cext} \cdot 100 \tag{4.8}$$

GERMINATION INDEX

The phytotoxicy of the final composts was evaluated by performing the germination test in accordance to Zucconi et al. [100]. 300 g of samples were air-dried and then distilled water was added until the moisture content was 85%wt. After two hours the mixtures were centrifuged at 600 rotation/minutes for 15 minutes, and then subjected to vacuum filtration at pore filters 0.8 µm. The filtered extracts were added with distilled water in order to obtain solutions diluted at 75% and 50%.

Ten Petri dishes containing laboratory filter paper were added with 1 mL of each of the obtained solutions. In each Petri dish, 10 *Lepidium sativum* seeds, previously allowed to swell in distilled water for one hour, were placed [61,73]. The test was conducted at 20°C for 72 h, as suggested by Masciandaro et al. [62]. The same procedure was applied using distilled water, and constituted the control. During the test, roots and sprouts developed. After 72 hours, germination was stopped by adding ethanol, and the roots were counted and measured.

For each solution (compost extracts diluted at 75% and 50%, and the control), the germination index was calculated using the Equation 4.9:

$$GI_d = \frac{G_d \cdot L_d}{G_b \cdot L_b} \cdot 100 \tag{4.9}$$

where:

GI_d is the germination index of the given solution,

G_d is the number of the seeds where germination occurred in the Petri dishes containing the given solution,

L_d is the average roots' length of the seeds where germination occurred in the Petri dishes containing the given solution,

G_b is the number of the seeds where germination occurred in the Petri dishes containing the control solution,

L_b is the average roots' length of the seeds where germination occurred in the Petri dishes containing the control solution.

For each compost, the average of the indices obtained for the two diluted extracts (75% and 50%) was calculated and compared to the one determined for the control.

4.3.7 Statistical analyses

Sampling was performed approximately every 10 days from each of the four reactors involved in the experiment. In the pilot-scale experiment, sub-samples of about 250 g were withdrawn from 4 collecting points (two at the top, one at the center and one at the bottom of each reactor), then mixed to form a single sample to be used for the analytical determinations. In the laboratory-scale experiment, where turnings were operated, 80 g sub-samples were collected from the core of the composting piles. All the analyses were conducted in triplicate and the results are presented as mean values ± standard deviation.

A one-way analysis of variance (ANOVA) was performed on the main process parameters (temperature, pH, volatile solids content) with the ash amount as the main factor. Post hoc Tukey HSD test was conducted when statistically significant differences were found. Statistical analyses were also performed to study the relationship between the volatile solid reduction and main physical properties. The correlations between VS and RA4, humic matter and the available P and K, and the germination indices were analyzed by simple regression analyses. All the statistical data were obtained using the Statgraphic Centurion XVI software.

4.4 Results pertaining the process evolution

In this paragraph the evolution of each process parameters in the pilot-scale, laboratory-scale set of trials, including C8*, is discussed. For each parameter, a comparison among the results attained in the various experimental tests is also presented.

4.4.1 Temperature

Pilot-scale experiment

In Figure 4.8 the temperature evolution and the amount of tap water added in the pilot-scale tests are displayed. At the early stage of the composting process a temperature increase was observed in all the mixtures and the hygiene requirements for pathogen reduction, consisting in temperature values higher than 55°C for at least three consecutive days, was fulfilled [22,67]. In particular, in the C8 mixture, values higher than 60°C for four days were observed and the maximum value of 71°C was reached, that was 10°C higher than in the control.

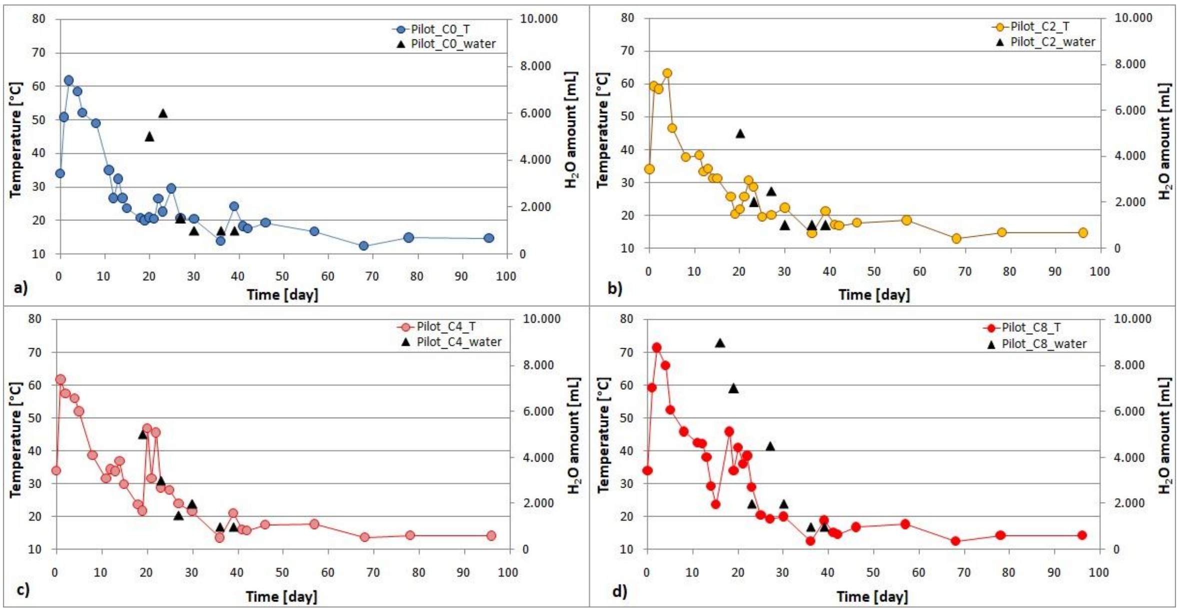

Fig. 4.8. Temperature evolution over time and water addition in the pilot-scale experiment: a) C0; b) C2; c) C4; d) C8.

After the initial peaks, temperature decreased in all the mixtures (days 4-15). Afterwards, the temperature values grew again (days 16-22), consistently with the moisture trend that is described later on in this Chapter. From day 15 to 30, statistically significant differences at the 0.1 level (ANOVA F(3,36) = 2.37, p = 0.087) were observed between the C0 and C8 composting mixtures. After day 38, the temperature values converged to constant values, close to the room temperature (10°C, since the tests were performed during winter) in all the composters.

Laboratory-scale experiment

In Figure 4.9 the temperature trend with respect to time is shown. In this picture, also the external water additions and turnings are depicted. On days 3 and 4 the maximum temperature values were reached, which ranged from 51°C in C0 to 56°C in C8 and C16. Temperature values higher than 50°C were maintained for three days in C8, two days in C4 and C16, and for one day in the control reactor. The small mass amount subjected to composting, that induces low heat capacity, and the turning operations conducted prevented the mixtures from reaching excessively high temperature values.

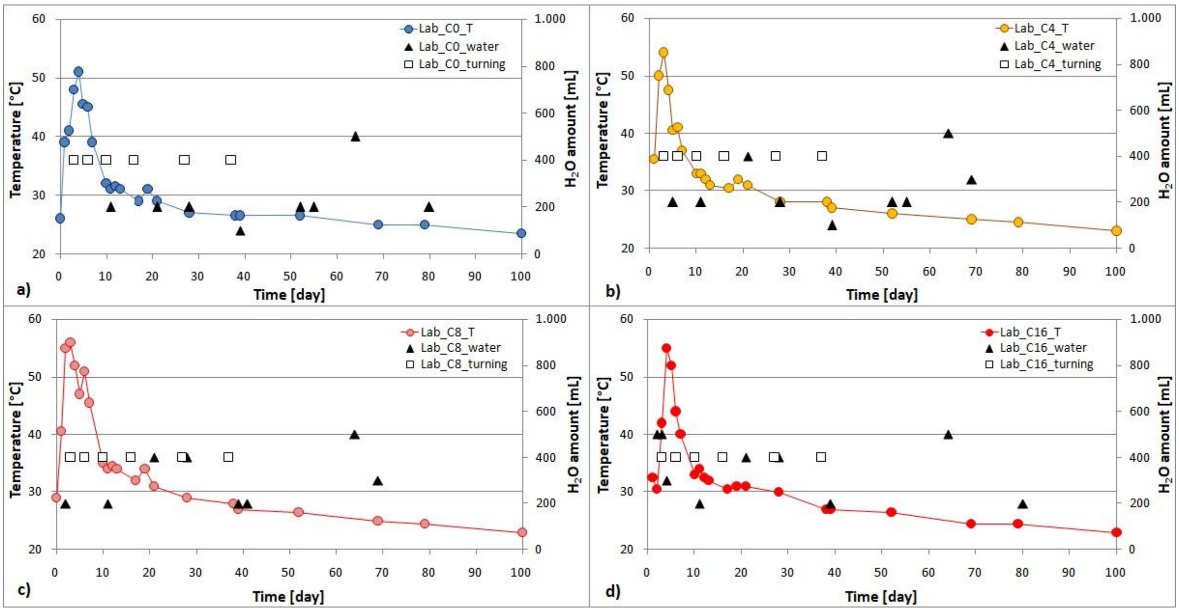

Fig. 4.9. Temperature evolution over time, water addition and turning operations in the laboratory-scale experiment: a) C0; b) C4; c) C8; d) C16.

After the initial peaks, the temperature values decreased in all the mixtures (days 4-17). The temperature evolution attained was similar in all the C0-C16 laboratory-scale mixtures. Statistically significant differences were not detected by the ANOVA analysis, which means that the temperature was not influenced significantly by the amount of ash added. After the last turning (day 37) and water addition (day 38), the temperature levels remained constant and close to room temperature (23°C, since the experimental campaign was conducted during summer) in all the mixtures.

*C8**

In the C8* mixture, the temperature evolved similarly to the C8 one (Fig. 4.10). The ANOVA tests did not highlight statistically significant differences between the two sets of trials. However, it should be noted that the C8* mixture reached the highest temperature value attained in the laboratory-scale experiment (61°C) and for three days temperature levels were higher than 50°C.

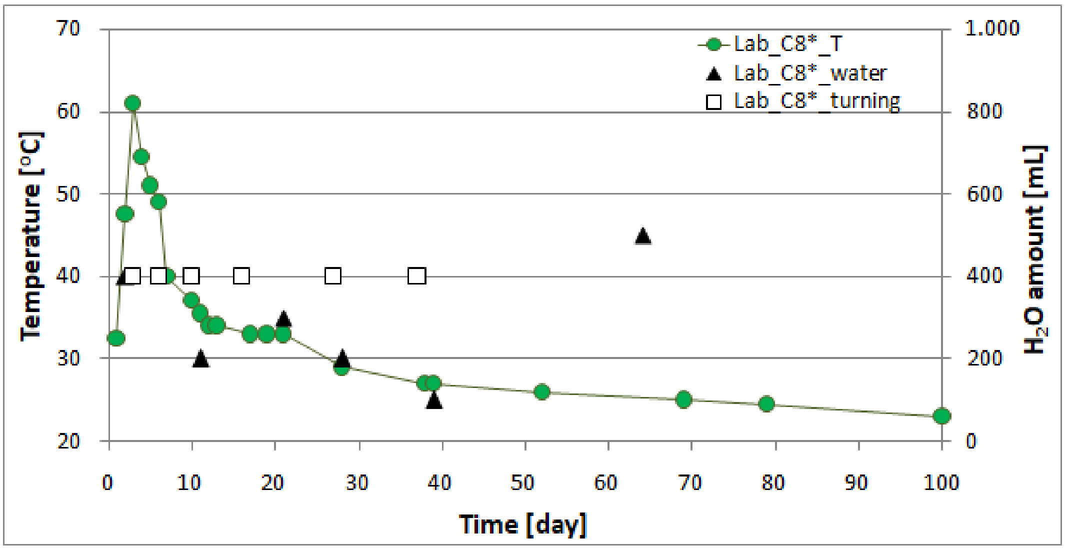

Fig. 4.10. Temperature evolution over time in the C8* mixture.

Comments

In all the tests, a temperature growth at the early stage of the composting process was observed, and the increase was more intense in the mixtures containing the highest ash amounts (C8 in both the experimental campaign, and C16 and C8* in the laboratory-scale run). This is consistent with what observed by other authors in mixtures amended with ash [55-56]. This effect could be attributed to the accelerated microbial activity, increased heat capacity, and carbonation exothermic reactions. The latter occurs because of the biomass ash alkalinity, as also suggested by Koivula et al. [53], Kuba et al. [55], and Mohee et al. [66], and could be considered one prevailing cause for the temperature increase. In all the experiments, the temperature evolution in the active and curing phases are clearly distinct, and in all the trials the active phase could be identified with the initial 30-days period.

As for the hygiene requirements, the Italian national standard (minimum 55°C for three consecutive days) was fulfilled by all the pilot-scale composting mixtures; the C8 pile maintained temperature values higher than 60°C for 4 days and was the only mixture to nearly meet the German requirements [21]. In the laboratory-scale experimental campaign the requirements were not met probably due to the small amount of the mass of waste involved, and the consequently lower heat capacity. Coherently, the highest temperature value among the laboratory-scale reactors was reached in C8*, that contained the biggest mass of waste.

It is also worth to mention that in the pilot-scale experiment the highest temperature peak corresponded to values (>70°C) that could be of harm for the biological process. It could be concluded that the ash addition could help in fulfilling the hygiene requirements but, on the counterpart, an accurate control on the temperature evolution should be exerted. To this purpose, turning could be of help in maintaining temperature values at lower levels.

4.4.2 Moisture

Pilot-scale experiment

The initial moisture content was similar in all the pilot-scale composting mixtures (55-60%wt) (Fig. 4.11). During the first 15 days of the pilot-scale experiment, no tap water was added in order to observe the effect of ash on the moisture content. In all the composters, including C0, a decrease in the moisture values down to levels below 50%wt occurred. The moisture drop was as dramatic as the ash amount was high, and values lower than 40%wt were reached in C4 and C8 that, according to several authors, correspond to conditions that slacken the composting process [50,58]. The decrease in the moisture levels was mainly caused by the loss of water vapor due to the temperature growth and subsequent evaporation [99]. Since in the pilot-scale mixtures temperature raised as much as the ash amount was higher, the moisture decrease was more intense in the ash-amended mixtures than in the control, and as high as the ash amount added was. External water was added in order to re-establish optimal moisture levels (Tab. 4.11). The addition of tap water allowed to contrast the decrease of moisture content and to re-establish a moisture level of 45-55%wt in all the final composts.

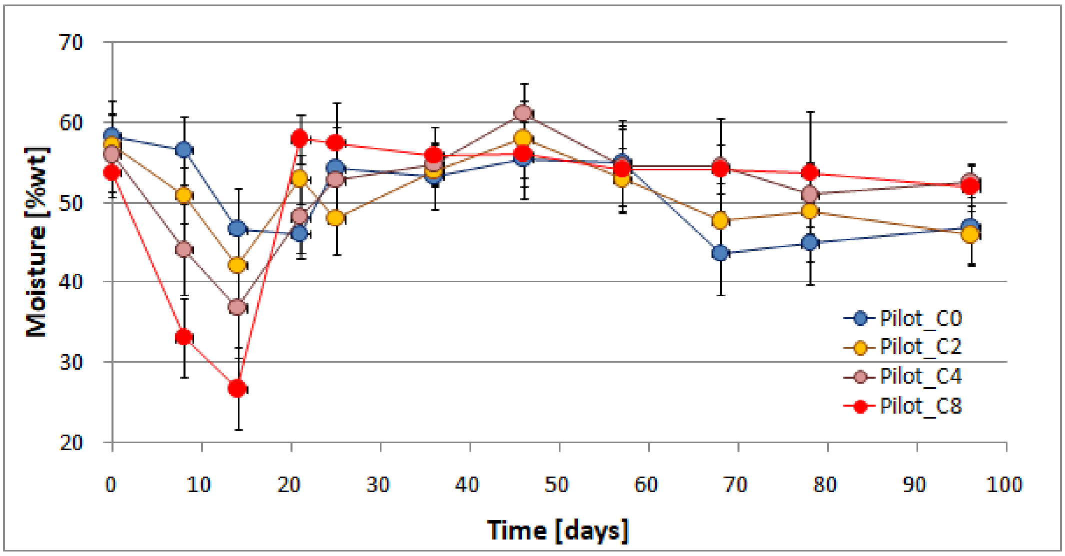

Fig. 4.11. Moisture evolution in the pilot-scale composting mixtures (error bars indicate standard deviation).

Tab. 4.11. Amount of tap water added to the composting mixtures of the pilot-scale test.

	C0	**C2**	**C4**	**C8**
Tap water added [L]	15.0	12.5	13.5	26.5

Laboratory-scale experiment

The moisture evolution in the laboratory-scale experiment is depicted in Figure 4.12. During the first 15 days, the moisture content in all the composting mixtures converged to values of approximately 50%wt, due to the combined effect of the water vapor evaporation and addition of tap water. In the C8 and C16 mixtures, the addition of external water started on day 2 in order to contrast an excessive decrease in moisture levels beforehand. The moisture levels were kept under control by doing additions of small amounts of tap water (each addition consisted of 100-500 mL of water, Tab. 4.12). The C8 and C16 mixtures reached the minimum moisture level of approximately 35%wt on days 20 and 28, respectively, which was adjusted by adding more water. The amount of additional water was higher in the composting mixtures containing ash than in the control. In the final composts, the moisture content was 54-57%wt.

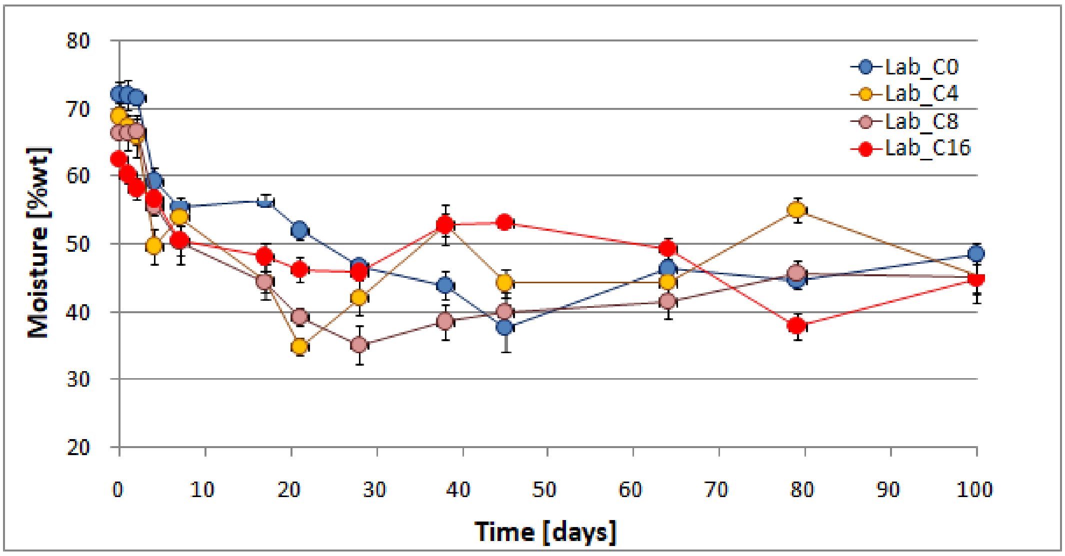

Fig. 4.12. Moisture evolution in the laboratory-scale composting mixtures (error bars indicate standard deviation).

Tab. 4.12. Amount of tap water added to the composting mixtures of the laboratory-scale test.

	C0	**C4**	**C8**	**C16**
Tap water added [L]	1.8	2.3	2.4	3.0

*C8**

The initial moisture content in the C8* substrate was higher than the ones in all the ash-amended mixtures of the laboratory-scale experiment because of the larger amount of OFMSW used (Fig. 4.13). During the first 20 days of the experiment, the moisture level in the C8* mixture was higher than in the C8 one; afterward, the moisture evolution in C8* and C8 became coinciding, and very close to the one observed in the C0 mixture too. The amount of external water added to the C8* mixture was lower than for the C8 one (Tab. 4.13). The final moisture levels in the C8*, C8 and C0 mixtures were similar and approximately equal to 55%wt.

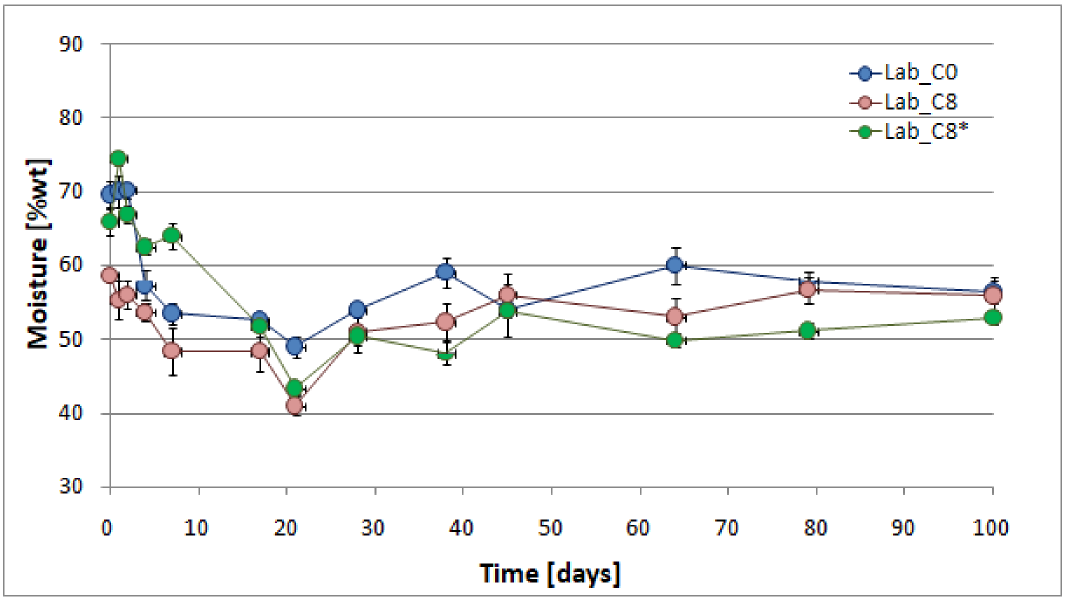

Fig. 4.13. Moisture evolution in C8*, C0 and C8 final composts of the laboratory-scale experiment (error bars indicate standard deviation).

Tab. 4.13. Amount of tap water added to the C8*, C0 and C8 composting mixtures of the laboratory-scale experiment.

	C0	**C8**	**C8***
Tap water added [L]	1.8	2.4	1.7

Comments

The initial and final moisture levels in all the trials are consistent with the ones reported by Fernández-Delgado Juárez et al. [36], who conducted a composting experiment using biowaste and wood ash. In all the trials, addition of external water was needed to contrast the drop of moisture content. The latter was higher in the pilot-scale tests than in the laboratory-scale ones because of the enhanced temperature growth and water loss due to evaporation.

The mixtures containing the highest amounts of ash (8%wt and 16%wt) required the biggest water addition. However, in the pilot-scale tests, the amount of tap water added to the mixtures was not aligned directly with the ash content (Fig. 4.14a).

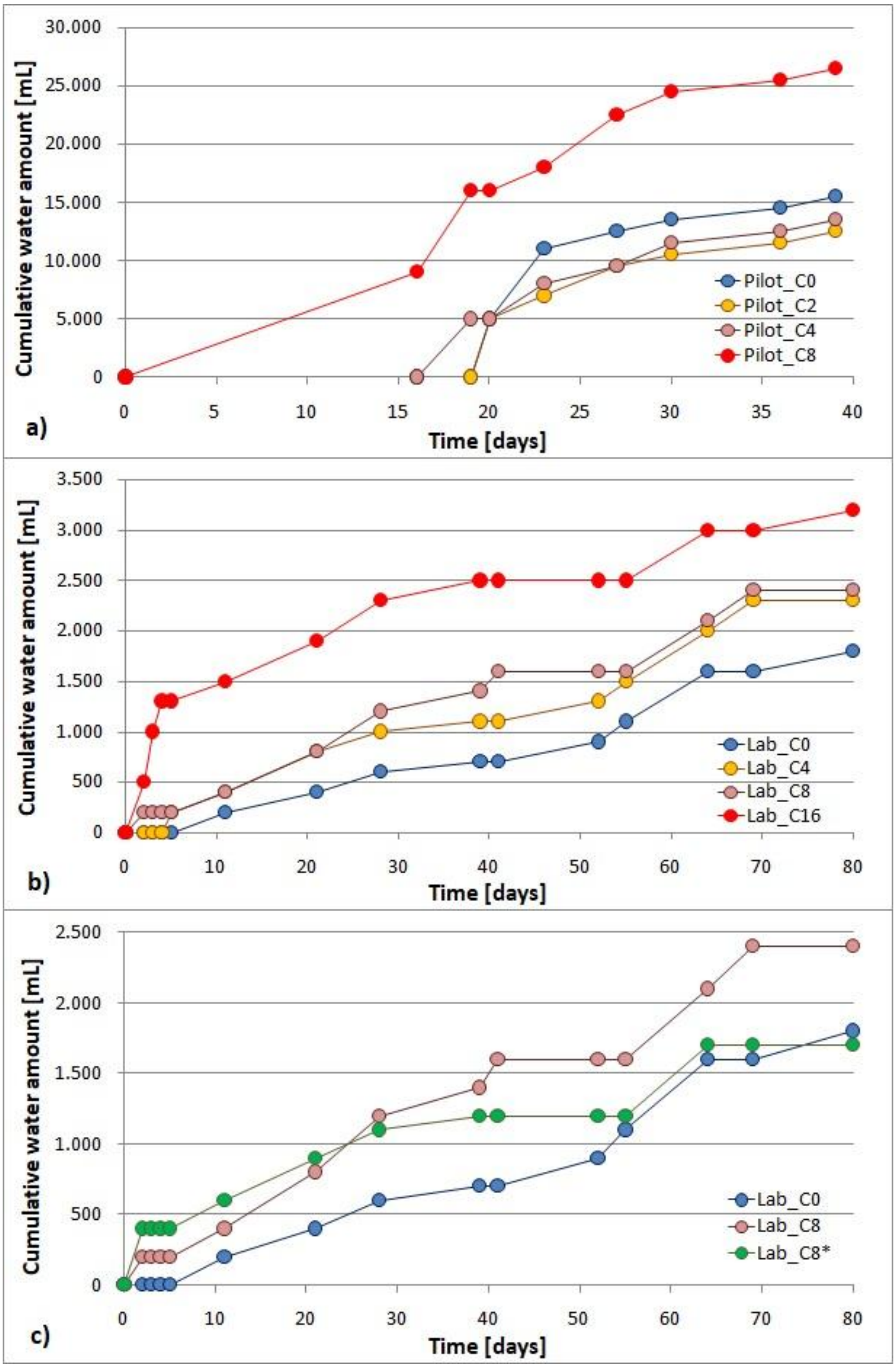

Fig. 4.14. Cumulative mass of water added to the composting mixtures in the (a) pilot-scale, (b) laboratory-scale experiment, and (c) C8*, C0 and C8 of the laboratory-scale experiment.

As shown in Figure 4.14b, the cumulative mass of water added to the laboratory-scale mixtures increased linearly with the ash amount. The moisture evolution in the C8* test confirmed this trend, though the amount of external water supplied during the curing phase in this test was smaller than in the C8 one (Fig. 4.14c).

In the laboratory-scale mixtures, the piles were also subjected to turnings during the first 38 days of the composting process, which also allowed to control the temperature increase and, consequently, to limit the moisture drop. The conditions operated at laboratory-scale allowed a tighter control on moisture drop and to attain a correspondence between the amounts of water added and the ash content, the latter being related to the amount of water required to re-establish the optimal moisture content. It is worth to notice, however, that the tighter control exerted in the laboratory-scale mixtures did not represent the operative conditions of the full-scale treatment plants, which were replicated more truthfully by the pilot-scale experiment.

4.4.3 Physical properties evolution

Pilot-scale experiment

The bulk density and free airspace evolution attained during the pilot-scale experimental campaign is shown in Figure 4.15. The bulk density in the wet substrate decreased during the first two weeks of the experiment in all the mixtures; during this period, $BD_{w.b.}$ was as low as the ash amount was high. Moisture affected this evolution; in particular, the drop in the bulk density values may have been correlated at a great extent to the moisture dramatic decrease at the beginning of the degradation process. Coherently, during the first two weeks, the lowest $BD_{w.b.}$ level and water content were exhibited by the C8 mixture. After this initial period, $BD_{w.b.}$ increased in all the mixture, which could have been provoked by the reduction of the waste particle size induced by degradation. From then on, the mixture that exhibited the highest bulk density level was C8, because of the high organic matter degradation achieved.

An increase in the FAS values was observed during the first two weeks of the experiment in all the mixtures, in accordance to the bulk density evolution. In the ash-amended mixtures, FAS was higher than in the control, in particular values higher than 70% were observed in C4 and C8. Since high FAS levels preserved the aerobic degradation process, this result was relevant. The high FAS values could be connected to the degradation performance achieved in these mixtures. After the first two weeks, FAS levels decreased in all the mixtures consistently with the increase of $BD_{w.b.}$.

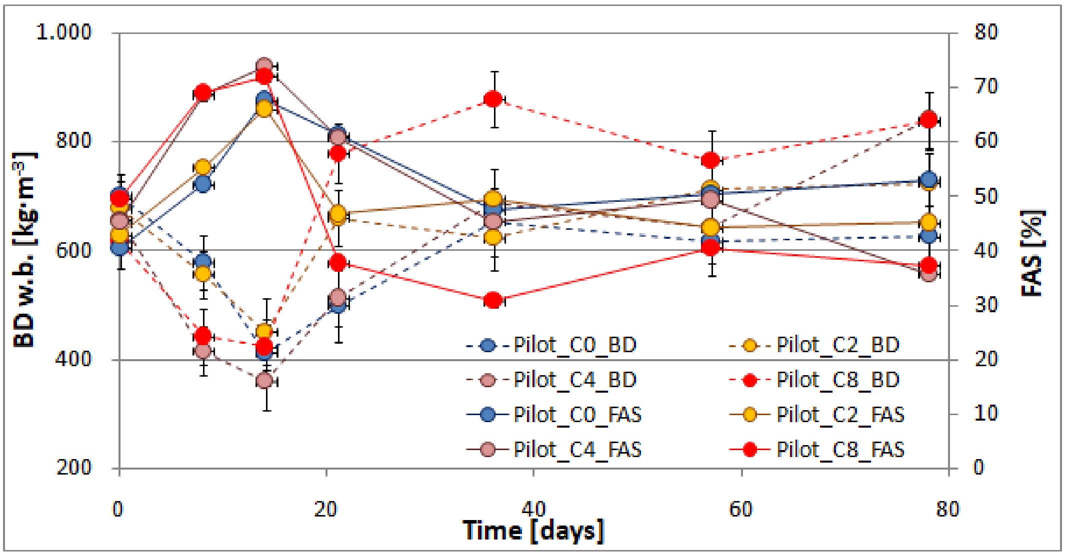

Fig. 4.15. Evolution of the bulk density (BD) and free airspace (FAS) in the composting mixtures of the pilot-scale experiment (error bars indicate standard deviation).

Laboratory-scale experiment

In Figure 4.16, the $BD_{w.b.}$ and FAS evolution attained during the laboratory-scale experiment is depicted. In the very first days of the composting tests, the $BD_{w.b.}$ in the C8 and C16 mixtures increased, because of the addition of tap water that was made on day 2 to prevent a dramatic water content decrease later on. However, after the first week the wet substrate bulk density converged to values of 400-450 kg·m^{-3} in all the mixtures. After day 20 the bulk density of the wet substrates increased in all the mixtures; despite some little differences, not significant variations in dependence on the ash amount were observed among the mixtures.

The FAS evolution was consistent with the $BD_{w.b.}$ trend. In this experiment, the starting FAS levels of the C8 and C16 mixtures were 62% and 71%, respectively (while C0 and C4 initial FAS was 48% and 50%, respectively) and showed a slight decrease on the successive two days as a consequence of the early water addition. In the first three days of composting, C8 and C16 had FAS levels higher than C0 and C4, then FAS converged to values very close to 65% in all the mixtures. After day 20, FAS decreased to values close to 40% and very few differences among the mixtures were observed.

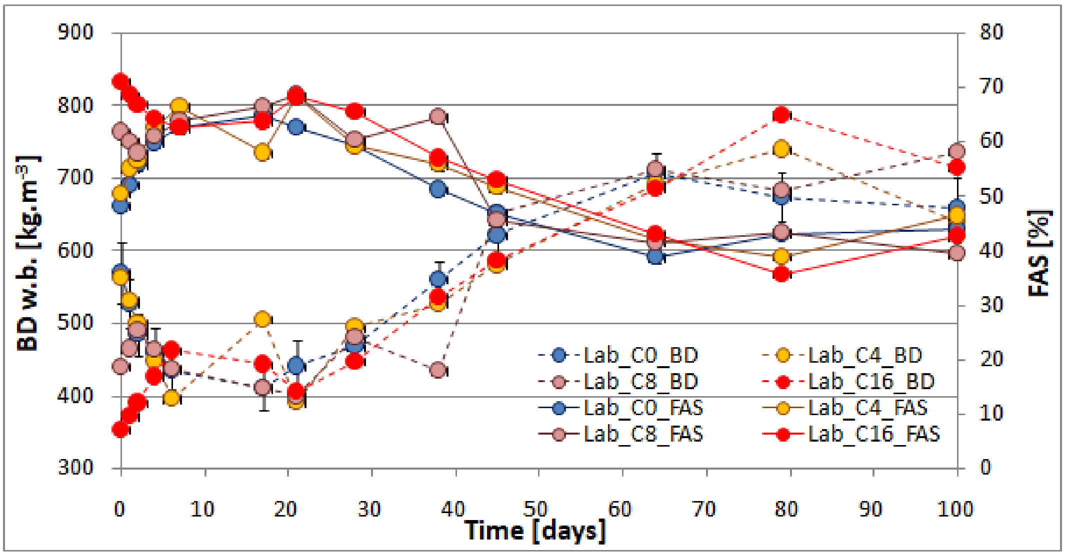

Fig. 4.16. Evolution of the bulk density (BD) and free airspace (FAS) in the composting mixtures of the laboratory-scale experiment (error bars indicate standard deviation).

*C8**

In the C8* trial, both $BD_{w.b.}$ and FAS evolved similarly to C8 (Fig. 4.17). In the C8* mixture a FAS value higher than 70% was reached on day 20, though a bigger mass of waste and smaller amount of bulking material was used in this test comparing to the other ones conducted at laboratory level.

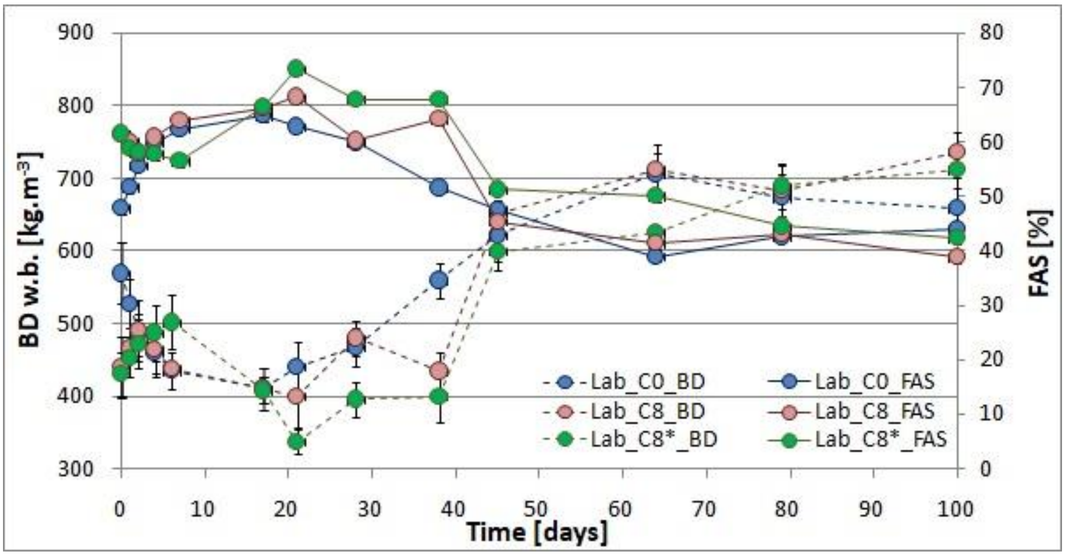

Fig. 4.17. Evolution of the bulk density (BD) and free airspace (FAS) in C8*, C0 and C8 final composts of the laboratory-scale experiment (error bars indicate standard deviation).

Comments

The $BD_{w.b.}$ evolution was similar in all the experiments, but some differences could be noticed among the tests. $BD_{w.b}$ was affected by a combination of factors: the extent of moisture decrease at the beginning of the process, tap water addition, organic matter degradation, compaction of the pile, type of bulking material. As for the latter aspect, the bulking material used in the laboratory-scale experiment (wood chips) was composed by bigger particles and by less easily degradable and compacting material than the one used in the pilot-scale tests (grass and tree prunings). This caused differences between the $BD_{w.b.}$ values attained in the two experiments: in the pilot-scale experiment $BD_{w.b.}$ ranged between 400 and 1000 $kg{\cdot}m^{-3}$, while in the laboratory-scale tests (including C8*) it varied from 350 to 800 $kg{\cdot}m^{-3}$. Because of the more marked drop in the moisture content at the early stage of the composting process, the differences in the physical properties among the mixtures were maximized in the pilot-scale experience. One of the purposes of using synthetic waste and wood chips in the laboratory-scale trials was to ensure an even distribution of waste and bulking material, and an adequate interconnectivity of the pores. In the laboratory-scale trials a more accurate control of the organic waste quality, BM distribution and moisture control allowed maintaining appropriate FAS levels for the first 40 days (equivalent to the high-rate phase). That said, as observed in the pilot-scale run, the laboratory-scale test confirmed that the highest FAS values were reached in the mixtures most enriched with ash. It could be due to the ash ability of absorbing water, which was expressed by the BOA and FA high water holding capacity (see Chapter 3), allowing more space for air diffusion.

4.4.4 pH

Pilot-scale experiment

The pH trend in the pilot-scale run is shown in Figure 4.18. The pH values of the initial mixtures ranged from 5.0 to 7.3, and increased with the time and the ash amount added. In this experimental set, a pH drop at the very early stage of composting was not observed. The pH evolution over time showed statistically significant differences in relation to the effect of the ash amount on pH values (ANOVA $F(3,36) = 3.84$, $p = 0.018$). The post hoc test showed that the pairs statistically significantly different were C0-C4, C0-C8, and C2-C8.

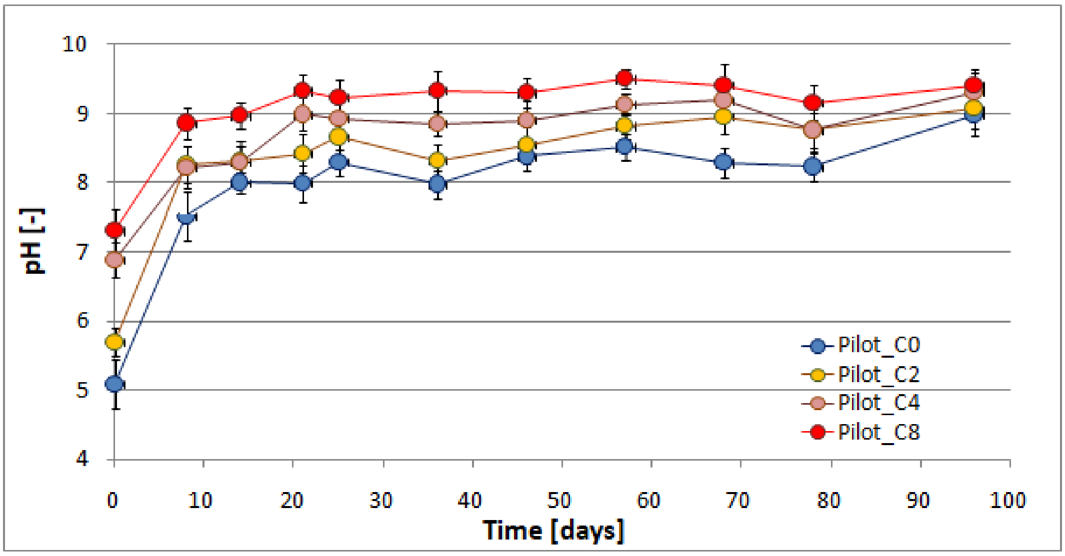

Fig. 4.18. pH evolution over time in the pilot-scale mixtures (error bars indicate standard deviation).

Laboratory-scale experiment

The evolution over time of the pH values in the laboratory-scale tests is shown in Figure 4.19. The initial mixtures showed pH values ranging from 4.7 to 7.4. On day 2 a pH drop down to 4.8 and 5.1 was observed in the C0 and C4 mixtures, respectively. In the C8 and C16 mixtures a slight pH decrease was observed as well, less intense as the ash amount added was higher. It could be deduced that the pH decrease, which is typical of the early stage of the OFMSW aerobic degradation process, was contrasted by the ash addition.

As for the pH evolution during the whole experiment, statistically significant differences in relation to the ash amount were observed (ANOVA F(3,40) = 6.26, p = 0.0014). According to the post hoc test, the pairs C0-C8 and C0-C16 were statistically significantly different.

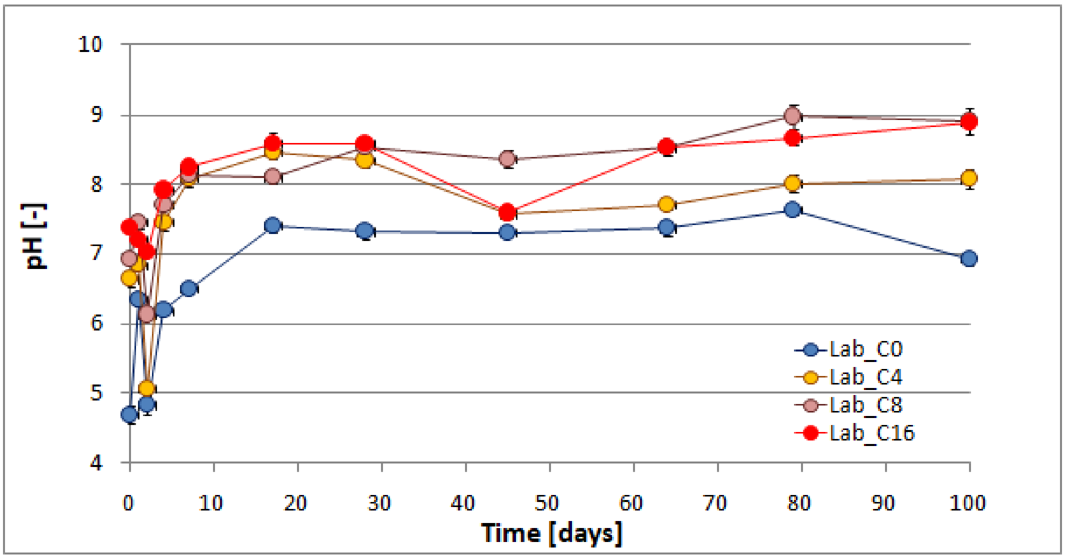

Fig. 4.19. pH evolution over time in the laboratory-scale mixtures (error bars indicate standard deviation).

*C8**

The pH trend observed in the C8* mixture is depicted in Figure 4.20. There are statistically significant differences in the pH evolution according to time and the ash amount (ANOVA F(1,2) = 21.18, p = 0.0001). The pairs C0-C8 and C0-C8* showed statistically significant differences, while the pH evolution in C8* and C8 was not.

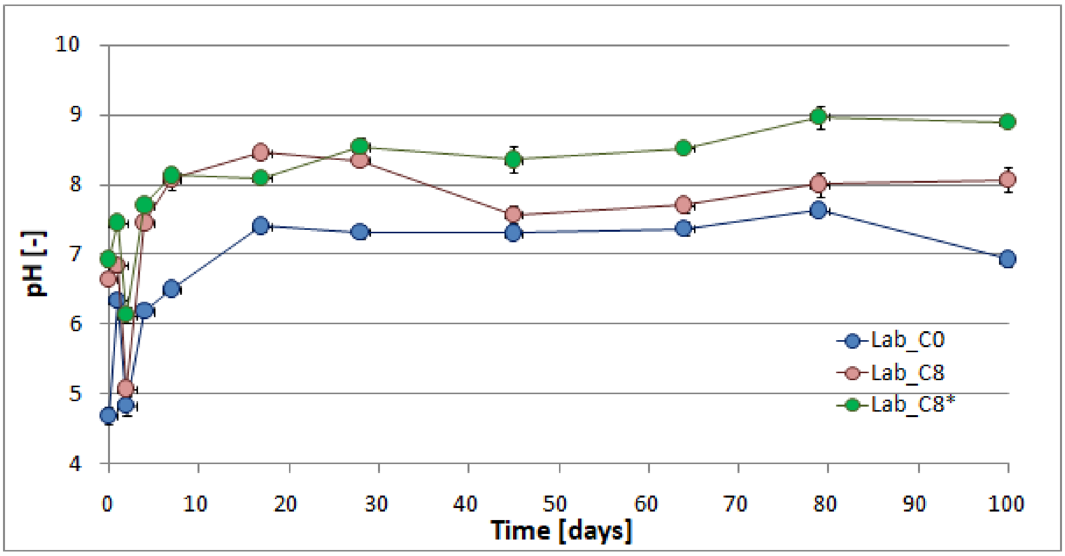

Fig. 4.20. pH evolution over time in C8*, C0 and C8 final composts of the laboratory-scale experiment (error bars indicate standard deviation).

Comments

The pH evolution during the composting process was similar in all the experiments, showing an increase throughout the process. The final pH values were higher in the ash-amended composts than in the corresponding control ones. At laboratory-scale, a tighter pH monitoring was exerted and this allowed to detect a pH drop on day 2, that was less intense as the ash amount added was higher. If the mixtures of the two experimental campaigns having the same amount of ash are compared (C4 and C8, and the control C0, Fig. 4.21), it could be noticed that the pH evolution was coincident in all the case; it could also be observed that the pilot-scale mixtures (that were prepared using source-separated OFMSW) had pH values higher than the laboratory-scale corresponding mixtures (where synthetic OFMSW was used) because of the difference in the pH values of the initial substrates pH. In the laboratory-scale experiment the pH final level of the C16 product corresponded to the ones of the C8* and pilot- and lab-scale C8 mixtures.

It could be concluded that the increase in the pH levels provoked by the use of an alkaline additive was helpful in contrasting the initial pH drop, and similar final pH values were observed when 16%wt or 8%wt of ash was added, irrespective to the type of the waste and bulking material, and OFMSW:BM ratio used.

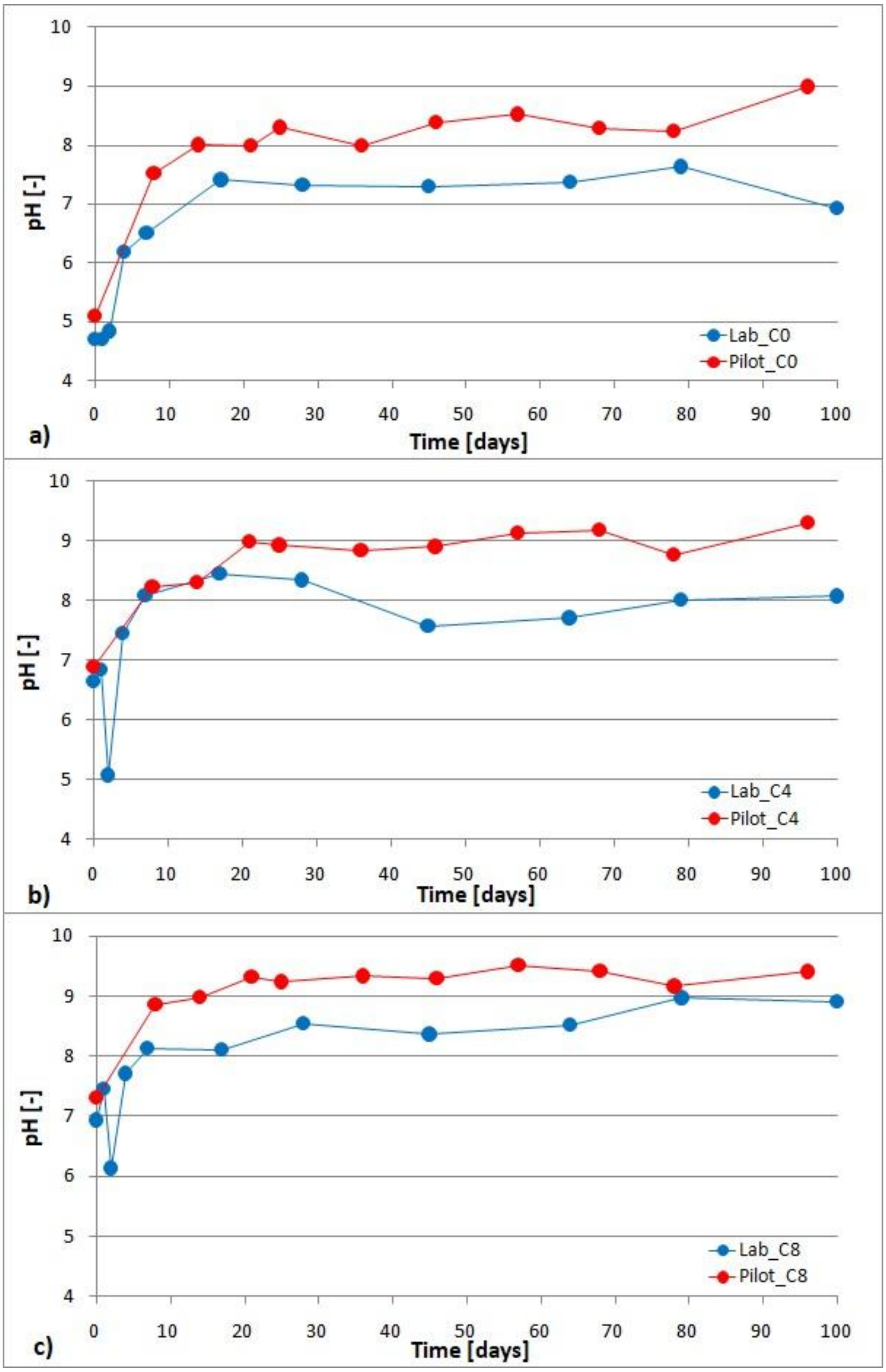

Fig. 4.21. pH evolution over time in the pilot-scale and laboratory-scale reactors: (a) C0; (b) C4; (c) C8.

4.4.5 Volatile solids content reduction

Pilot-scale experiment

In the pilot-scale mixtures, the volatile solids content at the beginning of the experiment ranged from 62 %$wt_{d.b.}$ to 67 %$wt_{d.b.}$. Larger variations were observed in the final composts (VS ranged from 32 %$wt_{d.b.}$ to 50 %$wt_{d.b.}$), because of the different extent of the VS reduction achieved in the four composting mixtures (Fig. 4.22). In particular, the VS content in the C8 final compost was 38% lower than in the unamended final product. Indeed, the volatile solids degradation was more marked in the ash-containing mixtures than in the control. If compared to the volatile solids content in the initial substrates, the final composts showed a reduction of 25.4%, 32.0%, 40.7% and 49.9% in C0, C2, C4 and C8, respectively.

The evolution in the volatile solids content showed statistically significant differences at $p < 0.05$ level (ANOVA F(3,36) = 10.34, p = 0.000) in relation to the amount of ash added. Similarly to what observed for the pH evolution, three pairs of composting mixtures showed statistically significant differences according to the Tukey's HSD test: C0-C4, C0-C8, and C2-C8.

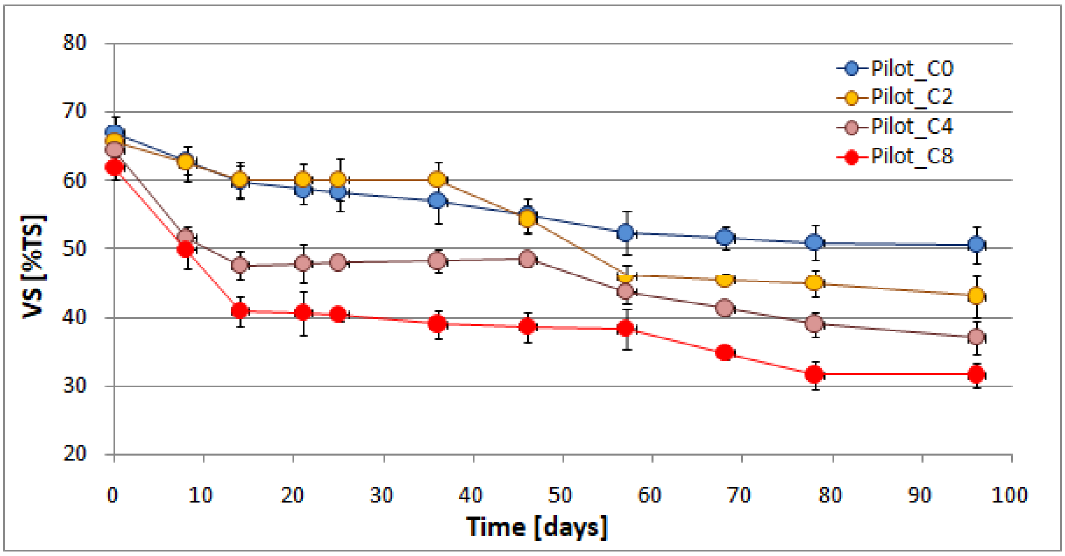

Fig. 4.22. Volatile solids content reduction over time in the pilot-scale mixtures (error bars indicate standard deviation).

Laboratory-scale experiment

In the laboratory-scale reactors, the initial VS levels were 87-97 %wt$_{d.b.}$, while the final volatile solids content ranged from 62 %wt$_{d.b.}$ to 76 %wt$_{d.b.}$. As observed at the pilot-scale level, a decrease in the volatile solids content, as high as the ash amount added, was found (Fig. 4.23). In the C16 final compost, the VS content was 29.4% lower than in the control. If compared to the volatile solids content in the initial substrates, the final composts showed a reduction of 14.4%, 21.9%, 28.2% and 31.5% in C0, C4, C8 and C16, respectively.

The volatile solids content reduction attained in the laboratory-scale mixtures showed statistically significant differences at the $p<0.1$ level (ANOVA F(3,48) = 10.74, p = 0.000) in the pairs C0-C8, C0-C16 and C4-C16.

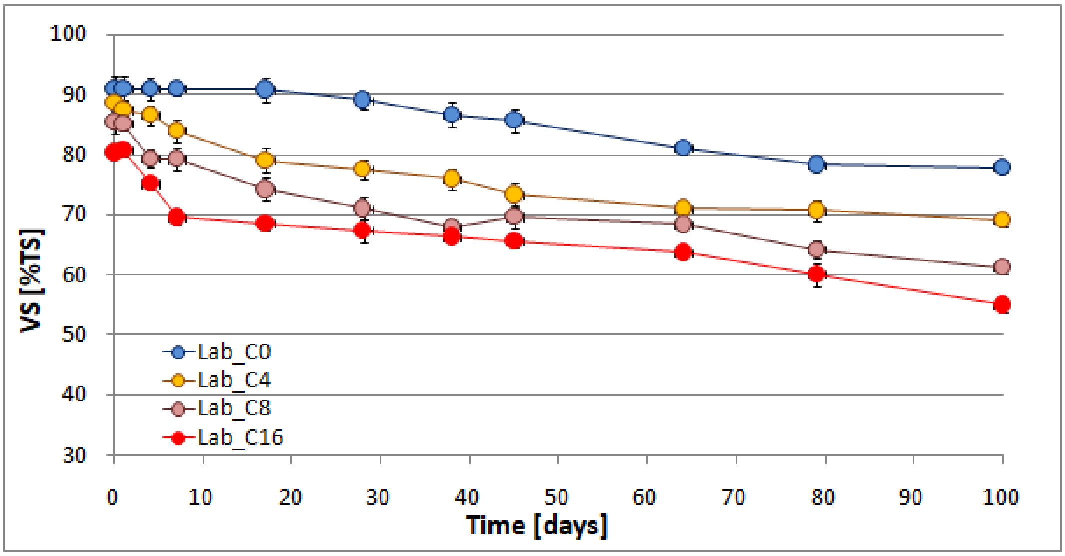

Fig. 4.23. Volatile solids content reduction over time in the laboratory-scale mixtures (error bars indicate standard deviation).

*C8**

The initial VS content in C8* was very close to the one observed in C8, so as the final volatile solids content (Fig. 4.24). However, the volatile solids content evolution over time in the C8 and C8* mixtures was dissimilar. Statistically significant differences were found (ANOVA F(1,2) = 135.97, p = 0.0000) among all the pairs: C0-C8, C0-C8*, C8-C8*.

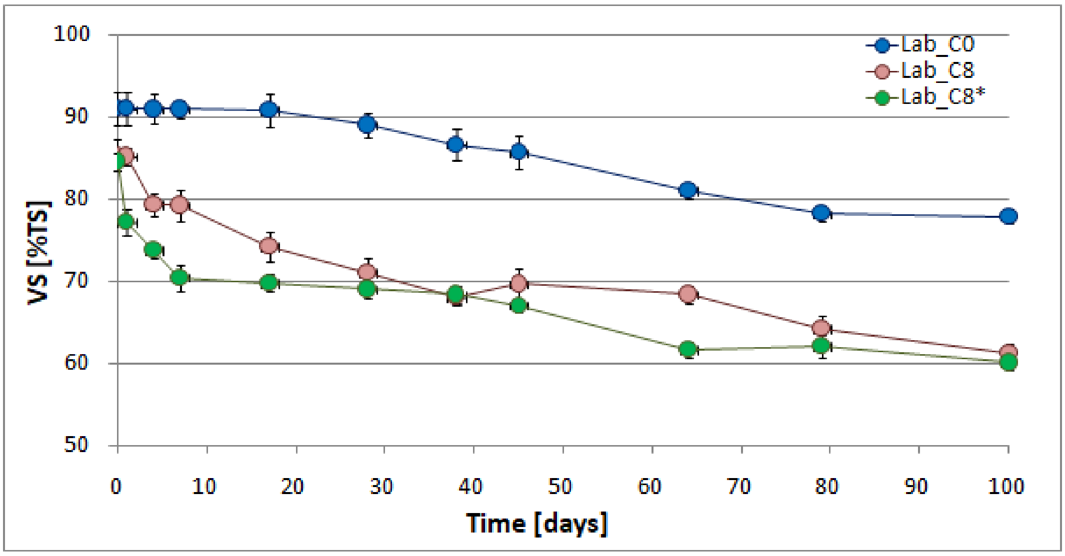

Fig. 4.24. Volatile solids content reduction over time in C8*, C0 and C8 final composts of the laboratory-scale experiment (error bars indicate standard deviation).

Comments

The initial VS values in the OFMSW:BM mixture used in the laboratory-scale tests was higher than in the real OFMSW:BM employed in the pilot-scale reactors because wood chips (that constituted the BM in the 64L tests) had a higher $VS_{d.b.}$ content than grass and prunings (that constitute the green waste employed as BM in the 250L experiment, see Chapter 2).

In both the experimental sets, higher VS reduction was observed in the ash-amended composts than in the unamended ones, and the reduction was more intense as the ash amount added was higher. These results suggest that ash addition favored the organic matter degradation. In Fig. 4.25 the comparison between the C0, C4 and C8 mixtures in the pilot- and laboratory-scale experiments is shown (the curves express the normalized $VS_{d.b.}$ decrease comparing to the initial values that are set equal to 100). It could be observed that the $VS_{d.b.}$ decrease in the C0 mixtures is coinciding, while the $VS_{d.b.}$ evolution in both the C4 and C8 mixtures of the pilot- and laboratory-scale tests was divergent, and the divergence was higher between the C8 mixtures than between the C4 ones, since the pilot-scale mixtures showed higher $VS_{d.b.}$ reduction in the ash-amended tests than the corresponding laboratory-scale ones. As pointed out by Fernández-Delgado Juárez et al. [36], it could be supposed that ash, being alkaline, made the ligno-cellulosic composition of the green waste more prone to deconstruction. Therefore, supposing that the green waste used as bulking agent in the pilot-scale experiment was more easily degradable than the wood chips used at lab-scale level, this fact could explain why the ash effect was magnified in the 250 L-tests.

Similar VS trends were observed in C8* and C8, suggesting that the ash addition exerted the same effect on the OFMSW irrespective of the OFMSW:BM ratio used.

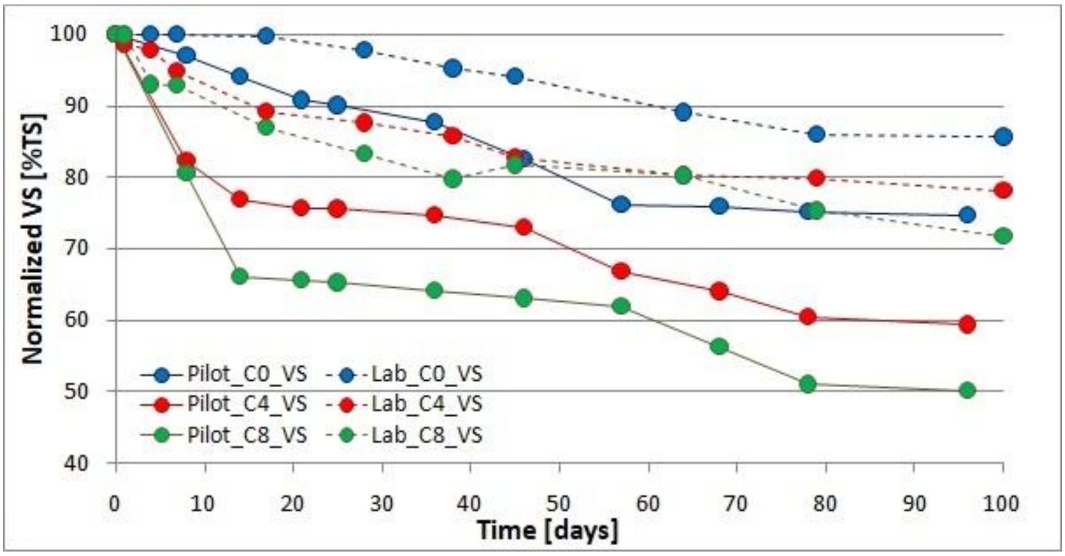

Fig. 4.25. Comparison of the normalized volatile solids in the C0, C4 and C8 mixtures of the pilot- and laboratory-scale experiments.

In order to provide a better understanding on the $VS_{d.b.}$ reduction, a multifactorial analysis of variance for $VS_{d.b.}$ was conducted referring to the factors:

- FAS and ash amounts
- Moisture and ash amounts.

In this statistical analysis, the evolution of $VS_{d.b.}$, FAS and moisture across time and taking into account the ash amount in the pilot- and laboratory-scale and C8* trials was compared.

In Table 4.14, the ANOVA table is reported where the influence of FAS and the ash content on the $VS_{d.b.}$ evolution is analyzed (Type III sums of squares). These factors had a statistically significant effect on $VS_{d.b.}$ at the 90.0% confidence level.

Tab. 4.14. Analysis of Variance for $VS_{d.b.}$ with covariate FAS and factor ash amount (Type III Sums of Squares).

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
COVARIATES					
FAS	1561.0	1	1561.0	39.2	0.000
MAIN EFFECTS					
A:ash	17596.3	8	2199.5	55.2	0.000
RESIDUAL	3787.1	95	39.9		
TOTAL (CORRECTED)	26667.2	104			

In Figure 4.26, the result of such multirange analysis (VS mean values with covariate FAS in dependence of the ash content) is reported. The tests grouped in squares showed no statistically significant differences. Pilot- and laboratory-scale tests clearly exhibited differences, while the C8* and C16 mixtures showed interactions between $VS_{d.b.}$ and FAS that are almost coinciding.

The Tukey HSD test showed that there were not statistically significant differences among the trials:

- C0 and C4; C4 and C8; C8, C16 and C8* of the laboratory-scale tests
- C0 and C2; C2 and C4; C4 and C8 of the pilot-scale tests.

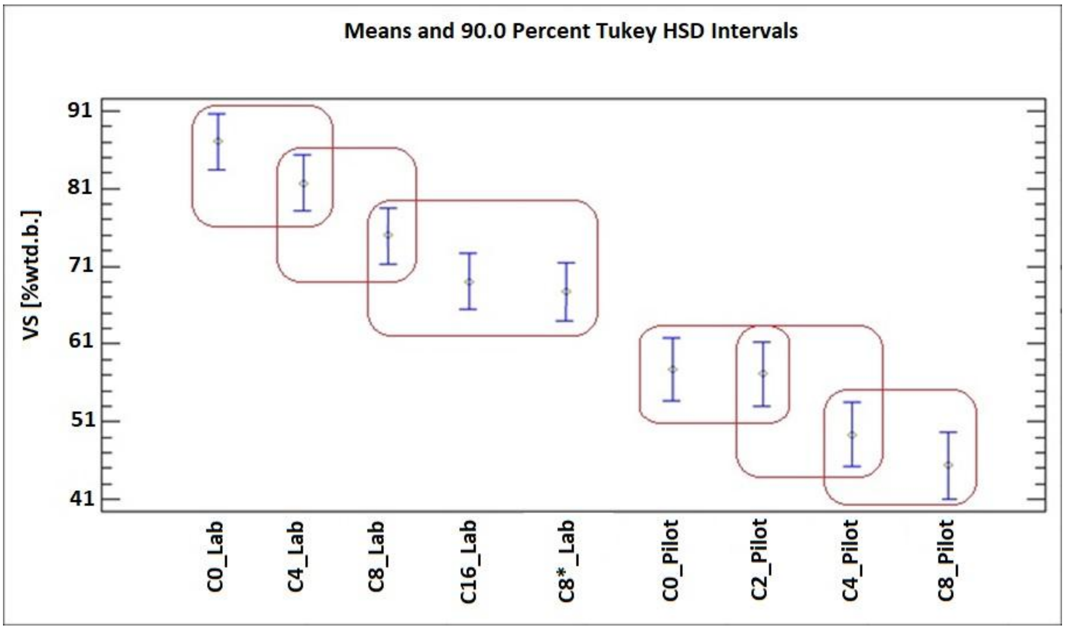

Fig. 4.26. Multirange analyses of the $VS_{d.b.}$ means values and covariate FAS with factor ash amount.

In Table 4.15, the ANOVA table evaluating the variability of $VS_{d.b.}$ in relation to the moisture content and the ash amount is reported (Type III sums of squares). These factors had a statistically significant effect on $VS_{d.b.}$ at the 90.0% confidence level.

Tab. 4.15. Analysis of Variance for $VS_{d.b.}$ with covariate moisture and factor ash amount (Type III Sums of Squares).

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-Ratio**	**P-Value**
COVARIATES					
Moisture	14.709	1	14.709	0.26	0.61
MAIN EFFECTS					
A:ash	20841	8	2605.1	46.4	0.00
RESIDUAL	5333.4	95	56.141		
TOTAL (CORRECTED)	26667	104			

The Tukey HSD test showed that there were not statistically significant differences among the following mixtures:

- C0 and C4; C4, C8 and C8*; C8, C16 and C8* of the laboratory-scale tests
- C0 and C2; C2 and C4; C4 and C8 of the pilot-scale tests.

In relation to the interaction between $VS_{d.b.}$ and moisture, the C8* mixture showed no statistically significant differences with C4, C8 and C16 (Fig. 4.27). The sets of experiments conducted at pilot- and laboratory-scale (including C8*) were statistically significantly different instead.

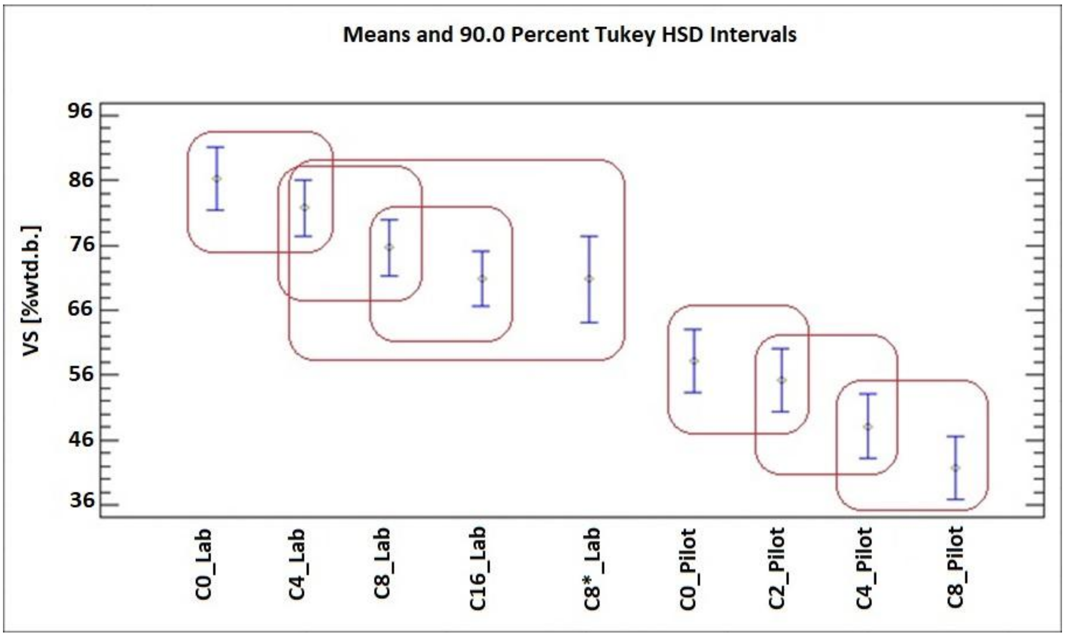

Fig. 4.27. Multirange analyses of the $VD_{d.b.}$ means values and covariate moisture with factor ash amount.

On the basis of these statistical results, it could be assumed that FAS, the experimental setup, and moisture and ash content had a statistically significant effect on the $VS_{d.b.}$ evolution, hence the observed organic matter degradation could be partially related to them.

4.4.6 Respiration activity

Pilot-scale experiment

The four days oxygen consumption (RA4, expressed as $mgO_2 \cdot gVS^{-1}$ or $mgO_2 \cdot gDM^{-1}$) was similar in all the initial substrates, while on day 46 and in the final composts the 4th day respiration activity varied significantly depending on the ash content (Tab. 4.16). If the RA4 values (expressed as $mgO_2 \cdot gVS^{-1}$) at day 46 are related to the corresponding initial levels, a reduction of 16.4%, 33.8%, 38.9% and 46.2% could be observed for C0, C2, C4 and C8, respectively. In the final C0, C2, C4 and C8 composts, the reduction of the RA4 values comparing to the corresponding initial levels was 35.9%, 54.4%, 48.9% and 66.6%, respectively. Therefore, the highest decrease in the respiration activity was achieved in the mixture amended with 8%wt of ash blend.

Tab. 4.16. Oxygen consumption in the pilot-scale mixtures.

	Day 0	**Day 46**	**Day 96**
C0	49.2 $mgO_2 \cdot gVS^{-1}$ 26.7 $mgO_2 \cdot gDM^{-1}$	41.2 $mgO_2 \cdot gVS^{-1}$ 22.6 $mgO_2 \cdot gDM^{-1}$	31.6 $mgO_2 \cdot gVS^{-1}$ 15.8 $mgO_2 \cdot gDM^{-1}$
C2	51.9 $mgO_2 \cdot gVS^{-1}$ 26.8 $mgO_2 \cdot gDM^{-1}$	34.4 $mgO_2 \cdot gVS^{-1}$ 18.7 $mgO_2 \cdot gDM^{-1}$	23.7 $mgO_2 \cdot gVS^{-1}$ 10.7 $mgO_2 \cdot gDM^{-1}$
C4	43.8 $mgO_2 \cdot gVS^{-1}$ 28.2 $mgO_2 \cdot gDM^{-1}$	26.7 $mgO_2 \cdot gVS^{-1}$ 13.0 $mgO_2 \cdot gDM^{-1}$	22.4 $mgO_2 \cdot gVS^{-1}$ 11.1 $mgO_2 \cdot gDM^{-1}$
C8	45.8 $mgO_2 \cdot gVS^{-1}$ 28.4 $mgO_2 \cdot gDM^{-1}$	24.7 $mgO_2 \cdot gVS^{-1}$ 8.0 $mgO_2 \cdot gDM^{-1}$	15.3 $mgO_2 \cdot gVS^{-1}$ 2.7 $mgO_2 \cdot gDM^{-1}$

Laboratory-scale experiment

The initial mixtures showed a respiration activity that differed consistently in dependence on the ash amount added (Tab. 4.17). In this experimental run, it should be considered that the bulking agent used in this experiment (wood chips), though having high volatile solids content, is not easily biodegradable and, together with ash, constituted a portion of mixture that did not contribute to the respiration activity.

On day 45, the RA4 values showed variations among the mixtures, with the highest value observed in C0 and the lowest in C4. The reduction in the RA4 (expressed as $mgO_2 \cdot gVS^{-1}$) achieved after 45 days was the highest in C4 (64%) and approximately 49% in the remaining mixtures (49.1%, 49.6% and 48.8% in C0, C8 and C16, respectively).

In the final composts, the RA4 value was the lowest in C16. The reduction of oxygen consumption in the final composts comparing to the one in the initial substrates was the lowest in C0 (58.3%) and the highest in C4 (82.2%; reduction levels in C8 and C16 were similar and equal to 74.7% and 79.3%, respectively).

Tab. 4.17. Oxygen consumption in the laboratory-scale mixtures.

	Day 0	**Day 45**	**Day 100**
C0	45.4 $mgO_2 \cdot gVS^{-1}$	23.1 $mgO_2 \cdot gVS^{-1}$	18.9 $mgO_2 \cdot gVS^{-1}$
	30.9 $mgO_2 \cdot gDM^{-1}$	20.5 $mgO_2 \cdot gDM^{-1}$	5.2 $mgO_2 \cdot gDM^{-1}$
C4	38.7 $mgO_2 \cdot gVS^{-1}$	13.9 $mgO_2 \cdot gVS^{-1}$	6.9 $mgO_2 \cdot gVS^{-1}$
	32.4 $mgO_2 \cdot gDM^{-1}$	12.4 $mgO_2 \cdot gDM^{-1}$	5.5 $mgO_2 \cdot gDM^{-1}$
C8	29.9 $mgO_2 \cdot gVS^{-1}$	15.1 $mgO_2 \cdot gVS^{-1}$	7.6 $mgO_2 \cdot gVS^{-1}$
	21.8 $mgO_2 \cdot gDM^{-1}$	12.2 $mgO_2 \cdot gDM^{-1}$	5.8 $mgO_2 \cdot gDM^{-1}$
C16	29.6 $mgO_2 \cdot gVS^{-1}$	15.2 $mgO_2 \cdot gVS^{-1}$	6.1 $mgO_2 \cdot gVS^{-1}$
	22.5 $mgO_2 \cdot gDM^{-1}$	11.0 $mgO_2 \cdot gDM^{-1}$	4.3 $mgO_2 \cdot gDM^{-1}$

*C8**

In the C8* mixture, the RA4 value differed slightly from the ones observed in C8 (Tab. 4.18). After 45 days, the reduction of the respiration activity (expressed as $mgO_2 \cdot gVS^{-1}$) comparing to the initial substrate was 39.5%, and it was 69.7% on the final day.

Tab. 4.18. Oxygen consumption in the C8* mixture.

	Day 0	**Day 45**	**Day 100**
C8*	26.6 $mgO_2 \cdot gVS^{-1}$	16.1 $mgO_2 \cdot gVS^{-1}$	8.1 $mgO_2 \cdot gVS^{-1}$
	21.0 $mgO_2 \cdot gDM^{-1}$	11.4 $mgO_2 \cdot gDM^{-1}$	5.0 $mgO_2 \cdot gDM^{-1}$

Comments

The RA4 values decreased over time in both the pilot- and laboratory-scale tests and the results from the respiration tests were consistent with the ones reported by literature [27]. In both the experimental campaigns, the ash-amended final composts manifested bigger RA4 reduction comparing to the unamended ones. This fact suggests that an enhanced organic matter degradation occurred when ash was added, as Fernández-Delgado Juárez et al. [36] also advanced.

The RA4 values in the initial mixtures were lower in the laboratory-scale experiment than in the pilot-scale tests. This could be due to the fact that the bulking agent used in the laboratory-scale experiment was constituted by wood chips that are recalcitrant to microbial attack [49] and do not consume oxygen, while the green waste (grass and tree prunings) used in the 250L tests is more easily biodegradable.

In the laboratory-scale tests, very high reduction rates in the oxygen consumption were achieved, even after 45 days. In addition, if the limit of 10 mg O_2·g DM^{-1} suggested by the European Union Biological Treatment Working Document [81] is considered, only the final C8 compost fulfilled the requirement in the pilot-scale experiment, while all the final composts produced in the laboratory-scale test had a respiratory activity lower than this limit value. In Fig. 4.28 the normalized RA4 decrease in the C0, C4 and C8 mixtures of the pilot- and laboratory-scale experiments is shown. The comparison between the oxygen consumption trend in the C0, C4 and C8 mixtures showed that the mixtures of the laboratory-scale experiment exhibited the highest RA4 reduction. These results could be explained by the fact that the organic matter degradation of a smaller mass of waste occurred in shorter time than in a larger one, especially under a more efficient air distribution and tighter moisture control.

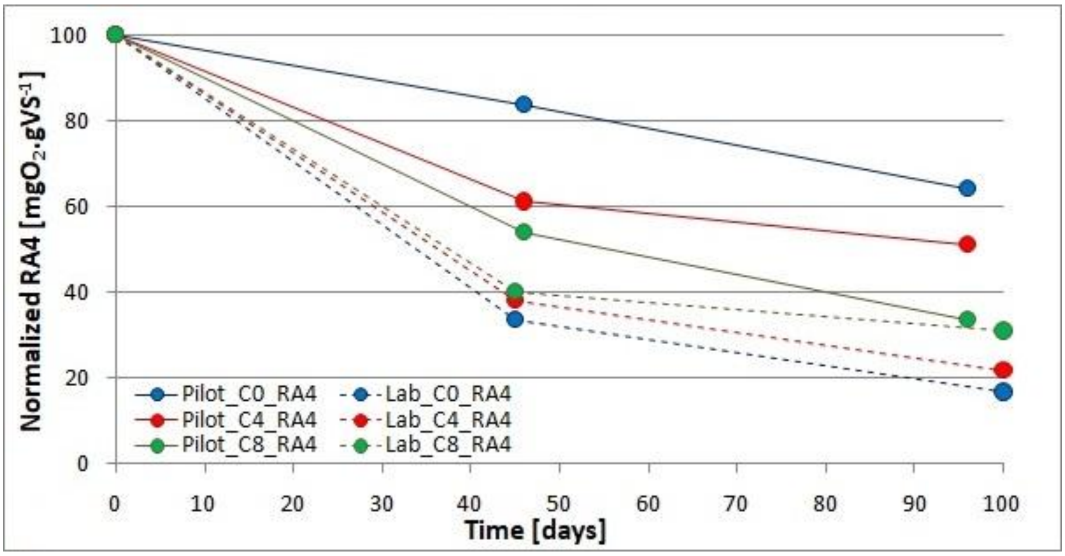

Fig. 4.28. Comparison of the normalized respiration activity evolution in the C0, C4 and C8 mixtures of the pilot- and laboratory-scale experiments.

In Figure 4.29 the normalized RA4 decrease for the C8*, C8 and C0 mixtures is depicted. The respiration activity on day 45 exhibited a smaller reduction in C8* than in the C0 and C8 mixtures, but the extent of the RA4 decrease was coinciding in the C8* and C8 final composts.

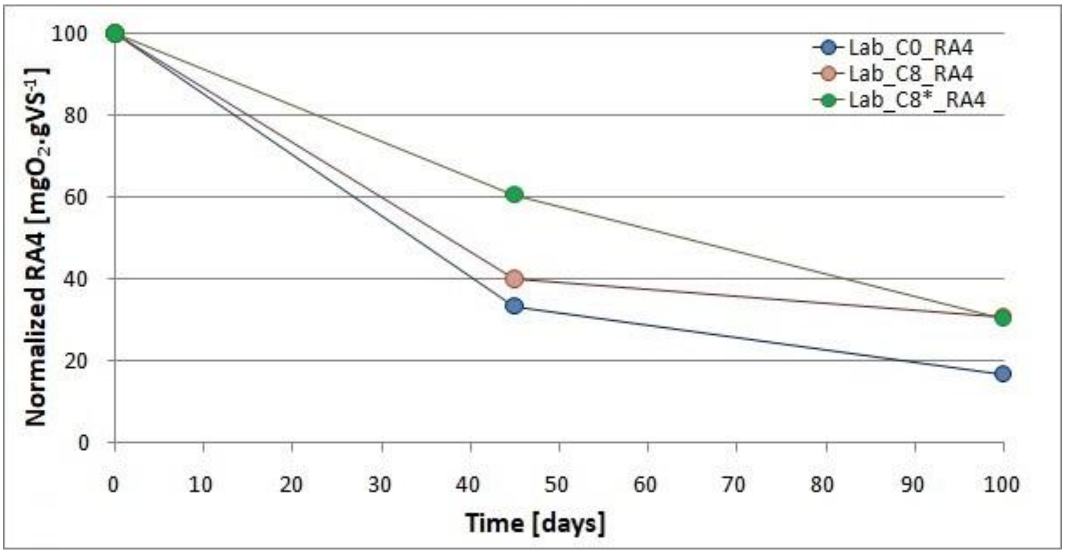

Fig. 4.29. Comparison of the normalized respiration activity evolution in C8*, C0 and C8 final composts of the laboratory-scale experiment.

In general, the VS$_{d.b.}$ and RA4 were related one each other. In Figures 4.30-4.32 the correlation between the VS$_{d.b.}$ and RA4 values are displayed.

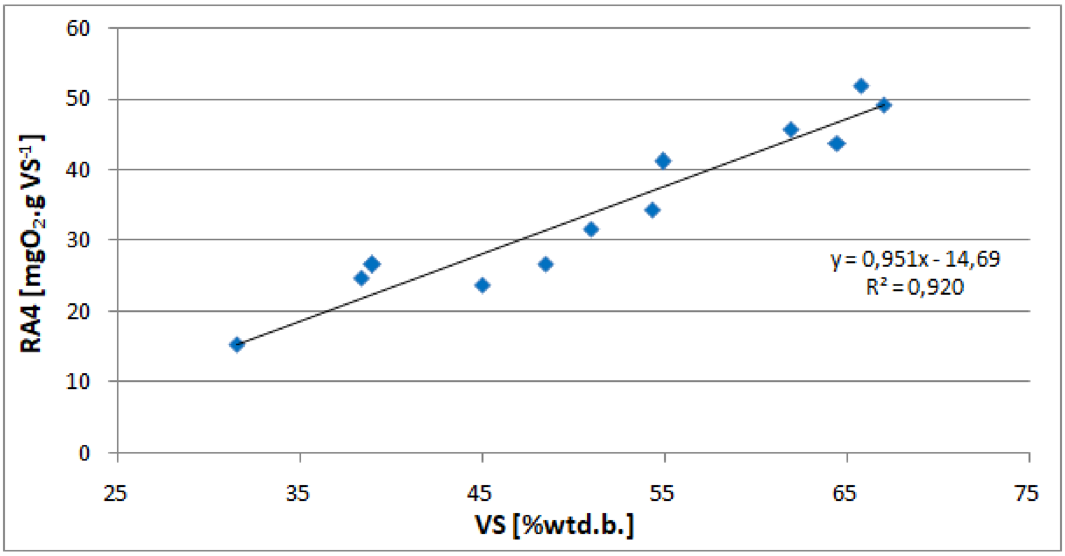

Fig. 4.30. Correlation between the volatile solids content and the respiration activity on days 0, 46, 96 in the pilot-scale experiment.

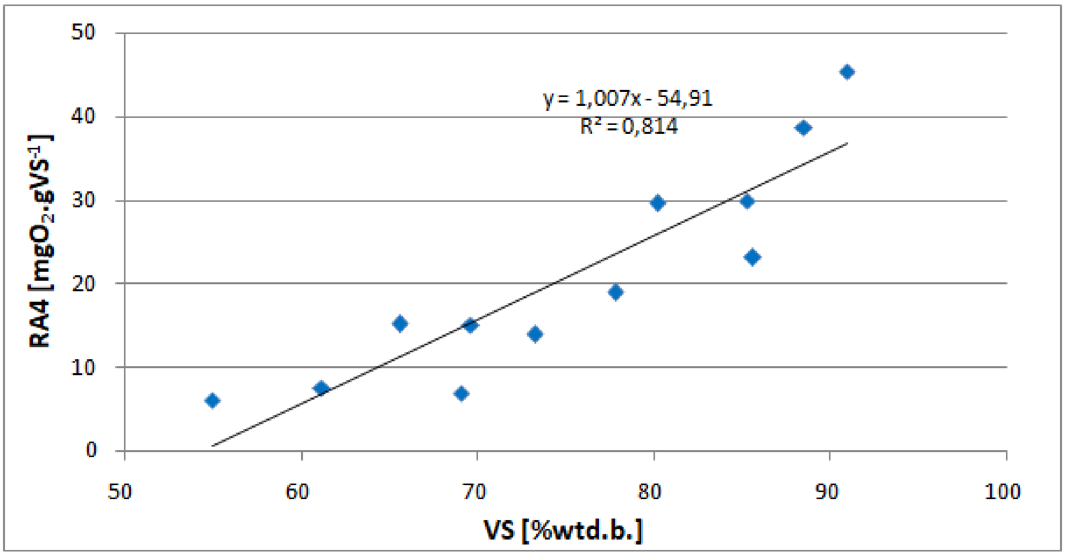

Fig. 4.31. Correlation between the volatile solids content and the respiration activity on days 0, 45, 100 in the laboratory-scale experiment.

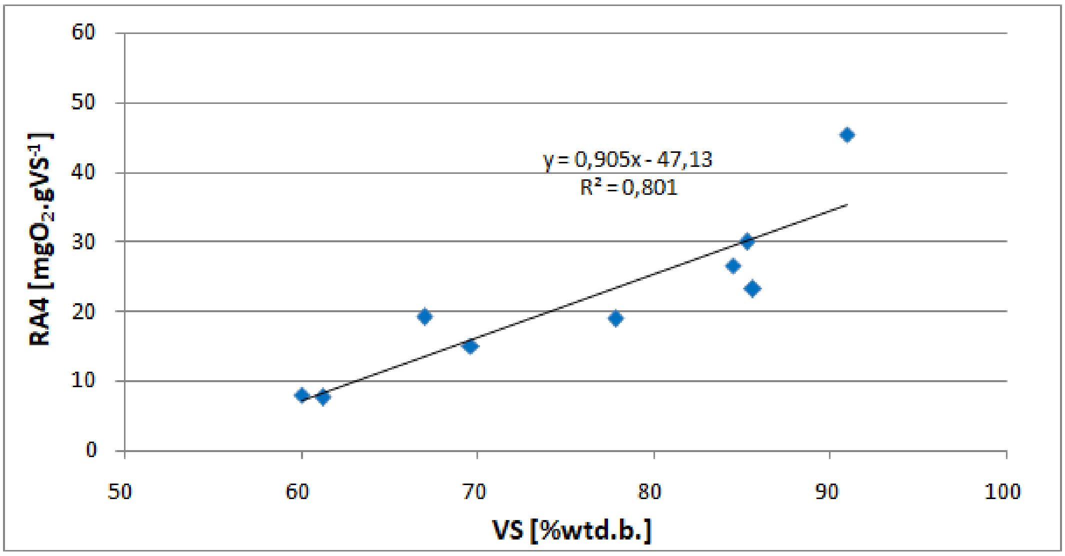

Fig. 4.32. Correlation between the volatile solids content and the respiration activity on days 0, 45, 100 in C8*, C0 and C8 final composts of the laboratory-scale experiment.

4.5 Final product quality

In this paragraph each property that describes the compost quality is discussed by analyzing the results attained in the pilot-scale, laboratory-scale and C8* tests. A comparison between the results attained in the two experimental sets is also given.

4.5.1 pH and electrical conductivity levels

Pilot-scale experiment

All the final composts produced in the 250 L reactors showed pH values higher than 8 and electrical conductivity levels higher than 4 $mS \cdot cm^{-1}$ (Tab. 4.19). These results could be due to the high pH and EC values in the starting substrate (5.09 and 4.22 $mS \cdot cm^{-1}$, respectively). In particular, the electrical conductivity of the starting OFMSW+BM mixture exceeded the reference value (3 $mS \cdot cm^{-1}$), possibly because of the presence of high salinity components of the real OFMSW, such as fireplace ash.

Tab. 4.19. Electrical conductivity (EC) in the final composts and initial OFMSW+BM mixture of the pilot-scale test (standard deviation is indicated in brackets).

	OFMSW+BM	**C0**	**C2**	**C4**	**C8**
pH [-]	5.09 (0.03)	8.23 (0.00)	8.76 (0.01)	8.77 (0.21)	9.16 (0.01)
EC [$mS \cdot cm^{-1}$]	4.22 (0.10)	4.08 (0.26)	5.48 (0.55)	6.06 (0.13)	6.23 (0.18)

The high electrical conductivity observed in the final composts produced at pilot-scale is connected to the high levels of water-soluble sodium and chlorides (Fig. 4.33). Both the water-soluble Na and Cl^- were lower in the ash-enriched composts than in the unamended one, except for the Cl^- value observed in the C2 final product. The latter could be related to the possible presence of an extraneous contaminant in the sample collected, while the general decreasing trend could be due to the high salinity of the initial substrate, in particular the real OFMSW, that affected the mixture EC more than biomass ash.

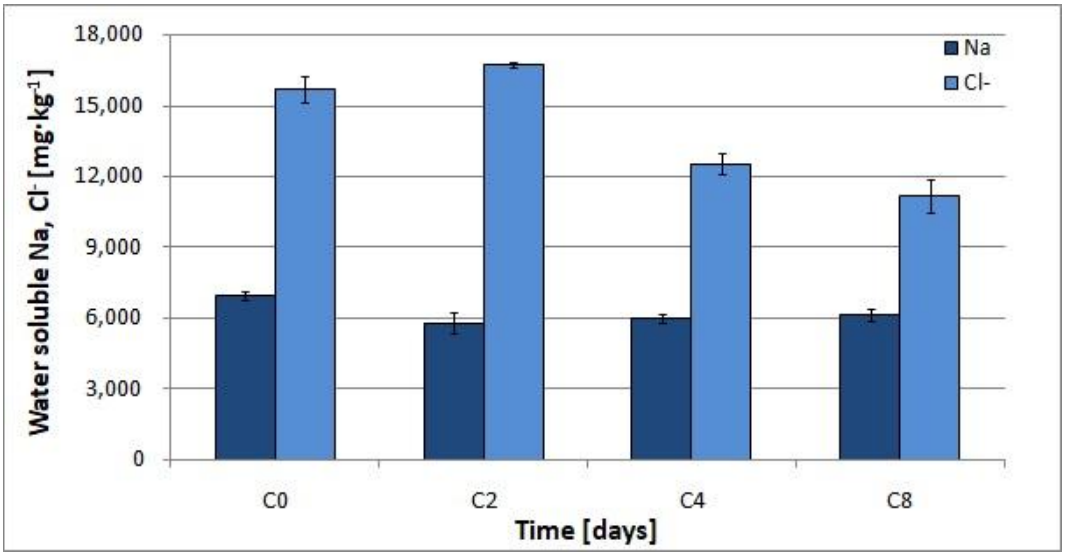

Fig. 4.33. Water soluble sodium and chlorides in the final composts produced in the pilot-scale experiment (error bars indicate standard deviation).

Laboratory-scale experiment

In the laboratory-scale reactors, pH levels higher than 8 were attained in the ash-amended composts. The EC values in the C8 and C16 final composts were higher than 3 mS·cm^{-1} (Tab. 4.20).

Tab. 4.20. Electrical conductivity (EC) in the final composts and the initial OFMSW+BM mixture of the laboratory-scale test (standard deviation is indicated in brackets).

	OFMSW+BM	**C0**	**C4**	**C8**	**C16**
pH [-]	4.69 (0.02)	6.93 (0.01)	8.08 (0.04)	8.90 (0.01)	8.99 (0.01)
EC [mS·cm^{-1}]	0.46 (0.03)	1.59 (0.11)	2.78 (0.25)	3.30 (0.13)	3.71 (0.04)

As expected, in the laboratory-scale experiment, where synthetic organic waste (totally free of contaminants) was used, the water-soluble Na and Cl$^-$ content was higher in the ash-amended final composts than in the unamended one (Fig. 4.34).

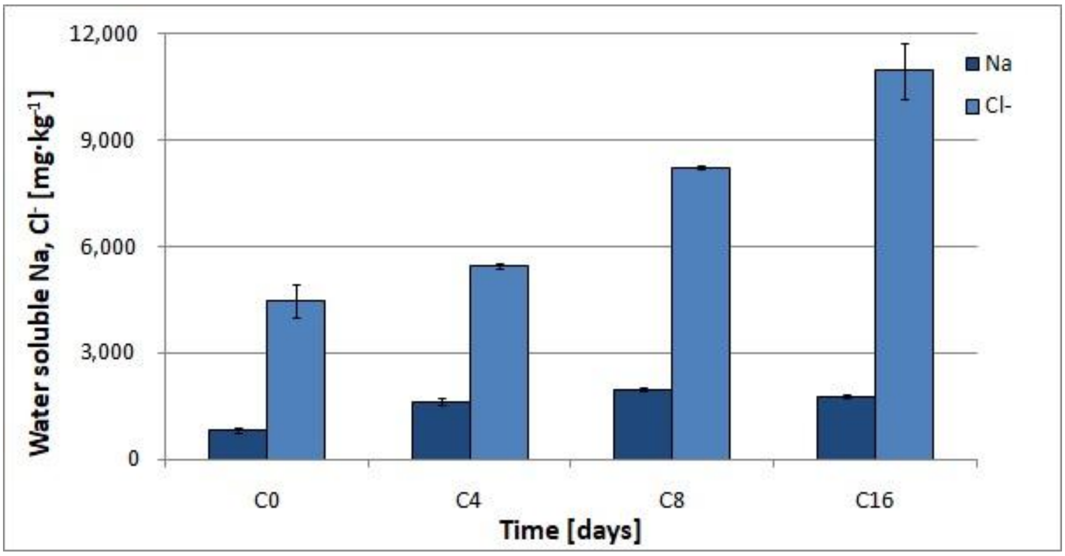

Fig. 4.34. Water soluble sodium and chlorides in the final composts produced in the laboratory-scale experiment (error bars indicate standard deviation).

*C8**

The C8* final compost pH and EC values are displayed in Table 4.21.

As shown in Fig. 4.35, the final C8* compost showed higher water-soluble Na and Cl^- content than C0. Comparing to the final C8 compost, C8* showed higher soluble sodium but lower soluble chlorides level. This figure could be explained by the contribution of wood chips, whose total sodium content was not detectable while the soluble chlorides level was 2000 $mg \cdot kg^{-1}$ (see Chapter 3).

Tab. 4.21. Electrical conductivity (EC) in the C8* final compost and initial OFMSW+BM mixture (standard deviation is indicated in brackets).

	OFMSW +BM	**C8***
pH [-]	4.70 (0.02)	8.70 (0.08)
EC [$mS \cdot cm^{-1}$]	0.41 (0.02)	3.57 (0.17)

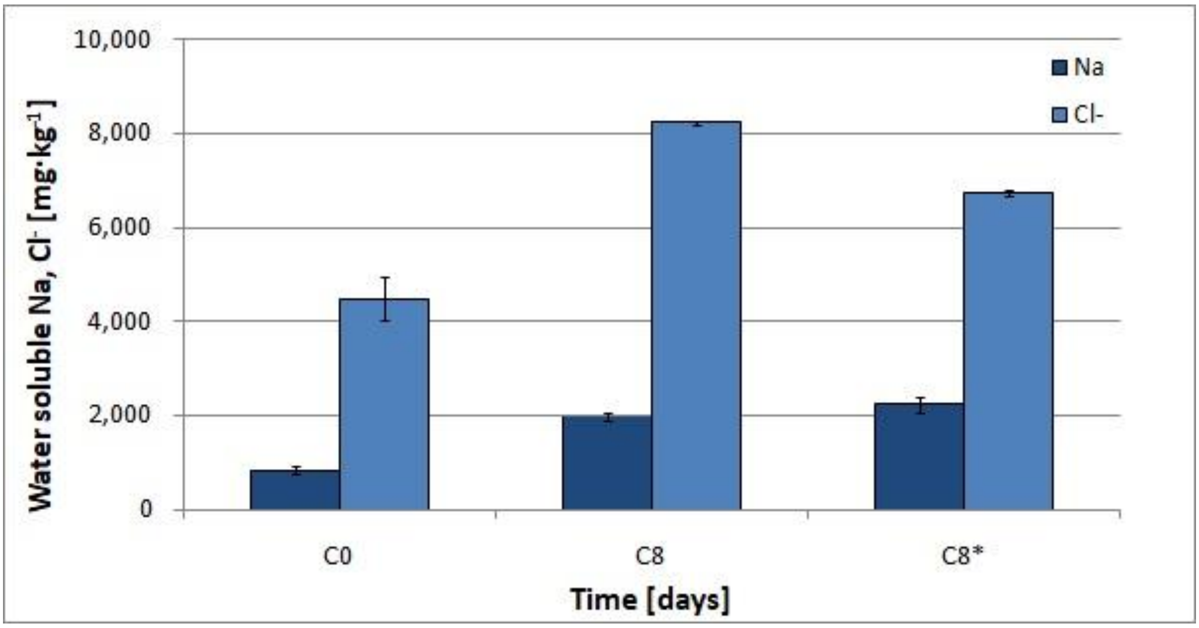

Fig. 4.35. Water soluble sodium and chlorides in the final composts produced in C8*, C0 and C8 final composts of the laboratory-scale experiment (error bars indicate standard deviation).

Comments

In all the experiments, both the final pH and EC values were higher in the ash-amended composts than in the related control ones, and as high as the ash amount added was. These values were also greatly affected by the initial pH and EC levels in the organic waste.

The mixtures enriched with 4%wt and 8%wt of ash produced in the pilot-scale experiment had pH values higher than the corresponding ones produced in the laboratory-scale run. This is coherent with the different pH values of the two initial substrates used in the 250L and 64L trials (i.e., 5.09 and 4.69, respectively). The pH values observed in the ash-amended composts could be either beneficial or adverse for plant growth depending on the properties of soil where the compost is supposed to be employed. Bougnom et al. [19], who conducted field experiments using an ash-amended compost characterized by pH value of 8.59 and produced in the experimental campaign described by Kuba et al. [55], observed an ameliorating effect when the compost was applied to an acidic soil. However, in the majority of cases, composts having high pH values are detrimental for plant growth (in Italy, the Legislative Decree on fertilizers sets a maximum pH value of 8.50 for the mature composts allowed for sale) and ash, which increases the final compost pH further, should be cautiously added.

The EC values in the final composts was higher when ash was added than in the control, and as high as the ash amount was. It is worth underlining that the electrical conductivity of the final composts varies in relation to the EC of the initial substrates. The electrical conductivity of the real OFMSW used in the pilot-scale tests (equal to 4.22 $mS\cdot cm^{-1}$) was unexpectedly high, eventually due to a possible contamination with a high salinity waste component, such as fireplace ash. Therefore, in all the composts produced in the pilot-scale tests, including the control, the EC values exceeded the levels of 3 $mS\cdot cm^{-1}$, that is recommended in order to avoid harm for the plants [36,53,55]. Conversely, in the laboratory-scale tests, where a OFMSW+BM mixture having electrical conductivity of 0.46 $mS\cdot cm^{-1}$ was used, only C8 and C16 EC levels exceeded the recommended value of 3 $mS\cdot cm^{-1}$. The C8* final compost showed final pH and EC values very similar to the C8 ones.

In relation to both the pH and EC values of the final composts, when synthetic (i.e., not contaminated) waste was used, the composts added with 8%wt (and 16%wt) of ash exceeded the limit values set by the Italian legislation (maximum pH value of 8.50) and the common practices in agriculture (maximum EC value of 3 $mS\cdot cm^{-1}$). Therefore, this ash amount (8%wt) could be suggested as the limit amount for obtaining a final compost admitted for commercialization according to the existing rules and accepted for common uses. However, the identification of the maximum ash amount should be completed by the knowledge of the real OFMSW properties, since the latter could impair the final compost quality even without any ash addition.

4.5.2 C_{tot}, TOC, N_{tot}, C_{tot}/N_{tot}

Pilot-scale experiment

Both the total carbon (C_{tot}) and the total organic carbon (TOC) content decreased with the time, and the values in the final composts were as low as the ash amount added was higher (Fig. 4.36). The TOC values in the final composts produced in the pilot-scale experiment ranged between 15.0 $\%wt_{d.b.}$ and 29.2 $\%wt_{d.b.}$. If a comparison between the initial TOC values and the ones manifested in the final composts is made, a reduction of 15.2%, 34.1%, 30.9% and 53.3% could be observed in the C0, C2, C4 and C8 mixtures, respectively. The total C content reduction was consequently more intense as the ash amount added was higher (the C_{tot} reduction was 28.4%, 33.7%, 32.7%, 36.4% in the C0, C2, C4 and C8 mixtures, respectively).

Nitrogen, that is the most important nutrient for plant growth, was approximately 2 $\%wt_{d.b.}$ in the initial mixtures, and ranged from 1.64 $\%wt_{d.b.}$ to 2.17 $\%wt_{d.b.}$ in the final composts. However, a great uncertainty (represented by the standard deviation and possibly due to the sample heterogeneity) was determined for the nitrogen content in the C0 and C8 final composts. The lowest N_{tot} level was found in the C8 final compost (where it could be supposed that the highest temperature and pH levels favored ammonia stripping) and the highest in C2.

The initial C_{tot}/N_{tot} ratio was approximately 17.6 in all the trials and close to 12 in the final composts. The lowest C/N value was observed in the C2 final compost and it was due to the higher N_{tot} final level.

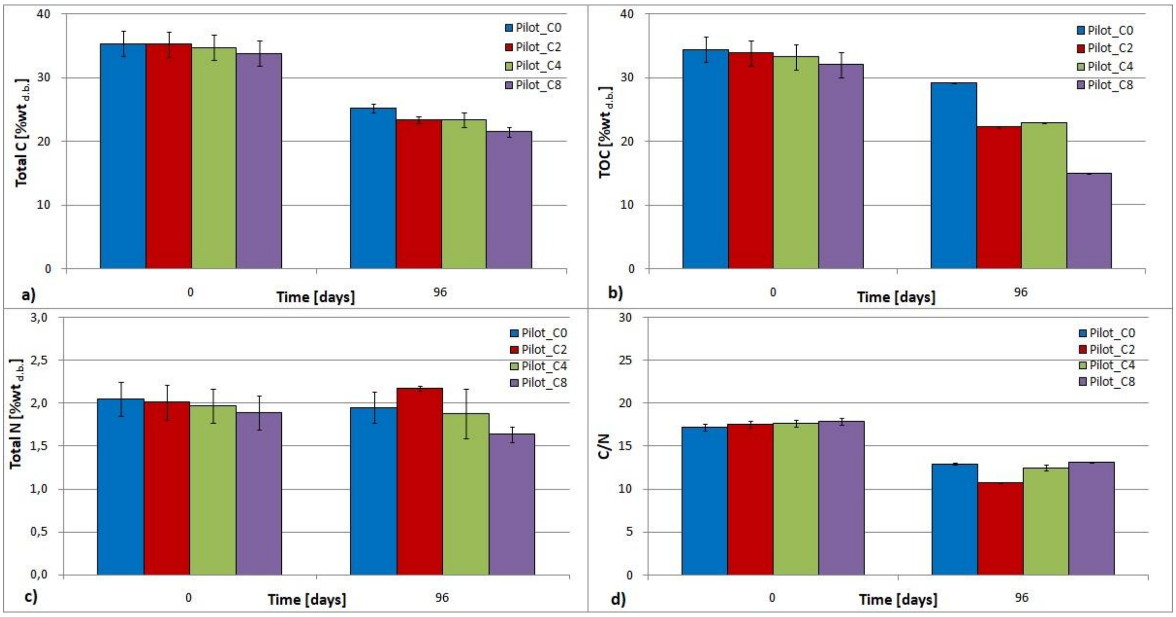

Fig. 4.36. Comparison of the: (a) total carbon content; (b) total organic carbon content; (c) total nitrogen content, and (d) C_{tot}/N_{tot} ratio in the initial mixtures and final composts of the pilot-scale experiment (error bars indicate standard deviation).

Laboratory-scale experiment

The initial mixtures exhibited similar total C levels (from 49.8 $\%wt_{d.b.}$ in C0 to 43.9 $\%wt_{d.b.}$ in C16). A reduction in the total C content was observed in the final composts comparing to the initial substrates, and the decrease was as high as the ash amount was.

The C_{tot} reduction was 17.1%, 21.9%, 28.3%, 39.0% in C0, C4, C8 and C16, respectively.

The initial total organic carbon (TOC) content varied from 49.8 $\%wt_{d.b.}$ to 38.7 $\%wt_{d.b.}$, while it ranged between 39.0 $\%wt_{d.b.}$ and 12.7 $\%wt_{d.b.}$ in the final composts (Fig. 4.37). The TOC content reduction attained in the C0, C4, C8 and C16 mixtures was 21.5%, 33.9%, 52.0% and 61.5%, respectively, therefore it was as high as the ash amount added was.

The total nitrogen content in the initial mixtures was 2.54-2.21 $\%wt_{d.b.}$ (and the lowest in C16), and it decreased over time in all the trials. The N_{tot} reduction was 9.1%, 9.4%, 11.0% and 27.7% in C0, C4, C8 and C16, respectively.

The ratio between the total carbon and nitrogen content was approximately 19.6 in all the initial mixtures of the laboratory-scale tests. In the final composts, it was approximately 15 in the ash-amended products, and the highest in the unamended compost.

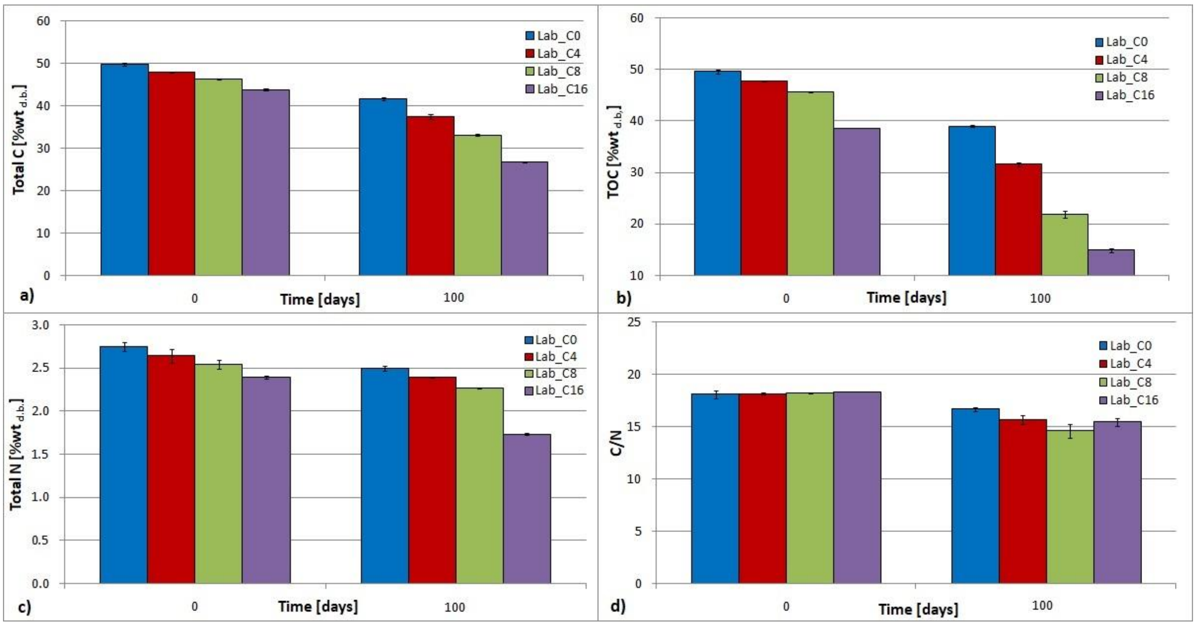

Fig. 4.37. Comparison of: (a) total carbon content; (b) total organic carbon content; (c) total nitrogen content, and (d) C_{tot}/N_{tot} ratio in the initial mixtures and final composts of the laboratory-scale experiment (error bars indicate standard deviation).

*C8**

The C8* initial mixture manifested lower levels of total and total organic carbon content than the corresponding C8 ones (Fig. 4.38). The C_{tot} reduction in the final C8* compost comparing to the initial substrate was significantly lower than in C8 (19.0% in C8* comparing to 28.5% in C8), while the TOC reduction over time exhibited a less marked divergence (47.9% and 52.0% in C8* and C8 final composts, respectively).

The N_{tot} reduction was dissimilar in the C8 and C8* mixtures (11.0% and 5.1%, respectively), and the C/N variation with the time differed in C8 and C8* as well (19.7% and 14.6%, respectively).

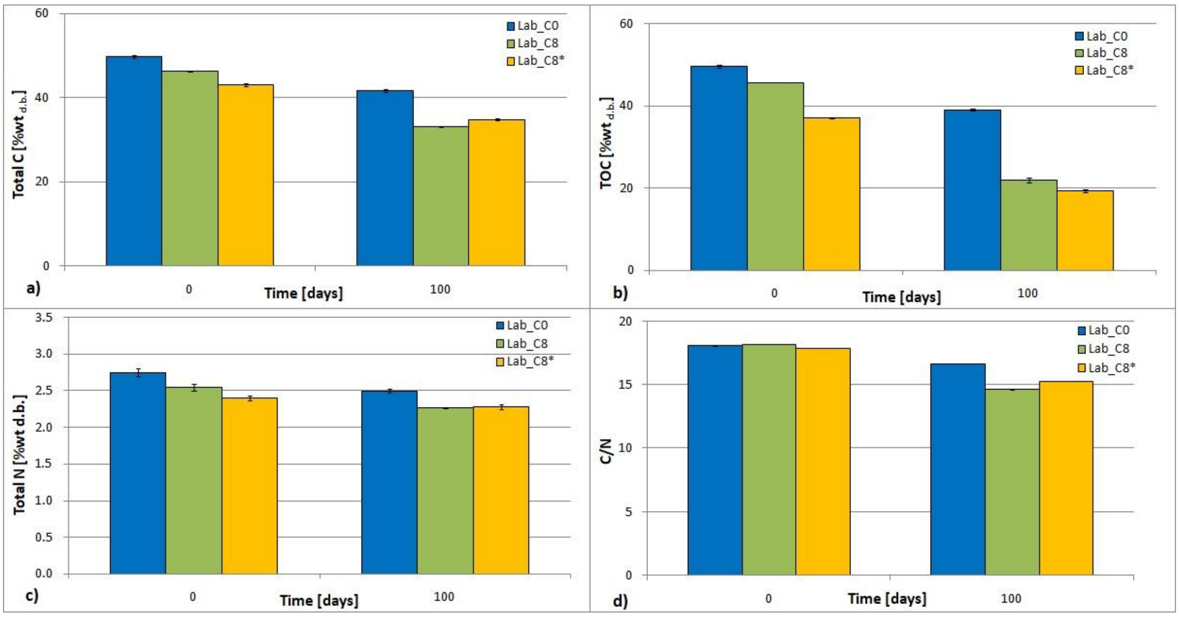

Fig. 4.38. Comparison of: (a) total carbon content; (b) total organic carbon content; (c) total nitrogen content, and (d) C_{tot}/N_{tot} ratio in C8*, C0 and C8 final composts of the laboratory-scale experiment (error bars indicate standard deviation).

Comments

The total and organic carbon content in the initial mixtures used in the pilot-scale experiment was lower than in the substrates used in the laboratory-scale because of the inert materials (impurities) present in the real OFMSW, that were avoided when synthetic organic waste was used in the 64 L tests.

Both the C_{tot} and TOC content decreased over time according to the increase of the ash amount added. The highest TOC reduction in the ash-amended composts could be explained by the improved organic matter degradation achieved when ash was used, and it affected the total carbon evolution as well [36,53,56]. In Figure 4.39 the comparison between the C_{tot} and TOC normalized values on the first and last days of the experiments in the C0, C4 and C8 mixtures of both the pilot- and laboratory-scale experiments is depicted. The total organic carbon content decreased as much as the ash amount added was higher, and at similar extent in each of the C0, C4 and C8 couples of mixtures of the two experimental campaigns conducted (Fig. 4.39a). Hence, the results obtained in the laboratory-scale test confirmed what observed in the pilot-scale experiment.

The Italian Legislative Decree n. 75/2010 establishes that the organic C in the soil amendments must be at least 20% of the dry matter. In the composts obtained in the described experiments this requirement was fulfilled by all the final products, except for the C8 compost produced in the pilot-scale trial, and the C16 and the C8* final composts. It could be concluded that the addition of 8%wt and 16%wt of ash blend affected the compost quality negatively in terms of total organic carbon, because of the low total organic C. The total C content decreased over time as well, and the reduction was more intense when ash was added (Fig. 4.39b). Since C_{tot} is given by the contribution of the total organic and inorganic carbon, its decrease is obviously influenced by the TOC reduction. However, it could be observed that this figure decreased at a lesser extent in the laboratory-scale tests than in the pilot-scale ones. It is plausible that the divergence among the C_{tot} evolution in the C0, C4 and C8 mixtures of the two experimental sets, was due to the extent of the carbonation reactions that must have involved ash during composting. It could be supposed that part of the CO_2 released by the aerobic degradation was fixed as a carbonate, and that these reactions were more intense in the laboratory-scale tests than in the pilot-scale ones, because of the more accurate distribution of ash in the mixtures.

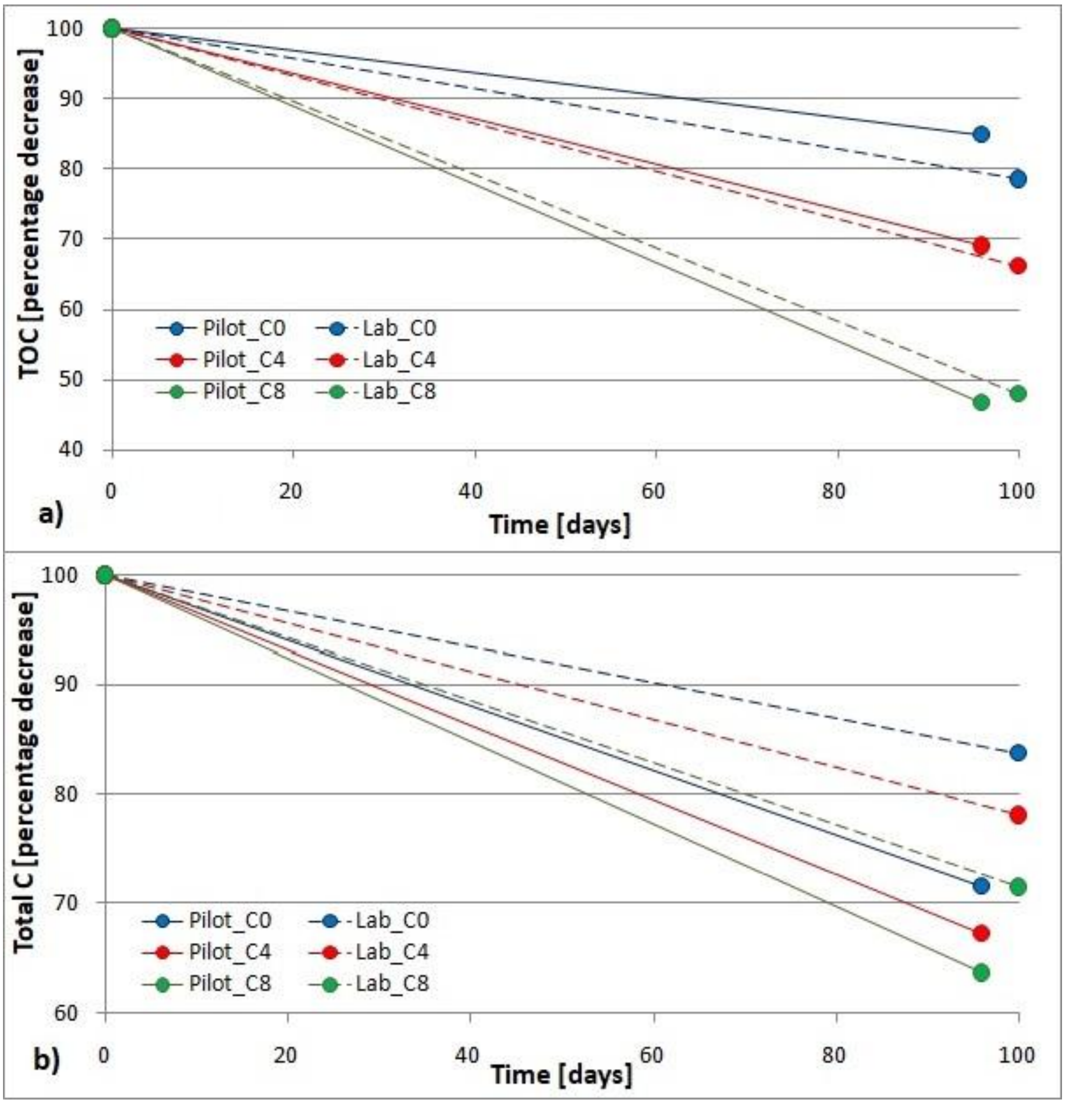

Fig. 4.39. Comparison of the normalized (a) total organic carbon and (b) total carbon content in the C0, C4 and C8 mixtures of the pilot- and laboratory-scale experiments.

In the pilot-scale experiment, a clear trend in the total nitrogen content in relation to time and the ash amount added could not be envisaged, while in the laboratory-scale tests a decrease with time and the ash addition was observed. It could be due to the heterogeneity of the real OFMSW that was used at pilot-scale level, that might have altered these results. In Figure 4.40a the normalized trend of the total nitrogen content in the C0, C4 and C8 mixtures at pilot- and laboratory-scale is compared. It could be observed that in both the experimental campaigns the same extent of the N_{tot} decrease was determined in the C0 and C4 mixtures. In both the pilot- and laboratory-scale tests, the total nitrogen content decreased in the C8 mixtures the most. While in the C0 and C4 pilot-scale mixtures the N_{tot} decrease was lower than the one observed in the corresponding laboratory-scale mixes, it was the contrary for the C8 products, so that the pilot-scale C8 compost exhibited the highest reduction in the N_{tot} content.

The nitrogen content in the final compost is affected by some factors, such as the dilution effect caused by the fact that the OFMSW is mixed with an additive (ash) poor or lacking of nitrogen content, while on the counterpart the concentration effect due to the organic matter degradation that was more intense when ash was added. In addition, the ammonia volatilization could have been favored when ash was added because of the higher temperature and pH values attained, as explained in 4.2.5, leading to a further decrease in the total N content.

The evolution of the C_{tot}/N_{tot} ratio is obviously conditioned by the decrease of both the total carbon and nitrogen content. The C_{tot}/N_{tot} ratio decreased in both the experimental campaigns with time and as much as the ash amount added was higher (Fig. 4.40b). Values lower than 20 are considered an indicator of sufficient nitrogen supply for plant growth [33], while the Legislative Decree no. 75/2010 sets maximum limit values of 50 and 25 for the soil amendments produced from green waste ("*ammendante compostato verde*") and mixed waste ("*ammendante compostato misto*"), respectively. These requirements were fulfilled by all the composts produced, irrespective of the amount of ash added. Indeed the C_{tot}/N_{tot} levels attained were approximately 15 in the laboratory-scale composts (slightly lower to the ones obtained by Kuba et al. [55]) and close to 12 in the pilot-scale final products. The reduction was more intense in the pilot-scale trials, showing the same evolution of the C_{tot} one. The C_{tot}/N_{tot} ratio is one of the parameters adopted to described compost maturity. In particular, Bernal et al. [15] proposed that C_{tot}/N_{tot} values lower than 12 were indicative of mature composts; in the present study, only the C2 final compost obtained in the 250 L test met this requirement. On the counterpart, it should be recalled that Iglesias-Jiménez and Pérez-García [48] suggested the C_{tot}/N_{tot} ratio was not descriptive of the compost maturity, which should be assessed by other more reliable parameters, such as the germination index, respiration rate, water-soluble TOC, organic carbon in the fulvic acid fraction and water-soluble nitrogen (total and organic) [16,29].

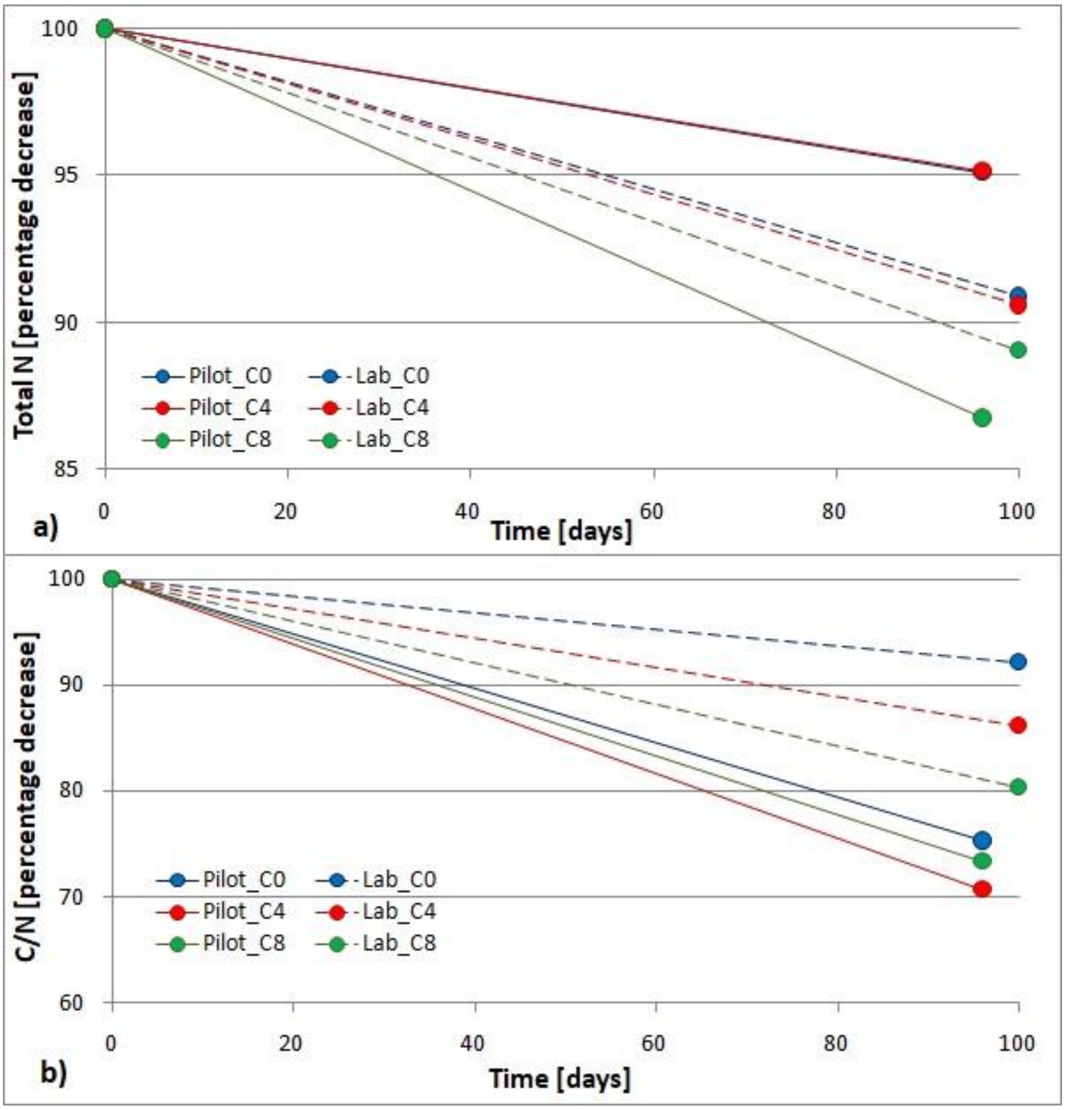

Fig. 4.40. Comparison of the normalized (a) total N and (b) C_{tot}/N_{tot} ratio content in the C0, C4 and C8 mixtures of the pilot- and laboratory-scale experiments.

4.5.3 Total, soluble and available nutrients content

Pilot-scale experiment

In the pilot-scale experiment, higher levels of Ca, Mg, K and P were attained in the ash-amended final composts than in the unamended one, except for the Ca and P total content in the C2 final compost (Fig. 4.41).

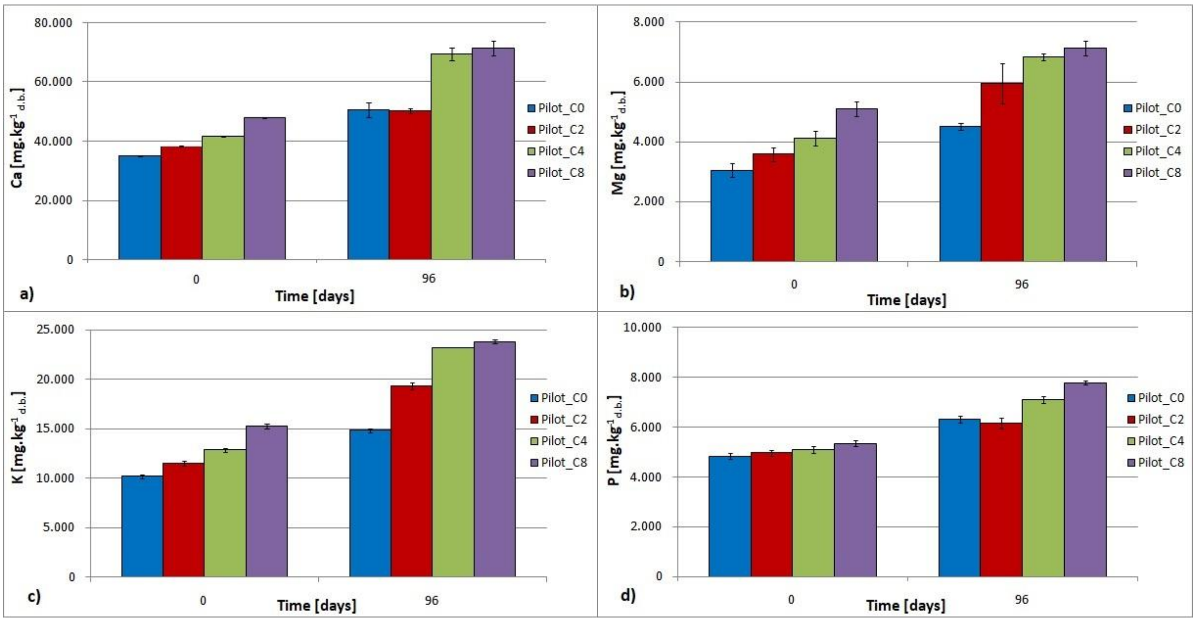

Fig. 4.41. Evolution of the total nutrients content in the pilot-scale experiment: (a) Ca; (b) Mg; (c) K; (d) P (error bars indicate standard deviation).

The Ca and Mg water-soluble and available content is displayed in Fig. 4.42, while the amounts of water-soluble and available K and P are depicted in Fig. 4.43.. The available Ca and Mg content was higher in the ash-amended composts than in the control one, while the Ca and Mg water-soluble content showed a slight decrease with the ash addition. The content of both the water-soluble and available potassium increased in the final composts as the ash amount added increased (Fig. 4.43a), while lower levels of the $NaHCO_3$-extractable phosphorus were observed in the composts containing ash comparing to the unamended one (Fig. 4.43b).

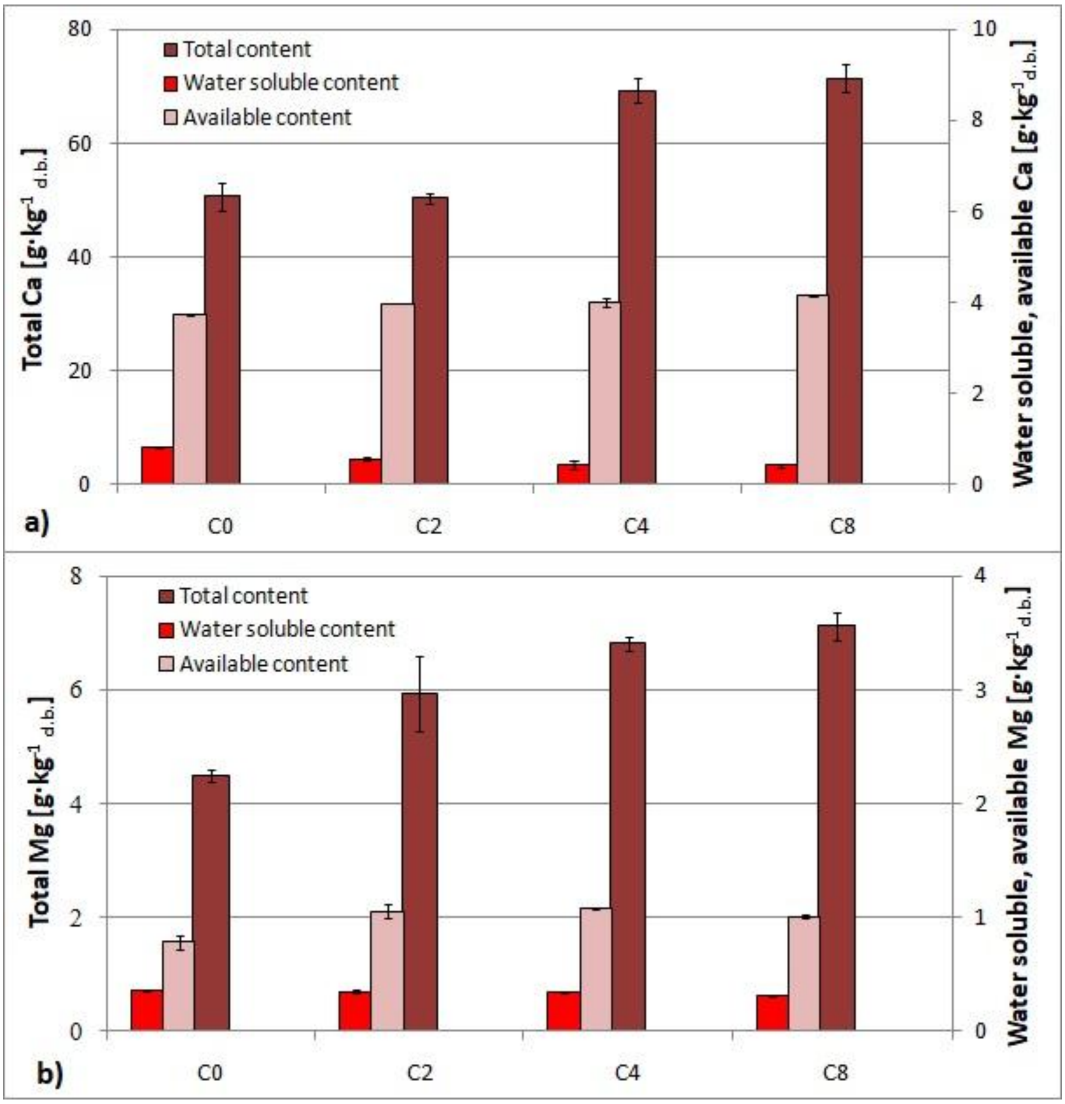

Fig. 4.42. Total, water-soluble and available content of (a) calcium and (b) magnesium in the final composts produced in the pilot-scale experiment (error bars indicate standard deviation).

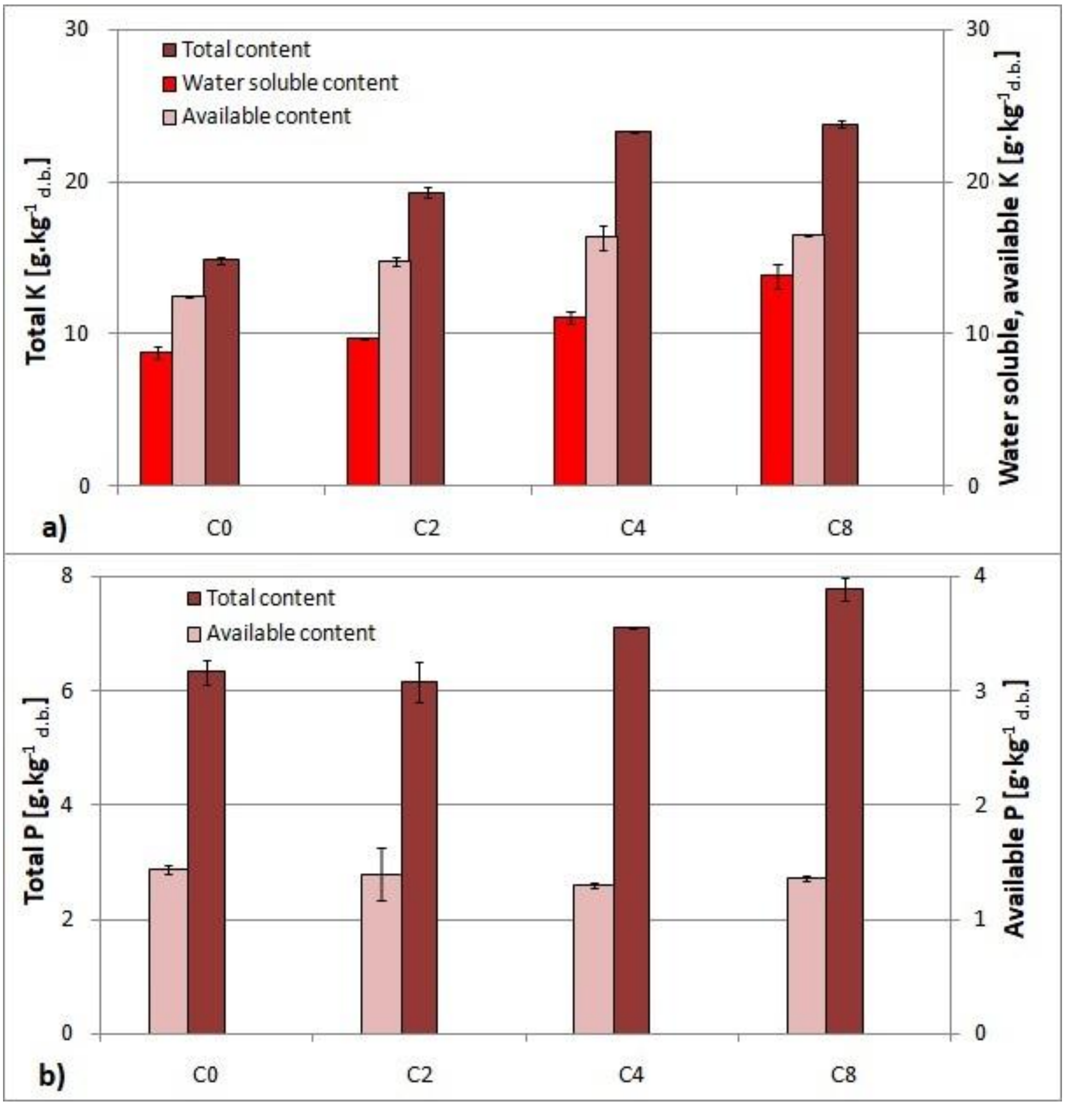

Fig. 4.43. Total, water-soluble and available content of (a) potassium and (b) phosphorus in the final composts produced in the pilot-scale experiment (error bars indicate standard deviation).

If the nutrient water-soluble and available fractions (i.e., % of the total content) are considered, lower values were observed in the ash-amended composts comparing to the control one (Tab. 4.22). The Ca and Mg water-soluble fractions were lower in the ash-enriched composts than in the unamended ones possibly due to the carbonation reactions that might have occurred in the aerated mixtures added with these alkaline residues [40,53]. Similarly, the lowest calcium and magnesium available fractions were observed in the most ash-enriched composts.

The K available fraction decreased with the increase in the ash amount added, while a clear trend in the K water-soluble fraction could not be envisaged. The P available fractions were lower in the ash-amended composts comparing to the control one.

Tab. 4.22. Nutrient total content, and soluble and available fractions in the final composts produced in the pilot-scale experiment (standard deviation is indicated in brackets).

	C0	**C2**	**C4**	**C8**
Ca [%wt$_{d.b.}$]	5.06 (0.25)	5.03 (0.08)	6.93 (0.21)	7.14 (0.08)
Soluble Ca [% total Ca]	1.6%	1.1%	0.6%	0.6%
Available Ca [% total Ca]	7.4%	7.9%	5.8%	5.8%
Mg [%wt$_{d.b.}$]	0.45 (0.01)	0.59 (0.07)	0.68 (0.01)	0.71 (0.02)
Soluble Mg [% total Mg]	8.0%	5.9%	5.0%	4.5%
Available Mg [% total Mg]	17.5%	17.8%	15.8%	14.2%
K [%wt$_{d.b.}$]	1.48 (0.02)	1.93 (0.03)	2.32 (0.00)	2.38 (0.05)
Soluble K [% total K]	59.4%	50.4%	47.8%	58.0%
Available K [% total K]	84.2%	77.1%	70.3%	68.4%
P [%wt$_{d.b.}$]	0.63 (0.02)	0.62 (0.03)	0.71 (0.00)	0.78 (0.01)
Available P [% total P]	22.6%	22.7%	18.3%	17.5%

Laboratory-scale experiment

The Ca, Mg, K and P total content in the ash-enriched composts was higher than in the C0 final product (Fig. 4.44).

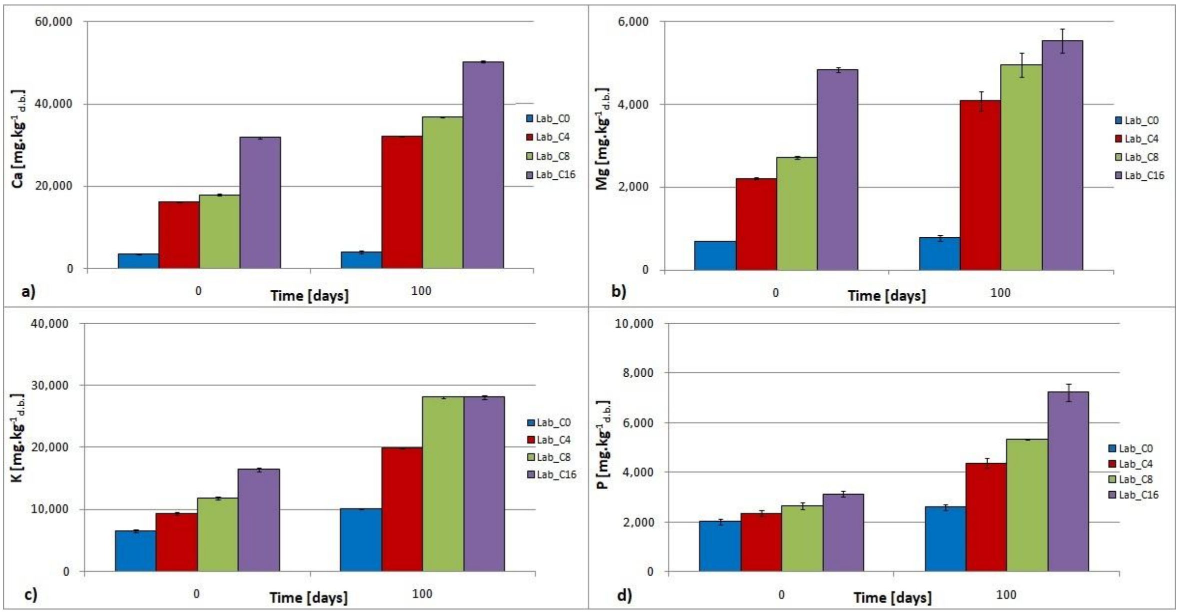

Fig. 4.44. Evolution of the total nutrients content in the laboratory-scale experiment: (a) Ca; (b) Mg; (c) K; (d) P (error bars indicate standard deviation).

The Ca and Mg water-soluble and available content is displayed in Fig. 4.45, while the correspondingamounts of potassium and phosphorus are depicted in Fig. 4.46. Higher available Ca and Mg content was observed in the ash-enriched composts than in the control, though there was not an increase proportional with the ash amount added. The corresponding water-soluble content slightly increased with the ash addition. The potassium water and available contents were higher in the composts containing ash than in the control one (Fig. 4.46a). On the contrary, the available P content was lower in the ash-enriched final products than in the unamended one (Fig. 4.46b).

In the C4, C8 and C16 final composts the Ca and Mg water-soluble and available fractions were lower than in C0 (Tab. 4.23). Also the K water, and K and P available fractions were lower in the ash-amended composts than in the unamended one (Fig. 4.46).

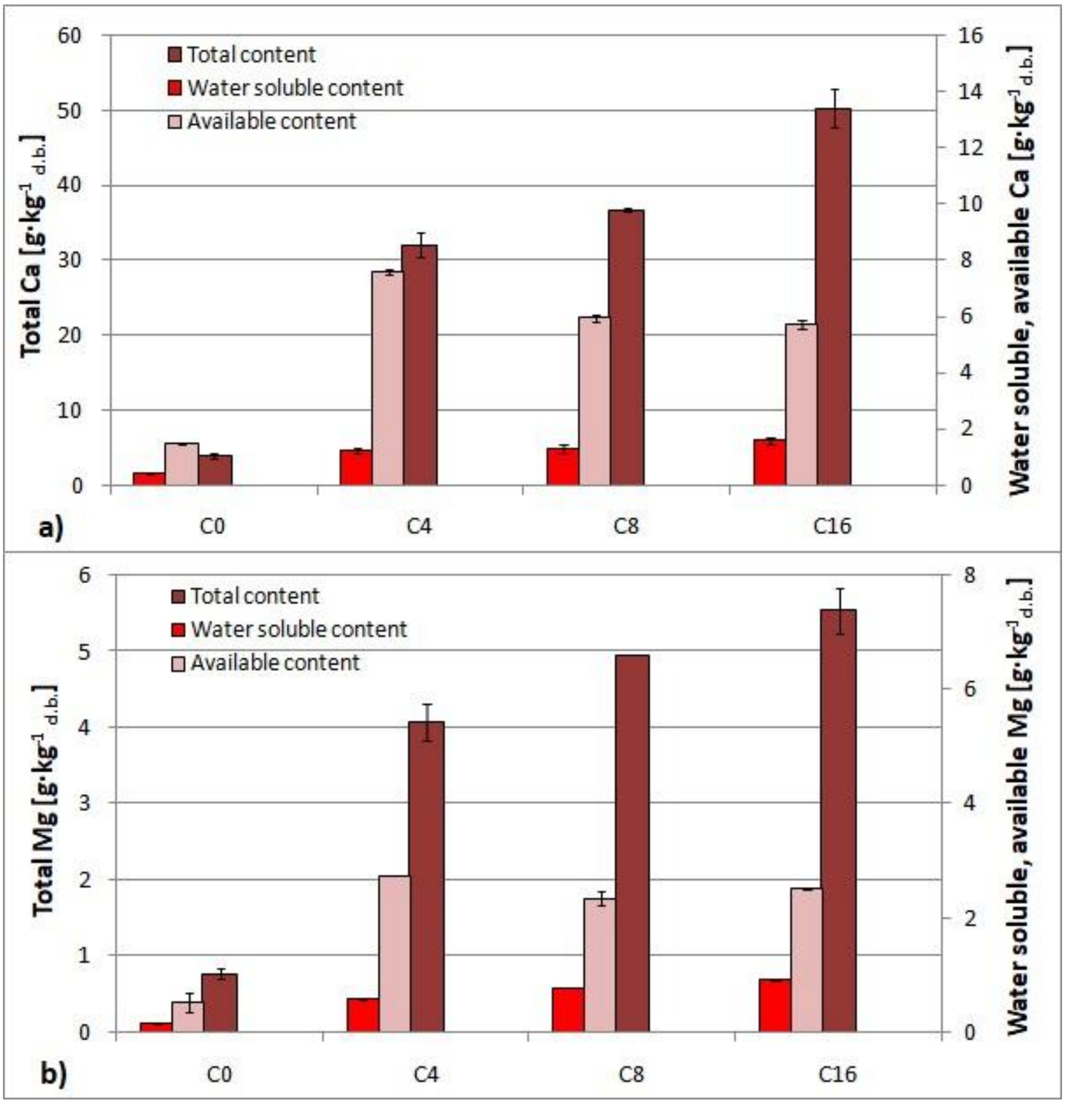

Fig. 4.45. Total, water-soluble and available content of (a) calcium and (b) magnesium in the final composts produced in the laboratory-scale experiment (error bars indicate standard deviation).

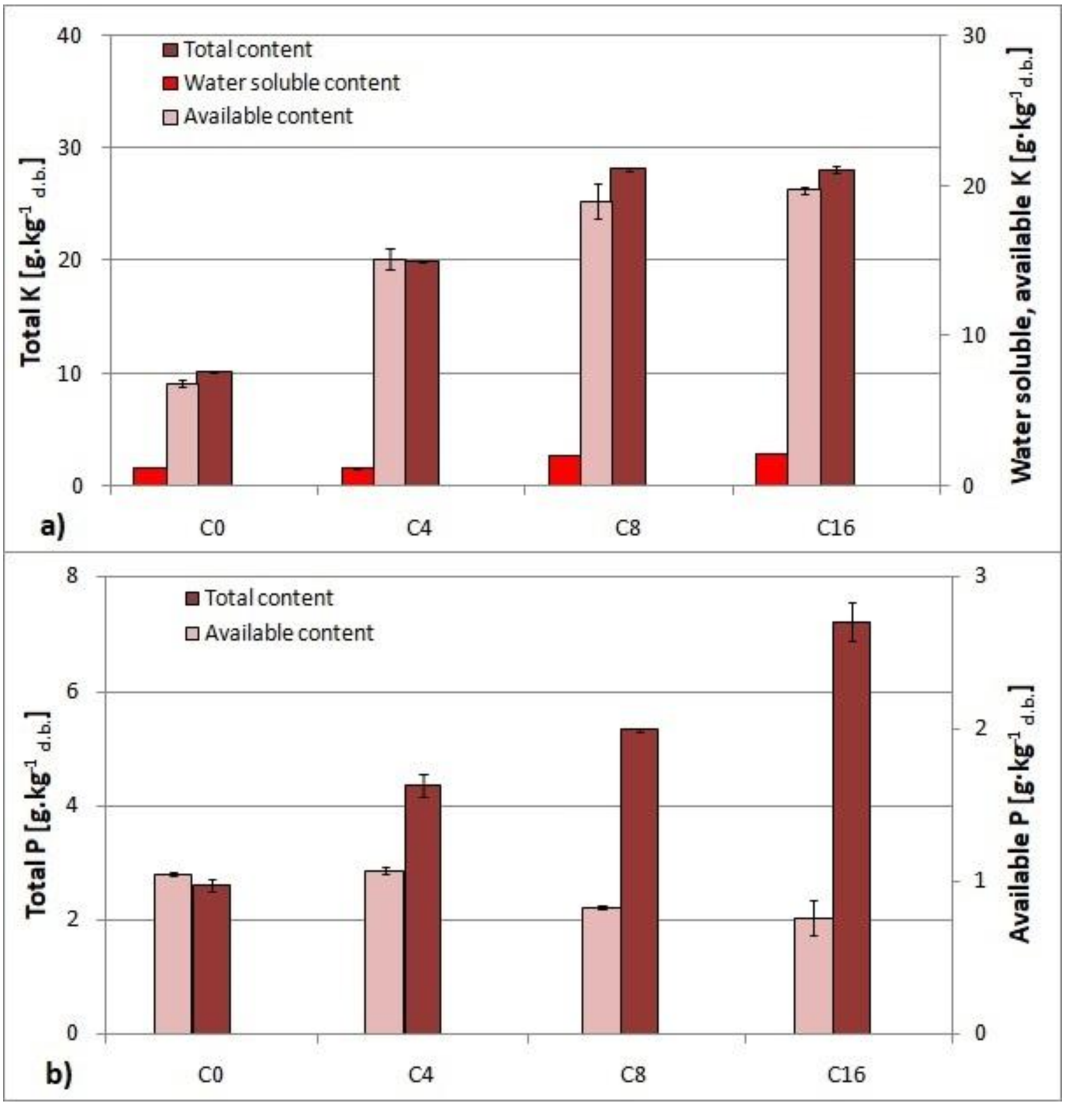

Fig. 4.46. Total, water-soluble and available content of (a) potassium and (b) phosphorus in the final composts produced in the laboratory-scale experiment (error bars indicate standard deviation).

Tab. 4.23. Nutrient total content, and soluble and available fractions in the final composts produced in the laboratory-scale experiment (standard deviation is indicated in brackets).

	C0	**C4**	**C8**	**C16**
Ca [%wt$_{d.b.}$]	0.40 (0.03)	3.21 (0.17)	3.68 (0.02)	5.03 (0.26)
Soluble Ca [% total Ca]	10.22%	3.85%	3.50%	3.17%
Available Ca [% total Ca]	36.93%	23.70%	16.18%	11.39%
Mg [%wt$_{d.b.}$]	0.08 (0.01)	0.39 (0.02)	0.50 (0.02)	0.55 (0.32)
Soluble Mg [% total Mg]	19.42%	14.37%	15.86%	16.89%
Available Mg [% total Mg]	68.22%	67.23%	47.38%	45.55%
K [%wt$_{d.b.}$]	1.00 (0.01)	2.00 (0.01)	2.81 (0.20)	2.81 (0.28)
Soluble K [% total K]	12.02%	5.98%	7.19%	7.52%
Available K [% total K]	76.45%	73.64%	70.03%	69.60%
P [%wt$_{d.b.}$]	0.26 (0.01)	0.44 (0.02)	0.53 (0.00)	0.72 (0.06)
Available P [% total P]	40.32%	24.62%	15.67%	10.57%

*C8**

The Ca, Mg, K and P total content in the C8* compost are depicted in Figure 4.47, and the comparison with the C0 and C8 corresponding levels is shown. It could be noticed that the Ca, Mg and K total content in the C8* and C8 final composts were coinciding, and much higher than the ones observed in the control. On the contrary, the phosphorus concentration in the C8* product was lower than the C8 one, though still remarkably higher than in the unamended compost.

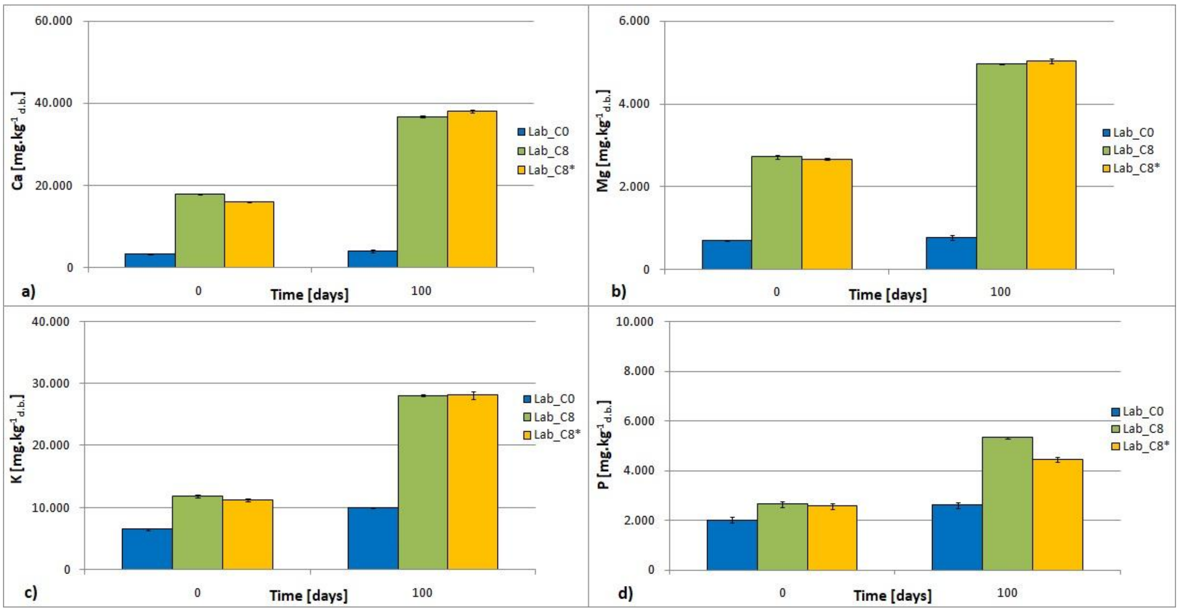

Fig. 4.47. Total nutrients content in C8*, C0 and C8 final composts of the laboratory-scale experiment (error bars indicate standard deviation).

In Figure 4.48 the water-soluble and available content of Ca, Mg, K and P in the C8* compost are shown. While the Ca and Mg total content was coinciding to the ones found in the C8 final compost, both the potassium and phosphorus levels were lower in the C8* product than in the C8 one.

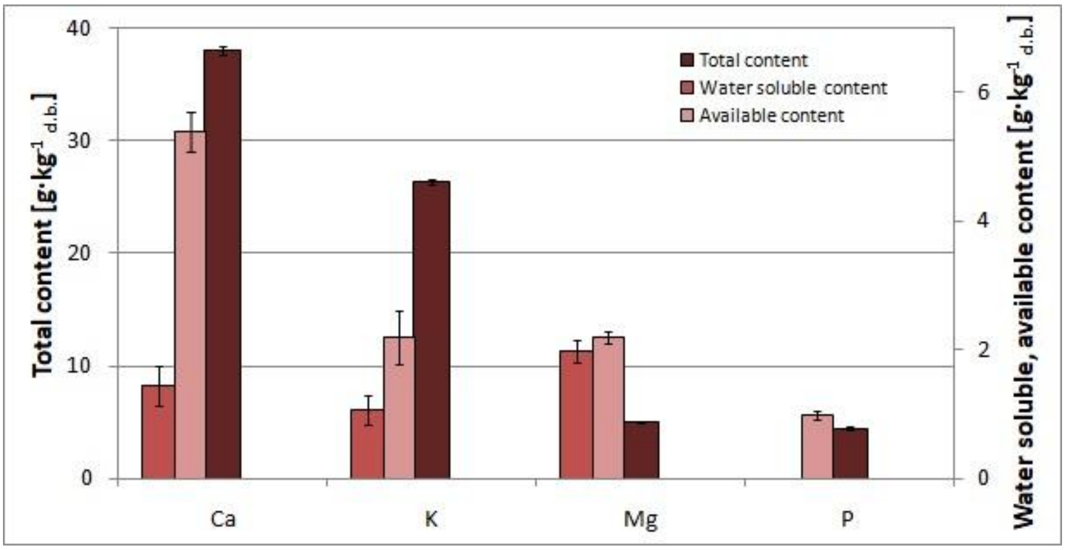

Fig. 4.48. Nutrients total, water soluble and available content in the C8* final compost (error bars indicate standard deviation).

The Ca, Mg and K water-soluble fractions in the C8* compost were higher than in the corresponding C8 one. Also the available K and P fractions were higher in the C8* final product than in the C8 one, while the available Ca and Mg fractions did not (Tab. 4.24).

Tab. 4.24. Nutrient total content, and soluble and available fractions in the final C8* compost (standard deviation is indicated in brackets).

	C8*		**C8***
Ca [%wt$_{d.b.}$]	3.80 (0.04)	K [%wt$_{d.b.}$]	2.63 (0.07)
Soluble Ca [% total Ca]	3.80%	Soluble K [% total K]	7.53%
Available Ca [% total Ca]	14.17%	Available K [% total K]	80.62%
Mg [%wt$_{d.b.}$]	0.50 (0.01)	P [%wt$_{d.b.}$]	0.45 (0.01)
Soluble Mg [% total Mg]	21.08%	Available P [% total P]	21.88%
Available Mg [% total Mg]	43.62%	-	-

Comments

The total nutrient content normally increases during the composting process because of the organic matter degradation and the resulting concentration effect [83]. In this study, the final total content was further increased when ash was added because of the high calcium, magnesium, potassium, and phosphorus levels present in BOA and FA, and the enhanced organic matter degradation achieved when ash was added. This result is relevant, since Ca, Mg, K and P are important macronutrients for plant growth [72], and consistent with what described by Fernández-Delgado Juárez et al. [36] and Kurola et al. [56].

In Figure 4.49, the initial nutrients (Ca, Mg, K, P) content (set equal to 100) in the C0, C4 and C8 mixtures of the two experimental sets (250 L and 64L reactors) and the percentage increase from the beginning to the end of the experiments are depicted.

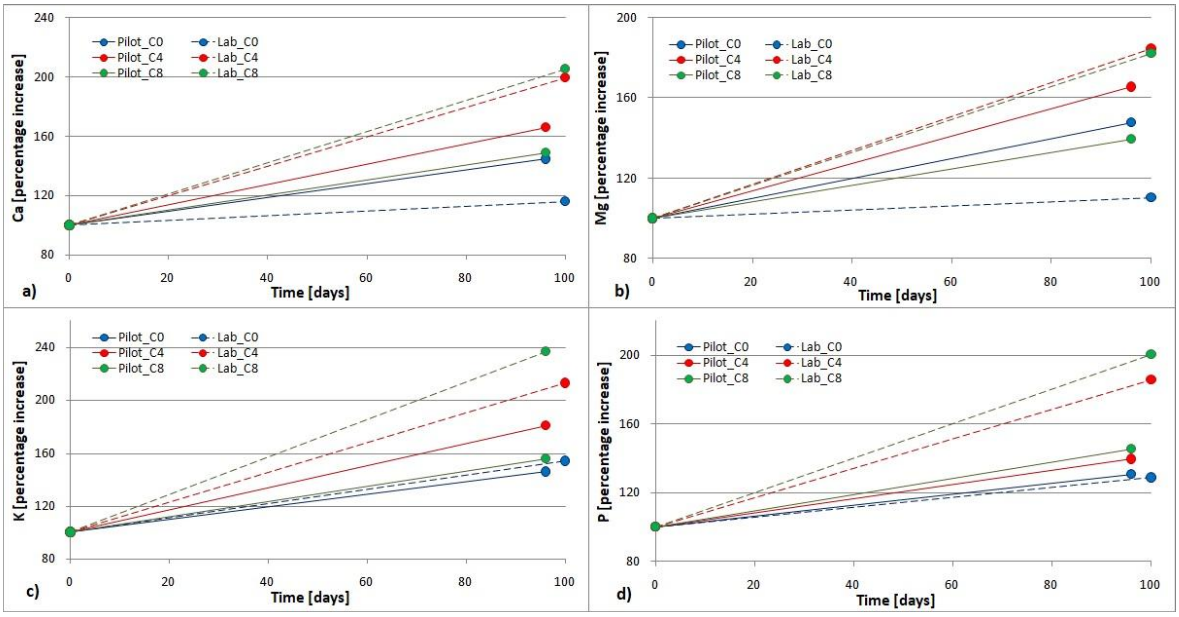

Fig. 4.49. Comparison among the normalized (a) calcium, (b) magnesium, (c) potassium and (d) phosphorus content in the C0, C4 and C8 mixtures of the pilot- and laboratory-scale experiments.

In the C0, C4 and C8 mixtures, the increase in the nutrient content differed at a lesser extent in the pilot-scale experiment than in the laboratory-scale mixtures. This could be due to the fact that the nutrients total content in the initial substrates of the pilot-scale test were higher than in the laboratory-scale ones (possibly because of the presence of contaminants such as fireplace ash, as previously suggested), which lessened the magnitude of the biomass ash effect. In the laboratory-scale tests, the lower nutrients level in the initial substrate allowed appreciating more intensively the extent of the nutrient enrichment.

In both the experimental campaigns, the Ca and Mg water-soluble and available fractions were lower in the ash-enriched composts than in the unamended ones, possibly due to the carbonation reactions that might have occurred in the aerated mixtures added with alkaline residues [40,53].

The water-soluble and available potassium fractions were lower in the ash-enriched composts comparing to the control one as well. Since the K total content increased with ash addition, it might be supposed that other forms of potassium were favored by ash addition, which could represent sources of slowly releasable K [17].

Lower levels of $NaHCO_3$-extractable phosphorus, that represents inorganic, labile P and easily hydrolysable organic P [54,90] were observed in the composts containing ash comparing to the unamended one. Consequently, the corresponding P available fractions were lower in the ash-amended composts comparing to the control one. However, it is worth underlining that part of the most stable P is organically-bound, and, since the phosphorus organically-bound to humic substances constitutes a slow release P source, it is available as well, though in the long term [71,90].

The higher K water-soluble, and K and P available fractions observed in the C8* final compost comparing to the C8 one could be related to the lower humification degree attained in the C8* final compost comparing to C8 (see paragraph 4.5.4).

4.5.4 Humification parameters

Pilot-scale experiment

The chemical characteristics in terms of humic substances in the final composts are displayed in Figure 4.50 and Table 4.25. The total humic carbon (Cext), humic acid carbon (CHA), fulvic acid carbon (CFA), and the humification ratio (HR) and index (HI) were higher in the ash-amended composts than in the unamended one. The highest Cext and CFA were observed in C4, while CHA, HR and HI were the highest in the C8 final composts. On the contrary, lower percentages of humic acids (PHA) were attained in the ash-enriched composts than in the unamended one.

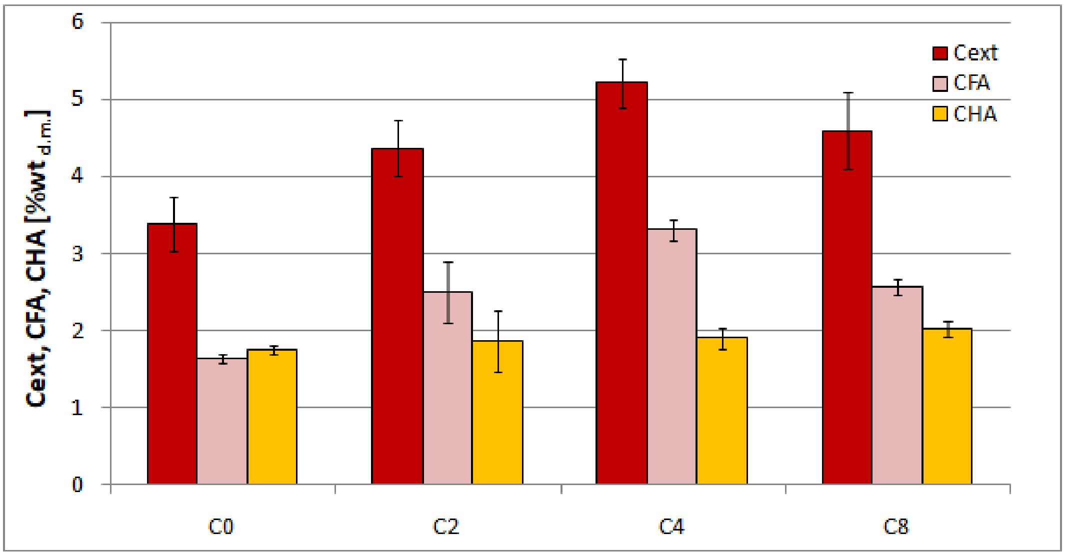

Fig. 4.50. Total humic, acid and fulvic acid carbon content in the final composts produced at pilot-scale (error bars indicate standard deviation).

Tab. 4.25. Humic substances and humification parameters in the final composts produced in the pilot-scale experiment (standard deviation is indicated in brackets).

	C0	**C2**	**C4**	**C8**
Cext [%wt$_{d.b.}$]	3.39 (0.35)	4.37 (0.36)	5.21 (0.32)	4.60 (0.51)
CFA [%wt$_{d.b.}$]	1.64 (0.06)	2.50 (0.39)	3.31 (0.14)	2.58 (0.10)
CHA [%wt$_{d.b.}$]	1.75	1.87	1.90	2.02
HR [%]	11.61	19.79	22.70	30.69
HI [%]	5.99	8.39	8.28	14.39
PHA [%]	51.53	42.81	36.46	43.96

Laboratory-scale experiment

Figure 4.51 and Table 4.26 show the chemical characteristics in terms of humic substances in the final composts produced in the laboratory-scale experiment.

The total humic carbon was higher in the ash-enriched composts than in the control one, and as high as the ash amount added was. In the C8 and C16 final products CFA was the highest as well. Similar Cext, CFA and CHA values were observed in the C8 and C16 final products. Among the composts produced at laboratory-scale, the C4 one exhibited the highest CFA and the lowest CHA.

The humification ratio (HR) and index (HI) increased with the ash amount. On the contrary, the PHA value was the highest in C8 and the lowest in C4.

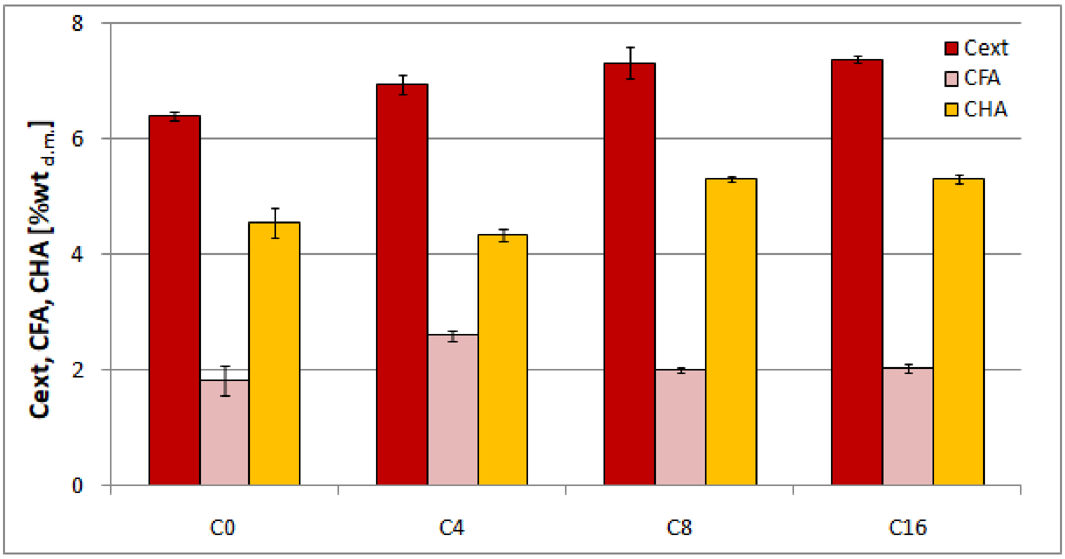

Fig. 4.51. Total humic, acid and fulvic acid carbon content in the final composts produced at laboratory-scale (error bars indicate standard deviation).

Tab. 4.26. Humic substances and humification parameters in the final composts produced in the laboratory-scale experiment (standard deviation is indicated in brackets).

	C0	**C4**	**C8**	**C16**
Cext [%wt$_{d.b.}$]	6.40 (0.08)	6.94 (0.17)	7.32 (0.27)	7.37 (0.43)
CFA [%wt$_{d.b.}$]	1.84 (0.23)	2.60 (0.09)	2.00 (0.05)	2.05 (0.06)
CHA [%wt$_{d.b.}$]	4.56	4.34	5.32	5.32
HR [%]	16.43	21.97	32.16	57.93
HI [%]	11.71	13.73	23.37	41.81
PHA [%]	71.26	62.47	72.67	72.18

*C8**

In Figure 4.52 and Table 4.27 the humic matter chemical characteristics in the C8* final compost are reported and compared to the ones of the C0 and C8 final products.

The total humic and humic acid carbon content was lower in the C8* final product than in C8. The fulvic acid carbon, and humification ratio and index in C8* and C8 were comparable, while the percentage of humic acid was lower in the C8* compost than in the corresponding C8 one.

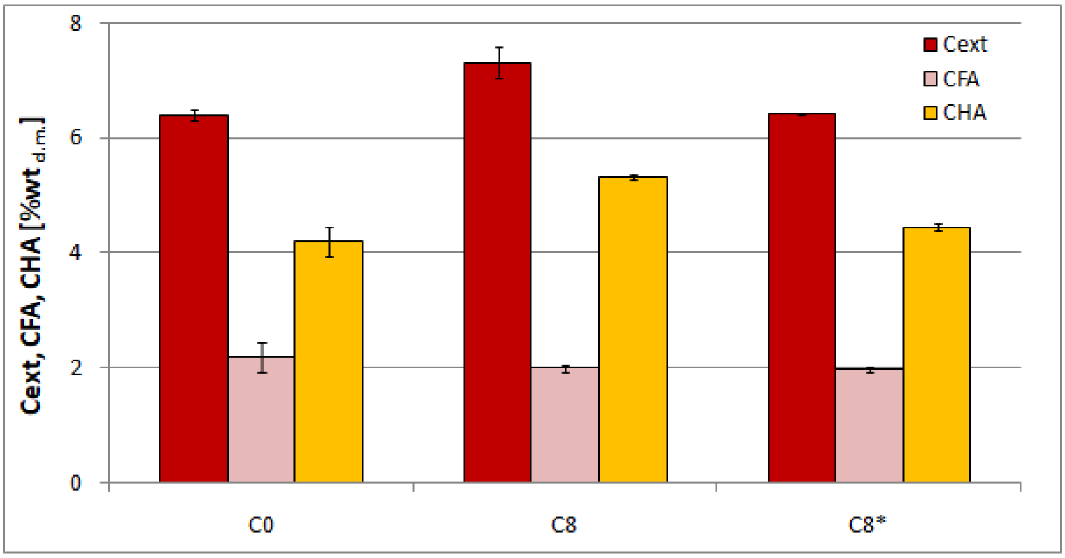

Fig. 4.52. Total humic, acid and fulvic acid carbon content in C8*, C0 and C8 final composts of the laboratory-scale experiment (error bars indicate standard deviation).

Tab. 4.27. Humic substances and humification parameters in the C8* final compost (standard deviation is indicated in brackets).

	C8*		**C8***
Cext [$\%wt_{d.b.}$]	6.42 (0.02)	HR [%]	33.26
CFA [$\%wt_{d.b.}$]	1.97 (0.05)	HI [%]	23.07
CHA [$\%wt_{d.b.}$]	4.45	PHA [%]	69.34

Comments

The total humic and humic acid carbon levels obtained in the pilot-scale experiment were comparable to the ones, pertinent to mature organic fertilizers, reported by Roletto et al. [79], while the corresponding figures in the laboratory-scale composts were higher. The fulvic acid carbon in all the trials of both the experimental setups was consistent with the CFA levels reported by Roletto et al. [79], except for the pilot-scale C4 final compost that was significantly higher.

The CHA fraction, which is related to compost maturity according to Huang et al. [44], was higher in the ash-amended composts than in the unamended one (except for the C4 product obtained at laboratory-scale). The CHA highest values were observed in the C8 final composts of both the experimental campaigns and in C16 (in the laboratory-scale test C8 and C16 final composts showed the same CHA values).

With the aim of assessing compost maturity, Roletto et al. [79] suggested a set of minimum values for Cext, HR and HI equal to 3.0 %$wt_{d.b.}$, 7.0% and 3.5%, respectively. With the same purpose, Bernal et al. [16] reported that a limit of minimum 50.0% was suggested for PHA. Referring to these limit values, all the four final composts obtained in the pilot-scale experiment met the maturity requirements in terms of Cext, HR and HI, while the minimum limit for the percentage of humic acids was fulfilled only by the unamended final compost. On the contrary, all the final composts produced in the 64L reactors (including C8*) met the maturity requirements proposed by Bernal et al. [16] and Roletto et al. [79] for assessing compost maturity.

It should be mentioned that Roletto et al. [79] emphasized the fact that, among the humification parameter for assessing the compost maturity, the humification index was the most reliable. According to the data obtained, the humification index in the C4 final composts of the pilot- and laboratory-scale experiments, was 1.38 and 1.17 times higher than in the control ones, respectively. In the C8 final composts of the pilot- and laboratory-scale experiments, HI was 2.25 and 2.00 times higher than in the control ones, respectively. The humification indices in C8* and C8 were almost coinciding (23.07% and 23.37%, respectively). It could be concluded that ash addition increased the humification index, and the extent of this effect was bigger in the pilot-scale tests than in the laboratory-scale ones. This results could be due to the fact that the unamended compost produced from synthetic waste, showed a high HI (11.7%) itself.

P exhibits a great affinity for the humic substances that are naturally formed during composting. It should be noted that in the pilot-scale C4 compost the highest total humic carbon and the lowest level of available P were observed. Similarly, the highest Cext and lowest available phosphorus level were observed in the C16 compost produced at laboratory-scale. The total humic carbon and the available phosphorus of all the composts produced showed a statistically significant relationship at < 0.1 level (ANOVA $F(1,7) = 49.06$, $p = 0.0002$). Moreover, if the linear regression analysis between these variables is considered, a correlation coefficient equal to -0.93549 is found (Fig. 4.53).

Also the potassium exchangeable content was compared to the amount of Cext. The available K had a statistically significant relationship with the total humic carbon at <0 .1 level (ANOVA $F(1,7) = 19.59$, $p = 0.0031$). A simple regression showed a correlation coefficient of 0.85832 (Fig. 4.53). The data are better fitted by other models, the better of which is the Reciprocal-Y squared-X one (correlation coefficient equal to -0.9616). These results show that the Cext in the final composts had a relatively strong relationship with the amounts of available P and K. The data displayed in Figure 4.53 could be grouped in two sets, that well represent the results obtained from the pilot-scale experience and the laboratory-scale one.

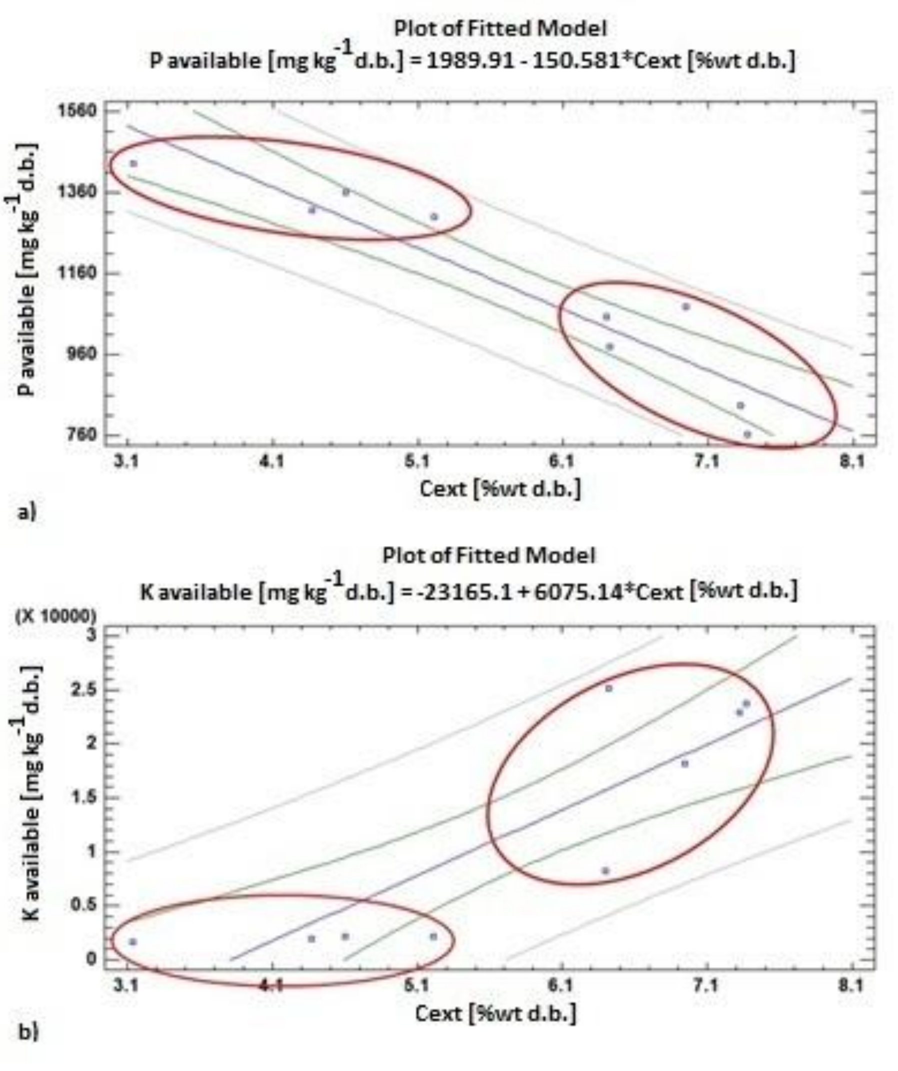

Fig. 4.53. Relationship between the total humic carbon and the phosphorus (up) and potassium (bottom) available content.

4.5.5 Heavy metal total content and the potential metal release to soil

Pilot-scale experiment

The real OFMSW used as a substrate in the pilot-scale experiment showed a higher concentration of Be, Cr, Ni and Sb than the ash blend used as an additive itself. This feature is due to the high heterogeneity and presence of extraneous materials in the real OFMSW, which affected the significance of the heavy metal content in the final composts. This was confirmed by the fact that in the pilot-scale final composts the total content of most of the heavy metals could not be uniquely related to the ash amount added, and for some metals, similar concentrations were observed in the final composts irrespective to the ash amount added. For instance, the Cr content in the final products was 34.63, 33.47, 35.84 and 37.46 mg·kg^{-1} in the C0, C2, C4 and C8 composts, respectively. Similarly, in the C0, C2, C4 and C8 final composts the Cu and Fe concentrations were 37.56, 29.70, 34.18 and 34.54 mg·kg^{-1}, and 7089, 7023, 6527 and 6991 mg·kg^{-1} respectively. Finally, in the C0, C2, C4 and C8 products the Ni content was 17.94, 17.57, 20.00 and 18.87 mg·kg^{-1}, and the Zn concentrations were 76.81, 87.86, 75.86 and 75.35 mg·kg^{-1} respectively.

In the pilot-scale tests, a relation between the concentration levels and the ash content, could be envisaged for Al and Mn only (Fig. 4.54). The Al and Mn total content in the ash-amended composts were higher than in the unamended one, and as high as the ash amount added was. This result could be due to the fact that the leachable fractions of aluminum and manganese in the considered ash types used were very low (see Chapter 3). As for the water-soluble fractions of these elements in the final composts, the Al and Mn ones decreased with the increase of the ash amount added: the Al water-soluble fraction was 0.17%, 0.16%, 0.10% and 0.09% of the total Al, and the Mn water-soluble fraction was 0.55%, 0.50%, 0.29% and 0.19% of the total Mn in C0, C2, C4 and C8, respectively.

The total zinc and copper content did not manifest a clear trend in relation to the ash amount. However, the Zn water-soluble fraction decreased as the ash amount increased, and was 3.68%, 3.30%, 2.57% and 1.47% of the total Zn content in C0, C2, C4 and C8, respectively; on the contrary, the copper water-soluble fraction increased with the ash amount added and was 4.03%, 7.64%, 7.66% and 8.96% in the final C0, C2, C4 and C8 composts, respectively.

Because of the mentioned factors that affected the data obtained in the pilot-scale tests, more significant results on the heavy metal total content in final composts and the potential metal release to soil were sought in the laboratory-scale experimental tests.

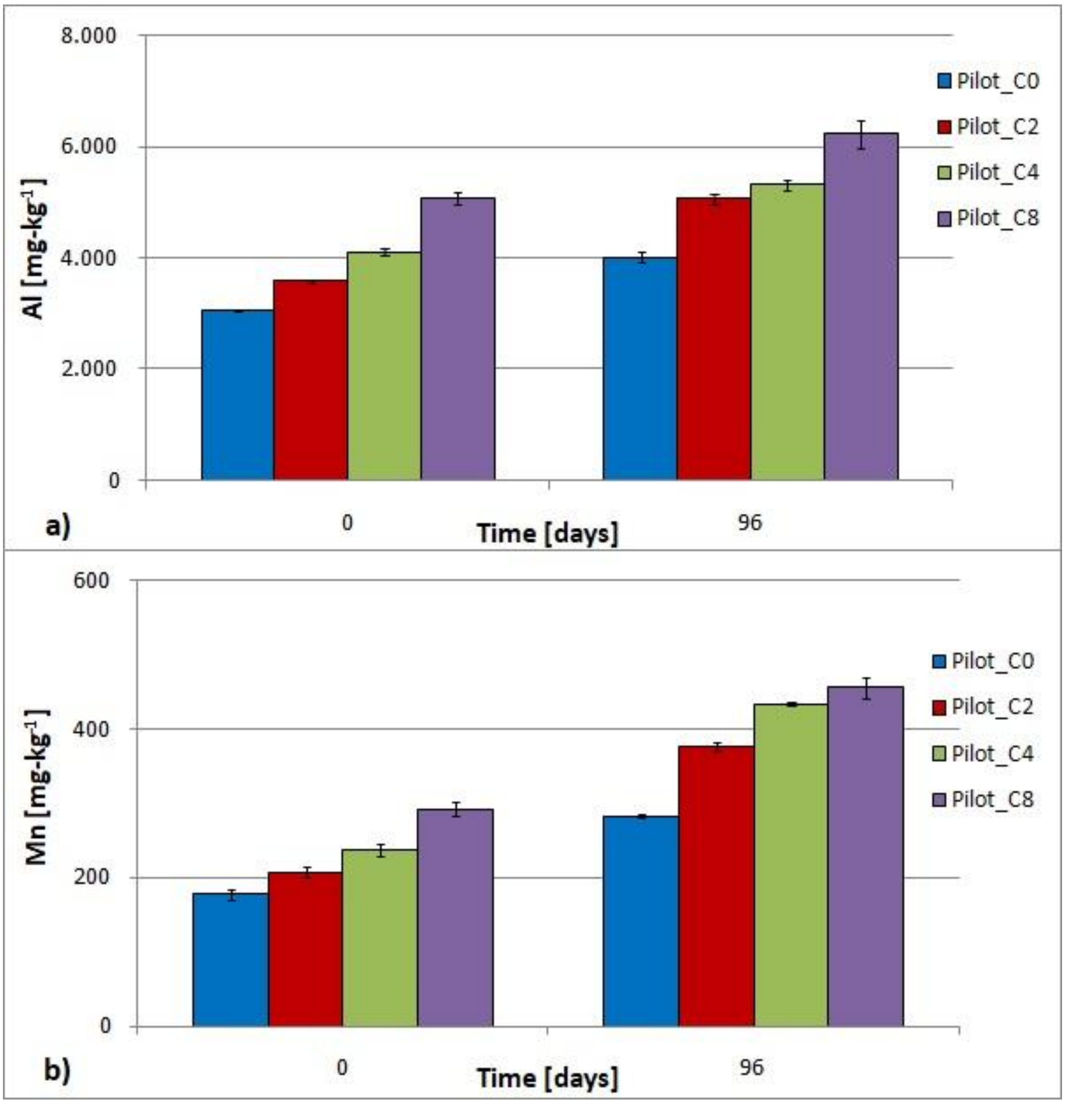

Fig. 4.54. Heavy metals total content in the initial mixtures and the final composts produced at pilot-scale: (a) Al; (b) Mn (error bars indicate standard deviation).

Laboratory-scale experiment

The total Be, Mo, Sb and V levels in the final composts were below the detection limit. The total content of most of the other heavy metals in the final products was as high as the ash amount added was (Fig. 4.55). The selenium total content was below the detection limit in the ash-amended composts, while it was 4.95 mg·kg^{-1} in the C0 final product. It has to be mentioned that the Se leaching behaviour is affected by the carbonation reactions that presumably occurs in composting piles amended with ash, in a way that selenium leachability increases after carbonation (see Chapter 5). It is reasonably for this fact that a higher amount of selenium was retained in the unamended compost than in the ash-amended ones.

The Al, Ba, Fe and Sr total content in the final C0 compost was lower than the corresponding levels in the initial unamended substrate, which could be related to the metal solubility of these metals during composting and the loss with the leaching water. In the ash-amended products, the final concentrations of these elements were higher than in the corresponding initial substrate, which was aligned to the concentration effect provoked by the degradation of the organic matter and to the fact that the metal solubility was lowered by the ash addition. The nickel total content in the ash-amended final composts did not manifest significant differences and was lower than in the C0 final product.

In the C16 final product all the heavy metals, except for nickel, exhibited concentrations remarkably higher than in the other composts obtained, as a consequence of the higher amount of ash added. If the values observed are compared to the limits set by the Italian legislation for the heavy metals in composts, it could be observed that the C16 final compost exceeded the maximum Cd total content accepted by the law.

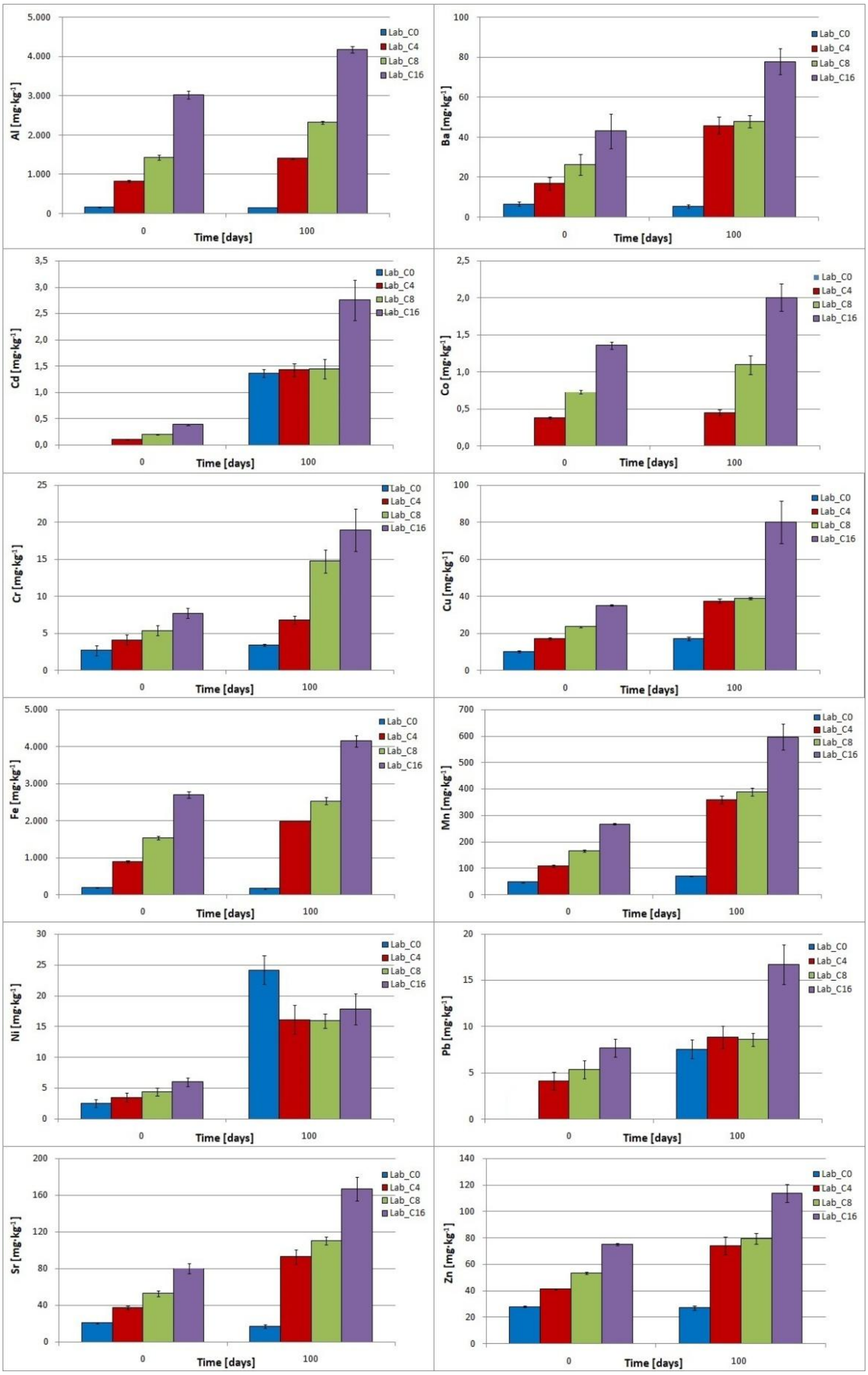

Fig. 4.55. Heavy metal total content in the initial mixtures and the final composts produced at laboratory-scale (error bars indicate standard deviation).

As for the heavy metal water-soluble content, it was below the detection limits for Ba, Cd, Co, Cr, Ni Mo, Se and Pb, while only Al, Cu, Fe, Mn, Sr and Zn exhibited detectable values (Tab. 4.28). The Al, Mn and Zn water-soluble fractions decreased according to the ash amount added. In the ash-containing composts, the Fe and Sr water-soluble fractions were lower than in the C0 final composts as well, but the decrease was not linearly related to the ash amount. A linear relation between the Cu water-soluble fraction and the ash amount was not envisaged but in the ash-amended composts the copper soluble fractions were higher than in the unamended one.

Tab. 4.28. Heavy metals water soluble fractions in the final composts produced in the laboratory-scale experiment (< d.l.: below detection limit).

	C0	**C4**	**C8**	**C16**
Soluble Al [% total Al]	17.33%	1.45%	0.74%	0.41%
Soluble Cu [% total Cu]	<d.l.	1.68%	6.39%	3.51%
Soluble Fe [% total Fe]	4.90%	0.71%	0.80%	0.68%
Soluble Mn [% total Mn]	7.78%	1.23%	0.99%	0.63%
Soluble Sr [% total Sr]	9.63%	4.73%	4.11%	3.59%
Soluble Zn [% total Zn]	3.98%	1.22%	1.44%	1.07%

*C8**

The heavy metal total content in the C8* final compost is depicted in Figure 4.56. The total Be, Mo, Sb, Se and V levels in the final C8* compost were below the detection limit. For the majority of the elements, the heavy metal level in C8* and in C8 were not statistically different. Conversely, the Cu and Pb total contents were statistically different in the C8* and C8 final composts, and higher in the C8* product than in the C8 one.

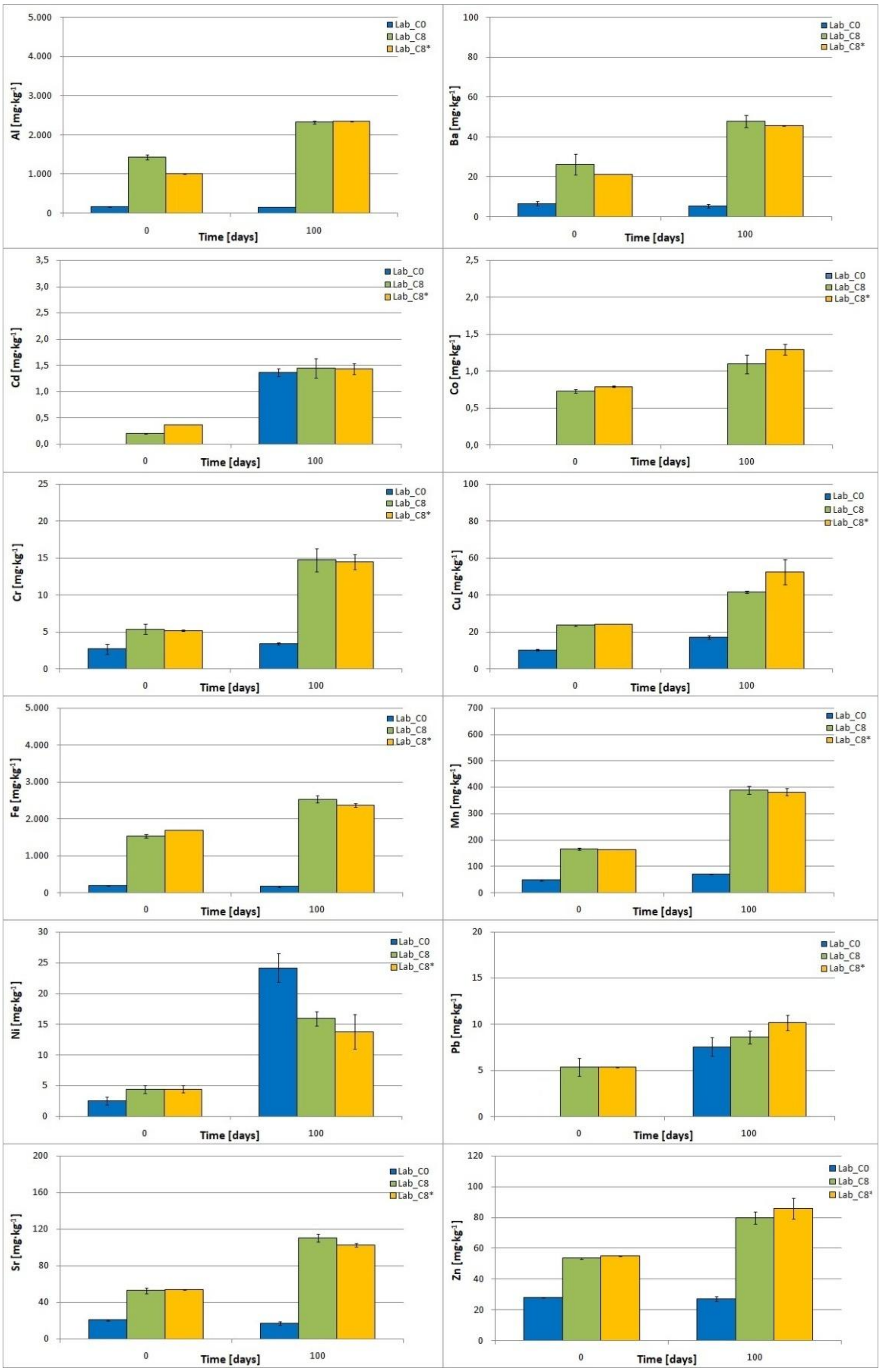

Fig. 4.56. Heavy metals total content in C8*, C0 and C8 final composts of the laboratory-scale experiment (error bars indicate standard deviation).

All the heavy metal water-soluble fractions observed in the C8* final compost were comparable to the ones attained for the C8 final compost.

Tab. 4.29. Heavy metals water soluble fractions in the final C8* compost.

	C8*		**C8***
Soluble Al [% total Al]	0.87%	Soluble Mn [% total Mn]	1.06%
Soluble Cu [% total Cu]	6.32%	Soluble Sr [% total Sr]	5.13%
Soluble Fe [% total Fe]	1.15%	Soluble Zn [% total Zn]	1.26%

Comments

The evolution of the heavy metal content in the final ash-amended composts depends on the amount retained in the waste mass, as opposite to the leaching behavior of the given species. Indeed, it is known that leaching with the water added to the composting mixtures could reduce the metals content in the final products, as suggested by Manohara and Belagali [60] in a study on municipal waste composting. It is also acknowledged that the organic matter decomposition and formation of humic compounds influence the metal water solubility [7,69]. Some heavy metals, such as Cr, could form stable and organically bound compounds with the humic matter developed during composting [41], and they are prone to be retained in the waste mass, rather than leach with the water added. The carbonation reactions occurring in the composting piles must have influenced the leaching behavior of some of the metal species as well. For instance, the Se leachability in the ash-amended mixtures must have been higher than in the unamended mixtures because of the effect of carbonation reactions (see Chapter 5).

The Al, Fe, Mn, Sr and Zn water-soluble fractions in the final composts decreased with the increase of the ash amount (this behavior in Al, Mn and Zn was observed in both the pilot- and laboratory scale sets). Ifansyah [47] reported that the humic acids lowered the aluminum and iron solubility. Similarly, Amir et al. [7] observed that, as humification increases, Zn is converted from exchangeable to more stable forms (organic complexes with the humic matter), thus its solubility decreases as the humification improves. In the final composts, the decrease of the Mn water-soluble fraction with the increase of the ash amountcould be related to the increase in the pH levels in the composts where ash was added. This fact was also observed by Hue and Mai [45], who investigated the effect of adding lime and compost to soils. Finally, also Sr solubility decreases as pH value increases. Therefore, the reduction of metals solubility when ash was added could be explained by the increase in the compost pH and humification degree in the ash-amended products. On the contrary, the laboratory-scale tests showed that the final Ni total content in composts was not aligned with the ash content, and the Ni total content was higher in the unamended compost than in the ones amended with ash. The nickel fate might have been influenced by the break down of the metal complexes that it forms with the organic matter, as Singh and Kalamdhad [83] explained. Attention should be paid on Cu, since the copper water-soluble fraction was higher in the ash-amended composts than in the unamended one. Copper has high affinity with the soluble fraction of the humic matter [1] that increases with the pH growth [51] and, since pH increases with ash addition, higher soluble Cu fractions were observed in the ash-enriched composts than in the unamended one. Higher Cu soluble fractions in the composts with high pH values were reported also by Neaman et al. [69], who conducted an experiment where lime and compost were added to soils.

The results pertaining the C16 final compost showed that the Cd total content exceeded the limit set by the Italian legislation for fertilizers. This result raises an issue about the existence of a maximum amount of biomass ash that might be added as a composting additive without being of harm for the health and the environment.

As for the heavy metals total content and solubility in the C8* final compost, results coinciding with the C8 ones were obtained.

4.5.6 Phytotoxicity (Germination Index)

Pilot-scale experiment

The results of the germination test, aimed at evaluating the phytotoxicity and, in turn, the achieved stability level of the final composts, are displayed in Figure 4.57. In the pilot-scale C2, C4 and C8 composts, germination indices were 13%, 19%, and 8% greater than C0, respectively.

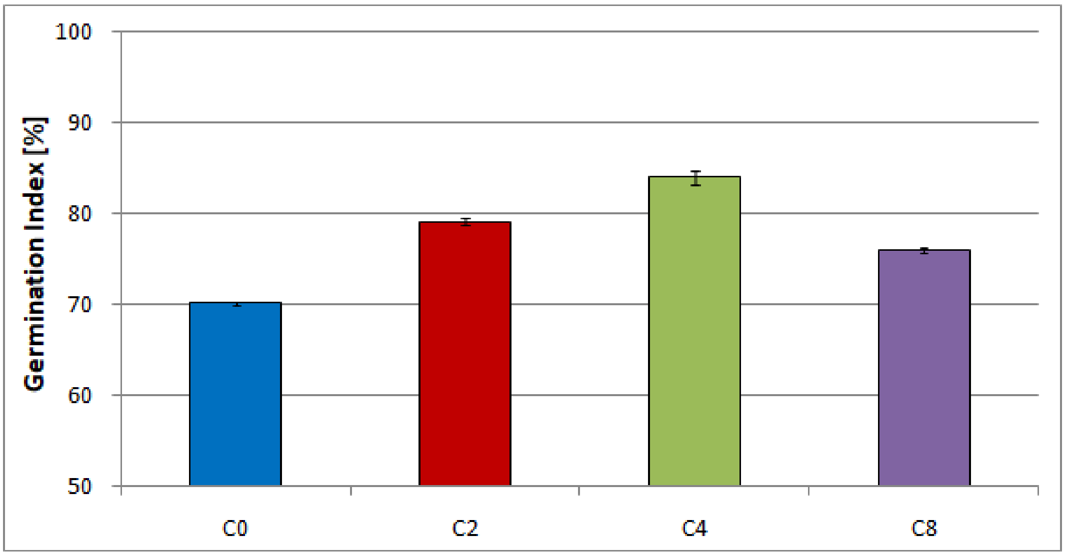

Fig. 4.57. Germination indices of the final composts produced in the pilot-scale experiment (error bars indicate standard deviation).

Laboratory-scale experiment

In the laboratory-scale C4, C8 and C16 composts the germination indices were 2%, 6% and 13% higher than in the control, respectively (Fig. 4.58).

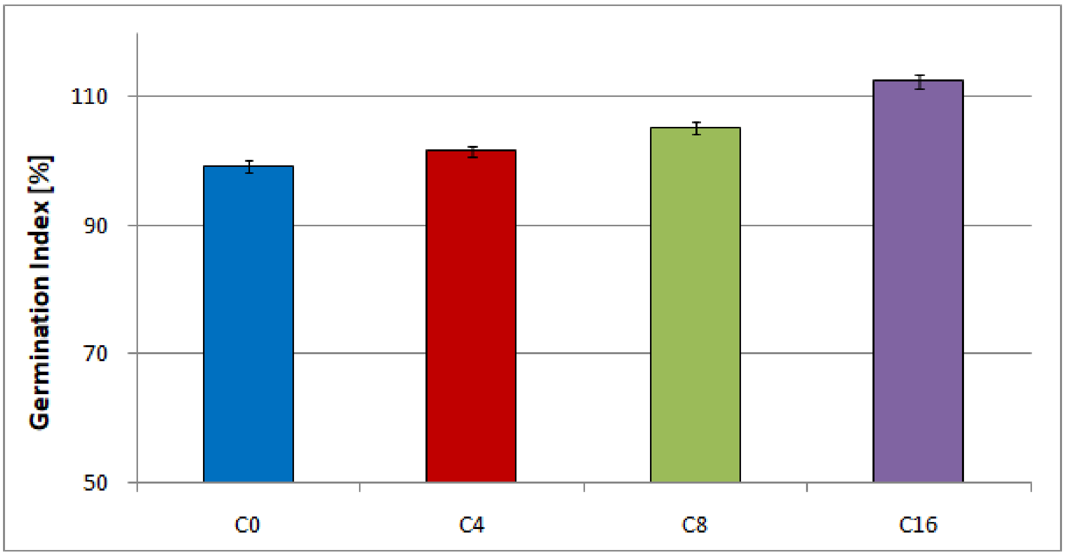

Fig. 4.58. Germination indices of the final composts produced in the laboratory-scale experiment (error bars indicate standard deviation).

*C8**

The C8* compost exhibited a germination index of 106.78%, slightly higher than the C8 one (105.12%, Fig. 4.59).

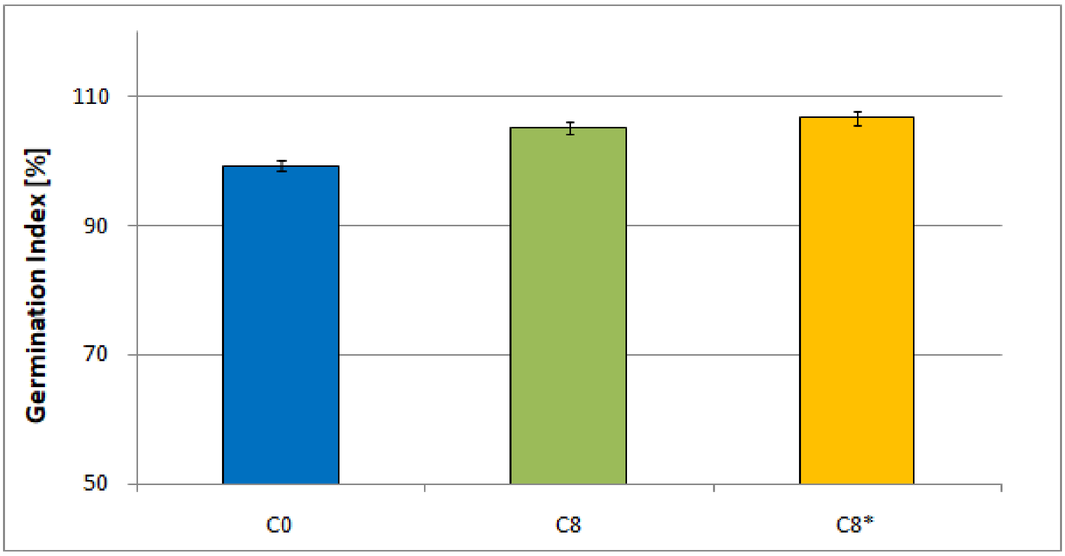

Fig. 4.59. Germination index of C8*, C0 and C8 final composts of the laboratory-scale experiment (error bars indicate standard deviation).

Comments

Many aspects influence the germination performance. The inhibiting factors that are usually considered a concern when combustion ash are recycled (such as salinity, heavy metals), may affect germination negatively. In the experiments conducted, the composts obtained in the laboratory-scale tests produced better performances than the ones deriving from the pilot-scale trials, which confirmed the importance of the good quality of the starting substrate.

In all the trials, the ash-amended composts exhibited germination indices higher than the unamended ones, meaning that the ash-amended composts had a lower inhibitory effect on plant growth than C0. Himanen and Hänninen [43] observed a relationship between higher germination performances and the improved stability in composts amended with commercial additives based on calcium and magnesium-bearing compounds. The higher stability of the ash-enriched composts comparing to the control, that was suggested also by the lower respiration activity of the ash-amended composts comparing to the unamended one, could be the reason for the higher germination indices observed. The germination indices could have also benefited by the presence of nutrients essential for plant growth and humic matter.

In addition, it can be noticed that the germination indices of all the composts produced in the pilot-scale tests were lower than 100%, meaning that they had a bigger inhibitory effect comparing to distilled water [13]. This result could be related to the presence of toxic or inhibiting compounds, such as metabolites of the organic matter degradation, and high salinity levels as suggested by Belyaeva et al. [14], who observed an accumulation of soluble salts in low germinating composts produced from green waste and digested sewage sludge. On the counterpart, the laboratory-scale composts had germination indices higher (for the ash-amended composts) or very close to 100% (C0 showed a germination index of 99.31%), which is coherent with the better control of the process conditions, more homogeneous aeration, absence of extraneous materials, low electrical conductivity levels and more extended enrichment in nutrients essential for plant growth observed in the small scale composts. Consistently to the latter aspect, the C16 final compost exhibited the highest germination index (>110%).

The final C8* compost manifested a germination index very close to the one pertaining C8, showing that the reduction in the amount of bulking material used did not lead to a worsening of the germination performance.

At last, a relatively strong correlation (coefficient equal to 0.96313) was found between the germination indices and the humic matter content in the data set that includes all the final composts produced in the pilot- and laboratory scale experiments and C8*, as displayed in Figure 4.60.

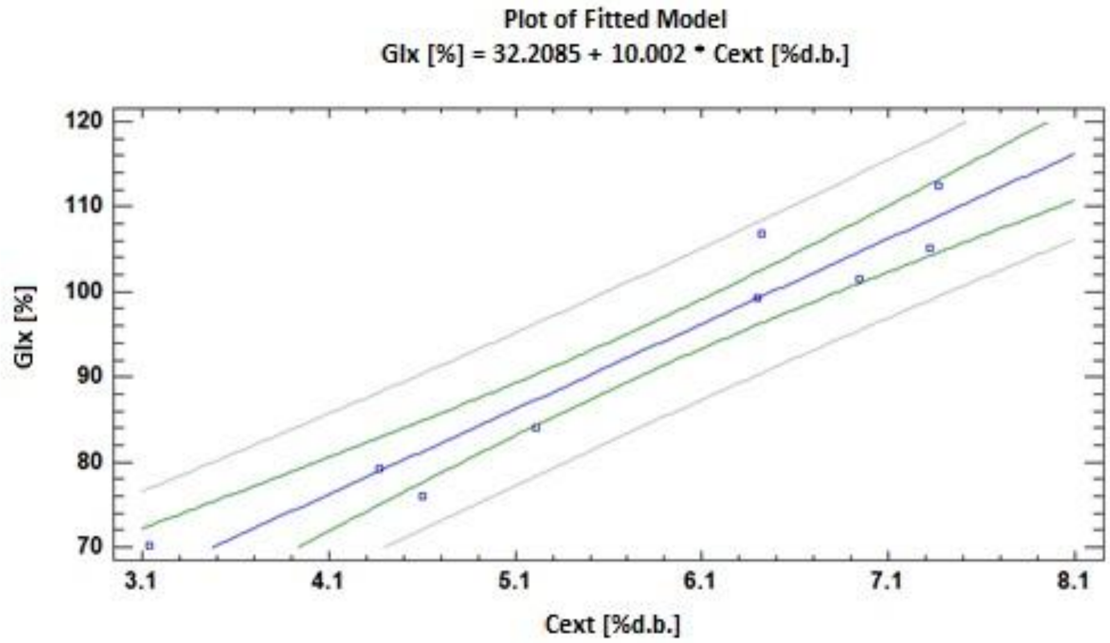

Fig. 4.60. Relationship between the germination indices (GIx) and total humic carbon (Cext) in the final composts produced in the pilot- and laboratory scale experiments.

4.6 Conclusions

In this research line, two experimental campaigns at pilot- and laboratory-scale were conducted using selected types of biomass combustion ash as an additive in the OFMSW composting, with the main objective of assessing the effects of the addition of a biomass ash blend on the process itself and the final product quality.

In the pilot-scale experiment real OFMSW and green waste were used as principal source of organic matter and bulking agent, respectively. The former was highly heterogeneous and contaminated by extraneous materials, while the latter was constituted by grass and tree pruning that were partially degraded during the aerobic treatment. In the laboratory-scale tests synthetic OFMSW and wood chips were used instead, and the previously mentioned additional variables (heterogeneity, presence of extraneous materials, the bulking material contribution to the degradation process) were avoided. In addition, in the pilot-scale experimental setup, the moisture control was made difficult by the significant temperature increase. The tighter control exerted at laboratory-scale comparing to the pilot-scale allowed to limit some of the problems connected to the management and control of “real” waste composting. Therefore, differences were observed between the ash effects exerted under the “ideal” (synthetic waste and wood chips) and “real” (source-separated waste and a more degradable bulking agent) conditions. However, the properties of the real OFMSW and the large mass of waste used in the pilot-scale experiment better simulated the conditions that actually characterize the waste treatment facilities. The parameters that resulted to be affected by the real operating conditions the most were the pH and electrical conductivity levels, the final heavy metals total content, and the volatile solids content and respiration activity evolution (influenced by the degradation of the bulking agent).

However, beyond all these differences provoked by the various operating conditions reproduced in the pilot- and laboratory-scale tests, two main results were obtained:

i. Firstly, biomass ash addition was beneficial for the composting process and the final compost quality, by determining a set of effects on the physical characteristics of the mixtures subjected to composting, the evolution and extent of the stabilization process and characteristics of the final product, and the magnitude of these effects was generally proportional to the amount of ash added.
ii. Secondly, in the ash-amended mixtures the process was improved comparing to the unamended one irrespective of the amount of bulking agent used, thus ash could have a potential as a physical conditioner.

In particular, in relation to the ash effects on the process and final product quality, the blend of biomass fly and boiler ash influenced the composting process and final compost quality as follows:

- Ash addition provoked an increase of the pH and electrical conductivity levels in the final composts, even beyond the limits set by the law or suggested by the common use; however the pH and EC final levels were, for the pilot scale tests, strongly affected by the ones of the initial waste that could impair the compost quality even without using any additive.
- In both the experimental setups, the organic matter stabilization, assessed as the reduction of the VS total content or respiration activity, was improved by ash addition. The organic matter degradation could have been partially related to the FAS levels in the composting mixtures, which was increased by the ash addition. Tuomela et al. [89] and Fernández-Delgado Juárez et al. [36] suggested that ash could facilitate the degradation of lignin, cellulose and hemicellulose, therefore the extent of the organic matter degradation could be influenced by the contribution of the bulking agent used when it is decomposed as well.

- Ash addition influenced the moisture content and, in relation to this aspect, the resulting physical properties. This fact suggests that biomass ash had a role as a physical conditioner. Therefore, ash could be proposed as an additive that enhances the effectiveness of traditional bulking agents, that typically consist of wood chips and may represent a cost for the waste treatment facilities.
- Pertaining the total C and the total organic C, the results of the laboratory-scale tests confirmed the results attained at the pilot scale level, and a decrease with time and the ash amount added was observed. The total organic carbon reduction was found to be excessively large in some of the composts obtained, so that this figure could provide essential information pertaining the possible limitation of ash use as an additive.
- Ash did not generate an enrichment in total nitrogen content, which is the most important nutrient for plant growth, and presumably affected the N_{tot} content in the final composts in various ways (because of the low or absence of nitrogen in the ash, or because of the enhanced ammonia volatilization provoked by the ash alkalinity). However, the C_{tot}/N_{tot} ratio fulfilled the requirements in all the composts thanks to the high reduction in the total carbon content attained.
- As for the other nutrients content, the results of the pilot- and laboratory-scale tests were consistent and an increase in the Ca, Mg, K and P total content with the ash addition was observed; hence, biomass ash reintroduction in the organic waste composting complies with the goal of recovering nutrient-rich waste in the production of soil improvers.
- A decrease in the Ca, Mg, K, and P water-soluble and available fractions when ash was added was observed in both the experimental campaigns. This could suggest the formation of not available forms of nutrient when ash was added, at some extent favored by carbonation (i.e. formation of Ca- and Mg-bearing carbonates). More slowly releasable forms of nutrients might also manifest, which could have been favored by ash addition (i.e. related to the improved humification) and represents an issue that deserves further investigation.
- In general, in the final products higher humification of organic matter, which is related to compost maturity, was observed when higher amounts of ash were added. In this context, it was also found that the total humic carbon, and potassium and phosphorus available amounts were connected with statistically significant relationships (i.e. lower available P and higher available K concentrations were

related to higher total humic carbon content).

- As for the most feared negative effects, which is the presence of heavy metals, the mobility of most of the heavy metals was limited by ash addition, possibly because of the increase in the pH levels of the composts, improved humification and the complexes that might have formed; however, for some species, such as Cu, a different behavior was observed that deserves a particular attention.
- In both the experiments described in this Chapter, ash-added composts were connected to higher germination indices comparing to the unamended products.

In the mixture having 16%wt of ash blend the figures were affected by the ash addition the most intensively. In general, it could be concluded that the effect of ash addition on most of the parameters increased according to the amount of ash added.

Ash amounts of 8%wt and 16%wt were found to provoke adverse effects on the final product quality in terms of organic carbon and Cd total content, respectively, that did not meet the limits set by the Italian legislation. These results raise an issue about the existence of a maximum amount of biomass ash that might be added as a composting additive without being of harm for the health and the environment. In the present study it could be concluded that an ash amount close to 8%wt could be evaluated as a limit, however a wider knowledge of the properties that this kind of residues typically have should be acquired, and this limit should be confirmed by further studies as it could be also case-sensitive with respect to the biomass origin. Also, it is advisable that in future each residue will be analyzed before recycling by means of routine analyses established by the law or on the basis of a voluntary analytical program, in order to ascertain possible cases of occasional contamination.

The additional goal of evaluating the effect of ash when the BM share in the OFMSW+BM mixture was reduced, was also pursued. In the test aimed at evaluating the ash influence when varying the OFMSW:BM ratio, little differences among the ash-amended reactors (C8* and C8) were observed in most of the parameters analyzed, while significant differences were found among them and C0. Interestingly, a higher mass reduction and a higher germination performance were observed for the compost produced using a lower amount of wood chips. In general, it could suggest that the amount of bulking agent employed in composting could be reduced in presence of a certain amount of ash, maintaining similar processing performance and final compost quality. This would produce a cost saving for the composting facilities, though further investigations at pilot scale are suggested.

These results open to new perspectives and are consistent with a full implementation of the Circular Economy concepts. According to this approach, it is important to study synergistic approaches for the valorization of residues, having eventually different origins, but being available in the same area. In addition to minimizing the flow of waste sent to the final disposal, the recycling option described in this Chapter could also allow for a greater added value to the final products, which in turn enhances the possibility of placing them on the market.

However, the reuse in composting should be conditioned by the assessment of the contamination risk for any specific case. The reuse of ash in composting should not affect the final compost quality, and the quality standards already existing should always be fulfilled. It is also worth mentioning here that several European countries have adopted certification programs aimed at ensuring that the compost has been produced from well-defined starting materials and by following appropriate procedures. In some countries [55-56] there are quality requirements for each of the materials involved in the compost production, besides of the final product, and the extensive adoption of such approach could be suggested. It is the authors' opinion that any compost produced using ash as additive, even if complying with current regulations, should be marked to distinguish it from ash-free products.

To deepen the present study, some more detailed aspects could be eventually investigated:

- The formation of non-humic or humic bounds and complexes should be studied by conducting specific analyses, in particular aimed at clarifying the fate of nutrients and heavy metals.
- The carbon balance and effects on the microbial activity.
- The ash-amended compost should be tested on field, so that the effect on plant growth will be verified.

In the future, the research on the biomass ash recycling as a composting additive could give raise to:

- Firstly, the definition of the maximum ash amount that might induce benefits to the compost quality, while avoiding the disadvantages highlighted in this work.
- Secondly, further studies aimed at confirming that the ash addition could lead to a

reduction in the amount of the bulking material used, and induce to a possible cost saving for the composting facilities.

4.7 References

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CHAPTER 5

Reuse of ash as a substrate for CO_2 sequestration

5.1 Introduction

Some types of biomass ash have chemical and mineralogical composition that make them subjected to several chemical reactions when exposed to atmosphere. As other alkaline waste, biomass ash is spontaneously prone to carbonation, that constitutes the most important phenomenon in the ageing/weathering process and has an impact on the environmental behavior, that is worthy for investigation. Indeed, carbonation causes a pH decrease and a subsequent change in the leaching properties, which could be either positive or negative for the environment on the basis of the chemical species taken into consideration. On one side, most of the metals and metalloids are fixed into insoluble minerals, but on the other side, some others could become more soluble; as a whole, these effects should be regarded for any management option that might eventually be proposed.

In additiom, since the early 2000s, accelerated carbonation of alkaline waste has been considered one technique for pursuing the carbon dioxide sequestration. This option is considered safer and faster than geological sequestration and is recommended by the IPCC [28]. Following this scope, many studies on the accelerated carbonation of several alkaline industrial residues were developed in order to accelerate and/or maximize the CO_2 uptake.

Based on these assumptions, this Chapter focuses on the effect of carbonation on selected types of biomass combustion residues (fly and boiler ash) in terms of chemical and mineralogical composition, and the performance of such residues as a substrate for CO_2 sequestration.

The objectives of the research line presented in this Chapter were:

(i) the study of the environmental behavior of boiler and fly ash when subjected to carbonation, that is the most representative transformation occurring during the spontaneous ageing process,

(ii) the assessment of the potential CO_2 sequestration capacity of such residues in the view of proposing them as a substrate for mineralogical carbon capture and sequestration (CCS).

Leaching tests and XRD analysis were conducted on ash that underwent carbonation. Several accelerated carbonation tests were conducted and the process conditions optimal for sequestering CO_2 were sought. The assessment of the potential carbon dioxide sequestration was finally conducted taking into account the amount of ash produced within a timeframe. These results were compared to the greenhouse gases (GHG) direct and indirect emissions generated by a typical supply chain, trying to ideally merge two environmental issues concerning power generation: the solid waste generation and greenhouse gaseous emissions.

5.2 State of the art

Carbonation is a chemical process naturally occurring when alkaline materials are exposed to wet conditions and atmospheric CO_2 [23]. Basically, carbonation consists in a process where CO_2 is fixed in mineral forms that are thermodinamically stable. A certain degree of carbonation occurs when waste is exposed to the described conditions prior (through a pre-treatment method) or as a consequence of the planned disposal. Yan [47] described the phenomena that concur to ash weathering with the scheme reported in Figure 5.1, among which there is carbonation.

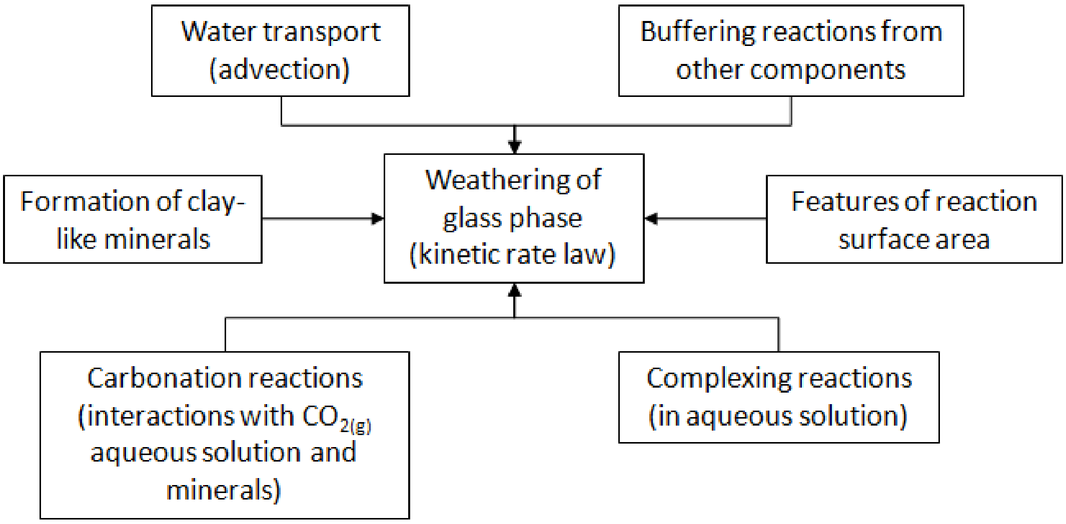

Fig. 5.1. Phenomena that influence the ash weathering process [48].

Weathering affects the waste properties on a time scale of decades, so that waste exposed for a long time to atmospheric CO_2 have chemical and physical properties different from fresh waste. Long-time exposure generates effects on the environmental behavior of an alkaline residue, of which the one of major concern is leaching. Though carbonation is not the unique transformation occurring during ageing and other types of chemical and mineralogical changes affect alkaline residues [6], carbonation is the one that affect leaching the most and well represents long-time weathering [13,37]. Though it is important to know at what extent it will affect the environmental impact of the waste disposed, the knowledge on this issue is still scarce [24].

On the other side, mineralogical carbonation constitutes a way to immobilize CO_2 and IPCC [28] has recommended it as a valid option among the carbon capture and storage (CCS) or carbon capture and utilization (CCU) techniques, the latter being attained when recycling of the produced carbonates into low-cost construction materials is also viable [3,11,34]. In particular, mineralogical carbonation is introduced as an alternative to geological sequestration, that raises many concerns about safety and manifests slow uptake kinetics. Following to IPCC [28] recommendations, the tendency of some alkaline waste to sequestering CO_2 was widely studied with the aim of assessing the potential carbon dioxide sequestration. Several industrial waste have an alkaline and earth-alkaline composition similar to the minerals typically proposed for mineralogical carbonation (Tab. 5.1-5.2). Industrial waste demonstrated to be more reactive than natural minerals, and this feature contributed to push mineralogical sequestration forward. Particular attention was paid to the ash generated by thermal processes, such as coal combustion and municipal waste incineration, whose residues are presented in Table 5.3, because they contain the chemical species mainly involved in natural carbonation, particularly calcium and magnesium oxides (as a result of the oxidation reactions) and silicates.

There are several methods to conduct mineral carbonation, which were summarized by Pan et al. [34] according to the scheme reported in Figure 5.2.

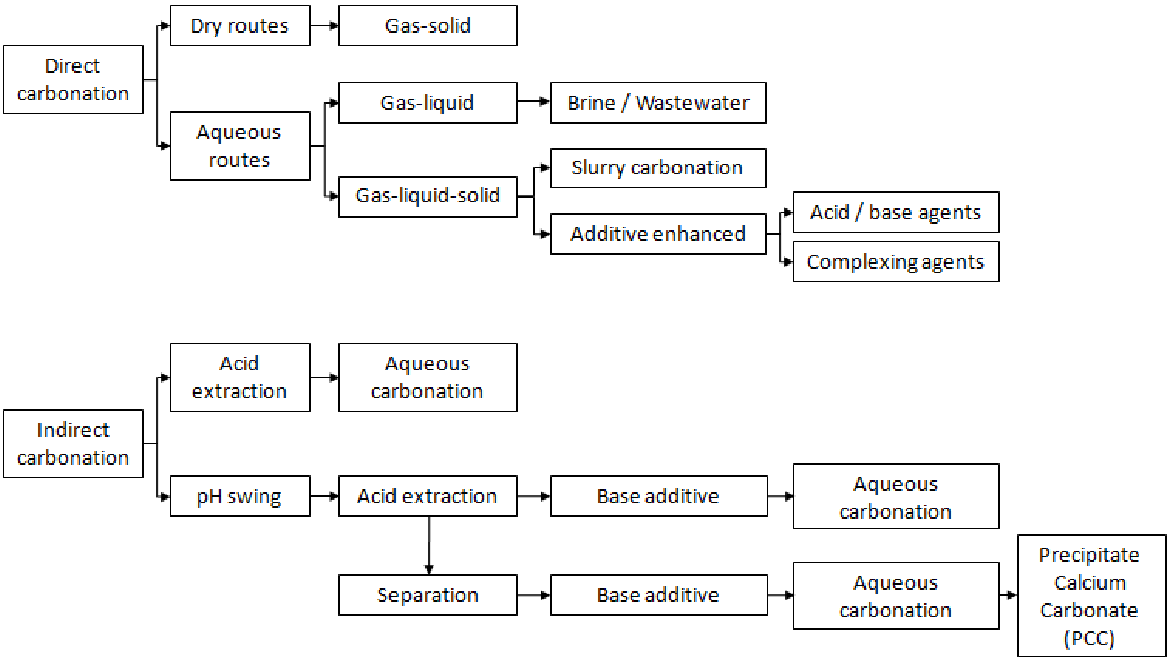

Fig. 5.2. Paths for conducting accelerated carbonation [34].

Firstly, a distinction between direct and indirect carbonation could be made. The former consists in a one-step process where the material is directly subjected to carbonation; in the latter, the alkaline metal is extracted from the mineral matrix by means of acid extraction or pH swing before being subjected to carbonation. While indirect carbonation requires high amounts of alkaline materials and conducts to the formation of intermediate products, direct carbonation is considered less energy-consuming and easier to manage [34].

Direct carbonation could be conducted under several liquid to solid (L/S) ratios, meaning that various ways for CO_2 diffusion in the substrate exist: the gas-solid carbonation occurs under dry conditions ($L/S < 0.2\ L \cdot kg^{-1}$), the liquid-solid carbonation under wet conditions (L/S > 5 L·kg^{-1}), and the gas-liquid-solid carbonation is obtained where gas bubbles are diffused in an aqueous medium. The direct aqueous carbonation consists in a set of at least three stages, which are related to:

(i) the dissolution of the gaseous CO_2 ($CO_{2(g)}$) in water ($CO_{2(l)}$).

(ii) The dissociation of $CO_{2(l)}$, as described by Equation 5.1:

$$CO_{2(g)} + H_2O_{(l)} \leftrightarrow CO_3^{2-} + 2H^+ \qquad (5.1)$$

Therefore, moisture is essential to make carbonation happens, because this step basicly consists in the hydration of carbon dioxide into carbonic acid.

(iii) the formation of carbonates because of the reactions with some chemical species present in the material used. The tendency of absorbing CO_2 is related to the chemical and mineralogical composition of the substrate; in particular, (hydro)oxides of calcium, magnesium, sodium and potassium are reactive to CO_2 exposure. Among them, calcium hydroxide (portlandite, $Ca(OH)_2$) is the most reactive and forms calcium carbonate ($CaCO_3$) spontaneously with the CO_2 dissolved in the aqueous medium according to the reaction expressed by Equation 5.2.

$$Ca(OH)_{2(s)} + H_2CO_{3(l)} \leftrightarrow CaCO_{3(s)} + 2H_2O_{(l)} \qquad (5.2)$$

Portlandite is generated by the calcium oxide hydration (Equation 5.3):

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} \qquad (5.3)$$

These two steps could be described as a whole, as reported in Equation 5.4:

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} \qquad (5.4)$$

Similarly, magnesium oxide participates to carbonation reactions, according to the reactions reported in Equations 5.5-5.6. Also sodium and potassium (Na_2O or NaOH, and K_2O or KOH) are subjected to carbonation but their contribution is usually negligible.

$$MgO_{(s)} + H_2O_{(l)} \rightarrow Mg(OH)_{2(s)} \qquad (5.5)$$

$$Mg(OH)_{2(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)} + H_2O_{(l)} \qquad (5.6)$$

Tab. 5.1. Chemical composition [%wt$_{d.b.}$] of some industrial waste (BF: blast furnace ; CBD: cement bypass dust; CKD: cement kiln dust; GGBS: ground granulated blast furnace slag; LF: ladle furnace; PS: phosphorus slag; SS: steel slag; SWS: steel wastewater sludge; n.d.: not determined).

	BF [17]	**CBD** [24]	**CKD** [24]	**GGBS** [16]	**LF slag** [4]	**PS** [16]	**Red mud** [47]	**SS** [16]	**SWS** [24]
Al_2O_3	9.4	4.4	4.6	12.5	4.6	2.6	20.1	2.7	2.0
CaO	40.6	66.3	46.2	39.0	58.1	46.7	3.0	38.4	7.9
Fe_2O_3	0.9	2.7	2.9	0.5	4.8	0.8	31.9	22.5	71.7
K_2O	0.6	1.7	3.9	n.d.	0.0	n.d.	n.d.	n.d.	0.1
MgO	10.7	1.1	1.5	8.7	6.2	1.2	n.d.	9.0	2.6
MnO	0.5	n.d.	n.d.	0.3	2.2	0.1	n.d.	3.6	n.d.
Na_2O	n.d.	0.3	0.5	n.d.	n.d.	n.d.	6.0	n.d.	0.3
SiO_2	34.1	17.8	16.4	34.6	26.4	43.1	8.5	12.1	0.8
SO_3	4.3	4.6	22.3	n.d.	0.4	n.d.	n.d.	n.d.	8.0

Tab. 5.2. Chemical composition [%wt$_{d.b.}$] of some natural minerals (n.d.: not determined).

	Bauxite [24]	**HT, non-mag antigorite** [34]	**Magnetic antigorite** [34]	**Non-mag antigorite** [34]	**Non-mag lizardite** [34]	**Olivine** [34]	**Olivine** [48]	**Serpentine** [34]	**Serpentine** [48]	**Wollastonite** [48]
Al_2O_3	79.6	0.3	0.2	0.2	1.5	0.2	4.6	0.2	2.2	0.9
CaO	0.1	0.2	0.1	0.0	0.3	0.1	5.9	0.1	0.0	42.1
Fe_2O_3	13.6	n.d.	n.d.	n.d.	n.d.	n.d.	6.8	n.d.	1.2	0.2
K_2O	0.1	0.0	0.0	0.0	0.0	0.0	n.d.	0.0	n.d.	n.d.
MgO	0.0	49.7	25.7	38.5	39.5	49.7	32.3	40.6	40.6	1.2
MnO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Na_2O	0.0	0.0	0.0	0.0	0.0	0.1	n.d.	0.0	n.d.	n.d.
SiO_2	3.4	42.7	19.9	37.2	38.8	41.4	48.7	36.2	52.1	55.6
SO_3	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	n.d.	0.1	n.d.

Tab. 5.3. Chemical composition [%wt$_{d.b.}$] of some residues from thermal processes (APC: air pollution control; BA: bottom ash; FA: fly ash; MSWI: municipal solid waste incinerator; PSIA: paper sludge incinerator ash; n.d.: not determined).

	APC [7]	**Coal FA** [31]	**MSWI-BA** [24]	**MSWI-FA** [24]	**PSIA** [24]
Al_2O_3	0.7	n.d.	14.5	15.8	5.5
CaO	30.8	5.0	33.1	32.1	60.0
Fe_2O_3	0.2	3.9	7.9	3.4	1.7
K_2O	4.1	n.d.	1.1	0.8	0.2
MgO	2.9	n.d.	2.8	3.4	1.4
MnO	0.0	n.d.	n.d.	n.d.	n.d.
Na_2O	2.0	n.d.	2.2	1.8	0.3
SiO_2	3.0	n.d.	5.2	32.4	23.8
SO_3	0.0	n.d.	27.9	3.6	5.1

Generally, substrates having highly reactive calcium and magnesium species are more prone to carbonation under common conditions of moisture and pressure. Though calcium and magnesium oxides are the most prone to react with CO_2, other mineral forms such as silicates bearing calcium or other alkaline species could participate to the CO_2 fixation as well, as shown in Equation 5.7 [9].

$$2CaO_{(s)} \cdot SiO_{2(s)} + 2H_2CO_{3(l)} \rightarrow 2CaCO_{3(s)} + SiO_{2(s)} + 2H_2O_{(l)} \tag{5.7}$$

All the Equations 5.2-5.7 are characterized by negative enthalpy of formation, that means they can occur spontaneously, though very slowly.

Since the ability of a substrate of sequestering CO_2 depends on the chemical and mineralogical composition, several formulas to calculate the theoretical CO_2 uptake on the basis of the elemental and mineralogical analyses were proposed. The Steinour formula relates the theoretical carbon sequestration capacity to the total content of the chemical species that are the most relevant for this purpose. In relation to the chemical and mineral species present in each waste, various modified expressions of such relationship were proposed.

$$CO_2(\%) = 0.785(CaO - 0.7SO_3) + 1.091Na_2O + 0.935K_2O \tag{5.8}$$

$$CO_2(\%) = 0.785CaO + 1.091MgO + 1.41Na_2O + 0.935K_2O - 0.55SO_3 \quad (5.9)$$

$$CO_2(\%) = 0.785\,(CaO - 0.56\,CaCO_3) \; + \; 1.091\,MgO + 0.276Fe_2O_3 + 0.62MnO - 0.55SO_3 \quad (5.10)$$

$$CO_2(\%) = 0.785(CaO - 0.53CaCO_3 - 0.7SO_3) + 1.091MgO + 0.71Na_2O + 0.468(K_2O - 0.632KCl) \quad (5.11)$$

In Equation 5.11, the positive action of calcium, magnesium, potassium and sodium total content is considered. Calcium carbonate and sulfur are accounted for their negative contribution to carbon sequestration because calcite and metal sulfates are mineral forms that result from carbonation reactions already occurred in the substrate before the treatment [35].

The extent of carbonation in the exposed waste depends on the ambient conditions existing at the time of exposure. The variables influencing carbonation are temperature, water content, CO_2 partial pressure, presence of acid rains, particle size of the alkaline residues that constitute the substrate of interest [9].

- Moisture is a key parameter since it provides the water content essential for carbon dioxide hydration and formation of carbonic acid. The water content allows the gas to permeate the substrate, but excess water hinders the CO_2 diffusion in the medium [20,23,42]. Hence, if the aqueous route for carbonation is the path pursued, various experiments should be made to assess what liquid-solid ratio would be the most preferable. Water is an essential factor in natural ageing as well (i.e. rains), and strictly affects the reaction time [25].

- Temperature influences the CO_2 solubility and carbonation kinetics in terms of buffering reaction rate. In particular, the calcium ions are dissolved in an aqueous medium more efficiently when temperature increases, but CO_2 solubility decreases [34]. As a whole, according to some authors, temperature does not affect carbonation positively [9,23,42] and, whenever it was improved by the temperature increase (values higher than 40°C), it is plausible that, after a certain time exposure, the yields of carbonation reactions occurring at room temperature would equalize the ones attained at higher temperature.

- Carbon dioxide partial pressure is relevant because it is connected to the CO_2 solubilization; the maximum amount of carbon dioxide involved in solubilization does not change though, while the carbonation kinetics are influenced by CO_2 partial pressure positively [35].

- Acid rains affect the CO_2 uptake negatively, since the carbonates dissolution is favored by an acid environment and CO_2 is released to the atmosphere [1].
- As for the particle size, it has proven to be effective in influencing the carbon dioxide uptake because the particle size reduction increases in the specific surface that reacts with CO_2, as Baciocchi et al. [2] demonstrated.

Accelerated carbonation was introduced as a way to maximize and accelerate the CO_2 uptake. Indeed, it is aimed at attaining complete carbonation in a shorter time than under natural conditions by the control of parameters such as the CO_2 partial pressure and substrate moisture content, and approaching the maximum CO_2 uptake that the chemical and mineralogical composition of a given residue might predict. The maximum level of CO_2 sequestration attainable is represented by the theoretical carbon dioxide uptake, however everyone of the formulas proposed does not consider most of the substrate mineralogy. Mineral stable forms of the reactive chemical species do not participate to carbonation reactions, so that their contribution has to be detracted from the total amount of the respective elements. The only way to assess the effective CO_2 potential is to conduct experimental tests where the carbonation process is performed under controlled conditions. Many experimental works were conducted by other authors, and the theoretical and effective CO_2 uptake determined for some waste types are displayed in Table 5.4. The corresponding equipment and operating conditions used are also reported.

Tab. 5.4. Theoretical and effective CO_2 uptake for industrial waste (APC: air pollution control; BA: bottom ash; BF: blast furnace; CBD: cement bypass dust; CKD: cement kiln dust; FA: fly ash; GGBS: ground granulated blast furnace slag; LF: ladle furnace; MSWI: municipal solid waste incinerator; PS: phosphorus slag; PSIA: paper sludge incinerator ash; SS: steel slag; SWS: steel wastewater sludge).

Reference	**Waste**	**Theor. uptake [g $CO_2 \cdot kg^{-1}$ residue]**	**Eff. uptake [g $CO_2 \cdot kg^{-1}$ residue]**	**Method**	**Equipment**	**Operating conditions**
[4]	LF slag	522	247	Direct carbonation	Stirred Pyrex flask (250 mL)	15% CO_2 at atmospheric pressure; 20°C; L/S 10.0 $L \cdot kg^{-1}$; T = ambient; t = 24 h
[7]	APC	434	200	Direct aqueous carbonation	Open vessel	100% CO_2 at atmospheric pressure; L/S 2.5 $L \cdot kg^{-1}$; T = 20°C; t = 3 h
[16]	GGBS	401	271	Indirect carbonation:dissolution with NH_4HSO_4 or $(NH_4)_2CO_3$ and pH adjustment	500 mL stirred necks glass flask	L/S from 15 to 50 $L \cdot kg^{-1}$; T = 65°C; t = 1 h
	PS	380	226			
	SS	400	358			
[17]	BF	415	227	Indirect carbonation: (pH-swing) with NaOH and CH_3COOH addition	Stirred glass reactor (400 mL)	100% CO_2 from 1 to 40 bar; L/S 2.5 $L \cdot kg^{-1}$; T = 20°C; t = 3 h
[24]	CBD	517	255	Direct aqueous carbonation	Pressurized reaction vessel	100% CO_2 at 2 bar; Relative Humidity = 75%; t = 72 h
	CKD	278	88			
	MSWI-BA	158	45			
	MSWI-FA	286	67			
	PSIA	461	250			
	SWS	49	0			

continue

Reference	**Waste**	**Theor. uptake [g $CO_2 \cdot kg^{-1}$ residue]**	**Eff. uptake [g $CO_2 \cdot kg^{-1}$ residue]**	**Method**	**Equipment**	**Operating conditions**
[28]	CKD	298 377	227 290	Direct carbonation	Ventilated stainless steel 288 L box Packed glass column (L = 6 cm; D = 5 cm)	100% RH; 80% CO_2 at atmospheric pressure; L/S from 0 to 1.25 $L \cdot kg^{-1}$; 8 days
[31]	Coal FA	39	26	Direct aqueous carbonation	Stirred titanium reactor	CO_2 10, 20, 30, 40 bar; 30 or 60°C; 2 h
[47]	Red Mud	66	38	Direct carbonation	Stainless steel chamber	100% CO_2 at atmospheric pressure at 3.5 bar; L/S from 0.3 to 0.5 $L \cdot kg^{-1}$; t = 11 h

Several physical transformation could be observed in the residues that underwent carbonation. Temperature increases because of exothermic carbonation reactions; sample dry mass increase because of the fixation of CO_2 [35]; sample volume increases [23]; and the pH level of the water/residue suspension decreases as CO_2 reacts. The pH decrease is the most important transformation and involves the environmental properties because pH affects metal mobilization. The initial pH value of the alkaline waste undergoing carbonation is very high [9]. During carbonation, a buffering effect could be observed and pH decreases from a initial values of 12-13 to final levels of 8-9, when and the waste becomes stable. The final pH corresponds to the level where most of the heavy metals show their minimum solubility. Indeed, the minimum release of most of the heavy metals is observed at pH around 8-9, so that carbonation is often beneficial for the environment. Some heavy metals could also form insoluble precipitates with the newly constituted carbonates, which also contributes to diminish the pollutants release. So, there are two mechanisms that relate carbonation to the immobilization of metals: the direct metal stabilization into insoluble minerals, and the reduction of metal solubility indirectly obtained by changing the pH value of the aqueous medium. For this reason Diener et al. [13] suggested that carbonation is the transformation that affect the leaching behavior the most, and many authors studied carbonation as a way to stabilize heavy metals in alkaline waste, reducing hazardousness and allowing a safe disposal [20,23]. Several studies focused on the reduced solubility of most of the heavy metals [5,7,9,35,42]. For instance, Gunning et al. [24] reported that in electric arc furnace slags, Ba and Sr solubility was diminished by carbonation. In fly ash generated by municipal solid waste incineration Bosio et al. [5] described the beneficial effects of carbonation on the Pb and Zn solubility, and Cappai et al. [7] also observed a reduction in the Cu and Cr release. Nonetheless, the solubility of some other metals, present as oxyanionic species (Sb, Mo, As), increased after carbonation. Cappai et al. [7] observed an increase in Sb solubility in municipal incineration residues subjected to carbonation, and other authors reported higher selenium and vanadium release in the carbonated residues than in the untreated ones [24,42].

Similarly to such alkaline waste, selected types of biomass combustion ash could be subjected to carbonation. Biomass ash is naturally prone to carbonation when exposed to weathering conditions and natural ageing, after it is intentionally spread to the soil, or wood stumps and invasive weeds are burnt, or fires occur. Burning biomass, which is a long-lasting practice in many countries, has the scope of returning organic carbon and minerals to the soil, but in a time of decades it could provoke some adverse effects on the soil chemistry. Till now, these effects, particularly in relation to the exposure to moisture and atmospheric CO_2, has not been fully investigated [24]. Due to its physical properties and chemical composition, biomass ash could also be a promising CCS substrate (Tab. 5.5). The theoretical and effective CO_2 uptake determined for biomass ash, and the equipment and operating conditions used by other authors are displayed in Table 5.6.

Tab. 5.5. Chemical composition [$\%wt_{d.b.}$] of ash generated by the combustion of biomass proposed as a substrate for accelerated carbonation (BA: biomass ash; BTA: bottom ash; BOA: boiler ash; CFBF: circulating fluidized bed furnace; GF: grate furnace; WA: wood ash; n.d.: not determined).

	BA [24]	**BTA GF** [44]	**BTA BOA GF** [44]	**FA CFBF** [44]	**WA** [24]
Al_2O_3	0.3	7.5	7.6	3.3	2.6
CaO	24.2	38.8	38.8	6.7	45.5
Fe_2O_3	0.7	3.7	3.6	0.4	1.3
K_2O	21.2	5.0	5.2	5.4	14.0
MgO	8.8	7.4	7.3	1.0	6.9
MnO	n.d.	1.3	1.4	0.2	n.d.
Na_2O	0.3	0.6	0.7	0.4	0.9
SiO_2	5.1	25.0	25.2	80.6	17.0
SO_3	3.3	0.2	0.3	0.2	0.6

Tab. 5.6. Theoretical and effective CO_2 uptake for ash generated by the combustion of biomass (BA: biomass ash; BTA: bottom ash; BOA: boiler ash; CFBF: circulating fluidized bed furnace; GF: grate furnace; WA: wood ash).

Reference	**Biomass ash**	**Theor. uptake [g $CO_2 \cdot kg^{-1}$ g residue]**	**Eff. uptake [g $CO_2 \cdot kg^{-1}$ residue]**	**Method**	**Equipment**	**Operating conditions**
[24]	BA	369	8	Direct aqueous carbonation	Pressurized reaction vessel	100% CO_2 atmosphere at 2 bar; Relative Humidity = 75%; t = 72 h
	WA	501	75			
[44]	BTA GF	412	178	Direct carbonation	Open and airtight storage	Sample moisture = 16.7%; t = 16 weeks
	BTA BOA GF	412	299		Open	Sample moisture = 16.7%; t = 16 weeks
	FA CFBF	91	47		Open	Sample moisture = 17.4%; t = 16 weeks

If the composition of biomass ash samples proposed by other authors as a substrate for accelerated carbonation is observed (Tab. 5.5), it could be noticed that in almost all of the samples calcium is the most abundant element. The sample where the lowest calcium level was observed (FA CFBF), displayed the lowest theoretical and effective CO_2 uptake. The theoretical carbon dioxide uptake values were comparable to the ones reported for other industrial residues, such as paper sludge incineration ash, air pollution control waste, ground granulated blast furnace slag, phosphorous slag and steel slag (Tab. 5.6). The effective CO_2 uptake varied greatly, as also happened for the industrial residues, possibly in dependence to the different operating conditions operated. It should be deduced that, for each residue, specific conditions should be identified that maximize its potential as a substrate for accelerated carbonation.

The reuse of biomass ash as a substrate for mineralogical CCS would provide the power generation from biomass with a higher degree of sustainability. Indeed, sustainability of energy production from biomass is nowadays argued. However, few literature works are available on its use for reducing CO_2 emissions. Biomass combustion is conventionally considered carbon neutral in relation to the direct emissions, because it is assumed that the CO_2 generated by thermal plants will be counterbalanced by the carbon captured by the next crop [39]. This assumption is adopted by the current European Union Emission Trading System [14], so that the direct GHG emissions generated by biomass combustion is set to zero, though it does not represent the emissions actually generated at the thermal power plants' stacks and by the supply chain of feed biomass.

Though biomass is regarded as a "green" energy source [31], the combustion emits greenhouse gases and its massive recourse raises an environmental concern related to the gaseous emissions. Of great importance are the indirect emissions generated by the production, harvesting and transport operations. Indeed, if referred to the whole biomass supply chain, carbon dioxide emissions become more significant, and a concern on the biomass environmental impact raises. The unsustainable use of natural resources and the impact related to the biomass supply chain management contribute to the GHG overall emissions at any scale. For this reason, a revision of the EU GHG inventory is under study, in order to include the land use, change of land use and forestry sector in the emissions accountability [19].

The assessment of the potential carbon dioxide sequestration of biomass ash is a piece of information useful to compare biomass ash to other similar alkaline residues, at present considered as a valuable CCS substrate, and a step forward into the awareness of the environmental impact, in terms of gaseous emissions, that power generation for biomass actually provokes.

5.3 Materials and Methods

5.3.1 Chemical and mineralogical determinations

Fly and boiler ash were considered as a substrate for accelerated carbonation because of their alkaline composition. According to the ash chemical and mineralogical composition described in Chapter 3, calcium oxide represented 41.4 $\%wt_{d.b.}$ and 24.7 $\%wt_{d.b.}$ of the dried fly and boiler ash, respectively; while, magnesium oxide was 4.3 $\%wt_{d.b.}$ and 5.5 $\%wt_{d.b.}$ of the total dry fly and boiler ash mass, respectively. The mineralogical analysis showed that fly ash contained portlandite ($Ca(OH)_2$) and in both BOA and FA calcium silicate hydrate was present.

In addition to the chemical characteristics and physical properties reported in Chapter 3, the buffering capacity and mineralogical composition of the selected biomass ash were determined. After carbonation, treated ash was characterized in terms of total carbon and calcite content, mineralogical composition, and leaching behavior.

ACID NEUTRALIZATION CAPACITY

The buffering capacity of uncarbonated fly and boiler ash was evaluated by means of the acid neutralization capacity (ANC) tests by the addition of increasing pre-selected amounts of nitric acid (HNO_3) at L/S 10.0 $L \cdot kg^{-1}$ and stirring the suspension for 48 hours, according to UNI 15364:2006.

MINERALOGICAL COMPOSITION

The ash mineralogy before and after carbonation was determined using a Rigaku Geigerflex X-ray diffractometer (XRD), with application of Cu-Kα radiation at 30 kV/30 mA and scan speed equal to 2° of 2θ/min between 4 and 60°.

TOTAL AND INORGANIC CARBON

An elemental analyzer (CHN-1000, LECO Corporation, MI, USA) was used to determine the total carbon content in ash after carbonation in accordance to ASTM D 5373. Calcimetry analysis was conducted in order to determine the calcite content in the untreated and treated ash, by placing 0.5 - 1.0 g of dried sample in a Dietrich-Fruehling apparatus and adding 10 ml of HCl 1:1 v/v.

LEACHING TEST

Batch, one-stage leaching tests were performed on ash after carbonation at a liquid to solid ratio of 10.0 L·kg^{-1} according to UNI EN 12457-2:2004 for materials with particle size below 4 mm. The eluates were analyzed for the water-soluble fractions of major and minor elements by ICP Spectrometry (ICP-OES, Optima 7000DV, PerkinElmer, MA, USA). The pH of the eluates was determined according to UNI EN 15933:2012. These results were compared to the corresponding values obtained for untreated ash.

5.3.2 Experimental setup

Carbonation tests were performed on suspensions of ash and distilled water at several liquid/solid ratios. Liquid to solid ratios of 1.0, 2.5, 5.0, and 10.0 L·kg^{-1} were tested. Each suspension was prepared by using 100 g of dried ash and the corresponding amount of distilled water in a glass beaker and mixing with a magnetic stirrer until the suspension was homogeneous. A preliminary test at 2.5 L·kg^{-1} was conducted to investigate the behavior of the biomass ash types when subjected to CO_2 exposure. The equipment used was constituted by an airtight glass reactor, whose bottom was provided with a bed of water and salt to saturate the incoming CO_2, that was blown through the water/residues mixtures at constant flow, ambient temperature and atmospheric pressure. The CO_2 pressure inside the glass reactor was maintained at 1 bar by regulating the gas gauge of the pressurized tank. The weighing dishes containing the wet suspension samples were placed in the reactor as shown in Figure 5.3, and withdrawn at pre-selected set times of 6, 24, 30, 48 and 72 hours.

After the preliminary trials, a pressurized reactor filled with CO_2, whose details are shown in Figure 5.4, was used to conduct the accelerated carbonation tests. In Figure 5.5 a fly ash sample before (i.e. wetted) and after an experiment is depicted.

Fig. 5.3. Airtight glass reactor.

Fig. 5.4. Stainless steel reactor.

Fig. 5.5. Fly ash before (left) and after (right) the accelerated carbonation treatment.

The pressurized reactor was constituted by an inner Teflon vessel having a 1700 mL working capacity inserted in an outer stainless steel cylinder SS 316TI. The reactor had a maximum operating pressure of 200 bar and could be heated by an electrical resistance placed in the outer cylinder. Nonetheless, the carbonation tests described hereby were conducted at room temperature. A stirrer and a sampling tube in PTFE were connected to the lid and sank inside the Teflon vessel, the former being additionally connected to a speed regulator (0-500 rpm). The reactor lid was made in stainless steel SS 316TI and equipped with ports for the gas inlet and outlet valves, and liquid sample extraction. A pressure gauge was mounted on the reactor lid to control the inner pressure of the reactor.

The L/S 1.0 and 2.5 $L \cdot kg^{-1}$ suspensions were used for a wet route process, placed in thin layers inside weighing dishes and then inserted into the Teflon inner vessel of carbonation reactor; while the L/S 5.0 and 10.0 $L \cdot kg^{-1}$ suspensions underwent a slurry route process and were poured directly inside the inner carbonation vessel. When conducting the tests under wet route process, a solution of water and salt to saturate the incoming CO_2 was also placed inside the Teflon vessel.

Analytical grade carbon dioxide supplied by a pressurized tank was used. The CO_2 inlet pressure was maintained equal to 1 bar to simulate the least burdensome conditions. When the internal pressure decreased because of CO_2 consumption, and at each set time, pressure of 1 bar was manually restored.

During carbonation tests, sampling at set times between 5 and 360 minutes was performed. As for wet route processes, this required the reactor being depressurized and opened, and the pre-set conditions restored, whilst during the slurry carbonation tests, samples of treated ash were extracted by means of a sampling duct.

Samples from the wet routes were oven-dried at 40°C for 48 hours and prepared for the successive analyses; while, samples from the slurry suspensions were filtered at 1.2 μm before being oven-dried at 40°C for 48 hours. The liquid obtained was used for pH determinations.

5.3.3 Calculations

The ash chemical and mineralogical composition described in Chapter 3 suggests that Equation 5.11 is the most complete for this kind of residue, and is therefore the one used in Section 5.4 for the theoretical CO_2 uptake calculation.

On the basis of the total carbon content of the ash untreated and treated, the corresponding effective CO_2 uptake was calculated by using Equation 5.12 or Equation 5.13, which consider the total carbon content or the calcite amount, respectively.

$$CO_{2(any\ time)} = 3.67 \cdot C_{(any\ time)} \tag{5.12}$$

$$CO_{2(any\ time)} = 0.4397 \cdot \frac{CaCO_{3(any\ time)}}{10} \tag{5.13}$$

where:

$CO_{2(any\ time)}$ is the equivalent carbon dioxide amount [%wt$_{d.b.}$].

$C_{(any\ time)}$ is the total carbon content [%wt$_{d.b.}$];

$CaCO_{3(any\ time)}$ is the calcium carbonate content [g·kg$^{-1}_{d.b.}$].

The effective carbon dioxide uptake was evaluated by determining the variations, calculated with Equation 5.12 or 5.13, between the untreated and treated samples, using Equation 5.14.

$$CO_2 uptake = \frac{CO_{2(aftercarbonation)} - CO_{2(initial)}}{100 - CO_{2(aftercarbonation)}} \tag{5.14}$$

where:

$CO_{2\,uptake}$ is the carbon dioxide effective sequestration [%wt$_{d.b.}$];

$CO_{2(after\ carbonation)}$ is the equivalent CO_2 amount at any time [%wt$_{d.b.}$];

$CO_{2(initial)}$ is the equivalent CO_2 amount in the initial (untreated) sample [%wt$_{d.b.}$].

For each carbonation test, the effective CO_2 uptake was compared to the theoretical one, in order to evaluate whether the maximum degree of carbonation was reached and which conditions generated the highest CO_2 uptake level.

The assessment of the potential carbon dioxide sequestration was conducted taking into account the amount of ash produced in a timeframe and the plant emission factor. Finally, estimates of the net GHG emissions generated by using biomass as a fuel and the comparison with the CO_2 potentially absorbed by ash that underwent carbonation were made.

5.4 Results

5.4.1 Results of the characterization targeted to accelerated carbonation

The mineralogical analyses revealed the presence of calcium-bearing minerals, such as CaO, that influences carbonation reactions [23]. In particular, the mineralogical composition, as described by the X-ray diffraction, revealed the prevalence of calcium-bearing minerals in FA, and also identified different calcium-bearing minerals contained in both the ash types analyzed. Calcium was present as silicate, carbonate and sulfate hydrate in BOA and FA, and as hydroxide in FA. In particular, portlandite ($Ca(OH)_2$) was one of the most representative minerals in FA, where gehlenite ($Ca_2Al_2SiO_7$), albite ($(N,Ca)(Si,Al)_4O_8$), aphthitalite ($K_3Na(SO_4)_2$), syngenite ($K_2Ca(SO_4)_2$) were also identified. In BOA, calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$) were present. $CaCO_3$ was present in FA as well and might represent the result of a carbonation process already ongoing in both the ash types. Cliftonite (C) is a form of graphite and was observed in FA as well. These results are coherent with the above described chemical composition and consistent with literature studies [22,40-41,44].

As reported in Chapter 3, BOA and FA had an alkaline pH (12 and 13, respectively), due to the presence of alkali compounds, such as calcium hydroxides in fly ash. Fernández-Delgado Juárez et al. [21] observed that the presence of Ca, Mg and K, hydroxides and carbonates is responsible for the biomass ash buffering capacity at very strong alkaline pH values.

In order to acquire information about the reactivity of the selected ash types, the ANC curves were obtained. The results of the ANC test performed on BOA and FA are shown in Figure 5.6.

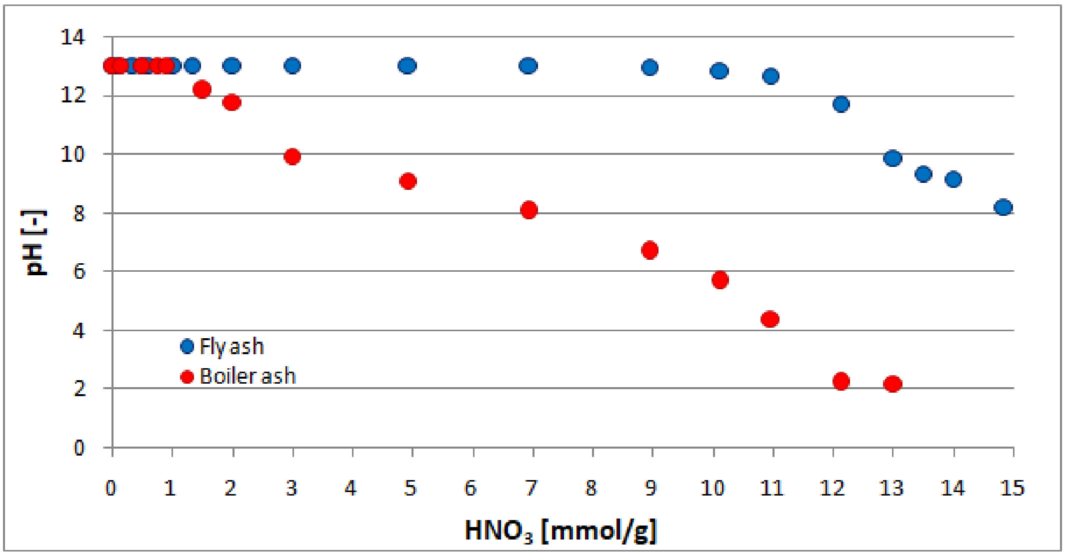

Fig. 5.6. ANC curves performed on boiler and fly ash.

The ANC was used by Cho et al. [9] as a way to estimate the carbon sequestration potential. As CO_2 dissolution and CO_3^{2-} formation proceeds, H^+ is released and pH decreases; nonetheless, the ability to do so changes as the pH value varies across the whole pH range, and only a qualitative information on the capacity of a given material to sequester CO_2 could be presumed from the ANC curve. On the other side, through the ANC curve, the ability to resist to acid attack maintaining alkaline pH levels is determined and, since metal solubility usually increases when pH drops to acid values, it represents an indicator of the environmental hazard under long-lasting atmospheric exposure [23,25]. The ANC curve obtained for FA showed that this ash type had a very high buffering capacity at alkaline values, expressed by the ability of maintaining the initial pH value above 8.0 even after a strong acid attack. The ANC curve obtained for BOA showed a very narrow plateau at alkaline values, followed by a decrease to pH values around 2.0 earlier and more irregularly than the one manifested by FA, suggesting that there are less mineral species that buffer. These trends suggest that FA is more suitable for the use as a CCS substrate than BOA, as the chemical and mineralogical analyses also predict.

5.4.2 Theoretical CO_2 uptake

The ash chemical composition allows estimating, through Equation 5.11, the theoretical CO_2 uptake, and the results are shown in Table 5.7.

Tab. 5.7. The BOA and FA theoretical CO_2 uptake.

	BOA	**FA**
Theoretical CO_2 uptake [g $CO_2 \cdot kg^{-1}$ residue]	291	390

A difference could be observed in the theoretical CO_2 uptake levels attained for BOA and FA that is coherent with the different chemical composition of the two types of residues. The theoretical uptake ascribable to FA is aligned with the values attained for the majority of the residues of biomass combustion proposed by other authors as substrates for accelerated carbonation and displayed in Table 5.6.

5.4.3 Preliminary carbonation tests

The carbonation tests carried out in the airtight glass vessel and stainless steel reactor gave the results described hereby. First, boiler and fly ash were subjected to a wet route carbonation in the glass reactor at L/S 2.5 $L \cdot kg^{-1}$, and the results were expressed in terms of total carbon and calcium carbonate content. These analytical determination conducted on the treated samples provided information on the process kinetics (Fig. 5.7). The total carbon content in fly and boiler ash subjected to carbonation increased along time. These results show that changes in the total carbon content of both the ash types occurred within 24 hours after the beginning of the test.

Tab. 5.8. Evolution of the total carbon content in BOA and FA during the carbonation test conducted at L/S 2.5 $L \cdot kg^{-1}$ in the airtight glass reactor (n.d.: not determined; standard deviation is indicated in brackets).

		Airtight glass reactor		
Time [hours]	**BOA C_{tot} [$\%wt_{d.b.}$]**	**BOA $CaCO_3$ [$g \cdot kg^{-1}_{d.b.}$]**	**FA C_{tot} [$\%wt_{d.b.}$]**	**FA $CaCO_3$ [$g \cdot kg^{-1}_{d.b.}$]**
0	5.55 (0.02)	109 (5)	2.44 (0.03)	263 (6)
6	5.65 (0.28)	198 (13)	6.91 (0.15)	515 (0)
24	5.90 (0.28)	221 (2)	7.03 (0.19)	532 (3)
30	6.07 (0.52)	n.d.	7.02 (0.06)	n.d.
48	6.34 (0.45)	224 (0)	7.24 (0.06)	568 (0)
72	5.98 (0.10)	224 (1)	7.24 (0.13)	600 (2)

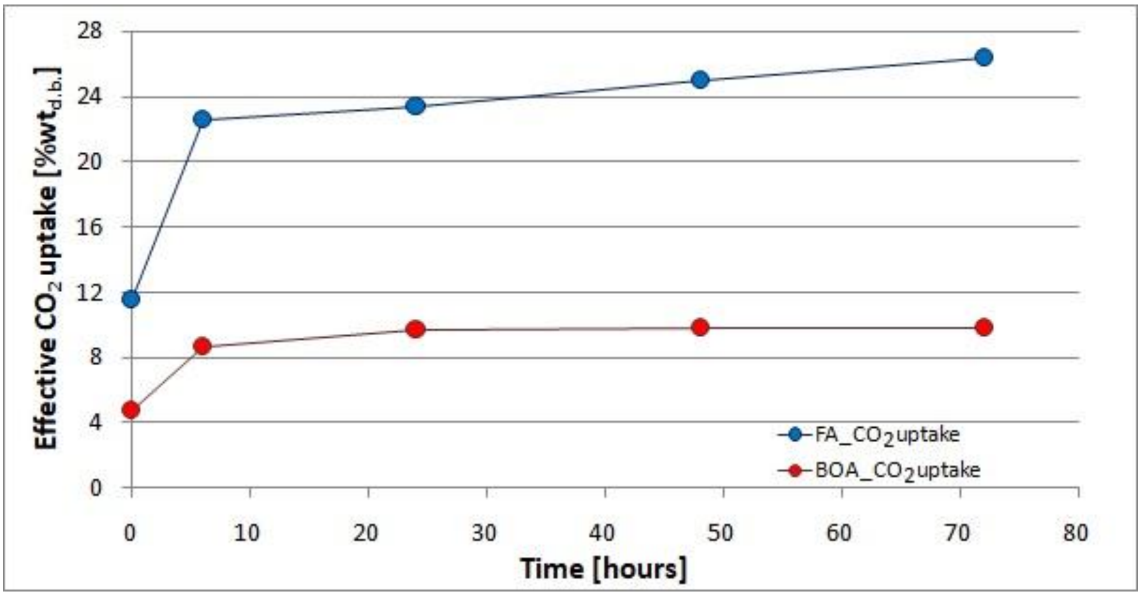

Fig. 5.7. Evolution of the effective CO_2 uptake during the carbonation tests performed at L/S 2.5 L·kg^{-1} in the airtight glass reactor.

A comparison between the two ash types highlighted that FA was far more reactive than BOA (effective CO_2 uptake of 26.4%wt and 9.8%wt, respectively), therefore the subsequent tests were conducted on FA only.

The FA wet route process at L/S 2.5 L·kg^{-1} was tested in both the reactor types. The results are shown in Figure 5.8 and Table 5.9.

Different reaction rates depending on the reactor configuration were observed and the carbonation kinetics was accelerated in the stainless steel reactor. Having different timescale, time was normalized by dividing the effective time values by the final time value of each experiment; the plot reported in Figure 5.8 was therefore obtained. Though attained in different timescale, the effective CO_2 uptake values attained at L/S 2.5 L·kg^{-1} with the two experimental equipments were comparable.

Tab. 5.9. Evolution of the total carbon content in FA during the carbonation tests conducted at L/S 2.5 L·kg^{-1} (n.d.: not determined; standard deviation is indicated in brackets).

Airtight glass reactor		**Stainless steel reactor**	
Time [hours]	**C_{tot} [%wt$_{d.b.}$]**	**Time [min]**	**C_{tot} [%wt$_{d.b.}$]**
0	2.44 (0.03)	0	2.99 (0.28)
6	6.91 (0.15)	15	6.38 (0.22)
24	7.03 (0.19)	30	6.67 (0.70)
30	7.02 (0.06)	60	6.69 (0.26)
48	7.24 (0.06)	120	7.23 (0.23)
72	7.24 (0.13)	150	7.30 (0.08)
n.d.	n.d.	180	7.21 (0.28)
n.d.	n.d.	240	7.48 (0.07)
n.d.	n.d.	270	7.38 (0.00)
n.d.	n.d.	300	7.07 (0.05)
n.d.	n.d.	360	7.22 (0.00)
n.d.	n.d.	420	7.37 (0.00)
n.d.	n.d.	480	7.52 (0.00)

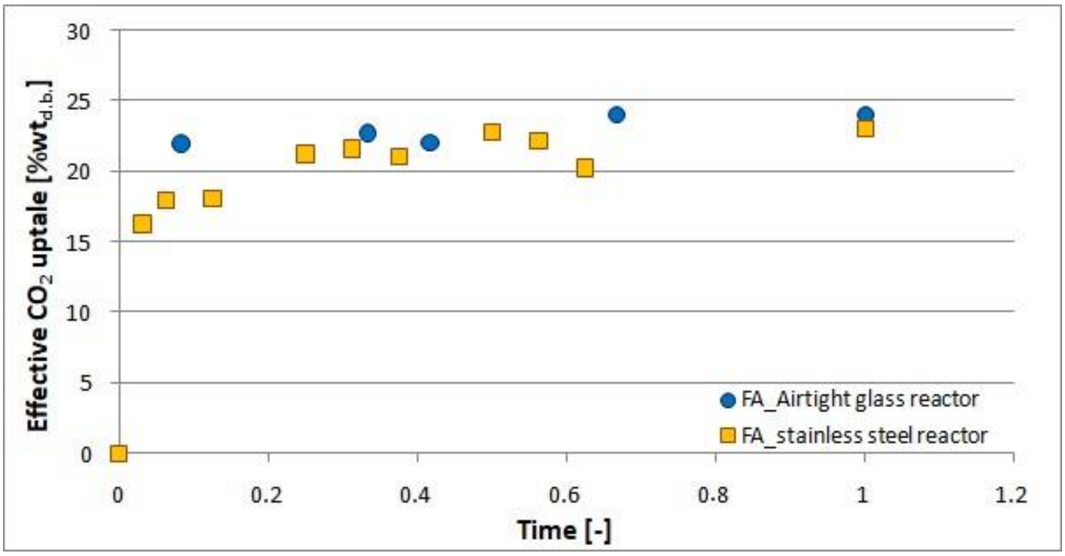

Fig. 5.8. Evolution of the effective CO$_2$ uptake during the carbonation tests performed at L/S 2.5 L·kg^{-1}.

5.4.4 Modifications in the leaching properties after carbonation

The heavy metal leachability is a fundamental analysis to determine the potential environmental hazard entailed with carbonation, being it a natural process or a treatment aimed at immobilizing CO_2. The results of the leaching test conducted on boiler and fly ash are shown in Tables 5.10-5.11.

Among the macro-elements, potassium is the most abundant one in the carbonated FA and BOA eluates, and chromium, molybdenum and selenium are the only heavy metals whose amounts are above the detection limit. By comparing the results before and after carbonation, Mo and Se were higher in the leachate of the carbonated ash than in the one of the untreated residues since, as previously said, oxyanions leachability increases after carbonation.

Chromium, copper (in fly ash) and zinc leachability decreased after carbonation, as also observed by Cappai et al. [7]. Barium leachability decreased after carbonation treatment, which could be explained by the fact that Ba is present as a trace in the newly formed calcite [26]. Lead leachability was lower in the carbonated fly ash than in the untreated one, as a consequence of the great affinity Pb has with calcite [36].

If a comparison between the results attained and the limit values set by the European Union legislation for the acceptance of waste at landfills [10] is made, selenium exceeded the limit value in both the treated boiler and fly ash, with a noticeable difference between the value observed in BOA and the limit set. It is relevant to remark such result, because it may represent a limit to the diffusion of biomass ash carbonation. On the other hand, these results are a useful information about the behavior of ash exposed to moisture and aerobic conditions.

Tab. 5.10. Results of the leaching test performed on FA before and after carbonation (at L/S 2.5 L·kg^{-1}), according to UNI EN 12457:2004 (< d.l.: below detection limit; standard deviation is indicated in brackets).

	Uncarbonated FA	**Carbonated FA**	**Limit values for non hazardous waste [10]**
pH	13.20 (0.03)	8.66 (0.99)	-
Al_2O_5 [mg·kg$^{-1}_{d.b.}$]	0.86 (0.00)	0.11 (0.00)	-
CaO [%wt$_{d.b.}$]	1.02 (0.10)	0.03 (0.00)	-
Fe_2O_3 [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	-
K_2O [%wt$_{d.b.}$]	12.06 (0.20)	0.84 (0.00)	-
MgO [mg·kg$^{-1}_{d.b.}$]	0.49 (0.05)	0.07 (0.00)	-
MnO_2 [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	-
Na_2O [%wt$_{d.b.}$]	0.81 (0.00)	0.05 (0.00)	-
As [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	2
Ba [mg·kg$^{-1}_{d.b.}$]	4.14 (0.23)	< d.l.	100
Cd [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	1
Co [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	-
Cr [mg·kg$^{-1}_{d.b.}$]	1.29 (0.01)	1.23 (0.00)	10
Cu [mg·kg$^{-1}_{d.b.}$]	0.05 (0.00)	< d.l.	50
Mo [mg·kg$^{-1}_{d.b.}$]	2.88 (0.00)	3.28 (0.00)	10
Ni [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	10
Pb [mg·kg$^{-1}_{d.b.}$]	0.83 (0.05)	< d.l.	10
Sb [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	0.7
Se [mg·kg$^{-1}_{d.b.}$]	0.40 (0.05)	0.58 (0.00)	0.5
V [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	-
Zn [mg·kg$^{-1}_{d.b.}$]	0.82 (0.00)	< d.l.	50

Tab. 5.11. Results of the leaching test performed on BOA before and after carbonation (at L/S 2.5 L·kg^{-1}), according to UNI EN 12457:2004 (< d.l.: below detection limit; standard deviation is indicated in brackets).

	Uncarbonated BOA	**Carbonated BOA**	**Limit values for non hazardous waste [10]**
pH	12.70 (0.06)	9.57 (0.11)	-
Al_2O_5 [mg·kg$^{-1}_{d.b.}$]	14.25 (2.04)	0.02 (0.00)	-
CaO [%wt$_{d.b.}$]	0.90 (0.00)	0.00 (0.00)	-
Fe_2O_3 [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	-
K_2O [%wt$_{d.b.}$]	1.80 (0.01)	0.15 (0.00)	-
MgO [mg·kg$^{-1}_{d.b.}$]	0.31 (0.00)	0.02 (0.00)	-
MnO_2 [mg·kg$^{-1}_{d.b.}$]	0.05 (0.00)	< d.l.	-
Na_2O [%wt$_{d.b.}$]	0.11 (0.01)	0.01 (0.00)	-
As [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	2
Ba [mg·kg$^{-1}_{d.b.}$]	3.00 (0.03)	< d.l.	100
Cd [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	1
Co [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	-
Cr [mg·kg$^{-1}_{d.b.}$]	1.71 (0.08)	0.11 (0.00)	10
Cu [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	50
Mo [mg·kg$^{-1}_{d.b.}$]	0.60 (0.01)	0.80 (0.00)	10
Ni [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	10
Pb [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	10
Sb [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	0.7
Se [mg·kg$^{-1}_{d.b.}$]	0.32 (0.01)	1.63 (0.00)	0.5
V [mg·kg$^{-1}_{d.b.}$]	< d.l.	< d.l.	-
Zn [mg·kg$^{-1}_{d.b.}$]	0.17 (0.10)	< d.l.	50

5.4.5 Subsequent carbonation tests: Effective CO_2 uptake

In the light of the above mentioned results, FA could be considered more promising than BOA as a CCS substrate. For this reason, further experiments were conducted on fly ash only. Further accelerated carbonation tests were performed using the pressurized reactor at different L/S ratios, with the aim of seeking the most favorable operating conditions for maximizing the CO_2 sequestration. In particular, the comparison of the results obtained allowed to evaluate the effect of water content on the final CO_2 uptake (Fig. 5.9, Tab. 5.12).

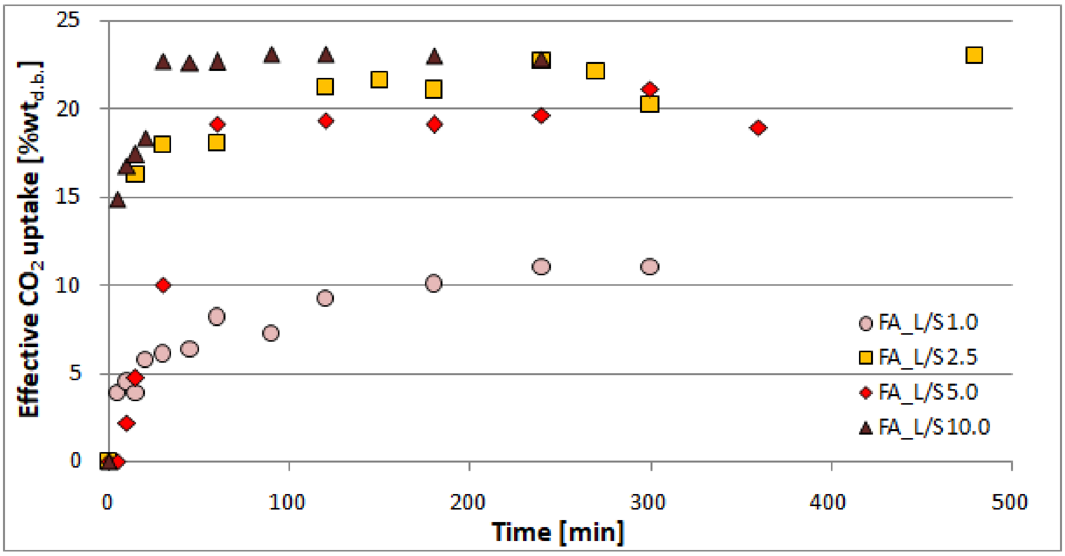

Fig. 5.9. Evolution of the effective CO_2 uptake during the carbonation tests performed at different L/S ratios in the pressurized reactor.

The results obtained are consistent with the ones reported by Gunning et al. [24] for similar substrates and comparable to what described by Cappai et al. [7] for other waste types. Biomass fly ash could be regarded as interesting for CO_2 sequestration.

The effective CO_2 uptake achieved at L/S 2.5 and 10.0 $L \cdot kg^{-1}$ were similar, though the kinetics at the beginning of the two tests were different, showing an earlier increase of the CO_2 uptake when L/S was 10.0 $L \cdot kg^{-1}$ comparing to that at L/S 2.5 $L \cdot kg^{-1}$.

If the kinetics is considered, the most promising result was obtained when the L/S 10.0 $L \cdot kg^{-1}$ ratio was applied. However, L/S 2.5 $L \cdot kg^{-1}$ could represent the most preferable condition because of the savings in the amount of water used and the smaller volume involved. The evolution of the CO_2 uptake attained at L/S 5.0 $L \cdot kg^{-1}$ exhibited kinetics slighter slower at the early stage of the tests comparing to the corresponding experiments conducted at L/S 2.5 and 10.0 $L \cdot kg^{-1}$, and the reason for this behavior is worthy of further investigation. If compared to the theoretical CO_2 uptake, the effective one corresponded to 60% of the maximum sequestration attainable. In the studies reported by other authors the effective CO_2 uptake observed ranged from 2% to 73% (Tab. 5.6).

Tab. 5.12. Evolution of the total carbon content in FA during the carbonation tests conducted at different L/S ratios in the pressurized reactor (n.d.: not determined; standard deviation is indicated in brackets).

Time [min]	**L/S 1.0 L·kg^{-1} C$_{tot}$ [%wt]**	**L/S 2.5 L·kg^{-1} C$_{tot}$ [%wt]**	**L/S 5.0 L·kg^{-1} C$_{tot}$ [%wt]**	**L/S 10.0 L·kg^{-1} C$_{tot}$ [%wt]**
0	5.45 (0.00)	2.99 (0.28)	5.50 (0.07)	2.74 (0.00)
5	6.25 (0.63)	n.d.	5.32 (0.24)	4.41 (0.77)
10	6.38 (0.58)	n.d.	5.95 (0.28)	4.41 (0.30)
15	6.25 (0.46)	6.38 (0.22)	6.48 (0.13)	4.43 (0.19)
20	6.63 (0.07)	n.d.	n.d.	4.49 (0.08)
30	6.70 (0.08)	6.67 (0.70)	7.47 (0.12)	4.75 (0.02)
45	6.75 (0.14)	n.d.	n.d.	4.73 (0.05)
60	7.10 (0.09)	6.69 (0.26)	8.99 (0.13)	4.76 (0.01)
90	6.92 (0.06)	n.d.	n.d.	n.d.
120	7.29 (0.04)	7.23 (0.23)	9.03 (0.01)	n.d.
150	n.d.	7.30 (0.08)	n.d.	n.d.
180	7.44 (0.18)	7.21 (0.28)	8.99 (0.04)	n.d.
240	7.61 (0.09)	7.48 (0.07)	9.07 (0.04)	n.d.
270	n.d.	7.38 (0.00)	n.d.	n.d.
300	7.60 (0.23)	7.07 (0.05)	9.25 (0.01)	n.d.
360	n.d.	7.22 (0.00)	8.92 (0.14)	n.d.
420	n.d.	7.37 (0.00)	n.d.	n.d.
480	n.d.	7.52 (0.00)	n.d.	n.d.

Tab. 5.13. Fly ash effective CO_2 uptake (standard deviation is indicated in brackets).

	L/S 1.0 L·kg^{-1}	**L/S 2.5 L·kg^{-1}**	**L/S 5.0 L·kg^{-1}**	**L/S 10.0 L·kg^{-1}**
Theoretical CO_2 uptake [g CO_2·kg^{-1} residue]	390	390	390	390
Effective CO_2 uptake [g CO_2·kg^{-1} residue]	110 (13)	235 (7)	197 (1)	227 (1)

Not only the chemical composition is a key factor for the proneness of a substrate to react. Calcium availability is the limiting factor for carbonation reactions [36], and some factors have to be considered. Firstly, whether calcium is prone to dissolve in the distilled water/residue suspension, it depends on the mineral phase it is present in [16]. For instance, calcium carbonate is a mineral form thermodynamically stable at ambient condition, is present at some extent in biomass ash even before carbonation, and does not react further; while, calcium oxide and hydroxide are the minerals most apt to react under carbonation conditions. Another form that could be found in biomass fly ash is $Ca_3(PO_4)_2$, as reported by Dong et al. [15], which is poorly soluble under alkaline conditions. This fact limits the phosphorus leachability as well, as recalled in Chapter 4. Secondly, calcium dissolution also depends on the water properties that affect the solubility, such as temperature, pH, and salinity [36].

5.4.6 Modifications in the mineralogical composition after carbonation

The mineralogical composition of the untreated fly ash is shown in Figure 5.10. As previously said, it was characterized by calcium silicate, sylvite (KCl), calcite ($CaCO_3$), aphthitalite ($K_3Na(SO_4)_2$), syngenite ($K_2Ca(SO_4)_2$), vaterite ($CaCO_3$), cliftonite (C) and portlandite ($Ca(OH)_2$), the latter of which is a compound very reactive to carbonation. Calcium carbonate in the form of vaterite was observed, which is a polymorph of calcium carbonate and is less stable than calcite. In their work, Saito et al. [37] studied the mechanism of formation of vaterite caused by the carbonation of γ-Ca_2SiO_4 starting from cement paste containing quartz via the path expressed by Equations 5.1 and 5.7. Vaterite resulted to be the preferred form of $CaCO_3$ rather than calcite and aragonite (a third form of calcium carbonate) because of the similarities between the crystallography of vaterite and the starting silicate [37].

Aphthitalite, syngenite and sylvite, that were present in the initial fly ash under investigation, were also observed by other authors [30,39]. These compounds (sulfates and chlorides) are generally soluble, particularly sylvite: as reported by Sarenbo et al. [39] sylvite is ten times more soluble than syngenite. However, the fate of these species after carbonation is questionable, though; some authors observed that the sulfates and chlorides solubility do not change after carbonation [39], while others reported a decrease in potassium solubility [30].

The XRD analysis of the carbonated fly ash (Fig. 5.11) showed that all the identified peaks corresponded to carbonates: calcite, vaterite, aragonite (which are the three forms of $CaCO_3$), and magnesian calcite ($(Ca,Mg)CO_3$) which consists in calcite with random substitution of Ca atoms with Mg ones. These results suggest that the carbonation process was efficient. However, it could have happened that granules of vaterite and aragonite were coated by carbonated materials while the nucleus remained unreacted, as described by Huntzinger [28] for CKD subjected to carbonation. If this situation occurred, eventually favored by the fast carbonation kinetics, then there could be conditions to improve carbonation further and it will be the basis for deeper future investigations.

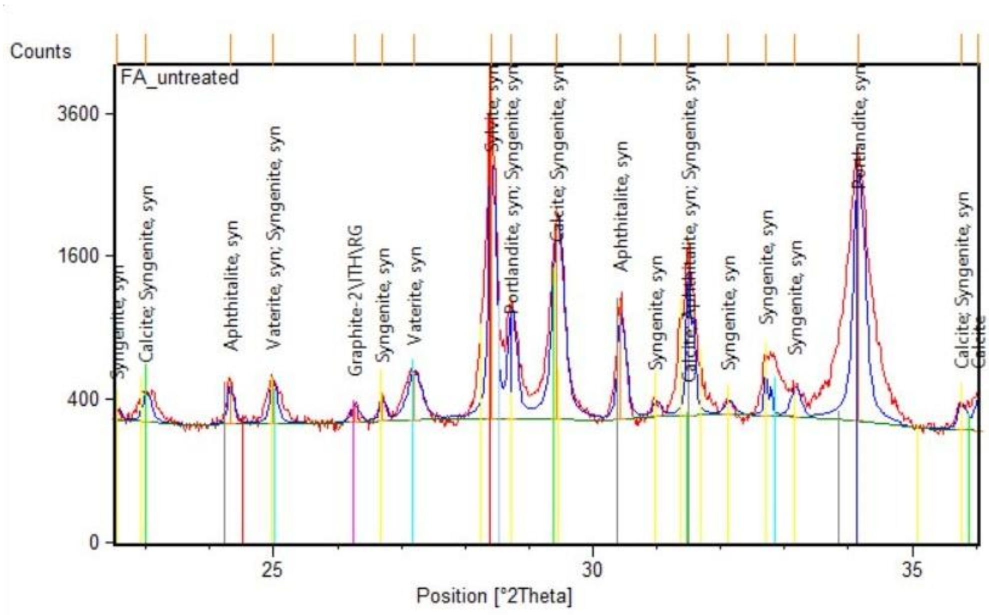

Fig. 5.10. XRD analysis for uncarbonated fly ash.

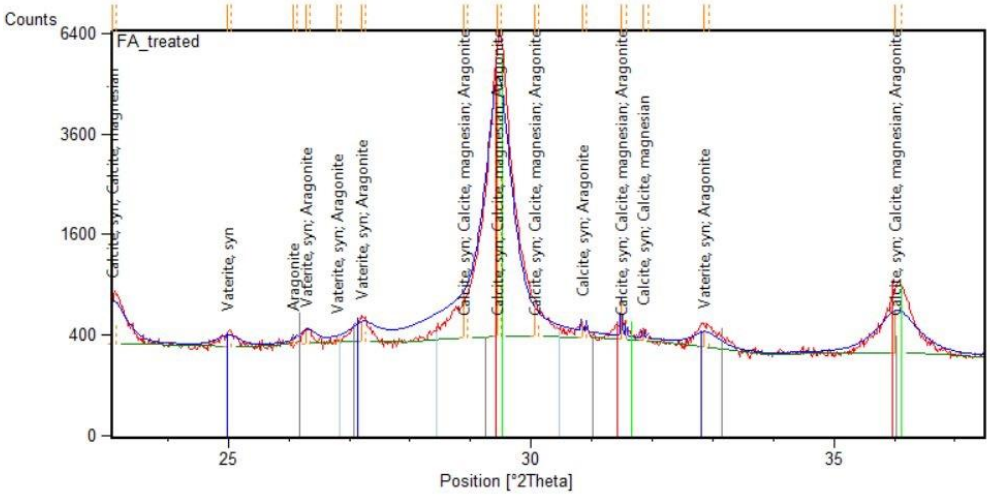

Fig. 5.11. XRD analysis for fly ash carbonated at L/S 10.0 L·kg^{-1}.

5.4.7 Potential CO_2 sequestration

The actual CO_2 sequestration potential depends on the total amount of each ash type generated, and thus potentially available for the reuse as a CCS substrate. As Obernberger et al. [33] reported, bottom ash accounts for approximately 90%wt of the residues generated by fixed-bed combustion systems, and the remaining amount is composed approximately by 3%wt of boiler ash and 7%wt of fly ash.

As previously said, though emitting greenhouse gases at the thermal power plants' stacks, energy generation from biomass is conventionally accounted as carbon neutral, according to the EU ETS [14]. Nonetheless, the Environmental Protection Agency [18], highlighted that wood biomass contributed to the total carbon dioxide emissions from the energy sector for 214,434 kt CO_2eq in 2014 (this value takes into account CH_4 and N_2O emissions, since they represent a large portion of the greenhouse emissions in the energy sector: 45% and 10% of total U.S. emissions, respectively, [18]).

Estimates from the Intergovernmental Panel on Climate Change [29] attribute to wood combustion an emission factor of 112,034 kg CO_2·TJ^{-1}, which corresponds to 0.403 kg CO_2·kWh^{-1}. This value is consistent with what declared by the European Member States in the reports produced in the fulfillment of the article 21 of the EU ETS Directive [19], that is 90,000 kg CO_2eq·TJ^{-1}.

To obtain the given emission factors, it was assumed that 1.3 kg biomass generates 1 kWh of energy [18], while the amount of ash produced during combustion was set equal to 0.04 $kg_{ash}\cdot kg^{-1}_{biomass}$.

Tab. 5.14. Direct plant emission factors.

	IPCC [29]	**MS's report** [19]
Plant emission factor [kg $CO_2eq\cdot TJ^{-1}$]	112,034	90,000
Plant emission factor [kg $CO_2eq\cdot MWh^{-1}$]	403	324
Plant emission factor [kg $CO_2eq\cdot t^{-1}$ biomass]	310	249
Plant emission factor [kg $CO_2eq\cdot kg^{-1}$ ash]	7.76	6.23

From the factors displayed in Table 5.14, an average plant emission factor of 6.99 kg $CO_2eq\cdot kg^{-1}$ ash was considered and used in the following calculation. Considering also the effective CO_2 uptake value reported in 5.4.5, the reduction of the CO_2 direct emissions is estimated to be equal to 0.25%.

Tab. 5.15. Reduction of the CO_2 direct emissions.

	Values for FA
Plant emission factor [kg $CO_2\cdot kg^{-1}$ ash]	6.99
Reduction of CO_2 emissions (on the maximum uptake basis) [%]	0.46
Reduction of CO_2 emissions (on the measured uptake basis) [%]	0.25

Nowadays, the indirect emissions generated by biomass systems are considered relevant to an extent that a revision of the EU GHG inventory is under study, in order to include the land use, change of land use and forestry sector in the emissions accountability [20]. The indirect GHG emissions generated by biomass combustion are also related to the fuel biomass supply chain, particularly to harvesting and transport.

The plant emission factor proposed by the British Department for Environment, Food and Rural Affairs [12], equal to 61.41 kg $CO_2eq\cdot t^{-1}$ biomass, was considered for accounting for the indirect GHG emissions generated by the use of wood chips in an average supply chain in the UK. This value includes the emissions produced by the activities related to cultivation, harvesting, processing (i.e. drying) and transport of the fuel biomass, and the ones directly emitted by the combustion plants. The emission factor proposed by DEFRA is consistent with the ones reported by Thornley et al. [46] for small and large electricity facilities, that are 60 and 55 kg $CO_2\cdot MWh^{-1}$, respectively, and consider all the activities needed for the biomass production (from the preparation to restoring of soil), processing, transport and combustion for power generation (Tab. 5.16).

Tab. 5.16. Indirect plant emission factors.

	DEFRA [12]	**Small facility** [46]	**Large facility** [46]
Plant emission factor [kg $CO_2eq\cdot MWh^{-1}$]	80.0	60.0	55.0
Plant emission factor [kg $CO_2eq\cdot t^{-1}$ biomass]	61.4	46.0	42.0
Plant emission factor [kg $CO_2eq\cdot kg^{-1}$ ash]	1.54	1.15	1.06

Given the mentioned assumption, the average plant emission factor of 1.25 kg $CO_2eq\cdot kg^{-1}$ ash was used in the following calculation (Tab. 5.17).

Tab. 5.17. Reduction of the CO_2 indirect emissions.

	Values for FA
Plant emission factor [kg $CO_2\cdot kg^{-1}$ ash]	1.25
Reduction of CO_2 emissions (on the maximum uptake basis) [%]	2.58
Reduction of CO_2 emissions (on the measured uptake basis) [%]	1.41

The reduction of CO_2 indirect emissions attainable by using biomass fly ash and considering the effective CO_2 uptake observed in the experiments described in this Chapter is 1.4%. Shall the theoretical (maximum) CO_2 uptake be attained, the emission reduction will correspond to 2.6%. These values are comparable to what could be obtained by using other industrial waste, such as the residues of municipal solid waste combustion and red mud from alumina production, as calculated by Cappai et al. [8], and open to promising perspectives in the limitation of the environmental impacts generated by power generation from biomass.

5.5 Conclusions

Carbonation is a phenomenon that naturally occurs when biomass ash is exposed to moisture and atmospheric CO_2, which produces variations in the ash physical, chemical and mineralogical properties, among which the most important for the environmental impact is leaching. When conducted under controlled conditions of CO_2 partial pressure and moisture content, carbonation is accelerated and constitutes an efficient technique to achieve CO_2 capture and sequestration. In this work, selected types of biomass combustion ash were exposed to accelerated carbonation under various L/S ratios in order to assess the potential environmental hazard when undergoing weathering and their possible reuse as a substrate for mineral CCS.

Fly ash manifested a remarkable reactivity and the highest effective CO_2 uptake attained from the carbonation tests conducted was 235 g $CO_2 \cdot kg^{-1}_{residue}$. The operating condition that favored the CO_2 uptake the most corresponded to a liquid to solid ratio equal or higher than 2.5 $L \cdot kg^{-1}$ at atmospheric pressure and ambient temperature. However, the carbon dioxide uptake kinetics was maximized at L/S ratio of 10.0 $L \cdot kg^{-1}$.

If compared to the maximum CO_2 uptake deduced by the ash chemical and mineralogical composition, it could be concluded that the effective value was 60% of the theoretical one and, considering that the least burdensome operating conditions in terms of temperature and CO_2 pressure were applied, this result confirms that FA could be an interesting substrate for the CO_2 capture and sequestration via accelerated carbonation. However, some aspects should be further investigated that might clarify why the extent of the effective CO_2 uptake was lower than the maximum value attainable. The presence of grains coated with calcium carbonate, that did not react completely in the nucleus, should be verified, and the performances achievable by expanding the sets of operating conditions should be determined.

Fly ash manifested an interesting potential in reducing the carbon dioxide emissions produced by the use of biomass for power generation. This potential was evaluated taking into account both the direct and indirect GHG emissions produced by the recourse to biomass as a fuel. Though biomass is a renewable energy source conventionally considered carbon neutral, some concerns about the actual impact exerted on the environment and about the sustainability of the supply chains that cover large distances (often intercontinental transports are made) are raised. In particular, the use of biomass ash as a substrate for CCS could diminish the indirect CO_2 emissions provoked by a typical supply chain of 2.6% (calculated on the basis of the theoretical CO_2 uptake). Despite the fact that a limited amount of ash is produced at present comparing to other residues that are equally promising, this result is of interest because the amount of ash available for this purpose will predictably increase as a consequence of the growth in the number of power plants fueled with biomass. Concomitantly, the concern about the environmental impact generated by long distance supply and intensive conditions of cultivation and harvesting will predictably lead to new managerial strategies that limit the related indirect GHG emissions.

However, one of the most important environmental aspect related to accelerated carbonation, which is the variation of heavy metals leachability as a consequence of the pH decrease, showed that the selenium and molybdenum leachable amounts increased after carbonation comparing to the levels observed in the untreated ash. This result arises an important environmental level of criticality when ash is exposed to moisture and aerobic conditions, as happens in natural processes, uncontrolled ageing and the reuse of fly ash as a CCS substrate. Facing any environmental aspect of the carbonated ash management should be an aspect to study more deeply in the next future.

5.6 References

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CHAPTER 6

Conclusions

The work done during the three years of PhD, presented in this thesis manuscript, was aimed at widening the understanding of the biomass combustion ash characteristics and recovery options, under the motivation of the dramatic diffusion of biomass as a renewable energy source and increasing amounts of waste generated. In the next future, the ash amount will predictably grow up to levels that require an accurate management plan, and a variety of recycling options should be developed in accordance to the peculiarities of these residues.

In this research work, the first point that was discussed consisted in the properties of typical fuel biomass, and the characteristics of the related combustion ash, which need to be considered when developing dedicated recycling paths for this waste stream. To do so, all the three ash types (bottom, boiler and fly ash) generated at a plant considered as representative example were sampled and characterized. The outcome was that the ash properties were greatly affected by the section of the thermal plant where the specific ash type was discharged. The understanding of the biomass ash variability drove the selection of the recycling options that were subject of the subsequent experimental activities.

In particular, two ash types, the boiler and fly ash, arouse the interest the most, in the light of innovative paths for recycling. Indeed, boiler and fly ash resulted to be enriched in macro- (Ca, K, Mg and P) and micro-nutrients (Cu and Zn) content, have high total porosity, water holding capacity and pH levels. These properties make them a promising material for the reuse as a composting additive, that constituted one research line developed in this work.

These residues also had alkaline properties and high portlandite content that make these biomass ash types prone to carbonation, which is the most representative transformation occurring during the spontaneous ageing process and could be used as a method to achieve the CO_2 sequestration.

That said, the **main findings** of the present research could be summarized as follows:

- The combustion residues under concern were affected to large variations in the amounts produced, physical properties and chemical composition.
- Overall, a blend of boiler and fly ash resulted beneficial for the composting process and final compost quality. The results of the experimental activities demonstrated that a proper blend of fly and boiler ash could have a potential as a physical conditioner, mineral additive and improver of humification in the composts produced from organic fractions of municipal solid waste. In a perspective of full-scale implementation, biomass ash addition could provide the final composts from organic fractions of municipal solid waste with a greater added value and enhance the possibility of placing them on the market.
- For most of the parameters, the magnitude of the effect exerted by ash addition increased according to the amount added, however ash amounts of 8% seemed to represent a possible maximum limit for ash addition, as adverse effects in terms of total organic carbon impoverishment and heavy metal contamination were observed. In fact, the reuse of ash in composting should be conditioned by the assessment of the contamination risk for any specific case, and should not affect the final compost quality according to the already existing quality standards.
- Similar process performance and final compost quality were attained even when a significant amount of structuring agent was replaced by a mass of the biomass ash blend, which suggests that ash could have a potential as a

physical conditioner and give a contribution in the partial replacement of the traditional bulking materials.

- Fly ash manifested a remarkable reactivity to CO_2 exposure and proved to be eligible as a substrate for carbon capture and sequestration. The reuse of fly ash as a substrate for CCS could potentially lead to a reduction of the impact generated by the recourse to biomass as a fuel, particularly in terms of the indirect GHG emissions.
- However, a potential environmental hazard was detected when both boiler and fly ash were subjected to carbonation, in relation to the varied leaching behavior of some heavy metals after the treatment. This result arises an important environmental issue related to the natural process of weathering, which ash are subjected to, and suggests a potential criticality in the application of ash as a substrate for CCS.

These results open to new perspectives for a full implementation of the Circular Economy concepts and allow to draw some suggestions for **further research**:

- A wider understanding of the biomass combustion residues with respect to the biomass origin, combustion technology and operating conditions should be pursued, since a scarce understanding of their characteristics would not allow to maximize the ash potential. In the future, a voluntary analytical program might eventually be introduced to improve the knowledge of the ash characteristics and environmental behavior, and make easier the evaluation of the technical requirements needed for any future recycling path. Certification programs for specific recycling options could be proposed, which would be based on the extensive adoption of adequate analytical protocols.
- The evaluation of pros and cons of the ash reuse as a composting additive should be continued at a deeper extent, by extending the number of parameters under study. A more solid statements on some of the issues raised by the present study is suggested, such as carbon balances, humification, availability of nutrients, fixation/solubilization of metals, effects on microbial activity and assessment of the long-term effects of the final products on plants. Further studies should also be aimed at confirming the maximum ash amount that might induce benefits to the

compost quality, without being of harm for the health and the environment, and contributing in the definition of a possible regulation in this sector. Concomitantly, further experiments should be conducted in order to confirm that the ash addition would allow a reduction in the amount of bulking agent used, and could be effective in producing a cost saving for the composting facilities.

- In relation to the reuse of fly ash as a substrate for CO_2 sequestration, the performance achievable by accelerated carbonation of ash could be further enhanced by expanding the sets of operating conditions to apply. A deeper understanding of possible factors that might have limited the effective CO_2 uptake attained, and the mineralogical modifications that occur during the process should also be pursued.

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