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Merging two waste streams, wood ash and biowaste, results in improved composting process and end products

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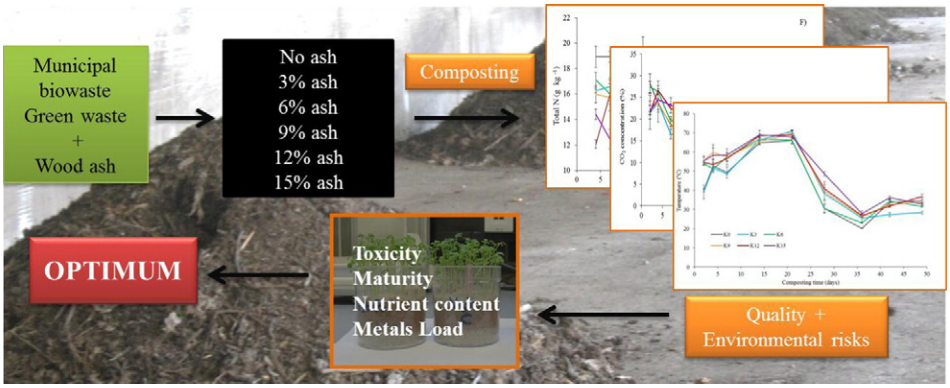
HIGHLIGHTS

- Addition of wood ash to biowaste improved composting kinetics.
- Higher C/N ratios in ash amended composts do not evidence lower maturity stages.
- Use of wood ash increased macronutrient content of the final products.
- An admixture of 8–9% of wood ash to biowaste was found to be optimal.

GRAPHICAL ABSTRACT



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ABSTRACT

A trial was carried out to evaluate the influence of wood ash admixture on biowaste composting. The aim was to find the optimal dosage of ash addition to enhance the composting process without endangering the final compost characteristics and use.

Six treatments including an unamended control (*K*0) and composts with additions of 3% (*K*3), 6% (*K*6), 9% (*K*9), 12% (*K*12) and 15% (*K*15) of wood ash (w/w) were studied. The composting process was monitored in situ for 49 days, by measuring temperature, CO_2, O_2, and CH_4 in the piles and pH, electric conductivity (EC), and inorganic N in the laboratory. At the end of the process, the products were tested for Reifegrad (maturity), toxicity and quality.

The addition of up to 15% of wood ash to biowaste did not negatively affect the composting process, and the initial differences found between both the low and high ash-treated composts were attenuated with the ongoing process development. Nevertheless, and mainly due to Cd level, composts with higher ash amendment did not comply with the highest quality standards established by the Austrian Compost Ordinance. The failure of obtaining class A^+ quality after ash amendment emphasizes the need for a rigid quality selection of (bottom) ashes and thus reducing environmental risks related to high pollutant loads originating from the ashes.

1. Introduction

Fostering the use of renewable energies for power generation constitutes one of the main environmental policies of the European Union (European Commission, 2010). By 2020, the biomass utilization in

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Europe is expected to increase by up to 129 million tonnes of oil equivalents (M toe) in order to meet the demands from the heat and electricity sectors (AEBIOM, 2011). As a consequence, this increase will be accompanied by the production of huge amounts of waste ashes, which must be managed with appropriate disposal practices to avoid a negative impact on the environment. In fact, the implementation of the end-of waste criteria by the European Waste Framework Directive (Directive 2008/98/EC on waste (Waste Framework Directive), 2008/98/EC) marks a shift in thinking about waste from an unwanted burden to a valued resource, emphasizing waste prevention and new recycling goals.

Specifically, forestry and forest-based industries account for the majority of biomass supply, with wood being one of the main renewable energy sources from biomass in EU countries such as Finland, Lithuania, Hungary and Austria (AEBIOM, 2011). According to James et al. (2012), the future trend in the use of biomass for energy might lead to a production of 15.5×10^7 tons of ash in the EU-27 by 2020. In Austria alone, the quantities of wood ash produced increased from 100,000 tonnes in 2004 to 149,000 tonnes in 2008, of which 50% was landfilled (Umweltbundesamt, 2011). The disposal of ashes in landfills implies considerable costs for biomass plant operators and negates the recycling potential of ashes. Previous studies have shown that wood ash may act as a mineral fertilizer and aid in the replacement of lime (Augusto et al., 2008; Bougnom et al., 2012; Brod et al., 2012; Demeyer et al., 2001; Fernández-Delgado Juárez et al., 2013; Pitman, 2006). On the one hand, it contains major elements such as P, Ca, Mg and K, along with a variety of micronutrients including Fe, Mn, Zn and Cu, all needed in plant production (Knapp and Insam, 2011). In addition, ash has a high acid-neutralizing effect on soils, due to the formation of hydroxides and carbonates during the combustion and conditioning processes (Steenari et al., 1999). Wood ash has also been used as an additive in composting due to its known capability to buffer pH and reduce compost malodours (Bougnom and Insam, 2009; Gabhane et al., 2012; Koivula et al., 2004; Kuba et al., 2008; Kurola et al., 2011; Rosenfeld et al., 2004), and having similar effects as lime (Bergersen et al., 2009), which opens new avenues for entrepreneurship in the waste management sector. Accordingly, Himanen and Hänninen (2009) observed that the addition of high alkalinity additives to a biowaste-peat mixture (1:1, v/v) led to a rise in pH, an earlier elimination of water-soluble NH_4–N, together with an increase in NO_3–N and a shortened phytotoxic period during composting. Nevertheless, they established that the use of peat as a bulking agent could have resulted in a lower pH, thereby giving additional importance to these types of additives.

Kurola et al. (2011) found that the admixture of low doses (4 and 8%) of wood ash to biowaste resulted in a rise in composting temperature and pH, and stimulated mineralisation in both pilot and large-scale systems. Nonetheless, the use of wood ash at low doses was not effective in reducing the concentration of both volatile sulphuric compounds and ammonia in the pilot-scale process. These authors suggested two plausible explanations, either that the chemical composition of the applied ash was inappropriate to reduce the total odour emission, or that the addition of 8% of wood ash was too low to fulfil this purpose. Indeed, Koivula et al. (2004) reported a reduction in H_2S evolution following 20% of ash amendment in biowaste composting. Moreover, Kuba et al. (2008) found that wood ash may be safely added to biowaste in quantities of up to 16%. In both studies, no adverse effects on the dynamics of the process were observed. In addition, the compost produced with a 16% of ash admixture had an improved nutrient balance and met the requirements of the Austrian Compost Ordinance (2001) on heavy metal content.

Furthermore, changes in both bacterial and fungal community structure have been found following the use of ash as a compost additive (8 and 16%) relative to unamended composts (Bougnom et al., 2010). Bougnom and Insam (2009) also observed that composts produced with 8% of wood ash admixture enhanced the utilization of C sources by soil microbial communities, as revealed by MicroResp^{TM}; whereas, no such changes were recorded with 16% of ash amendment. All together this indicates that the amount of wood ash used for composting is a major factor influencing the process itself and the quality of the final product. This is of utmost importance for the safe use of compost as a soil fertilizer, as wood ash may contain considerable amounts of heavy metals like cadmium and lead (Knapp and Insam, 2011; Kuba et al., 2008).

Despite the fact that previous studies dealing with the use of wood ash as a compost additive exist, the optimal ratio of ash and biowaste still needs to be investigated in order to delve deeper into the potential benefits and drawbacks of using this type of additive for the composting process. Therefore, the objective of the present study was to determine the effects of the addition of low and high doses of wood ash on the gas emissions and the chemical process parameters throughout the composting of communal biowaste. Moreover, we evaluated the impact of the different ash doses on the quality of the final product, by determining several parameters widely-used as maturity indicators.

2. Material and methods

2.1. Composting performance and sampling

The experiment was set-up at the municipal composting plant in Völs (Tyrol, Austria) on the 28th of February, 2011. To study the effect of wood ash amendment on the composting process, six different windrows made up of communal biowaste from the small town of Völs, consisting of source-separated organic waste (SSOW): food and garden waste, and occasionally paper fibres and compostable packaging, as well as chopped (100 mm long) tree-bush-cuttings from areas around the composting plant. Biowaste was mixed with tree cuttings in the ratio of 70:30 (w/w) and after that, different proportions of 0% (*K*0), 3% (*K*3), 6% (*K*6), 9% (*K*9), 12% (*K*12) and 15% (*K*15) of wood ash (w/w) were amended and composting windrows were formed. Each windrow had a triangle-shaped profile (1.2 m high, 2 m long and 1.5 m wide) and was composed of 1 ton of biowaste–biomass ash admixture. The physico-chemical properties of the biowaste, expressed on an oven-dry weight basis (mean ± S.E.) were: pH 5.48 ± 0.11, electrical conductivity (EC) 2.12 ± 0.04 mS cm^{-1}, organic matter content 60.6 ± 0.2%, total N 1.93 ± 0.04% and total C content 32.05 ± 0.45%. The wood ash was supplied from the power boiler of an incineration plant located in Kufstein (Tyrol, Austria), in which bark, sawdust and wood chips are used as input materials. The physico-chemical properties of the wood ash and the nutrient and heavy metal contents are shown in Table 1.

After the second week of composting, the compost piles were mechanically turned using a windrow turner on a weekly basis. Temperature and gas (CO_2, O_2 and CH_4) evolution were determined for the whole composting period (until April 18). Compost maturation was assessed by determining the C-to-N ratio, ammonium and nitrate content. Each of the three samples per pile was a composite sample comprised of 10 sub-samples collected from different locations within the composting pile (surface material excluded). In addition, at the end of the process, a Dewar self-heating test was performed to evaluate the Reifegrad (maturity grade) of the final compost. Mature composts were sieved with a 1 cm-sieve and analysed to determine the pH and EC, heavy metal (Pb, Cd, Cr, Cu, Ni, Zn) and nutrient (C, N, Ca, Mg, K, P) contents, and used in plant growth tests.

2.2. Analytical methods

Temperature and gas measurements were done in triplicate in each pile and always immediately prior to the collection of composite compost samples. The composting pile temperature was measured using a stainless steel temperature probe with NiCr–Ni component (Model 4009, Pronova Analysentechnik, Bad Klosterlausnitz, Germany) connected to a digital thermometer (Testo 925 Testo, Vienna, Austria). Gas emissions were determined using a probe composed of a 1.5 m

Table 1
Elemental composition of wood ash used in the present study and limit values for the use of wood ash in composting according to the Austrian Compost Ordinance (2001). Values expressed on a dry mass basis, n = 3 (standard error in brackets).

Parameters	Wood ash	Legal limits
pH	12.5 (0.1)	
EC (mS cm^{-1})	15.0 (0.1)	
OM (g kg^{-1})[a]	228 (5)	
Dry weight (%)	75.0 (0.8)	
Ca (g kg^{-1})	160	–
P (g kg^{-1})	7	–
Mg (g kg^{-1})	27	–
Mn (g kg^{-1})	5.7	–
Fe (g kg^{-1})	12	–
Si (g kg^{-1})	57	–
Cd (mg kg^{-1})	2.3	8
Co (mg kg^{-1})	6.4	100
Cr (mg kg^{-1})	45	250
Cu (mg kg^{-1})	71	250
Hg (mg kg^{-1})	0.05	–
Mo (mg kg^{-1})	<2.0	20
Ni (mg kg^{-1})	25	100
Pb (mg kg^{-1})	11	100
As (mg kg^{-1})	4.3	20
V (mg kg^{-1})	22	100
Zn (mg kg^{-1})	330	1500

[a] OM: organic matter.

metal pipe connected to a 1 m silicone tube (2 mm in diameter). A gastight Fortuna® Optima® glass syringe was used to take gas measurements. Firstly, 50 mL of compost gas were discharged to avoid possible mixing with the air present in the probe, and then 100 mL gas was sampled. Gas quality (CH_4 [%], O_2 [%], CO_2 [%]) was determined in situ with a portable Biogas Check BM 2000 instrument (Geotechnical Instruments, Warwickshire, UK).

Chemical analyses were performed according to the standard protocols proposed by the Austrian Compost Ordinance (2001) for compost samples, with some minor modifications. Compost samples (10 g fresh weight) were placed in a Petri dish, oven-dried (105 °C) for at least 18 h, and re-weighed for calculating total solids. The volatile solid content (VS) was determined from the weight loss following ignition in a muffle furnace (Carbolite, CWF 1000) at 550 °C for 5 h. pH was determined in 25 g compost with 200 mL solution of 0.01 M $CaCl_2$ using a pH-metre (MLP4, WTW, Weilheim, Germany). Electrical conductivity (EC) was measured in compost/deionized water (1:10, w/v) using a LF 330 conductivity metre with a standard cell TetraCon 325 (WTW, Weilheim, Germany). Total C and N contents were analysed in dried samples, using a CN analyser (TruSpec CHN; LECO, Michigan, U.S.A.). Inorganic nitrogen (NH_4^+ and NO_3^-) was determined in 0.0125 M $CaCl_2$ extracts (1:8, w/v), as described by Kandeler (1993, 1993).

The Dewar self-heating test was performed in duplicate for each compost treatment, to test compost stability and maturity. Temperature development was measured for 4 days. Briefly, the interpretation of the results is based on increments of the compost temperature compared to a fixed external temperature (22 ± 0.5 °C). According to this three major categories are defined: I) fresh compost (50°–40 °C increment), II) active compost (40°–20 °C increment), and III) finished compost (increase < 20 °C) (Itävaara et al., 1997; Weppen, 2002).

Nutrient and heavy metal contents in mature composts were determined according to the Austrian Compost Ordinance (2001), using a digestion procedure with aqua regia. Compost samples were dried at 45 °C for at least 48 h, ground and sieved (Ø 0.5 mm). One gramme of compost was placed into pre-cleaned vessels and 5 mL of aqua regia (HCl (12 M):HNO_3 (15 M), 3:1 (v/v)) were added, followed by the sample digestion using a microwave system MLS-1200 mega (MLS GmbH, Germany). The digested extracts were then transferred into 25 mL calibrated flasks, filled with Milli-Q water, filtered and stored at 4 °C until analysis. The content of nutrients and heavy metals was determined with a GF-AAS contrAA® 600 (Analytic Jena, Jena, Germany).

A plant growth test was performed according to the Austrian Compost Ordinance (2001). Glass dishes (12 cm diameter, 6 cm high) were filled with 100 mL of glass sand and 200 g of a mixture composed of tennis sand, standard soil and 0, 15 and 30% (w/w) of compost were placed on top of the sand layer, as shown by Kuba et al. (2008). Cress seeds (0.4 g) were then spread on the surface and covered with another 50 g of glass sand. Distilled water was added until saturation, and treatments were covered with black foil until germination. The aboveground dry mass of the cress was determined after nine days.

2.3. Statistical analyses

Data were analysed by repeated measures analysis of variance (ANOVAR) in which compost windrows represented the subjects, ash concentration was fixed as the between-subject factor, and the sampling time was fixed as a within-subject factor. All the variables met the sphericity condition (Mauchly's test), except for CO_2 concentration, pH, ammonia and nitrate contents. In these cases, the sphericity violation was corrected with the Geisser–Greenhouse (G–G) procedure (Potvin et al., 1990). Data corresponding to mature composts were analysed by ANOVA, with ash addition as the main factor. Significant differences in the main effects were analysed by paired comparisons with the Tukey HSD test. The normality and the variance homogeneity of the data were tested prior to ANOVA. Data were transformed when they did not resemble a normal distribution. All statistical analyses were performed with the Statistica software programme v9.

3. Results and discussion

3.1. Changes in physico-chemical parameters during the composting process

In the current study in which biowaste and green wastes were composted for 49 days, a typical temperature graph was observed throughout the process of composting (Fig. 1), consisting of an initial mesophilic phase, a thermophilic phase, a subsequent second mesophilic phase and a final maturing stage (Insam and de Bertoldi, 2007; Kuba et al., 2008; Ryckeboer et al., 2003). As shown in Fig. 1, the temperature was found to be significantly different over time (ANOVAR $F_{8,96} = 401.6$, $p < 0.001$) and with respect to the ash concentration (ANOVAR $F_{5,12} = 22.17$, $p < 0.001$). Specifically, higher temperature values were recorded in ash-amended composts, primarily in those treatments with a higher ash dose, in comparison with the control (*K0*). However, the differences to the control became less evident towards the end of the process (Fig. 1), where the lowest temperature (27.3 ± 1.03) was reported for *K3* after 42 days of composting, resulting in a significant interaction between ash concentration and time (ANOVAR time*ash conc. $F_{40,96} = 3.64$, $p < 0.001$). An increase in the temperature was seen after 2 days of composting, with temperatures 15 °C higher being recorded in *K6*, *K9*, *K12* and *K15* compared with *K0* and *K3*. The maximum temperature values reached in the ash-amended-compost piles after 21 days of composting were 70.8, 66.2, 69.6, 69.1 and 68.0 °C for *K3*, *K6*, *K9*, *K12* and *K15*. Such increases relative to the control were probably due to the enhancement of abiotic heat production due to ash carbonation, as previously shown by Koivula et al. (2004). In line with this, Kuba et al. (2008) established that an onset of an exothermic carbonatization process is expected as a consequence of ash addition, which results in abiotic heat production and thus, in a higher temperature in ash-amended composts. Kurola et al. (2011) also reported an increase in the temperature when wood ash (8%) was used as a biowaste compost additive, and this increase was observed after 2 days of composting. In our study (Fig. 1) such trend is reflected in the first 7 days of composting. During this period *K0* and *K3* showed lower temperatures than compost with higher dosages of ash, but after 14 days all composts reached similar temperatures. All the ash-amended composts in this study met the current legislative hygiene requirements, which demand that the temperature should exceed 65 °C

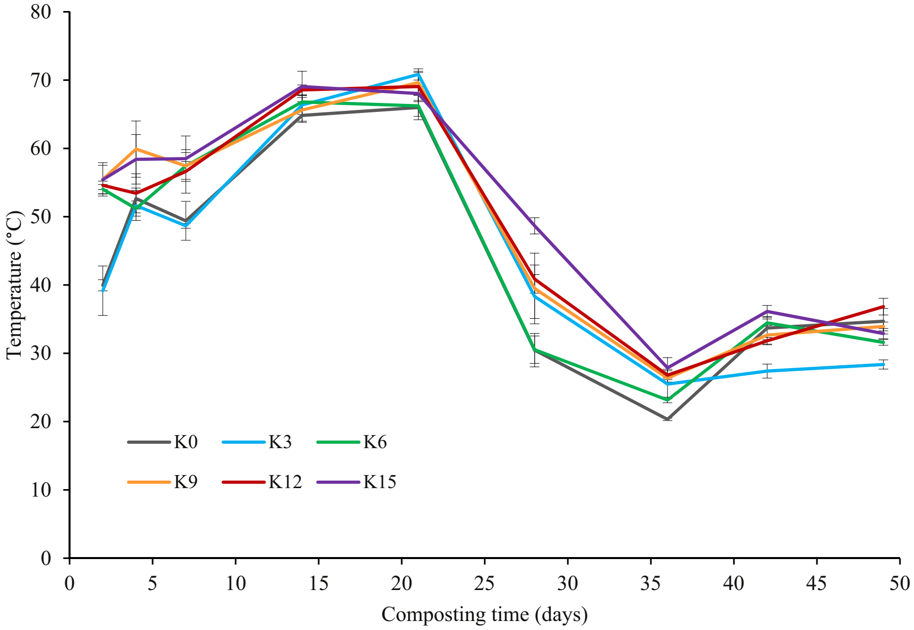

Fig. 1. Evolution of temperature in the compost piles produced without, and with different percentages of ash addition (3, 6, 9, 12 and 15%). Means of triplicate measurements with standard errors are shown.

at least twice during the process (i.e., after 14 and 21 days in this study) with one pile turnover in between; and that such temperatures should be maintained for 3 days (Bundesminister für Land-und Forstwirtschaft, 2001). In the case of *K0* (unamended compost), the pile temperature only exceeded 65 °C after 21 days; even though the temperature of 64.8 °C ± 0.84 reached in *K0* after 14 days was close to meeting sanitation requirements.

The course of O_2 evolution changed significantly over time (ANOVAR $F_{8,96} = 475.01$, $p < 0.001$). Overall, a low O_2 content (ranging between 1 and 5%) was recorded for all the treatments, regardless of the ash dose, during the first 21 days of composting (Fig. 2A). Similarly, Koivula et al. (2004) found O_2 levels below 5% in composts with up to 20% of ash addition after 7 days of composting. After this day there was a sharp increase in O_2 levels, ranging from 12.3% to 18.5%, until the end of the process (Fig. 2A). In fact, oxygen concentration should not fall below 10% in order to avoid the overgrowth of aerobic zones by anaerobic microorganisms (Diaz and Savage, 2007; Vallini et al., 2002). For windrow composting, O_2 concentrations should be about 15% so as to achieve an optimal process and in turn, to avoid the formation of anaerobic zones (Amlinger et al., 2005; Sundberg and Jönsson, 2008).

Carbon dioxide (CO_2) concentration followed the inverse trend to that observed for O_2 levels throughout the composting process (Fig. 2B). Significant differences in CO_2 concentration were recorded over time (ANOVAR $F_{8,96} = 246.2$, $p < 0.001$) and with the ash dose (ANOVAR $F_{5,12} = 28.84$, $p < 0.05$). In general, all the ash-amended composts, with the exception of *K3*, had a higher CO_2 level than that in the control (*K0*) during the initial phases of the composting process (Fig. 2B); and they became more similar towards the end of the process (Fig. 2B), leading to a significant interaction between ash concentration and time (ANOVAR time*ash conc. $F_{40,96} = 1.87$, $p \leq 0.05$). A similar trend was found by Kurola et al. (2011). Moreover, these authors observed that the CO_2 evolution matched heat production in the ash-amended composts, which is indicative of an apparent boost of microbial activity as a consequence of ash addition. Kuba et al. (2008) observed, on the other hand, that CO_2 content was lower in the treatment with the highest ash dose (16%) in the first weeks of composting. The authors attributed this fact to an improved aggregate formation allowing for larger pores.

CH_4 concentration changed significantly over time (Fig. 2C; ANOVAR $F_{5,60} = 20.02$, $p < 0.001$) and in function of the ash dose (ANOVAR $F_{5,12} = 11.35$, $p < 0.001$), resulting in a significant interaction between ash concentration and time (ANOVAR time*ash conc. $F_{25,60} = 2.50$, $p \leq 0.005$). Overall, CH_4 concentration was higher in ash-amended composts, with the exception of *K3*, in comparison with the control treatment during the first 21 days of composting (Fig. 2C). As stated by Kurola et al. (2011), amending compost with a higher dose of ashes (8%) led to an increase in CH_4 content at the beginning of the process in comparison with a lower dose (2%), probably due to the occurrence of anaerobic niches in the piles. However, in the present work the highest level of CH_4 was unexpectedly recorded in *K6* (up to 8.5%) until day 14 (Fig. 2C). After 21 days of composting there was a drastic reduction in CH_4 content in all the compost piles (Fig. 2C), and the levels were close to 0% (around 0.4%) after 28 days. From day 36 until the end of the process, there was no CH_4 found in any of the compost piles. It is well known that methane emissions during aerobic processes of organic wastes mostly occur during the thermophilic phase of composting (Koivula et al., 2004; Sommer and Moller, 2000), when oxygen consumption is at its peak and anaerobic microniches are likely to be formed in aggregates (Kurola et al., 2011; Sommer and Moller, 2000). Also, in our study the drop in methane content matched the drop recorded in temperature. High methane contents within the compost piles, however, do not mean that high methane emissions are to be expected. Methane consumption by methanotrophic microorganisms in the outer layers of the piles may considerably lower the methane content of the emitted gas (Jäckel et al., 2005).

Dry matter content changed significantly with the composting time (ANOVAR $F_{7,84} = 62.67$, $p < 0.001$) and the ash concentration (ANOVAR $F_{5,12} = 15.52$, $p < 0.001$). Overall, higher values of DM content were observed in ash-amended composts (except for *K3*) in comparison with the control (*K0*) throughout the process (Fig. 3A). More specifically, until day 30, *K12* and *K15* had a greater DM content compared to the other ash-amended treatments (Fig. 3A). However, from then on, the differences were less pronounced with respect to *K6* and *K9* (Fig. 3A), leading to a significant interaction between ash concentration and time (ANOVAR time*ash conc. $F_{35,84} = 3.14$, $p \leq 0.001$). Water content is an important indicator during the composting process, because at moisture levels below 40–45% the degradation activity is restrained by osmotic stress (Vinnerås et al., 2010). In the current study, the moisture content ranged from 55% to 62% at the beginning, while at the end of the

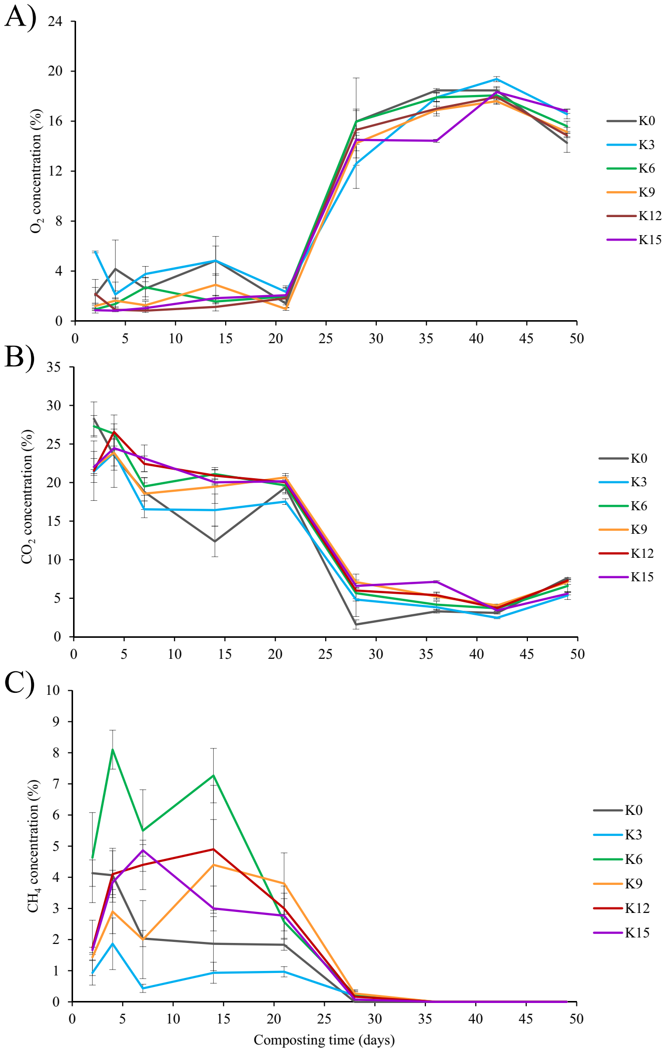

Fig. 2. Airfilled pore space concentrations of O_2 (A), CO_2 (B), and CH_4 (C) in the compost piles produced without, and with the different percentages of ash amendment (3, 6, 9, 12 and 15%). Means of triplicate measurements with standard errors are shown.

process the moisture level was 53% for *K0* and 40% for *K15*. According to Diaz and Savage (2007) the water content of a compost pile should be around 30% towards the end of the process in order to prevent any further biological activity in the mature compost. In our study, however, all the ash-amended piles exceeded 30% of their water content after 49 days of composting (Fig. 3A). The treatment containing 3% of ash had the highest level, with 53.1% water content. In composts with addition of ashes from 6% up to 15%, the water content was lower, with values between 40.2% and 45.7% (Fig. 3A). The differences between amended and unamended composts may be attributed to the higher DM content of the ash compared to the biowaste.

Organic matter (OM) content also changed significantly with time (ANOVAR $F_{7,84} = 2.26$, $p < 0.05$) and ash concentration (ANOVAR $F_{5,12} = 2.27$, $p < 0.001$); however, there was no significant influence of the interaction between ash concentration and time on this parameter. At the beginning of the process the OM content ranged from 573 g kg^{-1} to 467 g kg^{-1}, and it was approximately 10% lower after 49 days of composting, ranging between 528 g kg^{-1} and 423 g kg^{-1} (Fig. 3B). Overall, lower OM levels were observed in ash-amended composts (except for *K3* after 42 days of composting) in comparison with the control (*K0*) throughout the process (Fig. 3B). More specifically, lower OM values were recorded in those composts treated with a higher dose of ashes (9, 12 and 15%), compared to lower-dose treatments (*K3* and *K6*) (Fig. 3B). The lowest OM content was found for *K15* (402 g kg^{-1} after 14 days composting) (Fig. 3B). It is widely known that OM is decomposed during the composting process, emitting the CO_2 heat and water vapour as residual products (Insam and de Bertoldi, 2007). In this study the organic matter content (Table 1) of the used ash was unexpectedly higher than that of standard bottom ash, and being closer to what could be considered as biochar (Enders et al., 2012). Wood ash had, however, lower VS content than the biowaste used in this study. Therefore, the lower OM values following ash addition could be due not only to the dilution effect from the mineral components of ash, but to the increased OM degradation (Vandecasteele et al., 2013).

Acidity also varied with the time of composting (ANOVAR $F_{7,84} = 40.15$, $p < 0.001$) and the ash concentration (ANOVAR $F_{5,12} = 11.18$, $p < 0.005$). Overall, higher pH-values were recorded in ash-amended composts, mainly in those treated with a higher dose of ashes (7.4, 7.3 and 7.4 for *K9*, *K12* and *K15* during the first 28 days of composting) in comparison with the control treatment, which had an average pH of 6.9 (Fig. 3C). Nevertheless, from then on, no clear differences were found among the treatments (Fig. 3C), leading to a significant interaction between ash concentration and time (ANOVAR time*ash conc. $F_{35,84} = 8.85$, $p \leq 0.001$). A pH of 7.1 was recorded for *K0* at the end of the process (after 49 days of composting), whereas in the ash-amended composts the recorded pH was slightly lower, ranging from 6.6 to 6.9 (Fig. 3C). It has been reported that a pH below 6.0 might inhibit the transition from the mesophilic to the thermophilic temperature stages during the composting process (Sundberg et al., 2013). Nonetheless, wood ash addition reduces this risk by increasing the pH from the beginning. Kuba et al. (2008) also found that ash additions up to 16% significantly increased the pH of biowaste compost from 6.9 to 7.7 compared to the unamended control. Our results show that after 4 composting days, the buffering capacity of the ashes (Fig. 3C), was remarkable, being different between *K0*, and all ash-amended treatments. Accordingly, Kurola et al. (2011) observed that in biowaste tunnel composting, the addition of wood ash (4%) led to an increase of pH by 1.5 units, relative to the control, after 8–9 composting days. The observed effect was also confirmed in studies using lime to buffer compost pH (Bergersen et al., 2009), where the amendment effect of 5% lime persisted for about 20 days.

There were significant differences in EC concerning the time (ANOVAR $F_{7,84} = 4.98$, $p = 0.001$) and ash concentration (ANOVAR $F_{5,12} = 61.34$, $p < 0.001$), resulting in a significant interaction between both factors (ANOVAR time*ash conc. $F_{35,84} = 2.04$, $p \leq 0.005$). Overall, EC values were higher in ash-amended composts in comparison with the control (Fig. 3D). In general, those composts with higher ash doses, (*K15*, *K12* and *K9*) showed a higher EC than those with lower ash amendments (*K6* and *K3*) throughout the process, as shown in Fig. 3D. An exception to this trend was found after 42 days of composting, at which point *K15* and *K12* showed EC values (1.98 and 1.91 mS cm^{-1}, respectively) closer to that registered in *K0* (1.8 mS cm^{-1}; Fig. 3D); whereas *K3*, *K6*, and *K9* exhibited higher EC levels (2.23, 2.27 and 2.59 mS cm^{-1}; Fig. 3D). The EC is considered as a relevant parameter concerning the suitability of composts as organic amendments, because plants may face osmotic problems due to high salt concentrations (Thangarajan et al., 2013). A maximum level of 3 mS cm^{-1} has been established by the Austrian Compost Ordinance (2001) for the use of composts as organic amendments. This threshold value was not reached for any of the ash doses used in our study.

The initial biowaste had a carbon content of 320 g kg^{-1}. The composting time and the ash concentration greatly affected this parameter (time: ANOVAR $F_{7,84} = 6.38$, $p < 0.001$; ash treatment: ANOVAR $F_{5,12} = 10.27$, $p < 0.001$), even though the interaction between both factors was not significant. Overall, total C values ranged from 200 g kg^{-1} to 284 g kg^{-1} throughout the composting process (Fig. 3E). Moreover, lower C contents were in general observed in ash-amended composts in comparison with the control (*K0*) along the process (Fig. 3E). More specifically, *K15* had the lowest C content over time (between 201 and 260 g kg^{-1}; Fig. 3E), with the exception at 42 days of composting. The C content was lower in *K12* (Fig. 3E) at this time point. In this case

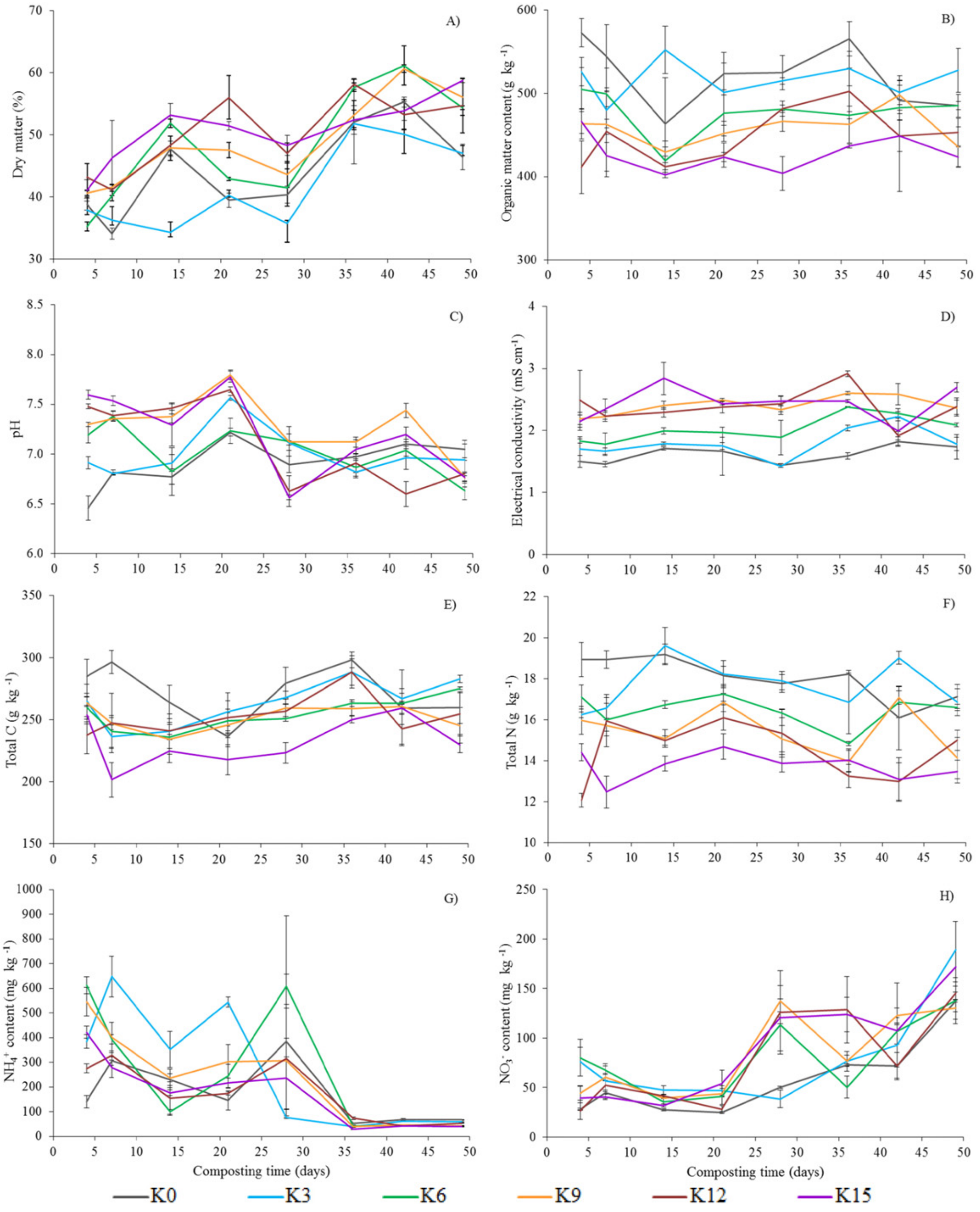

Fig. 3. Dynamics of dry matter content (A), organic matter content (B), pH (C), electrical conductivity (D), total carbon content (E), total nitrogen content (F), ammonium (G), and nitrate content (H), in the compost piles produced without, and with the different percentages of ash amendment (3, 6, 9, 12 and 15%). Means of triplicate measurements with standard errors are shown.

lower C_{tot} contents in compost with higher dosages are explained not only by the "dilution" effect of the amendment, but also by a higher gaseous carbon emission (Fig. 2B). Another plausible explanation to the results is that part of the CO_2 was fixed in a stabilization process of the ashes, and $CaCO_3$ (Kuba et al., 2008) was formed during the composting process since the C_{tot} reduction over time was not so strong for the ash-amended composts compared to *K0*.

As with total C, a significant effect of both time and ash amendment was observed for total N (time: ANOVAR $F_{7,84} = 3.78$, $p < 0.005$; ash treatment: ANOVAR $F_{5,12} = 71.8$ $p < 0.001$). A significant interaction was also found between both factors (ANOVAR time*ash conc. $F_{35,84} = 2.38$, $p \leq 0.001$) regarding this parameter. Overall, the highest total N of 19.9 g kg^{-1} at the beginning of composting was recorded in the control treatment (*K0*) throughout the process (Fig. 3F); lower values were observed for ash-amended composts, mainly for those treated with the higher doses of 12 and 15% (Fig. 3F). Additionally, in the current study, it was observed that from day 14 to day 36 of composting, the total N content in *K3* was found to be similar to that in the control (Fig. 3E), being even higher in *K3* after 42 days of composting. Similar to our findings, Kurola et al. (2011) reported that amending compost with higher ash doses (up to 8%) resulted in a lower total N content. Accordingly, Kuba et al. (2008) also observed slightly lower values of total N in biowaste compost amended with 16% of wood ash in comparison with a lower ash dosage (8%) and the unamended control; moreover, they observed that N levels did not change significantly over time. The lower N content of compost with higher ash addition (*K12* and *K 15*) might be attributed to the "dilution" effect of the ashes, since it is known that the nitrogen content of wood ashes is very low (Knapp and Insam, 2011; Schiemenz et al., 2011).

C/N ratio from all treatments (data not shown) decreased over time, nevertheless there were no outstanding differences between treatments.

NH_4^+ content varied significantly over time (ANOVAR $F_{7,84} = 22.08$, $p = 0.001$), and this effect was dependent on the ash concentration (ANOVAR time*ash conc. $F_{35,84} = 2.08$, $p \leq 0.005$). As shown in Fig. 3G, after 4 days of composting NH_4^+ content ranged from 140 mg kg^{-1} in the unamended compost (*K0*) to 612 mg kg^{-1} in *K6* treatment. Afterwards, the highest NH_4^+ level was detected in *K3* until day 14 of composting (Fig. 3G). From day 21 on, a reduction in NH_4^+ content was recorded, which was clearer up to day 28 for all the compost piles. An average value of 46.6 mg kg^{-1} on day 36 (Fig. 3G), which remained constant until the end of the process. Therefore, all the ash-amended composts, even those treated with the doses of 12 and 15%, did not exceed the limit value of 400 mg kg^{-1} as suggested by Zucconi and de Bertoldi (1987) for the level of NH_4^+ in stable composts.

Significant differences in NO_3^- concentration were recorded over time (ANOVAR $F_{7,84} = 33.12$, $p < 0.001$) and with the ash dosage (ANOVAR $F_{5,12} = 61.34$, $p < 0.05$). At the beginning of the process NO_3^- content reached a value of 74.7 mg kg^{-1} in *K3* and *K6* (Fig. 3H), whereas lower levels (around 30 mg kg^{-1}) were observed in the remaining treatments on the second day of composting (Fig. 3H). From this day on and until day 21 of composting no significant differences were found in NO_3^- levels among the treatments over time (Fig. 3H) although a pronounced increase in NO_3^- content was registered for all the treatments, except for *K0* and *K3*, on day 28 (Fig. 3H). Afterwards, a significant reduction in NO_3^- levels was found in *K6* and *K9* on day 36 of composting (Fig. 3H), while no changes were recorded for the higher ash doses of 12 and 15% (Fig. 3H). This resulted in a significant interaction between ash concentration and time (ANOVAR time*ash conc. $F_{35,84} = 1.91$, $p \leq 0.001$). At the end of the process there was an increase in NO_3^- content in all the treatments relative to the previous sampling (Fig. 3H), with values ranging from 130 to 190 mg kg^{-1} obtained in the ash-amended composts. In general, after 49 days of composting the addition of ashes led to the highest NO_3^- levels in *K3* (189 mg kg^{-1}) followed by *K15* and *K12* (189 and 172 mg kg^{-1}, respectively). The lowest levels were found in the unamended compost (137 mg kg^{-1}, Fig. 3H). This indicates that amending biowaste compost with high ash doses (12% and 15%) also favoured the composts stability in terms of nitrification, a process that mainly takes place during the maturation stage when temperatures are close to ambient temperatures. Himanen and Hänninen (2009) reported similar dynamics for the mineral nitrogen forms NH_4^+ and NO_3^- when biowaste compost was amended with high alkaline additives, with an earlier elimination of water-soluble NH_4^+, followed by an increase in NO_3^- level. Kurola et al. (2011) observed that the addition of wood ash to biowaste composts at a dosage of 4% did not reduce NH_4^+ content, relative to the unamended compost, and it led to an increase in NO_3^- content at the maturation stage.

3.2. Evaluation of compost maturity and quality

The application of immature composts to soil can have harmful effects on plants and on ecosystem functioning (Déportes et al., 1995) and can lead to a competition for oxygen between microbial biomass and plant roots, resulting in the production of NO_2^- and H_2S (Brinton and Evans, 2002; Chukwujindu et al., 2006). Another problem relies on the nitrogen starvation of plants, as microorganisms scavenge soil N to make up for the deficit derived from the use of immature composts with a high C/N ratio (Butler et al., 2001). Phytotoxic compounds (e,g. phenolic compounds and ethylene oxide) in immature composts may further impair plant growth (Senesi, 1989; Zucconi et al., 1981). Thus, it is of paramount importance to evaluate the maturity of composts for their successful application to soils. There exists a wide range of physical, chemical and microbial parameters for assessing compost maturity (Itävaara et al., 2002; Pinzari et al., 2002; Rynk, 2003), and the combined use of different parameters seems to be the most reliable option for this purpose (Bernal et al., 2009; Gómez-Brandón et al., 2008, 2013). As such, in the present study the maturity of the composted materials from the six different piles was evaluated after 49 days of composting by determining the changes in C-to-N ratio and by using a self-heating test and a plant toxicity test.

According to the criteria proposed by Brinton et al. (1995) for the Dewar self-heating test, all the amended composts in this study, irrespective of the ash dose, can be classified as finished compost, with a degree V of decomposition (Itävaara et al., 1997; Weppen, 2002). The increases in temperature, compared to the external stable temperature (22 °C), were never higher than 2.5 °C (data not shown); moreover, no differences were found between the control treatment (*K0*) and the ash-amended treatments (from *K3* up to *K15*; data not shown). Butler et al. (2001) pointed out that the Dewar test was the most reliable procedure for determining the Reifegrad of composts from different sources.

The C_{tot}/N_{tot} ratio ranged from 14 to 18 in the ash-amended composts after 49 days of composting (Table 2). A C/N ratio lower than the cut-off value of 20 is recommended for the safe application of compost into soil in order to ensure enough plant-available N (Hue and Sobieszczyk, 1999). In our study, all the composts met this requirement irrespective of the ash dose used, but as clear trend, the higher the ash amendment, the higher the C/N ratio. These obtained results are probably due to two main factors: first of all the low nitrogen content of the ashes implies lower total nitrogen content since the early process stages. This low nitrogen content may be also due to the higher pH of ash amended compost, which enhanced nitrogen volatilization (as NH_3) (Kurola et al., 2011; Pagans et al., 2006). A second factor relies on the high VS content of the ashes. The organic content of the ash is to a high proportion in the form of unburnt OM recalcitrant to biodegradation (Insam et al., 2009). This OM is not degradable in a short period of time and only the easy degradable organic matter from the biowaste fraction is decomposed during the 49-day composting period. Another plausible factor is the above mentioned fixation of CO_2 as $CaCO_3$ as a consequence of ash carbonation process (Kuba et al., 2008; Zimmermann and Frey, 2002), due to this part of the decomposed C may be fixed as mineral fraction of ash-amended composts. This is of utmost importance since a higher C/N ratio in ash amended composts does not evidence lower maturity stages.

According to the Austrian Compost Ordinance (2001), a compost is considered to be non-toxic, when there is no reduction in the amount of total plant biomass produced upon growth in a soil containing 15% of compost, relative to a standard soil. In the present study, all composts met the aforementioned requirement; the unamended compost (*K0*) allowed higher biomass yields than those with ash addition, independent of the percentage of ash used Fig. 4. Bougnom and Insam (2009) observed a positive effect of composts with 8% of ash in germination tests, while composts amended with 16% of ashes showed inhibitory effects.

Wu et al. (2000) suggested that pH and EC might be used to monitor compost stabilization, as long as the source waste composition is relatively consistent and other tests are conducted. In the current study, adding wood ash at higher doses resulted in an increase in pH, ranging from 7.3 in *K0* to 8.5 in *K15* (Table 2). The presence of quickly soluble compounds such as oxides, hydroxides and carbonates could be responsible for the higher compost pH following wood ash addition. According to Diaz and Savage (2007), the pH at the end of the composting process should range between 8.0 and 8.5, indicating total mineralization. In particular, acid metabolite intermediates should have been neutralized. All the ash-amended composts, primarily those treated with a higher dose, met this requirement. These results match previous findings (Kuba et al., 2008; Kurola et al., 2011), in which pH values up to 8.8

Table 2
Chemical parameters and nutrient contents in the composts produced without, and with the different proportions of ashes (3, 6, 9, 12 and 15%). Values expressed on a dry mass basis for n = 3 (standard error in brackets), except for total C and N, N–NO_3 and N–NH_4 for which n = 5.

	K0	K3	K6	K9	K12	K15
pH	7.31 (0.09) a	7.69 (0.03) c	8.12 (0.1) b	8.22 (0.07) bd	8.23 (0.06) bd	8.48 (0.06) d
EC (mS cm^{-1})[a]	1.59 (0.04) a	2.33 (0.02) b	2.52 (0.06) b	2.61 (0.003) bd	3.06 (0.07) c	2.87 (0.12) cd
O_2 (%)	17.6 (0.14) a	18.5 (0.26) b	18.1 (0.07) ab	18.3 (0.03) ab	18.6 (0.11) b	18.4 (0.26) b
CO_2 (%)	2.27 (0.39) a	1.4 (0.06) ac	1.40 (0.00) ac	1.00 (0.06) bc	0.87 (0.07) b	0.93 (0.07) b
OM (g kg^{-1})[b]	494 (1.90) a	480 (10.7) a	410 (10.3) a	432 (20.0) a	387 (3.46) a	397 (12.9) a
Total C (g kg^{-1})	258 (5.96) a	248 (3.99) ab	228 (2.45) b	245 (11.38) ab	227 (4.54) b	229 (5.97) b
Total N (g kg^{-1})	19.6 (0.42) a	18 (0.19) b	14.6 (0.14) c	15.3 (0.21) c	13.4 (0.12) d	13.3 (0.36) d
N–NO_3^- (mg kg^{-1})	125 (2.98) a	208 (3.21) c	195 (3.42) bc	187 (4.29) bd	177 (5.07) d	239 (1.85) e
N–NH_4^+ (mg kg^{-1})	18.3 (1.14) a	12.4 (0.59) b	14.4 (0.71) bc	15.1 (0.73) bc	16.2 (0.42) ac	18.9 (0.48) a
P (g kg^{-1})	3.64 (0.07) a	5.45 (0.06) ac	6.28 (0.27) bc	5.86 (0.16) acd	6.63 (0.18) bd	6.76 (0.17) b
K (g kg^{-1})	14.4 (0.97) a	17.3 (0.32) ac	21.3 (0.67) bc	22.7 (0.29) bc	24.3 (0.65) b	27.9 (4.95) b
Ca (g kg^{-1})	50.9 (2.88) a	66.1 (0.60) ac	90.3 (4.68) bc	86.7 (4.22) bc	102 (4.28) b	94.5 (11.4) b
Mg (g kg^{-1})	11.6 (0.40) a	12.0 (0.30) a	13.2 (0.37) ab	13.4 (0.38) ab	13.6 (0.16) ab	15.4 (1.79) b

Dissimilar letters in a row indicate statistically significant differences among the ash treatments (Tukey HSD-test).

[a] E.C.: Electrical Conductivity.

[b] OM: Organic Matter.

were obtained in mature composts amended with 8% of ashes. This buffering capacity is an important property of wood ash, making it appropriate for application to acidic soils (Bougnom et al., 2009). The increase in EC due to ash addition is in contrast to the results of Bougnom et al. (2010). All composts except *K12* had EC values below the recommended limit of 3 mS cm^{-1}, according to the Compost Ordinance.

Inorganic N forms (i.e., ammonia and nitrate) not only indicate compost maturity (Itävaara et al., 2010), but also provide information about the fertilizing effect of compost on soil in the short-term (easily plant available N-forms). It has been previously shown that ash-like amendment ($Ca(OH)_2$, CaO_2, CaO) significantly reduces total ammonia content of biowaste compost (Himanen and Hänninen, 2009). In our study, a similar trend was observed when composts were amended with up to 9% of ash addition (Table 2), however, it can be seen that amending compost with higher ash doses (*K12* and *K15*) led to an increase in ammonia levels probably due to the production of anaerobic niches in these compost piles (Kurola et al., 2011). The formation of more oxidized N forms was incremented following ash addition, and the highest NO_3^- content was recorded for *K15* (Table 2). The fertilizing value of composts, in terms of NO_3^- content, was therefore favoured by ash addition. Ash addition significantly reduced total N content compared to the unamended control (*K0*). Composts with higher ash addition (*K12* and *K15*) presented significantly lower total N levels (Table 2) than composts with lower dosage (*K3*, *K6*, *K9*), however, values were in the usual range (between 0.6 and 2.3% d.m.) for a normal compost (Baumgarten, 2010). The lower N contents are attributed to the dilution effect by ash amendment.

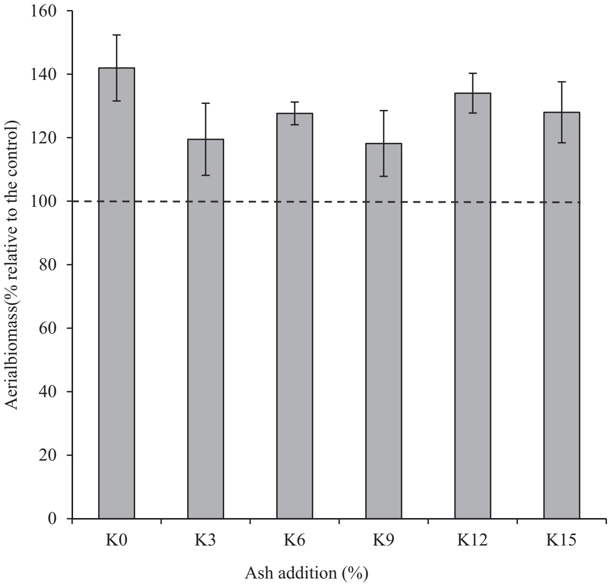

Fig. 4. Plant-growth bioassay (*Lepidium sativum*) in mature composts produced without, and with the different percentages of ash amendment (3, 6, 9, 12 and 15%). Measured values; the dotted line at 100% indicate the level that should be achieved with 15% of compost addition to the standard soil, according to the Austrian Compost Ordinance (2001). Means of triplicate measurements with standard errors are shown.

Of great interest is also the fact that ash addition had a positive effect on the content of nutrients of the final composts, as shown in Table 2. Indeed, there was a significant increase in the amount of P, Ca, K and Mg with the ash doses of 12 and 15%, in comparison with the control *K0*. Similar results were previously found by Koivula et al. (2004), Kuba et al. (2008), and Kurola et al. (2011), reinforcing the fertilizer potential of wood ash as a compost additive.

The heavy metal content in the wood ash used in this study was below the limits established by the Austrian Compost Ordinance (Table 1). Interestingly, as shown in Table 3, all the final composts, irrespective of the ash dose, met the requirements for compost quality A^+ regarding the amount of Cr, Ni and Pb. The Cu content for the treatments *K3*, *K9* and *K12* exceeded the limit of 70 mg kg^{-1} established for A^+ class (Table 3). For *K6*, the amount of Cu was circa 70 mg kg^{-1} (Table 3), and unexpectedly *K15* had a Cu content that fell into the A^+ class (58.3 mg kg^{-1}, Table 3), being close to the Cu level registered for unamended compost (Table 3). In the case of Cd, only *K0* and *K3* met the limits for compost class A^+ (Table 3), while *K6* and *K9* fell into class A (Table 3). The treatments with the highest ash dose, *K12* and *K15*, fell into class B (Table 3). Due to the high dry matter content of the ashes, compared to the biowaste, there was a more pronounced effect on composts with a high ash proportion, (*K12*, *K15*). For this reason, these treatments showed Cd levels closer to the original ash values (Table 1). Concerning the Zn content in the final composts, the control *K0* was classified into class A^+ and *K3* into class A (Table 3). The remaining treatments belonged to class B, although their levels of Zn were close to the cutoff value for class A (Table 3).

Therefore, only the treatment without ash addition (*K0*) could be strictly classified as compost A^+ quality taking into account all the analysed heavy metals (Table 3). In contrast to our findings, Kuba et al. (2008) observed that biowaste composts amended with up to 16% of ash admixture met the quality requirements for A^+ class. On the other hand, Koivula et al. (2004) also reported increasing values of heavy metals (Cd, Ni, Pb, Cu) with increasing ash addition (up to 20%) to kitchen biowaste compost. It is important to bear in mind that both the pollutant content and amount of the ashes on a dry matter basis, have a major influence on the final pollutant content on the compost. A mass flow simulation of a composting process from Obernberger

Table 3
Heavy metal contents in composts produced without, and with the different proportions of ashes (3, 6, 9, 12 and 15%), and the limit values for quality composts A^+, A and B according to the Austrian Compost Ordinance (2001). Values expressed on a dry mass basis for $n = 3$ (standard error in brackets).

	Heavy metal contents in mature compost (mg kg^{-1})						Limits for different compost qualities		
	K0	K3	K6	K9	K12	K15	A^+	A	B
Cd	0.01 (0.0005) a	0.07 (0.01) a	0.91 (0.29) ab	0.73 (0.44) ab	1.65 (0.43) b	1.51 (0.08) b	0.7	1	3
Cr	36.9 (5.34) a	36.1 (2.64) a	30.6 (1.76) a	32.6 (1.90) a	25.5 (0.36) a	26.3 (0.33) a	70	70	250
Cu	54.1 (3.78) a	95.1 (35.4) a	67 (6.37) a	71.9 (1.51) a	85.3 a[1]	58.3 (1.05) a	70	150	500
Ni	20.6 (1.06) a	20.2 (0.58) a	24.8 (0.88) b	24.1 (0.80) bc	20.6 (0.58) a	20.9 (0.36) ac	25	60	100
Pb	0.50 (0.27) a	0.69 (0.19) a	0.19 (0.10) a	0.36 (0.23) a	0.79 (0.29) a	0.48 (0.24) a	45	120	200
Zn	142 (5.29) a	263 (4.65) a	515 (25.5) a	511 (23.1) a	534 (32.0) a	554 (24.9) a	200	500	1800

Dissimilar letters in a row indicate statistically significant differences among the variants (Tukey HSD-test).

[1] $n = 2$.

(2010) concluded that an A+ class compost could be obtained from pure bottom ashes from fluidised furnaces, containing a maximum Cd level of 2 mg kg^{-1} d.m., using a maximum of up to 8% of ash addition.

4. Conclusions

The addition of up to 15% of wood ash to biowaste did not negatively affect the composting process, and the initial differences found between both the low and high ash-treated composts at the early stages of composting were attenuated with the ongoing process development. The final composts, regardless of the dose of ashes, reached Reifegrad V according to the Dewar test. The C/N ratio of all the ash-amended composts was lower than the cut-off value of 20 recommended for the safe application of composts as organic amendments. Furthermore, the highest NO_3^- content was recorded following the addition of 15% of ashes, which was also accompanied by an increase in the amount of macronutrients. Due to their heavy metal load, none of the ash-amended composts met the quality criteria for A+ class, according to the Austrian Compost Ordinance. Due to Cd levels, composts with 12 and 15% of ash did not qualify for class A. Thus, to avoid the risk of too high pollutant content, we suggest an amendment of not more than 9% of ashes to composts, and prior to the addition considering ashes as well as feedstock dry matter. The failure of obtaining class A+ quality after ash amendment emphasizes the need for a rigid quality-based selection of (bottom) ashes.

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