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Abstract: In this work the effects of selected types of biomass ash on the composting process and final product quality were studied by conducting an experimental campaign where the source separated organic fraction of municipal waste, mixed with wood prunings that served as bulking agent, was added with 0%, 2%, 4% and 8% wt/wt of biomass ash. The evolution over time of the main process parameters was observed, and the final composts were characterised. On the basis of the experimental results, the composting process was improved by ash addition; indeed, enhanced volatile solids reduction and biological stability were attained when ash was added, since ash favored the aerobic degradation by acting as a physical conditioner. In the final products, higher humification of organic matter, better germination performances, higher total Ca, Mg, K and P contents were observed when ash was used. The latter aspect may influence the composts marketability positively, particularly with regards to potassium and phosphorus. For this reason, the effect of ash on the K and P availability for plants was investigated too. However, some controversial effects of ash, related to the moisture and temperature values attained during the process, and pH and electrical conductivity levels in the final composts, were also observed. In the study, also heavy metals total content and their potential release to soil were investigated.

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COVER LETTER

In the present work the reuse of biomass combustion ash as an additive in the organic waste composting process is investigated. Biomass covers a prominent role among the renewable energy sources, whose diffusion is associated to energetic, economic and environmental advantages. The increasing amount of combustion ash produced worldwide is an emerging environmental issue related to the dramatic recourse to biomass. The definition of suitable reuse options for this special waste stream is, therefore, needed.

The utilization of biomass ash as an additive in the composting process has been studied by very few authors, though it is a valid option to recycle the nutrients and micronutrients contained in this waste stream. In particular, only one of the ash types valuable as a composting additive is considered in the existing published research, or only a part of all the properties relevant for assessing the final compost quality is investigated.

The present work focuses on the reuse of two ash types and demonstrates that the mixture of the two has a role as physical conditioner, and enhances the organic matter degradation and humification.

For these reasons, the Authors think the paper introduces new results on the biomass ash reutilisation and should be considered for publishing.

In order to investigate the effects of ash on the organic waste composting, an experimental campaign has been conducted in four pilot-scale composters using different biomass ash/organic waste ratios. The process, which lasted 96 days, was monitored continuously and the final composts were characterized. The data, obtained with methodological accuracy, were statistically analyzed and discussed.

Since this paper addresses an issue of emerging concern, is based on a solid state of the art and adheres to rigorous scientific methods, the Authors think it could appeal to both a popular and a scientific audience.

The article has been checked by a native tongue speaker with expertise in the field.

Authors are available as reviewers for at least three other articles for WM during the current year.

1 BIOMASS ASH REUTILISATION AS AN 2 ADDITIVE IN THE COMPOSTING PROCESS

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21 agent, was added with 0%, 2%, 4% and 8% wt/wt of biomass ash. The evolution over time of the
22 main process parameters was observed, and the final composts were characterised. On the basis of
23 the experimental results, the composting process was improved by ash addition; indeed, enhanced
24 volatile solids reduction and biological stability were attained when ash was added, since ash
25 favored the aerobic degradation by acting as a physical conditioner. In the final products, higher
26 humification of organic matter, better germination performances, higher total Ca, Mg, K and P
27 contents were observed when ash was used. The latter aspect may influence the composts
28 marketability positively, particularly with regards to potassium and phosphorus. For this reason, the
29 effect of ash on the K and P availability for plants was investigated too. However, some
30 controversial effects of ash, related to the moisture and temperature values attained during the
31 process, and pH and electrical conductivity levels in the final composts, were also observed. In the
32 study, also heavy metals total content and their potential release to soil were investigated.

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35

36 **1. INTRODUCTION¹**

37 In the recent years, a new strategy for achieving a more sustainable economic growth, based on the
38 circular economy approach, has been adopted by the European Commission (European
39 Commission, 2015). The aim of circular economy is to contrast the depletion of natural resources,
40 protect the biosphere, and increase the valorisation of residues in the production cycles (European
41 Commission, 2014), which could be also pursued by actions such as the recycling of nutrients-rich

¹ ANOVA: analysis of variance; BAsh: biomass ash; BD: bulk density; BOA: boiler ash; EC: electrical conductivity; FA: fly ash; FuA: fulvic acids; FAS: free airspace; HA: humic acids; HSD: honest significant difference; NREAPs: national renewable energy action plans; OFMSW: organic fraction of municipal solid waste; PD: particle density; RA4: 4-days respiration activity test; TOC: total organic carbon; TS: total solids; VS: volatile solid; WP: wood prunings

42 waste into soil improvers.

43 The last decade was marked by the spread of biomass plants as an attempt of a partial transition
44 from fossil fuels to renewable energy sources (Fernández-Delgado Juárez et al., 2015). In the
45 European Union, the National Renewable Energy Action Plans (NREAPs) estimate an increase in
46 biomass consumption of about 22% by 2020 comparing to the 2012 level (European Commission,
47 2014), which will result in a dramatic growth in the amounts of the related residues. Particular
48 attention should be paid to combustion, that is the most common biomass conversion technology,
49 and the residues generated, which consist of ash (James et al., 2012). Vassilev et al. (2010)
50 estimated that the amount of ash produced worldwide annually from biomass combustion was
51 approximately 480 million tonnes. James et al. (2012) reported that the biomass ash amount
52 produced in 2005 in Europe ranged from 1.6×10^7 to 3×10^7 tonnes, and suggested that the future
53 trend in the use of biomass for energy production could potentially lead to a production of $15.5 \times$
54 10^7 tonnes of ash in the EU-27 by 2020.

55 Biomass ash composition varies significantly according to the feed properties, combustion
56 technology, operating conditions and discharging point (Cuenca et al., 2013; Singh et al., 2011;
57 Teixeira et al., 2013; Vamvuka and Kakaras, 2011; Vassilev et al., 2010). In relation to the latter
58 point, some ash types could be discerned that are characterised by chemical-physical properties, and
59 a high content of macro-elements (such as Ca, Mg, K and P) and micro-nutrients (including Fe, Mn,
60 Zn and Cu), which could be relevant for maximising the potential of this waste product in the light
61 of the circular economy objectives (James et al., 2012).

62 In particular, though some studies suggest that selected biomass ash types may enhance the
63 composting process itself and improve the final compost quality if added to the organic waste at the
64 beginning of the process, to the authors' knowledge few published research is available on this issue
65 so far (Fernández-Delgado Juárez et al., 2015; Koivula et al., 2004; Kuba et al., 2008; Kurola et al.,
66 2011).

67 Moreover, in these studies only one of the ash types usually produced and valuable as a composting
68 additive was considered, or they focus on a part of the properties relevant for assessing the final
69 compost quality.

70 Therefore, the reutilisation of ash as a composting additive is worthy of further investigation,
71 considering the various chemical and physical characteristics, and their potential impacts on the
72 process and the final compost quality. Some physical characteristics of ash, such as low bulk density
73 and moisture, could have a positive impact on the composting process. In addition, since biomass
74 ash is enriched in elements important for plant growth (such as Ca, Mg, K and P), it could influence
75 the final compost quality positively so as to place it on the market with a higher added value
76 (Tittarelli et al., 2007). In particular, phosphorus is an essential nutrient that often constitutes the
77 limiting factor for plant growth, and potassium is usually low in the composts derived from organic
78 waste (Tittarelli et al., 2007). The K and P total content and availability in the composts are,
79 therefore, aspects of great significance.

80 On the counterpart, the use of biomass combustion ash as a composting additive may increase the
81 heavy metals content and salinity in the final compost, and dilute the total nitrogen content that ash
82 contains in small amounts or is lacking of (Fernández-Delgado Juárez et al., 2015; Kurola et al.,
83 2011).

84 With this aim to deepen the understanding on this issue, a composting experimental campaign was
85 conducted where a mixture of two biomass ash types, selected on the basis of their physical-
86 chemical characteristics, was added to the initial admixture of organic waste and bulking agent
87 according to ratios of 0%, 2%, 4% and 8% wt/wt.

88 **2. MATERIALS AND METHODS**

89 Two types of biomass combustion ash were used, that were collected from an industrial thermal
90 power plant located in Sardinia (Italy) and fed entirely with wood biomass. The ash types used were

91 boiler ash (BOA) and fly ash (FA) sampled from the super-heater placed after the boiler, and the
92 electrostatic filters, respectively. A mixture of BOA and FA (called BAsh in the manuscript)
93 according to 71:29% wt/wt (50:50% vol/vol ratio), which corresponds to the shares that are actually
94 produced in the thermal power plant, was used as additive during the composting tests.
95 A 96 days long composting experimental campaign was conducted using four static aerobic reactors
96 filled with approximately 133 kg of organic fraction of municipal solid waste (OFMSW) and wood
97 prunings (WP, used as bulking agent), mixed together according to the 70:30% wt/wt ratio, and
98 amended with BAsh. Biomass ash was added to the OFMSW+WP admixture in the amounts of 2%,
99 4% and 8% wt/wt in reactors that were called C2, C4 and C8, respectively. A fourth reactor did not
100 contain ash and served as the control (C0).
101 In Table 1 the chemical-physical characterisation of the OFMSW+WP admixture and the BAsh
102 blend used in this experiment is shown.
103 The composting admixtures were forced aerated by means of a compressed air circuit, that supplied
104 an aeration rate calculated according to the formulas proposed by Haug (1993) and set equal to 0.12
105 $\text{m}^3_{\text{air}} \cdot \text{m}^{-3}_{\text{substrate}} \cdot \text{min}^{-1}$, which is also consistent with the air rates provided by Ming et al. (2008) and
106 Zhang et al. (2016) for similar purposes.
107 The composting process was monitored on a daily basis by measuring the temperature values with a
108 thermocouple at the core of the composting admixtures. The moisture and volatile solids (VS)
109 content were determined by using a thermostatic oven at 105°C according to UNI 14774:2009, and
110 a furnace at 550°C according to UNI 15169:2007, respectively. The pH and electrical conductivity
111 (EC) levels were determined using a pH-meter (Orion4 Star, Thermo Fisher Scientific, MA, USA)
112 and a conductivity meter (HQ30d, Hach Company, CO, USA), respectively, according to UNI EN
113 15933:2012.
114 The evolution over time of the physical properties of concern was also monitored during the
115 composting process. The bulk density (BD) was measured on a weekly basis in accordance to UNI

116 15103:2010, while particle density (PD) was determined using a gas pycnometer (Accupyc II 1340,
117 Micromeritics Instrument Corporation, GA, USA) in accordance to ASTM B 923:2010. The free
118 airspace (FAS) was calculated by using the formula reported by Mohee and Mudhoo (2005) and
119 expressed by Eq. (1):

$$120 \quad FAS = 100 - BD_{w.b.} \cdot \left(\frac{M}{BD_{water}} + \frac{100 - M}{PD} \right) \quad (1)$$

121 where

122 FAS is the free airspace [%],

123 $BD_{w.b.}$ is the wet bulk density of the material [$\text{kg}\cdot\text{m}^{-3}$],

124 M is the moisture content of the material [%],

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

126 PD is the particle density of the material [$\text{kg}\cdot\text{m}^{-3}$].

127 The 4-days respiration activity test (RA4) was performed in the composting admixtures at the
128 beginning and the end of the experimental campaign by using a Sapromat respirometer (H+P
129 Labortechnik AG, Germany).

130 A total organic carbon analyser (TOC-VCSN and SSM-5000A, Shimadzu Corporation, Japan) and
131 an elemental analyser (CHN-1000, LECO Corporation, MI, USA) were used to determine the total
132 organic carbon (TOC) and total carbon and nitrogen contents in final composts, respectively. In
133 addition, the final products were characterised in terms of total content of major and minor elements
134 by inductively coupled plasma spectrometry (ICP-OES, Optima 7000DV, PerkinElmer, MA, USA)
135 after a microwave-assisted acid digestion, according to EPA Method 3052. Mercury was determined
136 by using a Direct Mercury Analyser (DMA-80, MilestoneS.r.l., Italy). The water soluble fraction of
137 heavy metals was assessed by extracting with distilled water, filtering and analysing using
138 spectrometry (ICP-OES, Optima 7000DV, PerkinElmer, MA, USA). A colorimetric determination
139 and spectrophotometry (U-2000, Hitachi Ltd., Japan) were used to measure the total phosphorus

140 content (Li et al., 2013; Masto et al., 2013) and available fraction of phosphorus, the latter after
141 extraction with 0.5 M NaHCO₃ (Olsen et al., 1954). The potassium water soluble and exchangeable
142 fractions were determined after extraction with distilled water (Singh and Kalamdhad, 2013), and
143 with 1 M ammonium acetate at pH 7.0 (Rayment and Higginson, 1992), respectively. Afterwards,
144 liquid samples were filtered and analysed using spectrometry (ICP-OES, Optima 7000DV,
145 PerkinElmer, MA, USA).

146 Germination tests were performed on the final composts using *Lepidium sativum* seeds according to
147 the procedure proposed by Masciandaro et al. (2010) and Zucchini et al. (1981).

148 Finally, humic matter, and fulvic (FuA) and humic acids (HA) were determined by extracting the
149 humic substances according to UNI 10780:1998; then the humic carbon in the obtained solutions
150 was determined by means of a TOC analyser (TOC-VCSN and SSM-5000A, Shimadzu Corporation,
151 Japan).

152 A one-way analysis of variance (ANOVA) was performed on the main process parameters
153 (temperature, pH, volatile solids content) with the ash amount as the main factor. Post hoc Tukey
154 HSD test was conducted when statistically significant differences were found. In addition, a
155 comparison between regression lines was made on the volatile solids content and free airspace
156 values across the ash amount levels used. Simple regression analyses between the humic matter and
157 available P and K content were also performed. All the statistical data were obtained using the
158 Statgraphic Centurion XVI software.

159 All the analyses were conducted in triplicate and the results are presented as mean values \pm standard
160 deviation.

161 **3. RESULTS AND DISCUSSION**

162 **3.1 Evolution of the composting process**

163 The temperature and moisture evolution in C0, C2, C4 and C8 with respect to time is displayed in

164 Fig. 1. At the early stage of the composting process an increase in temperature levels was observed
165 in all the reactors, and values higher than 55°C were achieved and maintained for more than three
166 days, which is one of the hygiene requirements for pathogens reduction (Cesaro et al., 2015; Nair et
167 al., 2006). In the composting admixture with 8% of BAsh, values higher than 60°C for almost one
168 week were observed. The higher temperature values observed in C8 at the early stage of the process
169 could be related to accelerated microbial activity, higher ability to retain heat, and carbonation
170 exothermic reactions that normally occur when an alkaline material, such as ash, is subjected to
171 aerobic processes (Koivula et al., 2004; Kuba et al., 2008; Kurola et al., 2011). The initial
172 temperature peaks influenced the moisture evolution because of the loss of water vapour (Zhang et
173 al., 2016), so that a decrease in the moisture content was observed in all the reactors, and was as
174 marked as the ash amount added was greater. After the addition of tap water, on day 15, moisture
175 levels of approximately 55% were re-established in all the reactors and new temperature peaks were
176 observed. From day 15 to 30, temperature values showed statistically significant differences at the
177 0.1 level (ANOVA $F(3,36) = 2.37$, $p = 0.087$) between the C0 and C8 composting admixtures.
178 Consistently, the admixture containing 8% of BAsh required the biggest amount of water to restore
179 a proper moisture level (26 L for C8 comparing to approximately 15 L for C0, C2 and C4).
180 Successive water additions did not lead to significant temperature increase, values close to ambient
181 temperature (10°C, since tests were performed during winter time) were detected, and the biological
182 stability was supposed to be achieved (Haug, 1993).
183 In the final composts the moisture content ranged from 43% to 54%, with values similar to the ones
184 reported by Fernández-Delgado Juárez et al. (2015).
185 The evolution over time of pH values and the volatile solids content is shown in Fig. 2. The pH
186 values evolved during the composting process similarly in all the composters, with higher values
187 observed in correspondence to the admixtures with the highest ash amounts because of the ash
188 alkaline properties. Statistically significant differences were observed in relation to the effect of the

189 ash amount on pH values (ANOVA $F(3,36) = 3.84$, $p = 0.018$). The post hoc test revealed that the
190 pairs C0-C4, C0-C8, and C2-C8 were significantly different. The ash reuse as an additive could be
191 beneficial for contrasting an excessive pH decrease that eventually might occur at the initial acid
192 phase of organic waste composting (Kurola et al., 2011) and provoke a microbial activity decrease
193 at pH values lower than 5 (Cheung et al., 2010). On the other hand, too high pH values could be
194 inhibitory for the biological activity during the thermophilic phase and cause N losses due to
195 ammonia stripping (Fang et al., 1999). According to Nakasaki et al. (1993), the optimal pH values
196 for a rapid degradation at the early stage of composting range from 6 to 9.

197 The volatile solids reduction was more marked in the ash-amended admixtures comparing to the
198 control. A statistically significant effect of ash addition on the volatile solids content at the $p < 0.05$
199 level (ANOVA $F(3,36) = 10.34$, $p = 0.000$) was observed. As underlined for the effects on pH, three
200 pairs of composting admixtures showed statistically significant differences according to the Tukey's
201 HSD test: C0-C4, C0-C8, and C2-C8. In particular, the volatile solids content in the final C8
202 compost was 38% lower than in the final unamended product. This result suggests that ash addition
203 improved organic matter degradation. Fernández-Delgado Juárez et al. (2015) observed a similar
204 result and suggested that ash, being an alkaline additive, could facilitate the degradation of lignin,
205 cellulose and hemicellulose, whose decomposition under aerobic conditions is otherwise uneasy.

206 The respiration activity assessed over time confirmed this figure. The 4 days total oxygen
207 consumption for the initial substrates, expressed as RA4, was between 26.7 and 28.4 $\text{mg O}_2 \cdot \text{gTS}^{-1}$,
208 and ranged from 2.7 to 15.8 $\text{mg O}_2 \cdot \text{gTS}^{-1}$ in the final composts. The lowest RA4 value was
209 observed for the C8 final product, 52% lower than for the control reactor. Interestingly, only the C8
210 final product fulfilled the limit value of 10 $\text{mg O}_2 \cdot \text{gTS}^{-1}$ suggested by the European Union
211 Biological Treatment Working Document to identify a stable compost (Sánchez Arias et al., 2012).
212 Therefore, ash addition seems to enhance the achievement of a higher biological stability degree.
213 The bulk density and free airspace evolution attained during the experimental campaign is shown in

214 Fig. 3. Particle density, that is needed for the determination of FAS, was also calculated (data not
215 shown). If the initial and final bulk density values are considered, an increase could be observed in
216 all the composting admixtures, with higher values attained for the composting mixtures with 4%
217 and 8% of BAsh, though a decrease at the beginning of the experiment could also be noticed. An
218 increase in the FAS values was observed during the first two weeks of the experiment in all the
219 admixtures in accordance to the BD evolution in the same period and, in particular, values higher
220 than 70% were observed in C4 and C8. A comparison of regression lines was conducted to evaluate
221 the variation of the volatile solids content against the FAS values evolution across categories
222 constituted by the ash amounts added. A linear regression model describes the relationship between
223 $VS_{w.b.}$, FAS and BAsh amounts, as expressed by Equations (2-5), that correspond to the conditions:
224 BAsh = 0%, BAsh = 2%, BAsh = 4%, and BAsh = 8%, respectively.

$$225 \quad VS_{w.b.} = 16.2137 + 0.22546 \cdot FAS \quad (2)$$

$$226 \quad VS_{w.b.} = 5.7058 + 0.44262 \cdot FAS \quad (3)$$

$$227 \quad VS_{w.b.} = 13.818 + 0.20644 \cdot FAS \quad (4)$$

$$228 \quad VS_{w.b.} = 3.3733 + 0.40997 \cdot FAS \quad (5)$$

229 This model explains 79.4% of the variability of $VS_{w.b.}$. There is a statistically significant
230 relationship between $VS_{w.b.}$ and FAS at the 0.05 level (ANOVA $F(7,20) = 10.98$, $p=0.000$).

231 On the basis of the statistical results, the observed organic matter degradation could be partially
232 related to the FAS evolution.

233 **3.2 Final compost quality**

234 The main characteristics of the obtained composts are reported in Tab. 2.

235 Both the final pH and EC values were higher in the ash-amended composts than in the control one,
236 and as high as the ash amounts added were. The pH levels in the final C0, C2, C4 and C8 composts
237 were 8.2, 8.8, 8.8 and 9.2, respectively. These high values could be either beneficial or adverse for

238 plant growth depending on the properties of soils where the composts are supposed to be employed.
239 Bougnom et al. (2010), who conducted field experiments using an ash-amended compost
240 characterised by pH value of 8.59 and produced in the experimental campaign described by Kuba et
241 al. (2008), observed an ameliorating effect when the compost was applied to an acidic soil.
242 The final EC in C2, C4 and C8 composts were 35%, 49% and 53% higher than in the control one. It
243 is worth underlining that in all the reactors, including the control, EC values exceeded the
244 recommended level, that is set between 3 and 4 $\text{mS}\cdot\text{cm}^{-1}$ (Fernández-Delgado Juárez et al., 2015;
245 Koivula et al., 2004; Kuba et al., 2008). Therefore, to determine this figure it could have contributed
246 the initial OFMSW electrical conductivity value (equal to $4.2 \text{ mS}\cdot\text{cm}^{-1}$), that was unexpected high,
247 eventually due to a possible contamination with a high salinity waste component such as fireplace
248 ash.
249 The increase in the ash amount added resulted in lower total organic carbon content in the final
250 products. The TOC values ranged between 24.9% $\text{wt}_{\text{d.m.}}$ and 19.0% $\text{wt}_{\text{d.m.}}$ in the final composts,
251 because of the dilution effect due to the low organic fraction of the combustion residues and the
252 improved organic matter degradation achieved in the ash-amended composts (Fernández-Delgado
253 Juárez et al., 2015; Koivula et al., 2004; Kurola et al., 2011).
254 Nitrogen, that is the most important nutrient for plant growth, was lower in C4 and C8 than in C0.
255 Since the total nitrogen level in BAsh was very low (below the detection limit, $<0.006\%$), a dilution
256 effect might have influenced the N content in the final products where ash was added. In addition,
257 the increased temperature and process pH observed when BAsh was added could have favored
258 ammonia volatilisation during composting, further reducing the total N content. As for the
259 $C_{\text{total}}/N_{\text{total}}$ ratio, it ranged between 10.8 and 13.1 in the four final composts.
260 As also reported by Singh and Kalamdhad (2013), the total nutrients content is expected to increase
261 during the composting process because of the concentration effect caused by the organic matter
262 degradation. In this work, the levels of P, Ca, K and Mg, that are important macronutrients for

263 plants (Park et al., 2012), in the final composts were investigated (Tab. 2). Because of the high P,
264 Ca, K and Mg levels in BOA and FA, and the enhanced organic matter degradation achieved when
265 ash was added, a more evident increase was observed in the ash-amended composting admixtures.
266 Comparable results were described by Fernández-Delgado Juárez et al. (2015) and Kurola et al.
267 (2011). This figure could provide ash-amended composts with a wider marketability because of the
268 increased agronomic value, particularly in relation to phosphorus and potassium (Tittarelli et al.,
269 2007).

270 The potassium water-extractable and exchangeable fractions represent the K soluble salts and the
271 bioavailable K, respectively; while the NaHCO_3 -extractable P is related to both the soluble fraction
272 and the one bound to soil surface by weak adsorption, which correspond to the amount of
273 phosphorus readily available for plant growth (Glaser et al., 2002).

274 The levels of both the water soluble and exchangeable potassium increased in the final composts
275 according to the increase of the ash amount added, as depicted in Fig. 4a. If the corresponding
276 fractions are considered, lower values were observed in the ash-amended composts comparing to
277 the control one; in particular, the K bioavailable fraction was 84.2% $\text{wt}_{\text{d.m.}}$, 77.1% $\text{wt}_{\text{d.m.}}$, 70.3% $\text{wt}_{\text{d.m.}}$
278 and 68.4% $\text{wt}_{\text{d.m.}}$ of the total potassium content in C0, C2, C4 and C8, respectively. Therefore, other
279 forms of potassium must had been favored by ash addition, which might represent sources of slowly
280 releasable K (Bhattacharyya et al., 2007).

281 Lower levels of NaHCO_3 -extractable phosphorus, that represents inorganic, labile P and easily
282 hydrolysable organic P (Kolahchi and Jalali, 2012; Verma, 2013) were observed in the composts
283 containing the highest amounts of ash comparing to the unamended one (Fig. 4b); as a consequence,
284 also the corresponding P available fractions were lower in the ash-amended composts comparing to
285 the control one (22.6% $\text{wt}_{\text{d.m.}}$, 22.7% $\text{wt}_{\text{d.m.}}$, 18.3% $\text{wt}_{\text{d.m.}}$ and 17.5% $\text{wt}_{\text{d.m.}}$ in C0, C2, C4 and C8,
286 respectively). Nonetheless, part of the more stable P is organically-bound and, since the phosphorus
287 organically-bound to humic substances constitutes a slow release P source, it is available as well,

288 though in the long term (Palanivell et al., 2013; Verma, 2013).

289 In this study, the overall humic matter was 59.8% wt_{d.m.}, 65.7% wt_{d.m.}, 67.8% wt_{d.m.} and 66.8% wt_{d.m.}

290 of the total carbon content in the final C0, C2, C4 and C8 composts, respectively, as shown in Fig.

291 5. According to these results, humification in the final composts was improved when BAsh was

292 added. In addition, the HA fraction of the overall humic matter, which is related to compost

293 maturity (Huang et al., 2006), was higher in the ash-amended composts comparing to the

294 unamended one, and the highest value was observed in C8. It should be noted that in C4 the highest

295 overall humic matter content and the lowest level of available P (that exhibits a great affinity for the

296 humic substances that are naturally formed during composting) were observed. If the linear

297 regression analysis between the total humic substances and available phosphorus is considered, a

298 correlation coefficient equal to -0.91812 is found between the variables. In the final composts, also

299 the potassium exchangeable fraction was compared to the amount of humic matter; a simple

300 regression analysis was performed and a correlation coefficient of 0.945173 is found. These two

301 statistical analyses indicate that the humic matter content in the final composts had a relatively

302 strong relationship with these forms of available P and K.

303 The total Be, Cd, Co, Pb, Sb, Se and V levels in the final composts were below the detection limit.

304 The total content of the other heavy metals is shown in Tab. 3. The heavy metals water soluble

305 fractions, that represent the share of elements that could be easily mobilised (Singh and Kalamdhad,

306 2013), are also reported in Tab. 3.

307 For most of the elements, the total content variations among the final composts could not be clearly

308 related to the ash amount added. On the contrary, the Al and Mn total content in the ash-amended

309 composts were higher than in the unamended one, and as high as the ash amount added was. This

310 result could be due to the fact that the Al and Mn levels in BAsh were higher than in the organic

311 waste, and that the leachable fractions of aluminum and manganese in the considered ash blend

312 were very low or not detectable (data not shown).

313 As for the heavy metals water soluble fractions in the final composts, the Al, Mn and Zn ones
314 decreased along with the increase of the ash amount added. The decrease in the Mn water soluble
315 fraction could be related to the increase in the compost pH levels when ash was used, as Hue and
316 Mai (2002) observed when they investigated the effect of lime and compost in soils. It is also
317 acknowledged that the organic matter decomposition and formation of humic compounds influence
318 the metals water solubility (Amir et al., 2005; Neaman et al., 2012). Amir et al. (2005) observed that
319 as humification increases, Zn is converted from exchangeable to more stable forms (organic
320 complexes with the humic matter), and Ifansyah (2013) reported that the humic acids lowered the
321 aluminum solubility.

322 The copper water soluble fraction was higher in the ash-amended composts, and as high as the ash
323 amount added was. Copper has high affinity with the soluble fraction of the humic matter
324 (Adekunle, 2009) that increases with the pH growth (Kipton et al., 1992) and, since pH increases
325 with ash addition, higher soluble Cu fractions are attained in the ash-enriched composts. Also
326 Neaman et al. (2012), who conducted an experimental campaign where lime and compost were
327 added to soils, observed higher Cu soluble fractions in the composts with high pH values comparing
328 to the control.

329 In this study, the water soluble fractions of Fe and Ni were higher in the ash-amended composts
330 than in the unamended one, but a relation between the increase of Fe and Ni water soluble fractions
331 and the ash amount added could not be envisaged.

332 In general, these results suggest that ash-amended composts could be effective in immobilising
333 some of heavy metals (as for Zn), though attention should be paid to the different leaching
334 behaviour of copper comparing to the other metals.

335 In order to evaluate the phytotoxicity of the final composts, germination tests using *Lepidium*
336 *sativum* seeds were performed, and the results attained are displayed in Fig. 6. The composts
337 enriched with ash showed germination indices 13%, 19% and 8% higher than the control one,

338 respectively. The highest germination index was observed for the C4 final compost. These results
339 suggest that ash-amended composts had a lower inhibitory effect on plant growth than C0. Himanen
340 and Hänninen (2009) observed a relation between higher germination performances and the
341 improved stability in composts amended with commercial additives based on calcium and
342 magnesium-bearing compounds. In this study, a moderately strong correlation (with coefficient
343 equal to 0.8403) was found between the germination indices and the humic matter in the final
344 composts. On the other hand, all the composts reported germination indices lower than distilled
345 water, possibly because of the high salinity as suggested by Belyaeva et al. (2012), who studied the
346 effect of coal fly ash on compost quality.

347 **4. CONCLUSIONS**

348 In this work the effects of the ash addition on organic waste composting were studied and discussed.
349 An experimental campaign was conducted, where a blend of two biomass combustion ash types was
350 added to a mixture of OFMSW and bulking agent according to ash amounts of 2%, 4% and 8%
351 wt/wt. The addition of ash has determined a set of effects in terms of physical characteristics of the
352 admixtures subjected to composting, evolution and extent of the stabilisation process and
353 characteristics of the final product. The magnitude of these effects was generally proportional to the
354 amount of added ash and, overall, the combination of these can be evaluated positively.
355 Higher free airspace values in the ash enriched admixtures were also calculated, which suggest
356 biomass ash had a role as a physical conditioner. Beneficial effects on the evolution of the process
357 were observed in terms of enhanced organic matter degradation and bio-stability in the ash-amended
358 admixtures. As for the final composts quality, the total nutrients content (Ca, Mg, K and P), and
359 germination and humification indices were higher in the composts where ash was added than in the
360 control one. The water-soluble and exchangeable K were higher in the ash-amended composts
361 comparing to the control one. On the contrary, the available P was slightly lower in the ash-enriched

362 composts than in the unamended one, for the benefit of the slowly releasable form that is bound to
363 the humic substances. Though ash addition was adverse for the total nitrogen content, similar final
364 C_{total}/N_{total} values were observed in all the composts. The heavy metals content, that is regarded as
365 the main environmental disadvantage when using ash as a composting additive, was also
366 investigated; it is plausible to assume that part of the heavy metals content in the ash blend was
367 released with the leachate produced during the composting process, and this figure is worthy of
368 further investigation. As for the heavy metals share remaining in the end product, for Al, Mn and Zn
369 the solubility in the ash-amended composts was lower than in the control one, which suggests that
370 ash addition favored the heavy metals immobilisation. Conversely, copper showed a different
371 leaching behaviour comparing to the other metals, so that attention should be paid to it. Regarding
372 the most controversial aspects, higher temperature, pH and EC values, as well as lower moisture
373 levels, were observed in the ash-amended composting admixtures than in the unamended one.
374 In the perspective of a full implementation of the circular economy concepts, it is important to study
375 synergistic approaches for the valorisation of residues, eventually having different origins, but all
376 available in the same area. This approach, in addition to minimising the flow of waste sent to final
377 disposal, could also allow for a greater added value to the products of the recovery action, in turn
378 enhancing the possibility of placing them on the market, as pursued in the present study.

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496 **TABLES**

497 Table 1. Characteristics of the OFMSW and WP admixture, and the BAsh (ash blend) used;
 498 standard deviation is indicated in brackets (< d.l.: below the detection limit; n.d.: value not
 499 detected).

	OFMSW+WP	BAsh
Moisture [%]	58.30 (0.01)	1.21 (0.02)
VS [% wt _{d.m.}]	66.88 (0.03)	2.26 (0.15)
pH	5.09 (0.03)	12.77 (0.01)
EC [mS·cm ⁻¹]	4.22 (0.10)	26.38 (4.5)
TOC [% wt _{d.m.}]	34.77 (1.97)	4.56 (0.02)
N _{total} [% wt _{d.m.}]	2.05 (0.20)	<d.l.

$C_{\text{total}}/N_{\text{total}}$	16.96	n.d.
CaO [%wt _{d.m.}]	2.37 (0.07)	29.01 (0.12)
MgO [%wt _{d.m.}]	0.25 (0.02)	5.18 (0.07)
K ₂ O [%wt _{d.m.}]	0.61 (0.01)	9.43 (0.14)
P ₂ O ₅ [%wt _{d.m.}]	0.44 (0.01)	2.77 (0.05)
Na ₂ O [%wt _{d.m.}]	0.35 (0.00)	1.18 (0.01)
Fe ₂ O ₃ [%wt _{d.m.}]	0.34 (0.00)	2.61 (0.08)
Al ₂ O ₃ [%wt _{d.m.}]	0.29 (0.02)	6.00 (0.14)
MnO ₂ [mg·kg ⁻¹ _{d.m.}]	116.93 (3.08)	2319.87 (0.01)
Be [mg·kg ⁻¹ _{d.m.}]	0.83 (0.00)	0.06 (0.00)
Cd [mg·kg ⁻¹ _{d.m.}]	<d.l.	2.80 (0.09)
Co [mg·kg ⁻¹ _{d.m.}]	1.66 (0.00)	9.83 (0.36)
Cr [mg·kg ⁻¹ _{d.m.}]	87.38 (1.07)	39.11 (0.72)
Cu [mg·kg ⁻¹ _{d.m.}]	17.76 (0.95)	191.47 (0.35)
Hg [mg·kg ⁻¹ _{d.m.}]	0.02 (0.00)	0.28 (0.02)
Ni [mg·kg ⁻¹ _{d.m.}]	43.69 (0.54)	27.45 (0.96)
Pb [mg·kg ⁻¹ _{d.m.}]	<d.l.	44.67 (0.73)
Sb [mg·kg ⁻¹ _{d.m.}]	1.25 (0.59)	1.04 (0.15)
Se [mg·kg ⁻¹ _{d.m.}]	0.83 (0.00)	1.31 (2.20)
V [mg·kg ⁻¹ _{d.m.}]	3.61 (0.48)	42.74 (0.44)
Zn [mg·kg ⁻¹ _{d.m.}]	56.64 (2.36)	371.06 (3.32)

500

501

502 Table 2. Characteristics of the final composts; standard deviation is indicated in brackets (<d.l.:

503 below the detection limit).

	C0	C2	C4	C8
VS [% wt _{d.m.}]	50.91 (0.110)	44.99 (1.240)	38.98 (1.271)	31.54 (1.099)
pH	8.23 (0.000)	8.76 (0.014)	8.77 (0.205)	9.16 (0.014)
EC [mS·cm ⁻¹]	4.08 (0.262)	5.48 (0.552)	6.06 (0.127)	6.23 (0.184)
TOC [% wt _{d.m.}]	24.91 (0.841)	22.78 (0.262)	21.98 (0.813)	18.96 (1.937)
N [% wt _{d.m.}]	1.95 (0.178)	2.17 (0.029)	1.87 (0.291)	1.64 (0.093)
C _{total} /N _{total}	12.96	10.75	12.47	13.14
Total Ca [g·kg ⁻¹ _{d.m.}]	50.60 (2.46)	50.30 (0.83)	69.27 (2.10)	72.71 (0.79)
Total Mg [g·kg ⁻¹ _{d.m.}]	4.50 (0.12)	5.93 (0.67)	6.81 (0.12)	7.13 (0.25)
Total K [g·kg ⁻¹ _{d.m.}]	14.67 (0.20)	19.06 (0.34)	22.95 (0.03)	23.77 (0.46)
Total P [g·kg ⁻¹ _{d.m.}]	6.33 (0.19)	6.16 (0.30)	7.11 (0.00)	7.79 (0.08)

504

505

506 Table 3. Heavy metals total content and soluble fraction in the final composts; standard deviation is
507 indicated in brackets (< d.l.: below the detection limit).

	C0	C2	C4	C8
Al [mg·kg ⁻¹ _{d.m.}]	4022.92 (249.99)	5068.97 (247.90)	5315.73 (98.50)	6227.81 (108.94)
Soluble Al [% of the total content]	0.17	0.16	0.10	0.09
Ba [mg·kg ⁻¹ _{d.m.}]	77.64 (9.75)	68.19 (2.92)	67.52 (2.06)	72.44 (0.02)
Soluble Ba [% of the total content]	0.68	1.80	0.35	0.16
Cr [mg·kg ⁻¹ _{d.m.}]	34.63 (0.45)	33.47 (1.16)	35.84 (3.38)	37.46 (1.20)
Soluble Cr [% of the total content]	<d.l.	<d.l.	<d.l.	<d.l.

Cu [mg·kg ⁻¹ _{d.m.}]	37.56 (3.69)	29.70 (0.61)	34.18 (1.03)	34.54 (0.56)
Soluble Cu [% of the total content]	4.03	7.64	7.66	8.96
Fe [mg·kg ⁻¹ _{d.m.}]	0.71 (0.01)	0.86 (0.04)	0.65 (0.00)	0.70 (0.00)
Soluble Fe [% of the total content]	0.34	0.48	0.42	0.36
Hg [mg·kg ⁻¹ _{d.m.}]	0.062 (0.005)	0.073 (0.000)	0.082 (0.001)	0.055 (0.003)
Soluble Hg [% of the total content]	n.d.	n.d.	n.d.	n.d.
Mn [mg·kg ⁻¹ _{d.m.}]	283.11 (2.52)	377.17 (5.72)	433.26 (2.80)	455.30 (13.22)
Soluble Mn [% of the total content]	0.55	0.50	0.29	0.19
Ni [mg·kg ⁻¹ _{d.m.}]	17.94 (0.51)	17.57 (1.17)	20.00 (3.45)	18.87 (1.26)
Soluble Ni [% of the total content]	1.80	2.38	2.09	2.08
Zn [mg·kg ⁻¹ _{d.m.}]	76.81 (14.47)	87.86 (8.34)	75.86 (0.85)	75.35 (1.68)
Soluble Zn [% of the total content]	3.68	3.30	2.57	1.47

508

509

510 **Captions**

511 Figure 1. Temperature and moisture evolution over time in: a) C0; b) C2; c) C4; d) C8 composting
512 admixtures.

513 Figure 2. Evolution of: a) pH; b) volatile solid content (VS_{d.m.}) in the C0, C2, C4 and C8
514 composting admixtures.

515 Figure 3. Evolution of the bulk density (BD) and free airspace (FAS) in the C0, C2, C4 and C8
516 composting admixtures.

517 Figure 4. Total content, and water soluble and available fractions of: a) potassium; b) phosphorus..

518 Figure 5. Humic substances and fulvic (FuA) and humic (HA) fractions content (% wt_{d.m.}) in the
519 final C0, C2, C4 and C8 composts (error bars represent the standard deviation).

520 Figure 6. Germination indices of the final composts C0, C2, C4 and C8 (error bars represent the
521 standard deviation).

BIOMASS ASH REUTILISATION AS AN ADDITIVE IN THE COMPOSTING PROCESS

HIGHLIGHTS

- A blend of boiler and fly ash is added to organic waste undergoing composting.
- The ash blend improves free airspace and organic matter degradation.
- The ash addition improves biostability and the humification of organic matter.
- The ash-amended composts are enriched in nutrients, in particular P and K.
- Biomass ash could be used as an additive in the organic waste composting.

Figure

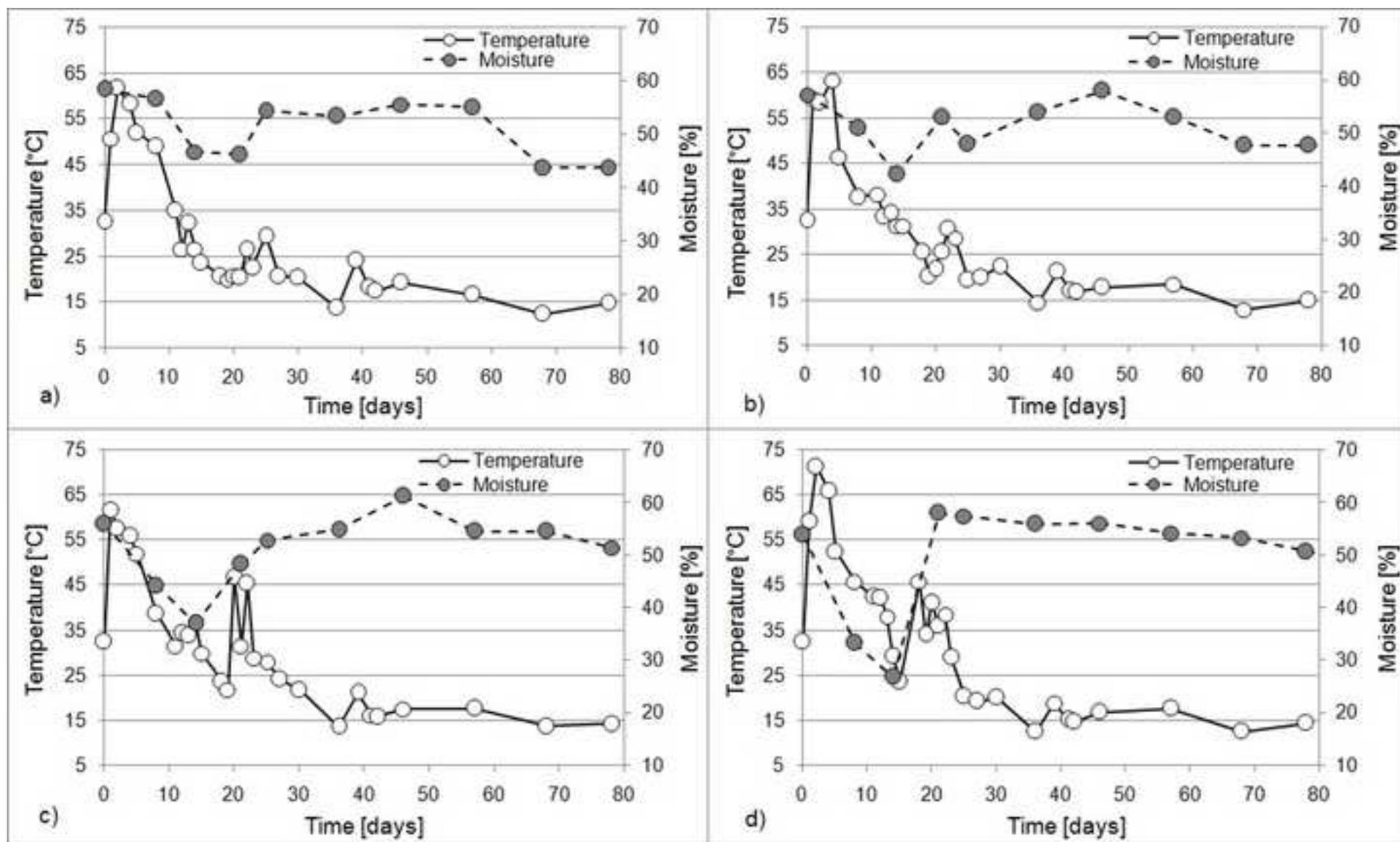
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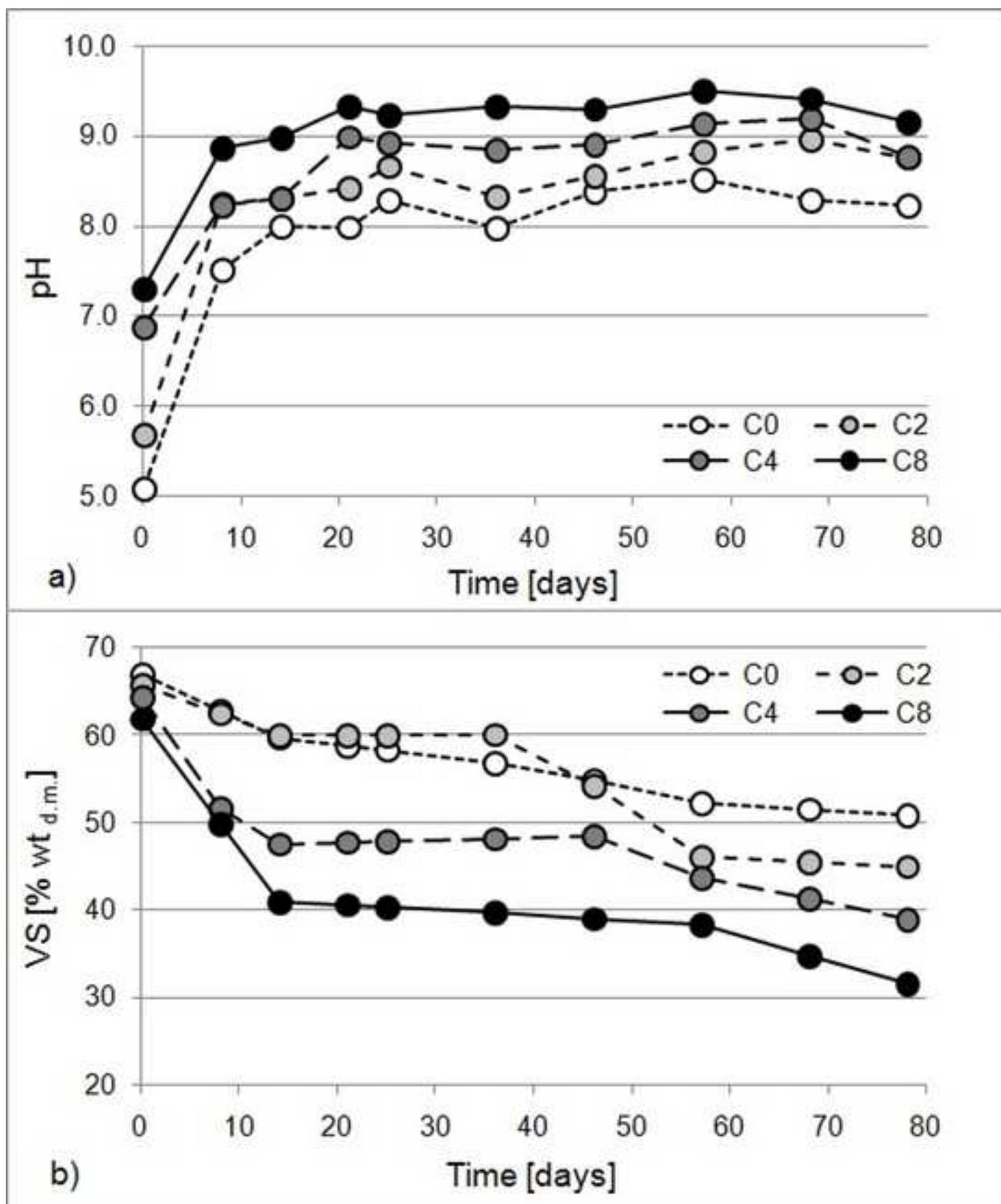


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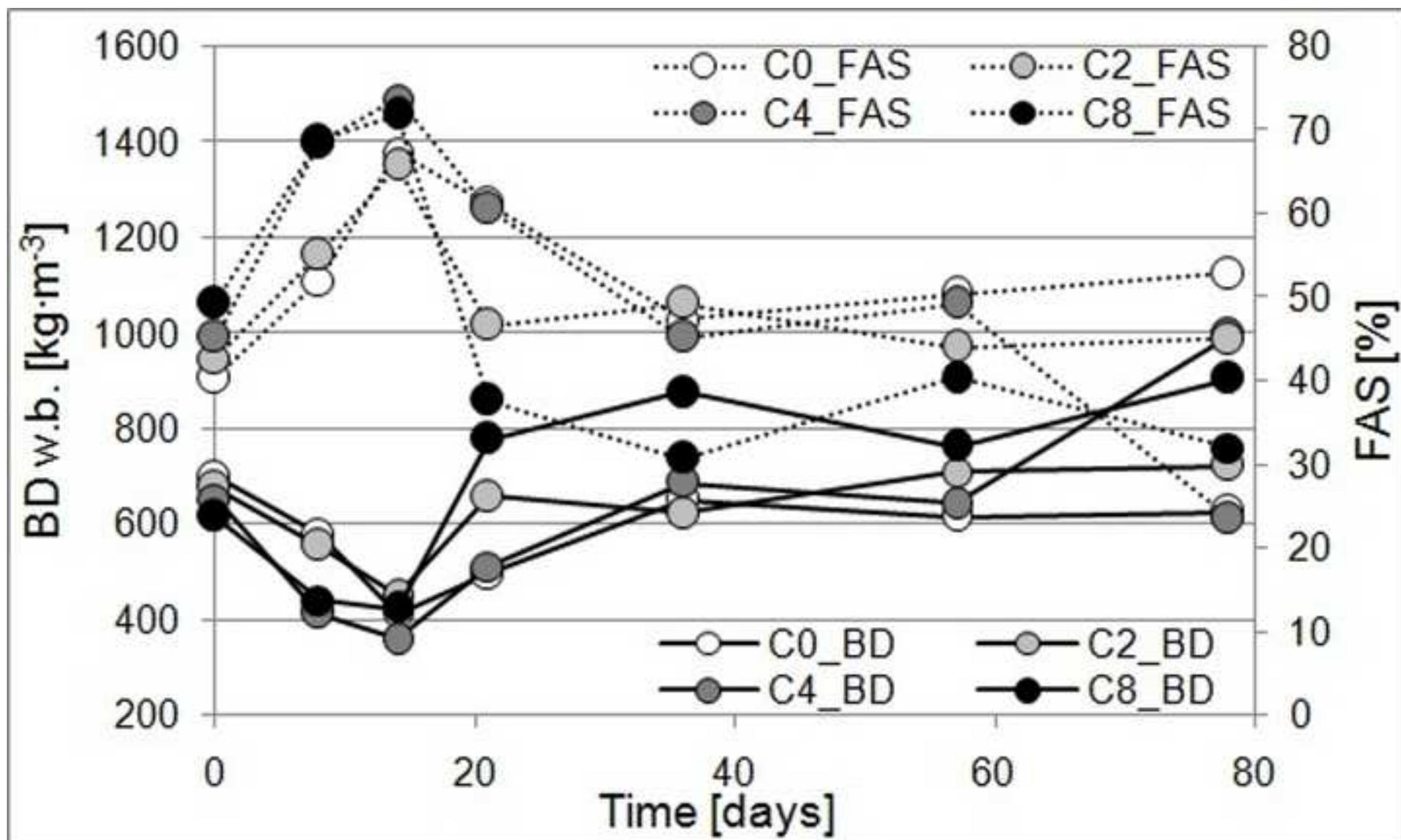
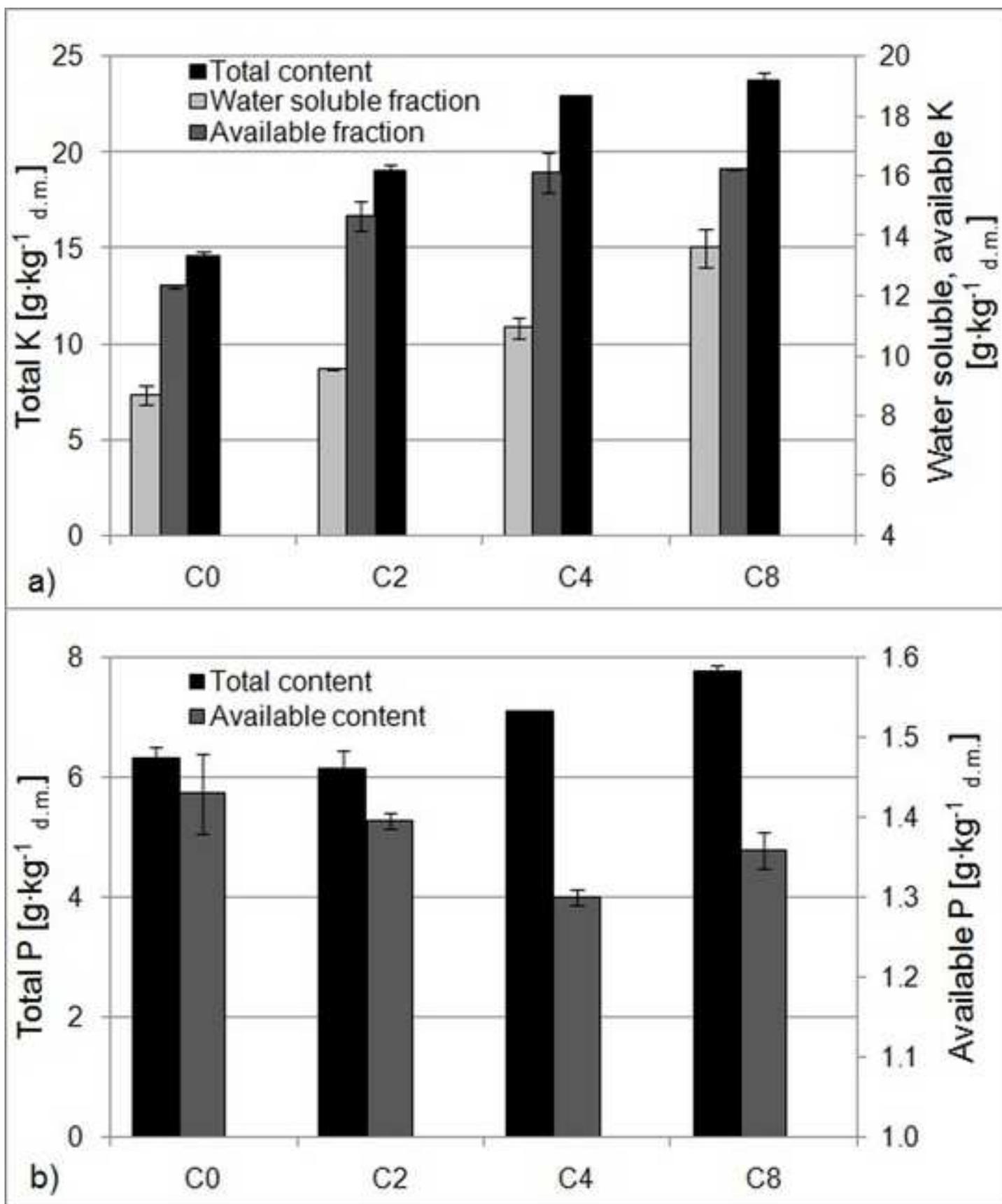


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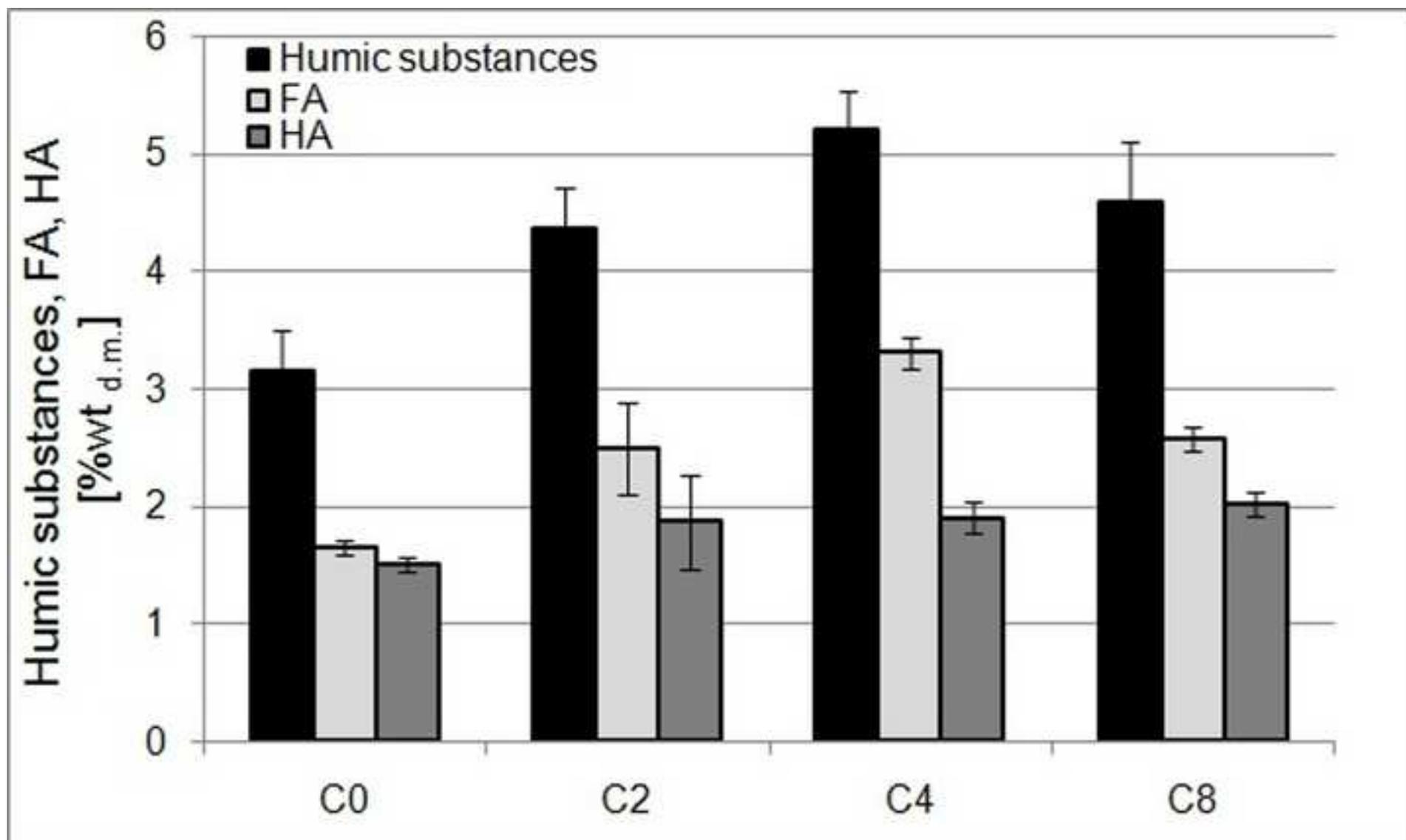


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