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## **Effect of industrial and domestic ash from biomass combustion, and spent coffee grounds, on soil fertility and plant growth: Experiments at field conditions**

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### **Abstract**

A study was conducted at field conditions in order to evaluate the effect of application of ash from biomass combustion on some soil fertility characteristics and plant growth. Application of 7.5 Mg ha<sup>-1</sup> industrial (fly) ash, domestic ash and a 50:50 mix of domestic ash and spent coffee grounds was made in different soil parcels. *Lolium perenne* seeds were sown and the grown biomass was harvested and quantified after 60 days. Soil samples from each parcel were also collected after that period and characterized. Both soil and grown biomass samples were analyzed for Ca, Mg, Na, K, P, Fe, Mn, Zn and Al contents. Soil pH was determined before and after amendment. All applications rose significantly soil pH. Domestic ash, whether combined with coffee grounds or not, proved to be efficient at supplying available macronutrients Ca, Mg, K, P to the soil and also reducing availability of Al (more than industrial ash). However, it inhibited plant growth, even more when combined with spent coffee grounds. As regards to elemental abundance in plant tissue, both domestic ash treatments reduced Ca and enhanced Al contents, unlike industrial ash, which proved less harmful for the load applied in the soil. Hence, it was possible to conclude that application load should be a limiting factor for this management option for the studied materials.

**Keywords:** biomass ash, spent coffee grounds, soil, fertilization, nutrients, plant growth

## 1 **1. Introduction**

2 Biomass is perhaps the most promising source of renewable energy regarding the use of  
3 alternatives to using fossil fuels, with all countries having a trend of increasing their share of  
4 biomass in the process of industrial combustion (Fuller et al. 2015). Biomass ash may be  
5 defined as the inorganic uncombustible part of fuel which remains after complete combustion of  
6 a biomass fuel (Khan et al. 2009; Melotti et al. 2013; Vassilev et al. 2010, 2013). Fly ash is the  
7 finest fraction of it that is collected in dedusting equipment downstream to the combustion  
8 chamber (Jala and Goyal 2006; Melotti et al. 2013; Pandey and Singh 2010; Tarelho et al.  
9 2015), with bulk density depending on several factors but reported to be roughly in the range of  
10  $0.27\text{-}1.80\text{ g cm}^{-3}$  (Augusto et al. 2001; Demeyer et al. 2001; Jala and Goyal 2006; Lanzerstorfer  
11 2015). Chemically, fly ash is usually characterized by high pH, in the range 8-13 (Augusto et al.  
12 2008; Basu et al. 2009; Demeyer et al. 2001; Park et al. 2012; Tarelho et al. 2012, 2015). Its  
13 elemental composition is very rich in macronutrients essential to plants, such as Ca, Mg, K, P or  
14 S, besides a variety of other elements like Na, Fe, Mn, Zn, Al, Si, B, Mo, Ti, etc. (Girón et al.  
15 2013; Herbert and Krishnan 2016; Lanzerstorfer 2015; Li et al. 2012; Nunes et al. 2016;  
16 Rajamma et al. 2015; Tarelho et al. 2015; Vassilev et al. 2013). These characteristics make  
17 biomass ashes attractive for soil amendment, subject which has been explored previously by  
18 other authors with positive and promising results (Augusto et al. 2008; Lopez et al. 2009; Matsi  
19 and Keramidas, 1999; Niu et al. 2016; Nkana et al. 2002; Park et al. 2012; Saarsalmi et al.  
20 2012). Several other potential benefits from application of biomass ash in soils have been listed  
21 in the literature (e.g. Demeyer et al. 2001; Fuller et al. 2015; Niu et al. 2016), namely: alteration  
22 in soil texture (higher porosity, aeration and water holding capacity), improving enzymatic  
23 activity or immobilization of heavy metals. The application of biomass ashes on the soil has also  
24 been studied, although more poorly, in terms of their effect on plant growth stimulation/inhibition  
25 and nutrient uptake. In this field, however, there are some contradictory results. For example,  
26 Etiegni et al. (1991), Matsi and Keramidas (1999) and Nkana et al. (1998) observed a significant  
27 increase in plant yield and in its content in Ca, Mg and K after fly ash application. Saarsalmi et  
28 al. (2012) reported that wood ash given together with N increased microbial biomass when  
29 compared to values from unamended soils and from soils treated only with N. On the other

30 hand, Augusto et al. (2008) suggested that tree growth improvement should only be expected  
31 for organic soils, since nitrogen is the first liming agent in most mineral soils, and ash is virtually  
32 N-free. Basu et al. (2009) further stated that the application of fly ash (both biomass and coal fly  
33 ash), particularly if unweathered, may reduce plant development by inhibiting the microbial  
34 respiration, enzymatic activity and soil N cycling processes. Also Brännvall et al. (2015) found in  
35 their work that soil fertilization with fly ash (from combustion of tree bark) mixed with biosolids  
36 (anaerobically digested) did not enhance biomass production neither nutrient uptake by plants  
37 (quite the contrary).

38 Spent coffee ground is a residue with fine particle size and high moisture content (80% to 85%),  
39 organic load and acidity, obtained during instant coffee preparation from raw coffee powder with  
40 hot water or steam (Mussatto et al. 2011). This material may represent a pollutant material  
41 when discharged to the environment, due to its high content in caffeine, tannins and  
42 polyphenols (Limousy et al. 2013). Since coffee has been consumed for over 1000 years and is  
43 nowadays one of the most widely consumed beverages around the world, a significant amount  
44 of this residue is produced daily. Since the development of small coffee machines that one can  
45 purchase to domestic use, each coffee home-consumer is now a producer of spent coffee  
46 grounds. This residue has been studied in recent years in order to find a sustainable  
47 environmental application to it. It has been proved to be suitable for a variety of practices, such  
48 as composting, or other agricultural purposes (Hachicha et al. 2012; Liu and Price 2011), non-  
49 structural fill applications, like road embankment extremities (Arulrajah et al. 2014), co-  
50 combustion fuel (Limousy et al. 2013), renewable resource in the tannin extraction process  
51 (Low et al. 2015), or production of CO<sub>2</sub> adsorbent materials (Plaza et al. 2012).

52 This work aimed to assess the effect of biomass ash (from industrial and domestic combustion)  
53 and spent coffee grounds on soil fertilization and plant growth. The field work was performed in  
54 a slightly acidic Portuguese soil, aiming at extending to this Southern European region the  
55 knowledge that has been developed especially for Northern Europe and tropical acidic soils.  
56 The field experiment aimed not only at finding a feasible way to recover industrial biomass ash,  
57 diverting it from landfills, but also at a residential level, testing beneficial effects of applying ash  
58 produced domestically in one's garden. The management of our own residues is the driven  
59 force for studying the application of domestic ash and spent coffee grounds into the soil.

60

## 61 **2. Materials and methods**

62 In this study experimental size soil plots were carried out at field conditions aiming to assess the  
63 effects of biomass ash application on soil properties and plant growth. Two types of ash from  
64 biomass combustion were tested: i) industrial fly ash (IA) collected at the electrostatic  
65 precipitator from a fluidized bed combustion system of a pulp and paper industrial facility, and ii)  
66 domestic ash (DA) collected at the grate of a conventional domestic woodstove operating with a  
67 mix of biomass fuels. The latter aimed at representing the regular operation of a typical  
68 residential biomass combustion equipment for heating purposes under day life practices in  
69 typical winter conditions. Another application consisted of a 50:50 mixture (weight, dry basis) of  
70 the domestic ash from the wood stove with spent coffee grounds (SCG) collected from a coffee-  
71 shop. The material applied on the soil resulted from a combined 2-day sample of SCG, and was  
72 used as received, without any pre-treatment, in order to better simulate what would be the  
73 behavior of any person who wanted to manage its own waste (the quantity that was mixed with  
74 DA was the necessary to produce a 50:50 dry basis mixture). The studied materials were  
75 applied on soil parcels in a load of 7.5 Mg ha<sup>-1</sup> (dry basis). The materials were applied on the  
76 surface of the soil parcels, taking care so that the entire plot area would receive equal  
77 distribution of material. In the case of DA+SCG application, the materials were previously mixed  
78 and then the resulting mixture was applied in similar manner. The 7.5 Mg ha<sup>-1</sup> load was chosen  
79 considering literature about application of biomass ash loads in soil (Augusto et al. 2008; Basu  
80 et al. 2009; Matsi and Keramidas 1999; Park et al. 2012; Perucci et al. 2008; Saarsalmi et al.  
81 2012), and also considering a high enough ash load in order to notice some effects of the  
82 treatment. On the other hand, it should not be high at a level incompatible with domestic  
83 management of solid wastes such as DA or SCG. A control test (CT) was included in the  
84 experiment, consisting of a parcel of soil to which no material was added. The field experiment  
85 was conducted in a typical, slightly acidic, soil of the central coastal region of Portugal, in the  
86 district of Aveiro (40°45'30.65"N, 8°29'20.11"W). The studied soil is classified by the Portuguese  
87 soil map as a cambisol (APA, 2011). The tested field was divided into a grid of 12 parcels, each  
88 one of 0.25 m<sup>2</sup> (square parcels of 0.5 m side). Each parcel was separated from the next one by  
89 at least 0.2 m. The layout of the grid is shown in Figure 1, where it can be seen that each line of

90 the grid had one parcel of each tested condition (that is, an ash treatment type) and that each  
91 condition was replicated 3 times.

92 The rationale behind the adopted spatial distribution of samples was made in order to minimize  
93 the role that environmental conditions (e.g., minor changes in orography or soil properties)  
94 could have in the behavior of the amended soil parcels, that is, an empirical experimental  
95 design was conceived to have the experimental plots with the same treatment at distinct  
96 locations in the experimental field. The size of sample plots was chosen considering soil field  
97 conditions, namely to guarantee minimum effects of variation in natural soil properties for the  
98 distinct samples, and conceived in order to have at least three replicates for each type of test.  
99 Small plots allow a better level of control of the experiment, and this is important in the field in  
100 order to minimize the number of variables that can influence the results. This way, we have  
101 submitted the distinct tests and replicates to a field soil that can be considered uniform in  
102 properties, and thus decreasing the number of variables that can influence the experiment. In  
103 selecting the size of the test-field it was also considered the domestic type of application,  
104 considering the limited amount of domestic ash and spent coffee grounds that can be generated  
105 by family houses and the subsequent local application of those wastes.

106 Ryegrass (*Lolium perenne*), a feed crop commonly grown in Portugal, was sown in all soil  
107 parcels in order to evaluate the stimulation/inhibition effect of the different tested materials in  
108 plant growth. 5.55 g of seeds were sown in each soil parcel, according to a commercially  
109 advised rate of 20 to 25 g<sub>seeds</sub> m<sup>-2</sup> and to other studies, e.g. Matsi and Keramidas (1999).

110 Sixty days after seeding, the aboveground biomass (cut at about 2-3 cm above the surface of  
111 the soils) was harvested from the different soil parcels, dried in an oven (at 105 °C) for 24h and  
112 weighed. The germination index (GI) was calculated for each parcel according to Equation 1,  
113 where *m* designates mass.

114

$$115 \quad GI = (m_{\text{biomass grown}}/m_{\text{seeds sown}}) / (m_{\text{biomass grown in CT}}/m_{\text{seeds sown in CT}}) \quad (1)$$

116

117 The GI has been used in previous studies, since it has been proved to be a very sensitive index  
118 (Tiquia et al. 1996). When greater than 0.8 GI indicates the inexistence of phytotoxicity of the  
119 amendment material (Araújo and Monteiro 2005).

120 Sub-samples of the dry biomass were ashed at 550°C according to CEN/TS 14775:2004. The  
121 produced ash was then digested according to CEN/TS 15290:2006, with the suitable ratio of the  
122 four recommended reagents: 2 mL of 30% (w/w) hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), 3 mL of 65% (w/w)  
123 nitric acid (HNO<sub>3</sub>) and 0.75 mL of 40% (w/w) hydrofluoric acid (HF), plus 7.5 mL of 4% (w/w)  
124 boric acid (H<sub>3</sub>BO<sub>3</sub>), and 20 mL distilled water, all of them commercial analytical grade reagents.  
125 This procedure was also adopted for the determination of the chemical composition of the  
126 amendment materials applied to the different soil parcels. The digestion procedure was  
127 performed in a Berghof Speedwave<sup>®</sup> Four microwave system, with TFM<sup>™</sup> digestion vessels.  
128 Soil samples (0-15 cm depth) were also collected from each parcel after the 60 days period.  
129 Those samples were air-dried to constant mass and sieved to 2 mm (ASTM Retsch Test Sieve).  
130 After this pre-treatment, soil samples were extracted by the Mehlich-3 (M3) extraction  
131 technique, which allows to quantify the exchangeable (and thus plant available) concentration of  
132 nutrients. The M3 extractant comprises 0.2 M CH<sub>3</sub>COOH, 0.015 M NH<sub>4</sub>F, 0.013 M HNO<sub>3</sub>, 0.001  
133 M ethylene diamine tetraacetic acid (EDTA), and 0.25 M NH<sub>4</sub>NO<sub>3</sub>. In this procedure,  
134 phosphorous is extracted by reaction with acetic acid and fluoride compounds, while  
135 exchangeable K, Na, Mg and Ca are extracted by the action of ammonium nitrate and nitric  
136 acid. The micronutrients (Mn and Fe, plus Zn) are extracted by NH<sub>4</sub> and EDTA.  
137 The content of sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe),  
138 manganese (Mn), aluminum (Al) and zinc (Zn) in the digested biomass and soil amendment  
139 materials samples, and Mehlich 3 extracted soil samples were analyzed by atomic  
140 absorption/emission spectroscopy, with a PerkinElmer AAnalyst 200 – Atomic Absorption  
141 Spectrometer. Phosphorous content was determined by colorimetric determination, using a  
142 Camspec<sup>®</sup> M501 Single Beam Scanning UV/Visible Spectrophotometer with infrared  
143 phototube. For this purpose, the methodology proposed in Greenberg et al. (1992) was  
144 adopted. In this procedure, ammonium molybdate and potassium antimonyl tartrate react in acid  
145 medium (provided by sulphuric acid) with orthophosphate to form a heteropoly acid –  
146 phosphomolybdic acid – that is reduced to intensely colored molybdenum blue by acid ascorbic,  
147 detectable by spectrophotometry at 880 nm.  
148 All soil samples and applied materials (IA, DA and SCG) were analyzed for pH in a 1:5 (v/v)  
149 ratio of soil in water, accordingly to ISO 10390:2005. The measurement was performed in a

150 Denver Instrument® model 25 pH/ion meter. In order to characterize the soil and the suitability of  
151 the amendment materials to apply on it, a determination of the organic matter content was  
152 performed adapting the procedure described in CEN/TS 14775:2004. A vertical undisturbed  
153 sample of the original untreated soil was also taken in order to determine soil dry bulk density  
154 (according to ASTM D7263-09) and field capacity (by means of staged water addition until  
155 saturation is reached, quantifying the amount of water that the soil can retain).

156 A two-sample t-test procedure ( $p < 0.05$ ) was applied to the experimental results to statistically  
157 differentiate the means at 95% confidence level.

158

### 159 **3. Results and discussion**

160 Table 1 compiles some relevant data on the physical characteristics of the soil used in the  
161 experiment at field conditions, prior to any material addition. The elemental composition of the  
162 original soil selected to experiments in the field is reflected in the analysis of the control soil  
163 (CT) and is shown in Figure 3, in order to allow comparison to the elemental composition of the  
164 amended soil parcels. The soil is originally an acidic, very rich in organic matter (13% wt., dry  
165 basis) soil. Previous studies in this field of research have shown that typical values of pH in  
166 Portuguese soils fall in the range of 4.2-7.2 in urban areas and 4.0-5.8 in rural areas, while the  
167 organic matter (as carbon) content varies in the ranges 0.6-11% wt. and 2.2-5.0% wt. in urban  
168 and rural areas, respectively (Rodrigues et al. 2010, 2013). Soil's dry bulk density is low (0.596  
169  $\text{g cm}^{-3}$ ), when compared to literature values of 1.1-1.6  $\text{g cm}^{-3}$  (Hillel 1980). Naturally, if the soil  
170 has low density, it will be more porous and, consequently, it will have higher water holding  
171 capacity, which is characteristic of cambisols. Table 2 summarizes the main physical-chemical  
172 characteristics of the materials applied in the soil. Their chemical composition is shown in Figure  
173 2. As expected, both types of biomass ash are highly alkaline, with pH in the range of 11.8 to  
174 12.4.

175 Differences in the organic matter content of the ashes, with higher values (15.7%wt.) in the case  
176 of domestic ashes, are related to the higher amount of unburnt carbon content in these ashes,  
177 due probably to lower combustion temperature or inadequate load of fuel/combustion air in the  
178 domestic woodstove, which promote a lower fuel conversion.



179 Spent coffee grounds are almost entirely not stabilized organic matter (about 98% wt.) and have  
180 pH lower than 6, which is in agreement with data provided in the literature (Arulrajah et al. 2014;  
181 Liu and Price 2011).

182 Among the analyzed elements, Ca and K are the most abundant elements in industrial and  
183 domestic ash's composition (especially in the latter), reflecting the original composition of the  
184 type of biomass burnt, in accordance with the literature (e.g. Vassilev et al. 2010). Both ash  
185 types also show considerable amounts of Na, Mg (especially DA), P, Fe and Al (especially IA),  
186 which is also in accordance with reported information in the literature for some types of biomass  
187 ash (Vassilev et al. 2013). Spent coffee grounds are particularly rich in K, but also in Mg and P,  
188 the macronutrients in which domestic ash is poorer.

189 The pH of the soil at the end of the field experiment is shown in Table 3. All applications  
190 significantly ( $p < 0.0001$ ) increased soil pH compared to the control test, to which no material was  
191 added. Amendment with domestic ash was the most efficient in raising soil pH, with a value of  
192  $7.88 \pm 0.06$  two months after application. All values are considerably high and fall near (either  
193 below or above) the top limit of the range pointed out in the literature for maximum nutrient  
194 availability of 6 to 7.5 (UNIDO and IFDC 1996). It is worth noting that even when combined with  
195 slightly acidic SCG, domestic ash caused greater raise in soil pH than industrial ash. This  
196 suggests high neutralizing capacity of domestic ash, possibly due to its greater richness in Ca,  
197 comparatively to the other materials used.

198 As regards to biomass yield (see Table 4), no significant difference ( $p = 0.8117$ ) was observed  
199 between the mass of biomass grown in control parcels and parcels of soil treated with IA. This  
200 is not an unprecedented result, since Park et al. (2012) and Brännvall et al. (2015) both  
201 recorded similar results. This means that application of  $7.5 \text{ Mg ha}^{-1}$  industrial fly ash did not  
202 produce any contamination in soil that would inhibit plant growth (phytotoxicity). On the other  
203 hand, application of DA seems to have caused a significant ( $p = 0.0352$ ) inhibiting effect on  
204 biomass development, which could be related with excessive pH raise or most likely to  
205 excessive nutrient enrichment, which may have caused excessive increase in the soil salinity  
206 and lead to a counter-productive effect. When combining DA with SCG, the effect was even  
207 worse, with the yield of biomass being approximately half of the quantity harvested from the  
208 control parcel. Since the effect in soil pH was very similar among the three treatments, this

209 inhibitory effect of the plant growth is more likely due to the composition of the SCG, not only in  
210 terms of the possibility of excessive content of some chemical elements, but also in terms of its  
211 98% wt. composition in organic matter. In fact, the literature has reported that organic wastes  
212 may induce phytotoxicity in plants, pointing out possible explanations for this effect, such as the  
213 presence of heavy metals, ammonia, salts and low molecular weight organic acids (e.g. Zucconi  
214 et al. 1985). Hence, at this load of application ( $7.5 \text{ Mg ha}^{-1}$ ), only industrial ash proved to not  
215 induce negative effects on the growth of the studied plant. Soil amendment with DA combined  
216 with SCG revealed to be the most hazardous application, with a GI of  $0.51 \pm 0.08$ . Figure 3  
217 shows the elemental concentration of the M3 extracted macro and micronutrients in all soil  
218 parcels, comparing the treated soils with the control soil.

219 All treatments produced noticeable raise (and statistically significant,  $p < 0.05$ ) on the  
220 concentrations of available macronutrients Ca, Mg and K in the soil. This was probably due to  
221 the chemical composition of the materials applied, which are rich in those elements, and also to  
222 the raise in soil pH, which may have enhanced these nutrient's availability. Similar effects are  
223 well documented in the literature (e.g. Augusto et al. 2008; Nkana et al. 1998, 2002; Pandey  
224 and Singh 2010; Saarsalmi et al. 2012). Application of DA or DA+SCG proved to deliver a  
225 higher raise in the abundance and availability of those macronutrients in the soil when  
226 compared to the application of IA. This is most likely due to the greater amount of those  
227 chemical elements in the composition of DA, which become available in the soil with rising pH.  
228 Moreover, it should be noted that the raise in pH caused by these treatments was in fact greater  
229 than the one produced by IA application. Similarly to that registered for the pH, the application  
230 to the soil of DA or DA+SCG did not differ statistically from each other in what availability of Ca,  
231 Mg and K is concerned ( $0.0681 < p < 0.2832$ ). Thus, despite SCG having more (total) Mg and  
232 much more (total) K than DA in its composition, the available fraction (M3 available) of those  
233 chemical elements in SCG proved to be relatively small. Regarding the P availability, there was  
234 no statistically significant effect of the application of industrial ash ( $p = 0.0779$ ). This may be due  
235 to the low solubility of P from ash, since it is usually bound to compounds of low solubility, like  
236 apatite (Augusto et al. 2008). However, contradictory results about P can be found in the  
237 literature. On the other hand, the application of DA or DA+SCG did rise significantly ( $p = 0.0725$ )

238 the levels of M3 available P in the treated soil, when compared to CT, but, once again, with no  
239 significant difference between these two treatments.

240 Regarding the other analyzed elements, Fe, Mn and Zn are recognized as essential plant  
241 micronutrients; Na can be an important cause of excess salinity in some soils (saline-sodic and  
242 saline soils); and Al may enhance soil acidity to levels not compatible with the development of  
243 most plant species. In the case of IA application, it did not produce any significant difference  
244 comparatively to the concentrations of Al and Fe registered in the control plot, while DA  
245 application significantly reduced the available Al and Fe concentration in the soil, whether  
246 combined with SCG or not; the outcome of the two treatments was once again statistically  
247 identical. The raise in soil pH produced by DA (whether combined with SCG or not) is likely to  
248 be responsible for this reduction in micronutrients availability, namely Al, which has been  
249 previously reported in other literature studies (e.g. Brännvall et al. 2015; Nkana et al. 1998;  
250 Pandey and Singh 2010). Brännvall et al. (2015) states that Al solubility and availability is low  
251 enough for soil pH above 5, which has been surpassed by the adopted amendments. According  
252 to Nkana et al. (1998), also the raises in exchangeable base cations may be associated with  
253 decrease in Al availability and toxicity. All applications rose bioavailability of Na and Mn. It is  
254 worth noting that IA rose statistically more ( $p=0.0464$ ) the Na level than DA, although the latter  
255 had a greater concentration of (total, not necessarily available) Na in its composition. The  
256 available Zn concentration remained statistically unaltered in result of the three soil additives  
257 application.

258 Figure 4 shows the elemental concentration of the macro and micronutrients, and also Na and  
259 Al, present in the biomass harvested after the 60 days field experiment.

260 In what macronutrients Mg, K and P are concerned, the t-test showed that the registered  
261 differences between biomass grown in treated soil and in the control soil parcels were not  
262 statistically significant. On the other hand, DA and DA+SCG applications reduced Ca  
263 concentrations in the plant tissue ( $p=0.0031$ ) from around 25 to around 10 g Ca kg<sup>-1</sup>, possibly  
264 due to excessive pH raise in the root of the plant, inhibiting the uptake of the available Ca.  
265 Contradictory results have been found in the literature regarding this. Several authors have  
266 registered significant increase Ca and K (Augusto et al. 2008; Demeyer et al. 2001; Nkana et al.  
267 1998), while Brännvall et al. (2015) found decrease in this nutrients content in plant tissue, as

268 well as for P, Fe and Mn. Park et al. (2012) only registered significant increase in the content of  
269 K. These results show the variability of plants' responses to the amendment of soil with biomass  
270 ash. This may be due to soil type, plant type, pH of the initial soil and pH achieved after  
271 amendment, the form of nutrients in the ash composition and ash load. In the case of P,  
272 availability above pH 7 may become limited due to the formation of insoluble calcium phosphate  
273 compounds, since it is strongly dictated by precipitation and surface adsorption reactions (Park  
274 et al. 2012). This can help explain the results obtained. The lack of increase in Ca and Mg  
275 content in plant tissue may also be due to the antagonist effect of Mg with Ca/K (Demeyer et al.  
276 2001; Nkana et al. 1998), or perhaps with excess salinity, namely Na content (UNIDO and IFDC  
277 1996).

278 As regards to micronutrients, the differences registered in Fe and Mn contents were always  
279 marginal, statistically non-significant. Similar results were obtained for the Na content. Total Al  
280 content in the plant was enhanced by addition of DA and DA+SCG (equal magnitude among  
281 treatments) from around 1.0 to around 2.3 g Al kg<sup>-1</sup>.

282 Repeating the harvest in time would have been adequate to further test and confirm these  
283 results, and even to compare the response of ryegrass to ash amendment amid different  
284 weather seasons. However, and since perennial ryegrass tends to die in April-May and should be  
285 replanted every year, sequential harvesting procedures would be made for different seeding  
286 procedures, which would not allow straight comparison amid results obtained.

287

#### 288 **4. Conclusions**

289 All three amendments significantly raised soil pH to levels very close to the recommended limit  
290 for optimum for plant growth, especially domestic ash. Perhaps in accordance with this,  
291 application of 7.5 Mg ha<sup>-1</sup> domestic ash seemed to significantly inhibit plant growth, especially  
292 when combined with spent coffee grounds. That hazardous effect was not observed when using  
293 industrial ash as amendment.

294 All treatments produced noticeable raises on the concentrations of available macronutrients Ca,  
295 Mg and K in the soil, especially the application of DA (whether combined with SCG or not). The  
296 two applications involving DA were also capable of significantly rising M3 available P content in  
297 the soil.

298 DA and DA+SCG application on the soil showed some concerning effects on plant tissue,  
299 reducing Ca content and enhancing Al content. Lowering the ash load, weathering the domestic  
300 ash or substituting the powder application by a granular or pelletized-form application could  
301 improve DA performance. A higher load could, however, be suitable for IA application, in order  
302 to potentiate its benefits to the soil, while evaluating if it maintains a harmless behavior with  
303 regard to plant growth and nutrition. Spent coffee grounds could possibly be suitable for soil  
304 amending if previously stabilized.

305 Further investigation is still needed in this subject, namely, by repeating these experiments at  
306 field conditions (seeding, amendment and harvesting) in time and space, for example  
307 throughout a year, to perform tests and harvest campaigns during the different seasons. Other  
308 types of soil should also be tested.

309

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314

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427

428 Table 1. Initial characteristics of the field soil where the experiments were developed

pH	5.03 ± 0.29
Organic matter content (% wt., db <sup>a</sup> )	13.9 ± 0.3
(Dry) Bulk density [g cm <sup>-3</sup> ]	0.59630
Field capacity [kg <sub>water</sub> kg <sup>-1</sup> <sub>dry soil</sub> ]	0.63431

432 <sup>a</sup>db - dry basis

433

434 Table 2. Initial characteristics of the applied amendment materials

	Industrial Ash	Domestic Ash	Spent Coffee Grounds
Moisture content (% wt., wb <sup>a</sup> )	0.46 ± 0.20	4.52 ± 0.81	55.8 ± 0.12
Organic Matter Content (% wt., db <sup>b</sup> )	7.09 ± 1.03	15.7 ± 2.33	98.1 ± 0.02
pH	12.4 ± 0.01	11.8 ± 0.03	5.76 ± 0.11

435 <sup>a</sup>wb – wet basis or as received basis

436 <sup>b</sup>db – dry basis

437

438 Table 3. Soil pH at 60 days after application of the different tested amendment materials (plus  
439 control soil)

	pH
Control Soil CT	5.86 ± 0.05
Soil IA	7.36 ± 0.10
Soil DA	7.88 ± 0.06
Soil DA+SCG	7.67 ± 0.03

440

441

442 Table 4. Biomass yield [g per parcel] and germination index for the different tested conditions

Soil parcel	Biomass yield	Germination Index (GI)
Control Soil CT	12.4 ± 1.03	-
Soil IA	12.6 ± 0.89	1.02 ± 0.07
Soil DA	10.2 ± 0.65	0.82 ± 0.05
Soil DA+SCG	6.27 ± 0.97	0.51 ± 0.08

443

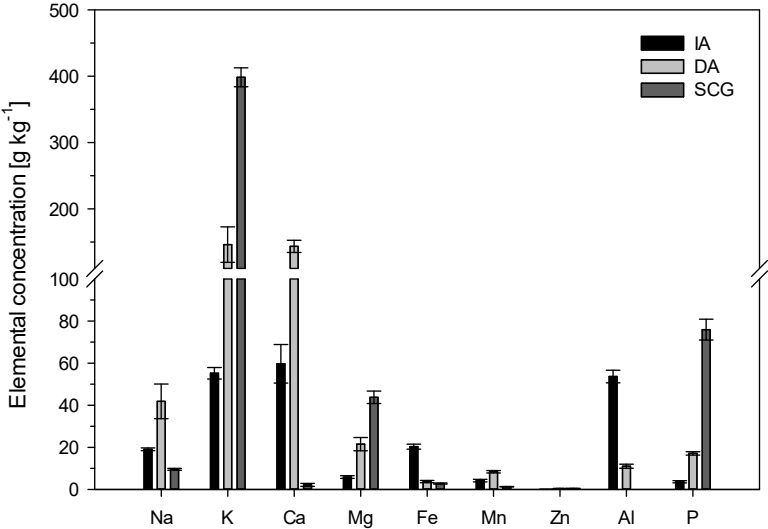
444

CT #1		IA #1		DA #1		DA+SCG #1
DA+SCG #2		CT #2		IA #2		DA #2
DA #3		DA+SCG #3		CT #3		IA #3

445

446 **Fig 1** Field layout of the different soil parcels (CT=control soil, IA=soil treated with IA, DA= soil  
 447 treated with DA, DA+SCG=soil treated with DA+SCG mixture)

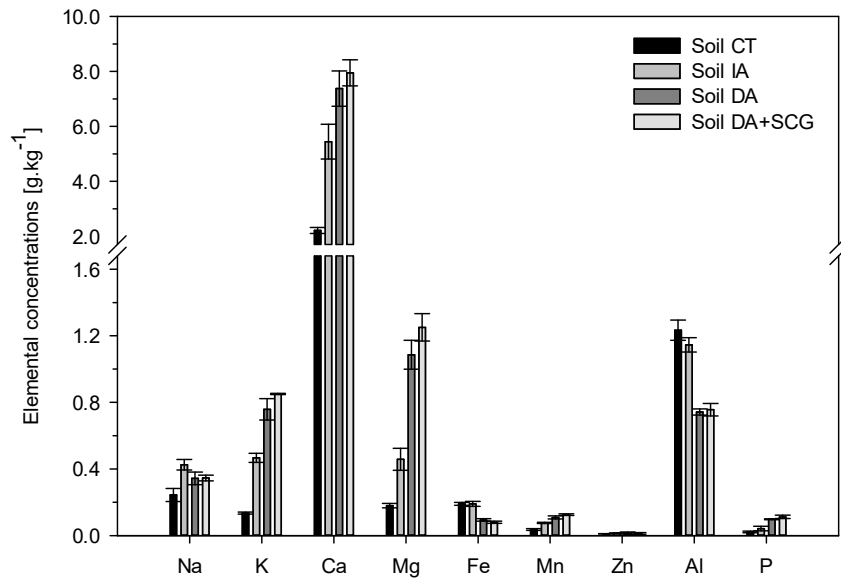
448



450

451 **Fig 2** Concentration [g kg<sup>-1</sup>] of the different chemical elements analyzed in the three amendment  
452 materials (IA= Industrial Ash; DA=Domestic Ash and SCG=Spent Coffee Grounds)

453

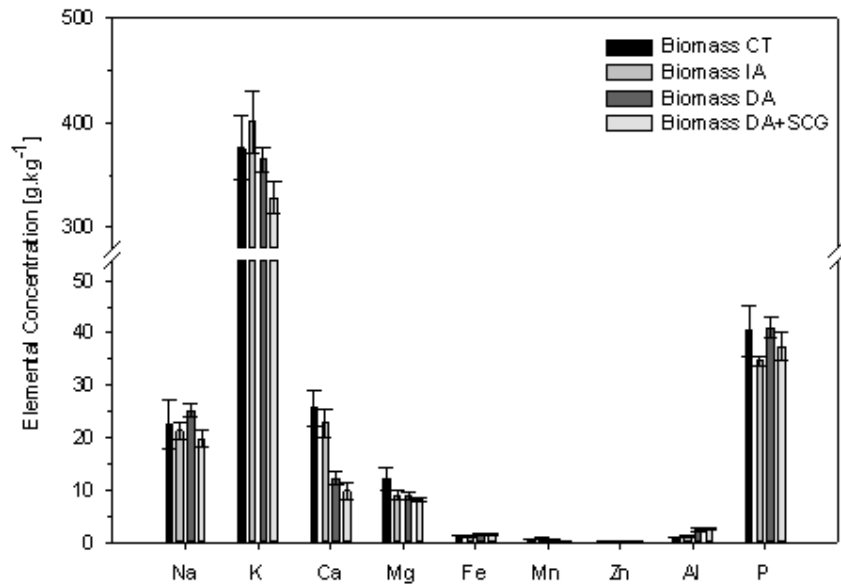


454

455 **Fig 3** Concentration [ $\text{g kg}^{-1}$ ] of plant available chemical elements in the soil 60 days after  
 456 amendment

457





458

459 **Fig 4** Concentration [ $\text{g kg}^{-1}$ ] of total chemical elements in the biomass harvested from the  
 460 different soil parcels

461