



## Use of pulp mill inorganic wastes as alternative liming materials

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### ABSTRACT

A laboratory aerobic incubation study was performed during 18 weeks under controlled conditions to assess the effects of applying different doses of pulp mill inorganic wastes on the physical–chemical properties of an acid Dystric Cambissol. Three different inorganic wastes were tested – wood ash, dregs and grits, and an agriculture limestone was used as reference. Results showed that increasing the dose applied of the different inorganic wastes tested always led to significant raises of soil pH at different incubation times demonstrating that its use as alternative-liming materials could be a valid and less expensive option to the use of commercial agricultural limestone. Moreover, no immediate concerns seem to be expected related to soil exchangeable sodium (Na) content, at least for the doses needed to increase soil pH until the targeted value 6.5. Particularly for wood ash a pronounced increase on soil extractable potassium and phosphorous was observed, indicating that besides the liming effect this waste can contribute to improve soil fertility by supplying significant available amounts of these nutrients. Finally, metals do not seem to be a limiting factor for the application to land of these by-products.

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### 1. Introduction

All over the world increasing attention is being paid to the ecological impacts associated with the forest industry in general and pulp and paper production in particular, as well as the means to minimize these impacts (Kissinger et al., 2007). Currently, there are about six thousand pulp and paper mills that produced during 2003 about 188 million tonnes of pulp and 325 million tonnes of paper (CELPA, 2005). Since this is an activity with strong environmental impact, especially on air and groundwater quality, the pulp and paper industry is greatly interested on improving processes and technology to eliminate constraints and reduce pollution. Significant progress has been made in last years, and modern technologies have greatly reduced the volume and toxicity of the effluents produced (Mahmood and Elliot, 2006). However, the effluents processing that consists of a pre-treatment, followed by both primary and secondary treatments and sometimes even a tertiary treatment, makes this industry one of the leading generators of inorganic and organic semi-solid and solid wastes. A significant fraction of these wastes are frequently burnt and/or deposited on the soil surface or landfilled with no treatment creating very negative environmental impacts (Cabral et al., 1998; Jordan et al., 2002). On the other hand, the increasing of costs to control landfilling and the decreasing of landfill areas are forcing mills to find

alternative disposal methods (Muse and Mitchell, 1995; Jordan et al., 2002; Jordan and Rodriguez, 2004).

According to the composition of the different wastes generated, it is possible to identify a group consisting of inorganic residues that are alkaline in nature. This group includes ashes (from the burning of biomass) and lime by-products as green liquor dregs (dregs) and slacker grits (grits), which are the inorganic precipitates, originated during liquor causticizing process (Jordan et al., 2002).

Rigorous studies conducted to assess alternative uses of these inorganic wastes are scarce, especially regarding dregs and grits. Some of these studies suggest that amendments to soil of these wastes may improve the chemical availability of nutrients by increasing soil pH that can result in a positive effect, especially in acid soils with low organic matter and nutrients content (Ritter et al., 1992; Muse and Mitchell, 1995); while other authors defend that these wastes may be harmful due to their chlorinated compounds and heavy metal content (Jordan et al., 2002).

In acidic soils the improvement of the productivity of different species depends on a large scale of soil appropriate management practices. So, in an effort to recycle and keep potentially valuable waste materials out of landfills, the incorporation into the soils of these wastes in raw as liming materials can constitute an acceptable environmentally friendly safe and economical alternative to other methods of disposal substituting traditional agricultural limestone (Jordan and Rodriguez, 2004; Muse and Mitchell, 1995; Ritter et al., 1992).

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Therefore, the present study focused on the potential and effectiveness as soil liming agents of inorganic wastes from the pulp and paper processing industry, using an agriculture limestone as reference. Furthermore, the effect on soil chemical characteristics resulting from inorganic wastes amendments will be investigated to evaluate eventual potential constraints to its utilization.

## 2. Methods

Three different inorganic wastes obtained from a Kraft pulp mill plant located in Setubal, South of Portugal, were tested: wood ash, dregs and grits. The wood ash is “fly ash” produced in a grate-fired boiler and the fuels used are bark, rejected wood wastes and fuel oil.

Dregs and grits are obtained during the causticizing process (part of the pulp mill chemical recovery circuit). Dregs are the non soluble compounds obtained from green liquor clarifier/filter (green liquor dregs), while grits are the insoluble materials removed from slackers after the reaction between green liquor and lime (slacker grits).

During 12 months, samplings of wood ash, dregs and grits were collected at four different times, at the pulp plant. Each inorganic waste sample was air-dried, sieved through a 2 mm  $\varnothing$  sieve (except for wood ash), and chemically analysed (Table 1). For each waste, a composite sample based on the four sub-samples was prepared and its potential use as liming agent for acid soils was evaluated in an incubation experiment conducted under controlled conditions. As comparative reference, an agricultural ground calcitic limestone was also used, with a calcium carbonate equivalent (CCE) of 87% (AOAC, 1990). Total nitrogen content in wastes was determined by the Kjeldhal method (Horneck and Miller, 1998). Other chemical elements, including heavy metals were obtained after digestion with *aqua regia* (Berrow and Stein, 1983). The adsorbable organic halogen compounds (AOX) in wastes were extracted by leaching with water according to the method DIN 38414-S4, and determined in the eluates using Analytical Jena Multi X-2000 equipment according to the standard method ISO 9562 (2004).

The soil selected for this experiment is a Dystric Cambissol (WRB, 2006), loamy textured with an acid pH (5.50), low organic matter content (4.40 g kg<sup>-1</sup>), very low extractable P (4.90 mg kg<sup>-1</sup>)

and medium extractable K contents (47.3 mg kg<sup>-1</sup>). The following amounts of air-dried wastes were individually and thoroughly mixed with 1 kg of soil (fraction <2 mm): 1; 2; 4 and 8 g of dregs, grits and limestone, and 1.25; 2.5; 5 and 10 g for wood ash. A control treatment consisting only of soil was also included. After distilled water was added as needed to achieve approximately 60% of soil–water holding capacity, four replicates of each mixture were prepared. Mixtures of soil–waste were placed in plastic containers and an aerobic incubation experiment was carried out over 18 weeks (temperature 25  $\pm$  1 °C). The containers were opened weekly to ensure aerobic conditions. Sub-samples of 10 g soil were taken at setting time–time zero (T0) and after at 1, 4, 8, and 18 weeks, for monitoring pH (H<sub>2</sub>O) evolution.

At the end of the incubation period the following parameters were evaluated in the soil:pH in a soil–water (1:2.5 w/v) suspension (pH<sub>H<sub>2</sub>O</sub>); exchangeable cations – after soil leaching with a barium chloride and trietanolamine solution at pH 8.1 (Mehlich, 1953), extractable potassium (K) and phosphorus (P) – after soil extraction with ammonium lactate and acetic acid solution buffered at pH 3.65–3.75 (Egner et al., 1960); extractable iron (Fe), copper (Cu), zinc (Zn) and manganese (Mn) – after soil extraction with EDTA solution at pH 4.65 (Lakanen and Ervio, 1971); and total heavy metals – after soil digestion with *aqua regia* (Berrow and Stein, 1983).

Chemical elements in wastes (Table 1) and soil were quantified through atomic absorption spectrometry using a Unicam M Series instrument equipped with a graphite furnace GF95, except for phosphorous, which was determined by molecular absorption spectrometry in a Hitachi 2000 VIS/UV equipment.

Results obtained were submitted to ANOVA followed by averages comparison using the least significant difference (LSD) method (Zar, 1996).

## 3. Results and discussion

### 3.1. Soil pH

At the end of the incubation period, pH of control soil was 5.6 and increasing the dose applied of the different inorganic materials always led to significant raises of soil pH at different incubation times (Table 2). Wood ash generally shows a high neutralizing

**Table 1**  
Chemical characteristics of the wastes used in this study (dry weight basis)

Characteristic	Wastes											
	Wood ash				Dregs				Grits			
	Max.	Min.	Average	sd <sup>†</sup>	Max.	Min.	Average	sd <sup>†</sup>	Max.	Min.	Average	sd <sup>†</sup>
pH (H <sub>2</sub> O)	13.0	12.5	12.8	0.20	12.3	12.1	12.2	0.1	13.1	12.4	12.6	0.30
AOX (mg L <sup>-1</sup> )	0.33	0.08	0.21	0.18	nd	nd	–	–	nd	nd	–	–
Calcium carbonate equivalent (%) (CCE)	77.7	54.30	66.0	4.00	95.6	64.4	80.0	12.9	100.6	69.4	85.0	8.18
Kjeldahl N (g kg <sup>-1</sup> )	0.40	0.02	0.17	0.20	0.10	0.00	0.07	0.06	0.10	0.02	0.05	0.04
Phosphorus (P) (g kg <sup>-1</sup> )	5.70	4.80	5.30	0.50	2.10	0.90	1.60	0.60	2.40	0.70	1.70	0.90
Potassium (K) (g kg <sup>-1</sup> )	30.9	20.4	27.3	4.80	6.60	0.90	3.10	2.40	1.40	0.50	0.80	0.40
Calcium (Ca) (g kg <sup>-1</sup> )	314.9	238.7	281.0	38.2	347.0	118.2	249.5	98.9	519.7	356.1	417.2	72.4
Magnesium (Mg) (g kg <sup>-1</sup> )	32.8	23.4	27.1	4.10	51.1	21.0	35.4	15.5	5.70	1.30	3.60	1.80
Sodium (Na) (g kg <sup>-1</sup> )	6.60	3.70	5.20	1.30	144.4	29.8	70.8	54.0	15.6	6.90	10.4	3.70
Aluminium (Al) (g kg <sup>-1</sup> )	6.70	3.20	5.70	1.70	4.10	0.30	2.50	1.60	2.50	0.50	1.70	1.10
Iron (Fe) (g kg <sup>-1</sup> )	7.40	7.20	7.30	0.10	5.40	2.60	4.10	1.50	3.70	1.20	2.20	1.30
Copper (Cu) (mg kg <sup>-1</sup> )	33.0	15.5	25.8	8.20	102.0	30.2	80.9	34.2	5.04	4.16	4.60	0.62
Zinc (Zn) (mg kg <sup>-1</sup> )	92.5	53.5	68.9	17.1	258.0	48.8	160.2	87.6	15.0	15.0	15.0	0
Manganese (Mn) (mg kg <sup>-1</sup> )	10000	7200	9000	1240	7800	1600	4720	3030	200	100	150	60
Nickel (Ni) (mg kg <sup>-1</sup> )	249.0	29.0	97.4	101.9	254.0	119.0	189.0	58.2	38.2	11.1	25.2	11.1
Lead (Pb) (mg kg <sup>-1</sup> )	51.0	39.1	44.3	5.06	62.4	31.1	46.8	16.4	47.3	14.1	34.1	14.3
Cadmium (Cd) (mg kg <sup>-1</sup> )	5.44	3.26	4.72	0.99	6.12	4.07	5.19	0.97	5.90	3.17	4.75	1.31
Chromium (Cr) (mg kg <sup>-1</sup> )	26.9	21.3	24.1	3.96	68.9	47.4	56.03	9.50	14.4	10.3	12.4	2.90
Cobalt (Co) (mg kg <sup>-1</sup> )	23.9	19.9	22.1	1.75	25.1	18.7	22.05	2.89	24.2	17.2	20.7	3.82

nd – Not detected.

<sup>†</sup> sd-standard deviation.

**Table 2**  
Soil pH at different incubation times

Treatment	Weeks				
	0	1	4	8	18
Control	5.46 a	5.45 a	5.34 a	5.30 a	5.58 a
Wood ash (g kg <sup>-1</sup> )					
1.25	6.17 b	5.70 b	5.59 b	5.59 b	5.74 b
2.5	7.16 c	6.78 c	6.68 c	6.58 c	6.71 c
5.0	8.20 d	7.97 d	8.08 d	7.98 d	7.88 d
10.0	9.42 e	8.40 e	8.55 e	8.38 e	8.38 e
Dregs (g kg <sup>-1</sup> )					
1.0	5.83 b	5.99 b	5.97 b	5.76 b	5.93 b
2.0	6.26 c	6.98 c	6.76 c	6.79 c	6.67 c
4.0	6.78 d	7.78 d	7.86 d	7.78 d	7.78 d
8.0	7.04 e	8.22 e	8.16 e	8.11 e	8.01 e
Grits (g kg <sup>-1</sup> )					
1.0	5.76 b	5.87 b	5.89 b	5.74 b	5.95 b
2.0	5.96 b	6.86 c	6.70 c	6.85 c	6.85 c
4.0	6.15 b	7.39 d	7.64 d	7.62 d	7.76 d
8.0	6.53 c	7.88 e	8.13 e	8.09 e	7.97 d
Limestone (g kg <sup>-1</sup> )					
1.0	5.90 b	6.11 b	5.98 b	5.95 b	6.11 b
2.0	6.02 b	7.02 c	7.06 c	6.92 c	7.17 c
4.0	6.80 c	7.73 d	7.60 d	7.70 d	7.85 d
8.0	6.86 c	8.07 e	8.04 e	8.14 e	8.32 e

Means followed by the same letter, in the column, do not differ at  $p \leq 0.05$  by the LSD-test.

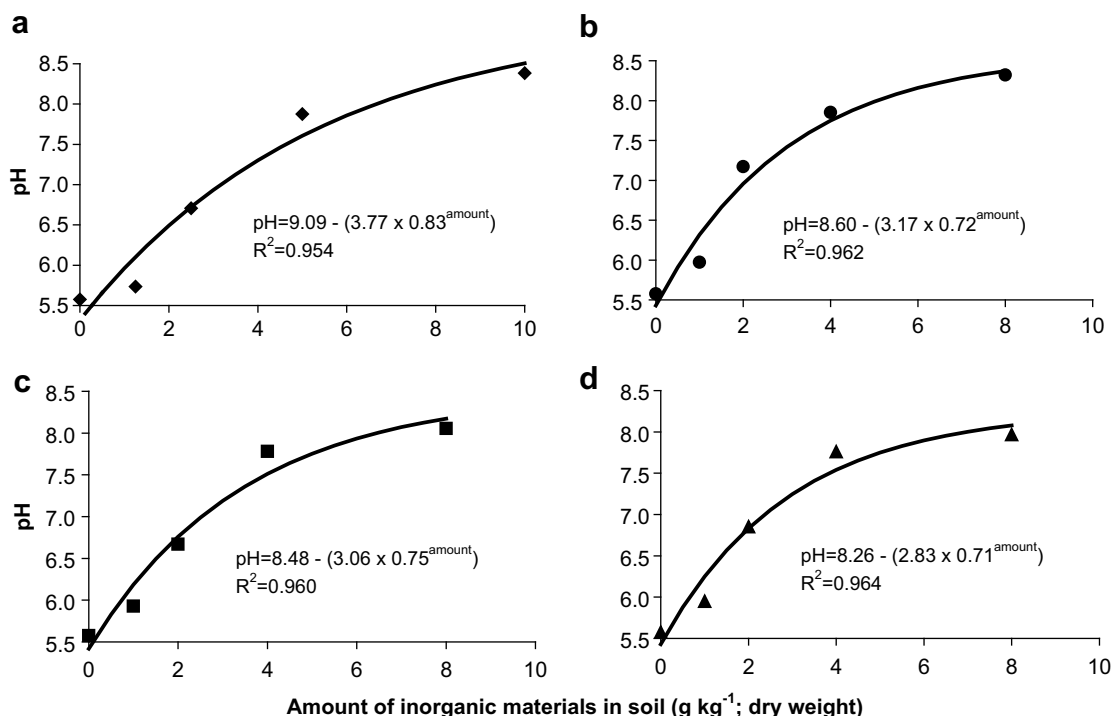
capacity due to the presence of significant amounts of carbonates, oxides, hydroxides and silicates of calcium, potassium, magnesium and sodium (Demeyer et al., 2001). The hydroxyl ions formed as a result of the dissolution of the CaO, MgO, K<sub>2</sub>O and NaOH in the ash neutralize the protons in the soil solution and those bound on cation exchange sites in the soil (Saarsalmi et al., 2006). On the other hand, several studies have shown that wood ash reacts more quickly with soils than agricultural limestone, resulting in a stronger pH increase, but only for a short period of time, since hydroxides that are dominant in the complex wood ash composition and

principally responsible for the neutralizing capacity, are highly reactive fractions than carbonates (Muse and Mitchell, 1995; Meiwes, 1995; Ohno and Erich, 1990).

The wood ash utilized in the present study with a calcium carbonate equivalent (CCE) equal to 66% (Table 1), showed a different behaviour relatively to the other inorganic liming materials tested. In fact, at the setting time (time zero) of the incubation study and for every dose tested, a strong increase on soil pH was observed (Table 2), that can be explained by the presence of highly reactive fractions on ash composition as well as by the very small size of the powdered ash particles (Vance, 1996). However, after one-week incubation, soil pH decreased and stabilized until the end of the incubation period (Table 2). On the contrary, for the other inorganic materials, an increase of soil pH was observed from time zero until one-week incubation and after pH stabilization occurred (Table 2). Composite samples of dregs and grits used in the present study with CCE's of 80% and 85%, respectively, expressed a similar behaviour as the reference agricultural limestone. These results are consistent with those obtained by Muse and Mitchell (1995) with dregs and grits samples from pulp and paper mills located in Alabama – USA, with calcium carbonate equivalents (CCEs) ranging from 79% to 97% for dregs and 96% to 118% for grits.

Fig. 1 shows the influence of the different inorganic liming materials tested on soil pH, at the end of the incubation study, confirming its high neutralizing capacity. The effect of the doses on soil pH was described by the mathematical model  $pH = c - (a \times b^{\text{amount}})$  that was fitted to the incubation data. The model allowed good fits to the data, and the determination coefficients ( $r^2$ ) were 0.954, 0.960, 0.964, and 0.962, respectively, for wood ash, dregs, grits and limestone (Fig. 1). According to the model the amounts of each waste needed to increase soil pH until the reference targeted value 6.5, are 2.0 g, 1.53 g, 1.40 g, and 1.26 g kg<sup>-1</sup> soil, for wood ash, dregs, grits and limestone, respectively.

A significant negative linear relationship ( $r^2 = 0.99$ ) between the dose of the liming material needed to increase soil pH until 6.5 and



**Fig. 1.** Soil pH at the end of the incubation period and pH values predicted according to model  $pH = c - (a \times b^{\text{amount}})$  for: (a) ash; (b) limestone; (c) dregs; and (d) grits.

the CCE of the corresponding inorganic material was also observed, revealing that the knowledge of both lime requirement of a particular soil and the CCE of a particular inorganic waste, can be used to adequately estimate the maximum amount of waste to be applied to soil without affecting nutrients dynamics in the soil.

### 3.2. Soil exchangeable cations

The composition of the soil exchangeable complex (Table 3), at the end of the incubation period, shows that for every inorganic liming material tested the increasing of the dose applied led to significant increases of soil total exchangeable cations especially for calcium. High Ca content in the inorganic materials may explain this fact (Table 1). On the contrary, a significant decrease of exchangeable Mg was detected with the increase of the dose applied, which results on an improvement of soil Ca/Mg ratio. Regarding soil exchangeable K a significant increase was detected with the increasing of the dose but only for wood ash. Moreover an increase of soil exchangeable Na was found for dregs and grits relatively to control, but only for the highest dose of both wastes applied (Table 3). In fact, the highest doses of dregs and grits added to soil were much higher than the amounts of each waste needed to increase soil pH until the targeted value 6.5. According to Tisdale et al. (1999), sodium (Na) is not of immediate concern unless exchangeable sodium percentage (ESP) is greater than 15%. Thus, potential negative effects on soil physical characteristics due to the presence of high exchangeable Na and for the wastes tested, do not seem to be a problem to this soil, since the ESP values found were always minor than 15%. High Ca in the inorganic wastes may explain this fact by the eventual replacement of Na on soil complex exchangeable sites, allowing Na to be leached from soil and preventing Na accumulation (Muse and Mitchell, 1995).

### 3.3. Soil extractable nutrients

At the end of the incubation study, the application of wood ash led to a significant increase on soil extractable K ranging from 48.0 mg kg<sup>-1</sup> in control to 326 mg kg<sup>-1</sup> for the highest dose ap-

plied, indicating that wood ash supplies considerable amounts of available K. Also, an increase of soil extractable P was observed relatively to control, for the greater doses of wood ash applied (Table 4). These results are consistent with those found for boiler ash and wood ash by Muse and Mitchell (1995) and Saarsalmi et al. (2006), respectively.

The application of the highest doses of both dregs and grits led to a significant increase in soil extractable P, that is probably a consequence of soil pH increase (Muse and Mitchell, 1995). Similarly, the extractability of other nutrients was affected by soil pH increase. In fact, soil available zinc (Zn) significantly decreased with the application of the different liming materials. Identical results

**Table 4**  
Soil extractable P, K, Fe, Cu, Zn and Mn at the end of the incubation

Treatment	Soil extractable nutrients (mg kg <sup>-1</sup> ; dry weight)					
	K	P	Fe	Cu	Zn	Mn
Control	48.0 ab	7.5 abcd	16.0 fg	0.68 a	3.05 f	14.7d
Wood ash (g kg <sup>-1</sup> )						
1.25	82.5 f	8.5 cd	12.2 abcd	0.73 a	1.00 cd	20.2 f
2.5	106.0 g	16.0 f	11.2 abc	0.50 a	0.65 ab	17.4 e
5.0	145.6 h	29.0 g	22.2 h	0.65 a	0.90 bcd	21.5 f
10.0	326.0 i	50.3 h	41.7 j	0.68 a	0.31 d	42.0 g
Dregs (g kg <sup>-1</sup> )						
1.0	56.8 bcd	6.8 abcd	12.7 bcde	0.78 a	1.00 cd	17.5 e
2.0	50.0 abc	7.8 abcd	11.0 ab	0.68 a	0.48 a	13.6 cd
4.0	60.8 cde	11.0 e	17.7 g	0.73 a	0.88 bcd	13.0 cd
8.0	59.5 bcde	16.5 f	26.5 i	1.23 b	1.10 d	14.7 d
Grits (g kg <sup>-1</sup> )						
1.0	52.0 abc	6.0 ab	12.5 bcd	0.65 a	0.90 bcd	13.4 cd
2.0	52.0 abc	9.0 de	10.6 ab	0.58 a	0.43 a	7.0 b
4.0	68.3 de	11.0 e	13.6 cdef	0.70 a	0.78 bc	6.3 ab
8.0	70.8 ef	14.8 f	15.2 efg	0.50 a	0.78 bc	4.9 a
Limestone (g kg <sup>-1</sup> )						
1.0	41.5 a	6.3 abc	11.6 abc	0.63 a	0.93 bcd	11.9 c
2.0	49.8 abc	5.5 a	9.8 a	0.50 a	0.48 a	6.7 ab
4.0	57.5 bcd	8.0 bcd	12.6 bcd	0.55 a	0.83 bcd	5.2 ab
8.0	68.5 de	8.8 de	14.1 def	0.53 a	0.70 ab	5.3 ab

Means followed by the same letter, in the column, do not differ at  $p \leq 0.05$  by the LSD-test.

**Table 3**  
Soil exchangeable bases at the end of the incubation

Treatment	Exchangeable bases (cmol(+) kg <sup>-1</sup> ; dry weight)					Na/total (%)
	Ca	Mg	K	Na	Total	
Control	2.98 a	1.95 cd	0.04 a	0.28 ab	5.24 a	5.3 ef
Ash (g kg <sup>-1</sup> )						
1.25	4.10 ab	2.23 de	0.06 ab	0.27 a	6.67 bc	4.1 bcd
2.5	5.96 c	2.54 e	0.08 b	0.27 a	8.86 gh	3.1 ab
5.0	7.07 cdef	1.74 bc	0.17 c	0.32 abc	9.30 ghi	3.4 abc
10.0	7.51 ef	1.22 a	0.31 d	0.49 bcd	9.52 hi	5.1 def
Dregs (g kg <sup>-1</sup> )						
1.0	3.99 ab	1.97 cd	0.03 a	0.25 a	6.24 ab	4.0 bcde
2.0	4.81 b	2.13 cd	0.03 a	0.31 abc	7.28 bcdef	4.3 cde
4.0	6.54 cde	2.07 cd	0.06 ab	0.51 cd	9.18 ghi	5.6 f
8.0	7.85 f	1.76 bc	0.07 ab	0.73 e	10.40 i	7.0 g
Grits (g kg <sup>-1</sup> )						
1.0	4.51 b	2.10 cd	0.03 a	0.29 ab	6.92 bcd	4.2 bcd
2.0	6.13 cd	2.05 cd	0.03 a	0.29 ab	8.50 fgh	3.4 abc
4.0	6.57 cde	1.48 ab	0.04 a	0.28 ab	8.37 efgh	3.3 abc
8.0	7.38 ef	1.23 a	0.06 ab	0.63 de	9.30 ghi	6.8 g
Limestone (g kg <sup>-1</sup> )						
1.0	4.72 b	2.06 cd	0.03 a	0.22 a	7.03 bcde	3.1 ab
2.0	6.13 cd	1.88 bcd	0.03 a	0.20 a	8.24 defgh	2.4 a
4.0	6.50 cde	1.26 a	0.04 a	0.18 a	7.98 cdefg	2.3 a
8.0	7.11 def	1.14 a	0.06 ab	0.20 a	8.51 fgh	2.4 a

Means followed by the same letter, in the column, do not differ at  $p \leq 0.05$  by the LSD-test.

**Table 5**  
Total heavy metals content (mg kg<sup>-1</sup>; dry weight) in soil at the end of the incubation

Treatment	Cu	Zn	Pb	Ni	Cd	Cr
Control	6.5 abcd	101.8 a	22.6 a	3.0 ab	0.27 a	11.9 a
Wood ash (g kg <sup>-1</sup> )						
1.25	6.2 abc	99.8 a	22.6 a	2.9 ab	0.23 a	12.1 a
2.5	5.8 ab	99.6 a	23.0 a	2.7 ab	0.23 a	11.9 a
5.0	6.0 abc	98.5 a	24.8 a	2.9 ab	0.23 a	12.5 a
10.0	6.0 abc	99.1 a	25.5 a	2.9 ab	0.23 a	11.4 a
Dregs (g kg <sup>-1</sup> )						
1.0	6.5 abcd	98.3 a	26.1 a	2.7 ab	0.27 a	11.1a
2.0	6.3 abc	100.8 a	23.2 a	2.8 ab	0.22 a	10.9 a
4.0	7.3 de	100.0 a	22.2 a	3.7 b	0.23 a	10.9 a
8.0	8.0 e	102.1 a	24.9 a	5.5 c	0.29 a	11.0 a
Grits (g kg <sup>-1</sup> )						
1.0	5.7 a	100.0 a	24.0 a	2.6 a	0.22 a	11.5 a
2.0	6.3 abc	97.0 a	23.3 a	3.2 ab	0.23 a	10.9 a
4.0	6.3 abc	99.3 a	24.7 a	3.1 ab	0.23 a	10.8 a
8.0	6.7 bcd	97.2 a	21.6 a	3.2 ab	0.22 a	10.6 a
Limestone (g kg <sup>-1</sup> )						
1.0	5.7 a	101.0 a	23.9 a	3.3 ab	0.27 a	10.2 a
2.0	6.8 abc	99.8 a	22.1 a	3.1 ab	0.24 a	10.9 a
4.0	6.8 cd	100.6 a	23.9 a	3.0 ab	0.28 a	9.8 a
8.0	6.7 bcd	104.0 a	22.3 a	3.1 ab	0.26 a	10.0 a

Means followed by the same letter, in the column, do not differ at  $p \geq 0.05$  by the LSD-test.

were observed for soil available manganese (Mn) when grits and limestone were applied. On the contrary, the application of dregs did not affect soil extractable Mn while for wood ash a significant increase was observed. These results may be explained taking into account the high Mn content present in dregs and especially in wood ash composition (Table 1).

#### 3.4. Soil total heavy metals content

According to the results obtained at the end of the incubation study, there was no evidence of excessive heavy metals concentrations in soil as a result of the liming materials additions (Table 5). The only exception was with respect to the significant increase observed on soil nickel (Ni) content for the highest dose of dregs applied (Table 5), which is probably a consequence of the high Ni content present in these wastes (Table 1). However, even in this case all the values found were much lower than the limit values admitted for concentrations of heavy metals in soil according to the European Council Directive 86/278/EC (1986).

#### 4. Conclusions

The inorganic materials tested showed high calcium carbonate equivalents (CCEs) responsible for neutralizing soil acidity. Additions to soil of these wastes as alternative-liming materials could be a valid option to the use of commercial agricultural limestone. Moreover, no immediate concerns seem to be expected related to soil exchangeable sodium (Na), at least for the amounts needed to increase soil pH until 6.5. This was also an evidence for dregs and grits, which presented the higher amounts of Na on its composition. Also, particularly for wood ash, the pronounced increase observed on soil extractable potassium and phosphorous, indicates

that ashes can also contribute to improve soil fertility supplying significant amounts of these nutrients. Finally, metals do not seem to be a limiting factor for the application to land of these by-products.

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