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## ABSTRACT

P-spiked Linz-Donawitz (LD) slag was used as a soil additive to improve physico-chemical soil properties and *in situ* stabilize Cu and other trace metals in a sandy Cu-contaminated soil (630 mg kg$^{-1}$ soil) from a former wood preservation site. The LD slag was incorporated into the contaminated soil to consist four treatments: 0 % (T1), 1 % (T2), 2 % (T3), and 4 % (T4) per air-dried soil weight. A similar uncontaminated soil was used as a control (CTRL). After a one-month reaction period, potted soils (1kg) were used for a 2-week growth experiment with dwarf beans (*Phaseolus vulgaris* L.). Soil pH increased with the incorporation rate of LD slag from 5.7 in the T1 soil up to 7.9 in the T4 soil. Similarly the soil electrical conductivity (EC, in mS cm$^{-1}$) rose from 0.15 (T1 soil) up to 1.17 (T4 soil). Bean plants grown on the T1 soil showed a high phytotoxicity. All incorporation rates of LD slag increased the root and shoot dry weight yields compared to the untreated soil (T1). The foliar Ca concentration of beans was enhanced for all LD slag-amended soils, while the foliar Mg, K, and P concentrations were not increased. Foliar Cu, Zn, and Cr concentrations of beans decreased with the LD slag incorporation rate. The 2% incorporation rate was sufficient to obtain the highest bean growth and foliar Ca concentration, to reduce foliar Cu concentration below its upper critical value, and to avoid an excessive soil EC and Zn deficiency.

## 1. INTRODUCTION

Soil contamination by potentially toxic trace elements (PTTE) due to anthropogenic activities is of concern in many world parts (He et al., 2005; Mathieu et al., 2008). Since the 18th century, the fungicidal Cu properties are recognized, and many Cu-based wood preservatives have been widely used (Bhattacharya et al., 2002; Karjalainen et al., 2009; Mench and Bes, 2009). The volume of wood products treated with Cu-based preservatives grew exponentially during the 1970s and 1980s and Cu remains today one of the primary biocide components used to protect wood used in ground contact or fully exposed to the weather (Freeman and McIntyre, 2008). Several PTTE, i.e. As, B, Cu, Cr, and Zn can occur in excess in contaminated soils at wood preservation sites, depending on Cu-based preservatives used against insects and fungi, which may result in soil ecotoxicity and PTTE dispersion through natural agencies (Bhattacharya et al., 2002; Kumpiene et al., 2008; Girouard and Zagury, 2009; Mench and Bes, 2009; Bes et al., 2010). Consequently, important aims are to remove (Gabrielli dos Santos et al., 2010; Kolbas et al., 2011) or to stabilize such PTTE in excess in these contaminated soils to minimise pollutant linkages such as root exposure, plant uptake, and leaching from the root zone (Mench et al., 2010). Several *in situ* stabilization techniques of PTTE in contaminated soils have been developed by incorporating amendments which reduce their labile pool, their root uptake and soil ecotoxicity (Mench et al. 2006; Kumpiene et al. 2008). In particular neutralizing agents in the form of alkaline materials have been added to acid soils to ameliorate their physico-chemical properties and reduce metal phytoavailability (Brallier et al., 1996; Brown et al., 1997; Bolan and Duraisamy, 2003; Gray et al., 2006; Tlustoš et al., 2006). Many alkaline materials are available to neutralize the soil acidity including calcite ($CaCO_3$), burnt lime (CaO), slaked lime ($Ca(OH)_2$), dolomitic limestone ($CaMg(CO_3)$), and slag ($CaSiO_3$) (Bolan and Duraisamy, 2003). They can reduce the negative effects of PTTE such as As, Cr, Cu, Pb, Cd, and Zn, and improve the quality of

contaminated soils (Mench et al., 2000; Oste et al., 2002; Bolan and Duraisamy, 2003; Adriano et al., 2004; Pérez de Mora et al., 2005; Raicevic et al., 2005; Kumpiene et al., 2006; 2008).

According to changes in soil pH, alkaline materials may be effective to induce metal hydrolysis reactions and/or co-precipitation with carbonates and to act as a precipitating agent for metals in the soil solution (Tyler and McBride, 1982; Mench et al., 1998; Singh and Oste, 2001; Bes and Mench, 2008). Liming of acid soils decreased the soluble fraction and plant uptake of Ni, Cd, Zn and Cu as well as increased the crop yield (Brallier et al., 1996; Krebs et al., 1998; Singh and Oste, 2001). Alkaline materials incorporated into Cu-contaminated soils improved the plant growth and reduced Cu concentration in the soil pore water (Fessenden and Sutherland, 1979; Bes and Mench, 2008). The incorporation of $Ca(H_2PO_4)_2$ and $CaCO_3$ into a multi-metal contaminated soil decreased the extractable concentrations of Cd, Cu, Pb, Ni, and Zn by more than 96% (Wang et al., 2001). Phosphogypsum improved soil properties such as pH, soil electrical conductivity (EC), cation exchange capacity (CEC), exchangeable Ca, Mg, and metal phytoavailability, and increased the crop yield (Alva and Sumner, 1990). Phosphates and related materials such as phosphoric acid, phosphate rocks, and synthesized apatites have been successfully applied to stabilize Pb, Cd, Zn, and Cu in contaminated soils, sediments and solid wastes, reducing their phytoavailability, their mobility in soils, and subsequently their leaching from the root zone to the groundwater (Bolan et al., 2003; Liu and Zhao, 2007). Phosphate minerals have the potential to sorb and /or co-precipitate trace metals (Barrow, 1987; Pierzynski and Schwab, 1993; Xu et al., 1994; Ma, 1996; Mench et al., 1998). The use of hydroxyapatite for the *in situ* stabilization of metals (Zn, Pb, Cu, and Cd) in contaminated soils decreased the exchangeable metal contents in soil, promoted plant growth and reduced the foliar metal concentrations of plants (Boisson et al., 1999a, b). In that case, the stabilization of trace metals of the soils could occurre through cations exchanges or by a dissolution – reprecipitation mechanisms. Iron phosphate (vivianite) incorporated into Cu-contaminated soils likely induced precipitation and adsorption processes decreasing available soil Cu (Liu and Zhao 2007).

Slags, which usually consist of Ca, Al, Si, Fe, and other metal oxides, are alkaline by-products of metallurgical processes and residues of incineration processes. Several slag types have been used as amendment for metal-contaminated soils (Mench et al, 1994a, 2000), but the use and environmental assessment of Linz-Donawitz (LD) slags is more recent (Proctor et al., 2002; Gahan et al., 2009; Yilmaz et al., 2010). Copper mainly precipitates with hydroxide dissolved from the slag rather than adsorbs on the slag surface (Kim et al., 2008). Blast-furnace slag is an effective sorbent for Cu, Zn, Ni, and Pb ions for a wide range of ion concentrations and pH values (Dimitrova, 1996; Dimitrova and Mehandjiev, 1998). The use of blast furnace slag to correct the soil

acidity promoted root length, shoot dry matter (DM) and grain yield (Carvalho-Pupatto et al., 2004). Calcium silicate slag can reduce the soil acidity, increase Ca, Mg, Si and P availability (Besga et al., 1996; Barbosa Filho et al., 2004), and lessen exchangeable soil Al, Mn, Cu, and Zn (Besga et al., 1996). Slag application in a tea garden and rice field soils increased the soil pH, shoot DM yield and P and Mn uptake (Ali and Shahram, 2007); plant Fe and K uptake increased in the rice field, while K uptake decreased and Fe uptake was not changed in the tea garden. Thomas phosphate basic slag used in several contaminated soils cut down the mobility and phytoavailability of Cd, Zn, Pb, and Cu, and can promote plant growth (Mench et al., 1994a, b; Bes and Mench, 2008).

This study aimed at determining (1) if the incorporation of a P-spiked LD slag into a Cu-contaminated topsoil from a French wood preservation site can improve soil properties, i.e. pH and EC, and (2) the LD addition rate which promotes the growth of bean plants and optimizes foliar mineral concentrations in their primary leaves.

## 2. MATERIAL and METHODS

### 2.1. Soils

The site (6 ha) is located in Gironde, SW France (N 44°43.353, W 000°30.938) and has been used for over a century to preserve and store timbers, posts and utility poles (Mench and Bes, 2009). Creosote and Cu-based salts (i.e. mainly $CuSO_4$, and chromated copper arsenate to a lesser extent) have been successively used as wood preservatives. Assessment of established vegetation and site characteristics were previously reported (Mench and Bes, 2009; Bes et al., 2010). Anthropogenic soils are developed on an alluvial soil (Fluviosol). Soil investigation pits (0-1.5m) have demonstrated a major contamination of topsoils with Cu due to wood washing (Table 1) with spatial variation (65 to 2400 mg Cu $kg^{-1}$ soil DW) whereas total soil As and Cr, i.e. 10-53 mg As and 20-87 mg Cr $kg^{-1}$ in topsoils, remained relatively low in all soil layers (Mench and Bes, 2009). The contaminated topsoil (0-25 cm, 50 kg from a 4m² area, Table 1) was collected with a stainless spade near the sub-site P7 where there are evidences that polycyclic aromatic hydrocarbons (PAH) in the topsoil are below the French guideline values for residential and industrial uses (Mench and Bes 2009). A similar uncontaminated Fluviosol soil was sampled (0-25 cm, 10 kg) in a kitchen garden (Gradignan, Gironde, France) and used as a control soil (CTRL, Table 1). Soils were air-dried, homogenized and sieved (2 mm). Soil material (50 g) was used for particle size distribution analysis by sieving and pipette methods (Richards, 1954; Jackson, 1969). The

soil pH was determined in 1:1 soil:water suspension using a glass electrode pH meter (Jackson, 1967). The soil EC was measured in 1:1 soil:water suspension with a conductivity meter (WTW 340i), Jackson, 1967). Total nitrogen was determined at the INRA, Laboratoire d'Analyses des Sols (LAS), Arras, France using standard methods (INRA LAS, 2007). The organic matter (OM) content was determined by a modified Walkely-Blake method; 0.5 g air-dried soil was placed in a 500 mL conical flask and mixed with 10 mL of 0.17M $K_2Cr_2O_7$, followed by addition of 20 mL of $H_2SO_4$, 200 mL of water, 10 mL of $H_3PO_4$ and one mL of diphenylamine indicator. The contents were backtitrated with 0.5M $FeSO_4.7H_2O$. The OM estimation (±7-8 %) assumes that 77% of the organic carbon is oxidized by the method and that soil OM contains 58% C (Jackson, 1967). The total cation exchange capacity (CEC) was determined by the cobaltihexamine chloride method (Ciesielski and Sterckeman, 1997). Total concentrations of trace elements in soils were determined by inductively coupled plasma emission (ICP-AES, Ultima1 from Jobin-Yvon, Horiba) after wet digestion in HF and $HClO_4$ (AFNOR NF X 31-147, Ciesielski et al., 1997). Table 1 gives the main physico-chemical properties of the contaminated (T1) and control (CTRL) soils. Compared to the control soil (CTRL), the contaminated soil (T1) displayed a high value for total soil Cu (Table 1). It largely exceeded Cu background concentrations in French sandy soils and the threshold value justifying a contamination assessment, i.e. 35 mg Cu kg-1 (Baize, 1997) (Table 1). Total soil As and Cr in the contaminated soil were similar to upper whisker values for French sandy soils. The composition of the contaminated soil mostly reflected the use of Cu-based wood preservatives.

The X-EDS maps showed a higher content of P, widely distributed, in the LD slag than in the initial slag (Fig. 1). The LD slag consisted of a complex mixture of Ca phases, i.e. Ca silicates such as Larnite, Ca ferroaluminates such as Brownmillerite and Sreboldoskite, calcite and hydrated calcite such as Portlandite, Fe oxides such as Wustite, Si oxide (silica), and P phases such as oxides and phosphates. The phosphate crystals in the LD slag mainly belonged to the Analcime and Apatite families, which are wellknown to sorb trace metals and to act as P fertilizer for plant growth.

### 2.2. Soil amendment

The Linz-Donawitz (LD) slag from electric steel furnace, also known as basic oxygen furnace, was furnished by the Centre Technique et de Promotion des Laitiers Sidérurgiques (CTPL, La Plaine Saint-Denis, France). This by-product of the steelmaking industry generally contained about 30% Ca, 20% Fe, 15% $SiO_2$, 5% Mg, 5% Al, 1.4% P and trace metals such as Cr, V, and Ba in low concentrations (Gahan et al. 2009; Yilmaz et al., 2010). These elements are combined to form a mix of calco-alumina silicates, iron oxides, lime and other

metal oxides which usually sorb trace metals. The initial Linz-Donawitz slag was chemically modified by precipitation of mineral phosphates to increase its P content (F. Amin, 1993) and henceforth called LD slag in the following text. The X-EDS maps were performed on two thin blades of initial and LD slags using a JEOL SEM (6400) equiped with an Oxford X-EDS detector. Total contents of major elements in the LD slag were determined by atomic absorption spectrophotometry (Perkin-Elmer, AAnalyst400) after sample digestion in pure HF solution (1M). Arsenic was determined by GF-AAS (norm NF EN ISO 15586, T90-119) after digestion with aqua regia (norm NF EN 13346). Other trace elements were analysed by ICP-AES (norm NF EN ISO 11885) after total digestion (norm NFX31-147, Cieselski et al., 1997). The pH and EC of LD slag were measured using a glass electrode pH meter and a conductivity meter (WTW 340i). The LD slag incorporation into the contaminated soil significantly increased the soil pH and EC (Fig. 2). The soil pH varied from 5.7 in the untreated contaminated soil (T1) to 7 , 7.4 and 7.9 in the T2, T3, and T4 soils, respectively (Fig. 2a). Soil pH in the T3 soil and the control soil (7.41) were similar. The soil EC (in mS cm-1) increased from 0.15 (T1) to 0.47, 0.51, and 1.17 for the T2, T3, and T4 soils, respectively (Fig. 2b). The soil EC was higher in the T2, T3, and T4 soils than in the control soil (0.41 mS cm-1). These increases in soil pH and EC in all LD slag-amended soils were related to the composition of LD slag which released P, Ca, and alkaline products. A relatively small LD slag amount induced a rapid change of the soil pH and EC as for the liming of acid soils (Su and Evans, 1996). Additionally, liming of metal-contaminated soils increased the net negative charge of variably charged soil colloids such as clays and OM (Gray et al., 2006). Increases in soil pH and EC after slag incorporation have been previously reported (Alva and Sumner, 1990), notably for basic slag with and without NPK fertilization (Pinto et al., 1995; Besga et al., 1996; Jamali and Forghani, 2008) and for Thomas basic slag (TBS) in a similar Cu-contaminated soil from a wood preservation site (Bes and Mench, 2008). Our results confirmed that LD slag incorporation in an acid, contaminated soil can ameliorate its properties such as soil pH and EC. However soil EC in the T4 soil (Fig. 2b) exceeded the suitable values for plant growth, i.e. 0 -0.45 mS cm-1 (Omafra, 2008).

### 2.3. Pot experiment

The LD slag was incorporated into the contaminated soil at increasing rate (in % by air-dried soil weight) to consist four soil treatments, i.e. 0 % (T1), 1 % (T2), 2 % (T3), and 4 % (T4). Three replicates (1 kg air-dried soil) for each treatment were homogenised by rotation in 2-L plastic flasks, and transferred into 1.3-L plastic pots. The control soil (CTRL) was treated in the same way. After the LD slag incorporation, the soil moisture content was raised to 70 % of the water holding capacity (WHC, 10% of air-dried soil weight) by

manual irrigation with distilled water and soils were allowed to react for four weeks at 20°C. Thereafter, four dwarf beans (*Phaseolus vulgaris* L. cv. vroege Limburgs) were sown in all pots. Plants were cultivated in the laboratory under controlled environmental conditions: illumination 12 h light/12 h darkness regime, intensity 150 µmol m$^{-2}$ s$^{-1}$, temperature 25°C/22°C, and 50% relative humidity. Pots were arranged in a fully randomised block design on a bench and watered daily with deionised water (at 50% WHC) without loss from drainage. The plant growth was monitored on a daily basis using an index based on plant development steps for two weeks and then plants were harvested. Phenotype traits, *i.e.* the fresh weight of roots, shoots and primary leaves, were measured. Plant parts were washed with deionised water (2 times) and distilled water, dried in an oven at 70 °C, and weighted to determine the DW biomass production. Plant samples (0.5 g) were wet digested in 5 mL 14M HNO$_3$, 2 mL H$_2$O$_2$ and 1 mL distilled water at 180°C in PFA (perfluoroalkoxy copolymer resin) tubes under microwaves (MarXpress, CEM) corresponding to an oxidation step from a pure chemical point of view. Mineral composition in the plant digests were determined by ICP-AES (Ultima, Jobin Yvon Horiba, Longjumeau, France). Soil samples were taken from all pots to measure the soil pH and EC as described above.

### *2.4 Statistical analysis*

All analytical determinations were triplicated. For the pot experiment, soil and plant data were statistically analysed (ANOVA, Kruskall-Wallis and Tukey test) with the SAS software (version 9.1) to evaluate changes in soil properties (soil pH and EC), root and shoot yields, mineral concentrations of primary leaves and their mineral mass [µg plant$^{-1}$, calculated by multiplying the biomass of primary leaves (µg DW plant$^{-1}$) by their element concentration (µg kg$^{-1}$ DW)].

### 3. RESULTS and DISCUSSION

### *3.1. Effect of LD slag on Plants*

### *3.1.2.Effect of the LD slag incorporation on the shoot DW yield*

The shoot DW yield of beans peaked for the control soil and displayed the lowest value for the untreated soil (T1) (Fig. 3). This confirmed that soils from the sub-site P7 negatively impact bean plants (Bes and Mench, 2008). The shoot DW yield rose (3 – 4 times) in all LD slag-amended soils compared to the T1 soil. Numerically, higher values occurred at the 2% and 4% addition rates, but differences were not significant between the T2, T3 and T4 soils. Values for the T3 and T4 treatments represented 61 % and 67 % compared to

the CTRL treatment. Positive effects of the LD slag incorporation on soil properties such as soil pH and EC and labile nutrient pool would contribute to promote the bean growth. Our results agreed with previous findings showing that slag incorporation corrects soil acidity and promotes shoot and grain DW yields (Alva and Sumner, 1990; Barbosa Filho et al., 2004; Carvalho-Pupatto et al., 2004; Bes and Mench, 2008). Best soil pH values for bean growth range from 6.0 to 7.5 (Gardener's Network, 2009), and the T2, T3 and CTRL values fell in this range (Fig. 2a). In addition, the soil EC values suitable for plant growth vary between 0 and 0.45 mS cm$^{-1}$ whereas values in the 0.46 - 0.7 mS cm$^{-1}$ range may decrease the plant growth and cause a slight to severe damage to salt sensitive plants (Omafra, 2008). That soil EC peaked in the T4 soil (Fig. 2b) may counteract the potential beneficial effect related to the increasing incorporation rate and explain that T3 and T4 soils did not differ for shoot DW yield (Fig. 3).

### 3.1.2. Effect of LD slag incorporation on the root DW yield

Root DW yield increased for all LD slag-amended soils compared to the untreated contaminated soil (T1) (Fig. 4). Root DW yield peaked for the 4% incorporation rate (T4 treatment) and its value was even higher than for the control soil. Root DW yield correlated to the LD slag incorporation rate and the value distribution fitted well with a 2$^{nd}$-order polynomial function (R²=0.97). Root DW yield increased 3 and 3.5 times in the T3 and T4 treatments, respectively, compared to the untreated soil (T1). These results confirmed previous studies reporting that slag application to correct soil acidity increases the root biomass (Carvalho-Pupatto et al., 2004; Bes and Mench, 2008). In contrast TBS incorporated into several contaminated soils did not increase the production of plant biomass but reduced the mobility and phytoavailability of Cd, Zn, and Pb (Mench et al., 1994a, b).

### 3.1.3. Effect of the LD slag incorporation on the foliar concentrations and mineral mass of trace elements

Foliar Al, Cu, Cr, and Zn concentrations of beans decreased for all LD slag-amended soils compared to the untreated contaminated soil (Table 3). The decrease in foliar metal concentrations may be due to the release of Ca and P by the LD slag, increase in soil pH and metal sorption, Ca competition with metals for root uptake, and the dilution effect due to the increased biomass of primary leaves. Foliar Al mass ranged from 2.6 (T1 plants) to 5.9 μg plant$^{-1}$ (CTRL plants) but differences were not significant (Table 4). In the literature, liming on acid soil surface increased the soil pH and reduced Al phytotoxicity (Brown et al., 2008). In most cases P

addition to acid soils resulted in Al precipitation (Wright, 1937). Calcium silicate slag decreased both soil acidity and exchangeable Al in soils (Besga et al., 1996).

Foliar Cu concentrations varied between 6.2 (CTRL plants) and 35.7 mg kg$^{-1}$ DW (T1 plants) (Table 3) and ranked in the following order: T1 > T2 > T3 > T4 > CTRL. Foliar Cu concentrations in the T3 and T4 plants decreased 2 and 2.5 times, respectively, compared to the T1 plants. Frequent values for Cu concentration in bean primary leaves were exceeded in all treatments except CTRL (Table 3). Upper critical foliar Cu concentration for beans is 15-30 mg Cu kg$^{-1}$ DW (MacNicol and Beckett, 1985). This explained that bean growth was limited on the T1 soil (Fig. 3 and 4). Foliar Cu mass varied from 1.9 (CTRL plant) to 3.4 (T3 plants) µg plant$^{-1}$ (Table 4). The LD slag incorporation into the contaminated soil may reduce Cu mobility by precipitation due to increased soil pH and/or sorption with LD slag and native soil compounds. At pH 7, Cu tends to precipitate in the forms of carbonate and hydroxide (Sipos et al., 2008). Such pH value was reached in all LD slag-amended soils (Fig. 2a). Generally, Cu was render less soluble by precipitation of Cu carbonates and oxy-hydroxides, ion exchange, and formation of ternary cation-anion ($SO_4$, $PO_4$) complexes on the surface of Fe and Al oxy-hydroxides (Kumpiene et al., 2008). Kim et al. (2008) suggested that Cu precipitates with hydroxides dissolved from slag rather than adsorbs on the slag surface. Liu and Zhao (2007) reported that the application of iron phosphate decreased Cu availability in Cu-contaminated soils by precipitation and adsorption processes. Usually incorporation of alkaline materials in acid soils decreased Cu concentration in soil solution and plants and increased crop yield (Brallier et al. 1996; Krebs et al., 1998; Singh and Oste, 2001; Bes and Mench, 2008).

Foliar Cr concentrations ranged from 0.4 (CTRL plants) to 6.0 mg kg$^{-1}$ DW (T1 plants) with the following order: T1 > T2, T3, T4 and CTRL. Foliar Cr concentration in the T1 plants exceeded frequent values in primary leaves of dwarf beans grown on uncontaminated soils, i.e. 0.13-1.7 mg Cr kg$^{-1}$ DW (Mench et al., 1996). The Cr mobility in soils is decreased by the presence of OM and divalent iron (Kumpiene et al., 2008). The higher OM content in the control soil (Table 1) may contribute to the lowest foliar Cr concentration in CTRL plants (Table 3). The LD slag also contained Fe and Mn oxides (Table 2). Kumpiene et al. (2006) reported that the incorporation of zerovalent iron grit into a CCA-contaminated soil, which resulted in newly-formed Fe and Mn oxides, reduced shoot Cr concentration by 95%. At pH values greater than 5, such as in the LD slag amended soils (Fig. 2a), the low Cr(III) hydroxyl solubility and its retention on soil surfaces such as iron oxides limits its bioavailability and mobility in soils (Fendorf, 1995). That foliar Cr concentration was higher for the T1 plants compared to all other plants (Table 3) was also assumed related to decrease in shoot DW yield (Fig. 2). Foliar Cr mass did not significantly differ across the soil treatments (Table 4).

Foliar Zn concentrations ranged between 2.9 (T4 plants) and 10.9 g kg$^{-1}$ DW (CTRL plants) and were lower than frequent values for beans grown on uncontaminated soils (Table 3). According to Mench et al. (2000), increase of soil pH reduces Zn availability in the soil solution and increase in bean leaf yield cuts down foliar Zn concentration. The lowest foliar Zn concentration occurred in the T4 plants, with a decrease of 3.5 and 3.8 times compared to the T1 and control plants, respectively (Table 3). At the 4% incorporation rate, LD slag may induce an excessive Zn sorption and low Zn supply may limit bean growth compared to CTRL (Fig. 3). In previous findings, TBS incorporation into contaminated soils decreased Zn mobility and phytoavailability (Mench et al., 1994a, b). Foliar Zn mass did not differ across the LD slag-amended and contaminated soils but peaked in the control soil (Table 4).

### 3.1.4. Effect of the LD slag incorporation on the foliar nutrient concentrations and mass

Foliar Ca concentrations ranged between 2.5 (T1 plants) to 21.3 g kg$^{-1}$ DW (CTRL plants) (Table 3) and significantly increased in all LD slag-amended soils compared to the T1 soil. Foliar Ca concentration peaked in the T3 and T4 plants, being 7.9 and 7.6 times higher compared to the T1 plants, respectively. However foliar Ca concentration did not significantly differ between the T2, T3, T4 and CTRL plants. Foliar Ca concentration in plants frequently ranges between 1 and 50 g kg$^{-1}$ DW (Marschner, 1995) and Ca concentration in the primary leaves of dwarf beans grown on uncontaminated soils varies between 6.4 and 28 g kg$^{-1}$ DW (Table 3, Mench et al., 1996). Low foliar Ca concentration vs. foliar Cu concentration especially in the T1 plants can limit bean growth, Ca sub-cellular homeostasis and the detoxification of oxidative stress (Cuin, 2006). The TBS incorporation into a Cu-contaminated soil from a wood preservation site also increased the foliar Ca concentration and reduced the foliar Cu one in beans (Bes and Mench, 2008). Foliar Ca mass significantly increased in all LD slag-amended plants compared to the T1 plants, peaked in the CTRL plants, and was the lowest in the T1 plants (Table 4). Increased foliar Ca mass in plants from LD slag-amended soils may contribute to enhance pectin methylesterase functioning (Micheli, 2001) and Cu sorption by various ligands (Pilon et al., 2006) and may reduce perturbations in Ca$^{2+}$ homeostasis and effects of oxidative stress (Cuin, 2006).

Foliar Mg concentration was lower in all plants from LD slag amended soils than in the T1 and CTRL plants (Table 3). It varied from 1.5 (T4 plants) to 3.0 g Mg kg DW$^{-1}$ (T1 plants). Lower shoot DW yield in the T4 plants compared to the CTRL plants (Fig. 3) may be partly related to a low foliar Mg concentration in the T4 plants, which was below the frequent values (Table 3). Generally, Mg concentrations in plants range between 1.5 and 3.5 g kg$^{-1}$ DW (Marschner, 1995). The increases in leaf biomass (Fig. 3) and foliar Ca concentration (Table

3) for the T3 and T4 plants may contribute to reduce their foliar Mg concentration. Foliar Mg mass was higher in the CTRL plants than in other ones (Table 4).

Foliar P concentrations varied from 2.3 (T4 plants) to 5.3 g kg$^{-1}$ DW (CTRL plants) and ranked in the following order: CTRL, T1 > T2 > T3, T4 (Table 3). The P concentration in the primary leaves of dwarf beans grown on uncontaminated soils usually ranged between 1.6 and 6 g kg$^{-1}$ DW (Mench et al., 1996). The highest foliar P concentration in CTRL plants may result from P supplied by OM decay in the control soil and its past P fertilization. High foliar P concentration in the T1 plants (Table 3) may be related both to low soil pH and biomass production. In acid soils the P availability of TBS is similar to that of other water soluble P fertilizers (Sinaj et al., 1994). However the LD slag despite their phosphatation did not promote foliar P concentration (Table 3). Decreased foliar P concentrations with increasing LD slag incorporation rate would be related to increases in soil pH (Fig. 2a), phosphate sorption, soil Ca availability, and plant biomass (Fig. 3 and 4). Pinto et al. (1995) reported that slag addition in acid soil increases exchangeable soil Ca and Ca concentration in soil solution. Due to the LD slag composition, and notably phosphate sorption and precipitation with cations such as Ca, Fe and Al, phosphates would be less available in the soil solution for root uptake. The potential chemical mechanisms responsible of such trend could be a pure phosphate sorption or a phosphate complexation at the solid/liquid interface which could be precise by a specific study. The foliar P mass was higher in the CTRL plants than in all other ones (Table 4).

Foliar K concentrations (in g kg$^{-1}$ DW) were in the 13.0 (T2 plants) - 21.9 (T1 plants) range and decreased in the T2 and T3 plants (Table 3). Generally, critical K concentrations in plants range between 20 and 50 g kg$^{-1}$ DW (Marschner, 1995), while the K concentration in the primary leaves of dwarf beans grown on uncontaminated soils varied between 13 and 22 g kg$^{-1}$ DW (Mench et al., 1996). For all soil treatments, foliar K concentration of bean plants fell in this range (Table 3). Foliar K mass increased in the T3 and T4 plants compared to the T1 plants (Table 4). Pinto et al. (1995) suggested that slag application in an acid soil decreased soil exchangeable K due to the CEC increase. Based on foliar K concentration and mass, decrease in K supply was not marked here and changes in foliar K concentration were more related to the increases of root and shoot yields in plants grown on LD slag amended soil (Fig. 3 and 4).

## 4. CONCLUSION

Linz-Donawitz (LD) slag is an alkaline by-product from electric steel furnace with a potential for ameliorating physico-chemical soil properties and metal stabilization in contaminated soils. A LD slag spiked with P was incorporated at increasing rates (0%, 1%, 2%, and 4%) into an acid, sandy Cu-contaminated soil (630

mg Cu kg$^{-1}$) from a wood preservation site. Depending on the incorporation rate, the soil pH was increased from 5.7 in the untreated contaminated soil up to 7.9 in the 4 % LD slag-amended soil. Similarly, the soil EC (in mS cm$^{-1}$) rose from 0.15 in the untreated contaminated soil up to 1.17 in the 4% LD slag-amended soils. The LD slag incorporation increased both root and shoot DW yields of bean plants for all amended soils compared to the untreated contaminated soil. Compared to plants grown in the untreated contaminated soil, foliar Cu, Al, and Cr concentrations decreased in all plants grown in the amended soils and foliar Zn concentration at the 4% LD slag rate. Foliar Ca concentration and mass in plants were enhanced for all amended soils compared to the untreated contaminated soil. Foliar Mg and P concentrations and masses in plants were not enhanced by LD slag incorporation into the Cu-contaminated soil. Both foliar K concentration and mass increased in beans at the 2% and 4% LD slag incorporation rates. These rates resulted in the highest bean growth and foliar Ca concentrations and the lowest foliar Cu ones. However the 4% incorporation rate reduced too much the foliar Zn concentration. Foliar Cu mass of beans was higher in all amended soils than in the contaminated soil, notably due to the restoration of root and shoot DW yields.

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