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Mobility and phytoavailability of Cu, Cr, Zn, and As in a contaminated soil at a wood preservation site after four years of aided phytostabilization

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Abstract:

The remediation of copper-contaminated soils by aided-phytostabilisation in 16 field plots at a wood preservation site was investigated. The mobility and bioavailability of four potentially toxic trace elements (PTTE), i.e. Cu, Zn, Cr, and As, were investigated in these soils four years after the incorporation of compost (OM, 5% w/w) and dolomite limestone (DL, 0.2% w/w), singly and in combination (OMDL), and the transplantation of mycorrhizal poplar and willows. Topsoil samples were collected in all field plots and potted in the laboratory. Total PTTE concentrations were determined in soil pore water (SPW) collected by Rhizon soil moisture samplers. Soil exposure intensity was assessed by Chelex100-DGT (diffusive gradient in thin films) probes. The PTTE phytoavailability was characterized by growing dwarf beans on potted soils and analyzing their foliar PTTE concentrations. OM and DL, singly and in combination (OMDL), were effective to decrease foliar Cu, Cr, Zn, and As concentrations of beans, the lowest values being numerically for the OM plants. The soil treatments did not reduce the Cu and Zn mineral masses of the bean primary leaves, but those of Cr and As decreased for the OM and DL plants. The Cu concentration in SPW was increased in the OM soil and remained unchanged in the DL and OMDL soils. The available Cu measured by DGT used to assess the soil exposure intensity correlated with the foliar Cu concentration. The Zn concentrations in SPW was reduced in the DL soil. All amendments increased As in the SPW. Based on DGT data, Cu availability was reduced in both OM and OMDL soils, while DL was the most effective to decrease soil Zn availability.

39 **1. Introduction**

40

41 Phytostabilization is a less invasive, low-cost phytotechnology, singly and in combination with
42 amendments (i.e. aided phytostabilisation) is a potential options to restore the physical, chemical, and biological
43 properties of potentially toxic trace elements (PTTE)-contaminated soils (Bolan et al. 2003; Kumpiene et al.
44 2008). The fate of PTTE in soils is influenced by physical and chemical reactions between the solid components
45 of soil and the liquid phase (Morel et al. 2006). Soil factors such as pH, soil organic matter (SOM), texture,
46 redox potential and temperature (Alloway 1995) and biological processes controlled by soil microorganisms and
47 plants are key-players in the root zone for the PTTE mobility and bioavailability (Chaignon and Hinsinger 2002;
48 2003). Roots can indeed modify the PTTE mobility by changing soil pH, electrochemical potentials through
49 element sorption in the apoplast and functioning of membrane transporters and their rhizodeposition or
50 complexation in the rhizosphere, including soluble root exudates and mucilages (Hinsinger 1998, 2001a, b;
51 Lombi et al. 2001; Chaignon and Hinsinger 2002).

52 Several mineral and organic amendments such as lime, coal fly ashes, phosphates, red muds, compost,
53 biosolids, iron grit and Fe/Mn/Al oxides can improve phytostabilization and production of plant-based feedstock
54 through decrease in the PTTE bioavailability (Lombi et al. 2002; Bolan et al. 2003; Brown et al. 2004; Geebelen
55 et al. 2003; Kumpiene et al. 2008; Mench et al. 2010). Case studies assessing the PTTE mobility and
56 bioavailability in the long-term for contaminated soils managed by (aided) phytostabilization are needed to
57 better define the pros and cons of such management options (Mench et al. 2010). The main thrust of this article
58 was to investigate the effects of the amendments and understand the factors involved in aided phytostabilization
59 of Cu and chromated copper arsenate (CCA) salt contaminated soils by liming and addition of compost.
60 Therefore, this work aimed at assessing the mobility, soil exposure intensity and phytoavailability of Cu, Zn, Cr,
61 and As in top soils (0-25 cm) of 16 field plots at a wood preservation site in Southwest France, four years after
62 their implementation for testing four options of (aided) phytostabilization. These options were either to
63 incorporate compost (OM) and dolomitic limestone (DL), singly and in combination (OMDL), or not into the
64 contaminated soil prior the transplantation of mycorrhizal poplar and willows. The efficiency of the four aided-
65 phytostabilisation options to reduce the mobility and phytoavailability of Cu, Cr, Zn, and As was compared.

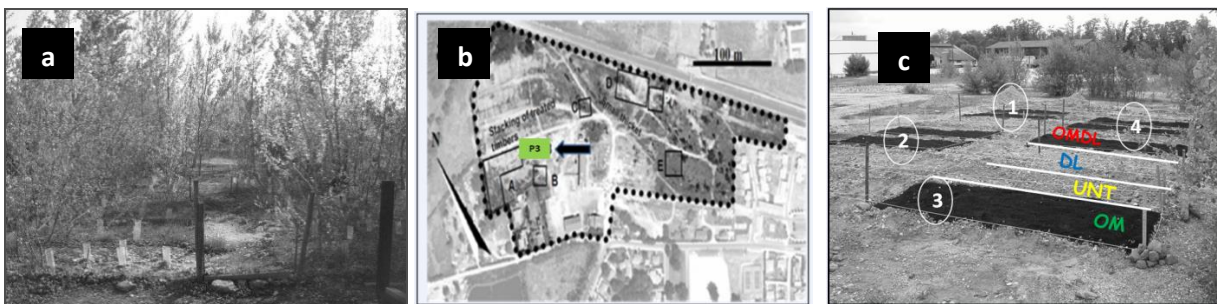
66 **2. Material and Methods**

67 **2.1. Site, soil sampling and soil characterization**

68 The wood preservation site (6 ha are partially active and 4 ha with historical activities were used for an
69 allotment) is located in the Gironde County (44°43'N; 0°30'O), Southwest France. It has been used for over a
70 century to preserve and store timbers, posts and utility poles and various Cu-based salts were successively
71 utilized (Mench and Bes 2009). Plant communities and soil characteristics were previously assessed. Cu is the
72 main contaminant in topsoils (i.e. 65 to 2600 mg kg⁻¹, Mench and Bes 2009; Bes et al. 2010; 2013). Soil Cu
73 contamination mainly results from washings of the treated timbers. Plant communities in the zone of the field
74 trial included *Agrostis capillaris*, *Elytrigia repens*, *Rumex acetosella*, *Portulaca oleracea*, *Hypericum*

75 *perforatum*, *Hypochaeris radicata*, *Euphorbia chamaesyce*, *Echium vulgare*, *Agrostis stolonifera*, *Lotus*
 76 *corniculatus*, *Cerastium glomeratum*, and *Populus nigra* (Fig. 1a) (Bes et al. 2010). The geological structure of
 77 the site consists of two layers. The first one is a mixture of brown sand and gravels, from the medium Pleistocen
 78 (Riss); with a depth in the range 2.5- 4.5 m whereas the second layer is composed of marls and decalcification
 79 clays related to eroded Stampien materials. Fifteen sub-sites were previously defined (labeled from A to E and
 80 P1 to P10) depending on total topsoil Cu concentration (Fig. 1b) (Mench and Bes 2009; Bes et al. 2010). Long-
 81 term phytostabilization experiments are established at the P3 and P7 sub-sites. The field trial (150 m²)
 82 established in 2006 at the site P1-3, formerly used for stacking treated wood and utility poles (Fig. 1b, Bes 2008;
 83 Lagomarsino et al. 2011), has been cultivated as a short rotation coppice including mycorrhizal poplar (*P. nigra*
 84 L.) and willows (*Salix caprea* and *S. viminalis*) (Bes 2008). It consists in 16 plots (1 m x 3 m) that have received
 85 one of the following four initial treatments, at the beginning of the experiment only, randomly replicated in four
 86 blocks: untreated (UNT), dolomitic limestone (DL, 0.2% by air dried soil, w/w, NF U 44 001, 30% CaO and
 87 20% MgO combined with carbonates, 80% < 0.16 cm, Prodical Carneuse, Orthez, France), compost (OM, 5%
 88 w/w), and DL combined with OM (OMDL) (Fig.1c). Thus each treatment was repeated 4 times. Compost
 89 derived from composting (9-12 months) poultry manure and pine bark chips (ORISOL, Cestas, France, Bes and
 90 Mench 2008). Soil amendments were carefully mixed in the topsoil (0-0.30 m) with a stainless spade. Topsoils
 91 (0-25 cm, alluvial origin, Fluviosol) were sampled in April 2010 (average sample made of three sub-samples of
 92 1 kg) with a stainless spade in the 16 plots. Main characteristics of topsoil's at the site P3 are presented in Table
 93 1. Their texture is sandy. Organic matter content is low as well as the cation exchange capacity (CEC). Total soil
 94 concentrations were in the common range of French sandy soils for Cr, As, and Zn but total soil Cu was in
 95 excess for these coarse sandy soils *i.e.* 35 mg Cu kg⁻¹ (Tab. 1, Baize and Tercé. 2002).

96



97

98 Figure 1. (a) implementation of the plots of the field trial (2006) carried out with soil amendments and
 99 mycorrhizal trees since 2006 at the Biogeco phytoremediation platform (adapted from Bes et al.2010), (b)
 100 location of the studied site, the arrow indicating the site P3 and (c) Photo of the field plots (P3 sub-site) in April
 101 2010, 4 replicated blocks, each block treated with 4 types of amendments (OM, DL, OMDL and UNT)

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Table 1. Main characteristics of the P3 and control soils (0-0.25 m soil layer)

Parameters	Site P3	Control soil	Background values in French sandy soils ^a
Sand %	83.5 ± 1.1	66.5	
Silt %	11.5 ± 0.9	15.5	
Clay %	3.8 ± 1.2	18.0	
C/N	17.2	13.8	
SOM (g. kg ⁻¹)	15.9	69.9	
CEC (cmol+/kg)	3.49	16.1	
organic C (g. kg ⁻¹)	9.19	40.4	
total N (g. kg ⁻¹)	0.534	2.94	
pH	7.0 ± 0.23	7.01	
As (mg.kg ⁻¹)	9.8	3.6	1.0-25 ^b
Co (mg.kg ⁻¹)	2	2.62	1.4-6.8
Cu (mg.kg ⁻¹)	674 ± 126	21.5	3.2-4.8
Cr (mg.kg ⁻¹)	23	17.9	14.1-40.2
Mn (mg.kg ⁻¹)	181	189	72-376
Ni (mg.kg ⁻¹)	5	7.46	4.2-14.5
Zn (mg.kg ⁻¹)	46	50.9	17-48

108 ^a median and high vibrissae values except for As (Baize. 1997; Baize and Tercé 2002):. ^b common As mean values for all French soil
 109 types (Baize and Tercé 2002).

110

111 2.2. Germination tests

112

113 For each of the 16 plots, 1 kg of soil was potted after sieving (2 mm). Similarly, two samples of an
 114 uncontaminated control soil (CTRL) from a kitchen garden (0-0.25 m Gradignan, France) from the same alluvial
 115 terrace were taken and potted (Tab 1). Four seeds of dwarf beans (*Phaseolus vulgaris*) were sown in all pots and
 116 cultivated for 18 days in controlled conditions (16 h light/8 h darkness regime, 25°C/21°C). The soil moisture
 117 was maintained at around 50% of the field water capacity with additions of deionized water after weighing, then
 118 the soil moisture was raised to 80% at the beginning of seed germination. At harvest, the dry weight (DW) of
 119 bean primary leaves (BLDW) was determined after drying at 70°C. Aliquots of primary leaves (BL) were
 120 weighed (35-150 mg) directly into Savillex Polytetrafluoroethylene PTFE 50 mL vessels, 2 mL H₂O and 2 mL
 121 of 14 M HNO₃ were added and heated open at 65°C for 2 hours. Then the caps were closed and the containers
 122 were left overnight at 65°C (12-14h). Thereafter, they were opened, 0.5 mL of H₂O₂ (30%) was added to each
 123 sample and left at 75°C open for 3 hours. Then 1.5 ± 0.5 mL of *fluorhydric acid* (HF, 48%) was added to each
 124 sample, caps closed and left at 100°C overnight. Containers were opened and kept at 120°C for 4-5 hours
 125 evaporating to dryness, taken off heat, 1 mL HNO₃ + 5 mL H₂O + 0.1 mL H₂O₂ were added to each, gently
 126 warmed up (65°C) and after cooling down made up to 50 mL with distilled water. Finally, trace element
 127 concentrations in digests were determined by ICP-MS (Varian 810-MS) using standard solutions of trace
 128 elements diluted from a stock solution 1000ppm ±1%/Certified). The accuracy of the metals determination was
 129 checked by performing calibrations with a standard reference solution. Strong correlation was found between the
 130 measured and the reference results (R²=0.9992) indicating that the measurement are accurate. After the
 131 calibration phase, 4 repeated measurements were performed for each digest. The precision of the trace element

132 content measurement was assessed by the standard deviation (SD). All foliar element concentrations are
133 expressed in mg kg^{-1} DW. The mineral mass of each PTTE in BL was computed based on their elemental
134 concentrations and the BLDW.

135 **2.3. Characterization of the soil pore water**

136

137 Soil pore waters (SPW) were extracted from each pot by Rhizon soil moisture samplers (SMS, model
138 MOM, Rhizosphere Research Products, Wageningen, The Netherlands) with a nominal porosity of $0.15 \mu\text{m}$
139 after harvesting the dwarf beans. The capped end was inserted into each potted soil during filling. A syringe
140 needle was connected to the female lock and inserted into a 10 mL glass vacuum tube, for extracting the SPW
141 by vacuum (Cattani et al. 2006). Before putting the samplers in the soils, the SMS devices were previously
142 cleaned with 5% HNO_3 and then washed twice with deionised water.

143 Three SMS devices were placed at 45° in the soils. The soil moisture was maintained at 80% for 15 days.
144 Each device was then let under vacuum for 24 hours for collecting the SPW ($\sim 30 \text{ mL}$) from all pots (18 soil
145 samples, three SMS/pot). The SPW were stored at 4°C . An aliquot (3 mL) of each SPW was acidified with 0.1
146 M HNO_3 for measuring the concentrations of Cu, Zn, Cr, and As in the SPW samples by HR-ICP-MS (Element
147 2, Thermofischer). All the reagents used to prepare the extracting solutions were products of analytical-grade
148 quality (Merck pro-analysis, Darmstadt, Germany). All solutions and dilutions were prepared using doubly
149 deionized water ($18.2 \text{ M}\Omega\text{cm}^{-1}$) (Thermo Scientific Barnstead Easy pure II systems). Standard stock solutions of
150 $1000 \text{ mg}\cdot\text{l}^{-1}$ of different elements were prepared from metal wires or salts of purity higher than 99.998% (VWR
151 international, BDH Prolabo ICP Standards, Belgium). Diluted standard working solutions were prepared from
152 these on a daily basis. All laboratory glassware and plastic ware were rinsed three times with double deionized
153 water after being soaked in a HNO_3 (10%, v/v) bath for 24h. A certified reference material (drinking water) EP-
154 L-3 diluted 1000 times certified by SPS Science (Baie d'Urfé, QC, Canada) was used to assess the precision and
155 accuracy of the analysis of the soil solutions and DGT elution's for Cu, Zn, Cr and As. Measurements lied in the
156 interval of confidence and precision and accuracy was better than 5% RSD.

157 In all SPW samples, dissolved organic carbon (DOC) was determined by a carbon analyzer (Shimadzu[®]
158 TOC 5000A), and concentrations of major cations (Na^+ , K^+ and Ca^{2+}) and anions (NO_3^- , SO_4^{2-} , and Cl^-) were
159 analyzed by ionic chromatography (Dionex ICS-2000, Sunnyvale, CA using the columns CS16A for measuring
160 cations and AS17 for anions).

161

162 **2.4. DGT measurements**

163

164 For measuring available metals in the soils and characterizing the soil exposure, standard cylindrical
165 Chelex 100-DGT (diffusive gradient in thin films) units with an active surface area of 3.14 cm^2 were manually
166 inserted for 24 h directly into the humid topsoil (80%) of each pot. Two DGT probes were inserted per pot. The
167 DGT probes consist of three layers: the first one is a $0.45 \mu\text{m}$ filter; the second layer is a diffusion layer which
168 consists of a polyacrylamide gel layer and the third one a polyacrylamide gel layer that incorporates a Chelex-
169 100 resin that binds strongly the labile trace metal species (Davison et al. 2000; Ernstberger et al. 2002a, b).

170 DGT has proved to be an efficient tool to assess the exposure of PTTE in contaminated soils (Zhang et al.,
171 2001).

172 DGT continuously accumulates metals on the resin gel during deployment. The total mass of each metal
173 (M) accumulated per unit area over the deployment time (T) is given by integrating the flux over the deployment
174 time (eq. 1):

$$175 \quad M = \sum_{t=0}^T F(T)dt \quad (\text{eq. 1})$$

176
177
178
179 The total mass of each metal (M) is determined analytically through the area exposed to the solution (A)
180 by measurement of the eluent concentration (C_e) after elution of the resin gel (volume, V_{gel}) with 1 M HNO_3
181 (volume, V_{HNO_3}),

$$182 \quad M = C_e (V_{\text{HNO}_3} + V_{\text{gel}})/fe \quad (\text{eq. 2})$$

183
184 With $f=0.8$ for Cu, Cr and Zn.

185 The strong binding of metals in the resin gel leads to the creation of a linear concentration gradient in the
186 diffusive gel. This gradient depends on several factors such as the interfacial concentration of labile trace metal
187 species, C_i and the thickness of the diffusion layer, Δg (cm), All these factors determines the flux, $F(t)$, of metal
188 from the soil to the resin-gel according to Flick's first law (eq. 3):

$$189 \quad F(t) = \theta d D d \frac{C_i(t)}{\Delta g} \quad (\text{eq. 3})$$

190
191 where θd is the porosity of the diffusion gel and $D d$ ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient of the labile
192 trace metal species in the diffusion layer. The diffusion coefficients were taken from Zhang et al. (2001).

193
194 The averaged interfacial concentration, C_{DGT} , or available concentration can be calculated from M (eq. 4)

$$195 \quad C_{\text{DGT}} = \frac{M \Delta g}{\theta d D d} \quad (\text{eq. 4})$$

196
197
198 For each metal, the division of the available concentration (C_{DGT}) on the total concentration measured in
199 the SPW, C_{SPW} , give the ratio, R , which indicates the extent of the depletion of soil pore water concentrations
200 at the DGT interface (eq. 5)

$$201 \quad R = C_{\text{DGT}}/C_{\text{SPW}} \quad (\text{eq. 5})$$

202
203
204 For each metal, the mass accumulated in the resin-gel layer was determined after extraction of the resin
205 gel by 1 mL of HNO_3 5% for 24h. This solution was further diluted 10 times and analyzed by HR-ICP-MS
206 (Element 2, Thermo Fischer) for determining metal concentrations (Cu, Cr and Zn).

207
208
209

210 **2.5. Statistical analysis**

211 Analysis of variance (ANOVA), Tukey Post Hoc test (Statistica) and Pearson correlation coefficients
212 (linear regression) (significance level, $p < 0.05$) were performed on the total SPW concentrations, DGT
213 concentrations, R ratios, foliar element concentrations, foliar mineral masses of elements and leaf DW yields to
214 evaluate the treatment influence. All analytical determinations were performed in four replicates. Differences
215 were considered statistically significant at $p < 0.05$. All statistical analyses were performed using the statistical
216 software Statistica (version 6).

218 **3. Results and discussion**

219 **3.1. Soils and soil pore waters**

220 Table 2 shows the physico-chemical parameters of soils (i.e. pH, EC and TOC) and of the SPW (i.e. DOC
221 and major cation and anion concentrations) depending on soil treatments, i.e. phytostabilization (UNT) and
222 aided phytostabilization (OM, DL, and OMDL). Aided phytostabilization based on treatment incorporation into
223 the soil followed by tree transplantation increased slightly the soil pH from 7.16 up to 7.45 in the treated soils
224 compared with the untreated one, mean soil pH values following the decreasing order: DL > OMDL > OM >
225 UNT > CTRL. However, differences in the soil pH and TOC (0.53-1.68%) and in DOC of SPW (29-63 mg C.
226 L⁻¹) were only significant between the contaminated soils (UNT, OM, DL, and OMDL) and the uncontaminated
227 control soil (CTRL) ($P=0.0019$, $P= 1.45E^{-6}$, $P= 0.0013$). They were insignificant between the treated and
228 untreated contaminated soils. The soil EC values varied in the 157-192 $\mu\text{S cm}^{-1}$ range but did not differ between
229 all investigated soils.

230 Four years after, amendments added to the contaminated soils had little influence on the cation
231 concentrations in the SPW (Tab. 2). The SPW Mg²⁺ concentrations varied from 10.9 mg L⁻¹ (Unt) to 41.3 mg L⁻¹
232 (DL) and was significantly higher for the DL soil compared to the UNT soil ($P=0.014$). The SPW Na⁺, K⁺, and
233 Ca²⁺ concentrations were respectively in the 8-38 mg L⁻¹ Na⁺, 16-49 mg L⁻¹ K⁺, and 87-272 mg L⁻¹ Ca²⁺ ranges,
234 but differences between soils were insignificant. For the anion concentrations in the SPW, Cl⁻, NO₃⁻, and SO₄²⁻
235 varied respectively between 9.6-42.9 mg L⁻¹, 300-914 mg L⁻¹, and 13.9-42.7 mg L⁻¹, without significant
236 differences across the soil series (Tab. 2).

237 Metal concentrations in SPW generally mirror root exposure to metals (Sauvé 2003; Tandy et al. 2006;
238 Forsberg et al. 2009). Soil pore waters collected from the potted contaminated and uncontaminated soils
239 showed significant differences in total metal concentrations (Fig. 2). On this soil series, total PTTE
240 concentrations in the SPW were generally in decreasing order: Cu > Zn > As > Cr (mean values in $\mu\text{g L}^{-1}$ on
241 the soil series: Cu = 676, Zn = 22, As = 3.0, and Cr = 0.68). This ranking reflected total PTTE concentrations
242 in the soils, except that total soil Cr was higher than total soil As (Tab.1).

243

244

245

246

247 Table 2. Physico-chemical characteristics of the soils and soil pore water. Values are mean \pm standard deviation
 248 (n=4). Different letters indicate a significant difference ($p < 0.05$)

Soils	pH	EC ($\mu\text{S. cm}^{-1}$)	TOC %	DOC (mg C.L^{-1})	Cations (mg. L^{-1})				Anions (mg. L^{-1})		
					Na ⁺	Mg ²⁺	K ⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
UNT	7.16 \pm 0.12 a**	161 \pm 64.0 NS	0.64 \pm 0.02 a***	29.4 \pm 8.80 a**	21.0 \pm 6.60 NS	10.9 \pm 6.3 a*	21.9 \pm 19.6 NS	156 \pm 56.5 NS	16.9 \pm 2.10 NS	495 \pm 207 NS	19.6 \pm 4.2 NS
OM	7.27 \pm 0.38 a**	168 \pm 51.0 NS	1.68 \pm 0.33 a***	38.0 \pm 7.10 a**	38.7 \pm 35.3 NS	22.9 \pm 14.0 ab*	41.4 \pm 26.6 NS	167 \pm 114 NS	42.9 \pm 45.7 NS	548 \pm 35 NS	39.3 \pm 28.4 NS
DL	7.45 \pm 0.15 a**	157 \pm 16.0 NS	0.53 \pm 0.05 a***	39.4 \pm 6.50 a**	28.2 \pm 11.9 NS	41.3 \pm 18.9 b*	24.7 \pm 18.4 NS	273 \pm 148NS	26.7 \pm 17.8 NS	914 \pm 527 NS	42.7 \pm 28.0 NS
OMDL	7.32 \pm 0.11 a**	192 \pm 39.0 NS	0.72 \pm 0.09 a***	40.9 \pm 4.70 a**	19.5 \pm 5.70 NS	21.8 \pm 9.40 ab*	16.4 \pm 3.8 NS	87.5 \pm 41.7 NS	18.3 \pm 7.20 NS	301 \pm 166 NS	18.4 \pm 7.7 NS
CTRL	6.45 \pm 0.07 b**	169 \pm 22.0 NS	0.62 \pm 0.30 b***	63.06 \pm 1.70 b**	8.6 \pm 8.50 NS	23.2 \pm 10.7 ab*	49.7 \pm 7.9 NS	113.7 \pm 60.8 NS	9.6 \pm 12.8 NS	ND	13.9 \pm 9.8 NS

249 0.01 < (*) P < 0.05, 0.01 > (**) p > 0.001, (***) p < 0.0001, (NS) insignificant difference; ND: not determined. Unt : untreated,
 250 OM : Compost, DL : Dolomitic limestone, OMDL : compost and dolomitic limestone, CTRL : uncontaminated control soil.
 251 EC: electrical conductivity, TOC: total organic carbon; DOC: dissolved organic carbon

252

253 3.1.1. Soil Cu exposure

254 The addition of OM and OMDL numerically increased 2 fold and 1.3 fold respectively the total dissolved
 255 Cu concentration in the SPW (Cu_{spw}) whereas the DL treatment slightly decreased it (0.8 fold) compared to the
 256 UNT soil; however only the OM soil differed from the UNT soil (Fig. 2a). The Cu_{spw} value of the CTRL soil
 257 was 58%, 79%, 52% and 67% lower than those of the UNT, OM, DL and OMDL soils, respectively, i.e. 2-5
 258 fold less than for these contaminated soils. Compost (OM) incorporation into the contaminated soil significantly
 259 increased Cu_{spw} compared to other amendments ($P = 9.0 \text{ E}^{-19}$) and the uncontaminated soil (CTRL) ($P = 1.12 \text{ E}^{-10}$)
 260 (Fig. 2a). All amendments significantly decreased the available Cu concentration (Cu_{DGT}) in the contaminated
 261 soils by roughly a factor 2 ($P = 1.38 \text{ E}^{-14}$) (Fig. 2e). Cu_{DGT} peaked in the UNT soil and was the lowest in the
 262 CTRL soil ($P = 5.4 \text{ E}^{-16}$). In contrast with Cu_{spw} (Fig. 2a), Cu_{DGT} was lower in the OM and OMDL soils than in
 263 the DL soil (Fig. 2e). The Cu_{spw} values in the OM and OMDL soils were respectively 7 fold and 5 fold higher
 264 than the Cu_{DGT} values, i.e. (in $\mu\text{g Cu L}^{-1}$) OM: 1065 and 157 respectively; OMDL: 665 and 147 respectively)
 265 (Fig. 2. a and e). Similar comparison showed a 2-fold factor for the UNT soil (519 $\mu\text{g Cu L}^{-1}$ and 280 $\mu\text{g Cu L}^{-1}$)
 266 and the DL soil (456 $\mu\text{g Cu L}^{-1}$ and 197 $\mu\text{g Cu L}^{-1}$).

267 On the whole soil series, the Cu_{spw} values were not correlated to the Cu_{DGT} ones ($r = -0.16$ the correlation
 268 in the contaminated and the control soil, $r = -0.57$ the correlation calculated in the contaminated soil without the
 269 control one), but highly positively correlated with the soil TOC values ($r = 0.86$ "contaminated soil with control
 270 one") (Tab. 3). The correlation between Cu_{spw} and TOC was even stronger when only the Cu-contaminated soils
 271 are considered ($r = 0.93$) (Tab. 4). The Cu_{spw} did not significantly correlate to soil pH ($r = 0.35$ "in the presence
 272 of control soil, $r = -0.11$ only in contaminated soils, Tab. 3), The correlation was significant and negative between
 273 Cu_{DGT} and the DOC measured in the SPW ($r = -0.68$) (Tab. 3,4).

274 Table 5 presents the R ratio ($R_{Cu} = Cu_{DGT}/Cu_{spw}$) values for the whole soil series. The R_{Cu} values of all
275 amended soils were lower than that for the UNT soil. The soil amendments reduced R_{Cu} and led to the increasing
276 order: OM < OMDL < DL < UNT, this reduction reaching respectively 73% (OM), 59% (OMDL), and 20%
277 (DL) compared to the UNT soil. The R_{Cu} of the control soil was 35% lower than that of the UNT soil.

278 The Cu phytotoxicity in soils depends mainly on its solubility and chemical speciation, which are
279 influenced by its sorption onto mineral and soil organic matter (SOM) (Garrido et al. 2005). Here the total
280 dissolved Cu concentration in SPW increased significantly in the OM-amended soils and slightly in the OMDL
281 soils (Fig. 2a). The DOM (dissolved organic matter) may mobilize soil Cu and bound it in the SPW (Beesley
282 and Dickinson 2011). However, four years after adding OM and OMDL, DOC in SPW as well as soil pH were
283 rather similar in both compost-amended soils and the DL soil (Tab. 2). One week after compost incorporation
284 into the soil, Cu mobility can be reduced by 71% (Ruttens et al. 2006). The SOM and DOM in the SPW react
285 with Cu, and their complexes modify Cu solubility, chemical species, and re-supply from soil bearing phases
286 (Ashworth and Alloway 2007). Fulvic acid bound Cu in the SPW increases its mobility from the solid phase to
287 the liquid phase of soils, notably in compost-amended soils (Hsu and Lo 2000). Soluble Cu may also increase in
288 the SPW in the presence of DOM whereas high molecular mass organic compounds can sorb Cu (McBride and
289 Martinez, 2000; Docekal et al. 2005). After one year, Cu bound to organic matter increased 3-fold in compost-
290 amended soils at this wood preservation site (Lagomarsino et al. 2011). The Cu-SOM complexes, particularly
291 with non-soluble, high molecular mass organic acids can decrease Cu phytoavailability (Chirenje and Ma 1999;
292 Balasoiu et al. 2001; Bolan and Duraisamy 2003). Regulation of Cu mobility from soil to plants by SOM in
293 relation to the ligand functional groups was suggested by Hsu and Lo (2000) and Thakali et al. (2006). In
294 calcareous soils OM may reduce the retention of Cu by $CaCO_3$ and increase its solubility in the soil (Saha et
295 al.1991) as in the OMDL soil (Fig. 2a). The insignificant, small reduction in Cu_{spw} (0.8 fold) in the DL soil can
296 be explained by the slight increase in soil pH (Sauve´ et al. 1997). The DL addition may limit Cu_{spw} by Cu
297 precipitation and complexation and increasing the Cu sorption on solid bearing phases such as organic matter,
298 clays, Fe/Mn (hydr) oxides, carbonates and phosphates (Filius et al. 1998; Kabata-Pendias and Pendias 2000;
299 Garrido et al. 2005 Kumpiene et al. 2006; Lagomarsino et al. 2011). The DL addition induced a similar trend
300 when OM and OMDL soils were compared (Fig. 2a). Similarly, liming soils from pH 4.6 to 6.9 can decrease the
301 water soluble and exchangeable Cu fraction from 11.7 to 4.6 mg kg⁻¹ in sludged soils (Brallier et al. 1996).

302

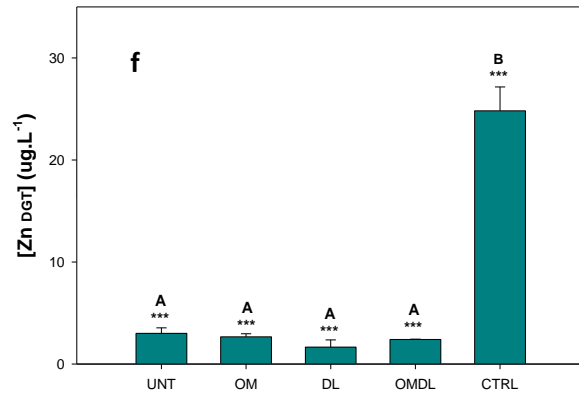
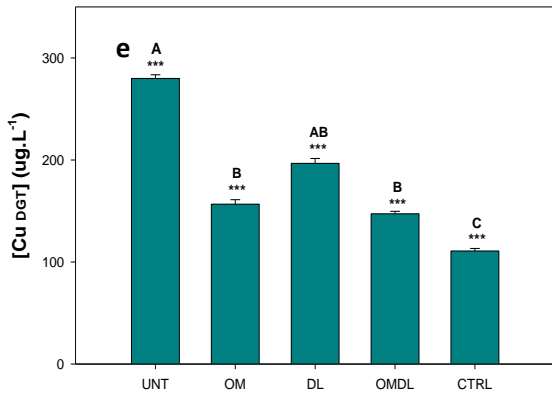
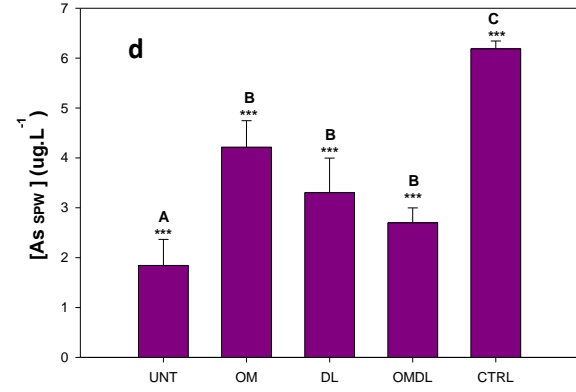
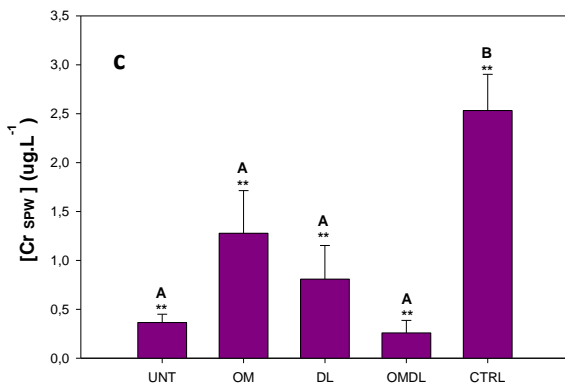
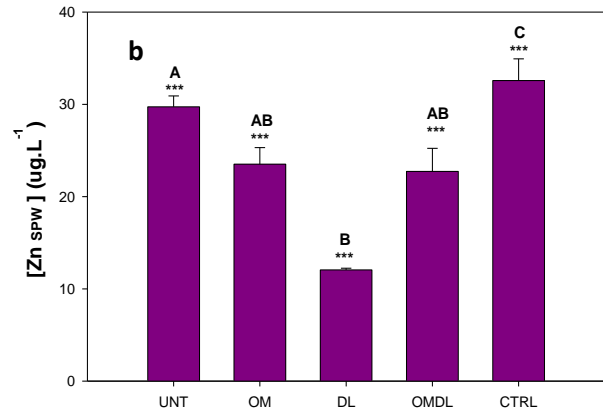
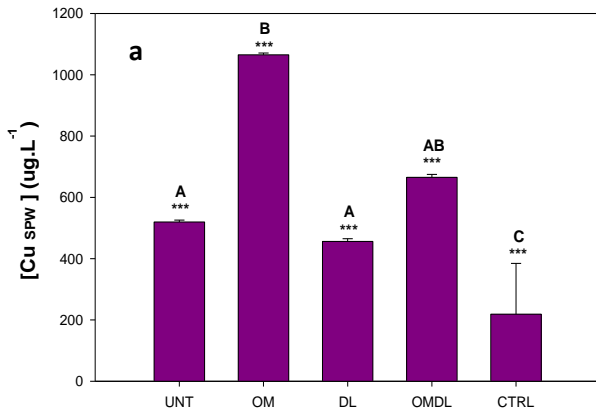
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311 Figure 2. Concentrations of Cu, Zn, Cr, and As in the soil pore waters and intensity of Cu and Zn exposure in
 312 the soils determined by DGT. Values are mean \pm standard deviation (n=4). Different letters on bar graphs
 313 indicate a significant difference ($p < 0.05$)

314

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318 Table 3: Pearson's correlation coefficients between the parameters of soils and soil pore waters of the
 319 contaminated and control soil.

	Amendement	pH	EC ($\mu\text{S. cm}^{-1}$)	TOC (%)	DOC (mg.L^{-1})	[Cu _{tot}]	[Cu _{spw}]	[Cu _{DGT}]	R
Amendement	1.00								
pH	-0.56**	1.00							
EC ($\mu\text{S. cm}^{-1}$)	0.10 ^{NS}	-0.17 ^{NS}	1.00						
TOC (%)	-0.26 ^{NS}	0.10 ^{NS}	0.10 ^{NS}	1.00					
DOC (mg.L^{-1})	0.83***	-0.47**	0.10 ^{NS}	-0.03 ^{NS}	1.00				
[Cu _{tot}]	-0.65**	0.61**	0.24 ^{NS}	0.14 ^{NS}	-0.65**	1.00			
[Cu _{spw}]	-0.49**	0.35 ^{NS}	0.09 ^{NS}	0.86***	-0.33 ^{NS}	0.46**	1.00		
[Cu _{DGT}]	-0.75***	0.23 ^{NS}	-0.18 ^{NS}	-0.29 ^{NS}	-0.68**	0.30 ^{NS}	-0.16 ^{NS}	1.00	
R	-0.23 ^{NS}	-0.06 ^{NS}	-0.21 ^{NS}	-0.69**	-0.26 ^{NS}	-0.12 ^{NS}	-0.71***	0.80***	1.00

320 Significance level: 0.01<(*)P <0.05, 0.01>(**) p >0.001, (***) p < 0.0001, (NS) insignificant difference.
 321 TOC: total organic carbon, Cu_{DGT}: interfacial Cu concentration determined by DGT, Cu_{spw}: total Cu concentration in the soil pore water;
 322 DOC: dissolved organic carbon, EC: electrical conductivity, Cu_{tot}: total soil Cu, Amendement: the four types of soil treatments (UNT,
 323 OM, DL, and OMDL).
 324

325 Table 4: Pearson's correlation coefficients between soil and soil pore water parameters in the contaminated soil
 326 (without control).

	Amendement	pH	EC ($\mu\text{S. cm}^{-1}$)	TOC (%)	DOC (mg.L^{-1})	[Cu _{tot}]	[Cu _{spw}]	[Cu _{DGT}]	R
Amendement	1.00								
pH	0.35 ^{NS}	1.00							
EC ($\mu\text{S. cm}^{-1}$)	0.21 ^{NS}	-0.27 ^{NS}	1.00						
TOC (%)	-0.21 ^{NS}	-0.07 ^{NS}	0.11 ^{NS}	1.00					
DOC (mg.L^{-1})	0.54*	0.31 ^{NS}	0.18 ^{NS}	0.16 ^{NS}	1.00				
[Cu _{tot}]	0.11 ^{NS}	0.62*	-0.08 ^{NS}	0.24 ^{NS}	0.46 ^{NS}	1.00			
[Cu _{spw}]	-0.08 ^{NS}	-0.11 ^{NS}	0.09 ^{NS}	0.93***	0.14 ^{NS}	0.23 ^{NS}	1.00		
[Cu _{DGT}]	-0.76**	-0.25 ^{NS}	-0.21 ^{NS}	-0.43 ^{NS}	-0.55*	-0.32 ^{NS}	-0.57*	1.00	
R	-0.47 ^{NS}	-0.09 ^{NS}	-0.21 ^{NS}	-0.70**	-0.41 ^{NS}	-0.26 ^{NS}	-0.84***	0.91***	1.00

327 Significance level: 0.01<(*)P <0.05, 0.01>(**) p >0.001, (***) p < 0.0001, (NS) insignificant difference.
 328 TOC: total organic carbon, Cu_{DGT}: interfacial Cu concentration determined by DGT, Cu_{spw}: total Cu concentration in the soil pore
 329 water; DOC: dissolved organic carbon, EC: electrical conductivity, Cu_{tot}: total soil Cu, Amendement: the four types of soil treatments
 330 (UNT, OM, DL, and OMDL).
 331

332 Table 5: Capacity of the solid phase to resupply Cu, Zn, and Cr to the pore water: Ratio of the available
 333 concentration determined by DGT vs. total dissolved soil pore water concentration (C_{DGT}/C_{spw})

Amendment	R(Cu)	R(Zn)
UNT	0.54 a ±0.01	0.10 a ±0.02
OM	0.15 b ±0.00	0.12 a ±0.01
DL	0.43 ab ±0.02	0.16 a ±0.60
OMDL	0.22 c ±0.01	0.15 a ±0.03
CTRL	0.34 abc ±0.01	0.76 b ±0.02

334 R > 0.95: high capacity of the solid phase to resupply the pore water ; R < 1 : the DGT device is supplied only by the
 335 diffusion of solutes through the pore water which becomes progressively depleted. Other R values : partial resupply from
 336 the solid phase, but insufficient to sustain fully pore water concentrations. Mean values in a column followed by the same
 337 letter did not differ at the 5% level

338
 339

340 3.1.2. Soil Zn exposure

341 The Zn concentration in the SPW (Zn_{spw}) was reduced for the amended soils, i.e. OM: 21%, OMDL: 24%
342 and DL: 59% ($P= 5.35E^{-05}$) compared with the UNT soil (Fig. 2b). The DL influence was the most significant.
343 The Zn_{spw} value for the CTRL soil was higher than for all the contaminated soils, i.e. UNT: 1.09 fold, DL: 2.7
344 fold, and OM and OMDL: 1.4 fold ($P= 5.94E^{-07}$). In soils amended with 5% compost, with and without 5%
345 cyclonic ashes, the Zn mobility was reduced after one week by 87% and 96% respectively compared with the
346 UNT soil (Ruttens et al. 2006). Limestone, biosolids, cyclonic ashes, iron grit and red muds can also decrease
347 soil Zn mobility (Brown et al. 2005). For instance the decrease in Zn_{spw} in compost- and biochar-amended soils
348 over a 60-day field exposure was due to the Zn presence mainly in water-soluble fractions whereas other
349 elements such as Cu and As formed more stable complexes in the soil (Beesley et al. 2010). Conversely, Zn was
350 immobilized in an acid soil by humic acids isolated from organic materials, whilst Cu mobility was enhanced by
351 the same humic acids (Clemente and Bernal 2006). Zinc is generally relatively insoluble at $pH > 7$ (Ross 1994),
352 so the higher Zn_{spw} value in the CTRL soil would be related to its lower soil pH (Tab. 1). Soluble Zn
353 concentrations in SPW from environmentally exposed green waste compost are generally low compared to other
354 PTTE such as Cu and As (Beesley and Dickinson 2010). The OM addition rate may influence Zn mobility and
355 increase negatively-charged adsorption sites in the OM-treated soils (Hartley et al. 2010). In González et al.
356 (2012), an OM addition rate of 6%, compared to 5% in our experiment, decreased Zn_{spw} while it increased at
357 2%.

358 Red mud was more effective than limestone and furnace slags to decrease shoot Zn concentration of
359 lettuce (Lee et al. 2009). Reduced concentrations of soluble and extractable Zn in the amended soils were partly
360 attributed to increase in the soil pH. Addition of alkaline materials such as coal fly ash and red mud also
361 decreased Zn leaching by 99.7% and 99.6%, respectively (Ciccu et al. 2003), compared to 59% in our study.
362 Large reductions in Zn extractability (up to 21.9%) and phytoavailability can be obtained from alkaline organic
363 treatments, i.e. lime-stabilized biosolid and N-Viro Soil, by forming metal-carbonate precipitates (Basta et al.
364 2001).

365 The DL treatment decreased Zn_{DGT} by 45% compared to the UNT soil, being more effective than OM
366 (11%) and OMDL (20%) (Fig. 2f). Zn_{DGT} was 8- 12 times higher in the uncontaminated soil than in the
367 contaminated ones ($P=2.30 E^{-08}$) (Fig. 2f).

368 Zn_{spw} in the OM, DL and OMDL treated soils was respectively 9, 7 and 9.5 fold higher than Zn_{DGT} . This
369 ratio peaked up to 10 for the UNT soil (29.7 and 3, $\mu g Zn L^{-1}$, respectively). The DOC correlated with Zn_{DGT}
370 ($r=0.776$) in the contaminated and control soils, and Zn_{DGT} with Zn_{spw} as well ($r=0.57$). The $Zn_{DGT}:Zn_{spw}$ ratio
371 (R) was roughly 7 fold higher in the control soil than the UNT soil, the solid phase of this last one having a low
372 capacity to resupply Zn the pore water (Tab. 5). The R value was numerically slightly lower in the UNT soil
373 than in the treated soils and peaked in the DL soil, but differences were not significant.

374 In another study the Zn availability in a contaminated soil can be reduced after the incorporation of
375 various amendments (i.e. limestone, biosolids, cyclonic ashes, iron grit and red muds), but ecosystem services

376 were not fully restored due the residual Zn bioavailability (Brown et al. 2005). Increase in the soil pH, due to
377 organic and inorganic amendments, was suggested in line with Zn precipitation and sorption on mineral phases
378 (Lee et al. 2009). Similar findings were reported with six cost-effective amendments (CaCO₃, iron grit, fly ash,
379 manure, bentonite and bone meal) for Cd, Zn and Pb leaching and phytoavailability (Houben et al. 2012). Here,
380 the DL incorporation into the soil slightly increased soil pH (Tab. 2), significantly decreased Zn_{SPW}, but did not
381 change Zn_{DGT} which was initially low.

382

383 3.1.3. Soil Cr exposure

384 The total dissolved Cr concentration in the SPW of contaminated soils (Cr_{spw}) (in µg. L⁻¹) varied between
385 0.3 (OMDL) and 1.3 (OM). However this variation was not significant for the treated (OM, DL and OMDL) and
386 untreated (UNT) contaminated soils. In contrast the control soil (CTRL) presented the highest total dissolved Cr
387 concentration in the SPW (Cr_{spw}) (in µg. L⁻¹) (2.5), this concentration was significant compared with the others
388 contaminated soils (p=0.002)(Fig. 2c).

389 Cr_{spw} concentration was related to TOC of the treated and untreated contaminated soils (r=0.65).
390 Similarly the Cr_{spw} concentration was related to the DOC (r= 0.82) measured in the contaminated (UNT, OM,
391 DL and OMDL) and uncontaminated soils (CTRL). Cr_{DGT} was below the detection limit for all contaminated
392 soils. Thus the Cr_{DGT}:Cr_{SPW} ratio was Zero in the four type of soil.

393 Cr mobility depends on several key-factors such as soil pH, clay mineral content, competing major ions,
394 and complexing agents (Pantsar-Kallio et al. 2001). The oxidation state of Cr in contaminated soils is an
395 important indicator of toxicity and potential mobility. Chromium in the hexavalent Cr (VI) state is highly toxic
396 and soluble, whereas the trivalent state Cr (III) is much less toxic and relatively insoluble. Increased Cr_{spw} after a
397 single addition of both organic or inorganic amendment, and correlation between the soluble Cr fraction and the
398 total and dissolved organic matter in the soil were previously reported (Kumpiene et al. 2008; Hartley et al.
399 2010). As Cr (III) is relatively insoluble and resistant to leaching (Palmer and Puls 1984), the fraction we
400 measured may include chromate (hexavalent chromium; Cr (VI)) which is more mobile under alkaline to
401 slightly acidic conditions (e.g. pH=7.27±0.38 in the OM soil) Kimbrough et al. 1999). Higher chromate mobility
402 may be due to the presence of other competing anions which were abundant in the compost (Jardine et al. 1999).
403 Based on Pantsar-Kallio et al. (2001) several alkaline materials, e.g. fly ash, hydroxyapatite, and CaCO₃, can
404 increase soil pH above neutral, which favor the oxidation of Cr(III) to Cr(VI), and thus enhances the Cr mobility
405 and uptake by roots (Rai et al. 2004). This agrees with the higher Cr_{spw} value measured in the DL soil. Barnhart
406 et al. (1997) indicated lower sorption of Cr species at higher pH. Decline in Cr_{SPW} in the OMDL soil can be due
407 to the capacity of soil organic matter (SOM) to reduce Cr (VI) to Cr (III), which is more stable in the soil, and
408 the negative functional groups on SOM surface which can increase Cr (III) adsorption (Bolan et al. 2003; Banks
409 et al. 2006; Jiang et al. 2008). Simultaneously, the DL addition into the OMDL soil slightly increased soil pH
410 (Tab. 2), which may promote Cr (III) sorption by SOM.

411 Available Cr fraction determined by DGT was not detected in the contaminated topsoil's, suggesting that
412 soil Cr may be mainly under the Cr (III) form, which is more stable or not available to the DGT probe
413 (Ernstberger et al. 2002). Even though chromates are not expected to bind to the chelex resin due to their anionic
414 form, they can diffuse in the gel layer but this one was not analyzed.

415

416 **3.1.4. Soil As exposure**

417 The total dissolved As concentration in the SPW (As_{spw} , in $\mu\text{g. L}^{-1}$) increased from 1.8 to 4.2 in all
418 amended soils compared to the UNT soil, and ranked as: OM > DL > OMDL > UNT (Fig. 2d). The As_{spw}
419 peaked in both the OM soil ($P=0.0003$) and the CTRL soil, which had a relatively high SOM content. As_{spw} well
420 correlated with TOC for our soil series ($r= 0.69$) and DOC concentrations in soil pore water ($r= 0.73$).

421 All amendments incorporated into the soil increased the As mobility in the treated soils but As_{SPW}
422 remained below the control soil value (Fig. 2d). Influences of organic and inorganic amendments on the
423 mobility, availability and phytotoxicity of soil As in the soil are controversial. Increases in As mobility after
424 dressing of organic matter are reported (Mench et al. 2003). DOM generally presents in SPW in anionic form
425 and compost-borne anions such as phosphates may compete with As for sorption sites such as Fe oxides (Sadiq
426 1997)). This could enhance As leaching from the soil material (Lombi et al. 2000). In the OMDL treatment,
427 changes in the soil pH (Tab. 2) and addition of Ca and Mg, may promote precipitation of Ca- and Mg
428 phosphates and arsenates, metal arsenates such as those of Cu(II), which are less soluble and more stable in the
429 neutral pH region than Ca arsenates, and may limit DOM influence. In CCA-spiked mineral soils, 92% of total
430 As is As(V), which is less mobile and less toxic, while the proportion of mobile, toxic and bioavailable As(III)
431 in CCA-spiked organic soils increased to one third of the total soil As (BalasoIU et al. 2001). Other mechanisms
432 have been suggested: (1) organic anions may block As adsorption sites (Carey et al. 1996) and (2) formation of
433 soluble As-organic complexes (Chen et al. 2006; Dobran and Zagury 2006).

434 DL incorporation into the contaminated soil increased the mobility of As by 2 fold (Fig. 2d), confirming
435 previous findings (Seaman et al. 2003; Mench et al. 2003). Alkaline materials such as lime, dolomitic limestone,
436 fly ashes, and hydroxyapatites, are indeed undesirable in As-contaminated soils as they can increase As release
437 from the soil to the SPW, due to the higher As mobility at a higher pH range. However, lime could slightly
438 reduce As leaching in soil through possible formation of As-Ca complexes. Calcium hydrogen arsenate
439 ($CaHAsO_4$) and calcium arsenate ($Ca_3(AsO_4)_2$) can precipitate in the Ca presence under oxidizing and moderate
440 pH conditions (Porter et al. 2004).

441

442 **3.2. Biomass of primary leaves and PTTE phytoavailability**

443 Liming and organic amendments, singly and in combination, can increase plant yields and reduce the
444 plant exposure to Cu and Zn in metal-contaminated soils (Brallier et al. 1996; Sanchez-Monedero et al. 2004; Su
445 and Wong 2004; Bes and Mench 2008). In our study the BLDW of Cu and Zn was numerically higher for all

446 contaminated soils compared to the CTRL soil (Tab. 6). For the contaminated soils the lowest BLDW value was
447 for the UNT beans: based on the UNT plants, the OM, OMDL, and DL treatments numerically enhanced BLDW
448 by 50%, 44%, and 23% respectively (Tab. 6).

449 The UNT beans had higher foliar Cu, Cr, As, and Zn concentrations than the other beans (Tab. 6). Foliar
450 metal concentrations were reduced in the OM, OMDL and DL plants compared to UNT plants, which agreed
451 with Bes and Mench (2008). The addition of dolomite residue and to a lesser extent gypsum and
452 phosphogypsum can also reduce both soil Cu exposure and plant Cu concentration (Garrido et al. 2005). Foliar
453 Cu, Cr, and As concentrations of plants grow on the contaminated soils exceeded those of CTRL plants, except
454 foliar Zn concentration which was similar. Differences between the treated soils and the UNT soils and between
455 the contaminated soils and the CTRL soil were significant for Cu, Cr, As and Zn, except for foliar Zn
456 concentration between contaminated and CTRL soils. Except for CTRL beans, foliar Cu concentration exceeded
457 its upper critical threshold value (in mg kg⁻¹ DW: 15-30 (MacNicol and Beckett 1985); 20 (Kabata-Pendias and
458 Pendias 2000)). Foliar Cu concentration was predicted by Cu_{DGT} (r=0.78) and was correlated to soil
459 pH (r= 0.62). Upper critical threshold values for foliar Cr, As and Zn concentrations, i.e. 1-5, 1-5, and 100-450
460 mg kg⁻¹ DW, respectively (MacNicol and Beckett 1985; Kabata-Pendias and Pendias 2000) were just reached in
461 the UNT plants and in overall decrease in bean growth mainly mirrored Cu phytotoxicity confirming previous
462 findings (Bes and Mench 2008).

463 Total element amount in primary leaves (µg plant⁻¹), so-called mineral mass, was computed for Cu, Cr, Zn
464 and As by multiplying the foliar element concentration (µg kg⁻¹ DW) by the leaf biomass (µg DW plant⁻¹). For
465 Cu, Cr and As, mineral masses of UNT plants were higher than those of the CTRL plants (Fig. 3). Soil treatment
466 influenced mineral masses for Cr, Cu and As but not for Zn. This reflected a dilution effect of the biomass on
467 Zn concentrations, i.e. foliar Zn concentration = 176.93e^{-10,61} foliar DW yield (R² = 0.93). Compared to the UNT
468 plants, mineral masses of OM and DL plants decreased by 2 fold for Cr, 2.5 fold for As and ,1.3 and 3.6 for the
469 Cu respectively, whereas mineral mass of Cr and Cu in OMDL plants increased by 16% and 23% respectively.
470 Differences between OM and OMDL plants were significant for Cr and Cu mineral masses. Lowest values of
471 As_{spw} and Cr_{spw} in OMDL soil were not reflected by Cr and As mineral mass of OMDL bean (Fig. 3) the
472 variance of Cu mineral masse was significant also between the contaminated soils (UNT, OM ,DL and
473 OM+DL) and the CTRL soil (p=0.00005).

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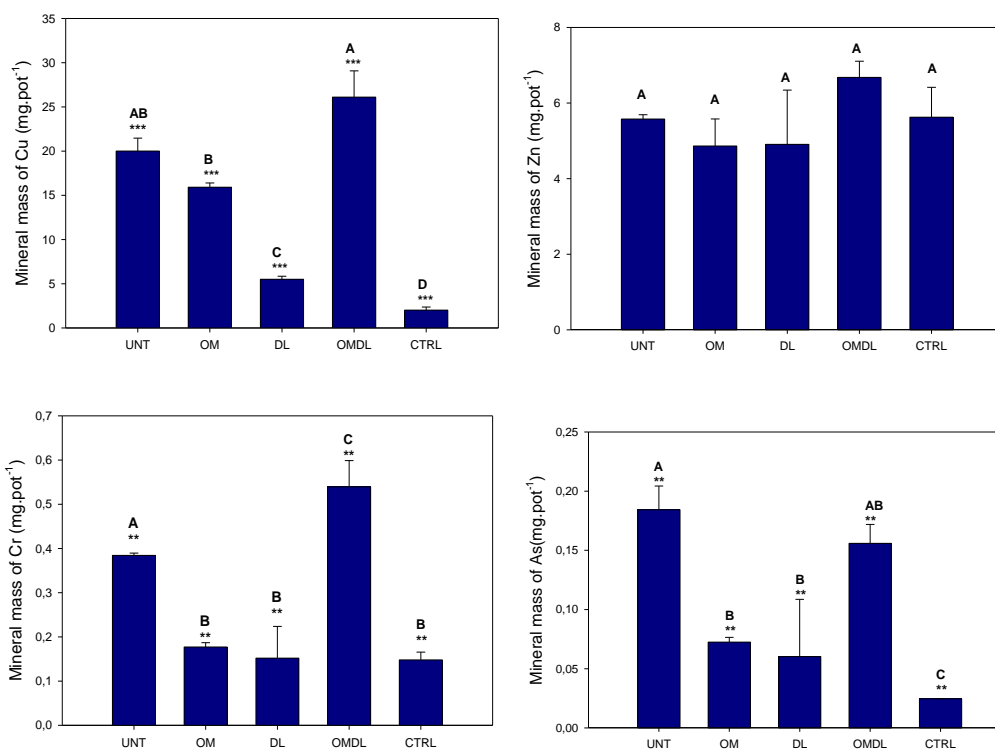
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480 Table 6: Dry weight (DW) of bean primary leaves BL (BLDW) and PTTE concentrations of bean primary
 481 leaves. Values are mean \pm standard deviation (n=4).

traitements	Dry weight (DW) of bean primary leaves BL(BLDW) (g DWplant ⁻¹)	Foliar concentrations (mg. kg ⁻¹)			
		Cr	Cu	As	Zn
UNT	0.06 \pm 0.01	6.89 a \pm 0.54	357 a \pm 48.8	3.29 a \pm 0.56	100 a \pm 11.2
OM	0.11 \pm 0.00	1.58 b \pm 0.03	142. b \pm 23.7	0.65 b \pm 0.01	52.2 b \pm 4.43
DL	0.07 \pm 0.09	2.31 b \pm 0.25	211 b \pm 20.9	1.15 b \pm 0.39	75.9 b \pm 22.9
OMDL	0.10 \pm 0.01	5.37ab \pm 0.30	260 b \pm 15.8	1.55 ab \pm 0.07	66.7 b \pm 22.2
CTRL	0.13 \pm 0.00	1.18 c \pm 0.14	16,0 c \pm 2.80	0.19 c \pm 0.00	44.7 c \pm 6.34
Anova with CTRL	NS	**	**	**	*
Anova without CTRL	NS	**	**	**	NS

482 0.01<(*)P <0.05, 0.01>(**) p >0.001, (***) p < 0.0001, (NS) insignificant difference.



483

484

485

486 Figure 3: Mineral masses of Cu, Cr, Zn and As in the bean primary leaves. Values are mean \pm standard deviation
 487 (n=4). Different letters on bar graphs indicate a significant difference (p<0.05)
 488

489 4. Conclusion

490

491 The present work was focused on assessing the effectiveness of several aided-phytostabilisation options
 492 based on liming and the addition of compost to remediate PTTE in contaminated soils. Changes in mobility and
 493 phytoavailability of Cu, Zn, Cr and As were investigated at a wood preservation site in topsoils of field plots
 494 amended with DL and OM, singly and in combination, and phystabilized with mycorrhizal trees, after four years.
 495 The OM incorporation into the contaminated soil decreased the Cu, Cr, Zn and As concentrations of bean
 496 primary leaves to the highest extent, but only their Cr and As mineral masses were reduced. The Cu

497 concentration in the SPW increased for OM and OMDL soils whereas it slightly decreased for the DL soil. The
498 Zn concentration in SPW significantly decreased only for the DL soil. The Cr concentration in SPW was
499 enhanced for both DL and OM soils but slightly decreased for the OMDL soil. The As concentration in SPW
500 increased for all amended soils, notably for the OM soil. The addition of OM and DL, singly and in
501 combination, decreased the available fraction of Cu in soil determined by DGT. Mobilization of Cu from the soil
502 to the SPW was slower than root uptake and soil amendments reduced the replenishment of Cu in SPW.
503 Conversely, based on the DGT R ratio, Zn remobilization from the solid phases was enhanced in the DL soil.

504 In overall, data suggested the influence of both pH and DOM on metals and As concentrations in the SPW
505 and their phytoavailability to dwarf beans. The DL addition promoted Cu and Zn sorption in relation with pH
506 rise but enhanced remobilization of Cr and As, likely as chromates and arsenates from Fe oxides. Nevertheless
507 foliar Cr and As concentrations in the DL beans were lower than in the UNT beans likely due to the decrease in
508 soil Cu exposure, partial restoration of root growth and subsequent Cr and As storage in roots. Compost likely
509 increased Cu–DOM complexes in the SPW, which are less available for root uptake, and consequently enhanced
510 the DW yield of bean primary leaves. Subsequently, decreased soil Cu exposure in both OM-amended soils
511 allowed roots to better control metals and As uptake and promote a dilution effect in the bean plant aerial parts.

512 In conclusion both aided-phytostabilisation options were found to be able to reduce the SPW
513 concentrations or phytoavailability of PTTE and provide interesting technologies for the remediation of Cu and
514 CCA salt contaminated soils.

515

516

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524

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