

Effect of organic amendments on the mobility of trace elements in phytoremediated techno-soils: role of the humic substances

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Abstract The efficiency of aided phytostabilization using organic amendments such as ramial chipped wood (RCW) and composted sewage sludge (CSS) was studied on contaminated techno-soils, on nine experimental plots. The objective was to characterize the role of fulvic (FA) and humic acids (HA) on the mobilization of trace elements, specifically As, Cu, Mo, Pb and Zn. Results showed that the addition of CSS increased the total organic carbon and nitrogen content more than with RCW and as a result, the C/N ratio in the CSS soil was higher than in the RCW and non-amended (NE) soil, reflecting the high decomposition of soil organic matter in the CSS soil compared with the other soils. The RCW and CSS amendments increased the hydrogen index (HI) values and the oxygen index (OI) values compared with the NE soil, especially for the soil treated with CSS which contained more aliphatic than aromatic compounds. The addition of CSS to the techno-soil significantly increased the percentage of C_{org} associated with the HA fractions compared with the RCW and

NE soils. The soil amended with CSS showed the highest E_4/E_6 ratio and the lowest E_2/E_3 ratio of FA. Zn and As were more abundant in the FA fraction than in the HA fraction, whereas Pb, Cu and Mo were more associated to HA than to FA in the treated and untreated soils, which may explain the difference in their mobility and availability.

Keywords Contaminated techno-soil · Trace element · Humic acid · Fulvic acid · Mobility

Introduction

Techno-soil is a soil “whose properties and function are dominated by technical human activity as evidenced by either a substantial presence of artifact” (WRB 2006). Moreover, all techno-soils are not necessary contaminated by inorganic or organic contaminants. The pollution of anthropogenic soils with a high concentration of trace elements (TE) is more problematic than for other types of soils as the properties of these techno-soils change over time, making handling more difficult (Kelly et al. 1996). Moreover, they present a real risk for human health and especially for children's health (De Burbure et al. 2006).

The contamination of a techno-soil with TE requires special soil-management techniques to limit the TE solubility and thus plant availability. Among remediation techniques, phytoremediation has attracted attention as it is a low-cost and ecologically sustainable alternative to physicochemical methods, can be applied to large areas, and is accepted by local populations (Mench et al. 2010). Aided phytostabilization is a phytoremediation technique that is recognized as a potentially cost-effective and ecologically sound approach to the containment of TE-polluted soils and mine tailings. Its principal objective is to reduce the mobility, ecotoxicity, and dispersion of metals/metalloids through the

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environment (Mendez and Maier 2008; Ginocchio et al. 2007; Mench et al. 2010). Aided phytostabilisation requires the incorporation of both plant species and organic or inorganic amendments that are appropriate for the type of contamination in order to immobilize TE such as metals/metalloids and reduce their availability in these soils (Mendez and Maier 2008; Berti and Cunningham 2000) and to restore the physical, chemical and biological properties of contaminated soils (Mench et al. 2000; Bolan and Duraisamy 2003; Pérez de Mora A et al. 2005; Raicevic et al. 2005; Kumpiene et al. 2006, 2008). Several mineral and organic amendments such as lime, coal fly ashes, phosphates, red muds, compost, biosolids, iron grit and Fe/Mn/Al oxides can improve phytostabilization and the production of plant-based feedstock through the decrease in the solubility, leaching and bioavailability of TE (Lombi et al. 2002; Bolan and Duraisamy 2003; Brown et al. 2004; Geebelen et al. 2003; Basta and McGowen 2004; Kumpiene et al. 2008; Mench et al. 2010). This reduction is achieved via various complex processes, e.g., adsorption onto mineral surfaces, formation of stable compounds with organic ligands, surface precipitation and ion exchange (Kumpiene et al. 2008; Ahmad et al. 2011).

The addition of organic matter amendments such as compost, manure or various organic wastes with the plants is a common practice for the remediation of contaminated soils. The effect of organic matter amendments on TE bioavailability depends on the nature of the organic matter, its microbial degradability, salt content and effects on soil pH and redox potential as well as on the particular soil type and metals concerned (Walker et al. 2003, 2004). Organic amendments may contain a high proportion of humified organic matter, which has a large capacity to interact with metal ions and mobilize or immobilize TE through the formation of more or less stable complexes. The formation of these insoluble metal compounds reduces their mobility through the soil profile and the pool available for biota (Geebelen et al. 2003). The characteristics of humus fractions have proven useful in the interpretation of organic matter dynamics in soil. There is an extensive literature on the characterization of humic substances (HS) (Abbt-Braun and Frimmel 1999; Gondar et al. 2005; Shirshova et al. 2006) and on the binding of metals to HS, mainly concerning laboratory experiments with humic or fulvic fractions purified from water or soil (Vaca-Paulin et al. 2006; Gondar et al. 2006; Doig and Liber 2007; Evangelou et al. 2007). The ability of HS to react with TE has long been recognized (Wu et al. 2002; Clemente and Bernal 2006; Evangelou et al. 2007). HS have the capacity to control the behavior of TE in the environment. However the reactions between TE and HS are highly complex and depend on the TE itself, the humic material and pH. There are two possible outcomes of humic–metal binding: (1) metal ions may form soluble organic complexes with the potential to contaminate groundwater and to retain the metal in soil solution; and (2)

insoluble complexes can form and result in a reduction in bioavailability and consequently, in the ecotoxicity of the metals (Logan et al. 1997).

In the present work we assess the role of HS (humic acid [HA] and fulvic acid [FA]) extracted from two different organic soil amendments — composted sewage sludge (CSS) and fresh ramial chipped wood (RCW) — and from a untreated soil on the mobility of several TE in metallurgical technosols treated by aided phytostabilisation.

Materials and methods

Site description and experimental design

The studied site is a metallurgical landfill (Industeel-Loire; 45°32'N; 4°38'E) located near Lyon, France. It is located behind a steel and iron factory which is still in operating. The site was used from about 1850 to 2001 to dispose of foundry waste, slag, fire-bricks, and other by-products from the industrial process, such as more or less hydrated lime. It extends over nearly 15 ha and is 8–10 m thick. The soil (“foundry technosol” type) is highly contaminated with iron (Fe) and different metals used in various alloys: mainly molybdenum (Mo), arsenic (As), copper (Cu), lead (Pb) and zinc (Zn). This site is part of a French network of contaminated sites (“SAFIR” network. <http://www.safir-network.com>) and is partly dedicated to research into contaminant transfer, the biological impact of pollution and remediation technologies.

In this context, the efficiency of aided phytostabilization using organic amendments was studied on nine 50 m² (5 × 10 m) experimental plots. Plots were prepared in December 2009 by shallow ploughing (10 to 15 cm depth) and they were enriched using the following materials: (1) RCW applied on approx. 500 m³/ha (three plots), (2) SS applied on approx. 120 t DM/ha (three plots) and (3) no organic enrichment (NE) (three plots). An extensive pedo-geochemical characterization of the different plots was performed in March 2010, i.e., 4 months after preparation of the plots.

The soils were air-dried and sieved to <2 mm. The main pedological characteristics of the soils studied (taken at 0–20 cm depth), and their chemical composition are given in Table 1. The soil pH was measured in 1:2.5 soil/water suspension using a glass electrode pH meter (NF ISO 10390 procedure; AFNOR 1994). Total organic carbon (TOC) was determined in the soil samples by Rock-Eval pyrolysis. Total N contents were determined using a Fisons Instruments (Crowley, UK) elemental analyzer model EA 1108. The cation exchange capacity (CEC) was determined by the Metson method at pH=7. Particle size distribution of the <2-mm fraction was determined by sieving and using the pipette method. Extraction of the major and metallic elements was

Table 1 The main pedological characteristics and chemical composition of the studied soils

		Treatment		
		RCW	CSS	NE
Physicochemical parameters	Texture	sandy	sandy	sandy
	pH	9.08±0.07	9.07±0.12	9.34±0.18
	C_{org} (g kg ⁻¹)	19.7±0.34	31.4±0.34	8.9±0.24
	N (g kg ⁻¹)	0.9±0.03	3.9±0.13	0.6±0.01
	C/N	22.67±4.31	8.45±2.01	15.76±4.73
	CEC (Cmol/kg)	5.63±1.10	6.77±0.15	5.77±0.55
Major elements	P ₂ O ₅ (g kg ⁻¹)	0.03±0.00	0.25±0.04	0.02±0.00
	K ₂ O (g kg ⁻¹)	0.29±0.05	0.59±0.07	0.09±0.07
	CaO (g kg ⁻¹)	18.88±6.71	20.70±1.13	24.67±2.17
	MgO (g kg ⁻¹)	2.66±0.44	1.29±0.09	2.79±0.44
	Na ₂ O (g kg ⁻¹)	0.08±0.07	0.14±0.02	0.14±0.03
Trace elements	Zn (mg kg ⁻¹)	1,719.00±777.78	1,348.33±560.02	1,326.00±739.13
	Pb (mg kg ⁻¹)	688.33±453.8	623.00±246.43	839.00±390.20
	Mo (mg kg ⁻¹)	523.66±142.30	652.66±69.28	682.33±124.44
	Cu (mg kg ⁻¹)	399.00±84.01	410.33±78.23	523.00±160.36
	As (mg kg ⁻¹)	76.66±22.47	73.00±11.78	91.33±15.54

For each treatment, data are the mean of 30 measures (ten samples per plot)

RCW ramial chipped wood, CSS composted sewage sludge, NE non-amended soil

performed using hydrofluoric (HF) and perchloric (HClO₄) acids, according to the NF X 31-147 procedure. The contents of major and metallic elements in various extracts were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Horiba Jobin-Yvon apparatus.

Characterization of soil organic matter by Rock-Eval pyrolysis

Rock-Eval pyrolysis (Rock-Eval 6 Turbo; Vinci Technologies, France) is used to identify the type and maturity of organic matter (Béhar et al. 2001; Disnar et al. 2003; Sebag et al. 2006). This technique can be applied to soils (Di Giovanni et al. 1998). The analysis comprised two steps. First, pyrolysis under nitrogen adsorption of hydrocarbon is maintained at 200 °C for 5 min. Then cracking occurs between 200 °C and 650 °C at 30 °C min⁻¹.

In summary, the four basic parameters obtained by pyrolysis are as follows: S_1 is the amount of free hydrocarbons in the sample (in milligrams of hydrocarbon per gram of sample); S_2 is the amount of hydrocarbons generated through thermal cracking of nonvolatile organic matter; S_3 is the amount of CO₂ (in milligrams CO₂ per gram of sample) produced during pyrolysis of kerogen. S_3 is an indication of the amount of oxygen in the kerogen and is used to calculate the OI; T_{max} is the temperature at which the maximum release

of hydrocarbons from cracking of kerogen occurs during pyrolysis (T_{max} is an indication of the stage of maturation of the organic matter).

The type and maturity of organic matter in our soils was characterized from Rock Eval pyrolysis data using the following parameters: HI ($HI=[100 \times S_2]/TOC$). This parameter is used to characterize the origin of organic matter. Marine organisms and algae, in general, are composed of lipid- and protein-rich organic matter, where the ratio of H to C is higher than in the carbohydrate-rich constituents of land plants. OI ($OI=[100 \times S_3]/TOC$) is a parameter that correlates with the ratio of O to C, which is high for polysaccharide-rich remains of land plants and inert organic material (residual organic matter) encountered as background in marine sediments. OI values range from near 0 to ~150.

TOC was determined in the soil samples by Rock-Eval pyrolysis. This instrument uses a ramped temperature pyrolysis technique in which a small amount of sample (70–100 mg) is heated in an inert atmosphere (helium or nitrogen) and also combusted with air to obtain several key geochemical parameters such as the TOC.

In the present work a small amount of sample (70–100 mg) is heated with a precision over 0.5 mg in an inert atmosphere (helium or nitrogen) and also combusted with air to obtain several key geochemical parameters. Only the TOC and HI versus OI were considered as the main parameters, following the original work by van Krevelen (1950).

Extraction and characterization of humic substances

Briefly, 100 g of each soil sample was extracted with 500 ml of 0.5 N NaOH (Schnitzer and Schuppli 1989). The HAs and FAs used were extracted following the procedure given by Holtzclaw et al. (1976). The mixture was stirred for 17 h under N₂ gas. HAs were precipitated with 6 M HCl (pH=1) and separated by centrifugation (3,000 rpm, 15 min). The TOC of each solution was determined by hot catalytic combustion (Teckmar – Dohrman Phoenix 8000).

Total metal contents in FA and in the mixture of FA+HA were determined by HR-ICP-MS (Element 2; Thermofischer, Waltham, USA) using a Twinna bar cyclonic spray chamber with a Micromist nebulizer (Glass Expansion, Melbourne, Australia) for As, Cu, Mo, Pb and Zn.

The ultraviolet–visible (UV–vis) is an instrumental technique used to identify the functional groups present in organic compounds by measuring their absorption of infrared radiation over a range of frequencies. The absorption pattern is then compared to the infrared spectra of known substances for identification. The UV–vis absorption spectra of separated FA and HA were recorded by a Jasco V-530 spectrophotometer. The E_4/E_6 ratios were calculated as the ratio of absorbance at 465 and at 665 nm according to Chen et al. (1997). The E_2/E_3 ratios were calculated as the ratio of absorbance at 280 and at 365 nm. The SUVA index was calculated by dividing the UV absorbance measured at $\lambda=254$ nm by the TOC concentration (Weishaar et al. 2003).

Infrared characterizations in the region of 400–4,000 cm⁻¹ were undertaken in transmission mode for several samples in classical pellet form. The preparation of the pellets was as follows: the sample was finely ground in an agate mortar and 1 to 1.5 mg of the resulting powder was mixed with KBr, previously dried at 120 °C for 24 h. to make a 150-mg pellet. The mixture was homogenized and pressed in an evaluable die to prepare a 13 mm diameter pellet. The operating conditions were 256 scans, 2 cm⁻¹ resolution over the 400–4,000 cm⁻¹ range without ambient H₂O and CO₂ correction.

Statistical analyses

All statistical analyses were performed using StatSoft Statistica (version 6). All analytical determinations were performed in three replicates for each plot. Differences were considered statistically significant at $p < 0.05$.

Results and discussion

Physicochemical properties

The physicochemical properties of these samples are presented in Table 1. The studied soils are alkaline (pH between 9.08

and 9.34), sandy and with CEC ranging from 5.63 to 6.77 cmol/kg. As expected, application of the organic amendments slightly modified the physicochemical properties of the soil (Larney and Angers 2012). A significant decrease in pH and an increase in the CEC are observed. In the case of carbonated soils, Séré et al. (2010) showed that the application of organic amendments as compost can lead to a decrease in pH by soil decarbonization. The increase in CEC can be explained by the increase in the TOC measured in treated soils ($p=0.00037$) compared with untreated soil (NE). Soil amended with RCW and CSS contained 2.2- and 3.5-fold more TOC, respectively, than the NE soil. TOC in the soil treated with RCW was less than that measured in the CSS soil. This could be due to microbial decomposition of carbon and its subsequent release as CO₂ (Basiramakenga and Simard 1998). Moreover, Soumare et al. (2003) showed that an increase in the concentration of organic matter is related to the decomposition of organic amendments in soil, and RCW decomposes more slowly than compost sewage sludge. RCW and CSS added to the soil significantly increased the total nitrogen by 1.6- and 7-fold, respectively, compared with the NE soil ($p=0.0047$) (Table 1). This result agrees well with that found by Vaca-Paulin et al. (2006), who reported that the addition of compost and sewage sludge increased the total nitrogen in the soil threefold compared with the control soil. Our results are also in good agreement with those of Kaschl et al. (2002) who investigated the effect of compost added to a calcareous soil on the physicochemical characteristics of the soil. They found a positive correlation between the addition of compost and soil organic carbon contents. Crecchio et al. (2001) also reported that amendment with municipal compost increased the total C and N in the soil significantly compared with the other treated and control soils. RCW added to the soil increased the C/N ratio by 1.4-fold, whereas the addition of CSS reduced the C/N ratio by 1.9-fold compared with the NE soil. The decrease in the C/N ratio in the CSS soil reflects the high microbial activity, which leads to a high decomposition of organic matter (Hsu and Lo 2001; Amir et al. 2005) and a greater degree of humification.

Organic geochemistry

Rock-Eval analyses of the treated (RCW and CSS) and untreated soil (NE) was conducted in order to recognize the origin and the evolution of the MO contained in each soil. Examination of the results obtained leads to the following conclusions: (1) the TOC content in treated soils was significantly higher than that measured in the untreated one (Table. 1); (2) the same behavior was marked for the HI, where RCW and CSS presented 63 % and 75 % of HI more than the NE soil. However, addition of organic amendment to the soil increased slightly soil OI by 23 % and 13 % in soil amended with RCW and CSS, respectively (Table 2). The

Table 2 Rock-Eval pyrolysis

Soil	TOC (%)	HI (mg g ⁻¹)	OI (mg g ⁻¹)	HI/OI
RCW	1.97ab±0.34***	181.41ab±15.08***	188.86a±23.84 NS	0.965
CSS	3.14a±0.34***	264.54a±11.50***	165.52a±7.58 NS	1.600
NE	0.89b±0.24***	66.01b±13.43***	143.67a±28.99 NS	0.459

TOC total organic carbon (%), HI hydrogen index (mg g⁻¹), OI oxygen index (mg g⁻¹), RCW ramial chipped wood, CSS composted sewage sludge, NE non-amended soil

0.01 < (*) $p < 0.05$, 0.01 > (**) $p > 0.001$, (***) $p < 0.0001$; NS insignificant difference

HI values presented by the soil amended with CSS were nearly 2-fold higher than that presented by RCW, whereas RCW presented 1.8-fold of OI higher than that present by the soil amended with the CSS (Table. 2). This result is in agreement with the low organic content in the untreated soil (low TOC), and thereafter the expression of the nature of the two organic amendments in the RCW and CSS respective values: their addition in the soil increases the TOC and the HI index (RCW). Thereafter a very strong correlation was observed between TOC and HI measured in the three types of soils ($r=0.94$). Our results are in agreement with that reported by Walter et al. (1982), who found very good correlation between TOC content and the kerogen HI.

The relation between the HI and OI values is shown in Fig. 1, which plots the origin of the organic matter in the three types of soil studied here on the well-known van Krevelen diagram. This diagram consists of three lines highlighting the natural origin of the organic matter in the soil (Tissot and Welte 1984; Espitalié et al. 1997; Hassen et al. 2009). Lines I and II correspond to organic material of microbial or planktonic origin, line III corresponds to the OM of higher continental plants.

It can be clearly seen in Fig. 1 that the points representing the treated and untreated soils studied here plot along lineage III, indicating the terrestrial origin of the organic matter in the untreated soil. It also shows that the values obtained in the

amended soils are highly dependent on that of the amendment itself. RCW has a higher OI because of the presence of wood cellulose. As the original kerogen of the non-treated soil is not abundant and also because its OI is low, RCW soil has the highest OI, close to that of wood. Due to its origin, CSS has a higher HI because it is richer in aliphatic groups than wood. The soil amended with CSS therefore has a higher HI value than the others soils.

Characterization of the humic fraction

HS (FA and HA) extracted from the control and amended soils accounted for 7.0 % to 12.9 % of the soil organic C (C-HS/C_{org}). The addition of CSS significantly increased the proportion of C_{org} associated with HS compared to control soil. Usman et al. (2004) explained this result by the high proportion of easily biodegradable organic components in sewage sludge. In contrast, RCW residues have a high lignin concentration, inducing a slower rate of decomposition of these residues compared to sludge. Amendment with RCW had no effect on the proportion of HS (N'dayegamiye and Angers 1993). The proportion of FA extracted to soil organic carbon (C-FA/C_{org}) ranged from 3.7 % to 4.4 % (Fig. 2a) and the organic amendments (RCW and CSS) added to the soil had no significant effect on the percentage of organic carbon associated with the FA fractions. The HA fractions represent from 2.7 % to 9.1 % of the SOC (C-HA/C_{org}). Moreover, the addition of CSS to the soil significantly increased ($p < 0.001$) the percentage of C_{org} associated with the HA fractions compared with the RCW and NE soils. The increase in the organic carbon fraction in the form of HA despite the drastic extraction procedures used suggests that part of the organic carbon from organic amendments (CSS) has been incorporated into the HA fraction. The maturity and stability of organic matter are expressed by the C-HA/C-FA ratio and shown in Fig. 2b. A significant increase in the C-HA/C-FA ratio for CSS soil ($p < 0.0001$), by 3.9-fold compared to RCW and NE soils was observed which is not the case for the RCW-type amendment. These results indicate a higher degree of humification of organic matter in the CSS soil compared to RCW and NE soils (Hsu and Lo 2001).

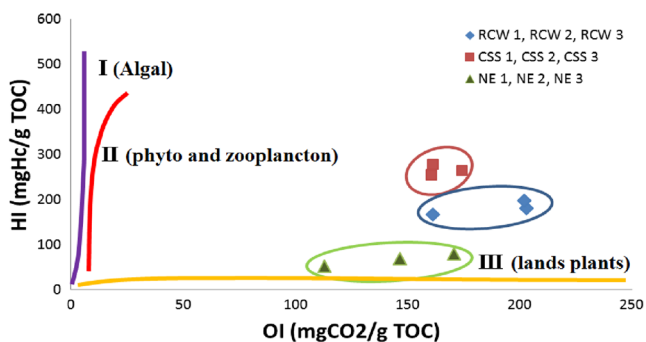
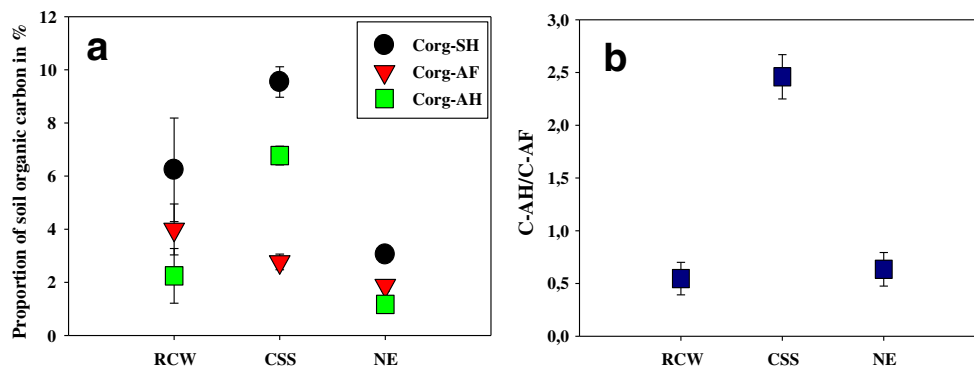


Fig. 1 Origin of the organic matter in the three types of soils: RCW (blue diamond), CSS (red square) and NE (green triangle) as a function of the hydrogen and oxygen indices

Fig. 2 a Proportion in % of total organic carbon between HS, HA and FA. **b** C-HA/C-FA ratio measured in the three soils. Values are: *box*, median; *whisker*, error bars ($n=9$)



UV–visible spectroscopy results

The absorbance ratio E_2/E_3 is considered in the literature as an indicator of the size of the organic molecules and their hydrophilicity (Thomsen et al. 2002). The addition of CSS significantly decreased the E_2/E_3 ratio ($p<0.0001$), whereas in soil amended with RCW the E_2/E_3 ratio of FA increased weakly compared with NE soil (Table 3). This means that the organic particle size of the RCW and NE soils was larger than that of CSS, and that the hydrophobic properties in the RCW and NE soils were lower than that in CSS soil (Guo and Chorover 2003).

Typically, the E_4/E_6 ratio is considered to be inversely related to the following: the particle size (Chen et al. 1997), the molecular weight (Christl et al. 2000), and the degree of condensation of the aromatic network in HS macromolecules (Senesi and Loffredo 1999). Table 3 shows that the addition of CSS to the soil increased the E_4/E_6 ratio by 30 % in comparison with the NE soil, whereas in soil amended with RCW, the E_4/E_6 ratio decreased by 19 % compared with the NE soil. Our results show that CSS soil has a low degree of aromatic condensation, indicating the presence of low-molecular-weight organic acids (Senesi and Loffredo 1999; Chen et al. 1997; Christl et al. 2000; Thomsen et al. 2002). Finally, it can be seen that the highest E_4/E_6 ratio and the lowest E_2/E_3 ratio of FAs were extracted from the soil amended with CSS, indicating that this soil contains more hydrophilic and

aliphatic compounds and fewer condensed and aromatic structures than RCW and NE soils.

FTIR

FTIR has been widely used for the characterization of HS extracted from soils. Even if the interpretation of the analysis may be difficult due to the overlapping of spectral features of the two fractions, the assignment of the absorption bands, determined by several studies, highlights certain differences once soils have been amended with RCW and CSS. The FTIR spectra of HAs and FAs show typical absorption bands relative to the organic groups of the polyfunctionality of humic substances (Piccolo and Stevenson 1982; Baes and Bloom 1989; Vaca Paulin et al. 2006). The most important features are: (1) the two peaks of variable intensity at 2,918–2,926 and 2,850–2,855 cm^{-1} due to aliphatic C–H stretching; (2) the strong peak centered between 1,615 and 1,624 cm^{-1} mostly attributed to structural vibrations of aromatic C=C and antisymmetrical stretching of COO– groups; (3) the medium intensity absorption centered between 1,398 and 1,450 cm^{-1} , mostly due to aliphatic C–H bending and symmetrical COO– stretching; and (4) absorption at 1,030 and 1,090 cm^{-1} associated with C–O stretching of alcohols. The aliphatic group absorptions are often associated with weak peaks of aliphatic CH chains centered at about 770–778 cm^{-1} as both spectra show. Moreover, the weak absorption bands at 1,220 and 1,260 cm^{-1} , due to the C–O stretching of carboxylic groups, phenols and/or aromatic ethers appear more intense for HS and more particularly in a soil treated by RCW. The sharp bands at 1,375 cm^{-1} present on all the spectra are attributed to residual inorganic salts resulting from the extraction of organic matter. The wide bands centered around 1,100 cm^{-1} are attributed to inorganic Si–O vibrations of clay impurities coprecipitated with both FAs and HAs and not eliminated by the purification process (Fig. 3).

The most significant differences in absorption bands were found for the humic fractions. The FTIR spectra of soils treated with RCW and CSS show a more pronounced absorption band at 1,720 cm^{-1} than the raw or standard one,

Table 3 E_2/E_3 , E_4/E_6 and $SUVA_{254}$ values calculated for fulvic acid (FA) fraction by UV–visible spectroscopy

	E_2/E_3	E_4/E_6
RCW (FA)	5.44 a $\pm 0.41^{***}$	5.12 NS ± 1.56
CSS (FA)	2.40 ab $\pm 0.21^{***}$	9.06 NS ± 1.53
NE (FA)	4.41 b $\pm 0.67^{***}$	6.33 NS ± 3.18

RCW ramial chipped wood, CSS composted sewage sludge, NE non-amended soil, FA fulvic acid

0.01 < (*) $p < 0.05$, 0.01 > (**) $p > 0.001$, (***) $p < 0.0001$; NS insignificant difference

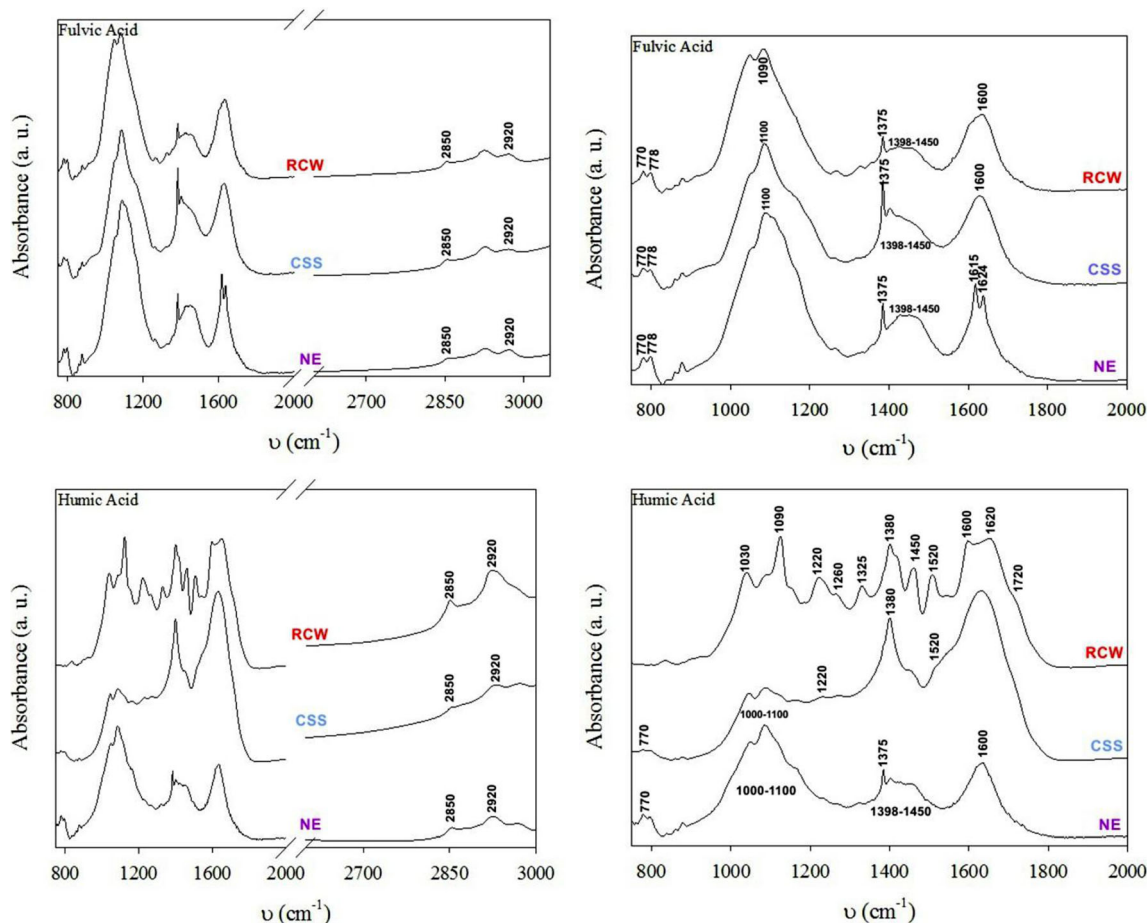


Fig. 3 FTIR analysis of the treated (RCW and CSS) and untreated soils (NE). Typical absorption vibration bands of both humic and fulvic substances were labeled and assigned in the main text. The two

amendments contribute to the formation of high molecular weight and humification substances which are highlighted with additional bands for the extracted humic acids

indicating a larger content in carboxylic groups. The pH values of the untreated and treated soils confirm that this band (shoulder around $1,720\text{ cm}^{-1}$) results from COOH groups. The introduction of amendments decreases soil pH and consequently increases such bands. This is further confirmed by the concomitant appearance of two new bands in the $1,620$ and $1,380\text{ cm}^{-1}$ regions ascribed to COO^- ions resulting from the conversion of HAs to their salts. Another difference in the spectra of HA fractions is the appearance of weak absorption bands at $1,520\text{ cm}^{-1}$ for amended soils, relative to N–H vibration of amide groups. The identification of these bands suggests the presence of complex structural components with a high molecular weight and high humification.

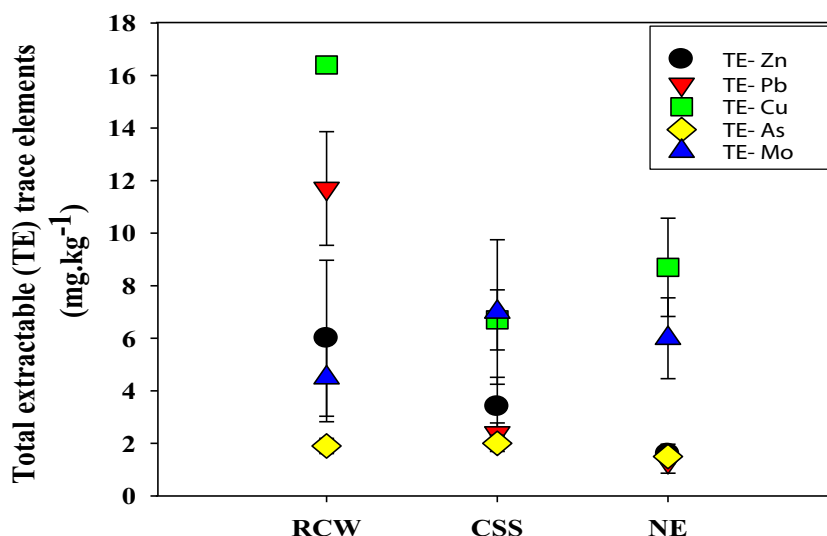
Effect of organic amendments on trace element dynamics

The ecological effects of TE, metals and metalloids, in soils are closely related to the concentration and speciation of the elements in the soil (Brummer et al. 1986). Whatever the elements, their contents are considerably higher than natural background (Baize 2000) (Table 1), which confirms the high

level of polymetallic contamination in the soils. Moreover, the addition of CSS and RCW to the soil has no significant effect on the total metal concentrations compared with the NE soil.

The contents of As, Cu, Mo, Pb and Zn associated to HS extracted from all soils are presented in Fig. 4. Cu, Pb and Zn were extracted from the fractions bound to organic constituents by NaOH in higher amounts than Mo and As. Our results show that RCW added to the soil significantly increased the concentration of extractable Zn, Pb and Cu by 4.9- and 2-fold and slightly increased the extractable arsenic by 1.3-fold in the solution, whereas it decreased the extractable fraction of Mo by 0.8-fold compared with the NE soil. The effect of CSS added to the soil on the concentration of extractable TE was less than that shown by RCW: the addition of CSS increased the extractable Zn, Pb, Mo and As by 2-, 1.8-, 1.2- and 1.3-fold and decreased Cu by 1.3-fold compared with the NE soil. In general, we can note that organic amendments (RCW and CSS) added to the soil increased the extractable TE especially in the case of RCW amendment in comparison with the NE soil.

Fig. 4 Total extractable Zn, Pb, Cu, As and Mo (from the NaOH extract) in mg kg⁻¹



HS constitute a large fraction of soil organic matter (SOM) and their binding capacities affect the mobility of TE in soils. FAs are the most mobile fraction and a major component of dissolved organic matter (DOM) in soil (Stevenson 1994). Therefore, the presence of soluble organic matter (as FAs) may be responsible for the solubilization of TE in soils whereas insoluble organic matter (such as HAs) may contribute to TE immobilization in soils. Indeed, FA is characterized by smaller molecular size fractions and a high ability to form complexes with trace metals that are more mobile than those formed with HA (Stevenson 1982). As Hsu and Lo point out (2001), knowledge about the distribution of TE between HA and FA fractions is essential for understanding and predicting the mobility of TE in contaminated soils after organic amendments. The distribution of TE in FA and HA fractions show a large variability depending on the chemical elements and the treatment (Fig. 5).

Figure 5a shows that Zn in the amended soils is more abundant in the FA fraction than in the HA fraction. The proportion of Zn bound to FA was about 23 % and 32 % higher than that bound to HA in the soils treated with RCW and CSS, respectively. Almas et al. (2000) and Usman et al. (2004) found that the addition of sewage sludge increased the solubility of Zn due to the formation of soluble organo-metallic complexes. Our results concerning Zn agree with Donisa et al. (2003), who studied the distribution of trace metals between humic and fulvic fractions in natural soils. They found that Zn associated more with FA than with HA. Boruvka and Drabek (2004) also found that 95.7 % of Zn bound to FA compared to HA, whereas over 75 % of Pb and Cu fractions bound to HA in treated and untreated soils, e.g., in soil amended with CSS, 80 % of Cu associated with HA compared with 20 % associated with FA (Fig. 5b,c). He et al. (1995) also found that more Cu in the compost was recovered in HA than in FA. In a study of the irrigation of Mediterranean

sandy soil by treated wastewater, Tarchouna Gharbi et al. (2010) demonstrated that copper had a high affinity for the HA fraction. Concerning Pb and Cu, our results do not agree with those reported by Donisa et al. (2003) or Boruvka and Drabek (2004), who investigated the distribution of TE between the dissolved organic fraction and found that Pb and Cu were more abundant in FA than in HA. Hsu and Lo (2001) isolated the HS from several separated swine manures (SSW) to investigate the effect of HS on the leachability and availability of TE. They found that more than 98 % of Cu and Zn complexed with FA.

Arsenic is more abundant in the fulvic fraction than in the humic fraction for all soils. The proportion of arsenic associated with FA was 13 %, 8 % and 35 % higher than that associated with HA in the soils treated with RCW, CSS and NE, respectively (Fig. 5d). Mo is about 60 % more abundant in HA than in FA in the soil treated with RCW and about 25 % and 60 % less abundant in HA than in FA in the soil treated with CSS and NE, respectively (Fig. 5e). This result can be explained by the capacity of RCW soil to provide a greater quantity of organic carbon in the form of FA than CSS soil.

Conclusion

In aided phytostabilization, the additions of organic amendments of various natures (RCW and CSS) were utilized: (1) for improve the physical, chemical and biological properties of contaminated soils and (2) to immobilize the TE and reduce their availability in contaminated soils. This study showed that the quantity and quality of SOM were modified according to the type of organic amendments. Although the two amendments significantly increase the content of SOM, only CSS increased the proportions of HA in soil highlighting that added

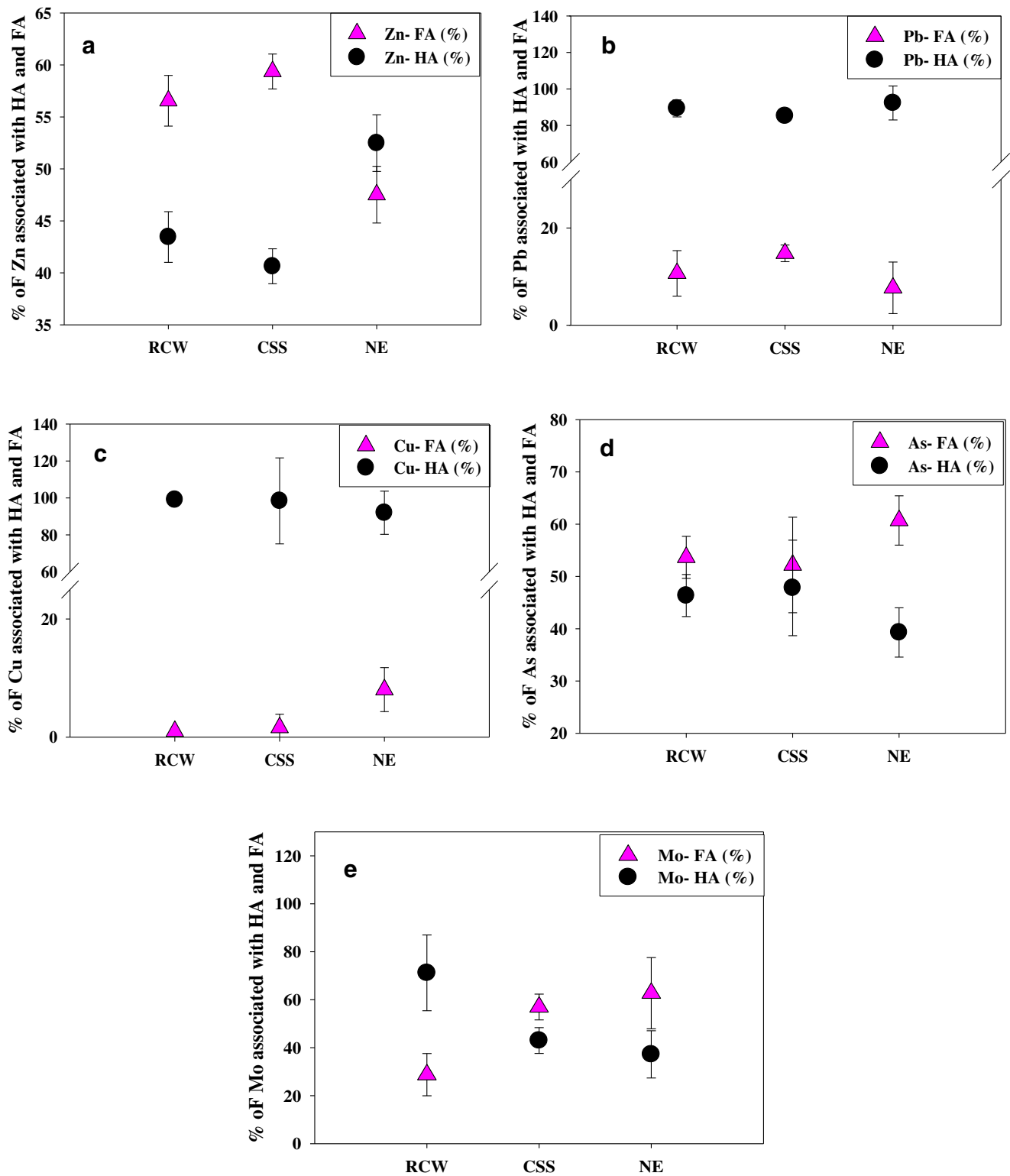


Fig. 5 Percentage of Zn, Pb, Cu, As and Mo associated with HA and FA

organic matter was more mature and stable in the time. In treated and untreated soils, humic acids are the main organic fraction associated to Pb, Cu and Mo and contribute to their immobilization in soil. However, formation of a large amount

of soluble Zn- and As-FA complexes can result in their mobilization in the soil profile, and then play an important role in term of contamination risks. Moreover, whatever the type of organic amendments, an increase in the proportion of zinc

associated with FA is highlighted, indicating a high risk of Zn leaching at short and long term.

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