Soil remediation using *in situ* immobilisation techniques

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The main objective of this study was to investigate the efficiency of different substrates to reduce the extraction of heavy metals concentration in a heavily contaminated soil. Two contaminated soils by Cu and Zn were used to evaluate the effectiveness of eight substrates (calcium carbonate, bentonite, kaolinite, charcoal, manganese oxide, iron oxide, zeolite, phosphate) to reduce metal availability and to study the change of metals speciation in different forms using sequential extraction technique (single step). Sequential extraction technique (single step, 0.11 M acetic acid, $HONH_3Cl$, $H_2O_2 + NH_4OAc$, Aqua regia) was applied on contaminated soils after and before treatment to evaluate metals speciation. Results indicate that the most effective treatments in decreasing available metal concentrations were calcium carbonate, zeolite and manganese or iron oxide. Metal sequential fractionations indicate that the exchangeable fraction of Cu and Zn in contaminated soils can be transformed into unavailable forms after chemical remediation.

Keywords: heavy metals; soil remediation; amendments; sequential extraction technique

1. Introduction

Human activities have introduced numerous potentially hazardous trace elements in the environment after the industrial growth [1]. The alterations of environmental conditions and the growing use of agrochemicals increase the public concern on the potential effects of the accumulation of heavy metals and other contaminants in the soils [2]. Elevated concentrations of these contaminants (especially heavy metals) are dangerous for the environment and human health due to their persistence and cumulative tendency in the environment and their direct toxic effects for organisms. To a certain extent, soils are able to limit the toxic effects [3]. However, when the concentrations of heavy metals become too high to allow the soil to limit their potential effects, contaminants can be mobilised, resulting in contamination of agricultural products or groundwater.

The study of trace metals speciation is important since slight changes in the metal availability and in environmental conditions can determine toxic effects to animals and plants. The mobility of trace metals and their bioavailability strongly depend on their specific chemical forms

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or ways of binding. However, the determination of specific chemical species or binding forms is rather difficult. Therefore, the determinations of broader forms (e.g. 'mobile' or 'carbonate-bound' forms), using extraction procedures, can be a good compromise to give information on environmental contamination risk. As a result of this practicality, single and sequential extraction schemes have been designed for the determination of binding forms of trace metals in soil [3–8].

According to da Silva et al. [9], the determination of specific chemical forms or the nature of binding, is much more valuable than the determination of the total metal content, since the toxic effects and the geochemical pathways of heavy metals are mainly determined by their mobile species. The knowledge of such chemical forms enables prediction and prevention of the adverse effects of heavy metals to affected communities. Many soil remediation techniques have been applied to polluted soils [10–14].

The soil remediation techniques include: (1) chemical stabilisation method to reduce the solubility of heavy metals by adding some non-toxic materials into the soils, (2) removal of polluted surface soils and replacement with clean soils, (3) covering the original polluted soil surface with clean soils, (4) on-site chemical leaching with acid agents, (5) dilution method, mixing polluted soils with surface and subsurface clean soils to reduce the concentration of heavy metals, or (6) phytoremediation by plants such as woody trees. The chemical stabilisation method was evaluated as the most low cost-effective remediation technique involving removal of polluted soils and addition of clean soils to the surface. Also phytoremediation is recommended [12]. The aim of this study is to evaluate the possibility to use using different substrates to reduce the extractable of heavy metals in a heavily contaminated soil.

2. Materials and methods

2.1. *Soil collection*

Samples were collected between August and September 2005 in two soils, one located in a sugar factory and influenced by industrial wastes, and one located in the El Morash village and influenced by urban and wastewater. Contaminated surface soil samples (0–20 cm) were collected from each site (ca 15 samples from each site), using sterile polyethylene bags.

2.2. *Analytical procedure*

The samples were air-dried for 3 days and then hand-crushed using mortar and sieved through 2 mm stainless steel (screen) sieves to remove large debris, stones and pebbles. Samples were finally homogenised and stored until the analyses.

2.3. *Chemical treatments for contaminated soil*

Eight chemical treatments were used to compare and evaluate the effectiveness of chemical remediation techniques. Nine different slurries of soil (1 g soil:25 ml H_2O) were put in polyethylene bottles and treated according the following methods: (1) 1 g calcium carbonate ($CaCO_3$) added to increase soil pH to 7.0; (2) a high quantity of calcium phosphate (10 mg P); (3) 1% manganese oxide (5 g); (4) 1% iron oxide (5 g); (5) 1 g charcoal; (6) 1 g kaolinite ore; (7) 1% synthetic zeolite (5 g., Sigma Chemical Company, USA); and (8) 1 g bentonite ore; and (9) kept as a control. Each treatment was performed in triplicate and incubated for two weeks at room temperature (25 °C).

2.4. *Physico-chemical parameters*

After 24 h, in each treatment (1 g soil:25 ml H_2O), soil pH and electrical conductivity (EC) were measured using a pH-meter (Orion Research, Model SA520, USA) and conductivity meter (HANNA Instruments, HI 8033 Italy), respectively [15]. Calcium carbonate and organic carbon contents were determined by back-titrating an excess of 0.5 M HCl added to 1 g of the sample [16], and wet oxidation [17], respectively.

2.5. *Extraction of Cu and Zn in soil*

Extraction of Cu and Zn in the experimental soils was determined by several different extraction solutions for eight treatments [18]. These extraction reagents included distilled water [19], 0.05M EDTA (pH 7.0) [18], 0.43M HOAC [19], and 0.1 M HCl [20]. The extraction suspensions were centrifuged at 8000 rpm for 15 min, then the supernatants diluted to 50 ml using double-distilled water.

2.6. *Sequential extraction of Cu and Zn in soil*

The mobility of metals in soil samples was evaluated using protocol proposed by Ure et al. [21]; Chen et al. [13] and da Silva et al. [9]. Table 1 reports the four steps sequential extraction technique used to validate the methods applied in the speciation studies in soil samples. The method is based on step 1: acetic acid extraction (0.11 M acetic acid), step 2: hydroxylamine hydrochloride and ammonium acetate extraction, step 3: hydrogen peroxide oxidation and step 4: complete acids attack (conc. HF, HNO_3 and HCl, mixture technique). These extractions are based on the exchangeable, water and acid soluble phases (bound to carbonate, step 1), the reducible phase (occluded Fe/Mn oxide fraction, step 2), oxidisable phase (organically bound and sulphide fractions, step 3) and detrital fractions (structurally bound in residual fraction, step 4). Generally, heavy metals in the exchangeable and carbonate-bound fractions are considered readily and potentially bioavailable, while the Fe- -Mn oxide and organic/sulphide fractions are relatively stable under normal soil conditions. Heavy metals in the residual fraction are entrapped within the crystal structure of the minerals and, thus represent the least liable fraction.

The steps and the operationally defined fractions of metal are summarised in Table 1. The sequential extractions were carried out, in triplicate, on 1 g soil sample, in 85 ml polyethylene bottles. After digestion, the sample suspensions with extractant were decanted into polyethylene tubes and centrifuged at 8000 rpm for 15 min. The supernatants were carefully removed and stored in polyethylene bottles at 4 °C. The analytical performance of the laboratory was evaluated by

Table 1. Sequential extraction scheme for metal speciation in soil samples.

Reagent	Shaking time and temperature	Fraction
40 ml of 0.11 mol/l acetic acid	16 h at room temperature	Water-soluble (Available)
40 ml of 0.1mol/l hydroxylamine hydrochloride (pH 2)	16 h at room temperature	Occluded in Fe or Mn oxides (Reducible)
10 ml 30% H_2O_2(pH 2)	1 h at room temperature and 1 h at 85 °C	Organically bound and sulphides (Oxidisable)
then 10 ml 30% H_2O_2(pH 2)	1 h at 85 °C	
cool, add 50 ml mol/1 ammonium acetate (pH 2)	16 h at ambient temperature	
Conc. acid mixture (HCl: HNO_3: HF)		Structurally bound (Residual fractions)

analysis of Certified Reference Material (two NIST standard reference soil materials, NIST SRM 2709 and NIST SRM 2711 [22]).

2.7. *Atomic absorption spectrophotometry*

The composition of digested samples was determined with atomic absorption spectrophotometry (Model Solaar 969, ATI Unicam Comp.) equipped with a digital direct concentration read out and an air–acetylene burner using single element hollow cathode lamps (ATI Unicam Comp.). When the concentrations were under the detection limit of flame, the AAS External standards in diluted acid were used to calibrate the accuracy of atomic absorption.

3. Results and discussion

This study was conducted to evaluate Cu and Zn concentrations of study soil, to examine chemical partitioning of the heavy metals and to compare the ability of different amendments to reduce the heavy metals in a heavily contaminated soil.

Chemical properties of both contaminated soils are shown in Table 2. The pH values were 7.23 at the Sugar factory soil and 6.82 at El Morash village soil. The hydrogen ion concentration (pH) is probably the most important factor influencing metal adsorption onto both inorganic and organic surface. The hydrous metal oxide surface can act as weak acid in solution, undergoing protonation in response to change in solution pH [23,24]. Lindsay [25] reported that the solubility of Zn soil solutes increased 100 times for each unit decreased in pH. High conductivity (CE) and concentration of organic matter (OM) ($920 \mu S\,cm^{-1}$ and $23.1\,mg\,g^{-1}$, for CE and OM, respectively) were reported in El Morash village comparing with site 1 where values were $80 \mu S\,cm^{-1}$ and $18.96\,mg\,g^{-1}$ for CE and OM, respectively. The differences in CE content between the two contaminated soils could be due to that the Sugar factory soil has potentially stronger adsorption of heavy metals. High organic matter values reported at El Morash village soil is due to sewage discharge (Table 2), suggesting that all geochemical processes, leading to recycle and accumulate the trace metals in soils, are associated and influenced by the concentration of the organic matter.

Total metal content is still used as an important index in the long run, which, together with the changing environmental condition determines the bioavailability of heavy metals [26]. Our results display that, the highest total Cu and Zn concentrations are reported at Sugar factory soil than at El Morash village soil (87.5 and $315\,\mu g\,g^{-1}$, and 5.0 and $253.25\,\mu g\,g^{-1}$, for Cu and Zn respectively in the Sugar factory and El Morash village, respectively) (Table 2). 0.1 M HCl extractable metals reflects higher Cu and Zn concentrations (106.25 and $179.75\,\mu g\,g^{-1}$, respectively) at Sugar factory soil compared with El Morash village soil (47.25 and $110.5\,\mu g\,g^{-1}$, for Cu and Zn concentrations, respectively; Table 2). This suggests that Sugar factory soil is more contaminated than El Morash village soil.

Table 2. Physicochemical characteristic of contaminated soils.

					0.1 M HCl		Total content ($\mu g\,g^{-1}$ dry soil)	
Location	pH	cond. $\mu S\,cm^{-1}$	O.M $Mg\,g^{-1}$	$CaCO_3$ $Mg\,g^{-1}$	Cu	Zn	Cu	Zn
Sugar cane Factory Soil	7.23	80	18.96	22.5	106.25	179.75	87.5	315
El-Morash Village Soil	6.82	920	23.1	2.5	47.25	110.5	5.0	253.25

3.1. *Extraction of Cu and Zn in soil*

The application of substrates in soils that can immobilise heavy metals *in situ* may provide a cost effective and sustainable solution for remediation of contaminants in soils [27–30]. Gray et al. [30] evaluated the effectiveness of lime and red mud (the product of aluminum manufacturing) to reduce metal availability to *Festuca rubra*. They found that, the application of either lime or red mud induced a significant increase in soil pH ($p < 0.05$) from 4.7 to ca 6–7 in the control soil (for lime and 5% red mud soils, respectively). At the same time the application of lime reduced the concentrations of soluble and extractable Pb, Zn, Cd, Cu and Ni from 4.58, 250, 6.11, 2.58 and 0.3 mgl^{-1} to 0.0, 4.05, 0.32, 2.15 and 0.03 mgl^{-1}, respectively. The application of 5% red mud reduced the concentrations of soluble and extractable Pb, Zn, Cd, Cu and Ni from 4.58, 250, 6.11, 2.58 and 0.3 mgl^{-1} to 0.71, 2.32, 0.3, 1.63 and 0.01 mgl^{-1}, respectively. The concentration of the investigated metals (based on water, EDTA, 0.43 M HOAC and 0.1 M HCl) in the two contaminated study soils treated with different substrates can be compared and evaluated by different extractants. These results reflect significant decrease in the extractability of Zn concentration at El Morash village soil treated with manganese oxide, zeolite or calcium carbonate (based on EDTA, 0.43 M HOAC and 0.1 M HCl) while for Sugar cane soil significant difference were reported in zinc extracted with 0.43 M HOAC (Table 3). The decrease of soluble and extractable metal concentrations in the amended soils can be attributed to the significant increase in soil pH after the amendment with lime. This increase in soil pH has been reported in other studies where lime has been used as a soil amendment [30–33] and can be also the result of the alkaline nature of the substrate. Other studies have indicated that application of hydrous iron or manganese oxides can significant reduce the solubility of heavy metals in soil [13,19,34–36]. Triplicate of seven chemical treatments were tested to compare and evaluate the remediation techniques for contaminated soils using pot experiments [13]. It was found that there are significant decreases in the extractability of Cd and Pb in both contaminated soils after the amendments with calcium carbonate, manganese oxide, or zeolite ($p < 0.01$). On the other hand,

Table 3. Mean zinc concentration (μg g^{-1}.dry soil) extracted by different extractants in both contaminated soils treated with different amendments.

Treatment	Water	EDTA	HoAc (0.43M)	HCl (0.1M)	Range of four extractants	SD
El- Morash Village Soil						
Control	9.5	120	43.5	110.5	48	24.6
CaCo$_3$	33	83.5	20	89	18.5	8.3
Bentonite	21	120	159.5	196.5	40	18.7
Kaolinite	67	88	112.5	197.5	48.5	22.7
Charcoal	20	91.5	134	197	187.75	88.1
MO	20.5	85	42.5	109	83	37.35
FO	24	94.5	220	181	18.5	8.8
Zeolite	26.5	90	23.5	90	20.5	9.7
Phosphate	28.5	80	146.5	178.5	29	13.4
Sugar factory Soil						
Control	21	189	143.5	179.75	94.5	39.8
CaCo$_3$	12	140	352	162	52.7	23.11
Bentonite	19.5	303.75	231	120.75	76.5	36.7
Kaolinite	19	350	421.5	298	82	40.1
Charcoal	21	246.5	293.5	334.5	171.5	77.9
MO	22	181.5	184	163.5	106.5	44.8
FO	N/A	244	187.5	240.5	63	28.4
Zeolite	57.5	141.5	184	168	71.5	36.3
Phosphate	296	130	313.5	255	106	45.9

FO: iron oxide; MO: manganese oxide.

Table 4. Mean copper concentration ($\mu g\,g^{-1}$.dry soil) extracted by different extractants in both contaminated soils treated with different amendments.

Treatment	Water	EDTA	HoAc(0.43M)	HCl (0.1M)	Range of four extractants	SD
El- Morash Village Soil						
Control	N/D	48	11.5	47.25	110.5	53.2
CaCo₃	25	19	23	6.5	69	34.97
Bentonite	ND	40	23.5	39	175.5	75.59
Kaolinite	23	26.5	29.5	71.5	130.5	57.27
Charcoal	11	156.5	194.1	198.75	177	74.35
MO	ND	83	26.5	64.6	88.5	40.1
FO	3.5	22	20	21	196	87.9
Zeolite	ND	20	14.5	20.5	66.5	37.5
Phosphate	ND	29	24.5	26	150	67.2
Sugar Factory Soil						
Control	11.75	38.5	54.25	106.25	168	77.4
CaCo₃	9.29	20	62	22.25	340	140.2
Bentonite	8.5	42.5	83.5	85	284	124.7
Kaolinite	11.5	90	93.5	91.5	402.5	176.18
Charcoal	42	192.4	180.3	213.5	313.5	139.9
MO	6	112.5	79	77	162	77.7
FO	14.5	26	77.5	24.15	244	114.9
Zeolite	30	25	82.5	96.5	126.5	56.29
Phosphate	22.5	128.5	82	107.5	183.5	82.8

FO: iron oxide; MO: manganese oxide; ND: not detectable.

manganese oxide and zeolite could reduce the soluble heavy metal concentrations in soils [30]. The results indicated that calcium carbonate (leads to increase the soil pH up to 7) is more efficient to reduce Zn solubility compared with other amendments, therefore soil pH is regarded as a main factor to controlling the extractability of heavy metals in contaminated soil.

Copper contents (Table 4), also reflect significant decrease in its extractable concentration in soil treated with either calcium carbonate, iron oxide or zeolite. These decreases in Cu extractability were based on EDTA and HCl extracts for both soils. This agrees with other studies where the application of lime [13,19,37–39], also for hydrous iron or manganese oxide [19,35,36] can significantly reduce the solubility of heavy metals in the soil. The metal removal efficiency, increased with the increasing of pH, can be explained on the basis of decrease in competition between protons and metal cations for the same functional groups and by decrease in the positive surface charge resulting in a lower electrostatic repulsion between the surface and metal ions [40]. All metals display a low solubility with increasing of pH values as the result of the onset of metal hydrolysis and the beginning of the precipitation [41], so the most important factor influencing heavy metals mobility is soil reaction [42]. Generally, high pH values also increase heavy metals sorption to soil particles. Nevertheless, every metal has a maximum limit for mobility in the soil [42].

3.2. *Sequential extraction technique*

The extractable concentrations of heavy metals in soil reflect their solubility and are influenced by different factors. Therefore, the sequential chemical extraction procedure can be considered a practically useful method to detach the chemical phase distribution of heavy metals in soils that is related to their behaviour in the environment.

The follow-up of the measured metal concentrations in different sequential extractions exhibited that the organically bound and sulphidic fraction of Cu (with extractability 59.8% of the total metal content) is the major chemical form in Sugar factory soil (Table 5). The stronger association between soil Cu and the organic matter is in agreement with the general findings that Cu forms

Table 5. Sequential fractionation ($\mu g\,g^{-1}$.dry soil) of Cu, Zn and their extractability (E%) as a percentage of total metal contents in two contaminated soils.

Soil	HoAc (0.11 M)	Extraction NH$_2$OH.HCl	Solutions H$_2$O$_2$+ NH$_4$OAC	Total acids digest.	Sum of all fractions
Copper					
El-Morash	35.2	73.6	1.2	5.0	115
Village Soil	*(30.6)	*(64)	*(1.04)		
Sugar factory	79.2	135.2	318.6	87.5	620.5
Soil	*(12.8)	*(21.8)	*(51.35)		
Zinc					
El-Morash	123.2	7.2	198.6	253.25	582.25
Village Soil	*(21.15)	*(1.2)	*(34.1)		
Sugar factory	132	91.2	228.8	315	767
Soil	*(17.2)	*(11.89)	*(29.8)		

*Value in parentheses is the percentage of each fraction on the sum of all fractions.

the most stable complexes with organic matter [2,43]. Guy et al. [44] found that the extraction of Cu bound to humic acid or clay minerals in the presence of the other component recovered less amounts of metal than in the absense of these components. Kheboian and Bauer [45], using the synthetic sediment model, reported similar results in which selective extraction used for Cu in exchangeable or reducible fractions did not reflect exactly the chemical phase distributions set up beforehand. They assumed that although an element in a certain fraction may be dissolved with an extract selective for the fraction, the element would be reabsorbed on other residual fractions during the process of extraction. Cu actually present as an exchangeable form may be a form bound to organic matter due to the readsorption on organic matter during the extraction process for an exchangeable fraction. Cu having the high proportion in the fraction bound to Fe/Mn oxide state with extractability 64% of the total metal content –(at El-Morash village), changing the chemical phase distribution with the oxidation of soil, increase (decreasing) the proportion of the exchangeable form. Soil Zn in the exchangeable fraction accounted for <22% of total soil Zn, while its major chemical form is the residual fraction followed by organically bound and sulphidic fraction (Table 6). These results indicate that a significant fraction of soil Zn is relatively stable. For example Takenaga et al. [46] displayed that the order for increasing affinities of metals to a humic acid is Zn (log $K = 7.15$) <Cu (log $K = 12.6$).

The application of sequential extraction technique for both soils (and after remediation with different substrates) indicate that, exchangeable form of Cu, extracted using 0.11 M acetic acid mixed with calcium carbonate, iron oxide or zeolite can be transformed to other three bounded forms (Table 7). The forms of Zn combined with calcium carbonate or zeolite in El Morash village soil were transformed in unavailable forms (Table 6). The fraction of available form of Zn in Sugar factory soil can be transformed to other three unavailable forms after the combination with calcium carbonate, zeolite or phosphate (Table 6). It can be assumed that Cu and Zn would be also changed from potentially mobile phase to stable phase. Transformations of the exchangeable to the sulfidic/organic fraction and reducible phases. It can be assumed that this is affected by complexed factors comprising of the extraction procedure and the chemical properties of these elements [47].

Several studies [31,32], based on the chemical sequential fractionation, display that the application of different treatments in contaminated soils results in a redistribution of heavy metals from soluble and exchangeable pools to other fractions. Once heavy metals are specifically sorbed onto these fractions surfaces, potentially they may become irreversibly fixed as a result of several mechanisms, including migration of metal ion into micro pores on the surface of the oxides

Table 6.   Sequential extraction distribution of Zn (μg g^{-1}.dry soil) in both contaminated soils after different treatments.

Treatment	HoAc	NH$_2$OH.HCl	H$_2$O$_2$+NH$_4$OAC	Total acids digest.
El-Morash village soil				
Control	123.2	7.2	198.6	253.25
CaCo$_3$	54.5	518.3	265.2	287.75
Bentonite	71.2	248	149.2	149.8
Kaolinite	98.4	96.8	13.8	218
Charcoal	97.5	739.8	153.2	148.5
MO	168	124.8	103.2	36.5
FO	80	152	36	229.5
Zeolite	48	16	211	316.5
Phosphate	108	152	31	129
Sugar factory soil				
Control	132	91.2	228.8	315
CaCo$_3$	53.2	324.8	292	397.5
Bentonite	113.6	313.6	75.8	273.5
Kaolinite	68	763.2	38.8	108.75
Charcoal	144.8	276	213.2	299.75
MO	134.4	280.8	201.8	208
FO	155.2	164	82.8	388.5
Zeolite	316	100	304	290.5
Phosphate	69.6	319.2	273.2	399.0

FO: iron oxide; MO: manganese oxide.

Table 7.   Sequential extraction distribution of Cu (μg g^{-1}.dry soil) in both contaminated soils after different treatments.

Treatment	HoAc	NH$_2$OH.HCl	H$_2$O$_2$+NH$_4$OAC	Total acids digest.
El-Morash village soil				
Control	35.2	73.6	1.2	5.0
CaCo$_3$	3.2	95	4.0	330.5
Bentonite	13.2	39	1.2	1.5
Kaolinite	ND	49.6	0.4	1.75
Charcoal	115.3	159.1	42.9	640.45
MO	16.3	149.7	9	110.6
FO	4.8	97.6	11.6	21
Zeolite	7.2	93.6	3.2	22
Phosphate	23.2	28	18.8	89
Sugar factory soil				
Control	79.2	135.2	318.6	87.5
CaCo$_3$	52	80	325	70.22
Bentonite	55.2	37.15	480.63	102
Kaolinite	124	220	2.0	1.5
Charcoal	190.4	147	69.2	513.9
MO	56.8	324.8	293.4	19.5
FO	61.6	87.2	46.6	104.6
Zeolite	6.25	378.75	415	100
Phosphate	63.2	112	124.8	210

FO: iron oxide; MO: manganese oxide; ND: not detectable.

[48], solid state diffusion of ions into the crystal lattice of oxides [49], or perhaps occlusion of metal ions.

Soil solution of heavy metals concentrations are generally considered to be the most readily available for plant uptake [50], hence decreasing the soluble pool of heavy metals in soils is likely to have the most immediate impact on metal bioavailability.

4. Conclusions

The application of calcium carbonate can increase soil pH and, at the same time, decrease the concentration of soluble and extractable heavy metals in threatened soils compared to the control soil. Both zeolite and manganese or iron oxide display comparable effects in reducing the available Zn and Cu concentrations. This means that, exchangeable forms of Zn and Cu in both contaminated soils can be transformed to unavailable fractions after amendment with calcium carbonate (to increase pH to 7) or 1% manganese or iron oxide or zeolite. It is recommended further investigations to study the potentiality of different substrates to reduce heavy metal available over a long term and the effects of different treatments on biodiversity and ecosystem functioning of the restored ecosystems.

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