

Mobilization of Accumulated Heavy Metals from Soils in the Vicinity of Municipal Solid Waste Dumpsites, Alexandria, Egypt

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Abstract: The environmental impact of heavy metal contaminants strongly depends on the metals speciation, mobility, and bioavailability in soil. The chemical behavior of heavy metals in soils is controlled by a number of processes, including metal cation release from contamination source materials (e.g., fertilizers, sludge, smelter dust, slag, dump sites), cation exchange and specific adsorption onto mineral surfaces and soil organic matter (OM), and precipitation of secondary minerals. The relative importance of these processes depends on soil composition and pH. In general, cation exchange reactions and complexation to organic matter are most important in acidic soils, while specific adsorption and precipitation become more important at near neutral to alkaline pH values. The release of heavy metals (Zn, Cu, Cd and Pb) from two soils by column leaching, single batch (CaCl₂ pH 3 and pH 6) and the modified European Community Bureau of Reference (BCR) three-step sequential extraction procedures was investigated. Homogeneously packed soil columns were leached with 720 ml/g 10 mmol_c L⁻¹ CaCl₂ (pH 6) for 1440 h to investigate the exchangeable metal pool and subsequently with 720 ml/g 10 mmol_c L⁻¹ CaCl₂ adjusted to pH 3 to study the potential of metal release in response to soil acidification. Two calcareous soils (pH 8.1 and 7.9) were used in this study, pronounced release peaks for Zn and Cu were observed for these soils by Ca exchange. Chemical composition of the leached solution was discussed concerning the most dominant cations and anions (Ca²⁺, Na⁺ and SO₄²⁻) in the studied soils. Slight changes were observed for metal distributions in all BCR steps in both soils. The comparison between heavy metal released amounts in column leaching and batch techniques related to the total metal contents reflected that Cd and Cu were most mobile, especially with the acidified solution in both soils. In general, between 7 and 50% of total metal contents were mobilized by Ca exchange and subsequent leaching at pH 3 except for Pb, which was described as an immobile metal.

Key words: Heavy metals; Mobilization; Alkaline soil; Column leaching.

INTRODUCTION

The environmental impact of heavy metal contaminants strongly depends on the metals speciation, mobility, and bioavailability in soil. The chemical behavior of heavy metals in soils is controlled by a number of processes, including metal cation release from contamination source materials (e.g., fertilizers, sludge, smelter dust, slag, dump sites), cation exchange and specific adsorption onto mineral surfaces and soil organic matter (OM), and precipitation of secondary minerals (Manceau *et al.*, 2000; McBride *et al.*, 1997; McBride, 1999; Morin *et al.*, 1999; Voegelin *et al.*, 2003). The relative importance of these processes depends on soil composition and pH. In general, cation exchange reactions and complexation to organic matter are most important in acidic soils, while specific adsorption and precipitation become more important at near neutral to alkaline pH values (Voegelin *et al.*, 2003).

High exchangeable sodium percentages and low soil solution salt concentrations can disperse colloids and this may facilitate mobilization of accumulated heavy metals from soil into surface waters and ground waters via colloid-assisted transport (Amrhein *et al.*, 1992; Grolimund *et al.*, 1996; Norrström and G. Jacks, 1998). Transport of organic carbon and nitrogen to surface water may also be facilitated.

There are several approaches commonly used to estimate heavy metal pools (*mobile, labile, or bioavailable*) in soils and/or contaminated soils. The most important methods include: (i) single batch extraction of soil samples with salt solutions (e.g. NH₄NO₃ or CaCl₂), this method form the basis of environmental regulations in many countries (Gupta *et al.*, 1996; McLaughlin *et al.*, 2000a,b), (ii) sequential batch extractions with increasingly harsh extractants designed to dissolve metals associated with different solid phases, this approach is often used to obtain information on the possible heavy metal binding forms in soil (Ahnstrom and

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Parker, 1999; Tessier *et al.*, 1979; Zeien and Brümmer, 1989), (iii) isotope exchange methods are useful to determine the bioavailable pool and (v) column leaching experiments which provide information on heavy metals release and transport in soil, and are also useful for testing possible soil remediation or stabilization treatments, to assess heavy metal binding and desorption kinetics, or to study processes such as colloid-facilitated metal transport at the laboratory scale (Grolimund *et al.*, 1996; Kedziorek *et al.*, 1998; Kretzschmar and Sticher, 1997; Rashad *et al.*, 2010; Temminghoff *et al.*, 1997).

The addition of organic matter may affect metal mobility by increasing soluble organic matter and Cu mobility may be enhanced, especially in soils of high pH (McBride *et al.*, 1999). Soils in our study often show relatively high pH and CaCO₃ content and low organic matter content at the soil surface. The addition of manure to these soils represents an increase of organic matter and metals that, combined with the soil characteristics, may show differential responses depending on the metal and on the studied soil. Thus, the objectives of this study were to (i) investigate mobilization of some accumulated heavy metals such as Zn, Cu, Cd and Pb from alkaline soil after five years application of municipal solid waste compost (MSWC) and (ii) compare the amounts of heavy metals released in column leachates with the amounts in batch extractions.

MATERIALS AND METHODS

2.1. Study Site:

The plough layer (0-20 cm depth) of the soil was collected from two sites in the vicinity of two municipal solid waste dumpsites in Alexandria, Egypt. Both dump sites produce MSWC to be used as an organic fertilizer. The first site is called Abees, represents soil 1, located at 31° 08' 47.59'' N and 29° 55' 52.04'' E. The second site is called Elmontazah, represents soil 2, located at 31° 16' 07.24'' N and 30° 01' 45.84'' E. Generally, these soils contain clay ~ 26 %, crypto calcareous, non saline to moderately saline and 1-2% slope. Surface irrigation is the common system in this area and the water table in the open drains is generally maintained at 2.5 m below ground surface. Cultivated crops were Tomatoes and Carrot in soil 1 and Potatoes in soil 2, MSWC is applied in both soils for about 5 years. The evaporation rate is far in excess of precipitation it ranges from 1,500 mm/yr in the north to 2,400 mm/yr in the deep south (DRI 2001, Achthoven *et al.*, 2004). According to X-ray diffraction and FT-IR spectroscopy, the clay fraction for both soil samples contained high amount of quartz and mica, and traces of kaolinite were also detected.

2.2. Soil Properties and Sample Preparation:

The collected samples were air-dried and sieved \square 1 mm. The resulting fine soil samples consist mostly of aggregates with a size close to 1 mm in diameter. The texture determined by sieving and sedimentation (pipette method) is 60 % sand, 16 % silt and 24 % clay for soil 1 and 55 % sand, 19 % silt and 26 % clay for soil 2. The CaCO₃ content quantified by gaseous CO₂ release from the fine soil upon acidification with 10% HCl is 230 mg g⁻¹ and 115 mg g⁻¹ for soil 1 and soil 2 respectively. Organic C, quantified by subtracting inorganic C from total C, the latter determined with a CNS analyzer (elementar, Vario EL III) is 20 mg g⁻¹ for soil1 and 18 mg g⁻¹ for soil 2. The C/N ratio is 16 and 15.2 for soil 1 and soil 2 respectively. The cation exchange capacity (CEC) of the fine soil determined with the Ag thiourea method (Van Reeuwijk, 2002) using the acetate buffer at pH 8.2 was found to be 127 mmol_c kg⁻¹ for soil 1 and 209 mmol_c kg⁻¹ for soil 2. Dithionite-citrate-bicarbonate (DCB) soluble Fe and Al of the fine soil 1 is 6.4 and 3.8 mg g⁻¹ respectively and for soil 2 is 6.8 and 3.2 mg g⁻¹ respectively.

Electrical conductivity (EC) for soil 1 and soil 2 was measured in a 1:10 (solid: liquid) aqueous extract is 1380 μS/cm and 1420 μS/cm respectively. Soluble cations and anions were extracted with deionized water (1:10) and quantified by atomic absorption spectroscopy (Perkin Elmer, PE 3300) and anion chromatography (DIONEX, ICS-90). Na⁺ was extracted in higher amounts than the sum of Ca²⁺ and Mg²⁺ divalent cations (Table 1). Among the anions, Cl⁻ dominated (0.62 mol_c kg⁻¹) and SO₄²⁻ represented one third (0.21 mol_c kg⁻¹) of Cl⁻ concentration. In the charge balance, where the charge of HCO₃⁻ and dissolved organic matter (DOM) are not considered, the sum of cations is much larger than that of the anions. As the pH determined in a 1:2.5 suspension of deionized water is 8.1 for soil 1 and 7.9 for soil 2, it can be concluded, that carbonates are present as HCO₃⁻ and distinct amounts of functional groups of DOM are deprotonated. Dissolved organic carbon (DOC) concentrations in a 1:5 aqueous extract, quantified with a TOC analyzer (elementar, liquiTOC trace) were 62 mg C L⁻¹ and 70 mg C L⁻¹ for soil 1 and soil 2 respectively.

The clay fraction was separated by dispersing the fine soil by shaking overnight in deionized water and repeated sedimentation and decantation. The suspension was centrifuged, washed until salt free and finally the clay fraction was freeze-dried. The specific surface area (SSA) determined by N₂-adsorption (Quantasorb, Quantachrome) was found to be 31 m² g⁻¹ for soil1 and 26 m² g⁻¹ for soil 2. The total content of heavy metals in soil samples were determined by hot *aqua regia* digestion. Zn, Cu, Cd and Pb contents in solution (Table 2) were measured with an inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Liberty 200; Varian).

Table 1: Soluble cations and anions in the 1:10 aqueous extract of the A-horizon in both soils.

Soil	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Σ cations	Σ anions
	mol. kg ⁻¹									
1	1.20	0.13	0.23	0.40	0.62	0.02	0.001	0.21	1.96	0.85
2	1.32	0.16	0.27	0.46	0.56	0.02	0.001	0.18	2.21	0.76

2.3. Setup of Column Leaching Experiments:

The experiments were conducted to investigate the release of accumulated heavy metals from contaminated soils in response to large concentration of CaCl₂ (pH 6 and EC 2300 μS cm⁻¹). The first set of these experiments was performed in polypropylene tubes having an inner diameter of 3 cm and filled with 20 g air-dried fine soil aggregates \square 1 mm, the length of soil columns was 15 cm. A Whatman glass microfiber filter was placed at the bottom of each column. The column inlet was then connected to a peristaltic pump (IPC-ISMATIC) and percolated with 10 mmol_c L⁻¹ CaCl₂ solution (unbuffered pH of 6). The interpretation of column leaching experiments may be further complicated by the occurrence of slow desorption or dissolution reactions, which could influence the metal release patterns (Voegelin *et al.*, 2003). Therefore, in previous work (Rashad *et al.*, 2010) a flow rate of 0.5 ml h⁻¹ proved to avoid column blocking during the total run time of the experiments (720 h), in this work to assess the importance of kinetic effects we used the same flow rate for total run time (1440 h). The relatively low flow rate helped to keep the partially saturated state of the packed aggregates until the end of the experiments. A number of four columns were set up for two soils with two percolating solutions. The leachates were collected every 24 h for 60 days (1440 h) in total. About 720 ml were percolated through each column during this period. The concentrations of Zn, Cu, Cd and Pb in the collected leachates were measured using an ICP-AES. pH and EC were also measured in the leachates.

Due to the high pH values of the studied soils a second set of column experiments was carried out to study the further release of heavy metals induced by soil acidification. In this part we followed the procedure reported by (Voegelin *et al.*, 2003), but with some modifications according to our environmental conditions. The experiments were performed in smaller polypropylene tubes having an inner diameter of 1 cm and filled with 3 g of the fine soil aggregates \square 1 mm, the length of soil columns was 2.2 cm, in this case the effluent will be monitored over a much larger number of pore volumes for the same period of the later experiments i.e., 1440 h. We used the same leaching solution 10 mmol_c L⁻¹ CaCl₂ adjusted to pH 3 by HCl addition. Column leachates were collected and the concentrations of Zn, Cu, Cd and Pb were measured using an ICP-AES.

2.4. Batch Extractions:

The same electrolyte solutions used in column experiments were used to perform single batch extractions in order to compare the amounts of heavy metals released in column leachates with the amounts in batch extractions. Each 5 g fine soil sample was equilibrated in polycarbonate centrifuge tubes with 25 ml of a solution containing 10 mmol_c L⁻¹ of CaCl₂ (pH 6 and EC 2300 μS cm⁻¹). After shaking for 24 h, the pH of the suspensions was alkaline (7.6 to 8), the suspensions were centrifuged, Zn, Cu, Cd and Pb concentrations were measured in the supernatants using an ICP-AES. In addition, the modified European Community Bureau of Reference (BCR) three-step sequential extraction procedure (Li *et al.*, 2010; Pueyo *et al.*, 2008) was applied to investigate the mobility of accumulated heavy metals in soil. This procedure can be described as follows (Rauret *et al.*, 1999): **First step** (Exchangeable and weak acid soluble fraction): 1 g soil sample was extracted with 40 mL of 0.11 mol L⁻¹ acetic acid (Merck Suprapur) solution by shaking in a mechanical, end-over-end shaker at 30 ± 10 rpm at 22 ± 5 °C for 16 h. The extract was separated by centrifugation for 20 min, collected in polyethylene bottles and stored at 4 °C until analysis. The residue was washed by shaking for 15 min with 20 mL of doubly deionised water and then centrifuged, discarding the supernatant. **Second step** (Reducible fraction): 40 mL of 0.5 mol/L hydroxylammonium chloride (Merck pro-analysis) solution was added to the residue from the first step, and the mixture was shaken 30 ± 10 rpm at 22 ± 5 °C for 16 h. The acidification of this reagent is by the addition of a 2.5% (v/v) 2 mol L⁻¹ HNO₃ solutions (prepared by weighing from a suitable concentrated solution). The extract was separated and the residue was washed as in the first step. **Third step** (Oxidisable fraction): 10 mL of 8.8 mol L⁻¹ hydrogen peroxide (Merck Suprapur) solution was carefully added to the residue from the second step. The mixture was digested for 1 h at 22 ± 5 °C and for 1 h at 85 ± 2 °C, and the volume was reduced to less than 3 mL. A second aliquot of 10 mL of H₂O₂ was added, the mixture was digested for 1 h at 85 ± 2 °C, and the volume was reduced to about 1 mL. The residue was extracted with 50 mL of 1 mol L⁻¹ ammonium acetate (Merck pro-analysis) solution, adjusted to pH 2.0, at 30 ± 10 rpm and 22 ± 5 °C for 16 h. The extract was separated and the residue was washed as in previous steps. **Residue from the third step** (Residual fraction): the residue from step 3 was digested with aqua regia, following the ISO 11466 (ISO, 1995b). In this case, the amount of acid used to attack 1 g of sample was reduced to keep the same volume/mass ratio: 7.0 mL of HCl (37%) and 2.3 mL of HNO₃ (70%) were added.

RESULTS AND DISCUSSION

The results of heavy metals analysis confirmed our expectation of high heavy metals contaminated soils. Heavy metal concentrations in mg kg^{-1} and % of total contents obtained using aqua regia, single extraction and three-step BCR sequential extraction procedures are reported in (Table 2 and Table 3).

Table 2: Selected properties and heavy metal contents (aqua regia) of soils 1 and 2 (aggregate fraction $\square 1$ mm).

Soil	Soil properties			Total heavy metal contents			
	pH	Organic C	CEC	Zn	Cu	Cd	Pb
		g/kg	$\text{mmol}_e \text{kg}^{-1}$	mgkg^{-1}			
1	8.1	20	127	105.62	73.82	10.58	60.52
2	7.9	18	209	108.51	68.23	11.21	69.18

Table 3: BCR three-step sequential extraction and single (CaCl_2 pH3) batch extraction data as percentages of total heavy metal contents (aqua regia) for soil 1 and soil 2.

Step	Soil	Extracted heavy metals			
		Zn	Cu	Cd	Pb
		% of total contents			
1	1	30.5	25.2	51.2	7.3
2	1	18.0	17.2	31.9	4.6
3	1	9.7	28.8	8.9	3.1
Sum	1	58.2	71.2	92.0	15.0
Residue	1	41.8	28.8	8.0	85.0
1	2	33.9	26.5	46.2	9.4
2	2	18.5	15.9	29.0	6.7
3	2	8.8	33.9	13.6	4.5
Sum	2	61.2	76.3	88.8	20.6
Residue	2	38.8	23.7	11.2	79.4
CaCl_2 (pH 3)	1	23.4	12.7	24.3	0.3
	2	25.7	11.5	27.4	0.2

3.1. Effect of CaCl_2 on Metal Release from Soil Columns:

Despite the high contamination of the studied soils no critical heavy metal contents referring to groundwater pollution were found in the column leachates. Relatively high soil pH values (Table 2); clay contents (24 % and 26 %) for soil 1 and soil 2 respectively, large amounts of iron oxides (Kalbitz, 1996) and CaCO_3 may slow mobilization of heavy metals from both contaminated soils. Therefore, the further presentation is focused on the second set of column experiments which conducted to study the release of heavy metals in response to soil acidification (Voegelin *et al.*, 2003). The released amounts of Zn, Cu and Cd from Soil 1 in response to the effluent volume of $10 \text{ mmol}_e \text{ L}^{-1} \text{ CaCl}_2$ (pH 6) are presented in Fig. 1a. Only small amounts of Zn, Cu and Cd were released during the initial conditioning phase, possibly in association with the mobile colloidal particles resulting from column packing (Voegelin *et al.*, 2003). The results revealed a sharp increase followed by pronounced tailing in the released amount of Zn and Cu with increasing effluent volume from about 250 to 400 ml/g soil depending on the solubility and tendency of each metal for complex ion formation with DOM in soil as stated by Ashworth and Alloway (2008) they showed that the solubility of heavy metals has a strong positive relationship to the solubility of organic matter, particularly at high soil pH. Zn, Cu and Cd can be adsorbed to organic OM, phyllosilicates, or soil carbonates (Kabata-Pendias and Pendias, 2001); thus, the low mobility of metals in alkaline soils may be related to high CaCO_3 and organic matter content. The relatively low clay content of studied soil may result in increase of the leaching of both Zn and Cu as compared to Cd. Under neutral to basic conditions in presence of OM (i) deprotonation of the hydroxyl groups at mineral surfaces decreases the positive net surface charge and (ii) organic molecules become more electronegative. Thus, mineral surfaces and OM repel each other and DOM is released into solution (Avena and Koopal, 1998). Then, the heavy metals could be mobilized to soil solution by release of metal-organic complexes adsorbed onto soil solid surfaces in response to alkaline pH (Grybos *et al.*, 2007). Note that Zn, Cu and Cd showed similar release patterns, but Zn peaks in the leachates were about 12 times higher than peaks of Cu and 45 times higher than those of Cd reflecting different contamination levels (Table 2), this investigation is in agreement with Voegelin *et al.*, (2003). Comparable results were obtained for Soil 2 as illustrated in Fig. 2a. The main difference between the two soils was that Zn, Cu and Cd exhibited short plateaus started at the same effluent volume ~ 280 ml/g soil and ended at ~ 380 ml g^{-1} soil for Cu and Cd, but there was a little shift to smaller volume for Zn. The disappearing of those plateaus followed by a long tailing may be attributed to the depletion of the exchangeable cations in soil solution (Voegelin *et al.*, 2003), note that we used CaCl_2 as a percolating solution and there are soluble forms of Ca^{2+} and Mg^{2+} in soil solution (Table 1).

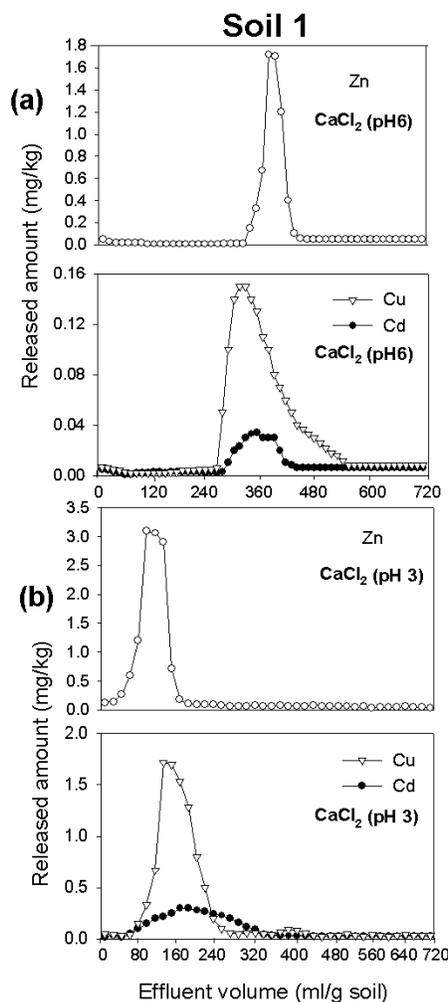


Fig. 1: Heavy metal amount released from soil 1 (fine soil aggregates \square 1mm, column experiment). a) Leaching of metals with 10 mmol/L CaCl_2 solution (pH 6). An effluent volume of 1 ml/g corresponds to approximately 1.6 pore volumes. b) Leaching of metals with 10 mmol/L CaCl_2 solution (pH 3). An effluent volume of 1 ml/g corresponds to approximately 1.1 pore volumes.

3.2. Metal Release by Acidification:

The same leaching behavior was observed under acidification for both soils using CaCl_2 (pH 3) as shown in Fig. 1b and Fig. 2b. Because both soils are calcareous, sandy clay loam soils with high buffering capacity, due to the large CaCO_3 concentrations, 230 mg g^{-1} and 115 mg g^{-1} for soil 1 and soil 2 respectively, the pH decreased shortly during the first set after introducing the pH 6 solutions. At effluent volume of 240 to 360 ml g^{-1} soil a fluctuation in pH values was observed (Fig. 3) and the pH of leachates started to increase close to the initial soil pH (7.9 for soil 1 and 8.1 and soil 2). In contrast after introducing the pH 3 solutions the leachates pH decreased for both soils with about 0.6 values until the end of the experiment. Addition of the pH 3 solutions increased the released amounts of Zn, Cu and Cd in both soils. The released amounts of heavy metals increased immediately using the acidified effluent solution at 80 ml g^{-1} for both soil samples. The peak amount released of Zn with acidified solution was approximately 2 times higher than that leached with nonacidified CaCl_2 solution in both soils. While, the peaks of the released amounts of Cu and Cd using acidified CaCl_2 solution were about 12 times higher than those released using the nonacidified solution.

A completely different leaching behavior for Pb among other heavy metals was identified in both soils. Although the total Pb contents in both soils were roughly 6 times higher than those of Cd (Table 2 and Table 3), effluent Pb concentrations in soil 1 and soil 2 were negligible using either acidified or nonacidified CaCl_2 solutions. This indicates that Pb is adsorbed much more strongly than Zn, Cu and Cd which is in good agreement with previous adsorption studies of heavy metals in soils (Abd-Elfattah and Wada, 1981; Buchter *et al.*, 1989; Hooda and Alloway, 1998; Voegelin *et al.*, 2003).

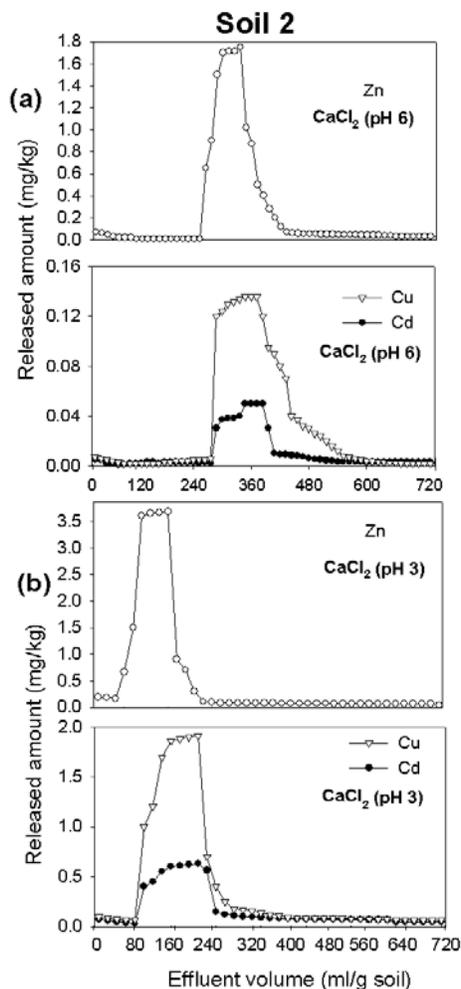


Fig. 2: Heavy metal amount released from soil 2 (fine soil aggregates \square 1mm, column experiment). a) Leaching of metals with 10 mmol/L CaCl_2 solution (pH 6). An effluent volume of 1 ml/g corresponds to approximately 2.1 pore volumes. b) Leaching of metals with 10 mmol/L CaCl_2 solution (pH 3). An effluent volume of 1 ml/g corresponds to approximately 1.7 pore volumes.

3.3. Salinity and Chemical Composition of The Leached Solution:

The EC was measured in the leachates (Fig. 4) at different effluent volumes in order to identify the effect of the percolating solution (CaCl_2) on the chemical composition of the leachates. In previous work (Rashad, *et al.*, 2010) the effect of CaCl_2 and other electrolytes in the leaching solutions, column experiment, on DOM retention led to distinct time dependent changes in chemical composition of the leachates. In the current study, the EC of the leachates also showed time dependent behavior during column experiment. The CaCl_2 solute caused ion exchange and release of anions and cations (Table 1). As a consequence of CaCl_2 addition, relatively large Na^+ concentrations 42 and 47 mmol L^{-1} for Soil 1 and Soil 2 respectively at 360 to 420 effluent volumes were detected. Concurrently, a strong decrease in the EC was observed with the progression of the experiment, consequently Na^+ decreased to 13 and 17 mmol L^{-1} for Soil 1 and Soil 2 respectively. The released amounts of SO_4^{2-} due to CaCl_2 addition were small i.e., 1.1 and 0.7 mmol L^{-1} for Soil 1 and Soil 2 respectively. The small SO_4^{2-} concentrations in the leachates may be attributed to the presence of Ca^{2+} , which enhance SO_4^{2-} adsorption due to the co-sorption of Ca^{2+} and SO_4^{2-} as ion pairs CaSO_4^0 (Bolan *et al.*, 1993).

3.4. Batch Extraction:

From the tabulated data in Table 3 heavy metal concentrations obtained from the three steps BCR-sequential extraction procedure are expressed in percent of the total metal contents of Soil 1 and Soil 2 (Table 2). Using 10 mmol L^{-1} CaCl_2 (pH 6) as a batch extracting solution reflects good comparison with the released metal amounts in column experiments (Table 4), but CaCl_2 extracted small concentrations compared with the BCR 1st step using 0.11 mol L^{-1} acetic acid.

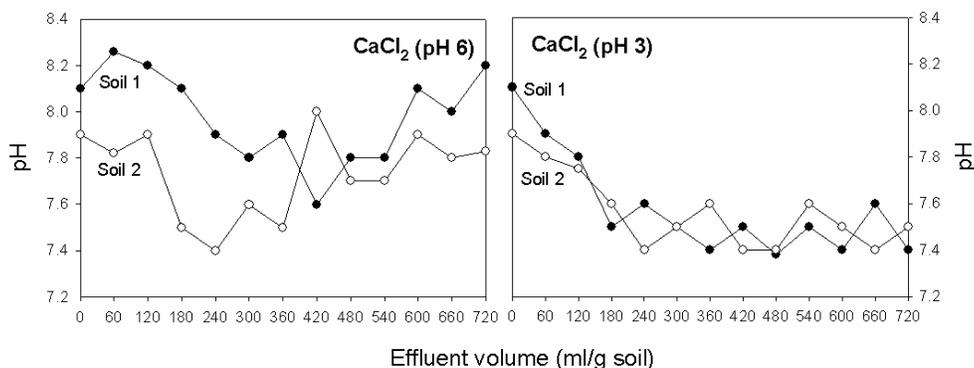


Fig. 3: Changes of pH in leachates from both soils (column experiment, 720 ml/g as a total effluent volume for 1440 h) using CaCl₂ solution (pH 6 and pH 3; the initial soil pH is written at 0 effluent volume).

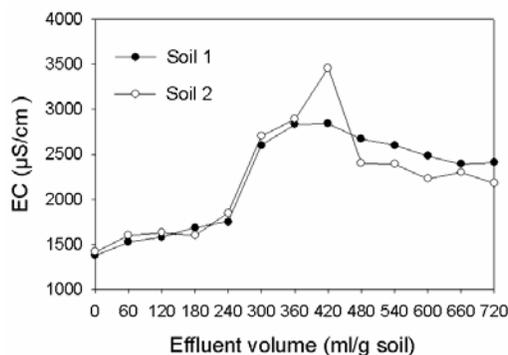


Fig. 4: Changes of electrical conductivity (EC) in leachates from both soils (column experiment, 720 ml/g as a total effluent volume for 1440 h) using CaCl₂ solution (pH 6, the initial soil EC is written at 0 effluent volume).

The temporal changes in Zn, Cu, Cd and Pb distribution patterns indicated the dissolution of main soil fractions and similarities between the samples. Changes in heavy metal distributions between Soil 1 and Soil 2 were useful for exploring the dynamic nature of the studied metal interactions in these soils. The potential mechanism affected this dynamic is the natural attenuation processes in which element may diffused to internal sorption sites in solid phases by migration, by surface precipitation or by changing a solid solution into more crystalline and stable structural sites, which provoke an increase in trace element fixation in the soil over time (Tessier *et al.*, 1996; Ford *et al.*, 1997; Gong and Donahoe, 1997; Thompson *et al.*, 1999; Banwart and Malmstrom, 2001; Yong *et al.*, 2001). Heavy metal distributions for Soil 1 and Soil 2 are shown in Fig. 5. Only slight changes were observed for metal distributions in all steps in both soils. The obtained data indicated the parent material type of the studied soils, where the potential increase in the extractability of the most mobile elements (Cd, Cu and Zn) due to the decrease in pH associated with the calcareous nature of the studied soils (Pueyo *et al.*, 2008). It is important to highlight the high extractability (sum of three steps), especially for Cd (92 % Soil 1, 88.8 % Soil 2) and Cu (71.2 % Soil 1, 76.3 % Soil 2) relative to which can be deduced from the desorption yields obtained in the first step in both soil samples. Extracted amounts of Zn in both soils (58 % to 62 %) reflected the high tendency of these calcareous soils to precipitate Zn in carbonate form compared with Cd and Cu. In case of Pb, no significant changes were observed in its distribution due to the association of this element with insoluble weathering products which may formed by the oxidation of the insoluble soil fractions (Yanful and Orlandea, 2000). The increase in Pb fixation or precipitation was observed in both soils in which the residual fraction increased with time. Despite the acidic pH during the BCR steps, Pb showed low solubility and high residual fraction. The extracted Pb amounts using 10 mmol_c L⁻¹ CaCl₂ were negligible.

3.5. Column and Batch Results Comparison:

In order to compare between column and batch results, cumulative release of heavy metals from soil columns using acidified (CaCl₂ pH3) and nonacidified (CaCl₂ pH6) solutions was calculated (Table 4) and illustrated by Fig. 6. Comparison between the total metal contents (Table 2) and the released amounts (Table 4) shows that Cd and Cu were most mobile, especially with the acidified solution in both soils. Small fractions of Zn and much smaller amounts of Pb were released compared with their total content. The released Pb amounts

reflected the immobile behavior of this metal in both soils even under acidifying conditions. In the column experiment, strong Pb fixation, adsorption or precipitation resulted in Pb release at low or negligible concentrations (Table 4). Consequently, the mobilized Pb fraction is much lower than the pool determined in 10 mmol_c L⁻¹ CaCl₂ batch extractions.

Metal extraction in batch not only depends on the salt concentration and solution to soil ratio (SSR), but also on the adsorption affinity of the exchange cation (Gupta and Aten, 1993). Significantly less heavy metal amounts were extracted and/or released using 10 mmol/L CaCl₂ as batch extraction solution or as leaching solution in column experiments compared with the BCR-sequential extraction procedure. As presented in (Table 3) in the BCR-sequential extraction (step 1 “exchangeable fraction”) using acetic acid is followed by an extraction with 0.5 mol/L hydroxylammonium chloride (step 2 “specifically adsorbed fraction”) acidified with HNO₃. Metal-acetate complexes formed during step 1 are considerably more stable than metal-nitrate complexes formed during step 2. This leads to an effective decrease of the free metal cation activity in step 2 and, consequently, to the release of more strongly adsorbed metals from the soil matrix. In contrast in a flow-through column, the activity of the released metals in solution is kept low by constant leaching with fresh metal-free extractant solution, thereby favoring desorption reactions.

In Fig. 5 and Fig. 6 we compare the cumulative amounts of Zn, Cu, Cd and Pb released from soil columns in response to Ca exchange (CaCl₂ pH 6) and acidification (CaCl₂ pH 3) with the results of the BCR-sequential extraction and 10 mmol_c L⁻¹ CaCl₂ batch extractions. From this comparison we can conclude the following points:

- I. For weakly adsorbed metals, Zn and Cd in Soil 1 and Soil 2, the released amounts in column experiments for Zn were about 10 % less than the amounts extracted in batch with 10 mmol/L CaCl₂ solutions, but Cd amounts released were corresponded well with the extracted amounts using the later solution. While, the extracted amounts of Zn in the sum of the 3 steps BCR-sequential extraction were about 35 % higher than the extracted in batch with 10 mmol_c L⁻¹ CaCl₂ solutions for both soils and the BCR extracted Cd amounts were about 64 % in average higher than the extracted Cd in batch for both soils.
- II. For strongly adsorbed metals, Cu and Pb for Soil 1 and Soil 2, the released amounts in column leachates were always lower than the batch extracted amounts either in single CaCl₂ solution or in the BCR sequential extraction. But the released Pb amounts can be described as negligible amounts compared with the BCR extracted amounts.
- III. In both soils the sum of the BCR-sequential extraction was generally higher than the amount extracted with 10 mmol_c L⁻¹ CaCl₂ solution. This difference can be attributed to release of carbonate bound metals by ammonium acetate (formed in step 2), which could not be extracted with CaCl₂ (Voegelin *et al.*, 2003).

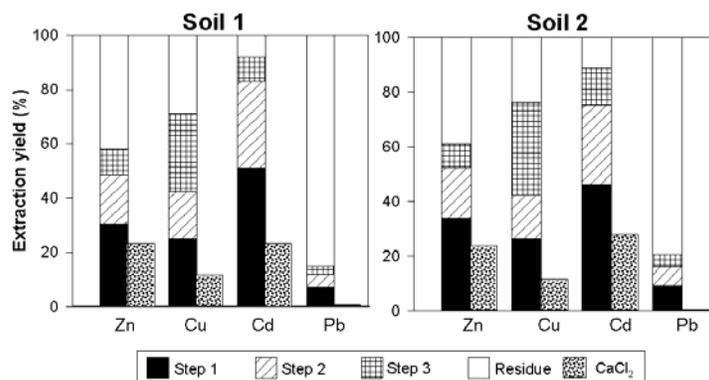


Fig. 5: Heavy metal distributions obtained at 2 months (1440 h) for Soil samples using single batch extraction with 10 mmol/L CaCl₂ solution (pH 6) at a solution to soil ratio (SSR) = 5 ml/g, and BCR sequential extraction procedures. All results are given in percent of the respective total metal concentrations (Table 2).

Table 4: Cumulative release of heavy metals from soil columns (leaching solution pH 6) compared with subsequent acidification to pH 3.

Leaching solution	Soil	Released heavy metals			
		Zn	Cu	Cd	Pb
CaCl ₂ (pH 6)	1	8.42	1.96	0.73	ND
CaCl ₂ (pH 3)	1	14.33	10.10	5.32	0.08
CaCl ₂ (pH 6)	2	6.12	1.89	0.92	ND
CaCl ₂ (pH 3)	2	18.20	14.26	8.70	0.12

ND: Not determined.

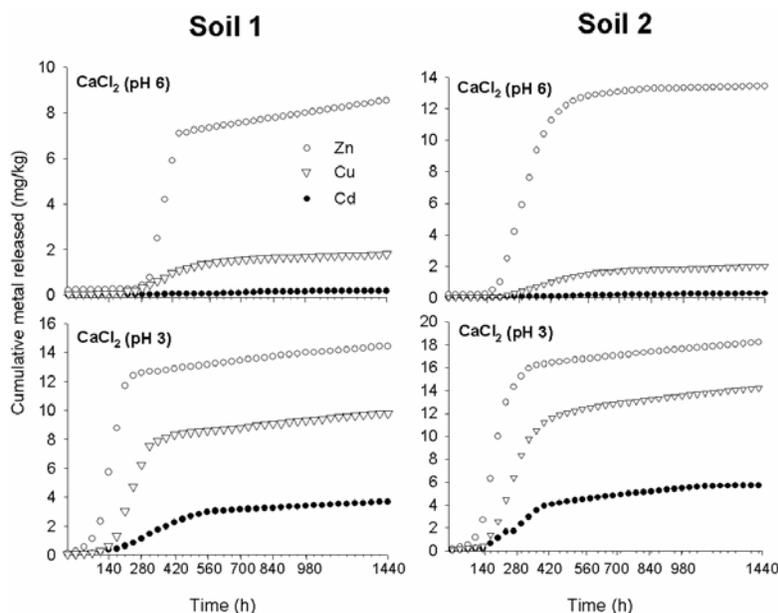


Fig. 6: Cumulative heavy metal amounts released from soils (fine soil aggregates \square 1 mm, column experiments) with time (1440 h) using percolating solutions of CaCl_2 (10 mmol/L, pH 6 and 3). The percolation rate is 0.5 ml/h.

Conclusion:

Location of the studied soils in the vicinity of municipal solid waste dumpsites in addition to the yearly application of the MSWC for five successive years increased the accumulation of heavy metals in the A-horizon of both soils; the same conclusion is reported by (Aicha, *et al.*, 2009). Thus, application of MSWC led to a significant increase of heavy metal concentrations in the top soils. Consequently, it would be recommended to separate metal-rich wastes from the municipal wastes prior to composting. Column leaching experiments provide valuable information on labile metal pools and the importance of slow reaction kinetics in metal leaching. Our results indicated that the cumulative amounts of metal cations released is poorly defined because it can include metal cations released from high affinity sorption sites on organic matter and oxides, metal released by dissolution of metal-bearing solid phases (Voegelin *et al.*, 2003). Thus, the metals released by acidification only revealed information on the potential of heavy metal release as a result of strong soil acidification. In general, between 7 and 50% of total metal contents were mobilized by Ca exchange and subsequent leaching at pH 3 except for Pb, which was described as an immobile metal.

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