HEAVY METALS EXTRACTABILITY IN A SOIL AMENDED WITH SEWAGE SLUDGE

Giuliano Marchi1*; Luiz Roberto Guimarães Guilherme2; Andrew C. Chang3; Clístenes Williams Araújo do Nascimento4

1 Embrapa Cerrados; Rodovia BR020, km 18 - C.P. 08223 - 73310-970 - Planaltina, DF, Brasil.
2 UFLA - Depto. de Ciência do Solo, C.P. 3037 - 37200-000 - Lavras, MG - Brasil.
3 University of California, Riverside - CA 92521 - USA.
*Corresponding author <giuliano.marchi@cpac.embrapa.br>

ABSTRACT: Few investigations have been carried out about the comparison of desorption rate and amount of heavy metals extracted successively by organic acid mixtures mimicking the rhizosphere and routine extractants in sewage sludge-amended soils. Extractions of Zn, Cd, Ni, Cr, and Cu were performed in samples of a sewage sludge-amended soil using seven extractants: four organic acid mixtures and three routine extractants (DTPA, Mehlich-I, and ammonium acetate). Results from single pass extractions, in which the extractable metal contents were determined by simply extracting the soil a single time, as well as from 15 successive extractions, in which the solid residues of the first extraction was successively extracted 14 additional times, of heavy metals were analyzed. The extractability of heavy metals in a single pass extraction was, in general, as follows: Mehlich-I > DTPA > organic acids > NH₄OAc. The highest rates of extraction followed the general order: DTPA > Mehlich-I > organic acids > NH₄OAc. While Mehlich-I presented the highest extractability of heavy metals among studied extractants, DTPA showed a high extractability of Zn, Cd, Ni, and Cu in a single extraction as well as the highest rates of extraction among the studied extractants. The transfer of heavy metals from soil to organic acid solutions is slower than to DTPA and Mehlich-I extractants.

Key words: Oxisol, extraction rate, trace elements

EXTRACTABILIDADE DE METAIS PESADOS EM UM SOLO TRATADO COM LODO DE ESGOTO

RESUMO: Poucos trabalhos têm sido realizados sobre a comparação da taxa de dessorção e da quantidade de metais extraídos sucessivamente por misturas de ácidos orgânicos que imitam a composição da rizosfera e por extratores usados na rotina em amostras de solo tratado com lodo de esgoto. Extrações de Zn, Cd, Ni, Cr e Cu foram realizadas em amostras de solo de carga variável tratado com lodo de esgoto usando-se sete extratores: quatro misturas com ácidos orgânicos e três extratores usados na rotina (DTPA, Mehlich-I e acetato de amônio). Os resultados para uma única extração, em que o conteúdo de metais extrai-áveis foi determinado simplesmente extraíndo-os do solo uma única vez, bem como após 15 extrações sucessivas, em que o resíduo sólido da primeira extração foi extraído sucessivamente por mais 14 vezes, foram analisados. A extractabilidade dos metais em uma extração simples foi, em geral, como segue: Mehlich-I > DTPA > ácidos orgânicos > NH₄OAc. As mais elevadas taxas de extração seguiram a ordem: DTPA > Mehlich-I > ácidos orgânicos > NH₄OAc. A maior extração de metais foi obtida com Mehlich-I, enquanto, o DTPA também extraiu alta quantidade de Zn, Cd, Ni e Cu em uma extração simples, bem como obteve as mais altas taxas de extração entre os extratores estudados. A transferência de metais do solo para as soluções de ácidos orgânicos foi mais lenta que para os extratores DTPA e Mehlich-I.

Palavras-chave: Latossolo, extração de metais, elementos-traço

INTRODUCTION

Sewage sludge may be rich in heavy metals, which are, therefore, introduced into agricultural soils when sewage sludges are land applied. These metals loading may pose a serious risk for food chain contamination through accumulation in plants, as well as for soil contamination and surface-water pollution that may arise from runoff (Benítez et al., 2001). To assess the potential health risk of cropland, it is imperative that the plant availability of heavy metals in receiving soils may be accurately projected over time.
Several routine extraction methods, either acid or complexing solutions, such as Mehlich-I (Nelson et al., 1953), DTPA (Lindsay & Norvell, 1978), and ammonium acetate (Ure et al., 1993) have been long used to assess the availability of heavy metals in soils. These single pass extractions are one-time point measurements that are not able to mimic the reactions taking place at the rhizosphere (Abreu et al., 2002), and are not likely to recover all of the plant available metals (Bermond & Ghestem, 2001). So far, there has not been a satisfactory protocol that fully gauges the extent and rates to which metals can be released from soil particles (Zhang et al., 2001). The fate, transport, and bioavailability of heavy metals in soils are dependent on the extent and rate the metals may be desorbed at the soil colloid-extractant interfaces especially in those soils amended with sewage sludge (Zhang et al., 2001; Ernstberger et al., 2005; Shirvani et al., 2007).

To overcome such drawback, methods using organic acid solutions that mimic the rhizosphere have been developed (Pires et al., 2004; 2007). Koo et al. (2008) stipulated that the plant availability of metals in cropland soils should be expressed in terms of capacity i.e., total available pool of the soil, and intensity i.e., the rate at which metals might be absorbed by plants. While it conceptually represented an improvement in the methodology to predict heavy metal mobility and bioavailability, the dynamics of organic acids on metal desorption requires further exploration (Qin et al., 2004), especially in Oxisols, where organic acids interact with soil colloids causing significant changes in surface charge properties (Marchi et al., 2006a, b).

We compared the dynamics of extracting heavy metals in sewage sludge-amended Oxisols by comparing the outcomes of extractions employing the rhizosphere based organic acids and those employing the conventional approaches.

### MATERIAL AND METHODS

A soil sample of a sewage sludge-amended Kandiuadox (Soil Survey Staff, 1999) was collected from an experimental field in Jaguariúna, São Paulo state, Brazil (22°41’ S, 47° W). Its physical and chemical characteristics were as follows: pH_H2O = 5.5; exchangeable Ca\(^{2+}\), Mg\(^{2+}\), and Al\(^{3+}\) (1 mol L\(^{-1}\) KCl) = 27.5, 8.5, and 1 mmol\(_c\) dm\(^{-3}\), respectively, and exchangeable K\(^+\) = 1.51 mmol dm\(^{-3}\); Mehlich-I extractable P = 3.5 mg dm\(^{-3}\); total acidity extracted with 0.5 mol L\(^{-1}\) calcium acetate at pH 7.0 (H\(^+\)Al\(^{3+}\)) = 35 mmol dm\(^{-3}\), organic matter based on the Walkley-Black method = 25.5 g kg\(^{-1}\), and clay = 450 g kg\(^{-1}\).

The Jaguariúna’s experimental field was established in 1999 and received sewage sludge from the Franca Sewage Sludge Treatment Station (São Paulo State, Brazil). This sludge was applied for five consecutive years at 24.11, 26.03, 30.13, 35.45, and 34.80 t ha\(^{-1}\) yr\(^{-1}\) dry weight equivalent rate, respectively. The characteristics of the sewage sludge had been reported elsewhere (Bettiol et al., 2006). A soil sample, composed of ten subsamples, was collected and digested using the USEPA Method 3052 that employed microwave digestion of soil aliquot in HCl-HNO\(_3\)-HF mixture (USEPA, 1996). The total contents were 71.74, 0.21, 15.90, 58.12, and 37.44 mg kg\(^{-1}\) for Zn, Cd, Ni, Cr, and Cu, respectively.

#### Extraction of heavy metals

Seven extractants were used to successively extract heavy metals from the soil samples. Four extractants were composed by low-molecular-weight organic acids: i) modified organic acids mixture (MOAS, Table 1); ii) simplified organic acid mixtures (SOAS, Table 2); iii) lactic acid; and, iv) acetic acid. The latter three extractants were: Mehlich-I, ammonium acetate (Ure et al., 1993), and DTPA (Lindsay & Norvell, 1978). Table 1 presents the concentrations of organic acids used to prepare the MOAS extractant solutions.

<table>
<thead>
<tr>
<th>Organic acid</th>
<th>Molecular</th>
<th>Formula</th>
<th>COOH mole fraction</th>
<th>COOH</th>
<th>mmol(_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic</td>
<td>60.05</td>
<td>C(_2)H(_4)O(_2)</td>
<td>0.2998</td>
<td>1</td>
<td>29.98</td>
</tr>
<tr>
<td>Butyric</td>
<td>88.11</td>
<td>C(_3)H(_6)O(_3)</td>
<td>0.2183</td>
<td>1</td>
<td>21.83</td>
</tr>
<tr>
<td>Glutaric</td>
<td>132.12</td>
<td>C(_4)H(_6)O(_4)</td>
<td>0.0042</td>
<td>2</td>
<td>0.21</td>
</tr>
<tr>
<td>Lactic</td>
<td>90.08</td>
<td>C(_4)H(_6)O(_3)</td>
<td>0.3823</td>
<td>1</td>
<td>38.23</td>
</tr>
<tr>
<td>Maleic</td>
<td>116.07</td>
<td>C(_5)H(_8)O(_4)</td>
<td>0.0439</td>
<td>2</td>
<td>2.19</td>
</tr>
<tr>
<td>Propionic</td>
<td>74.08</td>
<td>C(_5)H(_6)O(_2)</td>
<td>0.0104</td>
<td>1</td>
<td>1.04</td>
</tr>
<tr>
<td>Pyruvic</td>
<td>88.06</td>
<td>C(_6)H(_8)O(_3)</td>
<td>0.0004</td>
<td>1</td>
<td>0.04</td>
</tr>
<tr>
<td>Succinic</td>
<td>118.09</td>
<td>C(_7)H(_8)O(_4)</td>
<td>0.0063</td>
<td>2</td>
<td>0.31</td>
</tr>
<tr>
<td>Tartaric</td>
<td>150.09</td>
<td>C(_8)H(_6)O(_4)</td>
<td>0.0334</td>
<td>2</td>
<td>1.67</td>
</tr>
<tr>
<td>Valeric</td>
<td>102.13</td>
<td>C(_9)H(_8)O(_2)</td>
<td>0.0010</td>
<td>1</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 1. Modified organic acid solution (MOAS) composition\(^{a}\).

\(^{a}\)Modified from rhizosphere organic acid profiles developed by Koo et al. (2006); *mmol\(_c\)* concentration of organic acid used to prepare MOAS.
nium acetate, and DTPA. Extractants composed by organic acids were made up to 0.1 mol L\(^{-1}\) of COOH in a background matrix containing 4 mmol L\(^{-1}\) CaSO\(_4\) and 0.05 mmol L\(^{-1}\) NaCl. The background matrix was determined with basis on the main mono and divalent cations and anions present in saturation extracts from the sewage sludge-amended soil sample. The pH of these solutions was adjusted to 4.8 ± 0.1, comparable to the pH range of rhizosphere (Koo et al., 2006).

One and half-gram of soil material was placed into 50-mL tubes containing 30 mL of each extractant. The tubes were shaken for 24 hours at 25°C, 2 rpm, using a rotary mixer. One percent (v/v) of chloroform was added to each bulk solution to control microbial activity and prevent organic acid decomposition during the extraction.

The routine analysis extractants (Mehlich-I, ammonium acetate, and DTPA) were also used for heavy metals extraction. The procedures of such extractions were: (i) Mehlich-I – 30 mL of 0.05 mol L\(^{-1}\) HCl, and 0.0125 mol L\(^{-1}\) H\(_2\)SO\(_4\) were mixed with 7.8 g of sample and shaken for 5 minutes (Nelson et al., 1953); (ii) Ammonium acetate – 30 mL of 1 mol L\(^{-1}\) ammonium acetate, pH 7, were mixed with 1.875 g of sample and shaken for 14 h (Ure et al., 1993); and, (iii) DTPA – 20 mL of 0.005 mol L\(^{-1}\) dietilenetriaminepentacetic acid, 0.1 mol L\(^{-1}\) TEA (trietanolamine), and 0.1 mol L\(^{-1}\) CaCl\(_2\), pH 7.3, were mixed with 10g of soil and shaken for 2 h (Lindsay & Norvell, 1978).

The above-outlined protocols are all single pass extractions where the extractable metal contents were determined by simply extracting the soil a single time. The solid residues of the first extractions were successively extracted fourteen additional times. Extractions were performed with three replications. Metals recovered at each extraction were separately analyzed and the cumulative metal recovery and cumulative volume of extractants used for the extractions were recorded.

The trends on the cumulative heavy metal removal with respect to the number of extractions were fitted to a first-order model (exponential rise to maximum model) where the cumulative desorption of an ion from the soil particles is given by (Bermond & Ghestem, 2001; Koo et al., 2008):

\[ Ct = C_1 (1 - e^{-kt}) \]  

In equation (1), \( Ct \) stands for the cumulative heavy metals removed (mg kg\(^{-1}\)) at the extraction \( t \), \( C_1 \) is the quantity of heavy metal extracted at equilibrium (mg kg\(^{-1}\)); and \( t \) is expressed as number of extractions (ε); \( k \) is the rate of extraction (ε\(^{-1}\)).

The experiment was set up in a randomized design. Results from single, as well as from successive extractions were statistically tested according to ANOVA and significant differences between treatments were determined according to the Tukey test (\( p < 0.05 \)).

### Heavy metals analysis

Following the extraction, the contents were centrifuged for 20 min at 8,000 rpm to separate the solution and solid phases. The solution phase was passed through a 0.45-μm filter with a polytetrafluoroethylene (PTFE) membrane. The filtrates were acidified with 1% (v/v) HNO\(_3\) and the Cd, Zn, Cr, Cu, and Ni contents of the filtrate were determined according to atomic absorption spectroscopy employing a Perkin-Elmer AAnalyst 800 atomic absorption spectrometer (Perkin-Elmer, Bodenseewerk, Germany), using flame for Zn and graphite furnace for analysis of Cd, Cr, Cu, and Ni. The trace metal-grade (TMG) reagents whenever available were selected and used without further purification to prepare the extracting solutions. The final preparations were all checked for purity. The Standard Reference Material (SRM) 1640, “trace elements in natural water” and SRM 2709, “San Joaquin Soil” certified by US NIST (National Institute of Standards and Technology) were used in the quality control and quality assurance protocol. For calibration of the instrument, the reference material “Lab Performance Check Standard 1” (LPC-1-100/500) supplied by SPEX, whose accuracy was based on SRM of US NIST, was used.

### RESULTS AND DISCUSSION

#### Single pass extractions

The amount of Zn, Ni, and Cu extracted by lactic acid was higher than by acetic acid, MOAS and SOAS (Table 3). This is probably due to the fact that the stability constants of complex compounds with Zn, Ni, and Cu are higher with lactic acid than with acetic acid.
(Martell & Smith, 2003). For Cd, on the other hand, the amount extracted by acetic acid was greater than with lactic acid (Table 3), corroborating the higher Cd stability constant with this acid (Martell & Smith, 2003; Gustafsson, 2006). Based on stability constants only, it is impossible to explain why the SOAS extracted more Cr than the other low-molecular-weight organic acid solutions. As a component of the SOAS the lactic acid should complex 95% of all available Cr according to Visual Minteq calculations (Gustafsson, 2006). Thus the amount of Cr extracted by SOAS should at most equal that extracted by the lactic acid solution.

The contents of Cd, Zn, Ni, Cr and Cu (Table 3) extracted by Mehlich-I were higher, when compared with the other extractants studied, except for Cr and Cu with respect to SOAS and DTPA, respectively. An acid extractant, such as Mehlich-I, often extracts greater amounts of heavy metals than DTPA and NH₄OAc (Martínez & Motto, 2000). The proportions of total Zn, Cd, Ni, and Cu extracted with Mehlich-I were of 37, 33, 6, and 10%, respectively, of the total contents extracted by the USEPA 3052 method. The proportion of Mehlich-I-extractable Cr was much lower (< 1%). In the cationic form, chromium-III is very immobile in soils, forming strong complexes with organic matter and chemisorbing onto oxides and silicate clays, even at quite low pH (McBride, 1994). Moreover, as an oxyanion, Cr can also be adsorbed onto metal oxides at low pH (Hayes & Traina, 1998), thus being less available for extraction.

The DTPA-extractable amounts of Zn, Cd, Ni, and Cu were significantly higher than that extracted by the organic acids. This high extraction capacity of DTPA, for Zn, Cd, Ni, and Cu, might be attributed to its two donor groups namely the amine "NH₂ and 2"carboxylate "COO groups (Agbenin et al., 1999), which hold great ability to complex metals. The organic ligands used in the present experiment contained only the carboxylate donor group, which affinity for trace metal ions is lower than that of amine "NH₂.

The very low amount of Cr recovered by DTPA (Table 3) indicates low extractability of Cr by DTPA in sewage sludge-amended samples, as found before by Fuentes et al. (2006) and Walter et al. (2006). This Cr behavior in DTPA solutions is due to Cr solubility, which decreases above pH 4, with complete precipitation above pH 5.5 (Alloway, 1995). Another reason could be the slow kinetics for the formation of Cr-DTPA complexes (Byegård et al., 1999). In soil columns experiments, Cr was found to leach out faster by organic acids as compared with DTPA (Wasay et al., 2001).

Ammonium acetate extracted the same amounts of Cd, Cr, and Cu than did the acetic acid (Table 3). However, for Zn and Ni, NH₄OAc extracted the lowest amount when compared with all other extractants. Among the three conventional single pass metal extraction protocols, the outcomes for each metal were different (p < 0.05). The chemical nature of the extracting reagents and the soil may affect the outcomes (McBride, 1994). For the rhizosphere organic acids based protocols, the amounts of metals extracted in the single pass were fairly consistent. The rhizosphere organic acid based extraction protocols were based on the premise that the total plant available metal pool of the soil may be obtained by employing successive extractions as previously depicted (Koo et al., 2008). The outcomes of the single pass extraction, nevertheless, demonstrated that the extractions were chemically plausible.

**Successive extractions**

The cumulative amount of heavy metals removed after 15 extractions (Ct15) was considerably higher than those extracted by the single pass extractions, and there was no definitive mathematical trend between corresponding values (Table 4). It is an indication that the single pass extraction failed to recover all of the reactive metals and probably do not reflect the plant availability metal pools of the soil. The objective of the

<table>
<thead>
<tr>
<th>Extractants</th>
<th>Zn</th>
<th>Cd</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOAS a</td>
<td>13.6</td>
<td>16.6</td>
<td>455.7</td>
<td>493.1</td>
<td>369.3</td>
</tr>
<tr>
<td>SOAS</td>
<td>13.9</td>
<td>15.4</td>
<td>481.2</td>
<td>667.6</td>
<td>405.0</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>15.5</td>
<td>13.3</td>
<td>527.2</td>
<td>494.1</td>
<td>567.2</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>9.7</td>
<td>21.8</td>
<td>335.8</td>
<td>75.8</td>
<td>237.2</td>
</tr>
<tr>
<td>Mehlich-I</td>
<td>26.8</td>
<td>70.3</td>
<td>1026.9</td>
<td>559.9</td>
<td>3565.1</td>
</tr>
<tr>
<td>DTPA</td>
<td>17.1</td>
<td>50.6</td>
<td>725.6</td>
<td>12.1</td>
<td>3876.4</td>
</tr>
<tr>
<td>NH₄OAc</td>
<td>1.9</td>
<td>21.6</td>
<td>93.7</td>
<td>51.2</td>
<td>311.2</td>
</tr>
</tbody>
</table>

*Standard error in parentheses; all the values are means of three replicates; no difference to same letters in columns (Tukey test, p < 0.05).* a MOAS: modified organic acid solution; SOAS: simplified organic acid solution.
Table 4 - Cumulative Zn, Cd, Ni, Cr, and Cu removed at the fifteenth extraction, $C_{15}$, in a sewage sludge-amended soil sample.

<table>
<thead>
<tr>
<th>Extractants</th>
<th>Zn</th>
<th>Cd</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOAS*</td>
<td>33.7(0.36)$^{b}$</td>
<td>82.6(0.76)$^{a}$</td>
<td>1978.5(0.45)$^{b}$</td>
<td>3647.8(1.33)$^{c}$</td>
<td>2457.7(1.37)$^{d}$</td>
</tr>
<tr>
<td>SOAS</td>
<td>33.9(1.34)$^{b}$</td>
<td>79.3(0.26)$^{a}$</td>
<td>2073.5(1.20)$^{a}$</td>
<td>4406.6(1.04)$^{b}$</td>
<td>2519.6(1.28)$^{d}$</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>36.5(0.59)$^{a}$</td>
<td>76.0(0.78)$^{a}$</td>
<td>1900.2(0.24)$^{b}$</td>
<td>4310.8(1.11)$^{c}$</td>
<td>2742.0(0.57)$^{e}$</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>28.3(0.81)$^{c}$</td>
<td>71.7(1.19)$^{a}$</td>
<td>1489.1(0.81)$^{d}$</td>
<td>542.3(0.04)$^{d}$</td>
<td>1103.5(0.10)$^{c}$</td>
</tr>
<tr>
<td>Mehlich-I</td>
<td>36.6(0.26)$^{a}$</td>
<td>85.7(0.39)$^{a}$</td>
<td>1702.0(1.23)$^{c}$</td>
<td>4750.0(0.18)$^{a}$</td>
<td>7706.5(1.35)$^{c}$</td>
</tr>
<tr>
<td>DTPA</td>
<td>23.0(0.92)$^{d}$</td>
<td>62.0(1.19)$^{c}$</td>
<td>1056.5(0.81)$^{c}$</td>
<td>113.3(1.04)$^{c}$</td>
<td>6551.9(1.27)$^{b}$</td>
</tr>
<tr>
<td>NH$_4$OAc</td>
<td>9.6(0.91)$^{e}$</td>
<td>49.3(0.50)$^{d}$</td>
<td>254.9(1.30)$^{d}$</td>
<td>176.4(1.41)$^{c}$</td>
<td>1289.7(1.40)$^{c}$</td>
</tr>
</tbody>
</table>

*Standard error in parentheses; all the values are means of three replicates; no difference to same letters in rows (Tukey test, $p < 0.05$).

*MOAS: modified organic acid solution; SOAS: simplified organic acid solution.

successive extractions is to obtain the total reactive metal content, which may be estimated according to Equation 1. The data points the cumulative metal extracted ($C_t$) vs. the number of extractions ($t$) and the fitted Equation 1 for each extraction protocol are shown in Figure 1.
The rate of heavy metal extraction ($k$) was very small for all organic acid extractants (Figure 1; $k < 0.005 \text{ e}^{-1}$), which means that heavy metals were slowly extracted from the soil. The Cr kinetic showed the lowest $k$ values ($< 0.0007 \text{ e}^{-1}$) in all extractants (Figure 1), indicating the strong adsorption of such metal onto this soil, or slow Cr dissolution. The $C_{t15}$ results obtained by Mehlich-I successive extractions were higher than those for other extractants, except for Ni (Table 4). The proportion of the $C_{t15}$ by Mehlich-I in relation to the total concentrations extracted by the USEPA 3052 method was: Zn 51.0%, Cd 40.5%, Ni 13.0%, Cr 8.2%, and Cu 20.6%.

Studies on diffusive gradients in thin films (Ernstberger et al., 2005) showed that Zn and Cd presented higher extraction rates than Ni. The present study shows that, while Zn ($k = 0.020 \text{ e}^{-1}$) and Cd ($k = 0.026 \text{ e}^{-1}$) in a single extraction by Mehlich-I were near the amount extracted at $C_{t15}$, Ni ($k = 0.012 \text{ e}^{-1}$), Cr ($k = 0.001 \text{ e}^{-1}$), and Cu ($k = 0.007 \text{ e}^{-1}$) needed some more extractions to get near the amount extracted at $C_{t15}$. This behavior is clearly related to the differences in metal binding strength to the surfaces of soil particles (Ernstberger et al., 2005; Fangueiro et al., 2005) or, for Cr, slow dissolution of mineral phases.

DTPA extracted smaller amounts of heavy metals when compared with $C_{t15}$ values obtained by Mehlich-I and organic acids, except for Cu (Figure 1). In such a case, DTPA extracted a higher amount of Cu than did the organic acids. For DTPA, the $k$ for Zn ($0.260 \text{ e}^{-1}$), Cd ($0.364 \text{ e}^{-1}$), Cu ($0.142 \text{ e}^{-1}$), Ni ($0.198 \text{ e}^{-1}$), and Cr ($0.006 \text{ e}^{-1}$) were also the highest among the extractants. The high $k$ values obtained by the DTPA extraction indicate a fast desorption during the first extractions when compared with the other studied extractions.

The NH$_4$OAc extracted the smallest amounts of heavy metals among the tested extractants (Table 4). The $k$ values for NH$_4$OAc successive extractions were also very low, approaching zero.

For the three conventional metal extraction protocols, the cumulative metal removal in 15 successive cycles was wide spread for each metal (Figure 1). For the four rhizosphere organic acids based metal extraction protocols, the cumulative metal removal in 15 successive cycles was narrowly distributed for each metal.

REFERENCES


Received April 08, 2008
Accepted April 22, 2009