Leachability of Cu and Ni in wood ash-amended soil as impacted by humic and fulvic acid

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Abstract

Land application is a cost-effective way of disposing of wood ash. However, high volume wood ash application tends to increase soil pH, solubilizing soil organic matter (SOM), and enhancing metal mobility. Column studies (1.5 × 20 cm) were conducted to determine the leachability of Cu and Ni in an ash-amended soil. In the first study, deionized water was used to leach three columns: ash, ash mixed with topsoil, and ash mixed with topsoil overlying a spodic horizon. In the second study, humic acid (HA), fulvic acid (FA), and a mixture of humic and fulvic acids (HAFA) were used to leach ash columns. Leaching was conducted, one pore volume (PV) at a time, under unsaturated conditions. Leachate concentrations of dissolved organic carbon (DOC), Cl, Cu, and Ni, as well as pH were determined. Leachate pH ranged from ~10 to ~11 in the water- and acid-leached columns, respectively. In the ash-only columns, Cu leaching was in the form of soluble complexes with Cl. When wood ash was mixed with soil, Cu leached as soluble complexes with DOC at high pH (~10). Columns with a Bh horizon had 30% less leaching of Cu, possibly due to increased metal retention. Nickel leachability was not affected to the same extent as Cu. Organic acid-leached ash columns showed lower DOC, Cu, and Ni leaching, suggesting that these two metals and DOC were precipitating out with DOC at the high ionic strengths of these solutions (>0.3 mol dm⁻³). Precipitation was greater in the more reactive FA-leached columns. This study shows the need to understand the system to which wood ash is applied to minimize potential harmful effects. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Spodic; Precipitation; Complexation; Humic/fulvic acid

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1. Introduction

Land application is fast becoming a cost-effective way of managing wood ash from the pulp and paper industries. Wood ash is produced from burning wood bark, chips, and shavings in boilers to produce energy at paper mills, plywood plants, and other electrical generating plants. It consists of salts, oxides, and hydroxides of Ca, K, Fe, Al, Mn, Na, and Mg, and other trace elements in lesser proportions (Pepin and Coleman, 1984). The high pH and salinity associated with most ashes result from the formation of oxides and salts of alkaline metals during combustion. Additives such as sodium hydroxide, used for priming by some plywood plants, also increase the alkalinity of ash. Thus, it is important to consider the impacts of high ionic strength and pH-induced solubilization of organic matter (OM) from ash on metal mobility to minimize the adverse effects of land application on the environment.

Organic matter is generally insoluble (stable) under low pH conditions (Chirenje and Ma, 1999; Rivero et al., 1998). On the other hand, high pH promotes the dissolution of OM and increases concentrations of dissolved organic carbon (DOC) and metal–DOC complexes (Sparks, 1995). Under alkaline conditions, the bonds that hold OM to metals are disrupted and acidic components of OM are converted to their soluble salt forms. Soluble organics thus increase the carrying capacity of soil solutions for metals at elevated pHs by forming soluble metal–OM complexes (McBride, 1995; Stevenson, 1994).

The extent of OM and colloidal complexation of metals, as well as the transport and dispersal of these complexes in the subsurface has been demonstrated by many authors (McCarthy and Zachara, 1989; Puls and Powell, 1992; Sheppard et al., 1980). In contrast to a simple exchange phenomenon where retention is determined by valence and ionic radius, metal selectivity by OM depends on the specific electrochemical and structural properties of the ligand and metal ion. Stevenson (1994) suggested that at least four mechanisms were involved in metal sorption by OM, including physical adsorption, electrostatic attraction, hydrogen bonding, and coordination complexation.

Copper generally reacts with OM by forming stable coordination complexes rather than by forming compounds via hydrogen bonding or electrostatic attraction because of its low hydration energy and low charge (Stevenson, 1994). Nickel, on the other hand, associates with OM to a lesser extent and complexes mostly with inorganic substances (Hickey and Kittrick, 1984). The high pH associated with the ash application and its potential to solubilize and mobilize OM make OM-facilitated metal transport a potentially significant mechanism for metal conveyance in soil. The presumption was that OM-complexed Cu is more mobile in soil than simple Cu under the alkaline conditions of the study (Chirenje and Ma, 1999).

In addition to pH, solution salinity affects the ionic strength and a plethora of other chemical reactions. The surface area blocked by a particle deposited on a spherical collector decreases as the ionic strength is increased and is generally several times smaller than the projected area of the particles. Daylin et al. (1995) suggested that ionic strength influences the dynamics of colloidal deposition and transport (in our case, OM–metal complexes) in heterogeneous porous media by controlling the range and magnitude of interparticle forces. McCarthy and Zachara (1989) observed that colloidal deposition within the soil matrix is influenced by interparticle attraction–repulsion, which depends on
ionic strength, and the prevailing process (attraction or repulsion) is determined by pH and the nature of the sorbing surfaces. The high salinity of the ash samples in this study and the high pH they induced in our system had significant implications on this relationship.

A previous study on wood ash showed that the leachability of metals was highly correlated with DOC leaching from the soil (Chirenje, 2000; Chirenje and Ma, 1999). The leachability of trace metals was reduced by acidification of the soil columns, which reduced the solubilization and subsequent mobilization of OM from these soil profiles. The objectives of this investigation were to study the role of humic acid (HA) and fulvic acid (FA) in the solubilization and leaching of Cu and Ni from ash and soil, and to determine the effects of soil material from different horizons on Cu and Ni dissolution and leachability from ash.

2. Materials and methods

2.1. Properties of soil and ash

The soil used for this study (located in Hawthorne, FL) was an acidic fine sand (Typic Quartzipsamment) with a spodic horizon below 2 m. The wood ash used was generated at a plywood plant in Hawthorne, FL, which produces approximately 4 mg of ash per day. Sodium hydroxide was used to prime the wood, causing extremely high pH and salinity in the ash. In contrast, the soil had a relatively low pH of 5.6. Selected chemical, physical, and mineralogical properties of the ash and soil are shown in Tables 1 and 2.

2.2. Set up of columns

High-density polyethylene (HDPE) columns, 20-cm long and 1.5-cm internal diameter, were used in this study. The columns were set up as described by Nielsen and Biggar (1961). The column packing material was placed in the vertically oriented columns, two columns per treatment. The bottom of each column contained a porous glass frit (Aldrich, Milwaukee, WI) to which a suction of 20 cm of water was applied (Fig. 1). At the top of the column, a glass frit, with a high entry value, supplied flushing solution at a suction that was adjusted to give flow rates of < 0.33 PV per day. The latter suction was also about 20 cm of water resulting in approximately unit hydraulic gradient. The soil or ash in the

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Elemental concentrations of the wood ash and soil (A horizon) used in this study</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Ca</th>
<th>Na</th>
<th>Mg</th>
<th>K</th>
<th>Al</th>
<th>Fe</th>
<th>P</th>
<th>Mn</th>
<th>Zn</th>
<th>Ba</th>
<th>Pb</th>
<th>Cu</th>
<th>Se</th>
<th>Ni</th>
<th>Cr</th>
<th>As</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>100</td>
<td>26.0</td>
<td>9.00</td>
<td>8.00</td>
<td>8.00</td>
<td>7.00</td>
<td>3.00</td>
<td>14.0</td>
<td>0.70</td>
<td>7.00</td>
<td>1.30</td>
<td>1.00</td>
<td>19.0</td>
<td>10.0</td>
<td>2.00</td>
<td>2.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Soil</td>
<td>0.10</td>
<td>0.04</td>
<td>0.90</td>
<td>0.03</td>
<td>2.00</td>
<td>0.80</td>
<td>0.10</td>
<td>14.0</td>
<td>0.70</td>
<td>7.00</td>
<td>1.30</td>
<td>1.00</td>
<td>0.70</td>
<td>5.00</td>
<td>4.00</td>
<td>0.40</td>
<td>0.50</td>
</tr>
</tbody>
</table>
column was packed carefully to ensure good contact between the material and the fritted glass membrane. All columns were packed dry and then wetted at the beginning of the experiment.

2.3. Extraction of humic and fulvic acid

The OM fractions used in this study were extracted using the method described by Schnitzer (1969). Ten grams of soil were shaken in 200 ml 0.1 N NaOH for 24 h and the supernatant separated from the residual soil by centrifugation at 10,000 rpm for 10 min. The residual soil was washed with 50 ml water and centrifuged, and the supernatant was added to the original supernatant and acidified to a pH < 2 using 2 N HCl. The soluble fraction (FA) was separated from the coagulate (HA) by centrifugation and purified.

![Diagram of the leaching experiment (under unsaturated conditions)](image)

Fig. 1. The set up of the leaching experiment (under unsaturated conditions).
Humic acid (the coagulate) was brought into solution by adding more NaOH and deionized water and both solutions were adjusted to a pH of 5.6 (using HCl). A pH of 5.6 was chosen because it corresponded with the pH of our experimental soil (Table 2). Coincidentally, the deionized water used in the experiment had a pH that was close to this value as well (pH ~ 5.5). The third extract used, a mixture of both fractions (HAFA), was extracted using 0.1 N NaOH and adjusted to pH 5.6 using 2 N HCl.

2.4. Metal leaching in water-leached soil/ash columns

Three columns were packed separately with (i) 5.3 g ash (ash), (ii) 5.3 g ash mixed with 14 g of soil from the A horizon (ash + A), and (iii) 5.3 g ash mixed with 14 g A horizon overlying a separate layer of 5.2 g of soil from the spodic horizon (ash + A + Bh). The ash + A treatment corresponded to an ash application rate equivalent to 900 mg ha$^{-1}$ (packed to field bulk density), which was used in the field where the soil was collected (Chirenje, 2000). The columns were leached with deionized water at a rate of one pore volume (PV) every 3 days to compare the effects of soil material from different horizons on the leachability of heavy metals from the ash. The PVs for the three treatments were different due to the different amounts of soil used in each treatment. The ash only, ash + A, and ash + A + Bh columns had PVs of 5.0, 8.7, and 10.7 ml, respectively. Pore water velocities in different columns were also different, with the ash, ash + A, and ash + A + Bh columns having flow velocities of 1.67, 4.00, and 5.33 cm day$^{-1}$, respectively.

2.5. Metal leaching in organic acid-leached ash columns

In this study, three columns, similar in dimensions to those in the first study, were packed with 5.3 g of ash. Three different leaching solutions, HA, FA, and HAFA, adjusted to pH 5.6 (pH of the soil and deionized water), were used to leach the ash columns. Fulvic acid, HA, and HAFA were used to leach the ash columns to determine the effects of these acids on metal leachability from the ash. This eliminates other factors that may have been introduced by the presence of soil. The organic acids used were extracted from the soil at the experimental site (Hawthorne, FL) in order to understand the exact conditions present at that site. All three columns had the same PV of 5.0 ml, with a pore water velocity of 1.67 cm day$^{-1}$.

2.6. Metal sorption and dissolution

Metal sorption curves for the soil were also determined. One gram of air-dry surface soil was weighed into a Nalgene bottle and different concentrations of Cu and Ni were added as nitrate salts (up to 500 mg l$^{-1}$). The solutions were shaken for a period of 16 h, filtered, and analysed for Cu and Ni concentrations. Sorption curves were then developed for the amounts of each metal in solution for each added concentration. For the dissolution of metals from ash, 1 and 2 g of ash samples were added to 40-ml containers and 20 ml of deionized water was added. These solutions were then shaken on a rotary shaker and a series of samples were taken after 0, 0.02, 0.2, 0.5, 1, 2, 6, 12, 24, and 48 h. Curves depicting dissolution of metals with time were then developed.
2.7. Chemical extraction and analyses

Water-soluble Cu and Ni concentrations were determined by shaking 1 g of ash in 10 ml water on a reciprocating shaker for 16 h, filtering the solution through a 0.2 μm filter. For total elemental concentration analyses, 0.5 g of soil or ash were weighed into a 120-ml Teflon pressure digestion vessel, mixed with 10 ml HNO₃ acid and digested in a CEM MDS-2000 microwave sample preparation system (Matthews, NC) using EPA method 3051 (USEPA, 1986). Total concentrations of Cu and Ni in the leachates and digestates were determined using a Perkin Elmer SIMAA 6000 GFAAS (Norwalk, CT) using EPA method 7060A (USEPA, 1986). Other elements were determined using a Thermo-Jarrell-Ash 61E Inductively Coupled Plasma Spectrometer (Franklin, MA). The spike recoveries for all elements were within 80% to 120% and the quality control samples were all within 10% of the known concentrations. The pH and electrical conductivity (EC) were determined using a Fisher Accumet model 20 pH/conductivity meter (Pittsburgh, PA). The total organic carbon (TOC) was determined on a Shimadzu TOC 5050 carbon analyser (Columbia, MD).

The association of HA and FA with Cu and Ni was investigated through the determination of $E_4/E_6$ ratio of HA and FA, Kumada classification parameters, and fluorescence spectra for HA (Rivero et al., 1998). The $E_4/E_6$ ratio was determined by reading the absorbance of a dilute solution containing 1.0 mg HA adjusted to a pH of 8.3 at 465 and 665 nm (Kononova, 1966) on a Shimadzu UV-160U spectrophotometer (Columbia, MD). The Kumada classification parameters were determined from the absorbance of a dilute solution containing between 200 and 300 mg HA at 400 and 600 nm and measuring the specific OC content of this solution (Kumada, 1987). The emission spectra were recorded between 380 and 550 nm at a fixed excitation wavelength of 360 nm (Rivero et al., 1998) using the Shimadzu RF-1501 spectrofluorophotometer (Columbia, MD). The ionic strengths $I$ (mol m⁻³) of the solutions were determined from the EC of leachates using the Marion–Babcock equation of “$\log I = 1.159 + 1.009 \log \kappa$”, where $\kappa$ is EC (dS m⁻¹).

3. Results and discussion

The leaching of chloride (Cl⁻), which was present in large concentrations in the ash, was used for comparison as a conservative tracer in the columns (Fig. 2). Over 99% of the potentially leachable Cl⁻ had leached out after the third PV in the water-leached columns. The delay in the breakthrough for Cl⁻ was probably due to the slow dissolution from the ash in the column rather than the flow characteristics of the leaching solution. The increased delay in the columns incorporating the Bh horizon (87% Cl⁻ leached out by the third PV) was possibly due to the significant reduction in hydraulic conductivity caused by layering (elluvial and spodic horizon, Chirenje, 2000). In the organic acid-leached ash columns, an average of 90% Cl⁻ had leached out by the end of the fourth PV.

Although the pHs of all solutions used in the column study were adjusted to 5.6 at the beginning of the study, the pHs of the first PV ranged from 10 in the water-leached ash-soil columns to 11 in the organic acid-leached ash columns (Table 3). This shows the extent of
alkalinity of the ash and the extent of influence of this strong alkalinity on the chemistry of the leaching solution. The pHs subsequently decreased to $\approx 9$ at the end of 10 PVs in all columns. Nonetheless, such high pHs have been shown to solubilize OM (Stevenson, 2001).

**Table 3**

<table>
<thead>
<tr>
<th>Leaching solution</th>
<th>Column material</th>
<th>Copper $^a$ (µg)</th>
<th>Nickel $^a$ (µg)</th>
<th>DOC $^a$ (mg)</th>
<th>In $^a$ C (mg)</th>
<th>$I$ (mol dm$^{-3}$) $^b$</th>
<th>Initial pH $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>Ash</td>
<td>360 a</td>
<td>50 a</td>
<td>48</td>
<td>580</td>
<td>0.20</td>
<td>10</td>
</tr>
<tr>
<td>Deionized water</td>
<td>Ash + A</td>
<td>320 b</td>
<td>79 a</td>
<td>210</td>
<td>660</td>
<td>0.23</td>
<td>10</td>
</tr>
<tr>
<td>Deionized water</td>
<td>Ash + A + Bh</td>
<td>320 b</td>
<td>73 b</td>
<td>390</td>
<td>1280</td>
<td>0.21</td>
<td>10</td>
</tr>
<tr>
<td>HA</td>
<td>Ash</td>
<td>66 c</td>
<td>35 b</td>
<td>4</td>
<td>450</td>
<td>0.38</td>
<td>11</td>
</tr>
<tr>
<td>FA</td>
<td>Ash</td>
<td>11 d</td>
<td>7 c</td>
<td>1</td>
<td>490</td>
<td>0.36</td>
<td>11</td>
</tr>
<tr>
<td>HAF A</td>
<td>Ash</td>
<td>64 c</td>
<td>44 a</td>
<td>14</td>
<td>850</td>
<td>0.39</td>
<td>11</td>
</tr>
</tbody>
</table>

Means within a column followed by the same letter are not significantly different ($p < 0.05$) using Student t-test.

$^a$ Measured in the first 50 ml of leachate.

$^b$ pH and ionic strength were measured in the first PV of leachate. pH values initially started off high in both sets of columns but they decreased to $\approx 9.5$ after 50 ml leachate had eluted through the columns.

Fig. 2. The variation of chloride in (A) water-leached and (B) organic acid-leached columns.
1994). In fact, the classical OC extraction methods employ an alkaline solution (NaOH) to solubilize OM (Schnitzer, 1969). The effects of such high pHs on OM–metal associations, solubility, and leachability are discussed in a latter section.

The ECs of the leachates from the water-leached columns were not significantly different \((p>0.05)\) from each other (13.8, 16, and 14.3 dS m\(^{-1}\) in the first PV in the ash, ash + A, and ash + A + Bh columns, respectively), but were at least six times higher than the typical EC of most soils \((<2\ \text{dS}\ \text{m}^{-1}\), Sposito, 1989). The ECs from the organic acid-leached ash columns were significantly higher than those from the water-leached ash columns \((p<0.05)\) but they were not significantly different from each other (25.3, 24.5, and 26 dS m\(^{-1}\) in the first PV of the HA, FA, and HAF-leached ash columns, respectively). The higher EC in the organic acid-leached columns (10–15 times higher than typical soil solutions) had a strong bearing on the solution chemistry of those columns. The ionic strength in those columns was almost double that of the water-leached columns \((\sim 0.21\ \text{vs.}\ 0.37\ \text{mol dm}^{-3}\) for water- and organic acid-leached ash columns, respectively, Table 3), hence, favouring precipitation of most of the soluble organics and affecting solute transport as discussed in subsequent sections. The ionic strength of most soil solutions ranges from \(\sim 0.005\ \text{mol dm}^{-3}\) in the tropics to \(\sim 0.1\ \text{mol dm}^{-3}\) in the less weathered temperate soils (Naidu et al., 1994).

The emission spectra of the soil and soil-ash samples showed an increase in the fluorescence intensity (Fig. 3, 900-A) immediately after ash incorporation but the intensity decreased with the time (Fig. 3, 900-B). The increase in fluorescence intensity is related to

![Fluorescence spectra of DOC from the experimental soil](image)
the presence of electron-donating groups, e.g., COOH, and the decrease is related to increase of the molecular size. This suggests that ash incorporation increased OM–metal interaction. Copper, in particular, has been shown to have high association with OM (Bloomfield and Pruden, 1980; McBride, 1981; Rivero et al., 1998). The shape of the peaks was generally not affected, suggesting that although ash was applied at these high rates, it did not significantly change the original soil HA. These observations were supported by the classification system by Kumada (1987). According to this system, the plot of RF against $\Delta \log k$ shows the degree of aromaticity and the relative contents of the various functional groups in the OM fraction (Fig. 4). The HA at the beginning of the study was classified as type A, signifying high aromaticity and high concentrations of functional groups of the carboxyl type. The HA fraction generally had relatively lower functional groups than those in the FA fraction. This is in agreement with current knowledge on the behaviour of HA and FA (Rivero et al., 1998; Stevenson, 1994). Nonetheless, the high aromaticity and high content of hydroxyl groups has important implications on the reactivity of both fractions with the ash. The high content of functional groups promotes OM–metal association. The $E_4/E_6$ ratio for FA and HA was 3.53 and 4.86, respectively, indicating high molecular condensation for both, with FA also showing the presence of relatively high molecular sizes.

The sandy soil used in this experiment did not sorb significant amounts of Cu (<5% sorbed from the 200 mg l$^{-1}$ solution, data not shown). By comparison, a considerable amount of Ni (up to 25% in the 50 mg l$^{-1}$ solution, data not shown) was sorbed. These two concentrations were used for comparison because they corresponded to the solution concentration of Cu and Ni added by the ash at the application rate used in this study. The relative Ni concentrations available in the ash were lower than those of Cu (Table 1). Therefore, a small reduction in Ni concentration had a noticeable effect on the different Ni

Fig. 4. The classification system according to Kumada (1987), where (A) HA with bigger evolution degree and stability, rich in aromatic carbon, and carboxylic groups. (B and $P_0$) Transitory forms of HA in the evolution towards the more stable (A), $R_p$ have high concentration of alkyl carbon. $P_1P_0$: Transitory forms of the HA, rich in functional groups, characteristic of soil with very low pH.
fractions. Batch studies also showed that 95% of the water-soluble Cu and Ni were dissolved from ash into solution within 12 h and continuous shaking over a period of 48 h did not lead to increased dissolution (data not shown).

3.1. Cu and Ni leaching in the water-leached soil/ash columns

Approximately 80% of the total water-leachable Cu and Ni were leached out by the fourth PV (Fig. 5). This represents an equivalent of 2 years of rainfall at the site where the ash was applied. Leachate Cu concentrations in water-leached ash and ash + soil columns were greater than those in the organic acid-leached ash columns in the first 50 ml of leachate ($p < 0.05$; Table 3). Due to the differences in the total weight of column constituents, 50 ml represent 10, 5.7, and 4.7 PV for the ash, ash + A, and ash + A + Bh columns, respectively.

A 30% to 66% of the water-soluble Cu was leached out from the ash. The lower concentrations in the columns with a Bh horizon were possibly due to the higher Cu retention in the Bh layer due to higher residence time of the leaching solution, a consequence of layering. The leaching patterns of Cu were different from those of Cl (did not follow the same breakthrough curves), indicating that Cu was actively interacting with the solid matrix, unlike Cl (Figs. 5 and 6).

Copper was directly dissolved from the ash matrix into solution where it may have been hydrolyzed to Cu$_2$(OH)$_2$$^{2+}$ and Cu(OH)$^+$ (Baes and Mesmer, 1976), both of which complex with both chloride and OM to form stable but readily leachable compounds. Although many researchers have reported most of the Cu in soils to be bound to OM (McBride, 1981), more than 80% of Cu can be complexed with Cl when Cl concentrations are sufficiently high (Doner et al., 1982). Although Cl exists mostly in free form, significant amounts can be found as complexes in solution. The average concentration of Cl in the first five PVs in the ash columns was $\sim 310$ mg l$^{-1}$ compared to 190 mg l$^{-1}$ for DOC (Table 3, Fig. 5). Doner (1978) showed that Cu(II) can complex with Cl to the same extent that it can with OM and that the stability of these complexes depends on Cl concentration. Copper commonly exists as Cu(CO$_3$)$_2$$^{2-}$ and Cu(OH)$_4$$^{2-}$ under alkaline conditions (McBride, 1981) similar to those in our study (pH 9–11) and may also have been leached out in these forms. Sanders and Bloomfield (1980) showed that the solubility of CuCO$_3$ was not pH dependent and this species accounted for a significant fraction of soluble inorganic Cu in solution at neutral and alkaline pH as long as there was sufficient carbonate present. However, the Cl complexes were more important due to high concentrations of Cl (>1200 mg l$^{-1}$ in first PV, Fig. 4).

In contrast to the ash-only columns where Cu–Cl played a significant role, Cu leaching in the ash + A and ash + A + Bh columns (Fig. 5) was influenced more by the presence of DOC because Cu preferentially complexes with DOC (Stevenson, 1994). The average DOC concentrations in the first five PVs were 210 and 390 mg l$^{-1}$ for the ash + A and ash + A + Bh columns, respectively, compared to 48 mg l$^{-1}$ in the ash-only columns (Table 3). The reduction in Cu leaching in the ash + A and ash + A + Bh columns was possibly due to complexation with DOC, which was subsequently immobilized due to the high EC in those columns. This is not unusual because there were sufficiently high concentrations of OM with a very high proportion of functional groups (Fig. 4) and the
extremely high ionic strength of the leaching solution. There are numerous comprehensive publications on Cu association with DOC. Baham and Sposito (1986) observed an increase in Cu solubility in the presence of excess metal complexing ligands and

Fig. 5. Variation of Ni and Cu with pore volume in (A) ash, (B) ash + A, and (C) ash + A + Bh columns.
postulated that this was due to the increase in stability of the metal–ligand complexes. High pH increases the stability of these complexes due to the decrease in proton competition (Innskeep and Baham, 1983; Elliot and Huang, 1979; Davis, 1984). The

Fig. 6. Variation of Ni and Cu with pore volume in (A) HA-, (B) FA-, and (C) HAFA-leached ash columns. The concentrations were normalized to those of the combined HAFA. The substantial decrease of Cu and Ni in FA-leached columns is evident.
disruption of OM-soil inorganic phase bonds at high pH maintains the solubility of OM and increases its availability for reaction (McBride and Blasiak, 1979). However, increased ionic strength negates this, leading to high proton competition and favouring precipitation of the organics with Fe and Al present in solution.

The total amounts of Cu leached in the first five PVs in the ash + A and ash + A + Bh columns (320 and 320 µg, respectively) were lower than \((p < 0.05)\) those in the ash-only columns (360 µg, Table 3). The presence of soil reduced Cu leaching from the columns. Organic matter has been shown to coat the exposed surfaces of materials in natural systems. For example, Davis (1982) and Tipping (1981) reported that almost all suspended solid surfaces in water were coated by adsorbed OM. Although the OM content of our soil was very low (<1%, Table 2), several researchers have shown that it has a capacity to contribute significant amounts of surface area. Peret et al. (1994) showed that 40% to 70% of the total surface area in a Rhine River sample was due to colloids \(<200 \text{ nm} \) despite the fact that this fraction accounted for only 1.5% of the total mass. Organic matter precipitation/adsorption is strongly favoured at high ionic strength, Fe, and Al concentrations. Therefore, Cu was possibly retained within the soil matrix in association with precipitated DOC in the ash and ash + soil columns. Both Cu and DOC leaching were strongly negatively correlated to ionic strength (with correlation coefficients of \(-0.97\) and \(-0.69\), respectively, data not shown). Therefore, while the mixing of ash with soil in our columns provided sufficient surface area that facilitated more OM to dissolve, the high ionic strength \((>0.2 \text{ mol dm}^{-3}, \text{ Table 3})\) promoted precipitation of the DOC, which in turn led to the retention of Cu within the columns. On the other hand, the ionic strength did not affect Cl leaching in these columns. Chloride dissolution rate from the ash and the solution flow rate were still the main factors affecting Cl leachability, hence, the difference in the leaching patterns of Cu and Cl.

Nickel leaching in the ash-only column was not significantly different \((p>0.05; \text{ Table 3})\) from the ash + A and ash + A + Bh columns. Mixing ash with the surface soil did not increase Ni leaching although the DOC increased from \(<50\) to \(210 \text{ mg l}^{-1}\) (Table 3). When the Bh horizon was included, 25% less Ni was leached \((p<0.05)\). This reduction in leached Ni may be due to increased adsorption in the Bh horizon. The increased leaching solution residence time in the Bh horizon columns may also have allowed adsorption or precipitation processes to reach equilibrium at higher values (favouring adsorption and precipitation). Clearly, Ni did not complex with DOC to the same extent as Cu in these columns.

The soil chemistry of Ni is relatively simple and is based on the divalent metal ion \(\text{Ni}^{2+}\). The \(\text{Ni}_4(\text{OH})_4^{4+}\) ion has been shown to be the predominant polymer in salt solutions of Ni(II) (Christensen et al., 1996). At high pH, Ni precipitates as \(\text{Ni(OH)}_2\), hence, this was not the species responsible for Ni loss in our columns. Nickel does not complex with OM as strongly as Cu. Christensen et al. (1996) observed that at these high pHs, chloro-complexes were negligible but carbonate complexes accounted for \(>90\%\) of dissolved Ni up to concentrations of 9%. Sposito and Page (1984) made similar observations, noting that the dominant species were \(\text{NiCO}_3^0\) and \(\text{NiHCO}_3^{+}\) in their system. These species may have contributed to the high initial leaching of Ni in our columns because of the high concentrations of carbonates and inorganic carbon in our ash (Table 3). The correlation coefficients of Cu and Ni with inorganic C were 0.40 and 0.60,
respectively (data not shown). Wang et al. (1997) showed that Ca competes for adsorption sites with Ni, hence, the presence of high concentrations of Ca and \( \text{CO}_3^{2-} \) may have led to the high Ni leachability (initial concentration in ash only, 10 mg/l) in this study.

3.2. Cu and Ni leaching in organic acid-leached ash columns

As noted previously, a smaller amount of Cl was leached at the end of the fourth PV in the organic acid-leached ash and ash + soil columns than that in water-leached columns (Fig. 4). This showed that the organic acids were dissolving less Cl from the ash than deionized water. We suspect that this might also apply to Cu and Ni, i.e., there might also have been differences in the dissolution of Cu and Ni from the ash due to the differences in leaching solutions. Chloride seemed to exhibit differential solubility in each organic acid, with the HAFA fraction leaching out the highest concentration of Cl, followed by HA, and FA. The differences between the HAFA- and HA-leached Cl were not statistically different. However, Cl leached from the FA columns was significantly lower than the other two fractions (\( p < 0.05 \)).

An interesting observation from this study was that the leachate pH of the acid-leached columns was even higher than that of the water-leached columns (~11 compared to ~10 for water-leached columns). This was a testament to the strong alkalinity of the ash and the nature of salts formed by the neutralization reaction between the ash and leaching solution. The ionic strengths of these solutions were also much higher than those from water-leached columns (~210 vs. 370 mmol dm\(^{-3}\) in the water- and acid-leached columns, respectively). Copper mobility from organic acid-leached ash columns was much lower than that in water-leached ash columns. The amounts of Cu leached in 50 ml were 66, 11, and 64 \( \mu \)g for HA, FA, and HAFA, respectively, compared to 360 \( \mu \)g for water (Table 3). Only 2%, 10%, and 12% of the total water-soluble Cu was leached out in the FA-, HA-, and HAFA-leached columns, respectively. This decrease in leaching can be explained by the flocculation of Cu–OM complexes due to the very high ion activity in the organic acid-leached columns (Table 3). The mean total DOC leached in the organic acid-leached columns was 5 mg compared to 48 mg in the water-leached columns, indicating higher precipitation in the acid-leached columns (Table 3). Each organic acid fraction (HA and FA) had DOC concentrations of approximately 1000 mg/l before being leached through the columns. The DOC concentration in the combined fraction (HAFA) was almost double that in each separate fraction. Significantly higher DOC was expected in the acid-leached columns because the acid fractions (constituting a large part of DOC) had been extracted by an alkali (stronger extractant than deionized water) from the topsoil and used as the leaching solution. Unlike the acid-leached ash columns, the DOC in the water-leached ash columns was a result of OM dissolution from the ash only as the leaching solution travelled through the column.

The presence of large quantities of Ca and Mg in our columns (100 and 9 g kg\(^{-1}\) Ca and Mg in ash, respectively) also possibly increased the formation of ternary complexes and/or acted as cationic bridges between OM and soil surfaces (Greenland, 1970). The reduction in Cu concentration was highest in the FA columns (Fig. 6B) possibly due to the higher reactivity of FA and its high tendency to flocculate faster under conditions of high ionic strength (Oden et al., 1993). While it is acknowledged that the solubility of Cl is
different from that of Cu, these results seem to suggest that the column material interacted more with Cu than Cl. Flocculation was more favoured in the organic acid-leached columns because we supplied readily available DOC to these salt-laden columns than in water-leached columns in which only water-soluble DOC (from ash) was dissolved by the leaching solution.

Nickel leaching in the HADA-leached columns was comparable to that in the water-leached columns (44 μg compared to 50 μg; Table 3). The lower concentration of FA-leached Ni suggested possible reaction and subsequent flocculation of Ni with the highly surface reactive FA. About 9% of the total Ni in the ash was leached in the water-leached columns compared to just above 8% (p>0.05) in the HADA-leached columns. Similar to Cu, Ni concentrations in the HA- and FA-leached fractions were additive (Fig. 6).

These observations are different from the results from an earlier study by Chirenje and Ma (1999) in which the presence of DOC resulted in greater metal leaching in all treatments. The difference may be in the fivefold change in the ionic strengths of the leaching solutions emanating from the different solution to solid ratios in the two studies (ionic strength in previous study ~ 0.05–0.08 compared to 0.2–0.4 mol dm$^{-3}$ in this study). The increased ionic strength as a result of lower solution to solid ratio in the current study (1.5 vs. 1), hence, favoured precipitation of DOC and reduced Cu leaching. However, since Ni does not complex with DOC to the same extent as Cu, the reduction in Ni leaching was much less than that of Cu in the organic acid-leached ash columns.

4. Conclusions

This study demonstrated that the extent of OM-facilitated metal transport in soil columns depends on the mobility of the OM–metal complexes within the system and this mobility is in itself governed by a variety of factors. While the soil used in this study was sandy, the addition of ash increased soil pH, which commonly favours OM dissolution but the high ionic strength resulting from the salts in the ash also created conditions favourable for flocculation and precipitation of OM. Trace elements that have a strong tendency to form complexes with OM (e.g., Cu) are affected by these dynamics to a greater extent than those with a lower tendency to form metal–organic matter complexes (e.g., Ni). It is important to note that the heterogeneous complexing nature of the organic ligands (where opposing processes occur simultaneously in the system) may have confounded our results. Nonetheless, in general, the prevailing soil chemical properties may be more important in determining the movement of metals through soil columns if the metals are moving in association with specific complexes (e.g., OM) than the properties of the metals themselves. However, these specific properties of the metals should not be ignored because they determine the type of associations these metals make with soil constituents.

References

Baham, J., Sposito, G., 1986. Proton and metal complexation by water soluble ligands extracted from anaerobically digested sewage sludge. J. Environ. Qual. 15, 239–244.


