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Leaching of As and Cr in Wood-Ash-Amended Soil Columns

Tait Chirenje, Carmen Rivero, and Lena Q. Ma*

High volume application of wood ash as a soil amendment in forested areas may introduce toxic elements to these ecosystems. Column studies were conducted under unsaturated conditions to determine As and Cr leachability in wood ash-amended soil columns. Three treatments were used in columns 1.8 cm diameter and 20 cm long: (a) ash alone, (b) ash mixed with topsoil at 900 Mg ha^{-1} application rate, and (c) ash mixed with topsoil overlying a spodic horizon. Water, humic, fulvic, and a mixture of humic and fulvic acids were also used to leach ash in separate columns. Leachate concentrations of organic carbon, Cl$^-$, As, and Cr and pH were determined. There was higher As and Cr leaching in the water-leached ash and soil-ash columns than in the acid-leached ash columns. The lower Cr leaching in HA-leached columns was due to the high reaction between Cr and HA. There was also lower dissolved organic carbon (DOC) leached in the acid-leached ash columns due to possible flocculation. Mixing ash with soil led to a higher increase in Cr leaching than As, which flocculated with DOC in the columns. High ash pH dissolved OC but high ionic strength led to DOC-oxyanion flocculation in this study.

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INTRODUCTION

Relatively few researchers have investigated the leachability of oxyanions under conditions of extremely high pH and salinity. This study examined the effects of high rate application of wood-fired boiler ash on the mobility of As and Cr. Chromium is treated as an oxyanion in this study because its only common stable cationic form, Cr^{3+}, is not very mobile under typical soil conditions (Shupak, 1991). The more mobile and toxic Cr (VI) does not exist as a free ion, but as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), or chromium trioxide (CrO_3), which all behave as divalent anions rather than hexavalent cations (Kimbrough *et al.*, 1999). This investigation is a compliment of a study presented elsewhere in a companion paper (Chirenje and Ma, 2002; in press) in which the leachability of the cationic metals (Cu and Ni) under the same conditions was determined.

Wood ash derives its salinity and alkalinity from wood bark processing methods (priming) and its constituents (principally salts and oxides of Ca, K, Fe, Al, Mn, Na, and Mg, and trace elements, including As and Cr [Pepin and Coleman, 1984]). While most of the factors that affect the solubility and availability of metals from ash apply equally to the dissolution and leachability of oxyanions, their effects may be opposite due to the differences in charge between these species (metal ions are positively charged, while oxyanions are negatively charged). The conditions under which these factors are most predominant also vary due to these charge differences. In general, trace element leaching is not of major concern when land application of wastes is carried out at agronomic rates. However, extremely high application rates were used erroneously at a forested site in this case, with the mistaken intention of increasing moisture content. While this turned out to be a bad idea, it gave the authors an opportunity to study the leachability of different trace elements under these extreme conditions of high pH and ionic strength when approached to find solutions to the problems at the site.

Understanding the processes governing the migration of oxyanions is essential for predicting the environmental and health impact of spreading wastes on land (Stumm and Morgan, 1981; Sposito *et al.*, 1982). For instance, large doses of Cr in human blood have been shown to cause chronic liver and kidney damage (National Institute of Occupational Safety and Health [NIOSH], 1999) and tubular necrosis. On the other hand, arsenic has been shown to be teratogenic and fetotoxic as well as being a possible carcinogen in humans (Kurzel and Cetrulo, 1981).

Earlier studies of the ash used in this study have shown the leachability of its constituent elements to be highly correlated with DOC leaching (Chirenje and Ma, 1999). We suspected that there could be other factors that were being masked by this association because, in general, oxyanions do not complex with organic acids. In general, organic matter (OM) is tied up by Fe and Al in naturally acid soils (Tyler and McBride, 1982). In neutral to alkaline soils, OM is considerably more capable of complexing with trace metals. However, there may have been other factors affecting the mobility and association of this "free" OM with oxyanions, hence the ash was leached with different organic acids.

An unintended artifact in our study, high ionic strength, added to the complexity of the leaching solution by increasing the likelihood of DOC to flocculate. All ions associated with DOC hence were taken out of the mobile phase. Another important consideration was the neutralization reaction between the organic acids used as leaching solutions and the calcite in the ash. That reaction yielded bicarbonate, which in turn buffered the pH of the resulting solution at a very high pH, affecting the solution chemistry of the mobile phase.

There is relatively little evidence in the literature of adsorption of Cr by OM. Eary and Rai (1991) showed that Cr (III) and Cr $(OH)^{2+}$ can bind to solids that have exposed negatively charged edges, for example, surfaces of OM, but the pH range under which Cr (III) exists is very low and narrow. In fact, Cr (III) does not exist as a free ion above pH 3.8 and Cr $(OH)^{2+}$ does not exist in solution above pH 6.3. Because Cr (VI) commonly exists as negatively charged chromate ions, these species do not have strong affinities for any DOC, unless they are bonded through Fe or other metals, for example, Al. Chromium (VI) does, however, have a strong affinity for HA (Rivero *et al.*, 1998). Hence, the presence of high concentrations of HA in solution had important implications in this study.

Arsenic association with OM has been well documented (Cullen and Reimer, 1989; Xu *et al.*, 1991). Arsenic is converted to volatile organics through biomethylation by microbes over a wide range of pH. Takamatsu *et al.* (1982) reported high levels of As (III) and dimethylarsinate ($(CH_3)_2AsO(OH)$) under high pH conditions; high levels of As (V) and monomethylarsonate ($(CH_3)AsO(OH)_2$ pK_a of 4.19 and 8.77, respectively) occurred at low pH and oxidized conditions. However, arsenic leaching from soils is generally limited by adsorption on Fe and Al oxides and clay surfaces. This is particularly so in our study where the highly saline and alkaline conditions limited microbial activity.

The behavior of As (V) has been shown to be similar to that of P due to the near similarities of the pK_as of their respective acids. The successive pK_as for H_3AsO_4 at 25°C are 2.2, 6.9, and 11.5, and the corresponding values for H_3PO_4 are 2.2, 7.2, and 12.4 (Cullen and Reimer, 1989). Therefore, under the conditions of this study, the high solubility of DOC (from the high pH) may facilitate arsenic leachability. In a study of sediments along the Xiangjiang River in China, Chunguo and Zihui (1988) showed that arsenic was mainly bound as Al-, Fe-, Ca-, and Fe-occluded arsenate, just like P. Lesser species were soluble As (III), and soluble and insoluble organic arsenic.

Similar to the Cu/Ni study (Chirenje *et al.*, 2002; in press), the specific objectives of this investigation were to study: (1) the role of organic acids (HA and FA) in the leaching of As and Cr, and (2) to determine the effects of soil from different horizons on As and Cr dissolution and leachability from ash.

MATERIALS AND METHODS

The materials (the soil and ash) and methods used in this article are discussed in detail in Chirenje *et al*. (2002; in press). The only difference was in the trace elements analyzed (oxyanions in this paper vs. cations in Chirenje *et al*., 2002). Selected chemical, physical, and other properties of the ash and soil are shown in Tables 1 and 2. The set up of the columns was done as described by Nielsen and Biggar (1961), with minor modifications as described by Chirenje *et al*. (2002). The set-up is shown in Figure 1. The polyethylene columns used in this study were 20 cm long, with 1.5 cm internal diameter. All columns were packed dry (to approximate field bulk density, ~ 1500 kg m^{-3}) and wetted at the beginning of the experiment.

The OM fractions used in this study were extracted from the soil found at the ash application site 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 (8 *g*) 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. Humic acid was brought into solution by adding deionized water and both solutions were adjusted to a pH of 5.6, which is the pH of the soil (Table 1). The third extract, a mixture of both fractions (HAFA), was extracted using 0.1 N NaOH and adjusted to pH 5.6 using 2 N HCl. Separate fractions of HA and FA were purified in preparation for further analysis.

Leaching of As/Cr in Water-Leached Soil/Ash Columns

Three columns were packed separately with (1) 5.3 g ash (ash), (2) 5.3 g ash mixed with 14 g of soil from the A horizon (ash + A), and (3) 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 columns were leached with deionized water at a rate of one PV every 3 days to compare the effects of soils from different horizons on the leachability of heavy metals.

Leaching of As/Cr in Organic Acid-Leached Ash Columns

In this study, three columns, similar in dimensions to those in the first study(water leached columns), 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 coincidentally, deionized water), were used to leach the ash columns.

TABLE 1
Elemental Concentraions of the Wood Ash and Soil (A Horizon) Used in This Study

	Element																
	$g\ kg^{-1}$							$mg\ kg^{-1}$									
	Ca	Na	Mg	K	Al	Fe	P	Mn	Zn	Ba	Pb	Cu	Se	Ni	Cr	As	Cd
Ash	100	26.0	9.00	8.00	8.00	7.00	3.00	14.0	0.70	7.00	1.30	1.00	19.0	10.0	2.00	2.00	3.00
Soil	0.10	0.04	0.90	0.03	2.00	0.80	0.10	14.0	0.70	7.00	1.30	1.00	0.70	5.00	4.00	0.40	0.50

TABLE 2
Comparison of Characteristics of Wood Ash and Soil (A Horizon) Used in This Study

	Soil / Ash Parameter										
	$CaCO_3$ (g kg^{-1})	pH	Alkalinity	EC (dS m^{-1})	OM (%)	Sand (%)	Silt (%)	Clay (%)	Minerals		
Ash	250	11.4	55000	78.0	25	48.1	34.0	17.9	Calcite ~20%	Gypsum ~2%	Quartz <5%
Soil	0.00	5.60	0.14	2.00	<1	94.9	1.90	3.20	Kaolinite >1%	Gibbsite >1%	Quartz >10%

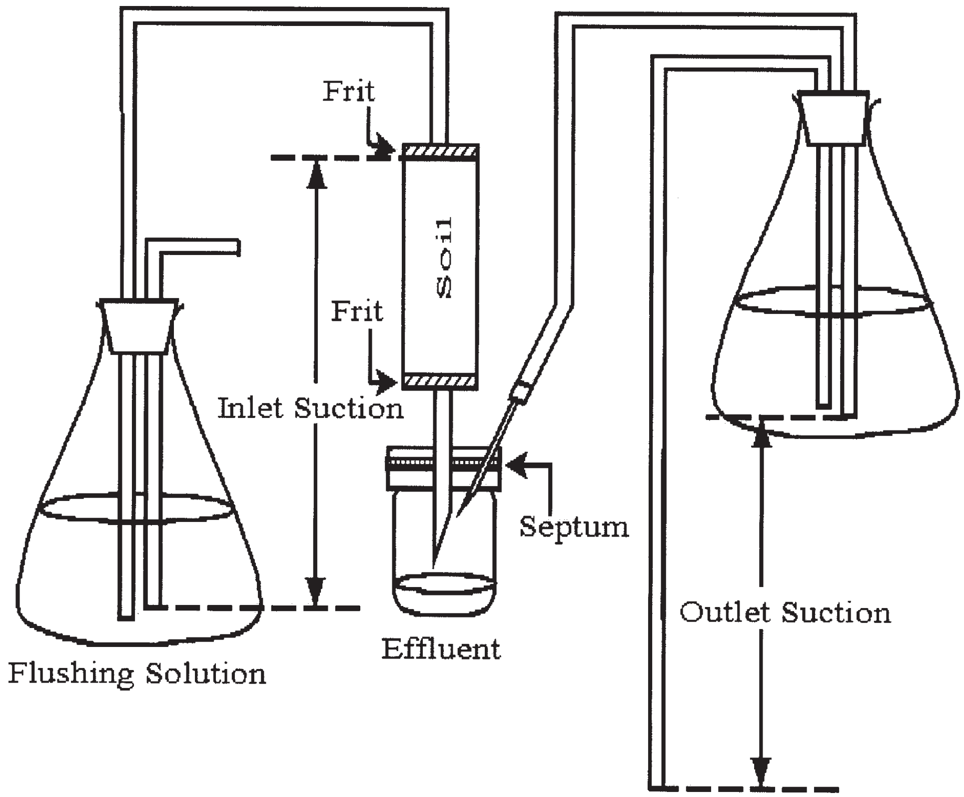

FIGURE 1

Set up of the leaching experiment under unsaturated conditions (figure by Dean Rhue).

Chemical Extraction and Analyses

Water-soluble As and Cr 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 HNO_3 acid, and digested in a CEM MDS-2000 microwave sample preparation system (Matthews, NC) using EPA method 3051 (USEPA, 1986). Total concentrations of As and Cr 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 pH and electrical conductivity (EC) were determined using a Fisher Accumet model 20 pH/conductivity meter (Pittsburgh, PA). The total organic carbon was determined on a Shimadzu TOC 5050 carbon analyzer (Columbia, MD). The bulk density of the control soil and ash were calculated from soil core samples collected from the field. The bulk density was determined by measuring the weight of soil in the core and dividing it by the volume of the core. Mineral characterization was done on the samples using X-ray diffractometer (Nicolet XRD Madison, WI) using CuKα radiation of aluminum powder mounts (Whitting and Allardice, 1986). The samples were also analyzed on a thermogravimetric analyzer (TGA, Omnitherm Corporation). Particle size analysis was done using Stoke's law of sedimentation. Fifty grams of soil were weighed into a 1000-mL cylinder and hydrometer readings were taken at predetermined intervals to determine the amount of sand and silt particles that had settled out.

The association of HA and FA with As and Cr 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 to 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 κ is EC (dS m^{-1}).

RESULTS AND DISCUSSION

The leaching of chloride (Cl^-) from the ash was used for comparison as a conservative tracer in the columns (Figure 2). Over 99% of the potentially leachable Cl^- had leached out after the third PV in the water-leached columns. Slow dissolution was probably the cause of the delay in the breakthrough for Cl^- 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). An average of 90% Cl^- had leached out by the end of the fourth PV in the organic acid-leached ash columns.

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). The pH of all solutions used in the column study had all been adjusted to 5.6 at the beginning of the study. This shows the extent of alkalinity of the ash and the extent of influence of this strong alkalinity on the solution chemistry of the leaching solution. There was a modest decrease in pH to ~9 at the end of 10 PVs in all columns.

The ECs of the leachates from the water-leached columns were much higher than the typical EC of most soils (<2 dS m^{-1}, Sposito, 1989), but they were not

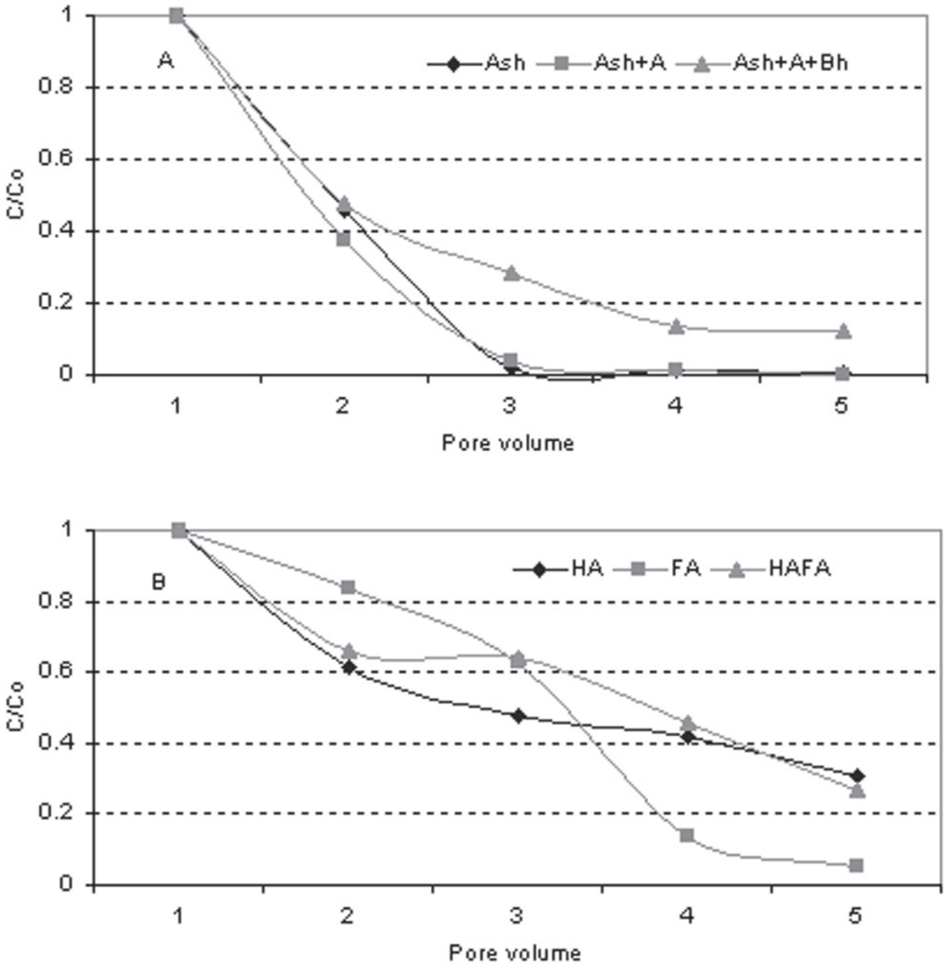

FIGURE 2

The variation of chloride in (a) water-leached columns and (b) organic acid-leached ash columns .

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). The EC from the organic acid-leached ash columns were significantly higher than those from the water-leached ash columns ($p < 0.05$), and they were also not significantly different from each other (25.3, 24.5, and 26 dS m^{-1} in the first PV of the HA, FA, and HAFA-leached ash columns, respectively). The ionic strength of most soil solutions ranges from ~0.005 mol dm^{-3} in the tropics to ~0.1 mol dm^{-3} in the less-weathered temperate soils (Naidu *et al*., 1994). The higher EC in the organic-acid-leached columns had a strong bearing on the solution chemistry of those columns.

TABLE 3
Total Amounts of As, Cr, Inorganic Carbon and DOC Leached in the First 50 mL and Ionic Strength and pH in First Pore Volume of Each Column

Leaching solution	Column material	Arsenic	Chromium	DOC	In C	I (mol dm^{-3})	Initial pH†
		------- µg ------		----- mg ----			
Deionized water	Ash	11^{a}	120^{a}	48^{a}	580^{a}	0.20^{a}	10
Deionized water	Ash + A	20^{b}	260^{b}	210^{b}	660^{a}	0.23^{a}	10
Deionized water	Ash + A + Bh	40^{c}	590^{c}	390^{c}	1280^{b}	0.21^{a}	10
HA	Ash	41^{c}	69^{d}	4^{d}	450^{c}	0.38^{b}	11
FA	Ash	22^{b}	240^{b}	1^{d}	490^{a}	0.36^{b}	11
HAFA	Ash	23^{b}	250^{b}	14^{d}	850^{d}	0.39^{b}	11

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

† pH values initially started off high in both sets of columns but they decreased to ~ 9.5 after 50 mL leachate had eluted through the columns.

The ionic strength in those columns was almost double that of the water-leached columns (~210 vs. 370 mol dm^{-3} for water- and organic acid-leached ash columns, respectively, Table 3), hence favoring precipitation of most of the soluble organics and affecting solute transport, as discussed in subsequent sections.

As discussed in Chirenje *et al.* (2002), the emission spectra of the soil and soil-ash samples showed an increase in the fluorescence intensity (Figure 3, 900-A) immediately after ash incorporation. However, the intensity decreased with the time (Figure 3, 900-B). The increase in fluorescence intensity can be attributed to the presence of electron-donating groups, for example, COOH, and the decrease is related to increase of the molecular size. Therefore, ash incorporation increased OM-metal interaction. Although ash was applied at these high rates, it did not significantly change the original soil HA, as observed from the small change in the shape of the peaks. These observations were supported by the classification system by Kumada (1987).

According to the Kumada classification 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 (Figure 4). According to Figure 4, the HA at the beginning of the study was classified as type A, signifying high aromaticity and high concentrations of carboxyl functional groups. The HA fraction generally had relatively lower functional groups than those in the FA fraction. However, the high aromaticity and high content of hydroxyl groups has important implications on the reactivity of both fractions with the ash. 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.

Although only very low concentrations of arsenic were added in the batch study (as As trioxide), the soil used in this experiment did not adsorb significant amounts of arsenic (data not shown). Considerably higher amounts of Cr, added as potas-

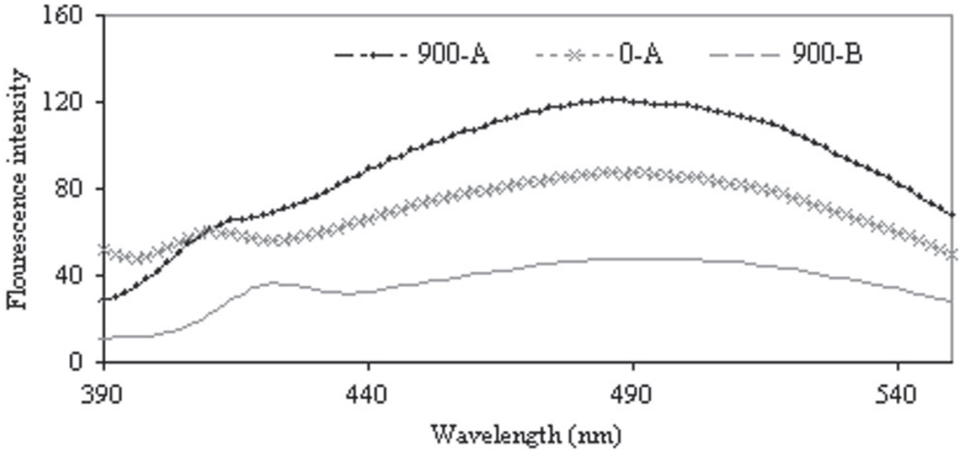

FIGURE 3

Flourescence spectra of soil humic acid, where: Control = 0 mt/ha ash treatment at the beginning of the study, 900-A = 900 mt/ha ash treatment at the beginning of the study, 900-B = 900 mt/ha ash treatment after 20 months.

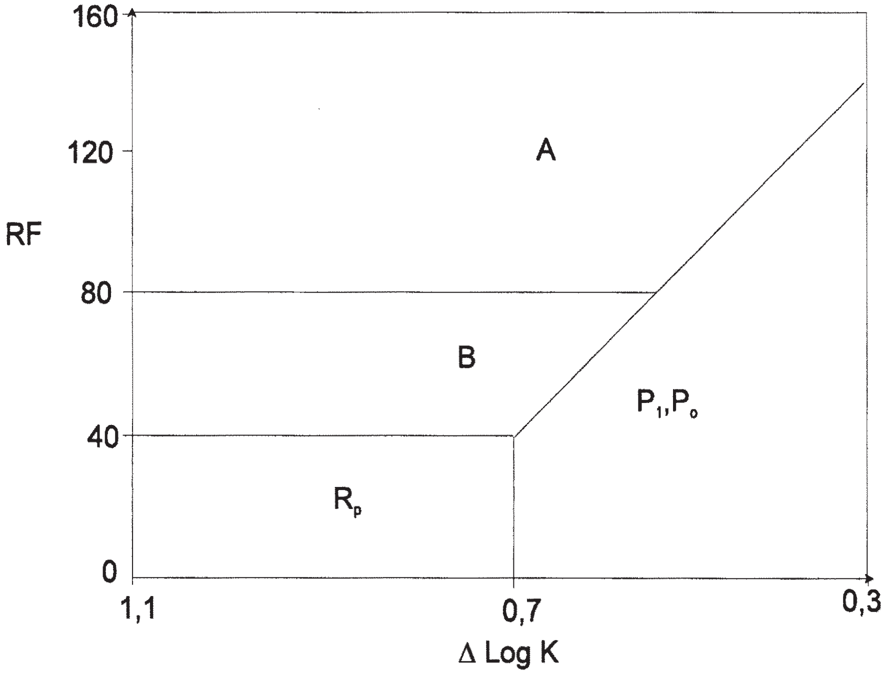

FIGURE 4

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 Rp: Transitory forms of HA in the evolution towards the more stable A, Rp have high concentration of alkyl carbon, P_1,P_0: Transitory forms of the HA, rich in functional groups, characteristic of soil with very low pH.

sium dichromate ($K_2Cr_2O_7$), were adsorbed by the soil (data not shown). Batch studies showed that Cr desorption was very fast and nearly 25% of the total Cr was desorbed within 6 h of shaking. The relative amounts of Cr and As desorbed in these batch studies was much higher than the corresponding concentrations of these elements in the column leaching experiments. This was possibly due to the shaking, longer contact time, and exposure of more solution to ash surfaces allowing more Cr to dissolve in the batch study. Dynamic equilibrium between leaching solution and particle surfaces was possibly reached at lower absolute concentrations in the columns due to the lower liquid to solid ratios used. Up to one-eighth of the total arsenic was also desorbed at the end of 12 h. Continuous shaking over a period of 48 h did not lead to increased desorption in either element.

In general, the two oxyanions (Cr and As) leached faster than the cations (Cu and Ni, Chirenje *et al.*, 2002; in press). More than 90% of the water-soluble As and Cr had been leached out by the end of the third PV (Figure 5) compared with 4 PV in the case of Cu and Ni (Chirenje *et al.*, 2002; in press). The increased concentration in the fourth PV leachate was due to the delay in leaching the columns. A period of 2 weeks was used as the interval compared with 3 days in all the other samples and this gave As and Cr more time to dissolve.

Arsenic/Chromium Leaching in Water-Leached Soil/Ash Columns

The total concentration of both Cr and As in the ash was 2 mg kg^{-1}, and this was 0.5 and five times the concentrations in the soil respectively (Table 1). Although these concentrations seem relatively low, the high solubility of both elements from the ash matrix and the large amounts of ash applied in the field plots warranted

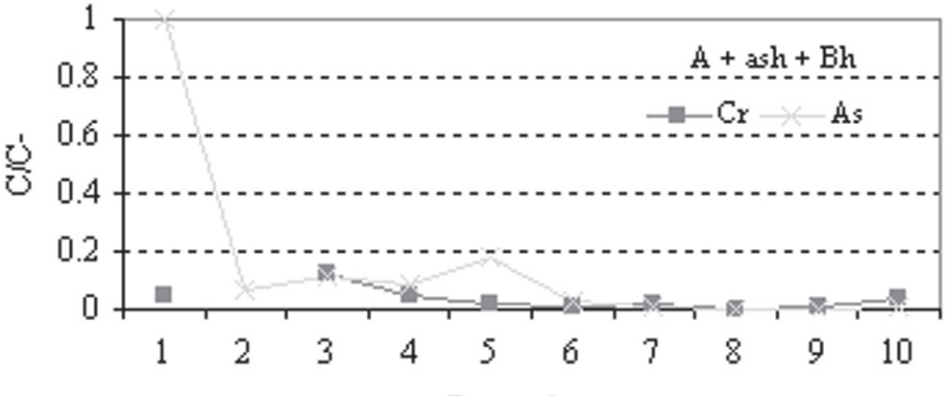

FIGURE 5

Variation of As and Cr with pore volume in ash, ash+A and ash+A+Bh concern about toxicity. Table 3 highlights this concern, especially for Cr, the leaching of which was about 10 times that of arsenic (w/w).

The influence of the different soil layers on the leaching patterns of As and Cr are shown in Figure 5. It must be emphasized that although the amount of ash used in each column was the same, the amount of soil and the resulting depth of packing materials were different for each treatment in this part of the study.

Although 10 times as much Cr than As was leached from the columns, the leaching pattern of Cr was not different from that of As in the ash-only columns (Figure 5). Nonetheless, the curve of the Cr slope was much steeper than that of arsenic (Figure 5), and when flow was interrupted after the third pore volume even more Cr was leached from the soil-ash mixture.

The average concentration of water-leached Cr in the ash-only columns was lower than that leached from the Ash + A columns in the first 50 mL (260 μg compared with 120 μg in the first 50 mL; Table 3). Mixing ash with soil possibly exposed Cr to more reaction sites on the soil surfaces, promoting more dissolution. More than 100% more Cr was leached from the Ash + A + Bh column. The hydraulic conductivity of Ash + A + Bh columns was lower than that of Ash + A and ash-only columns (Chirenje, 2000), leading to higher residence time of the leaching solution.

Although Cr (III) is the most stable form of Cr under the slightly acidic conditions common in most natural soils and sediments, the combustion process from which the ash used in this study was produced, and the high pHs involved tend to favor the oxidation of Cr (III) to the more mobile Cr (VI). The dissolved species of Cr (VI), (hydrochromate ($HCrO_4^-$), dichromate ($Cr_2O_7^-$), and chromate (CrO_4^{2-}) are more mobile in soils (Bartlett and James, 1979; James and Bartlett, 1983), and their leaching can be coupled to that of any of the major cations present in the ash. Therefore, Cr (VI) constituted the highest proportion of leached Cr in this study.

The average water-leached arsenic was lower than organic acid-leached arsenic in the ash-only columns (24 μg compared with above 29 μg in the first 50 mL; Table 2). Mixing ash with topsoil did not change concentrations of water-leached arsenic despite the increase in the amount of DOC leached (Table 2). In studies conducted on two wetland sites, Kalbitz and Wennrich (1998) noted that arsenic was only marginally mobilized by DOC in the site with low soil pH and highly mobilized in the site where the pH was slightly higher. Similar to our study, the fraction of DOC was also much higher at the second site. The inclusion of the Bh horizon in our study led to an increase in the amount of arsenic leached, corresponding also to significantly higher DOC leaching than in the first two columns.

Arsenic/Chromium Leaching in Acid-Leached Ash Columns

The effects of the different leaching solutions on As and Cr solubility and mobility are shown in Figure 6. There was less Cr leaching in the HA than the FA-treated

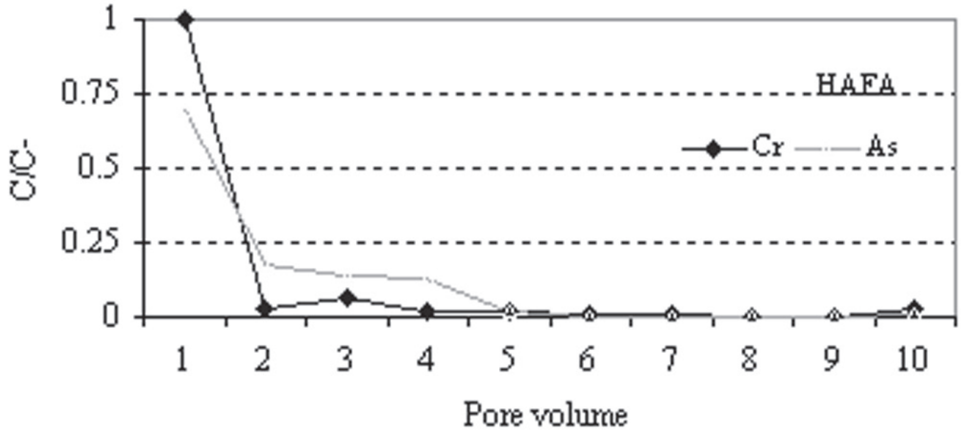

FIGURE 6

Variation of As and Cr with pore volume in HA, FA and HAFA leached amended columns ash columns

ash columns in the first 50 mL (69 vs. 240 μg in the first 50 mL, Table 3). Humic acids are less reactive than the smaller-sized and more surface reactive FA. In the Cu/Ni study (Chirenje *et al.*, 2002; in press), it was postulated that the organic acids precipitated out at the high ECs in the columns. This postulation equally applies here. Less than 10% of the total DOC leached in the water-leached soil-ash columns (48 mg, Table 3) was leached in the acid-leached ash columns (4 and 1 mg for HA and FA, respectively, Table 3). Chromate was easily leached in the FA columns because it was not associated with the FA that flocculated and stayed in the soil matrix. In the HA ash columns, leaching was also affected by flocculation, but HA was not retained in the matrix to the same extent as FA. The solubility of Cr and the leaching characteristics of the column played a more significant part. However, the chromate species has been shown to react with the HA used (with relatively high concentration of carboxyl groups), which are larger, more complex, and consequently less mobile than FA. This explains the low leaching and retardation in leaching of Cr in the HA-leached ash columns (Figure 6).

Water-leached soil/ash columns had lower Cr concentrations than FA- and HAFA-leached ash columns (120 μg compared with 240 and 250 μg, respectively, in the first 50 mL, Table 3). As previously discussed, HA-leached ash columns had lower Cr concentrations due to the retention of Cr in association with humates in the column. Mixing ash with soil only led to insignificant increases in Cr leaching, while the inclusion of the Bh horizon slowed leaching rate and increased the total amount of Cr leached due to increased time of exposure of the eluting solution to potentially soluble Cr. Significantly higher DOC was leached in the two soil-ash columns than the ash-only columns ($p < 0.05$). There was, indeed, significant reduction in Cr leaching in the columns in all the acid-leached columns compared with the Ash + A + Bh columns. However, the same pattern was not observed between Cr leaching in acid-leached columns and that in Ash + A columns. This can be explained by the lower concentration of DOC in the Ash + A columns compared with the Ash + A + Bh columns.

The average water-leached arsenic was lower than that leached by HA and FA (24 μg compared with above 29 μg in the first 50 mL; Table 3). The relative amount of arsenic leached in our columns was lower than that of Cr ($p < 0.05$), suggesting that either Cr was relatively more soluble from our ash or arsenic was retained in the columns to a greater extent than Cr. Batch studies confirmed that Cr was more soluble from the ash matrix (20 times as much Cr than As was desorbed from the ash after 48 h of shaking; data not shown). Mixing ash with topsoil more than quadrupled the amount of DOC, but the corresponding increase in arsenic leaching was only twofold (Table 2). The relationship between DOC and arsenic was not clear due, in part, to the complex nature of the leaching solutions (high pH and I).

The HA fraction leached more arsenic than the FA fraction (Table 3), possibly due to higher association of arsenic with FA than HA. Humic acid was not immobilized to the same extent as FA, hence more of the soluble arsenic leached out with the eluting HA solution. As discussed previously, FA is more surface reactive and was retained to a greater extent in the columns than HA (Table 3). There was negligible microbial activity in these columns because the ash had a very high pH and salt content (Chirenje, 2000). Therefore, both As immobilization into the organic fraction and volatilization through methylation were not significant.

Mixing soil with ash increased both DOC and arsenic leaching. The presence of higher DOC concentrations seemed to impact arsenic leaching, but the mechanism of this effect is not clear from this study. It cannot be explained simply in terms of association with either HA or FA. The preponderance of negative charge in the acid-leached columns may, in fact, have led to the repulsion of the negatively charged arsenic species leading to increased arsenic leaching. Breslin and Duedall (1983) found that both As (V) and As (III) leached from fly ash, but arsenate was predominant (77%). Turner (1981) noted that arsenic was initially leached as As (III) in his study, but As (V) increased with leaching and postulated that adsorption or catalytic oxidation was responsible for this. The columns in this study had high levels of Mn oxides (Table 1), making this a likely possibility. Fulvic acid, used as one of the leaching solutions here, has also been shown to have a higher impact on the desorption isotherms of As (V) than As (III) (Xu *et al*., 1991).

The behavior of As and Cr in this study was different from their behavior under saturated conditions (Chirenje and Ma, 1999), where the leachability of both elements was reduced by the immobilization of DOC. The difference must have been due to the changes in solution chemistry, namely, changes in flow velocity and solution to solid ratio, which led to increase in ionic strength, which in turn induced precipitation of DOC fractions. The differences in the prevailing pH between the two studies is also significant (maximum pH of 7 in Chirenje and Ma (1999) vs. ~11 in this study).

CONCLUSIONS

This study showed that although both As and Cr move in the soil as oxyanions, the extent of their mobility very much depends on their individual chemical properties (e.g., solubility) and how they interact with the soil solution and matrix. Both oxyanions leached faster than the cations showing that they had less interaction with the solid matrix. The main limitations from this study were that the extremely high pH of the leaching solution, coupled with the high ionic strength of the leaching solution may have masked some of the relatively simple but important reactions governing metal solubility and subsequent leaching in our columns. Therefore, it is extremely difficult to isolate the predominant mechanisms against such a background.

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