Effects of Soil on Trace Metal Leachability from Papermill Ashes and Sludge

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ABSTRACT

Understanding trace metal leachability is important for successful land application of papermill residues. Trace metal leachability from papermill ashes (Ash 1 and Ash 2) and papermill sludge (Sludge), and the effects of a soil on their leachability were determined by leaching the three papermill residues packed on top of a soil in a column. The leachates were analyzed for pH, electrical conductivity (EC), dissolved organic carbon (DOC), and concentrations of six metals (Cd, Cr, Cu, Pb, Se, and Zn). Ash 1 behaved significantly differently from Ash 2 during the leaching experiment, primarily due to its high pH and Na contents. Application of papermill residues significantly increased the pH, EC, and DOC concentrations in leachates, with Ash 1 having significantly greater impacts than Ash 2 and sludge. Soil columns under alkaline leaching of Ash 1 appeared bleached due to the dissolution of solid-phase organic matter. Significant amounts of Zn were leached from all papermill residues, whereas significant amounts of Cr, Se, and Cu were leached only in the Ash 1 treatments. The presence of a soil (especially a B horizon) generally enhanced metal leachability in the Ash 1 treatments due to the extremely high pH of Ash 1, whereas it decreased metal leachability in the Ash 2 and sludge treatments. Thus, organic matter enhances metal sorption when present as a solid phase, but it increases metal leachability when present in dissolved form under alkaline conditions.

The USA obtains approximately 2.7 quads of energy from burning biomass while producing 1.5 to 3.0 million Mg of ash annually (Campbell, 1990). The pulp and paper industry alone produces an estimated 0.8 million Mg of boiler ash (Thacker, 1986) and 2.1 million Mg of sludge on a dry-weight basis annually (Fuller and Warrick, 1985).

During the past two decades, much progress has been made in our knowledge of the chemical composition in papermill ash and sludge (Pepin and Coleman, 1984; Someshwar, 1996). Papermill sludge consists of both primary and secondary forms, and papermill ash includes both fly ash and bottom ash, a mixture of which is termed boiler ash (Pepin and Coleman, 1984). Primary sludge is produced in the primary clarifier and consists of rejected wood fibers, sand, and small amounts of fly ash, which are derived from bark or coal burned for energy. Secondary sludge is produced in aeration basins and consists of dead bacteria and other microorganisms. Generally speaking, papermill sludges are typically low in trace metals and contain two basic groups of materials: organics including cellulose, microorganisms, lignin and wood extracts; and inorganics including lime, clay, calcium carbonate, and trace metals (Pepin and Coleman, 1984). Unlike sludges, boiler ashes from papermill are mainly inorganic and consist primarily of Fe, Al, Mn, and Mg with an array of other chemical elements in lesser quantities (Pepin and Coleman, 1984).

The potential benefits to forest soils from applying the nutrients inherent in papermill residues have been investigated extensively. Land application of papermill residues, when properly mixed and incorporated at acceptable loading rates, could provide substantial benefits to soils that are low in nutrients and organic matter (OM), and might benefit forest growth with minimal adverse effects on groundwater quality (Bramryd and Fransman, 1995; Muse and Mitchell, 1995). Some studies have shown that direct application of papermill sludge to forested sites enhances growth of existing stands (Eck, 1986; Henry, 1991) and improves levels of Ca and K in forest soils (Naylor and Schmidt, 1989). Papermill ash is an alkaline material with pH typically ranging from 8.5 to 13, and contains plant nutrients extracted from the soil during tree growth. Previous research has demonstrated that ash can be applied to land as a liming agent and soil additive (Campbell, 1990). Papermill sludge can be used as an organic amendment to improve soil water holding capacity, OM content, nutrient retention, and cation exchange capacity. Another use for papermill sludge is as an amendment to improve plant growth on disturbed or degraded landscapes. There have been several large-scale operations involving the spreading of papermill ash and sludge on forest land in the eastern USA (Campbell, 1990).

Our understanding of the effects of papermill-residue-borne trace metals and of the papermill residue themselves on forest ecosystems, and especially on po-

Abbreviations: DOC, dissolved organic carbon; EC, electrical conductivity; XRD, x-ray diffraction; TG, thermogravimetry; DTA, differential thermal analysis; OM, organic matter.
Concerns have been raised with respect to direct application of papermill ash and sludge to soils. These concerns are based on uncertainty related to the composition and environmental fate of trace metals and organic compounds present in papermill ash and sludge. Among the possible negative effects are potential release of trace metals into the environment including transfer of these elements from soil into groundwater. The extent to which trace metals can be released from land-applied coal fly ash and sewage sludge into the environment has been studied extensively (Bilski and Alva, 1995; Fleming et al., 1996; Logan et al., 1997; Schmidt, 1997). However, little information is available on the leachability and availability of trace metals from land-applied papermill ash and sludge.

This study employs column-leaching techniques in a laboratory setting to understand mobility and leachability of trace metals from papermill ashes and sludge. Although a column leaching study cannot completely simulate leaching under natural rainfall in the field, it is useful for evaluating the relative leachability of salts and metals in papermill residues (Buchholz and Landsberger, 1995; Camobreco et al., 1996; Chichester and Landsberger, 1996; Fleming et al., 1996). The laboratory leaching test was designed to investigate the mobility of environmentally sensitive trace metals (As, Cr, Cu, Pb, Se, and Zn) from papermill ashes and sludge, and the effects of different soil horizons on metal leachability from these papermill residues.

### MATERIALS AND METHODS

#### Selection and Characterization of Soil and Papermill Residues

In November 1995, three papermill residues from the Georgia Pacific Corporation—two ashes and one primary sludge—were land-applied to two sandy forest soils. One papermill ash (Ash 1) from the Hawthorne plant of Florida was applied to a former timberland in Hawthorne, FL. Another papermill ash (Ash 2) and sludge (Sludge) from the Brunswick plant of Georgia were applied to a sandy forest soil in Brunswick, GA. The two soils are sandy in nature, rendering the local area susceptible to both drought stress and nutrient loss due to leaching. Such soils should benefit from the conditioning effects and nutritive values of the papermill residues. These three papermill residues were thus chosen to conduct the laboratory leaching study.

Soil samples collected from a control plot in Hawthorne, FL, where Ash 1 was applied, were used, including three depths (representing the A, E, and Bh horizons). This soil is an acidic fine sand (Typic Quartzamment) with a spodic horizon below 2 m. All soil samples were air-dried, well-mixed, and sieved through a 1-mm sieve after removing roots and rocks. The soil and papermill ash and sludge samples were digested in a CEM MDS-2000 microwave digestion oven using USEPA Method 3051 (USEPA, 1986). Concentrations of Al, B, Ba, Ca, Mg, K, Na, Fe, Mn, P, Cd, Cu, Ni, Pb, and Zn were determined using a Thermo-Jarrell-Ash 61E ICP and those of As, Cr, and Se using a Perkin-Elmer Model 2380 graphite furnace atomic absorption spectrometer (Table 1).

The two ash samples were also analyzed by x-ray diffraction (XRD). Qualitative assessments of minerals in the ash samples

### Table 1. Elemental concentrations in different horizons of a forest soil and in papermill ashes and sludge used in this study.

| Element | As | Cr | Cu | Pb | Se | Zn | Ca | Mg | K | Na | Fe | Mn | P | Al | Mg | K | Ca | Ba | Sr | Zr |
|---------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ash 1   | 1.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Ash 2   | 2.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| Sludge  | 3.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |

**Notes:**
- Concentrations are in mg kg⁻¹.
- Data represent averages from replicate samples.
- Concentrations of As, Cr, Cu, Pb, Se, and Zn were determined using a Thermo-Jarrell-ASH 61E ICP.
- Concentrations of Al, B, Ba, Ca, Mg, K, Na, Fe, Mn, P, Cd, Cu, Ni, Pb, and Zn were determined using USEPA Method 3051.
were also performed using thermoanalytical techniques, i.e., threogravimetry (TG) and differential thermal analysis (DTA).

**Column Experiment**

To determine the effects of a soil from different horizons on trace metal leachability of papermill residues, 20 g of each of the ashes and 10 g of the sludge were placed on top of 20 g of soil from each of three pedogenic horizons in 60-mL syringes (13 cm length by 2.8 cm diam.). The three soil horizons include the A (surface), E (subsurface bleached, light color), and Bh (subsurface black or dark brown in color). To determine trace metal leachability from papermill residues, a control consisting of the three papermill residues alone was included. The columns were packed in duplicate, resulting in a total of 24 columns (3 papermill residues × 3 soil horizons × 2 replicates + 3 controls × 2 replicates). A small amount of glass fiber was packed in the bottom of each syringe to prevent soil loss during leaching. The columns were then leached with deionized water using a Zero-Max extractor model 24-01. Sixty mL of water, which was equivalent to 1.8, 2.0, and 1.7 pore volumes for the Ash 1, Ash 2, and Sludge treatments, respectively, was leached through each column over a 24-h period. A second leaching was conducted after a 24-h equilibrium time. A total of seven leachings (420 mL, being equivalent to 74 cm of water) were applied to each column. Leachates were filtered through 0.22-µm membrane filters and analyzed for pH, electrical conductivity (EC), and dissolved organic carbon (DOC) using a Shimadzu 5000A carbon analyzer. Trace elements (Cd, Cr, Cu, Pb, Se, and Zn) were determined using a Perkin-Elmer Model 2380 atomic absorption spectrometer. Selected anion concentrations (SO\textsubscript{4}\textsuperscript{2-}, PO\textsubscript{4}\textsuperscript{3-}, and NO\textsubscript{3}\textsuperscript{-}) were analyzed in leachates using a Dionex 2000i ion chromatograph.

In addition to leachate analysis following each leaching, the ashkludge–soil columns after the seventh leaching were allowed to drain freely until gravitational flow ceased and then were put into a freezer. The frozen ash/sludge–soil samples were subsequently removed from the syringes without breaking them apart and sectioned into two fractions: papermill residues (top) and soil (bottom). Sections where the papermill residues and soil had become intermixed during leaching were discarded. Concentrations of As, Cd, Cr, Cu, Ni, Pb, Se, and Zn in the samples were determined using a Perkin-Elmer Model 2380 atomic absorption spectrometer after they had been digested in a CEM MDS-2000 microwave digestion oven using USEPA Method 3051.

**RESULTS AND DISCUSSION**

**Characterization of the Papermill Residues**

Composition of the two papermill ashes varied widely (Table 1). Papermill ash is often generated from burning wood and waste papermill sludge, and thus contains higher levels of Al than the soil (Table 1). The elevated Al levels in papermill sludge are likely due both to alumino-silicate clays and to aluminum sulfate, which is added during paper manufacturing. Most of the Ca and Mg in papermill ash are probably present as carbonates (Erich and Ohno, 1992). Papermill ash primarily consists of inorganics; however, some organic residues remain after combustion as well. Ash content and chemical composition vary among tree species and also depend on soil type and climate (McGinnis, 1995). Alkali metals and alkaline earth elements exist mainly as oxides, hydroxides, and carbonates in such ashes, with a typical pH range of 10 to 13 (Campbell, 1990). Among the trace metals, Se (<3 mg kg\textsuperscript{-1}) and Cd (<25 mg kg\textsuperscript{-1}) levels in papermill ashes are relatively low. Concentrations of Ni, As, and Cr are somewhat higher but generally still <50 mg kg\textsuperscript{-1}, whereas levels of Pb and Cu range from 50 to 110 mg kg\textsuperscript{-1}. Zinc has the highest levels of all microelements in typical papermill ashes, with a median level of 329 mg kg\textsuperscript{-1} (Someshwar, 1996). Meiwes (1995) reported that Zn and Pb contents in untreated wood ashes are 250 and 100 mg kg\textsuperscript{-1}, respectively, whereas Cu contents range from 130 to 240 mg kg\textsuperscript{-1}, Cr from 0.2 to 200 mg kg\textsuperscript{-1}, and Cd from 3 to 21 mg kg\textsuperscript{-1}, respectively. Although concentrations of trace metals among the two papermill ashes displayed high variability, all with the exception of Ni in Ash 2 were within published ranges (Table 1).

Compared with background soil concentrations, the levels of target metals in both ashes and sludge were significantly greater than concentrations in the control soil. In addition, this sandy soil (~96% sand) has a low cation exchange capacity (0.85–3.08 cmol, kg\textsuperscript{-1}, Ma et al., 1997), reflecting its low capacity to retain trace metals. Therefore, it is critical to study potential groundwater contamination for this soil after application of papermill residues.

The XRD and thermoanalytical results showed that the two papermill ashes in this study contained primarily calcite, silica, and gypsum. After the leaching test, gypsum had nearly disappeared, whereas the calcite and silica remained (data not shown).

**Leachate Analysis**

**pH**

The pH values for all leachates from the ash- and sludge-amended soil columns were high (Fig. 1). Leachate pH values for Ash 1, Ash 2, and Sludge following the first leaching were 12.6, 7.2, and 8.7, respectively, in the absence of soil. Clearly, the pH of Ash 1 was 3.3 to 5.4 units greater than for either Ash 2 or Sludge, causing it to behave differently. The leachate pH of Ash 1 increased from 12.6 to only 9.63 after the seventh leaching (a total of 74 cm of water). Leachate pH of 12.6 from Ash 1 was probably due to the presence of free OH- in Ash 1, since NaOH was used to soak the wood during the manufacturing process. A solution in equilibrium with calcite would have a pH of only ~8.2 assuming a CO\textsubscript{2} pressure of 0.00003 MPa (McBride, 1994). It seemed that, after leaching with 74 cm of water, Ash 1 still contained free CO\textsubscript{3}\textsuperscript{2-}, elevating the leachate pH to 9.63 (Fig. 1). Leachate pH would remain high as long as CaCO\textsubscript{3} was present in this ash. It is reasonable to conclude that it would take years of natural leaching before all CaCO\textsubscript{3} could be leached from Ash 1 if it were land-applied at a high rate. The presence of soil from different horizons had little effect on the leachate pH of Ash 1 (Fig. 1).

Compared with an initial pH value of 8.7 from the
Ash 2 control, leachate pH of Ash 2 had decreased slightly to 8.0 after the seventh leaching (Fig. 1). In contrast to Ash 1, 74 cm of water effectively leached free CO$_3^{2-}$ from Ash 2, causing leachate pH to decrease to below 8.2. Leachate pH values in the presence of soil were generally lower than those of corresponding controls for all leachates, demonstrating the pH buffering capacity of the soil. Leachate pH for the Ash 2 control remained constant during leaching, whereas pH values in the presence of soil gradually increased with leaching, suggesting that the soil’s buffering capacity was gradually being overcome. Leachate pH from the sludge treatments remained relatively constant at 7.5 to 8.0 (Fig. 1). The pH of the first leachate from the sludge-amended soil column, especially for the A and Bh horizons, was approximately one unit lower than the pH for leachate from the sludge alone, again demonstrating the role of soil buffering capacity in controlling leachate pH.

Dissolved Organic Carbon

The first leachates from the Ash 1 + Bh treatments were coffee-colored and extremely difficult to pass through the membrane filters, suggesting high concentrations of colloidal OM. Leachate color from the Ash 1 + Bh treatments changed gradually with increased leaching, from coffee color to a final light-yellow color after the seventh leaching. Leachates from the Ash 1 + A treatment also had a dark brown color during the first three leachings, whereas a light yellow color was observed for Ash 1 alone and for the Ash 1 + E horizon treatments, suggesting that Ash 1 contained some soluble OM itself. After the seventh leaching, colors of the A, E, and Bh soil horizons in the columns were bleached to a white color for all of the Ash 1 treatments, suggesting that most of the solid-phase OM in the soil had been dissolved in the alkaline solutions and subsequently leached from the ash-soil columns (Brady and Weil, 1996). This was substantiated by the DOC data (Fig. 2). In contrast, little soil color change was observed for the Ash 2 and sludge treatments, which is mainly due to the pH difference between the papermill residues (9.4-12.9, Fig. 1).

Significant amounts of DOC were leached from the soil columns amended with Ash 1, especially in the pres-

![Fig. 1. Measured pH in leachates of different soil horizons amended with papermill residues.](image-url)
ence of soil horizons A and Bh. Both the A and Bh horizons contained greater initial amounts of OM than the E horizon (Table 1). Concentrations of DOC from the first leachates for treatments Ash 1, Ash 1 + A horizon, and Ash 1 + Bh horizon increased from 195 to 1158 and 1399 mg L\(^{-1}\), a more than sixfold increase in the presence of soil. This suggested that soil OM was dissolved by alkaline solution with an initial pH of 12.6 (Fig. 1). The DOC results were thus consistent with the observation of coffee-colored leachates from the Ash 1 + Bh treatments. In the second leachates, DOC decreased sharply (=10-fold) for the Ash 1 treatments compared with the first leachates, suggesting that most of the labile OM from the soil had been rapidly dissolved and leached already. Concentrations of DOC continuously decreased with subsequent leaching and, in all leachates, concentrations of DOC from the Ash 1 control were significantly lower than those in the presence of soil (Fig. 2).

Considerably less (=10-fold) DOC was leached from Ash 2 than Ash 1 (Fig. 2) as a result of pH reduction from 12.6 (Ash 1) to 8.7 (Ash 2). Concentrations of DOC in the Ash 2 control (16 mg L\(^{-1}\)) also were generally greater than those in the presence of soil (9.6–14.3 mg L\(^{-1}\)) during the first leaching, suggesting the retention of soluble OM by the soil (Fig. 2). Concentrations of DOC in the sludge treatments for the first leachates were relatively high, ranging from 214 to 362 mg L\(^{-1}\), with the sludge control having the highest DOC concentration (Fig. 2). This suggests that the presence of soil decreased DOC levels from the sludge as well. Even though DOC concentrations in the leachate of sludge alone (avg. 362 mg L\(^{-1}\)) were much greater than that for Ash 1 alone (avg. 195 mg L\(^{-1}\)), much less DOC was leached from the sludge treatments than for the Ash 1 treatments in the presence of soil. Like Ash 1, concentrations of DOC in the second leachates were consistently lower than those in the first leachate for the Ash 2 and sludge treatments (Fig. 2).

Among the three papermill residues used in this study, DOC concentrations in the absence of soil decreased in the order: sludge > Ash 1 > Ash 2 (Fig. 2), suggesting that papermill sludge, which is rich in fiber, contains relatively high amounts of easily dissolved and mobile OM. However, in the presence of soil, DOC concentrations were greatest for the Ash 1 + A and Ash 1 + Bh treatments, which can be attributed to the extremely high pH of Ash 1 and to subsequent OM
Table 2. Correlation coefficients between various parameters determined in the leachates.

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<tr>
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<tr>
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<td>0.97**</td>
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<td>0.98**</td>
<td>0.98**</td>
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</tr>
<tr>
<td>Cu</td>
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<td>0.61*</td>
<td>0.95**</td>
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<tr>
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<td>0.67*</td>
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<td>0.15ns</td>
<td>0.04ns</td>
<td>0.07ns</td>
</tr>
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</table>

* ** Significant at the 0.05 and 0.01 probability levels in a two-tailed t test. ns, not significant.

dissolution under the resultant highly alkaline conditions (Brady and Weil, 1996; Fig. 2). This is supported by relatively high correlation coefficient (r = 0.60) between pH and DOC for the first leachates of all treatments (Table 2).

Electrical Conductivity and Major Cations and Anions

Relatively high electrical conductivities (EC values) in the first leachates from all three papermill residues were observed, especially for Ash 1 (Fig. 3). The EC of Ash 1, Ash 2, and sludge were 24.2, 2.32, and 1.19 dS m⁻¹, respectively. Ash 1 was thus not only very alkaline in nature, but also very saline. Its salinity was much greater than the 4 dS m⁻¹ criteria for a saline soil (McBride, 1994). The EC for Ash 1 was ~10 times greater than for Ash 2 or sludge throughout the leaching experiment. However, the EC of all leachates reduced ~sixfold from the first to the second leaching, suggesting that most of the ions in these papermill residues were quite soluble. Electrical conductivity for all first leachates was highly correlated with pH (r = 0.96), and was also correlated with DOC (r = 0.59) (Table 2).

Concentrations of Na in the first leachates from Ash 1, Ash 2, and sludge averaged 10000, 334, and 244 mg L⁻¹, respectively, with Na concentrations for Ash 1 being 30- to 40-fold greater than those for Ash 2 or sludge (Fig. 4). This was consistent with their respective total Na concentrations, since Ash 1 contained 15 to 20 times more soluble Na than the other two materials (Table 1). Sodium concentrations declined 8- to 15-fold, to 638, 23.1, and 29.9 mg L⁻¹, respectively, in the second leachates. This suggests that most soluble Na had been re-
moved during the first leaching. Concentrations of Na in all leachates from the Ash 1 treatments decreased gradually with leaching, to ≈86 mg L⁻¹ after seven leachings. Meanwhile, concentrations of Na in leachates from Ash 2 and sludge remained relatively constant, in the range 3 to 20 mg L⁻¹, during the last six leachings. The presence of soil had little effect on Na leachability in these columns. Based on the empirical relationship of total cations (mmol(+)) L⁻¹ = EC (dS m⁻¹) × 10 (McBride, 1994), the EC values contributed by Na represented 43, 1.5, and 1.1 dS m⁻¹ in the first leachates from Ash 1, Ash 2, and sludge alone. The above equation applies reasonably well to soil solutions of differing compositions except under very acidic or very alkaline conditions (McBride, 1994). The EC value calculated from Na concentration (43 dS m⁻¹) for Ash 1 was much greater than the measured EC (24.2 dS m⁻¹) in the leachate. The above equation thus was not valid for Ash 1, possibly due to its high alkalinity (pH = 12.6). Sodium contributed ≈65 and 92% of the EC values for Ash 2 and sludge alone, assuming the validity of the above equation. This is consistent with the fact that Na was highly correlated to EC for all leachates, with r = 0.97 (Table 2).

Like Na, significant amounts of anions (SO₄²⁻ > 3500 mg L⁻¹, PO₄³⁻ > 150 mg L⁻¹, and NO₃⁻ > 45 mg L⁻¹) were detected in the first leachates from the Ash 1 treatments. Little anions were detected in the subsequent leachates, suggesting that soluble anions were completely removed during the first leaching.

**Trace Metals**

Significant amounts of Zn, up to 213 mg L⁻¹, were leached from the three papermill residues (Fig. 5). It is interesting to note that Zn concentrations in the second and third leachates from the Ash 1 + Bh treatments were greater than those for the Ash 1 treatment alone. Such enhanced metal leaching was more pronounced in the Ash 2 treatments for all leachates. For example, Zn concentration in the first leachate from the Ash 2 + Bh treatment was 134 mg L⁻¹, which was significantly greater than for the Ash 2 control of 53 mg L⁻¹. The elevated Zn concentration could not be attributed to DOC or pH effect alone, because Zn concentrations correlated poorly with both DOC and pH (r ≤ 0.25; Table 2) in all leachates.

It should be noted that Zn concentrations in Ash 2
(3864 mg kg⁻¹) averaged fivefold greater than in Ash 1 (849 mg kg⁻¹), with both far greater than those in soil alone (0.01 mg kg⁻¹, Table 1). However, the amounts of Zn leached from Ash 1, with the exception of the first and sixth leachates, were consistently greater (two- to sixfold) than those from Ash 2 in the absence of soil (Fig. 5). This suggests poor correlation between Zn leachability and total Zn concentrations in the ashes. Minimum Zn solubility occurs at pH = 7 to 8, with a maximum near pH 4.5. Zinc shows a marked increase in solubility for pH values > 8 as a result of the formation of more soluble anionic hydroxo complexes (McBride, 1994). In this study, the pH values for all leachates from Ash 1 treatments ranged from 9.1 to 12.6, which is consistent with the formation of more soluble anionic hydroxo complexes of Zn.

Concentrations of Cr from both ash treatments decreased gradually with leaching, whereas those from the sludge treatments decreased to essentially zero after the first leaching (Fig. 6). Extremely high concentrations of Cr were detected in the first leachates of the Ash 1 treatments. Chromium concentrations averaged 1042, 836, 357, and 879 μg L⁻¹ for the Ash 1, Ash 1 + A, Ash 1 + E, and Ash 1 + Bh treatments, respectively. They then decreased to 30 to 86 μg L⁻¹ in the second leachate, and to <10 μg L⁻¹ by the sixth leaching. It was clear that the presence of soil, and especially of Bh horizon material, significantly increased Cr concentrations of the leachates except during the first leaching for the Ash 1 treatment. This again can be attributed to OM-enhanced metal leaching, since DOC concentrations in Ash 1 + soil ranged from 47 to 88 mg L⁻¹ compared with 0 mg L⁻¹ for the Ash 1 control during the last six leachings (Fig. 2). This is also supported by the high correlation coefficients between Cr concentrations and pH (r = 0.88) and DOC (r = 0.67) in all leachates for the first leaching (Table 2).

Little Cr was leached from the Ash 2 and sludge treatments, even during the first leaching, with Cr concentrations <6 μg L⁻¹ (Fig. 6). Unlike the Ash 1 treatments, the presence of soil significantly decreased Cr concentrations in leachates of the Ash 2 treatments,
except for the first and sixth leaching. The DOC concentrations in leachates from the Ash 2 + soil treatments (7–9 mg L\(^{-1}\)) were lower than for the Ash 2 control (12 mg L\(^{-1}\); Fig. 2). Even though Cr concentrations in these papermill residues were similar (22–36 mg kg\(^{-1}\)), their leachability varied greatly. Chromium leachability for Ash 1 averaged 180 to 442 times greater than for Ash 2 or sludge (Fig. 6).

As for Cr, significant amounts of Se were detected in all leachates from the Ash 1 treatments, especially in the first leaching. Selenium concentrations ranged from 722 to 1039 µg L\(^{-1}\) (Fig. 7A). Concentrations of Se decreased to ≤ 175 µg L\(^{-1}\) in the second leaching, and dropped to < 25 µg L\(^{-1}\) by the sixth leaching (data not shown after the second leaching). In general, the presence of soil, and especially of Bh horizon, enhanced Se leaching for Ash 1 treatments. For example, Se concentrations in the first leachates increased from 794 µg L\(^{-1}\) for the Ash 1 treatment to 1039 µg L\(^{-1}\) for the Ash 1 + Bh treatment. Compared with Se concentrations for Ash 1, relatively low Se concentrations were detected in the first leachates from the Ash 2 and sludge treatments, with Se concentrations ≤ 32 µg L\(^{-1}\) (Fig. 7A). However, unlike the Ash 1 treatments, the presence of soil in Ash 2 and sludge treatments reduced metal concentrations in the leachates. Unlike Zn and Cr, Se concentrations in all three papermill residues were low (< 2 mg L\(^{-1}\); Table 1). However, Se concentrations for all leachates were greater than those for Zn and comparable to those for Cr (Fig. 5–7). Selenium, an oxyanionic trace element, has a maximum solubility at pH 10 to 12, and reduced solubility at higher (>12) and lower pH values (<9, Jones, 1995). Selenite is known to be the predominant Se form in leachates from coal fly ash, regardless of the pH of ash–water mixtures; even though, selenate, the highest oxidation state of Se

![Graph](image-url)
Fig. 7. Selenium and Cu concentrations in leachates of different soil horizons amended with papermill residues, where AAS stands for Ash 1, Ash 2, or sludge.

(i.e., SeO$_3^{2-}$), is predicted to be the most stable form at alkaline pH (Wadge and Hutton, 1987). In our studies, Se leachability can be attributed not only to pH ($r = 0.84$) but also to DOC ($r = 0.61$) for the first leachates (Table 2). In addition, it was interesting to note that Se concentrations were highly correlated to Cr concentrations for the first leaching ($r = 0.96$, Table 2).

Similar to Cr and Se, significant amounts of Cu were detected in all leachates during the first leaching, with values for Ash 1 treatments being the highest (Fig. 7B). Copper levels were ≤1039, 42, and 43 µg L$^{-1}$ for the Ash 1, Ash 2, and sludge controls, respectively. Even though Cu concentrations in the Ash 1 and Ash 2 both averaged 89 mg kg$^{-1}$, their Cu leachability was significantly different. Again, as for Zn, Cr, and Se, the presence of soil significantly enhanced Cu leaching for the Ash 1 treatment (Fig. 7B). However, the opposite was true for the Ash 2 and sludge treatments. Unlike Se, however, little Cu was detected after the first three leachings for the Ash 1, Ash 2, and sludge treatments, respectively (data not shown after second leaching). This indicates that most of the Cu was leached out after only a few leachings. Like Cr and Se, Cu concentrations were highly correlated to both pH ($r = 0.94$) and DOC ($r = 0.72$) for the first leaching (Table 2). Greater solubility of trace metals in alkaline solution was attributed to enhanced formation of OM–metal complexes. Most dissolved trace metals are present as metal-soluble organic ligand complexes in this pH range (in our case pH > 8) (Leita and Nobili, 1991). Although the solubility of humic C was low (0.04–0.06 g L$^{-1}$), Cu ions probably saturated most of the complexing capacity of dissolved humic substances in our system (Shuman, 1985).

Even though Pb concentrations in all three papermill residues were relatively high, ranging from 4 to 99 mg kg$^{-1}$ (Table 1), significant Pb (up to 90 µg L$^{-1}$ in the first two leachates) was detected only in leachates from the Ash 1 + Bh treatment (data not shown). Lead concentrations rapidly decreased to <30 µg L$^{-1}$ in the third leachate and to <2 µg L$^{-1}$ in the sixth leachate. Unlike for all other metals discussed thus far, no Cd was detected in leachates from papermill residues, even though Ash 1 contained 4 mg kg$^{-1}$ Cd (Table 1). This suggests that Cd is relatively immobile in Ash 1.
Differences in chemical composition and properties of the two papermill ash samples appeared to reflect differences in fuel type and could explain observed differences in their release of trace metals. Ash 1 had high alkalinity and high soluble salts, a result of additions of strong alkali for presoaking wood during the plywood manufacturing process. Our observations showed that most of the soluble constituents were leached from the papermill residues during the first few leachings, and that alkalinity and soluble elements in all initial leachates were markedly elevated. Under high alkalinity, OM in the soil, especially the A and Bh horizons, tended to dissolve, greatly enhancing metal mobility in the soil. Thus, application of high rates of Ash 1 could increase the risk of elevated pH, soluble salt concentrations (EC values), and DOC for both soil and groundwater.

It has been reported that mobilization of trace metals from coal ash depends on distribution of each element in the solid phase, which controls initial leaching rates. Elements that are enriched on particle surfaces should be more accessible to percolating solution. Consequently, they may be leached initially at more rapid rates, especially if they are present as readily soluble phases, than elements that are uniformly distributed throughout the waste matrix. Studies of coal ash show that elements (As, Cd, Cu, Pb, Se, and Zn) that tend to be present as sulfide minerals, and/or associated with the organic fraction, are generally more volatile during combustion and tend to become more enriched on particle surfaces than elements that are associated with silicate and oxide minerals in coals (Eary et al., 1990). Significant amounts of Cu, Se, and Zn were leached, whereas little As, Cd, and Pb were leached from the papermill ashes in our experiment. Thus, elemental distribution in ash particles was only one of the factors controlling metal leachability. In our case, ash pH proved to be important in controlling metal leachability.

Some trace metals, and particularly Pb, are relatively immobile once complexed by forest floor OM (Herrick and Friedland, 1990). This is consistent with our data. The amounts of Zn, Cu, Ni, and Cd in the forest floor were positively correlated with OM contents. The considerable losses of trace metals from the A horizon of forest soils may occur under conditions favoring the leaching of OM, such as Ash 1 in our case. Organic C plays a major role in the transport of metals during downward migration in soils and into groundwater. A strong relationship between concentrations of Pb, Cu, and DOC has been shown in other studies (Domergue and Vedy, 1992), which is also consistent with our data. Organic matter may facilitate metal transport when it is dissolved under alkaline conditions (in the case of Ash 1), however, whereas it may enhance a soil's ability to sorb metals when present as solid phase (in the cases of Ash 2 and sludge).

Concentrations of Trace Metals in the Ash/ Sludge–Soil Columns after Leaching

After the leaching test, concentrations of seven trace metals in the ash/sludge–soil columns were analyzed. Concentrations of most trace metals were significantly elevated in all soil horizons, especially the Bh horizon, compared with background soil concentrations after application of papermill residues (Table 3). The metal enrichment factor was calculated as metal concentrations in ash/sludge–impacted soil (A, E, or Bh horizons) divided by the corresponding metal concentrations in unimpacted soil horizons from Table 1. Metal accumulation for an element in a given soil horizon was directly proportional to the soil's ability to retain metals. Among the three soil horizons, excluding Ash 1 treatments, generally the Bh horizon had the highest and the E horizon the lowest enrichment factor. Bleaching of the Bh horizon by high-alkalinity solution in Ash 1 treatments resulted in lower metals enrichment for the Bh than for the A or E horizons.

Among the four metals (Zn, Cr, Se, and Cu) determined for the leachates, Zn had the highest and Se the lowest enrichment factor (Table 3). This is consistent with our leachate data, in that significant amounts of Se were leached from the three papermill residues (<1039 µg L⁻¹ for Ash 1 and <32 µg L⁻¹ for Ash 2 and sludge in the first leachates) even though the total amounts of Se in these residues were relatively low (<2 mg kg⁻¹). Zinc concentrations in the Ash 1, Ash 2, and sludge were 849, 3864, and 75.9 mg kg⁻¹, respectively, with Ash 2 evidencing the highest levels (Table 1). However, in terms of enrichment factor, Ash 2 was generally the greatest among the three papermill residues (Table 3). The enrichment factor for Cu was much lower than for Zn, ranging from only 1.4 to 5.6. This was probably due to the fact that Cu complexed with OM much more strongly than did Zn (McBride, 1994). Much lower Cu concentrations (10–89 mg kg⁻¹) than Zn concentrations in the papermill residues were also another possible reason. Greater Zn loading may have resulted in greater Zn retention by the soil.

Like Zn, significant Pb enrichment in the soil was observed (Table 3), with Pb for the ash/sludge + Bh treatments having the highest enrichment factor among the three horizons. This suggests that Pb is strongly associated with soil OM and accumulates in horizons high in OM (McBride, 1994). Although Ash 1 contained the highest Pb concentrations (99.2 compared with 37.3 and 4.0 mg kg⁻¹) among the three papermill residues (Table 1), the Ash 1–impacted soils had the lowest Pb accumulation (Table 3). This was consistent with our leachate data. High alkalinity solution from Ash 1 dissolved most OM from the soils, thus reducing its ability to sorb metals. The high alkalinity of Ash 1 released Pb and Cu, which are highly mobile in soils at high pH. Pb and Cu are known to be mobile in soils with pH values greater than 7 (EPA, 1994).

| Table 3. Ratios of metal concentrations in ash/sludge-impacted soil horizons to the corresponding horizons of the control soil (metal enrichment factor). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Zn   | Cr   | Se   | Cu   | Pb   | As   | Ni   |
| Ash 1 + A      | 1160 | 0.95 | 0.31 | 3.68 | 133  | 1.22 | 118  |
| Ash 1 + E      | 1040 | 1.09 | 0.34 | 5.41 | 61   | 0.68 | 146  |
| Ash 1 + B      | 792  | 0.70 | 0.45 | 2.13 | 313  | 1.30 | 35   |
| Ash 2 + A      | 1790 | 1.06 | 0.44 | 2.13 | 254  | 1.44 | 309  |
| Ash 2 + B      | 564  | 0.71 | 0.39 | 2.82 | 567  | 0.84 | 97   |
| Ash 3 + A      | 1180 | 1.66 | 0.62 | 6.09 | 1170 | 2.26 | 295  |
| Ash 3 + B      | 786  | 0.65 | 0.64 | 1.40 | 172  | 1.83 | 106  |
| Sludge + A     | 781  | 0.96 | 0.37 | 2.53 | 260  | 0.42 | 46   |
| Sludge + B     | 394  | 2.16 | 1.30 | 5.63 | 1080 | 1.13 | 133  |
to retain Pb (Fig. 2) and leading to detectable leachate Pb concentrations. In contrast, no detectable Pb was observed for the Ash 2- and sludge-impacted leachates due to great Pb accumulation in the soils, with enrichment factors ranging from 254 to 1170 (Table 3). These findings are consistent with other studies on the behavior of Pb in contaminated soils, where Pb accumulates at the surface with little evidence of downward movement (Thornton, 1981).

However, Cu concentrations in both ashes (89 mg kg⁻¹) were greater than Zn concentrations in sludge (75.9 mg kg⁻¹), and yet Zn enrichment factors for the sludge-impacted soils were several orders of magnitude greater than for the ash-impacted soils. This may again be attributed to much greater Cu association with OM than for Zn (McBride, 1994), which greatly reduces Zn mobility in the soil. Little enrichment was observed for Cr and Se, suggesting that most Cr or Se were leached from the papermill residues. This was consistent with the leachate data (Fig. 6 and 7).

Concentrations of As and Ni were not determined for the leachates, but they were determined for the ash/sludge-soil columns after the leaching test. Like Zn and Pb, significant amounts of Ni were accumulated in the soil as expected, with enrichment factors ranging from 35 to 309 (Table 3). Slight elevation of As concentrations was observed for most ash/sludge + A and + Bh treatments, ranging from 1.13 to 2.26, but little As was accumulated in the E horizon. It was obvious that soil had greater ability to retain metal cations such as Zn, Ni, and Pb (with the exception of Cu, which complexes strongly with DOC and solid OM) than for oxyanion such as As, Cr, and Se. Our soil column data were consistent with the leachate data, with As, Cr, and Se having greater mobility than for Pb and Zn. This leads to the conclusion that considerable care must be taken when land-applying papermill residues containing high concentrations of As, Cr, and Se.

Soil OM form both soluble and insoluble complexes with metal ions and thereby play a dual role in soils. Low molecular-weight compounds (e.g., fulvic acids) serve as carriers of trace elements in the soil solution. In contrast, high molecular-weight compounds (e.g., humic acids) function as a sink for cations. Although estimates vary, the results obtained thus far suggest that those trace elements in soil that form strong complexes (e.g., Cu²⁺) occur mostly in organically complexed forms; whereas those that form weak complexes (e.g., Zn²⁺) occur mostly in free forms or as inorganic complexes (Stevenson, 1994, p. 380-401). Our results have demonstrated that Cu, Zn, Pb, Cr, and Se were significantly mobilized by Ash 1 (OM was dissolved to become DOC), whereas Pb, Zn, Ni, Cu, Cr, and As were significantly accumulated in the Bh soil layer for the Ash 2 and sludge treatments.

CONCLUSIONS

Overall results suggested that the impacts of papermill-residue amendment on forest soils depend on the properties of the materials. High alkalinity and soluble salts of materials such as Ash 1 can cause severe adverse effects at high application rates. Soil OM may be dissolved under highly alkaline leaching, and Bh horizon OM may even be destroyed if high application rates of Ash 1 are employed. The dissolved OM could enhance trace metal leachability. Preleaching and acidification of this type ash should reduce the high alkalinity and salinity and enhance its benefits as a soil amendment (Ghodrati et al., 1995). On the other hand, Ash 2 and sludge have only minor adverse attributes with respect to land application, and Bh horizon soil, with its high OM content, can represent a considerable buffering capacity against metals leaching below the Bh horizon and then into groundwater.

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