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Research Article

In Situ Generated Colloid Transport of Cu and Zn in Reclaimed Mine Soil Profiles Associated with Biosolids Application

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Areas reclaimed for agricultural uses following coal mining often receive biosolids applications to increase organic matter and fertility. Transport of heavy metals within these soils may be enhanced by the additional presence of biosolids colloids. Intact monoliths from reclaimed and undisturbed soils in Virginia and Kentucky were leached to observe Cu and Zn mobility with and without biosolids application. Transport of Cu and Zn was observed in both solution and colloid associated phases in reclaimed and undisturbed forest soils, where the presence of unweathered spoil material and biosolids amendments contributed to higher metal release in solution fractions. Up to 81% of mobile Cu was associated with the colloid fraction, particularly when gibbsite was present, while only up to 18% of mobile Zn was associated with the colloid fraction. The colloid bound Cu was exchangeable by ammonium acetate, suggesting that it will release into groundwater resources.

1. Introduction

Water dispersible colloids may be a carrier vector for contaminants in the unsaturated soils zone, transporting metals to surface and groundwater [1–4]. The soil matrix is assumed to be a buffer to contaminant transport, due to its ability to sorb metals [2], but the mobilization of dispersible colloids from this matrix have been shown to transport contaminants [3, 4]. Reclaimed mine soils can be a source of heavy metals, released from unweathered spoil material, industrial wastes, fertilizers, power station fly ash, or biosolids applied during reclamation [5]. Copper (Cu), lead (Pb), or zinc (Zn) sulfides can leach from fresh spoil material [6], while cadmium (Cd), chromium (Cr), iron (Fe), manganese (Mn), and Pb can all be contained in phosphorus fertilizers [5].

Up to 95% of biosolids associated metals have been accounted for in the soil profile following biosolids application [7, 8], while under increasingly acidic conditions trace metals were observed to at least a 1 m depth in mine soils receiving biosolids [9]. Within this soil matrix, metal sorption is controlled by pH, clay mineralogy [10], or complexation with soil organic matter [11, 12]. It is commonly assumed that metals are adsorbed in the upper 15 to 30 cm of the soil matrix, thereby reducing their mobility [13, 14], but studies have observed significant metal transport by dispersed colloidal material [15, 16]. Therefore, early models which partition metals between an immobile solid and mobile liquid phase only have to be revised to include colloid particulate material as a third mobile solid phase, and a potential vector of metal transport [17].

Factors that affect colloid mobilization include clay mineralogy, ionic strength, pH, total clay content, soil moisture, and soil management [4]. Coal mining can destroy the original soil matrix, causing the loss of aggregation due to mining equipment and the oxidation of organic binding agents, both of which can increasing mineral colloid release from the soil. Application of biosolids, a common reclamation procedure [18], may also be a source of organic colloids [19, 20]. Organic acids and humic material in the biosolids can chelate and bind metals, reducing, at least temporarily, their transport into groundwater [21]. Lime stabilized biosolids raise the soil solution pH, thus reducing metal solubility [18]. However, a basic pH can also cause
organic colloids to be suspended into pore water, increasing the likelihood of being leached through the system [19].

Formation of pseudokarst channels is likely in reclaimed soils [6, 22, 23], and colloid transport through macropores can bypass impermeable spoil layers [3, 24]. On the other hand, high salt content is commonly associated with fresh mine spoils [6, 23], and increased ionic strength can aggregate colloids and reduce their mobility [17].

Due to their high surface area and charge density, colloids can be an important vector in transport of contaminants in the soil [25, 26]. Higher concentrations of Cd, Cu, and Zn within the dispersible clay fraction have been observed in soils receiving increasing rates of biosolids [8]. Colloid facilitated transport of dichlorodiphenyltrichloroethane (DDT), atrazine, and metals (Cu, Cr, Ni, Pb, Zn) have all been observed in packed and undisturbed columns [4]. Because of their affinity for pollutants, mobile colloids can also strip contaminants such as atrazine and zinc from the soil matrix [27]. Given that colloids can sorb metals from the soil matrix, it is likely that their presence will increase metal transport.

The objectives of this study were (1) to assess the mobility of Cu and Zn within reclaimed soils when spoil materials are placed beneath, (2) to assess the mobility of Cu and Zn within reclaimed soils receiving biosolids application, (3) compare metal mobilization to that occurring in similar undisturbed (natural) forest soils, and (4) to evaluate colloid, soil, and reclamation practices enhancing or inhibiting metal transport.

2. Materials and Methods

2.1. Soil Monolith Preparation. Intact soil monoliths and disturbed material were obtained from the Powell River Project (PRP), near Wise, Virginia, in the southern Appalachian Mountains (30-year-old mine soils) and from Robinson Forest, near Jackson, Kentucky (5-year-old mine soils). This was done to observe any differences in colloid production as mine soils age. All reclaimed soils were from surface mined coal operations, where a top soil is replaced overtop of spoil materials. The monoliths were subjected to the following treatments for each study area (Figure 1): two replicated unmined forest soils, referred to as natural monoliths (VN), which were used as controls. Soils disturbed by coal mining constituted the reclaimed (VR), reclaimed soil + mine spoil material (VS), and reclaimed soil + mine spoil material + biosolids application treatments (VB). Kentucky treatments were natural monoliths (KN), reclaimed monoliths (KR), reclaimed soil and spoil (KS), while biosolids applied treatment (KB) constituted only of reclaimed soil + biosolids application, following low colloid elution from VB monoliths. This was done so that within Kentucky treatments, the effects of spoil and biosolids could be observed separately.

The soil and disturbed monoliths (30 cm height by 18 cm diameter) were extracted from the Virginia study area by carving a pedestal, then trimming them with knives and soil picks to fit within a polyvinyl chloride (PVC) tube of 20 cm internal diameter and 30 cm height. The 2 cm gap between the PVC and the soil was sealed with expandable Poly-U-Foam (Kardol, 1-800-252-7365) to stabilize monoliths and prevent preferential flow along the walls. These intact monoliths preserve all of the structure and soil porosity present at the time of sampling. The PRP site in Virginia had been reclaimed by placing a spoil layer of siltstone and coal underneath a sandy soil material. These two layers were sampled separately as intact reclaimed and spoil monoliths, where each was 30 cm in height. Due to this, the reclaimed soil treatments were only 30 cm tall, while the reclaimed plus spoil treatments combined two separate 30 cm monoliths, for a total height of 60 cm (Figure 1). The soil and spoil materials were combined by placing the PVC encased monoliths flush with each other and sealing the edges with silicone to prevent leaking. Rock fragment content prevented consistently sized intact monoliths from being extracted from the reclaimed and spoil sites (for treatments KR, KS, and KB) from University of Kentucky’s Robinson Forest. Instead, loose soil and spoil material were obtained to build monoliths in the lab. The reclaimed soils were obtained in two forms: (a) an intact, granular surface horizon of about 15 cm in thickness, and (b) a bucket of loose material from the subsurface. The material was taken back to the lab and combined into a 30
by 18 cm soil monolith. Wire mesh was made into a cylinder and placed into an empty PVC tube with a 20 cm internal diameter and 30 cm height. This mesh provided a mold for the loose soil and spoil material. Then a section of intact reclaimed surface horizon was placed on top to bring the total height to 30 cm. The 2 cm gap between the PVC and the soil was sealed with expandable Poly-U-Foam to stabilize monoliths and prevent preferential flow along the walls. The 30 cm tall spoil monolith was built in the same way for the KS treatment, but another 30 cm tall PVC column with wire mesh was placed above the spoil and Kentucky reclaimed soil material was placed above it, bringing the total height to 60 cm. Reclaimed soils receiving biosolids (KB) did not have a spoil monolith below them, while KN monoliths were

to 60 cm. Reclaimed soils receiving biosolids (KB) did not have a spoil monolith below them, while KN monoliths were obtained intact as described for the Virginia monoliths.

The lime stabilized biosolids material used in the study came from a local municipal wastewater treatment facility in Winchester (Clark County), Kentucky. It was applied to the surface of the soil at a rate of 40 dry Mg ha$^{-1}$. A lower rate than normally applied (80 to 125 Mg ha$^{-1}$) was done due to the small surface area of the monoliths and the difficulty in mixing the biosolids into the surface of the monoliths without spilling over the sides. Instead, lower rates of biosolids were mixed by hand with the upper 6 inches of the reclaimed soils. The biosolids contained 7.0 g kg$^{-1}$ P, 27.5 g kg$^{-1}$ TKN, and had a calcium carbonate equivalent of 730 g kg$^{-1}$ (Table 1).

2.2. Bulk Soil Cu and Zn Analysis. Natural, reclaimed, spoil, and biosolids materials were air-dried and passed through a 2 mm sieve. EPA method 3050b was used to extract Cu and Zn from 20 g of soil, spoil, or biosolids materials using HNO$_3$ and HCl and heating to 95°C. Extractants were analyzed by a Varian Vista Pro inductively coupled plasma analyzer (ICP) to determine preliminary levels of each metal in the materials. The pH and electrical conductivity (EC) were determined with a Denver Instrument Model 250 pH$^{+}$ISE$^{-}$ conductivity meter. Ammonium acetate extracts were used to determine cation exchange capacity (CEC) and total exchangeable bases (TEB).

2.3. In Situ Colloid Elution. In situ colloid generation and elution from monoliths were assessed with leaching experiments using a rainfall simulator previously described by Miller et al. [28]. Deionized water (18 μS cm$^{-1}$) at a rate of 250 ml hour$^{-1}$ (1.0 cm h$^{-1}$) was applied to the surface of each monolith with a peristaltic pump for approximately 2-3 pore volumes. Leaching was done in 6 hour pulses for Virginia monoliths and increased to 8 hour pulses for Kentucky monoliths. The cycle was repeated for 6 days until at least 2 pore volumes (pv) were achieved. The lower monolith boundary was kept at −10 cm using a Mariotte device.

Leachate was collected at the bottom of the monolith and tested for suspension concentrations, EC, pH, dissolved organic carbon (DOC), aromatic content of DOC [29], mineralogical composition of the colloids; and colloid particle size [28]. Larger particles were allowed to settle before sampling for suspended colloids. Mineralogical composition was performed on composite samples from each leaching cycle by X-ray diffraction (XRD) and thermogravimetric analysis (TGA) using a Phillips PW 1840 diffractometer/PW 1729 X-ray generator and a TA 2000 thermogravimetric analyzer interfaced with a 951 DuPont TG module, respectively [30]. Colloidal particle size was determined on a Beckman Coulter N5 Submicron Particle Size analyzer on the first sample eluted from every cycle, if colloids were present. The software reports an average representative particle size for the sample.

Eluents were also tested for dissolved metals by taking a 50 mL aliquot from each hourly sample and passing it through a 0.2 μm filter to remove the colloidal material. Some colloids may be smaller than 0.2 μm from these eluents, but observations of filtrates passing thru 0.2, 0.1, and 0.05 μm filters showed no differences in colloid concentration. The filtered material was analyzed for dissolved metals by ICP. Following filtration, 20 mL of 1 M HCl/HNO$_3$ was passed through the same 0.2 μm filter containing the colloids to strip any bound metals. The HCl/HNO$_3$ filtrate was analyzed for metals by ICP and represents the colloid bound fraction.

3. Results and Discussion

3.1. Metal Concentrations in Bulk Samples. Zinc concentrations in the digested samples ranged from 14.7 to 60.8 mg kg$^{-1}$, and Cu from 1.7 to 23.0 (Table 2). The highest recovered concentration of Zn was observed in the biosolids materials (60.8 mg kg$^{-1}$), while the highest Cu levels were extracted from the Kentucky spoil (23.0 mg kg$^{-1}$) and biosolids (21.4 mg kg$^{-1}$) materials, respectively. Biosolids may contain metals that are potential contaminants to the groundwater [31], but levels within these biosolids were well below EPA limits. Within the Virginia sites, Cu was highest in the spoil material, while Zn was highest in the reclaimed soils. The Kentucky spoil was recently exposed from a roadside cut at a surface mine, which probably explains the higher Cu and Zn concentrations observed within this material, possibly present as sulfate compounds. In contrast, the 30-year-old Virginia spoil material had roughly half the extractable Cu and Zn observed in the fresh Kentucky spoil. This indicates that the Virginia spoil may have released metals over time as it weathered, and we could expect the same with the Kentucky materials. Other properties of the bulk soil material have been discussed in Miller et al. [28, 32].

<table>
<thead>
<tr>
<th>Biosolids characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>12.7</td>
</tr>
<tr>
<td>Percent Total Solids</td>
<td>41</td>
</tr>
<tr>
<td>Calcium carbonate equivalent (CCE)</td>
<td>730</td>
</tr>
<tr>
<td>Total Kjeldahl Nitrogen</td>
<td>27.5</td>
</tr>
<tr>
<td>Ammonia Nitrogen</td>
<td>1.2</td>
</tr>
<tr>
<td>Nitrate Nitrogen</td>
<td>0.03</td>
</tr>
<tr>
<td>Total P</td>
<td>7.0</td>
</tr>
<tr>
<td>Total K</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 1: Selected chemical properties of the biosolids (processed by the EnviroData Group, Lexington, KY).
3.2. Cu and Zn Elution in Virginia Mine Soils. While VN monoliths had the largest mass of eluted colloids [32], they did not show a significant elution of colloidal Cu or Zn. The largest total (solution and colloid) mass of Cu was eluted from VB monoliths. However, there were no significant differences in the mass of soluble or colloidal Cu fractions in any of the Virginia treatments (Table 3). The VB monoliths also produced the highest mass of soluble (20.75 mg) and colloidal-bound (0.78 mg) Zn fractions, while all other treatments were similar. The high initial breakthrough of dissolved Cu and Zn observed in this study is consistent with leachate differences in the mass of soluble or colloidal Cu fractions in any of the Virginia treatments (Table 3). The VB monoliths also produced the highest mass of soluble (20.75 mg) and colloidal-bound (0.78 mg) Zn fractions, while all other treatments were similar. The high initial breakthrough of dissolved Cu and Zn observed in this study is consistent with leachate properties observed in other mine soil profiles receiving biosolids [33–35].

The percentage of total Cu transport mediated by colloids (Table 3) was highest in the VR monoliths (82.0%), while all other treatments were similar. Eluents from VR monoliths also had the highest portion of colloid bound Zn (18.2%) compared to other Virginia treatments, but the differences were not significant. The higher Cu levels in the VR colloid fraction may be due to the mineralogical makeup of the eluted colloids [36, 37], which were dominated by 2:1 minerals and gibbsite [32]. Zinc eluted from VN monoliths was similar in total (solution + colloid) mass to VR and VS treatments, but less than 1% was colloid bound compared to 27.3% for Cu. Less than 4% of eluted Zn was transported in the VN, VS, and VB treatments; suggesting that Zn is dominantly transported in the dissolved fraction, unless gibbsite is present. The increased mobility of soluble metals may be attributed to the acidic eluents observed in VN, VS, and VB monoliths [9].

When spoil material was placed below the Virginia reclaimed monoliths (VS), colloid transport was significantly inhibited [32, 38], thus reducing the chance of colloid mediated transport of metals. Only trace amounts of total Cu (0.04 mg) were present in the eluent, with only up to 30% being colloid bound (Table 3). Within the VR eluents, Cu was dominantly transported in the colloid phase, but the restriction of colloid movement by a dense spoil reduced the overall total Cu mobility, with similar amounts of soluble Cu being released from VR and VS monoliths. Zinc, on the other hand, increased 2 fold in the dissolved phase when spoil was added to reclaimed soils, although extractable Zn was slightly lower in the spoil material. This may be due to the more acidic pH of the VS eluents [32], which allowed for greater soluble Zn mobility [38].

Concentrations of eluted colloids in VN, VR, and VS monoliths generally started off at their highest concentrations, and dropped throughout the leaching cycle [32]. Only in the VB monoliths was there a low but consistent release of colloidal material. Patterns of Cu and Zn elution

---

Table 2: Extractions of Cu and Zn in mg kg
-1 by HCl/HNO
3 in soils, spoil, and biosolids.

<table>
<thead>
<tr>
<th></th>
<th>VN</th>
<th>VR</th>
<th>VS</th>
<th>KN</th>
<th>KR</th>
<th>KS</th>
<th>Biosolids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.7 (0.2)</td>
<td>4.3 (0.3)</td>
<td>11.3 (1.2)</td>
<td>4.9 (2.7)</td>
<td>2.4 (0.1)</td>
<td>23.0 (0.4)</td>
<td>21.4 (1.0)</td>
</tr>
<tr>
<td>Zn</td>
<td>14.7 (2.5)</td>
<td>23.6 (1.1)</td>
<td>16.5 (3.1)</td>
<td>19.1 (4.6)</td>
<td>17.8 (1.4)</td>
<td>49.8 (13.3)</td>
<td>60.8 (0.6)</td>
</tr>
</tbody>
</table>

*represent average value with standard deviation in parenthesis.

Table 3: Total, colloidal, and percent-bound Cu and Zn for eluents from the Virginia and Kentucky treatments*.

<table>
<thead>
<tr>
<th></th>
<th>VN</th>
<th>VR</th>
<th>VS</th>
<th>VB</th>
<th>KN</th>
<th>KR</th>
<th>KS</th>
<th>KB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Cu (mg)</td>
<td>0.04 a</td>
<td>0.32 a</td>
<td>0.04 a</td>
<td>0.93 a</td>
<td>0.12 b</td>
<td>0.0 b</td>
<td>0.49 b</td>
<td>3.30 a</td>
</tr>
<tr>
<td>Dissolved Cu (mg)</td>
<td>0.03 a</td>
<td>0.05 a</td>
<td>0.04 a</td>
<td>0.87 a</td>
<td>0.02 b</td>
<td>0.0 b</td>
<td>0.75 b</td>
<td>3.04 a</td>
</tr>
<tr>
<td>Colloid Cu (mg)</td>
<td>0.01 a</td>
<td>0.23 a</td>
<td>0.01 a</td>
<td>0.07 a</td>
<td>0.10 b</td>
<td>0.0 c</td>
<td>0.0 c (na)</td>
<td>0.26 a</td>
</tr>
<tr>
<td>Bound Cu (%)</td>
<td>27.3 b</td>
<td>82.0 a</td>
<td>29.9 b</td>
<td>6.5 b</td>
<td>80.9 a</td>
<td>0.0 c</td>
<td>0.0 c (na)</td>
<td>8.2 b</td>
</tr>
<tr>
<td>Total Zn (mg)</td>
<td>5.13 b</td>
<td>3.29 b</td>
<td>6.78 b</td>
<td>21.53 a</td>
<td>11.76 a</td>
<td>2.75 a</td>
<td>50.73 a</td>
<td>7.04 a</td>
</tr>
<tr>
<td>Dissolved Zn (mg)</td>
<td>5.09 b</td>
<td>2.93 b</td>
<td>6.74 b</td>
<td>20.75 a</td>
<td>11.44 a</td>
<td>2.41 a</td>
<td>50.73 a</td>
<td>6.39 a</td>
</tr>
<tr>
<td>Colloid Zn (mg)</td>
<td>0.04 b</td>
<td>0.36 b</td>
<td>0.04 b</td>
<td>0.78 a</td>
<td>0.32 a</td>
<td>0.34 a</td>
<td>0.0 a (na)</td>
<td>0.65 a</td>
</tr>
<tr>
<td>Bound Zn (%)</td>
<td>0.7 a</td>
<td>18.2 a</td>
<td>0.5 a</td>
<td>3.7 a</td>
<td>2.7 ab</td>
<td>15.4 a</td>
<td>0.0 b (na)</td>
<td>9.7 ab</td>
</tr>
</tbody>
</table>

= Statistical differences (LSD = 0.05) are represented by letters and are compared within row by sites only, standard deviations are in parenthesis, na = not applicable.
(Figures 2(a) and 2(b)) were more erratic, with colloid associated metals showing spikes at several instances during leaching. A relatively large mass of Cu associated with VR colloids was eluted during an initial flushing stage, with another spike occurring at about 1 pv (Figure 2(a)). Colloids eluted from VB monoliths on the other hand, had several Cu spikes within 1 pv and another after 2 pv. This irregular elution pattern suggests that the variability in colloid particle size and mineralogy may make colloid mediated Cu transport difficult to predict. Combining eluted soluble and colloid-bound Cu phases in Figures 3(a) and 3(b) does not contribute much more to the understanding of Cu mobility. Although it rose the overall total Cu mass eluted from VB monoliths, the spikes in concentration contributed by colloids remain, as with the VR and VN monoliths.

Within the VN monoliths, total Zn was observed regularly in all eluent samples (Figure 3(b)), with most of the colloid fraction Zn eluted within 1 pv (Figure 2(b)), following colloid elution patterns [32]. Not many samples contained colloids [32] or bound metals after 1 pv in VR eluents (Figure 2(b)), but solution phase Zn was present in all samples (Figure 3(b)). The Zn concentration spikes observed in the VS breakthrough curves at the beginning of each leaching cycle are probably due to the diffusion of Zn from smaller pore spaces during periods of zero to low flow (Figure 3(b)). For biosolids amended treatments, the elution of soluble Zn (Figure 3(b)) was much smoother than the erratic behavior seen in Figure 2(b), except after 2 pv, where an upward shift in pH and colloid elution was observed [32]. The total mass of eluted Zn reached a peak concentration by 0.5 pv, (probably due to free and DOC complexed Zn released from the biosolids), tailing quickly thereafter (Figure 3(b)). While this elution pattern may be alarming for an initial flushing stage of metals to the groundwater following biosolids application, it may also suggest a quick depletion over repeated rainfall events [35].

3.3. Cu and Zn Elution in Kentucky Mine Soils. Eluents from KB monoliths had the greatest total, soluble, and colloid associated Cu, while all other Kentucky treatments were similar (Table 3). Increased Cu mobility has been previously observed in soil leachates due to surficial biosolids applications [33–35]. Within the Kentucky reclaimed soils (KR) no Cu was detected in either the soluble or colloid fractions, even though KR monoliths had the largest mass of colloids eluted and Cu was present in the bulk soil extracts (Table 2). The addition of unweathered spoil material (KS) beneath reclaimed monoliths resulted in detectable levels of
Cu compared to reclaimed soils alone (KR). Colloid elution was not detected within 2 pv of leaching [28], so all reported Cu and Zn eluted from KS monoliths is from the solution phase.

Dissolved Zn increased 25 fold in KS eluents compared to other treatments, suggesting that the fresh unweathered spoil material contributed to Zn mobilization. The chemical properties of the eluents reflect only what it comes into contact with in the soil/spoil matrix [23], so the effects of toxic materials on pore water cannot be easily predicted by average carbonate and pyrite contents of spoils. In this case, the fresh spoil probably had unoxidized Zn minerals throughout the matrix, but if it had been mixed with other spoil types, Zn loads may have been lower. The application of biosolids also doubled Zn elution compared to reclaimed soils alone. Even the natural forest soil treatments (KN) had five times more Zn than KR eluents. This is probably associated with the leached sandy nature of the KR soils, due to their inherent characteristics as an Appalachian topsoil replacement. In spite of the large range in Zn elution, the high variability between the duplicated monoliths prevented significant statistical differences between the treatments.

The transport of soluble and colloidal Zn also doubled with biosolids application. An increase in DOC was observed in KB versus KR eluents [28], which may explain the increased transport of dissolved Cu and Zn. The greater mass of Zn associated with KB colloids, even with a lower colloid mass [28], indicates that these colloids carried a larger metal load. Colloids from KB monoliths may have more mineral-organic complexes due to the biosolids, thus increasing their ability to carry Cu and Zn. Overall; there was a greater cumulative release of Zn compared to Cu with biosolid application, which has been correlated with soil acidity in other mine soils receiving biosolids [9].

Although KN eluents had a low total Cu elution (0.12 mg), nearly 81% was bound to mobile colloids, greater than any other treatment. Kentucky reclaimed (KR) monoliths eluted no detectable Cu, while KS monoliths eluted no detectable colloids. The larger colloid bound transport of Cu in undisturbed forest soils may be due to the presence of colloidal gibbsite [28], suggesting that colloid mineralogical composition may be more influential than total colloid mass [36, 37]. Dissolved organic carbon was also higher in KN eluents, which may have influenced solution and colloidal transport of both Cu and Zn [28]. Cumulative Zn loads were the lowest in KR monoliths, but these soils also had the lowest extracted levels from bulk samples (Table 2).

Colloid associated leaching patterns of Cu and Zn for all four Kentucky treatments are shown in Figures 2(c) and 2(d). Again it can be observed that no colloidal Cu was

![Figure 3: Total (colloid and solution) concentrations (mg L$^{-1}$) of Cu and Zn in Virginia (a, b) and Kentucky (c, d) monoliths over the entire leaching. VN: Virginia Natural, VR: Virginia Reclaimed, VS: Virginia Spoil, VB: Virginia Biosolids, KN: Kentucky Natural, KR: Kentucky Reclaimed, KS: Kentucky Spoil, KB: Kentucky Biosolids.](image-url)
detected within KR eluents, while no colloids were detected in KS eluents (Figure 2(c)). The pattern of colloid bound Cu from natural (KN) monoliths is erratic, often containing spikes in eluted colloidal Cu, which can be associated with pulses from flushing events [28]. Although colloids from KB (biosolids amended) monoliths typically carried greater Cu loads than KN colloids, at two sampling points Cu dropped below detection (Figure 1(c)), even though colloid concentration in KB eluents remained stable [28]. Colloids from KN monoliths, on the other hand, always had detectable amounts of bound Cu. This indicates that colloid mediated Cu transport may not be exclusively associated with high colloid concentrations, but may also be controlled by colloid mineralogy and particle size. When dissolved Cu is accounted for, elution patterns are much smoother, as larger concentrations of Cu in solution mask the variability in the colloid bound phase (Figure 3(c)). The addition of spoil material to reclaimed soils caused an initial flush of Cu elution, before a constant rate is observed. Therefore, fresh spoil material with unweathered Cu bearing minerals could be a long-term source of mobile Cu.

Similar results can be seen with Zn in Kentucky mine soils, where colloid bound Zn showed several spikes (Figure 2(d)). Some of these peaks between VN, VR, and VB monoliths occurred at the same point, and can be associated with initial pulses from the daily leaching cycle (Figure 2(d)). Other variations are more likely tied to differences in colloid mineralogy and particle size. These flushing cycle pulses can be better observed in Figure 3(d), where spikes in soluble Zn from KS eluents are evident for every initial leaching cycle samples.

### 3.4. Virginia versus Kentucky

Reclaimed soils in Virginia and Kentucky eluted a similar colloid bound and total mass of Zn, while Cu was not detectable in KR samples (Table 3). While KR monoliths produced almost 7 fold more colloids than their VR counterparts, total metal elution did not vary. This may indicate that reclaimed soils alone will not contribute to metal transport in solution or colloid phases. It is with the addition of spoil or biosolids that increases the potential for metal release in these systems.

The total mass of Zn was greater when spoil was added to KS treatments compared to VS treatments. Fresh spoil material in KS monoliths was also a more likely source of soluble Zn compared to the spoil that had undergone weathering for 30 years in VS monoliths. Colloid contribution to metal transport in both treatments with spoil was limited by bulk density and EC [28, 32], so the majority of this transport could be dominated by pH. Because most of the metal mobility within spoil amended monoliths was solution dominated, flushing patterns are more evident in the leaching cycles.

The addition of biosolids to reclaimed soils resulted in similar colloid bound metal transport patterns for both Zn and Cu (Figure 2). Release was largely unpredictable, with several peaks and valleys, but not often dropping below detection. This may indicate that soil water chemistry shifts may be moving through different pore sizes at varying rates, releasing colloids and metals in an unpredictable pattern. While the average pH of VB eluents is acidic, Miller et al. [32] reported sharp increases in sample pH following 2 pv of elution. The alkaline biosolids may release dissolved metals quickly, but it takes more time to overcome the pH buffer capacity of the soil. Cumulative mass Cu was 3 fold higher in KB eluents; probably due to the different overall length of the monoliths, which were 60 and 30 cm for VB and KB monoliths, respectively. While movement of metals associated with organic complexes below 80 cm has been observed with high loading rates [33], mobility beyond 30 cm appears to be limited with the lower application rates to these soils.

A comparison of natural forest soils from each study area does not yield similar results in colloid or metal elution. Total mass of colloids, Cu, and Zn were greater in KN eluents [28], indicating that undisturbed forest soils from different regions of Appalachia will vary in mobility, which should be expected. The ratio of total mass Zn:Cu was similar between the two forest soils, both being 100 fold higher in Zn and both dominantly showing greater Zn mobility in the dissolved phase.

### 3.5. Metal Associations

Selected colloid samples were treated with ammonium acetate (NH$_4^+$) and 1 M HCl/HNO$_3$ to determine the exchangeable load of colloid bound metals (Table 4). The ammonium acetate method extracted Cu and Zn from all colloids, but the double acid extraction method exchanged significantly more Cu. This would verify the exchangeable nature of the Virginia and Kentucky eluted colloid bound metals (particularly Zn), and the increased potential for release to water resources.

### 4. Conclusions

The transport of Cu and Zn was observed in both the dissolved and colloid phases, with Zn being present in all treatments and Cu being detected in all but the KR eluents. The presence of unweathered spoil material and biosolids amendments contributed to higher metal release in soluble fractions, particularly Zn. The mobility of Cu was enhanced in the presence of gibbsite containing colloids but was less exchangeable than Zn. Therefore, Cu mobility was more limited and dependent on colloid movement, while dissolved Zn was ubiquitous in all systems. The total mass of eluted Zn in older reclaimed soils (VR, VS) was very similar, indicating that the contribution of Zn to pore waters in younger spoil

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**Table 4: Colloid bound metals extracted by ammonium acetate (NH$_4^+$) and 1 M acid in mg L$^{-1}$ in selected samples, with letters representing differences at 0.01 between the extraction methods.**

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4^+$</td>
<td>0.003 b</td>
<td>0.261 a</td>
</tr>
<tr>
<td>HCl/HNO$_3$</td>
<td>0.017 a</td>
<td>0.266 a</td>
</tr>
<tr>
<td>% Exchangeable</td>
<td>17.6</td>
<td>98.1</td>
</tr>
</tbody>
</table>
materials (KS) will mitigate over time. Within the younger mine soils (KR), increases in surface organic material and plant uptake may also reduce metal leaching over time [39].

Except for the case of the younger spoil material, total metal concentrations were below 1 ppm and within drinking water standards. The total accumulation of metals was also not very high, considering the intensity of leaching in these lab experiments. In the case of the older, weathered forest soils, the presence of Cu and Zn in leachates indicates that natural release and leaching of these metals in the Appalachians must be low.

The application rate of biosolids used in the study was lower than the typical levels applied in the field and the concentration of the metals below the EPA limits. Therefore, our findings may underestimate actual field occurrences. However, our results indicate that an increase in transport of soluble metals directly after biosolids application is to be expected. Furthermore, mineral and organic colloid mobilization through larger diameter, saturated conduits occurring in cracks of disturbed soils may enhance transportability of larger metal loads. Whether these metal loads reach surface or groundwater will depend on the overall path length and the possibility of being adsorbed to the soil matrix. The addition of a dense spoil (VS) and salt laden fresh spoil (KS) limited colloid bound metal transport. This may also be the case in the field if saturated conduits are not present.

The large spatial and vertical matrix variability existing within mine land environments will make colloid contributions to mobility difficult though. Dispersion and movement of colloids cannot be retarded; therefore the application of biosolids to reclaimed lands should be offset by the depth to the water table, or runoff potential. Spoil materials which have the potential to release large amounts of salts should also be placed in upland positions, where longer path lengths to groundwater will reduce colloid and soluble metal loads.

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References


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