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COLLOID MEDIATED TRANSPORT OF HEAVY METALS IN SOILS FOLLOWING RECLAMATION WITH AND WITHOUT BIOSOLID APPLICATION

Jarrod O. Miller
University of Kentucky

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ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the
requirements for the degree of Doctor of Philosophy in the
College of Agriculture at
the University of Kentucky

By

Jarrod O. Miller

Lexington, Kentucky

Director: Dr. A.D. Karathanasis, Professor of Plant and Soil Sciences

Lexington, Kentucky

2008

ABSTRACT OF DISSERTATION

COLLOID MEDIATED TRANSPORT OF HEAVY METALS IN SOILS FOLLOWING
RECLAMATION WITH AND WITHOUT BIOSOLID APPLICATION

Soils disturbed by strip mining practices may have increased colloid loads moving to groundwater resources, also enhancing the transport of contaminants into our water resources. We hypothesize that contaminant transport within soils following mining is enhanced by colloid mobility. Two sites were chosen for this study, a 30-year old reclaimed strip mine in southwest Virginia and a recently mined area from eastern Kentucky. Intact reclaimed soil monoliths were retrieved from sandstone derived soils in southwestern Virginia. Reclaimed monoliths from eastern Kentucky were recreated in the lab. Intact undisturbed (native) soil monoliths representing the soils before mining were also sampled for comparison. Biosolids were added to an additional reclaimed monolith at a rate of 20 T/acre. Leaching experiments with deionized water at a rate of 1.0 cm/h involved 6 cycles of 8 hours each, giving each monolith at least 2 pore volumes of leaching. Native soil monoliths from Virginia had an average colloid elution of 857 mg over all cycles, reclaimed soil monoliths had an elution of 1460 mg, reclaimed soil monoliths with spoil material had a colloid elution of 76 mg, and when biosolids were amended to reclaimed soil and spoil monoliths, 870 mg colloids were eluted. Native soil monoliths from eastern Kentucky eluted 7269 mg colloids, reclaimed monoliths from eastern Kentucky eluted 10,935 mg colloids, and reclaimed soils with spoil material eluted no colloids. Lime stabilized biosolids enhanced colloid elution due to high pH dispersing material within the monoliths, while spoil materials with high density and salt content reduced colloid elution. Metal loads in solution were mobilized by DOC, particularly in low sulfate environments, while colloid bound metals increased the total metal loads in the order of Pb > Ni > Cu > Cd > Zn > Cr.

Jarrod O. Miller
  Jarrod O. Miller

May 12, 2008
  Date

COLLOID MEDIATED TRANSPORT OF HEAVY METALS IN SOILS FOLLOWING
RECLAMATION WITH AND WITHOUT BIOSOLID APPLICATION

By

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DISSERTATION

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To my parents – who will never know I did this

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CHAPTER 1   GENERAL INTRODUCTION

In the southeastern United States, land reclaimed after coal mining is becoming ubiquitous wherever coal is present. Within Kentucky it is estimated that 272,000 acres have been disturbed by coal mining due to the states larger coal deposits in both the eastern and western coalfields. The Surface Mining Control and Reclamation Act (SMCRA) passed in 1977 regulated and standardized the reclamation of drastically disturbed lands, and required the return of the land to pre-existing conditions. To reclaim the land in a manner consistent with good environmental practices, toxic materials with high acidity of heavy metal content had to be buried, a suitable topsoil replacement found (particularly in the Appalachians where natural topsoil replacement was thin and hard to store) and additions of fertilizer, lime, and biosolids were commonly applied to promote natural regrowth (Daniels and Stewart, 2000).

Detrimental environmental effects from coal mining are well-established through studies of acid mine drainage (Geidel and Caruccio, 2000; Skousen et al., 2000), and increasing contaminant transport through surface runoff (Al and Blowes, 1996; Shukla et al., 2004; Rogowski and Jacoby, 1979; Gubert and Gardner, 2001). Reclaimed mine soil properties have also been observed (Haering et al., 2004) as well as methods for reclaiming these soils using organic amendments to increase organic matter content and reduce metal transport (Haering et al., 2000). While it is assumed that metals are bound to immobile mineral and organic aggregates in the soil, recent studies have observed increased contamination due to colloid transport (McCarthy and Zachara, 1989; Seta and Karathanasis, 1997). Since many studies must filter samples through a 0.45 μm filter before analysis, colloids that can potentially transport pollutants into groundwater are often overlooked.

In Eastern Kentucky topsoil replacement is typically limited to overburden material because of the lack of topsoil. These overburden materials can produce acid mine drainage (AMD) from pyrite oxidation, salt accumulation from oxidation of pyrite, and heavy metal release causing contamination of groundwater (Geidel and Caruccio, 2000). The application of lime stabilized biosolids to reclaimed lands will

reduce acidity and precipitate heavy metals while simultaneously adding organic matter (Haering et al., 2000).

Colloids are ubiquitous in natural waters, where they can control the chemistry of reactive elements and pollutants in solution (Stumm and Morgan, 1996). These particles are microscopic in size, typically in the range of 1 nm to 1 um, and they can be organic or inorganic. Metals can be strongly sorbed to colloids because of their high surface area and charge density and have been observed to strip metals directly from the soil matrix (Stumm and Morgan, 1996; Karathanasis, 2003; Barton and Karathanasis, 2003). Increased organic carbon content and surface charge density has been found to increase metal transport by increasing their dispersivity (Barton and Karathanasis, 2003). Even when flocculated, colloids may travel through macropore spaces, where as much as 70% of water flux has been observed to flow through (De Novio et al., 2002).

In reclaimed areas both mineral and organic colloid sources are present and the application of biosolids could contribute organic colloids to the matrix. The principles which control colloid activity in soil matrices depend upon three general functions including colloid mobilization, colloid stabilization, and colloid transport (McCarthy and Zachara, 1989). It is likely that colloid mobilization and transport will occur in reclaimed mine soils and the underlying spoil material when disturbed. Disturbed soils are similar to colluvial material, as they are sometimes loosely consolidated material. Although these soils can be compacted during reclamation, fractures and desiccation cracks have been observed in spoil material (Al and Blowes, 1996), where preferential flow for colloid transport may occur. Organic materials from biosolids may also sorb to mineral colloid surfaces lowering their zero point of charge (ZPC) and causing dispersion (Parker and Zelazny, 1983). If the material added has been lime stabilized, the pH will rise, potentially increasing dispersion. Transport, however, may be reduced by the high concentration of soluble salts in spoil materials, which may cause flocculation of colloids and sometimes cementation to the pore walls during dry periods (Weisbrod et al., 2002). The dispersion or flocculation of colloids will affect their size and potential to be filtered by the matrix (Karathanasis, 2003).

Not only is the presence of colloids likely in reclaimed areas, but heavy metals can be found in concentrations above their normal background levels. In the reclaimed material (soil and spoil), metals such as As, Cu, Pb, and Zn are often associated with sulfide minerals. While it has been observed that the addition of lime stabilized biosolids will reduce metal solubility (Haering et al, 2000), Karathanasis and Ming (2002) observed that higher pH associated with lime-stabilized biosolids increased colloid dispersion and breakthrough. Although metal solubility may decrease, the likelihood of transport by colloids increases as they become more dispersed.

Colloid transport is important when predicting the overall health of the watershed, due to the long terms effects of contaminant transport through surface and interflow. Colloid transport is often overlooked in studies of metal contamination by reclaimed minelands. This study will help define whether or not colloid transport contributes enough to warrant its factoring into reclamation strategies.

We hypothesize that colloid mobilization is reduced in reclaimed soils when compared to their natural counterparts, and that colloids will enhance the transport of metals within the reclaimed soils systems.

CHAPTER 2   IN-SITU COLLOID GENERATION AND TRANSPORT IN RECLAIMED MINE SOIL PROFILES WITH AND WITHOUT BIOSOLID APPLICATION

2.1   Introduction

Within soil profiles, colloids are dynamic and diverse components which can be involved in chemical, biological and physical reactions (Stumm and Morgan, 1996), including the transport of pollutants (McCarthy and Zachara, 1989). Metal transport has been associated with colloid movement through soil profiles by mineral (Karathanasis, 2003) and organic colloids (Karathanasis and Ming, 2002). Soils which have been disturbed by strip mining could be a source of mineral colloids and organic colloids from biosolid application as well as metals from spoil materials, a byproduct of strip mining (Geidel and Caruccio, 2000).

Spoil, or refuse, is often assumed to be acidic and toxic in nature, but overburden materials can have varying amounts of oxidized or unoxidized strata, as well as varying amounts of acid producing pyrite or neutralizing carbonates (Haering et al., 2004). Because of the potential for acid mine drainage (AMD) or toxic metals entering surface and groundwater from coal mining waste, the Surface Mining Control and Reclamation Act (SMCRA, 1977) and other state specific regulations were passed. These regulations have established that toxic materials must be covered with a standard 1.2 m of topsoil or suitable substitute (Stewart and Daniels, 1992), while it has been observed that a minimum of 30 cm is needed to establish vegetation (Daniels et al. 2000).

Within the Appalachians this topsoil and spoil material are usually distributed as valley fill with easily eroded slopes (Daniels and Stewart, 2000) and are coarsely textured (Shulka et al. 2004), because their finer materials are usually placed in slurry. Colloids are generally considered to be < 2 μm in diameter (Stumm and Morgan, 1996; Valsaraj et al., 1996), so younger , less weathered spoil materials may not produce many colloids due to their coarse texture. As these materials mature and coarse materials weather into silt and clay size particles, more colloid mobilization may occur. Unoxidized spoil materials can contain high amounts of sulfur (S) in the

form of pyrite (FeS_2), or Zn, Pb, or Cu sulfides (Geidel and Caruccio, 2000), which oxidize upon exposure to water and air. This reaction increases acidity, soluble salts (ionic strength), and heavy metals within the soil solution, (Sengupta, 1993; Geidel and Caruccio, 2000; Skousen et al., 2000), which can all have significant effects on colloid stability. Colloids will be resistant to gravitational settling unless they are flocculated by increases in ionic strength or cation valence (Vinton and Nye, 1985; Westall and Gschwend, 1993). Salt content may also cement colloids to the matrix during dry periods, allowing for greater peak breakthrough with high intensity rainfall events (Weisbrod et al. 2002). Flocculation is also enhanced when mineral colloids are at their point of zero charge (PZC), which changes with pH and when coated by oxides or organic matter (Kretzschmar et al., 1998; Bertsch and Seaman, 1999; Karathanasis, 2003; Seta and Karathanasis, 1996). The buffering capacity of mine spoils can be controlled by inherent $CaCO_3$ content in the refuse (Skousen et al., 2000; Geidel and Caruccio, 2000), making the predictions of pH effects on colloid aggregation difficult without combining pyrite and carbonate content into a measure of potential acidity.

Aggregation of colloids makes them susceptible to filtration by smaller pores or soils with low hydraulic conductivity. Mineralogy can also affect filtration, as kaolinitic colloids with larger diameters may be physically filtered from the soil before smectitic colloids (Karathanasis, 2003; Seta and Karathanasis, 1997). The density of the spoil material is controlled by the reclamation method (Haering et al., 2004), where spoil material may increase in density as it settles (Ragowski and Jacoby, 1979), while over 20-year periods density may decrease as soil carbon increases (Shukla et al., 2004). Mine soils typically have lower water infiltration due to the loss of structure, increased bulk density, and lower porosity and pore continuity (Guebert and Gardner, 2001; Ward et al., 1983). However in some cases, backfill hydraulic conductivity is greater than the original hard rock overburden due to the formation of karst-like channels (Al and Blowes, 1996; Skousen et al., 2000; Geidel and Carcuccio, 2000), and may increase colloid transport. These soil cracks are typically found next to rock fragments in reclaimed soils, so mine spoil with higher

rock content may have a higher probability of preferential flow (Guebert and Gardner, 2001).

Preferential flow can enable increased colloid transport through larger macropores which will bypass impermeable spoil layers (MCcarthy and Shevenell, 1998; Seta and Karathanasis, 1997; Guebert and Gardner, 2001; Ragowski and Jacoby, 1979). Colloid transport through the soil depends on flow rates, where faster rates will move colloids by convection through saturated macropores (Christ and Hoffman, 2002; McCarthy and Zachara, 1989; Ranville et al., 2005) or through diffusion when rates are slower (Noack et al., 2000). Faster rates of flow through fractures and macropores will decrease the chance of filtration of larger particle diameters, as well as reduce the chance that colloids will have the chance to interact with the soil matrix (Kaplan et al., 1993; Ranville et al., 2005; McCarthy and Shevnell, 1998; Seta and Karathanasis, 1996). Transient flow has been observed to increase colloid concentrations as capillary pressure head was raised from -18.5 cm to -9.5 cm, and overall colloid concentrations were higher at less negative water potentials (Levin et al., 2002). Schelde et al. (2002) reported that flow rates were not as important as cumulative flow. Within their study colloid mobilization was time dependent and occurred when flow ceased and colloids were allowed to diffuse from the matrix into macropores.

Karst channels may also influence the effects of pyrite and carbonates since the chemistry of the water does not reflect the average content of the fill, but rather what it comes in contact with (Skousen et al., 2000), so reducing inflitration through the spoil is often done to reduce acidity. Reducing inflitration is done by diverting water, adding topsoil or revegetation (Daniels and Stewart, 2000). Quick establishment of vegetation is accomplished by adding topsoil and biosolids (Haering et al., 2000).

Biosolids typically add nutrients, water holding capacity, and structure to the soil to help revegetate the reclaimed land (Sopper, 1993; Haering et al., 2000), as well as reducing soluble metal loads in surface horizons (Haering and Daniels, 2000). Organic acids and humic material in the biosolids can chelate and bind metals, reducing their transport into groundwater (Sopper, 1993). Lime stabilized biosolids are often used to raise the pH, which reduces metal solubility (Haering et al., 2000),

but a higher pH can also cause organic colloids to be suspended, increasing the likelihood that they are leached through the system (Karathanasis and Ming, 2002). While most studies have observed that metals in solution decrease with application of biosolids, none have directly observed the potential for colloid transport in reclaimed mine refuse. We hypothesize that colloid transport will be reduced by disturbance within reclaimed soils, but increased through the addition of organic amendments with an alkaline pH.

Prediction of colloid transport in reclaimed minesoils presents various challenges due to large variation in reclaimed properties. The objectives of this chapter are to (1) observe the in-situ colloid generation and transport through soils disturbed by coal mining and reclaimed prior and after the passage of SMCRA, (2) evaluate the effects of drying on colloid generation, (3) and to determine if the addition of lime stabilized biosolids will increase colloid transport through soils disturbed by coal mining.

2.2 Materials and Methods

2.2.1 Soil Monolith Preparation

Intact soil monoliths were obtained from the Powell River Project (PRP), near Wise, Virginia, in the southern Appalachian Mountains, representing 30 year old reclaimed soils and from Robinson Forest, near Jackson, Kentucky, representing recently reclaimed mine soils.

The monoliths were subjected to the following for each study area (Figure 2.1). There were two replicated unmined forest soils, referred to as (1) Natural monoliths, which were used as controls. Three replicated soils disturbed by coal mining per site constituted the: (2) Reclaimed (3) Reclaimed soil + mine spoil material, and (4) Reclaimed soil + mine spoil material + biosolid application. Kentucky treatments were adjusted so that (4) constituted only Reclaimed soil + biosolid application following results from Virginia monoliths.

The disturbed, spoil, and natural soils in Virginia and the natural soils in Kentucky were obtained as intact soil monoliths, 30 cm in height and 18 cm in

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diameter. The reclaimed soils in Virginia had been deposited above a black spoil material varying in thickness from 30 cm to 1 m and containing fragments of siltstone. The Virginia reclaimed soils and spoil materials were obtained from their upper 30 cm depth and recombined in the lab for treatments 2 and 3 to ensure similar thickness. Monoliths were removed by digging a pedestal approximately 50 x 50 x 40 cm, then trimming them with knives and soil picks so to fit within a polyvinyl chloride (PVC) tube of 20 cm internal diameter and 30 cm height. The 1 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. The natural soil for both Virginia and Kentucky treatments was comprised by intact soil monoliths 30 x 18 cm obtained from adjacent undisturbed sites.

Rock fragment content prevented intact monoliths from being extracted from the 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, an intact surface horizon of about 15 cm in thickness, and 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. Subsurface material was packed in the column to obtain a bulk density of around 1.4 g/cm^3 up to about 15 cm. 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 spoil column was built the same way and a separate reclaimed mine soil monolith was built above it before filling with Poly-U-Foam.

The lime stabilized (CaO) biosolid material use in the study came from a local municipal wastewater treatment facility in Winchester (Clark County), Kentucky. It was dried and applied to the surface of the soil at a rate of 20 T/ha.

2.2.2 Bulk Soil Analysis

Natural, reclaimed, spoil, and biosolid materials were air dried and passed through a 2 mm sieve. EPA method 3050b was used to extract environmentally available Cd, Cr, Cu, Pb, Ni, and Zn from 1 g of soil, spoil, or biosolid materials using HNO_3 and HCl and heating to 95ºC. Extractants were analyzed by inductively coupled plasma spectrophotometer (ICP-MS) to determine initial levels of each metal in the materials. The pH and electrical conductivity (EC) were determined on 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). Mineralogical composition was performed by X-ray diffraction (XRD) and thermogravimetric analysis (TA) 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 (Karathanasis and Hajek, 1982).

2.2.3 Colloid Fractionation and Characterization

To determine which minerals within the bulk soil and spoil materials may be more mobile, water dispersible colloids were fractionated from bulk samples of soil, spoil and biosolid materials. A 50 g sample was placed in a 1 L centrifuge bottle and filled with D.I water. The slurry was mixed on a shaker for 1 hour and centrifuged at 750 rpm for 3.5 minutes. The colloid particles in suspension were decanted and the procedure was repeated on the same 50 g sample twice. Mineralogical composition was performed by x-ray diffraction (XRD) and thermogravimetric analysis (TA) using the methods described above. Adsorption isotherms were conducted on 100 mg dried colloid samples added to 50 mL test tubes containing 0 – 5 mg/L metal concentrations to compare to bulk soil isotherms. Further analyses were similar to the bulk samples above.

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2.2.4   In-Situ Colloid Elution

In-situ colloid generation and elution from monoliths was assessed with leaching experiments. A rainfall simulator was set up to apply D.I. water at a rate of 250 ml/hour (1.0 cm/hour) to the surface of each monolith. The application rate was controlled with a peristaltic pump. The upper boundary condition of the monolith was the 1.0 cm/hr infiltration rate and the lower boundary was kept at -10 cm using a Mariotte device. To control the lower boundary at -10 cm the monolith was placed in a large funnel and sealed around the edges with a silicone gel. A tube was attached from the funnel into a sealed 2 L flask for the leachate to drip into. This 2 L flask was also connected to a second flask, which was filled with water to create a positive tension beneath the monolith and maintain the lower boundary condition at the desired level. This second flask was sealed except for two openings, one of which connected to the tubing used to apply suction, and the other contained a thin PVC pipe which was open to the atmosphere. The bottom of the pipe was placed below the water surface, so that when suction was applied, air entered through the PVC and pushed through the water, creating a negative pressure within the system. A tensimeter was used to monitor the pressure within the funnel, which was adjusted to -10 cm by raising or lowering the pipe.

The leaching of each monolith was conducted in six cycles, corresponding to 2-3 pore volumes (pv) of elution. It was observed that after 6 cycles in preliminary studies that most monoliths did not elute additional colloids. Each cycle consisted of 2 L of water elution at 24-hour intervals. Leachate was collected at the bottom of the monolith every hour for a total of 8 hours, then allowed to equilibrate over 16 hours before leaching commenced again. This was done to observe if any colloid regeneration occurred between intense leaching cylces. Suspension concentrations were determined gravimetrically taking a 20 mL aliquot from each hourly sample and drying it at 105 ºC in a pre-weighed aluminum tin for 24 hours. Electrical conductivity was multiplied by 0.61 to convert to salt concentration which was then subtracted from the suspension concentrations to determine actual colloid concentration (US Salinity Laboratory, 1954). To correct for salts in the biosolid application treatments a glass membrane filter was used to remove mineral and

organic colloids in selected samples and create a regression equation of salt concentration versus electrical conductivity. A 20 mL aliquot eluent was filtered through a 0.2 μm filter and dried in a pre-weighed aluminum tin at 105 ºC for 24 hours before converting to mg/L salt content. Electrical conductivities for each sample were used to determine salt content using the regression equation, where salt content was subtracted from suspension concentration to determine colloid concentration.

The pH and EC were determined for each hourly elution. Dissolved organic carbon (DOC) was analyzed by taking a 20 mL subsample from each elution and acidifying it with one drop of concentrated H_2SO_4 to evaluate dissolved organic carbon on a Shimadzu TOC 500DA carbon analyzer.

Mineralogical composition of the samples was determined by x-ray diffraction (XRD) and thermogravimetric analysis (TA) (Karathanasis and Hajek, 1982). To extract colloids from the eluent samples were filtered through a 0.45 μm filter which was taped to a glass slide for XRD analysis. 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.

Natural and reclaimed monoliths were dried in an oven at 60ºC following the original leaching. During drying, the monoliths were weighed daily until no change was seen in the mass. A new leaching cycle was then conducted on each monolith to determine if drying would induce colloid regeneration following an intense leaching. It was assumed that colloids would regenerate through diffusion from smaller pores and physical weathering of soil particles during drying. Eluents were measured for colloid concentration, pH, and EC, and compared to the first leaching cycle.

2.3   Results and Discussion

Virginia Sites

2.3.1   Soil and Biosolid Properties

The Virginia reclaimed soils (Table 2.1) had a higher sand content and lower silt and clay than their natural counterparts, because there is a loss of finer materials

during reclamation (Daniels and Stewart, 2000). Consequently, in-situ colloid release within mine soils may be lower because of the lower clay content. The Virginia natural soils had low bulk density (1.18 g/cm^3), probably due to maturity and organic matter incorporation, while reclaimed soils had a bulk density of 1.34 g/cm^3. The Virginia spoil material had the highest bulk density (1.87 g/cm^3), apparently due to compaction from heavy mining equipment. The spoil material also had the lowest particle density (1.87 g/cm^3) compared to natural (2.54 g/cm^3) and reclaimed soils (2.61 g/cm^3), probably due to the high silt and coal content. The natural soils had the highest pore volume (4.1 L) due to their lower bulk density, followed by reclaimed (3.62 L), and the spoil material (0.42 L). The high bulk density and low pore volume of the spoil material suggest that they may be inherently restrictive to flow and colloid transport.

The Virginia natural (5.1), reclaimed (5.4), and spoil material (4.5) all had acidic pH values compared to the 12.7 of the lime stabilized biosolids. Therefore, the addition of biosolids may raise the pH of reclaimed and spoil materials, increasing the likelihood of colloid release. The spoil material also had the highest electrical conductivity (287 μS/cm), followed by natural (31 μS/cm), reclaimed (23 μS/cm), and biosolids (9 μS/cm). Leaching through the spoil material may increase the ionic strength of the reclaimed pore water and aggregate colloids in suspension. The biosolids had the highest (62.8 cmol/kg) cation exchange capacity (CEC), followed by the spoil material (35.8 cmol/kg), natural soils (8.2 cmol/kg), and reclaimed soils (5.1 cmol/kg). The higher CEC of the biosolids and spoil materials may be due to organic matter. The potential acidity of the spoil material was 103.7 tons/acre, so it would take that much calcium carbonate to neutralize the acidity. The biosolids had a 70 % calcium carbonate equivalent (CCE) and with an application rate of 20 tons/ha of biosolids, only 5.6 tons of CCE were applied to the Virginia monoliths.

2.3.2 Elution pH and EC

Average pH (Figure 2.2) over the entire leaching was highest in the reclaimed monoliths (6.1), while the reclaimed with spoil (4.9), natural (4.6), and biosolid amended (4.3) monoliths were all similar. Organic acids in the natural monolith may

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have contributed to the low pH, while the more acidic spoil in the spoil and biosolid treatments kept the pH lower than reclaimed and natural treatments. Overall pH trends can be seen in Figure 2.3, where reclaimed monoliths remained consistently higher over the entire leaching cycle. There was a decrease in the elution pH (Figure 2.2) for the natural (5.9 to 4.3), reclaimed (7.3 to 5.7), and spoil (5.5 to 5.0) treatments, but the biosolid treatment rose from 4.0 to 5.0 after about 2 pore volumes (Figure 2.2). The decrease in pH for most treatments may come from a loss of basic cations during leaching, while the rise in the biosolid amended monolith pH is caused by the alkaline nature of the lime stabilized biosolids. The rise in pH within the biosolid amended monoliths may increase in-situ colloid transport (Karathanasis and Ming, 2002). None of the pH changes across the leaching cycles were significant.

Average electrical conductivity (Figure 2.4) was highest in the biosolid amended monoliths (859 µS/cm), while the spoil (506 µS/cm), reclaimed (375 µS/cm), and natural (354 µS/cm) monolith eluents were all similar. The EC values dropped in all treatments following leaching (Figure 2.3b), with the largest drop in the biosolid amended monoliths (1415 to 290 uS/cm), followed by reclaimed (700 to 226 uS/cm), spoil (701 to 404 uS/cm), and natural (519 to 267 uS/cm). The additional salts present in the biosolid amended monoliths contributed to the higher EC, with the peak salt content occurring just before 0.5 pore volumes (Figure 2.3). While the higher pH of the biosolid amended monoliths may suspend more colloids, the higher salt content may flocculate and cause filtration by smaller pores.

2.3.3   DOC Elution

The Virginia natural monolith eluents contained higher average DOC levels (605.2 mg/L), followed by the reclaimed (401.9 mg/L), spoil (251.7 mg/L), and biosolid amended treatments (44.5 mg/L) over the entire elution period (Figure 2.5). The forest litter of the natural monoliths contributed to their high DOC, while the reclaimed soils have possibly regained some organic carbon after 30 years under forest management. The low DOC in biosolid amended monolith eluents suggests that within two pore volumes, limited DOC or colloidal material was released from the biosolids. Biosolid during initial application may not produce biosolids as they high

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Ca content may keep the material flocculated. Overtime colloids may release from this material. Colloids may also have been limited in their transport from the surface of monoliths to the collection flask during the short time that these monoliths were observed.

The decrease in carbon over the leaching cycle was largest for the natural monoliths (1888 to 119 mg/L), followed by reclaimed (980 to 172 mg/L), spoil (229 to 135 mg/L), and biosolid monoliths (66 to 22 mg/L). After 2 pore volumes the natural, reclaimed, and spoil amended treatments had similar DOC. The biosolid treatment started at the lowest DOC values out of all the treatments, suggesting that the spoil material associated with this treatment did not produce much DOC and applied biosolids did not contribute to DOC eluted within 2 pore volumes.

2.3.4 Colloid Elution

Cumulative colloid elution through the natural Virginia monoliths ranged from 751 to 964 mg (Figure 2.6). However, the elution pattern between the duplicate monoliths was somewhat different, with the Natural I monolith producing no colloids after 0.5 pore volumes, while the Natural II monolith produced slightly more colloids between 0.5 and 1.0 pore volumes. By the end of the leaching, no colloids were detected in the eluent of either monolith, and the lines appeared flat. Variability in colloid content, pore connectivity, or loose material during extraction of the natural monoliths may have caused the Natural II monolith to produce more colloids after 0.5 P.V.

Cumulative colloid load eluted from the reclaimed monoliths was very similar, but with different patterns of elution (Figure 2.7). The Reclaimed I monolith eluted 1469 mg of total colloids within 1 pore volume in an irregular pattern, ceasing and resuming twice before the maximum colloid elution was observed. The Reclaimed II eluted 1452 mg within 1 pore volume, with a smooth transition to its maximum colloid elution. The stuttered elution occurring in the Reclaimed I monolith may have occurred due to diffusion of colloids from smaller pores, dispersion of colloids with small changes in pore water chemistry, or shear along pore walls as water cycles were discontinued and restarted the next day.

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Reclaimed monoliths underlain by spoil material also eluted similar total colloid loads, (79 and 83 mg, respectively), but showing contrasting elution patterns (Figure 2.8). Monolith I eluted all of it's colloids within the first 0.3 pore volumes, while monolith II did not elute any colloidal material before 0.3 pore volumes. Thereafter it showed two colloid flushing events at 0.35 and 0.65 P.V. before reaching a plateau at about 0.7 P.V. Within the spoil monoliths flushing events may have occurred in the second monolith due to clogged pores releasing their colloids.

In-situ colloid production and transport through these soils is apparently limited by either pore size or source (Barton and Karathanasis, 2003). It is difficult to determine within each elution cycle whether the source of the colloids was the entire monolith or only the lower portion. Colloids from the upper 15 cm of any monolith could have been filtered out by smaller pores before they could become eluted from the monolith, keeping in mind the model of formation of argillic horizons through clay elluviation/illuviation processes. The soils stayed close to saturation (-1 to -5 cm) through each leaching cycle, possibly flushing all colloids within the monolith in 1.0 P.V. and preventing the release of new colloids through diffusive mechanisms (Schelde et al., 2002). It is also difficult to discern if the source of colloids came entirely from the larger macropores within each monolith. Diffusion of colloids from smaller pores may have occurred during the short time between cycles, but a majority of the colloids eluted probably came from the macropores, where colloid size restrictions were the least and flow was the fastest.

In contrast to the Virginia natural, reclaimed, and spoil treatments that showed colloid elution plateaus before or at 1 P.V., the biosolid amended treatments continued to elute colloids beyond 2 P.V., reaching maximums of 1104 and 637 mg, respectively (Figure 2.9). Biosolid additions apparently have affected the chemistry of the reclaimed and spoil monoliths through increased pH after about 2 P.V. (Figure 2.2). A higher pH may have increased the dispersion of colloidal material, increasing the colloid load eluted from those treatments (Karathanasis and Ming, 2002).

For natural, reclaimed, and spoil monoliths, colloid concentration was highest near the beginning of the elution, while the biosolid monoliths had higher eluted colloid concentrations between 0.1 and 1 P.V. (Figure 2.10). Both natural and

reclaimed monoliths started out with colloid concentrations above 1000 mg/L, but quickly tapered off to levels similar to the other treatments. Average colloid concentration (representing the average concentration from every eluent sample) within all treatments (Figure 2.11) was highest in reclaimed soils (207 mg/L), followed by natural monoliths (105 mg/L) and reclaimed with spoils and biosolids (79 mg/L), while reclaimed monoliths with spoil material (11 mg/L) had the lowest colloid concentration.

The reclaimed monoliths (Figure 2.11) had the highest eluted cumulative colloid loads (1460 mg), followed by the natural (858 mg) and biosolid amended monoliths (871 mg), while reclaimed monoliths with spoil material had the lowest (76 mg). The reclaimed soils had about 1.5 times the colloids of natural monoliths (Shukla et al., 2004), which may be caused by the loss of aggregation by clay and organic materials, resulting in the smaller eluted particle size (Table 2.2) and the larger cumulative colloid elution. The reclaimed monoliths eluted (Figure 2.12) a higher amount of cumulative colloids than the other treatments over the entire elution. Reclaimed monoliths (Figure 2.12) are also the only treatment where cumulative colloids eluted in a disrupted pattern. These monoliths may have macropores which occasionally clog or terminate into smaller pores. The spoil material presented a physical or chemical barrier to the colloids eluted within the reclaimed monoliths. The biosolid amendment may have caused a larger amount of colloid release because of pH effects, but it is also possible that the spoil material is variable between all monoliths and would have produced more eluted colloids regardless of biosolid addition. The biosolid amended monoliths were the only treatment which released colloids in a steady linear pattern (Figure 2.12). This may indicate that monoliths amended with biosolids will not reach a plateau within 2 P.V., and may release a higher cumulative colloid amount than reclaimed monoliths in the long run.

2.3.5 Particle Size and Mineralogy of Eluted Colloids

Average eluted colloid particle size (Table 2.2) was highest within the biosolid amended monoliths (2662 nm), followed by natural (721 nm), reclaimed (521 nm), and reclaimed with spoil (460 nm). Colloids extracted by mechanical shaking and

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centrifugation were smaller than eluted colloids for the natural, spoil, and biosolid amended monoliths and larger in the reclaimed monoliths (Table 2.2). Average colloid diameter was larger than 200 nm for all measured eluents, so filtrations by a 0.2 um filter should successfully capture all suspended colloids.

Reclaimed monoliths had both the most cumulative colloids eluted (Figure 2.11) and a smaller eluted colloid particle size when compared to natural and biosolid amended monoliths. The smaller colloid size within reclaimed monoliths may have reduced the likelihood that they would be filtered by clogging. Although biosolid amended monoliths had a much larger particle size diameter, they eluted a similar amount of total colloids as the natural monoliths (Figure 2.11).

Mica and kaolinite made up a greater portion of the overall mineralogy in eluted colloids compared to centrifuge derived colloids (Table 2.2). Although 2:1 minerals such as smectite and illite have been observed to break through in higher concentrations (Karathanasis, 2003), and kaolinite has shown lower water dispersability at low pH than 2:1 minerals (Seta and Karathanasis, 1996), it appears that mica and kaolinite were more mobile than other minerals within these monoliths. The higher amounts of kaolinite within natural and biosolids amended monoliths explain the larger colloid diameter observed (Table 2.2), while the lower quartz percentage in reclaimed monoliths may have contributed to the smaller diameter of those eluted colloids. Overall, quartz was consistently lower in the eluted colloids, probably due to the inert qualities of quartz and its larger particle diameter, which may cause it to be filtered in smaller pores. Gibbsite was also present in higher quantities in Virginia reclaimed monoliths, which may have been mobilized as the pH and ionic strength dropped within the reclaimed monolith eluents.

2.3.6   Bromide Tracer Elution

For the natural (Figure 2.13), reclaimed (Figure 2.14), and reclaimed-spoil combination (Figure 2.15) monoliths, in-situ colloids eluted earlier than Br⁻ as a function of pore volumes. It should also be noted that the Br⁻ experiments were conducted following colloid leaching experiments. Water dispersible colloids applied to the surface of soil monoliths have shown rapid breakthrough ahead of a

conservative (Cl⁻) tracer, usually following preferential flow paths (Seta and Karathanasis, 1997). The bromide within these monoliths was applied to the surface, while in-situ colloids could exit from the lower portions of the monoliths immediately, allowing for earlier breakthrough. Within the biosolid amended monoliths (Figure 2.16) colloids continued to be eluted past 2 P.V. While colloids were eluted before the tracer, they had not reached a maximum elution before the bromide reached its initial concentration.

The natural monoliths (Figure 2.17) eluted $0.5(C_o)$ of the tracer earlier than any other treatment, revealing more preferential flow than the other monoliths. This is probably due to the maturity of the soil and the lack of disturbance which would have destroyed macropores within the soil. A mature forest soil should have root channels and macrofauna passages which allow for more preferential flow. The reclaimed and reclaimed-spoil combination monoliths had similar tracer patterns, suggesting that both monoliths have similar pore distributions. The monoliths amended with biosolids reached the initial concentration earlier than the other reclaimed treatments, so these soils may have more macropores than the former treatments inducing faster elution of the tracer when the monoliths are saturated.

2.3.7 Colloid Elution Following One Drying Cycle

Treatment monoliths were leached a second time following drying at 60ºC to determine if colloids would regenerate. Following drying the average pH (Figure 2.18) was similar for both the natural (4.6 vs. 4.4) and reclaimed monoliths (6.1 vs. 5.6), being slightly higher before drying in both. The average conductivity (Figure 2.18) of eluents from monoliths was lower after drying in both natural (354 vs. 246) and reclaimed (375 vs. 152) treatments, suggesting that salts have difficulty regenerating from the soil matrix to the soil solution. This was similar to the findings of Klitzke and Lang (2007), who observed that with drying that there was not much difference in eluent pH and conductivity.

Both the Virginia natural and reclaimed monoliths eluted more colloids following drying (Figure 2.19), even though they had been producing none after one P.V. in the original leaching. The natural monoliths eluted four times more total

colloids following drying than the first elution, while colloid elution within reclaimed monoliths was 0.8 times lower. Colloid regeneration is possible within soils following drying, and is quicker than salt regeneration. This is possibly because salts derive from mineral dissolution and cation exchange, slowing their regeneration after intense leaching. Colloids may come from several sources including loss of aggregation, release from previously clogged pores, and diffusion from the soil matrix. Drying the column may increase the rate of release for any of these processes.

The drying cycles may be compared to seasonal wet/dry effects. Rainfall in the spring will be conducive to colloid generation through leaching. The intensity of these events will probably be more dynamic than the lab experiments, so it is likely that several spring and early summer rains could mobilize a significant amount of colloids in these soils. Following a dry and hot summer, more colloids may be potentially released in these soils, and subsequently leached in the fall or following spring as the post drying and leaching cycles suggest. Therefore colloid release would probably be cyclical, peaking in the spring or fall, and subsiding in the summer.

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2.3.8   Soil and Biosolid Properties

The reclaimed soils (Table 2.3) had a higher sand content and lower silt and clay than the natural soils, probably due to some loss of finer materials during reclamation (Daniels and Stewart, 2000). This may result in lower colloid release within mine soils because of the lower clay content. The spoil material had a similar particle size distribution as the natural soils, but much greater rock content. The natural soils had low bulk density (1.04 g/cm^3), probably due to maturity and organic matter incorporation, compared to 1.39 g/cm^3 of the reclaimed soils and 1.42 g/cm^3 of the spoil material, which were both constructed to have a higher bulk density. The particle density of natural (2.33 g/cm^3) and reclaimed soils (2.32 g/cm^3) were similar, even though reclaimed soils had a slightly higher sand content. The natural soils had the highest pore volume (4.2 L) due to the lower bulk density, followed by reclaimed (2.8 L), and the spoil material (2.7 L). The higher bulk density and lower pore volume of the reclaimed and spoil monoliths suggest that they may restrict colloid transport

more than native monoliths. Compaction may reduce pore connectivity as well as diameter, directly influencing the transport of colloids through the monoliths.

The natural (6.1) and spoil material (4.5) had acidic pH values compared to the reclaimed (7.2) and the lime stabilized biosolids (12.7). The higher pH of reclaimed monoliths particularly in the presence of biosolids may be increasing the likelihood of colloid release (Karathanasis and Ming, 2002). The spoil material also had the highest electrical conductivity (2240 $\mu S/cm$), followed by reclaimed (78 $\mu S/cm$), natural (36 $\mu S/cm$), and biosolids (9 $\mu S/cm$). As the EC of a solution rises, so does the ionic strength (US Salinity Laboratory, 1954). Therefore colloid suspension and mobilization through the spoil material may be inhibited due to the increase in ionic strength of the reclaimed pore water that is conducive to aggregation of the suspended particles. The biosolids had the highest (62.8 cmol/kg) cation exchange capacity (CEC), followed by the natural soils (10.3 cmol/kg), spoil material (6.1 cmol/kg), and reclaimed soils (2.3 cmol/kg). The higher CEC of the biosolids and natural soils is attributed to their higher organic matter content. The potential acidity of the spoil material was 6.6 tons/acre, so it would take that much calcium carbonate to neutralize the acidity. However, its near neutral buffered pH (6.8) suggests that acidity may be easily neutralized.

2.3.9   Elution pH and EC

Average pH (Figure 2.20) over the entire leaching was 6.3 for eluents from the natural monoliths and did not change much over the leaching cycle (Figure 2.21). Average pH was highest in the reclaimed monoliths (7.7) and remained relatively stable when biosolids were added to the monolith (7.9). Even though the addition of lime stabilized biosolids did not raise the pH higher, this eluent pH range is conducive to colloid mobilization and transport. The addition of spoil material beneath the reclaimed monoliths dropped the average eluent pH to 4.2, thus potentially limiting further colloid generation and transport. The pH levels for eluents of reclaimed and biosolid amended monoliths remained consistently higher over the entire leaching cycle (Figure 2.21). In spite of some small pH variability during the leaching process, none of the pH changes within the leaching cycles were significant.

Therefore, amongst the treatments, pH either did not or had similar changes between all of the monoliths observed.

Average electrical conductivity (Figure 2.22) was highest in the reclaimed-spoil combination monoliths (4541 uS/cm), while the biosolid amended (651 uS/cm), reclaimed (441 uS/cm), and natural (192 uS/cm) monolith eluents were all similar. The EC values dropped in all treatments following leaching (Figure 2.21, 2.3), with the largest drop in the reclaimed-spoil combination monoliths. The reclaimed-spoil combination monolith eluents remained at 4000 uS/cm even after 3 P.V., suggesting that it will take considerable time to leach all of the salts from these monoliths. Both the high ionic strength of the reclaimed-spoil eluents and acidic pH can aggregate colloids and restrict mobilization.

2.3.10 DOC Elution

The natural monolith eluents contained higher average DOC levels (1522 mg/L), followed by the reclaimed (204 mg/L), biosolid amended (162 mg/L), and reclaimed-spoil monoliths (42 mg/L) over the entire elution period (Figure 2.23). The forest litter of the natural monoliths contributed to their high DOC, while the reclaimed soils have possibly regained some organic carbon in the surface horizons from decaying grass roots. There was no increase in DOC when biosolids were added to reclaimed monoliths, suggesting that within 2 pore volumes the DOC and biocolloids were effectively filtrated by the monolith matrix. The decrease in carbon over the leaching cycle was largest for the natural monoliths, followed by reclaimed, biosolid, and reclaimed-spoil monoliths. After 2 pore volumes all monoliths had similar DOC levels.

2.3.11 Colloid Elution

Cumulative colloid elution through the natural Kentucky monoliths ranged from 6610 to 7926 mg (Figure 2.24). After 1.5 P.V. of leaching, no colloids were detected in the eluent of the Natural I monolith while the Natural II duplicate monolith continued to elute colloids at a lower rate beyond 2 pore volumes.

Cumulative colloid loads eluted from the reclaimed monoliths were highly variable, with the Reclaimed I monolith eluting 1074 mg and the Reclaimed II monolith eluting 20,738 mg of colloids (Figure 2.25). There was an opportunity to observe two more reclaimed monoliths because of the biosolid amended treatments. To differentiate between colloid and mineral loads, two reclaimed monoliths were built and leached to remove mineral colloids before the biosolid application was made. These two monoliths are reported before biosolid application as Reclaimed III (1955 mg cumulative colloids) and Reclaimed IV (2335 mg cumulative colloids) in Figure 2.25, and can be observed to be closer to Reclaimed I in total colloids eluted. This indicated the measure of heterogeneity that can be expected from recently reclaimed soils and the highly variable colloid output of the replaced soil materials. The good agreement between the three monoliths also suggests that the 20,000 mg of colloids eluted from the Reclaimed II monolith is probably an exception.

Both the reclaimed monoliths underlain by spoil material did not elute any colloids (Figure 2.26), probably due to their high salt content and acidic pH values in the eluent. Colloids entering the spoil material will probably be slightly different in mineralogy and particle size and could be removed by the change in pore water chemistry, aggregating and being filtered out in the pore channels. It is difficult to determine within each elution cycle whether the source of the colloids was the entire monolith or only the lower portion. Colloids from the upper 15 cm of any monolith could have been filtered out by smaller pores before they could become eluted from the monolith, assuming natural eluviation/illuviation processes. The transport of colloids generated within the reclaimed and the spoil matrix may be inhibited by the chemistry of the spoil material. The lower clay content (13%) of the spoil may have also been a deterrent in colloid generation.

The natural and reclaimed monoliths stayed saturated through each leaching cycle, possibly flushing all colloids within the monolith in 1.0 P.V. and preventing the release of new colloids through diffusive mechanisms (Schelde et al., 2002). In contrast to these monoliths, the biosolid amended treatments continued to elute colloids beyond the 2 P.V., reaching maximums of 1063 and 1356 mg, respectively (Figure 2.27).

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The reclaimed (III, IV) monoliths had been leached prior to biosolid addition and had both reached plateaus in colloid elution (Figure 2.25). The Biosolid I monolith showed a small plateau at 1 P.V. before starting to release more colloids at 3 P.V., while the Biosolid II monoliths had a linear elution during the entire leaching. Biosolid additions were not shown to raise the pH (Figure 2.20), but the presence of organic ligands may have enhanced the dispersion of colloidal material and the eluted load from those treatments.

For the natural and reclaimed monoliths, colloid concentration was highest near the beginning of the elution, while the biosolid monoliths had a consistent concentration of colloids throughout the elution (Figure 2.28). The natural monoliths started out with colloid concentrations above 5000 mg/L, but quickly tapered off to levels similar to the reclaimed treatment. Average colloid concentration within all treatments (Figure 2.29) was highest in the reclaimed soils (1016 mg/L), followed by natural monoliths (655 mg/L) and reclaimed with biosolids (104 mg/L), while the reclaimed monoliths with spoil material (0 mg/L) had the lowest colloid concentration.

The reclaimed (6525 mg) and natural monoliths (7269 mg) had the highest eluted cumulative colloid loads (Figure 2.29 a); however, the abnormally high colloid elution from the Reclaimed II monolith distorted the statistical comparisons. When the Reclaimed IV monolith was substituted for Reclaimed II in the ANOVA, the natural monoliths became significantly higher than all other treatments (Figure 2.29 b).

A larger sample size for all the treatments within this study may be necessary to determine the real relationship. The natural monoliths eluted a significant amount of colloids, possibly due to the macroporosity from the root channels and higher clay content than reclaimed monoliths. The reclaimed monoliths though, based on the more consistent elution patterns of Reclaimed I, III, and IV, may have fewer colloids because of lower clay content and lower macroporosity. On the other hand the excessively large amount of colloids eluted from Reclaimed II is a sign of the extreme variability in these soils that may make them difficult to predict.

The spoil material presented a chemical barrier to the colloids eluted within the reclaimed monoliths, probably due to its high salt content. The addition of biosolids caused a larger amount of colloid release, probably because of pH effects, that may prolong colloid elution beyond 2 P.V., and could result in a higher cumulative colloid mass than unamended reclaimed monoliths in the long run.

2.3.12 Particle Size and Mineralogy of Eluted Colloids

Average eluted colloid particle size (Table 2.4) was highest within the reclaimed monoliths (1127 nm), followed by biosolid amended monoliths (721 nm) and natural monoliths (314 nm). No colloids were detected in the reclaimed-spoil monolith eluents. Colloids extracted by mechanical shaking and centrifugation were larger than eluted colloids for the natural and biosolid amended monoliths and similar in size to the reclaimed monoliths (Table 2.4). Average colloid diameter was larger than 200 nm for all measured eluents, so filtration by a 0.2 µm filter should successfully capture a large majority of the suspended colloids.

The large diameter of the eluted colloids from reclaimed monoliths is consistent with the age of the material and its particle size distribution. The natural monoliths had one of the highest average colloid loads and the smallest particle size. The smaller particle size of natural colloids may have allowed for easier dispersion and greater mobilization and transport within the monoliths. Three of the reclaimed monoliths had lower colloid loads than both natural monoliths. Apparently, the lower macroporosity and the large colloid diameter increased the likelihood of filtration of the reclaimed colloids.

Mica and kaolinite made up a great portion of the mineralogy of eluted colloids (Table 2.6). Although kaolinite has generally shown lower water dispersability at low pH than 2:1 minerals (Seta and Karathanasis, 1996; Karathanasis, 2002), it appeared to be more mobile than hydroxyl interlayered vermiculite (HIV) within these monoliths. Generally, quartz was consistently lower in the eluted colloids, except for the biosolid amended monoliths, where a quartz increase was probably caused by a matrix detachment from the bottom of the monoliths.

2.3.13 Bromide Tracer Elution

In the natural (Figure 2.31), reclaimed (Figure 2.32), reclaimed-spoil (Figure 2.33), and biosolid amended monoliths (Figure 2.34), the bromide tracer was rapidly eluted to the initial concentration within one pore volume. Only the natural monoliths released colloids faster than the bromide tracer (Figure 2.31). The natural monoliths have more root channels from being under forest management, and ex-situ water dispersible colloids applied to the surface of soil monoliths have shown rapid breakthrough ahead of a conservative (Cl⁻) tracer, usually following preferential flow paths (Seta and Karathanasis, 1997). However, the bromide within these monoliths was applied to the surface, while in-situ colloids exit from the lower sections of the monoliths immediately, allowing for earlier colloid breakthrough.

Within the reclaimed (Figure 2.32) and biosolid amended monoliths (Figure 2.34), almost all observed colloids were eluted after the bromide tracer, indicating restricted movement of colloids within the monoliths. Because colloids were not applied to the monoliths like the tracer, it is hard to compare the two curves. The rapid breakthrough of the tracer does suggest that colloids may be transported from throughout the reclaimed monoliths by preferential flow, and may not only come from the lower sections of the monoliths.

In spite of differences in their matrix makeups, all monoliths (Figure 2.35) eluted $0.5(C_o)$ of the tracer at similar pore volumes. Most of the monoliths overlapped each other in either the beginning or the end of the elution, and reached the initial bromide concentration around one pore volume.

2.3.14 Colloid Elution Following One Drying Cycle

The natural and reclaimed monoliths were leached a second time following drying at 60ºC to determine if colloids would regenerate. The reclaimed monoliths (III, IV) that were amended with biosolids were not dried, so all colloid averages refer to reclaimed monoliths I and II.

Following drying the average pH (Figure 2.36) was similar for both natural (6.3 vs. 6.5) and reclaimed monoliths (7.4 vs. 7.4). The average conductivity (Figure 2.36)

of eluents from monoliths was higher after drying in natural monoliths (192 vs. 345), and was higher over the entire elution. Drying the monolith may have concentrated some salts onto the pore walls through desiccation, which only explains the higher initial salt content and not the consistently higher EC. In reclaimed monoliths electrical conductivity was similar (441 vs. 444), which is consistent with the findings of Klitzke and Lang (2007), who observed that with drying there is not much difference in eluent pH and conductivity.

Both natural and reclaimed monoliths eluted additional colloids following drying (Figure 2.37), even though they had been producing none after one pore volume in the original leaching. However, the total colloid mass eluted was only 1/3 of that eluted from natural monoliths and only 1/10 of the reclaimed monoliths before drying. Only the Reclaimed I and II monoliths were oven dried, and the colloid load eluted from both monoliths following drying was similar to Reclaimed I, III, and IV before drying. This is further evidence that the large colloid load from Reclaimed II before drying may be an exception to other reclaimed monoliths. The results suggest that colloid regeneration is likely within soils following drying. Colloids may come from several sources, including loss of aggregation, release from previously clogged pores, and diffusion from the soil matrix.

2.3.15 Comparison of Virginia and Kentucky Sites

Overall, the highest eluent pH (Figure 2.38) was associated with the Kentucky reclaimed (KR) and Kentucky reclaimed and biosolid amended monoliths (KRB), but did not appear to have any significant effect on colloid elution (Figure 2.39). The siderite content of the KR monoliths along with lime stabilized biosolids of the KRB monoliths increased their eluent pH, while the acidic spoil material lowered the eluent pH in the Virginia reclaimed with spoil (VRS), Virginia reclaimed with spoil and biosolid amendment (VRSB), and Kentucky reclaimed with spoil (KRS) treatments. Within these monoliths other factors, such as bulk density and salt content, probably confound pH effects. High salt contents because of fresh spoil material contributed to high EC in the eluents (Figure 2.38), of the KRS monoliths, and their subsequent low colloid release (Figure 2.39). The Virginia natural (VN), Virginia reclaimed (VR),

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and Kentucky natural (KN) treatments had the lowest electrical conductivity; hence young spoil material or unweathered parent material mixed with the matrix of reclaimed soils may be a long term source of salts that could impede colloid mobilization.

The low colloid elution in VRS monoliths indicated that besides salt content, compaction may also impede colloid transport, as evidenced by the high bulk density of the Virginia spoil monoliths (1.75 g/cm^3). When KR monoliths with similar colloid loads were compared to all other treatments, the model was significant for all treatments. The KN monoliths eluted the highest colloid loads, while both VRS and KRS monoliths eluted the least amount of colloids. A larger sample size could add some additional reliability to these trends. The high colloid load in the KN monoliths may be due to the large root channels which were observed on extraction, compared to VN monoliths. Besides the spoil material reducing the amount of colloids eluted, there were not many differences between reclamation methods on colloid elution. All reclaimed monoliths regenerated and eluted more colloids following wet/dry cycles, but with lower loads.

2.4   Summary and Conclusions

All duplicated monoliths eluted similar total cumulative colloid loads, except the KR II monolith, suggesting little variability in colloid generation and transport within monolith treatments. When comparing the average cumulative colloid elution between VR soils (over 30 years old) and the younger KR monoliths, there is not much difference, except for the abnormal behavior of the KR II monolith. This variability suggests that recently reclaimed soils release high amounts of colloids, possibly due to their low consolidation and loss of aggregation, but over time they will reach a steady state and be relatively similar to other soils in colloid production. Natural soils from Virginia produced a lower colloid load than those in Kentucky. Variability amongst natural forest soils may be high due to site location, including colluvial versus sideslope positions and proximity to large tree roots. Higher clay content in natural versus reclaimed monoliths may increase colloid elution due to the larger source of colloidal material.

Across Virginia and Kentucky monoliths, pH did not influence colloid concentration, unless it was associated with lime stabilized biosolids. Lime stabilized biosolid amendments increased colloid release through dispersion, resulting in a continual release of colloids after 1 P.V. This dispersion probably occurs because of organic ligands sorbing to mineral colloid surfaces, creating a more pH dependent charge, as well as the raise in pH due to the lime stabilized nature of the biosolids. Biosolids had a similar colloid elution effect on both reclaimed soils, showing a continuous linear release pattern. There was no increase in DOC observed within biosolid amended monoliths, so the increase in colloidal material was more likely due to pH changes affecting mineral colloids.

The opposite effect occurred with increasing EC, which enhanced flocculation thus increasing the chances for filtration in the Kentucky spoil material. The presence of spoil material beneath the VR monoliths reduced colloid load transport mainly due to its high density rather than ionic strength. Therefore over time, the Kentucky spoil material may have a better chance of leaching out the salts and facilitating more colloid transport.

In spite of the fact that natural and reclaimed monoliths from both study areas ceased producing colloids after 1 pv, drying the monoliths at 60ºC regenerated colloid elution. This is consistent with the findings of Schelde et al. (2002), suggesting that colloids are regenerated by diffusion from the matrix after throughflow has ceased within the soils. Although soils may not always become this dry in the field, they will experience cyclical seasonal effects, with colloid elution peaks occurring during spring rains and after dry periods in the summer.

In-situ production of colloids appears to be a perpetual regeneration process in natural and reclaimed soils, but results vary when spoil and biosolids are factored in, due to variance in pH, EC, and bulk density. Predicting colloid generation and transport in these soils may be difficult because of the heterogeneity inherent in lands reclaimed following strip mining, but through leaching and wet/dry cycles, a steady state colloid release is inevitable. Considering in-situ colloid production a constant regeneration process, colloid mediated pollutant transport may be expected to follow a similar pattern. Since mining may increase average metal content from exposure of

fresh unweathered spoil material, or the application of biosolids, colloid transport of metals to groundwater should be anticipated and even expected in these systems. Therefore, groundwater pollution prediction and prevention strategies should always take into account colloid transport potential by observing soil properties such as ionic strength, pH, mineralogy, bulk density, and organic content.

Table 2.1: Chemical and physical properties of the Virginia soils and biosolids.

	Natural	Reclaimed	Spoil Material	Biosolids
Sand %	34.5	78.1	52.8	-
Silt %	46.1	16.8	26.4	-
Clay %	19.4	5.1	20.8	-
D_b (g/cm^3)	1.18	1.34	1.75	-
D_p (g/cm^3)	2.54	2.61	1.87	-
pH	5.1	5.4	4.5	12.7
EC (µS/cm)	31	23	287	9
CEC (meq/100g)	8.2	5.1	35.8	62.8
Potential Acidity (tons/acre)	-	-	103.7	-
Pore Volume (L)*	4.09	3.67	0.42	-

* Total liters of pore space per one column.

Table 2.2: Estimated mineralogy (%) and particle size (nm) of centrifuged and eluted Virginia colloids (Relative peak intensity by ½ width).

	Natural		Reclaimed		Reclaimed with Spoil**		Reclaimed with Spoil + Biosolids	
	Cfg*	Elu.	Cfg	Elu.	Cfg	Elu.	Cfg	Elu.
Mineral	--%--							
HIV	29	18↓	13	15	8	-	8	0↓
Int	6	0↓	22	3↓	14	-	14	9↓
Mica	4	13↑	20	37↑	42	-	42	39
Kaolinite	23	53↑	17	14	10	-	10	33↑
Quartz	38	16↓	25	6↓	26	-	26	13↓
Gibbsite	0	0	20	25↑	0	-	0	6↑
	-------------------------------------Particle Size (nm)-------------------------------------							
Avg	308	721	700	521	320	460	320	2662
Std Dev	-	404	-	370	-	121	-	4309

* Cfg= centrifuged colloid, Elu = eluted colloid.
** Colloid concentration was not high enough to measure eluted colloids.
↑↓ Increasing or decreasing trend

Table 2.3: Chemical and physical properties of the Kentucky soils and biosolids.

	Natural	Reclaimed	Spoil Material	Biosolids
Sand%	58.1	73.5	59.0	-
Silt%	30.9	18.7	27.5	-
Clay%	11.0	7.8	13.5	-
D_b (g/cm^3)	1.04	1.39	1.42	-
D_p (g/cm^3)	2.33	2.32	-	-
pH	6.1	7.2	4.5	12.7
EC (μS/cm)	36	78	2240	9
CEC (meq/100g)	10.3	2.3	6.1	62.8
Potential Acidity (tons/acre)	-	-	6.6	-
Pore Volume (L)*	4.23	2.83	2.66	-

* Total liters of pore space per one column.

Table 2.4: Estimated mineralogy (%) and particle size (nm) of centrifuged and eluted Kentucky colloids (Relative peak intensity by ½ width).

	Natural		Reclaimed		Reclaimed with Spoil**		Reclaimed with Spoil + Biosolids	
	Cfg*	Elu.	Cfg	Elu.	Cfg	Elu.	Cfg	Elu.
Mineral	--%--							
HIV	35	12↓	8	5	15	-	8	11
Int	1	8↑	17	6↓	0	-	17	0↓
Mica	21	24	12	37↑	32	-	12	24↑
Kaolinite	28	40↑	44	40	17	-	44	27↓
Quartz	11	10	13	10	32	-	13	37↑
Gibbsite	4	6	-	-	-	-	-	0
Siderite	-	-	6	3	5	-	6	1↓
	----------------------------------Particle Size (nm)----------------------------------							
Avg	1564	314	1200	1127	4156	-	1200	4704
Std Dev	-	182	-	1125	-	-	-	3755

* Cfg= centrifuged colloid, Elu = eluted colloid.
** Colloid concentration was not high enough to get eluted colloids.
↑↓ - Indicates increasing or decreasing trend.
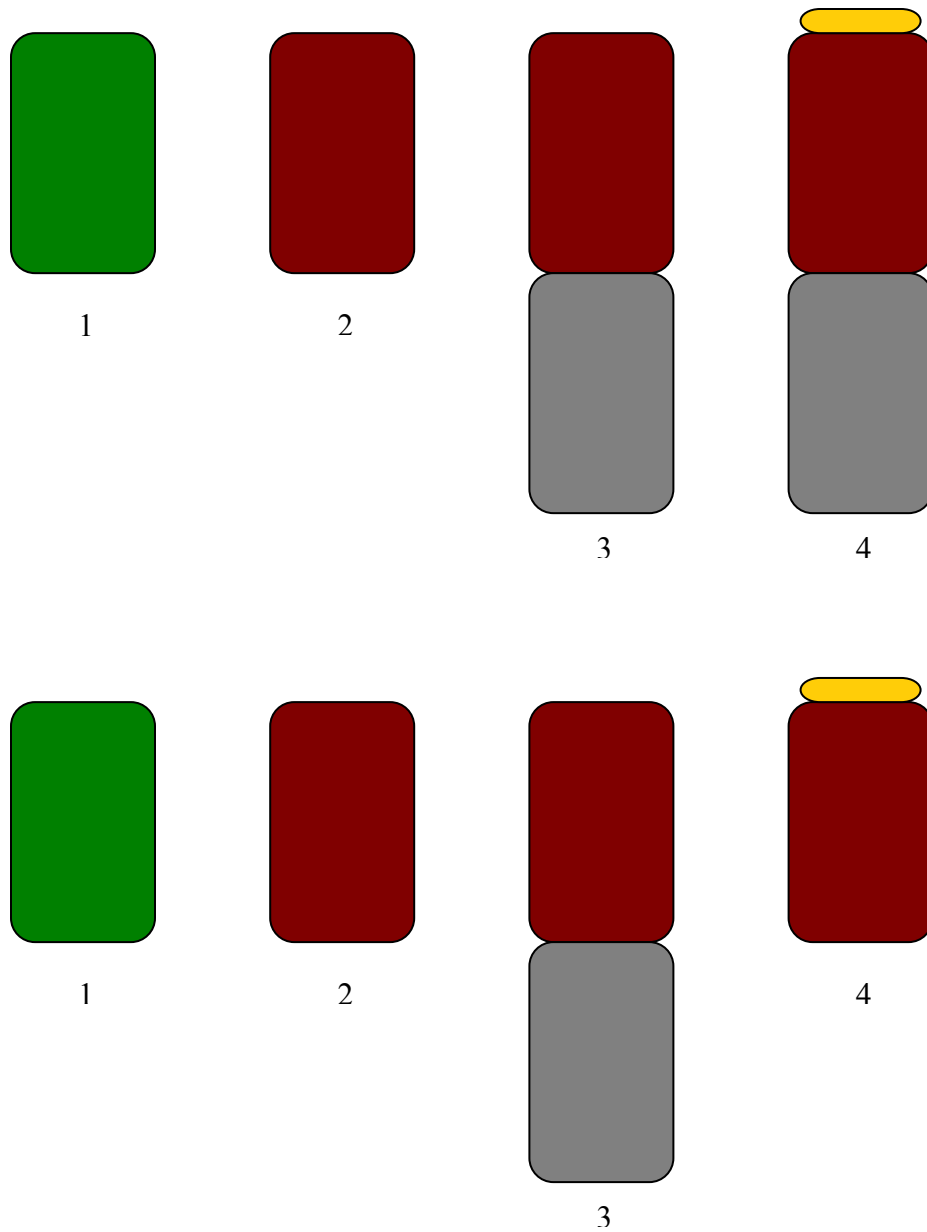
Figure 2.1: Diagram of (1) natural monolith, (2) reclaimed monolith, (3) reclaimed combined with spoil monolith, and (4) Reclaimed combined with spoil monolith and biosolid amendment treatments for Virginia and Kentucky monoliths.
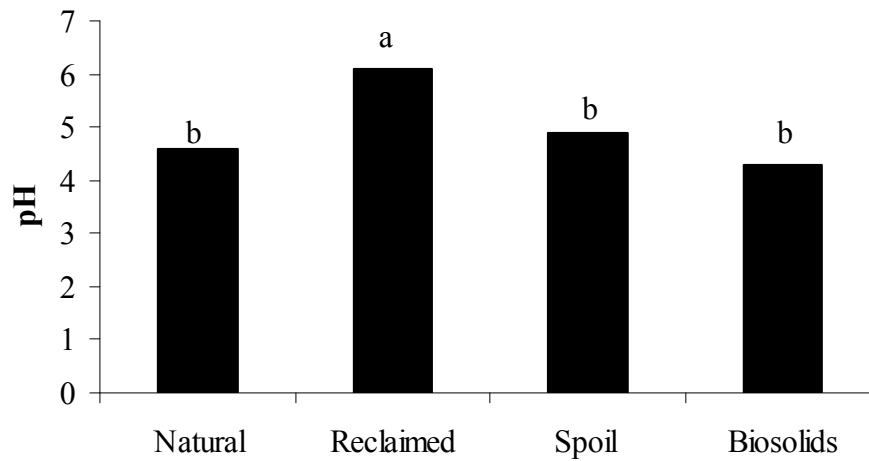
(a)
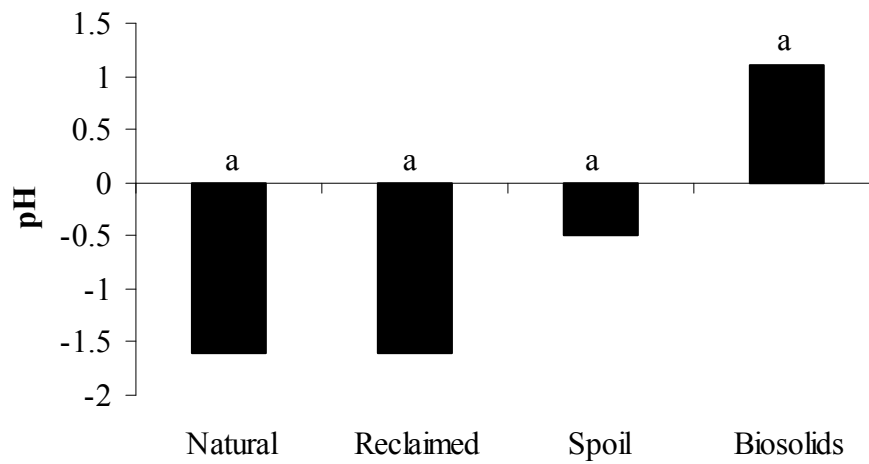
(b)

Figure 2.2: (a) Average pH and (b) change in pH (final minus initial pH) within the Virginia monolith treatments with letters representing statistical differences. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed and spoil monoliths combination amended with biosolids.)
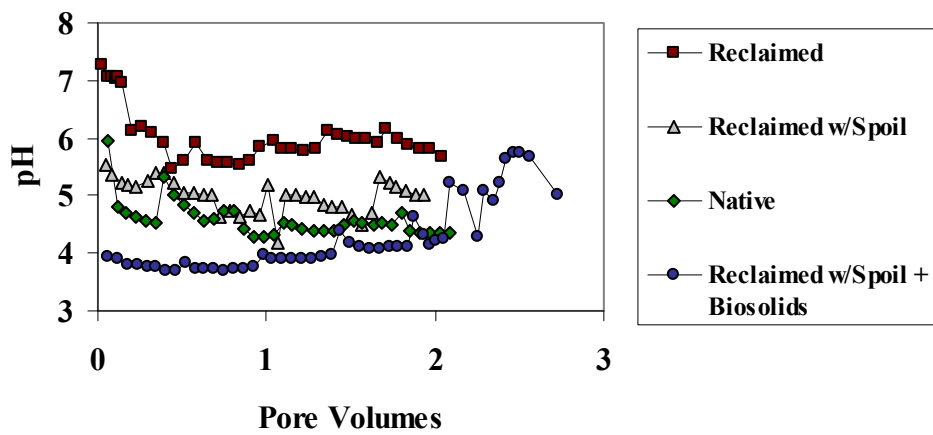
(a)
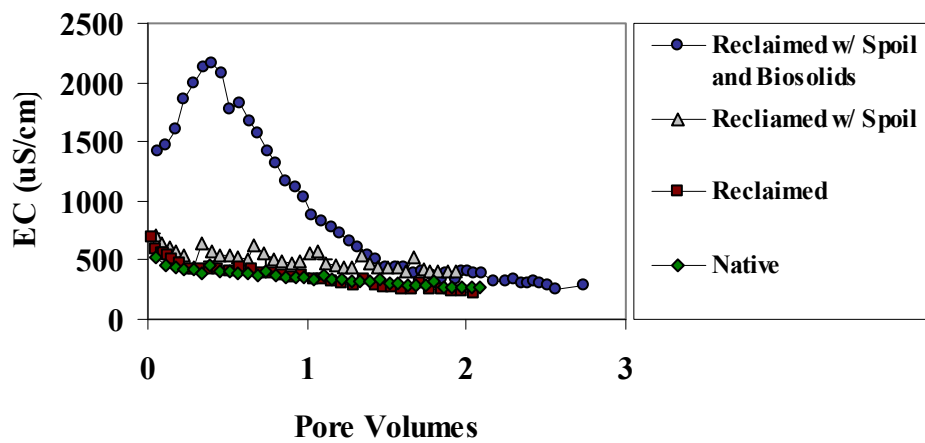
(b)

Figure 2.3: (a) pH within and (b) EC (μS/cm) within the Virginia monolith treatments over the entire elution. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed and spoil monoliths combination amended with biosolids.)
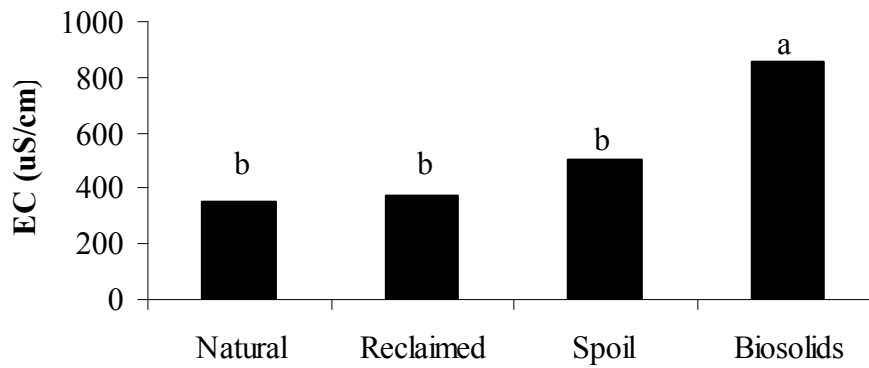
(a)
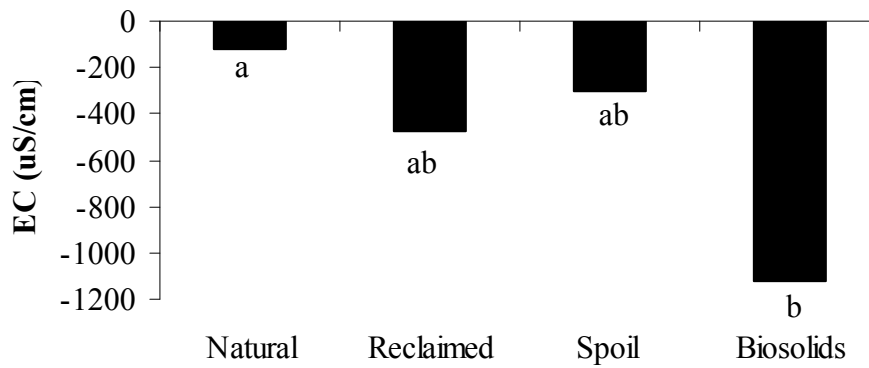
(b)

Figure 2.4 (a) Average EC (μS/cm) and (b) change in EC (final minus initial EC) within the Virginia monolith treatments with letters representing statistical differences. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed and spoil monoliths combination amended with biosolids.)
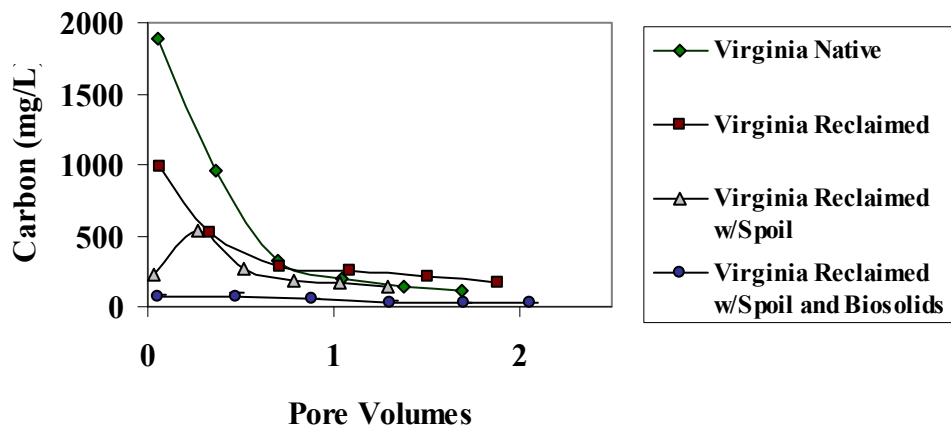
Figure 2.5: Average dissolved organic carbon (mg/L) eluted from Virginia treatments. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed and spoil monoliths combination amended with biosolids.)
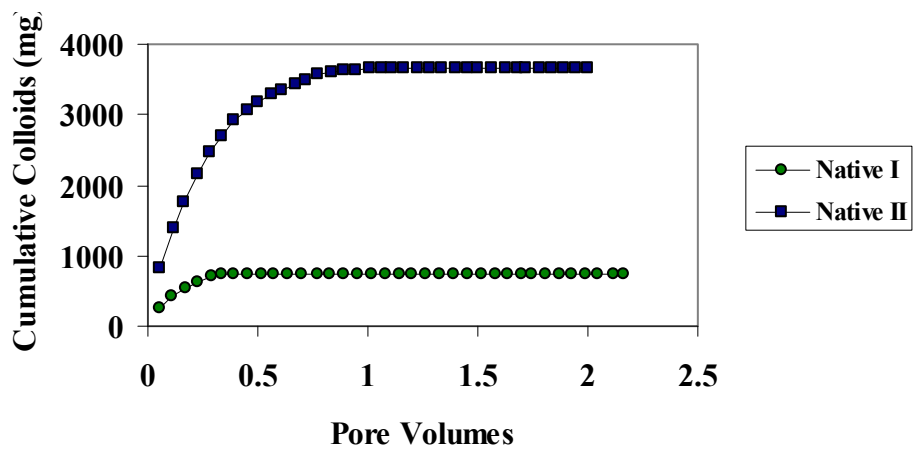
Figure 2.6: Cumulative colloid loads (mg) eluted from duplicate Virginia natural monoliths.
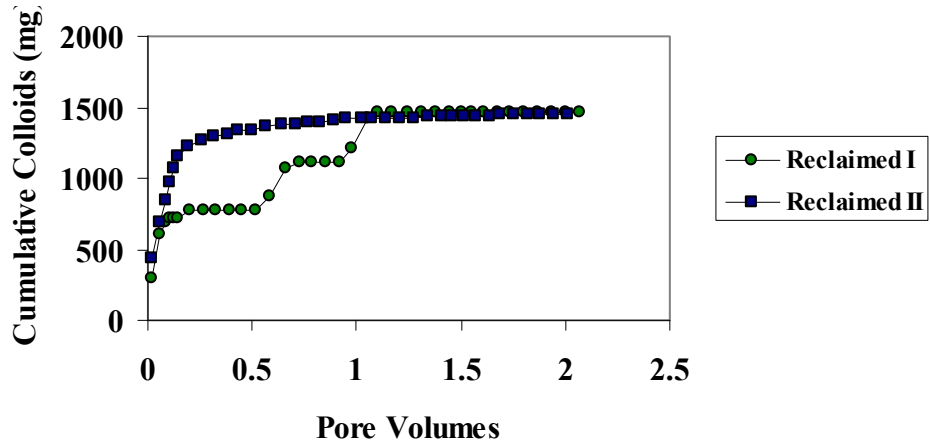
Figure 2.7: Cumulative colloid loads (mg) eluted from Virginia duplicate reclaimed monoliths.
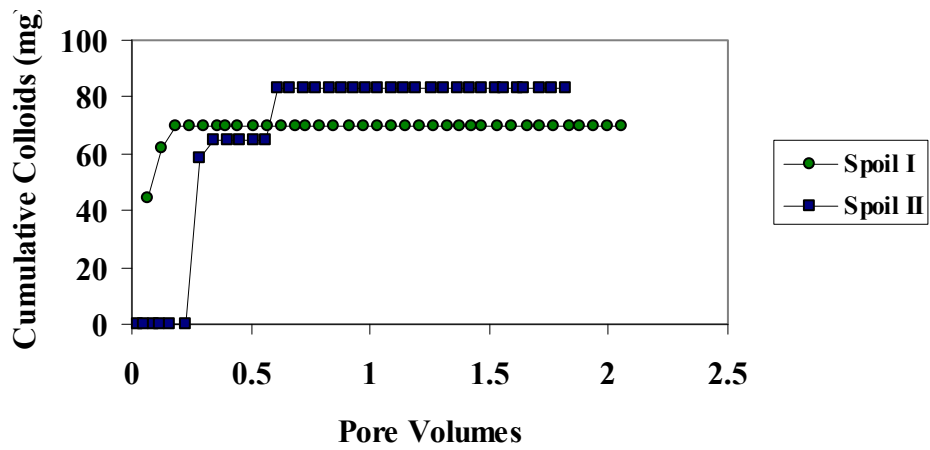
Figure 2.8: Cumulative colloid loads (mg) eluted from duplicate Virginia reclaimed-spoil combination monoliths.
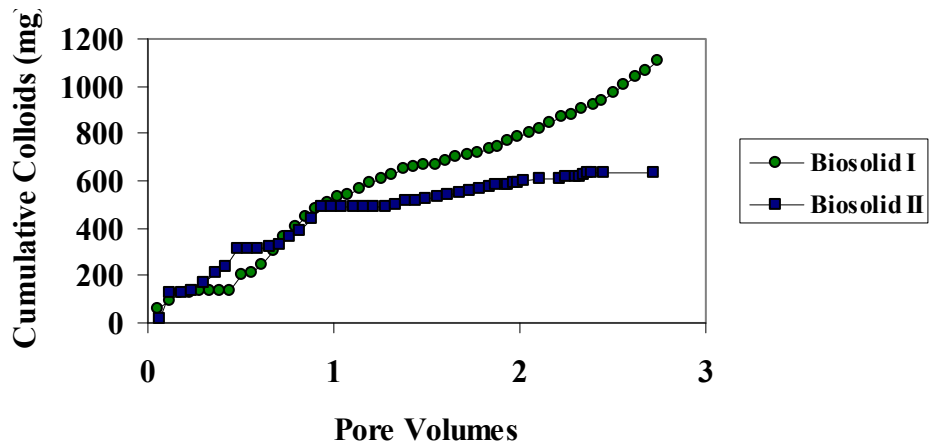
Figure 2.9: Cumulative colloid loads (mg) eluted from duplicate Virginia reclaimed-spoil combination monoliths amended with biosolids.
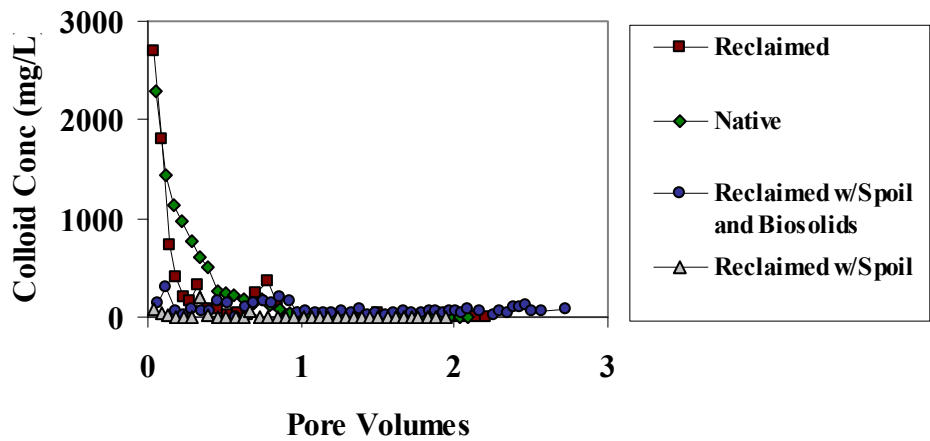
Figure 2.10: Average colloid concentrations (mg/L) as a function of monolith pore volumes eluted from the different treatments. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed and spoil monoliths combination amended with biosolids.)
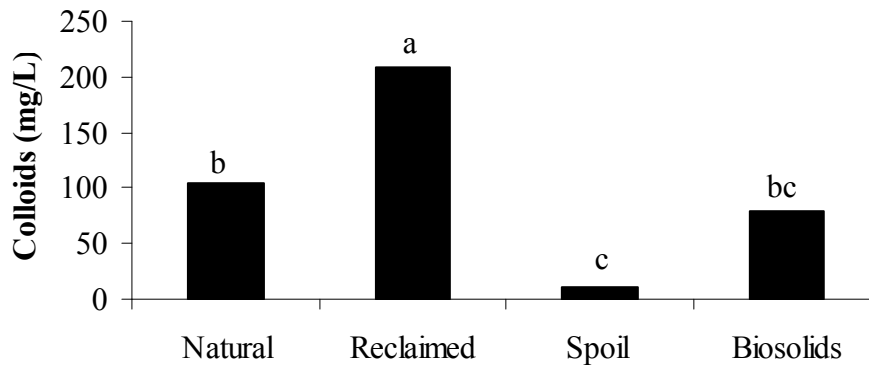
(a)
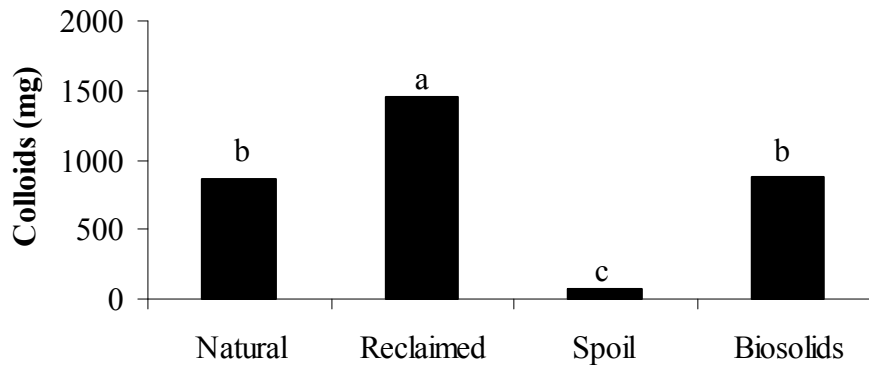
(b)

Figure 2.11: (a) Average colloid concentration (mg/L) (b) and average total eluted colloid loads (mg) within Virginia monolith treatments with letters representing statistical differences. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed and spoil monoliths combination amended with biosolids.)
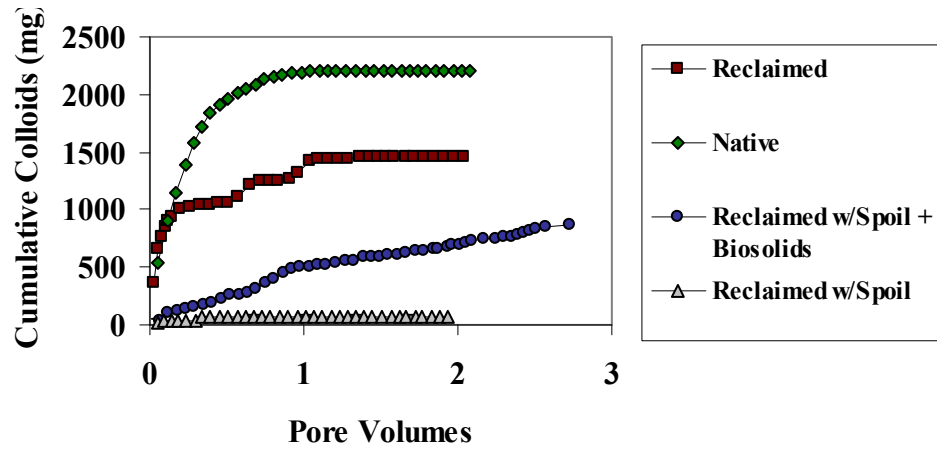
Figure 2.12: Average Virginia cumulative colloid loads (mg) as a function of pore volumes eluted from the different treatments. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed and spoil monoliths combination amended with biosolids.)
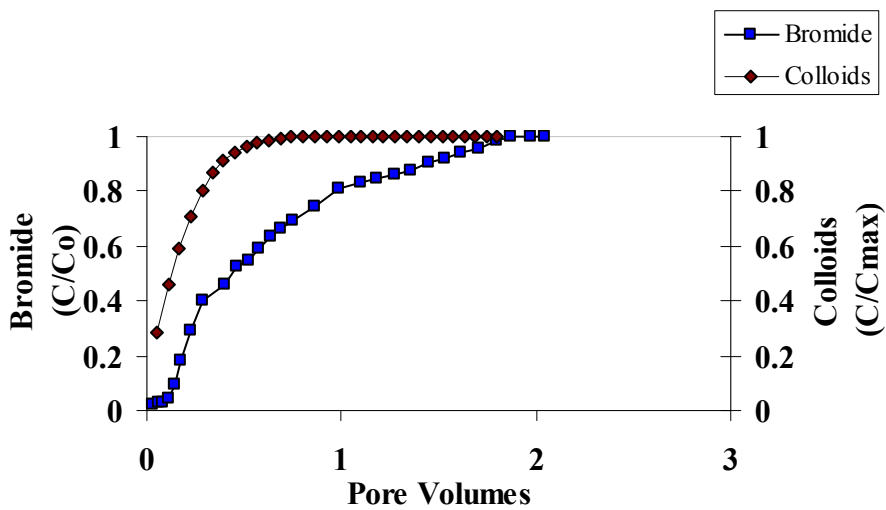
Figure 2.13: Bromide tracer (C/Co) and cumulative colloids (Cum Colloids/ Maximum Colloids) as a function of pore volumes in the Virginia natural monoliths.
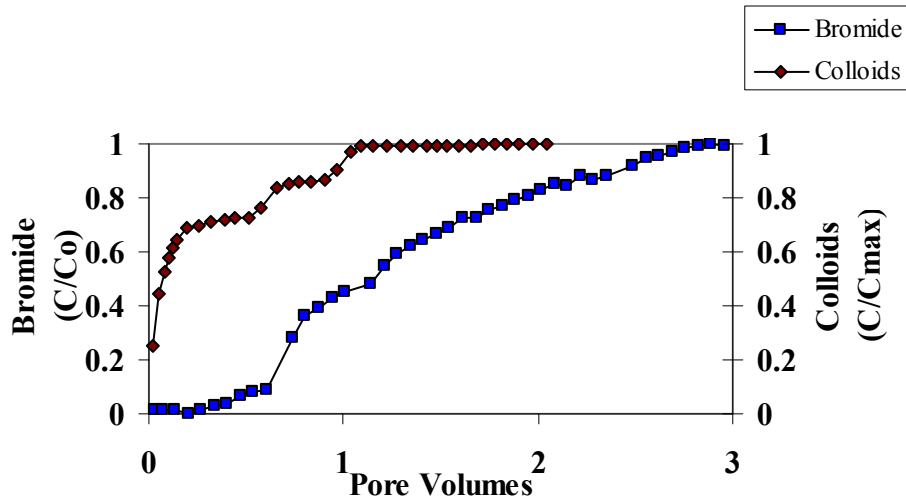
Figure 2.14: Bromide tracer (C/Co) and cumulative colloids (Cum Colloids/ Maximum Colloids) as a function of pore volumes eluted in the reclaimed monoliths.
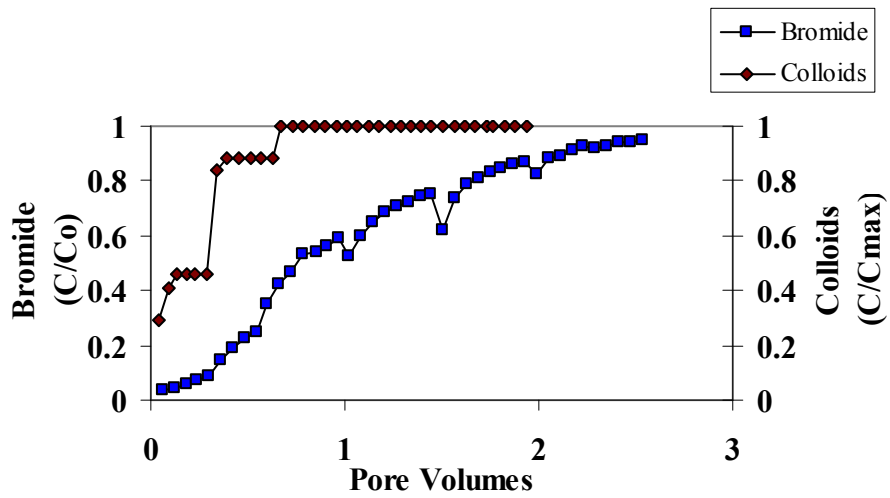
Figure 2.15: Bromide tracer (C/Co) and cumulative colloids (Cum Colloids/ Maximum Colloids) as a function of pore volumes eluted in the reclaimed with spoil monoliths.
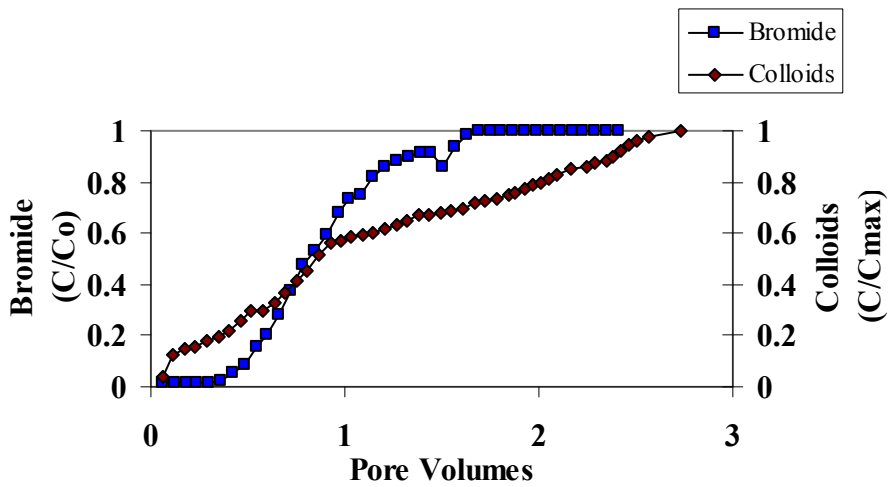
Figure 2.16: Bromide tracer (C/Co) and cumulative colloids (Cum Colloids/
Maximum Colloids) as a function of pore volumes eluted in the
biosolid amended monoliths.
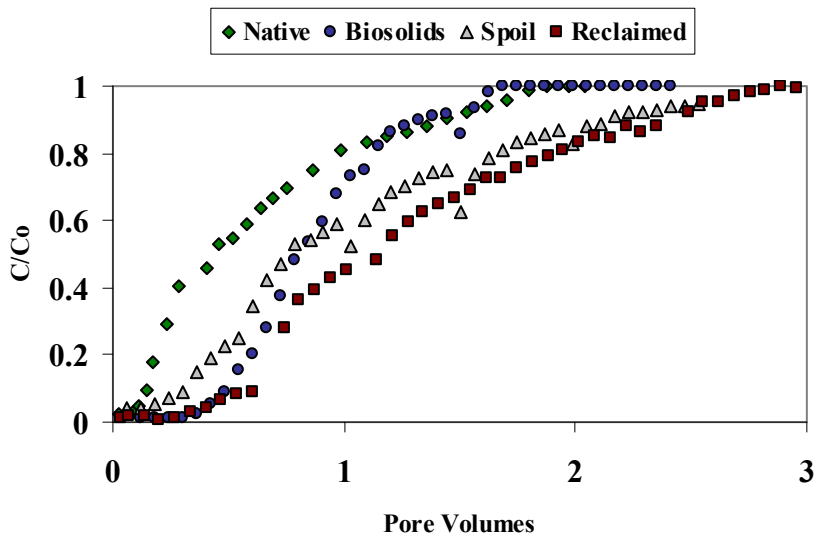
Figure 2.17: Bromide tracer (C/Co) and cumulative colloids (Cum Colloids/
Maximum Colloids) as a function of pore volumes eluted in the
different Virginia treatments.
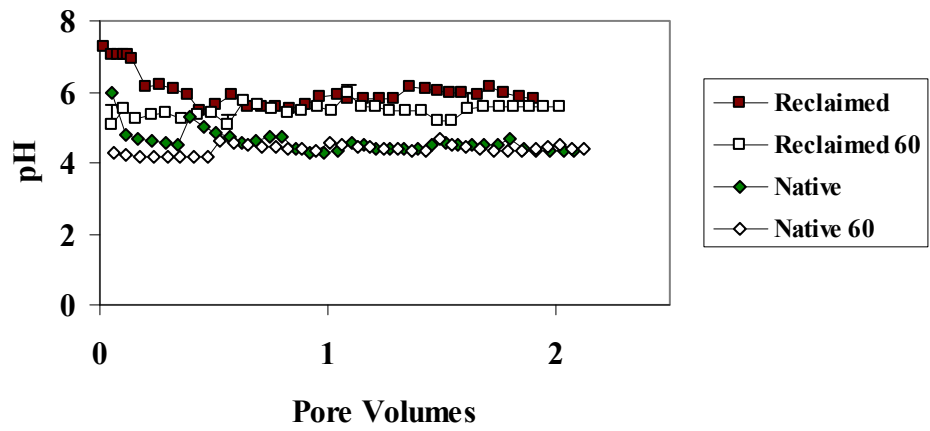
(a)
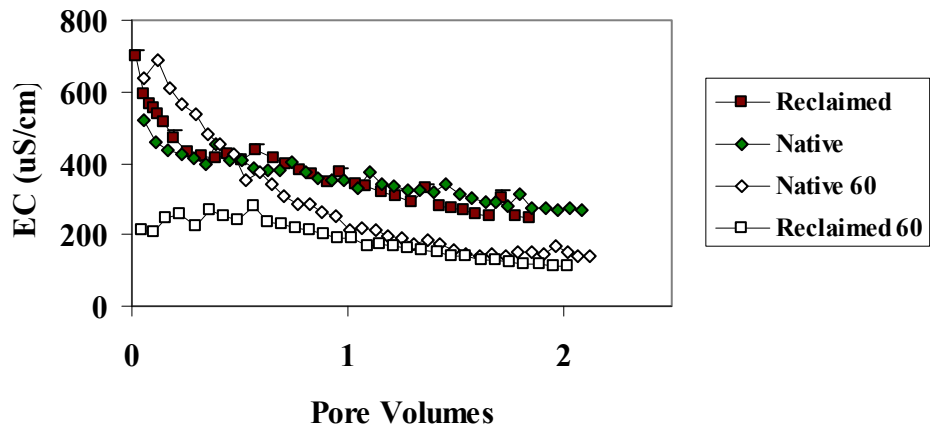
(b)

Figure 2.18: (a) Average eluent pH and (b) average eluent EC (µS/cm) of Virginia natural and reclaimed monoliths before and after drying at 60ºC.
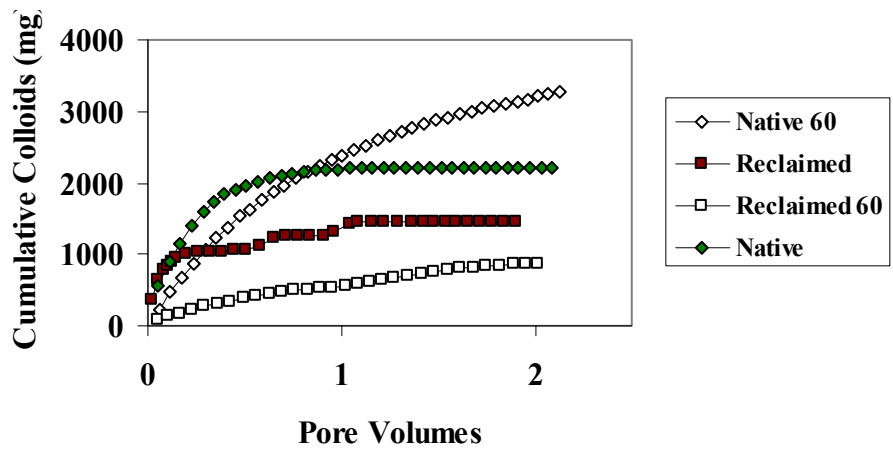
Figure 2.19: Average cumulative colloid loads eluted (mg) from Virginia natural and reclaimed monoliths before and after drying at 60ºC.
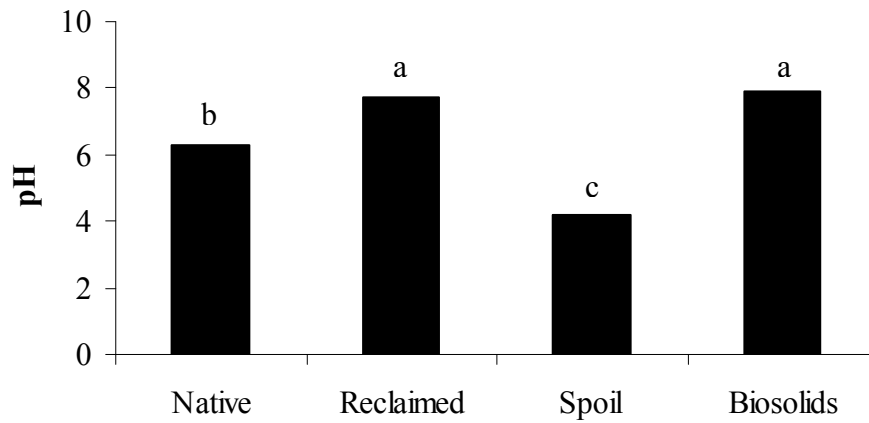
(a)
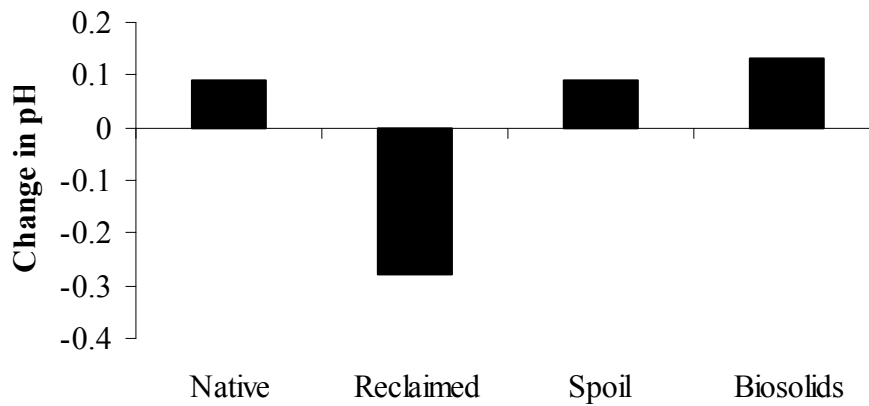
(b)

Figure 2.20: (a) Average pH and (b) change in pH (initial minus final pH) within the Kentucky monolith treatments. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed monoliths amended with biosolids.)
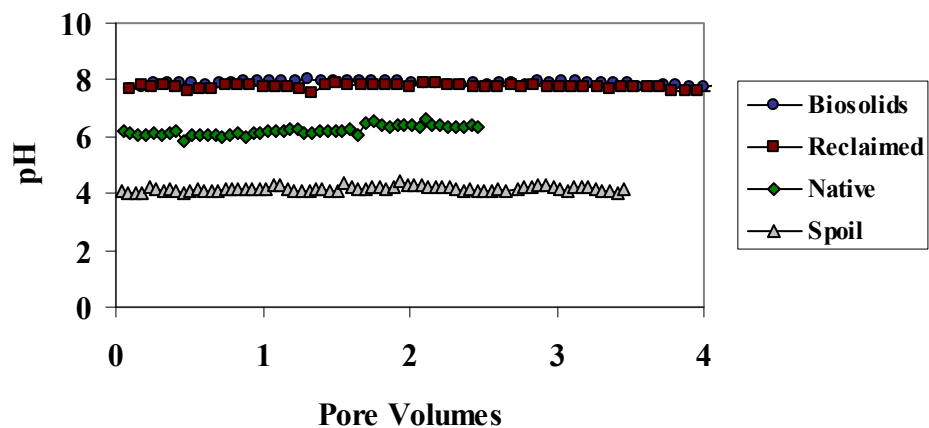
(a)
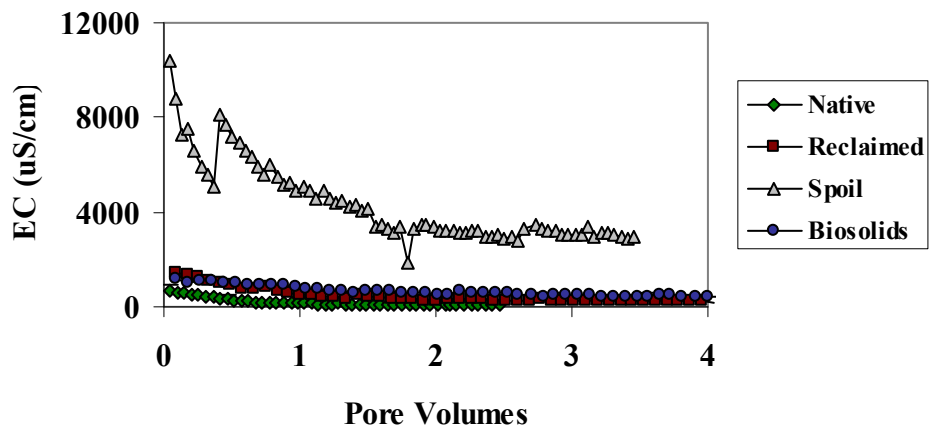
(b)

Figure 2.21: (a) pH within and (b) EC (uS/cm) within the Kentucky monolith
treatments over the entire elution. (Spoil represents the reclaimed and
spoil treatment combination; biosolids represents the reclaimed
monoliths amended with biosolids.)
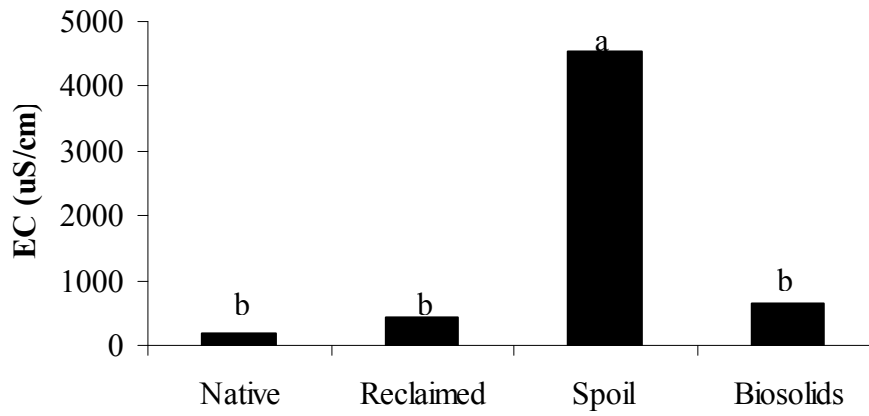
(a)
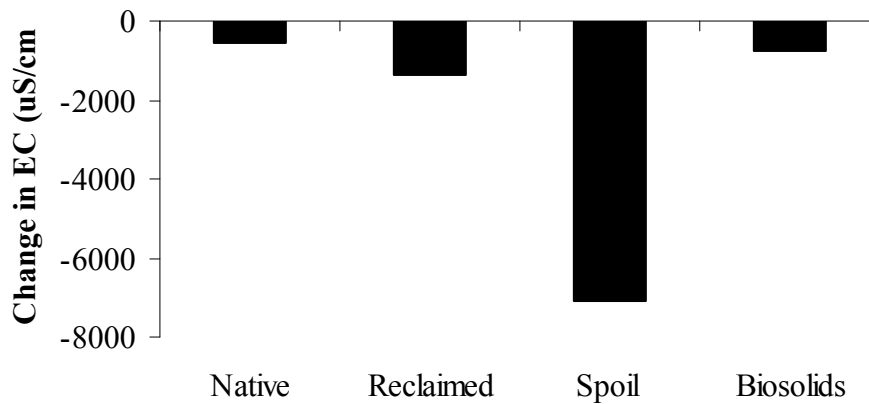
(b)

Figure 2.22: (a) Average EC (µS/cm) and (b) change in EC (initial minus final EC) within the Kentucky monolith treatments. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed monoliths amended with biosolids.)
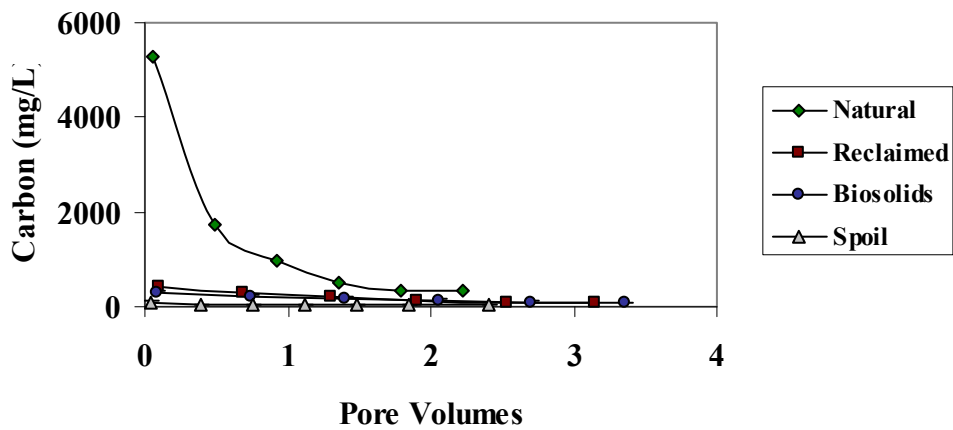
Figure 2.23: Average dissolved organic carbon (mg/L) eluted from different Kentucky treatments. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed monoliths amended with biosolids.)
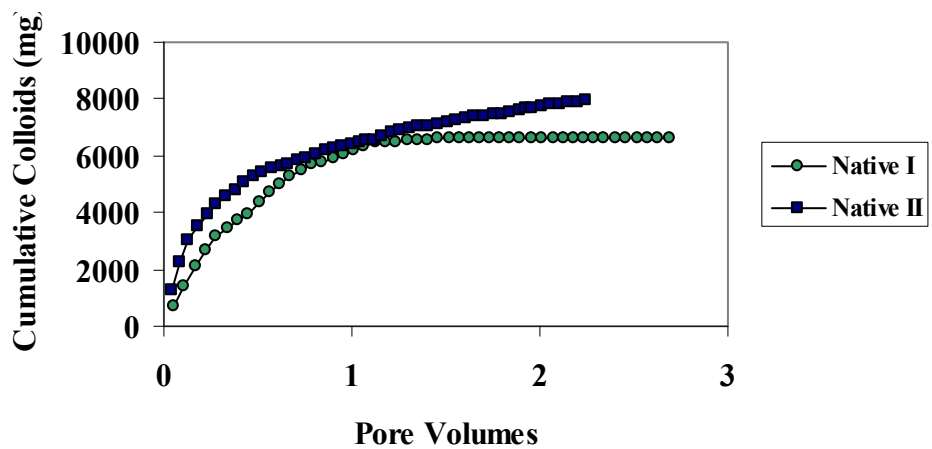
Figure 2.24: Cumulative colloid loads (mg) eluted from duplicate Kentucky natural monoliths.
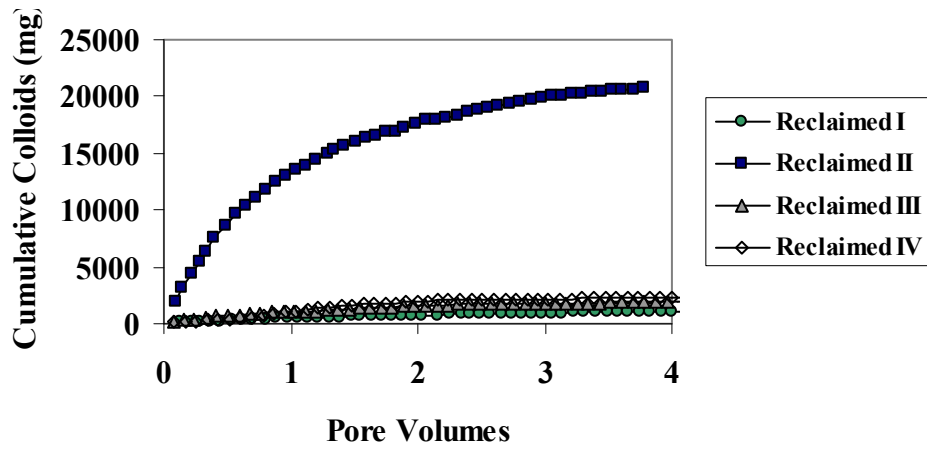
Figure 2.25: Cumulative colloid loads (mg) eluted from Kentucky duplicate reclaimed monoliths.
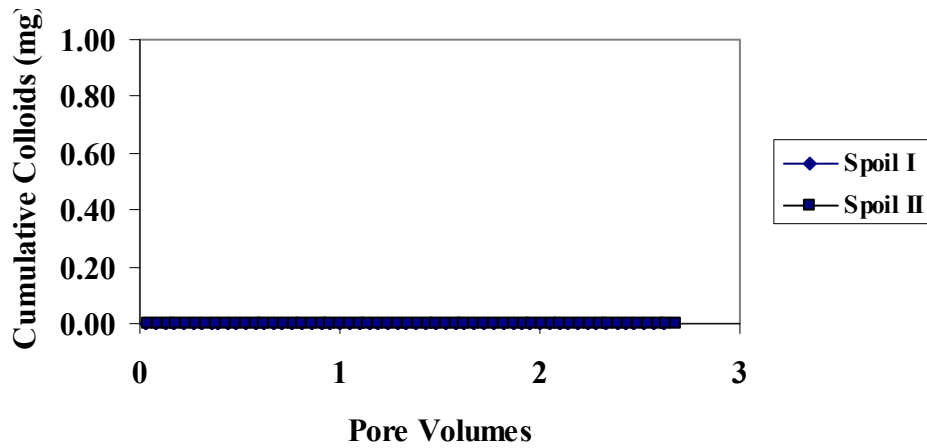
Figure 2.26: Cumulative colloid loads (mg) eluted from duplicate Kentucky reclaimed-spoil combination monoliths.
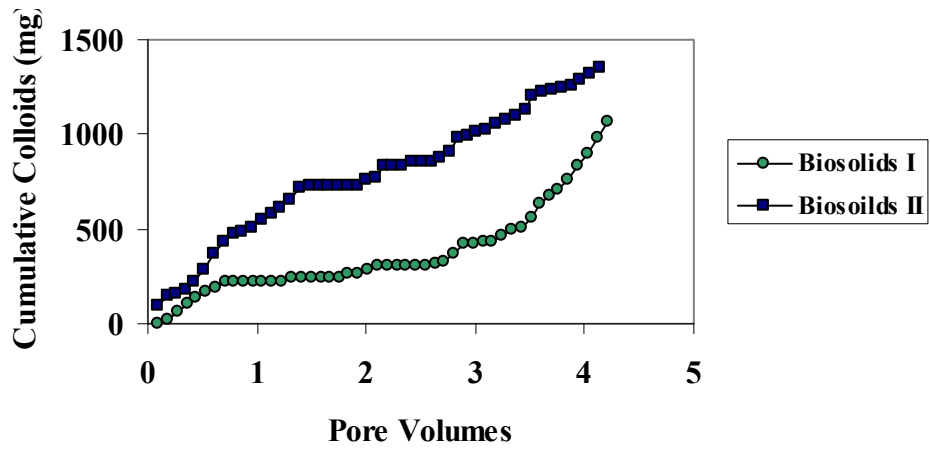
Figure 2.27: Cumulative colloid loads (mg) eluted from duplicate Kentucky
reclaimed monoliths amended with biosolids.
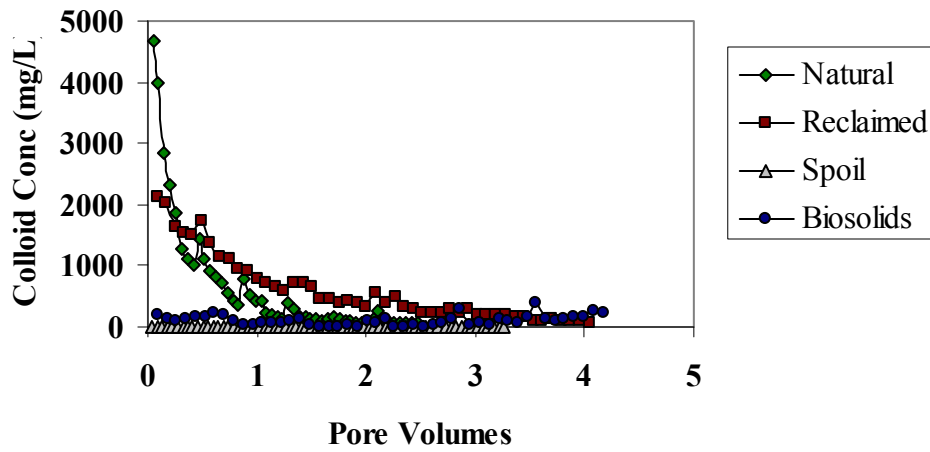
Figure 2.28: Average colloid concentrations (mg/L) as a function of monolith pore
volumes eluted from the different Kentucky treatments. (Spoil
represents the reclaimed and spoil treatment combination; biosolids
represents the reclaimed monoliths amended with biosolids.)

(a)
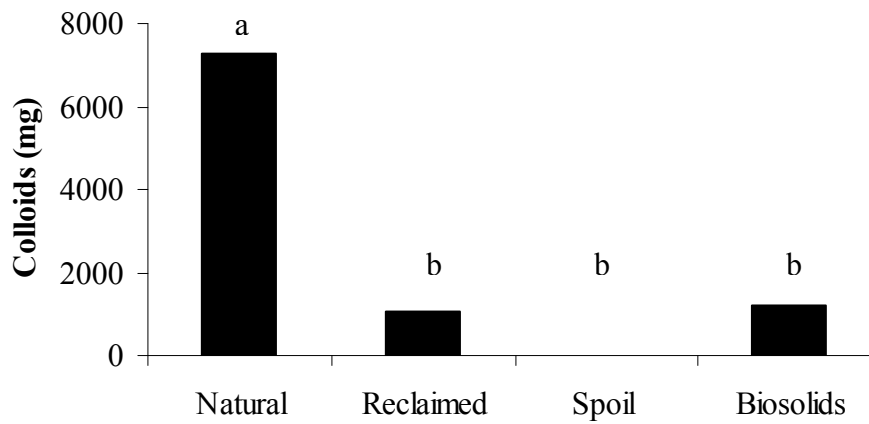
(b)

Figure 2.29: (a) Average total eluted colloid loads of all treatments, including all four recalimed Kentucky monoliths (mg) (b) and average total eluted colloid loads (mg) within all treatments with only two reclaimed Kentucky monolith treatments. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed monoliths amended with biosolids.)
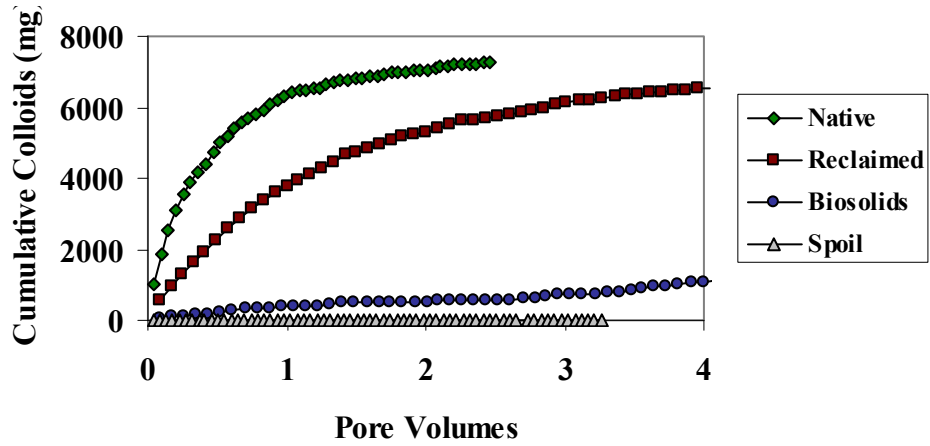
Figure 2.30: Average Kentucky cumulative colloid loads within (mg) as a function of pore volumes eluted from the different treatments, including all four reclaimed monoliths. (Spoil represents the reclaimed and spoil treatment combination; biosolids represents the reclaimed monoliths amended with biosolids.)
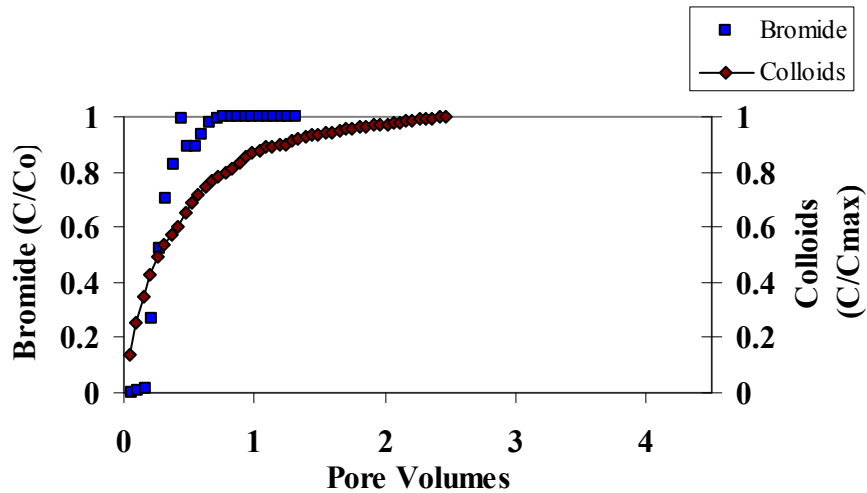

Figure 2.31: Bromide tracer (C/Co) and cumulative colloids (Cum Colloids/ Maximum Colloids) as a function of pore volumes in the Kentucky natural monoliths.
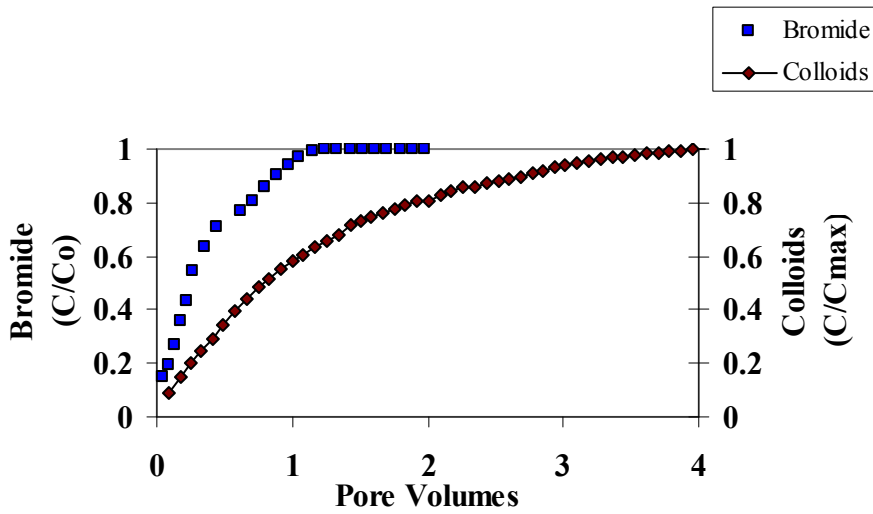
Figure 2.32: Bromide tracer (C/Co) and cumulative colloids (Cum Colloids/ Maximum Colloids) as a function of pore volumes eluted in the reclaimed monoliths.
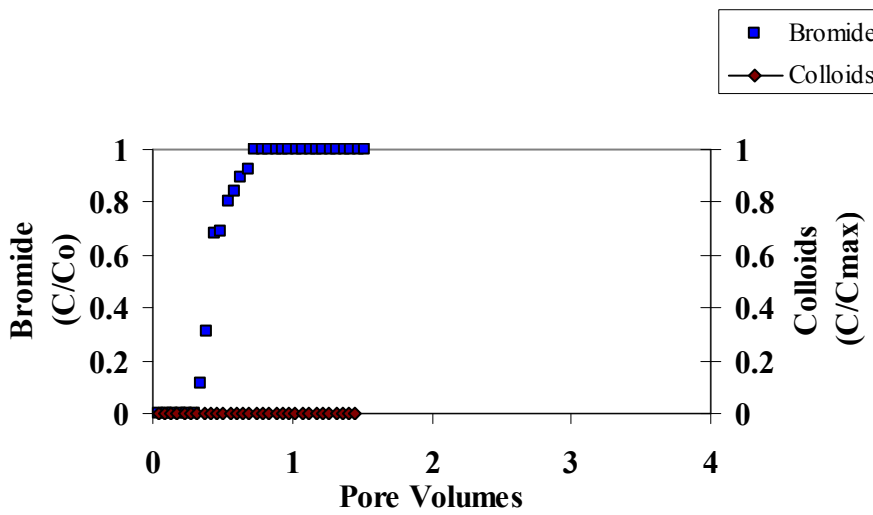
Figure 2.33: Bromide tracer (C/Co) and cumulative colloids (Cum Colloids/ Maximum Colloids) as a function of pore volumes eluted in the reclaimed with spoil monoliths.
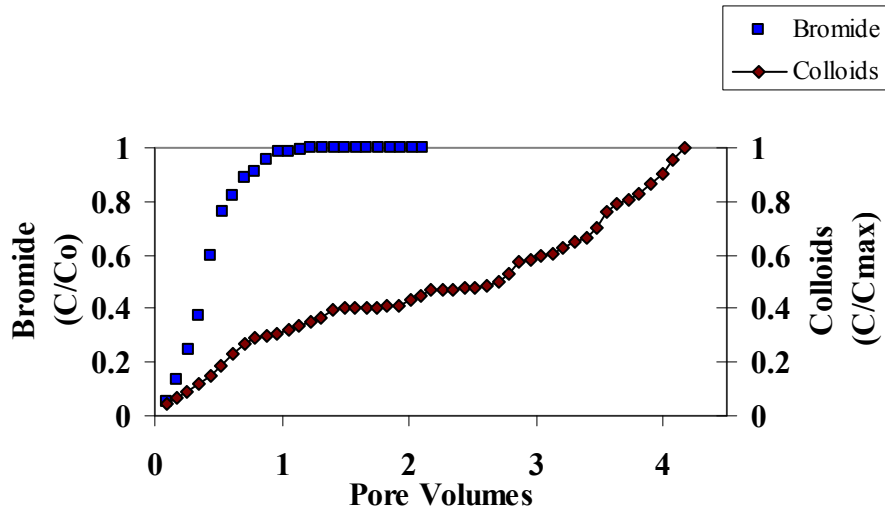
Figure 2.34: Bromide tracer (C/Co) and cumulative colloids (Cum Colloids/ Maximum Colloids) as a function of pore volumes eluted in the biosolid amended monoliths.
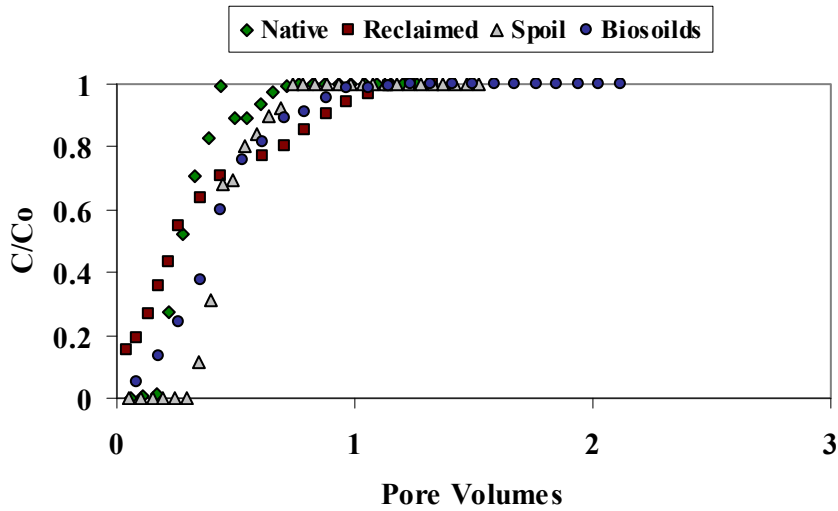
Figure 2.35: Bromide tracer (C/Co) and cumulative colloids (Cum Colloids/ Maximum Colloids) as a function of pore volumes eluted in the different treatments.
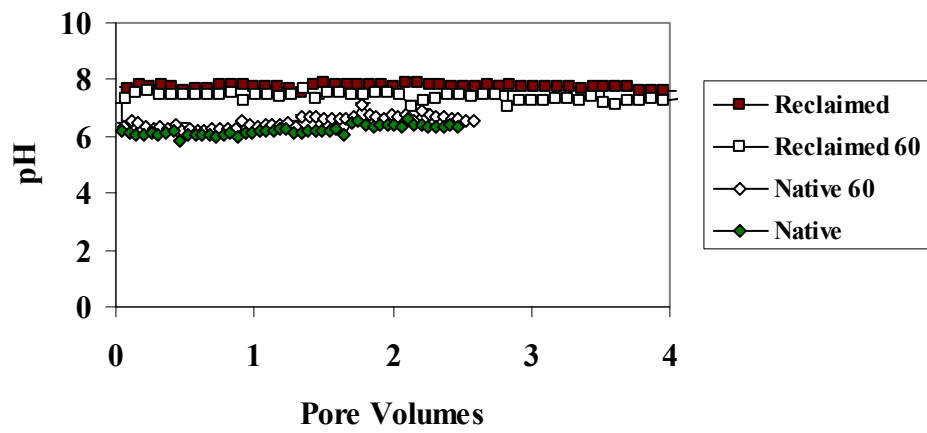
(a)
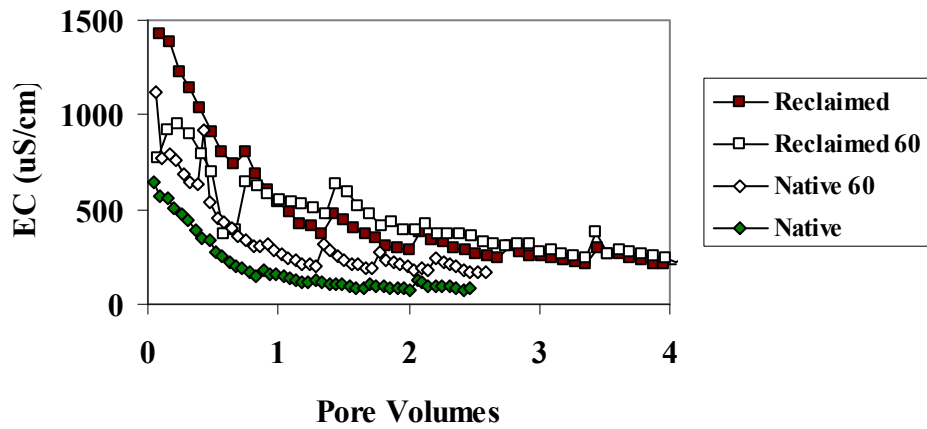
(b)

Figure 2.36: (a) Average eluent pH and (b) average eluent EC (uS/cm) of Kentucky
natural and reclaimed monoliths before and after drying at 60ºC.
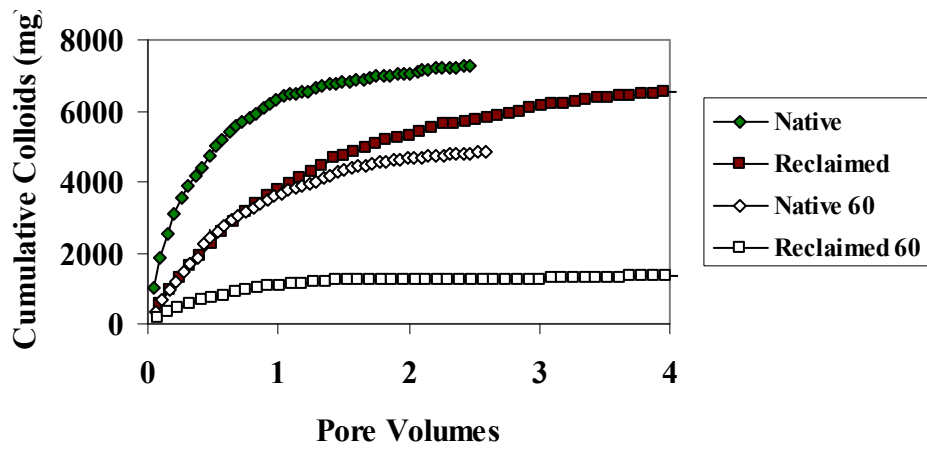
Figure 2.37: Average cumulative colloid loads eluted (mg) from Kentucky natural
and reclaimed monoliths before and after drying at 60ºC.
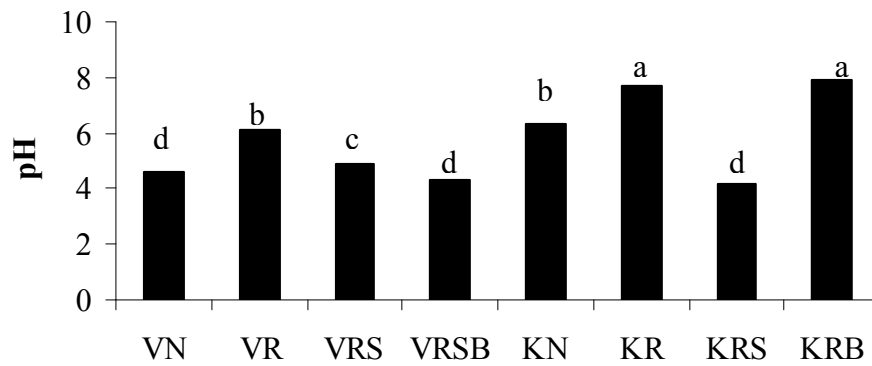
(a)
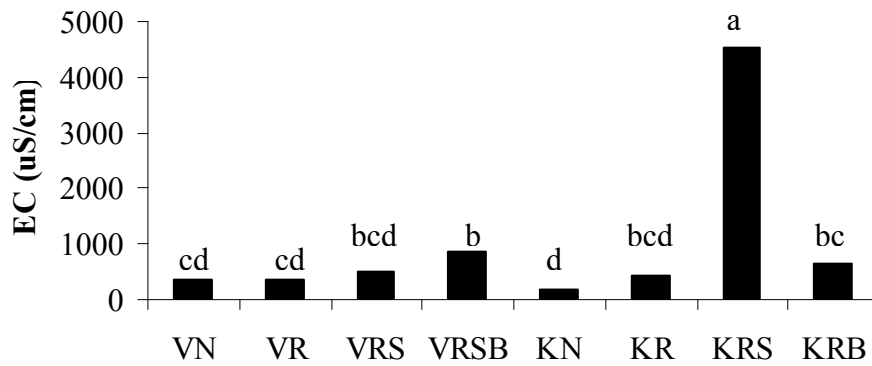
(b)

Figure 2.38: Virginia and Kentucky monolith (a) pH and (b) EC (µS/cm) averages for all treatments. (V = Virginia, K = Kentucky, N = Natural, R= Reclaimed, S = Spoil, and B = Biosoilds)
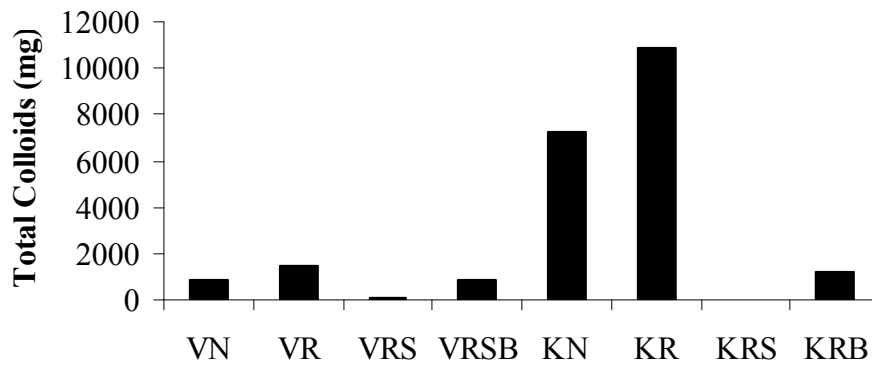
(a)
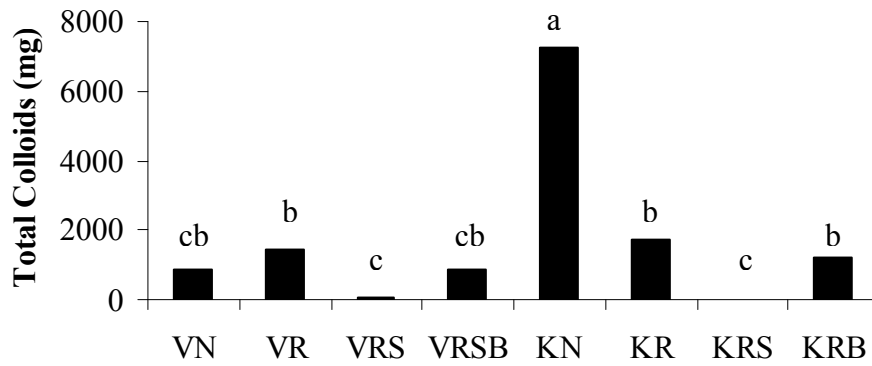
(b)

Figure 2.39: Virginia and Kentucky cumulative colloids eluted from monoliths with (a) original Kentucky reclaimed monoliths (b) replacement Kentucky reclaimed monolith. (V = Virginia, K = Kentucky, N = Natural, R= Reclaimed, S = Spoil, and B = Biosoilds)

CHAPTER 3   IN-SITU COLLOID TRANSPORT OF CD, CR, CU, NI, PB, AND ZN IN RECLAIMED MINE SOIL PROFILES WITH AND WITHOUT BIOSOLID APPLICATION

3.1   Introduction

Contaminants are usually concentrated in the unsaturated soil zone (McCarthy et al., 2002), which is assumed to act as a buffer for groundwater pollution since metals can be immobilized by sorption onto the soil matrix (Levin et al., 2002). However, what is frequently overlooked is that water dispersible colloids can be released from the soil matrix and subsequently transported to surface and groundwater resources, carrying previously immobilized pollutants in the soil (Seta and Karathanasis, 1997; de Jonge et al., 2004). Reclaimed mine soils can be a source of heavy metals, derived either from the original unweathered spoil material or from industrial wastes, fertilizers, power station fly ash, or biosolids applied during reclamation (Haigh, 1995). Unoxidized spoil material can contain Cu, Pb, or Zn sulfides (Geidel and Caruccio, 2000), while rock phosphate fertilizers can contain cadmium (Cd), chromium (Cr), iron (Fe), manganese (Mn), and lead (Pb) (Haigh, 1995).

Metal mobility in soils can be controlled by pH, mineralogy, surface adsorption (Konig et al., 1986), or complexation by organic compounds (Sposito et al., 1982; Pohlman and McColl, 1986). Mass balance studies of soils receiving biosolid applications have indicated that up to 95% of biosolid associated metals could be accounted for in the soil profile (McGrath and Lane, 1989; Sukkariyah, 2005). It is commonly assumed that metals are adsorbed in the upper 15 to 30 cm of the soil matrix, thereby reducing their mobility (Streck and Richter, 1997; Gove et al., 2001), but recent studies have observed significant contaminant transport by dispersed colloidal material (McCarthy and Zachara, 1989; Grolimund et al., 1996). 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 potential vector of contaminant transport (Grolimund et al., 2007).

Clay mineralogy, ionic strength, pH, total clay content, soil moisture, and soil management are all factors that affect colloid mobilization (de Jonge et al., 2004). Following coal mining, reclaimed soils may become a source of mineral colloids due

to the disturbance of the original soil matrix. Loss of aggregation due to mechanical disturbance by mining equipment, or loss of binding agents such as organic matter and carbonates, can increase the possibility of mineral colloid suspension. Application of biosolids, a common reclamation procedure (Haering et al., 2000), may be a source of organic colloids (Karathanasis and Ming, 2002; Karathanasis and Johnson, 2006). Formation of pseudo-karst channels is also common in reclaimed soils (Al and Blowes, 1996; Skousen et al., 2000; Geidel and Carcuccio, 2000), and colloid transport through macropores can bypass impermeable spoil layers (MCcarthy and Shevenell, 1998; Seta and Karathanasis, 1997). On the other hand, high salt content has also been observed in fresh mine spoils (Geidel and Caruccio, 2000; Skousen et al., 2000), and increased ionic strength can aggregate colloids and reduce their mobility (Grolimund et al., 2007).

Due to their high surface area and charge density, colloids can be an important vector in transport of contaminants in the soil (Karathanasis, 1999; Bertsch and Seaman, 1999). Higher concentrations of Cd, Cu, and Zn within the dispersible clay fraction have been observed in soils receiving increasing rates of biosolid application (Sukkariyah et al., 2005). Colloid facilitated transport of DDT, atrazine, Cu, Cr, Ni, Pb, and Zn have all been observed in packed and undisturbed columns (de Jonge et al., 2004). Because of their affinity for pollutants, mobile colloids can also strip contaminants such as atrazine and zinc from the soil matrix (Barton and Karathanasis, 2003). Given the likelihood that colloids can migrate through the soil matrix, and their high affinity to sorb metals, it is likely that their presence will increase metal transport.

The practice of biosolid application to reclaimed lands is favored because it promotes revegetation and reduces soluble metal loads in surface horizons (Haering and Daniels, 2000). Organic acids and humic material in the biosolids can chelate and bind metals, reducing, at least temporarily, their transport into groundwater (Sopper, 1993). Lime stabilized biosolids raise the soil solution pH, thus reducing metal solubility (Haering et al., 2000), however, a basic pH can also cause organic colloids to be suspended, increasing the likelihood of being leached through the system (Karathanasis and Ming, 2002). The contribution of biosolids to metal transport can

vary with soil properties. Clay loam soils receiving biosolid applications retained 90% of Cu, Ni, and Zn within the upper 25 cm 17 years after the original application (Sukkariyah et al., 2005), but movement of Cu and Zn in coarse textured soils may be more likely (Sukkariyah et al., 2007). Biosolid derived colloids applied to undisturbed soil monoliths considerably enhanced the transport of Cu, Zn, Pb, Cd, Cr, and Mo (Karathanasis et al., 2005; Karathanasis and Johnson, 2006).

The objectives of this study were: 1) to assess the mobility of Cd, Cr, Cu, Ni, Pb, and Zn within reclaimed mine soils with or without spoil materials and with or without biosolid application;

2) compare metal mobilization to that occurring in similar undisturbed (natural) forest soils; and

3) to evaluate colloid, soil, and reclamation practices enhancing or inhibiting metal transport.

3.2   Materials and Methods

3.2.1   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 to represent 30 year old reclaimed soils and from Robinson Forest, near Jackson, Kentucky, to represent recently reclaimed mine soils.

The monoliths were subjected to the following treatments for each study area (Figure 1). There were two replicated unmined forest soils, referred to as (1) natural monoliths, which were used as controls. Three replicated soils disturbed by coal mining per site constituted the: (2) reclaimed (3) reclaimed soil + mine spoil material, and (4) reclaimed soil + mine spoil material + biosolid application. Kentucky treatments were adjusted so that (4) constituted only reclaimed soil + biosolid application, following results from Virginia monoliths.

The disturbed, spoil, and natural soils in Virginia and the natural soils in Kentucky were obtained as intact soil monoliths, 30 cm in height and 18 cm in diameter. The reclaimed soils in Virginia had been deposited above a black spoil

material varying in thickness from 30 cm to 1 m and containing fragments of siltstone. The Virginia reclaimed soils and spoil materials were obtained from the upper 30 cm and recombined in the lab for treatments 2 and 3 to ensure similar thickness. Monoliths were removed by digging a pedestal approximately 50 x 50 x 40 cm, then trimming them with knives and soil picks so to fit within a polyvinyl chloride (PVC) tube of 20 cm internal diameter and 30 cm height. The 1 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. The natural soil for both Virginia and Kentucky treatments was comprised by intact soil monoliths 30 x 18 cm obtained from adjacent undisturbed sites.

Rock fragment content prevented intact monoliths from being extracted from the 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, an intact surface horizon of about 15 cm in thickness, and 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. Subsurface material was packed in the column to obtain a bulk density of around 1.4 g/cm^3 up to about 15 cm. 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 spoil column was built the same way and a separate reclaimed mine soil monolith was built above it before filling with Poly-U-Foam.

The lime stabilized biosolid material used in the study came from a local municipal wastewater treatment facility in Winchester (Clark County), Kentucky. It was dried and applied to the surface of the soil at a rate of 20 T/ha.

3.2.2 Bulk Soil Analysis

Natural, reclaimed, spoils representing the entire monoliths, and biosolid materials were air-dried and passed through a 2 mm sieve. EPA method 3050b was

used to extract environmentally available Cd, Cr, Cu, Ni, Pb, and Zn from 1 g of soil, spoil, or biosolid materials using HNO_3 and HCl and heating to 95ºC. Extractants were analyzed by inductively coupled plasma (ICP-MS) to determine preliminary levels of each metal in the materials. The pH and electrical conductivity (EC) was determined on 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). Mineralogical composition was performed by X-ray diffraction (XRD) and thermogravimetric analysis (TA) 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 (Karathanasis and Hajek, 1982). Adsorption isotherms were generated to evaluate the affinity of Cd, Cr, Cu, Ni, Pb, and Zn to the bulk soils, spoils, and biosolids. Duplicate 1 g soil, spoil, and biosolid samples were added to a 50 mL centrifuge tube with 20 mL of 0 – 5 mg/L metal concentrations. Samples were shaken on a reciprocating shaker for 24 h at room temperature and centrifuged for 1 h at 3500 rpm. Supernatants were collected and analyzed for Cd, Cr, Cu, Ni, Pb, and Zn via inductively coupled plasma spectrophotometer analysis (ICP). Freundlich isotherms fitted on log-scale by linear regression were used to describe the experimental adsorption data.

3.2.3 Colloid Fractionation and Characterization

To determine which minerals within the bulk soil and spoil materials may be more mobile, water dispersible colloids were fractionated from bulk samples of soil, spoil and biosolid materials. A 50 g sample was placed in a 1 L centrifuge bottle and filled with D.I water. The slurry was mixed on a shaker for 1 hour and centrifuged at 750 rpm for 3.5 minutes. The colloid particles in suspension were decanted and the procedure was repeated on the same 50 g sample twice. Mineralogical composition was performed by X-ray diffraction (XRD) and thermogravimetric analysis (TA) using the methods described above. Adsorption isotherms were conducted on 100 mg dried colloid samples added to 50 mL test tubes containing 0 – 5 mg/L metal concentrations to compare to bulk soil isotherms. Further analyses were similar to the bulk samples above.

3.2.4   In-Situ Colloid Elution

In situ colloid generation and elution from monoliths was assessed with leaching experiments. A rainfall simulator was set up to apply D.I. water at a rate of 250 ml/hour (1.0 cm/hour) to the surface of each monolith. The application rate was controlled with a peristaltic pump. The upper boundary condition of the monolith was 0 cm and the lower boundary was kept at -10 cm using a Mariotte device. To keep the lower boundary at -10 cm the monolith was placed in a large funnel and sealed around the edges with a silicone gel. A tube was attached from the funnel into a sealed 2 L flask for the leachate to drip into. This 2 L flask was also connected to a second flask, which was filled with water to control the pressure beneath the monolith and maintain the lower boundary condition at the desired level. This second flask was sealed except for two openings, one of which connected to the tubing used to apply suction, and the other which contained a thin PVC pipe which was open to the atmosphere. The bottom of the pipe was placed below the water surface, so that when suction was applied, air entered through the PVC and pushed through the water, creating a negative tension within the system. A tensimeter was used to monitor the pressure within the funnel, which was adjusted to -10 cm by raising or lowering the pipe.

The leaching of each monolith was conducted in six cycles, corresponding to 2-3 pore volumes (PV) of elution. Each cycle consisted of 2 L of water elution at 24 hour intervals. Leachate was collected at the bottom of the monolith every hour for a total of 8 hours. Suspension concentrations were determined gravimetrically taking a 20 mL aliquot from each hourly sample and drying it at 105 ºC in a pre-weighed aluminum tin for 24 hours. Electrical conductivity was multiplied by 0.61 to convert to salt concentration, which was then subtracted from the suspension concentrations to determine actual colloid concentration (US Salinity Laboratory, 1954). To correct for salts in the biosolid application treatments, a glass membrane filter was used to remove mineral and organic colloids in selected samples and create a regression equation of salt concentration versus electrical conductivity. A 20 mL aliquot of eluent was filtered through a 0.2 μm filter and dried in a pre-weighed aluminum tin at

105 ºC for 24 hours before converting to mg/L salt content. The pH and electrical conductivity (EC) were determined for each hourly elution.

Eluted dissolved organic carbon (DOC) was analyzed by taking a 20 mL subsample from each elution and acidifying with 1 drop of concentrated H_2SO_4 to evaluate dissolved organic carbon on a Shimadzu TOC 500DA carbon analyzer. Aromatic content of DOC was observed by taking selected unfiltered samples and reading light absorbance at 270 nm on a Shimadzu UV-3101PC UV-VIS-NIR scanning spectrophotometer. The absorbance values were converted to aromaticity by dividing by DOC content.

The mineralogical composition of the samples was determined by X-ray diffraction (XRD) and thermogravimetric analysis (TA) (Karathanasis and Hajek, 1982). To extract colloids from the eluent, samples were filtered through a 0.45 μm filter, which was taped to a glass slide for XRD analysis. 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.

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. The filtered material was analyzed for dissolved metals by ICP. Following filtration, 20 mL of 1M HCl/HNO_3 were 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.

Concentrations of anions (F, NO_2, NO_3, Br, PO_4, and SO_4) were measured on selected samples so that metal speciation could be determined. The selected samples were analyzed for anions by filtering through a 0.2 μm filter and passing through a Metrohm 792 Basic ion chromatograph (IC). Concentrations of DOC, Cd, Cr, Cr, Ni, Pb, Zn, and the anions were entered into Visual Minteq to calculate dissolved metal speciation.

3.3 Results and Discussion

3.3.1 Metal Concentrations in Bulk Samples

All metals, with the exception of Cd, were detected in all of the soil, spoil, and biosolid materials using the EPA total recoverable metals digestion (Table 3.1). Zinc had the highest concentration in all of the samples, ranging from 0.4 to 1.7 ppm, followed by Cu (0.05 to 0.64), with Cr (0.03 to 0.15) typically present in the lowest concentrations. In the Kentucky spoil and the biosolid materials Zn was present in concentrations above 1 ppm, while most other metals had concentrations below 0.5 ppm. Kentucky spoil materials also had the highest Cr (0.15), Cu (0.64), Ni (0.3), and Pb (0.18) concentrations, and the second highest Zn (1.4) concentrations of all the treatment materials. Although the spoil material from Robinson Forest was minimally weathered, the similarity in metal content and affinity suggested limited potential for significant difference in metal elution across treatments.

3.3.2 Adsorption Isotherms

The linear Freundlich isotherm had the best fit for the sorption data, with most fits of the 6 points having an r^2 above 0.8, and was used to describe the affinity of metals to colloids and soils. Whole biosolid materials had the highest overall affinity for Cd, Pb, and Zn, both Cu and Ni had a higher affinity for the Kentucky natural soils, while Cr showed the highest affinity for the Kentucky spoil material (Table 3.2). Within soil samples, Cu consistently showed the highest affinity, while Ni and Zn often had the lowest. Within soil systems Cu has a greater binding strength to humus, clay, and sesquioxides, while Zn and Ni have the lowest (Blume and Brummer, 1990).

Among colloids, the biosolid samples showed higher affinities for Cd, the Virginia natural colloids for Cr and Zn, and the Kentucky reclaimed colloids for Cu and Ni. The Virginia spoil materials (bulk and colloid) showed the highest affinity for Pb, probably due to their high coal content. Generally, most soil and spoil groups showed higher affinity for Pb rather than other metals. Surprisingly, extracted colloids did not always have higher affinities for individual metals than their bulk soil

counterparts, suggesting that surface area was not the only factor controlling metal sorption processes. Coatings of oxides and organic matter may play a roll in adsorption of metals in these materials as well. Overall, there were no drastic differences in values across metals, soils, or colloids, suggesting that any of these metals had an equal probability of being transported by colloids through the matrix. This is not surprising since Cd, Cu, Ni and Zn all have similar charge, giving them equal chances for adsorption to surfaces. Considering that Cr is commonly an anion in soil systems (Bartlett, 1991), it is surprising that similar adsorption coefficients were observed.

3.3.3   Metal Elution in Virginia Monoliths

Within the Virginia natural monoliths only Cu, Ni, and Zn were observed regularly during the elution period with Zn present in all eluent samples (Figure 3.1). No Cd or Pb was detectable, although Pb was observed in the original soil extractions, and had similar affinities among the soil matrix and natural colloids (Table 3.2). Low concentrations of Cr were observed twice, but only in solution and not bound by colloids. Total mg Zn was also 100 fold higher than total Ni and Cu combined (Table 3.3). A larger fraction of the total Cu was colloid bound (27%), than Zn (1%) or Ni (10%). Zinc had the lowest percentage of bound load but the greatest cumulative mass, which corresponds to the higher Zn content in the soil extractions and higher affinity for natural colloids. The lower % Zn bound compared to Cu can be partially attributed to the lack of colloids released after 1 PV (Figure 3.1), and the steady release of Zn in solution after 1 PV.

The Virginia reclaimed monoliths (Figure 3.2) eluted trace amounts of each metal. Although no Cd was present in bulk soil extractions, it was present in a colloid bound form within 1.5 PV, and three times in the solution phase. Trace amounts of Cr, Cu, Pb, and Ni were also present, but were released sparsely. Colloid transport increased the mobility of Cr, Cu, and Pb by 85-92%, while only 14% of the total Ni transported was colloid bound. Both Cd and Cu displayed a pattern similar to colloid elution at 0.75 PV, while Cd, Cr, Cu, and Ni have all released at similar times following 1 PV of elution. However, of these three metals, only Ni was dominantly

transported as a solute. Zinc was released over the entire leaching cycle, but only 11% (Table 3.3) was colloid bound. Total Zn was much higher and the % colloid bound lower due to its consistent release as a solute after colloids ceased to elute from the monoliths, in a pattern similar to the natural monoliths above. Zinc release resembled the leaching cycle pattern, with peaks occurring at the beginning of each cycle and descending as the 8 hour cycle continued. The Virginia reclaimed monolith colloids carried the highest fraction of metals of any treatment (Table 3.3). This could be attributed to the higher total colloid load released from these monoliths, which was influenced by the higher pH and smaller colloid particle diameter (Table 3.4). The reclaimed colloids also had a higher percentage of more reactive 2:1 minerals and gibbsite to bind the metals.

When spoil material was placed below reclaimed monoliths, colloid transport was significantly inhibited (Figure 3.3, Table 3.4), thus reducing the chance of colloid mediated transport of metals. Trace amounts of Cd, Cu, and Ni were present in the eluent, with only up to 15% being colloid bound (Table 3.3). Of those three metals only Ni had a consistent release throughout the leaching cycle. More total Zn was released from reclaimed soils when spoil material was present, with less than 1% being colloid bound. The Zn elution pattern also resembled the leaching cycle of the reclaimed monoliths discussed above.

When biosolids were applied to the reclaimed-spoil combination monoliths, the colloid elution pattern was constant but irregular throughout the leaching. Metal elution was continuous for Cd, Cu, and Zn, with peak concentrations occurring within the first 0.5 PV. This pattern is probably due to the salts leaching from the biosolids, and is similar to the EC elution pattern of these monoliths. Although there was no peak concentration, Cu was eluted throughout the entire leaching cycle, showing an erratic colloid elution pattern. Carbonates from the lime stabilized biosolids probably precipitated any traces of Pb as insoluble $PbCO_3(s)$ within the monoliths, thus reducing the possibility of Pb transport. The entire amount of Pb observed in the eluent was bound to colloidal materials. Colloid transport of Cd, Cr, Cu, Ni, and Zn accounted for less than 5% of their accumulated mass, although colloids were continuously released from biosolid amended monoliths at total amounts similar to

natural monoliths (Table 3.4). Total Cu, Ni, and Zn were higher in biosolid amended eluents than any other Virginia treatment, suggesting that initial leaching may flush the most soluble metals through to groundwater.

3.3.4   Metal Elution in Kentucky Monoliths

Unlike the Virginia natural monoliths, eluents from the Kentucky natural monoliths contained trace amounts of Cd and Pb which were released in a discontinuous pattern (Figure 3.5). Several peaks in the Cd elution coincided with colloid flushing peaks at the beginning of the leaching cycle, while later peaks were mostly associated with dissolved Cd. Apparently initial Cd is transported bound to colloids, but over longer periods of leaching some Cd will become dissociated from the matrix and move through the monoliths. The entire Pb load was eluted within the first PV and was completely associated with the colloid fraction (Table 3.3). Both Cu and Zn were released throughout the leaching process, but the majority of Cu was associated with the colloid fraction, while Zn was dominantly eluted in the dissolved fraction. Both Cu and Pb had higher affinities for the Kentucky reclaimed colloids than for Zn or Cd, thus supporting their greater colloid facilitated transport potential. The pattern of Zn elution coincided with flushing events at the beginning of each leaching cycle.

The Kentucky reclaimed monoliths (Figure 3.6) released Cd, Ni, and Pb in single flushing events, coinciding with those of colloids and usually at the start of the leaching cycle. However, only trace amounts of each metal were released, with Ni detected only in the first eluent sample taken. Although Cu was present in the bulk soil extractions and showed a high affinity for reclaimed colloids, no Cu was observed in eluents from reclaimed monoliths. Overall, less total Zn was eluted in the Kentucky reclaimed monoliths (Table 3.3) than in the natural monoliths, but more of it was associated with colloids, which may be the result of the continual release of colloids throughout the leaching process. The pattern of Zn elution coincided with flushing events at the beginning of each leaching cycle. Although both colloid concentration and total mg of colloids released were greater in reclaimed monoliths, higher metal elution was not observed when compared to natural monoliths. This may

be due to the lower overall metal content of the reclaimed samples (Table 3.1). The Kentucky reclaimed soils were regulated by SMCRA, which may explain their lower metal content compared to natural forest soils.

When unweathered spoil material was placed beneath reclaimed monoliths, colloid transport was completely inhibited within 2 PV of elution (Table 3.4). Each metal was observed starting at peak concentration and descending during the leaching. Both Cr and Pb dropped to levels below ICP detection within 1 PV, showing the lowest extracted concentrations of all six metals. Copper and Ni descended to equilibrium concentrations, and did not drop below detection within 2.5 PV. Both Cd and Zn had spikes in concentration, with the Zn pattern closely following the resumption of each leaching cycle. Across all treatments, total Zn was highest in eluents of the Kentucky spoil material.

The application of biosolids to the Kentucky reclaimed monoliths resulted in the additional release of Cr and Ni compared to reclaimed monoliths alone. Initial peak concentrations of Cu, Ni, and Zn were observed at about 1 PV before descending to levels similar to the biosolid amended Virginia monoliths. Colloid mediated transport of Cr, Cu, Ni, and Zn was relatively low, but nearly 100% of Pb eluted from the biosolid amended Kentucky monoliths was associated with colloids. Total Cu was higher than other treatments, while total Ni was only higher in the Virginia biosolid monoliths. Peaks in Ni and Zn elution coincided with the beginning of leaching cycles.

3.3.5   Metal Associations

Selected colloid samples were treated with ammonium acetate (NH_4^+) and 1 M HCl/HNO$_3$ to determine if colloid bound metals were exchangeable (Table 3.5). Only Cr and Pb were not detected when NH$_4$ was used as an exchangeable cation, but both metals had acid extractable concentrations low enough to see any differences found. Only Cu had significantly higher concentrations extracted from colloids using the double acid extraction versus NH_4^+. This would indicate that the metals detected in the Virginia and Kentucky monoliths were exchangeable, thus having increased an potential to be released from colloids to water resources.

Selected samples from the Kentucky eluents were analyzed by ion chromatography to determine anion content, which was combined with data for all 6 metals plus Ca, Mg, K, Na, Al, Fe, and DOC. Concentrations of various complexed forms of Cd, Cr, Cu, Ni, Pb, and Zn were calculated by Visual Minteq in the solution phase. For the Kentucky natural and reclaimed monoliths all of the dissolved Cd, Cu, and Zn were found to be complexed by the DOC (Table 3.6). The selected natural and reclaimed samples did not have Cr, Ni, or Pb above the ICP detection limits to determine speciation. The Kentucky reclaimed monoliths underlain by spoil did have all 6 metals present, but only Cr was entirely complexed by DOC (Bartlett, 1991). The spoil material contained higher amounts of SO_4^{2-} than the other treatments (Figure 3.9). Up to 50% of the Cd, Ni, or Zn, was free in solution, with the remaining 40% associated with SO_4^{2-}, and less than 10% complexed by DOC. Both Cu and Pb were either complexed by DOC or associated with SO_4^{2-}, without any free solution species. The Kentucky reclaimed and reclaimed-spoil combination monoliths had similar average concentrations of DOC, but the extremely high SO_4^{2-} content in spoil materials competed with the complexing ability of DOC. Kentucky reclaimed monoliths amended with biosolids also showed variability between the metals and DOC association. All of the Cu and a majority of the Cd and Ni in solution were complexed by DOC, but only 37% of the soluble Zn was associated with organic carbon. Most of the Zn was in free divalent form, even though SO_4^{2-} and DOC contents were comparable to those seen in reclaimed and natural monoliths.

The aromatic C content of the DOC observed using spectrophotometry was higher in the reclaimed-spoil eluents than either the natural or reclaimed-biosolid eluents. Natural and biosolid amended eluents resembled values reported from forest soils at depths of 15-30 cm, while spoil eluents resembled values from 0-15 cm depths (Jaffrain et al., 2007). This may indicate that most of the DOC from natural and reclaimed-biosolid eluents was derived from the lower portion of the monolith, while spoil material had fresh organic matter similar to surface soils, due to the source of spoil material being sluff from a roadside cut. The higher aromatic content of biosolid derived eluents may explain why less Zn was complexed by DOC.

3.4   Conclusions

Generally the transport of Cd, Cr, Cu, Ni, Pb, and Zn was increased by their association with colloids in most treatments. The results varied between metals and treatments, but the presence of unweathered spoil material and biosolid amendments contributed to higher metal release in solution and colloidal fractions. Monoliths with greater colloid release and a greater fraction of 2:1 minerals in the colloid fraction had higher percentages of colloid bound metals. Recently reclaimed Kentucky soils following SMCRA guidelines appeared to have lower levels of contamination than the 30 year old non regulated Virginia reclaimed soils and their natural counterparts. Natural forest soils contain considerable in-situ levels of heavy metals, particularly Cu and Zn, which may be released in both the solute and colloidal fractions. Only Zn was present in all treatments, while Cu and Ni were present in all but one treatment each. Trace amounts of Cd, Cr, and Pb were observed in most eluents, with Pb being predominantly colloid associated. Nearly all of the colloid bound metals were exchangeable, increasing the importance of colloid transport to the overall health of a watershed. Dissolved metals were mostly associated with DOC, unless high sulfate contents were present. Therefore, the addition of biosolid amendments to reclaimed soils could increase transport of metals through both dissolved and colloid phase mobilization.

Reclamation methods must be carefully planned to limit the amount of heavy metals transported to groundwater resources, since metal concentrations in these systems are inherently elevated and can be mobilized further following the disturbance. The application of biosolids should follow strict EPA guidelines governing the concentration of metals within the materials applied. While it may not be possible to restrict the amount of toxic spoil replaced within reclaimed soils, tests should be done to indicate the type and amounts of metals present within unweathered spoil, so predictions can be made on the possibility of groundwater contamination.

Table 3.1: Extractions of Cd, Cr, Cu, Ni, Pb, and Zn in mg/L by HCl/HNO$_3$ in soils, spoil, and biosolids.

| | Virginia | | | Kentucky | | | |
	Natural	Reclaimed	Spoil	Natural	Reclaimed	Spoil	Biosolids
	---mg/L---						
Cd	nd*	nd	nd	nd	nd	nd	nd
Cr	0.09	0.06	0.11	0.07	0.03	0.15	0.06
Cu	0.05	0.12	0.32	0.14	0.07	0.64	0.60
Ni	0.05	0.13	0.20	0.12	0.08	0.31	0.04
Pb	0.08	0.08	0.13	0.11	0.15	0.18	0.06
Zn	0.41	0.66	0.46	0.54	0.49	1.4	1.70

*nd = none detected

Table 3.2: Adsorption isotherm K_d (L/kg) constants for Cd, Cr, Cu, Ni, Pb, and Zn in Virginia and Kentucky bulk soil and colloid samples.*

| | Soils | | | | | | | Colloids | | | | | | |
	VN	VR	VS	KN	KR	KS	B	VN	VR	VS	KN	KR	KS	B
							L/kg							
Cd	1.13	1.43	2.15	2.33	1.88	1.17	3.11	1.79	1.52	1.57	1.88	1.58	1.56	3.26
Cr	1.78	1.29	1.58	1.45	1.02	2.17	1.49	3.00	1.95	2.16	2.62	1.92	1.89	1.63
Cu	1.54	1.76	2.48	2.70	2.08	2.02	1.15	2.60	1.67	2.28	2.64	4.54	1.15	1.72
Ni	1.08	1.42	1.92	2.16	1.67	0.97	1.01	0.80	1.53	1.77	1.67	2.03	1.16	1.64
Pb	1.99	1.92	2.73	2.66	1.58	2.65	2.74	2.81	2.07	5.57	3.59	2.52	2.39	2.53
Zn	1.39	1.26	1.69	2.03	1.58	1.49	3.39	3.09	1.09	1.50	1.80	1.88	1.12	2.96

* V = Virginia, K = Kentucky, B = Biosolid, N = Natural, R = Reclaimed, S = Spoil.

Table 3.3: Total (mg) and colloid bound (%) Cd, Cr, Cu, Ni, Pb, and Zn loads in Virginia and Kentucky treatments.*

	Cd		Cr		Cu		Ni		Pb		Zn	
	Total (mg)	Colloid Bound (%)	Total (mg)	Colloid Bound (%)	Total (mg)	Colloid Bound (%)	Total (mg)	Colloid Bound (%)	Total (mg)	Colloid Bound (%)	Total (mg)	Colloid Bound (%)
VN	nd	nd	< 0.01	nd	0.04	27.2	0.01	10.2	nd	nd	5.13	0.8
VR	0.01	87.5	0.09	92.0	0.40	86.5	0.66	13.6	0.02	85.0	3.29	10.9
VRS	< 0.01	nd	nd	nd	0.04	12.8	0.12	14.7	nd	nd	6.78	0.4
VRSB	0.02	0.8	< 0.01	2.0	0.93	7.02	3.31	25.9	< 0.01	100	21.53	3.62
KN	0.01	16.7	nd	nd	0.12	81.0	nd	nd	< 0.01	100	11.76	2.72
KR	< 0.01	39.0	nd	nd	nd	nd	0.01	87.0	< 0.01	55.6	2.75	12.2
KRS	0.18	nd	0.03	nd	0.96	nd	7.20	nd	0.03	nd	61.52	nd
KRB	0.16	42.7	< 0.01	16.7	3.30	8.09	2.87	2.2	< 0.01	100	7.04	9.3

* V = Virginia, K = Kentucky, B = Biosolid, N = Natural, R = Reclaimed, S = Spoil, nd = none detected.

Table 3.4: Selective properties of eluents and colloids for Virginia and Kentucky treatments.

	Virginia Eluents/Colloids				Kentucky Eluents/Colloids			
	Natural	Reclaimed	Spoil Amended	Biosolid Amended	Natural	Reclaimed	Spoil Amended	Biosolid Amended
pH	4.6	6.1	4.9	4.3	6.3	7.7	4.2	7.9
EC (µS/cm)	354	375	506	859	192	441	4541	651
Kaolinite (%)	53	14	-	33	40	40	-	27
2:1 Minerals (%)	31	55	-	48	44	48	-	35
Quartz (%)	16	6	-	13	10	10	-	37
Gibbsite	0	25	-	6	6	0	-	0
Particle Size (nm)	721	521	460	2662	182	1125	-	4704
Total Colloid Mass (mg)	857	1460	76	871	7269	10906	0	1209
Colloid Conc (mg/L)	105	208	11	79	655	1016	0	104

Table 3.5: Colloid bound metals extracted by ammonium acetate (NH_4^+) and 1 M acid in mg/L in selected samples, with letters representing differences at 0.01.

	Cd	Cr	Cu	Ni	Pb	Zn	All Metals
				-ppm-			
NH_4^+	< 0.01	nd	< 0.01 b	0.01	nd	0.26	0.05
HCl/HNO_3	< 0.01	< 0.01	0.02 a	0.01	< 0.01	0.27	0.05

* nd = none detected

Table 3.6: Metal complexation of metals by DOC (%) in Kentucky natural, reclaimed, reclaimed-spoil combination, and biosolid amended monoliths indicated by Minteq, DOC concentrations (mg/L), and aromatic content (L/mg cm).

	Natural	Reclaimed	Spoil	Biosolids
			-%-	
Cd	100	100	10.6	97.6
Cr	nd*	nd	100	nd
Cu	100	100	77.2	100
Ni	nd	nd	1.2	68.3
Pb	nd	nd	58.9	nd
Zn	100	100	0.2	36.9
DOC (mg/L)	1522.6	44.5	42.2	162.4
Aromatics (L/ mg cm)	0.001	-	0.018	0.006

* nd = none detected, otherwise not determined.
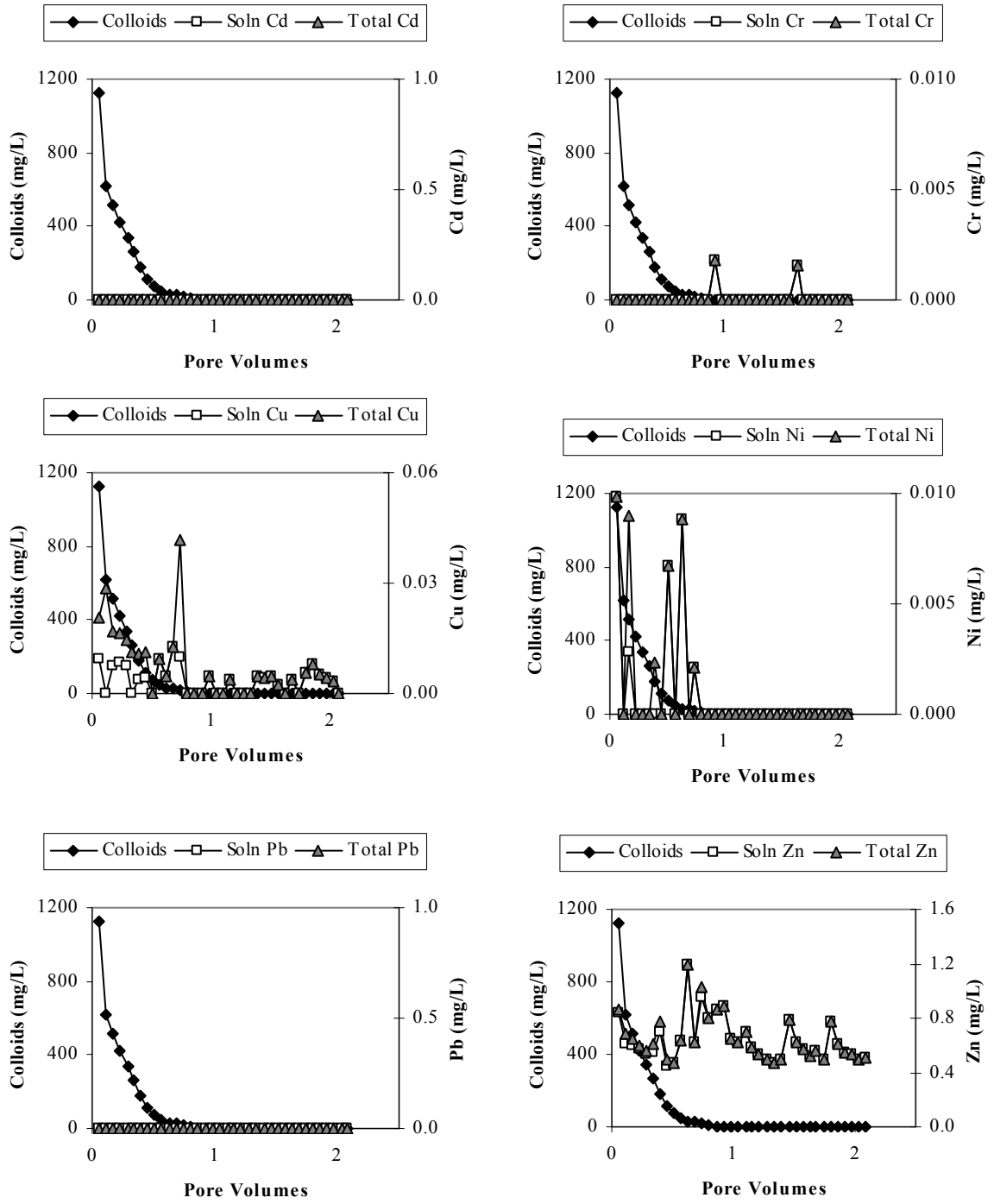
Figure 3.1: Colloid and metal concentrations (mg/L) of Cd, Cr, Cu, Ni, Pb, Zn in Virginia natural monolith eluents.
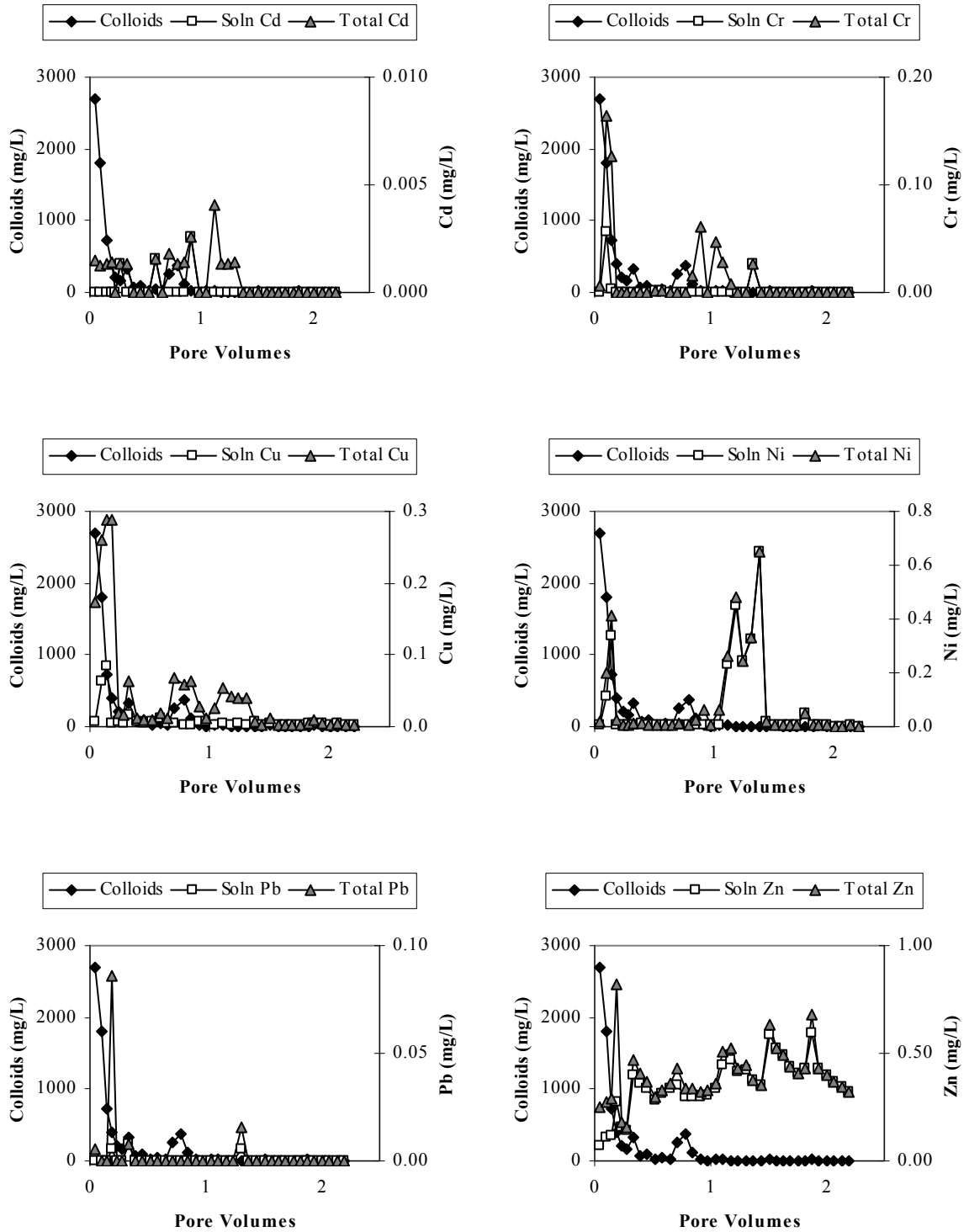
Figure 3.2: Colloid and metal concentrations (mg/L) of Cd, Cr, Cu, Ni, Pb, Zn in Virginia reclaimed monolith eluents.
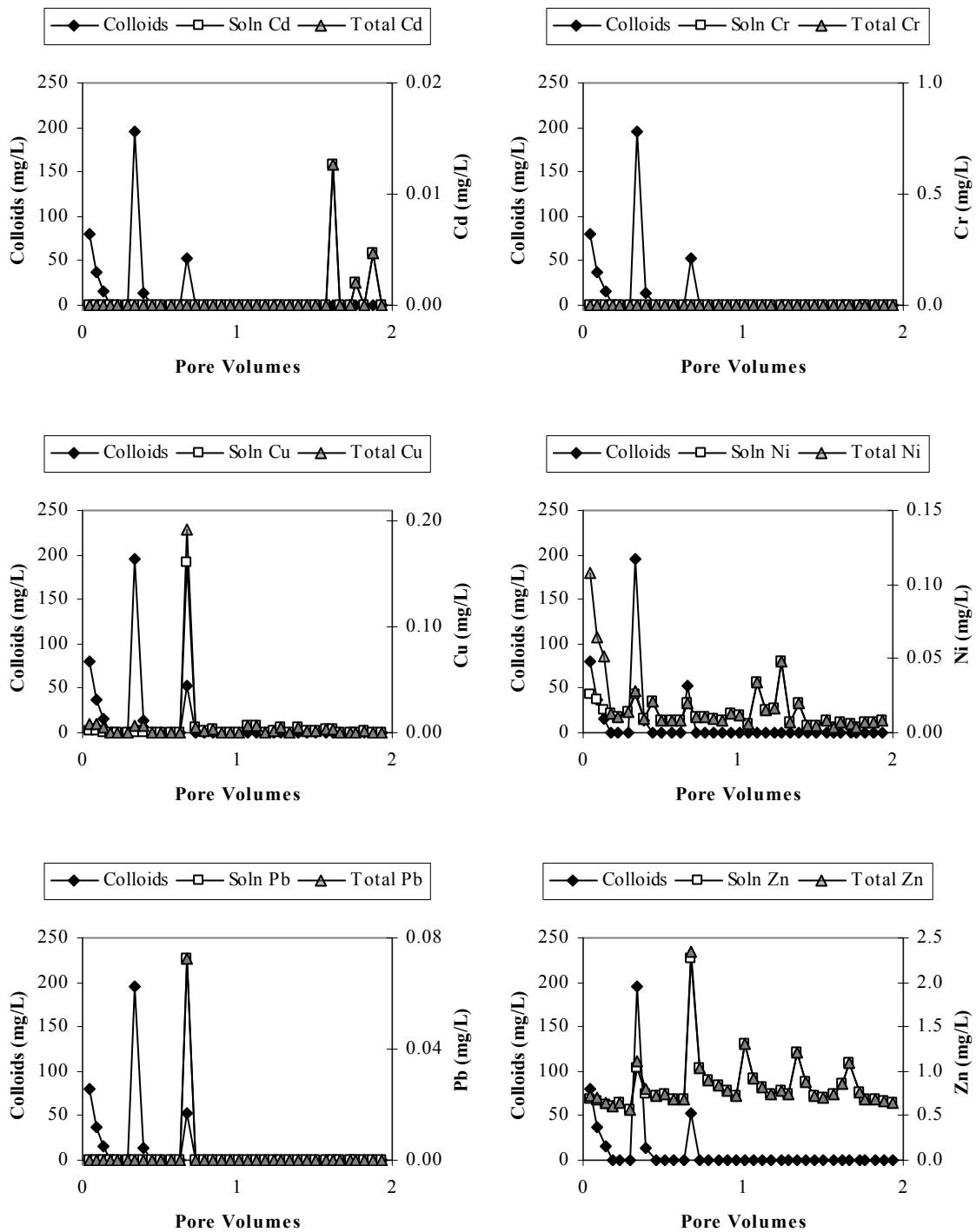
Figure 3.3: Colloid and metal concentrations (mg/L) of Cd, Cr, Cu, Ni, Pb, Zn in Virginia reclaimed-spoil combination monolith eluents.
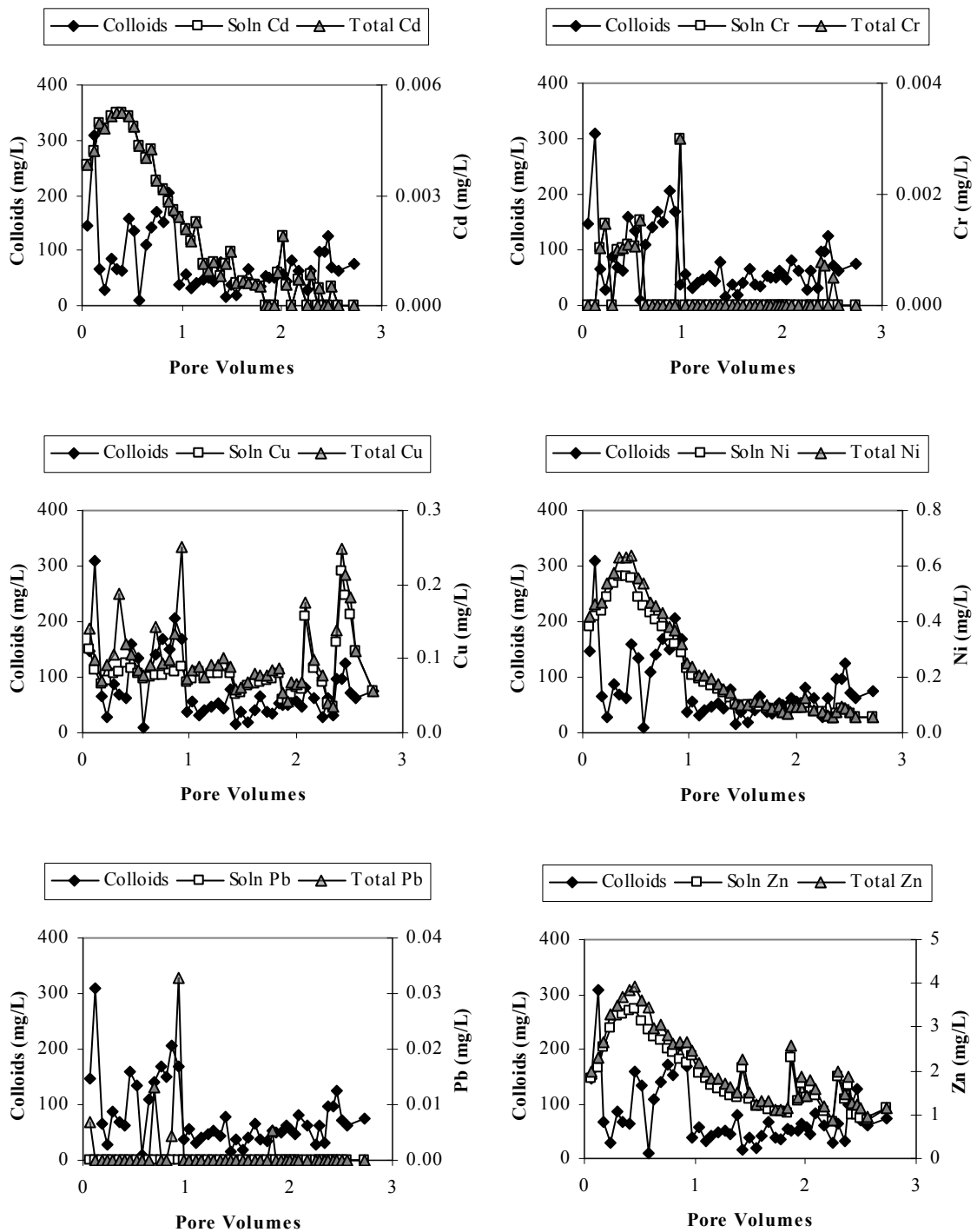
Figure 3.4: Colloid and metal concentrations (mg/L) of Cd, Cr, Cu, Ni, Pb, Zn in Virginia reclaimed-spoil-biosolid combination monolith eluents.

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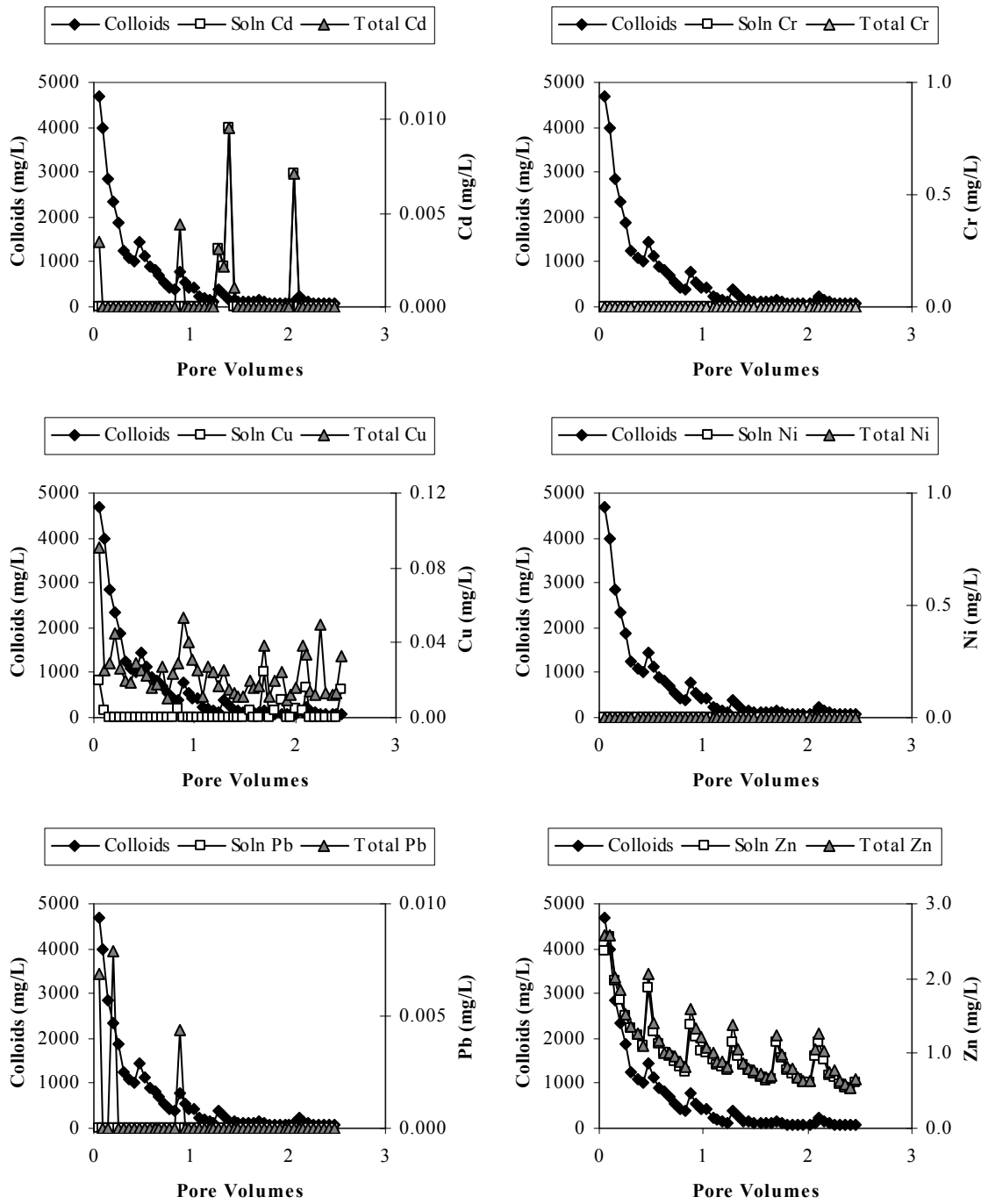
Figure 3.5: Colloid and metal concentrations (mg/L) of Cd, Cr, Cu, Ni, Pb, Zn in Kentucky natural monolith eluents.
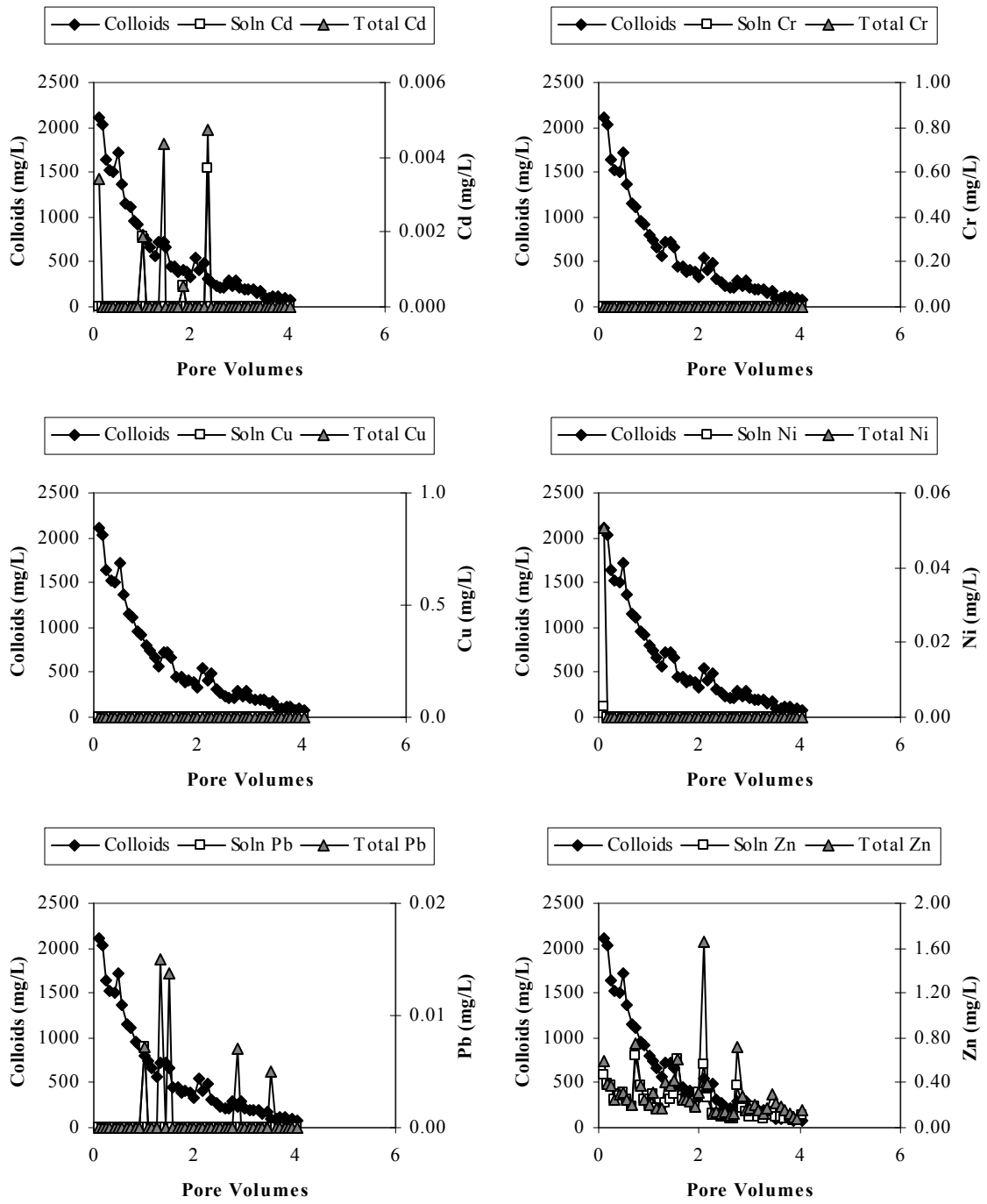
Figure 3.6: Colloid and metal concentrations (mg/L) of Cd, Cr, Cu, Ni, Pb, Zn in Kentucky reclaimed monolith eluents.
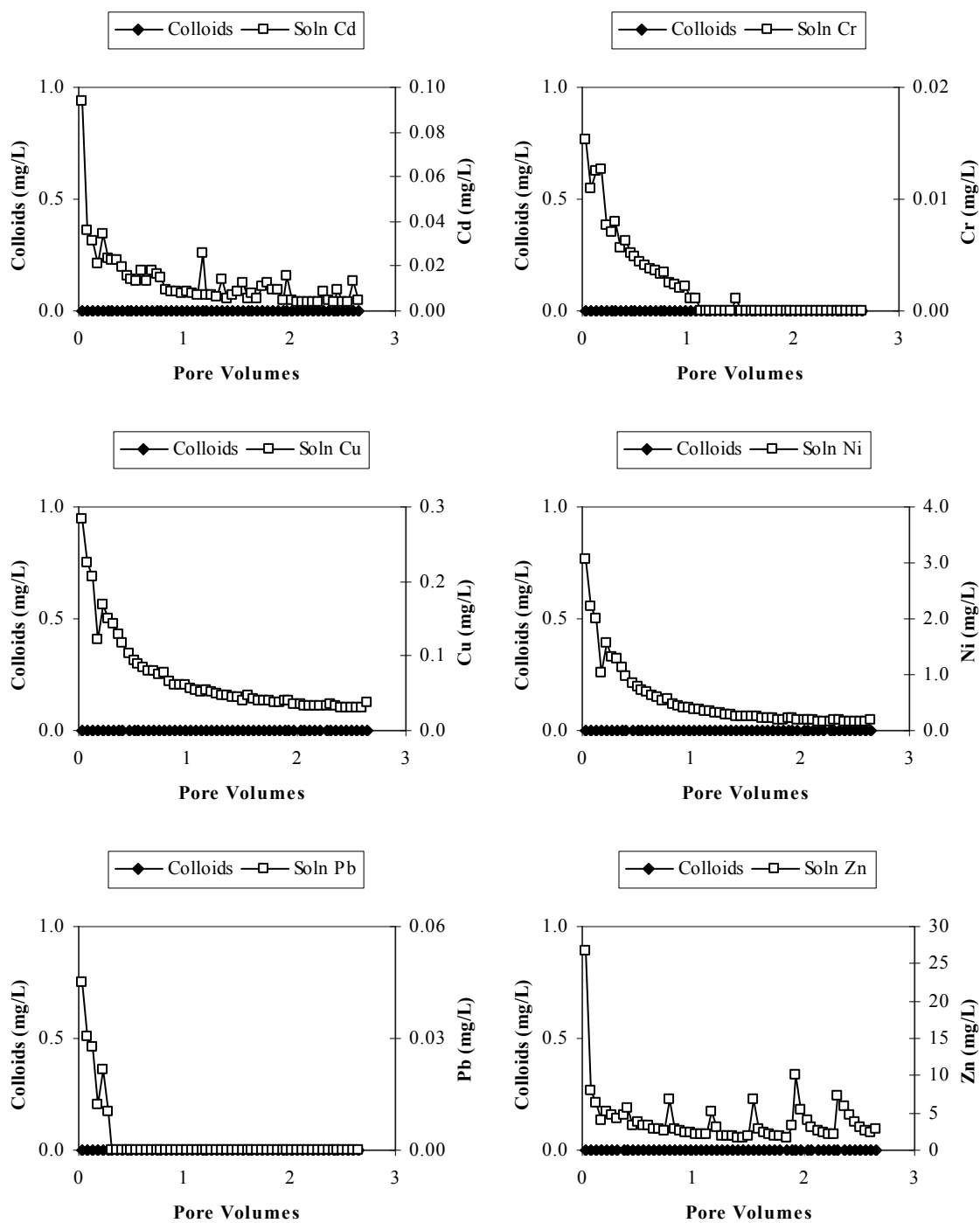
Figure 3.7: Colloid and metal concentrations (mg/L) of Cd, Cr, Cu, Ni, Pb, Zn in Kentucky reclaimed-spoil combination monolith eluents.
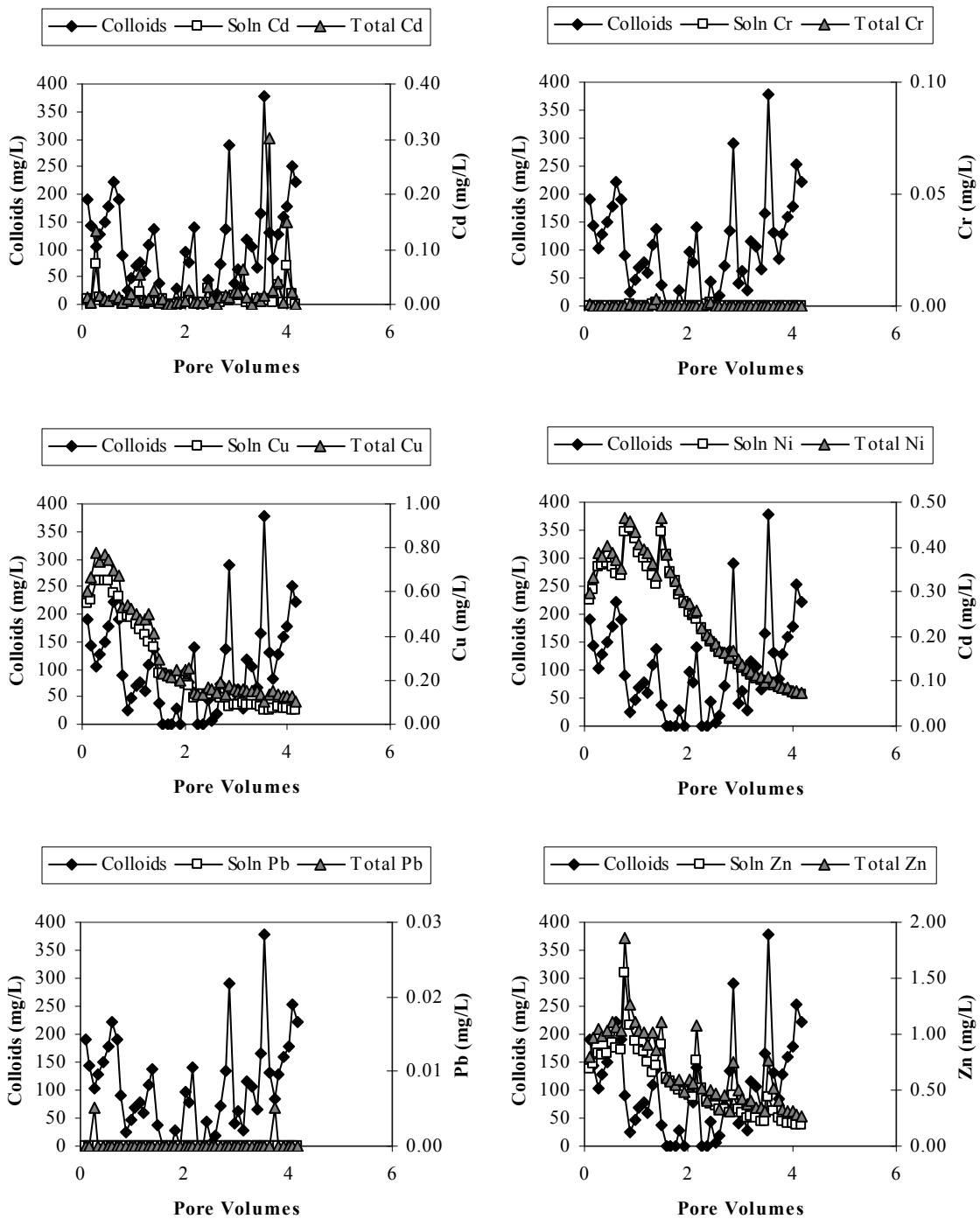
Figure 3.8: Colloid and metal concentrations (mg/L) of Cd, Cr, Cu, Ni, Pb, Zn in Kentucky biosolid amended reclaimed monolith eluents.
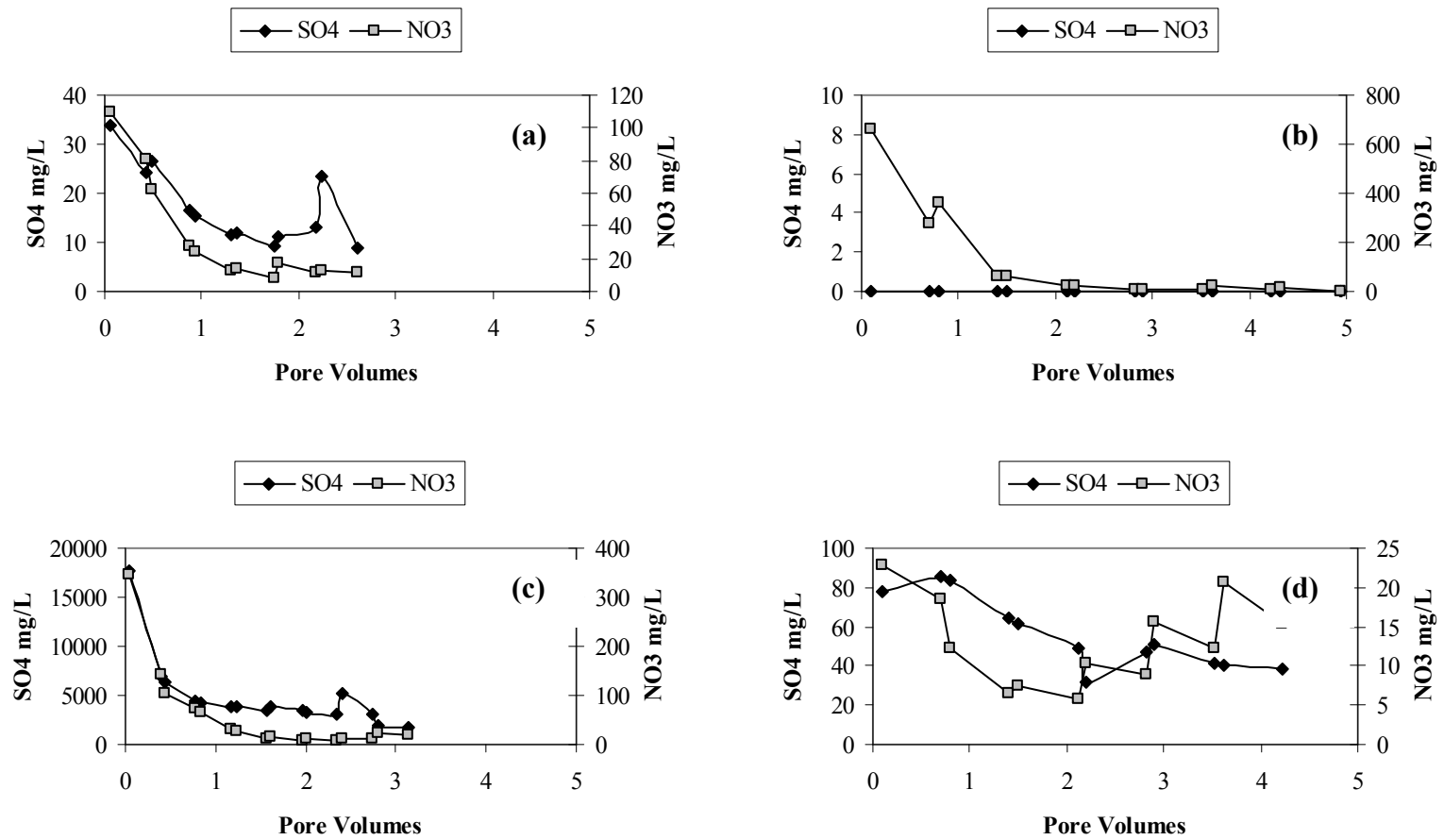
Figure 3.9: Concentration (mg/L) of SO_4 and NO_3 in eluents of Kentucky (a) natural, (b) reclaimed, (c) reclaimed-spoil combination, and (d) biosolid amended reclaimed monoliths.

CHAPTER 4   HYDRAULIC CONDUCTIVITY AND IN-SITU COLLOID TRANSPORT WITHIN RECLAIMED MINE SOILS

4.1   Introduction

Soils disturbed by coal mining experience changes in water infiltration rate and hydraulic conductivity depending through the destruction of pore structure and compaction. Understanding saturated and unsaturated flow within mine soil profiles is important in predicting colloid transport. The pore size distribution of reclaimed mine soils will contribute to the filtration of colloids (Kaplan et al., 1993; Karathanasis, 2003), which may be carriers of inorganic pollutants into groundwater. Therefore, understanding the changes in hydraulic conductivity within disturbed soils is an important precondition for predicting colloid mobility within reclaimed soils.

The Surface Mining Control and Reclamation Act of 1977 (SMCRA) requires reclamation methods which cover toxic (spoil) materials with at least 1.2 m of a non-toxic topsoil (Stewart and Daniels, 1992). Degradation of soil structure, increased bulk density, and lower porosity often occur when soils are disturbed by strip mining practices (Guebert and Gardner, 2001; Ward et al., 1983). In some cases water infiltration is reduced on purpose to divert percolation through spoils and prevent the production of acid mine drainage (Daniels and Stewart, 2000). The higher bulk densities of spoil materials are a direct result of the reclamation methods used (Haering et al., 2004). Density may increase over time as settling occurs (Rogowski and Jacoby, 1979), or decrease at the surface through the incorporation of organic materials (Shukla et al., 2004). As the density of reclaimed soils increases, physical straining of larger colloids occurs (Kaplan et al., 1993), and smaller colloids may diffuse into the matrix, reducing their mobility as well (Cumbie and McKay, 1999). While increased bulk density may restrict flow due to reduced porosity, macropores or cracks within the spoil may induce preferential flow, even within a compacted soil. Macropores are more effectively defined by their channeling capacity than by an arbitrary pore size, as a small volume of macroporosity may dominate vertical flow during some rainfall events (Beven and Germann, 1982).

Macropores and fracture flow are often a characteristic of reclaimed soils, due to the formation of karst-like channels following reclamation(Al and Blowes, 1996; Skousen et al., 2000; Geidel and Carcuccio, 2000). These fractures are typically located adjacent to rock fragments, providing mine spoils with greater rock content and increased preferential flow (Guebert and Gardner, 2001). Increased colloid transport through larger macropores can occur relative to adjacent impermeable spoil layers (McCarthy and Shevenell, 1998; Seta and Karathanasis, 1997; Guebert and Gardner, 2001; Rogowski and Jacoby, 1979). Colloid transport through fractured soils depends upon flow rates, where faster rates will move colloids through macropores by convection or as film flow along pore walls (Christ and Hoffman, 2002; McCarthy and Zachara, 1989; Ranville et al., 2005), while slower rates promote colloid transport through diffusion (Noack et al., 2000). Faster flow will inhibit colloid filtration due to reduced colloid contact with the soil matrix, as well as by directing larger colloids into marcopores where they are less likely to be filtered (Kaplan et al., 1993; Ranville et al., 2005; McCarthy and Shevenell, 1998; Seta and Karathanasis, 1996). On the other hand, mobilization of in-situ colloids may be limited by preferential flow due to limited contact of the matrix with low ionic strength rainwater, which increases dispersion of colloids (Kjaergaard et al., 2004).

Macropores more effectively move colloids when soils are saturated, which is not often the condition (Beven and Germann, 1982). Diffusion of solutes and colloids becomes more important during unsaturated flow, which primarily passes through finer pores, where conductivity is slower (Nielsen and Biggar, 1961; Noack et al., 2000). Also, under decreasing volumetric moisture contents, steady state breakthrough of colloids is reduced through film straining and capture at air-water interfaces (Wan and Tokunaga, 1997; Lenhart and Saiers, 2002). In unsaturated soils, colloid mobility decreases as film thickness drops below the colloid diameter (Wan and Tokunaga, 1997), although colloids will continue to travel through any continuous ducts that exist (Lenhart and Saiers, 2002). Water film thickness depends on grain size, shape and roughness, as well as packing and aggregation (Wan and Tokunaga, 1997), which may be highly heterogeneous in reclaimed soils. Retention of colloids occurs as the gas content of porous media increases, particularly with

hydrophobic colloids (Wan and Wilson, 1994). As soils rewet, transient flow occurs, disturbing and releasing more colloids (Levin et al., 2002).

Predicting colloid mobilization and filtration in reclaimed soils depends on understanding pore size distribution, colloid particle size, and hydraulic conductivity under both saturated and unsaturated conditions. The objectives of this study were to (1) quantity the hydraulic conductivity function of 30 year old and recently reclaimed soil monoliths;

(2) compare saturated conductivity at different depths within natural, spoil, reclaimed, and reclaimed monoliths receiving biosolid applications;

(3) observe unsaturated conductivity at different depths within natural, spoil, reclaimed, and reclaimed monoliths receiving biosolid applications; and

(4) contrast eluted colloid loads to hydraulic conductivity of reclaimed monoliths at varying soil water contents.

4.2   Materials and Methods

4.2.1   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 to represent 30 year old reclaimed soils and from Robinson Forest, near Jackson, Kentucky, to represent recently reclaimed mine soils.

For each study area, monoliths were obtained to represent the following treatments: (1) natural monoliths (controls) collected in duplicate from unmined forest soils, and three duplicate monoliths per site obtained from soils disturbed by coal mining to represent (2) reclaimed soils, (3) reclaimed soil + spoil material, and (4) reclaimed soil + spoil material + biosolid application. The Kentucky treatments consisted only of (1) natural and (2) reclaimed soil monoliths.

The disturbed, spoil, and natural soils in Virginia and the natural soils in Kentucky were obtained as intact soil monoliths, 30 cm in height and 18 cm in diameter. The reclaimed soils in Virginia had been deposited above a black spoil material varying in thickness from 30 cm to 1 m depth and containing fragments of

siltstone. The Virginia reclaimed soils and spoil materials were obtained from their upper 30 cm depth and recombined in the lab for treatments 2 and 3 to ensure similar thickness. Monoliths were removed by digging a pedestal approximately 50 x 50 x 40 cm, then trimming them with knives and soil picks so to fit within a polyvinyl chloride (PVC) tube of 20 cm internal diameter and 30 cm height. The 1 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. The natural soil for both Virginia and Kentucky treatments was comprised by intact soil monoliths 30 x 18 cm obtained from adjacent undisturbed sites.

Rock fragment content prevented intact monoliths from being extracted from the 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, an intact surface horizon of about 15 cm in thickness, and 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. Subsurface material was packed in the column to obtain a bulk density of around 1.4 g/cm^3 up to about 15 cm. 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 lime stabilized biosolid material use in the study came from a local municipal wastewater treatment facility in Winchester (Clark County), Kentucky. It was dried and applied to the surface of the Virginia Reclaimed monoliths at a rate of 20 t/ha.

4.2.2 In-Situ Colloid Elution

In situ colloid generation and elution from monoliths was assessed with leaching experiments. A rainfall simulator was set up to apply D.I. water at a rate of 250 mL/hour (1.0 cm/hour) to the surface of each monolith. The application rate was controlled with a peristaltic pump. The upper boundary condition of the monolith was

open to the atmosphere and related to the infiltration rate of the surface, while the lower boundary was kept at -10 cm using a Mariotte device. To keep the lower boundary at -10 cm the monolith was placed in a large funnel and sealed around the edges with a silicone gel. A tube was attached from the funnel into a sealed 2 L flask for the leachate to drip into. This 2 L flask was also connected to a second flask, which was filled with water to control the pressure beneath the monolith and maintain the lower boundary condition at the desired level. This second flask was sealed except for two openings, one of which connected to the tubing used to apply suction, and the other which contained a thin PVC pipe that was open to the atmosphere. The bottom of the pipe was placed below the water surface, so that when suction was applied, air entered through the PVC and pushed through the water, creating a negative tension within the system. A tensimeter was used to monitor the pressure within the funnel, which was adjusted to -10 cm by raising or lowering the pipe. Tensiometers were placed at 5, 15, and 25 cm depths to monitor saturation. A Campbell Scientific CR10X datalogger monitored pressure transducer tensiometers readings in mV every minute during leaching. Voltage readings were converted to cm pressure head.

The leaching of each monolith was conducted in six cycles, corresponding to 2-3 pore volumes (PV) of elution. Each cycle consisted of 2 L of water elution at 24 hour intervals. Leachate was collected at the bottom of the monolith every hour for a total of 8 hours. Suspension concentrations were determined gravimetrically taking a 20 mL aliquot from each hourly sample and drying it at 105 ºC in a pre-weighed aluminum tin for 24 hours. Electrical conductivity was multiplied by 0.61 to convert to salt concentration, which was then subtracted from the suspension concentrations to determine actual colloid concentration (US Salinity Laboratory, 1954). To correct for salts in the biosolid application treatments a glass membrane filter was used to remove mineral and organic colloids in selected samples and create a regression equation of salt concentration versus electrical conductivity. A 20 mL aliquot eluent was filtered through a 0.2 μm filter and dried in a pre-weighed aluminum tin at 105 ºC for 24 hours before converting to mg/L salt content. The pH and EC were determined on a Denver Instrument Model 250 pH*ISE*conductivity meter for each hourly elution.

Mineralogical composition of the samples was determined by x-ray diffraction (XRD) and thermogravimetric analysis (TA) (Karathanasis and Hajek, 1982). To extract colloids from the eluent, samples were filtered through a 0.45 μm filter which was taped to a glass slide for XRD analysis. 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.

4.2.3   Evaporation of Kentucky and Virginia Monoliths

Laboratory evaporation experiments to determine unsaturated hydraulic properties of the Virginia and Kentucky natural and reclaimed monoliths were performed using the Wind (1968) method described by Wendroth and Wypler (2008). Monoliths which had been previously leached of colloids were saturated by capillary action by placing them in a tub of deionized water, capped with polywrap and left to equilibrate for 24 hours. Following equilibration, the capped monoliths were removed and allowed to drain before they were placed on a 30 by 30 cm sheet of Plexiglas and sealed at the bottom with silicone gel. Pressure transducer tensiometers to measure soil water pressure potential were placed at depths of 5, 15, and 25 cm and sealed with plumber lute. The tensiometers were logged overnight on a Campbell Scientific CR10X data logger until zero hydraulic gradients were observed, indicating hydraulic equilibrium.

The polywrap was removed to start the evaporation and the initial weight was taken on a $\pm$ 0.01 kg scale. Further mass readings were taken every four to five hours, or as a weight change was observed on the scale. For the sandier textured Kentucky reclaimed monoliths a fan was used to induce a faster evaporation rate. When the tensiometer at 5 cm depth reached readings of -700 cm, or air entry into the tensiometer was observed, evaporation was stopped by placing a cap on each monolith. The final weight was taken and monoliths were dried in an oven at 60ºC until no decrease in mass was observed. Subsamples were taken and dried at 105ºC to determine the gravimetric water content and calculate the bulk density of each monolith. Water storage for each monolith was calculated and an iterative procedure for calculating the van Genuchten function parameters α, n, θ_s, and θ_r

(van Genuchten, 1980) was performed using the procedures outlined in Wendroth and Wypler (2008). Subsequently, the hydraulic conductivity pressure head relation was calculated for different layers.

4.2.4 Hydraulic Conductivity of Cores from Virginia Monoliths

Hydraulic conductivity close to and at saturation was measured to observe the contribution of macropores to flow within the monoliths. To measure the hydraulic conductivity of different layers within the Virginia natural, reclaimed, and spoil monoliths, bulk density cores were sampled from within moistened monoliths. A bulk density core of 6 cm height and 8.6 cm diameter was taken from the monoliths using a self made bulk density hammer. Within each 30 cm tall monolith three to four bulk density cores were carefully extracted to preserve pore structure. Due to variability in soil integrity and rock fragment content, extracted depths varied within a few centimeters between monoliths. The excess soil was carefully trimmed to fit within each core, wrapped in polywrap, and stored in a refrigerator until needed for hydraulic conductivity measurements.

Saturated conductivity (K_{sat}) was performed in an Eijkelkamp K_{sat} permeameter (Netherlands) using upward constant head flow conditions (Reynolds and Elrick, 2002). Flow within soil cores was measured until three relatively similar conductivities were observed consecutively, then the experiment was stopped. The water level in the permeameter was slowly reduced and the soil cores were allowed to gently drain.

Unsaturated conductivity was measured because soils are not often under saturated conditions, and flow will occur much slower when soils are not saturated. To determine unsaturated conductivity at -1, -5, and -10 cm water pressure, a percolation method was used where the core sample was placed between two membranes to which the negative pressure was applied. Soil cores were placed on the infiltrometer and Mariotte devices at both the inlet and outlet were adjusted so that the upper and lower boundaries were set to either -1, -5, or -10 cm. Conductivity through each core was measured by calculating flow rates. When three relatively similar conductivities were observed consecutively, the experiment was stopped.

4.2.5   Thin Sections from Virginia Monoliths

Selected bulk density cores from the Virginia natural, reclaimed, reclaimed with biosolid amendment, and spoil monoliths were used for thin section analysis to visually observe macroporosity, connectivity, and tortuosity within the soil pores. The soil was carefully removed from each core, wrapped in a fine mesh hair net, polywrap, and aluminum foil. Samples were sent to National Petrographic Services (Houston, Texas) to be impregnated with saran, cut, mounted, and polished. Thin section samples were examined using a Leica M Stereo-microscope (Leica Microsystems Ltd., Heerbugg, Switzerland). A potential flow path (τ) of the pores was determined by drawing a line on each thin section photograph. The height of the photo was assumed to be the length of a straight (L_{tube}) path through the thin section and divided by the total proposed (L_{pore}) path length.

$$\tau = \frac{L_{tube}}{L_{pore}}$$

A smaller ratio was assumed to mean an increase in flow path.

4.3   Results and Discussion

4.3.1   Unsaturated Hydraulic Properties and Colloid Mobility

Water retention curves for the Virginia and Kentucky natural and reclaimed monoliths obtained with the evaporation method are shown in Figure 4.1. Because there were three tensiometers, water retention curves of each monolith were derived for the upper and lower layers.

Within Virginia natural (VNI, VNII) duplicates and layers, there was not a large difference in water retention (Figure 4.1 a,b). At drier conditions, VNII has slightly lower volumetric water content (θ) than VNI, which is not supported by the higher density of VNII monoliths (Table 4.1). Unsaturated conductivity (K(h)) of VN monoliths (Figure 4.2 a,b) also exhibited little variation, with VNII having higher K(h) at most tensions in both layers. Differences in pore size distribution (Figure 4.3 a,b) were difficult to discern under drier conditions, but VNII had a larger amount of

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macropores (> 75 μm) as observed at tensions of around -50 cm. This is indicated by the larger values of dθ/dh in the VNII monoliths (Figure 4.3 a,b) at wetter conditions. Larger macroporosity may explain the lower density observed in VNII monoliths. Colloid elution from the VNII monolith was slightly higher than VNI, which may be due to the slightly higher macroporosity (Table 4.1). Observations of soil water pressure head within VN monoliths during colloid leaching experiments indicated that both monoliths were close to saturation (0 to -5 cm) the entire time. Therefore, because the monoliths were close to saturation, and the VNII monolith had greater macroporosity, there was slightly higher mobility of water dispersible colloids within the VNII monolith when compared to VNI.

Colloid elution between the VR monoliths was not significantly different (Table 4.1), although there were some differences in hydraulic properties observed (Figures 3.1, 3.2, 3.3). These differences were seen in water retention between the Virginia reclaimed (VRI, VRII) monoliths (Figure 4.1 c,d). The VRII monolith had much lower water content, beginning to diverge as matric potentials (h) approached -50 cm, indicating that the VRII monolith did not hold as much water at lower pressure heads. Unsaturated conductivity (Figure 4.2 c,d) was not easily comparable between VR duplicates due to the VRII monolith exhibiting very different behavior. This may be due to the difficulty in measuring differences in mass during the evaporation experiment. The data obtained would indicate that the VRII monolith had a higher unsaturated conductivity (Figure 4.2 c,d) at lower pressure heads (-400 to -600 cm) in both layers. Change in θ as h dropped was greater in the VRII than the VRI monolith at most pressure heads observed in the upper layer (Figure 4.3), indicating that the VRII monolith had a greater porosity. At conditions closer to saturation, the lower section of the VRI monolith had a decrease in θ change, suggesting a lower contribution of macropores than in the VRII monolith. The larger amount of macropores in VRII monoliths apparently did not contribute to greater colloid mobility.

Cumulative colloids from Kentucky natural (KNI, KNII) duplicate monoliths were higher in the KNII monolith by about 1300 mg (Table 4.1). Only the water retention curves for KN monoliths had discernable differences (Figure 4.1 e,f). The

KNII monolith, like the Virginia natural monoliths, had lower water content at similar pressure heads than the reclaimed monoliths. Unsaturated conductivity (Figure 4.2 e,f) generally appeared to be similar between the KN monoliths, although the K(h) data were scattered and difficult to read. Pore size distribution did not vary between the KN monolith layers (Figure 4.3 e,f). Bulk density (Table 4.1) was lower in the KNII monolith, indicating more pore space, but water retention curves suggested that the KNII monolith held less water than the denser KNI monolith (Figure 4.1 e,f). This may be an indication of macropores within the KNII monolith reducing density measurements, or higher clay content within KNI monoliths allowing for a larger number of smaller pores. The slightly larger colloid load released from the KNII monolith compared to KNI may be related to chemical and mineralogical factor rather within the monoliths, rather than pore space. Without K(h) measurements closer to saturation, we cannot determine how the larger macropores may have contributed to flow within these two monoliths.

Eluted colloid loads were highly variable between the Kentucky reclaimed (KRI, KRII) monoliths (Table 4.1), where the KRII monolith released 20 times more colloids than the KRI monolith. Both of these treatments were the only monoliths constructed within the lab of recently disturbed material, which may explain the differences. There were no observable differences between the water retention, K(h), or the pore size distribution curves of the KR monoliths (Figures 3.1, 3.2, 3.3, g,h). There was difficulty in drying the KRI monolith below -200 cm tension, possibly due to sand content, where we may have observed greater differences in the water retention curve. The similarity in the hydraulic properties of the two monoliths should be expected since they were reconstructed in a similar manner, and the difference in colloid elution is probably due to the relative mixing of material within each monolith.

Considering all of the Virginia and Kentucky treatments, both of the natural forest soils had greater water retention at lower soil water potentials than their reclaimed counterparts, probably due to higher clay content (Figure 4.1). During the reclamation practice soils often lose their finer materials, probably due to wind or erosion. The KN monoliths were less dense than their reclaimed counterparts, which

was reflected in their slightly higher unsaturated conductivities and larger contribution of pores to change in θ (Figure 4.3). Although the KRII monolith eluted the largest load of colloids, this does not appear to be related to hydraulic properties observed from water pressure heads of -10 to -700. Macropore contribution to flow near saturated conditions may be larger in the KRII monolith, but could not be determined from this data. When monoliths were dried at 60ºC and leached to determine rejuvenation of colloid content within the matrix, the KRII monolith eluted a much lower cumulative colloid load, supporting the hypothesis that there was a larger portion of colloidal material in the recently constructed monolith. With leaching, the KR monoliths appeared to contain similar sized sources of colloids.

When both KN monoliths were compared to only the KRI monolith, they released a greater colloid load (Table 4.1), which may be due to higher clay content, as well as slightly higher macroporosity and overall pore space. The total pore volume within KN monoliths was almost double that of KR monoliths (Table 4.1). The KN monoliths released almost 6 to 7 times the colloid load that the VN monoliths did. Although they appear to have similar K(h) and pore size distribution, the VN monoliths showed higher water retention at all tensions. It is possible that the colluvial nature of KN monoliths provided them with a larger amount of loose material to be dispersed into the pore water. The VR monoliths had similar colloid load elutions to the KRI monolith, but different pore size distributions. Virginia reclaimed monoliths also had a similar density to their KR counterparts, but over 30 years may have formed more aggregated structure, and therefore greater porosity throughout the monoliths.

4.3.2   Hydraulic Conductivity within Virginia Cores

Bulk density cores were extracted from all Virginia natural, reclaimed, and spoil monoliths and examined for conductivity at 0, -1, -5, and -10 cm (Table 4.2, 3.3). Because of the difficulty of extracting the cores not all depths or number of cores extracted were similar. For Virginia natural and reclaimed cores, the original monoliths were only 30 cm tall. However, for treatments with spoil monoliths

attached, the height was increased to 60 cm, so any depth below 30 cm within those treatments represents conductivities from within spoil monoliths.

Saturated conductivities (K_{sat}) varied by depth within monoliths, probably due to the differences in macroporosity and pore connectivity within the soils. Conductivity within all monoliths dropped as water content or soil water pressure head fell, which was expected. Only within the spoil monolith associated with the biosolid amended reclaimed duplicate (VRSBII) was the conductivity at pressure heads below saturation so slow that it could not be measured.

Conductivities across depths within natural, reclaimed, and spoil monoliths were averaged in Figure 4.4 to make it easier to compare the data. There were four unamended reclaimed monoliths to compare, those with (VRSI, VRSII) and those without (VRI, VRII) a spoil monolith attached beneath. The reclaimed monoliths amended with biosolids (VRBI, VRBII) also had spoil monoliths beneath them.

The natural monoliths (VNI, VNII) and the VRII had similar K_{sat}, but the VRI monolith had a higher saturated conductivity than all three (Figure 4.4a). The higher conductivity observed in one out of both of the reclaimed monoliths may explain the higher colloid load eluted (Table 4.1) from reclaimed monoliths, although pore continuity and not just conductivity alone may have contributed (Ehlers et al., 1995). The lowest saturated conductivity was within the VRSI monolith, while the VRSII was similar to the VN monoliths (Figure 4.4a). The highest saturated conductivities when averaged across all depths (Figure 4.4a) were among two biosolid amended reclaimed monoliths (VRBI, VRBII), but this was not due to surface disturbance since they both had higher conductivities at lower depths than other reclaimed monoliths (Table 4.3). The biosolid amended reclaimed monoliths also maintained the highest conductivities as unsaturated flow occurred. The difference from colloids eluted within all treatments associated with reclaimed spoil combination monoliths was more likely related to preferential flow within spoil monoliths allowing for greater colloid mobility (Figure 4.4 b).

The spoil monoliths, separate from their reclaimed surfaces, had similar saturated conductivities to all other monoliths, but quickly dropped to the lowest conductivities as unsaturated flow occurred (Figure 4.4 b). This points to the presence of large

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cracks within the spoil monoliths that only become relevant for transport when the soils are close to saturation. Conductivities were averaged across all depths within reclaimed spoil combination monoliths, with and without biosolid additions (Figure 4.4). When averaged across all depths VRSB monoliths still maintained two of the highest conductivities, explaining their higher colloid load release that was not seen in VRS monoliths, which had two of the lowest. Conductivity within VRSB monoliths remained higher than VRS monoliths at all depth averaged saturations, higher than even natural monoliths. This is a factor that may explain why VRSB monoliths had colloid loads similar to natural monoliths.

Hydraulic conductivity data from the core infiltration and monolith evaporation experiments were combined in Figure 4.5. In the upper and lower compartments of the VN and VR monoliths three points representing average K(h) at -1, -5, and -10 cm pressure head were plotted with the K(h) from evaporation experiments. The data within VN monoliths was in general agreement, although there were no cores for the lower portion of the VNII monolith to obtain hydraulic conductivities close to saturation (Figure 4.5 b). The upper and lower portions of the KRII monolith (Figure 4.5 c,d), which for the evaporation experiment had two clusters of data, shows better agreement between the additional data points close to saturation and evaporation K(h) between -10 and -100 cm soil water pressure. Therefore, the large cluster of data between -100 and -1000 cm soil water pressure for the upper KRII monolith may be somewhat flawed (Figure 4.5 c,d). The KRI subsurface K(h) had a stronger relationship between tension infiltrometer and evaporation data (Figure 4.5 d), than in the KRI surface (Figure 4.5 c). Overall the tension infiltrometer data that observed K(h) close to saturation in subsampled cores and the evaporation method applied to large monoliths support each other. This may validate the application of evaporation experiments to larger soil samples.

4.3.3   Thin Sections from Virginia Cores

Thin sections from the Virginia cores were examined in a micromorphological approach to describing porosity and colloid mobility. The Virginia natural monoliths were porous (Figure 4.6 a,b), but many of the macropores had tortuous paths, which

probably limited colloid transport from the surface (1-7 cm). Two path lengths were proposed in Figure 4.6a for the surface of a VN monolith. The first path (α) represents a complete flow path with a value (τ) of 0.72. The second proposed path (β) presents a partial dead end pore situation to further emphasize the reduced likelihood of colloid mobility. The surface matrix (Figure 4.6 a) was also aggregated, containing intra (macro) and interaggregate (matrix) pores. Biological activity was probably the factor that caused pronounced aggregation and the continuous pores of the VN surface, and repeated wash cycles may flush colloids caught in tortuous pores from the surface over time. Colloids may also disperse into in the intraaggregate pores during periods of slow flow (Cumbie and McKay, 1993), reducing overall colloid elution. On the other hand, colloids would be washed easily from interaggregate pores, providing a diffusion gradient from intraaggregate pores as proposed by Schelde et al. (2002), and allowing for colloid regeneration during drier soil conditions. Evidence of this was seen in Table 4.1, where additional colloids were eluted after monoliths were allowed to dry at 60ºC.

The natural subsurface (16-22 cm) thin section (Figure 4.6 b) matrix was more compact, but still contained macropores. The proposed colloid pathway through the soil had a τ of 0.82, which implies that the VN subsurface was slightly shorter path than the surface. The subsurface also contained significant amounts of plasma (clay), which was probably a source for the eluted colloid load from natural monoliths. Thin films of both organic and mineral material were present along pore walls indicating illuviation processes within the soils. It is likely that many of the colloids from VN monoliths were dispersed and mobilized from the subsurface environment, due to the plasma content and lower τ.

Virginia reclaimed monoliths had 30 years to regenerate some porosity under forest conditions (Figure 4.7 a,b). The surface (3-9 cm) of these monoliths (Figure 4.7a) was dominated by sand grains and horizontal flow paths. These paths resulted in a higher τ (0.66) than was seen in surface of VN monoliths (Figure 4.6 a). The lower clay content and longer paths were probably a limiting factor to colloid mobility from the reclaimed surfaces. Some plasma can be observed along the pore walls, indicating that the minimal amount of clay present has been mobile within the monoliths. The

VR surface (Figure 4.7 a) appeared to be more compact than the VN surface (Figure 4.6 a).

The VR subsurface (17-23 cm) had a much lower τ (0.93) than the reclaimed surface (Figure 4.7 b). The macropores present appeared as diagonal cracks, and not the result of biological activity. The subsurface was also sandier when compared to the natural subsurface (Figure 4.6 b), with minimal amounts of plasma within aggregates or on pore walls. The low observable plasma in the reclaimed subsurface was interesting to note because VR monoliths released a higher colloid load than VN monoliths (Table 4.1).

The mixing of biosolids into the reclaimed surface (1-7 cm) resulted in a destruction of the original structure and incorporation of organic materials (Figure 4.8a). When compared to the surface of reclaimed monoliths lacking biosolid amendments (Figure 4.7 a), it can be observed that larger macropores were not as horizontal in their course (Figure 4.8 a). This resulted in a lower τ (0.91) than the original reclaimed surface (Figure 4.7 a). Continuity of the original pores may have been compromised in doing this, but leaving most of the textural porosity intact.

The subsurface of biosolid amended reclaimed monoliths was taken from just below the surface horizon, at a depth of 8-14 cm (Figure 4.8 b). Evidence of biocolloid movement could be observed along the pore walls, but it also appeared that the original influx of organic material may have clogged some of the pores. The subsurface of these monoliths was not disturbed, and probably retained the cracks also seen in the reclaimed monoliths above (Figure 4.7 b). The τ of the proposed flow path was 0.74, which is greater than that observed in the unamended reclaimed monoliths (Figure 4.7 b), implying that there is a range in τ in reclaimed subsurfaces. The total area represented by one thin section is small, so this variability should be expected. Over longer periods of time, any biocolloids not incorporated into soil aggregates will have the potential to be transported through the reclaimed monoliths. Shifts in the chemistry of pore water through the influx of lower ionic strength rainwater may eventually help disperse this material. The difficulty with the transport of mineral and organic colloids through reclaimed minelands will probably come from the spoil material located beneath.

From the hydraulic conductivities already mentioned above and the thin sections taken from a spoil monolith (Figure 4.9), it was obvious that connectivity of pores within these monoliths would be limiting to colloid transport. Large chunks of coal are evident within these monoliths, still present after 30 years. The matrix is compact and low in dispersible material for colloidal transport, so most of the colloids will have to come from the reclaimed material above. There are angular cracks present for movement of colloids and solutes, which posses a τ of 0.72 along the proposed pathway. These cracks will play a large role in colloid movement only when soils are saturated, since the micropore structure is compact and limited in connectivity.

4.4   Conclusions

Many factors contribute to colloid mobility within natural, reclaimed, and spoil monoliths, confounding any discussion of which soils may have larger colloid release. Macroporosity within soils did contribute to larger colloid release, particularly if the material is dense like spoil. Within macropores, significant contribution to colloid mobility could only occur if monoliths were under saturated conditions. Density does increase through reclamation, but it appears that colloid loads may differ because of the amount of dispersible colloidal material, and how recently the soils were reclaimed. Exchange between micro- and macropores probably occurs if a diffusion gradient is created as larger cracks become stripped of colloids. Variation between natural forest soils from different regions of the Appalachians also cannot be explained by simple pore structure, but also must account for soil pore water chemistry and the dispersability of colloidal material.

The density of soil and spoil materials alone did not describe the potential for colloid release from monoliths. The hydraulic conductivity within these soils is controlled by the volume, connectivity and path length of the pores, of which both path length and connectivity were more limiting in the surface of monoliths, indicating that many colloids came from the subsurface. Biosolids mixed within the surface of reclaimed soils did create biocolloids, but the large influx of colloids was limited in their movement by clogging within reclaimed soils. Over time these colloids would probably disperse and become mobile again, only to be limited in

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movement by a dense spoil material. It was obvious that only when the spoil material was under saturated conditions, would biocolloid transport be significant through preferential flow pathways. High rainfall events will be the most important factor in colloid movement within these monoliths, and therefore to pollutant transport as well.

Table 4.1: Monolith and eluent properties from Virginia and Kentucky duplicate (I,II) monoliths.

	VN		VR		VRS		VRB		KN		KR	
	I	II	I	II	I	II	I	II	I	II	I	II
Total Colloids (mg)	751	964	1469	1452	70	83	1104	638	6610	7927	1074	20738
Total Colloids after drying (mg)	5200	2315	593	1618	-	-	-	-	5883	3787	1305	1412
Colloid Particle Size (nm)	600	924	495	548	-	461	2073	768	-	-	-	-
Bulk Density (g/cm^3)	1.26	1.10	1.30	1.37	1.75	1.75	1.75	1.75	1.15	0.93	1.39	1.39
Pore Volume (L)	3.8	4.3	3.7	3.6	4.1	4.1	4.1	4.1	4.3	4.9	2.8	2.8

(V= Virginia, K= Kentucky, R=Reclaimed, S=Spoil, B=Biosolids, "-" = not determined).

Table 4.2: Hydraulic conductivity at saturation, -1, -5, and -10 cm tension in Virginia natural and reclaimed monoliths.

Core	Depth	Ksat	Tension		
			- 1 cm	- 5 cm	- 10 cm
	cm	------------------------------cm/d-----------------------------			
Natural I	1-7	164.7	87.7	22.2	14.8
	8-14	283.8	78.7	3.14	2.5
	16-22	981.9	61.5	8.1	6.6
	24-30	38.4	12.8	4.3	1.4
Natural II	2-8	338.7	50.6	8.0	3.5
	9-15	443.4	153.0	21.9	5.0
Reclaimed I	1-6	5230.6	97.3	51.5	45.2
	8-14	967.3	22.8	21.2	20.9
	23-29	7.2	2.4	1.9	1.5
Reclaimed II	3-9	164.7	125.6	3.5	1.0
	9-15	283.8	40.3	5.2	2.7
	17-23	981.9	7.0	2.8	1.7
	24-30	38.4	5.5	1.9	1.4

Table 4.3: Hydraulic conductivity at saturation, -1, -5, and -10 cm tension in Virginia reclaimed w/spoil and reclaimed w/spoil and biosolids amended monoliths.

Core	Depth*	Ksat	Tension		
			- 1 cm	- 5 cm	- 10 cm
	cm	------------------------------cm/d-----------------------------			
Reclaimed	2-8	501.6	60.1	15.3	18.1
w/Spoil I	10-16	20.7	11.5	4.0	3.3
	17-23	29.4	136.5	9.6	5.5
	24-30	114.2	9.4	7.0	6.0
	31-37	25.3	2.6	1.1	0.1
	38-44	1.7	1.3	1.1	1.1
	45-51	226.6	1.5	0.6	0.2
	53-59	1.6	1.3	0.7	0.2
Reclaimed	1-7	1227.0	9.8	7.4	3.1
w/Spoil II	8-13	33.7	160.5	58.3	27.7
	14-20	12.1	32.7	10.4	5.4
	31-36	37.4	3.0	1.0	0.7
	39-45	94.3	4.3	1.9	1.5
	47-53	16.8	2.5	0.9	0.5
	54-60	76.5	6.1	3.6	3.3
Reclaimed	1-7	26797.8	608.9	109.8	22.6
w/Spoil +	8-14	803.5	276.6	165.1	25.4
Biosolids I	23-29	509.0	30.8	33.7	21.1
	30-36	442.6	17.6	1.6	0.59
	38-44	669.9	24.1	1.6	0.62
	46-52	1607.5	13.4	7.3	0.27
	53-59	39.2	20.3	0.6	0.31
Reclaimed	0-7	3851.3	110.9	62.0	42.8
w/Spoil +	8-14	570.0	294.4	212.7	135.8
Biosolids II	16-22	3940.8	223.9	107.0	95.2
	30-36	0.3	-	-	-
	39-45	3.4	-	-	-
	46-52	0.7	-	-	-
	54-60	0.4	-	-	-

*Depths below 30 cm represent spoil monoliths.
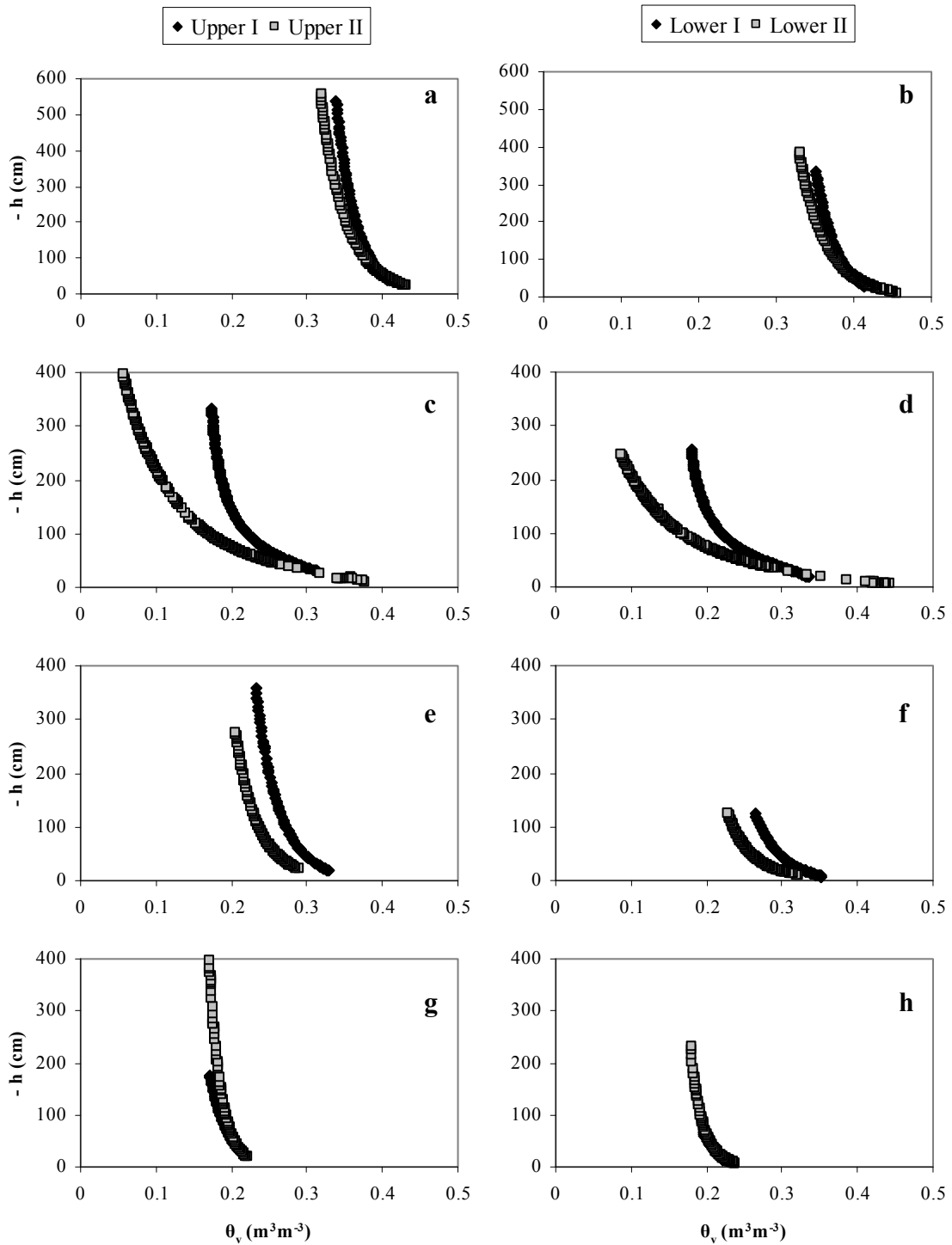
Figure 4.1: Water retention curves (h vs. θ_v) for duplicate (I vs. II) monoliths from the upper and lower compartments of (a,b) Virginia natural, (c,d) Virginia reclaimed, (e,f) Kentucky natural, and (g,h) Kentucky reclaimed monoliths.
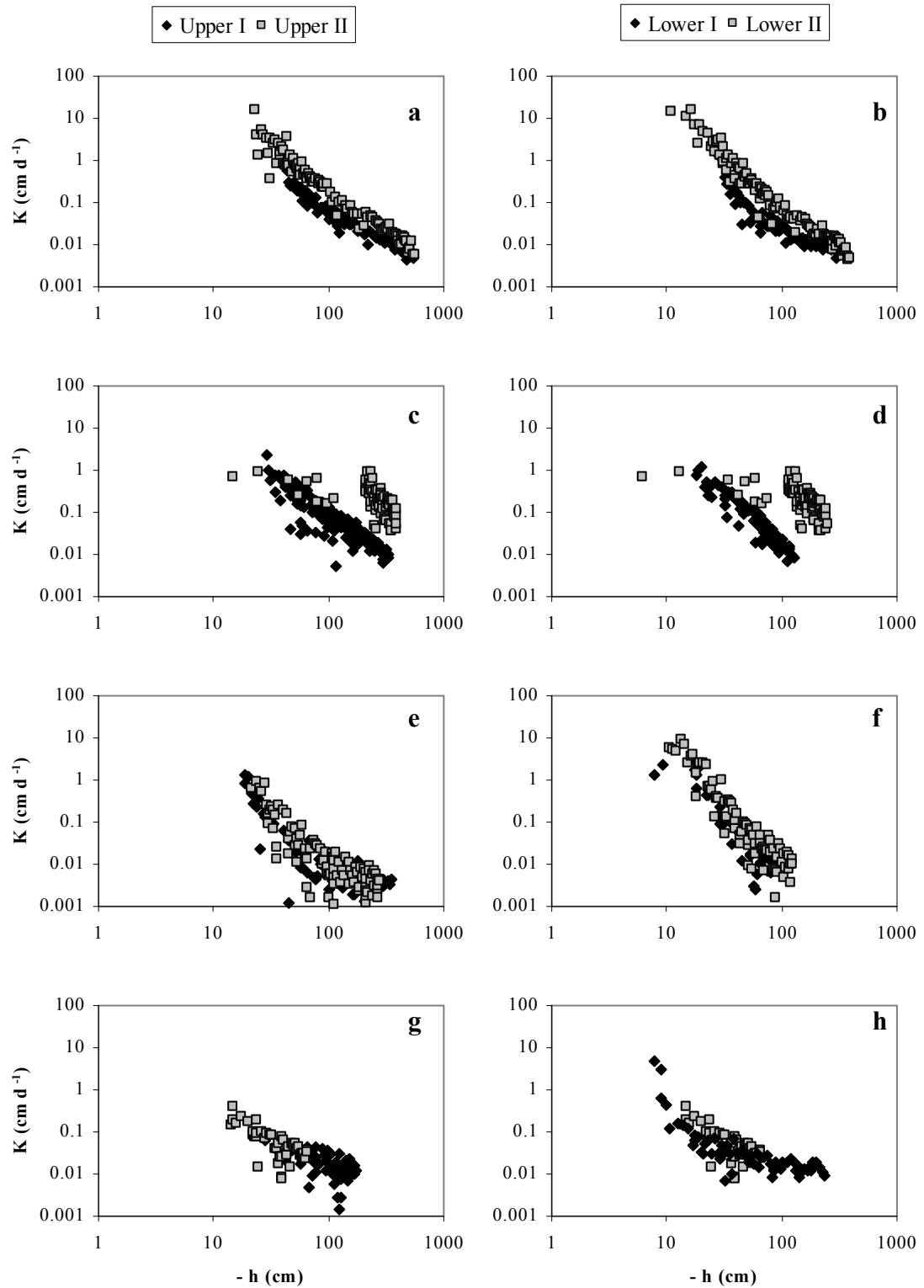
Figure 4.2: Unsaturated hydraulic conductivity (K_h) vs. soil water pressure head (h) for duplicate (I vs. II) monoliths from the upper and lower compartments of (a,b) Virginia natural, (c,d) Virginia reclaimed, (e,f) Kentucky natural, and (g,h) Kentucky reclaimed monoliths.
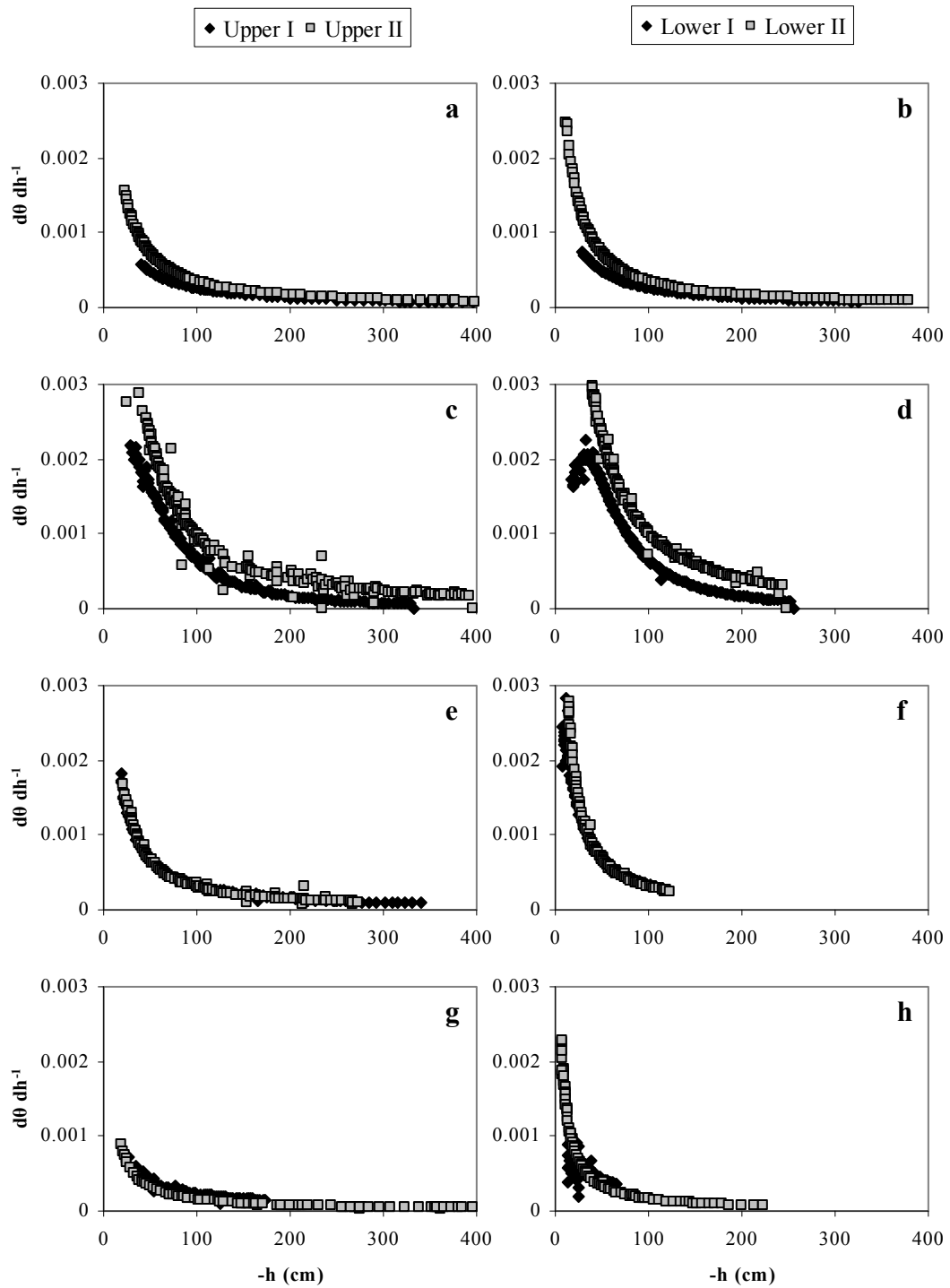
Figure 4.3: Pore size distribution by derivative vs. soil water pressure head (h) for duplicate (I vs. II) monoliths from the upper and lower compartments of (a,b) Virginia natural, (c,d) Virginia reclaimed, (e,f) Kentucky natural, and (g,h) Kentucky reclaimed monoliths.
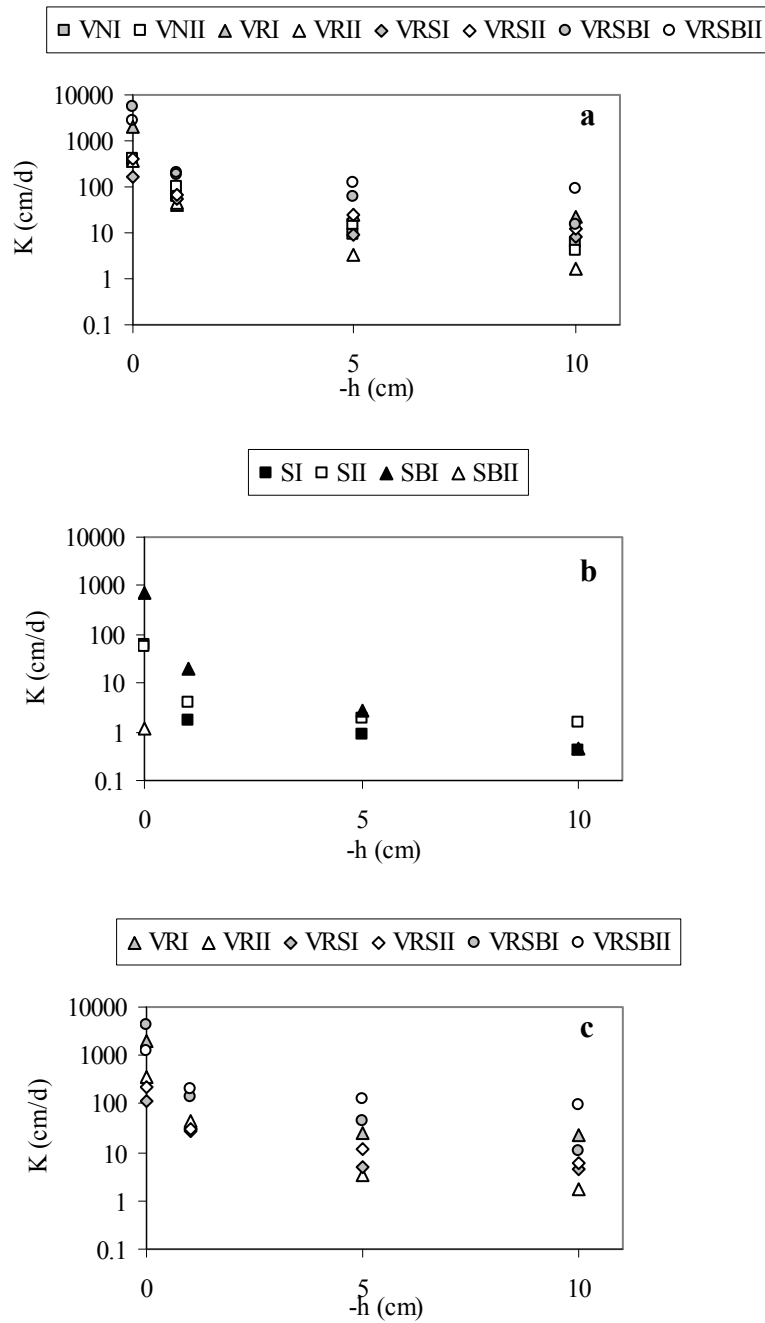
Figure 4.4: Average conductivities within Virginia cores for (a) natural and
reclaimed monoliths, (b) separated spoil monoliths, and (c)
conductivities averaged across all depths for combined reclaimed and
spoil monoliths.(N=natural, R=reclaimed, S=spoil, B=biosolids).
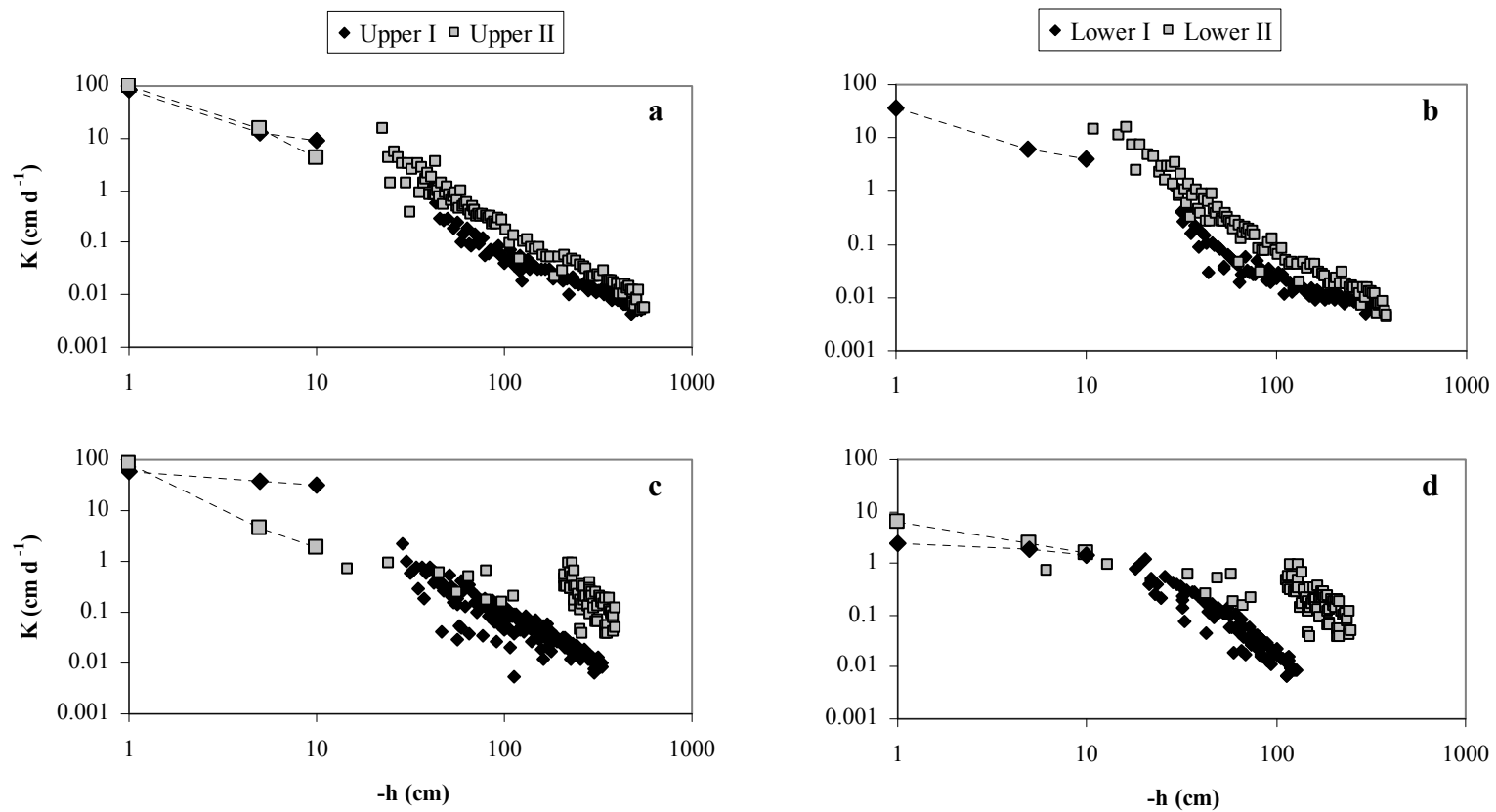
Figure 4.5: Hydraulic conductivity (K) vs. soil water pressure head (h) for duplicate (I vs. II) monoliths from the upper and lower compartments of (a,b) Virginia natural, (c,d) Virginia reclaimed including data from tension infiltrometers as connected points.
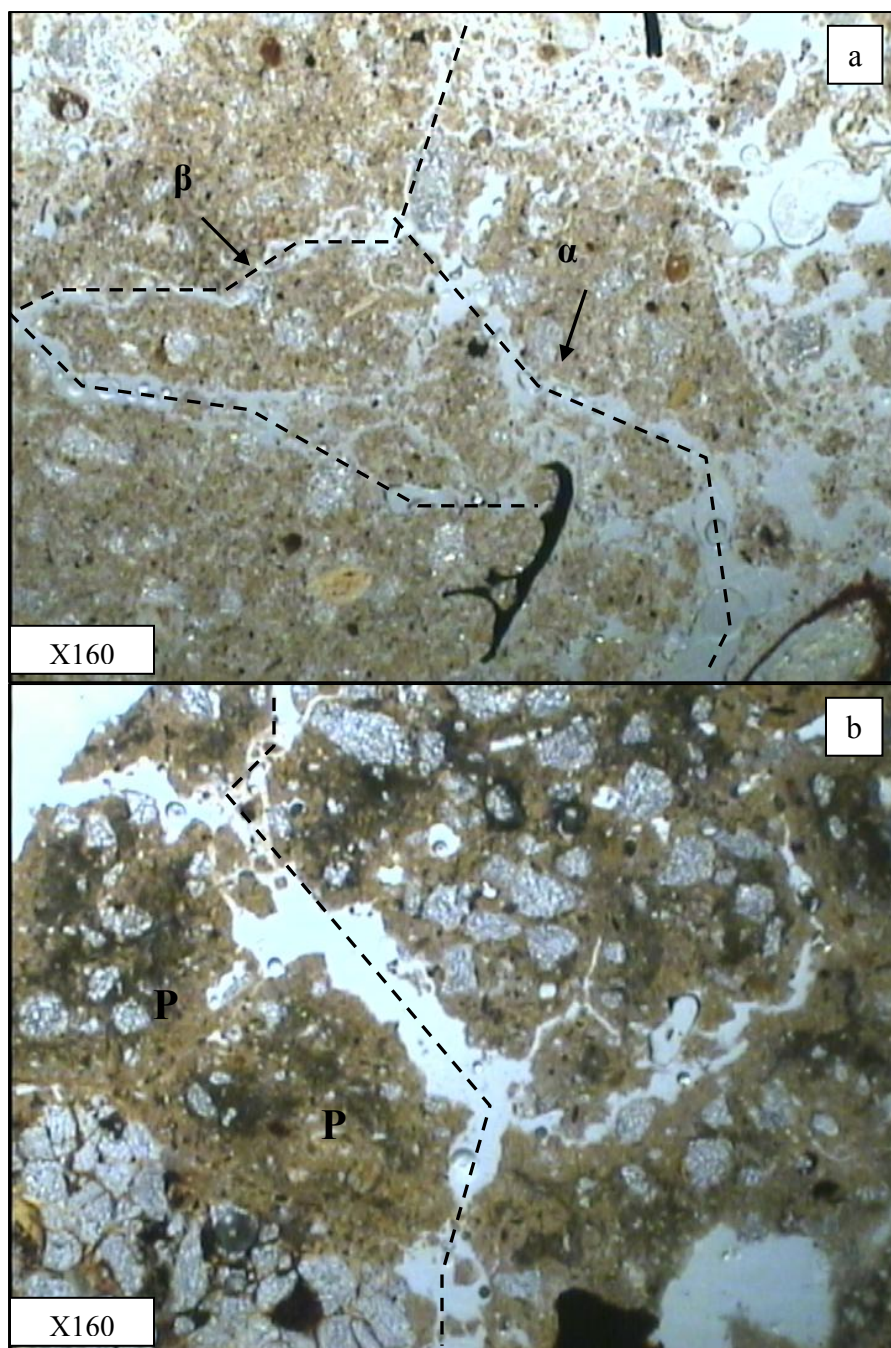
Figure 4.6: Thin sections of Virginia natural monoliths at (a) 1-7 cm with two potential pore flow paths labeled α and β and (b) 16-22 cm depths, with the P indicating plasma and a dashed line for a potential flow path.
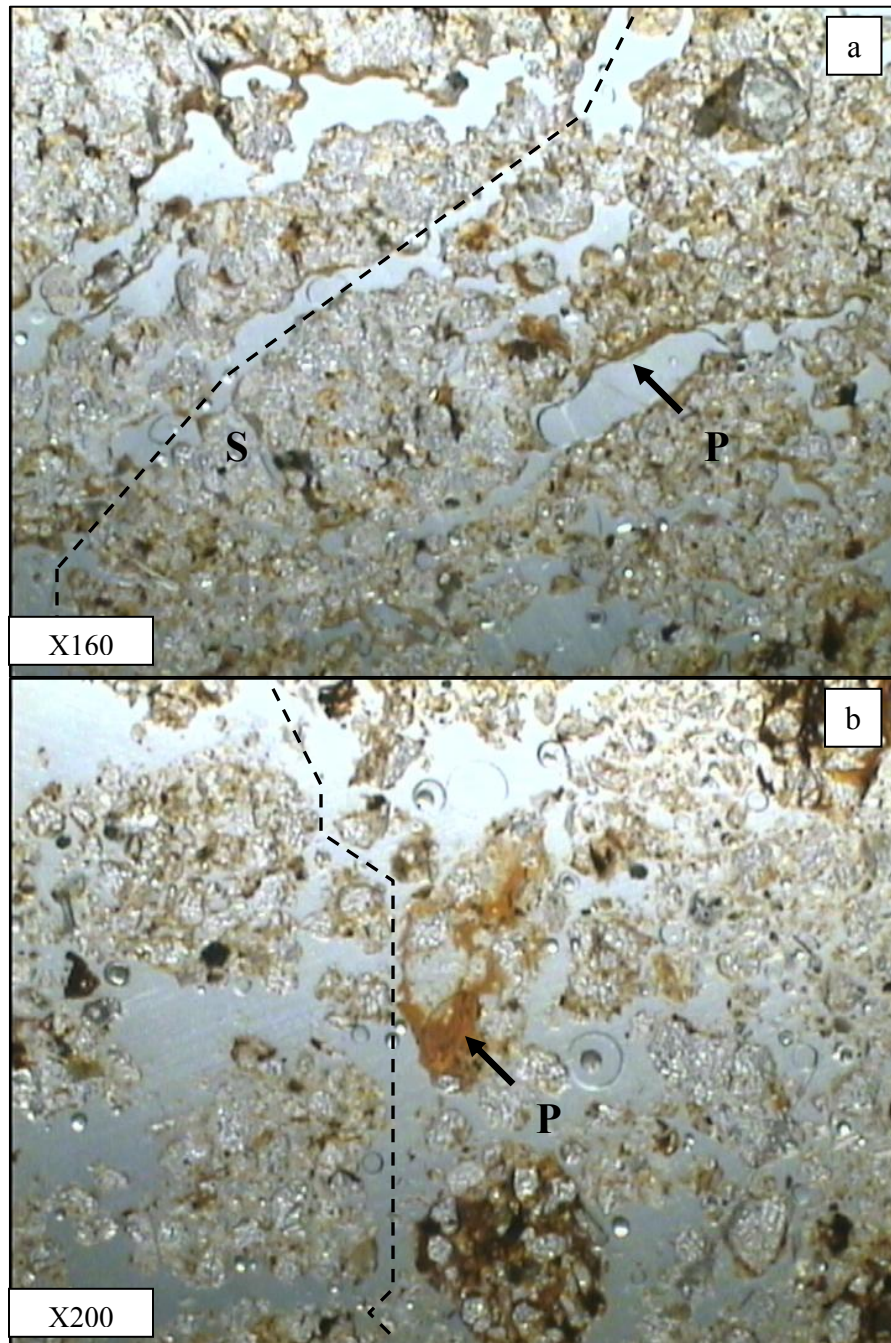
Figure 4.7: Thin sections of Virginia reclaimed monoliths at (a) 3-9 cm, and at (b) 17-23 cm depths, with the dashed line representing potential flow paths, and the P and S indicating plasma and sand, respectively.
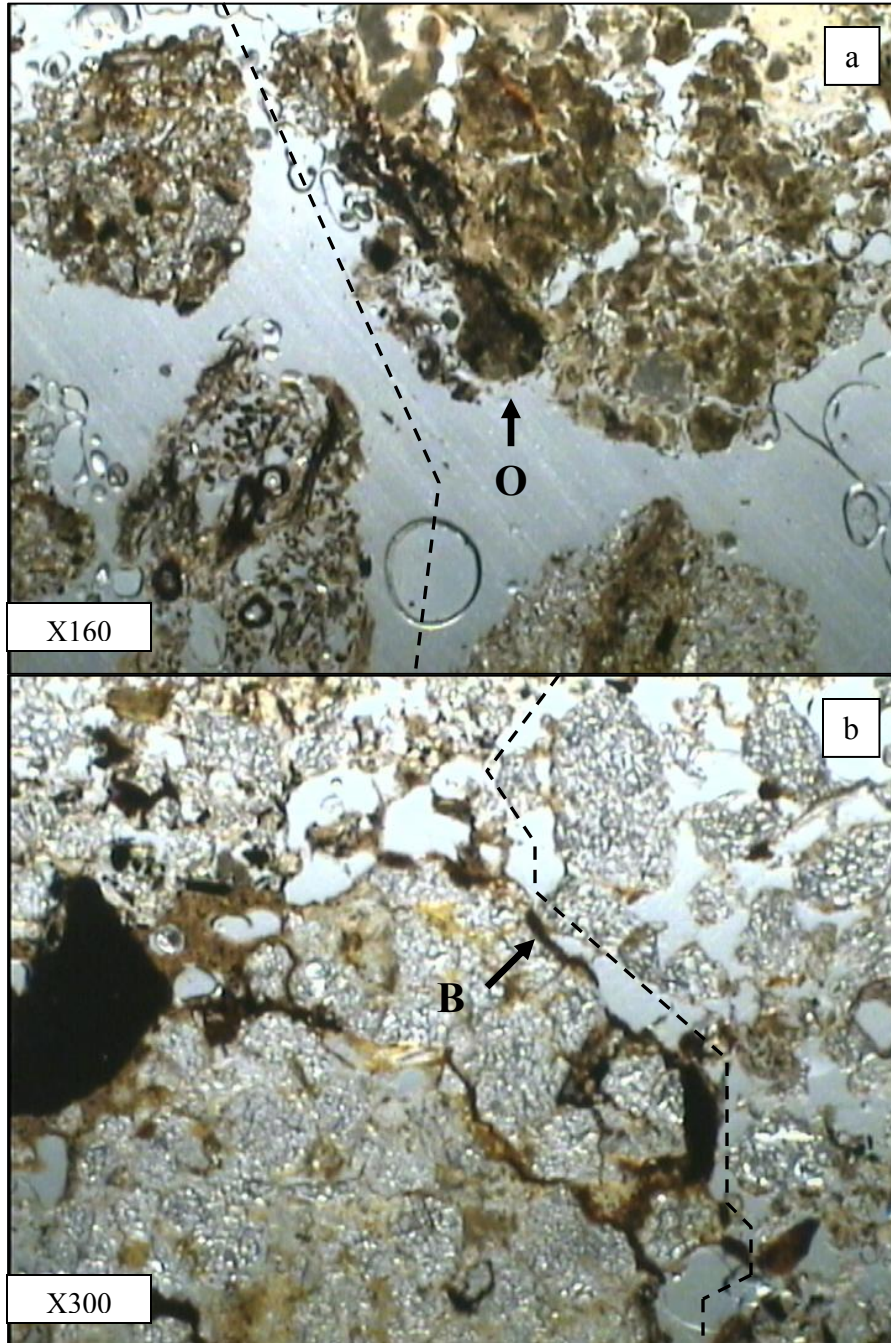
Figure 4.8: Thin sections of Virginia reclaimed monoliths amended with biosolids at (a)
1-7 cm and (b) 8-14 cm depths. The dashed lines represent possible flow
paths; the O indicates biosolids mixed with soil material, while the B
indicates biocolloid coatings on pore walls.
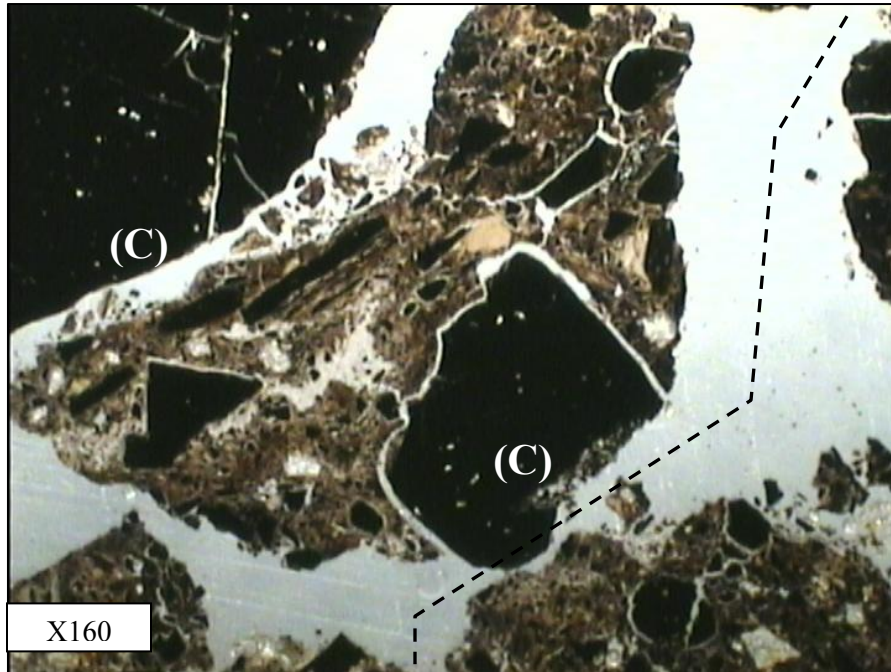
Figure 4.9: Thin section of the Virginia spoil monoliths at the contact between a reclaimed and spoil monolith (30-36 cm depth). The dashed line represents a possible flow path, while the C indicates coal material.

CHAPTER 5   GENERAL CONCLUSIONS

Predicting colloid mediated metal transport in reclaimed mine soils is very difficult because of the extreme variability in the physical and chemical properties of the soils. In spite of this inherent impediment, our study has shown a consistent trend for an increase in the transport of Cd, Cr, Cu, Ni, Pb, and Zn in association with colloids, but colloid and metal release both varied depending on treatment conditions.

Within treatments, the only notable difference in colloid elution was observed within recently reclaimed monoliths, but as these soils continued to leach over time they became similar to each other. Across all treatments clay content, biosolid application, and the age or bulk density of the spoil had the largest effects on colloid release within the monoliths. Monoliths with higher clay contents had a larger source to draw from for colloid generation and release, where reclaimed soils typically had lower amounts of clay due to the loss of finer materials during reclamation. Biosolid application induced a continuous release of colloids within reclaimed monoliths, while all other monoliths not receiving biosolid application ceased colloid release within 1 P.V. The addition of young spoil materials beneath monoliths reduced colloid transport in recent spoil due to high salt content flocculating colloids. Over time, these salts are expected to be leached from the system, thus increasing the potential for colloid mobility. High density of older spoil materials reduced colloidal transport due to size exclusion effects in smaller pores.

Macropores and cracks in the spoil and soil monoliths allowed for greater colloid mobility, but this was only possible under saturated conditions, as hydraulic conductivity quickly decreased with lower water contents. Spoil monoliths that were observed to have greater saturated hydraulic conductivity also released greater colloid loads. Besides pore size, path length also played a role in colloid mobility. There was evidence that path length of pores within soil surfaces reduced colloid mobility, suggesting that most of the generated colloids probably originated from the subsurface. Path length within reclaimed monoliths also reduced the mobility of biocolloids, where observation of thin sections showed that most of these organic colloids became clogged in surface pores. Colloids released from biosolids may be incorporated into the matrix or eventually transported through connected pores.

Biosolids also increased solution and colloid associated metal release, while the greatest metal release was observed in recently reclaimed monoliths underlain by unweathered spoil material. Natural forest soils released measurable amounts of heavy metals, particularly Cu and Zn, indicating that there is a baseline release of metals, even within unmined soils. Metal release within recently reclaimed monoliths was lower than older mine soils, possibly due to the effectiveness in SMCRA regulations for topsoil replacement materials. Treatment monoliths with greater colloid release had higher percentages of colloid bound metals, with the most variability across rather than within treatments.

Of all the metals observed, only Zn was present in all treatments, while Cu and Ni were present in all but one treatment each. Trace amounts of Cd, Cr, and Pb were observed in most eluents, with Pb being dominantly colloid associated. Nearly all of the colloid bound metals were exchangeable, increasing the importance of colloid transport to the overall health of the watershed.

Current regulations are set to reduce the toxicity of reclaimed mine lands. Burying toxic spoils with approved topsoil will not guarantee the quality of groundwater sources, and because of colloid mobility, it cannot be assumed that the addition of biosolids will prevent metal mobility within reclaimed soils. It is probably impossible to restrict all metal movement within soils, but with increased attention it can be reduced.

Addressing these concerns is a Catch-22, as any improvement in reducing throughflow through minesoils may result in more runoff and increased erosion. Biosolid applications can reduce the mobility of metals within minesoils by chelation and adsorption at the surface and still remains a viable option. It should not be assumed that this will stop all transport though, as biocolloid movement may occur. The rise in pH due to the addition of lime stabilized biosolids may also shift the pore water chemistry, causing the suspension and mobility of mineral colloids within the soils. Application of biosolids should follow stricter guidelines for heavy metal contamination than the EPA allows, because minelands already contain appreciable amounts of metals. These organic amendments will also increase the amount of aggregation, increasing pore size, which may lead to greater colloid mobility. However, it may also reduce the total number of colloids through aggregation itself.

If it is possible, spoil material that is more acidic could be piled and leached, collecting the drainage in a sealed containment pond for treatment. If this is not a viable option, quick establishment of vegetation may help to reduce through flow, allowing for a gradual release of toxic metals and salt content, rather than a large plug flow. There is no one solution to any specific site; each situation will require different management techniques depending on the chemical and physical properties of the reclaimed materials.

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Vita

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