Vegetative Potential to Reduce Total Dissolved Solid Nutrient Ions Generated from Reclaimed Mine Lands in Central Appalachia

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ABSTRACT (academic)

One of the major issues in surface coal mine land reclamation is the impact of total dissolved solids (TDS) on water quality. To address this issue, this study assessed whether vegetation could reduce TDS nutrient ion movement from the rooting zone in early reclamation stages when TDS generation is often highest. Vegetated and un-vegetated paired plots were established across eight sites with gradients in age, spoil material, and vegetative productivity. Ion exchange resin lysimeters were used to compare nutrient ion fluxes in soil solution that contribute to TDS between paired plots. Soil and vegetation properties (used as proxies for evapotranspiration and plant uptake) were characterized at each site and correlated with log ratios of common TDS contributing ions [i.e., base cations Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} (R_{BC}), sulfate ($R_{SO_4^{2-}}$), and total Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-} (R_{total})] between un-vegetated and vegetated plots. Strong Spearman correlations were found between R_{Total}, R_{BC}, and $R_{SO_4^{2-}}$ during the peak growing season, and ewere weakened overall during vegetative dormancy. Soil organic matter was shown to be a strong correlate through dormant periods. Correlations between TDS nutrient ions and vegetation suggest evapotranspiration in the growing season, and interception during dormant periods, exert an influence on nutrient ion fluxes. These findings indicate that aggrading forests may reduce TDS nutrient ion loading, through solute retention mechanisms driven by organic matter inputs and plant uptake.

ABSTRACT (public)

Total dissolved solids (TDS) coming from surface coal mines are greatly impacting water quality in Appalachia. This study investigated whether vegetation could reduce TDS (specifically calcium, potassium, magnesium, sodium and sulfate ions) in solution draining from the soil into streams. Vegetated and un-vegetated plots were established across eight sites that differed in age, rock material, and plant communities. Ion exchange resins that capture TDS ions in soil solution were used to compare nutrient ion fluxes that contribute to TDS between paired plots. Soil and vegetation properties (used as proxies for evapotranspiration and plant uptake) were characterized at each site and correlated with log ratios of common TDS contributing ions. Strong correlations were found during the peak growing season, suggesting that the presence of vegetation reduced the amount of dissolved ions in soil solution. In addition, soil organic matter was correlated with TDS contributing nutrient ions in all seasons. These finding suggests that productive, growing forests could reduce TDS contributing nutrient ions draining from soils into streams through plant and organic matter retention.

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Chapter 1. Introduction and Literature Review

1.1 Introduction

One of the major issues in surface coal mine land reclamation is the impact of total dissolved solids (TDS) on water quality. Surface mining practices in the central Appalachian Mountains involves the removal of overburden in order to reach underlying coal seams. After extraction of the coal seam, overburden (i.e., spoil) is replaced to the approximate original contour of the landscape (SMCRA [Sec.515(b)3]), with excess being placed in adjacent valleys or hollows, creating what are known as valley fills (US.EPA., 2011). The practice coal surface mining and the subsequent replacement of spoil has resulted in the removal of forested ecosystems, and consequently a loss of the valuable ecosystem services they provide. Most often they are replaced with herbaceous communities and early successional woody species post-mining. The Forestry Reclamation Approach (FRA) was developed to address this issue by re-establishing native hardwood forests on post-mining land, and restore the ecosystem services such as improved water quality and hydrology, carbon sequestration, wildlife habitat connectivity, and diverse plant communities often associated with forests (Zipper et al., 2011; Burger et al., 2005).

Mining practices have also increased TDS in soil solution that leaches into surface waters. The exposure and weathering of mine spoil releases ions often in excess of background concentrations, which contribute to the increased levels of TDS in soil solution and streams. This increase in TDS constituent ions causes elevated electrical conductivity (EC), impacting benthic macroinvertebrate communities (Pond et al., 2008; Lindberg et al., 2011; Timpano et al., 2015). The primary TDS constituent ions generated by weathering from central Appalachian mine spoils include Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}, SO_4^{2-} and HCO_3^{-} (Orndorff et al., 2015; Pond et al., 2008; Lindberg et al., 2011; Timpano et al., 2015). Four of these ions are also essential plant macronutrients: Ca^{2+}, K^{+}, Mg^{2+}, and SO_4^{2-}. Most of the current research has focused on how to limit TDS in drainage water by selecting weathered, coarser topsoil substitutes (e.g., sandstone vs. siltstone), and isolating materials that tend to produce high TDS concentrations in water by keeping them out of direct contact with drainage waters (Agouridis et al., 2012; Daniels et al., 2013; Daniels et al., 2014; Orndorff et al., 2015). Even though many studies have shown evapotranspiration to be an important factor effecting discharge to streams (Brown et al., 2005), little has been done to assess the role evapotranspiration and plant uptake may have in reducing TDS loading to surface waters in mine spoil settings.

1.2 Thesis Organization

This thesis is organized in manuscript format, where one manuscript will be submitted to a peer reviewed journal for publication. The manuscript is co-authored by Amy C. Gondran, Brian. D. Strahm, Kevin J. McGuire, Carl E. Zipper and John R. Seiler. It also contains a general literature review organized in the following sections:

1.3 Literature Review

1.3.1 The Forestry Reclamation Approach

Surface coal mining has caused the removal of forested ecosystems, which is most often replaced with herbaceous vegetation communities and early successional woody species post-mining. The Forestry Reclamation Approach (FRA) is a series of reclamation practices developed to re-establish native hardwood forests on post-mining land in the central Appalachians. It provides coal mine operators with a set of guidelines to successfully reclaim mined land in a cost effective and regulatory compliant manner, while re-establishing valuable ecosystem services to disturbed forest systems. The FRA calls for the following five strategies (Zipper et al., 2011; Burger et al., 2005):

1) Selection of topsoil or topsoil substitute materials that produces low soluble salts with a pH between 5 and 7 to create a rooting zone at least 4 feet deep. Weathered sandstone is best as a topsoil substitute.
2) Materials loosely dumped and un-compacted to promote tree growth and survival
3) Establish tree compatible ground-covers that are less competitive
4) Plant native crop trees that are commercially valuable and nurse trees for soil stability and wildlife
5) Use proper storage and planting techniques to aid seedling survival

These steps also support the restoration of different ecosystem services. Using weathered materials that are more compatible with tree growth and plant recruitment restores forest productivity and plant communities (Burger et al., 2007; Emerson et al., 2009; Miller et al., 2012; Sena et al., 2014; Agourdis et al., 2012). Further, materials low in soluble salts generate less TDS, protecting water quality (Agourdis et al., 2012, Sena et al., 2014, Daniels et al., 2014; Orndorff et al., 2015). Soil compaction limits root growth, water infiltration, and water holding capacity, thus impairing tree growth and survival (Skousen et al., 2009; Burger and Evans, 2010). By loosely grading topsoil or topsoil substitutes (i.e., spoil) root growth and water infiltration are improved, helping to restore hydrology. Competitive, herbaceous vegetation can outcompete tree seedlings and impact tree growth (Chaney et al., 1995; Burger et al., 2008; Skousen et al., 2006). The use of tree compatible groundcovers promotes seedling survival and diversifies the forest community, while also improving water quality by preventing erosion into surface waters (Zipper et al., 2011). With the implementation of the FRA on mined lands, native hardwood forests can be re-established on the post-mining landscape to restore the valuable ecosystem services a forest community provides.

1.3.2 TDS Impacting Water Quality in Appalachia

Surface mining practices in central Appalachia remove surface vegetation (typically forest), topsoil, and underlying bedrock (i.e. overburden) in order to reach underlying coal seams. The overburden, often referred to as mine spoil, is then replaced after the extraction of the coal seam, with excess spoil being placed into adjacent valleys or hollows, creating valley fills (US EPA, 2011). The placement of excess spoil into valley fills permanently buries headwater streams, causing alterations to flow regimes downstream. Destruction of vegetative communities in the construction and placement of valley fills decreases evapotranspiration, and compaction often reduces water infiltration, resulting in increased runoff. Together such alterations increase stream flow below valley fills (US EPA, 2011; Wiley et al., 2001).

In addition to the hydrological impacts, exposure and weathering of mine spoil releases ions often in excess of background concentrations, which contribute to increased levels of TDS in streams. Percolating waters through the placed overburden causes chemical reactions that release dissolve primary minerals, resulting in elevated levels of SO_4^{2-}, Ca^{2+}, Mn^{2+}, K^+, Mg^{2+}, total selenium, acidity, and alkalinity in soluble forms (Bryant et al., 2002). The primary TDS constituent ions generated by weathering from central Appalachian mine spoils include Ca^{2+}, K^+, Mg^{2+}, Na^+, SO_4^{2-}, and HCO_3^- (Orndorff et al., 2015; Pond et al., 2008; Lindberg et al., 2011; Timpano et al., 2015). This increase in TDS constituent ions causes elevated electrical conductivity (EC) in streams, impacting benthic macroinvertebrate communities (Pond et al., 2008; Lindberg et al., 2011; Timpano et al., 2015). EC, TDS, and SO_4^{2-} concentrations have been shown to be strongly and negatively correlated with the biological condition of macroinvertebrate communities (Timpano et al., 2015). Timpano et al. (2015) found SO_4^{2-} to be the dominant ion (on a mass basis) in water samples taken from 21 mining impacted streams, accounting for 46% of the ion composition. Further, SO_4^{2-} was strongly associated with the biological condition of the macroinvertebrate community. The Ephemeroptera taxa (i.e., mayflies) have especially been impacted. Ephemeroptera are a large component of the benthic invertebrate community, making up as much as 50% of the assemblage in Appalachian streams. Pond et al. (2008) showed loss of richness and relative abundance of Ephemeroptera within mined watersheds, indicating that elevated specific conductance is a cause of water quality impairment. Impaired streams have also had impacts on fish and amphibian communities. Fish communities downstream of valley fills have lower species richness (Stauffer and Ferreri, 2002; Ferrari et al., 2004), and salamanders have decreased abundance (Wood and Williams, 2004).

Elevated levels of EC have been shown to impact invertebrate and vertebrate communities, yet more research is required in order to determine how to effectively decrease elevated EC levels in streams caused by TDS leaching from reclaimed mine lands and valley fills. Current research has focused on limiting TDS generation by selecting weathered, coarser materials (i.e., weathered sandstone) for topsoil substitutes, and by keeping materials that generate high levels of TDS out of direct contact with drainage waters. Vegetation may play a role in reducing TDS loading to surface waters through plant uptake and increased evapotranspiration, but little has been done to assess the validity or magnitude of the effect.

1.3.3 Evapotranspiration as a Hydrologic Control

Research continually shows forest removal reduces evapotranspiration (ET) during the growing season, resulting in increased streamflow. At the Hubbard Brook Experimental Forest in New Hampshire, clearcutting watersheds increased streamflow more than 40% as compared to untreated estimates. Within the first two years, increases in water yield averaged 309.88 mm (Hornbeck et al., 1970). Further studies continue to show increases in water yield, in addition to increases of dissolved nutrient ions in the water. In one study, clearcutting caused a lack of nutrient uptake by vegetation, yet decomposition processes continued, causing increased Ca^{2+}, K^{+}, Mg^{2+} and Na^{+} by 29%, 218%, 7%, and 7%, respectively (Hornbeck et al., 1986). However, these observed increases in water yield are not indefinite. Increases are typically greatest in the first few years after clearcutting, and decline within the first decade as natural regrowth occurs (Douglass, 1983).

Similar hydrologic patterns have also been found on landscapes affected by mining (Messinger, 2003), though a post-mining landscapes exhibits conditions more akin to an urban area rather than what would be expected from simple deforestation (Ferrari et al., 2009). In general, mine lands reclaimed after the enactment of SMCRA in the late 1970s generate higher magnitudes of runoff from stormflow events, while valley fills may act as water storage reservoirs. This storage of water in valley fills may suppress the response to storm events, resulting in sustained base flows (Miller and Zegre, 2014). Newly reclaimed watersheds can also exhibit increases in peak and base flows in response to strong storm events (Evans et al. 2015). Wiley et al. (2001) compared streams from pre- and post-mining areas, and showed 90-percent flow durations in streams below valley fills were 6-7 times higher than that of unmined areas. Daily streamflow and base flow percentage were also generally greater. Modeling has also showed flood magnitude increases linearly in areas where the landscape has been altered by surface mining and reclamation (Ferrari et al., 2009).

Despite the many studies on the hydrologic impacts of mining, we still have a limited understanding of the altered flow paths and the implications of these processes. Studies can vary in their findings of altered discharge to streams from base flow and stormflow patterns (Miller and Zegre, 2014). On a large-scale surface mine in West Virginia, Messinger (2003) observed intense storms increasing runoff from a mined/valley filled watershed, but with less intense storms, peak unit flow was greater on the forested control. Stream storm response from the mined/valley filled site was attributed to surface compaction, valley fills storing water, and the absence of canopy and litter interception. Messinger (2003) concluded that on these altered landscapes, hydrologic response to rainfall can be site specific depending on the mining processes and reclamation practices. Negley and Eshleman (2006) compared annual runoff yields and response to storm events between a mined and reference site. Water balances showed the annual runoff between sites to not be significantly different, but on an event basis the reclaimed mine site on average produced greater storm runoff coefficients, total storm runoff, and peak hourly runoff rates. Bonta et al. (1997) had similar findings to Wiley et al. (2001) where daily runoff and peak flow responses to rainfall were higher on post-mining areas. However, changes in base flow were inconsistent. In contrast to Ferrari et al. (2009) who showed flood magnitude to increase with surface mining, Zegre et al. (2014) assessed land cover change with mining over time and found significant decreases in maximum streamflow. They concluded that the decrease in maximum streamflow could pose benefits to flood avoidance.

Previous research has linked some of these altered hydrologic process on mine sites to reduced ET. Messinger and Paybins (2003) observed increases in total flow from extensively mined catchments compared to partially mined and forested catchments. These increases in total flow were thought to be influenced by decreased ET from forest removal. Forest removal has been found to reduce ET, thus contributing to increased peak flows and shortened storm response in recently mined areas (Griffith et al., 2012). A third study in Tennessee attributed greater base flow durations and higher annual streamflow from five mined watersheds (as compared to an unmined reference) to reduced ET from loss of vegetation (Dickens et al., 1989). These studies suggest that re-establishing vegetation to recover ET functions on the post-mining landscape may reduce water that leaves the rooting zone and is discharged to streams, predominantly during the growing season.

There are still many unknowns regarding the mechanisms that govern hydrologic process in mined land reclamation. Most of the time, research suggests that recently reclaimed, heavily impacted mined surfaces have reduced infiltration and vegetative cover, producing flashier runoff responses to rainfall (Miller and Zegre, 2014). Base flow generally appears to be higher or more sustained in areas with valley fills, but this may be site specific. Similar responses have also been observed with forest removal from harvesting practices. Both areas of research indicate that evapotranspiration is an important control of the water budget, and forest removal most often results in increased water discharge to streams.

1.3.4 TDS Generation and Vegetative Reclamation

Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}, SO_4^{2-}, and HCO_3^{-} are the primary TDS ions generated by weathering from central Appalachian mine spoils (Orndorff et al., 2015; Pond et al., 2008; Lindberg et al., 2011; Timpano et al., 2015). Four of these ions are also essential plant macronutrients: Ca^{2+}, K^{+}, Mg^{2+}, and SO_4^{2-}. Most of the research to date has focused on limiting TDS generation by selecting weathered, coarser topsoil substitutes (e.g., sandstone vs siltstone), and isolating high TDS generating materials from drainage waters. Yet, little has been done to assess the role vegetation plays in reducing TDS loading to surface waters.

The amount of TDS generated is largely dependent on the parent rock material. EC is often used as a proxy for TDS since it is easier to measure, and has proven to be strongly correlated with TDS. (Daniels et al., 2009; Daniels et al., 2013). In general, weathered mine spoil of the same strata produces less EC than unweathered materials (Agouridis et al., 2012; Daniels et al., 2013). Column leaching experiments have shown that finer textured rock materials, such as shales and mudstones, produced leachates higher in EC, especially when unweathered (Daniels et al., 2013; Daniels et al., 2014). At Bent Mountain, KY, EC levels in drainage from mine spoils were highest in a mixture of shale and sandstone, unweathered sandstone being intermediate, and lowest in weathered sandstone (Agouridis et al., 2012). After 9 years, EC had decreased across all spoil types, with the trend in EC levels remaining the same. Sena et al. (2014) concluded that EC levels had reached an equilibrium where input from weathering materials was roughly equal to what was leached in discharge.

Native hardwood trees were also planted on the sites at Bent Mountain, KY to test tree growth and survivability. After three years, tree volume and height were highest on weathered sandstone, followed by the shale/sandstone mix, and lowest on unweathered sandstone (Agouridis et al., 2012). By year 9, tree volume was nearly 50 times greater, with 86% survivability, on the weathered sandstone. Though these sites were not seeded, volunteer vegetation provided groundcover. Percent cover and species richness were consistently highest on weathered sandstone (Sena et al., 2014). Thus, productivity and diversity were all highest on the spoil type with the lowest EC.

1.3.5 Plant Uptake and Nutrient Accumulation of Common TDS ions

Vegetation may reduce TDS loading via two mechanisms: evapotranspiration or plant uptake. Evapotranspiration decreases soil water and drainage in the rooting zone, and plant uptake of nutrients may reduce TDS ion concentrations in soil solution. It is likely that vegetation influences TDS by both mechanisms. Sena et al. (2014) showed decreased water discharge between the dormant and growing seasons from a surface mine in eastern Kentucky, indicating that transpirational demands from an aggrading forest can reduce waters draining from a reclaimed mine land. The study concluded that evapotranspiration from trees exerted a greater influence over the quality of discharged water than spoil type. Previous research has also shown vegetation to accumulate nutrient ions that are relevant to TDS (i.e., K^+, Ca^{2+}, and Mg^{2+}) through plant uptake.

Studies conducted on forests recovering from disturbance have demonstrated plant accumulation of nutrients. Woody species have been shown to account for over 60% of the nutrient accumulation in above ground biomass four years after forest disturbance (Hendrickson, 1988). Crow et al. (1991) demonstrated that woody and woodland herbaceous species accounted for more than 70% of the nutrients captured by vegetation, while early successional species and graminoids (e.g., grasses, sedges, and rushes) accounted for only a small percentage of the nutrient accumulation. Mou et al. (1993) also showed recovering tree species to accumulate higher amounts of nutrients than herbaceous species six years after forest disturbance. Other studies continue to show that understory vegetation accounts for a small percentage of the total nutrient mass. In one natural secondary forest, grasses accounted for 13% of the total nutrients accumulated (Zhang et al., 2009). In a maturing red alder stand, understory vegetation (predominantly ferns) contribution was greater (25% of the total nutrient mass) but still notably lower than what woody species account for in nutrient mass (Turner et al., 1976).

Further studies on older tree stands show even greater amounts of nutrient accumulation as a forest aggrades. Six years after forest disturbance, Mou et al. (1993) found trees to account for 85 kg K ha^{-1}, 94 kg Ca ha^{-1}, and 18 kg Mg ha^{-1}. Whereas a 25 year old loblolly pine stand can accumulate 155 kg K ha^{-1}, 231 kg Ca ha^{-1}, and 80 kg Mg ha^{-1} (Pehl et al., 1984), and a 34 year old red alder stand 99 kg K ha^{-1}, 299 kg Ca ha^{-1}, and 110 kg Mg ha^{-1} (Turner et al., 1976). The high amounts of nutrient accumulation in woody species compared to herbs may suggest that re-establishing trees along with herbs is more advantageous than reclaiming with herbs alone. The higher uptake of K^+, Ca^{2+}, and Mg^{2+} specifically could aid in the reduction of these TDS ions in soil solution.

Vegetation may also be capable of taking up TDS ions in amounts greater than what is present in drainage waters within the first three years of reclamation. Agouridis et al. (2012) characterized the elemental concentrations from water samples across spoil type for the first three years after spoil placement. Common ion concentrations were found to be as high as 100.3 Ca^{2+} mg L^{-1}, 45.6 K^+ mg L^{-1}, 88.8 Mg^{2+} mg L^{-1}, 22.6 Na^+ mg L^{-1}, and 225.5 SO_4^{2-} mg L^{-1}. Given the discharge volumes and area of the drainage basin, ion content exceeds 18 Ca^{2+}, 8 K^+, 16 Mg^{2+}, 4 Na^+, and 40 SO_4^{2-} kg ha^{-1} (Taylor et al., 2009; Agouridis et al., 2012). Experiments involving recovery from clear cutting and whole tree harvest showed trees were accumulating Ca^{2+} and K^+ in amounts greater than those leaching three years after disturbance, with Mg^{2+} exceeding by year four (Mou et al., 1993; Hendrickson, 1988). Trees, shrubs and herbaceous vegetation together accumulated Ca^{2+} and K^+ higher than 18 and 8 kg ha^{-1} respectively within two years (Mou et al., 1993). The data are summarized in Table 1.

Table 1.

Common ion concentrations in mg/L and ion content in kg/ha three years after spoil placement compared to nutrient uptake by trees within the first three years after disturbance.

TDS Ion Concentrations and Nutrient Uptake by Trees

	Ca^{+2}	K^+	Mg^{+2}	Na^+	SO_4^{2-}	Reference
Ion Concentrations (mg/L)	100.3	45.6	88.8	22.6	225.5	Agouridis et al., 2012
Ion Content (kg/ha)	18.4	8.4	16.3	4.2	41.5	Agouridis et al., 2012; Taylor et al., 2009
Nutrient Uptake (kg/ha)	40.6	45.1	9.5	---	---	Mou et al., 1993
Nutrient Uptake (kg/ha)	43.7	22.1	6.8	---	---	Hendrickson, 1988

1.3.6 Conclusion

Surface mining practices in central Appalachia have impacted water quality with increased levels of TDS. Research has shown that with the removal of forest cover, reduced evapotranspiration increases the amount of water discharged to streams, thus increasing water flux through the rooting zone. Though the FRA was developed to re-establish native hardwood forests on the post-mining landscape, it may also help restore hydrology and improve water quality. Previous research has demonstrated decreases in discharge with increased evapotranspiration from aggrading forests on reclaimed mines, trees and groundcover thriving on low EC spoils, and trees accumulating TDS ions as nutrients in amounts exceeding that which have been discharged. It is hypothesized that aggrading forests can reduce TDS nutrient ion loading both by decreasing the quantity of water leaving the rooting zone through increased transpiration, and decreasing the concentration of TDS nutrient ions in percolating waters through plant uptake. The outcomes to this research are especially pertinent to mine land reclamation as TDS loading to surface waters is a major water quality concern.

1.4 Research Objectives

The primary objectives for this study are to:

1. Quantify the effect of vegetation on reducing soil solution fluxes of common TDS nutrient ions in reclaimed mine lands,

2. Assess vegetation and soil properties to determine their effects on TDS nutrient ion loading, and

3. Recommend reclamation strategies that optimize vegetation communities for reducing TDS nutrient ion loading from reclaimed mined lands.

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Chapter 2. Vegetative Potential to Reduce Total Dissolved Solid Nutrient Ions Generated from Reclaimed Mine Lands in Central Appalachia

2.1 Introduction

One of the major issues in surface coal mine land reclamation is the impact of total dissolved solids (TDS) on water quality. Surface mining practices in the central Appalachian Mountains involves the removal of overburden in order to reach underlying coal seams. After extraction of the coal seam, overburden (i.e., spoil) is replaced to the approximate original contour of the landscape (SMCRA [Sec.515(b)3]), with excess being placed in adjacent valleys or hollows, creating what are known as valley fills (US.EPA., 2011). Exposure and weathering of mine spoil releases ions often in excess of background concentrations, contributing to the increased levels of TDS in streams. This increase in TDS constituent ions causes elevated electrical conductivity (EC) in surface waters, impacting benthic macroinvertebrate communities (Pond et al., 2008; Lindberg et al., 2011; Timpano et al., 2015). The primary TDS constituent ions generated by weathering from central Appalachian mine spoil include Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}, SO_4^{2-}, and HCO_3^{-} (Orndorff et al., 2015; Pond et al., 2008; Lindberg et al., 2011; Timpano et al., 2015). Four of these ions are also essential plant macronutrients: Ca^{2+}, K^{+}, Mg^{2+}, and SO_4^{2-}. Most of the current research has focused on how to limit TDS generation by selecting weathered, coarser topsoil substitutes (e.g., sandstone vs. siltstone), and isolating high TDS generating materials by keeping them out of direct contact with drainage waters (Agouridis et al., 2012; Orndorff et al., 2015; Daniels et al., 2013; Daniels et al., 2014). Little has been done to assess the role vegetation plays in reducing TDS loading to surface waters.

The amount of TDS generated is largely dependent on the parent rock material and degree of weathering. EC is often used as a proxy for TDS since it is easier to measure and has proven to be strongly correlated with TDS (Daniels et al., 2009; Daniels et al., 2013). In general, weathered mine spoil of the same strata produces less EC than unweathered materials (Agouridis et al., 2012; Daniels et al., 2013). Column leaching experiments have shown that finer textured rock materials, such as shales and mudstones, produce leachates higher in EC compared to sandstones, especially when unweathered (Daniels et al., 2013; Daniels et al., 2014). Research at Bent Mountain, KY, showed EC levels in drainage from mine spoils to be highest in a mixture of shale and sandstone, unweathered sandstone being intermediate, and lowest in weathered sandstone (Agouridis et al., 2012). After 9 years, EC had decreased across all spoil types (Sena et al., 2014). Native hardwood trees were also planted on the sites to test tree growth and survivability. After three years, tree volume and height were highest on weathered sandstone, followed by the shale/sandstone mix, and lowest on unweathered sandstone (Agouridis et al., 2012). By year 9, tree volume was nearly 50 times greater, with 86% survivability, on the weathered sandstone. Though sites were not seeded, volunteer vegetation did provide groundcover. Percent cover and species richness were consistently highest on weathered sandstone (Sena et al., 2014). Thus, productivity and diversity were all highest on the spoil type with the lowest EC.

Studies conducted on forest ecosystems recovering from disturbance have demonstrated the significant role of plants in regulating the balance and loss of nutrients (e.g., Ca^{2+}, K^{+}, and Mg^{2+}) (Vitousek and Reiners, 1975). This is particularly true in early successional ecosystems compared with mature ecosystems, where nutrient retention generally scales with net primary productivity. Woody species have been shown to account for over 60% of the nutrient accumulation in above ground biomass four years after forest disturbance (Hendrickson, 1988). Crow et al. (1991) demonstrated that woody and woodland herbaceous species together accounted for more than 70% of the nutrients captured by vegetation, while early successional graminoids (e.g., grasses, sedges, and rushes) accounted for only a small percentage of the nutrient accumulation. Mou et al. (1993) also showed recovering tree species to accumulate higher amounts of nutrients than herbaceous species six years after forest disturbance. Other studies continue to show that understory vegetation accounts for a small percentage of the total nutrient mass (Zhang et al., 2009; Turner et al., 1976). In a natural secondary forest, grasses accounted for 13% of the total nutrients accumulated (Zhang et al., 2009). Similarly, in a maturing red alder stand, understory vegetation (predominantly ferns) contribution was greater (25% of the total nutrient mass), but still notably lower than what woody species account for in nutrient mass (Turner et al., 1976).

Vegetation may reduce the potential for TDS export via two mechanisms: evapotranspiration and plant uptake. Evapotranspiration decreases water and drainage in the rooting zone, and plant uptake of nutrients may reduce concentrations of TDS nutrient ions in soil solution. Vegetation also plays an important role in the water budget of an ecosystem through transpiration and evaporation of intercepted water from canopy surfaces. It has been shown that with the removal of forest cover, reduced evapotranspiration increases the amount of water discharged to streams (Brown et al., 2005). Sena et al. (2014) have also shown decreased water discharge volumes between the dormant and growing seasons from a surface mine in eastern Kentucky, demonstrating that transpirational demands from an aggrading forest can reduce waters draining from a reclaimed mine land. The study concluded that evapotranspiration from trees exerted a greater influence over the quality of discharged water than spoil type. It is hypothesized that aggrading forests can reduce TDS loss from the rooting zone both by decreasing the quantity of water leaving the rooting zone through increased evapotranspiration, and decreasing the concentration of TDS nutrient ions in percolating waters through plant uptake. The outcomes to this research are especially pertinent to mine land reclamation as TDS loading to surface waters is a major water quality concern.

The primary objectives for this study are to 1) quantify the effect of vegetation on reducing soil solution fluxes of common TDS nutrient ions in reclaimed mine lands, 2) assess vegetation and soil properties to determine their effects on loading of TDS nutrient ions, and 3) recommend reclamation strategies that optimize vegetation communities for reducing TDS nutrient ion loading from reclaimed mined lands.

2.2 Methods

2.2.1 Site Description and Preparation

Study sites are located in southwest Virginia at the Powell River Project in Wise County (37°00'17"N 82°42'26"W). Climate of this area is humid, average annual precipitation of 1230 mm, with temperatures ranging from 5.4°C in January to 27°C in July and August. Local vegetation in unmined areas are mixed native hardwoods (Avera et al., 2015). The bedrock is characterized by sandstone and siltstone of the Pennsylvanian age Wise Formation (Haering et al., 2005).

Eight sites were selected across a range of post-reclamation ages (1-8 years). Due to logistical constraints of vegetation removal, sites greater than eight years post-reclamation were not included. In addition, it has been suggested that as reclamation age approaches 10 years, EC values diminish (Sena et al., 2013; Daniels et al., 2014; Orndorff et al., 2015). Where possible, multiple sites within a particular age were selected to represent various spoil materials and extents of weathering, thus providing gradients in both productivity and potential TDS generation. Overburden used as topsoil substitute primarily consisted of unweathered sandstone and siltstone, with fragments of shale and coal.

At each site, vegetated and un-vegetated paired plots were established to evaluate the effect of vegetation on common TDS nutrient ion fluxes (Figure 1). Plot sizes were variable (12 to 45 m^2) based upon the dominant vegetation height to buffer un-vegetated treatments from adjacent vegetation influencing canopy interception, soil moisture, and nutrient uptake. Plot perimeters extended from the center a minimum of one meter if the dominant vegetation was less than one meter tall. Otherwise, plot perimeters extended from the center a distance equal to the height of the dominant vegetation. Each set of paired plots were laid on the backslope of a hill, running parallel with the slope, and separated by a minimum distance equal to the plot width. In order to establish un-vegetated plots, vegetation was removed manually (pulling, clipping, and sawing as required) and with herbicide (BrushMaster® active ingredient: Glyphosate; Roundup® active ingredients: 2,4-D, 2,4-DP, and Dicamba). Regrowth was treated with herbicide and manual removal as needed, typically twice for each sampling period. Decomposition of roots releasing nutrient ions after herbicide application is likely minimal as previous research has indicated that less than three percent of dry matter for Ca^{2+}, K^+, Mg^{2+}, and sulfur accumulates in roots of grasses, herbaceous, and woody species (Mou et al., 1993; Peri et al., 2008; Zhang et al., 2009; Peri and Lasagno, 2010;).

2.2.2 TDS Sampling and Extraction

Sampling for common TDS nutrient ions (i.e., Ca^{2+}, K^+, Mg^{2+}, Na^+, SO_4^{2-}) took place in two month increments seasonally through 2015 and 2016. Ion exchange resins (Amberlite® IRA-400

Cl^- and Amberlite® IR-120 H^+) encapsulated in a screened PVC lysimeter were used to absorb cations and anions contributing to TDS in soil solution under locally saturated conditions (i.e., zero tension). Lysimeters were constructed from schedule 20 PVC by Hole Products with the following specifications: 20.3 X 2 cm, 0.25 mm width screening, 3.2 mm screened spacing for an overall screened section 10.2 cm with a pointed plug. Lysimeters attach to an unscreened PVC casing with flush threading. Casings were 61 cm in length with a slip cap. Resin lysimeters attached to PVC pipe were placed approximately 30 cm deep at an angle relative to the hillslope (for 60 percent slopes angle was approximately 60° and for 35 percent slopes angle was approximately 40°). Pilot holes using a 2.5 cm steel rod and hammer were created in order to place and collect the resin with minimal soil disturbance across three sampling periods. Three resin lysimeters were placed in each vegetated and un-vegetated plot, linearly in plot centers, spaced 2 meters (Figure 1). Vegetation was removed from un-vegetated plots five weeks prior to resin lysimeter deployment. Sampling periods took place July 6, 2015 to September 8, 2015 (peak growing season), October 9, 2015 to December 10, 2015 (fall), and January 14, 2016 to March 15, 2016 (winter). A fourth sampling period was planned for mid-April to mid-June, but a wildlife disturbance prematurely ended the study.

Resin lysimeters were soaked in a deionized (DI) water bath for 48 hours and rinsed in quadruplicate before use and between each sampling period. Cation and anion resins were combined in a ratio of 1:1.28 to account for the different exchange equivalencies. All resin lysimeters were stored refrigerated at 6°C before deployment.

Resins retrieved from the field were stored refrigerated at 6°C prior to extraction. Resins were removed from lysimeters and filtered using DI water and Whatman® # 1 filter paper. During the first sampling period, resins were extracted in 100ml of 2*N* HCl on a reciprocal shaker, and then filtered using Whatman® # 1 filters. Resins were extracted a second time with 175ml of 2*N* HCl following the same procedure described above and the values from ICP analysis were combined. For all other sampling periods, resins were extracted three times as previously described with 175 ml of 2*N* HCl, and extracting solutions from the three extractions were combined. All solutions were frozen at -20°C until analyzed for elemental Ca, K, Mg, Na, Fe, and S (subsequently converted to SO_4^{2-}). The first sampling period filtrates were sent to the Virginia Tech Soil Testing Lab and analyzed with a CirOS VISION ICP-AES. All following filtrates were analyzed using a Varian MPX ICP-OES.

2.2.3 Vegetation Characterization

Vegetation was classified into three categories: herbaceous, trees [>2.5 cm at diameter at breast height (DBH)], or other woody vegetation (OW) (<2.5 cm at DBH). Each category was characterized by measuring biomass, basal area, and leaf area index (LAI). Where destructive sampling was necessary, three 0.5 m^2 quadrats near but outside of plot boundaries were randomly located so as to minimize the effect of the disturbance on the fluxes of water and common TDS nutrient ions (Figure 1). Herbaceous vegetation within the quadrat was harvested and separated into live and dead categories. Vegetation was then oven dried at 65°C and weighed.

Within the full vegetated treatment plot, DBH (trees) or ground line diameter (OW) was measured. Basal areas for trees were calculated using DBH, and ground line basal area for OW using ground line diameter. Allometric equations from Chojnacky et al. (2014) were used to determine biomass estimates for trees. Volume index was determined for OW using methods modified from Emerson et al. (2009), with the formula:

$$\text{OW volume index (cm}^3\text{)} = \text{ground line diameter}^2\ (\text{cm}^2) \times \text{height (cm)}$$

Stem densities for trees and OW vegetation were recorded for each site.

LAI was measured using a Li-Cor LAI 2200 Plant Canopy Analyzer with a 90° view cap. K files for each site were compiled and scattering corrections applied to each LAI measurement using the FV2200 software. Measurements were taken inside each vegetated plot 6 inches above the ground, evenly spaced. Six readings were taken for plots whose dominant vegetation height was less than 1 meter, and eight readings for all others.

2.2.4 Soil Characterization

Three soil samples per 0-10 cm and 10-20 cm depth were taken at each site. Soil samples were randomly located outside of plot boundaries to minimize the effect of soil disturbance on TDS fluxes (Figure 1). Soils were air-dried and mineral soil separated from course fragments with a 2mm sieve. Mineral soil samples were analyzed for pH, particle size, and organic matter. Samples were sent to the Virginia Tech Soil Testing Lab for pH analysis using 1:1 (vol/vol) water to soil ratio (Kalra et al., 1995). Particle size was analyzed on mineral soil using the hydrometer method (Bouyoucos, 1962), and organic matter content was analyzed by loss on ignition (Ball, 1964). Coarse fragments from 0-10 cm and 10-20 cm depth were composited and ground to pass through a 2mm sieve for saturated paste EC analysis (Gartley, 2011; Rhoades et al., 1989). Hydraulic conductivities were calculated from infiltration rates that were measured using a Mini Disk tension infiltrometer by Decagon Devices, Inc. (Zhang, 1997). The infiltrometer was set to a capillary pressure head of -2 cm providing hydraulic conductivity estimates of the soil matrix excluding macropores with air entry values higher than that capillary pressure head. Six measurements were taken at each site.

2.2.5 Data and Statistical Analysis

Comparison of TDS nutrient ion fluxes between paired plots were expressed as the $\log_{10}$-transformed ratio (R) of measurements made in the un-vegetated plot relative to vegetated plot to both constrain the scale of the data and transform the distribution to one that is symmetrical. Thus, positive values represent un-vegetated fluxes that are greater than vegetated fluxes within a pair, and vice versa. A value of zero is no change. To determine the fluxes of common TDS nutrient ions, each analyte was averaged for the 3 lysimeters per plot and then summed with other analytes to obtain a plot-level value for total ions, base cations, and sulfate, expressed as µg day^{-1} basis. Equations for calculating plot level ratios for total ions (R_{Total}), base cations (R_{BC}), and sulfate ($R_{SO_4^{2-}}$) are as follows:

$R_{Total} = \log_{10}[(\text{Un-vegetated})\ \Sigma\ Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}, SO_4^{2-} / (\text{Vegetated})\ \Sigma\ Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}, SO_4^{2-}]$

$R_{BC} = \log_{10}[(\text{Un-vegetated})\ \Sigma\ Ca^{2+}, K^{+}, Mg^{2+}, Na^{+} / (\text{Vegetated})\ \Sigma\ Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}]$

$R_{SO_4^{2-}} = \log_{10}[(\text{Un-vegetated})\ SO_4^{2-} / (\text{Vegetated})\ SO_4^{2-}]$

Outlier box plots were used to assess whether outliers were present for sulfur and iron, which would be suggestive of pyrite oxidation. Data from two resin lysimeters, one in each plot of 3b, suggested pyrite oxidation across all seasons. Consequently, these resin lysimeters were excluded from the data. The Spearman rank correlation coefficient (ρ) was used due to small sample size. Fisher's LSD was used to determine differences in EC among sites. All data analysis was performed in JMP® Pro 11.0.0.

2.3 Results

During the peak growing season (sample period July to September), LAI and live herbaceous biomass tended to increase with post-reclamation age (Table 1). LAI ranged from 0.5 to 4.9, generally increasing with age with the exception of the one-year-old site (Table 1). Average live herbaceous biomass ranged from 15 g to 83 g. The one-year-old site (site 1) is comparatively higher in live herbaceous (46 g) when compared to sites 3 years (sites 3a and 3b) and 6 years (sites 6a and 6b) old (Table 1). This may be because site 1 had been recently hydroseeded and fertilized. Biomass and stem density of trees, and volume and stem density of OW, tended to be more variable than live herbaceous biomass, reflecting the different productivity gradients of each site. Only three sites supported trees (6a, 6b, and 8b), but OW vegetation was present on most sites. Tree stem density and biomass were highest on 8b (0.12 kg m^{-2} and 3.9 kg m^{-2}, respectively). Site 6a was slightly lower in stem density than 6b, but higher in biomass (Table 1). While 8a lacked trees, it was higher in OW stem density and volume than 8b (Table 1). OW volume and stem density increased across sites by age.

Soil properties of the study sites are shown in Table 2. On average, sandy loam was the dominant soil textural class across all sites. The pH ranged from 6.3 to 8.1 at 0-10 cm depth and 6.0 to 8.3 at 10-20 cm depth. EC of the combined coarse fragments ranged from 0.316 mmhos cm^{-1} to 0.871 mmhos cm^{-1}. Most sites had an EC value less than 0.600 mmhos cm^{-1}, but the two sites with the highest ECs (3a and 6a; $p<0.005$) exceeded 0.800 mmhos cm^{-1}. Percent organic matter ranged from 4.4 to 9.8% at 0-10 cm depth and 3.0 to 6.2% at 10-20 cm depth, generally increasing with age.

A correlation analysis was performed including and excluding sites 3a and 6a (EC > 0.800 mmhos cm^{-1}) to determine the effect high EC materials may have on vegetative influences on solute fluxes (Figure 2). Positive trends between TDS variables and site characteristics were expected. Figure 2a shows correlations for the peak growing season with all sites included. Most correlations were less than 0.40, with the exception of percent organic matter, age, and live herbaceous vegetation. When sites 3a and 6a with the highest EC values were excluded, correlations become stronger and more positive (Figure 2b). This suggests that initially selecting lower EC materials is necessary before a vegetative effect can be determined. Otherwise, mine spoil or topsoil substitute with EC greater than 0.800 mmhos cm^{-1} may generate TDS nutrient ions in amounts greater than the capacity for vegetation to mitigate.

Vegetated plots often yielded higher values for TDS nutrient ions than un-vegetated plots, contrary to the hypothesis (Appendix B). Despite this, the data shows positive Spearman correlations between calculated ratios (R_{Total}, R_{BC}, and $R_{SO_4^{2-}}$) and vegetative characteristics. The strongest of these correlations were between $R_{SO_4^{2-}}$ and live herbaceous vegetation (ρ = 0.89), LAI (ρ = 0.77), percent organic matter (0-10 cm ρ = 0.83; 10-20 cm ρ = 0.77), and OW volume (ρ = 0.60). Tree characteristics (ρ = -0.07), groundline basal area (ρ = 0.09), and volume (ρ = 0.09) were not correlated with R_{BC}, while live herbaceous (ρ = 0.71), percent organic matter (0-10 cm ρ = 0.60; 10-20 cm ρ = 0.54), and LAI (ρ = 0.54) were the most positively correlated characteristics with R_{BC}. Live herbaceous vegetation was most positively correlated in the peak growing season compared to the fall and winter dormant periods (Figure 3). During the fall sampling season (Figure 3b), all OW and tree characteristics exhibited moderate correlations (ρ = 0.44 to > 0.70), suggesting that even during dormant periods woody vegetation had an apparent influence on the flux of common TDS nutrient ions. During this period, OW volume had its strongest correlation with R_{BC} (ρ = 0.71), and trees were moderately correlated with R_{Total} (ρ = 0.44). Correlations during the winter sampling season (Figure 3c) for trees were weakly negative (ρ ≤ -0.3), while OW density (ρ = 0.67), groundline basal area (ρ = 0.77), and volume (ρ = 0.77) increased over the fall period with $R_{SO_4^{2-}}$.

During the peak growing season, percent organic matter exhibited moderate to strong correlations with R_{Total}, R_{BC} and $R_{SO_4^{2-}}$, with ρ values of 0.66, 0.60, and 0.83 for 0-10 cm, respectively, and 0.60, 0.54, 0.77 for 10-20 cm, respectively. Correlations with R_{Total}, R_{BC} and $R_{SO_4^{2-}}$ strengthen during the fall. For 0-10 cm depth, ρ values were 0.71, 0.77, and 0.90, respectively, and 0.66, 0.71, 0.84 for 10-20 cm depth, respectively. In winter, correlations weakened, but overall remained positive for R_{Total}, R_{BC} and $R_{SO_4^{2-}}$ (0-10 cm ρ = 0.37, 0.43, and 0.71, respectively; 10-20 cm ρ = 0.26, 0.31, and 0.60, respectively).

2.4 Discussion

Three key implications can be drawn from the results of this study. First, correlations indicate that herbaceous and woody vegetation exert an influence on common TDS nutrient ion fluxes during the growing season, and woody vegetation continues to affect fluxes of common TDS nutrient ions in the dormant season. Second, organic matter influences fluxes of common TDS nutrient ions across all sampling periods, exhibiting high ρ values during the growing season and fall (ρ = 0.60 to > 0.80). Last, vegetation may have a reduced effect on TDS nutrient ions fluxes if materials used for topsoil substitute are high in soluble salts (Figure 2). It is important to note that values for vegetated plots are often higher than values for un-vegetated plots (Appendix B), which does not conform to the hypothesis that vegetated plots would be lower in TDS nutrient ions in soil solution. The reason for this result is unclear. Perhaps on the sites where vegetation was already minimal, the disturbance effect of the vegetation control treatment outweighed any potential evapotranspirative or nutrient uptake effect. Still, the many positive correlations with vegetative parameters suggest a relationship with vegetation that is worthy of further exploration, even though the reduced sample size after removing outliers suggests low statistical power (e.g., power is 48% for n = 6 and ρ = 0.8).

2.4.1 Effect of Vegetation on TDS Nutrient Ion Fluxes

Research has shown forest removal in the Appalachians alters the natural water and nutrient ion budgets, particularly during the growing season (Brown et al., 2005; Adams and Kochendenfer, 2014; Hornbeck et al. 1986), which often coincides with increases in specific conductance (Likens et al., 1970; Kochenderfer and Wendel, 1983). Deforestation from mining practices have similar effects on discharge to streams, and have been attributed to decreases in evapotranspiration with forest removal (Messinger and Paybins, 2003; Griffith et al., 2012; Dickens et al., 1989). Correlations suggested some influence of vegetation and a potential effect on TDS nutrient ion fluxes via increased evapotranspiration and plant uptake. Some of the results show high positive correlation between vegetation characteristics and TDS nutrient ion fluxes seasonally, reflecting the differences in evapotranspiration and plant uptake between growing and dormant seasons. However, TDS nutrient ion fluxes were not always lower on sites with vegetation characteristics that would suggest higher productivity and evapotranspiration.

During the first sampling period, live herbaceous biomass, OW volume, and LAI were positively correlated with R_{Total} and $R_{SO_4^{2-}}$. During the growing season, interception and evapotranspiration are at their highest (Gerrits et al. 2010; Sun et al. 2008). A higher LAI typically indicates higher interception, thus having a greater influence on canopy interception storage and subsequent evaporation of precipitation from leaf surfaces (Swank and Douglass, 1974; Aston, 1979). Interception and transpiration of rainfall by vegetation reduces the amount of water percolating through the rooting zone, especially during the growing season when transpiration is highest. Precipitation losses to evapotranspiration can account for greater than 40% annually (Swank et al., 2001). In one study, 21 to 41% of the total precipitation was lost to vegetative interception alone (Kramer and Holscher, 2009), while other findings have shown canopy and forest floor interception combined can account for roughly 40% of annual evaporation (Gerrits et al. 2010). Another study found grasses to intercept 26% of total precipitation (Tsiko et al. 2011). On our study sites, grasses and other herbaceous vegetation are a major component of the recovering forest community, and likely account for more interception of rainfall than the trees and other woody species at the early stages of reclamation.

During the growing season, correlations between $R_{SO_4^{2-}}$ and live herbaceous, OW volume, and LAI, in addition to R_{BC} correlates with live herbaceous and LAI, suggests plant uptake of nutrient ions. Again, even though the vegetated plots often yielded higher fluxes of TDS ions compared to un-vegetated plots, the correlation of the log-ratios of paired plot data indicated some effect of the vegetation and soil characteristics. Moreover, two of the older sites that showed the strongest difference between the vegetated and un-vegetated plots (i.e., larger positive of log-ratios of paired plot data), suggested some vegetation control of TDS fluxes. Of the nutrient ions analyzed, Ca^{2+} and Mg^{2+} are the most abundant in vegetation. However, plant uptake through mass flow is also important for K^+ and SO_4^{2-} (Prenzel 1979). Within the first three years of recovery from forest disturbance, vegetation is known to accumulate 40 to 44 kg ha^{-1}, 22 to 45 kg ha^{-1}, and 7 to 10 kg ha^{-1} of Ca^{2+}, Mg^{2+}, and K^+ respectively (Mou et al., 1993; Hendrickson, 1988). In more mature stands, uptake can average 1097 kg ha^{-1}, 230 kg ha^{-1}, and 64 kg ha^{-1} for Ca^{2+}, Mg^{2+}, and K^+ respectively (Johnson and Todd, 1990). Calcium and magnesium are important components of plant function where calcium is required for structure of cell walls and membranes (White and Broadley, 2003), and magnesium is a core element in chlorophyll in addition to its structural role in tissues (Huber and Jones, 2013). Though sulfate is an important nutrient in proteins and chloroplasts, less than 3 kg ha^{-1} sulfate in vegetation may accumulate (Likens et al., 2002). Plants depend upon potassium for stomatal control and a variety of non-structural biochemical reactions; however, because it is highly soluble, it can be lost readily from ecosystems at high rates (Liken et al. 1994). Sodium is not considered an essential plant macronutrient, but vegetation does utilize sodium as an osmoregulator, generating high internal osmotic pressure to sustain tugor (Amtmann and Sanders, 1998). Vegetative uptake of these ions likely influences nutrient ion fluxes in combination with evapotranspiration.

Because interception and evapotranspiration are functions of LAI, they consequently fluctuate seasonally (Gerrits et al., 2012; Sun et al., 2008; Swift et al., 1975). It is not surprising that during fall when leaves drop and vegetation begins to senesce, correlations with live herbaceous vegetation and LAI overall decline. However, as the vegetation enters dormancy, tree biomass (along with all other tree characteristics) become more positively correlated with R_{Total}, R_{BC}, and $R_{SO_4^{2-}}$. OW volume correlations also increase with R_{BC}. These findings suggest that even as herbaceous vegetation senesces and woody species drop their foliage, woody vegetation continues to exert some influence over nutrient ion fluxes. With LAI showing an average correlation of 0.53, continued interception, albeit reduced, provides a possible explanation. Gerrits et al. (2010) found canopy interception during the leaf off period to be 5% of the rainfall amount, but when combined with litter interception it accounted for 26% of the rainfall loss to evaporation. In this study, most of the vegetation categorized as trees included pines, which are known to have greater rates of interception during the dormant season (Helvey, 1967; Swank and Douglas, 1974).

Transpiration may also be continuing into the first half of the fall sampling period. Between September 29th and October 13th, 2015 the area received approximately 82 mm of precipitation, followed by a dry period. Plant uptake and transpiration could have continued during this wet spell. At the nearby Fernow Experimental Forest (WV), water loss to transpiration has been shown to occur into October, and accounted for 65% of the precipitation in that month based on a water balance analysis (Patric, 1973). The observed fall correlations with trees and OW vegetation in this study were likely influenced by both interception and transpiration, with transpiration predominating at the beginning of the collection period.

Deep into the dormant season, interception and transpiration are at their lowest. This is reflected in the winter sampling period where correlations with LAI and all tree characteristics are no longer positively correlated. Surprisingly, OW volume continues to show a strong positive correlation with $R_{SO_4^{2-}}$ ($\rho = 0.77$). This is most likely due to some interception loss from OW vegetation.

2.4.2 Organic Matter Retention of TDS Nutrient Ions

Vegetation may have an indirect effect on TDS nutrient ion fluxes through the senescence and subsequent decomposition of biological material that forms soil organic matter. Soil organic matter is an indicator of restored ecosystem structure and function as it accumulates with age on reforested mined lands (Avera et al., 2015). A moderate correlation ($\rho = 0.65$ for 0-10 cm and 10-20 cm; data not shown) between soil organic matter and site age exists in our study, supporting that soil organic matter increases with time on reclaimed mined lands. Two out of three of the oldest sites (i.e., 8-year old) had large positive log-ratios for soil organic matter suggesting that once enough organic matter is present, there might be an effect of vegetation control on TDS nutrient ion fluxes. However, percent soil organic matter in this study is higher than what has been found in previous research (Acton et al., 2011; Avera et al., 2015), for both 0-10 cm depth and 10-20 cm depth, on all sites. This is likely due to the method used to analyze for soil organic carbon. Loss on ignition does not discriminate between geogenic organic carbon (i.e., coal fragments in mineral soil) and soil organic carbon, thus yielding in higher percent soil organic matter in older sites. Correlations between soil organic matter and R_{Total}, R_{BC}, and $R_{SO_4^{2-}}$ are likely leveraged by the high values in percent organic matter.

Results show strong positive relationships between percent soil organic matter and R_{Total}, R_{BC}, and $R_{SO_4^{2-}}$. Correlations for 0-10 cm and 10-20 cm strengthen from the growing season into the fall, with ρ values exceeding 0.70. In winter, R_{BC} ρ values decrease ($\rho < 0.45$), whereas $R_{SO_4^{2-}}$ remains strongly correlated. These positive correlations during dormancy suggest a year round retention mechanism for common TDS nutrient ions. This could be explained by two functions of soil organic matter: 1) increased water holding capacity and 2) adsorption of positively charged nutrient ions through the cation exchange complex.

Soil organic matter increases the water holding capacity of the soil (Hudson 1994, Saxton and Rawls 2006), thereby reducing water draining from the rooting zone, preventing losses of nutrient ions via leaching. It acts as a reservoir for plant available nutrients in mineral soil through adsorption of positively charged nutrient ions on negatively charged exchange sites, or by retaining dissolved ions in soil solution (Gosz et al., 1976). The cycle between immobilization and mineralization provides a buffer to the export of nutrient ions from the rooting zone (Bormann and Likens, 1967; Gosz et al., 1976). Loss of nutrients from soil organic matter occurs through either vegetative uptake or export from soil via erosion processes, draining waters, or to the atmosphere if the element possesses a gaseous phase, all of which are related to the availability of water.

Both water retention and adsorption of nutrient cations by organic matter likely influence TDS fluxes. These functions are especially important during dormancy when evapotranspiration is lower. During the fall sampling period R_{Total}, R_{BC}, and $R_{SO_4^{2-}}$ all are strongly correlated with percent organic matter ($\rho > 0.65$) for both depth increments. R_{BC} exhibits its strongest correlation during the fall, which may be due to organic matter retaining base cations as vegetative uptake decreases seasonally. However, this retention is not indefinite as it is lost in the winter sampling period. $R_{SO_4^{2-}}$ shows predominantly high correlations across all sampling periods. As SO_4^{2-} is an anion, and thus generally considered more mobile in alkaline systems like these, organic matter likely holds sulfate in soil solution via water retention, although cation bridging is also a possibility. However, these mechanisms alone do not fully explain the patterns in R_{BC} and $R_{SO_4^{2-}}$ during the winter. Further investigation is needed to explain the correlation between soil organic matter and R_{BC} and $R_{SO_4^{2-}}$.

2.4.3 High EC Impedes Vegetative Controls

Our findings support previous research that reclaiming with optimal spoil materials increases revegetation success (Zipper et al., 2011; Sena et al., 2014; Agouridis et al., 2012). When data for all sites were analyzed using Spearman correlation, woody vegetation and LAI were either negative or weakly positive ($\rho < 0.40$), whereas live herbaceous had ρ values up to 0.45. Stratifying the data by high EC (i.e., $\rho > 0.800$ mmhos cm^{-1}) demonstrated increasingly positive relationships between all parameters and R_{Total}, R_{BC}, and $R_{SO_4^{2-}}$ (Figure 2). The FRA suggests reclaiming materials that are low in soluble salts ranging in a pH of 5 to 7 (Zipper et al., 2011; Burger et al., 2005) to promote productivity. Most of the sites in this study fit these requirements, except those determined to have high EC. This is reflected in our findings where productive sites lower in EC exerted an influence on TDS nutrient ion fluxes, indicating that the selection of topsoil substitutes is a critical first step in mitigating TDS nutrient ion loading to surface waters draining reclaimed surface coal mines, and that the influence of vegetation on TDS nutrient ion fluxes is an important, but potentially secondary, best management practice for reclamation practitioners. It is also worth mentioning that even with high EC sites included in the analysis (Figure 2), organic matter was positively correlated with $R_{SO_4^{2-}}$, suggesting that organic matter could mitigate TDS nutrient ion loading from waters draining on sites that were unable to be reclaimed with spoils low in soluble salts.

2.4.4 Reclamation Strategies

The goal of this study was to investigate whether vegetation could mitigate TDS nutrient ion loading from reclaimed mine lands, and provide strategies for reclamation practitioners to utilize. Our findings suggest that both herbaceous and woody vegetation can reduce TDS nutrient ions leaching from the rooting zone when topsoil substitutes are low in soluble salts. Interception from woody vegetation and ion retention by organic matter may provide year round control. Three strategies are proposed to optimize vegetative control of TDS fluxes to surface waters draining from reclaimed surface coal mine lands:

1) Use spoil materials low in soluble salts. High EC materials may generate TDS nutrient ions in amounts greater than what vegetation is able to mitigate.
2) Establish non-competitive herbaceous vegetation in early reclamation stages to reduce TDS nutrient ion fluxes and build soil organic matter.
3) Establish woody species for year round control of TDS nutrient ion loading

The benefits of low EC are twofold. Vegetative productivity is higher on materials low in soluble salts, and low EC materials tend to yield drainage waters lower in specific conductance. Establishing tree compatible herbaceous ground cover increases evapotranspiration and plant uptake during the growing season, and builds organic matter via senescence and decomposition, which exerts an influence during the non-growing season. Tree compatible ground covers will also aid in seedling survival of woody species, whether they are established by planting or natural recruitment. As reclaimed forests aggrade, woody species will have greater influence on TDS nutrient ion fluxes through evapotranspiration and plant uptake during the growing season, and through interception in the dormant season. Together, these three strategies may help reclamation practitioners decrease the amount of TDS nutrient ions reaching surface waters, thereby mitigating water quality impacts.

2.5 Conclusions

One of the major issues in surface coal mine land reclamation is the impact of TDS on water quality. To address this water quality concern, we assessed whether vegetation could reduce TDS loading, specifically nutrient ions Ca^{2+}, Mg^{2+}, K^+, Na^+, and SO_4^{2-}, likely through increased evapotranspiration and plant uptake. Paired vegetated and un-vegetated plots were established, and vegetation properties (i.e., LAI, tree biomass, OW volume, etc.) measured as proxies for evapotranspiration and plant uptake. Results were not definite in this study. Vegetated plots often produced higher TDS nutrient ions than un-vegetated plots, which suggests that vegetation did not have a significant influence on reducing TDS nutrient ions in soil solution. However, Spearman correlations with vegetation characteristics, age, and percent organic matter followed expected patterns that TDS nutrient ions were reduced in soil solution within the rooting zone of more vegetated systems, which warrant exploration. Interception by woody vegetation and litter, and soil organic matter retention, may also influence TDS nutrient ion loading during the dormant season. These finding suggest that aggrading forests and good vegetative cover may reduce TDS nutrient ion loading by decreasing the quantity of water leaving the rooting zone through increased evapotranspiration, and decreasing TDS nutrient ions in percolating waters through plant uptake in the growing season. However, this study could not unquestionably show this effect. An increased sample size and including sites between the ages of 6 and 12 years of age may be needed to detect a vegetation effect. Based on implications from this study, it is recommended that reclamation practitioners 1) choose topsoil substitutes low in soluble salts, 2) establish non-competitive herbaceous vegetation in early reclamation stages to reduce TDS nutrient ion fluxes and build soil organic matter, and 3) establish woody species for year round control of TDS nutrient ion loading once EC levels are below 0.800 mmhos cm^{-1}. These three strategies combined may help reclamation practitioners decrease the amount of TDS nutrient ions reaching surface waters, thereby mitigating water quality impacts.

2.6 References

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2.7 Tables and Figures

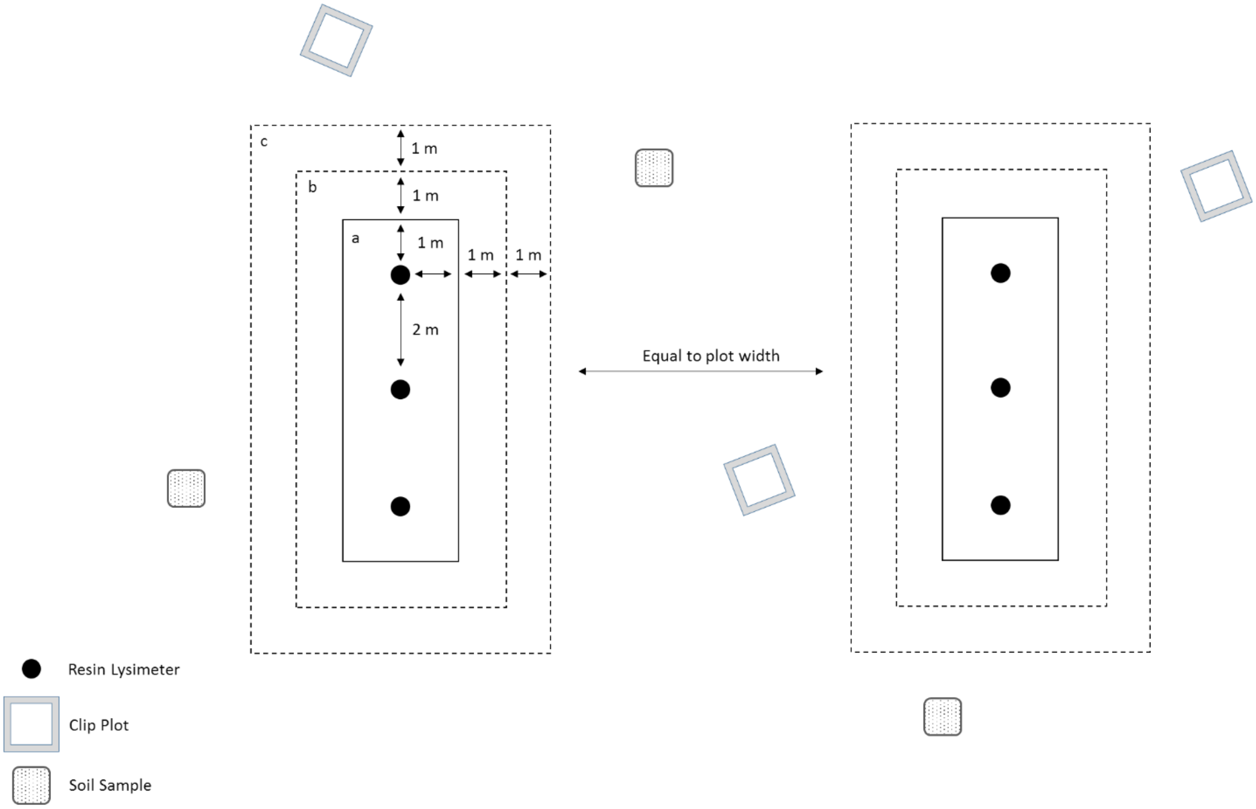


Figure 1. Plot layout, and soil and vegetation sampling. Plots were established on the backslope of the hills, parallel to the slope, and set apart at a minimum distance equal to the plot width**.** (a) is an example of a plot if dominant vegetation is less than 1 m in height, (b) if dominant vegetation is 2 m, and (c) if dominant vegetation is 3 m. Vegetation clip plots and soil samples were randomly selected near, but outside plot boundaries.

Table 1. Vegetation characteristics of study sites. Includes peak live herbaceous (mean and standard errors), stem densities, biomass, volume, and peak leaf area index (LAI).

Age Post-Reclamation	Herbaceous	Trees		Other Woody		LAI
	Live (g)	Stems (m^2)	Biomass (kg/m^2)	Stems (m^2)	Volume (cm^3/m^2)	
1	46 ± 14	0	0	0	0	1.7
3*a*	15 ± 3	0	0	0	0	0.5
3*b*	22 ± 3	0	0	0.1	3.56	0.5
6*a*	24 ± 14	0.03	1.7	0.2	444	2.3
6*b*	18 ± 11	0.04	0.9	0.2	79.5	1.4
8*a*	58 ± 4	0	0	0.5	2350	2.1
8*b*	83 ± 28	0.12	3.9	0.3	1730	4.9
8*c*	78 ± 24	0	0	0.2	987	2.8

Table 2. Means and standard errors for soil properties of each site. Includes percent sand, percent clay, percent organic matter, pH, EC of coarse fragments, and hydraulic conductivity (*K*).

Age Post-Reclamation	% Sand		% Clay		pH		% Organic Matter		EC (mmhos/cm)	*K* (cm/hr)
	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-20 cm	
1	58 ± 2	61 ± 10	12 ± 1	11 ± 3	6.3 ± 0.3	6.0 ± 0.5	4.4 ± 0.1	3.5 ± 0.5	0.316 ± 0.08	0.1 ± 0.1
3*a*	55 ± 2	60 ± 1	17 ± 1	16 ± 1	7.5 ± 0.2	7.5 ± 0.2	6.2 ± 0.5	4.3 ± 0.7	0.833 ± 0.03	0.4 ± 0.1
3*b*	62 ± 2	67 ± 2	13 ± 1	13 ± 1	7.7 ± 0.1	7.5 ± 0.3	3.8 ± 0.0	3.0 ± 0.2	0.474 ± 0.03	2.7 ± 0.6
6*a*	68 ± 1	67 ± 0	9 ± 1	10 ± 0	6.4 ± 0.0	6.7 ± 0.5	7.2 ± 0.8	5.0 ± 0.3	0.871 ± 0.05	0.6 ± 0.1
6*b*	64 ± 0	67 ± 2	10 ± 1	11 ± 1	7.8 ± 0.3	8.1 ± 0.2	4.3 ± 1.2	3.4 ± 0.5	0.640 ± 0.01	0.4 ± 0.0
8*a*	55 ± 2	54 ± 1	16 ± 1	19 ± 2	8.1 ± 0.1	8.3 ± 0.0	5.7 ± 0.2	3.9 ± 0.4	0.504 ± 0.01	0.5 ± 0.1
8*b*	61 ± 1	61 ± 2	11 ± 1	14 ± 1	6.6 ± 0.2	7.1 ± 0.2	7.9 ± 0.2	6.2 ± 0.3	0.464 ± 0.01	0.8 ± 0.2
8*c*	61 ± 2	64 ± 2	12 ± 1	13 ± 2	6.8 ± 0.2	7.2 ± 0.2	9.8 ± 0.8	6.1 ± 0.6	0.527 ± 0.06	0.9 ± 0.3

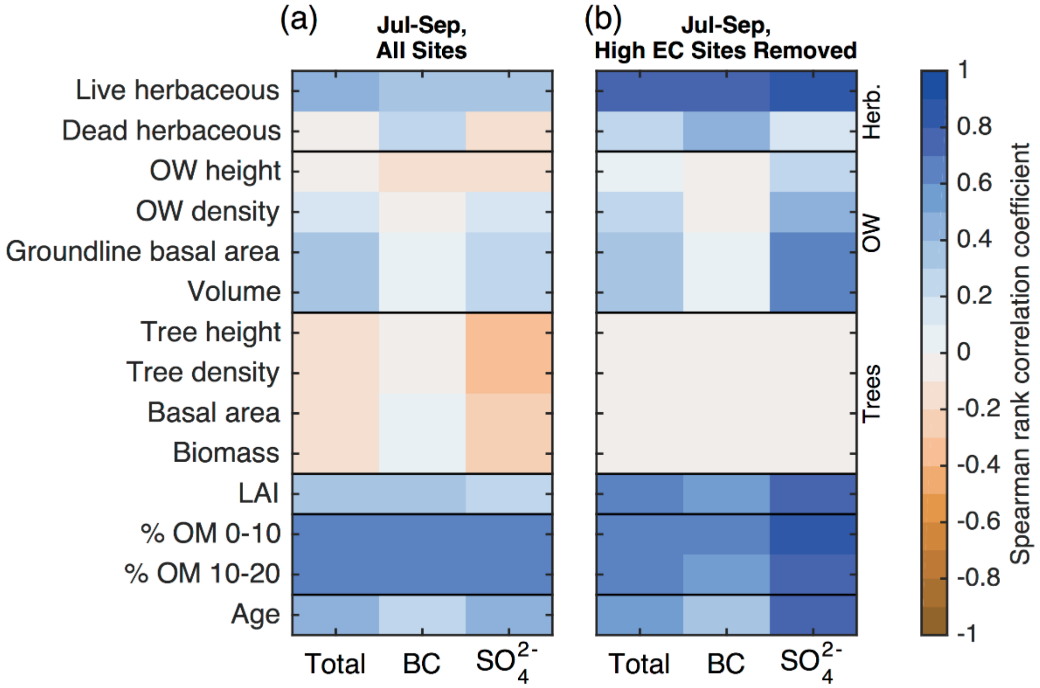


Figure 2. Spearman rank correlation coefficients where intensity of blue indicates the scale (or magnitude) of positive correlations and intensity of tan indicates the scale of negative correlations. Correlations are between ΔTDS, ΔBC, and ΔSO_4^{2-} and parameters for herbaceous vegetation, OW, Trees, and integrative characterizations (LAI and % Organic Matter) (a) shows correlations for all sites during peak growing season. (b) excludes sites 3a and 6a based on high EC.

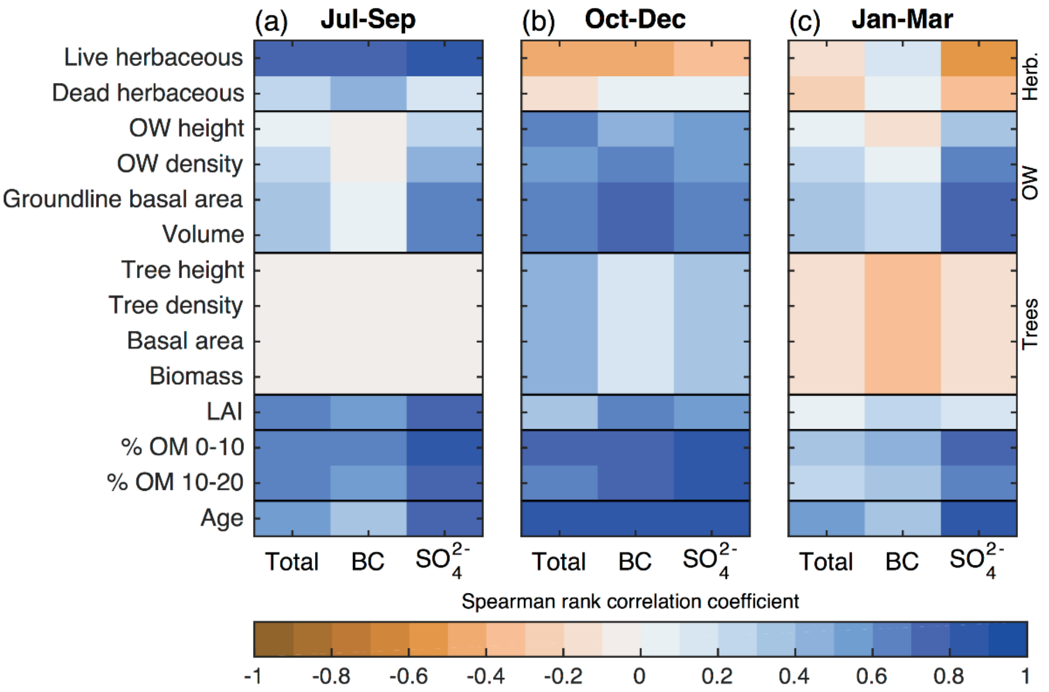


Figure 3. Spearman rank correlation coefficients where intensity of blue indicates the scale (or magnitude) of positive correlations and intensity of tan indicates the scale of negative correlations. Correlations are between ΔTDS, ΔBC, and ΔSO_4^{2-} and parameters for herbaceous vegetation, OW, Trees, and integrative characterizations (LAI and % Organic Matter) (a) shows the peak growing season, (b) fall, and (c) winter.

Chapter 3: Summary and Conclusions

Surface mining practices in central Appalachia have impacted water quality with increased levels of TDS. Research has shown that with the removal of forest cover, reduced evapotranspiration increases the amount of water discharged to streams, thus increasing TDS transport through watersheds. Similarly, as forests aggrade from disturbances, e.g., reclaimed mine sites, discharge from the sites typically decreases. This reduction of water throughput suggests that vegetation is capable of reducing TDS loading to surface waters. In this study, it was tested whether aggrading forests could reduce TDS nutrient ion loading by decreasing the quantity of water leaving the rooting zone through increased evapotranspiration, and decreasing the concentration of TDS nutrient ions in percolating waters through plant uptake. Specifically, common TDS nutrient ions Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, and SO_4^{2-} were analyzed as indicators of TDS in solution draining mine spoils from reclaimed sites of different age. Vegetated and un-vegetated paired plots were established across eight sites with gradients in age, mine spoil material, and vegetative productivity. Ion exchange resin lysimeters were used to compare TDS nutrient ion fluxes in soil solution between un-vegetated and vegetated paired plots. Soil and vegetation properties were characterized at each site, with vegetation properties being used as proxies for evapotranspiration and plant uptake, and correlated with TDS nutrient ion fluxes. Results suggest that evapotranspiration and plant uptake have an effect on reducing TDS nutrient ions in soil solution within the rooting zone. Interception by woody vegetation and litter may also influence TDS nutrient ion loading during the dormant season. Additionally, soil organic matter appears to be important for the retention of TDS nutrient ions during the dormant season. These findings suggest that aggrading forests may reduce TDS nutrient ion loading, through solute retention mechanisms driven by organic matter inputs and plant uptake. From this research, three strategies are suggested to reclamation practitioners to mitigate TDS nutrient ion loading from surface coal mines:

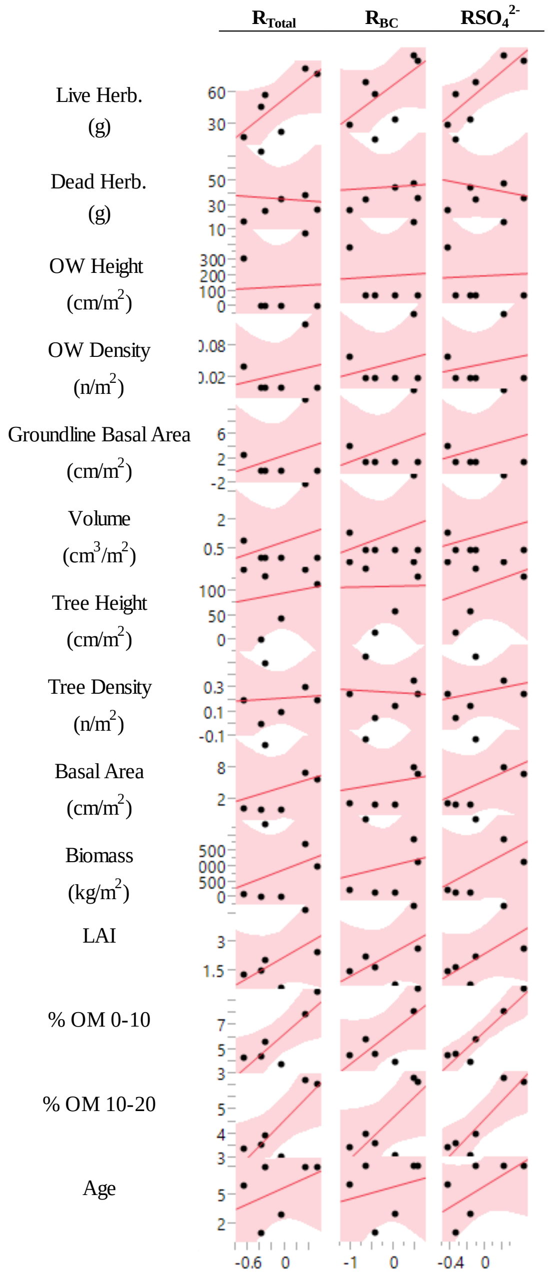
1) Use spoil materials low in soluble salts. High EC materials may generate TDS nutrient ions in amounts greater than what vegetation is able to mitigate.
2) Establish non-competitive herbaceous vegetation in early reclamation stages to reduce TDS nutrient ion fluxes and build soil organic matter.
3) Establish woody species for year round control of TDS nutrient ion loading

Together, these three strategies may help reclamation practitioners decrease the amount of TDS nutrient ions reaching surface waters, thereby mitigating water quality impacts in central Appalachia.

Appendix A

Spearman correlation plots and coefficients for July-September, October-December, and January-March sampling periods. Sites with EC greater than 0.800 mmhos cm^{-1} are not included in the correlation analysis.

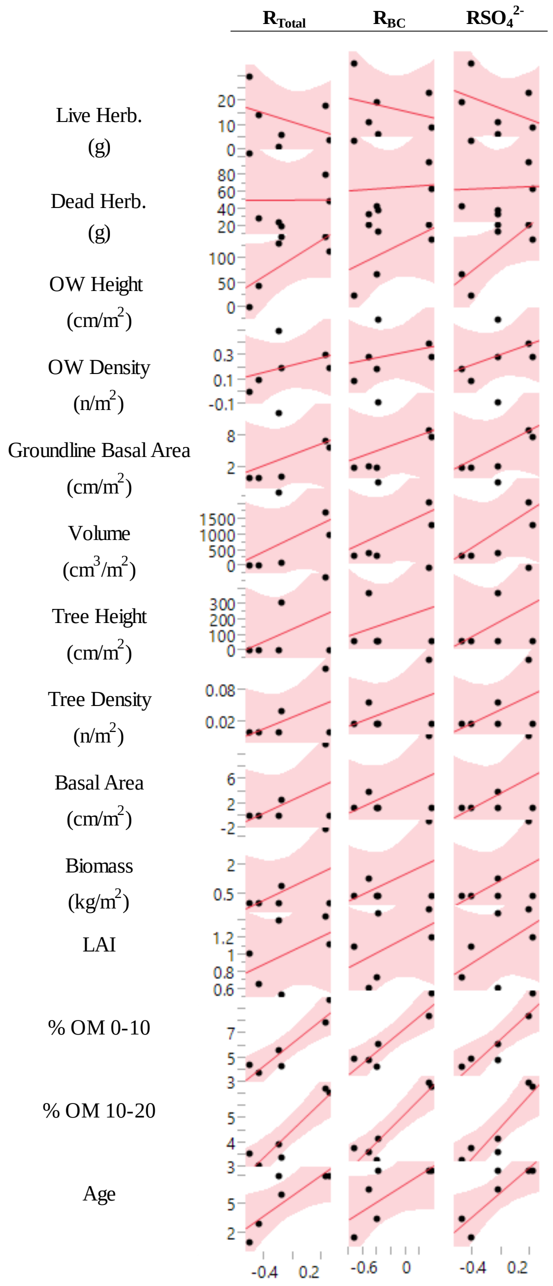
July-September



Spearman's Rank Correlation Coefficient

Parameter	R_{Total}	R_{BC}	RSO_4^{2-}
Live herbaceous	0.771	0.714	0.886
Dead herbaceous	0.257	0.486	0.143
OW height	0.086	-0.086	0.200
OW density	0.232	-0.058	0.464
Groundline basal area	0.371	0.086	0.600
Volume	0.371	0.086	0.600
Tree height	-0.068	-0.068	-0.068
Tree density	-0.068	-0.068	-0.068
Basal area	-0.068	-0.068	-0.068
Biomass	-0.068	-0.068	-0.068
LAI	0.600	0.543	0.771
% OM 0-10	0.657	0.600	0.829
% OM 10-20	0.600	0.543	0.771
Age	0.577	0.334	0.759

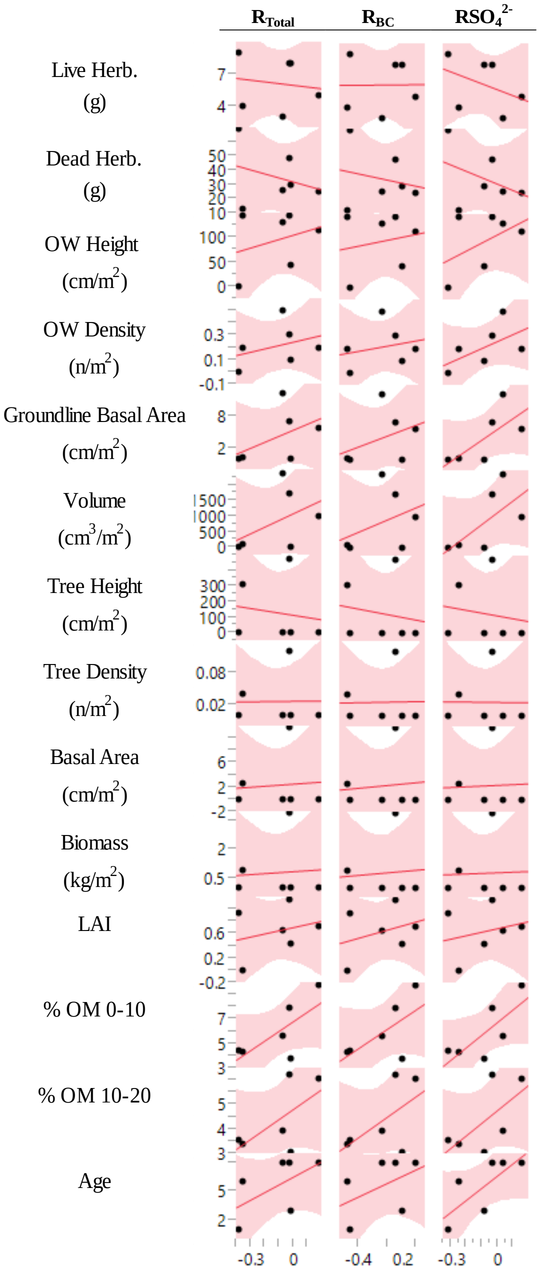
October-December



Spearman's Rank Correlation Coefficient

Parameter	R_{Total}	R_{BC}	RSO_4^{2-}
Live herbaceous	-0.429	-0.486	-0.377
Dead herbaceous	-0.143	0.029	0.058
OW height	0.657	0.429	0.580
OW density	0.551	0.609	0.574
Groundline basal area	0.600	0.714	0.638
Volume	0.600	0.714	0.638
Tree height	0.439	0.101	0.360
Tree density	0.439	0.101	0.360
Basal area	0.439	0.101	0.360
Biomass	0.439	0.101	0.360
LAI	0.371	0.657	0.551
% OM 0-10	0.714	0.771	0.899
% OM 10-20	0.657	0.714	0.841
Age	0.820	0.880	0.832

January-March



Spearman's Rank Correlation Coefficient

Parameter	R_{Total}	R_{BC}	RSO_4^{2-}
Live herbaceous	-0.116	0.116	-0.522
Dead herbaceous	-0.257	0.029	-0.371
OW height	0.086	-0.143	0.314
OW density	0.203	0.058	0.667
Groundline basal area	0.314	0.200	0.771
Volume	0.314	0.200	0.771
Tree height	-0.135	-0.304	-0.135
Tree density	-0.135	-0.304	-0.135
Basal area	-0.135	-0.304	-0.135
Biomass	-0.135	-0.304	-0.135
LAI	0.029	0.257	0.143
% OM 0-10	0.371	0.429	0.714
% OM 10-20	0.257	0.314	0.600
Age	0.516	0.395	0.880

Appendix B

Analyte values for vegetated and un-vegetated paired plots for each sampling season.

		Un-vegetated					Vegetated							
Period	**Site**	**Ca^{2+}**	**Mg^{2+}**	**K^{+1}**	**Na^{+1}**	**SO_4^{2-}**	**Ca^{2+}**	**Mg^{2+}**	**K^{+1}**	**Na^{+1}**	**SO_4^{2-}**	**R_{Total}**	**R_{BC}**	**RSO_4^{2-}**
Jul-Sep														
	1	61.19	21.15	71.1	4.943	188.2	178.1	71.25	182.3	10.58	418.6	-0.3135	-0.6516	-0.108
	3a	254.9	100.1	109.2	3.089	662.8	136.9	45.85	45.85	2.587	349.2	0.3319	0.4727	0.2183
	3b	586.7	337	202.1	16.53	688.3	585.1	323.4	176.1	16.56	1011	0.5323	0.5755	0.4589
	6a	30.06	26.09	6.444	0.7933	101.9	63.83	44.04	66.39	1.449	181.3	-0.3344	-0.4428	-0.2501
	6b	18.96	5.391	1.154	0.5755	87.35	175.1	64.18	47.75	2.293	240	-0.669	-1.045	-0.439
	8a	16.65	5.176	3.205	0.5581	79.97	71.37	30.62	11.71	1.03	102.5	-0.395	-0.4459	-0.3471
	8b	67.31	35.65	41.29	1.833	135.3	26.73	10.2	11.22	1.048	81.83	0.2893	0.3056	0.2782
	8c	214.6	92.77	195.9	5.09	261.1	65.89	53.49	14.41	1.316	90.77	-0.0621	0.016	-0.1669
Oct-Dec														
	1	235.8	67.81	107.1	13.39	702.7	973.6	339.5	848.2	42.92	1818	-0.2432	-0.3911	-0.1303
	3a	1019	400.4	238.1	6.638	3227	321.2	95.4	61.19	3.551	758.5	0.2406	0.3176	0.1926
	3b	583	319.9	120	14.56	970.9	1516	844.6	284.3	42.65	3134	0.2912	0.3671	0.2229
	6a	167.1	92.38	68.18	3.064	592.1	228.2	125.9	351.1	5.41	879.4	-0.2363	-0.3321	-0.1718
	6b	30.91	7.691	6.13	1.469	263.1	99.35	31.33	22.19	1.735	354.9	-0.2168	-0.5246	-0.13
	8a	119.2	50.44	22.42	2.419	344.3	305.4	122.8	46.17	4.165	464.7	-0.5527	-0.7158	-0.4129
	8b	187.9	88.2	58.77	3.546	471	85.52	36.45	38.18	2.721	302.3	0.596	0.5386	0.6288
	8c	356.1	144.5	131	4.963	600.5	157.4	52.27	61.02	2.675	359.4	-0.4622	-0.4134	-0.5089
Jan-Mar														
	1	227.6	73.39	52.82	12.95	662.9	539.8	194.5	361.5	26.94	1371	-0.0712	-0.1449	0.03864
	3a	267.8	117.1	105.6	6.567	702.7	365.1	146.8	99.18	8.461	561.3	-0.0239	-0.0159	-0.0299
	3b	883.2	594.8	211.3	33.65	1374	822.6	533.1	132.9	22.61	1675	0.1832	0.2059	0.1541
	6a	174.5	102.4	57.45	4.669	557.8	369.8	220.6	70.09	7.113	1732	-0.4275	-0.2943	-0.4921
	6b	61.53	27.34	14.26	3.169	240.1	217.9	83.83	43.84	3.863	426.5	-0.3503	-0.5168	-0.2496
	8a	248.6	151.6	36.74	5.605	366.1	395.9	170.5	45.9	5.45	334.9	-0.3841	-0.4859	-0.3155
	8b	133.3	68.86	59.68	3.733	356.3	123.1	75.51	67.82	9.067	381.6	0.00688	-0.0957	0.09759
	8c	296.4	123.7	107.8	6.218	392.4	205.2	78.92	44.73	3.617	275.2	-0.0123	0.05697	-0.086

Appendix C

Means (M), standard errors of the means (SEM), and p values for total ions [Ca2$^+$, Mg2$^+$, K$^+$, Na$^+$, and SO_4^{2-} (R_{Total})], base cations [Ca2$^+$, Mg2$^+$, K$^+$, and Na$^+$ (R_{BC})] and sulfate (RSO_4^{2-}) for each vegetated (v) and un-vegetated (nv) plot for all sampling periods.

			R_{Total}			R_{BC}			RSO_4^{2-}		
Period	**Site**	**V/NV**	**M**	**SEM**	**p >|t|**	**M**	**SEM**	**p >|t|**	**M**	**SEM**	**p >|t|**
July-Sep											
	8a										
		nv	105.559	22.865	0.272	25.592	23.5104	0.257	79.967	16.1382	0.3431
		v	217.272	75.043		114.728	99.2232		30.8848	17.831	
	8b										
		nv	281.347	15.606	0.0087	146.089	18.242	0.0237	135.259	3.325	0.0004
		v	131.023	23.409		49.196	20.084		81.827	3.649	
	8c										
		nv	769.51	244.59	0.1454	508.384	179.69	0.1618	261.126	64.915	0.113
		v	225.886	86.18		135.113	85.61		90.773	15.069	
	6a										
		nv	165.317	59.68	0.4049	63.389	38.78	0.3994	101.928	20.913	0.4147
		v	357.002	181.44		175.707	104.42		181.295	77.341	
	6b										
		nv	113.43	22.85	0.4465	26.084	14.05	0.444	87.345	9.03	0.451
		v	529.354	442.45		289.323	278.22		240.031	284.456	
	1										
		nv	346.604	135.26	0.0934	158.386	79.62	0.105	188.218	55.802	0.0826
		v	860.713	183.91		442.157	106.2		418.556	78.756	
	3a										
		nv	1130.06	896.27	0.6201	467.308	372.83	0.6102	662.753	523.75	0.6274
		v	580.46	426.21		231.215	181.22		349.246	245.03	
	3b										
		nv	1830.7	358.4	0.8844	1142.37	103.16	0.9674	688.33	255.27	0.7335
		v	2111.95	1522.1		1101.06	803.97		1010.89	718.14	
Oct-Dec											
	8a										
		nv	538.773	92.852	0.0409	194.471	54.575	0.0191	344.302	38.372	0.1799
		v	943.273	98.985		478.528	50.673		464.745	60.303	
	8b										
		nv	809.426	79.481	0.0313	338.433	40.847	0.0295	470.993	41.054	0.0442
		v	465.146	40.402		162.866	30.189		302.28	12.742	
	8c										
		nv	1237.02	315.78	0.1884	636.511	194.35	0.1962	600.506	127.02	0.1898
		v	632.72	170.844		273.313	55.67		359.403	45.35	
	6a										
		nv	922.81	343.26	0.271	330.763	184.13	0.3705	592.052	161.05	0.2135
		v	1589.97	392.37		710.616	315.83		879.354	90.53	
	6b										
		nv	309.308	10.67	0.4989	46.203	7.05	0.4925	263.106	10.99	0.5067
		v	509.549	244.49		154.61	225.38		354.939	114.38	

			R_{Total}			R_{BC}			RSO_4^{2-}		
Period	**Site**	**V/NV**	**M**	**SEM**	**p >|t|**	**M**	**SEM**	**p >|t|**	**M**	**SEM**	**p >|t|**
	1										
		nv	1126.81	268.7	0.4032	424.1	140.6	0.3759	702.72	128.6	0.4435
		v	4022.6	2752.4		2204.22	1576.1		1818.38	1177.1	
	3a										
		nv	4890.51	4151.3	0.4732	1663.78	1460.1	0.5063	3226.73	2691.3	0.4565
		v	1239.84	750.3		481.31	359.7		758.45	390.7	
	3b										
		nv	2008.34	841.7	0.2453	1037.45	400.26	0.257	970.89	441.44	0.2367
		v	5821.82	1805.3		2687.91	818.92		3133.91	986.39	
Jan-Mar											
	8a										
		nv	808.614	68.07	0.661	442.505	52.06	0.535	366.109	19.753	0.5782
		v	952.622	278.99		617.716	234.08		334.946	45.466	
	8b										
		nv	621.887	154.21	0.9106	265.595	101.97	0.9551	356.292	52.26	0.8581
		v	657.13	247.19		275.481	128.95		381.649	118.28	
	8c										
		nv	926.488	61.607	0.0244	534.117	54.515	0.047	392.371	19.646	0.0215
		v	607.624	66.045		332.467	43.192		275.157	24.283	
	6a										
		nv	896.75	25.5	0.2767	338.972	32.05	0.3606	557.78	39.65	0.2511
		v	2399.59	1014.5		667.581	279.51		1732.01	735.23	
	6b										
		nv	346.353	60.09	0.3801	106.296	41.48	0.4747	240.057	19.18	0.2579
		v	775.871	384.42		349.416	277.9		426.455	119.64	
	1										
		nv	1029.63	35.2	0.3961	366.74	12.07	0.3641	662.89	47.27	0.4281
		v	2493.47	1366.1		1122.76	648.75		1370.71	717.82	
	3a										
		nv	1199.7	493.22	0.9754	496.979	250.55	0.6986	702.719	243.13	0.6491
		v	1180.84	279.01		249.909	144.28		561.301	144.88	
	3b										
		nv	3097.32	1163.7	0.9796	1723.03	594.9	0.8978	1374.29	568.8	0.8718
		v	3186.48	2699.9		1511.19	1259.1		1675.29	1440.8	

Appendix D

Ionic charge balance for base cations and sulfate for all sampling periods. Three resin lysimeters for each vegetated (v) and un-vegetated (nv) plot per site are shown.

Charge Balance July-September (65 days)

			mmol per day					Ionic Charge							
Site	**v/nv**	**#**	**Ca**	**Mg**	**K**	**Na**	**SO_4^{2-}**	**Ca +2**	**Mg +2**	**K +1**	**Na +1**	**SO_4^{2-}**	**Σ BC**	**Σ SO_4^{2-}**	**Δ BC+ SO_4^{2-}**
8a	v	1	0.0018	0.0014	0.0015	0.0004	0.0004	0.0036	0.0027	0.0015	0.0004	-0.0007	0.0082	-0.0007	0.0075
8a	v	2	0.0003	0.0001	0.0002	0.0001	0.0002	0.0006	0.0002	0.0002	0.0001	-0.0005	0.0011	-0.0005	0.0006
8a	v	3	0.0032	0.0023	0.0049	0.0006	0.0005	0.0065	0.0046	0.0049	0.0006	-0.0009	0.0166	-0.0009	0.0157
8a	nv	1	0.0002	0.0001	0.0001	0.0001	0.0002	0.0004	0.0001	0.0001	0.0001	-0.0005	0.0008	-0.0005	0.0003
8a	nv	2	0.0003	0.0001	0.0001	0.0001	0.0003	0.0005	0.0002	0.0001	0.0001	-0.0005	0.0010	-0.0005	0.0005
8a	nv	3	0.0008	0.0005	0.0015	0.0002	0.0003	0.0016	0.0010	0.0015	0.0002	-0.0007	0.0043	-0.0007	0.0036
8b	v	1	0.0003	0.0001	0.0005	0.0002	0.0003	0.0005	0.0002	0.0005	0.0002	-0.0005	0.0014	-0.0005	0.0008
8b	v	2	0.0012	0.0008	0.0028	0.0004	0.0003	0.0025	0.0016	0.0028	0.0004	-0.0006	0.0073	-0.0006	0.0067
8b	v	3	0.0005	0.0004	0.0029	0.0003	0.0003	0.0010	0.0007	0.0029	0.0003	-0.0006	0.0049	-0.0006	0.0043
8b	nv	1	0.0018	0.0017	0.0085	0.0006	0.0005	0.0037	0.0034	0.0085	0.0006	-0.0009	0.0162	-0.0009	0.0153
8b	nv	2	0.0017	0.0015	0.0107	0.0005	0.0004	0.0035	0.0031	0.0107	0.0005	-0.0009	0.0178	-0.0009	0.0169
8b	nv	3	0.0015	0.0012	0.0039	0.0005	0.0005	0.0029	0.0023	0.0039	0.0005	-0.0010	0.0097	-0.0010	0.0087
8c	v	1	0.0002	0.0001	0.0002	0.0002	0.0002	0.0005	0.0001	0.0002	0.0002	-0.0005	0.0010	-0.0005	0.0005
8c	v	2	0.0033	0.0057	0.0033	0.0004	0.0003	0.0066	0.0115	0.0033	0.0004	-0.0006	0.0218	-0.0006	0.0213
8c	v	3	0.0014	0.0008	0.0029	0.0004	0.0004	0.0028	0.0016	0.0029	0.0004	-0.0008	0.0077	-0.0008	0.0069
8c	nv	1	0.0049	0.0033	0.0205	0.0014	0.0008	0.0099	0.0066	0.0205	0.0014	-0.0015	0.0383	-0.0015	0.0368
8c	nv	2	0.0084	0.0063	0.0696	0.0026	0.0014	0.0168	0.0127	0.0696	0.0026	-0.0027	0.1017	-0.0027	0.0990
8c	nv	3	0.0027	0.0018	0.0222	0.0013	0.0006	0.0054	0.0037	0.0222	0.0013	-0.0012	0.0326	-0.0012	0.0314
6a	v	1	0.0032	0.0034	0.0290	0.0008	0.0012	0.0064	0.0069	0.0290	0.0008	-0.0023	0.0431	-0.0023	0.0408
6a	v	2	0.0002	0.0001	0.0001	0.0001	0.0003	0.0005	0.0002	0.0001	0.0001	-0.0005	0.0008	-0.0005	0.0003
6a	v	3	0.0013	0.0019	0.0083	0.0004	0.0005	0.0027	0.0038	0.0083	0.0004	-0.0010	0.0152	-0.0010	0.0142
6a	nv	1	0.0015	0.0027	0.0016	0.0003	0.0005	0.0029	0.0055	0.0016	0.0003	-0.0010	0.0103	-0.0010	0.0094
6a	nv	2	0.0006	0.0004	0.0017	0.0003	0.0003	0.0012	0.0009	0.0017	0.0003	-0.0006	0.0040	-0.0006	0.0033
6a	nv	3	0.0002	0.0000	0.0000	0.0001	0.0002	0.0004	0.0001	0.0000	0.0001	-0.0005	0.0006	-0.0005	0.0001
6b	v	1	0.0002	0.0001	0.0001	0.0002	0.0003	0.0005	0.0001	0.0001	0.0002	-0.0005	0.0009	-0.0005	0.0003
6b	v	2	0.0127	0.0078	0.0266	0.0020	0.0020	0.0253	0.0156	0.0266	0.0020	-0.0040	0.0695	-0.0040	0.0656
6b	v	3	0.0002	0.0000	0.0001	0.0001	0.0003	0.0004	0.0001	0.0001	0.0001	-0.0005	0.0007	-0.0005	0.0002
6b	nv	1	0.0009	0.0006	0.0006	0.0003	0.0004	0.0018	0.0011	0.0006	0.0003	-0.0007	0.0038	-0.0007	0.0030
6b	nv	2	0.0002	0.0001	0.0001	0.0001	0.0003	0.0005	0.0001	0.0001	0.0001	-0.0006	0.0008	-0.0006	0.0002
6b	nv	3	0.0003	0.0000	0.0000	0.0001	0.0003	0.0006	0.0001	0.0000	0.0001	-0.0005	0.0007	-0.0005	0.0002
1	v	1	0.0034	0.0021	0.0290	0.0031	0.0011	0.0069	0.0042	0.0290	0.0031	-0.0022	0.0431	-0.0022	0.0409
1	v	2	0.0062	0.0038	0.0551	0.0055	0.0020	0.0124	0.0075	0.0551	0.0055	-0.0040	0.0805	-0.0040	0.0765
1	v	3	0.0037	0.0029	0.0184	0.0023	0.0013	0.0074	0.0059	0.0184	0.0023	-0.0025	0.0340	-0.0025	0.0315
1	nv	1	0.0016	0.0008	0.0109	0.0020	0.0007	0.0031	0.0017	0.0109	0.0020	-0.0013	0.0177	-0.0013	0.0164
1	nv	2	0.0004	0.0001	0.0011	0.0003	0.0003	0.0008	0.0003	0.0011	0.0003	-0.0006	0.0025	-0.0006	0.0019
1	nv	3	0.0026	0.0016	0.0285	0.0027	0.0010	0.0052	0.0033	0.0285	0.0027	-0.0020	0.0397	-0.0020	0.0377
3a	v	1	0.0090	0.0049	0.0271	0.0024	0.0029	0.0181	0.0099	0.0271	0.0024	-0.0058	0.0574	-0.0058	0.0516
3a	v	2	0.0007	0.0003	0.0043	0.0003	0.0004	0.0015	0.0007	0.0043	0.0003	-0.0008	0.0067	-0.0008	0.0060
3a	v	3	0.0005	0.0004	0.0015	0.0003	0.0003	0.0010	0.0008	0.0015	0.0003	-0.0007	0.0036	-0.0007	0.0029
3a	nv	1	0.0002	0.0001	0.0001	0.0001	0.0002	0.0005	0.0001	0.0001	0.0001	-0.0005	0.0008	-0.0005	0.0003
3a	nv	2	0.0021	0.0014	0.0117	0.0006	0.0007	0.0042	0.0028	0.0117	0.0006	-0.0015	0.0194	-0.0015	0.0179
3a	nv	3	0.0167	0.0109	0.0498	0.0023	0.0059	0.0335	0.0218	0.0498	0.0023	-0.0119	0.1073	-0.0119	0.0954
3b	v	1	0.0039	0.0033	0.0100	0.0021	0.0010	0.0078	0.0066	0.0100	0.0021	-0.0020	0.0265	-0.0020	0.0245
3b	v	2	0.0208	0.0188	0.0560	0.0165	0.0060	0.0416	0.0377	0.0560	0.0165	-0.0119	0.1518	-0.0119	0.1399
3b	v	3	0.0253	0.0233	0.0551	0.0091	0.0060	0.0506	0.0467	0.0551	0.0091	-0.0120	0.1614	-0.0120	0.1494
3b	nv	1	0.0165	0.0146	0.0385	0.0066	0.0033	0.0331	0.0293	0.0385	0.0066	-0.0066	0.1075	-0.0066	0.1010
3b	nv	2	0.0225	0.0212	0.0521	0.0108	0.0066	0.0449	0.0423	0.0521	0.0108	-0.0132	0.1502	-0.0132	0.1370
3b	nv	3	0.0127	0.0131	0.0356	0.0046	0.0015	0.0255	0.0262	0.0356	0.0046	-0.0030	0.0917	-0.0030	0.0887

Charge Balance October-December (63 days)

			mmol per day					**Ionic Charge**							
Site	**v/nv**	**#**	**Ca**	**Mg**	**K**	**Na**	**SO_4^{2-}**	**Ca +2**	**Mg +2**	**K +1**	**Na +1**	**SO_4^{2-}**	**Σ BC**	**Σ SO_4^{2-}**	**Δ BC+ SO_4^{2-}**
8a	v	1	0.0067	0.0042	0.0006	0.0002	0.0012	0.0133	0.0084	0.0006	0.0002	-0.0024	0.0225	-0.0024	0.0201
8a	v	2	0.0091	0.0063	0.0012	0.0002	0.0017	0.0182	0.0126	0.0012	0.0002	-0.0034	0.0323	-0.0034	0.0289
8a	v	3	0.0071	0.0046	0.0017	0.0002	0.0019	0.0142	0.0093	0.0017	0.0002	-0.0039	0.0253	-0.0039	0.0215
8a	nv	1	0.0042	0.0028	0.0009	0.0002	0.0014	0.0084	0.0055	0.0009	0.0002	-0.0028	0.0149	-0.0028	0.0121
8a	nv	2	0.0014	0.0008	0.0003	0.0000	0.0009	0.0028	0.0016	0.0003	0.0000	-0.0019	0.0048	-0.0019	0.0029
8a	nv	3	0.0033	0.0027	0.0005	0.0001	0.0012	0.0067	0.0053	0.0005	0.0001	-0.0025	0.0126	-0.0025	0.0101
8b	v	1	0.0014	0.0012	0.0011	0.0001	0.0010	0.0028	0.0024	0.0011	0.0001	-0.0019	0.0065	-0.0019	0.0045
8b	v	2	0.0033	0.0021	0.0010	0.0001	0.0011	0.0066	0.0041	0.0010	0.0001	-0.0022	0.0118	-0.0022	0.0096
8b	v	3	0.0017	0.0012	0.0008	0.0001	0.0011	0.0034	0.0025	0.0008	0.0001	-0.0021	0.0068	-0.0021	0.0047
8b	nv	1	0.0043	0.0034	0.0013	0.0002	0.0017	0.0086	0.0069	0.0013	0.0002	-0.0034	0.0170	-0.0034	0.0137
8b	nv	2	0.0059	0.0044	0.0018	0.0002	0.0019	0.0118	0.0088	0.0018	0.0002	-0.0037	0.0226	-0.0037	0.0189
8b	nv	3	0.0038	0.0030	0.0014	0.0001	0.0014	0.0077	0.0060	0.0014	0.0001	-0.0027	0.0152	-0.0027	0.0125
8c	v	1	0.0028	0.0015	0.0023	0.0001	0.0013	0.0056	0.0029	0.0023	0.0001	-0.0026	0.0110	-0.0026	0.0084
8c	v	2	0.0032	0.0017	0.0007	0.0001	0.0010	0.0064	0.0034	0.0007	0.0001	-0.0019	0.0105	-0.0019	0.0086
8c	v	3	0.0058	0.0033	0.0017	0.0002	0.0015	0.0116	0.0066	0.0017	0.0002	-0.0030	0.0200	-0.0030	0.0170
8c	nv	1	0.0126	0.0080	0.0030	0.0003	0.0028	0.0252	0.0160	0.0030	0.0003	-0.0055	0.0445	-0.0055	0.0390
8c	nv	2	0.0109	0.0078	0.0052	0.0003	0.0022	0.0218	0.0157	0.0052	0.0003	-0.0045	0.0430	-0.0045	0.0385
8c	nv	3	0.0031	0.0020	0.0018	0.0001	0.0013	0.0063	0.0040	0.0018	0.0001	-0.0025	0.0122	-0.0025	0.0097
6a	v	1	0.0077	0.0072	0.0211	0.0003	0.0034	0.0154	0.0144	0.0211	0.0003	-0.0069	0.0512	-0.0069	0.0443
6a	v	2	0.0035	0.0028	0.0010	0.0002	0.0024	0.0069	0.0056	0.0010	0.0002	-0.0049	0.0136	-0.0049	0.0088
6a	v	3	0.0059	0.0056	0.0049	0.0002	0.0033	0.0118	0.0111	0.0049	0.0002	-0.0066	0.0281	-0.0066	0.0215
6a	nv	1	0.0011	0.0007	0.0001	0.0000	0.0011	0.0023	0.0014	0.0001	0.0000	-0.0022	0.0038	-0.0022	0.0016
6a	nv	2	0.0035	0.0029	0.0007	0.0001	0.0020	0.0070	0.0057	0.0007	0.0001	-0.0040	0.0135	-0.0040	0.0095
6a	nv	3	0.0079	0.0078	0.0044	0.0003	0.0031	0.0158	0.0157	0.0044	0.0003	-0.0061	0.0361	-0.0061	0.0300
6b	v	1	0.0004	0.0001	0.0001	0.0000	0.0008	0.0007	0.0002	0.0001	0.0000	-0.0016	0.0011	-0.0016	-0.0006
6b	v	2	0.0066	0.0036	0.0015	0.0002	0.0020	0.0132	0.0073	0.0015	0.0002	-0.0041	0.0221	-0.0041	0.0180
6b	v	3	0.0005	0.0001	0.0001	0.0000	0.0009	0.0010	0.0003	0.0001	0.0000	-0.0017	0.0014	-0.0017	-0.0003
6b	nv	1	0.0008	0.0004	0.0002	0.0001	0.0008	0.0017	0.0007	0.0002	0.0001	-0.0017	0.0027	-0.0017	0.0010
6b	nv	2	0.0006	0.0002	0.0001	0.0000	0.0009	0.0011	0.0004	0.0001	0.0000	-0.0019	0.0017	-0.0019	-0.0002
6b	nv	3	0.0009	0.0004	0.0002	0.0001	0.0010	0.0018	0.0007	0.0002	0.0001	-0.0019	0.0028	-0.0019	0.0009
1	v	1	0.0046	0.0025	0.0036	0.0003	0.0019	0.0091	0.0050	0.0036	0.0003	-0.0039	0.0181	-0.0039	0.0142
1	v	2	0.0569	0.0339	0.0545	0.0047	0.0145	0.1138	0.0677	0.0545	0.0047	-0.0290	0.2408	-0.0290	0.2118
1	v	3	0.0114	0.0056	0.0069	0.0006	0.0025	0.0228	0.0111	0.0069	0.0006	-0.0051	0.0414	-0.0051	0.0363
1	nv	1	0.0096	0.0046	0.0048	0.0010	0.0033	0.0191	0.0092	0.0048	0.0010	-0.0066	0.0340	-0.0066	0.0274
1	nv	2	0.0045	0.0021	0.0019	0.0004	0.0022	0.0090	0.0042	0.0019	0.0004	-0.0044	0.0155	-0.0044	0.0111
1	nv	3	0.0036	0.0017	0.0016	0.0003	0.0018	0.0072	0.0034	0.0016	0.0003	-0.0036	0.0125	-0.0036	0.0089
3a	v	1	0.0199	0.0097	0.0039	0.0003	0.0053	0.0398	0.0194	0.0039	0.0003	-0.0107	0.0633	-0.0107	0.0527
3a	v	2	0.0037	0.0020	0.0007	0.0001	0.0016	0.0075	0.0040	0.0007	0.0001	-0.0032	0.0123	-0.0032	0.0091
3a	v	3	0.0004	0.0001	0.0001	0.0001	0.0010	0.0008	0.0002	0.0001	0.0001	-0.0020	0.0012	-0.0020	-0.0008
3a	nv	1	0.0047	0.0031	0.0009	0.0002	0.0022	0.0093	0.0063	0.0009	0.0002	-0.0044	0.0166	-0.0044	0.0122
3a	nv	2	0.0018	0.0009	0.0003	0.0001	0.0015	0.0037	0.0018	0.0003	0.0001	-0.0030	0.0059	-0.0030	0.0029
3a	nv	3	0.0697	0.0454	0.0171	0.0006	0.0299	0.1395	0.0908	0.0171	0.0006	-0.0599	0.2480	-0.0599	0.1881
3b	v	1	0.0498	0.0444	0.0094	0.0027	0.0143	0.0995	0.0889	0.0094	0.0027	-0.0287	0.2006	-0.0287	0.1719
3b	v	2	0.0909	0.0577	0.0057	0.0021	0.0382	0.1818	0.1153	0.0057	0.0021	-0.0765	0.3051	-0.0765	0.2286
3b	v	3	0.0259	0.0251	0.0051	0.0010	0.0075	0.0518	0.0501	0.0051	0.0010	-0.0149	0.1080	-0.0149	0.0931
3b	nv	1	0.0203	0.0173	0.0047	0.0008	0.0049	0.0407	0.0347	0.0047	0.0008	-0.0098	0.0808	-0.0098	0.0710
3b	nv	2	0.0398	0.0389	0.0108	0.0022	0.0125	0.0796	0.0778	0.0108	0.0022	-0.0251	0.1705	-0.0251	0.1454
3b	nv	3	0.0088	0.0090	0.0015	0.0004	0.0018	0.0175	0.0180	0.0015	0.0004	-0.0037	0.0374	-0.0037	0.0337
														Avg Δ	0.0361
														STDEV	0.0567
														SE	0.0082

Charge Balance January-March (61 days)

			mmol per day					Ionic Charge							
Site	**v/nv**	**#**	**Ca**	**Mg**	**K**	**Na**	**SO_4^{2-}**	**Ca +2**	**Mg +2**	**K +1**	**Na +1**	**SO_4^{2-}**	**Σ BC**	**Σ SO_4^{2-}**	**Δ BC+ SO_4^{2-}**
8a	v	1	0.0171	0.0121	0.0160	0.0028	0.0014	0.0343	0.0242	0.0160	0.0028	-0.0029	0.0773	-0.0029	0.0744
8a	v	2	0.0042	0.0031	0.0043	0.0013	0.0009	0.0084	0.0063	0.0043	0.0013	-0.0018	0.0202	-0.0018	0.0184
8a	v	3	0.0083	0.0058	0.0100	0.0020	0.0012	0.0166	0.0116	0.0100	0.0020	-0.0023	0.0403	-0.0023	0.0380
8a	nv	1	0.0048	0.0049	0.0057	0.0017	0.0012	0.0095	0.0098	0.0057	0.0017	-0.0024	0.0267	-0.0024	0.0243
8a	nv	2	0.0069	0.0075	0.0091	0.0029	0.0014	0.0139	0.0150	0.0091	0.0029	-0.0028	0.0409	-0.0028	0.0381
8a	nv	3	0.0069	0.0063	0.0094	0.0018	0.0012	0.0138	0.0126	0.0094	0.0018	-0.0024	0.0376	-0.0024	0.0351
8b	v	1	0.0051	0.0058	0.0357	0.0066	0.0021	0.0101	0.0116	0.0357	0.0066	-0.0042	0.0640	-0.0042	0.0598
8b	v	2	0.0014	0.0009	0.0027	0.0007	0.0007	0.0027	0.0018	0.0027	0.0007	-0.0014	0.0080	-0.0014	0.0066
8b	v	3	0.0028	0.0026	0.0064	0.0029	0.0012	0.0056	0.0052	0.0064	0.0029	-0.0023	0.0200	-0.0023	0.0177
8b	nv	1	0.0020	0.0018	0.0068	0.0010	0.0011	0.0041	0.0036	0.0068	0.0010	-0.0021	0.0156	-0.0021	0.0134
8b	nv	2	0.0059	0.0050	0.0234	0.0020	0.0016	0.0118	0.0100	0.0234	0.0020	-0.0032	0.0472	-0.0032	0.0440
8b	nv	3	0.0020	0.0017	0.0092	0.0011	0.0011	0.0041	0.0034	0.0092	0.0011	-0.0021	0.0178	-0.0021	0.0157
8c	v	1	0.0057	0.0039	0.0051	0.0016	0.0011	0.0115	0.0079	0.0051	0.0016	-0.0021	0.0260	-0.0021	0.0239
8c	v	2	0.0040	0.0024	0.0065	0.0010	0.0008	0.0079	0.0048	0.0065	0.0010	-0.0016	0.0203	-0.0016	0.0187
8c	v	3	0.0057	0.0034	0.0179	0.0014	0.0010	0.0113	0.0068	0.0179	0.0014	-0.0020	0.0375	-0.0020	0.0355
8c	nv	1	0.0066	0.0044	0.0104	0.0021	0.0013	0.0133	0.0088	0.0104	0.0021	-0.0027	0.0346	-0.0027	0.0319
8c	nv	2	0.0073	0.0055	0.0358	0.0026	0.0015	0.0146	0.0109	0.0358	0.0026	-0.0030	0.0639	-0.0030	0.0609
8c	nv	3	0.0082	0.0054	0.0249	0.0023	0.0013	0.0165	0.0109	0.0249	0.0023	-0.0025	0.0546	-0.0025	0.0521
6a	v	1	0.0166	0.0165	0.0234	0.0040	0.0108	0.0333	0.0330	0.0234	0.0040	-0.0217	0.0936	-0.0217	0.0719
6a	v	2	0.0031	0.0027	0.0060	0.0017	0.0021	0.0063	0.0055	0.0060	0.0017	-0.0042	0.0194	-0.0042	0.0152
6a	v	3	0.0079	0.0080	0.0169	0.0024	0.0051	0.0159	0.0160	0.0169	0.0024	-0.0102	0.0511	-0.0102	0.0409
6a	nv	1	0.0040	0.0037	0.0048	0.0016	0.0021	0.0080	0.0074	0.0048	0.0016	-0.0043	0.0217	-0.0043	0.0175
6a	nv	2	0.0048	0.0043	0.0138	0.0016	0.0020	0.0096	0.0086	0.0138	0.0016	-0.0040	0.0336	-0.0040	0.0295
6a	nv	3	0.0043	0.0046	0.0194	0.0020	0.0017	0.0086	0.0092	0.0194	0.0020	-0.0033	0.0393	-0.0033	0.0359
6b	v	1	0.0002	0.0001	0.0006	0.0006	0.0007	0.0003	0.0002	0.0006	0.0006	-0.0014	0.0018	-0.0014	0.0004
6b	v	2	0.0141	0.0087	0.0259	0.0026	0.0021	0.0282	0.0173	0.0259	0.0026	-0.0043	0.0740	-0.0043	0.0698
6b	v	3	0.0020	0.0016	0.0025	0.0011	0.0016	0.0041	0.0031	0.0025	0.0011	-0.0032	0.0107	-0.0032	0.0075
6b	nv	1	0.0011	0.0008	0.0020	0.0009	0.0008	0.0022	0.0016	0.0020	0.0009	-0.0015	0.0067	-0.0015	0.0052
6b	nv	2	0.0027	0.0021	0.0059	0.0018	0.0010	0.0053	0.0041	0.0059	0.0018	-0.0019	0.0172	-0.0019	0.0152
6b	nv	3	0.0009	0.0005	0.0015	0.0009	0.0008	0.0017	0.0010	0.0015	0.0009	-0.0016	0.0051	-0.0016	0.0035
1	v	1	0.0027	0.0016	0.0098	0.0024	0.0014	0.0053	0.0033	0.0098	0.0024	-0.0028	0.0208	-0.0028	0.0181
1	v	2	0.0264	0.0163	0.1894	0.0211	0.0096	0.0529	0.0327	0.1894	0.0211	-0.0193	0.2960	-0.0193	0.2767
1	v	3	0.0113	0.0060	0.0395	0.0068	0.0033	0.0226	0.0121	0.0395	0.0068	-0.0066	0.0810	-0.0066	0.0745
1	nv	1	0.0059	0.0031	0.0143	0.0050	0.0020	0.0118	0.0061	0.0143	0.0050	-0.0040	0.0373	-0.0040	0.0333
1	nv	2	0.0052	0.0029	0.0126	0.0051	0.0026	0.0103	0.0058	0.0126	0.0051	-0.0051	0.0338	-0.0051	0.0287
1	nv	3	0.0060	0.0031	0.0080	0.0044	0.0023	0.0119	0.0062	0.0080	0.0044	-0.0047	0.0305	-0.0047	0.0258
3a	v	1	0.0121	0.0067	0.0289	0.0053	0.0029	0.0243	0.0135	0.0289	0.0053	-0.0058	0.0719	-0.0058	0.0661
3a	v	2	0.0114	0.0066	0.0239	0.0019	0.0018	0.0228	0.0131	0.0239	0.0019	-0.0036	0.0617	-0.0036	0.0581
3a	v	3	0.0038	0.0048	0.0127	0.0023	0.0012	0.0076	0.0096	0.0127	0.0023	-0.0023	0.0323	-0.0023	0.0300
3a	nv	1	0.0041	0.0033	0.0091	0.0017	0.0016	0.0082	0.0065	0.0091	0.0017	-0.0032	0.0255	-0.0032	0.0223
3a	nv	2	0.0029	0.0018	0.0095	0.0015	0.0016	0.0058	0.0035	0.0095	0.0015	-0.0032	0.0202	-0.0032	0.0171
3a	nv	3	0.0130	0.0094	0.0512	0.0042	0.0041	0.0261	0.0189	0.0512	0.0042	-0.0083	0.1003	-0.0083	0.0921
3b	v	1	0.0375	0.0410	0.0504	0.0155	0.0108	0.0751	0.0819	0.0504	0.0155	-0.0217	0.2228	-0.0217	0.2012
3b	v	2	0.1052	0.0965	0.1718	0.0401	0.0274	0.2103	0.1930	0.1718	0.0401	-0.0548	0.6153	-0.0548	0.5606
3b	v	3	0.0035	0.0029	0.0082	0.0015	0.0008	0.0070	0.0058	0.0082	0.0015	-0.0016	0.0224	-0.0016	0.0208
3b	nv	1	0.0292	0.0343	0.0571	0.0198	0.0068	0.0584	0.0687	0.0571	0.0198	-0.0135	0.2040	-0.0135	0.1905
3b	nv	2	0.0884	0.0727	0.0647	0.0260	0.0282	0.1767	0.1454	0.0647	0.0260	-0.0564	0.4128	-0.0564	0.3565
3b	nv	3	0.0149	0.0146	0.0359	0.0054	0.0028	0.0297	0.0292	0.0359	0.0054	-0.0056	0.1002	-0.0056	0.0946
														Avg Δ	0.0643
														STDEV	0.1003
														SE	0.0145

Appendix E

Example field sites and ion exchange resin lysimeters.

Template 1.
A 1 year post reclamation site characterized by herbaceous ground cover.

Template 2.
A site six years post reclamation has seedlings and maturing trees present.

Template 3.
Ion exchange resins and screened resin lysimeter.

Template 4.
Screened resin lysimeter and PVC pole.

Appendix F

This appendix contains procedures for making a mixed bed resin, loading and removing ion exchange resins from resin lysimeters, and extracting resins with 2N HCl.

Procedure for Loading Resin Lysimeter

Materials:

Amberlite IRA-400 Cl$^-$
Amberlite IRA-120 H$^+$
2 spaculas
2 plastic dishes
Glass stir rod
Funnel
Bucket w/ lid
Lysimeter (screened pvc)
Casing (pvc pipe)
Quartz wool
Parafilm
200 ml beaker (or other appropriate size)

Determine Ion exchange resins to be used and their exchange equivalencies:

Amberlite IRA-400 Cl$^-$	1.4 exchange equivalency
Amberlite IRA-120 H$^+$	1.8 exchange equivalency

Determine difference in exchange equivalency

$[(Y2 - Y1)/ Y1] *100 = \%$ change
$[(1.8 - 1.4)/ 1.4] * 100 = 28.57 \%$

Want 28.57% more Cl$^-$ than H$^+$

Volume of Lysimeter

$V=\pi r^2 h$
$\pi\ (.375)^2\ (8) = 3.53\ in^3$

Convert to ml:

$3.53\ in^3 = 57.85$ ml

How much Cl^- to H^+ ?

- First sampling season:

½ lysimeter = 29 ml
Cl^- = 16 ml
H^+ = 12.5 ml

$$\frac{Cl^-}{H^+} = \frac{1.4}{1.8} = \frac{12.5ml}{x}$$

$$x = 16ml$$

$$\frac{16 - 12.5}{12.5} * 100 = 28\%$$

- All other sampling seasons:

48 ml resin used to leave enough room for quartz wool packing
Cl^- = 27 ml
H^+ = 21 ml

$$\frac{27 - 21}{21} * 100 = 28.57\ \%$$

- Alternatively, use the specific gravity for your chosen resins to determine the mass needed to fill a given volume

Material Prep

1. All storage containers and lysimeter components must be cleaned
   - Buckets with lids, casings, and slip caps DI rinsed 4X
   - Points and screened PVC 48 hour DI bath (in buckets with lids)
2. All lab dishes to be used must be acid washed
3. Screw pointed plugs onto screened PVC

Procedure for loading mix bed resins into resin lysimeters

1. Prepare two dishes with IRA 400 Cl^- and IRA 120 H^+
   - Use separate spaculas and stir bars for both
2. Using a 50 ml graduated cylinder to measure out resin 27 ml Cl^-
   - Scoop in small amounts to avoid overfilling
   - Gently tap base of graduated cylinder to even out resins for an accurate measurement (a sponge underneath absorbs the impact and keeps glassware from cracking)
   - Use DI water to rinse resin out of the graduated cylinder into a beaker (200 ml is an appropriate size). Set beaker aside
3. Repeat step 5 for 21 ml H^+

4. Combine H^+ and Cl^- into the same beaker. Use a stir bar and DI water to create a well-mixed slurry.
5. Pour into the lysimeter with a funnel
6. Pack the top with quartz wool and seal with parafilm
7. Store sealed in DI cleaned bucket (or other appropriate container). Refrigerate until use.

Removing Resins from Resin Lysimeter

Materials:

2 150 ml beakers
DI water squirt bottle
Whatman 1 filter paper
Funnel
Spacula with flat side
250 ml Nalgene bottle

Procedure:

1. Remove parafilm, quartz wool, and pointed plug (carefully). Set pointed plug aside for cleaning.
2. Using DI water, rinse resins from lysimeter into a small beaker (150 ml is appropriate). Use a DI squirt bottle to clean resins from plug and internal threading.
3. Set up Whatman 1 filter paper in funnel, and set on 150 ml beaker. Pour resins from 1st beaker into funnel to drain water.
4. After water has drained completely, remove resins from filter. Use the flat sided spacula to gently scrape resins out. Open filter paper up to remove resins that catch in crevices. Put into a labeled 250 ml Nalgene bottle.

Resin Extraction with 2N HCl

Materials:

Butt tons of 2N HCl (30 L)
Whatman 1 filter paper
Funnel
250 ml graduated cylinder
peristaltic pump (optional)
DI water
Shaker table
1L bottle
Preferred storage container (10ml bottles, 150 ml nalgenes)

Procedure:

1. Prepare 30L of 2N HCl. Each 250 ml Nalgene bottle will receive 3 175 ml extractions.

2. Peristaltic pump:
    - Before use clean all hoses on peristaltic pump and replace if needed.
    - Prime with DI water before pumping acid.
    - Calibrate the peristaltic pump to dispense 175 ml. Set desired flow rate. Use a 250 ml graduated cylinder to check calibration. Adjust if needed.
3. Dispense 175 ml of 2N HCl into graduated cylinder. Pour into bottle with resins. Seal.
4. Place on shaker table for 1 hr (about 20 can be done at one time per table)
5. Take off shaker and let stand until resins settle
6. Pour off solution into a liter bottle, leaving resins in the 250 ml nalgene. Pour slowly to get as much of the solution out without pouring resins off.
7. Repeat step 2-6 twice more.
8. Once all three extractions have been combined into the liter bottle, seal bottle and mix solution well.
9. Filter the solution using a Whatman 1 filter placed into a funnel. Filter into your preferred storage container (10 ml bottles, 150 ml nalgenes ect). Store frozen until ready to run on ICP