Biochar 2011 Data Summary

Mountain Studies Institute and Research Services LLC in cooperation with the Bureau of Land Management and the U.S Forest Service



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Executive Summary

More than 120 years of hardrock mining in the Upper Animas River basin has left a legacy of thousands of abandoned mine sites where surface disturbance and metal laden waters cause soil and water impairment.

Many of the larger sites in the basin have seen remediation efforts and been improved by past and ongoing actions of the Animas River Stakeholders Group (ARSG), Bureau of Land Management (BLM), U.S. Forest Service (USFS), U.S Environmental Protection Agency (EPA), and Sunnyside Gold Corporation. However, due to the magnitude of the problem (>5,000 sites), some sites have difficulty of access and associated costs, traditional remediation techniques like hydrologic and physical controls, and removal of material to other sites, that are prohibitively expensive.

As a result, the USFS, BLM and other parties have sought less costly alternatives to traditional remediation methods. Phytostabilization is one method that has shown promise at other contaminated sites. Phytostabilization involves establishing a vegetative cover, stabilizing soil, and reducing the potential for polluted material to enter watercourses. Successful when applied at certain sites, phytostabilization requires tolerant plant species and soil conditions which enable natural successional processes without repeated inputs of fertilizer or irrigation. Soil conditions can be especially limiting for phytostabilization on mining impacted soils, due in part to low soil pH and high concentrations of metals that are toxic to plants.

The harsh soil and climatic conditions of mine sites in the Upper Animas basin pose challenges for traditional soil improvement techniques. These challenges are due in part to a lack of available native soil and climatic conditions that limit the use of traditional remediation plant cultivars. In addition, many of the sites needing remediation contain soils with toxic levels of Cu, Ni, Mn, Pb and Zn. An alternative soil amendment, biochar, has been used successfully at other sites with heavy metal contamination. Biochar is a low density, carbon rich product that is the result of pyrolyzing biological material. For our trials, we used biochar sourced from Colorado Lodgepole pine and Ponderosa pine that were acquired from commercial distributors using single and multiple chamber pyrolysis units.

Our trials were conducted at sites near Silverton, Colorado, on soils ranging from pH <3.0 to minimally disturbed alpine forest soils (pH 5-6). Our trials included large ($^{1}/4$ acre) and small (2-3 m²) field plots, container trials, soil column tests, and laboratory analyses of soil and water chemistry.

Findings from two years of trials indicate that biochar significantly affects soil physical properties relative to control soils in the following ways:

- Soil moisture content is increased
- Soils retain moisture for longer periods following wetting events
- Bulk density is decreased
- Soil leachate concentrations for some analytes (Fe, Al) are decreased while others (Cd, Cu, As, Mn, Ni, Pb, and Zn) showed small increases no change

Vegetation responses to biochar additions are summarized by:

- Increased spatial extent of cover
- Above ground biomass is increased
- Faster biomass accumulation during initial season of growth

Our results suggest that biochar may be a suitable soil amendment (i.e., differential and significant improvement in soils and vegetation growth) for sites characterized by soil pH of less than five (pH <5) and metal concentrations that exceed plant toxicity levels. Conversely, our results indicate that biochar may not be suitable at sites with soil pH greater than or equal to six (pH \geq 6), and low concentrations of plant toxicity.

Using pyrolized biomass as part of a larger strategy of renewable energy, soil improvement, waste reduction and carbon storage may be an effective means to reduce risk to wildfire, improve forest health, improve degraded soils and water resources, and increase the productivity of lands across the Southwest, and in the San Juan Mountain region, especially. The decision to use biochar as a soil amendment should be guided by an understanding of the specific site conditions, goals for that location/site, origin and composition of the biochar material, and full cost accounting which should include the multiple externalities associated with using any material, especially a processed biomass material (e.g., energy requirement, harvest, processing, transportation, and application costs).

Introduction

To address the challenge of re-establishing native vegetation communities and reducing metal pollution at abandoned mine sites in the Upper Animas Basin, we sought to determine the suitability of biochar as a soil remediation and water quality treatment tool for abandoned mine lands in the San Juan Mountains, near Silverton, Colorado. Our research assessed the effect of biochar and other amendments on the mobility and potential toxicity of metalliferous contaminants in soils and acid mine drainage (AMD) emanating from abandoned mine sites. Our ongoing field and container trials continue to examine the effects of biochar treatments on vegetation establishment and growth, soil physical dynamics, and soil/water chemistry. Field sites are located on USFS and BLM abandoned mine lands and other disturbed soil sites. Sites were located near Silverton, CO at elevations of 2,800 to 3,700 meters, with soil conditions that ranged from pure waste rock to partially reclaimed forest soil.

Initial field trials were installed in 2009 at the Lackawanna Mill and Brooklyn mine sites. Based on this preliminary work, four additional sites were installed in 2010 (Highland Mary, Joe and John, Bonner, and Little Molas). Results from single season trials in 2010 indicated that when compared to seeding alone, the addition of a 30% by volume biochar soil amendment showed that on low pH soils, statistically significant (10 - 20%) increases in vegetation cover were observed. Conversely, there was no significant increase in cover for non-acidic soils. Biochar treatments also significantly increased water holding capacity in all soils by 12-19%. Seed emergence was faster with more emergence and longer sprouts (17 - 45 mm increase in length) at 120 hours for biochar treatments as compared to soil only; however the greatest numbers of seeds emerging, with the longest sprouts, were in treatments that contained both biochar and straw mulch. Above ground biomass was positively affected by biochar additions, with acid mine sites showing a 180% increase in biomass. The effect of biochar on above-ground biomass on nonacid sites was small, with a magnitude increase of 5-11%. The results for the effect of biochar on soil leachate chemistry are mixed, with some analytes showing a decrease in leachate concentration at 40 days (Al, Fe), some showing an increase in concentration (Cu) and most showing very small or no differences (Cd, As, Mn, Ni, Pb, Zn) in leachate concentration when compared to a soil only control. Confirmation of these results may indicate that biochar, when combined with organic mulch, may be a useful tool for soil restoration at abandoned mine sites, or at other locations with acidic soils.

Unresolved questions from our 2010 trials include:

- 1. What are optimal biochar application rates,
- 2. What is the long term effect of biochar additions on the accumulation of carbon,
- 3. What is the effect on metal mobility at the field scale,
- 4. How should land managers overcome some of the practical obstacles to mechanized use of biochar at abandoned mine sites,
- 5. Can biochar be used to treat Acid Mine Drainage/heavy metal laden waters?

In 2011 we built upon our experience in 2010 and sought to further evaluate the effect of biochar on vegetation growth, and soil physical and chemical properties, as well as answer some of our unresolved questions from 2010 trials. We focused on mining-affected sites as the results from our 2010 trials found little or no effect of biochar on vegetation growth nor above ground biomass in soils impacted by activities other than mining.

In addition to the empirical data we collected from our container and field trials, we benefited by the increasing number of peer-reviewed scientific articles published on the topic of biochar (305 papers since 1998), with 134 papers in 2011 alone. Though there is an increasing interest in using pyrolized

carbon rich material for soil improvement, waste reduction, and carbon storage, the number of citations that focus specifically on using biochar for remediating mining-affected soils is small. A recent Web of Science search (wokinfo.com; Dec., 2011) illustrates this pattern with only 26 published articles which included biochar and heavy metals as keywords, 17 of which were published in 2011 alone (**Figure 1**). Though there is a relative paucity of studies examining biochar and its efficacy as an amendment for mining impacted soils, the increasing number of publications indicates a growing consensus regarding the characterization of biochars and their utility for restoring degraded soils. For example, a recent paper by Beesley et al. (2011) summarizes the current understanding of biochar and its impact on mining affected soils:

- Biochars are biological residues combusted under low oxygen conditions, resulting in a porous, low density carbon rich material;
- Large surface areas and cation exchange capacities (CEC) are controlled by source material and pyrolysis temperature;
- Biochars surface area and CEC enables enhanced adsorption of both organic and inorganic contaminants to biochar surfaces, reducing organic and inorganic mobility/leachability in soils;
- Liming effects and/or the release of dissolved organic carbon (DOC) into soil water may increase arsenic mobility, and biochars enhanced retention of some plant nutrients may restrict re-vegetation on degraded soils amended only with biochar;
- Combinations of composts, manures and other amendments with biochar may be most effective for soils requiring stabilization by re-vegetation;
- Specific mechanisms of contaminant-biochar retention and release over time and the environmental impact of biochar amendments on soil organisms remain unclear and should be investigated to ensure that the management of environmental pollution coincides with ecological sustainability.

This report is for practitioners of mine land remediation and who are considering incorporating biochar as a part of their remediation tools. This report seeks to provide evidence based on practical examples of biochar use at a range of mining impacted sites. Our hope is that readers will use the information provided to enable a decision regarding whether to use biochar or not at their site. We have provided site-specific information regarding the soil, water, and environmental conditions of our sites with the hope that readers will be able to transfer the understanding provided here to other sites and to better evaluate whether biochar use should be a part of their remediation strategy

Setting

A comprehensive description of the geology of the Upper Animas Basin can be found in Yager and Bove (2007) and Yager, Choate and Stanton (2008). These reports include major units (**Figure 2**) where mining was concentrated and which have the greatest degree of mining-related impacts. As Yager and others have noted, the Upper Animas basin and the western San Juan Mountains record a relatively complete geologic record from the Precambrian to Cenozoic era. Evidence for this is demonstrated by Precambrian deposits found to the south of the upper Animas River (segments YXu) and Paleozoic through Tertiary stratigraphic sections visible to the west of Mineral Creek.

The two most significant geologic events that have shaped the current landscape of the San Juan Mountains, and subsequent human interactions with it, are related to mid-Tertiary volcanism (30-35 Ma) and subsequent hydrothermal alteration, and the late-Tertiary to Pleistocene glaciation (18,000 BP)

that led to widespread scour and erosion which gives us the high topographic relief and distinct alpine features we find in the San Juan Volcanic field (**Figure 3**).

Volcanism and Hydrothermal Alteration

The period of mid-Tertiary volcanism began around 35-30 Ma and lasted until roughly 26 Ma (Steven and Lipman, 1976; Yager et al., 2008; **Figure 4**). During this period, lavas and pyroclastic debris covered a large region including south-central Colorado and north-central New Mexico, building up andesite and rhyolite flows and breccias (Bove et al., 2001; **Figure 5**). The eruption of siliciclastic ash flows were followed by the formation of a number of calderas. In the upper Animas, two important calderas were formed: the San Juan-Uncompahgre and nested within, the Silverton caldera (Bove et al., 2001). The ash flows also resulted in the intra-caldera Eureka Member composed of dacite and rhyolite (Lipman, 1976; Ringrose, 1982; Bove et al., 2001, Yager et al., 2008). Ring-fracture volcanism, sedimentation, and landslide debris within the San Jan caldera contributed a thick layer (~1 km) of intermediate composition lava flows and volcaniclastic sedimentary rocks that became host to the majority of minerals mined in the region. As this sequence of lavas filled in the caldera, regional propylitic alterations affected most of the igneous rocks in the caldera complex, resulting in a mineral assemblage that includes quartz, chlorite, epidote, calcite, secondary potassium feldspar, pyrite, and iron oxides. Additionally, along the Silverton ring-fracture zone, multiple granitic stocks, dikes, and silicic intrusions formed.

Major episodes of hydrothermal alteration occurred in the Upper Animas Basin from a period of 26 and 10 Ma, following the collapse of the Silverton caldera. There were five general alteration events affecting the Animas basin that occurred following the collapse of the Silverton Caldera, and followed the caldera collapse by 1 - 5 million years (Yager and Bove, 2007). The five alteration periods include: regional propylitic alteration, weak sericite-pyrite, vein-related quartz-sericite-pyrite, quartz-sericite-pyrite, and acid-sulfate alteration

During this time, acidic, mineral-rich water traveled upwards through faults and cracks formed during the collapse. As the hydrothermal solutions moved upwards and cooled, minerals were precipitated out and deposited along the fault walls. The solutions contained many metals highly significant today for resource extraction: gold, silver, lead, zinc, and copper. Vein ores, some of the most productive deposits, formed within fault walls and along areas of multiple fractures. Volcanic rocks in the San Juan Mountains constitute the largest erosional remnant of a once nearly continuous volcanic field that extended over much of the southern Rocky Mountains and adjacent areas in Oligocene and later time (Lippman, 1970).

In the San Juan field, voluminous early lavas and breccias—mainly alkali andesite, rhyodacite, and mafic quartz latite—were erupted from numerous scattered central volcanoes onto an eroded, tectonically stable terrane. They formed mostly during the interval 35 to 30 Ma ago, but some likely erupted earlier and others up to several million years later.

Approximately 30 Ma, major volcanic activity changed to explosive ash-flow eruptions of quartz latite and low-silica rhyolite that persisted until about 26 Ma. Source areas for the ash flows are marked by large calderas in the central and western San Juan Mountains. Two groups of lavas and associated rocks of intermediate composition inter-tongue with the ash-flow sequence: (1) quartz latitic lavas that were erupted in and adjacent to caldera structures and are genetically related to the ash-flow activity; and (2) other, generally more mafic lavas and related rocks that are widely distributed without evident structural relation to the ash-flow eruptive centers. The second group apparently represents a continuation of the early intermediate activity into the period of major ash-flow eruption.

Much of the volcanic cover was eroded by glaciers between the late-Tertiary to Pleistocene period (**Figure 6**). Yager, Choate, and Stanton (2007) note that the high potential for erosion during this period was likely due to the offset of the San Juan Mountains relative to the adjacent Rio Grande rift basin to the east. This period of glaciated erosion and weathering was instrumental in exposing large areas of the mineralized terrain as well as depositing talus, debris-cone, and landslide rocks on the surface in the region. The mineral composition of these surface deposits is significant as they are the pathways for much of the surface and ground-water flow through the region, and may influence the acidity of these flows.

Climate

Located on the western edge of the Colorado plateau and rising from the highland deserts to over 14,000 feet, the San Juan mountains are subject to both winter storm tracks, bringing ~30% of annual precipitation as snow, from the northwest (Barry and Chorley, 1998; Sheppard et al., 2002) as well as North American monsoon events (Adams and Comrie, 1997) that occur typically from July through September. The dual sources of moisture to the region gives rise to a bi-modal precipitation regime with peaks occurring both in the December to April and July to August periods. This pattern and the magnitude of precipitation the San Juan Mountains receive each year can be strongly controlled by the interacting monsoon strength and its arrival date (Adams and Comrie, 1997).

Observations from the National Weather Service Cooperative Observer Program (COOP) have been recorded since 1907 (WRCC, 2012; National Climatic Data Center, 2012) and indicates this "monsoonal" pattern where precipitation is greatest in the form of snow during February and March and again in July, August and September in the form of rain (**Table 1; Figures 7 and 8**). The hydrology shows a typical snowmelt hydrograph, with occasional high flows associated with summer and fall rain events (**Figure 9**).

Study Sites

In the Upper Animas Basin, we established five long term field sites and collected soils for greenhouse and soil leachate experiments from ten total sites (**Figure 10**). All sites were located near Silverton, CO (**Table 2**) and are located at sites ranging in elevation from 2840 m (9,320 ft) to 3473 m (11,394 ft). Sites were selected based on input from the USFS and BLM.

Sites were established on BLM lands and near the USFS Little Molas Lake Campground in the Upper Animas river basin near Silverton. Sites were located on mill tailings, waste rock piles, partially restored mine sites, and other human disturbed landscapes. The range of chemical and soil physical disturbance at each site ranged in impact from relatively low to relatively high in terms of soil physical properties and high density metallic element concentrations. Site selection was based on a preliminary survey of sites and pilot trials in 2009, ease of access, and plans for restoration.

Bonner

The Bonner mine site is located south of CO Route 8, just upslope of the Middle Fork of Mineral Creek (**Figure 11**). This site consists primarily of waste rock and has the highest levels of minerals of all sites in the study area. The Bonner site covers 0.33 ha with an estimated volume of 18,700 m⁻³ and includes two draining adits (Church et al., E5 2007). Adit water chemistry, analyzed by the USGS, indicates high concentrations of cadmium, copper, iron, manganese, and zinc along with consistently low pH values (2.7 - 3.4; Mast et al., 2000; Church et al., E5, 2007; CDMG, 2000). Restoration work conducted in 2000 reshaped the pile to remove it from the avalanche chute and to divert water which had previously flowed across the pile

The Bonner site is divided into three terraces moving successively up-slope to the south, with block 1 at the highest (south) terrace, block 2 in the middle of the pile and block three at the lower end of the of the pile just north of the access trial (**Figure 12**).

In 2011 we installed two additional 5 x 2 meter blocks at each terrace, with plots randomly located within each block. Also in 2011, we installed two larger (5 X 5 meter) plots below block 1 near the extreme lowermost edge of the pile and adjacent to the lower draining adit (**Figure 13**). These two plots are orientated normal to the slope with the eastern plot receiving a 30% by volume application rate and the western plot receiving a 15% by volume application rate, and a flume filled with a biochar sand mix to capture the AMD from the lower adit (**Figure 14**).

On the upper terrace of the pile, Block 1 is located at the intersection of undisturbed forest soils and the top of the pile which has an average bulk density of 0.83 g/cm⁻³ and porosity of 0.7.. Additionally, an x-ray floresence soil chemistry test for block 1 shows plant toxicity levels of Ni (2,620 ppm), Pb (2,870 ppm) and Fe (51,700 ppm.) Block 2 had a soil bulk density of 1.1 g/cm⁻³ and a soil porosity of 0.58. Soil chemistry for block 2 was similar to block 1 in that high levels of Ni and Pb were observed (2,470 and 3,250 ppm). Block 2 also had plant toxicity levels of Zn (591 ppm), but much lower values for Fe (8,600 ppm). Block values similar to block 2 for bulk density (1.2 g/cm-3) and soil porosity (0.52). Block 3 was similar to block 1 in that high levels of Pb (2,320 ppm). Block 3 had the highest levels of Ni (3,070 ppm) and Zn (1,400 ppm), but the lowest level of Pb (2,320 ppm). Overall, the Bonner site had an average bulk density of 0.97 g/cm⁻³, with mean values for Fe, Ni, Pb, and Zn of 41,733 ppm, 2,720 ppm, 2,813 ppm, and 755 ppm respectively. These values are above levels described as plant toxic by Kataba-Pendias and Pendias (2001).

Joe John

The Joe John site (**Figure 15**) is located at the Lark Mine, north of Silverton in Prospect Basin, and is the highest elevation site in the study area at 10,864 feet. Waste rock from the Joe & John mine was transported about a quarter mile to the Lark mine, and waste rock from both mines was placed in a HPDE-wrapped repository. The wrap was capped with six inches of native material from the vicinity, which has elevated levels of acid-sulfate rocks derived primarily from Quartz-sericite-pyrite alterations. Biosolids and mulch were applied to this native material, and the site was seeded. That remediation effort did not meet project goals with low vegetation cover and almost no vegetation recruitment. Soil conditions indicated a heavy silt content of 35%, and high compaction (1.1 g^{-cm} bulk density). Soil chemistry for the site suggested that high levels of arsenic (92 ppm) could be limiting to plant growth. Additionally, the short growing season and the desiccation of plants due to the low water holding capacity (<5%) of the soils appeared to be plant limiting at the site.

Results from the 2010 trials were positive with the biochar treatments having increased cover relative to the mulch and seed only treatments. Based on these results, we proposed a large-scale application at the Joe John repository. Biochar application at the site included ~4,400 lbs. of applied to four quadrants of the site, at two (10-20%) application rates (**Figure 16**). The application rate was based on per volume calculations derived from an estimate of 4 lbs./m² for 30% per volume in the first 15 cm. As part of this trial, we sought to understand how much biochar would be measureable in the root zone (~15 cm depth of soil) following a large scale application. Results from this work are presented in the Joe John results section.

Lackawanna

The Lackawanna site is located at a reclaimed tailings site (**Figure 17**). This site is located on the south side of Silverton, above the floodplain and just upslope of a former tailings pile (**Figure 18**). The location

is within Silverton town limits and is of mixed ownership with the tailings site on BLM land and the mill owned by the Town of Silverton (BLM, 2002). Reclamation activities to the tailings pile were conducted in 2000 and 2001, relocating contaminated soil to a repository at the May Day mine site. Following removal, the site was reclaimed using jute mat and native grasses (Rudolph, 2007). Monitoring of chemical groundwater conditions at the site has been conducted annually since remediation. The site is now mostly reclaimed, except for the section at the base of the mill where remediation efforts have not yielded significant improvement.

Due to limited space, only one block was established in 2010 with continued monitoring of the 2009 plots done in conjunction with the 2010 efforts. The additional block has five plots with the same treatments as given at other field sites. Soil properties for the Lackawanna mill site include an average bulk density of 1.28 g/cm⁻³. Soil chemistry for Lackawanna indicates existing high-levels of metal pollution with Cu (316 ppm), Ni (2,210 ppm), Pb (887 ppm), and Zn (2,500 ppm) being above levels considered plant toxic. Levels of Mn (1,780 ppm) and Fe (21,000) were also high, but were not at levels considered plant toxic.

Highland Mary

The Highland Mary site is located at the end of the Cunningham Creek valley at a large tailings pile (~0.6 ha and 27,000 m⁻³), near the intersection of Royal Tiger and Cunningham Creeks (**Figure 19**). The Highland Mary mill was part of a larger mineral complex which includes the Shenandoah Dives and Mayflower mines (Ransome, 1901; King and Allsman, 1950; Nash, 1999; Church et al., E5, 2007). Mining in the area peaked between 1947-1955 and ceased following destruction of the mill works in a fire and subsequent avalanche.

The Highland Mary site is unique in its relation to other sites in this study because of high acid neutralizing capacity (ANC) of the ore, with the resulting millings having a neutral to alkaline pH. This is.most likely due to the nature of the Precambrian schist source rock (Nash, 1999). This site is ranked low in terms of its contribution to water quality impairment to the Animas River basin (Nash, 1999; Church et al. chap. E5, 2007).

Physical properties of the soil at the Highland Mary site showed a marked difference from the other sites as sediments were comparable to beach sand with well sorted and fine (<2 mm) sand (**Figure 20**). Chemical analysis of the Highland Mary soil indicated metal concentrations of Fe (7,620 ppm), Mn (983 ppm), Ni (873), and Zn (256) below levels considered plant toxic. In contrast, Pb (538 ppm) was recorded at levels considered plant toxic. Overall, Fe, Mn, Ni, and Zn were high but not considered plant toxic. On average, Pb was present in plant toxic concentrations. Soil pH at the site was among the highest of all the study sites (pH 8.5)

Little Molas

The two Little Molas sites are located near parking for the Colorado Trail (**Figure 21**). This campground site was the location of a campsite until 2009 when the road to it was decommissioned and an official USFS campsite was established nearby. The un-authorized campground site has a southern aspect, at an elevation of 3,304 meters. The primary impact at this site is from soil compaction; soils were visibly fine-grained and lacking an organic horizon in each of the installed blocks. The Little Molas Road site is located along the eastern edge of the Colorado Trail access road at Little Molas Lake Campground. Restoration work in 2009 decommissioned a road and spread pine bark chips across the area. This site is located on a sloping berm adjacent to the access road at an elevation of 3,323 meters. The eastern aspect of the site is shaded by nearby trees during the pre-noon hours. Soils at this site were the most

developed of all study sites, with an organic layer and vegetation growing in patches. The primary impact at this site was the deep layer (~10 cm) of wood chips.

Brooklyn

The Brooklyn site was one of the initial biochar sites established in 2009, and is located east of US Hwy 550 near the Ohio Peak area (**Figure 22**). The Brooklyn mine is set within a claim area of ~600 acres (Colorado Goldfields, 2009). The geology of the Brooklyn mine and property consists of the Burns formation of the Silverton Volcanic series (Yager and Bove, 2002). The property is located proximally to the western ring fault of the San Juan and the Silverton Calderas and on the eastern side of Mineral Creek (**Figure 23**). Soil chemistry for the site indicates plant toxic levels of Ni, Pb, and Mn. The pH of the soils at the site was on the higher end as compared to other sites (pH 5.17 - 5.79). Brooklyn was a soil collection site for 2011.

Red and Bonita

The Red and Bonita site is located in Upper Cement Creek, just north of the North Fork of Cement Creek (**Figure 24**). This site was selected as a soil collection site, with no field plots installed. This site has a larger discharge (>100 gal/min) of AMD across a waste rock pile located at the mouth of the collapsed tunnel. The volume of the mine waste is ~6,000 yd³ with a disturbed soil leachate area of ~1,100 m², and a pH on the lower end of soils collected (pH - 3.76; **Figure 25**).

Road Cut

The Road Cut site is located approximately 1.5 miles north of Silverton on the east side of highway 550 (**Figure 26**). The Road Cut site is a soil collection site (no field plots) and is located at the base of a land slide area where successive mass movements of snow and rock have left mineralized material exposed. Soil leachate pH at this site was on the higher end of soils collected (pH - 6.16).

Across from Bonner

The Across from Bonner site (AfB) is located approximately 700 meters north of the Bonner mine dump, one mile west along the Ophir Pass road (Colorado Route 8; **Figure 27**). Soil was collected from this site in 2011 with no field plots installed. Soil pH was in the higher range of soils collected (pH - 5.54)

Eveline

The Eveline Mine is located in the Cement Creek drainage basin of the Animas River, approximately six miles north of Silverton (**Figure 28**). The Eveline Mine consists of a flowing adit and small waste rock dump. The site is located on a steep north-facing hillside at an elevation of 10,550 feet, adjacent to North Dry Creek. Remediation work at this site was initiated in 2010 with the construction of a concrete tank with multiple cells. This is a water treatment test site, with no vegetation plots or soil collection, water chemistry for the site is presented in Table 8. In 2011 a column experiment was initiated to evaluate the effect of biochar on the improvement of hydraulic conductivity of the zero-valent (ZI) and sand mix. As part of this experiment, we installed multiple columns with different volumes of biochar and ZI combinations (**Figure 29**).

Boston Mine

The Boston Mine is an abandoned coal mine west of Durango in La Plata County (**Figure 30**). This site is not connected with the Silverton Caldera. The Boston Mine has undergone some remediation work with the construction of settling ponds and wetlands. This site is characterized as part of the Mesa Verde Group, Menefee coal formation, and was operated as a coal mine from 1901-1926. More than 1 million tons of coal had been mined at the site which now comprises 4,000 cubic yards of coal waste (Kirsten

Brown - DRMS). This area is now owned by the Colorado Division of Wildlife and subject to closures to protect wildlife (Brown, pers. comm.). The Boston site is a soil collection site only, with no field plots installed in 2011. Soil leachate at the site is among the lowest of any soils collected (pH - .44).

Biochar Engineering Process

The biochar used for a majority of this study, was acquired from Biochar Solutions Incorporated (BSI), (<u>www.biocharsolutions.com</u>) with the raw material sourced from Colorado Lodgepole pine (*Pinus contorta*) which had been killed by Mountain Pine Beetle (*Dendroctonus ponderosae*). Information was provided by BSI regarding the physical and chemical characteristics of the biochar product we used. This includes: Surface Area (m2/g) – 76, pH – 8.6, Total Base (meq/g) – 0.56, Ash content (%) – 7.4 (**Figure 31**).

A description of the Biochar Solutions process is provided below: (personal communication w/ Jonah Levine, BSI)

"Biochar Solutions Incorporated is a biochar production and fabrication company and co-produced energy production. The biochar produced at BSI from the BSI Beta Base Unit (a mobile 1/4ton biochar/hr. production unit) was made in a proprietary, two-stage process (**Figure 32**) described as a carbon optimized gasification process.

BSI production equipment optimizes biochar for characteristics fixed carbon and high surface area, through exothermic production. BSI equipment is capable of continuously processing woodchip and nut hull feedstock into biochar in a proprietary, two-stage process (**Figure 33**). Other feedstock is possible to run in the equipment using a variety of operation techniques not all of which are continuous. The following two stage process is focused on the processing of a dry woodchip feedstock free of dirt, rocks and fines.

In the first stage of the process, the material is carbonized in a controlled aerobic (O₂ limited) environment at a temperature between 500-700 °C for less than one minute. This process takes place in the primary reactor; this is the first large cylinder on the equipment skid. All the heat (thermal energy) for the process is produced in the exothermic partial oxidation reaction. Temperatures are controlled by managing the ratio of available air to biomass and ensuring that it is well below the combustion ratio. This management of air to biomass allows for the preservation of solid carbon (biochar) while driving off nitrogen, oxygen, hydrogen, and other biomass constituent components.

In the second stage, material is held in a hot gas environment for up to fourteen minutes at a temperature between 300-550 °C before the material is removed from the process and cooled. The pyrolysis gas produced in the first stage of the process is used as sweep gas for the second stage, and is primarily composed of N2, H2, CO, CH4, and other higher VOCs and trace gases. No oxygen is available in the second stage of the process. Two size fractions of biochar are produced with ~80% of the material in size fractions of 1.5 x 1 x 0.5 cm (0.75^{^3} cm). The remaining material (~20%) is comprised of a fine dust fraction ranging from 10_u to 100_u (1 x 10⁻⁶ m).

We also used biochar from Colorado Biochar LLC, which produces biochar from a proprietary, single chamber pyrolysis system (**Figure 34**).

Methods

Based on a literature review of earlier biochar research and abandoned mine land restoration studies, the 2010 effort sought to test the efficacy of biochar for promoting the establishment and vigor of grasses native to the region and, for reducing the amount of metals leached from the soil profile. To test for the establishment, growth, and vigor of grasses native to the region we conducted three separate trials with the format of a randomized complete block design (Adelman, 1969). Within this framework, we established six field sites, a phytotoxicity/bio-indicator test, a greenhouse trial, and a soil chemistry and leachate test.

At each field site, we installed up to three blocks within which five 2 x 1 meter plots were randomly placed. Container trials consisted of phytotoxicity/bio-indicator test (shoot height in mm after 120 hours in a darkened room held at 65°F), above ground biomass (all above ground vegetation harvested at 40 days, dried at 100°C for 24 hours), and a soil leachate chemistry analyses. Elemental content of the soils were analyzed by X-ray fluorescence, using a Niton–700 device. Soil leachate analysis was conducted by using inductively coupled plasma mass spectrometry (ICP-MS) at ACZ Laboratory, in Steamboat Springs, CO (www.acz.com). Trials in 2010 used a mix of seeds that included native grasses, supplied by Southwest Seed Inc. (www.southwestseed.com) (**Table 3**). In 2011 we used a different seed mix from Southwest Seed Inc. comprised mostly of perennial species (**Table 4**)

For our field vegetation plots, we generally followed the methods outlined in Madejon (2006) and Beesley (2010) by installing plot-based field trials at multiple sites impacted by mining and other land disturbances in the Upper Animas basin. Field sites generally consist of three individual blocks with four unique treatments in each block. Treatments are as follows; biochar at 30% by volume (top 15 cm of soil; Bio30), biochar + straw mulch (BioMulch), tilled in straw mulch (Mulch), seed only control (SCTL), and a no seed control (CTL).

At each field site multiple blocks were installed with five 2 x 5 m plots randomly located within each block. Soil in each blocks was disturbed to a depth of 15 - 30 cm and rocks larger than 10 cm diameter were removed (**Figure 35**). Soil was mixed with blochar on a per-volume basis, by filling a 5 gallon bucket with 2/3 soil and 1/3 blochar. Soil and blochar mixes were re-incorporated into the plot, and all plots were backfilled level to the existing surface grade of the surrounding soil.

Study blocks were established between June 20th and July 10th (year?) and were revisited twice, at 30 – 35 days and again at 60 days. Upon revisiting the sites measurements, of vegetation cover (%) and soil moisture (%) were made. Vegetation cover was estimated directly using 5% breakpoints (Mueller-Dombois and Ellenberg, 1974), with four or five independent estimates of cover made at each plot and all estimates averaged together for a final cover estimate. Soil moisture was measured at five locations within each plot using a time-domain reflectrometery (TDR) soil moisture probe (Hydrosense - Campbell Scientific, Utah).

Water Treatment

We examined the potential to use biochar as a passive treatment system for acid mine drainage. Biochar was tested for water treatment due to the potential for multiple benefits from using biochar for AMD treatment, e.g., low cost, re-use, local source, and the potential for sequenced or conjunctive use with other treatment media/strategies. Biochar may meet some of these requirements of multiple benefits as it has been demonstrated to bind Fe (Beesley, 2010), is potentially low cost if produced on site or

nearby, and could potentially provide secondary benefits as Fe impregnated biochar has been shown to provide additional metal precipitation in soils (Mench, 2010).

To test the efficacy of using biochar, either in isolation or in conjunction with other materials (i.e., zerovalent iron), we deployed concurrent trials at the Eveline and Bonner sites. Trials at the Bonner site consisted of a trench filled with ~200 lbs. of biochar and 160 lbs. of clean play-sand. AMD water from the lower Bonner adit is directed through the trench, with pH and water chemistry measured upstream and downstream from the biochar sand matrix. Flow at the Bonner adit is ~3 liters/min. Contact time at the Bonner trench was low, with slugs of water moving through the media in ~2-3 minutes.

The Eveline trial consisted of 10 columns where the AMD was directed to flow upward through 20 cm x 50 cm PVC tubes (**Figure 36**). Columns contained different ratios of biochar and zero-valent iron sand mix (10% ZI), and consisted of 20 cm X 50 cm PVC (8 inch X 24 inch) with treatments as follows: 10 columns of biochar at 10%, 20%, 30%, 50%, and 100% by volume with corresponding volumes of ZI ; 2 columns of a 100% ZI-sand mix collected from the existing treatment tank (**Figure 37**). Flow, pH, and water chemistry were measured at 7 and 14 days, with water samples acidified in the field and sent to ACZ Laboratories for analysis by ICP-MS (**Figure 38, 39**). Flow rate was measured using a bucket and a stopwatch. Time of flow was calculated as the number of days flow was observed moving through the tubes.

Container/Greenhouse Trials

In 2010, container trials were conducted in a greenhouse setting in Silverton, CO and generally followed the methods of Beesley et al. (2010) and Perez de Mora et al. (2007). For our trials, soil was collected from each field sites, dried, and sieved to 2 mm. Replicates for each trial were run in triplicate and followed the same treatment framework as the field sites, i.e., biochar (30%) + soil; biochar + straw mulch (~20 g) + soil; straw mulch + soil; and soil, with all containers receiving 10 grams of seed mix.

Soil and soil mixtures were placed in containers and equilibrated with 200 ml of deionized water (pH 8.0) and placed in a greenhouse subjected to ambient conditions (no heating or additional light). Containers were irrigated with deionized water at successive 3, 4, 5, 6, and 9 day intervals. Soil moisture was measured with a TDR probe prior to each watering. After 40 days, longest shoot height was measured (mm) and all above ground biomass (AGB) was harvested, dried in a 100°C oven for 24 hours and weighed (g). Measurements were combined and average values for each site and treatment are reported.

In 2011, we established container trials using soil from existing field (Joe John, Bonner) and soil collection sites (Brooklyn, Across from Bonner, Red and Bonita, and Boston) (**Figures 39, 40, 41**). These trials comprised of 3.5 inch containers with additions of 200 grams of soil and three levels of biochar additions (10% - 20g, 20% - 40g, 30% - 60g) and a soil only control. These additions are equal to 5,544, 10,355, and 14,295 lbs./acre or 1.4, 2.6, 3.5 lbs./meter (**Figure 42**). One gram of the 2011 seed mix and four individual Penstemon strictus seeds were added to the soil and biochar mixes. Containers were grown under full spectrum fluorescent lights, kept at 58°F (15 C). We irrigated soil and biochar mixes with 100 ml's of tap water on a weekly basis, with the leachate collected and measured for pH. Total irrigation added to the each container equates to ~8 inches of precipitation (approximately the amount of precipitation Silverton receives on average from late-June to mid-September). During each irrigation cycle, we recorded the height (mm) of green vegetation and the weight of the container prior and following irrigation. The trial was run from January 5th to April 9th when soil was washed from the

existing plant material (above and below ground). Plant material was dried for 24 hours at 100[°]C and weighed.

Soil Leachate and X-Ray Florescence Chemistry

Soil chemistry was analyzed with an X-Ray fluorescence test, using a Niton–700 device (<u>www.niton.com</u>). X-Ray fluorescence measures the emission of characteristic fluorescent X-rays from a material that has been excited by bombarding it with high-energy X-rays (Beckhoff et al., 2006). This method is a rapid and effective way to determine major, minor and trace elements in samples of soils, aerosols, and drinking water (Bamford et al., 2004). For our analysis, we followed the Niton manual and results are reported in mg/L.

In 2010 soil leachate was collected from the gallon containers at a 9, 17, 23, and 40 day interval for metals analysis. During each irrigation cycle 200 ml of deionized water was applied to each biochar and soil-only treatment. Following irrigation, leachate was collected from each container and homogenized with leachate samples from the same site and treatment. From this homogenized leachate a 100 ml sub-sample was collected, acidified with nitric acid (HNO₃) and kept refrigerated prior to shipping to an analytical laboratory (APHA, 1980; USEPA, 1979; USGS, 1982). Soil leachate was analyzed by inductively coupled plasma mass spectrometry (ICP-MS) at ACZ Laboratories (<u>www.acz.com</u>), using methods established in USEPA (1994), Methods for the Determination of Metals in Environmental Samples. Samples were analyzed for total concentrations of Ag, Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, V, and Zn.

Joe John Large Scale Application Trial

An unresolved question for large-scale biochar applications is: what is the effective application rate of biochar (i.e., the fraction that remains in the rhizosphere)? This is an important question, as it relates directly to the application rates and therefore cost of biochar usage. For example, we know that for carbonaceous sorbents (e.g. biochar) are effective for increasing vegetation growth, however, the material must be located in the soil profile so that plant roots grow within the soil and biochar matrix. Also unknown is that if material is placed only on the surface of the soil will it have a reduced effect on water holding capacity and soil chemistry improvement. Conversely, if the material becomes incorporated too deep in the soil profile for plant roots to quickly grow through, will the biochar be effective for plant growth response.

To answer the above questions we established a large-scale trial at the Joe John site. We selected the Joe John site for the trial due to the positive results from the 2010 effort, which indicated that biochar additions at this site had a positive effect on vegetation cover and above ground biomass. Based on the 2010 results the BLM/USFS elected to conduct a large-scale application trail of biochar in 2011. In four quadrants of 172 (A), 315 (B), 240 (C), and 343 (D) square meters, ~4,400 lbs. of biochar was applied using heavy equipment (backhoe and tractor) (**Figure 43, 44**) (**Table 5**).

To determine the effective rate of biochar application we collected soil cores from the first six inches of soil at the Joe John site two-weeks following the biochar application and subjected the soil samples to a density separation method to disaggregate the biochar fraction from the mineral soil. We followed guidelines for separating soil organic matter outlined in Elliot and Cambardella (1991) and Crow et al., 2007 and Sohi, 2009. Our task was made easier due to the very low amounts of soil carbon (especially black carbon) at the Joe John site, due primarily to the absence of an O horizon.

To separate the black carbon fraction from the mineral soil we placed the samples in a dense solution of water and salt (NaCl) (40 g/L), shaking the sample and solution to allow the mineral fraction to settle. We then collected the floating portion (biochar) and dried the sample. We then dried the soil samples, recording the dry soil and biochar volumes (ml) and mass (g).

Geostatistical Technique

Point estimates of soil carbon were used to predict percent biochar soil concentrations across the entire site. We used three geo-statistical techniques to predict soil carbon (biochar) concentrations across the study quadrants, Inverse Distance Weighting (IDW), Spline Fit (SP), and Ordinary Kriging (OK). These methods use a variety of interpolation techniques to predict values at locations between sampled points. The three methods all follow a mathematical form which assumes that items that are closer in coordinate space are more likely to be similar in value. IDW and Spline fit techniques are very typical of this, while Kriging is an interpolation method which uses weighted moving averages and is a more mathematically complex estimation method which accounts for more of the variability in values at measured points.

Statistical Analysis

Our study design was based on a randomized complete block design (Addelman, 1969), with multiple blocks at a site and randomly placed plots placed within each block. We controlled for micro-site factors by preparing all field blocks and containers in an equal fashion.

This design was selected for a number of reasons, including:

- 1. An ability to compare the treatments collectively, while controlling for a single source of variability, i.e., site level variability;
- 2. Design is efficient to implement and was transferrable across experiments;
- 3. Statistical analysis is simple though powerful enough to detect the effect of the treatment.

We recognize that this study design has some drawbacks, primarily that if the within-site variability is not adequately characterized then the effect of replicating multiple blocks at a site would result in pseudorepliction. We sought to avoid this problem by arranging the study blocks at a site along any topographic or hydraulic gradient, if one was present, such that each block was an independent measure of the treatment effect and pooled results for a site represented full range of impacts evident at a site. We further divided our analyses blocks up by sites that had similar attributes.

Our analysis generally employed a general linear model analysis of variance (ANOVA) to test for differences in means between treatments, site, and multiple pairwise comparisons of results within a site and within a site type (e.g., mining affected, non-mining affected; acid and non-acid). For pairwise comparisons we primarily used the Holm-Sidak method for multiple comparisons procedure (Holm, 1979). This method has greater sensitivity than the Bonferroni test and is recommended as a first-line procedure for pairwise comparison testing.

Results

Results are presented for aspects of vegetation establishment and growth, soil physical properties, and soil and water chemistry and include results from the 2010 and 2011 trials. A complete description of the 2010 results can be found in Peltz (2010).

Vegetation Cover

Vegetation cover results are presented for both 2010 and 2011 individually and combined and by site and site type. We analyzed the 2010 and 2011 both separately and individually as the mix of seeds used in 2010 included two annual species: (Annual Rye, Lolium – 16% and Small Grain Spring Wheat, Triticum – 27% by weight) which were not included in the 2011 seed mix, and comprised a large percentage of the 2010 cover (<50% of the species observed in plots), which is most likely the reason for the 10% percent decrease in cover across all sites and treatments (**Figure 45**)

The 2010 cover estimates indicated that the addition of a 30% by volume biochar soil amendment increases median vegetation cover relative to seed-only by ~16% (26.7% - biochar, 15% seed-only control), and by ~6% relative to straw mulch alone (20%) (p <0.001) (**Table 15**). The greatest increase in cover was found from the biochar + straw mulch treatments, with pooled results in 2010 showing median cover of 36% (**Figure 46**). Comparisons between treatment indicated that the only significant pairwise differences were between biochar treatments and the no-seed controls (p <0.05).

In 2011 similar analyses of cover values showed large decreases in overall cover, with the biochar only plot having a median value of 7.5%, biochar+mulch (15%), Mulch (5%), and the seed only control at 10% cover (p <0.001). Pairwise comparisons were significant at p <0.001 for the biochar and biochar + mulch vs. no-seed control, as well as the seed-only vs. the no-seed control.

In both 2010 and 2011 we analyzed our results by grouping sites with low soil pH (pH <5.5) "acid" sites (Bonner, Lackawanna, and Joe and John, n - 110) collectively and comparing cover values for the different treatments with values from the "non-acid" (pH <5.5) sites (Highland Mary and Little Molas, n - 145) (**Figure 47, 48**).

Results from the 2010 acid vs. non-acid groupings (**Figure 49**) indicated that the treatment effect on cover was significant (p = 0.004), though the greatest influence on cover is attributed to site type (mining or non-mining) (p < 0.001, F = 42.5). The same analysis (acid vs. non-acid sites) for the 2011 data indicated significant differences between treatment and site type (p < 0.001), however, the strength of the differences was diminished in 2011 (F = 39.1). Least square means for site type in 2011 indicated decreased cover values with acid sites showing average cover values of 9.8% (SEM 1.7) and non-acid sites having an average cover of 23.4% (SEM 1.4).

We also grouped sites by mining affected (Highland Mary, Bonner, Joe John, n - 180) and non-mining affected sites (Little Molas, n - 75) and performed the same two-way ANOVA and pairwise comparisons. Average cover in 2010 for mining affected sites was 18.5% (SEM 1.8), and 42.3% (SEM 3.2) for non-mining affected sites (**Figure 50**) (**Table 18**). In 2011 we saw the same pattern of decreased cover with site and treatment being significant (p < 0.001) however the strength of the differences was less with F values for site type (29.8) and treatment (11.6) lower than in 2010. Average cover in 2011 was lower than 2010, with cover at mining affected sites decreased to 7.5% (SEM 1.2) and 18.1% (SEM 1.5), at non-mining affected sites, both which were lower than cover values in 2010 by ~10% and ~22%.

Greenhouse Trials - 2010

We measured the above ground biomass (AGB) following a 40 day greenhouse trial (August – September, 2010) where one-gallon containers had ~10 grams of seed applied to the different biochar and control treatments. We placed containers in an outdoor, un-heated greenhouse located near Silverton, CO. Irrigation was conducted weekly with 200 ml of de-ionized water. Soil leachate was

collected during each irrigation cycle and was sent to ACZ laboratories for analysis of metal concentrations.

Results from these trials indicated that overall, the biochar treated containers had significant increases (p < 0.001) in biomass (4.1 grams, n - 56) relative to the non-biochar treatments (2.6 grams, n - 47) (**Table 25**). When results were grouped by treatment the BioMulch treatments had the greatest average mass with 4.3 g of biomass, followed by Bio30 with 3.7 g, Mulch 3.1 g, and SCTL 1.8 g (**Figure 51**). We conducted pairwise comparisons and found significant (p < 0.05) differences between BioMulch and SCTL, Bio30 and SCTL, and Mulch and SCTL, however we did not find significant differences in biomass between Bio30 and BioMulch.

The greatest amount of AGB was found at the Highland Mary site, treated with BioMulch (4.7 g) (**Table 27**). Containers with soils from the Highland Mary site had the highest overall average biomass (4.4 g), followed by Lackawanna (3.5 g), Bonner (2.7 g), and Joe John (2.2 g). When sites were grouped by acid and non-acid types, the greatest AGB was found in the BioMulch for both acid and non-acid sites (**Figure 52**), for example BioMulch treatments in the acid soils had AGB of 3.9 g, and 4.8 g in the non-acid soils, values which are relatively close together. This is contrasted by the differences in the SCTL treatments where AGB in the acid soils averaged 1.1 g, while in the non-acid soil AGB averaged 3.9 g. When the results were grouped by mining versus non-mining sites the differences were less striking however, none of the differences between treatments for the non-mining soils were significant. The differences in vegetation biomass can be seen in (**Figure 53**) when the containers were in the greenhouse, as well as following the trial with the differences for the Highland Mary site (**Figure 54**) showing little differences, contrasted with the Bonner site (**Figure 55**).

Vegetation Growth Rates

Results from the weekly height measurements show increased growth rates in the biochar treatments relative to the soil only controls (**Figure 56**). These differences were evident from the initial measurement on 1/19/12 where average vegetation height in the soil only containers was 1.3 mm, contrasted with the biochar treatments that ranged from 6.0 mm to 9.5 mm for the different levels of biochar addition. Vegetation heights differences between the biochar treatments begin to diverge significantly at 2-6 (fourth irrigation cycle since germination) with the Bio30 and Bio20 having increased vegetation heights (39, 35 mm) relative to the Bio10 (32 mm) as well as the soil only control (22 m). This divergence in heights continued with the Bio30 having the greatest height at all subsequent irrigation cycles, with a final average height of 64 mm. This is 10% greater than the Bio20 treatment, and 25% and 53% greater than the Bio10 and soil control heights (**Figure 57**).

Soil Moisture

As part of our trials we sought to better understand biochars influence on soil moisture dynamics. This was due in part to our hypothesis that, along with cation exchange and acid neutralizing capacity, soil moisture was one of the strong controls on seed germination and vegetation growth and a significant predictor for increased vegetation cover and above ground biomass. To understand this dynamic, we measured soil volumetric water content (%) at multiple times during the growing season (June – September) and during our measurements of vegetation cover at the end of the growing season.

In our field trials we observed that biochar amended plots (Bio30 and BioMulch) had median soil VWC values of 14% versus non-biochar amended plots (Mulch, SCTL, and NSCTL) which had median values of 6% (**Figure 58, Table 14**). This pattern of increased soil VWC in biochar amended plots was evident both in 2010 and 2011 (**Figure 59**), where median soil VWC in biochar treated plots was increased by 7% in

2010 and 10% in 2011 relative to non-biochar amended plots (**Table 15**). We also examined the differences in VWC between all field treatments in 2010 and 2011 and found that the highest mean VWC was observed in the Bio30 treatments in both 2010 (18.8%) and 2011 (19.4%), with the BioMulch showing similar, though slightly less VWC (17.8% - 2010, 18.5% - 2011). The pattern of increased soil moisture was evident at all sites in both 2010 and 2011 (**Figure 60, 61, 62**), as well as at mining affected and acid affected sites (**Figure 63**)

Results from the container trials found results similar to our field trials (**Figure 63**) with biochar treatments having median VWC values of 32% as compared to the non-biochar treatments (16%) (**Table 16**). Bio30 treatments also had the highest median VWC from the one way ANOVA analysis with a value of 35%, as compared to the BioMulch (29%), Mulch (16%), and Seed only Control (16%). In combining the results of the container trials into mine, non-mine and acid, non-acid and found that for mine and acid soils the Bio30 had the highest VWC (38.2% - mine, 42.8% - acid). However, for the non-mine and non-acid soils the highest VWC was found in the BioMulch treatments (35.7% – non-mine, 32.0% - non-acid). Mulch and SCTL had lower average VWC for all sites and site types.

In 2011 we also evaluated soil moisture dynamics throughout the growing season (June 31 – August 26,) by taking VWC measurements on a weekly basis (n - 9) at the Bonner and Highland Mary sites (**Table 19**). Results from these measurements indicate that soil moisture values in the biochar treatments responded to inputs of precipitation differentially from the non-biochar treatments, with the Bio30 and BioMulch treatments having increased soil VWC. This was particularly evident from the two measurements occurring on July 22 and July 29, between which 31 mm of precipitation had fallen. On the later date VWC had increased in the biochar plots from 17.7% to 24.2%, while conversely in non-biochar plots VWC increased from 7.9% to 9.1%. This pattern was observed between other precipitation events with biochar treated plots showing large relative increases in VWC as compared to the non-biochar treatments (**Figure 64**).

The large relative differences in VWC between treatments can be seen in (**Figure 65**) represents average soil volumetric water content (%) for Bonner and Highland Mary measured nine times at ~7 day intervals from June 21 (all plots snow free) to August 26, 2011 when vegetation cover was measured in plots. Points represent the mean value (n = 5) within a 1 x 2 meter plot. Horizontal lines represent a two period moving average between points. Vertical lines indicate precipitation totals (cm) from the Center for Snow and Ice Studies Swamp Angel Weather Station - elevation 3,368 meters (11,050 ft.). This period comprises the middle of the growing season at this altitude, with precipitation during this period strongly controlling the total available soil moisture for grasses and other plants that rely primarily on soil moisture storage. During this period soil moisture in the biochar treatments averaged 20%, while in the no-biochar treatments over the same period soil moisture averaged 8%.

Soil Leachate Chemical Results

In multiple applications and under varying conditions, we examined the use of biochar as metal sorbent and catalyst for metal precipitation into less environmentally mobile forms. As part of ongoing research into this topic, other researchers have found that biochar can increase soil pH and reduce trace metals in soil leachates (Novak et al, 2009), reduce phytotoxic concentrations of water-soluble Cd and Zn (Beesley et al., 2010) and increase the cation-exchange capacity of soils (Laird et al., 2010). Some studies have shown that the addition of biochar amendments can increase arsenic mobility, most likely due to competition with P for binding sites when greenwaste compost was added and increased alkalinity from the liming effect of recently applied biochar (Hartley et al., 2009; Madejon and Lepp, 2007, Lucas and Davis, 1961). In 2010, we examined the effect on soil water from a 30% biochar addition, with special emphasis on the metals of concern in the Upper Animas basin (Al, As, Cu, Cd, Fe, Mn, Pb, and Zn). Treatments were comprised of either, three liters of soil from Bonner and Joe John, or two liters of soil and one liter of biochar (30%/volume). Our results should be interpreted noting the different total volumes of soil between the treatments. During each irrigation cycle we recorded the mass of the container with the soil and soil/biochar mixers prior to, and following irrigation (100 ml tap water). As part of the irrigation process we recorded the soil leachate pH of the irrigation excess (typically 20-40%). pH was recorded using a YSI pH 100 with a 2-point calibration.

Joe John Large Scale Biochar Application

Soil Carbon Content

Following processing we had a final sample set of 97 samples that ranged in carbon content from 20% carbon volume to 0.3% by volume, with the average carbon volume across all the samples equaling 5.5%. This is lower than the expected average of 15% given the amounts applied (**Table 35**) (**Figure 79**).

Though the range of biochar content ranged across a 20% continuum of concentration we noticed that there were similar patches of higher soil carbon. We can see a consistent pattern of predicted soil carbon between the Spline (**Figure 80**) and IDW (**Figure 81**) interpolation techniques. We observe that the Kriging technique (**Figure 82**) predicted higher soil carbon volumes across quadrant C and D than predicted by SP and IDW. Most likely this is due to high values of soil C that appear discontinuous based on the point samples.

This interpolation will be useful for future monitoring to evaluate vegetation response at locations at the site, with the hypothesis that areas with higher carbon content will have increased vegetative cover in 2013 and beyond. It is recommended that additional soil cores are collected in the late summer of 2013 to evaluate the strength of the prediction of soil carbon and to evaluate the relationship between soil carbon content and vegetative response.

Soil pH

We were also interested in determining the range of soil pH conditions at the Joe John site as this factor may contribute strongly to the ultimate success of vegetation recovery at locations across the site. For our analysis we measured soil pH by measuring the solution pH (3:1) of the soils collected for the density separation. Our results indicate that pH varies somewhat from ~2.3 to 4.3 across the site (**Figure 83, 84**). We applied both the IDW and Spline interpolation techniques to the pH data to derive spatially continuous estimates of soil pH based on the assumption of continuously varying changes in soil chemistry. We also found that there was no relationship between carbon content and soil pH (**Figure 85**)

Ongoing Research

Colleen Rostad, Dave Rutherford, Charley Kelly - USGS

The USGS team is using laboratory column experiments designed to assess whether adding beetle-killed pine biochar to mine tailings is an effective approach for reclaiming abandoned mine lands (**Figure 86**, **87**). Using tailings from two mine sites near Silverton, CO we investigated the hypotheses that incorporating biochar into acidic mine tailings would 1) decrease heavy metals in leaching solution, 2) improve activity and diversity of microbial populations that might promote natural ecosystem succession processes, and 3) improve overall conditions for plant growth and soil formation by increasing nutrient and water holding capacity, increasing pH, and decreasing compaction, concretion, and bioavailable heavy metal concentrations. We also investigated the longevity of any ameliorating effects resulting from amending acidic mine tailings with biochar.

Doug Winter - Colorado University

Acid Mine Drainage Treatment Cells

Doug worked for MSI in 2011 as a summer intern and is currently a senior environmental engineering student at the University of Colorado. Doug is working on a senior thesis project where he is using various configurations of biochar, zero-valent iron, and wood chips to increase the pH and reduce metal loads of simulated AMD (**Figure 88**).

David Gonzales - Fort Lewis College

David has two students working in biochar related projects. Chad Quinn and Colin Frye are both seniors in geology at Fort Lewis, and who are conducting bench-top, laboratory experiments focusing on the sequestration potential and effect on pH of biochar on collected and simulated AMD solutions. The first of these experiments is looking at biochars effect on water, and include a soil column experiment with treatments of sand (10 cm), biochar (21 cm) and sand (2 cm.) The second experiment will examine the sequestration capabilities of biochar in simulated AMD solutions of 200 ppm Cu, Cd, Pb, and As. This second experiment will be conducted in flasks loaded with 200 ml biochar and 1000 ml solutions of simulated AMD. Flasks will be placed on shaker tables and stirred for two-weeks. Analyses will examine both the concentration of the simulated AMD following the two weeks as well as the adsorption onto biochar particles. Chemical and adsorption (Scanning Electron Microscope) analysis of the biochar pre and post treatment will be conducted at New Mexico Institute of Mining and Technology (New Mexico Tech).

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