NORTHERN BIOCHAR FOR NORTHERN REMEDIATION AND RESTORATION

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ABSTRACT

Biochar is a soil amendment that results from heating various biological ingredients, such as wood, fish or animal bone under oxygen limited conditions and has proven to promote plant growth, as well as, hydrocarbon degradation at contaminated sites in southern climates. We are working to identify different types of biochar that promote hydrocarbon degradation, as well as, re-vegetation success in mining-contaminated northern soils. Preliminary results from hydrocarbon contaminated soils indicate that under frozen conditions, 3% biochar was significantly effective, reducing the F2 and F3 fraction by up to 22%. In northern sandy soils biochar may improve the texture of the soil, enhancing water holding capacity, porosity, surface area and the availability of water under frozen conditions, which in turn may stimulate microbial activity that appears to be a driving factor in petroleum hydrocarbons degradation. The application of a biochar and lime treatment to mine tailings led to significantly higher germination rates and aboveground biomass compared with fertilizer only. There are a number of potential mechanisms by which biochar may have influenced germination and growth, including retention of soil moisture, increased temperature at the surface due to low albedo, increased nutrient retention and reduction in bioavailability of heavy metals.

Key Words: Hydrocarbons, Heavy Metals, Mine Tailings, Re-Vegetation, Frozen Soils.

INTRODUCTION

Bioremediation and restoration in northern Canada is a slow process with unique challenges related to cold-climate soil chemistry, short growing seasons and geographical isolation. Both hydrocarbons and heavy metals are common pollutants in the North (Mohn and Stewart 2000; Thomas et al. 1992). With increasing industrial activity in northern Canada there is a growing need to develop northern-specific remediation and restoration technologies.

Conventional methods of hydrocarbon remediation rely on fertilizer additions and soil turning to stimulate the microbial community to catabolize organic contaminants; however this approach has not proven to be consistently successful in polar environments (Paudyn et al. 2008). Biochar is a novel amendment that results from the oxygen-limited pyrolysis of various biological ingredients, which has received interest because of its ability to enhance growth and carbon storage in agricultural soils (Lehmann and Joseph 2009; Lehman et al. 2006). Biochar could have parallel effects on petroleum hydrocarbon (PHC) contaminated soil and has the potential to increase bioremediation rates. Few studies have been conducted on PHC contaminated soils in cold environments, but there have been successful reports of increased PHC degradation rates in biochar amended soils as compared to the control (Dias et al. 2012; Theis and Rillig 2009). However, the physical, chemical, and biological mechanisms driving these results are not well understood and further investigation into these mechanisms is required. Aged-diesel contaminated soil from Iqaluit, NU was used in a laboratory trial which investigated the use of biochar as an amendment to enhance PHC degradation. The aim of this study is to determine if biochar enhances PHC degradation in northern soils and to link this degradation to θ_{liquid} content and its affect on the soil microbial community.

Due to the lack of organic matter, low pH and high metal content the conditions on many mine sites may be too harsh for vascular plants to establish. Hence, the use of soil amendments may be necessary to allow for successful germination and growth. Several studies have found biochar can result in significant decreases in the bioavailability of heavy metals associated with mine impacted soils (Beesley and Marmiroli 2011; Fellet et al. 2011; Namgay et al. 2006) and simultaneously improve physical, chemical and biological soil properties (Laird et al. 2010). Biochar has many benefits for the environment and has been investigated extensively in southern climates, but very few studies have examined its use in northern mine site reclamation and restoration. The aim of this study is to examine various soil amendments and native species to determine optimal formulations that improve soil conditions and promote long term re-vegetative success in northern mine impacted soils. Determining the most appropriate reclamation and restoration option is heavily dependent on site characteristics and the contaminants of concern; however, development of soil amendments that are effective in northern soils with multiple contaminants may provide important cost-effective technologies.

METHODS

Hydrocarbon Remediation Trial

The soil had a background TPH concentration of 600 mg kg^{-1}, neutral pH (7.5), sandy texture (93.9% sand) nutrient deficiencies (i.e., 0.48 NO_3 mg kg^{-1}, NH_3 0.95 mg kg^{-1}, PO_4 0.23 mg kg^{-1}), and low moisture (9.81 gg^{-1}), and organic carbon contents (0.67% OM). Prior to trial setup, the soil was homogenized and amended in batches with urea (46-0-0) and mono-ammonium phosphate (11-52-0) fertilizer, compost, and bonemeal biochar. After the addition of amendments to each treatment, the soil was re-homogenized, weighed into amber glass vials and plugged with sterile cotton balls to prevent anaerobic conditions. Water was added to each vial to bring the soil up to 60% of field capacity, which was maintained throughout the experiment.

PHC degradation under thawed conditions was compared using control and amended treatments; fertilizer, 3% (w/w) bonemeal biochar plus fertilizer, 6% (w/w) bonemeal biochar plus fertilizer, 5% (w/w) compost plus fertilizer, and 10% (w/w) compost plus fertilizer. The vials were incubated under thawed (10°C) conditions and destructively sampled over 0, 30, 60, and 90 days. PHC degradation under frozen conditions was also compared using control and amended treatments; fertilizer and 3% (w/w) bonemeal biochar plus fertilizer. These vials were incubated at -5°C and destructively sampled over 0, 30, 60, and 90 days. Biochar and compost was added on a weight to weight (w/w) basis while urea and mono-ammonium phosphate fertilizer was added at a C_{TPH}:N:P ratio of 100:9:1 (Chang et al. 2010).

After destructive sampling, the vials were stored at -80°C until they were analyzed for total petroleum hydrocarbons (TPH) using ASE and GC-FID analysis, for θ_{liquid} content using time-domain reflectometry (TDR) methods and for total PHC-degrading microbial populations using Most Probable Number (MPN) counts. Gravimetric moisture content was determined for each sample and TPH was extracted using an ASE 200 Accelerated Solvent Extraction System; a patented technique developed by Dionex® to extract liquids from solid and semisolid matrices (Thermo Scientific, Sunnyvale, CA). Following ASE, the PHC extracts were run through sodium sulphate and silica gel cleanup columns to remove water and polar organic compounds, respectively (CCME 2001). Finally, PHC concentration in fractions F2 and F3 were quantified using a Varian 3800 CP gas chromatograph fitted with a flame ionization detector (Varian, Santa Clarita, CA).

Volumetric water content was measured by TDR, a technique that measures the dielectric constant of the medium. Because the dielectric constant of water ($K_{water} = 80$) is much higher than other soil constituents ($K_{air} = 1$; $3 > K_{soil} < 7$;$< K_{ice} = 3.2$), the dielectric constant of the medium is proportional to the amount of θ_{liquid} (Topp et al. 1980). This technique is capable of measuring small quantities of θ_{liquid} down to 0.05 m^3 H_2O m^{-3} soil (Topp et al. 1980). Soil θ_{liquid} content was measured using calibrated TDR probes and a Tektronix 1502B cable tester (Tektronix, Beaverton, OR). Waveform data were collected, compared to the gravimetric moisture content and plotted as a linear equation to obtain calibration.

Culturable, aerobic, diesel-degrading microbial populations were enumerated using 96-well microtiter plates. Filter sterilized No. 2 fuel oil (F2) was used as the selective substrate to quantify total PHC-degrading microorganisms (Haines et al. 1996). Minimal salts medium (180 µL) was added to each well and supplemented with 3 µL of 5000 mg/kg^{-1} F2 diesel (Yergeau 2009). Soil samples were diluted in a saline phosphate buffer solution (PBS); 1 g of soil was mixed with 9 mL of PBS to create a 1:10 dilution. The first row of wells was inoculated with 20 µL of the 1:10 dilution. The subsequent wells in each column were inoculated by transferring 20 µL from the previous well to create a dilution series ranging from 10^{-2} to 10^{-7}. The last row remained un-inoculated to serve as a sterile control. Following incubation at 23°C for three weeks, 50 µL of filter-sterilized iodonitrotetrazolium (INT) violet (3 g/L) was added to identify positive wells (Haines 1996). In positive wells, INT is reduced to an insoluble formazan that deposits as a red precipitate in the presence of respiring microorganisms (Wrenn and Venosa 1996). Red or pink positive wells were scored after an overnight, room-temperature incubation with INT. Final cell numbers were derived using an MPN calculator (Jarvis et al. 2010).

<u>Tailings Soil Amendment Trial</u>

The Keno Hill Silver District is one of the world's highest-grade silver districts located 330 km north of Whitehorse, Yukon, Canada. It is estimated that approximately 4,050,000 tonnes of tailings were deposited at a 130 ha site, known as the Valley Tailings, located in the McQuesten River Valley (63°55'26.4N, 135°29'76.1W). The tailings are highly variable with a pH ranging from 5.7 to 8.4 and texture varying from silt loam to sand. The tailings exceed the Canadian Council of Ministers of the Environment (CCME) industrial soil quality guidelines for allowable levels of Antimony (Sb), Arsenic (As), Cadmium (Cd), Copper (Cu), Lead (Pb), Silver (Ag), Titanium (Ti) and Zinc (Zn).

The original site consisted of boreal vegetation including small trees (*Picea glauca* (Moench) Voss, *Picea mariana* P. Mill., *Populus tremuloides* Michx., and *Populus balsamifera* L.), as well as, shrubs (*Salix* spp.) and moss mats (*Sphagnum* spp., *Pluerozium* spp.). Vegetation in the Valley Tailings area was eventually covered by tailings, which range from 0.1 to over 4m in thickness (Keller et al. 2010). Mean

January and July temperatures are -26.9°C and 15.6°C respectively. However, summer temperatures in the region can exceed 25°C and winter temperatures -50°C. The average total precipitation is 322 mm and discontinuous permafrost is found throughout the area (Clark and Hutchinson 2005).

We examined 8 soil amendment treatments and 1 control treatment (fertilizer and seed only). Soil amendments were applied to the Valley Tailings using a randomized block design with 14 blocks (5m x 10m). Leaving at least 1 m^2 between treatments, the 9 treatments (1 m^2 each) were randomly assigned within each block. Each soil amendment treatment had 14 replicates for a total of 126 plots.

The soil amendment treatments included the following materials: biochar (1 kg/m^2), smectite (calcium bentonite) (750g/m^2), dolomite lime (54.6% $CaCO_3$, 41.5% $MgCO_3$) (484 g/m^2), wood mulch (193 g/m^2) and the tackifier Guar Gum (12.7 g/m^2). The biochar (BC) was a phosphorus-rich bonemeal biochar (2-14-0) pyrolyzed at a temperature of 450°C for 6 hours. The grain size of the finished product was ≤ 2mm. The 8 soil amendment treatments were: biochar (BC); biochar and smectite (BCS); biochar and lime (BCL); smectite and lime (SL), biochar, smectite and lime (BCSL); mulch (M); mulch and lime (ML); biochar, smectite, lime and mulch (BCSLM). All soil amendment treatments were fertilized (19:19:19) at a rate of 110kg/ha and seeded at a rate of 30kg/ha with a native grass seed mix, containing Violet Wheatgrass (*Agropyron violaceum* Hornem. – 40%), Sheep Fescue (*Festuca ovina* L. – 23.3%), Rocky Mountain Fescue (*Festuca saximontana* Rydb. – 23.3%) and Glaucous Bluegrass *(Poa glauca* Vahl. – 13.4%). Guar Gum was present in all treatments. All of our amendments were applied as a slurry to simulate delivery via hydroseeding using 7.5L of water per m^2.

Plots were established between July 1-3, 2012. Germination was determined by counting the number of emerging stems in 0.25m^2 subplots for each replicate from July 25-26, 2012. Above and belowground biomass were sampled from August 27-29, 2012 in 0.5 m^2 subplots for each replicate. All biomass was dried at 90°C for 36 hours before determining dry weights.

Data from the hydrocarbon and soil amendment trials were examined to ensure the assumptions of Analysis of Variance (ANOVA) were met and log transformations were performed on some variables. A two-way ANOVA was used to detect significant differences between treatments over the duration of the hydrocarbon experiment. Soil amendment trial data was analyzed using a blocked ANOVA. All analyses were conducted in R (R package version 2.1.50).

RESULTS

<u>Hydrocarbon Remediation Trial</u>

Amended and control treatments had variable effects on TPH degradation under frozen versus thawed conditions (Figure 1). Under frozen conditions, 3% (w/w) bonemeal biochar significantly reduced the F3 fraction by 22%, as compared to fertilizer which only stimulated degradation by 3%. In the F2 fraction, both the 3% (w/w) biochar and fertilizer amendments stimulated degradation, by 42% and 33%, respectively. None of the amended and control thawed treatments exhibited a significant effect on TPH degradation, as compared to the standard fertilizer treatment.

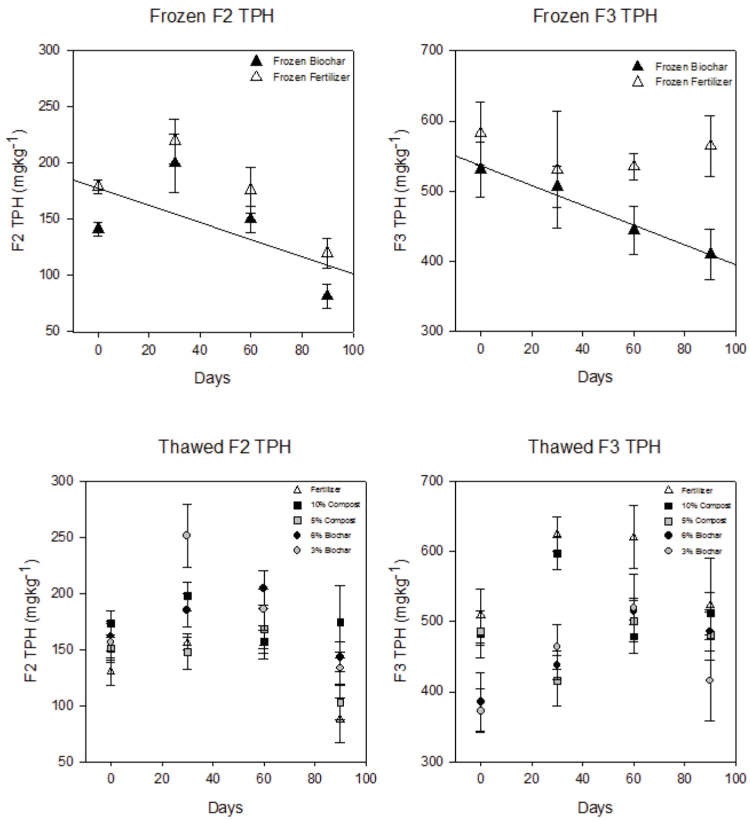

Figure 1. *PHC degradation in fractions F2 and F3 was monitored over 90 days in frozen and thawed soils. Under thawed conditions, no significant effect on degradation was observed in any treatments. However, under frozen conditions, 3% (w/w) biochar decreased concentrations in the F3 fraction, as compared to the standard fertilizer treatment. Both 3% (w/w) biochar and the fertilizer treatment stimulated degradation in the F2 fraction. The addition of biochar appears to have a significant effect on heavier PHC compounds, under frozen conditions.*

Under frozen conditions, θ_{liquid} of soil amended with 3% (w/w) biochar was higher than the fertilizer control, although differences were not significant. Trends suggest that biochar amendments can increase the θ_{liquid} content in frozen soils by increasing surface area and soil-water interactions.

Most probable number (MPN) counts indicated that total PHC-degrading populations were significantly higher in soil amended with 3% (w/w) bonemeal biochar incubated under frozen conditions (Figure 2a). Surprisingly, MPN with 3% (w/w) bonemeal biochar incubated under thawed conditions was not significantly different than the fertilizer control (Figure 2b).

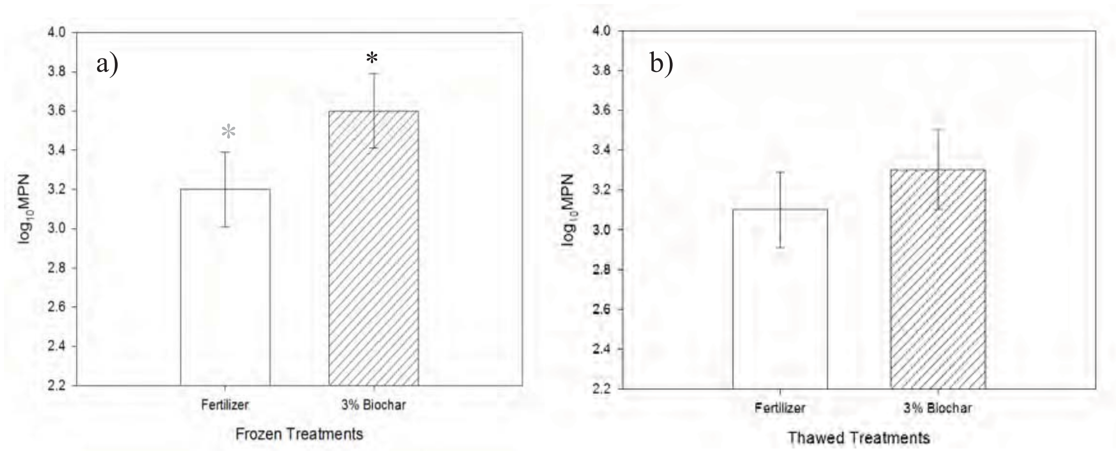

Figure 2. MPN counts from soils amended with bonemeal biochar as compared to the control treatment, incubated for 90 days under frozen (a) and thawed (b) conditions. Different shaded asterisks (*) indicate significantly different PHC degradation (ANOVA, p<0.05).

<u>Tailings Soil Amendment Trial</u>

Of the 8 amendment treatments examined, the biochar and lime treatment (BCL) had significantly higher germination rates (Figure 3) and significantly higher aboveground biomass (Figure 4a) when compared with the fertilizer only control treatment (CT). The BCL treatment also had higher germination rates than treatments that included mulch (i.e., M, ML and BCSLM).

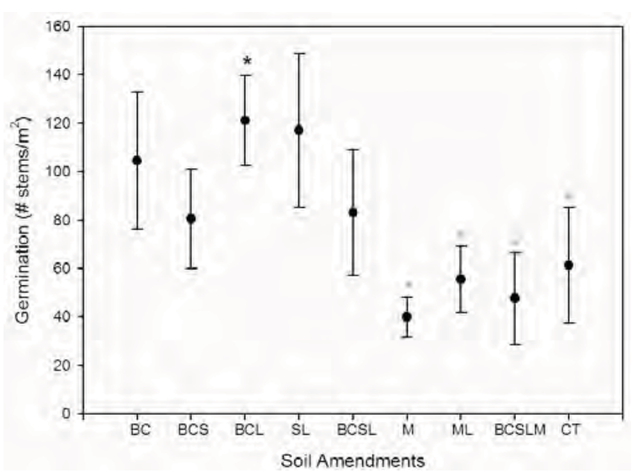

Figure 3. Germination of native grasses with different soil amendments 22 days after application at the Valley Tailings, Keno, YT. Soil amendment treatments are Biochar (BC), Biochar and Smectite (BCS), Smectite and Lime (SL), Biochar, Smectite and Lime (BCSL), Mulch (M), Mulch and Lime (ML), Biochar, Smectite, Lime and Mulch (BCSLM) and Control with fertilizer only (CT). Germination of the BCL treatment is significantly higher (*) than the M, ML, BCSLM and CT treatments (*) (ANOVA, p<0.05 for all comparisons).

None of the soil amendment treatments had significantly higher belowground biomass compared with the control. Average belowground biomass was slightly higher in the BCL treatment (2.9 g/m^2) compared with the control (2.0 g/m^2), however not significantly. The SL treatment had significantly higher belowground biomass compared with BCS, BCSL, ML and BCSLM (Figure 4b).

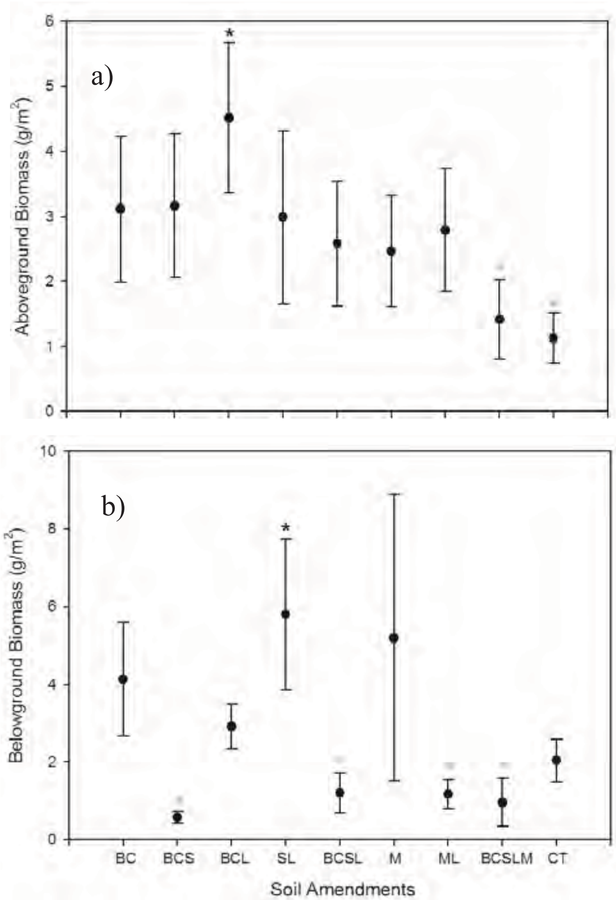

Figure 4. Aboveground (a) and belowground (b) biomass of native grasses with different soil amendments after 2 months grow on the Valley Tailings, Keno, YT. Soil amendment treatments are Biochar (BC), Biochar and Smectite (BCS), Smectite and Lime (SL), Biochar, Smectite and Lime (BCSL), Mulch (M), Mulch and Lime (ML), Biochar, Smectite, Lime and Mulch (BCSLM) and Control with fertilizer only (CT). The aboveground biomass of the BCL treatment is significantly higher (*) than the BCSLM and CT treatments (*) (ANOVA, p<0.05 for all comparisons). Note: Belowground biomass was only sampled within 5 plots per treatment.

DISCUSSION

<u>Hydrocarbon Remediation Trial</u>

Under frozen conditions, the addition of 3% (w/w) bonemeal biochar is effective at accelerating the degradation of PHC contaminated soils from a northern landfarm. Microbial activity appears to be a driving factor in the degradation of PHCs under frozen conditions, as amended soils had higher numbers of PHC-degrading microorganisms. Dias et al. (2012) similarly found higher PHC-degrading bacterial counts in biochar amended soils, as compared to the control. In soils with adequate nutrients, temperature, and θ_{liquid} there may be limited response from biochar applications (i.e., no significant differences in degradation were detected under thawed conditions). However, biochar can compensate for deficient soils that are limited by temperature, θ_{liquid}, nutrient supply rates and enhance microbial activity and PHC degradation. Areas with low rainfall and coarse textured or nutrient deficient soils have benefited the most from the addition of biochar to agricultural lands (Lehmann et al. 2006). Similar to previous studies, we found that biochar can increase θ_{liquid} in coarse textured soils under frozen conditions, due to increases in soil porosity and surface area (Amonette and Joseph 2009; Chan and Xu 2009; Downie et al. 2009).

Although the frozen and thawed treatments had similar soil properties and fertilizer additions, frozen soils are limited by temperature, θ_{liquid}, and nutrient and gas exchange. Liquid water (θ_{liquid}), limits microbial activity in frozen soil as unfrozen water allows the diffusion of microbial substrates and waste products (Ostoumov and Siegert 1996). Changes in θ_{liquid} may directly impact microbial activity and subsequently alter nutrient supply rates, which can also influence microbial activity and PHC degradation in frozen soils (Harvey et al. 2008; Harvey 2011). Trends suggest that θ_{liquid} content is higher in biochar amended soils so we expect that there will be significant differences between nutrient supply rates in biochar amended versus the control treatment under frozen conditions. We also expect that the abundance of catabolic functional genes will also be higher in biochar amended soils as compared to the control, under both frozen and thawed conditions. In subsequent experiments, we will attempt to examine linkages between functional gene copy numbers and microbial biomass to θ_{liquid} content, which influences nutrient supply rates and degradation rates.

If a deficient soil is lacking in essential macro and micronutrients, biochar additions may not directly supply enough nutrients, therefore, fertilizer additions may be necessary. However, biochar has a high cation-exchange capacity (CEC) and can reduce nutrient losses in the soil (Beesley et al. 2011); therefore, for soils with limited CEC or θ_{liquid}, biochar additions may be beneficial.

Current bioremediation strategies are targeted toward the short summer months (2 to 4 months/year), but this is often an insufficient amount of time to meet remediation targets and environmental criteria. Our results suggest that with biochar, remediation may be active under frozen conditions extending remediation periods and providing new cost-effective remediation strategies.

Tailings Soil Amendment Trial

Phytostabilization of mine tailings is highly difficult, not only due to phytotoxic effects of elevated heavy metal concentrations, but also due to extreme pH values, low fertility, low water-holding capacity and unfavorable substrate structure (Fellet et al. 2011). The BCL treatment promoted both germination and growth of the native grass seed mix. There are a number of potential mechanisms by which biochar may have influenced germination and growth including retention of soil moisture, increased temperature at the surface due to reduced albedo, increased nutrient retention and reduction in bioavailability of heavy metals. Biochar has a high surface area and porosity and can increase the water-holding capacity of the soil (Fellet et al. 2011). Biochars with a high volume of macropores greater than 50 nm diameter can make water available to plants (Lehmann and Joseph 2009). Higher moisture availability at the surface may have contributed to both higher rates of germination and initial growth.

The functional groups of biochar influence the sorption process depending on the nature of their surface charge so that both transition metals and non-transition metals can be sorbed onto the surface of biochar particles (Amonette and Joseph 2009). Several studies have found reduced availability or leachability of heavy metals following the application of biochar to contaminated soils (Beesely et al. 2011). In situ immobilization of metals using soil amendment processes is increasingly being considered as an effective and low cost remediation alternative (Fellet et al. 2011; Kumpiene et al. 2008; Mench et al. 2007). While liming is one of the oldest and most widely used metal immobilizing soil treatments, the effects of liming gradually reduce over time due to the dissolution and leaching of the liming agent, especially in highly acidic soils (Ruttens et al. 2010). Biochar however, is highly recalcitrant (Steiner et al. 2007) and its effects may persist over long time periods. In addition, most biochars tend to have neutral to basic pH and therefore commonly have a liming effect. However, it should be noted that this liming effect has been shown to increase As mobility and restrict re-vegetation (Beesely et al. 2011). Care should be taken to determine how various types of biochar may interact with the elements and conditions at a given site. Further studies are needed to examine the influence of biochar application methods and the adsorption and long-term immobilization of heavy metals with biochars.

WORK IN PROGRESS

In addition to the above studies our project is also working to overcome the logistical and technical hurdles associated with biochar production in the North, specifically in both Whitehorse, YT and Iqaluit, NU. Three further trials examining the use of biochars for hydrocarbon remediation are being undertaken: 1) a laboratory trial comparing the rates of PHC degradation in frozen soils amended with biochars made from wood, fishmeal and bonemeal feedstocks; 2) Land treatment facility trials in Whitehorse, YT and Iqaluit, NU to determine the specificity of biochar and role of direct additions of nutrients via biochar by evaluating PHC degradation under different biochar formulations; and 3) Land treatment trials in Whitehorse, YT and Iqaluit, NU to determine methods of applying biochar to soils (i.e., surface application, injection or homogenization) that optimize θ_{liquid}.

CONCLUSIONS

Soil amendments that promote the degradation of hydrocarbons, reduce the bioavailability of heavy metals, improve soil conditions and promote long term re-vegetative success are needed in northern Canada. By providing technological solutions for northern remediation and restoration, we aim to increase PHC bioremediation and mine restoration success in the North. Providing effective biochar formulations, optimal application rates and efficient application technologies specific to local restoration needs is essential to alleviate current challenges to cost-effective remediation.

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Overcoming Northern Challenges

Proceedings of the 2013 Northern Latitudes Mining Reclamation Workshop and

38th Annual Meeting of the Canadian Land Reclamation Association

Whitehorse, Yukon September 9 – 12, 2013

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Northern Latitudes Mining Reclamation Workshop

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Chang	Bioremediation in Northern Climates
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Hewitt, McPherson and Tokarek	Bioengineering Techniques for Re-vegetation of Riparian Areas at Colomac Mine, Northwest Territories
Bossy, Kwong, Beauchemin, Thibault	Potential As2Oc Dust conversion at Giant Mine (paper not included)
Waddell, Spiller and Davison,	The use of ChemOx to overcome the challenges of PHC contaminated soil and groundwater at contaminated sites
Douheret,	Physico-Chemical treatment with Geotube® filtration: Underground Mine Desludging in winter TTS, Iron (Fe) and Zinc treatment
Coulombe, Cote, Paridis, Straub	Field Assessment of Sulphide Oxidation Rate - Raglan Mine
Smirnova et al	Results of vegetation survey as a part of neutralizing lime sludge valorization assessment
Baker, Humbert, Boyd	Dominion Gurney Minesite Rehabilatation (paper not included)
Martínez, Borstad, Brown, Ersahin, Henley	Remote sensing in reclamation monitoring: What can it do for you?

Wednesday:	**Back To Tuesday**
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Knight	Galena Hill, Yukon, Ecosystem Mapping Project
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Pedlar-Hobbs, Ludgate and Luchinski	Key Factors in Developing and Implementing a Successful Reclamation Plan
Chang, et.al	Effects of Soil Aggregates Sizes (paper not attached)
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NORTHERN LATITUDES MINING RECLAMATION WORKSHOP

The Northern Latitudes Mining Reclamation Workshop is an international workshop on mining, land and urban reclamation and restoration methods. The objective of the workshop is to share information and experiences among governments, industry, consultants, Alaska Natives, northern First Nations and Inuit groups which undertake reclamation and restoration projects, or are involved in land management in the north or in comparable environments.

The first Workshop was held in Whitehorse, Yukon Territory, Canada in 2001 and it has been held every two years since, alternating between Canada and Alaska. The primary sponsors of the Workshop include the Yukon Geological Survey, Indian and Northern Affairs Canada, Natural Resources Canada, US Department of the Interior Bureau of Land Management, and the State of Alaska Department of Natural Resources.

CANADIAN LAND RECLAMATION ASSOCIATION

The CLRA/ACRSD is a non-profit organization incorporated in Canada with corresponding members throughout North America and other countries. The main objectives of CLRA/ACRSD are:

- To further knowledge and encourage investigation of problems and solutions in land reclamation.
- To provide opportunities for those interested in and concerned with land reclamation to meet and exchange information, ideas and experience.
- To incorporate the advances from research and practical experience into land reclamation planning and practice.
- To collect information relating to land reclamation and publish periodicals, books and leaflets which the Association may think desirable.
- To encourage education in the field of land reclamation.
- To provide awards for noteworthy achievements in the field of land reclamation.

ACKNOWLEDGEMENTS

The sponsoring organizations wish to acknowledge the work and support of all the people who made this conference a success, including:

- The Conference Organizing Committee: Alissa Sampson, Andrea Granger, Bill Price, David Polster, Diane Lister, Justin Ireys, Linda Jones, Mike Muller, Neil Salvin and Samantha Hudson.
- The Conference Papers and Posters Committee: Andy Etmanski, Bill Price, Chris Powter, David Polster, Diane Lister and Scott Davidson
- The Conference Sponsors (see next page)
- The Conference paper and poster presenters
- Dustin Rainey, Jocelyn Douheret and Brian Geddes for permission to use their photos on the Cover, Papers and Posters pages, respectively

CITATION

This report may be cited as:

Polster, D.F. and C.B. Powter (Compilers), 2013. Overcoming Northern Challenges. Proceedings of the 2013 Northern Latitudes Mining Reclamation Workshop and 38th Annual Meeting of the Canadian Land Reclamation Association. Whitehorse, Yukon September 9 – 12, 2013. 264 pp.