PYROLYSIS WITH PURPOSE:
SURVEYING RELATIVE BIOCHAR-TAILINGS COMPATIBILITY THROUGH NATIVE SEED GERMINATION TRIALS.

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Key Words: biochar, mining, heavy metals, acid mine drainage, tailings, germination, reforestation.

CONTEXT:

Introduction

Canada's diverse geological landscape is foundational to the country's long-standing global leadership in mining. At present, more than 60 minerals and metals are produced from domestic mine sites across Canada, representing a considerable contribution to the national economic portfolio (MAC, 2014). As a result of historical unregulated mining activities, contaminated inactive and abandoned mine sites generate both localized and widespread soil and water quality degradation (NRCAN, 2014). Orphaned mine sites fall under the jurisdiction of cash-strapped government ministries, who oversee an often slow, inadequate and impermanent remediation process (NOAMI, 2014). In recent years, the Canadian mining industry has been exposed to increasingly rigid environmental accountability. All the while, current mining and milling practices remain largely unchanged (NRCAN, 2014). Among the industry's direct operational products, tailings are generally considered the most difficult to manage responsibly and permanently (Bussière, 2007).

Following orebody mining, valuable mineral is separated from the gangue material through a milling process that involves initial size reduction (crushing, grinding) and subsequent chemical separation (floatation, hydrometallurgy) (Bussière, 2007). Mine tailings -the non-metal material produced during processing- is valueless and requires disposal. Precious metal mines are often profitable at very low cut-off grades and generate significant quantities of tailings while isolating very small fractions of valuable metals. These large volumes of tailings are pumped as slurry into a settlement area where they pose long-lasting physical stability risks. Moreover, once deposited into the impoundment area, tailings become geochemically volatile. Sulphides, inherent in most hard rock mine tailings, combine with oxygen in the atmosphere and form acid, which in turn solubilizes remnant trace metals. Heavy metal ions have been reported to infiltrate surrounding water networks and disperse extensively within aquatic and terrestrial ecosystems (Beesley et al., 2011).

Current practices in tailings management

To date, considerable research into environmental mine reclamation has focused on limiting the availability of either oxygen, water, or sulphide minerals within a tailings impoundment in an effort to prevent ionization of metals. Currently, the use of thickened tailings technology and engineered barrier systems are most common in both research and industrial practice (Cabral et al., 2000). Thickened tailings – or densified tailings – are emerging in hard rock mining due to their high physical stability and deposition predictability. Also, densified tailings generally raise the proximate water table and, thus, reduce oxygen flow and acidification within an impoundment (Bussière, 2007). Yet, given that some of the most toxic tailings contaminants, such as arsenic, are soluble at near neutral pH levels, oxygen limitation alone will not effectively mitigate heavy metal contamination. Moreover, lasting vegetation and forestation on thickened tailings impoundments- often a mandatory component within mine closure plans – is difficult if not impossible to achieve (Beesley et al., 2011).

Biochar as a tailings amendment

The introduction of select low-cost biochars at active and legacy mine sites could alter the reclamation scenario dramatically. Biochar is the term given to any pyrolyzed biomass material that is classified for use as a soil additive (Beesley et al., 2011). Biochar has been shown to sorb mine contaminants (heavy metals), encourage substrate water and nutrient retention, and promote fertility; thus could ultimately render reclamation more efficient (Hunt et al., 2010). Furthermore, development of a commercial biochar industry in mining communities would introduce diversity within a volatile, resource-based economic setting. The experimental addition of char onto soils has demonstrated increased crop yields and plant biomass, as well as lasting stress adaptation potential (Keske and Lohman, 2011). Recent findings suggest that the inputs to and conditions of pyrolysis influence a biochar's physical and chemical properties and its ultimate performance as an amendment (Hunt et al., 2010). Less understood, however, is the extent to which biochar behavior varies in different substrate environments, including diverse mining terrains.

Biochar performance determinants

The long-term nature of biochar's heavy metal sorption in addition to its proposed improvement to litter decomposition rates, pH, and nutrient availability in soils, have motivated research into the properties of chars and general char design (Thomas, 2013). Chen et al., Beesley et al., Gell et al., amongst others, have confirmed the positive relationship between pyrolysis temperature and select characteristics of biochar, namely adsorption surface area and carbon content (Beesley et al., 2011)(Chen et al., 2008) (Gell et al., 2011). Limited research has investigated the potential mutable role of biochar in different soil substrates. Laboratory experiments conducted by Yang et al. and Zhang et al. propose that tailored/pyrolysis-defined sorption features of a biochar amendment could react variably in soils with different native organic matter (Yang et al., 2003)(Zhang et al., 2010).

Within the context of land reclamation, arsenic ionization is especially toxic to plants and animals. Arsenic is also unique in its tendency to mobilize more readily within an increasingly alkaline substrate environment (Beesley et al., 2011). In contrast to most other metals, arsenic ions exist in an oxy-anion solution (negative charge) and will, thus, tend to bind to specific heavy metal oxides in soils (or in biochar, for that matter). Amendment through a mixture of biochar and iron oxide should promote arsenic retention. This particularity further highlights the variable amendment role that biochar takes within diverse substrates.

Grass and tree seed germination

The presence of a vegetative layer over soils helps to isolate water-born contaminants and reduce their overall mobility. Re-vegetation and re-forestation atop tailings is prioritized for motivations beyond solely ecosystem regeneration and aesthetics. Indeed, the reintroduction of trees, grasses and shrubs on tailings material (or any substrate) will also assist in stabilizing both physical and geochemical parameters of concern (Ranjan et al., 2015). A rapid rate of forestation on tailings would also encourage greenhouse gas offsets as operations continue or as reclamation work progresses. Biochar has been shown to increase soil water holding capacity and liming effects, and hence encourages vegetation success (Thomas, 2013). Nevertheless, limited research attention has been applied towards matching specific biochars and mine tailings to optimize restoration and regrowth.

RESEARCH QUESTION:

Is a biochar's influence on soil improvement and plant growth substrate-specific? Can the feedstock source and pyrolysis method of 'designed' lignocellulosic biochar be used to predict its ultimate amendment capacity on a particular mine tailing?

HYPOTHESES:

Under controlled conditions, the rate and magnitude of seed germination are expected to depend on the tailing-biochar composition of a substrate, suggesting that char may be customized to encourage optimal growth on a particular tailing. Furthermore, a slightly acidic char (pH = 6.54) is expected to decrease arsenic mobility most when added to an iron-rich tailing and could induce greatest seed fertility in this tailing subclass so long as overall substrate pH remains conducive for incubation. Germination rates and leaf emergence are projected to depend on the species of seed observed, as well, irrespective of the substrate.

METHODOLOGY:

The hypotheses were tested by way of both seed germination and plant experiments performed under the supervision of Dr. Sean C. Thomas, Ph.D., Canada (Tier 1) Research Chair. A series of eight-day germination experiments were conducted in a rooftop glasshouse at the University of Toronto. Three 'designed' biochars with unique feedstock and pyrolysis features and one natural 'high-ash' char sourced from a minesite forest fire were introduced into a variety of tailing-seed settings. The growth media were four distinctive unmodified gold mine tailings from operating sites in Northern Ontario, as well as one granitic sand from Haliburton, Ontario. The tailings selected for experimental application have been sourced exclusively from operational open-pit gold mines within Ontario's Abitibi Greenstone Belt mineral formation. All tailings exhibit various extents of acidification due to inherent sulphide oxidation (St. Andrew Goldfields, 2016). The pH levels and heavy metal effluent concentrations are within legal limits at all tailings source sites, however with no advanced geochemical tailings management in practice, the stability of these levels is unlikely. The four tailings have been produced from similar mineral extraction processes whereby sodium cyanide first leaches gold off ore particles and then activated carbon is used to absorb the gold from solution. All tailings applied contain varying amounts of Cu, Co, and Fe, whereas current mine technicians only identify two of the samples as also carrying trace amounts of arsenic.

In miniature field replicates of 50 cm^3 (n = 500), each biochar has been blended into individual samples of mine tailings or granitic sand at a common dosage of 50 t/ha, as employed in forestry and no-till agriculture (Thomas et al, 2013). Dry bulk density of each tailing was measured to accurately convert the application dose into a substrate-specific percent mass of biochar. Prior to sample preparation, the biochars were be pre-treated by washing with de-ionized water for a 24hr. period on a shaker table at 50 RPM, then subsequently dried for 24hrs. in a batch oven at 60°C, as displayed in Figure 1. Motivations for pre-washing chars stem from the highly porous and absorptive properties of biochar and the release of particles throughout pyrolysis. Any initial biochar pore saturation could influence amendment, overall substrate composition, and the char's ultimate sorption potential. The four tailings applied were fully dried in a batch oven at 60°C and then passed through a coarse screen, followed by standard mechanical analysis of tailings' particle size distribution in five size classes. Both biochar and tailings pH and Electrical Conductivity values were be measured and recorded prior to sample preparation, as well. Moreover, tailings samples was examined using Xray fluorescence technology to determine elemental status of Cu, Fe, Co, and As. Finally, the measured tailings data was cross-referenced to available data collected by each mining company in situ.

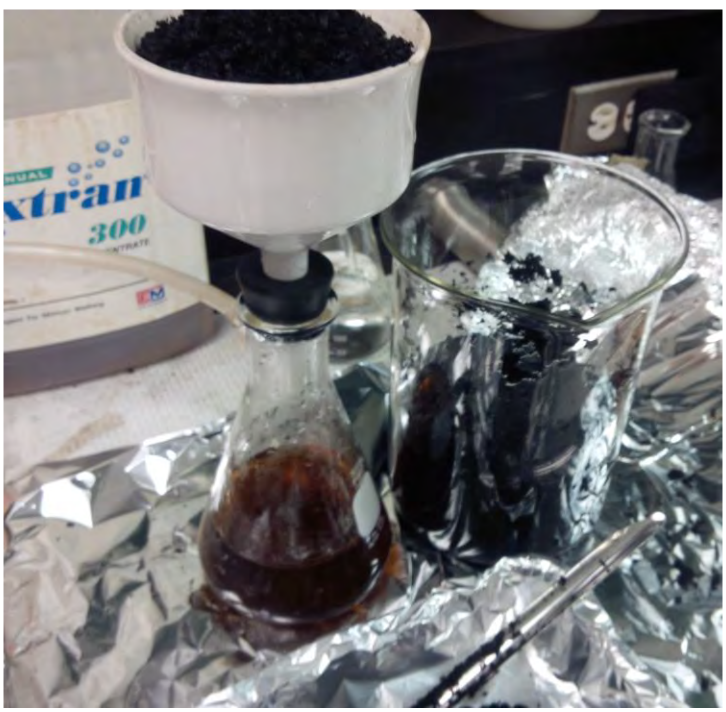

Figure 1: Pre-treatment (draining) of biochar.

Seeds of *Andropogon gerardii*, *Poa palustris*, *Picea mariana*, and *Pinus banksiana* were applied to the media (25 seeds/sample). Both grass and tree seeds were sourced from Natural Resources Canada's (NRCAN) National Seed Centre nurseries in close proximity to the pertinent mine sites, and located within the Boreal Forest Zone. The mine sites fall within the ‘3a’ Plant Hardiness Zone with mean summer daytime temperatures of 23°C and a maximum recent summer temperature near 35°C (Weather2, 2016). Systematic monitoring of % germination on 48 hour intervals as well as cumulative leaf emergence on day 8 and 10, is considered most crucial for judging amendment. One observer performed all data collection over the 8 (grasses) and 10 (trees) day trials in order to eliminate subjective variability in judging seed germination. So as to discern the relationship amongst experiment variables, a multiple regression analysis will be performed. The covariance of properties will likely require an ordination in order to reduce dimensionality for specific considerations. A typical experimental sample of tailings, biochar, and seedlings is depicted in Figure 2.

Figure 2: Substrate sample of tailings-biochar on Day 6 of a germination observation.

PRELIMINARY RESULTS/IMPLICATIONS:

Percentage of total germinated grass and tree seeds was observed to vary across the biochar-tailings substrates, with most dramatic variability observed across the various biochar`s applied to Goldcorp’s Porcupine Mine upper delta tailings. Seed germination success on this aforementioned substrate has been grouped based on biochar type and displayed in Figure 3 below. The natural forest fire charcoal (“M”) produced the second highest germination in all species when applied to the Goldcorp upper delta biochar.

In forecasting possible seed reactions to a substrate combination of natural forest fire charcoal and mine tailings, typical post-fire forest stands should be considered. Indeed, decades of research confirms that revegetation (including reforestation) increases following fire events due in large part to the resulting charcoal deposition, which increases litter decomposition, soil pH, and nitrogen availability (Thomas, 2013).

Substrates with both tailings and natural high-ash forest fire char were, hence, expected to exhibit increased germination rates compared to substrates composed of tailings alone. The natural char's propensity to match pyrolyzed chars in terms of germination response suggests it may be a viable, readily-available amendment. Typically, forest-fire char is produced as a result of complete wood combustion under relatively high oxygen exposure. Such conditions result in an alkaline, nitrogen-depleted substance, which if considered exclusively, should diminish germination potential. In combination with various acidic, contaminated tailings, however, its behavior is less predictable. Moreover, the natural char has been applied to samples in its in situ form and was likely collected in combination with some organics from the underlying terrain. Although the composition of this amendment is not one of "pure" char, the material was left untreated so as to verify the efficiency of a locally sourced amendment option.

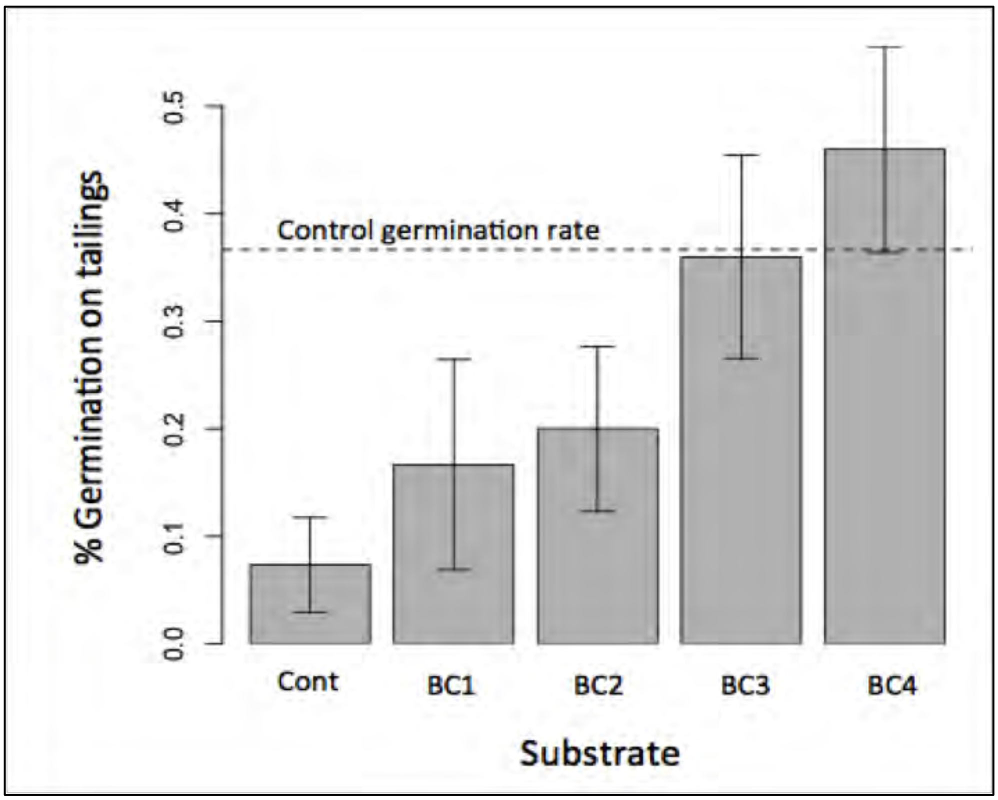

Figure 3: Goldcorp Porcupine Upper Delta Tailings: % Germination in Biochar Types.

Overall, further data analysis is to be conducted and germination rate and leaf emergence is predicted to vary among biochar-substrate groupings with some independent deviation between seed species. Of the biochars applied, that with highest pH and pyrolysis T–designed from mixed construction wood waste – was expected to prompt most rapid and robust germination in all species when combined with most tailings, yet was outperformed by the three other chars tested . Given the distinct toxicity and chemical behavior of arsenic, any biochar-specific germination trends will be of significant interest and likely the subject for further analysis. Since the mobility of arsenic ions is known to increase with increased soil pH, the most alkaline biochar may actually deter germination in this particular scenario. Any arsenic mobility is likely to introduce toxicity within the substrate water particles and, hence reduce seed germination.

CONCLUSIONS/SIGNIFICANCE:

Preliminary results would suggest that biochar might be tailored for use on a particular contaminated substrate, representing a value-added incentive for its application in the industrial context. Furthermore, if a natural mine site char increases seed germination rates in tailings, it may prove to be an internal, low-cost support to reforestation and reclamation. As the substrate-specific behavior of biochar becomes progressively more understood, development of a biochar treatment glossary for Canadian mine tailings could be realistic. Tailored biochar solutions would advance mine remediation and the biochar industry, and reduce the ultimate industrial footprint. Results of preliminary investigations should provide motivation for extended glasshouse experiments and eventual in-situ testing.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the project support from the Ontario Mining Association, as well as the resources provided by Goldcorp Inc., St. Andrew Goldfields, and Haliburton Research Forest. Both authors receive independent research funding from the Natural Sciences and Engineering Research Council. Finally, the authors acknowledge the great opportunity provided by the conference host, the Canadian Land Reclamation Association.

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