Abstract

Mineral (neutral mine tailings, quartz sand) and organic (sawdust, hay) mixes were subjected to a slow co-pyrolysis process (400°C, 30 minutes) to produce biochar-mineral mixtures with the intent of accelerating granular structure formation which is beneficial to the establishment of vegetation. Resulting products were examined for pH, CEC, water holding capacity and IR spectra, and compared to non-pyrolyzed samples. The changes in these soil properties with temperature of pyrolysis (200°C, 300°C and 400°C) were also examined. Differences were found in samples resulting from organic type, mineral type, temperature of pyrolysis, and the pyrolysis process. Aggregates formed in all samples containing organics. Aggregates were examined by scanning electron microscope and thin section microscopy revealing mineral particles embedded in an organic matrix. The results suggest a role of phase changes of carbon products (into bio-oil and bio-gas) during pyrolysis in the closed reactor system, rather than a biochar coating creating organo-mineral complexes.
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1 Introduction

Extractive industries are a major economic driver and provide raw materials for the manufacturing sector of the economy in Canada and for export. Canada’s Gross Domestic Product in 2011 related to mining, quarrying and oil and gas extractions was $57.4 billion (Industry Canada, 2013). Tailings are a common waste product of hard rock mining and are a fine-textured, sand/silt-like material produced from the crushing, milling and chemical processing of ore. Dry tailings may be stabilized against erosion from water or wind by plant cover; however, tailings often lack key nutrients and organic matter which is not supportive of plant growth (Mendez and Maier, 2008; Ibrahim and Goh, 2004).

The presence of a granular structure can serve as an indicator of soil fertility associated with improved aeration, water flow and availability, and high nutrient content (Arocena et al., 2012). Stable aggregates within soil are important for environmental quality and can influence both physical (water transport and capacity, aeration and erodibility) and biogeochemical processes (plant growth and soil biological activity) (Amezketa, 1999). Acidic hard rock mine tailings amended with organic matter and calcium carbonate have been shown to establish granular microstructure over time (Zanuzzi et al., 2009; Arocena et al., 2012). However, this pathway for the formation of granular structure takes time on the scale of years and one of the perceived drawbacks of phytoremediation as a site remediation treatment is the lengthy implementation time (Mendez and Maier, 2008). Ibrahim and Goh (2004) created macroaggregate structure in tailings amended with lime, humic substances (leonardite), and straw over a matter of months; however, their experiment was done in an incubator with consistent moisture and a temperature of 20°C, conditions that would not be reflected in most natural settings.
Formation of soil particles into micro and macro aggregates involves soil organic carbon (SOC), biota, ionic bridging, clay, and carbonates (Bronick and Lal, 2005), carried out by soil fauna, microorganisms such as bacteria and fungi, and plant roots while being influenced by environmental conditions (Six et al., 2004). Microaggregates (20-250µm) are composed of complexes of clay, polyvalent metals (such as Ca, Al, Fe,) and humified organic matter (Edwards and Bremner, 1967) with the most important mechanism likely being polyvalent-cationic bridging between clay particle surfaces and carboxyl groups of organic matter (Tisdall and Oades, 1982). Ibrahim and Goh (2004) attributed the correlation between increased aggregation and increased cation exchange capacity (CEC) to the increase in exchange sites from organo-mineral complex formation. The stability of microaggregates is high, due to several binding agents working in combination and stronger organic bonds because microaggregates contain less organic carbon (OC) than macroaggregates (>250µm) (Tisdall and Oades, 1982). Fernandez-Ugalde et al. (2013) found that clay content was proportionally greater in microaggregates compared to macroaggregates (defined as 250-500µm) and large macroaggregates (defined as 500-5000µm). They also found that OC levels decreased with decreasing aggregate size and that swelling clay levels were increased in microaggregates compared to larger aggregate sizes, which the study authors attributed to the large surface area, smaller particle size and mechanical properties of the swelling clays (Fernandez-Ugalde et al., 2013).

Biota make significant contributions to aggregation in soils by adding organic materials as carbon sources and/or binding agents, and through physical and chemical processes such as the intake and excretion of soil materials by soil fauna, resulting in organo-mineral complexes (Pulleman et al., 2005). These complexes show a variety of organic
functional groups present within the materials (Arocena et al., 1995). A recent study, using multi-element scanning transmission X-ray microscopy (STXM) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, found complex and extremely varied organic groups and organo-mineral interactions within soil microaggregates (Solomon et al., 2012).

Previous research has examined the potential of co-pyrolysis of organic matter and mine tailings to encapsulate metals and improve soil structure with the increase in soil organic matter (SOM) (Debela et al., 2012). Pyrolysis is a process in which organic matter is partially decomposed by the application of heat (usually at temperatures < 700°C) in a low-oxygen environment (Lehmann and Joseph, 2009). The resulting material is known as char, biochar, or black carbon, and will be referred to here as biochar for consistency. Previous encapsulation research (Debela et al., 2012) found that tailings particles were left with a surface coating of biochar, with mixed results for the leaching of different elements studied; for example: leaching was reduced 93% for Cd and Zn in tailings pyrolized at 400°C with 5-10% biomass addition, Zn leaching increased after pyrolysis at both 200°C and 400°C with 15% biomass addition, Pb leaching was reduced 43% after heat treatment at 400°C with no added biomass, and As leaching was increased after pyrolysis at 200°C with 0, 5, 10, and 15% biomass additions.

When applied as an agricultural amendment, biochar has been shown to improve aggregate stability in fertile agricultural soils (Alfisols and Andisols) (Herath et al., 2013), increase mean weight diameter of soil aggregates and reduce erosion (Jien and Wang, 2013), and improve soil biological and physiochemical properties (Jien and Wang 2013; Laird et al. 2010). Lei and Zhang (2013) found that biochar improved physical and hydraulic properties
of soil. A study comparing biochar carbon to other soil organic carbon (SOC) found that biochar appeared preferentially present in microaggregates and the authors speculated that the biochar may have a role in both formation and stabilization of microaggregate structures (Brodowski et al., 2006). Biochar was associated with increased incorporation of other organic matter into soil aggregates and the organo-mineral fraction (Liang et al., 2010).

The chemical and physical properties of biochar vary depending on reaction conditions (temperature, speed of reaction) and feedstock (Lehmann and Joseph, 2009; Heymann et al., 2011; Lee et al., 2013a; Lee et al., 2013b; Masek et al., 2013a; Masek et al., 2013b). Bruun et al. (2011) found temperature increments of 25°C in a fast pyrolysis process significantly changed the chemical properties and subsequent loss of carbon as a result of degradation in soil. In a comparison between fast and slow pyrolysis methods, the fast pyrolysis method resulted in a biochar with an unpyrolyzed carbohydrate fraction (8.8%), providing a labile source of carbon which may have caused the observed slight increase in CO₂ emission due to decomposition of the labile C, the increased microbial biomass, and the nitrogen immobilization rather than net nitrogen mineralization. In addition, the fast pyrolysis product showed a lower pH, smaller particle size, and higher Brunauer-Emmett-Teller (BET) surface area than the slow pyrolysis product (Bruun et al. 2012). Variations in temperature and feedstock (different livestock manures) have been found to result in different physiochemical characteristics. Generally, the study authors observed that the increase in pyrolysis temperature resulted in an increase in ash content, pH, BET surface area, and the removal of volatile matter, while finding mixed results for fixed carbon concentrations and electrical conductivity (EC) by feedstock (Cantrell et al., 2012). Biochar particles become smaller with increasing temperature, and the functional groups within the
biochar changed at different production temperatures and durations of the process, showing aromatic groups increasing with temperature and O, H and aliphatic C decreasing (Peng et al., 2011). Biochars have potential to be designed for specific characteristics suitable for different microbial processes in soils (Steinbeiss et al., 2009).

Artificially constructed soils are sometimes used for studying particular soil processes, such as aggregation due to microbial activity (Pronk et al., 2012). Constructed soil has been proposed as a method to design a medium with desired characteristics for a specific study (Guenet et al., 2011). Nutrient-poor soils, or non-soils such as mine tailings or geotechnical fill, will often be treated with various additives such as fertilizers, pH adjusters, or compost to improve their function as a plant growth medium.

The study undertaken in this thesis pursued a novel approach where the primary amendment, biochar, was created through a pyrolysis process in the presence of the nutrient-poor and non-soil materials to be amended. This was anticipated to create a bound mix of the organic biochar product and the mineral material, potentially resulting in improved opportunity for the formation of organo-mineral complexes and soil granular microstructure. If successful, a major benefit of the process would be a greatly reduced time period required to create granular microstructure compared to naturally occurring processes.

The experimental trials in this thesis involved different combinations of materials with the variables being: mineral material (tailings from a nearby molybdenum mine along with an industrial grade quartz sand), organic feedstock (low-ash wood sawdust and high-ash hay), and ratio of organic feedstock to mineral material. Initially, temperature and time of reaction were intended as variables; however, the inclusion of added variables would greatly
increase the number of samples, with each additional sample taking roughly four to five hours to produce. In order to keep the experiment straightforward and reasonable in scope and time, one temperature and one time of reaction were chosen. The literature review suggested that char yields drop with increased temperatures, favouring the production of bio-oils and bio-gas as temperatures go beyond 400-500°C. Logistically, the reactor used in this experiment had a stated maximum operational temperature of 450°C, and was found to have a real limit of 485°C. Preliminary lab testing determined that lower temperatures (<300°C) did not always produce completely charred materials, with the inner portion of the sample maintaining some degree of its original colour and appearance. To ensure complete charring in a relatively swift time, while maintaining a high yield of solid char, a temperature of 400°C and hold-time of 30 minutes were chosen. Mixtures were also made of the tailings/sand materials and separately-created biochar to observe differences between the co-pyrolysis method and separate pyrolysis of the feedstock.

1.1 Intended Benefits

Although the economic and material benefits of mining are significant, so is the potential for environmental degradation due to land disturbance and toxic waste products. Mine tailings present a management challenge due to their large quantity and potential for environmental degradation through metal leaching and acidification of receiving waters. In addition, tailings are usually a nutrient-poor material when considered as a growth medium and frequently carry the potential for being transported offsite via wind and water erosion. Phytostabilization of tailings is an attractive concept but its major drawback is the length of time required to establish plant communities within the poor substrate.
Co-pyrolysis of organic matter and tailings has the potential to introduce biochar to
the tailings as an excellent soil amendment thereby increasing nutrients and organic matter,
while accelerating the formation of granular microstructure which is preferable for plant
growth and ecosystem establishment. The research presented here is a starting point to
examine if microaggregates can be created through the co-pyrolysis process and to establish
relationships between the chosen feedstocks, mineral materials, and reaction conditions.
2 Methods and Materials

2.1 Co-pyrolysis

Co-pyrolysis is the combustion of organic matter together with mineral matter in the absence of oxygen to generate a partially oxidized material. For this experiment, a Parr 4575 500-mL bench top reactor (Parr Instrument Company, Moline, Illinois) was used (Fig. 2-1). The reactor has a sealable cylinder capable of withstanding a temperature of ~500 °C and an internal pressure of 3500 psi. The reactor is fitted with an external heater, and an internal cooling loop to accelerate cooling upon the completion of a heating cycle. There is a valve-controlled gas line hooked up to a nitrogen tank to purge ambient air from the sealed reactor chamber prior to heating (thus removing oxygen and preventing combustion), and an exhaust valve which can either be closed to retain reaction products (as was done in this study), or opened to release gases and liquid by-products of the pyrolysis process.

Figure 2-1 Schematic diagram of the Parr 4575 reactor (from Debela et al., 2012)
2.2 Sample Materials

The co-pyrolysis experiments conducted in this thesis used high and low ash content organic materials together with mine tailings and quartzitic sand for inorganic matter. A single species, relatively clean (free from visible dirt and debris), commercially-available Timothy grass (*Phleum pratense*) hay (high ash) and Douglas-fir (*Pseudotsuga menziesii*) shavings (low ash) were used as organic materials. The hay and wood shavings were then separately milled through a hammer mill fitted with a 1-mm screen (Mikro-Bantam T-Hammer Mill, model W, Hosokawa Micron Powder Systems) located in the UNBC Enhanced Forestry Laboratory. The wood shavings are referred to as "sawdust" throughout. It was noted that, with the hay being a fibrous material, the 1-mm screen size only applied to width and depth resulting in many hay particles being several millimeters in length. The milled organic materials were placed in individual aluminum trays (commercially purchased, disposable aluminum food bakeware) and dried in a laboratory oven (Fisher Scientific, Isotemp Oven) at 80 °C for 24 hours, then stored in an airtight container.

The mine tailings were collected from Tailings Pond #2 at the Endako Mine (a molybdenum mine located in central British Columbia) in April 2011, and stored moist in a closed plastic pail at ambient laboratory temperature until use. To obtain an average particle size distribution for the tailings material which could then be used to create a similar quartzitic material with the same particle size distribution, samples of the tailings were dried at 105 °C, weighed, placed in a dry sieve set with screen sizes of 425 µm, 180 µm, 90 µm and 53 µm, then shaken in a reciprocating shaker for 30 minutes. The dry sieving of a tailings sample was done three times to obtain the following average particle size distribution: >425 µm = 60%, 180 to 425 µm = 30%, 53 to 180 µm = 8%, <53 µm = 2%).
The quartzitic sand materials were then individually mixed to obtain the appropriate and comparable size distribution to the tailings sample. Small particle sized quartz sands were generated by grinding larger particle sized quartzitic materials in a ceramic mortar and pestle.

2.3 Production of co-pyrolyzed char materials

2.3.1 Main Experiment

Prior to the production of co-pyrolyzed materials for the experiment, multiple test runs were performed with the various combinations of organic and mineral materials and varying reactor conditions. These test-runs were designed both to gain familiarity with the equipment and materials, and to choose an appropriate temperature and heating time for the samples. The amount of material that could be included in one batch is limited by both the volume of the material and its mass. In effect, density matters. It was determined that a sample mass of 130 g of mineral material was the maximum which could be accommodated within the volume of the apparatus for the least dense of the mineral/organic mix samples (TS30 = 130g tailings and 39g sawdust). The same total mass was applied to all of the runs with other mineral and mineral/organic mixtures. In the case of pure sawdust and pure hay, a reduced weight of 60 g was utilized in order to fit all of the material into the apparatus. Mass was chosen as the independent variable as it is invariant during the treatment whereas volume changed significantly during pyrolysis.

\footnote{Addition of organics is based on +15% and +30% of mineral mass i.e. 19.5g is 15% of 130g, and 39g is 30% of 130g.}
A low temperature was targeted to favour char production; however, it was observed that, at low temperatures (≤300 °C), the organic material did not always appear to be completely charred. The 400 °C temperature was chosen to produce completely charred materials within the temperature limitations of the reactor and minimize the conversion of the biomass into the liquid and gaseous phases. Once the temperature of 400 [± 10] °C was reached, the condition was maintained for 30 min before the heat supply was shut off and the cooling cycle started. The range of temperatures varied slightly for the types and ratios of organics to mineral material. The range of the time period for the equipment to reach 400 °C varied from 75 min for the 100% mineral samples to 90 minutes for 100% organic samples. However, these temperature and time variations are believed to be minor and have no significant influence on the properties of the char products.

Once the equipment had cooled to a sufficient degree, the reactor was removed from the insulated cylinder and placed in a water bath until cool enough to remove the contents. Residual pressure from gaseous products was observed in the cooled reactor except for the 100% quartzitic sand and 100% tailings samples. This gaseous product was vented into a fume hood before the reactor was opened and a small amount of liquid product (not measured, but estimated at less than 5 mL) often bubbled out the reactor exhaust and into the vent tubing. The pyrolized product, along with the vented gases and liquids, had a very unpleasant odour and proved to be irritating to the respiratory tract so an air filter mask was used during the recovery of the char product and cleaning of the equipment.

Once the product was removed and placed in a labeled 250 mL sample jar, the inside of the reactor was scrubbed and cleaned with Alconox™ (an anionic detergent) and water. After cleaning, the equipment retained minimal carbonized residue buildup from both the
present and previous experiments; however, given the nature of the experiment (characterizing samples rather than looking for micro or nano-levels of contaminants within the samples), the very minimal residue accumulations compared to the sample volumes, and the resistance of the residue to removal, it is believed that the residue has no significant impact on any of the sample properties studied in this experiment either by decreasing sample volume or introducing sample contamination.

Once a complete set of samples from the 12 treatments (Table 2.1) was produced (each sample taking roughly five hours to create, completed samples were stored in air-tight sample jars until all 12 were completed), the samples were placed in individual open plastic trays (large weigh boats) and left in a fume hood for 17 days to release volatile compounds and condensates. After 17 days, the samples were returned to their air-tight sample jars. Three replicates of the 12 treatments were done. All 12 treatments were completed before the next set of replicates was started.

Table 2.1 Combinations of organic (sawdust, hay) and inorganic (mine tailings, quartzitic sand) used in the production of charred materials in the primary experiment

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Sample ID</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>TX0</td>
<td>100% tailings (130g dry weight)</td>
</tr>
<tr>
<td>T2</td>
<td>TS15</td>
<td>130g tailings, 19.5g sawdust</td>
</tr>
<tr>
<td>T3</td>
<td>TS30</td>
<td>130g tailings, 39g sawdust</td>
</tr>
<tr>
<td>T4</td>
<td>TH15</td>
<td>130g tailings, 19.5g hay</td>
</tr>
<tr>
<td>T5</td>
<td>TH30</td>
<td>130g tailings, 39g hay</td>
</tr>
<tr>
<td>T6</td>
<td>SX</td>
<td>100% sawdust (60g dry weight)</td>
</tr>
<tr>
<td>T7</td>
<td>QX0</td>
<td>100% quartz</td>
</tr>
<tr>
<td>T8</td>
<td>QS15</td>
<td>130g quartz, 19.5g sawdust</td>
</tr>
<tr>
<td>T9</td>
<td>QS30</td>
<td>130g quartz, 39g sawdust</td>
</tr>
<tr>
<td>T10</td>
<td>QH15</td>
<td>130g quartz, 19.5g hay</td>
</tr>
</tbody>
</table>
Each sample was then subjected to soil pH testing ($H_2O$ and $CaCl_2$), Cation Exchange Capacity (CEC) determination by $BaCl_2$ extraction and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis for Al, Ca, Fe, K, Mg, Mn. In addition, soil available water was determined using a pressure plate apparatus at 1/3 bar and 15 bars. Samples were also examined by Fourier Transform Infrared spectroscopy (FTIR) in KBr pellets, as well as analyzed for Total Carbon, Organic Carbon, and Total Nitrogen.

### 2.3.2 Temperature Experiment

A secondary experiment was a temperature trial in which samples containing one mix of material (130g quartzitic sand, 39g sawdust) were subjected to pyrolysis at three different temperatures. During the primary experiment, it was noted that the temperature would hold around particular values for several minutes then increase quickly before returning to a more regular rate of temperature increase. The sudden temperature increase corresponded to a sudden pressure increase. It was theorized that this showed the temperatures at which different products change phase and that products created at temperatures below and above those values should exhibit different characteristics. This secondary experiment sought to investigate any difference based on the same parameters (pH, CEC etc.) investigated in the primary experiment. Three temperature settings were chosen based on previously noted temperatures corresponding to pressure increases, 210°C, 310°C and 430°C, but it was observed that the temperature would rise above the 210°C setting (235-248°C), stabilize around 310°C for the 310°C setting (308-319°C), and not quite reach the temperature for the
430°C setting (411-419°C). This temperature discrepancy had been noted previously and was planned for in the choice of settings.

With these trials, the reactor was set to the chosen temperature and turned on, observed until it reached a point where the pressure stopped increasing (generally corresponding to the time it reached its highest temperature or within about 10 minutes after reaching that temperature), left for 30 minutes, then the reactor element was shut off and the cooling loop turned on. Pressure was used as the determinant as it indicates that products are changing phase. The three samples were replicated three times with each set of three being completed prior to the start of the next set of three. Each sample was then subjected to soil pH testing (H₂O and CaCl₂) and CEC determination by BaCl₂ extraction and ICP-OES analysis for Al, Ca, Fe, K, Mg, Mn. Samples were examined by FTIR spectroscopy in KBr pellets, as well as analyzed for total carbon, organic carbon, and total nitrogen. A test run of the pressure plate apparatus for determining soil available water was conducted with the temperature trial samples to ensure the instrument was operating within specifications.

Results indicated that the materials had very similar soil available water, which was not surprising given that the samples all had the same mineral/organic mix and the precision of this testing is not high, so minimal differences would not likely be observed. Two of the samples were damaged during the test (material spilled during handling), but because of the similarity in results and the time-consuming nature of the test (over a week to run it), another test was not run and results of the test-run are not reported as it is not believed to provide illuminating results within this relatively low temperature range. Had a larger temperature of pyrolysis range been studied, soil available water may have been reduced due to increased carbonization at higher temperatures.
Table 2-2 Combinations of sawdust and quartzitic sand used in the production of charred materials in the temperature experiment

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Sample ID</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>T13</td>
<td>T200</td>
<td>130g quartz, 39g sawdust, 210°C</td>
</tr>
<tr>
<td>T14</td>
<td>T300</td>
<td>130g quartz, 39g sawdust, 310°C</td>
</tr>
<tr>
<td>T15</td>
<td>T400</td>
<td>130g quartz, 39g sawdust, 430°C</td>
</tr>
</tbody>
</table>

2.3.3 Non-pyrolyzed (NP) Samples

For comparison of certain parameters with the co-pyrolysis samples, a set of non-pyrolyzed samples reflecting the same mixes as the tailings-containing samples and 100% organic samples were created. An additional sample was created by pyrolyzing sawdust separately from tailings (the tailings were also put in the reactor and subjected to the heating process), then mixed into a sample reflective of a 100% tailings, 30% sawdust by pre-pyrolysis weight, equivalent to the material found in the TS30 sample.

Table 2-3 Additional samples

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Sample ID</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>T16</td>
<td>100T30S</td>
<td>130g tailings heated in reactor, 39g sawdust pyrolyzed, with the two materials mixed after heat treatments completed.</td>
</tr>
<tr>
<td>T17</td>
<td>TX0NP</td>
<td>100% tailings (130g dry weight), no pyrolysis</td>
</tr>
<tr>
<td>T18</td>
<td>TS15NP</td>
<td>130g tailings, 19.5g sawdust, no pyrolysis</td>
</tr>
<tr>
<td>T19</td>
<td>TS30NP</td>
<td>130g tailings, 39g sawdust, no pyrolysis</td>
</tr>
<tr>
<td>T20</td>
<td>TH15NP</td>
<td>130g tailings, 19.5g hay, no pyrolysis</td>
</tr>
<tr>
<td>T21</td>
<td>TH30NP</td>
<td>130g tailings, 39g hay, no pyrolysis</td>
</tr>
<tr>
<td>T22</td>
<td>SXNP</td>
<td>100% sawdust (60g, dry weight), no pyrolysis</td>
</tr>
<tr>
<td>T23</td>
<td>HXNP</td>
<td>100% hay (60g, dry weight), no pyrolysis</td>
</tr>
</tbody>
</table>
2.4 Thin Section Samples

Thin sections provide important observations of the internal structure of an aggregate which is unique to this form of analysis. The production time of the thin sections (five months) and the slow development of aggregates within the stored samples did not allow sufficient time for thin sections to be prepared from samples in the main experiment and included in this thesis. Instead, thin sections displayed here were made using aggregates taken from samples created during trial runs of the equipment several months prior to the start of the main experiment. Samples T1-2 and T1-3 were most similar in constitution and production time to the main experiment samples and are believed to be suitable examples of the aggregates created by the co-pyrolysis process. T1-2 and T1-3 used the same tailings material as the main experiment, but a different source of sawdust (of unknown tree species). The two samples analyzed were created as follows:

Table 2-4 Thin section samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Material</th>
<th>Temperature Setting</th>
<th>Time spent at temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1-2</td>
<td>100% tailings + 20% additional weight in sawdust</td>
<td>275°C</td>
<td>1 hour</td>
</tr>
<tr>
<td>T1-3</td>
<td>100% tailings + 20% additional weight in sawdust</td>
<td>400°C</td>
<td>30 minutes</td>
</tr>
<tr>
<td>Control</td>
<td>Unprocessed mix of sawdust and tailings, no aggregation</td>
<td>No pyrolysis</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Although it was not optimal that the thin sectioned samples were created with different sawdust, and the varied times of processing from the main sample set, it was deemed a good opportunity to have some thin sections of aggregates created by the process used for the samples in the main experiments. These two test samples presented the best
option. It was observed that the T1-2 (lower temperature) aggregates were fewer and smaller in size as well as more fragile than the T1-3 aggregates. Pieces of aggregated sample material, as well as a sample of unprocessed sawdust/tailings mix were packed with cotton wool in rigid containers and sent to The University of Ghent, Belgium for thin section preparation. Thin sections were photographed in the UNBC labs using a Meiji Petrographic Microscope with cross-polarized option, at 4X and 10X magnification.

2.5 Laboratory Analyses

2.5.1 Total Elemental Analysis

A total elemental analysis was done on the tailings and quartz material to gain a greater understanding of the starting materials and to check for impurities within the quartz as it was industrial grade and not lab-grade quartz. Industrial grade is generally used as clean, fine-grained material for purposes such as water well installations. The samples were analyzed through HNO₃/HCl digestion and lithium metaborate fusion by the British Columbia Ministry of Environment Laboratory in Victoria, BC (BC MoE Laboratory).

2.5.2 pH

The pH of the char was determined in both distilled H₂O and 0.1M CaCl₂ solution following the procedure of Kalra and Maynard (1991). Ten grams of material was used for each sample except for the 100% hay or sawdust samples, for which only 1g of material was used due to the very low density (<1.0 g ml⁻¹) of those samples. For each sample, the 10g of material was placed in a beaker and 20 mL of either water or CaCl₂ solution was added.
Samples were stirred every 5 minutes for 30 minutes, then left to settle for an additional 30 minutes. It was noted that the samples appeared hydrophobic (except the mineral samples) as they tended to remain in a clump either at the bottom of the beaker or float to the surface with no water appearing to penetrate the clump. Vigorous stirring with a glass rod seemed to break this hydrophobic tendency and mixed the material with the water or CaCl₂ solution. After the 30 min settling time the samples were filtered and pH was measured in the filtrate. The pH was determined with a pH meter (Thermo Electron Corporation, Orion 550A) calibrated with pH 4, 7, and 10 buffers. The pH meter was checked and recalibrated against the buffers prior to measurement, after six samples, and after all the samples (12) in the set were completed.

Four key questions were addressed through statistical analysis of the pH testing:

1. Are there differences among the tailings-based sample treatments, and among the quartz-based sample treatments?

2. Do the tailings samples and quartz samples with the same organic matter and ratio differ (e.g. does TS15 differ from QS15)?

3. Do the samples differ between organic matter (OM) treatments (type of OM and ratio, e.g. does TS15 differ from TH15)? and,

4. Do the pyrolized tailings samples and 100% OM samples differ from their non-pyrolized (NP) counterparts?

The first question was addressed with a one-way ANOVA (in which the null hypothesis was rejected at p=0.05), followed by a post-hoc Tukey-Kramer test to determine
which treatments contributed significantly to the established variance. Questions 2-4 were addressed with two-tailed t-tests between pairs (at 95% confidence interval). Results for $pH_{H2O}$ and $pH_{CaCl2}$ were calculated separately. All statistical tests were run using Microsoft Excel.

2.5.3 Effective CEC

Cation exchange capacity was determined using the barium chloride extraction procedure (Hendershot and Duquette, 1986) and assumes that all exchange sites are occupied in the sample and all cations in those exchange sites are displaced into the extract by $Ba^{2+}$. Exactly 2.0 g (+/- 0.02g) of sample was weighed into a centrifuge tube. Thirty mL of a 0.1M $BaCl_2$ solution was added to each tube. Samples were shaken in a reciprocating shaker for two hours, and then centrifuged for 15 minutes at 700 rpm, filtered and the extract placed in labeled sample bottles. Extracts were sent to the BC MoE Laboratory for ICP-OES analysis of exchangeable cations (Al, Ca, Fe, K, Mg, Mn, Na). Results for exchangeable cations (Al, Ca, Fe, K, Mg, Mn, Na) were analyzed with one-way ANOVA, followed by a post hoc Tukey-Kramer test, and two tailed t-tests between specific pairings. Statistical analysis tests were based on total CEC (cmol/kg) and not individual cations.

2.5.4 Available Water

Available water or the water content held between -30 and -1500 kPa potential was determined using a pressure plate apparatus (Soilmoisture Equipment Corp., 5 bar and 15 bar extractor with dual pressure regulating manifold, and 220V compressor). Individual sample cells were created from ~1cm x 20 mm PVC pipe and glued to a piece of filter paper
(Whatman 42) at one end. This type of cell allowed the removal of water from the sample through the filter paper while containing all of the material. All empty cells with attached filter paper were numbered and weighed, with weights recorded. A saturated paste was made by mixing deionized water and a small amount of each sample. The paste was used to fill individual cells. Deionized water was then dripped onto each sample to ensure saturation. Light plastic covers (cut from small weigh boats) were placed over each cell to prevent evaporation from the surface. Cells were placed on a 30 kPa ceramic plate (soaked for 24 hours with deionized water to ensure plate saturation) and placed in the pressure apparatus under 30 kPa pressure. Water was drained from the sample through a plastic tube into a graduated cylinder outside of the apparatus to monitor the attainment of equilibrium condition (i.e., the water level in the cylinder ceased to increase). Once equilibrium had been established, the pressure was released from the apparatus and the ceramic plate and sample cells were removed. All cells were weighed (without their plastic covers) and the weights recorded in the prepared table. Cells were then placed on a 1500 kPa pressure plate (previously soaked for 24 hours in deionized water), covered again with their plastic covers, and placed in the 1500 kPa pressure apparatus. Once the water again ceased to increase in the draining tube, the pressure was slowly released and the cells were removed and weighed without their plastic covers. Finally, the cells were placed in an aluminum tray and dried for 24 hours at 80 °C to determine the oven-dried weight of the sample. Dried cells were weighed and the weights recorded. Differences between the cell weight, 30 kPa weight, 1500 kPa weight and dried material weight were used to determine the available soil water (in g of water/g of soil) for each sample following the equation below:
Available water \((g/g) = [(\text{Cell mass at 30 kPa}) - (\text{Cell mass at 1500 kPa})] / [(\text{Oven-dry cell mass}) - (\text{empty cell mass})]\)

Soil available water was assessed statistically by a one-way ANOVA between all samples, including the 100% organics samples XS and XH, as well as one-way ANOVAs between tailings-based samples and quartz-based samples separately. The tailings-based and quartz-based samples were followed by post-hoc Tukey-Kramer tests to indicate which pairs contributed significantly to the variance. Two-tailed t-test pairs were examined for differences between mineral and organic parameters.

**2.5.5 Organic Carbon, Inorganic Carbon, Nitrogen Content**

Samples were sent to the BC MoE Laboratory for analysis of organic carbon, inorganic carbon, and nitrogen content. Total C and N were measured by combustion elemental analysis using a Thermo Scientific Flash 2000 elemental analyzer. Organic and inorganic carbon were determined using the acid fumigation method described in Harris et al. (2001), whereby a sample is split, inorganic carbonates are removed from one sample via acid fumigation, then total carbon is determined for both samples with the difference providing the inorganic carbon content.

**2.5.6 X-Ray Diffraction (XRD)**

Samples were finely ground and applied to a slide for XRD analysis using a Bruker D8 Discover with GADDS system (with Co Kα radiation generated at 40 kV and 20 mA). XRD analysis was completed for samples of quartz (taken directly from source, no heating), tailings (this particular tailings sample had not been heat treated in the reactor at pyrolysis
temperatures, but rather was taken from a source which had been oven dried at 80°C), wood ash (created in muffle furnace at 400°C), hay ash (created in muffle furnace at 400°C), and samples TS30 (pyrolyzed sawdust with tailings) and TH30 (pyrolyzed hay with tailings).

2.5.7 Fourier Transform Infrared Spectroscopy (FTIR)

Small amounts of sample were finely ground with KBr and pressed into a pellet. Infrared spectra were then determined with a Perkin Elmer 2000 FTIR and Spectrum v5.3.1 software.

2.5.8 Scanning Electron Microscope (SEM)

Electron microscope images were taken using a Phillips XL30 Scanning Electron Microscope. Samples were placed on a mount and sputter-coated with gold, then placed in the SEM for imaging.
3 Results

3.1 Total Elemental Analysis

Results of the total elemental analysis are displayed in Table 3-1 below. All elements in the samples are below contaminant levels outlined in the BC Contaminated Sites Regulation with the exception of Zn in hay ash (362ppm), which exceeds the environmental quality criteria both for ingestion by livestock and for major microbial functional impairment (Contaminated Sites Regulation, BC Reg 375/96, Schedule 5). Ingestion by livestock is not considered to be of much concern at a mine site, but ingestion by wildlife could potentially be problematic and microbial impairment could affect soil processes and development. However, as it is the pure hay ash that has this elevated level of Zn, and not the final mineral/organic char product, this minor elevation in Zn level is not of concern. If the tailings were to contain unacceptable levels of contaminants, it would be a further practical avenue for concern for site remediation; however, this study does not address contaminants, but rather examines the combination of mineral and organic matter.

Table 3-1 Elemental Analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Quartzitic Sand</th>
<th>Tailings</th>
<th>Sawdust Ash</th>
<th>Hay Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.043</td>
<td>7.262</td>
<td>0.150</td>
<td>0.448</td>
</tr>
<tr>
<td>Ca</td>
<td>0.004</td>
<td>1.555</td>
<td>0.427</td>
<td>4.450</td>
</tr>
<tr>
<td>Fe</td>
<td>0.015</td>
<td>1.989</td>
<td>0.093</td>
<td>0.185</td>
</tr>
<tr>
<td>K</td>
<td>0.010</td>
<td>3.313</td>
<td>0.074</td>
<td>14.105</td>
</tr>
<tr>
<td>Mg</td>
<td>0.003</td>
<td>0.416</td>
<td>0.064</td>
<td>1.818</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;.001</td>
<td>0.057</td>
<td>0.018</td>
<td>0.042</td>
</tr>
<tr>
<td>Element</td>
<td>Quartzitic Sand</td>
<td>Tailings</td>
<td>Sawdust Ash</td>
<td>Hay Ash</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
<td>----------</td>
<td>-------------</td>
<td>---------</td>
</tr>
<tr>
<td>Na</td>
<td>&lt;.001</td>
<td>2.648</td>
<td>0.043</td>
<td>0.481</td>
</tr>
<tr>
<td>P</td>
<td>&lt;.001</td>
<td>0.055</td>
<td>0.038</td>
<td>2.236</td>
</tr>
<tr>
<td>S</td>
<td>&lt;.001</td>
<td>0.281</td>
<td>0.056</td>
<td>0.293</td>
</tr>
<tr>
<td>Si</td>
<td>45.77</td>
<td>31.89</td>
<td>0.72</td>
<td>16.72</td>
</tr>
</tbody>
</table>

Other Elements (HNO₃/HCl Digest) ppm

<table>
<thead>
<tr>
<th>Element</th>
<th>Quartzitic Sand</th>
<th>Tailings</th>
<th>Sawdust Ash</th>
<th>Hay Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Ba</td>
<td>7</td>
<td>941</td>
<td>145</td>
<td>304</td>
</tr>
<tr>
<td>Be</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Bi</td>
<td>&lt; 4.0</td>
<td>&lt; 4.0</td>
<td>&lt; 4.0</td>
<td>&lt; 4.0</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Co</td>
<td>29.1</td>
<td>25.2</td>
<td>7.3</td>
<td>21.8</td>
</tr>
<tr>
<td>Cr</td>
<td>2.0</td>
<td>6.0</td>
<td>16.5</td>
<td>46.8</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>16</td>
<td>19</td>
<td>49</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt; 1.0</td>
<td>98.8</td>
<td>1.2</td>
<td>2.7</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
<td>7.5</td>
<td>33.8</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt; 1.0</td>
<td>3.0</td>
<td>3.1</td>
<td>3.6</td>
</tr>
<tr>
<td>Sb</td>
<td>&lt; 4.0</td>
<td>&lt; 4.0</td>
<td>&lt; 4.0</td>
<td>&lt; 4.0</td>
</tr>
<tr>
<td>Se</td>
<td>&lt; 4.0</td>
<td>&lt; 4.0</td>
<td>&lt; 4.0</td>
<td>&lt; 4.0</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt; 1.0</td>
<td>&lt; 1.0</td>
<td>1.1</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Sr</td>
<td>2.0</td>
<td>288.3</td>
<td>49.6</td>
<td>208.4</td>
</tr>
<tr>
<td>Ti</td>
<td>70</td>
<td>3007</td>
<td>174</td>
<td>252</td>
</tr>
<tr>
<td>Tl</td>
<td>&lt; 2.0</td>
<td>&lt; 2.0</td>
<td>&lt; 2.0</td>
<td>&lt; 2.0</td>
</tr>
<tr>
<td>V</td>
<td>4.0</td>
<td>55.4</td>
<td>1.7</td>
<td>9.4</td>
</tr>
<tr>
<td>Y</td>
<td>2.0</td>
<td>15.1</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Zn</td>
<td>5</td>
<td>37</td>
<td>72</td>
<td>362</td>
</tr>
<tr>
<td>Zr</td>
<td>45</td>
<td>284</td>
<td>42</td>
<td>24</td>
</tr>
</tbody>
</table>
The quartzitic sand was found to be 45.77% Si, with very small amounts of other major mineral constituents, and trace amounts or below detection levels of other elements. As it is an industrial grade quartz product commonly used for drinking water infrastructure, this result is anticipated. In contrast with the relatively pure quartz, the tailings had a much more complex elemental profile reflecting the source, a hard rock mineral deposit. Total ash content (determined at 950°C) was much higher for hay than sawdust. Hay ash also contained much higher mineral content, and the prevalence of potassium is clear. Potassium in the hay is addressed later in the CEC section as it is the major contributor to CEC in the hay-containing samples. Looking at elemental analyses of different organics should be investigated for the potential to predict exchangeable cations.

3.2 X-Ray Diffraction Analysis

XRD diffractions patterns for tailings, quartz, hay ash, wood ash, TS30 and TH30 are displayed in Appendix A. XRD analysis identified quartz (SiO₂) mineral as the mineral component of the quartzitic sand and wood ash samples. The hay ash sample was found to contain both quartz and calcite (CaCO₃). The tailings sample was found to contain quartz, albite (NaAlSi₃O₈), and anorthite (CaAl₂Si₂O₈). The TS30 and TH30 both contain quartz, albite, and a microcline (KAlSi₃O₈). It is important to note that these results do not reflect complete mineral profiles of the materials, but rather recognize minerals with peaks which are clearly identifiable. The quartz sample is clear, showing only quartz peaks, while the other samples are more complex in constitution as would be expected.
3.3 pH

The pH means with standard deviation in H$_2$O and CaCl$_2$ for the main sample set and the non-pyrolyzed samples are displayed in Fig. 3.1 and 3.2 below. Mean values and standard deviations are calculated using pH values, not hydrogen ion concentrations. Tables containing pH values, means and standard deviation in H$_2$O and CaCl$_2$ are displayed in Appendix B.

Figure 3-1 pH means of main sample set with standard deviations
The pH measurements were significantly affected by mineral substrate, type and amount of organic matter, and the pyrolysis process (both H$_2$O and CaCl$_2$ tests). CaCl$_2$ tests showed slightly stronger variation among samples. The strongest variable influence on sample pH is the presence and amount of hay char, which contributed alkalinity to its samples and raised their pH above the mineral-only and sawdust samples. The addition of hay increased the pH more in the quartz-based samples than in the tailings-based samples.

3.3.1 Comparisons of pH Means

There were statistically significant differences in pH in both H$_2$O (F= 3.48, p = 0.02) and CaCl$_2$ (F = 3.83, p=0.04) values among the tailings-based samples (Fig. 3-3).
There was a statistically significant difference (F= 3.48, p = 1.79E-06) in pH in both H_2O and CaCl_2 (F= 3.48, p = 3.06E-05) values among the quartz-based samples (Fig. 3-4).

Two-tailed t-test pairs of tailings and quartz with the same organics added only found significant difference in pH between some of the sawdust-containing samples, and none of
the hay-containing samples. Two-tailed t-test pairs of the sample pH with the same mineral to organic ratio but with alternate organics (e.g. TS15 vs. TH15), shows a significant difference between most pairs. Two-tailed t-tests between the different amounts of organics added (e.g. TS15 vs. TS30) show no significant difference in pH for any pairs in the pH\textsubscript{H\textsubscript{2}O} tests, but do show significant difference between QS15 vs. QS30 and QH15 vs. QH30 with the pH\textsubscript{CaCl\textsubscript{2}} tests. These results suggest that both mineral type and organic type do influence the pH, with the organic type having the stronger influence. However, the influences on pH are not extreme at these concentrations and with these particular materials. It is suspected that using non-neutral mineral substrates would show a clearer influence of mineral substance on pH, and may offset the alkalinity of the hay char.

Comparison between non-pyrolyzed samples to their pyrolyzed counterparts (Fig 3-5) reveals a minor pH increase from the pyrolysis of the sawdust and stronger pH increase from the pyrolysis of the hay.

**Figure 3-5 pH means with standard deviations of non-pyrolyzed vs pyrolyzed samples**
The relatively weak increase in pH attributable to the sawdust is insignificant with lower content of sawdust. Interestingly, the non-pyrolyzed organics lower the pH of the samples while the pyrolyzed mixes, particularly the hay, show an increase in pH. The pH increase after pyrolysis of the TH15 and TH30 samples is particularly striking as it is approximately 2 pH units. Non-pyrolyzed samples were not created for the quartz samples as it was a secondary line of inquiry. Given that a major issue with mine tailings is a tendency towards developing acidity through sulfide mineral oxidation, a treatment that raises the pH is attractive. The difference in the pH increases for the hay treatment vs. the sawdust treatment shows that the choice of organics is important in pH alteration. The tailings in this study are not acid-generating and the study did not investigate potential for neutralizing acidity in acid tailings, however this may be an interesting topic for further research.

The separately pyrolyzed T100S30 sample did not show a difference in pH from the co-pyrolyzed TS30 sample, indicating no difference between the pyrolysis and co-pyrolysis products; however, it is also important to note that the sawdust does not show a strong influence on pH in any of the other tests. As it is hay char that shows a stronger pH influence and reaction with the tailings under pyrolysis, using hay as the feedstock in this comparison may have shown a pH difference in this comparison that is not seen with the sawdust.

3.4 Cation Exchange Capacity

Results for exchangeable cations (Al, Ca, Fe, K, Mg, Mn, Na) are based on total CEC (cmol/kg), not individual cations. Total CEC for all samples is displayed in Fig. 3-6 below.
Two-tailed t-test pairs between samples of different mineral and same organic content (e.g. TS15 vs. QS15) found significant differences in total CEC between all pairs except TH30 vs. QH30. Two-tailed t-test pairs between samples of the same mineral and different organics showed similar results with significant differences between all pairs except TS15 vs. TH15 (which had a p-value of 0.053, narrowly missing the 0.05 required to accept significance). Two-tailed t-test pairs between the same mineral with different ratio of the same organic (e.g. TS15 vs. TS30) showed significance only between the two pairs involving hay, TH15 vs. TH30, and QH15 vs. QH30. These results clearly show the stronger influence of hay over sawdust as a contributor to CEC, and the tailings over the quartz.

The tailings-based samples and 100% organic samples (Fig 3-7) show lower total CEC in the pyrolized samples compared to their non-pyrolized (NP) counterparts with the exception of XH vs. XHNP. However, the two-tailed t-test of the pairs reveals that only the differences for the hay containing samples are significant.
Hay is again seen as the major contributor to CEC, while sawdust contributions to CEC are negligible in both pyrolyzed and non-pyrolyzed samples. In six of the seven pairings, the non-pyrolyzed samples appear to have higher CEC than the pyrolyzed samples, although the difference between TX0 vs. TX0NP, TS15 vs. TS15NP, and TS30 vs. TS30NP are not significant. The XH vs. XHNP sample however, shows the pyrolyzed sample as having roughly 1.75 times the CEC of the non-pyrolyzed sample. A possible explanation for this is that the measurements are based on the same mass of material being used in the barium chloride extraction. The pyrolyzed XH sample has lost a large portion its original pre-pyrolysis mass, and it is likely that the remaining pyrolyzed material carries a greater proportion of exchangeable cations than the original non-pyrolyzed material so that when equal masses of pyrolyzed and non-pyrolyzed material are used in extractions, the proportion of exchangeable cations is higher in the pyrolyzed sample due to the larger mass of non-pyrolyzed material that was used to create the equal mass of pyrolyzed material. This
concentration of exchangeable cations due to pyrolysis could be present in the TH15 and TH30 samples, but is not apparent due to the lower levels of organic material in those samples. The concentration of cations is not apparent with the sawdust samples as sawdust does not appear to contribute substantially to CEC.

The separately pyrolyzed sample (T100S30) gives an interesting result for CEC, in that the results are not what were expected from looking at the constituents. In Table 3.6, it can be seen that the individual cations Ca\(^{2+}\), Mg\(^{2+}\), Na\(^+\) and the total CEC in T100S30 do not reflect the constituent mix of TX0 and XS (although the T100S30 was made from a separate batch of heated tailings and pyrolyzed sawdust, not these samples of TX0 and XS). The K\(^+\) and Mn\(^{2+}\) do reflect the constituent mix. The Ca\(^{2+}\) in particular is notable as it contributes heavily to total CEC, and was previously mentioned as interesting due to an apparent reaction during pyrolysis affecting the Ca\(^{2+}\) when hay is involved. Ca\(^{2+}\) is enhanced by co-pyrolysis and inhibited by mixing of separately-pyrolyzed samples. This provides an interesting venue for future investigation if particular cations are determined to be more or less desirable and could have implications for applications of biochars where metal contamination in the mineral material is at issue. Debela et al. (2012) found that metal ions (Pb, Zn, Cu, As, Cd) displayed differing adsorption and leaching behaviours after copyrolysis based on the individual elements, differing organic amounts, and time and temperature of reaction. Those results as well as the results of this study point to the complexity of interactions. Mechanisms involved are not yet understood and should be considered for future study.
Table 3-2 CEC of 100T30S, TS30, TX0, XS in cmol/kg

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al cmol/kg</th>
<th>Ca cmol/kg</th>
<th>Fe cmol/kg</th>
<th>K cmol/kg</th>
<th>Mg cmol/kg</th>
<th>Mn cmol/kg</th>
<th>Na cmol/kg</th>
<th>Total CEC cmol/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>100T30S</td>
<td>0.003885</td>
<td>1.703025</td>
<td>nd</td>
<td>0.222924</td>
<td>0.059662</td>
<td>0.056399</td>
<td>0.287206</td>
<td>2.333101</td>
</tr>
<tr>
<td>TS30</td>
<td>nd</td>
<td>3.037744</td>
<td>nd</td>
<td>0.155179</td>
<td>0.031273</td>
<td>0.04519</td>
<td>0.141125</td>
<td>3.41051</td>
</tr>
<tr>
<td>TX0</td>
<td>0.010564</td>
<td>2.820353</td>
<td>nd</td>
<td>0.218644</td>
<td>0.048203</td>
<td>0.062049</td>
<td>0.162705</td>
<td>3.322519</td>
</tr>
<tr>
<td>XS</td>
<td>nd</td>
<td>0.615978</td>
<td>nd</td>
<td>0.245005</td>
<td>0.040018</td>
<td>0.007853</td>
<td>0.030709</td>
<td>0.939563</td>
</tr>
</tbody>
</table>

The individual cation results (Fig 3-8 through 3-10) clearly show a difference in the cation contributions made by hay and tailings, with hay contributing cations mainly as potassium, and tailings as calcium (see fig. 3.8). Both quartz and sawdust are marginal contributors. What is most interesting in these results is the individual cations in the hay/tailings mixes, TH15 and TH30, in comparison with the TX0 (100% tailings) and XH (100% hay) samples. For the hay and tailings mixes, the results reflect a contribution to CEC from the tailings (as seen in TX0), yet CEC increases do not appear strictly additive (with hay addition): TH15 is only slightly higher in CEC than TX0, and the difference between TH30 and TH15 is far greater than the difference between TH15 and TX0. This suggests an interaction between the tailings and the hay. Comparison between the pyrolized and non-pyrolized samples shows the non-pyrolized samples as having an additive relationship for CEC with the addition of hay. Therefore the tailings and hay must be undergoing a chemical co-reaction under the pyrolysis conditions. The co-reaction appears to result in inhibition of CEC, including the removal of exchangeable Ca$^{2+}$ present in the TX0 sample (and Mn$^{2+}$, a minor CEC contributor), countered somewhat by an increase in K$^+$ (which originated from the hay).
Figure 3-8 Exchangeable Ca\(^{2+}\), K\(^{+}\) (cmol/kg)

*XH mean for K\(^{+}\) = 58.95, stdev = 3.60

Figure 3-9 Exchangeable Na\(^{+}\), Mg\(^{2+}\) (cmol/kg)

*XH mean for Mg\(^{2+}\) = 1.09, stdev = 0.27
3.5 Soil Available Water

Soil available water produced expected results (Fig 3-11), i.e. the more organics, the higher the water holding capacity of the sample. Results between the 15% and 30% organics show an approximately linear relationship between organic level and water holding capacity while statistical results and sample values suggest that sawdust samples have a higher ability to hold water than does hay. However, the statistical significance is impacted by the high variability within the sample groups. Due to both the equipment and the procedure, this is not a high-precision test; accuracy of results was further hampered by using only small amounts of sample during the test, necessitated by the limited amount of material available. Nevertheless, the results do show some significant difference in water holding capacity between the organics, which is consistent with visual observation in the lab.
Figure 3-11 Soil Available Water of samples in grams(water)/grams(soil)

3.6 Organic Carbon, Inorganic Carbon, and Total Nitrogen

Organic carbon (Fig 3-12) and total nitrogen (Fig 3-13) show predictable patterns based on the amount and type of organic matter added. The 15% OM is generally half the value of the 30% OM, levels for XS and XH are notably much higher, and levels for TX0 and QX0 are minimal for organic carbon, and zero for nitrogen. Both quartz-based and tailings-based samples appear additive for OC (organic carbon) and N suggesting (as expected) that the hay and sawdust are the contributors for organics in the samples, although with a minor amount of organics present in the tailings which is not unusual for such material.
Figure 3-12 Organic Carbon (%)

Figure 3-13 Total Nitrogen (%)

The results from the tests for inorganic carbon (IC) are different (Fig 3-14). The 100% mineral samples (TX0 and QX0) and the 100% hay sample (XH) have minimal IC present, however the mineral/organic mixes of TH30 and QH30 both show IC levels that are greater than that of their constituents. Conversely, the XS sample has relatively high IC, yet the
QS15 and QS30 samples do not show elevated IC that might be assumed from the sawdust content. This suggests that there may be some differences in carbonization during co-pyrolysis with the organic/minerals mixes vs. the 100% organics samples, with the presence of the mineral reducing the conversion of OC to IC in the sawdust, while increasing it in the hay, pointing again to feedstock-specific results. However, strong conclusions cannot be drawn here as the sample size is small and the standard deviation is high. Also, the levels of IC are still very low and likely not important.

Figure 3-14 Inorganic Carbon (%).

![Inorganic Carbon Graph]

3.7 Influence of temperature on pH and CEC

The pH increased with temperature of pyrolysis (Fig 3-15). This is expected due to increased ash content with higher temperatures. The pH increase between T200 and T300 was minor (T200 = 3.38_{H2O}, 3.19_{CaCl2}; T300 = 3.71_{H2O}, 3.58_{CaCl2}), while the pH increase between T300 and T400 was more pronounced (T400 = 4.78_{H2O}, 4.79_{CaCl2}). However, when
considered as proton concentrations rather than the logarithmic pH scale, the change in \([H^+]\) reflects a roughly linear relationship with temperature (pH of 3.38 = \([H^+]\) of 4.1 \(x\) 10\(^{-4}\) M, pH of 3.71 = \([H^+]\) of 1.9 \(x\) 10\(^{-4}\) M, pH of 4.78 = \([H^+]\) of 0.16 \(x\) 10\(^{-4}\) M). One-way ANOVA on the pH values showed the difference to be significant between all treatments for both pH\(_{H_2O}\) and pH\(_{CaCl_2}\).

**Figure 3-15 pH of pyrolysis products produced at 200°C, 300°C, and 400°C**

The temperature trials all used the same mix of quartz plus 30% sawdust by weight (the same as QS30). This mix was chosen before CEC results were completed and analyzed for the main experiment. Unfortunately, the CEC for QS30 is quite low to begin with, given that both the quartz and the sawdust contribute little to CEC. Because of this low CEC inherent in the sample materials, the CEC results for the temperature trials (Fig 3-16) are not believed to be a particularly good basis for drawing conclusions regarding the effect of temperature on CEC. The results did find that there was significant difference between the CEC for T300 and T400, with T400 being lower. The average CEC for T200 samples was
very similar in value to that of T300, and therefore higher than T400; however, the standard deviation of the T200 samples was relatively high and thus statistical tests found T200 not significantly different to either T300 or T400. Literature suggests that CEC should decrease with increased temperature of pyrolysis (Ippolito et al., 2015) although the rate of this decrease is reduced at higher temperatures (Mukherjee et al., 2011). It is believed that the results of this study are consistent with these observations even if statistical tests cannot be relied on for support with the T200 results.

**Figure 3-16 Total CEC of pyrolysis products produced at 200°C, 300°C, and 400°C.**

3.8 **FTIR**

Infrared spectra were taken for all regular samples and the temperature trials. One spectrum for each of the 12 treatments in the main experiment, as well as one spectrum from each of the three temperature treatments, is shown in Appendix C. Replicates are not shown as there was little variation between the three samples of each treatment. Literature suggests
three main wavelengths associated with biochars: aliphatic C-H stretching around 2900cm\(^{-1}\), -OH stretching between 3200-3600cm\(^{-1}\), and aromatic C=C bonds around 1600cm\(^{-1}\) (Al-Wabel et al., 2013; Keiluweit et al., 2010; Kim et al., 2012; Peng et al., 2011; Zhao et al., 2013), as well as cellulosic and ligneous transformation products between 700-1600cm\(^{-1}\) (Al-Wabel et al., 2013; Keiluweit et al., 2010).

The results from this experiment (displayed in Appendix C) generally agree with these findings, with the pure organic samples (XS and XH) conforming to these established patterns and the other samples showing the influence of the mineral materials seen in TX0 and QX0. Although the KBr was kept in a desiccator, all samples are suspected to show some contamination by water absorbed from ambient humidity into the KBr at 3440cm\(^{-1}\) as well as some compound showing absorbance at 1080cm\(^{-1}\) (KBr background spectra not shown), but stronger absorbance in the samples at 3400cm\(^{-1}\) and at slightly higher wavelengths suggest additional sources of -OH stretching in the samples. When undertaking this analysis it was believed that the different organics would show more distinct spectra; however, the XS and XH spectra are very similar.

### 3.9 SEM

Scanning Electron Microscope (SEM) images were taken for eight of the twelve main samples: TX0, QX0, TS30, TH30, QS30, QH30, XS, and XH (Figs. 3-17 to 3-31). Aggregates from the 15% organics samples were not included as it was felt they would not add to the examination of the phenomenon in ways not illustrated by the 30% organic samples.
All samples had some small aggregates available, except for the QX0. The TX0 aggregates were extremely fragile while the remaining samples had aggregates of varying fragility (as observed when attempting to pick up aggregates with tweezers in order to mount for microscopy). Generally, it was observed that decreased organic content resulted in increased fragility of the aggregate. The samples formed aggregates of varying size with the exception of QX0 (which had no aggregates) and TX0 (which had small and very fragile aggregates).

For the SEM images shown, aggregates were specifically selected for their small size. The mixes of mineral and organics samples tended to have aggregates 2mm to 10mm along the longest axis with the samples of higher organic matter containing more and larger aggregates. The XS and XH samples came out of the reactor a mix of individual particles, small aggregates, and large, fused chunks. Based on the shape of the fused material as it came out of the reactor, it appeared that some bio-liquids or gases had risen to the top of the chamber during pyrolysis and the fused material formed into a rough cylinder in the top area upon cooling. The SEM images show a smooth, glassy texture for some of the samples containing organics (see TS30 Figs. 3-20, 3-21, and XS Figs. 3-28, 3-29), often with vesicles, which could have formed from gas bubbles. The thin sections (see section below, 3.10) show void spaces within the organic matrix, also suggesting bubbles. To have some of the pyrolysis products as liquids or gases at the reaction temperature, which then cool and harden at ambient temperature, is not an unreasonable assertion and is believed to be part of what is happening in this experiment.

The QX0 and TX0 images (Fig. 3-17 and Figs. 3-18, 3-19, respectively) show the mineral particle(s) without any organics added. The quartz is a rounded single grain as there
was no aggregation of the particles in the bulk sample. The tailings aggregate is composed of angular mineral particles of varying sizes. Of the 100% organics images, the hay char in XH appears as a solid mass with many small, fibrous pieces coating the surface, likely remnants of decomposing tissue structure (Figs. 3-30, 3-31). In the closer range image (Fig. 3-31), the surface beneath the fibrous pieces appears to have a smooth texture. The sawdust char in the XS images appears as an angular mass with many vesicles (Figs. 3-28, 3-29). The solid portion shows the smooth texture previously noted, and the surface has few smaller particles adhered compared to the fibrous pieces of the XH sample. Images of TS30, TH30, QS30 and QH30 (Figs. 3-20 and 3-21, 3-24 and 3-25, 3-22 and 3-23, and 3-26 and 3-27, respectively) show the aggregates as mineral particles bound within the organic matrix. The organic portion can be seen as a smooth, often vesicled texture that appears to partially coat and tightly adhere to the mineral surfaces, indicating that at least a portion of the organics must have attained some fluidity during pyrolysis. Cracks at the mineral and organic interface (see QH30 at 50X, TH30 at 200X) indicate rigidity of the organic matrix once solidified.

Figure 3-17 Quartz particle (QX0), 150X
3.10 Thin Sections

Since individual aggregates have been sectioned rather than an in-situ soil sample, the descriptions refer to the aggregate microstructure, not a soil. In the T1-2 and T1-3 slides (Figs. 3-32 to 3-39), it can clearly be seen that there are mineral particles coated and captured within a matrix of organic material and void space. The organic matrix appears as a solid mass which is fusing the particles together. This appears consistent with the SEM photos showing a glassy-textured organic material holding on to the mineral particles. The cross-polarized photos (xpl) more clearly demonstrate the structure of the aggregate being composed of the mineral particles and void space within the organic (black) matrix. The control shows no aggregation and no char; the particles of sawdust and mineral are completely separate.
3.10.1 Samples T1-2, T1-3

These thin sections did not differ markedly and are described as one below in Table 3-7. Photos are shown in regular (Figs. 3-32, 3-33, 3-36, 3-37) and cross-polarized (Figs. 3-34, 3-35, 3-38, 3-39) light (xpl). The xpl photos show the void space as dark grey.

Figure 3-32 T1-2 (4X magnification)  
Figure 3-33 T1-2 (10X magnification)

Figure 3-34 T1-2 (4X magnification, xpl)  
Figure 3-35 T1-2 (10X magnification, xpl)

Black is char coating on mineral grains and char matrix bridging between grains.
Table 3-3 Micromorphology of Tl-2 and Tl-3

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Pellicular or intergrained microstructure, smooth, angular to sub-angular, blocky individual grains fused into unaccommodated aggregate mass with complex packing voids, 60% void space.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundmass</td>
<td>c/f 3:1, open enaulic-chitonic with coarse grains interspersed with void spaces and clusters of finer grains coated and fused with char. Overall abundance of mineral/char clusters ~40%, with coarse particles 25%, finer particles 5%. Organics - black char coating and bridging grains, 10%</td>
</tr>
</tbody>
</table>
3.10.2 Control Sample

The control sample was a loose assortment of individual sawdust pieces and smooth, angular, blocky individual mineral grains with no aggregation (Fig 3-40, 3-41). Only the cross-polarized slides are shown as the material was difficult to distinguish with regular light.
4 Discussion

The major objective of this thesis was to assess if aggregates could be created de novo, using the co-pyrolysis method. Indeed, macro-aggregates were created in all samples which were mineral/organic mixes or 100% organics. However, this was not an instantaneous result; immediately after removal from the reactor little macro-aggregation was apparent and the materials appeared a loose mix. The exception was the 100% organic samples, XS and XH, where the portion of the sample nearest to the top of the reactor chamber was lightly fused into a fragile cylinder of material and had to be broken off of the internal reactor components and into sample jars. As the reactor was not vented and remained sealed until cool to touch, it is believed the fused material resulted from bio-liquids or vapours formed during the pyrolysis interacting with the top layer of material and generating solidified material as it cooled. The material from the 100% organic samples in the lower portion of the reactor chamber was generally loose upon removal. Over time in storage jars, with no additional treatment or manipulation, aggregates formed (or continued to form in XS and XH) within the loose material and in addition were more resistant to breakage with continued time in the storage jars. The aggregation of the 100% organic samples continued to a point where larger pieces had to be intentionally broken up in order to be used in laboratory analytical tests as loose material became scarce within the sample jars.

In general, it was observed that the sawdust-containing samples formed more aggregates more quickly than the hay-containing samples. Further, the higher organic content samples contained the more abundant, large, and stable aggregates. The tailings sample (with no organics added) did have some small clumps in which a few particles held together; however, these aggregates were so weak that they were usually crushed when
trying to pick them up with tweezers or with any agitation of the sample. The quartzitic sand did not form aggregates at any time.

Although intended in the study design, aggregate counts/sizing and stability testing was deemed unsuitable for the samples in this study once the samples were completed. Much of the samples with larger aggregates were broken up during other analytical tests and the remaining samples would be altered or destroyed by aggregate testing. Also, given the observed tendency for increasing aggregation with increased storage time, it was felt that samples were not appropriately controlled to make this testing meaningful. In future work, it would be advisable to extract and store a portion of each sample immediately upon removal from the reactor, or to create samples specifically for testing desirable attributes such as aggregate count, size, and stability. However, the collection of such data would be complicated by the tendency for increased aggregation, size and stability of aggregates over time. A temporal factor should be included in the study design.

The results were more conclusive in documenting significant differences between the two organic treatments, as well as differences in the mineral interactions with the organic materials. The pH testing not only indicated differing contributions from both the two organics and the two mineral substrates, it showed an interaction between the hay char and the tailings which was also indicated by the CEC results. The tailings appear to have a neutralizing effect on the pH increase attributable to the hay char, which is not seen with the quartz (specifically chosen to be a relatively non-reactive substance) or the sawdust.

The CEC results have two particularly interesting features. Firstly, it is noteworthy that the choice of organics can contribute such vastly different amounts of exchangeable
cations to the mixtures, and that the contribution may be seen from primarily one cation. The sawdust contributed very little exchangeable cations, while the hay contributes a larger amount, mostly K. The second feature of note is the removal of availability of some of the exchangeable cations from the tailings when pyrolized with hay. The total exchangeable cation level is still increased due to the input of K from the hay, but it presents the possibility that exchangeable cations may be made unavailable by the co-pyrolysis, perhaps without the introduction of other cations from the organics, which could also be an important factor when selecting organics for this process.

The study was designed with a potential reaction between mineral and organics in mind and the quartz sand was chosen specifically to provide a relatively non-reactive mineral substrate for comparison to see if such interactions could be identified with the tailings. While the negligible contributions of quartz were anticipated, the low CEC from sawdust was surprising. However, even the non-pyrolized sawdust (XSNP) shows low CEC so it appears to be inherent in the material, and not greatly influenced by pyrolysis. However, a study by Suliman et al. (2016) using Douglas-fir wood and bark found much higher CEC in the biochar produced (~50-55 cmol/kg) compared to the XS sample in this study, and were more similar to the XH levels in this study. There is no easy explanation for this discrepancy between that study and ours, although a slightly different method of CEC determination was used by Suliman et al. (2016) (including pre-washing the biochar with an HCl solution followed by e-pure water rinse) as well as higher pyrolysis temperature (but higher pyrolysis temperature tends to decrease CEC). Mukherjee et al. (2011) used a KCl/NaNO₃ substitution process for CEC analysis and found CEC levels for pine, oak and grass pyrolyzed at 400°C in the 10-20 cmol/kg range. The difference in CEC values for similar
substances seen in studies by Suliman et al. (2016), Mukherjee et al. (2011), and our thesis demonstrates both the importance of consistency in the specific analytical methods chosen when data is being compared, and the utility of testing sample characteristics of any organic materials intended for application rather than depending solely on literature values when planning soil treatment programs.

The differences between the organics and minerals, and potential for reactions between the organic and mineral materials are very supportive of the idea of "designer" biochars, where a feedstock and the production conditions are chosen for their particular characteristics. An important factor in all soil biological and chemical processes is the pH of the aqueous components and these results suggest that organics could be specifically chosen for their pH contributions. In studies of just biochar (i.e. no co-pyrolysis with mineral material), increasing temperature of pyrolysis is associated with increasing alkalinity, and pH also varies with feedstock material (Al-Wabel et al., 2013; Novak et al., 2009; Novak et al., 2014; Yuan et al., 2011; Zhang et al., 2015; Zhao et al., 2013). Kloss et al. (2012) did not find a consistent increasing trend with temperature of reaction and pH; however, their study used temperatures of 400°C, 460°C and 525°C, which are relatively minor increments, while the other studies cited use increments of 100°C or greater. Ronsse et al. (2013) attributed pH increases with temperature to both the increase in ash as well as the reduction in carboxyl groups and the de-protonation of acidic functional groups into their conjugate bases.

Although unexplored in this thesis, the specific chemical changes of the organics and the co-reaction with the mineral substrate are an extremely interesting avenue for further research. From a practical standpoint, the co-reaction between the hay char and the tailings provides more potential for either manipulating the characteristics of the resulting products,
or experiencing results that differ from what was intended or expected. The soil available water results, although largely expected, also support the concept of designer biochar, showing some difference between the organics.

The SEM images and thin sections revealed the most unexpected results in this thesis, the contribution of a phase change in the organics to the formation of aggregates and the appearance of both the vesicles and the organic matrix binding the mineral particles. There are some hints of this in literature. Zhang *et al.* (2015) features SEM images of biochars created from straw and pulp waste at 200°C, 400°C and 600°C. In their images, an increase in the size of the vesicles can be clearly seen between the 200°C pulp waste biochar (small vesicles) and the higher temperature pulp waste biochars (larger vesicles). Differences are less apparent between their 400°C and 600°C images but, given that the production of oils and gas over char increases with temperature, it makes sense that more vesicles would form as the temperature increases. Lua *et al.* (2004) observed a release of volatiles and increase in pores with pyrolysis temperature in char made from pistachio-nut shells, as well as an "intermediate melt" phase evidenced by their own SEM images, which bear a strong resemblance to the smooth, glassy texture seen in this thesis. They describe it as intermediate because the texture is changed at higher temperatures as the "melted" material volatilizes. This same "intermediate melt" was observed by Soucemarianadin *et al.* (2013) in chars made from black spruce. As the formation of a liquid or gaseous phase, which then solidifies as a matrix around the mineral particles, was not expected at the start of the experiment, further investigation of the implications or possible manipulations of that feature was not explored. However, it does present an interesting opportunity for further study. This experiment used a closed reactor, keeping the oils and gases contained within the chamber.
until the mixtures were cooled. If the reactor could be fitted with an appropriate churning mechanism, then mixing of the liquid fractions could be encouraged within the reaction chamber, potentially coating more of the mineral particles rather than concentrating near the top of the reactor. It might also be of interest to increase the temperatures into the range that favours more oil and gaseous products which would be conserved and condensed/solidified when the reactor was cooled. Whether this would produce any desirable soil properties is unknown as it may instead result in reduced recalcitrant forms of carbon (as char) and more labile hydrocarbons from the bio-oils and gases which could be more readily broken down by soil organisms.

FTIR analysis was pursued to examine presumed differences in functional groups resulting from the use of differing feedstocks, mineral material and reaction temperatures. Against expectations, spectra of all main experiment samples and the temperature trial showed that few major differences exist in the functional groups present. It was primarily expected that there would be clear differences between the hay and sawdust as feedstocks, however the similarity between timothy hay and sawdust in this thesis is comparable to the similarity of results seen in Zhao et al. (2013). In that study, wheat straw and sawdust display similar spectra, although the study compares ten other biochars from both plant and animal feedstocks, some of which (notably bone dregs, waste paper, Chlorella and waterweeds) display distinctively different IR spectra. The temperature trials also agree with literature trends, showing a weakening in the -OH and C-H stretching wavelengths, and an expansion (but decreased sharpness of peaks) in the wavelengths associated with aromatics, carboxyl and carbonyl compounds, and C=O ester bonds (~1400-1750cm⁻¹), suggesting an increased variety of aromatic compounds are present. Literature suggests that the greatest
degradation of organic products within the biochar takes place at temperatures over 500°C (Keiluweit et al., 2010; Zhao et al., 2013), which is above the temperatures possible with the equipment used in our experiment.
5 Conclusions

5.1 Summary of conclusions regarding aggregation

Aggregates were found within the samples; however, evidence suggests the aggregates are a result of organic compounds physically fusing mineral particles together rather than forming aggregates via organo-mineral bridging and electrostatic forces. The thin sections and electron micrographs appear to show the mineral particles set in a solid or semi-solid organic carbon matrix. This could be attributed to varying carbon compounds present in pyrolized materials, with some of the heavier compounds existing at ambient temperature in a solid, or semi-solid state, while having been liquid or gaseous at the temperatures of the reaction. The smooth, vitreous appearance of organics in the electron micrographs suggests solidification from a liquid state, rather than the joining of multiple particles. Aggregates were observed to increase in frequency and size over storage time. Ambient lab temperature was relatively constant, but this continued formation could be explained by semi-solid hydrocarbons present in the samples enveloping and fusing particles over time. If this enveloping and fusing of mineral particles by semi-solid carbon compounds is what is responsible for forming the aggregates, does this mean that the process does not have potential in forming preliminary soil structure? Not necessarily, as the aggregates do form from organic and mineral clustering, and some of the function of aggregates in soils may still be intact.

The bulk material did show increased water holding capacity resulting from the organic additions, the aggregate clusters would provide some habitat for microorganisms, and the pyrolized materials would likely provide some labile carbon forms for use in
microbial metabolic processes which may then release exudates and other organic products that act as more traditional binders for aggregation. However, it is not clear that the char formed an organic and charged coating on the mineral particles, which would increase potential aggregation.

There was a very low clay content in the mineral materials used in this experiment. Clay particles are an important constituent of soil aggregates and, if the experiment was repeated, an increase in clay content may result in greater aggregation within the samples or better long-term aggregation if this process was implemented in a greenhouse or field experiment. The experiment did find an increase in exchangeable cations with the addition of hay, as well as cation contributions from the tailings material. These factors have potential to be positively utilized and manipulated if a field use was planned with a "designer" biochar.

5.2 Insights gained

With the benefit of hindsight, the design used in this experiment contained the assumption that the results would be as anticipated: a uniform product containing aggregates, with clear differences in characteristics resulting from the differing mineral materials and organic materials. The results did show the latter, differences resulting from differing mineral and organic constituents. However, the aggregation (which was visibly apparent) did not occur uniformly within the sample and therefore representative aggregate testing of the samples (aggregate size, frequency and stability) could not be performed with these samples. Also, the aggregates that did form appear to be mineral particles physically enveloped by a semi-solid hydrocarbon matrix, and not through organo-mineral bridging.
Given that the premise of the experiment was an attempt at accelerating and mimicking natural aggregate formation, the aggregates that did form may show some similar functionality as natural aggregates, but they are not so similar in creation. The co-pyrolysis process investigated in this study could still result in promoting accelerated aggregate formation and associated benefits if used in a field trial but that has yet to be tested. The more conclusive results of the study are seen in the influences of the different mineral and organic constituents (pH, CEC, water holding capacity) which have implications for designing biochars for particular purposes as well as possible interactions with mineral soil substrates.

An unclear and unanticipated factor that emerged in this study is the possible influence of the phase of the carbon products during and after the pyrolysis reaction. Although it was anticipated that the carbon products would coat the particles, the apparent process and results differed significantly from the anticipated results and this has implications for the samples. The process within the reactor involves the thermo-chemical breakdown of the original carbon-containing plant material. Unless the material was both of extremely fine particle size and agitated during the reaction (it was not), then in order to effectively coat the mineral particles some phase change to liquid or gaseous forms would be necessary. It is also known that pyrolysis produces solid, liquid and gaseous products so considering this may have lent itself to projecting that partitioning of products would occur within the reactor and the product would not be uniform. Further, it might have been anticipated that condensates and liquid/solid phase changes might be an important process in aggregate formation.
The experimenter held an expectation that the mineral particles would be coated with a char exhibiting electrostatic attractions to surrounding material, and not that the particles would be bound together in an organic matrix. It is likely that there is some degree of coating and potential for enhanced electrostatic interactions, but that might require more long-term subjection to real or simulated soil processes to be observed and tested. The intention of this study was to create "instant" granular structure, while the results show an enhancement of properties which affect aggregate formation and differ due to the co-pyrolysis process from products where biochar is formed separately and then added to the mineral substrate. It was shown that CEC of the mineral material could be increased with the co-pyrolysis with hay, but the aggregation that did occur was found with both the hay and sawdust-containing samples. If anything, it was observed that the sawdust, which did not show a large influence on CEC, appeared to result in more frequent and less fragile aggregates than the hay. This indicates that CEC was not a dominant influence in the aggregates formed in this study, but rather the organic matrix of the aggregates, attributed here to phase changes during the pyrolysis process, was more prevalent in the sawdust products, and resulted in a firmer condensation product.

During the production of the first set of samples, it was noticed that some of the samples that were placed in jars developed clear condensates on the insides of the jar, so a decision was made to place the samples in trays for 17 days and allow the volatile components to be released, as well as potentially 'drying out' any resinous products. Unfortunately, and particularly since phases do seem to play a role, there was no control on this venting of the samples, so whether or not the venting had any significant effect is untested and unknown.
The phase of the products also has implications for any future uses of this co-pyrolysis process. This experiment used a closed reactor with no venting during the reaction. Differing technologies exist for pyrolysis, some of which intentionally separate products and some of which may lose gaseous products due to a lack of a closed system. Further understanding the role that phases of the products play may be important in any future studies.

5.3 Summary of Significant Findings

This study had both original findings and confirmations of results found in studies of similar subject matter:

- Aggregates were created in this study, but featured mineral grains in an organic matrix, rather than the anticipated granular clusters.

- Characteristics of the end products after co-pyrolysis were influenced by both mineral material (pH and CEC) and organic material (pH, CEC and water holding capacity).

- The tailings appeared to react with the hay during co-pyrolysis, evidenced by a decrease in exchangeable Ca\(^{2+}\), Na\(^{+}\) and Mn\(^{2+}\) in the tailings-based samples and increase in K\(^{+}\) and Mg\(^{2+}\) in the hay-containing samples, which is not seen with quartz and sawdust. The pH changes and differences observed between pyrolyzed and non-pyrolyzed support this assertion.

- Co-pyrolysis of mineral and organic matter as opposed to pyrolysis of organics in isolation may minimally affect carbonization, either inhibiting conversion of organic carbon to inorganic in sawdust while enhancing the conversion in hay. Differences in
carbonization were modest at the temperatures used, but could show increased differences in carbonization between feedstocks at higher temperatures where more carbonization would be expected.

- The study confirmed the following literature findings for pyrolysis products:
  - differing feedstocks result in differing characteristics of products (pH, CEC and water holding capacity) suggesting potential for designer biochars;
  - the temperature of the reaction influenced product characteristics (pH and CEC);
  - IR spectra indicate functional groups do not vary greatly at the temperatures used in this study (~200°C - 400°C).

The original study goals were to examine if aggregates could be created though the co-pyrolysis process, and establish relationships between the chosen feedstocks, mineral materials and reaction conditions. While these goals were met, the form of aggregation (granular material in organic matrix) and temporal aspect of the formation (aggregation increased over time in storage jars) was unexpected, and aggregate testing for quantity, size and strength could not be undertaken due to non-uniformity with the samples (inability to make a representative splitting of the samples for separate aggregate testing), and the temporal aspect of increasing aggregation over time. The study did successfully indicate differing characteristics and possible co-reactions stemming from different organic feedstocks and different mineral materials.
5.4 Practical Considerations For Application of the Research

There are a few major drawbacks/obstacles to a real-world application of this co-pyrolysis process.

1. Volume: This study used mine tailings as a mineral material given that it is generally nutrient deficient, very low in any organic matter, and is frequently deposited in large quantities with a large spatial footprint which is then subjected to water and wind erosion and is therefore desirable to establish vegetative cover. However, the volume of tailings is frequently immense, into the millions of cubic metres of material. Such volumes would not only be challenging and time-consuming to process, but the amount of organics used in this study (15% and 30% by weight) would require enormous volumes of organics to treat a site, along with any associated shipping costs and energy required for the pyrolysis process. If this process were to be applied, likely only a thin top-layer would be prudent and/or feasible economically, or potentially a tilling in of co-pyrolyzed material into the top layer of the tailings deposit.

2. Equipment: Mobile pyrolysis equipment does exist, but is quite expensive and offers volumes which may be sufficient when producing biochar/oil/gas, but are not large enough with respect to volumes of material found in tailings deposits. Also, the energy required to run the equipment may be onerous, particularly in remote sites. It has been suggested that low-tech traditional pyrolysis methods (charcoal mounds) may be used to produce biochars in developing nations for agricultural purposes with a net economic benefit (Dickinson et al., 2015) and such traditional methods could conceivably be used for co-pyrolysis (although likely with higher organic content).
However, traditional methods tend to have poor yields and inconsistencies in production which are generally undesirable in a planned remediation program.

3. Organic requirements: Part of the attraction of biochar which is reflected in this research, is the potential for making a designer biochar which has features desirable for the purpose to which it is applied. Part of the attraction is also in using locally available organic wastes. However, what is locally available is not necessarily the best organic feedstock for the intended use and shipping in organics both increases the costs and the carbon footprint of the treatment.

These practical considerations add a great deal of logistical complexity to any attempts to apply the research to real situations. In order to maximize the benefits (and justify the expense) of this co-pyrolysis process, the right combination of positive soil enhancing qualities for the situation at hand, and availability of the particular organics and production technology that maximize those qualities must be found. It would also need to be determined if any co-reactions between the mineral and organics would occur and what the effect would be. Given this complexity, in a real-world situation it may be more tempting to either just add the organics as is (i.e. non-pyrolyzed), or just add previously manufactured char without the co-pyrolysis. Both those options, as well as the co-pyrolysis should result in increased bulk density, water holding capacity and SOM in the material, and the chars would likely offer more recalcitrant carbon. What the co-pyrolysis potentially offers is that jump-starting of soil aggregate processes which, while not immediate, did appear accelerated in this experiment. Aggregation occurred and increased as the samples sat in jars over the course of the experiment period. This was not observed in T100S30 samples which were separately pyrolyzed (reflecting a system where finished biochar is added to a mineral or
soil), and also was not observed in any of the non-pyrolyzed samples (reflecting systems where raw organics are added to a mineral or soil). Although there is a great deal of complexity to the co-pyrolysis process, these results are quite promising for accelerating soil formation and further study is warranted.

5.5 Recommendations for Future Research

Although this study's findings are promising, they are entirely lab-based and preliminary in nature and it is unknown how they might translate into a real world situation or simulation. Initially, more work should be done to further illuminate the process and resulting products. Of particular interest would be to better understand how the organic carbon and minerals are interacting. During this study period, it was noticed that when the sample products were put in water for the pH testing that there was a partition between material which floated and that which sank. This raised the question of how much of the organics was adhered to the mineral material and how much was just free pieces of biochar. An attempt was made to wash the floating part off of the samples and then run testing on the remaining material; however, the technique for the washing was not very precise and it was felt that any results would be unreliable and also that any fine mineral materials would be lost and they had great potential for participating in the formation of granular structure. Perhaps a better test would be to use soil columns with simulated precipitation and observe the migration of organics over time in both co-pyrolyzed samples and mixes where the biochar had been added to the minerals after pyrolysis. The assumption would be that, if the organics were adhered to the mineral material, it would be less likely to migrate downward, although fine mineral material may migrate also. At the end of the column testing, the
samples could also be analyzed for aggregate formation and stability, both in the co-
pyrolyzed and biochar-added samples.

Clays are an important contributor to aggregate formation, yet the material used in
this study were quite low in clay-sized particles. It would be interesting to further study the
coppyrolysis process with increased levels of clay particles to examine their influence on
aggregate formation and adherence with biochar. Additionally, CaCO₃ often plays a role in
aggregation as a cementation agent and additionally has the potential to increase pH which is
of particular interest in mine tailings. The role of additives such as CaCO₃ would be another
venue for further study. Higher pyrolysis temperatures may cause conversion of CaCO₃ to
CaO. CaO/CaOH is often added to mine tailings for its acid neutralizing ability. If this co-
pyrolysis process was used as part of a remediation plan for mine tailings sites, the addition
of CaCO₃ and a higher pyrolysis temperature may streamline the treatment process, adding
both increased acid neutralization and organic matter in one process, while encouraging the
formation of granular structure in the material.

Finally, the products of this process may function well as a growth medium and soil-
building amendment, or they may be better applied in tandem with other soil-building
processes, in particular the application of fertilizers, inoculation with microbiota, and the
inclusion of other sources of organic matter such as compost. The co-pyrolyzed mixture may
offer a more stable form of carbon that would be helpful as part of a soil-building system,
more so than on its own. Greenhouse or field studies of the co-pyrolysis products are seen as
an essential future step to move this research forward to a real-world application.
References


Appendix A: X-Ray Diffraction Patterns

a) X-ray diffraction pattern of quartz sand

b) X-ray diffraction pattern of tailings
c) X-ray diffraction pattern of hay ash

![X-ray diffraction pattern of hay ash](image1)

HAYASH-12Jan15, Corundum HAY

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d) X-ray diffraction pattern of wood ash

![X-ray diffraction pattern of wood ash](image2)

woodASH-12Jan15, Corundum wood
e) X-ray diffraction pattern of TS30

f) X-ray diffraction pattern of TH30
Appendix B: pH Values, Means and Standard Deviations

Table B-1 pH values, means and standard deviations of main experiment samples

<table>
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<tr>
<th>H2O</th>
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Table B-2 pH values, means and standard deviations for non-pyrolized samples

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CaC22

| TXONP | 6.64           | 6.62           | 6.70           | 6.65    | 0.03   |
| TS15NP| 6.28           | 6.25           | 6.33           | 6.29    | 0.03   |
| TS30NP| 5.61           | 5.55           | 5.52           | 5.56    | 0.04   |
| TH15NP| 5.62           | 5.68           | 5.64           | 5.65    | 0.02   |
| TH30NP| 5.86           | 5.92           | 5.83           | 5.87    | 0.04   |
| XSNP  | 4.34           | 4.39           | 4.27           | 4.33    | 0.05   |
| XHNP  | 5.89           | 5.82           | 5.80           | 5.84    | 0.04   |

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**Table B-3 pH values, means and standard deviations of temperature trial samples**

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**Table B-4 pH values, means and standard deviations for separately pyrolized sample**

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Appendix C: FTIR Spectra
a) IR spectra of TX0
b) IR spectra of QX0
e) IR spectra of TS15
d) IR spectra of TS30
e) IR spectra of TH15
1) IR spectra of TH30
g) IR spectra of QS15
h) IR spectra of QS30
i) IR spectra of QH15
j) IR spectra of QH30
k) IR spectra of XS
l) IR spectra of XH
m) IR spectra of T200
n) IR spectra of T300
o) IR spectra of T400