

**PRODUCTIVITY AND GREENHOUSE GAS EMISSIONS FROM  
LONGTERM STOCKPILED SOILS TREATED WITH ORGANIC  
AMENDMENTS**

By

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## ABSTRACT

Reclamation success depends on the final soil quality of stockpiled soils. This thesis research examined N<sub>2</sub>O emission, plant growth, and nitrogen and phosphorus availability in two stockpiled soils that were amended with biochar (BC), humalite (HU), peat (PT), and 50:50 blends of biochar/humalite (BCH) and biochar/peat (BCP). These amendments were applied at rates of 0, 6.55, 13.1 and 26.2 g C kg<sup>-1</sup> soil. Biochar, PT, and BCP at the highest rate reduced N<sub>2</sub>O emissions by 34, 54, and 70%, relative to the control. In the bioassay, BC and PT increased dry matter yield by 38 and 40%, respectively. In the mineralization experiment, all amendments but BC significantly reduced Olsen P concentration. Nitrate and ammonium concentrations were highest in PT-amended soils. In general, PT performed the best in both soils.

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## **1. INTRODUCTION**

Current methods of soil salvage in the Cold Lake and Athabasca Oil Sands Regions of Alberta, Canada, are highly consumptive of time, energy, and financial resources. Government approvals often require operators to separate soils based on ecosite and subsoil texture, as well as to segregate topsoil from subsoil - a process called two-lifting. Specifically, the two-lift salvaging method consists of (i) an upper lift comprising of a mixture of the organic (O) and A horizons and sometimes a portion of the B horizon to a maximum depth of 30 cm and (ii) a lower lift comprised of the material below the upper lift to a depth considered appropriate for the specific site. Typically, a total salvage depth of 0.5-1.0 m is observed within Alberta. During the two-lift process, bulldozers first salvage topsoil to the specified topsoil depth determined by pre-disturbance soil surveys and then push the salvaged material into windrows. In winter, soils are ripped using a dozer shank in two perpendicular directions (cross-ripping) to assist in topsoil salvage. Subsoil is then stripped to an appropriate depth (again, cross-ripping occurs at this stage in winter) and also windrowed separately. Windrows are then loaded out using excavators and haul trucks, and material is sent to the reclamation material stockpile (RMS), or, in rare cases, is used to immediately reclaim disturbed areas. Excavators then salvage the remaining undisturbed soil underneath the windrows while they are loading out material. This process is very involved and time consuming, and requires the double handling of materials. Further



double handling of material occurs during the placement and reclamation process of the land management life cycle. Materials have to be hauled out of stockpiles in two separate actions, and placed and contoured separately. Typically, placement is referred to as 'capping', and usually occurs overtop of overburden (material occurring beyond 1 m in depth, which gets placed into a separate pile), which acts to buffer the soils from naturally undesirable materials, such as Pleistocene clays, which can be highly sodic (i.e., Clearwater clays), tailings sand, or coke. It should be noted, however, that to our knowledge, the placement of salvaged upland soils has not occurred on a large scale for permanent reclamation in the Oil Sands Region (but has elsewhere). This is dominantly due to the abundance of peat on site, and the higher success rate of reclamation of peat-mineral mix as a reclamation material after extended storage.

Two-lift soil salvage is highly beneficial when the soils are directly placed (i.e., salvaged and then immediately placed) in areas in need of reclamation. However, there is often low demand for reclamation material early on, which causes much of the salvaged material to be stockpiled (Visser, et al. 1984). Both the short-term and long-term stockpiling of soils results in adverse soil quality changes, including reduced microbial activity; loss of or reduced viability of seeds, propagules and roots; lower water holding capacity; poor chemical properties; reduced nutrient cycling; and increased bulk density (Harris, et al. 1989). Additionally, soil organic carbon (SOC) losses, up to 30%, have been found to be one of the most immediate consequences of stockpiling (Visser, et al. 1984). Decreases in soil quality have also been attributed to the change from anaerobic to aerobic conditions (Picek, et al. 2000). It is thought that much of the carbon (C) and

nitrogen (N) in recently spread soil is either volatilized, lost through microbial processes, or lost as runoff (Picek, et al. 2000, Williamson and Johnson, 1990). The degradation of soil quality over time directly impacts the success of reclamation, and limits or eliminates the advantages two-lift salvage holds over one-lift salvage methods, where topsoil and subsoil are salvaged and stockpiled together.

In a one-lift system, soil is salvaged in one operation, to a total depth of 0.5-1.0 m. This lift is comprised of all horizons within the soil profile, unless they are deemed unsuitable for salvage. In one-lift salvage, excavators are used in soil salvage, a process that is much more efficient, since horizon admixing is no longer a concern. As a result, lift thickness is greater, and material can be immediately loaded into heavy-haulers without the need to windrow material. Any required ripping can also be done to a greater depth, eliminating the need for a double application of cross-ripping. Transitional areas (i.e., Gleysols and shallow organic soils) are also incorporated during salvage, increasing the overall average organic matter (OM) content of the reclamation material, and compensating for any OM dilution effects. Some advantages of the one-lift salvage method are reduced costs, lower greenhouse gas (GHG) emissions due to reduce machinery requirements, smaller RMS footprints (and therefore less overall disturbance), and potentially equivalent soil quality compared to current practices. However, to our knowledge, no published research has examined the relative changes in soil quality and productivity of one-lift salvaged vs. two-lift salvaged soils, or their differences after stockpiling for a prolonged period of time.

As stated earlier, stockpiling soils has been shown to decrease soil quality. Losses of 32-85% of original OM have been observed in 18 stockpiles with three different textures and aged between 1.5 and 7 years (Abdul-Kareem and McRae, 1984). Another study found that undisturbed soils with 0.72% OM had their OM reduced to 0.26% - 0.38% in soils that had been stockpiled from 1-10 years on a coal mine in India (Kundu and Ghose, 1997). These losses have been attributed to the continued mineralization of OM (and conversion into dissolved organic C) within the stockpile, which results in a highly mobile form of soil C (Williamson and Johnson, 1990). In addition to these losses, Kundu and Ghose (1997) also reported substantial decreases in N, from 220 kg ha<sup>-1</sup> to 120 kg ha<sup>-1</sup> over a period of 10 years. Phosphorous and potassium followed similar trends, decreasing from 8.5 kg ha<sup>-1</sup> to 6 kg ha<sup>-1</sup>, and from 220 kg ha<sup>-1</sup> to 125 kg ha<sup>-1</sup>, respectively (Kundu and Ghose, 1997). Soil pH in the same study decreased from 6.38 to 5.88 over 10 years due to the leaching of base cations (Kundu and Ghose, 1997). However, other studies in alkaline temperate soils (e.g., Abdul-Kareem and McRae, 1984) showed that pH also increased with depth within soil stockpiles as a result of anaerobic conditions, and the increase of ammonium levels, findings echoed by Williamson and Johnson (1990) in their intensive look at the continued N and C mineralization of OM within stockpiles. The large amount of ammonium N in stockpiled soils very quickly becomes transformed into nitrate N, a highly labile form of nitrogen (Williamson and Johnson, 1990). During rainfall events, much of this nitrate, along with large amounts of dissolved organic carbon (DOC), are lost from the soil, further depleting soil quality (Williamson and Johnson, 1990).

Once soils lose their quality, they are very slow to return to their pre-disturbance quality. Akala and Lal (2000) found that there was an initial decrease in SOC within the first 5 years due to the disruption of aggregates and the decomposition of OM. After this point, however, SOC began to increase, and eventually plateaued (Akala and Lal, 2001). Their study also showed initial C contents of 15.3 Mg ha<sup>-1</sup> and 10.8 Mg ha<sup>-1</sup> in the 0-15 and 15-30 cm depth intervals following reclamation in pasture systems, while forested systems had initial C concentrations of 12.7 Mg ha<sup>-1</sup> and 9.1 Mg ha<sup>-1</sup> in the respective depths (Akala and Lal, 2000). By the end of the study, C contents had increased to 44.4 Mg and 18.3 Mg ha<sup>-1</sup> in the 0-15 and 15-30 cm depth intervals of pasture systems, while soil C in forested soils increased to 45.3 Mg ha<sup>-1</sup> and 13.6 Mg C ha<sup>-1</sup> in these depths (Akala and Lal, 2000). When long-term reclaimed soils for both systems were compared directly to their undisturbed controls, reclaimed systems showed slight increases ranging between 0.7 and 1.8 Mg C ha<sup>-1</sup> in three of the four soils (Akala and Lal, 2000). The only C loss (-5.4 Mg C ha<sup>-1</sup>) occurred in the 15-30 cm depth interval in pasture systems (Akala and Lal, 2000). However, Akala and Lal (2000) also showed that these changes had a significant lag phase of 10 years in most depth intervals and systems, and that SOC up until these points remained close to initial restoration values. It may be possible to alter these curves and decrease the time to the plateau by adding amendments that provide slowly released nutrients and C, and as a result, decrease reclamation time.

To improve soil quality, amendments are required. While chemical fertilizers have been traditionally used in agricultural settings, they are expensive and can pose environmental hazards, unless slow release forms are utilized. These issues are magnified

in the oil sands regions of Alberta, where large volumes of soil are in need of amendment, and there are many environmentally sensitive areas. To address the deterioration of soil quality during long-term stockpiling of salvaged soil, several studies have been conducted over the years to identify suitable organic soil amendments for augmenting soil quality in reclamation programs utilizing long-term stockpiled soils.

Presently, peat is predominantly used as an amendment since it is widely abundant in the Alberta oil sands region (AOSR): approximately 64% of the oil sands region consists of peaty wetlands (Rooney, et al. 2012). Current management practices use a blend of peat and underlying mineral soil to create a peat-mineral mix reclamation material that is readily available onsite, minimizing transportation costs (Rowland, et al. 2009). From this mixture, entire soil profiles are created and used in reclamation to replace disturbed soils. It is possible that peat could be used to bolster reclaimed soil quality in upland soils as well, either by including it into the soil stockpiles during soil salvage, or by incorporating during reclamation. Despite its wide use in the oil sands, the behavior of peat as an amendment is poorly understood. It is generally accepted that peat, when applied to the soil, tends to increase SOC, soil porosity, and water holding capacity (Li, et al. 2004, Ojekanmi and Chang, 2014, Vano, et al. 2011). It has also been shown that the addition of peat typically results in yield increases in most crops (Li, et al. 2004, Vestberg, et al. 2009). However, peat has also been shown to decrease soil nitrification and mineralization rates and, correspondingly, nitrate and ammonium concentrations, which are key soil quality parameters (Li, et al. 2004, Vano, et al. 2011, Vestberg, et al. 2009). (Vestberg, et al. 2009). The stockpiling process may potentially enhance the

performance of peat, since when it was compared to other reclamation materials, such as forest floor-mineral mix (i.e., O + A horizons), peat-mineral-mix (PMM) significantly outperformed amendments with regards to height, biomass, and foliar N in trembling aspen (*Populus tremuloides* Michx.) (Pinno, et al. 2012).

Humalite (a form of lignite) is a potentially beneficial soil amendment that could be used in the oil sands region. Humalite refers to natural lithologies that are enriched in organic acids, especially humic and fluvic acids, and are formed by the natural weathering or oxidation of coal or carbonaceous sediment (Hoffman, et al. 1993). The term humalite (derived from “humic” and “Alberta”) has been used informally for the material occurring with the subbituminous coals of the Battle River and Sheerness coalfields of Alberta (Hoffman, et al. 1993). Important properties of humalite include high cation exchange capacity (CEC), buffering properties, and the ability to chelate metal ions (Freeman, 1969). Like other humic acid products, humalite is classified as a soil conditioner and often marketed as humate. The benefits of humalite in reclamation stems in part from its ability to increase OM content, thereby increasing microbial populations, soil quality, nutrient uptake, and biomass yields (Hoffman, et al. 1993). One limitation, however, is that humalite is not available on site in the AOSR; deposits are 350 to 500 km away, thus transport costs may prohibit its use.

Another amendment to consider for use in reclamation is biochar. Biochar has attracted tremendous attention due to its ability to sustain long term improvements in soil physical, chemical and biological properties (Enders, et al. 2012). Recent studies have demonstrated that biochar can decrease soil hydraulic conductivity, improve soil water

retention, ion exchange capacity, nutrient retention (Laird, et al. 2010), nitrogen use efficiency (van Zwieten, et al. 2010), and microbial biomass (Lehmann, et al. 2011). In multiple studies, both hydraulic conductivity and the moisture retention (which are inversely related) showed greater differences with increasing rates of biochar application than their respective controls (Ibriham, et al. 2013, Ghithinji 2013, Lei and Zhang, 2013). Additionally, because of the chemical changes taking place during pyrolysis, biochars are chemically recalcitrant and resistant to biological decomposition, and may provide a slow release of C and other nutrients (Baldock and Smernik, 2002). Biochar is also easy to produce and could be created on site, utilizing non-merchantable timber, which is simply cleared and burned under current management practices.

The three experiments reported in this thesis aimed to examine the effects of various organic amendments on soil quality. Specific objectives were to:

1. Compare GHG emissions from one-lift and two-lift salvaged soils treated with different organic amendments;
2. Characterize changes in soil quality parameters following application of different amendments to long-term stockpiled soils.
3. Characterize nutrient dynamics in long-term stockpiled one-lift and two-lift salvaged soils as affected by different organic amendments; and
4. Determine the effects of amendment application on Plant growth and biomass yield in long-term stockpiled one-lift and two-lift salvaged soils.

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## 2. ORGANIC AMENDMENT EFFECTS ON NITROUS OXIDE EMISSIONS FROM LONG-TERM STOCKPILED SOILS

### 2.1. ABSTRACT

The Alberta oil sands have created large reclamation challenges, as millions of cubic meters of soil have been salvaged and stockpiled, and will eventually require placement. Stockpiled soils tend to be highly prone to nitrogen (N) losses in particular, through leaching of nitrate ( $\text{NO}_3^-$ ) and through denitrification. Organic amendments may restore soil quality attributes and mitigate denitrification; hence reducing the environmental impact of  $\text{N}_2\text{O}$  from oil sands reclamation. In this study, 100 g of a long-term (24 yr. old) stockpiled soil was amended with 0, 6.55, 13.1, and 26.2 g C  $\text{kg}^{-1}$  of softwood biochar (BC), humalite (HU, a subbituminous coal), fibric peat (PT), and 50:50 blends of biochar and humalite (BCH) and biochar and peat (BCP). Amended soils were incubated for up to 45 days and sampled at intervals ranging from 1 to 7 d. Biochar, PT, and BCP applied at the rate of 26.2 g C  $\text{kg}^{-1}$  reduced  $\text{N}_2\text{O}$  emissions by 34, 54, and 70%, respectively, relative to the unamended soil (control). All amendments showed significant reductions in  $\text{N}_2\text{O}$  emission relative to the zero-rate control (ZRC) during peak emission. Overall,  $\text{N}_2\text{O}$  flux, averaged across amendments, decreased with increasing amendment rate, culminating in a 31% reduction in  $\text{N}_2\text{O}$  flux at the 26.2 g  $\text{kg}^{-1}$  rate when compared to the ZRC. Of all amendments, PT and BCP gave the greatest overall reductions in  $\text{N}_2\text{O}$  flux, and may provide a solution to  $\text{N}_2\text{O}$  losses from stockpiled soils.

These reductions, in conjunction with the wide availability of the two amendments, make PT and BCP better amendments for reducing soil N losses.

## **2.2. INTRODUCTION**

The deterioration in soil quality of salvaged soils following long-term stockpiling is one of the most serious challenges to successful land reclamation in the oil sands region of Alberta, Canada, where some of the largest earthworks in the world are located. Salvaged soil stockpiles on these mines often easily reach between tens of thousands and millions of cubic metres in volume, resulting in 144,334,880 m<sup>3</sup> of stockpiled soils throughout the oil sands as of 2013 (ESRD, 2014). The main determinant of final soil quality is the length of time salvaged soils are stockpiled and the anaerobic conditions that develop in these stockpiles (Abdul-Kareem and McRae, 1984, Harris, et al. 1989, Kundu and Ghose, 1997). Drastic decreases in quality occur even in soils that have been stockpiled for just one year (Kundu and Ghose, 1997). Despite the relatively poor quality of stored soils, it is much easier to salvage and store soils than it is to attempt to recreate soil profiles with other alternative materials (i.e. waste paper sludge). Additionally, salvaged soils are generally free of contaminants, whereas alternative materials can be high in metals, sodium, and cause problems for establishing plants.

Perhaps the two most vulnerable, but important soil parameters are organic carbon (C) and nitrogen (N). One study in India showed that soils stored for only one year had 47% lower C and 31% lower available N than undisturbed soils (Kundu and Ghose, 1997). The same soils had lost 94% and 95% of their original C and available N, respectively, when stockpiled for 6 to 10 years (Kundu and Ghose, 1997). While these

losses may be exacerbated due to the study area's tropical climate, it is suspected that the behaviour of Canadian stockpiles would be similar, but would occur less rapidly. The reasons for these losses are manifold. Salvaging soil essentially halts any inputs into the soil from the plant community; thus, annual organic matter inputs cease, while microbial activity does not. Additionally, the microbial community itself changes drastically. Thousands of cubic meters of topsoil which were aerated via soil macro and micropores are now piled together and the bulk of the stored soil is entombed beyond the first 1-2 m of the stockpile, and microbial communities shift to anaerobically dominant ecosystems (Harris, et al. 1989, Williamson and Johnson, 1990). This change in microbial community structure results in an alteration of the speciation of soil N from  $\text{NO}_3^-$  to  $\text{NH}_4^+$ , resulting in a large buildup of  $\text{NH}_4^+$  within the stockpile over time due to ongoing mineralization reactions (Williamson and Johnson, 1990). These anaerobic mineralization reactions also increase dissolved organic C in the soil and increase soil pH (Williamson and Johnson, 1990).

When stockpiled soils become re-aerated, a large fraction of  $\text{NH}_4^+$  once again transforms to  $\text{NO}_3^-$ , which can result in serious problems when reclamation occurs as these soils are prone to N loss via  $\text{NO}_3^-$  leaching and denitrification (Williamson and Johnson, 1990, Williamson and Johnson, 1994). Losses via denitrification can be substantial due to the abundance of substrate, created during soil stockpiling, needed for denitrification. Williamson and Johnson (1994) found that denitrification alone accounted for a 33% decrease in total soil N over 21 days under conducive, aerobic conditions. These losses were attributed to an increase in the denitrification potential of

the soil, the increased availability of substrate (soluble organic C and  $\text{NO}_3^-$ ) as a result of soil storage, and the disruption of soil pores, which created excellent conditions for denitrification to occur (Williamson and Johnson, 1994).

Biochar is a promising amendment that has been shown to decrease  $\text{N}_2\text{O}$  emissions. Alho et al. (2009) reported a 49% decrease in  $\text{N}_2\text{O}$  emissions in soils treated with waste wood biochar at rates of 6 and 9  $\text{Mg ha}^{-1}$ . They attributed the reduction to a decrease in water filled pore space, as biochar added large amounts of surface area to the soil, and a liming effect of the biochar on the soil (Alho, et al. 2012). In another study, woodchip biochar reduced  $\text{N}_2\text{O}$  emissions to 10% of those from untreated soil (Kammann, et al. 2012). In the presence of denitrification stimulating earthworms, (Augustenborg, et al. 2012) also found significant reductions in  $\text{N}_2\text{O}$  emission, after adjusting for changes in water filled pore space (WFPS), as a result of biochar amendment, indicating that the reductions in  $\text{N}_2\text{O}$  emission were not due to increased soil porosity and aeration. Perhaps one of the most appealing reasons to utilize biochar to improve soil quality and mitigate  $\text{N}_2\text{O}$  emissions in Alberta's oil sands is that there is an abundance of feedstock readily available on-site as all non-merchantable wood is burned when an area is cleared for oil sands development, causing huge emissions of  $\text{CO}_2$ .

Peat is known to act as a slow-release N source (Hemstock, et al. 2010) and is widely used throughout the oil sands as a reclamation material. The majority of the permanent reclamation projects conducted in the oil sands use a blend of peat and underlying mineral soil to create a peat-mineral mix reclamation material. Peat is dominantly used as it is widely abundant, with approximately 64% of the oil sands region

consisting of peaty wetlands, and because it is available on site, minimizing trucking costs. However, to increase the likelihood of successfully reclaiming upland areas to ecosites similar to pre-disturbance ecosites, upland soils are salvaged. As illustrated by Williamson and Johnson (1994), upland soils face numerous challenges when stored for long periods of time. Currently, the body of knowledge surrounding peat as an amendment, particularly with regards to its impact on denitrification is, poorly documented.

Humalite is a sub-bituminous coal that developed on non-marine bedrock, similar to leonardite. Varying forms of humalite have recently been sold to agricultural producers, as it tends to be high in nitrogen and humic and fluvic acids, which are known to be beneficial to soil quality, and improve wheat yields (Turgay, et al. 2011, Verlinden, et al. 2009). Though no humalite is found in the oil sands region, it may be possible to transport it from Forestburg, Alberta to site for reclamation purposes, should its benefits outweigh transit costs. With millions of cubic metres of stockpiled soils in need of placement, Alberta's oil sands are a large potential source of N<sub>2</sub>O emission. Nitrous oxide is known to be 310 times more potent than CO<sub>2</sub>, and 75% of N<sub>2</sub>O emissions come from agriculture and soil management (USEPA, 2014).

The objective of this study was to compare the effects of biochar, humalite, and peat application on N<sub>2</sub>O emissions from stockpiled oil sands soils to determine which amendment would provide the least environmental impact while providing the highest overall soil quality.

## **2.3. MATERIALS AND METHODS**

### **2.3.1. Soil Sampling and Analysis**

The soil was collected from 24-year old and an 8-year old stockpile on Imperial Oil Limited's Cold Lake, AB, Canada Operations (54° 36' N, -110° 28' E). Soils in the area consisted of a mix of Boralfs (Orthic Gray Luvisols), Cryochrepts (Eluviated Eutric Bruisols), Eutrochrepts (Orthic Melanic Brunisols), Hemists (Terric Mesisols) and Entisols (Orthic Regosols). Prior to sampling, multiple stockpiles were visually inspected to determine their overall quality, with regards to organic matter content. The stockpiles with the highest organic matter content were then selected, as they were expected to provide the highest rates of nitrous oxide flux, and thus illustrate a 'worst case scenario' for the AOSR. As a result of the stockpile survey, two sampling locations, 5 km apart, were chosen. The stockpiles at each location consisted of soils salvaged from corresponding well pads that were 1ha in size. The soils consisted of Boralfs for the two-lift soil (2LS) soil and its natural controls (NC) and Cryochrepts for the one-lift (1LS) soil and its NC. In both cases, the natural controls were located on mixed-wood ecosites that consisted of White Spruce and Birch as dominant vegetative species. Samples were taken from the 2 to 3-m in depth at one 2LS and two 1LS stockpiles at their respective sites. The 2LS stockpile consisted entirely of topsoil, while soils for the 1LS were taken from separate topsoil and subsoil piles at the 1LS sampling location. In each instance, stockpiles were approximately 25 m wide × 100 m long × 4 m high. Samples were collected from the stockpiles using a small excavator (Hitachi ZAXIS33U, Japan). Collected soils were then placed into 20-L plastic pails, and sealed with lids prior to



transportation. The soil was then screened through an 11-mm sieve, composited, and stored in pails for approximately 30 d at 20 °C, until the experiment commenced.

Using soils from the 8-year old stockpiles, a 20:80 topsoil:subsoil blend was prepared to mimic a one-lift salvaged (1LS) soil. The blend was placed into 125-L Rubbermaid tubs, which were kept in a walk-in incubator maintained at 25°C for two weeks. Approximately 6 L of reverse osmosis water were added to the bulk 1LS soil (approximately 50 kg) during incubation to simulate stockpile conditions in the AOSR. During the addition of moisture, soils were stirred to ensure uniform moisture distribution.

The soils were analyzed for baseline chemical properties (Table 2.1). Soil  $\text{NO}_3^-$  was determined using the KCl extraction and cadmium reduction method (Carter and Gregorich, 2007). Ammonium was determined with an Ammonia analyzer following extraction with KCl. Available soil P (Olsen P) was determined by the ammonium molybdate method following extraction with 0.5 M sodium bicarbonate at a pH of 8.5, and then analyzed using an Utraspec 2100 Pro Spectrophotometer (Holliston, MA, USA) (Carter and Gregorich, 2007). Organic matter was determined via the loss on ignition method using a Thermo Scientific™ Thermolyne™ muffle furnace (Waltham, MA, USA) (Carter and Gregorich, 2007), while pH was determined in a 1:1: soil to water suspension with a pH electrode (AB15 – Fisher Scientific, Waltham, MA. USA). Calcium (Ca), magnesium (Mg), and sodium (Na) were determined in ammonium acetate extracts by atomic absorption spectroscopy (iCE™ 3300 AAS; Thermo Scientific,

Waltham, MA, USA). Cation exchange capacity (CEC) was obtained by summing cation concentration in ammonium acetate extracts (Carter and Gregorich, 2007).

### **2.3.2. Organic Amendments**

The amendments tested in this study were biochar (BC), peat (PT), humalite (HU), a 50/50 mixture of biochar and humalite (BCH), and a 50/50 (w/w) mixture of biochar and peat (BCP). The biochar was obtained from Alterna Biocarbon (Prince George, BC) and was produced from wastewood from logging operations that utilized Douglas fir (*Pseudotsuga menziesii*), white spruce (*Picea glauca*), and various pine species. The biochar was pyrolyzed at an average temperature of 380°C, and then immediately cooled with water spray following carbonization. Humalite was provided by Black Earth Humic LP (Calgary, AB). Humalite is a sub-bituminous coal and is very similar to Leonardite; the main difference being that humalite is formed in non-marine environments and tends to be higher in humic content (Black Earth Inc., 2014). The peat utilized in this experiment was Sunshine<sup>®</sup> horticultural peat from Sun Gro Horticulture (Vancouver, BC) and was fibric in nature.

The amendments were analyzed for their baseline chemical properties (Table 2.2). Total carbon (C) concentration was determined using a carbon analyzer (FlashEA<sup>®</sup> 1112 Nitrogen and Carbon Analyzer; Thermo Scientific Waltham, MA, USA), while calcium carbonate equivalence (CCE) was determined using the pressure calcimeter method ((Loeppert and Suarez, 1996). Organic C concentration was determined as the difference between total C concentration and CCE. Total P, K, Ca, Mg, and S concentrations were

determined by atomic absorption spectrometry following digestion with hydrogen peroxide and nitric acid. Sodium adsorption ratio (SAR) was calculated from Na, Ca, and Mg concentrations, determined as described above, in saturated paste extracts.

### 2.3.3. Experimental Setup

The experiment was set up as a completely randomized design with a factorial treatment structure. The experiment design was: total [ $2_{\text{soil}} (5_{\text{amend}} \times 3_{\text{rate}} \times 3_{\text{reps}} + 6_{\text{control}})_{\text{reps}}$ ] yielding 102 units. The factors were the organic amendments described above and amendment rate (0, 6.55, 13.1, and 26.2 g C kg<sup>-1</sup> soil) (Table 2.3). Actual amendment rates corresponding to these C rates are presented in Table 2.2, along with their chemical properties in table 2.3. The 13.1 g C kg<sup>-1</sup> rate corresponds to the commonly recommended rate of biochar for agricultural purposes. Undisturbed soils from the stockpile sites (natural control soils, NC) were included for comparison.

Amendments were added at the above rates to 100 g (oven dry wt.) soil, thoroughly mixed in a 1-L mason jar, and transferred into a 6.2 cm ht. × 5.2 cm diam. PVC pipe covered with a piece of cloth at the base. Each resulting unit was fertilized with 6.87 mg urea (3.2 mg N), with the exception of the NC soils, following Rowland et al. 2009. The units were placed in 1-L mason jars, watered to approximately 50% WFPS, and immediately weighed for moist weight. After covering with perforated parafilm to minimize moisture loss and allow free airflow, the units were placed in a walk-in

Table 2.1. Selected Chemical Properties of the 1LS and 2LS Soils and Their Natural Controls Prior to Amendment (NC).†

Parameter	pH	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Olsen P	mg kg <sup>-1</sup>			Na	Organic C	CCE
					K	Mg	Ca			
								%		
<b>1LS</b>	7.6	5.0	0.8	13	100	375	2014	29	2.24	13.6
<b>2LS</b>	7.3	9.5	1.4	19	112	250	1674	20	4.47	10.8
<b>1LS NC</b>	6.1	23.0	0.2	37	73	109	743	20	1.20	4.9
<b>2LS NC</b>	5.6	12.5	7.7	9	186	273	1108	14	4.47	8.4

† NO<sub>3</sub><sup>-</sup> = nitrate, NH<sub>4</sub><sup>+</sup> = ammonium, CCE= calcium carbonate equivalent.

Table 2.2 Initial Chemical Properties of the Amendments Added to the 1LS and 2LS Soils.†

Amendment	pH	TOC	N	P	K	S	Ca	Mg	CEC	CCE	SAR
<b>Biochar</b>	7.2	648	0.4	67	1282	90	3350	722	1.7	0.3	0.21
<b>Humalite</b>	4.3	375	10.7	103	175	4169	14136	2140	21	0.2	5
<b>Peat</b>	4.5	273	7.2	157	0	792	7490	1076	4.6	0.3	0.18

† TOC, total organic carbon; CEC, cation exchange capacity; CCE, calcium carbonate equivalent; SAR, sodium adsorption ratio

incubator, which was set at 25°C for the duration of the experiment. A humidifier (Sunbeam SUL-496, Boca Raton, FL, USA) was placed inside the incubator to limit moisture loss from the units. The units were weighed every two to three days and watered if moisture content dropped below 5% of the target 50% WFPS. Any watering took place a minimum of three days prior to gas sampling to allow for the cores to equilibrate, thus preventing any influence of moisture on measurements.

Table 2.3. Amount of organic amendment added to each 100 g core. †

<b>Amendment</b>	<b>Rate of C Application g C kg<sup>-1</sup></b>	<b>BC added g</b>	<b>HU added g</b>	<b>PT added g</b>
<b>Biochar</b>	<b>6.55</b>	1.02	-	-
<b>Biochar/Humalite</b>	<b>6.55</b>	0.51	0.88	-
<b>Biochar/peat</b>	<b>6.55</b>	0.51	-	1.21
<b>Humalite</b>	<b>6.55</b>	-	1.76	-
<b>Peat</b>	<b>6.55</b>	-	-	2.42
<b>Biochar</b>	<b>13.1</b>	2.03	-	-
<b>Biochar/Humalite</b>	<b>13.1</b>	1.02	1.76	-
<b>Biochar/peat</b>	<b>13.1</b>	1.02	-	2.42
<b>Humalite</b>	<b>13.1</b>	-	3.52	-
<b>Peat</b>	<b>13.1</b>	-	-	4.84
<b>Biochar</b>	<b>26.2</b>	4.06	-	-
<b>Biochar/Humalite</b>	<b>26.2</b>	2.03	3.52	-
<b>Biochar/peat</b>	<b>26.2</b>	2.03	-	4.84
<b>Humalite</b>	<b>26.2</b>	-	7.04	-
<b>Peat</b>	<b>26.2</b>	-	-	9.67

† HU, humalite; PT, peat; BC, biochar;

#### 2.3.4. Gas Sampling and Analysis

Gas samples were collected on days 0, 1, 2, 3, 7, 10, 17, 24, 31, 38, and 45 using a static incubation system (Tenuta and Beauchamp, 2000; Velthof et al. 2003). Prior to sampling on each day, the headspace of each incubation unit was flushed with air for 45 s to ensure N<sub>2</sub>O was at ambient concentration. The units were then sealed with a Mason jar lid fitted with a rubber septum. The units were allowed to sit for 2 h to allow for gas accumulation before sampling (11 mL per unit) with a 23G1 PrecisionGlide® needle mounted on a 20 mL syringe (BD, Franklin Lakes, NJ, USA). Gas samples were placed into 6 mL Exetainer vials (Labco, High Wycombe, Buckinghamshire, England). Blank

units were spaced every 25 incubation units in the incubator to correct for background (ambient) N<sub>2</sub>O concentrations. Nitrous oxide concentrations in the samples were measured with a gas chromatograph (Varian 3800, Varian Instruments, Walnut Creek, CA, USA) equipped with a detector for N<sub>2</sub>O (i.e., electron capture detector; carrier gas 10% CH<sub>4</sub> and 90% Ar). Nitrous oxide concentrations were corrected for background concentrations prior to data analysis.

### **2.3.5. Residual Soil Inorganic Nitrogen**

At the end of the incubation, each soil core was emptied into a brown paper bag and allowed to air dry for three days prior to analysis. Subsamples were extracted and analyzed for NO<sub>3</sub>-N, NH<sub>4</sub>-N, and pH as described above.

### **2.3.6. Calculations**

Nitrous oxide fluxes were calculated from the rate of N<sub>2</sub>O accumulation in the headspace of each unit, with the assumption that N<sub>2</sub>O concentration increased linearly with time (Velthof and Oenema, 1995; Velthof et al. 2003). Dissolved N<sub>2</sub>O concentration was estimated according to the method described by Moraghan and Buresh (1977) and added to the N<sub>2</sub>O concentration in the headspace to give total flux. Nitrous oxide fluxes were integrated over the incubation period to give cumulative N<sub>2</sub>O emissions.

### **2.3.7. Statistical Analysis**

Analysis of variance of N<sub>2</sub>O flux data was performed using the generalized linear mixed models procedure (PROC GLIMMIX) of SAS v.9.3 (SAS Institute, 2004), with amendment and rate as fixed effects. Sampling time was modeled as a repeated factor using the compound symmetry (CS) covariance structure. Treatment differences were considered significant if  $P < 0.05$  using the Tukey-Kramer method.

## 2.5. RESULTS

### 2.5.1. Soil and Amendment Properties

The soils were relatively low in organic matter,  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  and tended to be slightly alkaline (Table 2.1). The amendments varied substantially in nutrient content and pH. Biochar had the highest pH, C, and K content, but the lowest N, P, S, Ca, Mg, and CEC (Table 2.2). Humalite was the highest in N, S, Ca, Mg, CEC, and SAR, but the lowest in pH and CCE. Peat was the highest in P and the lowest in K.

### 2.5.2. Nitrous Oxide Flux

Significant treatment effects on  $\text{N}_2\text{O}$  flux were observed in the 2LS but not in the 1LS soil. In the 2LS soil, fluxes peaked Day 3 for all amendments at all rates (Table 2.4, Fig. 2.1). On Day 3,  $\text{N}_2\text{O}$  flux from the  $6.55 \text{ g C kg}^{-1}$  PT treatment was 56% lower than flux from the unamended control. At the  $13.1 \text{ g C kg}^{-1}$  rate on Day 3; all amendments produced significantly lower  $\text{N}_2\text{O}$  fluxes than the control, with the flux being lowest for PT, which produced 68% lower  $\text{N}_2\text{O}$  flux than the control. Similarly, at the  $26.2 \text{ g C kg}^{-1}$  rate on Day 3,  $\text{N}_2\text{O}$  fluxes were lower in all amended soils than in the control, with PT having the lowest flux, which was 90% lower than that in the control. On Day 7, only PT at the  $26.2 \text{ g C kg}^{-1}$  showed a significant reduction in  $\text{N}_2\text{O}$  flux relative to the control, reducing the flux by 80%. The unamended soils included for comparison exhibited the lowest  $\text{N}_2\text{O}$  fluxes, and were significantly lower in flux than treated soils during most sampling times.

When  $\text{N}_2\text{O}$  fluxes from amended soils were compared, significant differences were observed on Day 2 at the  $26.2 \text{ g C kg}^{-1}$  rate, at which HU produced the greatest flux, which was 84, 185, 606, and 761% higher than fluxes from BCH, BC, PT and BCP, respectively. The only other significant difference between amendments was that between BCP and BCH. On Day 3, PT produced between 45 and 48% lower  $\text{N}_2\text{O}$  flux than BC, HU, and BCH at the  $13.1 \text{ g C kg}^{-1}$  rate, while at the  $26.2 \text{ g C kg}^{-1}$  rate,  $\text{N}_2\text{O}$  fluxes from 2LS soil amended with BC, BCP, and PT were 40, 64, and 86%, respectively, lower than that from BCH-amended soil, and BCP and PT produced 54 to 84% lower fluxes

than HU and BC. On Day 3, BC produced 29% lower flux than PT at the 6.55 g kg<sup>-1</sup> rate, but at the 13.1 g C kg<sup>-1</sup> rate, HU and PT produced 29 and 38% lower fluxes than BCP, while at the 26.2 g kg<sup>-1</sup> rate, PT produced between 70 and 76% lower flux than all the other amendments. However, amendment differences disappeared by Day 7. In general, amendment differences on N<sub>2</sub>O flux were most pronounced at the 26.2 g C kg<sup>-1</sup> rate. At that rate, PT produced the greatest reduction in N<sub>2</sub>O flux. Overall, N<sub>2</sub>O fluxes tended to decrease in the order of HU>BC>PT amongst the full strength amendments, and BCH>BC>BCP amongst biochar and its blends.

### **2.5.3. Cumulative Nitrous Oxide Emission**

When the cumulative emissions were analyzed, we found an amendment and rate main effect. When the 2LS amended soils were compared to the zero-rate control (ZRC), we found no significant differences. When compared the NC, all amendments were substantially higher in emissions, with differences of 1120 to 1616%. The HU treatment had the greatest cumulative flux, while PT had the lowest when compared to the NC, which yielded 5.63 μg N<sub>2</sub>O kg<sup>-1</sup> for the entire study. Amongst the amended soils, HU had 28, 39, and 41% higher than BCP, BC, and PT. Nitrous oxide emissions in the 13.1 and 26.2 g C kg<sup>-1</sup> rates were significantly lower than those seen in the 6.55; differences of 20 and 31% respectively. No significant differences in the 1LS soil were observed between the controls and the amendments, or the amendments themselves when cumulative values were analyzed.



Table 2.4. Amendment and rate effects on N<sub>2</sub>O flux and cumulative losses, soil pH, and available N concentration in the two-lift soil (2LS)†.

	One-lift salvaged soil					Two-lift salvaged soil				
	N <sub>2</sub> O Flux μg kg <sup>-1</sup> hr <sup>-1</sup>	Cumulative N <sub>2</sub> O loss μg kg <sup>-1</sup> 45 d <sup>-1</sup>	pH	NO <sub>3</sub> <sup>-</sup> mg kg <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> mg kg <sup>-1</sup>	N <sub>2</sub> O Flux μg kg <sup>-1</sup> hr <sup>-1</sup>	Cumulative N <sub>2</sub> O loss μg kg <sup>-1</sup> 45d <sup>-1</sup>	pH	NO <sub>3</sub> <sup>-</sup> mg kg <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> mg kg <sup>-1</sup>
<b>Amendment</b>										
BC	0.001	1.93 <sup>a</sup>	7.61	23.1	7.44	0.098	69.57 <sup>b</sup>	7.31	30.6	10.2
HU	0.005	3.76 <sup>a</sup>	6.73	31.3	10.0	0.132	96.71 <sup>b</sup>	6.44	39.7	15.1
PT	0.004	3.26 <sup>a</sup>	7.01	29.7	12.3	0.082	68.75 <sup>b</sup>	6.49	36.8	12.6
BCH	0.004	2.24 <sup>a</sup>	7.26	24.9	10.2	0.118	85.17 <sup>ab</sup>	6.83	36.1	9.69
BCP	0.006	8.16 <sup>a</sup>	7.17	26.5	10.8	0.095	75.43 <sup>b</sup>	6.92	34.56	9.53
<b>Rate</b>										
6.55 g C kg <sup>-1</sup>	0.005	6.26 <sup>a</sup>	7.46	29.3	9.29	0.127	95.52 <sup>a</sup>	7.07	35.6	9.62
13.1 g C kg <sup>-1</sup>	0.003	1.48 <sup>a</sup>	7.21	27.0	10.8	0.100	76.42 <sup>b</sup>	6.83	37.1	10.2
26.2 g C kg <sup>-1</sup>	0.004	3.86 <sup>a</sup>	6.80	25.0	10.4	0.088	65.44 <sup>b</sup>	6.51	34.1	14.4
						P value				
Amendment (A)	0.34	0.52	<0.001	0.01	0.29	<0.001	0.002	<0.001	<0.001	0.02
Rate (R)	0.41	0.31	<0.001	0.06	0.67	<0.001	<0.001	<0.001	0.046	0.01
Time (T)		-	-	-	-	<0.001	-	-	-	-
A × R	0.14	0.28	<0.001	0.32	0.69	<0.001	0.116	0.05	0.58	0.005
T × R	0.45	-	-	-	-	<0.001	-	-	-	-
A × T	0.33	-	-	-	-	<0.001	-	-	-	-
A × R × T	0.24	-	-	-	-	<0.001	-	-	-	-

† Time effect only applied to N<sub>2</sub>O flux and is not presented, along with interactions involving time, for the other response variables. NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> denote nitrate and ammonium respectively. 2LS NC cumulative flux= 5.63 μg kg<sup>-1</sup> 45 d<sup>-1</sup>. NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> values are residual soil values after the experiment. Means for the time main effect are not shown for brevity. Different letters in the same column denote significant differences between treatments.

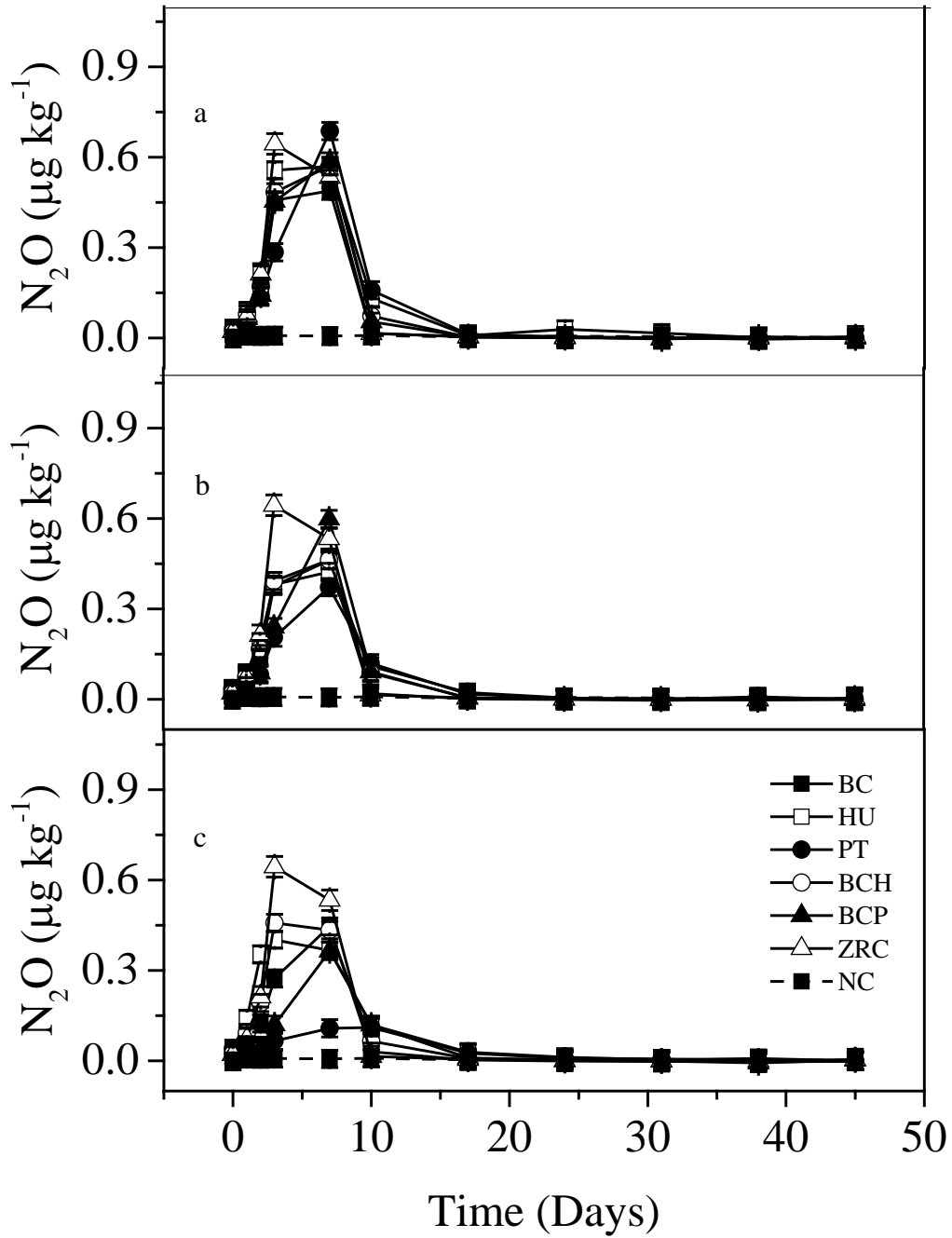


Fig. 2.1. N<sub>2</sub>O flux values by amendment, increasing rate of application, and time in the two-lift (2LS) soils. a) 6.55 g C kg<sup>-1</sup> rate, b) 13.1 g C kg<sup>-1</sup>, c) 26.2 g C kg<sup>-1</sup>

#### 2.5.4. Residual Available Soil Nitrogen and Soil pH

The 1LS treated soils did not differ from the unamended 1LS soils with respect to residual soil nitrate, but PT and HU produced 60 and 69% more soil nitrate than the unamended, undisturbed soil (Table 2.5). Amongst the amended soils, only HU BC had significantly different  $\text{NO}_3\text{-N}$  concentrations. Residual  $\text{NO}_3\text{-N}$  concentrations in the 2LS soil at the end of the incubation period did not differ significantly between the amended and unamended soil. However, the  $\text{NO}_3\text{-N}$  concentration in the unamended, undisturbed soil ranged from 39 to 81% greater than that in the amended and unamended 1LS soil. When the amended soils were compared to one another, HU produced significantly greater  $\text{NO}_3\text{-N}$  concentration in the soil than BCP and BC, while PT and BCH were not significantly different from HU, but outperformed BC by 18 and 13%, respectively.

There was a significant amendment  $\times$  rate interaction for  $\text{NH}_4\text{-N}$  concentration in the 2LS. The 26.2 g C  $\text{kg}^{-1}$  HU rate produced significantly greater  $\text{NH}_4\text{-N}$  concentration than the unamended 2LS soil, while no differences in  $\text{NH}_4\text{-N}$  concentration were observed between amended and unamended soils. Amongst the amendments, only HU at the 26.2 g C  $\text{kg}^{-1}$  rate produced significantly greater  $\text{NH}_4\text{-N}$  concentration than equivalent rates of BC, BCH, and BCP.

Soil pH tended to be significantly lower in amended than the unamended 1LS soil. At the 13.1 g C  $\text{kg}^{-1}$  rate, BCP, PT, and HU produced significantly lower soil pH values than the unamended 1LS, while at the 26.2 g C  $\text{kg}^{-1}$  rate, BCH, BCP, PT and HU produced lower pH. Amongst the amendments, BC produced the highest pH, but

differences did not show up until the 13.1 and 26.2 g kg<sup>-1</sup> rate, where it was higher than that in soils receiving the other amendments at equivalent rates. In the 2LS soil, there were significant amendment and rate effects on pH, which were again apparent at the 13.1 and 26.2 g C kg<sup>-1</sup> rates. The unamended 2LS produced higher pH than all the other amendments at equivalent rates. Amongst the treated soils, pH followed the following ranking BC > BCH = BCP > HU = PT, with differences ranging between 6 and 13%. Finally, the 6.55 g kg<sup>-1</sup> rate had the highest overall pHs. The 13.1 g kg<sup>-1</sup> rate produced higher pH than the 26.2 g kg<sup>-1</sup> rate.

Table 2.5: Residual soil N values by amendment type for the one-lift (1LS) and two-lift (2LS) soils.†

	Amendment	NO <sub>3</sub> -N mg kg <sup>-1</sup>	NH <sub>4</sub> -N mg kg <sup>-1</sup>
1LS	ZRC	27.00	7.43
	NC	18.50	27.40
	BC	23.11	7.44
	HU	31.33	10.02
	PT	29.67	12.27
	BCH	24.83	10.13
	BCP	26.50	10.80
2LS	ZRC	36.50	9.47
	NC	53.33	14.80
	BC	30.61	10.21
	HU	39.67	15.10
	PT	36.76	12.56
	BCH	36.11	9.69
	BCP	34.56	9.53

†BC, biochar; BCH, 50:50 biochar:humalite by mass (based on C content); BCP, 50:50 biochar:peat by mass (based on C content); HU, humalite; PT, peat; 1LS, one-lift soil; 2LS, two-lift soil; ZRC, zero-rate control; NC, natural control.

## 2.6. DISCUSSION

The low N<sub>2</sub>O flux in PT-amended soil may have been due to low microsite moisture levels in the soil as a result of bulking or hydrophobicity. Although moisture content was kept relative constant and similar in all treatments throughout the experiment, peat is known to be hydrophobic, and, at the micro-scale, this hydrophobicity may have inhibited nitrification, a step required for denitrification (Cheng, et al. 2012, Szajdak, et al. 2007). This decrease in N<sub>2</sub>O flux in PT-amended soil was even more pronounced as rate increased (Fig. 3.1). While hydrophobicity may play an important

role, we suspect that it is the bulking effect of the added peat that is creating the greatest reductions in N<sub>2</sub>O flux. Even though the WFPS of our amended soils was on average 50%, we suspect the pore distribution of the PT amended soils would be very different from those amended with finer additives, such as humalite. The large size of peat fibers and the large volume of peat added (Table 2.5) at the higher rates likely created an abundance of macropores within the soil cores, increasing aeration and reducing the available habitat for nitrifying and denitrifying bacteria.

Biochar also tended to do relatively well at reducing N<sub>2</sub>O flux in the 2LS soil during peak emissions. This may be, again, due to increases in soil porosity, and thus aeration, as biochar has been found to have a high surface area, and thus impacts bulk density and soil porosity, which may explain the increase in N<sub>2</sub>O reductions with increasing rate (Alho, et al. 2012, Mukherjee and Lal, 2013). Further, it was found that approximately 2% *w/w* biochar ( a rate corresponding to our 26.2 g C kg<sup>-1</sup> rate of application) was able to bring about significant decreases in bulk density (Mukherjee and Lal, 2013). Biochar also tends to be highly stable in the soil environment, with low concentrations of labile C, thus potentially limiting N<sub>2</sub>O flux, as microbes are carbon-limited (Kammann, et al. 2012, Novak, et al. 2009). Peat, on the other hand, is expected to contain more labile C than biochar or humalite. One study, which examined ten organic (peat) soil profiles, clearly showed that fibric bog peat, such as that used in the present study, had a large pool of mineralizable C (Grover and Baldock, 2012). Additionally, substrate quality played a significant role in decomposition, and therefore C mineralization; however, moisture content was crucial, and could influence the rate of

mineralization by up to 50% (Grover and Baldock, 2012). Another study found that at constant levels of  $\text{NO}_3^-$  in the soil, and the addition of glucose at increasing rates, different peat sources and compositions resulted in lower levels of  $\text{N}_2\text{O}$  flux versus peats with no glucose added (Amha and Bohne, 2011). The authors attributed these differences to the amount of decomposable organic compounds that could be used as electron donors for the denitrifying microbes in the organic soils. Therefore, the relative ease of peat decomposition compared with other amendments in conjunction with the increased aeration associated with the addition of peat to the soil may have resulted in the large  $\text{N}_2\text{O}$  flux reductions observed in the present study. The low cumulative  $\text{N}_2\text{O}$  emissions from PT-amended soils in our study reflected the low  $\text{N}_2\text{O}$  flux discussed above.

In general, emissions from both the 1LS and 2LS soils had very low nitrous oxide emissions, compared to other greenhouse gas studies. For instance, Chiyoka, et al. (2011) measured cumulative nitrous oxide emissions under similar conditions, in two agricultural soils, and the cumulative values of their unamended soils were typically one to three orders of magnitude lower in emissions. Further, our findings also clash with those of Williamson and Johnson (1994), who found up to 33% of N lost from stockpiled soils, was attributed to denitrification. This may indicate that denitrification does not play a large role in N losses from reclaimed soils under most conditions. However, our low nitrous oxide emissions are likely a result of drier conditions present in our study, which are more representative of field conditions. Further, we designed our experiment so as to also measure  $\text{CO}_2$  and  $\text{CH}_4$  (data not presented), the former of which requires some aeration to form. We suspect that under wetter conditions, we may have received

more nitrous oxide production on par with those found by Williamson and Johnson (1994), whose soils were completely saturated during their study.

Several published studies report a 10 to 90% reduction in cumulative N<sub>2</sub>O emissions in soils amended with biochar, yet the causes of these reductions are still not well understood (Cayuela, et al. 2013, Cayuela, et al. 2014). Although biochar significantly reduced N<sub>2</sub>O flux relative to the unamended soil during peak periods within the first week of incubation, it did not significantly reduce cumulative emissions. This is inconsistent with the findings in literature mentioned above, and may be due to the adverse effects of stockpiling on the microbial community, or the relatively poor quality of the soils used in our study, which contrasts markedly with agricultural soils. When compared to other amendments in the present study, biochar exhibited relatively strong reductions in cumulative N<sub>2</sub>O emissions, evidently due to its consistently low N<sub>2</sub>O emissions across a number of sampling days. We suspect that the high surface area of biochar played a large role in these reductions, by increasing soil porosity and aeration. This, combined with a low labile C pool (i.e., high C stability), likely caused these reductions (Cayuela, et al. 2014, Grover and Baldock, 2012, Kammann, et al. 2012, Novak, et al. 2009). The differences between the NC and the treated soils are not unexpected; in other experiments we conducted, the NC soils tended to perform poorly, particularly with regards to nitrification and mineralization. This may be because unlike the stockpiled soils, the NC's organic matter is likely less decomposed (i.e. more fresh) and have less substrate (i.e. dissolved organic carbon) to be utilized by microbes in the denitrification process. This sentiment is echoed by Williamson and Johnson (1990),



who noted copious amounts ammonium and dissolved organic carbon tended to build up in stockpiled soils. They found that the dissolved organic carbon and ammonium was rapidly converted to nitrate and was also rapidly denitrified (Williamson and Johnson, 1990, Williamson and Johnson, 1994).

The high soil nitrate and ammonium levels observed with HU addition were consistent with our observations in another experiment examining N availability in soils treated with the same amendments as in the present study (unpublished data). Humalite produced relatively large amounts of available N in the amended soil, and this may have resulted in its consistently high N<sub>2</sub>O emissions, as NO<sub>3</sub>-N is a precursor for N<sub>2</sub>O. Interestingly, however, PT tended to have similar nitrate and ammonium levels, yet had significantly lower N<sub>2</sub>O emission, further pointing to differences in soil physical properties as a result of amendment as a potential cause for differences in flux, rather than availability of denitrification substrate. Additionally, it is expected that PT would contain more labile C to support a larger population of the denitrifying microbes.

Although the PT and BCP treatments gave the lowest N<sub>2</sub>O fluxes, it remains unclear how long these benefits would last. It may be that once native or seeded Plant communities begin to establish on reclaimed soil, the in situ conditions may likely alter to favour denitrification, as more easily decomposable biomass and root exudates provide the substrates needed for denitrification to occur. Regardless, the reductions seen in N<sub>2</sub>O flux when soils were amended with PT were real and significant. Any reduction in the loss of N from the soil is beneficial to reclaimed soils as they generally tend to be highly depleted in available N, at least until normal soil function returns. Further, these

reductions occurred when the soil was most vulnerable to N losses, and may result in better performances of the soil microbial community early on in the reclamation process, and reduce the overall contribution of these soils to climate change, as N<sub>2</sub>O is 310 times more potent than CO<sub>2</sub> (USEPA, 2014).

## 2.7. CONCLUSIONS

Nitrous oxide emissions pose a huge challenge from both an environmental and soil quality perspective for oil sands developers. All five amendments tested in this study decreased N<sub>2</sub>O flux in amended soils on peak days when compared to the unamended soil, with BC and PT producing the greatest reductions. Biochar, BCP, and PT gave the lowest fluxes of all amendments during the 45 d incubation period, but did not significantly reduce cumulative emissions relative to the unamended soil, indicating that these amendments may provide little benefit to those seeking to reduce the global warming impact of the oil sands. While our findings are beneficial to the management of stockpiled soils, a closer look at how these amendments behave when stored within stockpiles over long periods of time may be beneficial and provide a more plausible method of reducing N<sub>2</sub>O losses. Biochar would be of particular interest, as it has been found to retain labile compounds, such as NO<sub>3</sub><sup>-</sup> in the soil, a property that may further reduce N losses through denitrification or leaching, and thus may prove to be the best amendment to apply in terms of reducing losses from the soil nitrogen pool; a phenomenon that could be measured in the field using lysimeters.

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### **3. A GROWTH ROOM BIOASSAY OF ORGANIC AMENDMENT EFFECTS ON THE PROPERTIES AND PRODUCTIVITY OF STOCKPILED SOILS**

#### **3.1. ABSTRACT**

Long-term stockpiling of soil salvaged from oil sands operations often leads to deterioration of soil quality and poor reclamation results when the soil is eventually used to reclaim disturbed sites. This bioassay examined the effects of organic amendments on the quality of a traditionally salvaged (two-lift salvaged, 2LS) topsoil, consisting of the O + A horizons, and a 20:80 mixture of topsoil (O + A) and subsoil, which was a surrogate for a one-lift salvaged (1LS) soil. Dry soil samples (4.2 kg) were placed into 5-L pots and amended with biochar (BC), humalite (HU), peat (PT), a 50:50 mixture of biochar and peat (BCP), and a 50:50 mixture of biochar and humalite (BCH) at rates corresponding to 0, 6.55, 13.1, and 26.2 g C kg<sup>-1</sup> soil. The pots were seeded with barley (*Hordeum vulgare*), fertilized according to standard practice, and placed in a growth chamber. Plants were allowed to grow for three crop cycles of 45-59 d each and harvested at the end of each cycle. Dry matter yields (DMY) were highest for BC and PT, which increased the DMY by 38 and 40%, respectively, in the 2LS soil compared with the non-amended soil. Humalite gave the highest Plant N and Plant P content, but these did not lead to an increase in DMY due to Plant toxicity in HU amended soils.

### 3.2. INTRODUCTION

Final quality of salvaged and stored soils is of great importance to oil sands developers and future generations. In Canada's Alberta oil sands region (AOSR), reclamation soil stockpiles range between tens of thousands to millions of cubic metres in volume, resulting in more than  $144 \times 10^6 \text{ m}^3$  of stockpiled soils throughout the oil sands as of 2013 (ESRD 2014). Time is considered the greatest factor that influences the final quality of stockpiled soil, and has been shown to negatively impact important soil quality parameters such as organic matter content, available nitrogen (N) and phosphorus (P), pH, and cation exchange capacity (CEC) (Abdul-Kareem and McRae, 1984, Harris, et al. 1989, Kundu and Ghose, 1997). Even with short-term storage, significant decreases in soil quality occur. Significant reductions in soil organic carbon (SOC, 47%), available N, available P (23%), and potassium (K, 28%) have been reported in soils following one year of stockpiling (Kundu and Ghose, 1997). After six to ten years, these nutrients had decreased by between 89 and 96% (Kundu and Ghose, 1997).

There are many reasons why stockpiling impacts soil quality so drastically. First, salvaging soil halts any inputs into the soil from the Plant community. While annual organic matter inputs cease, microbial activity does not, usually resulting in lower organic matter contents with time (Abdul-Kareem and McRae, 1984). Additionally, the composition of the microbial community is altered as thousands of cubic meters of topsoil, which were previously aerated via soil macro and micropores, are now buried

beneath the oxic zone (typically 1 to 2 m in depth) of the stockpile, and microbial communities shift to anaerobically dominant ecosystems (Ghose, 2004, Harris, et al. 1989). The change from aerobic to anaerobic conditions alters the dynamics of many reactions within the soil (Harris, et al. 1989, Williamson and Johnson, 1990). This change in community composition results in an alteration of soil N from  $\text{NO}_3\text{-N}$  to  $\text{NH}_4\text{-N}$ . When stored soils become aerated, a large amount of  $\text{NH}_4\text{-N}$  is transformed to  $\text{NO}_3\text{-N}$ , which can result in serious problems as these soils are much more prone to N loss via leaching of  $\text{NO}_3\text{-N}$  (Williamson and Johnson, 1990).

Differences in soil salvage methods may also play a role in final soil quality. Currently, two-lift soil salvage (2LS) is the approved method in the AOSR (CEMA, 2012). This method involves the combined removal of the O and A horizons to a maximum depth of 20 cm. The underlying subsoil is then salvaged to a maximum depth of 80 cm and stored in a different cell of the reclamation material stockpile (RMS), based on its overall texture (CEMA, 2012). This process is cycle intensive and difficult. Most salvage is conducted during winter, and in order to remove the soil, bulldozers must break up a salvageable horizon in two passes, in a process called “cross ripping”. The topsoil is windrowed in yet another pass and then hauled to the RMS, and the entire process is repeated for the subsoil horizon. It is also important to note that RMSs sit undisturbed for approximately 20 to 30 years, as the vast majority of soil salvage occurs



during the development phase of the mine's lifecycle, which presents limited opportunities for reclamation.

Since oil sands operators tend to end up with relatively poor soil quality compared to the undisturbed surrounding soils, the efficacy of the two-lift method may be lower than expected when utilized for long term storage and reclamation. A one-lift soil salvage (1LS) method, where topsoil and subsoil are salvaged together, may reduce cost and greenhouse gas emissions from equipment, while still potentially providing the operators with similar soil quality. The main concern with the one-lift method, however, is the dilution of the topsoil with the subsoil, as the two are admixed during salvage, resulting in poorer soil quality to begin with. However, over time, the final soil quality and productivity from the two soil salvage methods may be similar since long term storage will likely cause soil quality to deteriorate until it reaches an equilibrium state.

Organic amendments, such as peat (PT), biochar (BC), and humalite (HU) may help improve soil quality parameters and productivity during reclamation. Peat is known to act as a slow-release N source and is widely used throughout the oil sands as a reclamation material (Hemstock, et al. 2010). The majority of the permanent reclamation conducted in the oil sands uses a blend of peat and underlying mineral soil to create a peat-mineral mix reclamation material that is readily available on site, minimizing transportation costs (Rowland, et al. 2009). Peat is dominantly used since it is widely abundant, accounting for 64% of the landmass (Rooney, et al. 2012). However, peat's

effectiveness as an amendment has been shown to have mixed or negative effects on soil N concentration and on the microbial community. For instance, Piteola and Tanni (2003) reported an increase in soil organic carbon (SOC) concentration in topsoil, and a 30 to 45% increase in NO<sub>3</sub>-N concentration during the first year following peat amendment, while NO<sub>3</sub>-N concentration had decreased by 50% relative to non-amended soil three years later, possibly indicating immobilization. Peat decreased water soluble P concentration of soils, which could pose a problem in already degraded stockpiled soils (Pietola and Tanni, 2003). Further, the same study showed that peat fibers were still obvious after two years, indicating that the composition of peat made it resistant to breakdown and conversion to humus by the microbial community (Pietola and Tanni, 2003). Indeed, it was found that microbial biomass C and N, and mycorrhizal fungi populations decreased significantly with peat application; a mechanism that is not well understood, but attributed to antagonistic bacteria and fungi within peat (Vestberg, et al. 2009). However, another study showed that a variety of reclamation materials, including a forest floor-mineral mix, were significantly outperformed by a peat-mineral-mix, when height, biomass, and foliar N values were compared, indicating that the previous negative effects may not occur with stockpiled peat-mineral mix (Pinno, et al. 2012).

Biochar has garnered a lot of attention in recent years. The effectiveness of biochar in improving soil quality appears to depend largely on feedstock type and on pyrolysis temperatures. In one study, wheat derived biochar applied at 10 to 40 t ha<sup>-1</sup>

increased SOC by between 9.3 and 56% and rice yield by 9.5 to 29%, and decreased global warming potential by 7.1 to 34.8% (Zhang, et al. 2012). In another study, biochar was found to increase SOC by 33% and total N by 10%, while it decreased bulk density by 9%, but did not significantly affect rice yields (Huang, et al. 2013). When biochar application was paired with chemical fertilizers, similar results were obtained for the previously mentioned soil quality indicators, but BC amendment also resulted in a 5% increase in rice yield (Huang, et al. 2013). Steiner et al. (2007) reported large increases in sorghum yield of up to 75% when 11 t ha<sup>-1</sup> of biochar was applied, while another study showed yield increases of 28 to 140% when compared to non-amended soils, in a maize-soybean crop rotation that was treated with 20 t ha<sup>-1</sup> of biochar (Major, et al. 2010). The effect of biochar on the soil ecosystem also tends to be positive. Biochar increased basal soil respiration after two years in one study, a change attributed to biochar increasing Plant biomass, and therefore the rhizosphere effect on soil microbes (Jones, et al. 2012). The same study also showed that the aged biochar had a large potential to mineralize glucose, albeit at a slower rate than the control (Jones, et al. 2012). Additionally, biochar increased bacterial and fungal growth relative to the control (Jones, et al. 2012).

Humalite, a non-marine form of leonardite, has also been shown to improve soil quality. The sub-bituminous coal, similar to lignite, has recently been sold to agricultural producers, as it tends to be high in N and humic and fluvic acids, which are known to be beneficial to soil quality and yields (Turgay, et al. 2011, Verlinden, et al. 2009). Humic

substances are known to increase soil P content by impeding P fixation and by forming humophospho complexes, which are easily taken up by plants (Pietola and Tanni, 2003, Raina and Goswami, 1988). Additionally, combinations of lignite-derived humic acid and chemical fertilizers produced greater soil macronutrient and micronutrient concentrations compared with the control soils fertilized at identical rates (Nandakumar, et al. 2004). Differences between humic acid-amended treatments and fertilized controls ranged between 5 and 11% for N, P, and K in two different soils, and between 7 and 20% for Fe, Mn, Zn, and Cu (Nandakumar, et al. 2004). In another study, researchers found that the application of lignite increased potato tuber numbers by 22%, marketable potato yield by 38%, and total potato yield by 15% compared to the control (Sanli, et al. 2012). Although humalite is not found in the AOSR, it may be possible to transport it to site for reclamation purposes. However, the closest deposits of humalite are 345 km away, thus the benefit of this amendment would have to be quite substantial to offset transportation cost.

The objective of this study was to determine if applying the aforementioned organic amendments would result in increases in dry matter yield (DMY) and soil productivity, which may translate to better reclamation success in the AOSR. Upland soils in particular are vulnerable to soil degradation when compared to the salvaged peat soils currently used, but lend themselves to the redevelopment of soil profiles more typical of pre-disturbance conditions. Additionally, we wanted to determine the

behaviour of these organic amendments in temperate soils. Relatively few studies have been conducted in cold climates. Peat and humalite in particular have had a very limited number of studies conducted on their efficacy as soil conditioners. We hypothesized that biochar would provide the greatest overall benefit to the soil due to its ability to increase soil surface area, provide habitat for microbes and soil fauna, as well as its known ability to limit nitrate leaching and improve cation exchange capacity (CEC) in the soil (DeLuca, et al. 2009).

### **3.3. MATERIALS AND METHODS**

#### **3.3.1. Site and Soil**

The soil was collected from 24-year old and an 8-year old stockpile on Imperial Oil Limited's Cold Lake, AB, Canada Operations (54° 36' N, -110° 28' E). Soils in the area consisted of a mix of Boralfs (Orthic Gray Luvisols), Cryochrepts (Eluviated Eutric Bruisols), Eutrochrepts (Orthic Melanic Brunisols), Hemists (Terric Mesisols) and Entisols (Orthic Regosols). Prior to sampling, multiple stockpiles were visually inspected to determine their overall quality, with regards to organic matter content. The stockpiles with the highest organic matter content were then selected, as they were expected to provide the highest rates of nitrous oxide flux, and thus illustrate a 'worst case scenario' for the AOSR. As a result of the stockpile survey, two sampling locations, 5 km apart, were chosen. The stockpiles at each location consisted of soils

salvaged from corresponding well pads that were 1 ha in size. The soils consisted of Boralfs for the two-lift soil (2LS) soil and its natural controls (NC) and Cryochrepts for the one-lift (1LS) soil and its NC. In both cases, the natural controls were located on mixed-wood ecosites that consisted of White Spruce and Birch as dominant vegetative species. Samples were taken from the 2- to 3-m in depth at one 2LS and two 1LS stockpiles at their respective sites. The 2LS stockpile consisted entirely of topsoil, while soils for the 1LS were taken from separate topsoil and subsoil piles at the 1LS sampling location. In each instance, stockpiles were approximately 25 m wide × 100 m long × 4 m high. Samples were collected from the stockpiles using a small excavator (Hitachi ZAXIS33U, Japan). Collected soils were then placed into 20-L plastic pails, and sealed with lids prior to transportation. The soil was then screened through an 11-mm sieve, composited, and stored in pails for approximately 30 d at 20 °C, until the experiment commenced.

Using soils from the 8-year old stockpiles, a 20:80 topsoil:subsoil blend was prepared to mimic a one-lift salvaged (1LS) soil. The blend was placed into 125-L Rubbermaid tubs, which were kept in a walk-in incubator maintained at 25°C for two weeks. Approximately 6 L of reverse osmosis water were added to the bulk 1LS soil (approximately 50 kg) during incubation to simulate stockpile conditions in the AOSR. During the addition of moisture, soils were stirred to ensure uniform moisture distribution.

The soils were analyzed for baseline chemical properties (Table 2.1). Soil  $\text{NO}_3^-$  was determined using the KCl extraction and cadmium reduction method (Carter and Gregorich, 2007). Ammonium was determined with an Ammonia analyzer following extraction with KCl. Available soil P (Olsen P) was determined by the ammonium molybdate method following extraction with 0.5 M sodium bicarbonate at a pH of 8.5, and then analyzed using an Utraspec 2100 Pro Spectrophotometer (Holliston, MA, USA) (Carter and Gregorich, 2007). Organic matter was determined via the loss on ignition method using a Thermo Scientific™ Thermolyne™ muffle furnace (Waltham, MA, USA) (Carter and Gregorich, 2007), while pH was determined in a 1:1: soil to water suspension with a pH electrode (AB15 – Fisher Scientific, Waltham, MA, USA). Calcium (Ca), magnesium (Mg), and sodium (Na) were determined in ammonium acetate extracts by atomic absorption spectroscopy (iCE™ 3300 AAS; Thermo Scientific, Waltham, MA, USA). Cation exchange capacity (CEC) was obtained by summing cation concentration in ammonium acetate extracts (Carter and Gregorich, 2007).

### **3.3.2. Amendments and Rates**

The amendments tested were biochar (BC), humalite (HU), peat (PT), a 50:50 mixture of biochar and humalite (BCH), and a 50:50 mixture of biochar and peat (BCP). The roller-milled biochar was provided by Alterna Biocarbon (Prince George, BC) and

was produced using waste wood from Douglas Fir (*Pseudotsuga menziesii*), White Spruce (*Picea glauca*) and various pine species (*Pinus* spp.) from logging operations. The biochar was pyrolyzed at a temperature of 380 °C, and then immediately cooled with a water spray following carbonization. Humalite was provided by Black Earth Humic LP (Calgary, AB). The peat was Sunshine<sup>®</sup> horticultural peat from Sun Gro Horticulture (Vancouver, BC) and was fibric in nature. All amendment treatments were applied at rates of 0, 6.55, 13.1, and 26.2 g C kg<sup>-1</sup> (Table 3.1). The 0 g C kg<sup>-1</sup> rate was the zero rate control (ZRC), while natural controls (NC) were collected from sites approximately 50 m away from where the stockpiled soils were collected.



Table 3.1. Rates of amendment applied to the 1LS and 2LS soil, and the mass of carbon associated with them. †

<b>Amendment</b>	<b>Rate of C Application g C kg<sup>-1</sup></b>	<b>BC added g</b>	<b>HU added g</b>	<b>PT added g</b>
<b>Biochar</b>	<b>6.55</b>	1.02	-	-
<b>Biochar/Humalite</b>	<b>6.55</b>	0.51	0.88	-
<b>Biochar/peat</b>	<b>6.55</b>	0.51	-	1.21
<b>Humalite</b>	<b>6.55</b>	-	1.76	-
<b>Peat</b>	<b>6.55</b>	-	-	2.42
<b>Biochar</b>	<b>13.1</b>	2.03	-	-
<b>Biochar/Humalite</b>	<b>13.1</b>	1.02	1.76	-
<b>Biochar/peat</b>	<b>13.1</b>	1.02	-	2.42
<b>Humalite</b>	<b>13.1</b>	-	3.52	-
<b>Peat</b>	<b>13.1</b>	-	-	4.84
<b>Biochar</b>	<b>26.2</b>	4.06	-	-
<b>Biochar/Humalite</b>	<b>26.2</b>	2.03	3.52	-
<b>Biochar/peat</b>	<b>26.2</b>	2.03	-	4.84
<b>Humalite</b>	<b>26.2</b>	-	7.04	-
<b>Peat</b>	<b>26.2</b>	-	-	9.67

† HU, humalite; PT, peat; BC, biochar

### 3.3.3. Soil, Amendment and Plant Analysis

Soils and amendments were analyzed for pH; organic matter, nitrate (NO<sub>3</sub>-N), ammonium (NH<sub>4</sub>-N), Olsen P (Plant available P), potassium (K), sulfur (S), boron (B), zinc (Zn), iron (Fe), manganese (Mn), calcium (Ca), magnesium (Mg), and sodium (Na) concentrations; and cation exchange capacity (CEC) at the beginning of the study (Table 3.2, Table 3.3). At the end of each crop cycle, soil samples were analyzed for NO<sub>3</sub>-N, NH<sub>4</sub>-N, Olsen P, K, Ca, Mg, Na, and CEC. Soil NO<sub>3</sub><sup>-</sup> was determined in 2 M KCl

extracts with the cadmium reduction method using a Lachat QuikChem 8500 Flow Injection Analyzer (Loveland, CO, USA) (Carter and Gregorich, 2007). Ammonium was also determined using the same auto analyzer, using a different channel, following extraction with 2 M KCl. Available soil P (Olsen P) was determined by the ammonium molybdate method following extraction with 0.5 M sodium bicarbonate at a pH of 8.5 (Carter and Gregorich, 2007), and then analyzed using an Utraspec 2100 Pro Spectrophotometer (Holliston, MA, USA). Organic matter was determined via the loss on ignition method (Carter and Gregorich, 2007) using a Thermo Scientific™ Thermolyne™ muffle furnace (Waltham, MA, USA), while pH was determined in a 1:1 soil to water suspension with a pH electrode (AB15 – Fisher Scientific, Waltham, MA, USA). Calcium, Mg, and Na were determined in ammonium acetate extracts by atomic absorption spectroscopy (iCE™ 3300 AAS; Thermo Scientific, Waltham, MA, USA). Micronutrients (Fe, Mn, Cu, Zn) were extracted with 0.005 M DTPA and analyzed using atomic absorption spectroscopy, while B was determined by the hot water extraction method (Carter and Gregorich, 2007). Cation exchange capacity (CEC) was estimated by summing cation concentrations in ammonium acetate extracts. Finally, container moisture capacities for the 1LS and 2LS soils were determined by adding varying amounts of moisture to 100 g of each soil in clear plastic pill bottles and allowing the moist soils to sit for 24 h to allow for moisture equilibration, as per White and Mastalerz (1996). Total Plant N concentrations were analyzed using combustion in an Elementar

Table 3.2. Selected initial chemical properties of the one-lift (1LS) and two-lift (2LS) soils. †

	pH	OM	NO <sub>3</sub> -N	NH <sub>4</sub> -N	Olsen P	K	Cl	S	B	Zn	Fe	Mn	Cu	Mg	Ca	Na	CEC
		%	mg kg <sup>-1</sup>													cmol kg <sup>-1</sup>	
<b>2LS</b>	7.5	2.5	1.5	1.4	15	117	4.5	8	0.8	2.1	157	56	1.2	244	1633	14	10.6
<b>2LS NC</b>	5	2.6	12.5	7.7	9	186	-	-	-	-	-	-	-	273	1108	17	8.4
<b>1LS topsoil</b>	7.1	3.6	2.5	-	29	100	6	10	0.7	1.63	188	37.9	0.74	257	1424	16	9.6
<b>1LS subsoil</b>	7.6	0.8	8	-	10	100	16	48	0.3	2.89	5.73	1.3	0.58	411	2319	29	15.4
<b>1LS combined</b>	7.6	1.3	5	0.8	13	100	-	-	-	-	-	-	-	375	2014	29	13.6
<b>1LS NC</b>	6.1	0.7	23.0	0.2	37	73	-	-	-	-	-	-	-	109	743	20	4.9

†OM, organic matter; CEC, cation exchange capacity;

Table 3.3. Initial chemical properties of the organic amendments. †

<b>Amendment</b>	<b>pH</b>	<b>TOC</b>	<b>N</b>	<b>P</b>	<b>K</b>	<b>S</b>	<b>Ca</b>	<b>Mg</b>	<b>CEC</b>	<b>CCE</b>	<b>SAR.</b>
		— g kg <sup>-1</sup> —			mg kg <sup>-1</sup>			cmol <sub>c</sub> kg <sup>-1</sup>		%	
<b>BC</b>	7.2	648	0.4	67	1282	90	3,350	722	1.7	0.3	0.21
<b>HU</b>	4.3	375	10.7	103	175	4,169	14,136	2,140	21	0.2	5
<b>PT</b>	4.5	273	7.2	157	0	792	7,490	1,076	4.6	0.3	0.18

† TOC, total organic carbon; CEC, cation exchange capacity; CCE, calcium carbonate equivalent; SAR, sodium adsorption ratio; BC, biochar; HU, humalite; PT, peat

Vario Max CN analyzer (Mount Laurel, NJ, USA). Total P concentration in Plant tissue was determined in nitric acid and hydrogen peroxide digests using a Perkin Elmer 5400 ICP (Waltham, MA, USA).

### 3.3.4. Experimental Setup

Oven-dry soil samples (4.2 kg per pot) were thoroughly mixed with the five amendments at the rates indicated above. The soils also received 0.143 g urea, 0.338 g mono-ammonium phosphate, and 0.787 g potassium sulphate, after which they were placed into 5-L pots and seeded with 15 barley (*Hordeum vulgare*) seeds, which were randomly distributed and placed at least 2 cm apart. Container capacity was then determined, and pots were watered to match container capacity (White and Mastalerz, 1966).

The potted soils were watered with reverse osmosis water to attain volumetric water contents of 0.130 and 0.230 kg H<sub>2</sub>O kg<sup>-1</sup> for the 1LS and 2LS soils, respectively. These moisture contents corresponded to 34 and 50% water-filled pore space (WFPS). The pots were then placed inside a walk-in incubator, which was maintained at a 16-h photoperiod, with temperatures of 22 °C and 15 °C during the light and dark periods, respectively. Light intensity in the chamber was 270 μmole m<sup>-2</sup> s<sup>-1</sup> during the photoperiod, while relative humidity was set at 65% at all times. The pots were weighed every two to three days and watered to replace any moisture lost via evapotranspiration.

Plants were allowed to grow until full heading, after which they were harvested by clipping the above ground biomass at the soil surface. The cycle was repeated two more times, to give a total of three cycles (C1, C2, C3), each of which was 45 to 59 days long as a way of mimicking a three-year field study. Between cycles, a 10-day rest period occurred, in which soils left unplanted after sampling, and stored in the growth chamber.

In total, for each cycle the experiment design was as follows: [ $2_{\text{soil}} (5_{\text{amendments}} \times 3_{\text{rate}} \times 3_{\text{reps}} + 6_{\text{control reps}})$ ] yielding 102 units. There were signs of chlorosis and necrosis mid-way through C1, possibly due to micronutrient deficiency. A micronutrient mixture consisting of: 8 Zn, 7 Mn, 1 Mo, 5 B, 20 Cu, and 26 mg kg<sup>-1</sup> Fe was therefore added to each pot, except the NC soils, at the start of C2, along with the same rate of urea used in C1. Sulphur was also added with this mixture at 203 mg kg<sup>-1</sup> S was also added with the micronutrient solution. The micronutrient solution appeared to reduce necrosis somewhat, and was not reapplied with an additional application of urea at the beginning of C3.

### 3.3.5. Sampling

Above-ground biomass was harvested at the end of each cycle and oven-dried at 60°C for 48 h. Oven-dry samples were weighed for dry matter yield (DMY) determination. Subsamples were ground, passed through a 2-mm sieve and analyzed as described above. Soil samples (20 g) were collected immediately after each harvest for

laboratory analysis. Residual roots were then cut into approximately 0.5 to 1 cm pieces and then uniformly mixed back into the soil prior to the start of the next crop cycle.

### **3.3.6. Statistical Analysis**

Analysis of variance was performed on all data using the generalized linear mixed models procedure (PROC GLIMMIX) of SAS v.9.3 (SAS Institute, 2014), with amendment and rate as fixed effects. Sampling time was modeled as a repeated measures factor using the compound symmetry (CS) covariance structure. Treatment means were compared using the Tukey-Kramer multiple comparison procedure. Treatment differences were considered significant if  $P < 0.05$ . Data for the 1LS and 2LS soils were analyzed separately.

## **3.4. RESULTS**

### **3.4.1. Dry Matter Yield**

**One-Lift Soil.** There was a significant amendment x cycle interaction for DMY, but this only occurred in the factorial + control aspect of our study. Differences only occurred in C2 and C3 between all stockpiled soils and the natural controls (Table 3.4). Typically, differences in C2 were between 345 and 390%, but these differences decreased to between 244 and 306% in C3. There was also crop cycle x rate interaction for DMY, but no significant difference between amended and non-amended 1LS soil (Table 3.4,

Fig. 3.1). The rate effect was not significant in C1. In C2, DMY tends to decrease with increasing rate, with the 6.55, 13.1 and 26.2 g C kg<sup>-1</sup> rate soils being 73, 50, and 57% higher than the unamended soils. In C3, the 13.1 g C kg<sup>-1</sup> rate produced 34% greater DMY (mean of all amendments) than the 26.2 g C kg<sup>-1</sup> rate and 77% greater DMY than the control (zero rate), but did not differ significantly from the 6.55 g C kg<sup>-1</sup> rate (Fig. 3.1).

Across amendments, a comparison of rate effects within a cycle revealed that at the 6.55 g C kg<sup>-1</sup> rate, DMY in C1 was 41% greater than that in C2 and 91% greater than that in C3, while C2 DMY was 36% greater than that observed in C3. At the 13.1 g C kg<sup>-1</sup> rate, DMY in C1 was 49% greater than that in C2 and 52% greater than that in C3. At the 26.2 g C kg<sup>-1</sup> rate, DMY in C1 was 53 and 118% greater than those in C2 and C3, respectively, while C2 DMY was 43% greater than that observed in C3. In C2, DMY in the treated soils were 345 to 370% greater than in the NC (1.71 g pot<sup>-1</sup>), while in C3 amendments produced between 244 and 306% more DMY than the NC (1.70 g pot<sup>-1</sup>).

**Two-Lift Soil.** In the 2LS soil, there was a significant amendment × cycle interaction when the 2LS ZRC treatment was included in the analysis of variance (Table 3.5, Fig. 3.2). In C2, PT produced 174% more DMY than the ZRC, but there was no significant difference between the other four amendments and the ZRC. Furthermore, there was no significant treatment effect in Cycles 1 and 3. In the amended 2LS soil, PT outperformed BCP, BCH, and HU by 18, 21, and 22%, respectively, with respect to



DMY, while BC outperformed BCH and HU by 15 and 18%, respectively. Dry matter yields in amended soils were 151 and 215% greater in C1 than in C2 and C3, respectively, while C2 had 25% greater DMY than C3.

Table 3.4. Amendment, rate, and cycle effects on dry matter yield and soil quality parameters in the one-lift soil.†

	DMY	Cumulative DMY	Plant N content	Plant P content	OM	pH	NO <sub>3</sub> -N	NH <sub>4</sub> -N	Olsen P	CEC
	g pot <sup>-1</sup>	g pot <sup>-1</sup>	mg pot <sup>-1</sup>		g C kg <sub>soil</sub> <sup>-1</sup>		—————	mg kg <sup>-1</sup> —————		cmol <sub>c</sub> kg <sup>-1</sup>
<b>Amendment (A)</b>										
BC	8.33	25.00	78.14	14.98b	10.45	7.50	3.15	19.62	14.19a	13.20
HU	8.50	25.49	91.94	16.84a	18.27	6.42	0.70	20.42	11.96ab	14.74
PT	9.03	27.07	92.73	15.91ab	24.82	6.62	1.06	24.19	11.15ab	13.99
BCH	8.61	25.84	85.40	15.75b	14.33	6.95	2.06	21.81	12.11ab	13.79
BCP	8.62	25.86	81.25	15.25ab	17.04	7.09	1.96	22.74	13.04b	13.01
<b>Rate</b>										
6.55	8.96	26.88	88.09	16.10	11.76	7.31	1.49	19.64	13.93a	13.92
13.1	8.57	25.71	89.53	16.03	15.69	6.98	1.92	24.42	12.71a	13.63
26.2	8.33	24.98	80.46	15.10	23.78	6.45	1.94	21.15	10.82b	13.68
<b>Cycle</b>										
1	11.6	-	115.60	22.08	17.48	6.76c	1.62	25.17	13.84a	13.75
2	7.90	-	89.49	13.27	-	6.86b	1.65	12.18	13.13a	13.41
3	6.33	-	53.00	11.88	16.67	7.12a	2.08	27.86	10.49b	14.01
<b>P value</b>										
Amendment (A)	0.23	0.36	<0.001	0.01	<0.001	<0.001	<0.001	0.18	0.02	<0.001
Rate (R)	0.03	0.68	<0.001	0.04	<0.001	<0.001	<0.001	0.01	<0.001	0.51
A x R	0.10	0.25	0.01	0.32	<0.001	<0.001	0.02	0.40	0.93	<0.001
Cycle (C)	<0.001	-	<0.001	<0.001	0.09	<0.001	<0.001	<0.001	<0.001	0.13
A x C	0.78	-	0.01	0.11	<0.001	0.18	0.67	0.14	0.29	0.43
C x R	<0.001	-	0.01	0.01	0.95	0.07	<0.001	<0.001	0.46	<0.001
A x R x C	0.23	-	0.75	0.15	0.04	0.24	<0.001	<0.001	0.63	0.04

†BC, biochar; BCH, 50:50 biochar:humalite by mass (based on C content), BCP, 50:50 biochar:peat by mass (based on C content), HU, humalite, PT, peat; CEC, cation exchange capacity; DMY, dry matter yield; OM, organic matter.

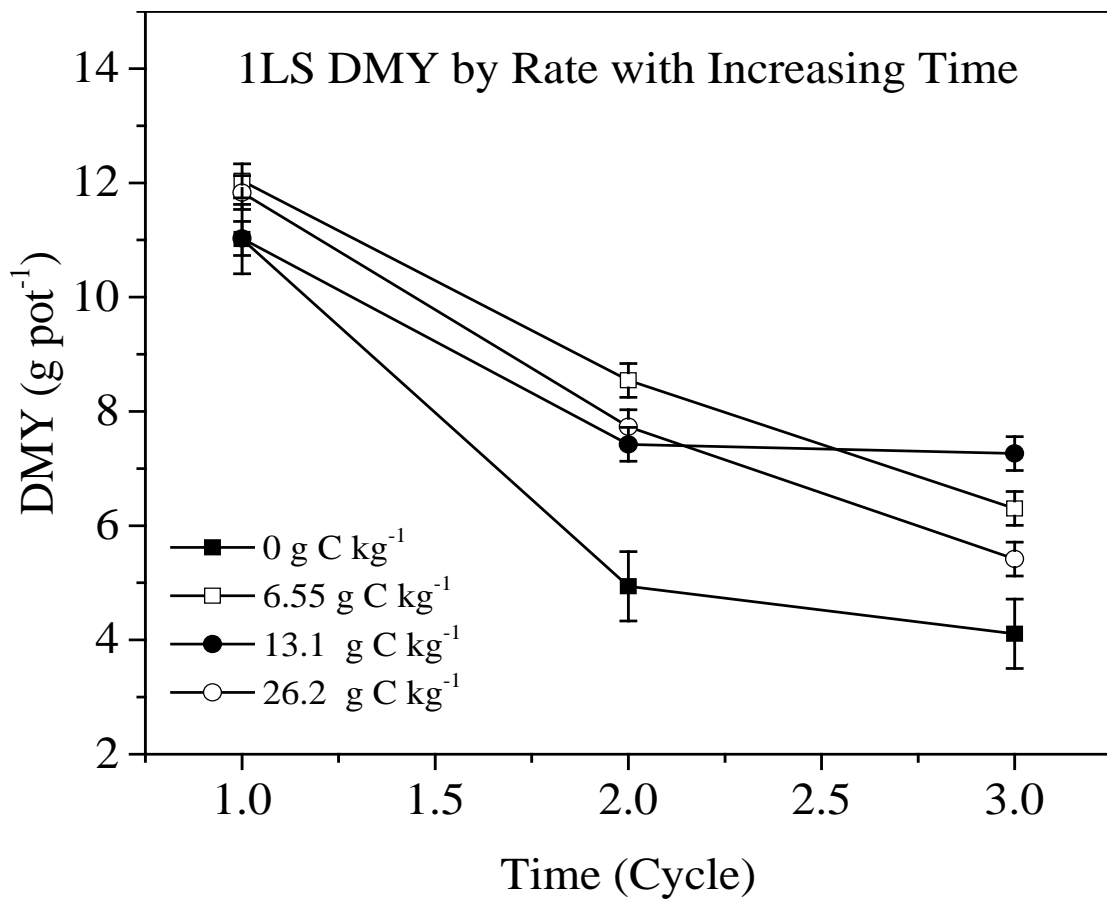


Fig. 3.1. Differences in Barley dry mater yield (DMY) by rate, by time in the one-lift soil (1LS). Rates of 0, 6.55, 13.1, and 26.2 g C kg<sup>-1</sup> represent the DMY values averaged across the amendments, which were applied at carbon equivalent rates.

Table 3.5. Amendment, rate, and cycle effects on dry matter yield, and soil quality parameters in the two-lift soil.†

	DMY†	Cumulative DMY†	Plant N content	Plant P content	OM†	pH	NO <sub>3</sub>	NH <sub>4</sub>	Olsen P	CEC†
	g pot <sup>-1</sup>	g pot <sup>-1</sup>	mg pot <sup>-1</sup>		g C kg <sub>soil</sub> <sup>-1</sup>		—————	mg kg <sup>-1</sup>		cmol <sub>c</sub> kg <sup>-1</sup>
<b>Amendment (A)</b>										
BC†	12.4	37.28ab	120.05	24.00	18.88c	7.25	2.91	16.84	14.19	10.86
HU†	10.3	31.00b	131.39	21.36	25.98b	6.40	0.59	19.36	13.81	13.44
PT†	12.7	37.96a	143.71	23.52	32.76b	6.55	0.72	15.56	13.44	12.47
BCH†	10.5	31.47ab	118.54	19.99	22.14bc	6.82	1.81	16.64	13.89	12.00
BCP†	10.8	32.29ab	121.48	21.31	24.79b	6.90	1.65	16.84	13.70	11.16
<b>Rate</b>										
6.55	11.4	34.16	123.75	21.85	19.39c	7.08	1.20	18.34	15.00	11.61
13.1	11.5	34.62	140.42	23.56	24.40b	6.85	1.61	16.75	14.40	12.25
26.2	11.1	33.24	116.93	20.69	30.95a	6.42	1.80	16.05	12.02	12.09
<b>Cycle</b>										
1	19.8	-	246.52	34.27	25.58a	6.66b	1.49	17.54	16.16	11.93a b
2	7.89	-	80.89	17.45	-	6.71b	1.67	13.32	14.13	12.35a
3	6.29	-	53.68	14.39	24.23b	6.97a	1.46	20.28	13.13	11.68b
<b>P value</b>										
Amendment (A)	<0.001	0.006	<0.001	0.02	<0.001	<0.001	<0.001	0.08	0.69	<0.001
Rate (R)	0.62	0.73	<0.001	0.02	<0.001	<0.001	<0.001	0.08	<0.001	0.01
A x R	<0.001	0.97	<0.001	<0.001	0.13	<0.001	0.03	<0.001	<0.001	0.01
Cycle (C)	0.92	-	0.04	0.51	<0.001	<0.001	<0.001	0.92	0.009	0.02
A x C	0.009	-	<0.001	0.04	0.38	0.77	0.60	0.81	0.26	0.54
C x R	0.07	-	0.37	0.54	0.19	0.11	<0.001	0.57	0.03	0.10
A x R x C	0.10	-	0.79	0.52	0.11	0.35	0.55	0.63	0.74	0.87

†BC, biochar; BCH, 50:50 biochar:humalite by mass (based on C content), BCP, 50:50 biochar:peat by mass (based on C content), HU, humalite, PT, peat; CEC, cation exchange capacity; DMY, dry matter yield; OM, organic matter.

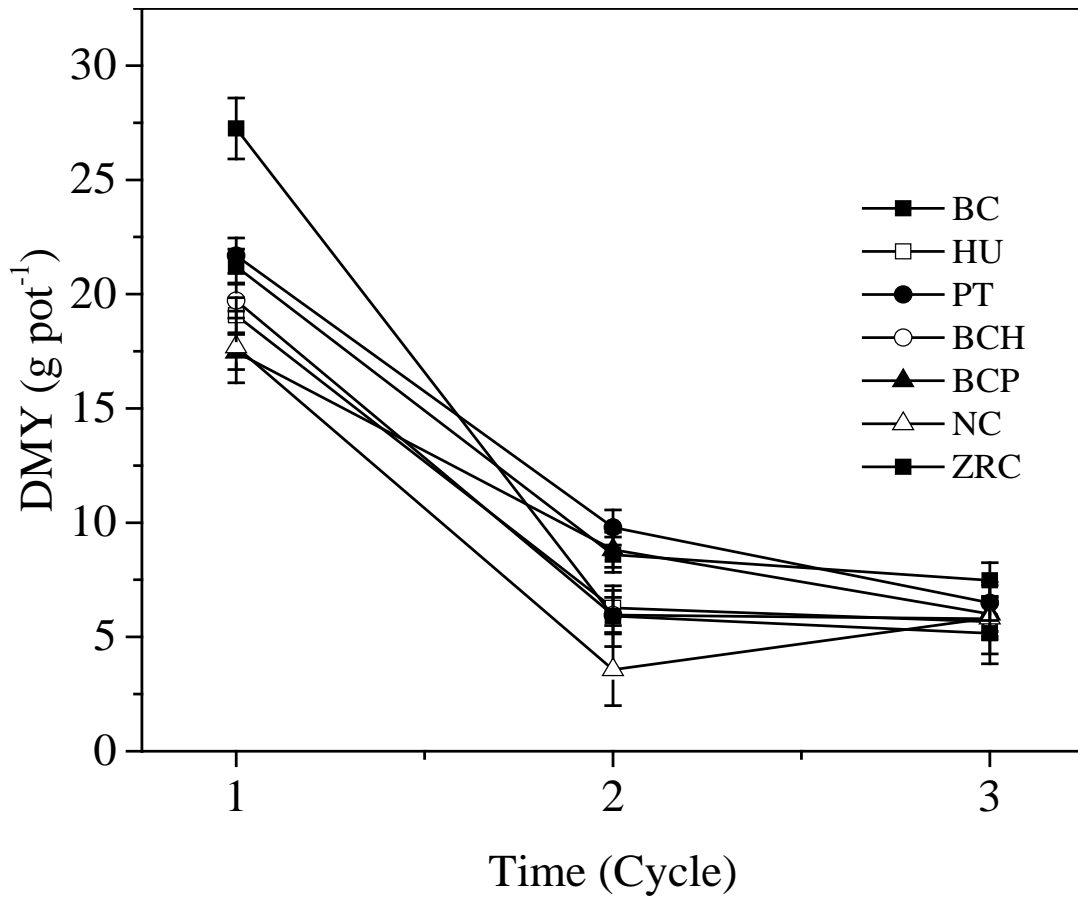


Fig. 3.2. Differences in Barley dry matter yield (DMY) for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC), over time in the two-lift soil (2LS).

### 3.4.2. Cumulative DMY

Amended 1LS soil showed significant differences in cumulative DMY (i.e., summed over C1 through C3). Amended soils produced between 70 and 85% greater cumulative DMY than the NC soils, with PT having the highest absolute values. There were no significant differences when compared to the ZRC or when the ZRC was excluded from the analysis. In the 2LS soil, BC and PT produced 38 and 40% greater DMY than the ZRC, but did not differ from the NC. Peat produced 22% greater DMY than HU, but PT and HU did not differ significantly from the other amendments with respect to DMY.

### 3.4.3. Above ground Plant N Content

**One-Lift Soil.** Plant N content was 51% lower in the NC soil than in the ZRC 1LS soil. All amendment and rate combinations produced 204 to 288% greater Plant N content than the NC soil, with HU and PT having the greatest Plant N content values at all rates. Plant N content from 1LS soil amended with PT was significantly greater than that from soil amended with HU at the 6.55 and 13.1 g C kg<sup>-1</sup> rates (Fig. 3.3). Humalite and PT produced 25 to 28% and 37 to 41% greater Plant N content, respectively, than the ZRC. Among the amendments, Plant N content was 36% greater for HU than BCP at the 13.1 g C kg<sup>-1</sup> rate, while PT gave 27 and 40% greater Plant N content than BC and BCP, respectively.

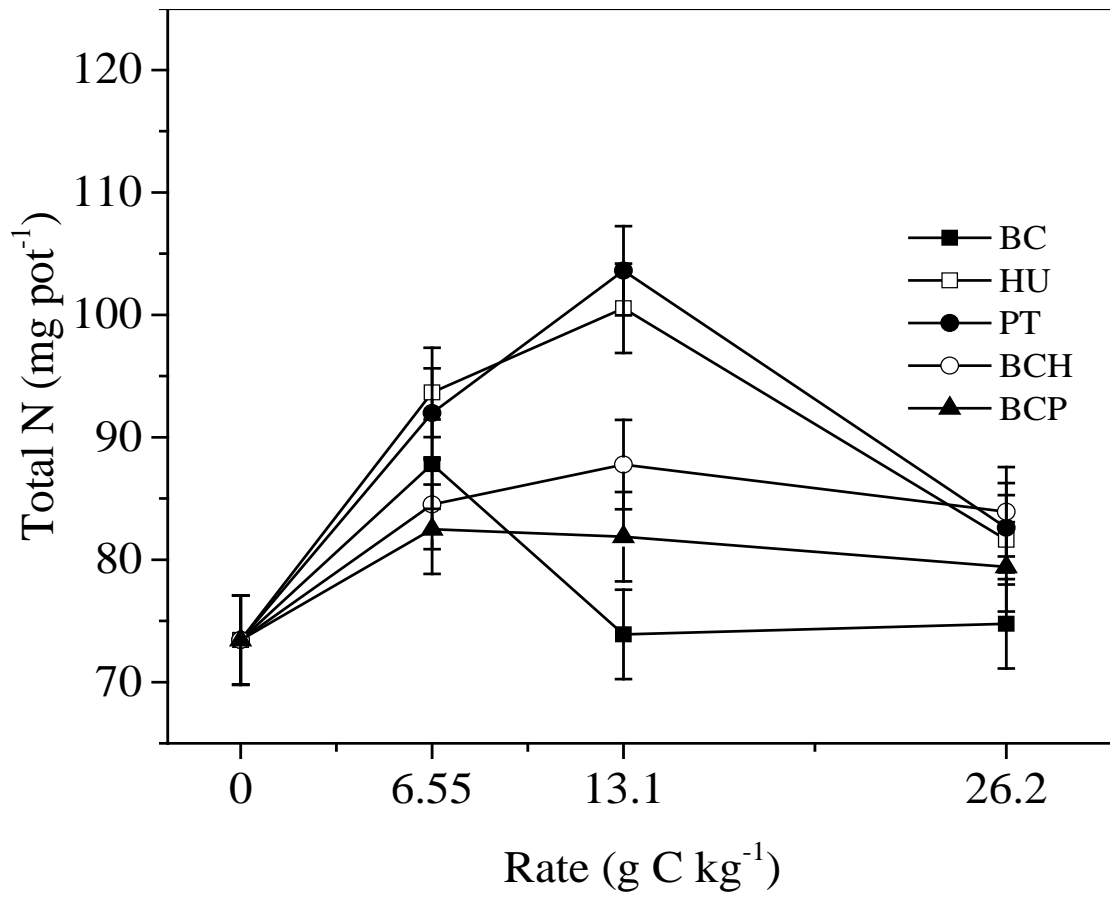


Fig. 3.3. Plant N content in Barley for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC), at varying rates of application in the one-lift soil (1LS).

In C1, amendments produced between 47 and 69% greater Plant N content than the NC, but did not differ significantly from the ZRC (Fig. 3.4). In C2, HU and PT again produced the greatest Plant N content. Differences in Plant N content between amended soils and the NC in this time period ranged from 383 to 525%. When the amendments in C2 were compared to the ZRC, HU and PT gave 38 and 43% greater Plant N content, while the NC had 77% lower Plant N content than the ZRC. In C3, differences versus the NC were lower than in C2, and ranged between 168 and 212%. There were no significant differences when the amendments were compared to the ZRC in C3. In HU- and PT-amended ILS soil, Plant N content decreased by 19 and 20%, respectively, when rates increased from 13.1 to 26.2 g C kg<sup>-1</sup>.

When individual treatments were compared across time, C1 had the highest values, and was between 23 and 40% higher than values in C2, and 96 to 131% higher than values in C3 (Fig. 3.5). Cycle 2 was also significantly different than C3, with values being between 52 to 84% higher. Within rates, Plant N content values again decreased with time. The 6.55 g C kg<sup>-1</sup> rate was between 36 and 115% higher, the 13.1 g C kg<sup>-1</sup> rate was 39 to 114% higher, and the 26.2 g C kg<sup>-1</sup> rate was 44 to 92% higher in Plant N content than the ZRC. Within rates and across time, values in C1 were 28 to 96% higher than in C2 and 104 to 149% higher than C3. C2 values were also 59 to 61% higher in Plant N content than in C3.



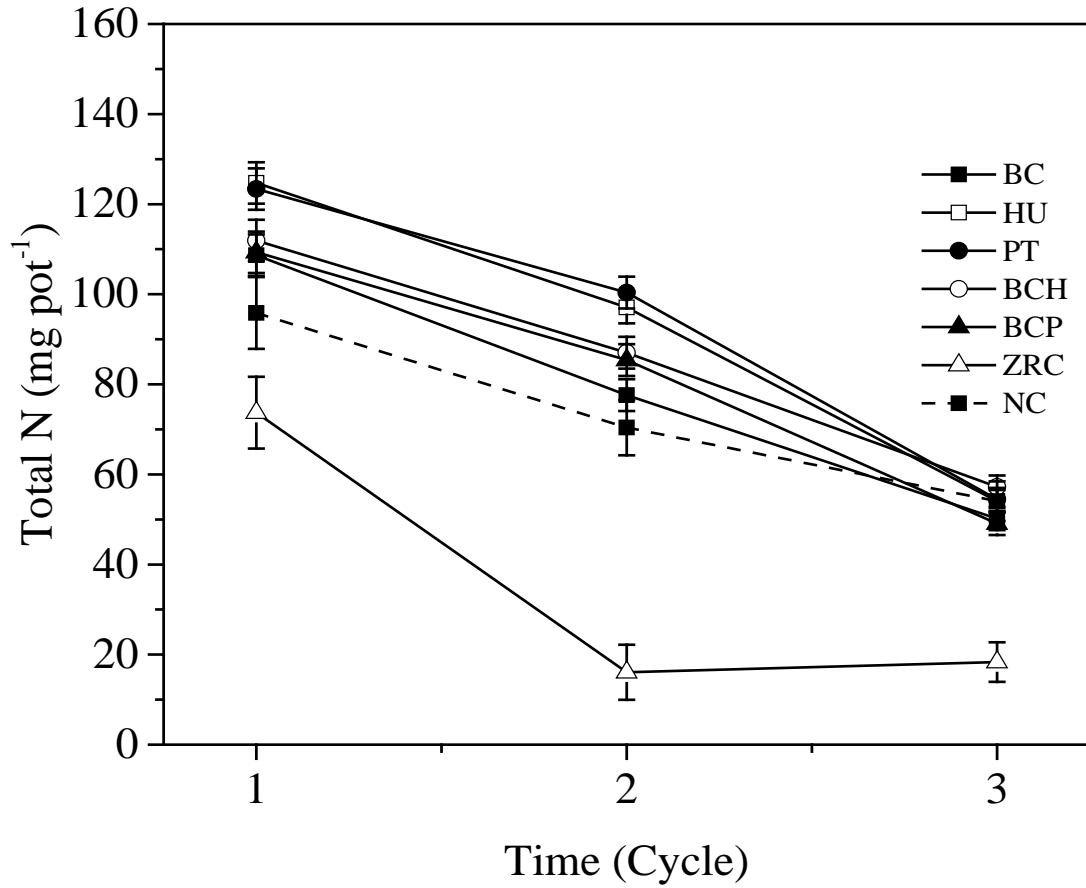


Fig 3.4. Plant N content in Barley for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC), over time in the one-lift soils (1LS).

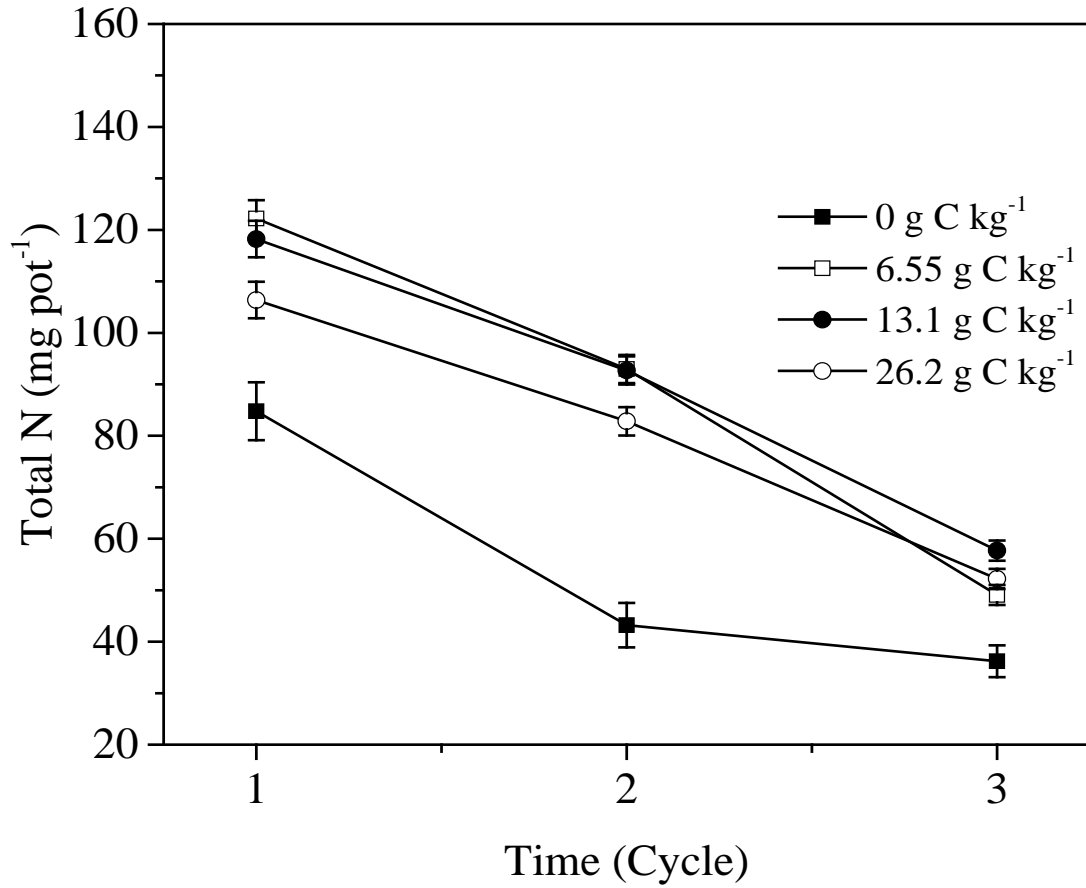


Fig. 3.5. Plant N content in Barley by rate of application over time in one-lift soils (1LS). Rates of 0, 6.55, 13.1, and 26.2 g C kg<sup>-1</sup> represent the Plant N content values averaged across the amendments, which were applied at carbon equivalent rates.

**Two-Lift Soil.** Plant N content was significantly greater for PT and HU at the 13.1 g C kg<sup>-1</sup> rate compared with the controls, with the two amendments producing 47 and 60% greater Plant N content than the ZRC and 60 and 74% greater Plant N content than the NC, respectively (Fig. 3.6). Among the treated soils, only the 13.1 g C kg<sup>-1</sup> HU amended soil showed a significant difference and gave 41% greater Plant N content than BC. There were no significant differences among amendments within each cycle. However, when individual amendments were compared within cycles, significant differences occurred. Plant N content in C1 was 69 to 77% greater than that in C2, and 69 to 81% greater than that in C3 (Fig. 3.7). Cycle 2 and Cycle 3, however, did not differ in any case.

#### 3.4.4. Plant Phosphorus Uptake

**One-Lift Soil.** An amendment x cycle interaction occurred, but this only took place in the factorial + control portion of the analysis (Fig. 3.8). There were no significant differences in Plant P content when the amendments were compared to the ZRC. However, BCP, PT, and BC treatments produced 24 to 29% lower Plant P content than the NC, while the ZRC produced 33% lower Plant P content than the NC in C1. In C2 and C3, all amendments produced 142 to 182% and 109 to 122% greater Plant N content than the NC. In both instances, both PT and HU had the highest uptake of the amendments, with values of 177 and 180% and 118 and 120% higher than the NC, correspondingly, in C2 and C3.

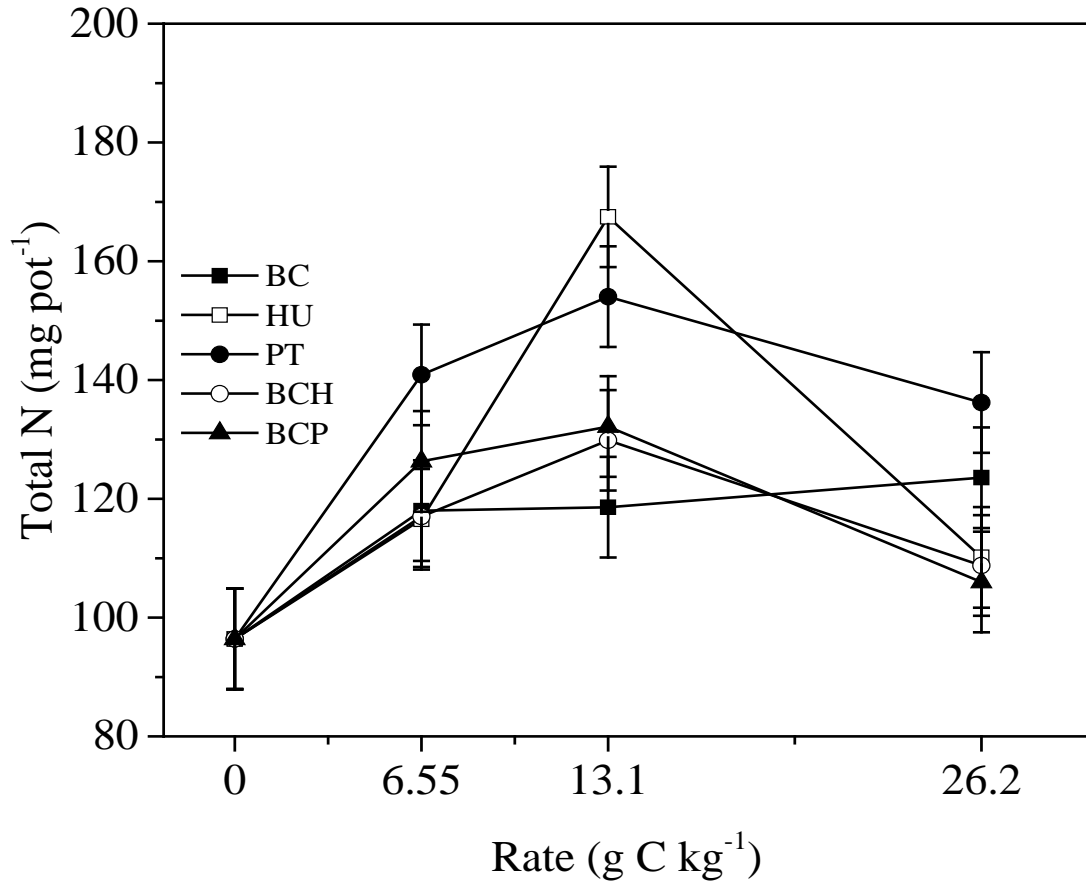


Fig. 3.6. Plant N content in Barley for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) across rates, in the two-lift soil (2LS).

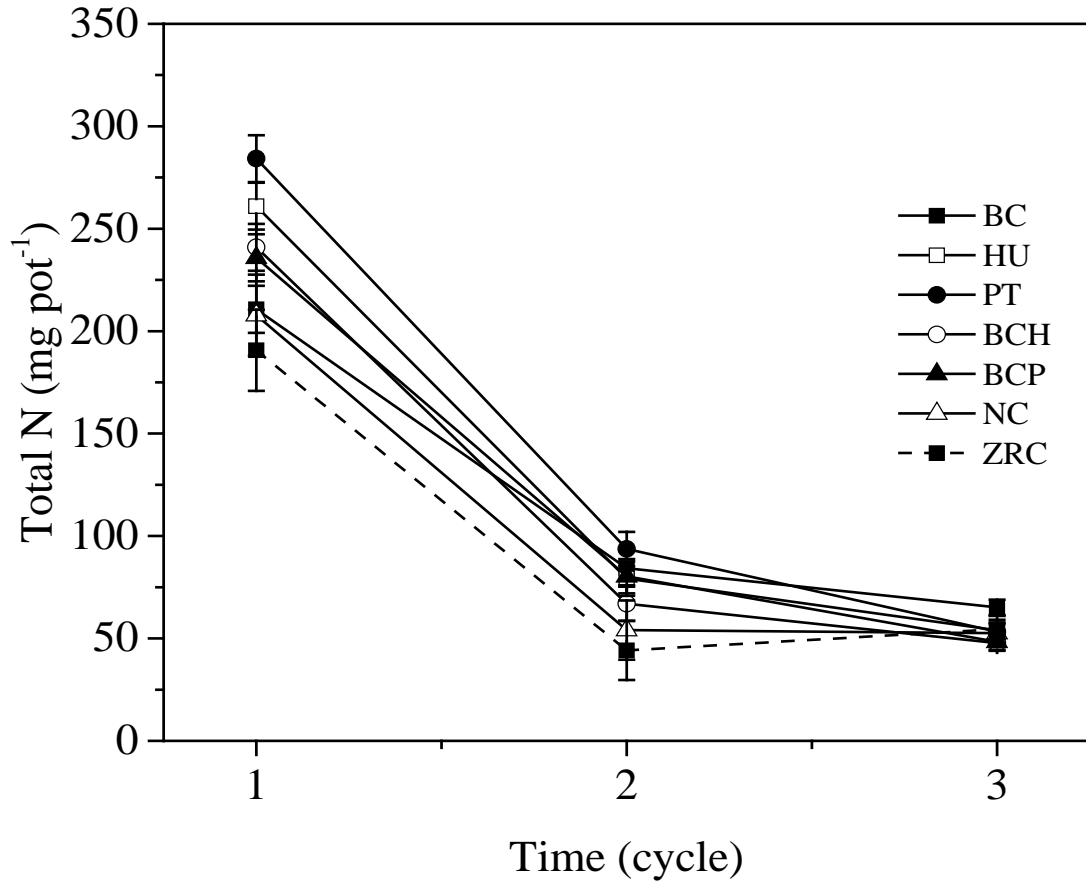


Fig. 3.7. Plant N content in Barley for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) over time in the two-lift soil (2LS).

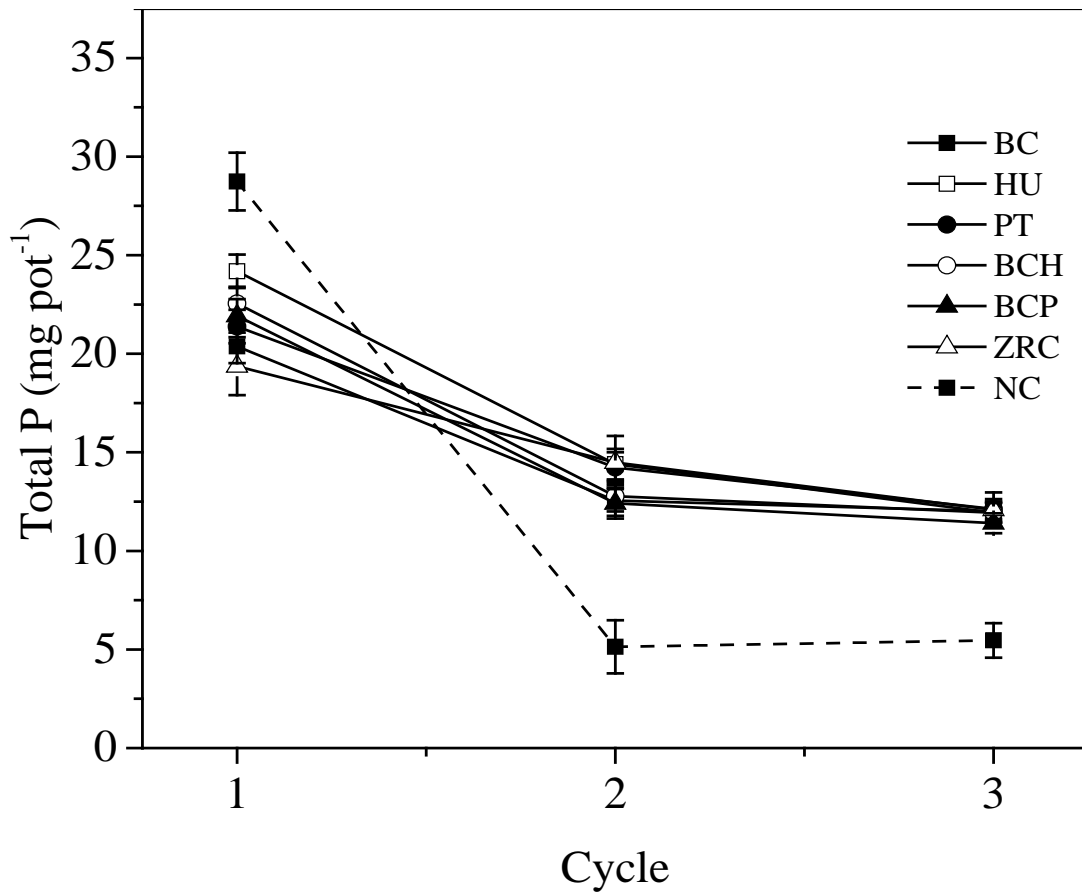


Fig. 3.8. Plant P content by Barley for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) across time in the one-lift soil (1LS).

The cycle × rate interaction was significant for Plant P content in the 1LS (Table 3.4; Fig. 3.9). Phosphorus uptake in Cycle 1 was 50 to 76% greater than that in C2, and 70 to 103% greater than that in C3, with largest differences occurring in the BCH and HU treatments. Across the cycles, only the 6.55 and 13.1 g C kg<sup>-1</sup> rates gave higher Plant P content than the ZRC.

**Two-Lift Soil.** The amendment × cycle interaction was significant for Plant P content in the 2LS soil (Table 3.5; Fig. 3.10). While there were no significant differences in Plant P content among amendments within cycles, Plant P content from individual amendments varied between cycles in a similar fashion to that described for the 1LS soil above. Differences in Plant P content between C1 and C2 ranged between 62 and 174% across the amendments, while the NC and ZRC gave 189 and 333% higher Plant P content respectively, in C1 than in C2. When cycle 1 was compared to C3, amended soils were 96 to 181% higher plant N content, while the NC and ZRC produced 206 and 180% greater Plant P content in C1, respectively, than in C3. In general, the greatest increases in Plant P content occurred in HU and PT amended soils.

#### 3.4.5. Soil Nitrate

**One-Lift Soil.** Nitrate concentrations in amended soils were 92 to 98% lower than NO<sub>3</sub>-N concentration in the NC in C2, whereas differences between amended soils

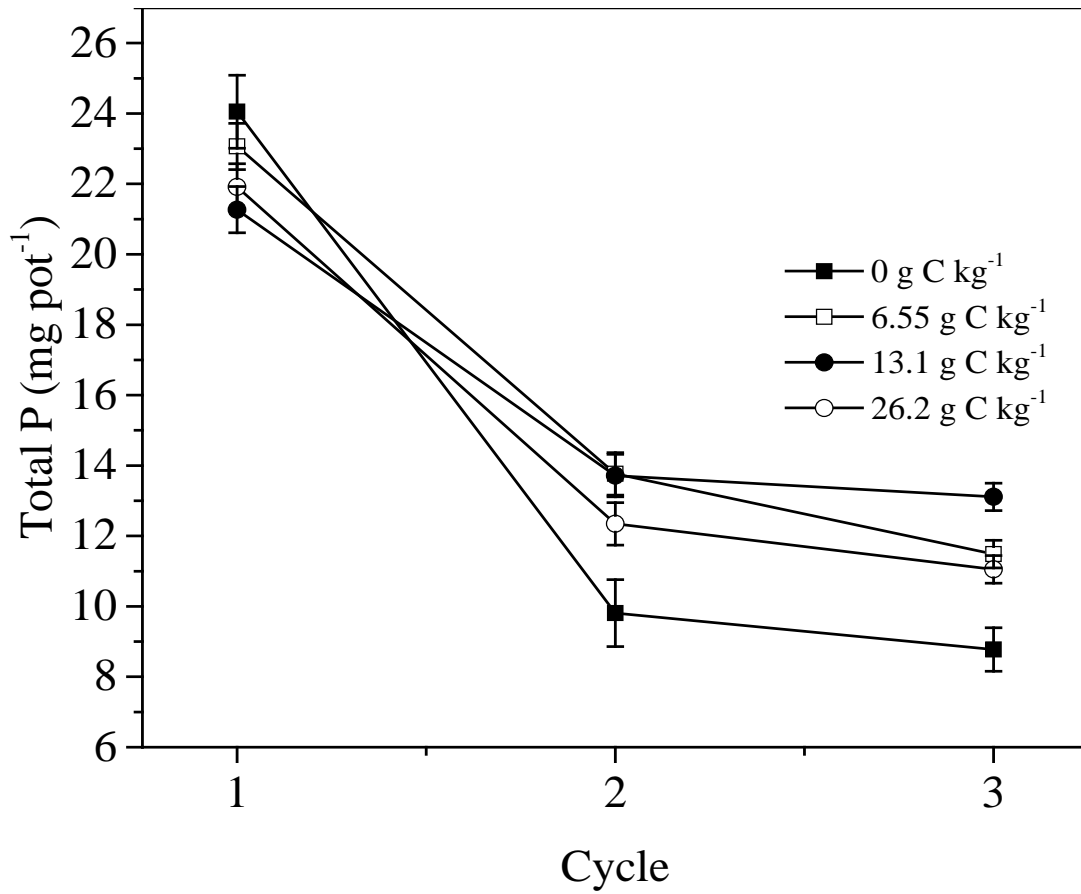


Fig. 3.9. Plant P content in Barley for the 0, 6.55, 13.1, and 26.2 g C kg<sup>-1</sup> rates of amendment application, averaged across all amended soils, and plotted against time in the one-lift soil (1LS).



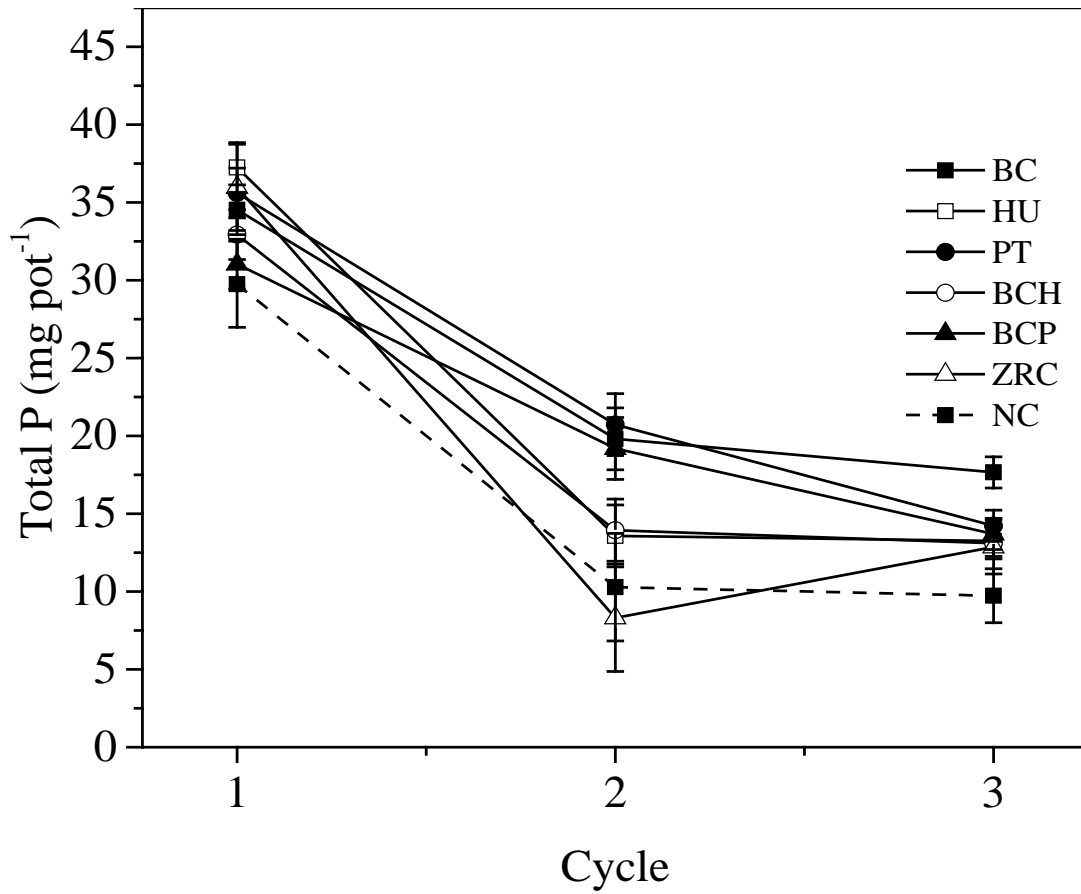


Fig. 3.10. Plant P content in Barley for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments and plotted across time, in the two-lift soil (2LS).

and the NC were not significant in C1 and C3. When the amendments were compared to one another in the 1LS soil, the amendment  $\times$  rate interaction was significant for  $\text{NO}_3\text{-N}$  concentration (Table 3.4; Fig. 3.11). At the  $6.55 \text{ g C kg}^{-1}$  rate,  $\text{NO}_3\text{-N}$  concentration in BC-amended soil was 150 and 221% higher than  $\text{NO}_3\text{-N}$  concentration in PT and HU, respectively. At the  $13.1 \text{ g C kg}^{-1}$  and  $26.2 \text{ g C kg}^{-1}$  rates,  $\text{NO}_3\text{-N}$  concentration in BC-amended soil was 66 to 425% greater than that for the other amendments. The rate  $\times$  cycle interaction was significant for  $\text{NO}_3\text{-N}$  concentration (Table 3.4; Fig.3.12). In Cycle 1, the  $26.2 \text{ g C kg}^{-1}$  rate, averaged across amendments, produced 112% greater  $\text{NO}_3\text{-N}$  concentration than the ZRC, but differences between the ZRC and  $6.55$  and  $13.1 \text{ g C kg}^{-1}$  rates were not significant.

**Two-Lift Soil.** There was a significant amendment  $\times$  rate interaction for  $\text{NO}_3\text{-N}$  concentration in the 2LS soil (Table 3.5; Fig. 3.13). Biochar at all rates produced significantly greater  $\text{NO}_3\text{-N}$  concentrations than the ZRC. Additionally, BCH and BCP amended soils at the  $13.1$  and  $26.2 \text{ g C kg}^{-1}$  were greater than the  $\text{NO}_3\text{-N}$  concentrations of the ZRC. Biochar-amended soil had between 140 and 333% higher  $\text{NO}_3\text{-N}$  concentration than the ZRC across the rates, with the  $26.2 \text{ g C kg}^{-1}$  rate giving the highest concentration, while BCH and BCP produced 140 to 180% greater  $\text{NO}_3\text{-N}$  concentrations than the ZRC. When compared to the NC, all amendments showed between 47 and 93% lower  $\text{NO}_3\text{-N}$  concentrations in the amended 2LS soil. Generally, these differences

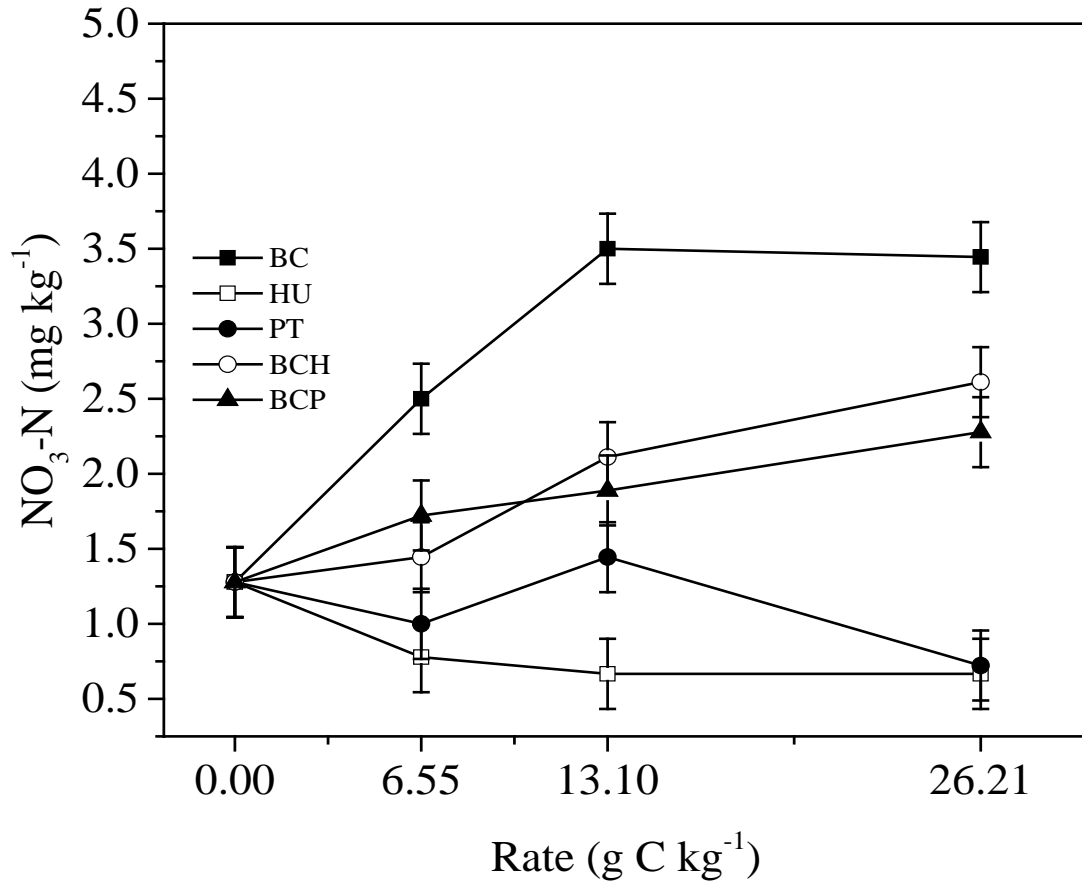


Fig 3.11. Soil nitrate values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) by increasing carbon equivalent rate of application.

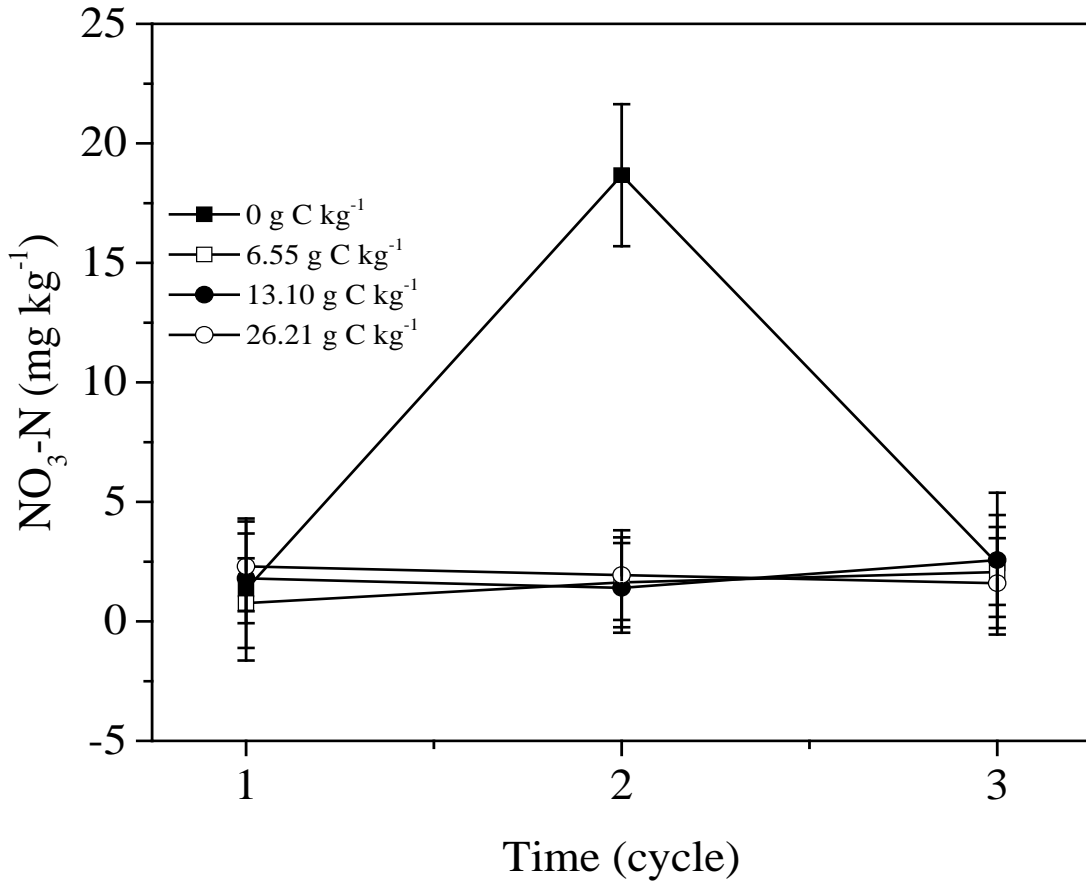


Fig. 3.12. Soil nitrate values at harvest for the 0, 6.55, 13.1, and 26.2 g C kg<sup>-1</sup> rate of application, averaged across all amended soils, and plotted against time in the one-lift soil (1LS).

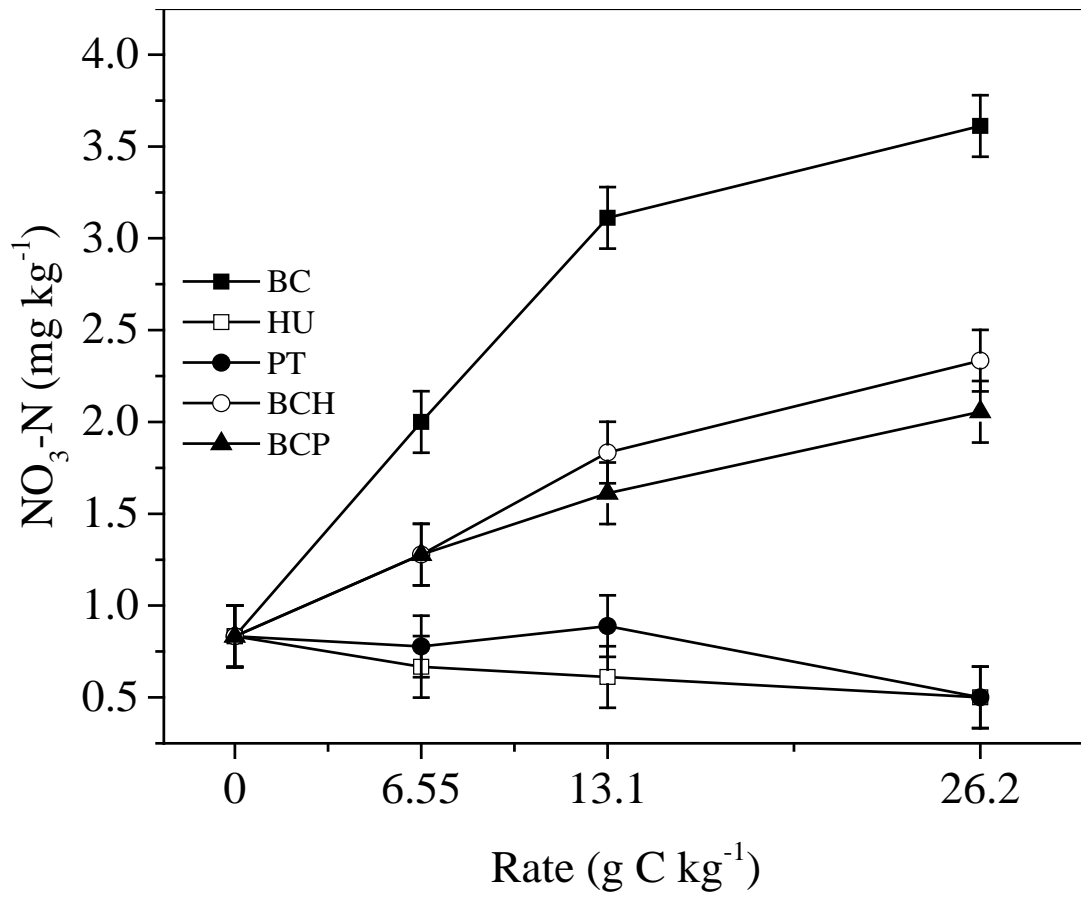


Fig. 3.13. Soil nitrate values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) by increasing carbon equivalent rate in the two-lift soil (2LS).

decreased with rate, except in soil amended with PT and within each cycle BC produced the highest NO<sub>3</sub>-N concentrations, which were 183 to 489% greater than those in the ZRC. When compared to the NC, in C1, NO<sub>3</sub>-N concentration in BC-amended soil was 253% higher, yet in C2 and C3 all amendments produced between 56 and 94% lower NO<sub>3</sub>-N concentration than the NC. Increasing the rate of application of the amendments resulted in an increase in NO<sub>3</sub>-N concentration across the cycles, but the non-amended controls still had higher concentrations.

When amendments were compared in the 2LS soils, the effects were similar to those reported above for the 1LS soil. Biochar produced significantly greater NO<sub>3</sub>-N concentration at all rates than all the other amendments. The largest differences occurred when BC was compared to PT and HU, while the least differences came when compared to BCH. Nitrate N concentrations in soil amended with BCH and BCP were significantly greater than that in soil amended with PT and HU only at the 13.1 and 26.2 g C kg<sup>-1</sup> rates. Increasing the amendment rate from 6.55 to 13.1 g C kg<sup>-1</sup> or 26.2 g C kg<sup>-1</sup> typically resulted in 34 to 90% higher NO<sub>3</sub>-N concentration. Finally, in general, unamended soils tended to have higher soil nitrate values than the amended soils (Fig. 3.14).

#### **3.4.6. Soil Ammonium Nitrogen Concentration**

**One-Lift Soil.** There was a significant amendment × rate × cycle interaction for NH<sub>4</sub>-N concentration in the 1LS soil (Table 3.4; Fig. 3.15). In C1, PT and BCP at the

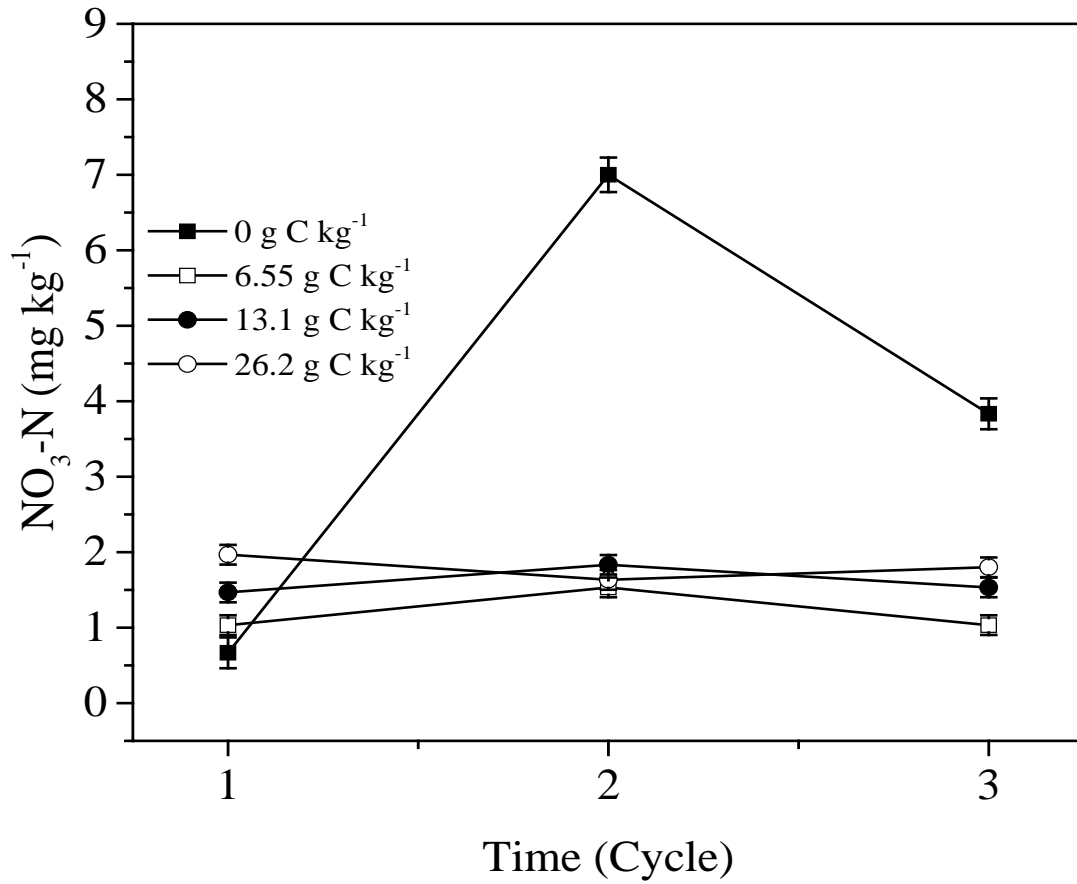


Fig. 3.14. Soil Nitrate values for the 0, 6.55, 13.1, and 26.2 g C kg<sup>-1</sup> rate of application, averaged across all amended soils, and plotted against time for the two-lift soil (2LS).

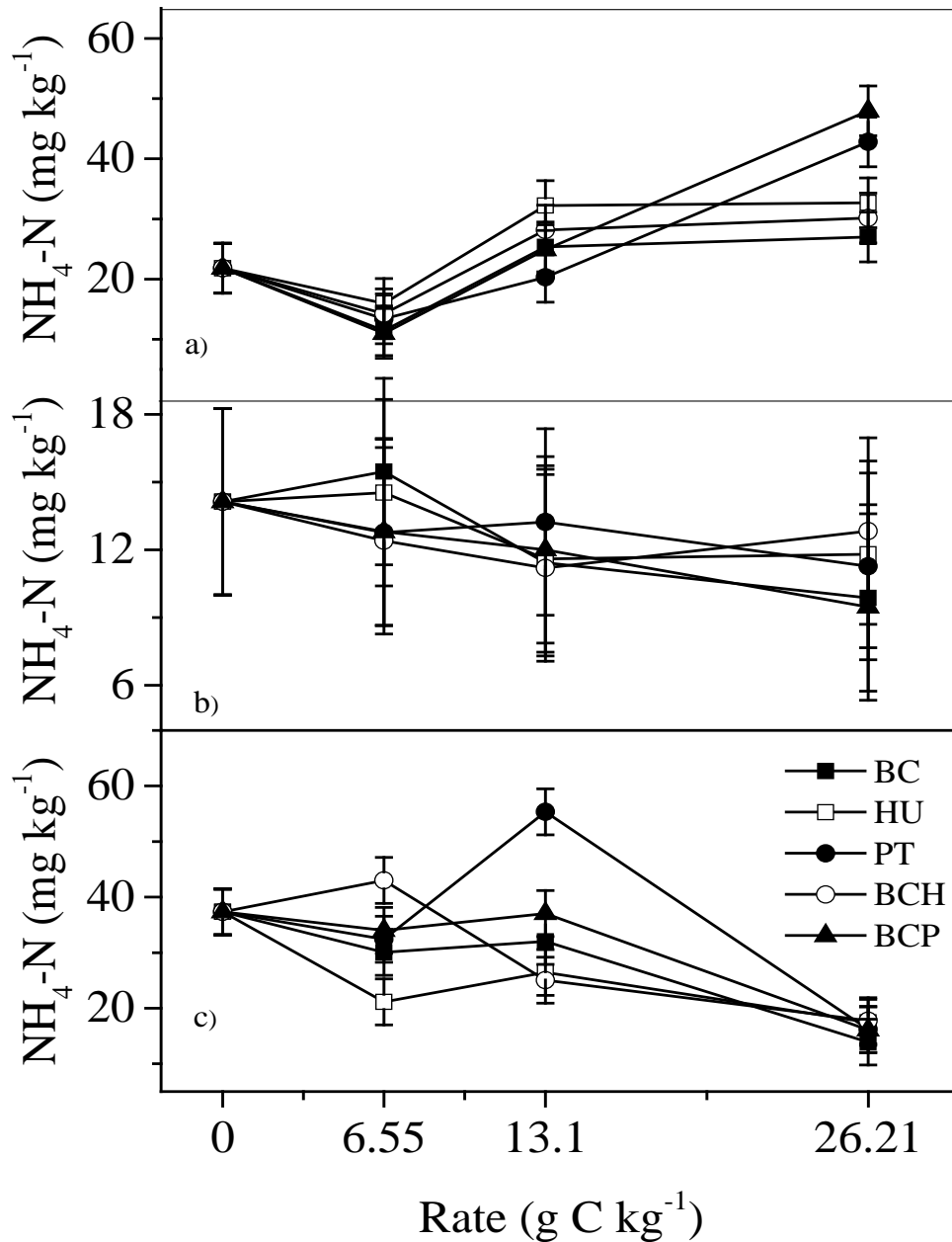


Fig. 3.15. The Amendment x rate x cycle interaction for ammonium values in biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments with increasing rate of application, in each cycle (a: cycle 1; b: cycle 2; c: cycle 3) in the one-lift soil (1LS).



26.2 g C kg<sup>-1</sup> rate produced significantly greater NH<sub>4</sub>-N concentrations than the ZRC, but differences in C2 and C3 were not significant. In C3, PT produced significantly greater NH<sub>4</sub>-N concentrations than BCH and HU at the 13.1 g C kg<sup>-1</sup>, but amendment differences were not significant in C2 and C3 and at the other amendment rates.

**Two-Lift Soil.** Ammonium N concentrations in the 2LS were 33 to 44% greater in the ZRC than in the amended soil. Ammonium N concentrations were also significantly greater in the ZRC than in the NC. Amended soils had significantly greater NH<sub>4</sub>-N concentrations in C3 than in C1 and C2, while NH<sub>4</sub>-N concentration was greater in C1 than in C2.

#### 3.4.7. Soil Olsen P

**One-Lift Soil.** In the 1LS soil, only the main effects of amendment, rate, and cycle were significant for Olsen P (Table 3.4). Among the amendments, only BC (14.2 mg Olsen P kg<sup>-1</sup>) and BCP (13.0 mg kg<sup>-1</sup>) produced significantly different Olsen P concentrations in the soil. Olsen P concentration was significantly lower for the 26.2 g C kg<sup>-1</sup> rate than the 6.55 and the 13.1 g C kg<sup>-1</sup> rates, whereas the difference between the latter two rates was not significant. Olsen P concentration, averaged across amendments and rates, decreased from 13.8 mg C kg<sup>-1</sup> in C1 through 13.1 mg C kg<sup>-1</sup> in C2 to 10.5 mg C kg<sup>-1</sup> in C3, with the differences between C3 and the first 2 cycles being significant. Compared with the ZRC, BCP, BCH, HU, and PT produced 26 to 37% lower Olsen P

concentration. When compared to the NC, the amendments produced 58 to 67% lower Olsen P concentration in the soil.

**Two-Lift Soil.** There was a significant amendment  $\times$  rate interaction for Olsen P concentration in the 2LS soil (Table 3.5; Fig. 3.16). At the 26.2 g C kg<sup>-1</sup> rate, PT, BCP, and HU produced 30 to 35% lower Olsen P concentrations than the ZRC. When compared to the NC, amendment application at the 6.55 g C kg<sup>-1</sup> rate produced 210 to 254% higher Olsen P concentration than the NC. At the 13.1 g C kg<sup>-1</sup> rate, Olsen P concentrations from amended soils were 207 to 232% higher than those in the NC, with BCH having the highest concentration. At the 26.2 g C kg<sup>-1</sup> rate, Olsen P concentrations in amended soils were 141 to 210% higher than those in the NC, with BC having the highest concentration. When the NC and the ZRC were compared, the NC had 73% lower Olsen P concentration.

The rate  $\times$  cycle interaction was significant for Olsen P concentration. In C1, amendment application at the 6.55, 13.1, and 26.2 g C kg<sup>-1</sup> rates produced 65, 66, and 33% higher Olsen P concentrations than the ZRC values. In C2, both the 6.55 and 13.11 g C kg<sup>-1</sup> rates produced 33% higher Olsen P concentration than the ZRC, while the 26.2 g C kg<sup>-1</sup> rate showed no difference. Differences between amended soils and the ZRC were not significant in C3. When only the amended soils were compared, HU at the 26.2 g C kg<sup>-1</sup> rate produced 22% lower Olsen P concentration than BC.

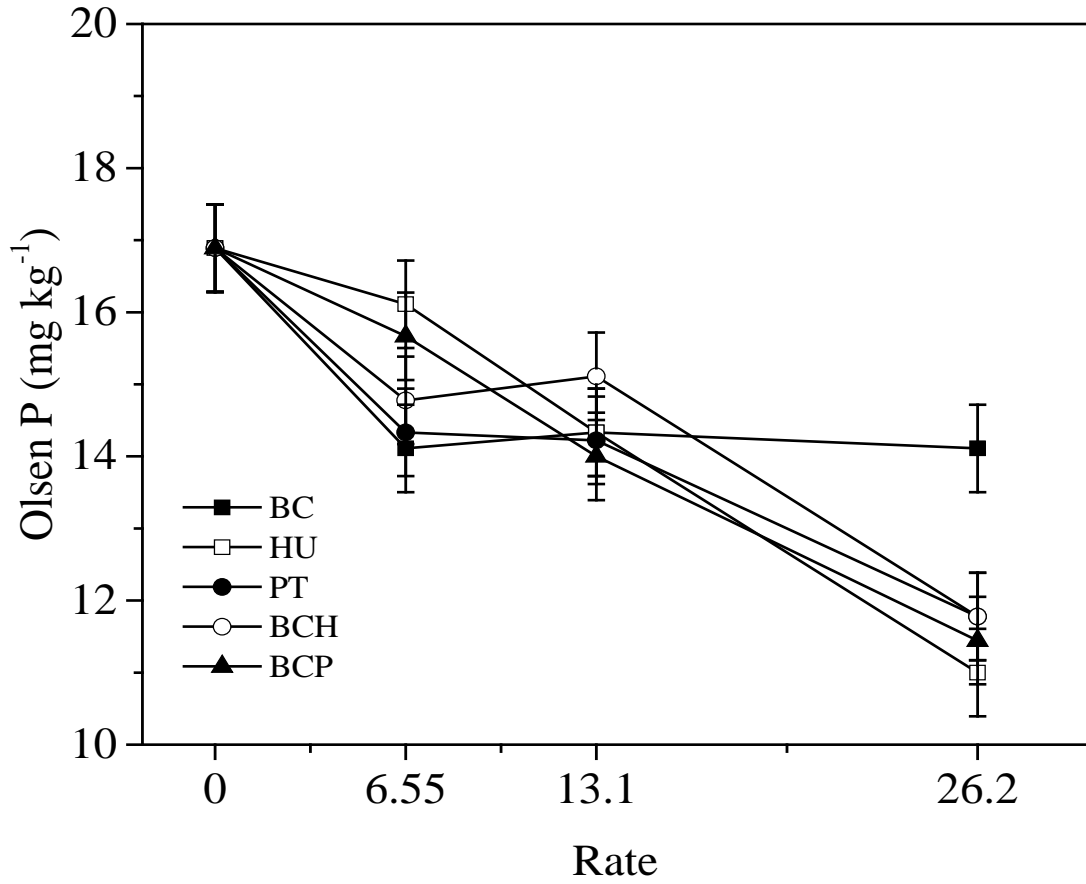


Fig. 3.16. Olsen P values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments, plotted against increasing rate of application in the two-lift soil (2LS).

The rate  $\times$  cycle interaction was significant for Olsen P concentration. Olsen P concentration at the 6.55 g C kg<sup>-1</sup> rate in C3 was 18 and 10% lower than in C2 and C1, respectively, while the concentration at the 13.1 g C kg<sup>-1</sup> rate was 30 and 11% lower. At the 26.2 g C kg<sup>-1</sup> rate, Olsen P concentrations in C2 and C3 were 17 and 29% lower than those in C1.

### 3.4.8. Soil pH

**One-Lift Soil.** In the 1LS soil, there was a significant amendment  $\times$  rate interaction for soil pH (Table 3.4; Fig. 3.17). For all amendments, soil pH decreased with amendment rate, but the decrease in soil pH per unit increase in amendment rate (pH units per g C kg<sup>-1</sup>) increased in the order BC (-0.007) < BCP (-0.04)  $\approx$  BCH (-0.04) < PT (-0.06)  $\approx$  HU (-0.07). When compared to the ZRC, all amendment and rate combinations, except for the BC treatment, produced lower pH values. Only HU and PT at the 26.2 g C kg<sup>-1</sup> rate gave lower pH values than the NC, reflecting their acidifying effects. In the amended 1LS soil, BC consistently produced the highest pH values, while HU and PT had the lowest. Generally, the two blends that included BC, that is, BCH and BCP, showed much smaller differences in pH than their full-strength counterparts. Soil pH also increased significantly in each subsequent crop cycle.

**Two-Lift Soil.** Similar to the 1LS soil, significant amendment  $\times$  rate interaction and cycle main effects were observed for pH in the 2LS soil (Table 3.5; Fig. 3.18). Changes in pH with increasing amendment rate and pairwise comparisons of slopes for

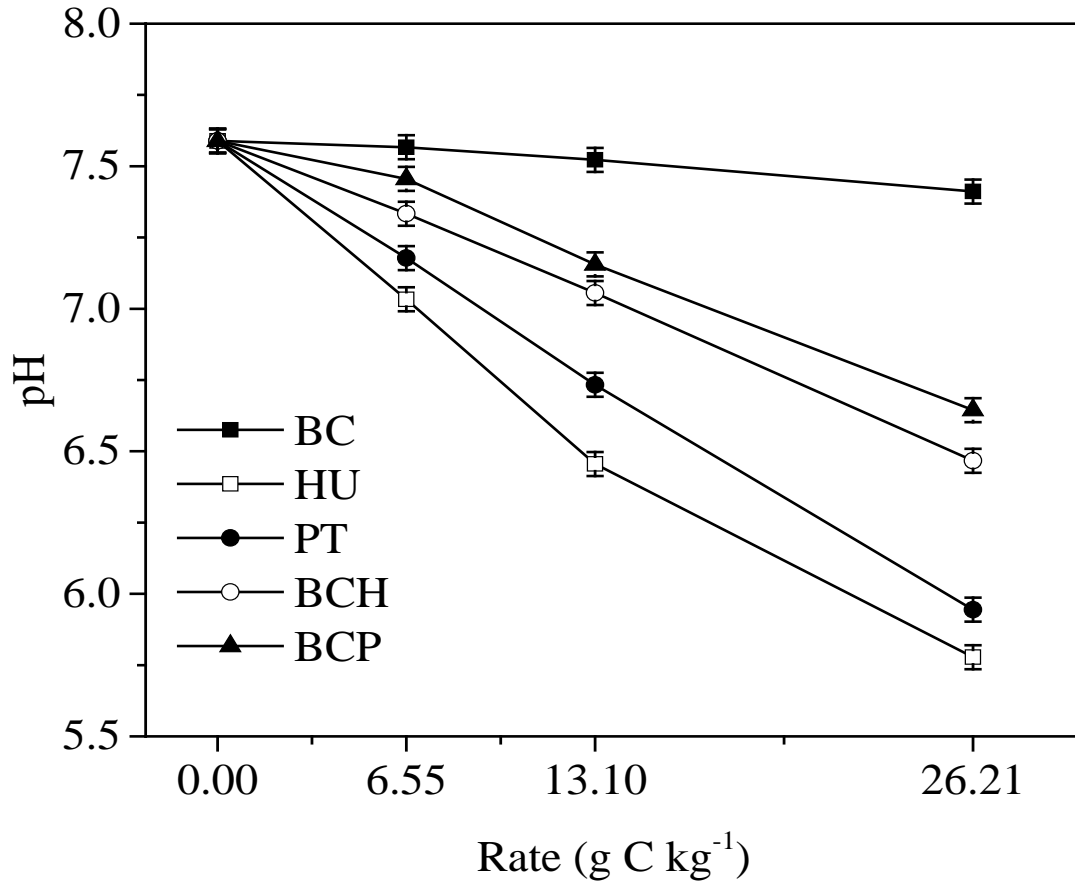


Fig. 3.17. Change in pH values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments plotted against increasing rate of amendment application, in the one-lift soil (1LS).

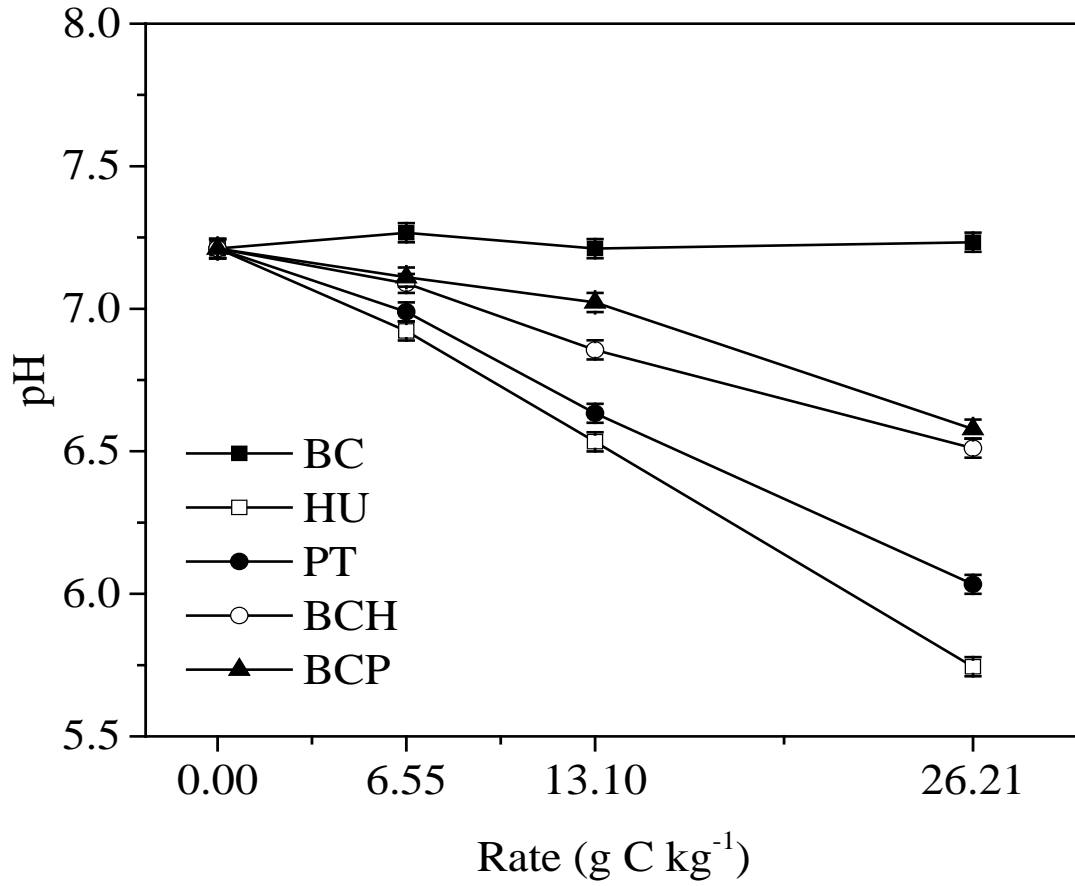


Fig. 3.18. Change in pH values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments plotted against increasing rate of amendment application, in the two-lift soil (2LS).

different amendments yielded the same results as reported for the 1LS soil above. Similarly, comparisons of amended vs. ZRC and NC soils mirrored those for the 1LS soil. Soil pH in the 2LS soil increased significantly in C3 relative to C1 and C2.

#### 3.4.9. Cation Exchange Capacity

**One-Lift Soil.** There was a significant amendment  $\times$  rate  $\times$  cycle interaction for CEC (Table 3.4; Fig. 3.19). Within the factorial + control analysis, no significant differences occurred between the ZRC and the treated soils. In all cases, however, amended soils were between 170 and 264, 179 and 287, and 152 and 226% higher than the NC across cycles. We were unable to determine trends with the aforementioned data, as amendment values changed substantially across rates and cycles. The only significant difference occurred when just the amended treatments were considered, was within the 13.1 g C kg<sup>-1</sup> rate PT treatment, in which values in C1 were 40% higher than those in C2, but not different from those in C3.

**Two-Lift Soil.** In the 2LS soil, there was a significant amendment  $\times$  rate interaction for CEC averaged across cycles (Table 3.5). Soils amended with 13.1 g C kg<sup>-1</sup> HU, 13.1 g C kg<sup>-1</sup> PT, and 26.2 g C kg<sup>-1</sup> HU treatments had 20, 18, and 26% higher CEC than the ZRC. When the treated soils were compared, PT and HU produced 19 to 26% higher CEC than BC and BCP at the 13.1 g C kg<sup>-1</sup> rate, while at the 26.2 g C kg<sup>-1</sup> rate, HU produced 15 to 33% higher CEC than all the other amendments. Cation exchange capacity in C2 was 6% higher than in C3, but did not differ from that in C1. Cation

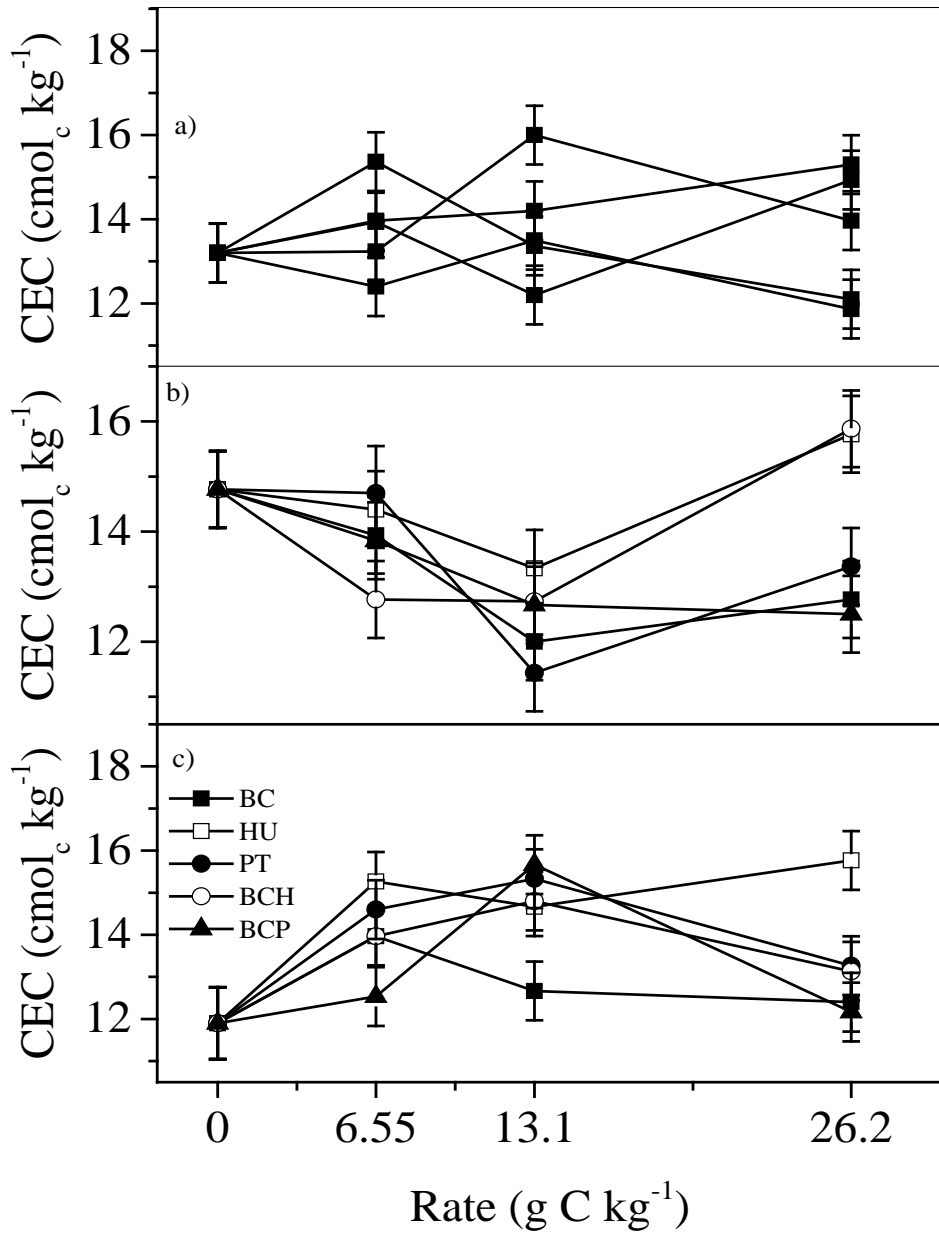


Fig. 3.19. The Amendment x rate x cycle interaction for cation exchange capacity (CEC), between biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments plotted against increasing rate of application, in each cycle (a: cycle 1; b: cycle 2; c: cycle 3) in the one-lift soil



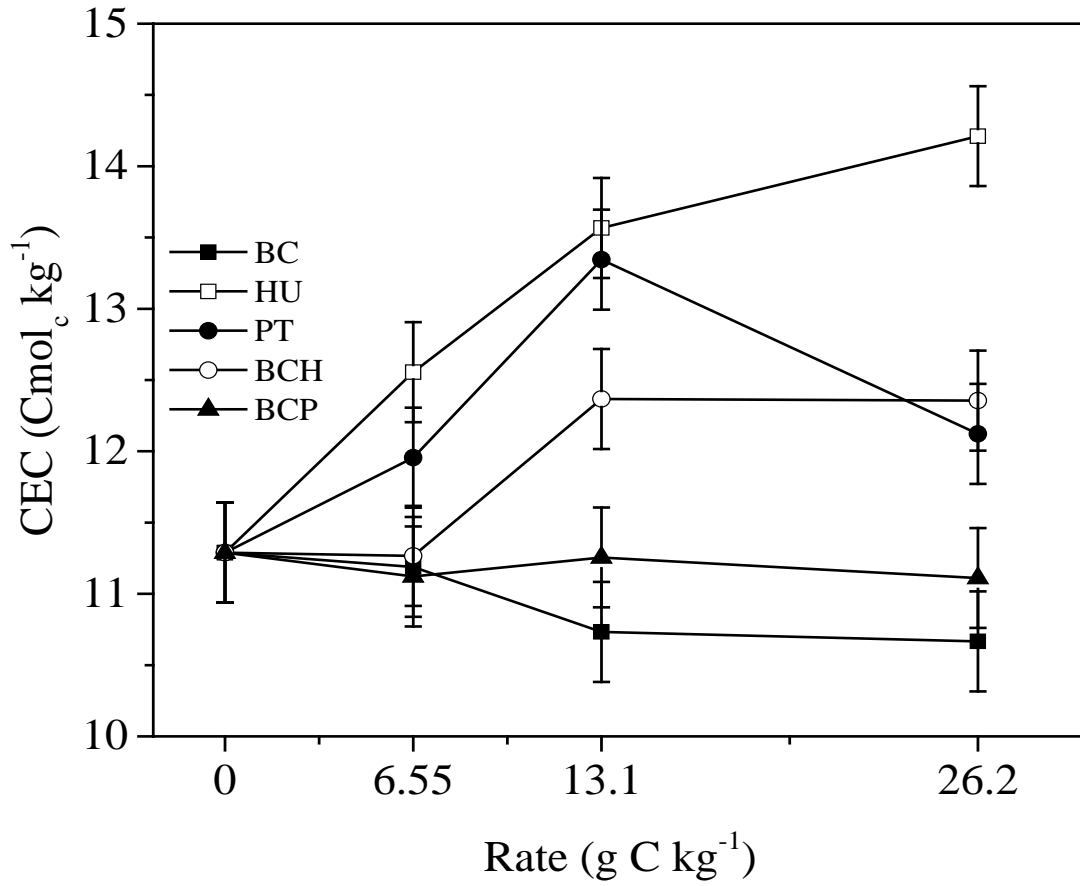


Fig. 3.20. Cation exchange capacity (CEC) values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments, with increasing rate of application in the two-lift soil (2LS).

exchange capacity was greater in the amended and unamended (ZRC) 2LS than in the NC, although the differences decreased with cropping cycle.

### **3.5. DISCUSSION**

#### **3.5.1. Dry Matter Yield**

The overall decrease in DMY with crop cycle, as highlighted in the 1LS soil, was likely due to the decreasing nutrient content of the soil, as nutrients such as N, P, and K are mined from the soils over time. Despite the replenishment of N at the start of C2 and C3, the other major and micronutrients were likely insufficient to sustain healthy Plant growth given the low fertility of the soils to begin with. Additionally, overall physical properties of the soils tended to degrade with cycle, particularly in the 1LS soil. Soils tended to crust easily, likely due to their relatively low organic matter, and highly disrupted structures, which made root penetration difficult.

The PT-treated 2LS soil produced significantly greater DMY than the ZRC. This finding corroborates those reported in the literature. One study reported increases of up to 30% in potato yield with the application of peat at 48 Mg ha<sup>-1</sup> (Li, et al. 2004). Li, et al.(2004) attributed the DMY increases were likely due to increased soil water holding capacity due to the increase in soil organic matter content at the high amendment rates, and an increase in available soil N due to fertilization (Li et al. 2004). The application of

peat in conjunction with mineral fertilizers also increased potato leaf N, Ca, Mg, and P concentrations; tuber dry weight; and tuber specific gravity (Li, et al. 2004). The performance differences we observed between PT and HU were likely due to the hydrophobic properties of HU and the coarse texture of the soils. Additionally, for unknown reasons, plants in HU-amended soils appeared to show symptoms of toxicity, which contributed to the lower DMY. Biochar performed similarly to PT with respect to DMY, and this may be due to its highly porous nature. The lower performance of BCH and BCP relative to BC reflect the lower amounts of BC added in the mixtures. Indeed, it has been shown that biochar increases moisture retention by 10 to 15% when compared to non-amended soils (Laird, et al. 2010).

### **3.5.2. Plant Nitrogen and Phosphorus Content**

#### **Soil Chemical Properties**

**Nitrate and Ammonium Concentrations.** The high NO<sub>3</sub>-N concentrations in both 1LS and 2LS soils amended with BC, when compared to other amendments and the controls, contradict those reported by Jones et al. (2012), who found that NO<sub>3</sub>-N concentration decreased significantly after BC application in a three year field study. The biochar in their study was produced from oak feedstock at a pyrolysis temperature of 450 °C, conditions that are somewhat similar to those under which our BC was produced, yet their results were vastly different (Jones, et al. 2012). Biochar was also found to decrease soil NO<sub>3</sub>-N concentration relative to control soils in two other studies (Dempster, et al.

2012, Nelson, et al. 2011). These decreases in  $\text{NO}_3\text{-N}$  were significant, and BC treatments were 4.2 to 8.8% lower in  $\text{NO}_3\text{-N}$  than unamended soils, and coincided with a decrease in  $\text{NH}_4\text{-N}$  (Nelson, et al. 2011). The decreases were attributed to volatile organic compounds found in biochar acting as a C source which caused N immobilization (Nelson, et al. 2011).

One interesting observation we found was that in almost all situations,  $\text{NO}_3\text{-N}$  concentrations in BC-amended soils were significantly greater than those in HU-amended soils, despite HU having higher initial N concentration. However, the lower  $\text{NO}_3\text{-N}$  concentrations in HU correlate well with the Plant uptake data and was higher in HU and BCH than in the other amendments in the 1LS and 2LS soils. This suggests that there was high N mineralization and nitrification in soil amended with HU, and that the nitrate was being taken up by the barley plants. The elevated  $\text{NO}_3\text{-N}$  concentrations in the BC-amended soils were likely a result of biochar increasing habitat for nitrifying bacteria. In the Jones et al. (2012) study, biochar increased observable basal soil respiration, microbial growth, and fungal growth (Jones, et al. 2012). Though their results did not show increases in soil  $\text{NO}_3\text{-N}$  concentration, this was likely because their study was conducted in a highly productive agricultural soil in contrast to the infertile soils used in our study, which could have potentially masked the benefits of biochar (Jones, et al. 2012). Further, the Jones et al. (2012) study utilized coarse biochar, with 83% of it greater than 2 mm in size. The biochar in the present study, on the other hand, was ball milled prior to the experiment, and larger pieces were removed by hand prior to

application. Additionally, biochar is known to decrease denitrification at moisture contents less than 75% WFPS, which could result in increased  $\text{NO}_3\text{-N}$  levels (Nelson, et al. 2011). Results from a related unpublished study showed that BC produced low cumulative  $\text{N}_2\text{O}$  emissions, which were significantly lower than all other amendments, except for PT, over a 45 d study, which could further explain BC's behaviour in the present study. The combined effect of increasing SWHC moisture retention, and the ability to stabilize nitrate within the soil, makes biochar an appealing amendment in reclamation, as stockpiled soils tend to emit large flushes of  $\text{N}_2\text{O}$  upon placement and aeration (Williamson and Johnson, 1990).

Generally,  $\text{NH}_4\text{-N}$  concentrations decreased with cycle regardless of amendment or rate of application. This could be due to increased nitrification, as we found that  $\text{NO}_3\text{-N}$  concentrations tended to increase with cycle, particularly in the amended 1LS soil. Ammonium levels could have decreased with cycle as  $\text{NO}_3\text{-N}$  concentrations increased, due to increased nitrification and decreased Plant N content by plants.

In most cases, HU and BCH produced significantly greater  $\text{NH}_4\text{-N}$  concentrations than the other amendments. As suggested earlier, this may be due to higher mineralization rates and perhaps relatively lower nitrification rates soils amended with HU and BCH. Purwanto et al. (2005) found that N mineralization decreased with increasing alkyl C/O-alkyl C ratios, which are a measure of (and increase with) the carbon stability and degree of decomposition of various amendments. As Humalite is

essentially solidified, highly humified peat, and biochar is known to lose much of its organic functional groups at high pyrolysis temperatures, it is possible that the ease of decomposition of PT relative to the other amendments in our study was responsible for the elevated  $\text{NH}_4\text{-N}$  levels seen in both the BCP- and PT-treated soils (DeLuca, et al. 2009).

**Olsen Phosphorous Concentration.** The observed decrease in 1LS and 2LS Olsen P concentration with increasing amendment rate likely reflected the corresponding general increase in Plant P content as a result of higher DMY at the higher rates. Olsen P concentration also decreased with cropping cycle for all amendments except BC, reflecting the decreasing Plant P content as DMY diminished along with progressive nutrient depletion. Increasing the rate of amendment application to the soil in most cases caused decreases in soil pH, which may also have resulted in soil P becoming less available within the soil. More plausibly, the high Ca and Mg concentrations of the soils, as well as that of the amendments, may have resulted in a decrease in Olsen P, as Ca and Mg are well known to form low solubility P precipitates (Wadu, et al. 2013). However, HU, which had the highest concentrations of Ca and Mg, resulted in the greatest amount of Plant P content and the second lowest soil P concentrations relative to the ZRC. Nevertheless, organic matter constituents, particularly humic and fluvic acids (of which HU has abundance), are known to increase P availability to plants via competition for Fe/Al oxides, and replaces  $\text{H}_2\text{PO}_4^-$  on anion exchange sites (Guppy, et al. 2005a, Guppy, et al. 2005b). The crop cycle effect observed in the 1LS soil was likely a result of the

lack of replenishment of P throughout the experiment, while the constant levels of P in the BC treatment as rate increased were likely due to the stability of biochar and the relatively low amounts of P in the biochar itself.

**Soil pH.** The differences in pH observed in amended soils reflected the pH values of the respective amendments. Biochar, which had a pH closest to that of the non-amended soil, had the least effect on soil pH. Humalite and PT, on the other hand, had much lower pHs, which reduced the pH of the amended soils. These findings corroborate those from previous studies (Nandakumar, et al. 2004, Sanli, et al. 2012). As expected, the blended amendments, BCH and BCP, had intermediate pHs. The liming effect of BC is well documented in the literature, and is thought to be one of the main reasons why biochar improves soil fertility (DeLuca, et al. 2009, Jones, et al. 2012, Laird, et al. 2010, Stavi, 2012).

**Cation Exchange Capacity.** In the 1LS soil, CEC peaked in C2, and did not differ among any of the amendments in C1 or C3. In contrast, we would expect significant differences to occur in C1, and CEC levels to remain high, or decrease gradually through the duration of the experiment as the effects of amendment on CEC would likely be rapid. In the 2LS soil, differences were clearer and consistent with those reported by Giannouli et al. (2009). In their study, they found that soils amended with lignite (which is similar to humalite) tended to have higher CEC values than peat

amended soils, mainly due to their higher humic acid contents (Giannouli, et al. 2009). This agrees with our findings, as HU produced the highest CECs of all amendments.

### **3.6. CONCLUSIONS**

Results from this experiment indicate that, of the five amendments tested, biochar and peat provide the greatest potential for use in upland soil reclamation, as they produced the greatest biomass yields. Overall biomass accumulation is the most important objective of reclamation as it mitigates erosion in reclaimed areas and occupies niche space, preventing weed encroachment. The ability of biochar to increase biomass yield and its ability to provide habitat for soil nitrifying bacteria make it a useful amendment. Humalite application to the subject soils resulted in toxicity symptoms and low overall biomass, making HU the least beneficial amendment to use for reclamation of these soils. In addition, HU would also be costly to transport to target AOSR sites in the quantities needed to effect reclamation, while its high sodium content may cause reclamation challenges at high amendment rates. Peat may be a useful amendment when trying to recreate acidic, sandy Jackpine ecosystems common throughout the AOSR, while biochar may be beneficial in creating neutral to basic, finer-textured, mixed-wood ecosystems. Additionally, if only one amendment were to be utilized for an entire site, biochar may prove to be the most beneficial. With the expected increase in humic acids following Plant establishment, as well as any acidifying or leaching effect from rainfall,



biochar may be the better option, as it may increase the buffering capacity of the soil, thus preventing or delaying any soil quality issues associated with acidic soils. Biochar's ability to maintain high soil nitrate concentrations, likely through providing habitat for soil microorganisms and nitrifying bacteria, make it highly promising as this may help kick-start initial re-vegetation of reclaimed sites. Also, the ability of biochar (and peat) to improve SWHC, as demonstrated in other studies, should not be understated, as soil moisture is a key factor in Plant establishment. Though the reclamation of the AOSR still poses large concerns to the public, the environment, and reclamation planners, the use of organic amendments, particularly on upland ecosites, may substantially alleviate some of these concerns, and aid in the restoration of these disturbed ecosystems.

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## **4. ORGANIC AMENDMENT EFFECTS ON THE AVAILABILITY OF NITROGEN AND PHOSPHORUS IN LONG-TERM STOCKPILED SOILS FROM THE ALBERTA OIL SANDS REGION**

### **4.1. ABSTRACT**

During oil sands mining in the Alberta Oil Sands Region (AOSR) of Canada, soils are salvaged using the approved two-lift salvage (2LS) method in which the 0 to 20 cm layer is salvaged as topsoil, while the 20 to 100 cm layer is salvaged as subsoil. The main challenge in successful reclamation is the degradation of soil quality during long-term stockpiling. The amendment of stockpiled soils during reclamation may potentially restore them to their pre-disturbance quality and productivity. This laboratory bioassay examined the effects of biochar (BC), peat (PT), humalite (HU), and 1:1 (by mass) mixtures of biochar and peat (BCP) and biochar and humalite (BCH) on nitrogen (N) mineralization and phosphorus (P) availability in a 2LS soil and a laboratory-prepared one-lift salvaged (1LS) soil (top and sub-soils mixed to mimic entire soil profile is salvaging in 1LS operations). Amendments were applied to 100 g of each soil at rates corresponding to 26.2 g C kg<sup>-1</sup>. The soils were then watered to 70% water filled pore space (WFPS). The microcosms were incubated at 25°C and watered periodically. Samples were taken on days 0, 7, 14, 30, 60, 90, and 120 for determination of available N



and P. All amendments, except BC, resulted in a net decrease in available P concentration in the 1LS soil. In the 2LS BC treated soils showed increased P levels when compared to the NC. In general, BC tended to have higher Olsen P values over the duration of the experiment than other amended soils, but these values were not significantly higher than the unamended controls. With regards to nitrate and ammonium, however, PT produced the highest values and showed benefit over the ZRC and NC soils, while BC tended to perform poorly, likely due to its high carbon stability.

## 4.2. INTRODUCTION

Oil sands mining operations in Canada's Alberta Oil Sands Region (AOSR) are of great environmental concern. Currently, oil sands developers strive to manage natural resources on their sites in such a way that the restoration of their disturbed areas will result in the homogenization of their leases back into the surrounding landscape. In order to accomplish this, soil quality must be maintained as it is a key driver for plant community establishment and ecosystem composition. As a result of the large amount of disturbance at the beginning of a project's lifecycle, the vast majority of salvaged soils are placed into stockpiles, rather than being used immediately in reclamation, as is often the case in strip coal mines (i.e., progressive reclamation). These stockpiles are often stored on site for 20 to 30 years, or until production has been completed. The stockpiles can be tens of thousands to millions of cubic metres in size (ESRD, 2014). The volume of stockpiled soils in the AOSR is estimated at  $>144 \times 10^6 \text{ m}^3$  (ESRD 2014). One of the

main challenges with reclamation, however, is that stockpiled soils degrade in quality with time, due to a lack of inputs, vast changes in porosity (i.e. destruction of soil structure), and the change in aeration status (particularly as topsoil is entombed), as soils that were once spread out over many hectares are heaped together in a pile (Abdul-Kareem and McRae, 1984, Harris, et al. 1989).

Length of storage greatly dictates final stockpiled soil quality and is known to decrease important soil quality parameters such as organic matter content, available N and P, pH, and cation exchange capacity (CEC) (Abdul-Kareem and McRae, 1984, Harris, et al. 1989, Kundu and Ghose, 1997). Even in cases of relatively short-term storage, on the order of one to three years, large decreases in soil quality have been reported. Kundu et al. (1997) found that soil organic C, available N, available P, and potassium (K) concentrations decreased by 47, 31, 23, and 28%, respectively. After six to ten years of storage, 89 to 96% of these nutrients had been lost from stockpiled tropical soils (Kundu and Ghose, 1997). These losses are due mainly to changes in microbial community composition. Soils that were once aerated are now entombed in an anoxic environment, resulting in a change from a community dominated by aerobic microbes to anaerobic microbes, which causes changes in soil microbial processes (Ghose, 2004, Harris, et al. 1989, Williamson and Johnson, 1990). For instance, nitrification dominant systems are changed to denitrification and mineralization dominant systems after stockpiling (Ghose, 2004, Harris, et al. 1989, Williamson and Johnson, 1990). These soils are further depleted in organic C and inorganic N when they are exposed again to oxygen, while the ammonium reserves that will have accumulated in the stockpiled soils

are transformed back into nitrate due to an abundance of substrates available for the microbial population (Williamson and Johnson, 1990).

The method used to salvage the soil also likely influences post-storage soil quality. Under Alberta regulations, the top 20 cm of O and A horizons are salvaged together utilizing bulldozers, excavators, and haul trucks. The underlying 80-cm thick layer, consisting of the B and C horizons, is salvaged separately from the top 20 cm layer. This two-operation salvaging process is called ‘two-lifting’ (CEMA, 2012). The process is time consuming and complex. Most salvaging occurs during winter, and to remove the soil, bulldozers must use their shanks to break up a salvageable horizon. This “cross ripping” is done in two perpendicular passes. Cross ripping essentially triples the work required to salvage soils, as the equipment must make three passes - two for ripping and a third to push the soil into a windrow - and is often needed for both topsoil and subsoil. Additionally, reclamation practitioners often end up with soil that is depleted in quality.

One-lifting, in which all horizons up to the 100-cm depth are salvaged in one operation, may alleviate some of the concerns associated with two-lift salvaging. Considering that the currently approved two-lift salvage method results in poor quality of long-term stockpiled soils, the one-lift method may result in similar quality reclamation material at significantly decreased fuel, labour, and environmental costs. However, admixing is the main concern of the one-lift method, as topsoil and subsoil are blended together during the salvage process, thus diluting organic matter and decreasing initial soil quality. Yet, over time, the quality of soil salvaged using the two methods may be

similar. It is likely that extended storage time may mask the poorer soil quality of the one-lift soil, and that the two-lift soil may degrade until it reaches a similar quality to the one-lift soil. Organic amendments may help restore the pre-disturbance quality of long-term stockpiled soils. A common example is peat (PT), which is widely used in reclamation projects in the AOSR, and is thought to act as a slow-release source of N (Hemstock, et al. 2010). Peat is often blended with underlying mineral soil to recreate entire soil profiles (Rowland, et al. 2009). Peat ecosystems account for up to 64% of the landmass in the AOSR, which explains its widespread use as an amendment (Rooney, et al. 2012). Peat also has complex effects on soil N concentration and the microbial ecosystem, and has been shown to slowly mineralize due to its relatively high stability (Pietola and Tanni, 2003, Purwanto, et al. 2005). Another study showed that peat had a negative impact on microbial populations and their C and N contents, suggesting that its relatively high C content may cause N immobilization (Pietola and Tanni, 2003). This may present a challenge in reclamation, as currently reclaimed soils generally tend to be low in nutrients and are highly susceptible to further nutrient loss via leaching (Hemstock, et al. 2010, Williamson and Johnson, 1990). However, one study showed that in 10, 30, and 50% v/v mixes of peat:mineral soil, SOC increased from 30 g kg<sup>-1</sup> to 35 g kg<sup>-1</sup>, with increasing amounts of peat application (Ojekanmi and Chang, 2014). Soil organic C has been closely tied to total N and P values as well as many other soil quality indicators, indicating that any immobilization from peat may be relatively temporary (Ojekanmi and Chang, 2014).

Numerous recent studies have demonstrated the effectiveness of biochar as an organic amendment for agricultural soils. Feedstock sources and pyrolysis temperatures appear to be key features that determine the effectiveness of biochar. Zhang et al. (2012) reported SOC increases of 9.3 to 56% following application of biochar in rice paddies. In another study, biochar increased total N concentration by 10% and SOC concentration by 33% compared with the unamended soil (Huang, et al. 2013). Yet another study showed that biochar increased microbial respiration two years after amendment, and that biological potential increased after three years and resulted in increased microbial and fungal growth when compared to the unamended soils (Jones, et al. 2012). Biochar itself is not considered an N source since most of the N in the feedstock is lost via volatilization at typical pyrolysis temperatures ( $>200^{\circ}\text{C}$ ) (DeLuca, et al. 2009). However, high temperature biochars may provide more extractable nitrate N, likely due to the higher temperatures liberating the nitrate from the feedstock, and making it available in the ash component of the biochar (DeLuca, et al. 2009). Further, biochar is thought to adsorb nitrification inhibiting compounds from the soil, thus increasing nitrification rates (DeLuca, et al. 2009).

Humalite, which is a sub-bituminous coal that developed on non-marine bedrock, similar to lignite and leonardite, is another amendment that could restore the quality of long-term stockpiled soils. Humalite derivatives have recently been sold to agricultural producers as an organic amendment. These derivatives are often humic and fluvic acids, which are typically applied as a foliar spray, or in liquid form, and in some cases have been shown to improve soil quality and yields (Turgay, et al. 2011, Verlinden, et al.

2009). Studies have shown that humic substances increase soil P content by fixing humophospho complexes, which are Plant available (Pietola and Tanni, 2003, Raina and Goswami, 1988). Nandakumar et al. (2004) found that soils treated with a combination of humic acids and chemical fertilizers had 5 to 11% higher N, P, and K concentrations than untreated soils (Nandakumar, et al. 2004). Though humalite would require transportation to the AOSR if it were to be used as an amendment in reclamation projects, its potential benefits may offset shipping costs. Sharif et al. (2002) found that lignite was mineralized as a C source in lignite-containing mine soils, and accounted for 24, 63, and 61% of the CO<sub>2</sub> evolved from a 37 year-old mine soil, a 14 year-old mine soil, and a lignite rich parent material, respectively (Sharif, et al. 2002).

While these amendments have been tested mostly on relatively fertile agricultural soils, their effectiveness in degraded, long-term stockpiled, alkaline temperate soils is currently not well understood. The overall objective of this study was to determine the effects of biochar, peat, humalite, and 1:1 mixtures (by mass) of biochar and peat (BCP) and biochar and humalite (BCH) on the availability of N and P in long-term stockpiled soils from the AOSR. Specific objectives were to (1) determine the effects of amendment rate on N and P availability and (2) compare amendment and rate effects on the availability of these nutrients in a two-lift vs. a one-lift salvaged soil.

### **4.3. MATERIALS AND METHODS**

#### **4.3.1. Soil Description**

The soil was collected from 24-year old and an 8-year old stockpile on Imperial Oil Limited's Cold Lake, AB, Canada Operations (54° 36' N, 110° 28' E). Soils in the area consisted of a mix of Boralfs (Orthic Gray Luvisols), Cryochrepts (Eluviated Eutric Bruisols), Eutrochrepts (Orthic Melanic Brunisols), Hemists (Terric Mesisols) and Entisols (Orthic Regosols). Prior to sampling, multiple stockpiles were visually inspected to determine their overall quality, with regards to organic matter content. The stockpiles with the highest organic matter content were then selected, as they were expected to provide the highest rates of nitrous oxide flux, and thus illustrate a 'worst case scenario' for the AOSR. As a result of the stockpile survey, two sampling locations, 5 km apart, were chosen. The stockpiles at each location consisted of soils salvaged from corresponding well pads that were 1 ha in size. The soils consisted of Boralfs for the two-lift soil (2LS) soil and its natural controls (NC) and Cryochrepts for the one-lift (1LS) soil and its NC. In both cases, the natural controls were located on mixed-wood ecosites that consisted of White Spruce and Birch as dominant vegetative species. Samples were taken from the 2- to 3-m in depth at one 2LS and two 1LS stockpiles at their respective sites. The 2LS stockpile consisted entirely of topsoil, while soils for the 1LS were taken from separate topsoil and subsoil piles at the 1LS sampling location. In each instance, stockpiles were approximately 25 m wide × 100 m long × 4 m high. Samples were collected from the stockpiles using a small excavator (Hitachi ZAXIS33U, Japan).

Collected soils were then placed into 20-L plastic pails, and sealed with lids prior to transportation. The soil was then screened through an 11-mm sieve, composited, and stored in pails for approximately 30 d at 20 °C, until the experiment commenced.

Using soils from the 8-year old stockpiles, a 20:80 topsoil:subsoil blend was prepared to mimic a one-lift salvaged (1LS) soil. The blend was placed into 125-L Rubbermaid tubs, which were kept in a walk-in incubator maintained at 25°C for two weeks. Approximately 6 L of reverse osmosis water were added to the bulk 1LS soil (approximately 50 kg) during incubation to simulate stockpile conditions in the AOSR. During the addition of moisture, soils were stirred to ensure uniform moisture distribution. Prior to the start of the experiment, both soils were roller-milled (<1.8 mm) to break up any remaining soil clods.

#### **4.3.2. Amendments and Rates**

Biochar was obtained from Alterna Biocarbon (Prince George, BC). The biochar feedstock was wastewood from logging operations, and consisted of Douglas Fir (*Pseudotsuga menziesii*), White Spruce (*Picea glauca*) and other coniferous species. The biochar was pyrolyzed at a temperature of approximately 380°C, immediately cooled with a water spray following carbonization, and roller-milled by the manufacturer prior to shipping. Humalite was provided by Black Earth Humic LP (Calgary, AB), while the fibric peat tested in this experiment was Sunshine<sup>®</sup> horticultural peat from Sun Gro Horticulture (Vancouver, BC). Amendments were passed through a 2-mm sieve prior to addition to the soil to improve homogeneity of mixing with the soil.



The amendment treatments tested were biochar (BC), humalite (HU), peat (PT) and 1:1 (by weight) mixtures of biochar and humalite (BCH) and biochar and peat (BCP). All amendments were applied to the soil at a rate corresponding to 26.2 g C kg<sup>-1</sup>. Unamended soils (controls) were included for comparison along with a natural control (NC), which was soil collected from an adjacent undisturbed site.

#### **4.3.3. Experimental Setup**

The experiment was set up as a completely randomized design with a one-way treatment (amendment) structure and three replicates. Sampling time (Days 0, 7, 14, 30, 60, 90 and 120) was a repeated factor. Amendments at the above rate were thoroughly mixed with 100 g (oven dry wt.) soil in a 1-L mason jar and then transferred into 120 ml specimen cups (Lake Charles Manufacturing, Lake Charles, LA, USA) Each unit was watered to approximately 50% water-filled water space (WFPS) and immediately weighed. The units were then sealed with lids on which four 2-mm holes had been drilled to promote aeration. The units were placed in a walk-in incubator, which was set at 25°C. A humidifier (Sunbeam SUL-496, Boca Raton, FL, USA) was placed inside the incubator to limit moisture loss from the units. The units were weighed every two to three days and watered if moisture content dropped below 95% of the target 50% WFPS. Any watering took place a minimum of 3 days prior to sampling to allow for core equilibration and minimize moisture effects on measurements.

#### **4.3.4. Sampling and Analysis**

Triplicate microcosms treated with each amendment were retrieved from the incubator on the sampling days indicated above (see ‘Experimental Setup’ subsection). The contents of each unit were thoroughly mixed and subsampled for Olsen P and KCl-extractable ( $\text{NO}_3^-$  and  $\text{NH}_4^-$ ) N determination using methods described below (see ‘Laboratory Analysis’ subsection). All samples were extracted fresh (without drying) immediately after sampling.

#### **4.3.5. Laboratory Analysis**

Soils and amendments were analyzed for baseline chemical properties using the same methods (Table 4.1, Table 4.2). Organic matter was determined by the loss on ignition method (Carter and Gregorich, 2007) using a Thermo Scientific™ Thermolyne™ muffle furnace (Waltham, MA, USA), while pH was determined in a 1:1 soil or amendment to water suspension with a pH electrode (AB15, Fisher Scientific, Waltham, MA, USA). Soil  $\text{NO}_3^-$  was determined in 2 M KCl extracts using the cadmium reduction method using a Lachat QuikChem 8500 Flow Injection Analyzer (Loveland, CO, USA) (Carter and Gregorich, 2007). Ammonium was also determined using the same auto analyzer, using a different channel, following extraction with 2 M KCl Available P (Olsen P) was determined by the ammonium molybdate method using an Utraspec 2100 Pro Spectrophotometer (Holliston, MA, USA) following extraction with 0.5 M sodium bicarbonate at a pH of 8.5 (Carter and Gregorich, 2007). Calcium, Mg, and Na were determined in ammonium acetate extracts by atomic absorption spectroscopy (iCE™

3300 AAS; Thermo Scientific, Waltham, MA, USA). Micronutrients (K, Fe, Mn, Zn) were extracted with 0.005 M DTPA and analyzed using atomic absorption spectroscopy, while B was determined by the hot water extraction method (Carter and Gregorich, 2007). Sulfur concentration was determined by automated turbidimetric determination barium sulfate in 1 M KCl extracts (Carter and Gregorich, 2007) Cation exchange capacity (CEC) was obtained by summing cation concentrations in ammonium acetate extracts. On sampling days, fresh (moist) subsamples from incubated microcosms were analyzed for Olsen P using an Utraspec 2100 Pro Spectrophotometer (Holliston, MA, USA) and available N ( $\text{NO}_3^-$  and  $\text{NH}_4\text{-N}$ ) using a Technicon auto-analyzer II (Oakland CA, USA) following extraction procedures described above.

Table 4.1 Initial soil quality values of the one-lift soil (1LS) and its topsoil and subsoil components, as well as the two-lift (2LS) stockpiled and natural control soils. †

Amendment	pH	OM	NO <sub>3</sub> -N	NH <sub>4</sub> -N	Olsen P	K	Cl	S	B	Zn	Fe	Mn	Cu	Mg	Ca	Na	CEC
		%															cmol <sub>c</sub> kg <sup>-1</sup>
<b>1LS Topsoil</b>	7.1	3.6	2.5	-	29	100	6	10	0.7	1.63	188	37.9	0.74	257	1424	16	9.6
<b>1LS Subsoil</b>	7.6	0.8	8	-	10	100	16	48	0.3	2.89	5.73	1.3	0.58	411	2319	29	15.4
<b>1LS blend</b>	7.6	1.3	5	-	13	100	-	-	-	-	-	-	-	375	-	29	13.6
<b>1:LTS NC</b>	7.5	0.6	1.0	1.8	12	122	-	-	-	-	-	-	-	252	1985	15	12.4
<b>2LS</b>	7.5	2.5	1.5	1.4	15	117	4.5	8	0.8	2.1	157	56	1.2	244	1633	14	10.6
<b>2LS NC</b>	5.0	2.6	12.5	7.7	9	186	-	-	-	-	-	-	-	273	1108	17	8.4

† OM= organic matter, NO<sub>3</sub>-N= nitrate, NH<sub>4</sub>-N= ammonium, CEC= cation exchange capacity.

Table 4.1: Chemical analysis of the biochar, humalite, and peat amendments used in the study. †

Amendment	pH	TOC	N	P	K	S	Ca	Mg	CEC	CCE	SAR
		g kg <sup>-1</sup>	g kg <sup>-1</sup>				mg kg <sup>-1</sup>	g kg <sup>-1</sup>		cmol <sub>c</sub> kg <sup>-1</sup>	g kg <sup>-1</sup>
<b>Biochar</b>	7.2	648	0.4	67	1282	90	3,350	722	1.7	3	0.21
<b>Humalite</b>	4.3	375	10.7	103	175	4,169	14,136	2,140	21	2	5
<b>Peat</b>	4.5	273	7.2	157	0	792	7,490	1,076	4.6	3	0.18

† TOC= total organic carbon, CEC= cation exchange capacity, CCE=calcium carbonate equivalent, S.A.R.= sodium adsorption ratio.

## **4.4. RESULTS**

### **4.4.1. Initial Soil Properties**

The 1LS soil was created from a 20:80 blend of 1LS topsoil and subsoil, and its soil quality values reflect this. The pH increased to match that found in the 1LS subsoil, while organic matter, nitrate, Olsen P and micronutrient values decreased to levels slightly higher than those found in the 1LS subsoil. The 1LS soil and the 1LS NC soil were also fairly similar in value, with the expected exception in nitrate values. The 2LS and 2LS NC also closely matched for the most part, again with most differences occurring in N based parameters.

### **4.4.2. Amendment Properties**

Biochar had both the highest pH and total organic carbon values of the amendments, while having very low N values in comparison to HU and PT, giving it a C:N of 1620 vs 35 and 38 for HU and PT respectively. Biochar also had the lowest amount of P and PT had the highest, while HU had the highest Ca, Mg, CEC, and SAR values.

### **4.4.3. Olsen Phosphorus**

In 1LS there was a significant amendment  $\times$  time interaction for Olsen P concentration in the 1LS soil (Table 4.3, Fig 4.3). Significant differences between the treated soils and the control occurred at all sampling times, except on Day 60. Olsen P

Table 4.3: Amendment and time effects on soil quality values in the one-lift (1LS) and two-lift (2LS) soils. †

Soil		NO <sub>3</sub> -N	NH <sub>4</sub> -N	Olsen P
1LS†	Amendment		mg kg <sup>-1</sup>	
	<b>BC</b>	7.27	0.75	6.55
	<b>HU†</b>	13.37	2.48	4.80
	<b>PT†</b>	16.31	3.26	4.94
	<b>BCH†</b>	10.27	1.60	4.91
	<b>BCP†</b>	9.02	1.73	5.34
		<b>p-Values</b>		
	<b>Amendment (A)</b>	<0.001	<0.001	<0.001
	<b>Time (T)</b>	<0.001	<0.001	<0.001
	<b>A x T</b>	<0.001	<0.001	0.0035
<b>2LS†</b>				
	<b>BC</b>	12.61	0.41	7.80
	<b>HU</b>	16.32	3.24	7.37
	<b>PT</b>	23.43	4.65	6.94
	<b>BCH</b>	13.14	1.24	6.99
	<b>BCP</b>	14.39	2.44	6.40
		<b>p-Values</b>		
	<b>Amendment (A)</b>	<0.001	<0.001	<0.001
	<b>Time (T)</b>	<0.001	<0.001	<0.001
	<b>A x T</b>	<0.001	0.0004	<0.0017

†BC, biochar; BCH, 50:50 biochar:humalite by mass (based on C content); BCP, 50:50 biochar:peat by mass (based on C content); HU, humalite; PT, peat; CEC, cation exchange capacity; DMY, dry matter yield; OM, organic matter.

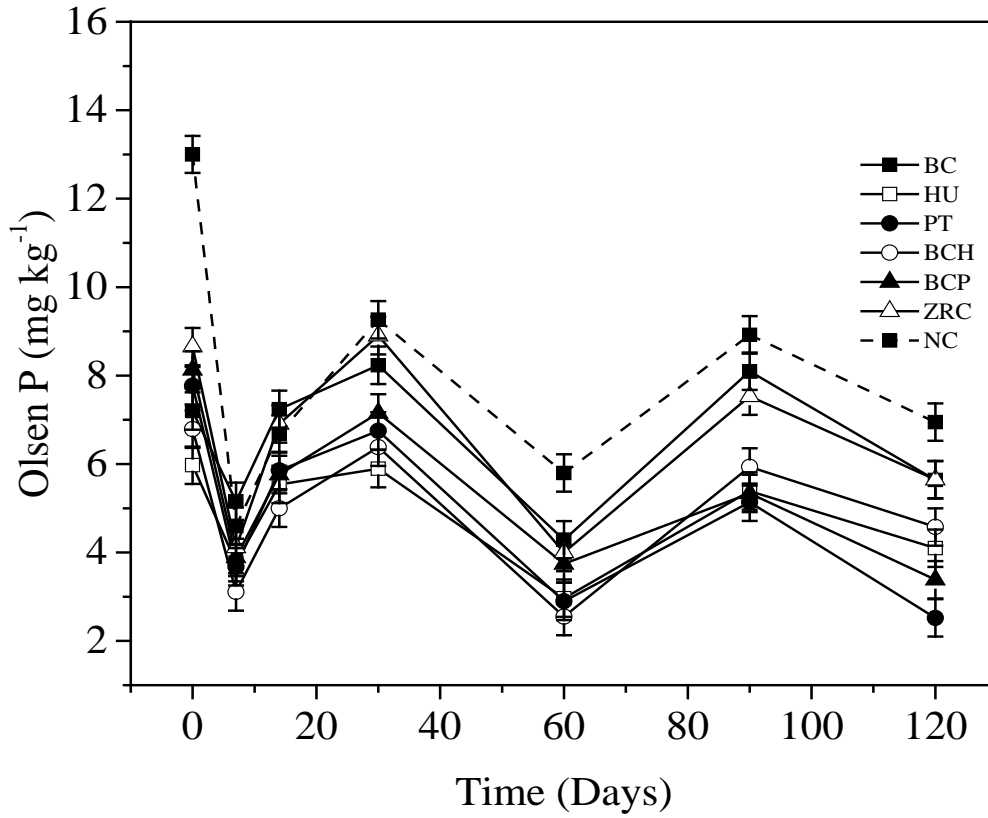


Fig. 4.1. One-lift (1LS) Olsen P values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments across a 120 day period.



concentrations in soil amended with HU and BCH were 28 to 34% lower than those in the control at all sampling times up to Day 30. On Days 90 and 120, respectively, PT produced 32 and 55% lower Olsen P concentrations than the control. Olsen P concentration was 21 to 36% higher in the NC than in all 1LS except BC (Fig. 4.1). When the amended 1LS units were compared to one another, differences were observed only on Days 90 and 120. On Day 90, BC had 50 to 58% greater Olsen P concentration than all but BCH-amended soils, while on Day 120 BC had 124% more Olsen P than PT.

In the 2LS soil, the amendment  $\times$  time interaction was significant for Olsen P concentration (Fig. 4.2). On Day 7, all amendments produced 91 to 137% higher Olsen P concentration than the ZRC, with the largest difference occurring in the PT-amended and the smallest difference in the BCP-amended soil (Fig. 4.2). After Day 7, however, there were no significant differences between any of the amended treatments and the ZRC soil, except on Days 60 and Day 90 when BCH produced 47% and BCP had 36% lower Olsen P concentration than the control. When the amended 2LS soil was compared to the NC on Day 7, PT was 63% higher in Olsen P and the only amendment that was different than the NC. On Days 30 and 60, Olsen P concentration was significantly greater in BC-amended soil than in the NC soil. However, these Olsen P concentrations did not differ significantly from those in the unamended 2LS soil. On Day 30, Olsen P concentrations in HU, BCH, BC, and the unamended 2LS were 32 to 56% higher than those in the NC soil. On Day 60, only BC-amended soil had significantly higher Olsen P concentration

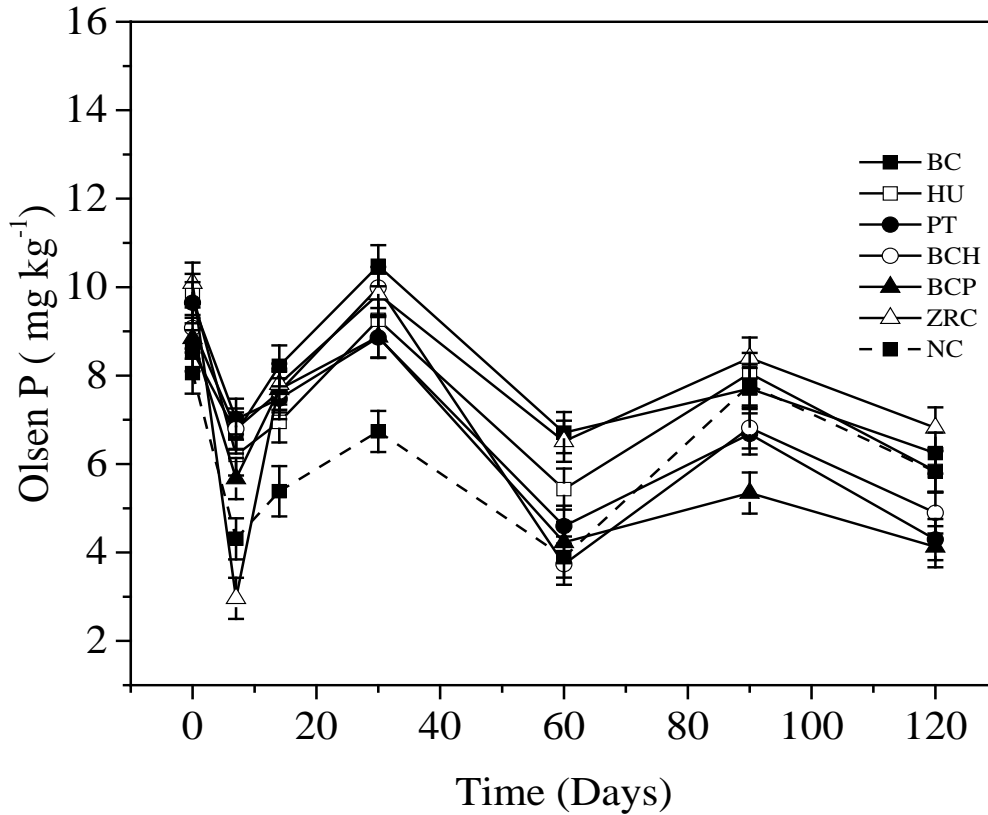


Fig. 4.2. Two-lift (2LS) Olsen P values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments across a 120 day period.

than the NC, a difference of 72%. When we compared only the amended 2LS microcosms, differences in Olsen P concentration only occurred on Days 60 when BC produced 59% and 80% higher Olsen P concentration than BCP and BCH, respectively, and on Day 90, when HU and BC, respectively, produced 44 and 51% higher Olsen P concentration than BCP.

#### 4.4.4. Available Nitrogen

##### Nitrate

In the 1LS soil, there was a significant amendment  $\times$  time interaction for  $\text{NO}_3\text{-N}$  concentration (Table 4.3, Fig. 4.3). Nitrate N concentration in PT-amended soil was significantly higher than that in the 1LS soil amended with HU, BC, BCP, and BCH on Days 30, 60, and 90, but amendment differences were not significant on the other sampling dates (Fig. 3.3). Humalite produced significantly greater  $\text{NO}_3\text{-N}$  concentration than BC on Days 60 and 90. Notably, while  $\text{NO}_3\text{-N}$  concentration did not vary significantly after sampling Day 30 for any of the other amendments, it decreased significantly for PT from about  $25 \text{ mg kg}^{-1}$  on Day 90 to about  $7.5 \text{ mg kg}^{-1}$  on Day 120.

Generally,  $\text{NO}_3\text{-N}$  concentration was significantly greater in the 1LS ZRC than in the corresponding NC soil. Nitrate N concentrations were significantly greater in HU- and PT-amended 1LS soil than in the ZRC on Day 30, while on Day 90,  $\text{NO}_3\text{-N}$  concentration was significantly greater in the ZRC than in the soil amended with BCP (Fig. 4.4).

In the 2LS soil, amendment effects also varied with rate, as indicated by the significant amendment  $\times$  rate interaction (Table 3). Similarly to the 1LS soil, PT produced the highest  $\text{NO}_3\text{-N}$  concentration on Days 30, 60, and 90, while the lowest  $\text{NO}_3\text{-N}$  concentration was in the soil amended with BC (Fig. 5). However, differences between PT and BCP on Day 30, and between PT and HU on Days 60 and 90 were not

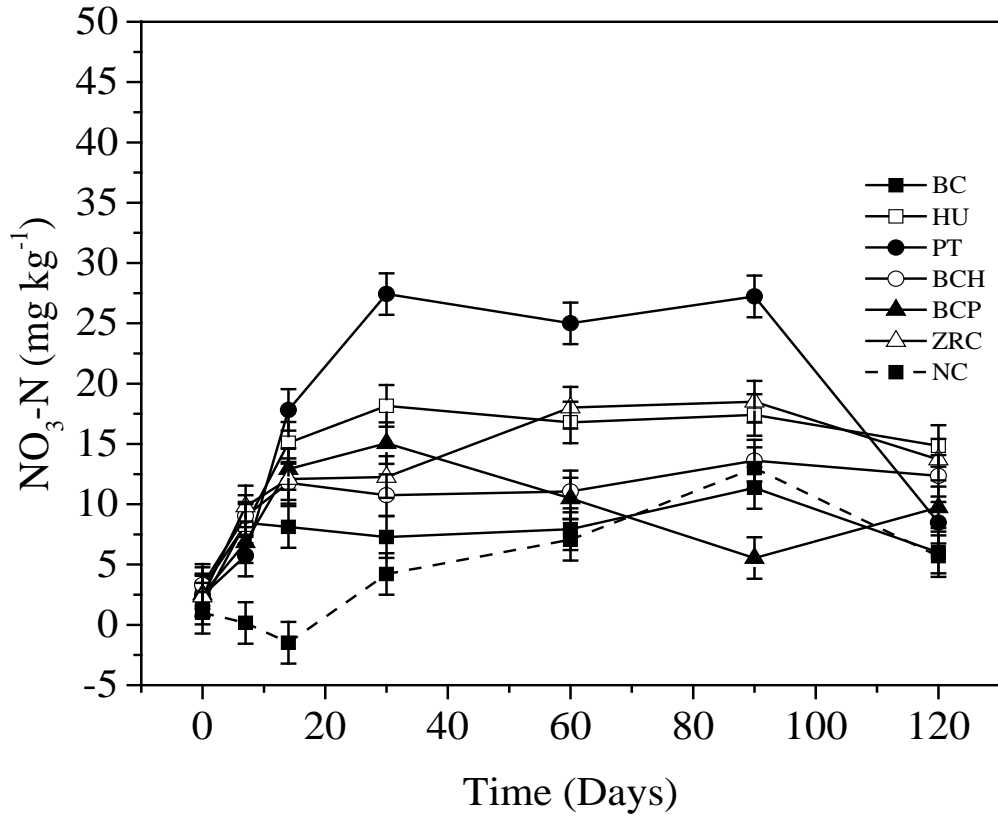


Fig. 4.3. One-lift (1LS) nitrate values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments across a 120 day period.

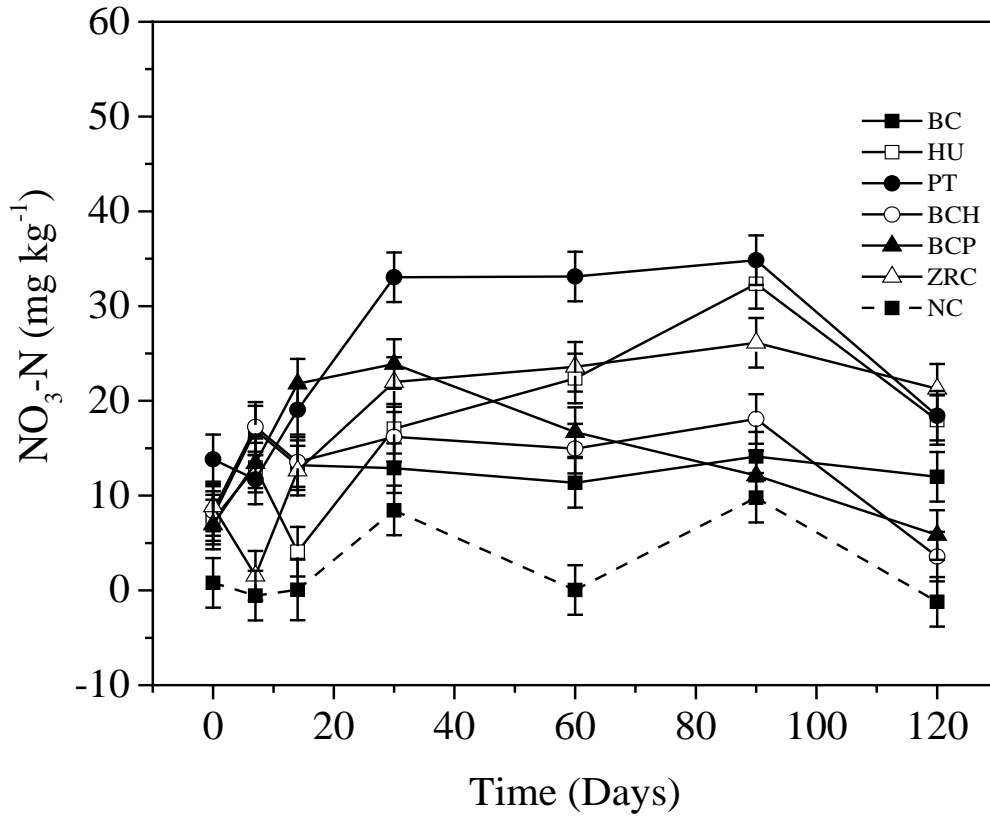


Fig. 4.4. Two-lift (2LS) Olsen P values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments across a 120 day period.

significant at  $\alpha = 0.05$ . Amendment differences on the rest of the sampling dates were not significant. When compared with the ZRC, BC and BCH increased  $\text{NO}_3\text{-N}$  concentration by 993 and 1018%, respectively, on Day 7 (Fig. 5). Amendments did not significantly change  $\text{NO}_3\text{-N}$  concentration relative to the ZRC thereafter, until Days 90 and 120 when BC and BCP decreased  $\text{NO}_3\text{-N}$  concentration relative to the ZRC. Nitrate N concentrations in the NC soil were lower than those in the ZRC and the amended soils throughout the sampling period.

### **Ammonium**

The amendment  $\times$  time interaction was significant for  $\text{NH}_4\text{-N}$  concentration in the 1LS and 2LS soils (Tables 4.3). In both salvaged soils,  $\text{NH}_4\text{-N}$  concentrations peaked on Day 7 and dropped to near zero by Day 30, remaining unchanged for the rest of the experiment (Figs. 4.5 and 4.6). Peat produced the highest peak  $\text{NH}_4\text{-N}$  concentration while BC produced the lowest on Day 7 in both soils. All amendments except BC produced significantly higher  $\text{NH}_4\text{-N}$  concentrations in the 1LS than in the ZRC on Day 7, while only PT produced significantly higher  $\text{NH}_4\text{-N}$  concentration than the ZRC on Day 14 (Fig. 4.6). Ammonium concentrations did not differ significantly between amended soils and the ZRC on all other sampling dates. On DAY 7, all amendments except BCP produced 49 to 293% higher  $\text{NH}_4\text{-N}$  concentration than the NC soil, which in turn had 54% higher  $\text{NH}_4\text{-N}$  concentration than the ZRC. On DAY 14, all amendments except PT gave 67 to 96% lower  $\text{NH}_4\text{-N}$  concentration than the NC soil, while the ZRC had 94% lower  $\text{NH}_4\text{-N}$  concentration than the NC soil.

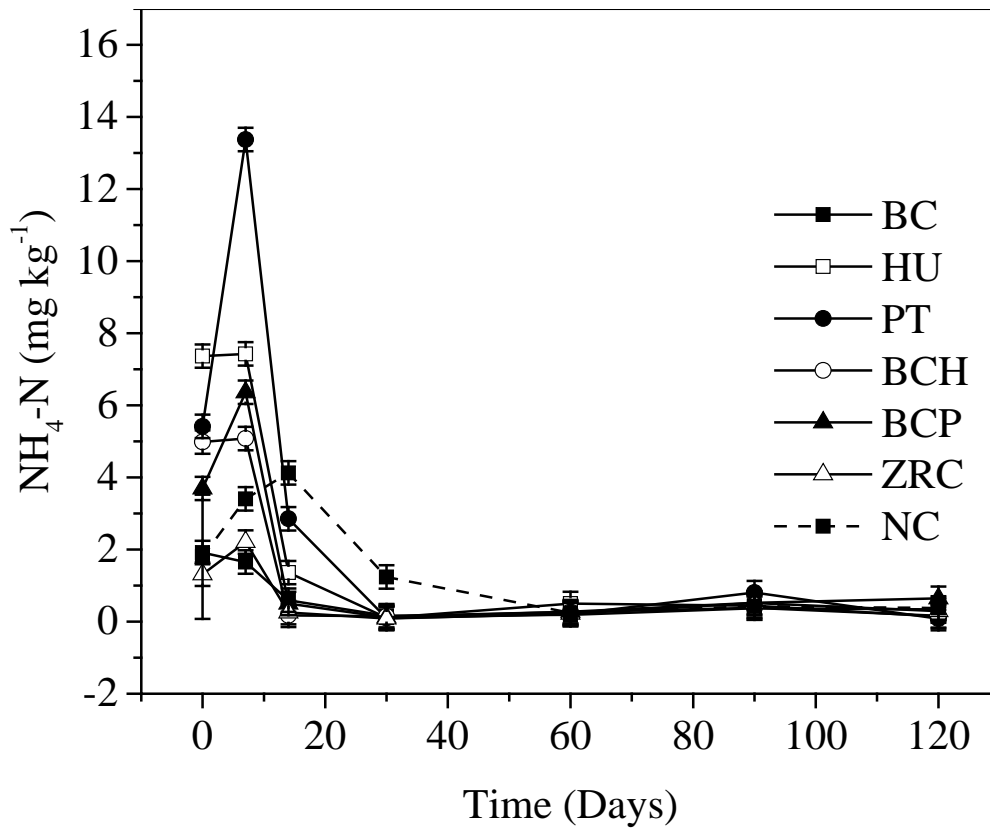


Fig. 4.5. One-lift (1LS) ammonium values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments across a 120 day period.

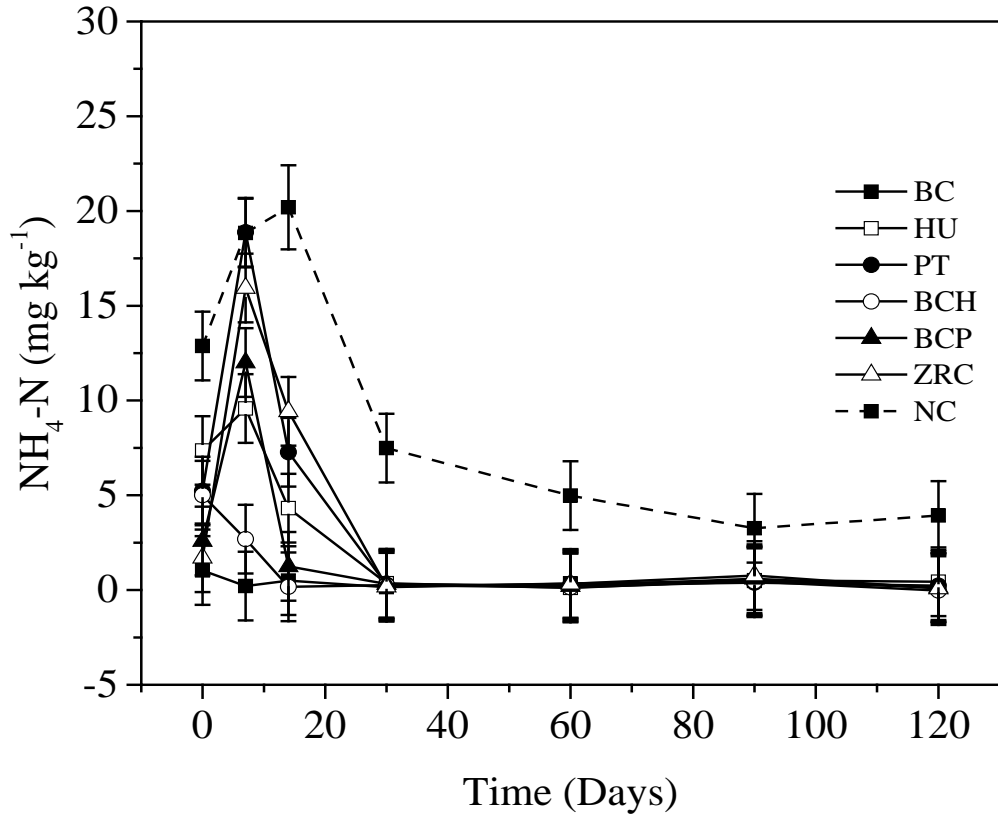


Fig. 4.6. Two-lift (2LS) ammonium values for biochar (BC), humalite (HU), peat (PT), biochar:humalite (BCH), biochar:peat (BCP), natural control (NC) and zero-rate control (ZRC) treatments across a 120 day period.



The only difference observed between the amended 2LS soil and the ZRC occurred on DAY 7, where BCH- and BC-amended soil, respectively, had 83 and 99% lower  $\text{NH}_4\text{-N}$  concentration than the ZRC (Fig. 7). When compared to the NC soil, all amended 2LS soil microcosms had substantially lower  $\text{NH}_4\text{-N}$  concentrations than on Days 0 to 14. After DAY 14, all differences disappeared, as soil ammonium values dropped to near zero, where they remained for the remainder of the experiment. Overall, however, NC soils tended to have noticeably higher  $\text{NH}_4\text{-N}$  concentrations even after DAY 14, when compared to the treated 2LS soil.

## **4.5. DISCUSSION**

### **4.5.1. Olsen Phosphorous Concentration**

The effects of amendment on Olsen P concentration tended to vary between the two soils. The lack of immobilization in BC amended units in the 1LS could be the result of high stability of biochar within the soil. Biochar has been shown to have a mean residence time of ~402 years in soil, and a decomposition rate of 0.3% under ideal (laboratory) conditions (Kuzyakov, et al. 2014). Kuzyakov et al. (2014) found that 88% of C in biochar was in the form of highly stable condensed aromatic compounds, which could explain its high stability (Kuzyakov, et al. 2014). The decrease in Olsen P concentration observed with the other amendments in the 1LS soil may be due to immobilization. This is consistent with results from a previous study which showed that when glucose was added to a subtropical soil in a 43-d incubation, it significantly decreased Olsen P concentrations, while treatments amended with much more stable

forms of C (rice straw) did not show immobilization (Wu, et al. 2007). However, such an effect was not evident in the 2LS soil in which amendment differences were minimal.

The amended 2LS soil behaved in a much more expected manner than the 1LS soil. In almost all cases where significant differences occurred, amended soils had significantly higher P concentrations than the corresponding ZRC and NC soils. Peat may initially supply P through easily decomposable P-containing organic compounds, as it produced the highest peak Olsen P concentration, yet BC and BCH followed closely behind in value. While PT's mechanism for P supply is relatively intuitive, and likely a result of quick mineralization, BC's is not. One possible explanation for the high Olsen P concentration in biochar-amended soils is that inorganic P could be supplied by the ash fraction of the biochar, and that mineralizable organic P may be supplied by the volatile acid-rich portion of the biochar (DeLuca, et al. 2009, Mukherjee and Zimmerman, 2013). This behaviour is relatively well documented in the scientific literature (DeLuca, et al. 2009, Liang, et al. 2014, Parvage, et al. 2013, Zhai, et al. 2015). In one study, manure based biochar released  $0.26 \text{ g P kg}_{\text{soil}}^{-1}$  from its ash, with release rates plateauing after 72 h and remaining high for the duration of the 240 h experiment (Liang, et al. 2014). The same study attributed the rate of P release to  $(\text{Ca, Mg})_3(\text{PO}_4)_2$  in the biochar itself, and was less influenced by soil properties. In another study, the ash fraction of maize biochar accounted for 77% of total biochar P, and biochar was found to increase Olsen P and soil microbial biomass P, and lower P sorption capacity (Zhai, et al. 2015). They also found that the P within the biochar was largely available, and the amount of available P increased with rate of application (Zhai, et al. 2015). However, another study found that

biochar at 1% *w/w* was found to increase soil P content by 11 to 253%, but beyond 1% *w/w*, biochar showed P immobilizing behaviour (Parvage, et al. 2013). We suspect that the relatively high Olsen P values we observed in BC amended soils throughout our study were derived from the ash of the biochar used. Further, we suspect that the P supplied by the biochar remained constant after an initial increase in value, in a manner similar to that observed by Liang, et al. 2014, while other amended soils underwent immobilization.

#### **4.5.2. Soil Nitrate Nitrogen Concentration**

Overall, in both the 1LS and 2LS soils, PT produced the highest NO<sub>3</sub>-N concentrations. This was likely due in part to the much higher labile N concentration in PT than in amendments such as BC and mixtures containing BC. Peat also has a higher amount of labile C than humalite or biochar. Purwanto et al. (2005) found that N mineralization decreased with increasing degree of degradation of peat organic matter and increasing C stability of the peat used in their study. Alkyl C/O-alkyl C ratios were highly important, and peat sources with higher ratios (i.e., less O-alkyl groups, such as carboxyl groups) were less easily degraded, and had lower mineralization rates (Purwanto, et al. 2005). The activation energy required for mineralization also plays a role in mineralization rates, but even peats with relatively high C:N ratios (31 - 34) had similar rates of mineralization as those with much lower ratios (15 – 18), indicating that C stability is more important (Purwanto, et al. 2005). The lag times for HU-amended soils to begin to behave similarly to PT treated soils in the present study is likely further evidence that C stability is a key driver in mineralization and thus NO<sub>3</sub>-N concentrations,

as the more complex forms of C expected in humalite would take longer to degrade and become accessible to the microbial population.

The minimal differences between the ZRC soil and the amended 1LS indicate that there is little benefit in adding amendments to the stockpiled soil in a one-lift scenario, and amendments may result in  $\text{NO}_3\text{-N}$  immobilization, as was observed in the 2LS soil. Nonetheless, amendments consistently produced higher  $\text{NO}_3\text{-N}$  concentrations in both salvaged soils than in the corresponding NC soils, indicating that amendments may result in better Plant and ecosystem establishment.

#### **4.5.3. Ammonium Nitrogen Concentration**

The lack of difference between the ZRC and the NC soils from Day 0 to Day 14 in both soils tends to illustrate that there is little difference in the mineralization rate between stockpiled and undisturbed soils. In the 1LS soil, all amendments except BC produced greater  $\text{NH}_4\text{-N}$  concentrations than the ZRC and NC soils. This was most evident on Day 7, but was also observed on Day 14. However, in the 2LS soil,  $\text{NH}_4\text{-N}$  concentrations were higher in the NC and ZRC soils than in the amended soils, likely due to the higher organic matter content of the 2LS soils which may have masked the benefit of the amendments, or, in the case of the 2LS NC, the relative freshness of the samples (i.e., more active microbial community, more easily decomposed material, etc.).

The impact of BC on  $\text{NH}_4\text{-N}$  concentration appeared to be minimal in both the 1LS and 2LS soils, a result that was expected on account of C stability in BC (Dempster,

et al. 2011, Kuzyakov, et al. 2014). Our findings match results in one study, where no change in C or N mineralization was observed with fresh and aged wheat biochar additions (Dempster, et al. 2012), and contradict those from another study where BC was found to have significant negative impacts on the microbial C pool and N mineralization rates (Dempster, et al. 2011), a mechanism that was not well understood by the study authors. (Dempster, et al. 2011, Dempster, et al. 2012). Biochar's inactivity within the soil is further highlighted in the BCH and BCP amended soils, which also had low NH<sub>4</sub>-N concentrations (but higher than those for BC). The differences between BC and the BCH and BCP mixtures were likely due to the humalite and peat in the mixtures, which is consistent with the lower NH<sub>4</sub>-N concentrations in soils amended with BCH and BCP compared with soils receiving the 100% HU and PT. The higher NH<sub>4</sub>-N concentrations from PT was likely due to the higher labile C content of PT, and its lower degree of degradation/humification compared to the other amendments. Peat's physical properties could also influence mineralization. The increase in soil porosity and void space due to the bulky nature of peat likely impacted soil aeration, and thus the microbial processes associated with mineralization (Halvin, et al. 2004).

#### **4.6. CONCLUSIONS**

In many cases, amendment of the 1LS and 2LS soils showed little, if any improvement over the corresponding controls. Amongst the amendments, however, PT clearly provided the greatest benefit, increasing available N concentration. However, BC appeared to produce the highest Olsen P concentration in the soils, particularly later in the experiment. Our results suggest that the degree of humification and the C stability of

the amendments played the greatest role in determining N and P availability in the two soils. Amendment performance therefore generally ranked in the order PT > HU > BCP = BCH > BC. Amendments such as PT may have larger benefits to the soil, which may not be apparent under lab conditions, thus a field study is recommended, as the more extreme field conditions may highlight differences more clearly.

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## 5. GENERAL SYNTHESIS

This research has demonstrated that amending stockpiled soils tends to have somewhat mixed results. The main driver for performance of our amendments appears to be the carbon stability of the amendments. Generally, biochar, which was the most stable, performed the worst, and had the lowest soil quality parameter values (except for nitrate) and the lowest mineralization, likely due to the highly crystalline nature of the biochar. Humalite, which has moderately stable carbon, had moderate quality values, while peat, which had the least stable form of carbon, had the highest values. Peat tended to perform the best overall in all three experiments. Peat bolstered cumulative DMY in the 2LS soil, provided the greatest overall reduction in soil N<sub>2</sub>O losses during the incubation experiment, and had the best overall nitrification and soil N mineralization rates of all the amendments. Humalite had the highest Plant N content, and performed well during the mineralization experiments, yet it reduced DMYs in our bioassay, likely as result of suspected boron toxicity, and yielded the greatest N<sub>2</sub>O losses. Biochar was also able to improve cumulative biomass, and had the highest soil nitrate values during the bioassay, but this nitrate may not have been Plant available. Further, biochar produced low nitrification and mineralization rates; however, unlike the other amendments, it did not cause P immobilization in the soil.

## 6. CONCLUSIONS AND RECOMMENDATIONS

Although soils for the 1LS and 2LS treatments were sourced from stockpiles that were within 5 km of each other, site and stockpile variability make it very difficult to compare 1LS and 2LS performance directly, especially in conjunction with the limited number of stockpiles that were available to create a 1LS soil. Even differences in soil fertility parameters ( $\text{NO}_3\text{-N}$ ,  $\text{NH}_4$ , and Olsen P) between the natural control soils and the stockpiled soils seemed to be large despite being collected only 50 m from one another. It is uncertain whether these differences between the stockpiled and natural soils can be attributed to the stockpiling process, or natural variability. Regardless, differences between the ZRC and the amended soils are more important than the differences between the amended soils and the natural sites, a fact the experimental design of this study deliberately emphasized. For the bioassay experiment, soil and DMY data were fairly comparable and trended in similar manners between the two soils. Individual amendments behaved similarly regardless of soil, thus indicating that amendment type may make the biggest difference in overall performance. In order to get a clear understanding of how salvage method impacts long-term soil quality, the creation a few small one-lift stockpiles (approximately 10 m  $\times$  4 m  $\times$  10) at the same time and at the same location as some two-lift stockpiles is recommended.

Given humalite's toxicity effects, it is advisable that this amendment is applied at low rates. The blends, BCP and BCH, generally behaved in a similar manner as their full strength HU and PT counterparts, but always had lower ammonium, nitrate, and Olsen P concentration levels as well as DMY weights, thus using non-blend amendments is suggested. Biochar had low N mineralization rates within the incubation study, indicating its high carbon stability. However, in the bioassay, it provided substantial benefits to the soil, particularly in terms of nitrate indicating that it creates habitat for nitrifying bacteria. Additionally, the bioassay provides a more holistic look at biochar's total benefit to stockpiled soils. Finally, the ability of biochar to sequester large amounts of carbon in very stable forms, prevent nitrate leaching, and generate energy from a biochar reactor via the bio-oils and bio-gases released during its production may still make it a useful product. Further, when applied to small sites with another organic amendment with much less stable carbon (i.e. manure), its performance may be greatly enhanced. Within our study, peat performed the best overall, and I suggest that it is the best amendment to utilize in the AOSR due to the rapid nature it provided benefits to the soil, and its abundance on site.

Of the amendments studied, the use of peat is recommended for improving soil quality of stockpiled and reclaimed soils in the Cold Lake Oil Sands Region. Though in some cases peat-amended soils did not show significant differences from the non-amended stockpiled soils, this may be due to the tightly control conditions in which our experiments were conducted. In a field scenario, differences, particularly with Plant biomass, benefits may be much more apparent as the moisture retention abilities of the

amendments may play a larger role in determining soil mineralization rates and biomass production.