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5 Tables, 4 Figures

Abstract

Reclamation practices in the oil sands region of Alberta involve the reconstruction of soil profiles using a combination of salvaged mineral substrates and organic matter-rich surface materials, including peat-mineral mix (PM) and forest floor-mineral mix (FFM). The successful re-establishment of vegetation on reclaimed sites is for a large part dependent on the nutrients these materials can provide. Hence, the overall objective of this study was to compare carbon (C), nitrogen (N) and phosphorus (P) release rates from PM and FFM materials used to cap reconstructed sandy soils. A 325-day laboratory incubation was conducted to measure these rates. The two materials released comparable amounts of N on a per kilogram of soil basis (111 to 118 mg_N kg⁻¹). However, when results were normalized based on each material's organic C content, N release was six times greater for FFM than for PM, in accordance with results of previous studies. In addition, overall C mineralization and P release rates were over one order of magnitude higher with FFM than with PM. As opposed to N, however, P release seemed to be controlled more by abiotic processes than by organic matter mineralization. While the FFM material overall released more N and P, it also degraded faster; in comparison, PM may provide a smaller but more stable release of N.

Introduction

Organic matter plays a central role in the functioning of the overall soil ecosystem; as such, it is often used as a proxy for soil quality in soils undergoing reclamation (Frouz et al. 2009; Turcotte et al. 2009). Sandy soils, more so than their finer-textured counterparts, depend on organic matter to store nutrients and retain water, sustain a healthy biota and support plant growth. Consequently, when reconstructing coarse-textured soils following land disturbance, it is essential that the right amount and the right type of organic matter amendment be used (Larney and Anger, 2012). Furthermore, monitoring how organic matter evolves and releases nutrients in reconstructed soils is key to understanding if, and how quickly, sustainable processes and functions can be restored in these soils (Quideau et al., 2013b; Macdonald et al., 2015).

In upland forest ecosystems of the Alberta oil sands region, clay to loam textured parent materials derived from morainal and glaciolacustrine deposits support the genesis of Gray Luvisols, while coarser textured parent material (sandy loam to sand) leads to the formation of Eutric and Dystric Brunisols (Natural Regions Committee, 2006). Luvisols occupy a large portion of the landscape around Fort McMurray, and give way to Brunisols moving northeast. Parent material of the Brunisols is mostly glaciofluvial outwash, with eolian landforms prevailing in the area south of Lake Athabasca (Turchenek and Lindsay, 1982). As oil sands mining extends north, it has become increasingly important to understand how to efficiently reconstruct these coarse-textured soils, as they will constitute a significant portion of the final reclaimed landscape.

Two types of organic matter-rich coversoils are used during oil sands reclamation; peat-mineral mix (PM) and forest floor-mineral mix (FFM). The extensive use of peat has been

motivated by its abundance in the pre-mining landscape, while forest floor salvaged from upland areas has been shown to be an excellent source of seeds and propagules for native forest communities (Mackenzie and Naeth 2006; Naeth et al., 2013). Additionally, FFM may promote soil microbial activity (Béasse et al., 2015), and the development of microbial communities more similar to those found on natural forest soils, although this may be due more to differences in the plant communities growing on the two types of reconstructed soils than to initial differences in the composition of PM and FFM (Hahn and Quideau, 2013).

While the superiority of FFM over PM as a native seed source is well established, studies that compared the two materials in term of their ability to release nitrogen (N) have yielded conflicting results. Measured N release rates ($\text{mg kg}^{-1} \text{ day}^{-1}$) were higher for FFM than for PM in a 30-day field incubation using the buried bag method (McMillan, 2005). On the other hand, PM was found to release more N than FFM in a similar field incubation established at a different reclaimed site (McMillan et al., 2007), as well as during a 315-day laboratory incubation (MacKenzie and Quideau, 2012). Field measurements using ion-exchange PRS probes ($\mu\text{g N } 10 \text{ cm}^{-2}$) have similarly reported either lower (Howell et al., 2016) or higher (Jamro et al., 2014) N release from FFM than from PM.

The primary objective of the current study was to quantify potential carbon (C), N, and phosphorus (P) release rates from PM and FFM materials used to reconstruct sandy soils following oil sands mining. To our knowledge, this is the first time that P release rates for these types of materials are being measured under controlled laboratory conditions. Several biochemical attributes of quality were also measured for each material, including carbon macromolecular chemistry using solid state NMR, and the ability of microbial communities to utilize various carbon substrates as measured by substrate induced respiration (SIR). The

last objective was to critically review results from past studies to assess whether differences among sites or chosen analytical protocols could explain reported differences in nitrogen release rates.

MATERIALS AND METHODS

Experimental Site and Soil Sampling

The Aurora Soil Capping Study, a large-scale trial located at the Syncrude Aurora North mine (57°19'20"N, 111°30'24"W) in northeastern Alberta, was established to test a number of soil cover types and capping depths to reclaim a lean oil sand overburden area. Once placed, the mineral subsoil materials were capped with coversoil (10, 20 or 30 cm) consisting of either PPM (a material of high organic content, salvaged from bogs and fens), or FFM (forest floor material obtained from upland forest that is typically mixed with the underlying A and potentially a portion of the B horizons during salvage, and often results in a material of lower organic content). The soil treatments were constructed in 2011, and the experimental plots were planted to a mixture of trembling aspen (*Populus tremuloides* Michx.), white spruce (*Picea glauca* (Moench) Voss), and jack pine (*Pinus banksiana* Lamb.) in spring 2012 (North Wind Land Resources Inc., 2013). The PM and FFM materials used in this study were sampled in summer 2014 from the Capping Study. Ten samples (0-20 cm) of each material were taken from different areas and composited to yield one large (20 litre) representative sample of each coversoil. Soil samples were kept at 4 °C until further analysis.

Soil Analyses

Upon arrival into the laboratory, field moist soils (FFM and PM) were sieved with a 4 mm sieve and carefully mixed. The water content of each material was evaluated at 0.1 bar ($pF = 2$; corresponding to field capacity) using ceramic Soil Moisture Equipment Corp. plates under pressure (Reynolds and Topp, 2008). Soil pH was measured using an Accumet XL200 pH meter in a 1:2 soil to water ratio following the method of Kalra and Maynard (1991). Soil texture was determined using the hydrometer method following pretreatment with H_2O_2 (30%) to remove organic matter. Extractable ammonium (NH_4^+) and nitrate concentrations (NO_3^-) were quantified by analyzing filtered 2M KCl extracts (1:10 soil to extractant ratios) on a SmartChem 200, and extractable phosphorus of the two materials was determined using the modified Kelowna method (Ashworth and Mrazek, 1995) with an extractant solution of 0.015 M ammonium fluoride, 1.0 M ammonium acetate and 0.5 M acetic acid in a 1:10 soil to solution ratio. Total inorganic phosphorus was determined by measuring P concentrations in 0.5M H_2SO_4 extracts (1:10 soil to solution ratio). Total organic phosphorus was estimated by the difference of inorganic P measured in one ignited sample (550°C for 4 hours) and an un-ignited sample (O'Halloran and Cade-Menun, 2008). Subsamples finely ground with a Retsch MM200 ball mill (Retsch Inc. Newtown, USA) were analyzed for total organic carbon and nitrogen by combustion on a Costech ECS 4010 Elemental Analyzer equipped with a thermocouple detector (Costech Analytical Technologies Inc., Valencia, USA). Organic matter content was calculated by loss on ignition at 550°C for 4 hours.

Solid-State Nuclear Magnetic Resonance

Three subsamples of FFM light fraction ($<1 \text{ g cm}^{-3}$) and PM were analyzed by solid-state ^{13}C ramped cross-polarization with magic angle spinning (RAMP-CPMAS) NMR using a

Bruker Avance ($B_0 = 9.4 \text{ T}$, $\nu_L(^{13}\text{C}) = 100.6 \text{ MHz}$) spectrometer with a 4.0 mm double resonance MAS probe according to Norris et al. (2016). Spectra were referenced to tetramethylsilane (0 ppm) by setting the CH_2 signal of the external adamantane peak to 38.56 ppm. Four thousand scans were acquired for each sample with the following experimental conditions: spinning rate of 13.0 kHz, ^1H 90° pulse width of 4.0 μs , 1 ms contact time, and a 5 s pulse delay. The resulting FID signals were processed using the Bruker's TopSpin 3.5 software, including phase and baseline correction and line broadening of 200 Hz. Assignment of the different spectral regions was based on previously published work (Simpson and Preston 2007): alkyl (0-47 ppm), methoxyl (47-58 ppm), O-alkyl (58-93 ppm), di-O-alkyl (93-112 ppm), aromatic-protonated (112-125 ppm), aromatic-carbon substituted (125-140 ppm), phenolic (140-165 ppm), carboxyl (165-190 ppm) and carbonyl (190-220 ppm).

Substrate Induced Respiration

The 4 mm-sieved field-moist PM and FFM materials were tested for microbial activity using seven substrates and a water control according to the protocol described in Swallow and Quideau (2015). Because the two materials greatly varied in terms of their original moisture content, water was added to the FFM samples to reach a moisture level comparable to that of the peat samples (40-50% wt). Stock solutions for the substrates were prepared and adjusted for each soil sample so that the final substrate concentrations in the soil solutions would be similar across samples. These concentrations ranged from 30 mg g^{-1} soil-water for the soluble substrates (malonic acid and quinic acid), 5 mg g^{-1} soil-water for the less soluble (threonine, N-acetyl glucosamine, pantothenic acid) and 0.05 mg g^{-1} soil-water for the least

soluble substrate (syringic acid). Following substrate addition, samples were incubated for 1.5 hours at 21°C. Microbial respiration was determined by measuring pre-incubation and final UV-Vis absorbance readings (572 nm) on a Synergy HT, Multidetector Microplate Reader (Bio-Tek Instruments, Inc. Winooski, VT, USA); measurements were repeated three times for each sample (n=3). Absorbance values were converted to respiration rates based on the equations of Swallow and Quideau (2015).

Carbon, Nitrogen and Phosphorus Release Rates

Ten replicates of the peat and FFM materials (< 4 mm) were incubated in the dark at room temperature (21°C) using microlysimeters (Nalgene, product number N3004050) to measure C, N and P release rates over a total of 325 days. Each microlysimeter contained 120 g of field moist material mixed with 60 g of sand to improve aeration and water flow.

Weekly headspace samples (20 ml) were taken from the microlysimeters and injected to evacuated (<0.03 kPa) 12 ml borosilicate exetainers (Labco Limited, High Wycombe, UK). Carbon dioxide concentrations were measured using a Hewlett Packard 5890 Series II gas chromatography unit (Hewlett Packard, Santa Clara, USA) with a 1m Supelco Porapak Q column with helium as the carrier gas and equipped with an Agilent Technologies GC Sampler 80. Following gas sampling, the microlysimeters were extracted with 100 ml of deionized water that was added to the top chamber. Soil extracts were obtained from the bottom chamber under vacuum (-0.1 bar), and were analyzed for NH_4^+ , NO_3^- , and PO_4^{3-} concentrations. As ammonium concentrations were below detection limit during the first two weeks of the incubation, this analysis was stopped and data are not presented here. Nitrate and phosphate were analyzed colorimetrically by reaction with vanadium cocktail and

malachite green respectively (Lajtha et al., 1997; Doane and Horwarth, 2003). Methods were modified to allow for the change in absorbance to be measured using a BioTek Synergy HT multi-detection microplate reader with the BioTek Gen5 software. A subset of extracts (day 3, 24, 45, 80, 166 and 236) were analyzed by a Shimadzu TOC-V with TN option (Mandel Scientific Company Inc., Guelph, CA) to determine dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concentrations. Total dissolved organic nitrogen (DON) concentrations were calculated by subtracting nitrate-N from the TDN concentrations.

Sample measurements occurred weekly for CO_2 , NO_3^- , and PO_4^{3-} for the first 243 days; after that, CO_2 continued to be analyzed weekly while NO_3^- and PO_4^{3-} were measured monthly until the end of the incubation.

Data Analyses

Data analysis, including the computation of mean and standard deviations was conducted in RStudio (0.99.485, RStudio, Inc.). Cumulative respiration, nitrate and phosphate release rates were determined from the sum of all sampling points. Catabolic evenness, which is a measure of relative variability in substrate use, was calculated from the respiration response profiles obtained during the Substrate Induced Respiration experiment according to Degens et al. (2001). These values, along with other PM and FFM data, were examined for statistical differences between substrates using a Welch two-sample t-test performed in R (version 2.15.1, the R Foundation for Statistical Computing).

RESULTS

Soil Characteristics

The mineral component of both materials was sandy ($> 90\%$ sand), but the PM samples contained five times more organic matter than the FFM (259 vs. 56 mg g^{-1} , Table 1), and consequently included much less mineral matter than the FFM. Total nitrogen concentration was seven times greater for PM than for FFM (7.0 vs. 0.8 mg g^{-1}). The PM material also exhibited a much greater water holding capacity than FFM, likely linked to its higher organic matter content. Extractable ammonium concentrations were slightly greater for FFM than for PM, while extractable nitrate concentrations were five times higher for PM than for FFM. Lastly, there were striking differences in extractable phosphate concentrations between the two soil types, with the FFM showing concentrations that were ten times greater than the PM samples (25 ± 2 vs. $2.5 \pm 0.7 \mu\text{g g}^{-1}$). On the other hand, total phosphorus values did not show big differences between materials.

Organic matter characterization by solid-state nuclear magnetic resonance spectroscopy identified similar signals for the two soil cover types, including the dominant O-alkyl carbon peak at 74 ppm for both the PM and FFM samples (Figure 1). The 74 ppm peak corresponds to the C-2, C-3, and C-5 carbons of carbohydrates (mostly cellulose and hemicelluloses), while the smaller peak at around 65 ppm can be assigned to C-6 carbons, and the anomeric (C-1) carbons appear at 105 ppm (Gaudinski et al., 2005). On all spectra, the second largest peak appeared in the alkyl carbon region around 30 ppm , which corresponds to polymethylene carbons found in waxes and resins. Additional peaks included the methoxyl carbon signal of lignins at 56 ppm , peaks around 115 and 132 ppm arising from C-substituted aromatic carbons, and a broad peak around 149 ppm corresponding to phenolic carbons (Turcotte et al., 2009). Carboxyl carbons were apparent at 173 ppm .

While peaks were present at comparable chemical shifts on all NMR spectra, the relative intensity of these peaks significantly differed between the PM and FFM materials (Table 2). More specifically, the PM materials contained significantly more alkyl, methoxyl and carboxyl carbons, while the FFM samples displayed significantly larger signals from carbohydrates, as well as from aromatic and phenolic carbons. The alkyl/O-alkyl carbon ratio further indicated that the organic matter was different between PM and FFM with a significantly higher ratio for PM (0.86) than for FFM (0.54).

When calculated on a g of soil basis, the PM samples respired significantly more CO₂ (>0.40 mg CO₂-C g⁻¹ soil hr⁻¹) than the FFM samples (<0.25 mg CO₂-C g⁻¹ soil hr⁻¹) in response to the substrates added during the substrate induced respiration (multi-SIR) experiment (data not shown). However, when normalized to the soil C contents (i.e.; calculated on a g⁻¹ C basis), FFM samples respired comparable amounts of CO₂ following addition of the two nitrogen-containing substrates threonine and N-acetyl glucosamine, the carbohydrate D-cellobiose, the aromatic substrate syringic acid, and the carboxylic acid pantothenic acid (Table 3). On the other hand, PM responded significantly more strongly (mg CO₂-C g⁻¹ C hr⁻¹) than FFM to the addition of the other two carboxylic acids, malonic and quinic acid (p-value ≤ 0.10). The microbial community of the FFM samples responded fairly similarly to all seven substrates, with a respiratory response varying over the relatively small range of 2.1 to 5.6 mg CO₂-C g⁻¹ C hr⁻¹. Consequently, the catabolic evenness for the FFM (6.2) was significantly greater than for PM (4.1; p=0.007). The lower catabolic evenness for the PM samples was more specifically due to their strong response to the addition of malonic acid and quinic acid (> 13 mg CO₂-C g⁻¹ C hr⁻¹) compared to the other substrates (<4.5 mg CO₂-C g⁻¹ C hr⁻¹) tested.

C, N and P Release Rates

The laboratory incubation results for the PM and FFM materials clearly illustrate the difference in CO₂ respiration and nutrient release of these two materials (Figure 2 and Table 4). Although the cumulative amount of nitrate leached over the 325 days of the experiment was similar for both materials relative to the amount of dry soil, the normalization relative to the organic carbon content of each material led to a significantly higher cumulative release of CO₂ and nitrate for the FFM than for the PM samples (Table 4). When taking into account only the initial and final states after 325 days, the average FFM respiration rate was over 12 times that of the PM material, and the cumulative release of N was six times higher from the FFM than PM.

Release rates did not stay constant over time (Figure 2). In fact, three different successive phases of CO₂ respiration rates could be distinguished for both materials. During Phase 1 (from 0 to about 150 days), a constant respiration rate was observed (5.0 and 81 $\mu\text{g C g}^{-1} \text{ day}^{-1}$ for PM and FFM, respectively, Table 4). A lower respiration rate was observed during Phase 2 (~150-250 days), while the highest respiration rate was recorded during Phase 3 (~250-325 days) for both materials (3 to 5 times higher than during Phase 2). Nitrate release overall also varied according to the three successive phases, but differences were observed between PM and FFM samples. While the rate of nitrate release from FFM samples followed the same trend as the rate of CO₂ respiration, *i.e.* a decrease in Phase 2 and an increase in Phase 3, the rate of nitrate release from PM samples was initially low during the first 40 days, then increased and remained constant until the end of Phase 2 (Figure 2).

As opposed to nitrate, the rate of phosphate release was independent of the three respiration phases and was better explained by the cumulative amount of water extracted from the microlysimeters (Figure 3 compared to Figure 2). The rate of P release relative to the cumulative amount of percolated water was constant for FFM samples over the whole experiment ($2.3 \mu\text{g P g soil}^{-1} \text{ L}^{-1}$); P release from PM samples was constant over the first 80 days ($0.19 \mu\text{g P g soil}^{-1} \text{ L}^{-1}$) and was then equal to $0.10 \mu\text{g P g soil}^{-1} \text{ L}^{-1}$ until the end of the experiment.

The loss of C and N as dissolved organic matter in the extracted water was significant, particularly in the first 100 days of the experiment (Figure 4). Overall, we estimated that 5.1% of the initial organic C present in the FFM samples was lost after 325 days, with 2.2% mineralized as $\text{CO}_2\text{-C}$ and 2.9% leached as dissolved organic C (DOC). Comparatively, only 0.5% of the organic C initially present in the PM material was lost at the end of the experiment, with 0.2% as $\text{CO}_2\text{-C}$ and 0.3% leached as DOC. Similarly, greater DON concentrations were found in the FFM leachates compared to the PM (Figure 4).

DISCUSSION

Chemical Forms of Soil C, N, and P

Characteristics of the two materials as described here were typical of the coversoils used in the oil sand region. In term of the NMR spectra (Figure 1), these were comparable to those reported by Béasse et al. (2015). More specifically, with its intense alkyl-C peak at 31 ppm, the NMR spectrum of the PM material used in our study was similar to the stockpiled peat from Béasse et al. (2015) but was very different from their sphagnum moss spectrum, which presented very minimal signals except for the dominant O-alkyl signal at 74 ppm. The

importance of the alkyl C signal could indicate an advanced stage of decomposition (Baldock et al., 1997). This is plausible considering that the peat had either been stockpiled (Béasse et al., 2015), or in the case of our study had been placed on site three years prior to our sampling. Alternatively, at least part of the PM material could originate from trees such as black spruce (*Picea mariana* (Mill) B.S.P.) and tamarack (*Larix laricina* (Du Roi) K. Koch), which would be characterized by a high alkyl C content from needle waxes and cutin (Preston et al., 2000).

Response of the soil microbial communities to carbon substrate addition (Table 3), were interestingly similar to the study by Timonen et al. (1998), where the only differences in substrate utilization between a nursery peat and forest floor from a Scots pine (*Pinus sylvestris* L.) forest were for quinic and malonic acids. Organic acids such as quinic and malonic acids are abundant in tree root exudates, and have been shown to affect soil microbial communities to a greater extent than soluble sugars (Shi et al., 2011). It is possible that the microbial community in the PM material was more carbon limited than the FFM, hence responded more strongly to the addition of these two labile substrates.

Inorganic N was primarily in nitrate form in the PM material (63% of extractable inorganic N), while 85% of inorganic N corresponded to ammonium in the forest floor (Table 1). The results are in line with results from several other studies conducted in the area (e.g.; McMillan et al. 2007; Rowland et al., 2009; MacKenzie and Quideau, 2012), where the dominance of nitrate in PM-reclaimed soils was hypothesized to be due to their relatively higher soil pH favoring rapid nitrification. Similarly, pH of the PM material examined in this study was higher than that of the FFM (Table 1). In addition to lower nitrification rates than in PM (g^{-1} soil), higher levels of ammonium in FFM-reclaimed soils have also been linked to

greater gross ammonification rates (McMillan et al., 2007).

Lastly, the FFM material contained significantly more extractable P than the PM material (Table 1). Our results are intermediate between those of Mackenzie (2006) who reported twice as much extractable P in FFM than in PM, and those in Pinno et al. (2014), which showed 16 times more P in FFM compared to PM. Contrary to N which is mostly stored in the materials in organic form, the organic fraction of P only represented 40 to 60% of the total P, in FFM and PM, respectively (Table 1), which suggests that the phosphate detected in the leachate may originate both from the mineralization of organic matter and from the alteration of inorganic-P carrying phases.

Mineralization of C and N in reclaimed materials

The results of the incubation experiment clearly indicated a faster release of C and N in FFM compared to PM. Overall C mineralization rate was over one order of magnitude higher with FFM than with PM. If we were to assume first-order decomposition with a fixed decay constant k , these numbers indicate that it would take about 40 years for most of the organic matter contained in FFM to decompose and almost 600 years for the PM. While relying on crude assumptions, these numbers illustrate the magnitude of difference in the initial ease of decomposition of the two materials. Differences do not seem to be directly linked to differences in microbial communities, as results from the MSIR analysis were comparable for both materials (Table 3). The NMR results reported here, on the other hand, suggest that the higher concentration of recalcitrant alkyl C moieties present in the PM (Table 2) may be in part responsible for its lower rate of decomposition.

The distinction of different phases of organic matter degradation in this experiment brings additional information regarding the link between C and N mineralization (Figure 2). The comparison between Phases 1 and 2 suggests a higher initial mineralization rate due to the presence of more easily degradable organic compounds and/or the presence of a significant amount of available mineral N. As the available stock of these compounds progressively decreased over time, a switch to Phase 2 was observed after about 150 days, with a lower CO₂ respiration rate for both materials. While the transition from Phase 1 to Phase 2 may reflect a normal succession, the apparition of a new increase in C mineralization after 250 days (Phase 3) was probably caused by a change in our laboratory protocol, where we switched from a weekly to a monthly extraction of water and therefore, nutrients. This likely led to an accumulation of nutrients in the microlysimeters, leading to a new shift in biological activity and a higher degradation rate. These observations, in particular the comparison between Phases 2 and 3 provide empirical evidence that carbon mineralization in these reclaimed materials may be controlled by the availability of N.

The higher N release from FFM than from PM becomes apparent when results are presented relative to the amount of carbon present in each material rather than on a soil weight basis (Table 4), as the FFM contained significantly less carbon than PM (Table 1). Similarly, past studies reported in the scientific literature comparing N mineralization rates between the two materials always show a lower carbon content for the FFM (Table 5). These studies have reported conflicting results where N mineralization rates were expressed on a soil weight basis. However, when recalculated relative to the total amount of carbon or nitrogen present in each material, the rates of mineral N release are always higher for FFM than for PM (Table 5). This is an especially interesting result considering the variability of

the materials included in Table 5, including finer-textured reclamation materials (McMillan et al., 2007) than in the current study, as well as materials salvaged from different forest and peat types.

In our study, as much as 17.5% of the initial N may have been leached from the FFM samples, with 14% as nitrate and 3.5% as dissolved organic nitrogen (DON). Only 2.2% of the total N present in PM was leached, with 1.7% as nitrate and 0.5% as DON. The temporal variation in N release rates was also different for the two materials, showing either a decrease (FFM) or a slight increase (PM) between Phase 1 and Phase 2 (Figure 2). A similar temporal pattern was observed in a previous incubation experiment (MacKenzie and Quideau, 2012), where N release from FFM decreased after 25 weeks, while it stayed constant for PM until the end of the 45-week incubation. Consequently, while PM is releasing N at a slower rate than FFM, it may continue to do so without plateauing and serve as a slow-release N fertilizer for many more years.

P dynamics

Our laboratory results confirmed past observations under field conditions, where higher P exchange between FFM and PRS probes was reported as compared to PM (Howell et al., 2016). Further, our laboratory experiment provides insight into the mechanisms underlying P release. The fact that P release solely depended on the volume of percolated water and not on the different mineralization phases suggests that abiotic rather than microbial processes governed its release; e.g., desorption from mineral phases or dissolution of phosphate precipitates (Bünemann, 2015). This does not however exclude the possibility that organic matter mineralization may have directly (by converting organic P into inorganic P) or

indirectly (by modifying soil chemical properties, e.g. by acidification through CO₂ production) contributed to the replenishment of the extractable pool of mineral P.

A higher phosphatase activity was previously observed in FFM materials compared to PM (Quideau et al., 2013a), which may suggest a higher mineralization rate of organic P. In addition, this study found that the PM material had a much wider ratio of C to organic P (P_o) than the FFM; i.e., 1100 for PM and 300 for FFM (Table 1). Such a wide C:P_o ratio, which is typical of the 800-2000 range found in peat deposits (Wang et al., 2015), is indicative of P deficiency (McGill and Cole, 1981) and would favor net P immobilization over mineralization in the PM material (Bünemann, 2015). In addition to a lower net mineralization, the relatively high pH of the PM material (pH > 7.0, Table 1), indicates that most of the inorganic P released by mineralization may remain as insoluble forms such as calcium phosphate associated with the abundant calcium carbonate phases, explaining its very low release rate over time (Figure 3). In comparison, the overall release of phosphate led to a decrease of 4% of the total P in the case of FFM. This means that over time, if large volumes of water percolate through the soil, the stock of P may progressively decrease or migrate to lower horizons unless it is taken up by vegetation. Leaching of P in the field is much more likely for the FFM than for the PM material due to its lower water holding capacity (Table 1).

Conclusions and practical implications

In the Alberta oil sands region, salvaging operations over-strip the forest floor layers and collect a portion of the underlying mineral soil profile. Variability in the forest floor and stripping depths across a salvage area results in coversoil materials with varying organic

matter contents. In particular, as was the case for this study, a thinner forest floor and lower amount of organic matter content is typical for coarse-textured (sandy loam to sand) Brunisolic soils compared to finer-textured (loam to clay) Luvisol soils. Due to the range of organic matter content of salvaged coversoil materials for reclamation, reporting nutrient release rates as a function of total soil nutrient stocks and/or carbon content rather than soil weight may be a more appropriate way to compare results of different studies. On the other hand, from an operational perspective, the total release per weight (or volume) is likely more important as this is how the reclamation material is deployed. For future studies, reporting rates both ways would be ideal to support both applications.

In our study, the FFM material released comparatively more P than N when compared to the PM. The ratio of N to P release rates was 15 for FFM, and 282 for PM. Such a wide N/P ratio for PM may result in plant P deficiency in the early years post-reclamation, in the absence of some other form of nutrient addition either by management (*e.g.*, fertilization) or normal soil processes. However, if P is indeed associated to carbonate phases in this PM material, the efficiency of phosphate fertilization would be decreased. On the other hand, a lowering of soil pH over time via normal soil weathering or enhanced biological activity from root exudates could enhance P availability.

Overall, our results clearly showed a higher C, N and P release from forest floor than PM. Results also underline the importance of rapidly establishing vegetation on sites undergoing reclamation with a FFM coversoil so that plants fully benefit from the flush of nutrients from the decomposing forest floor.

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For Review Only

Table 1. Average characteristics of the PM and FFM materials from the Aurora Soil Capping Study used for the incubation experiment. Results are tabulated on a dry soil weight basis; when indicated, standard deviations are calculated based on three replicates, and the p-values of the corresponding Welch t-tests are listed in the last column.

	PM	FFM	p-value
Textural class	Sand	Sand	n.a.
pH	7.4 ± 0.3	5.6 ± 0.4	<0.001
Water content at field capacity (mg g ⁻¹)	976	109	n.a.
Total organic C (mg g ⁻¹)	167 ± 5	26 ± 1	<0.001
Total organic matter (mg g ⁻¹)	259 ± 8	56 ± 1	<0.001
Total N (mg g ⁻¹)	7.0 ± 0.2	0.8 ± 0.1	<0.001
Extractable NH ₄ -N (µg g ⁻¹)	3.5 ± 0.1	2.6 ± 0.2	0.003
Extractable NO ₃ -N (µg g ⁻¹)	4.4 ± 0.1	0.8 ± 0.0	<0.001
Total P (µg g ⁻¹)	243 ± 2	222 ± 7	0.034
Total organic P (µg g ⁻¹)	148 ± 2	86 ± 13	0.011
Total inorganic P (µg g ⁻¹)	95 ± 0	136 ± 6	0.006
Extractable P (µg g ⁻¹)	2.5 ± 0.7	25 ± 2	<0.001

Table 2. Integration of ^{13}C NMR spectra (% total spectral area) for the PM and FFM materials from the Aurora Soil North Capping Study used for the incubation experiment. Standard deviations are calculated based on three replicates, and the p-values of the corresponding Welch t-tests are listed in the last column.

Carbon type	PM	FFM	p-value
Alkyl	24.8 ± 0.3	17.4 ± 1.1	0.005
Methoxyl	6.7 ± 0.1	5.9 ± 0.2	0.010
O-alkyl	28.9 ± 0.3	32.1 ± 1.3	0.040
Di-O-alkyl	8.5 ± 0.1	10.3 ± 0.2	0.004
Aromatic-protonated	5.9 ± 0.1	7.4 ± 0.2	<0.001
Aromatic-carbon substituted	7.7 ± 0.1	8.1 ± 0.1	0.007
Phenolic	7.6 ± 0.2	9.4 ± 0.3	0.002
Carboxyl	7.3 ± 0.3	6.2 ± 0.3	0.001
Carbonyl	2.8 ± 0.4	3.2 ± 1.0	>0.5
Alkyl/ O-alkyl	0.86 ± 0.01	0.54 ± 0.04	0.004

Table 3. Multiple Substrate Respiration results for the PM and FFM materials from the Aurora South Capping Study used for the incubation experiment. Results are tabulated on a dry unit weight basis; standard deviations are calculated based on three replicates, and the p-values of the corresponding Welch t-tests are listed in the last column.

	PM	FFM	p-value
	mg CO ₂ -C g ⁻¹ C hr ⁻¹	mg CO ₂ -C g ⁻¹ C hr ⁻¹	
Water	1.9 ± 2.2	2.8 ± 0.7	0.55
Threonine	3.4 ± 1.3	5.6 ± 1.6	0.16
N-acetyl glucosamine	4.1 ± 1.4	2.1 ± 1.1	0.13
D-cellobiose	4.0 ± 1.8	3.7 ± 0.4	0.77
Malonic acid	18.5 ± 9.2	3.5 ± 1.0	0.10
Quinic acid	13.6 ± 4.4	4.6 ± 1.2	0.06
Pantothenic acid	2.8 ± 0.4	4.2 ± 1.4	0.23
Syringic acid	3.4 ± 0.8	5.5 ± 1.7	0.15
Catabolic evenness (E)	4.1 ± 0.3	6.2 ± 0.5	0.007

Table 4. Release rates of CO₂-C and NO₃-N for the PM and FFM materials from the Aurora Soil Capping Study used for the 325-day incubation experiment. Results are calculated for each successive mineralization phase, and as an average for Phase 1 and Phase 2 or for the entire incubation. Rates are presented relative to the amount of organic C initially present in each material.

		CO ₂ -C (µg _C g _C ⁻¹ day ⁻¹)		NO ₃ -N (µg _N g _C ⁻¹ day ⁻¹)	
		PM	FFM	PM	FFM
Phase 1	0-150 days	5.0	81	2.2	18
Phase 2	150-250 days	3.1	20	2.5	6.6
Phase 1+2	0-250 days	4.3	59	2.3	14
Phase 3	250-325 days	10	100	1.3	9.7
Overall	0-325 days	5.4	66	2.1	13

Table 5. Nitrogen release rates from paired studies comparing PM and FFM coversoils used during oil sands reclamation.

Reference	Method	Length <i>days</i>	Org. C content		Total N content		Total N mineralized		Ratio of N mineralization rates		
			PM <i>g_C kg⁻¹</i>	FFM <i>g_C kg⁻¹</i>	PM <i>g_N kg⁻¹</i>	FFM <i>g_N kg⁻¹</i>	PM <i>mg_N kg⁻¹</i>	FFM <i>mg_N kg⁻¹</i>	FFM/PM, relative to:		
									<i>Soil weight</i>	<i>C content</i>	<i>N content</i>
Mc Millan 2005	Field (Buried bag)	30	80	40	2.8	0.8	20	16	2.1	3.8	3.9
Mc Millan et al. 2007	Field (Buried bag)	30	93	51	4.5	2.4	5	10	0.8	1.6	2.7
MacKenzie and Quideau 2012	Laboratory (Microlysimeter)	315	31	11	1.4	0.4	153	136	0.9	2.5	3.1
Jamro et al. 2014	Field (PRS probe)	730	107	54	3.4	3.0	14.6 ^a	28.5 ^a	2.0	3.9	2.2
Howell 2015	Field (PRS probe)	57	154	13	6.6	0.4	82 ^a	10 ^a	0.1	1.4	2.0
This study - Overall	Laboratory (Microlysimeter)	325	167	26	7.0	0.8	118	111	1.0	6.2	8.6
This study - Phase 1	Laboratory (Microlysimeter)	150	167	26	7.0	0.8	61	78	1.3	7.9	11.0
This study - Phase 2	Laboratory (Microlysimeter)	100	166	26	6.9	0.7	43	17	0.4	2.5	3.5
This study - Phase 3	Laboratory (Microlysimeter)	75	166	25	6.9	0.7	13	16	1.2	7.6	10.5

^a Unit for these data is $\mu\text{g N } 10 \text{ cm}^{-2}$ of PRS probe

List of Figures

Figure 1. Representative CPMAS ^{13}C NMR spectra for the PM and FFM materials used as coversoils at the Aurora Soil Capping Study.

Figure 2. Cumulative release of $\text{CO}_2\text{-C}$, nitrate-N and phosphate-P as a function of time from the PM and FFM materials. Results are expressed as the cumulative amount of elements relative to the weight of material for individual samples ($\mu\text{g g}_{\text{soil}}^{-1}$), with the bolded line corresponding to the average values of ten replicates. Average release rates for different time intervals (phases) are also indicated on the graphs.

Figure 3. Cumulative release of nitrate-N and phosphate-P as a function of water volume extracted from PM and FFM. Results are expressed as the cumulative amount of elements relative to the weight of material for individual samples ($\mu\text{g g}_{\text{soil}}^{-1}$), with the bolded line corresponding to the average values of ten replicates. Average release rates for different time intervals (phases) are also indicated on the graphs.

Figure 4. Concentrations of dissolved organic carbon (DOC) and nitrogen (DON) as a function of the amount of carbon present in the PM and FFM materials.

99x75mm (300 x 300 DPI)

190x227mm (300 x 300 DPI)

190x153mm (300 x 300 DPI)

190x150mm (300 x 300 DPI)