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Biomarkers of novel ecosystem development in boreal forest soils

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ABSTRACT

Novel ecosystem development is occurring within the western boreal forest of Canada due to land reclamation following oil sand surface mining. Sphagnum peat is the primary organic amendment used to reconstruct soil in these novel ecosystems. We hypothesised that ecosystem recovery would be indicated by an increasing similarity in the biomolecular characteristics of novel soil organic matter (SOM) derived from peat to those of natural boreal ecosystems. We evaluated the use of the homologous series of long chain ($\geqslant C_{21}$) *n*-alkanes with odd/even predominance to monitor the re-establishment of boreal forest on these anthropogenic soils. The lipids were extracted from dominant vegetation inputs and SOM from a series of natural and novel ecosystem reference plots. Twice the concentration of *n*-alkanes was extracted from natural than from novel ecosystem SOM ($p < 0.01$). We observed unique *n*-alkane signatures for the source vegetation, e.g. peat material was dominated by C_{31}, and aspen (*Populus tremuloides* Michx.) leaves by C_{25}. The *n*-alkane distribution differed between the two systems ($p < 0.001$) and reflected the dominant vegetation input, i.e. peat or tree species. Our results indicate that further research is required to clarify the influence of vegetation or disturbance on the signature of *n*-alkanes in SOM; however, the use of *n*-alkanes as biomarkers of novel ecosystem development is a promising application.

1. Introduction

Surface mining is a landscape-scale disturbance that effectively returns entire ecosystems to early stage succession in terms of soil genesis (Macdonald et al., 2012). The success of post-mining reclamation, by reconstructing soil to support ecosystem development, depends on recreating a soil surface horizon with sufficient soil organic matter (SOM) to sustain productivity (Akala and Lal, 2000). Thus, measurements of SOM stocks and other directly associated parameters, e.g. microbial activity, are used as indicators of the recovery of ecosystem processes that support the re-establishment of vegetation communities (e.g. Shrestha and Lal, 2007; Banning et al., 2008). A wide range of natural, agricultural and industrial organic amendments is used to reconstruct soils (see recent review by Larney and Angers, 2012). However, SOM dynamics differ between plant communities, leading Vetterlein and Hüttl (1999) to question whether or not applied organic amendments had the same quality, and thus the same function, as that in natural ecosystems. Reclamation guidelines require the re-establishment of vegetation within the natural range of ecotypes and wildlife capability similar to predisturbance conditions (Government of Alberta, 1993). Therefore, measures to solely increase SOM stocks as a proxy for successful reclamation may not always relate to the success of ecosystem rehabilitation. A more robust indicator of the generation of a natural ecosystem is the development of SOM accumulated through litter production from new vegetation (Vetterlein and Hüttl, 1999).

Reclamation practices following open pit mining in the Athabasca oil sands region (AOSR; Alberta, Canada) typically include reconstruction of soil-like profiles using a combination of native soil material, industrial by products and fertilizer. Peat (derived from *Sphagnum* spp.) is in plentiful supply in the region and is the major organic amendment used, specifically for its ability to decrease bulk density and increase moisture retention whilst increasing organic nutrient supply (Fung and Macyk, 2000). The AOSR lies within the western boreal forest, a region characterised by a mosaic of upland pioneering *Populus tremuloides* Michx. (trembling aspen) and slower growing *Picea glauca* (Moench) Voss (white spruce), with *Pinus banksiana* Lamb. (jack pine) on the drier sites (Macdonald et al., 2012). A near natural mixture of canopy cover by these three trees is the ultimate objective of the forest reclamation treatment. Novel ecosystems, as defined here, are those composed of reclaimed stands growing on anthropogenically reconstructed soil. Research in the AOSR has investigated the characteristics of SOM in a survey of reclamation and natural stands from long term soil and vegetation monitoring plots (LTMPs) and in a series of reclaimed stands that had been capped with peat (20–50 cm) and planted with the target tree species (Turcotte et al., 2009; Sorenson et al., 2011). Turcotte et al. (2009) compared changes in the characteristics of the light fraction of SOM in the LTMP using semi-quantitative solid-state nuclear magnetic

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resonance spectroscopy (NMR) as this fraction has been shown to be sensitive to cultivation and management practices (Six et al., 2002). NMR revealed that the novel sites had a significantly higher proportion of the whole spectral area in the O-alkyl C region (45–112 ppm), i.e. carbohydrate, whilst the natural sites displayed a significantly higher proportion in the alkyl region (30 ppm), i.e. aliphatic lipids. The authors suggested that the O-alkyl/alkyl ratio may be a good indicator of an overall system shift in the macromolecular chemistry of the organic matter (OM) between end member conditions, i.e. novel and natural ecosystems. However, the source of the OM as either the organic amendment, i.e. peat, or novel input from the colonising trees could not be confirmed. Vegetation biomarkers have been used in the Canadian prairies to investigate land-use change (Schnitzer et al., 2006) and sources of OM in grassland and forest soils (Otto and Simpson, 2006). To differentiate between OM sources using vegetation biomarkers could provide an important indicator of the development of true forest carbon dynamics.

Lipids are a minor component of soil [e.g. 4–8% of soil organic carbon (SOC)] but their functional diversity confers a variable rate of degradation/transformation that may be exploited to obtain quantitative information about soil processes (Bull et al., 2000). The *n*-alkanes of the epicuticular wax of vascular plants have distinctive distributions ($\geqslant C_{21}$) with a strong odd/even predominance (Eglinton and Hamilton, 1967) and are considered to be resistant to degradation (Derenne and Largeau, 2001). The greatest proportion of soil lipids originates directly from the local vegetation (van Bergen et al., 1997); therefore, the dominance of particular *n*-alkanes in surface soil horizons can provide chemotaxonomic and quantitative information on local plant input (Jansen et al., 2006). Jansen et al. (2006) found that the extractable straight chain lipid concentration in roots was generally much lower than in leaves of the same species and were in many cases less specific, so they recommended the use of leaf *n*-alkanes as the biomarkers of choice for plant input to soil. The dominance of specific *n*-alkanes in the leaf epicuticular waxes of major contributing plant species are typically C_{29} and C_{31} in monocots (Maffei, 1996a), C_{27} in woody species (Lockheart et al., 1995) and C_{23} and C_{25} in *Sphagnum* spp. (Baas et al., 2000). Consequently, soils are normally characterised by corresponding high proportions of these vegetation biomarkers for grassland soils (van Bergen et al., 1997; Jansen et al., 2006), forest soils (Marseille et al., 1999; Vancampenhout et al., 2009; Trendel et al., 2010) and *Sphagnum* spp. peat (Bingham et al., 2010), respectively. Thus, *n*-alkanes have been used to quantify the contributions of different sources of terrestrial OM in contemporary soil studies (Bull et al., 2000; Jandl et al., 2012), oceanic and lacustrine sediment research (Eglinton and Eglinton, 2008) and palaeoclimate investigations (Nott et al., 2000; Bingham et al., 2010) using established gas chromatography (GC) methods.

The re-establishment of a near-natural forest is the ultimate objective of reclamation strategies for the AOSR. Because of the fundamental role of SOM in ecosystem functioning (Schmidt et al., 2011), we hypothesised that the progression of long chain *n*-alkane signatures in reconstructed soils towards those of soils from natural sites of the same ecotype would indicate the advancing state of SOM development along chronosequences since reclamation began. Specifically, we hoped to observe a transition from the dominance of peat biomarkers (C_{23} and C_{25}) to woody biomarkers (C_{27}) from early (1 yr) to mid (< 30 yr) succession, that would correlate with the O-alkyl/alkyl ratio values described by Turcotte et al. (2009) and provide evidence for the source species contributing to the change in NMR spectra. Therefore, to test our hypothesis, we extracted and quantified *n*-alkanes from a chronosequence of soils from the AOSR to investigate the relationship between specific environmental variables (including ecosite classification, soil type, dominant vegetation and stand age) and *n*-alkane abundance and distribution.

2. Material and methods

2.1. Field sampling and preparation

Detailed site descriptions and sampling procedures have been described in full by Turcotte et al. (2009). Briefly, soil samples from natural and novel ecosystems were collected from the LTMPs to span the range of ecological conditions in the region within a 100 km radius of Fort McMurray (Alberta, Canada; Table 1). Ecosites representing natural ecosystems were classified on the basis of the Central Mixedwood Subregion of the Boreal Forest Region and included a range of tree cover with *P. tremuloides*, *P. glauca* and *P. banksiana* in pure or mixed stands (Beckingham and Archibald, 1996). Ecosites were chosen to span a range of nutrient regimes from less productive ecosites (e.g., a1, b1), on drier, nutrient poor, coarse textured Dystric Brunisol (FAO: Dystric Cambisol) soils, to those with a greater moisture content and richer nutrient regime (e.g., d1, d2), on fine textured Grey Luvisols (FAO: Albic Luvisols; Soil Classification Working Group, 1998). Reclaimed stands representing novel ecosystems on reconstructed soils were classified according to the six representative treatments of reclamation practices in the AOSR and included a similar range of tree cover. All treatments were capped with 20 cm of a mixture of salvaged peat (25–50% by volume) and mineral material. Treatment varied in the composition of material below 20 cm, with combinations of: pure tailings sand (H), salvaged mineral soil and tailings sand (A), salvaged mineral soil and geological substrate (E), pure geological substrate (I) and peat and mineral soil combination directly placed from an undisturbed site to the reconstructed landscape (B). Three plots of each ecosite type (a1, b1, b3, d1, d2, d3) were randomly selected ($n = 3$) from the LTMPs, to represent natural ecosystems and at least four reclaimed sites of each treatment were selected (A, B, E, H, I) to represent novel ecosystems (Table 1). At each plot, surface soil samples (0–10 cm from below the fresh litter layer) were randomly collected from 10 locations around the edge of the permanent LTMP using a trowel. The soils were then composited to one representative sample per plot. Soil samples were sieved to 4 mm, oven dried at 65 °C and finely ground with a ball mill before analysis of total organic carbon (TOC) concentration via dry combustion using a Costech ECS 4010 Elemental Analyzer (Costech Analytical Technologies Inc., Valencia, USA).

Peat material, representative of the material used in novel ecosystem construction, was collected as a composite sample from the top 10 cm of an Organic or Histosol from a representative *Sphagnum* peatland within the LTMP area in 2003, air dried and stored. Additional vegetation in the peatland included *Picea mariana* (Mill.) Britton, *Larix laricina* (Du Roi) K. Koch, *Vaccinium vitis-idaea* L., *Betula glandulosa* Michx and *Salix* spp. leaves were collected directly from a random selection of a dozen *P. tremuloides* trees on a novel ecosystem site within the radius of LTMPs in September 2010, air dried and ground using a ball mill to a fine powder. Needles of *P. banksiana* and *P. glauca* were collected from trees of Canadian origin from Bedgebury Pinetum (UK) in November 2012, oven dried at 85 °C and finely ground with a ball mill.

2.2. Extraction and analysis

The leaves and soils were extracted according to Bull et al. (2000). Samples (0.5–3.0 g) were Soxhlet extracted with dichloromethane (DCM) and Me_2CO (9:1) for 24 h. A known amount of C_{34} *n*-alkane was added as an internal standard before extraction. The extract was evaporated to dryness and hydrolysed with