ELSEVIER

Soil Biology & Biochemistry 40 (2008) 515–527

Soil Biology & Biochemistry

www.elsevier.com/locate/soilbio

FTIR spectroscopy can be used as a screening tool for organic matter quality in regenerating cutover peatlands

Rebekka R.E. Artz[a,*], Stephen J. Chapman[a], A.H. Jean Robertson[a], Jacqueline M. Potts[b], Fatima Laggoun-Défarge[c], Sébastien Gogo[c], Laure Comont[c], Jean-Robert Disnar[c], Andre-Jean Francez[d]

[a] *Soils Group, The Macaulay Institute, Craigiebuckler, Aberdeen AB15 8QH, UK*
[b] *Biomathematics and Statistics Scotland (BioSS), The Macaulay Institute, Craigiebuckler, Aberdeen AB15 8QH, UK*
[c] *Institut des Sciences de la Terre d'Orléans (ISTO), UMR 6113 CNRS/Université d'Orléans, Bt Géosciences, Rue de St Amand, BP 6759, 45067 Orléans Cedex 2, France*
[d] *Interactions Biologiques et Transferts de Matières, UMR CNRS 6553 Ecobio, Université de Rennes 1, 35042 Rennes Cedex, France*

Received 22 September 2006; received in revised form 20 September 2007; accepted 24 September 2007

Abstract

Vegetational changes during the restoration of cutover peatlands leave a legacy in terms of the organic matter quality of the newly formed peat. Current efforts to restore peatlands at a large scale therefore require low cost and high throughput techniques to monitor the evolution of organic matter. In this study, we assessed the merits of using Fourier transform infrared (FTIR) spectra to predict the organic matter composition in peat samples at various stages of peatland regeneration from five European countries. Using predictive partial least squares (PLS) analyses, we were able to reconstruct peat C:N ratio and carbohydrate signatures with reasonable accuracy, but not the micromorphological composition of vegetation remains. Despite utilising different size fractions, both carbohydrate ($<200\,\mu$m fraction) and FTIR (bulk soil) analyses report on the composition of plant cell wall constituents in the peat and therefore essentially reveal the composition of the parent vegetational material. The accuracy of the FTIR-based PLS models for C:N ratios and carbohydrate signatures was adequate to allow for their use as initial screening tools in the evaluation of the present and future organic matter composition of peat during monitoring of restoration efforts.

Keywords: Fourier-transform infrared spectroscopy; Peat; Organic matter quality; Carbohydrates; C:N ratio; Organic micro-remains

1. Introduction

Northern Peatlands are composed almost entirely of decomposing plant material and store approximately a third of all soil organic matter (Gorham, 1991) even though their total cover only extends to 3–5% of the global land area. Peat extraction for fuel and horticultural use has steadily diminished this carbon stock, with the largest quantities of peat having been extracted in the mid to late 20th century (Chapman et al., 2003). Various restoration programs have since been designed to encourage revegetation of cut-over peatlands (Gorham and Rochefort, 2003). Although some of these programs have demonstrated that annual gaseous emissions show a return to net carbon sequestration (Tuittila et al., 1999) or at least reduce net emissions (Waddington and Warner, 2001), it is not known how peatland restoration affects the pool of soil organic matter and hence the long-term regeneration of the carbon sequestration potential. Increased losses of dissolved organic carbon (DOC) have been observed from many peatland ecosystems in the past decades (Freeman et al., 2001), and some of this can be ascribed to increased turnover of the soil organic matter (Glatzel et al., 2003). Currently, monitoring efforts of the evolution of soil organic matter quality during restoration of peatlands have

---

[*] Corresponding author. Fax: +44 1224 498207.
E-mail address: r.artz@macaulay.ac.uk (R.R.E. Artz).

0038-0717/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.soilbio.2007.09.019

only a limited array of tools. Generally, bulk measures such as total and soluble organic carbon and nitrogen, and their ratios, have been most often used to assess restoration success (Andersen et al., 2006; Comont et al., 2006). Similarly, a technique often employed in peat organic matter compositional studies is analysis of the patterns of carbohydrate monomers derived from plant cellulose and hemicelluloses as these are indicative of the source plant composition and the preservation status of these remains (Cheshire, 1979; Moers et al., 1989, 1990; Bourdon et al., 2000). Comont et al. (2006) used peat C:N ratios combined with micromorphological and carbohydrate composition of peat in a pioneering study to elucidate the evolution of organic matter with regeneration. These techniques, however, are expensive and time consuming processes. Fourier Transform Infrared (FTIR) spectroscopy is a commonly used technique capable of distinguishing the principal chemical classes in soil organic matter, such as carbohydrates, lignins, cellulose, fats and/or lipids and proteinaceous compounds, through the vibrational characteristics of their structural chemical bonds. The use of attenuated total reflectance accessories, in particular those utilising very hard crystals such as diamond, has further advanced the use of FTIR in soils and other solid residues. Dilution with KBr is no longer necessary, reproducibility is increased and the nondestructive nature of this analysis allows the sample to be re-used for other analyses. FTIR spectroscopy has been used successfully on whole soils to describe the status of decomposition in different horizons (Haberhauer and Gerzabek, 1999; Haberhauer et al., 1998; Chapman et al., 2001), for example through following the reduction of the carbohydrate markers with depth. Using multivariate statistics, FTIR data can be used as quantitative indicators of the composition of the soil organic matter to distinguish soil horizons (Haberhauer et al., 1999, 2000). Models utilising partial least squares (PLS) analysis have been applied to FTIR data to predict various chemical and physical qualities of organic materials, including studies of the lignin and carbohydrate contents of wood and woody peat (Durig et al., 1988; Tucker et al., 2001; Bjarnestad and Dahlman, 2002) and the phenolic and carbohydrate contents of food (e.g. Coimbra et al., 2005). This study investigated the potential use of FTIR spectroscopy data as indicators of peat organic matter quality in regenerating peatlands. We determined various chemical and micromorphological characteristics of peat samples from profiles at sites at different stages of regeneration from five cutover European peatlands and tested the power of PLS analysis using FTIR data to predict these organic matter characteristics. In large-scale restoration projects, it would be advantageous to be able to use low cost and high throughput techniques in order to assess the success of restoration efforts. Our results are therefore discussed with respect to the utility of FTIR spectroscopy coupled to predictive PLS in the assessment of organic matter quality with peatland regeneration.

2. Materials and methods

2.1. Sampling procedure

Nineteen sites within gradients of unaided regeneration were selected in previously cut-over peatlands in five countries in Europe (Table 1). Single cores were obtained from each site with a double-skinned peat corer (to avoid compaction) and were sectioned into four horizons of different stages of decomposition. The horizons were designated horizons 3 (surface layer 0–5 cm), 4 (5–10 cm), 6 (22.5–27.5 cm) and 8 (42.5–47.5 cm). Where horizon 3 samples contained a mixture of new vegetation and cut surface peat, only the vegetation layer was sampled. Samples were cut into 1 cm^3 subsamples and the subsamples mixed to ensure homogeneity. Portions were shipped on ice packs to partner laboratories for the relevant analyses contributing to this study. Samples where not all analyses could be completed due to low sample size were excluded from statistical analyses, reducing the dataset for statistical analyses to $n = 13$ for horizon 3, $n = 18$ (horizon 4), $n = 18$ (horizon 6) and $n = 18$ (horizon 8; except for carbohydrates, where $n = 17$).

2.2. FTIR spectroscopy

Spectral characterisation of peat samples was performed by diamond attenuated total reflectance (DATR) FTIR spectroscopy using a Nicolet Magna-IR 550 FTIR spectrometer (Thermo Electron, Warwick, UK) fitted with a potassium bromide beam splitter and a deutroglycine sulphate detector. A DATR accessory, with a single-reflectance system, was used to produce transmission-like spectra. The samples were dehydrated by freeze drying and powdered by ball milling with zirconium balls. Samples were placed directly on a DATR/KRS-5 crystal and a flat tip powder press was used to achieve even distribution and contact. Spectra were acquired by averaging 200 scans at 4 cm^{-1} resolution over the range 4000–350 cm^{-1}. A correction was made to spectra for the ATR to allow for differences in depth of beam penetration at different wavelengths (Omnic software, version 7.2, Thermo Electron). All spectra were also corrected for attenuation by water vapour and CO_2. Minor differences in the amplitude and baseline between runs were corrected by normalisation of the data by subtraction of the sample minimum followed by division by the average of all data points per sample. First and second derivatives were calculated to determine and test correlations of organic matter variables which formed 'shoulders' rather than distinct peaks in the FTIR profiles. Occasionally, spectral signals from silicate minerals were observed in a few samples from sites on, or close to, nearly exhausted peatlands A notable example is shown in Fig. 1A in the Scottish sample from an advanced stage of regeneration at horizon 6 (22.5–27.5 cm depth), which shows the diagnostic peaks at 3700 and 467 cm^{-1} of kaolinite. Mineral interference also manifests itself in the