Spectroscopic investigation of soil organic matter composition for shelterbelt agroforestry systems

Gurbir Singh Dhillon [a,*], Adam Gillespie [b,c], Derek Peak [a], Ken C.J. Van Rees [a]

[a] Department of Soil Science, University of Saskatchewan, 51 Campus Drive, Saskatoon, SK S7N 5A8, Canada
[b] Canadian Light Source (CLS), 44 Innovation Blvd., Saskatoon, SK S7N 2V3, Canada
[c] Ontario Ministry of Agriculture, Food and Rural Affairs, 1 Stone Road West, Guelph, ON, N1G 4Y2, Canada

ARTICLE INFO

ABSTRACT

While the role of agroforestry systems in increasing soil organic matter (SOM) storage has been studied, insufficient information is available on their effect on the chemical composition of SOM. The objective of this study was to determine the carbon (C) functional group chemistry of SOM for shelterbelts and compare it to the adjacent agricultural fields by using attenuated total reflectance Fourier transform infrared (ATR-FTIR) and Carbon *K*-edge X-ray absorption near edge structure (XANES) spectroscopies. ATR-FTIR spectral analysis indicated larger proportions of conjugated carboxylic and aromatic C groups for hybrid poplar, white spruce and caragana shelterbelts, phenolic C for hybrid poplar and Manitoba maple shelterbelts and aliphatic and aromatic C for Manitoba maple shelterbelts compared to the adjacent agricultural fields. Polysaccharide, ether and alcoholic C functional groups were generally lower for shelterbelts compared to agricultural fields, with the exception of hybrid poplar species. Analysis by C *K*-edge XANES spectroscopy on a subset of soils showed the accumulation of aromatic C, ketones and carbohydrates in the surface soil layer (0–5 cm) for the shelterbelts compared to agricultural fields. Pearson correlation analysis indicated that the majority of SOM added under the shelterbelts was in the form of plant-derived aromatic, phenolic and carboxylic C groups. The results of this study suggested that the initial composition of litter and its decomposition rate had a strong influence on the composition of SOM under the shelterbelts. The higher proportion of processed forms of SOM, such as ketones, indicated that the SOM for shelterbelts was at a more advanced stage of decomposition compared to agricultural fields; likely due to the surface deposition of litter under shelterbelts.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Soil organic matter (SOM) is composed of diverse and heterogeneous organic substances that vary in structure and chemical complexity (Piccolo, 2002; Sutton and Sposito, 2005). Biological stability of SOM is dependent on its physical accessibility to microorganisms and their degradative enzymes, as well as on the inherent recalcitrance of SOM to microbial decomposition linked to its molecular structure and composition (Sollins et al., 1996; Six et al., 2002). While the role of the chemical composition of SOM in determining its turnover and storage has recently been debated (Schmidt et al., 2011; Dungait et al., 2012), it is nevertheless an important factor in regulating soil carbon (C) dynamics, especially during the initial phase of decomposition process, and in the surface soil layers (Krull et al., 2003; von Lützow et al., 2006). Advanced molecular-scale analytical techniques, such as attenuated total reflectance Fourier transform infrared (ATR-FTIR) and X-ray absorption near edge structure (XANES) spectroscopies may be useful in the characterization of chemical composition of SOM (Lehmann and Solomon, 2010). FTIR is a form of vibrational spectroscopy, that allows for the determination of principal chemical forms of organic compounds, through the vibrational characteristics of their structural chemical bonds (Artz et al., 2008). XANES, also known as near edge X-ray absorption fine structure (NEXAFS), is an X-ray absorption spectroscopic (XAS) technique, that employs synchrotron-based soft x-rays (photon energy <2000 eV) for excitation of core level electrons to unoccupied or partially occupied molecular orbitals, thus producing unique absorption spectra for the elements

(Lehmann et al., 2009). These absorption spectra can be used to assess the speciation and functional group chemistry of the specific elements such as C (Lehmann and Solomon, 2010). The knowledge of the structural characteristics of C and its speciation, obtained through techniques such as ATR-FTIR and Carbon *K*-edge XANES, can be used to determine the role of structural moieties to the inherent recalcitrance of organic matter (Lehmann et al., 2005) as well as to investigate the effect of land use and management practices on the composition and dynamics of organic C at molecular scale in the soils (Solomon et al., 2005, 2007).

Agroforestry practices, such as shelterbelts, are expected to influence not only the quantity of SOM (Nair et al., 2009), but also its quality and composition. Incorporation of shelterbelts into agricultural fields changes the quality of litter inputs (Lorenz and Lal, 2014), which may persist through the decomposition process leading to the differences in the molecular nature of SOM (Wickings et al., 2012). Shelterbelts also modify microclimatic conditions such as soil moisture and temperature (Kort, 1988; Scholten, 1988; Brandle et al., 2004), which may influence microbial decomposition, thus altering SOM composition (Davidson and Janssens, 2006; Hilli et al., 2008). Despite the importance of molecular composition in regulating soil C dynamics and sequestration (Krull et al., 2003), there is a lack of information on the effect of agroforestry practices on the composition of SOM. This study, therefore, attempts to explore the changes in SOM chemistry due to the incorporation of shelterbelts in agricultural fields using combined application of ATR-FTIR and C *K*-edge XANES spectroscopies. We examined the molecular composition of SOM for different shelterbelt species, including hybrid poplar, green ash, Manitoba maple, caragana, white spruce and Scots pine, and their adjacent agricultural fields up to 50 cm soil depth, in order to elucidate the effect of shelterbelts on SOM composition.

2. Materials and methods

2.1. Site selection and soil sampling

Sampling was performed for six major shelterbelt species - green ash (*Fraxinus pennsylvanica*), hybrid poplar (*Populus* spp.), Manitoba maple (*Acer negundo*), white spruce (*Picea glauca*), Scots pine (*Pinus sylvestris*) and caragana (*Caragana arborescens*). Saskatchewan has 106 ecodistricts, as defined by the National Ecological Framework for Canada, and they were grouped into 31 homogeneous clusters, based on the similarity between 42 climate, site and soil variables obtained from the National Ecological Framework for Canada and Soil Landscapes of Canada (SLC v3.2) datasets. Among these clusters, the ones with the highest number of trees shipped for shelterbelt planting of a particular species were chosen for sampling of that species, based on the Prairie Farm Rehabilitation Administration (PFRA) tree orders database. A randomized branch sampling (RBS) procedure was applied within the chosen clusters to select sampling sites for each species. In this way, a total of 59 sites were sampled, consisting of 10 sites each for hybrid poplar, Manitoba maple and caragana shelterbelts, 11 sites for Scots pine shelterbelts and nine sites for green ash and white spruce shelterbelts (Fig. 1). The procedure for selection of sampling sites has been described in more detail in Amichev et al. (2015, 2016).

At each site, soil samples were obtained at three locations, 20 m apart, along a transect in the shelterbelt and in adjacent agricultural field, for a total of three samples from the shelterbelt and agricultural field, each. Sampling within the agricultural fields was performed at more than twice the height of shelterbelt trees, ranging from 50 to 100 m apart from shelterbelt, to avoid the influence of shelterbelts. Soil samples were collected at 0–5, 5–10, 10–30 and 30–50 cm depths using a hand auger (6.58 cm dia.), air-dried at room temperature and ground to <250 μm in size prior to laboratory analysis.

2.2. Analysis by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy

Chemical composition of SOM for shelterbelts and agricultural fields was investigated by using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. A Bruker Optics Equinox 55 FTIR spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector was used for ATR-FTIR spectra acquisition of the finely ground whole soil samples. The spectra were collected by averaging 128 scans at 4 cm^{-1} resolution over a spectral range of 4000–400 cm^{-1} and were corrected against the spectrum with ambient air as background. Baseline correction of the spectra was performed using OPUS (ver. 6.5, Bruker Optik GmbH, Ettlingen, Germany) spectral processing software package.

The ATR-FTIR spectra of the mineral soils under shelterbelts and agricultural fields showed a number of characteristic major absorbance bands representing different functional groups in SOM (Fig. 2). Absorbance of the broad band at about 3600–3000 cm^{-1} arises from O—H stretching and is strongly influenced by water content (Ellerbrock et al., 2005), which may vary between the analysed soil samples. Hence, the relative intensity of this band was not considered in the present study. The spectral region between 2700 and 1800 cm^{-1} was excluded from the analysis because the information attributable to organic matter is masked by C—O noise from $CO_2(g)$ (Roman Dobarco, 2014). Similarly, the bands from 900 to 400 cm^{-1} are predominantly attributed to soil minerals (Haberhauer et al., 2000). Hence, the wavenumber range of 1800–900 cm^{-1} was considered for the analysis of C functional groups in this study. As there is a strong overlap among the bands of organic functional groups within this wavenumber range, the individual bands were resolved by spectral deconvolution. To resolve the spectra into individual bands, a series of Gaussian curves were fit to the infrared spectra using the Fityk software package (version 1.2.1; Wojdyr, 2010). Spectral deconvolution could be performed for only 54 of the 59 sites, as the ATR-FTIR spectra of the other 5 sites were of poor quality. Analysed sites included 11 sites for Scots pine, 10 sites for Manitoba maple, nine sites for hybrid poplar and green ash, eight sites for caragana and seven sites for white spruce shelterbelts. The curve parameters were constrained to ensure equal FWHM (full width at half maximum) of the curves. Individual spectral band identification was performed by using the second-degree spectral derivatives of the ATR-FTIR bands, along with the available knowledge of characteristic infrared peak positions of soil organic compounds as reported in the literature. The relative absorbance intensity (rA) of the deconvoluted bands was calculated by dividing the area of individual bands within the 1800–900 cm^{-1} wavenumber region (i.e. 917, 986, 1037, 1103, 1162, 1250, 1370, 1434, 1509, 1584, 1644, 1703 cm^{-1}) with the sum of total area of all the bands in this region (e.g., $rA_{1509} = A_{1509}/\Sigma A_{(917-1703cm^{-1})}$). Arithmetic means of the relative intensities of the absorption bands for three soil samples, collected at each sampling site, were calculated for each band to obtain the representative relative intensities of the bands for all sites ($n = 54$). The intensity of absorption bands depends on the amount of absorbing functional groups such that high absorption intensity indicates high content of the corresponding functional group and vice versa (Ellerbrock et al., 1999). Thus, the relative intensity of the bands was used as a semi-quantitative estimate of the relative proportion of C functional group within the soil sample.

2.3. Analysis by carbon K-edge X-ray absorption near edge structure (XANES) spectroscopy

X-ray absorption near edge structure (XANES) spectroscopy was used to investigate the SOM composition at the Carbon *K*-edge for three shelterbelt sites belonging to hybrid poplar, Scots pine and