Geoderma xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Evaluation of pre-treatment procedures for improved interpretation of mid infrared spectra of soil organic matter

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ARTICLE INFO

Article history:
Received 1 November 2015
Received in revised form 7 April 2016
Accepted 9 April 2016
Available online xxxx

Keywords:
Mid infrared spectroscopy
Spectral subtraction
Dry ashing
Sodium hypochlorite treatment
Hydrofluoric acid treatment
Soil organic matter composition

ABSTRACT

This study evaluated the effectiveness of dry ashing of soils and subsequent spectral subtraction procedure in comparison with alternative chemical methods in accentuating organics for diffuse reflectance infrared Fourier transform (DRIFT) spectroscopic analysis of soil organic matter composition. Chemical oxidation of soil with sodium hypochlorite (NaOCl) and demineralisation by hydrofluoric acid (HF) treatment were assessed as possible alternatives to the dry ashing method. Surface samples (0–10 cm) of four contrasting soils i.e., Ferralsol, Luvisol, Vertisol and Solonetz were used in the study. We observed the spectral changes before and after pre-treatments using DRIFT spectroscopy of bulk soils and their respective four separated density fractions (<1.8, 1.8–2.2, 2.2–2.6, and >2.6 g cm^{-3}). Dry ashing of soils altered the absorption bands of gibbsite and goethite in the Ferralsol; however, phyllosilicate bands in the Luvisol, Vertisol and Solonetz remained largely unaffected. The organic bands were incompletely removed by the dry ashing method and shifts in some major organic bands were also noticed. Thus the accuracy of the dry ashed spectral subtraction was limited due to the mineral and organic bands alteration. The NaOCl treatment oxidised labile organic carbon (OC) (e.g., aliphatics) without any mineral alteration, but the rest of the OC fractions remained largely unaffected. Therefore, the result of spectral subtraction of the NaOCl treated samples from original spectra was ambiguous. The HF treatment removed minerals efficiently from both bulk soils and density fractions, which noticeably highlighted the organic bands with little or no mineral interferences in the spectra of the treated samples. HF treatment also removed a small portion of the total OC that was associated with minerals. We conclude that HF treatment was more effective than dry ashing and NaOCl oxidation to accentuate organics in the soil DRIFT spectra, since it provided mineral interference free spectra with in general least affected organic bands. Thus, HF treatment of soil offers a potential pre-treatment method for improved spectroscopic characterisation of soil organic matter.

1. Introduction

Mid infrared (MIR) spectroscopy is a fast and non-destructive technique for assessing soil organic matter (SOM). This technique relies on the information derived from the interaction between the electromagnetic radiation and molecular bonds within the functional groups of SOM (Ellerbrock and Gerke, 2013; Calderón et al., 2011; Janik et al., 2007; Nguyen et al., 1991). The spectroscopic technique is capable of quantifying soil organic carbon (OC) and nitrogen (N), and other properties of soils when combined with chemometric methods (Zimmermann et al., 2007). A clear understanding of the qualitative and quantitative properties of SOM is important as such properties have significant implications on the turnover and dynamics of carbon (C) and the global C cycle (Gleixner et al., 2002; Lal, 2004). The application of MIR spectroscopy to characterise SOM composition in bulk soils is however limited due to the interference of dominant signals from the soil mineral components (Baldock and Broos, 2011). Even in organic matter (OM) rich soils, minerals can obstruct spectral assignment and their interpretation (Reddy et al., 2008; Reeves, 2012). For example, in soil spectra at the region smaller than 1050 cm^{-1}, multiple strong absorption bands of both silica (Si—O) and clays (O—H) occur which may overlay with the C—O stretching band of polysaccharides at 1080–1040 cm^{-1} (Calderón et al., 2011; Parikh et al., 2014).

Removal of OM from soil samples through thermal oxidation, followed by the subtraction of ashed soil spectrum from the original soil spectrum accentuates organic bands in the spectrum that better enables the characterisation of SOM functional groups (Calderón et al., 2011; Chefetz et al., 1998; Kaiser et al., 2007; Sarkhot et al., 2007). The assumption behind this procedure is the complete elimination of OM from the soil sample after thermal treatment with minimum effect on mineral structures. However, the accuracy of the subtracted spectra might be compromised by the thermal alteration of both mineral and organic components in the sample (Kamau-Rewe et al., 2011; Parikh

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http://dx.doi.org/10.1016/j.geoderma.2016.04.008
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Please cite this article as: Yeasmin, S., et al., Evaluation of pre-treatment procedures for improved interpretation of mid infrared spectra of soil organic matter, Geoderma (2015), http://dx.doi.org/10.1016/j.geoderma.2016.04.008

et al., 2014). As an example, the modification of oxide mineral phases by heating to 350 °C (Mikutta et al., 2005; Siregar et al., 2005) and artefacts in the organic bands after heating to 420 °C (Heller et al., 2015) were reported.

These limitations necessitate finding alternatives to dry ashing procedure for the spectroscopic analysis of SOM (Margenot et al., 2015; Reeves, 2012; Yang, 2014). Chemical oxidation of soil can be performed using oxidising agents, such as hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl) and disodium peroxodisulphate ($Na_2S_2O_8$) to remove OM. Among these oxidising chemicals, NaOCl is the most widely used because of its efficiency in removing SOM with little or no effect on minerals (Mikutta et al., 2005; Zimmermann et al., 2007). The results from several studies have reported between 19 and 96% OC removal by the NaOCl treatment from soils (Favilli et al., 2008; Kaiser et al., 2002; Mikutta et al., 2005; Siregar et al., 2005). The NaOCl oxidation method was first proposed for the mineralogical analysis of soils (Anderson, 1963) and subsequently the method has been used for multiple purposes such as, extraction of metals associated with SOM, metal sorption studies and to isolate a stable fraction of SOM (Kaiser et al., 2002; McDowell and Condron, 2001). However, few studies have explored using NaOCl oxidation as an alternative to the dry ashing method (Margenot et al., 2015; Reeves, 2012; Yang, 2014) for the MIR spectroscopic study of SOM. Yang (2014) concluded that both the dry ashing and chemical oxidation (NaOCl, H_2O_2 and $Na_2S_2O_8$) techniques are inappropriate for accurate interpretation of SOM spectra. However, Margenot et al. (2015) found the NaOCl oxidation method more effective in removing organics than the dry ashing for SOM spectroscopic analysis. However, these studies have used either pure soil minerals (Reeves, 2012), non SOM + humic acid extracts (Yang, 2014), or soils with similar mineralogy (Margenot et al., 2015; Reeves, 2012). So, there is a lack of understanding about the effectiveness of thermal and chemical oxidation methods for spectroscopic analysis of SOM in natural soils with contrasting mineral composition.

In addition to the oxidation of SOM, the removal of mineral or demineralisation of soil with hydrofluoric acid (HF) treatment can also be used for the spectroscopic analysis of SOM. The HF pre-treatment is commonly employed for solid state ^{13}C NMR spectroscopy of SOM; the treatment enhances the resolution of organic signals by removing the paramagnetic compounds and concentrating C in the sample (Rumpel et al., 2006; Skjemstad et al., 1994). Most of these studies reported negligible or no loss or alteration of C (Goncalves et al., 2003; Mathers et al., 2002; Schmidt et al., 1997; Skjemstad et al., 1994). Conversely, it was shown that HF can isolate mineral bound OM fraction by removing the minerals from the sample along with the OM associated with the mineral phase (Dai and Johnson, 1999; Eusterhues et al., 2007; Kaiser et al., 2002; Rumpel et al., 2008) and this OM removal was influenced by soil types (Eusterhues et al., 2007). However, Rumpel et al. (2006) observed improvement in organic bands in the spectrum of a mineral rich sample after HF treatment and suggested using HF as a pre-treatment for MIR study of SOM. To the best of our knowledge, there are only few studies where HF treatment has been used to improve MIR spectra for SOM characterisation (Dick et al., 2006; Lima et al., 2009; Poirier et al., 2005; Rumpel et al., 2006). These researchers have used single soil type (e.g., Luvisol: Lima et al., 2009; Poirier et al., 2005, and Cambisol: Rumpel et al., 2006) in the study, which raise the necessity to check whether HF pre-treatment is efficient to improve SOM spectra of other soil types.

Therefore, this study was undertaken to compare the effectiveness of dry ashing, chemical oxidation and demineralisation procedures for improving the interpretation of MIR spectra of SOM. Our aims were (i) to examine the effect of dry ashing on mineral spectra and to determine the efficiency in removing OM from contrasting soils, and (ii) to investigate NaOCl and HF treatments as alternatives to the dry ashing method as a pre-treatment for the MIR spectroscopic analysis of SOM. We used four bulk soils with contrasting mineralogy and four density fractions (<1.8 to >2.6 g cm^{-3}) of these soils. The density fractionation was done to separate particulate OM (POM) and distinct mineral-OM assemblages in the soils. This fractionation also helped to avoid the presence of mixed minerals in the samples which might assist to identify the treatments effect more clearly.

2. Materials and methods

2.1. Samples

Surface soils (0–10 cm) from long-term agricultural (pasture and/or cereals) fields were sampled from four sites located in the state of New South Wales in Australia. Each site represents a different soil type with unique mineral composition. The bulk soil samples were air dried, ground and passed through a 2 mm sieve. The detailed site descriptions and general characteristics of the soils are given in Tables 1a and 1b, respectively.

2.2. Methods

2.2.1. Sequential density fractionation of soils

The sequential density fractionation method, adopted from Jones and Singh (2014) and Sollins et al. (2006, 2009), was used to separate bulk soil samples into four density fractions, including <1.8 (POM), 1.8–2.2 (1.8DF), 2.2–2.6 (2.2DF) and >2.6 (>2.6DF) g cm^{-3}. Briefly, 30 g of air dried soil was weighed into a 250 ml centrifuge bottle; 125 ml of sodium polytungstate (SPT) solution with a density of 1.8 g cm^{-3} was added. The mixtures were shaken for 3 h on a horizontal shaker (300 rpm) and the suspension was centrifuged for 30 min at 970 *g*. The materials floating on the top of SPT were extracted under suction and SPT was recovered by filtering the supernatant liquid using 0.7 μm glass fiber filter and returned to the same centrifuge tube. The tube was shaken again for 1 h on a horizontal shaker, centrifuged as described above and the floating material aspirated for a second time. The two aspirated floating materials (POM, <1.8 g cm^{-3}) were combined and rinsed multiple times with deionised water on a 0.7 μm glass fiber filter to remove residual SPT until EC dropped below 50 μS cm^{-1}. The remaining sediment in the centrifuge bottle of the above fraction step was mixed with 125 ml SPT solution of 2.2 g cm^{-3} and the whole process was repeated to obtain the 1.8DF (1.8–2.2 g cm^{-3}). Similarly, the sediment left after 1.8DF extraction was *re*-suspended with 2.6 g cm^{-3} SPT solution, shaken and centrifuged to obtain the 2.2DF (supernatant, 2.2–2.6 g cm^{-3}) and >2.6DF (sediment, >2.6 g cm^{-3}). The only exception was for residual SPT removal from heavier clay rich fractions where washing with deionised water directly done in centrifuge bottles rather than on the filter paper, as fine clays instantly clogged the filter paper pores. After rinsing, all recovered fractions were oven dried at 40 °C, hand ground to a fine powder and stored in glass vial for further analyses.

2.2.2. Dry ashing

The dry ashing of both the bulk soils and density fractions was carried out at 400 °C for 8 h (Kaiser et al., 2007) in a muffle furnace. Sample mass was recorded before and after ashing for further calculations. After ashing, the samples were stored in a desiccator to minimise moisture absorption.

2.2.3. Chemical treatments

2.2.3.1. NaOCl oxidation. The oxidation of the bulk soils and density fractions was performed with 6% NaOCl (pH 8.0) at room temperature following the modified method of Mikutta et al. (2006). Between 15 and 90 mg of sample was mixed with 5 ml of NaOCl, the mixture was shaken on a rotary end-over-end shaker for 6 h, centrifuged and the supernatant was removed. This oxidation procedure was repeated 6 times and after the last treatment, the sediment was washed with deionised

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