Mapping micro-spatial patterns of C, and Fe and Al-oxides in gleysols: A means of understanding SOM-mineral interactions

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Abstract

To fully understand the role of mineral interactions in the sequestration of soil organic matter (SOM) these processes need to be studied at the micro-scales over which they occur. The spatial patterning of iron oxides as a result of redox reactions makes gleysols an ideal medium in which to study such processes. This paper outlines the methods being used in an on-going study of SOM – mineral interaction in gleysols. A combination of soil micromorphology, SEM-EDS, and selective dissolution using oxalate and citrate dithionite on undisturbed soil sections is teamed with sequential extraction of bulk soil samples also using oxalate and citrate dithionite, ICP-OES, FT-IR and CN analysis. The results of this study are still being collected, but will be presented in August once the study is complete.

Key Words

Soil organic matter, mineral interactions, gelysol, stagnosols, micro-analysis

Introduction

The stabilisation of SOM through its interaction with Fe and Al oxides is well documented (Eusterhues *et al.*, 2005; Wagai and Mayer, 2007; Wiseman and Püttman, 2005), but not well understood (Kögel-Knaber *et al.*, 2006). The nature of the interaction between organic matter (OM) and Fe/Al oxides is determined by the chemical characteristics of the OM and the type of mineral phases present. The reactive surfaces of Fe and Al oxides are often presumed to account for sorption and stabilisation of OM (Kaiser *et al.*, 2000), but recent research has suggested that simple sorption processes do not stabilise the bulk of SOC as the maximum sorption ratio of Fe oxides is only 0.22 g OC/1 g of Fe Wagai and Mayer, 2007). Ternary OM - Fe-oxide - clay associations (Wagai and Mayer, 2007) and the formation of unidentified chemical bonds (Spielvogel *et al.* 2008) have been suggested as possible mechanisms for stabilisation.

Gleyed (waterlogged) soils are characterised by highly localised patterns of Fe (hydr)oxides concentration and depletion, related to the reduction and mobilisation of Fe in anaerobic regions and its reprecipitation as Fe (hydr)oxides in oxidising areas of the soil. The spatial and temporal distribution of oxidising and reducing conditions in gleyed soils is linked to groundwater and soil water chemistry, microbial activity, OM distribution, aggregation and void patterns (Lovely, 1991; Ottow, 1970). In a gleyed soil where reducing and oxidising conditions alternate, the microbially mediated reduction and oxidation of Fe (hydr)oxides can lead not only to the stabilisation of carbon but also to its release as dissolved organic carbon (DOC) (Stemmler and Berthelin, 2003), CO_2 and CH_4.

The turnover of carbon in peaty gley soils is, therefore, highly complex with temporal and micro-spatial variation due to localised redox conditions. Few studies have investigated the chemical composition of the OM stabilised by Fe/Al oxides in gleyed soils (Kaiser *et al.*, 2000; Spielvogel *et al.*, 2008), and as far as we can establish, the complex spatial pattern of oxidising and reducing conditions over very small scales has not been considered in previous research using bulk soil chemical properties. Analysis of the distribution of SOC, Fe, Al, and other minerals (e.g. Si and Mn) in undisturbed gley soils over scales of µms to mms, carefully related to bulk SOC chemistry can provide a means of studying the complex processes of SOC chemical stabilisation *in-situ.* To this end the study combines direct micro-spatial analyses and bulk soil chemical techniques to map the relative distribution and concentrations of C, Fe and Al in gleysols in order to study carbon storage associated with Fe oxides and clay minerals and better understand the mechanisms of stabilisation.

Methods

Soils with contrasting hydrological regimes (gleysol, stagnosol and gleyic cambisol) were sampled from an experimental forest, Harwood Forest, Northumberland, UK, in which above and below gound carbon stocks have already been well characterised (Zerva *et al*., 2005). Undisturbed soils samples were taken from the top soil (10-20 cm) and sub soil (20-30 cm) using kubiena tins together with closely spatially associated bulk samples.

Concentrations of Fe, Al and Mn have been determined for bulk soils and extracted bulk soil residues (after microwave-assisted HNO_3/HBF_4 digestion) and for bulk soil and thin section extract solutions using ICP-OES. Bulk soil samples are also being analysed to determine concentrations of weakly and strongly crystalline Fe/Al oxides and associated with organic matter fractions by sequential selective extraction using oxalate and citrate-dithionite. Additionally, to study the chemical characteristics of the stable OM, extract solutions were purified and analysed using FT-IR spectroscopy. Carbon, nitrogen and OM contents were also measured for the bulk soils/residues.

The undisturbed samples were freeze-dried, resin impregnated under vacuum and then bonded to glass slides and lapped to produce thin sections with a thickness of 30 µm following standard procedures (www.thin.stir.ac.uk). Thin sections are currently being described micromorphologically following the terminology of Stoops (2003). Void space, organic matter, and iron depletion and concentration features, such as those shown in Figure 1, are in the process of being mapped and counted using point counting techniques with a spatial interval of 1.5 mm. The range of organic and iron features identified micromorphologically will then be analysed using SEM-EDX to quantify and map C, Fe, and Al distributions. Selective dissolution of the soil thin sections using oxalate and citrate dithionite will be followed by repeat micromorphological examination and SEM-EDX to determine the micro-spatial distribution of weakly and strongly crystalline Fe/Al oxides and their association with soil organic matter.

Figure 1. Amorphous iron oxide impregnation surrounding and within the organic tissues of a partially decomposed root.

Results

This is a scoping study that is on-going (due to report March 2010) hence results to date are preliminary and incomplete, but the final findings of the project will be presented at the WCSS in August 2010 once the study has been completed.

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