Geoderma 293 (2017) 44–53

Contents lists available at ScienceDirect

Geoderma

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

Microscale soil structures foster organic matter stabilization in permafrost soils

Carsten W. Mueller [a,*], Carmen Hoeschen [a], Markus Steffens [a], Henning Buddenbaum [b], Kenneth Hinkel [c], James G. Bockheim [d], Jenny Kao-Kniffin [e]

[a] Lehrstuhl für Bodenkunde, TU München, Freising-Weihenstephan 85356, Germany
[b] Environmental Remote Sensing and Geoinformatics, University of Trier, 54286 Trier, Germany
[c] University of Cincinnati, Department of Geography, Cincinnati, OH 45221, USA
[d] Department of Soil Science, University of Wisconsin-Madison, Madison, WI 53706, USA
[e] Department of Horticulture, Cornell University, Ithaca, NY 14853, USA

ARTICLE INFO

Article history:
Received 24 October 2016
Accepted 24 January 2017
Available online 1 February 2017

Keywords:
Particulate organic matter
Mineral associated organic matter
Micro aggregate
NanoSIMS
SEM
Supervised image classification

ABSTRACT

Organic carbon (OC) stored in permafrost affected soils of the higher northern latitudes is known to be highly vulnerable to ongoing climatic change. Although the ways to quantify soil OC and to study connected C dynamics from ecosystem to global scale in the Arctic has improved substantially over the last years, the basic mechanisms of OC sequestration are still not well understood. Here we demonstrate a first approach to directly study micro scale soil structures mainly responsible for soil OC (SOC) stabilization using nano scale secondary ion mass spectrometry (NanoSIMS). A cross section from a permafrost layer of a Cryosol from Northern Alaska was analysed using a cascade of imaging techniques from reflectance light microscopy (RLM) to scanning electron microscopy (SEM) to NanoSIMS. This allowed for the direct evaluation of micro scale soil structures known to be hot spots for microbial activity and SOC stabilization in temperate soils. The imaging techniques were supported by classical soil analyses. Using this unique set of techniques we are able to evidence the formation of micro-aggregate structures in the vicinity of plant residues in permafrost soils. This clearly indicates biogeochemical interfaces at plant surfaces as important spheres for the formation of more complex soil structures in permafrost soils. Organo-mineral associations from these hot spots of microbial activity were recovered from plant residues (free particulate organic matter, fPOM) as fine grained mineral fraction with a typically low C/N ratio. This nicely illustrates the link between classical bulk analysis and state of the art spectromicroscopic techniques.

1. Introduction

More than twice as much organic carbon (OC) than in the atmosphere is estimated to be stored in permafrost affected soils of the northern hemisphere (Hugelius et al., 2014). Predicted changes in the arctic carbon cycling solely consider the active layer thawing during summer while assuming it as a homogeneous carbon reservoir (Schuur et al., 2008). This is in clear contrast to the known heterogeneity of the composition and spatial distribution of soil OC (SOC) and thus possible future changes in microbial bioavailability (Gentsch et al., 2015; Höfle et al., 2013; Knoblauch et al., 2013; Mueller et al., 2015; Schädel et al., 2014; Vonk and Gustafsson, 2013). It is still not fully understood which mechanisms might replace the climatic stabilization of SOC (reduced mineralization due to low temperatures) (Trumbore, 2009) and thus possibly sustain long term SOC storage in the future with pronounced warming in polar regions. Due to the fact that active layers will deepen and large amounts of buried mostly labile OC (Gillespie et al., 2014; Mueller et al., 2015; Palmtag et al., 2016) might be exposed to more favorable conditions in terms of SOC mineralization. From temperate soils it is known that soil structure plays a vital role for the long term sequestration of OC by the occlusion of particulate organic matter (POM) within aggregates and the association of OC with mineral micro-aggregate structures (Vogel et al., 2014; von Lützow et al., 2008). Although permafrost affected soils are characterized by drastic freeze–thaw cycles leading to the vertical mixing of different soil compartments (cryoturbation), there is growing evidence that soil structural features (e.g. micro-aggregates) also affect SOC sequestration in permafrost affected soils. For instance for soils in northern Alaska and Siberia a substantial amount of particulate SOC was found to be sequestered occluded within aggregated soil structures (Höfle et al., 2013; Mueller et al., 2015). Recent incubation experiments highlighted the contribution and importance of organo-mineral associations for SOC sequestration in soils of the Siberian Arctic, with over 50% of soil OC bound to minerals (Gentsch et al., 2015).

* Corresponding author.
E-mail address: carsten.mueller@wzw.tum.de (C.W. Mueller).

http://dx.doi.org/10.1016/j.geoderma.2017.01.028
0016-7061/

However, these findings are based on bulk analyses which are defined by the destruction of the intact soil structure and thus integrate over a larger volume. To directly study soil structure and elemental distribution together, it is crucial to keep the soil microscale architecture intact (Mueller et al., 2013). The systematic study of intact in-situ soil structures dates back to the micropedological work of Kubiena (1938). Intact soil samples were resin embedded and polished, and pedological features were studied on the resulting thin sections using transmitted light microscopy. Over the years this technique was used to study a wide variety of soils including permafrost affected soils (Bullock and Murphy, 1980; Eickhorst and Tippkoetter, 2008; Fisk et al., 1999; Li et al., 2004; Murton et al., 2015; Pulleman et al., 2005; Smith et al., 1991; Szymanski et al., 2015). But the micromorphological approach is often restricted to the description of structural features due to the limited capabilities of visible light microscopic techniques. With the advent of microscopic techniques resolving soil features together with elemental and molecular information at the nano- to micro-scale (e.g. scanning electron microscopy (SEM), time of flight secondary ion mass spectrometry (TOF-SIMS), nano scale secondary ion mass spectrometry (NanoSIMS)), the micromorphological examination of soils may change from the pure description of soil structures to the identification of materials and analyses of soil processes. Thus, the increased accessibility of spectromicroscopic techniques allows nowadays for the evaluation of micro-scale structural entities and biogeochemical features and processes which determine the long term stabilization of SOC. In the present study we combine the classical micromorphological approach of soil embedding and sectioning with state of the art NanoSIMS to elucidate elemental distributions at soil microenvironments. To account for the spatial representation of the spots analysed at high resolution by NanoSIMS, we used conventional reflectance light microscopy together with supervised image classification. This allowed for the identification of structural domains representing specific biogeochemical interfaces and thus areas which may act as hot spots for SOC stabilization, microbial activity, nutrient sorption and cycling.

2. Materials and methods

2.1. Sampling site and soil material

Samples were taken at the Barrow Peninsula, on the Arctic Coastal Plain in April 2010. For a more detailed description of the sampling campaign see Mueller et al. (2015). The landscape is characterized by a mosaic of drained thaw lake basins with a different age since drainage. For the study we took samples from a soil core (at 71.27786 latitude and 156.44264 longitude) of an Aquiturbel (Soil Survey Staff, 2010), see Table 1 for basic soil properties. The core originated from a drained thaw lake basin of medium age (approx. 50 to 300 years after thaw lake drainage) according to the classification given by Hinkel et al. (2003). The parent material consists of unconsolidated sediments of the Late Pleistocene Gubik Formation (Hinkel et al., 2003). The soil core was obtained using a SIPRE corer attached to a Big Beaver earth drill apparatus (Little Beaver, Inc., Livingstone, TX) mounted on a sledge. The frozen core was further processed in a cold room in Barrow and after horizon description cut into sections of corresponding soil horizons. Samples for general soil properties were dried at 60 °C in an oven in Barrow and subsequently shipped to Germany.

Table 1
Soil properties of the analysed Cryosol core. The embedded soil section was taken from the deepest horizon (Cg/Oabfm).

Horizon	Depth [cm]	Bulk density [g^*cm^{-3}]	OC [mg^*g^{-1}]	N [mg^*g^{-1}]	C/N
Oi1	0–12	0.13	413.5	19.7	21.0
Oi2	12–14	0.27	324.8	14.3	22.7
Cg/Oijj	14–40	0.66	103.5	6.2	16.7
Cg/Oejjfm	40–80	0.60	97.9	6.5	15.0
Cg/Oabfm	80–126	0.67	30.3	1.9	16.4

2.2. Intact sample preparation and NanoSIMS

Subsections of the intact frozen cores were initially dried with acetone (row of different concentration) and then impregnated with a series of Araldite 502:acetone mixtures (1:3, 1:1 (vl:vl)) and finally with 100% Araldite 502 (Araldite kit 502, electron microscope sciences, Hatfield, USA). The blocks (24.5 mm in diameter) were cured at 60 °C for 48 h, cut into thin slices and carefully polished. Due to the insulating properties of the epoxy resin, the epoxy blocks were gold-coated by physical vapour deposition under argon atmosphere prior to SEM and NanoSIMS analysis. Prior to NanoSIMS analysis, the samples were investigated using a reflectance light microscope (further denominated as: RLM; Zeiss Axio Imager Z2) and a scanning electron microscope (SEM; Jeol JSM 5900LV, Freising, Germany) in backscatter electron mode. Due to the flat polishing of the section the material contrast of the backscattered electrons allowed for a good differentiation between organic and mineral compartments while also allowing the identification of soil pores filled with the epoxy resin.

The NanoSIMS images were recorded at the Cameca NanoSIMS 50 L (Gennevilliers, France) of the Lehrstuhl für Bodenkunde, TU München, Germany.

Electron multiplier secondary ion collectors were used for $^{12}C^-$, $^{16}O^-$, $^{12}C^{14}N^-$, $^{28}Si^-$, $^{32}S^-$, $^{27}Al^{16}O^-$ and $^{56}Fe^{16}O^-$. Charging was compensated by an electron beam generated by the electron flood gun of the NanoSIMS instrument. Prior to analysis, impurities and the coating layer were sputtered away by using a high primary beam current.

2.3. Physical soil fractionation

To relate the image data with the distribution of main soil constituents we conducted a combined density and particle size fractionation procedure according to Mueller et al. (2015). Air dried soil material (20 g) was capillary-saturated with sodium polytungstate solution (1.8 g cm^{-3}) and allowed to settle overnight. The floating free particulate organic matter (fPOM) was extracted prior to ultrasonic disruption (Bandelin, Sonopuls HD 2200; energy input of 440 J ml^{-1}) of aggregated soil structures and the recovery of occluded POM (oPOM). Excess salt from POM fractions was removed by washing with deionised water over a sieve of 20 μm mesh size until the electric conductivity dropped below 5 μS cm^{-1}. The procedure yielded two large POM fractions (fPOM, oPOM) and two smaller POM fractions <20 μm ($fPOM_{small}$ and $oPOM_{small}$). Mineral fractions larger than 20 μm were separated by wet sieving, all smaller mineral fractions were obtained by sedimentation. All fractions were freeze-dried, weighed and analysed for C and N content.

2.4. Chemical analyses

For bulk chemical analysis the soil material was ground using a ball mill (Fritsch, Germany, pulverisette 23). Carbon and nitrogen contents were measured in duplicate by dry combustion (EuroVector, Milan, Italy). Due to the absence of carbonates, the measured C concentrations equalled organic C.

2.5. Statistical analyses and image processing

To evaluate the spatial extent of the areas analysed using NanoSIMS, we conducted a supervised maximum likelihood classification (MaxLike) on the RLM image in the image processing software Envi (Version 5.2, ITT Visual Information Solutions). The MaxLike algorithm assumes that the statistics for each class in each band are normally distributed and calculates the probability that a given pixel belongs to a