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Comparison of soil organic carbon speciation using C NEXAFS and CPMAS ^{13}C NMR spectroscopy

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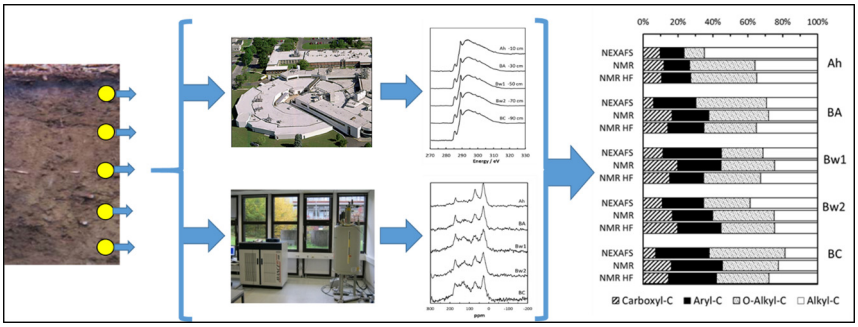
HIGHLIGHTS

- Comparison of soil carbon speciation using C NEXAFS and CPMAS ^{13}C NMR spectroscopy
- Analysis of defined mixtures of SOM sources, organic layer, mineral soil samples
- CPMAS ^{13}C NMR more accurate and precise than C NEXAFS spectroscopy
- C NEXAFS spectroscopy excellent method for analysis of C-poor subsoil horizons
- Combination of both methods: better understanding of SOM speciation and turnover

GRAPHICAL ABSTRACT



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ABSTRACT

We compared synchrotron-based C near-edge X-ray absorption fine structure (NEXAFS) and CPMAS ^{13}C nuclear magnetic resonance (NMR) spectroscopy with respect to their precision and accuracy to quantify different organic carbon (OC) species in defined mixtures of soil organic matter source compounds. We also used both methods to quantify different OC species in organic surface horizons of a Histic Leptosol as well as in mineral topsoil and subsoil horizons of two soils with different parent material, stage of pedogenesis, and OC content (Cambisol: 15–30 OC mg g^{-1}, Podzol: 0.9–7 OC mg g^{-1}). CPMAS ^{13}C NMR spectroscopy was more accurate and precise (mean recovery of different C functional groups 96–103%) than C NEXAFS spectroscopy (mean recovery 92–113%). For organic surface and topsoil samples, NMR spectroscopy consistently yielded larger O-alkyl C percentages and smaller alkyl C percentages than C NEXAFS spectroscopy. For the Cambisol subsoil samples both methods performed well and showed similar C speciation results. NEXAFS spectroscopy yielded excellent spectra with a high signal-to-noise ratio also for OC-poor Podzol subsoil samples, whereas this was not the case for CPMAS ^{13}C NMR spectroscopy even after sample treatment with HF. Our results confirm the analytical power of CPMAS ^{13}C NMR spectroscopy for a reliable quantitative OC speciation in soils with >10 mg OC g^{-1}. Moreover, they highlight the potential of synchrotron-based C NEXAFS spectroscopy as fast, non-invasive method to semi-quantify different C functional groups in soils with low C content (0.9–10 mg g^{-1}).

1. Introduction

The chemical nature of soil organic matter (SOM), namely the speciation of soil organic carbon (SOC, OC), is a key soil property, reflecting

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important SOM formation pathways as well as influencing ecological properties of humic topsoils (Cotrufo et al., 2015). Moreover, SOC speciation provides indicator properties for the SOM decomposition status (Baldock et al., 1997), as well as historic land-use (Chen et al., 2002), or vegetation (Prietzel et al., 2013). Therefore, a fast, accurate, and precise OC speciation in soils is desirable, and numerous methods (*e.g.* CPMAS ^{13}C NMR, Raman or FT-IR spectroscopy; gas chromatography, often after sample extraction, digestion, or derivatization) for the characterization of SOM are widely used. Most methods work fairly well for SOM-rich organic surface layers and humic topsoil horizons, but are less accurate in subsoil horizons with low SOM contents and/or large contents of pedogenic minerals (clay minerals; Fe, Al oxyhydroxides). With their large specific surfaces, these minerals interact strongly with SOM and often preferentially with particular C functional groups (O-alkyl C groups of polysaccharides; Schöning et al., 2005; Spielvogel et al., 2008). The presence of paramagnetic compounds (*e.g.* Fe oxyhydroxides) additionally results in signal broadening and functional group-specific quenching of CPMAS ^{13}C NMR signals, which bias SOM characterization at C:Fe ratios <1 (Arshad et al., 1988; Kögel-Knabner, 1997; Smernik and Oades, 2000; Schöning et al., 2005). Sample treatment with HF dissolves all minerals, resulting in SOM enrichment and removal of paramagnetic Fe oxyhydroxides (Skjemstad et al., 1994; Schmidt et al., 1997). However, it is still a matter of ongoing scientific debate (*e.g.* Sanderman et al., 2017), whether HF treatment yields a residual OM composition representing that before HF treatment or results in preferential removal of specific C functional groups with high affinity to soil oxyhydroxides (O-alkyl C; Schöning et al., 2005; Spielvogel et al., 2008). The deficit in available methods for a fast and reliable speciation of subsoil OM contrasts to the relevance of deep SOM for C sequestration and long-term OC storage in soils (Paul et al., 1997; Rumpel and Kögel-Knabner, 2011).

During recent decades, synchrotron-based X-ray spectroscopy has emerged as a powerful tool for soil analysis, allowing a direct, non-invasive speciation of many elements, including C, in soils (Lehmann and Solomon, 2010). Organic C speciation using this tool has been performed on soil extracts (Scheinost et al., 2001; Solomon et al., 2005; Christl and Kretzschmar, 2007), bulk soil samples (Jokic et al., 2003) and with sub-microspatial resolution also on soil aggregates and colloids (Wan et al., 2007; Lehmann et al., 2008; Keiluweit et al., 2012; Chen et al., 2014a, 2014b). These studies most often were qualitative, *i.e.* they fingerprinted OC speciation differences between soils, soil horizons, or aggregate regions rather than quantifying different C functional groups (*e.g.* Wan et al., 2007; Chen et al., 2014a, 2014b). Moreover, they mostly investigated SOM-rich topsoil rather than SOM-poor subsoil samples. Different C species in soils have also been quantified by C NEXAFS spectroscopy (*e.g.* Scheinost et al., 2001; Jokic et al., 2003; Solomon et al., 2005; Schumacher et al., 2005; Keiluweit et al., 2012). However, it is generally assumed that C NEXAFS spectroscopy performed on soils or soil extracts yields only "semi-quantitative" results, and that a quantitative interpretation of C NEAXFS spectra remains an unresolved challenge for several reasons summarized by Christl and Kretzschmar (2007).

With our study, we aimed to contribute to a reduction of the knowledge deficit concerning the ability of synchrotron-based C NEXAFS spectroscopy to quantify different soil C species. We investigated the accuracy and precision of C NEXAFS spectroscopy for the quantification of different C species in defined mixtures of organic compounds, which are enriched in particular C functional groups. Furthermore, we compared the accuracy and precision of C NEXAFS spectroscopy regarding the quantification of C functional groups in important SOM sources (lignin, cellulose, amino acids) with that of CPMAS ^{13}C NMR spectroscopy. Additionally, we compared the C speciation reported by both methods for surface, topsoil, and subsoil horizons of soils with different parent material, pedogenesis, and OC content.

2. Material and methods

2.1. Preparation of defined mixtures of organic compounds

We investigated the accuracy and precision of synchrotron-based C NEXAFS spectroscopy on two sample sets consisting of different defined mixtures of organic compounds. Set 1 comprised mixtures of four organic compounds specifically enriched in particular C functional groups or bonds between C atoms: **Graphite** (C_∞; consisting of solely aromatic C), **D-glucose** ($C_6H_{12}O_6$; solely O-alkyl C), **Ca formate** ($Ca[HCOO]_2$; solely carboxyl C), and ***L*-cysteine** ($C_3H_7NO_2S$; comprising carboxyl C, alkyl C, and C associated with amino or thiol groups). Set 2 comprised three major constituents of vascular plants, whose degradation products are considered important building blocks of SOM: **Cellulose** ($[C_6H_{10}O_5]_n$; 100% O-alkyl C), **lignin** ($C_9H_{10}O_2$,$C_{10}H_{12}O_3$,$C_{11}H_{14}O_4$; 61% aryl C; 30% O-alkyl C; 8% alkyl C; 1% carbonyl C), and ***L*-cysteine**, the latter representing proteins. Additionally, we included calcium carbonate ($CaCO_3$) as compound in Set 2 to test whether C NEXAFS spectroscopy can quantitate organic and inorganic C in calcareous soils. Cellulose (cotton linter; DP 7000) and lignin (spruce wood, "organocell" [ethanol/NaOH] processed) both were received from the Institute for Wood Research München, the other compounds were purchased from Sigma Aldrich. Seventeen different mixtures of graphite, glucose, *L*-cysteine, and Ca formate (Set 1) as well as 12 different mixtures of cellulose, lignin, *L*-cysteine, and $CaCO_3$ (Set 2) were prepared by careful homogenization in an agate ball Retsch minimill. Percentages of the different constituents in the mixing variants are presented on a C atom basis in Tables 1 and 2.

2.2. Selection and preparation of soil samples

We investigated the OC speciation of three German forest soils using C NEXAFS and CPMAS ^{13}C NMR spectroscopy. The soils differed in parent material, OC concentration, and content of pedogenic Fe minerals. Soil *Fall* (Table 3) is a Histic Leptosol ("Tangelrendzina"; Zech et al., 1985; Prietzel et al., 2013) formed on dolomite bedrock. It is located in the Bavarian Alps at an elevation of 1200 m a.s.l. and stocked with a mature *Picea abies–Abies alba* forest. Due to the cool and moist climate (MAT: 6.4 °C; MAP: 1767 mm), a thick organic surface layer (>40 cm) has accumulated on a shallow Ah horizon upon Triassic "Hauptdolomite" bedrock. From this soil, we sampled the organic surface layers (L, Of, Oh1, Oh2 horizons) and the Ah horizon. Soils *Mitterfels* and *Luess* are both stocked with mature *Fagus sylvatica* forest and have been studied intensively earlier (Lang et al., 2017; Werner et al., 2017a). *Mitterfels* is a Dystric Cambisol formed from Paleozoic gneiss. It is located in the Bavarian Forest at 1023 m a.s.l. The climate (MAT: 4.9 °C; MAP: 1300 mm) is less humid than that at *Fall*. The *Mitterfels* soil has a sand loam texture; it is acidic and has comparably high contents of OC (>15 mg g^{-1}) and Fe oxyhydroxides (Fe_d > 10 mg g^{-1}) in the entire mineral soil down to 90 cm depth (BC horizon; Table 3). We sampled the Ah, BA, Bw1, Bw2, and BC horizons of *Mitterfels*. Soil *Luess* is a Podzol formed from Pleistocene glaciofluvial outwash. It is located in N Germany in the Lüneburger Heide at 115 m a.s.l. Compared to *Fall* and *Mitterfels*, the climate at *Luess* is warmer and drier (MAT: 8.0 °C; MAP: 779 mm). The soil is characterized by a sandy texture, advanced podzolization (Werner et al., 2017a, 2017b) and low subsoil OC contents (<1 mg g^{-1}). We sampled the AE, Bh, Bs, Bw, and CB horizons down to 80 cm. After drying at 45 °C and sieving (<2 mm) the samples were finely ground, and their C speciation was analyzed by C NEXAFS and CPMAS ^{13}C NMR spectroscopy.

2.3. C NEXAFS spectroscopy

For nine pure C-bearing compounds, including those used for preparation of Sets 1 and 2, and additionally citric acid ($C_6H_8O_7$) as well as mannane ($C_{24}H_{42}O_{21}$), we acquired reference C NEXAFS spectra at the