Nature of soil organo-mineral assemblage examined by sequential density fractionation with and without sonication: Is allophanic soil different?

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ABSTRACT

Organic matter (OM) bound to soil mineral particles (higher-density particles) tends to be more stabilized, enriched in ^{13}C and ^{15}N, and has a lower C:N ratio. Yet how these variations in OM chemistry are linked to the nature of organo-mineral assemblage remains poorly understood, especially in allophanic soils where high amounts of OM are stabilized by interactions with reactive inorganic phases such as short-range-order (SRO) minerals. We thus assessed the extent to which the degree of aggregation and its disruption during fractionation control the distribution and chemistry of the soil organo-mineral particles across six density fractions using a volcanic soil (allophanic Andisol) based on selective dissolution, microscopy (SEM), solid-state ^{13}C NMR spectroscopy and $\delta^{13}C$ and $\delta^{15}N$ analyses. Intermediate-density fractions (2.0–2.5 g cm^{-3}) accounted for 63–86% of organic C and N, 73–93% of pyrophosphate-extractable iron and aluminum (Fep, Alp), and 78–95% of oxalate-extractable metals (Feo, Alo) in the bulk soil sample. While air-drying pretreatment had little effect, sonication during fractionation led to (i) fragmentation of both plant detritus and some of the aggregates of 30–100 mm sizes, (ii) release of occluded low-density fraction (<1.6 g cm^{-3}) which largely originated from the aggregates of 1.6–2.0 g cm^{-3} density range, and (iii) redistribution of organo-mineral particles (15–16% of total OM and 7–19% of the extractable metals) within the intermediate density fractions. Positive correlation of Alp with C:N ratio and negative correlation of Alp with $\delta^{15}N$ among the fractions suggest preferential binding of Alp phase (e.g., organo-Al complexes) to decaying plant detritus. Positive correlation of Alo and Feo with $\delta^{15}N$, together with theoretical density calculations of idealistic organo-mineral association modes, suggests that ^{15}N enrichment may be coupled with OM binding to SRO minerals and with the formation of physically-stable aggregates of micron/submicron sizes in accord with our conceptual model (Asano and Wagai, 2014). The general pattern of ^{13}C and ^{15}N enrichment and C:N decline with increasing particle density remained largely unchanged despite the sonication effects detected, indicating that sonication-resistant organo-mineral assemblages largely control the observed patterns. The similarity in the density-dependent changes of OM chemistry between the studied Andisol and the soils with crystalline clay and metal oxide mineralogies in previous studies strongly suggests a common biogeochemical control which deserves further investigation.

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1. Introduction

Cycling of carbon (C) and nitrogen (N) on land is mediated (driven) by microbial transformation of organic matter (OM) during which significant amounts of OM are transferred to soil and stored as organo-mineral assemblages. A variety of mechanisms are responsible for the organo-mineral interactions, from adsorption of dissolved organics and organo-metal coprecipitation at molecular scale to protective effect of mineral matrix or aggregation at larger scales (Baldock and Skjemstad, 2000; Keil and Mayer, 2014; Mikutta et al., 2009; Sollins et al., 1996). Thus, the separation of the multiple mechanisms present

in the physically-heterogeneous mixture has been a major challenge in soil and sedimentary OM studies. In this paper, we use the term "soil particle" to refer to the organo-mineral assemblages present after dispersive energy (e.g., mechanical shaking and sonication) as well as individual particles (mineral crystallite, particulate OM) given the aggregated nature of soil particles even in <0.2 mm fraction for soils rich in phyllosilicate clays (Chenu and Plante, 2006), in crystalline metal oxides (Santos et al., 1989), and in poorly-crystalline minerals (Asano and Wagai, 2014).

The fractionation of soil particles according to their density is an effective approach to examine biogeochemical nature of OM in soils (Christensen, 1992; Lajtha et al., 2014; Schrumpf et al., 2013). Decomposing plant detritus, the OM pool that is relatively labile and more accessible to microbes (e.g., Bird et al., 2008; Wagai et al.,

2013a), can be isolated as low-density fractions (LF) whereas the amorphous OM (e.g., microbial byproducts) associated more strongly to minerals and aggregates is recovered as higher-density fractions (e.g., Kleber et al., 2010; Mikutta et al., 2009). Based on previous studies (Turchenek and Oades, 1979; Kaiser and Guggenberger, 2007a), the two major factors controlling the density of soil particles and their distribution are (i) the absolute density of individual mineral and organic particles, and (ii) the relative amounts of OM and minerals in the case of organo-mineral particles. The absolute density of mineral particles generally ranges between 2.3 and 2.8 g cm^{-3} including allophane and imogolite (2.7–2.8 g cm^{-3}, Wada and Wada, 1977) except for iron oxides that can be up to 5.3 g cm^{-3} (Cornell and Schwertmann, 2003). Organic matter in soil has a density ca. 1.4 g cm^{-3} (e.g., Mayer et al., 2004; Kaiser and Guggenberger, 2007b). Thus the density of organo-mineral particles depends largely on their volumetric ratio.

Soil particles having different types and/or degrees of OM–mineral associations can be isolated by sequentially separating them by narrow density intervals (e.g., Spycher and Young, 1979). More recent studies showed the general patterns of increasing δ^{13}C, δ^{15}N, and ^{14}C-based mean residence time as well as decreasing C:N ratio with an increase in particle density across a range of mineral soils (Baisden et al., 2002; Castanha et al., 2008; Crow et al., 2014; Gunina and Kuzyakov, 2014; Lajtha et al., 2014; Sollins et al., 2006, 2009), suggesting that microbially-driven OM transformations occur in parallel with the physical association of OM and minerals. The separation procedure, however, has some variation in the literature with no standardized method (Cerli et al., 2012; Crow et al., 2007; Wagai et al., 2009), which may explain some of the variations in the density-dependent patterns among the previous studies. Two major methodological variations appeared to be the initial soil condition (field-moist vs. air-dried) and the degree of aggregate disruption (mechanical shaking vs. sonication at varying energy), which could result in systematic bias (Castanha et al., 2008; Kaiser and Guggenberger, 2007a).

Air-drying is not a recommended pretreatment for density separation especially for soils rich in metastable mineral phases such as hydrous iron oxides and poorly-crystalline aluminosilicates due to drying-induced aggregation (Sollins et al., 1999). While drying may lead cause air entrapment in soil aggregates (Wander, 2004), experiments showed proper density assignment for the hydrous metal oxides associated with organic matter (Kaiser and Guggenberger, 2007a). However, air-drying to minimize microbial activity is sometimes necessary for sieving, archiving soils, and processing large numbers of samples.

Soil dispersion is, on the other hand, a required step in density separation. Common techniques are mechanical shaking alone (e.g., Lajtha et al., 2014; Sollins et al., 2006), shaking with glass beads (Gunina and Kuzyakov, 2014; Paul et al., 2008), and sonication (ultrasound) at each density separation step (Baisden et al., 2002; Basile-Doelsch et al., 2007; Castanha et al., 2008). While the drying-induced aggregation may be reversed by the dispersion treatments, over-application of sonication energy can lead to undesired consequences including the fragmentation of plant detritus and mineral particles (Kaiser and Asefaw Berhe, 2014 and the references therein). Strong dispersion may also lead to the systematic bias of the soil particles towards lower density fractions especially for soils rich in hydrous metal oxides and OM due, presumably, to the formation of negatively-charged colloidal fragments (Kaiser and Guggenberger, 2007a). No study, however, has systematically examined these effects using field soils. Thus the validity of comparing the literature results and the extent to which the progressive changes in organic chemistry (C:N, isotopic ratios) with soil particle density are affected by these methodological variations are virtually unknown at present.

We thus tested to what extent the degree of aggregation and its disruption induced by air-drying and subsequent sonication affects the changes in C:N ratio and the isotopic ratio of ^{13}C and ^{15}N along the particle density gradient. A well-characterized allophanic Andisol was used for this study as this soil type is known for strong aggregate stability (especially after drying), and high OM accumulation via interactions with reactive inorganic phases (Garrido and Matus, 2012; Hernández et al., 2012; Parfitt, 2009; Percival et al., 2000; Sanderman et al., 2014), thus the pretreatment effect on density fractionation may be severe. Major inorganic phases that have high affinity for OM in Andisols are short-range-order (SRO) minerals and organo-metallic complexes (Nanzyo et al., 1993; Wada and Higashi, 1976). Yet how this organo-metallic phase, often approximated with some cautions by the aluminum and iron extracted by pyrophosphate (Parfitt and Childs, 1988; Wagai et al., 2013b), is associated with SRO and other mineral phases within bulk soil is poorly understood (Asano and Wagai, 2014; Basile-Doelsch et al., 2007). We thus examined the distribution of OM and the metals (Al and Fe) extracted by pyrophosphate and acid oxalate across six density fractions with and without sonication. To help elucidate the source of "occluded light fraction" (low-density material presumably occluded in sonication-resistant aggregates), we also examined the carbon forms for the lower three density fractions by solid-state ^{13}C NMR spectroscopy. Finally, the relationship between OM and the extractable metal phases along the particle density gradient was examined based on correlation approach and the volume/density considerations of specific organo-mineral associations.

2. Materials and methods

2.1. Soil sample source and handling

We examined the soil from the experimental agricultural field at the National Institute of Agro-Environmental Science (36°01′N, 140°07′E, 21 m a.s.l), Ibaraki, Japan. The soil was classified as Hydric Hapludand (Soil survey staff, 2010) and Hydric–Silic Andosol (IUSS Working Group WRB, 2006), developed from rhyolitic and/or basaltic volcanic ash deposits (from Mt. Asama, Fuji, and Hakone). Dominant clay minerals are SRO minerals with minor amounts of gibbsite, kaolinite, chrorite, hydroxyl-interlayered vermiculite, mica, quartz, and feldspar. Mean annual air temperature is 13.7 °C and rainfall is 1300 mm y^{-1}. Mean annual soil temperature at 0–50 cm is 15.2 °C (monthly mean ranged 1.3–29.2 °C).

The sample used in this study is a subset used for previous incubation and physical fractionation studies ("Till-1" in Wagai et al., 2013a and "TKB" in Asano and Wagai, 2014) that give fuller description of the field and sampling scheme. We sampled the entire plow layer (0–20 cm) from the field (soybean/winter-wheat rotation since 1983) under conventional tillage practice where all residues were removed from the field after each harvest and inorganic fertilizer (30 kg N, 100 kg P, 100 kg K) was applied annually. The sample was sieved (2 mm) and kept in a refrigerator until further analyses. Soil pH was 6.5. Soil texture was 45% clay, 31% silt, and 24% sand.

2.2. Density fractionation

We examined two treatment effects. Air-drying prior to the fractionation (air-dry) and sonication during the fractionation (sonication treatment) were compared with field-moist samples (control), all with three replicates. The samples for air-dry and sonication treatments were air-dried at room temperature for >2 weeks. We conducted a sequential density separation using sodium polytungstate solution (SPT-O grade, Sometsu, Germany) adjusted to 1.6, 1.8, 2.0, 2.25, and 2.5 g cm^{-3}. The organic C and total N concentrations in fresh SPT were within the acceptable range (<0.5 mg g^{-1}, Kramer et al., 2009).

For the control and air-dry treatments, we first mixed soil samples with the SPT solution to have a final density of 1.6 g cm^{-3} (soil:solution ratio = 10 g:40 mL) and shook for 30 min at 120 rpm. The mixture was centrifuged (20 min, 2330 g) and floating material (<1.6 g cm^{-3}) was collected on 0.22 mm membrane filter as the lowest density fraction (F1). These steps (shaking to centrifugation) were repeated three times to