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Does phyllosilicate mineralogy explain organic matter stabilization in different particle-size fractions in a 19-year C_3/C_4 chronosequence in a temperate Cambisol?

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ABSTRACT

Finely divided minerals play a key role on the stabilization of soil organic matter (SOM). Among them, phyllosilicates are known to be particularly efficient due to their surface properties. However, how the wide variety of phyllosilicates with contrasted surface properties results in differing abilities to stabilize SOM is still unclear. In this study, we used a C_3/C_4 chronosequence established in a temperate Cambisol to compare the quantity of organic C and the incorporation of maize-derived C associated to various particle-size fractions with contrasting phyllosilicate mineralogy. We separated sand, silt and clay fractions in samples from 0–20-cm and 45–60-cm horizons. In each fraction, we measured organic C, total N and C isotope signatures. Phyllosilicate mineralogy of fine-silt, coarse-clay, medium-clay, and fine-clay fractions (2–20 μm, 0.2–2 μm, 0.2–0.05 μm, <0.05 μm) was determined using X-ray diffraction. Although phyllosilicate mineralogy differed between fractions, no clear relation was observed between mineralogy and organic C among the various particle-size fractions in any horizon. Interestingly, coarse-clay fractions providing a lower specific surface area had the greatest content of organic C and the lowest incorporation of fresh maize-C. This supported the hypothesis that a significant part of organic C stabilized in these fractions is due to the presence of very stable clay-size aggregates (resistant to sonication) that encapsulate organic C. The differing ability of the various phyllosilicates to stabilize organic C should therefore be evaluated according to both their ability to adsorb organic C and to form stable clay-size aggregates. This may prevent from finding simple relationships between phyllosilicate mineralogy and organic C stabilization.

1. Introduction

In the most soils, a great proportion of organic matter is associated to the mineral matrix (Christensen, 1992). Minerals protect soil organic matter (SOM) from decomposition through two main mechanisms: (i) adsorption of organic compounds on mineral surfaces (physico-chemical protection) and (ii) entrapment of organic compounds within aggregates (physical protection) (Baldock and Skjemstad, 2000; Sollins et al., 2006; Lützow et al., 2006). Associations between SOM and minerals can stabilize organic C in the soil for several centuries (Wattel-Koekkoek and Buurman, 2004). Among soil minerals, finely divided minerals (clay fraction, <2 μm) are the most efficient ones to interact with SOM due to their large specific surface areas (SSA) and surface charges (Feller and Beare, 1997; Hassink, 1997). Three types of finely divided minerals are particularly efficient protecting SOM: (i) poorly crystallized aluminosilicates such as allophane or imogolite (Torn et al., 1997), (ii) metallic oxi-hydroxydes (Wiseman and Püttmann, 2006) and (iii) phyllosilicates (Pronk et al., 2013). The high efficiency of finely divided minerals to stabilize SOM by organo-mineral interactions has been emphasized in many case studies and several meta-analysis showing that the content of organic C is positively correlated to the fraction of finely divided minerals of soils (Hassink, 1997; Six et al., 2002; Feng et al., 2013). It has been also observed that organo-mineral interactions (both adsorption and entrapment) have an increasing role on the organic C stabilization in deep horizons (Moni et al., 2010; Rumpel and Kögel-Knabner, 2011), where organic carbon uses to be older than in surface (Rumpel and Kögel-Knabner, 2011).

Most temperate soils contain a variety of phyllosilicate minerals differing in surface properties and size (Laird, 2001; Churchman, 2010; Hubert et al., 2012). The surface properties (i.e. SSA and surface charges) control interactions of phyllosilicate minerals with ions, other mineral particles and organic matter in the soil. Thus, differences of surface properties among phyllosilicates minerals should lead to

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contrasting abilities to protect SOM (see Barré et al., 2014 for details). This premise has been validated in laboratory experiments using model organic and/or mineral materials, however results from less controlled experiments are not so clear (Barré et al., 2014). The meta-analyses carried out with different soil types by Six et al. (2002) and Feng et al. (2013) suggest that fractions of finely divided minerals dominated by 2:1 phyllosilicate minerals are more efficient in stabilizing organic C than fractions of finely divided minerals dominated by 1:1 phyllosilicate minerals. However, this conclusion is weakly supported by case studies and no clear relationship between the mineralogy of phyllosilicates and organic C stabilization has emerged yet, as discussed in the review by Barré et al. (2014).

The still unclear relationship between phyllosilicate mineralogy and SOM protection may due to the fact that most studies comparing the ability of various phyllosilicate minerals to stabilize SOM compare fractions of finely divided minerals extracted from very different soils. As a consequence, many parameters co-vary with mineralogy in such studies and no clear conclusion can be drawn from their results. An alternative approach to avoid co-varying parameters is to use the intrinsic variability of minerals of a given soil. This approach avoids other parameters co-varying with mineralogy. Several studies showed that the particle-size fractionation within clay fractions can indeed separate fractions with contrasted phyllosilicate mineralogy (Hubert et al., 2012) but this approach has seldom been used to study organo-mineral associations of differing mineralogy (Laird et al., 2001; Gonzalez and Laird, 2003). Density fractionation has also been used in few studies to separate fractions of elementary particles corresponding to different mineral species and their associated organic matter (Chenu and Plante, 2006; Bonnard et al., 2012), but the solubilization of a fraction of the organic matter in the solution used for the separation is a severe drawback. To our knowledge, a particle-size separation of different phyllosilicate species has never been combined with the use of ^{13}C natural abundance to describe the incorporation of organic C in relation to the mineralogy of a soil.

The aim of our study was to compare the ability of various phyllosilicates for stabilizing SOM in a temperate Cambisol, using the intrinsic mineral variability within the soil at two depths. We applied a particle-size fractionation to separate various silt- and clay-size fractions in soil samples from the surface and the deep horizons of a C_3/C_4 chronosequence. We analyzed mineralogy, and measured organic C and stable C isotope composition of the separated fractions. Although all organic C in the fractions is not necessarily stabilized by mineral associations, we assumed that a greater content of organic C and a lower incorporation of new organic C (C_4-derived C) indicated a greater stabilization of organic C in the fractions. This allowed us testing the following hypotheses: more stabilized organic C, indicated by a greater organic C and a lower incorporation of new C_4-derived C will be found (i) in fractions with a greater proportion of swelling minerals in both surface and deep horizons and (ii) in the deep horizon than in the surface horizon.

2. Material and methods

2.1. Soil description and sampling

The study was conducted in the Closeaux experimental field, at the INRA agricultural research site in Versailles (France). Climate in the area is temperate with annual mean rainfall 639 mm year^{-1} and annual mean temperature 10.5 °C. The soil is a Eutric Cambisol (IUSS Working Group WRB, 2006), with varying texture from silt-loam in the topsoil to silty-clay-loam in the subsoil, developed on loess deposits. The clay fraction (<2 μm) in the whole profile is characterized by a complex phyllosilicate mineralogy with 2:1 and 1:1 minerals. The 2:1 minerals are discrete illite, discrete smectite, discrete chlorite, and two R0 illite–smectite and chlorite–smectite mixed-layer minerals (MLM). The 1:1 mineral is discrete kaolinite (Hubert et al., 2009). Iron and aluminum oxides and hydroxides are negligible in the soil profile (Moni et al., 2010; Fernandez-Ugalde et al., 2013). The organic C content decreases from 13.7 mg g^{-1} soil in the surface horizon to 4.05 mg g^{-1} soil in the deep horizon. The cation exchange capacity is essentially saturated by calcium (11.7 cmol(+) kg^{-1} in the surface horizon and 13.5 cmol(+) kg^{-1} in the deep horizon). Carbonate content is negligible in the whole profile (Moni et al., 2010).

The experimental design of Les Closeaux is a chronosequence of wheat (C3)-maize (C4) transition established in 1993. The field was cultivated only with wheat before 1993, when it was divided into 32 plots. Between 1993 and 2002, three plots per year were converted into maize. Once converted, the plots were maintained with C4- vegetation. Four control plots were conserved with wheat in the field. Three plots of control-wheat (CW) and the three plots of 19-year maize (19 M, converted to maize in 1993) were sampled in March 2012. Undisturbed soil samples from the surface (0–25 cm) and the deep (45-60 cm) horizons were collected at each plot and treated as field replicates for statistical analyses. Field-moist samples (10% *w*/*w* on average) were carefully hand-sieved to 5 mm, air-dried and stored in the dark.

2.2. Particle-size fractionation

Soil samples were subjected to a combination of a two-step physical dispersion and a particle-size fractionation adapted from Balesdent et al. (1991) to separate the following organo-mineral particle-size fractions: sand fraction (>50 μm), two silt fractions (20–50 μm, 2–20 μm), and three clay fractions (0.2–2 μm, 0.05–0.2 μm, and <0.05 μm) (Laird et al., 1991; Hubert et al., 2012). Approximately 25 g of soil were shaken overnight with 15 glass beads in 100 ml of deionized water to break aggregates >50 μm. The resultant suspension from dispersion was then passed through a 50 μm sieve to separate the fraction >50 μm, sand and free particulate organic matter. This previous step avoided the disruption of particulate organic matter >50 μm during the subsequent ultrasonic dispersion (Balesdent et al., 1991). The suspension <50 μm was sonicated in an ice bath for a total input of 320 J mL^{-1} using a digital sonifier, max. Output = 120 W, probe with a flat tip of 2.5 cm diameter, operating at 20 kHz (Sonics model 500 W). These physical dispersion conditions were determined by Balesdent et al. (1991) for this specific soil to obtain amounts of sand, silt and clay equivalents to those obtained by a chemical dispersion (OM removal using H_2O_2 and Na polytungstate). This means that the full dispersion of aggregates is only guarantee for aggregates >2 μm. The dispersion conditions also guaranteed that mineralogical characteristics of organo-mineral complexes were not altered (Hubert et al., 2009). The sonicated suspension was then sequentially centrifuged at 16,221 g for 61 min to separate the fraction <0.05 μm, at 4053 g for 16 min to separate the fraction 0.05–0.2 μm, at 91 g for 10 min to separate the fraction 0.2–2 μm, and at 2 g for 6 min to separate the fractions 2–20 μm and 20-50 μm. All fractions were oven-dried at 60 °C and weighed.

2.3. Mineralogical analyses

The mineralogy of particle-size fractions 2–20 μm, 0.2–2 μm, 0.05–0.2 μm, and <0.05 μm of all samples (2 vegetation types × 2 depth × 3 replicate × 4 fractions) was determined by X-ray diffraction (XRD). Oriented deposits of an approximate density of 10 mg cm^{-2} were prepared with the fractions by using the filter transfer method (Moore and Reynolds, 1997). The air-dried, oriented deposits were analyzed with a RIGAKU UltraX18HF X-ray diffractometer (RIGAKU, Tokyo, Japan). The XRD patterns were accumulated at 0.05° step intervals for 3 s counting time in the range from 3 to 30° 2θ by using Cu $K\alpha_{1,2}$ radiations. The oriented deposits were then exposed to ethylene glycol vapor over 16 h at 60 °C for 16 h. The XRD patterns of glycolated deposits were acquired in the same conditions as the air-dried samples.