



Sequential chemical extractions of the mineral-associated soil organic matter: An integrated approach for the fractionation of organo-mineral complexes

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ABSTRACT

Long-term stabilisation of soil organic matter (SOM) largely depends on its interaction with the active mineral components of soils. SOM may become associated with the mineral active surfaces through a wide variety of linkages, with different strength. Thus, fractionation procedures capable of assessing the strength through which mineral-associated SOM is stabilised can be very useful. This paper presents a soil organo-mineral fractionation method (henceforth, SOF) that essentially resumes the work of classical pedologists, who aimed to quantify the different modes through which organic compounds are bound to the mineral matrix using sequential extractions with chemical reagents (0.1 M sodium tetraborate, 0.1 M sodium pyrophosphate, 0.1 M sodium hydroxide, 0.1 M sodium hydroxide after sodium dithionite pretreatment, and 0.1 M sodium hydroxide after hydrofluoric acid pretreatment). We added a previous extraction with 0.5 M potassium sulfate to remove soluble organic compounds, and a weak acid attack with 0.33 M sulfuric acid to destroy possible SOM-occluding carbonate films, which are often assumed to contribute to SOM stability in calcareous soils. The proposed sequence is applied only to the organo-mineral complexes (<20 µm), after the removal of the particulate organic matter (POM) by ultrasonic dispersion and wet sieving.

We tested the SOF method on four contrasting soils: two Haplic Calcisols (under crop and forest) and two Humic Cambisols (under forest and pasture), with organic C (OC) contents ranging from 1.8 to 3.4% and pH from 3.9 to 8.0. Our results showed that the mineral-associated SOM represents the largest SOM fraction (67–72% of the total organic C content), and that a substantial part of it is weakly associated with the mineral matrix, as it can be extracted by sodium tetraborate or sodium pyrophosphate. While the sodium tetraborate extract was the main fraction in acid soils, the sodium pyrophosphate extract was the main fraction in calcareous soils, thus highlighting the role of Ca in SOM stability. In contrast, our results suggest a small role of carbonate precipitation in the stabilisation of SOM < 20 µm. The sodium hydroxide extractions after both the sodium dithionite and HF treatments released little SOM in the studied soils, but the remaining (insoluble) residue accounted for 15–30% of total OC, and deserves further study. The SOF method can be a valuable tool for splitting mineral-associated SOM into different fractions regarding their proneness for extraction, and its thoroughness may prove most useful for comparative studies about SOM stabilisation.

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1. Introduction

The study of soil organic matter (SOM) dynamics through fractionation procedures has been practised for at least one century (Vaughan and Ord, 1985). Fractionation involves splitting SOM among several fractions, whose relative proportion provides us with information about SOM stability, which results in its long-

term persistence. Ideally, these fractions should account for SOM functional pools, reflecting the soil C cycle to some extent.

Chemical fractionation methods based on the solubility of SOM in specific solvents (usually alkalis, mainly sodium hydroxide) dominated SOM studies until the 1980s (Stevenson, 1982). These methods aimed to isolate the so-called humic substances, a stabilised yet chemically active SOM fraction. Humic substances were further divided into humic (soluble in alkaline solutions, insoluble in acid) and fulvic (soluble at all pHs) acids. Radiocarbon dating studies showed that these fractions actually represent distinct stabilisation pools: humic acids are usually more stable, resistant to

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biodegradation and much older than fulvic acids (Guillet, 1979). Although several refinements of this fractionation were proposed over the years (for instance, Schnitzer and Schuppli, 1989), the basic concept still remains.

In recent decades, the fractionation methods based on physical properties (density, particle-size, or a combination of both) have become the dominant ones in SOM studies. These methods, which primarily aim to isolate and further study soil organo-mineral complexes (Bruckert, 1979a), became increasingly popular in the last decades of XXth century (Christensen, 1992). Today's predominant physical fractionation procedures result from evidence that the obtained fractions are often good predictors of SOM stability and decomposition (Janzen et al., 1992; Rovira et al., 2010; Zimmerman et al., 2012, among many others).

Some studies have evidenced the relevance of organo-mineral interactions for SOM stability (Kaiser and Guggenberger, 2000; Kalbitz et al., 2005; Kögel-Knabner et al., 2008). A recent review (Schmidt et al., 2011) stressed that while chemical recalcitrance explains SOM persistence during the first decades, in the long-term – centuries or millenia – SOM stabilisation depends on its interaction with the active components of the mineral matrix. Thus, any fractionation method designed to understand SOM stabilisation in a given soil should start by quantifying the SOM attached to active mineral surfaces. Density- or particle-size fractionation methods are appropriate for this (Christensen, 1992). The problem, however, is that physical fractionation alone cannot resolve the exact nature of the bond between organic and active mineral components. The generic term 'associated with mineral matrix' involves many different and contrasting organo-mineral interactions, each one with its own properties: hydrogen bonds, weak electrostatic unions with clay particles, precipitation by cations, association with Fe and Al oxides and hydroxides, occlusion by fine carbonate coatings, etc. Neither density- nor size fractionation methods are useful for a complete and absolute quantification of the relevance of the different stabilisation modes.

An alternative way is to use specific chemical reagents capable of counteracting a particular type of binding, thus solubilising most, if not all, of the SOM stabilised by such an interaction. These chemicals are already known, some of them for many years. Here we emphasize old literature, precisely to stress this fact. Sodium tetraborate has been shown to displace the organic substances attached to mineral surfaces by Van der Waals and weak electrostatic forces (Bruckert, 1970, 1979b; Greenland, 1971). Sodium pyrophosphate is a very useful chelating agent to solubilise organic compounds precipitated by metallic elements (Bremner et al., 1946; McKeague, 1967; Kononova and Bel'chikova, 1970). Sodium dithionite is a known reductive agent of iron oxyhydroxides, enabling the extraction of their bound SOM (Gonzalez-Prieto et al., 1989). Traditional extraction with sodium hydroxide must also be considered given its powerful extractive properties.

The return to fractionation methods based on chemical extractions should not consist of merely repeating old recipes, but in designing new, sound fractionation protocols in which several extractants are arranged in a rational and well-ordered sequence. Indeed, attempts have been made to do just this. The sodium tetraborate–sodium pyrophosphate–sodium hydroxide sequence was recommended by French researchers (Chouliaras et al., 1975; Duchaufour 1976; Bruckert, 1979a; Bruckert and Kilbertus, 1980), and applied sometimes by Spanish researchers (Dorado et al., 1979). Schnitzer and Schuppli (1989) applied the sodium pyrophosphate–sodium hydroxide sequence to particle-size fractions after extracting lipids with organic solvents. After noting that the sodium hydroxide-insoluble fraction often

accounted for most of the SOM, Duchaufour (1976) suggested pursuing fractionation by applying further treatments, including reduction with sodium dithionite, hydrofluoric attack or density fractionation. Actually the protocol of Dabin (1976) already applied these ideas. On these grounds, Almendros et al. (1979) developed a quite exhaustive fractionation scheme, involving the previous isolation of free (= light) organic matter by density fractionation with organic solvents, and the further treatment of the organo-mineral (= dense) fraction with a sequence of extractants: sodium pyrophosphate, sodium hydroxide, hydrochloric acid (in calcareous soils), sodium dithionite and hydrofluoric acid. Sodium tetraborate was not included in the sequence. Gonzalez-Prieto et al. (1989) put together the previous sequences in a single and long one: after removing the light fraction by density fractionation, they carried out extractions with sodium tetraborate, sodium pyrophosphate, sodium hydroxide, sodium dithionite, and hydrofluoric acid. The protocol by Gonzalez-Prieto et al. (1989), though complex and time-consuming, represents in our view the right point of departure to perform a complete description of the mineral-associated SOM.

In this study, we propose a sequential, integrated fractionation procedure designed to quantify different organo-mineral fractions according to the strength of their bond. Rather than studying a single, specific interaction type, the soil organo-mineral fractionation (SOF) described herein aims to achieve a compelling insight into how – and to what extent – the SOM of a given soil sample is stabilised by its mineral components.

2. Materials and methods

2.1. Overview of the SOF procedure and reagents

Broadly, our proposal involves a two-step procedure. The soil sample was first subjected to physical fractionation by size fractionation after ultrasonic dispersion, in order to separate the particulate organic matter (POM > 20 µm) from the organo-mineral complexes. Whereas POM is assumed to account for the free organic debris, not associated with the mineral components, the organo-mineral fraction (<20 µm) was subjected to a sequential set of extracting solutions within the SOF procedure (Fig. 1) by using the following reagents:

- 1) Potassium sulfate, to extract the water-soluble organic compounds present (or potentially present) in the soil solution (Jones and Willett, 2006), thus easily available for microbes (Casals et al., 2009, 2011).
- 2) Sodium tetraborate buffer at pH 9.7 (Na₂B₄O₇), to extract mainly those organic molecules adsorbed to mineral surfaces by weak unions. Sodium tetraborate displaces, through anionic exchange or ionisation of the functional groups, those organic compounds weakly adsorbed to the mineral matrix by means of electrostatic or Van der Waals interactions, such as hydrogen or cationic bridges with clay particles (Greenland, 1971, Bruckert, 1979b). These chemical bonds are characteristic of the SOM recently adsorbed by the mineral matrix (Bruckert, 1979b, Evans and Wilson, 1985; Lemaître et al., 1995), less stabilised and more prone to be detached from its adsorption site during soil disturbances or microbial attack.
- 3) Sodium pyrophosphate buffer at pH 9.8 (Na₄P₂O₇), a well-known chelating reagent, to extract organic substances precipitated by metallic cations (Ca, Mg, Fe, Al). Multivalent cations can form insoluble complexes with organic molecules, inducing their coagulation (Oste et al., 2002). Sodium tetraborate does not extract these complexes (Bruckert, 1979a; Evans and Wilson, 1985). Sodium pyrophosphate extraction is

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