



REVIEW ARTICLE

STRATAGEMS FOR ISOLATION OF SOIL ORGANIC MATTER FRACTIONS IN SOIL MATRIX: A MINI-REVIEW

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ABSTRACT

Soil organic matter (SOM) have successfully been fractionated using physicochemical methods for many decades. Although, no single method will absolutely separate natural organic matter into its components, as there are several types of organic matter i.e. kerogen carbon (KC), hydrolysable carbon (HC), non-hydrolysable carbon (NHC), black carbon (BC) and aged organic carbon (AOC). A hybrid of physical (density or particle size separation) and chemical separation methods (chemical hydrolysis) provides useful experimental data for modelling soil carbon dynamics and sequestration in many soil types. The type of separation techniques to be employed, like every other analytical tool, depends on the cost implication, selectivity, time scale, level of purity required, end use of the isolates, amongst other criteria required by the analyst.

INTRODUCTION

Soil is a complex three-phase system composed of variety of solids, water and dissolved substances, as well as gases in pore air (Smets, 2007). The importance of soil, the thin layer of unconsolidated material on bedrock, may be difficult to comprehend by an average man. Nonetheless, soil is the “biogeochemical engine of Earth’s life support system (Valentín et al., 2013; Robinson et al., 2012). Soil organic matter often referred to as natural organic matter is a very important component of soil. A concept of “soft” carbon (or amorphous, rubbery state) and “hard” carbon (or condensed, glassy state) has been used to delineate the chemical heterogeneity of SOM and to elucidate the mechanisms for sorption by soils and sediments (Schjønning, 2012). Scientific researchers have established that soil organic matter (SOM) fractionates into the following types of organic carbons; kerogen carbon (KC), hydrolysable carbon (HC), non-hydrolysable carbon (NHC), black carbon (BC) and aged organic carbon (AOC) (Weber et al., 1992). Kerogen carbon is insoluble in acid, base and organic solvent, NHC is considered to be synonymous but not equal to the molecularly uncharacterized OC that constitute a significant component of resistant organic matter preserved in soils and sediments (Ran, 1953-1962). The black carbon and non-hydrolysable carbon are classified as condensed organic matter due to the heavy structural crosslinkage; they contain aromatic heterocyclic and monocyclic compounds connected or cross-linked with aliphatic carbons (Hedges et al., 2012).

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The difference between the BC and NHC is the presence of BC and other components such as kerogen and graphite carbon in NHC. The roles NOMs play are often contradictory in terms of their effect on the adsorption and desorption process. On the one hand, NOMs could facilitate the dispersion of sorbent in water and make more adsorption sites available for adsorbates, thus increasing the adsorption. Similarly, NOM would compete with organic compounds for the same adsorption sites or physically block some available adsorption sites for organic compounds, resulting in reduced adsorption. Even though NOMs adsorbed on the sorbent surface can function as a new adsorbent, their affinity with organic compounds appears to be smaller than the affinity between natural sorbents and organic compounds. Researchers concluded that the structural components of SOM affects the geochemistry of soil especially the sorption of hydrophobic organic compounds (HOCs) (Ran et al., 2007; Adeola, 2018). This report explains the various chemical, physical and/or physicochemical methods that have been employed over the last few decades to isolate, modify and fractionate the different forms of organic matter present in soils.

MATERIALS AND METHODS

Chemical Fractionation of Soil Organic Matter

Demineralization of Soil Samples (DM): Soil is a complex matrix constituted mainly by mineral and organic materials. The mineral phase which are mostly silicates, ferrites, aluminates etc, and some are complexed with organic compounds. Therefore to release or recover the soil organic matter, the minerals must first be removed i.e. *demineralization*. The soil samples must first be air-dried,

ground and sieved through a 0.6 micro meter mesh size (Ololade et al., 2018). Gelinás *et al.* (Gelinás et al., 2001) described comprehensively a chemical method that can be employed for the demineralization of soils. The powdered Bulk soil sample (10g), were firstly gently demineralized with HCl and HF following the procedure outlined to removed carbonates, salts, and sesquioxide coatings were removed, i.e. 10g of various replicate samples were weighed using an analytical weighing balance and dissolved in 1N HCl for 30minutes at room temperature. The residues were separated from the supernatant by centrifuging (3000g, 20mins) and rinsed with distilled water. To reduce the loss of black carbon associated with the particles that were not sediment at 3000g, the HCl and water supernatant were filtered. Silicates minerals were then removed using two successive 12-hour treatment in a mixture of 1N HCl and 10% HF at room temperature. The samples were then centrifuged, and the supernatant were filtered as described above. The solid residues were rinsed with distilled water and freeze-dried, the residue is believed to have removed around 98% of the mineral constituents.

Removal of Hydrolysable Organic Matter (HOM): Allard *et al.* (1998) described a method for the isolation of hydrolysable organic matter. After demineralization, the hydrolysable organic matter (HOM) was then removed using standard hydrolytic methods. Polysaccharides were liberated using trifluoroacetic acid (TFA) hydrolysis. Two successive 2N TFA hydrolysis were carried out at 100°C for 3 hours in polypropylene tubes followed by two additional ones (4N and 6N TFA respectively) at 100°C for 18 hours in a shaking water bath. Finally, the residual hydrolysable organic matter was removed with 6N HCl at 110°C for 24 hours. Following each hydrolysis, the supernatants were separated from the residues by centrifugation and filtration as described above. The samples were rinsed with distilled water after the last TFA treatment and HCl hydrolysis. The residues (nonhydrolysable carbon, NHC) were then freeze-dried (Ke Sun et al., 2010). The selective removal of sugars (and other forms of easily hydrolysable OM) with increasing TFA concentration and reaction time has been shown to be an efficient approach to reduce the potential for the formation of melanoidin-like materials during 6N HCl hydrolysis.

Thermal Oxidation/ Black Carbon Removal (BC): The demineralized and HOM-Free samples (NHC) were thermally oxidized in a muffle furnace at 1200°C for 12 hours. The samples were directly weighed in a pre-tared silver cups, placed in titanium holder, combusted and re-weighed after cooling in a desiccator for mass balance calculation following standard procedures.

Classical Separation Techniques of Soil Organic Matter: Prior to the use of chemicals for the separation of the organic matter fraction in soil, was the use of difference in the physical state as basis for separation.

Density Separation: The density separation extracts organic matter from soil of low density (<1.6-2.0 g cm⁻³) by flotation in heavy liquid. The low-density components of soils consist of plant matter and charcoal (Sollins et al., 1983; Spycher et al., 1983). Denser fractions of soils contain mineral-associated organic matter. generally, the low-density material has higher ¹⁴C values and turns over more rapidly than much of the SOM.

Charcoal may be isolated by dissolving other low-density material (except pollen) by treatment with strong acids and bases (Hammond et al., 1991; Gillespie et al., 1992; Susan, 1996).

Size Separation: The dynamics of cycling SOM to different size fractions have been studied in the last few decades (Cambardella, 1993; Cambardella, 1994). Findings led to hypothesis about the role of soil aggregates in limiting the decomposition of reactive SOM constituents by physically protecting OM from soil microbial degradation (Oades, 1993). Anderson and Paul (Anderson, 1984) shed light on the limited measurements of ¹⁴C in size-fractionated organic matter available. This also suggest a relation between the size of soil-associated organic material and stability of associated organic matter. Mayer (Mayer, 1994) reported that there is a relationship between organic matter content and surface area in many soils and sediments.

If organic matter is protected by stabilization on clay surfaces, there is high probability of a lower ¹⁴C values than organic matter, which are available for microbial degradation or utilization. Premised on folk (Folk, 1961) findings and reports, Mayer carried out SOM fractionation by size separation technique, using the <2-mm sieved samples, without density separation. The ¹⁴C content was measured for three size fractions: <2 mm but >63 μ, <63 μ but >2 μ, and <2 μ. The largest fraction was separated by dry sieving; the fractions greater and less than 2 μ were separated by settling from a suspension (Benoit et al., 2008). This method inherently breaks apart soil aggregates and promotes easy isolation and separation of particulate matter. Most of the carbon in coarser-textured soils was associated with the >631u fraction. whereas in more clay-rich, heavy-textured soils (Oxisols), most of the organic carbon is associated with the fine silt and clay fractions (<634u). The sorption capacity of organic matter is not only controlled by their chemical composition, but also by their size, due to a greater number of sorptive sites related to a greater surface area with decreasing particle size (26).

Comparison of fractionation methods for soil organic matter: Soil organic matter could either be particulate organic matter and volatile organic matter. The different proportion of kerogen carbon (KC), hydrolysable carbon (HC), non-hydrolysable carbon (NHC), black carbon (BC) and aged organic carbon (AOC) present as soil organic carbon is dependent on soil origin and anthropogenic activities. Studies have shown that the chemical fractionation techniques provide a wider spectrum of organic matter isolates that is recoverable in-situ and by chemical treatment. Also, the physical fractionation technique either density separation and/or size separation, has proven to be useful, but not without its deficiencies. The major advantage of the physical or classical approach to SOM fractionation over the chemical method is that chemical modifications or transformation take place due to the reaction between the reactive functional groups of SOM and the extractants (acid or base). However, Chemical treatment is most effective in coarse-textured soils, in part because more of the total carbon is removed in the hydrolysis procedure. Chemical extraction with acids and bases may not change the ¹⁴C content of organic matter, even though up to 90-95% of the original carbon was removed (Spycher, 1983). Chemical treatment is suitable for very complex soils with

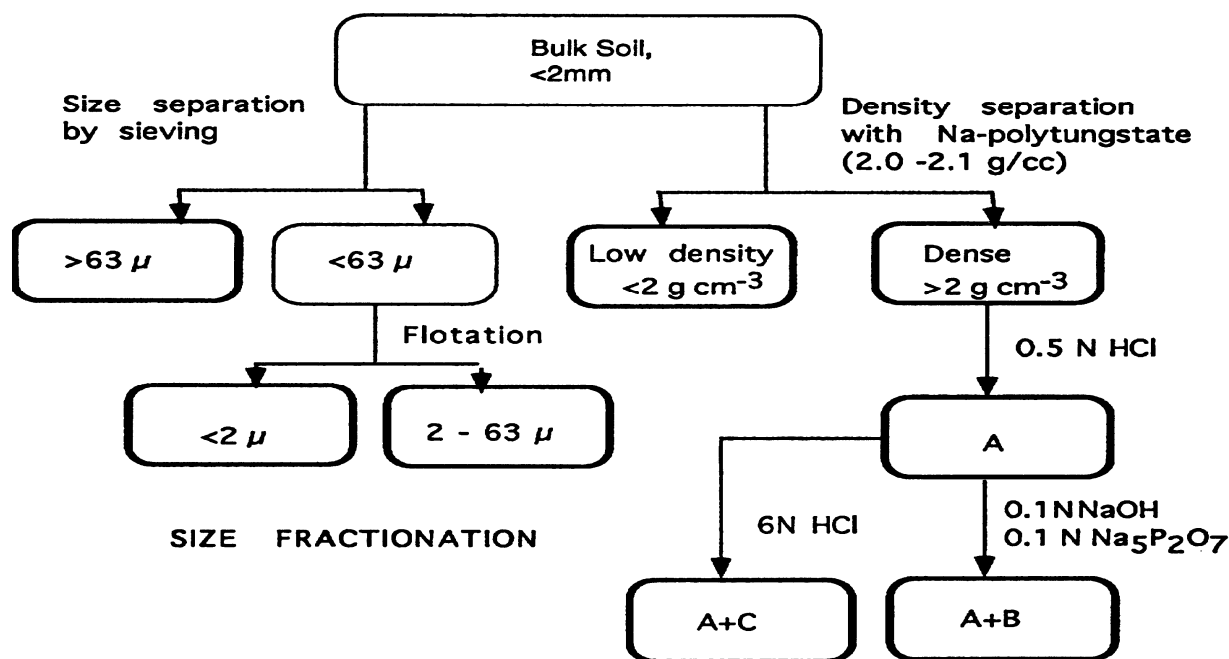


Fig. 1. Schematic diagram for the size and density fractionation of SOM (Susan, 1996)

mineral-organic complexation and for complete delineation of the various fractions of soil organic matter (SOM).

Future prospects: Soil as a heterogeneous mixture of several Constituents, which includes organic and inorganic compounds of varying compositions and surface activities, and may thereby considerably affect the behaviour of chemicals released e.g. herbicides, pesticides. It is an established fact that organic matter is very important in agriculture, essentially for plants growth and development (Lin et al., 1997; Morrica et al., 2008; Pusino et al., 2004). Various soil characteristics such as organic carbon content, clay content, pH, and cation exchange capacity (CEC) have been determined to affect the sorption-desorption of herbicides, however, there is need to extensively study the interaction of soil organics and wider scope or class of organic pollutants. The indiscriminate release of waste or chemicals to natural environment influences several biological and chemical activities in soils. Thus, studies on how and whether one form SOM can undergo bio-transformation in soils to give another form or fraction of SOM is needful in other to fully grasps the dynamics of soil organic matter and postulate what is would be obtainable in the nearest future in the natural environment. Furthermore, it is sacrosanct to understand how certain environmental variables such as temperature, pH, UV-radiation/sunlight etc., can influence the bio-transformation process.

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