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Effects of exchangeable cations, mineralogy and clay content on the mineralization of plant residue carbon

Fatemeh Rakhsh^{a,*}, Ahmad Golchin^a, Ali Beheshti Al Agha^b, Parisa Alamdari^a

^a Soil Science Department, Faculty of Agriculture, University of Zanjan, Zanjan, Iran

^b Soil Science Department, Faculty of Agriculture, Razi University, Kermanshah, Iran

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ABSTRACT

Interactions of clay minerals with organic materials and the consequences of these interactions on dynamics of organic carbon (OC) have been reviewed in detail. However, the effects of exchangeable cations and clay types on the turnover rate of OC have not been given much attention. Appropriate amounts of homoionic Na-, Ca- and Al-clays from Georgia kaolinite, Illinois illite and Wyoming bentonite were mixed with pure sand to prepare artificial soils with different clay contents, exchange cations and clay types. Alfalfa plant residues were incorporated into the artificial soils and the soils were inoculated with microbes from a natural soil and incubated for 184 days to study the effects of clay contents, exchangeable cations and clay types on the mineralization of OC and plant residue derived microbial biomass. Mineralization of plant residue carbon was significantly (*p < 0.01) more rapid in pure sand than in soils containing 5 and 10% clay, indicating that clay contents influence the capacity of soils to protect and store OC. The amounts of biomass carbon were lowest in pure sand and highest in soils with 10% clay. There was a significant influence (**p < 0.01) of exchangeable cations on microbial biomass and hence the mineralization of OC over a period of 184 days. At 5 and 10% clay contents, the amounts of microbial biomass carbon and the mineralization of plant residue carbon were highest in Ca-soils and lowest in Al-soils. Statistical analysis of data showed a significant effect (**p < 0.01) of clay type on mineralization of plant residue carbon and microbial biomass. However, the effects of clay types on the mineralization of OC were much less than those of clay contents and exchangeable cations. The mineralization of plant residue carbon was highest in soils with Georgia kaolinite clay and lowest in soils with Wyoming bentonite clay. The amounts of biomass carbon were slightly lower in soils with Wyoming bentonite clay than soils with Georgia kaolinite and Illinois illite clay minerals. The results of this study indicate that OC and microbial biomass are stabilized in soils through the interaction with clay minerals and a small amount of clay (5%) slows OC decomposition significantly and reduces carbon dioxide emission from soils. Exchangeable cations exert their influence on microbial biomass and hence carbon dynamics by controlling the size and activity of the microbial population through modifying the physicochemical characteristics of microbial habitats.

1. Introduction

Many studies have examined the mechanisms of organic matter (OM) preservation in soils. Decomposition and stabilization of organic materials in soils represent a complex set of processes involving the processing and decomposition of OM by diverse communities of soil fauna and microorganisms, as well as chemical-physical interactions with mineral soil particles (Giardina et al., 2014). The chemistry of OM is an important factor that influences microbial degradation rate of organic materials (Golchin et al., 1996). Recent studies on the turnover of OM in soils have demonstrated that, in addition to the chemistry, the location of biopolymers within the mineral matrix of the soil is another dominant factor regulating the microbially mediated decomposition processes (Van Veen and Kuikman, 1990; Ellerbrock et al., 2005; Sollins et al., 2006; Six and Paustian, 2014). Longer turnover times for organic materials occluded within aggregates, and those associated with clay particles, compared with the free organic materials present within the soil matrix, confirm the concept that the accessibility of soil organisms to organic materials decreases as a result of aggregation and adsorption to clay surfaces (Golchin et al., 1996; von Lützow et al., 2006; Schrumpf et al., 2013).

Studies have shown that clay particles are important in reducing the rate of decomposition of OM in soils (Jenkinson, 1977). Clays with the formation of clay-OM stable complexes and deactivation of

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^{*} Corresponding author. E-mail address: rakhsh.fatemeh@znu.ac.ir (F. Rakhsh).

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extracellular enzymes protect OM against microbial degradation in soils with high clay content. (Saggar et al., 1996). In fact, the amount of clays, as an abiotic factor, is effective on the microbial decomposition rate of organic materials and the size of soil organic matter (SOM) pools (Franko, 1996; Kleber et al., 2015). Clay minerals also by the formation of water stable aggregates decrease the accessibility of soil organisms to particulate OM occluded within aggregates and thus decrease the decomposition rate and increase the retention of organic materials in soils (Edwards and Bremner, 1967; Six et al., 2004).

Studies have shown that OM adsorbed onto the surfaces of clay minerals and oxides are more resistant against microbial degradation than the dissolved organic matter or OM with no interaction with minerals (Kalbitz et al., 2005; Mikutta et al., 2007; Schneider et al., 2010).

Organic biopolymers can adsorb onto the clay surfaces by different mechanisms. Positively charged organic molecules are adsorbed onto the clay surfaces by cation exchange mechanism. Since organic anions are repelled by the negatively charged clay surfaces, in cation bridging mechanism, the exchangeable polyvalent cations of the clays such as Ca^{2+} , Mg^{2+} , Fe^{3+} and Al^{3+} act as bridges to neutralize both the negative charges of the clay surfaces and organic anions and connect organic biopolymers to the clay surfaces (Kaiser et al., 2012; Kögelknabber and Kleber, 2011). Also, the organic anions can bind to the phyllosilicate clay minerals through the hydrogen bonding, van der Waals forces and hydrophobic interactions (Kögel-knabber and Kleber, 2011). Polysaccharides are bonded strongly to clay minerals via cation bridges and, thus, are preserved from the microbial decomposition (Chenu, 1995). In general, longevity and chemical stability of organic materials depend on how strong these materials are bonded with exchangeable and structural cations of the clay minerals, especially Ca²⁺, Fe³⁺ and Al³⁺ (Nguyen et al., 2004). Many studies have shown that SOM content has a positive correlation with the soil cation exchange capacity (CEC) (Zech et al., 1997; Wang and Wang, 2007). The microbial degradation rate of the OC in clavev soils is less than that of sandy soils (Brynhildsen and Rosswall, 1997; Cruz-Guzman et al., 2003) and this causes humic substances to accumulate in these soils (Varadachari et al., 1991; Wershaw, 1999).

Although sufficient information exists in the literature about the role of soil texture and spatial distribution of organic materials within the soil matrix on the dynamics of OC, the roles of exchangeable cations and clay types are not clear in this regard. Exchangeable cations by changing the physical and chemical properties of soil and influencing soil aggregation can have a major impact on OM dynamic (Golchin et al., 1996). Christensen (1992) concluded that the stabilization of organic compounds created during the decomposition of organic residues is highly influenced by the amounts of clay and silt in the soil and in sandy soils these compounds would be simply destroyed by the leaching and secondary decomposition. Six et al. (2002) observed that 1:1 clay minerals (kaolinite) relative to 2:1 clay minerals (illite, montmorillonite and vermiculite) had less OC retention. Saidy et al. (2012) observed that the OC mineralization was significantly influenced by the clay mineralogy and in the mixtures of sand and clay those contained kaolinite and illite had more OC mineralization than the mixtures contained illite and smectite. Bruun et al. (2010) measured soil respiration in tropical soils with different mineralogy and observed that OC stability in soils containing smectite, was less than that of soils containing kaolinite and allophane. Information about the role of mineralogy on soil organic carbon (SOC) storage and dynamics is limited and antithetic, But generally, it is accepted that the retention of SOM by allophane, smectite, illite and kaolinite decreases respectively (Bruun et al., 2010; von Lützow et al., 2006). The impact of clay mineralogy on OM dynamics mostly has been studied indirectly and fewer resources show its direct effects (Feng et al., 2013).

Li et al. (2007) stated that the OC content of soil increased as the amount of clay in the soil increased. Gonzalez and Laird (2003) reported that the coarse clay fractions generally had aromatic and humified OM, but the fine clay fractions contained unstable or less humified OM. They also showed that soils with high amounts of clay had less water extractable OC. Wang and Wang (2007) reported that the amounts of hot water extractable OC significantly decreased as the clay contents of the soils increased. In contrast, some studies have shown that the addition of clay increased OC mineralization in initial stages of decomposition which was due to the increased microbial activity on the clay surfaces (Van Loosdrecht et al., 1990).

The impacts of clay types on SOC decomposition rate have not been confirmed in all experiments, for instance, Varadachari et al. (1991, 1995) showed that the effects of clay types on the SOC retention and the dynamics were much less than that of clay content. Hassink and Whitmore (1997) also showed that the clay mineralogy had no effect on the retention of OC. Wattel-Koekkoek et al. (2001) did not observe any differences between the amount of OC in soils with 1:1 and 2:1 clay minerals.

Although the effects of soil texture on the retention and dynamics of SOC have been investigated in many studies, but research showing the direct effects of clay type is rare (Denef and Six, 2005; Denef et al., 2002; Reichert et al., 2009) and the effects of exchangeable cations in these regards are unknown. This study aimed to: (i) investigate the effects of kaolinite, illite and smectite clay minerals on mineralization of OC and plant residue derived microbial biomass, (ii) determine how retention and the dynamics of OC are affected by mono-, di- and trivalent exchangeable cations (Na⁺, Ca⁺², Al⁺³) present on the exchange complexes of clay minerals, and (iii) examine the influence of clay content on retention and the mineralization of OC. We hypothesized that exchangeable cations affect SOM dynamics by controlling the size and activity of soil microorganisms through modifying the physicochemical characteristics of microbial habitats and change the effects of clay mineralogy and clay content on SOM turnover.

2. Material and method

Mixtures of sand and clay (artificial soils) were used to study the simple and interactive effects of clay types, exchangeable cations and clay contents on mineralization of plant residue carbon and plant residue derived organic materials (Pronk et al., 2013). The clay minerals used in this study were Georgia kaolinite, Illinois illite and Wyoming bentonite and these clay minerals were saturated three times with three different cations (Na⁺, Ca²⁺ and Al³⁺) to prepare homoionic clays (Na-, Ca- and Al-clays) (Golchin et al., 1996). The homoionic clays were mixed with acid washed sand in appropriate proportions to yield 18 different artificial soils (50 g) with 5 and 10% clay.

2.1. Preparation of pure sand and homoionic clays

Sub-samples of sand were washed with water thoroughly and after removal of soluble salts and clay particles, the sand particles were passed through a 2 mm sieve and those remained on a 0.05 mm sieve were used for the incubation experiment. Initially, the sand particles were heated in the furnace at 550 °C for 4 h two times to remove OC and then the particles were washed with 2 M HCl for removing carbonates. Subsequently, the sand particles washed with distilled water and dried in the oven at 105 °C.

To prepare homoionic clays, samples of Georgia kaolinite, Illinois illite and Wyoming bentonite were treated with 1 M solution of NaCl to saturate clays with Na and facilitate their dispersion. The clays then were washed with distilled water until free from salt and dispersed by gentle ultrasonic energy to separate the $< 2 \mu m$ fraction. The $< 2 \mu m$ fractions of clays were used to prepare homoionic Na-, Ca-, and Al-clays by washing the clays three times with 1 M solutions of NaCl, CaCl₂ and AlCl₃, respectively (Golchin et al., 1996). After saturation of clays with different cations, the samples were dialysed against distilled water until free from salt and chlorine. The absence of chlorine in distilled water was tested with 1 M solution of silver nitrate (Yoder, 1919). The salt-free clay samples were freeze-dried and stored at room temperature.

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