



Relationship between soil clay mineralogy and carbon protection capacity as influenced by temperature and moisture



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ABSTRACT

Environmental conditions like temperature and moisture could affect the carbon protection capacity of various clay types in soils. Using dominantly kaolinitic-illitic, smectitic and allophanic soils, we conducted systematic incubation experiments over 42 days at different temperatures (4, 22 and 37 °C) and moisture contents (30, 60 and 90% of water holding capacity (available water)). The basal respiration was monitored to study the relative effect of moisture contents and temperature on the carbon protection capacities and mechanisms of the three clay types. The results indicated that carbon decomposition increased with increasing moisture and temperature. A two-component quadratic equation could explain the carbon mineralisation process. The highest C respiration was observed at 37 °C with a 60% moisture level in each of the soil types. Under these conditions, the smectitic soil recorded the highest carbon decomposition followed by the kaolinitic-illitic and allophanic soils. The study of the priming effect using ¹⁴C labelled malic acid confirmed the trend of the bulk respiration results. The allophanic soil showed the lowest amount of carbon mineralisation under all experimental conditions. A strong inverse correlation ($R^2 = 0.90$ at $p < 0.05$) was observed between CO₂ emission rate and total sesquioxides (Fe and Al oxides) content. As evidenced by the pore size distribution, micromorphologies and thermogravimetric analyses, the microporous structure and microaggregate formation in the allophanic soil enhanced carbon sequestration. This study indicated that soil carbon stabilisation was related more to the sesquioxides content than to the clay types or their relative specific surface areas.

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1. Introduction

The decomposition of soil organic carbon (SOC) is mainly controlled by microbial processes which are directly or indirectly influenced by soil moisture and temperature (Hao et al., 2016). In the terrestrial ecosystem, soils store the largest quantity of organic carbon (OC), of which nearly 80% C plays active role in the global carbon (C) cycle, compared to about 20% in vegetation. The OC is heterogeneous and made of various components, ranging from

easily decomposable sugars to recalcitrant aromatic compounds. Mean residence times of C in soils vary from a few hours to thousands of years (Torn et al., 1997; Trumbore and Torn, 2003). The mineralisation of stable OC, which makes 52–98% of the SOC pool (Tisdall, 1996), is directly related to the prevailing climatic conditions. Moreover, the variation in mineralisation times is dependent on the binding strength of organo-mineral associations (Christensen, 1996; Parfitt et al., 1997; Baldock and Skjemstad, 2000). Soil OC decomposition is affected by several environmental and soil properties including temperature (Wang et al., 2016), moisture (Suseela et al., 2012), quantity of organic residue (Roychand and Marschner, 2013), soil texture (Baldock, 2007), microbial community structure (Six et al., 2004) and land use patterns (Hassink, 1994).

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A small change in the amount of soil C stock may result in a large impact on the atmospheric CO₂ emission (Lal, 2008). Soil OC loss via heterotrophic respiration is one of the main reasons for global CO₂ emission from the terrestrial ecosystem to the atmosphere (Bond-Lamberty and Thomson, 2010). For this reason, a very good understanding of the relationship between environmental conditions (e.g., temperature and moisture) and SOC is needed in order to predict C fluxes from the terrestrial ecosystem (Davidson and Janssens, 2006). Temperature could have a more significant effect on the SOC decomposition than any other factor. The Q₁₀ value, which describes the change in the rate of SOC decomposition with each 10 °C rise in temperature, is commonly used to describe the sensitivity of temperature to SOC decomposition (Suseela et al., 2012). The Q₁₀ values may vary with the quantity and quality of SOC (Fierer et al., 2006), moisture and temperature (Wang et al., 2016). It is likely that the SOC stock in fine-textured soils is less susceptible to heterotrophic respiration than that in coarse-textured soils (Baldock and Skjemstad, 2000; Lal, 2007; Conant et al., 2008). However, it is still not very clear whether the heterotrophic respiration of SOC exhibits different responses to the global warming potential in soils with different mineral compositions. It was found that the mineralisation of OC associated with montmorillonite clay mineral showed a higher Q₁₀ value at a low temperature (2 °C) (Zhang, 2010). Contrarily, kaolinite dominated soils showed a greater sensitivity (higher Q₁₀ value) at an intermediate temperature (22 °C) (Zhang, 2010). Emission of C from soils can potentially exceed that from fossil fuel burning and land use change when there is a 20% increase in global temperature (Conant et al., 2008). Therefore, the functional relationships between clay mineral types and temperature are important for understanding this process better, and they warrant urgent research attention. The effect of soil moisture on SOC decomposition is reasonably well known, but the combined effect of temperature and moisture has not been studied to a great extent in soils with different textures and clay mineral compositions (Wang et al., 2016).

Because they have more reactive sites reflected in higher values for cation exchange capacities (CEC) and specific surface areas (SSA), clay and silt particles bind SOC to a greater extent and also more strongly than sand particles through polyvalent cation bridging and ligand exchange reactions (Hassink, 1997; Kögel-Knabner et al., 2008). Sand particles generally have only a weak bond with SOC (Baham and Sposito, 1994; Lützow et al., 2006). The strong bonds between clay minerals and SOC would inhibit C mineralisation and therefore may decrease its temperature sensitivity (Arevalo et al., 2012). The SOC associated with clay minerals with different SSA and CEC should respond differently to the global warming potential of soils.

Different soil clay minerals, such as kaolinite, illite, smectite and allophane, have very different physico-chemical properties. This is demonstrated by the different strengths of their interactions with dissolved organic C (Singh et al., 2016). While kaolinite and smectite have regular layered aluminosilicate crystal structures, allophane is only poorly- or non-crystalline (Churchman and Lowe, 2012). The order of these clay minerals according to their SSA was found to be: allophane > smectite > kaolinite, whereas that according to their CEC differed with pH, although smectite always had the highest value, with allophane and kaolinite each showing a strong component of pH-variable charge (Churchman and Lowe, 2012). The effects of changes in temperature and moisture content on associations of native and introduced OC with these clay minerals have not been reported until now.

Plant root exudates such as organic acids (e.g., acetic acid, malic acid and citric acid), amino acids (e.g., aspartic acid, glutamic acid and glycine) and carbohydrates (e.g., glucose and sucrose) contribute to SOC in the rhizosphere (Bolan et al., 1994). Some of

the native SOC can be mineralised during the decomposition of the theoretically easily decomposable root exudates; this is known as the priming effect (Kuzyakov et al., 2000; Chowdhury et al., 2014). The priming effect can be either positive or negative in relation to the mineralisation of native soil C (Hamer and Marschner, 2002; Chowdhury et al., 2016). It has been reported that montmorillonite was associated strongly with aromatic compounds whereas kaolinite was associated more with polysaccharide compounds (Wattel-Koekkoek et al., 2001). In addition, the different clay minerals give rise to different pore structures and different geometries of the soil aggregates, which together govern the access of OC to the microorganisms (Six et al., 2000). However, the effects of different soil clay minerals such as kaolinite, illite, smectite and allophane on the priming effect are still only poorly understood.

Therefore, the current study focused on the effect of different temperatures and moisture contents on the protection of SOC using three natural soils with different clay mineral compositions (kaolinite-illite, smectite and allophane). Natural soils were used because the clay minerals in the soils are likely to behave differently from those found in mineral deposits (Churchman and Lowe, 2012). The specific aims of the study are to (i) compare the effects of moisture and temperature on the mineralisation of occluded OC in soils with different types of clays, and (ii) examine the mineralisation of occluded OC in soils with different types of clay minerals as affected by the supply of an easily mineralisable ¹⁴C source (malic acid) to the microorganisms.

2. Materials and methods

2.1. Sample collection and preparation

This study included three soils which were each dominant in kaolinite and illite together (known as kaolinite-illite in the later text), smectite and allophane clay minerals (Stace et al., 1968; Lowe and Palmer, 2005; Churchman et al., 2010). The samples were collected respectively from Hoyleton (34.01°S, 138.33°E), the Waite campus of the University of Adelaide (34.96°S, 138.64°E) and Mt. Schank (37.56°S, 140.44°E) in South Australia. The mineralogical composition and physico-chemical properties of these soils were described earlier (Singh et al., 2016). After collection (at 5–20 cm depth), all visible gravels, roots and other plant materials were removed from the samples by passing them through a 2-mm sieve. The samples were stored in cold dark room (4 °C). Prior to the incubation experiments, soil was equilibrated by adding water (30% of water holding capacity) at room temperature (23 °C) for 2 weeks in order to ensure the maximum microbial activity. The physico-chemical characteristics of the soils are given in Table 1.

2.1.1. Measurement of total C, N, CEC and Fe/Al oxides

Total C concentration in the soils was analysed by combustion using a LECO® C/N analyser (LECO TruMac® CNS/NS, Saint Joseph, MI, USA). The combustion temperature and oxygen flow time were 1300 °C and 5 s, respectively. The CEC of soils was measured using a method described by Rayment and Lyons (2011). Citrate-dithionite-bicarbonate (CDB) treatment was employed for measuring the free (non-structural) Fe (Fe_d) and Al (Al_d) (Blakemore et al., 1987). To confirm the presence of allophane in Mt. Schank soils, acid oxalate-extractable Fe (Fe_o), Al (Al_o), and Si (Si_o), and pyrophosphate-extractable Fe (Fe_p) and Al (Al_p) contents were also measured by using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Model: 5300 V, Perkin Elmer, Waltham, MA, USA) (Blakemore et al., 1987). The subscripts ('d', 'o', 'p') represent the respective extractants (CDB, acid oxalate and pyrophosphate).

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