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Sorption of Water-Extractable Organic Carbon in Various Clay Subsoils: Effects of Soil Properties

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ABSTRACT

Clay-rich subsoils are added to sandy soils to improve crop yield and increase organic carbon (C) sequestration; however, little is known about the influence of clay subsoil properties on organic C sorption and desorption. Batch sorption experiments were conducted with nine clay subsoils with a range of properties. The clay subsoils were shaken for 16 h at 4 °C with water-extractable organic C (WEOC, $1\,224$ g C L^{-1}) from mature wheat residue at a soil to extract ratio of 1:10. After removal of the supernatant, the residual pellet was shaken with deionised water to determine organic C desorption. The WEOC sorption was positively correlated with smectite and illite contents, cation exchange capacity (CEC) and total organic C, but negatively correlated with kaolinite content. Desorption of WEOC expressed as a percentage of WEOC sorbed was negatively correlated with smectite and illite contents, CEC, total and exchangeable calcium (Ca) concentrations and clay content, but positively correlated with kaolinite content. The relative importance of these properties varied among soil types. The soils with a high WEOC sorption capacity had medium CEC and their dominant clay minerals were smectite and illite. In contrast, kaolinite was the dominant clay mineral in the soils with a low WEOC sorption capacity and low-to-medium CEC. However, most soils had properties which could increase WEOC sorption as well as those that could decrease WEOC sorption. The relative importance of properties increasing or decreasing WEOC sorption varied with soils. The soils with high desorption had a low total Ca concentration, low-to-medium CEC and low clay content, whereas the soils with low desorption were characterised by medium-to-high CEC and smectite and illite were the dominant clay minerals. We conclude that WEOC sorption and desorption depend not on a single property but rather a combination of several properties of the subsoils in this study.

Key Words: cation exchange capacity, clay mineral, illite, kaolinite, smectite

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INTRODUCTION

Dissolved organic carbon (DOC) accounts for only a small proportion of total soil organic carbon (SOC), but it is the most mobile and bioavailable fraction (Marschner and Kalbitz, 2003; McDowell, 2003). Mobility of DOC is influenced by its interactions with soil and clay minerals (Jardine *et al.*, 1989), including sorption and desorption (Trumbore, 1993; Kalbitz and Kaiser, 2008). Sorption of DOC to soil and clay surfaces affects not only its mobility and retention but also its decomposition rate because sorbed DOC is less accessible to soil microbes (Baldock, 2007).

The DOC and organic C sorption of clay minerals have been studied extensively (Kaiser and Zech, 1997; Nelson, 1997; Kalbitz *et al.*, 2005). Clay properties such as mineralogy, surface area, concentration of iron (Fe) and aluminum (Al) oxides and cation exchange capacity (CEC) play an important role in

DOC and organic C sorption. Sequestration of organic C is greater in smectite-rich sediments compared to clays dominated by chloride and illite (Ransom *et al.*, 1998; Gonzalez and Laird, 2003). Surface area of clay minerals is positively related to DOC and organic C sorption (Nelson *et al.*, 1993; Kaiser *et al.*, 1996). The DOC is predominantly negatively charged in soils (Jardine *et al.*, 1989) and therefore preferentially binds to positively charged surfaces. Clays also have a negative surface charge, but coating with Fe or Al oxides or binding of cations can provide positively charged sorption sites (Sumner, 1963). In soils, DOC sorption is positively correlated with concentrations of Al and Fe oxides/hydroxides and CEC (Amato and Ladd, 1992). However, this is not always the case. Riffaldi *et al.* (1998) found no correlation between organic C sorption and concentrations of Al and Fe oxides or CEC. The nature of cations on clay surfaces also influences DOC sorption. Multivalent cations (Ca^{2+}) increase positive

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surface charge which in turn increases binding of negatively charged organic C, whereas monovalent cations (*e.g.*, Na^+) do not have this effect (van Geen *et al.*, 1994). Therefore, DOC sorption is low if a high proportion of the exchange sites are occupied by monovalent cations (*e.g.*, Na^+); that is, high sodium absorption ratio (SAR) decreases DOC sorption (Mavi *et al.*, 2012). However, a high proportion of Ca^{2+} increases DOC sorption (Setia *et al.*, 2013). Sorption of DOC in clay soils is also affected by other properties such as pH and total organic carbon (TOC) and clay content. Soil sorption capacity of DOC is negatively correlated with soil pH (Kahle *et al.*, 2004), but positively correlated with soil clay content (Nelson *et al.*, 1997; Benke *et al.*, 1999). Native organic C can limit sorption of added DOC by coating the surfaces of soil particles (Kaiser and Zech, 2000).

Thus, it is well established that DOC sorption is influenced by clay and soil properties. However, the studies described above were conducted with less than three clay or soil types and the relative importance of different clay properties for DOC sorption is unclear. This requires comparison of a greater number of soils. Furthermore, the role of clay properties in the release of bound organic C is poorly understood.

The aim of this study was to investigate the effect of clay soil properties on sorption and desorption of water-extractable organic carbon (WEOC) in nine clay soils with a range of properties. We hypothesised that WEOC sorption and desorption depend on a number of soil properties and their relative importance will vary among soils. Clay subsoils were chosen because claying, *i.e.*, the addition of clay subsoil to sandy topsoil, is increasingly used by farmers to ameliorate texture-contrast (sand over clay) soils. Claying has been shown to increase yield, water and nutrient-holding capacity and, in some cases, organic C content (Hall *et al.*, 2010), but the effect on organic C content is variable. Therefore, more information about the relationship between subsoil properties and organic C sorption is required.

MATERIALS AND METHODS

Soils

Nine clay subsoils (40–90 cm depth) were used in this study (Table I). These soils were collected from Vermilion County, Illinois, USA (VE) and from Monarto (MO), Claremont (CL) and Urrbrae (UR) in Adelaide, the southeastern part (SE1 and SE2) and the Eyre Peninsula (EP1, EP2 and EP3) of South Australia. These soils were selected because they represent a broad range of clay subsoils. All soils were air-dried and sieved to ≤ 2 mm.

Water-extractable organic carbon

Water-extractable organic carbon (WEOC) was derived from dry mature wheat straw (ground and sieved to particle size ≤ 2 mm) by shaking 40 g of wheat straw with 1 200 mL of deionised water (1:30, weight/volume) for 1 h. The extract was centrifuged at 1 760 × *g* for 10 min and filtered through a Whatman No. 42 filter paper (pore size, 2.5 μm). We use the term WEOC because the filtered extract may not only

TABLE I

Basic properties[a] of the clay subsoils used in the study

Soil[b]	Particle size			Texture	$pH_{1:5}$	$EC_{1:5}$	Specific surface area	Total organic carbon	Clay mineral			Fe oxide	
	Clay	Silt	Sand						Kaolinite	Illite	Smectite	Haematite	Goethite
		%				μS cm^{-1}	m^2 g^{-1}	g kg^{-1}			g kg^{-1}		
VE	51.0[c]	36.1	12.9	Clay	6.4b[d]	1 789e	229a	4.2c	30	690	10	1	1
MO	77.3	1.1	21.6	Heavy clay	9.2e	1 876f	556e	1.5a	500	250	20	5	5
CL	61.0	19.9	19.1	Heavy clay	8.3c	456c	424cd	2.8b	110	50	400	1	1
UR	61.0	12.4	26.6	Heavy clay	8.5cd	143ab	313ab	6.0d	150	110	150	1	1
SE1	68.5	12.4	19.1	Heavy clay	9.1e	934d	502de	11.2e	10	100	430	1	1
SE2	50.3	11.3	38.5	Clay	6.4b	67a	361bc	4.2c	400	10	10	5	30
EP1	49.0	15.0	36.0	Clay	6.5b	154b	318ab	4.2c	300	50	10	5	5
EP2	49.0	12.5	38.5	Clay	5.5a	71a	286ab	4.2c	300	30	10	5	20
EP3	54.8	1.1	44.1	Clay	8.6d	214b	495de	2.5b	340	110	10	1	20

[a] $pH_{1:5}$ and $EC_{1:5}$ are pH and electrical conductivity measured in the 1:5 soil-water extract, respectively.
[b] VE is the soil collected from Vermilion County, Illinois, USA; MO, CL and UR are the soils collected from Monarto, Claremont and Urrbrae in Adelaide, South Australia, respectively; SE1 and SE2 are the soils collected from the southeastern part of South Australia; EP1, EP2 and EP3 are the soils collected from the Eyre Peninsula, South Australia.
[c] Values are means (*n* = 3).
[d] Means followed by the same letter(s) in a column are not significantly different (*P* < 0.05).