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Colloidal properties and potential release of water-dispersible colloids in an agricultural soil depth profile

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ABSTRACT

The effects of soil depth on the colloidal properties and potential release of water-dispersible colloids (WDCs) in an agricultural soil were investigated in batch experiments. Nine soil samples were collected along a trench at different depths (from −7.5 cm to −127.5 cm) from the TERENO test site located in Selhausen (Germany). A physical gentle soil fractionation confirmed the importance of the solution chemistry in controlling the depth distribution of WDC in the Luvisol soil. A maximal fraction of total clay (f_{WDC}) equal to approx. 45% was released at a depth of −37.5 cm to −52.5 cm below the surface. This was found to be related to the lowest electrical conductivity of the soil electrolyte phase where Ca^{2+} concentration played a major role. A rather constant content of metal oxyhydroxide (MO(OH)) accounting for about 10% in WDCs was found along the soil depth after a dithionite-citrate-bicarbonate (DCB) extraction. However, a decrease from 40% to 25% in the contribution of MO(OH) particles to SSA of WDC was calculated along the soil depth. Using photon correlation spectroscopy (PCS) and N_2 gas adsorption method, variations were measured in colloidal hydrodynamic diameters (d_z) and the mineral specific surface area (SSA) for WDC in water-dispersed and dried states, respectively. A function structure $f(n_p)$ was defined to relate the particle size variations between the two states along the soil depth. An inverse correlation was established between the particle size variations which assumed that the number of primary particle in the water-dispersed state increases in subsoil samples. The effects of different soil parameters such as pH, organic carbon (OC) coverage at MO(OH) surfaces and humification index (HIX) of dissolved organic carbon (DOC) on the WDC structure variations are discussed. It can be hypothesized that a maximal surface OC coverage at MO(OH) surfaces of WDCs facilitates the release of small particles through electrosteric dispersion in topsoil. Lower pHs and WDC(OC) content would favor the release of large WDC particles in subsoil where an OC content of a more aliphatic character can also facilitate hydrophobic interactions.

1. Introduction

The importance of the soil organic carbon (SOC) in the carbon cycle has often been reviewed. The SOC availability for CO_2 transformation or sequestration in mineral soil determines an equilibrium that varies depending on the soil properties. It is generally acknowledged that OC in soil is roughly distributed between non-associated and associated OC pools with the mineral soil particles, which can be characterized by different soil fractionation methods. The sequestration of an OC pool at the surface of soil particles is known to increase its stability in microbial decomposition processes. Thus, direct OC adsorption at the soil colloidal clay fraction (<2 μm) as organo-mineral complexes is a major sequestration process where aluminosilicate clay minerals and metal oxyhydroxide (MO(OH)) components mainly contribute to the specific surface area (SSA) of the bulk soil (Baldock and Skjemstad, 2000; Kaiser and Guggenberger, 2003; Kögel-Knabner et al., 2008). It has been demonstrated that the dominant mechanism of organic matter (OM) stabilization is associated with amorphous and crystalline MO(OH) (Mikutta et al., 2006). OC associated with water-dispersible colloids (WDC) can be transported in deeper soil layers or by soil erosion in depositional environments (Van Oost et al., 2007). Another sequestration process involves the inclusion of organic matter in soil silt-clay size aggregates (Virto et al. 2010; von Lützow et al., 2006), the architecture of which largely depends on clay particle contacts. However, in the case of tillage and slaking events, dispersions of soil clay content into WDC forms promote the accessibility of uncomplexed OC to microorganisms (Balesdent et al., 2000; Lal, 2003) and its further transport as dissolved organic carbon (DOC).

According to these sequestration processes, the prerequisite for OC mobility and biodegradability is thus a colloidal dispersion state of soil clay particles, which can be achieved by varying hydrodynamic

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Abbreviations: DOC, dissolved organic carbon; d_z, z-average diameter; $f(n_p)$, function structure; f_{WDC}, WDC fraction of TC content; HIX, humification index; M_d, dithionite extractable metal; MO(OH), metal oxyhydroxide; OC, organic carbon; SOC, soil organic carbon; SSA, specific surface area; TC, total clay; TOC, total organic carbon; WDC, water-dispersible colloid; WDC(OC), WDC-associated OC.

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and soil electrolyte conditions. Thus, the impact energy of raindrops, hydrodynamic shear forces and wetting physically disintegrate soil aggregates. Chemical conditions, such as the presence of organic matter, increasing pH, decreasing ionic strength and increasing sodium adsorption ratio (SAR), are also crucial factors for the concentration of mobile WDCs (Frenkel et al., 1978; Grolimund and Borkovec, 2006; Kaplan et al. 1996, 1997; Kjaergaard et al., 2004a, 2004b; Kretzschmar et al., 1993; Miller et al., 1990; Nelson et al., 1999; Ryan and Elimelech, 1996; Séquaris and Lewandowski, 2003; Seta and Karathanasis, 1996).

In the present work, we investigated WDCs from soil samples collected along a trench profile in the TERENO test field at Selhausen (Germany). The dispersibility of the soil clay fraction after gentle shaking in deionized water was compared in batch experiments. The distribution and colloidal properties of potentially mobile WDCs were investigated and related to chemical solution and soil parameters, which characterize the soil depth profile. In particular, results from the gas adsorption method were combined with the results from the analysis of metal oxyhydroxide (MO(OH)) and OC contents to characterize the surface of WDCs. The effects of OC content and pH on the release mechanisms were discussed by scaling particle size variations of WDC samples in water-dispersed and freeze-dried states with photon correlation spectroscopy (PCS) and the N_2 gas adsorption method, respectively.

2. Material and methods

2.1. Soil samples

Soil samples taken from the TERENO test site were investigated. The test site is located in Selhausen (50°52′09.34″N; 6°27′00.58″E) in the river Rur catchment (North Rhine-Westphalia, Germany). The underlying sediments are fluvial deposits from the Rhine/Meuse river and the Rur River system, which were covered by aeolian sediments during the Pleistocene. A detailed description of the test site is given by Weihermüller et al. (2007). The test site represents an intensively used agricultural area where lime and fertilizer were applied regularly. The soil was classified as a cutanic luvisol (ruptic and siltic) according to the World Reference Base for Soil Resources classification (IUSS Working Group WRB, 2007). It consists of three horizons ranging from 0 cm to 33 cm (Ap), 33 cm to 57 cm (EBw), and 57 cm to 130 cm (2Btw). The soil texture is a silt loam.

Soil samples were collected in a fresh wall along a trench. Samples were taken along 3 vertical profiles at 9 different depths (−7.5 cm to −127.5 cm) and mixed to provide a representative sample. The samples were air-dried. Stones and large pieces of plant material were removed by hand after soils were sieved through a 5 mm sieve. The mean grain size distribution and soil pH are listed in Table 1.

2.2. Soil fractionation

Wet sieving soil fractionation was performed after chemical dispersion according to Cambardella and Elliot (1992). Therefore, 10 g soil (<2 mm) was shaken overnight with 0.05 L fresh Na hexametaphosphate (5 g L^{-1}) solution (Séquaris et al., 2010a). The dispersed soil samples were passed sequentially through a 200 μm (Retsch GmbH, Haan, Germany) and a 53 μm sieve (Fritsch GmbH, Idar-Oberstein, Germany) and rinsed thoroughly with water until the rinsate was clear. The material remaining on the sieves was freeze-dried and weighed in order to analyze the organic carbon content. The particle size fractions used here are operationally defined by this widely used fractionation method. It is generally considered that the particle size fraction 0–53 μm passing through the 53 μm sieve contains the mineral-associated and water-soluble C, while the particle size fraction 53–2000 μm remaining on the 53 and 200 μm sieves contains the particulate organic matter (POM).

Table 1
Primary particles soil fractions, organic carbon content in bulk soil (SOC), mineral specific surface area of bulk soil ($SSA_{bulk\ soil}$) and soil pH.

Depth cm	Clay %	Silt %	Sand %	SOC g kg^{-1}	$SSA_{bulk\ soil}$ $m^2\ g^{-1}$	pH[a] H_2O	pH[a] 0.01 M $CaCl_2$
7.5	17.1 ± 1.0	67.5 ± 0.7	15.4 ± 0.4	10.23 ± 0.42	9.8 ± 1.1	7.0	6.5
22.5	16.6 ± 0.6	67.7 ± 0.2	15.6 ± 0.4	9.82 ± 0.24	11.6 ± 0.5	7.3	6.6
37.5	19.6 ± 0.5	66.2 ± 0.8	14.2 ± 0.6	4.46 ± 0.15	14.3 ± 1.1	7.3	6.3
52.5	22.0 ± 1.8	60.0 ± 2.7	18.1 ± 1.3	2.85 ± 0.06	18.0 ± 0.9	7.0	6.2
67.5	24.3 ± 1.3	63.3 ± 1.8	12.4 ± 1.1	2.53 ± 0.07	19.0 ± 0.4	6.7	6.1
82.5	25.0 ± 0.3	65.1 ± 0.8	9.8 ± 0.6	1.88 ± 0.03	18.7 ± 0.4	6.7	6.1
97.5	23.8 ± 0.1	64.7 ± 0.8	11.5 ± 0.9	1.43 ± 0.01	18.9 ± 1.0	6.7	6.2
112.5	21.9 ± 0.9	62.8 ± 0.7	15.3 ± 1.4	1.38 ± 0.02	17.3 ± 0.8	6.8	6.2
127.5	20.2 ± 1.0	58.9 ± 2.6	20.9 ± 2.3	0.82 ± 0.01	15.0 ± 0.5	6.7	6.1

[a] Soil/water or 0.01 M $CaCl_2$ (1/5).

2.3. Soil clay dispersibility and WDC fractionation

WDCs in soil samples along the soil depth were fractionated in a batch experiment to compare the dispersibility of the soil clay fraction. WDC fractionation was conducted gently in triplicate as follows: 100 g air-dried soil sample was added to a 1000 mL Duran bottle (Schott, Germany) containing 200 mL Millipore deionized water and shaken using a horizontal shaker (150 rpm) for 6 h. 600 mL deionized water was then added before starting sedimentation (Séquaris and Lewandowski, 2003). Aqueous phase containing non-settling colloids (colloidal phase) was obtained after a sedimentation time of 12 h at room temperature. This easily dispersed colloidal soil content in the aqueous phase was defined as WDC, the colloidal properties of which were characterized by electrokinetic and particle-size parameters (Table 2). The WDC size fraction from 0.05 μm to 2 μm was obtained by high-speed centrifugation (10,000 *g*; 90 min) of the soil colloidal phase without no filtration. After the centrifuged WDCs were freeze-dried, their OC (WDC(OC)) contents were analyzed and their mineral specific surface area (SSAs) were measured (Table 2). The mineralogical composition of WDC from XRD analyses comprises illite (abundant), kaolinite, smectite, chlorite/vermiculite (present or little) in Table 2. The freeze-dried WDC samples were characterized by the typical platelet-like structure of clay minerals (Supplementary data S.1). The aqueous phase remaining after centrifugation was designated as the electrolyte phase. The chemical composition of the electrolyte phase was also analyzed. The OC content of this phase was operationally defined as dissolved organic carbon (DOC).

Table 2
Organic carbon content in WDC (WDC(OC)), mineral specific surface area of WDC (SSA_{WDC}), particle size (d_z), zeta potential, and pH of electrolyte phase and minerals in WDC (XRD).

Depth cm	WDC(OC) g kg^{-1}	SSA_{WDC} $m^2\ g^{-1}$	d_z nm	Zeta potential mV	pH	Minerals in WDC[a]
7.5	26.53 ± 0.10	56.6 ± 0.5	611 ± 23	−(18 ± 5)	7.48	I^A, C/V^C, K^C
22.5	23.47 ± 0.25	59.3 ± 0.2	611 ± 70	−(18 ± 5)	7.54	I^A, C/V^C, K^C
37.5	14.07 ± 0.23	70.7 ± 0.6	499 ± 16	−(22 ± 5)	7.48	I^A, C/V^B, K^C, S^C
52.5	9.96 ± 0.07	80.5 ± 0.4	659 ± 63	−(20 ± 5)	7.03	I^A, C/V^B, K^C, S^C
67.5	8.20 ± 0.03	79.1 ± 2.3	691 ± 25	−(18 ± 5)	7.13	I^A, C/V^B, K^C, S^C
82.5	5.79 ± 0.10	78.5 ± 0.8	784 ± 90	−(17 ± 5)	6.82	I^A, C/V^B, K^C, S^C
97.5	4.82 ± 0.02	79.3 ± 1.6	779 ± 23	−(17 ± 5)	6.90	I^A, C/V^B, K^C, S^C
112.5	4.10 ± 0.02	80.2 ± 0.2	752 ± 30	−(17 ± 5)	6.93	I^A, C/V^B, S^B, K^C
127.5	4.31 ± 0.03	83.2 ± 0.2	790 ± 12	−(18 ± 5)	6.88	I^A, C/V^B, S^B, K^C

A = abundant; B = present; and C = little.

[a] XRD mineral analysis: I, illite; C/V, chlorite and/or vermiculite; K, kaolinite; and S, smectite.