Geoderma 235–236 (2014) 260–270

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Effect of metal oxide on surface area and pore size of water-dispersible colloids from three German silt loam topsoils

Canlan Jiang [a,1], Jean-Marie Séquaris [a,*], András Wacha [b], Attila Bóta [b], Harry Vereecken [a], Erwin Klumpp [a]

[a] Agrosphere, IBG 3, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
[b] Department of Biological Nanochemistry, Institute of Molecular Pharmacology, Research Centre for Natural Sciences, Hungarian Academy of Sciences (IMP RCNS HAS), Pusztaszeri út 59-67, H-1025 Budapest, Hungary

ARTICLE INFO

Article history:
Received 21 May 2013
Received in revised form 17 July 2014
Accepted 18 July 2014
Available online 1 August 2014

Keywords:
Metal oxide
Water dispersible colloid
Particle size
Surface area
Mesopore
Small-angle X-ray scattering
N_2 gas-adsorption
Dynamic light scattering
Microelectrophoretic method

ABSTRACT

The surface area and pore structure of easily dispersed soil particles <2 μm in size (water-dispersible colloids, WDCs) are important for carbon sequestration and transport in soil, two processes which are essential for the terrestrial carbon cycling. In this work, we determine the effects of dithionite–citrate–bicarbonate (DCB) extractable metal oxides, and oxalate extractable metal oxides on the specific surface area (SSA) and pore structure of WDCs from silt loam topsoils of three TERENO test sites with a similar clay content (20%) in Germany (arable (Selhausen), grassland (Rollesbroich) and forest (Wuestebach) soils). The N_2 gas-adsorption (−196 °C), small-angle X-ray scattering (SAXS), dynamic light scattering (DLS) and microelectrophoretic (ME) methods were used and compared. Results show that 1) the SSA of the WDCs from Selhausen, Rollesbroich, and Wuestebach decreased more after DCB treatment (27%, 35%, and 44%) than after oxalate treatment (5%, 14%, and 22%). DCB removed metal oxide nanoparticles from WDCs were found to have diameters (d_p) ranging from 4 nm to 8 nm and the surface loading ratios on the surface of aluminosilicate residues in WDCs were estimated to be 11% to 22% for three soils where the highest value was found in the acidic forest soil. 2) Pore sizes in the mesopore range (2 nm to 50 nm) were analyzed in the WDC fractions. The results were discussed in terms of accessible open pores for the pristine WDCs and WDC samples from which metal oxide nanoparticles and organic carbon (OC) had been removed. The lower average pore radius (R_p) measured by the N_2 gas-adsorption method based on the total volume (V_t) to SSA ratio variations in WDCs without metal oxides compared to WDC with metal oxides indicated a contraction of the porous structure of WDCs due to the presence of metal oxide nanoparticles. The pore size distribution (PSD) analysis showed a sensitive contribution of metal oxide nanoparticles in the low range of pore sizes (<25 nm) of WDCs. In SAXS measurements, higher surface fractal dimensions (D_s) were observed in WDCs before the metal oxide's removal, which supports a roughness increase of the interfaces in the presence of nanoparticles. The colloidal characterization of WDCs by the DLS and ME methods shows, at a μm scale, the role of positively charged metal oxide nanoparticles in forming WDCs with a more compact structure by decreasing the particle size (d_z) and the negative zeta potential (ζ). 3) The comparison of R_p, k, d_z and d_p results between different soils also indicates the dependence on the clay mineralogy of WDCs so that the heterocoagulation between kaolinite and illite (clay minerals of different aspect ratios) increases the size of soil mesopores (Rollesbroich). In conclusion, the results of this study clearly show that the combination of the N_2 gas-adsorption, SAXS, DLS and ME methods allows the characterization of soil porosity in the nanometer range where metal oxide nanoparticles contribute to a more compact structure of WDC.

1. Introduction

Soil structures have an important influence on environmental processes such as water filtration and carbon sequestration. The large specific surface area (SSA) of the soil clay fraction traps and stabilizes organic carbon (OC) through electrostatic and chemical complexations (Mikutta et al., 2007). The inclusion of the soil clay fraction in the narrow porous structure of soil hinders the accessibility of OC to microbial degradation (Baldock and Skjemstad, 2000; Six et al., 2002; Sollins et al., 1996). Water dispersible colloids (WDCs) that can be easily dispersed in contact with soil water are soil particles <2 μm from soil clay fractions.

Abbreviations: BJH, Barret–Joyner–Halenda; CB, citrate-carbonate; DCB, dithionite–citrate–bicarbonate; DLS, dynamic light scattering; D_m, mass fractal dimensions; DOC, dissolved organic carbon; D_s, surface fractal dimension; d_p, particle diameter; d_z, z-average particle diameter; k, pore fractal dimension; M_{CB}, citrate-bicarbonate extractable metal; M_{DCB}, dithionite–citrate–bicarbonate extractable metal; $M_{oxalate}$, oxalate-extractable metal; ME, microelectrophoretic; V_p, total pore volumes; q, scattering vector; Roll, Rollesbroich; R_p, pore radii; SAXS, small-angle X-ray scattering; Selh, Selhausen; SSA, specific surface area; TOC, total organic carbon; WDC, water-dispersible colloid; Wuest, Wuestebach; ζ, zeta potential; $_{70}$, before OC removal; $_{400}$, after OC removal.

* Corresponding author.
E-mail address: j.m.sequaris@fz-juelich.de (J.-M. Séquaris).
[1] Present address: The College of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing 210095, People's Republic of China.

http://dx.doi.org/10.1016/j.geoderma.2014.07.017
0016-7061/

They mainly include aluminosilicate and metal oxide particles, which can be released from soil aggregate structures. The dispersions of the soil clay content into a WDC form promotes the accessibility of uncomplexed organic matter and leads to its further transport as dissolved organic matter (DOM) (Kretzschmar et al., 1999; McCarthy and Zachara, 1989). By strongly associating with the clay surfaces of WDC, transport of OM into deeper soil layers is also possible (Séquaris et al., 2010). Mechanical and chemical processes in soil are key factors which affect the stability of soil aggregates and thus the release and stability of mobile WDCs such as a combination of hydrodynamic parameters (intensive rain, splash erosion, infiltration water rate) and chemical dispersion conditions (the presence of organic matter, increasing pH, decreasing ionic strength and increasing sodium adsorption ratio (SAR)) (Jarvis et al., 1999; Kjaergaard et al., 2004a, 2004b). It has been shown that shaking soil aggregates in low-ionic strength water simulates erosive dispersion (Séquaris et al., 2010). WDC release has been modeled by formulating a two-step mechanism (Ryan and Elimelech, 1996; Ryan and Gschwend, 1994). A rapid detachment step of WDC is shown by modeling the net-interaction energy potential between colloids and mineral grains. It is followed by a diffusion-controlled transport step of the mobilized WDC through immobile water layers at the soil aggregate surfaces in the low mechanical energy range of batch experiments (Jiang et al., 2013; Ryan and Gschwend, 1994).

The heterogeneous WDC structure contributes to the sequestration of organic matter. The organic matter is stabilized by physical inclusion and chemical reaction with metal oxide surfaces (Eusterhues et al., 2005; Kaiser and Guggenberger, 2000, 2003; Kiem and Kögel-Knabner, 2002; Wagai and Mayer, 2007). Various forms of iron oxides can be found in soils (Cornell and Schwertmann, 2003). Iron oxides in crystalline form such as goethite and in less-crystalline forms such as hydrous oxide ferrihydrite are the most abundant (Childs, 1992; Gaboriaud and Ehrhardt, 2003; Roden and Zachara, 1996). In the case of aluminum oxide, less-crystalline forms such as hydrous oxide gibbsite are the most common (Gilkes et al., 2006; Rosenqvist et al., 2003). These metal oxides can be selectively extracted by different dissolution methods. Dithionite–citrate–bicarbonate (DCB) treatment (Cornell and Schwertmann, 1996; Kiem and Kögel-Knabner, 2002; Mehra and Jackson, 1960; Turchenek and Oades, 1979) mainly extracts Fe oxyhydroxides, which can be used to calculate the total iron oxide (M_{DCB}) via reduction and parts of the dissolve oxides for Al and Si. Ammonium oxalate treatment (pH 3) (Kiem and Kögel-Knabner, 2002; Schwertmann, 1964) is generally used for the selective dissolution of Fe, Al, and Si ($M_{oxalate}$) from poorly crystalline aluminosilicates, ferrihydrite and Al- and Fe-humus complexes, but the Al, Fe, Si from gibbsite, goethite, hematite and layer silicates are not included (Mikutta et al., 2005). Despite the relatively low mass contribution of metal oxides to German soil, these nanometer-sized mineral particles have significant effects on the total surface of soil aggregates because of their inherently large surface area (Eusterhues et al., 2005; Kaiser and Guggenberger, 2003; Pronk et al., 2011). These particles are located as free clusters or cover the surface of much larger particles (Deshpande et al., 1968; Hendershot and Lavkulich, 1983). They contribute to the porous structure of WDC by their interactions with large plate-like particles of clay minerals. Thus, small organic molecules, such as organic acids, should be able to enter micropore space (<2 nm), where they would be protected from microorganisms and their enzymes (Eusterhues et al., 2005). A comprehensive characterization of the heterogeneous porosity of WDCs in air-dried and water-dispersed states requires different chemical and physical approaches. Pores can be defined as open pores if they communicate with the external surface and are accessible to molecules or ions from the surroundings. By contrast, closed pores are closed as individual voids in the mineral matrix which is not interconnected to the external surface (Radlinski et al., 2004). The N_2-gas adsorption method has been widely used to measure the specific surface area (SSA) and characterize the open porosity of air-dried soil particles, especially the mesoporosity (pore width between 2 and 50 nm) and microporosity (pore width not exceeding 2 nm) (Mayer et al., 2004; Pronk et al., 2011). The small-angle X-ray scattering (SAXS) technique (Guinier and Fournet, 1955) has been used more generally for the internal and external structural characterization of porous solid materials on a length scale of typically 1 nm to 100 nm as in the case of silica gel (Schmidt, 1991; Schmidt et al., 1991) and clay minerals (Pernyeszi and Dékány, 2003). It has been shown that SAXS technique is suitable for studying fractal dimensions, (D) of powders with porous or irregular surface (Höhr et al., 1988; Schmidt, 1991) where D values are provided from a power law of the measured scattered intensity $I(q)$ as a function of the scattering angle 2θ. D values have thus expressed the compactness of allophane aggregate clusters in andosols (Chevallier et al., 2010) and the surface roughness of soil grains (Borkovec et al., 1993). Broadly speaking, higher D values point to higher surface roughness, higher aggregation mechanism and higher cluster compactness (Marliere et al., 2001).

The effect of metal oxides on soil SSA and pores can be determined through N_2 gas-adsorption method while investigations using the SAXS method are not aware to our knowledge. Kaiser & Guggenberger found that the SSA of soils is highly correlated with the amount of Fe oxyhydroxides (Kaiser and Guggenberger, 2003). Eusterhues et al. (2005) studied two German acid forest soils and found only a few micropores remaining in samples after the dissolution of iron oxides. The soluble minerals in the DCB extraction method were identified as the main microporous phases in soil. Filimonova et al. (2006) demonstrated that the removal of iron oxides by DCB treatment decreases the SSA by up to 50%. In their study, the micropores completely vanished in two German luvisol and gleysol soils.

In the present study, both gas adsorption and SAXS were applied to investigate the effect of metal oxide particles in the SSA and porous structure of the mineral matrix in WDC samples in the freeze-dried state. The variations of colloidal properties of WDCs were detected in the water-dispersed state of WDC samples by dynamic light scattering (DLS) and microelectrophoretic (ME) methods. Soil samples were obtained from the TERENO project, whose observatories span Germany and supply data regarding the impact of long-term climate change on ecosystems, land use, and infrastructure at the regional level (www.TERENO.net) (Zacharias et al., 2011). This study is part of the SoilCan project (Puetz et al., 2009) of TERENO and mainly focuses on the stability of soil aggregates (Jiang et al., 2013; Séquaris et al., 2013). Three German silt loam topsoils were systematically analyzed after applying the DCB and oxalate extraction methods. The three soils were luvisol, cambisol, and gleysol, all of which are widespread and important for agriculture all over the world (Driessen et al., 2001). With N_2 gas-adsorption, SSA variations in WDC fractions and bulk soils were examined. In the case of WDC fractions, total pore volumes (V_p) were also measured to further calculate the distribution of pores and the average pore radii (R_p). Particular attention was paid to estimating the size extent of the coverage of metal oxide nanoparticles in the mesopore size range of the WDC mineral matrix. Information obtained by the SAXS method about the surface fractal dimensions from power law scattering intensity was recorded. The diameter and zeta potential of colloidal WDCs were further investigated by the DLS and ME methods, respectively. The results of the colloidal characterization of the samples in the micrometer range were related and compared to the N_2 gas-adsorption and SAXS results. This study aims to reconcile results using very different measurements and to provide information on WDC structure parameters affected by metal oxides.

2. Materials and methods

2.1. Soil samples

Topsoil samples (0 cm to 10 cm) were collected in July 2010 from three test sites in Germany, Selhausen (Selh) (50°52′08″N; 6°26′59″E; arable luvisol), Rollesbroich (Roll) (50°37′18″N; 6°18′15″E; grassland