Sorption of organic carbon compounds to the fine fraction of surface and subsurface soils

S. Jagadamma [a,*], M.A. Mayes [a], Y.L. Zinn [b], G. Gísladóttir [c], A.E. Russell [d]

[a] Climate Change Science Institute and Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[b] Department of Soil Science, Federal University of Lavras, MG 37200, Brazil
[c] Department of Geography and Tourism, University of Iceland, 101 Reykjavík, Iceland
[d] Department of Natural Resource Ecology & Management, Iowa State University, Ames, IA 50011, USA

A B S T R A C T

Dissolved organic carbon (DOC) transported from the soil surface is stabilized in deeper soil profiles by physico-chemical sorption processes. However, it is unclear how different forms of organic carbon (OC) compounds common in soil organic matter interact with soil minerals in the surface (A) and subsurface (B) horizons. We added four compounds (glucose, starch, cinnamic acid and stearic acid) to the silt- and clay-sized fraction (fine fraction) of A and B horizons of eight soils from varying climates (3 temperate, 3 tropical, 1 arctic and 1 sub-arctic). Equilibrium batch experiments were conducted using 0 to 100 mg C L^{-1} of ^{14}C-labeled compounds for 8 h. Sorption parameters (maximum sorption capacity, Q_{max} and binding coefficient, k) calculated by fitting sorption data to the Langmuir equation showed that Q_{max} of A and B horizons was very similar for all compounds. Both Q_{max} and k values were related to sorbate properties, with Q_{max} being lowest for glucose (20–500 mg kg^{-1}), highest for stearic acid (20,000–200,000 mg kg^{-1}), and intermediate for both cinnamic acid (200–4000 mg kg^{-1}) and starch (400–6000 mg kg^{-1}). Simple linear regression analysis revealed that physico-chemical properties of the sorbents influenced the Q_{max} of cinnamic acid and stearic acid, but not glucose and starch. The sorbent properties did not show predictive ability for binding coefficient k. By using the fine fraction as sorbent, we found that the mineral fractions of A horizons are equally reactive as the B horizons irrespective of soil organic carbon content.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Transport of dissolved organic carbon (DOC) from the litter layer and organic carbon (OC) rich surface soil layers constitutes an important component of OC flux into deeper soil horizons (Kalbitz et al., 2005). A major part of DOC is retained and chemically protected on mineral surfaces by sorption (Kaiser and Guggenberger, 2000). Chemical protection refers to various chemical bonds formed by the newly added OC functional groups with mineral surfaces or with the OC functional groups already attached to the mineral surfaces. Chemical protection tends to render sorbed OC less susceptible to enzymatic degradation or microbial uptake (Jones and Edwards, 1998; Kalbitz et al., 2005; van Hees et al., 2003). Physical protection, in contrast, refers to the occlusion of OC particles and molecules into mesopores and interstitial spaces of layered minerals (Kaiser and Guggenberger, 2003; Kögel-Knabner et al., 2008; Zimmerman et al., 2004). This process results in

the formation of stable soil aggregates that protect OC against microbial degradation (Jastrow, 1996; Oades, 1984, 1988) because diffusion of relatively large enzymes and microbes into small pores within soil aggregates is inhibited (McCarthy et al., 2008; Zhuang et al., 2008).

The fine fraction of soils (<53 μm) consists of silt and clay-sized organo-mineral associations, and it is believed that DOC is primarily sorbed to the fine fraction (Christensen, 2001; Kaiser et al., 1996). Most (25 to 98%) of the OC in soils is associated with the fine fraction and the dominant mechanism is chemical protection (Basile-Doelsch et al., 2007; Christensen, 1992; Schulten and Leinweber, 2000). Coarser soil fraction (>53 μm) consisting of sand and organic particles including roots, plants, and soil fauna debris are referred to as the particulate OC (POC) fraction. The POC fraction has relatively few reactive functional groups to support the sorption of DOC (Christensen, 2001; Hassink, 1997) and stabilization of POC tends to occur by the formation of soil aggregates. In most soils, surface (A) horizons are enriched with the POC fraction and stabilized aggregates, while subsurface (B) horizons are enriched with OC in the fine fraction (Feller and Beare, 1997; Kögel-Knabner et al., 2008; Swanston et al., 2005). Field studies demonstrate that concentrations and fluxes of DOC decrease significantly with increasing soil depth because of lower C inputs and greater stabilization

* Corresponding author at: Oak Ridge National Laboratory, 1 Bethel Valley Rd, PO BOX 2008, MS6036, Oak Ridge, TN 37831, USA. Tel.: +1 330 601 2134.
E-mail address: jagadammas@ornl.gov (S. Jagadamma).

Table 1
Soil collection locations and taxonomy.

Soils	Location	B horizon	Soil taxonomy
Temperate			
Alfisol	Milan, Tennessee, USA	Btx	Oxyaquic Fraglossudalfs
Mollisol	Batavia, Illinois, USA	Btg1	Typic Endoaquolls
Temp-Ultisol	Walker Br, Tennessee, USA	2Bt1	Typic Paleudults
Tropics			
Trop-Ultisol	Lavras, Minas Gerais, Brazil	Bt2	Typic Hapludult
Oxisol-1	Lavras, Minas Gerais, Brazil		Humic Rhodic Acrudox
Oxisol-2	La Selva Biological Station, Costa Rica	Bt1	Haplic Haploperox
Sub-arctic			
Gelisol	Fairbanks, Alaska, USA	Cgf[a]	Typic Aquiturbels
Andisol	Krýsuvíkurheiði, Reykjanes, Iceland	Bw	Haplic Andosol[b]

[a] Permafrost layer.
[b] Based on World Reference Base system, all others are based on USDA–NRCS system.

with soil minerals (Fröberg et al., 2007; Gjettermann et al., 2008; Jardine et al., 2006; Michalzik and Matzner, 1999; Qualls et al., 2002). However, it is unclear whether chemical sorption is greater in subsurface horizons as a result of real mineralogical differences between the surface and subsurface horizons. Alternatively, sorption may be less important in the A horizon because reactive mineral surfaces are hidden within stabilized aggregates.

The chemical structure of DOC also controls the sorption potential of reactive soil components. There are numerous studies of sorption of DOC extracted from natural aquatic and terrestrial systems (e.g. Kothawala et al., 2009; Mayes et al., 2012; Mikutta et al., 2007; Moore and Matos, 1999). Nevertheless, DOC is a complex mixture of a variety of compounds with varying properties, chemical structures, and molecular sizes. Each component molecule has specific sorption energy and sorptive characteristics, thus the overall sorption isotherm of DOC is the combined sorption isotherms of all the components (Wen et al., 2007). When natural DOC is used as a sorbent in sorption experiments, it is impossible to understand how the individual moieties in the DOC become sorbed onto the soil surface. Some studies used hydrophilic and hydrophobic components fractionated from the bulk DOC (Kaiser et al., 1996; Pérez et al., 2011). However there are two major problems with this approach: (i) composition of DOC in the equilibrium soil solution is determined not only by the sorption of the component molecules on soil solids, but also by the desorption of indigenous OC to the solution phase, and (ii) both hydrophilic and

hydrophobic fractions contain similar OC functional groups, e.g. carboxyl groups (Kothawala et al., 2012). Only a few studies have examined the sorption of specific DOC functional groups on soils using, e.g., dissolved carboxylic acids (e.g. Jones et al., 2003; Strahm and Harrison, 2008; Ström et al., 2001; van Hees et al., 2003), glucose, or amino acids (e.g. Fischer et al., 2010; Jones and Edwards, 1998) on an individual soil or a few soils. Studies using major classes of OC compounds as sorbates and wider range of soils as sorbents are needed to understand how specific molecules in DOC interact with soils.

To our knowledge, there have been no earlier attempts to assess the sorption capacity of reactive silt and clay-sized fractions in the A and B horizons of soils. The objective of the current study is to quantify the sorption capacity of the silt- and clay-sized (fine) fractions of a widely different group of soils as a function of soil horizon and sorbate chemistry. Thus, this study used the following approaches: (i) soils from temperate, tropical, arctic and sub-arctic ecosystems were used as sorbents, (ii) OC compounds were carefully selected to represent the common classes of C compounds present in DOC, and (iii) fine fraction of soils containing silt and clay-sized particles was isolated and used as sorbents in order to eliminate the interference of aggregation and plant residues on chemical sorption.

2. Materials and methods

2.1. Soils and fractionation

The soils selected for this study cover a broad geographical area and represent some of the common soil orders of temperate (Mollisol, Alfisol, and Ultisol), tropical (Ultisol and Oxisol), arctic (Gelisol) and sub-arctic (Andisol) climates (Table 1). Soils from A and B horizons were collected, air-dried and sieved to <2 mm. The fine fraction was isolated from <2 mm soil following a size-based fractionation protocol. Briefly, 25 g soil, 125 mL deionized water and 25 glass beads (4 mm diameter) were combined in a 250 mL polyethylene bottle and shaken on a reciprocal shaker for 16 h. Number of beads, and time and speed of shaking were optimized in preliminary tests to ensure satisfactory disruption of aggregates with minimal fragmentation of organic residues. The fine fraction (silt + clay-sized) was separated from the sand and POC fraction by wet sieving the soil suspension through a 53 μm sieve. The fine fraction passed through the sieve was collected and dried in an oven at 60 °C. We used glass beads to mechanically disperse the soil instead of other common dispersion methods, e.g., sodium hexametaphosphate or sonication, because glass beads are reported to be the most appropriate method for minimizing C loss and POC

Table 2
Physical and chemical characteristics of the silt- and clay-sized organic carbon fraction (fine fraction) of soils.

Soil	Horizon	pH	OC	Clay[a]	Fe_d	Al_d	Fe_o	Al_o	Fe_p	Al_p
			(g kg^{-1})							
Alfisol	A	5.24	5.25	305	17.74	5.51	3.50	1.24	0.85	0.55
	B	4.91	3.09	368	22.52	4.43	4.43	1.50	0.34	0.39
Mollisol	A	7.13	30.37	380	17.41	4.22	1.12	2.34	0.34	0.77
	B	7.54	7.04	321	23.45	3.89	0.70	1.53	0.05	0.22
Temp-Ultisol	A	6.44	11.59	342	14.74	3.27	0.80	1.34	0.91	0.53
	B	4.33	2.21	556	34.03	5.27	0.92	1.15	0.20	0.30
Trop-Ultisol	A	4.70	28.48	726	32.98	6.84	3.02	2.19	2.49	1.85
	B	4.12	8.05	792	36.73	7.04	1.54	2.02	2.03	1.63
Oxisol-1	A	3.70	50.02	770	107.95	14.76	6.16	3.98	10.23	6.57
	B	4.11	22.71	849	119.38	17.75	3.30	3.64	7.92	5.17
Oxisol-2	A	3.93	24.19	700	84.91	21.75	9.00	4.59	21.96	7.48
	B	4.15	8.38	809	113.85	25.78	2.92	3.95	2.57	1.58
Gelisol	Active	5.86	11.97	141	16.49	2.25	8.99	0.98	1.99	0.34
	Permafrost	7.50	11.16	144	20.2	1.96	9.97	1.19	1.82	0.18
Andisol	A	5.04	93.95	176	72.27	29.23	43.74	20.00	5.50	7.76
	B	5.24	86.01	128	84.76	39.16	48.10	28.26	7.71	8.67

OC is organic carbon; Fe_d and Al_d are dithionate–citrate–bicarbonate extractable Fe and Al; Fe_o and Al_o are ammonium oxalate (in the dark) extractable Fe and Al; Fe_p and Al_p by sodium pyrophosphate extractable Fe and Al.
[a] Clay + silt in fine fraction is 1000 g kg^{-1}.