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Selective adsorption of dissolved organic matter to mineral soils

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ABSTRACT

As soil solutions pass through forested mineral soils, the chemical and structural compositions of dissolved organic carbon (DOC) can alter substantially due to interactions with soil particle surfaces. Typically, adsorption processes dominate in mineral soils and the resulting concentration of DOC is reduced substantially. We studied changes in the molecular and structural compositions of DOC during equilibration with mineral soils collected across Canada ($n = 43$) and found that the overall aromatic content of DOC decreased with equilibration in almost all cases from using specific absorbance (SUVA) and the fluorescence index. The fluorescence index revealed that podzolic B horizons, with typically large adsorption capacity (*Qmax*), had the greatest reduction in aromaticity, which was partially explained by the much lower aromatic content of DOC desorbed from soils surfaces. In contrast, a decrease in DOC aromaticity for volcanic B horizons, also with high *Qmax*, was primarily due to adsorption. An unexpected finding was the release of extremely high (2.6×10^6 Da) and low (420 Da) molecular weight (MW) organic materials during equilibration using high performance size exclusion chromatography (HPLC), for luvisols and podzols, respectively. In general, the average number–average MW (M_n) of DOC decreased for all soil types, but the greatest decrease in M_n was observed for mineral soils with large *Qmax*, including the podzolic and volcanic B horizons. Analysis of changes in FTIR spectra revealed that the most prominent change to DOC functional groups was a reduction in carboxyl groups, which was even greater than the removal of aromatic DOC. The findings of this study emphasize that while DOC concentrations may decrease substantially during passage through mineral soils, it is valuable to consider the contribution of DOC from desorption of pre-existing soil C. Essential to the findings of this study was the inclusion of multiple analytical techniques to track changes to DOC character, and the inclusion of a wide range of mineral soils.

1. Introduction

Dissolved organic carbon (DOC) found in forest soil–solutions consists of a spectrum of molecules ranging in molecular size, solubility and functional group composition. The chemical and physical structures of DOC have been linked to ecological and environmentally relevant functions (Cabaniss et al., 2000; Chin et al., 1998). For instance, the transport and fate of heavy metals and organic contaminants are strongly influenced by chemical associations with DOC within soils (Tipping and Hurley, 1992; Tipping et al., 2003). In addition, the quality of DOC leached from forest soils can influence pH buffering capacity and nutrient availability in surface waters (Hruska et al., 1999; Qualls and Haines, 1991a).

An important abiotic process influencing the chemical composition of DOC in soil solutions is adsorption and desorption on soil particle surfaces (Kaiser et al., 2002; Qualls et al., 2002). Soil solutions leaching through mineral soil horizons often contain high concentrations of DOC generated from decomposing litter within upper organic rich horizons (McDowell and Likens, 1988; Michalzik et al., 2001). DOC contains a broad mixture of organic polyelectrolytes, and likewise, soil particle surfaces have positively and negatively charged sites. Consequently, a multitude of interactions can occur between DOC and soil surfaces. Mineral soil horizons with a high capacity to adsorb DOC have been found to contain high amounts of amorphous oxides and oxyhydroxides of Fe and Al, which are particularly abundant in the B horizons of acidic podzols and soils derived from volcanic parent materials (Kaiser et al., 1996; Kothawala et al., 2009; Moore et al., 1992). As a soil–solution infiltrates through mineral horizons, the concentration and chemical composition of DOC can vary substantially resulting from dominant interactions including ligand exchange, cation bridging, anion exchange and weaker van der Waals forces (Sposito, 2004; Tan, 2003). Changes to DOC composition may thus be highly variable depending on physical and mineralogical characteristics of the soil. Determining which soil

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properties influence the chemical partitioning of DOC during passage through mineral soils can further our understanding of how soil processes influence the quality and function of DOC entering aquatic systems.

Several studies have examined changes to the chemical characteristics of DOC before and after sorption to mineral soils under controlled conditions, providing useful insights into mechanisms of soil–DOC interactions (Ghosh et al., 2009; Gu et al., 1994; Kaiser, 2003). But, there is a gap in our understanding of how variable DOM partitioning may be over a broad range of mineral soils, as studies using soils collected from a narrow range of sites have a limited ability to compare among soil characteristics (Kaiser et al., 2002; van Hees et al., 2005). Similarly, studies using well-identified pure soil minerals such as goethite (FeO(OH)) are unable to assess the potential contribution of soil C desorption, which could be an important source of DOC.

Numerous analytical techniques have been developed and adapted over the past several decades to assess various measures of DOC quality (for example see Thacker et al., 2005), yet no single technique has proven to be fully effective as a means of characterizing DOC. Here, we apply four techniques to examine changes to soil–solution DOC before and after equilibration with mineral soils. Two optical techniques are the fluorescence index and SUVA, which provide surrogate measures of aromaticity and have been effective due to their simplicity to measure and interpret (McKnight et al., 2001; Weishaar et al., 2003). In addition, we include high performance size exclusion chromatography (HPSEC), allowing for the identification of shifts in the molecular weight distribution, and Fourier transform infra red (FTIR) spectrophotometry, to examine changes to the prominent functional groups of DOC. Our objectives are to identify changes to the chemical and structural character of DOC that result from exchange reactions with mineral soil surfaces. We use a wide range of mineral soils representative of Canadian temperate and boreal forests, that have been well-characterized in terms of adsorption capacity and desorption potential (Kothawala et al., 2009).

2. Methods

2.1. DOC source

DOC was extracted from the organic L, F, and H horizons of a podzol (Canada Soil Survey Committee, 1998) collected from Mt. Saint Hilaire, Québec (45°33′N, 73°08′W). The intact LFH horizon was soaked in deionized water overnight. The soil solution was decanted from the soil, filtered with 0.45 μm glass fiber filters (Rose Scientific), and stored at 4 °C, to produce an initial DOM solution with a concentration of 61 $mg \cdot L^{-1}$ for all batch sorption experiments, and had a pH of 4.8 and conductivity of 100 $\mu S \cdot cm^{-1}$.

2.2. Study sites

Mineral soil horizons included in the study were collected from 17 soil profiles across Canada and represent five soils orders including podzol, brunisol, luvisol, gleysol and an organic soil (Canada Soil Survey Committee, 1998). Soil horizons were grouped into four horizon groups, based on previously determined sorption characteristics (Kothawala et al., 2009). A horizons and B horizons are defined as not being enriched with Fe, while podzol B and volcanic B horizons are enriched with Fe (Table 1). Soils included in this study represent a sub-set ($n = 43$) of a previous study ($n = 52$) (Kothawala et al., 2009) and horizons not included in the current study include two A horizons (A/Ae), three volcanic B horizons (Bfj), four podzol B horizons (Bf/Bcc/Bfh) and two C horizons. Thus, soil properties (Table 1) and sorption characteristics (Fig. 1) only reflect the sub-set of soil horizons included in this study as identified in Table 2. We collected a sandy orthic dystric brunisol (Bf, Bfj) developed on volcanic ash from a Douglas fir (*Pseudotsuga menziessi*) stand on Vancouver Island (49°35′N, 124°56′W). Clay rich orthic humic gleysol (Bg) and orthic dystric brunisol (Ah, Bm), as well as one sandy gray luvisol (Ae, Bt), were collected from Waskesiu Lake, Saskatchewan (53°55′N, 106°04′W), under black spruce (*Picea mariana*), jack pine (*Pinus banksiana*) and aspen (*Populus tremuloides*), respectively. A heavily mottled clayey orthic gleysol, humic luvic gleysol and an organic soil (Ah, Ae, Bt, Bg, Bf, Bfj), were collected from Groundhog River, Northern Ontario (48°58′N, 82°19′W), under a mixed forest stand of aspen, black spruce, and white spruce (*Picea glauca*). Well-drained sandy lacustrine dystric

Table 1
Properties and sorption characteristics for four groups of mineral soil horizons. Values are averages ± standard deviation (range).

Properties	A horizons	B horizons	Podzol B	Volcanic B
Soil horizons	Ah/Ae	Bm/Bg	Bfj/Bf/Bfh/Bcc	Bfj/Bf
n	11	17	7	10
Soil C ($mg\ g^{-1}$)	18.4 ± 20.0 (4.5 to 72.6)	4.8 ± 4.8 (0.5 to 17.8)	46.0 ± 25.4 (7.2 to 84.8)	15.3 ± 7.1 (8.2 to 27.5)
Soil pH_{CaCl_2}	4.8 + 1.3 (3.4 to 7.5)	5.7 ± 0.9 (4.5 to 7.2)	4.3 ± 0.4 (3.7 to 5.3)	5.2 ± 0.3 (4.7 to 5.5)
Fe_{am} ($mg \cdot g^{-1}$)	0.6 ± 0.4 (0.1 to 1.3)	0.8 ± 0.4 (0.1 to 1.8)	6.1 ± 4.1 (2.5 to 14.5)	5.4 ± 2.6 (1.40 to 10.5)
Al_{am} ($mg \cdot g^{-1}$)	0.4 ± 0.2 (0.1 to 0.6)	0.7 ± 0.9 (0.1 to 3.8)	5.2 ± 3.2 (1.0 to 8.9)	8.7 ± 7.7 (0.9 to 25.9)
% sand	66 ± 29 (22 to 97)	55 ± 28 (22 to 98)	72 ± 23 (37 to 92)	70 ± 12 (48 to 88)
% clay	10 ± 7 (5 to 29)	16 ± 11 (5 to38)	10 ± 3 (6 to 17)	12 ± 8 (6 to 26)
Qmax ($mg\ kg^{-1}$)	259 ± 235 (60 to 855)	463 ± 466 (182 to 2200)	2022 ± 1891 (572 to 2006)	1041 ± 487 (630 to 4913)
b ($mg \cdot kg^{-1}$)	70 ± 43 (14 to 146)	50 ± 28 (4 to 96)	117 ± 64 (52 to 256)	46 ± 26 (15 to 83)

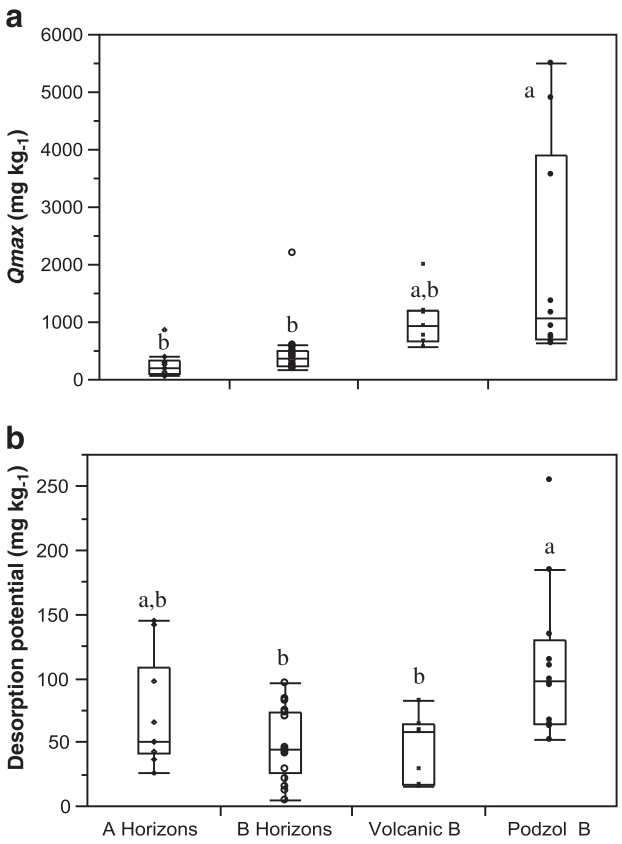

Fig. 1. Distribution of (a) adsorption capacity (*Qmax*), and (b) the desorption potential for soil horizon groups, A horizons ($n = 10$), B horizons ($n = 17$), volcanic B ($n = 10$) and podzol B ($n = 10$). Only groups not sharing the same lower case letter are significantly different from each other based on the Tukey–Kramer honestly significant test for comparison of means with uneven sample sizes ($p < 0.05$). The line in the middle of boxes represents the median, with lower and upper parts of the box representing 25% and 75% of the distribution, respectively.