

# Relation between Soil Order and Sorption of Dissolved Organic Carbon in Temperate Subsoils

## Melanie A. Mayes\*

Environmental Science Division  
Oak Ridge National Lab.  
P.O. Box 2008  
Oak Ridge, TN 37831

## Katherine R. Heal

Dep. of Oceanography  
Univ. of Washington  
Seattle, WA 98122

## Craig C. Brandt

Biosciences Division  
Oak Ridge National Lab.  
P.O. Box 2008  
Oak Ridge, TN 37831

## Jana R. Phillips

Environmental Science Division  
Oak Ridge National Lab.  
P.O. Box 2008  
Oak Ridge, TN 37831

## Philip M. Jardine

Dep. of Biosystems Engineering and  
Soil Science  
Institute for a Secure and Sustainable  
Environment  
Univ. of Tennessee  
Knoxville, TN 37996

Soils have historically been considered a temporary sink for organic C, but deeper soils may serve as longer term C sinks due to the sorption of dissolved organic C (DOC) onto Fe- and clay-rich mineral soil particles. This project provides an improved understanding and predictive capability of the physical and chemical properties of deep soils that control their sorptive capacities for DOC. Two hundred thirteen subsurface soil samples (72 series from five orders) were selected from the eastern and central United States. A characterized natural DOC source was added to the soils, and the Langmuir sorption equation was fitted to the observed data by adjusting the maximum DOC sorption capacity ( $Q_{\max}$ ) and the binding coefficient ( $k$ ). Different isotherm shapes were observed for Ultisols, Alfisols, and Mollisols due to statistically significant differences in the magnitude of  $k$ , while  $Q_{\max}$  was statistically invariant among these three orders. Linear regressions were performed on the entire database and as a function of soil order to correlate Langmuir fitted parameters with measured soil properties, e.g., pH, clay content, total organic C (TOC), and total Fe oxide content. Together, textural clay and Fe oxide content accounted for 35% of the variation in  $Q_{\max}$  in the database, and clay was most important for Alfisols and Ultisols. The TOC content, however, accounted for 27% of the variation in  $Q_{\max}$  in Mollisols. Soil pH accounted for 45% of the variation in  $k$  for the entire database, 41% for Mollisols, and 22% for Alfisols. Our findings demonstrate that correlations between Langmuir parameters and soil properties are different for different soil orders and that  $k$  is a more sensitive parameter for DOC sorption than is  $Q_{\max}$  for temperate soils from the central and eastern United States.

**Abbreviations:** DOC, dissolved organic carbon; NCSC, National Cooperative Soil Characterization; OC, organic carbon; SOC, soil organic carbon; TOC, total organic carbon.

The necessity of mitigating global climate change has led to a need for fundamental research on the processes of C sequestration in subsurface soils, which have been identified as a potentially significant C sink (Jardine et al., 1989, 1990, 2006; Sombroek et al., 1993; Kalbitz et al., 2005; Han et al., 2007). Soil is the largest terrestrial sink, with the soil organic C (SOC) fraction containing about twice as much C as inorganic pools (Houghton et al., 1983; Sombroek et al., 1993). For example, in the southeastern United States, SOC ranges from 50 to 95% of the total terrestrial C pools, depending on location and disturbance history (Han et al., 2007).

Organic C in the upper soil horizons consists of weathered organic particles bound together with mineral clay, mycorrhizal fungi, and other soil components. Because turnover of SOC ranges from years to decades, organic C content in up-

The submitted manuscript has been authored by a contractor of the U.S. Government under Contract DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

Supplementary material is available online.

Soil Sci. Soc. Am. J. 76:1027–1037

doi:10.2136/sssaj 2011.0340

Received 29 Sept. 2011.

\*Corresponding author (mayesma@ornl.gov).

© Soil Science Society of America, 5585 Guilford Rd., Madison WI 53711 USA

All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Permission for printing and for reprinting the material contained herein has been obtained by the publisher.

per horizons is sensitive to changes in inputs caused by seasons, land-use effects, altered local climates, and vegetative succession (Houghton et al., 1983; Cronan and Aiken, 1985; Parton et al., 1988; Dalva and Moore, 1991; Qualls and Haines, 1991; McGuire et al., 1995; Trumbore, 1997; van Dam et al., 1997). Stabilization of organic C in subsurface soil B and C horizons, however, occurs primarily via sorption of DOC onto soil minerals (Kaiser and Zech, 1996; Neff and Asner, 2001; Gjettermann et al., 2008), resulting in turnover times ranging from centuries to millennia (Trumbore, 1997; van Dam et al., 1997).

Although the native SOC in subsurface soils is much lower than in surface soils per unit mass, much higher mineralization has been observed in the O and A horizons vs. the B horizons (Kalbitz et al., 2003; Lumsdon et al., 2005; Han et al., 2007). Neff and Asner (2001) noted that physicochemical sorption mechanisms were a much more important control on DOC fluxes than biodegradation in field-scale experiments (van Dam et al., 1997; Kalbitz et al., 2005). The extent to which DOC is stabilized on the mineral surfaces of soils depends on a number of variables, including the quality of the substrate, clay content, pH, disruption of soil aggregates, and hydrologic transport to mineral soils (Jardine et al., 1989, 1990, 2006; Kalbitz et al., 2003; Moore and Turunen, 2004; Gjettermann et al., 2008; Kothawala et al., 2009). In many soils, deeper horizons with Fe-, Al-, and clay-rich mineralogies exhibit the potential to sequester significantly more organic C (OC) than is initially present on the solid (Jardine et al., 1989, 1990, 2006; Kothawala et al., 2009).

No specific chemical or physical property or properties have been shown to accurately predict the maximum DOC sorptive capacity onto the soil solid phase (Voice and Weber, 1983; Kalbitz et al., 2000). Several different mechanisms for DOC sorption onto mineral soils have been proposed including ligand exchange (Gu et al., 1994), cation bridging and anion exchange (Tipping, 1981; Sposito, 2004), and entropy-driven hydrophobic reactions (Jardine et al., 1989). Bacterial recycling of plant and microbial materials resulting in specific arrangements of organic compounds on the mineral interface has also been proposed (Kleber et al., 2007; Sollins et al., 2007, 2009). Dissolved organic C sorption involves many processes, and our scientific understanding remains inadequate to predict variations in the subsoil sorptive capacity due to soil physical, chemical, and mineralogical properties. Siemens (2003) suggested that DOC present in soil profiles is the “missing” flux in the European C budget; consequently, it is important to quantify the extent and potential for mineral-stabilized sorption of organic C in deep subsoils.

Our goal in this study was to provide an improved fundamental understanding and predictive capability of the physical and chemical properties that control the sorptive behavior and capacities of U.S. subsoils for DOC. The objectives of this project were to: (i) quantify the relationship between DOC sorption and the physical and geochemical properties of mineral soils; and (ii) provide statistical models that can be used to estimate the C sequestration potential of U.S. subsoils using extant soil property databases (e.g., the National Cooperative Soil Characterization [NCSC] database [<http://soils.usda.gov/survey/nscd/>], accessed on 1 Apr.

2010]). Although several studies have demonstrated the sorptive capacities of DOC in individual profiles in both the organic and mineral horizons, a consistent predictive model of sorptive capacity that can be coupled with existing soil chemistry databases is lacking. Previous studies have suggested that the chemical and physical properties of subsurface Alfisols, Ultisols, and Oxisols are ideal for maximizing DOC sorption on the solid phase (Jardine et al., 1989, 2006; Benke et al., 1999). The soils of the eastern and central United States are dominated by the former two soil orders, potentially making this region ideal for deep subsurface C sequestration.

## MATERIALS AND METHODS

### Sample Selection

We used the State Soil Geographic (STATSGO) database (Soil Survey Staff, 1994) to select soil series in the conterminous United States based on the area of the Great Group to which the series belonged. Series area was calculated by multiplying the area of each STATSGO map unit by the proportion of the series in the map unit and then summing by series to get the total area. To ensure that the most recent series classification was used, the STATSGO series list was updated with the soil taxonomy from the Soil Series Classification database (<http://soils.usda.gov/technical/classification/scfile/index.html>). Next, an area-weighted sample was selected from the compiled list of series. Using this approach, the probability of selecting a given series was directly proportional to its mapped area in the STATSGO database. If the selected series was not represented in the NCSC database, we removed it from the list and selected a different series.

Changes were made to the list of selected pedons after viewing their most recent pedon description and characterization data obtained from the NCSC database. The data were plotted to confirm that the selected soils were representative of the Great Groups in the database. Pedons with anomalous values were dropped from the list and replaced by another pedon of the same soil series with more representative values. Pedons that had been reassigned to a different series by the National Cooperative Soil Survey were dropped from the list and replaced with pedons of the selected series. Additional changes were made to the list of selected pedons based on discussions with state and county agents concerning pedon location and series representation, and the availability of archived soils. If a pedon was dropped from the list, another pedon of the same series was selected to replace it. In cases where this was not feasible, a new series of the same Great Group and similar aerial coverage was selected as a replacement.

Overall, 106 samples of individual soil horizons were obtained from the NCSC archived collections, while state and county agents provided an additional 55 samples from new dig sites located at historical pedon locations. An additional 63 samples of individual soil horizons collected from various sites around the United States for a variety of other projects were obtained from the stored archive at Oak Ridge National Laboratory (ORNL). Of the total of 213 B and C horizon samples, 72 series, 31 Great Groups, and five soil orders were represented. The five soil orders included Ultisols, Alfisols, Mollisols, Inceptisols, and Entisols. Information on loca-

tions, horizons, and source (NCSC or ORNL archive) of the sampled pedon is given in Table 1. Soil horizon depths, bulk density, and rock volume were obtained from either the NCSC database or from records of soil sample collections in the ORNL database.

## Soil Characterization and Dissolved Organic Carbon Isotherms

Samples were air or oven dried at 60°C, gently ground using a mortar and pestle, and sieved to collect the <2-mm soil fraction. The NCSC archived soils were prepared in the same manner by the NCSC laboratories. Soil properties data either were obtained from the NCSC database or were measured in our laboratory (Table 1).

Soil pH was measured on the supernatant of a 5 mmol L<sup>-1</sup> CaCl<sub>2</sub> solution at a 2:1 solution/solid ratio. Total Fe oxides were extracted by the dithionate–citrate–bicarbonate method (Loeppert and Inskeep, 1996) and analyzed using inductively coupled plasma mass spectrometry (ELAN-6100, PerkinElmer Corp.). Particle size analysis was performed using the Buoycous hydrometer method (Gee and Or, 2004), and total C and TOC were measured by combustion on a LECO TruSpec CN analyzer (LECO Corp.). Total organic C was determined by the standard method of removing the total inorganic C (TIC) by treating the soil with 3 mol L<sup>-1</sup> HCl for 1 h and rinsing three times. Soil TIC was computed from the difference between total soil C (untreated soil) and TOC.

The natural DOC sample used in this study was obtained from a surface stream near a peat deposit in Georgetown, SC, and has been previously studied (McCarthy et al., 1993; Gu et al., 1994; Chen et al., 2002). Fourier-transformed infrared and nuclear magnetic resonance spectroscopies showed that the DOC appears to resemble humic substances in aquatic systems and in soil fulvic acids. The DOC contains 48.3% (w/w) C, 42.1% O, 3.3% H, 3.1% S, and 1.6% N (corrected for ash content) (Gu et al., 1994). Dissolved organic C sorption isotherms were determined at a constant ionic strength of 0.01 using NaCl, constant indigenous soil pH, and room temperature as described in Jardine et al. (1989). To obtain isotherms, glass vials containing 0.5 g of soil were shaken with 0.03 L of varying concentrations (0–100 mg L<sup>-1</sup>) of the natural DOC solution for 48 h, centrifuged, decanted, and the supernatant was analyzed for DOC with a Shimadzu TOC-5000 Total Organic Carbon Analyzer (Shimadzu Corp.). The solutions were acidified to remove any potential dissolved TIC before analysis. Blanks (soil exposed to 0.01 mol L<sup>-1</sup> NaCl and no DOC) were analyzed in triplicate for each sample to determine desorption potential of indigenous soil organic C.

## Modeling Dissolved Organic Carbon Isotherms

Past studies have shown that DOC sorption onto mineral soils can best be described by the Langmuir isotherm (Gu et al., 1994; Kothawala et al., 2008). The amount of DOC adsorbed (mg DOC kg<sup>-1</sup> soil) or desorbed (RE) is a function of the final measured equilibrium solution concentration ( $X_f$ ) (mg DOC L<sup>-1</sup> solution), the maximum sorption capacity ( $Q_{\max}$ ) (mg DOC kg<sup>-1</sup> soil), and the binding affinity ( $k$ ) (L mg<sup>-1</sup>) according to the following model:

$$RE = \frac{k Q_{\max} X_f}{1 + k X_f} \quad [1]$$

In the soils studied here, negligible or small amounts of desorbed DOC were common in blanks (conducted in triplicate) containing no added DOC and when low concentrations of DOC were added to the soils. When this phenomenon was observed, all adsorbed concentrations were modified to remove the concentration of desorbed DOC measured by averaging the three blank samples. The adjustments were typically very small in comparison to the total sorption capacity of the soils. The overall modification to the Langmuir equation is similar to Kothawala et al. (2009), where an adjustable  $y$  intercept ( $b$ ) was added to describe the desorption potential (i.e., the intercept):

$$RE = \frac{k Q_{\max} X_f - b}{1 + k X_f} \quad [2]$$

The isotherms were subsequently fitted using the Langmuir equation in the nonlinearized optimizer from Bolster and Hornberger (2007) to obtain  $k$  and  $Q_{\max}$  and standard errors. An example of an isotherm fitted to the Langmuir equation is shown in Fig. 1.

## Statistical Relationships between Dissolved Organic Carbon Sorption and Soil Physicochemical Properties

Linear and multiple regressions in SigmaStat 3.5 (Systat Software Inc.) were used to construct statistical models to predict  $Q_{\max}$  and  $k$  for DOC sorbed onto soil horizons as a function of the aforementioned soil horizon properties. Using multiple horizons from a single pedon to determine correlations implies that some of the sample points may be autocorrelated, and thus the data used in the correlations may not be fully independent. Therefore, values representative of each pedon, i.e., values averaged from all horizons analyzed, for each soil property and Langmuir parameter were obtained by weighting the horizon values according to the soil mass. The soil mass was obtained using the bulk density and horizon thickness (assuming that the cross-sectional area of each horizon is equivalent to 1 cm<sup>2</sup>), and by removing the fraction of rock fragments. When bulk density and horizon thickness were unavailable, they were weighted equally. Values of pH were transformed into concentrations of the H<sub>3</sub>O<sup>+</sup> ion, weighted according to soil mass as above, and then the concentrations of H<sub>3</sub>O<sup>+</sup> were recalculated as pH values. Linear and multiple regressions in SAS (SAS Institute) were used to construct statistical models to predict  $Q_{\max}$  and  $k$  for DOC sorbed onto the soil pedons as a function of the soil pedon properties. Correlations were tested using both raw and log<sub>10</sub>-transformed data. Models were considered statistically rigorous at the 95% confidence interval ( $P < 0.05$ ).

## RESULTS AND DISCUSSION

### Soil Characteristics

Our soils were specifically selected to be representative of soil properties of soil orders in the eastern and central United States. The analyzed subsoil horizons contained a broad range

**Table 1. Soils analyzed in this study.**

Series	Origin†	Pedon	County, State	Great Group	Horizons	Analysis‡
Alfisol						
Acove	NCSC	09N0838	McCulloch, TX	Haplustalfs	Bt1, Bt2, Bt3, Cr	NCSC
Angola	ORNL	40A1184	Erie, NY	Endoaqualfs	B	ORNL
Apalona	NCSC	08N0828	Perry, IN	Fraguidalfs	Bt1, Bt2, Btx, 2Bt1, 2Bt2	NCSC
Arispe	NCSC	07N0567	Decatur, IA	Hapludalfs	Btg2, Btg3, 2BTg4, 2Btg5	NCSC
Blount	NCSC	95_0249	Elkhart, IN	Epiaqualfs	Bt1, Cd/Bt	ORNL, NCSC
Brewback	NCSC	08N0518	York, SC	Hapuldalfs	Bt1, Bt2, Btc, Cr	NCSC
Chetek	NCSC	75WI095	Polk, WI	Hapludalfs	Bt, B2, C1, C2	ORNL, NCSC
Crosby	NCSC	93_0236	Elkhart, IN	Epiaqualfs	2Bt2, 2Cd/Bt, 2Cd1	ORNL, NCSC
Darien	NCSC	07N0845	Crawford, PN	Epiaqualfs	Bt1, Bt2, BC, C	ORNL, NCSC
Grenada	ORNL		Gibson, TN	Fraglossudalfs	Btx, Bw2/E/Btx, C	ORNL
Lagonda	NCSC	07N0568	Lucas, IA	Hapludalfs	Btg1–3, 2btg4, 2btg5, 3bt1–3	NCSC
Lawrence	ORNL	98P367	Perry, TN	Fragiudalfs	Bt1	Stewart et al., 2003
Lenberg	ORNL	91P1084	Perry, IN	Paleudalfs	Bt1	Stewart et al., 2003
Malmö	NCSC	07N0113	Lancaster, NE	Hapludalfs	Bt1, Bt2, Bt3, Bt4, BCg, C, Cg	NCSC
Marlette	NCSC	40_1911	Gratiot, MI	Glossudalfs	B/E, Bt, BC, C	ORNL
Memphis	NCSC	85TN053	Gibson, TN	Hapludalfs	Bt1, Bt2	ORNL, NCSC
Nester	NCSC	93_0036	Iosco, MI	Glossudalfs	Bt, C1, C2	ORNL, NCSC
Paducah	NCSC	80P0279	Stonewall, TX	Haplustalfs	Bt11–13, Bt21, Bk, C1, C2	ORNL, NCSC
San Ysidro	ORNL		Napa, CA	Palexeralfs	B	ORNL
Susquehanna	NCSC	81_0559	George, MS	Paleudalfs	B	ORNL
Talbott	NCSC	40A4366	Williamson, TN	Hapludalfs	Bt11, Bt12, Bt13	ORNL, NCSC
Voca	NCSC	09N0837	McCulloch, TX	Paleustalfs	Bt1, Bt2, Bt3, BT4	ORNL, NCSC
Winfield	NCSC	83_0508	Lincoln, MO	Hapludalfs	Bt1, Bt2, Bt3	ORNL
Zanesville	NCSC	09N0873	Spencer, IN	Fragiudalfs	BE, Bt, Btx, 2BC1, 2BC2, 2BC3	ORNL, NCSC
Entisol						
Plainfield	NCSC	83P0249	Peoria, IL	Udipsamments	1Bw, 1BC, C	ORNL, NCSC
Wakeland	ORNL	85P257	Jasper, IL	Fluvaquents	Cg1	Stewart et al., 2003
Inceptisol						
Calvin	ORNL		Anderson, TN	Dystrudepts	B, B/C	ORNL
Lehew	ORNL		Anderson, TN	Dystrudepts	B2	ORNL
Mantachie	NCSC	82_0495	Smith, TX	Endoaquepts	Bg, Bg2–4	NCSC
Riverview	NCSC	81_0358	Macon, AL	Dystrudepts	Bt1b, Bt2b, Bw1, Bw2, BCb, C	ORNL
Weikert	ORNL	93P0796	Franklin, PA	Dystrudepts	BE	ORNL, Stewart et al., 2003
Mollisol						
Aksarben	NCSC	07N0112	Lancaster, NE	Argiudolls	Bt1, Bt2, Bt3, C	NCSC
Barnard	NCSC	72_0107	Modoc, CA	Durixerolls	Bt1, Bt2, B, Bqm1, Bqm2	ORNL, NCSC
Bearden	NCSC	08N0411	Walsh, ND	Calciaquolls	Bk1	NCSC
Bresser	NCSC	07N0126	Morgan, CO	Argiustolls	Bt1, Bt2, Bt3, BC, 2C3	ORNL, NCSC
Clarion	NCSC	93_0534	Moltrie, IL	Endoaquolls	Bw1, Bw3, C1, C3	NCSC
Colo	NCSC	90_01079	Moltrie, IL	Endoaquolls	Bg1, Bg2, Bg4	NCSC
Dennis	ORNL	86P869	Labette, KS	Argiudolls	Ba	ORNL, Stewart et al., 2003
Drummer	ORNL		Kane, IL	Endoaquolls	A/Ba, Bg/Btg1, Btg1/Btg2	ORNL
Edalgo	NCSC	02N0463	Cloud, KS	Argiustolls	3Bt	NCSC
Haxtun	NCSC	07N0122	Morgan, CO	Argiustolls	Bk1, Bk2, Bk3, C1	NCSC
Labette	NCSC	09N0935	Butler, KS	Argiustolls	Bt1, Bt2	NCSC
Lanton	NCSC	84P0823	Neosho, KS	Haplaquoll	Cg	NCSC
Longford	NCSC	09N0339	Washington, KS	Argiustolls	Bt1, Bt2, 2Bk1, 2Bk2, 2C	ORNL
Marshan	NCSC	08N0210	Buchanan, IA	Endoaquolls	Bg, BC	NCSC
Muir	NCSC	09N0218	Republic, KS	Haplustolls	2Bwb3	ORNL, NCSC
Pawnee	NCSC	07N0111	Lancaster, NE	Argiudolls	Bt1, Btss, Btkss, Bk1, Bk2	ORNL, NCSC
Pullman	NCSC	94_0644	Hansford, TX	Paleustolls	Bt1, Btk1, Btk5, Btk6	ORNL, NCSC
Sibley	ORNL	80P115	Clay, MS	Argiudolls	B1	ORNL, Stewart et al., 2003
Ultisol						
Unclassified	ORNL		Anderson, TN		E, B, 2B	ORNL
Allen	ORNL		Anderson, TN	Paleduldults	E, Ba, Bw, 2B, 2B2	ORNL, Stewart et al., 2003

(cont.)



Table 1. (cont.)

Series	Origin†	Pedon	County, State	Great Group	Horizons	Analysis‡
Armuchee	ORNL		Anderson, TN	Hapludults	Bt1, Bt2, B1, B2	ORNL
Bladen	NCSC	85P0163	Liberty, GA	Albaquults	Btg1, Btg2, Btg3, Btg4	NCSC
Bodine	ORNL		Anderson, TN	Paledults	B/E, Bt	ORNL
Cecil	NCSC	83P443	Dekalb, GA	Kanhapludults	Bt1	Stewart et al., 2003
Claiborne	ORNL		Anderson, TN	Paledults	B1, B2, Bt	ORNL
Collegedale	ORNL		Anderson, TN	Paledults	B21t, B22t,	ORNL
Cuthbert	NCSC	82_0497	Smith, TX	Hapludults	Bt, B/C	ORNL
Fullerton	NCSC	40_04976	Blount, TN	Paledults	B1, B21t, B22t, B3	ORNL
Gilpin	NCSC	81_0497	Wyoming, WV	Hapludults	Bt1, Bt2	NCSC
Hayesville	NCSC	92_0082	Buncombe, NC	Kanhapludults	Bt1, C1, C3	ORNL, NCSC
Holston	ORNL		Anderson, TN	Paledults	B2, Bt2	ORNL
Jefferson	ORNL		Anderson, TN	Hapludults	B1, Bt1, Bt2, 2Bt1	ORNL
Luverne	NCSC	90_0893	Anderson, TN	Hapludults	Bt1, Bt2, Bt3, Bt4	ORNL
Orangeburg	NCSC	85_0164	Jefferson, GA	Kandiudults	Bt1, Bt3	ORNL, NCSC
Rockaway	ORNL	80P692	Bergen, NJ	Fragiudults	B2t	Stewart et al., 2003
Towaliga	ORNL		Butts, GA	Hapludults	Bt1	ORNL
Troup	NCSC	40A5109	Escambia, FL	Kandiudults	Bw1, Bw2, Bt1, Bt3	ORNL, NCSC
Westphalia	ORNL		Prince George's, MD	Hapludults	Bt1, Bt2	ORNL
Wolftever	ORNL		Anderson, TN	Hapludults	Bt1, Bt2, Bt3, Bt4	ORNL

† NCSC, Natural Cooperative Soil Characterization database; ORNL, Oak Ridge National Laboratory.

‡ Location of analysis for Fe oxides, texture, and pH. Total inorganic and organic C, maximum sorption capacity, and binding coefficient were analyzed in our laboratory for all soils.

of physical and chemical properties that were expected to influence DOC sorption. (Supplementary Material available online contains soil physical and chemical information for each soil horizon and weighted pedon average.) The large variability in subsoil physical and chemical properties is ideal because it allows the prediction of  $Q_{\max}$  and  $k$  across a large range of soil physico-chemical characteristics for each of the soil orders. Figure 2 shows compiled, pedon-averaged values for pH, textural clay content, Fe oxide content, and TOC for Mollisols, Alfisols, and Ultisols, where statistically significant differences between soil orders at the 95% percentile level were evaluated according to Student's  $t$ -test or the Mann-Whitney rank sum test. There was insufficient data to interpret either horizon- or pedon-scale patterns of Entisol and Inceptisol soil orders. Ultisols had much lower pH values and Mollisols much higher pH values, while Alfisols were intermediate (Fig. 2a). Clay content was insensitive to soil order (Fig. 2b). The Fe oxide content was higher for Ultisols than for Alfisols and Mollisols (Fig. 2c). Total organic C was greater for Mollisols than for Alfisols and Ultisols (Fig. 2d).

### Correlations between Soil Properties and Langmuir Binding Coefficient

The binding coefficient  $k$  is a measurement of the shape of an isotherm, where higher  $k$  values indicate increasingly nonlinear isotherms. The estimates and standard errors of the fitted Langmuir parameters for each soil horizon and weighted pedon average are in the Supplemental Material. Differences in  $k$  were statistically distinct for each soil order (Fig. 2e). In Ultisols,  $k$  values were higher ( $0.091 \text{ L mg}^{-1}$ ) and exhibited a wider range of variation than in Alfisols ( $k = 0.061 \text{ L mg}^{-1}$ ), while Mollisols exhibited the lowest  $k$  ( $0.032 \text{ L mg}^{-1}$ ) and smallest range of varia-

tion (Fig. 2e). The differences in  $k$  values reflect the fact that sorption isotherms are more nonlinear in Ultisols (higher  $k$ ) and more linear in Mollisols (lower  $k$ ), with Alfisols being intermediate (Fig. 3). Curvature in the isotherm (high  $k$ ) indicates sorption to high-affinity sites at low DOC concentrations, and the decrease in slope observed at higher DOC concentrations may indicate progression to lower affinity chemical and physical adsorption sites (Gu et al., 1994). Differences observed according to soil order may therefore indicate different mixtures of high- and low-affinity sites. Higher binding coefficients, as observed for Ultisols,

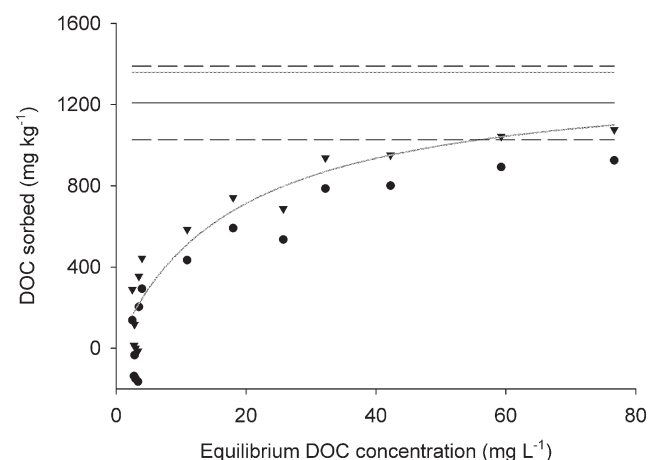


Fig. 1. Example of isotherm fitting. Raw data (circles) were adjusted after subtracting triplicate blanks to acquire additional dissolved organic C (DOC) sorbed data (triangles), which were fit to the Langmuir equation (gray curve) to find the maximum additional DOC sorption capacity (gray line at 1359) and binding coefficient (isotherm shape). Desorption potential (blanks) were subtracted from the maximum additional DOC sorption capacity to find the overall maximum sorption capacity (black line), shown with standard error (dashed lines).

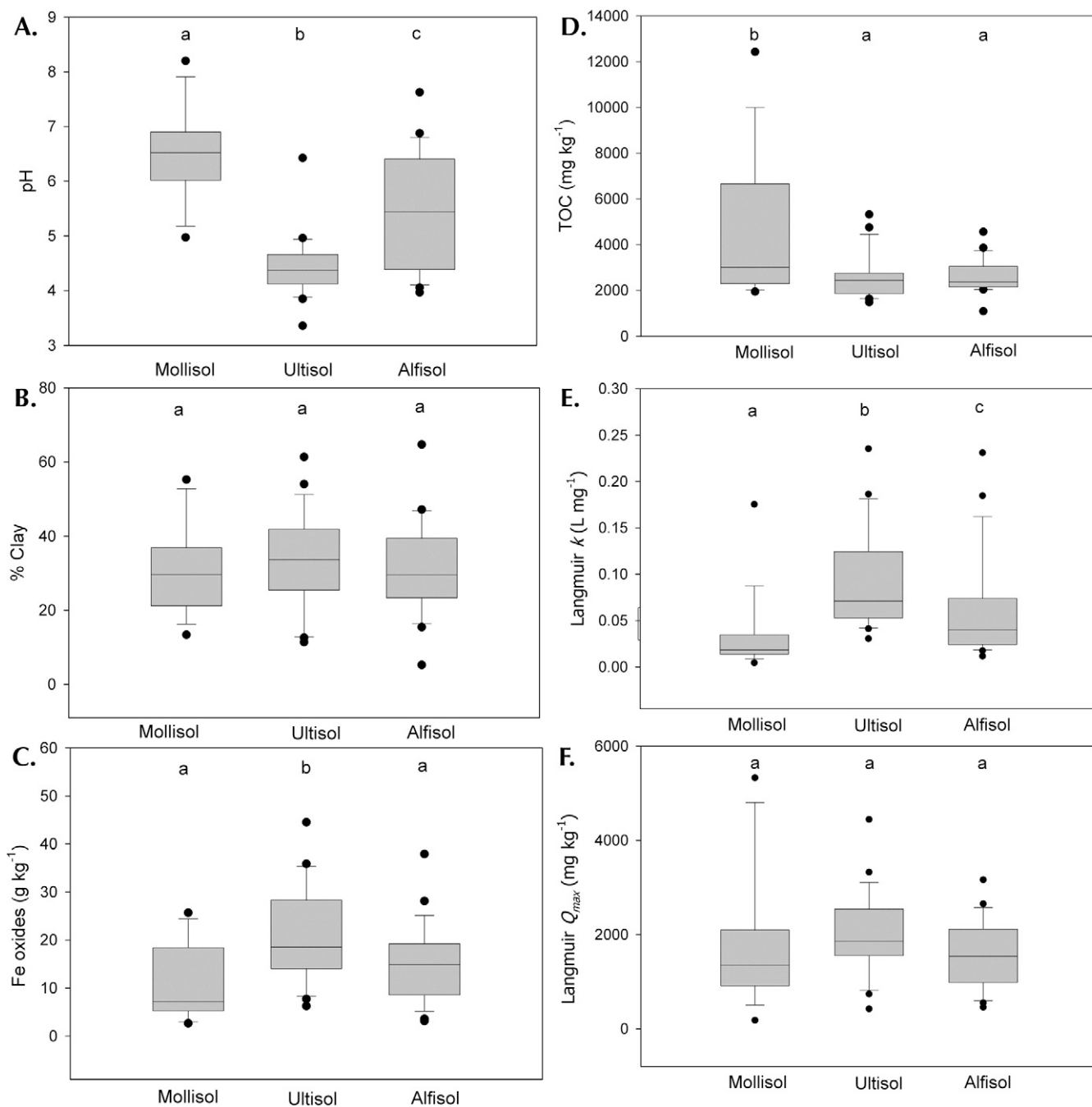
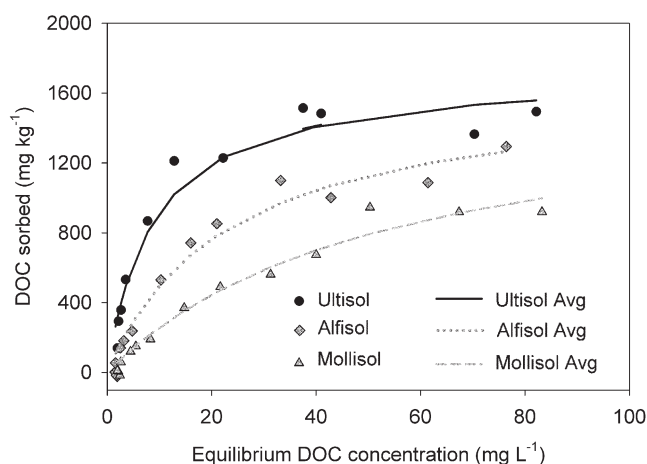


Fig. 2. Soil pedon characteristics of (a) soil pH, (b) clay content, (c) Fe oxide content, (d) total organic C (TOC), (e) Langmuir binding coefficient  $k$ , and (f) dissolved organic C (DOC) sorption capacity  $Q_{\text{max}}$ , grouped by order. The middle line in the box is the median, with 25 and 75% represented by lower and upper lines of the box, respectively, and 10 and 90% shown by whiskers, with each outlier represented by a dot. Sample size was 18 pedons (52 horizons) of Mollisols, 22 pedons (59 horizons) of Ultisols, and 25 pedons (86 horizons) of Alfisols. Statistical differences between populations are denoted by lowercase letters as determined using Student's  $t$ -test or the Mann–Whitney rank sum test at the 95% confidence interval, i.e.,  $P < 0.05$ .

reflect generally nonlinear isotherms that adsorb DOC to high-affinity sites when low concentrations of DOC are added (Fig. 3). The maximum sorption capacity, i.e., the asymptote, is readily reached for most Ultisols with the addition of low concentrations of DOC. In contrast, the low binding coefficients and more linear isotherms observed for Mollisols indicate fewer sites with a high affinity for added DOC. Consequently, the maximum sorption capacity, i.e., the asymptote, is reached for most Mollisols only after substantial addition of DOC, indicating selectivity of

Mollisols for certain DOC functional groups (Fig. 3). Alfisols are intermediate between Ultisols and Mollisols in terms of  $k$  values and isotherm curvature. This probably indicates greater preference for the type of functional group adsorbed than Ultisols and less preference for the type of functional group adsorbed than Mollisols. The DOC source is a natural and heterogeneous water sample obtained from a wetlands pond near Georgetown, SC, and subsequently filtered and concentrated, which consists of approximately 42% hydrophobic acids, 18% hydrophobic neu-

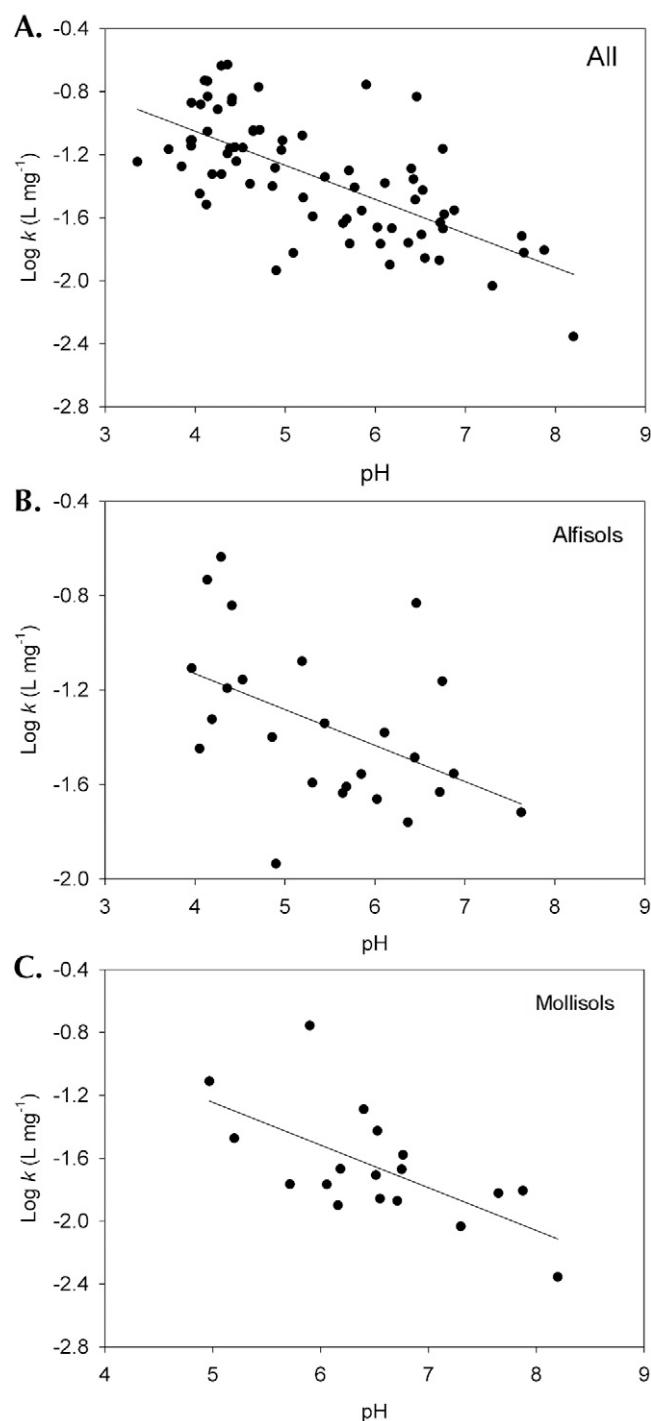


**Fig. 3. Representative isotherms.** Points are individual isotherms from each soil order (Alfisol, Apalona 2Bt2, Mollisol, Pawnee Btss, and Ultisol, Wolftever Bt2), and lines are the Langmuir equation fitted to the average dissolved organic C (DOC) sorption capacity  $Q_{\max}$  and binding coefficient  $k$  values for all horizons within each soil order (Alfisol  $Q_{\max} = 1750 \text{ mg kg}^{-1}$ ,  $k = 0.047 \text{ L mg}^{-1}$ ; Mollisol  $Q_{\max} = 1690 \text{ mg kg}^{-1}$ ,  $k = 0.024 \text{ L mg}^{-1}$ ; Ultisol  $Q_{\max} = 1800 \text{ mg kg}^{-1}$ ,  $k = 0.091 \text{ L mg}^{-1}$ ).

tral compounds, and 40% hydrophilic solutes (Gu et al., 1994), meaning that a wide variety of functional groups are present.

The values for the weighted pedon average for  $k$  were tested against soil properties in the database, and pH was found to be the strongest predictor of  $k$  (Fig. 4a), accounting for 45% of the variability when all pedons were grouped together (Table 2). As the pH increased,  $k$  decreased, which was also observed for the Alfisol (Fig. 4b) and Mollisol pedons (Fig. 4c). Correlation with pH accounted for 22% of the variability in Alfisols and 41% in Mollisols (Table 2). Surprisingly, pH was not a predictor of  $k$  in Ultisols, which is probably due to the narrow range of Ultisol pH values (Fig. 2a). No other soil characteristics were able to predict  $k$  for Ultisols. There were inadequate numbers of Entisols and Inceptisols to define any correlations with soil characteristics.

The mechanism for selectivity of sorbed DOC functional groups by different soil orders (Fig. 3) is potentially related to the dependence of  $k$  on the soil pH. The primary mechanism for DOC sorption onto clays is through pH-dependent, electrostatic interactions involving anion exchange (Feng et al., 2005). As the pH increases, clays and variably charged mineral surfaces (Fe and Al oxides) become less positive and aqueous species become more negative, both of which tend to minimize sorption via ligand and anion exchange (Jardine et al., 1989; Gu et al., 1994). These researchers found that the maximum DOC sorption on soil and Fe oxides occurs at pH 3 to 4 and decreases rapidly with increasing pH. Consequently, the higher pH of Mollisols (pH 6–7) implies that there are both fewer mineral surfaces available for sorption of DOC and fewer functional groups of DOC having charges that promote sorption. The lower pH of the Ultisols (pH 4–5, see Fig. 2a), in contrast, implies that the charge of most mineral surfaces in Ultisols promotes sorption of DOC and that many DOC functional groups are conducive to sorption. Thus, the soil pH is the mechanism for selectivity observed in Fig. 3 and provides the explanation for why Mollisols and Alfisols ex-



**Fig. 4. The observed (data points) and model fitted (lines) relationship between the most significant independent variable (pH) and the logarithm of the Langmuir binding coefficient  $k$  in (a) all pedons, where  $\log k = -0.186(\text{pH}) - 0.216$  and  $r^2 = 0.457$ , (b) Alfisols, where  $\log k = -0.152(\text{pH}) - 0.524$  and  $r^2 = 0.220$ , and (c) Mollisols, where  $\log k = -0.271(\text{pH}) + 0.112$  and  $r^2 = 0.415$ .**

hibited a strong relationship between pH and  $k$  and Ultisols did not exhibit a relationship (Fig. 4). Ultisols, because of their low soil pH, are conducive to sorption of DOC with less regard for its characteristics, while Mollisols and Alfisols sorb only the portions of DOC that have functional groups can be incorporated into the structure of their organic–mineral interface. Preferential sorption of hydrophobic compounds to OC-rich soils was ob-

**Table 2. Parameter estimates, standard errors, and statistics obtained from a linear regression analysis that related pedon properties to the log of the binding coefficient ( $k$ ) of dissolved organic C.**

Soil	Characteristic	Slope			Intercept			$r^2$	$n$
		Value	SE	$P$	Value	SE	$P$		
All	pH	-0.2163	0.0282	<0.0001	-0.1859	0.1536	0.2302	0.4573	72
Alfisols	pH	-0.1518	0.0596	0.0180	-0.5240	0.3303	0.1263	0.2202	25
Mollisols	pH	-0.2714	0.0805	0.0039	0.1122	0.5293	0.8349	0.4154	18

served in a large database of different temperate soils (Kaiser et al., 1996), resulting in a good correlation between pH and added DOC for subsurface soils. Although many studies have tended to ignore the Langmuir binding coefficient (Kothawala et al., 2009), our analysis suggests that pH is potentially a master variable controlling the sorption of DOC in soils.

### Correlations between Soil Properties and Maximum Sorptive Capacity

The DOC sorptive capacities ( $Q_{\max}$  values) are grouped according to soil order for the Mollisol, Alfisol, and Ultisol pedons (Fig. 2f). The average sorption capacity of pedons from the three orders was not statistically different according to Student's  $t$ -test or the rank sum test (Fig. 2f), which is very surprising and suggests that that organic-rich subsoils are nearly as capable of sorbing significant quantities of DOC as organic-poor, Fe-rich subsoils.

Multiple regression analysis was performed on all analyzed subsoil pedons from all five soil orders. When the data for all the soil types were pooled, textural clay and Fe oxide contents were together the strongest predictor of  $Q_{\max}$ , accounting for 35% of the variability (Table 3). These results are consistent with findings of increasing DOC sorptive capacity with increasing clay and Fe oxide contents (Fig. 5a) (Jardine et al., 1989, 1990, 2006; Kaiser et al., 1996; Shen, 1999; Qualls, 2000; Kaiser and Guggenberger, 2000; Mikutta et al., 2006; Gjettermann et al., 2008). Higher clay content provides more surface area for DOC–solid-phase interactions (Neff and Asner, 2001; Moore and Turunen, 2004; Jardine et al., 2006; Sutton and Sposito, 2006). These results differ from those of Percival et al. (2000), who found that DOC sequestration in numerous New Zealand soils was not significantly influenced by the soil clay fraction, but their soils were surface soils, which tend to contain smaller mineral fractions.

Many explanations for the correlation between Fe and clay contents and  $Q_{\max}$  have been discussed in previous studies. Regarding Fe, the amphoteric nature of Fe oxides creates a condition such that positive surface charges dominate at low pH and negative surface charges dominate at higher pH. Because Ultisol soils, in particular, are highly acidic (Fig. 2a), the high percent-

age of positively charged surface sites is ideal for DOC sorption via anion exchange (Jardine et al., 1989). Other studies have also suggested ligand exchange (surface complexation) as a possible mechanism for DOC sorption onto Fe and Al oxide dominated mineral soils (Gu et al., 1994; Kaiser et al., 1996, 1997; Kaiser and Guggenberger, 2000; Qualls et al., 2002; Feng et al., 2005). A study grouping 52 podzols, volcanic soils, and other A and B horizon soils from temperate and boreal forests in Canada observed a primary relationship between noncrystalline Al and Fe oxides and  $Q_{\max}$ , and a secondary relationship with clay content (Kothawala et al., 2009). Because our study relied extensively on the NCSC database, data on noncrystalline Al and Fe oxides was typically not available. These researchers noted that clay content was of secondary importance because coatings of Al and Fe oxides may have masked the influence of clay content on sorption, but in our study, clay content was a textural rather than a mineralogical classification. Regardless, additional correlations beyond those found here might be a result of sorption to poorly crystalline oxides (Kothawala et al., 2009); however, other studies involving large databases of soils have found a good relationship with total Fe oxides and sorption (Kaiser et al., 1996). Mechanisms such as van der Waals bonding and cation bridging are also potentially important; however, our experiments were conducted in a Na-based matrix, where the latter mechanism is unlikely. Cation bridging processes are more likely to occur with surface-bound divalent and trivalent cations (e.g.,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ , respectively).

When the data were analyzed according to soil order, somewhat different models predicted the  $Q_{\max}$  of Mollisols, Alfisols, and Ultisols, even though overall,  $Q_{\max}$  was insensitive to soil order (Fig. 2f). Sorption capacity in Mollisols was primarily dependent on TOC, where TOC accounted for 27% of the variability (Table 3). In Alfisols and Ultisols, clay content accounted for 32 and 30% of the variability, respectively (Table 3). Due to the sparse data sets available for Entisols and Inceptisols, no predictive models could be generated.

The model for the Mollisol pedons suggests that  $Q_{\max}$  increases with increasing indigenous OC content (Fig. 5b). Our findings differ significantly from studies observing no relation-

**Table 3. Parameter estimates, standard errors, and statistics obtained from a linear regression analysis that related pedon properties to the log of the maximum sorption capacity ( $Q_{\max}$ ) of dissolved organic C.**

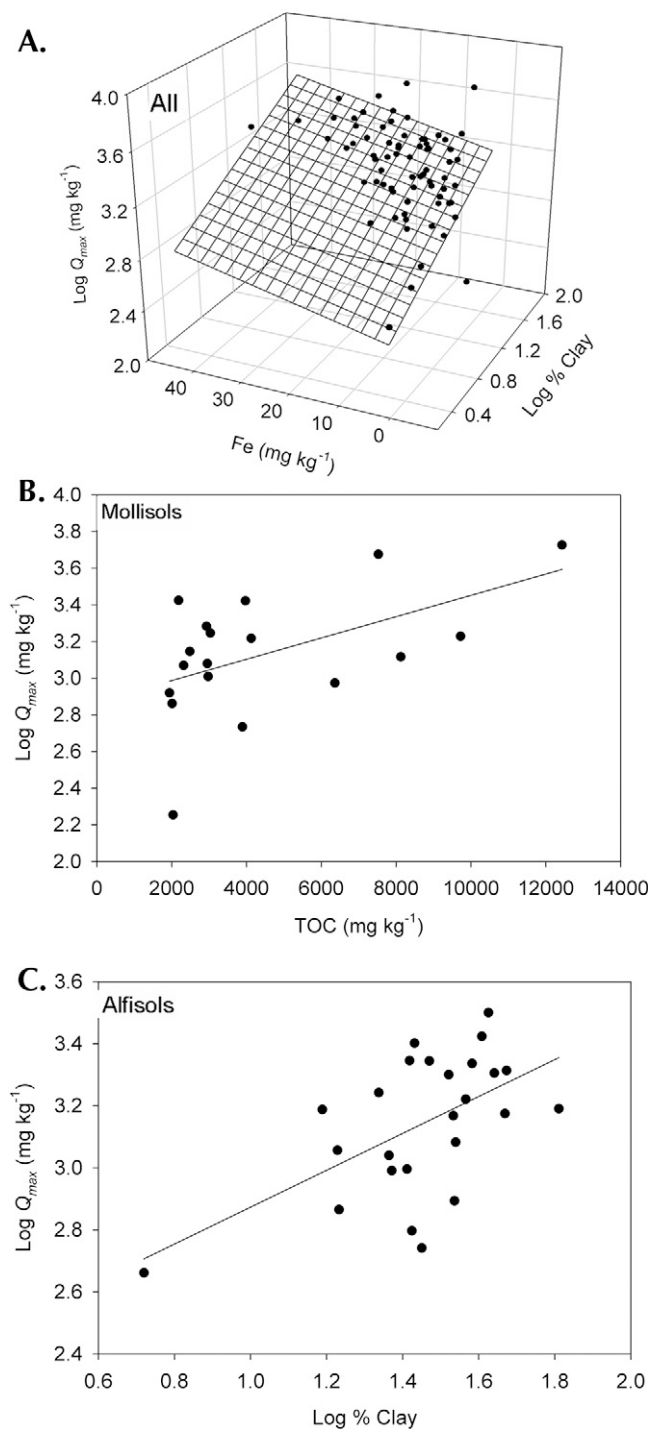
Soil	Characteristic	Slope			Intercept			$r^2$	$n$
		Value	SE	$P$	Value	SE	$P$		
All	log(%clay)	0.4833	0.1173	0.0001	2.3282	0.1619	<0.0001	0.3542	72
	%Fe	0.0087	0.0030	0.0049					
Alfisols	log(%clay)	0.5945	0.1798	0.0031	2.2788	0.2642	<0.0001	0.3222	25
Mollisols	Total organic C	5.81E-5	$2.37 \times 10^{-5}$	0.0260	2.8710	0.1279	<0.0001	0.2732	18
Ultisols	log(%clay)	0.5965	0.2046	0.0086	2.3549	0.3081	<0.0001	0.2982	22



ship or a negative relationship between SOC and  $Q_{\max}$ , all of which attributed the lack of correlation to blocking of mineral sites by SOC (Kaiser et al., 1996; Kaiser and Guggenberger, 2000; Guggenberger and Kaiser, 2003; Kothawala et al., 2009). The removal of TOC from Inceptisol and Ultisol soils, for example, resulted in increased sorption of DOC (Jardine et al., 1989). Moore and Turunen (2004) observed a positive relationship between TOC and DOC sorption, but noted a lack of mechanistic understanding as to why sorption affinity varied with TOC content. Kothawala et al. (2009) did observe sorption to OC-rich Podzol B horizons, resulting in high  $Q_{\max}$  (1800 mg kg<sup>-1</sup>), but the study also attributed sorption to other characteristics (low pH and high concentrations of poorly crystallized Fe and Al oxides).

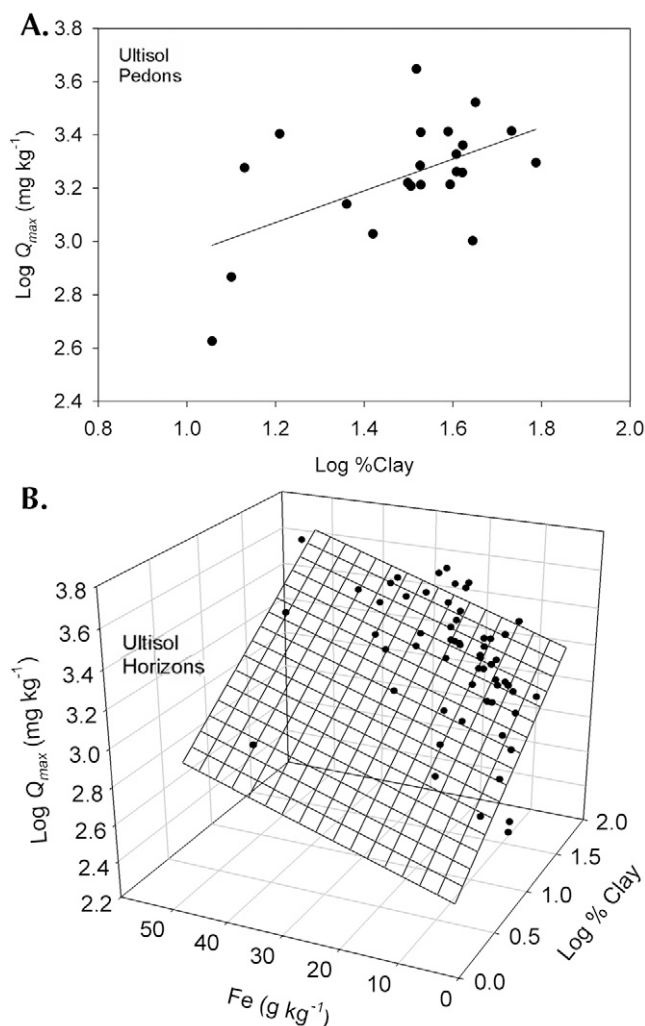
A conceptual mechanism describing the formation of complex arrangements of layers of organic C on mineral surfaces suggests that fresh mineral surfaces are not required for sorption of DOC (Kleber et al., 2007). The formation of layers of organic compounds on mineral surfaces (Kleber et al., 2007; Sollins et al., 2007, 2009) would potentially provide numerous sites for sorption. As discussed above, the differences in observed binding coefficients ( $k$ ) between Mollisols and Ultisols suggest that high-pH Mollisols may be selective for certain functional groups of a heterogeneous DOC source, while Ultisols do not exhibit selectivity because of their low pH, which strongly promotes sorption regardless of functional group interactions. In soils with higher amounts of TOC, higher concentrations of DOC may be necessary to maximize the sorption capacity (Fig. 3) because only certain portions of any heterogeneous DOC source may readily become incorporated into the layered structure of the mineral–organic interface. Kaiser et al. (1996) noted that the hydrophobic fraction was preferentially sorbed onto OC-rich soils, and Qualls (2000) noted that peat effectively exchanged different portions of DOC when it was added to the peat. For Ultisols, low SOC implies a less-developed OC–mineral complex and dominant sorption mechanisms therefore involve ligand or anion exchange directly onto Fe oxides. Validation of this theory will require further testing in future studies.

Both Alfisol (Fig. 5c) and Ultisol (Fig. 6a) pedons exhibited dependence of the sorption capacity on textural clay content, which is consistent with the patterns observed in the entire database. It was surprising that the DOC sorption capacity of Ultisols did not exhibit a significant dependence on the Fe oxide content, particularly because the entire database exhibited a secondary relationship with Fe oxides (Fig. 5a) and because Ultisols contain high concentrations of Fe oxide mineral surfaces (Fig. 2c) conducive to the sorption of DOC (Jardine et al., 1989, 1990, 2006; Kaiser and Guggenberger, 2000; Mikutta et al., 2006; Gjettermann et al., 2008). Indeed, correlations with Fe oxide content in the pedon-averaged database accounted for around 17% of the variation but had  $P$  values that slightly exceeded the 95th percentile (not shown). When both clay and Fe were tested for correlations with the pedon-averaged database, the  $P$  value for Fe far exceeded the 95th percentile (not shown), indicating that the results were not statistically significant. When the  $Q_{\max}$  of the horizons (vs. pedon-averaged  $Q_{\max}$ ) was tested



**Fig. 5.** The observed (data points) and model fitted (grid surface and/or lines) relationship between the dissolved organic C (DOC) sorption capacity ( $Q_{\max}$ ) and the most significant independent variable(s) for (a) all pedons, where  $\log(Q_{\max}) = 0.483 \log(\% \text{clay}) + 0.009(\text{Fe}) + 2.328$  and  $r^2 = 0.354$ , (b) Mollisols, where  $\log(Q_{\max}) = 5.81 \times 10^{-5}(\text{total organic C [TOC]}) + 2.871$  and  $r^2 = 0.273$  and (c), Alfisols, where  $\log(Q_{\max}) = 0.595 \log(\% \text{clay}) + 2.279$  and  $r^2 = 0.322$ .

for correlations with clay and Fe, however, a good correlation was observed (Fig. 6b), with  $P$  values  $< 0.0003$  for all variables and an  $r^2$  value of 0.49. The correlation using all the horizons, which are subsets of each pedon, however, potentially violates the expectation that all statistical input values are fully independent and are not related to each other. None of the correlations with the other



**Fig. 6.** The observed (data points) and model fitted (lines or grid surface) relationship between the dissolved organic C (DOC) sorption capacity ( $Q_{\max}$ ) and the most significant independent variables for (a) all Ultisol pedons, where  $\log(Q_{\max}) = 0.597 \log(\% \text{clay}) + 2.355$  and  $r^2 = 0.298$ , and (b) all Ultisol horizons, where  $\log(Q_{\max}) = 0.475 \log(\% \text{clay}) + 0.009 (\text{Fe}) + 2.311$  and  $r^2 = 0.494$ .

soil orders differed substantially between the pedon-averaged and horizon-specific values. This could suggest that improved correlations might be observed with the poorly crystalline oxides in Ultisols (e.g., Kothawala et al., 2009) compared with the total Fe oxides as used here and in the NCSC database.

## CONCLUSIONS

Recent modeling approaches have successfully used pedo-transfer functions incorporating TOC and Al and Fe oxide contents from a single site to model DOC dynamics through the soil profile (Gjettermann et al., 2008). Because different soil orders are composed of unique proportions and characteristics of reactive mineral and organic components, we tested the hypothesis that unique equations describing the controlling factors for sorptive capacity and binding of DOC could be generated for each soil order given a sufficiently representative data set (e.g., Kaiser et al., 1996; Kothawala et al., 2009).

The extensive nature of our database (Supplemental Material) lends credibility to our approach and goes well beyond what has been reported in the current scientific literature. Our study focused on collecting temperate subsoils representative of the midwestern and eastern United States, produced sorption and characterization information averaged across 72 different soil pedons, and tested for correlations between widely available soil properties (NCSC database) and Langmuir fitting parameters. We found that  $k$  was inversely related to pH for the entire database and for Alfisols and Mollisols individually, while no relations were found for Ultisols. Our results suggest that the binding coefficient is a measure of the amount of selectivity for sorption of DOC functional groups, where high  $k$  values (e.g., Ultisols) indicate little selectivity for DOC functional groups and low  $k$  values (e.g., Mollisols) indicate greater selectivity. Mollisols may have greater selectivity because of the extent of surface coverage by TOC (Fig. 2d). Because pH is inversely related to  $k$ , this suggests that high-pH soils (e.g., Mollisols) may have greater selectivity than low-pH soils.

Our modeling strategy can predict 35% of the variability describing the  $Q_{\max}$  using textural clay and total Fe oxide content. Around 30% of the variability in  $Q_{\max}$  of individual soil orders—Ultisols and Alfisols vs. Mollisols—was predicted using textural clay and TOC content, respectively. Although the findings were significant at the 95% confidence level, our inability to capture more of the variability in the data suggests that we are not considering all of the processes that are important drivers for DOC sorption on these soil types. Different physical and chemical characteristics were related to the maximum DOC sorption capacity ( $Q_{\max}$ )—texture and Fe oxides for the entire database, texture for Alfisols and Ultisols, and TOC for Mollisols—suggesting somewhat different sorption mechanisms depending on the soil order, even though  $Q_{\max}$  was similar for all three soil orders. Examination of horizon-level data for the Ultisols suggests the importance of Fe that was not detected by the pedon-level approach, and recent studies have suggested that extraction of poorly crystalline Al and Fe oxides might have improved our correlations for Ultisols. It was surprising to find an equivalent sorption capacity for the three soil orders. In particular, the significant sorption observed in the Mollisols suggests that more study should be devoted to understanding the function and structure of the organic–mineral interface in OC-rich soils.

## ACKNOWLEDGMENTS

This project is funded under the U.S. Department of Energy (DOE) Student Undergraduate Laboratory Internship (DOE SULI) and is part of Oak Ridge National Laboratory's Climate Mitigation Science Focus Area funded through DOE's Office of Biological and Environmental Research, Climate and Environmental Sciences Division. We would like to thank Larry West and Thomas Reinsch from the Natural Cooperative Soil Survey for providing many of the samples used in the study. We would also like to acknowledge Deanne Brice of ORNL for TOC analysis and Sindhu Jagadamma of ORNL for reviews and technical advice. Oak Ridge National Laboratory is managed by the UT–Battelle, LLC, under Contract DE-AC05-00OR22725 with the U.S. DOE.

## REFERENCES

Benke, M.B., A.R. Mermut, and H. Shariatmadari. 1999. Retention of dissolved

- organic carbon from vinasse by a tropical soil, kaolinite, and Fe-oxides. *Geoderma* 91:47–63. doi:10.1016/S0016-7061(98)00143-8
- Bolster, C.H., and G.M. Hornberger. 2007. On the use of linearized Langmuir equations. *Soil Sci. Soc. Am. J.* 71:1796–1806. doi:10.2136/sssaj2006.0304
- Chen, J., B. Gu, E.J. LeBoeuf, H. Pan, and S. Dai. 2002. Spectroscopic characterization of the structural and functional properties of natural organic matter fractions. *Chemosphere* 48:59–68. doi:10.1016/S0045-6535(02)00041-3
- Cronan, C.S., and G.R. Aiken. 1985. Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. *Geochim. Cosmochim. Acta* 49:1697–1705. doi:10.1016/0016-7037(85)90140-1
- Dalva, M., and T.R. Moore. 1991. Sources and sinks of dissolved organic carbon in a forested swamp catchment. *Biogeochemistry* 15:1–19. doi:10.1007/BF00002806
- Feng, X., A.J. Simpson, and M.J. Simpson. 2005. Chemical and mineralogical controls on humic acid sorption to clay mineral surfaces. *Org. Geochem.* 36:1553–1566. doi:10.1016/j.orggeochem.2005.06.008
- Gee, G.W., and D. Or. 2004. Particle size analysis: Hydrometer method. In: J.H. Dane and G.C. Topp, editors, *Methods of soil analysis. Part 4. Physical Methods*. SSSA Book Ser. 5. SSSA, Madison, WI. p. 278–283.
- Gjettermann, B., M. Styczen, H.C.B. Hansen, F.P. Vinther, and S. Hansen. 2008. Challenges in modeling dissolved organic matter dynamics in agricultural soil using DAISY. *Soil Biol. Biochem.* 40:1506–1518. doi:10.1016/j.soilbio.2008.01.005
- Gu, B., J. Schmitt, Z. Chen, L. Liang, and J.F. McCarthy. 1994. Adsorption and desorption of natural organic matter on iron oxide: Mechanisms and models. *Environ. Sci. Technol.* 28:38–46. doi:10.1021/es00050a007
- Guggenberger, G., and K. Kaiser. 2003. Dissolved organic matter in soil: Challenging the paradigm of sorptive preservation. *Geoderma* 113:293–310. doi:10.1016/S0016-7061(02)00366-X
- Han, F.X., M.J. Plodinec, Y. Su, D.L. Monts, and Z. Li. 2007. Terrestrial carbon pools in southeast and south-central United States. *Clim. Change* 84:191–202. doi:10.1007/s10584-007-9244-5
- Houghton, R.A., J.E. Hobbie, J.M. Melello, B. Moore, B.J. Peterson, G.R. Shaver, and G.M. Woodwell. 1983. Changes in the carbon content of terrestrial biota and soils between 1860 and 1980: A new release of CO<sub>2</sub> to the atmosphere. *Ecol. Monogr.* 53:235–262. doi:10.2307/1942531
- Jardine, P.M., M.A. Mayes, P.J. Mulholland, P.J. Hanson, J.R. Tarver, R.J. Luxmoore, J.F. McCarthy, and G.V. Wilson. 2006. Vadose zone flow and transport of dissolved organic carbon at multiple scales in humid regimes. *Vadose Zone J.* 5:140–152. doi:10.2136/vzj2005.0036
- Jardine, P.M., N.L. Weber, and J.F. McCarthy. 1989. Mechanisms of dissolved organic carbon adsorption on soil. *Soil Sci. Soc. Am. J.* 53:1378–1385. doi:10.2136/sssaj1989.03615995005300050013x
- Jardine, P.M., G.V. Wilson, J.F. McCarthy, R.J. Luxmoore, and D.L. Taylor. 1990. Hydrogeochemical processes controlling the transport of dissolved organic carbon through a forested hillslope. *J. Contam. Hydrol.* 6:3–19. doi:10.1016/0169-7722(90)90008-5
- Kaiser, K., and G. Guggenberger. 2000. The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. *Org. Geochem.* 31:711–725. doi:10.1016/S0146-6380(00)00046-2
- Kaiser, K., G. Guggenberger, L. Haumaier, and W. Zech. 1997. Dissolved organic matter on subsoils and minerals studied by <sup>13</sup>C-NMR and DRIFT spectroscopy. *Eur. J. Soil Sci.* 48:301–310. doi:10.1111/j.1365-2389.1997.tb00550.x
- Kaiser, K., G. Guggenberger, and W. Zech. 1996. Sorption of DOM and DOM fractions to forest soils. *Geoderma* 74:281–303. doi:10.1016/S0016-7061(96)00071-7
- Kaiser, K., and W. Zech. 1996. Nitrate, sulfate, and biphosphate retention in acid forest soils affected by natural dissolved organic carbon. *J. Environ. Qual.* 25:1325–1331. doi:10.2134/jeq1996.00472425002500060022x
- Kalbitz, K., S. Solinger, J.H. Park, B. Michalzik, and E. Matzner. 2000. Controls on the dynamics of dissolved organic matter in soils. *Soil Sci.* 165:277–304. doi:10.1097/00010694-200004000-00001
- Kalbitz, K., J. Schmerwitz, D. Schwesig, and E. Matzner. 2003. Biodegradation of soil-derived dissolved organic matter as related to its properties. *Geoderma* 113:273–291. doi:10.1016/S0016-7061(02)00365-8
- Kalbitz, K., D. Schwesig, J. Rethemeyer, and E. Matzner. 2005. Stabilization of dissolved organic matter by sorption to the mineral soil. *Soil Biol. Biochem.* 37:1319–1331. doi:10.1016/j.soilbio.2004.11.028
- Kleber, M., P. Sollins, and R. Sutton. 2007. A conceptual model of organo-mineral interactions in soils: Self-assembly of organic molecular fragments into zonal structures on mineral surfaces. *Biogeochemistry* 85:9–24. doi:10.1007/s10533-007-9103-5
- Kothawala, D.M., T.R. Moore, and W.H. Hendershot. 2008. Adsorption of dissolved organic carbon to mineral soils: A comparison of four isotherm approaches. *Geoderma* 148:43–50. doi:10.1016/j.geoderma.2008.09.004
- Kothawala, D.M., T.R. Moore, and W.H. Hendershot. 2009. Soil properties controlling the adsorption of dissolved organic carbon to mineral soils. *Soil Sci. Soc. Am. J.* 73:1831–1842. doi:10.2136/sssaj2008.0254
- Loeppert, R.H., and W.P. Inskeep. 1996. Iron. In: D.L. Sparks, editor, *Methods of soil analysis. Part 3. Chemical methods*. SSSA Book Ser. 5. SSSA, Madison, WI. p. 639–654.
- Lumsdon, D.G., M.I. Stutter, R.J. Cooper, and J.R. Manson. 2005. Model assessment of biogeochemical controls on dissolved organic carbon partitioning in an acid organic soil. *Environ. Sci. Technol.* 39:8057–8063. doi:10.1021/es050266b
- McCarthy, J.F., T. Williams, L. Liang, P.M. Jardine, A.V. Palumbo, L. Cooper, L.W. Jolley, and D.L. Taylor. 1993. Mobility of natural organic matter in a sandy aquifer. *Environ. Sci. Technol.* 27:667–676. doi:10.1021/es00041a010
- McGuire, A.D., J.M. Melillo, D.W. Kicklighter, and L.A. Joyce. 1995. Equilibrium responses of soil carbon to climate change: Empirical and process-based estimates. *J. Biogeogr.* 22:785–796. doi:10.2307/2845980
- Mikutta, R., M. Kleber, M.S. Torn, and R. Jahn. 2006. Stabilization of soil organic matter: Association with minerals or chemical recalcitrance? *Biogeochemistry* 77:25–56. doi:10.1007/s10533-005-0712-6
- Moore, T.R., and J. Turunen. 2004. Carbon accumulation and storage in mineral subsoil beneath peat. *Soil Sci. Soc. Am. J.* 68:690–696. doi:10.2136/sssaj2004.0690
- Neff, J.C., and G.P. Asner. 2001. Dissolved organic carbon in terrestrial ecosystems: Synthesis and a model. *Ecosystems* 4:29–48. doi:10.1007/s100210000058
- Parton, W.J., J.W.B. Stewart, and C.V. Cole. 1988. Dynamics of C, N, P and S in grassland soils: A model. *Biogeochemistry* 5:109–131. doi:10.1007/BF02180320
- Percival, H.J., R.L. Parfitt, and N.A. Scott. 2000. Factors controlling soil carbon levels in New Zealand grasslands: Is clay content important? *Soil Sci. Soc. Am. J.* 64:1623–1630. doi:10.2136/sssaj2000.6451623x
- Qualls, R.G. 2000. Comparison of the behavior of soluble organic and inorganic nutrients in forest soils. *For. Ecol. Manage.* 138:29–50. doi:10.1016/S0378-1127(00)00410-2
- Qualls, R.G., and B.L. Haines. 1991. Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. *Soil Sci. Soc. Am. J.* 55:1112–1123. doi:10.2136/sssaj1991.03615995005500040036x
- Qualls, R.G., B.L. Haines, W.T. Swank, and S.W. Tyler. 2002. Retention of soluble organic nutrients by a forested ecosystem. *Biogeochemistry* 61:135–171. doi:10.1023/A:1020239112586
- Shen, Y.-H. 1999. Sorption of natural dissolved organic matter on soil. *Chemosphere* 38:1505–1515. doi:10.1016/S0045-6535(98)00371-3
- Siemens, J. 2003. The European carbon budget: A gap. *Science* 302:1681. doi:10.1126/science.302.5651.1681a
- Soil Survey Staff. 1994. *State Soil Geographic (STATSGO) Data Base data use information*. Misc. Publ. 1492. NRCS, Washington, DC.
- Sollins, P., M.G. Kramer, and C. Swanston. 2007. Stabilization and destabilization of soil organic matter: A new focus. *Biogeochemistry* 85:1–7. doi:10.1007/s10533-007-9099-x
- Sollins, P., M.G. Kramer, C. Swanston, K. Lajtha, T. Filley, A.K. Aufdenkampe, R. Wagai, and R.D. Bowden. 2009. Sequential density fractionation across soils of contrasting mineralogy: Evidence for both microbial- and mineral-controlled soil organic matter stabilization. *Biogeochemistry* 96:209–231. doi:10.1007/s10533-009-9359-z
- Sombroek, W.G., F.O. Nachtergaele, and A. Hebel. 1993. Amounts, dynamics and sequestering of carbon in tropical and subtropical soils. *Ambio* 22:417–427.
- Sposito, G. 2004. *The surface chemistry of natural particles*. Oxford Univ. Press, New York. </bok>
- Stewart, M.A., P.M. Jardine, M.O. Barnett, T.L. Mehlhorn, L.K. Hyder, and L.D. McKay. 2003. Influence of soil geochemical and physical properties on the sorption and bioaccessibility of chromium(III). *J. Environ. Qual.* 32:129–137.
- Sutton, R., and G. Sposito. 2006. Molecular simulation of humic substance–Ca–montmorillonite complexes. *Geochim. Cosmochim. Acta* 70:3566–3581. doi:10.1016/j.gca.2006.04.032
- Tipping, E. 1981. The adsorption of aquatic humic substances by iron oxides. *Geochim. Cosmochim. Acta* 45:191–199. doi:10.1016/0016-7037(81)90162-9
- Trumbore, S. 1997. Potential responses of soil organic carbon to global environmental change. *Proc. Natl. Acad. Sci.* 94:8284–8291. doi:10.1073/pnas.94.16.8284
- van Dam, D., E. Veldkamp, and N. van Breemen. 1997. Soil organic carbon dynamics: Variability with depth in forested and deforested soils under pasture in Costa Rica. *Biogeochemistry* 39:343–375. doi:10.1023/A:1005880031579
- Voice, T.C., and J.W.J. Weber. 1983. Sorption of hydrophobic compounds by sediments, soils and suspended solids: I. Theory and background. *Water Res.* 17:1433–1441. doi:10.1016/0043-1354(83)90275-0

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.