ORIGINAL PAPER

Inhibition of phosphorus sorption to goethite, gibbsite, and kaolin by fresh and decomposed organic matter

James F. Hunt · Tsutomu Ohno · Zhongqi He ·
C. Wayne Honeycutt · D. Bryan Dail

Abstract The direct effects of dissolved organic matter (DOM) on the sorption of orthophosphate onto gibbsite, goethite, and kaolin were examined using a one-point phosphorus sorption index and the linear Tempkin isotherm model. DOM extracted from fresh and decomposed agricultural residues, as well as model organic and humic acids, were used. Changes in the chemical and sorptive characteristics of the DOM in the absence and presence of added orthophosphate (50 mg l^{-1}) were also determined. For residue-derived materials, DOM sorption to all minerals correlated well with percent hydrophobicity, apparent molecular weight, and phenolic acidity in the absence of added orthophosphate. Sorption of DOM to goethite and gibbsite was significantly decreased in the presence of added P. The correlation coefficient values of percent hydrophobicity, apparent molecular weight, and phenolic acidity to sorption also declined in the presence of added P. Thus, the addition of P substantially lowered fractionation of DOM after sorption to goethite and gibbsite. In contrast, few significant P sorption-induced differences were observed in the kaolin system. According to one-point P sorption results, DOM in the form of Aldrich humic acid, oxalate, and decomposed clover and corn residue, significantly inhibited P sorption to goethite at concentrations of 50 and 200 mg total soluble carbon (C_{TS} l^{-1}). Phosphorus

sorption to gibbsite was significantly inhibited by 50 mg C_{TS} l^{-1} derived from decomposed corn residue, fresh dairy manure residue, and oxalate solution. At 200 mg C_{TS} l^{-1}, all DOM solutions were found to inhibit P sorption to gibbsite. This study suggests that DOM inhibition of P sorption depends on the chemical properties of both the sorbent and the DOM itself. In general, DOM from decomposed organic materials inhibited P sorption to a greater extent than did DOM derived from fresh materials. This stronger inhibition highlights the importance of microbial processes in the release of soluble soil P, a key determinant of P availability to plants.

Keywords Dissolved organic matter · Phosphorus · Decomposition · Metal oxides · Sorption

Introduction

The plant availability of P in soils is often below that required for optimum crop production due to either precipitation of P with Ca, Fe, and Al, or to specific adsorption of P by metal hydrous oxides. To raise the fertility of soils, large inputs of inorganic P fertilizer are usually required, which may result in the excessive build up of soil-bound P. Subsequent erosion of these soils can lead to eutrophication in nearby surface waters (Sims et al. 1998). Additions of plant biomass and animal manures have been studied as one approach for moderating the problems associated with excessive inorganic P addition through increasing the bioavailability of the soil bound P fraction (Iyamuremye et al. 1996). Organic matter can interact with P in soils to influence the amount of available P in solution (Guppy et al. 2005a). The direct effects of dissolved organic matter (DOM) on P availability are

J. F. Hunt · T. Ohno (✉) · D. B. Dail
Department of Plant, Soil, and Environmental Sciences,
University of Maine,
5722 Deering Hall,
Orono, ME 04469-5722, USA
e-mail: ohno@maine.edu

Z. He · C. W. Honeycutt
New England Plant, Soil, and Water Laboratory, USDA-ARS,
Orono, ME 04469, USA

thought to involve four processes: (1) competition between DOM and P for mineral adsorption sites; (2) complexation of surface metals and release of these metals into solution, thereby removing adsorption sites; (3) increased repulsion of phosphate anions by sorption of DOM to positive sorption sites; and (4) formation of cation bridges leading to an increase in P sorption sites.

Because DOM released from soil amendments can result in both positive and negative effects regarding plant available P and P leaching, there is great interest in determining the importance of each of these possible fates. The relative importance of the first two direct effects on reducing soil P sorption has not been sufficiently resolved. Many studies have reported P sorption inhibition, due to either site competition or metal complexation and dissolution, by organic acids (Earl et al. 1979; Lopez-Hernandez et al. 1986; Hue 1991; Violante and Gianfreda 1993; Bhatti et al. 1998; Strom et al. 2002), humic substances (Leaver and Russell 1957; Sibanda and Young 1986; Gerke 1993), or DOM derived from green manures (Othieno 1973; Easterwood and Sartain 1990; Ohno and Crannell 1996; Erich et al. 2002). However, a number of works have found little or no evidence to support such DOM-mediated effects under more realistic soil conditions (LeMare et al. 1987; Borggaard et al. 2005; Guppy et al. 2005a). The uncertainty of the mechanisms involved in P–organic matter interactions in soils is discussed in a recent review article by Guppy et al. (2005b), which concludes that most of the increase in P availability observed in previous studies can be attributed to the P contained within the organic amendment itself.

The extent of DOM interactions with mineral surfaces is likely sensitive to the chemical properties of the DOM. Studies have shown, for instance, that there is preferential organic matter sorption for DOM fractions having greater hydrophobic character, aromatic content, apparent molecular weight (MW_{AP}), and total organic acidity (Jardine et al. 1989; Gu et al. 1995; Meier et al. 1999; Kaiser and Guggenberger 2000; Hur and Schlautman 2003). Carbon-rich soil amendments undergo microbial decomposition in soil that can alter these chemical characteristics, as well as their subsequent interaction with mineral surfaces (Hunt et al. 2007). In this study, DOM extracted from a diverse collection of agriculturally relevant organic materials was used to explore whether DOM at concentrations similar to those found in soils can directly inhibit the sorption of P onto goethite, gibbsite, and kaolin. The natural DOM was extracted using water from fresh and decomposed plant biomass and dairy manure. Reference materials used for comparison purposes were Aldrich humic acid (AHA), salicylic acid, and oxalic acid; the latter organic acids are usually among the most abundant found in soil (Fox and Comerford 1990; Kryzyzowska et al. 1996).

Materials and methods

Aqueous extracts

Plant shoot biomass was obtained from field-grown corn (*Zea mays* L.), crimson clover (*Trifolium incarnatum* L.), and hairy vetch (*Vicia villosa* L.), air-dried, and ground before passing through a 1-mm sieve. The dairy manure sample was acquired locally, air-dried, and passed through a 2-mm sieve. The DOM was extracted with a 40:1 (*v/w*) water to sample ratio using cold de-ionized distilled water (DI–H_2O) and refrigerating (4°C) the suspension for 18 h with periodic shaking by hand. The suspensions were then centrifuged (900×*g*) for 30 min before vacuum filtering through 0.4-μm pore size polycarbonate filters. Solutions of AHA, and oxalic and salicylic acids were chosen to examine the P sorption-inhibiting effects of materials known to sorb to metal hydrous oxides (AHA) or to solubilize hydrous oxide metals (oxalate). Salicylic acid was used because of its aromatic structure and high pKa carboxylic acid group positioned ortho to a hydroxyl substituent; it has been shown that this structural configuration is important in ligand exchange reactions involving metal hydrous oxide surfaces (Gu et al. 1994).

Decomposition

Decomposition of the plant biomass and dairy manure was conducted using a procedure modified from Merritt and Erich (2003). Briefly, 2.00 g of plant biomass or manure sample and 10 ml of DI–H_2O were added to 36 g of acid-washed silica sand in 125-ml polyethylene screw-top bottles. Thirty microliters of a fresh field-soil extract (1:10, soil/DI–H_2O) was added to each bottle to provide a microbial population representative of fresh field soils. The C/N ratios were determined for the plant and manure samples using a LECO CN-2000 carbon–nitrogen analyzer, and ammonium nitrate was added as necessary to attain a C/N ratio of 20 for each sample before incubation to assure that decomposition would proceed and N availability would not limit this process. The bottles were shaken, loosely capped, and placed in the dark at room temperature. Bottles were weighed and DI–H_2O added as necessary on alternate days to maintain the initial moisture level. The decomposed DOM was extracted on day 10 in the same manner as for the fresh samples. Three replicates of each material and a control consisting of sand, inoculant, and DI–H_2O were analyzed.

Chemical characterization

The concentrations of total-soluble organic carbon (C_{TS}) in each DOM solution were determined using a Shimadzu 5000 carbon analyzer. Except for an aliquot that was used

to determine hydrophobicity, each extract was then diluted to 50 mg C_{TS} l^{-1} and adjusted to pH 6 before further testing. Ultraviolet-visible spectra were collected using an Agilent 8453 diode-array spectrophotometer with a 1-cm quartz cuvette. The UV absorbance values at 254, 280, and 365 nm were used to calculate the molar absorptivities at 280 nm (absorbance at 280 nm divided by the C molar concentration) and the E2/E3 ratios (absorbance at 254 nm divided by absorbance at 365 nm) of each sample (Guo and Chorover 2003). Molar absorptivity at 280 nm has been found to correlate well with DOM aromaticity, while the E2/E3 ratio has been shown to be inversely related to DOM molecular weight (Chin et al. 1994). Total acidity was determined by potentiometric titration in a glass reaction beaker maintained at 25.0±0.1°C. The extracts were passed through a proton-saturated cation exchange resin before dilution to 20 mM C_{TS}, pH 3, using dilute HCl and 20 mM ionic strength using 1 M KCl solution. Nitrogen was bubbled through the solutions for 15 min before titration to minimize CO_2 contamination, and the resultant solutions were titrated with standardized 0.05 M NaOH. The molar quantity of OH^- consumed between the operational beginning and end points of pH 3 and 8 was defined to be equal to the molar quantity of carboxyl acidity present in the material. Phenolic acidity was estimated to be twice the NaOH consumption between pH 8 and 10 (Ritchie and Perdue 2003). Blank corrections were made by subtracting the quantity of the base consumed in titrating 20 mM KCl solutions from pH 3 to 10. Differences in the final solution volumes between the blank and each sample were included in the acidity calculations to normalize titrant consumption.

High performance-size exclusion chromatography was used to estimate the MW_{AP} of the DOM. The system consisted of a Hewlett Packard (Agilent, San Jose, CA, USA) 1100 high-performance liquid chromatography unit equipped with a G1311A quaternary pump, a G1314 auto sampler, and a G1315A photodiode array UV detector. A Waters Protein Pak 125 stainless-steel SEC column with a Waters guard column was used. The mobile phase consisted of a 0.1-M NaCl aqueous solution buffered to pH 6.8 with 5 mM phosphate buffer. Samples were matched to the mobile phase matrix by the addition of 0.1 ml of 1 M NaCl solution (phosphate buffered to pH 6.8) to 0.9 ml of sample. Calibration of molecular weight to retention time was accomplished using polystyrene sulfonate sodium standards (2.0 mg ml^{-1}) of nominal masses of 4.6, 8.0, and 18.0 kDa, and polydispersity values of less than 1.2 (Polymer Laboratories, Silver Spring, MD, USA). Benzoic acid and salicylic acid were used as the low-molecular-mass standards in the calibration. The injection volume for all samples was 100 μl, and the flow rate was 1.0 ml min^{-1} with detection at 230 and 254 nm (Zhou et al. 2000). All standards and samples were analyzed in duplicate.

Percent hydrophobicity was determined using 30 ml aliquots (200 mg C_{TS} l^{-1}) of each DOM extract and reference solutions that were acidified to pH 2 using dropwise additions of 6 M HCl. The solutions were passed through columns containing DAX-8 (Sigma Chemical, St. Louis) resin at a rate of 2 ml min^{-1}. The DAX-8 resin was prepared with three 50-ml rinses of 0.1 M NaOH and DI–H_2O, followed by Soxhlet extraction with methanol for 3 h. Ten milliliters of the resin was then added to a column and rinsed sequentially with 100 ml each of DI–H_2O, 0.01 M NaOH, and 0.01 M HCl (Ohno and Cronan 1997). Hydrophobicity was operationally defined as the percentage of DOC sorbed onto the DAX-8 resin relative to the total C and was calculated by:

$$\%\text{hydrophobicity} = [(\text{initial } C_{TS} - \text{eluent } C_{TS})/\text{initial } C_{TS}]*100$$

where C_{TS} is the total-soluble organic carbon concentration.

P sorption

The total P concentrations in the DOM and AHA solutions were determined using inductively coupled plasma-atomic-emission spectroscopy (ICP–AES), and the malachite green method (Ohno and Zibiliske 1991) was used to determine molybdate-reactive inorganic P concentrations. The difference between the results of these two methods was taken as the organic P fraction in the extract solutions. The P concentrations of the oxalic and salicylic acid solutions were determined by ICP–AES alone. Addition of P (as KH_2PO_4) to each extract was adjusted to normalize the amount measured in the extract source (final total P concentration of 50 mg l^{-1}) to reduce the possibility that any effects observed could be due to a release of P contained in the extract material.

Phosphorus sorption inhibition by the DOM solutions was examined using both a one-point P sorption index and five-point P sorption isotherms. Synthetic goethite (α-FeOOH) and gibbsite ($Al(OH)_3$) were used as representative metal hydrous oxides frequently present in soils, and kaolin was used as a representative aluminosilicate clay. The goethite was synthesized by using a method modified from Schwertmann and Cornell (1991). Briefly, 13.9 g of $FeSO_4·7H_2O$ was added to 1 l of DI–H_2O that was de-aerated with N_2 flushing. One hundred ten milliliters of 1 M $NaHCO_3$ solution was then added, and air was bubbled through the reaction vessel at 35 ml min^{-1} for 48 h. The suspension was then centrifuged (900×g, 30 min). The pellet was retained, washed three times with DI–H_2O, and then dried at 40°C for 24 h. The specific surface area of 58.3 m^2 g^{-1} was determined by triple point N_2 adsorption and is comparable to literature values that range from 48.5 to 70.9 m^2 g^{-1} (Wang et al. 1997). The gibbsite was prepared by the hydrolysis of aluminum nitrate as described

by Borggaard et al ([2005](#)) who reported a specific surface area of 264 m^2 g^{-1}. Commercial kaolin was purchased from Sigma and was found by triple point N$_2$ adsorption to have a surface area of 17.7 m^2 g^{-1}, which is comparable to the value of 14.3 m^2 g^{-1} determined by Hur and Schlautman ([2003](#)) for this material.

For the one-point index, sorbed P was taken to be the initial P solution concentration minus the final P solution concentration after shaking with the sorbent solutions. The P concentration was 50 mg P l^{-1} in the presence of DOM at either 50 or 200 mg C$_{TS}$ l^{-1}. All sorption experiments were conducted in triplicate, and the control consisted of 50 mg P l^{-1} with no added DOM. The phosphorus sorption isotherms were constructed from five P concentrations (5, 10, 20, 40, and 50 mg P l^{-1}). Data from these isotherms was then plotted using the Tempkin model: P sorbed=a log [solution P]+b, where a is the slope of the linear isotherm and b is the y-intercept. The Tempkin model allows for the calculation of linear parameters and is used to assess the affect of a treatment on the sorption of a sorbate over a range of concentrations.

DOM sorption

A one-point DOM adsorption index with an initial C solution concentration of 50 mg C$_{TS}$ l^{-1} was used to evaluate the extent of DOM sorption. The adsorption index for each DOM solution was determined in triplicate by reacting 25 ml of 50 mg C$_{TS}$ l^{-1} DOM solution adjusted to pH 6 and 20 mM ionic strength (using KCl), with 40 mg of gibbsite, 80 mg of goethite, and 1,500 mg of kaolin in 50-ml plastic centrifuge tubes. The different masses used reflect the differences in both mineral surface area and propensity to sorb orthophosphate, and were calculated from preliminary experiments designed to optimize the amount of sorption site competition between the DOM and P. The tubes were then placed on an orbital shaker at 120 rpm for 24 h at 4°C to minimize microbial degradation of the DOM solution (Zhou and Wong [2000](#)). No attempt was made to control the pH of the solutions during the experiment, and pH changes in the DOM solution were determined at the conclusion of the experiment. The tubes were then centrifuged (900×g) for 30 min, and the supernatants were filtered through 0.40-μm filters. The C$_{TS}$ concentration was determined as described above, and the quantity adsorbed was calculated by the difference from the initial solution. All post-sorption solutions were chemically characterized for MW$_{AP}$ and UV absorbance.

Statistical analysis

Analysis of variance (ANOVA) was used to test for differences in the one-point P sorption indexes, and the resulting mean separations were performed using the experiment-based Dunnett's test. The relationship between mineral sorption and selected extract chemical characteristics was examined through correlation analysis. Log transformations of the variables were necessary for the data to pass the Shipiro–Wilks test for normality and the Levene's test for variance equality. Student t tests were used to compare the parameters of the linear Tempkin regressions. Mean variations are reported as standard errors in all tables and text. All statistical analyses were performed using the statistical package SAS 9.1 for Windows.

Results and discussion

One-point P sorption index

Sorption of P (50 mg l^{-1}) solutions in the absence or presence of DOM (50 or 200 mg C$_{TS}$ l^{-1}) derived from various C sources is shown as one-point P sorption indexes in Fig. [1](#). The amount of P sorbed to goethite, gibbsite, and kaolin minerals in the absence of DOM was 5,270±54 μg P g^{-1}, 20,800±117 μg P g^{-1}, and 207±2 μg P g^{-1}, respectively. Phosphate sorbs to mineral surfaces through inner-sphere interactions (Sposito [1989](#)). The much greater P sorption by goethite and gibbsite compared with kaolin was likely due to both the preponderance of surface hydroxyl groups in the metal hydrous oxide minerals and to differences in the specific surface areas of the minerals present in solution.

Significant inhibition of P sorption to goethite was found for DOM derived from decomposed clover and corn residues, as well as AHA and oxalate at both 50 and 200 mg C$_{TS}$ l^{-1} concentrations levels (Fig. [1](#)). In contrast, for gibbsite, DOM concentration was a strong factor in P inhibition. At the 50 mg C$_{TS}$ l^{-1} concentration, only decomposed corn and clover DOM and oxalate were found to significantly inhibit P sorption. However, at the 200-mg C$_{TS}$ l^{-1} concentration, all DOM and reference materials significantly reduced P sorption. For kaolin, the only significant inhibitor was oxalate, and the strength of this inhibition led to the complete inhibition of P sorption (Fig. [1](#)). The pattern of inhibition of P sorption by DOM varied with the mineral surface studied, suggesting important interactions between DOM and P. Results from the one-point sorption indices demonstrate that P sorption inhibition by organic matter is dependent on both the nature of the organic matter and the mineral surface.

Tempkin isotherm analysis

The results of one-point sorption studies are sometimes criticized because they do not consider the slope of the

Fig. 1 Sorption of 50 mg P l^{-1} solutions to goethite, gibbsite, and kaolin in the presence of 50 and 200 mg total soluble carbon l^{-1} derived from fresh and decomposed organic matter. The *error bars* indicate the standard deviation of the mean of three replicates. The *dashed line* indicates P sorption potential in the absence of DOM. The *asterisk* represents the significance difference in P sorption between DOM containing solutions and control
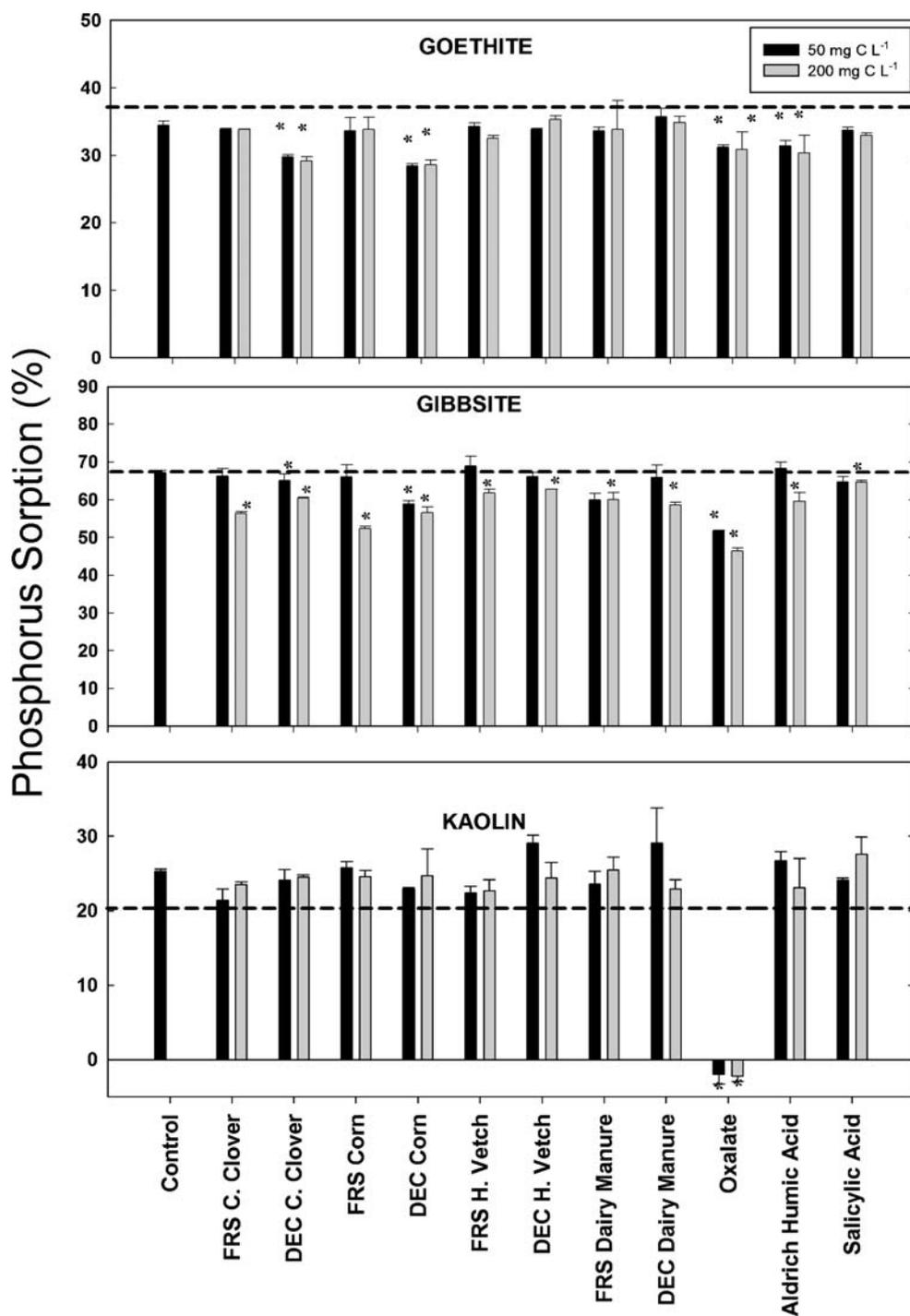
sorption isotherm. An additional study was, therefore, conducted using a range of P concentrations at a constant DOM concentration of 50 mg C$_{TS}$ l^{-1}. The resulting isotherms were interpreted using the Tempkin model (Bowden et al. 1980; Guppy et al. 2005b). In this model, displacement of the P sorption isotherm to the right (decrease in *y*-intercept) with no change in slope is interpreted as a decrease in P sorption sites due to competitive sorption, while displacement to the left

(increase in *y*-intercept) indicates creation of additional sorption sites with similar bonding energies. On the other hand, modifications in the P isotherm slope are taken to represent fundamental transformations in the P-related affinity of the mineral sorption sites. An increase in slope is associated with the creation of new sites, while a decreased slope may indicate permanent blocking of sorption sites. The Tempkin plot associated with the effects of the reference organic materials on P sorption to goethite
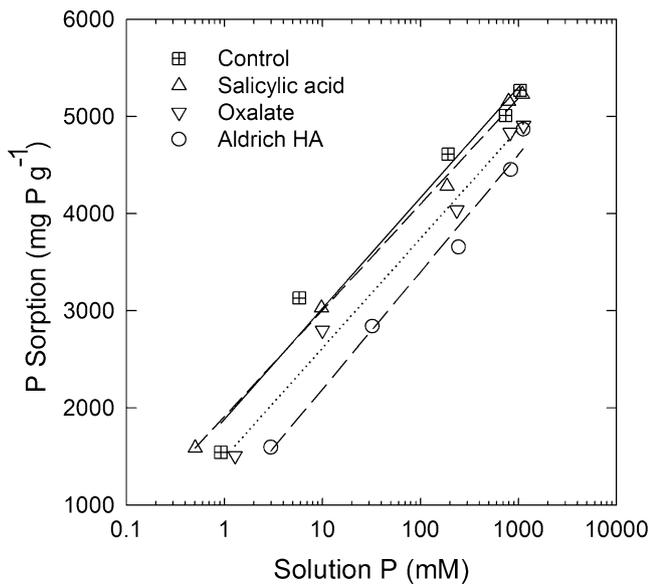
Fig. 2 Tempkin plot of phosphorus sorption to goethite in the presence of 50 mg total soluble carbon l^{-1} solutions of model organic compounds

is shown in Fig. 2. Two of the reference material solutions produced significant affects on the goethite P sorption isotherm. The AHA significantly lowered the P sorption y-intercept, while oxalate decreased both the slope and the y-intercept of the isotherm relative to that of the control in the goethite system (Table 1). This indicates that AHA may inhibit P sorption through a competitive mechanism alone, while oxalate appears to be reducing P sorption through an alteration in the sorption sites. These alterations may have been due to the dissolution of goethite, as oxalate has been

shown to strongly enhance the dissolution of iron oxides (Johnson and Loeppert 2006).

The slope and y-intercept values describing the Tempkin plots for all of the DOM materials and minerals are shown in Table 1. Although DOM derived from fresh plant biomass and manure generally decreased the amount of P sorbed to goethite, none of these effects were found to be significant. However, DOM derived from the decomposed residues of these sources, with the exception of hairy vetch, significantly inhibited P sorption to goethite. Decomposed clover and corn-derived extracts significantly reduced both the y-intercept and the slope of the P isotherm relative to that of the control. These changes indicate both a decrease in the number of available P sorption sites as well as decreases in the affinity of existing P sorption sites. Decomposed dairy manure-derived extract decreased the y-intercept value while also increasing the slope of the isotherm. We attribute the lack of any P sorption inhibition to the net result of these opposing effects. Overall, 5 of the 11 DOM tested significantly inhibited P sorption to goethite.

Plant biomass DOM inhibited P sorption to gibbsite in a manner similar to that observed with goethite. Only decomposed crimson clover and corn DOM inhibited P sorption by decreasing the y-intercept in the former case and by decreasing both the y-intercept and the slope in the latter case (Table 1). Decomposed hairy vetch DOM significantly increased the isotherm slope, indicating the formation of new P sorption sites. Overall, four of the eleven DOM extracts significantly inhibited P sorption to gibbsite.

Table 1 Tempkin plot values for phosphate adsorption by goethite, gibbsite, and kaolin in the presence of different 50 mg C l^{-1} solutions

DOC source	Goethite		Gibbsite		Kaolin	
	y-Intercept	Slope	y-Intercept	Slope	y-Intercept	Slope
Control (0 mg C l^{-1})	1,631±4.7	1,228±20	7,347±67	4,870±49	−235±37	145±13
Frech crimson clover	1,642±11	1,169±22	7,038±152	4,913±87	−157±35	114±17
Decomposed crimson clover	1,223±58*	1,110±44**	7,061±65**	4,976±61	−159±16	118±7.8
Fresh corn	1,585±33	1,234±36	7,202±96	4,870±9.9	−242±15	152±6.9
Decomposed corn	1,517±4.0**	1,025±32***	5,589±12***	4,527±77**	−201±22	135±7.2
Fresh hairy vetch	1,614±18	1,295±21	7,263±38	5,184±24	−175±45	113±16
Decomposed hairy vetch	1,597±13	1,311±21	5,010±1189	5,670±627**	−191±10	131±2.2
Fresh dairy manure	1,576±26	1,212±19	6,753±163*	4,872±7.6	−128±119	113±39
Decomposed dairy manure	1,585±11**	1,370±6.7**	6,459±1057	5,385±612	−184±25	142±13
Oxalate	1,490±15*	1,126±2.5**	4,525±6.8***	3,728±8.8***	−68±18	15.4±7.4*
Salicylic acid	1,533±77	1,219±19	7,103±101	4,657±140	−185±42	122±16
Aldrich humic acid	1,223±16*	1,313±64	7,103±83	4,954±52	−199±44	132±18

± Indicates the standard deviation of the mean.
*$p=0.01$, significant difference
**$p=0.05$, significant difference
***$p=0.001$, significant difference

With kaolin as a sorbent, the Tempkin isotherm analysis was consistent with the results observed in the one-point P sorption study by revealing no DOM effects on P sorption, except in the case of oxalate. Nevertheless, oxalate did decrease the slope of the P isotherm by nearly an order of magnitude, an effect likely due to the dissolution of Al metal from the aluminosilicate mineral.

DOM chemical properties

Selected chemical properties for the DOM investigated are shown in Table 2 and illustrate the diversity of the materials employed. In particular, values for the reference material DOM demonstrate the relationship between the selected chemical properties and known structural characteristics. For instance, the richly aromatic AHA has high molar absorptivity, MW_{AP}, and percent hydrophobicity values, as well as a very low E2/ E3 ratio value. Conversely, the low molecular weight aliphatic oxalate has very low values for absorptivity and percent hydrophobicity. For the plant- and animal manure-derived DOM, hydrophobicity, absorptivity, MW_{AP}, and phenolic acidity all increased significantly ($p<0.05$) in value after decomposition of the source materials, while E2/E3 values decreased after decomposition. These chemical changes indicate that the agricultural residues underwent substantial structural transformations during the 10-day incubation and are consistent with the literature relating decomposition with increasing humification (Stevenson 1994).

DOM sorption

Analysis of the Tempkin isotherm parameters suggests that DOM may inhibit P sorption by both competitive/negative surface charge effects and by dissolution of surface metal oxide sorption sites. Thus, sorption of the DOM ligand to

the mineral surface should be an important factor in the inhibition of P sorption. To investigate this in more detail, the sorption of DOM to the three minerals and the chemical characteristics of the DOM remaining in solution after sorption were determined in both the absence and presence of added phosphate (Fig. 3). The mean amount of DOM sorbed to the minerals in the absence of P followed the same order observed for P sorption: gibbsite (14,200 µg C_{TS} g^{-1}) > goethite (5,470 µg C_{TS} g^{-1}) > kaolin (322 µg C_{TS} g^{-1}). This ranking between the two metal oxides was expected as the relative affinity of both orthophosphate and C anions for mineral surfaces generally follows the order amorphous Al compounds > amorphous Fe compounds > goethite (Jones and Brassington 1998). As noted earlier, differences in the specific areas of the minerals may also be a factor in the observed ranking in this study. Visual inspection of the effects of P on DOM sorption reveals that P strongly inhibits DOM sorption to goethite, is intermediate for gibbsite, and does not inhibit DOM sorption to kaolin (Fig. 3).

The mean reduction in DOM sorption onto goethite in the presence of P was 85%, suggesting that P was a stronger competitor for sorption sites than was DOM. The initial percent hydrophobiticy, MW_{AP}, absorptivity, and phenolic acidity group content of the DOM were significantly correlated with DOM sorption in the absence of P for both the fresh and decomposed DOM (Table 4). In the presence of P, the correlation coefficient for molar absorptivity becomes non-significant, and the significance levels for percent hydrophobicity and MW_{AP} decrease. This suggests that it is the more humified (i.e., more aromatic and higher MW_{AP}) fraction of the DOM that is preferentially sorbed and that bonding involves the phenol functional group. Comparison of sorption densities with other studies is hindered by differences in solution: mineral ratios and

Table 2 Selected chemical characteristics of the fresh and decomposed extracts before sorption

Extract source	Fraction	Hydrophobicity (%)	Absorptivity (l mol^{-1} cm^{-1})	E2/E3 ratio	MW_{AP} (Da)	Carboxyl acidity (mmol$_{(-)}$ g^{-1})	Phenolic acidity (mmol$_{(-)}$ g^{-1})
Crimson clover shoot	Fresh	16.9 (0.3)	79.7 (1.2)	4.56 (0.1)	302 (21)	10.2 (0)	7.87 (0.2)
	Decomposed	33.7 (1.7)	131 (2.6)	5.03 (0.1)	427 (30)	9.15 (0)	11.4 (0.1)
Corn shoot	Fresh	13.9 (1.5)	100 (3.3)	4.46 (0.5)	525 (22)	9.08 (0)	3.54 (0.1)
	Decomposed	41.3 (1.2)	175 (4.6)	3.36 (0.4)	1295 (26)	11.9 (0)	16.1 (0.8)
Hairy vetch shoot	Fresh	9.84 (1.4)	52.6 (2.3)	5.52 (0.6)	240 (0.9)	9.80 (0)	6.56 (0.1)
	Decomposed	46.2 (0.9)	70.5 (1.1)	4.56 (0.7)	1,035 (25)	9.28 (0.1)	24.0 (1.8)
Dairy manure	Fresh	56.2 (1.2)	323 (5.4)	3.16 (0.5)	4,492 (52)	11.8 (0.1)	6.33 (0.1)
	Decomposed	76.5 (1.1)	426 (11)	2.94 (0.3)	5,688 (45)	8.42 (0.1)	12.4 (0.6)
Aldrich humic acid		71.8 (2.5)	845 (12.9)	2.73 (0.5)	4,457 (63)	7.49 (0.1)	4.05 (0.1)
Oxalate		0.13 (0.5)	5.62 (0.8)	Negative	90.0[a]	52.2 (0.4)	0.00 (0.1)
Salicylic acid		98.3 (0.4)	252 (3.1)	35.1 (2.9)	138[a]	8.88 (0.1)	1.89 (0.1)

Values in parenthesis are the standard error of the mean.
[a] Molecular weight

Fig. 3 Sorption of 50 mg total soluble carbon l^{-1} solutions derived from fresh and decomposed organic matter to goethite, gibbsite, and kaolin in the absence and presence of added phosphorus. The *error bars* indicate the standard deviation of the mean of three replicates
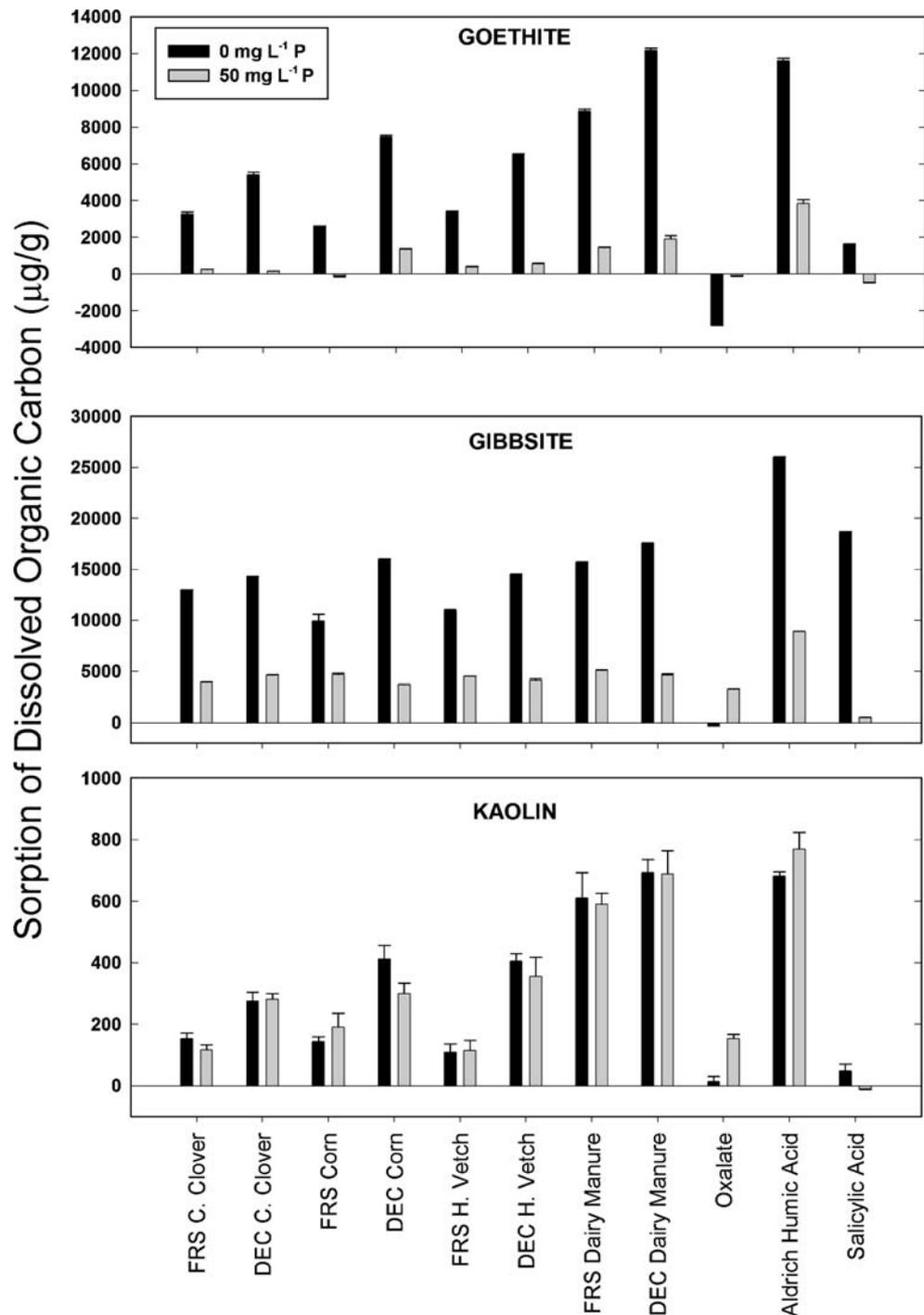
experimental pH values, both of which can affect the degree of C sorption. However, Ohno et al. (2007) reported that goethite sorption of DOM derived from similar types of fresh plant biomass and animal manures ranged between 1,370 and 3,360 μg C$_{TS}$ g^{-1}, and Kaiser and Zech (1997) found DOM sorption onto goethite from forest Oa horizon to be 4,450 μg C$_{TS}$ g^{-1}. Oxalate caused a net desorption of C from the goethite surface (Fig. 3). The source of this C was likely carbonate that had strongly bonded to the goethite

surface during synthesis and released into solution upon oxalate-mediated dissolution of the mineral.

The inhibition of DOM sorption to gibbsite by added P was generally less than that observed with respect to goethite with a mean reduction of 69% as compared to 85% for goethite (Fig. 3). The same chemical property descriptors (hydrophobicity, MW$_{AP}$, absorptivity, and phenolic acidity group content) were significant for sorption onto gibbsite as for goethite in the absence of P (Table 3).

Table 3 Pearson correlation coefficients relating sorption to the log transformed values of the chemical properties of dissolved organic carbon derived from fresh and decomposed extract sources

Sorbent	Phosphorus concentration (mg l^{-1})	DAX-8 hydrophobicity (%)	Molar absorptivity (l mol^{-1} cm^{-1})	Apparent molecular weight (Da)	Carboxylic acidity (mmol$_{(-)}$ g^{-1})	Phenolic acidity (mmol$_{(-)}$ g^{-1})
Goethite	0	0.946*	0.805*	0.885*	0.121 (NS)	0.593**
Goethite	50	0.617**	0.401 (NS)	0.508***	0.356 (NS)	0.565**
Gibbsite	0	0.894***	0.729*	0.756*	0.216 (NS)	0.687***
Gibbsite	50	0.046 (NS)	0.360 (NS)	0.305 (NS)	−0.229 (NS)	−0.606***
Kaolin	0	0.951*	0.803*	0.901*	0.098 (NS)	0.478 (NS)
Kaolin	50	0.903*	0.816*	0.900*	0.003 (NS)	0.284 (NS)

NS The correlation is not significant.
*$p=0.05$significant difference
**$p=0.01$, significant difference
***$p=0.001$, significant difference

In the presence of P, hydrophobicity, MW$_{AP}$, and absorptivity become non-significant, and the correlation coefficient for phenolic acidity content becomes negative. This implies that sorption of the more humified DOM, a fraction strongly sorbed onto the gibbsite surface in the absence of P, is significantly inhibited in the presence of P. Whereas P sorption to gibbsite was significantly inhibited in the presence of four of the eight plant biomass and dairy manure extract DOM sources (Table 1), DOM sorption in the presence of P was uniform for all plant biomass and dairy manure extracts 4,420±420 μg C$_{TS}$ g^{-1} (Fig. 2).

The mean DOM sorption onto kaolin was 322 μg C$_{TS}$ g^{-1} in both the absence and the presence of P, indicating that DOM is not involved in competitive sorption with P. This differs from the observed interactions between these two anions at the goethite and gibbsite surfaces. The much lower observed DOM sorption to kaolin compared to goethite and gibbsite is consistent with differences in both sorption site availability and to the predominant sorption mechanisms operating within the different mineral systems.

A number of previous studies have shown that surface complexation–ligand exchange reactions dominate the sorption of both P and acidic C moieties to aluminum and iron hydrous-oxide surfaces (Davis 1982; Gu et al. 1994, 1995; Hur and Schlautman 2004). Sorption of C onto aluminosilicate minerals, such as kaolin, can also be expected to occur through a number of different mechanisms such as ligand exchange, anion exchange, or entropy-driven interactions involving a partitioning of hydrophobic groups out of solution (Jardine et al. 1989; Sposito 1989; Baham and Sposito 1994; Balcke et al. 2002).

Phosphorus sorption onto kaolin has been shown to occur solely via ligand exchange at a limited number of edge aluminol sites (Sposito 1989; Tombacz et al. 2004). Thus, the C sorption mechanism predominating at the kaolin surface should determine the degree of P sorption inhibition. Edge aluminol sites have been found to have a point of net zero charge (PZC) of ~7.3 (Hur and Schlautman 2003), which is much higher than the PZC for the typical kaolin surface overall (~4.2) and should, therefore, still act as Lewis

Table 4 Percent change in absorptivity and apparent molecular weight of DOM due to adsorptive fractionation after sorption to goethite, gibbsite, and kaolin in the presence and absence of 50 mg P l^{-1}

DOM source	Absorptivity (280 nm)		MW$_{AP}$	
	0 ppm P	50 ppm P	0 ppm P	50 ppm P
Goethite				
Fresh extracts	−29.0	25.8	−56.6	−1.17
Decomposed extracts	−22.6	45.8	−80.0	−8.28
Aldrich humic acid	−21.1	22.7	112	191
Gibbsite				
Fresh extracts	−17.1	−8.91	−58.6	−9.29
Decomposed extracts	−13.3	−6.91	−81.8	−21.8
Aldrich humic acid	34.7	−4.14	33.9	−1.82
Kaolin				
Fresh extracts	−32.5	−19.0	−69.5	−65.9
Decomposed extracts	−26.9	−23.6	−79.3	−76.4
Aldrich humic acid	−76.9	−55.3	−85.1	−85.2

acid sites at our experimental pH of 6. Thus, if hydrophobic/ entropic effects dominate DOM sorption to kaolin, then little competitive interaction for sorption sites would be expected to occur between DOM and P, a result consistent with our observations (Fig. 3). The DOM sorption to kaolin in this study was significantly correlated with the humification-related properties (percent hydrophobity, molar absorptivity, and MW_{AP}) but not with carboxylic and phenolic acidity functional group content (Table 3). This suggests a role for the hydrophobic partitioning of DOC onto the kaolin surface and is consistent with the lack of P sorption inhibition observed with the DOM with kaolin.

The results of the correlation were generally verified by determining the changes in the absorptivity and MW_{AP} properties of the remaining DOM from the organic amendments and AHA in solution after sorption in the absence and presence of added P (Table 4). In the absence of added P, absorptivity and MW_{AP} generally decreased significantly after sorption to each mineral. This is consistent with numerous studies demonstrating organic matter fractionation as a result of the preferential sorption of DOM fractions with greater hydrophobic character, aromatic content, and MW_{AP} than the DOM remaining in solution (Gu et al. 1995; Kaiser and Zech 1997; Meier et al. 1999; Chorover and Amistadi 2001; Hur and Schlautman 2003; Ohno et al. 2007). Kaolin showed the strongest DOM fractionation despite sorbing DOM to a much lower extent than either goethite or gibbsite. This strong fractionation by kaolin has been observed previously and has been attributed to the sorbent-selective nature of kaolin (Namjesnik-Dejanovic et al. 2000). AHA was the only material in the absence of added P that showed significant increases in MW_{AP} after sorption to gibbsite and goethite but not kaolin. Similar anomalous MW_{AP} results have been observed previously for AHA and are believed to be due to the greater aromatic and acidic functional groups associated with the smaller size fractions of this material (Shin et al. 1999; Johnson et al. 2002; Hur and Schlautman 2003).

Carbon fractionation after DOM sorption to gibbsite and goethite in the presence of added P was, in almost all cases, much less than that observed in the absence of added P. This was expected because the extent of fractionation in aluminum and iron hydrous-oxide systems is likely proportional to the amount of C sorbed (Hur and Schlautman 2003). Higher than initial absorptivity values were found for most of the added P, post-goethite sorption solutions and were likely due to the dissolution of iron from the goethite surface by these DOM ligands. The subsequent formation of soluble or colloidal organo-iron complexes may have led to red-shifting and/or excessive scattering of the incident UV light that resulted in higher-than-expected absorbance readings (Meier et al. 1999).

Conclusion

It has been suggested that most of the decreases in P sorption attributed to OM solutions in previous studies could be due to mineralization of P contained within the OM itself (Guppy et al. 2005a). In this study, we have accounted for the P supplied directly by the DOM to reduce the possibility that the observed effects could be due to a release of P contained in the native DOM. Our results show P sorption inhibition by some DOM extracted from plant biomass and dairy manure, especially materials that were extracted after microbial decomposition. This finding clearly demonstrates the importance of considering microbially mediated processes, such as decomposition, when doing laboratory-based soil chemical studies of ecosystem processes.

The results of these studies clearly indicate that DOM can inhibit P sorption to metal hydrous oxide minerals (Table 1 and Fig. 1). However, the mechanism by which this inhibition operates remains unresolved. There was no clear correspondence between the observed pattern of DOM inhibition of P sorption (Table 1 and Fig. 1) and the DOM sorption to mineral surfaces, in the absence and presence of P (Fig. 3), discouraging the notion of direct competition between DOM and P. Although relatively high DOM sorption in the presence of P for AHA and decomposed corn and dairy manure suggested that competition between P and DOM ligands may contribute to the P sorption inhibition observed with these two DOM sources, decomposed crimson clover DOM significantly inhibited P sorption despite suppression of DOM sorption to near zero in the presence of P (Fig. 2). While determining the processes involved in the observed DOM inhibition of P sorption onto metal oxides will require further research, this study demonstrates that addition of plant biomass or manures to soil may reduce the sorption of P onto soil minerals and, thus, increase the bioavailability of P in the soil. The results also show that the extent of inhibition is closely related to the chemical structure of both the DOM molecule and the sorbing surface.

References

Baham J, Sposito G (1994) Adsorption of dissolved organic carbon extracted from sewage sludge on montmorillonite and kaolinite in the presence of metal ions. J Environ Qual 23:147–153

Balcke GU, Kulikova NA, Hesse S, Kopinke F-D, Perminova IV, Frimmel FH (2002) Adsorption of humic substances onto kaolin clay related to their structural features. Soil Sci Soc Am J 66:1805–1812

Bhatti JS, Comerford NB, Johnson CT (1998) Influence of oxalate and soil organic matter on sorption and desorption of phosphate onto a spodic horizon. Soil Sci Soc Am J 62:1089–1095

Borggaard OK, Raben-Lange B, Gimsing AL, Strobel BW (2005) Influence of humic substances on phosphate adsorption by aluminum and iron oxides. Geoderma 127:270–279

Bowden JW, Posner AM, Quirk JP (1980) Adsorption and charging phenomena in variable charge soils. In: Theng BKG (ed) Soils with variable charge. New Zealand Society of Soil Science, Lower Hutt, NZ, pp 147–166

Chin YP, Aiken G, O'Loughlin E (1994) Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environ Sci Technol 28:1853–1858

Chorover J, Amistadi MK (2001) Reaction of forest floor organic matter at goethite, birnessite and smectite surfaces. Geochim Cosmochim Acta 65:95–109

Davis JA (1982) Adsorption of natural dissolved organic matter at the oxide/water interface. Geochim Cosmochim Acta 46:2381–2393

Earl KD, Syers JK, McLaughlin JR (1979) Origin of the effect of citrate, tartrate and acetate on phosphate sorption by soils and synthetic gels. Soil Sci Soc Am J 43:674–678

Easterwood GW, Sartain JB (1990) Clover residue effectiveness in reducing orthophosphate sorption on ferric hydroxide coated soil. Soil Sci Soc Am J 54:1345–1350

Erich MS, Fitzgerald CB, Porter GA (2002) The effect of organic amendments on phosphorus chemistry in a potato cropping system. Agric Ecosyst Environ 88:79–88

Fox TR, Comerford NB (1990) Low-molecular weight organic acids in selected forest soils in the southeastern USA. Soil Sci Soc Am J 54:1139–1144

Gerke J (1993) Phosphate adsorption by humic/Fe-oxide mixtures aged at pH 4 and pH 7 and by poorly ordered Fe-oxide. Geoderma 59:279–288

Gu B, Schmitt J, Chen Z, Liang L, McCarthy JF (1994) Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. Environ Sci Technol 28:38–46

Gu B, Schmitt J, Chen Z, Liang L, McCarthy JF (1995) Adsorption and desorption of different organic matter fractions on iron oxide. Geochim Cosmochim Acta 59:219–229

Guo M, Chorover J (2003) Transport and fractionation of dissolved organic matter in soil columns. Soil Sci 168:108–118

Guppy CN, Menzies NW, Blamey FPC, Moody PW (2005a) Do decomposing organic matter residues reduce phosphorus sorption in highly weathered soils? Soil Sci Soc Am J 69:1405–1411

Guppy CN, Menzies NW, Moody PW, Blamey FPC (2005b) Competitive sorption reactions between phosphorus and organic matter in soil: a review. Austr J Soil Res 43:189–202

Hue NV (1991) Effects of organic acids/anions on P sorption and phytoavailability in soils with different mineralogies. Soil Sci 152:463–471

Hunt J, Ohno T, He Z, Honeycutt CW, Dail DB (2007) Influence of decomposition on the chemical properties of plant- and manure-derived dissolved organic matter and sorption to goethite. J Environ Qual 36:135–143

Hur J, Schlautman MA (2003) Molecular weight fractionation of humic substances by adsorption onto minerals. J Colloid Interface Sci 264:313–321

Hur J, Schlautman MA (2004) Effects of pH and phosphate on the adsorptive fractionation of purified Aldrich humic acid on kaolinite and hematite. J Colloid Interface Sci 277:264–270

Iyamuremye F, Dick RP, Baham J (1996) Organic amendments and phosphorus dynamics: I. Phosphorus chemistry and sorption. Soil Sci 161:426–435

Jardine PM, Weber NL, McCarthy JF (1989) Mechanisms of dissolved organic carbon adsorption on soil. Soil Sci Soc Am J 53:1378–1385

Johnson SE, Loeppert RH (2006) Role of organic acids in phosphate mobilization from iron oxide. Soil Sci Soc Am J 70:222–234

Johnson WP, Bao G, John WW (2002) Specific UV absorbance of Aldrich humic acid: changes during transport in aquifer sediment. Environ Sci Technol 36:608–616

Jones DL, Brassington DS (1998) Organic Acids in the rhizosphere—a critical review. Plant Soil 248:31–41

Kaiser K, Guggenberger G (2000) The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. Org Geochem 31:711–725

Kaiser K, Zech W (1997) Competitive sorption of dissolved organic matter fractions to soils and related mineral phases. Soil Sci Soc Am J 61:64–69

Kryzyzowska AJ, Blaylock MJ, Vance GF (1996) Ion chromatographic analysis of low-molecular-weight organic acids in Spodosol forest floor solutions. Soil Sci Soc Am J 60:1565–1571

Leaver JP, Russell EW (1957) The reaction between phosphate and phosphate-fixing soils. J Soil Sci 8:113–126

LeMare PH, Pereira J, WJ Goedert (1987) Effects of green manure on isotopically exchangeable phosphate in a dark latosol in Brazil. J Soil Sci 38:199–209

Lopez-Hernandez D, Siegert G, Rodriguez JV (1986) Competitive adsorption of phosphate with malate and oxalate by tropical soils. Soil Sci Soc Am J 50:1460–1462

Meier M, Namjesnik-Dejanovic K, Maurice PA, Chin Y-P, Aiken GR (1999) Fractionation of aquatic natural organic matter upon sorption to goethite and kaolinite. Chem Geol 157:275–284

Merritt KA, Erich MS (2003) Influence of organic matter decomposition on soluble carbon and its copper binding capacity. J Environ Qual 32:2122–2131

Namjesnik-Dejanovic K, Maurice PA, Aiken GR, Cabaniss S, Chin YP, Pullin MJ (2000) Adsorption and fractionation of a muck fulvic acid on kaolinite and goethite at pH 3.7, 6 and 8. Soil Sci 165:545–559

Ohno T, Crannell BS (1996) Green and animal manure-derived dissolved organic matter effects on phosphorus sorption. J Environ Qual 25:1137–1143

Ohno T, Cronan CS (1997) Comparative effects of ionic and nonionic-resin purification treatments on the chemistry of dissolved organic matter. Int J Environ Anal Chem 66:119–136

Ohno T, Zibiliske LM (1991) Determinations of low concentrations of phosphorus in soil extracts using malachite green. Soil Sci Soc Am J 55:892–895

Ohno T, Chorover J, Omoike A, Hunt J (2007) Molecular weight and humification index as a predictor of plant- and animal manure-derived dissolved organic matter to goethite. Eur J Soil Sci 58:125–132

Othieno CO (1973) The effect of organic mulches on yields and phosphorus utilization by plants in acid soils. Plant Soil 38:17–32

Ritchie JD, Perdue EM (2003) Proton-binding study of standard and reference fulvic acids, humic acids, and natural organic matter. Geochim Cosmochim Acta 67:85–96

Schwertmann U, Cornell P (1991) Iron oxides in the laboratory: preparation and characterization. VCH, New York

Shin H-S, Monsallier JM, Choppin GR (1999) Spectroscopic and chemical characterization of molecular size fractionated humic acid. Talanta 50:641–650

Sibanda HM, Young SD (1986) Competitive adsorption of humus acids and phosphate on goethite, gibbsite and two tropical soils. J Soil Sci 37:197–204

Sims JT, Simard RR, Joern BC (1998) Phosphorus loss in agricultural drainage: historical perspective and current research. J Environ Qual 27:277–293

Sposito G (1989) The chemistry of soils. Oxford University Press, New York

Stevenson FJ (1994) Humus chemistry: genesis, composition, reactions. Wiley, New York

Strom L, Owen AG, Godbold DL, Jones DL (2002) Organic acid mediated P mobilization in the rhizosphere and uptake by maize roots. Soil Biol Biochem 34:703–710

Tombacz E, Libor Z, Illes E, Majzik A, Klumpp E (2004) The role of reactive surface sites and complexation of clay mineral and iron oxide particles. Org Geochem 35:257–267

Violante A, Gianfreda L (1993) Competition in adsorption between phosphate and oxalate on an aluminum hydroxide montmorillonite complex. Soil Sci Soc Am J 57:1235–1241

Wang LL, Chin, Y-P, Traina SJ (1997) Adsorption of (poly)-maleic acid and an aquatic fulvic acid by goethite. Geochim Cosmochim Acta 61:5313–5324

Zhou LX, Wong JWC (2000) Microbial decomposition of dissolved organic matter and its control during a sorption experiment. J Environ Qual 29:1852–1856

Zhou Q, Cabaniss SE, Maurice PA (2000) Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances. Water Res 34:3505–3514