

# Adsorption of Dissolved Organic and Inorganic Phosphorus in Soils of a Weathering Chronosequence

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## ABSTRACT

Leaching of dissolved organic matter (DOM) and associated nutrients can be a significant loss from developing ecosystems. We studied how the adsorption of dissolved organic P (DOP) and  $\text{PO}_4$  changes during the development of young andesitic soils and determined which soil characteristics are responsible for these changes. We sampled 77, 255, 616, and about 1200+ yr-old andesitic soils at the 0- to 10-, 30- to 40-, and 140- to 150-cm soil depths and performed adsorption isotherm analyses that were described using a modified Langmuir (for DOP) or linear equation (for  $\text{PO}_4$ ). We also sampled soil solution at the 10-, 20-, 40-, and 150-cm soil depths during the main snow melt period in 2001 and 2002 and analyzed it for DOP and  $\text{PO}_4$ . The ability of the soils to adsorb DOP and  $\text{PO}_4$  increased with soil age. Stepwise multiple regression analyses between the adsorption capacity for DOP, or the slope of the adsorption isotherm for  $\text{PO}_4$ , and several soil parameters showed that allophane concentrations control the adsorption of DOP and  $\text{PO}_4$  in these soils. Tests of preferential adsorption of DOP vs.  $\text{PO}_4$  and DOC vs. DOP showed that the adsorption strength increased in the following order:  $\text{DOC} < \text{DOP} < \text{PO}_4$ . The preferential adsorption of  $\text{PO}_4$  vs. DOP and DOP vs. DOC increased significantly with increasing soil development, whereas the soil depth did not have a consistent and significant effect. Significant correlations between the null-point adsorption of DOP or  $\text{PO}_4$  and field soil solution concentrations indicated that the results obtained in laboratory experiments were applicable to field conditions. Consequently, the tendency of DOP and  $\text{PO}_4$  to leach from these andesitic soils decreases as soils and ecosystem develop.

**D**ISSOLVED ORGANIC MATTER plays an important role in soil development through the processes of illuviation and eluviation (Duchaufour, 1982). Movement of elements in DOM may conceivably be important in depositing nutrient elements in pores that are inaccessible to bacteria or into adsorbed phases protected by complexation to metals. Elements in DOM may also be lost from the rooting zone through leaching (Hedin et al., 1995; Seely et al., 1998; Qualls et al., 2002). Leaching of DOP might play a role in the trends in the stocks of P present in soil that have been observed during soil development (Walker and Syers, 1976). However, until now, the emphasis on cycling and leaching of nutrients has largely been focused on inorganic nutrients.

Inorganic  $\text{PO}_4$  anions are known to be strongly adsorbed by amorphous oxyhydroxides and aluminosilicates, which typically increase in concentration during soil development (Egawa, 1984; Schwertmann and Tay-

lor, 1989; Wada, 1989). However, little is known about the adsorption characteristics of DOP. Only one study has examined adsorption isotherms of DOP in natural DOM for soils. Kaiser (2001) compared the adsorption characteristics of DOP to those of DOC and found that the overall retention of DOP was smaller than that of DOC. Qualls and Haines (1991) studied the DOC/DOP ratios in soil solution in soil profiles of the Appalachian Mountains. They found that the DOC/DOP ratio decreased with increasing soil depth, concluding that DOC is preferentially adsorbed from the soil solution. However, no study has compared adsorption isotherms of natural DOP and  $\text{PO}_4$ .

Other authors have studied the differences in adsorption characteristics of specific dissolved organic and inorganic P compounds. Anderson et al. (1974) found that inositol hexaphosphate, with multiple negatively charged  $\text{PO}_4$  ester groups, was adsorbed more strongly than inorganic orthophosphate in acid soils. Additionally, organic P depressed the adsorption of inorganic P, whereas inorganic P did not depress the adsorption of organic P. The stronger adsorption of organic than inorganic P and the depression of inorganic P adsorption were more pronounced at pH 3 than at pH 6. Frossard et al. (1989), found that in forested Boralf soils, the mobility of various P compounds increased in the following order: adenosine triphosphate < orthophosphate anions < choline phosphate.

The contrasting results concerning the adsorption strength of DOP compounds might be due to different numbers of  $\text{PO}_4$ -ester groups in the organic molecule. Little is known about the structure of natural DOP. Only one study has been published on  $^{31}\text{P}$  NMR of DOP, in which the DOP was concentrated from seawater, and  $^{31}\text{P}$  NMR gives limited information on whether the functional groups are monoesters, diesters, or phosphonates (Kolowitz et al., 2001). Consequently, studies on the adsorption characteristics of model compounds cannot be easily extended to natural DOM.

In an earlier study, we showed that adsorption of dissolved organic C (DOC) and N (DON) in an andesitic soil chronosequence in northern California increased during soil development, mainly due to increases in allophane concentrations (Lilienfein et al., 2003, 2004). In this paper we focus on P and extend our earlier analysis to DOP and  $\text{PO}_4$ . Our objectives were to determine: (i) how the adsorption of DOP and  $\text{PO}_4$  of these young andesitic soils changes with soil development, (ii) which soil characteristics control the adsorption of DOP and  $\text{PO}_4$  in these soils, (iii) if there are any differences in

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**Abbreviations:** DOC, dissolved organic C; DOM, dissolved organic matter; DON, dissolved organic N; DOP, dissolved organic P; SOC, soil organic C.

the adsorption characteristics of DOP vs.  $\text{PO}_4$  or DOC vs. DOP, and (iv) whether adsorption isotherm parameters correlate with concentrations of DOP and  $\text{PO}_4$  in soil solution collected from the field.

## MATERIALS AND METHODS

### Study Sites

The study was performed at the Mt. Shasta Mudflow Research Natural Area in northern California, about 6 km north-east of McCloud, CA. The soils in the area were formed on cold, volcanic mudflows of coarse, sandy andesitic material, which originated from the south slope of Mt. Shasta. Topography and climate are similar across the chronosequence. As all mudflows originate from one common canyon on the south side of the mountain, parent material of all flows is similar in chemical composition (Sollins et al., 1983). Because the parent material originates from below a glacier (approximately 3000 m above sea level), the material in mudflows was chemically unweathered. Therefore, chemical weathering and soil formation started largely after the material had been deposited.

The parent material of all flows consists of ground rocks of hornblende-andesite composition (Dickson and Crocker, 1953). In 2001, the soils of the four different mudflows were 77, 255, 616, and 1200+ yr old (Lilienfein et al., 2003). The age of the oldest flow is not exactly known and was arbitrarily designated as 1200+ yr (Dickson and Crocker, 1953). Soils of the 77- and 255-yr-old mudflows were classified as Vitrandic Haploxerepts, and those of the 616- and 1200+ yr-old mudflows were Humic Haploxerands (Peter Van Susteren, U.S. Forest Service, McCloud Ranger District, personal communication, 2003). For the young soils the subgroup name "Vitrandic" was based on the content of volcanic glass (Dickson and Crocker, 1954).

On each of the flows we established five to six plots, which were randomly selected along transects. Areas of obvious disturbance, for example by fire or bark beetles (*Ips pin* or *Dendroctonus* spp.), were rejected. More detailed information concerning the study sites is given in Dickson and Crocker (1953) and Lilienfein et al. (2003).

### Equipment and Sampling

To compare field soil solution concentrations with the results of laboratory experiments, we installed three acid washed ceramic suction cup lysimeters (Soilmoisture Equipment Corp., Santa Barbara, CA) in each of the plots. The ceramic cups were model B02M2, made from a high fire silica body, with maximum pore size of 1.3  $\mu\text{m}$ . Preliminary tests using forest floor solution indicated no significant adsorption of DOC or  $\text{PO}_4$ . In each plot, one lysimeter was installed at the lower boundary of the A horizon (at 10-cm soil depth in the 77- and 255-yr-old soils, at 16-cm soil depth in the 616-yr-old soil, and at 20-cm soil depth in the 1200+ yr-old soil). A second lysimeter was installed at the lower boundary of the B horizon at the 40-cm soil depth, and the deepest suction cup lysimeter was installed at a 150-cm soil depth to represent the bottom of the rooting zone. Soil solution was sampled for five consecutive days per month during the time when the main water fluxes occurred in the soil due to snowmelt (February to May) in 2001 and 2002, for a total of eight soil solution events (Lilienfein et al., 2004). Additionally we took solid soil samples from 0- to 10-, 30- to 40-, and 140- to 150-cm soil depth. Because organic matter content tended to be more variable at the 0- to 10-cm soil depth (Lilienfein et al., 2004), three

samples were taken per plot at the 0- to 10-cm depth and then composited for analyses.

### Chemical Analyses

Soil samples for chemical analyses were dried at 40°C and passed through a 2-mm sieve for homogenization. Organic C content was determined on ground subsamples by dry combustion with a PerkinElmer 2400 CHN analyzer (Perkin Elmer, Norwalk, CT). Soil pH was measured in water with a soil/solution ratio of 1:1 and was reported as the arithmetic average (Baker et al., 1981).

Oxalate soluble Al ( $\text{Al}_o$ ), Fe ( $\text{Fe}_o$ ), and Si ( $\text{Si}_o$ ) were determined with the method of Schwertmann (1964). Total pedogenic Fe oxides ( $\text{Fe}_d$ ) were extracted with dithionite-citrate-bicarbonate (DCB, Holmgren, 1967), and organically bound Al ( $\text{Al}_p$ ) was extracted with pyrophosphate (McKeague, 1967). Metal concentrations in the extracts were determined using a PerkinElmer Plasma 1000 inductively coupled plasma emission spectrometer (Perkin Elmer, Norwalk, C.T.).

Concentrations of crystalline Fe oxides were calculated as follows:

$$\text{Fe}_{\text{cryst}} = \text{Fe}_d - \text{Fe}_o \quad [1]$$

Allophane concentrations, in terms of  $\text{g kg}^{-1}$  soil, can be calculated by as follows (Dahlgren, 1994):

$$\text{Allophane} = f \times \text{Si}_o \quad [2]$$

The factor  $f$  depends on the Si/Al molar ratio and distinguishes Si-rich allophane (Al/Si, 1:1) and either Al-rich allophane or imogolite (Al/Si, 2:1). The factor  $f$  can be determined as follows:

$$f = (\text{Al}_o - \text{Al}_p)/\text{Si}_o \quad [3]$$

For an Al/Si ratio of 1:1, the factor is 5, and for a ratio of 2:1, the factor is 7. We found an Al/Si ratio of 2:1, which suggests that we were not overestimating allophane content due to dissolution of Si from other soil materials (Lilienfein et al., 2003). In this paper we refer to allophane concentrations calculated from the dissolution analysis, but it should be understood that it could also include imogolite.

Specific surface area was determined by the ethylene glycol monoethyl ether (EGME) method according to Carter et al. (1986). This method requires drying of the soil, which could conceivably introduce artifacts.

Soil solution was analyzed for DOC with a TOC analyzer (TOC 5050 A, Shimadzu Corp. Columbia, MD), and for orthophosphate with the molybdate blue method (Murphy and Riley, 1962) using a spectrophotometer (Shimadzu UV-1201, Shimadzu Corp.). Total P was measured after digestion with persulfate (Wetzel and Likens, 1991) as orthophosphate. Concentrations of DOP were calculated as the difference between total P and orthophosphate.

### Sorption Experiments

Fresh field-moist soil taken from 0- to 10-, 30- to 40-, and 140- to 150-cm soil depths was used for the adsorption experiment. Forest floor materials from the youngest and the oldest mudflows, were used to make up stock DOM solution. Forest floor material was placed on netting and sprayed periodically with deionized water. The solutions that had percolated through from the forest floor material from both mudflows were mixed with a 1:1 ratio. The solution was filtered through 0.45- $\mu\text{m}$  cellulose acetate membrane filters (GN-6, Pall Corp., Ann Arbor, MI) to remove particulate organic matter from the solution. The stock solution contained 292  $\mu\text{g}$  DOP and

696  $\mu\text{g PO}_4$ . For the sorption experiment, initial solutions containing 0, 8, 18, 41, 292  $\mu\text{g DOP L}^{-1}$  and 4, 19, 51, 103, 696  $\mu\text{g PO}_4 \text{ L}^{-1}$ , respectively, were prepared by diluting the stock DOM solution with a solution containing similar inorganic ion composition as the stock solution (pH 5.2, 0.45 mmol  $\text{L}^{-1}$  for K, 0.72 mmol  $\text{L}^{-1}$  for Ca, 0.07 mmol  $\text{L}^{-1}$  for Mg, 0.13 mmol  $\text{L}^{-1}$  for Na, 0.12 mmol  $\text{L}^{-1}$  for  $\text{SO}_4^{2-}$ , and 1.86 mmol  $\text{L}^{-1}$  for  $\text{Cl}^-$ , for a total ionic strength of 2.16 mmol  $\text{L}^{-1}$ ). The concentration range was chosen to represent the concentrations of the forest floor leachate in the field.

For the sorption experiments, 30 mL of each of the five initial solutions were added to 3 g of each of the three soil depths in 21 plots and shaken for 24 h in an end-over-end shaker with one rpm. The low revolution rate was chosen to avoid a breakdown of the fragile soil structure of wet allophanic soil (Parfitt, 1990). The suspensions were centrifuged and the supernatants were then filtered through 0.45- $\mu\text{m}$  filters and analyzed for  $\text{PO}_4$  and total P as above.

### Sorption Isotherms

Sorption of DOP and  $\text{PO}_4$  was analyzed by using sorption isotherms in which the equilibrium (i.e., concentration after 24 h) DOP or  $\text{PO}_4$  concentration in solution is plotted against the mass of DOP or  $\text{PO}_4$  adsorbed per gram of dry soil. Adsorption isotherms data of DOP were fit to a modified Langmuir curve rather than a straight line because the fit to the Langmuir curve was better than to a straight line. Because we were working with soil samples that contained native adsorbed organic matter, we added a parameter  $a$  in the Langmuir equation, which allows for a nonzero  $y$ -intercept (Lilienfein et al., 2004).

$$x/m = [(KCb)/(1 + KC)] - a \quad [4]$$

In this equation  $x/m$  is the mass of adsorbed DOP per mass of soil,  $C$  is the DOP equilibrium concentration,  $K$  is a constant related to the binding strength,  $a$  is the  $y$ -intercept which describes the DOM released at low initial concentrations of added DOM, and  $b$  is the asymptote of the Langmuir curve plus parameter  $a$ . The asymptote of the Langmuir curve will be referred to as the adsorption capacity. Because of the inclusion of constant  $a$ , we could not transform the equation into the linear form as is commonly done (Bohn et al., 1985) to solve the Langmuir equation. Therefore, we used nonlinear regression to estimate the parameters  $K$ ,  $b$ , and  $a$  using a nonlinear curve-fitting program (Pezzullo, 2002).

The  $\text{PO}_4$  adsorption isotherms were fit to a straight line (using linear regression) because the fit was rather better than to the Langmuir curve.

We also determined the null-point concentration, which is defined as the DOP or  $\text{PO}_4$  equilibrium concentration at which there is no net adsorption or release of DOP or  $\text{PO}_4$ , calculated as the  $x$ -intercept of either the Langmuir or the linear equation.

### Preferential Adsorption of $\text{PO}_4$ vs. DOP and DOC vs. DOP

To test whether the degree of adsorption of DOP is different from that of DOC and  $\text{PO}_4$ , we compared the  $\text{PO}_4/\text{DOP}$  and the  $\text{DOC}/\text{DOP}$  ratios in the solution before and after the batch adsorption experiment. A difference in the ratio before and after adsorption was used to indicate a preferential adsorption of one or the other form. For example, a higher  $\text{DOC}/\text{DOP}$  ratio in the equilibrium solution than in the initial solution would indicate that more DOP is removed from the solution and therefore that it is preferentially adsorbed over DOC.

### Statistical Analyses

A multiple comparison of means of soil organic C (SOC), allophane,  $\text{Fe}_o$ , crystalline Fe concentrations, pH, and specific surface area in soils of different ages, within each soil depth, were done using Tukey's honest significant difference (HSD) test. A multiple comparison of means was also used to study the influence of soil age and depth on the  $\text{PO}_4/\text{DOP}$  and the  $\text{DOC}/\text{DOP}$  ratio in the equilibrium solution for the highest level of addition of  $\text{PO}_4$  and DOP. All multiple comparisons of means were performed on log-transformed data (except for pH) to ensure equal variances. To compare the  $\text{PO}_4/\text{DOP}$  and the  $\text{DOC}/\text{DOP}$  ratio of the DOM solution before and after the batch experiment, a two-tailed single sample  $t$  test was performed. Ratios were log transformed to normalize the data. Linear regression analyses were used (i) to fit lines to the  $\text{PO}_4$  adsorption isotherms, (ii) to test the influence of soil age on the adsorption parameters of DOP and  $\text{PO}_4$ , and (iii) to test the relationship between the null-point concentration of DOP or  $\text{PO}_4$  of the soils and the DOP or  $\text{PO}_4$  soil solution concentrations. To determine the soil characteristics that explain the variation in the adsorption of DOP and  $\text{PO}_4$  in these soils, we performed simple and stepwise multiple regression analyses between parameters of the adsorption curves (as the dependent variables) and various soil characteristics as the independent variables. For all statistical analyses, significance was set to  $P \leq 0.05$  and statistical analyses were performed with SPSS 11.5 (SPSS, Inc., 2000).

## RESULTS AND DISCUSSION

### Influence of Soil Weathering on Adsorption Characteristics of DOP and $\text{PO}_4$

Concentrations of organic C and N, allophane, ferrihydrite, and the surface area increase with increasing soil age (Table 1). It should be noted that oxalate also extracts some Fe from magnetite and that about 34% of  $\text{Fe}_o$  in the youngest soil and <19% in the oldest soil could be due to magnetite (Dickson and Crocker, 1954; Rhoton et al., 1981). Crystalline Fe oxides are absent in the younger mudflows and in the subsoil of the older mudflows. Even in the A horizon of the older flows, crystalline Fe was <24% of total DCB extractable Fe (Lilienfein et al., 2003).

The modified Langmuir equation (Eq. [4]) effectively described the adsorption dynamics for DOP in all of the soils with very good fits to the data ( $r^2 = 0.91$  to 0.99, Fig. 1). All soil samples released DOP at low initial DOP concentrations and adsorbed DOP at higher initial DOP concentrations. All soil samples also showed a tendency to approach an adsorption maximum, as did DOC and DON adsorption in an earlier study on the same study sites (Lilienfein et al., 2004). The predicted adsorption maximum (asymptote of the Langmuir curve, Eq. [4]) can be interpreted as the adsorption capacity for DOP. Overall, adsorption capacity increased significantly with increasing soil age for all depths (Fig. 2a).

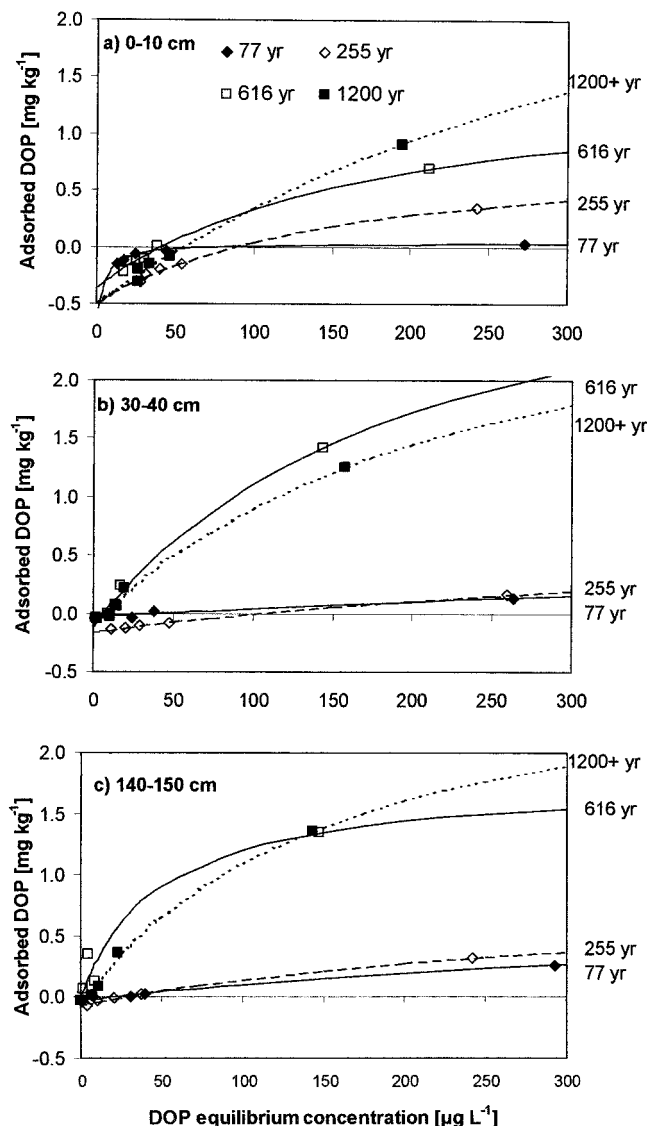
In contrast to DOP, the sorption dynamics of  $\text{PO}_4$  were best described by a linear regression, indicating that the  $\text{PO}_4$  concentrations used in this experiment did not approach the adsorption capacity of the soils (Fig. 3). All except two (the 140–150 cm of the 616 and 1200+

**Table 1.** Average concentrations ( $\pm$  standard deviations) of soil organic C (SOC), allophane, and ferrihydrite, crystalline Fe ( $\text{Fe}_{\text{cryst}}$ ), pH, and specific surface area (SSA) in the soils of the Mt. Shasta mudflow chronosequence (from Lilienfein et al., 2003).

Soil age	Soil depth	SOC	allophane	ferrihydrite	$\text{Fe}_{\text{cryst}}$	pH	SSA
yr	cm			$\text{g kg}^{-1}$			$\text{m}^2 \text{g}^{-1}$
77	0–10	$4.4 \pm 1.2\text{c}^\dagger$	$0.56 \pm 0.20$	$2.0 \pm 0.31\text{b}$	0	$4.7 \pm 0.3\text{b}$	$14 \pm 1.2\text{c}$
	30–40	$0.62 \pm 0.16\text{c}$	$0.95 \pm 0.25$	$1.8 \pm 0.12\text{b}$	0	$5.4 \pm 0.3\text{a}$	$13 \pm 2.1\text{b}$
	140–150	$0.60 \pm 0.16\text{b}$	$0.96 \pm 0.09$	$2.0 \pm 0.29\text{b}$	0	$5.8 \pm 0.3\text{a}$	$13 \pm 2.3\text{b}$
255	0–10	$19 \pm 5.9\text{b}$	$1.3 \pm 0.34$	$1.9 \pm 0.19\text{b}$	$0.59 \pm 0.34$	$5.6 \pm 0.2\text{a}$	$17 \pm 3.2\text{bc}$
	30–40	$3.6 \pm 3.9\text{b}$	$1.6 \pm 0.32$	$2.0 \pm 0.17\text{b}$	$0.27 \pm 0.15$	$5.5 \pm 0.5\text{a}$	$11 \pm 1.0\text{b}$
	140–150	$1.6 \pm 1.2\text{ab}$	$1.8 \pm 0.43$	$2.2 \pm 0.41\text{b}$	0	$5.4 \pm 0.2\text{a}$	$13 \pm 2.9\text{b}$
616	0–10	$49 \pm 22\text{a}$	$29 \pm 8.4$	$3.1 \pm 0.22\text{a}$	$0.66 \pm 0.21$	$5.3 \pm 0.3\text{a}$	$26 \pm 7.6\text{a}$
	30–40	$10 \pm 3.1\text{a}$	$50 \pm 15$	$3.8 \pm 0.37\text{a}$	$0.26 \pm 0.39$	$5.8 \pm 0.2\text{a}$	$25 \pm 4.6\text{a}$
	140–150	$3.0 \pm 2.5\text{a}$	$29 \pm 18$	$4.0 \pm 0.95\text{a}$	0	$5.8 \pm 0.2\text{a}$	$27 \pm 13\text{a}$
–1200+	0–10	$45 \pm 14\text{a}$	$21 \pm 7.8$	$3.1 \pm 0.63\text{a}$	$0.61 \pm 0.17$	$5.4 \pm 0.3\text{a}$	$25 \pm 3.7\text{a}$
	30–40	$16 \pm 7.0\text{a}$	$47 \pm 13$	$4.2 \pm 0.58\text{a}$	$0.35 \pm 0.35$	$5.7 \pm 0.2\text{a}$	$23 \pm 5.0\text{a}$
	140–150	$3.7 \pm 1.7\text{a}$	$33 \pm 20$	$4.0 \pm 0.59\text{a}$	0	$5.8 \pm 0.2\text{a}$	$28 \pm 4.2\text{a}$

$^\dagger$  Means with different letters indicate significant differences using a multiple comparison of means (Tukey's HSD) across soils of different ages within a given soil depth.

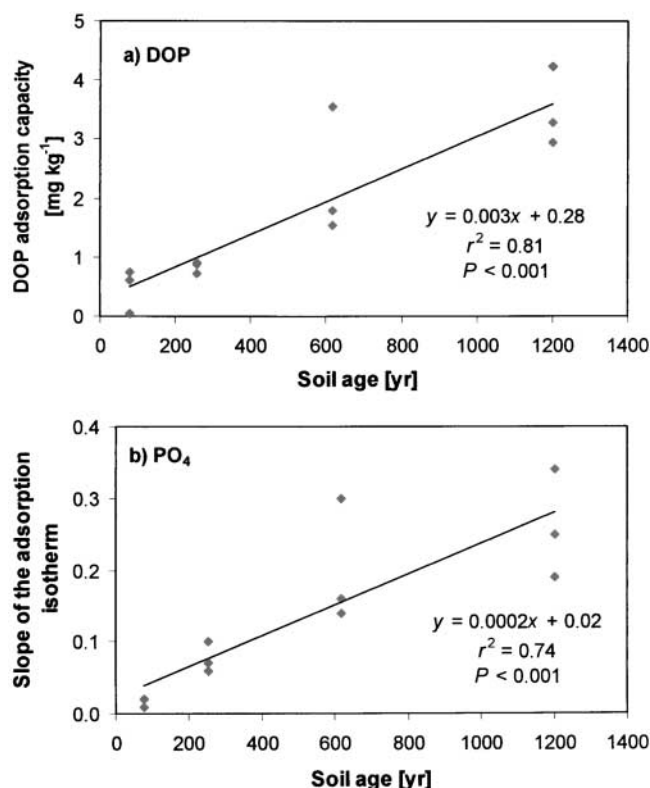
yr-old soils) of the soil samples released  $\text{PO}_4$  at low initial  $\text{PO}_4$  concentrations and adsorbed  $\text{PO}_4$  at higher initial  $\text{PO}_4$  concentrations. For all soil depths combined,



**Fig. 1.** Dissolved organic P (DOP) adsorption isotherms of Mt. Shasta mudflow soils at depths of (a) 0 to 10 cm, (b) 30 to 40 cm, and (c) 140 to 150 cm. Lines are fitted according to the Langmuir equation (Eq. [4]),  $r^2$  ranged from 0.91 to 0.99.

the increase of adsorption capacity with increasing soil age was highly significant (Fig. 2b).

To further investigate which soil characteristics control the adsorption of DOP and  $\text{PO}_4$  in these soils, we performed stepwise multiple regression analyses between the parameters of the adsorption isotherm (adsorption capacity for DOP, or the slope of the adsorption isotherm for  $\text{PO}_4$ ) and soil characteristics we thought might be controlling the adsorption of DOP and  $\text{PO}_4$  in these soils. The independent variables included in the regression analysis were: allophane, ferrihydrite, SOC concentrations, and specific surface area, as well as the following ratios: allophane/SOC concentration, ferrihydrite/SOC concentration, and specific surface area/SOC concentration. We included the ratios be-



**Fig. 2.** Regression analysis for (a) the adsorption capacity for DOP and the age of the soils and (b) the slope of the adsorption isotherm of  $\text{PO}_4$  and the age of the soils.

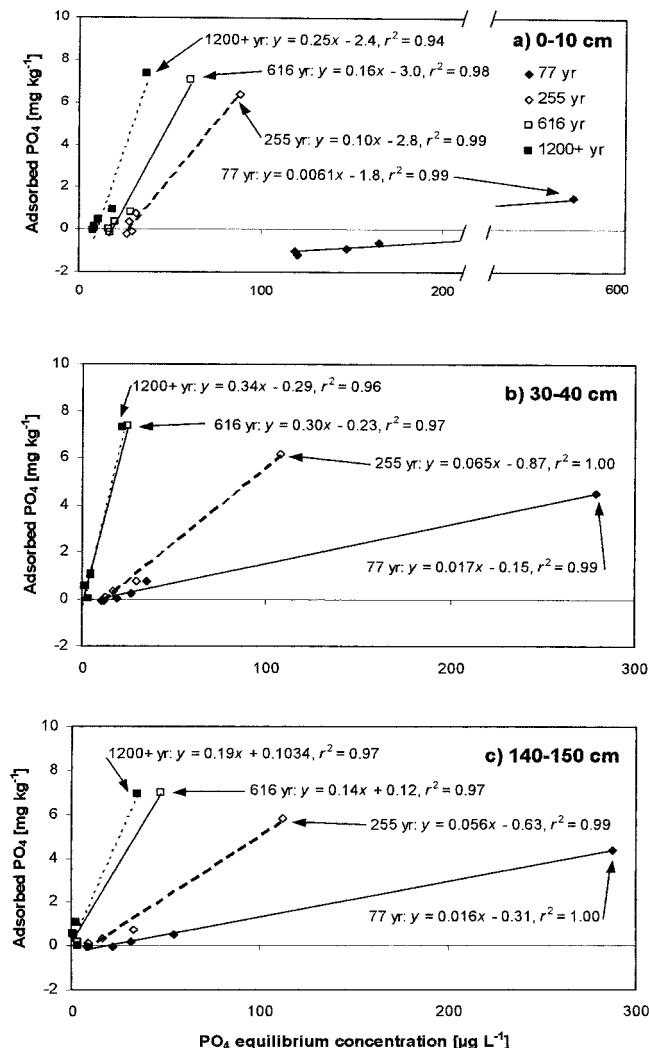


Fig. 3. Orthophosphate adsorption isotherms of Mt. Shasta mudflow soils at depths of (a) 0 to 10 cm, (b) 30 to 40 cm, and (c) 140 to 150 cm. Lines are linear regressions and are indicated on the figure.

cause we hypothesized that sorption of DOP might be inversely related to soil SOC concentration but directly related to allophane and ferrihydrite concentrations.

For both DOP and  $\text{PO}_4$ , the results of the stepwise multiple regression analysis showed a highly significant correlation between the parameters of the adsorption isotherm and the allophane concentration in the soil (Fig. 4). None of the other independent variables included in the stepwise multiple regression analysis significantly improved the coefficient of determination. Therefore, we conclude that the adsorption of DOP and  $\text{PO}_4$  in these soils is controlled predominantly by allophane in these young andesitic soils. This can be explained by the very high adsorption capacity of allophane for  $\text{PO}_4$  of 6.2 to 18.6 g P  $\text{kg}^{-1}$  allophane (Wada, 1989).

Although ferrihydrite was likely to play some role in adsorption in these soils, the failure to explain the increase of adsorption with soils age is due to two related factors: (i) the smaller increase in ferrihydrite concentrations with age compared with that of allophane, and (ii)

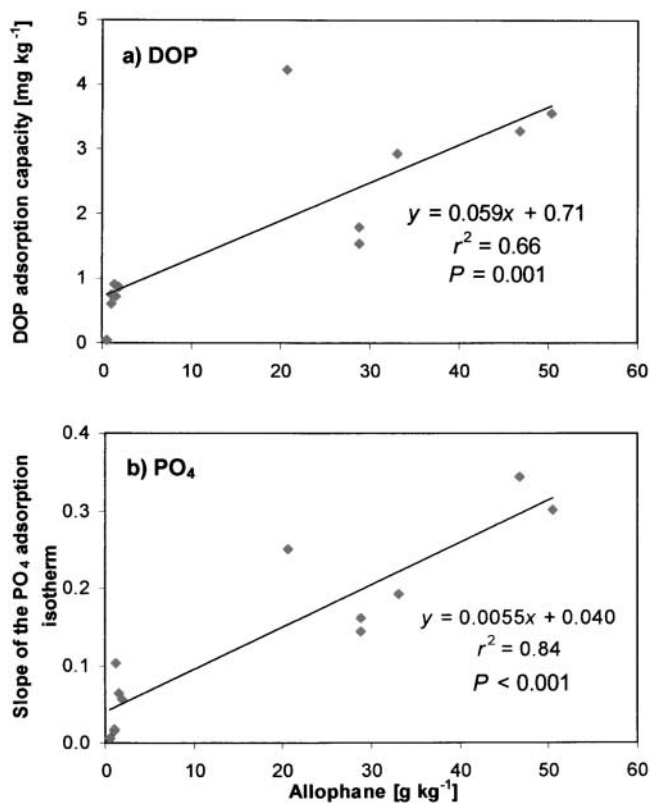


Fig. 4. Regression analysis between (a) the adsorption capacity for DOP and allophane concentrations and (b) the slope of the  $\text{PO}_4$  adsorption isotherms and allophane concentrations in the soils.

the much lower concentration of ferrihydrite compared to allophane in the older soils.

### Preferential Adsorption of $\text{PO}_4$ or DOP

To determine whether  $\text{PO}_4$  or DOP was preferentially adsorbed from solution, we compared the  $\text{PO}_4$ /DOP ratios of the equilibrium concentrations of the highest initial concentration for all three soil depths. All samples showed a net adsorption of  $\text{PO}_4$  and DOP from that solution (Fig. 1 and 3). The  $\text{PO}_4$ /DOP ratio of the initial solution was 2.4 (Fig. 5). A lower  $\text{PO}_4$ /DOP ratio in the equilibrium than in the initial solution would indicate that  $\text{PO}_4$  is preferentially adsorbed. For all except one (77-yr-old soil, 0–10 cm) of the soil samples, the  $\text{PO}_4$ /DOP ratio in the equilibrium solution was significantly lower than in the initial solution (Fig. 5), indicating preferential adsorption of  $\text{PO}_4$ . The initial solution contained more  $\text{PO}_4$  than DOP, whereas the equilibrium solution of all samples from the 255, 616, and 1200+-yr old soils contained more organic than inorganic P. A multiple comparison of means showed a significant influence of soil age on the  $\text{PO}_4$ /DOP ratio in the equilibrium solution (Fig. 5). The ratio significantly decreased with increasing soil age. This means that the adsorption of inorganic P increases more strong with soil age than the adsorption of organic P. The soil depth, however, did not consistently have a significant influence on the  $\text{PO}_4$ /DOP ratio in the equilibrium solution (Fig. 5).

Our results showing preferential adsorption of  $\text{PO}_4$

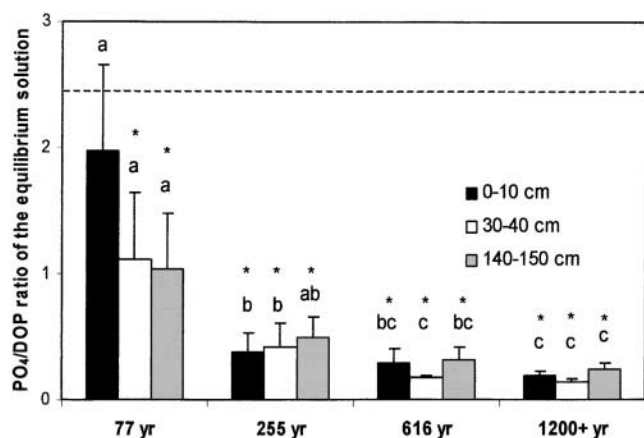


Fig. 5. Phosphate/DOP ratio in the equilibrium solution of the most concentrated initial solution ( $292 \mu\text{g DOP L}^{-1}$  and  $696 \mu\text{g PO}_4 \text{L}^{-1}$ ). The dashed line represents the  $\text{PO}_4/\text{DOP}$  ratio in the initial solution. Asterisk (\*) indicates a significant difference in the  $\text{PO}_4/\text{DOP}$  ratio in the equilibrium solution as compared with the initial solution ( $p \leq 0.05$ , two-tailed single sample paired  $t$  test); different letters indicate significant differences in the  $\text{PO}_4/\text{DOP}$  ratio among soils of different age and within one soil depth ( $P < 0.05$ , Tukey's HSD test).

over DOP might seem contrary to those of some experiments in which model organic P compounds were used. For example, Anderson et al. (1974) found stronger adsorption of inositol hexaphosphate, a compound with six phosphate ester groups, than inorganic P. Frossard et al. (1989) found either higher or lower adsorption depending on the organic P compound. Adenosine triphosphate was adsorbed more strongly than inorganic P, but choline phosphate was adsorbed less strongly than inorganic P. Adenosine triphosphate contains three P groups, and choline contains only one. Consequently, the strength with which a particular organic P compound is adsorbed seems to depend on the number of phosphate ester groups per unit of molecular size. In the case of DOP in natural DOM, the density of phosphate ester groups per molecule is unknown. The DOP/DOC ratio in soil solution can vary widely (Qualls and Haines, 1991), and this may also cause variation in the adsorption characteristics of DOP. Moreover, other functional groups, such as carboxyl groups, may determine the adsorption behavior of DOM (Qualls and Haines, 1991).

The preferential adsorption of  $\text{PO}_4$  over the organic forms may also be related to the reason we observed linear isotherms for  $\text{PO}_4$ . With increasing concentrations of  $\text{PO}_4$ , the high affinity of allophane surfaces for  $\text{PO}_4$  (Wada, 1989) may result in the displacement of other adsorbed species, while DOM molecules are unable to displace other adsorbed species and exhibit saturation of the adsorption isotherms.

### Preferential Adsorption of DOC or DOP

We also tested if there is any preferential adsorption of DOC vs. DOP. Therefore, we performed the same statistical analyses to compare DOC/DOP ratios as we did for  $\text{PO}_4$  and DOP. A higher DOC/DOP ratio in the equilibrium solution than in the initial solution would indicate that DOP was preferentially adsorbed. All sam-

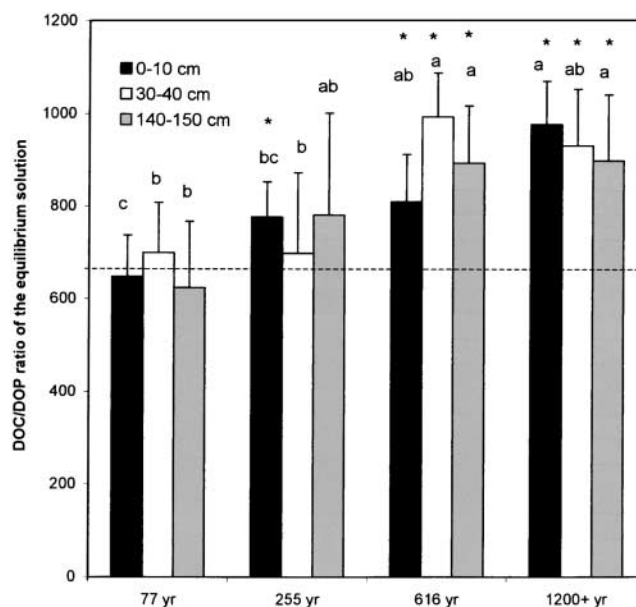


Fig. 6. The DOC/DOP ratio in the equilibrium solution of the most concentrated initial solution ( $200 \text{ mg DOC L}^{-1}$  and  $292 \mu\text{g DOP L}^{-1}$ ). The dashed line represents the DOC/DOP ratio in the initial solution. Asterisk (\*) indicates a significant difference in the  $\text{PO}_4/\text{DOP}$  ratio in the equilibrium solution as compared with the initial solution ( $p \leq 0.05$ , two-tailed single sample paired  $t$  test); different letters indicate significant differences in the  $\text{PO}_4/\text{DOP}$  ratio among soils of different age and within one soil depth ( $P < 0.05$ , Tukey's HSD test).

ples of the 77 and 255-yr old soils, except the 0- to 10-cm depth of the 255-yr old soil, showed no significant differences in the DOC/DOP ratio between the initial and equilibrium solutions (Fig. 6). However, all samples of the 616 and 1200+ yr-old soils showed a significantly higher DOC/DOP ratio in the equilibrium than in the initial solution, indicating a preferential adsorption of DOP vs. DOC. Thus, DOP was preferentially adsorbed in the older soils but not in the younger soils. A multiple comparison of means among soils of different ages, within each depth, showed that the ratio also significantly increased with increasing soil age (Fig. 6) indicating that the effect of preferential adsorption of DOP over DOC increases with the soil age. However there was no consistent trend in the DOC/DOP ratio with soil depth. The lack of a trend with the soil depth might mainly be explained by the fact that the allophane and ferrihydrite concentrations also show a much stronger trend with soil age than with soil depth.

These data indicated that DOC, DOP, and  $\text{PO}_4$  are adsorbed differently after a minimal period of soil development, and that these differences become more pronounced with the age and degree of pedogenesis of the soil. This is in contrast to the sorption behavior of DON for which we found no consistent difference in the adsorption strength compared with DOC with increasing soil age (Lilienfein et al., 2004). Consequently we can conclude that the adsorption strength increased in the following order:  $\text{DOC} = \text{DON} < \text{DOP} < \text{PO}_4$ .

**Table 2. Average PO<sub>4</sub> and DOP soil solution concentrations ( $\pm$  standard deviation) at the lower end of the A horizon (77 and 255 yr-old soil: 10-cm soil depth; 616: 16 cm, and 1200+ yr-old soil: 20 cm) B horizon (40-cm soil depth) and at 150-cm soil depth (C horizon) between February and May in 2001 and 2002.**

	Soil age, yr			
	77	255	616	1200+
	<b>DOP, <math>\mu\text{g L}^{-1}</math></b>			
A horizon	71 $\pm$ 60	32 $\pm$ 10	28 $\pm$ 9.4	15 $\pm$ 4.9
B horizon	29 $\pm$ 16	20 $\pm$ 5.1	27 $\pm$ 18	13 $\pm$ 7.5
C horizon	5.6 $\pm$ 2.8	5.7 $\pm$ 2.3	5.9 $\pm$ 3.5	3.0 $\pm$ 2.1
	<b>PO<sub>4</sub>, <math>\mu\text{g L}^{-1}</math></b>			
A horizon	187 $\pm$ 22	46 $\pm$ 19	18 $\pm$ 7.4	12 $\pm$ 9.3
B horizon	74 $\pm$ 48	27 $\pm$ 5.1	32 $\pm$ 27	9.2 $\pm$ 5.5
C horizon	18 $\pm$ 7.4	16 $\pm$ 7.0	10 $\pm$ 9.2	3.1 $\pm$ 1.7

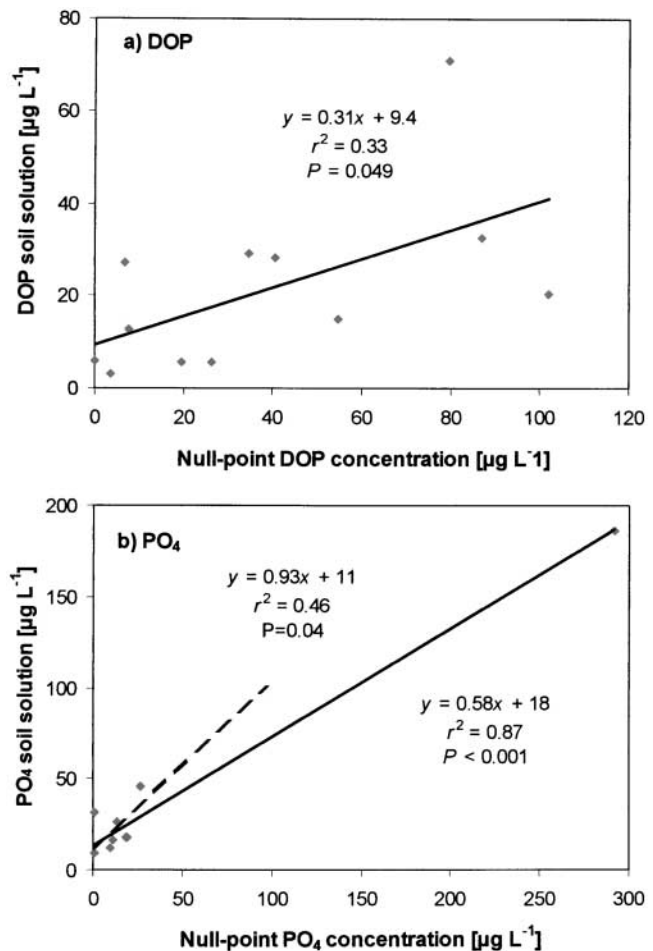
### Correlation with Soil Solution Concentrations

We tested whether the results of the adsorption experiments were correlated with soil solution concentrations during snowmelt in the field. Average DOP and PO<sub>4</sub> soil solution concentrations are presented in Table 2. The null-point concentration is the concentration for which the soil neither releases nor adsorbs PO<sub>4</sub> or DOP, respectively. If the soil solution is in equilibrium with the soil solid phase, the null-point concentration should be correlated to the soil solution concentration of the corresponding soil depths. Therefore, we performed regression analyses between the null-point concentrations of PO<sub>4</sub> or DOP at the 0- to 10-, 30- to 40-, and 140- to 150-cm soil depth and the measured PO<sub>4</sub> or DOP concentrations in the soil solution at 10-, 16- or 20-, 40-, and 150-cm soil depth, respectively.

We found that soil solution and null-point concentrations over all soil ages and soil depths were significantly correlated (Fig. 7). The regression for PO<sub>4</sub> was heavily influenced by one point with a very high null-point concentration (77 yr-old soil, 0–10 cm). The adsorption isotherm for this soil had a low slope and the null-point concentration is therefore less certain than for the other soil samples. When we excluded the 77 yr old soil data, the regression was still significant ( $r^2 = 0.46$ ,  $P = 0.04$ ).

### CONCLUSIONS

Adsorption of DOP and PO<sub>4</sub> increased with increasing soil age, and hence degree of development, mainly due to increased allophane concentrations. Although ferrihydrite was likely to play some role in adsorption in these soils, the increase in ferrihydrite concentrations with age, compared with that of allophane, was not high enough to explain the increase in adsorption of DOP and PO<sub>4</sub> with age. Despite the fact that the initial PO<sub>4</sub> concentrations in the adsorption experiments were 2.4 times higher than those of DOP, the adsorption isotherms of DOP were asymptotic and thus could be best described by Langmuir isotherms. However, the adsorption of inorganic PO<sub>4</sub> was linear, indicating a much higher adsorption capacity for PO<sub>4</sub> than for DOP. Significant regression analyses between the null-point concentrations and soil solution concentrations for DOP and PO<sub>4</sub> indicated that (i) the results obtained in laboratory



**Fig. 7. Regression analysis between the soil solution concentration of (a) DOP and (b) PO<sub>4</sub> at 10-, 16-, or 20-, 40-, and 150-cm soil depth and the null-point DOP and PO<sub>4</sub> concentration in soil samples from 0- to 10-, 30- to 40-, and 140- to 150-cm soil depth. The dashed line in 7(b) shows the regression analysis, excluding the influential point (77 yr-old soil, 0–10 cm).**

adsorption experiments were relevant to in situ field conditions, and (ii) the factors controlling adsorption under experimental conditions (i.e., soil age and allophane concentrations) were also important in controlling concentrations in soil solution.

A comparison of the ratios of PO<sub>4</sub>/DOP and DOC/DOP in the initial and equilibrium solution indicated that the adsorption strength increased in the following order DOC < DOP < PO<sub>4</sub>, and these differences in adsorption increased with soil age.

Because adsorption of DOP, DOC, and PO<sub>4</sub> increased with soil age the tendency to leach from the root zone is also likely to decrease with soil age. The finding supported this conclusion that concentrations of DOP, DOC, and PO<sub>4</sub> in soil solution at 150 cm were higher in the younger soils (Table 2, and Lilienfein et al., 2004). In addition, the finding that PO<sub>4</sub> was more strongly adsorbed than DOP and DOC also suggests that DOP and DOC are more susceptible to leaching. The factors controlling the leaching of organic and inorganic nutrients have been compared and classified as biological,

geochemical, and hydrological (Qualls, 2000). Phosphate, and perhaps some small organic P compounds may be directly taken up by roots and microbial cells. Dissolved organic P may also be biologically mineralized. Geochemical factors include adsorption. Hydrological factors include the water flux through the soil and four factors that may prevent soil solution from coming into equilibrium with soil surfaces (Qualls, 2000). Solution may fail to reach equilibrium due to lack of time to equilibrate with soil surfaces. Diffusion through particles may limit the time to reach equilibrium. Preferential flow may short circuit exposure of the entire soil surface (e.g., Akhtar, 2003). On a larger scale, flow paths through a watershed may bypass the most strongly adsorbing horizons, for example, surface flow, lateral flow, and throughfall on stream channels. However, in our study the concentrations of DOP, PO<sub>4</sub>, and DOC, at the 150-cm depths in general corresponded to the relative degree of adsorption.

Like many volcanic soils, the soils of the chronosequence underwent rapid weathering (Lilienfein et al., 2003) and increased in adsorption capacity in a relatively short-time period. However, many soils that weather far more slowly, characteristically increase in the adsorption capacity for PO<sub>4</sub> due to formation of pedogenic oxides, clays, and short-range order aluminosilicates (Jenny, 1980). In one dolomitic pedogenic sequence, increases in adsorption strength for PO<sub>4</sub> occurred largely because of concentration of Fe and Al as Ca and Mg leached from the soil (Carreira et al., 1997). Such increases in adsorption strength during pedogenesis are not likely universal however, since extreme podzolization (e.g., Walker et al., 1981) or pedogenesis under hydric conditions may result in decreasing adsorption capacity. In addition, increases in clay content, lowering hydraulic conductivity, and development of blocky structure may increase the occurrence of preferential flow (Aktar et al., 2003) during pedogenesis. The relationships of changing adsorption capacity during soil and ecosystem development have been widely appreciated in the case of PO<sub>4</sub> but are also very important in controlling leaching of DOP and DON.

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