

# Adsorption of Dissolved Organic Carbon and Nitrogen in Soils of a Weathering Chronosequence

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## ABSTRACT

Leaching of dissolved organic matter (DOM) and the associated nutrient elements can be a significant form of loss from developing ecosystems. We studied how the adsorption of dissolved organic C (DOC) and N (DON) changes during soil development and determined which soil characteristics control adsorption. We sampled 77, 255, 616, and about 1200+ yr-old andesitic soils at five depths and did adsorption isotherm experiments fit to a modified Langmuir equation. We measured DOC and DON in soil solution at the 10- to 20-, 40-, and 150-cm soil depths during the snowmelt period to compare with adsorption experiments. Ability of the soils to adsorb DOM increased with soil age. Regression analyses were performed between adsorption capacity or the null point concentration of either DOC or DON and the independent variables soil organic C (SOC), N, allophane, oxalate extractable Fe, crystalline Fe, and specific surface area. The best relationships were found between adsorption capacity and the allophane/SOC ratio ( $r^2 = 0.88$ ), and between the null point concentration of DOC or DON and the SOC/allophane ratio (DOC:  $r^2 = 0.85$ ; DON:  $r^2 = 0.77$ ). Stepwise multiple regression indicated that oxalate-extractable Fe and specific surface area contributed only small increases in the multiple  $R^2$ . High correlations between the null-point adsorption of DOC or DON and the DOC ( $r^2 = 0.92$ ) or DON ( $r^2 = 0.86$ ) field soil solution concentrations indicated that results obtained in laboratory experiments were applicable to field conditions. The cause of the increased ability of the soils to adsorb and retain DOM during soil development appears to be an increase in allophane concentrations.

**D**ISSOLVED ORGANIC MATTER PLAYS an important role in soil development and influences the potential for leaching of nutrient elements (Duchaufour, 1982). Dissolved organic N is the dominant form of dissolved N lost from many minimally disturbed forest ecosystems (Perakis and Hedin, 2002; Qualls et al., 2002). In stream water from 100 unpolluted watersheds in Chile and Argentina, DON comprised on average 80% of the total N. In streams draining 19 minimally disturbed watersheds in the USA, with atmospheric N deposition rates ranging from 1.0 to 7.5 kg ha<sup>-1</sup> yr<sup>-1</sup>, DON comprised 47% of total N and 63% of total dissolved N (Lewis, 2002). In some areas of high atmospheric N deposition, nitrate dominates the total dissolved N in stream water (Perakis and Hedin, 2002; Lewis, 2002) or water draining from the forest floor (Michalzik and Matzner, 1999), but DON can still be the dominant form (59%) in some watersheds with high N deposition (Campbell et al., 1999).

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Adsorption of DOM by soil has been implicated as a very important factor in controlling the loss of DOM from ecosystems in stream water (McDowell and Wood, 1984; Nelson et al., 1993; Qualls et al., 2002). Several authors have found positive correlations between parameters derived from DOC adsorption experiments and soil characteristics such as clay content, oxalate extractable Al and Fe, dithionite-citrate-bicarbonate (DCB) extractable Fe, and surface area (Donald et al., 1993; Moore et al., 1992; Nelson et al., 1993). Few studies exist, however, on the adsorption of DON (Kaiser and Zech, 2000b) despite N being the limiting nutrient in most terrestrial ecosystems (Schlesinger, 1997).

While several authors have studied the adsorption of DOC to ferrihydrite and aluminum hydroxides, much less is known about the adsorption of DOC to allophane, an aluminosilicate. Allophanic soils are known to accumulate organic matter rapidly and this has been attributed to their large surface area and positive surface charge (Wada, 1989; Parfitt, 1990). The short-range-order aluminosilicates, allophane, and imogolite strongly adsorb DOC (Parfitt et al., 1977; Yuan et al., 2000). Dahlgren and Marrett (1991) attributed the strong adsorption of DOC in the Bs horizon of a volcanic Spodosol to high concentrations of ferrihydrite and imogolite. Dahlgren et al. (1991) also found that most DOC was removed from solution in the A horizon of a nonallophanic Andisol in Japan. The mechanism of adsorption of organic matter to allophane surfaces is probably by ligand exchange.

Carbon and N cycles change during ecosystem development (Dickson and Crocker, 1953; Sollins et al., 1983). Soils of the Mt. Shasta soil weathering chronosequence were aged at 77, 255, 616, and 1200+ yr in 2001 with C and N accretion rates increasing linearly with age by 121 kg C ha<sup>-1</sup> yr<sup>-1</sup> and 4.5 kg N ha<sup>-1</sup> yr<sup>-1</sup>, respectively over the first 616 yr (Lilienfein et al., 2003). Concentrations of allophane and ferrihydrite as well as SSA, also increased with soil age. As we have discussed, there are many factors that influence adsorption of DOM in soils, and these factors tend to change during soil development. Consequently, we hypothesized that adsorption characteristics would differ between the soils of our chronosequence.

The aim of this work was to determine: (i) how the adsorption of DOC and DON in andesitic soils changes with soil development, (ii) which soil characteristics control the adsorption of DOM in these soils, (iii) if there are any differences in the adsorption characteristic of

**Abbreviations:** DOC, dissolved organic carbon; DOC<sub>np</sub>, null-point DOC concentration; DOM, dissolved organic matter; DON, dissolved organic nitrogen; DON<sub>np</sub>, null-point DON concentration; Fe<sub>o</sub>, oxalate extractable iron; IM, initial mass; SOC, soil organic C; SSA, specific surface area; TN, total nitrogen.

DOC vs. DON, and (iv) the correlation between adsorption isotherm parameters to concentrations in soil solution collected from the field.

## MATERIALS AND METHODS

### Study Sites

The study was performed in the Mount Shasta Mudflow Research Natural Area, about 10 km northeast of McCloud in northern California. 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. Consequently, chemical weathering and soil formation started largely after the material had been deposited.

The average annual precipitation in the last 50 yr was about 1300 mm with 80% occurring November to March, mainly as snow. The average annual temperature during the last 50 yr was 9.9°C, varying between 1.4°C in January and 20°C in July.

The parent material of all flows consists of ground rocks of hornblende-andesite composition (Dickson and Crocker, 1953). The soils of the two younger mudflows, which were 77 and 255 yr old in the Year 2001, were classified as Vitrandic Haploxerepts. The soils of the two older mudflows (616 and 1200+ yr old) were classified as Humic Haploxerands (Peter Van Susteren, U.S. Forest Service, McCloud Ranger District, personal communication, 2002). X-ray diffraction and differential thermal analyses of the clay fractions indicated small quantities of montmorillonite but no kaolinite (Dickson and Crocker, 1954). Dickson and Crocker's description of their analyses also suggested no indication of halloysite.

For soils aged 77, 616, and 1200+ yr, five plots were established. For soils aged 255 yr, six plots were established. Areas of obvious disturbance by fire or bark beetles were rejected. More detailed information concerning the study sites is given in Lilienfein et al. (2003) and Dickson and Crocker (1953).

### Equipment and Sampling

To compare field soil solution concentrations with the results of laboratory experiments, in each of the plots we installed three acid washed ceramic suction cup lysimeters (Soil-moisture Equipment Corp., Santa Barbara, CA). 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 DON. In each plot, one lysimeter was installed at the lower boundary of the A horizon (at the 10-cm soil depth in the 77- and 255-yr-old soils, at the 16-cm soil depth in the 616-yr-old soil, and at the 20-cm soil depth in the 1200+ year-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 was installed at the 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 the snowmelt (February to May) in 2001 and 2002, for a total of eight soil solution events. Additionally we took solid soil samples from 0- to 10-, 10- to 20-, 30- to 40-, 70- to 80-, and 140- to 150-cm soil depth. For the 0- to 10- and 10- to 20-cm

soil depths, three samples were taken per plot and then composited for analyses because organic matter content tended to be more variable near the surface, but below 20 cm, one sample was taken in each plot.

### Chemical Analyses

Soil samples for chemical analyses were oven dried at 40°C until a constant weight was obtained and then passed through a 2-mm sieve for homogenization. Organic C and N content was determined on ground subsamples by dry combustion with a Perkin Elmer 2400 CHN analyzer (Perkin Elmer, Norwalk, CT). Soil pH was measured in water with a soil/solution ratio of 1:1 (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 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 Perkin Elmer Plasma 1000 inductively coupled plasma emission spectrometer (Perkin Elmer, Norwalk, CT).

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 Eq. [2] as summarized by 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 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 dissolved organic C (DOC) with a DOC analyzer (TOC 5050 A, Shimadzu Corp., Columbia, MD), and  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were determined colorimetrically with a flow injection analyzer (Lachat QuickChem 8000, Lachat Instruments, Milwaukee, WI). Total N (TN) was determined after persulfate oxidation (Koroleff, 1983) as  $\text{NO}_3^-$ . Dissolved organic N was calculated by difference:  $\text{DON} = \text{TN} - (\text{NO}_3^- + \text{NH}_4^+)$ .

### Sorption Experiments

Fresh field moist soil taken from 0- to 10-, 10- to 20-, 30- to 40-, 70- to 80-, and 140- to 150-cm soil depth were used for the adsorption experiment. To make up stock DOM solution, forest floor material from the youngest and the oldest mudflows 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 and filtered through 0.45- $\mu\text{m}$  cellulose acetate membrane filters. The stock solution contained 200 mg DOC

L<sup>-1</sup> and 3.3 mg DON L<sup>-1</sup> and the pH was 5.2. For the sorption experiment, initial solutions containing 0, 6, 15, 30, and 200 mg DOC L<sup>-1</sup> and 0.017, 0.104, 0.278, 0.556, and 3.354 mg DON L<sup>-1</sup>, respectively, were prepared by diluting the stock DOM solution with a solution with an inorganic ion composition similar to the stock solution (pH 5.2, 0.45 mmol L<sup>-1</sup> for K, 0.72 mmol L<sup>-1</sup> for Ca, 0.07 mmol L<sup>-1</sup> for Mg, 0.13 mmol L<sup>-1</sup> for Na, 0.04 mmol L<sup>-1</sup> for SO<sub>4</sub><sup>2-</sup>, 0.16 mmol L<sup>-1</sup> for H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup>, and 1.86 mmol L<sup>-1</sup> for Cl<sup>-</sup>, for a total ionic strength of 2.16 mmol L<sup>-1</sup>). The highest concentration was chosen to better characterize the adsorption isotherm maximum as described by the Langmuir equation, and furthermore, it approximated the range of concentrations of DOC in the field, from a low of 0.5 (at the 150-cm depth) to a high of 286 mg L<sup>-1</sup> (in forest floor leachate).

Twenty milliliters of each of the five initial solutions were added to 2 g of each of the five soil depths from 21 plots and shaken for 24 h in an end-over-end shaker with 1 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 for 15 min at 3000 rpm and the supernatants were then filtered through 0.45- $\mu$ m cellulose acetate membrane filters and analyzed for DOC, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and TN.

### Selective Dissolution Experiment

To determine which soil characteristics control the adsorption of DOM, we selectively removed certain constituents from the soils which we thought might be responsible for the release (SOM) or adsorption (allophane, ferrihydrite) of DOM. Therefore we chose four soil samples with contrasting concentrations of C, N, allophane, ferrihydrite, and SSA (Table 1): the youngest and the oldest soil from 0- to 10- and 70- to 80-cm soil depth. Then we performed an adsorption experiment with the pretreated soil samples. With five subsamples of each of the four soil samples, the following treatments were performed:

- Destruction of the organic matter with 30% (v/v)H<sub>2</sub>O<sub>2</sub> at 70°C according to Kunze and Dixon (1986).
- Extraction with ammonium oxalate solution according to

Schwertmann (1964) to remove short-range order aluminosilicates and metal oxides.

- Sequential extraction with ammonium oxalate solution followed by DCB solution (Holmgren, 1967) to remove crystalline Fe in addition to short-range order aluminosilicates and metal oxides.
- Destruction of the organic matter and sequential extraction with ammonium oxalate solution, followed by DCB extraction.

After treatment, the samples were washed three times with deionized water to remove all extraction reagents. Afterwards, each of the pretreated soil samples was shaken with each of the initial DOC solutions used in the adsorption experiment described previously.

### Sorption Isotherms

Sorption of DOC and DON was analyzed by using sorption isotherms where the equilibrium DOC and DON concentration in solution is plotted against the mass of DOC and DON adsorbed per gram of dry soil. Measured adsorption isotherms were fitted to a modified Langmuir curve. Because we were working with soil samples, which contained native adsorbed organic matter, we added a parameter *a* in the Langmuir equation, which allows for a nonzero *y* intercept.

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

In this equation *x/m* is the mass of adsorbed DOM per mass of soil, *C* is the DOM 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).

We also determined the null-point concentration, which is

**Table 1.** Average concentrations ( $\pm$  standard deviations) of soil organic C (SOC), N, allophane, oxalate extractable (Fe<sub>o</sub>), crystalline Fe (Fe<sub>cryst</sub>), soil pH, and specific surface area (SSA) in the soils of the Mt. Shasta mudflow chronosequence.

Soil age	Soil depth	SOC	N	pH	Allophane	Fe <sub>o</sub>	Fe <sub>cryst</sub>	SSA
yr	cm	g kg <sup>-1</sup>						m <sup>2</sup> g <sup>-1</sup>
77	0-10	4.4 $\pm$ 1.2c†	0.20 $\pm$ 0.07c	4.7 $\pm$ 0.3b	0.56 $\pm$ 0.20c	1.2 $\pm$ 0.18b	0	14 $\pm$ 1.2c
	10-20	2.9 $\pm$ 0.6c	0.160 $\pm$ 0.05c	4.6 $\pm$ 0.1b	0.81 $\pm$ 0.13c	1.2 $\pm$ 0.10b	0	9.6 $\pm$ 1.5c
	30-40	0.62 $\pm$ 0.16c	0.08 $\pm$ 0.04b	5.4 $\pm$ 0.3a	0.95 $\pm$ 0.25c	1.1 $\pm$ 0.07b	0	13 $\pm$ 2.1b
	70-80	0.54 $\pm$ 0.11c	0.04 $\pm$ 0.05c	5.6 $\pm$ 0.2a	0.85 $\pm$ 0.19c	1.2 $\pm$ 0.11b	0	12 $\pm$ 2.4b
	140-150	0.60 $\pm$ 0.16b	0.04 $\pm$ 0.05b	5.8 $\pm$ 0.3a	0.96 $\pm$ 0.09b	1.2 $\pm$ 0.17b	0	13 $\pm$ 2.3b
255	0-10	19 $\pm$ 5.9b	0.85 $\pm$ 0.28b	5.6 $\pm$ 0.2a	1.3 $\pm$ 0.34b	1.1 $\pm$ 0.11b	0.59 $\pm$ 0.34	17 $\pm$ 3.2bc
	10-20	6.4 $\pm$ 1.4b	0.30 $\pm$ 0.06b	5.4 $\pm$ 0.1a	1.8 $\pm$ 0.45b	1.3 $\pm$ 0.15b	0.14 $\pm$ 0.16	14 $\pm$ 2.3bc
	30-40	3.6 $\pm$ 3.9b	0.18 $\pm$ 0.13b	5.5 $\pm$ 0.5a	1.6 $\pm$ 0.32b	1.2 $\pm$ 0.10b	0.27 $\pm$ 0.15	11 $\pm$ 1.0b
	70-80	1.0 $\pm$ 0.2b	0.10 $\pm$ 0.01b	5.6 $\pm$ 0.4a	1.5 $\pm$ 0.29b	1.2 $\pm$ 0.19b	0.27 $\pm$ 0.35	17 $\pm$ 4.4b
	140-150	1.6 $\pm$ 1.2ab	0.12 $\pm$ 0.04a	5.4 $\pm$ 0.2a	1.8 $\pm$ 0.43b	1.3 $\pm$ 0.24b	0	13 $\pm$ 2.9b
616	0-10	49 $\pm$ 22a	1.84 $\pm$ 0.65a	5.3 $\pm$ 0.3a	29 $\pm$ 8.4a	1.8 $\pm$ 0.13a	0.66 $\pm$ 0.21	26 $\pm$ 7.6a
	10-20	20 $\pm$ 5.2a	0.90 $\pm$ 0.25a	5.6 $\pm$ 0.2a	37 $\pm$ 7.0a	2.0 $\pm$ 0.07a	0.46 $\pm$ 0.30	30 $\pm$ 6.3a
	30-40	10 $\pm$ 3.1a	0.46 $\pm$ 0.17a	5.8 $\pm$ 0.2a	50 $\pm$ 15a	2.2 $\pm$ 0.22a	0.26 $\pm$ 0.39	25 $\pm$ 4.6a
	70-80	8.3 $\pm$ 2.9a	0.34 $\pm$ 0.09a	5.81 $\pm$ 0.2a	43 $\pm$ 12a	2.5 $\pm$ 0.19a	0	34 $\pm$ 5.3a
	140-150	3.0 $\pm$ 2.5a	0.12 $\pm$ 0.08a	5.8 $\pm$ 0.2a	29 $\pm$ 18a	2.3 $\pm$ 0.56a	0	27 $\pm$ 13a
~1200+	0-10	45 $\pm$ 14a	2.00 $\pm$ 0.56a	5.4 $\pm$ 0.3a	21 $\pm$ 7.8a	1.8 $\pm$ 0.37a	0.61 $\pm$ 0.17	25 $\pm$ 3.7a
	10-20	27 $\pm$ 8.3a	1.14 $\pm$ 0.34a	5.5 $\pm$ 0.5a	31 $\pm$ 12a	2.1 $\pm$ 0.42a	0.28 $\pm$ 0.22	21 $\pm$ 5.3a
	30-40	16 $\pm$ 7.0a	0.70 $\pm$ 0.20a	5.7 $\pm$ 0.2a	47 $\pm$ 13a	2.5 $\pm$ 0.34a	0.35 $\pm$ 0.35	23 $\pm$ 5.0a
	70-80	6.8 $\pm$ 1.8a	0.34 $\pm$ 0.05a	5.7 $\pm$ 0.2a	58 $\pm$ 9.3a	2.6 $\pm$ 0.21a	0.19 $\pm$ 0.31	33 $\pm$ 8.0a
	140-150	3.7 $\pm$ 1.7a	0.18 $\pm$ 0.08a	5.8 $\pm$ 0.2a	33 $\pm$ 20a	2.4 $\pm$ 0.35a	0	28 $\pm$ 4.2a

† 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.

defined as the DOC or DON equilibrium concentration at which there is no net adsorption or release of DOC or DON, that is, the  $x$  intercept of the fitted Langmuir curve.

### Preferential Adsorption of Dissolved Organic Carbon or Dissolved Organic Nitrogen

To test whether the degree of adsorption of DOC is different from that of DON, we compared the DOC/DON ratio in the solution before and after the batch adsorption experiment.

### Statistical Analyses

Replication for all reported data was for one sample taken in each of five or six plots in soils of each age. A multiple comparison of means of SOC, N, allophane, and  $Fe_0$ , crystalline Fe concentrations, pH, and specific SSA in soils of different ages, within each soil depth, was done using Tukey's honest significant difference (HSD) test. Log-transformed data were used (except for pH) to ensure equal variances. Analysis of variance and a multiple comparison of means were used to compare the DOC adsorbed between soils of different ages for the highest level of addition of DOC. To compare the DOC/DON 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. In the selective dissolution experiment, the effects of pretreatment of the soil on the adsorption characteristics relative to untreated soil samples were tested by using the Wilcoxon matched-pairs signed ranks test (using adsorbed DOC for the pretreated—untreated soil as the data pair). To determine the soil characteristics that explain the variation in the adsorption of DOC and DON 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. Linear regression analysis was also used to examine the relationship between the null-point concentration of DOC and DON of the soils and the DOC and DON soil solution concentration. For all statistical analyses, significance was set to  $P < 0.05$  and statistical analyses were performed with SPSS 11.5 (SPSS Inc., 2000).

## RESULTS AND DISCUSSION

### Influence of Soil Weathering on Adsorption Characteristics

Characteristics of the soils are given in Table 1. Concentrations of organic C and N, allophane,  $Fe_0$  and the surface area increased with increasing soil age. Most importantly for the process of adsorption, allophane concentrations were up to 68 times as high in the oldest soil than in the youngest while  $Fe_0$  concentrations were about 2.3 times as high in the oldest soil. Moreover, in the oldest soil allophane concentrations were about 10 times higher than  $Fe_0$  (compared on a mass basis if we assume that the mass of the  $Fe_0$  containing material is similar to ferrihydrite) (Lilienfein et al., 2003). 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 the crystalline Fe was <24% of the total DCB extractable Fe (Lilienfein et al., 2003). It should be noted that oxalate also extracts some Fe from magnetite. Rhoton et al. (1981) found that oxalate dissolved 50 g Fe per kg of standard magnetite. Dickson

and Crocker (1954) found 2.4% magnetite in the fine sand fraction, which comprised 36% of the soil, and found that it was the same percentage in soils of different ages. Using the percentage dissolution from Rhoton et al. (1981), and Dickson and Crocker's magnetite concentration, we estimate about  $0.4 \text{ g kg}^{-1} Fe_0$  would be due to magnetite, which is about 34% of  $Fe_0$  in the youngest soil and <19% in the oldest soil.

The amount of DOC released or adsorbed as a function of the DOC equilibrium concentration is presented in Fig. 1. All the studied soil samples released DOC at low initial DOC concentrations and adsorbed DOC at higher initial DOC concentrations. At the highest initial DOC concentrations the older soils tended to adsorb more DOC than the younger soils. An analysis of variance of the adsorbed DOC ( $\text{mg kg}^{-1}$ ) for the highest level of initial DOC added ( $200 \text{ mg L}^{-1}$ ) as the independent variable showed a significant effect of soil age at every soil depth. A multiple comparison of means (Tukey's HSD test) showed that the two older soils were significantly different from the two younger soils. The pH of the equilibrium solutions of the adsorption experiment was within 0 to 0.15 pH units of the soil pH listed in Table 1 for each level of initial DOC added.

In general, the shapes of the adsorption isotherms for DON are similar to those of DOC (Fig. 2). At low equilibrium concentrations of DON, the soil samples released DON into the solution, and at higher concentrations DON was adsorbed to the soil samples, except for the samples from the 255-yr-old soil at the 0- to 10-cm soil depth, where DON is released from the samples even at the highest equilibrium concentration.

To quantify how the adsorption characteristics of the study soils changed with increasing soil age, we determined the null-point concentration ( $x$  intercept of Langmuir curve) and the adsorption capacity (asymptote of the Langmuir curve) of the adsorption isotherms. Figure 3 shows how the null-point concentrations for DOC and DON changed with soil age and depth. Null-point concentrations decreased with increasing soil age, while concentrations of allophane and ferrihydrite and the specific surface area of the soil increased with soil age. The null-point concentration decreased with increasing soil depth due to decreasing concentrations of organic C and N and similar allophane concentrations in the soil solid phase (Table 1). This leads to increasing amounts of available active allophane surface area, that is, allophane that is not coated with humic substances. These findings are in agreement with those of Moore et al. (1992) and McLaughlin et al. (1994) who found increasing null-point concentrations with increasing concentrations of organic C and with decreasing concentrations of Fe and Al in the soil. The adsorption maxima increased clearly with increasing soil age and decreased slightly with increasing soil depth (Fig. 4).

Because the original Langmuir equation does not allow for the fact that DOM may be released from the soil, it is mainly used to describe adsorption of DOC to distinct minerals, which have no native adsorbed DOM (Baham and Sposito, 1994; Gu et al., 1995, 1996). Some authors have used the original Langmuir for DOM ad-

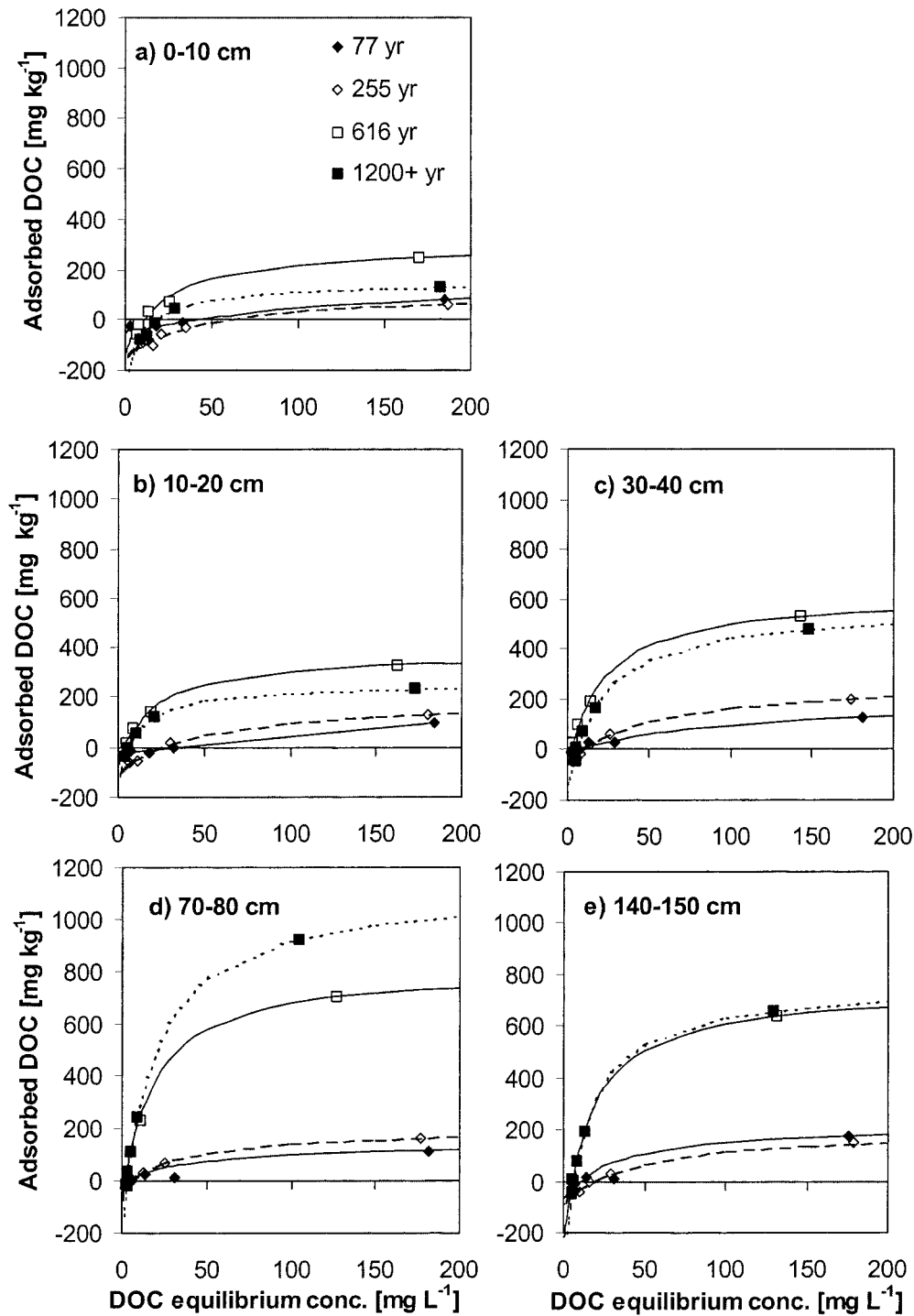


Fig. 1. Measured (points) and fitted (lines) dissolved organic C (DOC) adsorption isotherms of Mt. Shasta mudflow soils at depths of (a) 0 to 10 cm, (b) 10 to 20 cm, (c) 30 to 40 cm, (d) 70 to 80 cm, and (e) 140 to 150 cm.

sorption on soils (Shen, 1999; Benke et al., 1999) without correcting for the native adsorbed DOM.

Similar to the original unmodified Langmuir equation, the initial mass (IM) isotherm is inappropriate for our soils and our study purposes. Although commonly used to describe DOM adsorption in natural soils, the IM isotherm, developed by Nodvin et al. (1986), in which the amount of substance removed is plotted against the initial mass of DOC in solution, is designed to be used with low concentrations of DOC. The IM isotherm

allows the description of isotherms for soil samples that have native labile DOM, which is originally adsorbed to the soil and released into the solution for low initial DOC concentrations; and as such, Neff and Asner (2001) concluded in a recent review that the IM isotherm best represents the adsorption of DOC to soils. However, the IM isotherm only describes adsorption equilibria at low concentrations of DOC, and it therefore does not include a parameter for the adsorption maximum. The IM isotherm uses an adsorption term ( $m$ ), where

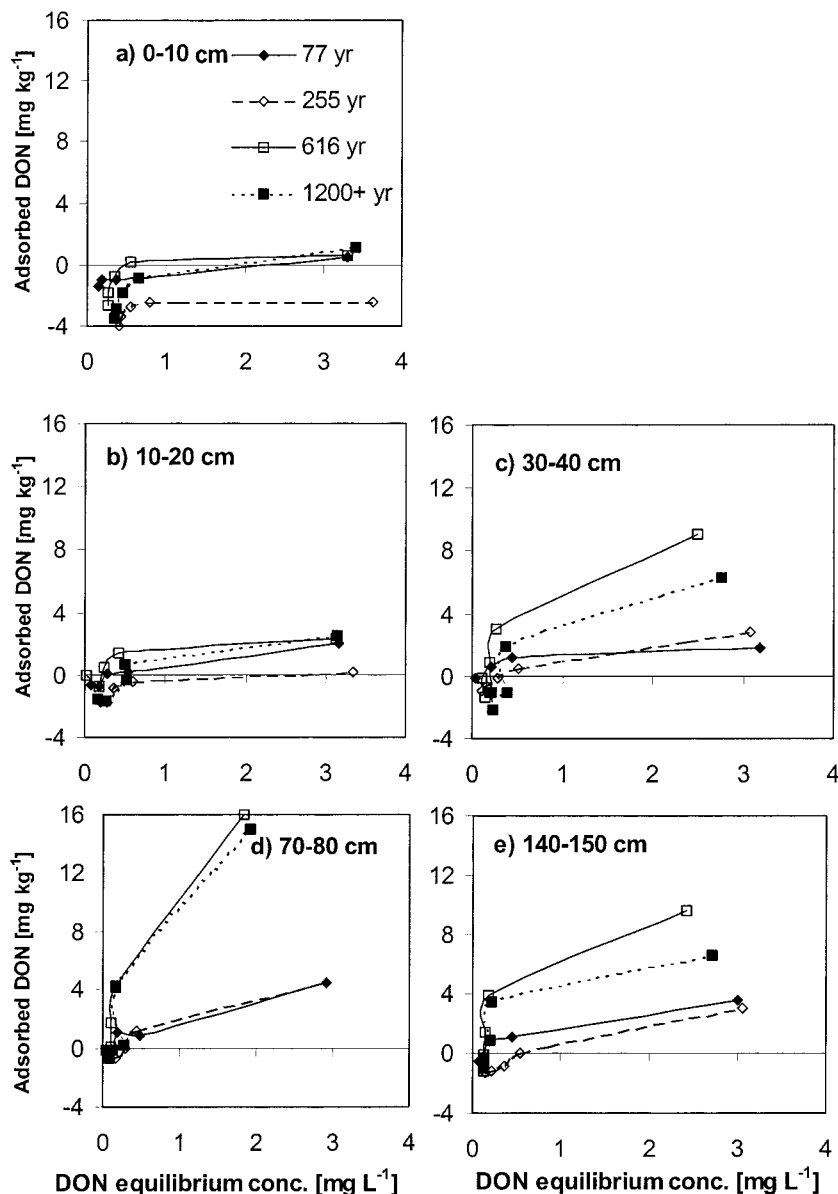


Fig. 2. Measured dissolved organic N (DON) adsorption isotherms of Mt. Shasta mudflow soils at depths of (a) 0 to 10 cm, (b) 10 to 20 cm, (c) 30 to 40 cm, (d) 70 to 80 cm, and (e) 140 to 150 cm.

$m$  is the slope of the linear regression and is interpreted as a partition coefficient, which is a measure of the affinity of sorbent (mineral soil) for the substance (DOC or DON) being sorbed. And, it assumes a linear relationship between the amount of adsorbed DOC and the amount of DOC in the initial solution. We used the modified Langmuir equation (Eq. [4]), because we were interested in estimating the adsorption maxima of our soil samples and therefore used high initial DOC concentrations of up to  $200 \text{ mg DOC L}^{-1}$ .

To enable the use of the Langmuir equation in the presence of native adsorbed DOC, without performing a separate analysis to determine the amount of originally adsorbed DOC, we modified the original Langmuir equation by adding the parameter  $a$  (see Eq. [4]) to correct for the amount of released DOC. This resulted in a good fit of the Langmuir curve to the measured data points. The coefficients of determination ( $r^2$ ) for

the fit of the predicted vs. measured points of the modified Langmuir equation for our soils ranged between 0.96 and 0.9999 (excluding the soil sample from the 77-yr-old soil at 10- to 20-cm soil depth for which the relationship was better described by a straight line).

Because of the greater analytical variability in the determination of DON compared with DOC, the isotherms for the adsorption of DON did not always fit the Langmuir model as well as those for DOC. Consequently, we simply presented data points connected with lines in Fig. 2.

#### Preferential adsorption of Dissolved Organic Carbon or Dissolved Organic Nitrogen

To determine whether DOC or DON was preferentially adsorbed, we compared the DOC/DON ratios of the equilibrium concentrations of the highest initial concentration for the three lower soil depths (30–40, 70–80,

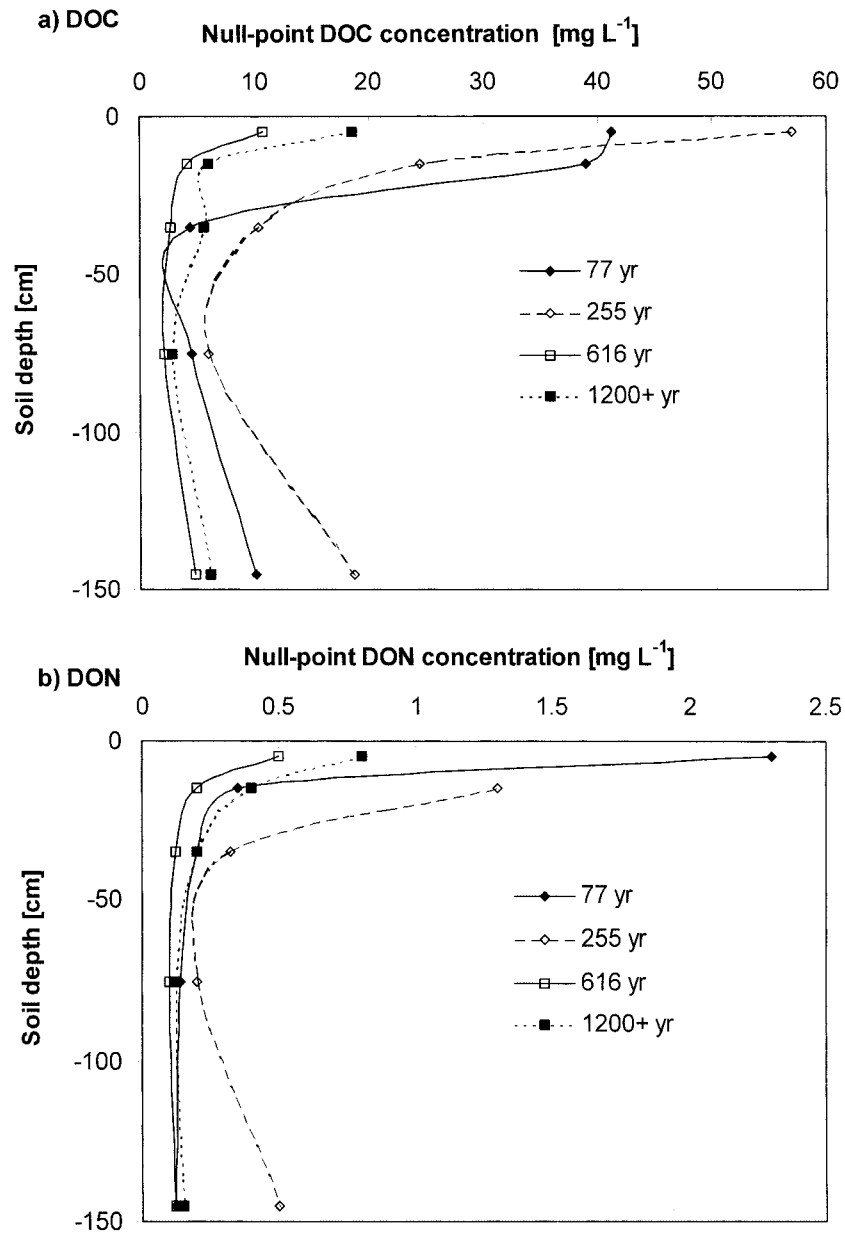


Fig. 3. Null-point (a) dissolved organic C (DOC) and (b) dissolved organic N (DON) concentrations of Mt. Shasta mudflow soil in relation to soil depth.

and 140–150 cm, Fig. 5). At these depths most samples showed a net adsorption of DOC and DON (Fig. 1 and 2). The DOC/DON ratio of the initial solution was 57. A higher DOC/DON ratio in the equilibrium solution than in the initial solution would indicate that DON is preferentially adsorbed over DOC and a lower DOC/DON ratio would indicate that DOC is preferentially adsorbed. For most soil samples the DOC/DON ratio in the equilibrium solution was not significantly different from that of the initial solution. Only four soil samples had a DOC/DON ratio of the equilibrium solution that was significantly different from that of the initial solution. For the 1200+ yr-old soil at 30- to 40- and 140- to 150-cm soil depths, the DOC/DON ratio was significantly lower in the equilibrium solution. For the 77- and 616-yr-old soils at 70- to 80-cm soil depth, the DOC/

DON ratio in the equilibrium solution was significantly higher than in the initial solution. Therefore, we concluded that there were no consistent trends indicating preferential adsorption of DOC or DON.

Kaiser and Zech (2000b) examined preferential adsorption of DOC or DON using separated fractions of DOC (hydrophobic fraction, hydrophilic fraction). They found that for a given fraction, there was no preferential adsorption of DOC or DON, and that there was only a slight preferential adsorption of the hydrophobic fraction that had a high DOC/DON ratio in soil samples. There was almost identical adsorption of DOC and DON to both amorphous  $\text{Al}(\text{OH})_3$  and goethite. They concluded that this indicated that N ligands were sorbed passively to the mineral soil as a part of other organic structures. Qualls and Haines (1991) found that the

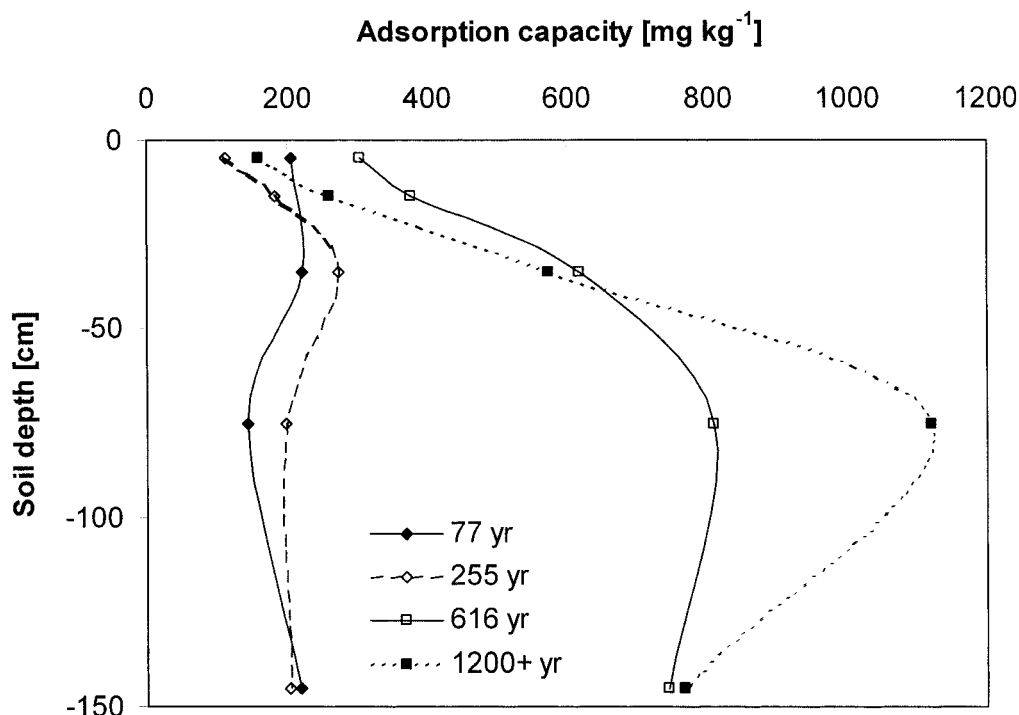


Fig. 4. Adsorption capacity for dissolved organic C (DOC) of Mt. Shasta mudflow soil in relation to soil depth.

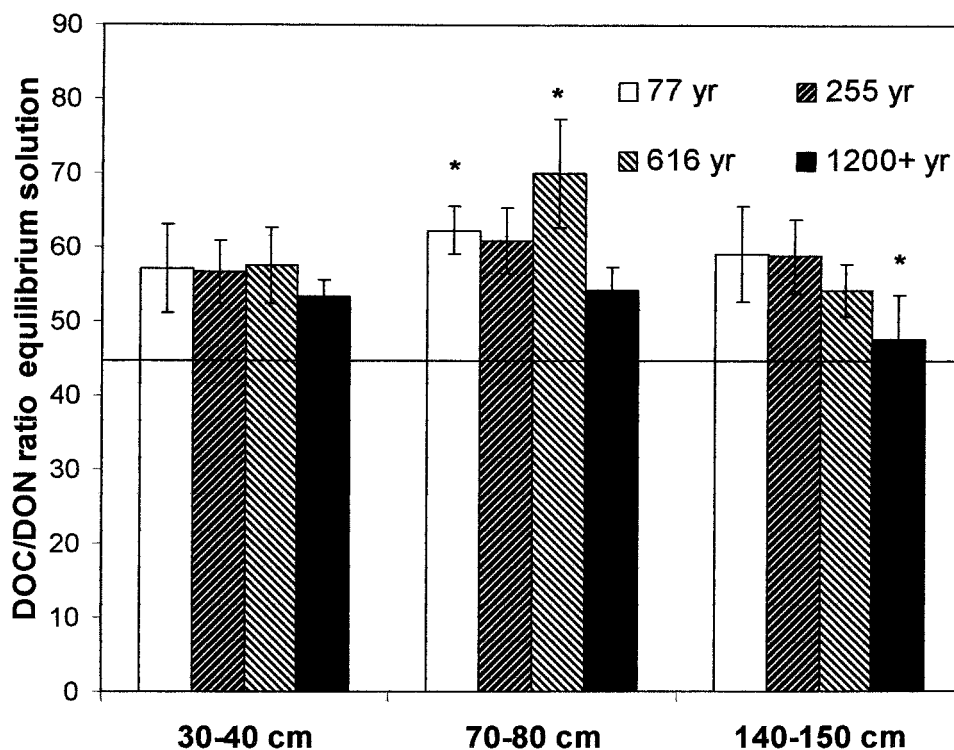


Fig. 5. Dissolved organic C/dissolved organic N (DOC/DON) ratio in the equilibrium solution of the highest concentration of initial solution ( $200 \text{ mg DOC L}^{-1}$  and  $3.3 \text{ mg DON L}^{-1}$ ). The line represents the DOC/DON ratio in the initial solution. Asterisk (\*) indicates a significant difference in the DOC/DON ratio in the equilibrium solution as compared with the initial solution ( $P < 0.05$ , single sample paired  $t$ -test).

DOC/DON ratio in the soil solution decreased with increasing soil depth indicating some degree of preferential leaching of DON over DOC. However, 98.4% of the DOC and 96.5% of the DON flux draining from the Oa horizon was retained in the mineral soil column in this same forest ecosystem (Qualls et al., 2002).

#### Soil Properties Influencing Dissolved Organic Matter Sorption

In the selective dissolution experiment, the effects of the sample pretreatment were stronger in the older than in the younger soils (Fig. 6). In the surface soil of the older soil, the removal of the organic material with  $\text{H}_2\text{O}_2$

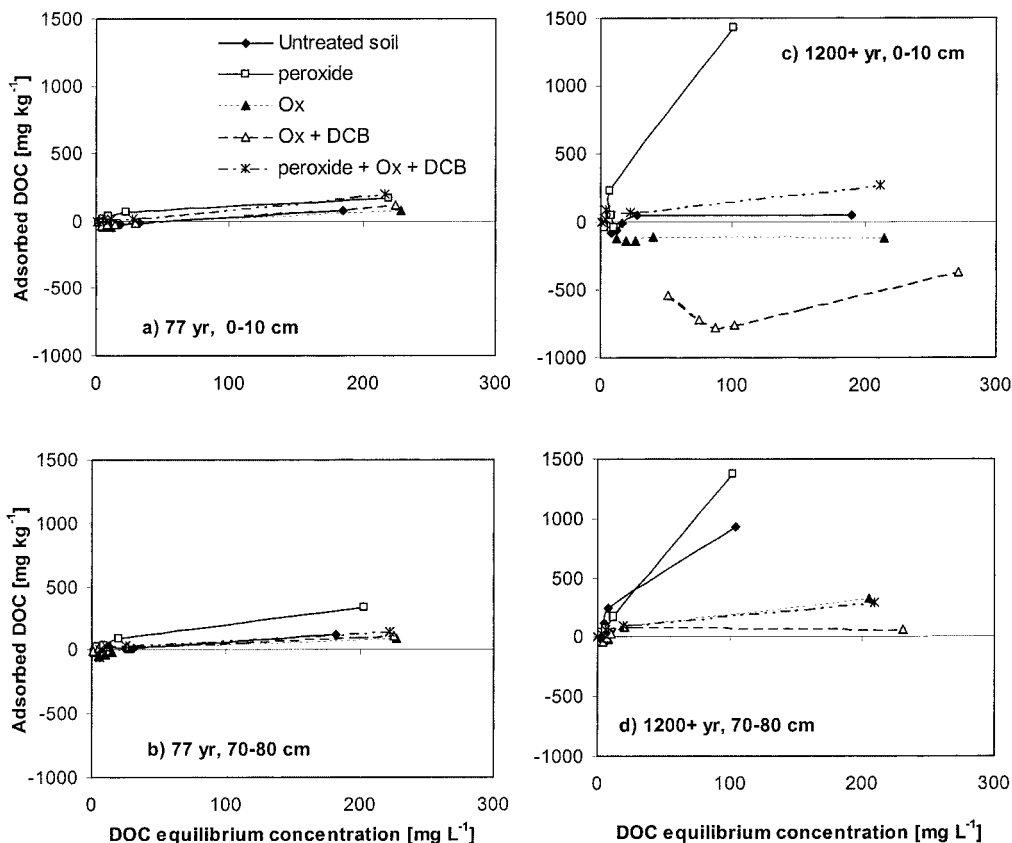


Fig. 6. Adsorption isotherms for pretreated soil samples (Ox: oxalate extraction, DCB: dithionite-citrate-bicarbonate extraction).

solution significantly increased the adsorption of DOC compared with the untreated soil samples ( $P = 0.04$ , using the Wilcoxon matched-pairs signed ranks test). The effect was weaker in the samples from a 70- to 80-cm soil depth because of the lower original SOC concentration (Table 1) and differences were not significant. The increase in adsorption after removal of the organic matter is in agreement with findings of Jardine et al. (1989) and Kaiser and Zech (2000a) who both found increased adsorption of DOM after removal of the organic matter. Removal of organic matter has two potential effects: (i) exposure of mineral surfaces that had been coated with adsorbed organic matter and (ii) removal of particulate organic matter in the soil. About 57% of the organic C in the 0- to 10-cm depth was associated with a low-density fraction probably corresponding to particulate organic matter not associated with mineral soil and the remainder was associated with denser mineral particles (Sollins et al., 1983). Qualls (2000) found that forest floor organic matter and peat both desorb and adsorb DOC, probably by H bonding mechanisms, so the presence of particulate organic matter probably contributed to the desorption of DOC that we observed in samples with high SOC content.

In contrast, the removal of allophane and ferrihydrite using oxalate, and a sequential extraction of oxalate and DCB solution, decreased the adsorption. In the oldest soil at the 70- to 80-cm depth, the removal of allophane and ferrihydrite significantly ( $P = 0.04$ ) reduced the adsorption capacity in comparison with the untreated

soil sample. In the 0- to 10-cm depth of the oldest soil, it led to a net release of DOC even for the highest initial concentration of  $200 \text{ mg DOC L}^{-1}$  as all adsorbing material was removed. The sequential extraction with oxalate and DCB solution further significantly decreased the adsorption capacity ( $P = 0.04$ ) compared with a single oxalate extraction in the 0- to 10-cm depth, perhaps due to the removal of crystalline Fe, which comprised 16% of the total DCB-extractable Fe in that sample. The DCB reagent has also been found to cause some dissolution of allophane (Wada, 1989) so the slight effect observed in the 70- to 80-cm depth could be caused by a more thorough removal of allophane by a second extraction. Jardine et al. (1989) found decreased adsorption of DOC after removal of the Fe and Al oxides with DCB extract in a soil that had far higher concentrations of crystalline oxides than did our soils. It should be noted that the effects of  $\text{H}_2\text{O}_2$ , oxalate, and DCB might have other effects on the soil beyond those of organic matter removal, or Fe and Al removal. For example, we noted some organic matter dissolution (color) in the oxalate and DCB extracts.

In all soils except in the 70- to 80-cm depth of the youngest soil, the combination of organic matter removal, oxalate and DCB extractions led to significantly ( $P = 0.04$ , using the Wilcoxon matched-pairs signed ranks test) different adsorption compared with the untreated soil. However, the effects differed because of the opposing effects of organic matter removal and oxalate and DCB extractions. Organic matter removal in-

creased adsorption while Al and Fe removal decreased adsorption, so the net effect of the combination of the two opposing treatments depended on the ratio of organic matter to Al and Fe in the original soil sample. In the 0- to 10-cm depth, the organic matter is the dominant factor in DOC adsorption, and there were small but consistent increases with the combination treatment. Kaiser and Zech (2000a), who performed a similar study on the clay fraction of subsurface soils, found an increase in adsorption after organic matter removal and a sharp decrease in adsorption after sequential removal of the Fe and Al oxides. In another study, Kaiser and Zech (1998) showed that coating of the soil with organic matter led to decreased DOC sorption, whereas coating with sesquioxides led to increased sorption of DOC. The effect on adsorption decreased in the following order: amorphous  $\text{Al}(\text{OH})_3$  > ferrihydrite > goethite.

Our selective dissolution experiment showed that organic matter decreased adsorption of DOC whereas Al and Fe oxides or silicates increased the adsorption of DOC. This led us to the hypothesis that the adsorption of DOC is correlated to the ratio of SOC to allophane and  $\text{Fe}_o$ . The selective dissolution experiment could not distinguish between the effects of allophane and  $\text{Fe}_o$ , because oxalate dissolves both, so we tested our hypothesis by performing the following linear regression analyses using soils of all ages and all depths together: (i) null-point concentration of DOC vs. (a) the ratio of SOC/allophane, (b) the ratio of SOC/ $\text{Fe}_o$ , (c) the ratio of SOC/surface area (d) allophane concentration, (e)  $\text{Fe}_o$  concentration, or (f) specific surface area; (ii) null-point concentration of DON vs. (a) the ratio of SON/allophane, (b) the ratio of SON/ferrihydrite, or (c) the ratio of SON/surface area; (iii) adsorption capacity of DOC vs. (a) the ratio of allophane/SOC, (b) the ratio of ferrihydrite/SOC, or (c) the ratio of surface area/SOC. We also performed the following stepwise multiple regressions: (iv) null-point concentration of DOC as the dependent variable and concentrations of SOC, allophane, and ferrihydrite; SSA and SOC/allophane; SOC/ferrihydrite and SOC/surface area as predictors; (v) null-point concentration of DON and concentrations of N, allophane, and ferrihydrite; SSA and N/allophane; N/ferrihydrite, and N/surface area as predictors; (vi) adsorption capacity of DOC and (a) allophane/SOC, (b) ferrihydrite/SOC, and (c) surface area/SOC.

We found a strong correlation between the null-point concentrations of DOC and DON and the ratio of SOC or N to allophane, respectively (Fig. 7). The coefficients of determination of null-point DOC vs. the following single variables were: 0.29 for allophane ( $P = 0.015$ ), 0.28 for  $\text{Fe}_o$  ( $P = 0.016$ ), and 0.21 for null-point SSA ( $P = 0.042$ ) (not shown). These relationships were weaker because they did not take organic C concentrations into consideration. The regressions of null point DOC or DON vs. other variables were not significant.

We also found high and significant coefficients of determination between the adsorption capacity of DOC and the allophane/SOC ratio across all soil ages and depths (Fig. 8), whereas the other regressions tested were not significant (not shown).

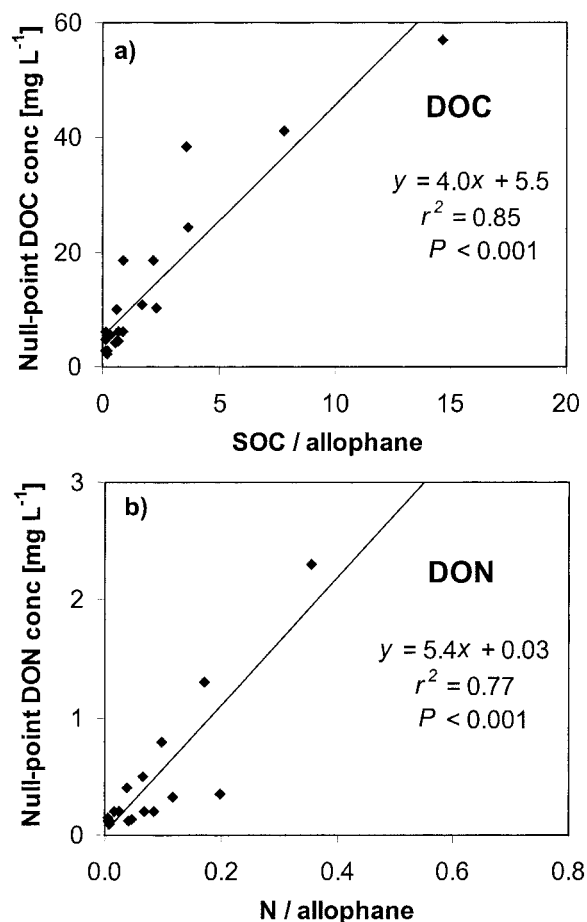


Fig. 7. Relationships between null-point dissolved organic C (DOC) and dissolved organic N (DON) concentrations and the C/allophane and N/allophane. Regressions of null-point DOC concentration vs. soil organic C (SOC)/ $\text{Fe}_o$  or SOC/specific surface area (SSA), and regressions of null point DON concentrations vs. N/ $\text{Fe}_o$ , or N/SSA were not significant ( $r^2 = 0.03$  to  $0.05$ ) and are not shown.

In the stepwise multiple regression analyses, with the null-point concentration of DOC as the dependent variable, the only predictor variable that significantly increased the  $R^2$  of the model was SOC/allophane with a coefficient of determination of 0.85 ( $P < 0.001$ ). The same analyses performed for the null-point concentration of DON and the respective predictor variables gave an adjusted  $R^2$  of 0.77 for N/allophane ( $P < 0.001$ ) and of 0.81 if surface area is included ( $P = 0.025$ ). The results of this analysis confirmed that SOC/allophane and N/allophane are the most important predictor variables for the null-point concentration of DOC and DON, respectively.

The stepwise multiple regression analyses with the adsorption capacity of the soil for DOC as the dependent variable indicated that the ratio of allophane/SOC alone gave an  $r^2$  of 0.88 (an adjusted  $R^2$  of 0.87,  $P < 0.001$ ), and the inclusion of ferrihydrite/SOC significantly increased the adjusted  $R^2$  to 0.95 ( $P = 0.016$ ). The further inclusion of ferrihydrite increased it to 0.96 ( $P = 0.027$ ). Thus, the ratio of allophane/SOC predicted most of the variation in the adsorption capacity of the soil for DOC. In summary, the results of individual and

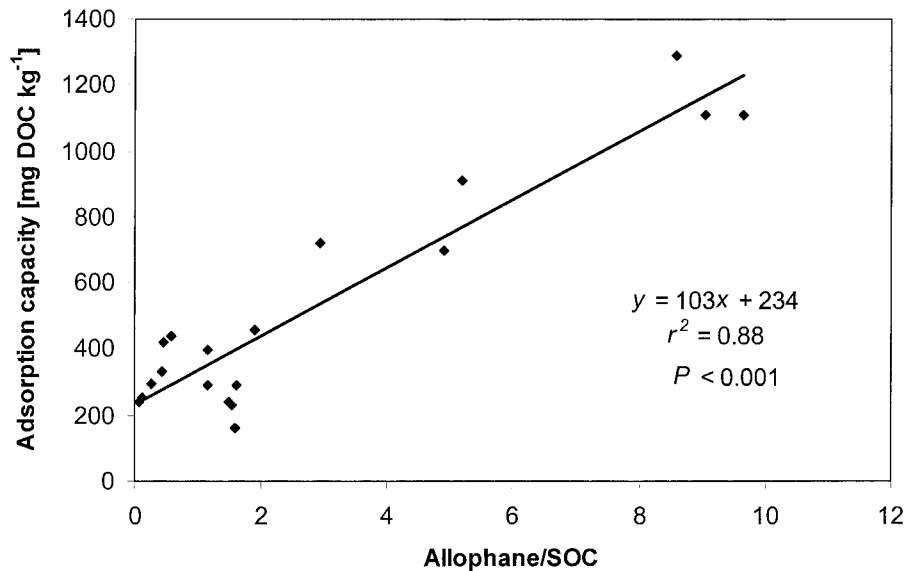


Fig. 8. Relationships between the adsorption capacity of dissolved organic C (DOC) and the allophane/soil organic C (SOC) ratio.

stepwise multiple regression analyses confirmed that both adsorption capacity and null-point concentration were largely predictable from some ratio of SOC or N and allophane.

Yuan et al. (2000) found that allophane has a large capacity for adsorbing humic acids and that capacity was about one order of magnitude larger than for kaolinite (Huang and Yang, 1995). Adsorption studies of DOM to individual mineral phases have shown that the adsorption of DOC to ferrihydrite and amorphous  $\text{Al}(\text{OH})_3$  was stronger than that to clay minerals like kaolinite and illite (Kaiser and Zech, 2000b). Nambu and Yonebayashi (2000) reported that adsorption isotherms of DOM for Andisols were similar to those for pure gibbsite or goethite minerals. However, there has been no comparison of the sorption characteristics of pure allophane and Al or Fe hydroxides. In nonallophanic soils, Donald et al. (1993) and Moore et al. (1992) reported positive correlations between the adsorption of DOC and both oxalate extractable Al and DCB extractable Fe. Likewise, McLaughlin et al. (1994) found a negative correlation between the concentrations of DCB-extractable Al and Fe and the DOC concentration

in soil solution. We conclude that in the Mt. Shasta mudflow Andisol chronosequence, allophane was a much better predictor of adsorption than ferrihydrite simply because it was present in 10 to 20 times higher concentrations in the older soils, and because it has a very high capacity for adsorption of DOM.

Nelson et al. (1993) found a positive correlation between the SSA and the adsorption of DOC when they compared a sandy and a clayey soil. The failure of SSA predict adsorption in our soils can be explained by the presence of different surfaces with very different adsorption capacities. Lilienfein et al. (2003) found that in the Mt. Shasta mudflow chronosequence, the apparent surface area because of allophane increased from a range of  $0.3 (\pm 0.1)$  to  $0.5 (\pm 0.04) \text{ m}^2 \text{ g}^{-1}$  in the youngest soil, to a range of  $10 (\pm 3.8)$  to  $28 (\pm 4.5) \text{ m}^2 \text{ g}^{-1}$  in the oldest soil over all depths. However, the surface area of the nonallophanic fraction remained about the same (youngest soil:  $9 [\pm 1.4]$  to  $14 [\pm 1.2] \text{ m}^2 \text{ g}^{-1}$ ; oldest soil:  $4.5 [\pm 6.5]$  to  $15 [\pm 2.4] \text{ m}^2 \text{ g}^{-1}$ ). Consequently, the highly reactive surface area of the allophane increased greatly while the total specific area only increased by an average factor of 2.6 between the youngest and oldest soils.

Table 2. Average dissolved organic C (DOC) and dissolved organic N (DON) 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 yr-old soil: 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, the time of the main snow melt. Averages were not volume or flux weighted.

Soil age	77 yr	255 yr	616 yr	1200+ yr
		DOC, mg L <sup>-1</sup>		
A horizon	50 $\pm$ 11	45 $\pm$ 15	22 $\pm$ 9	27 $\pm$ 13
B horizon	20 $\pm$ 7	30 $\pm$ 18	20 $\pm$ 19	11 $\pm$ 7
C horizon	8 $\pm$ 4	7 $\pm$ 3	3 $\pm$ 0.7	1.5 $\pm$ 0.3
		DON, mg L <sup>-1</sup>		
A horizon	1.1 $\pm$ 0.58	1.1 $\pm$ 0.29	0.57 $\pm$ 0.18	0.59 $\pm$ 0.30
B horizon	0.35 $\pm$ 0.10	0.63 $\pm$ 0.32	0.34 $\pm$ 0.22	0.27 $\pm$ 0.14
C horizon	0.12 $\pm$ 0.06	0.35 $\pm$ 0.41	0.07 $\pm$ 0.02	0.03 $\pm$ 0.009

### Correlation with Soil Solution Concentrations

As a final analysis, we tested whether the results of the adsorption experiments were correlated with soil solution concentrations in the field. Average DOC and DON soil solution concentrations are presented in Table 2. 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 DOC or DON at the 0- to 10-cm depth, and measured DOC or DON concentrations in the soil solution at 10-, 16- or 20-cm depths (depending on soil age). Null-point concentrations at the 30- to 40-cm depth were correlated with solution from the 40-cm depth. We chose the null-

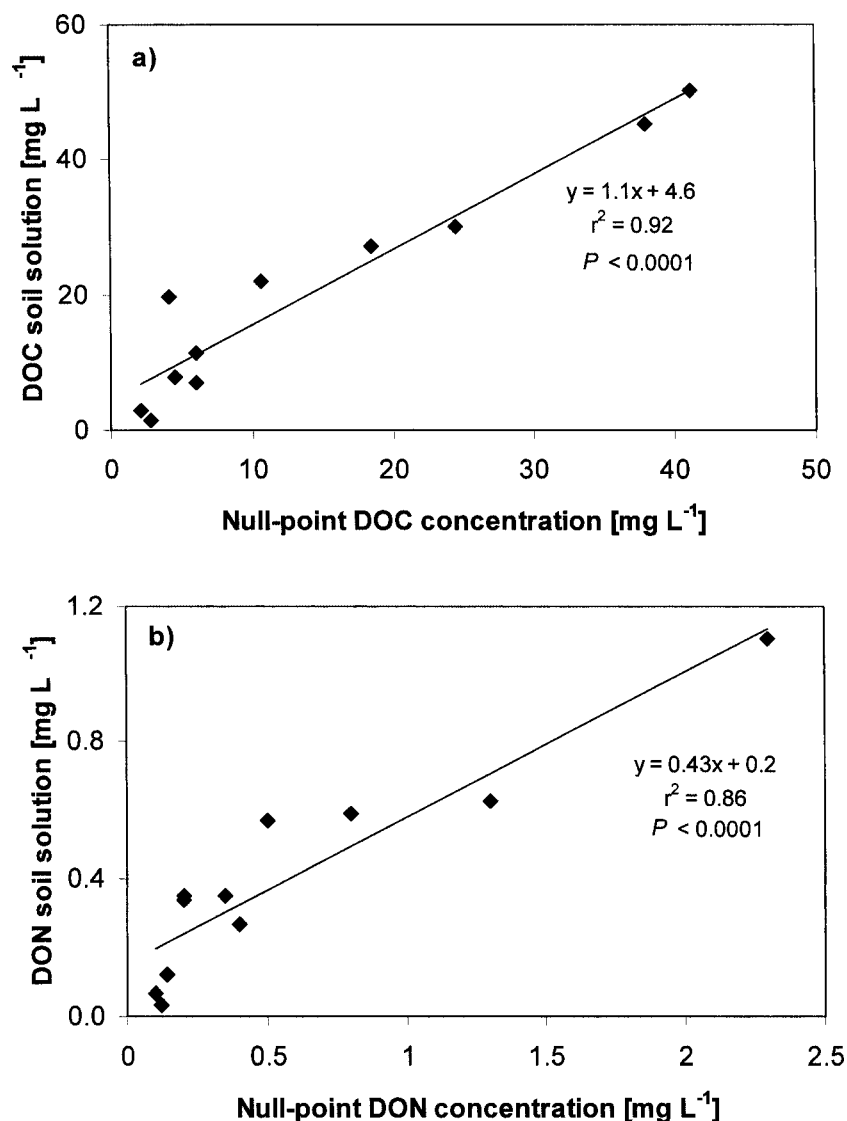


Fig. 9. Relationships between the soil solution concentration of (a) dissolved organic C (DOC) and (b) dissolved organic N (DON) at 10-, 16-, or 20-, 40-, and 150-cm soil depth and the null-point DOC and DON concentration in soil samples from 0- to 10-, 30- to 40-, and 70- to 80-cm soil depth.

point concentrations for the 70- to 80-cm soil depth to correlate with soil solution concentrations from the 150-cm soil depth, because we reasoned that the soil depth with the strongest degree of adsorption controlled the soil solution concentration at the 150-cm soil depth. We found that soil solution and null-point concentrations over all soil ages and soil depths were highly correlated (Fig. 9). In fact, in the case of DOC, the slope is close to 1 indicating a close correspondence between the null-point concentrations and the actual soil solution concentrations (Fig. 9a). However, in the case of DON, this correspondence is not as good (Fig. 9b). In summary, the highly significant coefficients of determination suggest that the soil solution is in equilibrium with the soil solid phase and the results obtained in the adsorption experiment are relevant to field conditions.

## CONCLUSIONS

Our approach in this study has been to (i) observe changes in adsorption properties with soil age, (ii) deter-

mine what factors control the changes in adsorption with soil age by (iia) experimental manipulation of these properties by selective dissolution and (iib) correlation with soil characteristics, and finally, (iii) to relate adsorption properties to soil solution concentrations observed in the field.

As the soils developed in the volcanic mudflows, increasing concentrations of allophane and SOM exerted the strongest influence on adsorption of DOC and DON. While allophane concentrations tended to increase adsorption capacity and decrease null-point concentrations, SOC increases in the upper horizons tended to decrease adsorption capacity and increase null-point concentration. Consequently, the ratio of allophane/SOC was the best prediction of adsorption capacity. While the concentration of Fe<sub>o</sub> increased with soil age, and contributed to adsorption capacity, its concentration in the oldest soil was much less than that of allophane. Adsorption of DOC and DON was controlled by similar factors and we could not find any consistent

preferential adsorption of DOC vs. DON. Good relationships between the null-point concentrations for DOC ( $r^2 = 0.92$ ) or DON ( $r^2 = 0.86$ ) from adsorption isotherms and soil solution concentrations indicated the relevance of the adsorption experiments to in situ field conditions. The increase in adsorption capacity as these soils age results in a decrease in the tendency for DOC and DON to be leached from the soil column.

### ACKNOWLEDGMENTS

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