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Mobilization of metals and phosphorus from intact forest soil cores by dissolved inorganic carbon

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Abstract Increased dissolved inorganic carbon (DIC) enhances the mobilization of metals and nutrients in soil solutions. Our objective was to investigate the mobilization of Al, Ca, Fe, and P in forest soils due to fluctuating DIC concentrations. Intact soil cores were taken from the O and B horizons at the Bear Brook Watershed in Maine (BBWM) to conduct soil column transport experiments. Solutions with DIC concentrations (~20–600 ppm) were introduced into the columns. DIC was reversibly sorbed and its migration was retarded by a factor of 1.2 to 2.1 compared to the conservative sodium bromide tracer, corresponding to a log $K_D = -0.82$ to -0.07. Elevated DIC significantly enhanced the mobilization of all Al, Fe, Ca, and P. Particulate (>0.4 μm) Al and Fe were mobilized during chemical and flow transitions, such as increasing DIC and dissolved organic carbon (DOC), and resumption of flow after draining the columns. Calcium and P were primarily in dissolved forms. Mechanisms such as ion exchange (Al, Fe, Ca), ligand- and proton-promoted dissolution (Al and Fe), and ligand exchange (P) were the likely chemical mechanisms for the mobilization of these species. One column was packed with dried and sieved B-horizon soil. The effluent from this column had DOC, Al, and Fe concentrations considerably higher than those in the intact columns, suggesting that these species were mobilized from soil's microporous structure that was otherwise not exposed to the advective flow. Calcium and P concentrations, however, were similar to those in the intact columns, suggesting that these elements were less occluded in soil particles.

Keywords Forest soils · Aluminum · Iron · Phosphorus · Calcium · Dissolved inorganic carbon · Bear Brook Watershed Maine

Introduction

Enhanced mobilization of metal species and P from soils into surface waters in forested ecosystems can be a significant water quality problem. Metals such as Al are not essential nutrients and can be toxic to fish, whereas excesses of the plant

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nutrient P in surface waters can lead to eutrophication. Aluminum precipitated in the water column of surface waters, on the other hand, can scavenge dissolved P (Kopáček et al. 2001; Norton et al. 2006) and trace metals in surface waters.

Mobilization of metals and P from forest soils occurs due to many factors. Acid deposition decreases the pH of soil solution, leading to an increase in the mobilization of cations, especially Al (Cronan and Schofield 1979). Concerns about global climate change have focused primarily on carbon dioxide (CO_2; Robinson et al. 1998). Although changing the CO_2 concentration in the atmosphere from $10^{-3.5}$ to $10^{-3.3}$ does little to the soil atmosphere, high concentrations of CO_2 in subsoils due to microbial and root respiration can increase metal mobilization, including base cations (Norton et al. 2001), Fe, and Al (David and Vance 1989; Su and Suarez 1997). Dissolved inorganic carbon (DIC) is the sum of carbonic acid ($H_2CO_3{}^* \approx CO_{2(aq)}$), bicarbonate anion ($HCO_3{}^-$), and carbonate anion ($CO_3{}^{2-}$) in water, with the concentration of each species depending on solution pH. Mechanisms for DIC adsorption to mineral oxides have been studied (Villalobos and Leckie 2000, 2001; Bruno et al. 1992; van Geen et al. 1994; Schulthess et al. 1998). Bruno et al. (1992) reported that the dissolution of metal oxide surfaces through ligand-promoted dissolution was related to the concentration of DIC bound to the surface sites.

Dissolved organic carbon (DOC) increases the dissolution rate of minerals by decreasing the pH, forming complexes at the mineral surface, and sequestering dissolution products as organic complexes (Furrer and Stumm 1986; Zinder et al. 1986; Pohlman and McColl 1988; Drever and Stillings 1996; Ochs 1996). More specifically, low molecular weight organic acids (LMWOA) that originate primarily from root exudates and soil fungi can also be transported through the soil. Although they make up <10% of DOC in soils, LMWOA greatly affect soil processes due to their small size, high solubility, continual formation, and ability to form strong complexes with metals (Homann and Grigal 1992; Fox 1995). LMWOA are more likely to increase the dissolution rate of mineral surfaces than larger molecular weight humic and fulvic acids. This is due to the ability of the LMWOA to form mononuclear bidentate complexes with surface metal centers during mineral dissolution (Furrer and Stumm 1986). Humic and fulvic acids, on the other hand, largely form monodentate multinuclear complexes that do not promote mineral dissolution.

Although studies have shown that the mobility of P largely depends on the mobility of cations such as Al, Fe, and Ca in the soil (Lindsay 1979; Kaiser and Zech 1996), ortho-P is also involved in anion exchange in the soil–soil water system. The most important competing anion in soil water is DOC that competes through ligand exchange and competitive sorption mechanisms (Parfitt et al. 1976; Turner and Kramer 1991).

Transition in the flow regime and solution chemistry can also lead to mobilization of particulate metal and P species. In unsaturated porous media, colloids attach at the air–water interface (Wan and Wilson 1994). The movement of these colloids in the soil is proportional to the density of air bubbles (Gomez-Suarez et al. 1999). In situ field experiments with ponded water found that colloids were mobilized due to the water surface level fluctuations (El-Farhan et al. 2000). Colloid mobility can also increase in a packed soil column when subjected to natural rainwater, resulting in higher colloidal repulsive surface energy, if ionic strength in the water decreases (Kaplan et al. 1993).

In our study, solutions with DIC concentration ranging between approximately 20 and 600 ppm were introduced into intact soil columns taken from reference and acidified forest soils at the Bear Brook Watershed in Maine (BBWM). Dissolved, particulate, and organically bound forms of Al, Ca, Fe, and P mobilized by the influents were analyzed from solutions taken at different times and depths along the soil column. We compared the response of intact and homogenized soil columns to assess mechanisms that control mobilization of Al, Fe, Ca, and P by variable DIC concentration and soil solution flow rate.

Materials and methods

The BBWM is a paired watershed consisting of the East Bear (reference) and West Bear (treated) watersheds located in eastern Maine approximately 50 km from the Gulf of Maine (44°52′ N, 68°06′ W). The soils are Spodosols, Inceptisols, and Folists with a mean thickness of ~1 m (Fernandez et al. 2003). Bimonthly treatments of 1,800 eq $(NH_4)_2SO_4$ ha^{-1} a^{-1} have been applied to West Bear since 1989. The untreated East Bear watershed serves as the reference.

Intact soil cores, 4.45 cm in diameter and ~16–24 cm long, were collected using a piston corer in acrylic casings. Six cores were removed from East Bear, four consisting of the B horizon only and two including the O and B horizons. One core from West Bear included the O and B horizons. The casings used for core collection were fitted with end caps in the laboratory and used as flow-through columns. The columns had side ports at 3.5 cm depth increments with one immediately below the top of the B horizon for sample collection at different depths. Soil characterization at BBWM is presented in Fernandez et al. (2003) and Sherman et al. (2006).

An experiment was conducted with homogenized B horizon from East Bear in a 5.0 × 17.8-cm column. Soils were dried at room temperature and sieved to isolate materials retained between a 0.5-mm and a #140 sieve. The columns were packed while using slight vibrations to promote settling. Nine sampling ports were spaced along the side of the column. The three upper ports were spaced 1.0 cm apart, and the lower six were spaced 2.0 cm apart.

Varying volumes of solutions containing degassed 0.1 mM NaCl were initially passed through the columns. A background ionic strength of 0.1 mM was adjusted by NaCl to simulate natural conditions in BBWM water. Columns were then subjected to solutions with different concentrations of DIC ranging from ~20 to 600 ppm at a flow rate between 1.10 and 1.55 ml min^{-1}. Although the higher DIC concentrations do not occur in the soil water at BBWM, the purpose of this study was to examine mechanisms of enhanced metal and P mobilization using the natural agent of DIC. Pure CO_2 gas was bubbled through 0.1 mM NaCl solution in the influent reservoir for different periods to obtain the desired DIC concentrations.

The sequence of manipulations of the columns is in Table 1. Each experiment began with an initial conditioning phase where a degassed 0.1-mM NaCl solution was run through the column. This was followed by an influent pulse with a specific DIC concentration and duration and then by a pulse of background 0.1 mM NaCl solution again followed by a pulse of higher DIC concentration. Columns 4–7 were allowed to drain under gravity for approximately 48 h after two discrete DIC pulses, followed by 0.1 mM NaCl solution and a high concentration DIC solution.

Table 1 Sequence of treatment steps for influent solutions and DIC concentrations

Sequence of treatment steps		Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7
0.1 mM NaCl	PV	0.6	0.5	1.2	11.2	5.7	18.1	4.5
DIC pulse 1	ppm	20	24	173	213	582	0[a]	443
	PV	2.4	4.4	8.6	25.9	17.2	20.5	15.9
0.1 mM NaCl	PV	21.6	4.7	7.0	12.3	22.2	18.2	2.2
DIC pulse 2[b]	ppm	40	40	347	309	–	470	–
	PV	16.1	6.4	15.3	28.7	–	19.3	–
0.1 mM NaCl	PV	7.0	5.4	8.4	11.3	–	4.1	–
0.1 mM NaCl[c]	PV	–	–	–	13.9	5.4	4.2	6.3
DIC pulse 3	ppm	–	–	–	185	547	460	460
	PV	–	–	–	25.3	22.2	36.7	14.7
0.1 mM NaCl	PV	–	–	–	3.8	4.2	2.6	2.9

PV pore volume

[a] 2.5 ppm DOC from Bear Brook O Horizon in influent

[b] Only when columns had a second continuous DIC run

[c] These columns were drained prior to introducing the 0.1-mM NaCl solution

Effluent samples were collected regularly from the bottom port. The effluent pH was continuously monitored in a closed cell using a combination pH electrode (Orion). Samples for DIC measurements were withdrawn using a 50-μL syringe and immediately injected into a total carbon analyzer (OI Analytical TOC Analyzer Model 1010) to avoid CO_2 degassing. When steady-state DIC concentration occurred at the bottom port, effluent samples were taken from the side ports to study transport along the depth. Samples were analyzed for DOC, Al, Ca, Fe, and P. Metals and P were fractionated into total, dissolved, and organically bound forms. Dissolved fraction samples were filtered through 0.4-μm polycarbonate filters immediately after collection. Samples for organically bound fractions were filtered through 0.4-μm polycarbonate filters and then passed through Dowex HCR-S cation-exchange resin in H^+ form. The resin was periodically regenerated using a 0.008% HCl, 0.575 g L^{-1} NaCl solution, as recommended by the manufacturer. All samples were acidified with 0.1 M ultrapure nitric acid after processing. Samples were stored at 4°C in the dark until analysis. Metal and P samples were analyzed using an inductively coupled plasma atomic emission spectrometer (Varian).

Results

Influent solutions of varying DIC concentrations were passed through homogenized and intact soil columns. Table 2 shows the influent DIC and effluent DOC, total Al (Al_t), Ca (Ca_t), Fe (Fe_t), and P (P_t) concentrations. The influent DIC concentrations in the homogenized soil column were 15 ppm with pH 4.6, compared to DIC concentrations in the intact soil columns 1 and 2 that ranged from 20 to 40 with pH 4.1 to 3.8. The DIC concentration for intact soil columns 3–7 ranged from 185 to 582 ppm with pH 4.1 to 3.8. Effluent concentrations of DOC, Al_t, and Fe_t were all considerably higher in the column with homogenized soil than those in the columns with intact soils. However, the effluent P_t concentrations were higher and the Ca_t was similar in the intact soil columns 1 and 2 compared to the homogenized soil column. To describe the physical characteristics of the intact soil columns with respect to solute transport, NaBr, a conservative tracer, was run through columns 1–5, and the breakthrough curves were modeled using the analytical solution to the advection–dispersion equation (Parker and van Ganuchten 1984). The breakthrough results of soil columns with high influent DIC concentrations (185–582 ppm) are presented first, followed by those of low DIC concentrations (20–40 ppm).

High DIC columns

The influent solutions in columns 3 to 7 had DIC concentrations in the ~300–550 ppm range (Table 1). The breakthrough curves for DIC, pH, Al_t, Ca_t, Fe_t, and P_t from column 7 are shown in Fig. 1a, b. Breakthrough curves from other columns are qualitatively similar to those of column 7 (Holmes 2007). Column 7 consisted of a 21.8-h conditioning phase with 0.1 mM NaCl solution followed by a ~24-h pulse of 443 ppm DIC solution. This was followed by another 3.2-h pulse of 0.1 mM NaCl solution. The influent solution was then stopped and the column was allowed to drain under gravity for 48 h. After this, 24.8 h of 0.1 mM NaCl solution was introduced into the column, followed by a final 22.1-h pulse of 460 ppm DIC that was then followed by a 4.3-h pulse of 0.1 mM NaCl solution.

During the initial conditioning phase, the concentrations of DOC, Al_t, Ca_t, Fe_t, and P_t were quite high (Fig. 1a, b) and then decreased relatively rapidly. Within ~3.2 pore volumes (6.8 h), the effluent concentrations of Al_t, Ca_t, Fe_t, and DOC dropped 40–70% of the initial effluent concentration.

The introduction of high DIC concentrations into the columns caused an immediate increase in the Al_t, Ca_t, Fe_t, and P_t concentrations (Fig. 1a, b). Al_t, Ca_t, and Fe_t concentrations varied proportionally throughout both pulses in the effluent solution with the DIC concentration, with r^2 values of 0.54, 0.26, and 0.15, respectively. These concentrations decreased sharply after the influent DIC solution was replaced by the 0.1-mM NaCl solution with no added DIC. However, while P_t concentration did increase substantially with the introduction of DIC, its behavior was much more

Table 2 Effluent concentrations and percentages of total NH_4Cl-extractable Al, Ca, Fe, and P released from the soil pools of each column

	Homogenized column	Intact column 1	Intact column 2	Intact column 3	Intact column 4	Intact column 5	Intact column 6	Intact column 7
Watershed	East Bear	East Bear	East Bear	East Bear	East Bear	East Bear	East Bear	West Bear
Soil horizon	B	B	O, B	B	B	O, B	B	O, B
Treatment DIC					213		0	
(ppm)		20	24	173	309	582	470	443
	15	40	40	347	185	547	460	460
Effluent pH range	4.1–4.83	4.4–4.87	4.57–4.71	4.24–4.76	4.22–4.89	4.32–4.97	4.07–4.91	4.19–4.81
Total solution (L)	–	10.9	6.6	8.4	27.7	10.1	14.5	6.5
Total solution (PV)	–	47.6	21.3	40.6	132	76.9	123	46.5
% Al released[a]	–	1	2	4	12	5	6	5
% Ca released[a]	–	15	5	46	52	61	160	18
% Fe released[a]	–	2	3	6	13	105	150	21
% P released[a]	–	670	620	2100	2700	1300	950	450
Effluent Al_t							1.2 ± 0.5	
(ppm)[b,c]		0.2 ± 0.02	0.3 ± 0.04	0.8 ± 0.2	1.2 ± 0.2	1.2 ± 0.5	0.6 ± 0.1	2.2 ± 1.4
	10.3 ± 5.2	0.3 ± 0.01	0.3 ± 0.02	1.3 ± 0.4	1.5 ± 0.6	0.6 ± 0.1	1.0 ± 0.3	1.9 ± 0.6
Effluent Ca_t							1.4 ± 0.7	
(ppm)[b,c]		0.3 ± 0.01	0.4 ± 0.03	1.3 ± 0.3	0.6 ± 0.3	1.9 ± 0.2	2.7 ± 0.8	3.4 ± 1.0
	0.4 ± 0.4	0.2 ± 0.09	0.2 ± 0.08	0.8 ± 0.2	0.5 ± 0.3	3.2 ± 3.1	3.0 ± 0.9	2.5 ± 0.2
Effluent Fe_t							1.2 ± 0.8	
(ppm)[b,c]		0.04 ± 0.02	0.07 ± 0.04	0.07 ± 0.04	0.07 ± 0.08	1.2 ± 0.8	1.3 ± 0.3	0.6 ± 0.4
	4.7 ± 3.2	0.04 ± 0.04	0.02 ± 0.01	0.14 ± 0.09	0.12 ± 0.12	2.9 ± 2.2	5.0 ± 2.1	0.6 ± 0.3
Effluent P_t							0.09 ± 0.05	
(ppm)[b,c]		0.4 ± 0.4	1.4 ± 0.6	5.2 ± 3.1	0.8 ± 1.4	4.7 ± 5.2	2.2 ± 2.8	2.1 ± 3.4
	0.07 ± 0.04	1.1 ± 1.3	1.5 ± 0.7	6.4 ± 4.1	1.1 ± 1.8	1.6 ± 2.2	0.2 ± 0.2	2.3 ± 3.6
Effluent DOC							16.4 ± 4.1	
(ppm)[b,c]		6.6 ± 4.9	5.8 ± 4.6	–	9.8 ± 15.1	4.1 ± 0.9	7.9 ± 2.7	9.2 ± 2.7
	500 ± 275	2.2 ± 0.9	3.4 ± 2.6	–	4.1 ± 3.3	4.9 ± 1.3	11.0 ± 5.0	7.9 ± 1.4

PV pore volumes

[a] Species released with respect to the solid-phase NH_4Cl-extractable concentrations reported by Fernandez et al. (2003)

[b] Volume-averaged effluent concentrations and standard deviations corresponding to the maximum DIC concentration

[c] Each row of metal and P concentrations corresponds to the same row of treatment DIC concentration above

erratic than for the other species. Although the DIC concentrations in the two pulses were similar in column 7, the maximum concentrations of each species changed between the two DIC pulses (Table 1). As the DIC reached its maximum steady-state concentration of 443 ppm in pulse 1, the maximum effluent concentrations of Al_t, Ca_t, Fe_t, and P_t were 4.2, 4.7, 1.2, and 11.1 mg L^{-1}, respectively. Pulse 2 began after the column was drained by gravity for 48 h. Pulse 2 had maximum effluent concentrations of Al_t, Ca_t, Fe_t, and P_t of 2.4, 2.6, 0.8, and 8.7 mg L^{-1}, respectively, showing a decrease in all concentrations compared to pulse 1.

The mobilized Al_t, Ca_t, Fe_t, and P_t, as a percentage of NH_4Cl-extractable fractions, are reported in Table 2. For the high DIC columns, the total mass of Al released ranged from 4% to 12% of the mass of NH_4Cl-extractable (highly labile) Al, while mobilized Ca and Fe were somewhat higher, ranging from 17% to 160% and 6% to 150%, respectively, of their NH_4Cl-extractable fractions. Mobilized P_t, however, was considerably higher, ranging from 450% to 2,700% of the NH_4Cl-extractable P.

Figure 2a, b shows the breakthrough curves of the speciated Al and Fe for column 7, respectively. A subset of effluent Al_t, Ca_t, Fe_t, and P_t samples were filtered through 0.45-µm filters to separate particulate (subscript p, calculated by difference) and total dissolved (subscript d) fractions. For some samples, the total dissolved fraction was

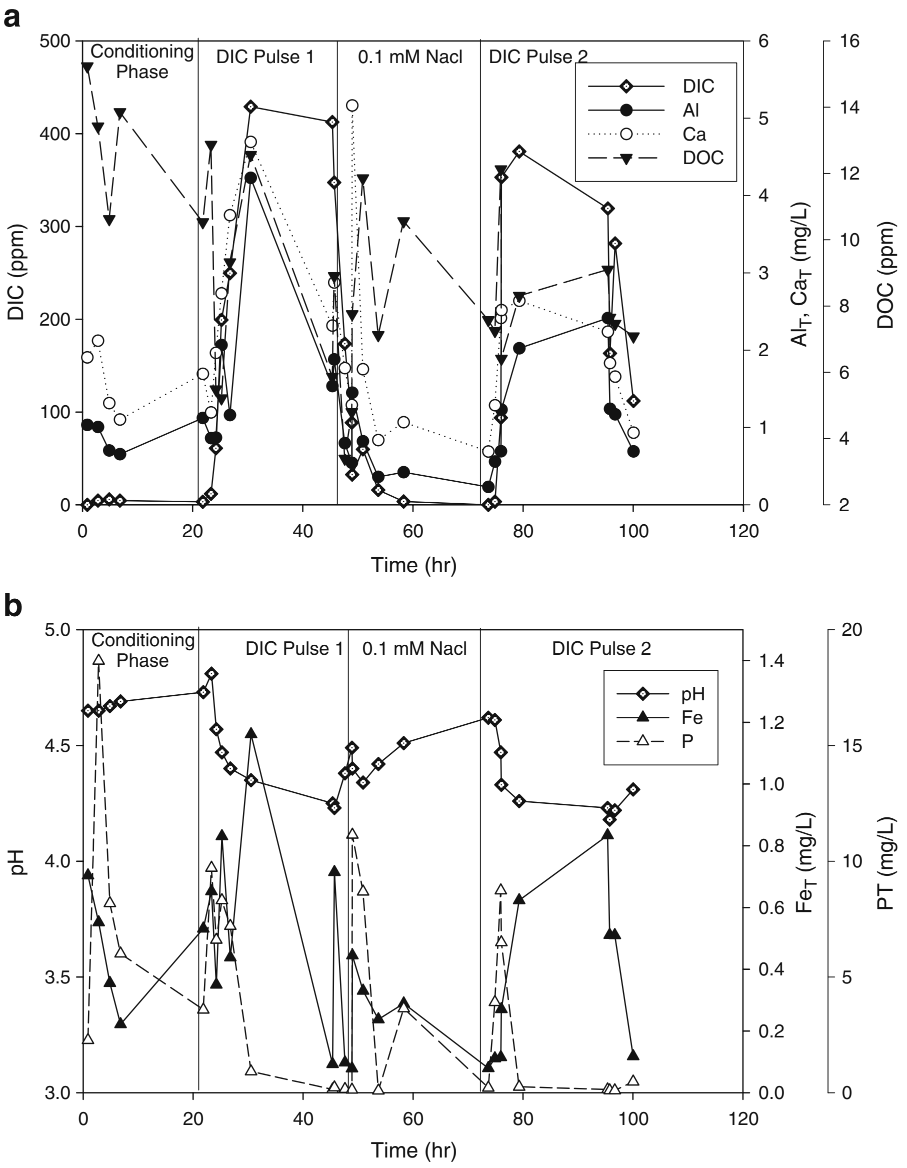


Fig. 1 **a** Breakthrough curves for DIC, Al_t, Ca_t, and DOC in column 7. **b** Breakthrough curves for pH, Fe_t, and P_t in column 7

then passed through a cation-exchange resin. In the case of metals, this procedure separates the freely dissolved species (subscript f), which are predominantly cationic in this pH range, from the organically bound species (subscript o), which carry an overall negative charge.

Al_d, Al_o, and Al_p concentrations all increased with increasing DIC concentrations, with Al_p showing the highest concentrations of all Al species and the strongest correlation with DIC ($r^2 = 0.57$) compared to other analytes in column 7 (Fig. 2a). Al_p was rapidly mobilized in all of the high DIC columns where samples were speciated. Rapid increases in Al_p occurred at the beginning of the conditioning phase and at the beginning of the DIC pulse 1 and to a lesser extent when the 0.1-mM NaCl solution was introduced at the beginning of the experiment and 48 h after the column was drained (Fig. 2a). For example, just before DIC pulse 1 was introduced in column 7, Al_p concentration was 0.26 ppm, and after its introduction, the Al_p concentration

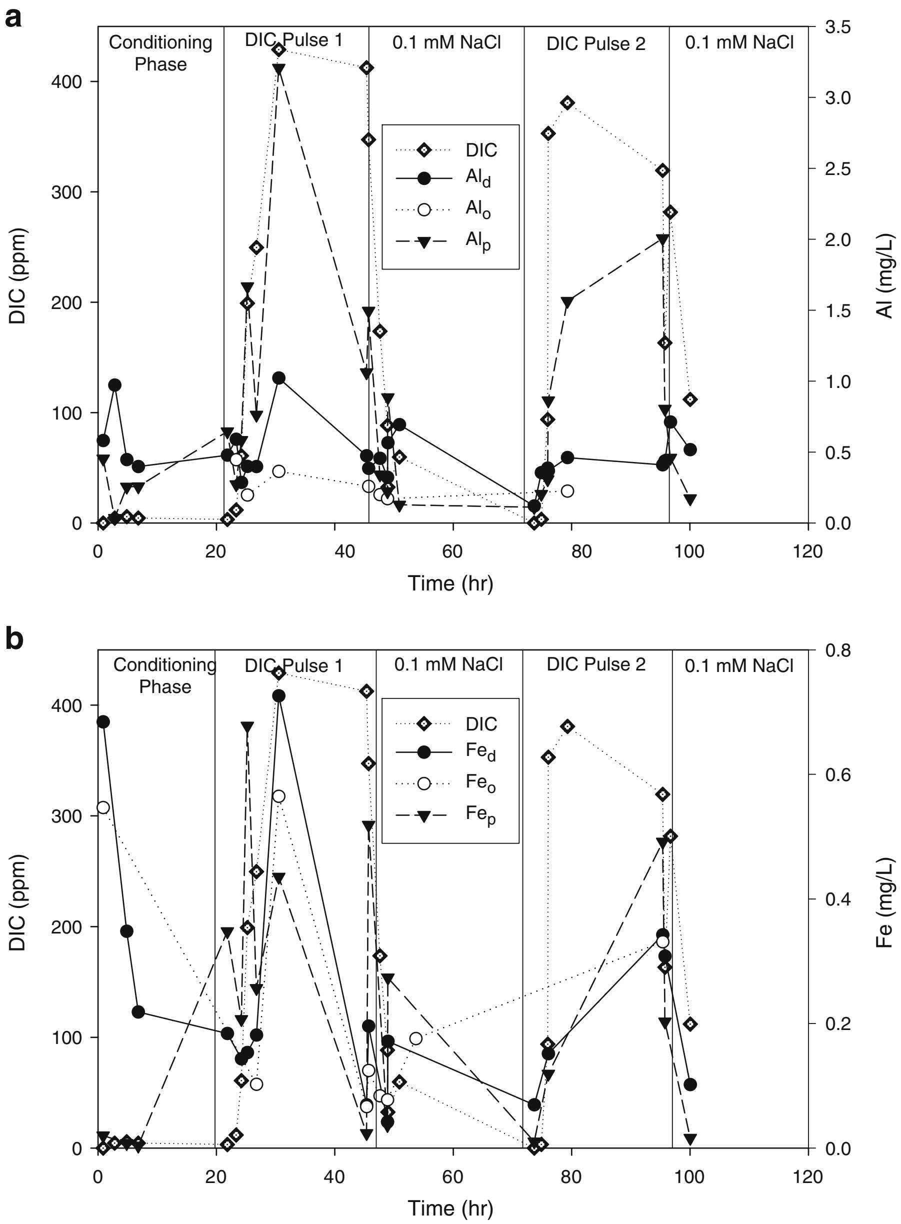


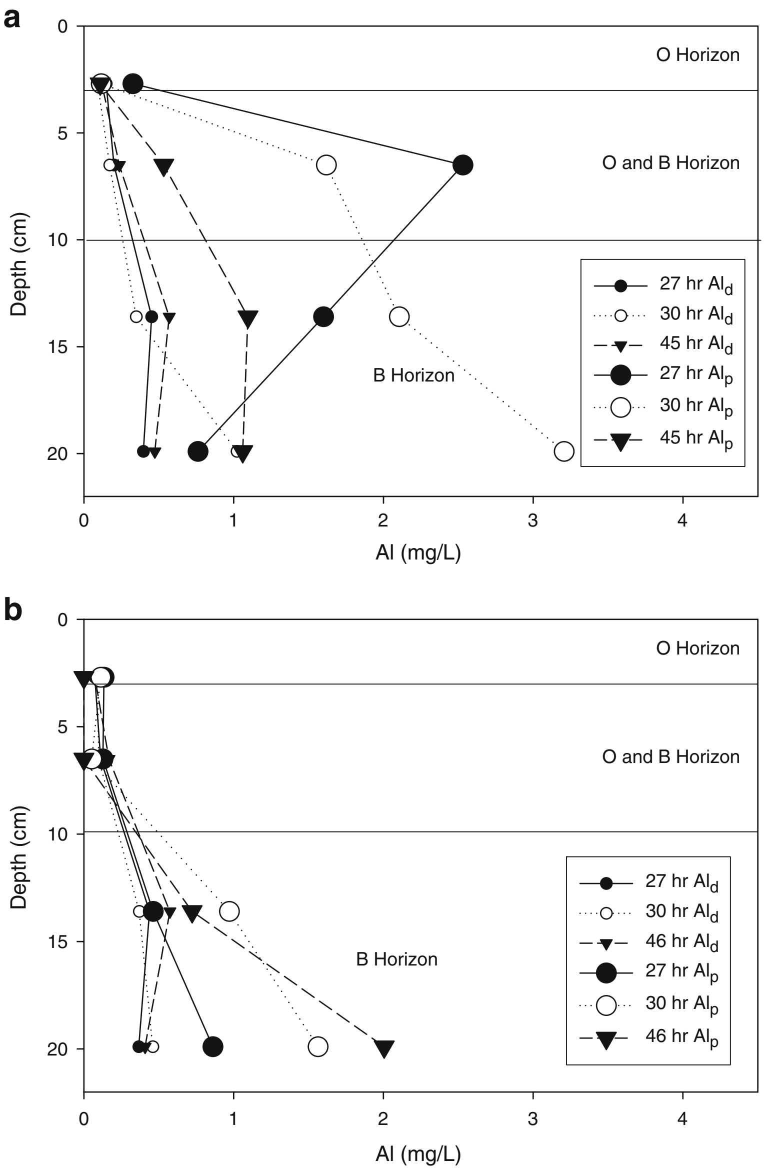
Fig. 2 **a** Breakthrough curves of DIC and Al_d, Al_o, and Al_p in column 7. **b** Breakthrough curves of DIC and Fe_d, Fe_o, and Fe_p in Column 7

rapidly increased to 3.21 ppm and then decreased to an average concentration of 1.92 ± 1.13 ppm for the remainder of the DIC pulse.

Similar to Al, effluent Fe species increased with increasing DIC concentrations (Fig. 2b). Individual Fe species did not show strong correlations with the DIC concentrations in any of the columns ($r^2 = 0.01$ to 0.06). Fe_p was the dominant Fe species in column 7 most of the time (Fig. 2b), but this behavior was not consistent among all columns. Fe_p increased with increasing DIC concentration in all high DIC columns. Fe_p also rapidly increased when a DIC pulse was introduced (Fig. 2b) and when the 0.1 mM NaCl solution was introduced at the beginning of the experiment and after the column was drained (for columns 5, 6, and 7).

Transport of Al and Fe species with depth in the soil profile for columns 4 to 7 was evaluated. Figures 3a, b and 4a, b represent samples taken

Fig. 3 **a** Al_d and Al_p concentrations along the depth of column 7 at different times during the steady-state maximum concentration of DIC pulse 1. DIC = 443 ppm. **b** Al_d and Al_p concentrations along the depth of column 7 at different times during the steady-state maximum concentration of DIC pulse 2. DIC = 460 ppm



simultaneously at four different side ports in column 7 during the steady-state maximum DIC concentrations of 443 and 460 ppm, corresponding to DIC pulses 1 and 2, respectively (Table 1). A gradual increase in the Al_d concentration with depth in column 7 occurred (Fig. 3a, b), even though the concentrations were relatively similar at different times for a given DIC pulse and between DIC pulses 1 and 2 (Fig. 3a, b). During the DIC pulse 1, the Al_p concentrations, however, increased sharply with depth, especially initially (Fig. 3a). At $t = 27$ h, which corresponds to the time when the effluent DIC concentration reached its steady-state maximum, a sharp initial increase in Al_p was followed by a decrease over the depth of the soil core. With time, the Al_p concentration diminished higher in the column, and at $t = 45$ h, lower Al_p concentrations were observed at all depths compared to $t = 30$ h (Fig. 3a). For DIC pulse 2, Al_p was mobilized but at lower concentrations than during DIC pulse 1 (Fig. 3b).

Figure 4a, b shows the effluent Fe_d and Fe_p with depth in column 7 during the steady-state maxi-

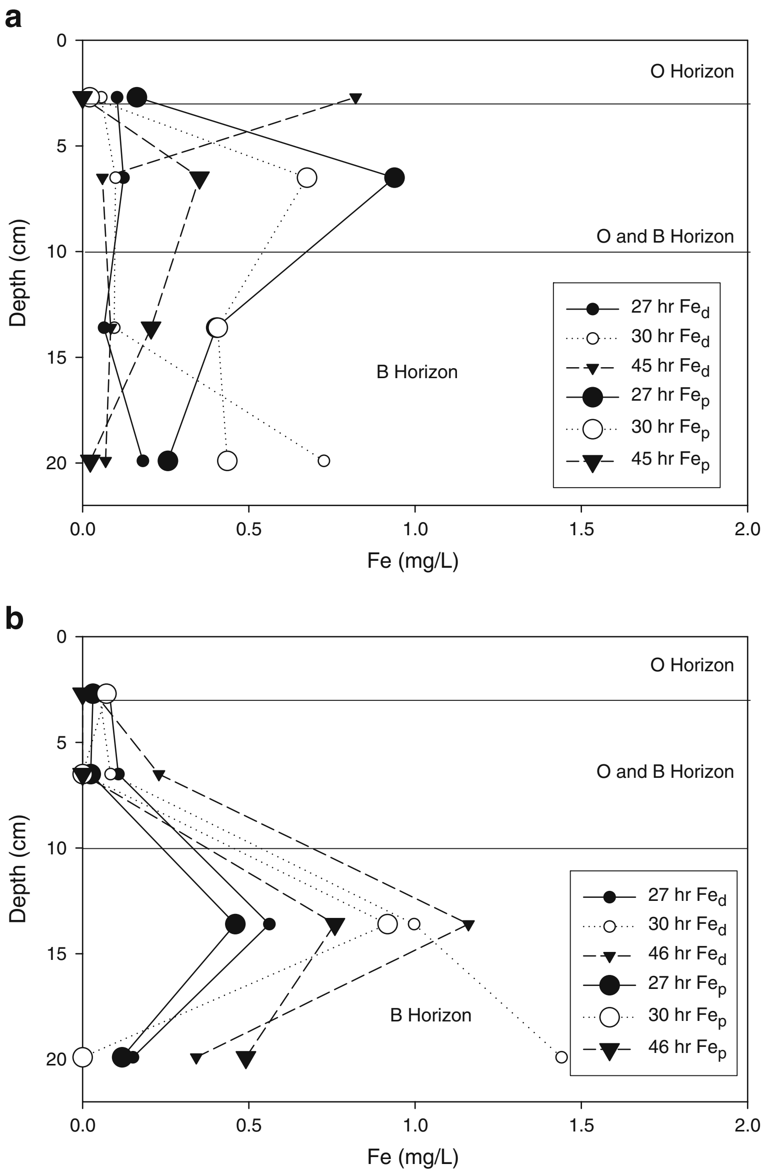


Fig. 4 **a** Fe_d and Fe_p concentrations along the depth of column 7 at different times during the steady-state maximum concentration of DIC pulse 1. DIC = 443 ppm. **b** Fe_d and Fe_p concentrations along the depth of column 7 at different times during the steady-state maximum concentration of DIC pulse 2. DIC = 460 ppm

mum DIC concentrations of 443 and 460 ppm, corresponding to DIC pulses 1 and 2, respectively (Table 1). During DIC pulse 1, Fe_p was mobilized in the mixed zone of O and B horizons, but its concentration decreased with time due to the depletion of labile Fe_p with depth due to colloid reattachment to the soil matrix (Fig. 4a). The peak Fe_p concentration was observed deeper in the column during DIC pulse 2 (Fig. 4b).

In all of the high DIC columns, Ca was almost completely in dissolved form. For example, in column 7, at the steady-state concentrations of DIC pulses 1 and 2, Ca_d was 86 ± 12% and 92 ± 40% of the Ca_t in solution, respectively. Ca_p is thought to be associated with Al_p and Fe_p because it was mobilized only during chemical and flow transients. Organic Ca (Ca_o) was 42 ± 11% and 55 ± 11% of the overall Ca_d in DIC pulses 1 and 2 in column 7, respectively.

Phosphorus was also almost completely in the dissolved form in the high DIC columns. During the steady-state concentrations of DIC pulses 1 and 2 in column 7, P_d was 87 ± 3% and 92 ± 15% of P_t, respectively. However, P_p was mobilized similarly compared to Ca_p during chemical and flow transients. For example, in column 7, P_p concentration increased from 0.91 to 3.09 ppm immediately after the introduction of the DIC pulse 1. The P_p concentration reached 0.56 ± 0.77 ppm when the DIC was at its steady-state concentration. P_p mobilization also occurred at the beginning of the conditioning phase in column 7 (not shown). Along the depth of column 7, P_d had a maximum concentration in the initial measurement varying from 6.7 to 1.0 ppm (data not shown here). Over time, P_d concentrations decreased to 0.02 ppm.

Concentrations of DIC and mobilized DOC were poorly correlated ($r^2 = 0.08$) in column 7. In column 6, the initial pulse contained no additional DIC and only a 2.5-ppm addition of DOC taken from the East Bear's O horizon (Table 1). Strong positive correlations between effluent concentrations of Al_t, Ca_t, Fe_t, and P_t and the effluent DOC concentration in the absence of elevated DIC were observed in this column (Fig. 5). Al_o, Ca_o, and Fe_o constituted 76 ± 10%, 69 ± 10%, and 70 ± 18% of the total dissolved concentration of each species, respectively. However, after the introduction of 470 ppm of DIC into column 6, poor correlations between Al_t, Ca_t, Fe_t, and DOC were observed, and the correlation between P_t and DOC remained relatively unchanged. Al_o, Ca_o, and Fe_o fractions decreased to 53 ± 8%, 49 ± 4%, and 66 ± 13% in DIC pulse 2, respectively. Elevated DIC also caused higher mobilization rates of these species.

Low DIC columns

Columns 1 and 2 had DIC concentrations between 20 and 40 ppm (Table 1). The DIC pulse concentrations used for the low DIC columns were in the range of realistic field values for groundwater environments that are reported to be between 60 and 96 ppm (Stumm and Morgan 1996). Fernandez and Kosian (1987) found forest soil air at BBWM to consist of 0.3% to 0.8% of CO_2. Assuming a Henry's law constant of $10^{-1.27}$ L atm^{-1} at 10°C, DIC concentrations are likely to be 2 to 5 ppm in the soil water. Therefore, 20 and 40 ppm could be at the high end of what will occur in the natural environment of these acidic New England forest soils.

The breakthrough curves of effluent DIC, pH, Al_t, Ca_t, Fe_t, P_t, and DOC concentrations for column 1 are shown in Fig. 6a, b and consist of a 2.8-h conditioning phase with 0.1 mM NaCl solution, followed by an 8.5-h pulse of 20 ppm DIC. Following a 74.8-h 0.1 mM NaCl solution, a 55.8-h pulse of 40 ppm DIC solution was

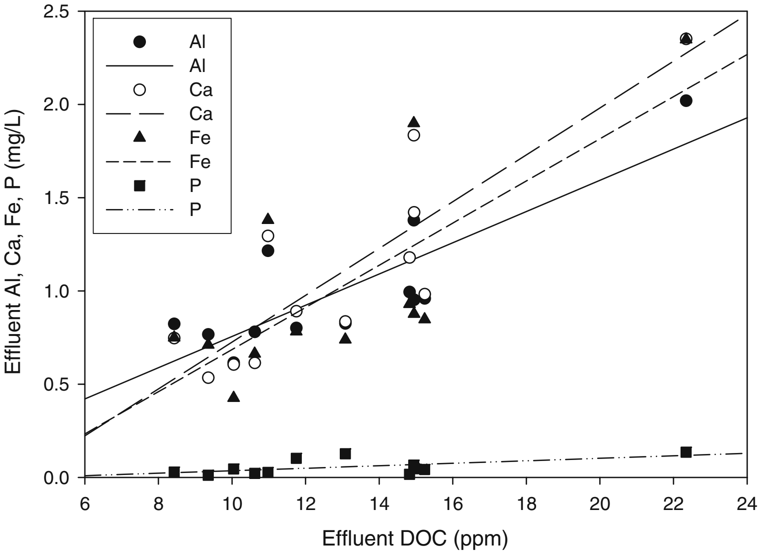


Fig. 5 Effluent Al, Ca, Fe, and P vs. DOC for the DOC-spiked pulse in column 6. Al, Ca, Fe, and P vs. DOC with $r^2 = 0.70$, 0.70, 0.65, and 0.54, respectively

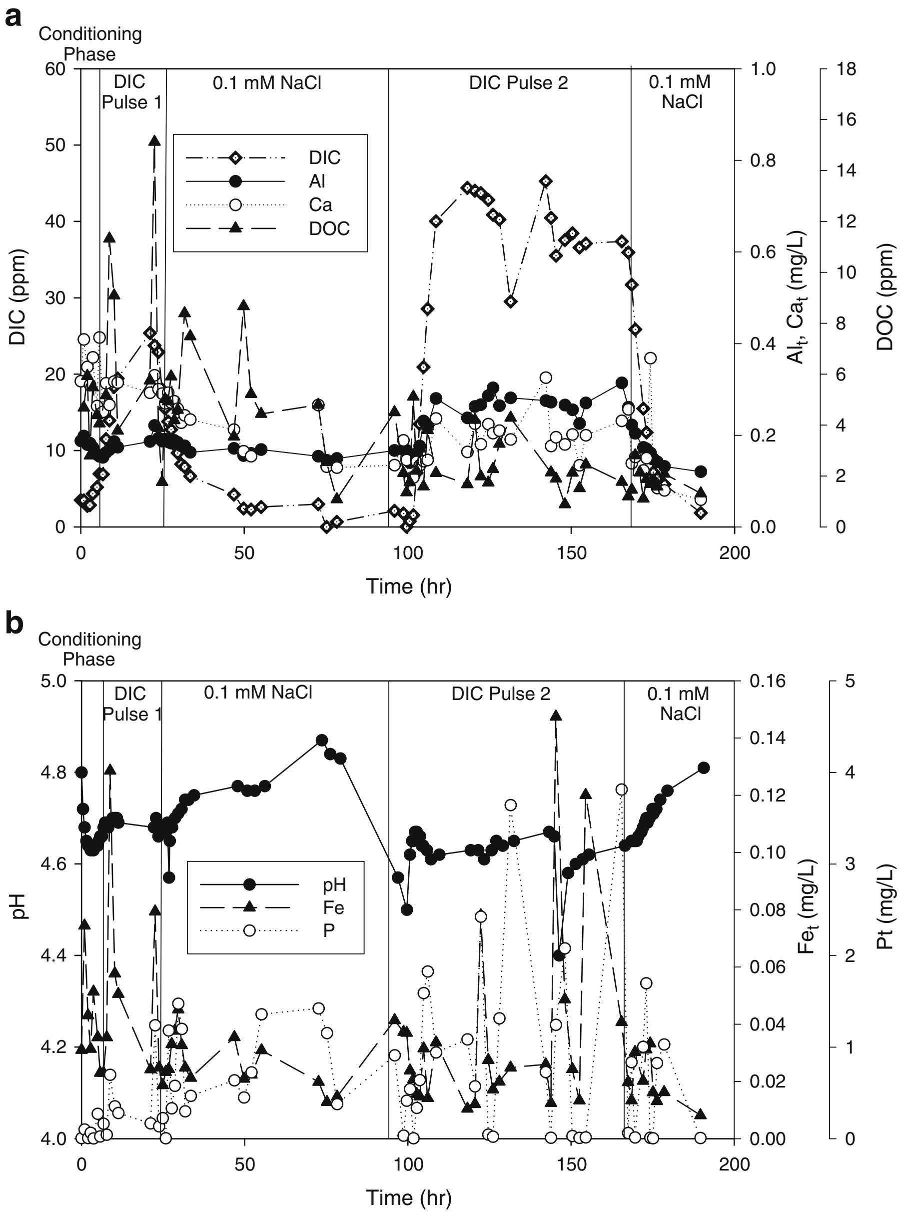


Fig. 6 **a** Breakthrough curves of DIC, Al_t, Ca_t, and DOC in column 1. **b** Breakthrough curves of pH, Fe_t, and P_t in column 1

introduced into the column. This was followed by a final 24.2-h pulse of 0.1 mM NaCl solution.

Similar to the high DIC columns, the low DIC conditioning step included the 0.1-mM NaCl solution. During this phase, the concentrations of DOC, Al_t, Ca_t, Fe_t, and P_t were initially quite high (Fig. 6a, b). The introduction of the first DIC pulse (20 ppm) did not cause a significant increase in the Al_t concentration (Fig. 6a). Such increase, however, was observed during the second DIC pulse (40 ppm). The Al_t concentration in the effluent of the low DIC columns varied proportionally with the DIC concentration ($r^2 = 0.40$), similar to the high DIC columns. P_t concentrations were unrelated to DIC ($r^2 = 0.02$), as also occurred in the high DIC columns. Ca_t and Fe_t decreased throughout the entire 20-ppm DIC pulse (Fig. 6a, b). At the beginning of the 20-ppm DIC pulse, the column had received less than one pore volume of 0.1 mM NaCl solution, which is perhaps insufficient to mobilize the more labile forms of Ca_t and Fe_t. The poor correlation between DIC and Ca_t and Fe_t concentrations ($r^2 = 0.00$ and 0.05, respectively) and lack of any shifts in the concentrations of these species indicate that DIC at 20 ppm did not mobilize Ca and Fe.

The 40-ppm DIC pulse that followed 74.8 h of background electrolyte caused a measurable response. The Al_t effluent concentration was proportional to the DIC concentration ($r^2 = 0.49$), while Ca_t and Fe_t were poorly correlated ($r^2 =$ 0.24 and 0.04, respectively) with DIC. However, the P_t concentration increased erratically ($r^2 =$ 0.06) compared to the trends of the other metals and nutrients. As the DIC reached its maximum steady-state concentration of 40 ppm in pulse 2, the maximum effluent concentrations of Al_t, Ca_t, Fe_t, and P_t were 0.31, 0.33, 0.15, and 3.6 ppm, respectively. The pH varied from 4.84 to 4.40 in the second pulse.

Lower concentrations of Al, Ca, Fe, and P were released in the low DIC than in high DIC columns, suggesting a direct relationship between DIC concentration and mobilization of these species. The mobilized species as a fraction of NH_4Cl-extractable species in low DIC columns were less than those in high DIC columns. The difference in the maximum amounts of NH_4Cl-extractable Al_t, Ca_t, Fe_t, and P_t in low DIC columns was 30% and increased in high DIC columns to 99%.

Discussion

Homogenized soil vs. intact soil cores

Metal mobilization is expected to increase with decreasing pH and increasing DIC concentrations (David and Vance 1989; Su and Suarez 1997). Table 2 shows that considerably higher concentrations of total Al, Fe, and DOC were released from the homogenized soil column than from the intact soil columns under otherwise similar conditions. Therefore, the higher Al_t, Fe_t, and DOC mobilization from the homogenized soil, where a considerably lower DIC concentration was introduced, could be attributed to disturbance of soil aggregates and changes in surface physicochemical characteristics brought about by drying, sieving, and repacking the soil. Even though we expect some disturbance to the soil column in the intact cores due to the action of the piston corer during sample collection, breakup of the soil microstructure did not take place to the same degree as in the homogenized soil.

Average effluent Ca_t concentration from the homogenized core was in the same range as that in the low DIC columns 1 and 2, but considerably lower than in the high DIC columns 3 to 7 (Table 2). Average P_t concentration was higher in all of the intact soil columns compared to the homogenized soil column (Table 2). The released Ca and P, unlike Al and Fe, were likely to have been primarily initially introduced into the soil from mineralization processes, such as P in leaf litter (Colpaert and Van Tichelen 1996) and Ca in leaf or branch litter (Songwe et al. 1997). As such, they can exist primarily in the exchangeable or sorbed forms at the external surfaces of the soil aggregates. However, the difference in the behavior of Ca and P can be linked to Al mobilization.

Homogenization destroys soil's microporous structure and, therefore, exposes surfaces that were otherwise physically inaccessible to advective flow. Soil aggregates in Spodosols are stabilized primarily by soil organic matter that originates from plants, animals, and microorganisms. Also, organometallic compounds act as bridges between the particles, resulting in aggregation (Bronick and Lal 2005). Soil homogenization leads to the mobilization of otherwise protected organic matter and Al and Fe pools that are not kinetically available in an intact soil column.

Metal and P mobilization

The rapid decrease of DOC, Al_t, Ca_t, Fe_t, and P_t following the initial introduction of the background electrolyte solution could perhaps be because of the depletion of the labile and easily mobilized fractions (Fig. 1a, b). This behavior was observed by Totsche et al. (2000) in a homogenized forest soil sample where they reported rapid initial mobilization of Al, Fe, and DOC followed by a rapid decrease in their concentrations. In nine pore volumes and at a flow rate of 1.74 ml h^{-1}, Al and DOC decreased approximately by 60% and 85%, respectively (Totsche et al. 2000).

In general, Al and Fe can be mobilized due to the direct interaction of proton and DIC species with the soil surfaces. DIC species adsorb to the surface sites of Fe(III) and Al (oxy)hydroxides (van Geen et al. 1994; Schulthess et al. 1998). van Geen et al. (1994) and Villalobos and Leckie (2001) proposed coordination of H_2CO_3 and HCO_3^- with the goethite (α-FeOOH) surface as inner sphere surface complexes that result in the displacement of surface hydroxyl groups. DIC species adsorb most effectively to Fe(III) and Al (oxy)hydroxides at pH between 5 and 7, which is slightly higher than the pH of our effluent solutions in Fig. 1b (van Geen et al. 1994; Schulthess et al. 1998; Bruno et al. 1992). Bruno et al. (1992) showed a direct correlation between the dissolution rate of hematite (α-Fe_2O_3) and the surface concentrations of $HCO_3{}^-$ and $CO_3{}^{2-}$. The introduction of DIC caused a decrease in pH (Fig. 1b). Therefore, mechanisms such as ion exchange, ligand-promoted dissolution proposed by Bruno et al. (1992), and proton-promoted dissolution due to the decreased pH (Stumm and Morgan 1996) may all contribute to the dissolution of Al and Fe in our soil columns. It should be noted that some of the mobilized Fe might be due to the microbially catalyzed reductive dissolution of soil Fe(III) hydroxide, following the depletion of dissolved oxygen due to microbial respiration, especially in some of the pore space.

Effluent Al_t and Fe_t concentrations varied with the DIC concentration (Fig. 1a, b). Mobilized Al_t and Fe_t were lower than (for Al) or approximately equal (for Fe) to their respective labile NH_4Cl-extractable fractions (Table 2). NH_4Cl extractions of BBWM soils were performed on homogenized samples from the site but not on the soil cores collected for this study (Fernandez et al. 2003). Therefore, the concentrations of exchangeable soil cations reported are likely not exact representations of the core composition.

In column 7, Al_p and Fe_p constituted the major mobilized fractions of Al_t and Fe_t. In all other columns, colloidal fractions of these species were also observed in the effluent, even though not as the dominant fraction. Furthermore, there were sharp increases in the release of these species due to chemical perturbations. Abrupt changes in solution chemistry and flow rate can lead to destabilization of the colloidal aggregates in soil, as observed in this study (Fig. 2a, b). Changes in ionic strength and composition (Kaplan et al. 1993; Nightingale and Bianchi 1977; Faure et al. 1997; Seaman et al. 1995; Grolimund and Borkovec 1999; Bunn et al. 2002), increases in pH (Ryan and Gschwend 1994; Swartz and Gschwend 1998, 1999; Roy and Dzombak 1996; Bunn et al. 2002), and introduction of ligands (Hubbe 1987; Ryan and Gschwend 1994; Swartz and Gschwend 1998; Seaman and Bertsch 2000; Liang et al. 2000) have resulted in colloid mobilization in porous media. El-Farhan et al. (2000) showed that abrupt changes in flow rate, such as those introduced in the soil at the beginning of the experiment and after draining columns 4–7, simulate rainfall or snowmelt events and may cause an increase in colloid mobilization. Bunn et al. (2002) proposed that the dissolution of the Fe (oxy)hydroxide-coated aquifer material due to chemical perturbation resulted in colloid mobilization. A similar mechanism could have occurred in this study, whereby DIC interaction with and dissolution of surface Al and Fe (oxy)hydroxides can result in colloid mobilization, shown especially in the results of column 7.

To study DIC interaction with the soil surfaces, we compared the breakthrough of DIC with that of the assumed conservative Br tracer (Fig. 7). Analysis of the DIC breakthrough curves allows the characterization of DIC sorption onto soil. Equilibrium reaction for reversible sorption of inorganic carbon onto soil surfaces may be written as:

$$\mathrm{DIC} \Leftrightarrow \mathrm{IC}_{\mathrm{ads}} \qquad K_{\mathrm{D}}$$

where IC_{ads} is the adsorbed inorganic carbon concentration (in milligrams per gram of dry solid) and K_D is the equilibrium constant for this reaction.

The assumption of reversible equilibrium sorption is justified in this case because the effluent-to-influent ratio for DIC approaches 1, suggesting no irreversible sorption. Values of log K_D for columns 1, 3, and 5 are shown in Table 3. Columns 1 and 3 contained the B horizon only, and column

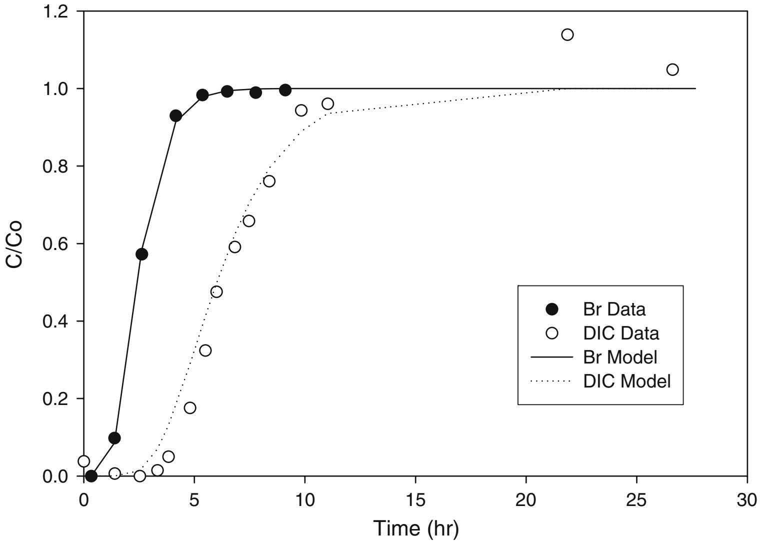


Fig. 7 Experimental and modeled breakthrough curves for Br and DIC in column 3 for a total DIC = 347 ppm

5 contained the O and B horizons. Log K_D values ranged between −0.82 and −0.07, showing small variations among the columns, as well as between the influent DIC concentrations, except for column 5 where they were nearly similar. The relatively low K_D values suggest a weak but reversible sorption of inorganic carbon to soil surfaces.

The mass of IC_{ads} can be estimated from Fig. 7 by accounting for the difference between the Br and DIC breakthrough curves. Table 3 shows the molar mass of IC_{ads} and released P_t for columns 1, 3, and 5. The linear relationship between the IC_{ads} and released P_t suggests that P can be mobilized due to a ligand-exchange mechanism following the adsorption of DIC species at the soil surfaces (Fig. 8). This mechanism is especially plausible because the nearly equal stoichiometry between the released P vs. Al and Fe (Table 2) preclude $Al(OH)_3$ and $Fe(OH)_3$ mineral dissolution as the P release mechanism.

Figure 3a, b shows a gradual increase in the Al_d concentration along the depth of column 7, except at the lowest depth, with the majority of mobilization in the B horizon. Al_d concentration remains relatively constant for the duration of the DIC pulses. Al_p, however, displays a much higher concentration with depth at $t = 27$ h, suggesting colloid mobilization followed by attachment to the soil matrix (Fig. 3a). At $t = 30$ h, Al_p concentration increases with depth, implying its mobilization throughout the length of the column. At $t = 45$ h, Al_p mobilization decreased by nearly 70% compared to at $t = 30$ h (Fig. 3a). During pulse 2, Al_p mobilization rate is slower than during pulse 1, even though the DIC concentration is slightly higher in pulse 2 (Fig. 3b). This can be attributed to the release of more easily mobilized (more labile) Al_p fractions during pulse 1. Al_p mobilization rate increases with time and depth in the B horizon during pulse 2 (Fig. 3b).

Table 3 Log K_D, adsorbed inorganic carbon (IC), and P_t released for columns 1, 3, and 5 and their corresponding DIC concentrations

	Column 1		Column 3		Column 5	
Influent DIC (ppm)	20	40	173	347	582	547
Log K_D	−0.25	−0.59	−0.24	−0.07	−0.80	−0.82
DIC (moles adsorbed)	1.9×10^{-4}	3.7×10^{-4}	1.8×10^{-3}	8.3×10^{-3}	1.1×10^{-3}	4.1×10^{-4}
P_t (moles released)	4.5×10^{-6}	4.3×10^{-5}	6.9×10^{-5}	1.5×10^{-4}	1.3×10^{-4}	4.5×10^{-5}
IC_{ads}/P_t ratio	43.5	8.6	25.4	56.6	7.9	9.1

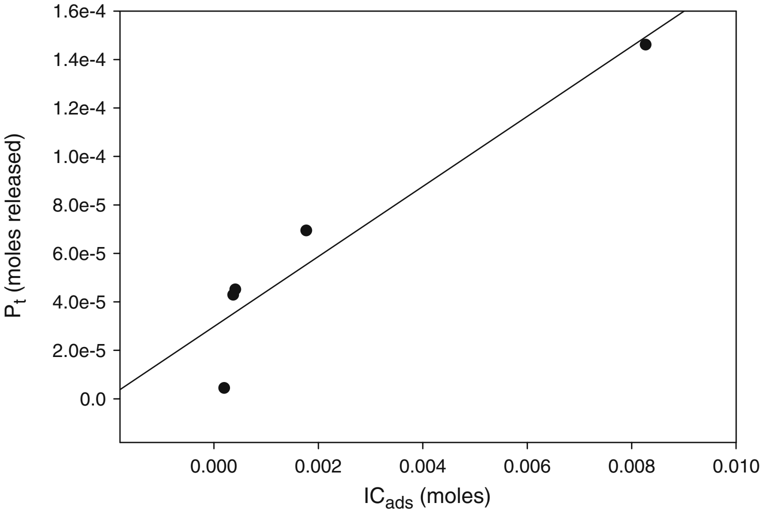


Fig. 8 Total moles of phosphorous released vs. moles of inorganic carbon adsorbed during the breakthrough of DIC in columns 1, 3 and 5. $r^2 = 0.90$

Similar to Al_d, Fe_d is initially mobilized primarily in the B horizon along column 7 (Fig. 4a, b). Fe_p shows an initial sharp peak at $t = 27$ h during pulse 1 in the mixed O and B horizons, with the peak decreasing with time, perhaps due to the depletion of the more labile Fe_p fraction (Fig. 4a). The location of the peak in Fe_p concentration moved lower in the column during pulse 2. Following its peak, Fe_p decreased with depth during both pulses due to attachment to the soil matrix in the B horizon.

Phosphorus is mobilized by a different mechanism than for Al and Fe. Phosphate can be mobilized by a ligand-exchange mechanism involving DIC and DOC. Sibanda and Young (1986) found that phosphate competes for surface adsorption sites on goethite, gibbsite, and two different B-horizon soils with humic and fulvic acids. Although P_t showed a poor correlation with respect to DIC in both high and low DIC columns, there was a substantial increase in the concentrations of P_t with DIC (Figs. 1b and 6b). Roy et al. (1999) found that total P concentrations in the East and West Bear streams were 2 and 4 ppb, respectively, during low flow and increased an order of magnitude during high flow. Most of the increase was as particulate P. In this study, P_t concentrations mobilized in the presence of DIC exceed the stream concentrations significantly (Figs. 1b and 6b). Mobilized P was significantly higher than the NH_4Cl-extractable P where the latter only made up ~6% of the inorganic P pools in the soils in BBWM (Sherman et al. 2006). As mentioned above, ligand exchange with DIC could be responsible for the large export of P from the column. Table 3 shows that increasing the influent DIC concentration in a given column results in the increase of mobilized P_t in that column. The variable IC_{ads}/P_t molar ratios among the columns (Table 3), however, reflect the heterogeneous nature of soil surfaces and possibly the labile P in each column.

High DIC columns released a higher concentration of Ca_t than the low DIC columns as well as the homogenized column. Also, Ca was primarily in the dissolved form, suggesting that it was not associated with the Al_p or Fe_p. The fact that the total mobilized Ca_t was less than or approximately equal to the NH_4Cl-extractable fraction and given that Ca is perhaps largely associated with the external soil surfaces as described above, ion exchange is the primary mechanism for its mobilization.

DOC relationship

Ligands mobilize DOC in soil columns. For example, Totsche et al. (2000) observed a direct relationship between DOC and added fluoride (F) as high as 171 ppm, suggesting that F displaced DOC from the soil surface via a ligand-exchange mechanism. They also observed correlations between

F and Al, Fe, and several other metals. Our results suggest that, even though DIC is effective in mobilizing metals, it is not effective in mobilizing DOC, even at concentrations as high as 443 ppm.

At pH > 4, more than half of the functional groups on natural organic acids that make up the DOC are deprotonated (Stumm and Morgan 1996). Ochs (1996) suggested that this allows larger molecular weight organic acids to bind at many surface sites, forming a stable multidentate surface complex. This may explain why DIC that adsorbs only weakly and reversibly to soil surfaces as shown above could not displace DOC at any significant rate.

We observed an increase in Al_t, Ca_t, Fe_t, and P_t concentrations with increasing DOC concentration (Fig. 6). Drever and Stillings (1996) found that, while the humic and fulvic acids do not increase and can inhibit mineral dissolution, the LMWOA increase dissolution through complexation of the surface metals in a mononuclear bidentate formation. It is expected that LMWOA are likely present and act as complexing ligands to mobilize Al_t, Ca_t, Fe_t, and P_t.

Conclusions

Addition of DIC as CO_2 to soil cores increases the mobilization of Al, Fe, and P. Soil homogenization, through drying and sieving, resulted in the release of considerably higher concentrations of Al, Fe, and DOC compared to the intact soil columns. The alterations of soil aggregate structure and surface physiochemical characteristics in these columns were likely the cause of these increases, underscoring the importance of using intact soils for laboratory simulations of the field environment. In the intact cores, mobilized Al_t and Fe_t varied proportionally with the rising and falling influent DIC concentrations for the most part, except that, in some cases, abrupt changes in solution chemistry or flow rate caused significant increases in the colloid mobilization. Mechanisms such as ion exchange and ligand- and proton-promoted dissolution were responsible for mobilizing Al and Fe. P mobilization in these soil columns was clearly altered by the presence of DIC despite the poor correlation between the two. The mobilized P concentration was considerably higher than soil's ion-exchangeable fraction, suggesting that ligand exchange with DIC plays an important role in P mobilization with changing soil air CO_2 concentrations. Ca was mobilized primarily through ion exchange due to the increase in proton concentration as a result of higher P_{CO2}. Both effluent P and Ca existed mainly in dissolved forms.

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