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Mobilization of Metals and Phosphorous from Intact Forest Soil Cores by Dissolved Inorganic Carbon: A Laboratory Column Study

Brett Holmes
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MOBILIZATION OF METALS AND PHOSPHOROUS FROM INTACT FOREST SOIL CORES BY DISSOLVED INORGANIC CARBON: A LABORATORY COLUMN STUDY

By

Brett Holmes

B.S. Worcester Polytechnic Institute, 2003

A THESIS Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science (in Civil Engineering)

The Graduate School
The University of Maine
May, 2007

Advisory Committee:

Aria Amirbahman, Associate Professor of Environmental Engineering, Advisor
Ivan J. Fernandez, Professor of Plant, Soil and Environmental Sciences
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Dissolved inorganic carbon (DIC) causes increased mobilization of dissolved, organically bound and particulate aluminum (Al), calcium (Ca), iron (Fe), and phosphorus (P) from the soils. Our objective was to examine whether increased metal solubility is attributed to increased DIC concentration in solution. Intact soil cores of 16.35 – 24.10 cm were taken from the O and B horizons from the East and West Bear Brook Watershed in Maine (BBWM) to conduct seven soil column transport experiments. DIC concentrations ranging from approximately 20 to 600 ppm with a background electrolyte solution of 0.1 M NaCl were introduced into the soil columns. To one column, a solution containing 2.5 ppm of dissolved organic carbon (DOC) extracted from the East Bear O horizon was added. DIC was introduced in two pulses of varying concentrations. Samples were continuously taken at the end of the column, and when steady-state condition with respect
to DIC concentration was achieved, samples were taken along the depth of the columns. Columns were characterized with a conservative tracer that showed an average porosity of $0.61 \pm 0.12$ and a dispersion coefficient of $0.88 \pm 1.12 \text{ m}^2 \text{s}^{-1}$. DIC was subject to reversible sorption and its movement was retarded by a factor of 1.2 to 2.1 compared to the conservative tracer corresponding to a $\log K_D = -0.82$ to -0.07. DIC significantly enhanced the mobilization of all metals and P. Colloidal Al and Fe were mobilized as a response to changes in the solution chemistry and flow regime. Ca and P were primarily in dissolved form. Mechanisms such as ion exchange (Al, Fe, Ca), ligand- and proton-promoted dissolution (Al and Fe) and ligand exchange (P) may explain mobilization of the species studied here. One column was packed with dried and sieved B-horizon material. The effluent from this column showed DOC, Al and Fe concentrations considerably higher than the intact columns, suggesting that these species were mobilized from the soil’s microporous structure that is otherwise not exposed to the advective flow. Ca and P concentrations, however, were similar to the intact columns, suggesting that these species are associated primarily with the soil’s external surface.
ACKNOWLEDGEMENTS

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I would also like to thank the staff at Dr. Ivan Fernandez’ Soil Science Lab for providing both technical and soil collection assistance in the lab and at the Bear Brook Watershed. Johanna Szillery and Micheal Sanclements were especially helpful in the field collection.

I thank the members of my advisory committee, Stephen Norton, Ivan Fernandez, and my primary advisor Aria Amirbahman. I would like to especially thank Aria for his patience, guidance, and sincerity in this process. I can not express my gratitude enough for his help in pushing me along in this project.

I would also like to thank my Mother, Kelly Coughlin, and Father, Michael Holmes for listening to my concerns, problems and giving me words of encouragement. I am lucky to have them to push me through all the tough times.
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1 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 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 metals in surface waters.

Mobilization of metals and P from forest soils occurs due to many factors. Acid rain 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 (CO₂) (Robinson et al., 1998). Although changing the CO₂ concentration in the atmosphere from $10^{-3.5}$ to $10^{-3.3}$ does little to the soil atmosphere, CO₂ in the subsurface environment can increase metal mobilization, especially Fe and Al (David and Vance, 1989; Su and Suarez, 1997; Villalobos and Leckie, 2000; Villalobos and Leckie, 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 (Drever and Stillings, 1996; Ochs, 1996; Zinder et al., 1986; Furrer and Stumm, 1986; Pohlman and McColl, 1988). More specifically, low molecular weight organic acids (LMWOAs) that originate primarily from root exudates and soil fungi can
also be transported through the soil. Although they make up less than 10% of DOC in soils, they 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 the 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 that has been shown to be effective in 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 (Kaiser and Zech, 1996; Lindsay, 1979), anionic P is also released through anion exchange in the soil-soil water system. The most important competing anions in soil water are inorganic anions and DOC that act through ligand exchange and competitive sorption mechanisms (Partiff et al., 1976; Turner and Kramer, 1991).

Phosphorus and surface metals can also be mobilized in particulate form. 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). Transition in the flow regime and solution chemistry can also lead to mobilization of particulate species. In-situ field experiments with ponded water found that colloids were mobilized as the water flux through the soil was rising and falling (El-Farhan et al., 2000). Increasing the flow rate in a packed soil column can increase colloid mobility (Kaplan et al., 1997). Colloid mobility can also increase in a
packed soil column when subjected to natural rainwater that results in higher colloidal repulsive surface energy caused by the decreased ionic strength in the water (Kaplan et al., 1993).

In this study, solutions with DIC concentration ranging between approximately 20 and 600 ppm were introduced into intact soil columns taken from the East and West streams of 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 locations along the soil column. Mobilization was studied as a function of influent DIC concentration and flow regime, and we compared the response of intact and homogenized soil columns to assess mechanisms that control mobilization of Al, Fe, Ca, and P by DIC and soil solution flow.
2 MATERIALS AND METHODS

Bear Brook Watershed in Maine is a paired watershed consisting of the East and West Brooks, located in eastern Maine approximately 50 km from the Gulf of Maine (44°52’ N, 68°06’ W). The soils are Spodosals, Inceptisols, and Folists along with accumulation of sesquioxides (Fernandez et al., 2003). Bimonthly treatments of 1800 eq (NH₄)₂SO₄ ha⁻¹ a⁻¹ have been applied to the West watershed since 1989. The untreated East watershed is the reference watershed for these studies.

Homogenized columns consisted of pre-fabricated columns, 5.0 cm in diameter and 17.8 cm long that were packed with soils from the B horizon in the East watershed. Soils were dug and frozen until use. Prior to use the soils were sieved to isolate materials that fell between a 0.5 mm screen and a #140 sieve. Soils were dried and then packed while using slight vibrations to promote settling. Nine sampling ports were spaced along the side of the column. The 6 upper ports were evenly spaced at a 2.0 cm distance and the last 3 were 1.0 cm apart.

Intact cores, 4.45 cm in diameter and approximately 16 – 24 cm long, were collected using a piston corer. Six intact soil cores were removed from the East watershed, four consisting of the B horizon only and two including the O and B horizons. One intact soil core from the West watershed included the O and B horizons. The soil cores were kept frozen until use. The casings used for core collection were fitted with end-caps in the laboratory and used as columns. The columns had side ports for collection of samples at different depths. The side ports were at 3.5 cm apart with one immediately below the top of the B horizon.
Varying volumes of solutions containing degassed 0.1 mM NaCl were initially passed through the columns. Even though BBWM water is less than 0.1mM NaCl, this concentration was chosen too have enough ionic strength to avoid colloid mobilization due to no ionic strength, which could effectively block flow through the column.

Columns were then subjected to different concentration DIC solutions ranging from approximately 20 to 600 ppm at a constant flow rate between 1.10 and 1.55 ml min$^{-1}$ (3.2 to 6.4 cm/s). Although the higher concentrations do not occur in the soil water at BBWM, the purpose was to see the increased mobilization due to the increase of DIC.

Pure CO$_2$ gas was bubbled through the 0.1 mM NaCl solution in the reservoir for different periods to obtain elevated DIC concentrations.

Effluent samples were collected frequently from the bottom port. When steady-state DIC concentration was reached, samples were taken from the side ports to follow the evolution of chemistry along the length of the column. Samples for DIC measurements were withdrawn using a 50 μL syringe and immediately injected into a total carbon (TC) analyzer (OI Analytical TOC Analyzer Model 1010). Samples were also analyzed for DOC, Al, Ca, Fe and P. Metals and P were fractionated into total, dissolved, organically-bound forms. Only approximately 50% of the total samples were analyzed for organically-bound forms. Samples for totals were collected from the sample ports and diluted prior to analysis. Dissolved fraction samples were filtered through 0.4 μm polycarbonate filters. Samples for organically-bound fractions were filtered 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. After filtration and exchange, these samples were acidified to 0.1 M Nitric Acid concentration.

The effluent pH was continuously monitored in a closed-cell using an Orion® Ross® glass-bodied, standard, ultra combination pH electrode. DIC and DOC were measured using a TC analyzer (OI Analytical 1010). Metal and P samples were analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Varian).
Influent solutions containing elevated DIC were run through homogenized and intact soil columns. Table 1 shows the influent DIC and effluent DOC, total Al (Al\textsubscript{t}), Ca (Ca\textsubscript{t}), Fe (Fe\textsubscript{t}) and P (P\textsubscript{t}) concentrations. The values listed are means and standard deviations for each run in the column. The influent DIC concentrations in the homogenized soil column was 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\textsubscript{t}, and Fe\textsubscript{t} were all considerably higher in the column with homogenized soil than those in the columns with intact soils. However, the effluent P\textsubscript{t} concentrations were higher, and the Ca\textsubscript{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 (results not shown here), and the breakthrough curves were modeled using the analytical solution to the advection-dispersion equation (Parker and van Genuchten, 1984). Using the dispersion coefficient and porosity as the fitting parameters, porosities from 0.45 to 0.74 and dispersion coefficients from 0.11 to 2.30 cm\textsuperscript{2} min\textsuperscript{-1} were obtained for these columns.
Table 1: Effluent concentrations and percentages of total NH₄Cl-extractable Al, Ca, Fe and P released from the soil pools of each column (from Fernandez et al. 2003). PV = pore volumes.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Homogenized Column</th>
<th>Intact Column 1</th>
<th>Intact Column 2</th>
<th>Intact Column 3</th>
<th>Intact Column 4</th>
<th>Intact Column 5</th>
<th>Intact Column 6</th>
<th>Intact Column 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil horizon</td>
<td>East Bear</td>
<td>East Bear</td>
<td>East Bear</td>
<td>East Bear</td>
<td>East Bear</td>
<td>East Bear</td>
<td>East Bear</td>
<td>East Bear</td>
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<tr>
<td></td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Treatment (ppm DIC)</td>
<td>15</td>
<td>40</td>
<td>40</td>
<td>173</td>
<td>309</td>
<td>582</td>
<td>470</td>
<td>443</td>
</tr>
<tr>
<td>Effluent pH range</td>
<td>4.1 - 4.83</td>
<td>4.4 - 4.87</td>
<td>4.57 - 4.71</td>
<td>4.24 - 4.76</td>
<td>4.22 - 4.89</td>
<td>4.32 - 4.97</td>
<td>4.07 - 4.91</td>
<td>4.19 - 4.81</td>
</tr>
<tr>
<td>Total Solution (L)</td>
<td>-</td>
<td>47.6</td>
<td>21.3</td>
<td>40.6</td>
<td>132</td>
<td>76.9</td>
<td>123</td>
<td>46.5</td>
</tr>
<tr>
<td>% Al released</td>
<td>-</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>12</td>
<td>5</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>% Ca released</td>
<td>-</td>
<td>15</td>
<td>5</td>
<td>46</td>
<td>52</td>
<td>61</td>
<td>61</td>
<td>18</td>
</tr>
<tr>
<td>% Fe released</td>
<td>-</td>
<td>2</td>
<td>3</td>
<td>6</td>
<td>13</td>
<td>105</td>
<td>150</td>
<td>21</td>
</tr>
<tr>
<td>% P released</td>
<td>-</td>
<td>670</td>
<td>620</td>
<td>2100</td>
<td>2700</td>
<td>1300</td>
<td>950</td>
<td>450</td>
</tr>
<tr>
<td>Effluent Al (ppm)*</td>
<td>0.2 ± 0.02</td>
<td>0.3 ± 0.04</td>
<td>0.8 ± 0.2</td>
<td>1.2 ± 0.2</td>
<td>1.2 ± 0.5</td>
<td>0.6 ± 0.1</td>
<td>2.2 ± 1.4</td>
<td>1.4 ± 0.7</td>
</tr>
<tr>
<td>Effluent Ca (ppm)*</td>
<td>0.4 ± 0.4</td>
<td>0.2 ± 0.09</td>
<td>0.2 ± 0.08</td>
<td>0.8 ± 0.2</td>
<td>0.6 ± 0.3</td>
<td>1.9 ± 0.2</td>
<td>2.7 ± 0.8</td>
<td>3.4 ± 1.0</td>
</tr>
<tr>
<td>Effluent Fe (ppm)*</td>
<td>4.7 ± 3.2</td>
<td>0.04 ± 0.04</td>
<td>0.07 ± 0.04</td>
<td>0.07 ± 0.04</td>
<td>0.07 ± 0.08</td>
<td>1.2 ± 0.8</td>
<td>1.3 ± 0.3</td>
<td>0.6 ± 0.4</td>
</tr>
<tr>
<td>Effluent P (ppm)*</td>
<td>0.4 ± 0.4</td>
<td>0.1 ± 1.0</td>
<td>1.4 ± 0.6</td>
<td>5.2 ± 3.1</td>
<td>0.8 ± 1.4</td>
<td>4.7 ± 5.2</td>
<td>2.2 ± 2.8</td>
<td>2.1 ± 3.4</td>
</tr>
<tr>
<td>Effluent DOC (ppm)*</td>
<td>500 ± 275</td>
<td>6.6 ± 4.9</td>
<td>5.8 ± 4.6</td>
<td>-</td>
<td>9.8 ± 15.1</td>
<td>4.1 ± 0.9</td>
<td>7.9 ± 2.7</td>
<td>9.2 ± 2.7</td>
</tr>
</tbody>
</table>

* Average effluent concentrations and standard deviations corresponding to the maximum DIC concentration
The sequence of manipulations of the columns is in Table 2. Each experiment was initiated by an initial conditioning phase, where a background 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 hr after two discrete DIC pulses, followed by 0.1 mM NaCl solution and a high concentration DIC solution. The breakthrough results of soil columns with high influent DIC concentrations (185 – 582 ppm) will be discussed first, followed by those of low DIC concentrations (20 – 40 ppm).

3.1 High DIC Columns

Columns 3 to 7 were high DIC, with DIC concentrations ranging from approximately 300 to 550 ppm (Table 2). The breakthrough curves for DIC, pH, Al, Ca, Fe, and P, from column 7 are in Figures 1a and 1b. Breakthrough curves from other columns are similar to those of column 7. Column 7 run consisted of a 21.8 hr conditioning with 0.1 mM NaCl solution followed by a ~24 hr pulse of 443 ppm DIC solution. This was followed by another 3.2 hr pulse of 0.1 mM NaCl solution. The influent solution was then stopped and the column was allowed to drain under gravity for 48 hr. After this, 24.8 hr of 0.1 mM NaCl solution was introduced into the column, followed by a final 22.1 hr pulse of 460 ppm DIC that was then followed by a 4.3 hr pulse of 0.1 mM NaCl solution.
Table 2: Influent Solutions and DIC Concentrations for Each Column. PV = pore volumes.

<table>
<thead>
<tr>
<th></th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
<th>Column 4</th>
<th>Column 5</th>
<th>Column 6</th>
<th>Column 7</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0.1 mM NaCl Solution, PV</strong></td>
<td>0.6</td>
<td>0.5</td>
<td>1.2</td>
<td>11.2</td>
<td>5.7</td>
<td>18.1</td>
<td>4.5</td>
</tr>
<tr>
<td>DIC Pulse ppm</td>
<td>20</td>
<td>24</td>
<td>173</td>
<td>213</td>
<td>582</td>
<td>0**</td>
<td>443</td>
</tr>
<tr>
<td>DIC Pulse PV</td>
<td>2.4</td>
<td>4.4</td>
<td>8.6</td>
<td>25.9</td>
<td>17.2</td>
<td>20.5</td>
<td>15.9</td>
</tr>
<tr>
<td><strong>0.1 mM NaCl Solution, PV</strong></td>
<td>21.6</td>
<td>4.7</td>
<td>7.0</td>
<td>12.3</td>
<td>22.2</td>
<td>18.2</td>
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<td>DIC Pulse* ppm</td>
<td>40</td>
<td>40</td>
<td>347</td>
<td>309</td>
<td>-</td>
<td>470</td>
<td>-</td>
</tr>
<tr>
<td>DIC Pulse* PV</td>
<td>16.1</td>
<td>6.4</td>
<td>15.3</td>
<td>28.7</td>
<td>-</td>
<td>19.3</td>
<td>-</td>
</tr>
<tr>
<td><strong>0.1 mM NaCl Solution</strong>*, PV</td>
<td>7.0</td>
<td>5.4</td>
<td>8.4</td>
<td>11.3</td>
<td>-</td>
<td>4.1</td>
<td>-</td>
</tr>
<tr>
<td>DIC Pulse ppm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>185</td>
<td>547</td>
<td>460</td>
<td>460</td>
</tr>
<tr>
<td>DIC Pulse PV</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>25.3</td>
<td>22.2</td>
<td>36.7</td>
<td>14.7</td>
</tr>
<tr>
<td><strong>0.1 mM NaCl Solution, PV</strong></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.8</td>
<td>4.2</td>
<td>2.6</td>
<td>2.9</td>
</tr>
</tbody>
</table>

* Only when columns had a second continuous DIC run  
** 2.5 ppm DOC from Bear Brook O Horizon in influent  
*** These columns were drained prior to introducing the 0.1 mM NaCl Solution

3.1.1 The Conditioning Phase

During the initial conditioning phase, the concentrations of DOC, Al{_t}, Ca{_t}, Fe{_t} and P{_t} were quite high (Figs. 1a and 1b), and then decreased relatively rapidly. Within approximately 3.2 pore volumes (6.8 hr), the effluent concentrations of Al{_t}, Ca{_t}, Fe{_t}, and DOC dropped up to 70% of the initial effluent concentration.
Figure 1a: Breakthrough curves for DIC, Al, Ca, and DOC in column 7

Figure 1b: Breakthrough curves for pH, Fe, and P in column 7
3.1.2 The DIC Pulse

The introduction of high DIC concentrations into the columns caused an immediate increase in the Al, Ca, Fe, and P concentrations (Figs. 1a and 1b). Al, Ca, and Fe concentrations varied proportionally throughout both pulses in the effluent solution with the DIC concentration, with r² 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 concentration did increase substantially with the introduction of DIC, its behavior was much more 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 2). As the DIC reached its maximum steady-state concentration of 443 ppm in pulse 1, the maximum effluent concentrations of Al, Ca, Fe and P 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 hr. Pulse 2 had maximum effluent concentrations of Al, Ca, Fe and P 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 DIC concentration showed correlations with pH (r² = 0.58) in the columns. For example, in the conditioning phase the average pH was 4.81 (Fig. 1b). Following the introduction of the 443 ppm DIC solution, pH steadily decreased to a minimum of 4.23. In pulse 2 of column 7, just before the 460 ppm DIC solution was introduced, pH was 4.62, and after the DIC solution was introduced it decreased to 4.18.

The mobilized Al, Ca, Fe and P, as a percentage of NH₄Cl-extractable fractions, are reported in Table 1. For the high DIC columns, the total mass of Al released ranged from
4 to 12% of the mass of NH$_4$Cl-extractable Al, while mobilized Ca and Fe were somewhat higher in comparison ranging from 17% to 160% and 6% to 150%, respectively, of their NH$_4$Cl-extractable fractions. Mobilized P, however, was considerably higher than the NH$_4$Cl-extractable P ranging from 450% to 2700%.

3.1.3 Speciation of Al, Ca, Fe and P

A subset of 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 fractions (subscript d). In some cases, the total dissolved fraction was then passed through a cation exchange resin to separate the freely dissolved (subscript f) from the organically-bound (subscript o) metal species.

Figures 2a and 2b show the breakthrough curves of the speciated Al and Fe, respectively, for column 7, and Figs. 3a and 3b show the same for column 6. Al$_d$, Al$_o$ and Al$_p$ in both columns (Figs. 2a and 3a) show similar trends compared to Al$_t$ in the conditioning phase. 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 ($r^2 = 0.57$) in column 7 (Fig. 2a). Al$_p$ was rapidly mobilized in all of the high DIC columns where samples were speciated. The rapid increases in Al$_p$ occurred when a DIC pulse solution was introduced, such as in DIC pulse 1 in column 7, and when the change 0.1 mM NaCl solution was introduced at the beginning of the experiment and 48 hr after the column was drained (Fig. 2a). Rapid increases in Al$_p$ occurred at the beginning of the conditioning phase and at the beginning of the DIC pulse 1 (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 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. In contrast to column 7, Al₄ was the most dominant Al species in column 6 (Fig. 3a). Even though all Al species increased with increasing DIC concentration in column 6, they are poorly correlated with respect to DIC ($r^2 = 0.02$ to 0.05). As for Al, Fe species increased with increasing DIC concentrations (Figs. 2b and 3b). Individual Fe species did not show strong correlations with the DIC concentrations in any of the columns ($r^2 = 0.01$ to 0.06). During the conditioning phase, Fe₄, Fe₀, and Feₚ initially increased and then decreased. Similar to Alₚ, Feₚ was the dominant Fe species in column 7 (Fig. 2b), and Fe₄ was the dominant Fe species in column 6 (Fig. 3b). Feₚ increased with increasing DIC concentration in all high DIC columns. Feₚ also rapidly increased when a DIC pulse solution was introduced (Figs. 2b and 3b), 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). For example, Feₚ concentration increased from 0.003 to 0.68 ppm immediately after the introduction of the DIC solution, followed by a decrease to an average concentration of 0.31 (±0.22) ppm for the remainder of the steady-state DIC concentration in column 7.
Figure 2a: Breakthrough curves of DIC and Al$_d$, Al$_o$ and Al$_p$ in Column 7

Figure 2b: Breakthrough curves of DIC and Fe$_d$, Fe$_o$ and Fe$_p$ in Column 7
Figure 3a: Breakthrough curves of DIC and Al₄, Al₀ and Alₚ in Column 6. Note break in scale.

Figure 3b: Breakthrough curves of DIC and Fe₄, Fe₀ and Feₚ in Column 6.
Transport of Al and Fe species along the length of columns 4 to 7 was evaluated. Figures 4a, 4b, 5a and 5b represent samples taken 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 2). A gradual increase in the \( \text{Al}_d \) concentration with depth in column 7 occurred (Figs. 4a and 4b), even though the concentrations are relatively similar at different times for a given DIC pulse, and between DIC pulses 1 and 2 (Figs. 4a and 4b). During the DIC pulse 1, the \( \text{Al}_p \) concentrations, however, increased sharply with depth, especially initially (Fig. 4a). At \( t = 27 \) hr that corresponds to the time when the effluent DIC concentration reached its steady-state maximum, a sharp initial increase in \( \text{Al}_p \) was followed by a decrease. At \( t = 30 \) and 45 hr less \( \text{Al}_p \) is initially mobilized, but no decrease with depth occurred. For DIC pulse 2, \( \text{Al}_p \) was mobilized but at lower concentrations than during DIC pulse 1 (Fig. 4b).

Figures 5a and 5b show the effluent \( \text{Fe}_d \) and \( \text{Fe}_p \) with depth in column 7 during the steady-state maximum DIC concentrations of 443 and 460 ppm, corresponding to DIC pulses 1 and 2, respectively (Table 2). During DIC pulse 1, \( \text{Fe}_p \) was mobilized in the mixed zone of O and B horizons, but its concentration decreased with time due to the depletion of labile \( \text{Fe}_p \), and depth due to colloid re-attachment to the soil matrix (Fig. 5a).
Figure 4a: $\text{Al}_d$ and $\text{Al}_p$ concentrations along the depth of column 7 at different times during the steady-state maximum concentration of DIC pulse 1. DIC = 443 ppm.

Figure 4b: $\text{Al}_d$ and $\text{Al}_p$ concentrations along the depth of column 7 at different times during the steady-state maximum concentration of DIC pulse 2. DIC = 460 ppm.
Figure 5a: $\text{Fe}_d$ and $\text{Fe}_p$ concentrations along the depth of column 7 at different times during the steady-state maximum concentration of DIC pulse 1. DIC = 443 ppm.

Figure 5b: $\text{Fe}_d$ and $\text{Fe}_p$ concentrations along the depth of column 7 at different times during the steady-state maximum concentration of DIC pulse 2. DIC = 460 ppm.
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, $C_{a_d}$ was 86% ($\pm 12\%$) and 92% ($\pm 40\%$) of the $C_{a_t}$ in solution, respectively. $C_{a_p}$ is thought to be associated with $A_{i_p}$ and $F_{e_p}$ because it was mobilized only during chemical and flow transients. Organic Ca ($C_{a_o}$) was 42% ($\pm 11\%$) and 55% ($\pm 11\%$) of the overall $C_{a_d}$ 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% ($\pm 3\%$) and 92% ($\pm 15\%$) of $P_{t}$, respectively. $P_{p}$ was mobilized similarly compared to $C_{a_p}$ 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 ($\pm 0.77$) 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). $P_{o}$ was 70% of $P_{d}$ (one data point) for DIC pulse 1 and was 33% ($\pm 23\%$) for DIC pulse 2. 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.

### 3.1.4 Effect of DOC

DIC concentration and the 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 2). Figure 4 relates the effluent $A_{i_t}$, $C_{a_t}$, $F_{e_t}$ and $P_{t}$ versus the effluent DOC concentrations during column 6’s DOC pulse. There was a strong correlation between effluent concentrations of $A_{i_t}$, $C_{a_t}$,
Fe, and P, with the effluent DOC in the absence of elevated DIC (Fig. 6). Al, Ca, Fe, and P constituted 76% (±10%), 69% (±10%), 70% (±18%), and 47% (±16%) of the total dissolved concentration of each species, respectively. However, after the introduction of 470 ppm of DIC into column 6, poor correlations between the same species and DOC occurred (r² from 0.03 to 0.54). Al, Ca, Fe, and P fractions decreased to 53% (±8%), 49% (±4%), 66% (±13%), and 31% (±20%) in DIC Pulse 2, respectively. Elevated DIC also caused faster mobilization rates of these species.

![Figure 6: Effluent Al, Ca, Fe, and P vs. DOC for the DOC-spiked pulse in column 6. Al, Ca, Fe, and P vs. DOC with r² = 0.70, 0.70, 0.65, and 0.54, respectively.](image)

3.2 Low DIC Columns

Columns 1 and 2, had DIC concentrations between 20 and 40 ppm (Table 2). The DIC pulse concentrations used for the low DIC columns are 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 Bear
Brook to consist of 0.3 to 0.8% of CO₂. Assuming a Henry’s Law constant of 10⁻¹.⁵ L atm⁻¹ at 25°C, DIC concentrations were likely 1 to 3 ppm in the soil water. Therefore, 20 and 40 ppm are at the high side of what will occur in the natural environment.

The breakthrough curves of effluent DIC, pH, Alₜ, Caₜ, Feₜ, Pₜ and DOC concentrations for column 1 are shown in Figs. 7a and 7b and consist of a 2.8 hr conditioning phase with 0.1 mM NaCl solution, followed by an 8.5 hr pulse of 20 ppm DIC. Following a 74.8 hr 0.1 mM NaCl solution, a 55.8 hr pulse of 40 ppm DIC solution was introduced into the column. This was followed by a final 24.2 hr pulse of change 0.1 mM NaCl solution.

3.2.1 Conditioning Phase

Similar to the high DIC columns, the low DIC conditioning step included the 0.1mM NaCl solution. During this phase, the concentrations of DOC, Alₜ, Caₜ, Feₜ and Pₜ were quite high, initially (Figs. 7a and 7b).

3.2.2 DIC Pulse Phase

The introduction of the 20 ppm pulse caused an immediate increase in the Alₜ concentration (Fig. 7a). The Alₜ concentration in the effluent of the low DIC columns varied proportionally with the DIC concentration (r² = 0.40), similar to the high DIC columns. The Alₜ concentration decreased sharply after the influent DIC solution was replaced by the 0.1 mM NaCl solution. Pₜ varied substantially in relation to DIC (r² = 0.02), as also occurred in the high DIC columns. Caₜ and Feₜ decreased throughout the entire 20 ppm DIC pulse (Figs. 7a and 7b). At the beginning of the 20 ppm DIC pulse, the column had received less than one pore volume of change 0.1 mM NaCl solution, which is perhaps insufficient to mobilize the more labile forms of Caₜ and Feₜ. 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 hr of background change 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 demonstrated by 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 were less than the 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%.
Figure 7a: Breakthrough curves of DIC, Al, Ca, and DOC in column 1.

Figure 7b: Breakthrough Curves of pH, Fe, and P in column 1.
4 DISCUSSION

4.1 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 1 shows that considerably higher concentrations of total Al, Fe and DOC were released from the homogenized soil column than from the intact soil columns. Therefore, the higher Al, Fe, and DOC mobilization from the homogenized soil, where a considerably lower DIC concentration was introduced, could be attributed disturbance of soil aggregates and changes in surface physicochemical characteristics brought about by drying, sieving and repacking the soil. Natural organic matter, however, is more soluble at a higher pH. Average effluent Ca concentration from homogenized cores 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 1). Average P concentration was higher in all of the intact soil columns compared to the homogenized soil column (Table 1). The released Ca and P, unlike Al and Fe, could have had different initial introductions to the parent material and are likely introduced into the soil via external pathways, such as P from 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 ion-exchangeable or sorbed forms at the external surfaces of the soil aggregates. However, the difference in the behavior of Ca and P can be attributed to Al mobilized that fixes the P, making it insoluble.

Homogenization destroys soil's microporous structure, and therefore, exposes surfaces that were otherwise physically not easily accessible to advective flow. Soil aggregates in Spodosols are stabilized primarily by the soil organic matter that originates from plants,
animals, and microorganisms. Also, organo-metallic compounds act as bridges between the particles resulting in aggregation (Bronick and Lal, 2004).

4.2 Metal and P Mobilization

The high concentrations of DOC, Al, Ca, Fe, and P that occurred initially in the conditioning phase can be attributed to desorption and ion-exchange reactions involving the more labile species. However, chemical transients, such as a decrease in the solution's ionic strength (Kaplan et al., 1993), the increased presence of complexing ligands in solution (Bunn et al., 2000) can lead to destabilization of the colloidal aggregates in the soils, as seen especially for column 6 (Figs. 3a and b). El-Farhan et al. (2000) showed that flow transients, such as those introduced in the soil at the beginning of the experiment and after draining the column to simulate rainfall or snowmelt events, cause a very rapid increase in colloid mobilization.

The rapid decrease of DOC, Al, Ca, Fe, and P following the initial introduction of the background change electrolyte solution could perhaps because of the depletion of the labile and easily mobilized fractions (Figs. 1a and 1b). This behavior was observed by Totsche et al. (2000) in a homogenized forest soil sample, where they reported 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 hr⁻¹, Al and DOC decreased approximately by 60% and 85%, respectively.

In general, Al and Fe can be mobilized due to the direct interaction of proton and carbonate species with the soil surfaces. Carbonate species adsorb to the surface sites of Fe(III) and Al (oxy)hydroxides (van Geen et al., 1994; Shulthess et al., 1998). Van Geen et al. (1994) and Villalobos and Leckie (2001) proposed coordination of carbonic acid
and bicarbonate with the goethite (α-FeOOH) surface as inner sphere surface complexes that result in the displacement of surface hydroxyl groups. Carbonate species adsorbed most effectively to Fe(III) and Al (oxy)hydroxides at pH between 5 to 7, which is slightly higher than the pH of our effluent solutions in Figure 1b (van Geen et al., 1994; Shulthess et al., 1998; Bruno et al., 1992). Bruno et al. (1992) showed a direct correlation between the dissolution rate of hematite (α-Fe₂O₃) and the surface concentrations of HCO₃⁻ and CO₃²⁻. As expected, introduction of DIC results in a decrease in pH (Figure 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) are all likely responsible for the dissolution of Al and Fe in our soil columns.

Effluent Alₜ and Feₜ concentrations varied with the DIC concentration (Figs. 1a and 1b). Mobilized Alₜ and Feₜ were lower than (for Al) or approximately equal (for Fe) to their respective labile NH₄Cl-extractable fractions (Table 1). NH₄Cl extractions of BBWM soils were performed on homogenized samples but not on the same samples tested in the lab. Although we recognize that the intact soil core collection procedure could lead to potential release of many nutrients, metals, etc., the concentration of this ion exchangeable fraction can not be an exact representation for our intact soils. The NH₄Cl-extractable fraction can be mobilized due to ion exchange with protons or dissolution following the reversible sorption of carbonate species. In column 7, Alₚ and Feₚ constituted the major mobilized fractions of Alₜ and Feₜ. In all other columns, colloidal fraction of these species was also observed, even though not as the dominant fraction. Furthermore, there were sharp increases in the release of these species due to chemical
perturbations. Changes in ionic strength and composition (Nightingale and Bianchi, 1997; 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; Swartz and Gschwend, 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. 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 carbonate 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 carbonate interaction with the soil surfaces, we compared the breakthrough of DIC with that of the assumed conservative Br tracer (Fig. 8). Analysis of the DIC breakthrough curves allows the characterization of DIC sorption onto soil. Equation 1 is the mass balance equation including advection, dispersion and linear equilibrium adsorption, the analytical solution of which can be used to estimate the equilibrium adsorption constant for a solute (Parker and van Genuchten, 1984).

\[
R \frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}
\]  

(1)

In equation 1, \( C \) is the solute concentration at time \( t \), \( t \) is time, \( x \) is the distance, \( v \) is the pore velocity, \( D_L \) is the hydrodynamic dispersion coefficient, and \( R \) is the solute’s linear retardation coefficient. \( D_L \) was first determined independently by fitting the breakthrough of the Br tracer. The DIC breakthrough data were then used to determine
$R$, the ratio of velocity of the DIC to that of the conservative tracer. Assuming a linear local equilibrium for the sorption of inorganic carbon,

$$R = 1 + \frac{\rho_b K_D}{\theta}$$  \hspace{1cm} (2)

where $\rho_b$ is the bulk density, $\theta$ is the average porosity, and $K_D$ is the equilibrium constant for the reversible sorption of inorganic carbon (largely HCO$_3^-$) onto soil surfaces for the equilibrium reaction

$$\text{DIC} \leftrightarrow \text{IC}_{\text{ads}} \ ; \ K_D$$  \hspace{1cm} (3)

where, $\text{IC}_{\text{ads}}$ is the adsorbed inorganic carbon concentration (mg g$^{-1}$ dry solid).

The assumption of reversible equilibrium sorption is justified in this case, because $C/C_0$ for DIC approaches one, suggesting no irreversible sorption. This is based on the assumption that NaBr itself is truly conservative. Values of $R$ and $\log K_D$ for columns 1, 3 and 5 are reported in Table 3. Columns 1 and 3 contained the B horizon only, and columns 5 contained the O and the B horizons. $\log K_D$ values ranged between -0.82 to -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.
Figure 8: Experimental and modeled breakthrough curves for Br and DIC in column 3 for a total DIC = 347 ppm.

Table 3: Retardation Coefficient \((R)\), Porosity \((\theta)\), \(\log(K_D)\), DIC adsorbed and \(P_t\) released for columns 1, 3, and 5 and their corresponding DIC concentrations

<table>
<thead>
<tr>
<th></th>
<th>Column 1</th>
<th>Column 3</th>
<th>Column 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent DIC (ppm)</td>
<td>20</td>
<td>40</td>
<td>173</td>
</tr>
<tr>
<td>(R)</td>
<td>1.95</td>
<td>1.44</td>
<td>1.74</td>
</tr>
<tr>
<td>(\theta)</td>
<td>0.534</td>
<td>0.72</td>
<td>0.72</td>
</tr>
<tr>
<td>(\log(K_D))</td>
<td>-0.25</td>
<td>-0.59</td>
<td>-0.24</td>
</tr>
<tr>
<td>DIC (moles adsorbed)</td>
<td>1.9E-04</td>
<td>3.7E-04</td>
<td>1.8E-03</td>
</tr>
<tr>
<td>(P_t) (moles released)</td>
<td>4.5E-06</td>
<td>4.3E-05</td>
<td>6.9E-05</td>
</tr>
<tr>
<td>(IC_{ads}/P_t) ratio</td>
<td>43.5</td>
<td>8.6</td>
<td>25.4</td>
</tr>
</tbody>
</table>
Figure 9: Total moles of Phosphorous released vs. moles of DIC adsorbed during the breakthrough curves of Columns 1, 3 and 5. \( r^2 = 0.90 \).

The mass of IC\(_{ads}\) may be estimated from Fig. 8 by accounting for the difference between the Br and DIC breakthrough curves. Table 4 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 is perhaps mobilized due to a ligand exchange mechanism following the adsorption of carbon species at the soil surfaces (Fig. 9). This mechanism is especially plausible since the nearly equal stoichiometries between the released P vs. Al and Fe (Table 1) preclude Al and Fe mineral dissolution as the P release mechanism.

Figures 4a and 4b show a gradual increase in the Al\(_d\) concentration downward in column 7, 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 $t = 27$ hr, suggesting colloid mobilization followed by attachment to the soil matrix (Fig. 4a). At $t = 30$ and $45$ hr, net $\text{Al}_p$ concentration appears nearly constant throughout the length of the column implying a relatively steady mobilization rate through out the depth. At $t = 45$ hr, the colloid mobilization rate has decreased by nearly 70% compared to earlier times (Fig. 4a). During pulse 2, $\text{Al}_p$ mobilization rate is slower than during pulse 1, even though the DIC concentration is slightly higher in pulse 2 (Fig. 4b). This can be attributed to the release of more easily mobilized $\text{Al}_p$ fractions during pulse 1. $\text{Al}_p$ mobilization rate increases with time and depth in the B horizon during pulse 2 (Fig. 4b).

Similar to $\text{Al}_a$, $\text{Fe}_a$ is initially mobilized primarily in the initial B horizon along column 7 (Figs. 5a and 5b). $\text{Fe}_p$ shows an initial sharp peak at $t = 27$ hr during pulse 1 in the mixed O an B horizons, with the peak decreasing with time, perhaps due to the depletion of the more labile $\text{Fe}_p$ fraction (Fig. 5a). The location of the peak in $\text{Fe}_p$ concentration moved lower in the column during pulse 2. Following its peak, $\text{Fe}_p$ decreased with depth during both pulses due to attachment to soil matrix in the B horizon.

Phosphorus is mobilized by a different mechanism altogether. 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 $\text{P}_i$ showed a poor correlation with respect to DIC in both high and low DIC columns, there was a substantial increase in the concentrations of $\text{P}_i$ with DIC (Figs. 1b and 7b). 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. In this study, P concentrations mobilized in the presence of DIC exceed the stream concentrations by more than two orders of magnitude. For example, P concentrations as high as 12.6 ppm occurred in column 4. Other columns had similar P concentrations. Mobilized P is significantly higher than the NH₄Cl-extractable P, where the latter only made up approximately 6% of the inorganic P pools in the soils in BBWM (Sherman et al., 2006). As mentioned above, ligand exchange with DIC may be responsible for the large export of P from the column. Table 4 shows that increasing the influent DIC concentration in a given column results in the increase of mobilized P in that column. The variable ICₐ/d/Pₐ molar ratios between the columns (Table 4), 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 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 Alₚ or Feₚ. The fact that the total mobilized Ca was less than or approximately equal to the NH₄Cl-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.

4.3 DOC Relationship

Ligands have been shown to mobilize DOC in soil columns. 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 above 4, many of the functional groups on natural organic acids that make up the DOC are deprotonated (Stumm and Morgan, 1996). Ochs et al. (1996) suggested that this allows larger molecular weight organic acids to bind at many surface sites forming a stable multidentate surface complex. This can 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<sub>t</sub>, Ca<sub>t</sub>, Fe<sub>t</sub> and P<sub>t</sub> concentrations with increasing DOC concentration (Fig. 7). Drever and Stillings (1996) found that while the humic and fulvic acids do not increase, and can inhibit, mineral dissolution, the low molecular weight organic acids increase dissolution through complexation of the surface metals in a mononuclear bidentate formation. It is expected that low molecular weight organic acids are likely present and act as complexing ligands to mobilize Al<sub>t</sub>, Ca<sub>t</sub>, Fe<sub>t</sub> and P<sub>t</sub>.
5 SUMMARY AND CONCLUSIONS

Addition of DIC to soil cores has shown that an increase in CO$_2$ concentration increases the mobilization of the metals and nutrients studied. 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 alteration of the soil aggregate structure and surface physiochemical characteristics in these columns were likely the cause of this drastic increase, indicating that laboratory simulations of field environment should be conducted using intact soils. In the intact cores, mobilized Al$_i$ and Fe$_i$ varied proportionally with the rising and falling influent DIC concentrations for the most part except for when chemical or flow transients caused rapid increases in the colloid mobilization causing the particulate species to dominate in one column. 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 part. Ca was mobilized primarily through ion exchange due to the increase in proton concentration as a result of mobilized metals and nutrients such as Al and Fe. Both effluent P and Ca existed mainly in dissolved forms.
REFERENCES


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Appendix A: Unreported Variable Distance Plots
Figure A-1: Column 4 Variable Distance Total Al. Run 1 = 213 ppm DIC, Run 2 = 309 ppm DIC, Run 3 = 185 ppm DIC.

Figure A-2: Column 4 Variable Distance Dissolved and Particulate Al. Run 1 = 213 ppm DIC, Run 2 = 309 ppm DIC, Run 3 = 185 ppm DIC.
Figure A-3: Column 4 Variable Distance Total Ca. Run 1 = 213 ppm DIC, Run 2 = 309 ppm DIC, Run 3 = 185 ppm DIC.

Figure A-4: Column 4 Variable Distance Dissolved and Particulate Ca. Run 1 = 213 ppm DIC, Run 2 = 309 ppm DIC, Run 3 = 185 ppm DIC.
Figure A-5: Column 4 Variable Distance Total Fe. Run 1 = 213 ppm DIC, Run 2 = 309 ppm DIC, Run 3 = 185 ppm DIC.

Figure A-6: Column 4 Variable Distance Dissolved and Particulate Fe. Run 1 = 213 ppm DIC, Run 2 = 309 ppm DIC, Run 3 = 185 ppm DIC.
Figure A-7: Column 4 Variable Distance Total P. Run 1 = 213 ppm DIC, Run 2 = 309 ppm DIC, Run 3 = 185 ppm DIC.

Figure A-8: Column 4 Variable Distance Dissolved and Particulate P. Run 1 = 213 ppm DIC, Run 2 = 309 ppm DIC, Run 3 = 185 ppm DIC.
Figure A-9: Column 4 Variable Distance Total DOC. Run 1 = 213 ppm DIC, Run 2 = 309 ppm DIC, Run 3 = 185 ppm DIC.

Figure A-10: Column 5 Variable Distance Total Al. Run 1 = 582 ppm DIC, Run 2 = 547 ppm DIC.
Figure A-11: Column 5 Variable Distance Total Ca. Run 1 = 582 ppm DIC, Run 2 = 547 ppm DIC.

Figure A-12: Column 5 Variable Distance Total Fe. Run 1 = 582 ppm DIC, Run 2 = 547 ppm DIC.
Figure A-13: Column 5 Variable Distance Total P. Run 1 = 582 ppm DIC, Run 2 = 547 ppm DIC.

Figure A-14: Column 5 Variable Distance Total DOC. Run 1 = 582 ppm DIC, Run 2 = 547 ppm DIC.
Figure A-15: Column 6 Run 1 Variable Distance Total Al. Run 1 = 2.5 ppm DOC, Run 2 = 470 ppm DIC, Run 3 = 460 ppm DIC.

Figure A-16: Column 6 Run 2 Variable Distance Total Al. Run 1 = 2.5 ppm DOC, Run 2 = 470 ppm DIC, Run 3 = 460 ppm DIC.
Figure A-17: Column 6 Run 3 Variable Distance Total Al. Run 1 = 2.5 ppm DOC, Run 2 = 470 ppm DIC, Run 3 = 460 ppm DIC.

Figure A-18: Column 6 Run 1 Variable Distance Total Ca. Run 1 = 2.5 ppm DOC.
Figure A-19: Column 6 Run 2 Variable Distance Total Ca. 460 ppm DIC.

Figure A-20: Column 6 Run 3 Variable Distance Total Ca. 460 ppm DIC.
Figure A-21: Column 6 Run 1 Variable Distance Total Fe. 2.5 ppm DOC.

Figure A-22: Column 6 Run 2 Variable Distance Total Fe. 470 ppm DIC.
Figure A-23: Column 6 Run 3 Variable Distance Total Fe. 460 ppm DIC.

Figure A-24: Column 6 Run 1 Variable Distance Total P. 2.5 ppm DOC.
Figure A-25: Column 6 Run 2 Variable Distance Total P. 470 ppm DIC.

Figure A-26: Column 6 Run 3 Variable Distance Total P. 460 ppm DIC.
Figure A-27: Column 6 Run 1 Variable Distance Total DOC. 2.5 ppm DOC.

Figure A-28: Column 6 Run 2 Variable Distance Total DOC. 470 ppm DIC.
Figure A-29: Column 6 Run 3 Variable Distance Total DOC

Figure A-30: Column 7 Run 1 Variable Distance Dissolved and Particulate Al. 443 ppm DIC.
Figure A-31: Column 7 Run 1 Variable Distance Organically Bound Al. 443 ppm DIC.

Figure A-32: Column 7 Run 2 Variable Distance Dissolved and Particulate Al. 460 ppm DIC.
Figure A-33: Column 7 Run 2 Variable Distance Organically Bound Al. 460 ppm DIC.

Figure A-34: Column 7 Run 1 Variable Distance Dissolved and Particulate Ca. 443 ppm DIC.
Figure A-35: Column 7 Run 1 Variable Distance Organically Bound Ca. 443 ppm DIC.

Figure A-36: Column 7 Run 2 Variable Distance Dissolved and Particulate Ca. 460 ppm DIC.
Figure A-37: Column 7 Run 2 Variable Distance Organically Bound Ca. 460 ppm DIC.

Figure A-38: Column 7 Run 1 Variable Distance Dissolved and Particulate Fe. 443 ppm DIC.
Figure A-39: Column 7 Run 1 Variable Distance Organically Bound Fe. 443 ppm DIC.

Figure A-40: Column 7 Run 2 Variable Distance Dissolved and Particulate Fe. 460 ppm DIC.
Figure A-41: Column 7 Run 2 Variable Distance Organically Bound Fe. 460 ppm DIC.

Figure A-42: Column 7 Run 1 Variable Distance Dissolved and Particulate P. 443 ppm DIC.
Figure A-43: Column 7 Run 1 Variable Distance Organically Bound P. 443 ppm DIC.

Figure A-44: Column 7 Run 2 Variable Distance Dissolved and Particulate P. 460 ppm DIC.
Figure A-45: Column 7 Run 2 Variable Distance Organically Bound P. 460 ppm DIC.

Figure A-46: Column 7 Run 1 Variable Distance Total DOC. 443 ppm DIC.
Figure A-47: Column 7 Run 2 Variable Distance Total DOC. 460 ppm DIC.
Appendix B: Unreported Al, Ca, Fe, P, DOC, and pH vs. Time Plots
Figure B-1: Column 2 Al, Ca, Fe, P and DIC vs. Time

Figure B-2: Column 3 Al, Ca, Fe, P and DIC vs. Time
Figure B-3: Column 4 Al, Ca, Fe, P and DIC vs. Time

Figure B-4: Column 5 Al, Ca, Fe, P and DIC vs. Time
Figure B-5: Column 2 pH and DIC vs. Time

Figure B-6: Column 3 pH and DIC vs. Time
Figure B-7: Column 4 pH and DIC vs. Time

Figure B-8: Column 5 pH and DIC vs. Time
Figure B-9: Column 2 DOC vs. Time

Figure B-10: Column 3 DOC vs. Time
Figure B-11: Column 4 DOC vs. Time

Figure B-12: Column 5 DOC vs. Time
Figure B-13: Column 7 DOC vs. Time
Appendix C: Unreported Conditioning Phase Plots
Figure C-1: Column 2 Conditioning Phase

Figure C-2: Column 3 Conditioning Phase
Figure C-3: Column 4 Conditioning Phase

Figure C-4: Column 5 Conditioning Phase
Figure C-5: Column 7 Conditioning Phase
Appendix D: Unreported Bromide Plots
Figure D-1: Column 2 Bromide Breakthrough Curve

Figure D-2: Column 3 Bromide Breakthrough Curve
Figure D-3: Column 4 Bromide Breakthrough Curve

Figure D-4: Column 5 Bromide Breakthrough Curve
Appendix E: Unreported Breakthrough Curves
Figure E-1: Column 2 breakthrough curve for Pulse 1

Figure E-2: Column 3 breakthrough curve for Pulse 1
Figure E-3: Column 3 breakthrough curve for Pulse 2

Figure E-4: Column 4 breakthrough curve for Pulse 1
Figure E-5: Column 4 breakthrough curve for Pulse 2

Figure E-6: Column 4 breakthrough curve for Pulse 3
Figure E-7: Column 5 breakthrough curve for Pulse 1

Figure E-8: Column 5 breakthrough curve for Pulse 2
BIOGRAPHY OF AUTHOR

Brett Holmes was born in Strong, Maine on May 13, 1981. He was raised in Skowhegan, Maine and was graduated from Skowhegan Area High School in 1999. He attended Worcester Polytechnic Institute, and was graduated in 2003 with a Bachelor of Science degree in Chemical Engineering. Upon completion of his undergraduate degree he was employed he worked for a year and a half for Geosyntec Consultants as a Field Engineering Technician. In January of 2005 he entered the Civil Engineering graduate program at the University of Maine.

Brett is the son of Kelly Coughlin and Michael Holmes. He is very close to his brothers Chad, Scott and Logan and sister Jessica. He began employment with Contech Stormwater Solutions in December of 2006. Brett is a candidate for the Master of Science degree in Civil Engineering from the University of Maine in May of 2007.