

Report for 2001ME1481G: Does aluminum geochemistry control the trophic status of oligotrophic lakes?

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- unclassified:
 - Reinhardt, R. L., Norton, S. A., Handley, M., and Amirbahman, A. 2002, Mobilization and linkages among P, Al, and Fe during high discharge events at the Bear Brook Watershed in Maine, USA: 4th International Symposium on Ecosystem Behavior (BIOGEOMON), Reading, England.
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Report Follows

Mobilization of and linkages among P, Al, and Fe during high discharge episodic acidification at the Bear Brook Watershed in Maine, USA

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1. ABSTRACT

Phosphorus (P), aluminum (Al), and iron (Fe) stream chemistry were assessed for high discharge snowmelt events at the Bear Brook Watershed, Maine (BBWM) during December 2001 and February 2002 and compared with results from Roy et al. (1999) from a January 1995 study of the same streams. The West Bear catchment has been subjected to artificial acidification since 1989. The East Bear catchment is the untreated reference. Most of the P export was with acid-soluble particulate Al in the 1995 event. Particulate P was co-precipitated with, occluded in, or adsorbed on acid-soluble $\text{Al}(\text{OH})_3$, which precipitated as emerging acidic groundwater degassed CO_2 and pH rose, or as the groundwater mixed with higher pH stream water. Induced acidification of the treated catchment resulted in increased transport of Al and P from soil to the stream, leading to greater Al and P export from the treated catchment, compared to the reference (Roy et al., 1999).

Particulate Al, Fe, and P were positively correlated with discharge during the 2001-2002 events. However, dissolved P concentrations remained low ($\leq 0.1 \mu\text{M}$) during high discharge events as pH decreased in both streams. For example, in 2001, total P concentration (acid-soluble) increased to $1.7 \mu\text{M}$ during the rising limb of the hydrograph in West Bear, approximately five times the value in East Bear. In 1995, the peak was $1.9 \mu\text{M}$ total P in West Bear, four times the value in East Bear. During the December 2001 event, dissolved Al concentrations increased to maxima of 21 and $6.3 \mu\text{M}$ in West Bear and East Bear, respectively, lower than maxima of 43 and $9.3 \mu\text{M}$ in 1995. Acid-soluble particulate Al concentrations in 2001 increased to 166 and $30 \mu\text{M}$ for West Bear and East Bear, respectively, up from 1995 maxima of 155 and $6.7 \mu\text{M}$. Dissolved Fe

concentrations remained $\leq 0.9 \mu\text{M}$ in both streams during all study events. However, acid-soluble particulate Fe concentrations in 2001 increased to 239 and $4.1 \mu\text{M}$ for West Bear and East Bear, respectively, up from 9.5 and $0.54 \mu\text{M}$ in 1995. Acid-soluble particulate Al and Fe declined parallel to total P after peaking during all study periods.

Nearly all of the base cations were in dissolved form during the three events, indicating that particulate Al in West and East Bear Brooks is not associated with primary minerals such as feldspars. Particulate acid-soluble Al concentrations substantially exceeded concentrations of particulate base cations in both streams during all sampling events. We conclude that particulate Al, Fe, and P are chemically linked during transport at high discharge in these episodically and chronically acidified streams.

Key words: acidification, aluminum, episodic acidification, iron, phosphorus, watershed manipulation

2. INTRODUCTION

Understanding the relationship between acid rain and phosphorus (P) mobilization in headwater systems is essential in the study of lake eutrophication. Lake eutrophication from excess P is a significant water quality problem. For example, one third of the natural water systems on Maine's threatened waters list are lakes, and 77% of those lakes are listed due to non-point pollution by P.

Particulate P increases with increasing discharge due to surface runoff and entrainment of material eroded from the stream bed or banks (Likens et al., 1977). Therefore, the bulk of annual particulate P export from northeastern U.S. forested

watersheds typically coincides with brief, high discharge events (i.e., fall rains, snowmelt). Dissolved P, on the other hand, is highly variable in relation to stream discharge among watersheds, and fluctuations may be correlated with, but not caused by, declining pH (Likens et al., 1977; Meyer and Likens, 1979; Munn and Prepas, 1986; Prairie and Kalff, 1988). Phosphorus adsorbed to secondary Al and Fe phases on soil particle surfaces may dissolve as acidified groundwater rises into the solum during high discharge (Fernandez and Struchtemeyer, 1985). Dissolution of these surface coatings would have the same net effect on the stream chemistry as transport and dissolution of the streambed material.

During catchment acidification, the accumulation of $\text{Al}(\text{OH})_3$ and P varies episodically and reversibly in stream sediments (Norton, 1975). Aluminum (Al) mobilization is attributed primarily to the acid-catalyzed dissolution of Al-bearing secondary minerals in the soil. Aluminum mobilization from soil and subsequent precipitation downstream may reduce the concentration of dissolved P by adsorption or co-precipitation (Kopacek et al., 2000).

Mobilization of other metals, including iron (Fe), may occur naturally in some watersheds during high flow events and is promoted by acidic and anoxic soil solutions with a high PCO_2 . Metal mobilization is enhanced in catchments subject to acidic precipitation, as observed in the two catchments in Bear Brook Watershed in Maine (BBWM), USA.

Release of Al, Fe, and P at BBWM was first addressed by Roy et al. (1999). They hypothesized that particulate Al, Fe, and P are chemically associated during transport, with the Al phase dominating. Roy et al. compared the chemistry of artificially

acidified West Bear Brook and untreated East Bear Brook catchments during a January 1995 high discharge event, when pH declined. The pH minimum was lower in the manipulated West Bear (4.8) than in the untreated East Bear (5.2). The pH decline was typical of episodic acidification of Maine streams (Kahl et al., 1992; Roy et al., 1999). Lower pH in West Bear Brook was attributed to higher concentrations of NO_3 and SO_4 , resulting from chemical manipulation, that were not wholly compensated by increased base cations. Higher concentration ranges for base cations in West Bear were attributed to cation desorption induced by the chemical manipulation. Concentrations of NO_3 , DOC, and dissolved Al increased in West and East Bear Brooks, consistent with the assumption of shallow flow paths. Concentrations of total P and Al were too high to be controlled by DOC, which only increased by 1 to 2 ppm.

The covariance of particulate Al and Fe with total P during the January 1995 event suggested that P- and Al- or Fe-bearing primary acid-soluble materials were eroded from the catchment, streambed, or stream banks, or P is chemically associated with particulate Al and Fe derived from the soil (Roy et al., 1999). The molar ratios of particulate Al to total P (50:1 to 100:1) did not suggest stoichiometric precipitation of P as an essential element of some mineral phase, but rather that P is adsorbed to or co-precipitated with $\text{Al}(\text{OH})_3$ (Norton and Henriksen, 1983; Roy et al., 1999). Iron should behave similarly to Al in the acidifying soils (Norton, 1989; Roy et al., 1999). Release and dissolution of Al and Fe particulate hydroxides from the stream bed as well as dissolution of Al and Fe adsorbed to stream substrates would occur during the rising limb of the hydrograph as pH decreases. Particulate Al and Fe may also be formed during high flow as CO_2 -rich, Al- and Fe-rich groundwater emerge to the higher pH and oxygen-

rich stream and degas CO₂, producing an increase in pH and precipitation of Al(OH)₃ and Fe(OH)₃.

Particulate and dissolved Al, Fe, and P during high discharge events at BBWM in December 2001 and February 2002 have been determined and compared to those reported by Roy et al. for January 1995. From 1995 to 2002, continuous artificial acidification of the West Bear catchment has affected the mobilization rates of Al, Fe, and P in the stream. We infer mechanisms controlling P export in surface waters undergoing chronic and episodic acidification.

3. METHODS

BBWM is comprised of the adjacent catchments of West and East Bear Brooks with areas of 10.7 and 10.2 ha, respectively. Soils in this catchment are primarily Spodosols, Inceptisols, and Folists with subsoil accumulations of sesquioxides (Fernandez and Struchtemeyer, 1985). Bimonthly treatments of 1,800 eq (NH₄)₂SO₄ ha⁻¹ yr⁻¹ have been applied to the West Bear catchment since 1989. The East Bear catchment is an untreated reference.

Stream water samples were collected simultaneously at short intervals from West and East Bear Brooks during periods of high discharge in December 2001 and February 2002. We used ISCOTM automated samplers fitted with 1 L acid-washed, plastic containers. Equilibrated pH was determined on 30 ml unfiltered aliquots equilibrated with air containing 300 ppm CO₂ at room temperature using a Radiometer combination pH electrode (model GK273920B). Alkalinity (ANC) was determined on 50 ml aliquots

via Gran Titration using a Radiometer Titration Manager with the same electrode. Sixty ml aliquots were filtered through Fisher 0.45 μm polyethylene filters into HDPE bottles, preserved with 2 drops of H_2SO_4 , and stored at 4°C until analysis for dissolved organic carbon (DOC) with an OI Corporation model 1010 TOC analyzer.

Total P and dissolved P were each determined on 50 ml aliquots by colorimetry. Samples for dissolved P were filtered through a 0.45 μm polyethylene filter prior to digestion. Total and dissolved P samples were digested by ammonium persulfate oxidation, autoclaved, and analyzed using the ascorbic acid method (Standard Method #4500 P-E) on a Thermospectronics Genesys5 Spectrophotometer. The detection limit was $1 \mu\text{g L}^{-1}$ with a precision of $\pm 1 \mu\text{g L}^{-1}$.

Samples for dissolved fractions of base cations and metals were filtered through a Fisher 0.45 μm polypropylene filter and acidified to $\text{pH} < 2$ with HNO_3 . Samples for total base cations and other metals were microwave-digested with HNO_3 at 180°C for 15 minutes prior to analysis. The remaining sample volume in the ISCO field container was acidified to 0.5% HNO_3 to dissolve any particulate Al and Fe hydroxides and associated P which had adhered to the walls of the sample container or had precipitated in the field container. The resulting concentrations using this “field total” method likely exaggerate total metal concentrations in the sample because the original volume had been reduced and any metals adsorbed on the container walls become concentrated in a smaller volume of acidified solution. Therefore, this field total method provides a maximum estimate of the concentration of metals initially in the container. Here we report total metal concentrations determined by the former method. The method of determining total metals concentrations for the December 2001 event differs from the method used for the

February 2002 events in that the aliquot for total metals was removed from the field container after the acidification for the field total method was done. Base cations (Ca, K, Mg, Na) and Al, Fe, and Si were determined using a Perkin-Elmer Optima 3300XL inductively coupled plasma optical emission spectrometer (ICP-OES) with axially-viewed plasma and a CETAC International, Inc. ultrasonic nebulizer.

4. RESULTS

Stream discharge for the three events at West and East Bear Brooks are reported in Figures 1-3. Maximum discharge increased in each successive event. Discharge ranged from 0.71 to 24.85 L s⁻¹ (28 L s⁻¹ = 1 mm/h) in East Bear during the 23-26 December 2001 event (Figure 1). The hydrograph in West Bear failed. Discharge ranges in West and East Bear Brooks were 0.73 to 35.76 and 0.73 to 46.95 L s⁻¹ for the 10-12 February 2002 event (Figure 2), and 2.46 to 126.15 and 3.45 to 132.55 L s⁻¹ for the 26-28 February 2002 event (Figure 3). The minimum equilibrated pH decreased in each successive event. Equilibrated pH decreased from 6.20 to 4.99 and 6.10 to 5.60 in December 2001 in West Bear and East Bear, respectively (Figure 1). Equilibrated pH decreased from 5.5 to 4.9 and 6.1 to 5.5 in West Bear and East Bear, respectively, during the early February event (Figure 2) and from 5 to 4.7 and 5.7 to 5.2 during the late February event (Figure 3).

Dissolved P concentrations remained low ($\leq 0.10 \mu\text{mol L}^{-1}$) in both streams during high discharge events during all three study periods (Figures 1-3). In December 2001, total P concentration (acid-soluble) increased to 1.7 μM during the rising limb of

the hydrograph in West Bear compared to 0.3 μM in East Bear (Figure 1). Acid-soluble total P concentrations reached 0.6 μM in both streams during the early February 2002 event (Figure 2). These concentrations were 3 and 1.5 μM during the late February event in West Bear and East Bear Brook, respectively (Figure 3).

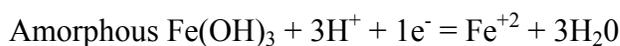
Maximum concentrations of dissolved Al increased with each successive event, consistent with the decreasing pH. Dissolved Al concentrations increased to maxima of 20.0 and 6.30 μM in West Bear and East Bear, respectively, during the December 2001 event (Figure 1). Dissolved Al concentrations reached 28.5 and 7.04 μM in West and East Bear, respectively during early February 2002 (Figure 2), and 40.0 and 11.5 μM during late February 2002 (Figure 3). Acid-soluble particulate Al concentrations in 2001 increased to 186 and 35.6 μM in West Bear and East Bear, respectively (Figure 1). Acid-soluble particulate Al concentrations reached maxima of 40.0 and 18.5 μM during the early February 2002 event (Figure 2), and 138 and 126 μM during the late February event (Figure 3), in West and East Bear Brooks, respectively. Thus the particulate Al maxima did not correspond to the maximum dissolved Al although the maxima could have occurred between sampling times.

Dissolved Fe concentrations remained low ($\leq 0.895 \mu\text{M}$) in both streams during the three events (Figures 1-3). However, acid-soluble particulate Fe concentrations in December 2001 increased to 251 and 4.12 μM for West Bear and East Bear, respectively (Figure 1). Concentrations of acid-soluble particulate Fe in West and East Bear Brooks reached maxima of 23.6 and 6.86 μM during the early February 2002 event (Figure 2), and 13.4 and 20.2 μM during the late February event (Figure 3). The particulate maximum for Fe occurred during the least acidic event, and vice versa.

Dissolved base cations comprised nearly all of the total base cations and remained relatively constant or decreased slightly as discharge increased during the three events (Table I). The difference between total and dissolved base cation concentrations was typically one to three $\mu\text{moles L}^{-1}$. Differences in base cation concentration ranges between West and East Bear Brook are attributed to cation desorption caused by the chemical manipulation of West Bear Brook (Norton et al., this volume). Particulate acid-soluble Al concentration also substantially exceeded concentrations of particulate base cations in both streams during each of the events. The difference between total and dissolved Al was on the order of approximately 100 micromoles per liter. From peak values, acid-soluble particulate Al and Fe declined parallel to total P during all events.

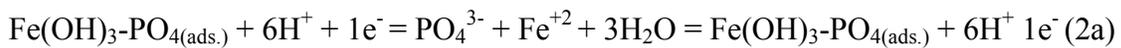
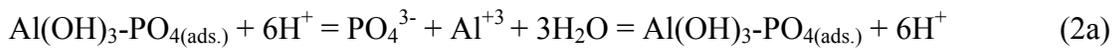
5. DISCUSSION

During periods of low flow, Al, Fe, and P are translocated from the mineral-rich B horizon soils to accumulate in the streambed. The particulate $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ in stream water during high flow likely originate from the streambed and from precipitated colloids from solutions leached directly from B horizon soil. The particulate $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ is likely formed as a consequence of increased pH caused by CO_2 degassing from soil solutions emerging into the stream, and mixing with higher pH and oxygen-rich water. The generalized reactions are, within the soil:



(1b)

These reactions consume alkalinity. The anion accompanying the release of the Al and Fe is HCO_3^{1-} , which is relatively abundant even at low pH because of the high PCO_2 in the soil. As the pH of the stream water rises because of CO_2 degassing, mixing with higher pH water, and oxygen is introduced, the reactions reverse. Phosphorus sequestered (adsorbed and occluded) in the sesquioxide-rich forest soils is released as the Al and Fe are mobilized, and is recaptured as the Al and Fe are precipitated in the stream water. These reversed reactions consume alkalinity with no net gain for the whole process.



Induced acidification of the treated catchment resulted in increased transport of Al, Fe, and P from the treated catchment compared to the reference catchment. The positive correlation between the particulate Al and P species, discharge, and lower pH is clear. Particulate Fe is higher during high discharge but is not as strongly related as Al. Dissolved P, however, does correlate with the discharge. Roy et al. (1999) observed the same lack of relationship. However, concentrations of total Al (160 μM) were significantly higher compared to total Fe (10 μM) in West Bear Brook during the 1995 discharge event. As a result, Roy et al. (1999) concluded that most of the particulate P was associated then with Al(OH)_3 , and to a lesser extent with Fe(OH)_3 .

Concentrations of total Al and Fe were comparable in West Bear Brook during the 2001-2002 events. Particulate P seems to track particulate Fe more closely in time during a single event. Total Al and P concentrations observed in West Bear in 2001-2002 were comparable to those observed in 1995. However, 2001-2002 discharge events had

higher total Fe concentrations compared to the 1995 event, perhaps due to earlier selective dissolution of more labile Al phases and lower pH.

Two lines of evidence indicate that the total P is not in primary minerals. Nearly all base cations are in dissolved form (Table 1). The presence of Ca primarily in a dissolved form precludes P associated with phosphate minerals such as apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) in the streams. Particulate P ranges up to $100 \mu\text{moles l}^{-1}$ whereas particulate Ca is in the few $\mu\text{moles L}^{-1}$ range and dissolved Ca is less than $100 \mu\text{moles L}^{-1}$, at all flows. Second, there is no stoichiometric relationship between P and Al or Fe or Si. By similar arguments, the particulate Al in both streams is not associated with primary minerals such as feldspars (KAlSi_3O_8 or $\text{NaAlSi}_3\text{O}_8$). It is too easily and quickly dissolved and little Ca occurs in the particulate fraction. Roy et al. (1999) also concluded from the January 1995 event that Al is not strongly associated with silicate minerals in the suspended material at either the West or East Bear Brook catchments on the basis of concentrations of particulate Al and base cations.

Particulate total Al was high in each of the three events, suggesting that much of the Al was derived directly from the soil as discharge increased, with relatively little intervening precipitation of Al in the stream substrates. The maximum total Fe decreased in each successive event, suggesting a slightly different mechanisms for mobilization and greater dependence on storage in the stream substrate.

Unlike dissolved Al that increased in both streams with a decreasing pH, dissolved Fe did not exhibit a dependence on pH. Dependence of dissolved Al on pH suggests relatively fast dissolution kinetics of $\text{Al}(\text{OH})_3$ in the soil leading to equilibrium with respect to this mineral. Lack of dependence of dissolved Fe and P concentrations on

pH may relate to the high redox conditions (low solubility) of the stream as well as kinetics of precipitation. Alternatively for P, the concentration of dissolved Al may be controlled in the stream by adsorption onto colloidal Fe and Al hydroxide. Colloidal $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ are effective adsorbents for many anions including P.

6.0 SUMMARY

Aluminum- and Fe-linked export of P appears to be episodic, occurring concurrently with increasing discharge and depressed pH at the Bear Brook Watershed in Maine. There are substantial difficulties in accurately determining the dissolved and particulate species because of time-dependent processes that are causing dissolved Al and Fe to precipitate. These processes include:

- Degassing of excess PCO_2
- Mixing of acidic groundwater with higher pH stream water
- Increasing the PO_2 as groundwater emerges into the stream

At BBWM export of Al and Fe in particulate acid-soluble form dominates the stream budget for these two elements. P is strongly associated with these particulate metals, with P in particulate form exceeding dissolved P by a factor of approximately 50. The pH does not control either dissolved Fe or P to an appreciable extent but dissolved Al is strongly controlled. Mobilization of these elements has been accelerated by progressive chronic acidification of the catchment and is particularly enhanced at high flow. Most mobilization to the stream appears to be a one-stage process from the soil to the stream water. However, temporary storage of precipitated Al and Fe, with adsorbed P, may occur in the stream substrate at lower flow. The mobilization of Al and Fe in this fashion

does not provide any net alkalinity to the system, only a removal of the solid phase from the soil. However, downstream P budgets may be substantially affected by the presence of the Al and Fe solids, both of which strongly adsorb P, thereby affecting trophic status of water.

7.0 ACKNOWLEDGMENTS

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Figure Captions

Figure 1. from top to bottom: (a) equilibrated pH (EqpH) and discharge (Q) ($L s^{-1}$) versus time (h) in West (WB) and East (EB) Bear Brooks from December 23-26, 2001; evolution of total and dissolved Al, Fe, and P ($\mu moles L^{-1}$) versus time (h) in (b) West Bear Brook and (c) East Bear Brook. Time zero equals 1600 h on 12/23/01). Subscripts 'Tot' and 'Diss' refer to total and dissolved concentrations, respectively.

Figure 2. from top to bottom: (a) equilibrated pH (EqpH) and discharge (Q) ($L s^{-1}$) versus time (h) in West (WB) and East (EB) Bear Brooks from February 10-12, 2002; evolution of total and dissolved Al, Fe, and P ($\mu moles L^{-1}$) versus time (h) in (b) West Bear Brook and (c) East Bear Brook. Time zero equals 1600 h on 2/10/02. Subscripts 'Tot' and 'Diss' refer to total and dissolved concentrations, respectively.

Figure 3. from top to bottom: (a) equilibrated pH and discharge ($L s^{-1}$) versus time (h) in West and East Bear Brooks from February 26-28, 2002; evolution of total and

dissolved Al, Fe, and P ($\mu\text{moles L}^{-1}$) versus time (h) in (b) West Bear Brook and (c) East Bear Brook from February 26-28, 2002 (time zero = 1600 h on 2/26/02). Subscripts 'Tot' and 'Diss' refer to total and dissolved concentrations, respectively.

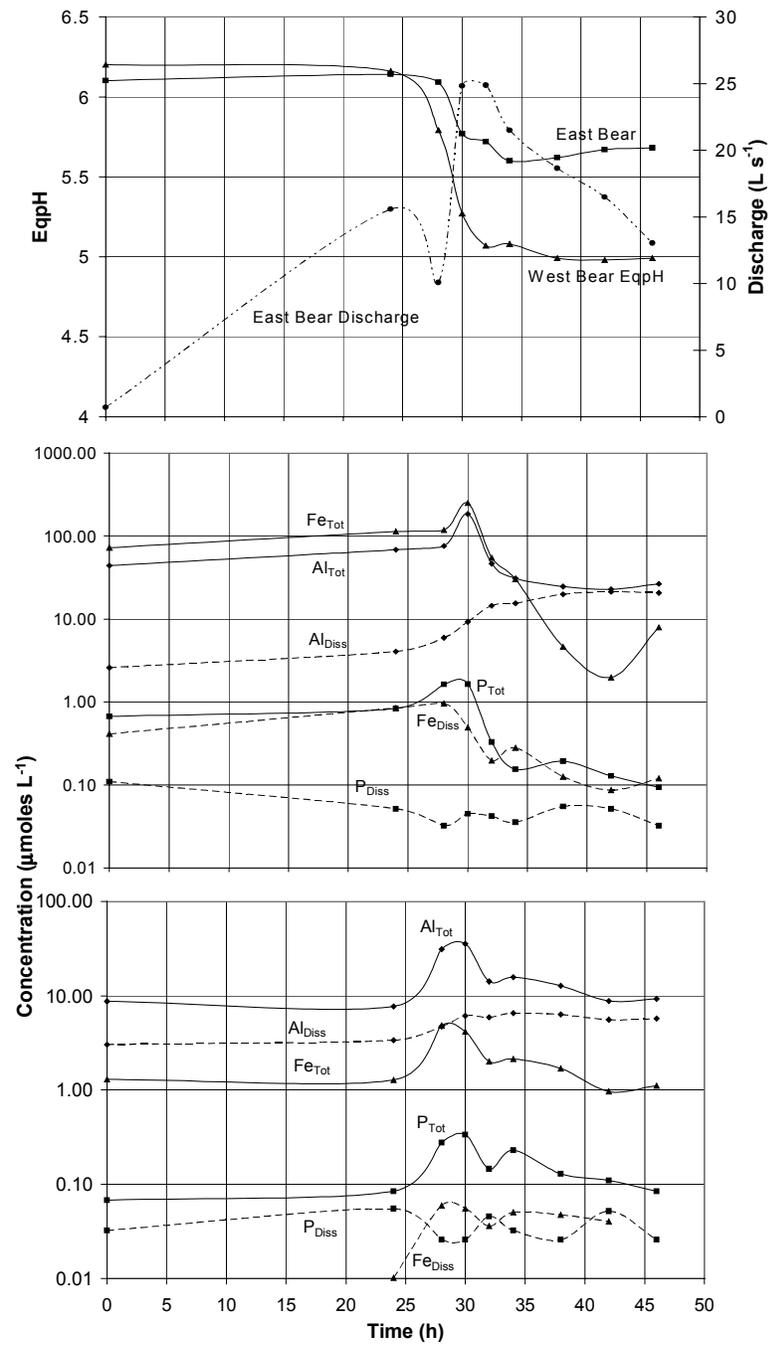


Figure 1.

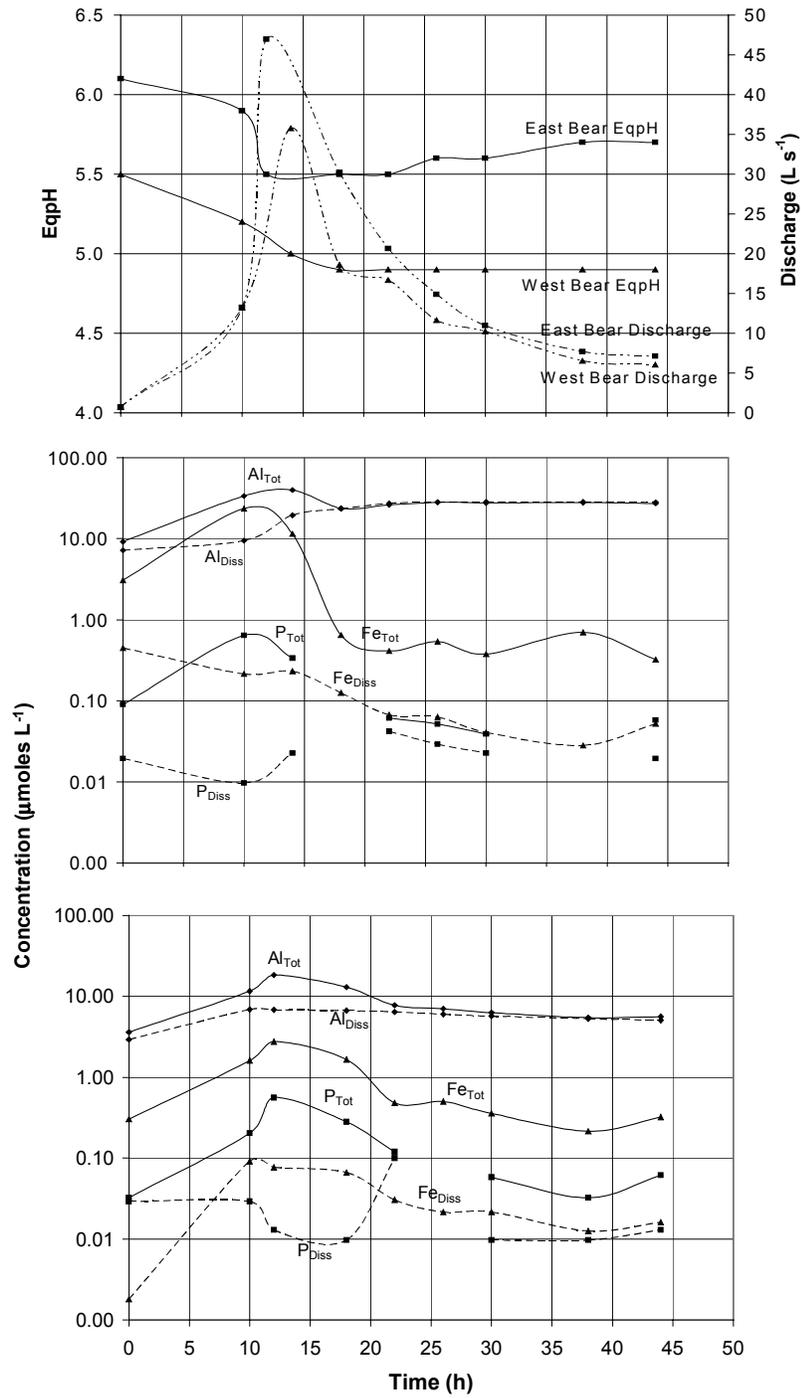


Figure 2

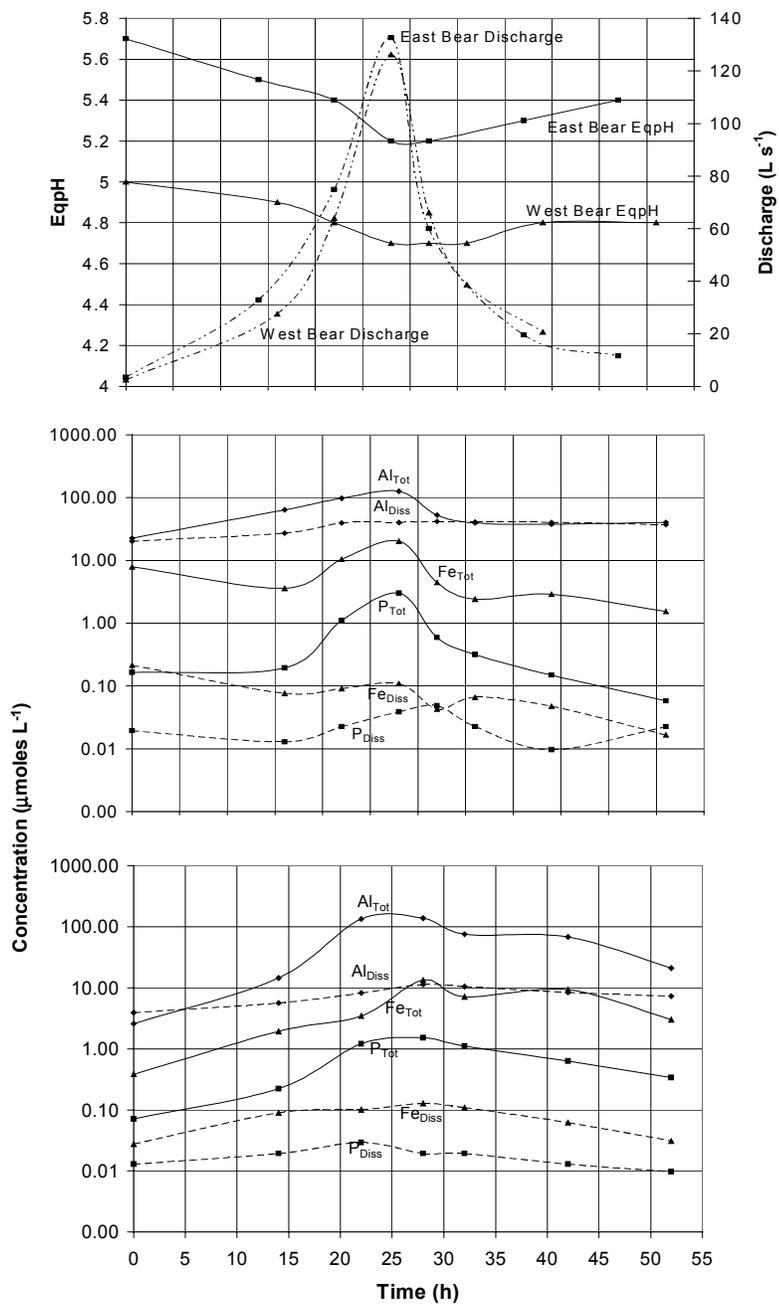


Figure 3

Table I
West and East Bear Brook chemistry for February 26-28, 2002

Date	Time	Discharge	DOC	Ca, mM	Ca, mM	K, mM	K, mM	Mg, mM	Mg, mM	Na, mM	Na
	h	L s ⁻¹	mg L ⁻¹	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dis
West Bear Brook											
26-Feb-2002	1600	2.46	1.75	0.054	0.055	0.007	0.007	0.020	0.020	0.095	
27-Feb-2002	800	27.58	2.24	0.050	0.051	0.008	0.008	0.019	0.020	0.089	
27-Feb-2002	1400	64.00	2.66	0.050	0.048	0.013	0.012	0.021	0.020	0.096	
27-Feb-2002	2000	126.15	3.47	0.064	0.050	0.020	0.016	0.022	0.021	0.087	
28-Feb-2002	0	66.09	3.08	0.052	0.051	0.014	0.013	0.021	0.022	0.084	
28-Feb-2002	400	38.74	2.89	0.050	0.051	0.012	0.012	0.021	0.021	0.095	
28-Feb-2002	1200	20.67	2.52	0.050	0.051	0.011	0.011	0.021	0.021	0.090	
1-Mar-2002	0	11.67	2.22	0.051	0.051	0.009	0.009	0.021	0.021	0.084	
East Bear Brook											
26-Feb-2002	1600	3.45	2.09	0.031	0.032	0.004	0.003	0.012	0.012	0.077	
27-Feb-2002	600	32.90	2.54	0.030	0.031	0.005	0.005	0.012	0.012	0.079	
27-Feb-2002	1400	74.95	3.41	0.039	0.029	0.008	0.007	0.013	0.012	0.076	
27-Feb-2002	2000	132.55	4.17	0.031	0.025	0.010	0.008	0.011	0.011	0.066	
28-Feb-2002	0	59.95	3.49	0.030	0.025	0.008	0.007	0.011	0.011	0.070	
28-Feb-2002	1000	19.62	2.96	0.030	0.026	0.006	0.007	0.011	0.011	0.074	
28-Feb-2002	2000	11.67	2.72	0.028	0.026	0.006	0.005	0.011	0.011	0.069	