

## USING ION-EXCHANGE RESINS TO STUDY SOIL RESPONSE TO EXPERIMENTAL WATERSHED ACIDIFICATION

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**Abstract.** Ion-exchange resins (IER) offer alternative approaches to measuring ionic movement in soils that may have advantages over traditional approaches in some settings, but more information is needed to understand how IER compare with traditional methods of measurement in forested ecosystems. At the Bear Brook Watershed in Maine (BBWM), one of two paired, forested watersheds is treated bi-monthly with S and N (28.8 and 25.2 kg ha<sup>-1</sup> yr<sup>-1</sup> of S and N, respectively). Both IER and ceramic cup tension lysimeters were used to study soil solution responses after ~11 years of treatment. Results from both methods showed treatments resulted in the mobilization of base cations and Al, and higher SO<sub>4</sub>-S and inorganic N in the treated watershed. Both methods indicated similar differences in results associated with forest type (hardwoods versus softwoods), a result of differences in litter quality and atmospheric aerosol interception capacity. The correlation between lysimeter and IER data for individual analytes varied greatly. Significant correlations were evident for Na ( $r = 0.75$ ), Al ( $r = 0.65$ ), Mn ( $r = 0.61$ ), Fe ( $r = 0.57$ ), Ca ( $r = 0.49$ ), K ( $r = 0.41$ ) and NO<sub>3</sub>-N ( $r = 0.59$ ). No correlation was evident between IER and soil solution data for NH<sub>4</sub>-N and Pb. Both IER and soil solution techniques suggested similar interpretations of biogeochemical behavior in the watershed.

**Keywords:** acidification, ion-exchange resin, nitrogen, soil solution, sulfur, watershed processes

### 1. Introduction

Studies of soil and soil solution chemical responses to elevated atmospheric nitrogen (N) and sulfur (S) deposition have shown that base cation depletion, accelerated N cycling, and sulfate (SO<sub>4</sub>-S) adsorption initially occur in surface or upper mineral horizons and progress with time into subsoil mineral horizons as acidification progresses deeper into the soil profile (Adams *et al.*, 1997; Fernandez *et al.*, 2003; Johnson *et al.*, 1988; Knoepp and Swank, 1994; Markewitz *et al.*, 1998; Meiwes *et al.*, 1998; Rustad *et al.*, 1993; Stuanes and Kjønaas, 1998). Differences in stream chemistry between peak and base flow (Edwards *et al.*, 2002; Moldan and Wright, 1998; Reinhardt *et al.*, 2004; Wright and Tietema, 1995) have confirmed progressive acidification with soil depth, as these stream chemistry differences were a result of soil chemistry differences during deep and shallow solution flow.

Organic horizons (or upper mineral [A] horizons) have important roles in nutrient cycling and storage in forested ecosystems. About 50% of the exchangeable calcium (Ca) was in the organic (O) horizon in soils in western Denmark (Vejre and Hoppe, 1998). Similarly, at the Cone Pond Watershed, New Hampshire, USA, over half ( $108 \text{ kg Ca ha}^{-1}$ ) of the total exchangeable Ca pool ( $195 \text{ kg Ca ha}^{-1}$ ) was in the O horizon (Bailey *et al.*, 1996). The upper 25–30 cm of soil at the Coweeta Hydrological Laboratory, North Carolina, USA, contained 31–46%, 31–43% and 12–25% of the total exchangeable Ca, potassium (K), and magnesium (Mg), respectively, with variations by soil type (Knoepp and Swank, 1994). Depletion of base cations from surface horizons, both organic and mineral, is problematic not only because these horizons contain a large part of the exchangeable pool, but also because a large proportion of the fine root mass is located in these horizons (Fahey *et al.*, 1988), making it likely that nutrient depletion impacts vegetation health and productivity. In addition, as soil acidification progresses into lower mineral horizons, Al that has been cycled by vegetative uptake and litter fall or has been mixed upward from mineral soil can displace base cations from the large bioavailable pool typical in surface forest soils (Lawrence *et al.*, 1995).

Soil solution flux data provide the best information on current soil dynamics (Marques *et al.*, 1996; Ranger *et al.*, 2001), but are difficult to measure in O horizons. Tension lysimeters, which sample both freely draining soil water and water held under tension, give information on solutions that have had more time to interact with soils than solutions sampled by zero-tension lysimeters. However, tension lysimeters are impractical to install in porous and commonly thin O horizons. For this reason, some researchers have experimented with ion-exchange resins (IER) to sample soil and soil solution chemistry.

The behavior of IER is analogous to soil particles (Skogley and Dobermann, 1996) and IER provide several advantages over traditional soil solution sampling: holding times prior to analysis are less stringent (Giblin *et al.*, 1994), installation and sampling are less time consuming (Johnson *et al.*, 2001; Giblin *et al.*, 1994), and the sampled area is less disturbed by resin installation (Gibson, 1986).

Several researchers (Binkley and Matson, 1983; Binkley *et al.*, 1992; Giblin *et al.*, 1994; Hart and Binkley, 1985; Lajtha, 1988; Lundell, 1989) have concluded that IER may provide a better relative measure of nutrient availability and may be more sensitive to site conditions compared to traditional methods. Good correlations between ions extracted with resins and traditional measures of nutrient availability have been found in laboratory and controlled greenhouse experiments (Binkley and Matson, 1983; McLaughlin *et al.*, 1993; Saggat *et al.*, 1990; Subler *et al.*, 1995; van Raij *et al.*, 1986), and in few field studies (Lajtha, 1988). In a comparison of conventional laboratory techniques with resin extraction for the measurement of exchangeable cations, McLaughlin *et al.* (1993) found that laboratory resin methods were comparable to traditional methods, with good regressions for Ca ( $r^2 = 0.87$ ), Mg ( $r^2 = 0.92$ ), K ( $r^2 = 0.73$ ), and other analytes. In month-long laboratory incubations, Subler *et al.* (1995) found that resin membrane measures of N dynamics

were more similar to soil N concentrations ( $r^2 = 0.85\text{--}0.96$ ) when an initial equilibration period was disregarded in data analysis. Binkley and Matson (1983) found that in greenhouse experiments, IER provided comparable N availability results to traditional measures ( $r = 0.71\text{--}0.87$ , varying by method). Lajtha (1988) found a good relationship ( $r^2 = 0.73$ ) between total mineral N on *in situ* resins and laboratory N mineralization rates. Most field researchers have found weak correlations between amount or accumulation rates of ions on IER when compared with extractable nutrients or *in situ* incubations (Binkley and Matson, 1983; Binkley *et al.*, 1992; Giblin *et al.*, 1994; Hart and Binkley, 1985; Lundell, 1989). Laboratory incubations for N availability compared to *in situ* resin extractions for nitrate ( $\text{NO}_3\text{-N}$ ) and  $\text{NH}_4\text{-N}$  resulted in low correlations coefficients ( $r = 0.08\text{--}0.41$ , based on incubation method) (Hart and Binkley, 1985). Other researchers in the literature also have reported weak correlations between traditional methods and IER methods (Giblin *et al.*, 1994; Lundell, 1989). In both laboratory and field studies, researchers have pointed out that measurements of nutrient availability by IER can incorporate site factors not assessed by other measures, such as moisture and temperature, that could have advantages over traditional methods (Binkley and Matson, 1983; Hart and Binkley, 1985; Lajtha, 1988; Lundell, 1989).

Previous investigators have used IER primarily for the quantification of N and P dynamics, and typically under ambient conditions not subjected to chemical manipulations. This study utilized IER techniques to evaluate soil solutions in treated and reference watersheds at the Bear Brook Watershed in Maine (BBWM), which is the site of a long-term, whole-watershed chemical manipulation using N and S. The objective of this study was to compare IER data with tension lysimeter soil solution data at BBWM for the effects of chemical treatments and forest types.

## 2. Methods

### 2.1. STUDY SITE

The Bear Brook Watershed in Maine (BBWM) is located in eastern Maine, USA, on the upper southeastern slope of Lead Mountain, approximately 60 km from the Atlantic Ocean (Norton *et al.*, 1999). Adjacent East and West Bear Brooks form the paired watershed experiment at BBWM, and drain 11.0 and 10.3 ha of forest land, respectively. Elevation within the watersheds ranges from 210 m to 475 m, with an average slope of 31%. Mean annual temperature is  $\sim 5^\circ\text{C}$ . Mean daily temperatures typically range from  $25^\circ\text{C}$  in the summer to  $-20^\circ\text{C}$  in winter. Annual precipitation is  $\sim 1.3$  to 1.4 m, with  $\sim 25\%$  as snow.

The dominant soils at BBWM are loamy, mixed, frigid Typic Haplorthods formed in till. Soils associated with softwoods tend to be thin mineral soils with O horizons  $\sim 12$  cm thick, or organic soils (Folists) on steeper slopes; in contrast,

soils in hardwood-dominated areas have thicker mineral horizons with thinner O horizons that are ~7 cm thick. All study pedons were well-drained mineral soils. Soils were generally acidic, and had relatively low base saturations, sulfate adsorption capacities, and cation exchange capacities. Based on these characteristics, BBWM was considered vulnerable to acidification (Norton *et al.*, 1999).

Bedrock consists of non-calcareous, non-sulfidic meta-pelites and quartzites at higher elevations, whereas calc-silicate gneiss predominates lower in the watersheds. Granite dikes and sills are common in the bedrock, and bedrock outcrops are common in the upper portion of the watershed (Norton *et al.*, 1999). Till covering the bedrock ranges in thickness from 0 to 5 m, with an average thickness of ~1 m.

Vegetation consists of hardwoods at lower elevations, a mid-zone of mixed hardwoods and softwood (i.e., mixed woods), and softwoods at higher elevations. The lower limit for softwoods resulted from logging in the 1950s (Norton *et al.*, 1999). Hardwoods were ~55 years old, and softwoods were >100 years old, with individuals >150 years old (Elvir, 2001). Major hardwood species at BBWM were American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), and red maple (*Acer rubrum*) with smaller amounts of yellow birch (*Betula alleghaniensis*) and paper birch (*Betula papyrifera*). Red spruce (*Picea rubens*) accounts for the majority of the softwood stand, with minor amounts of balsam fir (*Abies balsamea*) and hemlock (*Tsuga canadensis*). Species composition and extent for each forest type are similar in both East and West Bear (Elvir, 2001).

## 2.2. TREATMENT

East and West Bear streams were hydrologically and chemically similar before the treatments began in November 1989, based on observations from 1987–1989 (Norton *et al.*, 1999). West Bear watershed has been treated by helicopter since 1989 with bi-monthly additions of 300 eq  $(\text{NH}_4)_2\text{SO}_4 \text{ ha}^{-1}$ , for a total annual loading of 1800 eq  $\text{ha}^{-1}$  (25.2 kg N  $\text{ha}^{-1} \text{ yr}^{-1}$  and 28.8 kg S  $\text{ha}^{-1} \text{ yr}^{-1}$ ). Treatments were applied on: 25 June 2001, 22 Aug. 2001, 11 Oct. 2001, 4 Dec. 2001, 7 Feb. 2002, 5 Apr. 2002, and 25 June 2002. East Bear serves as the untreated reference watershed. Ambient wet deposition to BBWM averaged 118 eq  $\text{ha}^{-1} \text{ yr}^{-1}$  for  $\text{NH}_4\text{-N}$ , 192 eq  $\text{ha}^{-1} \text{ yr}^{-1}$  for  $\text{NO}_3\text{-N}$  and 350 eq  $\text{ha}^{-1} \text{ yr}^{-1}$  for  $\text{SO}_4\text{-S}$  (4.3 kg N  $\text{ha}^{-1} \text{ yr}^{-1}$  and 5.6 kg S  $\text{ha}^{-1} \text{ yr}^{-1}$ ) for calendar years 1998–2000 (unpublished data).

## 2.3. RESIN PREPARATION AND UNIT ASSEMBLY

Bio-Rad® AG50W-X8 (BioRad® Laboratories, California, USA), a strong cation resin, was used in the  $\text{H}^+$  form, 20–50 mesh. Bio-Rad® AG1-X8 (BioRad® Laboratories, California, USA), a strong anion resin, was used in the  $\text{Cl}^-$  form, 20–50 mesh. Three grams of either anion or cation resin were enclosed in circular (45-mm diameter) Nitex® nylon bags. After assembly, the resin bags were soaked

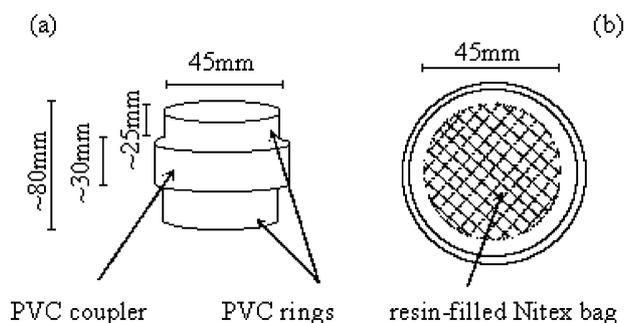


Figure 1. Side (a) and top (b) view of the ion exchange resin unit.

separately in 0.5 M hydrochloric acid (HCl) for one hour and then rinsed six times in deionized water.

One resin bag was placed in each PVC assembly unit, which consisted of a coupler into which two rings were inserted (Figure 1) to hold the Nitex<sup>®</sup> resin-filled bag firmly in place. All PVC components were washed in 10% HCl and rinsed six times in deionized water prior to inserting the resin bags. During assembly, installation, collection and extraction of the resins, workers wore powder-free nitrile laboratory gloves to reduce the possibility of resin contamination.

#### 2.4. EXPERIMENTAL DESIGN AND RESIN INSTALLATION

Five 5-by 5-m plots were established in June 2001 in each combination of forest type and watershed (referred to hereafter as compartment); i.e., (1) East Bear hardwood, (2) East Bear softwood, (3) West Bear hardwood, (4) West Bear softwood. Within each of the 20 plots, ion exchange resins and lysimeters were used to monitor soil solution chemistry.

Resin units (the PVC assembly with Nitex<sup>®</sup> resin-filled bag) were deployed in June 2001, Oct. 2001, and May 2002 for a period of 116, 192, and 142 days, respectively. At each lysimeter plot, one anion and two cation resin units were installed at the bottom of the organic horizon. The organic horizon was gently lifted, and the resin assembly was gently pressed into the top of the mineral soil surface. The organic horizon was replaced in its original position with as little disturbance as possible. This placement at the interface of the abrupt boundary between the organic and underlying mineral soil was intended to capture soil solution leaching from the bottom of the organic horizon prior to interaction with mineral soil. This design did allow for the possibility of capillary contact between the resin bag and underlying mineral soil where settling of the assembly allowed mineral soil to completely fill the void beneath. In most instances there was an air-filled void beneath the resin, and all sites were well drained so solution flux was downward. Field resin blanks were made by placing resin units into plastic bags, then installing blanks under the

organic horizon. These field blanks were treated similarly to other resin units prior to and following placement in plots.

In order to determine the minimum amount of time resins needed to be in the field, we conducted a study of resin adsorption after deployments of 32, 53, 95 and 116 days. Based on the results of this trial, we concluded that at least 95 days were needed before IER adsorbed enough ions to provide a clear concentration signal readily detectable above background concentrations in the resin extracts. When resin deployment was 95 days or greater, the concentrations of ions in field blanks were at least an order of magnitude smaller than field sample values. When field blanks were compared with fresh unused resin, concentrations of ions in field blanks were an average of 4.5 times higher than new resin, and ranged from 1–15 $\times$ .

## 2.5. RESIN COLLECTION, EXTRACTION, AND ANALYSES

Resins installed in June 2001 were collected in Aug., Sept. and Oct. 2001; resins installed in Oct. 2001 were collected in May 2002, and resins installed in May 2002 were collected Oct. 2002. Soil and debris were removed from the unit upon collection, and it was placed in a plastic bag and sealed. Resin units were stored at 4 °C after collection. Within a week of collection, resin units were disassembled, and resin bags with their contents were rinsed in deionized water to remove remaining soil particles and stored at 4 °C until extraction.

For extraction, resins were placed in a 150 ml Erlenmeyer flask with 100 ml of the extracting solution. The flasks, covered with parafilm, were placed on a mechanical shaker and shaken for 30 min, then filtered through a 0.45- $\mu$ m membrane filter and stored at 4 °C until analysis. One set of cation resins was extracted with 0.5 M hydrochloric acid (HCl) and analyzed for Ca, Mg, Al, manganese (Mn), potassium (K), sodium (Na), iron (Fe) and lead (Pb) by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The second set of cation resins was extracted with 1 M KCl and analyzed colorimetrically for NH<sub>4</sub>-N by flow injection analysis (FIA). The anion resin was extracted with 1 M NH<sub>4</sub>Cl and analyzed for total S by ICP-AES and for NO<sub>3</sub>-N by cadmium reduction with flow injection analysis (FIA).

Quality assurance included field blanks, laboratory blanks, reagent blanks, and triplicate splits of solution extracts. Concentrations of analytes extracted from the resins were normalized to an areal per day basis, and all means were weighted by days of deployment to account for different deployment periods. The molar ratios Ca/Al and Ca/Mg were calculated from means of extracted Ca, Al, and Mg.

## 2.6. LYSIMETERS

In May 2001, 40 mm inner diameter ceramic-cup tension lysimeters were installed in the 5- by 5-m plots. Resins were installed in a diagonal plot corner to reduce any disturbance effect associated with the lysimeter installation. In all 20 plots, one tension lysimeter was installed 25 cm below the mineral soil surface. These

lysimeters were right-angled so that they could be installed horizontally from an adjacent soil pit, thereby minimizing disturbance of the area above the ceramic cup. There were 11 soil solution collection dates between July 2001 and June 2002. Prior to collection,  $-300$  to  $-500$  kPa tension was applied to each lysimeter, and lysimeters were sampled within 1–2 days. Soil solutions were refrigerated at  $4^{\circ}\text{C}$  until analysis. Within 10 days of collection, solutions were filtered through a  $0.45\text{-}\mu\text{m}$  membrane filter before analysis for major cations and anions. Calcium, Mg, K, Na, Al, Fe, and Mn were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES);  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  were determined colorimetrically by flow injection analysis (FIA);  $\text{SO}_4\text{-S}$  and chloride (Cl) were determined by ion chromatography (IC). Extracts of IER were analyzed for total S by ICP because of the high ionic strength of these extracts which would quickly degrade IC columns. The ICP measures all forms of S present. Therefore correlations for S between soil solution and IER in this study could have been strengthened or weakened by the non- $\text{SO}_4\text{-S}$  forms of S present.

## 2.7. DATA ANALYSES

All data were evaluated for normality using skewness, kurtosis, the Shapiro-Wilk W statistic, and histogram plots. All data were log transformed to meet the assumptions of normality, with the exception of Pb, which required no transformation, and  $\text{NO}_3\text{-N}$ , which required a rank transformation. Mixed-model analysis of variance was used to model the variance structure of the data. This ANOVA was used to test for significant differences between watersheds and forest types. When the interaction between watershed and forest type was significant, a protected Tukey's HSD means separation was used to detect differences between these means. Using overall means for the study period, resin data and lysimeter data were aggregated to the plot level and Spearman correlation coefficients were calculated to assist in evaluating the relationship between analytes extracted from resin and analytes in soil solution. Statistical analyses were performed using the Statistical Analysis System (SAS, 1999) at an *a priori* determined significance level of 0.10, unless otherwise stated.

## 3. Results and Discussion

### 3.1. TREATMENT AND FOREST TYPE EFFECTS

Mean concentrations of analytes extracted from IER, expressed on a per day basis, are shown in Table I for the interaction between watershed (East Bear, reference watershed and West Bear, treated watershed) and forest type. Only resin Pb accumulation rates resulted in a significant interaction between watershed and forest type, and the numerical differences in accumulation rates were small. Higher Pb accumulation rates in softwoods was likely attributable to higher dissolved organic

TABLE I

Time- and area-weighted means of selected analytes extracted from ion-exchange resins (and standard errors in parentheses) for the interaction between watershed and forest type

Analyte <sup>a</sup>	East Bear		West Bear	
	Hardwood	Softwood	Hardwood	Softwood
Ca	83.8 (29.5)	33.5 (5.5)	67.8 (13.3)	54.9 (18.1)
Mg	57.9 (18.0)	63.2 (13.8)	40.4 (8.5)	115.7 (36.4)
K	42.4 (11.5)	81.5 (26.0)	49.3 (14.0)	128.4 (52.4)
Na	133.0 (68.2)	186.2 (44.9)	10.5 (3.6)	367.1 (111.2)
Al	1.41 (0.51)	6.35 (1.90)	0.434 (0.211)	51.4 (24.0)
Fe	0.236 (0.062)	2.06 (0.63)	0.215 (0.073)	1.01 (0.23)
Mn	0.587 (0.145)	1.37 (0.38)	6.10 (1.43)	2.25 (0.70)
Pb	0.014 (0.003) a	0.022 (0.005) ab	0.017 (0.005) a	0.043 (0.013) b
NO <sub>3</sub> -N	16.8 (5.0)	218.0 (64.2)	113.3 (43.1)	405.1 (167.7)
NH <sub>4</sub> -N	45.1 (15.3)	65.4 (20.3)	220.8 (72.4)	291.1 (108.1)
S	130.8 (45.5)	476.4 (115.9)	150.3 (75.4)	1568.2 (135.2)
Ca/Mg	1.45	0.52	1.70	0.47
Ca/Al <sup>b</sup>	30.0	2.62	85.0	0.54

*Note.* Means within rows followed by the same letter, or without letters, are not significantly different from each other at  $\alpha = 0.10$ .

<sup>a</sup> Units are  $\mu\text{eq m}^{-2} \text{d}^{-1}$  for all analytes, except  $\mu\text{mol m}^{-2} \text{d}^{-1}$  for Al, Fe, Mn and Pb.

<sup>b</sup> Molar ratio (mol/mol).

carbon (DOC) concentrations in softwoods (Fernandez *et al.*, 1999) which would be an effective mechanism for the transport of complexed Pb in these soils, and higher atmospheric inputs of Pb deposition due to greater interception efficiencies in softwood canopies.

Table II shows mean IER accumulation rates for the main effects of forest type and watershed. For watershed differences, all analytes had numerically higher mean accumulation rates on IER in the treated West Bear compared to East Bear watersheds, with the exception of Fe. Statistically significant differences between West Bear and East Bear are shown in Table II for Mn, NO<sub>3</sub>-N, and NH<sub>4</sub>-N, which were 450, 230, and 440% higher in West Bear compared to East Bear, respectively. These differences are consistent with accelerated N dynamics in West Bear compared to East Bear (Jefts *et al.*, 2004) in response to the N additions. For forest type effects, accumulations of Na, Al, Fe, and Pb on IER were significantly greater in softwood stands than in hardwoods, and most analytes exhibited parallel numerical differences. Calcium and Mn were the exceptions, with numerically higher accumulation rates in hardwoods. Higher Ca to Mg ratios (Ca/Mg) and Ca to Al ratios (Ca/Al) in hardwood stands were primarily the result of higher resin Ca concentrations in hardwoods. In some instances the main effect differences are

TABLE II

Time- and area-weighted means of selected analytes extracted from ion-exchange resins (and standard errors in parentheses) in the reference and experimental watersheds and hardwood and softwood forest types

Analyte <sup>a</sup>	Watershed		Forest type	
	East Bear	West Bear	Hardwood	Softwood
Ca	58.6 (14.8)	61.3 (11.2)	75.8 (15.6)	44.1 (9.4)
Mg	60.6 (11.1)	78.1 (19.0)	49.2 (9.7)	89.5 (19.5)
K	62.0 (14.5)	88.8 (27.7)	45.9 (9.0)	104.9 (29.3)
Na	159.6 (39.9)	188.8 (61.7)	71.7 (33.5)	276.7 (61.1)*
Al	3.88 (1.1)	25.9 (12.3)	0.920 (0.274)	28.9 (12.2)*
Fe	1.16 (0.35)	0.610 (0.133)	0.240 (0.047)	1.50 (0.34)*
Mn	0.980 (0.21)	4.20 (0.85)*	3.40 (0.87)	1.80 (0.40)
Pb	0.018 (0.003)	0.030 (0.007)	0.016 (0.032)	0.033 (0.007)*
NO <sub>3</sub> -N	117.3 (34.3)	259.2 (89.6)*	65.0 (23.0)	311.6 (89.6)
NH <sub>4</sub> -N	55.3 (12.6)	255.9 (64.3)*	133.0 (40.3)	178.2 (57.8)
S	303.6 (65.8)	859.2 (676.7)	140.5 (43.0)	1022.3 (653.2)
Ca/Mg	0.97	0.78	1.55	0.49
Ca/Al <sup>b</sup>	7.6	1.17	42.2	0.76

Note. Means followed by \* are statistically different by watershed or forest type at  $\alpha = 0.10$ .

<sup>a</sup>Units are  $\mu\text{eq m}^{-2} \text{d}^{-1}$  for all analytes, except  $\mu\text{mol m}^{-2} \text{d}^{-1}$  for Al, Fe, Mn and Pb.

<sup>b</sup>Molar ratio (mol/mol).

largely driven by only one forest type, such as watershed differences largely due to West Bear hardwood for Mn, and West Bear softwood for Al and NO<sub>3</sub>-N. In contrast, the significant response of NH<sub>4</sub>-N to treatment (Table II) was consistent across forest types in West Bear.

Quantitative pedon soil sampling by Fernandez *et al.* (2003) found lower exchangeable Ca and Mg in West Bear which they attributed to treatment effects. Szillery (2003) found higher soil solution Ca and Mg concentrations in West Bear compared to East Bear. Although not statistically significant, numerically higher rates of Ca and Mg accumulation on IER in West Bear (Table II) are consistent with these results. When base saturation is sufficient, base cation acid neutralization mechanisms initially respond to treatments resulting in the desorption of exchangeable Ca and Mg from soil colloidal surfaces. As a result of this exchange process, soil solution concentrations of base cations initially increase, which can result in net base cation depletion from the soil exchange complex if rates of base cation supply from mineral weathering, atmospheric deposition, or management cannot keep pace. As base cations are depleted from soils, acid neutralization mechanisms shift from base cation exchange to the hydrolysis and mobilization of Al and other metals. Aluminum is mobilized from soils below pH  $\sim 5.5$  from oxyhydroxide minerals, and becomes increasingly prevalent in soil solutions with

acidification (Reuss, 1983) and can displace more base cations through biocycling or capillary action (Lawrence *et al.*, 1995). Aluminum accumulation rates on IER were not significantly different between East Bear and West Bear (Table II), but the numerical trends for higher Al in West Bear were consistent with mobilization of Al in response to treatment. Although the relative difference in Mn accumulation was 400% greater for West Bear, the absolute difference was small. Thus, the role of Mn in acid neutralization is small.

Recent work at BBWM has suggested that Fe mobilization could also be a significant acid neutralization mechanism after over a decade of treatments (Norton *et al.*, 2003). Soil solution Fe concentrations from this study did not show evidence of Fe mobilization in response to acidification. This lack of response for Fe in soil solutions could indicate that stream Fe changes due to acidification are originating from watershed positions or soil depths beyond the soil zone sampled by our resins, or artifacts of sample processing (e.g., filtration) are excluding a particulate Fe phase and with it the signal of response to treatments (Norton *et al.*, 2003). Soil solution data (Szillery, 2003) showed that Al mobilization had become the most important acid neutralization mechanism in these forest soils after a decade of treatments, and IER data support that interpretation.

Sodium and Pb had larger responses to forest type than to treatment, based on IER accumulation rates. Higher concentrations of analytes under softwood stands compared to hardwoods were interpreted to be the result of a higher aerosol interception capacity of softwood canopies (Currie *et al.*, 1999; Houle *et al.*, 1999; Hultberg and Grenfeldt, 1992; Norton *et al.*, 1988; Rustad *et al.*, 1994; Waring *et al.*, 1981). Because of the proximity of BBWM to the Atlantic Ocean, evidence of a greater aerosol interception capacity in the canopy for softwoods compared to hardwoods was best expressed as higher accumulations of Na and Mg on IER in softwood stands due to marine aerosol interception. Higher IER N, S, and Pb accumulation rates were attributable to a greater interception of dry and occult deposition by softwood canopies. By contrast, Ca accumulation rates on IER were higher in hardwoods than softwoods. The Ca results reflect higher Ca content in hardwood vegetation and faster biogeochemical cycling between litter, soil, and biomass (Clarholm, 2002; Cole and Rapp, 1981; Hart *et al.*, 2003).

Significantly higher accumulation rates for Al, Fe, and Pb on IER were detected in softwoods compared to hardwoods. Higher DOC and lower pH in soil solutions under softwood stands (Szillery, 2003) would have enhanced mobilization of these metals (Huang and Kiang, 1972). The exception to this pattern among metals was for higher Mn accumulation rates on IER in hardwoods stands (Table II), and no clear explanation for the Mn response is evident. Szillery (2003) surmised that because of historically elevated net N mineralization and nitrification rates in West Bear hardwoods (Wang and Fernandez, 1999; Jefts *et al.*, 2004), the more labile Al oxyhydroxide coatings on soil particles may have been depleted by acidification resulting in a mobilization of Mn from these materials. This could result in

elevated concentrations of Mn in West Bear hardwoods as compared with other compartments.

Higher accumulation rates of  $\text{NH}_4\text{-N}$  and total S on IER in West Bear were expected as a direct result of treatments to West Bear with  $(\text{NH}_4)_2\text{SO}_4$  (Table II). The significantly higher accumulation rates of  $\text{NO}_3\text{-N}$  in West Bear reflect high rates of nitrification, consistent with previous studies of soil N transformations at BBWM (Nadelhoffer *et al.*, 1999; Jefts *et al.*, 2004). The highest rates of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  accumulation on IER were in West Bear softwood stands (Table I). Although softwood organic horizons are thought to have lower rates of N turnover than hardwoods, Jefts *et al.* (2004) found that in West Bear, O horizons under softwoods had significantly higher rates of net N mineralization than under hardwoods. They suggested that this unexpected contrast in N mineralization between forest types at BBWM may reflect changes in the response of West Bear softwoods as a result of the build-up of soil N pools over the first decade of treatment. After over a decade of N enrichment they surmised that threshold carbon to nitrogen (C/N) ratios may have been attained that resulted in measurable increases in N mineralization.

### 3.2. COMPARISON OF RESIN AND LYSIMETER DATA

Spearman correlations were determined using data aggregated to the plot level to assess the relationship between analyte accumulations on IER and soil solution concentrations (Table III). Graphical representations of the data for Ca, Al, Na,

TABLE III  
Spearman correlation coefficients ( $r$ ) and  $p$ -values for the relationship between analytes extracted from ion-exchange resins and soil solution analyte concentrations

Analyte <sup>a</sup>	$r$	$P$ -value
Ca	0.49	0.05
Mg	0.35	0.17
K	0.41	0.10
Na	0.75	<0.001
Al	0.65	0.006
Fe	0.57	0.02
Mn	0.61	0.01
Pb	-0.10	0.70
$\text{NO}_3\text{-N}$	0.59	0.01
$\text{NH}_4\text{-N}$	0.03	0.92
S/ $\text{SO}_4\text{-S}$	0.01	0.72

<sup>a</sup>Units for resin data are as noted in Tables I and II. Units for soil solution data are  $\mu\text{mol}_e \text{L}^{-1}$  for all analytes, except  $\mu\text{mol} \text{L}^{-1}$  for Al, Fe, and Mn.

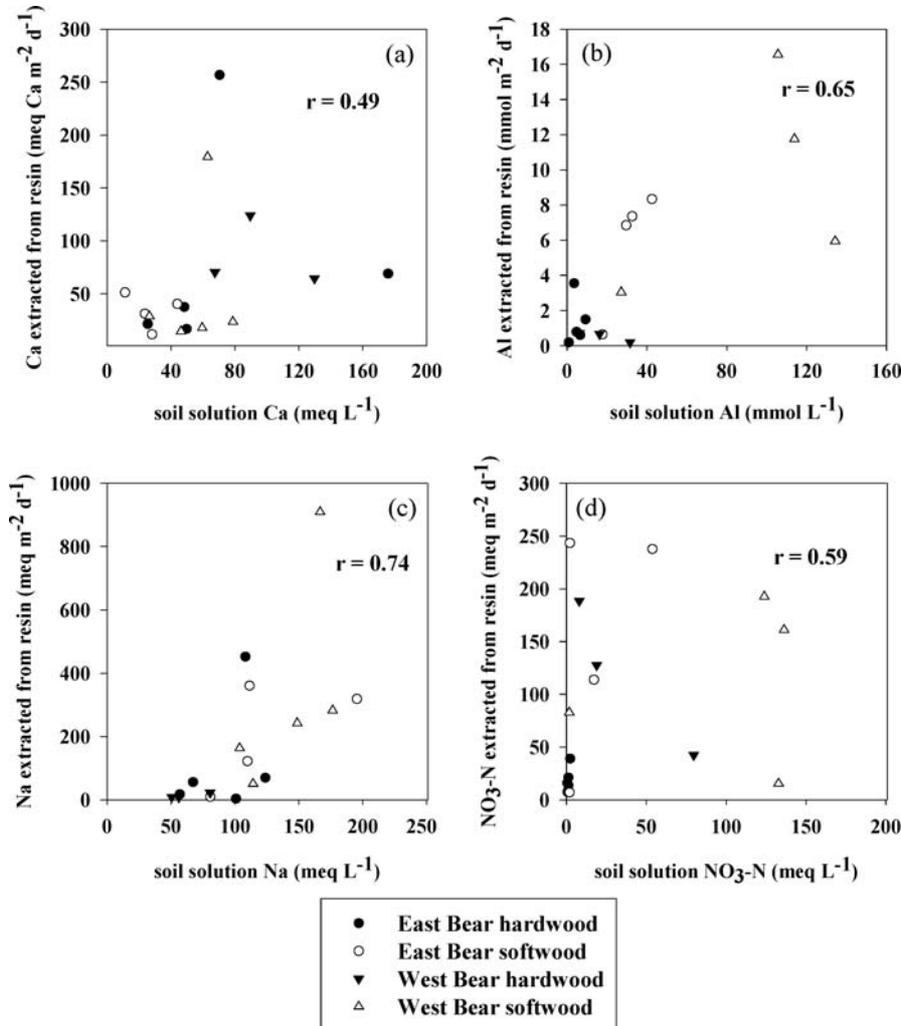


Figure 2. Spearman correlation between analytes extracted from ion-exchange resins and analytes in soil solution for: (a) Ca (b) Al (c) Na and (d) NO<sub>3</sub>-N.

and NO<sub>3</sub>-N are shown in Figure 2. Only 17 of the possible 20 plot-level lysimeter means were available for these correlations due to low collection efficiencies for three plots as a result of drought conditions during the summer of 2001.

The correlations between IER-extracted and soil solution Na and Al concentrations were the strongest among the analytes in this study, with  $r = 0.75$  and  $0.65$ , respectively (Table III). Figure 2 also shows a tendency for individual plot data within compartments (e.g. West Bear watershed, softwood forest type) to cluster reflecting the influence of both of the main effects in some instances. Other analytes such as Ca and NO<sub>3</sub>-N showed greater variability among plots within

compartments and between IER and soil solution data. As soil solution  $\text{NO}_3\text{-N}$  concentrations increased, the variability of  $\text{NO}_3\text{-N}$  extracted from IER increased (Figure 2d). From these data it appeared that IER may be better suited to estimates of  $\text{NO}_3\text{-N}$  than  $\text{NH}_4\text{-N}$  when used as surrogates for soil solutions because soil solution and IER  $\text{NO}_3\text{-N}$  concentrations were better correlated than resin and soil solution  $\text{NH}_4\text{-N}$  concentrations (Table III). However, Hart and Binkley (1985) reported that IER underestimated  $\text{NH}_4\text{-N}$  but overestimated  $\text{NO}_3\text{-N}$ , compared with traditional measures of N availability.

#### 4. Conclusions

The goal of the IER system used in this study was to provide a cumulative sample of solutes percolating downward in soil solutions under the O horizons of forest soils by a system that required minimal field work compared to conventional lysimetric methods. Our findings suggested that ion-exchange resins, as deployed here, were not highly correlated with tension lysimeter solution composition. However, the IER assembly used in this study resulted in IER analyte accumulation rates that indicated similar ecological processes were important in the response of a forested watershed to N and S additions as were seen in soil solutions and are supported by other BBWM studies in the literature. This supports IER techniques for the characterization of relative soil solution chemical losses. IER have the advantage of providing an integration of leaching losses over time without multiple samplings and the hydrological uncertainties typical of traditional lysimeter techniques. This approach to the use of IER *in situ* should be carried out on a wider range of soil and forest community conditions, with intensive simultaneous lysimetry to provide quantitative comparisons between these techniques.

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