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Trace metal loss following whole-tree harvest of a northeastern deciduous forest, U.S.A.

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Abstract. We examined changes in the biogeochemistry of trace metals following a commercial whole-tree harvest (WTH) at the Hubbard Brook Experimental Forest in New Hampshire. Within 6 months after completion of the WTH, maximum streamwater concentrations of Ni, Cd, Ba, Sr, Mn, Zn and Fe increased two- to nine-fold. Streamwater concentration of Cu remained unchanged after harvest. Streamwater pH decreased from 5.2 to 4.5 after the harvest, and correlated strongly with trace metal concentrations except for Fe. The decrease in pH apparently resulted from increased nitrogen mineralization and nitrification following harvest. All streamwater metal concentrations (except Mn and Fe) in the disturbed watershed increased prior to the decrease in streamwater pH, suggesting that the loss of readily exchangeable metals, not increased mineral dissolution, was responsible for the initial increase in streamwater trace metal concentrations. In contrast, streamwater Mn concentrations did not increase until streamwater pH dropped to 4.5, due in part to increased mineral dissolution. Although pH related strongly to trace metal concentrations in the harvested watershed, it did not account for much of the variation in metal concentrations in the reference (W6) watershed. Annual flux of trace metals increased two- to eight-fold following WTH. Annual losses of Mn and Sr were 14% and 12% respectively of the forest floor pool for each element, and less than 10% of forest floor pools for all other elements. Except for Cd and Cu, annual trace metal losses in streamwater exceeded annual inputs in bulk precipitation.

Introduction

Trace metals can influence ecosystem function in several ways. Some trace metals (e.g. Cu, Ni, B, Zn, Fe, Mo) are required as micronutrients and enzyme cofactors. However, at high concentrations, these essential elements can become toxic to fresh-water (Whitton 1970; Lithner 1989) and soil organisms (Bengtsson et al. 1988; Bååth 1989; Leyval et al. 1997). Other trace metals (e.g. Pb, Cd) have no known benefit to organisms, and may be toxic even at very low concentrations. At the plant community scale, elevated trace metal concentrations can depress tree seedling growth (Hecht- Buchholz et al. 1987). Numerous studies have shown that elevated concentrations of trace metals in soils arising from sludge disposal can influence soil processes (e.g. McGrath et al. 1995). Trace metals have also been implicated as contributing to forest decline (Gawel et al. 1996). In spite of their importance in terrestrial and aquatic ecosystems, few studies have examined the impact of forest disturbance on trace metal biogeochemistry and budgets.

Disturbance can alter biogeochemical cycles of forest ecosystems dramatically. At the Hubbard Brook Experimental Forest (HBEF), devegetation (Bormann et al. 1968; Likens et al. 1969; Likens et al. 1970), and forest harvesting (Likens & Bormann 1974; Bormann & Likens 1979; Hornbeck et al. 1986) caused major changes in the biogeochemical cycles of several major elements. Other studies have also demonstrated major changes in element fluxes and cycling in response to forest management practices (e.g. McClurkin et al. 1987; Tiedemann et al. 1988; Johnson et al. 1988; Hendrickson et al. 1989). Most of these studies have focussed on the cycling of major chemical elements. Far fewer studies have examined trace metal biogeochemistry in intact forests (Foster & Nicolson 1986; Bergkvist 1987a,b; Aastrup et al. 1995; Johnson et al. 1995) or after forest disturbance. Likens et al. (1970) and Lawrence et al. (1987) found that streamwater Al concentrations increased following forest disturbance at HBEF. Fuller et al. (1988) found that trace metal concentrations in soil solution and streamwater increased following whole-tree harvest (WTH), but the results varied with elevation, suggesting that multiple factors may influence trace metal biogeochemistry at the watershed scale. Similar spatial variation (i.e. elevation, soil horizon) in trace metal biogeochemistry in an undisturbed watershed (Driscoll et al. 1988) also suggests that multiple factors influence catchment-scale production and export of trace metals in soil.

Forest harvest may alter trace metal biogeochemistry through several mechanisms. Mineralization rates of trace elements contained in soil organic matter (both mineral soil and forest floor) may increase following forest harvest (e.g. Likens et al. 1970; Bormann et al. 1974; Bormann & Likens 1979; Vitousek et al. 1979). Increased forest floor mineralization could increase dissolved organic carbon (DOC) production, potentially enhancing the loss of trace metals forming complexes with DOC (Lawrence et al. 1987). Soil disturbance can expose new mineral surfaces to weathering of trace elements. Increased nitrification and decreased NO_3^- uptake following harvest may lower soil solution pH, increasing trace metal solubility (Likens et al.

1969; Fuller et al. 1987; Lawrence et al. 1987) and the loss of exchangeable metals. Soil acidification has been shown to influence trace metal biogeochemistry elsewhere besides HBEF (e.g. Bergkvist 1986; LaZerte 1986; LaZerte et al. 1989), possibly by changing the mobility of organometallic complexes (Hayes & Swift 1978). Finally, increased run-off and erosion following forest harvest can enhance the transport of trace metals adsorbed onto soil particles.

We examined changes in trace metal biogeochemistry and losses from a watershed following an experimental WTH at the HBEF. First, we quantified trace metal concentrations and fluxes in streamwater before and after (for two years) WTH. Second, we examined the factors controlling trace metal biogeochemistry, and their relative importance in a control and disturbed (WTH) watershed.

Methods

The HBEF is located in the White Mountains of New Hampshire. This study was conducted in Watersheds 5 (WTH watershed, W5) and 6 (reference watershed, W6). These adjacent watersheds have shallow (0.55 m) well-drained soils (Typic Haplorthods) and vegetation characteristic of northern hardwoods (predominantly *Betula alleghaniensis* Britt., *Fagus grandifolia* Ehrh. and *Acer saccharum* Marsh. at low elevation; *Betula papyrifera* Marsh., *Picea rubens* Sarg. and *Abies balsamea* (L.) Mill. at high elevation). Prior to WTH, both watersheds had experienced similar disturbance histories after 1900. Both watersheds are gauged continuously for streamflow at a weir located at the base of the watershed. For more information on these watersheds see Likens and Bormann (1995).

Whole-tree harvest of W5 began in the fall of 1983 and continued through the spring of 1984. All trees >2 cm dbh were cut and about 88% of above-ground biomass was removed from the watershed (Fahey et al. 1988). Beginning in May 1984, weekly streamwater and precipitation samples were collected for trace metal analysis. Stream samples were collected above the weir near the bottom of the watershed and acidified with Ultrex HNO_3 (0.8% v/v, $pH < 1$). A separate streamwater sample was collected for pH and electrical conductivity measurements. We sampled at the base of the watershed primarily to integrate changes in hydrology and biogeochemistry at the watershed scale (Bormann & Likens 1967). Precipitation samples were collected from a wet/dry collector located in W6 and acidified with Ultrex HNO_3 (0.8% v/v). All trace metal samples were split and sent to 2 laboratories to facilitate quality control. All of the analyses reported here were done at the Institute of Ecosystem Studies in Millbrook, NY. Additional samples for comparison were analyzed through Yale University at the Environmental Trace Substances Research Center, University of Missouri. Samples were not filtered, so the metal fraction measured includes both particulate and dissolved trace metals.

Samples were analyzed for Zn, Mn, Sr, Ba on a plasma emission spectrometer (Perkin Elmer ICP-6000). Concentrations of Fe, Cu, Cd and Ni were determined on a graphite furnace/atomic absorption spectrophotometer (Perkin Elmer HGA-400). Streamwater pH was measured potentiometrically in the lab (air equilibrated) with a glass electrode. Nitrate was measured with a Dionex 2000i ion chromatograph (Tabatabai & Dick 1983).

Pre-harvest trace metal data for W5 and W6 were limited. Monthly samples collected in 1983 from W5 and W6 showed relatively small differences in trace metal concentrations between the two streams (Mn 19% higher and Zn 15% lower in W6, CV >22% for all means; T.G. Siccama unpublished data). In addition, concentrations of major cations and anions were similar prior to WTH (Lawrence et al. 1987), and streamwater conductivity and nitrate-N concentrations were also similar prior to harvest (Figure 1, $p = 0.72$ and 0.92, respectively), although pH was slightly higher in W5 ($p < 0.01$). The two watersheds have similar vegetation, aspect, slope and soil type. Thus, we are confident that streamwater trace metal chemistry did not differ significantly in the two watersheds prior to WTH.

Although sample collection began in May 1984, it was irregular between August 1984 and April 1985. To fill in the data gaps for calculating annual trace metal fluxes, we compared our acidified samples with stored (preserved with chloroform), unacidified samples collected weekly at the same location in W5 and W6. For Mn, Sr, and Ba there was no significant difference between the different samples ($p > 0.05$), so we used the stored samples to fill in the temporal gaps for these three elements. Missing values for the other elements were estimated as described below.

Metal fluxes from both watersheds were calculated by averaging metal concentrations one week apart, then multiplying this value by total streamflow for that particular week. For dates when metal concentrations were missing, we estimated concentrations of Zn, Ni, Cd, and Cu in W5, and Fe concentrations in both W5 and W6, using streamwater conductivity and streamflow data, respectively (Table 1). We chose these factors because they showed the greatest correlation (highest R^2) with concentrations of these particular elements (Table 2). Since concentrations of Zn, Ni, Cd, and Cu varied little through time in W6, we used an average (based on the entire data set) value for these elements to fill in temporal data gaps in W6. Over the 2.5 y sampling period, about 25% of the weekly trace metal data points for these

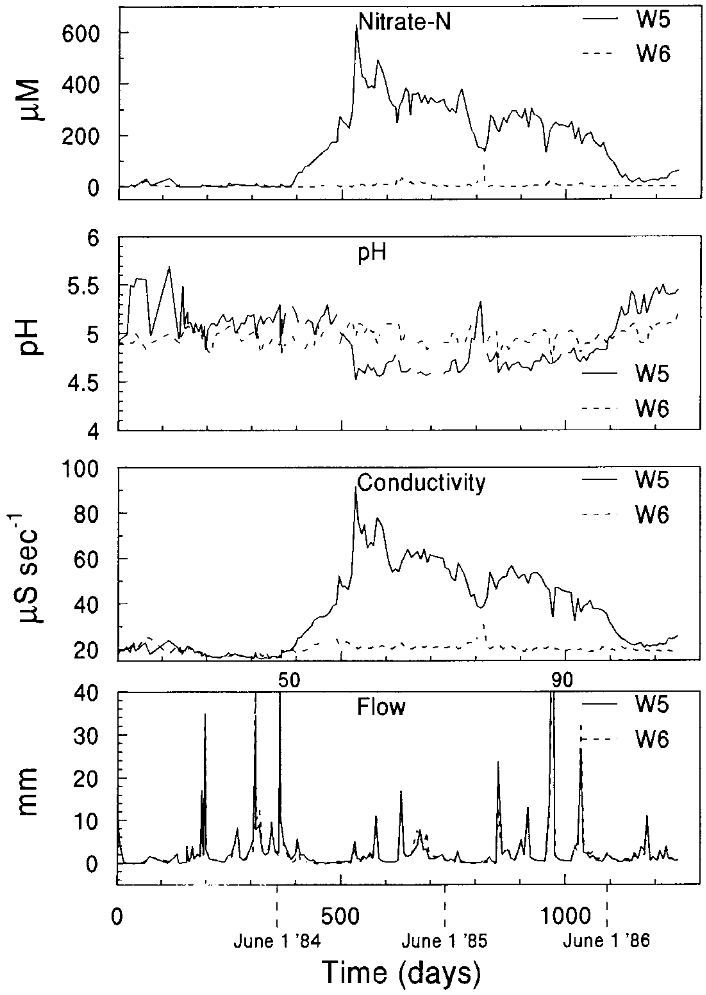

Figure 1. Streamwater NO_3^- concentration, pH, conductivity and flow for the reference watershed (W6) and the whole-tree harvested watershed (W5). Weekly measurements are shown from May 1983 (day 0 = May 31 1983) through November 1986. Whole-tree harvest was done during fall 1983–spring 1984.

five elements were estimated to facilitate the flux calculation (Figure 2, open symbols). We calculated average annual trace metal fluxes over two years beginning in May 1984 and ending in June 1986 (two water years).

Table 1. Regression equations used to predict values for missing trace element streamwater concentrations for Watersheds 5 and 6. All regressions were highly significant ($P < 0.01$). For elements besides Fe in W6, mean values based on the entire data set were used to fill data gaps

Element	Regression equation	R^2
	Watershed 5	
Zn	$[Zn] = 0.015 * COND - 0.15$	0.94
Ni	$[Ni] = 0.0011 * COND - 0.0043$	0.90
Cd	$[Cd] = 0.000051 * COND + 0.000084$	0.56
Cu	$[Cu] = -0.000055 * COND + 0.0054$	0.40
Fe	$[Fe] = 0.59 * FLOW + 0.33$	0.49
	Watershed 6	
Fe	$[Fe] = 0.0078 * FLOW + 0.059$	0.35

Table 2. R^2 values for the relationship between pH, electrical conductivity, streamflow, and NO_3^- concentration vs. trace metal concentration in streamwater (all regressions significant at $p < 0.05$)

	Ni	Cd	Zn	Cu	Fe	Sr	Ba	Mn
Watershed 5 (whole-tree harvested)								
H^+ activity	0.80	0.56	0.82	0.24	—	0.60	0.71	0.84
Conductivity	0.90	0.56	0.94	0.40	—	0.91	0.93	0.80
Flow	—	—	—	0.11	0.49	—	—	—
$[NO_3^-]$	0.86	0.61	0.91	0.36	—	0.90	0.92	0.79
Watershed 6 (reference)								
H^+ activity	0.17	0.05	0.22	0.15	0.26	—	0.12	0.29
Conductivity	0.05	—	—	—	—	0.51	0.42	0.12
Flow	—	0.09	0.07	—	0.35	0.07	—	0.31
$[NO_3^-]$	—	—	0.04	—	—	0.36	0.32	0.10

— Denotes non significant regression ($p > 0.05$).

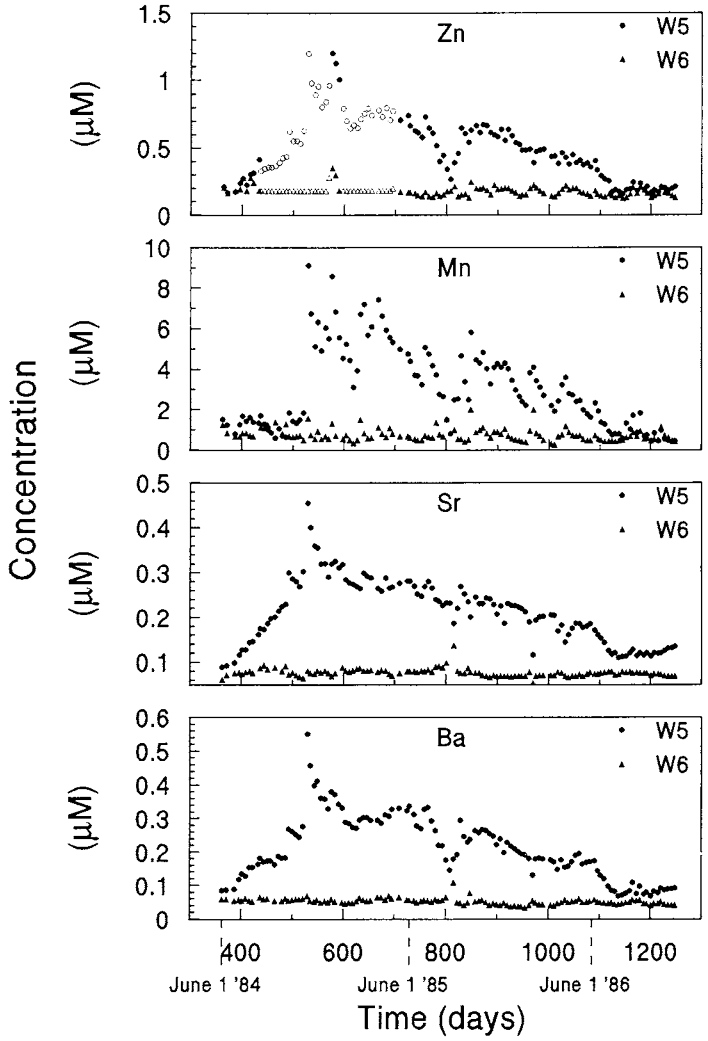

Figure 2. Streamwater trace metal concentrations in the reference (W6) and whole-tree harvested (W5) watershed. Estimated data are shown with open symbols, and actual measurements with solid symbols. Weekly sample collection began in late May 1984 and ended in November 1986. The X-axis has been expanded, but numeric X-values correspond directly to those in Figure 1. Whole-tree harvest was done between fall 1983 and spring 1984.

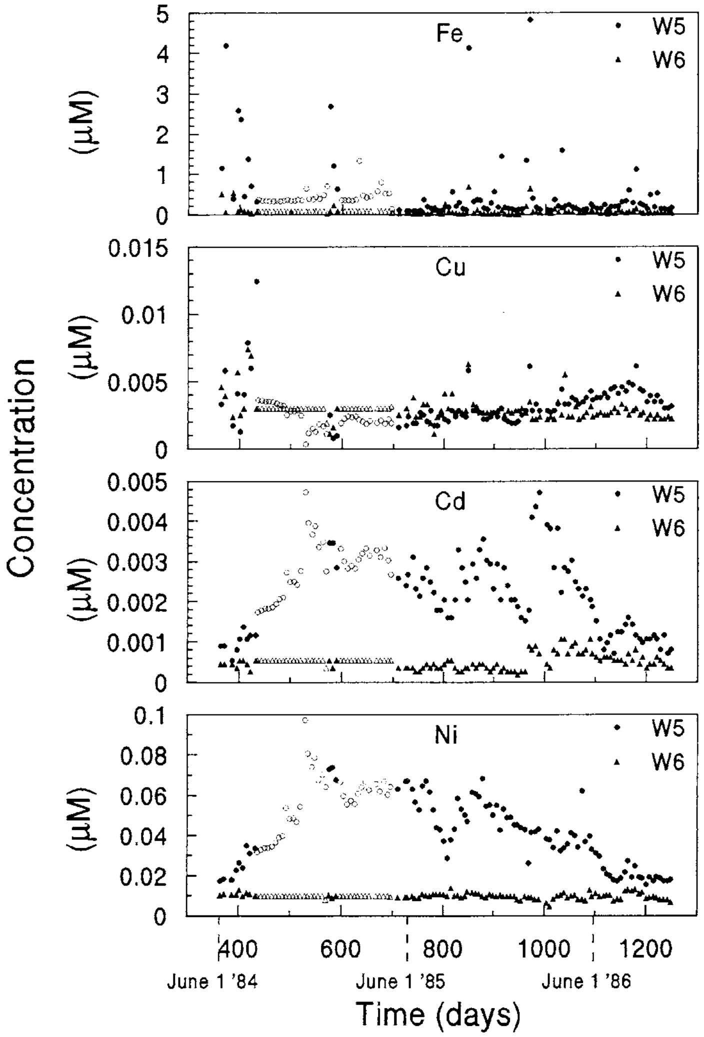

Figure 2. Continued.

Statistical analyses

We examined differences between W5 and W6 using the non-parametric Wilcoxon Matched-Pairs Signed Rank Test (procedure NPAR (SPSS 1988)). We also compared watersheds by examining cross-correlation of the time series for the two watersheds (procedure SERIES/CCF (SYSTAT 1992). In all cases, cross-correlations were performed on differences to remove upward or downward trends in the data.

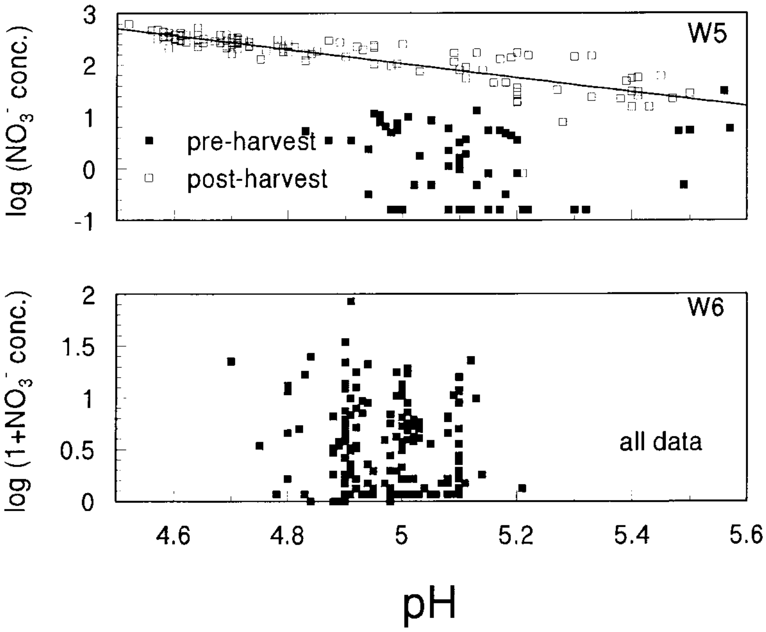

Figure 3. Relationship between streamwater pH and the log of streamwater NO_3^- concentration for the whole-tree harvested watershed (W5) and the reference watershed (W6). Log values of NO_3^- concentration in the reference watershed (W6) were calculated by taking the log of (1 + NO_3^- concentration). Pre-harvest points shown for W5 were from the period May 1983–May 1984. The regression relationship was not significant ($p = 0.23$) for the reference watershed and for the pre-harvest data in W5 ($p = 0.43$), but highly significant for the post-harvest results in W5 ($R^2 = 0.68$, $p < 0.001$).

Results

Although the magnitude differed, changes in streamwater NO_3^- and pH resembled those from prior watershed manipulations at HBEF and elsewhere in the White Mountains (Likens et al. 1970; Bormann & Likens 1979; Hornbeck et al. 1986). Forest disturbance stimulated NO_3^- production, increased streamwater conductivity, and lowered streamwater pH (Figure 1) (Likens et al. 1969, 1970; Lawrence et al. 1987). Nitrate concentrations and streamwater conductivity increased steadily beginning in May 1984 and peaked in Nov. 1984. Streamwater pH did not change significantly until November 1984, when pH dropped by about 0.6 units (Figure 1). Streamwater NO_3^- concentrations correlated strongly with pH during the post-harvest period (after day 370; Figure 1), especially below pH 4.8 ($R^2 = 0.68$, $p < 0.001$; Figure 3). No statistically significant relationship existed between pH and NO_3^- in the reference watershed during this period ($p = 0.23$, Figure 3).

Streamwater concentrations of Ni, Cd, Zn, Fe, Sr, Ba, and Mn increased significantly following WTH (Figure 2), with peak concentrations (November 1984) almost five-fold higher than pre-harvest concentrations (Figure 2). Of these elements, concentrations of all except Fe and Mn (Figure 2) increased steadily from May 1984 in conjunction with increasing streamwater NO_3^- concentrations (almost immediately after completion of the harvest), peaking in November 1984. Concentrations of Mn remained relatively similar in both watersheds until November 1984, when concentrations in W5 increased almost five-fold over a one-week interval (Figure 2) in conjunction with a large decrease in pH in W5 (Figure 1). Although Fe concentrations were significantly higher in the WTH watershed ($p < 0.01$, $r = 0.37$) (no significant correlation based on results from time series analysis), the differences between W5 and W6 varied greatly through time, the largest differences coinciding with high streamflow events (Figures 1, 2).

Concentrations of Zn, Sr, Ba, and Ni (Figure 2) correlated strongly with electrical conductivity and streamwater NO_3^- concentrations (Table 2). Although Mn concentrations also correlated strongly with conductivity (Table 2), streamwater pH correlated slightly more strongly with Mn concentrations (Figures 1, 2; Table 2). This result suggests that increased concentrations of Zn, Sr, Ba, and Ni were related more to losses of readily exchangeable metals (drive in part by pH changes), whereas Mn concentrations were influenced in part by the effect of pH on mineral dissolution. Streamwater Fe concentrations correlated positively with streamflow, which increased significantly ($p < 0.01$) following WTH. Streamwater NO_3^-, pH, and conductivity did not change in the reference watershed (W6) during the study (Figure 1).

In both watersheds, streamwater trace metal concentrations generally correlated negatively with streamwater pH (not Cu and Fe), the correlations being stronger in W5 than in W6 (Table 2). To examine whether pH influenced trace metal concentrations similarly in both watersheds, we compared the relationships between pH and metal concentration between the two watersheds. The slope of the relationship between log of metal concentration and streamwater pH differed significantly between watersheds except for Cd, Zn, and Mn ($p \leq 0.05$) (Table 3). This finding suggests that increased trace metal solubility with decreased pH is an important controlling mechanism for streamwater concentrations of Cd, Zn, and Mn in both watersheds, not surprising given their similar mineralogy (Bormann & Likens 1979; Likens & Bormann 1995). Likewise, it is not surprising that the relationship between pH and metal concentration differs for Sr, Ba, and Ni (Figure 4) since loss of the readily exchangeable pool appears important for these metals. All intercept values differed between watersheds except for Cu.

Table 3. p values from comparison of linear regression equations of log metal concentration vs. pH. p $\leq$ 0.05 represents a significant difference between the whole-tree harvested watershed (W5) and the reference watershed (W6)

Element	Slope	Intercept
Ni	0.01	<0.001
Cd	0.33	<0.001
Zn	0.10	<0.001
Cu	<0.001	0.31
Fe	0.001	<0.001
Sr	<0.001	<0.001
Ba	<0.001	<0.001
Mn	0.06	<0.001

Table 4. Trace metal flux from whole-tree harvested watershed (W5) and reference watershed (W6) between May 1984 and June 1986 relative to forest floor pool sizes, atmospheric inputs, streamwater outputs, and net accumulation prior to harvest. Forest floor pools measured for W6 in early 1980's. Annual inputs and outputs prior to whole-tree harvest are averaged over the period 1975–1984

Flux or pool	Ni	Cd	Zn	Cu	Fe	Sr	Ba	Mn
			After whole- tree harvest					
W5 streamwater outputs (moles ha^{-1} y^{-1})	0.41	0.022	4.79	0.027	9.42	1.87	1.96	33.66
W6 streamwater outputs (moles ha^{-1} y^{-1})	0.088	0.005	1.69	0.028	1.25	0.60	0.44	7.21
			Prior to whole-tree harvest					
Forest floor (moles ha^{-1})^{1}	13.6	—	98.0	12.3	12000	34.2	—	498
Bulk precipitation inputs (moles ha^{-1} y^{-1})^{2}	0.25	0.11	2.13	0.25	8.3	—	—	1.79
Streamwater outputs (moles ha^{-1} y^{-1})^{2}	0.18	0.013	2.23	0.08	10.45	—	—	8.38
Net gain (loss)	0.07	0.097	(0.10)	0.17	(2.15)	—	—	(6.59)

[1] Estimated from Smith (1990).

[2] Smith et al. (1986).

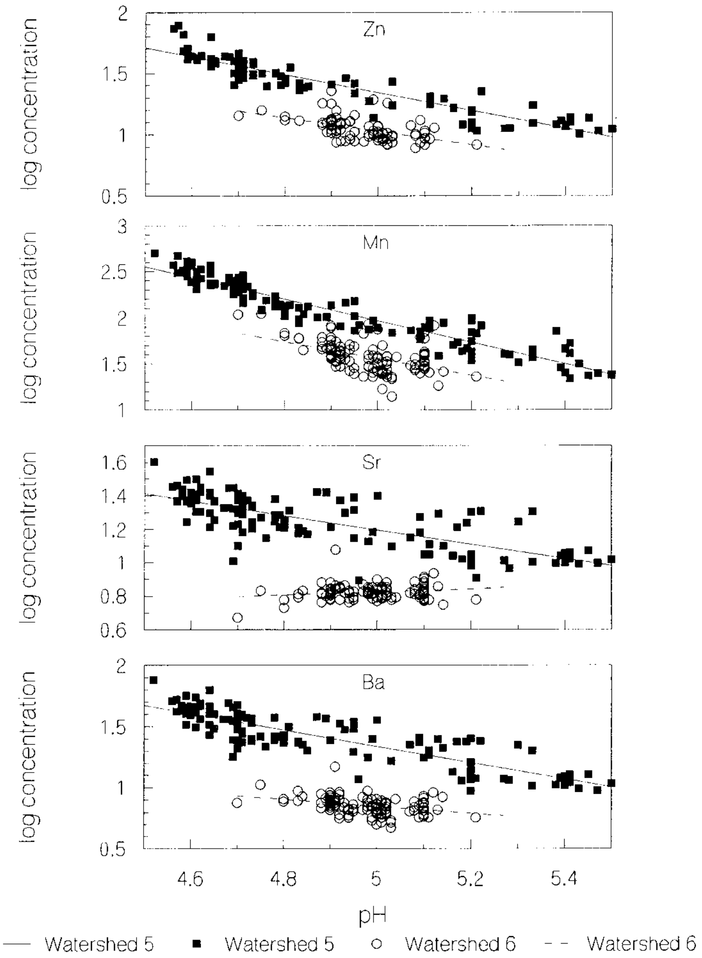

Figure 4. Relationship between the log of streamwater metal concentration (μg L^{-1} of Zn, Mn, Sr, Ba, Fe, Cu, Cd, Ni) and pH for reference watershed (W6) and whole-tree harvested watershed (W5). Where no regression line is shown (Fe in W5) the regression was not significant ($p > 0.05$).

Total annual flux of Ni, Cd, Zn, Fe, Sr, Ba, and Mn was higher from W5 than from W6 following the WTH (Table 4). Compared to estimated outputs averaged over a ten-year period prior to WTH, annual metal fluxes were markedly higher as a result of WTH (Table 4). The annual loss of Mn was about four-fold higher as a result of WTH. The main exception to this was for

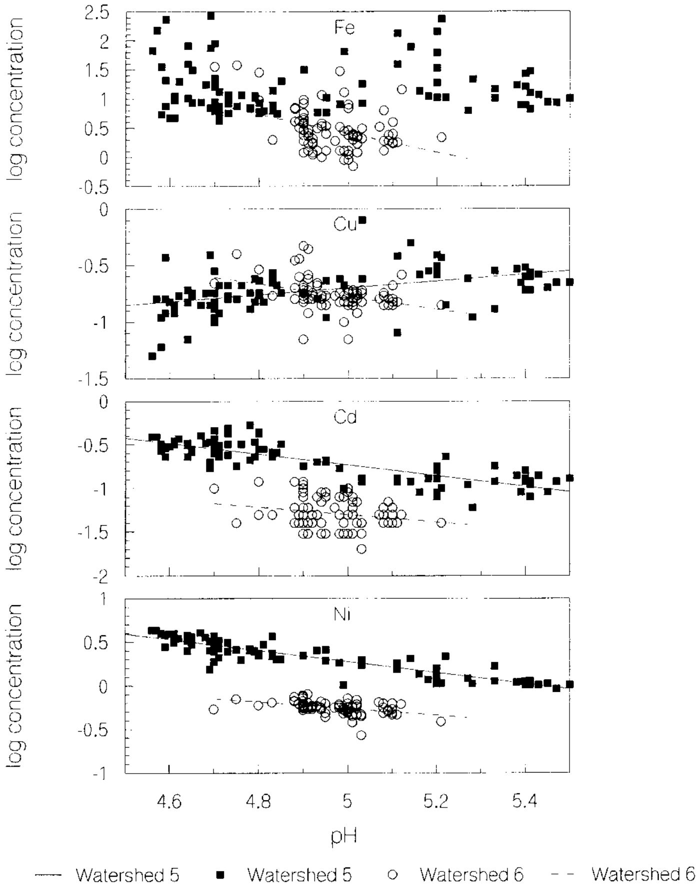

Figure 4. Continued.

Fe, where annual fluxes post-harvest appeared similar to annual streamwater fluxes for the preceding period 1975–1984 (Table 4). If the post-harvest metal fluxes had been calculated for one year post-harvest (June 1984–May 1985), the harvest effect would have been much greater, as metal concentrations generally decreased in the second year after harvest (Figure 2).

Discussion

Several factors interact to control trace metal biogeochemistry at the watershed scale. Previous work at HBEF has examined how these factors vary spatially (by altitude and soil horizon) in W6 (Driscoll et al. 1988) and W5 (Lawrence et al. 1987; Fuller et al. 1988). Based on monthly sampling from

January 1984 to October 1985, Fuller et al. (1988) found increased trace metal concentrations in soil solutions and streamwater at different elevations in W5 following WTH, with high spatial variation. Our results, based on weekly sampling from May 1984 to November 1986, indicate large (two- to nine-fold) increases in streamwater trace metal concentrations at the base of W5 after WTH, with the disturbance effect lasting about two years. The changes we observed in streamwater likely reflected changes that occurred in the soil solution and not in the streamwater, as Fuller et al. (1988) observed similar changes in soil solution trace metal concentrations following WTH. Here, we examine how different factors may have influenced trace metal biogeochemistry following WTH.

Changes in trace metal biogeochemistry following WTH appeared to be influenced primarily by changes in soil solution ionic strength and pH. Increased nitrification following harvest led to increased acidity production (Smith et al. 1968; Likens et al. 1969, 1970; Binkley & Richter 1987), causing an increase in solution ionic strength and (eventually) a significant pH decline for about two years post harvest (Figure 1). The relative impact of pH and soil solution ionic strength on changes in trace metal concentrations varies for different elements. Initial changes in streamwater concentrations of Zn, Sr, Ba, Cd, and Ni appeared to be caused by the release of readily exchangeable metals resulting from H^+ production and increased soil solution ionic strength. Conductivity increased gradually from about day 380 (May 1984), peaking on about day 500 (Figure 1). Lawrence et al. (1987) suggested that during this time increased H^+ production displaced exchangeable cations, which could include trace metals such as Sr, Ba, Zn, Cd, and Ni (Figure 2). By September (day 500), the exchange complex lost its ability to buffer solution pH, causing a large decrease in streamwater pH (Figure 1). This decrease in pH caused a further increase in trace metal concentrations except for Fe and Cu (Figure 2). The tight coupling between solution ionic strength, pH and trace metal concentration is further demonstrated near day 600 (June 1985) and day 800 (March 1986) (Figures 1, 2). Over a period of several weeks, streamwater NO_3^- concentration and conductivity decreased, pH increased (Figure 1) and trace metal concentrations decreased (Figure 2) in W5.

In contrast, the temporal pattern of streamwater Mn concentrations suggests that pH driven changes in mineral dissolution is an important controlling factor. Changes in pH explained as much or slightly more of the variation in streamwater Mn concentration (Table 2), suggesting that increased mineral dissolution contributed to increased streamwater Mn concentrations. Manganese concentrations did not increase until November 1984 (about day 500), when concentrations suddenly increased from about 1 μM to over 8 μM during one week in conjunction with a pH change from about 5.2 to 4.5 (Figure 1). A similar response in streamwater Al concentration was also observed (Lawrence et al. 1987). An alternative hypothesis is that vegetation regrowth during the summer may have helped retain Mn within the catchment, as vegetation influences Mn biogeochemistry in non-disturbed watersheds (Driscoll et al. 1988). However, changes in vegetation Mn uptake are unlikely to result in such rapid changes in streamwater Mn concentrations. Our results suggest that changes in mineral dissolution accompanying decreased pH lead to increased streamwater Mn concentrations after WTH. Minerals containing Mn are sensitive to changes in pH (Lindsay 1979), so it is not surprising that we observed such large changes in Mn concentration following solution acidification.

Forest floor mineralization and root decay could also contribute trace elements (e.g. Mn) to the soil solution following WTH (Bormann et al. 1974; Bormann & Likens 1979; Covington 1981; Fahey et al. 1988), although some studies suggest that harvest has little impact on forest floor mass (Mattson & Swank 1989). Measurements taken 2 years after the harvest showed no significant post-harvest decrease in forest floor C and N (Huntington & Ryan 1990), but there was a significant relocation of Oi and Oe material into the Oa horizon due to mechanical mixing during the harvest. Streamwater concentrations of DOC (produced during forest floor mineralization) did not increase after harvest (Lawrence et al. 1987). The forest floor is a major pool of Pb at Hubbard Brook (Smith & Siccama 1981; Friedland & Johnson 1985; Johnson et al. 1995), yet there was no increase in Pb concentrations of soil solution and streamwater following the harvest (Fuller et al. 1988). Finally, Fuller et al. (1988) found large increases in soil solution Mn concentration after WTH in the Bs_2 horizon, not the O horizon. The forest floor may have been the main Mn source prior to harvest, but the mineral soil apparently became a more important source post-harvest. Our results suggest that increased forest floor mineralization was not an important source of trace metals in W5 following the WTH.

The temporal pattern of post-harvest Fe loss contrasted sharply with the other metals. Prior to the WTH, streamwater Fe concentrations correlated with pH and DOC (Driscoll et al. 1988); chelated Fe was probably an important component of the mobile Fe pool. Unfortunately, we did not measure streamwater DOC concentrations in the two watersheds to match our trace metal data. We were, however, able to compare a subset of our trace metal data to (almost) monthly DOC collections during 1984–1985 (Lawrence et al. 1987). During this time, we found no significant relationship between streamwater DOC and Fe (or any metal) concentration ($n = 12$ for all metals, $R^2 < 0.01$ and $p = 0.90$) in the WTH watershed. Streamwater DOC concentrations in W5 and W6 between June 1982 and May 1983 were similar to those collected from June 1984 to May 1985 (about 200 μM DOC-C; Lawrence et al. 1986; Lawrence et al. 1987). Furthermore, DOC concentrations did not increase in W5 following harvest (Lawrence et al. 1987). Concentrations of Fe following WTH were lower (4.5×) than the increase in flux (7.6×), suggesting that increased streamflow enhanced post-harvest Fe losses. Variation in streamflow was, in fact, the best predictor of streamwater Fe concentration in both watersheds (Table 2); the largest differences in Fe concentrations between W5 and W6 occurred during high flow events (Figures 1, 2). Previous work demonstrated that particulate- bound Fe was the major form of Fe exported in streamwater from W6 (Bormann et al. 1974; Smith et al. 1986; Likens & Bormann 1995), and sediment export did increase after WTH (Martin & Hornbeck 1994). Our results suggest that increased flow and soil disturbance associated with WTH increased the export of particulate-bound Fe, especially during high flow events. Interestingly, Fe and sediment losses from W5 and W6 were nearly as high during the 1960's, possibly related to the occurrence of some high intensity rainfall events. In the period September to November 1966, 71% of the particulate output for a two-year period occurred (Bormann et al. 1969).

Neither changes in ionic strength, NO_3^- concentration, nor pH correlated with trace metal concentrations in the reference watershed (Table 2). This result was due in part to the small variation in these properties in W6. The different intercept values for Cd, Zn and Mn in the two watersheds (Table 3) probably result from either the contribution of a small, but different sized, exchangeable metal pool or to the differential contribution of metal complexes formed with dissolved or particulate organic carbon. If changes in mineral dissolution in response to pH changes explains the variation in trace metal concentrations in W5, pH should related to trace metal concentrations similarly in W6, as both watersheds have similar mineralogy (Bormann & Likens 1979; Barton et al. 1997). However, pH changes in W6 were small compared to W5 (Figure 1), so large changes in mineral dissolution likely did not occur in W6.

Although trace metal flux increased from 2.8- to 7.5-fold following WTH as compared to W6, the annual loss was small relative to estimated forest floor pools (Table 4) (Smith 1990). Total loss of Mn and Sr from W5 was 14% and 12%, respectively, of the total forest floor pool. Loss of all other elements represented less than 10% of the forest floor metal pool. We do not know how important these losses were relative to the biologically active pools of trace metals in W5. However, it is likely that the biologically active pools are smaller than the total pools, so losses of Mn following WTH were probably >14% of the active Mn pool. This loss could have important consequences for Mn availability to plants during post-harvest forest regeneration.

In spite of increased trace metal loss following WTH, some of the losses were not that large compared to previous losses and atmospheric inputs (Table 4). Annual trace metal losses for two years following WTH were 1.7 to 4.0 times higher than average annual outputs measured between 1975 and 1984 (Smith et al. 1986) except for Cu and Fe (Table 4). Although Fe losses were higher in W5 than in W6 post harvest, they were lower than annual losses in the late 1970's (Smith et al. 1986), and very similar to average atmospheric inputs between 1975 and 1984. Annual Cd inputs via bulk precipitation were 5 times higher than annual losses in W5 following WTH and 22 times higher than streamwater losses in W6 (Table 4). In contrast, annual export of Mn via streamwater was about 18 times higher following WTH than annual atmospheric inputs. In fact, annual Mn export was also higher in the reference watershed (W6) than atmospheric inputs, a similar trend to that observed from 1975 to 1984 (Smith et al. 1986). All other annual streamwater losses from W6 were lower than atmospheric inputs. In Sweden, long-term catchment monitoring showed that metals such as Pb and Cu accumulate in the catchment, while more mobile elements (e.g. Zn, Cd) cycle through more rapidly; the net catchment balance determined largely by the degree of acidification (Aastrup et al. 1995). In terms of maintaining ecosystem function, our results suggest that increased losses of Mn, Zn, and Ni are particularly important as they are not readily replenished via atmospheric inputs. This is especially important for Mn, where annual losses of Mn exceed inputs even without disturbance.

How could increased trace metal loss influence ecosystem function? First, as described above, the loss of some of these elements could represent a relatively large proportion of available trace metal pools. This loss could have implications for the nutritional requirements of plants and soil organisms when replenishment via atmospheric inputs is small. If these losses were to occur in plantation forests with relatively short rotations, the long-term implications for productivity would be large in areas where atmospheric deposition of these elements is low. Second, decreases in the available pool of elements such as Mn could have implications for wood decay. Manganese is required as part of the enzyme complex that breaks down lignin, and lignin decay rates are often proportional to tissue Mn concentrations (Perez & Jeffries 1992). Third, high concentrations of certain metals in soil solution can impact microbial physiology (Insam et al. 1996), altering microbially-mediated nutrient cycling rates and (possibly) nutrient availability.

Summary

We found that streamwater concentrations of several trace metals increased from two- to nine-fold and trace metal flux from two- to eight-fold after WTH at HBEF. In the case of Zn and Cd, streamwater concentrations exceeded levels known to impact populations of aquatic organisms (Whitton 1970; Lithner 1989). Increased nitrification followed by a decrease in solution pH led to increased trace metal concentrations in streamwater and increased metal flux from W5 following WTH. These concentration changes were primarily responsible for increased trace metal loss after harvest for all elements except Fe and Cu. Annual streamwater outputs of Ni, Zn, Fe, and especially Mn after WTH exceeded annual inputs in bulk precipitation. As such, these losses may be particularly important for maintaining ecosystem function.

The response of trace metal biogeochemisty at the watershed scale is poorly understood. Trace metals are, however, an interesting and potentially important group of elements to consider when assessing ecosystem response to disturbance or different forest management practices. Changes in trace metal flux following forest disturbance is a good example of how changes in terrestrial ecosystems can alter the dynamics of associated ecosystems like streams and lakes. The forestry practice used for the WTH of W5 was not unusual, so these post-harvest trace element losses may not be extreme.

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