

Processes regulating sulphate flux after whole-tree harvesting

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Terrestrial processes that regulate transfer of strong-acid anions (for example SO_4^{2-} , NO_3^- , Cl^-) play an important role in determining the acid-base status of surface waters¹. Anthropogenic perturbations of forested watersheds can alter these processes, resulting in changes of surface-water chemistry^{2,3}. Much controversy has arisen over the relative importance of acidic deposition, natural processes of soil acidification and the effects of changes in land use on the acidification of surface waters^{4,5,6}. Forest clearcutting represents a useful experimental tool to evaluate the effects of changes in strong-acid loading on biogeochemical processes controlling SO_4^{2-} retention and release. Here we report that after the whole-tree harvesting of an experimental watershed at the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire, USA, increased mineralization and nitrification led to substantial NO_3^- loss, acidification of soil solutions and increased soil adsorption of SO_4^{2-} . As a consequence, solution concentrations and streamwater efflux of SO_4^{2-} declined. Substantial increases in streamwater concentrations of H^+ and potentially toxic inorganic Al^{3+} after removal of biomass also occurred. A similar disruption of the soil N cycle observed in areas of forest decline^{7,8} suggests that decreased vegetation uptake of N may adversely affect surface water quality in acid-sensitive regions.

Previous research at the HBEF has demonstrated the importance of ecosystem processes in nutrient retention. After devegetation of watershed 2 (W2) at the HBEF in 1965, a substantial increase in the efflux of NO_3^- , H^+ , Al^{3+} and basic cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) occurred with streamflow. In these experiments, conventional commercial clearcutting practices were not used. Rather, trees were felled, left in place, and herbicides applied to prevent vegetation regrowth. These treatments were designed to separate the effects of vegetation uptake from increased decomposition on the mobilization of dissolved nutrients^{9,10}.

Although acidification and basic cation mobilization were evident, both concentration and efflux of stream SO_4^{2-} declined for the three years of herbicide treatment afterwards. The onset

Table 1 Saturation indices (SI) for lower mineral soil (Bs2) and stream solutions from November 1984 to March 1985 in W6 (reference watershed) and W5 (whole-tree harvested watershed)

Site	Watershed	Saturation index	
		Jurbanite	Gibbsite
Spruce-fir* (750 m)	W6 soil	-0.99	-0.40
	W6 stream	-1.38	-1.54
	W5 soil	-0.78	-0.85
Transition (730 m)	W5 stream	-0.99	0.20
	W6 soil	-0.75	0.14
	W6 stream	-0.78	-0.11
Hardwood (600 m)	W5 soil	-0.58	0.17
	W5 stream	-0.79	0.51
	W6 soil	-1.87	0.54
	W6 stream	-1.13	0.28
	W5 soil	-0.87	0.01
	W5 stream	-0.82	0.21

SI = $\log(Q_p/K_p)$, where Q_p is the ion activity product and K_p is the equilibrium constant. Positive values indicate oversaturation, negative values undersaturation with respect to the mineral phase of interest.

*Spruce-fir soil and stream solutions are typically undersaturated with respect to all mineral phases, owing to a combination of shallow soils (short hydrologic residence time), low pH and high dissolved organic C concentration, all of which favour a kinetic restraint on attaining saturation.

of vegetation regrowth after the cessation of herbicide treatment coincided with a decrease in the acidity of drainage water and an increase in the concentration and transport of SO_4^{2-} . A number of alternative hypotheses could explain the decrease in stream SO_4^{2-} concentrations after devegetation: H1: herbicide application selectively altered soil S transformations; H2: loss of foliar surface area decreased inputs of dry deposition¹¹; H3: decomposition of forest-floor organic matter increased, enhancing microbial immobilization of SO_4^{2-} into organic forms¹², or inhibiting organic S mineralization¹⁰; H4: decreased transpiration resulted in increased hydrological flux and dilution of stream SO_4^{2-} concentrations¹⁰; H5: sulphate was reduced to gaseous (for example H_2S) or solid (FeS) phases¹⁰; H6: sulphate was retained owing to precipitation of aluminium hydroxysulphate minerals, such as jurbanite ($\text{Al}(\text{OH})\text{SO}_4 \cdot 5\text{H}_2\text{O}$); H7: adsorption of SO_4^{2-} to free Al and/or Fe oxide surfaces increased owing to acidification of soil solutions¹³.

To test these hypotheses, a watershed manipulation experiment was done at the HBEF. From autumn 1983 through spring 1984 an experimental watershed (W5) underwent a commercial whole-tree harvest involving the removal of all aboveground tree biomass. This manipulation was evaluated using the paired watershed approach, in which the experimental watershed and an adjacent untreated reference watershed (W6) were

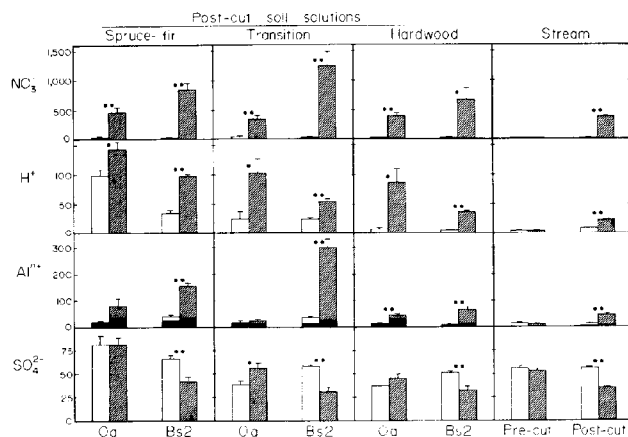


Fig. 1 Soil solution and stream concentrations ($\mu\text{mol l}^{-1}$) after whole-tree harvesting of watershed 5 (shaded bars) and the reference watershed 6 (clear bars). Darkened (lower) portions of the Al bars represent non-labile monomeric (organically complexed) Al, and the top portion labile monomeric (inorganic) $\text{Al}^{20,21}$. Post-cut solutions were collected between 20 November 1984 and 15 March 1985, the dormant period before snowmelt when hydrological fluxes are unaffected by transpiration. Stream solutions before cutting were sampled during the same period in 1983-84, before any clearcut effects. Asterisks denote significant differences between means at the $P < 0.05$ (*) and $P < 0.01$ (**) levels.

monitored. Both watersheds were instrumented with stream gauging weirs, bulk precipitation and throughfall collectors, and 'tension-free' soil lysimeters¹⁴ beneath the Oa (forest floor) and within Bs2 horizons above impervious schist bedrock. Watersheds 5 and 6 are dominated largely by northern hardwood forest vegetation, consisting of yellow birch (*Betula alleghaniensis*), American beech (*Fagus grandifolia*) and sugar maple (*Acer saccharum*). A spruce-fir zone at the top of each watershed is dominated by red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*). Elevational differences in vegetation and soil depth contribute to substantial spatial variability in the chemistry of drainage waters in these catchments^{15,16}. Consequently, replicate lysimeters were installed in a low-elevation hardwood zone (600 m; $n=3$) near the base of each watershed, in a hardwood transition zone (730 m; $n=3$) and in a high-elevation spruce-fir zone (750 m; $n=2$) near the top of each watershed.

After whole-tree harvesting of W5, patterns of element concentration and transport (Fig. 1) were similar to those after devegetation of W2. Increased concentrations of NO_3^- were released from soil to stream solutions owing to reduced vegetative uptake coupled with increased mineralization and nitrification caused by higher soil moisture and temperature^{7,17}. Mineralization and nitrification of soil organic N produces one mole of H^+ for each mole of NO_3^- ; however, increases in H^+ concentration were not stoichiometric with respect to NO_3^- release. Rather, increased concentrations of basic cations and Al were also leached from both organic and mineral soil horizons owing to a combination of mineralization, exchange and dissolution reactions. Increases in Al concentration largely occurred as the labile (inorganic) monomeric form, which has been shown to be toxic to aquatic organisms^{18,19}. Concentrations of SO_4^{2-} declined significantly ($P < 0.01$) after the whole-tree harvest (Fig. 1) in both lower-mineral soil solutions (W5, Bs2) and streamwater. Beneath the forest floor (Oa), however, SO_4^{2-} concentrations remained stable or significantly increased after the manipulation.

Patterns of solute release enabled us to test the research hypotheses (H1-H7) posed to explain decreases in the SO_4^{2-} concentration of drainage water after forest removal. As herbicides were not applied in the experiment, a selective action of the herbicide on S transformations was not possible (H1). Decreases in dry deposition inputs to the canopy as a result of canopy loss (H2), increases or decreases in S immobilization or mineralization rates, respectively, in the forest floor (H3), and dilution of SO_4^{2-} due to increased hydrologic flux (H4) would all be expected to result in decreased concentrations of SO_4^{2-} in Oa-horizon leachates. Consequently these hypotheses can be rejected as the proximate cause of decreased SO_4^{2-} concentra-

tions in mineral soil and stream solutions after clearcutting. Decreases in SO_4^{2-} concentration due to reduced dry deposition of S were probably compensated for by increased mineralization of organic S to SO_4^{2-} in the forest floor¹². Microbial reduction of SO_4^{2-} to S^{2-} (H5) is also unlikely, owing to the high concentrations of NO_3^- in soil solution and the fact that of NO_3^- reduction is more energetically favourable²² and would proceed before SO_4^{2-} reduction.

Possible control of solution SO_4^{2-} concentrations by jurbanite ($\text{Al}(\text{OH})\text{SO}_4 \cdot 5\text{H}_2\text{O}$) precipitation (H6) was investigated by calculating mineral saturation indices (Table 1) for jurbanite and natural gibbsite using the chemical equilibrium model ALCHEMI²³. This computer model calculates the distribution of inorganic Al complexes, adjusting for temperature and ionic strength effects²³. Soil and stream solutions were undersaturated with respect to the solubility of jurbanite in both watersheds at all elevations (Table 1), suggesting that jurbanite precipitation was not thermodynamically favourable and probably not responsible for the decline in solution SO_4^{2-} concentrations after the whole-tree harvest. Soil and stream solutions in the transition and low-elevation zones were closer to saturation with respect to the solubility of natural gibbsite, or a mineral of similar solubility. Although the solubility of $\text{Al}(\text{OH})\text{SO}_4 \cdot 5\text{H}_2\text{O}$ apparently does not control SO_4^{2-} concentrations at the HBEF, this process is considered important in regions with high atmospheric inputs of SO_4^{2-} , such as parts of the Federal Republic of Germany and The Netherlands^{24,25}.

Adsorption of SO_4^{2-} onto free sesquioxide surfaces (H7) was investigated using batch titration studies in which Na_2SO_4 was added to suspensions of Bs2 mineral horizon soil (taken from 30 soil pits in W5) with solution pH adjusted between 3.5 and 6.5 with HNO_3 or NaOH . After centrifugation, pH and soluble SO_4^{2-} were measured and adsorbed SO_4^{2-} was calculated from the amount removed from or added to solution. Acidification of the soil solution greatly enhanced retention of SO_4^{2-} (Fig. 2). In the range of pH values experienced by lower mineral soil solutions at the HBEF (4.5 to 5.3), SO_4^{2-} adsorption is highly dependent on pH²⁶. As pH decreases to 4.3, the extent of SO_4^{2-} adsorption increases owing to protonation of variable-charge surfaces such as $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$. Below pH 4.3, the extent of SO_4^{2-} adsorption diminishes. We attribute this decrease to dissolution of soil Al, which forms soluble $\text{Al}-\text{SO}_4^{2-}$ complexes which compete with the adsorbent phase for SO_4^{2-} .

On the basis of laboratory and field soil solution monitoring studies, all of the hypotheses advanced to explain the reductions in stream SO_4^{2-} concentrations after whole-tree harvesting can be rejected with the exception of acidification-induced SO_4^{2-} adsorption in lower mineral soil horizons. Furthermore, adsorption appears to be an important factor regulating seasonal variability in stream SO_4^{2-} concentrations in undisturbed watersheds²⁷. Regression analysis of stream SO_4^{2-} and H^+ concentrations (μ equiv. l^{-1}) in the reference watershed over a 2.5 year period yielded a significant inverse relationship ($[\text{SO}_4^{2-}] = 145 - 3.25 [\text{H}^+]$; $r^2 = 0.49$; $P < 0.0001$; $n = 31$), consistent with the pH-dependent SO_4^{2-} adsorption hypothesis.

Current models developed to simulate the response of forest ecosystems to strong-acid inputs generally fail to consider pH-dependent SO_4^{2-} adsorption²⁸⁻³¹. Results of this whole-tree harvest experiment indicate that strong-acid inputs, even though they may change soil solution pH only slightly, can facilitate SO_4^{2-} retention, which buffers surface water acidification. Therefore simulation models that fail to account for pH-dependent SO_4^{2-} adsorption may overestimate the consequences of increased inputs of strong acids to waters draining forest ecosystems.

The whole-tree harvest experiment also demonstrated that disruption of the soil N cycle resulting from biomass removal can cause short-term acidification of soil solutions and streams and the release of toxic inorganic Al to surface waters¹⁸. In view of current concerns about forest decline³², a link between forest degradation and surface-water acidification is especially

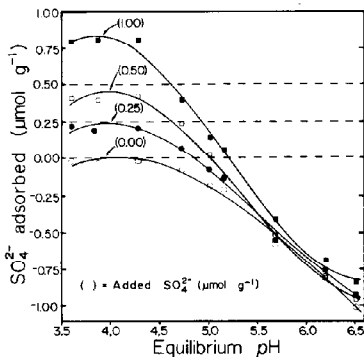


Fig. 2 Sulphate adsorbed by HBEF Bs2 horizon soil at different concentrations of added sulphate across a range of equilibrium solution pHs. Negative adsorption numbers are due to desorption of ambient sulphate. Lines represent the best fit of a third-order polynomial equation.

noteworthy. If forest decline is accompanied by substantial NO_3^- efflux, as has been observed in the Federal Republic of Germany⁷ and Czechoslovakia⁸, then the potential for damage to surface-water quality is present.

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