Reports

Forest Floor Leaching: Contributions from Mineral, Organic, and Carbonic Acids in New Hampshire Subalpine Forests

Abstract. *Analyses of soil water and groundwater samples from a high-elevation coniferous ecosystem in New England indicate that sulfate anions supply 76 percent of the electrical charge balance in the leaching solution. This result implies that atmospheric inputs of sulfuric acid provide the dominant source of both* H^+ *for cation replacement and mobile anions for cation transport in subalpine soils of the northeastern region affected by acid precipitation. In soils of relatively unpolluted regions, carbonic and organic acids dominate the leaching processes.*

Results from the literature indicate that two general leaching mechanisms account for most cation transport through forest floors and soil profiles. The data supporting these interpretations are derived primarily from relatively nonpolluted regions such as the Pacific Northwest, the U.S. Southwest, interior Central America, and portions of the Soviet Union (*1-5*). According to that evidence, carbonic acid and organic acids produced by biological activity are the principal agents responsible for the replacement and transport of exchangeable cations. Thus, within those regions where there is sufficient moisture and where there are no major atmospheric inputs of leaching agents, available cations are thought to be transported from the forest floor and soil in proportion to the availability of HCO_3^- or organic acid anions, or both, provided from within the soil system. In general, such a paradigm appears to be an apt description of the soil-leaching process to be expected in regions where incoming precipitation exhibits a relatively small acid strength in comparison to the acid-base buffering capacity of the canopy and soil.

For regions such as New Hampshire, which are subject to intense acid precipitation, it seemed to us that an alternative hypothesis might explain cation movement from the forest floor and through the soil profile. As recent studies have suggested, precipitation in the northeastern United States absorbs quantities of SO_2 and NO_x gases and aerosols from the atmosphere, so that water entering the forest ecosystem typically has a pH of 4 or less and high concentrations of SO_4^{2-} and NO_3^- (*6-10*). This being the case, we hypothesized that the biologically controlled production of carbonic acid and organic acids would not be as critical to soil leaching as the input of anthropogenic mineral acids introduced by precipitation. Gorham (*11*) and Johnson (*4*) have independently suggested or implied similar hypotheses.

In this report, we present findings from a 2-year field and laboratory study of the processes which control cation transport from forest floors of ecosystems receiving acid precipitation. Specifically, we compare the relative contributions of carbonic acid, organic acids, and precipitation-borne mineral acids to cation replacement and transport processes in the forest floor of a cool, moist balsam fir [*Abies balsamea* (L.) Mill.] subalpine forest. We selected this New England forest type for study because (i) it is widespread and well described in the mountains of the Northeast (*12*); (ii) it is characterized by a very prominent forest floor (*13*), the horizon of prime interest in this study; (iii) it receives large inputs of atmospheric pollutants that are accentuated by extreme horizontal impaction (*14*); and (iv) it is a system where organic acid production is potentially great, and also where extreme atmospheric inputs of H_2SO_4 seem likely to exert effects upon the processes of cation transport. This combination of factors offered us an opportunity to examine the dynamic interplay between naturally produced organic and carbonic acid leaching and anthropogenically derived mineral acid leaching.

We focused on the hypothesis that in geographic areas experiencing acid sulfate rain in the range pH 4.0, SO_4^{2-} is the major counterion for cation movement through the forest floor. The alternative hypothesis for regions of acid precipitation predicts that the unbuffered mineral acids are quickly neutralized, so that most of the mobile anions for cation transport are actually provided by the integrated contributions from organic acid and CO_2 reservoirs. We evaluated these alternate hypotheses by means of an analysis of electrical charge balance in forest floor leachates (*15*). In this approach it is assumed that by measuring the sum totals of major anions (micro-

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equivalents per liter of SO_4^{2-}, NO_3^-, HCO_3^-, and Cl^-) and major cations (microequivalents per liter of Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, NH_4^+, Al^{3+}, Fe^{2+}, and Mn^{2+}), one can (i) indirectly estimate the organic anion concentrations and (ii) evaluate the relative contributions of different acid anions in maintaining electrical neutrality for the dissolved cations of the leaching solution.

We sampled both soil solution and groundwater seepage during the periods July through September 1975 and May through October 1976 on Mount Moosilauke (71°50′W, 44°1′N) in the White Mountains of New Hampshire. Water samples were collected within 1 week of major rain events from permanent east-slope and west-slope sites located at an elevation of 1250 m (4100 feet) in the balsam fir zone (*12*). We sampled soil solution as saturated flow with plastic zero-tension lysimeters (8 by 30 cm) (*16*) placed beneath the undisturbed O2 horizon of the forest floor (mean forest floor depth, 12.2 cm). A total of 100 soil percolate samples were collected over the course of 15 rain events during both years. Groundwater was sampled eight times from a persistent spring located near the east-slope site.

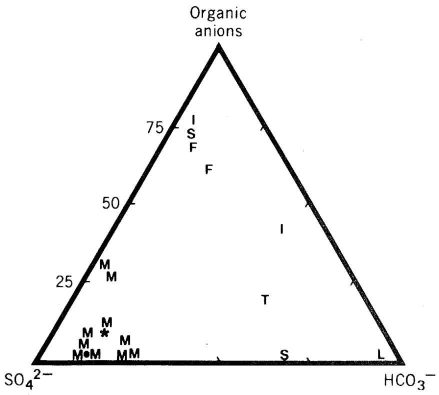

Fig. 1. The contrasting major anion composition of soil water and stream water samples from different geographic regions of North America. For each water sample, the coordinates are determined by the percentage of charge balance provided by SO_4^{2-}, HCO_3^-, and organic anions. As shown for organic anions on the left side of the triangle, the percentage for each anion decreases from 100 percent at the given apex to 0 percent at the side opposite that apex. The Mt. Moosilauke samples (M1 through M10) cluster in the lower left-hand corner of SO_4^{2-} dominance. The Mt. Moosilauke lysimeter mean for 1976 is designated by the asterisk; the Mt. Moosilauke 1976 spring mean is represented by the dot. Samples *F*, *T*, and *L* are Al-horizon leachates from northwestern alpine, northwestern temperate, and tropical sites, respectively (*4*). The upper sample marked *I* is from a perched bog watershed in Itasca County, Minnesota, and the lower *I* designates a groundwater fen watershed from the same county (*29*). The upper *S* is a leachate from a depth of 30 cm, and the lower *S* is a leachate from a depth of 100 cm from a spruce fir stand in the Sangre de Christo Mountains, New Mexico (*30*).

Table 1. Comparative charge-balance contributions from HCO_3^-, SO_4^{2-}, and organic acid anions in soil leachates and spring water collected in the fir zone of Mt. Moosilauke during the summer of 1976. Data from several other studies of soil leachates and stream water are presented for comparison.

Site	*p*H	Contribution (μeq/liter)				
		Total cations*	Total anions†	HCO_3^-	SO_4^{2-}	Anion deficit‡
		SO_4^{2-} dominance				
Moosilauke M1	4.05	174	148	0	130	26
Moosilauke M2	4.32	150	136	0	126	14
Moosilauke M3	3.64	747	692	0	647	55
Moosilauke M4	3.87	310	313	0	238	0
Moosilauke M5	4.52	183	169	0	135	14
Moosilauke M6	4.36	157	111	0	105	46
Moosilauke M7	4.17	266	258	0	194	8
Moosilauke M8	4.07	196	135	0	131	61
Moosilauke M9	4.67	164	158	0	138	6
Moosilauke M10	4.66	155	149	0	134	6
Moosilauke lysimeter mean	4.12	225	200	0	172	25
Moosilauke spring mean	4.70	159	157	0	135	2
Moosilauke overall range						
Minimum	3.54	106	79	0	71	0
Maximum	4.77	747	693	0	647	61
		Organic anion dominance				
Findley lake site, Wash. (*4*)	4.41	210	80	9§	49	130
Findley lake site	4.25	221	84	11§	44	137
Bog watershed, Minn. (*29*)	3.6	509	116	0	96	393
Sangre de Christo Mts., N.M. (*30*)	5.3	690	220	44	153	470
		HCO_3^- dominance				
Thompson site, Wash. (*4*)	6.14	252	228	114	47	24
La Selva, Costa Rica (*4*)	5.72	231	289	263	15	0
Fen watershed, Minn. (*29*)	6.5	1180	679	542	125	501
Sangre de Christo Mts., N.M. (*30*)	>6.0	350	410	302	108	0

*Total cations = $H^+ + Ca^{2+} + Mg^{2+} + K^+ + Na^+ + NH_4^+ + Al^{3+} + Fe^{2+} + Mn^{2+}$. †Total anions = $SO_4^{2-} + NO_3^- + Cl^- + HCO_3^-$. ‡The anion deficit is assumed to represent organic anions; this has been confirmed on the basis of results from GLC and ultraviolet irradiation experiments. §These values result from yearly averaging.

Water samples were placed in polyethylene bottles that had been washed with acid and rinsed with distilled water; these samples were analyzed for *p*H (Accumet model 210) within several hours of collection. Aliquots of each sample were then filtered through ashless paper (Whatman 44) for major cation and anion analyses, glass fiber filters (Reeve-Angel 934AH) for organic acid analyses, and 0.1-μm filters (Millipore) for trace metal analyses. The organic acid and trace metal samples were stored at 4°C in the dark, and the other samples were frozen. We analyzed for Ca^{2+}, Mg^{2+}, K^+, and Na^+ by atomic absorption spectroscopy (Perkin-Elmer 303) with sample aliquots and standards containing appropriate amounts of lanthanum. We measured Al^{3+}, Fe^{2+}, and Mn^{2+} by atomic absorption on a spectrophotometer (Perkin-Elmer 503) equipped with a graphite furnace (HGA 2100). The speciation of aluminum at different sample *p*H values was calculated from thermodynamic data. Standard colorimetric methods adapted for the Technicon AutoAnalyzer II were used to estimate NO_3^-, NH_4^+, Cl^-, and SO_4^{2-} (*17*). Relative precision was estimated for each test (*18*). Changes in *p*H following ultraviolet irradiation were used to confirm the organic nature (*19*) of the anion deficits calculated from ionic charge-balance differences. The HCO_3^- and volatile alkalinity were checked by *p*H measurement and N_2 purging (*20*). Organic acids were evaluated by gas-liquid chromatography (GLC) (*21*).

Results from these analyses indicate that SO_4^{2-}, rather than HCO_3^- or organic acid anions, supplies most of the electrical charge balance in the leaching solution. This implies that atmospheric inputs of H_2SO_4 (*22*) provide the dominant source of both H^+ for cation replacement and mobile anions for cation transport throughout the forest floor and, in fact, for the entire soil profile (*23*). A representative range of charge-balance data from eight separate lysimeter and two spring seepage samples (samples M1 through M10) are presented in Table 1. Mean values for all lysimeter and spring samples are also shown. In both the forest floor and spring seepage samples, SO_4^{2-} provides 61 to 92 percent (mean, 76 percent) of the equivalent anionic charge, whereas organic acids account for 0 to 31 percent (mean, 11 percent) of the anion equivalents; HCO_3^- is virtually absent at those low *p*H values (*24*). This same pattern of SO_4^{2-} dominance was observed in all samples collected, both from forest floor percolates and groundwater seepage. For comparison, samples from other geographic regions are presented in Table 1 to show the contrasting chemistries of soil solutions dominated by organic acids and carbonic acid.

To illustrate better the distinctly different character of cation transport in this New Hampshire system, we have plotted the data for samples M1 through M10 on the triangular diagram in Fig. 1. Here, the relative position of each sample is determined by the percentage of charge balance provided by SO_4^{2-}, HCO_3^-, and organic anions. It is clear that the H_2SO_4 dominance of high-elevation soil water in New Hampshire differs markedly from the chemistry of percolates representing other major leaching regimes (for example, the *F* symbols in Fig. 1 represent a Pacific Northwest alpine site dominated by organic acids). Viewed in terms of a broad pattern of forest soil transport processes across the United States, Fig. 1 illustrates that the balsam fir zone of the White Mountains (and perhaps other forests of the Northeast) exhibits a cation transport mechanism that is in distinct contrast with the leaching processes dominated by carbonic and organic acids prevailing over other portions of the continent. The geographic patterns of leaching implied in Fig. 1 may be broadly summarized as follows. Carbonic acid leaching tends to predominate in tropical and warm temperate soil profiles and may also prevail in the deeper horizons of many cooler soils (*3, 5*); organic acid leaching generally occurs in cool temperate and arctic and alpine acid soils; and H_2SO_4 leaching dominates in the mountains of New England and may be the dominant leaching process throughout the soils of the northeastern United States, at least in upper soil horizons, during unusually acid rain events. It remains to be seen whether other sites experiencing acid precipitation will be shown to have SO_4^{2-}-dominated leaching (*25*). Certain areas probably experience H_2SO_4 leaching derived from the oxidation of sulfur-rich organic and sulfide-rich inorganic materials (*26*).

At present, it is difficult to assess the consequences for eastern soils of this presumably modern regime of leaching by anthropogenic mineral acids. Evidence bearing on this subject is just becoming available (*2, 7, 27*). In our laboratory, we are evaluating the ecosystem implications of leaching processes dominated by atmospheric mineral acids versus intrinsic carbonic and organic acids. Preliminary analyses of field and laboratory data suggest that cation leaching increases in our system as the *p*H of rainfall drops below 4 to 4.5. Such leaching acceleration may lead to problems with nutrient availability in poorer sites or eventually to increased rates of soil and rock weathering, or both (*8*). With the strongly *p*H-dependent solubility of metals such as aluminum, increased concentrations of dissolved trace metals may also present toxicity problems for plants (*28*).

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19. This technique was suggested in the work of F. A. J. Armstrong, P. M. Williams, and J. D. H. Strickland [*Nature (London)* **211**, 481 (1966)]. For this procedure, the *p*H of an aliquot of sample that has been purged with N_2 is measured. Then, an aliquot that has been irradiated with ultraviolet light for 6+ hours is purged and the *p*H measured. Assuming that organic anions are oxidized to CO_2 by this method, there should be an increase in $[OH^-]$ commensurate with the decrease in organic anions. For example, a sample with an anion deficit of 43 μeq/liter showed a change in $[H^+]$ of 39 μeq/liter, whereas one with a deficit of 0 showed a change of 6 μeq/liter. Such results appear to follow predictions for *p*H changes resulting from the destruction of organic acids.
20. N. Johnson, personal communication. In this technique it is assumed that N_2 purging will remove excess CO_2, HCO_3^- alkalinity, and organic volatile alkalinity, producing a *p*H change proportional to the removed HCO_3^- or volatile organic anions, or both.
21. Organic acids were analyzed by GLC with trimethyl silyl derivatives and underivatized aqueous samples (60/80 Carbopack with 3 percent Carbowax 20M and 0.5 percent H_3PO_4). Prominent acid peaks appear to include formic, acetic, and malic acids.
22. The correlation coefficients between SO_4^{2-} and H^+ for bulk precipitation and throughfall are 0.89 and 0.85, respectively.
23. Another possible source of H_2SO_4 is the internal production from mineralization and oxidation of organic sulfur and iron sulfide. By using Cl^- as a relatively inert tracer, one should be able to compare SO_4^{2-}/Cl^- ratios in throughfall and soil solution to examine mineralization contributions to H_2SO_4. The SO_4^{2-}/Cl^- ratios averaged from over 80 samples actually dropped slightly from a throughfall value of 11.0 to a soil solution value of 9.5. This result suggests that SO_4^{2-} does not increase in passage through the soil and may decrease as a result of adsorption or absorption.
24. The technique described in (*20*) produced no *p*H change in any of 16 samples surveyed. From this and from thermodynamic considerations of HCO_3^- alkalinity at low *p*H, we concluded that HCO_3^- was absent. The local bedrock parent material is a minor source of sulfur compared to atmospheric inputs [N. M. Johnson, G. E. Likens, F. H. Bormann, D. W. Fisher, R. S. Pierce, *Water Resour. Res.* **5**, 1353 (1969)]. The mean NO_3^- contribution to anionic charge is 4 percent, so that the summed contribution from SO_4^{2-} and NO_3^- is 80 percent.
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30. W. C. Graustein, unpublished data.
31. We thank K. H. Cronan, D. Deuring, W. C. Graustein, J. Hornbeck, J. F. Hornig, N. M. Johnson, and S. O. Ornstein for their help and advice on various portions of this work. The work was supported in part by grants from the Cramer Fund of Dartmouth College, National Science Foundation grant DEB 76-09984, and Energy Research and Development Administrations grant EE77-S-02-4498.

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