DIVISION S-7—FOREST AND RANGE SOILS

Acidification Sources in Red Alder and Douglas Fir Soils—Importance of Nitrification¹

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ABSTRACT

Precipitation, throughfall, forest floor, and soil leachate samples were monitored continuously in 1981 and 1982 in a N-poor Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] forest and a red alder (*Alnus rubra* Bong.) forest growing adjacently on a glacial soil in western Washington. The purpose of the study was to quantify the relative importance of atmospheric vs. natural sources of H^+ input to forest soil acidification, and to determine the role of N transformation processes in the overall H^+ balance of soils with different N status. Rainwater samples had an avg pH of 4.7 and annual H^+ deposition via precipitation averaged $320 \text{ mol } H^+ \text{ ha}^{-1} \text{ yr}^{-1}$. This was modest compared to internal H^+ production associated with HCO_3^- and NO_3^- formation. In the soil under alder cover, which was naturally enriched in N through symbiotic N_2 -fixation, nitrification released up to $4500 \text{ mol } H^+ \text{ ha}^{-1}$ annually to the solution percolating through the upper part of the soil profile. In the N-poor soil no nitrification could be observed and N transformation processes had a minor influence on the soil H^+ balance. The main internal acidification source in this case was H_2CO_3 dissociation releasing $420 \text{ mol } H^+ \text{ ha}^{-1} \text{ yr}^{-1}$. In both instances, soil solutions appeared well buffered against these external and internal acidification sources, and few H^+ leached below the 40-cm soil depth.

Additional Index Words: leaching, acid deposition, soil acidification, pH buffering, *Pseudotsuga menziesii* (Mirb.) Franco, *Alnus rubra* Bong.

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NUMEROUS STUDIES in the last decade have addressed the potential impact of atmospheric inputs of acidic substances on terrestrial and aquatic ecosystems, sometimes leading to contradictory conclusions in this respect (Braekke, 1976; D'Itri, 1982; Dochinger and Seliga, 1976; Drablos and Tollan, 1980; Hutchinson and Havas, 1980; Shriner et al., 1980; Ulrich and Pankrath, 1983). These differences stem in part from the fact that forest soil acidification can occur as a direct consequence of acid deposition as well as from sources internal to the ecosystem (Bache, 1980; Krug and Frink, 1983). In addition, the anions associated with acid rain, NO_3^- , and SO_4^{2-} , can cause accelerated cation leaching from the rooting zone when not adsorbed or biologically immobilized in that part of the soil profile. Both processes, leaching and acidification, are in turn connected by and partly dependent on the amount of base cations in the soil and the rate of base displacement from the cation exchange complex (Johnson, 1981; McFee et al., 1977). The

overall effect of acid deposition thus depends on the nature and concentration of the acidifying components entering from the atmosphere, and will vary with ecosystem characteristics.

Soil and solution pH values reflect the relative balance between H^+ generating and H^+ consuming processes at any given point across the soil profile. Acid precipitation is an additional H^+ source, superimposed on a combination of H^+ sources and sinks which are found in all ecosystems. The ability of atmospheric H^+ input to acidify an ecosystem then depends on the magnitude of such external H^+ source, relative to the strength of the internal acidification processes and the buffering capacity of the system (Bache, 1980; Krug and Frink, 1983). Forest soil acidification occurs naturally as a result of the presence of plant roots and microorganisms in the soil and a detailed description of the biological transformation processes involved can be found in the literature (Bache, 1980; Krug and Frink, 1983; Reuss, 1977; Ulrich, 1980).

The effect of nutrient uptake by plants or soil microorganisms on soil and solution pH stems from the requirement for electroneutrality both in the external (soil) solution and the internal organism fluid. To maintain such a double charge balance at all times, cation uptake must either take place in association with an equivalent amount of anions, or must be countered by the extrusion of an equivalent amount of H^+ ions. Anion uptake is basically compensated by the release of an equivalent amount of OH^- , or the consumption of the necessary H^+ ions (Nye, 1981). Accumulation of cations in excess of anion uptake, as occurs when N is absorbed by the vegetation primarily in NH_4^+ form, causes a drop in rhizosphere pH. The opposite pH effect is observed in soil systems where NO_3^- is the major N source for plants (Nye, 1981; Reuss, 1977; Ulrich, 1980).

Microbial and root respiration releases substantial amounts of CO_2 gas which mostly leaves the soil through volatilization. Part of it dissolves and hydrolyzes in the percolating soil solution forming H_2CO_3 , which may subsequently dissociate into equivalent amounts of HCO_3^- and H^+ ions. This dissociation reaction increases with increasing solution pH, and represents an important natural source of H^+ ions and mobile leaching agents in many forest soils (Cronan et al., 1978; Johnson et al., 1977). Since H_2CO_3 is a very weak acid the role of its dissociation in soil acidification and cation leaching remains very limited in extremely acid soils (pH <4.4) such as organic acid dominated Spodosols (Johnson et al., 1977; Krug and Frink, 1983; Ugolini et al., 1977).

Finally, the effect of organic matter decomposition on soil acidity has to be considered. Decomposition constitutes a H^+ sink, when cations previously incorporated into the biomass are released as strong bases (Ulrich, 1980 and Eq. [1]).

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Mineralization of organic C compounds represents a net H^+ source, either directly through the formation of organic acids associated with partial oxidation, or through the production and hydrolysis of CO_2 following complete breakdown of organics. In arctic and alpine forest soils, organic acids strongly regulate the pH and chemical composition of the percolating solution, whereas H_2CO_3 dissociation plays an important role in the solution chemistry of temperate and tropical forest soils (Cronan et al., 1978; Johnson et al., 1977; Ugolini et al., 1977). Microbial breakdown of organic P directly releases a strong acid without a change in oxidation state (Eq. [2]), while N or S mineralization acts as a H^+ source only when the inorganic end-products are fully oxidized (Reuss, 1977; Ulrich 1980, Eq. [3] to [5]).

Equations [4] and [5] are of particular interest, in that they illustrate the importance of soil N status and N transformation processes in regulating the H^+ budget of forest soils. In forest soils which are N deficient, as is the case in many glacial and newly formed soils, various organism groups will strongly compete for the limited supply of available N. The NH_4^+ released during organic matter decomposition will be readily taken up and immobilized biologically, and little substrate will be left for further microbial oxidation. With nitrification thus curtailed, N loss from the soil through NO_3^- leaching will be severely restricted (Ulrich, 1980). Under these circumstances the N transformations constitute a closed and complete N cycle and no net change in the overall H^+ balance of the system occurs, as H^+ consumption during ammonification balances H^+ released during NH_4^+ uptake (Reuss, 1977). Only biomass removal or an external N source (atmospheric deposition, fertilization) may influence the system's overall H^+ budget (Ulrich, 1980; Van Breemen et al., 1983) in that biological immobilization of extra N input may represent an additional H^+ source or sink, depending on whether N enters the soil in NH_4^+ or NO_3^- form.

In forest soils with ample N supply, the competition between plants and soil microorganisms will be less severe and sufficient NH_4^+ will be available for nitrification. This oxidation reaction is a strongly acidifying process (Reuss, 1977; Ulrich, 1980; Van Breemen et al., 1983; Eq. [5]). As N is no longer deficient, and due to the mobile nature of the NO_3^- anion (Kinjo and Pratt, 1971; Wiklander, 1976), NO_3^- is likely to leach out of the rooting zone, leaving a net H^+ surplus in the upper part of the soil profile (Reuss, 1977; Ulrich 1980). Given appropriate environmental conditions, NO_3^- may also be lost from forest soils via de-

nitrification. In that case disappearance of each NO_3^- is accompanied by the consumption of one H^+ ion (Eq. [6]), and thus has an alkalizing effect on the soil.

The objective of the research reported in this paper was to determine the importance of the above natural sources of acidification in two western Washington forest soils relative to current atmospheric H^+ inputs and, more specifically, show the importance of N transformation processes on the soil H^+ balance. This was achieved by comparing soil properties and solution chemistry between a N-poor Douglas-fir ecosystem and a naturally N-rich red alder ecosystem, both of which developed on the same soil series.

MATERIALS AND METHODS

Site Description

The study was conducted at the Univ. of Washington's Thompson Research Center in the Cedar River Watershed, located 56-km SE from Seattle at 220-m elevation in the low foothills of the Cascade Mountains. The climate in that area is maritime with cool, dry summers and wet, moderate winters. Mean annual temperature is 9.8°C and mean annual precipitation is approximately 130 cm, most of which falls as rain between October and March.

At the research site, a naturally established stand of red alder (*Alnus rubra* Bong.) abuts against a Douglas-fir plantation. (*Pseudotsuga menziesii* (Mirb.) Franco). The soil at the sites belongs to the Alderwood series (Dystric Entic Dur ochrepts), developed from ablation till overlying a compacted basal till and has a gravelly, sandy loam texture (Cole and Gessel, 1968). The two stands developed almost simultaneously following logging of the original old growth forest approximately 50-yr ago. Thus parent material, microclimate, stand age, or prior logging history are excluded as significant sources of variability between the forest ecosystems. Observed differences in soil and solution chemistry are attributed primarily to differences in vegetation composition and associated changes in N status.

Field Measurements

Precipitation, throughfall, and soil solutions were continuously collected in 1981 and 1982. Precipitation samples were taken using an automatic sensing wet/dry precipitation collector (Aerochem Metrics, Miami, FL) placed above canopy level in an area close to the study sites. Throughfall solutions were collected in triplicate at each site by means of open funnels (17.5-cm diam) covered with 1-mm mesh screen, and placed on plastic bottles. Soil leachates were monitored by means of tension lysimeters at -10 kPa (Cole 1968) installed in triplicate immediately below the forest floor, and at the 10- and 40-cm soil depth. Solution samples were collected at 28 d intervals and transported to the laboratory where pH was measured promptly by means of a calomel electrode. Concentrations of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} were determined with an atomic absorption spectrophotometer, while analyses for NH_4^+ , NO_3^- , Cl^- , SO_4^{2-} , and $\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$ were performed on a Technicon Auto-analyzer. The HCO_3^- concentration was calculated from the alkalinity determined by titration to pH 4.5 with 0.01 mol H_2SO_4 L^{-1} . Presence and concentration of organic acids were evaluated indirectly from anion deficits, i.e., from differences between

$$\Sigma (\text{H}^+ + \text{NH}_4^+ + \text{Na}^+ + \text{K}^+ + \text{Mg}^{2+} + \text{Ca}^{2+})$$

Table 1. Bulk density (D_b), gravel content, N content, pH, cation exchange capacity, percent base saturation, and total exchangeable base content for the different soil horizons in the Douglas-fir and red alder sites.

Horizon and depth	D_b	> 2 mm†	N†	pH†	CEC†	% BS†	Total exchangeable cations		
							Ca ²⁺	Mg ²⁺	K ⁺
cm	Mg cm ⁻³	g kg ⁻¹	g kg ⁻¹		cmol (+) kg ⁻¹		kmol (+) ha ⁻¹		
Douglas-fir									
A1 (0-7)	1.03	464	1.9 ± 0.1†**	5.0 ± 0.1	12.3 ± 1.4	31 ± 6	10.3	1.2	1.3
A2 (7-15)	1.03	499	1.3 ± 0.2**	5.2 ± 0.03**	9.1 ± 1.0	16 ± 4	4.5	0.7	0.8
B21 (15-30)	1.13	499	1.0 ± 0.2	5.1 ± 0.03	8.1 ± 0.7	9 ± 2	4.0	1.0	1.2
B22 (30-45)	1.34	467	0.8 ± 0.1	5.1 ± 0.1	5.8 ± 0.6	8 ± 1	2.2	0.7	1.6
Total							21.0	3.6	4.9
Red Alder									
A1 (0-7)	0.96	620	3.4 ± 0.3**	4.6 ± 0.2	10.1 ± 0.8	15 ± 4	2.6	0.4	0.8
A2 (7-15)	0.96	620	2.3 ± 0.1**	4.8 ± 0.1**	9.8 ± 0.9	16 ± 2	3.4	0.4	0.7
B21 (15-30)	1.89	786	1.5 ± 0.1	5.2 ± 0.1	7.4 ± 0.5	19 ± 5	6.9	0.6	1.3
B22 (30-45)	1.30	595	1.1 ± 0.1	5.2 ± 0.1	5.7 ± 1.4	26 ± 13	6.2	0.7	1.7
Total							19.1	2.1	4.5

** Significant difference ($p = 0.01$) at a given depth between Douglas-fir and red alder soil.

† Johnson et al., 1981.

‡ Mean ± standard error of mean.

Fig. 1. Average pH of the precipitation, throughfall, forest floor, A horizon, and B horizon soil solutions in the Douglas-fir and red alder ecosystem in 1981 (mean ± standard deviation).

and

in solution (Johnson, 1975). Average solution pH values for the collection period were derived from weighted average H^+ concentrations. Annual precipitation, throughfall, and soil drainage flux rates for the various ions were calculated by multiplying weighted mean ion concentration by the appropriate H_2O volumes. It was observed that during periods of heavy precipitation, excess water was collected by the lysimeter plates due to the presence of the impermeable basal till layer. Therefore, during these periods theoretical maximum volumes were used to calculate the total ion fluxes mentioned above. These volumes were derived from a hydrological model developed for this area and based on precipitation volume, seasonality, and vegetation type (Knutson, 1965). Otherwise, collected soil drainage volumes were incorporated into the total ion flux calculation. In addition, soil samples were taken and analyzed, using methods described by Johnson et al. (1981) (Table 1).

Statistical significance of differences in mean value between the Douglas-fir and red alder soil and solution properties was determined by means of the Student's t -test.

RESULTS AND DISCUSSION

The average pH of the rainwater solution for the observation period was 4.7 (Fig. 1), with monthly means ranging between 4.1 and 5.4. Sulfate-sulfur was a major precipitation component, accounting for one third of the total atmospheric anion input (Table 2). This atmospheric H^+ and SO_4^{2-} deposition may be in part anthropogenic due to the presence of industrial activity 50-km west of the research site. However, the relative close proximity of the ocean and the recent volcanic activity in this region suggests that part of the dissolved SO_4^{2-} and H^+ may be also of natural origin. The precipitation samples also contained measurable amounts of inorganic N (Table 2) and wet deposition of N amounted to an average of $4.2 \text{ kg ha}^{-1} \text{ yr}^{-1}$, two-thirds of which occurred in NO_3^- form, and approximately 1.5 kg as NH_4^+ . These annual input rates were similar to wet fallout values observed in the San Francisco Bay area (McColl et al., 1982).

The precipitation fluxes reported in this paper should be considered an approximation of total atmospheric input in that dry deposition rates could not be satisfactorily determined at the site. The problem in obtaining such values lies with the typical rainfall pattern at our site which is more continuous, especially during the late fall, winter, and spring months. Under such circumstances, dry-wetfall collectors often are unable to clearly distinguish both components of atmospheric input. Furthermore, no dry fall data specific to this geographic area are available in the literature. However, since rain events are long in duration, it is our belief that the chemical composition of the wetfall samples are similar to that of bulk precipitation (wetfall + dissolved dryfall), especially during the wet season (October through April). The assumption that dry (particulate) input was accounted for in the rainwater chemistry was further supported by indirect determination of H^+ and S dry deposition using accepted calculation methods developed in Germany (Mayer and Ulrich, 1974; Mayer and Ulrich, 1980; Ulrich, 1983). Application of this technique using Na^+ and Cl^- enrichment of throughfall vs. precipitation as a measure of particulate filtering action by forest can-

Table 2. Annual H^+ , NH_4^+ , NO_3^- , SO_4^{2-} , HCO_3^- , and total anion flux in the Douglas-fir and red alder ecosystems for 1981 and 1982 ($mol_c ha^{-1} yr^{-1}$).

	H^+	NH_4^+	NO_3^-	SO_4^{2-}	HCO_3^-	Total anion flux†	H^+	NH_4^+	NO_3^-	SO_4^{2-}	HCO_3^-	Total anion flux†
Douglas-fir												
1981							1982					
Precipitation	248	125	125	649	231	1430	396	85	149	431	287	1540
Throughfall	108	45	11	705	240	1440	183	26	8	705	308	1820
Stemflow	8	2	0	78	12	132	15	2	0	58	3	94
Forest Floor	37	7	6	677	400	1490	52	11	11	498	193	1080
10 cm	11	32	6	650	584	1610	12	28	15	510	491	1450
40 cm	7	33	10	658	671	1690	13	70	17	721	684	2020
Balance‡	+241	+92	+115	-9	-440	-260	+383	+15	+132	-290	-397	-480
Red alder												
1981							1982					
Precipitation	248	125	125	649	231	1430	396	85	149	431	287	1540
Throughfall	77	30	35	444	618	1590	59	48	2	629	412	1900
Stemflow	0	1	1	1	16	21	0	0	0	5	6	14
Forest Floor	174	93	3020	940	207	4930	172	54	1250	973	78	2990
10 cm	204	33	4700	444	127	5690	215	24	2450	564	158	3840
40 cm	43	96	4980	509	595	6610	29	43	2310	274	490	3600
Balance‡	+205	+29	-4860	+140	-364	-5180	+396	+42	-2160	+157	-203	-2060

† Total Anion = $HCO_3^- + NO_3^- + SO_4^{2-} + Cl^- + (H_2PO_4^- + HPO_4^{2-})$.

‡ + = Net accumulation within the ecosystem and - = Net loss from the ecosystem.

opies with subsequent derivation of gaseous and particulate acid input failed to show a further increase in atmospheric inputs over the measured precipitation values.

A considerable portion of dissolved N input to the site was immobilized in the forest canopy. Only 5 to 10% of the NO_3^- and roughly one-third of the NH_4^+ added with the precipitation solution reached the forest floor with throughfall. Stemflow provided very little additional N input to the sites (Table 2). Direct effects of atmospheric N input and its biological transformation on the H^+ balance of the sites is thus rather limited, especially when compared to the rate of annual N return via litterfall (Cole and Rapp, 1981). To determine the relative importance of internal (natural) N transformation processes on the overall soil H^+ budget soil leachate composition was examined for the three depths discussed previously. Belowground annual NH_4^+ flux rates did not follow consistent patterns (Table 2) and remained small compared to the size of the available soil N capital and the annual N uptake and turnover rates in these particular forest ecosystems (Cole and Rapp, 1981). Annual NH_4^+ production and immobilization seemed fairly well balanced, and observed differences were expected to be of minor importance to the overall soil H^+ budget of either site.

However, the N-poor and naturally N-enriched soils showed marked differences with respect to NO_3^- . All soil solution samples collected below Douglas-fir were consistently low in NO_3^- ($0.001 mmol NO_3^- L^{-1}$) (Fig. 2). Differences between annual NO_3^- input via throughfall and leaching output below 40-cm soil depth was nearly zero (Table 2), causing an insignificant change in the soil H^+ balance. This closed N cycle, with N uptake rates closely coupled to N release during mineralization is characteristic for ecosystems under N stress (Cole and Rapp, 1981). In forest ecosystems with a limited amount of available N and optimal N conservation, N transformation processes can be

Fig. 2. Weighted average concentration of NO_3^- , HCO_3^- , $SO_4^{2-} + Cl^-$, total anions (●) and total cations (▲) in precipitation (P), throughfall (T), forest floor (FF), A horizon (A), and B horizon (B) solutions collected in the Douglas-fir and red alder ecosystem in 1981 and 1982 [$mmol (\pm) L^{-1}$].

expected to play a minor role in determining soil acidity (Reuss, 1977).

In the soil occupied by red alder, solution chemistry was highly dominated by NO_3^- , which accounted for as much as 75% of total anion flux past the 40-cm soil depth (Table 2). As there was little NO_3^- influx to the soil via the throughfall or stemflow solution (Table 2), most dissolved NO_3^- had to be produced within the below-ground part of the ecosystem. Such intensive nitrification was undoubtedly made possible by the greater N availability in the red alder soil, which in turn resulted from the symbiotic N_2 -fixing properties of alder species. Earlier studies have documented annual N accretion rates due to symbiotic N_2 -fixation by red alder ranging from 50 to 200 $kg N ha^{-1}$ (Bormann and DeBell, 1981; Cole et al., 1978; Zavitskovski and Newton, 1968). Most of the NO_3^- addition to the solution in this site took place in the forest floor and on the top 10 cm of the soil profile (Table 2), which was generally the locus of greatest N enrichment (Table 1, Bormann and DeBell, 1981).

The difference between NO_3^- leaching below 40 cm and annual NO_3^- input via throughfall + stemflow

could be taken as a measure of net annual nitrification rate. It did not account for the NO_3^- formed (Eq. [4] and [5]), but subsequently reduced during uptake by roots and/or microorganisms. In such cases, however, the cycle of N transformations is completed without a net change in the overall H^+ balance of the system (Reuss, 1977). If denitrification took place, which is not unlikely during periods of occasional H_2O saturation of this soil (Waring and Gilliam, 1983), then again the H^+ consumption associated with the reduction of each NO_3^- (Eq. [6]) would have balanced the H^+ release during NO_3^- formation (Eq. [4] and [5]). The production of all NO_3^- lost annually from the red alder ecosystem through leaching (4940 and 2310 mol $\text{NO}_3^- \text{ ha}^{-1} \text{ yr}^{-1}$ in 1981 and 1982, respectively) had to be accompanied by the release of equivalent amounts of H^+ ions. This microbial oxidation process thus represented an internal (natural) H^+ source on the avg 10 times stronger than atmospheric H^+ inputs (Table 3), and basically had the acidifying potential of 150 cm of annual rainfall with an avg pH of 3.6.

The increase in HCO_3^- leaching output over atmospheric input (Table 2) similarly provided a measure for internal production and dissociation of H_2CO_3 associated with root and microbial respiration. The smaller HCO_3^- flux in the upper part of the alder soil profile compared to the adjacent Douglas-fir soil profile (Table 2), was mainly attributed to a decrease in H_2CO_3 dissociation with decreasing solution pH (Fig. 1). Calculated annual H^+ release due to this natural respiration process ranged from 200 mol $\text{H}^+ \text{ ha}^{-1}$ to 440 mol $\text{H}^+ \text{ ha}^{-1}$ (Table 3), which was comparable to, or even exceeded, annual H^+ deposition from the atmosphere (Table 2 and 3). This is in all likelihood a conservative measure of internal H^+ production, in that the HCO_3^- input via rainwater appears high in view of observed rainwater pH and normal atmospheric pCO_2 . This potential overestimation of the rainwater HCO_3^- concentration may have resulted from the fact that alkalinity was determined by titration to the theoretical endpoint pH 4.5 (Stumm and Morgan, 1981). Titration to pH 5.0 to 5.3, assuming $[\text{HCO}_3^-] = 0$ at lower pH values, as suggested by Barnes (1964) for solutions with low HCO_3^- concentrations [$<0.160 \text{ mmol } (-) \text{ L}^{-1}$] would probably have yielded much lower HCO_3^- input values. Based on this approach, the internal H^+ production estimates would be increased by as much as 250 mol $\text{H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$. Organic acids were insignificant contributors to the overall H^+ budget (Table 3), as no measurable amounts could be detected in the soil solution samples collected at the 40-cm depth (Fig. 2).

Irrespective the origin and the magnitude of H^+ input to the soil, $<1.4\%$ of total annual H^+ input to the solutions percolated beyond the 40-cm soil depth (Table 3). Throughfall, forest floor, and soil solutions collected in the N-poor system where no nitrification was observed, had significantly higher pH values ($p = 0.001$) than the incident rainwater (Fig. 1). In the red alder forest on the other hand, the H^+ flux increased considerably underneath the forest floor (Table 2), and the soil solutions were always significantly more acid ($p = 0.001$) than those collected at the same depth in

Table 3. Mean annual H^+ input via precipitation vs. internal H^+ production by H_2CO_3 , HNO_3 , and organic acid formation and annual H^+ leaching loss in adjacent Douglas-fir and red alder forest soils.

Ecosystem	Atmospheric input	Internal production by:			
		H_2CO_3	HNO_3	Organic acids	Leaching output
		mol $\text{ha}^{-1} \text{ yr}^{-1}$			
Douglas-fir	320	420	tr†	tr	10
Red Alder	320	280	3450	tr	40

† tr = insignificant amount.

the Douglas-fir site (Fig. 1). Observed differences in solution pH between the two soil types were largest in the A horizon and decreased with increasing sampling depth (Fig. 1). The fact that the solution acidification pattern in the N-rich soil coincided with an increase in NO_3^- flux in that particular part of the soil profile (Fig. 1, Fig. 2, Table 2), suggested nitrification as the major H^+ source. Nevertheless, measured H^+ flux was considerably lower than what could be expected from the net increase in NO_3^- flux (Table 2), indicating strong pH buffering of the soil solutions. A concurrent increase in cation flux (Fig. 2) and decline in exchangeable cations in the upper part of the N-rich soil (Table 1) suggested cation displacement from the exchange sites as one of the buffer mechanisms involved (Van Miegroet and Cole, 1984). Franklin et al. (1968) similarly noted that the presence of red alder in the vegetative cover significantly lowered soil pH and caused a significant drop (from 10–16% to 4–5%) in the base saturation of the A horizons.

It should be recognized that the soil H^+ budgets presented here did not account for the effect of net cation accumulation in woody biomass. Calculations for various forest types in Tennessee estimated this natural H^+ source to be equal if not more important than H^+ release due to soil respiration (Johnson et al., 1983; Richter and Johnson, 1983). Quantification of such an additional internal H^+ source would only emphasize the relative importance of internal acidification processes, and provide further evidence on the strong buffering capacity of these particular soils against solution acidification. As pointed out earlier, annual atmospheric acid deposition rates were based on the chemical composition of the precipitation solution and did not include separate dryfall measurements. Studies in northern California showed that while dry deposition of NO_3^- comprised a substantial portion of total atmospheric N input (McColl et al., 1982) only a small portion of total atmospheric H^+ input entered in particulate form. If this was also the case at our study sites, then this important unaccounted input of NO_3^- -N would have been readily immobilized by root or microbial uptake in the N-deficient soil, causing a net alkalizing, rather than an acidifying effect, on the system. While rapid biological immobilization would have been less likely in the N-rich soil, dry deposition of NO_3^- could nevertheless not account for the large NO_3^- flux observed in the red alder soil. In both instances incorporation of dry deposition would not have altered the relative magnitude of internal vs. external sources of acidification.

CONCLUSIONS

At current acid deposition rates in western Washington, the H^+ input from the atmosphere is smaller than the amount of H^+ ions released naturally within two forest soils under Douglas-fir and red alder cover. In the red alder soil, naturally enriched in N through symbiotic N_2 -fixation, N transformation processes, and nitrification more specifically, exert a strong influence on soil and solution acidity. Latter microbial oxidation process releases considerable amounts of H^+ and mobile NO_3^- , causing accelerated downward displacement of exchangeable bases and a significant drop in pH of the soil and soil solution in the upper part of the profile. In the N-poor Douglas-fir soil, H_2CO_3 is the main internal acidification source, while N transformation processes have little effect on the overall H^+ budget. Up to 99% of all H^+ ions originating from external and internal sources are neutralized in the top 40 cm of either soil system. This is an indication of the capacity of these soils to act as a strong buffer against acidification of percolating solutions, whether caused by acid precipitation or through natural processes.

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