CANOPY INTERACTIONS WITH ATMOSPHERIC DEPOSITION AT THREE HARDWOOD FOREST SITES

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Abstract.--Annual ion fluxes in bulk precipitation and throughfall were compared at three deciduous forest sites to examine the role of hydrogen ions and organic compounds in canopy cation exchange. Hydrogen ions explained from 31 to 83% of annual canopy cation losses. Organic compounds played a significant role in canopy cation exchange as either weak acids or neutral salts.

INTRODUCTION

Loss of base cations from a forest canopy can be due to H^+ exchange, washoff of surface deposits, or leaching of neutral salts from tissue (Cronan and Reiners, 1983). Hydrogen ions from strong acids in atmospheric deposition and dissociated weak organic acids from the canopy can exchange for base cations from the canopy. Alternatively, washoff of surface deposited neutral salts or leaching of neutral salts from canopy tissue can represent a major cation loss. Loss of base cations via H^+ exchange has been linked to atmospheric deposition of H^+ (Price and Watters, 1988), while washoff and leaching of neutral salts can be largely determined by canopy cation availability.

Whether canopy cation losses due to elevated H^+ deposition may lead to excessive nutrient loss and soil acidification is unknown. Canopy cation losses are resupplied from the soil by the transpiration stream. If cation supplies from mineralization of organic matter or mineral weathering are insufficient to replenish the losses, soil acidification could result (Ulrich, 1983). Reduced soil and plant pH could increase availability of heavy metals toxic to plants and increase concentrations of Al^{3+} to toxic levels to trout in soil drainage water reaching streams.

The purpose of this paper is to report the results of a year-long study of canopy exchange at three hardwood forest sites with varying fertility on the eastern edge of the Central Hardwood region in an area with some of the highest atmospheric wet deposition of SO_4^{2-} and H^+ in North America. The objective of the study was to determine the role of H^+ exchange versus washoff and leaching of neutral salts in controlling canopy cation losses, with special attention to the role of organic acids. Overall biogeochemistry for these sites has been described by DeWalle et al. (1988) and DeWalle and Sharpe (1985).

THEORY

Two methods can be used to estimate the net flux of H^+ involved in cation exchange within the canopy: 1) pH measurements and 2) net canopy ion balance. By the first method pH differences between bulk precipitation and throughfall can be used to compute the net H^+ flux in the forest canopy (F_{H^+}) as:

$$F_{H^+} = PH^+_{bp} - TH^+_t \qquad (1)$$

where P is the amount of precipitation in cm yr^{-1}, T is the amount of throughfall in cm yr^{-1}, and subscripts bp and t refer to concentrations of H^+ in meq L^{-1} in bulk precipitation and throughfall,

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respectively. Equation (1) assumes no generation of H^+ within the canopy from dissociating organic acids or that organic compounds behave as neutral salts. If organic compounds derived from the canopy occur as organic acids then an additional H^+ flux equal to the net flux of organic anions in the canopy (bulk precipitation - throughfall) should be added. Equation 1 then becomes

$$F_{H^+} = PH^+_{bp} - T\,H^+_t + P\,|A^-o_{bp}| - T\,|A^-o_t| \qquad (2)$$

where Ao^- represents the organic anion concentration in meq L^{-1}.

The second method of estimating the net flux of H^+ in the canopy is the use of an ion balance suggested by Cronan and Reiners (1983). With this method the net flux of cations, excluding H^+, in the canopy (bulk precipitation-throughfall) is equal to the total canopy exchange by H^+ exchange as well as neutral salt washoff or leaching. The part of the cation flux due to neutral salt washoff and leaching equals the net flux of anions (bulk precipitation - throughfall) in the canopy, since a charge balance must be obtained between cations and anions of neutral salts. The remaining cation flux in the canopy is due to H^+ exchange. Thus, the net flux of H^+ by this method becomes

$$F_{H^+} = (P\,C^+_{bp} - T\,C^+_t) - (P\,|A^-_{bp}| - T\,|A^-_t|) \qquad (3)$$

or, by rearranging

$$F_{H^+} = (P\,C^+ - |A^-|)_{bp} - T\,(C^+ - |A^-|)_t \qquad (4)$$

where C^+ is the base cation sum and A^- is the anion sum both in meq L^{-1}. If organic anions are assumed to be derived from neutral salts, the anion sums in Equations 3 and 4 represent total anions and Equation 1 above pertains. If organic compounds exist as weak acids, then the anion sums in Equations 3 and 4 represent only inorganic anions and Equation 2 must be used.

Ideally the ionic concentrations in wet plus dry fallout should be used in the foregoing calculations, rather than bulk precipitation concentrations. However, no reliable method is available to continuously measure dry deposition inputs. Since bulk precipitation flux does include some inputs from larger particulate dry deposition (Lindberg et al., 1986), it is used here as the best available estimate of total atmospheric deposition.

STUDY SITES

The three deciduous forest sites studied were Peavine Hill on Laurel Mountain in southwest Pennsylvania, Fork Mountain on the Fernow Experimental Forest in north central West Virginia, and Sand Mountain in central Pennsylvania. All sites were gently-sloping, ridge-top sites in the Appalachian Mountains. Forest on Peavine Hill was dominated by saw-timber sized red oak (Quercus rubra) and black cherry (Prunus serotina) with a fern and Vaccinium spp. understory. Fork Mountain forest was also mature, saw-timber sized and primarily included red oak, black cherry, and sugar maple (Acer saccharum) with a dense herbaceous understory. Forest at Sand Mountain was composed of large-pole sized chestnut oak (Quercus prinus) and white oak (Quercus alba) with a mountain-laurel (Kalmia latifolia) understory. All sites were underlain by acidic sandstone and shale bedrock. Soils were fine-loamy, mixed, mesic typic Hapludults (Peavine Hill and Stone Mtn.) and loamy-skeletal, mixed, mesic, Typic Dystrochrepts (Fork Mtn.).

METHODS

Field

Field methods included biweekly measurement of precipitation and throughfall amounts and collection of bulk precipitation, throughfall and wet fallout samples from November 30, 1983 to November 14, 1984. Precipitation amounts were measured in standard non-recording rain gauges in forest openings near each site. Throughfall amounts were collected beneath the forest canopy with plastic rain gauges randomly located at ten points at Peavine Hill and five locations at each of the remaining two forest sites.

Bulk precipitation and throughfall samples for chemical analysis were collected using composite samples from 17-cm diameter plastic funnels during the growing season. Twelve funnels were employed at Peavine Hill and three funnels were employed at each of the other two sites. During winter, four 36-cm W x 52-cm L x 52 cm-D plastic tubs were used to collect bulk precipitation at Peavine Hill and one tub at each of the remaining two sites.

Laboratory

Standard methods (EPA, 1983) were employed for water anlyses. Analysis for Ca^{2+}, Mg^{2+}, Na^+, K^+, Mn^{2+}, Al^{3+}, and Zn^{2+} were conducted using atomic absorption spectrophotometry, NH_4^+ and NO_3^- analyses were conducted using a Technicon autoanalyzer, SO_4^{2-} was analyzed using both the turbidimetric method and chromatography (Dionex), Cl^- was analyzed using both a chloride titrator and chromatography (Dionex), and pH was measured using an Orion Ionanalyzer. Further details are given in DeWalle, et al. (1988).

Lower canopy tree leaves of species common to all sites were collected in August 1984 for chemical analysis. Three composite samples from leaves of at least ten trees of each species were digested and analyzed using inductively coupled plasma emission spectroscopy for total K, Ca, and Mg content.

Computations

Annual net flux of H^+ using Equations 1 and 2 were computed using annual ion fluxes. Due to the limited number of throughfall collectors used in the study, emphasis was placed on annual ion fluxes. Annual ion fluxes were computed as the product of mean biweekly ion concentration for the one-year period and the measured precipitation or throughfall totals.

Organic anion concentrations were computed as the difference between all measured cations minus all measured anions. As a check on this procedure, mean annual organic anion concentrations for bulk precipitation computed in this manner of 5, 8, and 9 $\mu eq\ L^{-1}$ at Peavine Hill, Fork Mountain and Sand Mountain, respectively, were found to agree well with organic anion concentrations of 6.8 to 14.9 $\mu eq\ L^{-1}$ found in NADP wet deposition samples by Keene and Galloway (1984). Thus, this procedure was deemed reasonable.

RESULTS AND DISCUSSION

Ion and water fluxes at the three forest sites for the November 1983-84 period are given in Table 1. Bulk precipitation deposition of H^+ at Peavine Hill was 63% greater than that at Fork Mountain and 79% greater than that at Sand Mountain primarily due to lower precipitation pH at Peavine Hill. Bulk precipitation of other cation and anion sums were similar among sites. Throughfall flux of H^+ was also greater at Peavine Hill, again due to lower pH. Throughfall flux of other cation and anion sums was greater at Fork Mountain., apparently due to greater canopy washoff, leaching and/or H^+ exchange. Regardless, canopy water at all sites remained relatively acidic with the maximum pH of 4.40 occurring in Fork Mountain throughfall.

The assumed role of organic compounds had a profound effect on the computed net fluxes of H^+ in the canopy (Table 2). If organic compounds act as weak organic acids, then the computed H^+ flux in the canopy is greater and equivalent to a larger fraction of total canopy cation loss than for the neutral salt scenario. For example, computed net H^+ exchange at Peavine Hill, Fork Mtn. and Sand Mtn. equals 83, 67, and 55% of total canopy cation losses, respectively, with organics acting as a weak acid. These percentages reduce to 64, 36, and 31% at Peavine Hill, Fork Mtn. and Sand Mtn., respectively, if organics act as neutral salts. Cronan and Reiners (1983) found H^+ exchange only explained 20% of canopy cation losses in a northern hardwood forest in New Hampshire with little or no organic anion contribution. Their results compare more favorably with the neutral salt scenario in this paper, but the true role of organics can not be determined.

Table 1. Ion and Water Fluxes at Three Deciduous Forest Sites for November 1983 to November 1984

Flux	Peavine Hill	Fork Mtn.	Sand Mtn.
	($meq\ m^{-2}\ yr^{-1}$)		
Cations[1]			
bulk precip.	130	160	142
throughfall	188	286	191
Anions			
bulk precip.			
total[2]	-288	-257	-230
organic[3]	-8	-12	-11
throughfall			
total	-309	-337	-264
organic	-19	-50	-23
H^+			
bulk precip.	158	97	88
(pH)	(4.00)	(4.21)	(4.16)
throughfall	120	51	74
(pH)	(4.05)	(4.40)	(4.19)
	($cm\ yr^{-1}$)		
Water			
precipitation	157	156	128
throughfall	134	127	115

1/ Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, Mn^{2+}, Al^{3+}, Zn^{2+}
2/ SO_4^{2-}, NO_3^-, Cl^-, organic anions
3/ organic anions estimated as cations including H^+ minus anions

Table 2. Canopy Exchange of Hydrogen Ions Using Two Scenarios for Organic Compounds and Two Estimation Methods

Net Flux[1]	Peavine Hill	Fork Mtn.	Sand Mtn.
	($meq\ m^{-2}\ yr^{-1}$)		
Organic Compounds as Neutral Salts			
1. Net H^+ flux from ion balance			
Base cations	-58	-126	-49
Neutral salts	-21	-80	-34
H^+	37	46	15
2. Net H^+ flux from pH measurement	38	46	14
Organic Compounds as Weak Acids			
1. Net H^+ flux from ion balance			
Base cations	-58	-126	-49
Neutral salts	-10	-42	-22
H^+	48	84	27
2. Net H^+ from pH measurement			
pH measurement	38	46	14
Organic acids	11	38	12
H^+	49	84	26

1/Net flux = bulk precipitation - throughfall

Excellent agreement was indicated between methods for computing the H^+ flux in the canopy (Table 2). Ion balance estimates based upon Equation 4 agreed within 1 $meq\ m^{-2}\ yr^{-1}$ with estimates based upon pH measurement (Equation 1 or 2).

Results suggest that annual canopy cation losses due to H^+ exchange do not vary simply with annual total H^+ deposition in bulk precipitation. The greatest H^+ exchange in the canopy (46 or 84 $meq\ m^{-2}\ yr^{-1}$) occurred at Fork Mountain where bulk precipitation deposition of H^+ (97 $meq\ m^{-2}\ yr^{-1}$) was intermediate in rank among the three sites. Similarly, maximum H^+ deposition at Peavine Hill of 158 $meq\ m^{-2}\ yr^{-1}$ was associated with intermediate canopy H^+ exchange (38 or 49 $meq\ m^{-2}\ yr^{-1}$). However, minimum H^+ deposition did

correspond to minimum H^+ canopy exchange at Sand Mountain. Although H^+ deposition probably directly influences canopy H^+ exchange, other factors, such as cation availability in the canopy, also probably play a role.

Total content of K, Ca, and Mg in tree leaves comprising the canopy at these three sites (Table 3) helps to explain canopy H^+ exchange. The generally higher total tree leaf content of K, Ca, and Mg at Fork Mountain may have led to greater availability of these cations for exchange with H^+ at this site than the other two sites. Thus H^+ exchange for cations in the canopy at Fork Mountain could be more efficient. Indeed, over one-half of H^+ in bulk precipitation was exchanged in the canopy at Fork Mountain. In contrast, tree leaves at Peavine Hill had the lowest total K, Ca, and Mg content (Table 3) which contributed to reduced canopy H^+ exchange and the fact that only about 23-30% of H^+ from bulk precipitation was involved in canopy exchange. At Sand Mountain tree leaf K, Ca, and Mg content was intermediate among the three sites and the fraction of H^+ from bulk precipitation involved in canopy exchange (16-31%) was similar to that at Peavine Hill.

Table 3. Mean Chemical Composition of Lower Canopy Tree Leaves at Three Forest Sites in August 1984

Tree Species	n	Element	Peavine Hill (%)	Fork Mtn. (%)	Sand Mtn. (%)
Prunus serotina	3	K	1.63 a[1]	2.47 b	-
		Ca	0.95 a	1.26 b	-
		Mg	0.28 a	0.68 a	-
Quercus prinus	3	K	0.81 a	1.37 b	1.05 c
		Ca	0.49 a	0.61 b	0.79 c
		Mg	0.10 a	0.20 b	0.15 c
Quercus rubra	3	K	0.84 b	1.35 b	0.94 b
		Ca	0.49 a	0.79 b	0.75 c
		Mg	0.09 a	0.18 b	0.15 c

[1]Means in the same row followed by the same letter are not significantly different between sites at the 95% confidence level.

CONCLUSIONS

Hydrogen ion exchange explained 31 to 83% of total annual canopy cation exchange at three deciduous forest sites. High canopy H^+ cation exchange was associated with both high tree leaf total K, Ca, and Mg content and high H^+ deposition in bulk precipitation. Assuming organic compounds acted as weak acids also increased the magnitude of the computed H^+ exchange. Annual canopy H^+ cation exchange was equivalent to 29 to 86% of annual H^+ in bulk precipitation for these stands; suggesting that a varying proportion of changes in H^+ deposition from the atmosphere would be translated into canopy H^+ cation exchange.

The role of organic compounds in canopy cation exchange was important, but ambiguous. As either a weak acid or neutral salt, organic compounds could have contributed from 19 to 30% of annual canopy cation exchange.

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