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Fluxes of undissociated acids to terrestrial ecosystems by atmospheric deposition

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ABSTRACT

Undissociated acids in the troposphere are transferred to terrestrial ecosystems as wet deposition in rain and cloud/fog water and as particulate and gaseous dry deposition during interstorm intervals. Wet deposition can be measured directly, and the sum of dry deposition and canopy release of undissociated acids can be estimated from net canopy wash-off into throughfall (TF). Samples of rain, cloud and fog water, and TF were collected from April 1986 through March 1987 at low-elevation (230 m) and high-elevation (1730 m) coniferous forests in Tennessee, USA. The samples were titrated for total acidity by Gran's method, and undissociated acidity was calculated as total acid (Gran) minus free acidity (pH measurement). During that 12-month period, the undissociated acid fluxes in wet deposition at these sites were both 34 mmol m^{-2}, comparable to the free acid fluxes in wet deposition. Fog water fluxes at the lower site were negligible, but at the high-elevation site cloud water was potentially responsible for considerable deposition of undissociated acids to the forest canopy. Dry deposition plus canopy fluxes of undissociated acids were greater at the higher site. Dry deposition plus canopy fluxes averaged 54 mmol m^{-2} y^{-1} (range 36–77) at the low-elevation site and 82 mmol m^{-2} y^{-1} (range 77–86) at the high-elevation site. Undissociated acidity in TF consists of biological metabolites and cuticular decomposition products and dry-deposited compounds washed from plant surfaces. Formic and acetic acid concentrations in TF do not exceed those found in rain, therefore dry depositions of those acids cannot account for the undissociated acidity of TF. The relative importance of wet and dry deposition of undissociated acid to terrestrial ecosystems would be further clarified by identifying the weak acids in TF.

1. Introduction

Acidity as measured by pH presents an incomplete picture of acid fluxes from the troposphere to forests by rain, in that undissociated weak acids are not detected (Galloway et al., 1976; Keene et al., 1983; Keene and Galloway, 1984). Dry deposition acid fluxes are generally measured in terms of free acids (e.g., HNO_3; Lovett and Lindberg, 1986) and may be underestimated for the same reason.

Formic and acetic acids are the predominant weak acids in rain (Galloway et al., 1982; Chapman et al., 1986), but aromatic and C_2–C_{30} linear alkyl acids (Kawamura and Kaplan, 1986), as well as other high molecular-weight organic compounds (Hoffman et al., 1980b) have also been isolated from rain. Weak acids present in gaseous (Dawson et al., 1980; Kawamura and Kaplan, 1987), particulate (Grosjean et al., 1978), and cloud droplet (Keene and Galloway, 1988; Munger et al., 1989; Winiwarter et al., 1988) phases can deposit on forest canopies as well.

Atmospheric inputs, as well as decomposition and exchange processes taking place within the canopy, all transfer acidity to the forest floor in

throughfall (TF). Thus, it has been recognized that pH measurements of TF yield an incomplete picture of the total acid fluxes in TF (Hoffman et al., 1980a, b; Lovett et al., 1985; Hantschel and Klemm, 1987).

Complete chemical analysis of TF has been impeded by its complexity, but the determination of its total acidity has been attempted in several ways. Hoffman et al. (1980b) used solvent extraction and gas chromatography to identify a wide variety of high-molecular-weight organics, including some carboxylates, in TF. The short-chain organic acids expected in wet and dry deposition were presumably volatilized during sample preparation in that study. Hoffman et al. (1980a), Lindberg et al. (1984), and Lovett et al. (1985) used Gran's plot titrations, and Hantschel and Klemm (1987) used stepwise titrations to pH 8.3, to obtain the total acidity of TF.

Net TF has been used to estimate dry deposition fluxes of trace metals (Lindberg and Harriss, 1981) and other inorganic ions (Lovett et al., 1985) to forest canopies. The application of this method to the estimation of undissociated acid fluxes is complicated by several factors. To the extent that dry-deposited acids react with, or are retained by the canopy and not released to TF, this method will underestimate the dry-deposited component in TF. On the other hand, the release of undissociated acidity from the foliage will cause this method to overestimate the dry deposition flux. To estimate dry deposition of undissociated acids from net TF fluxes requires the separation of these two distinctly different sources.

The undissociated acidity of TF, therefore, provides only a rough comparison of acid fluxes in wet and dry deposition. A further reason to examine the undissociated acidity of TF is related to the possibility that weak acids in net TF arises from the canopy itself. Forest canopies can buffer the acidity of atmospheric inputs by releasing acid anions that are subsequently protonated (e.g., Cronan and Reiners, 1983). Such compounds, synthesized by plants and released in TF, constitute a drain of metabolic resources. In the past, the metabolic consequences of inorganic ion loss only have been considered (e.g., Amthor, 1986).

The objectives of this work were: (1) to determine the undissociated acid fluxes by wet deposition to coniferous forests in two strongly contrasting environments; (2) to measure undissociated acid fluxes in net TF, arising from canopy internal sources and dry deposition washoff. We expected that both wet and dry deposition and canopy releases of undissociated acids could be affected by these contrasts in species composition and exposure conditions. One site was in a low-elevation loblolly pine plantation in an area exposed to substantial acid deposition from sulfur dioxide and nitric acid vapor (Lindberg et al., 1986). The other site was a high-elevation forest, consistimg primarily of old-growth red spruce, which received much more rain and snow and was frequently exposed to acidic cloud water as well (Lindberg et al., 1988). This study measured undissociated acid concentration of acids with pK_a from about 4 to 8. These undissociated acids constitute an acid "reserve" that buffers pH if free acidity in deposition is reduced.

2. Methods

2.1. Sites

Rain and throughfall (TF) samples were collected at two sites in Tennessee, USA. The high-elevation (1730 m) site is an old growth red spruce (*Picea rubens* Sarg.) forest on Clingmans Dome (34°34′N, 83°28′W) in the Great Smoky Mountains National Park. The low-elevation (230 m) site is an approximately 40-year-old loblolly pine (*Pinus Taeda* L.) plantation in Oak Ridge (35°52′N, 83°24′W).

2.2. Sample collection

2.2.1. Rain and throughfall. Automatic wet-only collectors (Aerochem Metrics ACM-1) were used for both rain and TF collections at these sites. At each site, rain was collected in forest clearings adjacent to the sampled plots. TF was collected in two collectors located randomly under the canopy at the spruce site and in five collectors at the pine site. Within each collector, water was collected in a 12.7-cm-diameter polyethylene funnel inserted in a 1-L polyethylene bottle. Samples were collected on an event basis and sample bottles were capped and returned to the laboratory within 12 h after each rain event. Depth (cm) of rain and TF were determined with

two Trucheck™ wedge gauges adjacent to each collector. The polyethylene collection and storage equipment was cleaned prior to use with several rinses with distilled, deionized (conductivity ≤ 2 μSiemens) water. No detergents or acids were used for cleaning this equipment.

At the pine site, 5 dormant season (November 1986 through March 1987; 5 months in duration) and 17 growing season (April 1986 through October 1986; 7 months in duration) rain events were analyzed. At the spruce site, 5 dormant season and 19 growing season rain events (based on the same defined seasons) were analyzed. The ranges of concentrations obtained with the two TF collectors at the spruce site, and the standard errors obtained with the five TF collectors at the pine site are reported as measures of spatial variability in TF chemistry. Spatial variability was not determined for the wet deposition inputs, since only one wet-only collector was available at each site. Seasonal and annual hydrologic fluxes were determined with continuous rain gauge data collected both in the open and below the canopy at each site.

2.2.2. Cloud and fog water. Cloud and fog water samples were collected intermittently during rain-free periods at both sites. At the pine site, a Global Geochemistry Corporation MIFS-1 active sampler (with polyethylene collection surfaces) was used. At the spruce site, a non-commercial passive impaction collector (with teflon collection surfaces) was used. Because of the limited volumes of the samples, only four cloud water samples from the spruce site and eight fog water samples from the pine site were titrated. The cloud and fog inputs were not separated into growing and dormant seasons because of the small number of samples.

2.3. Sample analyses

Sample pH measurements were made on the day of collection with an Orion 8152 "Ross" combination of pH electrode and a Beckman pHI 21 meter. Unfiltered rain, cloud and fog water, and TF samples were then preserved with 0.5% reagent $CHCl_3$ and stored in sealed polyethylene bottles until titration. The Gran titrations (Gran, 1952) were performed with a Brinkman "Metrohm" autotitrator/Hewlett Packard 85 microcomputer combination (Lindberg et al., 1984), with the sample equilibrated to ambient room temperature (± 2°C). A slow stream of N_2 gas (after passage through a mixed $CaSO_4$/ascarite trap and 1 M oxalic acid) was bubbled through the samples for 2 min prior to, and throughout the titrations. A N_2 atmosphere is essential to avoid the titration of bicarbonate from atmospheric CO_2, but the initial pH of these samples (<4.5) made long initial N_2 purges unnecessary (Galloway et al., 1976). On the other hand, volatile weak acids could be displaced from the solutions by longer N_2 purges (Galloway et al., 1979). The NaOH titrant was prepared by diluting saturated aqueous NaOH (from which absorbed CO_2 precipitates as Na_2CO_3) into boiled and N_2-purged distilled deionized water under a nitrogen atmosphere. This titrant entered the autotitrator syringe directly through a teflon tube. The titrant reservoir was vented through a mixed $CaSO_4$/ascarite trap mounted 30° below horizontal.

Excess ammonium (as 1 M Fisher A.C.S. reagent NH_4Cl to a final concentration of 250 μmol L^{-1}) was added to each sample prior to titration. With excess $[OH^-]$, pH plateaus were obtained from pH 8.2 to 8.4, where the titrations were stopped. This technique excludes ammonium and other proton donors with pK_a greater than 9 from the assay, and uses the ammonium–ammonia buffer to define a known and consistent intercept for the total acid function. Similar techniques have been used to define the strong acid function intercept of the Gran's titration (Lee and Brossett, 1978).

At the beginning and end of each day of titrations, a standard solution of reagent potassium hydrogen phthalate (Fisher A.C.S. reagent, 1640 μeq. L^{-1}) was titrated to determine the strength of the titrant base. This value varied by $<10\%$ for the entire course of the experiment. Titrations of formic, acetic, propionic, oxalic and citric acids yielded total acidities within 5% of their gravimetrically determined values (Table 1).

Gran titrations of pH 4.0 HNO_3 solutions (from concentrated reagent HNO_3 and distilled, deionized H_2O) that had been rinsed through funnels, collection bottles, and storage bottles showed total acidity equal to free acidity, indicating that acids were not extracted from the plastic at typical sample pH values.

Repeated analyses of individual samples following storage at 2°C for periods as long as

Table 1. *Gran's plot titrations showing total acidity (in μmol(c) L^{-1} of carboxylic acid standard solutions*

Acid	Theoretical	pH	Measured	T/M
formic	2350	3.84	2380	0.99
acetic	1750	3.86	1770	0.99
propionic	1340	3.87	1350	0.99
oxalic	880	4.28	920	0.96
citric	1050	3.95	1080	0.97

4 months showed changes of 5% or less in both pH and total acidity. Similar results (for up to 3 weeks) have recently been reported (Bachman and Peden, 1987).

Potential overestimation of free acid by the strong acid intercept of Gran's plot has been suggested (Lindberg et al., 1984; Keene and Galloway, 1985). Lindberg et al. (1984) avoided this problem by using only the total acid intercept of the Gran function, and using the original pH to measure free acidity. The calculated difference between these two quantities underestimates undissociated acidity to the extent that the weak acids present are deprotonated (present as free acidity) at the original solution pH (Lindberg et al., 1984; Keene and Galloway, 1985). Certain inorganic ions of aluminum, iron, manganese and phosphorus will also appear as titratable acidity by this method (Galloway et al., 1976). In this study, we also analyzed several rain and TF samples for aluminum (as Al^{3+}) and phosphate (as $H_2PO_4^-$), and found the sum of these titratable inorganic ions to account for less than 10% of the undissociated acidity. Manganese and iron concentrations in rain and TF were measured by Lindberg and Harriss (1981) in a nearby forest and found to make an insignificant contribution to undissociated acidity.

Ion chromatography analyses were performed with a Dionex HP ICE AS1 column (Dionex Corporation, 1987).

2.4. *Flux determinations*

The undissociated acidity ([HA], in μmol L^{-1}) of each sample was calculated using the following formula:

$$[HA] = (\text{Gran total acidity}) - (\text{pH free acidity}).$$

Rain fluxes and net TF (TF minus rain) fluxes by site and season were derived from depth-weighted averages. The rain fluxes of undissociated acid (HA, in mmol m^{-2} $event^{-1}$) were defined as:

$$([HA]_{rain} \times \text{cm rain}).$$

For seasonal fluxes, the TF concentrations were weighted by TF event depth and averaged. The net TF fluxes of HA (as mmol m^{-2} $event^{-1}$) were defined as:

$$([HA]_{TF} \times \text{cm TF}) - ([HA]_{rain} \times \text{cm rain}).$$

Neither free nor undissociated acidity is necessarily conserved when samples are combined. These volume-weighted fluxes do not necessarily yield the same results as concentration measurements on a composite sample, but ecosystems receive wet deposition as events and not as a single annual pulse. Galloway et al. (1982) advocated the estimation of free acid wet deposition with volume weighted sample pH measurements, and we adopted this procedure to estimate undissociated acid fluxes. Appendix A is an analysis of the potential errors in estimating concentrations of strong and weak acids arising from volume-weighting two samples of partially dissociated weak acids. This analysis indicates that:

(A) In this "worst case" (only two samples of very different volumes, with weak acidity comparable to their free acidity), the error in estimating undissociated acidity from volume weighting can exceed 30%.

(B) The error is positive (undissociated concentrations are overestimated by volume weighting) for acids whose pK_a is lower than the solution pH, and negative for acids whose pK_a is higher than the solution pH. We expect this error to be $<10\%$ for acids whose pK_a values differ from the solution pH by more than 0.5 units.

(C) The error in estimating composite undissociated acidity from volume weighting is in that example (and may generally be) smaller than the error in estimating free acidity by the same method.

3. Results

The undissociated acidity of rain determined in this study was comparable to that reported else-

where (Table 2), and as reported previously for sites in this region (Hoffman et al., 1980a; Lindberg et al., 1984; Lovett et al., 1985), the undissociated acidity of rain was comparable to its more commonly measured free acidity (Table 3).

Ranges of undissociated acidity (in μmol L^{-1}) in event rain samples were 14–45 (pine, DS), 0–78 (pine, GS), 4–49 (spruce, DS), and 0–87 (spruce, GS). The use of a single rain sampler at each site precluded rigorous statistical comparisons, but rain collected at the pine site had higher median and mean concentrations of undissociated acids than did rain collected at the spruce site (Table 3). A similar trend in inorganic ion concentrations has also been noted (Lindberg, 1988). Undissociated acidity in rain collected at the pine site was higher during the growing season, but no seasonal differences were noted in rain collected at the spruce site. At both sites, the concentrations of undissociated acidity in cloud and fog water (Table 3) exceeded those in rain water (t-test, $p < 0.05$). In the cloud water samples from the spruce site, undissociated acidity was >8 times higher than the mean concentration in spruce site rain water.

Table 2. *Organic acid concentrations (ranges, in μmol L^{-1}) in precipitation samples measured by a number of investigators and methods, from both remote and industrialized areas*

Location	Concentrations	Method
Northeast USA (Galloway et al., 1976)	1–16	GC
Tennessee (Hoffman et al., 1980)	26–89	GT–pH
Remote global (Keene et al., 1983)	1–44	IC*
Eastern USA (Keene and Galloway, 1984)	1–36	IC†
Tennessee (Lindberg et al., 1984)	47	GT–pH‡
Tennessee (Lovett et al., 1985)	42	GT–pH‡
Bayreuth, FRG (Hantschel and Klemm, 1987)	15–79	ST–pH
Continental (Keene and Galloway, 1988)	2–28	IC*
Marine (Keene and Galloway, 1988)	1–7	IC*
Ivory Coast (Servant)[1]	12–54	IC
Los Angeles, CA (Kawamura and Kaplan)[1]	<200	IC§
Tennessee (this study)	0–87	GT–pH

Analytical methods were gas chromatography (GC), ion chromatography (IC), stepwise titration (to pH 8.3)–free acidity (as measured by pH) (ST–pH), and Gran's total acidity–free acidity (as measured by pH) (GT–pH).

* Total organic acidity, not undissociated.

† Dissociated acidity only.

‡ Simple average of several determinations.

§ Only maximum value reported.

[1] Personal communication.

For both sites, wet deposition fluxes of undissociated acids during the growing season were comparable to those of the dormant season. Extrapolated to the entire year, wet deposition fluxes of undissociated acids were 34 mmol m^{-2} at both the pine and spruce sites (Fig. 1A), despite nearly twice as much precipitation at the spruce site (211 versus 107 cm annually). This relationship suggests a dilution effect for undissociated acidity in rain at the higher-rainfall site, as has been observed for inorganic ions there (Lindberg, 1988). Undissociated acid fluxes in precipitation during the dormant and growing seasons are very similar at both of these sites, although mean and median concentrations of undissociated acidity in rain at the pine site are higher during the growing season (Table 3).

Ranges of undissociated acidity (μmol L^{-1}) in event TF samples were 23–89 (pine, DS), 5–357 (pine, GS), 7–126 (spruce, DS), and 0–209 (spruce, GS). At the spruce site, GS median concentrations of undissociated acidity in TF were greater than the DS median (Table 2), and GS mean concentrations were 50% higher than the DS median concentrations (t-test, $p < 0.05$). The analogous seasonal change at the pine site was not significant. Concentrations of C_1–C_3 acids in throughfall (TF) did not exceed those in rain (Table 4), although dry deposition of these acids would cause such an increase. As noted in the methods section, all samples were poisoned with $CHCl_3$ within 24 h after the rain event ended, but this does not completely exclude the possibility that certain weak acids were assimilated or degraded prior to that treatment. This could take place either on canopy surfaces, or in the TF sample itself.

Table 3. *Free [H^+] and undissociated acidity [HA] in rain (R), throughfall (TF), and cloud or fog water, (C/F), at the loblolly pine and red spruce sites (μmol L^{-1})*

Type	Pine–DS	Pine–GS	Spruce–DS	Spruce–GS
R–[H^+]	39	61	24	35
R–[HA]	29 {29}	40 {41}	18 {14}	23 {18}
N	5	17	5	19
R–cm	54	53	103	88
TF–[H^+]	60 (4)	60 (4)	83 (10)	111 (5)
TF–[HA]	53 (4) {51}	62 (12) {52}	49 (6) {46}	76 (7) {58}
N	25	85	10	38
TF–cm	53	50	127	84
C/F–[H^+]	36 (7)*		220 (90)*†	
C/F–[HA]	55 (14)*		130 (40)*	
N	8		4	

Samples are segregated into dormant season (DS) and growing season (GS). Numbers in parentheses are standard errors (SE), median concentrations are in {brackets}. In the spruce forest there are only 2 TF collectors, and one-half the range is given instead of SE. There is only one R collector at each site, so concentrations ranges are not presented. Samples sizes (N) for undissociated and free acidity determinations are presented, followed by seasonal R and TF fluxes (cm).

* These samples not segregated into seasons.

† From 20 additional spruce site cloud water samples, mean [H^+] = 172 μeq. L^{-1}, SE = 21.

Table 4. *Median and mean concentrations (μmol L^{-1}) of formic (C_1), acetic (C_2) and propionic (C_3) acids in paired rain (R) and loblolly pine throughfall (TF) samples, determined by ion chromatography (IC)*

Type	Median	Mean	SE	Range*
R–C_1	0.1	1.0	0.5	0.1–5.3
–C_2	0.1	0.3	0.1	0.1–1.5
–C_3	0.1	0.3	0.2	0.1–1.8
R–IC	0.5	1.6	0.6	0.3–6.8
R–HA	20	19	4.6	0–44
TF–C_1	0.1	0.2	0.1	0.1–0.9
–C_2	0.1	1.8	1.6	0.1–17.9
–C_3	0.1	1.2	0.6	0.1–6.2
TF–IC	0.3	3.2	0.1	0.3–18
TF–HA	47	57	13	9–163

Undissociated acid concentrations (HA, by Gran's titration–$[H^+]_{pH}$) are presented for comparison with the summed IC concentrations of C_1–C_3 acids (IC). Standard errors (SE) and ranges of values obtained are also presented. Sample size = 11 in each case.

* Detection limit for IC is 0.2 μmol L^{-1}, so baseline and trace values are reported as $\frac{1}{2}$ of the detection limit.

At both sites and for both seasons, undissociated acid fluxes in TF exceed those in rain (Fig. 1A). The difference between the bars plotted represents net TF (dry deposition and canopy fluxes); this difference equals or exceeds the precipitation fluxes. Net TF fluxes of free and undissociated acids are presented by season in Fig. 1B.

4. Discussion

Undissociated acids in rain include natural and anthropogenic compounds scavenged by rain, whereas such acids in TF have several additional sources. In addition to dry deposition of natural and anthropogenic compounds from particulate and vapor phases, certain high-elevation sites such as the spruce forest may receive significant cloud deposition (Lindberg et al., 1988). Canopy sources of undissociated acids include decomposition of the plant cuticle (Hoffman et al., 1980b) and metabolic intermediates from within the plant cells themselves (Lovett et al., 1985). In the spruce canopy, epiphytic lichens are a potential source of decomposition products and metabolites to TF, as noted by Carroll (1980) for epiphytic mosses.

The undissociated acidity of cloud water

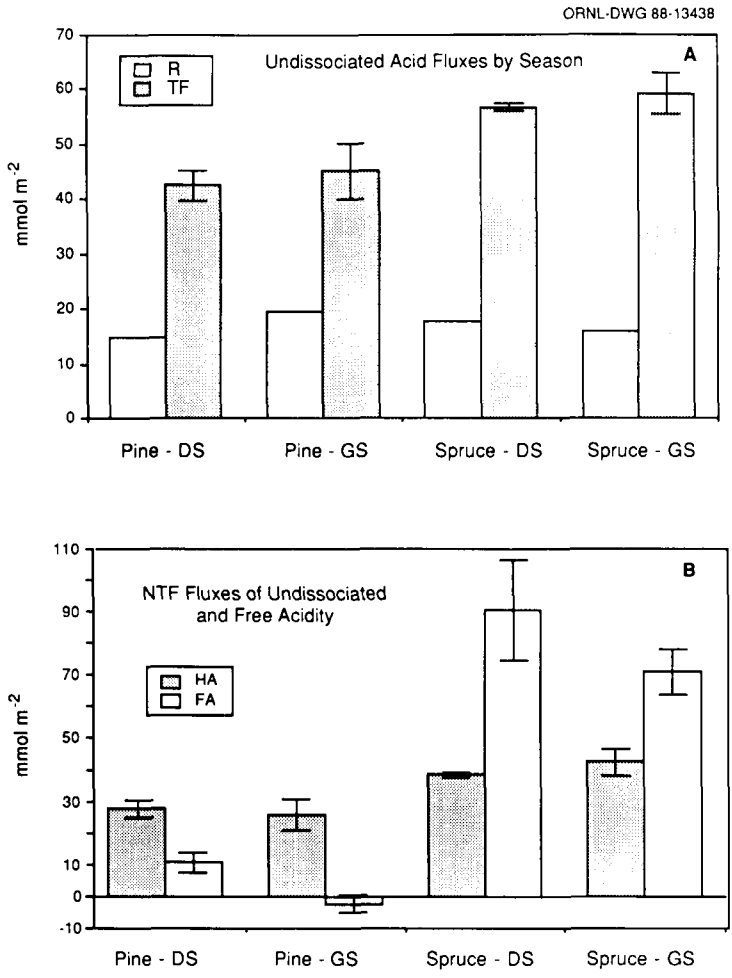

Fig. 1. (a) Fluxes of undissociated acidity (HA; mmol m^{-2} $season^{-1}$) in rain (R) and throughfall (TF) at the loblolly pine and red spruce sites during the five-month dormant season (DS) and seven-month growing season (GS). (b) Seasonal net throughfall fluxes (NTF; mmol m^{-2} $season^{-1}$) of HA and free acidity (FA). Standard error bars are shown for TF and NTF at the pine site ($n = 5$ collectors), and the bars represent one-half the range at the spruce site ($n = 2$ collectors). $NTF = [HA]_{TF} \times cm_{TF} - [HA]_R \times cm_R$.

measured at the spruce site (130 μmol L^{-1}, standard error = 40, $n = 4$) is high compared with that of fog water at the pine site (mean = 55 μmol L^{-1}, standard error = 14, $n = 8$). Spruce site cloud water undissociated acidity is also high compared with summed formic and acetic acid concentrations in cloud water that have been reported elsewhere (3–50 μmol L^{-1}, Keene and Galloway, 1988; 50 μmol L^{-1}, Murano et al., 1988; 20–150 μmol L^{-1}, Winiwarter et al., 1988), but Munger et al. (1989) reported that summed concentrations of formic and acetic acid could exceed 1000 μmol L^{-1} in cloud water. The cloud and fog water samples collected in this study were not analyzed for individual acids. Due to the highly variable nature of cloud chemistry and the limited sample size, we cannot estimate with confidence the fraction of net TF undissociated acidity that results from cloud water deposition at the spruce site.

Undissociated acids in net TF include dry-deposited natural and anthropogenic compounds washed from the canopy during rain. Formic and acetic acids are expected to dominate dry deposition (Dawson et al., 1980; R. W. Talbot, NASA Langley Research Center, personal communication), so that if dry deposition is a major source of undissociated acid fluxes in TF, the concentrations of these acids in TF would be higher than those in rain. Assuming that dry-deposited formic and acetic acids remain on the canopy to be removed by a subsequent rain event, the data presented in Table 4 argue against a major dry deposition source for these acids in TF.

Biological sources of undissociated acids to the atmosphere during the growing season should exceed those during the dormant season (Albritton et al., 1987). In addition, photochemical conversion of anthropogenic precursors (e.g., aldehydes) to acids should decrease during the winter months (Albritton et al., 1987). Together, these suggest that more undissociated acids will be present in the troposphere during the growing season, resulting in greater dry deposition during that period. If dry deposition were the major source of undissociated acids to these forests, this seasonal pattern would be observed at both sites. At the spruce site, undissociated acidity in TF is higher during the growing season than during the dormant season, but this seasonal pattern does not occur at the pine site.

The seasonal pattern contrasts between sites noted above is consistent with canopy sources being the primary contributors of undissociated acids in net TF. This contrast results from considerably milder winter temperatures at the low-elevation site, allowing the pines to remain metabolically active for much of the year (S. B. McLaughlin, Oak Ridge National Laboratory, personal communication).

Decomposition products of plant cuticles and epicuticular waxes may also be present in TF. Approximately half of the foliage is lost in 1 and 4 years at the pine and spruce sites, respectively. Foliar biomass at these sites is about 3000 and 9000 kg dry weight ha^{-1}, respectively (D. W. Johnson, Oak Ridge National Laboratory, personal communication). Conifer foliage has approximately 50 mg of cuticle (C_{16} acid monomer) and 6 mg of epicuticular wax (C_{30} acid monomer) per gram dry weight (calculated from data in Hunneman and Eglinton, 1972; Baig and Tranquillini, 1976; Chabot and Chabot, 1977; and Franich et al., 1978). If these polymers decompose completely and linearly into monocarboxylic acid monomers during the lifespan of the foliage, as much as 40 and 30 mmol m^{-2} $year^{-1}$ of these acids could be released from the spruce and pine canopies, respectively. These values are of the same magnitude as the annual undissociated acid fluxes measured in net TF (Fig. 1). However, foliage is abscised with at least some of its cuticle intact, so this decomposition is not the only source of undissociated acidity in net TF. Hoffman et al. (1980b) showed the presence of long-chain organic acids in deciduous forest TF. Kawamura and Kaplan (1986) detected long-chain fatty acids in rain, and suggested the weathering of plant surfaces as the source. The actual contribution of foliar structural degradation products to the undissociated acid fluxes measured here cannot be assessed without further chemical analyses.

For forests in general, short-chain acids (such as malic) may be in part associated with canopy releases of inorganic cations (Hoffman et al., 1980a; Cronan and Reiners, 1983; Lovett et al., 1985). Cationic releases from the spruce and pine canopies in net TF (Lindberg et al., 1988) are of the same order of magnitude as the undissociated acid net TF fluxes presented here.

While the threefold-greater foliar biomass of the spruce forest is a logical explanation for the greater undissociated acid fluxes in net TF at the high-elevation site, other possible causes should be considered. This montane forest is exposed to chronic high levels of atmospheric strong acids and oxidants (Lindberg et al., 1988). Cellular or cuticular disruption in foliage resulting from acidic and/or oxidant deposition (Miller, 1984; Landolt and Keller, 1985; McLaughlin, 1985) may accelerate canopy losses of undissociated acids unrelated to the inorganic cations in net TF.

Dry deposition of undissociated acidity may also be greater at the spruce site because of higher wind speeds and greater canopy surface area, relative to the pine site (Lindberg et al., 1988). We have not measured particulate or vapor phase concentrations of weak acids at either site, so direct comparisons of dry deposition to these sites cannot be made.

Compared to many coniferous forests, deciduous forest canopies show a greater potential to buffer wet deposition inputs of free acidity by reactions on canopy surfaces (e.g., Hoffman et al., 1980a; Richter et al., 1983; Foster, 1985). However, net TF fluxes of undissociated acids in these coniferous canopies exceed those measured in nearby deciduous forests by Lovett et al. (1985). Unless the weak acids released from deciduous canopies have greater potential to reduce the free acidity of rain (i.e., these acids have pK_a's which are greater than those released from coniferous canopies), the greater potential of deciduous forest canopies to buffer free acidity inputs does not result from weak acid releases. Testing this hypothesis requires the identification of the weak acids released from coniferous and deciduous canopies in TF.

Dry deposition should contribute primarily formic and acetic acids to net TF, but these compounds account for only a small fraction of the weak acids in TF (Tables 2, 3). Our attempts to identify the acids in TF below both deciduous and coniferous canopies have consistently indicated that only a small fraction of the titratable acidity in TF can be accounted for by these short-chain monocarboxylic acids.

Canopy sources of other acids, whether from metabolism or decomposition, are likely to be chemically quite distinct from deposition sources. For example, succinic acid has been suggested as being a major component of TF (O. Klemm, personal communication). The characterization of specific acids in rain, cloud and fog water, and TF was not a major part of this study, but would clarify the sources of acid deposition to terrestrial ecosystems.

5. Summary

We measured free and undissociated acid fluxes in rain and net TF at two strongly contrasting coniferous forests. At both forests, the undissociated acidity of precipitation was comparable to its free acidity. Only a small fraction of the undissociated acids in TF below these coniferous canopies are the short-chain acids anticipated to result from dry deposition, suggesting a canopy internal source for the undissociated acids in net TF. Lower undissociated acidity in precipitation at the spruce site was offset by greater rainfall there, resulting in identical undissociated acid precipitation fluxes to both sites. The undissociated acid fluxes in net TF were greater at the higher-elevation site. Cloud deposition at the higher-elevation site is potentially a substantial source of undissociated acids from the atmosphere. We showed that fluxes of undissociated acids in net TF equals or exceeds such fluxes in wet deposition, and that these net TF fluxes increase with canopy biomass. Seasonal fluctuations in undissociated acid concentrations in TF were greater at the site with the more severe winter temperatures.

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7. Appendix A

Errors resulting from volume weighting concentrations in mixtures of partially dissociated weak acids

We contend that volume weighted event measurements are the best available method to estimate long-term weak acid fluxes. This is an analysis of the potential errors in estimating concentrations of strong and weak acids arising from volume-weighting two samples of partially dissociated weak acids.

Combine 1000 ml of 100 μmol L^{-1} (total concentration) formic acid (pK_a 3.76), with measured pH of 4.00 (free acidity of 100 μmol L^{-1}), with 100 ml of 100 μmol L^{-1} (total concentration) acetic acid (pK_a 4.75), with measured pH of 4.30 (free acidity of 50 μmol L^{-1}). Solve for dissociated and undissociated concentrations with the Henderson–Hasselbalch equation:

$$pH = pK_a + (\log[Ac^-]/\log[HAc])$$

and the conservation of mass and charge, and compare the result with volume-weighting the original concentrations.

Solve for undissociated formic acid [HF] in the first solution:

$4.00 = 3.76 + (\log[F^-]/\log[HF])$;

$10 \wedge (0.24) = ([F^-]/HF]) = 1.73$,

and $[F^-] = [HF] * 1.73$.

Since total formic acid $= [F^-] + [HF] = 100$,

$([HF] * 1.73) + [HF] = 100 = 2.73 * [HF]$;

and $[HF] = 36.6$ μmol L^{-1}.

Solve for undissociated acetic acid [HA] in the second solution:

$4.30 = 4.75 + (\log[A^-]/\log[HA])$;

$10 \wedge (-0.45) = ([A^-]/HA]) = 0.355$,

and $[A^-] = [HA] * 0.355$.

Since total acetic acid $= [A^-] + [HA] = 100$,

$([HF] * 0.355) + [HF] = 100 = 1.36 * [HA]$;

and $[HA] = 73.5$ μmol L^{-1}.

Volume weight these two solutions:

1000 ml 36.6 μmol L^{-1} undissociated formic acid and 100 μmol L^{-1} $[H^+]$

100 ml 73.5 μmol L^{-1} undissociated acetic acid and 50 μmol L^{-1} $[H^+]$

yields the volume weighted estimates (in 1100 ml):

$(1000/1100) * 36.6 = 33.3$ μmol L^{-1} undissociated formic acid,

$(100/1100) * 73.5 = 6.7$ μmol L^{-1} undissociated acetic acid, and

$((1000 * 100) + (100 * 50))/1100 = 95.5$ μmol L^{-1} $[H^+]$, or pH = 4.02.

To solve for these concentrations explicitly, determine total acid concentrations in the final 1100 ml:

total formic acid $= 100 * (1000/1100)$
$= 90.9$ μmol $L^{-1} = 9.09 * 10^{-5}$,

total acetic acid $= 100 * (100/1100)$
$= 9.09$ μmol $L^{-1} = 9.09 * 10^{-6}$.

These set the "mass balances":

$[F^-] + [HF] = 9.09 * 10^{-5}$;

$[A^-] + [HA] = 9.09 * 10^{-6}$.

Dissociation relationships (recasting Henderson–Hasselbalch):

$[H^+] * [F^-] = [HF] * 1.74 * 10^{-4}$

$[H^+] * [A^-] = [HA] * 1.78 * 10^{-5}$.

Charge balance is also invoked:

$[H^+] = [F^-] + [A^-] + [OH^-]$.

Show $[A^-]$ in terms of only $[H^+]$:

$[A^-] = 9.09 * 10^{-6} - [HA]$

$[H^+] * [A^-] = [HA] * 1.78 * 10^{-5}$,

so $[HA] = ([H^+] * [A^-])/(1.78 * 10^{-5})$

$[A^-] = 9.09 * 10^{-6} - ([H^+] * [A^-])/(1.78 * 10^{-5})$

$[A^-] + ([H^+] * [A^-])/(1.78 * 10^{-5}) = 9.09 * 10^{-6}$

$[A^-] * (1 + [H^+]/(1.78 * 10^{-5}) = 9.09 * 10^{-6}$

$[A^-] * ((1.78 * 10^{-5} + [H^+])/(1.78 * 10^{-5}) = 9.09 * 10^{-6}$

$[A^-] = 9.09 * 10^{-6} * (1.78 * 10^{-5})/(1.78 * 10^{-5} + [H^+])$

$[A^-] = (1.62 * 10^{-10})/(1.78 * 10^{-5} + [H^+])$.

Now show $[F^-]$ in terms of only $[H^+]$:

$[F^-] = 90.9 - [HF]$

$[H^+] * [F^-] = [HF] * 1.74 * 10^{-4}$,

so $[HF] = ([H^+] * [F^-])/(1.74 * 10^{-4})$.

A series of rearrangements analogous to those for acetate leads to:

$[F^-] = 9.09 * 10^{-5} * (1.74 * 10^{-4})/(1.74 * 10^{-4} + [H^+])$

$[F^-] = (1.58 * 10^{-8})/(1.74 * 10^{-4} + [H^+])$.

This system of equations becomes tenable with the assumption that $[OH^-]$ is negligible in these

acidic solutions, so charge balance yields:

$$[H^+] = [F^-] + [A^-],$$

or:

$$[H^+] = (1.62 * 10^{-10})/(1.78 * 10^{-5} + [H^+]) + (1.58 * 10^{-8})/(1.74 * 10^{-4} + [H^+]).$$

To generate a first approximation of $[H^+]$, the standard approach (Butler, 1962) is to assume that the additive constants in the denominator are insignificant relative to $[H^+]$, so:

$$[H^+] = (1.62 * 10^{-10}/[H^+]) + (1.58 * 10^{-8}/[H^+])$$

$$([H^+])^2 = 1.62 * 10^{-10} + 1.58 * 10^{-8} = 1.6 * 10^{-8}$$

$$[H^+] = 1.26 * 10^{-4}.$$

The $[H^+]$ value derived in the first approximation is substituted into the right hand side for a second approximation of $[H^+]$:

$$[H^+] = (1.62 * 10^{-10})/(1.78 * 10^{-5} + 1.26 * 10^{-4}) + (1.58 * 10^{-8})/(1.74 * 10^{-4} + 1.26 * 10^{-4})$$

$$[H^+] = 5.38 * 10^{-5}.$$

After several more iterations, this equation converges on:

$$[H^+] = 6.74 * 10^{-5}, \text{ or } 67.4\ \mu\text{mol L}^{-1}, \text{ pH} = 4.17.$$

Also note that this $[H^+]$ value implies that $[OH^-] = 10^{-14}/6.74 * 10^{-5}$, or $1.48 * 10^{-10}$, validating the initial assumption of its insignificance. From this $[H^+]$ value calculate [HF] and [HA]:

$$[HF] = 2.54 * 10^{-5}, \text{ or } 25.4\ \mu\text{mol L}^{-1}$$

$$[HA] = 7.2 * 10^{-6}, \text{ or } 7.2\ \mu\text{mol L}^{-1}.$$

Compare these exact solutions with those approximated by volume weighting:

Species	VW prediction (μmol L^{-1})	Exact solution (μmol L^{-1})	Error	Relative error %
$[H^+]$	95.5	67.4	28.1	42 (0.15 pH)
[HF]	33.3	25.4	7.9	31
[HA]	6.7	7.2	−0.5	−7

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