

Reports

Atmospheric Deposition and Canopy Interactions of Major Ions in a Forest

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Airborne particles and vapors contributed significantly to the nutrient requirements and the pollutant load of a mixed hardwood forest in the eastern United States. Dry deposition was an important mechanism of atmospheric input to the foliar canopy, occurring primarily by vapor uptake for sulfur, nitrogen, and free acidity and by particle deposition for calcium and potassium. The canopy retained 50 to 70 percent of the deposited free acidity and nitrogen, but released calcium and potassium. Atmospheric deposition supplied 40 and 100 percent of the nitrogen and sulfur requirements, respectively, for the annual woody increment. This contribution was underestimated significantly by standard bulk deposition collectors.

MEASURING THE ATMOSPHERIC contribution to element cycles in a forest is a complex task that is often approached in a simplistic manner. While some investigators have reported detailed field measurements of wet or dry deposition (1), few have simultaneously sampled dry deposition, precipitation before and after its interception by the forest canopy, and the concentrations of airborne particles and vapors needed for reliable estimates of atmospheric input to the canopy and forest floor.

Deposition is typically determined from bulk precipitation collected periodically in continuously open containers. While this method may be useful in remote locations, where precipitation dominates input because of insignificant aerosol and vapor dry deposition, it is generally acknowledged to produce unreliable results (2). This is particularly true for forests near industrialized

areas, where canopies of large surface area can interact with anthropogenic particles and vapors to produce significant fluxes in dry deposition.

In 1982 we reported results of a summer-time study of the wet and dry deposition of trace metals to a mature oak-hickory forest at Walker Branch Watershed, Tennessee (3). We have since expanded our efforts in a deposition and nutrient cycling study to include major ions and atmospheric vapors over a 2-year period. Our data support our earlier results showing the importance of dry deposition in a forest typical of the ridge and valley physiographic province of the eastern United States.

During 1981 to 1983 we used automatic samplers in a clearing and beneath the forest canopy (*Quercus prinus*, *Quercus alba*) to collect incident precipitation and throughfall as wetfall-only on an event basis (4). Bulk precipitation and stemflow were col-

lected monthly by standard methods (5). Suspended particle concentrations and size distributions were measured above the canopy by filtration and impaction methods (6). We sampled 99 percent of the recorded precipitation (mean, 128 cm/year), obtained continuous flame photometric measurements of SO_2 (7), measured total airborne nitrate concentrations for 2000 hours with a filter pack (4, 8), and sampled airborne and deposited particles for 4000 hours. All analyses were done in accordance with standard atomic absorption and ion chromatography procedures (5).

Coarse ($>2 \mu\text{m}$), dry-deposited particles were collected on replicate plates situated on towers extending above the 20-m-high canopy and attached to tree branches in the upper canopy. Direct comparisons of the flux, chemistry, size distribution, and morphology of particles deposited to oak leaves and adjacent deposition plates have been published elsewhere (9).

Rates of coarse-particle deposition to plates were scaled to the canopy by factors determined from statistical analysis of throughfall fluxes of calcium, which exists primarily in the coarse size class of airborne particles (9). Linear regression was used to separate throughfall into its component parts of foliar exchange and dry deposition washoff (4). The scaling factors represent the ratio of the mean dry deposition rate of coarse particles to the whole canopy (4) to the mean dry deposition rate to individual plates (9); they are 2.76 for the growing season (April to October) and 1.0 for the dormant season (November to March).

Vapor and fine-particle ($\leq 2 \mu\text{m}$) dry deposition rates were calculated from atmospheric concentration data collected above the canopy and from appropriate deposition velocities measured independently at this site by eddy correlation and profile methods (8, 10), or taken from the literature (11). Deposition velocities were as follows (centimeters per second): SO_2 , 0.5; HNO_3 vapor, 2; fine particles, 0.2 during the growing season; and SO_2 , 0.2; HNO_3 vapor, 0.5; and fine particles, 0.05 during dormancy.

Relative to the total atmospheric input of each ion (Table 1), precipitation was the most important deposition process for SO_4^{2-} and NH_4^+ , dry deposition of vapors was most important for NO_3^- and H^+ , and dry deposition of coarse particles was most important for K^+ and Ca^{2+} . Dry deposition was a significant mechanism in the total annual flux of each of these ions to the

Table 1. Total annual atmospheric deposition of major ions to an oak forest at Walker Branch Watershed. Values are means $\pm$ standard errors for 2 years of data. Numbers of observations range from 15 (HNO_3) to 26 (particles) to 128 (precipitation) to 730 (SO_2). In comparing these deposition rates it must be recalled that any such estimates are subject to considerable uncertainty (2, 11). The standard errors given provide only a measure of uncertainty in the calculated sample means relative to the population means; hence, additional uncertainties in analytical results, hydrologic measurements, scaling factors, and deposition velocities must be included. The overall uncertainty for wet deposition fluxes is about 20 percent and that for dry deposition fluxes is approximately 50 percent for SO_4^{2-} , Ca^{2+} , K^+ , and NH_4^+ and approximately 75 percent for NO_3^- and H^+ .

Process	Atmospheric deposition ($\text{mEq}/\text{m}^2\text{-year}$)					
	SO_4^{2-}	NO_3^-	H^+	NH_4^+	Ca^{2+}	K^+
Precipitation	70 ± 5	20 ± 2	69 ± 5	12 ± 1	12 ± 2	0.9 ± 0.1
Dry deposition						
Fine particles	7 ± 2	0.1 ± 0.02	2.0 ± 0.9	3.6 ± 1.3	1.0 ± 0.2	0.1 ± 0.05
Coarse particles	19 ± 2	8.3 ± 0.8	0.5 ± 0.2	0.8 ± 0.3	30 ± 3	1.2 ± 0.2
Vapors*	62 ± 7	26 ± 4	85 ± 8	1.3	0	0
Total deposition	160 ± 9	54 ± 4	160 ± 9	18 ± 2	43 ± 4	2.2 ± 0.3

*Includes SO_2 , HNO_3 , and NH_3 . Complete conversion of deposited SO_2 to H_2SO_4 and of NH_3 to NH_4^+ was assumed in determining the vapor input of H^+ . NH_3 deposition was estimated from the literature (29).

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Table 2. Mean relative contribution of several major ions to the total analyzed chemistry of wet and dry deposition on a charge-equivalent basis. The values represent the range in the means for two separate years. The contribution of the other major ions not reported in this study to the total charge equivalents in precipitation at this site was minimal. The ions listed contributed 0.144 (92 percent) of a total of 0.157 mEq/liter for the 2-year weighted mean concentration of major ions in precipitation (12). The ions not reported here contributed the remaining 8 percent as follows (milliequivalents per liter): Na^+ , 0.005; Mg^{2+} , 0.001; PO_4^{3-} , <0.001; and Cl^- , 0.007. On the basis of a more complete analysis of the ion composition of selected samples of fine aerosols and deposited coarse particles, the major ions not included contributed 15 and 12 percent of the mean total charge equivalents, respectively.

Ion	Precipitation (%)	Dry deposition (%)	
		Fine particles	Coarse particles
SO_4^{2-}	38 to 39	51 to 57	30 to 32
NO_3^-	10 to 11	0.3 to 2.0	14 to 15
H^+	36 to 39	5 to 14	<0.1
NH_4^+	6.4 to 6.7	27 to 28	1.1 to 1.9
Ca^{2+}	5.5 to 8.0	6.3 to 6.8	49 to 53
K^+	<0.3 to 0.6	0.5 to 1.2	1.9 to 2.0

forest, contributing 32 percent of NH_4^+ , ~50 percent of SO_4^{2-} and H^+ , ~60 percent of K^+ and NO_3^- , and ~70 percent of Ca^{2+} . Dry deposition occurred primarily by vapors for SO_4^{2-} , NO_3^- , and H^+ (70, 76, and 97 percent of the total dry input, respectively); by fine particles for NH_4^+ (63 percent); and by coarse particles for K^+ and Ca^{2+} (~95 percent each). Deposition estimates are subject to considerable uncertainty (2): ~20 percent for wet deposition and 50 to 75 percent for dry (Table 1).

The contribution of individual ions to total input by each deposition process reflects the chemistry of the contributing material (Table 2). Precipitation at the site was dominated by SO_4^{2-} and H^+ , with sufficient SO_4^{2-} to account for all the free acidity, although NO_3^- could contribute up to 30 percent considering the probable contributions of calcium- and ammonium-sulfate salts. The fine-particle portion of dry deposition was primarily a mixture of H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and intermediates, with up to 27 percent of the SO_4^{2-} occurring as acid sulfate. Coarse particles in dry deposition were dominated by calcium salts of NO_3^- and SO_4^{2-} . In support of these conclusions, concentrations of H^+ , NH_4^+ , SO_4^{2-} , and NO_3^- in precipitation were all significantly intercorrelated, as were those of H^+ , SO_4^{2-} and NH_4^+ in fine aerosol and those of Ca^{2+} and NO_3^- in deposited coarse particles (12).

The comparability between wet and dry deposition rates for SO_4^{2-} (Table 1) has been suggested (11, 13), but to our knowledge has not been confirmed by extensive field measurements. Dry deposition of sulfur oxides is generally thought to be dominated by SO_2 and fine-particle SO_4^{2-} (2, 11). The mean annual concentration of sulfur oxides at the site was 10.4 μg of sulfur per cubic meter of air (standard error, 1.5), 75 percent as SO_2 and 22 percent as fine-

particle sulfate. The importance of dry deposition of SO_2 was confirmed by our results. However, sulfate associated with coarse particles was particularly important, contributing a disproportionate share of the sulfur input. Coarse-particle sulfate contributed ~20 percent of the total dry deposited sulfur, while constituting only 3 percent of the airborne sulfur oxide mass (Fig. 1).

Coarse-particle SO_4^{2-} is an important fraction of the total aerosol because of its effi-

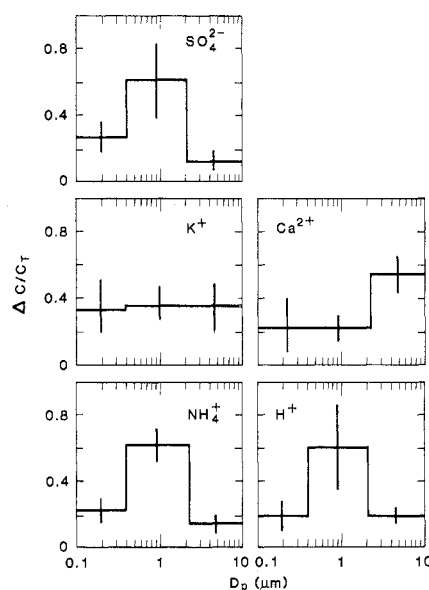


Fig. 1. Particle size distributions of airborne SO_4^{2-} , Ca^{2+} , K^+ , NH_4^+ , and H^+ collected above the forest canopy at Walker Branch Watershed from 1981 to 1983. Nitrate is discussed elsewhere (12, 16). Mean concentrations and standard errors (vertical bars) are given on a relative scale, where ΔC represents the concentration in a given size range, C_T the total particle concentration, and D_p the particle diameter. Absolute values of C_T for each ion are as follows (micrograms per cubic meter, means $\pm$ standard errors): SO_4^{2-} , 8.1 ± 0.8 ; K^+ , 0.11 ± 0.01 ; Ca^{2+} , 0.80 ± 0.10 ; H^+ , 0.048 ± 0.011 ; and NH_4^+ , 1.5 ± 0.2 .

cient removal from the atmosphere by sedimentation and impaction (14). Our measurements suggest a mean annual dry deposition velocity for coarse-particle SO_4^{2-} to the canopy of 0.4 cm/sec (standard error, 0.1) (9, 12, 15). This value is similar to deposition velocities for fine-particle SO_4^{2-} of 0.2 to 0.7 cm/sec measured for forests in short-term field studies, but much larger than the <0.1 cm/sec calculated on the basis of wind tunnel studies (11). Recent measurements by our methods of coarse-particle SO_4^{2-} flux in other areas have yielded mean dry deposition rates to inert surfaces that are similar to the mean measured at this site (9, 12, 14).

The importance of dry deposition was more pronounced for NO_3^- than for SO_4^{2-} , exceeding wet deposition by 70 percent (Table 1). Particle deposition is apparently controlled by NO_3^- in the coarse fraction (12, 16). However, most airborne NO_3^- at this site existed as HNO_3 vapor, a species not considered in deposition studies until recently (8). Nitric acid vapor is a major sink for atmospheric NO_x (2) characterized by a high solubility, resulting in efficient dry deposition to plant canopies (8). The mean annual concentration of total NO_3^- (particle plus vapor forms) above the forest was 1.0 μg of nitrogen per cubic meter (standard error, 0.13), ~70 percent of which was HNO_3 vapor (0.73 ± 0.06 μg of nitrogen per cubic meter). Our measurements suggest that dry deposition of HNO_3 vapor contributes nearly 50 percent of the total annual atmospheric flux of NO_3^- to the canopy, making it the most important nitrogen oxide species studied.

Because of the apparent importance of NO_3^- dry deposition to the forest and the acknowledged uncertainty in determining dry deposition (2, 11), we used three other approaches to estimate the dry NO_3^- input: (i) a statistical analysis of NO_3^- fluxes in throughfall (4), (ii) application of published deposition velocities (8, 11) to our concentration data for air, and (iii) collection of dry deposited HNO_3 plus particle NO_3^- on reactive surfaces situated throughout the canopy (12). The methods yielded values of total NO_3^- dry deposition of 13, 24, and 56 mEq/m² per year, respectively (17). These values bracket our best estimate of 32 mEq/m² per year (Table 1) and provide a measure of the uncertainty of dry deposition estimates.

Despite this uncertainty, and knowing that the lowest value in this range is an underestimate because of NO_3^- absorption by leaves (4, 17), we conclude that dry deposition is the dominant mechanism in the airborne flux of NO_3^- to this forest, contributing up to 70 percent of the total.

Including estimates of NO and NO₂ input (18) further increases the dry deposition contribution to over 80 percent. We know of no directly comparable field studies of nitrogen deposition to forests; however, our results suggest a somewhat greater role for dry deposition than the 50 percent measured for a grassland during a 1-month study (8).

The contribution of dry deposition to the total flux of K⁺ and Ca²⁺ was 60 to 70 percent (Table 1). This is expected from their aerosol size distributions: 34 percent of the airborne K⁺ and 55 percent of the Ca²⁺ were associated with particles greater than 2 μm in diameter (Fig. 1). The smaller fraction of coarse-particle K⁺ in the atmosphere may explain the somewhat lower relative contribution of dry deposition to its total input compared to that of Ca²⁺.

The source of Ca²⁺ and K⁺ in dry deposition may be suspended soil or biological material of local origin and may not represent "new" inputs (14). Measurements of K⁺ aerosol concentrations and deposition rates below, within, and above the canopy indicate that the highest values occur in the canopy itself, decreasing both above and below, suggesting an in-canopy source of K⁺. This material consists of weathered leaf cuticle, leaf hairs, and pollen (12). Because most of the dry deposition of K⁺ occurred during the growing season (Fig. 2), it is possible that as much as 50 percent of the annual K⁺ "deposition" actually represents an internal forest cycle (4). However, similar measurements of Ca²⁺ revealed that aerosol concentrations and deposition rates to inert surfaces each increase with increasing height above the forest floor (12), indicating an airborne source and a canopy sink. Although this suggests that the immediate Ca²⁺ source was particles in the air over this forest, the ultimate source was primarily resuspended soil and road dust originating outside our sampling site (6).

Wet deposition clearly dominates the input only of NH₄⁺, as might be suggested by the atmospheric chemistry of the NH₃-NH₄⁺ system (19). Ammonia vapor is highly soluble in acidic rain droplets and cloud water and can account for a significant portion of dissolved NH₄⁺ in such solutions. In part because of its solubility, NH₃ has been reported to represent a minor fraction (~5 to 20 percent) of the airborne burden of NH₃ plus particulate NH₄⁺ in studies in the Northeast (20) and Southeast (19). Because of these characteristics of the vapor, and because 85 percent of the particulate NH₄⁺ exists in the fine size range (Fig. 1), removal by precipitation may be favored over dry deposition.

Deposition of free H⁺ is difficult to quan-

tify because of its reactivity in solutions of precipitation and atmospheric particles and because vapors may experience various degrees of oxidation once deposited, thus representing various amounts of potential free acidity. Our analyses (Table 1) suggest that ~60 percent of the total input of H⁺ to the forest canopy occurred through the dry deposition of HNO₃ vapor and SO₂. These species represented 97 percent of the dry deposition of free acidity, with the remainder attributable to fine particles. This is reflected in air concentrations at the site: the mean total acidic vapor concentration in potential H⁺ equivalents was 0.54 ± 0.07 μEq/m³, while that of particle-associated H⁺ was 0.046 ± 0.012 μEq/m³, 80 percent of which occurred in the fine size range (Fig. 1).

Given the alkaline nature of some coarse particles and vapors (2), it is useful to estimate the net acidity of total deposition to the forest. With some simple assumptions regarding Ca²⁺ dry deposition (all or none could have been deposited as CaCO₃), NH₄⁺ dry deposition (all or none of the NH₄⁺ in aerosols and deposited particles could have originated from artifact NH₃ sorbed during collection), and SO₂ oxidation (up to 20 percent could have been adsorbed onto leaf surfaces and degassed before oxidation) (21), we can bracket our best estimate of total atmospheric deposition of free H⁺: 90 to 200 mEq/m² per year.

Comparison of our results with deposi-

tion estimates from bulk precipitation collected in a clearing at ground level indicates that bulk deposition significantly underestimates wet plus dry deposition for those ions with a major vapor or fine-particle component in the atmosphere (Fig. 2). Total deposition of H⁺, NO₃⁻, SO₄²⁻, and NH₄⁺ was underestimated by 50 to 70 percent. The underestimate of Ca²⁺ input was smaller (30 percent) because of its control by the dry deposition of large particles, which are captured to some extent by bulk collectors. However, bulk K⁺ deposition exceeded wet plus dry estimates (based on above-canopy sampling) by a factor of 2, reflecting the complication of the in-canopy source of K⁺. These comparisons suggest that the results of biogeochemical cycling studies in which system inputs are based solely on measurements of bulk deposition must be interpreted cautiously.

In the absence of dry deposition measurements, some have calculated total input to forests on the basis of various assumptions, including that of a constant annual ratio of dry to total deposition (22). However, the relative contribution of each deposition process is not constant throughout the year (Fig. 3). Dry deposition generally dominates ion input during the growing season. Wet deposition is the most important process during the dormant season, when most particle constituents in the air are at a minimum and the levels of SO₂ and HNO₃ vapor are only moderately higher than sum-

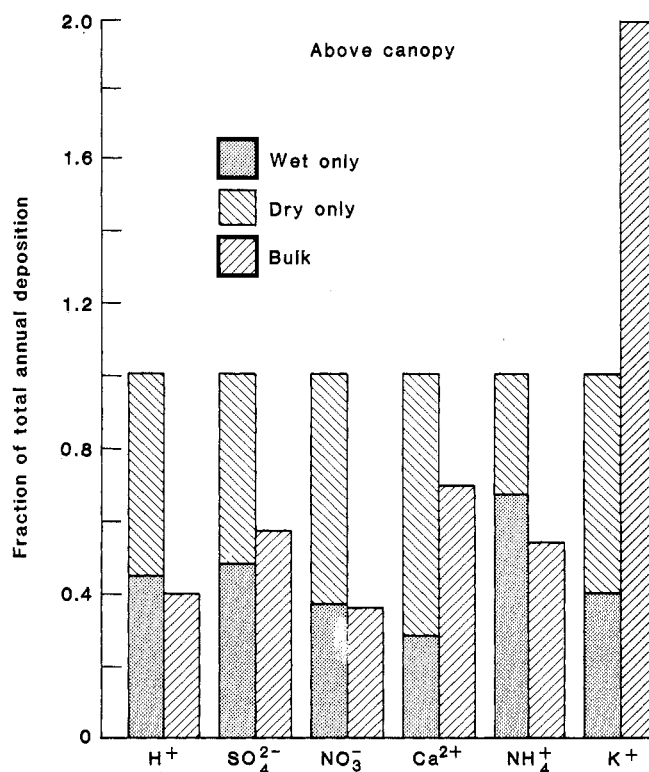


Fig. 2. Comparison of annual atmospheric deposition to a mixed deciduous forest, as determined by bulk deposition measurements and by separate collection of wet and dry deposition. All values have been normalized to the total annual wet plus dry fluxes shown in Table 1, which also gives the uncertainties and standard errors for these fluxes. For bulk deposition, standard errors relative to the means ($n = 24$ samples) are 0.23 for NO₃⁻ and between 0.06 and 0.09 for the remaining ions.

mer values (12). As a result, the ratio of total summer atmospheric deposition to total winter deposition is between ~2 and 3 for all ions.

The fate of material deposited on the forest canopy is reflected in the seasonal ion flux in throughfall and stemflow below the canopy (Fig. 3). During dormancy, the above- and below-canopy fluxes are comparable for SO_4^{2-} , NO_3^- , and NH_4^+ , indicating only a moderate influence of the defoliated canopy on these ions. However, deposited H^+ is apparently exchanged for K^+ and Ca^{2+} during canopy interception; 20 mEq of H^+ per square meter was removed in the canopy and 23 mEq of K^+ plus Ca^{2+} per square meter was released to throughfall and stemflow.

During the growing season, interactions in the canopy have a significant influence on the quantity of deposition reaching the forest floor for all ions except SO_4^{2-} . Canopy uptake decreases the flux of atmospheric H^+ , NO_3^- , and NH_4^+ by ~50 to 70 percent, while canopy leaching increases the flux of Ca^{2+} (by 55 percent) and K^+ (by a factor of 24). The flux of SO_4^{2-} is increased less than 5 percent. Thus during the growing season the total deposition to the canopy is acidic, consisting primarily of H_2SO_4 and HNO_3 and minor amounts of their NH_4^+ and Ca^{2+} salts. Below the canopy, however, the ion

flux is dominated by Ca^{2+} and K^+ salts of SO_4^{2-} .

Previous studies indicated that forest canopies removed 30 to 40 percent of the free H^+ from precipitation (23); this canopy apparently removes over 70 percent of the total wet plus dry deposition of free H^+ during the growing season. The removal process involves both ion-exchange and weak-base buffering reactions (23, 24). Deposited H^+ may remove canopy nutrients by cation exchange, as reflected in the growing season data for Ca^{2+} and K^+ (Fig. 3). The higher flux of these cations below the canopy compared to above (~20 mEq/m² for Ca^{2+} and ~50 mEq/m² for K^+) represents leaching of internal plant nutrients from the foliage. Using an ion charge balance of the deposition-canopy exchange and measurement of mobile organic anions in throughfall, we reported that 40 to 60 percent of the nutrient cation leaching from this forest canopy is due to exchange for deposited free acidity (24). The effects of nutrient leaching from the canopy depend on the ability of the trees to replenish these foliar pools.

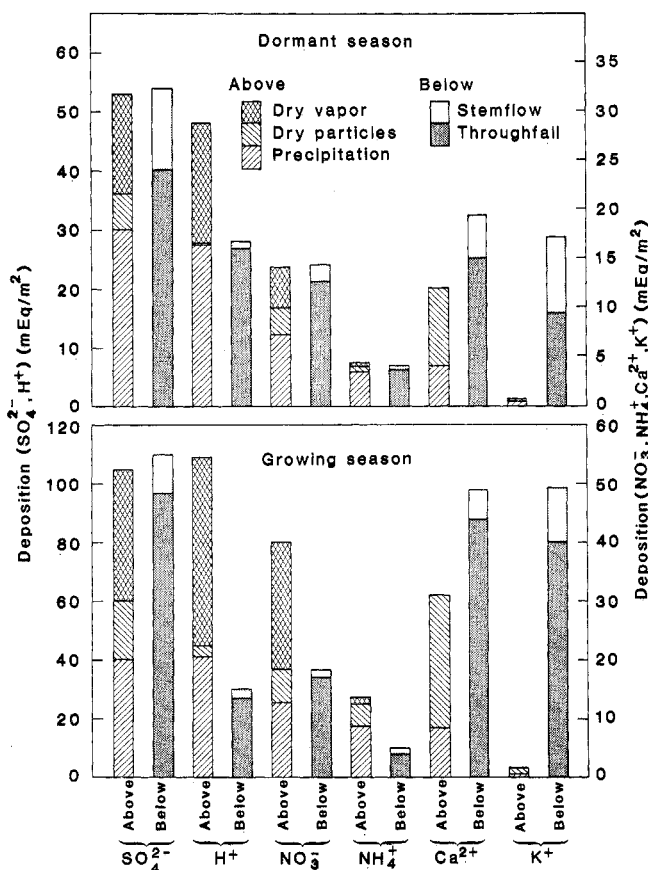
The absorption of NO_3^- and NH_4^+ in the forest canopy is not surprising for a nitrogen-deficient ecosystem. The similarity between the growing season dry input of HNO_3 and the quantity of NO_3^- removed in

the canopy (Fig. 3) suggests that dry deposition may be the form preferentially retained. The longer contact time of dry deposition with foliage compared to wet deposition (3) supports this idea, although absorption of NO_3^- from rain also occurs to some extent (4, 25). The NO_3^- in the canopy may be utilized primarily by epiphytes on canopy surfaces or directly assimilated in the leaves (26).

Deposited sulfur was not retained by foliage in this sulfur-rich (27) ecosystem (Fig. 3). Precipitation plus washed-off dry deposition could have accounted for 96 percent of the annual below-canopy flux, suggesting little or no leaching of internal plant SO_4^{2-} . Independent evidence from earlier tree fertilization (5) and biogeochemical cycling (27) studies of sulfur at this site support the idea that rainfall leaching of internally cycled plant sulfur is a minor contributor (~5 percent) to the total annual flux of SO_4^{2-} to the forest floor. Thus, although 40 percent of the total annual SO_4^{2-} deposition occurs as SO_2 , much of this may be leached from foliage by subsequent rain events. We determined that SO_4^{2-} removed from the canopy consists of two fractions having different kinetics of removal, one indicating surface wash-off and the other internal diffusion (4). Surface wash-off suggests soluble SO_4^{2-} in dry-deposited particles on the foliage, while internal diffusion suggests SO_4^{2-} removed from within the leaf. Without isotopic tracer studies it is difficult to identify the original source of this internal material as either soil SO_4^{2-} absorbed and translocated from roots or airborne SO_2 absorbed and oxidized in the foliage itself (11).

Our data support the hypothesis of a major role of dry deposition in atmospheric inputs to this deciduous forest. Chronic exposure of the canopy to dry deposition increases deposition-foliage interactions because of the long in-canopy residence time (3). These interactions can result in ion uptake and loss. We estimate that atmospheric deposition supplies calcium and nitrogen at a rate equal to 40 percent of the annual woody increment of this forest and supplies sulfur at a rate exceeding 100 percent of the increment (25, 27). Even the total forest requirement for sulfur is exceeded by deposition, while inorganic nitrogen input is 5 to 10 percent of the total requirement (25). If these proportions are raised because of increased industrial and automotive emissions, forests may satisfy increasing portions of their nutrient requirements by assimilation of airborne material, while simultaneously being exposed to increasing levels of air pollutants. It is possible that the effects of excess sulfur, nitrogen, and trace metal deposition by atmosphere-dominated

Fig. 3. Contribution of several atmospheric deposition and internal transfer processes to the total ion flux above and below the canopy of a mixed deciduous forest for the dormant and growing seasons (note different scales for SO_4^{2-} and H^+ relative to the other ions). The overall uncertainties and standard errors of the means for the above-canopy fluxes are given in Table 1. For below-canopy fluxes the standard errors relative to the means ($n = 80$ samples) are 0.35 for NH_4^+ , ~0.25 for Ca^{2+} and K^+ , and ~0.15 for the remaining ions.



element cycles are already being manifested in high-elevation forests in the eastern United States and Europe (28).

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- Although our data (12) and those of G. T. Wolff [*Atmos. Environ.* **18**, 977 (1984)] suggest that airborne particle NO₃ is dominated by coarse particles, all NO₃ particle size data must be considered cautiously because of artifacts due to HNO₃ vapor adsorption and NH₄NO₃ volatilization [B. R. Appel and Y. Tokiwa, *ibid.* **15**, 1087 (1981)].
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- Dry deposition of NH₃ to the forest canopy was estimated by using a deposition velocity for the growing season of 1 cm/sec [published elsewhere (20)] and assuming the same ratio of mean concentrations of NH₃ to NH₄⁺ (0.05) as measured by those authors. The seasonal and annual mean atmospheric concentrations of NH₄⁺ measured in our study and reported by those authors were within 10 percent of each other. Dry deposition during the dormant season was estimated from the growing season value by assuming that the ratio of growing season dry deposition to dormant season dry deposition was the same as that for SO₂ as determined in our study.
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Modification of the Active Site of Alkaline Phosphatase by Site-Directed Mutagenesis

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The catalytically essential amino acid in the active site of bacterial alkaline phosphatase (Ser-102) has been replaced with a cysteine by site-directed mutagenesis. The resulting thiol enzyme catalyzes the hydrolysis of a variety of phosphate monoesters. The rate-determining step of hydrolysis, however, is no longer the same for catalysis when the active protein nucleophile is changed from the hydroxyl of serine to the thiol of cysteine. Unlike the steady-state kinetics of native alkaline phosphatase, those of the mutant show sensitivity to the leaving group of the phosphate ester.

CHEMICAL MODIFICATION AND RECOMBINANT DNA studies directed toward the substitution of active site nucleophiles by other potentially competent nucleophiles have so far been limited to acyl transfer enzymes (1, 2). In every case, either the nucleophilic thiol of a cysteine was replaced by the nucleophilic hydroxyl of a serine or the converse substitution was effected. The general result of these modifications was to lower considerably the catalytic activity of the mutated enzymes relative to native enzymes toward all but the most highly activated substrates. The catalytic path of most acyl transfer reactions involves the formation and decomposition of tetrahedral intermediates; since it is the efficiency of these reactions that often dictates the overall enzyme activity, serine-cysteine substitutions may not be well tolerated because of stringent geometric requirements of the active site proton transfer system for a particular molecular environment. Thus, mutation of the active site nucleophile may result in a substantial retardation in the rate of one or more important proton transfer steps.

We now report our observations on the consequences of changing the nucleophilic-

ty of a crucial amino acid side chain at an active site in an enzyme catalyzing another type of group transfer reaction, one that does not require rapid proton transfer in a step affecting the rate. The model system that we investigated is the hydrolysis of phosphate monoesters catalyzed by *Escherichia coli* alkaline phosphatase (BAP) (3). The amino acid sequence (4) and x-ray map (3.4 Å) of BAP (5), a Zn(II) metalloprotein, have been described.

Alkaline phosphatase-catalyzed phosphate ester hydrolysis is initiated by attack of Ser-102 on the phosphoryl group to give a phosphorylated enzyme intermediate that can be isolated at low pH (6). Subsequently, the phosphorylated enzyme is hydrolyzed and the free enzyme is regenerated. Spectroscopic and kinetic evidence (7, 8) indicate that at acidic pH the dephosphorylation of intermediate I (Fig. 1) is rate-limiting while

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