HYDROLOGICAL AND BIOGEOCHEMICAL RESEARCH IN THE SHINGOBEE RIVER HEADWATERS AREA, NORTH-CENTRAL MINNESOTA

U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 96–4215

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Edited by Thomas C. Winter

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 96–4215

Denver, Colorado
1997

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Atmospheric Input to the Shingobee River Headwaters Area

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INTRODUCTION

Atmospheric deposition contributes to the chemical and isotopic budgets of forested ecosystems and influences forest decline and lake acidification (Crocker and Forster, 1986; Asbury and others, 1989; Baker and others, 1991; Psenner and Schmidt, 1992). Understanding of nutrient, contaminant, and elemental cycling in northern forested ecosystems requires evaluation and characterization of atmospheric inputs (Shepard and others, 1989).

Atmospheric inputs include wet (rain and snow) and dry (gas and particulate) deposition. Collection-vessel methods, referred to as bulk (open for collection at all times) or wet-only (open for collection only during rain or snow) precipitation methods, measure wet plus dry and wet-deposition fluxes. In contrast, indirect procedures monitor dry-deposition fluxes. Hicks, for example, developed inferential techniques to estimate dry-deposition fluxes, although problems associated with large particle-size material deposition remain to be overcome (Hicks and others, 1991; Meyers and others, 1991). In addition, forest-canopy interception complicates estimation of ecosystem atmospheric input. Canopy interception (throughfall), aided by leaf uptake, modifies inputs of inorganic species.

Several groups have contributed to the understanding of atmospheric deposition. Hicks, for example, pioneered the use of filter packs to infer dry-deposition flux to watersheds (Hicks and others, 1991; Meyers and others, 1991). Puckett (1991) characterized the role of the forest canopy in the chemical budgets of watersheds. Claassen and others (1986) used atmospheric inputs to develop hydrologic budgets.

This report presents a brief review of ongoing field measurements and computational strategies to evaluate wet and dry deposition to the Shingobee River Headwaters Area. These preliminary results allow the evaluation of the wet and dry atmospheric deposition contribution to elemental budgets of the Shingobee River Headwaters Area.

The working hypothesis is that atmospheric inputs to forested ecosystems can be determined with a combination of suitable field measurements and computational techniques. This hypothesis is tested by comparing estimated atmospheric inputs to those obtained by other chemical and hydrological studies at the study site. Nitrogen and sulfur deposition serve as a focus of field-measurement efforts to test the working hypothesis.

Chemical and isotopic composition of wet-deposition inputs are determined by using collection-vessel methods (Claassen and others, 1986; Reddy and Claassen, 1985). Dry-deposition inputs are inferred from the product, $F = V(d) * [C]$ where $V(d)$ is an appropriate deposition velocity and $[C]$ is the atmospheric concentration of the species of interest (Hicks and others, 1991; Meyers and others, 1991). Throughfall measurements evaluate atmospheric input-forest canopy interaction and subsequent bioaccumulation (Puckett, 1991).

This report summarizes measurement protocols for atmospheric input of major chemical species. Research in progress includes precipitation collection at sites in the Shingobee River Headwaters Area followed by analysis of chemical constituents and stable isotopes. Dry deposition and canopy throughfall have been measured on an intermittent basis.

METHODS

The physiography of the Shingobee River Headwaters Area and the physical characteristics of the principal surface-water bodies are described by Winter and Rosenberry (this volume). Local vegetation consists of second-growth aspen and conifer forest interspersed with pastureland and wetlands. The locations of the precipitation-collection vessels and the filterpacks in the Shingobee River Headwaters Area are shown on plate 1. Atmospheric inputs to the Shingobee River Headwaters Area were monitored using an array of sampling devices. A brief description of materials, techniques, and laboratory procedures follows.

Bulk precipitation was collected in polyethylene bags housed inside a steel drum (fig. 25a) (Claassen and others, 1986; Reddy and Claassen, 1985). A restriction incorporated into the bag limited evaporation. Samples were collected biweekly (coinciding with wet-only precipitation collection) during the warmer months and monthly during the colder months (typically December through February). The collection vessel was open to the atmosphere continuously. Volume and pH were recorded at the time of collection. Samples were sent to the laboratory for analysis of chemical constituents.

An Aerochem Metrics wet/dry precipitation sampler (fig. 25b) collected cumulative bi-weekly samples of wet-only precipitation during the warmer months (typically March through November). The collector consists of two polyethylene buckets and a rain sensor. Volume and pH were recorded at the time of collection. Samples were sent to the laboratory for analysis of major ions. The "wet-side" bucket is uncovered only during rainfall and covered during dry periods to prevent evaporation and contamination by dry deposition.

A filterpack system was used to monitor dry deposition. This approach was modified slightly from that used by Barrie and others (1980), Hicks and others (1991), Meyers and others (1991), and the National Dry Deposition Network (NDDN). Air was passed through a series of filters at the rate of 5 L/m using a pump equipped with a special back pressure regulator for exact flow control (fig. 25c). Filters were changed every 2 weeks. Particles larger than 8 μm accumulate on the first filter (Teflon, 8 μm porosity). The second filter (Teflon, 1-μm porosity) collected particulates between 1 and 8 μm in size. The third filter (nylon, 1-μm porosity) removed HNO_3 vapor. Finally, a pair of cellulose filters, pretreated by immersion in a solution of K_2CO_3 and glycerol, removed SO_2.

Throughfall collection used high-density polyethylene (HDPE) funnels inserted in the mouth of 1-liter HDPE bottles (fig. 25d). Collectors attached to stakes stood at a height of about 1 meter above the forest floor. Samples were collected in triplicate under representative coniferous and deciduous canopies and open atmosphere (precipitation). Each set of samples was collected and composited on a single-storm basis. Volume, temperature, and pH were recorded at the time of collection. Samples were sent to the laboratory for analysis of major ions. Collector funnels were left uncovered between storms but were rinsed with deionized water on a regular basis to limit accumulation of material from dry-deposition; time between precipitation events was also noted.

RESULTS

Bulk precipitation has been collected in the Shingobee River Headwaters Area since April 1990. Annual volume-weighted average concentrations of six major ions (chloride, sodium, magnesium, calcium, nitrate, and sulfate) and isotopes ($D/^{18}O$ and tritium) in bulk precipitation during 1991 agreed well between collection site locations (see sites C_L in plate 1). Average ion concentrations during 1992 exhibited somewhat larger differences between collection sites than during 1991. Overall, these results suggest uniformity in precipitation volume and composition within the headwaters area. This result allows comparison of precipitation-input budgets with those developed from other basinwide chemical and hydrological techniques. Ion loadings in the Shingobee River Headwaters Area are similar to loading values at other temperate terrestrial ecosystems.

Wet-only precipitation has been collected at Williams Lake since 1985. There were no significant differences in ion loadings of chloride and sulfur between collection-vessel types (bulk and wet only). Average annual ion loadings calculated from wet-only precipitation for nitrate, sodium, magnesium, and calcium were 17, 26, 27, and 44 percent less, respectively, than average annual ion loadings calculated from bulk precipitation.

Seasonal variation in ion concentrations and loadings in precipitation occurred at both sites. Calcium, nitrate, and sulfate ion concentrations varied by as much as a factor of 10 during the year (fig. 26).

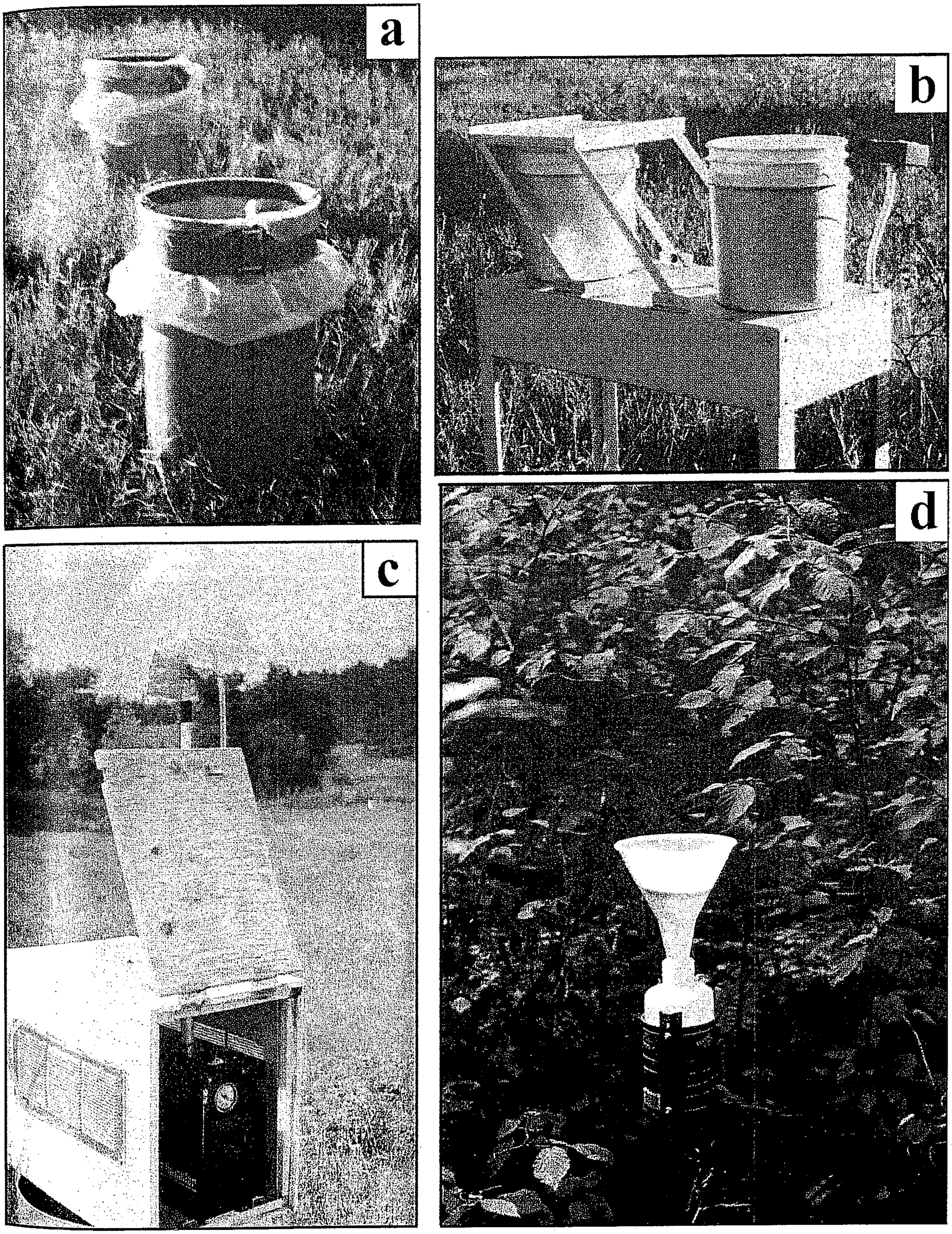


Figure 25. Sampling equipment used to monitor atmospheric inputs to the Shingobee River Headwaters Area: (a) bulk precipitation collectors; (b) wet-only precipitation collector; (c) filterpack system for dry deposition; and (d) throughfall collector.

Concentrations well above the mean value occurred several times throughout the year. Isotope values showed typical seasonal trends and all precipitation isotope data plotted on the meteoric water line.

Dry-deposition loadings of nitric acid, sulfur dioxide, and sulfate aerosol were measured continuously during the late summer and fall of 1991. Nitric acid loadings were the greatest (as much as a maximum of 40 grams/hectare/week). Values peaked at the start of sampling (August 28), decreased regularly thereafter, and increased again in late fall (November 4). Sulfur dioxide loadings, an order of magnitude smaller than those for nitric acid, exhibited a small peak at the start of the sampling period. Sulfate aerosol loadings, consistently the lowest values of the three parameters measured, varied from 0 to 3 grams/hectare/week.

Comparison of wet and dry loading values indicates that gaseous nitrogen (as nitric acid) makes a substantial contribution to the nitrogen atmospheric input budget. Gaseous sulfur dioxide, on the other hand, appears to be quantitatively unimportant. Particulate (> 8 μm) chloride, nitrogen, and sulfur contribute as much as 10 percent of the bulk precipitation concentrations. Particulate calcium and magnesium contribute as much as 20 percent of the bulk precipitation concentrations.

Throughfall precipitation (site P_t, plate 1) was collected during the 1991 and 1992 growing seasons (June-September). Regression analysis of ion deposition against the time between storms and the amount of rainfall during a storm was used to estimate the rate at which those ions accumulate in the canopy between storms and the rate at which they are leached from the canopy during storms (Puckett, 1990). The resulting regression relations were used to estimate ion leaching from and dry deposition to the canopies during the 1991 and 1992 growing seasons.

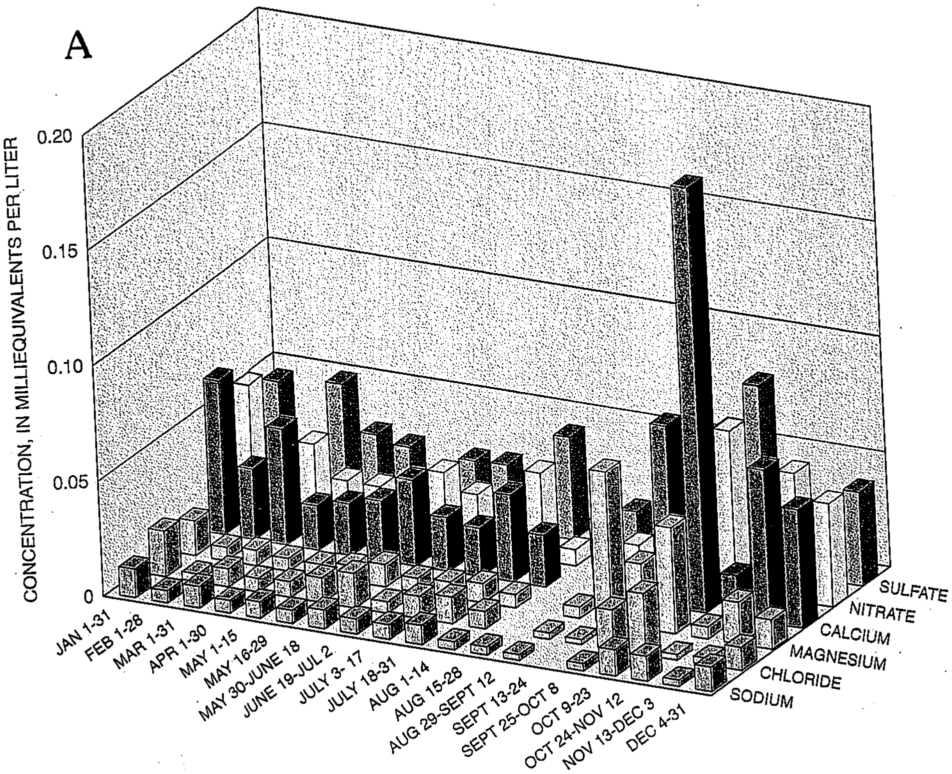
Net fluxes were greatest for calcium ion during both 1991 and 1992 under both canopies. Magnesium and chloride ion net fluxes were about equal under both canopies during the same years with the exception of 1991, when the coniferous canopy chloride ion net flux was essentially the same as that for calcium ion. There was net retention of nitrogen under both canopies during both years, probably due to limited nitrate (as nitrogen) availability in the forest soils. Sodium and sulfate (as sulfur) net fluxes were small, and in 1991 and 1992 they were negative, indicating retention by the canopy during those years.

The throughfall regression analyses against the time between storm events were statistically significant ($a = 0.05$) for calcium ion and magnesium ion under the deciduous canopy, and sodium ion and chloride ion under both canopies. Canopy leaching rate estimates were statistically significant for calcium ion and magnesium ion, and for nitrate nitrogen under the coniferous canopy only. For both calcium ion and magnesium ion under both canopies, leaching rates were several times those previously observed in the northern Shenandoah Valley of Virginia (Puckett, 1990). Nitrate leaching rates were significant only for the coniferous canopy, and were negative, reflecting net retention by the canopy. The statistically nonsignificant results for sulfate (as sulfur) suggest there is little uptake of sulfur from either the atmosphere or the soil, consequently little is available in either canopy for either washoff or leaching.

Canopy leaching and dry deposition contributions to throughfall were estimated by multiplying the appropriate regression coefficients by precipitation amounts and the time between events during the 1991 and 1992 growing seasons. For both canopies, leaching of calcium ion and magnesium ion and dry deposition of chloride ion accounted for the majority, if not all, of the net flux of those ions during both growing seasons. Dry deposition of calcium ion and magnesium ion was significant under both canopies but, with the exception of magnesium ion under the deciduous canopy in 1991, it represented less than half of the leaching estimate.

The relatively large amount of leaching of both calcium ion and magnesium ion under both canopies is probably related to their availability in the glacially derived soil which contains calcite and dolomite. This soil is also the likely source of the dry deposited calcium ion and magnesium ion in the deciduous canopy. Given the forested nature and general lack of agriculture in much of the surrounding area, suspension of dust from local unpaved roads probably provides most of these two constituents in dry deposition and in precipitation.

In spite of the relatively remote north-central United States location of the Shingobee site, nitrate (as nitrogen) appears to be the constituent delivered in greatest quantities from outside the watershed. During the growing season, this amounted to 0.6-0.8 kg/ha and was 2.1 kg/ha on an annual basis. In comparison, nitrate (as nitrogen) inputs to the northern Shenandoah



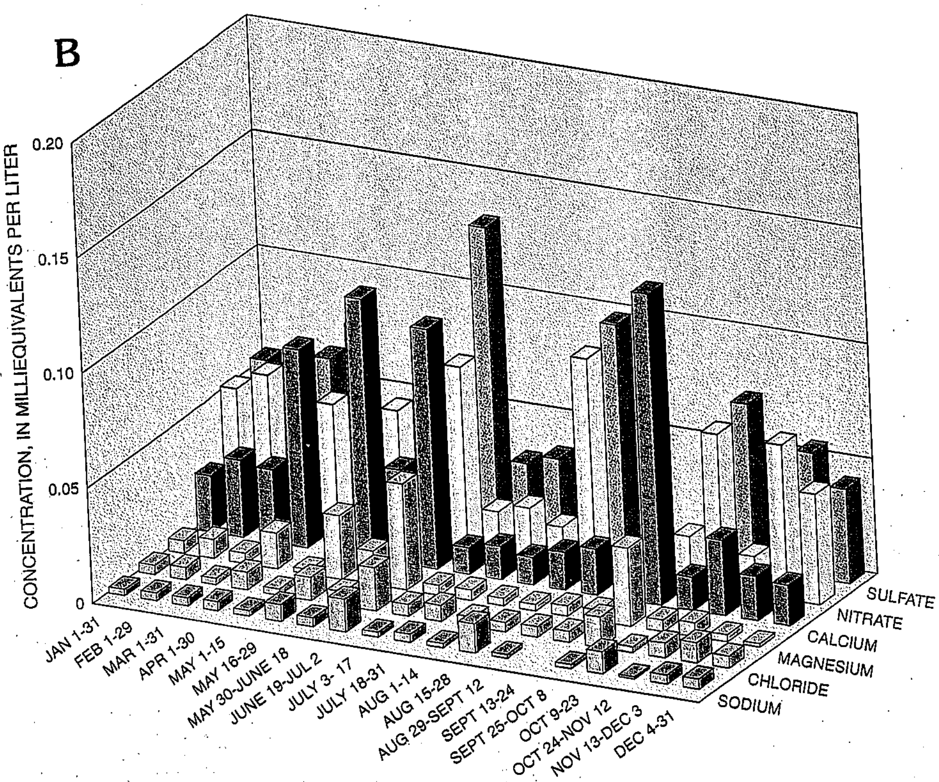


Figure 26. Concentrations of major ions in bulk precipitation in the Shingobee River Headwaters Area during (A) 1991 and (B) 1992.

Valley of Virginia in 1983 were approximately 1.8 and 2.8 kg/ha during the growing season and the entire year, respectively. Based on comparisons of the wet and bulk deposition chemistry it would appear that most (84 percent) of the nitrate (as nitrogen) enters the watershed in wet precipitation, whereas at the Virginia site wet and dry deposition contributions were about equal. It is important to note that the forest canopy at the Shingobee site is much more efficient at retaining nitrate (as nitrogen) inputs than the Virginia site as evidenced by the net retention at the Shingobee site compared to positive fluxes in Virginia. This pattern suggests that these northern Minnesota trees may be more nitrogen limited and therefore dependent on precipitation inputs of nitrogen.

Deposition of sulfate (as sulfur) in precipitation at the Shingobee site was about 0.9-1 kg/ha during the growing season and 3.1 kg/ha on an annual basis. Both deciduous and coniferous throughfall fluxes were about equal to the precipitation inputs. The fact that both the leaching and dry deposition estimates for sulfate (as sulfur) under both canopy types were not significant, suggests that most of the sulfur entering the Shingobee watersheds is in precipitation. This is important in that dry deposition in its various forms in eastern watersheds usually accounts for about one-half to one times the amount of sulfate (as sulfur) as wet deposition. For example, at the Virginia site wet deposition was about 5 kg/ha during the growing season compared to 8.7 and 8.5 kg/ha under the deciduous and coniferous canopies, respectively. Furthermore, wet deposition of sulfate (as sulfur) at the Shingobee site (3.1 kg/ha/yr) was less than half that in Virginia (7.1 kg/ha/yr), and represented about 97 percent of the total (bulk) deposition. Overall, these results suggest that dry deposition of gases, aerosols, or particles is a minor source of sulfur to the Shingobee River Headwaters Area.

CONCLUSION

Atmospheric inputs to the Shingobee River Headwaters Area comprise an important component of the chemical and isotopic budgets for Williams and Shingobee Lakes. Understanding of chemical distributions and fluxes in this forested ecosystem requires knowledge of atmospheric deposition processes throughout the year. These atmospheric inputs, which are one of the sources of chemical constituents in ground-water recharge, establish an end member for chemical and stable isotopic concentrations for the ground water-surface water system in the study area. That is, the source chemical and isotopic composition of recharge water in this area is ultimately controlled by atmospheric inputs and subsequent transformations.

A comparison of samples from 2 collection sites indicates uniformity in precipitation volume and composition within the headwaters area. Loadings calculated from wet-only precipitation were as much as 44 percent less than those calculated from bulk precipitation. Seasonal variation in precipitation ionic composition ranged by as much as a factor of 10. Isotope values showed typical seasonal trends and plotted on the meteoric water line. Nitrogen and to a smaller extent, sulfur, accumulate in the forested ecosystem by gas-phase dry deposition. Particulate (>8 μm) chloride, nitrogen, and sulfur contribute up to 10 percent of the bulk precipitation concentrations. Particulate calcium and magnesium contribute up to 20 percent of the bulk precipitation concentrations. Throughfall precipitation data are consistent with dry and wet deposition data, reflecting the relative contributions of dry deposition and the importance of wet deposition to the Shingobee River Headwaters Area.

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