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CONTRIBUTION OF FOLIAR LEACHING AND DRY DEPOSITION TO SULFATE IN NET THROUGHFALL BELOW DECIDUOUS TREES

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Abstract—Experiments were conducted at Walker Branch Watershed, TN, in 1986 with radioactive ^{35}S (87 day half-life) to quantify the contribution of foliar leaching and dry deposition to sulfate (SO_4^{2-}) in net throughfall (NTF). Two red maple (*Acer rubrum*) and two yellow poplar (*Liriodendron tulipifera*) trees (12–15 m tall) were radiolabeled by stem well injection. Total S and ^{35}S were measured in leaves; ^{35}S and SO_4^{2-} were measured in throughfall (THF). The contribution of foliar leaching to SO_4^{2-} in NTF, THF minus incident precipitation, was estimated by isotope dilution of ^{35}S in NTF arising from nonradioactive S in dry deposition. The per cent contribution of foliar leaching to SO_4^{2-} in NTF was greatest during the week following isotope labeling and during the period of autumn leaf fall. During the growing season, foliar leaching accounted for < 20% and dry deposition accounted for > 80% of the SO_4^{2-} in NTF beneath the study trees. Dry deposition of S to these tree species can be reasonably approximated during summer from the measurement of SO_4^{2-} flux in NTF.

Key word index: Sulfur, sulfate, sulfur dioxide, dry deposition, foliar leaching, deciduous trees, throughfall.

INTRODUCTION

The deposition of sulfate-S to Walker Branch Watershed (WBW), near Oak Ridge National Laboratory (ORNL), TN, in bulk precipitation is among the highest measured in the U.S. Lindberg *et al.* (1986) showed that bulk precipitation measurements significantly underestimated total annual atmospheric SO_4^{2-} deposition to the forest, which was about 75 kg ha^{-1} from 1981 to 1983. About half of the total SO_4^{2-} deposition to the forest canopy (*Quercus* sp.) occurred in wet deposition, and about half occurred as dry deposition of particles and vapors (Lindberg *et al.*, 1986). Therefore, dry deposition was a major contributor to the total annual sulfate-S flux to the watershed.

Various methods (Lovett and Lindberg, 1984; Mayer and Ulrich, 1978) have been proposed for estimating the dry deposition of SO_4^{2-} by collecting throughfall (precipitation passing through the forest canopy). The net throughfall SO_4^{2-} flux, that is the flux in throughfall minus the flux in rainfall, is one such proposed estimate. However, confusion about the sources of SO_4^{2-} in throughfall, particularly the amount originating from internal leaf pools, has curtailed its application for estimating dry deposition. For example, dry deposition based on the net throughfall flux may be overestimated due to leaching of foliar SO_4^{2-} that originates from root uptake and not atmospheric deposition.

Mayer and Ulrich (1978) estimated the contribution of dry deposition to a deciduous beech forest in Germany by comparing seasonal changes in the net sulfate-S flux. More than 75% of the S flux increase in throughfall during the growing season was attributed to dry deposition, and the contribution from foliar leaching was estimated to be at most 25%. Lindberg *et al.* (1986) indicated that rainfall leaching of internally cycled plant S was a minor contributor (5%) to the total annual flux of sulfate-S reaching the forest floor on WBW.

Based on the above work, it would appear that throughfall measurements might be used to estimate the dry deposition of SO_4^{2-} in forests near major emission sources. However, a review by Parker (1983) showed that literature estimates of the leaching (removal of internal plant S) contribution to net throughfall S flux ranged from 13 to 100% with no clear trends. Mis-estimation of the relative contribution of external and internal sources to net throughfall can have broad consequences for estimated input/output budgets of whole forests (Parker, 1983).

In 1986, we conducted experiments on WBW with radioactive ^{35}S to quantify the contribution of foliar leaching to net throughfall SO_4^{2-} concentrations beneath two deciduous tree species, yellow poplar (*Liriodendron tulipifera*) and red maple (*Acer rubrum*). Our objective was to explore the mobility of foliar S, traced by injected ^{35}S, and to quantify its leachability in a forest canopy where atmospheric deposition of S is far in excess of the forest's nutritional requirements (Johnson *et al.*, 1982; Lindberg *et al.*, 1986).

REPOSITORY Oak Ridge Energy Systems
COLLECTION
BOX No.
FOLDER

A-00083

Human Subjects Project

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EXPERIMENTAL

Terminology and technical approach

The throughfall transfer terminology described by Parker (1983) is used throughout this paper. The SO_4^{2-} concentration in total throughfall (THF) is a combination of SO_4^{2-} from (1) the interior of tree leaves, (2) dry deposition, and (3) wet deposition (incident rainfall) (Fig. 1). Net throughfall (NTF) SO_4^{2-} is the concentration in total throughfall minus the concentration in wet deposition. Net stemflow (NSF) was similarly defined. Net throughfall includes SO_4^{2-} in dry deposition (particulate and vapor) on the foliage that is washed off by rainfall, and internal leaf SO_4^{2-} that is leached from the leaves by rainfall. ^{35}S in NTF or NSF represents foliar leaching (i.e. the removal of internal leaf S) because tree leaves are the only source for ^{35}S present in THF (Fig. 1).

^{35}S was measured as disintegrations min^{-1} (d.p.m.) g^{-1} leaf dry weight (DW) or d.p.m ℓ^{-1} of THF, corrected for radioactive decay to the time of radiolabeling, and converted to mg g^{-1} DW or mg ℓ^{-1} using a conversion factor of 2.34 $\times 10^{-2}$ mg ^{35}S Ci^{-1} (1 Ci = 2.22 $\times 10^{12}$ d.p.m.). The concentration of total S was measured in foliage (mg g^{-1} DW), and the concentration of SO_4^{2-} was measured in THF (mg ℓ^{-1}). The specific activity (S.A.) of ^{35}S in the leaf (i.e. the ratio of the concentration of ^{35}S to the concentration of total S at the same time) was assumed to be unique to all forms of S in the leaf.

The principle of isotope dilution was used to determine the contribution of dry SO_4^{2-} deposition to NTF. Differences between the specific activity of ^{35}S in the leaf and in NTF arise from the dilution of ^{35}S in NTF from SO_4^{2-} in dry deposition (Fig. 1). It was assumed that isotopes are not differentially leached from foliage by rainfall. The per cent contribution of dry deposition (D_d) to NTF SO_4^{2-} was calculated based on an equation for the mixing of two sources with known isotopic composition:

$$\%D_d = [(S.A._{NTF} - S.A._{leaf})/(S.A._{dry\ deposition} - S.A._{leaf})] \times 100, \quad (1)$$

which (because $S.A._{dry\ deposition}$ is zero) reduces to

$$\%D_d = [(S.A._{NTF} - S.A._{leaf})/(-S.A._{leaf})] \times 100. \quad (2)$$

The per cent contribution of foliar leaching (L) to NTF SO_4^{2-} is simply

$$\%L = 100 - \%D_d. \quad (3)$$

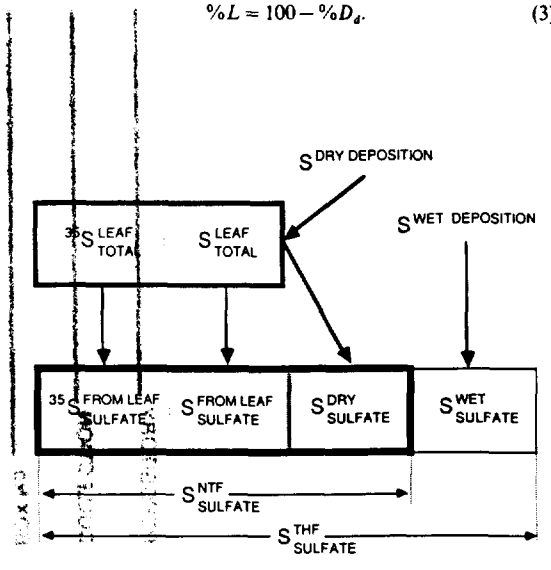

Fig. 1. Schematic representation of ^{35}S and SO_4^{2-} sources to throughfall (THF) and net throughfall (NTF) beneath the study trees.

Field methods

Two red maples and two yellow poplars (12–15 m tall and 15–19 cm diameter at breast height) were located along ridges on WBW on a Fullerton cherty silt loam soil. One tree of each species (indicated by tree '2' throughout the paper) was girdled to study volatilization and root turnover of ^{35}S; the bark, phloem, and cambial layers were removed at the girdle several weeks prior to radiolabeling (Garten, in press). Since there is no indication of increased fine root death for up to 6 months after girdling in yellow poplar trees (Edwards and Ross-Todd, 1979), girdling was regarded as a minimal disturbance in the current experiment.

The area beneath each tree (plot size) was determined by tracing the drip line of the tree onto the ground with a long pole. Regulated zones were established around each tree with fences and perimeter signs. We followed health physics procedures prescribed by the ORNL health physics procedures manual (Anonymous, 1985) for personnel monitoring and environmental protection.

Each tree was radiolabeled with between 182 and 243 μCi of ^{35}S (as sodium sulfate) on 25 and 26 June 1986. The amount of total S, as SO_4^{2-}, in the labeling solution was $< 20\ \mu g$. The calculated amount of ^{35}S in each labeling solution was confirmed by liquid scintillation counting (LSC). A leakproof collar was built around each trunk, above the girdle (when present). The collar was filled with distilled water, and 10–12 chisel cuts (0.6 cm wide) were made, about 1 cm deep into the xylem, where the collar met the trunk. ^{35}S was then added to the water which was drawn into the tree by xylem transport. The injection site on each trunk was covered with plastic to prevent contamination of other samples.

Stemflow (STF) was collected with a leakproof collar around the trunk (similar to the injection collar) about 25 cm above the injection collar. The stemflow collar drained into a calibrated 58-ℓ polyethylene carboy. Following rainfall, the volume of STF in each carboy was measured, mixed, and a 1-ℓ sample was removed for analysis. Background samples were obtained from an unlabeled maple tree fitted with a stemflow collar.

Throughfall was sampled on a 1 m × 1 m grid beneath each tree using four high-density polyethylene buckets (638-cm^2 opening, 18-ℓ capacity) (Fig. 2). The buckets were covered with a nylon screen (3-mm mesh) to exclude falling leaves and debris. Laboratory tests showed that the screen did not sorb $^{35}SO_4^{2-}$. Bucket positions were selected using a random numbers table and a stratified design (one bucket was always placed within 1 m of the trunk). Bucket positions were changed when THF was collected. The first clear day following rainfall, the THF in the four buckets was combined, measured, mixed, and a 1-ℓ sample was removed for analysis. Background THF samples were obtained from beneath an unlabeled maple tree.

Mean weekly rainfall amount was determined from continuous recorders located at two clearings < 400 m from the trees. Precipitation measurements were confirmed using rain gauges located at each tree. The rainfall amounts measured at the clearings were highly correlated ($r > 0.98$) with both rainfall and THF measurements at the individual trees. Weekly data on SO_4^{2-} deposition in rainfall was obtained at a precipitation chemistry collection site (part of the National Atmospheric Deposition Program/National Trends Network) located within 350 m of the radiolabeled trees.

Leaf samples were obtained from 4 to 8 m above the ground with a pole pruner at approximately monthly intervals. Leaf samples from different sides of each tree were composited and analyzed for ^{35}S and total S. The girdled maple and the girdled poplar trees were felled prior to autumn leaf fall (13 and 15 weeks after radiolabeling, respectively). The nongirdled trees were felled several weeks after autumn leaf fall (all foliage had fallen from the trees by 21 weeks after radiolabeling). At that time, the amount of ^{35}S present above ground in each tree was inventoried (Garten, in press).

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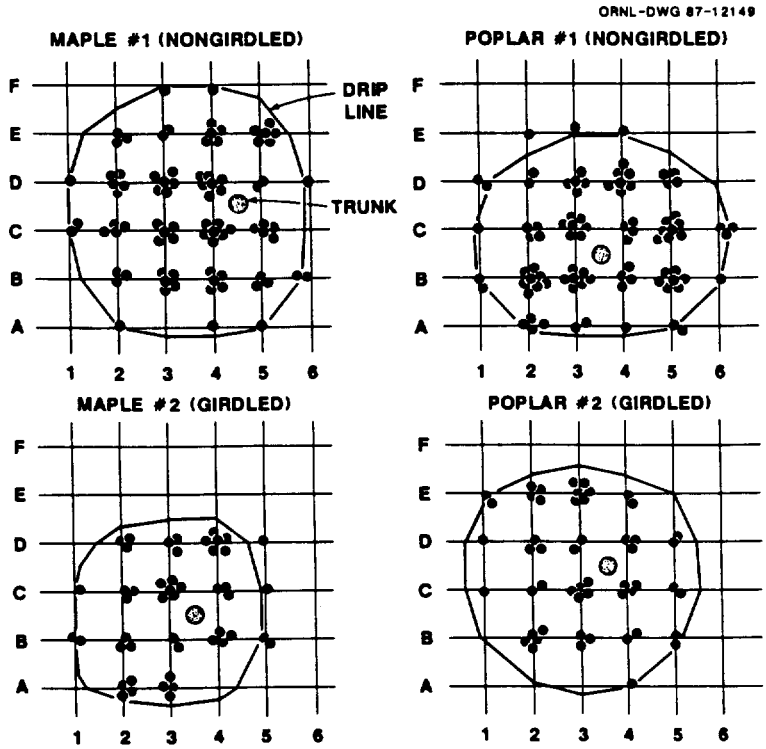

Fig. 2. Positions of throughfall buckets beneath the four trees during the experiment. The drip line is an approximate tracing.

Laboratory methods

Leaves were freeze-dried, weighed, and crushed into small fragments by manipulating the dry samples in zip-lock polyethylene bags. Samples were prepared for ^{35}S analysis using methods for total S analysis outlined by the Association of Official Analytical Chemists (Williams, 1984). One g of dry leaves was weighed into a large crucible and saturated with 7.5 ml of 3.7 M magnesium nitrate (AR grade) solution. The crucibles were heated on a hot plate until no further reaction occurred and were then ashed in a furnace (maximum temperature was 450 °C). All forms of ^{35}S in the leaf had been converted to $^{35}SO_4^{2-}$ in the ash, which was dissolved in 1 M HCl (known weight). Subsamples of the acid solution were analyzed for ^{35}S by LSC.

Methods outlined by Bushman *et al.* (1983) were followed for determining total S concentrations in foliage samples. Dry leaves were ground in a blender and 50-mg portions were burned in a Schoniger-type oxygen flask containing deionized water and a few drops of H_2O_2. After combustion, the flasks were allowed to stand for 1 h during which the gases produced on combustion were absorbed into the solution. Sulfate in the absorbing solutions was determined turbidimetrically as $BaSO_4$ (Bardsley and Lancaster, 1960), as well as by ion chromatography in the ORNL Analytical Chemistry Division.

Throughfall and STF were frozen until samples were prepared for analysis. Samples were passed through Whatman No. 541 filter papers and 15-ml samples were taken for SO_4^{2-} analysis by ion chromatography. Ten ml of 30% H_2O_2 was added to each filtered THF and STF sample, ranging in volume from 400 to 600 ml, after neutralization with NH_4OH. Samples were evaporated to approx. 75 ml on a hot plate and transferred to 150-ml tall-form beakers with two 5-ml washes of 1 N HCl. One ml of 30% H_2O_2 was added to each sample before evaporation to complete dryness with gentle heat. The residues were taken up in 2 ml of 1 N HCl and analyzed for ^{35}S by LSC.

Inorganic $^{35}SO_4^{2-}$ and total SO_4^{2-} in tree leaves was determined by extraction with dilute HCl at room temperature (Richter and Johnson, 1983.) A 1-g sample of crushed, dry leaves was placed in a centrifuge tube, covered with 25 ml of 0.01 M HCl, and shaken for 30 min at room temperature. The acid extract was filtered through a Whatman No. 541 filter and portions of the filtrate were analyzed for ^{35}S by LSC. A portion of each filtrate was also analyzed for SO_4^{2-} turbidimetrically, following precipitation as $BaSO_4$ (Bardsley and Lancaster, 1960). The per cent leaf $^{35}SO_4^{2-}$ and the per cent leaf SO_4^{2-} extracted was based on the total ^{35}S or total S concentration in the whole leaf, respectively.

Leaf area : dry weight ratios were determined for red maple and yellow poplar leaves in August. The areas of fresh leaves ($N = 20$) were read directly with a Li-Cor LI 3100 Area Meter. Leaves were then dried (72 h at 100 °C) and weighed.

Quality assurance

Quality assurance measures included the following: (1) analysis of background samples to correct for naturally occurring radioactivity in leaves, THF, and STF, (2) repeated counting of selected samples to follow the decay rate of ^{35}S, (3) trial analyses of leaves and STF with known additions of ^{35}S, (4) replicate analysis of THF, STF, and tree tissue samples, (5) comparison of ^{35}S concentrations in tree tissue samples ashed by the magnesium nitrate method and the Schoniger flask method, and (6) comparison of turbidimetrically determined SO_4^{2-} concentrations with analyses by ion chromatography.

RESULTS

Quality assurance

Repeated measurements of 12 samples (including STF, THF, and tissue samples) over a period of

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100–150 days showed that sample radioactivity decayed with a mean half-life of 84 (SD = 10) days. Therefore, the radioactive decay in these samples was consistent with that of ^{35}S and not ^{40}K (half-life = 1.2 × 10^9 years). ^{40}K was expected to be the principal natural radiocontaminant in low-level samples.

Analysis of leaf and STF samples ($N = 10$), with known additions of ^{35}S (as $NaSO_4$), showed that from 94 to 102% of the ^{35}S was recovered. Seventeen samples of THF and STF were analyzed twice, and ^{35}S determinations in ~ 90% of the replicate samples were within 10% of the first analysis. Twenty tissue samples (including leaves, leaf fall, and wood) from the radiolabeled trees were analyzed twice using the $Mg(NO_3)_2$ ashing procedure, and ^{35}S determinations in ~ 85% of the replicate samples were within 15% of the first analysis. Ten tissue samples were analyzed for ^{35}S using the $Mg(NO_3)_2$ ashing method and the Schoniger flask method. The mean difference between the two sets (3%) was not statistically significant (at the $P = 0.05$ level). There was also no difference between SO_4^{2-} determinations made turbidimetrically after precipitation as $BaSO_4$ and those made by ion chromatography. Results from the two methods were highly correlated ($r = 0.99$) and 86% of the samples analyzed differed by < 10%.

Study tree properties

Time intervals from injection to harvest of the four trees ranged from 13 to 20 weeks. The trees were relatively similar with respect to foliage biomass (Table 1). The total one-sided leaf area, determined from leaf area:dry weight ratios, ranged from 148 to 159 m^2 for maple trees and 106–116 m^2 for poplar trees. Of the four trees, red maple tree No. 2 had the highest leaf area index (LAI) because of a small crown diameter and small plot size (Table 1). The aboveground woody biomass ranged from 74 to 92 kg DW for the two maples and from 81 to 84 kg DW for the two poplars.

Specific activity in leaves

The experiment was divided into four time periods prior to autumn leaf fall and a separate period during autumn leaf fall (Table 2). The first period (25 June–3 July) consisted of the 8 days immediately after isotope labeling and corresponded to the time required for foliar ^{35}S concentrations to reach steady state (Garten, in press). From 4 July to 15 October, ^{35}S concentrations and the specific activity of ^{35}S in tree leaves varied by less than a factor of two (Table 3). The specific activity of ^{35}S in leaves showed the contri-

Table 1. Properties of the four study trees

Species	Tree	Exposure* (weeks)	Max. foliar biomass (kg DW)	Plot area† (m^2)	Estimated LAI‡ (m^2:m^2)
Red maple	1	19	6.5	23	6.4
	2	13	7.0	12	13.3
Yellow poplar	1	20	6.2	18	5.9
	2	15	6.8	22	5.3

* Duration of experiment from isotope labeling to end of autumn leaf fall (tree 1) or to the time a tree was felled (tree 2).
† Ground area circumscribed by the drip line of each tree.
‡ LAI–Leaf Area Index—leaf area (one-sided) per unit area of ground.

Table 2. Rainfall amounts, number of events, and SO_4^{2-} in wet deposition to Walker Branch Watershed for various periods during the experiment

Dates	Length of period (days)	Rainfall during period (mm)	No. of events*	Rainfall sulfate ($mg\ l^{-1}$)†	Rainfall sulfate ($mg\ m^{-2}$)†
Prior to leaf fall					
25 June–3 July	8	37	2	1.24	46
4 July–1 August	29	78	4	2.62	204
2 August–3 September	33	129	14	3.35	432
3 September–15 October	42	124	14	3.00	372
During leaf fall					
16 October–12 November	28	102	5	1.97	201

* An event is preceded and followed by 6 h of rainfall < 0.25 mm.
† From National Atmospheric Deposition Program/National Trends Network precipitation chemistry collection site.

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Table 3. ^{35}S concentrations and the specific activity (S.A.) of ^{35}S in leaves collected at various times throughout the study

	Leaf ^{35}S 10^{-15} g g^{-1} DW				^{35}S S.A.* in leaf $\times 10^{-12}$			
	Maple		Poplar		Maple		Poplar	
Dates	1	2†	1	2†	1	2	1	2
Prior to leaf fall								
25 June–3 July‡	170	5.7	33	150	150	5.9	12	100
4 July–1 August	160	6.3	71	220	140	6.7	26	130
2 August–3 September	120	8.0	90	220	120	9.2	32	140
4 September–15 October	99	9.2	110	220	78	11	37	120
During leaf fall								
16 October–12 November	78		140		60		47	
Mean (4 July–15 October)	130	7.8	93	220	113	8.7	33	127

* Specific activity = g ^{35}S g^{-1} DW:g S g^{-1} DW.
† Trees felled prior to autumn leaf fall.
‡ Pre-steady-state period.

bution of ^{35}S to total S was so small that concentrations of total S could be considered entirely due to stable S.

Analysis of variance (two-way, no replication) showed that foliar S concentrations were significantly different (at the $P = 0.05$ level) between the four trees. Total foliar S concentrations (mg g^{-1} DW) in leaves from maple No. 1 (1.15) and maple No. 2 (0.90) were not significantly different; concentrations in leaves from poplar No. 1 (2.85) and poplar No. 2 (1.73) were significantly different from each other and significantly different from the maples. Within each tree, foliar S concentrations did not change significantly over the time period of 25 June–15 October.

Dilute HCl extractions indicated that there were differences between trees in per cent leaf $^{35}SO_4^{2-}$ and per cent total leaf SO_4^{2-} (Fig. 3). On a percentage basis, leaf $^{35}SO_4^{2-}$ appeared to be slightly higher than leaf SO_4^{2-} within each tree, although the differences did not appear to be statistically significant (based on overlapping confidence intervals). The percentage of $^{35}SO_4^{2-}$ in maple and poplar leaves during the first week after radiolabeling (25 June–3 July) and also during the period of autumn leaf fall (16 October–12 November) was approximately twice that shown in Fig. 3.

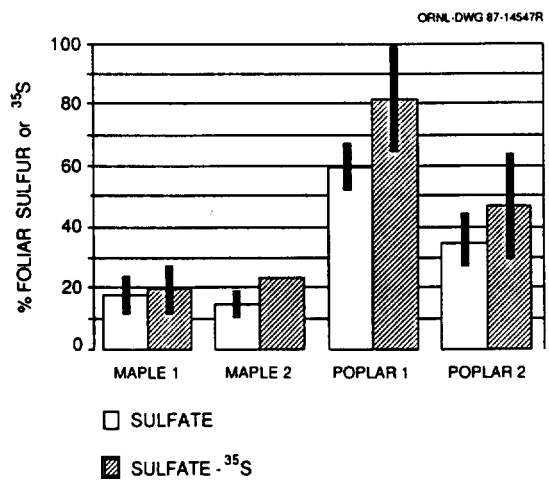

Fig. 3. Total SO_4^{2-} and $^{35}SO_4^{2-}$ in leaves sampled from 4 July to 15 October as a percentage of total leaf S or total leaf ^{35}S, respectively; determined by extraction with dilute HCl. Error bars show ± 2 SD about the mean.

Precipitation, throughfall, and stemflow

Rainfall in July, August, September, October, and November 1986, was 110, 93, 82, 121, and 107 mm, respectively, compared with normal rainfall (based on 35-year means) of 134, 95, 92, 75, and 119 mm for the same months. Deposition of SO_4^{2-} to the watershed was greatest during August, September and early October, corresponding to higher amounts of incident precipitation and a greater number of rainfall events (Table 2).

Figure 2 shows the coverage of THF sampling beneath each tree over the period of study. Most of the total SO_4^{2-} flux reaching the forest floor arrived in THF. Stemflow contributed 4–13% of the net SO_4^{2-} flux and < 10% of the total SO_4^{2-} flux reaching the forest floor beneath each tree. ^{35}S concentrations in THF and STF were significantly correlated ($r = 0.73$, $P < 0.001$). Total SO_4^{2-} concentrations in THF and STF were also significantly correlated ($r = 0.82$, $P < 0.001$).

^{35}S concentrations in THF were greatest during the week immediately after isotope labeling and during the period of autumn leaf fall (Table 4). The concentration data presented in Table 4 are means for each time interval, weighted by THF volume. Concentrations of SO_4^{2-} in NTF reached maximum values in the period immediately prior to and during autumn leaf fall (Fig. 4). The specific activity of ^{35}S in NTF

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Table 4. ^{35}S concentrations in throughfall (weighted for THF amount) and ^{35}S specific activity (S.A.) in net throughfall (NTF) at various times throughout the study

	^{35}S in THF d.p.m. ℓ^{-1}*				^{35}S S.A.† in NTF $\times 10^{-12}$			
	Maple		Poplar		Maple		Poplar	
Dates	1	2‡	1	2‡	1	2	1	2
Prior to leaf fall								
25 June–3 July§	196	284	394	589	1.5	4.9	3.7	6.0
4 July–1 August	149	39	221	303	1.6	0.97	4.8	3.9
2 August–3 September	157	70	242	171	2.0	1.0	3.7	3.1
4 September–15 October	207	66	1113	312	1.3	0.49	8.9	1.6
During leaf fall								
16 October–12 November	926		5081		4.3		46	
Weighted mean (4 July–15 October)	173	58	528	234	1.6	0.94	6.2	2.5

* d.p.m. ℓ^{-1}—disintegrations per minute per liter.
† Specific activity = mg $^{35}S\,\ell^{-1}$: mg $S\,\ell^{-1}$.
‡ Tree felled prior to leaf fall.
§ Pre-steady-state period.

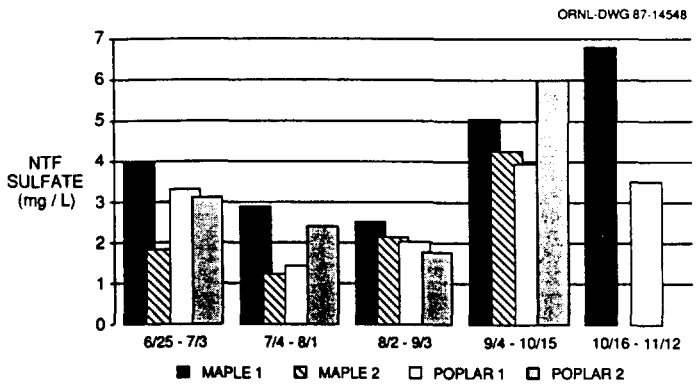

Fig. 4. Weighted mean concentrations of SO_4^{2-} in net throughfall (NTF) beneath the study trees prior to leaf fall (25 June–15 October) and during autumn leaf fall (16 October–12 November).

increased during leaf fall because of a large increase in NTF concentrations of ^{35}S relative to total SO_4^{2-} (Table 4).

Estimated leaching of foliar sulfur

During the period from 4 July to 15 October (104 days), the contribution of foliar leaching to the SO_4^{2-} concentration in NTF beneath the trees ranged from 1 to 24% (Fig. 5), and the mean contribution of foliar leaching to NTF SO_4^{2-} was calculated to be between 1 and 19% (Table 5). Estimates of the mean contribution of foliar leaching to the NSF SO_4^{2-} concentrations were similar to those for NTF (the range was 1–19%). Therefore, dry deposition accounted for more than 80% of the SO_4^{2-} in NTF beneath the four trees.

The contribution of foliar leaching to NTF SO_4^{2-} concentrations increased to ~ 100% during autumn leaf fall (15 October–12 November) in poplar No. 1 (Fig. 5). During the latter period, foliar leaching contributed ~ 7% to the SO_4^{2-} in NTF beneath maple tree No. 1. This was a striking species difference. The large contribution of foliar leaching to SO_4^{2-} in NTF during the week after radiolabeling (Fig. 5) was an apparent artefact of isotope labeling; foliar ^{35}S concentrations were increasing and there was more leaf $^{35}SO_4^{2-}$ relative to leaf SO_4^{2-} as measured by extraction with HCl.

DISCUSSION

Dry deposition dominates the SO_4^{2-} flux to WBW during the growing season (Lindberg *et al.*, 1986), but dry deposition is difficult to quantify because of the problem of calibrating or scaling indirect measurement methods to the complex architecture of the forest canopy. The present experiments show that foliar leaching does not contribute more than 20% to SO_4^{2-} in NTF and NSF beneath red maple and yellow poplar trees over the growing season (Table 5). Minor

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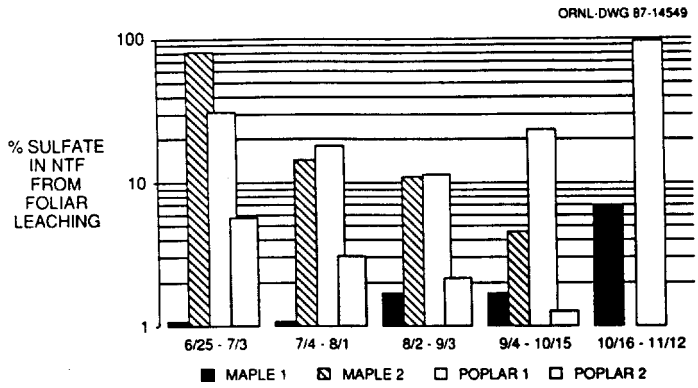

Fig. 5. Per cent contribution of foliar leaching to net throughfall (NTF) SO_4^{2-} concentrations beneath the study trees prior to leaf fall (25 June–15 October) and during autumn leaf fall (16 October–12 November).

Table 5. Summary of the mean contribution of foliar leaching and dry deposition to net throughfall (NTF) SO_4^{2-} concentrations beneath the four study trees during the period 4 July–15 October

	Mean % contribution to NTF SO_4^{2-}			
Source	Maple 1	Maple 2	Poplar 1	Poplar 2
Foliar leaching	1	11	19	2
Dry deposition	97	89	81	98

leaching of foliar incorporated S by rainfall is consistent with experiments showing an apparent agreement between dry deposition rates measured to inert surfaces and estimates based on briefly washing tree leaves (Lindberg and Lovett, 1983).

Greater leachability of foliar ^{35}S relative to foliar S would cause an overestimation of the ^{35}S specific activity in NTF, and therefore underestimate the percentage contribution of dry deposition to NTF SO_4^{2-}. Measurements by Johnson *et al.* (1982) of the SO_4^{2-} present in yellow poplar leaves (39%) and red maple leaves (21%) from WBW were in reasonable agreement with extractions of leaf SO_4^{2-} and $^{35}SO_4^{2-}$ reported here (Fig. 3), with the exception of poplar tree No. 1. This tree had higher total foliar S concentrations, a higher percentage of SO_4^{2-} in leaves, and a higher percentage contribution of foliar leaching to NTF SO_4^{2-} (Table 5).

Radiolabeling the trees with ^{35}S involved the addition of a negligible amount of total SO_4^{2-} to each tree. Therefore, the injection should not have affected normal S metabolism. There were no consistent differences between girdled and nongirdled trees in the contribution of foliar leaching to SO_4^{2-} in NTF (Table 5). Measurements of the per cent SO_4^{2-} in leaves from the girdled trees (Fig. 3) were similar to values previously measured for nongirdled yellow poplars and red maples on WBW (Johnson *et al.*, 1982).

The importance of foliar leaching to NTF SO_4^{2-} concentrations appears to vary seasonally (Fig. 5). ^{35}S and SO_4^{2-} concentrations in NTF increased just prior to and during autumn leaf fall; the increase beneath the maple tree was also accompanied by increased HCl extractability of ^{35}S from leaves. Autumnal peaks in THF SO_4^{2-} concentrations have been previously attributed to SO_4^{2-} leaching accompanying leaf senescence (Parker *et al.*, 1980).

From 4 July to 15 October (104 days), the specific activity of ^{35}S in leaves differed by less than a factor of two, therefore the ^{35}S was not markedly diluted by additions to the leaf S pool through root uptake or the assimilation of gaseous S from the atmosphere. Injection of the trees in late June, after leaf formation, probably helped to minimize dilution of the ^{35}S by additions of nonradioactive S to the leaf from root uptake.

Dry deposition estimates calculated from NTF measurements should complement other types of indirect estimates because the tree canopy itself is used to measure how much dry deposition occurs. The dry deposition SO_4^{2-}-S flux to the trees was calculated based on the SO_4^{2-} concentrations in NTF (Fig. 4), estimates of the percentage contribution of dry deposition to NTF SO_4^{2-} (Table 5), and the measured amounts of THF collected beneath the nongirdled trees over the time period 25 June–15 October. The dry deposition SO_4^{2-}-S flux to poplar No. 1 and maple No. 1 based on NTF measurements was 0.27 and 0.35 $g\,m^{-2}$, respectively.

Based on monthly mean SO_2 concentrations ($\sim 10\,\mu g\,m^{-3}$) and a canopy-scale SO_2 deposition velocity of $0.5\,cm\,s^{-1}$ (Lindberg *et al.*, 1986), the SO_2-S flux to the trees from 25 June to 15 October was $0.24\,g\,m^{-2}$. Dry deposition of additional sub-μm aerosol SO_4^{2-} ($\sim 0.05\,g\,m^{-2}$) was estimated empirically for the same time period using natural radionuclide-derived, biomass-normalized deposition velocities (Bondietti *et al.*, 1984), radionuclide–SO_4^{2-} relationships (Bondietti *et al.*, 1988), a SO_4^{2-} concen-

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tration of 10 $\mu g\,m^{-3}$ air, and leaf biomass densities (Table 1). The calculated total S flux, $\sim 0.29\,g\,m^{-2}$, compares favorably with estimates based on NTF SO_4^{2-}, indicating that both gaseous and aerosol S deposition was estimated by measurements of SO_4^{2-} concentrations in NTF.

The present data are consistent with prior studies (Mayer and Ulrich, 1978; Lindberg *et al.*, 1986), indicating that rainfall leaching of S from tree foliage is a minor contributor to the SO_4^{2-} flux reaching the forest soil in watersheds heavily impacted by atmospheric SO_4^{2-} pollution. In environments where there is little dry deposition of S, foliar leaching could still be a significant contributor to NTF SO_4^{2-}. The contribution of STF to the total SO_4^{2-} flux beneath the trees was < 10% (Garten, in press). Therefore, dry deposition of atmospheric S to red maple and yellow poplar trees on WBW was reasonably approximated during the growing season based only on the measurement of SO_4^{2-} flux in NTF.

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