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CONF-880351--1

Isotope Studies to Determine Dry Deposition of Sulfate to Deciduous and Coniferous Trees*

CONF-880351--1

DE88 006182

Task Group Project: 5C-05

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MASTER

IMPORTANCE

Experiments have been conducted at two locations near Oak Ridge, Tennessee, with radioactive ^{35}S (87 day half-life) to examine the cycling behavior of sulfur in yellow poplar (*Liriodendron tulipifera*), red maple (*Acer rubrum*), and loblolly pine (*Pinus taeda*) trees. Although these studies are funded under Task Group V, some findings pertain to methods development for estimating dry deposition of sulfur to forest canopies and the magnitude of sulfur emissions from natural sources (Task II).

PROJECT OBJECTIVES

(1) To determine through field studies, the internal cycling, storage, and biogenic emission of sulfur, as traced by $^{35}SO_4^{2-}$, in environments impacted by atmospheric sulfate deposition.

(2) To determine through isotope dilution studies, the contribution of foliar leaching and dry deposition to net throughfall (NTF) sulfate concentrations beneath deciduous and coniferous trees in such environments.

TECHNICAL APPROACH

Walker Branch Watershed (WBW) is located within 20 km of three coal-fired power plants. Approximately half of the annual sulfate input to the WBW forest is in the form of precipitation, and the other half is dry deposition (mostly vapors) (Lindberg et al. 1986). Johnson et al. (1982) showed that the atmospheric input of sulfur to the watershed far exceeded the calculated total annual sulfur requirement of the forest.

Little is known about the way that forest trees cope with sulfur in environments (like WBW) heavily impacted by atmospheric sulfate deposition. In this work, sulfur behavior in trees was studied with radioactive ^{35}S as a tracer for stable sulfur. Trees were radiolabeled by introducing the isotope into the transpiration stream (injection into the trunk).

In trees radiolabeled with ^{35}S, the initial total activity injected (corrected for radioactive decay) must balance the sum of aboveground leaching losses, leaf fall, amounts present in aboveground biomass at harvest, root storage or turnover, and biogenic emissions of volatile sulfur compounds from the tree. Using an activity balance approach, the biogenic emission of ^{35}S was estimated as the difference between the amount injected and remaining amounts measured in girdled trees.

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*Research sponsored by the Office of Health and Environmental Research, U. S. Department of Energy under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., and in part by the National Acid Precipitation Assessment Program (through the U. S. Department of Energy). Research conducted on the Oak Ridge National Environmental Research Park.

Some trees were girdled to prevent the downward translocation of ^{35}S and thereby remove the role of roots from the activity balance. In pine trees, it was possible to make field measurements of ^{35}S emissions from fascicles using a 4 L plastic chamber.

Some prior work indicates that throughfall measurements might be used to estimate dry deposition of sulfate in forests near major emission sources. The principle of isotope dilution was used to determine the contribution of dry sulfate deposition to sulfate concentrations in net throughfall (the concentration in total throughfall minus the concentration in wet deposition) collected beneath deciduous and coniferous trees. Differences between the specific activity of ^{35}S in the leaf and in net throughfall arise from the dilution of ^{35}S in net throughfall from stable sulfate in dry deposition (Figure 1). The percent contribution from dry deposition to net throughfall sulfate was calculated based on an equation for the mixing of two sources with known isotopic composition.

Each tree was radiolabeled with between 150 and 250 µCi of $^{35}SO_4^{2-}$. The amount of total S, as SO_4^{2-}, added to each tree in the labeling solution was < 20 µg. At least one tree of each species was girdled near the ground by carefully removing the bark, phloem, and cambium several weeks prior to isotope labeling. Stemflow and throughfall were collected at each tree over a period of 13 to 21 weeks after radiolabeling. Leaf fall amounts were measured and analyzed. Foliage, wood, and stump samples were obtained at regular intervals to track the distribution of ^{35}S. In order to obtain a complete accounting of aboveground amounts of ^{35}S, the trees were harvested, divided into sections, weighed, sampled, and analyzed for ^{35}S and total S.

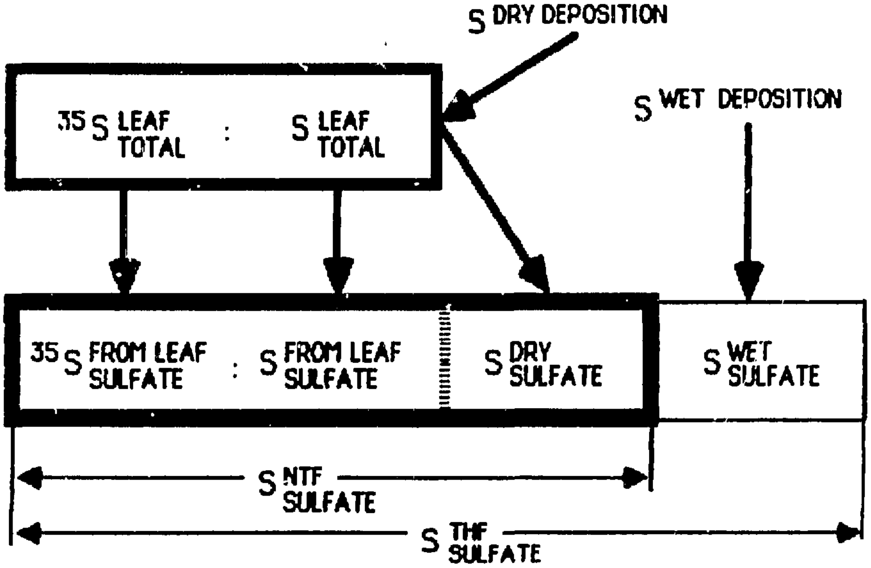


Figure 1. Schematic representation of ^{35}S and sulfate sources to throughfall (THF) and net throughfall (NTF) beneath the study trees.

Quality assurance measures included the following: 1) analysis of background samples to correct for naturally-occurring radioactivity in leaves, throughfall, and stemflow, 2) repeated counting of selected samples to follow the decay rate of ^{35}S, 3) trial analyses of leaves and stemflow with known additions of ^{35}S, 4) replicate analysis of throughfall, stemflow, 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 sulfate concentrations with analyses by ion chromatography.

RESULTS

Sulfur-35 concentrations in the study trees reached asymptotic levels within two weeks after radiolabeling. Analysis of ^{35}S concentrations in tree stumps confirmed that girdling prevented significant basipetal translocation of ^{35}S in the trees. With the exception of the girdled maple, the highest ^{35}S concentrations were usually found in the upper portions of each tree.

The final distribution of ^{35}S in the nongirdled trees (Table 1) indicated little aboveground storage of sulfur in biomass and appreciable (> 60%) capacity to cycle sulfur either to the belowground system by means of translocation or to the atmosphere by means of biogenic sulfur emissions. Foliar leaching of the ^{35}S and leaf fall represented relatively unimportant return pathways to the forest soil. Losses of volatile ^{35}S were estimated from the amount of isotope missing (approx. 33%) in the final inventories of girdled trees (Table 1). Estimated ^{35}S emission rates from the girdled trees were approximately 10^{-5} to 10^{-4} $\mu Ci\ g^{-1}$ leaf d^{-1}, and corresponded to an estimated gaseous sulfur emission of approximately 25 to 250 $\mu g\ S\ g^{-1}$ leaf d^{-1}.

Table 1. Activity balance for ^{35}S in the four study trees; all amounts are a percentage of the amount injected (I).

Item	Nongirdled Maple	Girdled Maple	Nongirdled Poplar	Girdled Poplar
Leached prior to harvest (L)	0.5	<0.1	2.4	0.4
Cumulative leaf fall (LF)	6.2	0.2	13.1	22.1
Total in aboveground biomass at harvest (W)	24.0	68.1	21.7	43.8
Volatile sulfur emission $V = I - (L + LF + W)$	29.3[a]	31.6	43.2[a]	33.7
Root storage and losses $R = I - (L + LF + W + V)$	40.0	(b)	19.7	(b)

[a] Estimate based on ^{35}S loss rate from girdled trees.

[b] Root losses were considered negligible in girdled trees.

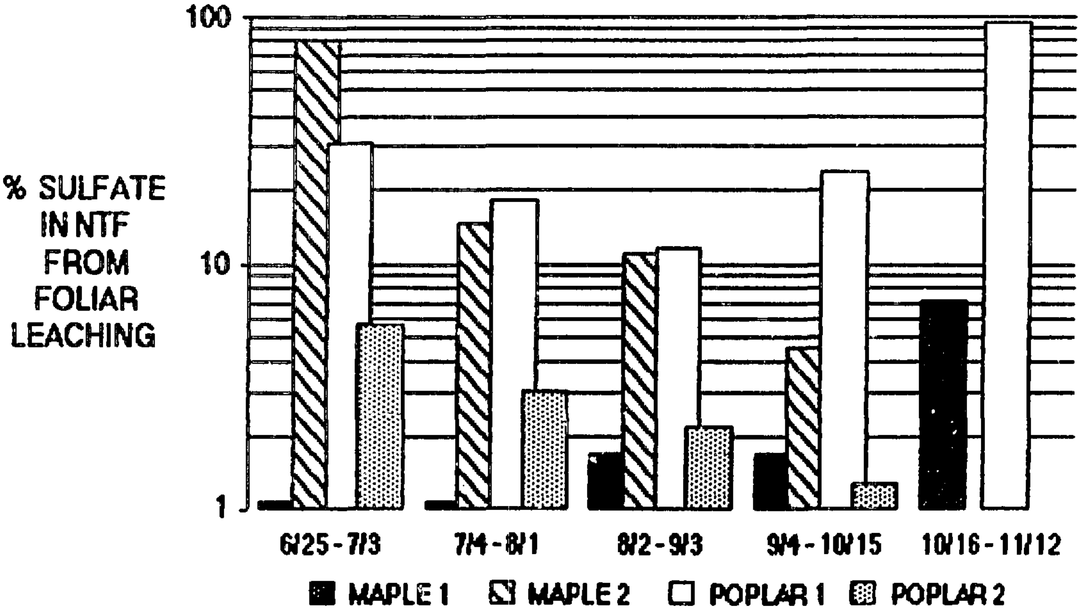
The study of isotope dilution in net throughfall was divided into four time periods prior to autumn leaf fall and a separate period during autumn leaf fall. The first period (June 25 to July 3) consisted of the eight days immediately after isotope labeling and corresponded to the time required for foliar ^{35}S concentrations to reach asymptotic levels in each tree. During the other time periods (July 4 to October 15), ^{35}S concentrations and the specific activity of ^{35}S in tree leaves varied by less than a factor of two.

During the period from July 4 to Oct. 15 (104 days), the contribution of foliar leaching to the sulfate concentration in net throughfall below red maple and yellow poplar trees ranged from 1 to

24% (Figure 2). The contribution of foliar leaching to net throughfall sulfate increased to approximately 100% during autumn leaf fall (October 15 to November 12) in the nongirdled poplar tree (Figure 2). The large contribution of foliar leaching to sulfate in net throughfall during the week after isotope labeling was an apparent artifact of isotope labeling; foliar ^{35}S concentrations were increasing and there was more leaf $^{35}SO_4^{2-}$ relative to leaf sulfate as measured by extractions with dilute HCl.

The mean contribution of foliar leaching to net throughfall sulfate concentrations was calculated to be between 1 and 19% during the summer months. Therefore, dry deposition accounted for 81 to 98% of the sulfate in net throughfall beneath the deciduous trees over the same time period. Although the contribution of stemflow to the total sulfate flux beneath the trees was < 10%, the mean contribution of foliar leaching to the net stemflow sulfate concentrations was similar to that in net throughfall.

Figure 2. Percent contribution of foliar leaching to net throughfall (NTF) sulfate concentrations beneath the study trees prior to leaf fall (June 25 - October 15) and during autumn leaf fall (October 16 - November 12).



Experiments with loblolly pine trees were begun in summer 1987 and the trees were harvested in October and November 1987. The pines ranged from 8.5 to 11.6 m in height. Aboveground portions weighed between 85 and 138 kg dry weight at harvest. Sample analyses from the pine tree study are proceeding; few data were available at the time this summary was written.

Emissions of ^{35}S from pine fascicles (approx. 10 g fresh weight) were measured using a 4 L plastic chamber. Air exiting the chamber (1.25 L min^{-1}) passed through two traps containing an alkaline cadmium hydroxide suspension. Based on literature data, this solution was > 95% efficient for trapping $H_2{}^{35}S$ emissions from the pine fascicles. Preliminary data indicated an emission rate of 10^{-6} to 10^{-4} µCi g^{-1} leaf d^{-1} and corresponded to an estimated range in volatile sulfur emission of 0.2 to 20 µg S g^{-1} leaf d^{-1}. This measured biogenic emission rate was about 10 to 100 times less than that derived for deciduous trees using a mass balance approach.

DISCUSSION

Dry deposition dominates the atmospheric sulfate 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 sulfate in net throughfall and net stemflow beneath these red maple and yellow poplar trees over the growing season. Minor leaching of foliar incorporated sulfur 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, 1985). However, the importance of foliar leaching to net throughfall sulfate concentrations appears to vary seasonally (Figure 2). Autumnal peaks in throughfall sulfate concentrations have been previously attributed to sulfate leaching accompanying leaf senescence (Parker et al., 1980).

Dry deposition estimates calculated from net throughfall 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 sulfate-S flux to the trees was calculated based on the sulfate concentrations in net throughfall, estimates of the percentage contribution of dry deposition to net throughfall sulfate (Figure 2), and the measured amounts of throughfall collected beneath the nongirdled trees over the time period June 25 - Oct. 15. The dry deposition sulfate-S flux to the trees ranged from 0.27 to 0.35 g m^{-2}, respectively.

Based on monthly mean SO_2 concentrations (10 µg 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 June 25 to Oct. 15 was 0.24 g m^{-2}. Dry deposition of additional submicron aerosol sulfate (0.05 g m^{-2}) was estimated empirically for the same time period using natural radionuclide-derived, biomass-normalized deposition velocities, radionuclide-sulfate relationships, a sulfate concentration of 10 µg m^{-3} air, and leaf biomass densities. The calculated total S flux, 0.29 g m^{-2}, compared favorably with the above estimates based on net throughfall sulfate, indicating that the sum of gaseous and aerosol S deposition was estimated by measurements of sulfate in net throughfall.

The present data are consistent with prior studies (Mayer and Ulrich, 1978; Lindberg et al., 1986) indicating that rainfall leaching of sulfur from deciduous foliage is a minor contributor to the sulfate flux reaching the forest soil in watersheds impacted by atmospheric sulfate pollution. In environments where there is little dry deposition of S, foliar leaching could still be a significant contributor to net throughfall sulfate.

CONCLUSIONS

1) During the growing season, foliar leaching accounted for <20% and dry deposition accounted for >80% of the sulfate in net throughfall beneath deciduous trees on a watershed impacted by deposition of atmospheric sulfate, therefore dry deposition of sulfur to some deciduous species in similar environments can be reasonably approximated during the summer from the measurement of sulfate flux in net throughfall.

2) The final distribution of ^{35}S in the study trees indicated little aboveground storage of sulfur in biomass and appreciable (>60%) capacity to translocate sulfur to the tree roots or release S to the atmosphere by means of biogenic sulfur emissions. Research on forest biogeochemical sulfur cycles should further explore biogenic sulfur emissions from trees as a potential process of sulfur flux from forest ecosystems.

REFERENCES

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Parker, G. G., S. E. Lindberg, and J. M. Kelly. (1980) Atmosphere-canopy interactions of sulfur in the southeastern United States, pp. 477-493. IN Atmospheric Sulfur Deposition, Environmental Impact and Health Effects (D. S. Shriner, C. R. Richmond, and S. E. Lindberg, ed.) Ann Arbor Science Publishers Inc., Ann Arbor, Michigan.

DELIVERABLES

1) Publication: Garten, Jr., C. T., E. A. Bondietti, and R. D. Lomax. Contribution of foliar leaching and dry deposition to sulfate in net throughfall below deciduous trees. Atmospheric Environment (in press).

2) Publication: Garten, Jr., C. T. Fate and distribution of sulfur-35 in yellow poplar and red maple trees. Oecologia (submitted).

3) Publication: Foliar leaching, translocation, storage, and emission of sulfur-35 from radiolabeled loblolly pine trees. (to be submitted to Ecology). Due: October 1988.

RELATIONSHIP TO OTHER WORK

This work was originally funded through the Office of Health and Environmental Research, U.S. Department of Energy, as part of a larger proposal entitled "Radionuclides in the Environment." Results from the described study will be applicable to atmospheric deposition research at a nearby site that is part of the Integrated Forest Study (IFS) supported by the Electric Power Research Institute.

ACTIVITIES

"Whole tree studies with sulfur-35 tracer." Presentation at NAPAP Terrestrial Effects Research Peer Review, Atlanta, March 8-13, 1987

"Whole tree studies with sulfur-35 tracer." Presentation at 194th ACS National Meeting, New Orleans, August 30 - September 4, 1987.

"Contribution of foliar leaching and dry deposition to sulfate in net throughfall." Presentation at Fourth Annual Gatlinburg Acid Rain Conference, Gatlinburg, October 26-27, 1987.

SUPPORT

FY 1987 $ 40 K from NAPAP (through DOE); other OHER-DOE $ 160 K; Total $ 200 K
FY 1988 $ 40 K from NAPAP (through DOE); other OHER-DOE $ 80 K; Total $ 120 K

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