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CAN SULFATE FLUXES IN FOREST CANOPY THROUGHFALL BE USED TO ESTIMATE ATMOSPHERIC SULFUR DEPOSITION?- A SUMMARY OF RECENT RESULTS

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ABSTRACT

The flux of sulfate in forest throughfall and stemflow (the sum of which is designated here as TF) may be an indicator of the atmospheric deposition of S, particularly if foliar leaching of internal plant S is small relative to washoff of deposition. Extensive data from 13 forests indicate that annual sulfate fluxes in TF and in atmospheric deposition are very similar, and recent studies with ^{35}S tracers indicate that leaching is only a few percent of total TF. However, some short-term deposition/TF comparisons show large differences, and there remain questions about interpretation of tracer results. Considering the data, we conclude that TF may be used under some conditions to estimate deposition within acceptable uncertainty limits, but that some assumptions need further testing. If TF does reflect deposition, these data suggest that commonly used methods and models seriously underestimate total S deposition at some sites.

1. INTRODUCTION AND BACKGROUND

Analysis of TF in forests (the water which falls to the ground beneath plant canopies during precipitation) has become an increasingly attractive tool for studies of atmospheric S fluxes. This method holds some advantages over other techniques such as the ability to provide long-term mean fluxes, and to estimate fluxes in highly complex terrain. However, sulfate ions in TF have both internal (foliar leaching) and external (atmospheric deposition) origins. Despite considerable recent research on the method in general, and on the importance of different sources of sulfate in TF, there remain questions about some of the method's assumptions.

The use of TF to estimate S deposition is common in the literature. In its simplest application, long-term mean TF fluxes of sulfate are suggested to be direct estimates of the total atmospheric deposition of S oxides. This assumes: 1) there is quantitative removal of deposited S by precipitation falling through the canopy, and 2) foliar leaching of internal plant S by rain is small. The term 'foliar leaching' refers to only that S which enters the plant by root uptake, is encorporated in foliage, and 'leaches' into TF during a rain event. If this is significant, it will clearly bias TF results. Stomatal uptake of deposited SO_2 may also 'leach' into TF, but does not bias TF results. SO_2 may also be irreversibly 'fixed' in the canopy to some extent, causing TF to underestimate deposition (see below). Table 1 summarizes several studies using a variety of approaches which, together, support the assumptions that 'washoff' of deposited S occurs to some extent, and that foliar leaching is a relatively small contributor of S

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to TF. If the results of these studies are universal, and if the method stands up to scrutiny, TF may provide as accurate an estimate of the long-term total atmospheric deposition of S as is possible with current techniques (± 20-30%; Hicks et al. 1986). We highlight here five field intercomparison and isotope studies of the assumptions and applicability of the TF method based on an ongoing critique of recent results (Lindberg et al. in preparation).

2. FIELD INTERCOMPARISONS

The most extensive, long-term direct comparisons between sulfate fluxes in TF and estimates of atmospheric S deposition were performed during the Integrated Forest Study (IFS) at 13 forests in the U.S., Canada, and Norway including stands of southern pine, northern hardwood, western conifer, and spruce/fir (Johnson and Lindberg in press). Using common protocols and samplers, IFS researchers measured coarse particle sulfate fluxes, and S concentrations in air, precipitation, and cloud water, and measured sulfate fluxes in TF below the forest canopy during 1986-1989. Dry and cloudwater deposition were determined using measured air concentrations and modelled deposition velocities based on meteorological and canopy structure data from each site (Hicks et al. 1987; Lindberg et al. 1988; Lovett 1988). Uncertainties in annual S fluxes were estimated to be on the order of ±30% for deposition and ±20% for TF.

The measured fluxes of sulfate in TF below these canopies strongly reflected the estimates of atmospheric S deposition. Figure 1 illustrates this relationship using mean annual fluxes at each site (from Lindberg 1991). The strength of the relationship is clear, with the variance in TF fluxes accounting for 97% of the variance in the estimated total deposition. Although the slope (0.84 ± 0.03) and intercept (170 ± 100) are different from 1 and 0, the relative difference between the two fluxes at any site (±20% or less) is within the typical uncertainty of total deposition estimates (Hicks et al. 1986). The difference between the flux of sulfate in TF and deposition (TF-deposition) indicates the general fate of sulfate in the canopy. These differences are subject to considerable uncertainty, but the trends across sites are consistent (deposition > TF at 11 sites), suggesting net foliar uptake of deposited S, most logically as SO_2 (Lindberg 1991). The data indicated a median net uptake of ~50% of deposited SO_2, which implies that the same amount washed off into TF, on average (cf. Table 1). However, the actual fate of SO_2 in the canopy may not be critical to use of the TF method in the IFS forests since SO_2 was a relatively small fraction of the total S deposition (median ~20%).

Eddy correlation measurements in a Scots pine plantation at Devilla Forest near Edinburgh (Fowler and Cape 1983) have been used to estimate dry deposition of SO_2 for a short-term comparison with simultaneous measurements of sulfate fluxes in NTF. A simple stomatal uptake model suggested that dry deposition of SO_2 could account for the sulfate deposited in NTF during summer if all stomatally absorbed S (70% of total) was removed by leaching. However, a similar calculation during autumn accounted for <10% of the sulfate in NTF, suggesting that foliar leaching was important. This conclusion was supported by a lack of temporal correlation between gas phase concentrations of SO_2 and sulfate in NTF, and by a strong relationship between rainfall amount and sulfate in NTF (Cape et al. 1987). Though the deposition of particle sulfate was not measured in this study, industrial areas with a wet, maritime climate such as this often exhibit concentrations and deposition of SO_2 that are large relative to those of aerosol sulfate (Cape et al. 1988) (eg. the mass ratio of the mean air concentrations of SO_2/SO_4^{2-} at Devilla = 5.3, while the range across the IFS sites = 0.3-1.6). Perhaps the sources of sulfate in NTF are very different in pollution climates where SO_2 dominates dry deposition. The fact that the measured sulfate flux in NTF at Devilla during autumn greatly exceeded estimates of dry deposition highlights the contrast with the better agreement between TF and deposition fluxes at the more continental IFS sites where the dry deposition of SO_2 and sulfate particles were comparable (Lindberg 1991).

It is also possible that fog and mist interception may add significantly to NTF at Devilla. The mean daily flux of sulfate in NTF at Devilla was an order of magnitude higher than the mean flux at the low elevation IFS sites (8.6 vs 0.8 mg S m^{-2}), but was in the range of values reported for the IFS mountain sites and for other European forests where fog, cloud, and mist inputs are often important (Unsworth and Fowler 1988). However, if this were not true at Devilla (Cape et al., 1988, used limited data to conclude that fog/mist inputs were small) and most of the S in NTF were actually due to foliar leaching, then this leaching flux would be 10-30 times higher than previous estimates, and would suggest a far more rapid turnover of internal S than is thought to occur in forests (Johnson 1984). On the other hand, if leaching of soil-derived sulfate is not unusually high here, then occult deposition of fog and mist must be significant, and/or conventional estimates of dry deposition rates for SO_2 and fine aerosols for this site are far too small. Input of SO_2 may be enhanced by co-deposition with NH_3 (Draaijers et al. 1989), and coarse particle fluxes (not measured at Devilla) are often significant (Davidson et al. 1985; Lindberg et al. 1990). Unfortunately, the comprehensive data to rule out any of these possibilities, including that of a significant leaching of soil-derived sulfate in the Devilla pine stand, are not yet available.

On a longer time scale, Ivens et al. (1990) compiled TF sulfate measurements from 1967-1988 at 65 forest stands in Europe. Deposition of S over this period was modelled with the Regional Acidification INformation and Simulation model (RAINS) developed at IIASA (Alcamo et al. 1990). In RAINS, the modelled wet and dry (but not occult) deposition of S is based on the average annual transport and transformation patterns provided by the EMEP II long-range transport model for 150 x 150 km grids (Eliassen and Saltbones 1983). Model estimates of S concentrations in air and rain agree with annual means within factors of two, and exhibit no obvious bias (Eliassen & Saltbones 1983, Lehmhaus et al. 1986). The comparisons showed that TF fluxes in coniferous stands (N=52) were significantly greater than modelled deposition estimates (pair t-test, $\alpha<0.05$) (Fig. 2). The mean ratio between the two was 1.8±0.9 (TF/model). A regression of TF (y) on modelled deposition (x) indicated that TF exceeded model estimates of S deposition by ~2.2 g S m^{-2} y^{-1} across a wide range of S pollution levels ($y = 0.96x+2.2$; $\alpha<0.05$). Hence, either TF flux overestimates deposition to coniferous forests, or modelled deposition underestimates the actual deposition to these forests. The overestimate of deposition by TF could be due to foliar leaching. However, the published low internal S cycling rate in many forests (~0.2 g S m^{-2} y^{-1}; Table 1), suggests that the major part of the excess observed S in NTF (~2.0 g S m^{-2} y^{-1}) is caused by an underestimate of the atmospheric deposition by the model. This underestimate of the total S deposition by the model could be due to the omission of occult deposition and co-deposition of S with NH_3, and/or to uncertainties in grid-average roughness lengths.

Interestingly, annual TF fluxes in the few deciduous (hardwood) stands studied (N=13) were not significantly different from S deposition estimated with this model ($\alpha>0.05$; mean ratio TF/model=0.9±0.3). The difference between the model behavior for deciduous and coniferous stands could be due to the smaller receptor surface of the deciduous trees during winter, an effect not accounted for in the model. Hence, one may hypothesize that the good model fit for TF in deciduous stands is valid only for annual data, due to averaging of summer and winter deposition. We are in the process of performing further comparisons on a seasonal basis to test this idea (Lindberg et al. in preparation). Although the predicted values of S deposition onto deciduous forests may be acceptable given the potential sources of uncertainty in these data, the S model clearly underestimates deposition onto areas dominated by conifers if one accepts the premise of minor foliar leaching in these stands (see following discussion).

3. ISOTOPE TRACER STUDIES

Garten and colleagues were the first to actually quantify the foliar leaching of S from tree

canopies using tracer techniques (Garten et al. 1988; Garten 1990). Eight mature red maple, yellow poplar, and loblolly pine trees located in and near the Walker Branch forest at Oak Ridge were labeled by the direct injection of $Na^{35}SO_4^{2-}$ into the tree trunks (a pulse input such as that simulated in Fig 3A). Foliar leaching of S was quantified from inventories of the tracer at the end of the study and from isotopic measurements (see below). During the growing season less than 20% of the tracer in the canopy of the labeled trees was leached by rainfall. Overall, leaching of stable S accounted for 4±12, 6±15 and 10±19%, respectively, of the sulfate in net TF (NTF) beneath the study trees (NTF=TF-precipitation). Therefore, the washoff of dry deposition from foliar surfaces was the major contributor to NTF sulfate concentrations, and total TF fluxes were dominated by wet and dry deposition (mean contribution >96%) (Lindberg and Garten 1988).

The use of isotopes in tracer experiments relies on a number of assumptions concerning the pathways and dynamics of the tracer and the substance being traced. One must assume the rapid equilibration of the isotope with non-labelled S in the tree. Since the contribution of foliar leaching to NTF sulfate in these studies was calculated from differences between the relative specific activity (RSA) in the leaf and in NTF, the issue of equilibrium is important (RSA = tracer concentration/stable S concentration in units of Bq/mg S). The RSA in the leaf and in NTF changed dynamically following addition of the tracer such that the contribution of foliar leaching to NTF sulfate could not be accurately estimated immediately following application of the tracer (Garten et al. 1988; Garten 1990). We are developing a model of S dynamics in the leaf which helps to explain this behavior of the tracer, and also why foliar S is not expected to be readily leached from tree leaves (Fig. 3).

Simulations with the model illustrate several points. First, there is a period of time required for ^{35}S tracer to reach equilibrium between various S pools in the leaf. This behavior by the model is consistent with observations from the field that show an increase in leaf ^{35}S concentrations and leaf RSA following tracer application (Garten 1988; also Cape et al. 1991- see below). Hence, immediately after addition of the tracer to the system, the behavior of the tracer is not representative of stable S. Second, different types of input (pulse or step applications) do not markedly affect estimates of the fractional leaching of S from tree leaves by rainfall over a period of several months. In the simulations presented in Figure 3, a large fraction of the tracer ^{35}S in the leaf was leached immediately after application. However, once ^{35}S reached equilibrium with stable S pools in the leaf, only ~10 to 30% of the tracer S was leached (a fractional leaching comparable to stable S). Finally, when at steady state, the calculated amount of foliar leaching based on simulations with the model is essentially in agreement with findings in the field studies at Oak Ridge; there is only minor leaching of internal foliar S by rainfall.

Despite their success, the studies at Oak Ridge do not directly demonstrate that soil-derived sulfate cannot contribute significantly to sulfate in TF. In order to study the complete cycle of sulfate from soil to canopy and back to soil, an experiment was conducted in the Scots pine forest at Devilla, in which $^{35}SO_4^{2-}$ was applied to the forest floor, and followed into the canopy and TF (Cape et al. 1991a). Unlike the Oak Ridge experiments, there was a continuous, but not constant, flux of tracer into the canopy, even over winter (such as simulated in Figure 3B). However, the gradual increase in activity in the canopy was not reflected in the amount of tracer observed in TF. The RSA in NTF was initially very high, then fell over a period of three weeks to a fairly constant low level where it remained. If it is assumed that equilibration of the tracer with unlabelled S in the canopy was relatively rapid, then the apparent contribution of soil-derived sulfate to the flux in NTF is shown in Figure 4. The initial large apparent contribution decreased to an approximately constant value within 2 months of the initial application, and implied a very small contribution (~3%) of soil-derived sulfate to the sulfate in NTF after mid-summer, as also seen in the Oak Ridge studies.

The assumption of rapid equilibration of the isotope with non-labelled S in the tree was addressed in an experiment at Devilla where shoots from 6 trees growing in the treated area were immersed in distilled water for 10 minutes, then removed and immersed similarly for 24 h (Cape and Sheppard 1991). Analysis of the resultant solutions showed that the initial washing removed 10±2 $\mu g\ g^{-1}$ dry wt sulfate with RSA=1.1±0.4 Bq mg S^{-1}, and the subsequent 24 h immersion yielded a further 10±3 $\mu g\ g^{-1}$ dry wt sulfate with RSA=40±20 Bq mg S^{-1}. For comparison, the RSA of the foliage was 76±10 Bq mg S^{-1}. The initial washoff is likely to be surface derived material from dry deposition of gas and particulate sulfate, while the second fraction has incorporated measurable root-derived tracer. Two important observations can be made: the total amount of water-leachable sulfate under these conditions was only 1% of the total S content of the needles, and the RSA of the 24-h leachate was about half that of the whole foliage. This suggests that the fraction of leachable sulfate is a small part of the total leaf sulfate content, but that the sulfate which can be leached appears to have a different isotopic composition than the total S remaining in the leaf. If the RSA of the leachable sulfate was half that of the whole leaf, the assumption of equilibrium in the tracer method would be violated and the results would lead to an underestimate of the contribution of leaching.

Thus, there are two alternative hypotheses to explain the Devilla results. The initial large RSA of NTF (Figure 4) may be seen as a period of non-equilibrium when sulfate entering the tree from the soil had very large RSA as the tracer had been concentrated near the tree roots. A quasi-steady state was then established with equilibrated soil sulfate containing a small amount of tracer continuously passing into the canopy, being fixed and equilibrating with sulfate in the tissue, and with only a small amount of sulfate removed by canopy leaching ($\sim$3%). This hypothesis (favored by the Oak Ridge group) requires a reassessment of our ideas on dry deposition of SO_2, particulate sulfate, and/or fog/mist at this site, since it implies much higher than expected S deposition. Alternatively, we (Cape et al.) may suggest that root-available sulfate is never in true equilibrium with the bulk of the soil sulfate, at least on a timescale similar to the frequency of deposition of sulfate in rain, and that what is leached from the canopy reflects the composition of root-available sulfate. The RSA of NTF then reflects the RSA of root-available sulfate rather than the RSA of the foliage as a whole, and canopy leaching actually contributes a larger (but unknown) proportion of the sulfate in NTF.

4. SUMMARY AND UNRESOLVED QUESTIONS

Data from a variety of approaches generally support the important assumptions made in using TF fluxes in forests to estimate S deposition (deposition washoff occurs and foliar leaching of plant S is minor). One could conclude from the studies described here that periodic mean sulfate fluxes in TF can be used to estimate deposition within generally acceptable uncertainty limits. If this is uniformly true, then some models and methods significantly underestimate S fluxes under certain circumstances. These may be whenever the following are important: fog/mist interception, coarse aerosol dry deposition, or co-deposition of SO_2 with NH_3. However, the Devilla data raise unresolved questions about tracer behavior and the processes which control deposition: 1) Both tracer studies show significant, but ephemeral, pulses of internal plant sulfate in TF, followed by very minor amounts. Which behavior is representative of the true contribution of internal foliar leaching? 2) What are the transport dynamics of both atmosphere- and root-absorbed sulfate through the canopy? 3) How does foliar leaching vary over the year, and across deposition gradients? 4) How important are the often-unsampled forms of S deposition (fog/mist etc.)? 5) Why are the differences between long-range transport/deposition models and TF fluxes of S in European forests geographically 'constant'? and 6) Are there 'rules of thumb' for deciding whether it is 'safe' to use TF as a surrogate of deposition (eg. in areas where the concentration ratios of SO_2/SO_4^{2-} in air are below some critical value)?

As we address these questions and continue to quantify the processes which influence S deposition, we may learn that fluxes have commonly been underestimated, and that TF does approximate deposition. For example, recent data indicate an important link between fluxes of sulfate and ammonium ions in forest TF, suggesting that S deposition is enhanced in the presence of NH_3 (Ivens, this volume). If the TF method is supported by further analyses, then TF will be important for characterizing S inputs to forests on scales where results of both long-range-transport and process-level models may be inappropriate or inaccurate.

Acknowledgements and a note to the reader. We thank the IFS research group for the data in Figure 1, and P. Kauppi, J. Alcamo and M. Posch from IIASA for providing model data for the RAINS model/TF comparison study. If the reader is struck by an apparent lack of consensus in this paper, he or she is correct. This paper has been truly 'coauthored'. Each of us contributed a summary and analysis of our recent data on the TF method, but have yet to resolve the issue of the apparent disagreement among studies. At this writing, it is equally possible that we will conclude the method to be of limited use or to be universally applicable; this awaits further debate (Lindberg et al. in preparation).

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Table 1. Studies of sulfur "washoff" from plant surfaces and of "foliar leaching" of sulfur from plant canopies.

Location	Vegetation Type	Methods	Results
laboratory[1]	isolated cuticles	$^{35}SO_4^{2-}$	SO_4^{2-} washes off completely.
laboratory[2]	spruce branches	wind tunnel	Soluble particles are washed off.
Tennessee[3]	oak leaves	leaf washing	Aerosol SO_4^{2-} washes off.
California[4]	chaparral leaves	leaf washing	Aerosol SO_4^{2-} washes off.
Georgia[5]	pine shoots	$^{35}SO_2$	~50% of SO_2 washes off.
Sweden[6]	spruce forested catchment	watershed mass balance	Internal S does not influence TF.
Germany[7]	several forests	ecosystem S cycles	S foliar leaching minor part of TF.
Tennessee[8]	oak/hickory forest	ecosystem S cycles	S foliar leaching minor part of TF.
Tennessee[9]	(same forest)	canopy balance	S foliar leaching minor part of TF.
Tennessee[10]	pine forest	sequential TF	S washoff indicates surface removal.
N. Carolina[11]	deciduous leaves	leaf washing	S washoff indicates surface removal.
Tennessee[12]	oak/hickory forest	N fertilizing	Foliar SO_4^{2-} reduced by fertilizing, but TF flux of SO_4^{2-} not effected; conclude that foliar leaching is minor.
Germany[13,14]	spruce forests	soil amendments	Adding H_2SO_4, $(NH_4)_2SO_4$, or $MgSO_4$ does not effect TF flux of SO_4^{2-}.
Sweden[15]	spruce forests	soil amendments	Adding Na_2SO_4, or elemental S does not effect TF flux of SO_4^{2-}.

[1](Yamada et al., 1964, 1966); [2](McCune and Lauver, 1986); [3](Lindberg and Lovett, 1985); [4](Bytnerowicz et al., 1987); [5](Gay and Murphy, 1989); [6](Hultberg, 1985); [7](Meiwes and Khanna, 1983); [8](Johnson, 1984); [9](Lindberg et al., 1986); [10](Schaefer and Reiners, 1990); [11](Potter and Ragsdale, 1991); [12](Richter et al., 1983); [13](Zöttl et al., 1989); [14](Kreutzer, 1989); [15](Hultberg and Grennfelt, 1990).

FIGURE CAPTIONS

Figure 1. Relationship between the estimated total atmospheric deposition of SO_4^{2-} and the measured flux of SO_4^{2-} in throughfall for sites in the Integrated Forest Study.

Figure 2. The flux of S in throughfall vs. RAINS/EMEP-II long-range transport and deposition model estimates of S deposition at 52 coniferous stands in Europe.

Figure 3. Model simulation of the fraction of stable S and tracer ^{35}S leached by rainfall from tree leaves when the tracer is applied as a pulse input (A) or a continuous, step input (B).

Figure 4. Apparent contribution of the leaching of soil-derived sulfate to the flux sulfate in net throughfall (NTF), assuming rapid tracer equilibration in the canopy; calculated as (relative specific activity in NTF)/(relative specific activity in canopy due to soil uptake of $^{35}SO_4^{2-}$)X100%.

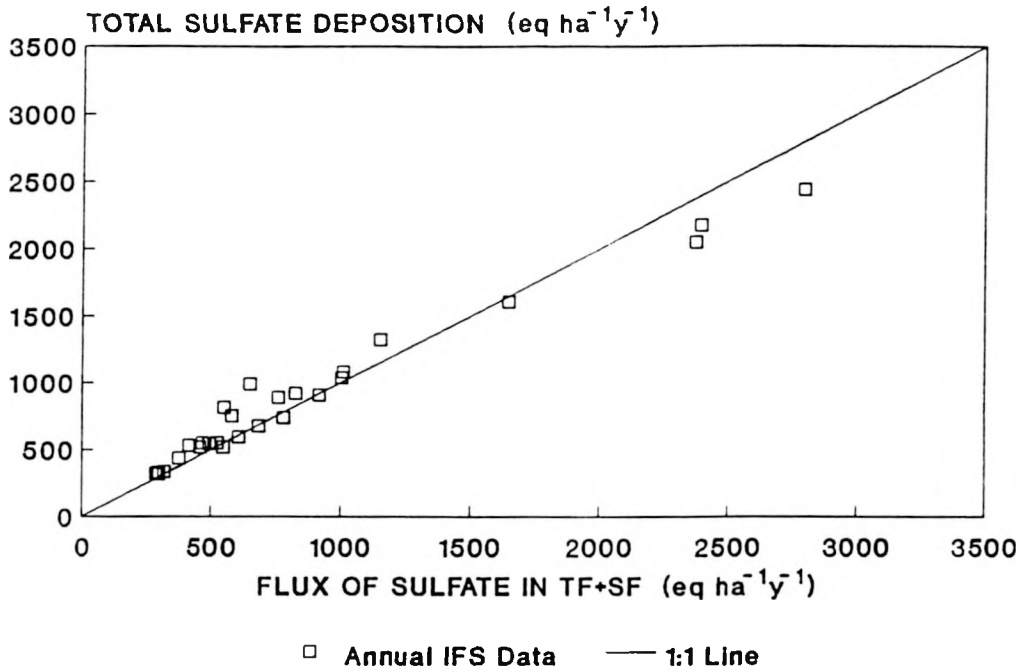
TOTAL SULFATE DEPOSITION (eq ha⁻¹y⁻¹)
3500
3000
2500
2000
1500
1000
500
0
0
500
1000
1500
2000
2500
3000
3500
FLUX OF SULFATE IN TF+SF (eq ha⁻¹y⁻¹)
Annual IFS Data
1:1 Line

Fig. 1

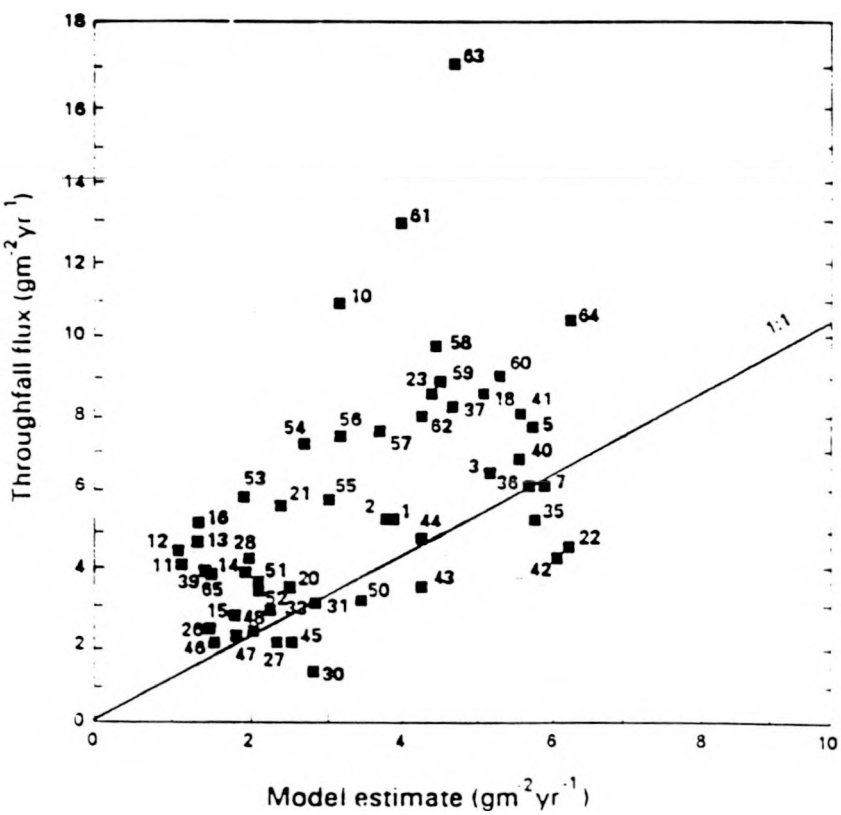
Throughfall flux (gm⁻²yr⁻¹)
Model estimate (gm⁻²yr⁻¹)
1:1
0
2
4
6
8
10
12
14
16
18
63
61
10
64
58
60
59
23
18
41
37
5
62
56
54
57
40
3
38
7
53
21
55
2
1
44
35
22
16
12
13
28
11
14
51
20
42
39
65
43
50
31
15
45
27
30

Fig. 2

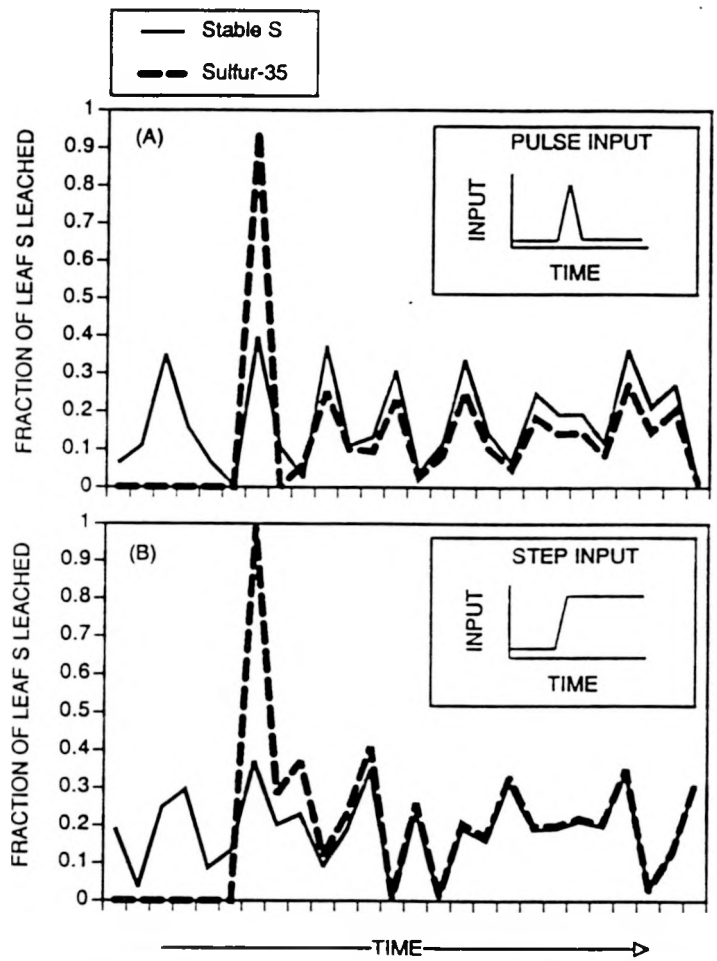
Stable S
Sulfur-35
(A)
PULSE INPUT
INPUT
TIME
FRACTION OF LEAF S LEACHED
(B)
STEP INPUT
INPUT
TIME
FRACTION OF LEAF S LEACHED
TIME

Fig. 3

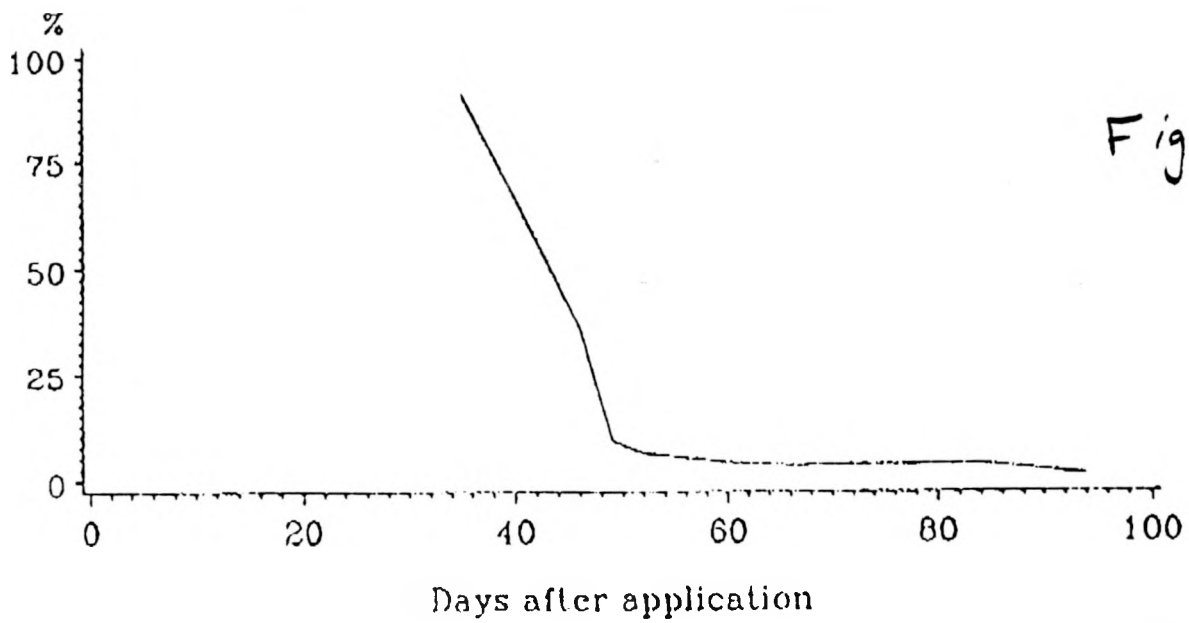
%
100
75
50
25
0
0
20
40
60
80
100
Days after application

Fig. 4