

IVL REPORT

SN

L91-25

Sulphur and seasalt deposition as reflected by throughfall and runoff chemistry in forested catchments

Göteborg 1991-02-13

SWEDISH ENVIRONMENTAL RESEARCH INSTITUTE

Hans Hultberg
Peringe Grennfelt

Presented at the International Conference on Acid Deposition in Glasgow 16-21 September 1990. To be published in Environmental Pollution 1991.

B-1009
Göteborg
1991

IVL
INSTITUTET FÖR VATTEN- OCH LUFTVÅRDSFORSKNING
SWEDISH ENVIRONMENTAL RESEARCH INSTITUTE

Organisation/Organization IVL INSTITUTET FÖR VATTEN- OCH LUFTVÅRDS- FORSKNING Address/Address Box 47086 402 58 GÖTEBORG Telefonnr/Telephone 031-460080	RAPPORTSAMMANFATTNING Report Summary
Rapportförfattare (efternamn, tilltalsnamn) Author (surname, christian name) Hans Hultberg Peringe Grennfelt	Projekttitel och ev SERIX projektnr Anslagsgivare för projektet/Project sponsor SNV IVL programbudget m fl
Rapportens titel och undertitel/Title and subtitle of the report Sulphur and seasalt deposition as reflected by throughfall and runoff chemistry in forested catchments.	
Sammanfattning/Summary At forested catchments at Lake Gårdsjön on the Swedish west coast the deposition and runoff chemistry has been followed during the period 1979-1990 by throughfall and runoff measurements as well as by measurements of atmospheric concentrations. The 10 year means in throughfall and runoff is very similar for sulphur and the main seasalt ions sodium and chloride; for sulphur 26.1 and 27.6 kg/ha/yr, for sodium 49 and 52 kg/ha/yr and for chloride 96 kg/ha/yr and 93 kg/ha/yr respectively. The actual flows are 100 - 200% higher than the wet deposition as collected in open bulk precipitation collectors indicating a very large input by dry deposition. One important question is to what extent the throughfall and runoff values can be used as measures of total deposition. From throughfall and runoff studies at different experimental catchments we will present a number of results illustrating the possibilities of using throughfall and runoff data as measures of atmospheric deposition of sulphur and seasalt.	
Förslag till nyckelord samt ev anknytning till geografiskt område, näringsgren eller vattendrag/Keywords Catchment, sulphur, nitrogen, acidification, deposition.	
Bibliografiska uppgifter/Bibliographic data IVL - publ. B-1009	
Beställningsadress för rapporten/Ordering address IVL, Biblioteket Box 21060, S-100 31 Stockholm, Sweden	

Sulphur and seasalt deposition as reflected by throughfall and runoff chemistry in forested catchments

Hans Hultberg and Peringe Grennfelt, Swedish Environmental Research Institute, P O Box 47086, S-40258 Göteborg, Sweden

ABSTRACT

At forested catchments at Lake Gårdsjön on the Swedish west coast the deposition and runoff chemistry has been followed during the period 1979-1990 by throughfall and runoff measurements as well as by measurements of atmospheric concentrations. The 10 year means in throughfall and runoff is very similar for sulphur and the main seasalt ions sodium and chloride; for sulphur 26.1 and 27.6 kg/ha/yr, for sodium 49 and 52 kg/ha/yr and for chloride 96 kg/ha/yr and 93 kg/ha/yr respectively. The actual flows are 100 - 200% higher than the wet deposition as collected in open bulk precipitation collectors indicating a very large input by dry deposition. One important question is to what extent the throughfall and runoff values can be used as measures of total deposition. From throughfall and runoff studies at different experimental catchments we will present a number of results illustrating the possibilities of using throughfall and runoff data as measures of atmospheric deposition of sulphur and seasalt.

INTRODUCTION

Within the UN ECE Convention for long range transported transboundary air pollution, critical loads are being applied as a basis for the development of abatement strategies. In this work it is necessary to compare the maps of critical loads with the deposition and link the deposition back to the sources. In linking the deposition with the emissions the intention is to use models describing transboundary fluxes, e.g. those developed within the EMEP programme. One essential drawback with these models today is that they are estimating mean depositions over large areas, e.g. 150x150 kilometres, and not taking into account the variability in surface structure, which in many cases may severely affect the deposition. This is especially the case for the deposition to coniferous forests, where deposition may be much larger than to open land. Forests are moreover often grown on soils which are more sensitive to acidification and thus being the determining receptor areas for the critical loads.

Quantifying inputs of acidifying substances to different types of receptors has been a major research area for many years. In most cases this problem has been tackled from the atmosphere, using different micrometeorological methods in order to quantify the flux. The micrometeorological approaches have many drawbacks, the limitation to certain terrain situations (mostly flat land) being one of the most important.

Another way to determine the input to forested areas has been the use of throughfall measurements. This method has been widely used at least for the quantification of the input of sulphur. The most important drawback of the throughfall method is probably the risk of interaction with the forest canopy, which for ammonium and nitrate may cause losses and for potassium and calcium may give extra fluxes due to internal circulation in the forest stand.

A third way of monitoring is to use outflow monitoring from small catchments. This method is only applicable to elements which are transported through the system without any large losses or without leaching.

In the Lake Gårdsjön acidification research area on the Swedish west coast we have, since 1979, studied deposition and flows within small catchments in order to quantify processes and changes in a forested ecosystem under stress from acid deposition. The studies have been undertaken in a number of catchments, some of them used for different experiments, e.g. treatments with acidifying or neutralizing agents in order to understand and quantify the effects of different changes in deposition or land use. (Hultberg 1985, Hultberg and Grennfelt 1986, Hultberg et al 1990, Westling and Hultberg 1990)

In our studies we have found that the small catchments within the watershed behaved very similarly although there might be differences in the absolute levels of the flows. This parallel behaviour makes it possible, after calibration, to experimentally treat different catchments and follow the changes caused by the treatment.

EXPERIMENTS AND STUDIES IN CATCHMENTS

Lake Gårdsjön is surrounded by many well-defined headwater catchments in which soils and water are chemically acidified due to sulphur deposition (Hultberg and Grennfelt 1986). Nitrogen deposition is high, yet most of the incoming nitrogen is retained in the terrestrial ecosystem (Grennfelt and Hultberg 1986).

The area is characteristic of acidified regions of the Swedish west coast and southern Norway with granite and gneissic bedrock overlain by thin podsollic soils developed from glacial material. Vegetation is dominated by Norway spruce stands of various ages up to > 80 years.

Whole catchment manipulation experiments have been performed since 1984 (Table 1). These manipulations have included fertilizer addition of nitrogen, liming and acidification with elemental sulphur as well as addition of sodium sulphate as a neutral salt. Clearfellings have also been performed in the area in order to study possible effects on the dry deposition of sulphur and sea salts. These experiments and ongoing long term studies provide details on dry and wet deposition which are summarized below.

In a new experiment, we also plan to decrease atmospheric deposition by building a roof in one 6000 m² catchment. This experiment is mainly designed to study the effect of decreased sulphur, nitrogen and mercury deposition in a forest ecosystem severely affected by acid deposition.

RESULTS

Element fluxes through the catchments

The yearly means of wet deposition, throughfall and runoff for chloride, sodium and sulphate are presented in Table 2. The mean fluxes in runoff and throughfall are very similar for the three ions. For chloride, the mean runoff is 93.3 kg/ha/yr and the mean throughfall is 96.0 kg/ha/yr. The agreements between outflow and throughfall are almost as good for sulphur (27.6 kg/ha/yr and 26.1 kg/ha/yr) and sodium (52.0 and 49.0 kg/ha/yr respectively). The large deposition of chloride and sodium is because the catchment is situated less than 20 kilometres from the sea. In fact sodium and chloride are the dominating ions in the flow through the catchment. Comparison with the wet deposition shows that the runoff and the throughfall are about 100-200% larger than the input by precipitation. The difference between the wet deposition and outflow/throughfall is largest for sodium and chloride and smallest for sulphur.

*Particulate dep
or wet
outflow !!!*

total S etc ?

The very close connection between outflow and throughfall as well as the similar difference between wet deposition and throughfall/runoff may suggest that

- throughfall and runoff in these areas are good measures of the total deposition of the elements sulphur, sodium and chloride, and
- the difference between throughfall/runoff and wet deposition is a good measure of the dry deposition.

(and fog)

Deposition of seasalt

Comparing the chloride and sodium fluxes with the seasalt composition shows that there is a balance between chloride and sodium in the wet deposition, an excess of chloride (7.8 kg/ha/yr, 9%) in the throughfall while there is a slight excess of sodium (2.8 kg/ha/yr, 6%) in the runoff. In throughfall, excess chloride occurs over the whole period 1980-1990 except for 1988/89. Less than 1 kg/ha/yr may be attributed to the excess chloride in wet deposition, but is the rest due to deposition or may there be internal circulation of chloride? The excess chloride in throughfall may be due to deposition of chloride from other sources or to deposition of HCl formed by the decomposition of seasalt into gaseous HCl and sodium-enriched seasalt particles. Such reactions may occur between gaseous nitric acid and sea salt

particles. The studies undertaken so far give no clear evidence of the importance of the different processes, but as will be mentioned below treatment with sodium sulphate gave a parallel pulse in chloride, indicating that chloride, at least during certain circumstances, may be a mobile anion giving extra throughfall fluxes.

We have studied the addition of sodium to the soil to see if this will give increased circulation of sodium within the forest (Hultberg et al 1990). In one catchment 285 kg/ha/yr sodium as sodium sulphate was applied; approx 130 kg in the autumn 1985 and the rest about one year later. At the first treatment we detected a small peak of sodium (< 5 kg/ha) in throughfall during the first month after application. The reason may be caused by the extra input of sodium but there may be other, indirect, reasons. The difficulties in explaining the effect are due to other ions e.g. potassium, chloride and ammonium also increasing compared to the reference catchment (Figure 1). After this short term peak no extra sodium was observed in the throughfall, not even after the second treatment with sodium sulphate.

In the runoff there is an excess in sodium, compared to the amount expected from the Na/Cl ratio in sea salt, caused by leaching of sodium from weathering of soil minerals.

Our conclusions are that throughfall and outflow monitoring mostly give fairly good measures of the sea salt deposition although there might be problems with internal circulation of chloride and leaching of sodium.

Sulphur deposition

One important question for the understanding and quantification of sulphur deposition is the importance of the receptor. The Lake Gårdsjön watershed consists of a number of small catchments with varying forest cover due to clearfelling during the last 10-20 years. In mass balance studies the sulphur outflows from these catchments were determined. By plotting the outflow of sulphur per hectare and year against the forest cover we found a strong linear relationship, showing a relative runoff of approx 30 kg S/ha/yr for the catchments with 100% mature forests and about 12 kg sulphur per hectare and year for the completely clearcut area (Figure 2) (Hultberg 1985). The clearcut area gave about the same outflow as the monitored wet deposition measured by open gauges.

The importance of forest cover is further illustrated in Figure 3, where the yearly runoff of sulphur is shown for the reference catchment and a catchment which was initially 40% covered by trees and was then clearcut. The runoff of sulphur decreased immediately indicating a very short retention time of deposited sulphur in the catchment. We had expected an increase in sulphur outflow due to mineralisation of the sulphur pool in the soil. Thus the sulphur pool seems bound very strongly to the soil. Not even treatment with limestone (6.5

tonnes per hectare) showed a significant increase in the sulphur output. This is important as the total amount of sulphur in the soil is approx 1 tonne sulphur per hectare. This sulphur seems, however, to be rather stable, due to binding to the organic compounds in the soil (Olsson et al 1985).

The retention time for sulphur may be further illustrated by results from the experimental treatment with sodium sulphate (Figure 4). In this experiment the outflow of sulphur was comparatively fast and approx 70 % was released from the catchment in one year and 95% had left the catchment 3 years after the second application. Figure 4 also shows the results of a model calculation for the water transport through the catchment. Sulphur is transported as fast through the catchment as the water (Hultberg et al 1990). The present retention capacity of sulphur in the soil is obviously low.

Internal circulation of sulphur has for many years been one of the most serious objections against the throughfall method. In two of our experiments, those where the soil was treated with extra inputs of sulphur (sodium sulphate and elemental sulphur), it is possible to clarify the problem to some extent. In the treatment with sulphate as well as with elemental sulphur we found no increase in sulphur concentrations in throughfall (Figure 5). In the treatment with elemental sulphur the concentrations of sulphate in the runoff increased with approx 60% throughout the following three years (Figure 6). Since the elemental sulphur is oxidized to sulphate in the upper part of the soil the tree roots were exposed to significantly higher sulphate concentrations. The higher sulphate concentrations did not show any increase in the throughfall of sulphate throughout the whole experimental period. Thus, uptake of sulphur by tree roots and transport to the tree canopy seems to be of minor importance for sulphur in throughfall. Accumulation of sulphur in the canopy of the tree is also of minor importance. In a study of net accumulation of elements in forest biomass we found that approx 0.5 kg S/ha/yr was bound in the forest trees (including roots) (Hultberg 1985). The accumulation of sulphur in the remaining vegetation was not determined but total accumulation will not exceed 1 kg/ha/yr.

The deposited sulphur has essentially two origins. One part is of anthropogenic origin and the rest is mainly sea salt particles. Assuming that all sodium in precipitation and throughfall is of marine origin and that sea salt sulphur is associated with sodium in the same ratio as in sea water, it is possible to estimate the marine seasalt contribution to the sulphur deposition. (Table 3) The sulphur from sea salt estimated in this way may account for about 10% of the wet deposition and almost 14 % of the throughfall flux. Based on the averages for the ten hydrological years 79/80 to 89/90 the non-marine wet deposition of sulphur is calculated to 11.6 kg/ha/yr. The remaining part in throughfall, after subtracting for the wet deposition, we assume to be the dry non-marine sulphur deposition and is calculated to 10.5 kg/ha/yr. If the

runoff is treated in the same way we get a "non-marine dry deposition" of 11.6 kg/ha/yr. The large variations in sulphur output by runoff (± 5 kg/ha/yr) reflect the large variations in water fluxes between years.

The commonly used approach for estimating the dry deposition of sulphur to forest ecosystems has been the use of atmospheric concentration data and deposition velocities. In an early study of the deposition to the Lake Gårdsjön using the data for the first two years of monitoring we applied a deposition calculation model using different deposition velocities, depending on the actual deposition situation (Grennfelt et al 1985). The calculated sulphur deposition 25-31 kg/ha/yr was in good agreement with the monitored throughfall and runoff of sulphur, 25 and 29 kg/ha/yr respectively (Hultberg 1985).

Another way of considering the deposition problem is to use the calculated deposition, monitored atmospheric concentrations and estimate the deposition velocities. At the reference catchment the non-marine dry sulphur deposition was, as calculated earlier, 10.5 and 11.6 kg S/ha/yr respectively. The concentrations of sulphur dioxide and particulate sulphate were $3.4 \mu\text{g S/m}^3$ and $1.3 \mu\text{g S/m}^3$ respectively. If we assume that sulphur dioxide and particulate sulphate were deposited by the same deposition velocity we get a mean deposition velocity for the 10 year period of 0.7 to 0.8 cm/s. For the clearcut area where the dry deposition was less than 2 kg S/ha/yr the corresponding deposition velocity was calculated to less 0.15 cm/s.

FINAL REMARKS

Monitoring of catchments over long periods may be an essential tool in judging long term changes in deposition. It is of course important that the catchments do not undergo large changes in terms of clearcutting, storm felling or increased filtering biomass by growth as in young forests. In the Lake Gårdsjön area we have studied mature forests with very small changes in forest growth during the studied period.

From 1979/80, when the measurements started, there has been reported a substantial decrease in sulphur emissions in west Europe, in many countries a decrease of about 50% during the ten year period 1980-1990. It is important to know to what extent these reductions may be reflected in the deposition or other measurements in the field. Although we know that there are many difficulties in observing long term trends, such as yearly variations in meteorological conditions and that our data only represent one monitoring station, it is intriguing to see that there is no downward trend in the observed sulphate concentrations, neither in wet deposition nor in throughfall (Figure 7). In fact throughfall monitoring indicates an increase in sulphate concentrations. H^+ concentrations in precipitation and throughfall also shows no downward trend.

The very close connection between sulphur flux in throughfall and outflow, as well as the lack of increased leaching from the canopy in the sulphate-treated catchments, support the hypothesis that throughfall and runoff monitoring will give a reasonably good measure of the total sulphur deposition for Norway spruce stands as well as deciduous forests (Likens et al 1990). Similar results have been described for deciduous forests, where root uptake was shown to be unimportant for the crown leaching of sulphate (Lindberg et al 1986). Increased sulphur leaching from Sitka spruce plantations have, however, been observed when sulphate concentrations in soil water increased. (Hornung, pers comm.). Some tree species may therefore lack the ability to avoid excess root uptake.

The use of throughfall monitoring has during the last years been the focus of increasing interest. Westling and Hultberg (1990) and Lövblad et al (1990) have compiled and evaluated throughfall data from a number of stations in northern Europe. They show that the throughfall may vary considerably depending on tree species, exposure situation etc, but the data all show that dry deposition is a very important part of the total deposition to forest ecosystems especially for Norway spruce.

REFERENCES

- Grennfelt, P., Larsson, S., Leyton, P. and Olsson, B. (1985). Atmospheric Deposition in the Lake Gårdsjön Area, SW Sweden. *Ecol. Bull.* 37, 101-108.
- Grennfelt, P. and Hultberg, H. (1986). Effects of Nitrogen Deposition on the Acidification of Terrestrial and Aquatic Ecosystems. *Water, Air and Soil Pollut.* 30, 946-963.
- Hornung, M. (1990). Personal Communication. Institute of Terrestrial Ecology, Grange-on-Sands, Cumbria, UK.
- Hultberg, H. and Grennfelt, P. (1986). Gårdsjön Project: Lake Acidification, Chemistry in Catchment Runoff, Lake Liming and Microcatchment Manipulations. *Water, Air and Soil Pollut.* 30, 31-46.
- Hultberg, H., Lee, Y.H., Nyström, U. and Nilsson, S.I. (1990). Chemical Effects on Surface-, Ground and Soil-Water of Adding Acid and Neutral Sulphate to Catchments. *Phil. Trans. R. Soc. Lond. A.* (In press).
- Likens, G.E., Bormann, F.H., Hedin L.O., Driscoll, C.T. and Eaton, J.S. (1990). Dry deposition of sulfur: a 23-year record for the Hubbard Brook Forest ecosystem. *Tellus* 42B, 319-329.

Lindberg, S.E., Lovett, G.M., Richter, D.D. and Johnson, D.W. (1986). Atmospheric Deposition and Canopy Interactions of Major Ions in a Forest. *Science* 231, 141-145.

Lövblad, G., Westling, O., Ivens, W. and Kauppi, P. (1990). Throughfall Monitoring as a Means of Monitoring Deposition to Forest Ecosystems - Evaluation of European Data. Prepared for the UN-ECE and the Nordic Council of Ministers (NMR). (In press).

Olsson, B., Hallbäcken, L., Johansson, S., Melkerud, P-A., Nilsson, I. and Nilsson, T. (1985). The Lake Gårdsjön area - physiological and biological features. *Ecol. Bull.* 37, 10-28.

Westling, O. and Hultberg, H. (1990). Liming and Fertilization of Acid Forest Soils - Short-term Effects on Runoff from Small Catchments. *Water, Air and Soil Pollut.* (In press).

TABLE 1
The Gårdsjön projekt. Overview of experimental catchments and treatments
conducted since 1984.

Catchment	Treatment	Area (ha)	Treatment date
F1	Control	3.7	-
F2	Liming, dolomite	3.4	June 1984
F3	Clearfelling	3.0	April 1984
F4	NH ₄ NO ₃	2.6	August 1984
F5	Elemental S	3.1	October 1985
L1	Na ₂ SO ₄	2.5	October 1985
BE	Liming + NH ₄ NO ₃	4.1	August 1985
BW	Liming	5.3	October 1985
KN	Liming + NH ₄ NO ₃	3.9	August 1985
G1	Roof	0.6	Winter 1990
G2	NITREX	0.5	Winter 1990

TABLE 2

Chloride, sulphur and sodium in runoff (RO), throughfall (TF) and wet deposition (WD) at the reference catchment at the Lake Gårdsjön watershed 1979-1989. The flows are expressed as kg/ha/yr of each element.

YEAR	CHLORIDE			SULPHUR			SODIUM		
	Cl			SO ₄ -S			Na		
	RO	TF	WD	RO	TF	WD	RO	TF	WD
79/80	74.7	-	12.4	27.9	-	13.3	47.4	-	5.6
80/81	85.2	78.5	21.4	29.5	23.8	10.1	49.1	41.6	11.9
81/82	116.5	98.4	40.3	31.1	25.7	11.1	51.5	41.1	19.8
82/83	130.5	124.3	50.7	38.7	30.9	16.7	69.3	64.5	25.1
83/84	104.3	100.7	40.5	18.2	21.7	11.8	47.4	53.5	21.2
84/85	91.6	63.7	24.6	29.6	28.1	14.3	56.4	32.1	11.3
85/86	72.6	73.1	27.8	29.3	22.1	11.7	51.0	34.7	16.7
86/87	96.4	104.3	29.4	33.7	30.9	15.7	64.4	54.0	16.7
87/88	49.7	60.8	19.9	23.8	26.9	15.3	37.0	32.0	13.7
88/89	82.3	123.7	30.5	16.0	26.4	11.4	39.0	71.4	17.7
89/90	104.2	132.4	36.3	26.2	25.0	12.5	54.8	65.4	21.2
Average									
11 yr	91.6±21.3	--	30.3±10.5	27.6±6.2	--	13.1±2.0	51.6±9.2	--	16.4±5.3
80/81-									
89/90									
10 yr	93.3±21.6	96.0±24.7	32.1±9.2	27.6±6.5	26.1±3.0	13.1±2.1	52.0±9.5	49.0±14.0	17.5±4.2

TABLE 3

Yearly means of total sulphur and excess sulphur in throughfall (TF), runoff (RO), and wet deposition (WD) and excess "non-marine dry deposition" (DD) of sulphur in throughfall and runoff (kg/ha/yr).

YEAR	TF _{tot}	TF _{excess}	RO _{excess}	WD _{excess}	DD (TF) _{excess}	DD (RO) _{excess}
80/81	23.8	20.4	25.5	9.1	11.3	16.4
81/82	25.7	22.3	25.6	9.5	12.8	16.1
82/83	30.9	25.5	32.5	14.6	10.9	17.9
83/84	21.7	17.3	13.3	10.1	7.2	3.2
84/85	28.1	25.4	25.3	13.3	12.1	12.0
85/86	22.1	19.2	25.8	10.3	8.9	15.5
86/87	30.9	26.4	29.2	14.3	12.1	14.9
87/88	26.9	24.2	21.4	14.2	10.0	7.2
88/89	26.4	20.4	12.1	9.5	10.9	2.6
89/90	25.0	19.6	21.3	10.7	8.9	10.6
Average 10 yr	26.1±3.0	22.1±3.0	23.2±6.1	11.6±2.1	10.5±1.7	11.6±5.3

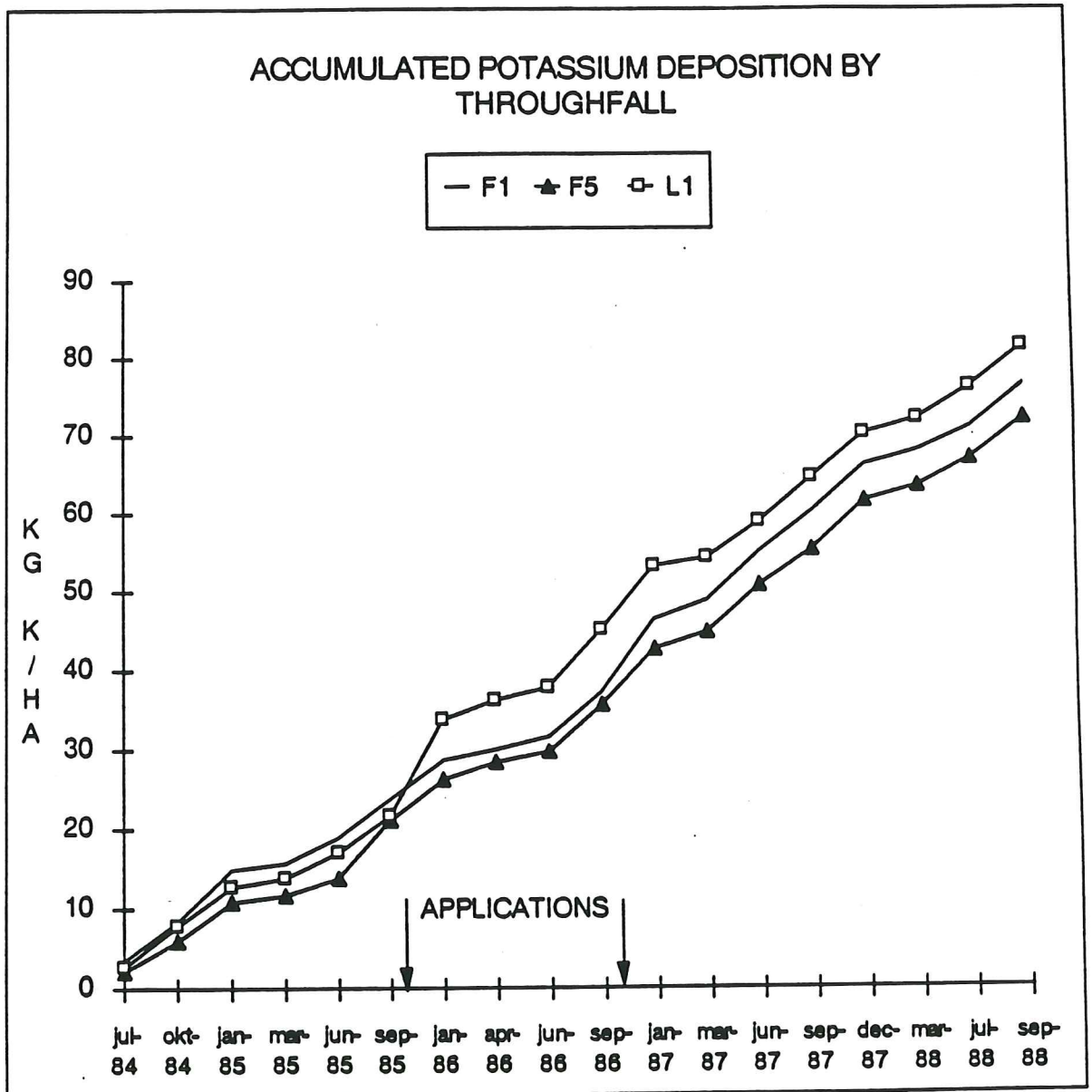


Fig. 1. Accumulated potassium deposition by throughfall after applications of Na_2SO_4 to catchment L1 and elemental sulphur to catchment F5. F1 is the reference catchment.

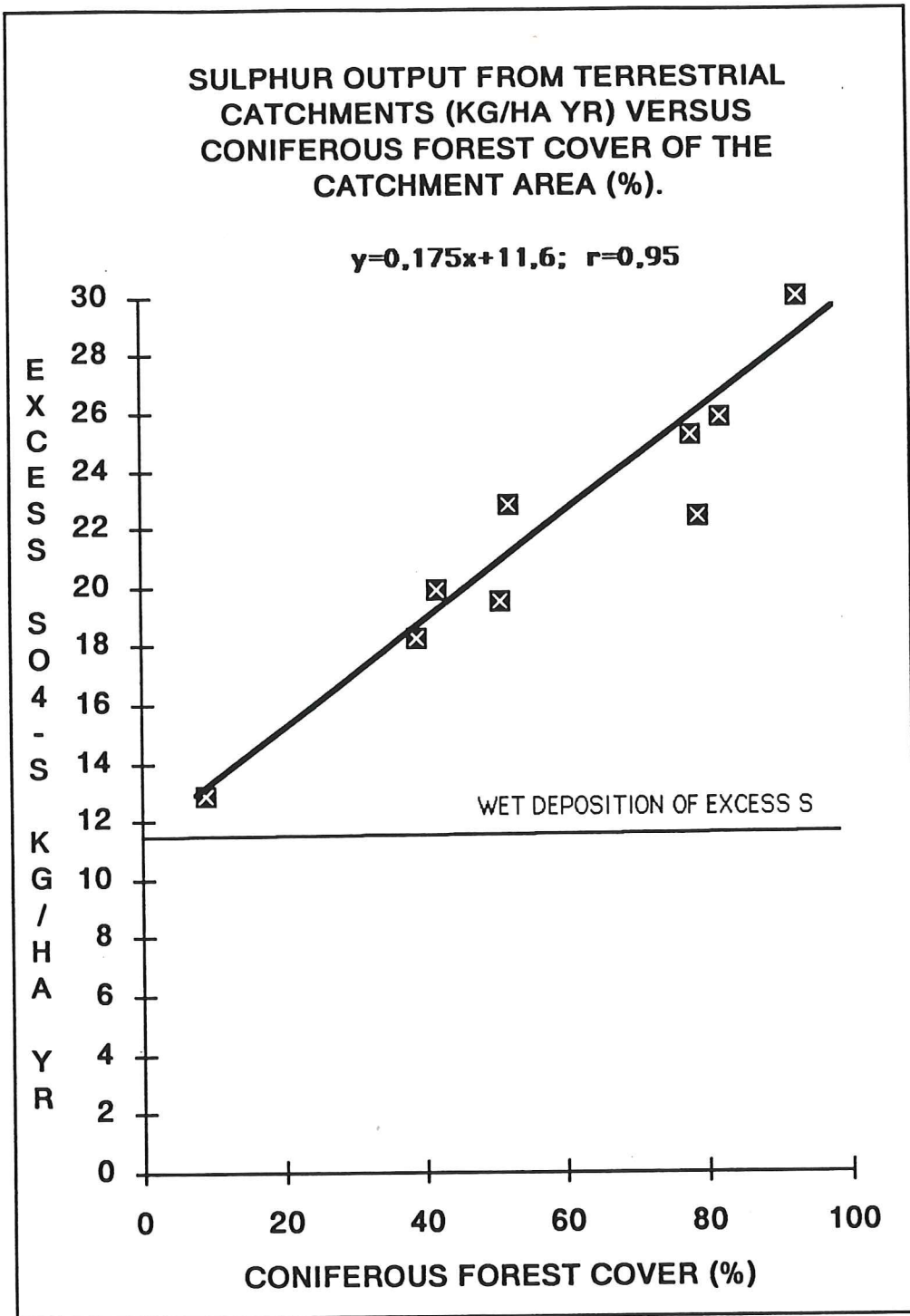


Fig. 2. Linear regression between output of sulphur from terrestrial sub-catchments versus the percentage of coniferous forest cover within the Lake Gårdsjön area. (Hultberg 1985).

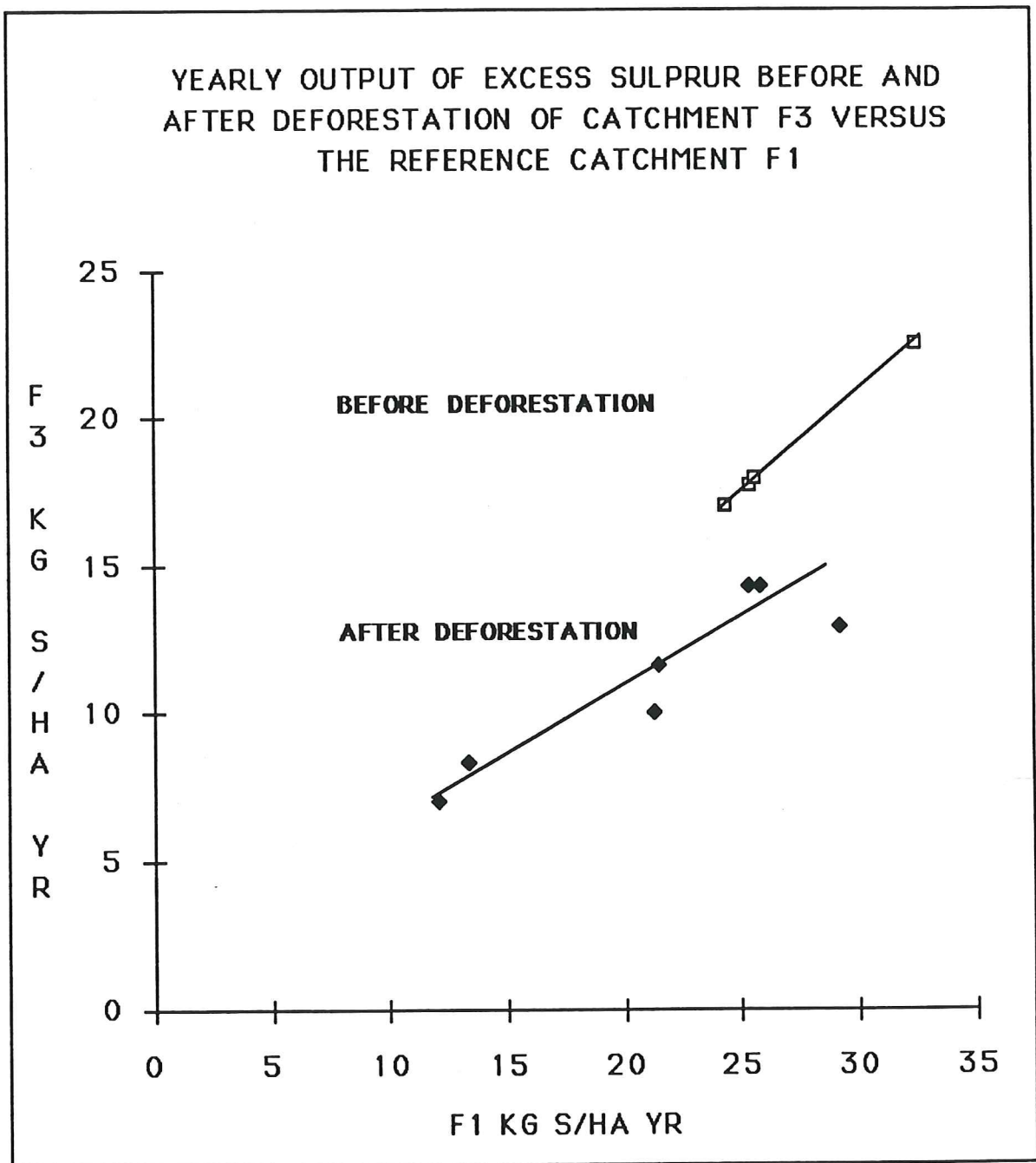


Fig. 3. Yearly output of excess sulphur (kg/ha,yr) before and after deforestation of catchment F3 versus the reference catchment. Before deforestation represents the years 1979/80-82/83. After deforestation 1983/84-89/90.

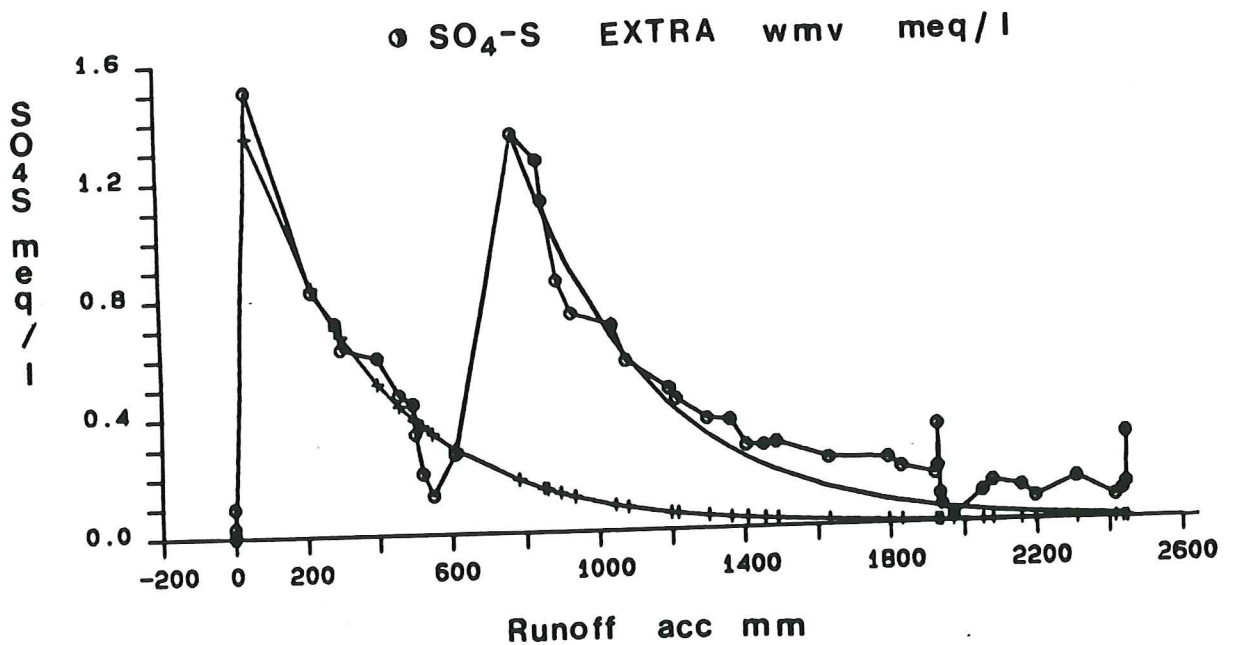
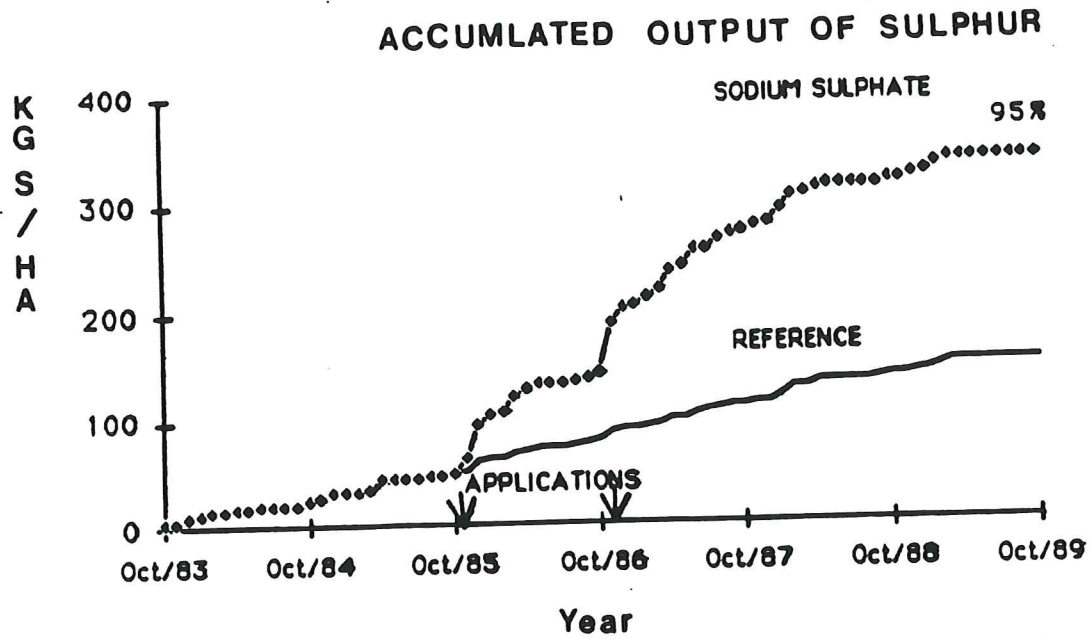


Fig. 4. Accumulated monthly flux of sulphur output (kg/ha) from reference catchment and from catchment treated with sodium sulphate (upper). Extra sulphate concentration, (meq/l) due to treatments with sodium sulphate versus accumulated water runoff together with model estimates (dilution curve) of the change in sulphur concentration in runoff (lower).

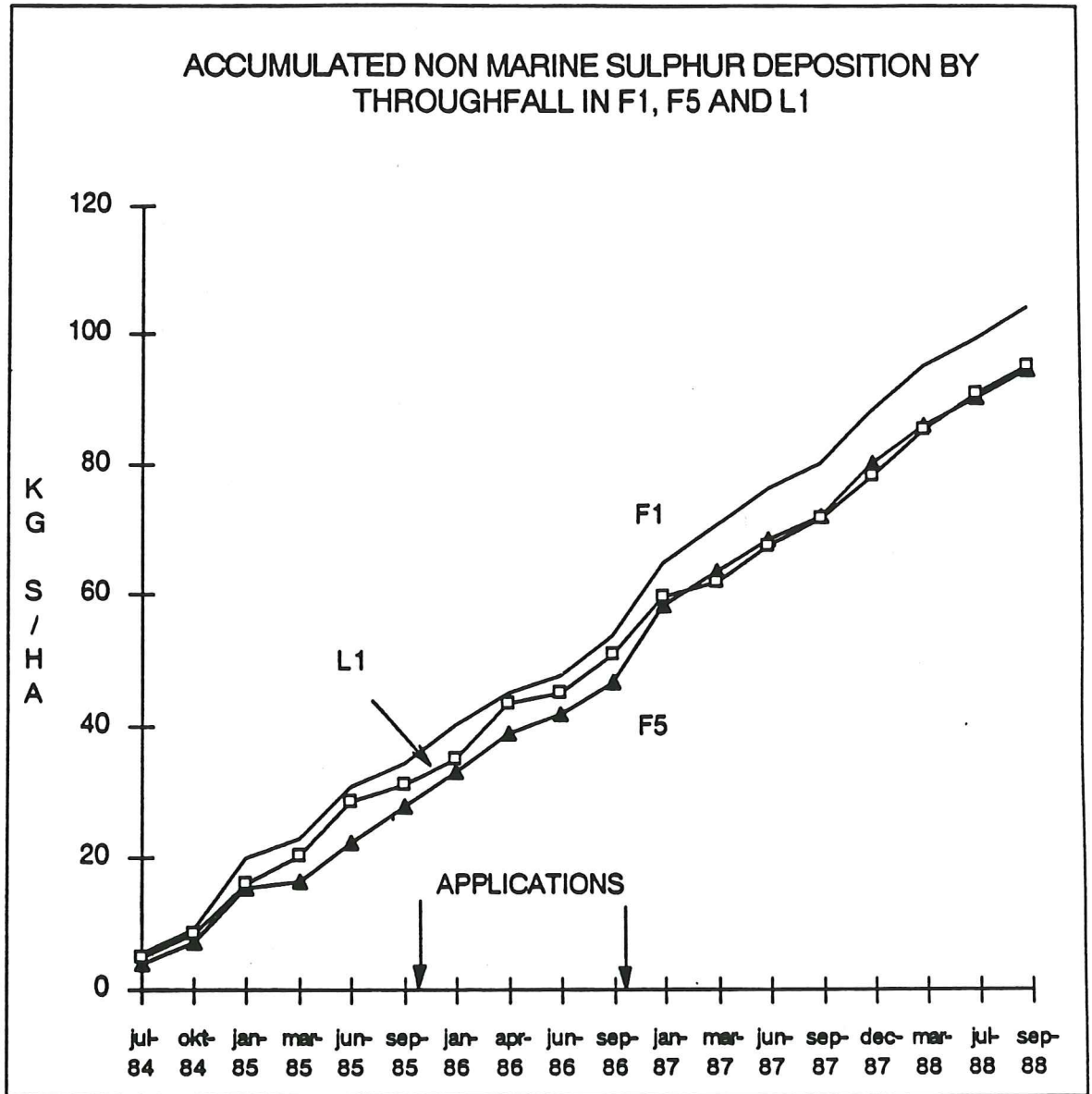


Fig. 5. Accumulated excess sulphur deposition by throughfall after treatments with sodium sulphate and elemental sulphur. F1 is reference catchment.

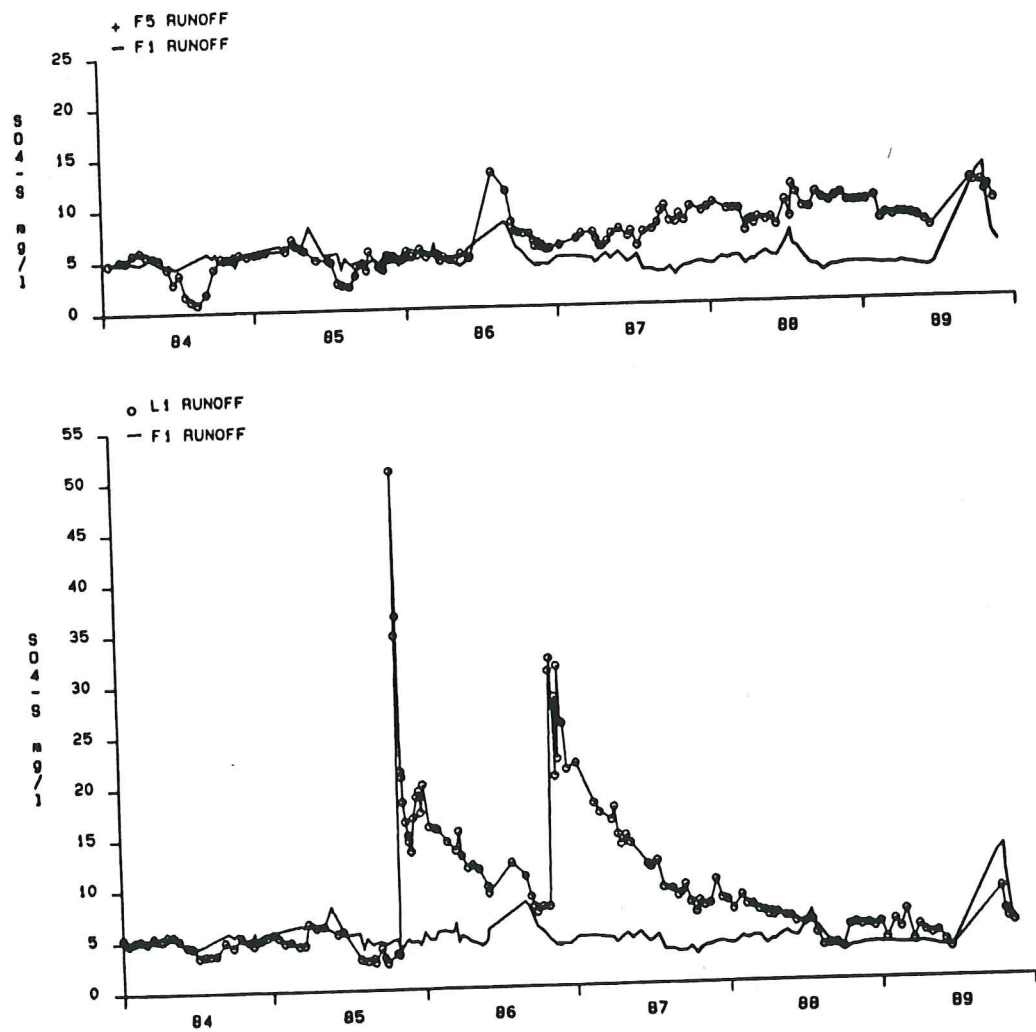
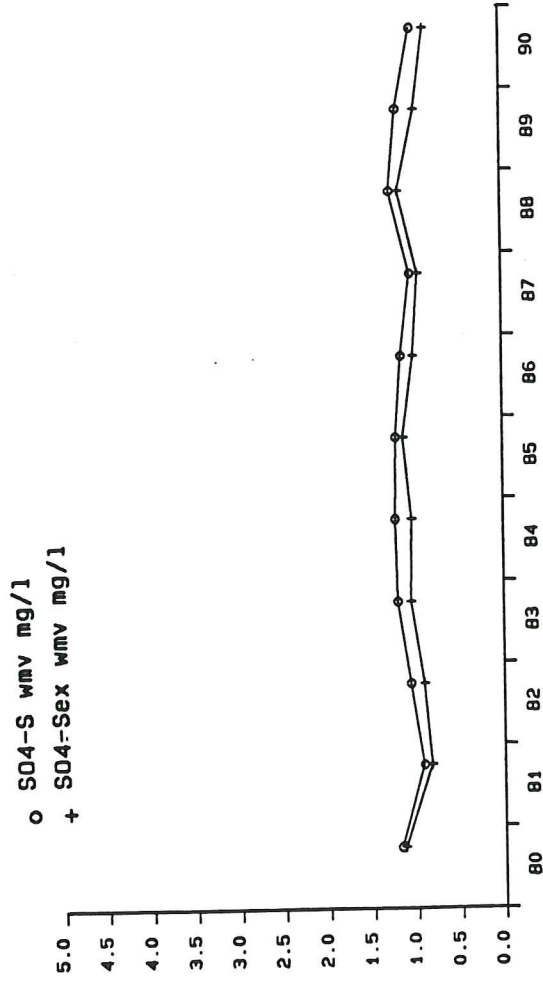
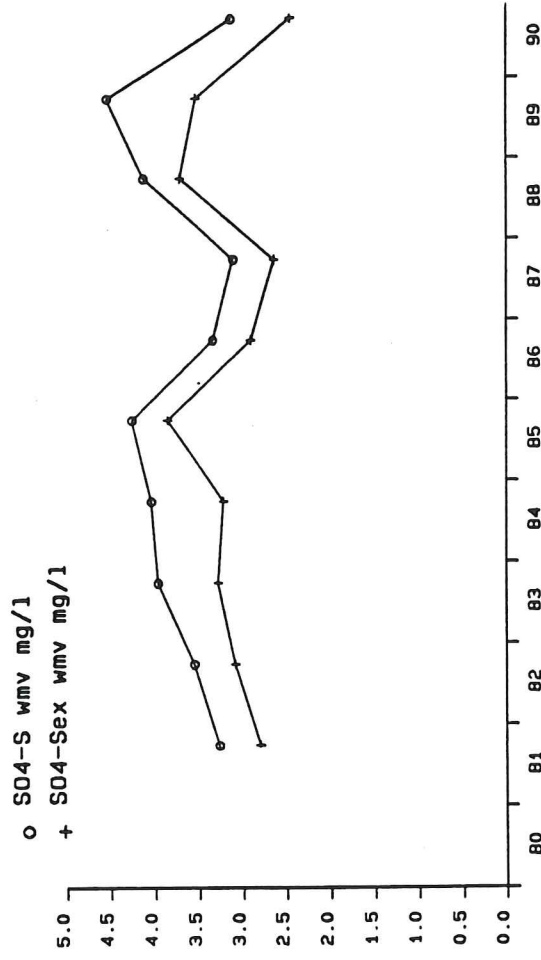


Fig. 6. Sulphate concentrations in runoff from the control catchment (F1) and the experimental treatment with elemental sulphur (F5) (upper) and the experimental treatment with sodium sulphate (L1) (lower). Treatments were performed in November 1985 and November 1986 at both catchments.

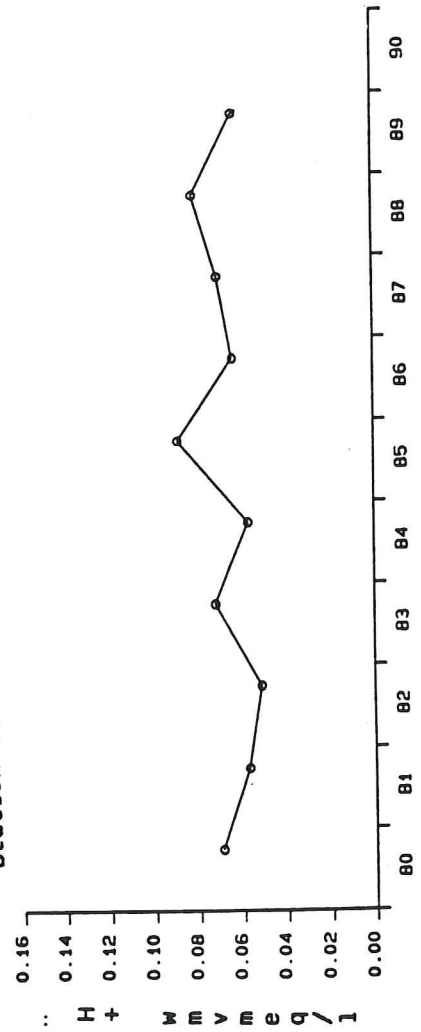
Station TV2



Station TFF1



Station TV2



Station TFF1

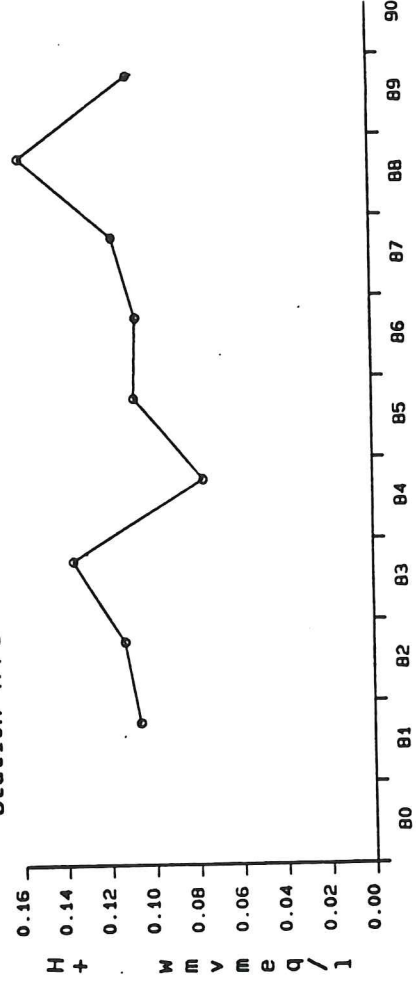


Fig.7. Weighted yearly sulphur and H⁺ concentrations in throughfall (TFF1) and bulk precipitation (TV2) during the years 1980 to 1990.