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# Atmospheric deposition and sulphur cycling in chalk grassland

## *A mechanistic model simulating field observations*

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**Key words**: acid rain, atmospheric deposition, chalk grassland, simulation model, throughfall, sulphur cycling

**Abstract**. Sulphate fluxes in bulk deposition, throughfall and soil solution were monitored during two years, and integrated within a model describing the cycling of S in a chalk grassland ecosystem. Throughfall fluxes were strongly determined by interceptive properties of the grassland canopy. Seasonal variation in Leaf Area Index resulted in dry deposition velocities for $SO_2$ varying between 0.1 $cm.s^{-1}$ (snow cover, almost no aerodynamic resistance) to 0.9–1.8 $cm.s^{-1}$ in periods with a fully developed canopy. On an annual basis net canopy exchange (assimilation of $SO_2$ minus foliar leaching) was estimated to be $-15\%$ of net throughfall. Simulated soil solution concentrations, being the result of throughfall input, leaching, adsorption, biomass uptake and mineralization, closely fitted actual values ($r > 0.92$; $p < 0.001$). Actual and simulated leaching were $1.74 \pm 0.03$ and 2.00 $keq.ha^{-1}.yr^{-1}$, respectively. Sulphur budgets for the soil showed net accumulation from April to October and net losses from October to April. Annual budgets for the ecosystem showed atmospheric input (2.02 $keq.ha^{-1}.yr^{-2}$) and actual output (2.05 $keq.ha^{-1}.yr^{-1}$) to be almost balanced. Apart from increased soil solution concentrations, additional input of sulphate (3.55 $keq.ha^{-1}.yr^{-1}$) to experimental plots resulted in additional accumulation in the ecosystem of 0.62 $keq.ha^{-1}.yr^{-1}$.

## Introduction

The influence of input of air pollutants on nutrient cycling has been frequently studied for forest ecosystems (Johnson 1984, Johnson et al. 1982, 1986; Mayer & Ulrich 1978; Meiwes & Khanna 1981; Richter et al. 1983; Stednick 1982; Strickland & Fitzgerald 1984; Ulrich et al. 1987). However, such studies for grasslands are scarce (Coughenour 1980, 1981; Coughenour et al. 1979; Gilliam 1987; Seastedt 1985), and it is obvious that measurements of throughfall below grassland canopies are much more complicated. Although atmospheric input can be directly measured with micrometeorological methods (Baldocchi et al. 1988), many biogeochemical studies rely on measurements of throughfall and stemflow to incorporate atmospheric input in cycling of elements (Likens et al. 1977; Ulrich et al. 1979; van Breemen et al. 1988). Canopy exchange processes however, may substantially modify atmospheric input (Parker 1983; Lindberg & Garten 1988), especially for ammonium and nitrate (uptake) and potassium, magnesium and calcium (leaching).

In Western Europe, especially in areas with high densities of animal husbandry, ammonia emissions are elevated (Buysman et al. 1984, 1985). $SO_2$- and $NH_3$-deposition were shown to be strongly correlated and mutually stimulated due to their opposite pH-dependent behaviour (Adema et al. 1986; van Breemen et al. 1982, 1988) and $NH_x$ deposition locally exceeds $50\,kg\,N\,ha^{-1}.yr^{-1}$ (Schneider & Bresser 1988). This results in eutrophication of nutrient-poor ecosystems and an increasing species dominance, while the total species diversity is impoverished (Heil & Diemont 1983; Bobbink & Willems 1987).

In West-European chalk grasslands, a strong increase of Brachypodium pinnatum (L) Beauv. has been observed (Bobbink & Willems 1987). Bobbink et al. (1988) showed that Brachypodium responds strongly to additional input of nitrogen compounds. So far, interceptive properties of chalk grassland vegetation were insufficiently known, however, to reliably estimate atmospheric input. We developed methods to quantify throughfall in grasslands (Heil & van Dam 1986; van Dam et al. 1987; Heil et al. 1988) and evaluated the effects of atmospheric input of nutrients to chalk grassland. In the present study we integrated measured fluxes of sulphate in bulk deposition, throughfall and soil solution within a model for sulphur cycling in chalk grassland, and showed the importance of atmospheric S-input for this ecosystem.

## Study area

The study was carried out in the southernmost part of the Netherlands (south Limburg, 50°50′N, 5°51′E), a region with high $SO_2$ concentrations (annual mean $23\,\mu gr.m^{-3}$). At the nearest long-range weather station (50°55′N, 5°47′E) average annual precipitation amounts to 767 mm and rainfall is evenly distributed over the year. Annual Penman evaporation amounts to 710 mm (KNMI 1972). Snow is recorded on 19 days a year, but snowcover is only occasionally persistent. February and March 1987 experienced considerable snowfall, however, and snow cover lasted until 19 March 1987. Vegetation at the study site was classified as Mesobrometum erecti (Willems 1982), with Brachypodium pinnatum (L.) Beauv. being the dominant species. Topography is undulating, with small valleys rather steeply incised in Pleistocene plateaus covered with loess. On valley slopes Upper-Cretaceous limestone deposits underly Rendoll soils. Our study site was situated at the higher part of a short valley slope and showed Eutrochreptic Rendoll soils (pH 7–8), developed from a mixture of calcareous loess and weathered limestone ($51\% < 50\,\mu m$). A paralithic contact of Maasstrichtian limestone was situated just below 50 cm.

## Methods

Bulk deposition was collected twice a month (from 31 October 1985 to 13 July 1988) in polythene funnels with a diameter of 14.5 cm at a height of 40 cm above soil surface (4 replicates). Black PVC sheet was used to suppress vegetation around the funnels. Collecting polythene bottles were kept in the dark within PVC pipes, to prevent photochemical conversions within samples and assimilation of nutrients by algae.

Throughfall below chalk grassland canopies was collected using a system with slanting PVC-pipes (Heil & van Dam 1986; Heil et al. 1988), samples being collected in polythene bottles dug in the soil (4 replicates). From 31 October 1985 to 15 April 1986 throughfall fluxes were measured below Brachypodium pinnatum growing on lysimeters. These throughfall fluxes were used to initiate sulphate concentrations for model calculations. To investigate the response of chalk grassland vegetation to nutrient input, six experimental plots of 2 by 2 m (with a buffer zone of 0.5 m) were used to receive nutrients in addition to atmospheric input. Two plots received $(NH_4)_2SO_4$, two received $Ca(NO_3)_2$, one plot received $CaSO_4$ and one plot received demineralized water. Two mm (8 liter per plot) of nutrient solution with a concentration of $7.75\,eq.m^{-3}$ was added, usually twice a month, from 15 May 1986 to 13 July 1988. The plots were designed for both nitrogen and sulphur cycling studies. For evaluating sulphur cycling, plots receiving $(NH_4)_2SO_4$ or $CaSO_4$ were pooled (sulphate plots), as were the plots receiving demineralized water or $Ca(NO_3)_2$ (control plots).

Soil solution below experimental plots was sampled with 30 high-flow porous ceramic cups (Soil Moisture Corporation, Santa Barbara, California) at depths of 12, 24 and 48 cm. A tension of 120 hP was continuously applied with a siphon system. Samples were collected in 100 ml polythene bottles dug in the soil.

Soil water content at sample depths was determined with 6 sensors measuring the moisture dependent relative complex permittivity of the soil (Hillhorst 1984) and data were recorded every 4 hours. Samples from bulk deposition, throughfall and soil solution were stored in the dark at a temperature of 4 °C before being analyzed with a continuous flow autoanalyser (Skalar) within 8 days after collecting. For sulphate analysis the Skalar colorimetric method with molybdene blue was used, removing interfering cations with a $H^+$-saturated ion exchange resin (Reynders et al. 1979).

Daily mean $SO_2$ concentrations for the two nearest measuring sites (50°47′N, 5°42′E and 50°49′N, 6°00′E) were supplied by the National Institute of Public Health and Environmental Protection. Mean $SO_2$ concentrations at the two stations were used to investigate relations with fluxes of sulphate in throughfall.

## Model calculations

Fluxes of sulphate in bulk deposition, throughfall and soil solution were integrated within a mechanistic model for sulphur cycling in chalk grassland. A flow diagram showing the general structure of the model is presented in Fig. 1. Model calculations of moisture transport were performed prior to calculations of solute transport, because ion transport is strongly dependent on moisture transport.

Precipitation input to the model was derived from precipitation data collected twice a month over the full period of measurements at the experimental site. Conversion to daily amounts was achieved by using the day to day distribution of precipitation at the nearest long range weather station recorded by the Royal Netherlands Meteorological Institute (KNMI 1985–1988). Recordings of daily precipitation at the measuring site with a pluviograph were used to trace heavy rainstorms in summer. During periods with snow, precipitation accumulates in a snowpack. Model calculations assumed melting to occur at a rate of 0.5 mm/hour during periods with temperatures above 0 °C.

Evaporation was deduced from Penman evaporation (KNMI 1985–1988) and from a modified Penman method for data after 1 April 1987 (de Bruin 1987), resulting in a reference crop evapotranspiration. Applying a crop factor of 1.1 from May through September (with grass higher than 15 cm) and a value of 1.0 for the remaining months gives a good approximation of real evapotranspiration (Makkink 1987). Interception evaporation was assumed to depend on a canopy storage capacity of 0.8 mm from May to September and of 0.4 mm for the remaining months. Transpiration was assumed to be zero until interception evaporation resulted in a dry grassland canopy. Transpiration of the chalk grassland vegetation was equated to moisture uptake by roots. For a 20-day period with only 0.6 mm of rain

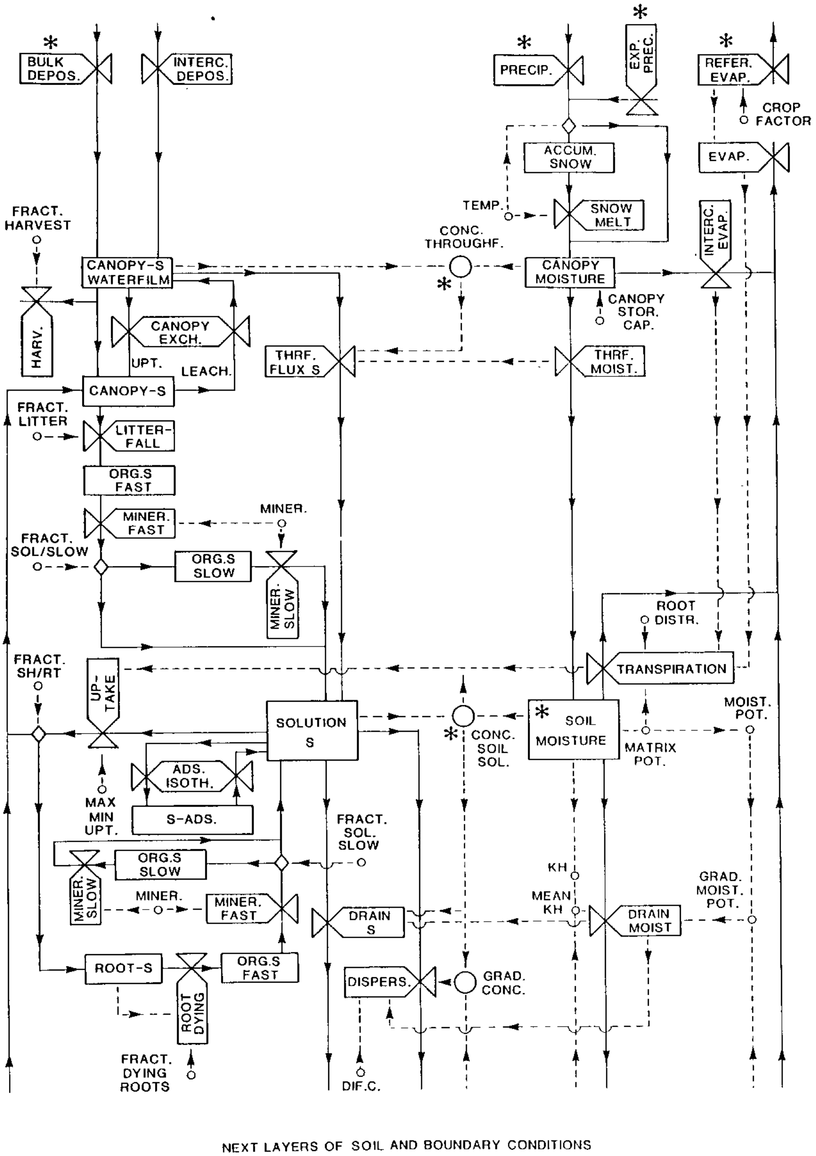

*Fig. 1.* General structure of model for cycling of sulphur. Pools are represented by squares, parameters by small circles and rates of processes by ⋈▭ = symbols. Material flow is represented by full lines, information flow by dashed lines. Measured variables have been indicated with asterixes.

(from 7 to 27 June 1988) the depth-dependent moisture uptake was calibrated using data from moisture sensors at 12, 24 and 48 cm depth. For intermediate depths the depth-dependent distribution of moisture uptake was calculated by interpolation.

Actual transpiration and thus moisture uptake by roots was assumed to be limited to a fraction (1 − A/B) of potential transpiration, with A being the pressure potential of the soil and B the pressure potential at wilting point (pF 4.2). This will result in soil water content asymptotically approaching wilting point values. Moisture fluxes between layers of 3 cm thickness were calculated using Darcy's law:

$$F = -Kh * GRAD$$

where Kh is the hydraulic conductivity at a particular moisture content, and GRAD the gradient of soil moisture potential between adjacent layers. The relations between moisture content and hydraulic conductivity and between moisture content and matrix potential (pF-curve) are most important model parameters to calculate moisture fluxes. Hysteresis was not included in the model.

Ion transport of sulphate is mainly governed by massflow and adsorption, but diffusion was also included in our model. Moreover model calculations give rise to pseudo-dispersion, due to mixing of solutes within layers of soil with finite thickness. The latter effect is proportional to moisture fluxes and inversely proportional to the amount of soil layers used for transport calculations (17 layers of 3 cm in this model). For sulphate adsorption/desorption to the soil linear adsorption isotherms were used:

$$SO4_{sol} = ISO * SO4_{ads}$$

where ISO is the slope of the adsorption isotherm, $SO4_{sol}$ the sulphate concentration in the soil solution (eq.dm$^{-3}$) and $SO4_{ads}$ the amount adsorbed to the ion exchange complex of the soil (eq.dm$^{-3}$). Sulphate adsorption/desorption of the calcareous soil was considered to be completely reversible. For sulphate plots and control plots the same adsorption isotherms were used, which were calculated with a procedure for least residual sum of squares between calculated and observed sulphate concentrations for plots receiving additional sulphate. The travelling speed and concentrations of the solute front were strongly dependent on sulphate adsorption isotherms. The slope (ISO) of the sulphate adsorption isotherm for the topsoil (0–9 cm depth) was 0.26, gradually decreasing to values less than 0.08 below 24 cm depth. Root uptake of sulphate was assumed to originate from mass flow. This results in equal depth-distributions for ion uptake and calibrated moisture uptake (if sulphate concentrations would be equal at various depths).

For control plots mineralization was assumed to be in a steady state with the amounts of S annually returned in litterfall and dying roots. Organic matter from litterfall was assumed to be (bio)mechanically mixed within the upper 6 cm of the soil profile (2/3 in 0–3 cm layer, 1/3 in 3–6 cm layer). Mineralization was described as a cascade process (Swift et al. 1979), with two fractions of organic S with different residence times. Mineralization of S from the fraction with a short residence time (1 year in our model) will result in output of sulphate entering the soil solution, and output of organic S entering the fraction with a long residence time (20 years). For mineralization from the latter fraction all output is returned to the soil solution as sulphate. For control plots and for plots receiving experimental input of sulphate the same residence times of organic S were used. Although this could easily be implemented, mineralization in our model was not dependent on actual moisture contents and soil temperature; mineralization rates (fraction of S mineralized/residence time) were a priori distributed over the months of a year with maximum values (16% of annual mean) in September and a minimum of 1% in February. Residence time of roots in the model was 1 year.

## Results and discussion

### *Bulk deposition, throughfall and dry deposition velocities*

Between 15 April 1986 and 14 April 1988 the flux of sulphate in bulk deposition amounted to 0.88 ± 0.011 $\text{keq.ha}^{-1}.\text{yr}^{-1}$. Sulphate concentrations in bulk deposition and amounts of precipitation were inversely correlated ($SO_4 = 0.53/P + 0.15$; $r = 0.72$; st.err. of regr. coeff. = 0.08; $n = 243$; $SO_4$ = sulphate concentration ($\text{eq.m}^{-3}$); $P$ = amount of precipitation (mm per sampling period)). Apart from Na and Cl ($r = 0.85$) correlation between ion fluxes in bulk deposition was highest between sulphate and nitrate ($NO_3 = 0.44 * SO_4 + 0.029$; $r = 0.81$; st.err. of regr.coeff. = 0.02; $n = 243$). Throughfall fluxes were calculated by multiplying actual concentrations with simulated throughfall volumes and amounted to 2.22 ± 0.22 $\text{keq.ha}^{-1}.\text{yr}^{-1}$ (simulated throughfall volumes were calculated from actual precipitation minus simulated interception evaporation; sampled throughfall volumes were always lower than calculated throughfall volumes, because throughfall in grassland canopies is conducted for a large part as leaf flow (Raybold et al. 1977; Seastedt 1985)).

Bulk deposition represents wet only deposition plus sedimentation of coarse (> 10 μm) particles (Fowler 1980), while throughfall represents bulk deposition + interception deposition + canopy exchange. The difference between throughfall fluxes and fluxes in bulk deposition is called net throughfall. If canopy exchange would be insignificant net throughfall would represent dry deposition as a result of aerodynamic roughness of the canopy, and could be expected to correlate with concentrations of $SO_2$, because in the Netherlands dry deposition of $SO_x$ originates for more than 90% from dry deposition of $SO_2$, with only a minor contribution of sulphate aerosols (Schneider & Bresser 1988). Deposition velocities of $SO_2$ were calculated from net throughfall and concomitant concentrations of $SO_2$. Calculated deposition velocities for $SO_2$ and measured $SO_2$ concentrations are shown in Fig. 2.

Canopy assimilation of $SO_2$ and foliar leaching of sulphate are opposite processes with respect to their influence on net throughfall. These canopy-exchange processes will influence the calculated deposition velocities. Several methods have been employed to separate leaching from net throughfall (Cape et al. 1987; Lovett & Lindberg 1984; Mayer & Ulrich 1978; Raybould et al. 1977). With labelled S it has recently been shown (Lindberg & Garten 1988; Garten et al. 1988) that leaching of sulphate from the canopy of deciduous trees was less than 20% of net throughfall on an annual basis. Measurements of dry deposition of $SO_2$ and throughfall of sulphate below a pine forest by Bache (1977) also showed foliar leaching to be only a small part (11%) of net throughfall.

If either net canopy exchange (assimilation of $SO_2$ – foliar leaching) or interception deposition are known, total atmospheric input to ecosystems can be calculated from bulk deposition and throughfall. Input/output budgets of the aboveground biomass of grasslands can be used to estimate interception deposition. In contrast to forests, net annual increments of S in biomass of grasslands can be ignored, because differences in the pool of S in aboveground biomass are almost zero at the start of successive growing seasons. Therefore annual input/output budgets of grassland canopies will satisfy equation (1):

$$\text{CANOPY INPUT} = \text{CANOPY OUTPUT} \tag{1}$$

specified to:

$$\begin{aligned}\text{BULK} + \text{INTERCEPTION} + \text{UPTAKE} &= \text{THROUGHFALL}\\ &\quad + \text{HARVEST} + \text{LITTERFALL}\end{aligned} \tag{2}$$

and rearranged to:

$$\text{INTERCEPTION} = \text{THROUGHFALL} + \text{HARVEST} + \text{LITTERFALL} - \text{BULK} - \text{UPTAKE} \quad (3)$$

Harvest + litterfall was equated to the amount of S determined in biomass at peak standing crop (0.87 ± 0.12 keq.ha$^{-1}$). Equation (3) then reads:

$$\text{INTERCEPTION} = 2.22 + 0.87 - 0.88 - \text{UPTAKE} \quad (4)$$

Equation (4) prompts to determine uptake from roots. We calculated uptake from simulated mass flow uptake of sulphate (0.90 keq.ha$^{-1}$.yr$^{-1}$). Interception deposition then amounts to 1.31 ± 0.35 keq.ha$^{-1}$.yr$^{-1}$. Total atmospheric input (bulk deposition + interception deposition) will thus amount to 2.19 keq.ha$^{-1}$.yr$^{-1}$, and net canopy exchange to $-0.03$ keq.ha$^{-1}$.yr$^{-1}$ (atmospheric input − throughfall). Interception deposition can also be determined from the total input/output budget of the ecosystem, with:

$$\text{INPUT} - \text{OUTPUT} = \text{NET INPUT} \quad (5)$$

specified to:

$$\text{INTERCEPTION} = \text{LEACHING} + \text{HARVEST} - \text{BULK} + \text{NET INPUT} \quad (6)$$

Our simulation model resulted in a net input to the ecosystem of $-0.20$ keq.ha$^{-1}$.yr$^{-1}$, of which $-0.18$ keq.ha$^{-1}$.yr$^{-1}$ was due to a decreased pool of sulphate in the soil solution (this was caused by exceptionally high precipitation with low sulphate concentrations at the end of the 2 year period for which the input/output budget was calculated). During the two year experimental period output with harvested biomass was 0.31 ± 0.05 keq.ha$^{-1}$.yr$^{-1}$ (only harvested once on 2 October 1987).

Interception deposition calculated with formula (6) amounts to $1.74 + 0.31 - 0.88 - 0.20 = 0.97$ keq.ha$^{-1}$.yr$^{-1}$, resulting in a total ecosystem input of 1.85 and a net canopy exchange of $-0.37$ keq.ha$^{-1}$.yr$^{-1}$. The values of $-0.03$ and $-0.37$ keq.ha$^{-1}$.yr$^{-1}$ for net canopy exchange were independently derived from our model. Both values are subject to equally unknown simulated fluxes. Reliability of the first value depends on

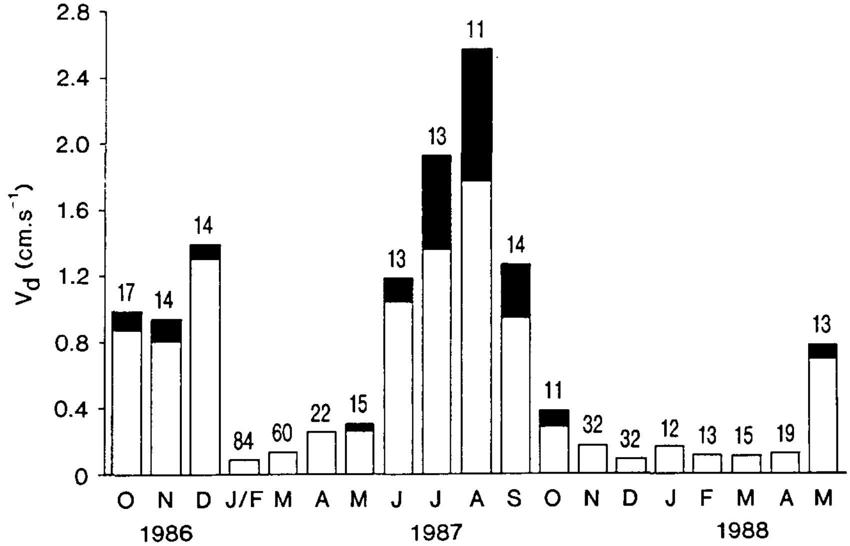

*Fig. 2.* $SO_2$-concentrations ($\mu$gr.m$^{-3}$) (indicated above bars) and dry deposition velocity of $SO_2$ (Vd), calculated from net throughfall below chalk grassland canopies. The contribution of foliar leaching(estimated to be 15% of net throughfall, see text) to apparent deposition velocities is represented by the upper part of bars.

simulated root uptake, whereas reliability of the second value depends on simulated adsorption and total organic S. A value of $-0.20$ keq.ha$^{-1}$.yr$^{-1}$ (mean of both methods) implies that 15% of net throughfall would represent net canopy exchange (leaching > canopy assimilation of $SO_2$).

Especially in periods with vegetation becoming partly senescent, foliar leaching of sulphate can exceed canopy assimilation of $SO_2$. This conclusion is supported by significantly lower ($p < 0.02$) sulphate concentrations in demineralized water extracts of standing dead (0.104 ± 0.033) than in extracts of living biomass (0.145 ± 0.029 for Brachypodium pinnatum, 0.167 ± 0.022 for other graminoids and 0.158 ± 0.051 eq/kg for herbs).

If foliar leaching exceeds canopy assimilation of $SO_2$, deposition velocities derived from net throughfall will be overestimated. We therefore recalculated deposition velocities by assuming that:

— 15% of annual net throughfall of sulphate represents net canopy exchange;

— net throughfall of potassium represents only leaching;

— seasonal distributions of leaching of potassium and sulphate are equal.

Deposition velocities of $SO_2$ calculated with and without this correction for net canopy exchange are shown in Fig. 2.

Aerodynamic characteristics, which are related to the Leaf Area Index of the vegetation canopy (Heil et al. 1988), will be responsible for the seasonal pattern of deposition velocities. From October through December 1986 LAI values of standing dead (no mowing, LAI values of 5–8) correspond with deposition velocities of 0.8–1.3 cm.$s^{-1}$. From January through March 1987 LAI values were much lower (1–2), prolonged periods with a snowcover occurred, and very low deposition velocities (0.1–0.2 cm.$s^{-1}$) were observed. From April to August 1987 increasing deposition velocities coincided with increasing LAI's (3–8). During the period with a fully developed canopy from June to September 1987, calculated deposition velocities of $SO_2$ were 0.9–1.8 cm.$s^{-1}$, compared to values of 0.7–1.3 generally cited in literature (McMahon & Denison 1979, Matt et al. 1987). After mowing (October 1987, LAI = 1–2) deposition velocities of $SO_2$ did not exceed 0.3 cm.$s^{-1}$. On an annual basis our data resulted in an average deposition velocity for $SO_2$ of 0.51 cm.$s^{-1}$. This result closely corresponds with deposition velocities employed in regional atmospheric transport models employed by the National Institute for Public Health and Environmental Protection in the Netherlands (Schneider & Bresser 1988) (0.66 cm.$s^{-1}$ for summer, 0.55 cm.$s^{-1}$ for winter and 0.20 cm.$s^{-1}$ when a snowcover is present). From Fig. 2 it is clear however, that in our case deposition velocities varied greatly between summer and winter periods.

### *Soil moisture*

Actual and simulated moisture contents were compared for the period from 19 December 1987 to 13 July 1988. Sensor data were collected every 4 hours, but for model calculations precipitation was evenly distributed over a day. Therefore actual moisture contents fluctuated more rapidly than simulated values. Nevertheless, actual moisture contents were closely fitted by the model and showed only 9.0, 5.9 and 5.7% root mean square error at 12, 24 and 48 cm, respectively. It is therefore to be expected that for the period from October 1985 to December 1987 calculated moisture contents will also accurately approach the hydrological behaviour of the soil. Model validation for previous hydrological years was not possible, however, because of malfunctioning sensors before December 1987.

Calculated moisture contents for a depth of 24 cm, daily amounts of precipitation and drainage are shown in Fig. 3. Striking differences between moisture contents during the summer of 1987 and those of 1986 and 1988 are due to the exceptionally wet summer of 1987. Hydrological characteristics for two hydrological years included in our measuring period are summarized in Table 1.

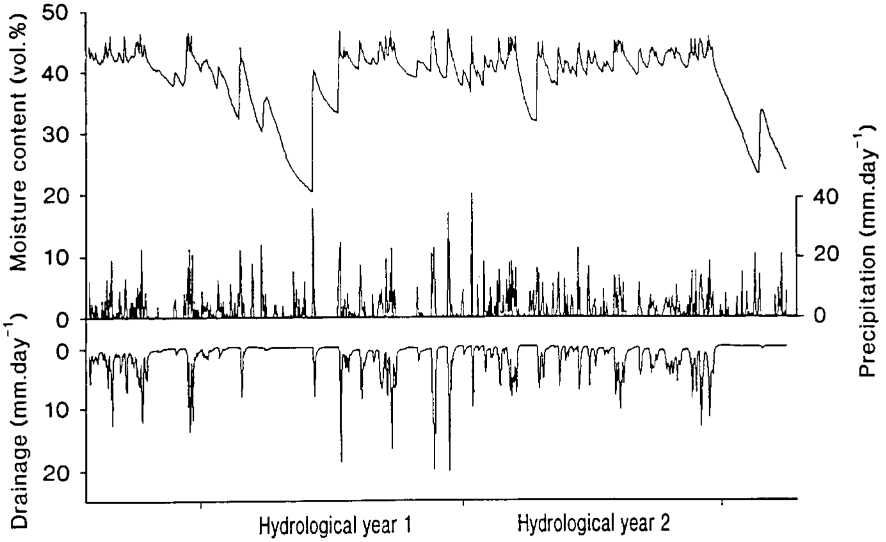

*Fig. 3.* Soil moisture content and drainage at 24 cm depth and concomitant precipitation for two hydrological years (15 April 1986 to 14 April 1988).

### *Sulphate concentrations in soil solution*

Concentrations of sulphate in the soil solution reflect input and output by throughfall, mineralization, leaching, adsorption and uptake by biomass. The pool of sulphate in the soil solution is a central point in our model. Actual and simulated concentrations of sulphate in the soil solution at 12 cm depth of the control and experimental plots are shown in Fig. 4. Seasonal patterns of high concentrations in autumn and low concentrations in spring are apparent for actual as well as for simulated concentrations. The seasonal patterns of solute

*Table 1.* Moisture fluxes (mm.year$^{-1}$) during two hydrological years (starting at 15 April of each year).

| | 1986–87 | 1987–88 |
|---|---|---|
| Precipitation | 817 | 999 |
| Throughfall at 0 cm | 729 | 871 |
| Drainage at 12 cm | 573 | 751 |
| Drainage at 24 cm | 444 | 640 |
| Drainage at 48 cm | 396 | 599 |
| Transpiration | 338 | 270 |
| Interception evaporation | 88 | 119 |
| Evapotranspiration | 426 | 389 |
| Ref. crop evapotranspiration | 403 | 345 |

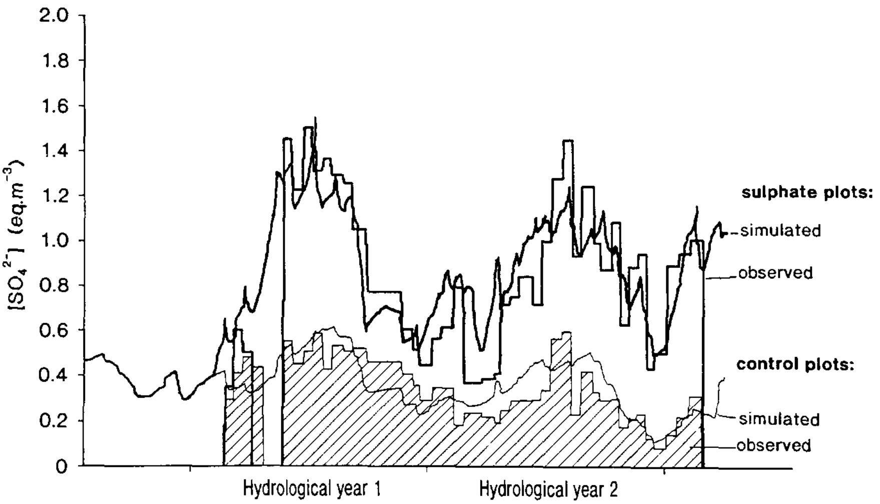

*Fig. 4.* Actual (bars) and simulated concentrations of sulphate at 12 cm depth for sulphate plots (bold) and control plots (hatched). Experimental addition of sulphate started at 15 May 1986.

concentrations result from accumulation due to precipitation deficits compared to evapotranspiration in summer, and leaching during autumn and winter. Moreover seasonal patterns of ion uptake and mineralization (Fig. 5)

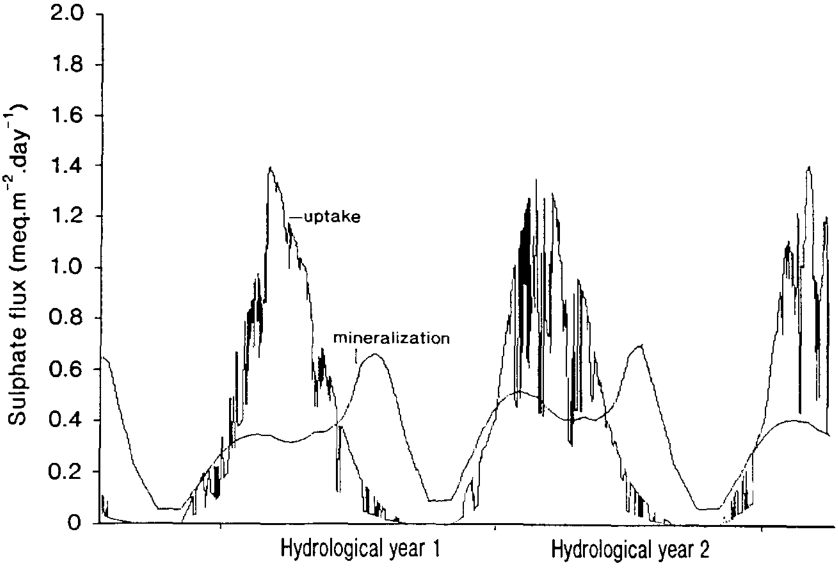

*Fig. 5.* Simulated root uptake and net mineralization for plots receiving additional input of sulphate (3.55 keq.ha$^{-1}$.yr$^{-1}$).

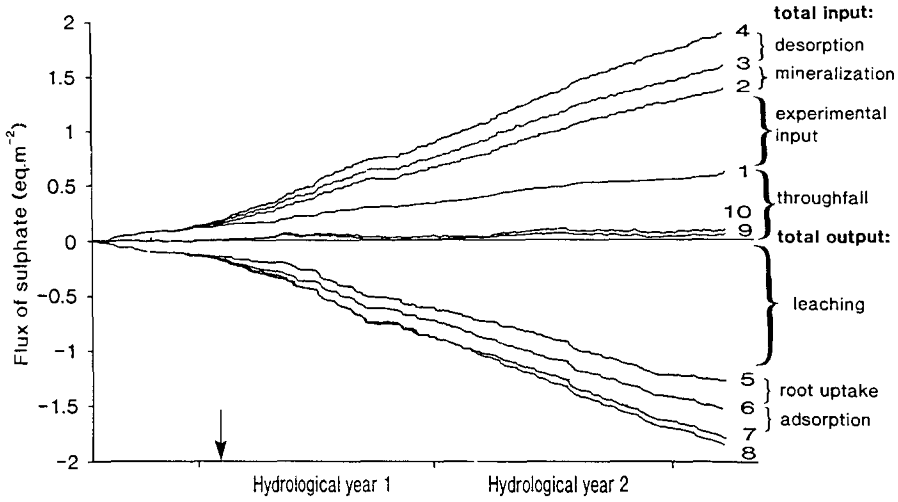

*Fig. 6.* Cumulative fluxes of sulphate from 31 October 1985 to 13 July 1988 for soil solution from 0–12 cm depth of plots receiving additional input of sulphate. Arrow indicates start of experimental input and output measurements (15 April 1986). (1) throughfall, (2) throughfall + additional input, (3) throughfall + additional input + simulated mineralization, (4) total input to soil solution (throughfall + additional input + simulated mineralization + simulated desorption), (5) actual leaching, (6) actual leaching + simulated root uptake, (7) total output from soil solution (actual leaching + simulated root uptake + simulated adsorption), (8) total output from soil solution (simulated leaching + simulated root uptake + simulated adsorption), (9) difference between input (4) and output (8), (10) difference between input (4) and output (7).

contribute to the observed seasonal patterns. For the control plots concentrations appear to be underestimated from January through March 1987 and overestimated during the exceptionally wet summer of 1987.

An input/output budget of the soil solution from 0 to 12 cm depth for plots receiving additional input of sulphate is shown in Fig. 6. The cumulative fluxes presented in this figure show that mineralization and uptake are only about 15% of total input and 20% of total output, respectively. Input fluxes minus output fluxes represent net changes in the soil solution. Compared to total fluxes small positive net changes are apparent during spring and summer and small negative changes during autumn and winter. Model assumptions on processes involving transport from or to the soil solution do not conflict with actual input in throughfall and output in leaching, since total input (actual throughfall + experimental input + simulated mineralization + simulated desorption) is very close to total output (actual leaching + simulated uptake + simulated adsorption).

## *Model results for sulphur cycling*

For the control plots a cumulative input/output budget for the whole ecosystem (vegetation + soil to maximum rooting depth [48 cm]) is presented in Fig. 7. The budget indicates that throughfall fluxes (2.22 ± 0.22 keq.-ha$^{-1}$.yr$^{-1}$) are almost equal to output with leaching + harvest (2.05 keq.-ha$^{-1}$.yr$^{-1}$). We showed that about 15% of net throughfall is derived from foliar leaching. Atmospheric input to the ecosystem is then calculated to be 2.02 keq.ha$^{-1}$.yr$^{-1}$. With respect to cycling of S this indicates that the ecosystem is close to a steady state. Because simulated output (2.26 keq.-ha$^{-1}$.yr$^{-1}$) exceeds actual output (2.05 keq.ha$^{-1}$.yr$^{-1}$), this either indicates that atmospheric input is slightly overestimated or that net ecosystem input is underestimated. If actual net input exceeds simulated values, this would indicate that some irreversible sulphate adsorption occurs, or that organic S deviates from a steady state on an annual basis.

In our model we assumed that soil-organic S in control plots is in a steady state on an annual basis if mowing and harvesting is practiced once a year in autumn (being the usual managing practice in chalk grassland). If turnover of organic S is slower than assumed in our model, the difference

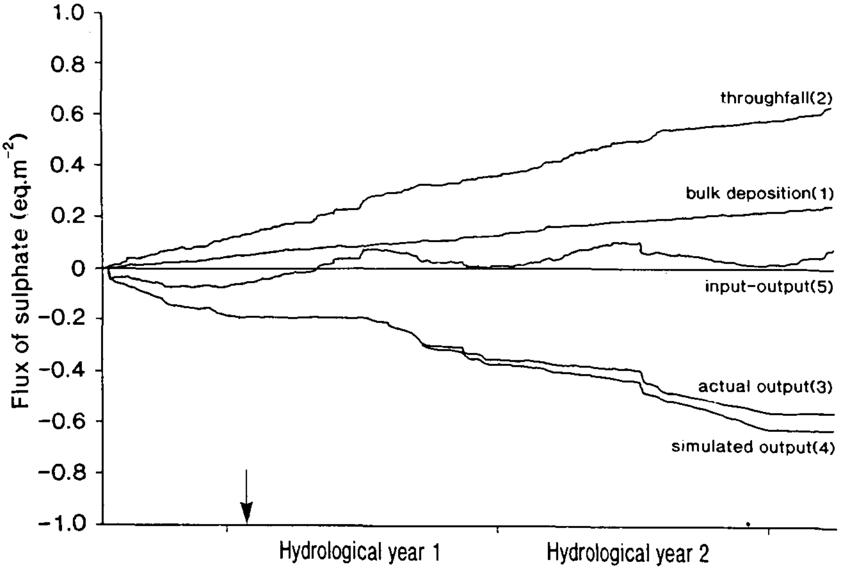

*Fig. 7.* Cumulative input and output of sulphate for chalk grassland. Arrow indicates start of output measurements. (1) input in bulk precipitation, (2) input to soil in throughfall, (3) actual output with leaching + harvest, (4) simulated output with leaching + harvest, (5) difference between input (2) and output (3).

*Table 2.* Summary statistics for sulphate leaching ($\mu$eq.m$^{-2}$.day$^{-1}$) during two hydrological years. Indicated are means of observed and simulated values, correlation coefficients, mean square errors, bias, difference in variances and incomplete covariances between simulated and observed values.

| Year | Depth (cm) | Mean obs. | Mean sim. | r | mse | Bias | dif. var. | Incompl. covar. |
|---|---|---|---|---|---|---|---|---|
| | | | | Sulphate plots | | | | |
| 1 | 12 | 1393 | 1338 | 0.982 | 0.035 | 0.006 | 0.146 | 0.846 |
| | 24 | 1137 | 1127 | 0.994 | 0.053 | 0.001 | 0.004 | 0.995 |
| | 48 | 1082 | 1035 | 0.980 | 0.031 | 0.011 | 0.003 | 0.986 |
| 2 | 12 | 1542 | 1740 | 0.947 | 0.144 | 0.055 | 0.067 | 0.879 |
| | 24 | 1288 | 1584 | 0.924 | 0.251 | 0.126 | 0.087 | 0.786 |
| | 48 | 1254 | 1517 | 0.920 | 0.184 | 0.120 | 0.174 | 0.705 |
| | | | | Control plots | | | | |
| 1 | 12 | 712 | 640 | 0.979 | 0.040 | 0.034 | 0.255 | 0.711 |
| | 24 | 537 | 548 | 0.989 | 0.017 | 0.004 | 0.044 | 0.952 |
| | 48 | 474 | 512 | 0.992 | 0.046 | 0.067 | 0.152 | 0.782 |
| 2 | 12 | 535 | 648 | 0.930 | 0.194 | 0.087 | 0.093 | 0.821 |
| | 24 | 410 | 591 | 0.967 | 0.399 | 0.363 | 0.325 | 0.312 |
| | 48 | 443 | 581 | 0.933 | 0.338 | 0.236 | 0.162 | 0.601 |

between the net gain of S observed and predicted by the model could be explained by additional accumulation of S in soil organic matter. Although annual input is almost equal to annual output, seasonal accumulation of S in the ecosystem is apparent. Similar crossover patterns between seasonally alternating net input and net output were also observed in forest ecosystems by Likens et al. (1977) and Christopherson & Wright (1981). Seasonal net input is predominant from April to October and net output from November to March (line 5 in Fig. 7).

Summary statistics (Sterman 1984) for actual and simulated sulphate fluxes between soil compartments are presented in Table 2. It shows that mean sulphate fluxes during the second hydrological year are overestimated by the model, especially at 24 and 48 cm depth, with bias showing a maximum value of 0.363 for the blank plots at 24 cm depth for the second hydrological year. Mean square errors are mainly due to incomplete covariances between observed and simulated leaching. For a large part this is the result of different time resolutions between simulated (one day) and actual leaching of sulphate (soil moisture sampled and analyzed for sulphate twice a month).

Sulphur cycling in chalk grassland as calculated with the present model is illustrated in Fig. 8. Fluxes and changes within pools are annual means of

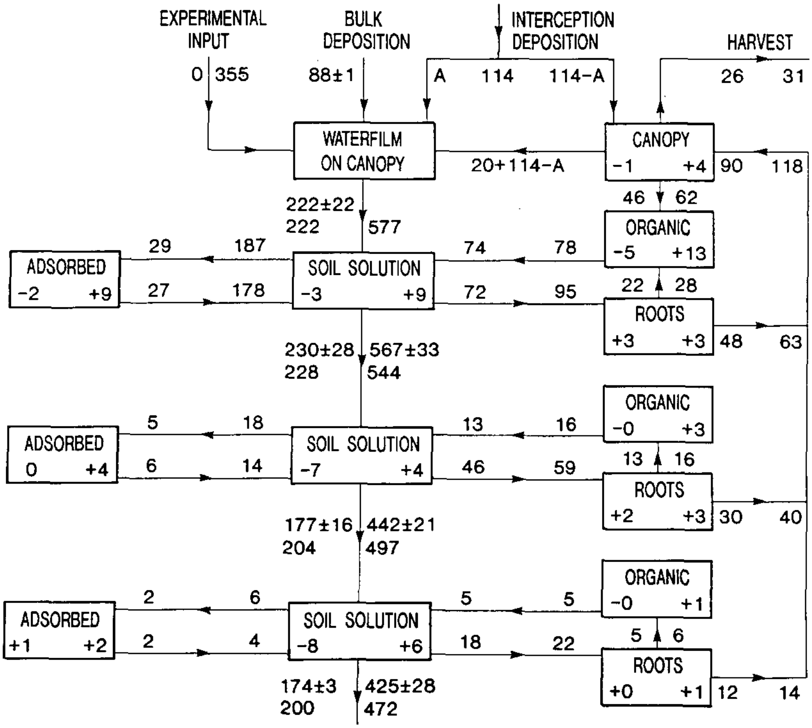

*Fig. 8.* Cycling of sulphur in chalk grassland during two hydrological years (eq.ha$^{-1}$.yr$^{-1}$ * 10). Measured fluxes are shown with standard deviations, while values without standard deviations represent simulated fluxes. First values of each pair are for control plots, and second ones for plots receiving experimental input (3.55 keq.ha$^{-1}$.yr$^{-1}$) of sulphate. Boundaries between repeated compartments are at 12, 24 and 48 cm depth.

two hydrological years (86/87 and 87/88, with 15 April being the beginning of each particular year). For the control plots, observed mean annual leaching of sulphate at 12 cm depth is not different from simulated leaching. At 24 and 48 cm, however, observed leaching is slightly lower (13.2 and 13.0%, respectively) than simulated values. Except for the topsoil (0–12 cm), root uptake is distinctly higher than mineralization. Without net annual changes in the pool of the solid mineral phase, this inevitably results in decreased leaching at greater depth. For plots receiving experimental additions of sulphate (3.55 keq.ha$^{-1}$.yr$^{-1}$), additional accumulation in the ecosystem (0.85 keq.ha$^{-1}$.yr$^{-1}$) is 23% of additional input. A large part (45%) of the additional accumulation is in the soil solution and not tightly locked up in the ecosystem, because concentrations in soil solution are much higher than in blank plots.

It is concluded that retention capacity for sulphate of the chalk grassland is very limited and that atmospheric input to the ecosystem is almost completely recovered in output.

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