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Effects of decreased atmospheric deposition on the sulfur budgets of two Dutch moorland pools

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Abstract. The chemical composition of surface waters of two Dutch moorland pools and of incident precipitation, was monitored from 1982 to 1990. For this period, sulfur and water budgets were calculated using a hydrochemical model developed for well-mixed non-stratifying lakes. Total atmospheric deposition of S decreased significantly after 1986 at both locations. A model describing the sulfur budget in terms of input, output and reduction/oxidation processes predicted a fast decrease of pool water SO_4^{2-} concentrations after a decrease of atmospheric input. However, SO_4^{2-} concentrations in the surface water was lowered only slightly or remained constant. Apparently a source within the lake caused the unexpectedly high SO_4^{2-} concentrations. The possible supply of SO_4^{2-} from the sediment through regulation by (K-)Al-SO_4 containing minerals or desorption of SO_4^{2-} from positively charged surfaces in the sediment was evaluated. Solubility calculations of pore water with respect to alunite, basaluminite and jurbanite indicated that SO_4^{2-} concentration was not regulated by these minerals. It is suggested here (1) that desorption of SO_4^{2-} from peaty sediments may account for the estimated SO_4^{2-} supply provided that the adsorption complex is periodically recharged by partial oxidation of the upper bottom sediments and (2) that because of exposure of a part of the pool bottom to the atmosphere during dry summers and subsequent oxidation of reduced S, the amount of SO_4^{2-} may be provided which complements the decreasing depositional SO_4^{2-} input. In future research these two mechanisms need to be investigated.

Introduction

Over the past decade, concern over the impact of elevated loading of anthropogenic acid on freshwater has initiated much research. The main attention has been focused on the influence of acid precipitation on the biogeochemistry of freshwater systems in acid-sensitive areas (e.g. Kelly 1982; Rudd 1986). In extremely acid-vulnerable lakes, within-lake biogeochemical processes appeared to be important sources of alkalinity (Schindler 1980; Cook et al. 1986). During an acidification experiment of a Canadian Shield Lake, about 70% of the H_2SO_4 added over a 7-year period, was lost by SO_4^{2-} reduction in epilimnetic sediments. Sulfate reduction and subsequent retention accounted for 85% of the internal alkalinity generation (Cook et al. 1986). In an experimentally acidified Wisconsin seepage lake, seston deposition appeared to be the most important SO_4^{2-} sink (Baker et al. 1989).

In the Netherlands a large number of oligotrophic to mesotrophic moorland pools occur in poorly buffered, non-calcareous sandy areas. Since the pools are largely fed by atmospheric deposition, they are vulnerable to environmental changes (Van Dam & Buskens 1993). Moorland pools act as important habitats for a variety of plants and animals, characteristic of these environments. Because these biota are comparatively rare in The Netherlands and surrounding countries, they have a high value for nature conservation. Acidification by acid atmospheric deposition is a major threat to isolated moorland pool ecosystems and results in biological impoverishment of the pools (Van Dam & Buskens 1993). Restoration of these pools may possibly be accomplished by the reduction of the acid load.

Although the total potential acid deposition (480 mmol m^{-2} y^{-1} in 1989, Erisman (1989)) still exceeds the critical potential acid load (25 mmol m^{-2} y^{-1}, i.e. the quantity of acid above which these types of waters may acidify within a short period, Schuurkes et al. 1987; Van Dam & Buskens 1993), the total potential acid deposition has decreased by about 30% over the years 1980—1989, mainly due to decreased wet and dry SO_x deposition (Erisman 1992). To assess how these types of ecosystems react to a decrease in atmospheric S-deposition, two moorland pools that differ in trophic status and morphometry were studied in detail. In this paper we present S budgets of the moorland pools over the period 1982—1990. Trends in SO_4^{2-} concentrations of pool water and deposition were evaluated based on calculations by hydrochemical models and short-term variations in S chemistry. The reaction of the pool water S chemistry on the decrease of atmospheric S deposition was evaluated by means of a simple model.

Study area

Investigations were conducted in two moorland pools, Gerritsfles and Kliplo, in the Netherlands (Fig. 1). Both pools are seepage pools with

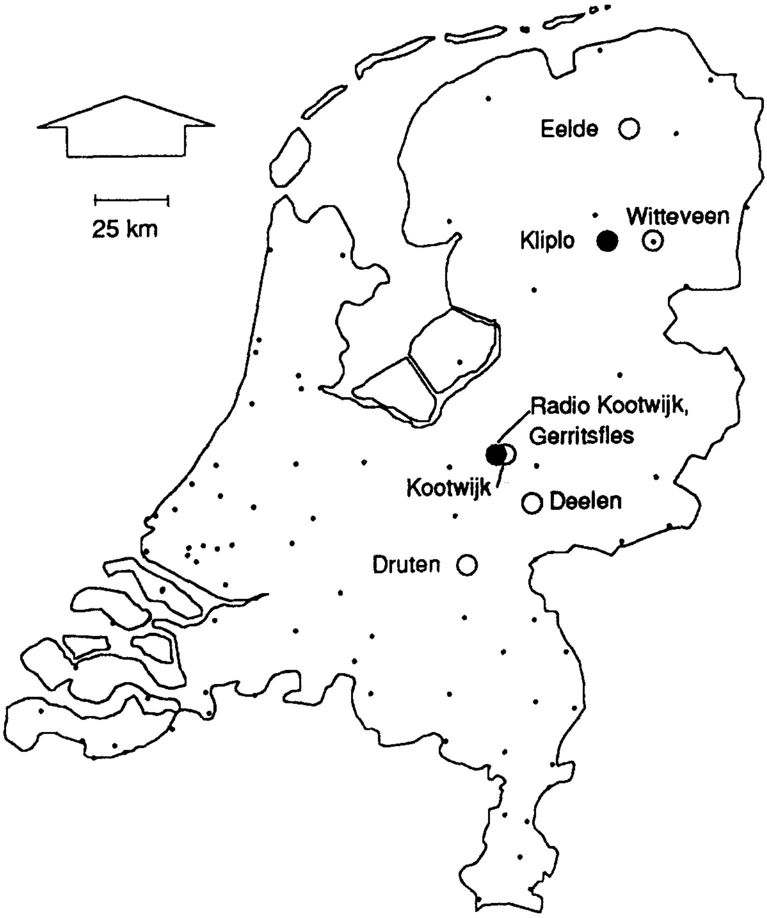

Fig. 1. Meteorological stations (open circles, except for Kootwijk) and the study locations Gerritsfles and Kliplo (solid circles). At Kootwijk another research location of the Agricultural University Wageningen is located. The small dots indicate the locations of the National Air Quality Monitoring Network where SO_2 concentrations were measured.

small catchment areas and they have a perched water table. Gerritsfles (52°10′N, 5°49′E, 40 m above MSL) is an oligotrophic pool, located in a health-dominated ecosystem. The bottom sediments are unconsolidated quartz sands which are covered by a detrital layer. This organic layer varies in thickness and is absent at some places. The detrital material is mainly derived from peat-moss (*Sphagnum*) which is abundant in Gerritsfles. The surface area of the pool is approximately 7 ha and the mean depth is 0.65 m. Kliplo (52°50′N, 6°26′E, 13 m above MSL), an oligo-mesotrophic pool, is located in an area that is characterized by the occurrence of aeolian sands. The bottom sediments consist of organic material which is mainly derived from decomposing algae. Kliplo has a surface area of approximately 0.5 ha and a mean water depth of about 1 m. At the western side of a strip of bog (5—10 m in length) separates the pool from a heathland. The pool has a sandy beach at the southeastern side. Otherwise the pool is enclosed by forest. More detailed descriptions are provided by Van Dobben et al. (1992) and Van Dam & Buskens (1993).

Methods

Modelling

Budgets of SO_4^{2-} and water in two moorland pools were calculated using two models. The model VENSIM (Van Dobben et al. 1992) simulates the water volume of the moorland pools. The model BUDGET (Van Dobben et al. 1992) calculates budgets for SO_4^{2-} in both pools. The *Sulfate* model was specifically developed to investigate how pool water SO_4^{2-} concentrations react to a change in S-deposition. The function of the different models and their relationships are depicted in Fig. 2.

Mass budgets of water

The model VENSIM (Van Dobben et al. 1992) simulated water and Cl^- budgets of the moorland pools from 1982—1990. VENSIM applies to

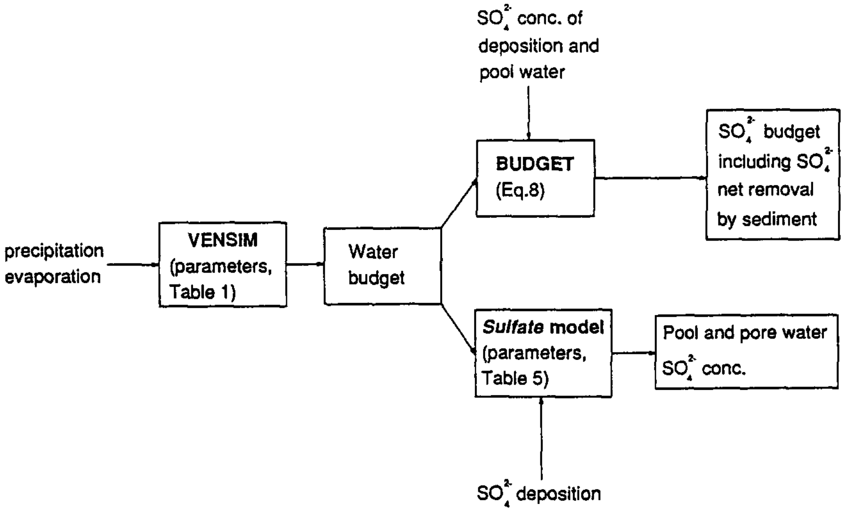

Fig. 2. Schematic representation of the function and relationship between the models used.

well-mixed non-stratifying lakes. The water budget can be described as follows:

$$dV_l/dt + \sum F_i = 0 \qquad (1)$$

where

t = time [y]
V_l = water volume of the pool [m^3]
ΣF_i = sum of inflow and outflow fluxes [$m^3\ y^{-1}$].

If Cl^- is considered to be conservative and the pool water is well-mixed, the chloride budget equation can be written as

$$d(V_l{*}C_l)/dt + \sum (F_i{*}C_i) = 0 \qquad (2)$$

where

C_l = Cl^- concentration in the pool [mmol m^{-3}]
C_i = Cl^- concentration in F_i (inflow and outflow fluxes) [mmol m^{-3}]

Figure 3 is a schematic representation of the pool system. The surface area of the pool depends on the water level. The hydraulic resistance of the pool bottom decreases near the border. The parameters and variables of the model are listed in Table 1. Since both pools have a perched water table, inseepage does not occur. The concentration of Cl^- ions in the evaporation flux is neglected so $F_e{*}C_e$ can be left out from Eq. (2) and the

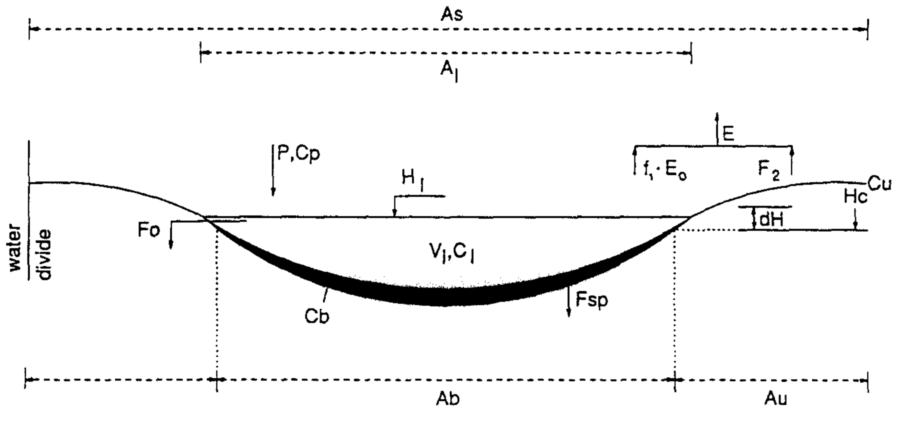

Fig. 3. Schematic representation of the pool system (for explanation of the symbols see Table 1 and text).

Table 1. Variables and parameters of the VENSIM model.

	Symbol	Unit	
Input variables			
Precipitation per 10 days	P	mm	
Evaporation per 10 days	E_o	mm	
Cl^- concentration in precipitation	C_p	mmol m^{-3}	
State variables			
Cl^- concentration in pool water	C_l	mmol m^{-3}	
Pool water volume	V_l	m^{-3}	
Parameters			
Catchment area	A_s	m^2	*
Pool water area	Al	m^2	
Surface area of the border strip with hydraulic bottom resistance c_u	A_u	m^2	
Surface area of the central part of the pool with hydraulic bottom resistance c_b	A_b	m^2	
Empirical evaporation coefficient in resp. around pool	f_1, f_2	—	*
Hydraulic resistance of pool bottom	c_b	d	*
Hydraulic resistance of pool bottom above H_c + dH	c_u	d	*
Highest level where hydraulic bottom resistance is c_b	H_c	m + MSL	*
Range over which c_b reduces to c_u	dH	m	*
Water pressure below pool bottom	H_r	m + MSL	

* Calibrated parameters.

concentration of Cl^- in the outflow fluxes equals the pool water concentration. With these assumptions Eqs. (1) and (2) can be written as

$$F_p + F_e + F_{sp} + F_o + dV_l/dt = 0 \tag{3}$$

$$F_p * C_p + (F_{sp} + F_o) * C_l + d(V_l * C_l)/dt = 0 \tag{4}$$

where the subscripts p, e, sp and o denote precipitation, evaporation, outseepage and overflow respectively. We use the convention that inflow and decrease of storage have a positive sign. The components of Eqs. (3) and (4) are calculated as follows:

$$F_p = P \cdot A_s \tag{5}$$

$$F_e = f_1 \cdot E_o \cdot A_l + F_2 \cdot (A_s - A_l) \tag{6}$$

where

$F_2 = f_2 \cdot E_o \quad \text{if } P > f_2 \cdot E_o$
$F_2 = P \quad \text{if } P \leqslant f_2 \cdot E_o$

$$F_{sp} = (H_l - H_r) \cdot (A_b/c_b + A_u/c_u) \tag{7}$$

VENSIM integrates Eqs. (3) and (4). The initial values of the state variables are taken from observations. The pool water surface A_l, the pool water level H_l and the pool water volume V_l are related by morphometric data. The model was calibrated by minimizing the root mean square difference between observed and calculated pool water levels and chloride concentrations over the period 1982—1990. With the calibrated model components of the water budget are calculated with Eq. (3).

Mass budgets of SO_4^{2-}

The model BUDGET (Van Dobben et al. 1992) was applied to calculate budgets of SO_4^{2-} for the years 1982—1990 using Eq. (4), extended with the term LOSS:

$$F_p * C_p + (F_{sp} + F_o) * C_l + d(V_l * C_l)/dt = -LOSS \tag{8}$$

where C denotes the concentration of SO_4^{2-}. The LOSS term is used to balance the budget and refers to the amount of SO_4^{2-} that is removed or gained from the pool water by processes other than by mass transport with water, i.e. biogeochemical reactions. We will refer to the LOSS as the net removal of SO_4^{2-}. The water fluxes and pool water volume are taken from the VENSIM output (Fig. 2). Pool water SO_4^{2-} concentrations are measured values.

Modelling of pool water SO_4^{2-} concentrations

To investigate how pool waters react to a change in S-deposition, we developed a simple model, the *Sulfate* model. Gerritsfles and Kliplo were represented as box-shaped lakes with a constant water level. The nine-year average water budgets were used as hydrological input (Fig. 2). Overflow, outseepage and evaporation were expressed as a fraction of precipitation, and the change of storage was set to zero (while in fact it amounted ~ 2% of the precipitation). Two dissolved sulfur species were considered; SO_4^{2-} and any form of reduced dissolved sulfur. We estimated the uptake of SO_4^{2-} in the water column by *Sphagnum* (in Gerritsfles) and by algae (in Kliplo) from the concentration of organic S in the upper 2 cm of the sediment (non-publ.) and the sedimentation rate (for both pools about 1 mm y^{-1}, Van Dam 1987). Sulfate reduction rates in the sediment, sulfur oxidation rates in the water column and sulfur fixation rates in the sediment were modelled by first order reaction kinetics using the parameters Kred, Kox and Kfix respectively. Transport of sulfur species occurs via diffusion and mass flow (downward transport).

Because values for the parameters Kox, Kred and Kfix in Gerritsfles and Kliplo are not known, we made a combination of these parameters such that (1) a steady state SO_4^{2-} pore water profile was reached which agreed with periodic measurements during 1990 of SO_4^{2-} concentrations in pore waters within a range of ± SD, (2) a steady state SO_4^{2-} pool water concentration was reached i.e. the mean SO_4^{2-} concentration over 1982—1990, (3) the modelled steady state SO_4^{2-} flux across the sediment water interface was of the same order of magnitude as that observed in the field. We used mean pool water SO_4^{2-} concentrations instead of the individual values because it requires a much more simple model and it serves our purpose, i.e. to investigate whether SO_4^{2-} pool water concentrations were reacting fast to a decrease of SO_4^{2-} input or whether there was a slow reaction yielding SO_4^{2-} pool water concentrations within the range of the measured fluctuations.

Deposition estimates

Model input consists of data collected at Gerritsfles and Kliplo during the period 1982—1990. The amount of precipitation and its chemical composition were not monitored continuously at both locations. Missing data were replaced by data from nearest monitoring stations (Table 2, Fig. 1). Bulk deposition of Cl^- and precipitation at the Gerritsfles and Kliplo locations were measured by open funnel samplers. The total deposition of SO_x onto both pool surfaces was estimated by the sum of the wet S-deposition and the dry S-deposition.

Up to 1988, wet S-deposition in The Netherlands was measured using open funnel samplers (bulk samplers), which also included dry S-deposition onto the capture surface. Since 1988, wet-only collectors were used with the funnel open to the atmosphere during rain events only. Deposition of SO_4^{2-} calculated from precipitation data collected by bulk samplers was estimated to be about 25% higher than those collected with wet-only samplers (Erisman et al. 1989). The wet S-deposition estimates before 1988 are corrected accordingly. Yearly average wet deposition fluxes for each monitoring station in the Netherlands (20 in 1982 and 14 in 1987 and following years) were calculated by multiplying the SO_4^{2-} concentra-

Table 2. Monitoring stations and data that were used for calculating budgets in Gerritsfles and Kliplo.

	amount evap.	amount prec.	Cl^- prec.	water level	solutes in prec.	solutes in lake water
Gerritsfles site						
Gerritsfles[1,2]		+	+	+	+	+
Radio Kootwijk[3]	+	+				
Kootwijk[2]			+			
Deelen[3]					+	
Druten[3]					+	
Kliplo site						
Kliplo[1,2]		+	+	+	+	+
Witteveen[3]	+	+			+	
Eelde[3]	+					

evap. = evaporation, prec. = precipitation.

[1] Monitoring site of the DLO Institute for Forestry and Nature Research.

[2] Monitoring site of the Agricultural University.

[3] Monitoring station of The Royal Meteorological Institute.
Monitoring at station Deelen was moved to Druten starting at 01-01-1986.

tion and the amount of rain. The local fluxes at Gerritsfles and Kliplo were subsequently estimated by interpolation. The uncertainty in the annual average wet deposition flux is 25% (Erisman 1992).

Dry S-deposition at Gerritsfles and Kliplo was estimated using interpolated SO_2 and particulate SO_4^{2-} concentrations and meteorological parameters (10 × 10 km^2 grid) based on measurements at stations of the National Air Quality Monitoring Network (NAQMN, Elskamp 1989, Fig. 1). Roughness characteristics of the areas surrounding the stations differ from those of water surfaces. Therefore, before interpolation of SO_2 and SO_4^{2-} concentrations to the Gerritsfles and Kliplo site, the measured concentrations and meteorological data were extrapolated to a height (50 m) where deposition and roughness characteristics do not influence the concentration profile of SO_2 (Erisman 1993). Hourly average dry deposition was then inferred from interpolated concentrations and an estimated local dry deposition velocity. The dry deposition velocities were calculated with the resistance analogy (Hicks et al. 1987) using interpolated meteorological data and the roughness characteristics for water surfaces. The annual average dry deposition flux is calculated by summing two-hourly average values. This dry deposition flux is currently the best estimate available for the locations Gerritsfles and Kliplo. The uncertainty in the annual average dry deposition flux is 45% (Erisman 1992, 1993). For the year 1986 we do not have a reliable estimate of dry and wet S-deposition because the configuration of the monitoring network was changed. For budget calculations of 1986 we therefore used interpolated values between 1985 and 1987.

Analyses of Cl^-, SO_4^{2-} were carried out by different laboratories. Chloride was determined by potentiometrical titration with a silver nitrate solution (Waterleidingbedrijf Midden-Nederland, WMN and National Institute of Public Health and Environmental Protection, RIVM) or by ion chromatography (Dionex or HPLC, Agricultural University, LUW). Sulfate was analyzed through coloring of excess barium with thorium after addition of a barium perchlorate solution (RIVM, WMN) or by ion chromatography (Dionex or HPLC, LUW). pH was determined potentiometrically using a combination electrode. Parallel samples of several pools were taken to compare the different methods. No appreciable differences between results of the methods were found for Cl^- and SO_4^{2-} (Van Dobben et al. 1992, two tailed T-Test, $p > 0.31$).

Pore water analysis and fluxes

Fluxes across the sediment/water interface were determined to estimate within-year variation in SO_4^{2-} fluxes and to compare the fluxes with modelled net removal of SO_4^{2-} from the water column. To assess fluxes of SO_4^{2-} over the sediment water interface, pore water was collected during the year 1990 in Gerritsfles and Kliplo.

Pore water was sampled by *in situ* dialysis using a sampling device ('peeper', l × h × w = 60 × 30 × 4 cm) that contained 10 membrane cells (modified after Oenema 1990) with slits parallel to the sediment-water interface, covered with a 0.2 μm biologically inert acrylic copolymer membrane filter (Versapor-200: Gelman Sciences). The upper 6 cells (width of slit 5 mm) of the peeper comprised about 40 ml, the lower 4 cells (width of slit 10 mm) about 80 m. Pore water samples were withdrawn through tubing that was connected with the cells and that reached to the water surface. Sulfate was measured by High Performance Liquid Chromatography (KH-phtalate, pH 4 as eluent). The peeper was installed permanently for one year. The water inside the membrane cells was allowed to equilibrate with the pore water for about a month.

Fluxes were calculated according to the equation (Lerman 1978)

$$J_{SO_4^{2-}} = -\phi \cdot D_s \cdot \frac{d[SO_4^{2-}]}{dx} \qquad (9)$$

where ϕ is porosity and D_s denotes the whole sediment diffusion coefficient. The D_s was determined in the lab on duplicate cores using tritiated water (Sweerts et al. 1991; Marnette et al. 1992a) and was corrected for temperature.

Pore water Al, SO_4^{2-} and K^+ were used to calculate equilibria with (K-)Al-SO_4^{2-} phases. Al was determined colorimetrically on acidified samples (pH ~ 2) using pyrocatechol violet. Pyrocatechol violet complexes essentially all dissolved Al except very strong organic-Al complexes as Al-citrate or Al-salicylate (J Mulder, pers. comm.). Potassium was determined by Atomic Absorption Spectrometry.

Results

Mass budgets of water

To test the model assumption that the pool waters are well-mixed, Cl^- and SO_4^{2-} concentrations were determined at the surface, at ca. 30 cm and at ca. 80 cm depth (Table 3). The coefficient of variation (CV) of SO_4^{2-} and Cl^- concentrations in Gerritsfles was less than 2% except for Cl^- and SO_4^{2-} concentrations in July. The CV at Kliplo was somewhat higher than in Gerritsfles but still less than 4%, with exception of SO_4^{2-} in June, July and December and of Cl^- in December. Although these data only cover a limited period, they indicate that in most cases the pool waters approach a well-mixed state.

Table 3. Variation of pool water Cl^- and SO_4^{2-} concentrations in Gerritsfles and Kliplo. Values represent means (± SD) of three samples collected at one sampling date, each sample taken at a different depth (surface, 30 cm and 80 cm depth).

Gerritsfles			Kliplo		
Date	$[Cl^-$	$[SO_4^{2-}]$	Date	$[Cl^-$	$[SO_4^{2-}]$
			1 May 90	400 ± 1	75 ± 1
1 Jun 90	389*	136 ± 1.3	1 Jun 90	438 ± 17	93 ± 18
2 Jul 90	191 ± 9	116 ± 9.4	2 Jul 90	267 ± 4	92 ± 12
31 Jul 90	332 ± 4	109 ± 0.4	3 Aug 90	448 ± 8	92 ± 1
4 Sep 90	318 ± 2	102 ± 1.1	4 Sep 90	395 ± 4	80 ± 2
1 Oct 90	317 ± 1	101 ± 0.2	1 Oct 90	391 ± 2	75 ± 1
1 Nov 90	315 ± 4	95 ± 0.5	1 Nov 90	389 ± 5	78 ± 1
3 Dec 90	318 ± 4	103 ± 0.6	3 Dec 90	399 ± 30	82 ± 8

* $[Cl^-]$ at surface and at 30 cm depth.

The water levels in Gerritsfles could be simulated rather precisely using VENSIM (Fig. 4). The root mean square error (RMSE) between measured and simulated water levels was 2.83 cm (~ 4% of mean depth). Chloride concentrations could be simulated reasonably well (Fig. 4), with a RMSE between measured and calculated values of 33.9 mmol m^{-3} (~ 14% of mean Cl^- concentration). Chloride concentrations were overestimated during 1987 and slightly underestimated during the following period. The trends of measured and simulated Cl^- concentrations, however, agreed well. Simulation of water levels in Kliplo (Fig. 5) resulted in a RMSE of 4.12 cm (~ 5.5% of mean depth). Simulation of the Cl^- concentration was slightly more accurate as in Gerritsfles (RMSE 32.4 mmol m^{-3}, ~ 10% of mean Cl^- concentration). Also in Kliplo, Cl^- concentrations were underestimated during the period 1988—1990.

The budgets of water and SO_4^{2-} in Gerritsfles and Kliplo are depicted in Fig. 6. The outseepage flux depends on bottom resistance, water level and the water pressure below the pool water, neither of which varied much over the whole period. Annual precipitation varies from 719 mm (1982) to 1013 mm (1983) in Gerritsfles and from 667 mm (1989) to 1042 mm

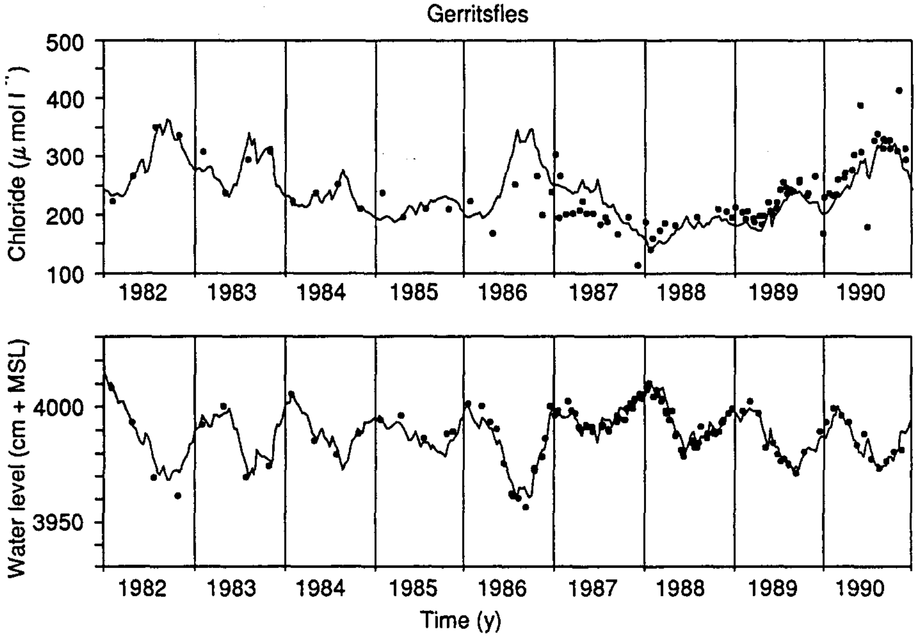

Fig. 4. Measured and simulated Gerritsfles pool water Cl^- concentrations and pool water levels. Dots represent measurements, solid lines simulations.

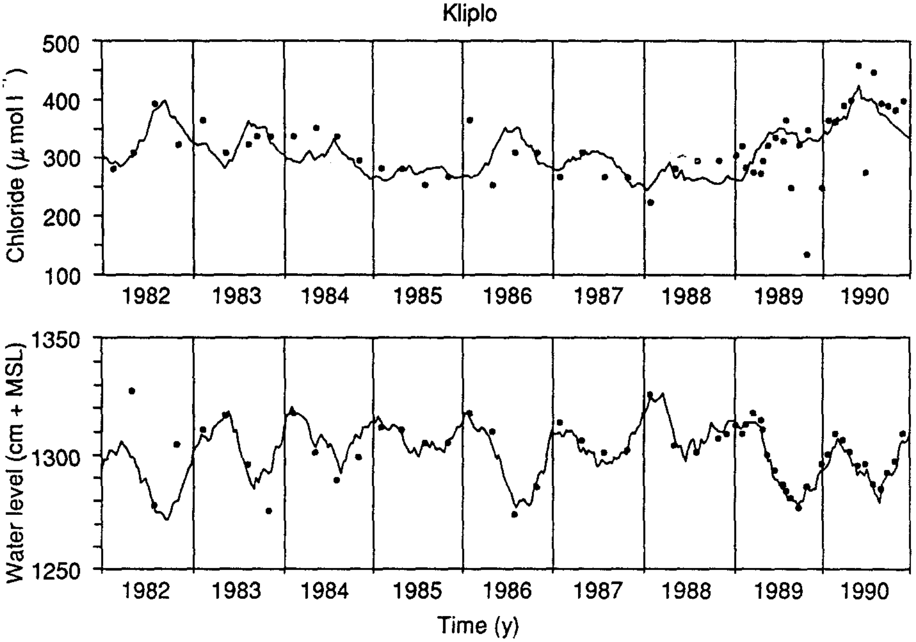

Fig. 5. Measured and simulated Kliplo pool water Cl^- concentrations and pool water levels. Dots represent measurements, solid lines simulations.

(1988) in Kliplo. Generally the change of water storage in Gerritsfles and Kliplo is small compared to precipitation. The total change of storage over nine years comprises about 2% of the total precipitation.

Input and output budgets of SO_4^{2-}

The budgets of SO_4^{2-} (from the BUDGET model, eq. (8)) in Gerritsfles and Kliplo are shown in Fig. 6. In Gerritsfles the annual net removal of SO_4^{2-} to the sediment clearly decreased after 1986 (Fig. 6). In Kliplo the net removal follows the same trend but the decrease was less pronounced than in Gerritsfles.

Estimates for the annual total S deposition and for the wet S deposition at Gerritsfles and Kliplo are shown in Figs. 7a, b. Wet S-deposition fluxes were rather constant over the years at both locations, whereas total deposition showed a clear decrease after 1986 as a result of a decrease in SO_2 concentrations (in the Netherlands, the annual average SO_2 concentration decreased from 22 $\mu g\ m^{-3}$ in 1980 to 10 $\mu g\ m^{-3}$ in 1989, Erisman 1992).

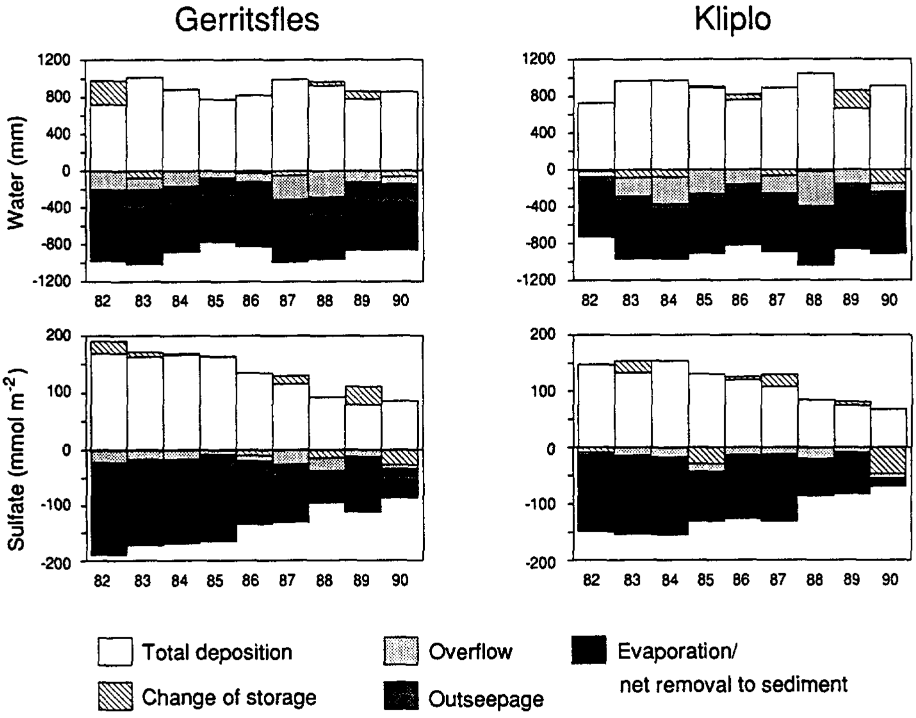

Fig. 6. Water and SO_4^{2-} budgets of Gerritsfles and Kliplo over the period 1982—1990.

Pool waters

Temporal variation in SO_4^{2-} concentrations of Gerritsfles and Kliplo pool waters is considerable (Figs. 7c, d). In Gerritsfles pool water SO_4^{2-} concentrations decreased significantly (t-test, $p < 0.0001$) from about 140 μmol l^{-1} (over 1982 and 1983) to around 100 μmol l^{-1} (1984—1990). The decrease of SO_4^{2-} concentration in pool water did not coincide with that of total S deposition (Fig. 7). A trend analysis (procedure Autoreg, SAS) over the years 1982—1990, using a linear model with corrections for periodicity, gave a significant ($p < 0.005$) decrease of pool water SO_4^{2-} concentrations but a poor fit ($R^2 = 0.34$). Sulfate pool water concentrations in Kliplo did not follow a linear trend in time and neither did they show a significant decrease over 1982—1990.

Fluxes

The temporal variation of sulfate pool and pore water concentrations in

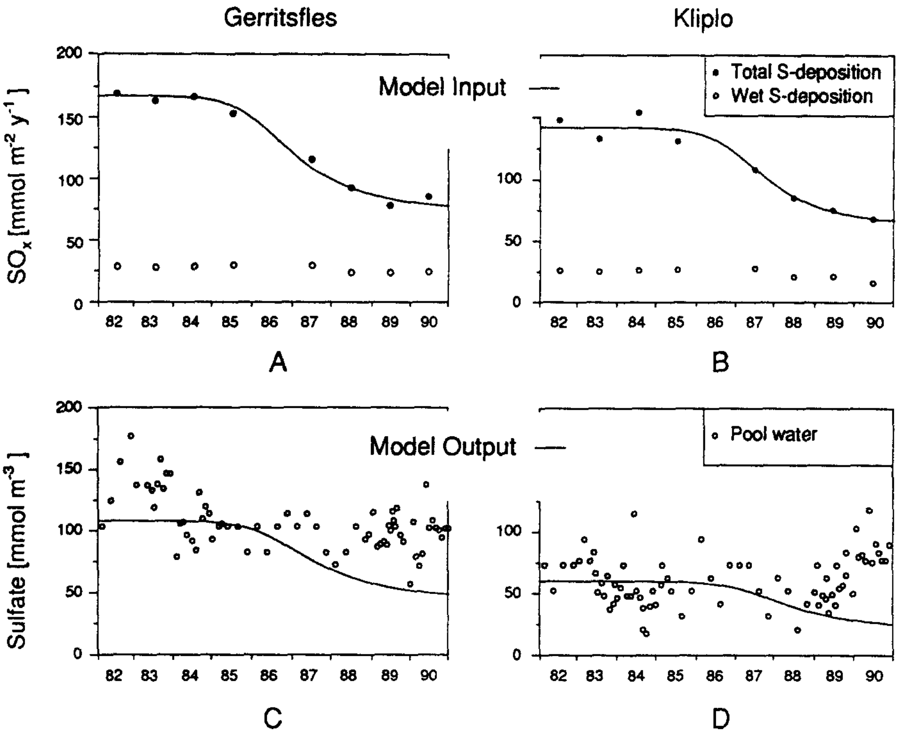

Fig. 7. (A, B) Annual total and wet deposition of SO_x and/or SO_4^{2-}. Total S deposition was fitted as a function of time and was used as input for the *Sulfate* model. (C, D) Pool water SO_4^{2-} concentrations as function of time, measured and modelled by the *Sulfate* model.

Gerritsfles and Kliplo (Fig. 8) and calculated fluxes across the sediment water interface (Table 4) was large. In both Gerritsfles and Kliplo fluxes from the sediment into the water column (negative sign) temporarily occurred, although at different times of the year.

Modelling of pool water SO_4^{2-} concentrations

The main purpose of the *Sulfate* model was to investigate whether SO_4^{2-} pool water concentrations were reacting fast to a decrease of SO_4^{2-} input or whether there was a slow reaction yielding SO_4^{2-} pool water concentrations within the range of the measured fluctuations (Figs. 7c, d).

The most important model parameters and their (steady state) values are listed in Table 5. Before imposing the decrease of S-deposition on the model system (Figs. 7a, b), the unknown reduction, oxidation and fixation rate constants (Kred, Kox and Kfix) were tuned to achieve a steady state

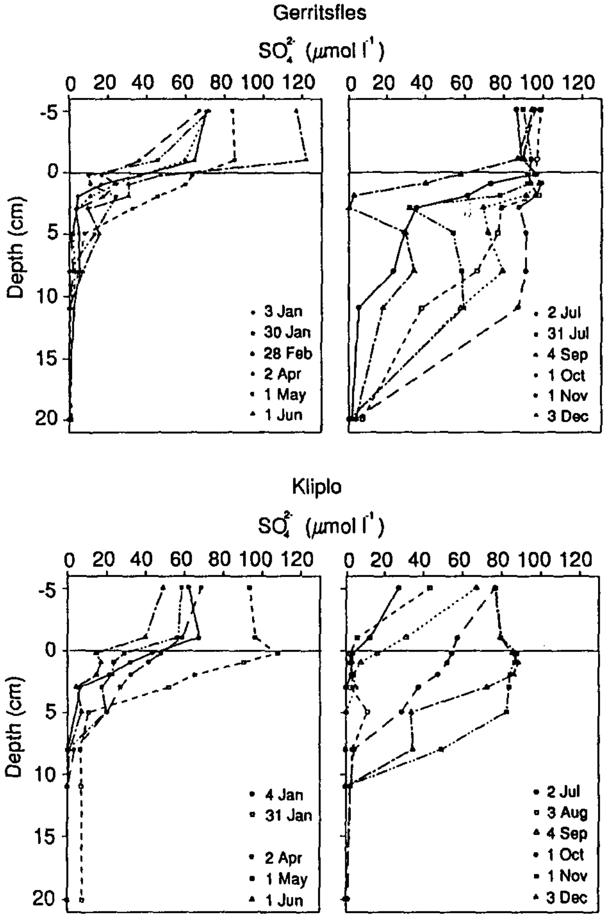

Fig. 8. Pore water concentrations of SO_4^{2-} in Gerritsfles and Kliplo sediment during 1990.

pool water SO_4^{2-} concentration. Only Kred has been estimated earlier in Gerritsfles and varied considerably with time and depth (0.6—5 d^{-1}, Feijtel et al. 1989). As steady state concentrations were used the mean values of pool water SO_4^{2-} concentrations over the whole period 1982—1990 (Table 5). The oxidation (in the water column) and fixation (in the sediment) rate constants have never been estimated in these sediments. Biological uptake of sulfate in the water column calculated from organic-S contents in the upper 2 cm of the sediment (13.3 μmol cm^{-3} for Gerritsfles and 28.3 μmol cm^{-3} for Kliplo) and sedimentation rates (1 mm y^{-1}), was estimated as 6.7 mmol m^{-2} y^{-1} and 14.2 mmol m^{-2} y^{-1} for Gerritsfles and Kliplo respectively. These values can be considered as

Table 4. Diffusive flux of SO_4^{2-} over the sediment-water interface in Gerritsfles and Kliplo during the year 1990, calculated from pore water gradients. Positive fluxes are directed downwards.

Gerritsfles		Kliplo	
Date	SO_4^{2-} flux mmol m^{-2} d^{-1}	Date	SO_4^{2-} flux mmol m^{-2} d^{-1}
03-Jan-90	0.12	04-Jan-90	0.09
30-Jan-90	0.08	31-Jan-90	−0.04
28-Feb-90	0.11		
02-Apr-90	0.10	02-Apr-90	0.05
01-May-90	0.21	01-May-90	0.15
01-Jun-90	0.49	01-Jun-90	0.15
02-Jul-90	−0.05	02-Jul-90	0.06
31-Jul-90	0.01	03-Aug-90	0.03
04-Sep-90	−0.03	04-Sep-90	0.10
01-Oct-90	−0.04	01-Oct-90	0.02
01-Nov-90	0.01	01-Nov-90	0.04
03-Dec-90	0.13	03-Dec-90	−0.02

either under- or overestimates because organic S may be mineralized by (an)aerobic decomposition or diagenetically formed by reaction of sulfides with organic matter. The uptake of S from the water column in Gerritsfles however agrees rather well with the 5.5 mmol m^{-2} y^{-1} estimated from the annual production of *Sphagnum* and its S content (Feijtel et al. 1989).

We listed five different combinations of Kred, Kox and Kfix that yielded a steady state (Table 5). All these combinations of rate constant values for Gerritsfles yielded steady state interstitial SO_4^{2-} concentrations that just fall within the range of pore water measurements (Fig. 9). For Kliplo the pore water steady state SO_4^{2-} concentrations were below the range of measured concentrations and could not be improved using the current model. The model could not reach steady state below a Kred value of 0.38 (Gerritsfles) and 2.28 d^{-1} (Kliplo), because the SO_4^{2-} concentration of the deposition was so much higher than that of the pool water. Only reduction rate constants above these values could bring the pool water SO_4^{2-} concentration at the preset steady state level (mean SO_4^{2-} pool water concentration over the whole period). The change in modelled pool water SO_4^{2-} concentrations is only dependent on the change in S deposition; different combinations of Kred, Kox and Kfix that lead to steady state situation resulted in the same rates of change of pool water SO_4^{2-} concentrations.

Over the period that the S deposition did not decrease and the model

Table 5. The most important parameters used for predicting the SO_4^{2-} pool water concentration using the *Sulfate* model.

	Gerritsfles	Kliplo	units
amount of precipitation	0.00236	0.00238	$m\ d^{-1}$
biol. uptake of SO_4^{2-} in water	6.7	14.2	$mmol\ m^{-2}\ y^{-1}$
overflow	0.17	0.23	frac. of prec.
seepage	0.23	0.08	frac. of prec.
evaporation	0.60	0.69	frac. of prec.
depth	0.68	0.82	m
area	56000	6500	m^2
number of sediment layers	10	10	—
thickness of sediment layer	0.01	0.01	m
mean pool water SO_4^{2-} concn. used for tuning Kred, Kox and Kfix	108	60	$mmol\ m^{-3}$

	model run #	Kred (d^{-1})	Kox (d^{-1})	Kfix (d^{-1})	SO_4^{2-} flux*
Gerritsfles	1	0.410	1.00e-3	0.9	127
	2	0.382	1.00e-4	0.9	123
	3	0.384	1.00e-4	0.5	124
	4	0.381	1.00e-4	1.5	123
	5	0.500	4.38e-3	0.9	137
Kliplo	1	2.345	1.00e-4	0.9	112
	2	2.283	1.00e-5	0.9	112
	3	2.285	1.00e-5	0.5	112
	4	2.281	1.00e-5	1.5	112
	5	3.000	9.36e-4	0.9	117

* SO_4^{2-} flux across sediment water interface ($mmol\ m^{-2}\ y^{-1}$).

was at steady state (Fig. 7) we calculated a SO_4^{2-} flux across the sediment/ water interface of 123 mmol $m^{-2}\ y^{-1}$, which is in fair agreement with measured integrated annual SO_4^{2-} flux of 111 mmol $m^{-2}\ y^{-1}$ in 1987 (Feijtel et al. 1989).

When steady state was reached, the model was run for 9 years which included a decrease in S-deposition according to sigmoid function (Figs. 7a, b). The model runs with different combinations of rate constants (Table 5) yielded the same results; the model calculated a decrease of the pool water SO_4^{2-} concentration as a reaction on decreased S deposition that clearly did not match the measured SO_4^{2-} concentrations (Figs. 7c, d).

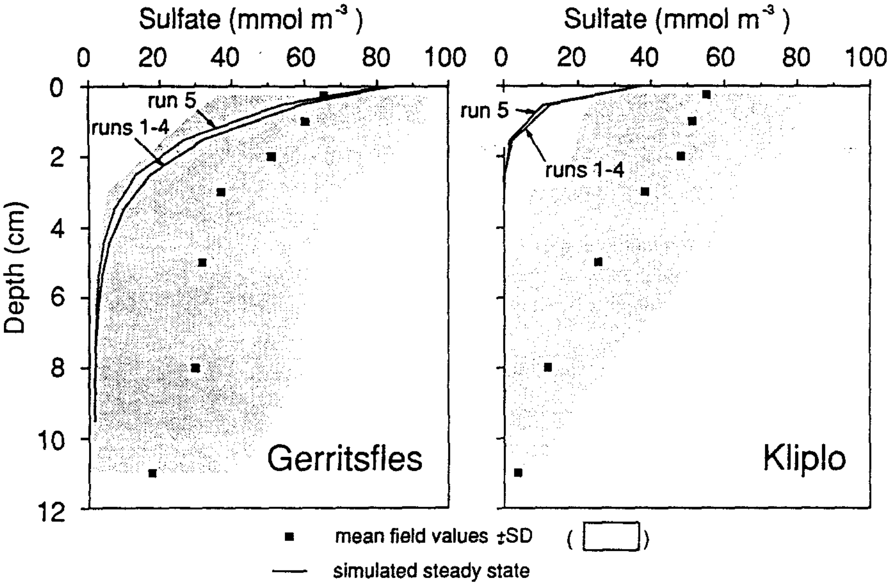

Fig. 9. Mean pore water SO_4^{2-} concentrations (± SD) during the year 1990 and steady state SO_4^{2-} profiles as calculated by different runs of the *Sulfate* model.

Discussion

Baker et al. (1986) and Kelly et al. (1987) developed a model that predicts the SO_4^{2-} removal and the resulting acid neutralization within acid-sensitive lakes requiring the water residence time, mean depth and the average mass transfer coefficient for SO_4^{2-}. The model only applies to lakes with oxic hypolimnia and might be used for Gerritsfles and Kliplo. At steady state, the removal of SO_4^{2-} by in-lake processes is expressed by the removal coefficient R, which is the proportion of incoming mass which is removed from the water column, either to the sediments or to the atmosphere or to a new form within the water column (Kelly et al. 1987):

$$R = \frac{mass\ in - mass\ out}{mass\ in} \tag{10}$$

At steady state, mass in = mass out + mass lost within the lake. We may consider the amount of SO_4^{2-} in Gerritsfles and Kliplo is in a steady state over the period 1982—1990 because the change of storage is only 2.5% of the SO_4^{2-} input for Gerritsfles and 3% for Kliplo. The change of storage for the individual years however may be high and ranges from 0.7—41% for Gerritsfles and from 0.3—69% for Kliplo. So the model of Baker et al. (1986) and Kelly et al. (1987) is only applicable when using mean data values during 1982—1990. The removal coefficient of Gerritsfles and Kliplo can easily be calculated from the SO_4^{2-} budgets (Fig. 6) with Eq. (10) where 'mass in − mass out' equals the net SO_4^{2-} removal and 'mass in' equals the total S deposition. Mass balance data were related with the SO_4^{2-} mass transfer coefficient S, the water residence time τ_w and the mean depth $\bar{z}$ (Kelly et al. 1987) according

$$R = \frac{S}{(\bar{z}/\tau_w) + S} \tag{11}$$

with the assumption that SO_4^{2-} reduction follows first order kinetics. The mass transfer coefficient S (in m y^{-1}) can be seen as the height of the water column from which SO_4^{2-} is removed each year. Estimates of the mass transfer coefficient were calculated as follows (Kelly et al. 1987):

$$S = \frac{f}{[SO_4^{2-}]} \tag{12}$$

where $[SO_4^{2-}]$ is the mean pool water SO_4^{2-} concentration (mmol m^{-3}) and f the SO_4^{2-} reduction rate (mmol m^{-2} y^{-1}) estimated as the net removal of SO_4^{2-} from the water column derived from the mass budgets.

To compare our budget calculations with the model developed by Baker et al. (1986) and Kelly et al. (1987), the SO_4^{2-} removal coefficient (Table 6) was calculated from mass budgets of Gerritsfles and Kliplo using Eq. (10) and from the model formulations of Baker et al. (1986) and Kelly et al. (1987) using Eqs. (11) and (12). The removal coefficients derived directly from the mass budgets are much lower than those which were modelled (Baker et al. 1986), perhaps because the net removal did not follow a first order function of the pool water SO_4^{2-} concentration (one of the model conditions) for both pools. This is supported by the fact that we observe a decrease in the net SO_4^{2-} removal while there is not a concomitant decrease of pool water SO_4^{2-} concentrations (Figs. 6 and 7).

The removal coefficients of Gerritsfles and Kliplo as function of $\bar{z}/\tau_w$ (the height of the water column that is displaced by new water each year) fit rather well in the trend reported by Baker et al. (1986) and Kelly et al. (1987) for a number of lakes (Fig. 10). The authors concluded that the contact time of the water with sediments is crucial in determining the fraction of SO_4^{2-} removed from water as it passes through the lake which

Table 6. Removal coefficients calculated from (1) mass transfer coefficients (S), mean depth ($\bar{z}$) and water residence time (τ_w), ($R^{\#}$) and from (2) mass budgets (R). Data are means over the period 1982—1990.

	$\bar{z}$ (m)	τ_w (y)	$[SO_4^{2-}]$ (mmol m^{-3})	f* (mmol m^{-2} y^{-1})*	S (m y^{-1})	$R^{\#}$ (Eq. 11) (−)	R (Eq. 10) (−)
Gerritsfles	0.68	0.77	108	96	0.89	0.50	0.74
Kliplo	0.82	0.96	60	95	1.58	0.65	0.83

* f is the mean net SO_4^{2-} removal rate over 1982—1990 estimated from budgets.

\# calculated with the model developed by Baker et al. (1986) and Kelly et al. (1987).

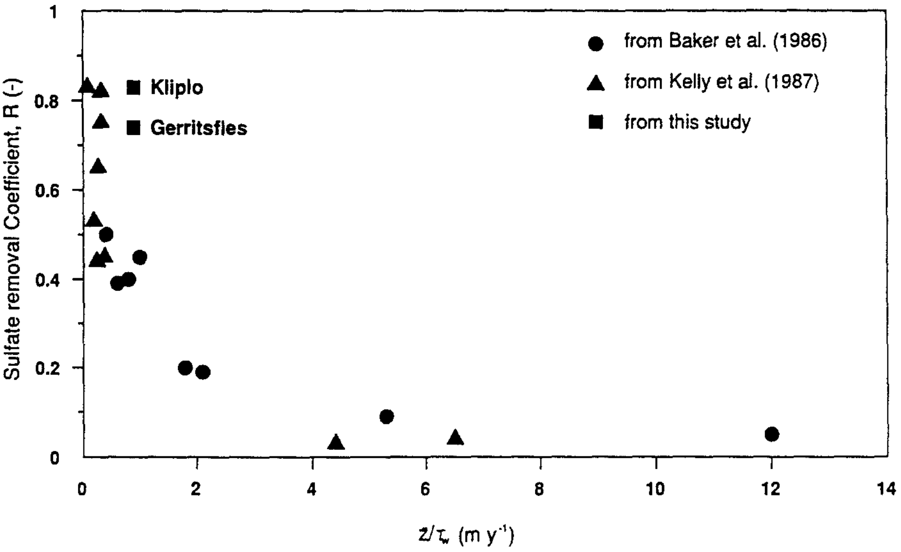

Fig. 10. Removal coefficients of SO_4^{2-} as function of $\bar{z}/\tau_w$ for a number of lakes. The removal coefficients and $\bar{z}/\tau_w$ of Gerritsfles and Kliplo are mean values over 1982—1990 derived from mass balances of SO_4^{2-} and water.

is evidenced by a decreasing SO_4^{2-} removal coefficient with increasing $\bar{z}/\tau_w$.

As an independent check of the SO_4^{2-} net removal calculated by the BUDGET model, we used annual fluxes across the sediment/water interface. The time-integrated flux of SO_4^{2-} over 1987 was estimated by Feijtel et al. (1989). In our study SO_4^{2-} fluxes were calculated from pore water concentrations over the year 1990 (Table 4). In some cases fluxes may have been underestimated because the spatial resolution at which pore water concentrations were measured (1 cm above the sediment and 0.25 cm below) may have been insufficient to reliably estimate the concentration gradients. In most cases there is a gradual decrease of SO_4^{2-} with depth (Fig. 8) and fluxes are considered to be well estimated.

In Table 7 the diffusive transport of SO_4^{2-} into the sediment is compared with the net removal of SO_4^{2-} by the sediment from the budget calculations. The annual fluxes and modelled net removal are in the same order of magnitude and, especially for Gerritsfles in 1990, agree very well. Also they both show a decrease from 1987 to 1990 for Gerritsfles. The calculation of the net diffusive SO_4^{2-} flux from pore water gradients is a completely different approach to estimate net removal of SO_4^{2-} from the water column than is the budget calculation using hydrochemical models. The good agreement between these approaches indicated that the net SO_4^{2-} removal has been fairly well estimated.

Table 7. Annual net removal of SO_4^{2-} from the water column in Gerritsfles and Kliplo from budget calculations and from diffusive fluxes of SO_4^{2-} across the sediment/water interface calculated from pore water gradients.

		Net removal to sediment (from mass budgets), mmol m^{-2}	Net removal into sediment (from diffusive fluxes), mmol m^{-2}
Gerritsfles	1987	83#	111*
	1990	32#	35#
Kliplo	1990	9#	22#

* from Feijtel et al. 1989.
\# from this study.

The total S-deposition in The Netherlands has decreased considerably after 1986. This temporal change in S deposition is mainly the result of a decrease in West European SO_2 emissions and thus SO_2 concentrations (Erisman 1992). Also a decline in total S-deposition at our study sites, based on regional data, has been calculated (Figs. 7a, b). There is a large discrepancy between measured lake water SO_4^{2-} concentrations in both pools and SO_4^{2-} concentrations modelled by the *Sulfate* model (Fig. 7). Measured pool water concentrations remained about constant while model calculations indicated a fast decrease of lake water SO_4^{2-} concentrations to the lowering of the S-deposition. So most likely, a net source of SO_4^{2-} makes up for the lowered input of atmospheric S. From the model simulations a supply rate of 89 mmol m^{-2} y^{-1} SO_4^{2-} for Gerritsfles and 75 mmol m^{-2} y^{-1} for Kliplo at the end of 1990 was estimated in order to maintain constant pool water SO_4^{2-} concentrations. Uptake of SO_4^{2-} by primary production in the water column or on top of the sediment is accounted for in the model. Therefore, the most likely source of extra SO_4^{2-} is the sediment, because besides atmospheric S deposition there are no other quantitatively important sources of SO_4^{2-}. We suggest three processes that may result in more or less constant SO_4^{2-} concentrations in spite of declining SO_4^{2-} inputs: (1) equilibrium control by SO_4^{2-} containing mineral phases, (2) desorption of SO_4^{2-} from positively charged surfaces and (3) input of SO_4^{2-} formed by oxidation of sedimentary reduced S through desiccation of a part of the pool bottom after dry summers. The first two processes represent a causal link between the supply of SO_4^{2-} and the decreased S-deposition, whereas the last process would be coincidental.

We investigated the possibility of equilibrium control of porewaters by SO_4^{2-}-containing minerals using data on pH, SO_4^{2-} total Al and K porewater concentrations collected in 1989 (not published), and equilibria constants as reported by Von Freiesleben (1988). Solubility curves, calculated for the SO_4^{2-} containing minerals alunite, basaluminite and jurbanite, minerals that might form at the observed porewaters concentrations, indicated that porewaters were not regulated by equilibrium control of these SO_4^{2-} containing minerals.

Sulfate concentration may be regulated by adsorption or desorption at positively charged surfaces in the sediment. Ensminger (1954) carried out extractions with sodium acetate (pH 4.8) on Florida peat which was presaturated with SO_4^{2-}. The peat released 160 mg S per kg material. Taking a dry bulk density of peat of 0.35 g cm^{-3} for the Dutch study sites, the potential adsorption of SO_4^{2-} can be estimated as about 175 mmol S per $m^2 \cdot 10$ cm sediment depth. If Gerritsfles and Kliplo sediments would possess the same properties as the peat used for the extractions, the release of SO_4^{2-} from the sediment as estimated by the *Sulfate* model (about 75—89 mmol m^{-2} y^{-1}) could be explained by desorption of SO_4^{2-} from peat. Recharging of the adsorption complex is necessary to provide a sustained supply of SO_4^{2-} to the water column. We have indications that periodical shifts of the redox boundary occur (Marnette et al. 1992a, b), so the adsorption complex can be recharged by SO_4^{2-} that has been supplied by reoxidation of reduced S compounds.

Van Dam (1987) reported a concomitant increase of SO_4^{2-} concentrations and a decrease of alkalinity and pH in Gerritsfles and several other pools after the extremely dry summer of 1976. Because of exposure of a part of the pool bottom to the atmosphere and subsequent oxidation of large quantities of reduced S, SO_4^{2-} concentrations reached extremely high levels of about 450 μmol l^{-1} (Van Dam & Buskens, 1993). During the following years, SO_4^{2-} concentrations decreased again through dilution with rain and by SO_4^{2-} reduction. The dry summers of 1986, 1989 and 1990 may have lead to pulses of SO_4^{2-} that replenished the amount of pool water SO_4^{2-}. However, since there is no causal link between increased S-oxidation through desication and decrease of S-deposition, this replenishment of SO_4^{2-} only could have happened by chance, since the amount of SO_4^{2-} released through oxidation should have been in the same order of magnitude in order to complement decreasing depositional SO_4^{2-} input. Nevertheless this might be a possible mechanism to explain the more or less constant pool water SO_4^{2-} concentrations in Gerritsfles in spite of decreasing S-deposition. In Kliplo after the dry summer in 1976, the SO_4^{2-} concentrations and pH remained relatively constant because the pool morphometry does not allow large parts of the bottom to desiccate.

In any case it is clear that the mechanism which is responsible for the net release of SO_4^{2-} to the water column will eventually lead to a strong decrease in sedimentary S.

Conclusions

The decrease of total S deposition onto two moorland pool systems, did not lead to decreased pool water SO_4^{2-} concentrations. Apparently a source of SO_4^{2-} within the lake caused the unexpectedly high SO_4^{2-} concentrations. The supply of SO_4^{2-} cannot be explained by the regulation of SO_4^{2-}-containing minerals but might be achieved by desorption processes in the sediment or by pulse-releases of SO_4^{2-} through desiccation of a part of the pool bottom after dry summers.

Future research will be necessary to establish the mechanisms which are responsible for the delivery of SO_4^{2-} from sediments to the water column.

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