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Sinks of anthropogenic nitrogen and sulphate in the Lehstenbach catchment (Fichtel gebirge): lessons learnt concerning reversibility

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Abstract

The Lehstenbach Catchment Study in the Fichtelgebirge region was one of many set up in 1987 to investigate the impact of sulphur and nitrogen emissions on soil, groundwater and freshwater quality. Sulphate immissions as determined by throughfall decreased by 50% down to 1 kmol ha^{-1} a^{-1} in the last 12 years. So far, recovery seems to be restricted to the top soil layers, whereas sulphate accumulation still continues in the deeper layers of the aquifer. Based on the analysis of nine cores of 10 m depth, the total sulphate pool in this layer is estimated to be about 90 kmol ha^{-1}. This pool is clearly reversibly bound. Its dynamics can be described by desorption isotherms. For nitrogen, export via the catchment runoff and net uptake by plants accounts for only one third of the total nitrogen sink. Redox processes have been shown to occur locally. However, this seems to be only a minor sink for both sulphur and nitrogen at the catchment scale. Instead, there is strong evidence that a substantial proportion of the nitrogen in the catchment is bound by adsorption to the solid phase in the deeper layers of the aquifer. This process is at present not well understood.

Key words: sulphur, nitrogen, deposition, reversibility, water quality

Introduction

Substantially increased sulphur and nitrogen emissions up to the eighties and decreasing sulphur emissions thereafter provide an excellent opportunity to test current hypotheses concerning the turnover of these substances in remote catchments (STODDARD & al. 1999). To assess the long-term development of groundwater and freshwater quality, the quantity stored underground needs to be evaluated. Furthermore, the kinetics of turnover of sulphur and nitrogen under varying boundary conditions have to be assessed.

It is widely accepted that sulphate is predominantly stored by adsorption of inorganic sulphate (VAN MIEGROET 1994, ALEWELL & al. 1997). Much of this seems to be reversibly bound and will be leached for decades even following a dramatic decrease in sulphate deposition. For nitrogen, many questions remain unsolved (FENN & al. 1998, LOVETT & al. 2000). Due to dry deposition, uptake, and leaching in the canopies of the trees, there is considerable uncertainty about the total amount deposited at single sites (ROSS & LINDBERG 1994). Furthermore, the magnitude of denitrification is not easily quantified at the catchment scale. Thus, the identification of additional sinks remains highly uncertain (c.f. MAGILL & al. 1997). This has important consequences for the assessment of the long-term development of freshwater quality: Whereas denitrification acts as a final sink, reversibility and limited storage capacity have to be taken into account in case of other sinks.

This paper summarises results of the Lehstenbach catchment study with respect to the magnitude, kinetics, and reversibility of the prevailing sinks of sulphur and nitrogen in a forested catchment. The focus is to assess the uncertainty of our knowledge with respect to single processes. It aims to delineate investigations necessary to quantitatively assess the future development of freshwater quality.

Site Description and Measurements

The Lehstenbach catchment is located in the Fichtelgebirge region in north-eastern Bavaria, approximately 30 km north-east of Bayreuth and 35 km west of Cheb (N. Latitude 50°08'; E. Longitude 11°52'). The catchment has an area of about 4.2 km^2 and lies at an altitude 695 to 877 m a.s.l. The bedrock consists of deeply weathered granite. Thickness of the regolith is 30 to 40 m. Among the soils, dystric cambisols and podzols prevail. One third of the catchment area is covered by wetlands. The vegetation is dominated by Norway spruce (> 95%). Annual mean air temperature is about 5 – 6.5 °C, mean annual precipitation sums up to 1000 mm (MANDERSCHEID & GÖTTLEIN 1995).

Since 1987, a comprehensive biogeochemical monitoring program has been carried out by the Bavarian State Office for Water Management, the Bavarian State Institute of Forestry, and the Bayreuth Institute for Terrestrial Ecosystem Research (BITÖK) (MORITZ & al. 1994, MANDERSCHEID & GÖTTLEIN 1995, LISCHEID & al. 1998). Bulk precipitation was collected at up to three plots, and throughfall at up to seven plots in biweekly intervals. The same holds for soil solution in 20 to 300 cm depth. Meteorological parameters have been measured at up to three different sites. Soil matrix potential, soil water content and soil temperature was measured at different plots. Groundwater data were available for 13 wells. Continuous streamwater sampling was performed at biweekly intervals at least at different sites, including the catchment's outlet. In addition, a variety of auxiliary studies have been performed in the catchment.

As the monitoring program was split between two different institutes and covered a 14 year period, a variety of instruments were used. In general, pH, electric conductivity and oxygen concentration were measured on site with WTW meters and electrodes of different types. Anions (NO_3^-, SO_4^{2-}, Cl^-, PO_4^{3-}) were determined by ion chromatography, Ca, Mg, Na, K and total Al by atomic emission spectometry with inductively coupled plasma. The total nitrogen content was determined by chemiluminescence (TN Analyzer), and NH_4^+ photometrically by flow injection analysis.

Results and Discussion

Mass Balance

Input fluxes were assessed by throughfall samplers at up to seven stands of different age. Output fluxes were quantified by streamwater export. In the 1988–1996 period mean annual precipitation was 950 mm, a little below the long-term mean of approximately 1000 mm a^{-1}. Evaporation of the canopy (bulk precipitation minus throughfall) was around 200 mm a^{-1} and net evapotranspiration (throughfall minus runoff) approximately 300 mm a^{-1}. Sulphate input

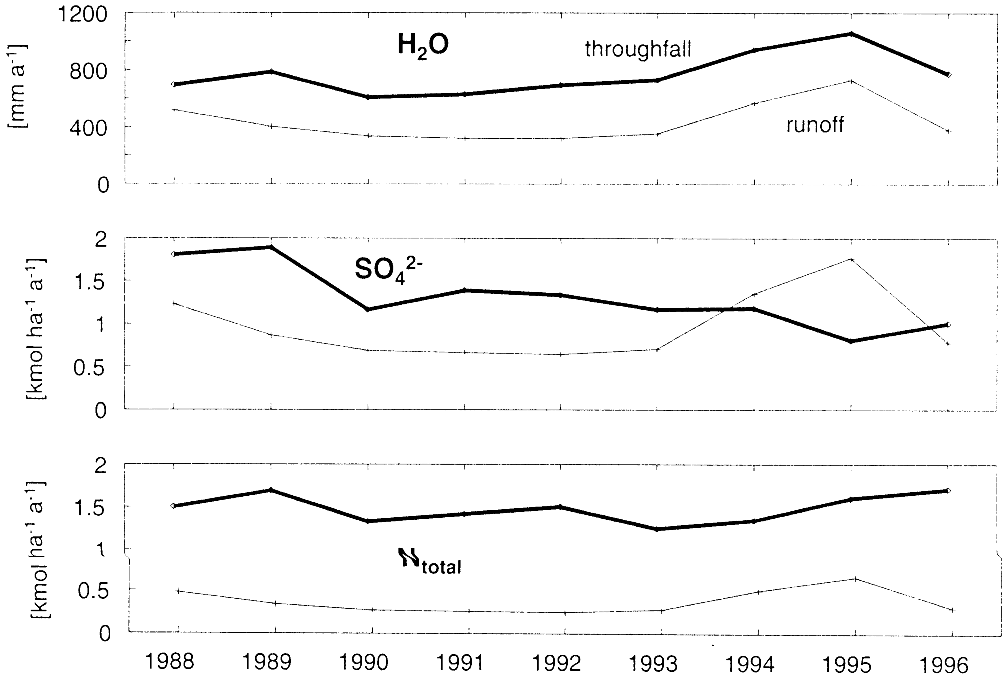

Fig. 1. – Input (bold line) and output fluxes (thin line) in the Lehstenbach catchment 1988–1996. Input fluxes are determined by throughfall samplers at up to seven sites, output fluxes are determined by the catchment runoff.

by throughfall exhibited a decrease of roughly 50%. Nitrogen did not show a clear trend (Fig. 1). Nitrate and ammonium each contributed approximately half of the total nitrogen deposition. There was only a small contribution from organic nitrogen. Ammonium and organic nitrogen were usually close to or at the detection limit in the streams of the catchment. The annual output of sulphate and nitrogen by the catchment runoff mainly depends on the water fluxes. In addition, there was no clear trend for either SO_4^{2-} or NO_3^- in the catchment runoff (Fig. 1).

Sulphate

In contrast to the mass balance approach, the short-term dynamics of SO_4^{2-} in the catchment runoff give some evidence for the onset of recovery. The SO_4^{2-} concentration peaks show a clear decrease in the last decade (Fig. 2). This has been confirmed by an artificial neural network approach (LISCHEID 2000) which explained about 80% of the variance by a non-linear regression with three variables. These variables were a sliding mean of SO_4^{2-} concentration in the throughfall, discharge measured at the catchment outlet, and a measure for the distance from the preceding baseflow period. The latter was expressed as runoff summed up since the last time runoff exceeded a threshold value to distinguish between baseflow and non-baseflow periods. According to the network, there is a clear decrease of SO_4^{2-} concentration especially during the first heavy rain events at the end of the vegetation period (LISCHEID 2000). Streamwater chemistry during these discharge peaks mainly reflects the soil solution in the riparian zone, which becomes mobilised during discharge peaks. Here, the mean residence

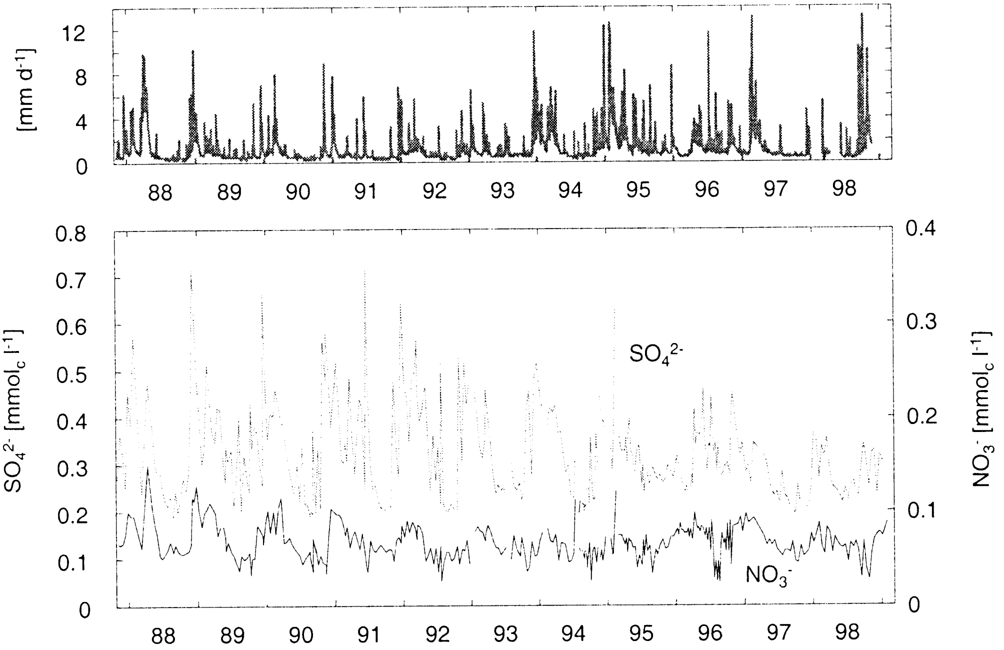

Fig. 2. – Time series of discharge (upper panel), SO_4^{2-}, and NO_3^- concentration (lower panel) in the catchment runoff.

time of the water is likely to be rather short. Thus, it is plausible that the soil's response on decreasing SO_4^{2-} deposition is the clearest visible during these events.

Isotope values suggest that dissimilatory SO_4^{2-} reduction occurs in the catchment (ALEWELL & GEHRE 1999). This is confirmed by laboratory experiments (GROSCHEOVÁ & al. 2000). However, the magnitude of this sink at the catchment scale can be assessed only indirectly. First, sulphate concentration in the catchment runoff is about twice the annual mean concentration in throughfall (volume weighted) during the first discharge peaks at the end of the summer period. As stated above, these peaks are generated mainly from riparian zone soil water where SO_4^{2-} reduction is most likely to occur. However, if SO_4^{2-} reduction would account for substantial amounts, SO_4^{2-} concentration peaks during these storms should be considerably less than twice that of SO_4^{2-} concentration in the throughfall, which is equal to the ratio between annual throughfall and annual runoff sum. Thus, these SO_4^{2-} concentration peaks likely reflect preferential uptake of water by plants during the summer period rather than a sulphate sink. Second, even during extended baseflow periods when the SO_4^{2-} concentration in the catchment runoff is the lowest, it is still in the range (mean ± standard deviation) of SO_4^{2-} concentration in the groundwater (Fig. 3). In addition, the summer depression is the most pronounced in the deepest parts of the catchment whereas SO_4^{2-} concentrations differ much less between low order streams and the catchment runoff in the winter period (Fig. 3). Thus, SO_4^{2-} concentration minima in the catchment runoff can be explained entirely by the fact that baseflow is exclusively generated by discharge of deeper groundwater. Substantial depletion of SO_4^{2-} which can be ascribed to reduction is visible only in two out of 12 low order streams monitored during that period (Fig. 3).

To assess the time scale of recovery, an extensive survey of the total sulphur stores in the underground has been performed. Samples were taken at 43 points of a rectangular grid over

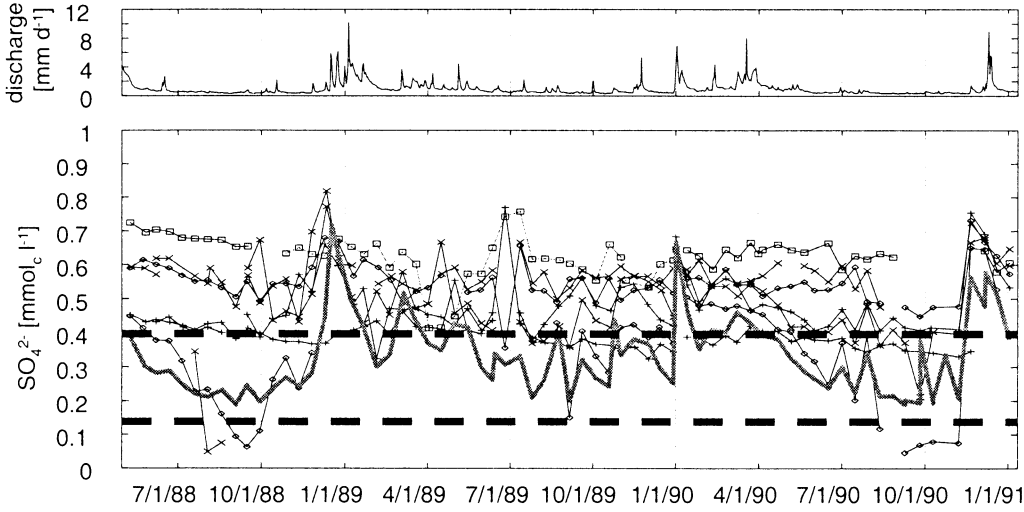

Fig. 3. – Time series of discharge at the catchment outlet (upper panel), and of SO_4^{2-} concentration in the catchment runoff (bold grey line) and of low order streams and springs (thin black lines with different symbols) in the June 1998 – January 1991 period. The bold slashed line denotes mean SO_4^{2-} concentration ± standard deviation in six groundwater wells for the same period.

the whole catchment area down to 0.5 m depth (JUNGNICKEL 1996) and from 9 borehole cores down to 10 m depth (MANDERSCHEID & al. 2000). The total sulphur store amounts to about 15 kmol ha^{-1} in the upper 0.5 m layer, and to 90 kmol ha^{-1} down to 10 m depth. This is about 10^2 times the annual output via the catchment runoff and is exclusively due to past deposition. The sulphur pool in deeper layers is not included in this estimation. However, there is a clear decrease with depth. Most of the sulphur is stored as sulphate and easily dissolves in water. The dynamics can be described by a Langmuir desorption isotherm. Local SO_4^{2-} concentration in most of the 13 groundwater wells is in equilibrium with the local desorption isotherms.

Six out of 13 groundwater wells were installed in 1987. At two wells, where mean groundwater level is the deepest (6.5 and 13.7 m below surface, respectively), there is a highly significant ($p < 0.01$) increase of SO_4^{2-} concentration up to now (Fig. 4). It is concluded that in contrast to the onset of depletion of the SO_4^{2-} pool in the topsoil, SO_4^{2-} accumulation in the deeper layers still continues due to vertical relocation. Thus, SO_4^{2-} concentration in the streamwater during storms starts to decrease but is likely to increase under baseflow conditions in the long-term.

Nitrogen

The overall picture is much less clear for nitrogen than for sulphate. Whereas the input of the latter can accurately be determined by throughfall samplers, quantifying the nitrogen input is compounded by the problem of dry deposition, nitrogen uptake and leaching of the tree canopies. It is likely that throughfall samplers underestimate the total nitrogen input substantially (ROSS & LINDBERG 1994). Taking into account measured gaseous and particle nitrogen compounds in the atmosphere, and estimating a mean deposition velocity, the total nitrogen input into the catchment is assessed to be about 2 kmol ha^{-1} a^{-1} (O. KLEMM, pers. comm.). This is about 40% more than throughfall fluxes. It has to be noted that another assessment

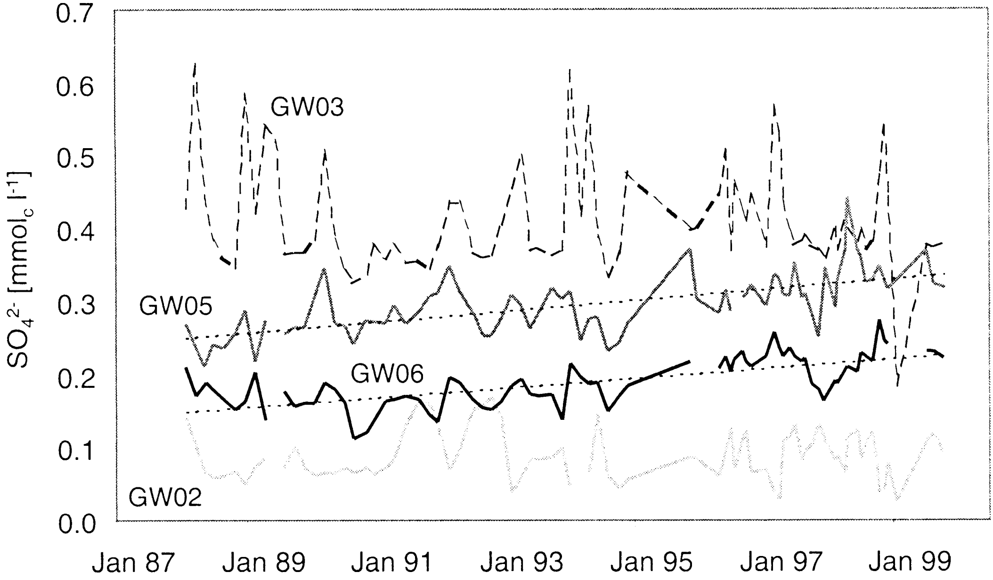

Fig. 4. – Time series of SO_4^{2-} concentration in different groundwater wells. Linear trends are indicated by dotted lines for well GW05 (mean groundwater level 13.7 m below surface) and GW06 (mean groundwater level 6.5 m below surface).

for a similar stand in the vicinity of the Lehstenbach catchment yielded about 4 kmol ha^{-1} a^{-1} (Bruckner-Schatt 1996).

Mean output via the catchment runoff for the 1988–1996 period amounts to 0.36 kmol ha^{-1} a^{-1}. Tree nitrogen uptake was assessed by determining the total biomass of trees of five stands of different age classes in the catchment and dividing by tree age (Mund 1996). For stem, bark and major branches the net nitrogen uptake amounts to 0.32 kmol ha^{-1} a^{-1}. There is no increase of needle mass with age except for very young trees so this parameter was not taken into account. Another nitrogen sink that should be considered is the build-up of the humus layer (c.f. Berg & Matzner 1997). Unfortunately, up to now only data from one plot are available. No significant increase of the nitrogen store of the topsoil, including the forest floor, could be found between 1988 and 1999. Data from a more comprehensive survey are still to be processed. However, changes of the total nitrogen store are not easily to determine, as the expected changes amount only for a minuscule part of the total nitrogen store. In addition, substantial spatial heterogeneity has to be taken into account.

Denitrification is often assumed to cover the difference between known sinks and sources of nitrogen. N_2O measurements prove that denitrification occurs in the boggy areas of the catchment (Horn 2000). A crude assessment by steel rod oxidation (c.f. Bridgham & al. 1991) confirms that low redox potential is widespread in the boggy areas (U. Reinhart, pers. comm.). However, direct quantification of nitrogen losses due to denitrification is not feasible at the catchment scale. Groundwater is substantially depleted of oxygen and nitrate only at one out of 13 wells. Thus, it is concluded that denitrification accounts only for a part of the catchment nitrogen sinks.

Instead, there is some evidence for an additional nitrogen sink in the deeper aquifer. In the groundwater, NH_4^+ and organic nitrogen rarely exceed the detection limit. Nitrate exhibits a clear spatial pattern. There is a continuous decrease from the watershed boundary towards the central boggy area and the catchment outlet, respectively. Correspondingly, nitrate concentration is significantly negatively correlated with silicon concentration ($p < 0.01$). Mean residence time of the groundwater is about 4 years (ZAHN 1995), and the maximum residence time, assessed by a groundwater model, about 12 years. As nitrogen deposition does not show any trend after 1988, this spatial pattern can not be ascribed to lower deposition in the past. On the other hand, deposition data do not exhibit any corresponding spatial pattern. However, it can not be excluded that existing patterns are not discernible as deposition has been measured only at six sites in parallel.

A series of laboratory experiments has been started to investigate underground nitrogen sinks in more detail. Only very limited results are available so far for two samples from about 5 and 8 m depth (T. RÖTTING, pers. comm.). 20 mg of the aquifer matrix has been shaken for 10 minutes at 5°C with 200 mg of solution which corresponds to the mean groundwater solution, except for organic carbon. Different amounts of nitrate were added. For nitrate concentrations below mean concentration in the groundwater (about 0.09 $\mathrm{mmol_c\ l^{-1}}$), nitrogen is released by the sample. For nitrogen added at 0.2 $\mathrm{mmol_c\ l^{-1}}$, more than 80% of the added nitrate is removed from the solution. Extending the time of shaking to 48 h does not have any effect. This provides strong evidence for an abiotic sink in the deeper aquifer.

In the literature, some more processes are discussed which could act as a transitory or final sink in forested catchments. Some authors emphasize that denitrification can occur in anoxic micro-sites in soils and aquifers, which appear to be oxic at the usual scale of sampling (TIEDJE & al. 1982, KÜSEL & DRAKE 1999). Further it has been shown that denitrification occurs under snowpack even at temperatures less than 0°C (DORLAND & BEAUCHAMP 1991, BROOKS & al. 1997). NH_4^+ adsorption to clay minerals (c.f. MAGILL & al. 1997) has been proven for the Lehstenbach catchment, too (MATSCHONAT & MATZNER 1996). However, the capacity of this process seems to be rather low. Last but not least, accumulation of organic mass might occur even in the deeper aquifer. Although the portion of organic carbon is very small, it might add up to considerable amounts in the 30–40 m thick regolith.

Little is known about the capacity, kinetics and the reversibility of these processes. Taking into account changing boundary conditions, e.g., global warming, further complicates any assessment of future trends. Future studies will focus on these processes.

Conclusions

Sulphate

The turnover of deposited sulphate in the soil and regolith of the catchment obviously is well understood and allows for a quantitative assessment. The total pool of sulphate in the regolith exceeds the annual output via the catchment runoff by two orders of magnitude. This pool is highly reversible. Its dynamics can be described by a desorption isotherm approach. There is evidence that the sulphate pool of the topsoil layers starts to be depleted due to decreasing deposition. This is reflected in streamwater chemistry during discharge peaks. On the other hand, SO_4^{2-} continues to accumulate in the deeper layers of the aquifer. It is likely that future stream water quality will deteriorate under baseflow conditions.

Nitrogen

For nitrogen many more uncertainties remain. In spite of the uncertainties associated with the assessment of the nitrogen input it seems to be clear that net plant uptake accounts only for a minor part of the deposited nitrogen. The same seems to be true for denitrification. Instead, there is some evidence for an additional abiotic nitrogen sink in the deeper aquifer. Such processes deserve much more attention than previously paid in order to quantitatively assess their capacity, kinetics and reversibility.

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