Comparative Analysis of Hydrochemical Time Series of Adjacent Catchments by Process-based and Data-oriented Modeling

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ABSTRACT

Time series of nitrate and sulfate concentration in the runoff of two forested catchments are investigated. Artificial neural networks and the mechanistic SUNFLOW model are applied. The results strongly indicate that the interplay between nitrogen turnover by biota and short-term mobilization in the riparian zone during rainstorms predominates the nitrogen dynamics at both sites. The differences of the observed short-term dynamics are ascribed to different runoff generation processes. The different sulfate dynamics of the two streams can be traced back to the change of sulfate concentration in the shallow and in the deep groundwater in response to decreasing sulfur deposition during the last decades. It is concluded that in contrast to the nitrate dynamics the sulfate dynamics more clearly reflect processes that occur at greater distance from the stream.

1 INTRODUCTION

Analysing the short-term dynamics of solute concentration in streams is a common way to investigate biogeochemical processes at the catchment scale. In addition, the change of these dynamics in the long-term can be used as an early indicator for long-term changes. Moreover, comparing the short-term dynamic of different streams can be used as an additional source of information. However, it should be clear where and how the dynamics are generated. In this study, nitrate and sulfate time series of two forested catchments with similar geochemical properties are investigated.

2 SITES

The catchments are located close to the Czech-German border at about 60 km distance. The Lysina catchment is part of the Slavkovský les (Slavkov Forest) in the Czech Republic, at 50°03' N and 12°40' E. The Lehstenbach catchment belongs to the Fichtelgebirge mountain region and is located at 50°08' N and 11°52' E. The size of the catchment is 0.273 km² at Lysina, and 4.2 km² at Lehstenbach. Elevation ranges between 829 and 942 m a.m.s.l. at Lysina, and between 695 and 877 m a.m.s.l. at Lehstenbach. The thickness of the regolith is about 2.5 m in the Lysina catchment, and up to 40 m in the Lehstenbach catchment. In both catchments the bedrock consists of granite, overlain by dystric cambisols and podzols that are susceptible to atmospheric deposition of sulfur and nitrogen. In addition, fabric histosols and dystric gleysoils predominate in the riparian zone. A dense network of natural streams and artificial channels exists in both catchments.

Annual mean precipitation of the last decade was 933 mm at Lysina and 985 mm at Lehstenbach. Annual mean runoff was 432 mm and 470 mm, respectively. Annual mean air temperature is about 5.2°C at Lysina, and 5 - 6.5°C in the Lehstenbach catchment, depending on altitude. Snowpack usually develops in December or January and final snowmelt occurs in March or April. Landuse is forestry exclusively, consisting of Norway spruce (*Picea abies* (L.) Karst.) stands.

An extensive monitoring program has been performed at both sites since the end of the 1980s. Beside others, discharge at the catchment is measured continuously. Concentration of the major solutes of the catchment runoff have been determined at biweekly intervals at least. Both sites have been severely impacted by nitrogen and sulfate deposition. Sulfate deposition peaked in the 1970s and decreased by more than 50% during the last decade at both sites. In contrast, neither nitrogen deposition nor nitrogen in the streams exhibit any clear trend at Lehstenbach. At Lysina, nitrogen deposition 1998-2000 was only 73% of that in 1991-1993 (Hruška et al. 2002), and the nitrate peaks in the winter season started to decrease in the end of the 1990s.
3 METHODS

3.1 Artificial Neural Networks

For the analysis of the time series of solute concentration, a universal model structure is required that is able to
map multi-variate, non-linear relationships, including time-lags between input and output, in a self-optimizing
way. Artificial neural networks meet these requirements and are widely used to analyze hydrological and

Here the feedforward multilayer perceptron type is used. The number of hidden layers is one. The logistic
function is used as activity function. The learning algorithm is the resilient propagation (Riedmiller and Braun,
1992), combined with a stochastic approach: To overcome the problem of getting stuck in a local minimum of
the error hyperplane, the weight matrix is altered randomly within a given range when the network fails to
decrease the model error. As is usual, the data set is split into training, validation and testing subsets. The
software package used is the Stuttgart Neural Network Simulator (SNNS) (Zell et al. 1995) with a slight
modification by the first author. Technical details are given in Lisched (2001).

3.2 The SUNFLOW model

The SUNFLOW (sulfate transport and sorption along flowpaths) model was developed to test the hypothesis that
sulfate sorption and desorption along the subsoil flowpaths of differing lengths account for the observed
differences of sulfate dynamics at various sites in the Lehstenbach and the Lysina catchment (Bütcher 2001).
Parameter values were not fitted to allow a more rigorous test of the model. A Monte-Carlo simulation provides
for the observed spatial heterogeneity of sorption isotherms.

In the model, the only difference between individual sampling sites within a catchment is the different shape of
their subcatchments. This is represented in the model by the respective flowpath lengths distribution. According
to the model, short flowpaths which react very rapidly to decreasing atmospheric sulfur deposition are decisive
for the decrease of sulfate concentration at single stream water sampling sites. In contrast, long flowpaths, which
lead to a greater delay, are characterized by still increasing concentrations.

4 RESULTS AND DISCUSSION

4.1 Nitrate

Nitrate is the predominating nitrogen component in the Lehstenbach. At Lysina, dissolved organic nitrogen
comprises about 50% of the total dissolved nitrogen in the mid 1990s, and increased to 82-88% in 1999 (Krám,
unpublished data). In contrast, ammonium, nitrite and organic nitrogen can be neglected at both sites. The short-
term nitrate dynamics can be reproduced by artificial neural networks as site-specific functions of discharge and
air temperature (Figure 1, Figure 2). Both the local discharge and temperature values of the sampling day, and
the mean values for the preceding 30 days period were used as input variables.

The neural network models explain about 50% of the observed variance at both sites. In addition to the seasonal
pattern, the models depict a substantial part of the short-term dynamics. The artificial neural network analysis
reveals inverse short-term relationships between nitrate concentration and discharge during stormflow: At
Lehstenbach, the nitrate concentration decreases with increasing discharge. The opposite is true for the Lysina
runoff. The former can be explained by source-limited nitrogen dynamics: The amount of inorganic nitrogen that
can be mobilized during rainstorms depends on the interplay between decomposition and plant uptake. Thus,
during heavy rainstorms, soil solution and stream water become diluted with respect to nitrate.

At Lysina, nitrate concentration is clearly less compared to Lehstenbach. Kinetic limitations of plant nitrogen
uptake and denitrification are likely to be the reason for the observed increase of nitrate concentration during
rainstorms. This is in accordance with the substantial contribution of soil water to the catchment runoff during
rainstorms (Buzek et al. 1995), whereas that component is less important in the Lehstenbach catchment (Lisched
et al. 2002). This might be due to the thicker regolith and longer flowpaths at Lehstenbach (Bütcher 2001).
Thus, it is concluded that part of the differences of the nitrate dynamics of the Lehstenbach and the Lysina runoff
can be traced back to differences of the stormflow generation processes.

4.2 Sulfate

About 80% of the short-term variance of sulfate concentration of the Lehstenbach catchment runoff is explained
by an artificial neural network. The model uses discharge data and the sliding mean of annual mean sulfate
concentration in throughfall (Lischeid 2001). Baseflow concentration did not change significantly since 1987, but peak concentration during discharge peaks decreased by a factor of two (Figure 3). This is ascribed to clearly decreasing sulfate concentration in soil solution and shallow groundwater that contribute to runoff generation only during discharge peaks. At Lysina, the short-term relationship between discharge and sulfate concentration is inverse: During the discharge peaks, sulfate concentration of the catchment runoff clearly decreases. This has been observed since the start of the monitoring program in 1989, but tended to become even more pronounced during the last years.

The SUNFLOW model (Bütcher 2001) succeeds in explaining these different dynamics. According to the model, the breakthrough of the sulfate concentration peak has not occurred yet in the long flowpaths, whereas short flowpaths clearly reflect the decrease of sulfate deposition. The latter comprise the soil solution and the shallow groundwater, that contribute to stream runoff only during stormflow. In the end of the 1990s, the difference between the shallow and the deep groundwater became less clear. Correspondingly, the sulfate concentration peaks clearly decreased (Figure 3). At Lysina, flowpaths of less than 50 m length comprise more than 50% of the catchment area, and maximum flowpath length is only 600 m, compared to more than 2000 m at Lehstenbach. As a consequence, sulfate concentration of the soil solution and the shallow groundwater at Lysina now is clearly less compared to deeper groundwater. This is decisive for the decrease of sulfate concentration during stormflow peaks (Figure 4). Thus, the SUNFLOW model succeeds in tracing back the change of short-term sulfate dynamics to long-term changes.

5 CONCLUSIONS

Investigating time series is a common way of hydrological and ecological research. However, the information provided by short-term dynamics differs for different solutes. The nitrate dynamics are likely to reflect processes in the riparian zone, including plant uptake, denitrification, decomposition, and runoff generation processes. In contrast, the short-term sulfate dynamics reflect more clearly processes of up-slope parts of the catchment as well. Thus, the short-term sulfate dynamics provides more information about catchment scale processes, as shown by the SUNFLOW results.

REFERENCES


FIGURES

Figure 1: Measured and simulated nitrate concentration of the Lehstenbach catchment runoff.

Figure 2: Measured and simulated nitrate concentration of the Lysina catchment runoff.

Figure 3: Measured and simulated sulfate concentration in the Lehstenbach catchment runoff. Three shortest flowpath length classes (< 150 m length) are combined to yield "stormflow", and the remaining flowpaths to yield "baseflow". Minimum and maximum values of ten model runs are given that account for the observed spatial heterogeneity of sorption isotherms.
Figure 4: Simulated and observed sulfate concentration in the Lysina catchment runoff. The shortest flowpath represents „stormflow“, and the longest flowpath „baseflow“. Minimum and maximum values of ten model runs are given that account for the observed spatial heterogeneity of sorption isotherms.
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