

Conservative mixing or chemically reacting: scale-dependency of processes at the stream water–groundwater interface

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Abstract Due to hypoxic conditions, the riparian zone at the interface between groundwater and stream water can have substantial impacts on stream water quality. This was investigated in a small-forested catchment. The extension of the hypoxic zone was determined by depth oriented groundwater sampling and a steel rod survey. Concentrations of the major solutes were determined simultaneously in the stream water, the shallow and the deeper groundwater. Based on the steel rod survey, the first order stream is entirely contained within a thin hypoxic zone above the deeper oxidic aquifer. In general, hypoxia has an impact on NO_3^- , Fe and Mn, but not on SO_4^{2-} concentrations in the shallow groundwater and the stream water. However, during storm flow, this zone is by-passed by a substantial portion of the runoff, which occurs in the topsoil layer above the hypoxic zone.

Key words groundwater; hypoxia; riparian zone; runoff generation; stream water; water quality

INTRODUCTION

The interface between groundwater and stream water is characterized by steep gradients with respect to physical and chemical parameters. Furthermore, substantial fluctuations in space and time, e.g. reversal of hydraulic gradients, and processes interacting at different time scales have to be taken into account. In addition, the riparian zone exhibits unique chemical conditions. Due to the permanent water saturation and the high organic matter content, hypoxic conditions often prevail. As groundwater discharging into the stream has to pass through the riparian zone, the latter has a substantial impact on the turnover of solutes that are susceptible to a low redox potential, e.g. nitrate and sulphate. The intention of this paper is to quantify these effects and their impacts on stream water quality. The paper focuses on the period outside the growing season when nutrient uptake by plant roots is negligible.

SITE DESCRIPTION

The investigation site is located within the Lehstenbach catchment in the Fichtelgebirge Region, southern Germany (50°08'N, 11°52'E) (Lischied *et al.*, 1998). The elevation of the catchment is 695–877 m a.s.l. The thickness of the regolith overlying the granite bedrock is approximately 30–40 m. It consists of a heterogeneous interbedding of sand, loam, gravel and granite boulders. The groundwater level is less

than 1 m below the surface in about a third of the catchment area, and deeper than 10 m close to the watershed boundary. The catchment is drained by a dense network of natural streams and artificial ditches. The vegetation is dominated by a Norway spruce forest, even in the boggy areas. For the 1988–1999 period, the mean annual precipitation was 985 mm, and mean annual discharge measured at the catchment outlet was 461 mm. Mean annual air temperature for the period 1994–1999, measured at 765 m a.s.l., was 6.4°C.

Results are presented from a groundwater discharge zone where a perennial short first-order stream flows into a high order stream. The groundwater flow is roughly parallel to the direction of the first-order stream (Fig. 1). The maximum amplitude of the groundwater level, measured at well B02 in the period 1987–2000, was 0.7 m. The mean groundwater level was 0.47 m below the surface, corresponding exactly to the elevation of the nearest point of the streambed at 8.3 m distance. Groundwater recharge by the high order stream was not observed during the study.

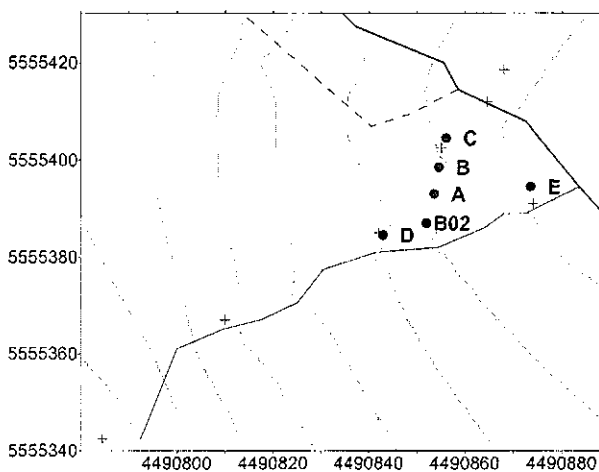


Fig. 1 Streams, wells (●), and location of some of the steel rods (+) at the field site. Contours of the surface elevation are given in grey at 1 m intervals. Gauss-Krüger coordinates are given in metres at the axes. Bold solid line: main stream; thin solid line: low order perennial stream; dashed line: low order ephemeral stream.

MEASUREMENTS

Stream water samples were taken manually or by an autosampler at 12-h intervals. Groundwater samples were taken using a submersed pump in well B02, at roughly bi-monthly intervals commencing in 1987. In addition, sampling at specific depths was performed in well B02 in 1999 and 2000. In an initial crude approach, a small pump was operated at different depths at a rate of 0.05 l s⁻¹. In spring 2000, an adaptation of the dual pumping technique (Rapp *et al.*, 1998) was used. Two pumps were operated at either end of the well screen. Varying the ratio of the pumping rates of the two pumps (between 0.3 and 0.6 l s⁻¹) shifts the water divide inside the well, which is determined by a tracer dilution technique (Rötting, 2000). Then samples are taken by a third pump using a very low pumping rate of about 0.01 l s⁻¹. Thus samples from a more clearly

defined depth can be collected in wells with a long screen. As this technique requires higher pumping rates to produce a clearly measurable water divide in the well, it can not be performed without a substantial drawdown. Thus the minimal depth of sampling was 5.2 m at this well.

The groundwater level has been measured at well B02 since 1987. In 1996, five additional observation wells were installed to 1.8 m maximum depth (Fig. 1). The groundwater level is measured at hourly intervals in three of the new wells. The discharge of the first-order stream was measured at a 60° V-notch weir near well E (Fig. 1) by manual stage level readings. Since November 1999, a pressure transducer has provided measurements at ten-minute intervals.

To investigate the spatial extension of the hypoxic zone, the steel rod approach of Bridgham *et al.* (1991) was used. Thirteen polished steel rods were installed in the soil to 1.8 m depth in April 2000 (Fig. 1). They were removed in June 2000. Hypoxic conditions are indicated by the absence of a rust layer on the polished rods; rust would develop under humid oxic conditions.

RESULTS

Spatial extension of the hypoxic zone

The steel rod method yielded fairly homogeneous results. In all cases, a rust layer developed only on the upper part of the rods. The minimum depth below the surface was 0.05 m and the maximum depth 0.5 m, mean depth 0.3 m. As hypoxic conditions are indicated even uphill from the spring, the first-order stream is entirely contained within in this zone.

According to the steel rod survey, the depth of the hypoxic layer is at least 1.8 m. Groundwater samples taken immediately prior to pumping on April 2000, from 1 and 3 m depth showed very low O₂ concentration, whereas even the most shallow groundwater sample taken using the depth-specific sampling method at 5.2 m depth, was saturated with respect to oxygen.

However, temporal variability has to be taken into account. After mid November 1999, even at 1.3 m depth, the O₂ concentration was as high as 8.8 mg l⁻¹, whereas hypoxia was never observed in either the depth-specific samples from greater depth (at least 5.2 m), or by depth integrated sampling.

Mean solute concentration

From October through to December 1999, seven samples were taken in the first-order stream, and from the shallow and the deeper groundwater at the same time. The stream water usually was saturated, and the deeper groundwater nearly saturated with respect to O₂, whereas the O₂ concentration was occasionally as low as 2.4 mg l⁻¹ at a depth of 1.3 m (Fig. 2). The Fe, Mn and DOC concentrations in the deeper groundwater only occasionally exceeded the detection limits (0.08 mg l⁻¹, 0.02 mg l⁻¹ and 1 mg l⁻¹, respectively), in contrast to the stream water and the shallow groundwater. The silica concentration is substantially lower in the stream water, but does not differ very much

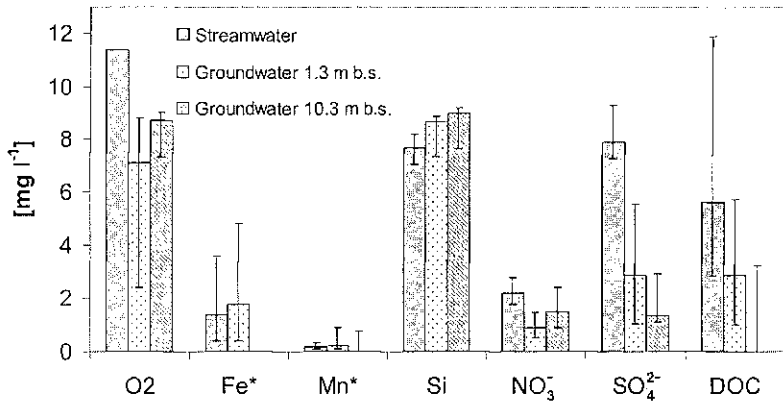


Fig. 2 Solute concentration in the stream water, shallow and deep groundwater. The median, minimum and maximum is given for seven samples taken in October–December 1999.

*For the sake of clarity Fe and Mn concentrations are multiplied by a factor of 10.

between shallow and deeper groundwater. The sulphate concentration exhibits a clear decrease with increasing depth. In contrast, the nitrate concentration is lowest in the shallow groundwater.

Dynamics of solute concentration

In general, the pH and silica concentrations decrease (Fig. 3), and SO_4^{2-} , Al and DOC increase with increasing discharge in the first-order stream. For the first four dates, the NO_3^- concentration in the shallow groundwater is only half of that in the deeper groundwater (Fig. 3). The SO_4^{2-} and DOC concentrations are substantially higher compared to the deeper groundwater in this period. During the subsequent samplings, however, the shallow groundwater resembles the deeper groundwater with respect to O_2 , NO_3^- , SO_4^{2-} , and DOC (Fig. 3).

DISCUSSION

Due to long lasting emissions of nitrogen and sulphate the pH increases, and the SO_4^{2-} and Al concentration in the soil water and groundwater decreases with depth in the Lehstenbach catchment (Lischeid *et al.*, 1998; Manderscheid *et al.*, 2000). In addition, DOC concentration decreases with depth, and Si concentration increases. This is reflected by a rapid increase of the SO_4^{2-} , Al and DOC concentration, and a corresponding decrease of the pH and Si concentration in the stream water during discharge peaks in this first-order stream, as well as in many of the other Lehstenbach streams (Lischeid, 2001).

Hypoxia in the riparian zone imposes an additional signal on solute concentration. Here, the Fe and Mn concentration is substantially higher, and the NO_3^- concentration only half compared to the deeper groundwater. However, there is no evidence for SO_4^{2-}

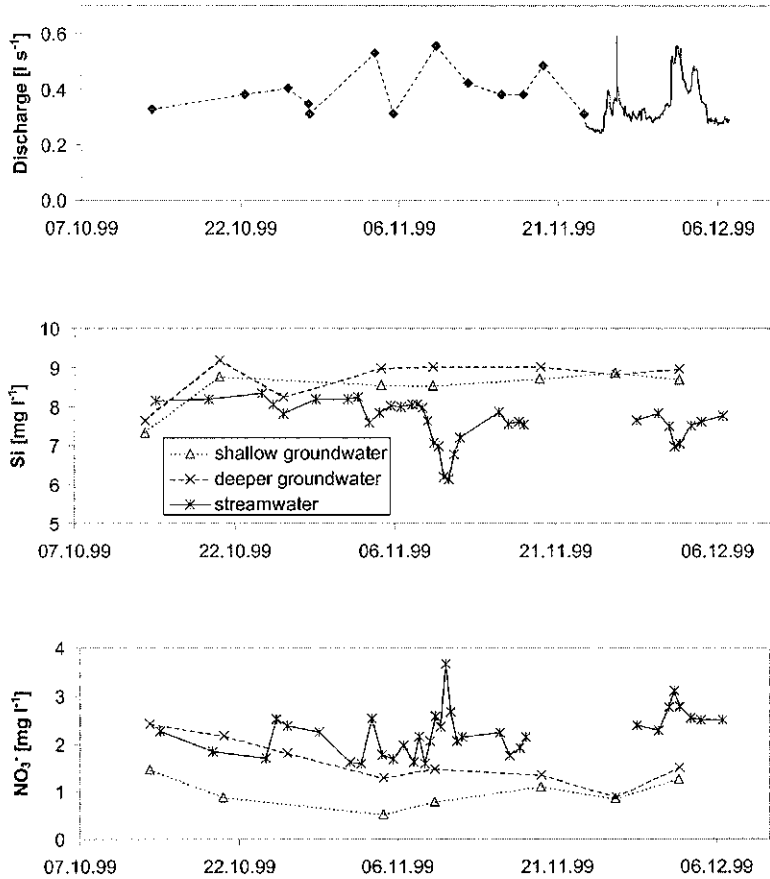


Fig. 3 Time series of stream discharge, Si and NO_3^- concentration in the stream water, shallow and deeper groundwater, in autumn 1999.

reduction. This corresponds to the expected order of time scales of the kinetics depending on the redox potential. Correspondingly, hypoxic groundwater immediately saturates with O_2 when it discharges into the stream, whereas NO_3^- behaves like a conservative tracer at that time scale.

Mean discharge in the low order stream was 0.31 s^{-1} during the period 23 November 1999–24 October 2000. Based on the annual mean discharge of 461 mm, this would require a subcatchment of about $20\,000 \text{ m}^2$. The water divide of the subcatchment can not clearly be determined on the basis of topography or groundwater head data (Fig. 1). However, it seems to be rather unlikely that the subcatchment would be restricted to the 100 m wide strip along the main stream that is characterized by hypoxic conditions. Instead, it is more likely that a major part of the groundwater that discharges into the low order stream infiltrated in the upslope part of the catchment. This groundwater is obviously oxygen saturated until it passes through the hypoxic zone close to the stream.

Correspondingly, stream water resembles the shallow groundwater much more than the deeper groundwater during baseflow conditions. This holds for Fe and Mn as

well, tracing back to the hypoxic conditions in the shallow groundwater. However, this does not hold for NO_3^- . In addition, a third component is required to explain stream water solute concentration especially during stormflow. Stream water exhibits significantly lower pH and Si concentrations, and much higher Al, NO_3^- , SO_4^{2-} and DOC concentrations during high flow periods. As mentioned above, this is typical for soil water in the top soil layer. It is concluded that during stormflow, a substantial portion of stream runoff is generated by rapid flow in the occasionally saturated upper soil layer, thus by-passing the hypoxic zone. This is confirmed by additional studies in the catchment (Lischeid, 2001). Except for oxygen, short-term dynamics (i.e. within hours) are best characterized as a conservative mixing process, whereas redox processes are discernible only on longer time scales.

The degree of hypoxia is not constant in time. Substantial undersaturation with respect to oxygen was observed in the shallow groundwater only until mid November. After that, the concentration of O_2 , NO_3^- , Fe and Mn in the shallow groundwater was very close to that of the deeper groundwater. This is partly ascribed to the more rapid groundwater turnover in this zone due to increasing groundwater heads further upslope. On the other hand, microbial activity and the corresponding oxygen consumption is likely to decrease with decreasing soil temperature at the end of the year.

CONCLUSIONS

The hypoxic zone of a few metres thickness underneath the stream bed has a substantial effect on stream water quality. This is the most clearly visible with respect to NO_3^- , Fe and Mn concentrations during baseflow conditions. During stormflow, however, most of the stream runoff is generated by soil water from outside the riparian zone that transiently by-passes the hypoxic zone. The degree of hypoxia varies in time, which is ascribed to the varying groundwater residence time and microbial oxygen consumption in this zone. Due to kinetic constraints, stream water quality is determined by short-term conservative mixing during stormflow, and by redox processes under baseflow conditions.

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