Abstract

Understanding of interactions between hydrological and biogeochemical responses of catchments on rainfall events which is usually unclear from periodic measurements and requires tracing of the temporal dynamics of the processes. Smaller streams reflect strong connections between hydrological processes of the rainfall runoff formation and biogeochemical processes in the watershed, consequently, the responsiveness of the streamwater chemistry to changed hydrological states is very high. The study was carried out in 2006, within the 42 km² forested Padež watershed in the southwestern part of Slovenia, which is characterized by distinctive flushing, an almost torrential hydrological regime influenced by impermeable flysch geological settings. More than 15 recorded hydrographs which, in the hydrological and biogeochemical sense, differed substantially, disclosed a highly variable but at the same time a strong linkage between hydrological and biogeochemical controls of nitrate exports from the spatial perspective of a watershed.

Keywords: watershed hydrology, high-frequency measurements, forest biogeochemistry, streamwater chemistry, streamwater nitrate, electrical conductivity.

1 INTRODUCTION

Forest hydrology studies show a great complexity of interacting influences on the water cycle. Forest systems notably affect the hydrological responses of the basins. In order to understand the formation of forest hydrologic flowpaths and the way how these flowpaths affect stream chemistry, we need chemical measurements at time scales that correspond to hydrological dynamics. Conversely, the stream chemistry tracing enables us to decipher the hydrological processes (Goodale et al., 2002; Kirchner et al., 2004; Heathwaite et al., 1993). High frequency chemical measurements are also essential for testing hydrological models. Hydrological data alone are rarely sufficient to test the process assumptions embedded into a typical hydrological model. Both, hydrological and geochemical or other water chemistry time-series data are needed to identify appropriate model structures and constrain their parameters (Quinn, 2004).

The understanding of how hydrological conditions trigger flushing of labile nutrients on a watershed scale is still rather poor, especially if we move from the timescale of seasonal variability towards the timescale of a single hydrological event. This paper presents a study that examines the seasonality of the nitrate dynamics on a mesoscale watershed in Slovenia covered mainly by deciduous forest, with the emphasis on high-frequency measurements of streamwater nitrate concentration.
during rainfall events of contrasting magnitudes occurring in different seasons. We believe that for progress to be made in understanding the role of integral hydrological controls on nitrate flushing, a shift away from the complexity of individual microscale processes observed at low time frequency is needed towards making improvements of observations on a time step of hydrological events.

2 STUDY AREA DESCRIPTION AND MONITORING SYSTEM

The Padež stream watershed comprises 42.1 km² and is situated in the Southwestern part of Slovenia (Figure 1). The Padež stream is a tributary of the Reka river, one of the widest known sinking streams of the Classic Karst area in Slovenia. The Padež watershed reaches deeply into the hilly area of Brkini in the south (altitude up to 811 m a.s.l.), the outflow to the Reka river is at 368 m a.s.l. The Brkini hilly area, and the Padež watershed as its part, consist of Eocene flysch (mainly marl and sandstone layers) underlain by deep cretaceous carbonate bedrocks which also surround the wider area of the Brkini flysch pool. From the hydrogeological point of view, the Padež watershed has a uniform structure characterized by low permeability of erodible flysch layers and a consequent well developed, dense and highly incised stream channel network with a drainage density of 1.94 km/km². In the climatic sense, the Brkini hilly area is a transitional area between the mediterranean and continental climate with mean annual temperature of 9.6 °C. Mean annual precipitation is approximately 1440 mm (Rusjan et al., 2006). The prevailing movement of the wet air masses is in the southwest–northeast direction. The majority of the precipitation falls during the October–March period with periodical snowfall on the highest parts of the Brkini hills, which does not have substantial influence on the watershed hydrology.

The monitoring system at the Padež watershed which was established in 2005 is shown in Figure 1. Precipitation data were obtained from 6 Onset RG2-M tipping bucket rain gauges located within the Padež watershed; the meteorological data were gathered from the Vaisala MAWS201 automatic meteorological station positioned in the middle of the watershed. Water level was recorded continuously with a 5-minute time step on four locations using a Unidata Starflow model 6526-51 1-D Doppler instrument with an integrated logger. Stream chemistry was measured continuously on a 15-minute time step using a Hydrolab MiniSonde 4a water quality multi-parameter data-sonde. The multi-parameter sonde is designed for on-site and flow-through applications and measures water chemistry parameters simultaneously (Brilly et al., 2006). The multiple parameters include: nitrate, temperature, electric conductivity, depth, dissolved oxygen, Total Dissolved Solids (TDS), Oxidation Reduction Potential (ORP) and pH. In order to achieve accurate water chemistry readings of the multi-parameter sonde, the maintenance and calibration procedures including regular cleaning of the sensors and replacement of the ion-selective nitrate sensor were carefully followed.
3 RESULTS

3.1 Continuous streamwater nitrate concentration measurements

The time series of nitrate concentration shown in Figures 2 and 3 point out a variety of hydrologically induced nitrate concentration oscillations during the late spring and summer hydrological events. During the sequence of the May–June hydrographs the streamwater nitrate concentration varied substantially and the maximum nitrate concentration reached 4 mg/l-N (Figure 2). The situation became even more complex during the sequence of August hydrographs (Figure 3). During the August event, which followed a 2-month dry summer period without substantial precipitation high concentrations of nitrate (up to 6.5 mg/l-N) were observed during the first two smaller storms. The last hydrograph with peak discharge 5.69 m$^3$/s raised the nitrate concentration only slightly higher (7.3 mg/l-N) than the second hydrograph with peak discharge 1.16 m$^3$/s.

The overall decreases of the nitrate concentrations in the falling limbs of the hydrographs were gradual, with different time intervals necessary for the nitrate concentrations to return to the pre-event baseflow concentrations. In the case of the May hydrograph, the recurrence interval was only 3 to 4 days, whereas during other sequences of hydrographs, the recurrence interval extended to more than a week.
Figure 2: Nitrate concentration oscillations during the May-June rainfall event.

The probable cause for the decrease of the nitrate concentration during the May–June hydrograph (Figure 2) is preceding wetting of the watershed which enabled the additional rainfall to drain down without considerable contact with the biogeochemical environment of forest soils.

Figure 3: Nitrate concentration oscillations during the August rainfall event.

3.2 Continuous measurements of streamwater electrical conductivity

The high frequency measurements of conductivity enable us a better separation between base flow (higher electrical conductivity) and rainfall runoff (lower electrical conductivity). The electrical conductivity of baseflow was above 0.30 mS/cm and remained relatively constant during the low flow periods. In the time of hydrograph peaks the electrical conductivity of streamwater dropped markedly to less than 0.15 mS/cm in the case of the major hydrographs through the sequence of hydrographs (Figures 4 and 5).
The results of the hydrograph separations indicate that smaller precipitation produces more pre-event water and that a surprisingly high proportion of the total flow is subsurface flow (Shultz, 1999). Event water could be interpreted as saturation excess overland flow if the contact time of the rainfall on the hillslopes is relatively short, which could be the case during some of the studied hydrographs with short times to peak.

![Graph](image1)

**Figure 4:** Continuous measurements of electrical conductivity during the May-June rainfall event.

![Graph](image2)

**Figure 5:** Continuous measurements of electrical conductivity during the August rainfall event.

Very fast decline in the streamwater electrical conductivity observed in Figures 4 and 5 can be linked to high hydrological response of the watershed. The impermeable flysch geological settings enable the rainfall runoff to drain rapidly without the prolonged contact with the forest floor which would undoubtedly raised the electrical conductivity of streamwater. The soil profile becomes saturated due to low hydraulic conductivity of the clayish and silt soils. Quick wetting of the watershed during the rainfall events also caused already mentioned decrease in the streamwater nitrate concentration during intensive rainfall.
events as the accumulated nitrate in the forest floor is washed out towards the stream less intensively.

4 CONCLUSION

We believe that presented high-frequency measurements of hydrological events and associated water chemistry oscillations would disclose the role of specific rainfall events in the total annual budgets of nutrient releases from the forested Padež stream watershed. Furthermore, through the continuous measurements of water chemistry parameters, we have obtain an insight into the capacity of forested watersheds to control water chemistry constituent exports and investigate the relations between the forest hydrologic and biotic export mechanisms over the dissolved nitrogen inorganic constituents in different seasons.

High frequency measurements of streamwater nitrate concentrations in the Padež stream throughout different hydrological and seasonal biogeochemical settings disclosed a highly variable but strong linkage between the hydrological and biogeochemical controls of the nitrate export from the spatial perspective of a watershed. The role of specific hydrological events proved to be important for predicting the rates of nitrate flushing whose size in the soil pool is large, although it can vary considerably. Consequently, the predicted rates of N cycling and nitrate losses from watersheds can alter greatly from year to year due to the climatic variations and their relative effect on plant growth and soil processes of mineralization and nitrification.

References