# Seasonal variability of diurnal in-stream nitrate concentration oscillations under hydrologically stable conditions

**Simon Rusjan · Matjaž Mikoš**

**Abstract** Seasonal and diurnal variations of in-stream $NO_3$-N concentration oscillations were studied through high-frequency measurements of stream-water's physical, chemical parameters (in-stream $NO_3$-N concentration, water temperature, dissolved oxygen, pH) and hydrometeorological variables (stream discharge, solar radiation) under hydrologically stable conditions. The study was carried out in 2006, within the 42 $km^2$ forested Padež stream watershed in the southwestern part of Slovenia, which is characterized by distinctive hydrogeological settings (flysch) and climate conditions (transitional area between the Mediterranean and continental climate). Fine temporal data resolution (15-min interval) enabled identification of the factors responsible for seasonal variability in the diurnal pattern of the streamwater $NO_3$-N concentrations versus seasonal and diurnal behavior of meteorological and other water chemistry constituents. The observed seasonal variability of in-stream $NO_3$-N daily oscillations indicates the important role of primary production uptake, particularly during seasons when deciduous vegetation is dormant and light levels in the stream are high. Highest daily $NO_3$-N concentration amplitudes (0.3 mg/l-N) and daily changes in the $NO_3$-N flux (0.4–0.5 g/s-N) were observed in spring; the $NO_3$-N concentration oscillations in summer showed a considerably smaller effect of the in-stream uptake (maximum $NO_3$-N daily concentration amplitude 0.1 mg/l-N; daily change in the $NO_3$-N flux 0.02 g/s-N). Seasonal shifts in the timing of daily maximum (up to 6 h) and minimum $NO_3$-N concentrations (between 1 and 3 h) provided some additional indications of seasonal changes in the in-stream primary production uptake and its relation to the terrestrial component of the forested watershed.

**Keywords** Diurnal oscillations · Forested watersheds · High-frequency measurements · Seasonality · Slovenia · In-stream nitrate

## Introduction

Imbalances in nitrogen biogeochemical cycle have become an important environmental issue on both local and global scale as changes in relationships between different forms of N can be useful leading indicators of environmental change. Nitrate leaching to streams draining forested watersheds is a sensitive indicator of the biogeochemical status of forest ecosystem and has been used as a response variable in the studies of the forest management practices (Aber et al. 1991; Likens and Bormann 1995;

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Goodale et al. 2002), atmospheric deposition alterations (Aber et al. 1997; Binkley et al. 2000; Aber et al. 2003; Burns 2004), soil characteristics (Gundersen et al. 1998; Fitzhugh et al. 2003) and hydrologically induced flushing of nutrients (Cirmo and McDonnell 1997; Band et al. 2001; Inamdar et al. 2004). Nitrate generally dominates leaching in forests with excess of N (Fenn et al. 1998; Gundersen et al. 2006); the streamwater nitrate exports could be limited by the availability of the accumulated nitrate in the soil pool and alternatively, by the absence of the sufficient movement of water to provide transport.

Understanding the cause of natural variability of streamwater nitrate concentration in unpolluted sites is essential for providing baseline information against which data from elevated nitrate concentration sites can be compared (Vanderbilt et al. 2003; Beachtold et al. 2003). Furthermore, nitrate concentrations in streams draining forested watersheds provide additional information about the processing of N in the forest and the possibility to study wide range of environmental physical and biogeochemical factors which are well known to play an important, yet a highly changeable role. N cycling and leaching loss depend on the interactions among a suite of potentially important physical variables; therefore in a particular study region, a large relative range in one of those variables may cause it to dominate and mask the role of the others. A great deal of the observed discrepancies found in the literature may be ascribed to the variability of the N alteration controlling variables.

Contemporaneous seasonal changes in biotic activity, physical and hydrologic conditions make it difficult to determine whether nitrate leaching is driven solely by a seasonal increase in nitrate availability through increased mineralization and nitrification rates, or whether it is simply due to flushing of nitrate that has accumulated over longer, hydrologically inactive periods of time. The greatest variability of the in-stream nutrient concentration is usually observed during the periods of changing hydrological conditions. The event-scale observations of nitrate flushing are highly complex in terms of simultaneous hydrological and water chemistry monitoring; however they offer additional opportunities to study the interactions between the hydrological characteristics and biogeochemical background of a particular forested watershed (Arheimer et al. 1996; Andersson and Lepisto 1998; McHale et al. 2002;

McGlynn and McDonnell 2003; Rusjan et al. 2008). On the other hand, various hydrologically induced streamwater nitrate concentration responses mask the connectivity between the in-stream nitrogen transformations and seasonal biogeochemical settings which occur continuously. As discussed by Kirchner et al. (2004) one might assume that nothing interesting would be observed during hydrologically "inactive" periods between rainfall events. However, it is during just such periods that interesting biogeochemical signs may appear, precisely because they are not obscured by hydrological fluctuations. Unfortunately, important biogeochemical signs are usually hidden behind the low temporal resolution of the measurements. Moreover, factors that affect the temporal variations are not necessarily the same ones as those which control the spatial variations across the study area.

Streamwater chemistry in small streams strongly reflects the processes in the biogeochemical surrounding. Additionally, in-stream N transformations, processes by which N is converted among its various inorganic oxidation states or between organic and inorganic or dissolved and particulate forms, are important in many stream ecosystems (Christensen et al. 1990; Mulholland 1992; Holmes et al. 1996; Bernhardt et al. 2002). Usually, in-stream processing of nitrogen is ignored as a potentially important component in determining the watershed output (Bernhardt et al. 2005). This is partly true in studies of the hydrologically triggered nitrate fluxes, where contact times in small streams are very short and the actual biogeochemical signs in the stream are defined well in advance by biogeochemical processing of nitrogen in periods preceding rainfall events. However, in-stream N transformations may significantly affect the interpretations about terrestrial processes and mass balances for watershed ecosystems made from samples taken at a particular point along the stream channel. Studies have shown that despite their relatively small proportion of watershed surface area, streams can be important sites for transformations and retention of nutrients (Burns 1998; Alexander et al. 2000; Peterson et al. 2001). Thus, ignoring in-stream nutrient processing and its temporal variability may lead to erroneous conclusions about the role of terrestrial processes in controlling streamwater nutrient concentrations (Mulholland 2004; Roberts and Mulholland 2007).

In this study we analyze high frequency in-stream $NO_3$-N concentration dynamics observed in the period March–November 2006 in a mesoscale watershed in Slovenia covered mainly by a deciduous forest. Synchronous high-frequency measurements of streamwater chemistry and hydrometeorological conditions during hydrologically stable periods in different seasons disclosed interesting interconnections between the in-stream dynamics of the physical parameters and chemical constituents on one hand, and meteorological variables on the other which emerge simultaneously on a daily basis. Although the main focus was on the high-frequency variations of the $NO_3$-N concentration, we tried to connect the high-frequency observations to the role of the well known seasonal patterns. The fine temporal resolution of the data enabled us to identify

driving factors responsible for the daily streamwater $NO_3$-N oscillating behavior and to make some distinctions between the roles of the biogeochemical "background" of the forest ecosystem surrounding the stream and the processes which take place inside the stream water body.

## Study area

The Padež stream watershed comprises 42.1 km$^2$ and is situated in the Southwestern part of Slovenia (Fig. 1). The Padež stream is a tributary of the Reka river, one of the best known sinking streams of the Classic Karst area in Slovenia. The Padež watershed reaches deeply into the hilly area of Brkini in the

**Fig. 1** The Padež stream watershed and the monitoring system
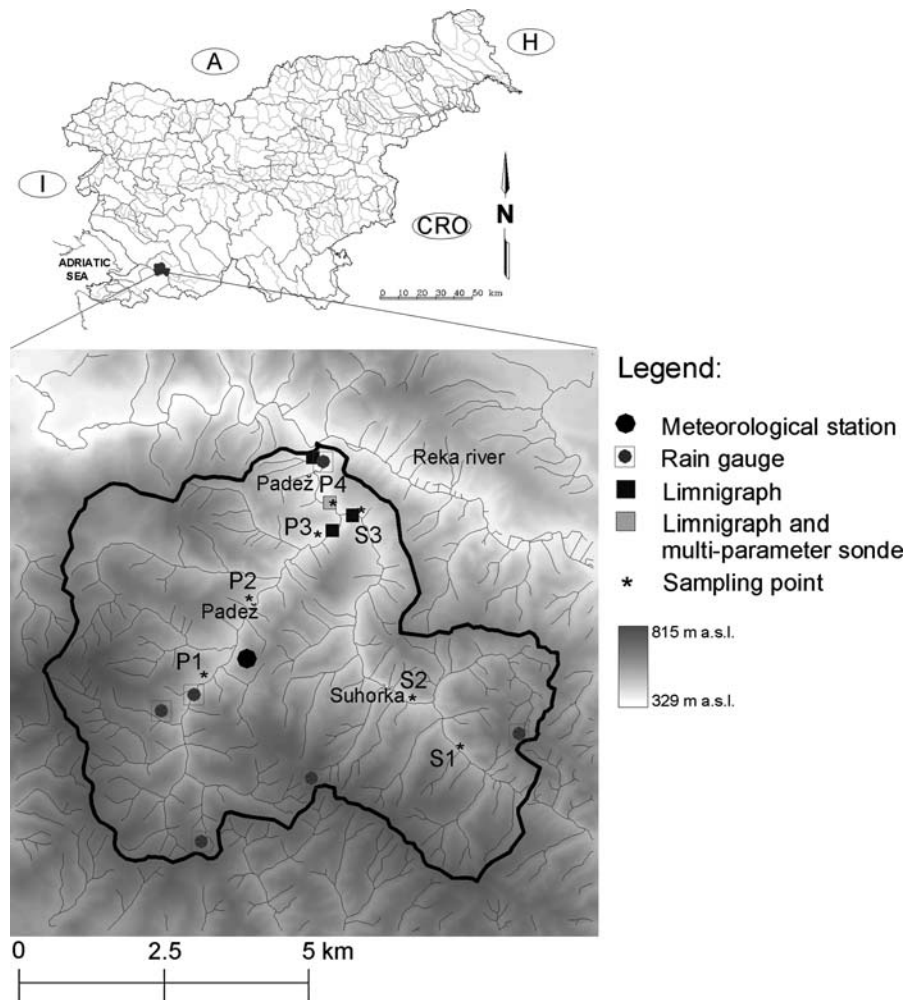
south (altitude up to 811 m a.s.l.); the outflow to the Reka River is at 368 m a.s.l. The wider Brkini hilly area is climatically a transitional area between the Mediterranean and continental climate with a mean annual temperature of 9.6°C (Šebenik 1996). Mean annual precipitation is approximately 1,440 mm. 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; periodical snowfall on the highest parts of the Brkini hills does not have a substantial influence on watershed hydrology.

The Brkini hilly area and the Padež watershed 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 basin. From the hydrogeological point of view, the Padež watershed has a uniform structure characterized by low permeability of erodible flysch layers and a consequently well developed, dense and highly incised stream channel network with a drainage density of 1.94 km/km$^2$. The lowest parts of the main valleys (the Padež and Suhorka stream valleys) are covered by up to 4-m thick alluvial deposits. The hydraulic conductivity of flysch is low (in the range $10^{-6}$ to $10^{-5}$ m/s), the hillslopes are steep (average slope derived from the digital elevation model amounts to 33%), the average slope of the Padež stream channel being almost 3%.

Soils in the study area are spatially uniform. According to the WRB 2006 soil classification they are classified as Haplic Cambisol (Humic, Hyperdystric, Endoskeletic) with 5 cm thick O horizon, shallow 1–2 cm thick A horizon and up to 1-m thick mineral layers; pH varies between 3.5 and 4, the C/N ratio of O–A and upper mineral horizons is 18.4 and 15.8, respectively. Regarding the textural composition, 35% of particles are sand, 46% silt and 19% clay-sized. The hydraulic conductivity of soils is low (around $10^{-5}$ m/s).

Mean discharge of the Padež stream in the year 2006 was 0.67 m$^3$/s; the long-term mean annual discharge of the Padež stream amounts to 1.12 m$^3$/s (Rusjan et al. 2008). The hydrologic response of the watershed is very fast (lag time ∼ 3 h), rainfall runoff drains very quickly which is on one hand reflected in the flushing, almost torrential regime of the Padež stream (yearly hydrograph peaks above 10 m$^3$/s) and on the other through low stream discharges during

dry periods (low summer baseflow less than 50 l/s). Most of the year, water is present only in the Padež stream and its major tributary, the Suhorka stream, other smaller streams in the watershed being intermittent. The streambed in the Padež and Suhorka stream is composed mainly of coarse gravel and cobble; due to the torrential regime of the streams, the streambed of the two main streams is considerably wide (8–10 m at the sampling point P4 stream section; Fig. 1), therefore during the periods of low to mean discharges the depth of water in the stream channel is shallow.

The Padež watershed is minimally disturbed by human activity; it has been used for local drinking water supplies and, as such, it is also foreseen as an additional source of drinking water for the water-deficient area of the Slovenian coastal region. According to the CORINE 2000 land cover data, 82% of the watershed is covered by forest (79% by broad-leaved forest), and 18% of the watershed comprises complex cultivation patterns (mainly meadows with significant areas of natural vegetation) which discontinuously appear on top of the hills and are all in the state of intensive successive reforestation. Steep hillslopes and narrow lower parts of the valleys are completely covered by deciduous forest. Sessile oak (*Quercus petraea*), Black alder (*Alnus glutinosa*), Beech (*Fagus sylvatica L.*), and Hornbeam (*Carpinus betulus*) are main tree species that can be found at the Padež watershed (Slovenian Forest Service 2000).

## Methods

### Data acquisition

The monitoring system at the Padež watershed is shown in Fig. 1. Rainfall 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 (Fig. 1). The meteorological station was equipped with a wind sensor, global solar radiation detector (silicon pyranometer), relative humidity and temperature probe. Water levels in the streams were recorded continuously with a 5-min time step at four locations using a Unidata Starflow model 6526-51

1-D Doppler instrument with an integrated logger. The instrument records water velocity (ultrasonic Doppler principle), water stage (hydrostatic pressure sensor referenced to atmospheric pressure) and water temperature. Flow was gauged on stream sections equipped with limnigraphs using two instruments. During low flow conditions, Flo-Tracer, a salt-dilution flowmeter was used, whereas during middle to high flows, a 2D/3D handheld Sontek ADV Doppler velocimeter was applied. Water level records were converted to volumetric discharges by empirical ratings that were validated by gauging at different water levels.

Stream chemistry was measured on a 15-min 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 sonde includes the following sensors: ion-selective nitrate electrode, 30 k ohm variable resistance temperature sensor, electric conductivity and total dissolved solids (TDS) sensor with graphite electrodes, pressure sensor, Clark Cell design dissolved oxygen (DO) sensor and KCl impregnated glass bulb pH sensor. The concentration of inorganic nitrogen atmospheric deposition (ammonium + nitrate) was measured in bulk rainfall samples at the Škocjan meteorological station positioned 8 km NW of the studied area.

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. Grab water samples were taken monthly from January to November 2006 and approximately biweekly during the periods of continuous streamwater chemistry measurements at the site where the multi-parameter sonde was installed. Laboratory analysis of the grab samples were used for calibration control of the multi-parameter sonde readings. The samples were collected and preserved according to ISO 5667-6 and ISO 5667-3 standards, respectively. $NO_3$-N was measured according to ISO 10304-1 standard with the ion chromatograph. The $t$-test was used to statistically compare the results of the measurements of nitrate concentration by the ion-selective sensor and through laboratory analysis (confidence interval 0.95). The ion-selective nitrate sensor showed slightly higher $NO_3$-N concentrations than laboratory analysis, but the differences between the readings were not statistically significant ($N = 14$; $p = 0.12$). The mean absolute difference between the laboratory analysis and the nitrate sensor was 0.4 mg/l-N ($R^2 = 0.82$; RMSE = 0.6 mg/l-N) considering the measurements during rainfall events and hydrologically inactive periods. If comparing only the measurement made during dry periods, the difference between the laboratory analysis and the nitrate sensor readings were even lower ($N = 6$; $p = 0.31$; mean absolute difference <0.2 mg/l-N).

Time series analysis

Standard statistical analyses were applied to original data in order to investigate the main underlying temporal patterns in the time series datasets. The data were inspected by means of auto-correlation function and smoothers. The relationships between seasonal temporal patterns of individual parameters (water chemistry and meteorological variables) and the streamwater nitrate concentration were assessed by cross-correlation. Cross-correlations of $NO_3$-N concentrations with water temperature, DO concentrations and pH were significant at a 0.95 confidence interval.

In addition to statistical analysis, a stationary wavelet transform was applied on normalized $NO_3$-N, DOsat and pH datasets. Normalization of the datasets was done by removing the seasonal differences in the mean values (between each parameter datasets) and the presence of temporal trends (increasing or decreasing parameter readings throughout the time series). Therefore, only the differences in the amplitude and timing of the daily oscillations have remained in the normalized datasets. The stationary wavelet transform was further used to decompose the input signals into lower resolution components. In this way, pure frequencies (harmonics) of the parameters oscillations were derived and separated from the noise in the input signal. The parameter signals were de-noised using Daubechies No. 5 wavelet and 5 decomposition levels. Details about the use of wavelet analysis can be found in Percival and Walden (2000). The statistical analysis and the wavelet analysis were done using MATLAB 7.3® software. Pure, de-noised parameter signals were used to evaluate typical seasonal differences in the

oscillations' amplitudes and daily minimum and maximum timing.

## Results

Spatial variations in the streamwater $NO_3$-N concentrations

The study of spatial distribution of streamwater $NO_3$-N concentrations along the main stream, and the Padež and the Suhorka tributaries, was carried out with the intention to investigate spatial anomalies in the $NO_3$-N concentration across the Padež watershed. Three campaigns of spot measurements were performed in the beginning of May, July and the end of September 2006. All three campaigns temporally coincided with antecedent dry periods and baseflow conditions. The spatial distribution of sampling points is indicated in Fig. 1; the results of the spot $NO_3$-N concentration measurements at selected sampling points during each campaign, campaign mean values and standard deviations (SD) are summarized in Table 1.

In-stream $NO_3$-N concentrations along the streams had only minor spatial variations in $NO_3$-N. In the case of May and September series, a slight increase in the $NO_3$-N concentration (between 20 and 30%) was observed from the headwater parts of the watershed downstream towards the measuring section equipped with the multi-parameter sonde (sampling point P4 in Fig. 1). The increase in the concentration was negligible in the July campaign when low $NO_3$-N

Table 1 Spatial distribution of the streamwater $NO_3$-N concentrations from spot measurements at selected sampling points across the Padež watershed (for the position of sampling points see Fig. 1)

| Sampling point | May (mg/l-N) | July (mg/l-N) | September (mg/l-N) |
|---|---|---|---|
| S1 | 1.4 | 1.2 | 1.1 |
| S2 | 1.7 | 1.3 | 1.3 |
| S3 | 1.9 | 1.4 | 1.7 |
| P1 | 1.2 | 1.2 | 1.0 |
| P2 | 1.5 | 1 | 1.2 |
| P3 | 1.6 | 1.1 | 1.1 |
| P4 | 1.7 | 1.2 | 1.5 |
| Mean | 1.57 | 1.13 | 1.28 |
| SD | 0.23 | 0.13 | 0.25 |

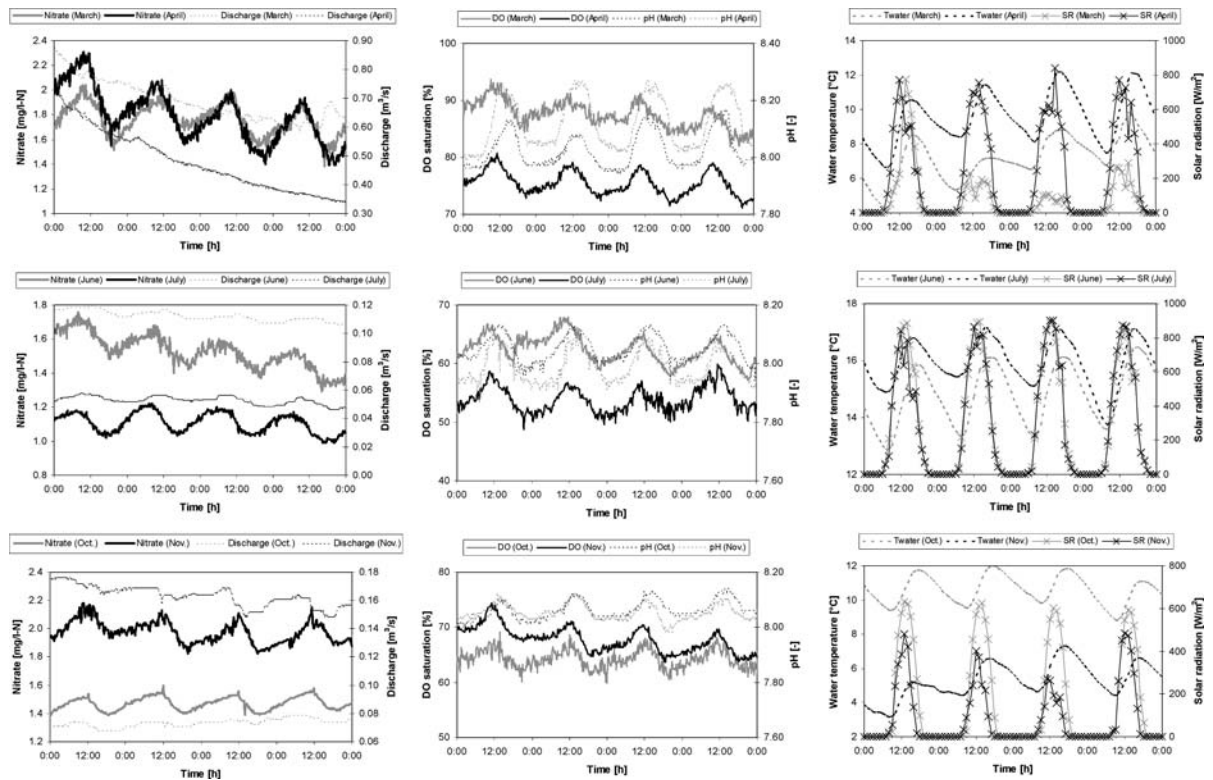concentrations coincided with low summer baseflow conditions.

Time series of the streamwater chemistry and meteorological conditions

Figure 2 shows synchronous high-frequency measurements of streamwater parameters ($NO_3$-N concentration, DO saturation, pH, water temperature), stream discharge and meteorological conditions (solar radiation) during hydrologically inactive periods in spring (March and April dataset), summer (June and July dataset) and fall (October and November campaign). Air temperature was not included into the dataset as it expressed high correlation with water temperature data and therefore did not provide additional information. The water chemistry was not monitored during the dry winter period which was in 2006 extremely cold (air temperatures down to $-10°C$) as the freezing of the stream could have damaged the multi-parameter sonde. The datasets cover dry periods without precipitation, except minor rainfall event at the end of the March dataset. Although the stream discharges during the spring observations in March and April were rather high (more than 0.80 $m^3$/s in the case of the March dataset) compared to other periods in summer and fall (discharges between 0.05 and 0.18 $m^3$/s, respectively), the water depth remained relatively shallow. Considering the cross-section geometry at sampling point P4, at discharge 0.8 $m^3$/s the average water depth amounts $\sim 25$ cm whereas the water surface width is $\sim 9$ m. Specific stream channel geometry seemed to reduce the effect of higher discharges on the diurnal dynamics of the streamwater chemistry. All datasets cover the periods of 4 days.

The water chemistry and meteorological parameters have a diurnal pattern of oscillation (Fig. 2); the temporal occurrence of the minimum and maximum values of the parameters varies on a daily basis. The solar radiation was measured at an open location; the solar radiation peaks were measured between noon and 2 pm. The peak diurnal water temperature lagged behind the solar radiation peaks by 3–5 h; whereas, minimum water temperature occurred between 7 and 9 am. Diurnal dissolved oxygen (DO) saturation peaks were observed between 11 am and 1 pm, the daily minimum appeared between 9 and 11 pm, while the peak diurnal pH values occurred at 1–3 pm and

**Fig. 2** Synchronous high frequency dynamics of the streamwater chemistry and meteorological conditions in spring (March and April), summer (June and July) and fall (October and November). For the sonde location see Fig. 1

pH daily minimum at 1–3 am. Stream discharges showed minor and less distinctive diurnal oscillating behavior which could be observed especially during low flow conditions in summer and fall. In these periods, maximum discharges could be noticed between 9 and 11 am and discharge minimums between 9 and 11 pm.

The $NO_3$-N concentration pattern was also diurnal, but with greater temporal variability, especially for the nitrate concentration diel peak. The minimum daily nitrate concentrations were generally measured between 6 and 9 pm, whereas the maximum concentrations seasonally shifted from 6 am in the summer (July dataset) to 1 pm in fall (November dataset). Simple regression revealed relatively little relationship between the parameters because the parameter oscillations are temporally shifted. Diurnal oscillations shown in Fig. 2 indicate a visually strong positive correlation between DO saturation and pH, and a negative correlation between water temperature and $NO_3$-N.

## Discussion

### Seasonal pattern of the in-stream $NO_3$-N concentration and implications of N status of the watershed

The seasonal trends of streamwater nitrate concentrations and their relationship with other in-stream and climatic parameters (especially water and air temperatures) have been reported in studies of natural, temperate forested catchments (Cirmo and McDonnell 1997; Fenn et al. 1998; Murdoch et al. 2000; Rogora 2007). Van Miegroet et al. (2001) showed that temperature control on N production and hydrological control on nitrate leaching during the growing season could cause an interannual variation of nitrate concentrations and export. During the warmer months, although mineralization of soil organic N is more rapid, nitrate can be immobilized by microbial and plant uptake. In colder months, the biological uptake and transformation of nitrate is

greatly reduced; thus the soil has a reduced ability to retain nitrate during the winter compared to summer (Clark et al. 2004). It is therefore not surprising that mean monthly air and water temperatures were used as a predictor of streamwater nitrate concentration in papers by Heathwaite et al. (1993), Arheimer et al. (1996), Mitchell et al. (1996), Sickman et al. (2003) and others.

The seasonal variability of time series values of streamwater $NO_3$-N concentration, water temperature (Twater), dissolved oxygen saturation (DOsat) and pH at the sonde location are shown in Fig. 3. Although pH did not have a notable seasonal cycle, DOsat and Twater did have a negatively related seasonal pattern. In addition to the positive effect of low water temperature on DO concentration, higher DOsat values in the spring could also be ascribed to in-stream primary production during the open canopy period (March–April) and intensified aeration in the coarse sediment stream channel during higher stream discharges.

The water temperature's seasonal pattern effect on the streamwater $NO_3$-N concentrations can be clearly seen and agrees with the findings of other studies. However, simultaneous changes in seasonal biotic activity and hydrological conditions make it difficult

to identify the prevailing cause for the seasonal streamwater $NO_3$-N concentration pattern. Higher mean streamwater $NO_3$-N concentrations during spring campaigns in March and April ($\sim 1.8$ mg/l-N), together with the reduced immobilizing capacity of soils and plants, could be partially associated with higher discharges and therefore intensified hydrologically induced transport of $NO_3$-N to the stream; however in the summer and fall this could not be the case, because of the low baseflow conditions. During the summer campaign (June and July), the mean $NO_3$-N concentration was 1.5 and 1.1 mg/l-N; in fall (November) the mean $NO_3$-N concentration was 1.9 mg/l-N. The difference between the mean streamwater $NO_3$-N concentrations in summer and fall could therefore be more clearly associated with the contrasting seasonal biogeochemical settings.

The cumulative atmospheric deposition of inorganic nitrogen in 2006 (derived from mean concentrations in bulk rainfall samples) was around 8 kg/ha (ARSO 2007). Mean in-stream $NO_3$-N concentration calculated on all sonde measurements was 1.6 mg/l-N, which is relatively high if compared to other studies of nitrate variability in forests. However, a great number of these studies were carried out in highland or even mountainous watersheds with variable



Fig. 3 Seasonal variability of the time series values of $NO_3$-N concentration, streamwater temperature (Twater), dissolved oxygen saturation (DOsat) and pH at the sonde location
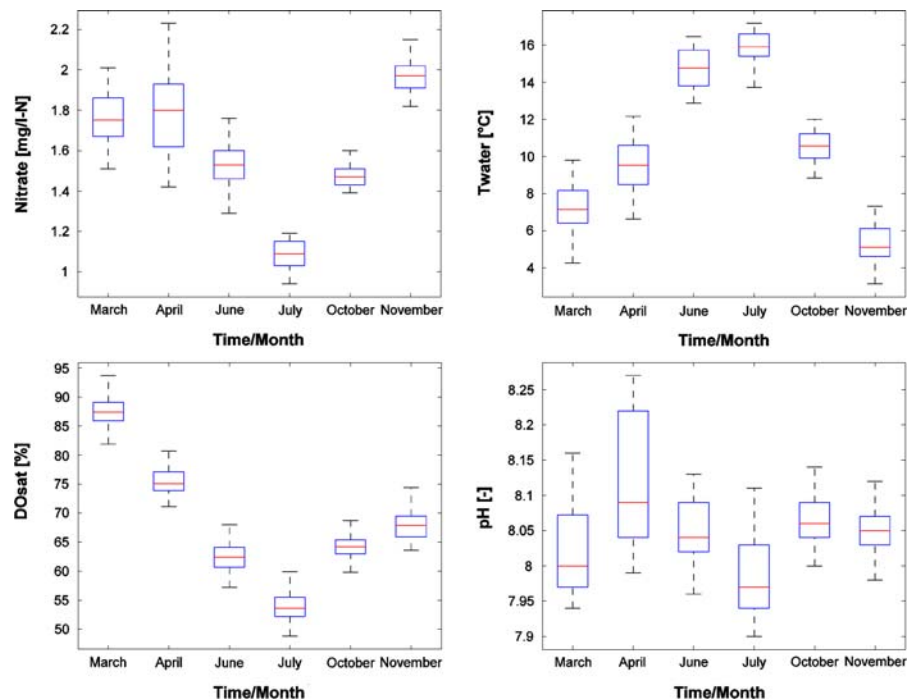
atmospheric N deposition levels and mean annual temperatures (Likens and Bormann 1995; Arheimer et al. 1996; Hood et al. 2003; Sickman et al. 2003, Clark et al. 2004). Higher NO$_3$-N concentrations (by a factor of 2 or 3) are reported in streams draining deciduous forests than in those draining watersheds covered by coniferous forests (Binkley et al. 2004). Bernal et al. (2005) have suggested that dissolved inorganic N (DIN) might be leaching more easily in forested Mediterranean catchments than in temperate ones as a consequence of high soil mineralization rates. Increased DIN leaching could further also be related to the presence of an asynchrony between the availability of mineral N and the ability of vegetation to use it, as suggested for Mediterranean regions in CA (USA) (Holloway and Dahlgren 2001).

Tree species can markedly influence forest ecosystem N cycling (Lovett et al. 2004). While the Padež watershed is covered mainly by old-growth, broad-leaved forest, the prevailing tree species on the narrow riparian areas is black alder (*Alnus glutinosa*). Alder is particularly noted for its symbiotic relationship with a bacterium (*Frankia alni*), which forms nodules on tree roots (Binkley et al. 1992; Hart et al. 1997). This nitrogen-fixing bacterium absorbs N from the air and makes it available to the tree, with the annual rate of fixation estimated at up to 125 kg of N/ha, leading to higher rates of N mineralization and nitrification (Pastor and Binkley 1998). Due to the lack of detailed understanding of the role of forest composition in the studied area on the seasonal extent of the forest soil N pool and further, on streamwater NO$_3$-N dynamics, one cannot develop further hypotheses, but the presence of N-fixing tree species in riparian areas could be a cause for elevated in-stream NO$_3$-N concentrations. Moreover, changes in streamwater NO$_3$-N concentrations particularly in its seasonal pattern have been proposed as an indicator of terrestrial N saturation (Stoddard 1994). Increased NO$_3$-N leaching to groundwater or streams is the primary symptom of nitrogen excess (Fenn et al. 1998). Aber et al. (1995) have discussed the influence of the N saturation on forest biochemistry and primary production in northern temperate and boreal forests in North America, while Goodale et al. (2000) report elevated losses and decreased retention of N in old-growth systems. Furthermore, a strong negative association between forest soil C/N ratio and NO$_3$-N leaching was identified as a highly descriptive variable (Lovett et al. 2002; Ollinger et al. 2002); Gundersen et al. (1998) even stated that the forest ecosystem N-saturation status is controlled by the forest floor C/N ratio.

At the Padež watershed, the presence of old-growth forest and N-fixing tree species (riparian black alders), low soil C/N ratio (15–18) and further, relatively high streamwater NO$_3$-N concentrations accompanied by a seasonal pattern provide some support for the N saturation status of the forested watershed. Additionally, the cumulative atmospheric deposition of DIN in the studied region might also represent a supplementary factor which could significantly affect the watershed N status.

## Seasonal changes in amplitude of in-stream NO$_3$-N concentration diurnal oscillations

In hydrologically stable periods under low-flow conditions, diurnal cycles of streamwater nitrate concentration were discernible in datasets reported by others (Mulholland 1992; Hessen et al. 1997; Burns 1998; Scholefield et al. 2005; Roberts and Mulholland 2007). The findings of these studies generally agree with our diurnal NO$_3$-N results: the lowest concentrations in the late afternoon and highest concentrations early in the morning. Temporal changes to in-stream NO$_3$-N concentrations in the literature are usually associated with changes in diurnal photoautotrophic activity. The overall observation of lower streamwater NO$_3$-N during daylight hours than at night suggests that in-stream NO$_3$-N uptake is greater during the day.

In our case, some further evidence for the role of biological activity is provided by the visually inverse relation between pH, DOsat versus NO$_3$-N concentrations, especially during summer datasets (June and July). The uptake of NO$_3$-N and carbon dioxide by photoautotrophs increases pH during the day (Fig. 2). The diurnal oscillations in NO$_3$-N concentration also could be a result of diurnal oscillations in discharge (summer and fall datasets) and the consequently increased leaching of NO$_3$-N from forest soils; however, the potential role of leaching appears rather limited as the NO$_3$-N oscillations are even greater in the spring, when no diurnal discharge pattern is evident.

In order to directly compare seasonal changes in the NO$_3$-N diurnal pattern, the NO$_3$-N concentrations have been normalized firstly by removing seasonal differences in the mean NO$_3$-N concentration (presented in Fig. 3), and secondly, concentration temporal trends (decreasing or increasing) during each NO$_3$-N concentration time series. The moving averages for 8 periods (2 h) of normalized values of the streamwater NO$_3$-N concentrations for the spring (April dataset), summer (July dataset) and fall (November dataset) are compared in Fig. 4.

Seasonal differences between the diel amplitudes in the NO$_3$-N concentration oscillations can be seen in Fig. 4. In the April dataset the amplitude moved within the range of 0.2–0.3 mg/l-N around the mean concentration, while in the July dataset the amplitude did not exceed 0.1 mg/l-N. In the November dataset an increase in the amplitude could be noticed in comparison to the July dataset. The amplitude of the NO$_3$-N concentration oscillations could be linked to the amplitude of other in-stream parameters' oscillations, e.g., pH amplitude during the April dataset (Fig. 3); but the overall seasonal relation between NO$_3$-N concentration amplitudes and amplitudes of other parameters (Twater, DOsat and pH) remains rather unclear. Linear regression revealed that 81% of the seasonal variance in NO$_3$-N amplitudes can be explained by the diel Twater amplitudes. The relation between diurnal variations in Twater and NO$_3$-N concentration is consistent with the results presented by Mulholland et al. (2006), where greater diurnal variations in nitrate uptake particularly in late spring were possibly a result of diurnal variation in water temperature.
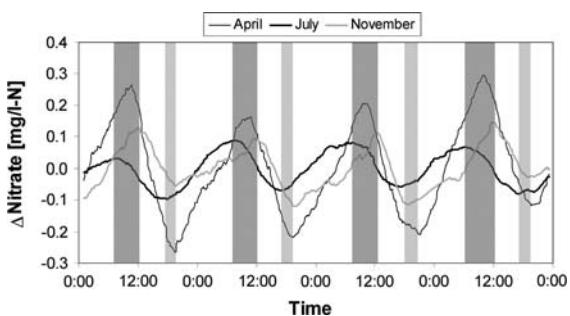


**Fig. 4** moving averages for 8 periods (2 h) of normalized values of the NO$_3$-N concentration with removed temporal trends for the spring (April), summer (July) and fall (November) dataset

On the other hand, diel pH and DOsat amplitudes explained only 53 and 19% of the seasonal variance in diel NO$_3$-N amplitude. Consequently, it is difficult to interpret the seasonal variability of the diel NO$_3$-N amplitudes in terms of the seasonal diel amplitude changes in DOsat and pH as indicators of in-stream autotrophic activity.

Nevertheless, the seasonal change in oscillation amplitudes could be related to seasonal ambient light conditions in the stream channel and, consequently, to a light-dependent intensity of the biological activity as discussed by Triska et al. (1983), Burns (1998) and Hamilton et al. (2001). The presence of the seasonal variations in stream metabolic activity and its relation to the diurnal variations in streamwater NO$_3$-N concentration was confirmed by Roberts and Mulholland (2007).

Since the canopy on deciduous trees at the forested Padež watershed had not developed by April, the available light would have reached the stream more readily at a time when the water temperature had became favorable for photoautotrophic activity. In the summer, the stream was heavily shaded by the overhanging trees. Therefore, light was not able to penetrate to the stream and the intensity of the primary producers' activity became strongly inhibited, resulting in a suppressed diurnal streamwater NO$_3$-N signal.

Additional factors which in combination with seasonal ambient light conditions at the stream surface could contribute to observed changes in streamwater NO$_3$-N diurnal amplitude are the high stream channel wetted perimeter and shallow water depths during periods of low to medium flows, conditions suitable for in-stream biotic activity. Alexander et al. (2000) found that in-stream N retention rates were inversely and exponentially related to river depth, probably reflecting the strong influence of high surface/volume ratios on the enhanced role of biotic and abiotic processes in regulating stream water chemistry.

Due to the flushing regime of the streams at the Padež watershed, the channels of the main streams (the Suhorka and the Padež stream) are rather wide; variations in the discharge contribute to substantial changes to the channel wetted perimeter and water surface width. The water surface width (channel geometry of the cross-section at sampling point P4) against stream discharge is shown in Fig. 5. Although

the relation between discharge and water surface width is reported for a particular channel cross-section, it could also be used to represent the basic geometric characteristics of the channel along the stream section downstream of the confluence of the Suhorka and the Padež stream (Fig. 1).

By linking the stream channel geometry data to the stream discharges for the periods of our datasets, variations in the water surface width can be observed (Fig. 5). During the July dataset, in accordance with low summer flows (around 0.06 m$^3$/s), the water surface widths were ~3 m, whereas in spring (March and April datasets) during higher discharges (average discharge during March dataset was 0.69 m$^3$/s and during April dataset 0.47 m$^3$/s, respectively), the water surface span was between 8 and 9 m. Consequently, the average water depth remained shallow or could even decrease as water moved laterally into broad and shallow channel areas that are not flooded during lower discharges. Through increased surface/volume ratio, a much wider stream channel wetted perimeter was made available as a substratum for the stream autotrophs during somewhat higher discharges in spring, which could result in a strengthened daily NO$_3$-N signal.

Seasonal shifts in the timing of daily minimum and maximum streamwater NO$_3$-N concentration

Further comparison of normalized NO$_3$-N concentration series shown in Fig. 4 clearly indicate some additional differences among them. The time sequence of daily minimum values is seasonally much less dispersed than that of the daily maximum

values. While the daily minimum values occur between 6 and 9 pm (light grey areas in Fig. 4), the occurrence of the daily maximum values shifted seasonally from 10–11 am in April to 6–7 am in July, and back to 12–1 pm in November (dark grey areas in Fig. 4).

A cross-correlation was applied on the time series of the streamwater NO$_3$-N concentrations in order to investigate the seasonal temporal shifts in diurnal streamwater NO$_3$-N oscillations. The results are summarized in Table 2. Lags present the amount of temporal shift (in full hours) for which the NO$_3$-N concentration time series in rows are shifted versus NO$_3$-N concentrations in columns to maximize the cross-correlation function (XCF); (e.g., temporal shift between March NO$_3$-N time series and other time series of NO$_3$-N concentration). The longest, a 5-h temporal shift, was detected between the July and November NO$_3$-N concentration dataset.

The cross-correlation function was also used to study the seasonal behavior of other parameters (water temperature, DO saturation, pH, solar radiation). The seasonal temporal shifts between particular parameter datasets did not exceed one hour, therefore no significant seasonal differences in the daily pattern of the oscillations could be stated.

Additional analysis of the seasonal changes in the timing of daily NO$_3$-N concentration minimums and maximums has been done by de-noising the normalized NO$_3$-N concentration, DOsat and pH original signals using wavelet analysis. Original and clean signals for all datasets are presented in Fig. 6.

As discussed earlier and is also evident from Fig. 6, only the NO$_3$-N concentration diel amplitudes

**Fig. 5** Water surface width against stream discharge in the channel cross-section at sampling point P4
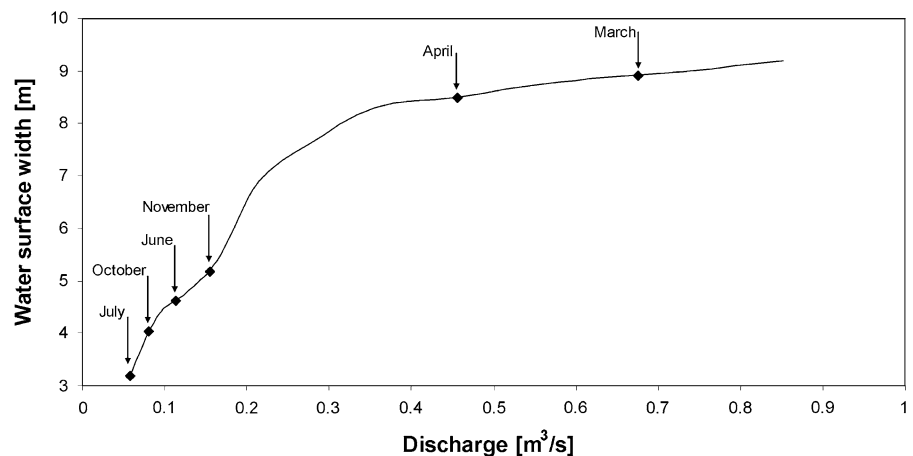
**Table 2** Cross-correlation analysis of the streamwater $NO_3$-N concentration datasets (XCF—cross-correlation function), lags are given in full hours

|          | March | | April | | June | | July | | October | | November | |
|----------|-------|------|-------|------|------|------|------|------|---------|------|----------|------|
|          | XCF   | Lags | XCF   | Lags | XCF  | Lags | XCF  | Lags | XCF     | Lags | XCF      | Lags |
| March    | –     | –    |       |      |      |      |      |      |         |      |          |      |
| April    | 0.816 | 0    | –     | –    |      |      |      |      |         |      |          |      |
| June     | 0.762 | −1   | 0.882 | 0    | –    | –    |      |      |         |      |          |      |
| July     | 0.706 | −2   | 0.855 | −3   | 0.677| −1   | –    | –    |         |      |          |      |
| October  | 0.688 | 0    | 0.539 | 0    | 0.574| 2    | 0.748| 3    | –       | –    |          |      |
| November | 0.759 | 2    | 0.843 | 2    | 0.690| 3    | 0.826| 5    | 0.667   | 2    | –        | –    |

have a considerable seasonal pattern. Seasonal changes in pH diel amplitudes are much less discernible (higher amplitudes in spring and minor amplitude decrease towards summer and fall), and there is practically no seasonal difference in the DOsat oscillation amplitudes. Mean daily oscillations of $NO_3$-N concentration, DOsat and pH clean signals for each dataset are shown in Fig. 7. The mean daily oscillation for each dataset was calculated as an average of daily oscillations throughout the period of each dataset (4 days); the mean daily oscillation therefore presents a typical daily behavior of the parameters during a particular dataset.

By cross-correlation analysis, the seasonally independent daily behavior of DOsat and pH has been identified; additionally, a seasonally consistent temporal pattern of DOsat, pH daily minimum and maximum can be clearly seen in Fig. 7 and agrees with the commonly observed dynamics, indicating the role of in-stream primary production. In view of daily $NO_3$-N variations, the influence of the uptake by in-stream photoautotrophs becomes rather unclear due to seasonal time lags. Especially the daily $NO_3$-N variability in March and November dataset is difficult to explain by the in-stream photoautotroph uptake when the daily $NO_3$-N concentration peak moved towards daily DOsat and pH peaks. The most consistent pattern in terms of primary producers' uptake could be observed in July, when DOsat and pH daily maximums almost coincided with $NO_3$-N minimums and vice versa (Fig. 7). The clearer indication of the primary production $NO_3$-N uptake could be a result of both, the diurnal in-stream activity of primary producers and strong immobilization of $NO_3$-N in forest soil by microbial and plant

uptake which resulted in low streamwater $NO_3$-N concentration in summer.

Mulholland et al. (2006) also indicated the presence of a 24-h cycle in nitrate uptake with highest rates during the middle to latter part of the daylight period and lowest rates at night just before dawn. The 24-h cycle in nitrate uptake could be presumably responsible for temporal decoupling and lag of daily $NO_3$-N concentration oscillations after the DOsat and pH daily pattern (Fig. 7). The slow decrease in the $NO_3$-N highest uptake rates from middle to latter part of the daylight period towards midnight, as described by Mulholland et al. (2006), agrees with our $NO_3$-N concentration observations. Seasonally relatively independent daily $NO_3$-N concentration minimums in the early evening period could be a consequence of seasonally unchanged temporal occurrence of highest daily $NO_3$-N uptake rates by primary producers (also indicated by the timing of DOsat and pH daily peaks, Fig. 7). On the other hand, seasonal variability of the $NO_3$-N concentration daily maximums could be associated with seasonal lags in the daily lowest $NO_3$-N uptake rates which in other studies (e.g., Burns 1998; Mulholland et al. 2006) were observed before dawn. An additional factor that could influence the shift of the $NO_3$-N daily maximums in spring and autumn towards midday is the greater supply of $NO_3$-N to the stream due to reduced terrestrial retention and daily water temperature fluctuation. The temperature effect on in-stream microbial activity is not disputed, but there is not always consensus as to how much it affects the activity and changes of bacterial communities in streams; with sufficient nutrients, increases in temperature up to the temperature optima will increase

**Fig. 6** Original and clean signals of $NO_3$-N, DOsat and pH sonde measurements for all datasets
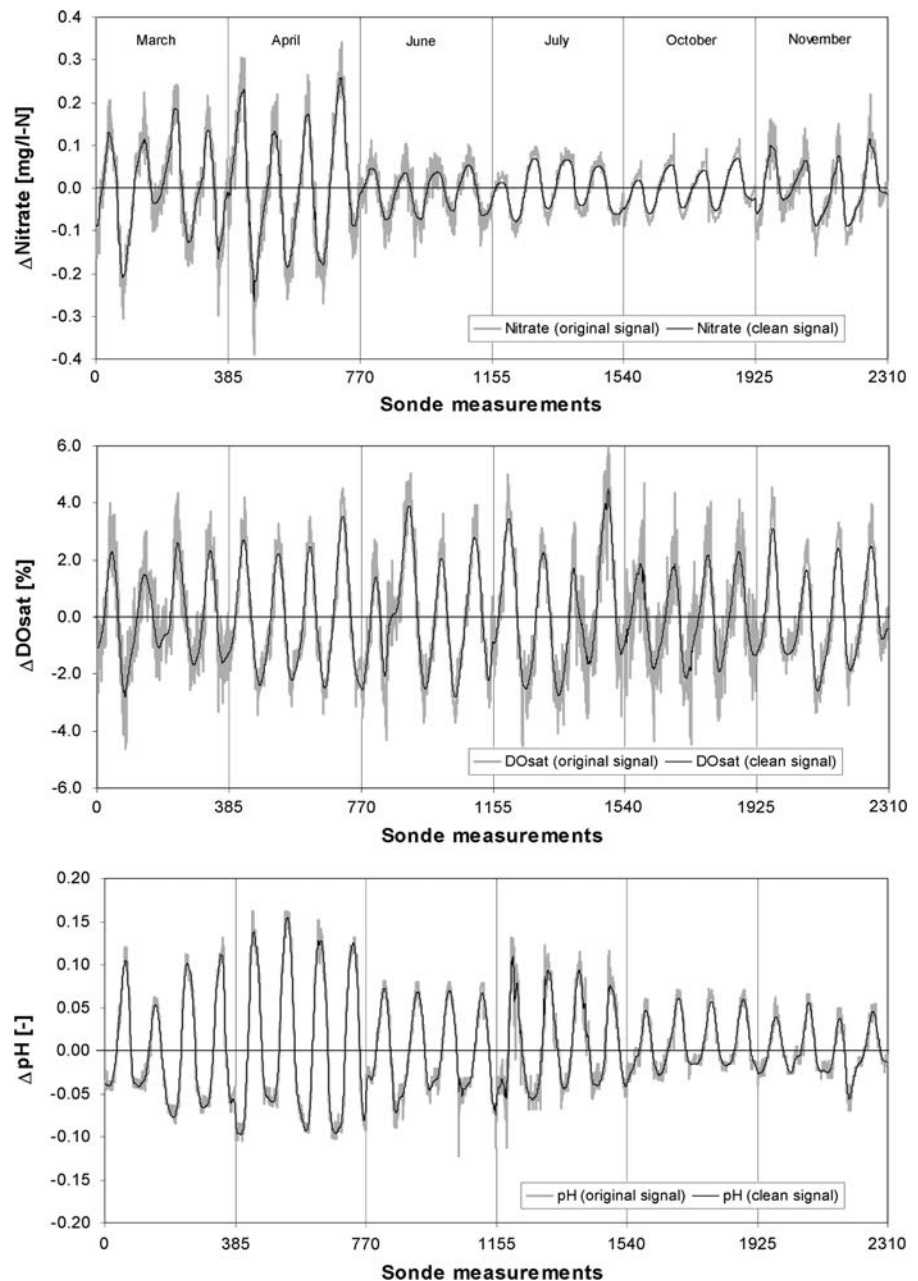


streambed metabolic activity (Kaplan and Bott 1989). Net freshwater photosynthesis varies little in the temperature range between 10° and 20°C; by lowering the temperature, the photosynthetic activity diminishes providing that other environmental factors remain stable (DeNicola 1996). In summer (July dataset), the $NO_3$-N supply to the stream was low, the water temperature range (above 14°C) could not significantly influence the timing of the $NO_3$-N daily

peaks, and they appeared around dawn. Especially during the March and November dataset early morning water temperatures were low (down to 3–4°C, Fig. 2). Consequently, the $NO_3$-N uptake by photoautotrophs could be additionally reduced in the morning, the $NO_3$-N supply to the stream was high and the daily $NO_3$-N maximums might accordingly move towards midday. Due to diel water temperature rise, the temperature conditions could become less
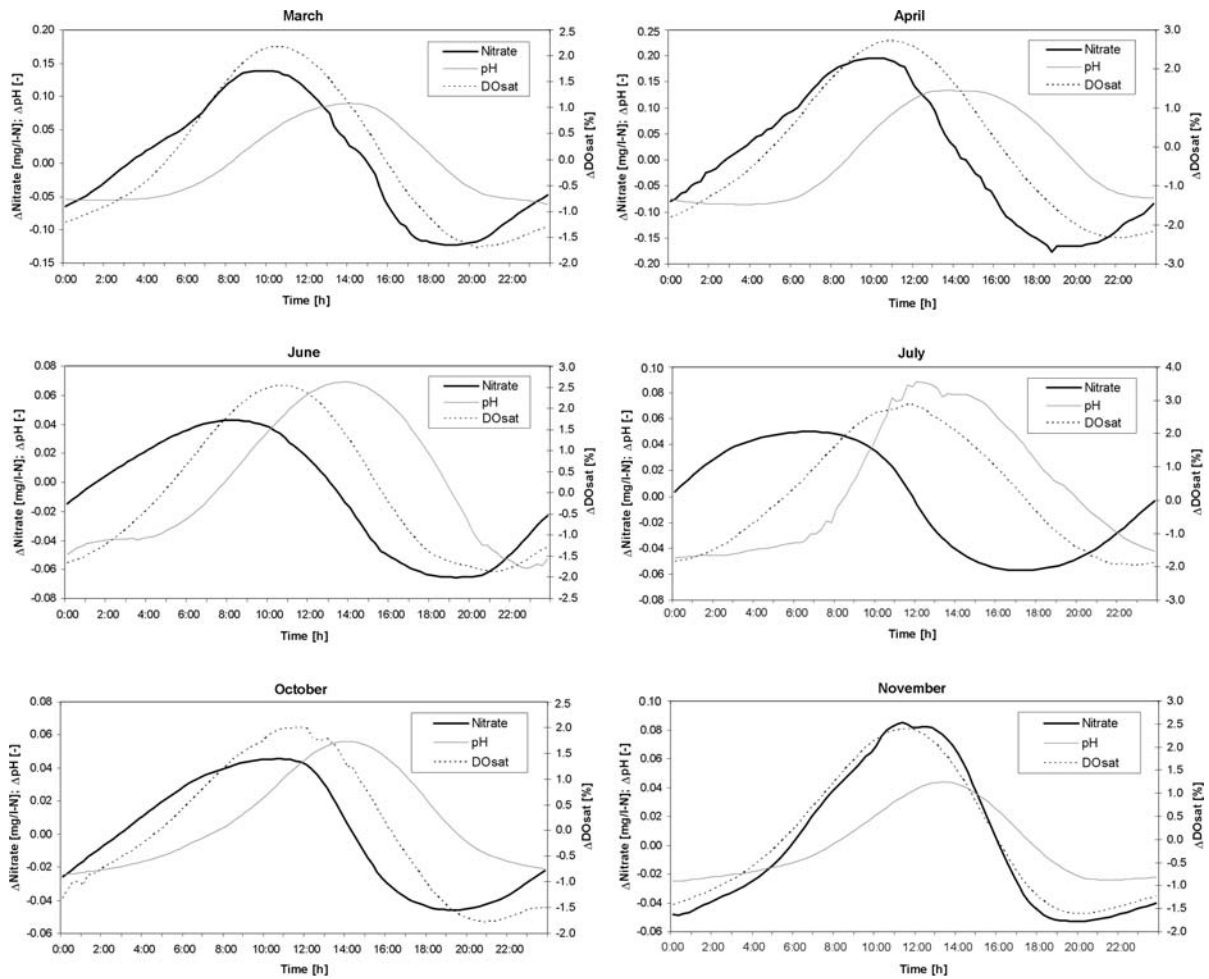
**Fig. 7** Mean daily oscillations of NO$_3$-N concentration, DOsat and pH clean signals

restrictive for the primary producers' activity, causing a decline in the NO$_3$-N concentration from midday towards late afternoon.

Terrestrial versus in-stream processing of NO$_3$-N

Despite the powerful impact of the terrestrial component of the watershed on stream nutrient export, it is increasingly evident that processes within the stream contribute substantially to,—and at times may dominate—watershed N export, thus affecting our interpretation of overall watershed processes (Likens and Bormann 1995; Bernhardt et al. 2005). The availability of N for in-stream processing depends ultimately on the amount of N that is transported from the terrestrial system and atmospheric environment to the stream, but the N processing capacity of

aquatic systems relative to the rates of N supply is not well known (Burns 1998; Bernhardt et al. 2002).

Seasonal changes in the daily nitrate flux as a product of NO$_3$-N concentration and discharge could be used to examine the seasonal differences in the daily in-stream nitrate uptake. Due to considerable differences in discharge, the seasonal NO$_3$-N flux changes are much more distinctive than the differences in the concentration. By normalizing and thus neglecting the differences in mean NO$_3$-N flux between different datasets and temporal trends due to changeable discharges, the seasonal differences in the daily NO$_3$-N flux change become also much more pronounced (Fig. 8). In the case of the March and April dataset, the daily flux change was between 0.4 and 0.5 g/s-N whereas the maximum July daily flux change was only 0.02 g/s-N. Accordingly, during the

spring datasets, the daily $NO_3$-N flux change was more than 20 times higher than during the summer dataset.

Seasonal daily flux variability therefore suggests important seasonal changes in the extent of the in-stream processing and retention of $NO_3$-N. During the March and April dataset, the $NO_3$-N supply to the stream was high; the daily change in the $NO_3$-N flux was the greatest, suggesting that the in-stream $NO_3$-N uptake was at its peak. In spring, the in-stream uptake could therefore have an important role in assessing the flux of nitrate from the forest. In summer during low flows, the supply of the $NO_3$-N from the terrestrial system to the stream is considerably reduced and so is the in-stream uptake, whose potential effect on the total flux assessment is greatly diminished.

It has been argued that in-stream retention or processing of N is a major factor influencing in-stream nitrate concentration in a variety of ecosystems (Peterson et al. 2001). However, in our study as in Lovett et al. (2002), conditions in headwater streams which are steep, rocky and shaded by overhanging trees tend to reduce in-stream N biogeochemical transformations and retention. Spatial distribution of the streamwater $NO_3$-N concentrations along the streams at the Padež watershed could indicate that a great part of the in-stream $NO_3$-N is set while the water percolates through the forest soils before reaching the stream. Furthermore, the input of $NO_3$-N to the stream during baseflow conditions clearly follows a seasonal pattern which is presumably controlled by the $NO_3$-N immobilizing capacity of the forest floor (Fig. 3). The observed increase in the

$NO_3$-N concentration downstream in May and September (Table 1) could be related to increased leaching of nitrate from the forest soils. During the July campaign, both the spatial variability of the streamwater concentrations across the watershed and also the in-stream concentrations were the lowest and apparently associated with maximum, mid-summer immobilization of nitrate by microbial and plant uptake.

The overall supply of the $NO_3$-N from the Padež watershed to the streams is high, and the in-stream $NO_3$-N uptake seems to be inadequate to cause a downstream decrease in the $NO_3$-N concentration. Nevertheless, the diurnal temporal dynamics of the in-stream $NO_3$-N concentration is most likely driven by the primary production uptake. The early morning daily $NO_3$-N concentration maximum could present an input of $NO_3$-N from the terrestrial system (forest) to the stream, which is minimally obscured by the in-stream processes taking place during the daylight.

## Conclusions

High-frequency observations during the periods which are not obscured by the changeability of hydrological conditions provided additional opportunities to explain the role of the simultaneous variations of seasonal meteorological conditions and water chemistry on the dynamics of the diurnal streamwater $NO_3$-N oscillations. Seasonal variability in the diurnal streamwater $NO_3$-N concentration behavior versus the seasonally relatively uniform behavior of other water chemistry constituents in terms of the timing of daily maximum and minimum values and furthermore, the seasonal variations in the amplitude of the daily oscillations offer some supplementary evidence of the in-stream $NO_3$-N uptake by primary producers.

Our results showing seasonal in-stream $NO_3$-N concentration variability indicate the potentially important role of primary production uptake on the daily dynamics of $NO_3$-N in forested streams, particularly during seasons when deciduous vegetation is dormant and light levels in the stream are high. In spring, highest daily amplitudes in $NO_3$-N concentration and daily changes in the $NO_3$-N flux have been observed as a result of the seasonal ambient light conditions. Additionally, increased in-stream uptake could also be related to increased stream surface/volume ratios and the stream channel wetted
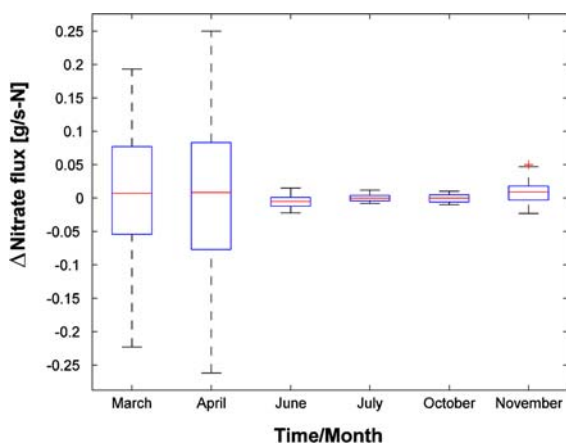


Fig. 8 Seasonal differences in the daily $NO_3$-N flux change

perimeter, and thus higher in-stream processing during periods of somewhat higher discharges. The NO$_3$-N concentration oscillations in summer show the smaller effect of the in-stream uptake, which could be additionally confined by low supply of the NO$_3$-N to the stream due to high immobilization in forest soils. The observed diurnal NO$_3$-N concentration variations have important implications for the long-term assessments of N cycling in streams and calculation of NO$_3$-N flux from the forested watersheds; the seasonal changes in the patterns of the NO$_3$-N concentration indicate considerable seasonal variability in the in-stream uptake, which should be properly considered in such calculations.

The seasonal behavior of the NO$_3$-N flushing from the Padež watershed under hydrologically changeable conditions has been discussed by Rusjan et al. (2008). The analysis presented here could, according to the previous results, lead to an important new conclusion. Whereas NO$_3$-N flushing during rainfall events depends on the seasonal transitions between the flush-limited and source-limited states of the forested watershed, by contrast the drying of the watershed after the rainfall events shifts the controlling factors responsible for the in-stream NO$_3$-N dynamics from the forested areas surrounding the stream into the stream. Therefore, during dry periods, the observed diurnal in-stream NO$_3$-N oscillations are mainly controlled by daily in-stream NO$_3$-N processing, namely the uptake by photoautotrophs. The shift of the mechanisms responsible for continuous regulation of in-stream NO$_3$-N dynamics requires further analysis, which would have to be supplemented by a more detailed understanding of temporal changes in the forest soil N pool.

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