Chapter 1

Inter- and Intra-Annual Variability of Nitrogen Concentrations in the Headwaters of the Mero River

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Abstract

This study examines the inter- and intra-annual variability of different forms of N [total nitrogen (TN), nitrate-nitrogen (N-NO_3) and total Kjeldahl nitrogen (TKN)] in stream waters of a rural headwater catchment in Galicia (NW Spain) during a 5-year period, covering 2004–2009 water years (October–September). Daily time series were used to verify the temporal variability and to characterize the nitrogen pollution. The TN concentrations were low, although the values constantly exceeded the critical range (0.5–1.0 mg L^{-1}) over which potential risk of eutrophication of water systems exists. Nitrate was the predominant form of nitrogen in the river throughout the study period, accounting for 82–85% of the TN. Significant differences were found for different forms of N between water years and seasons, indicative of wide inter- and intra-annual variability of nitrogen concentrations, mainly related to rainfall and flow oscillations. The seasonal pattern in the concentrations of TN, N-NO_3 and TKN in stream water was similar to many humid and temperate catchments, with higher concentrations in winter, when variability was also the highest in the period, and lower values in summer.

Keywords: nitrogen, variability, rural headwater catchment, temperate humid climate, NW Spain

1. Introduction

A large number of biological, chemical and physical processes are involved in the production, transformation and translocation of N compound in terrestrial and aquatic systems [1]. The most important natural factors controlling nitrogen losses from soils to surface waters are climatology, topography and hydrology, and soil characteristics. For example, the temperature acts on N transformation processes, whereas rainfall distribution and intensity plays a decisive role in the leachate. The distribution of water flow over and through the soil has a great influence on nitrate discharges into the waters [2, 3]. These factors are dynamic and highly variable in space and time, and their action can result in heavy discharges of nitrogen into the watercourses. The impact of natural factors on nitrogen losses can be modified by anthropogenic factors, including soil use and crop rotation, the application of slurry and other fertilizers, as well as the amount and method of application [4–6]. The diffuse pollution of water resources by nitrogen is a problem that affects the whole world, with agriculture being the main primary source of diffuse pollution of water resources [6, 7]. Ultimately, the interaction between the factors involved in the N loss from the soils and those related to N transport determine the final losses of nitrogen to surface waters, as well as the N concentrations and N forms in the rivers; hence, these interactions must be understood in order to manage diffuse losses of agricultural nutrients efficiently.

The dynamics and distribution of N forms in the aquatic system is not easy to understand since N concentrations vary markedly from one catchment to another, depending not only on land use, agricultural management, the type and quantity of fertilizer applied but also on the climatological and hydrological characteristics of the basins [8]. Several authors relate variability in N concentrations to catchment size and, in general, attribute small spatial and temporal variability to small river basins [9, 10]. In addition, the N concentrations display wide variability within the same catchment. For example, for a given rainfall event, the N concentrations may differ greatly at different times of the year [11, 12]. Climate and land use change is expected to alter the transfer of nutrients from land to water, although the results are controversial [13–16]. Some studies show that nitrogen loads will increase under climate change and may be affected equally by climate and land use change [15]. However, other studies indicate that nitrogen loads will decrease under climate change mainly due to decreases in runoff, which may be runoff, may be more affected by climate change than changes in land use [13, 16].

A good knowledge of the temporal variation of nitrogen concentrations is a key for understanding the N transport at the catchment scale, for modelling their behaviour and, ultimately for designing agricultural practices management to reduce potential N losses in a more effective manner under current and changing climate and land uses conditions. Therefore, it is essential to have good data on N for long-term periods. Most of studies on temporal changes of N concentration were mainly focused on catchments with a marked anthropogenic influence and only on one form of N, generally nitrate [9, 10]. Less attention has been paid to understanding the N dynamics at headwater streams with minimal human impact, even though they serve as a reference point against which data from more disturbed catchments can be compared. All this makes clear the need for more detailed long-term studies in small, minimally disturbed, headwater catchments to clarify the behaviour of different forms of N and understand the factors governing the temporal variability of N concentrations. Therefore, there is a clear need to monitor N concentrations in detail over a long-term period to investigate the N dynamics.

In this context, the aim of this study was to investigate the inter-annual and seasonal variations of different forms of nitrogen (TN, N-NO_3 and TKN) concentrations in the headwaters of Mero River basin, a typical groundwater-dominated rural catchment in Galicia (NW Spain) located upstream from the Cecebre reservoir, which has unique characteristics, since it is important both strategically (the only drinking water source of the city of A Coruña and its metropolitan area, approximately 450,000 inhabitants) and ecologically (site of community importance included in the Nature 2000 network). Additionally, the data collected in the catchment study are of great use in evaluating of several models.

2. Material and methods

2.1. Study site description

The study was conducted on a small headwater catchment of the Mero River basin (Galicia, NW Spain; **Figure 1**). The Corbeira has a catchment area of 16 km^2 and a total length of approximately 10 km. The geology of the catchment is homogeneous and dominated by basic metamorphic schist of the Órdenes Complex [17]. The main soil types are umbrisols and cambisols [18], which are relatively deep because of heavy weathering. The surface soil layer has a silt and silt-loam texture, high organic content (2.5–11.5%) and acid pH (4.5–5.6).

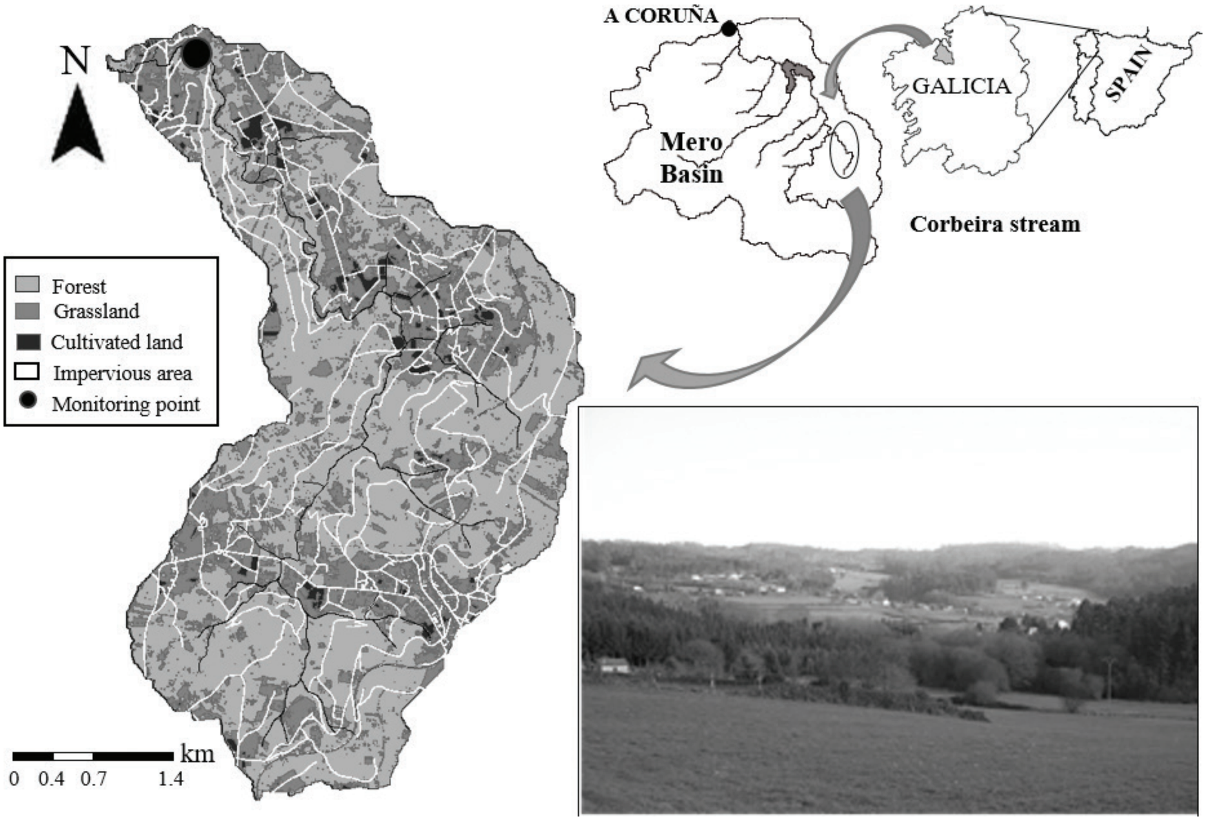

Figure 1. Localization of the study area, land-use map and general view of the Corbeira catchment.

The C/N of the upper layer is almost 10 (9.2–12). The Corbeira catchment is minimally disturbed by human activity; it is predominantly covered by forest (65%) and agricultural land (30%). The agricultural area is primarily used for meadows and natural pastures (83% of agricultural land), with the latter being located in more or less humid areas, mainly in flood areas, where they produce fodder for consumption in green, dry or as silage. Croplands comprise 3.8% of the catchment area and are mainly used for fodder crops, such as maize, and for winter cereals. Other crops—potatoes, turnips, vegetables or fruit trees—are consigned to small family farms oriented to self-consumption. Finally, a small percentage (about 5%) of the catchment is made up of areas occupied by buildings and roads. Agriculture and forestry are interspersed throughout the catchment (**Figure 1**). Forest areas (dominated mainly by commercial eucalyptus and pines) occupy areas with steep slopes. Two distinct agricultural areas can be distinguished in the catchment (**Figure 1**): one is located in the upper part of the catchment, where the slopes are moderately steep, with some cropland near the drainage network and the largest cattle load in the study area, which presents a great risk of erosion, with sediments and nutrients delivery to the stream. The other zone, located on the right margin of the river, in the middle-lower part of the catchment, is where most agricultural activity in the catchment takes place and is where the widest area of cultivated land is found, some with good connectivity to the drainage network. It also highlights the mosaic vegetation in agricultural areas, with most of the croplands bordered by meadows and even, in some cases, by small stone walls, which can obstruct connectivity of croplands with the drainage network, resulting in a decrease in the potential pollutant effect in surface waters.

The Corbeira catchment is a rural area characterized by the presence of small population centres (population density 35 inhabitants km^2). The vast majority of households lack sewerage, so domestic sewage, mainly faecal water, is stored in individual septic tanks. Livestock density was estimated at 0.29 livestock units ha^{-1}, with a predominance of cattle heads (75%). Organic wastes (slurries and manures) generated by agricultural and livestock activity are the most frequently used fertilizers in agriculture in the catchment, with mineral fertilizers supporting these organic ones. Slurries (mainly cattle) are primarily used in meadows and grasslands several times a year, even in the rainy season (October–December), whereas manures are used on croplands, especially in small orchards and in croplands given to maize production, generally prior to planting. Forest areas do not receive fertilizers.

The climate of the study area is Atlantic (temperate oceanic). The mean annual rainfall for the 1983–2009 period reaches a value of 1050 mm. Rainfall is distributed quite evenly throughout the year, although it is concentrated in the autumn and winter months, with October, November and December being the rainiest months and July and August the driest. In general, long-term rainfall causes high rainfall volume but rarely achieves high rainfall intensity, although this can vary substantially, depending on the type of front passing over. The temperature of the study area is characterized by its evenness, with a mean annual of 13°C and a thermal amplitude of 10°C for the period 1983–2009. Concerning the monthly temperature evolution throughout the year, the minimum values occurred in January and the maximum in July. The mean annual discharge of the Corbeira stream amounts to 0.20 m^3 s^{-1}. The hydrological regime is pluvial, with a seasonal pattern in hydrological response characterized by a dry summer period lasting up to first rainfall events in autumn, when the soil reserves recover, followed by a wet period that extends through the autumn and winter seasons [19]. Consequently, the maximum monthly mean discharge is observed in March (0.31 $m^3 s^{-1}$), whereas the minimum monthly mean discharge is registered in September (0.06 $m^3 s^{-1}$). The baseflow index, a measure of the proportion of stream flow delivered from groundwater, is about 0.80, indicative of a high contribution of groundwater to stream flow. A more detailed description of the study catchment characteristics can be found in the study of Rodríguez-Blanco et al. [19–21].

3. Hydrological monitoring, sampling and water analysis

Stream discharge and N concentrations have been measured at the catchment outlet from October 2004 to September 2009. Discharge was calculated from measuring water levels (ISCO 720) using the rating curve. Water level data were measured continuously (every min) and recorded at 10-min intervals. Water samples were collected during both baseflow and runoff events. Under baseflow conditions, water samples were manually collected every 10–15 days, whereas under runoff events, they were collected using an automatic sampler (ISCO 6712-FS) at short-time intervals, depending on the characteristics of the runoff events (magnitude, duration).

Stream water samples were analysed for total Kjeldahl nitrogen (TKN), nitrate (NO_3), nitrite (NO_2) and ammonium (NH_4). The TKN concentrations, which represent the sum of ammoniacal and organic nitrogen, were determined by Kjeldahl digestion of unfiltered samples, following the American Public Health Association method [22]. After filtration (0.45 μm), NO_3 and NO_2 concentrations were analysed by capillary electrophoresis, whereas the NH_4+ concentrations were measured using an ammonia-selective electrode. The NO_2 and NH_4 concentrations were below the detection limit in all cases.

Daily flow-weighted mean N concentrations were used to analyse the temporal variability and to characterize the N pollution. Data were organized into four seasons: autumn (October, November and December), winter (January, February and March), spring (April, May and June) and summer (July, August and September). For annual data, the hydrological year was used instead of the calendar year. The flow-weighted mean concentrations were calculated for each year or season by dividing the daily load (N-NO_3 and TKN) by the daily stream flow.

An analysis of variance (ANOVA) was performed to examine the effect of inter-annual variability (five levels: 2004/05, 2005/06, 2006/07, 2007/08 and 2008/09) and intra-annual variability (four levels: autumn, winter, spring and summer) on N (N-NO_3 and TKN) concentrations in the stream. The Tukey test was used as a *post-hoc* test whenever the ANOVA indicated a significance. For all analyses, a significance value of 0.05 was used. All statistical analyses were carried out using the PASW Statistics 18 for Windows program package (SPSS Inc.).

4. Results and discussion

4.1. Weather and discharge

Rainfall and stream discharge were highly variable during the study period (**Table 1**). Annual rainfall for 2004/2005–2008/2009 averaged 1147 mm, 97 mm above the mean of the 1983–2009 (1050 mm), and ranged from 895 mm in 2004/2005 to 1397 mm in 2006/2007. Rainfall distribution throughout the year was also variable. For example, in the hydrological year 2005/2006, more than 80% (963 mm) of annual rainfall occurred in the first half of the year, whereas in 2006/2007 about 55% (750.4 mm) was registered during autumn (October, November and December), reaching record autumn rainfall in the study area. Dry conditions occurred in the second half of the year 2007 and in the autumn 2007/2008, giving rise to the most severe drought episode registered in north-western of Spain over the last half century. Rainfall evolution throughout 2007/2008 was also complex. A dry autumn was followed by a very wet period, mainly January, March, April and May (62% of annual rainfall), in which rainfall events of great magnitude and intensity were registered.

Temperatures during the study period were also variable, although less than for rainfall. The 5-year study period mean temperature was 13.2°C, i.e. 0.2°C above the mean of the 1983–2009 period. Note that 2006/2007 was, together with 2000/2001, the hottest hydrological year in the historical record, whereas 2008/2009 was the coldest in the past 20 years. The annual thermal amplitude, i.e. the difference between the mean temperature of the warmest and the coldest month, varied substantially between years. Thus, the amplitude of the year 2005/2006 (14.1°C) was more than 50% of that registered in the year 2006/2007 (9.2°C). There is a clear seasonality, reaching the lowest mean temperatures in winter and the highest temperatures during the summer (**Figure 2**).

Annual flow, as with rainfall, has a high inter-annual variability, oscillating between 234 mm in 2007/2008 and 449 mm in 2005/2006, with a mean flow during the study period of 364 mm. Direct runoff makes up only a small proportion of streamflow, since it only represents between 20 and 38% of the annual flow. Although the annual flow was highest in 2005/2006, direct runoff was higher in 2006/2007 and 2008/2009 than in 2005/2006, i.e. in the wettest hydrological years, reflecting the role of soil water content in the runoff generation, as has been shown in a previous study in this catchment [19]. Streamflow also showed a clear seasonality, with maximum flows occurring in January–February and minimum flows occurring in September–October (**Figure 2**). This behaviour is typical of baseflow-dominated catchments, such as the Corbeira, resulting from the seasonality in rainfall distribution, although there was a lack of linearity between rainfall and streamflow attributed to differences in soil water balance [19].

	2004/2005	2005/2006	2006/2007	2007/2008	2008/2009
Rainfall (mm)	895	1192	1397	1054	1196
Temperature (°C)	13.2	13.5	13.7	13.0	12.6
Streamflow (mm)	298	449	412	240	421

Table 1. Annual variability of rainfall, temperature and streamflow during the five hydrological years of the study period.

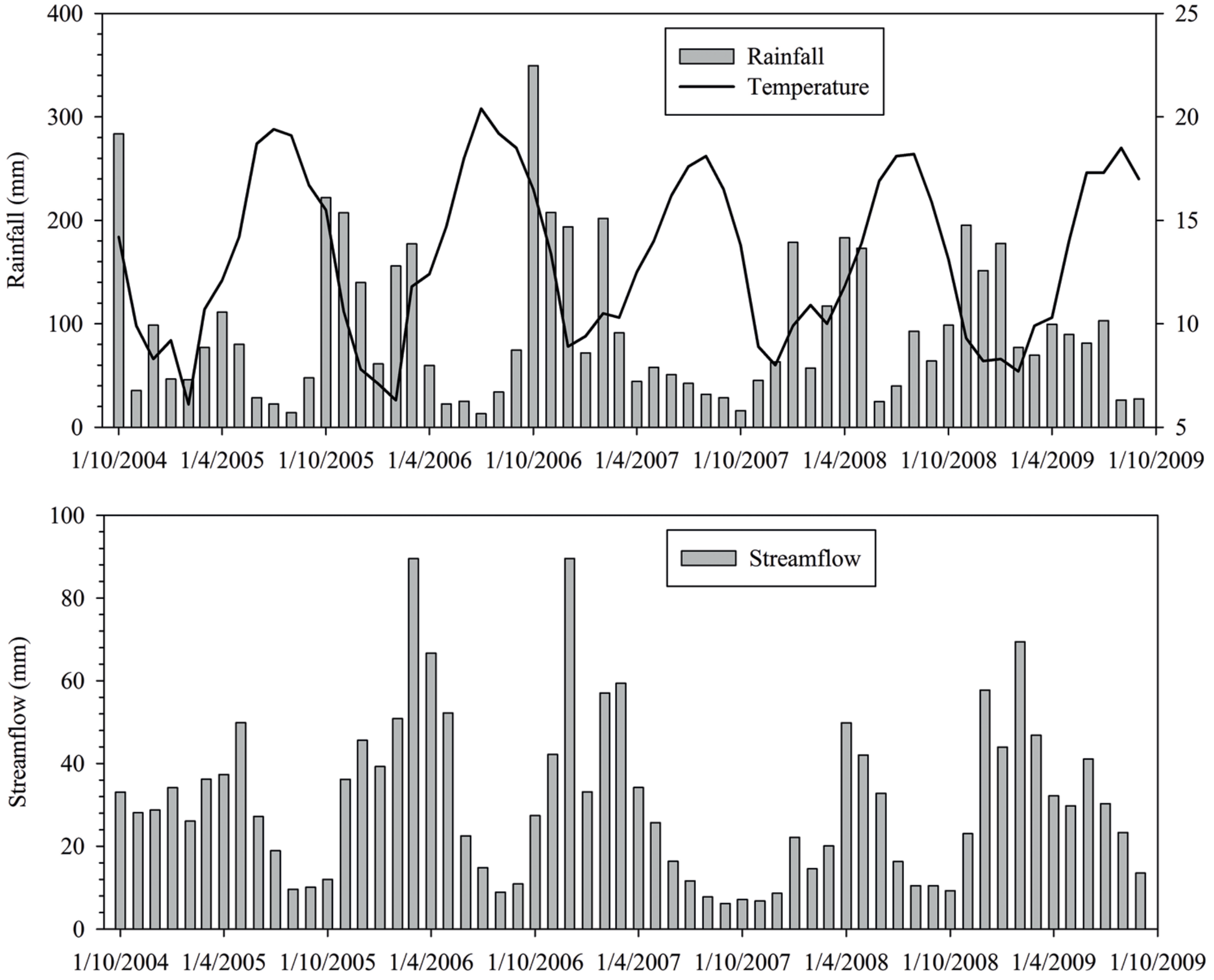

Figure 2. Monthly variation of rainfall, temperature and streamflow during the five hydrological years of the study period.

4.2. Inter-annual variation of N concentrations

Over the study period, the mean annual flow-weighted concentrations were 1.40, 1.15 and 0.26 mg L^{-1} for TN, N-NO_3 and TKN, respectively (**Table 2**). These low N concentrations are typical of streams draining minimally perturbed catchments, i.e. with low N deposition, high percentage of forest area and low agriculture activity, as is the case of Corbeira catchment, so the concentrations there were lower than typical concentrations for catchments with more intense land use, such as agriculture and urban. They were also lower than those reported by Serrano et al. [23] for the Mero basin headwater (mean concentrations of 2.23, 1.88 and 0.35 mg L^{-1} for TN, N-NO_3 and TKN, respectively), which shows similar climatic characteristic, landform and soil management of the study area, but with a higher percentage of agricultural land and livestock density. However, they were considerably higher than the levels in minimally disturbed, natural water draining areas in the north-western region of Spain [24] as well as the reference values proposed by Meybeck et al. [25] for pristine river systems, suggesting some N enrichment in the stream water, probably as a result of the agricultural practices in the catchment. In the Corbeira catchment, in addition to its presence as a natural component, N derives from agriculture, mainly because agricultural lands receive

	2004/2005	2005/2006	2006/2007	2007/2008	2008/2009
TN (mg L $^{-1}$)	1.30 (0.36)	1.50 (0.57)	1.37 (0.40)	1.39 (0.55)	1.45 (0.34)
N-NO$_3$ (mg L^{-1})	1.09 (0.17)	1.21 (0.29)	1.16 (0.22)	1.13 (0.27)	1.15 (0.22)
TKN (mg L^{-1})	0.21 (0.29)	0.29 (0.38)	0.21 (0.24)	0.28 (0.38)	0.30 (0.22)

Table 2. Flow-weighted TN, N-NO$_3$, TKN concentrations and standard deviation during the five hydrological years of study period.

a contribution of nitrogen fertilizers considerably higher than that of the forest areas and the N entry of N coming from the population nuclei is low.

The TN, N-NO$_3$ and TKN concentrations differed among the observed years (**Table 2**). The concentrations of TN ranged from 1.30 to 1.49 mg L^{-1}, whereas N-NO$_3$and NTKN contents varied from 1.09 to 1.21 mg L^{-1} and from 0.21 and 0.29 mg L^{-1}, respectively. For all N forms, the minimum values were registered in 2004/2005, an exceptionally dry water year with rainfall 17% lower than the mean rainfall for the period 1983–2009. Maximum concentrations were recorded in 2006/2007 for N-NO$_3$ and TN, i.e. in the rainiest water year of the study period, and in 2008/2009 for TKN (highest SS yield, data not shown). The observed changes in stream N concentrations most likely reflected the effects of change in hydro-climatic factors, such as hydrology of the catchment and temperature, because potential drivers of N, such as land use and soil management have not varied substantially in the area over the last few decades and, in consequence, fertilization rates have been stable during the monitoring period. However, the trend in mean annual stream N (both N-NO$_3$ and TKN) concentrations were not synchronous with changes in stream flow (**Table 1**), suggesting that changes in the timing and magnitude of rainfall episodes could lead to changes in the relationship between N transport per unit of water volume, in agreement with other studies [9, 26], as they affect N availability and transformation processes.

All of the water samples had higher N-NO$_3$ concentrations than TKN, so the N-NO$_3$ was the predominant form of N in the study catchment, accounting for, on average, 82% of the TN (80–85%). These rates are consistent with those commonly recorded in agricultural and rural groundwater-dominated catchments worldwide, with organic nitrogen comprising 10–20% of TN [23, 27]. However, the fractionation in this study contrasts with results obtained in a widely variety of catchments minimally disturbed catchments with TN concentrations lower than 2 mg L^{-1}, where frequently more than 80–90% of TN is commonly delivered in the form of organic N [28, 29], constituting a substantial component of TN in many ecosystems receiving low N enrichment. Mean annual N-NO$_3$ concentrations as a percentage of TN decreased from 85% in 2006/2007 to 80% in 2008/2009, the water year of highest particulate material which could favour higher N transport in organic form.

Daily flow-weighted TN concentrations were consistently below the threshold level of 2 mg L^{-1}, threshold identified in the European Nitrogen Assessment [30] as an appropriate target for the delivery of good ecological status in European water. However, daily flow-weighted TN concentrations exceeded the critical range of 0.5–1.0 mg N L^{-1} above which there is a potential risk of eutrophication of water systems [31], highlighting a possible negative effect on agricultural practices in the stream waters.

4.3. Intra-annual variation of N concentrations

The daily TN, N-NO$_3$ and TKN concentrations were characterized by a marked intra-annual variability (**Figure 3**), with the highest concentrations (and standard deviation) in winter, when the supply of N on both landscape and streamflow is usually abundant (**Figure 4**). Fertilization in the catchment takes place in autumn and spring. The lowest concentrations were obtained in summer, in combination with low streamflow, the maximum baseflow contribution to streamflow and higher biological activity within the catchment and stream, reducing the flushing of leaching soil NO$_3$ and thus reducing the N concentrations in the stream. Significant differences were detected between seasons, except for N-NO$_3$ between autumn and winter ($p > 0.05$) and for TKN between autumn and spring ($p > 0.05$) and between spring and summer (0.05). This pattern was also observed in many other rivers draining forest and agricultural catchments, irrespective of the importance of groundwater to river flow volume [32], and it is frequently related to water moving through the soil, less plant nitrogen uptake and microbial immobilisation during winter in addition to more intensive erosion, which all contribute to higher N levels during the winter. However, this general pattern varied among years depending on the weather and discharge patterns. For examples, in the 2008/2009 hydrological year, TN, N-NO$_3$ and TKN concentrations were significantly lower in spring than summer, when it reached the highest daily flow-weighted mean TKN concentration, which was notably influenced by two large rainfall-runoff events in July of 2009. The summer of the 2008/2009 water year was characterized by elevated rainfall in July (170% higher than mean rainfall for July in the period 1983–2009) concentrated in two intense rainfall events, which caused high surface runoff and particulate material delivery to the stream [11] and consequently high TKN concentrations were observed. However, the very dry autumn 2007/2008 led to very low TKN concentrations, very similar to those observed in summer. These results suggest that temperature-dependent biological uptake is not the more important factor controlling the seasonal nitrogen dynamics as frequently it occurs in more natural systems [28], but that delivery of nitrogen to the stream is driving the dynamics, with maximum concentrations when N availability and flow, and thus the transport capacity, is at their highest.

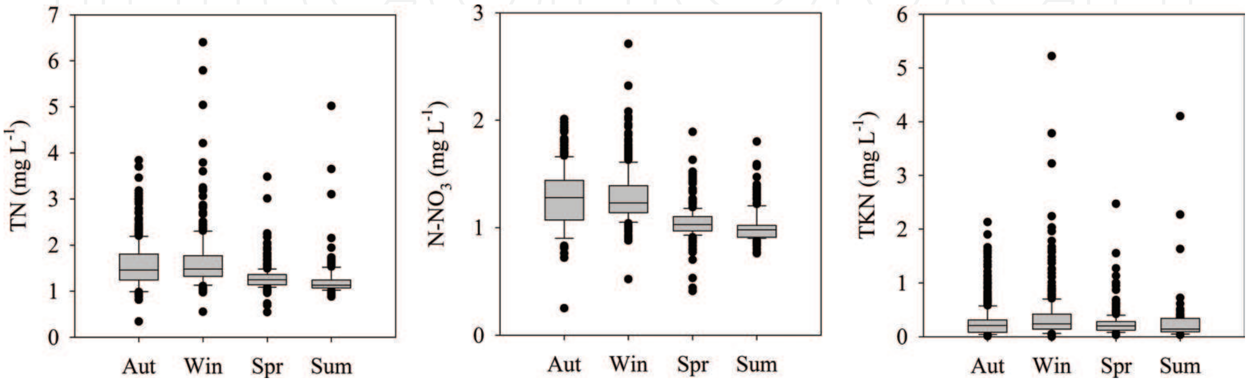

Figure 3. Box plot showing nitrogen seasonal variations. Aut: autumn, Win: winter, Spr: spring, Sum: summer.

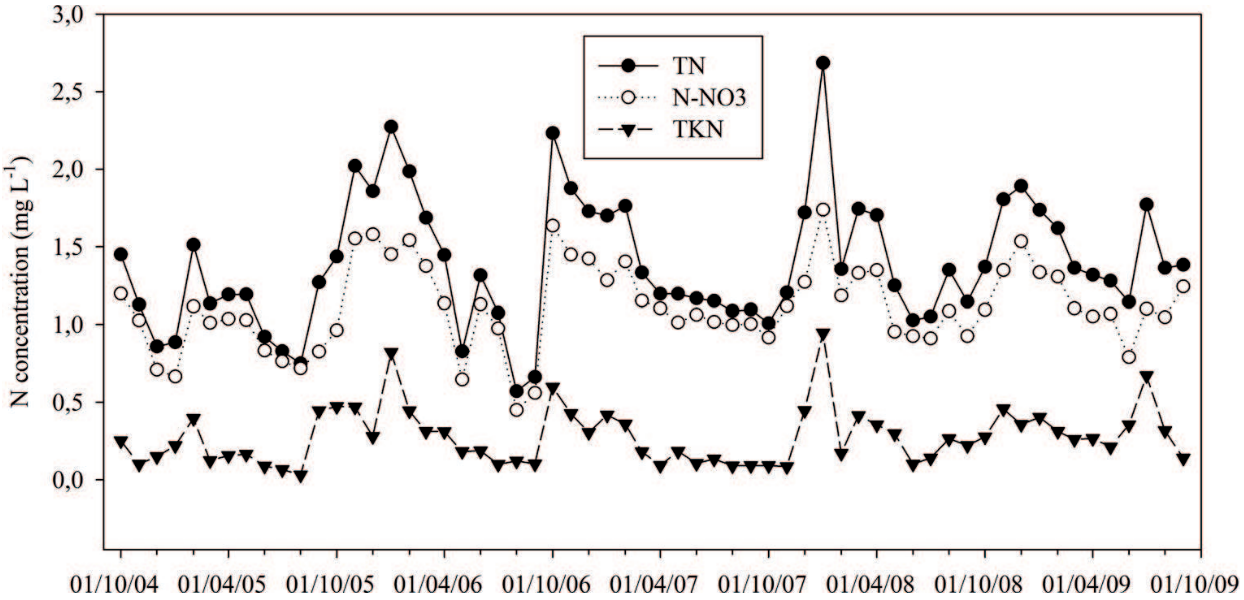

Figure 4. Variation of monthly flow-weighted nitrogen (N-NO_3 and TKN) concentrations during the five hydrological years of study period.

The contribution of the individual fractions made to the TN also showed an intra-annual variability. Thus, N-NO_3 contributed to more than 83% of TN during autumn and spring, representing about 86% in summer, but this contribution decreases during winter (77%), i.e. in the season with higher streamflow. This reflects an increase in the organic nitrogen during winter, probably due to more intense erosion during high flow periods.

In all seasons, a positive relationship exists between daily N concentrations and flow, suggesting a predominantly diffuse source of N. However, the relationship was highly variable between seasons. Thus, in autumn and winter, N-NO_3 was more strongly related to stream flow, whereas in spring and summer, TKN was more strongly related to flow, as expected in view of the role of shear stress in moving particles. These results suggest that although N-NO_3 and TKN may display a similar seasonal pattern, controls of N-NO_3 differ substantially from controls on TKN. Nitrate is originated from subsurface paths whereas TKN is delivered from surface flow paths.

5. Conclusions

Total nitrogen concentrations were relatively low, consistent with the lack of significant anthropogenic pressure in the catchment. However, the N concentrations were always over the critical range over which there is a potential risk of eutrophication of water systems. Most of the N flushed from the Corbeira catchment is in the form of nitrate (82–85%), so management practices could target nitrate, particularly that from fertilizer. In the study area, rainfall and stream flow change annually and seasonally, so the total nitrogen, nitrate and Kjeldahl nitrogen concentrations also showed an important inter- and intra-annual variability linked to rainfall and flow oscillations; showing that N concentrations are mainly controlled by hydrology processes. These findings have particular relevance in the current global context of climate change, which is predicted to bring more frequent heat waves and an increase extreme rainfall events (mainly during winter) in the study area. These changes will have impacts on the hydrological cycle and, consequently, in nitrogen concentrations, and may increase the transfer of nitrogen from soils to stream water during winter and impact on stream water quality.

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