Synchronous trends in N–NO$_3$ export from N-saturated river catchments in relation to climate

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Abstract Long term trends (1978–2005) of N–NO$_3$ concentrations in river water were investigated for 10 rivers draining forested catchments in Piedmont, North-Western Italy, and Canton Ticino, Switzerland. All the river catchments come into the category of the medium-high stage of N saturation (levels 2–3 of the Stoddard's classification). The seasonal signal in N–NO$_3$ concentrations and its changes in time over the course of the study period was also evaluated. Single trends were analysed for significance and magnitude; statistical techniques for the detection of common trends were then applied to identify a common pattern in the N–NO$_3$ time series. Both the increasing NO$_3$ levels and the limited seasonal pattern in recent years indicate an aggrading level of N saturation in time. Synchronous trends of N–NO$_3$ export were found for 8 rivers. The main common trend was used to test relationships with: (i) temperature, (ii) precipitation, and (iii) N deposition. Step-changes in the data series were also assessed, and the main points of change are discussed in relation to meteorological factors and response to the N saturation status. Temperature proved to be the main factor affecting the temporal pattern of N–NO$_3$ concentrations: warm periods were usually followed by an N–NO$_3$ increase in river water due to enhanced mineralisation and nitrification in soil.

Keywords Climate · Nitrate · Nitrogen saturation · Northern Italy · Trend · Water chemistry

Introduction

During the 20th century, emissions of oxidised nitrogen (N) species from combustion of fossil fuels and of reduced N compounds from manure management in livestock and agricultural soils increased dramatically in Europe peaking in the 1980s. This strong input of N into the atmosphere from anthropogenic activities dramatically increased the mobility and deposition of reactive forms of N (Galloway et al. 2003). After the peak values recorded in the 1980s, NO$_x$ emissions and deposition levelled off or decreased slightly in most European countries (Tarrason and Schaug 2000). Despite that, the investigations of chemical trends in European surface water showed a general absence of trends in NO$_3$ concentrations, with only a few regions exhibiting a significant decline of NO$_3$ (Wright et al. 2001; Skjelkvåle et al. 2005).

Long-term studies on the chemistry of atmospheric deposition have been performed in the area of Lake Maggiore watershed, located between Italy and Switzerland, since the 1970s. Nitrogen deposition is extremely high in this area: wet deposition of

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inorganic N, as the sum of ammonium and nitrate, is between 20 and 25 kg N ha^{-1} y^{-1} and it has been estimated that total N deposition, including the contribution of dry deposition, is close to 30 kg N ha^{-1} y^{-1} (Rogora et al. 2006). This huge N load from the atmosphere is due to a combination of high precipitation amount (1700–2000 mm) and elevate concentration of N compounds in atmospheric deposition. Indeed atmospheric pollutants are transported from the Plain of the River Po, the most industrialised and urbanised area in Italy, towards the Alpine relief, where they are deposited via atmospheric deposition (Della Lucia et al. 1996). N deposition in Lake Maggiore area proved to be among the highest in Europe (Evans et al. 2001) and it has not changed significantly in the last two decades. This huge flux of N from the atmosphere is causing N saturation of terrestrial catchments and increasing levels of NO$_3$ in rivers and lakes (Mosello et al. 2000; Rogora and Mosello 2007). According to pan European studies, the Italian sites located in the Lake Maggiore area are among the few sites in Europe showing a significant increase of N–NO$_3$ concentrations (Wright et al. 2001; Skjelkvåle et al. 2005).

In N saturated catchments, N in excess of the uptake capacity of plants and microorganisms is leached from the soil to surface waters (Aber et al. 1989). Since NO$_3$ is a strong acid anion, increased leaching of NO$_3$ enhances acidification of soils and surface waters (Murdoch and Stoddard 1992). Nitrogen is also the growth-limiting nutrient in many forest ecosystems. Hence excess N deposition may lead to nutrient imbalance and damage the health of forests and semi-natural terrestrial ecosystems (Tamm 1991; Dise and Wright 1995; Aber et al. 2003). Further detrimental effects of N excess in watersheds are increased emissions of nitrogenous greenhouse gases from soil, reduced methane consumption in soil, decreased water quality, toxic effects on freshwater biota, and eutrophication of coastal marine waters (see Fenn et al. 1998 for a review).

Aggrading forests usually act as major sinks for N by accumulating it in wood (Whittaker et al. 1979). On the other hand, old forest stands tend to have high rates of nitrogen loss to streamwater. Net ecosystem production is expected to be low or negligible in old-growth forest. As a consequence nutrient demand is also low, with little or no overall retention of nitrogen

(Vitousek and Reiners 1975). Hence unmanaged old-growth forests, such as those covering the catchments considered in this study, are expected to be particularly sensitive to developing nitrogen saturation in response to atmospheric N inputs (Aber et al. 1991; Stevens et al. 1994).

There are a number of studies demonstrating that temporal variations of N compounds in surface water may also be affected by climatic factors (e.g. Mitchell et al. 1996; Murdoch et al. 1998, 2000; Monteith et al. 2000; Park et al. 2003; Watmough et al. 2004). Increasing temperature and change in precipitation regime may affect biological processes taking place in soil and water which are involved in the retention and release of N. For instance, rates of both N mineralization and -nitrification are sensitive to changes in air temperature and soil moisture (Stark and Hart 1997; Hong et al. 2005). Hence, the long-term records of NO$_3$ concentrations in streamwater are affected by both short-term and long-term change in climate and these variations can mask trends in response to changes in N deposition. In particular, climatic variations must be taken into account in any evaluation of the response of terrestrial and aquatic ecosystems to an elevated atmospheric input of nitrogen. Van Miegroet et al. (2001) showed that temperature control on N production and hydrologic control on NO$_3$ leaching during the growing season caused the interannual variation of NO$_3$ concentrations and export. Murdoch et al. (1998) reported a positive relationship between mean annual air temperature and NO$_3$ concentrations in streamwater, suggesting that it could be due to higher rates of N mineralisation and nitrification in warmer years. Wright et al. (1998) suggested that climate warming may lead to an increasing release to surface waters of N in excess of that taken up by plants or immobilised in the soil. The CLIMEX experiment at the N saturated site of Risdalsheia, Norway showed that a permanent increase in temperature of 3–5°C resulted in a long-term increase in NO$_3$ concentrations in runoff (Wright 1998; Wright and Jenkins 2001).

A modelling exercise by Hong et al. (2005) demonstrated that the long-term nitrate export from a watershed at the Hubbard Brook Experimental Forest was mainly driven by N mineralization, not atmospheric N deposition. Murdoch et al. (2000) observed that extended dry periods were frequently followed by high N–NO$_3$ export and Watmough et al.

(2004) reported results from laboratory experiment supporting the hypothesis that increasing NO_3 in stream water may occur following droughts.

In this study we performed trend analysis of N–NO_3 concentrations for a number of rivers draining forested catchments in North-Western Italy, to evaluate the magnitude and geographical extent of the N saturation status. Along with trends, we also focused on seasonal and short-term variations of N–NO_3 levels. The eventual role of climate in the temporal pattern of N–NO_3 was investigated by considering long-term data series of temperature, precipitation and N deposition. The main aims of our analysis were to: (i) identify common patterns in N–NO_3 time series; (ii) evaluate common trends in relation to drivers such as meteorology and N deposition; (iii) investigate the combined role of temperature and precipitation in determining short-term changes of N–NO_3 levels.

Study area and methods

The study rivers belong to the watershed of Lake Maggiore, one of the main Italian lakes. This area is shared between the Piedmont region, in North-Western Italy, and the Canton Ticino, Switzerland (Fig. 1). The chemistry of several water bodies in this area has been monitored since the 1970s, in the framework of studies on eutrophication and acidification (e.g. Marchetto et al. 1994; Mosello et al. 2000; 2001). In particular the main tributaries of the lake (14 rivers in total) have been sampled monthly and analysed for the major chemical determinants since 1971. For our study, we excluded four of these tributaries which were clearly affected by point source pollution. Despite river data being available since 1971, we selected the period 1978–2005 for statistical analysis, as there were some gaps in the data in previous years. The main characteristics of the selected rivers and their catchments are listed in Table 1.

Two of the tributaries, Rivers Tresa and Verzasca, are lake outlets, of Lake Lugano and of an artificial reservoir, respectively. Seasonal and long-term variations of N compounds in lake outlets are influenced by biological processes taking place in the lake, mainly uptake by phytoplanktonic algae and denitrification in bottom water (Ito et al. 2005; Seitzinger

et al. 2006). Both rivers were included in the present study, to test whether they showed different temporal patterns from the others.

Precipitation in the study area is mainly determined by warm, moist air masses entering the Po valley from the Mediterranean and colliding with the Alps. Due to this orographic effect, the mean precipitation amount is rather high (1700 mm as mean annual value for the period 1978–2004). The yearly average temperature in the Lake Maggiore area, calculated for the period 1951–2005, is 12.3°C, with a minimum of 11.2°C recorded in 1956 and a maximum of 14.3°C in 2003. The winter minima are between 2.2 and 4.9°C and the summer maxima between 18.8 and 26.0°C (Ambrosetti et al. 2006).

The study rivers span a wide range of geographical and morphometric characteristics. Catchment areas ranged from 30–50 km^2 for the smallest rivers to more than 1500 km^2 in the case of the major tributaries of Lake Maggiore, the Ticino and the Toce. Most of the catchments are characterised by a steep altitudinal gradient, with the highest portion located above 2500 m a.s.l. As a consequence, the mean annual temperature may vary significantly in the catchments, from values between –1.0 and 0.5°C in the portion above 2000 m a.s.l. to about 13.0°C in the areas close to the lake shore. Precipitation amount is rather variable in the study catchments (Table 2), due to the presence of the relieves which determines an irregular spatial distribution of precipitation, with local maxima near the topographic highs (Mosello et al. 2001).

The river catchments are mainly covered by forest (from 40 to 80% of the total area), with broadleaves generally dominating on coniferous plants (Table 1). Detailed information about geology and soil characteristics are available only for very limited areas. From a very general point of view, granitic and granodioritic rocks, mainly with orthogneiss and micaschists, are dominating and soils are mainly acidic, with low base saturation and low C:N ratio.

Atmospheric deposition is the main source of N to the rivers. The morphological characteristics of the area do not permit extensive agriculture, so that the use of nitrogen fertilisers is negligible. The contribution of population to the N load affecting the study rivers has been estimated in previous studies (Mosello et al. 2001) at between 1% and 10% of the

Fig. 1 Location of the study rivers in the area of Lake Maggiore watershed, between Italy and Switzerland. Numbers refer to Table 1. The triangle shows the location of the meteorological and atmospheric deposition sampling station
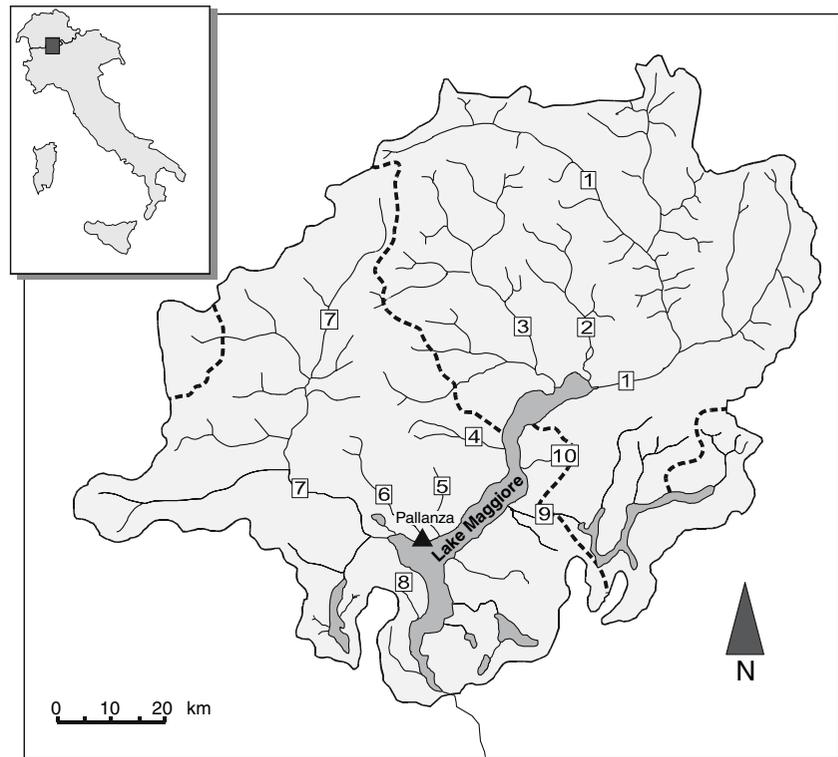

Table 1 Main characteristics of the selected rivers and their catchments

	River	Abbr.	River length (km)	Max altitude (m a.s.l.)	Mean altitude (m a.s.l.)	Catchment area (km²)	Annual average precipitation (mm)	Annual average discharge (m³ s⁻¹)	Forest cover (coniferous–broadleaves) (%)
1	Ticino	Tic	90	3402	1720	1616	1600	66.7	38 (23–15)
2	Verzasca	Ver	33	2864	1611	237	1720	–	53 (4–49)
3	Maggia	Mag	56	3273	1550	926	1960	23.1	68 (42–26)
4	Cannobino	Can	27	2193	1057	110	2160	5.3	80 (3–77)
5	S. Giovanni	SGi	18	2156	914	61	1980	2.4	70 (4–66)
6	S. Bernardino	SBe	29	2301	1228	131	2190	7.3	81 (1–80)
7	Toce	Toc	80	4633	1570	1547	1510	66.3	46 (14–32)
8	Erno	Ern	15	1491	657	26	1100	1.0	70 (6–64)
9	Tresa	Tre	58	2245	650	754	1690	23.9	68 (28–39)
10	Giona	Gio	14	1962	998	50	1900	–	69 (5–64)

total N load in most of the catchments, reaching 25% in the densely populated catchment of the River Tresa. The remaining percentage can be ascribed entirely to atmospheric deposition.

The chemistry of atmospheric deposition in this area has been monitored on a weekly basis since 1975 in the sampling site of Pallanza, located in the central part of the area (Fig. 1). A number of atmospheric

deposition sampling stations were put in operation afterwards, both in the Italian and the Swiss part of Lake Maggiore watershed (Mosello et al. 2001), in order to evaluate the atmospheric load of the main inorganic pollutants to surface water bodies in this area. However, data collected at these sampling stations do not cover such a long period as that of river chemistry. For this reason the long-term series

Table 2 Average values (2001–2005) of selected chemical variables in the study rivers

River	pH	Cond. (μS cm^{-1})	TA (μeq l^{-1})	$\sum$ ions (μeq l^{-1})	TP (μg P l^{-1})	TN (mg N l^{-1})	RSi (mg Si l^{-1})	NO$_3$ (μeq l^{-1})	NH$_4$ (μeq l^{-1})	ON (μeq l^{-1})
Tic	7.77	244.1	1053	5288	8	0.95	2.45	58	1	9
Ver	6.96	46.9	260	932	8	0.97	2.75	60	1	9
Mag	7.70	65.3	430	1351	8	0.99	3.06	61	1	9
Can	7.32	43.1	223	858	7	0.91	3.46	56	1	8
SGi	7.34	63.0	274	1240	20	1.67	4.42	106	2	11
SBe	7.39	58.6	313	1180	9	1.36	3.17	87	1	9
Toc	7.46	174.3	846	3692	23	0.91	2.72	50	5	11
Ern	7.37	113.4	343	2167	24	1.99	4.33	129	1	12
Tre	8.10	205.9	1827	4692	40	1.48	0.97	73	8	24
Gio	7.62	85.2	386	1693	40	1.53	4.06	97	3	10

Cond.: conductivity at 20°C; TA: total alkalinity; TP: total phosphorus; TN: total nitrogen; RSi: reactive silica; ON: organic nitrogen

of data available for Pallanza was used here, as it can be considered representative of the whole study area from the point of view of N loads. A bulk sampler has been used in Pallanza since the beginning, while a wet-only sampler was adopted in 1984. Paired measurements performed with the two sampling methods in the period 1984–2002 showed that the differences were very limited for inorganic N compounds (below 10%; Rogora et al. 2004), so that the long-term series of bulk data (1975–2005) was used here to calculate N deposition. Yearly values of inorganic N fluxes (Fig. 2a) were calculated as the product of annual precipitation amounts and yearly average concentrations of inorganic N (N–NH$_4$ + N–NO$_3$); the latter were obtained as volume weighted means of the weekly values.

Since monitoring started, river samples and atmospheric deposition have been analysed for the main chemical variables using standard techniques (see Mosello et al. 2001 for the analytical methods used). N–NO$_3$ was determined by spectrophotometry (salycilate) until 1986, and thereafter by ion chromatography. After the analytical method was changed, paired analyses were performed for about a year to detect possible systematic differences in the results. About 520 paired analyses were performed, and differences between the two methods proved to be low (mean value of the differences: 0.02 mg N l^{-1}) and not statistically significant (Tartari and Mosello 1997).

To check analytical quality for each analysis a comparison between the sum of anions and cations and between measured and calculated conductivity was performed. Further quality assurance measures

involved the use of control charts and the analysis of synthetic samples on a regular basis. Participation in several inter-laboratory comparisons on rain and surface water analysis allowed a further quality check of the results and the comparability of the data in time (e.g. Mosello et al. 1998).

Meteorological data (air temperature and precipitation) are regularly collected at a number of sites in the study area. Because our aim was to investigate relationships between meteorological variables and the main N–NO$_3$ trend in river water, a single time series had to be used for each variable (minimum, maximum and mean temperature, and precipitation amount). We selected the meteorological station of Pallanza, run by the CNR ISE, which is located centrally in the study area and is in possession of a series of daily data which goes back to the 1950s (Ambrosetti et al. 2006).

Before selecting Pallanza, we compared the data from this site to the data series available for other meteorological stations located in the various river catchments. Absolute values of temperature and precipitation amount differed at the various sites. However, our major interest for this study was the temporal pattern of the data (trends and step-changes). Despite occasional differences, the meteorological data series showed a high temporal coherence (all cross-correlation coefficients >0.60). Furthermore the Pallanza data records were continuous in time and the most reliable in terms of data quality. Hence they were used for all explanatory variables in the analysis of relationships with N–NO$_3$ data.

Fig. 2 Long-term trends of mean annual inorganic N deposition (TIN = N-NH$_4$ + N–NO$_3$) at the sampling site of Pallanza since 1975 (**a**) and mean annual values of N–NO$_3$ concentrations in the study rivers in the period 1978–2005 (**b**)
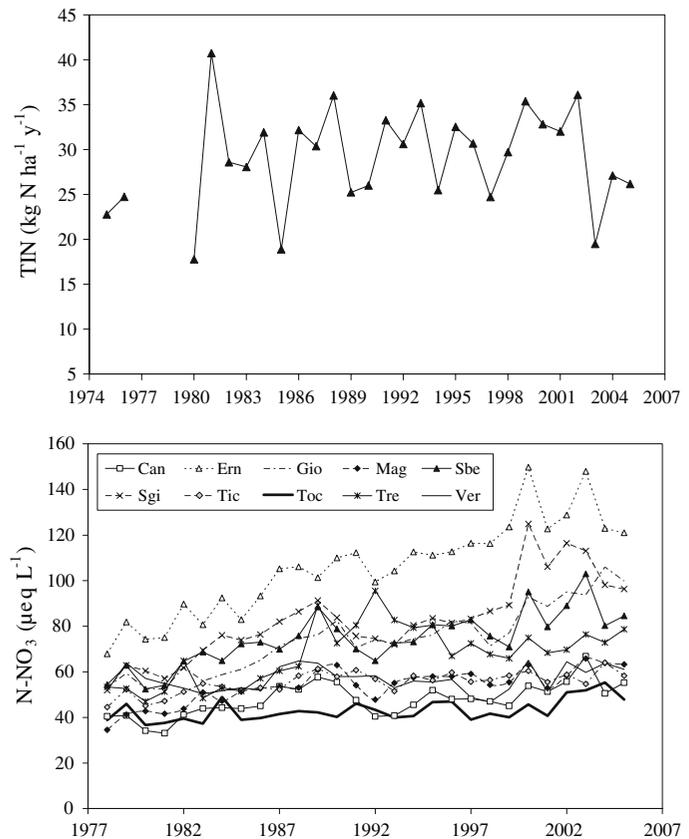
Stoddard's approach (Stoddard and Traaen 1994) was applied to monthly concentrations of N–NO$_3$ in the study rivers (mean values of 5-year periods) to classify them into N saturation stages. This method interprets monthly N–NO$_3$ concentrations in terms of seasonal vegetation cycles, defining four different N saturation stages, which correspond to a hypothetical process affecting terrestrial ecosystems if atmospheric nitrogen deposition remains high. Saturation proceeds from stage 0, when the N cycle is dominated by forest and microbial uptake governing the seasonal nitrate pattern of runoff water, to stage 3, when there is no seasonal pattern to nitrate output (Stoddard and Traaen 1994).

Time series analysis

Standard statistical analyses were applied to original data to describe the main temporal pattern and investigate data for the presence of trends. Exploratory data analysis (EDA) was used for an initial investigation of the dataset: data distribution, outliers, presence of seasonality or cycles in the data. Trend significance and slope were calculated with the Seasonal Kendall test (SKT) (Hirsch et al. 1982) and the Sen's method, respectively (Sen 1968). The presence of a seasonal signal in the data was tested using the Kruskall Wallis test. The data were visually inspected by means of auto-correlation function (ACF) and smoothers. Cross-correlation function (CCF) was used to assess the relationships among the river N–NO$_3$ time series and between N–NO$_3$ and explanatory variables (meteorological data and N deposition).

In addition to these techniques, some recently described statistical analyses for time series data were used in this study. Repeated loess smoothing (Cleveland et al. 1990) was applied to remove the seasonal signal from the data (de-seasonalisation). This technique can be used to identify the most important underlying patterns in a time series data set. Each time series is decomposed in a long term pattern and a shorter term pattern. The output is a long term

trend, seasonal component and residual information for each time series.

MAFA (min-max factor analysis) was applied to de-seasonalised data to look for common trends within time series. MAFA belongs to the so-called structural time series models, which can be used to analyse univariate time series. Developed by Solow (1994), and Shapiro and Switzer (1989), MAFA is a technique similar to principal component analysis (PCA). While PCA estimates axes with maximum variance, the MAFA axes have maximum autocorrelation with time lag k. By setting k = 1, a first axis with the highest autocorrelation is obtained. Each axis is typically associated with a trend, or smoothing curve. The second axis (second smoothing curve) has the second highest autocorrelation, etc. The MAFA axes are independent, and significance level (P value) can be estimated for each axis. Correlations between the axes and explanatory variables can be calculated after the analysis, which makes it a so-called indirect gradient analysis.

Sudden changes in the data (step-changes or breakpoints) were assessed by Webster's method, which is used to detect discontinuities (structural changes) in multivariate time series datasets (Legendre and Legendre 1998).

All statistical analyses were performed with the following softwares: Brodgar vers. 2.5.1 (Highland Statistics Ltd) and S-plus 2000 (Math Soft).

Results and discussion

River chemistry and N saturation status

The average values (2001–2005) of the main chemical variables in the study rivers are shown in Table 2, while the long-term trends of N–NO_3 concentrations in river water, as mean annual values, are shown in Fig. 2b.

The selected rivers differ widely in ionic concentrations according to the geology of the catchments: conductivity varied from 40–60 μS cm^{-1} in siliceous catchments to 200–250 μS cm^{-1} in catchments with carbonatic, highly weatherable rocks. Similarly the total ionic content varied between 800–900 μeq l^{-1} (Rivers Cannobino and Verzasca) and 4700–5300 μeq l^{-1} (Rivers Tresa and Ticino). River water is well buffered, with average pH values between 7.0

and 8.1 and alkalinity above 200 μeq l^{-1} at all the sites (Table 2).

Low phosphorus concentrations (<20 μg P l^{-1}) are found in most of the rivers, with higher concentrations (40 μg P l^{-1}) in the Tresa and the Giona (Table 2).

Nitrate is the dominant form of N in all the rivers, representing 80–90% of total N. Nitrate concentrations varies between 50–60 μeq l^{-1} in the rivers draining the northern part of the study area (Ticino, Maggia, Verzasca, Cannobino, Toce) up to 130 μeq l^{-1} in the southernmost River Erno (Table 2, Fig. 2b). Ammonium concentrations are almost negligible (1–2 μeq l^{-1}) in most of the rivers, with slightly higher values in the Toce and Tresa (5–8 μeq l^{-1}). Organic N concentrations are between 9 and 12 μeq l^{-1} (24 μeq l^{-1} in the Tresa), with a contribution to the total N content of river water between 9–10% (Rivers S. Bernardino, Erno, Giona) and 23% (Tresa). These results confirmed the good water quality and the lack of significant point source pollution for most of the rivers; only the Tresa and at a less extent the Giona are affected by occasional episodes of pollution attributable to contamination by urban sewage (Mosello et al. 2001).

Previous studies showed that the difference in the mean N–NO_3 levels in streamwater is partly attributable to the atmospheric N inputs, showing a north-south gradient in the study area with the highest deposition in the southern part (Della Lucia et al. 1996; Mosello et al. 2001). Nevertheless, deposition gradient alone was not able to explain the difference in stream water NO_3. Several studies demonstrated how catchment characteristics affect N retention or losses, possibly altering the relationships between N inputs and outputs (Clow and Sueker 2000; Campbell et al. 2004; Ito et al. 2005). For instance, forest composition (Lovett et al. 2002; Compton et al. 2003), bedrock geology (Williard et al. 2004), topography (Dillon and Molot 1992; Creed and Band 1998), wetland or peat cover (Chapman et al. 2001) proved to be relevant in affecting concentrations or fluxes of N compounds in surface water.

The possible role of other factors than atmospheric input in affecting NO_3 levels in the study rivers was investigated by means of linear regression: slightly significant negative relationships were found with catchment altitude and area (R^2 0.52 and 0.42, respectively; $P < 0.05$) and river length (R^2 0.50;

$P < 0.05$), but it must be emphasised that both these regressions were highly effected by two of the rivers, the Toce and the Ticino. The negative relationship between N–NO_3 and catchment elevation was mainly due to the fact that the higher N–NO_3 concentrations are found in the low-elevation southernmost rivers (Erno, S. Giovanni, Giona), subject to the highest N deposition level. Nitrogen retention by soils and vegetation, tough limited at these N saturated sites, coupled with in-stream removal mechanisms such as microbial uptake and denitrification may partly explain the decreasing NO_3 concentrations with increasing river length and catchment area (Seitzinger et al. 2002).

Nitrate should also be higher in watersheds covered by deciduous forest species, due to higher net N mineralization and nitrification rates compared to coniferous forests (Vitousek and Melillo 1979). Our findings did not confirm this hypothesis, being N–NO_3 not significantly related to the forest cover (as % of the total catchment area), nor to the proportion of broadleaves or conifers in the catchment. The limited number of sites considered in the present study, together with the lack of detailed information about land cover and soil characteristics prevent any further hypothesis about the possible influence of catchment attributes on streamwater NO_3.

The relationship between N–NO_3 concentration and discharge was also considered, but no significant regressions were found for any of the rivers. As suggested by Creed and Band (1998), this result could be due to the use of low-frequency data, as the monthly data of the present study. Monthly discharge data are indeed composites of multiple hydrologic events; significant concentration-discharge relationships may exist for discrete hydrologic events, but they could be obscured by the effect of the hydrologic events occurring in the same month.

Nitrate concentrations in the study rivers (between 50 and 100 μeq l^{-1} as mean values of the period 2001–2005) proved to be markedly higher compared to those reported in a number of studies for rivers draining forested catchments which were subject to moderate or high N deposition (e.g. Mulder et al. 1997; Harriman et al. 1998; Murdoch et al. 1998; Lovett et al. 2002; Aber et al. 2003; Goodale et al. 2003; Watmough et al. 2004). The study area is subject to N input sharply above 10 kg N ha^{-1} y^{-1},

which has been indicated as a critical threshold above which elevated concentrations of NO_3 in surface waters may occur (Dise and Wright 1995). Elevated NO_3 leaching to groundwater or surface waters is the primary symptom of N excess (Fenn et al. 1998). Hence the observed steady loss of NO_3 to running waters from the study catchments can be interpreted as a clear symptom of N saturation.

The presence of unmanaged, old-growth forest stands and the low C/N ratio (15–16) measured in the soils of selected catchments within the study area (Rogora and Mosello 2007) also provided some support to this hypothesis. Indeed, elevated losses and essentially no net retention are usually observed in steady-state old-growth systems (Vitousek and Reiners 1975; Goodale et al. 2000) and the soil C:N ratio proved to be inversely related to forest NO_3 leaching (Dise et al. 1998; Lovett et al. 2002).

The critical situation of the study catchments from the point of view of N saturation was already put in evidence by the N budgets calculated in a previous study (Mosello et al. 2001): the retention of total N input by soils and vegetation varied between 40% and 60% for the forested catchments with low population density in the central-northern part of the study area, to values close to zero or even negative in the south, indicating a net leaching from the soils. The output of N occurred mainly in inorganic form, with organic N representing between 10% and 20% of the total N exported from the catchments (Mosello et al. 2001).

According to Stoddard and Traaen (1994), when the mean monthly N–NO_3 concentrations of the period 2001–2005 were considered, all rivers came into the category of stage 3, i.e. the highest N saturation level, with the exception of the River Toce (stage 2). The recent N–NO_3 levels in river water were compared with those recorded in 1978–1982. A shift towards higher values was evident in all the rivers, which passed from level 1–2 to level 2–3 of Stoddard's classification. The only exception to this tendency was the River Verzasca, which showed similar N–NO_3 levels in the two periods.

A seasonal signal was present in 1978–82 in several rivers, showing a decrease of concentrations in June-July with respect to the previous months. On the other hand N–NO_3 levels seemed to be more stable in the period 2001–2005, with the values rarely falling below 50 μeq l^{-1} (Fig. 3). The lack of seasonality in N–NO_3 concentrations may be a
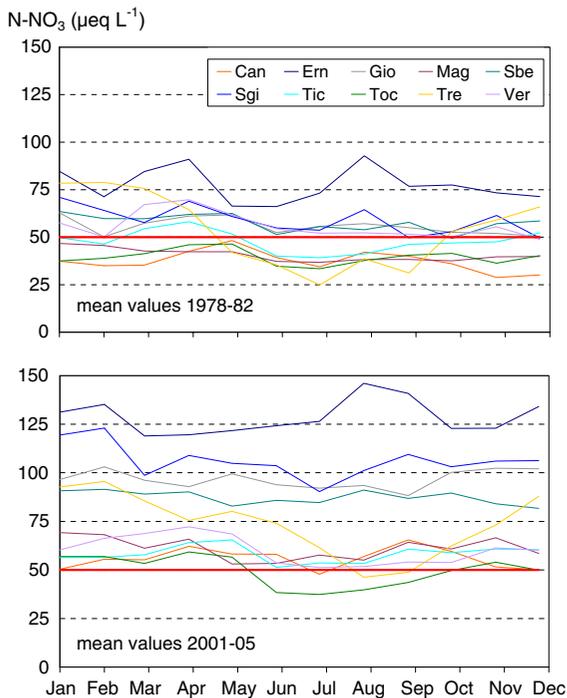
N-NO$_3$ (μeq L^{-1})

Fig. 3 Monthly N–NO$_3$ concentrations in the study rivers. Mean values of the periods 1978–82 (upper panel) and 2001–2005 (lower panel). Thick horizontal line shows the limit of 50 μeq L^{-1} used in the Stoddard' classification of N saturation (Stoddard and Traaen 1994)

further indication that N limitation has been overcome and biological demand no longer controls nitrate concentrations even in the growing season (Stoddard and Traaen 1994).

N–NO$_3$ trends

Monthly N–NO$_3$ data for the period 1978–2005 were tested for trends (Table 3). Significant positive trends ($P < 0.0001$) were found for all rivers except the Verzasca. Trend slopes were between 0.30 (River Toce) and 2.16 (River Erno) μeq l^{-1} y^{-1}, corresponding to an overall increase of 8 and 60 μeq l^{-1}, respectively. River Verzasca also showed a positive trend, though not significant ($P > 0.05$).

Auto-correlation functions were calculated for all rivers; they all showed smoothed decreasing lines, confirming the presence of trends in the data.

Smoothers (LOESS) were used to better visualise the temporal pattern of the data (Fig. 4). A span width of 0.1 was chosen in order to reduce the noising

in the data, though maintaining the main pattern, and each series was decomposed into a trend and a residual component. Smoothing highlighted some very general characteristics of the time series, such as the presence of a positive trend from the beginning of the record until 2000, followed by a period of high variability. Most of the river data behaved in similar way especially in the last part of the record. Nevertheless some deviations from the main pattern were observed: the Tresa and the Verzasca in particular deviated sharply from the main trend in 1991–95 and 1996–99, respectively (Fig. 4).

Co-plots were used to visualise the N–NO$_3$ trends in the different months. Figure 5 shows examples of these plots for two rivers with low and high N–NO$_3$ levels (Cannobino and Erno, respectively). A positive trend was visible in every month, and this result was common to all the study rivers. A slightly steeper slope can be seen in spring and summer than in the winter months. However, the increasing release of N–NO$_3$ in time seemed to be unrelated to a specific season.

Although the seasonality of N–NO$_3$ concentrations has become less and less evident in recent years, the data still present a seasonal pattern. Differences among groups were significant for all the rivers according to the Kruskall-Wallis Test ($P < 0.001$), when considering both seasons and months as groups. N–NO$_3$ data were accordingly de-seasonalised using repeated loess smoothing before proceeding with further analysis.

Before applying MAFA to identify the main common trends in the data, cross-correlation functions (CCF) were used to group rivers according to their temporal pattern. Table 4 shows the cross-correlation values among N–NO$_3$ time series. High CCF values indicate a temporal coherence between the data series, i.e. NO$_3$ temporal pattern is similar at the two sites, both as long-term trends and short-term variations. Seven rivers (Cannobino, Erno, Giona, Maggia, S. Bernardino, S. Giovanni, Ticino) were highly correlated with each other (correlation >0.70); the Toce also was well correlated with this group, though with lower coefficients (0.55–0.60). On the other hand the Tresa and the Verzasca showed a low correlation with each other and compared to the other rivers (Table 4). Cross-correlation analysis thus confirmed the different temporal pattern of NO$_3$ in these two rivers.

Table 3 Results of the SKT (Seasonal Kendall Test) applied to monthly N–NO$_3$ concentrations in the study rivers and to monthly meteorological data (1978–2005)

	P[a]	B[b]
Can	***	0.57
Ern	***	2.16
Gio	***	1.59
Mag	***	0.76
SBe	***	1.09
SGi	***	1.67
Tic	***	0.42
Toc	***	0.30
Tre	***	0.86
Ver	n.s.	0.11
Tx	***	0.08
Tn	***	0.06
Tm	***	0.06
mm	n.s.	–0.18
Ndep	n.s.	–0.02

Tx: maximum temperature; Tn: minimum temperature; Tm: medium temperature; mm: precipitation amount; Ndep: N deposition; [a] P levels: *** < 0.0001; ** < 0.001; * < 0.01; n.s.: not significant

[b] Trend's slope according to Sen (1968). Units: μeq L^{-1} y^{-1} for N–NO$_3$ concentrations; °C y^{-1} for temperature data; mm y^{-1} for precipitation amount; meq m^{-2} y^{-1} for N deposition

Three MAFA axes were initially extracted, to find all the main patterns present in the original data. The axes are shown in Fig. 6 together with canonical correlation values of each river with the axes. The first and most significant axis ($P < 0.001$) was a positive trend, regularly increasing since the beginning of the record and with a tendency towards stable values in the last part. All rivers except the Versasca correlated highly with this axis, confirming the presence of a common increasing trend of N–NO$_3$.

The second and third axes ($P = 0.003$ and $P = 0.005$, respectively) represented the temporal pattern of River Tresa and River Verzasca, respectively. While most of the river time series can be described by axis 1, the N–NO$_3$ series of the Cannobino and the Toce rivers are partially explained also by axis 3 (Fig. 6). The presence of this component in the River Cannobino trend may be due to the sharp increase of N–NO$_3$ in this river after 2000, contrasting with the stable or decreasing levels at the other sites.

In the case of the River Toce, the correlation with axis 3 was explained by a period of relatively high N–NO$_3$ concentrations at the beginning of the record. In the late 70s-early 80s the Toce was partly affected by inflowing water high in N–NO$_3$ coming from the highly polluted Lake Orta. This contribution was markedly reduced in the 80s due to lake restoration measures (Calderoni et al. 1994).

The River Tresa showed an increasing trend (positive correlation with axis 1) but also deviated from the common pattern, mainly due to a period of high concentrations in the central part of the record (1988–95) (Fig. 4). This river series actually had a significant negative correlation with MAFA axis 2, i.e. its temporal pattern can be represented by the opposite of axis 2 (Fig. 6). In general the Tresa showed a smoother trend compared to the other rivers; for instance, it was not characterised by the strongly oscillating pattern which affected the other sites between 2000 and 2005. As this rivers is the outlet of Lake Lugano, its N–NO$_3$ pattern is clearly affected by processes taking place in the lake, the most important being: (i) seasonal fluctuations of

Fig. 4 Long-term trends of N–NO$_3$ concentrations in 10 rivers after the application of LOESS smoothers (span width: 0.1) and the normalisation of the data. Data are unitless due to normalisation
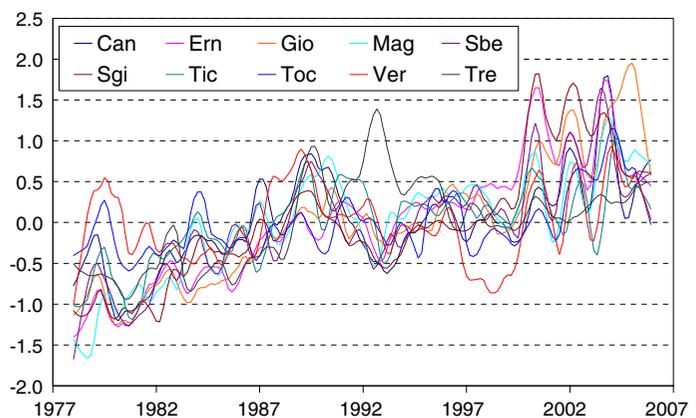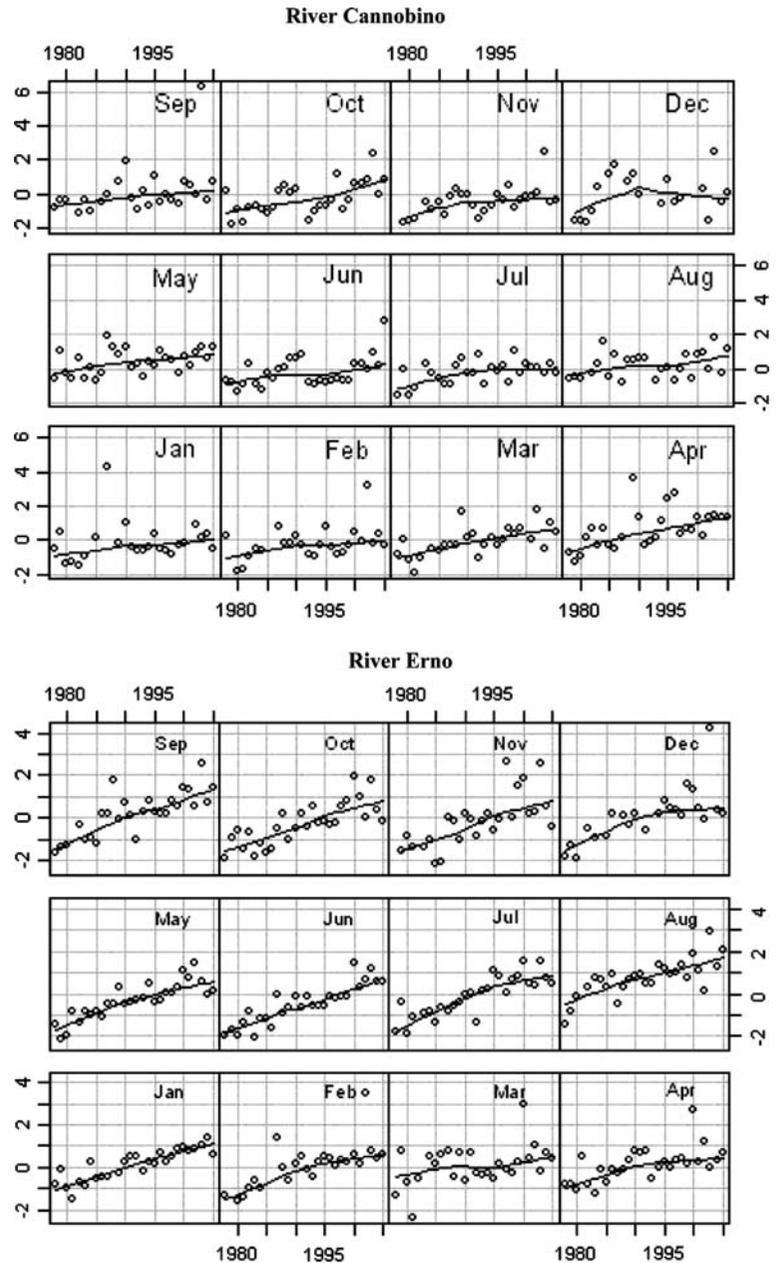
Fig. 5 Co-plots of N–NO₃
concentrations (1978–2005)
for River Cannobino
(above) and River Erno
(below): the trend of N–
NO₃ concentrations is
shown for each month of
the year. Data were
normalised and a smoothing
line added to each plot

N–NO₃ levels in relation to uptake by algae; (ii) stratification and mixing of lake water, which occur to a very high extent in the meromictic Lake Lugano. The period of high N–NO₃ levels in the Tresa above referred to is in fact related to a sharp increase of N–NO₃ concentration in Lake Lugano between 1986 and 1990 (Barbieri and Simona 2001). A further factor explaining the different temporal pattern of nitrate in the Tresa could be N fixation within the

stream. Being N retention greater in eutrophic weater bodies (Berge et al. 1997), it may be of some importance in the Tresa, characterised by rather high phosphorus concentrations (Table 2).

The lack of correlation between the River Verzasca and the other sites is due to the absence of a significant increasing trend. In fact, N–NO₃ concentrations in this river were relatively high at the beginning of the record (1979–81), and did not show the steep increase

Table 4 Cross-correlations (lag 0) among time series of N–NO$_3$ concentrations in the study rivers (de-seasonalised monthly data)

	Can	Ern	Gio	Mag	SBe	SGi	Tic	Toc	Tre	Ver
Can	–									
Ern	0.76	–								
Gio	0.76	0.88	–							
Mag	0.80	0.83	0.82	–						
SBe	0.89	0.86	0.83	0.89	–					
SGi	0.80	0.92	0.86	0.79	0.89	–				
Tic	0.64	0.75	0.73	0.79	0.69	0.67	–			
Toc	0.61	0.60	0.70	0.56	0.61	0.60	0.61	–		
Tre	0.45	0.56	0.58	0.58	0.52	0.44	0.60	0.31	–	
Ver	0.47	0.32	0.46	0.32	0.36	0.39	0.43	0.53	0.27	–
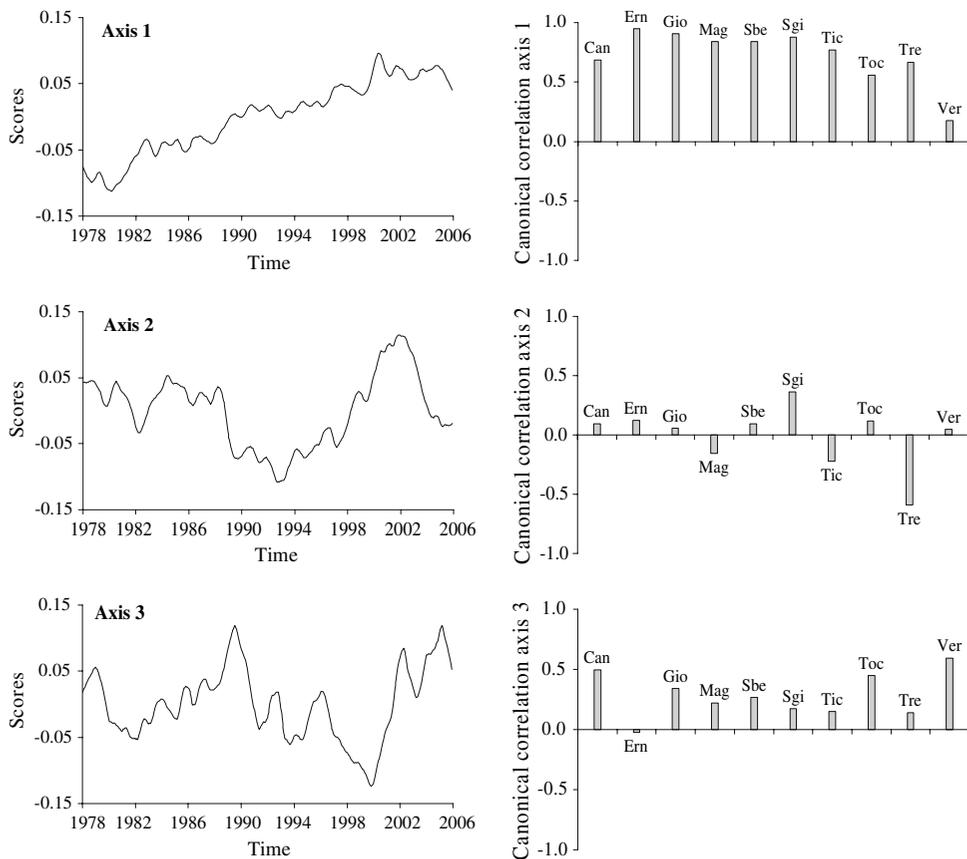
Fig. 6 Principal axis extracted by MAFA (min-max factor analysis) using N–NO$_3$ time series ($n = 10$) (left) and canonical correlations of river data with each axis (right). Significance levels of the axis were as follows: axis 1 $P = 0.001$; axis 2 $P = 0.003$; axis 3 $P = 0.005$

affecting the other rivers in the 1980s. The River Verzasca data are represented by axis 3 of the MAFA (Fig. 6): a period of low N–NO$_3$ levels was found between 1995 and 2000 which had no equal in the other data series. The presence of the reservoir certainly had some effects on the temporal pattern of N–NO$_3$ in the Verzasca. Part of the incoming nitrogen may have been retained by uptake processes

in lake, preventing the increasing trend of N–NO₃ in the outlet. The regulation of the reservoir level, and the timing of the discharge and recharge periods, were probably the main factors regulating the nitrogen retention capacity of the basin. In contrast with the Tresa, the Verzasca time series showed the same marked oscillations of the period 2000–2005 observed in the other rivers (Fig. 4). This means that this river did not entirely deviate from the common temporal pattern, and seasonal and interannual variability were partly explained by the same driving forces acting at the other sites.

Both CCF and MAFA revealed a group of 8 rivers co-varying in time. Their main temporal pattern is represented by MAFA axis 1 (positive trend). This group of rivers was selected for further analyses investigating step-changes and relationships between N–NO₃ and external drivers. To do this, a new MAFA was performed only on the 8 sites, to extract the main common trend excluding the noise component due to the Tresa and the Verzasca. Successively, Webster's method (multivariate choice) was applied to the 8 time series to find the major common discontinuities and these were plotted on the main trend in Fig. 7.

Eight discontinuities were found, the most important being at the end of 1980, between 1988 and 1989, and in 1999–2000 (Fig. 7). According to them, the long-term N–NO₃ trend can be roughly divided into three main sub-periods: a steep positive trend from the beginning of the record till 1988, a period with stable or slightly increasing values until 1999, and a period with sharp oscillations between 2000 and 2005. After 2000 there was also a slight tendency towards lower values, tough still above those recorded in the 80s and 90s (Fig. 7).

Effects of meteorology and N deposition

Some explanatory variables were introduced in the second step of the time series analysis, with the aim to investigate their possible role in the temporal pattern of streamwater nitrate: temperature (minimum, maximum and mean values), precipitation and N deposition. Monthly values data collected at Pallanza were used, covering the same period as the river chemical data (1978–2005).

Trend analysis by means of SKT was also performed for meteorological data and N deposition

(Table 3). Ambrosetti et al. (2006) analysed 50 years of meteorological data in the study area and reported significant increasing trends for temperature (about 1°C since 1951, with the steepest increase since 1980) and no significant changes for precipitation amount. The data series of Pallanza analysed here confirmed these results: Tn, Tx and Tm all increased significantly $(P < 0.001)$, with Tx showing the steepest trend slope $(0.08°C\ y^{-1})$. The overall increase of Tn and Tx in the period 1978–2005 was of 2.2 and 1.7°C, respectively. Both precipitation amount and N deposition decreased, tough not significantly (Table 3).

Because all the explanatory variables showed an evident seasonal pattern, data were de-seasonalised by repeated loess smoothing before further analysis.

Relationships between N–NO₃ data and explanatory variables were investigated by means of cross-correlation (Table 5). Lags of 1, 2, 3 and 4 months were considered. Rivers with positive N–NO₃ trend, belonging to the same group according to MAFA, correlated highly with temperature time series. Five rivers out of 8 showed the highest correlation with Tx values. Furthermore correlation increased when a lag of 2–4 months between temperature and N–NO₃ was considered (Tab. 5). The MAFA axis is compared with the de-seasonalised time series of Tx in Fig. 7: the lagged co-variation of the two series (peaks of Tx preceding peaks of N–NO₃) is mainly evident in the first part of the record (e.g. 1979, 1981, 1983) and after 2000, despite a tendency towards decreasing nitrate in the last few years of the record.

This result suggests that N–NO₃ concentrations in rivers are partly controlled by temperature, especially that recorded 2–4 months before river sampling. In contrast, no significant correlations were found between N–NO₃ and precipitation amount or N deposition, even when shifting these variables by different time lags.

Explanatory variables were included in the MAFA and their relationships with the various axes investigated by means of canonical correlations (Table 6). This analysis confirmed the strict relationship between increasing N–NO₃ and temperature: the first MAFA axis (positive trend) was significantly related to temperature data (correlation coefficients > 0.80). Axis 3, representing the River Verzasca and to a lesser extent the Cannobino and the Toce, negatively correlated with precipitation amount and N
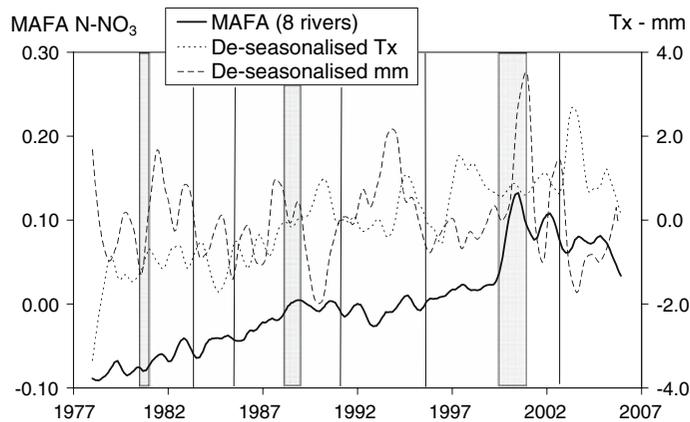
Fig. 7 Main common trend of N–NO$_3$ concentration in 8 rivers according to MAFA (straight line), and series of maximum temperature (Tx; dotted line) and precipitation amount (mm; dashed line) after de-seasonalisation and normalisation of the data. Data are unitless due to normalisation. Vertical lines and bars show the main discontinuities identified by Webster's method (multivariate, window size 30)

deposition, showing that the two drivers are also important at these sites.

Despite the lack of a significant correlation with precipitation amount, this variable still played a role in the temporal pattern of N–NO$_3$. As heavy rains or droughts were limited to a few episodes, their effects were not revealed by statistical analyses. Furthermore low frequency data such as the monthly data used here were not entirely suitable for the detection of short-term episodes. However, some examples of the N–NO$_3$ response to precipitation patterns emerged from the data (Fig. 7): rainy periods such as those recorded in the autumn of 2000 and 2002 determined a temporary decrease of N–NO$_3$ concentration by dilution effect. On the other hand the dry autumns/winters of 1999, 2001 and 2003 were followed by

strong N–NO$_3$ pulses in river water once it started raining. It has been observed that extended periods of drought are frequently followed by high N–NO$_3$ export (Murdoch et al. 2000; Watmough et al. 2004). We hypothesised that rain falling after prolonged dry periods leached previously stored N from the soil, determining temporary N–NO$_3$ increases. Furthermore, the rapid flushing of runoff water prevented its interaction with soil and vegetation, limiting N retention (Arheimer et al. 1996). Both long-term field studies (e.g. Murdoch and Stoddard 1992; Creed and Band 1998) and ecosystem manipulation experiments (Bechtold et al. 2004) supported this hypothesis, demonstrating that soil nitrate may accumulate over dry periods and then be rapidly leached from soils during rainstorms. Also Watmough et al.

Table 5 Cross-correlations (lag 0) between time series of N–NO$_3$ concentrations in the study rivers and explanatory variables. Abbreviations as in table 2. De-seasonalised monthly data were used for all variables. For Tx also the cross-correlations with time lags of 1, 2, 3 and 4 months are shown

	Can	Ern	Gio	Mag	SBe	SGi	Tic	Toc	Tre	Ver
Tx	0.68	0.85	0.78	0.80	0.84	0.76	0.59	0.43	0.58	0.16
Tn	0.66	0.84	0.75	0.75	0.79	0.79	0.62	0.47	0.58	0.28
Tm	0.63	0.82	0.69	0.78	0.80	0.72	0.62	0.34	0.63	0.15
mm	−0.24	0.03	0.05	−0.17	−0.20	−0.02	0.17	0.13	0.12	0.01
Ndep	−0.33	0.02	−0.10	−0.22	−0.25	−0.05	−0.06	−0.20	−0.06	−0.08
Tx lag1	0.70	0.85	0.78	0.81	0.83	0.77	0.60	0.45	0.58	0.16
Tx lag2	0.71	0.86	0.79	0.81	0.82	0.77	0.61	0.47	0.59	0.17
Tx lag3	0.71	0.86	0.79	0.81	0.81	0.77	0.63	0.50	0.59	0.17
Tx lag4	0.71	0.86	0.79	0.81	0.79	0.77	0.64	0.53	0.59	0.18

Table 6 Correlations between explanatory variables and MAFA axis (*n* = 10). Abbreviations as in Table 2. See Fig. 5 for the MAFA axis

	Axis 1	Axis 2	Axis 3
Tx	0.855	–0.046	0.007
Tn	0.819	0.021	0.016
Tm	0.823	0.129	–0.100
mm	0.093	–0.016	–0.156
Ndep	–0.009	0.086	–0.433

(2004) suggested that increase of streamwater nitrate following droughts may be due to the effect of changing moisture condition on mineralization and nitrification in organic surface soil.

Step-change analysis also revealed a main discontinuity between 1999 and 2000, when N–NO$_3$ showed a steep increase in a limited period of time. The pulse occurred immediately after a dry, mild winter (no precipitation occurred in January and February and the mean winter temperatures of 1999–2000 were the highest of the whole period). We hypothesised that the spring rainfall, in March-April, leached a huge amount of N which had accumulated in the soil during the previous months. Nevertheless similar meteorological conditions were also detected in other periods, but they did not cause analogous N–NO$_3$ flushes.

Conclusion

The data analysis presented here shows a synchronous increasing trend of N–NO$_3$ in a group of rivers draining the watershed of Lake Maggiore. The N saturation status of the river catchments is aggrading in time and is the main cause of the increasing N–NO$_3$ concentrations in streamwater.

The wide range of N–NO$_3$ concentrations measured at the various sites (from 50–60 to 130 μeq l^{-1} as average values) is mainly attributable to the atmospheric N input which was higher in the southernmost part of the study area. In addition to N deposition, catchment attributes certainly play a role in streamwater N–NO$_3$ levels. Indeed the river catchments considered differed greatly from the point of view of geographical characteristics (length, catchment area, slope). However, this topic was not fully investigated in the present study due to the limited information available on geology, soil and vegetation cover in the study catchments.

A temporal coherence in streamwater nitrate emerged clearly for 8 out of 10 rivers. The presence of this common temporal pattern in N levels leads to the hypothesis that N export to surface waters from the study catchments is affected by climatic factors.

N–NO$_3$ in river water was related neither to precipitation nor to atmospheric deposition of N considered on a monthly basis. In contrast, air temperature, particularly the maximum temperature recorded 2–4 months before the river sampling, was significantly correlated to N–NO$_3$ concentrations. It can be hypothesised that enhanced mineralization of N previously stored in soil during warm periods determined a net release of N from the catchments and increasing levels of N–NO$_3$ in running waters with a lag of the order of weeks or a few months.

Our results agree with those from other studies showing a positive correlation between temperature and N–NO$_3$ concentrations in runoff (Murdoch et al. 1998; Wright 1998; Watmough et al. 2004). Theoretically, increasing temperature would have contrasting effects on N leaching: it can stimulate N uptake by vegetation, but can also speed up processes like mineralisation, nitrification and denitrification. In N saturated catchments, like those of the present study, N uptake is no longer a dominant process regulating N leaching, even in the growing season. N export is mainly under the control of the mineralization and nitrification rates of organic matter. Our findings confirmed the hypothesis by Murdoch et al. (1998), that the correlation between climatic variables and streamwater nitrate is more evident at N saturated sites, being the N–NO$_3$ availability for leaching mainly controlled by temperature-dependent microbial processes.

Temperature also contributes to explain the short-term variability in streamwater N–NO$_3$, especially in the most recent part of the record: warm periods, coupled with dry conditions, determined nitrate pulses in river water. This effect may be due to the rapid flushing of previously stored N in the upper portion of the soils.

The temporal pattern of N–NO$_3$ concentrations was undoubtedly controlled by a number of factors other than temperature and precipitation regime. For instance the interannual variability, in particular

low-level following high-level periods, could be explained by a reduction of N availability in the soil due to elevated losses (Aber and Driscoll 1997). In the same manner N–NO$_3$ pulses may occur after periods with low or constant levels due to the accumulation of N in soil. This could partly explain the phase of relatively stable N–NO$_3$ concentrations in the study rivers between 1989 and 1999 after the steep increase of the 1980s.

Atmospheric deposition is certainly the main source factor of N to the river catchments and, through leaching from soils, to running water (Mosello et al. 2001). However, according to the present study, the measured N load was not the only driver of change for streamwater nitrate. The synchronous pattern of concentrations in the majority of the study rivers demonstrated that temperature-dependent processes and hydrological changes in response to dry or rainy periods play an important role in the temporal pattern of N export.

This study shows that climate warming coupled with extreme episodes of drought and heavy rain will have a major impact in the near future on ecosystem response to N deposition. Most regional climate models predict a further increase of temperature in the next decades, as well as increasing frequency of extreme events (IPCC 2001). Our findings suggest that both of these factors may exacerbate the effect of N deposition, enhancing N release from soils to surface waters and increasing N load to coastal marine ecosystems.

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