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Catchment features controlling nitrogen dynamics in running waters above the tree line (Central Italian Alps)

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Abstract

The study of nitrogen cycling in mountain areas has a long tradition, both to better understand and describe ecosystem functioning and to quantify the long-distance effect of human activities on remote environments. Nonetheless, especially in Europe, very few studies paid attention on catchment features controlling nitrogen dynamics above the tree line, with focus on running waters. In this study, relationships between some water chemistry descriptors, including nitrogen species and dissolved organic carbon (DOC), and catchment characteristics were evaluated for a range of sites located above the tree line (1950–2650 m a.s.l.) at Val Masino, in the Central Italian Alps. Land cover categories as well as elevation and slope were assessed at each site. Water samples were collected during the 2007 and 2008 snow free periods, with a nearly monthly frequency. Differently to dissolved organic nitrogen, nitrate concentration in running waters showed a spatial pattern strictly connected to the fractional extension of tundra and talus in each basin. Exponential models significantly described the relationships between maximum NO_3-N and the fraction of vegetated soil cover (negative relation) and talus (positive relation), explaining almost 90 % of nitrate variation in running waters. Similarly to nitrate, but with an opposite behavior, DOC was positively correlated with vegetated soil cover and negatively correlated with talus. Therefore, land cover can be considered one of the most important factors affecting water quality in high elevation catchments, with a contrasting effect on N and C pools.

1 Introduction

Human activities have dramatically altered the nitrogen (N) cycle by increasing the rate of transformation of N_2 into reactive nitrogen (RN) that includes all the N forms biologically functional. From the late 19th century to the late 20th the amount of RN from mainly food and energy production globally increased by an order of magnitude (Galloway, 2004). On a global basis, atmospheric transport and subsequent deposition

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have become the dominant N distribution processes and increasing atmospheric deposition of N occurs over so much of the Earth's surface that the cumulative effect amounts to global-scale change.

Most alpine regions, both in Europe and in the United States, receive rate of N deposition exceeding 0.5 $kg\,N\,ha^{-1}\,yr^{-1}$, the expected level for ecosystems in the absence of human influence (Burns, 2003; Fenn et al., 2003; Hiltbrunner et al., 2005; Balestrini et al., 2006). Historically N limited high-elevation ecosystems show symptoms of N saturation at relatively low N deposition rate, 2–4 $kg\,N\,ha^{-1}\,yr^{-1}$, as in the case of the Rocky Mountains (Williams et al., 1996). The fluxes reported for European alpine sites at elevation above 2000 m a.s.l. are between 0.5–3 $kg\,N\,ha^{-1}\,yr^{-1}$, but at lower altitude sites the rates greatly increase (Hiltbrunner et al., 2005; Rogora et al., 2006).

Mountain ecosystems and mainly the landscape above the tree line are highly vulnerable to changes in climate, pollutants and nutrient input. Complex topography, harsh climate, extensive snow cover and short growing season all combine to reduce the ability of these ecosystems to face alterations that affect physical structure and biological communities. These extreme environments are also key components of water cycle since they supply drinking water to major metropolitan areas world-wide. While the effects of N deposition on forest ecosystems have been studied extensively, analogous studies in high elevation areas are rare partly because of the logistical constraints in carrying out field sampling campaigns in such isolated environments. Intensive and long-term researches about nitrogen cycling on alpine ecosystems have been carried out in the United States (Brooks and Williams, 1999; Williams et al., 2011) but to date only few studies are available from high elevation areas of the European Alps (Psenner, 1989; Tockner et al., 2002; Kopacek et al., 2005) and most of them provide N concentrations in snowpack (Hiltbrunner et al., 2005; Kuhn et al., 1998) or ice cores drilled in glaciers (Schwikowski et al., 1999).

A significant environmental indicator of N saturation, the condition in which the availability of inorganic N exceeds the N assimilation capacity of biological processes (Aber et al., 1998), is the temporal variation of nitrate in the waters of uncontaminated

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catchments (Traaen and Stoddard, 1995). In N-limited systems the nitrate concentrations are very low with slight seasonal variations between vegetative and dormant periods. Several researches have associated changes in surface water chemistry with increased N deposition (Dise and Wright, 1995). Nonetheless in high elevation ecosystems establishing the cause of changes in stream water chemistry is not simple. Recent researches on the microbiology of alpine soils suggested a great role of bacterial community in controlling the N cycling and nitrate export in these basins (Lipson et al., 1999; Nemergut et al., 2005). Physical features of the catchment strongly influence the chemical composition of stream water and may control the ecosystem responses to global perturbations such as the atmospheric deposition of nitrogen and/or changes in climate (Clow and Sueker, 2000; Lovett et al., 2000; Sickman et al., 2002; Lewis, 2002; Kopaceck et al., 2005; Helliwell et al., 2008). The importance of physical landscape components in the amplification and attenuation of biogeochemical processes has been recently highlighted in a conceptual model for high elevation ecosystems named Landscape Continuum Model (Seastedt et al., 2004). The model was developed to predict where inorganic and organic matter is likely to accumulate or being exported and emphasizes the downward transfer of water and nutrients via physical transport vectors such as rivers, wind, rockslides, and snow avalanches. It provides a mechanistic interpretation for how different portions of the high-elevation landscape can experience excesses and limitations of the same nutrient, e.g. N, also in response to global changes.

Given the increasing availability of digital version of thematic maps and geographic information systems the analysis of relationships between the stream water chemistry and a wide variety of physical features of basins is now easier than in the past. This type of analysis can be very useful to identify habitat and catchment features influencing the N retention of high elevation ecosystems. The possibility to find powerful predictors of N fluxes and concentrations and to develop statistical models becomes very interesting especially for lakes and streams rather inaccessible such as those at high altitude. This approach could enhance our knowledge of the impact of increased N deposition on

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water quality scaling up the results obtained from intensively studied areas to a regional scale.

In the present study we investigate the relations between some descriptors of water chemistry, including nitrogen species, and some catchment physical variables at 16 sites located in a high elevation valley of the Central Italian Alps. Since 1994, a number of investigations have been performed in that valley (Val Masino), but at lower elevation (1190 m a.s.l.), in order to understand interactions between the atmospheric fluxes and the forest compartment (Balestrini et al., 2001, 2002). Given a N atmospheric input equal to 15 kg N ha^{-1} yr^{-1}, several findings, notably the strong soil N retention, seem to indicate a N-limitation status of the forested portion of the basin. Other observations, such as the monthly nitrate (NO_3-N) concentrations in the river Masino, point in the opposite direction, suggesting a surplus of N bioavailability in the terrestrial ecosystem (Balestrini et al., 2006). Our aims are to characterize the chemical composition of the running waters at the upper basin of river Masino and to test the hypothesis that nitrogen water chemistry and the N retention capacity could be predicted using some environmental and terrain variables.

2 Material and methods

2.1 Study area

The study area is located in the upper basin of the river Masino (Northern Italy), a typical glacial valley (Val Masino) extended for 25.2 km^2, on the north side of the main valley, Valtellina. Around 85 % of the basin of Val Masino is above 1850 m a.s.l. and is delimited by three alpine glacial circus with peaks rising to 3400 m a.s.l. A substantial shrinkage of glaciers occurred in this area, like most of the glaciers in the European Alps (Cannone et al., 2008) and, at present the glaciers occupy less than 5 % of the basin. At the lower limit of alpine meadows (around 2400 m a.s.l.), the vegetation is characterized almost exclusively by herbaceous formations with a predominance of

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Carex curvula and *Nardus stricta*. Most of these natural grasslands, above the tree-line, have been subjected to grazing until the sixties. Moving upward, the turf is fragmented into individual clumps, initially more dense and confluent, then more isolated and scattered. Prairie species are replaced by plants adapted to live on screes or in the interstices between the stones, at altitudes higher than 2500 m. The species more represented in this area are acidophilic (e.g. *Cryptogramma crispa, Oxyria digyna, Rumex scutatus, Saxifraga bryoides*).

The overall soil cover percentage of the catchment is 66 % and only 13 % of the catchment is forested. The soils developed on a volcanic granodiorite also called "Ghiandone" and are characterized in the upper horizons by a significant content of organic matter.

At lower elevation (1190 m a.s.l.), a study area (Bagni di Masino) belonging to the LTER and ICP-Forest networks is located. Within these programmes a number of monitoring studies has been carried out: throughfall and open field deposition measurements, chemical and hydrological monitoring of river Masino, soil solution and litterfall chemical characterisation (Balestrini et al., 2000, 2002, 2006; Balestrini and Tagliaferri, 2001).

In particular, at the Bagni di Masino study site, the mean precipitation amount, from 1995 to 2008, is 1589 mm yr^{-1} of which 30 % occurred as snowfall from November to April. The climate is continental, with the highest amount of precipitation in summer and the least in winter. The mean annual air temperature is +7 °C.

2.2 Sampling and analysis

In order to select the sampling sites for the seasonal monitoring a preliminary campaign was conducted in June 2007, in the upper Val Masino basin, at 2000–2650 m a.s.l. Thirty five water samples were collected from (i) springs outcroping from moraines formed by detritus of different size (medium to cyclopic), (ii) running waters along vegetated slopes and (iii) stream stretches. The location of these sites is shown in Fig. 1. On the base of the preliminary results obtained, sixteen sites were chosen and sampled

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during the snow free period, during the years 2007 and 2008, from the end of June till October, with a nearly monthly frequency.

The analysis were performed on filtered samples (0.45 µm), except for measurements of electrical conductivity and pH. The alkalinity of samples with pH > 5.6 was measured by two-endpoint potentiometric titration with HCl. NH_4-N was analyzed by molecular absorption spectrometry (Perkin Elmer UV-VIS Lambda25) using the indophenol-blue method. NO_3-N, SO_4 and Cl were determined by ion chromatography using a Dionex LC25 equipped with an AS11 column and KOH eluent. Ca, Mg, Na and K were measured by a Dionex ICS2000 ion chromatograph with a CS12 column. Total dissolved nitrogen (TDN) was measured using molecular absorption spectrometry UV-VIS, after a persulphate digestion in an autoclave at 120 °C. The dissolved organic nitrogen (DON) was estimated from the difference between TDN and inorganic N (NH_4-N plus NO_3-N).

Dissolved organic carbon (DOC) was assayed by high temperature catalytic oxidation using a Shimadzu TOC-5000 A analyser.

The quality of chemical analysis was checked by including method blanks, repeated measurements of internal and certified reference samples and by regular interlaboratory tests and international intercomparisons (Marchetto et al., 2006). The repeatabilities, based on repeated measurements of internal quality controls at different concentrations, were 3 % for NH_4-N, 2 % for NO_3-N, 4 % for TDN, 3 % for SO_4, 6 % for Cl. Detection limits were 5 $\mu g\,l^{-1}$ for NH_4-N, 0.02 $mg\,l^{-1}$ for NO_3-N and Cl, 0.05 $mg\,l^{-1}$ for SO_4 and 0.1 $mg\,l^{-1}$ for TDN.

A geographic information system (GIS) was used to delineate the catchment for each sampling site. Topographic coverages were derived from digitized Regional Technical Map, which have a scale of 1 : 10 000. We used a 20 m digital elevation model (DEM) for deriving the average slope, aspect and elevation for each basin. Basin land cover characteristics were quantified using digital map with a scale of 1 : 10 000 (DUSAF 1.1 – Regione Lombardia, 2001). Derived from this map, 7 categories were identified and basin specific land use percentages were determined (Table 1).

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2.3 Estimate of nitrate retention

We estimated the biological retention of nitrate by comparing the concentrations of NO_3 and a geochemical descriptor such as calcium in the analysed running waters. Analogously to NO_3, Ca reached the maximum concentration in October but the trend, starting from July, was generally more gradual than NO_3 one. For each site we calculated the expected concentration of NO_3 on the basis of Ca content. We used the ratio Ca/NO_3 measured at June to derive the values expected for the other months. An example for July is reported below.

$$\frac{Ca_{Jun}}{NO_{3\ Jun} \cdot Ca_{Jul}} = \text{expected } NO_{3\ Jul}$$

The data from late June can be a common basis for almost all sites in that they represent a condition where the running waters are composed mostly of water from melting snow after the effect of "ionic pulse" of the first spring thawing. Expected values higher than measured values indicate consumption of nitrate by biological processes, while the contrary means biological production of nitrate, e.g. nitrification. The percentage of NO_3 retention for each site was calculated as the mean ratio between measured and estimated concentration of all 2008 sampling dates.

3 Results

3.1 Hydrology and catchment features

At Bagni di Masino site, the amount of precipitation during 2007 and 2008 was 1321 mm (15 % as snow) and 1926 mm (28 % as snow), respectively, thus 17 % less and 21 % more than the long-term average (1589 mm yr^{-1}). The snowfall period was longer during 2008 (from the beginning of December to middle May) than the previous year (from the beginning of December till the middle April).

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The Masino river annual hydrograph for 2007 and 2008 (Fig. 2) reflects the typical seasonal trend of snowmelt dominated catchments. After the winter base flow, the discharge begins to increase during April/May, with the beginning of spring snowmelt and peaks in late June. The autumn decline is often interrupted by some peaks during the intense November rainfall. The annual median of hydrometric height, at Bagni di Masino, was 16 cm and 28 cm during 2007 and 2008, respectively. During the first studied year the snow melt pulse occurred earlier, at late April, in conjunction with an increase in air temperature. Conversely, a higher discharge was measured in July 2008.

Table 2 shows the morphological and topographic features of the selected sites monitored for two years. The elevation range was quite wide, from 1950 to 2634 m a.s.l., as well as the catchment area varying from 6.7 ha to 895 ha. On the contrary, the mean slopes slightly vary from 22° to 35°, with an overall mean equal to 30° that indicates that most of the sites were located on quite steep slopes. The overall average soil cover percentage was 21.7 % and the 90 % of sites had values ranging from 2.6 % and 35.4 %. In catchments with low soil coverage, rock debris (talus)/bedrock (R1) comprised the majority of the catchment area. The predominant land cover category was the herbaceous and shrub vegetation colonizing rocks and screes (N3). Only in some sites located at lower elevation (e.g. P31 site) other vegetation habitats, such as shrub vegetation (N8) and meadow vegetation (P4), occupied substantial portions of the catchments.

Some catchment characteristics were highly correlated (Table 3) and may identify habitats that have common physical features. Mean elevation and slope were positively correlated with each other and with R1 percentage. Conversely they were negatively correlated with the fractional amount of N3 in the catchments. This indicates that talus and bedrocks are mostly located at higher altitude on steep slopes. The vegetated soil (veg. soil) percentage was negatively correlated with mean slope suggesting that steeper basins contain a less amount of developed soil. Since R1 and N3 represent the main habitats in the studied basin they are also negatively related themselves. On the

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other hand, N3, that is the more represented vegetated habitat, is strongly correlated with vegetated soil cover percentage resulting from the sum of N3, N8 and P4.

3.2 Chemistry of running waters

As shown in Table 4 the ionic content of the analysed waters was very low, with electrical conductivity values ranging from 4.5 to 19 $\mu S\,cm^{-1}$. The predominant ionic species were HCO_3 and Ca, both significantly related with conductivity as expressed by correlation coefficients of 0.78 ($p < 0.001$) and 0.95 ($p < 0.001$), respectively. The values of alkalinity, ranging from 2 to 104 $\mu eq\,l^{-1}$, indicate that the surface waters are very sensitive to acidification. On a molar basis the abundance of major cations follows the order Ca > Na > K > Mg. The mean Ca/Na ratio (2.2), was much higher than the ratios available in literature for the plagioclase, that is the main constituent of granodiorite (Must et al., 1990). As reported for other catchments underlined by granitic rocks the weathering of calcite greatly contributes to the cations delivered to the waters thanks to its chemical reactivity and the high rate of physical erosion in alpine environments (Must et al., 1990).

Nitrate was the principal nitrogen species in the running waters with a mean concentration equal to 17.6 $\mu mol\,l^{-1}$ while ammonia was close to the detection limit. The mean concentration of DON was 2 $\mu mol\,l^{-1}$, one order of magnitude lower than inorganic nitrogen content. Contrary to NH_4-N, the values of NO_3-N were quite variable ranging from the detection limit to 45 $\mu mol\,l^{-1}$. For comparison, the NO_3-N concentration measured during 2008 in the rain and in the snow, at Bagni di Masino and in the snow, in the study area, were 18.4 and 8.1 $\mu mol\,l^{-1}$, respectively (Balestrini et al., 2009).

The correlation analysis revealed that the principal chemical constituents were not very good predictors of changes in N species concentrations. H^+ concentration and Ca/Na ratio were positively correlated with NO_3-N ($p < 0.001$), but with low correlation coefficients ($r = 0.43$ and $r = 0.39$, respectively), while DOC concentration was negatively correlated with NO_3-N ($p < 0.001$, $r = -0.38$).

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Nitrate concentration in most of the sites exhibited a temporal trend characterised by minimum levels in the middle of summer and a marked increase during October (Fig. 3). Other ion species such as Ca (Fig. 3) and SO_4 shown an increasing trend starting from June/July, while Cl, a conservative species, remains stable during the whole period. The DOC concentration did not show any trend during 2007, while higher values were measured in 2008, with the maximum occurring in July.

In Table 2 the estimate of the biological retention of nitrate, as result of both in-stream and soil retention processes, is shown for every study sites. Figure 4 gives an example of the obtained results, in a case where the NO_3 retention was about 70 % (site G12) and another where there was no biological consumption (H1). The estimated retention values, were homogeneously distributed varying from 0 to 100 % with a mean of 36 % and they were significantly and linearly related to the mean concentration of DOC measured in 2007 ($p < 0.0001$, $r = 0.80$).

3.3 Correlation and regression analysis between landscape patterns and solutes

We analysed patterns in correlations between specific groups of solutes (NO_3, DOC and Ca) and groups of landscape characteristics (Table 5). Since NO_3 and Ca exhibited monthly variations, the minimum, the maximum and the mean values were used in the correlations. For DOC we kept separated the values of 2007 and 2008 as they significantly differed between the two years.

The analysis showed that the percentages of vegetated soil cover (Veg. Soil) and N3 were strongly negatively related to nitrate concentration. The highest correlation coefficient was found considering the maximum concentrations mostly coincident with the values measured in October. Conversely R1 % was positively correlated to nitrate. Nitrate was also significantly correlated with the mean slope and elevation of the basins. Similarly to nitrate, but with an opposite behaviour, DOC measured during 2007 was positively correlated with soil cover and N3 % and negatively correlated with R1 % and the mean slope. Likewise DOC, the percentage of nitrate retention was strongly

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positively correlated with soil cover and N3 % and negatively with R1 %, mean slope and with a weaker significance to the mean elevation too.

The soil cover was not influent in controlling the Ca concentration in surface waters, but a high significant correlation was found between Ca and the mean aspect of the basins (Table 5). The correlation between Ca and the mean elevation was less significant.

It is worth to note that the minimum values of both NO_3 and Ca concentration were mostly measured at the end of June when the snowmelt had a dilution effect on the surface waters. This could explain the lower significance of some correlations between the concentration of some chemical species and the physical features of the basins as the melting waters modified the hydrological connection between substrates and surface waters.

The linear model using the N3 % was a good predictor for NO_3 concentration in the surface waters; 85 % of the variation in the maximum NO_3 values was explained by this linear equation (Fig. 5). An exponential model better described the relationship between maximum NO_3 and R1 % explaining almost 89 % of nitrate variation. The same model using vegetated soil cover was also a very good predictor of both peak nitrate (R^2 = 0.899) and mean nitrate concentration (R^2 = 0.803) in the studied sites. The exponential models using the mean elevation and the slope were slight less predictable (67 and 78 % respectively) compared to the soil use (Figs. 5 and 6).

The NO_3 retention declined linearly with decreasing N3 % and this linear model explained about 70 % of the variation in % NO_3 retention (Fig. 7).

4 Discussion

The range of NO_3-N concentrations in the high Val Masino is consistent with the data reported for a glacial valley in the Swiss Alps (Tockner et al., 2002) and for 73 high-elevation lakes of Eastern Alps in Austria (Psenner, 1989). Higher NO_3-N values (26 $\mu mol\,l^{-1}$, as median) were reported for alpine lakes in Tatra Mountains (Kopaceck et al., 2005), while slightly lower NO_3-N concentrations (about 12 μmol l^{-1}) were measured in an Italian alpine valley (Stelvio National Park), at 1950–3768 m a.s.l., located about 100 km East from Val Masino (Boscaini et al., 2003). The comparison with high elevation ecosystems in the United States reveals that our data are similar to the mean values (16–24 μmol l^{-1}) reported for some Rocky Mountain sites (Campbell et al., 1995; Baron and Campbell, 1997), but greater than Sierra Nevada sites (mean of 5.4 μmol l^{-1}) (Sickman et al., 2002).

Nitrate was the dominant form of N in the analysed waters since ammonia and organic nitrogen contributed, on a mean basis, only for the 3 and 10 % respectively. Both species occurred at concentrations often close to the detection limit and did not show any significant correlation with the physical features analysed in the present study. Comparable concentration and percentage of DON have been reported from alpine watersheds in Colorado Front Range (Hood et al., 2003). In that study, Hood et al. (2003) also reported an increase of DON moving downstream toward the forested portion of the catchment where DON contribution to the total N reached the 45 %. Differently, at the high-elevation Emerald Lake watershed in the Sierra Nevada, organic N was the major form of N export in stream water (Williams et al., 2001). Organic nitrogen is not commonly measured in remote ecosystems and its role in N cycling in high elevation systems is still unknown. Accordingly to Williams et al. (2001), our results suggest that the “leaky faucet hypothesis”, could be appropriate also for explaining DON behaviour in temperate ecosystems above the treeline where talus and tundra areas are predominant.

Differently to DON, nitrate in running waters showed a spatial pattern strictly connected to the abundance of the different land cover categories within the basin, each characterised by specific and common physical features. Our results clearly demonstrate that in an ecosystem rather simplified in terms of habitat and homogenous as geology, the relative proportions of the two main environmental types, talus (R1) and tundra (N3), become powerful predictors of the nitrate concentration in surface waters. Other indices related to catchment topography such as slope and elevation are both useful to predict NO_3 concentration, but the obtained relationships were partially due to the covariance of slope and elevation with R1 and N3. The substantial feature that distinguishes these two environments is the soil cover. N3 includes the fraction of the basin covered with vegetated soil while, with the exception of some patches of fine particles within the boulder matrix, soil is largely absent in talus fields (R1). The nitrate export in stream water diminished along with the increasing size of the vegetated soil fraction within each catchment. The presence of soil is the strongest discriminating factor in determining the possibility that nitrate could be retained. This means that the biological community represented by microorganisms and plants living in soils is efficient in consuming the N available in the water matrix, despite the adverse environmental conditions such as low temperature, short growing season, extensive and deep snow cover (Schmidt et al., 1999; Freppaz et al., 2007). The biological nature of the N consuming processes is also supported by the estimate of N retention that declined in a linear way with decreasing N3 percentage.

The area of the basins, that can be considered a proxy for the hydrological flowpath because it takes into account the time and distance from the source, resulted not significant to explain NO_3 variability. The relationship between discharge and some chemical species was analysed in Balestrini et al. (2006) for the Masino stream at the closing section of the basin (Bagni di Masino). There was an inverse, highly significant correlation between flow and SO_4, Ca, Mg, K, and Na concentrations, indicating the importance of the dilution process in controlling the variability of these solutes. Conversely, the hydrological regime was not significant in explaining the variation of NO_3 suggesting that other factors, apart from discharge, controlled the temporal trends of inorganic N in Masino stream water.

In the recent years, several studies investigated the relationships between surface water nitrogen and the physical features of the catchments but few of them were focused on ecosystems above the tree line. Lovett et al. (2000) reported that NO_3 concentration of 39 streams in a forested catchment (750–1250 m) in the Catskill Mountains (NY) was poorly correlated with some physical features (e.g. slope, relief,

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watershed area) which may influence hydrologic residence time. The same authors hypothesized that the key factor able to produce variation in stream NO_3 content had to be find in forest species composition induced by past land use practices. The relation between N yield and simple catchment features such as area, elevation and runoff was investigated by Lewis (2002) in 19 minimally disturbed watersheds spread all over the United States and mostly located below the treeline. Statistical analysis showed that elevation and watershed area bear no significant relationship to nitrogen yield for these watersheds. Only runoff was strongly related to the yields of total nitrogen and nitrogen fractions.

Clow and Sueker (2000) analysed the relation between stream water chemistry and topographic, vegetative, and geologic characteristics of nine alpine/subalpine basins in the Rocky Mountain National Park, Colorado. Similarly to the results of the present study, NO_3 concentration was positively correlated with steep slopes, unvegetated terrain, and young debris and was negatively correlated with subalpine meadow vegetation. On the other side, differently to our findings, they did not find any significant correlation between solute concentrations and the percentage of each basin covered by tundra plant species. Based on these data the Authors developed some regression models able to explain most variation in nitrate chemistry of these nine catchments. However the same models tested with existing synoptic stream-survey data from the Rocky Mountains revealed a poor performance. The authors explained this with a high proportion of small, high-elevation catchments with limited areas of subalpine soils comprised in the original data set, compared to the calibration data. These findings along with those obtained in the present study suggest that the modelling approach possibly will be really successful only when applied on homogenous data set since the processes, both abiotic and biotic, could act in different ways in controlling the N in water bodies located in different bioclimatic zone (e.g. the alpine versus the montane zone) and this can limit the overall suitability of simple regression models.

Sickman et al. (2000) found that soil cover and elevation were good predictors for stream nitrate concentrations and dissolved inorganic nitrogen (DIN) retention in alpine and subalpine ecosystems in both the Sierra Nevada and Rocky Mountains. Particularly, in both mountain ranges, the annual volume-weighted mean nitrate concentration decreased in a logarithmic fashion as soil cover increased. Similarly, the NO_3 concentrations measured in alpine lakes in Tatras Mountains (Slovakia-Poland) correlated negatively with parameters characterising land cover in the catchments, i.e. percent land cover with meadow, soil depth and soil pool (Kopacek et al., 2005).

In Fig. 8 we compared our data of nitrate concentration and land cover percentage to those reported by Sickman (2002) and Kopacek (2005). This comparison revealed that the proportion of the soil extension within the catchments exerted an analogous effect on nitrate concentrations across the alpine regions of Italy and both Poland and Western United States. The exponential coefficient of Sierra Nevada equation was about 2, 2.4 and 3 folds the coefficients of Masino valley, Rocky Mountains and Tatra Mountains equations, respectively. This suggests that the Sierra Nevada soils are more efficient in retaining NO_3, possibly because of differences in climate soil properties (Sickman, 2002) and latitude compared to the other three areas. On the other hand the equation intercepts, following the decreasing order Tatra Mountains $\gg$ Masino valley $>$ Rocky Mountains $\gg$ Sierra Nevada, may reflect different N atmospheric inputs. The annual mean of wet deposition flux of inorganic nitrogen (for the period 1995–2010) is 10.5 kg ha^{-1} yr^{-1}, at the closing section of the basin, Bagni di Masino (1190 m a.s.l.). The inorganic N pool stored in snowpack was measured during spring 2008, between 1950 m and 2250 m a.s.l., within the Masino catchment (Balestrini et al., 2009). The resulting mean N load of 1.08 kg ha^{-1} for the full length of the snow period (November 2007–May 2008) accounted for 40 % of the load measured at Bagni di Masino. Such percentage was used to estimate the total DIN loading for the most elevated part of the catchment. This estimate (4.2 kg ha^{-1} yr^{-1}) together with the deposition rate at Sierra Nevada (1.8 kg ha^{-1} yr^{-1}), Rocky Mountains (3.6 kg ha^{-1} yr^{-1}) and Tatra Mountains (8.5 kg ha^{-1} yr^{-1}) have been plotted (Fig. 9) against the intercepts of the equations reported in Fig. 8. It is apparent that the relationship between the two variables is really well accounted by a linear model. These observations are comparable to the MAGIC

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model predictions in which simulated NO_3 leaching is related to soil carbon pool by a curvilinear relationship dependent from the N deposition rate (Evans et al., 2006). Previous studies (e.g. Helliwell et al., 2008; Evans et al., 2006), aimed at analyzing control on NO_3 leaching in mountain freshwaters, reached similar conclusions about the importance of soil carbon pool in controlling N retention. Nonetheless, our findings suggest that in homogenous environments as those above the tree line, the percentage of soil cover may be sufficient for predicting N water concentration independently from carbon pool entity whose measurements are rather difficult to obtain. Some Authors (Hope et al., 1997) reported significant linear relationships between soil C pool and DOC export and Evans et al. (2006) used DOC as a proxy for C pool in the relationships with NO_3 concentration in surface waters. In the present study the analyzed relationship between DOC and NO_3 as well as DOC and the vegetated land cover fractions within the catchments were significant but not so strong as that reported between NO_3 and soil cover percent. Since also the significant differences in DOC concentrations we found between 2007 and 2008, we hypothesized that DOC in the surface waters sampled at high elevation may originate not only from the soil but also from the algae and bacterial growing in the water. For these reasons the relationships between NO_3 and DOC could be more complex than that with soil cover percent. A recent study by Taylor and Townsend (2010) proposed that the dissolved organic carbon to nitrate ratio (DOC/NO_3) of a substrate resource (freshwater, ocean, soil) strongly influences nitrate accumulation or uptake by regulating a host of microbial processes such as the nitrification and denitrification. The DOC/NO_3 ratio at our sites ranged from 2.3 to 97. A scatterplot of nitrate retention (%) versus the DOC/NO_3 ratio shows that lower percentages of nitrate retention were associated with DOC/NO_3 of about 2.5 (Fig. 10). This value falls below the 3.5 threshold identified by Taylor and Townsend for microbial biomass below which an increase of nitrate in water is expected. Accordingly to our data, Williams et al. (2011) found DOC/NO_3 less than 5 anchored to high elevation stream samples characterized by high NO_3 concentrations.

These findings enhance the role of vegetated soil in N retention as it may provide a certain organic carbon availability such to avoid the occurrence of a carbon limitation that may drive the accrual of nitrate in the system.

The fact that soils above the tree line could be effective in controlling the nitrate dynamics gives rise to some reflections on the current theories on nitrogen saturation whose mechanisms and effects have been widely studied in forest ecosystems across the United States and Europe (Aber et al., 1998; Gundersen et al., 1998; Earl et al., 2006; Curtis et al., 2011). However, especially in Europe, few studies have analysed the stream water nitrate signals in remote portions of high elevation ecosystems such as alpine tundra. The present study describes some catchments spread in a relatively small area of about 1000 ha along an elevational gradient of 700 m (from 1950 to 2650 m a.s.l.) and exposed to the same N deposition rate. Following the approach of Traaen and Stoddard (1995) the different seasonal patterns in surface water nitrate concentrations observed for the study basins could suggest the degree of the natural variability in response to a N loading of about 4 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$. Some basins showing growing season NO_3-N concentrations near the detection limit, could be included in the stage 0 or 1 of the sequence of N-saturation. On the contrary summer concentration of about 20 $\mathrm{\mu eq\,l^{-1}}$ may lead to suppose that the basins were already at stage 2–3. According to the theoretical approach proposed by Curtis et al. (2011), we think that these elevated NO_3 concentrations does not necessarily imply N saturation in the terrestrial ecosystem, but could indicate a pathway of nitrate leaching dominated by a hydrological bypass or the presence of carbon poor locations (e.g. talus slopes) not able to store N for long term. On the other hand the low nitrate output found in some other sub-basins demonstrate that the soils of the high Val Masino represent carbon rich pools where retention and/or accumulation of N could occur for long term. What diversifies the forest ecosystems and the alpine tundra is the size of the pool where N transformations occur, i.e. the % of developed soil, usually present in smaller extent in the catchments at high elevation than in forest areas. The sensitivity of the environments above the tree line to the N deposition is so mainly due to the relative proportion of vegetated soil within the catchments.

5 Conclusions

The chemical characterization of the surface waters along with the assessment of the landscape features of the portion of the basin located above the tree line added a noteworthy piece to the study of the nitrogen dynamics in a "Long Term Environmental Research" station of the Italian Alps (Val Masino). This study revealed important and differentiated relationships between a geochemical descriptor (Ca) and two biological active species (NO_3 and DOC) with some topographic features and land cover of the basin.

From our findings, we deduce that land cover can be considered one of the most important factors affecting water quality of streams in high elevation catchments, with a contrasting effect on N and C pools. The areal extension of developed soils is strictly related to the retention of N and this suggests the fundamental role of microbial community and plant roots in limiting the leaching losses of nitrate also in high elevation ecosystems. Therefore any variation of land cover due to global change could significantly affect the quality of running waters. According to the climate change scenarios in the alpine space, we might expect an upward shift of alpine plants and an increase in the plant species richness of high alpine and nival vegetation (Walther et al., 2005; Pauli et al., 2007). Nevertheless, at high elevation, even if the climatic conditions could be favorable, the diffusion of the tundra plant species could be limited by the low rate of soil formation, limiting the increase of the vegetated soil area (Letey et al., 2010). At the same time changes of the characteristics of the talus areas, due for example to permafrost degradation, could significantly affect water quality (Caine, 2010). All these changes could appreciably influence the quality of running waters above the tree line and have to be considered in the water resource management and planning in alpine areas.

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Furthermore, the comparison of the results obtained here with those from the Tatra Mountains, the Rocky Mountains and Sierra Nevada supports our overall findings, and suggests that the efficiency of soils in retaining N could be influenced by the N atmospheric loading. Since the equations linking the soil cover and the stream nitrate concentration could be used to quantify the effect of N loading on the N export, they may also contribute to the evaluation of critical N loads in alpine ecosystems.

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Table 1. Land cover categories used to characterize the study basin.

	Land cover
A1	Glaciers and snowfields
A2	Lakes and ponds
N3	Vegetation on rocks and rock debris
R1	Rock debris and bedrock
N8	Shrub vegetation
P4	Meadow vegetation
B4	Coniferous forest

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Table 2. Physical features and estimate of NO_3 retention (%) of study sites. R1, N3 and veg. soil are expressed as percentage of the catchment area.

Site Code	Site Elevation (m a.s.l.)	Mean Elevation (m a.s.l.)	Area (ha)	Slope (deg)	Aspect (deg)	R1 (%)	N3 (%)	Veg. soil (%)	NO_3 retention (%)
F13	2634	2773	23.8	29.87	168.4	95.1	4.7	4.7	37.2
F14	2608	2754	27.7	29.49	166.1	90.1	9.7	9.7	46.4
N22	2555	2633	6.7	30.81	173.7	86.8	13.2	13.2	28.3
H1	2542	2788	19.7	32.68	136.5	99.9	0.1	0.1	0.0
H2	2520	2773	21.2	31.44	136.0	97.4	2.6	2.6	7.1
H3	2519	2773	21.2	31.44	136.0	97.4	2.6	2.6	14.3
H30	2385	2777	71.4	28.66	160.6	86.4	8.7	11.1	17.7
MS1	2350	2805	114.2	31.13	182.2	79.6	13.7	17.5	33.5
G9	2275	2718	51.4	29.26	141.9	79.0	21.0	21.0	80.0
G10	2272	2718	51.4	29.26	141.9	79.0	21.0	21.0	47.0
G11	2252	2702	53.8	28.88	142.7	75.5	24.3	24.5	57.5
G12	2223	2653	118.3	27.90	147.1	66.8	32.1	33.1	68.9
P31	2134	2236	7.6	21.63	148.0	0.0	53.1	100.0	95.0
MS2	2000	2594	895.4	30.32	196.1	61.7	19.9	35.9	19.7
T5	1953	2477	203.0	35.07	264.1	61.7	20.2	35.0	25.4
T3	1951	2694	121.4	31.02	210.9	73.2	10.2	19.3	1.2

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Table 3. Summary of Pearson Product Moment correlations among catchment landscape features.

	Area	Slope	Aspect	Mean elevation	Site elevation	R1 %	N3 %
Slope	0.138 ns						
Aspect	0.414 ns	0.459 ns					
Mean elevation	−0.180 ns	0.506 [a]	−0.304 ns				
Site elevation	−0.530 [a]	0.070 ns	−0.576 [a]	0.569 [a]			
R1 %	−0.201 ns	0.681 [b]	−0.193 ns	0.928 [c]	0.639 [b]		
N3 %	0.105 ns	−0.737 [b]	0.013 ns	−0.828 [c]	−0.556 [a]	−0.923 [c]	
Veg. Soil %	0.185 ns	−0.705 [b]	0.139 ns	−0.931 [c]	−0.597 [a]	−0.996 [c]	0.942 [c]

[a] = $p < 0.05$,
[b] = $p < 0.01$,
[c] = $p < 0.001$,
ns = not significant correlations.

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Table 4. Mean ± Standard Deviation of pH and concentrations ($\mu mol\,l^{-1}$) of the major chemical species measured at 16 sites during 2007 and 2008.

	N	Mean ± S.D	Min	Max
pH	112	6.67 ± 0.45	5.57	8.19
Alkalinity	112	44.4 ± 26.7	2.0	104.3
NO_3-N	113	17.6 ± 10.8	< D.L	45.0
NH_4-N	113	0.55 ± 0.88	< D.L	6.57
SO_4	112	10.8 ± 3.7	4.2	25.0
Cl	111	3.9 ± 3.5	0.5	22.0
Ca	112	31.5 ± 12.2	11.2	66.1
Mg	112	2.6 ± 1.0	0.8	5.8
Na	111	13.9 ± 5.2	5.1	34.8
K	113	7.3 ± 2.7	3.1	17.8
DON	112	1.8 ± 2.7	< D.L	17.0
DOC	113	95 ± 39	31	250

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Table 5. Summary of Pearson Product Moment correlations between some catchment features and concentration of some chemical species and NO_3 retention (%).

	Ca Max	Ca Min	Ca Mean	NO_3-N Max	NO_3-N Min	NO_3-N Mean	DOC 2008	DOC 2007	% NO_3 Retention
Area	0.313 ns	0.307 ns	0.358 ns	−0.219 ns	−0.022 ns	−0.104 ns	−0.033 ns	−0.114 ns	−0.060 ns
Mean slope	0.221 ns	0.029 ns	0.185 ns	0.669 [b]	0.511 [a]	0.724 [b]	−0.454 ns	−0.569 [a]	−0.754 [b]
Mean aspect	0.830 [c]	0.510 [a]	0.789 [c]	−0.147 ns	−0.177 ns	−0.022 ns	−0.226 ns	−0.254 ns	−0. 263 ns
Mean elevation	−0.457 ns	−0.632 [b]	−0.608 [a]	0.722 [b]	0.510 [a]	0.575 [a]	−0.123 ns	−0.432 ns	−0.554 [a]
Site elevation	−0.342 ns	−0.296 ns	−0.414 ns	0.664 [b]	0.473 ns	0.493 ns	0.139 ns	−0.368 ns	−0.194 ns
R1 %	−0.276 ns	−0.418 ns	−0.391 ns	0.855 [c]	0.619 [a]	0.733 [b]	−0.285 ns	−0.561 [a]	−0.642 [b]
N3 %	0.137 ns	0.301 ns	0.277 ns	−0.918 [c]	−0.754 [b]	−0.836 [c]	0.287 ns	0.720 [b]	0.835 [c]
Soil cover %	0.245 ns	0.410 ns	0.374 ns	−0.854 [c]	−0.628 [b]	−0.740 [b]	0.299 ns	0.589 [a]	0.688 [b]

[a] = significant correlations $p < 0.05$,
[b] = significant correlations $p < 0.01$,
[c] = significant correlations $p < 0.001$,
ns = not significant correlations.

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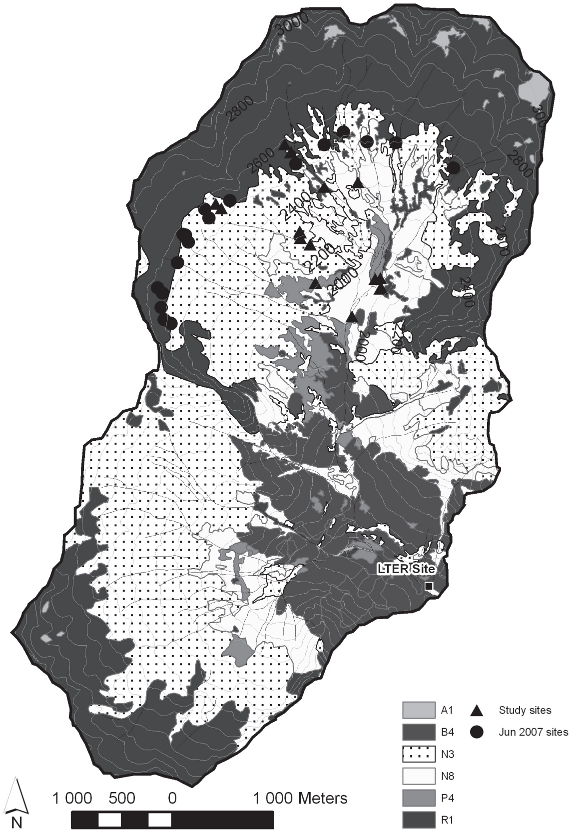

Fig. 1. Map of the of the Masino stream upper basin indicating the location of the sampling sites and the land cover categories (A1 = glaciers and snowfields, B4 = coniferous forest, N3 = vegetation on rocks and rock debris, N8 = shrub vegetation, P4 = meadow vegetation, R1 = rock debris and bedrock).

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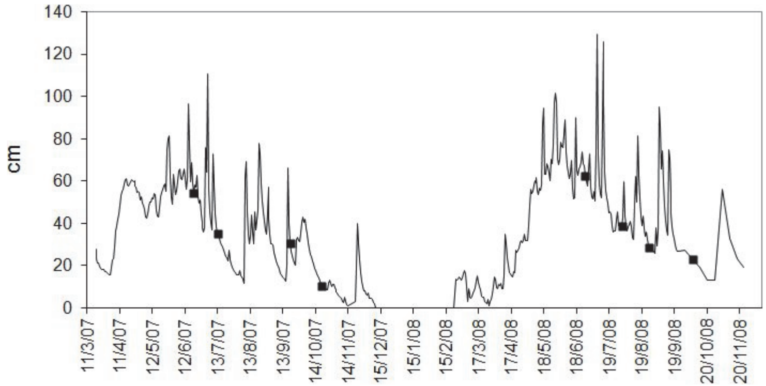

Fig. 2. Stream annual hydrograph (Masino stream) as hydrometric height (cm). The dots refer to sampling campaigns.

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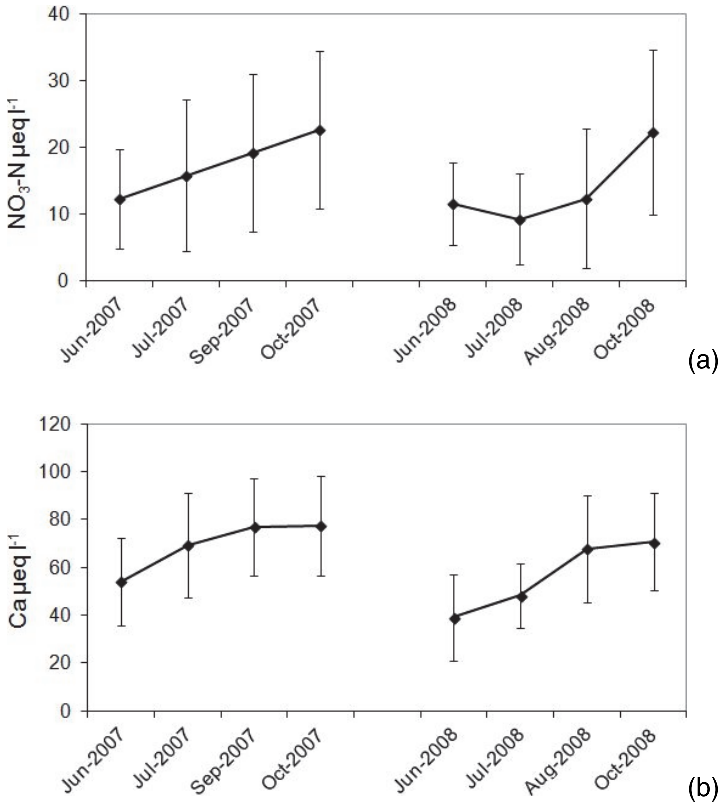

Fig. 3. Mean and standard deviation of NO_3-N **(a)** and Ca **(b)** concentrations measured in the running waters during the study period.

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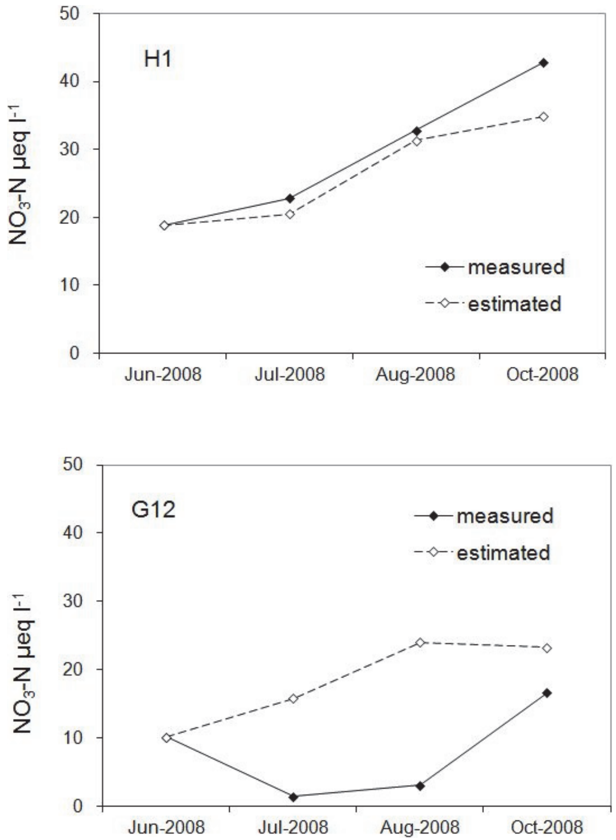

Fig. 4. Measured and estimated NO_3-N concentrations at H1 and G12 sites from June to October 2008.

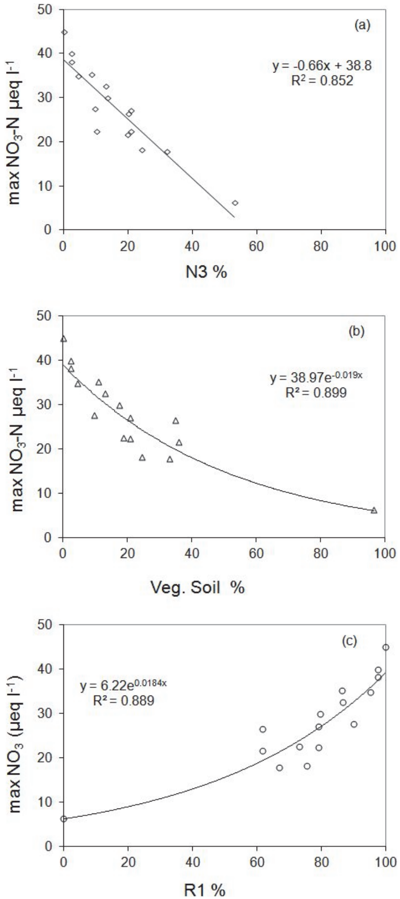

Fig. 5. Relationship between the maximum nitrate concentration in catchment outflow and **(a)** tundra (N3) percentage **(b)** vegetated soil percentage and **(c)** talus and bedrock (R1) percentage, for high elevation watersheds of the Val Masino.

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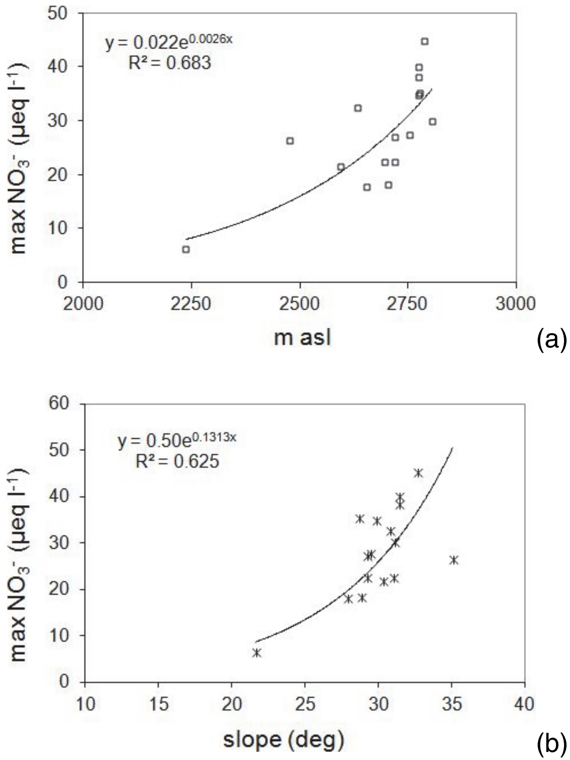

Fig. 6. Relationship between the maximum nitrate concentration in catchment outflow and **(a)** elevation, **(b)** slope, for high elevation watersheds of the Val Masino.

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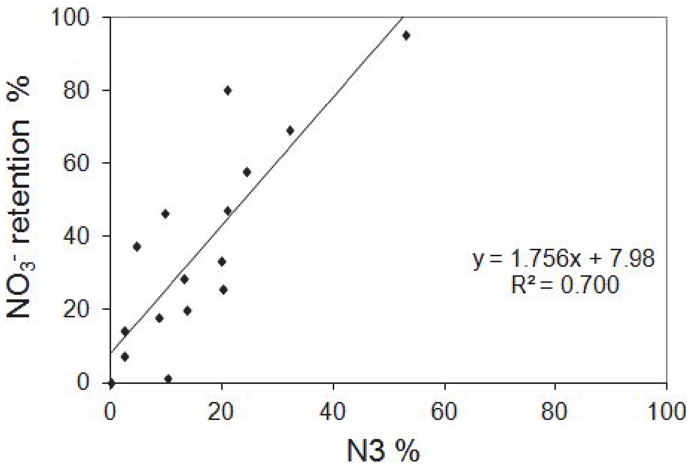

Fig. 7. Relationship between nitrate retention in catchment outflow and tundra (N) percentage, for high elevation watersheds of the Val Masino.

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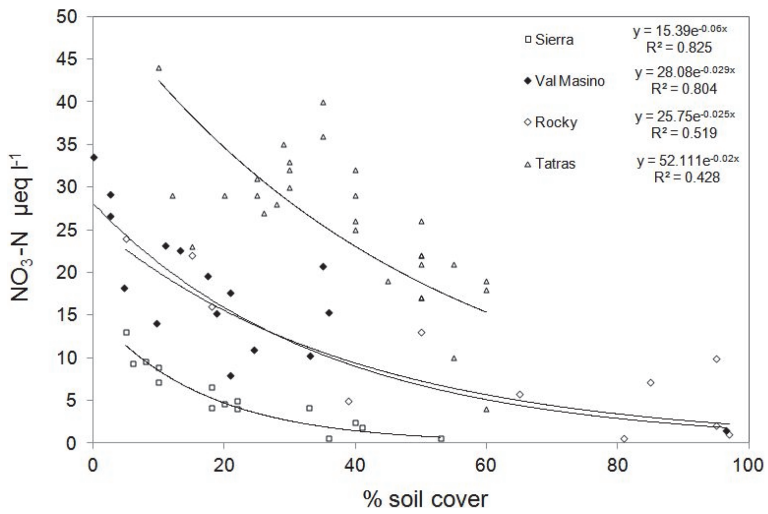

Fig. 8. Relationship between the mean nitrate concentration in catchment outflow and soil cover for high elevation watersheds of the Val Masino (present study), the Sierra Nevada, the Rocky Mountains and the Tatra Mountains (from Sickman et al. (2002) and Kopacek et al. (2005)).

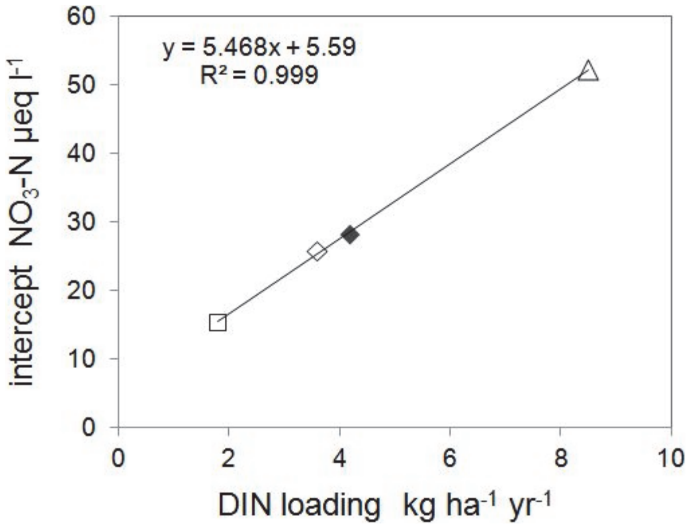

Fig. 9. Relationship between the intercepts of the equations reported in Fig. 8 (N-NO_3 concentration expected for basins without soil cover) and DIN deposition loading measured at Val Masino (present study), the Sierra Nevada, the Rocky Mountains (Sickman et al., 2002) and the Tatra Mountains (Kopacek et al., 2005).

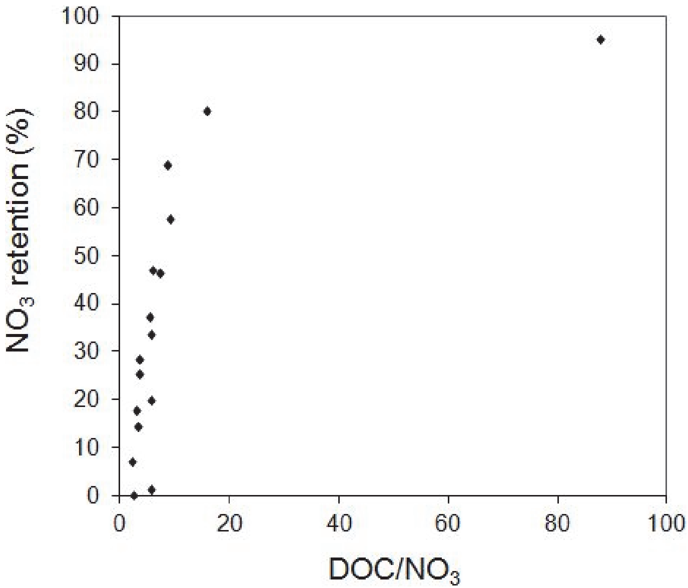

Fig. 10. Scatterplot of the percentage of nitrate retention versus the DOC/NO_3 calculated using the mean concentrations measured in the stream water samples.

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Nitrogen in running waters above the tree line

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