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Nitrogen cycling and mass balance for a forested catchment in the Italian Alps. Assessment of nitrogen status

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Abstract. During 1999–2001 the chemical composition and fluxes were measured in rainfall, throughfall, soil solution and stream water in a remote forested site in the Italian Alps. The analysis of temporal patterns revealed the differential behaviour of nitrogen and sulphur and suggested that different mechanisms controlled their flux. No important changes in sulphate concentration and fluxes emerged as the solution passed through the various components of the forest ecosystem, and temporal variations of SO_4 in the soil solution and stream were likely driven by the physical process of dilution. The availability of nitrate and ammonia, by contrast, was drastically reduced as throughfall water entered the soil and passed through the mineral layers, irrespective of season. The calculated hydrochemical budget based on throughfall and soil solution N fluxes revealed that ~80% N retention in the forest soil, corresponding to 12 kg ha^{-1} yr^{-1}, despite a relatively high N deposition loading (15 kg ha^{-1} yr^{-1}). Most of the leached nitrogen (90%) was in the organic form. Indicators of the N status of this ecosystem, such as C/N ratio in solid and solution phase of the soil and N foliage content as well as land use history were examined. Despite the strong N retention in the forested part of the catchment, the stream water N–NO_3 levels were consistently above 10 μg l^{-1} suggesting that the Val Masino catchment as a whole was less efficient in processing atmospheric N inputs. This contrasting N behaviour illustrates the role of landscape features, such as the soil cover and vegetation type, that is characteristic of an alpine catchment.

Introduction

In the last decade the anthropogenic emissions of SO_2 over much of the northern hemisphere have significantly decreased; the emissions of NO_x, by contrast, have tended to increase or remain constant (Wright et al. 2001). The rate of SO_2 emissions in Italy, in millions of tons per year, was about 3.8 in 1980, drastically decreased to 2.0 in 1985, and slightly declined to 1.3 in 1997. Emissions of NO_x, in the same units, increased from 1.6 in 1980 to about 2.0 in 1992, and have subsequently remained at about 1.6 (Ministero dell'Ambiente 2001).

There is a growing concern about the long-term potential effects of nitrogen (N) deposition on the aquatic and terrestrial ecosystems and, particularly, the response of the temperate forests, representing typical N-limited systems, seem to be particularly complex. Chronic inputs of N deposition can over time lead to ‘N saturation’, a condition in which the availability of inorganic N exceeds the N assimilation capacity of biological processes (Aber et al. 1989, 1998). The effects of excess of N include: (i) increased N mineralisation and nitrification in soils, (ii) nutrient imbalance in plant tissues, (iii) increased soil acidification with the leaching of acidifying compounds and the mobilisation of toxic species such as aluminium (Gundersen and Rasmussen 1990; Gilliam et al. 1996; Stoddard et al. 1999), and (iv) reduced biodiversity in aquatic and terrestrial ecosystems (Vitousek et al. 1997; Bobbink et al. 1998). Global climatic changes may add to these effects by mobilising the organic N stored in soils (Wright 1998). Besides the atmospheric inputs, a number of factors may predispose a forest to move towards N saturation including: stand age, nutrient soil status, water availability, climate, and prior land use (Fenn et al. 1998). Results from several experiments carried out in Europe and the US generate a very complex picture of N saturation processes. The response of some forests to the N addition experiments (Magill et al. 1996; Gundersen et al. 1998; Mitchell et al. 2001) has led to the formulation of new hypotheses on the role of soil organic matter in the N storage by both biotic (Aber et al. 1998; Tietema 1998) and abiotic processes (Johnson et al. 2000; Davidson et al. 2003).

The N atmospheric deposition is likely to have a heavy impact on alpine and subalpine regions as they are characterised by extreme climatic conditions (e.g. low temperature, high wind, high precipitation amounts). Alpine communities are considered very sensitive to changes in N deposition because a combination of short growing seasons, strong seasonal variation in moisture and temperature, shallow and poorly developed soils, steep terrain, sparse vegetation, and low rates of primary productivity generally limit the N uptake and retention capacity of the ecosystem (Baron 1992; Fisk et al. 1998; Burns 2004). Although relatively far from major pollution sources, the Alps receive a variable amount of chemical substances in the form of atmospheric deposition to terrestrial and aquatic surfaces transported by air masses. Weather phenomena like orographic barrier effects and katabatic wind systems can result in high precipitation amounts and specific deposition patterns in the Alps. Recent data for Italian alpine forests indicate rates of atmospheric deposition ranging from 7 to 24 and 5 to 11 kg ha^{-1} yr^{-1}, respectively, for N and sulphur (S) (Mosello et al. 2002a). While the levels of S are relatively low compared to the maximum critical loads (16–32 S kg ha^{-1} yr^{-1}), the N deposition loads are likely to exceed, on a rough base, the critical loads for nutrient N (3–7 N kg ha^{-1} yr^{-1}) (Posch et al. 1997).

Val Masino forest in the Rhetic Alps (Lombardy region) is a remote site relatively far (150 km) from the industrialised area of Milan, and not directly influenced by human pressures. Since 1994, a number of investigations have been performed in this area, in order to understand interactions between the atmospheric fluxes and the biological compartment (Azienda Regionale delle

Foreste 1998; Ballarin-Denti et al. 1998; Balestrini and Tagliaferri 2001). This forest site is part of the national network CON.ECO.FOR, a multidisciplinary monitoring programme for the study of the effects of atmospheric pollution and climate change on forest ecosystems (www.corpoforestale.it/conecofor). The overall purpose of this study is to evaluate the biogeochemistry of the principal elements at Val Masino forest. In the present paper, the specific objectives are to (i) compare the chemical composition of precipitation, throughfall, soil solution, and stream water; (ii) analyse temporal patterns in solute chemistry to assess the relative importance of biotic versus abiotic processes to biogeochemistry; and (iii) estimate the mass balance of N species in order to investigate the role of soil system in controlling the sequestration or the release of N.

Materials and methods

Site description

The study area, Val Masino (46°14′16″ N, 9°33′16″ E), at 1190 m a.s.l. and a mean slope of 10%, is situated in the upper basin of the river Masino (northern Italy), in a typical glacial valley on the north side of the main valley, Valtellina. Around 85% of the basin is above 1850 m and is delimited by mountains rising to 3500 m. The overall soil cover percentage is 66 and only 13% of the catchment is forested (Figure 1). The climate is continental, with the highest amount of precipitation in summer and the least in winter (Balestrini and Tagliaferri 2001). The mean rainfall amount from 1995 to 2003 is 1698 mm yr^{-1}, coincident with the 50 years (1920–1970) mean value of 1670 mm yr^{-1}. During the study period (1999–2001) about 30% of annual precipitation occurred as snowfall from November to April. The mean air temperature is 8 °C.

A throughfall plot (30 × 30 m) was established in the lower conifer forest component of the catchment (Figure 1). The vegetation belongs to the *Veronico urticifoliae-Piceetum* with *Picea abies*(L.) Karst. making up 52% of the trees. The secondary overstory species are *Abies alba* Mill. (22%), *Larix decidua* Mill. (11%), *Betula alba* L. (9%), *Fagus silvatica* L. (6%). The Norway spruces are between 50–80 years old.

The geological substratum is volcanic granodiorite and the soils are Humic Cambisol. As shown in Table 1, the soil is very acid, with very low base saturation and exchangeable acidity occupying most of the cation exchange capacity (CEC).

Sampling and analysis

The sampling protocols and analyses are in strict agreement with the international procedures adopted within the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forest (ICP Forests) (UN-ECE 1998). Atmospheric inputs have been collected at Val Masino site since 1994 and sampling is still ongoing (Balestrini and Tagliaferri

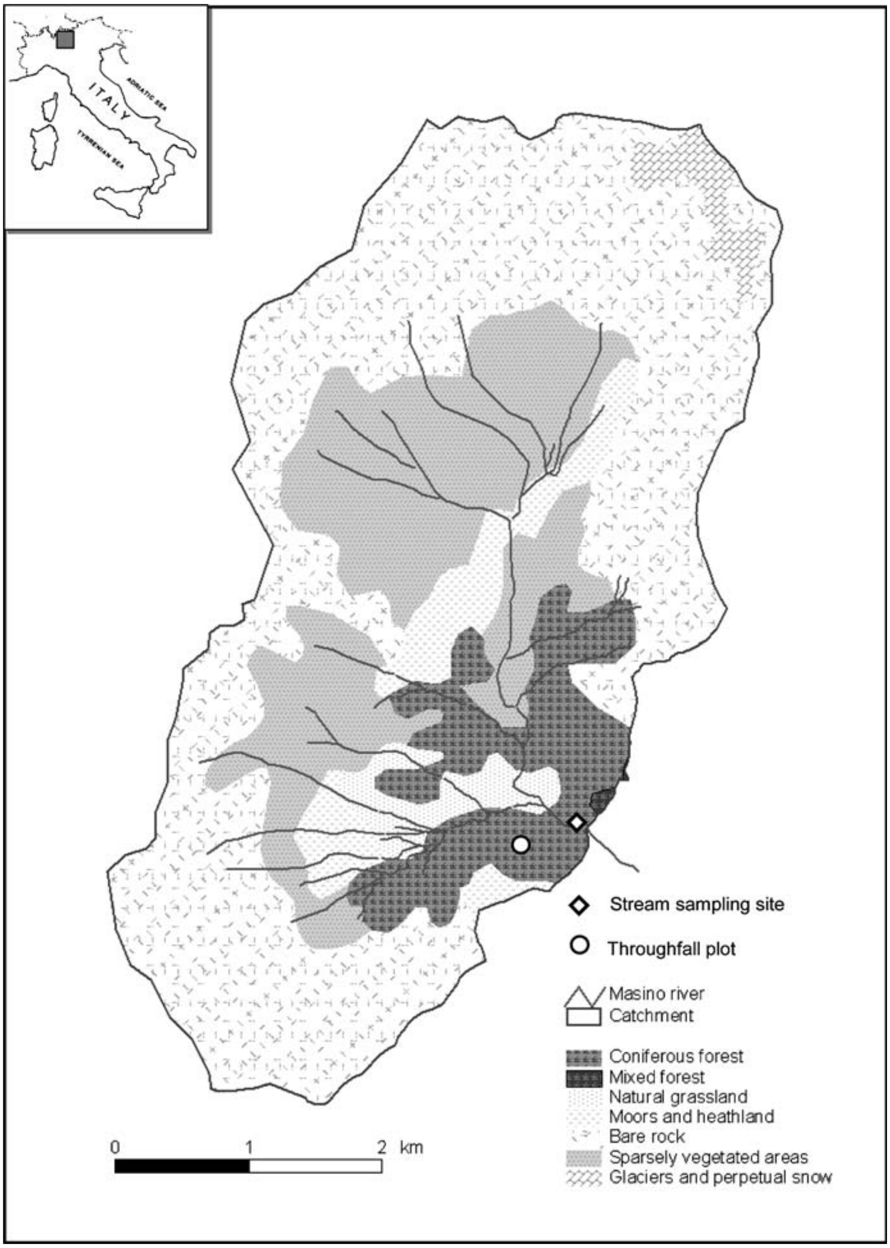

Figure 1. Map location of the upper catchment of the River Masino.

Table 1. Chemical properties of soil collected at Val Masino study area during 1997.

Horizon	Depth	pH	Exch. acidity	CEC	BS	C	N	C/N
	cm	($CaCl_2$)	cM kg^{-1}	cM kg^{-1}	%	g kg^{-1}	g kg^{-1}	
Organic		3.6				140	7.0	20.0
Surface	0–10	3.9	5	7.4	34	100	5.5	18.2
Sub surface	10–20	3.8	4	4.2	12	40	2.5	16.0

From Alianello et al. 2002.

2001). In a 30×30 m plot 9 throughfall samplers, composed of a 5-litre polyethylene bucket with an 18 cm diameter funnel, were systematically placed (Figure 1). Bulk precipitation was collected using a 33.5 cm polyethylene funnel fitted on a 15-litre polyethylene bucket that was installed in a nearby clearing, approximately 200 m from the throughfall plot. Both bulk precipitation and throughfall samplers were equipped with plastic nets to prevent birds from alighting. During the winter months (December–April) both bulk precipitation and throughfall collectors were replaced by snow collectors, consisting of cylindrical PVC containers (diameter = 20 cm, height = 80 cm). Precipitation and throughfall samples were collected weekly. Soil solution was collected using tension lysimeters, ceramic cups (P80, Staatliche Portzellanmanufaktor), with pore size of 1 μm, length of 60 mm and diameter of 20 mm, installed in the B-horizon (at 30 cm depth) and in the upper parts of the C-horizon (50 cm) in October 1998. Two replicate lysimeters per depth were placed near six throughfall samplers, for a total of 24 lysimeters. Prior to installation, ceramic cups were washed with 0,1 M HCl and rinsed with distilled water. Since soil disturbance due to installation may affect water chemistry, samples collected in the first six months were discarded until regular collection of soil solution started in May 1999. A tension of 0.3–0.6 bar was applied by a pump and samples were collected every 2 weeks, except during the coldest period (December–April), when soil solution in the connection tubes was frozen. During the three-year study period, stream water samples were collected weekly from the snowmelt (March or April) to November. The sampling was interrupted during the winter period since the stream was frozen and nearly dry. The depth of the water is measured by a hydrometric gauge placed at the sampling site. Due to lack of detailed stream discharge data, we did not estimate stream nutrient fluxes. Instead, mass balance calculations were based on deposition and soil solution data specific to the forested part of the catchment.

Prior to chemical analysis, throughfall and soil solution samples were combined proportionally to obtain one throughfall sample weekly and one soil solution sample for each depth biweekly. The analysis was performed on filtered samples (0.40 μm), except for measurements of electrical conductivity and total phosphorous (TP) and nitrogen (TN), for which unfiltered samples were used. The alkalinity of samples with pH > 5.6 was measured by two-endpoint potentiometric titration with HCl. N-NH4 was analysed by molecular absorption spectrometry (Perkin Elmer UV-VISLambda2) using the indophenol-blue method. N-NO_3, SO_4 and Cl were determined by ion chromatography using a Dionex 2000i equipped with AS4A column. Ca, Mg, Na and K were measured by a Dionex 4500i ion chromatograph with a CS12 column. The difference between cation and anions was assumed to be an estimation of weak organic acids (OA) (Driscoll et al. 1989). TP and TN were measured using molecular absorption spectrometry, after persulphate digestion in autoclave at 120 °C. The total organic nitrogen (TON) was estimated from the difference between TN and inorganic N (N-NH_4 plus N-NO_3). As soil solution was collected by lysimeters with pore size of 1 μm, it is comparable to a filtered sample, therefore in this case, TON corresponds to dissolved organic nitrogen (DON). Dissolved organic carbon (DOC) was assayed by high temperature catalytic oxidation using a Shimadzu TOC-5000 A analyser. Total aluminium (Al) and iron (Fe) were measured on the soil solution samples by inductively coupled plasma atomic emission spectrophotometry (ICP-AE).

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 (Mosello et al. 2002b). The repeatabilities, based on repeated measurements of internal quality controls at different concentrations, were 3% for N-NH_4, 2% N-NO_3, 4% for TN, 3% for SO_4, 6% for Cl, 5% for Ca, 4% for Mg and Na, 6% for K. Detection limits were 5 μg/l for N-NH_4, 0.02 mg/l for N-NO_3, Cl, Mg, Na and K, 0.05 mg/l for SO_4 and Ca, 0.1 mg/l for TN.

Hydrochemical budget

Water budget was assessed from measured precipitation and throughfall fluxes and estimated evapotranspiration. Potential evapotranspiration (ETp) was calculated from the Penman-Monteith equation (Allen et al. 2001) based on meteorological data observed in the study area. Soil water flux was estimated as throughfall amount minus evapotranspiration, since surface runoff and change in the soil water content are negligible in forest ecosystems in southern and central Europe (UN-ECE 1998). Since monthly rainfall amount was always higher than ETp during the three-year observation period, ETp reflected actual evapotranspiration. In this calculation method, Etp is equated to soil evaporation + transpiration and does not include interception losses in the canopy. While this distinction could possibly lead to an overestimation of ET, we found that our interception (bulk precipitation-throughfall) and ET values (356 mm and 479 mm, respectively) were very similar to median interception (290 mm) and transpiration + soil evaporation (417 mm) reported by de Vries et al. (2001) for 98 spruce stands. In addition, the chloride balance method, comparing throughfall and shallow soil solutions (30 cm) was used to validate the calculation of soil water infiltration flux. There were negligible differences (less than 5% on 3 years basis) between the soil water amounts estimated by these two methods. Annual nutrient fluxes were based on annual volume-weighted average concentrations multiplied by the water volume flux, for a period from May 1999 to December 2001.

Statistics

Differences between bulk precipitation and throughfall as well as soil solution at the two different depths were tested by Wilcoxon signed-rank test. A linear regression model was used to relate the concentrations of some measured variables in the soil solution. Correlations between water flow and stream water ion concentrations were tested with Spearman rank correlations.

Results and discussion

Ionic composition and organic constituents

Table 2 summarizes average chemical composition of aqueous samples for the period 1999–2001. Bulk precipitation and throughfall concentration are volume-weighted means; soil solutions and stream water are arithmetic means. Bulk precipitation (BP) was dominated by SO_4 and N-NO_3 as anions and Ca and N-NH_4 as cations. As solution passed through the canopy all ions significantly increased in concentration ($p < 0.0001$), except for N-NH_4, which declined. The chemical enrichment through spruce canopy filtering was particularly pronounced for K, known to be highly soluble and leachable (Tukey 1970). Charge deficit between anion and cation concentration also indicated an increase in organic acids, which accounted for the 31% of the total anion concentration. In throughfall, Ca was the main cation followed by K.

Once solution entered the soil profile, there was a considerable change in chemical composition that did not change significantly as the water percolated through the mineral soil. There was a significant reduction in both inorganic N species (N-NH_4 and N-NO_3), and both SO_4 and organic acids dominated the anion load. The vertical pattern in SO_4 concentration and flux (Tables 2 and 3) suggests little or no SO_4 adsorption in the mineral soil. The decrease in K concentration was accompanied by an increase of Ca and Mg. Organic acids were linearly related to Ca ($R^2 = 0.57$; $p < 0.0001$), Mg ($R^2 = 0.58$; $p < 0.0001$) and K ($R^2 = 0.44$; $p < 0.001$) at B horizon, but insignificant correlations were found at greater soil depth. Total aluminium was measured in the soil water during 2000–2001 period ranged between 9 and 31 μmol l^{-1}. The molar Ca/Al ratio was 1.6 over the threshold limit of 1, therefore indicative of no risk condition for roots damage (Cronan and Grigal 1995).

In the stream water, HCO_3 was the prevailing anion followed by SO_4 and N-NO_3 (Table 2). On the basis of the mean concentration of HCO_3 (0.058 meq l^{-1}), the stream can be defined as sensitive to acidification (Turner et al. 1986). Ca, the dominant cation, doubled in concentration relative to the soil solution, while Mg was lower than in the soil solution. In the streamwater the

Table 2. Average concentrations from bulk precipitation (BP), throughfall (TF), soil solution at B and C horizons, and stream water samples collected from Val Masino, between 1999 and 2001.

	pH	HCO_3	N-NH_4	N-NO_3	SO_4	Cl	Ca	Mg	Na	K	OA	Al[a]	Fe[a]	TON	TP	DOC[c]
		μeq l^{-1}										μmol l^{-1}		mg l^{-1}		
BP	5.08	20	24	22	29	7	31	5	7	3	13			0.10	0.009	
n	118	41	113	114	114	110	108	114	111	114	84			104	106	
TF	5.55	34	18	27	32	11	44	12	9	34	37			0.44	0.046	7.1
n	119	56	118	118	118	118	116	118	118	118	104			109	108	37
Bhs[a]	5.40	24	1.2	3.3	42	17	51	32	18	8	41	15	0.89	0.22	0.004	5.6
n	41	12	48	48	48	48	41	48	48	48	41	22	22	45	45	28
Chs[b]	5.51	21	0.8	1.6	45	13	47	34	20	9	38	14	1.42	0.20	0.003	5.1
n	41	15	45	45	45	44	41	45	45	45	41	22	22	41	40	24
Stream	6.68	58	1	20	39	6	105	13	21	10	29			0.10	0.006	
n	104	103	106	106	106	106	100	102	102	102	97	26	26	86	98	

The number of analysed samples is also indicated (*n*).

[a] Denotes at 30 cm depth.

[b] Denotes at 50 cm depth.

[c] Denotes data referred to June 2000–December 2001.

Table 3. Average solute fluxes at various level in the forest [above canopy (BP), and below canopy (TF), and in soil solution (Bhs and Chs)] measured at Val Masino during a 3 years period (1999–2001).

	H_2O	N-NH_4	N-NO_3	TON	DOC[a]	SO_4	Cl	Ca	Mg	Na	K
	mm yr^{-1}					kg ha^{-1} yr^{-1}					
BP	1959(35)	6.57(13)	6.02(16)	2.67(68)		27.9(25)	4.73(33)	12.5(39)	1.26(37)	3.10(27)	1.99(23)
TF	1603(29)	4.16(4)	5.92(9)	6.82(7)	100	24.6(15)	6.21(22)	14.5(42)	2.33(27)	3.30(29)	22.2(14)
Bhs(30 cm depth)	1124(41)	0.16(36)	0.49(29)	2.49(31)	63	22.6(37)	6.51(38)	10.9(26)	4.25(36)	4.51(42)	3.36(41)
Chs (50 cm depth)	1124(41)	0.11(44)	0.23(64)	2.52(67)	57	24.9(42)	4.89(38)	10.5(40)	4.66(40)	5.02(34)	3.72(24)

Coefficient of variation is indicated in brackets.

[a] Denotes DOC fluxes are based on 1.5 yr of solution chemistry data.

composition of basic cations likely reflected the major rock-forming minerals of the watershed, considering that nearly one-third of the catchment consisted of bare rock. Streamwater N-NO_3 showed a significant increase over soil solutions levels and approached concentrations measured in the precipitation. Ammonium was nearly undetectable in soil and stream water. This N-NO_3 concentration difference between streamwater and soil solution was likely due to the hydrologic contribution of bare rocks, which form one third of the catchment, and other source areas located at higher elevations and on steeper slopes than the conifer forest and with a lower capacity to buffer or modify atmospheric inputs (e.g. Campbell et al. 2000a).

The analysis of organic components such as TON, TP and DOC revealed the importance of throughfall as source of organic compounds. Organic matter in throughfall derives mainly from the leaching of plant tissues and consists principally of carbohydrates, and to a lesser extent aminoacids, pectic and phenolic substances, vitamins, and hormones (Tukey 1970; Guggenberger and Zech 1994). Epiphytes and micro-organisms in the canopy could represent further contributors of organic C and N at the study site since the abundance of lichens occurs on the trees. The TON average concentration, 0.44 mg l^{-1}, was approximately four-fold the concentrations measured in the bulk precipitation and stream water and was quite similar to those reported for some European coniferous sites in Eastern Finland, Bavaria and Norway, as well as in the USA (Michalzik et al. 2001). Lovett and Lindberg (1993) also observed net retention of inorganic N coupled to net release of DON with passage of rainwater though forest canopies. Even in the soil solution, where the inorganic N concentrations and fluxes were nearly undetectable (Tables 2 and 3), organic N was the predominant N species. The mean organic N concentration declined in the mineral soil relative to the throughfall solutions and was lower than most values reported by Michalzik et al. (2001). Average TON in stream water, 0.10 mg l^{-1}, was slightly high relative to unpolluted forested sites in the Oregon Cascades (USA) (Vanderbilt et al. 2002), similar to the concentrations measured in small forested watersheds in New Hampshire (Campbell et al. 2000b; Goodale et al. 2000), but lower than values reported by Hedin et al. (1995) for pristine old-growth forested watershed in the southern hemisphere.

Throughfall and soil solution DOC concentrations fell in the lowest part of the concentration ranges (3–35 mg l^{-1} and 2–35 mg l^{-1}, respectively) measured in 42 forest sites in temperate regions (Michalzik et al. 2001). Balestrini and Tagliaferri (2001) reported close correlations between DOC and TON on the basis of a large throughfall data set collected at Val Masino. In the B horizon soil solution, DOC concentration was significantly linearly related with estimated organic anions ($p < 0.001$), TON ($p < 0.001$), Al ($p < 0.001$) and Fe ($p < 0.001$) (Figure 2). None of these correlations was significant in the C horizon. These results suggest that the process of podzolization is effective in the Val Masino soil. This is would also account for the lack of measurable SO_4 adsorption on the mineral soil (e.g. Johnson and Todd 1983). Many studies have shown that in the organic and eluvial horizons of a podzolic soil, Al is

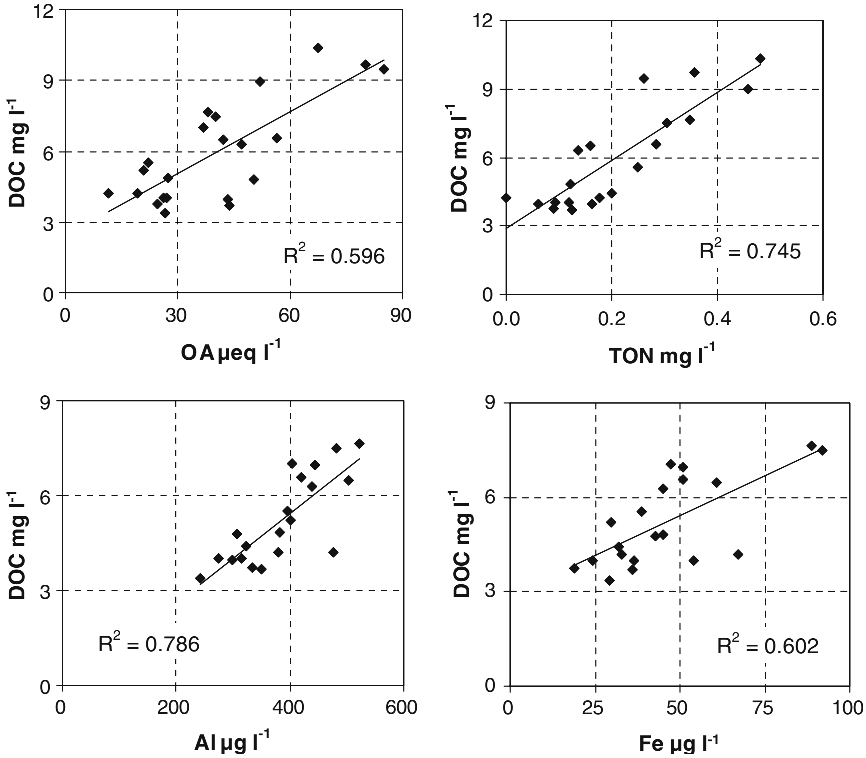

Figure 2. Linear regression between dissolved organic carbon (DOC) vs. organic acid (OA), organic nitrogen (TON), Al and Fe in the soil solution collected at B horizon.

strongly complexed with organic substances (Lundstrom et al. 2000). Given the strong correlation with DOC, the Al in the soil solution of Val Masino site, was probably in a complexed and therefore in a non-toxic form. The average DOC/TON ratios for throughfall, soil solution at 30 and 50 cm (19, 33, 42 respectively), referred to the period (May 2000–December 2001) for which both data were available, indicated a N impoverishment of DOM moving through the soil profile at Val Masino.

Temporal trends

Figures 3 through 5 show the monthly variations of the concentration means of the N species and SO_4 measured at Val Masino during the 1999–2001 period.

The atmospheric input, both in terms of bulk precipitation and throughfall, exhibited a marked seasonality for N-NH_4, N-NO_3 and SO_4, showing maximum concentrations during the spring–summer period and minimum values in winter. These temporal variations, already observed for a longer

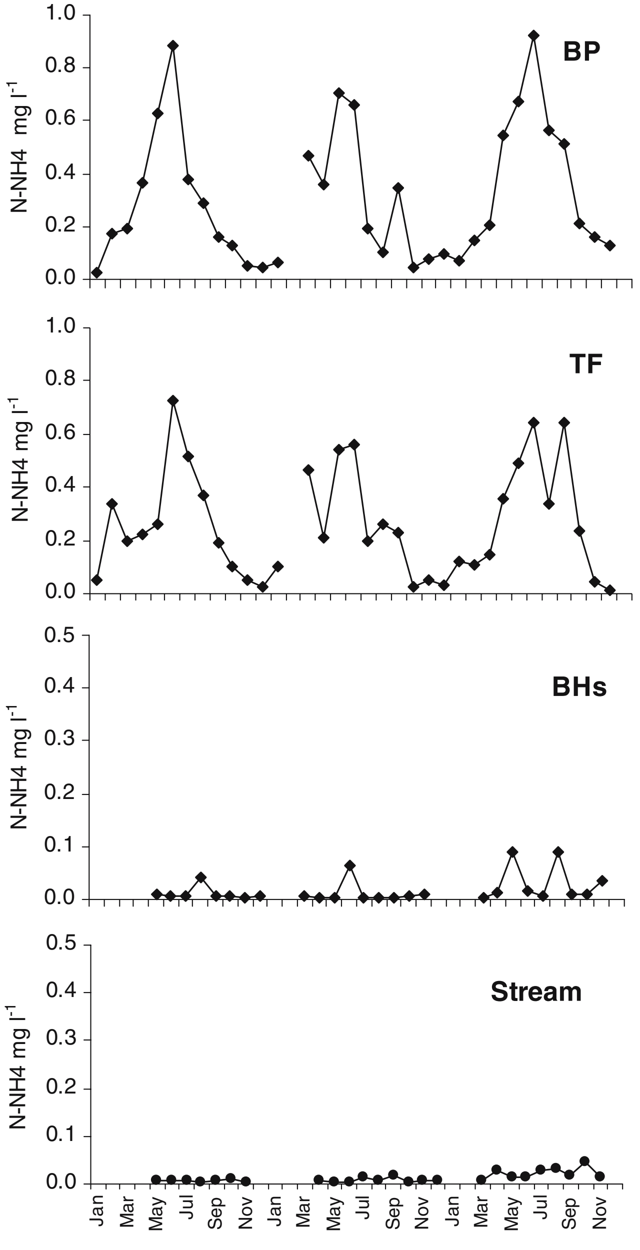

Figure 3. Monthly variations of N-NH$_4$ concentration in bulk precipitation (BP), throughfall (TF), soil solution from the B horizon (Bhs) and stream water, during the period March 1999 through December 2001.

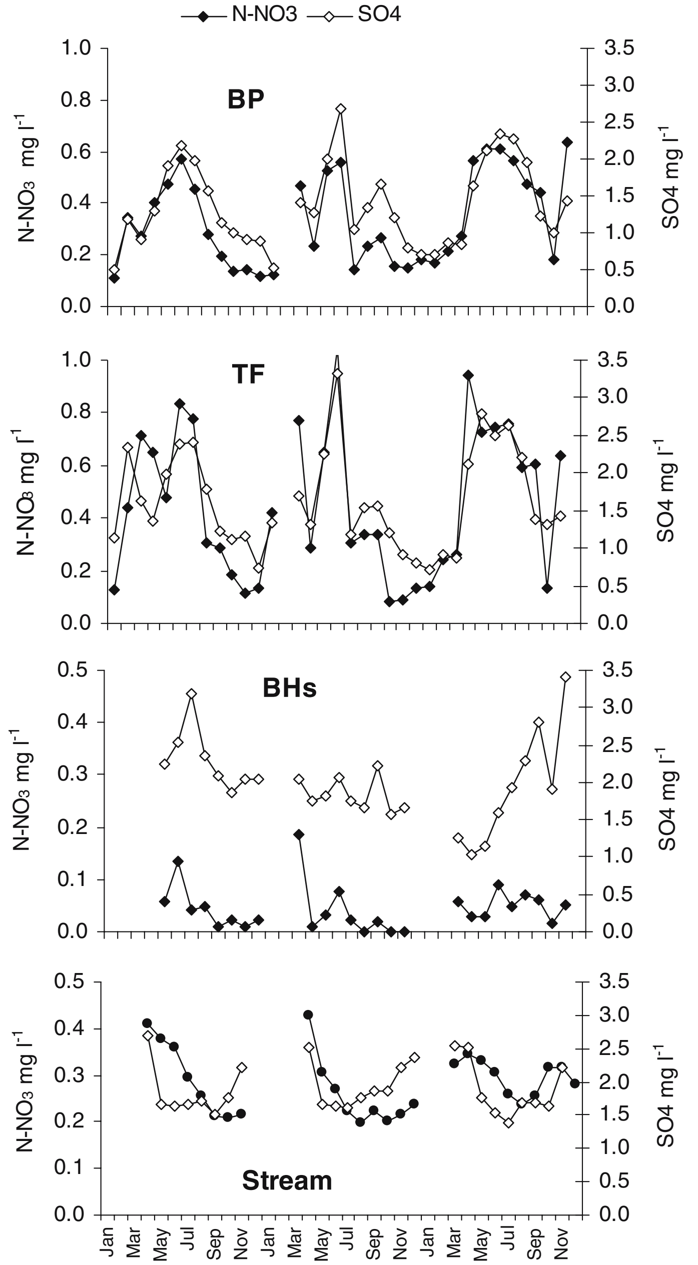

Figure 4. Monthly variations of N-NO_3 and SO_4 concentration in bulk precipitation (BP), throughfall (TF), soil solution from the B horizon (Bhs) and stream water, during the period March 1999 through December 2001.

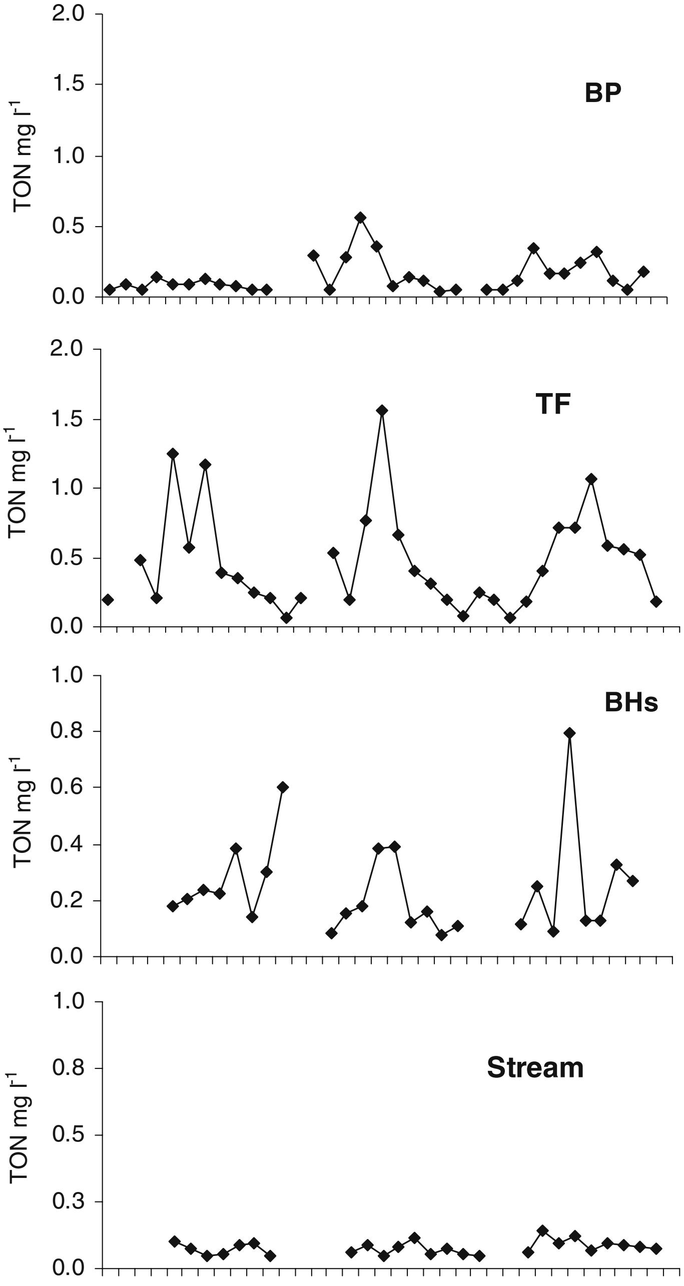

Figure 5. Monthly variations of TON concentration in bulk precipitation (BP9, throughfall (TF), soil solution from the B horizon (Bhs) and stream water, during the period March 1999 through December 2001.

period (1994–1999) in the same area (Balestrini and Tagliaferri 2001), are likely to be related to seasonal changes in the atmospheric stability. During summer, most pollutants in precipitation are probably transported into the region from long distances; in winter, the atmospheric deposition tends to contain ions of local origin. In the case of N-NH_4, the concentration increase during the warmer period is also connected to the biological processes within the soil favoured by high temperatures. The similarity in SO_4 concentration values between bulk precipitation and throughfall (Figure 4) does not indicate foliar washing of dry deposition.

No distinct temporal trends of N species were identified in the soil solution at both depths. The availability of N-NO_3 and N-NH_4 was attenuated as water passed through the mineral soil layers independent of season, although N-NO_3 showed some variability with highest concentrations in early spring. Ammonium concentrations were always close to the detection limit even in the stream. We can assume that during the growing season, coincident with the highest atmospheric N fluxes, all inorganic N was consumed by plants and microbiological community. During dormancy, the presence of the snow cover along with temperatures below 0 °C, interrupted the water flux through the soil. Subsequent thawing could account for the temporary flushing of N-NO_3 in early spring (e.g. Creed et al. 1996). The variation of SO_4 in the soil solution was similar to those observed for Cl, Ca, Mg and K. Particularly, this trend is characterised by (i) a peak during June–July 1999, (ii) roughly constant levels during 2000, (iii) an evident progressive increase of concentrations from April to November 2001. These concentration changes could depend on physical process of dilution, thus reflecting the availability of water in the soil. In effect, 2000 was the most rainy year with 2770 mm, while we measured the smallest amount of rainfall, 1600 mm, during 2001.

Stream water chemistry was characterised by distinct temporal variations, particularly evident for N-NO_3, SO_4 and base cations (data not shown). As shown in Figure 4, SO_4 exhibited higher levels in April, a rapid decrease to the summer months followed by an increase from the beginning of fall to the frozen period. This trend, observed also for the base cations, mirrored discharge, which reached the maximum in summer and the minimum in winter. There was indeed an inverse, highly significant ($p < 0.00001$) correlation between flow, expressed as hydrometric height, and SO_4 ($R^2 = 0.62$), Ca ($R^2 = 0.52$), Mg ($R^2 = 0.45$), K ($R^2 = 0.56$), and Na ($R^2 = 0.52$) concentrations, indicating the importance of the dilution process in controlling the variability of some solutes. Soil mineral weathering and cation exchange are the main source of base cations in stream water in most regions. Masino stream water SO_4 concentration was correlated to Mg and Ca ($R^2 = 0.52$; $p < 0.00001$) indicating that mineral weathering contributes to SO_4 export. On the other hand, given the low base saturation of the Val Masino forest soils (Table 1), little Ca and Mg could derive from displacement from the CEC. Soils also exerted a limited impact on modifying the SO_4 signal.

The N-NO_3 in the stream showed a maximum in April, a gradual decline with minimum in summer, followed by a stable period lasting until the end of autumn. Subsequently, the data seem to indicate trend of increasing N-NO_3 during the winter months. N-NO_3 was not related to the hydrometric height and this suggests that other factors, apart from discharge, controlled the seasonal trends of inorganic N in stream water. Where snowmelt dominates the annual stream hydrograph, an important factor affecting the seasonal variation of the stream water chemistry is the degree to which snowmelt is partitioned between surface overland flow and soil solution (Stottlemyer 1997). N-NO_3 concentrations in stream water were lower than those in precipitation from May to September and higher during the following winter months. The melting of snow characterised by low N-NO_3 concentrations and biological processes consuming N could explain the declining level during spring and summer. The release of soil inorganic N to stream water may become more important than atmospheric deposition in the cold (dormant) season (fall and winter) and during the beginning of snowmelt, generally occurring in April. With initial snowmelt, the draining of the upper organic soil layers can result in a small pulse in stream water N-NO_3 concentration (Campbell et al. 1995; Stottlemeyer 1997). The reduced biological sequestering in winter could account for the relatively high stream water N-NO_3 concentration observed in the river Masino during October–December period. Other studies on snowmelt-dominated streams underline the importance of flushing of soil water in influencing the stream water chemistry (Foster et al. 1989; Arthur and Fahey 1993; Creed et al. 1996; Stottlemeyer 1997). On the other hand, the substantial lower inorganic N concentration measured in the soil solution of mineral horizons at our study area, could indicate a lack of connection between deeper soil water draining the forest ecosystem and the stream water. Alternatively, it suggests that the stream water chemistry at the sampling point is not solely controlled by biogeochemical processes in the lower part of the catchment, dominated by conifer forest. It likely also reflects the hydrologic contribution of the higher parts of the catchment, where the massive presence of bare rocks limit the retention of atmospheric N inputs.

In throughfall, TON concentration showed a distinct seasonal variation (Figure 5) with maximum values in summer months and values close to detection limits in December. On monthly basis, the volume-weighted mean concentration of TON was positively correlated to temperature ($R^2 = 0.77$; $p < 0.0001$). These findings, consistent to those reported by Solinger et al. (2001), suggest the role of biological processes occurring in the canopy (e.g. by epiphytes and lichens) in changing the throughfall TON concentrations. While average concentration and annual fluxes of TON were generally lower in soil solutions than in throughfall, indicating net retention also of organic N in the soil, Figure 5 shows that TON in the soil solution was more seasonally variable than inorganic N. However, no discernable seasonal pattern emerged and concentrations did not appear to be driven by the magnitude and/or temporal variability of throughfall N inputs.

In stream water, the TON remained steady throughout the study period, but concentrations were too low to detect a seasonal pattern. In other studies in US forested sites in New England (Campbell et al. 2000b) and in Oregon (Vanderbilt et al. 2002), TON in stream water did not exhibit any strong temporal trend. There is a growing body of literature on the physical and biological mechanism that control DOC and dissolved organic matter (DOM) in mineral soils and water (e.g. Kalbitz et al. 2000; Neff and Asner 2001), but far less has been published on DON control mechanism. Comparison of temporal patterns would suggest that inorganic and organic N are subject to different control mechanisms.

Input–output fluxes

Solution fluxes through the various levels of the forest, estimated on a three-year basis (1999–2001), are presented in Table 3. The contribution of dry deposition was assessed by applying the canopy budget model (Balestrini and Tagliaferri 2001) and by direct measurements by using a modified wet and dry sampler (Balestrini et al. 2000). Both methods revealed a negligible contribution of the dry component for N and S species. Therefore in the current analysis bulk precipitation was considered a good measure of total N and S input to the site. The input of N and S species estimated for this short period were comparable to the 9-year (1995–2003) average reported in Table 4.

Average annual N input was around 15 kg ha^{-1} yr^{-1} with $N\text{-}NO_3$ and $N\text{-}NH_4$ contributing comparable amounts (~6 kg ha^{-1} yr^{-1}), and organic N representing only 20% of the total bulk input. The N flux in throughfall was somewhat higher (17 kg ha^{-1} yr^{-1}) and N species composition was different from bulk precipitation in that organic N comprised more than 40% of the total N. A similar throughfall N speciation was reported for a number of Italian alpine sites (Mosello et al. 2002a). Several studies have shown that DON can cover 50% or more of the total dissolved N flux in throughfall (Qualls et al. 1991; Lajtha et al. 1995). The reduction in inorganic N loading below the canopy was compensated by the marked increased in the organic N suggesting that $N\text{-}NH_4$ in solution has been replaced or metabolised to the organic form. Our data suggest a net canopy release of TON in the order of

Table 4. Bulk precipitation (BP) and throughfall (TF) fluxes measured at Val Masino during a nine years period (1995–2003).

	SO_4	Cl	$N\text{-}NO_3$	$N\text{-}NH_4$	TON
BP	25.0(24)	4.4(23)	5.7(17)	5.9(20)	3.1(32)
TF	22.5(21)	6.0(23)	6.0(17)	3.7(24)	7.4(18)

Average and coefficient of variation, in brackets, are indicated.

4 kg ha^{-1} yr^{-1}, and some retention of N-NH$_4$. This is consistent with other studies of net canopy exchange of N species (Lovett and Lindberg 1993; Sutton et al. 1995).

The three-year average N output (~3 kg ha^{-1} yr^{-1}) indicates that 80% of the input to the site is retained within the mineral soil. While there was some retention or transformation of N-NH$_4$ in the forest canopy, 98% of the N-NH$_4$ and 96% of N-NO$_3$ was removed in the soil. The depletion of N-NH$_4$ in the mineral soil solution may have resulted to some extent from fixation on the cation exchange complex, but was most likely due to biological uptake. The microbial conversion to N-NO$_3$ may occur in the upper soil layer, but no data are available for Val Masino soils. The root and microbial uptake is like to be the major process affecting the great retention of N-NO$_3$ in the soil solution. Soils that remain mostly wet and are high in organic matter represent ideal conditions for N-NO$_3$ removal through denitrification. However, no direct measures of this process are currently available for this study site or similar ecosystems nearby. Below the rooting zone the retention of N-NO$_3$ is almost complete. At both soil depths the measured fluxes were lower than the value of 1 kg ha^{-1} yr^{-1} reported in literature for N-limited forests (Gundersen and Rasmussen 1990).

More than 40% of both TON and DOC was removed as throughfall water percolated through the soil profile. The retention of dissolved organic N and C in the mineral soil layers, observed in several experimental forest sites (Michalzik et al. 2001), may be due to the decomposition or adsorption processes. The results from biodegradability studies of DOM in a forest ecosystem profile (Qualls and Haines 1992; Guggenberger and Kaiser 2003) have suggested that physical (adsorption) rather than biological processes are primarily responsible for the removal of organic N and C in the mineral soil, although some authors have not excluded the possibility of microbial DOM decomposition which favours transport of residual, recalcitrant DOC at greater soil depth (Kalbitz et al. 2000; Neff and Asner 2001). Qualls and Haines (1992) and Hedin et al. (1995) have further hypothesised that DON in the streams is mainly composed by refractory fulvic acids, a form that is relatively unavailable to the biota. Flux of DOC at the Hubbard Brook Watershed also increased with passage of water through the forest canopy and forest floor and subsequently decreased due to the abiotic sorption in the mineral soil (McDowell and Likens 1988). At Val Masino the organic N output (2.5 kg ha^{-1} yr^{-1}), accounting for 90% of the total N in the mineral horizon, is quite comparable to the values reported by Lajtha et al. (1995) (~3.5 kg ha^{-1} yr^{-1}) and Friedland et al. (1991) (about 1.5 kg ha^{-1} yr^{-1}) who observed organic N retention of 50–57% in the soil solution. A much smaller N load has been observed in the B horizon of a mixed boreal forest in Finland (~0.1 kg ha^{-1} yr^{-1}) where the retention was almost total (90%) (Pirainen et al. 1998). In these four study sites (including our site) the TON outputs likely originated from throughfall. Until recently, many studies of ecosystem N budget calculations did not include organic N and degree of N saturation of catchments is still largely assessed based streamwater N-NO_3 signals (Stoddard 1994). Inclusion of TON in the Val Masino mass balance slightly reduced the total ecosystem N retention to 82%. In many instances, as was for example case in the Harvard Forest, the inclusion of DON losses in N balance reduced the total N retention efficiencies at moderate rate of atmospheric N deposition (8 kg ha^{-1} yr^{-1}). In that study, little change in DON exports was observed at higher levels of N additions (50 and 150 kg ha^{-1} yr^{-1}) (Aber et al. 1998).

Average input of SO_4 in bulk precipitation between 1999–2001 was 28 kg ha^{-1} yr^{-1}, somewhat higher than the 9-year average of 25 kg ha^{-1} yr^{-1}. No important variation emerged examining the changes in SO_4 fluxes as the solution passes through the various components of the forest ecosystem. The slight reduction in the throughfall, between 3–20% on a yearly basis, may be related to the concomitant decrease in the water flux (13–22%). The SO_4 fluxes in the mineral soil layers had a high coefficient of variation (~40%), relative to SO_4 concentrations showed a (11–14%), suggesting that even in the soil, SO_4 flux seemed more dependent on water movement through the system than on internal soil processes such as adsorption. Thus, in general, higher precipitation resulted in greater the bulk deposition input and the soil solution output. This interpretation is in agreement with observations of Likens et al. (2002) and Friedland and Miller (1999) indicating a strong relation between sulphur cycle and hydrology in some forest ecosystems.

Nitrogen status

The comparison with the critical loads estimates of N and S for forest soils in Italy (Posch et al. 1997) indicates that the critical load for N as a nutrient (C.L.N.), 5.8 kg ha^{-1} yr^{-1}, has been exceeded at Val Masino site. In contrast, values for SO_4 were well below critical loads (54.6 kg ha^{-1} yr^{-1}). The great retention of N (12 kg ha^{-1} yr^{-1} or 80% overall) in the mineral soil level suggests that the coniferous forest at Val Masino is still limited by N, despite the relatively moderate atmospheric N deposition inputs to the ecosystem relative to more typical N inputs to the forest ecosystems ranging more than 40 kg ha^{-1} yr^{-1} to a low of 2 kg ha^{-1} yr^{-1} for the uncontaminated areas.

The comparison to other N budgets reported in the literature indicates a high N-NH_4 retention, which appears independent from the N input, but a variable response for N-NO_3. An analysis of an European data base (65 forest catchments) showed that at N inputs < 10 kg ha^{-1} yr^{-1}, N was mostly retained, while sites receiving about 25 kg N ha^{-1} yr^{-1} exhibited variable N outputs with some locations retaining all the N and other leaching significant amounts (Dise and Wright 1995). Johnson (1992) likewise showed that N retention efficiency under high chronic N input regimes was highly variable, and could only partially be explained by tree uptake. Furthermore, high retention of experimental addition of inorganic N to forest has been reported in a number of investigations carried out over Europe and the USA (Gundersen et al. 1998a; Mitchell et al. 2001).

Even after 6 years of huge N-addition (50 and 150 kg ha^{-1} yr^{-1}) at the Harvard Forest, Magill et al. (1996) observed that 85–99% of N was retained. The poor relationship between N retention and N deposition that has emerged from N fertilisation studies, points at the role of the soil, rather than plants, as the dominant sinks for atmospheric N deposition. Aber et al. (1998) has suggested mycorrhizal assimilation as a potential biological mechanism for N immobilisation in the soil without biomass production, and a shift in the dominant soil community from fungal (mycorrhizae) to bacterial could be a key process in the evolution of an ecosystem towards N saturation (Aber et al. 1998; Tietema 1998). However, these hypotheses have not been currently demonstrated by direct measurements of mycorrhizal assimilation efficiencies. There is also increasing evidence of abiotic N-NO_3 immobilisation process in forest soils (Johnson et al 2000; Davidson et al. 2003), or abiotic transformation of N-NO_3 into dissolved organic N in organic horizons of Harvard Forest, USA (Dail et al. 2001) and of temperate forests in Chile (Perakis and Hedin 2001).

Using three European independent datasets, Gundersen et al. (1998b) found a close negative correlation between N-NO_3 leaching and forest floor C/N ratios, with a lower threshold at C/N ratio of 25 where N-NO_3 leaching seem to increase. Likewise, observations within the Integrated Forest Study (IFS) showed that forest soils with C/N ratios >20 generally retained N (Van Miegroet et al. 1992). In the current study the organic horizon had C/N ratio of about 20, yet no leaching has been observed. On the other hand, the DOC/TON values in the soil solutions (around 35) are lower than the stream water ratio (61) reported for pristine unpolluted watershed in Chile (Hedin et al. 1995; Perakis and Hedin 2002) and similar to the ratios in losses from North American forests (Campbell et al. 2000b).

Prior land use, such as massive export of N due to agricultural conversion, fire, or harvesting, seems to play an important role as a predisposing factor in N saturation (Aber et al. 1998; Fenn et al. 1998), in part by reducing soil N pools in the soil and thus N losses in solution (Van Miegroet et al. 1992). Dendrochronologic surveys carried on in the Val Masino indicate a significant alteration event corresponding to the removal of a large portion of the forest during the early fifties (Azienda Regionale delle Foreste 1998). Such change in ecosystem structure and age composition has been shown to impact N retention and N-NO_3 losses even in systems receiving far higher N deposition inputs (Silsbee and Larson 1983; Emmett et al 1993).

Another important indicator of the N status of a forest ecosystem is the N concentration in the needles because of its positive correlation with N in throughfall and N-NO_3 leaching (Gundersen et al. 1998a; Mc Nulty et al. 1996). In response to long-term N additions, an increase in foliar N concentrations and a decrease in Mg/N ratios were also observed in the Harvard

Table 5. Nutrient foliar concentrations and relative ratios measured in the current needles of spruces at Val Masino (from Ballarin-Denti et al. 1998 and Matteucci et al. 1999).

Years	N	P	K	Ca	Mg	N/P	N/K	N/Ca	N/Mg
	mg g^{-1}								
1994	13.4	2.15	7.45	5.1	1.15	6.2	1.8	2.6	11.6
1995	11.8	1.2	4.95	4.75	1.35	9.8	2.4	2.5	8.7
1996	10.7	1.6	6.4	2.18	0.76	6.7	1.7	4.9	14.1
1997	11.6	1.81	3.67	5.37	1.50	6.4	3.2	2.2	7.7
1999	16.1	1.7	5.97	8.36	1.27	9.4	2.7	1.9	12.6
2001	20.0	2.03	6.38	5.72	1.44	9.9	3.1	3.5	13.9

Forest pine stand and at the Mt. Ascutney site (Aber et al. 1998). Measurements of foliar nutrients were performed at Bagni di Masino since 1994 (Table 5) (Ballarin-Denti et al. 1998; Matteucci et al. 1999). While the increase in N concentration as of 1999 has to consider a change in the analytical method to determine N in foliar tissues (from Kjeldahl to CHN device), overall the N values and related nutrient ratios are in the range reported in the literature for spruce in a ‘normal or adequate’ condition (De Vries et al. 2000).

While a number of observations, notably the strong N retention, seem to indicate N-limitation in the forested portion within Val Masino, other observations, such as the composition of the DOM and the foliage, point in the opposite direction. Also, the multi-annual monitoring of surface waters indicates relatively high N-NO_3 concentrations in the Masino river, never below 10 μeq l^{-1}, suggesting a surplus of N bioavailability in the terrestrial ecosystem, corresponding to a transition between the stage 1 and 2 of the N saturation on the basis of the approach of Traaen and Stoddard (1995). Furthermore, the mass balance of the catchment, using the water of the River Masino as output, even if based on only one year of measurements, revealed that only 50% of inorganic N is retained (Balestrini et al. 2002). This apparent contradiction is very useful to illustrate the complexity of the alpine catchments where rapid changing in altitudinal levels correspond to a wide variety of environments (e.g. forest, shrubs, meadow, etc.) with their own specificity in response to and processing of atmospheric N input. The multiple value (ecological, economical, recreational) of forests drives the scientific interest in this component of the alpine ecosystem, despite the fact that is only occupies a fraction of the entire catchment (less than 15% in this study). The N export over a broad area (catchment level) is heavily affected by the geomorphological characteristics of the catchment, such as elevation, runoff, soil cover percentage, slope, roughness, as well as the N deposition loading (Flury et al. 1994; Sickman et al. 2002). Particularly, the soil cover resulted the principal factor explaining the 90% of the inorganic N retention in several high-elevation basins in the Rocky Mountains, USA (Sickman et al. 2002). The Val Masino catchment is characterised by steep rocky slopes, heterogeneous soil structure, low soil cover percentage (almost one third of the catchment consists of bare rock), and low percentage of forested area. These features do not favour strong interaction between nutrients in the water and biological community, and consequently curtail efficient retention of N. Schleppi et al. (1998) hypothesised that quick preferential water flow constrains the retention of N-NO_3 from rain or snowmelt before entering the water runoff pathways in an experimental headwater catchment in Swiss Prealps. In that area, the leaching of inorganic N, mainly as N-NO_3, was estimated to be 4 kg ha^{-1} yr^{-1}. Different conclusions were drawn from other studies showing that N-NO_3 leaching during snowmelt had an isotopic signature that indicated biological transformation (nitrification) in both forested and alpine catchments (Kendall et al. 1995). While authors agree that the type of processes governing N retention and leaching in alpine environments are similar to those taking place in the forest, what fundamentally changes is the size of the N pools (Sickman et al. 2002). In a study of the alpine soils and lakes in the Tatra Mountains, the negative correlation between lake N-NO_3 concentrations and catchment soil pools was explained by the greater retention of inorganic N in the catchment with larger soil pools (Kopacek et al. 2004). The N levels in the river Masino may be mainly regulated by the water inputs interacting with the organic soil layers and bare rocks where the biological N demands are well below the N deposition rates measured during the last decade in Val Masino.

Conclusion

The hydrochemical data collection at different levels (rainfall, throughfall, soil leachates and stream water) has given us some useful insights into the N biogeochemistry of N at Val Masino forest ecosystem.

Based on our three-years study, the response of this forest to N atmospheric inputs, which are higher than those expected for unpolluted areas, seems to indicate a balanced condition. The high retention efficiency of N observed in the soil, as well as consistently low N-NO_3 and N-NH_4 concentrations in soil solutions, suggest a condition of N limitation. Other indicators of N status, such as N foliar content and the assessment of crown condition indicate a healthy spruce forest (Azienda Regionale delle Foreste 1998). While this study did not allow us to identify specific mechanisms, we hypothesize that abiotic of N-NO_3 immobilisation involving the soil organic matter as well as denitrification may have occurred, but further research on the fate and the dynamics of organic and inorganic N is essential. Continued soil solution monitoring in the future, including sampling in the surface layer (15 cm depth), will allow us ascertain long-term trends in soil solution chemistry.

The high N-NO_3 concentrations measured in the stream were somewhat unexpected and suggest a surplus of N bioavailability at the level of the catchment. The chemistry of the stream integrates prevailing processes acting in the entire catchment where different types of land cover are present, some of which with N retention capacities vastly different from those observed in the conifer forest. Additional investigations at Val Masino should therefore focus on the herbaceous communities above the treeline, which cover a large portion of the catchment and they might represent the more fragile component of the alpine ecosystems.

Our findings also suggest the importance of distinguishing between N-NO_3 export data obtained from stream water monitoring versus lysimeter samples and highlight the need for combined micro-scale and catchment-level investigations.

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