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**Variability in
mountain lake water
N isotopes**

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Nitrogen stable isotopes of ammonium and nitrate in high mountain lakes of the Pyrenees

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Abstract

Nitrogen stable isotopes ($\delta^{15}\text{N}$) are increasingly used to trace food web relationships and the flow of matter in lakes. However, there is high variability in $\delta^{15}\text{N}$ among primary producers and other primary energy resources that can eventually propagate throughout the lake food web. To increase our understanding of the origin of this variability, we measured ammonium and nitrate $\delta^{15}\text{N}$ in atmospheric deposition (AD), epilimnetic water (EW), deep chlorophyll maximum water (DCMW), and sediment porewater (SPW) in eight mountain lakes. A general $\delta^{15}\text{N}$ (-3.4‰) for AD was estimated as the signature for AD ammonium and nitrate did not differ. All lakes showed similar high $\delta^{15}\text{N}\text{-NH}_4^+$ values for SPW (ca. 2.2‰). In contrast, the variability among lakes in water column values was high, although differences between EW and DCMW within a lake were low. $\delta^{15}\text{N}\text{-NO}_3^-$ correlated with the altitude of the lakes, and its variability was interpreted as the influence of catchment nitrification, which is higher in talus landscapes. $\delta^{15}\text{N}\text{-NH}_4^+$ distribution had two modes, positive values (ca. 3‰) were associated to DCMW of shallow lakes, and probably reflect the SPW influence. Lower values (ca. -3‰) occur in EW and DCMW of deep lakes, and its variability was related to the degree that NO_3^- was up taken by primary producers and recycled within the food-web when NH_4^+ availability was low compared to demand. Overall, altitude, lake depth and seasonal cumulative primary production largely explain the patterns of $\delta^{15}\text{N}$ variability observed in nitrogen dissolved compounds.

1 Introduction

Stable isotopes of nitrogen are increasingly used to trace food web relationships and the flow of matter in aquatic ecosystems (Fry, 2006). Beyond discussions of the fractionation values at each trophic level, a key aspect that is still a source of major uncertainty is the understanding of the variability in primary producers (Vander Zanden and Rasmussen, 1999). Occasionally, this variability can be so high locally that researchers

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prefer to use primary consumers as the trophic level for reference (Post, 2000). Much of the variability of the nitrogen stable isotope ratio in primary producers comes from the specific source of nitrogen used and the biogeochemical pathways behind it. Ammonium and nitrate are the predominant inorganic nitrogen forms in natural waters. They are the main nitrogen sources for algal and bacterial growth and, consequently, for the food web as a whole. In this study, we examine the patterns of variability of the nitrogen stable isotope ratio of dissolved ammonium ($\delta^{15}\text{N-NH}_4^+$) and nitrate ($\delta^{15}\text{N-NO}_3^-$) in high mountain lakes.

Atmospheric deposition is the dominant source of N compounds in most high mountain catchments (Wookey et al., 2009). Although nitrate and ammonium are deposited in similar proportions (Camarero and Catalan, 1996), nitrate is the major N form that enters lakes from catchments (Hood et al., 2003). Indeed, ammonium is either highly retained in the catchment, by biological assimilation and sorption in mineral soil horizons, or transformed into nitrate by bacterial nitrification (Campbell et al., 2000). Within the lake, ammonium is abundant in the sediment porewater, due to organic matter mineralization, and diffuses to overlying water. NH_4^+ is also excreted by organisms living in the lake as a by-product of their metabolic activity. In general, NH_4^+ is preferred over NO_3^- as the N source by primary producers, as it does not require internal reduction (Falkowski, 1983). However, it is advantageous to use NO_3^- when NH_4^+ is scarce (ca. $<1 \mu\text{mol L}^{-1}$; McCarthy (1980)). NO_3^- and NH_4^+ can also be resources or products in several bacteria-mediated biogeochemical pathways.

Any reactive or diffusive process where NO_3^- and NH_4^+ are involved can provide N isotopic fractionation, e.g., nitrification (Mariotti et al., 1981), denitrification (Choi et al., 2001), N uptake by osmotrophs (Hogberg, 1997), ammonia volatilization (Hogberg 1997), organic matter mineralization (Lehmann et al., 2002), atmospheric N_2 fixation (Shearer and Kohl, 1986), assimilation (Wada and Hattori, 1978; Doi et al., 2004) and diffusive processes between compartments (e.g., sediment-water (Owens, 1987)). However, not all the potential processes are equally relevant in a specific ecosystem as sources of variability in nitrogen stable isotope ratios. On the one hand, some

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processes require particular environmental conditions, for instance, concerning oxygen or light conditions. On the other hand, fractionation generally occurs if there is a large pool of substrate and the amount actually used in the process is small compared to the pool size (Hoch et al., 1992; York et al., 2007).

In mountain lakes there are two main large pools of nitrogen that can supply the water column, namely, soil catchment and sediment pools. They have contrasting characteristics. Supply from the catchment is mostly in nitrate form (Campbell et al., 2002), which originates directly from deposition or from catchment nitrification of ammonium. Talus landscapes show higher nitrification and mineralization rates (Campbell et al., 2000), and eventually higher nitrate loadings to the lakes, than flatter and more vegetated areas which retain more nitrogen from deposition. In contrast, sediments are rich in ammonium from recycled organic matter. Nitrogen stable isotope ratios in the water column ($\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NH}_4^+$) largely depend on the relative importance of the contribution of these two large pools and the characteristics of their use and recycling within the water column.

High mountain lakes are essentially oligotrophic ecosystems. Variability in catchment characteristics mostly depend on the altitudinal position (Korner, 2007), which also has a large influence on lake thermal characteristics (Catalan et al., 2009b). Lake area or depth, which are highly correlated between them in these systems (Catalan et al., 2009b), provide an additional source of variability in lake dynamics. However, while lake changes in altitude are relatively gradual, depth mostly divides lakes into two types of contrasting characteristics (Catalan et al., 2009a): deep lakes (ca. >15 m depth) are characterised by a large volume hypolimnion with a zone where processes of mineralisation of organic matter permanently predominate over photosynthetic ones; whereas shallow lakes (ca. <15 m depth), show a relatively small hypolimnion, highly affected by metalimnetic and boundary layer transport, and mostly phototrophic because of the high transparency of the water in these lakes (Buchaca and Catalan, 2008). Therefore, to investigate the variability in $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NH}_4^+$, we selected an altitudinal gradient of lakes including deep and shallow types. For each lake we measured the

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NO_3^- and NH_4^+ concentrations and their nitrogen isotopic ratio in three compartments during stratification, namely, epilimnetic water (EW), deep chlorophyll maximum water (DCMW), which typically occurs in the hypolimnion in these lakes, and sediment porewater (SPW). In addition, we also measured the isotopic composition of both compounds in atmospheric deposition. The aims of our study were:

1. to assess how the two main phototrophic areas in these lakes (i.e., EW, DCMW) differentiate in $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{15}\text{N}\text{-NH}_4^+$ depending on the lake position in the altitudinal gradient, and lake size; and
2. to what extent in each case it may depend on catchment (mostly NO_3^-) and sediment loadings (mostly NH_4^+), and water column processes.

2 Materials and methods

2.1 Study sites

The lakes are located in three catchments within an area of less than 15 km radius. All basins are on granodioritic bedrock of the Maladeta batholith in the Central Pyrenees (NE Spain) (Fig. 1). The eight lakes cover an altitudinal gradient of 1068 m (Table 1). This gradient reflects a shift in land-cover type from bare rock and thin and poor soils in high altitude areas to extensive vegetation and well-developed soils at lower sites. The tree line is at ca. 2200 m a.s.l. Other general physical and chemical characteristics of the lakes are relatively similar (Table 1), with the exception of depth. The lakes are dimictic, covered by ice for 5 to 8 months a year, oligotrophic, and with low ionic content and acid-buffering capacity. After the snow and ice cover melting, deep water column mixes and ammonium and nitrate concentrations homogenise throughout the water column (Catalan, 1992). As soon as lake water reaches 4°C, the water column stratifies and phytoplankton blooms. During summer stratification, the photic zone is deeper than the thermocline. Light penetration is high and the Secchi disk depth may reach up to 20 m in the deep lakes and usually reaches the bottom in shallow lakes.

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Deep chlorophyll maximum develops at about 1.5 times the Secchi disk depth or just a few centimetres above the bottom in shallow lakes (Catalan et al., 2002). We used dissolved reactive silica (DRSi) as a proxy for water column productivity during early summer, as it is a primary nutrient for diatoms, we assumed that the lower DRSi the higher the seasonally accumulated primary productivity (Catalan et al., 2002).

2.2 Sampling

Deposition sampling was carried out fortnightly from 1 June to 25 August 2006. Samples were collected at 2240 m a.s.l., which corresponds to the centre of the lake altitudinal distribution. Deposition at this point was considered representative, due to the previously observed lack of significant differences in the chemistry of bulk precipitation within the altitudinal range in this area (Camarero and Catalan, 1996). Water samples for $\delta^{15}\text{N-NO}_3^-$ analysis were field-filtered (pre-ashed Whatman GF/F, 0.7 μm pore size) into clean polypropylene hermetic bottles and refrigerated (-20°C) until analysis, following Spoelstra et al. (2004). With this method, Spoelstra et al. (2004) found no detectable nitrate production or assimilation in the samples during a two-week incubation period, and, that atmospheric nitrate isotopic ratios were preserved.

Lakes were surveyed during the first week of August 2004. Within each lake, EW, DCMW and SPW were sampled for NO_3^- , NH_4^+ , $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NH}_4^+$ analyses. EW was sampled at 1 m depth, DCMW at 1.5 times the Secchi disk depth or, alternatively, from 1 m above the bottom when the Secchi disk was still visible at the lake bottom. These two water column samples were collected by means of a Ruttner bottle and treated in the same way as described for deposition samples. SPW was sampled using a gravity core. Immediately, the first five centimetres were extruded and stored in a polypropylene hermetic bag without air. This bag was transported cold to the lab where it was frozen. SPW was finally obtained after defrosting by high-pressure squeezing-filtration with Whatman GF/F 0.7 μm pore size. NO_3^- concentrations in SPW were very low. As a result, SPW NO_3^- isotopic composition could not be determined as it would have required about 4 L of porewater.

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2.3 Chemistry analysis

NH_4^+ was determined according to Solórzano (1969). NO_3^- was determined using a Waters Quanta 4000 Capillary Electrophoresis system. pH was measured with an Orion Research model 720 A pHmeter, with a low ionic strength filling solution in the pH electrode (KCl1M). Sediment loss on ignition (LOI) was carried out at 550°C , as an estimation of the organic content of the sediment samples (Heiri et al., 2001). Acid neutralising capacity (ANC) was determined by Gran titration. Conductivity was determined with an Instran-10 conductimeter. Dissolved inorganic carbon (DIC) was determined on a Shimadzu TOC-5000 analyzer by IR absorption. Total phosphorus was determined according to the Malachite green method, with previous acid persulphate digestion (Camarero, 1994). Dissolved reactive silica (DRSi) was determined with the blue silicon-molybdenum method (Grasshoff et al., 1983).

Stable isotopic ratios of NH_4^+ and NO_3^- were determined by the alkaline headspace diffusion methods of Holmes et al. (1998) and Sigman et al. (1997), respectively. For the $\delta^{15}\text{N}$ of NH_4^+ , magnesium oxide (MgO) was added to increase the pH and to convert NH_4^+ to NH_3 . A filter pack consisting of an acidified (KHSO_4 2.5 M) glass fibre filter sandwiched between two Teflon filters was placed in each sample bottle in the field. Back in the lab, the samples were incubated on a shaker table at 40°C for 14 days, to promote diffusion of NH_3 towards the filter pack. To determine the $\delta^{15}\text{N}$ of NO_3^- , samples were initially boiled, with MgO added, and vaporised up to 100 mL to concentrate and drive off NH_4^+ as NH_3 . Thereafter, Devarda's alloy was added to samples, which were placed in an oven at 60°C for 48 h to reduce NO_3^- to NH_4^+ . The rest of the $\delta^{15}\text{N}$ - NO_3^- procedure continued as for the $\delta^{15}\text{N}$ - NH_4^+ procedure. Filter packs from these analyses were analysed for the nitrogen isotopic ratio on a Europa Integra mass spectrometer (Sercon) at the University of California Davis Stable Isotope Facility. During analysis, samples were interspersed with several replicates of at least two different laboratory standards. These laboratory standards, which were selected to be compositionally similar to the samples being analysed, had been previously calibrated

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against NIST Standard Reference Materials (IAEA-N1, IAEA-N2, IAEA-N3 and IAEA-CH7) (Gonfiantini, 1978). A sample's preliminary isotope ratio was measured relative to reference gases analysed with each sample. These preliminary values were finalised by adjusting the values for the entire batch based on the known values of the included laboratory standards. The precision of replicate analyses of standards was 0.2%. Corrections to isotope values were calculated according to Holmes et al. (1998) and Sigman et al. (1997). Standards were analysed concurrently, with every set of samples analysed for NO_3^- and $\text{NH}_4^+ \delta^{15}\text{N}$. They were prepared by adding an ammonium stock solution of known isotopic composition to the same bottles to achieve an ammonium concentration similar to that expected. We used deviations between the known concentration and isotopic composition of the standards and the values obtained after the procedure to correct the sample results. $\delta^{15}\text{N}\text{-NO}_3^-$ values were also corrected for any N added due to Devarda's alloy contamination (Devarda's blanks), as described in Sigman et al. (1997). Deviations due to the different bottle volumes used during the analysis were also corrected according to Holmes et al. (1998).

3 Results

3.1 General patterns

There were very distinctive patterns in NO_3^- and NH_4^+ concentrations and stable isotope ratios among the compartments studied (Fig. 2). The largest concentrations were found in deposition and porewater, but stable isotope ratios were contrasting between them. NO_3^- and NH_4^+ concentrations in atmospheric deposition were $40 \pm 17 \mu\text{mol L}^{-1}$ and $47 \pm 29 \mu\text{mol L}^{-1}$, respectively, differences between them being not significant ($t = -0.6$, $\text{df} = 10$, $p\text{-value} > 0.5$), which was also the case for $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{15}\text{N}\text{-NH}_4^+$ ($t = 0.6$, $\text{df} = 10$, $p\text{-value} > 0.5$). Therefore, a tentative weighted average value of $-3.43 \pm 1.13\text{‰}$ was estimated for atmospheric $\delta^{15}\text{N}$ in the area. SPW NH_4^+ concentrations were remarkably high, $98 \pm 72 \mu\text{mol L}^{-1}$, whereas SPW NO_3^- was below $1 \mu\text{mol L}^{-1}$ in four

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lakes, and average concentration was low ($1.5 \pm 1.7 \mu\text{mol L}^{-1}$). This low concentration prevented the determination of $\delta^{15}\text{N-NO}_3^-$ in porewater. SPW $\delta^{15}\text{N-NH}_4^+$ was $2.2 \pm 1.5\text{‰}$, contrasting with the negative values in the deposition nitrogen. It is worth to highlight the low variability in SPW $\delta^{15}\text{N-NH}_4^+$ among lakes.

Nitrogen concentrations in water column compartments were lower than in deposition and porewater. NH_4^+ concentrations were particularly low compared to nitrate, the average was $0.8 \pm 0.3 \mu\text{mol L}^{-1}$, with no significant differences between EW and DCMW values ($t=0.6$, $\text{df}=14$, $\text{p-value}<0.5$). NO_3^- average in the water column was $8 \pm 5 \mu\text{mol L}^{-1}$, the range of values found was large compared to NH_4^+ concentrations (Fig. 2). In contrast, the range of $\delta^{15}\text{N-NH}_4^+$ values was much larger than for $\delta^{15}\text{N-NO}_3^-$, the former covering the whole range found in deposition and porewater, and going beyond that at both extremes (Fig. 2). Water column $\delta^{15}\text{N-NO}_3^-$ values were generally lower than in deposition ($t=-8.0$, $\text{df}=15$, $\text{p-value}<0.000$), without major apparent differences between EW and DCMW (paired $t=0.6$, $\text{df}=7$, $\text{p-value}=0.6$). The average value was $-6.5 \pm 2.0\text{‰}$.

3.2 Relationship between water column patterns and environmental lake features

Both $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NH}_4^+$ showed large variability in the water column among lakes (Fig. 2). EW and DCMW $\delta^{15}\text{N-NO}_3^-$ were both significantly related to lake altitude, the more negative the higher the elevation ($r^2=0.48$, $\text{p-value}<0.05$ and $r^2=0.55$, $\text{p-value}<0.05$, respectively, Fig. 3). $\delta^{15}\text{N-NH}_4^+$ showed the largest range of variability, which covered from negative values similar to $\delta^{15}\text{N-NO}_3^-$ to values more positive than those found in SPW. The $\delta^{15}\text{N-NH}_4^+$ variability was not significantly related to altitude; however, DCMW values were significantly different between shallow (ca. $+3\text{‰}$) and deep lakes (ca. -3‰), with ratios mostly positive in the former ($t=2.7$, $\text{df}=6$, $\text{p-value}<0.05$, Fig. 3). DRSi correlated with $\delta^{15}\text{N-NH}_4^+$ and $\delta^{15}\text{N-NO}_3^-$ of EW ($r^2=0.85$,

p-value<0.001 and $r^2=0.56$, p-value<0.05, respectively) but not with DCMW ratios (Fig. 3).

The stable isotope ratios were not fully independent of the compound concentrations (Fig. 4). For NO_3^- , ratio and concentration were correlated for both EW and DCMW ($r^2=0.50$, p-value<0.05 and $r^2=0.75$, p-value<0.05, respectively). In the case of NH_4^+ only EW correlated ($r^2=0.68$, p-value<0.05).

4 Conclusions

In high mountain lakes there are two large pools potentially supplying nitrogen to the water column: catchment soils through runoff, and sediments through diffusion and seasonal mixing. Catchment nitrogen loading is mostly in form of NO_3^- (Hood et al., 2003), whereas internal loading from sediments is mostly NH_4^+ . Interestingly, these two main nitrogen sources show contrasting $\delta^{15}\text{N}$ values and, as a consequence, their influence on the lake water column nitrogen pool can be traced. From our results, it is remarkable the scarce variability of NH_4^+ sediment porewater among lakes, both in terms of concentration and $\delta^{15}\text{N}$, despite the large changes in catchment characteristics (i.e., altitudinal gradient) and lake size. The SPW constancy contrasts with the high variability in the water column values. This fact suggests a powerful buffering mechanism within the nitrogen cycling from the water column to sediments and back to water column. Preferential use of NH_4^+ by primary producers could be a candidate mechanism; however, $\delta^{15}\text{N-NH}_4^+$ variability in the water column is extremely large (Fig. 2). Therefore, the SPW convergence among lakes has to occur during the process of organic matter mineralisation in the sediments and subsequent NH_4^+ diffusion to the water column. Because diffusion is slow, mineralization builds up high NH_4^+ concentrations in SPW, and thus fractionation during the diffusive process tends to be high. Lake primary productivity, oxygen conditions and bottom temperature in these lakes

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are relatively similar; as a consequence, the systems converge to similar sediment steady states in terms of concentration and NH_4^+ stable isotope ratios.

The negative values of $\delta^{15}\text{N}$ in deposition indicate the pollution origin of a large part of the nitrogen (Moore, 1977; Freyer, 1991; Hastings et al., 2003). $\delta^{15}\text{N}\text{-NO}_3^-$ values in the water column were always below the atmospheric ratios in our study, which indicates the influence of an additional fractionation. Catchment nitrification is the most likely candidate. There are several reasons to support this view. NH_4^+ is as much abundant as NO_3^- in deposition, and they show similar $\delta^{15}\text{N}$. However, inflow water to the lakes is extremely poor in NH_4^+ (Campbell et al., 2000). Therefore, NH_4^+ is either assimilated by plants and microorganisms, or is nitrified to NO_3^- . Nitrification has a large capacity of fractionation if occurring based on a large pool of substrate (i.e. 18–40%, Delwiche and Steyn (1970) and Mariotti et al. (1981)). Since NH_4^+ concentrations in deposition are high, we can expect relevant fractionation in catchment nitrification. Mayer et al. (2002) has already shown that in mountain catchments nitrification is higher in talus landscapes. This explains why we found more negative $\delta^{15}\text{N}\text{-NO}_3^-$ values the higher the lake altitude (Fig. 3), both in EW and DCMW. In addition, the nitrification influence can be more apparent at lower the NO_3^- concentrations (Fig. 4). Influence of within lake nitrification on $\delta^{15}\text{N}\text{-NO}_3^-$ is less likely, because NH_4^+ levels are much lower in water column water than in deposition and, therefore, fractionation is probably less pronounced.

In the water column, NH_4^+ concentrations are low and similar among lakes and compartments, average concentration ca. $0.8 \mu\text{mol L}^{-1}$. This responds to the preferential use of NH_4^+ in front of NO_3^- by primary producers up to values ca. $1 \mu\text{mol L}^{-1}$ (McCarthy, 1980). In contrast, water column $\delta^{15}\text{N}\text{-NH}_4^+$ variability is enormous, covering beyond the range in all other compartments. High fractionation during assimilation is unlikely, because this occurs against a small available pool. Therefore, the variability has to arise from sources providing NH_4^+ to the water column pools. There are two main NH_4^+ potential sources, transport from the SPW pool ($\delta^{15}\text{N}>0$) and food web recycling within

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the water column ($\delta^{15}\text{N} < 0$, if NO_3^- is the main N source for primary producers). Lake external sources are only relevant during thawing, and are quickly depleted (Catalan, 1992).

The significantly higher $\delta^{15}\text{N-NH}_4^+$ values in DCMW of shallow lakes (<15 m depth) agree with an internal supply from the sediments. Hypolimnion characteristics, where DCMW occur, with a relatively small volume and high influence of transport linked to turbulent mixing in boundary layers and internal wave fields, favour a higher relative influence of NH_4^+ pool in shallow lake DCMW and thus significantly higher $\delta^{15}\text{N-NH}_4^+$ values respect DCMW in deep lakes and EW of any lake.

Influence of N food web recycling on water column $\delta^{15}\text{N-NH}_4^+$ would be more relevant the higher the contribution of NO_3^- to primary producer nitrogen assimilation, for two reasons. First, because $\delta^{15}\text{N}$ values of NO_3^- uptaken are usually much lower than those of NH_4^+ (Fig. 2). Second, because during organism excretion there is fractionation that enhances the shift towards more $\delta^{15}\text{N}$ negatives values. Low NH_4^+ availability in EW or DCMW will make the use of alternative NO_3^- source ($\delta^{15}\text{N} < 0$) more likely and, as a result, there is a correspondence between low NH_4^+ concentration values and negative $\delta^{15}\text{N-NH}_4^+$ (Fig. 4). This might be ultimately related to factors driving primary production that were not considered in this study. However, correlation between low silicate, as a proxy of seasonal cumulative production, and $\delta^{15}\text{N-NH}_4^+$ points towards the same interpretation. The higher the productivity, the higher the relative use of NO_3^- compared to NH_4^+ and thus eventual low $\delta^{15}\text{N-NH}_4^+$ values in the excretion.

Certainly, there are many other processes taking place in the nitrogen cycle of high mountain lakes than here discussed (Robinson, 2001). However, if we apply the principle that high fractionation requires a large pool of substrate, the processes here depicted, and the environmental factors affecting them, appear as the most relevant. For instance, the influence of denitrification in sediments (Payne, 1973) probably has irrelevant consequences for $\delta^{15}\text{N-NO}_3^-$ values in the water column, as the remaining sediment NO_3^- concentrations are extremely low. In summary, variability in nitrogen

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stable isotopes of dissolved ammonium and nitrate in high mountain lakes mostly respond to factors determining the relative influence of three components:

1. the nitrate loading from the catchment with a negative $\delta^{15}\text{N}$, due to the starting atmospheric deposition values and the added nitrification influence;
2. the ammonium loading from the sediments with a positive $\delta^{15}\text{N}$, due to organic matter mineralization and slow diffusion from porewater to water column; and
3. the relative influence of NO_3^- uptake and organism NH_4^+ excretion in the within water column nitrogen cycling.

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Table 1. Physical and chemical characteristics of the lakes.

	Llebreta	Llong	Redó d'Aiguestortes	Redon	Xic de Colomina	Bergús	Gelat de Bergús	Vidal d'Amunt
Latitude – N	42.55	42.57	42.58	42.64	42.52	42.59	42.59	42.53
Longitude – E	0.89	0.95	0.96	0.78	1.00	0.96	0.96	0.99
Altitude (m)	1620	2000	2150	2240	2425	2449	2500	2688
Catchment area (ha)	5438	1111	322	153	35	101	24	17
Lake area (ha)	8.0	7.1	6.0	24.1	1.8	6.5	1.4	2.3
Depth (m)	10.5	12	10	73	11	50	7.5	18
Secchi disk depth (m)	10.5	12	10	30	11	20	7.5	7
Sediment organic matter (%)	26.4	23.3	22.9	22.1	26.0	18.3	16.3	24.5
pH	7.4	7.5	7.0	7.0	7.5	7.0	6.8	7.5
Acid-neutralizing capacity ($\mu\text{eq L}^{-1}$)	327	235	71	59	209	73	42	201
Conductivity ($\mu\text{S cm}^{-1}$)	42	29	12	11	25	13	8	24
Dissolved organic carbon (mg L^{-1})	1.4	1.7	1.0	1.3	2.1	1.0	1.1	2.2
Total phosphorous ($\mu\text{g L}^{-1}$)	7.8	9.5	7.5	5.2	6.3	4.3	5.4	7.9
Dissolved reactive silica ($\mu\text{mol L}^{-1}$)	48	25	31	8	21	30	18	16

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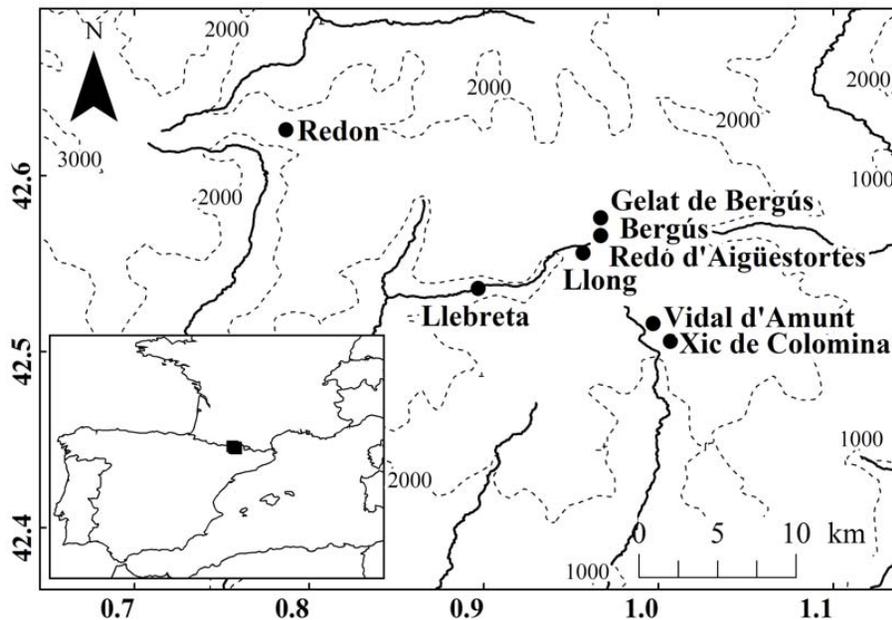


Fig. 1. Map showing the location of the eight lakes in the “Aigüestortes i Estany de Sant Maurici” National Park, Central Pyrenees (Spain).

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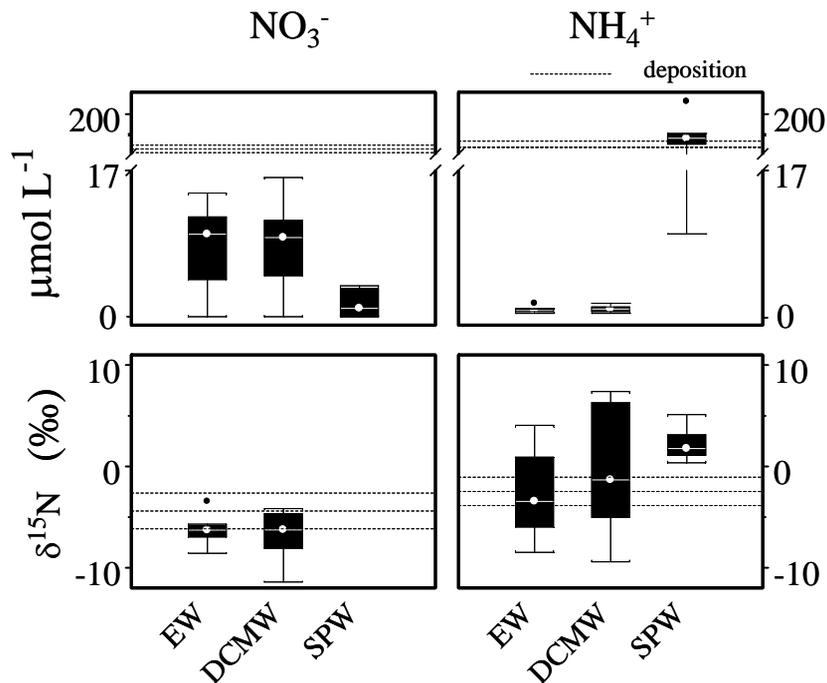


Fig. 2. Box plots of nitrate and ammonium concentration and $\delta^{15}\text{N}$, for epilimnetic water (EW), deep chlorophyll maximum water (DCMW) and sediment porewater (SPW) from the eight Pyrenean lakes studied. Mean, 25th and 75th percentiles are represented, whiskers are drawn to the nearest value that is not beyond a standard deviation span from the quartiles and, any points beyond this value (outliers), are drawn individually. Mean deposition values and the range are indicated in broken lines as a reference.

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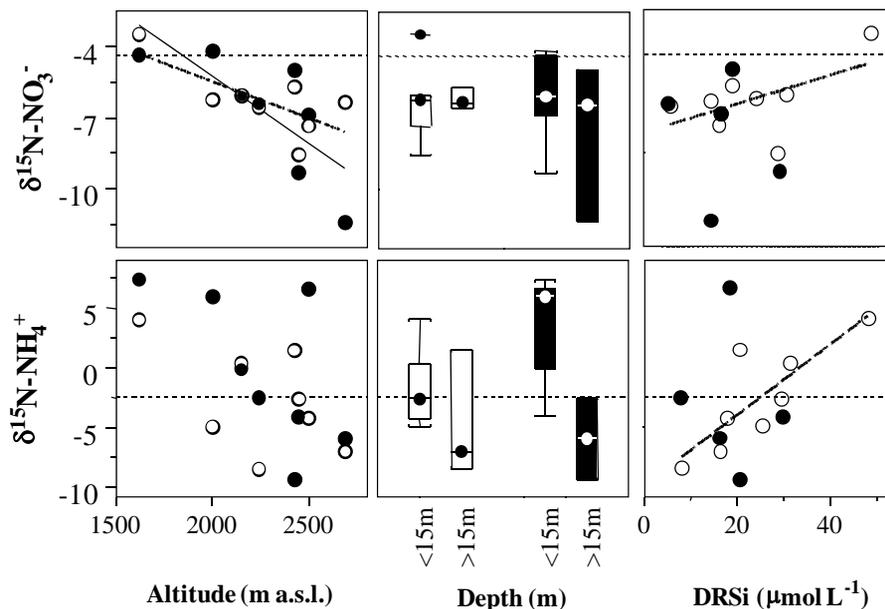


Fig. 3. Relationships of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NH}_4^+$, from epilimnetic (EW, empty circles or box plots) and deep chlorophyll maximum (DCMW, solid circles or box plots) waters, with altitude, depth, and dissolved reactive silica (DRSi), respectively. Mean deposition values are indicated with a broken line as a reference. Significant linear relationships are indicated respectively by solid (DCMW) and slashed (EW) lines in the plots.

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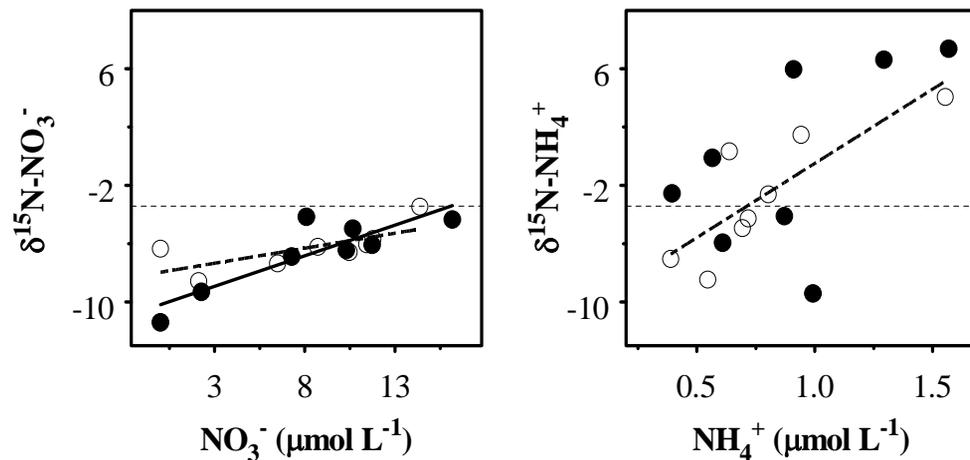


Fig. 4. Relationships between concentration and $\delta^{15}\text{N}$ for NO_3^- and NH_4^+ from epilimnetic (EW, empty circles) and deep chlorophyll maximum (DCMW, solid circles) waters. Significant linear relationships are indicated respectively by solid (DCMW) and slashed (EW) lines in the plots.

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