

Interactive comment on “Nitrogen stable isotopes of ammonium and nitrate in high mountain lakes of the Pyrenees” by M. Bartrons et al.

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Final Response:

Below we respond to each individual comment of the referees. Our answers follow each of their statements and are highlighted in bold. As a general comment, we want to remark that we are aware this is fundamentally a descriptive paper on natural variability. This kind of research is sometimes dismissed, but then we complain about the lack of references when we plan process-oriented research or we are unable to interpret unexpected results for other purposes (e.g. food web relationships). We think, knowledge on range and patterns of variability are fundamental in biogeosciences, and it is particularly applicable to relatively remote environments such as mountain aquatic ecosystems.

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The comments of the referees will be very helpful to emphasize more the strong points of our results and polishing unnecessary speculation. Mountain lake systems around the Northern Hemisphere have many aspects in common. Although the degree of atmospheric pollution (N deposition) differs from place to place, many findings from one place in Europe or North America have been found applicable to other sites. In that sense, this is not a contribution of only regional interest; we think there are at least three main conclusions that are of broad application:

1) Scarce differences between epilimnetic DIN and hypolimnetic DIN at the deep chlorophyll maxima both in concentrations and isotopic composition. However, there are marked differences among lakes. The two patterns together indicate that differences arise from external constraints or particular internal conditions that affect the overall nitrogen cycle of the lake.

2) Ammonium in porewater of mountain lakes shows a low range of variability in concentration and $\delta^{15}\text{N}$. Given the variability in catchment and lake conditions, and in the water column dissolved nitrogen values, this convergence towards a similar value is remarkable.

3) Correlation of $\delta^{15}\text{N}$ of nitrate and ammonium with altitude, and, some patterns with depth, suggests that there are a few constraining mechanisms of higher relevance than others of the nitrogen cycle. For future research, we hypothesize they are nitrification in the soils of the catchment for nitrate $\delta^{15}\text{N}$ and ammonium/nitrate differential uptake by algae in the water column for ammonium $\delta^{15}\text{N}$.

Anonymous Referee 1

General comments:

“This manuscript presents a dataset on variations in ^{15}N isotope signatures in lakes in the Spanish Pyrenees. It is a valuable dataset that will be useful in the community. However, the paper needs significant revisions before it should be considered for pub-

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lication in Biogeosciences. One major issue is that some of the interpretation of the data needs to be reconsidered. For example, one of the major conclusions of the paper is that catchment nitrification has a large influence on the N cycle of these lakes, but there are no data from streams or soils to defend this claim. Also, much of the data interpretation is from the perspective of explaining algal ^{15}N patterns, but there are no primary producer data presented to back this up. Finally, the conclusions section contains many apparent errors and is contradictory in parts. In general, I think this is a good dataset worthy of publication, but in the present form the manuscript is not suitable for this journal”.

We do not see major problems in incorporating the specific comments and views of referee 1.

Here we comment on the main three criticisms included in the statement above.

1. “One of the major conclusions of the paper is that catchment nitrification has a large influence on the N cycle of these lakes, but there are no data from streams or soils to defend this claim”.

We accept this should not be a conclusion but a hypothesis for further research. There is some ambiguity in our text around what clear conclusions from our data are and what just interpretations about potential processes that can be behind some of the patterns found are. In the revised version we will be more cautious in that aspect and we will focus on highlighting patterns of variability. Particularly, those related to altitude and depth of the lakes (as suggested by referee 2), rather than speculating about the processes behind. However, we will bring some new data (see specific comments) to support some of our interpretations (e.g. nitrate values in inflows of some lakes).

2. “Much of the data interpretation is from the perspective of explaining algal ^{15}N patterns, but there are no primary producer data presented to back this up”.

Ammonium and nitrate are the sources of nitrogen to phytoplankton and from them to

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the rest of the food-web in the water column. It does make sense, from a lake ecosystem perspective, to justify the interest of our study for food-web studies. However, we do not have any inconvenient in decreasing the attention paid to phytoplankton, except for the explanation of an ammonium value around $1 \mu\text{mol l}^{-1}$. In this case, we are using accumulated experimental evidence from algal physiological studies to explain our result.

3. “Finally, the conclusions section contains many apparent errors and is contradictory in parts”.

This is not completely correct, as we will explicitly indicate in the answers to the specific comments. In some cases, the referee was confusing statements referred to concentrations with statements referred to isotopic composition. In other occasions, the sentences or the paragraph were not clear enough. In a few cases, there were mistakes. See specific comments for the details.

Specific comments:

“Page 480, abstract: Overall I would like to see more strong conclusions in the abstract. This will help attract readers to your paper”.

We accept the abstract was rather descriptive, with little punch. We will revise it highlighting the main point listed above.

“Page 480, lines 8-9: Was the ^{15}N of atmospheric N estimated or measured? Can you add a sentence explaining the concentration patterns observed in atmospheric deposition”.

The ^{15}N of atmospheric N deposition was measured (Page 484, lines 7-9). We will make it clear in the revised abstract.

“Page 480, line 12: What kinds of samples are you referring to in this sentence?”

In this sentence (line 12) we are referring to ^{15}N samples. For instance, from line 5 to

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20 (Page 480), we are referring to 15N. It will be clarified.

“Introduction, first paragraph: I think this paragraph should be rewritten to minimize the focus on interpreting primary producer 15N data, since you don’t actually address this question in the paper. Why not frame the paper as an exploration of the variability of 15N of lake water versus altitude and how environmental variables can affect observed isotope ratios? This seems to be the main question that the paper can address. You can also say that 15N data such as yours can be valuable for studies of, yes, primary producer N sources, but also as tracers of atmospheric pollution and N cycling pathways”.

This is a good suggestion. We will follow the advice. In fact, our topic is patterns of isotopic variability in dissolved inorganic nitrogen in mountain lakes.

“Page 481, lines 10-12: I thought oxidized nitrogen such as nitrate was the primary form of atmospheric N deposition. Can you cite more papers that show that NO₃⁻ and NH₄⁺ are deposited in equal proportions?”

There are many papers showing that NO₃⁻ and NH₄⁺ are deposited in similar proportions throughout most of Europe. In page 481, lines 10-12, we already cited a paper from the Pyrenees (Camarero and Catalan, 1996). The pattern was already observed in previous studies (Camarero and Catalan, 1993) and has been maintained since then for 15 years in the data of our field observatory in lake Redon at 2240 m a.s.l. Similar proportions are indicated from other sites in France (Croisé et al., 2005), the Italian Alps (Rogora et al., 2001), or over Europe (www.emep.int). Obviously, this can change locally and in time, but in our study we have our own measurements, and they show no change.

References: Camarero, L. and J. Catalan. 1993. Chemistry of bulk precipitation in the central and eastern Pyrenees, northeast Spain. *Atmospheric Environment* 27:83-94. Camarero, L. and J. Catalan. 1996. Variability in the chemistry of precipitation in the Pyrenees (northeastern Spain): Dominance of storm origin and lack of altitude

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influence. *Journal of Geophysical Research* 101:29491-29498. Croisé, L., E. Ulrich, P. Duplat, and O. Jaquet. 2005. Two independent methods for mapping bulk deposition in France. *Atmospheric Environment* 39:3923-3941. Rogora, M., A. Marchetto, and R. Mosello. 2001. Trends in the chemistry of atmospheric deposition and surface waters in the Lake Maggiore catchment. *Hydrology and Earth System Sciences* 5:379-390.

“Page 482, lines 16-18. Here you say that there are two main sources of N to mountain lakes, soil catchment (I think you mean soils in the catchment) and sediment pools. But on the previous Page, in lines 9-10, you say that atmospheric deposition is the dominant source of N to mountain catchments. Don't these two paragraphs contradict each other?”

There is no contradiction. One thing is inputs to the catchments, the other inputs to the lake. Inputs to the catchment can be deposition, fixation by bacteria (in soils and/or with symbiosis with some plants), and massive deposition of animal excrements in some cases. In the case of high mountains, deposition is the main process. In contrast, inputs to the lake water column can be from soils in the catchment through runoff, direct deposition and the sediment pool. Direct deposition as we show below is irrelevant in these small lakes.

“Is there a way you can estimate the main source of N to your lakes with your concentration data? For example, can you estimate the N flux from streams, sediments, and the atmosphere? This would really make your paper stronger”.

We do not have data for all lakes. However, from a parallel study we can include data for two lakes, which are part of our study too (Table FR1). It can be seen that direct deposition is irrelevant, because the small size of the lakes, and that nitrate loading is two orders of magnitude higher than ammonium one. Table FR1. Input, export and deposition N fluxes of NO₃⁻ and NH₄⁺ in Liebreta and Llong lakes during year 2006.

Lake NO₃⁻ NH₄⁺ NO₃⁻ NH₄⁺ NO₃⁻ NH₄⁺ Inflow input Inflow input deposition deposition
(kmol yr⁻¹) (kmol yr⁻¹) (kmol yr⁻¹) (kmol yr⁻¹) Liebreta 528.9 2.7 3.0 2.5 Llong 140.0

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1.8 2.9 2.4

“Page 482, last paragraph: Can you make this paragraph more clear? It might be helpful to state how you expect $\delta^{15}\text{N}$ to vary with depth and altitude, perhaps in the form of hypotheses”.

We will revise this paragraph according to the referee’s suggestion. We will enhance the focus of the paper on patterns of variability related to altitude and lake depth.

“Page 482, lines 16-18: Can you be more specific about how altitude affects lake biogeochemistry? Is it just because of temperature?”

Certainly, the altitudinal gradient in mountains is more than just temperature, particularly for lakes. The most conspicuous aspect related to the nitrogen cycle is the progressive decrease with altitude of vegetation and related soils, and the increase of rocky areas, such as outcrops, scree, scarps, etc. Studies in other mountain ranges have shown that catchments with a higher proportion of talus areas have higher nitrification rates. This may sound counterintuitive but is related to the fact of maintaining oxygenated conditions in the reactive soil solutions; air diffusion is easier in rocky soils.

The advice of the referee is helpful. We will rewrite the introduction explicitly indicating what the patterns are that we might expect according to current knowledge.

“Page 484, lines 7-16: This paragraph needs more specifics. Are you collecting wet or dry deposition, or both? How was it collected?”

As stated in the methods section, we collected bulk deposition, which by definition means wet and dry deposition. Atmospheric bulk deposition was collected with a 22 cm diameter polyethylene funnel connected to an 8 L polyethylene reservoir by a tube, in which a 250 mm nylon mesh was placed to prevent large particles, such as insects or leaves, from entering the water tank. The amount of precipitation was estimated as the average of the volume collected in the sampler and two more collectors deployed for other purposes. These estimates were additionally checked against the measures pro-

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vided by an automatic weather station (AWS). Immediately after collection, $\delta^{15}\text{N-NO}_3^-$ samples were field-filtered in a field laboratory on-site using pre-ashed Whatman cellulose nitrate filters (GF/F, 47 mm diameter and $0.7\ \mu\text{m}$ pore size) into clean polypropylene hermetic bottles at the Redon field station and freezing (-20°C) until analysis. This information can be included in the manuscript.

“Why don’t you describe the 15N-NH_4^+ analysis here?”

We could describe the 15N-NH_4^+ analysis here, but we consider that explaining it together with $\delta^{15}\text{N-NO}_3^-$ analysis facilitates the explanation and logic understanding of both methodologies.

“Also, isn’t refrigeration at -20°C essentially freezing?”

Yes

“Page 485, lines 5-9. Some of the methods described here don’t have data shown in the results or Figures (e.g., LOI, DIC). Conversely, some of the parameters shown in the table are not explained in the methods (like DOC)”.

The LOI from the eight lakes is shown in Table 1 as sediment organic matter. We will harmonise the terms in the new version. The methods for DIC will be removed from the text, and the methods for DOC will be introduced as following: “Dissolved organic carbon (DOC) was determined on a Shimadzu TOC-5000 analyzer.”

“Page 486, line 18: I don’t think the isotope data are “very distinctive” as stated here. But, this may be because of the way Figure 2 is shown. Most of the $\delta^{15}\text{N}$ values do not appear to be different from each other”.

The referee is right. For the isotopic ratio, what is distinctive is the range of variability. In fact, concerning isotopic mean values, the only one that is statistically different is $\delta^{15}\text{N-NH}_4^+$ for SPW. We will restate the comment in a different way.

“Page 486, line 23: Can you provide all the data for $\delta^{15}\text{N}$ of NO_3^- and NH_4^- of depo-

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sition in a table, perhaps with the concentration data? This will be valuable for other researchers”.

Our time series is too short for discussing issues on deposition temporal variability. We think that reporting mean values is more informative at this stage. There is an ongoing research dealing with variability among precipitation events, which will be based on longer time series.

“Page 487, lines 3-4: “It is worth to highlight the low variability:”Can you be more specific here? What about the average the standard deviation?”

This was detailed just in the sentence before this one (Page 487, lines 2-3): “SPW $\delta^{15}\text{N-NH}_4^+$ was 2.2 ± 1.5 ‰ 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”. Anyway, we will revise the paragraph and make it clearer.

“Page 487, line 5: Aren’t nitrate concentrations higher in the water column than in porewaters? I think the statement here is only true for NH_4^+ ”.

Here we are referring to total dissolved inorganic nitrogen (DIN), which in the text was referred as “nitrogen concentrations” (Page 487, line 5). It will be clarified in the revised version.

“Page 488, line 5: Here again you state that most of the N loading from the catchment is in the form of nitrate. You need to be able to provide some data to back this up or else just cite that in other studies (on other continents!), the dominant N species in streams is NO_3^- . As I said above, I’m not really sure this is actually true. There may be a substantial DON component to these streams”.

N loading from the catchment is mostly in the form of NO_3^- as was indicated in previous comments (Table FR1). In Table FR2, we show inflow NH_4^+ , NO_3^- and DON concentrations of Liebreita and Llong lakes for the period between June 2004 and April 2006. NO_3^- inflow concentration is between three to four times higher than the DON inflow

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concentration. Table FR2. Inflow NH₄⁺, NO₃⁻ and DON concentrations of Llebreta and Llong lakes.

Inflow Llebreta Inflow Llong ($\mu\text{eq L}^{-1}$) ($\mu\text{eq L}^{-1}$)

NH₄⁺ 0.2 ± 0.2 0.2 ± 0.2 0.3 ± 0.2 NO₃⁻ 18 ± 2 15 ± 4 12 ± 3 DON 4 ± 4 5 ± 4 5 ± 4

This are the most vegetated catchments at lower altitude, we assume that external sources of DON will even decrease with altitude.

“Page 488, line 15: It seems like from Figure 2 that there is actually a very high standard deviation of NH₄⁺ concentration in porewaters. Be careful not to oversimplify your data”.

The data are as follow SPW NH₄⁺: 98 ± 72 $\mu\text{mol L}^{-1}$; SPW NO₃⁻: 1.5 ± 1.7 $\mu\text{mol L}^{-1}$; SPW $\delta^{15}\text{N}$ - NH₄⁺: 2.2 ± 1.5 ‰. The coefficient of variation is similar between ammonium and nitrate in pore waters, 0.73 and 1.13, respectively. In fact, variability for ammonium comes mostly from a single lake (Bergús), with 9.6 $\mu\text{mol/L}$ ammonium concentration. Excluding this lake the mean and standard deviation of the NH₄⁺ concentration becomes 110 ± 68 $\mu\text{mol L}^{-1}$, that is a coefficient of variation of 0.61.

“Page 488, line 17: “high variability in water column values” – again, this seems wrong to me. In Figure 2, it appears that NH₄⁺ concentration is not variable at all in water column samples?”

Here the text is referring to $\delta^{15}\text{N}$ not concentration. $\delta^{15}\text{N}$ in the water column are more variable than in porewater. It will be rewritten and clarified.

“Page 488, line 17: “buffering mechanism”. I don’t know what this means! I’m pretty sure you don’t mean a buffering of pH changes, but I don’t know what else it could mean. Please explain!”

Here “buffering mechanism” refers to a storage compartment that releases something

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(ammonium in this case) at a more constant rate than it receives. We will rephrase the sentence using other terms.

“Page 488, line 21: “SPW convergence among lakes” – what do you mean by this?”

Despite the high variability in the water column $\delta^{15}\text{N}$ values, related to the altitude or the N concentration, SPW $\delta^{15}\text{N}$ is fairly constant among lakes. Therefore, there is a mechanism that tends to constraint the variability SPW $\delta^{15}\text{N}$ ammonium and makes it less lower than in the water column. The term convergence is used to indicate this tendency to “become together”, to “tend to the same value” among lakes. We will rephrase the paragraph in a different way.

“Page 489, line 9: Here you cite a study on lakes in Colorado to defend your statement that inflow waters to the lake are low in NH_4^+ . You need to explain why you feel this is justified”.

In addition to the reference, we will add data from our lakes corroborating the statement (Tables FR1 and FR2).

“Page 489, lines 16-17: “In addition, the nitrification influence can be more apparent at lower the NO_3^- concentrations.” What is the significance here? Why does Figure 4 back this statement up? Wouldn’t more nitrification cause higher NO_3^- concentrations?”

The NO_3^- resulting from nitrification is highly depleted in ^{15}N (Mariotti et al. 1981). The impact of this “new” nitrate coming from NH_4^+ on the $\delta^{15}\text{N}$ of the “bulk” of nitrate existing in the water column will be higher the lower the NO_3^- concentration in the water column is. Again, the sense of our sentence depended on previous sentences; we will rephrase it to make it clear.

Reference: Mariotti, A., Germon, J. C., Hubert, P., Kaiser, P., Letolle, R., Tardieux, A., and Tardieux, P.: Experimental-determination of nitrogen kinetic isotope fractionation - Some principles - Illustration for the denitrification and nitrification processes, Plant

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Soil, 62, 413-430, 1981.

“Page 489, lines 21-30: Here you say that NH_4^+ concentrations are low and similar among lakes. On the previous Page, you say that there is high variability in NH_4^+ water column values? Please get these issues straightened out”.

Comments about $\delta^{15}\text{N}$ and concentration are confounded. In the previous page (Page 487, line 20) we are talking about $\delta^{15}\text{N-NH}_4^+$ and here (Page 489, line 21) we are talking about NH_4^+ concentration.

“Page 490, lines 2-3: Here you say that external sources of N are only relevant during thawing. But you have dedicated a significant portion of this paper to explaining why nitrification in soils is a major control on your observed N isotope patterns. This doesn't seem to add up”.

This paragraph (Page 489, line 21- Page 490, line 3) only refers to NH_4^+ . During thaw there is a peak in ammonium input. We will make clearer this point.

“Page 490, line 4: Are you sure there is a significantly higher $\delta^{15}\text{N}$ of NH_4^+ in deep waters as opposed to epilimnetic water? In Figure 2, it seems clear that there is no difference”.

Page 490, line 4 doesn't state this. This sentence says that the DCM $\delta^{15}\text{N-NH}_4^+$ from shallow lakes is significantly more positive than the DCM $\delta^{15}\text{N-NH}_4^+$ from the deep ones. This pattern can be observed in Figure 3. It will be make clearer in the revised text.

“Page 490, lines 10-21: I'm not sure how to interpret this paragraph. Why would greater NO_3^- uptake affect NH_4^+ isotopes? And why is this relevant to the paper?”

When nitrate (with more depleted $\delta^{15}\text{N}$, Figure 2) is assimilated by primary producers, it cycles through the food web, and it is partially excreted back by different organisms of the planktonic food web in form of ammonium. We think this is the reason why there is certain correlation between $\delta^{15}\text{N}$ of ammonium and nitrate.

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“Page 490, line 23: Can you add some examples of other N cycling processes that may be taking place in these lakes?”

They are already detailed in the introduction: denitrification, ammonia volatilization, atmospheric N₂ fixation, and ammonia oxidation (Anammox).

“Page 490, line 26: I think you haven’t quite explored the denitrification angle here. If denitrification in the sediments is so prevalent, it seems unlikely that you would see no signature in $\delta^{15}\text{N}$ of NO_3^- emitted”.

We could not measure $\delta^{15}\text{N}$ of porewater nitrate, because concentrations were low and the volume of water we could extract was limited. However, denitrification has little chance to leave any relevant signature in dissolved inorganic nitrogen in the water column or porewater. First, nitrate consumption results in nitrogen emission to the atmosphere (N₂, N₂O), so the product disappears from the system. On the other hand, the nitrate pool remaining in porewater is very low, when pools are low then fractionation is scarce. A comment about this will be introduced in the paper.

“Page 491, lines 1-8: I think you really need to provide some quantitative information here about these different processes. Using your data, can you make estimates of the magnitude of these rates?”

We cannot provide direct evidence of these or other processes beyond the data shown on Table FR1 and FR2 for concentrations. Our paper is about the description of the patterns of variability among lakes and within lake compartments, and their correlation with general geomorphological features. The processes behind are introduced here as hypothesis to explain the patterns found. Further studies should determine whether they are correct or not. We understand the referee’s objections, so we will clearly distinguish between patterns, landscape correlations and tentative hypothesis in our revised version. We will emphasize the relationships between concentration and isotopic values, and each of them with altitude and depth.

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“Also, I’m unclear on how NO₃⁻ uptake is relevant to your data. You state repeatedly in the paper how primary producers don’t like to use NO₃⁻. So why is it such a major process in your lakes?”

Primary producers do not “like” but “must” uptake NO₃⁻ when NH₄⁺ concentration drops below 1 μmol/L. As soon as NH₄⁺ concentration increases above ca. 1 μmol/L, primary producers switch again to NH₄⁺, and obviously deplete it to values lower than 1 μmol/L. For this reason, at the end, NH₄⁺ values tend to remain around 1 μmol/L. This threshold around 1 μmol/L is known since the 1980s by people studying phytoplankton physiology. These phytoplankton feed-backs, we think, are crucial for understanding why lakes with different environmental context tend to similar values.
 Anonymous Referee 2

General comment

“The study by Bartrons et al. investigates the N isotopic composition of dissolved inorganic nitrogen in different N-pools in high-mountain lakes in the Pyrenees. It did not become clear to me what we can learn from this study and how we could apply findings to other environments”.

We think that there is new information that could not be simply “guess” from current knowledge. For instance, the systematic changes in the isotopic signature of dissolved inorganic nitrogen following an altitudinal gradient. Or that porewater signature is quite similar among mountain lakes located in catchments of contrasting land cover. These patterns suggest there are key mechanisms that constrain the patterns beyond the complexities of the nitrogen cycle acting in each lake.

“The paper compares the N isotopic composition of different lakes and lake reservoirs, and tries to relate it to environmental constraint, yet it does not explain the mechanisms behind these possible links (e.g., altitude vs. δ¹⁵N)”.

The referee is right; the paper describes patterns of variation across the altitudinal gra-

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dient. To our knowledge this is the first paper reporting data on isotopic composition of nitrate and ammonium from mountain lakes and how they vary along the usually main environmental gradient in this lake districts: altitude. We do find certain patterns that open new questions and may guide future research oriented to particular processes.

“It also completely ignores the fact that there are strong spatial and temporal variations in the lakes $\delta^{15}N_{DIN}$ due to internal N cycle processes”.

This is not correct. In our group we have been studying distinct biogeochemical and biological processes in mountain lakes and we have a clear view of the seasonal and spatial variability within lakes and differences among lakes in space (mostly altitude). For this reason, we sampled the lakes during a short period of time when they are stratified and difference between upper layers and deep layers can be larger. In order to enhance the potential differences between these two samples, we chose the depth where the deep maximum chlorophyll maximum occurs in oligotrophic lakes (1.5x time the Secchi disk depth). As can be seen in our results differences between the two compartments were not significant, only differences between lakes were relevant and this correlated with external features (altitude) and lake morphology (depth).

We also considered porewater as a third compartment with high potential for showing distinct isotopic signatures for DIN. The difference were quite marked respect those of the water column. However, surprisingly, difference among lakes was much lower than one could expect from the differences observed in the water column.

“All in all, the lines of argumentation are weak, the discussion is speculative, and the conclusions are trivial, as are the initial objectives”.

Our previous comments show that the results are not so trivial, according the referee's comments, he/she would expect more differences between lake upper and deeper layers, perhaps. Also the low variability in porewater signatures among lakes is not trivial. We accept that objective are simple (not trivial) and that the argumentation may be circumstantial in some cases. In the revised version we will stick to facts, observed

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patterns with altitude and depth, and will shorten the part dedicated to the hypothesis about the process behind.

“The conclusion is written in an awkward style”.

No comment. We appreciate the constructive comments made by referee 1 and will follow his/her advice.

Specific comments:

“The informational value of the abstract is low”.

We do not think information is low, results are reported in detail. However, we agree that the abstract should emphasize the main results as suggested by referee 1.

“P11481, l. 22: How certain biogeochemical processes fractionate the N isotopes should be presented in more detail, and reduced to the processes that will be pertinent to the discussion of the paper”.

The most important reactions fractionating N isotopes are cited in the text with the corresponding citation of the article describing in detail the fractionation. The processes pertinent in the text are well specified when necessary.

“There is no information as to what kind of DIN- $\delta^{15}\text{N}$ values to expect in the various lakes, and what the potential environmental controls could be”.

The referee stated in their general comments that the objectives were trivial. Could he/she guess the expected DIN- $\delta^{15}\text{N}$ values and whether there is any pattern among lakes? We do not think so, as was our case. There is no information available. So, although simple, we thought it is worth exploring the patterns of variation throughout the altitudinal gradient during the period of stratification of the lakes. As mentioned before, we will rewrite the introduction trying to make clearer our goals:

1) to assess how the two main phototrophic zones 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 alti-

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tudinal gradient, and lake size;

2) to what extent we can differentiate from internal and external influence by comparing water column DIN isotopic composition with porewater DIN.

“It is not discussed at all why the porewater DIN has a much different $\delta^{15}\text{N}$ than the external N. If the lakes represent closed systems, the OM produced will reflect the $\delta^{15}\text{N}$ of the source. The original N signature will be incorporated into the sediments, and will also modulate the $\delta^{15}\text{N}$ N of ammonium that fluxes out of the sediments. Any discrepancy between these two main sources of DIN to the water column have to be explained by N-isotope partitioning during transformations in the lake, i.e., N burial or denitrification”.

It is not correct we were not discussing why porewater DIN is enriched. We suggested fractionation by diffusion, which we accept now it sounds unlikely as the main mechanism, even though there are some studies indicating that this may happen. Probably, it has more relevance the quicker mineralization of peptides with lighter nitrogen isotopes. The main nitrogen source to the sediments is the sinking of organic matter. During the synthesis of this organic matter there is nitrogen fractionation ($\delta^{15}\text{N}$ decreases), and when it cycles through the food web, there are more fractionations ($\delta^{15}\text{N}$ increases). Therefore, inputs to sediment have a different isotopic signature than the original dissolved sources, and their signature can be very variable in time within a lake, and among lakes. Therefore, similar porewater $\delta^{15}\text{N}$ among lakes indicates the existence of a constraining mechanism that takes place in the sediment. Denitrification has little differential effects among lakes. As explained before, denitrification uses nitrate, its concentration decline to low values in the sediment, and when the pool is small fractionation is scarce. In addition, the nitrogen by-product of the process is released to the atmosphere (N_2 , N_2O). We do not know the effects of burial, but according to the literature peptides with lower $\delta^{15}\text{N}$ are mineralised first. Therefore, now, we think that porewater ammonium $\delta^{15}\text{N}$ might reflect this fractionation during mineralisation. In these lakes, sediment conditions are similar, they are rich in organic matter and

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temperature is during all year around 4 oC. This may explain the convergence towards similar $\delta^{15}\text{N}$.

“Use of DRSi as proxy for water column productivity: Do you assume that productivity high when Si is high? Or that it is high when Si is low, i.e., all Si is being used during high productivity”.

It was explained in Page 11484 line 2-5 (materials and methods): 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).

“What is the yield for your ammonium diffusions? How can you analyze $\delta^{15}\text{N}$ of NH_4^+ at very low concentrations ($1\mu\text{M}$), while you cannot measure these levels in nitrate samples? What explains the high variability in ammonium concentration?”

The explanation is very simple. Isotopic analysis is limited by the total nitrogen available, not by concentration. We were analyzing 4 litres of water from the water column to overpass the limit of detection for the analysis of $\delta^{15}\text{N}\text{-NH}_4^+$. However, obtaining four litres of porewater for the analysis of $\delta^{15}\text{N}\text{-NO}_3^-$ was not feasible.

“In section 3.2, relationships between $\delta^{15}\text{N}\text{-DIN}$ and lake features are presented. No information is provided as to why or why not the $\delta^{15}\text{N}$ of ammonium in the lake, for example, should be related to the altitude of the lakes”.

Section 3.2 is a results section. This is discussed in section 4 (Conclusions, Page 489, line 24 – Page 490, line 3). However, in the revised version we will develop in the introduction why we expect a relationship as suggested by referee 1.

“p. 11488: Diffusive processes barely fractionate the N isotopes. This has to do with the fact that most solutes are hydrated, and the effective mass difference between the molecules is minor”.

This concept applies to diffusion in water, but diffusion in porewater offers the potential

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for NH_4^+ to interact with charged sites. There is some literature mentioning fractionation related to sediment diffusion (Prokopenko et al. 2006, Donahue et al. 2008). We understand this is pure speculation and will reduce it to a minimum. We will propose fractionation during mineralisation as main hypothesis and diffusion as a less likely alternative or complementary hypothesis.

References: Donahue, M. A., J. P. Werne, C. Meile, and T. W. Lyons. 2008. Modeling sulfur isotope fractionation and differential diffusion during sulfate reduction in sediments of the Cariaco Basin. *Geochimica et Cosmochimica Acta* 72:2287-2297. Prokopenko, M. G., D. E. Hammond, W. M. Berelson, J. M. Bernhard, L. Stott, and R. Douglas. 2006. Nitrogen cycling in the sediments of Santa Barbara basin and Eastern Subtropical North Pacific: Nitrogen isotopes, diagenesis and possible chemosymbiosis between two lithotrophs (*Thioploca* and *Anammox*) - "riding on a glider". *Earth and Planetary Science Letters* 242:186-204.

“p.11489, l. 23: use of NH_4^+ in front of NO_3^- ?? Covering beyond the range??”

Correct, it should say: preferential use of NH_4^+ in front of NO_3^- by primary producers when NH_4^+ values are above ca. $1\ \mu\text{mol/L}$.

“p. 11490, l.20-21: I cannot follow the logic of this sentence”.

It is already explained above. Concentrations of ammonium in the water column are just around $1\ \mu\text{mol/L}$, the threshold where it is more advantageous to use nitrate than ammonium for algae. When the concentration of ammonium is higher than $1\ \mu\text{mol/L}$, phytoplankton start to assimilate ammonium and the concentration of ammonium in the water column decreases. In contrast, when it is depleted to $1\ \mu\text{mol/L}$, primary producers start to assimilate nitrate. This is the reason why the concentration in the water column of these lakes is so close to $1\ \mu\text{mol/L}$.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/6/C4629/2010/bgd-6-C4629-2010->

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