

**Interactive comment on “Winter atmospheric nutrients and pollutants deposition on West Sayan mountain lakes (Siberia)” by Daniel Diaz-de-Quijano et al. Anonymous Referee #2**

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**General comments**

The manuscript topic falls within the scope of BG. It presents interesting data from an unexplored region. I think it is a valuable contribution on a relevant scientific topic i.e. pollutant/nutrient deposition in remote areas and the possible effects on the ecology of mountain lakes. The results are reported in a clear way but some sections could be shortened and presented more concisely. Some more information on lake features and lake chemical data could be provided (see specific comments).

**Specific comments**

**REFEREE #2 COMMENT 1:**

Lines 47-48: There is no mention here and in the manuscript of the modelled deposition estimates made by EMEP (Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe; <https://www.emep.int/mscw/index.html>): I would suggest the authors to consider these estimates and possibly compare them with the measured deposition deriving from their snowpack analyses. I think that s could be an added value to the paper.

**AUTHORS ANSWER 1:**

We are preparing a revised manuscript. We added the references there (lines 47-48) and included the EMEP deposition model results for 2017 in the discussion (line 337, former line numbers). The EMEP deposition estimates are within the ranges of Lamarque and colleagues (2013), so they don't modify our main conclusions. The EMEP deposition model is more accurate in time (for year 2017, when we sampled the snowpack) but, unfortunately, less accurate in space because our sampling site is located 200 Km east from the EMEP deposition map boundaries.

**REFEREE #2 COMMENT 2:**

Line 54: “warmed”: do the author mean subject to global warming?

**AUTHORS ANSWER 2:**

Yes, we changed that sentence (line 54). It is now: “According to published global models (IPCC, 2013; Lamarque et al., 2013), the West Sayan mountains, in south central Siberia, correspond to a low atmospheric nitrogen deposition area with a cold but increasingly warming climate in the last decades”

**REFEREE #2 COMMENT 3:**

Some more information could be provided on the lake sites e.g. in Tab. S2, such as lake surface area and depth, land cover. This information could help in understand the differences in nutrient levels among the lakes. Deposition is indeed a relevant but not the unique driver of nutrients lake water.

**AUTHORS ANSWER 3:**

We fully agree with this comment: the role of the watershed is crucial and might explain differences in water chemistry between lakes. We suggest to include a new supplementary table (Table S1 in the new manuscript version) with the fields: lake name, coordinates, altitude, maximum depth, Secchi disk,

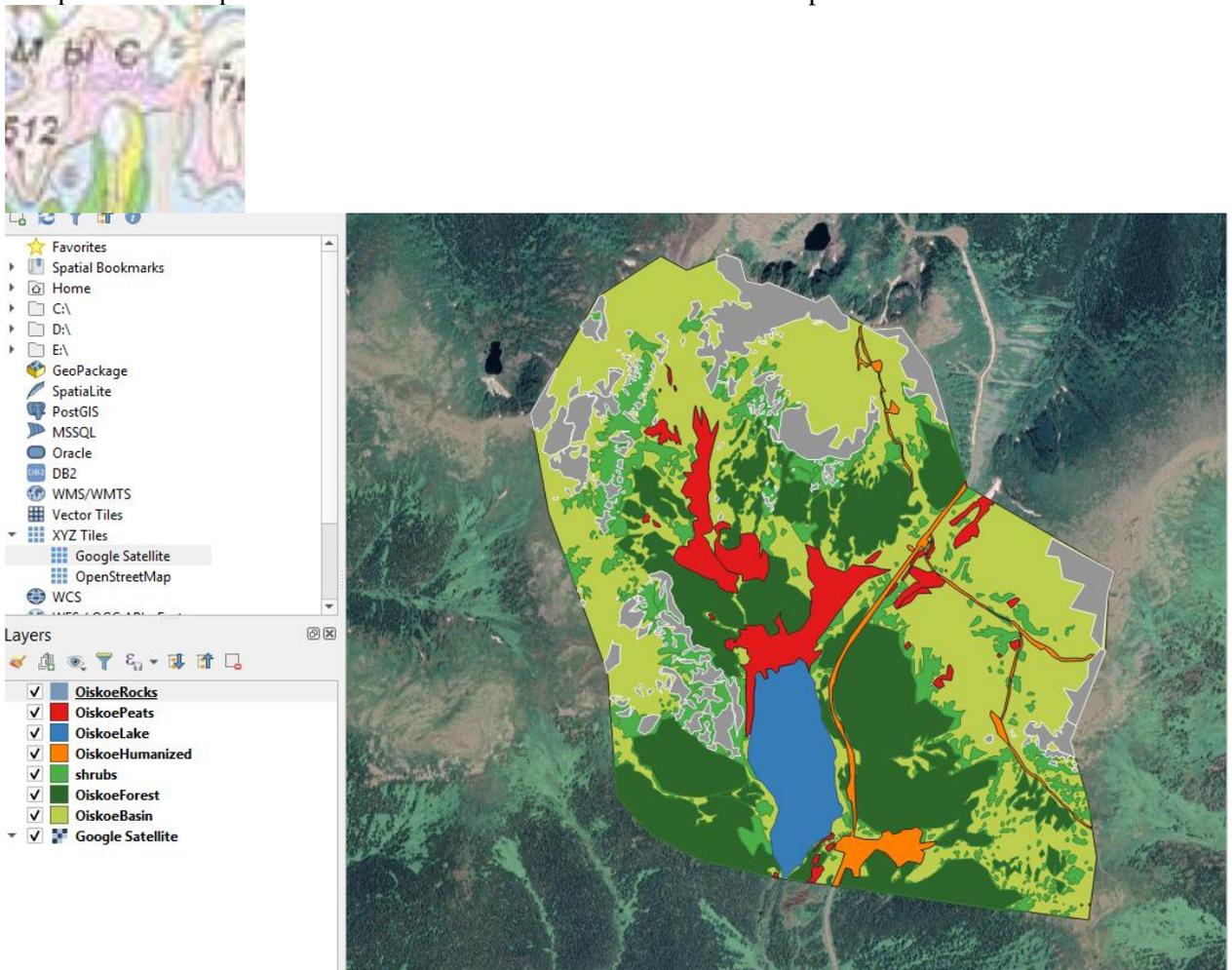
subsurface chlorophyll a concentration, lake area, watershed area, area of the lake/area of the watershed, watershed land use/land cover area %. Official whole Russia or Krasnoyarsk Territory vegetation cover and soil maps are not enough detailed for the purposes of our study (see the attached Atlas of Specially Protected Natural Territories of the Siberian Circle of the Russian Geographic Society, 2012, pp. 248-249). Therefore, detailed watershed land cover/land use maps have been manually defined for each lake. Polygons have been defined using QGIS 3.14.16-Pi on the basis of Google Satellite and Open Street Map XYZ tiles. Lake, whole watershed and watershed cover areas have been calculated using ellipsoidal project.

Oiskoe and Svetloe are relatively large forest lakes (0.57 and 0.37 Km<sup>2</sup>, 21 and 24 m maximum depth) with low water transparency (4 and 8 m Secchi disk, respectively). Tsirkovoe, Raduzhnoe and Karovoe are located at an alpine landscape and are smaller and shallower (0.02, 0.03, and 0.08 Km<sup>2</sup>, respectively; 15, 4 and 7m deep, respectively). Raduzhnoe and Karovoe lake beds were visible. Secchi disk was not tested at Tsirkovoe. Karovoe and Svetloe lakes represent a 7% of the watershed area, Tsirkovoe and Oiskoe, a 5%, and Raduzhnoe is only a 1.4% of its watershed area.

As for vegetation cover, Oiskoe and Svetloe watersheds have a 25 and 28% forest cover whereas the other lakes have less than 10% forest covers. These two watersheds are quite similar in terms of land cover: they have quite equilibrated percentages of forests, shrubs, meadows and scree. Oiskoe is also the watershed with higher peatland cover (6%), followed by Svetloe (3%) and Radushnoe (1.6%). Karovoe and Raduzhnoe watersheds are dominated by scree (73% and 52%, respectively) and meadows (14% and 24%, respectively), whereas Tsirkovoe watershed is dominated by shrubs (56%) and scree (37%).

The abovementioned information will be included in the study site description. Nevertheless, our aim was not to compare differences between watersheds or lakes but to study a representative group of lakes that informed about regional processes, as far as possible.

Comparison of snapshots of the mentioned atlas and the self-made map for Oiskoe basin:



**REFEREE #2 COMMENT 4:**

Line 122: please specify sampling depths

**AUTHORS ANSWER 4:**

The sampling depths were not homogeneous, as it was reported in table S2. We will add an explicit mention to it and cite table S2 at this point of the text to avoid any misunderstanding.

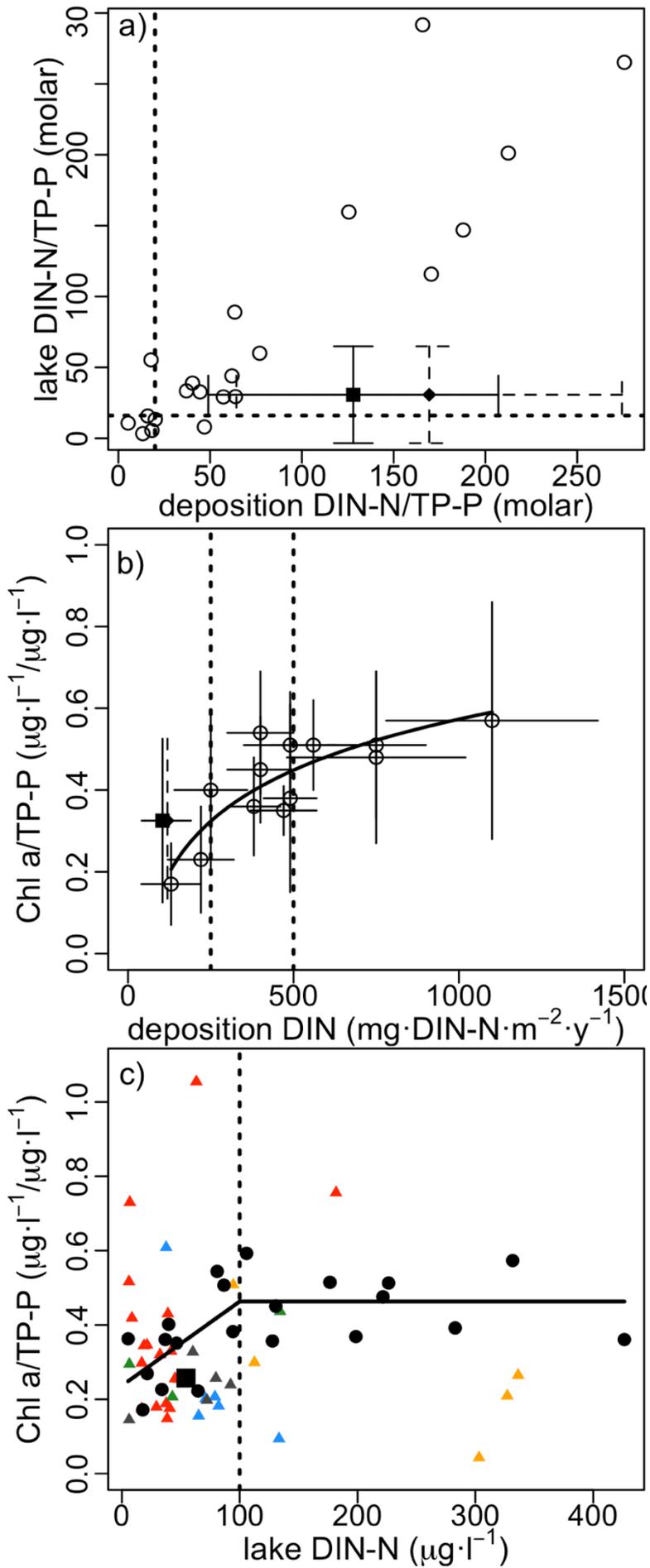
**REFEREE #2 COMMENT 5:**

Lines 122-124: the authors used data from a previous lake surveys: Were sampling and analytical methods comparable with the present study? For instance, the sampling period was slightly different in the two surveys (June-Aug in 2011-2012, Aug-Sept in 2015-2017): could this affect the differences in water chemistry between the two surveys (see comment below about Table S2)

**AUTHORS ANSWER 5:**

Yes, sampling periods are different and that might explain a particular percentage of the differences in water chemistry and chlorophyll across years because ecological succession was at different stages in different years samplings. Of course, the non-systematic sampling is an important minus of our lake chemistry data set. For that reason, we clearly state that limitation of our data set here in the methods section (lines 122-125), as well as in the discussion (lines 471-472 and 478-479) and in Table S2 (sample column). See discussion and graph below, on this same point.

As for analytical methods, there NO<sub>3</sub>, NO<sub>2</sub> and NH<sub>4</sub> were analysed according to the Russian standard method in 2011 and 2012. In this method the water sample is filtered through a paper filter. In 2015 and 2017 the same method was used but using an 0.45 µm pore membrane filter. In spite of the fact that porus size was not the same in the case of paper filter, only free ions would react in the analysis, so results are comparable. The important difference in DIN values for 2011-12 and 2015-17 were not due to due to different analytical methods but to a mistake between ionic and element units. The same occurred with TP in 2017. We have amended that mistakes in the new version of the manuscript. Now results look different, sections 3.6, 3.7 and conclusions will be changed. The corrected versions of figure 6 and table 3 will be as follows:



New figure 6

Year	month	Lake	DIN-N/TP-P (mol/mol)	TN/TP (mol/mol)	Limiting nutrient
2011	early June and August	Oiskoe	4.3		N
		Svetloe	4.3		N
		Raduzhnoe	16.2		N-P
		Karovoe	6.5		N
		mean	7.9		N
2012	early June and August	Oiskoe	109.2		P
		Svetloe	49.5		P
		Raduzhnoe	42.1		P
		Karovoe	29.6		P
		mean	57.6		P
2015	early September	Oiskoe	3.7	11.6	N
		Raduzhnoe	10.5	30.9	N
		Tsirkovoe	23.6	82.8	P
		mean	12.6	41.8	N
2017	late August	Oiskoe	6	56.6	N
		Karovoe	25.8	61.9	P
		Tsirkovoe	97.9	164.1	P
		mean	43.3	94.2	P

New table 3

Basically, the new conclusions are that the study site is a typical low atmospheric nitrogen deposition area, with lower deposition than the northern Sweden average, as it was described in the seminal paper by Bergström and colleagues where they formulated a new paradigm for phytoplankton growth limitation in oligotrophic lakes (figure 6 b). The studied West Sayan district is safely located in the nitrogen limited realm (figure 6 c). The idea that atmospheric nutrient deposition is quite unimportant for lake water chemistry and phytoplankton growth in these lakes is confirmed by the fact that DIN-N/TP-P ratios of atmospheric deposition and lake water clearly differ (figure 6 a). In conclusion, according to our data, both nitrogen and phosphorus limiting conditions occurred in the studied West Sayan mountain lakes (new table 3 and new figure 6 a) but the region as a whole would be predominantly located at the nitrogen limiting realm (new figure 6 a and c) and constitutes an excellent site to study the effects of global warming with a relative independence of atmospheric nitrogen deposition.

**REFEREE #2 COMMENT 6:**

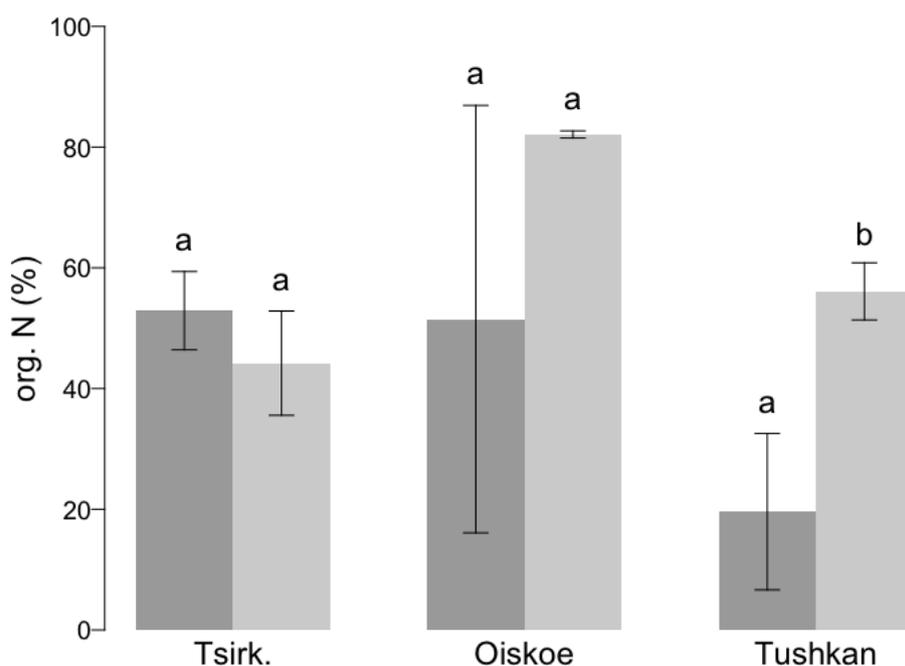
Lines 236-237: less than 50% of TN is in the form of NO<sub>3</sub>. Because NH<sub>4</sub> and NO<sub>2</sub> are negligible, the remaining part is organic N, Is there an hypothesis for such a high amount of the organic part? The comparison with deposition at other remote sites (lines 216-234) could consider also the relevance of inorganic vs organic N (if these information are available for the mentioned sites e.g. Pyrenees, Alps, Sierra Nevada).

**AUTHORS ANSWER 6:**

We didn't pay special attention to this fact, as organic nitrogen is not directly usable as a nutrient by lake phytoplankton. Nevertheless, it might be interesting to mention that, because organic nitrogen is especially important in the studied Ergaki mountain snowpack. We suggest to add a paragraph like this:

“The organic nitrogen in Ergaki snowpack represented a 56±19% of the total nitrogen, which is a high but reasonable value as compared to the literature. The relative share of organic to total nitrogen in the snowpacks of the Pyrenees, Alps and Sierra Nevada (USA) mountains, as well as on the Baltic sea were 10±9%, 41±13% ,49±17% and 21±12%, respectively (Catalan, 1989; Clement et al., 2012; Pearson et al.,

2015; Rahm et al., 1995). Organic nitrogen has been reported elsewhere to be higher in snowpack records than in wet deposition because dry deposition of organic nitrogen is integrated in the snowpack and because microbial uptake and assimilation of inorganic nitrogen might occur in the snowpack (Clement et al., 2012; Pearson et al., 2015). In the case of microbial conversion from inorganic to organic nitrogen, it could be hypothesised that deeper and older snow layers should have higher organic nitrogen shares. Such a pattern was only observed at Tushkan (ANOVA, p-value= 0.0178) whereas no significant differences were found in the percentage of organic nitrogen between upper and lower snow layers at Oiskoe and Tsirkovoe sites. We, therefore, hypothesise that a different combination of phenomena might be responsible for organic nitrogen dominance at different sites.”



Column pairs with “a” and “b” letters are significantly different (one-way ANOVA, p-v<0.05; n=3 except in Tsirkovoe, where upper layer n=4 and lower layer n=2).

**REFEREE #2 COMMENT 7:**

Tab. 2: It should be briefly mentioned in the table caption that “\_ time” and “\_ precipitation” referred to different approaches for estimated deposition, and then referred to the text for the explanation.

**AUTHORS ANSWER 7:**

OK, we will add these sentences to the table caption:  
 “Yearly deposition rates were estimated on the basis of measured winter depositions and either assuming a constant deposition rate (time weighted estimate, row 3) or a precipitation-dependent deposition rate (precipitation-weighted estimate, row 4). See section 3.3 for further discussion.”

**REFEREE #2 COMMENT 8:**

Lines 238-243: SO4 values are indeed quite high. The authors stated that these values are possibly overestimated because referred only to the winter period: why deposition

should be “expectably lower during summer” (line 353)? Do the authors totally exclude long-range transport from large sources, which could explain this high SO<sub>4</sub> deposition?

**AUTHORS ANSWER 8:**

We suggest that the high SO<sub>4</sub> values in the snowpack could be due to combustion of coal, which is commonly used for domestic and central heating in villages and cities at a regional scale. Therefore, we do not exclude long-range transport from large sources. That is discussed in section 3.5. We will change the phrase “Finally, our yearly sulphate deposition estimate should be cautiously considered, as it could be overestimated due to expectably lower deposition during summer” by:

“Finally, our yearly sulphate deposition estimate should be cautiously considered, as it could be overestimated due to regionally widespread coal combustion for heating during winter (see section 3.5).”

**REFEREE #2 COMMENT 9:**

Paragraph 3.3 I would suggest reorganising this paragraph and shorten it. The comparison of the deposition estimates of the present study (Tab.2) with other studies or with global deposition models could be eventually summarised in a table in the SM.

**AUTHORS ANSWER 9:**

OK, that is true. This section is written in an inductive way. It will be reformulated to a deductive structure of the speech, which will probably be more communicative and, hopefully, also shorter. A summarising table with the deposition estimates of the present study and those of global deposition models will be added in the SM if the manuscript is allowed to pass to the following revision step.

**REFEREE #2 COMMENT 10:**

Lines 284-295: Personally, I think this paragraph does not add any useful information on the estimate of P deposition and could be skipped. As the authors said, the use of pollen is an inaccurate method for the estimate: type and coverage by vegetation, meteorological features, and other factors should be considered. Furthermore, other sources than pollen could contribute to P deposition.

**AUTHORS ANSWER 10:**

Well, that is true that this paragraph does not add any especially valuable information but it rather reinforces the idea that the previous TP deposition estimate could be a credible value (or, alternatively, an underestimate). Moreover, it has also been criticized by the other referee. The paragraph was not present in the original manuscript but added on request of a reviewer in a previous submission to another journal. It will be deleted if the editor allows us to submit a new version of the manuscript.

**REFEREE #2 COMMENT 11:**

Lines 300-305: I agree that a seasonality in NO<sub>3</sub> deposition could be scarcely evident at remote sites with very low deposition rates. However, precipitation amount is probably more important at these sites in shaping the seasonal pattern of deposition.

**AUTHORS ANSWER 11:**

Yes, remote sites have a low seasonal variation of atmospheric NO<sub>3</sub> concentration, so the seasonal NO<sub>3</sub> deposition is basically ruled by precipitation seasonality in these remote and humid environments. We concluded that from the detailed discussion of a couple of study cases with seasonal information on

atmospheric NO<sub>3</sub> deposition and precipitation (in Czech Republic) and atmospheric NO<sub>3</sub> concentrations (China) (lines 300-317). That is why we chose the precipitation-weighted estimate of yearly NO<sub>3</sub> deposition (lines 330-331).

**REFEREE #2 COMMENT 12:**

Lines 360-361: The cited site in the Alps was an example of a remote site affected by long-range transport of air pollutants from the lowlands. Furthermore, the SCP values referred to periods of markedly high pollutant deposition (1980s-early 1990s). This holds for many sites, at least in Europe, where deposition of air pollutants, especially SO<sub>4</sub>, decreased significantly in the last 3 decades. I would suggest considering this temporal discrepancy when making the comparison with other sites. Conclusions: this paragraph can be shortened too, also because the content is partly already provided in the discussion. Conclusions can be maybe provided in the form of a few concise statements summarising the main outcomes of the study and the future research needs.

**AUTHORS ANSWER 12:**

We added the specification that data from the Alps refers to the more polluted times of 1980s and early 1990s. We also reviewed that all the comparisons with values found in the literature always included the information about the years when they were measured, if distant from the publication date. On the other hand, we suggest not to shorten this paragraph, as it is the only one in the discussion where we compare our calculated SCPs deposition rate to those in the literature.

OK. Conclusions will be shortened.

**REFEREE #2 COMMENT 13:**

Tab. 1: I would speak about “local pollution sources” more than “local perturbations”

**AUTHORS ANSWER 13:**

OK. We changed it.

**REFEREE #2 COMMENT 14:**

Table S2:

- SO<sub>4</sub> is lacking. It could be interesting to see the SO<sub>4</sub> level in lake water, considering the quite high atmospheric input of SO<sub>4</sub> estimated from snowpack analysis.

**AUTHORS ANSWER 14:**

We have added SO<sub>4</sub> measurements for lake water in the lake water chemistry table at SM. Values range from 0 to 1900 µg SO<sub>4</sub>-S/l. In 2015 it was not measured.

**REFEREE #2 COMMENT 15:**

- Further, there are quite sharp differences in some variables (e.g. NO<sub>3</sub>, TP) between the 2011-2012 and the present survey e.g. NO<sub>3</sub> in Oiskoe and Raduzhnoe was markedly higher in the first survey. On the opposite, TP seem to be significantly higher in the most recent survey. Could this be due to the different sampling procedure (composite vs grab surface sampling) or to the slightly different period of the year?

**AUTHORS ANSWER 15:**

Yes, that was true according to the submitted manuscript. As we already mentioned, we found a mistake in our lake water chemistry data. We did two mistakes. Firstly, we took 2011 and 2012 DIN data as N-NO<sub>3</sub>, N-NO<sub>2</sub> and N-NH<sub>4</sub> but in fact the ionic forms had been measured (NO<sub>3</sub>, NO<sub>2</sub> and NH<sub>4</sub>). Secondly, we did also a mistake when converting from total ionic PO<sub>4</sub> (after digestion) measured in 2017 into TP. All the units of the original data and the necessary conversion factors have been checked during this revision of the manuscript. After the corrected data, the difference in DIN levels between 2011-12 and 2015-17 is much more moderate than it appeared to be before. As for TP, changes are minor.

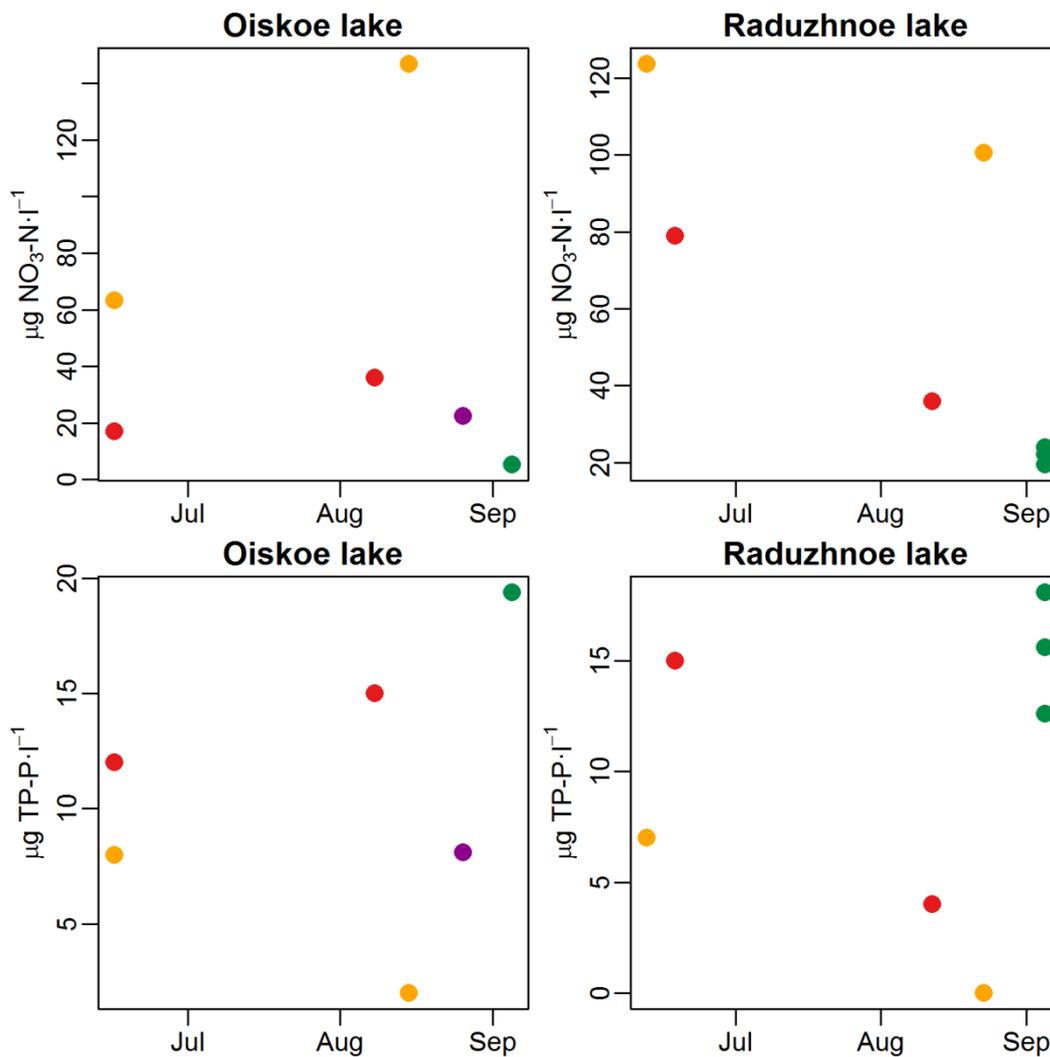
In any case, even after the corrected data, the question posed by the reviewer remains completely pertinent. As we previously said, the non-systematic sampling is a minus of our data set and we need to be very cautious when extracting any conclusion from that. Nevertheless, the data set is still informative. We expose our rationale here:

All sources of variability are important: composite vs. surface water sampling (sampling), stage of yearly plankton succession (season), and year variability (year). Oiskoe lake was sampled as composite samples (2011 and 2012) and at different depths (2015 and 2017). The differences between composite or discrete depth sampling can be minimised. The separate values obtained from different depths at 2015 and 2017 expeditions can be averaged to simulate a composite sample analysis and make data comparable across years and plankton succession stages. This cannot be done in the case of Raduzhnoe where samplings were either composite sample (2011) or surface water (2012-15). Nevertheless, Raduzhnoe is a small shallow lake. Its maximum depth at a very particular place in the middle of the lake, amongst rock boulders at the bottom of the lake, is 4m but most of the lake is generally no more than 2 m deep. Therefore, mixing might be important in this lake and, consequently, the differences in chemical composition are likely to be moderate between different depth water layers.

The other two sources of variability (season and year) cannot be disentangled in any way. That is a limitation of our data set. Nevertheless, there are some patterns that can be mentioned (see graph below):

- Both, at Oiskoe and Raduzhnoe lakes, late summer NO<sub>3</sub> was lower than early summer NO<sub>3</sub>, and/or 2015-17 NO<sub>3</sub> was lower than 2011-12 NO<sub>3</sub>.
- Both, at Oiskoe and Raduzhnoe NO<sub>3</sub> values were intermediate in 2011 (early and mid summer), higher in 2012 (early and mid summer) and low in 2015 and 2017 (late summer). If we removed 2012 outlier, the trend still would be to decrease in time (months and/or years).
- In the case of TP, there is a high variability in the values within any of the plotted lakes and there is no clear temporal trend (along succession and/or years). It should be noted that the TP values corresponding to 2015 are slightly higher than in the other years. TP in 2015 survey samples was measured differently from all the other cases: instead of directly analyzing TP, they were the sum of dissolved inorganic phosphorus (DIP) and particulate phosphorus (PP). This information was missing in the former manuscript version (!) but it has been included in the next version.

In conclusion, N tends to decrease in time (although it is uncertain if it is a seasonal and/or an interannual trend), but because P values oscillate, the N:P ratio also behaves this way (see corrected table 3 above in this document).



Lake water nitrate and total phosphorus concentrations at different time points of the plankton succession sampled at different years: 2011 (red), 2012 (yellow), 2015 (green) and 2017 (purple).

**REFeree #2 COMMENT 16:**

- TP values are quite high, especially in Oiskoe in 2015, pointing to a mesotrophic status of the lake: is there any hypothesis for that? Deposition is discussed in the manuscript as a P input, but these values lead to hypothesised other inputs (catchment sources)

**AUTHORS ANSWER 16:**

Yes, as we stated in Table 1, Oiskoe has the most human-modified watershed including an inflow from nearby houses. We add a new phrase underlying this fact also in the discussion, in former line 477. We will add:

“The effects of atmospheric nutrient deposition could be blurred by watershed processes at this lake [Oiskoe]. Forest and peat cover (25% and 6%, respectively) are important in comparison to the other lakes and, more importantly, the lake receives an inflow passing by nearby houses (table 1). Nevertheless, that houses and land covers were present during the whole studied period and the local anthropogenic impact-free Karovoe and Raduzhnoe lakes also showed a decrease in DIN-N/TP-P ratios in time.”

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