

Dear Editor

We agree with all remarks of the reviewers and directly addressed them in the revised manuscript. Below, we specified the line numbers in the manuscript where the changes have been made. We also highlighted the changes in our reply compared to its first version.

### **Responses to reviewer No 1.**

*Given the large quantity of data I wonder if it would have been worth attempting a principal component analysis to further disentangle TE mobilization.* In request to this important remark we performed the PCA treatment of the data as described below and presented in section 2 (L 172-181) and section 3.5 (L392-417) of the revised manuscript.

The data consisted of ~130 lake water samples grouped into three distinct seasons (spring, summer and autumn). Statistical PCA analyses were applied in order to derive a distinctive view of the influence of various parameters, notably the seasons, on the lake water chemical composition variability. Both normed and non-normed PCA treatment was attempted. For this step, the STATISTICA package (<http://www.statsoft.com>) which is also designed to compute and render graphics, was used to interpret the spatial structures.). Statistical analysis considered each chemical element as a variable (35 in total) for all lakes. Considering all seasons together, the first factor was responsible for 16% variation and included B, Na, Si, K, Ca, Ti, V, Cr, Ni, Zn, Rb, Mo, Sb, Cs, Ba, La, Ce and U whereas the 2<sup>nd</sup> factor (6.3%) included Al, Fe, Co, As, and Cd. Separation of F1 and F2 factors in June and August was uncertain since they provided 9% and 6.7% (June) and 11.8% and 5.8% (August). In contrast, October's data could be explained by 18.8% variation of F1 (B, Na, Si, K, Ca, Ti, V, Cr, Ni, Zn, Rb, Sr, Zr, Mo, Sb, Cs, Ba, La, Ce and U) and 4.4% F2 (SO<sub>4</sub>, Cu, Co, Fe, As). The list of elements and corresponding factors for each season is given in Table S5 and illustrated in Figure S7-A of the Supporting Information. The correlation profiles for F1 and F2 and various seasons are given in Fig S7-B.

This PCA treatment demonstrated rather high variability of lake chemical composition, mostly pronounced during June and August. In June, multiple factors are responsible for element enrichment in the lake water, namely the lateral input from thaw snow and lake ice, dissolution of colloid coagulation products, leaching of plant litter. The F1 factor in June is very poorly pronounced. Nevertheless, it may mark the colloidal transport of TE (organic complexes) whereas the 2<sup>nd</sup> factor may correspond to the degree of snow input (typical atmospheric aerosol –originated elements). In August, internal (autochthonous) processes and subsurface feeding are likely to strongly modify lake water chemical composition both for major (pH and DIC of the F2 factor) and TE. In addition, atmospheric precipitation in the form of rain which dilute lithogenic TE but also deliver marine aerosols and dust (via dissolution) can strongly modify the role of individual correlations. Finally, October represents the period when the first factor is mostly pronounced, as also translated in the PCA results of all seasons together. Presumably, the period of the beginning of ice formation corresponds to the maximal stability of the F1 x F2 structure; during this time, the influence of both allochthonous (lateral and subsurface TE influx from peat, mineral soil horizons and ground vegetation) and autochthonous (bio- and photo-destruction of organic colloids, primary productivity) processes are minimal.

*Maybe the authors should consider having another or enhanced conceptual figure that explains TC cycling in their systems. Is it possible to add vegetation and deeper peat element leaching to figure 11 ?* This conceptual figure illustrates the freezing concentration processes occurring in thermokarst lakes within a confined and frozen surrounding substrate. Note that the lake bottom is always frozen. During the period of October to May, shown in this figure, surrounding moss and peat are also frozen and do not suppose to leach any solutes to the lake

water. There are certainly exchange reactions between the lake sediment and the water column, thoroughly considered in our previous works (i.e., Audry et al., Biogeosciences, 2011). Following this recommendation, we added the possibility for lateral feeding in the beginning of the cold season and we also added the mobilization of solutes from lake interstitial sediments via pressure squeezing at the end of the glacial season (Figure 9 of the revised manuscript).

*The authors hint that large parts of the particulate Fe bound TE do not make it into the river systems. I think this is an important observation that might deserve a little more discussion. Is this a plausible mechanism for TE enrichment in sediments ?* This is very good point. Such a mechanism of TE enrichment in the sediment may be fully plausible. Last summer, we collected the core sediments in the lakes subjected to freezing and currently we are estimating the possible degree of such enrichment. We would like to avoid the speculations on unfinished work; however we will add this possibility to the discussion. Note that the thermokarst lakes studied in this work are not directly connected to the rivers. Neither particulate, no dissolved Fe-bound TE will ever make into the river system, even during spring flood. We added an explicatory sentence to revised text (L573-575).

*No effort was made to model the distribution of elements using chemical equilibrium modelling such as WHAM VII or VisualMinteq, why ?* This point is well taken; detailed description of visual MINTEQ chemical speciation modeling of studied lakes is given below and presented in section 3.6 (L419-454) of the revised manuscript.

We used the geochemical program Visual MINTEQ (Gustafsson, 1999), version 3.1 (October 2014) for Windows, a recent adaption of the original code written by Allison et al. (1991) (see Unsworth et al. (2006) for vMINTEQ application example) in conjunction with a database and the NICA-Donnan humic ion binding model (Benedetti et al., 1995; Milne et al., 2003) and Stockholm Humic Model (SHM). Speciation calculations were performed for Ba, Ca, Cd, Co, Cu, K, Mg, Mn, Na, Ni, Pb, Sr, Zn, and Al, Fe<sup>III</sup>, Th<sup>IV</sup>, and U<sup>VI</sup>O<sub>2</sub> for average lake water composition in spring, summer, autumn and winter as well as the average August composition of large (> 500,000 m<sup>2</sup>) and small (100-500,000 m<sup>2</sup>) lakes (Table 3) without modification of the default database (Milne et al., 2003). Note that significant proportion of data used to create this database represents soil humic and fulvic acids, and all aquatic FA and HA originated from temperate rivers and lakes which may be quite different from boreal subarctic waters studied in this work. In addition to NICA-Donnan approach, Stockholm Humic Model (SHM) of visual MINTEQ was used to calculate metal speciation in the lake water.

Results of the calculation of metals degree of complexation with DOM are listed in Table S6 and illustrated in Figures S8 and S9 of the Supplement. It can be seen that, according to NICA-Donnan model, the majority of divalent major and trace element is bound to organic (Donnan-like) complexes. Only Na and K exhibited a decrease of 80 to 10% complexed fraction from spring to winter. Extremely high complexation of metals with DOM (up to 80 to 90%) within the Nica-Donnan concept is supported by dialysis experiments conducted by our group in various lakes of western Siberian subarctic (Pokrovsky et al., 2013; Shirokova et al., 2013). In contrast to the Nica-Donnan, the Stockholm Humic Model (SHM) predicts moderate and quite variable association of divalent metals with DOM, with the lowest values for Ba and Mn (40% in spring and 20% in winter) and the highest values for Cu and Pb (80-90% for all seasons). It is important to note that the highest proportion of organic complexes is observed in summer, presumably due to the highest pH recorded during this season which facilitates the deprotonation of functional groups of the DOM. The lowest proportion of organic complexes in winter could be due to competition between metals for

organic ligand binding sites, given significant increase of  $Me^{2+}$  compared to DOC during solute concentration by freezing. The lake size has significant impact on metal complexation with DOM as illustrated in Fig. S9. Even within the “conservative“ SHM model, the TE in small thaw ponds exhibit 100% complexation with DOM. The degree of complexation is smaller in large lakes having a factor of 2 lower DOC concentration, despite that their pH is higher than that of small lakes (5.49 and 4.72, respectively). Interestingly, this may indicate higher bioavailability of metal micronutrients in large lakes, in line with the hydro biological evolution of western Siberia thermokarst lakes (elevated productivity and the presence of macrophytes and phytoplankton blooms in large mature thermokarst lakes, Pokrovsky et al., 2014).

*The authors measured pH but did not use it to explain some of their observations. Are their results independent of pH ? There is evidence in the literature that pH has a large control on both TE binding and Fe speciation. How much is pH controlled by DOC and how much by acid anions ?* The pH value is now explicitly included in our chemical equilibrium modelling by Visual MINTEQ (see our response to the previous question). The main result of this modeling is that the DOC concentration has more pronounced impact on metal speciation (notably the % of organic complexes) than the pH - both across the seasons and different lake size groups. Note that the simple carboxylic acids were below the detection limits by our HPLC technique used for anion analysis. The role of acid anions (Cl,  $SO_4$ ) at their concentration of 4 to 5  $\mu M$  in overall pH control ranged from 10 to 50% with the major influence exerted by DOM, especially in small lakes (< 500,000  $m^2$ ), most abundant in this region. We presented this information in L 446-454 of the revised manuscript.

*This is a long list of authors. Is it possible to describe the individual contribution of the authors to this manuscript?* Without referencing to a recent 12-author paper of Walter Anthony (2014) on Siberian yedoma thermokarst lakes, or a 20-author paper of J Boike (2011) on the Lena Delta permafrost system, we would like to point out that such a multidisciplinary study in remote region requested 4 heavy expeditions in 2013-2014, so that all the researchers (all but one have their PhD degrees) participated in the design planning of sample collection, its practical realization, analysis and interpretation of results.

Specifically,

Manasypov performed sampling, analysis of major cations and trace elements, interpretation and writing; Vorobiev and Kirpotin were responsible for the choice of sampling objects and statistical treatment; Kritzkov was the leader of winter sampling campaign and interpretation of lake freezing results; Loiko and Kulizhsky provided the background information on soil, peat, and contributed to design of summer and winter sampling campaigns; Shirokova was in charge of DOC, DIC and anion measurements and their interpretation; Shevchenko provided the expertise and practical performance of ice core sampling, handling and analyses; Kolesnichenko provided GIS-based interpretation, mapping and identification of sampled water bodies; Zemtsov and Sinkinov performed all primary hydrological data collection, their analysis and interpretation; Pokrovsky and Kirpotin provided supervision and placing this work in the context of current knowledge of western Siberia thermokarst lakes. All 12 authors spent significant amount of time in the field of Khanymey and Nojabrsk test sites. Each co-author have seen and approved the final paper and contributed to writing the manuscript. We added the requested text in the end of the paper (L736-749)

*From figure 2 to 5 it seems that there are no small lakes available in summer. The question arises which lakes change size?* This is true, small lakes were not sampled in summer for two reasons. First, many small depressions (10-100  $m^2$ ) were already dry in Augusts. Second, the

summer sampling campaign in this work was focused on medium and large size lakes. The small lakes from our test site (Fig. 1) sampled in wet/normal summer 2010 are described in our previous work (Shirokova et al., 2013). There was no significant change in the lake size (as it happened during heatwave in 2012, see Pokrovsky et al., 2013). However, the water depressions of 10-1000 m<sup>2</sup> size abundant in spring were often dry in summer 2013. Statistical treatment of our data (L23-25 p. 1982 and see also response to Rev No 2) demonstrated the lack of lake size effect (from 1000 to 500,000 m<sup>2</sup>) on element concentration. **We amended the text with necessary explanations (section 3.1 L193-L200).**

*P. 9 L 12 Were these slopes corrected for the presence of dissolved iron ? You have only three winter samples it seems. Maybe remove the sequence in the figure caption of figure 3. We agree to modify the sequence as “spring < summer < autumn”. Even three winter samples shown in Fig. 3 are useful as they illustrate the similarity of the UV absorbances among different contrasting seasons. We do not think that the dissolved iron can interfere significantly to this sequence as the molar ratio DOC/Fe remains very high during all seasons (between 220 and 480). Specifically, corrections for Fe<sup>3+</sup> imply subtracting a term of 0.08×[Fe, ppm] (Weichaars et al., 2003) from the UV absorbency. At relatively low Fe concentration in studied lakes (100 to 400 ppb), this will change the measured UV<sub>280 nm</sub> value (typically, from 0.2 to 0.5 cm<sup>-1</sup>) by less than 10% which is negligible compared to the variability among different seasons and lake sizes. **We added this information in the text (L488-490).***

*Did you do any statistical analysis of TE and UV<sub>280</sub> ? Maybe you could relate that to the element leaching of vegetation as opposed to peat leaching ?* The statistical treatment of the data did not reveal significant ( $p > 0.05$ ) links between TE concentration and UV<sub>280 nm</sub>. Rather poor correlations shown in Fig S4 (Supplement) of the manuscript are illustrative for both UV and DOC. The concentration of TE in peat unfrozen horizon and in ground vegetation (green and brown mosses) in the discontinuous permafrost zone of western Siberia are rather similar (Stepanova et al., 2015) and thus we do not expect that UV<sub>280</sub> can help to distinguish between the element leaching from vegetation as opposed to peat leaching. Rather, the similarity of specific UV absorbances across the seasons and lake size strongly suggests the dominance of terrestrial (soil and litter) sources of OC with minimal aquatic DOM. **We added this in the text (L235-243).**

*P 13 L. 28 and P 14 L. 2 : This is probably a good back of the envelope calculation but it is difficult to follow. Could you please explain with two more sentences your assumptions. I.e. Kd values for water/ice...maybe consider 1 m<sup>2</sup> of lake.*

In this calculation, we assumed a conservative scenario of element concentration evolution in thermokarst lakes. Based on thorough hydrological observations, we accepted, for 1 m<sup>2</sup> of the surface area, an average lake depth of 75±25cm in summer, to which we added 20 cm flooding in spring and from which we removed 20 cm of the water layer for ice formation in October. The 3 sampled lakes exhibited almost full freezing in February with therefore 10 cm of bottom water left and 65 cm of the ice. The concentration factor was calculated as the ratio of the water volume under 1 m<sup>2</sup> in a given season to that in spring. It was equalled to 1, 1.3, 2.0 and 9.5 for June, August, October and February, respectively. **The text was corrected accordingly (section 3.3, L 337-345).**

*P. 16 L. 10 This is a large difference I agree. I would still suggest that the authors make an effort to correct that data for the contribution from dissolved iron. We added an explicatory note: Correcting the UV absorbance for dissolved Fe<sup>3+</sup> (Weichaars et al., 2003) via subtracting a term of 0.08×[Fe, ppm] will change the UV<sub>280 nm</sub> value by less than 10% which*

is beyond the variability of the seasons and the lake size. Note also that a recent study of DOC properties in a boreal site demonstrated the absence of the influence of nitrate and iron on UV and visual absorbance up to 2.2 mg/L of Fe(III), (Avagyan et al., 2014, J Hydrology). We added this information in L 491-492 of the revised manuscript.

*P. 18 L. 8 Was that Fe(II) method mentioned in the methods section ?* No. We have not used ferrozine technique for Fe(II) analysis in this study. Here we refer to previously elaborated technique of Fe(II) analysis using dialysis membranes deployed directly in the lake water (Pokrovsky et al., 2012 Aquatic Geochemistry). We added this in L548-549 of the revised manuscript.

*P. 18 L. 25 This should eventually lead to an enrichment of trace elements in the solid phase. Would you happen to have any evidence of that from sediment samples ?* Yes, but only in the northern part of discontinuous permafrost zone some 400 km north of the present study site: the lake sediments are indeed enriched in Fe and trivalent and tetravalent hydrolysates (Audry et al., 2011, Biogeosciences). The work on sediments from lakes subjected to freezing collected during last summer on the Khanymey test site is in progress. We added necessary sentence in L 573-575.

*P.19 L. 8 Is that process maybe worth adding to a conceptual figure ? May be add to figure 11?* We added the proposed possibility to the upper diagram of Fig. 11 (see Fig. 9 of revised manuscript). Note that the input of fresh vegetation products and the leaching of the upper peat layer occur in June-August. The revised Fig 9 illustrates the processes occurring during glacial period, when topsoil and plant litter are frozen, between October and May.

*P. 20 L. 6 Here and earlier it would be nice if the authors would make an attempt to model the speciation. Why would Cu not be dependent on DOM colloids ?* As stated in the text (L 610-612), we hypothesized that these metals (including Cu) are less dependent on large-size DOM colloids than Fe, Ni, Cd and Pb. The large-size colloids are mostly subjected to coagulation during cryoconcentration. It is possible that these metals may be bound to LMW<sub><1 kDa</sub> organic complexes and thus remain in unfrozen water in the lake bottom layer. The speciation calculations (see section 3.6) do not help to distinguish between Fe, Pb and Cu: all three metals are 99%-bound with DOM. However, the LMW ligands are known to be most strongly pronounced for Cu (Pokrovsky et al., 2012 Geobiology and references therein) and as such this element can be “protected” from freezing-induced coagulation.

*P.20 L. 13 I assume that you made some solubility calculations...please explain.* Good point. The necessary information is given in (Shirokova et al., 2013); all the thermokarst water bodies of western Siberia are strongly supersaturated with respect to atmospheric pCO<sub>2</sub>. We referenced this work accordingly (L 621-622).

*Figure 3: Please remove winter in the sequence. You have only three samples it seems.* We agree. Note that the trend of progressive increase of the aromaticity from spring to autumn still remains. Revised Fig. 3 now has no winter data point.

*Figure 4: Did you attempt to normalize TE by Ca so see which elements could originate from litter leachate ? I assume that element ratios from a number of mosses are known.* This is very pertinent remark. Thanks to our recent work on elementary moss and peat composition in western Siberia (Stepanova et al., Applied Geochemistry, 2015), such a normalization becomes possible. However, significant variations of Ca concentration, over 2 orders of magnitude for the same lake size and the same season, actually preclude any quantitative

resolution of the TE source in the lake water, i.e., discriminating between peat versus surface moss layer leaching. Given the weak efficiency of Ca normalization, we did not modify the text in response to this comment.

*Figure 5: How much of the pH variation is explained by the presence of DOC. You seem to have data on ANC (major cations and major anions).*

The role of acid anions (Cl, SO<sub>4</sub>) at their concentration of 4 to 5 μM in overall pH control ranged from 10 to 50% with the major influence exerted by DOM, especially in small lakes (< 500,000 m<sup>2</sup>), most abundant in this region. This comment is partially addressed in L 444-454.

*Figure 6. is this figure needed ?* Not necessary in the main text, we moved it to the Supplementary. Now this is Fig. S3 of the supplement.

*Figure 9: Do you have any explanation for the high Zn values during winter ?* The main reason for such an increase of Zn concentration could be its high mobility in acidic, organic-rich aquatic systems. The additional mobilization of Zn from moss cover at the lake border during its freezing can be linked to the release of Zn from the cell cytoplasm during freeze-induced submerged vegetation cell damage. However we do not know any experimental works devoted to quantification of this potentially important phenomena. Note however that the concentration factor for Zn is not dramatically different from that of the other elements: it is similar to that of Cu, Zr, B, Na, K, REEs and U and even lower than that of Pb. As such we consider high element concentration during winter as being the consequence of solute concentration during freezing rather than specific mechanisms of metal mobilization from ground and bottom vegetation subjected to freezing. We added requested explanation in section 4.2 (L 556-564) of the revised manuscript.

*Figure 10: Fe should be ppb instead of ppm.* Thank you. Corrected.

*Figure 11: This figure could be complemented by TE mobility from either leached vegetation, litter or peat.* This figure schematizes the events during glacial cover period. We consider that the majority of surrounding organic substrate is already frozen. The main impact of fresh and litter vegetation as well as surround peat leaching occurs in May and summer period, not considered in this Figure. We added a possibility of lateral (subsurface) peat leaching in September-October in the revised Figure 9.

## Responses to Reviewer No 2

*It appears that the sampled ponds and lakes were not the same from a season to another (Table 1, Fig. 1). Apart from 3 lakes out of 130, in each sampling season the sampled sites were thus different, and in very contrasting abundance (June: n = 64; August: n = 31; October: n = 31; February: n = 3). How can we talk about seasonal trends if the data do not come from the same sampling sites? Moreover, only 3 sites are presented for winter, which seems a poor number compared to other seasons. Without further explanation on why the authors chose different lakes in different seasons (instead of coming back to the same sampling sites to be able to compare from a season to another), and without a demonstration that comparable lakes (of the same size) will show comparable hydro-chemical trends throughout the year, the inferred seasonal trends are not well supported. This should be further explained or justified.*

Highly variable number of sampled lakes during each season was basically due to the difficulties in sampling logistics, and the access to the site. Only five lakes (now labelled A, B, C, D, E in the Table 1) could be collected during all three open water seasons. In winter, we could not sample more than 3 lakes (both ice core and bottom water), because out of > 10 lakes we drilled in February, only 3 had any water at the bottom. All small lakes (< 1000 m<sup>2</sup>) were frozen solid in October (autumn period). We did not focus in this work on small size (< 500 m<sup>2</sup>) lakes in summer, because the small water objects were thoroughly studied in our previous work (Shirokova et al., 2013). Besides, many small ponds (10-100 m<sup>2</sup>) were dried in August 2013. For this reason, the size range of the sampled lakes is different among seasons.

**(We added this information in revised text L193-200)**

In addition to particular features of these shallow water bodies, the main reason why we discuss full data set is that we demonstrate, using rigorous statistical treatment, that the effect of the lake size on all measured chemical parameters is absent ( $p > 0.05$ ). In other words, given very similar depth of these shallow, non-stratified water bodies, all located in the same watershed divide, they are chemically indistinguishable, at least for the size range below 0.5 km<sup>2</sup>. The seasonal trends shown in **Fig. 7** of the manuscript are based on rigorous statistics of many lakes (except winter) and as such can be considered as highly representative for the territory.

To further illustrate the validity of our approach, we plotted in **Figure S10 of the Supplement** below two selected elements, also present in **Fig. 7** of the ms, Al and Cu, for the same 5 lakes sampled in spring, summer and autumn. For a large range of lake surface area, the trend spring < summer < autumn is clearly visible and statistically significant ( $p < 0.05$ ). The same treatment can be performed for all other dissolved components; however we believe that only simultaneous treatment of all lakes provides most reliable results.

*One way to provide more information would be to display correlation lines, slopes and coefficients ( $R^2$ ) on the Figures that present separate seasonal data (Figs. 2 to 6, and 10). At several places in the main text, the authors mention slopes and correlations, but do not provide such information on the graphs.*

In response to this comment we provided Table S1 (Supplement of the revised manuscript) that lists all the equations and correlation coefficients for the data shown in Figs 2, 3, 4, 8 of the main text and Fig. S2, S3 and S4 of the Supplement.

## Responses to specific comments of reviewer No 2

P1977, L2-6. Except only two words ('and vegetation', L4), this sentence is identical to the first sentence of the Introduction (P1978, L10-14). One would expect the abstract to recapitulate, summarize, condense the main points of the manuscript. Not just routinely copy-paste a few sentences. We agree. The first sentence of the revised abstract was modified as following "Despite relatively good knowledge of the biogeochemistry of Siberian thermokarst lakes during summer base flow, their seasonal dynamics remains almost unexplored (L 19-20)."

P1977, L2-3 (same as P1978, L10-11). The authors should provide a reference to support the assertion that thermokarst lakes 'extend over a territory spanning over a million km<sup>2</sup>'. We corrected this sentence as "Western and central Siberia's thermokarst (thaw) lakes extend over a territory spanning over a million km<sup>2</sup> (half of Western Siberia Lowland, 0.5 million km<sup>2</sup> and all North Siberian Lowland, 0.84 million km<sup>2</sup>)", L50-52.

P1977, L10-12. This sentence is hard to understand. We revised as: "The lakes larger than 1000 m<sup>2</sup> did not exhibit any statistically significant control of the lake size on Dissolved Organic Carbon (DOC), the major and trace element concentrations over three major open water seasons." L 24-27.

P1977, L16. Is the observed increase 'between spring and summer' on the one hand, and 'autumn and winter' on the other hand? If yes, maybe put a comma between the two? We agree and completely revised this sentence as following: "The concentration of most trace elements (TE) increased in the order spring > summer > autumn > winter." L 29-30.

P1977, L20-23. When reporting depths, I don't think we can use 'at the beginning'. Better to use 'near the surface', 'towards the bottom', etc. Also, at the end of the sentence: 'to the depth': : : of what? Do the authors mean 'to the bottom'? Please reword. We revised these two sentences as following: "As a result, the DOC and metal (Mn, Fe, Ni, Cu, Zn, As, Ba and Pb) concentrations were the highest near the surface of the ice column (0 to 20 cm) and decreased by a factor of 2 towards the bottom." L 33-35

P1977, L24. Do the authors mean 'implications' (instead of 'consequences')? Yes, corrected. (L35)

P1978, L1. For the non-specialist: what is a 'kDa'? Low molecular weight here means < 1 kDa, or < 1-2 nm. Corrected in L 40.

P1978, L6-8. How can a higher DOC concentration automatically mean a strong heterotrophic status and thus elevated CO<sub>2</sub> flux to the atmosphere? This assertion, although possible, is not strongly supported by the results from this study. In this part of the text, we



do not claim the elevated flux of CO<sub>2</sub> to the atmosphere from thermokarst lakes. Arctic thermokarst lakes may as well absorb CO<sub>2</sub>. Later in the text we do discuss the heterotrophic status of lakes from the Khanymey test site of this study and we reference our previous work in this region (Shirokova et al., 2013, Biogeochemistry). **We have not corrected the text in response to this comment.**

*P1978, L10-17 (first paragraph). The authors do not provide references here. Where do statements like ‘a territory spanning over a million km<sup>2</sup>’ or ‘permafrost thaw being heavily intensified in Western Siberia’ come from? We revised the sentence on geographic coverage with numbers taken from the Encyclopedia which does not require specific reference. We did add the reference to works of Frey and Smith (2005) **(L 50-56)***

*P1978, L24. Only in ‘boreal lakes’? I would say subarctic/arctic lakes as well. We agree and corrected accordingly **(L 66)**.*

*P1979, L1. Maybe I am too strict on words here, but if these shallow aquatic systems fully freeze to the bottom during winter, shouldn’t we name them ponds instead of lakes? Yes, these water objects could be called ponds. However, for consistency with previous works, we would like to maintain the use of term “lakes” in this study. We do agree that a 10 m large, 40 cm deep water object is hard to call “lake” and thus prefer a more general name “water body”. **We did not change the text in response to this comment.***

*If so, these western Siberia systems would not be that particular or different from other ponds from elsewhere around the Arctic (e.g., Laurion et al., 2010; Negandhi et al., 2013). P1979, L2-9. To my knowledge, Laurion et al. (2010) and Negandhi et al. (2013) do not report on thermokarst lakes, but rather on shallow ponds (< 2 m deep, mostly ~ 1 m deep) that do freeze to the bottom during winter.*

This is only partially true. Our point here is that 0.5 to 1.5 m deep, non-stratified western Siberian lakes having  $4 \leq \text{pH} \leq 6$  and  $10 \leq \text{DOC} \leq 40$  mg/L are still different from much less acidic, less organic and most importantly, redox stratified,  $2 \pm 1$  m deep thermokarst ponds of Quebec and NW Territories, despite the fact that both type of lakes freeze solid in winter. In most recent compilation of studied circumpolar ponds (Rautio et al., 2011, *Ecoscience*), only 1 region among 16 (thaw pond of Boniface, Quebec) exhibits a pH of  $5.4 \pm 0.6$ , Cond. of  $18 \mu\text{S cm}^{-1}$  and a DOC of  $13.4 \pm 4.7$  which is comparable to western Siberia water bodies (Table 3). We added a description of other studies in **L 80-86**.

*P1979, L9-13. Again, thaw ponds from Canada (Laurion et al., 2010; Negandhi et al., 2013) also lack a groundwater network because they are either overlying impermeable silty clays (subarctic ponds) or located in the continuous permafrost zone (arctic ponds). So these systems are also connected to the hydrological network via surface flows only, and thus the ‘uniqueness’ of western Siberia systems might not be true in that regard.*

We agree with this remark and modified the text as following: “Another important difference of thermokarst western Siberia lakes from well-studied river delta / river valley lakes is the lack of connection to the underground network in the formers **(L 76-78)**.”

*P1979, L17-24. The specific questions are clearly mentioned and interesting, but what about the general question(s), the main goal(s) of the study? The reader feels that it is referred to in the next paragraph (P1979, L25 to P1980, L4), but not explicitly stated. Please clearly mention the general objective(s) of this study. Our primary goal was to better understand the thermokarst lake biogeochemical functioning which should allow to constrain the impact of lake water metal and carbon cycling on river water composition and greenhouse gas exchange with the atmosphere in the course of year. On a larger perspective, we aimed at the understanding seasonal pattern of dissolved organic carbon and metal micronutrients in these shallow but highly abundant water bodies, different from previously studied glacial and deep thermokarst/yedoma lakes. This knowledge should allow predictions of phytoplankton activity, sedimentation and microbial respiration on the annual scale, necessary for evaluation of the net ecosystem exchange under various climate change scenarios. We greatly modified the text in L 90-99.*

*P1980, L5. Why specify 'analytical and statistical methods'? If so, the authors should also add 'sampling' methods. Why not just 'methods', in general? Agree and corrected accordingly: 2. Study site description, sampling, analytical and statistical methods (L 107).*

*P1980, L12. What are 'normal precipitation/evaporation conditions'? What are the variations during drier or wetter years? (in terms of mm of precipitation/evaporation, for example). The normal precipitation in this region is close to 450 mm. During dry summer, the lakes can decrease their depth two-fold (Pokrovsky et al., 2013, Biogeosciences). Corrected in L 113-114.*

*P1980, L19-22. We understand that precipitation and evapotranspiration data are provided by the nearby meteo station, but what about 'the annual runoff of the territory? Where do these data come from? There should be references for that. The annual runoff of the territory is between 200 and 250 mm (Novikov et al., 2009 and Frey et al., 2007). Added in L 123.*

*And finally, I am guessing that lake water volumes were calculated from the depth mapping (echosounder)? If yes, please make it clear. Yes, a GPS-echosounder was used for the depth mapping. L124.*

*P1980, L23. From the 'PVC' what? PVC tube, container, platform? This is not clear. Water samples were collected from the PVC boat for large lakes; we corrected accordingly (L 125).*

*P1980, L24. Again, if we talk about small and shallow water bodies, shouldn't we refer to them as ponds? (see my comment above, P1979, L1). Agree and added a term "ponds" in this line 126.*

*P1981, L19. [: :.] except for B and P (30 %). Were these elements discarded for further analyses? If yes, please mention. B is still in Table 3. While P was discarded for further analyses, B concentrations in most lakes are a factor of 3 to 7 higher than those in the SLSRS-5 and thus were retained for presentation. In addition to Agilent ICP MS, the Element XR ICP-MS measurement allowed to better assess the B concentration. L 146-148.*

P1981, L28. 'The ice of the lake water column': : : Do the authors simply mean 'lake ice'?  
Yes, corrected accordingly in L 155.

P1981, L29. Ice cores were cut using a Ti saw. How could contamination of samples by Ti be avoided? Ti appears in Table 3.

Note that Ti is covered (passivated) by highly inert TiO<sub>2</sub> (rutile) oxidized layer which is extremely stable at low temperatures, whose solubility in the water film formed during drilling is several orders of magnitude lower than the Ti concentration we measured in the samples. Ti pressure devise is widely used for extracting interstitial soil solutions for TE analysis (Pokrovsky et al., 2006, GCA). In this study, before and after fieldwork, blank samples were run by filling the pre-cleaned PVC container with MilliQ water and submerged Ti blades, at neutral pH and letting it to react for several hours. No detectable contamination of Ti, any major and trace elements was observed. We added necessary explanation in L 157-160.

P1982, L22-25. Where can we see the data? These do not appear in Table 1 or Fig. 1, mentioned earlier in the paragraph. Good point. See Table S1 of the Supplement.

P1983, L1-9. Same comment as just above: where can we see the data? A figure or a table, with the mentioned correlations, would help in following the text. The correlation parameters are now presented in Table S1 (see above).

P1983, L10-11. As mentioned above and below, if all the lakes (except 3, labelled with \* in Table 1) were sampled during different seasons, then such interpretation is not fully supported. Now the detailed answer can be found in L193-200 and a description above. Actually, five lakes of various size were sampled during all open water seasons.

For example, in Figure 2 the DOC concentration shows a maximum for micro-depressions (< 1 m<sup>2</sup>) in spring, but the same concentration was not measured in these ponds during the rest of the year. This is correct, small depressions were dry in August and fully frozen in October and February; we added this information in L 196-198.

Indeed, we might expect DOC in small ponds to be even more concentrated in summer and autumn, which would strongly modify the general trends of Fig. 2 (and the other mentioned relationships). Detailed study of small depressions, thaw ponds and small lakes is presented both for normal (Shirokova et al., 2013) and extremely dry (Pokrovsky et al., 2013) summers, L 197-199.

Same for the maximum at 1000-10000 m<sup>2</sup> surface areas: how can we know that DOC concentrations were not higher during other seasons for these particular lakes?  
Unfortunately, these ponds were frozen during winter baseflow. As described in the beginning of our reply, given very similar depth of these shallow, non-stratified water bodies are all located in the same watershed divide, and they are chemically indistinguishable. We did not modify the text in response to this comment.

P1983, L11-14. *This sentence apparently refers to Fig. 3, not Fig. 2. This is a bit confusing with the preceding sentence.* We agree and revised this § (L 235-242)

P1983, L12. *The slope or the values (y-axis) on the graph? It would help to have such slopes/lines on the graph.* The slopes are given now in a separate Table S1 of the Supplement (see above)

P1983, L14-16. *Again, such seasonal trends are inferred from data that were not obtained in the same lakes (except 3 lakes out of 130). Moreover, there are only 3 samples from the winter campaign, so it would be better to remove this season from the whole year.* We agree with the reviewer to remove winter data from this trend. However we believe that 30 to 60 similar lakes sampled during 3 open water seasons provide better statistics on the chemical evolution than that of 3 single data points for each individual lake. Besides, all trend described in this work on numerous lake analysis are confirmed by the data of 5 lakes sampled throughout the year (L 458-461).

P1983, L21-22. *Again, since the pH was not measured in the same lakes during all seasons, this statement is not supported by the data, unless the authors can demonstrate that comparable lakes of comparable area show comparable pH values throughout the year. Such demonstration is not provided in the manuscript as currently written.* This is now illustrated by the regression parameters listed in Table S1. In addition, we plotted pH and DOC concentration as a function of lake surface area for 5 selected lakes, sampled during all three open-water seasons (Figure S10 of the Supplement). The trend of pH increase with the lake size, the DOC increase in small size lakes, and the overall sequence spring < summer < autumn are visible on these plots (L458-461)

P1983, L22. *The small-size lakes were sampled ONLY in spring, according to the figure. So why mention the season here?* The pH trend is mostly pronounced for large lakes, which were sampled during all seasons (see Figure S10 for 5 selected lakes samples during all 3 open-water seasons)

P1985, L9-12. *This is interesting, but it's not presented in the figures. Where can we find these data?* As stated in the Footnote of Table 1 of the manuscript, oxygen concentration in samples OZ-13 to OZ-31 represents surface/bottom values. We have not corrected the text in response to this comment.

P1985, L11-12. *What do the authors mean by 'some redox stratification'? A drop in O<sub>2</sub> concentration? Fluctuations in the Eh? Please be more specific.* There was a ~50% drop in O<sub>2</sub> concentration at the sediment-water interface relative to the bottom of the ice core. These measurements were not quite reliable due to low temperatures and instability of the electrode potential in muddy bottom water. For this reason, they were not reported in Table 1. The text was corrected in L272-273.

P1985, L26-27. *This is important information that explains why only 3 lakes were sampled for the winter season. It should appear in the methods section, otherwise the reader assumes that all the lakes could be sampled throughout the whole year.* We agree and modified the

sampling section accordingly. Only 3 out of 10 sampled lakes were sampled for both ice and liquid water and we stated **it in L 285, 328, and 483.**

*P1986, L1-11. This paragraph is really interesting, but it is valid for only 3 lakes out of the ~ 130 lakes sampled. That should be acknowledged in the discussion. We fully agree and amended the text accordingly **in L 161, 285, 311 and 483.***

*P1986, L18-10. Where do these results come from? I might have missed something, but I don't think XRD was mentioned in the methods. As it is stated in L 7-9 of p. 1982, "The freeze-dried precipitates were characterized by scanning electron microscopy (SEM) using a Jeol JSM840a, and by X-ray diffraction using an INEL CPS 120 CoK $\alpha$ ." **We did not modify the text in response to this comment.***

*P1987, L20-21. This is a long list. Report as a table or remove this sentence. Some examples are provided in Fig. 9 anyway. We generally agree; however, the results of this statistically-based treatment are important to present in the main text. **In the revised version, these elements are presented in Fig. 7.***

*P1988, L8-14. I don't fully understand the relevance of this paragraph. What does it bring to further understand the data? This result might be empirical, but it clearly distinguishes two groups of elements: elements whose concentrations are affected by the seasons by a factor of 2 or higher and elements do not significantly increasing their concentration in summer relative to the spring seasons. For example, the increase of Si and metal micronutrients (Zn, Co, Ni, Cu, Cd, Ba and Mn) might indicate some preferential release of these elements during active plant and upper moss litter leaching in summer. High concentrations of B, Na, Mg, Ca, Cs, Pb in early spring relative to the end of summer may indicate their input with atmospheric precipitates. **We added this information in revised text (L355-L361).***

*P1988, L15-22. This paragraph is more Discussion than Results material. We believe that this information is novel and important for the reader. In fact, the small study site presented in this work can be a good surrogate for much larger region of western Siberia (described in Manasypov et al., 2014) in terms of seasonal evolution of thermokarst lake chemical composition. **The text was amended in L 368 – 371.***

*P1990, L10. Winter values are for only 3 lakes. This should be acknowledged. **Done in L 483-484.***

*P1992, L8-9. Where do these results come from? Was this mentioned in the methods? Good point. Here we refer to previously elaborated technique of Fe(II) analysis using dialysis membranes deployed directly in the lake water (Pokrovsky et al., 2012 Aquatic Geochemistry). **L 537-538.***

*P1992, L14-16. This is interesting, but it should be supported by data or a reference. Analysis of bacterial activity in the ice and bottom water was beyond the scope of this work and will be a subject of another manuscript. Here, we moderated our suggestion stating the possibility of such a heterotrophic consumption. Highly non-conservative behavior of DOC during the*

winter time demonstrating significant depletion in February (Fig. 9 A) may suggest some heterotrophic respiration of DOM under the ice (L 552).

*P1994, L25. Leaching of DOM from plant litter is very fast. How fast? Hours, days, weeks? The time scale is hours as confirmed by laboratory experiments.* added to L625-626.

*P1995, L12. The title is hard to follow. Maybe a shorter title would be more efficient. We renamed this section as “4.4. Seasonal evolution of stock of carbon and TE in thermokarst lakes”,* L 641.

*P1996, L4-15. This paragraph is interesting. I am wondering if the authors have explored other mechanisms of CO<sub>2</sub> enrichment during spring melt (CH<sub>4</sub> oxidation, for example?). This could be a possibility. At present, we do not know of any seasonal measurements of CO<sub>2</sub> and CH<sub>4</sub> in thermokarst water bodies of western Siberia. Our unpublished data (Figure S11) do not demonstrate any significant enrichment in CO<sub>2</sub> or CH<sub>4</sub> during spring flood. Only in very small depressions (< 10 m<sup>2</sup>), the CO<sub>2</sub> level does increase. Given that the concentration of methane is 1 to 2 orders of magnitude lower than that of CO<sub>2</sub> and [CH<sub>4</sub>] is independent on the depression size, we doubt the significant role of methane oxidation in CO<sub>2</sub> enrichment. We added explicatory sentences in the text* (L 663-669).

*Also, what local conditions in/around these shallow ponds and lakes would preclude CO<sub>2</sub> build-up under ice, as observed in deeper boreal lakes (Karlsson et al.,2013)? The reasons for this contrast could be low volume of the thermokarst lake water and relatively short period suitable or this accumulation in western Siberia, since already in February, there is a lack of liquid water under the ice, or very low fraction (between 10 and 20%) of this unfrozen water stock. We added this information in L 671-674.*

*P1996, L17-24. Again, the text as written suggests that each individual lake was sampled 4 times during the year, which is not the case (only 3 lakes out of 130 were sampled in each season). So this first conclusion, although interesting ‘per se’, is not clearly supported by the results. The authors state that in spring, there is a clear correlation between chemical concentrations and lake sizes, but this is the only season when lakes of all sizes have been sampled. Who knows what the results for other seasons would have been if small lakes had been sampled in summer, autumn and winter?*

Our conclusion “Most of dissolved elements and organic carbon decreased their concentration following the order June < August < October, regardless of the lake size range, from 2·10<sup>2</sup> to 2·10<sup>6</sup> m<sup>2</sup>” is supported by statistics (see Table S1) and also confirmed in the individual lakes sample during all three open-water seasons (see Figures S10 A-D as examples for some components). In revised version, we specified the seasons in L 686-687 and L 692.

*The lack of repeated sampling in the same lakes during successive seasons weakens this part of the conclusions. Maybe this can be explained by logistical reasons, but the authors do not*

give them. Now it is all explained in the first page of our reply, together with pertinent figures. Such small ponds disappear in summer due to evaporation and they are subjected to full freezing at the very beginning of the glacial seasons (L193-200; L686-687).

*P1997, L7-11. To my knowledge, this is the first time that ice formation and related changes in the composition of many chemical elements via pressure cracks is reported. Really interesting, and as far as I can tell, supported by the data (Figure 7). We believe that this is very general mechanisms operating across hundred thousands km<sup>2</sup> of frozen lakes in western and northern Siberia. From the helicopter flight in the beginning of the winter, most lakes in western Siberia permafrost zone exhibited this yellowish color at the surface, certainly linked to ice cracks and DOM-rich water seeping, see **Figure** below*



**Figure.** Typical thermokarst lake surface from the helicopter in the beginning of the winter taken 300 km NW from the study site. Cracks of ice produced OM-rich water seeping.

*P1997, L12-14. Were these ‘macroscopic and organic- and Fe-rich amorphous particles’ observed in the lake bottom sediments? Presumably, yes, since the sediment is enriched in Fe (Audry et al., 2011). Analyses of sedimentary cores sampled in shallow lakes of this site in August 2014 is in progress. We cited a pertinent reference in the revised version (L 572-574).*

*P1998, L2-3. This is interesting, but speculative. Can the authors provide any support for that (measurements, reference)? That would make the statement substantially stronger. We would like to avoid adding references in the Conclusion section. However, supports of this increased stocks are from seasonal observations of lake coverage in western Siberia (Zakharova et al., 2014), described in L15-25 of p. 1995 (section 4.4, now L 648 - 652).*

*P2003-2004 (Table 1). I don’t fully understand here. The ‘June lakes’ are labelled from Z-43 to Z-107; the August lakes, from Z-1 to Z-31; the October lakes, from OZ-1 to OZ-31, and the*

February lakes, from LF1 to LFS. So they are all different lakes? Besides the only three lakes labelled with an asterisk (Z-96, Z-2, and OZ-17), do I understand that the other lakes were not sampled during the 4 sampling seasons? If so, then how can we compare seasonal trends if the data don't come from the same lakes? Detailed answers to these questions are given in the first § of our reply and illustrated by **Figure S10 of the Supplement**. Five lakes were sampled during all open-water seasons as now shown in revised Table 1 by A, B, C, D, and E letters.

Also, I guess that 'R' ( $\mu\text{S cm}^{-1}$ ) stands for conductivity? Please specify. In fact, all acronyms and letters (column headings) should be defined somewhere. In Table 1, R stands for specific conductivity and N.D. for non-determined, **as explained in the revised version**.

P2007 (Figure 1). For people not familiar with western Siberia, it would be helpful to provide a map of the regional context of the study area, showing other northern regions (at least Siberia as a whole). Also, the figure resolution is not high enough to distinguish individual lakes. Maybe a higher-resolution file was submitted to the journal? Yes, we submitted HR image to the journal. **Hi-resolution Figure 1 is presented in revised version**.

P2009 (Figure 3). I don't really see increasing  $UV_{280}/\text{DOC}$  here. Maybe the authors could add regression lines (for each season) on the graph? **In the revised version, we listed in Table S1 of the Supplement** the regression coefficients. The average values of  $UV_{280\text{ nm}}/[\text{DOC}]$  are equal to  $0.024 \pm 0.0037$ ,  $0.030 \pm 0.0072$ ,  $0.035 \pm 0.0069$ , and  $0.0354 \pm 0.0068$  in spring, summer, autumn and winter, respectively.

P2010 (Figure 4). Is this figure absolutely necessary? (or could be included as Supplement) We agree and will move it to the Supplement; **now this is Fig. S2 of the Supplement**.

P2011 (Figure 5). Please display the correlation lines, with their slope and  $R^2$  values. These values are given in **Table S1** of this reply.

Otherwise, except for summer we don't really see 'increase in lake water pH with the increase in the lake size'. We agree, this increase should be visible only during summer due to the increase of primary productivity and occasional underground feeding. The increase of the pH in the cycle of thermokarst lake maturation based on previous summer period observations is fairly well documented for western Siberia (Pokrovsky et al., 2011, 2014), **L 220 of the revised text**.

P2012 (Figure 6). Is this figure absolutely necessary? (or could be included as Supplement) We agree and will move it to the Supplement; **now this is Fig. S4**.

P2013 (Figure 7). I presume 'LF-1' and 'LF-5' refer to sampled lakes? Yes, we added this explanation in the figure caption, **L 1005**.

**We took into account all technical corrections of this reviewer**

*General comment for the whole text: ice and snow melt. Permafrost thaws. Thank you for this very useful remark. We edited the text accordingly*