

### **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 added the PCA treatment of the data as described below.

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 1** and illustrated in **Figure 1 A –D**. The correlation profiles for F1 and F2 and various seasons are given in **Figure 2**.

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 photodestruction 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 3**).

*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 connected to the rivers. Neither particulate, no dissolved Fe-bound TE will never make into the river system, even during high spring flood.

*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.

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). 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 2** and illustrated in **Figures 4 and 5**. 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<sup>2+</sup> compared to DOC during solute concentration by freezing. The lake size has significant impact on metal complexation with DOM as illustrated in **Fig. 5**. 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 response to 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<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 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 very 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.

*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<sup>2</sup>) 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.*

*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.

*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 6 A and C 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 these two sources. 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 aquagenic DOM.

*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.

*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).*

*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)

*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.

*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. 3 of this response). Note that the input of fresh vegetation products and the leaching of the upper peat layer occur in June-August. The Fig 11 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 oif the authors would make an attempt to model the speciation. Why would Cu not be dependent on DOM colloids ? As stated in the text, 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 response above) 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 **Figure 6** of this response (Shirokova et al., 2013); all the thermokarst water bodies of western Siberia are strongly supersaturated with respect to atmopsheric pCO<sub>2</sub>.*

*Figure 3: Please remover 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.*

*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.*

*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.

*Figure 6. is this figure needed ? Not necessarily; we will remove it in the final version.*

*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.

*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 schematize 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 did add a possibility of lateral (subsurface) peat leaching in September-October in the revised Figure 11 (see Fig. 3 of this Reply)*

**Table 1.** PCA analysis of lake water chemical composition revealed two factors, with F1 mostly pronounced in October.

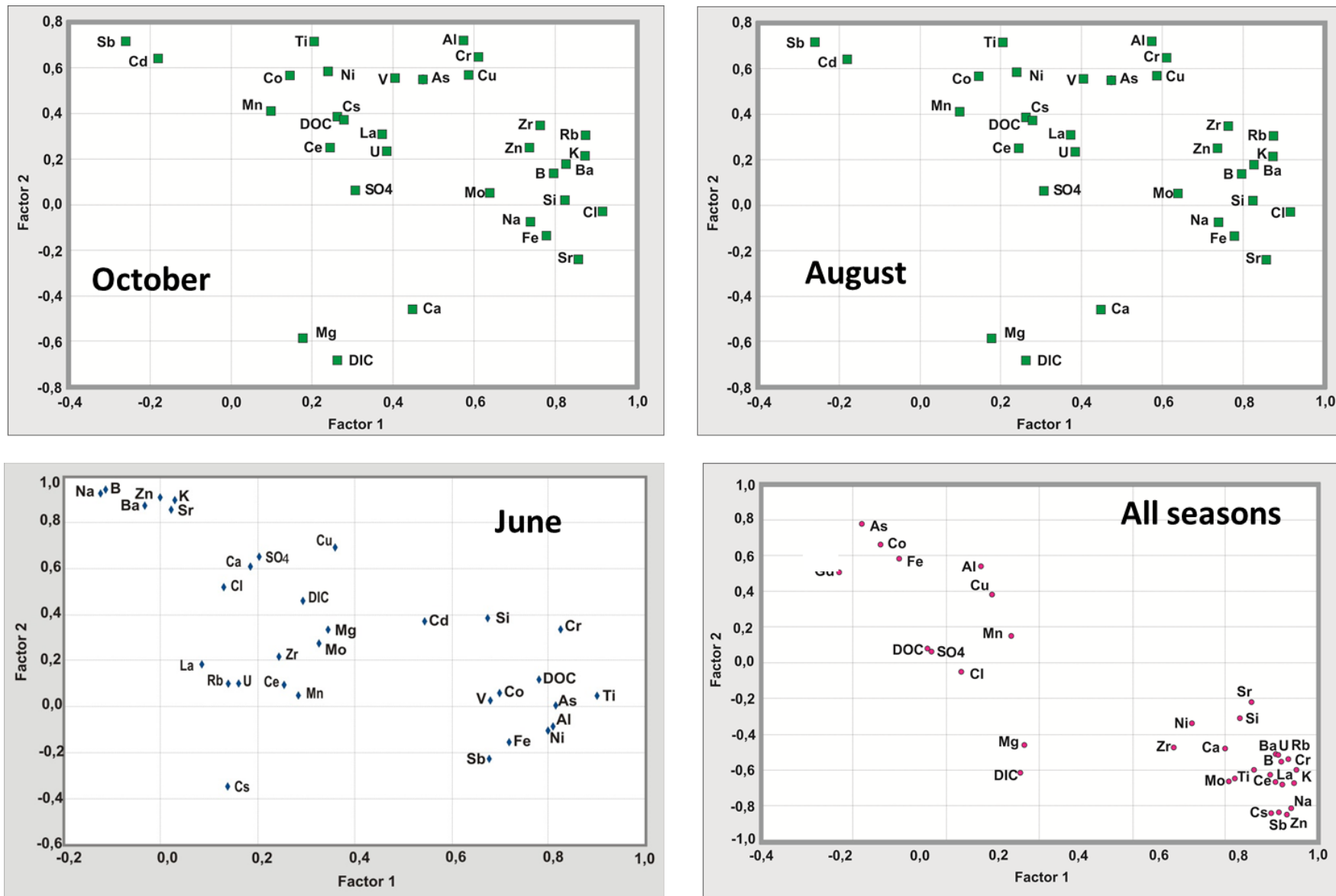
	<b>June</b>	<b>August</b>	<b>October</b>	<b>All seasons</b>
<b>F1</b>	8.1 % (DOC, UV, Al, Ti, Cr, Ni, As, Sb)	11.8% (Cl, B, Al, Si, K, Cr, Fe, Cu, Zn, Rb, Sr, Ba, Zr)	18.8 % (B, Na, Si, K, Ca, Ti, V, Cr, Ni, Zn, Rb, Sr, Zr, Mo, Sb, Cs, Ba, La, Ce and U)	16.6% (B, Na, Si, K, Ca, Ti, V, Cr, Ni, Zn, Rb, Mo, Sb, Cs, Ba, La, Ce, U)
<b>F2</b>	7.6% (B, Na, K, Cu, Zn, Sr, Ba)	5.8% (pH, DIC)	4.4% (Fe, Al, Cu, Co, As).	6.3% (Al, Fe, Co, As, Cd)

**Table 2A.** Percentage of complexed trace element with organic ligands calculated using NICA-Donnan model for the average lake composition in spring, summer, autumn and winter as listed in Table 3 of the manuscript.

	% complexed with organics (NICA-Donnan)			
	SPRING	SUMMER	AUTUMN	WINTER
Al+3	100	100	100	99.8
Ba+2	100	100	99	92
Ca+2	100	100	99	92
Cd+2	100	100	100	99
Cu+2	100	100	100	100
Fe+3	100	100	100	100
K+1	83	71	46	15
La+3	100	100	100	100
Mg+2	100	100	99	92
Mn+2	100	100	99	93
Na+1	83	71	46	15
Ni+2	100	100	100	95
Pb+2	100	100	100	100
Sr+2	100	100	99	92
UO2+2	100	100	100	100
Zn+2	100	100	99	92

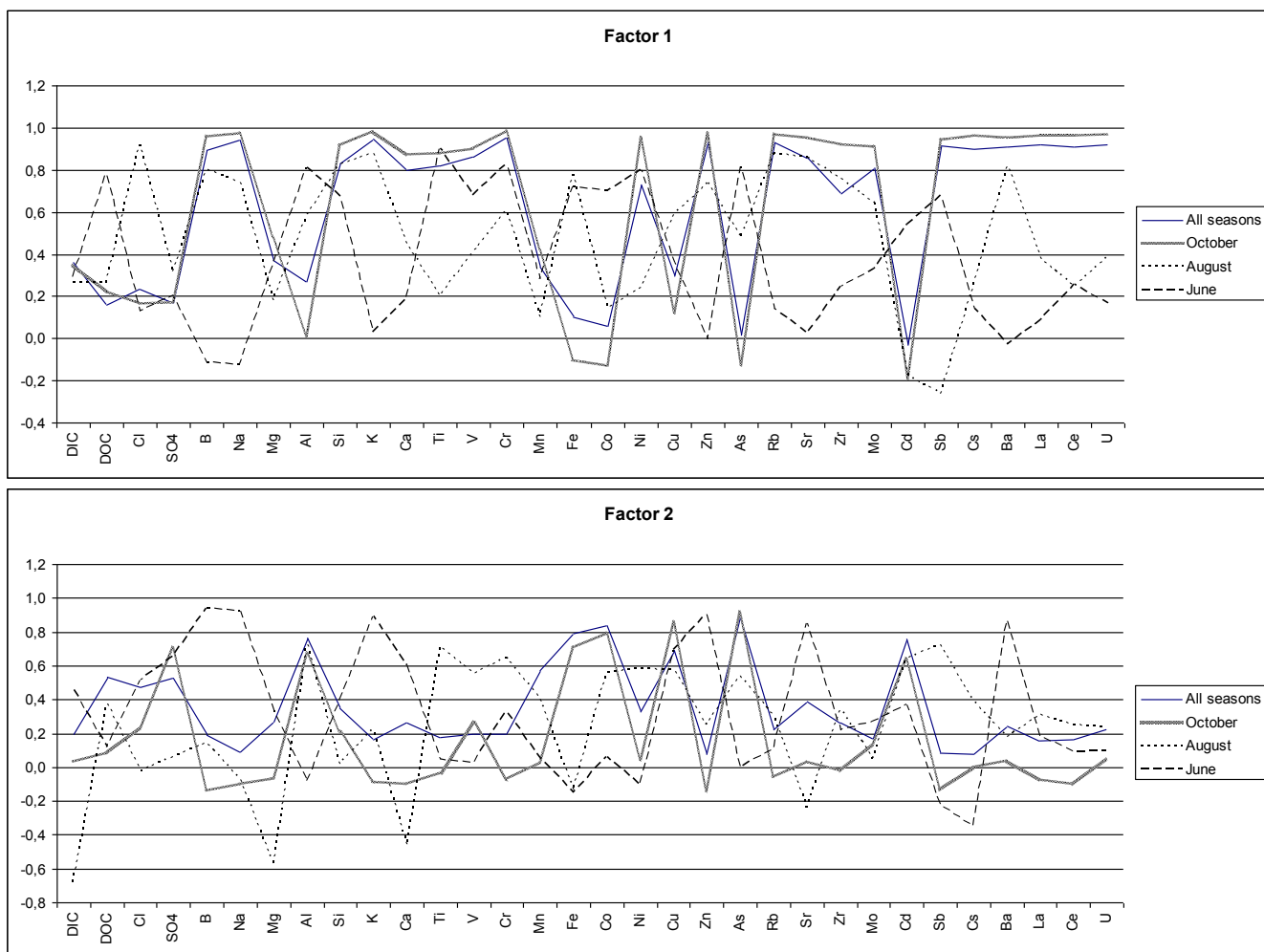
**Table 2 B.** Percentage of complexed trace element with organic ligands calculated using Stockholm Humic Model for the average lake composition in spring, summer, autumn and winter as listed in Table 3 of the manuscript.

	% complexed with organics (SHM)			
	SPRING	SUMMER	AUTUMN	WINTER
Al+3	99	100	99	99
Ba+2	40	47	34	23
Ca+2	41	50	37	25
Cd+2	48	63	52	38
Cu+2	88	96	93	86
Fe+3	100	100	100	100
La+3	99	100	99	97
Mg+2	41	49	36	24
Mn+2	41	50	37	25
Na+1	0	1	1	0
Ni+2	59	78	69	57
Pb+2	79	94	91	84
Sr+2	40	48	34	23
UO2+2	100	100	100	100
Zn+2	45	62	49	36

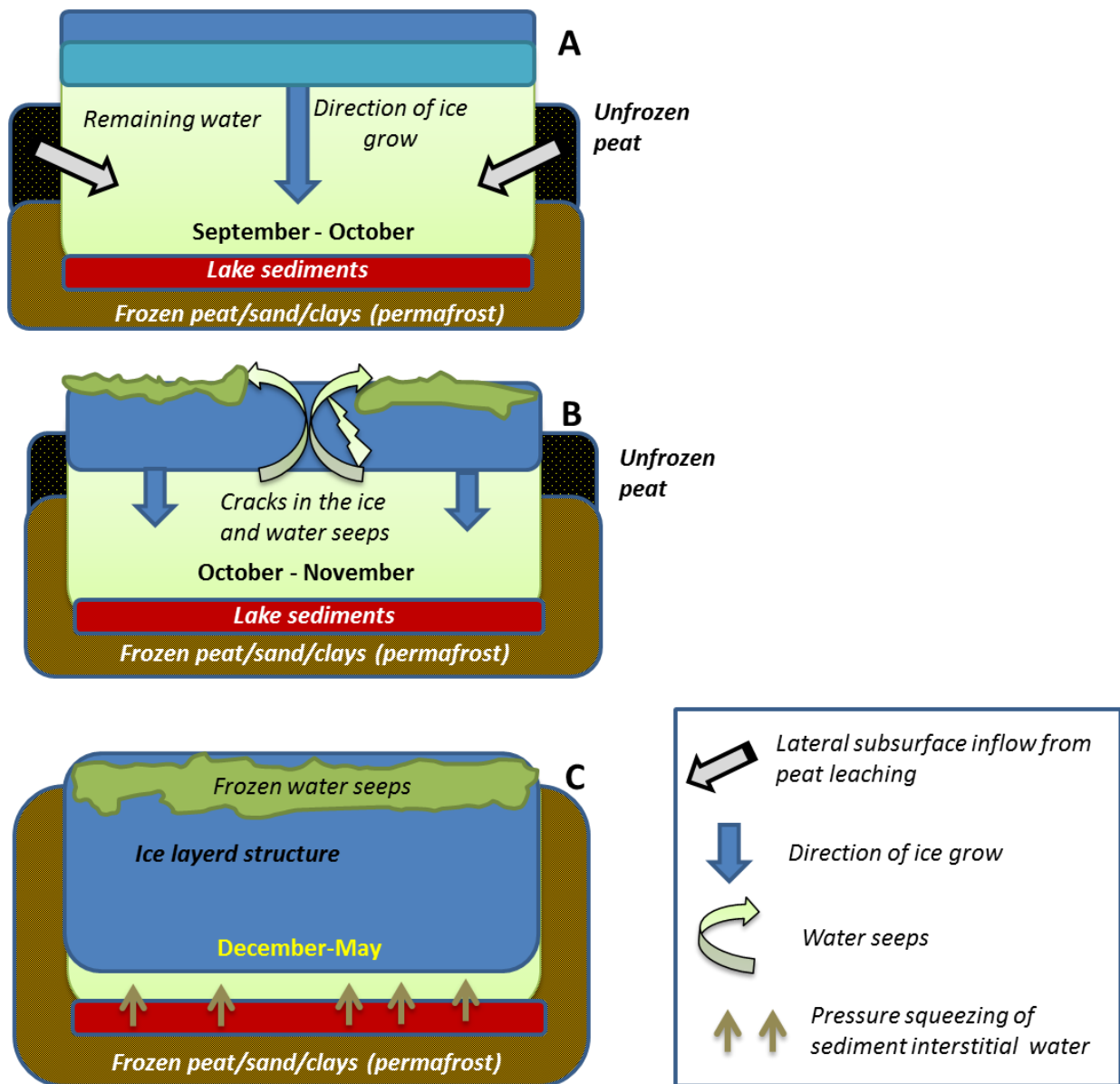


**Fig 1.** PCA matrix of F1XF2 factors on the lake water chemical composition during different seasons.

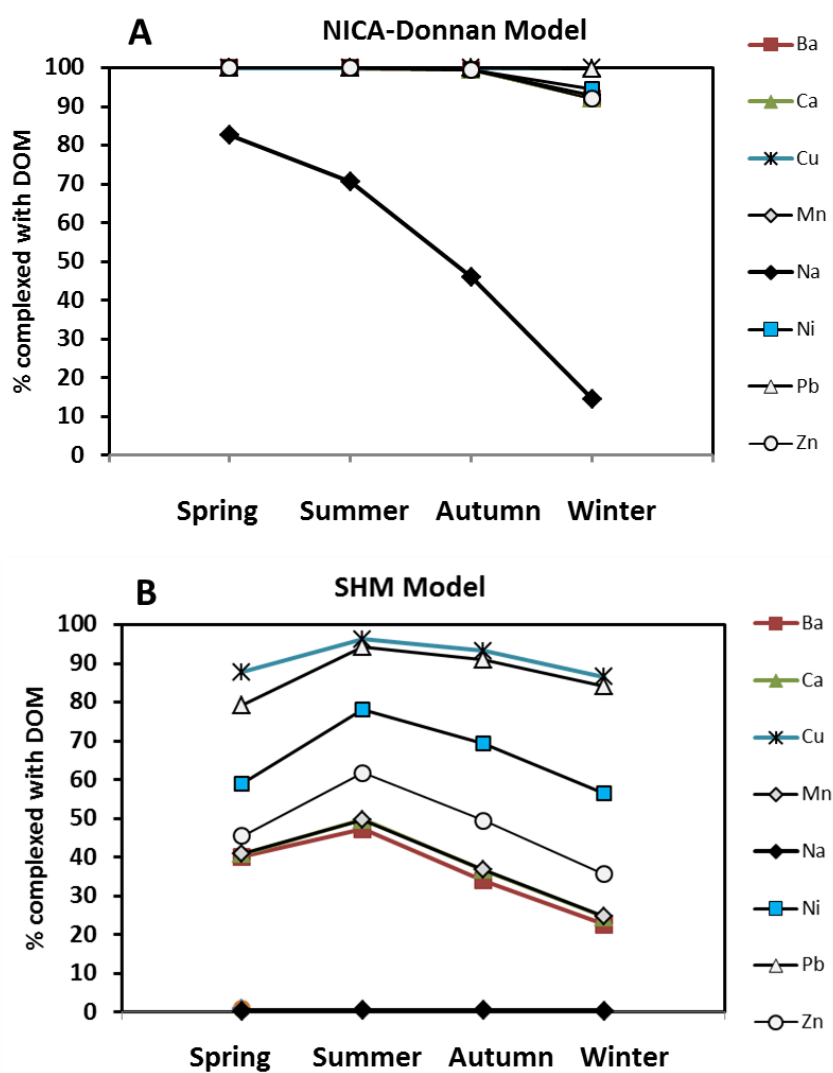




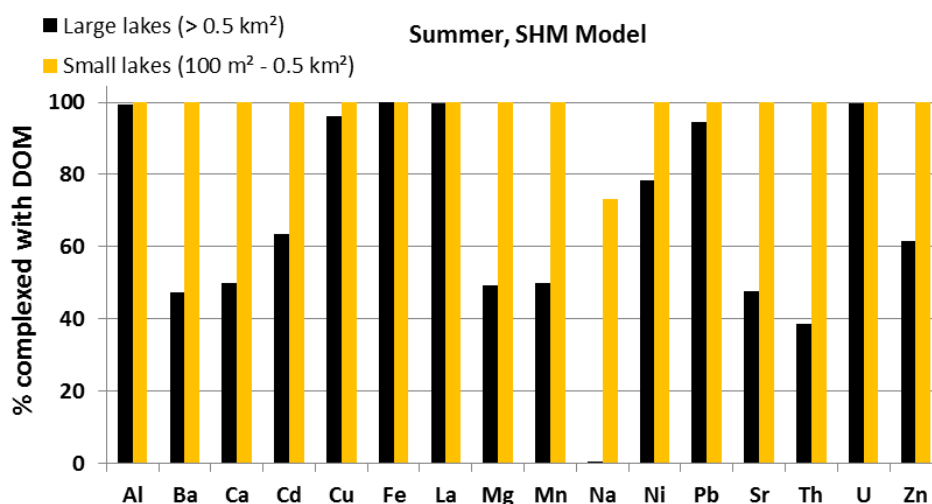
**Figure 2.** Correlation profiles of F1 (upper graph) and F2 (bottom graph) separately for each season and for all seasons together.



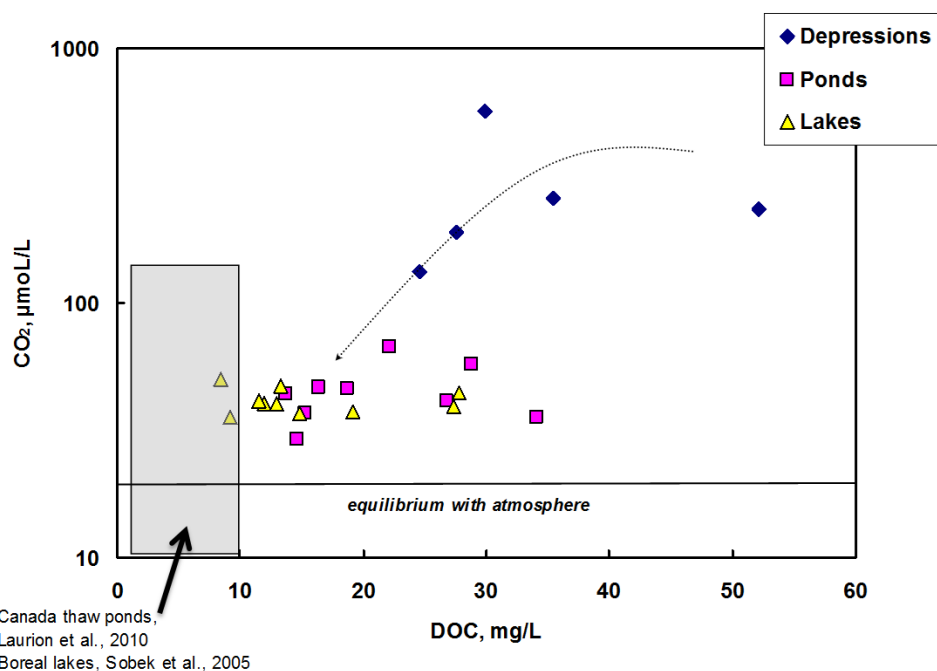
**Figure 3.** Sequence of ice crystallization events during the glacial period on the shallow (< 1 m depth) thermokarst lakes of western Siberia. A: start of the ice formation, when the lateral subsurface inflow from leached peat is still possible; B: squeezing water towards the surface via seeps; C: freezing of water pockets and seeps and multi-layer ice formation. At this stage, confined pressure squeezing of interstitial sediment water is possible which can provide additional source of solutes to the remaining water.



**Figure 4.** Proportion of TE bound to complexes with dissolved organic matter during different seasons, calculated using visual MINTEQ within the NICA-Donnan (A) and SHM model (B). Note that  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{La}^{3+}$  and  $\text{UO}_2^{2+}$  are predicted to be 100% complexed with DOM in all systems.



**Figure 5.** Percentage of organic-complexed TE in large and small thermokarst lakes in summer.



**Fig. 6.** High supersaturation of western Siberia thermokarst lake water with respect to atmospheric CO<sub>2</sub>.