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**Dissolved organic matter controls on seasonal and spatial selenium concentration variability in thaw lakes across a permafrost gradient**

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**Abstract**

Little is known about sources and processing of selenium (Se), an important toxicant and essential micronutrient, within boreal and subarctic environments. Upon climate warming and permafrost thaw, behavior of Se in northern peatlands becomes an issue of major concern, because sizeable amount of Se can be emitted to the atmosphere from thawing soils and inland water surfaces and exported to downstream waters, thus impacting the Arctic biota. Working towards providing a first-order assessment of spatial and temporal variation of Se concentration in thermokarst waters of the largest frozen peatland in the world, we sampled thaw lakes and rivers across a 750-km latitudinal profile. This profile covered sporadic, discontinuous and continuous permafrost regions of western Siberia Lowland (WSL), where we measured dissolved ( $< 0.45 \mu\text{m}$ ) Se concentration during spring (June), summer (August), and autumn (September). We found maximum Se concentration in the discontinuous permafrost zone. Considering all sampled lakes, Se exhibited linear relationship ( $R^2 = 0.7$  to  $0.9$ ,  $p < 0.05$ ,  $n \approx 70$ ) with dissolved organic carbon (DOC) concentration during summer and autumn. Across the permafrost gradient, the lakes in discontinuous permafrost regions demonstrated stronger relationship with DOC and UV-absorbance compared to lakes in sporadic/isolated and continuous permafrost zones. Both seasonal and spatial features of Se distribution in thermokarst lakes and ponds suggest that Se is mainly released during thawing of frozen peat. Mobilization and immobilization of Se within peat – lake – river watersheds likely occurs as organic and organo-Fe, Al colloids, probably associated with reduced and elemental Se forms. The increase of active layer thickness may enhance leaching of Se in the form of organic complexes with aromatic carbon from the deep horizons of the peat profile. Further, the northward shift of permafrost boundaries in WSL may sizably increase Se concentration in lakes of continuous permafrost zone.

## 1. Introduction

High-latitude arctic and subarctic lakes are recognized to be an important source of greenhouse gas (GHG) emissions to the atmosphere<sup>1</sup>, further pronounced under climate warming and permafrost thaw.<sup>2</sup> In contrast to numerous works addressing the role of inland waters in carbon storage and emission<sup>3-4</sup>, relatively few studies elucidate the behavior of other volatile, environmentally important and potentially threatening components in lake water at high latitudes<sup>5-6</sup>. Thus, although thawing of frozen peatlands is recognized as an important process capable of delivering volatile toxicants stored in peat to the atmosphere<sup>7-8</sup>, or toxic metal release from soil and sediments to the water column and hydrological network<sup>9-12</sup>, very little is known about the magnitude of these processes in the subarctic. This lack of knowledge is strongly evidenced in the vast West Siberian Lowland (WSL) extending over an area of more than 2 million km<sup>2</sup> and representing a hot spot of CO<sub>2</sub> and CH<sub>4</sub> emission from inland waters. The WSL also contains a large organic carbon stock in soil and surface waters thus regulating carbon and related element export from land to the Arctic Ocean. Almost half of the WSL is covered by frozen peatlands subject to active thermokarst development. This creates numerous lakes and thaw ponds whose inventory, in terms of toxic volatile element storage and potential emission, is just at the beginning.

In contrast to fairly good knowledge of non-volatile trace metal concentrations and transport in inland waters of permafrost-affected territories, Se (selenium), an essential micronutrient and toxicant<sup>13-14</sup>, has been rarely investigated in pristine boreal and subarctic environments. Over the past decade detailed reviews of Se biogeochemistry, emission fluxes and toxicity in biological, aquatic and soil systems have greatly improved understanding of distribution of Se stocks, its dynamics and toxicity thresholds<sup>15-19</sup>. The bulk of knowledge on Se biogeochemistry originates from research in temperate and tropical regions<sup>20-22</sup>, however the emission of Se from northern peatlands under climate warming scenarios is an issue of major

concern<sup>6</sup>. Depending on the amount of Se deposited via atmospheric influx and marine contribution<sup>23,24</sup>, sizeable amounts of Se can be lost to downstream waters, which in turn may be controlled by speciation of dissolved Se<sup>25</sup>. However, the change in magnitude of these processes under climate warming scenarios is poorly constrained. Furthermore, it can be expected that thawing of frozen peat can release a sizable amount of Se to aquatic systems upon widespread permafrost thaw<sup>6</sup> and thereby impact living organisms—from aquatic bacteria to humans—via food chain from upland rivers to the Arctic Ocean.

Increased Se concentrations in inland waters can have both toxic and beneficial effects on aquatic organisms as well as our food supply<sup>17-20</sup>. This is especially true for Siberian and arctic environments subjected to permafrost development, where peat and soil Se content and respective leaching potential to hydrological systems are poorly understood. Working towards providing a first-order assessment of the mechanisms controlling spatial and temporal variation of Se concentration in thermokarst waters of the largest frozen peatland in the world, we sampled ~70 lakes and ~10 rivers across a 700-km long transect. This transect coincides with sporadic, discontinuous and continuous permafrost of western Siberia Lowland (WSL) during 3 main hydrological seasons. Our specific objectives were to (i) quantify the effect of seasons (spring flood, summer baseflow and autumn) across the latitudinal gradient; (ii) characterize the effect of permafrost coverage on Se concentration in lakes over each season, and finally (iii) to assess the role of major hydrochemical parameters (pH, DOC, major and trace elements) on Se concentration patterns. We anticipate that quantifying Se reservoir in thermokarst water bodies of the WSL territory, combined with known trends of lake and thaw pond region evolution over the past decades should allow prediction of future Se storage and atmospheric emissions from lakes of permafrost-affected western Siberia.

## 2. Study Site and Methods

### *2.1. Thermokarst lakes and thaw ponds of western Siberia*

Shallow thermokarst lakes and ponds of WSL are abundant north of 60°N, and formed due to thawing of frozen peat (**Fig. 1**). Along a latitudinal gradient of ca. 700 km, 4 key study sites (Kogalym, Khanymey, Urengoy and Tazovsky) were selected corresponding to sporadic, isolated, discontinuous and continuous permafrost coverage. Climate ranges from moderately humid and cool summers with cold and snowy winters in Kogalym to humid and cold summers and cold and snow-deficient winters in Tazovsky. Mean annual temperatures are -4.0, -5.6, -6.4, and -9.1°C for Kogalym, Khanymey, Pandogy and Tazovsky, respectively. The WSL territory presents a very homogeneous lithology dominated by sands and silts in all four study sites. Peat thickness ranges from 1 to 3 m and has no correlation to latitude.<sup>26</sup>

All sampled bodies of water are located within the peat palsa and bog-lake complexes. Thaw ponds and thermokarst lakes were formed approximately 2500 BP as a result of increased temperature and precipitation as well as associated thermokarst activity.<sup>27</sup> The territory is dominated by flat watershed divides represented by palsa peat bog and polygonal tundra.<sup>28-29</sup> The depth of WSL thaw ponds and thermokarst lakes typically varies from 0.5 to 1.5 m<sup>30</sup>; none of the sampled lakes were deeper than 2 meters. It's important to note that in the very flat terrain of WSL peat palsa bogs, the majority of closed thermokarst lakes do not have inlets and outlets, and catchment areas are roughly comparable to respective lake surface areas.

### *2.2. Sampling and analyses*

To study seasonal and spatial variability of Se concentration, complete sampling along a gradient from sporadic and isolated to continuous permafrost<sup>30</sup> was performed during 3 seasons in 2016 (spring, summer and autumn). This included 76 lakes sampled from 20 May to 13 June, 67 lakes sampled from 9 to 24 August, and 67 lakes sampled from 25 September to 8

October. To study inter-seasonal variability, 24 lakes were also sampled in July 2012 (summer heat wave<sup>31</sup>) with another 16 lakes being sampled in October 2013 (under ice) in the discontinuous permafrost region near Khanymey. In general the same lakes were sampled across the seasons. In addition, 9 rivers not connected to lakes were sampled across the same latitudinal gradient with 9 rivers sampled in August 2015 and another 4 rivers sampled in February 2014.

Water from the thermokarst lakes ( $> 1000 \text{ m}^2$ ) and thaw ponds ( $< 1000 \text{ m}^2$ ) were collected from the middle of the water body at 0.2-0.3 m depth using vinyl gloves and pre-washed polypropylene (PP) jars. In addition to surface sampling, bottom water (ca 10-20 cm above the sediment-water interface) was sampled for DOC,  $\text{CO}_2$  and  $\text{O}_2$ . Shallow thermokarst lakes of the WSL are not thermally stratified. We did not find any measurable difference in DOC and  $\text{CO}_2$  between surface and bottom water. Regarding degree of  $\text{O}_2$  saturation between lakes of different size we found all lakes were fully oxygenated over 0.5-1.5 m depth<sup>28,32</sup>. This allowed us to assume uniform Se concentration throughout the water column. The sampling points of rivers were located some 100-200 m upstream where it crossed a regional road. Collected waters were immediately filtered into cleaned 60-mL PP Nalgene® bottles through single-use,  $\text{HNO}_3$ -, MilliQ-prewashed filter units Minisart (Sartorius, acetate cellulose filter) having a diameter of 33 mm and a pore size of  $0.45 \mu\text{m}$ . All preparation and cleaning of material were performed in a class A 10,000 clean room. Prior to filling the bottle, the first 20 to 50 mL of filtrate were discarded, with the second portion of 20 to 30 mL of filtrate used to rinse the bottle. The bottles were finally filled without air bubbles and preserved in the refrigerator. They were used for Se analyses within 1-2 months after sampling.

Total Se concentration was measured in Pau (IPREM) with Agilent 7500ce or 7900 ICP-MS instruments (Agilent Technologies, Tokyo, Japan) both equipped with an octopole reaction cell, concentric nebulizer and a Scott double pass spray chamber cooled to  $2^\circ\text{C}$ . Argon-based

polyatomic interferences were reduced by using H<sub>2</sub> as cell gas at a flow rate of 5 ml min<sup>-1</sup>. Acquisition parameters were: integration time, 200 ms per isotope; 15 replicates; monitored *m/z* 77 and 78. External calibration was performed. The instrumental detection limits of Se (based on <sup>78</sup>Se) were in the range 1.6-13 ng L<sup>-1</sup>. Typical analytical precision was < 5% (relative standard deviation, 15 replicates). In a series of representative lake water samples, inorganic Se species were identified and quantified by hyphenating High Performance Liquid Chromatography (1100 series, Agilent) with the same ICP-MS<sup>33</sup>. Quantification of total Se and Se species has been performed by standard additions to correct for matrix effects as developed for soil extracts<sup>33</sup>. Within the limits of analysis, no inorganic Se<sup>IV</sup> and Se<sup>VI</sup> was detected in lake waters, and the majority (90-95%) of dissolved Se was not in ionic form.

The second portion of filtrate was filled in polypropylene vials for analyses of DOC and DIC using a Carbon Total Analyzer (Shimadzu TOC VSCN) with an uncertainty better than 3%, and UV absorbance at 245 and 254 nm (using quartz 10-mm cuvette on Cary-50 spectrophotometer). The third aliquot was used for trace element analyses and acidified (pH ~ 2) with ultrapure double-distilled HNO<sub>3</sub>. The preparation of polypropylene bottles for sample storage was performed in a clean bench room (ISO A 10,000). Blanks of MilliQ water were processed in the field in parallel to samples in order to control the level of pollution induced by sampling and filtration. All blanks were less than 5-10% of the element concentration in the sample. Trace elements were determined in Toulouse (GET) with an ICP-MS Agilent 7500 ce with In and Re as internal standards and 3 various external standards, placed each 10 samples in a series of river water. The international geostandard SLRS-5 (Riverine Water Reference Material for Trace Metals) was used to check the validity and reproducibility of analysis. All certified major (Ca, Mg, K, Na, Si) and trace elements (Al, As, B, Ba, Co, Cr, Cu, Fe, Ga, Li, Mn, Mo, Ni, Pb, all REEs, Sb, Sr, Th, Ti, U, V, Zn) concentrations of the SLRS-5 standard and the measured concentrations agreed with an uncertainty of 10-20%. Further details of TE

analysis in boreal organic-rich surface waters, uncertainties and detection limits are presented in previous publications of our group.<sup>29,34</sup> The main interest of using a suite of various trace elements is that these elements can serve as proxy for colloidal forms of Se, which are unavailable via direct observations. According to our recent data, organic and organo-mineral (Fe, Al)-rich colloids essentially control the transport and speciation of a number of trace elements<sup>28,34</sup> including probably Se.

### *2.3. Statistical treatment of the data and element speciation in the river water*

The concentrations of Se and related elements in lakes and rivers were treated using the least squares method, Pearson correlation and one-way ANOVA (SigmaPlot version 11.0/Systat Software, Inc). Regressions were used to examine the relationships between Se concentrations and the lake area, latitude, and river watershed area. In the case of normal distribution of the data, linear regressions were run between Se concentration and UV<sub>254 nm</sub> or DOC concentration. These correlations were significant at  $p < 0.001$ . Pearson correlation of dissolved Se concentration with major and trace components was conducted at  $p < 0.05$  for lakes, separately for each site and each season, and for all sites, with all seasons grouped together. We applied a Bonferroni correction to the significance threshold used in these correlations assessment. In addition, a multivariate analytical approach, a Partial Least Square (PLS) regression, was used to predict Se concentrations in sampled lakes based on most relevant variables capable of explaining the observed patterns. The normality of Se concentration was assessed by using the Shapiro-Wilk test. In the case that data were not normally distributed, we used the median, 1<sup>st</sup> and 3<sup>rd</sup> quartiles, to trace the dependence of Se concentration on the type of permafrost distribution. The difference in Se concentration between each two adjacent permafrost zones and between various seasons at the same site was tested using Mann-Whitney U test for paired data set with significance level at 0.05.

### 3. Results

#### 3.1. Spatial, seasonal and annual variability of Se concentration in thaw ponds and lakes

The full set of measured Se concentrations is given in **Table S1 of the Supplement**. The highest concentrations of Se are observed in summer and the lowest in spring. There was no clear effect of latitude, which is a proxy for permafrost continuity and climate, on Se concentration (**Fig. 2**). However, the Khanymey site of the discontinuous permafrost zone exhibited the highest Se concentrations in summer and autumn forming a local maximum on the latitudinal transect. The geometric mean Se concentrations in thermokarst lakes of different permafrost zone was assessed separately for each season (**Table 1**) and yielded an overall concentration trend which followed the order August  $\geq$  September > June, significant at  $p < 0.05$ . There was no statistically significant (at  $p < 0.05$ ) trend of Se concentration with lake surface area, which was tested in all three permafrost zones (**Fig. 3**). The highest Se concentrations were revealed in the Khanymey site, discontinuous permafrost zone, during summer 2012 heat wave (**Fig. 3 B**) as well as in October 2013, during sampling under ice (**Fig. 3 C**).

**Table 1.** Compilation of Se concentrations in pristine thermokarst lakes of Western Siberia Lowland. The data obtained during anomalously hot summer (July 2012) and under-ice sampling in October 2013 are excluded.

Permafrost zone	June	August	September	All seasons
<b>Sporadic</b> (62.2° N) Kogalym	25±5.3	28.8±8.4	28.7±5.3	27.4±6.6
<b>Discontinuous</b> (63.6 °N) Khanymey	26.4±7.7	57.3±21	53.1±12.3	43.8±20
<b>Continuous</b> (Urengoy and Tazovsky)	20.5±8.8	46.2±19.2	40.4±10.2	35.4±17.4

Se concentrations in rivers were independent on the size of the watershed (**Fig. S1 A** of the **Supplement**). The latitudinal trend in Se river water concentration between 58 and 67.5°N (permafrost-free to continuous permafrost zone) was not pronounced. In winter, under ice, there was a sizeable increase in Se concentration in rivers north of 67°N, within the continuous permafrost zone (**Fig. S1 B**). There was no difference ( $p > 0.05$ , Mann Whitney U-test) in Se concentration between lakes and rivers for the mean of full year and for each season separately.

### *3.2. Correlation between Se concentration and DOC, UV absorbance and trace elements*

The Se concentration in lakes was correlated ( $p < 0.05$ ) with Specific Conductivity,  $UV_{254\text{ nm}}$  absorbance, DOC, major dissolved cations (Mg, Ca) components, inorganic colloid constituents (Fe, Al, P, Ti), micronutrients (V, Cr, Mn), low mobile hydrolysates (Ga, Th), some toxic metals (Cd, Pb, U) and metalloids (As, Sb) (**Table S2** of Supplement). The highest correlation coefficients were observed between Se and specific UV absorbance at 254 nm and between Se and DOC (**Table S3** of Supplement) although a number of insoluble low-mobile elements (Al, Fe, trivalent and tetravalent hydrolysates, Pb, U) also demonstrated sizable correlations with Se. The strongest links, detectable in the highest number of sites were observed between Se and DOC in summer and autumn, whereas in spring, the correlations between Se and DOC were quite weak (**Fig. 4 A-C**). The relationship between Se concentration and  $SUVA_{254\text{ nm}}$  was especially strong in the discontinuous permafrost zone (Khanymey and Urengoy, see **Fig S2 and Table S3**). It is worth noting the highest correlations of Se with DOC,  $UV_{254\text{ nm}}$  and Fe ( $R = 0.92, 0.97$  and  $0.85$ , respectively, **Table S2**) were observed during the anomalously hot summer of 2012. During the summer heat wave period in July 2012 and after ice formation on lakes in October 2013, Se exhibited the highest concentrations, between 100 and 300 ng/L (**Fig. 4 B and C**). Given the anoxic conditions of the lake water under ice<sup>32</sup>, these high Se concentrations were not associated with selenate and selenite as proved by HPLC-ICP

MS speciation analysis (not shown). The PLS analysis performed for all Se concentration data in lakes and rivers revealed that 13 key parameters including SUVA explain 89.4% of overall Se variability (**Fig. S3**). First 6 most important components were DOC, As, Ga, Sb, Cd and Al.

## 4. Discussion

### 4.1. Se concentration range in WSL lakes and rivers

The typical Se concentrations in western Siberian lakes and rivers ranged from 20 to 100 ng/L. This is in the lower range of Se concentrations in temperate and tropical European and Asian lake waters (30 to 1520 ng/L) as reviewed by Conde and Sanz Alaejos.<sup>35</sup> In temperate lakes of North America, Se concentrations ranged between 200 and 500 ng/L.<sup>5</sup> Aqueous Se concentrations above 200 ng/L are considered to be contaminated<sup>36</sup>. Thus, no Se contamination occurs in WSL lakes based on this threshold value. Comparable mean dissolved Se concentrations ranging from 20 to 60 ng/L have been measured in lakes of southern Norway<sup>37</sup>; Finish<sup>38</sup> and Canadian<sup>39</sup> lakes also exhibited Se concentrations lower than 100 ng/L. The rivers of western Siberia exhibited Se concentration ( $40 \pm 20$  ng/L) lower or comparable to that of boreal organic-rich rivers in Sweden (30 to 400 ng/L)<sup>25</sup> and Finland ( $\sim 100$  ng/L)<sup>38</sup>. This is lower than in industrially affected European, American or Asian rivers (from 100 up to 1000 ng/L)<sup>35</sup>.

The highest concentrations in our dataset were observed in lakes of discontinuous permafrost zone, during the anomalous summer draught (heat wave in July 2012) and after ice-on in October (between 100 and 300 ng/L). In both cases, mere decrease in liquid water volume by a factor of 2 to 5 due to evaporation during prolonged heating<sup>31</sup>, or freezing in the confined space in October<sup>32</sup>, could be responsible for the observed two to five fold increase in Se concentration.

#### *4.2. Mechanisms of Se mobilization from soil to inland waters*

The thermokarst lakes of the WSL demonstrate a linear relationship between their surface area and water residence time<sup>32</sup>. The observed independence of Se concentration on lake surface area therefore implies a lack of effect of water residence time on Se biogeochemical cycle in lakes. Further, this indicates a weak role of heterotrophic mineralization or photo-degradation of Se-organic complexes possibly occurring in the water column. Recent hydrological studies across WSL permafrost-affected zone<sup>40,41</sup> demonstrated a possibility of direct impact of lakes on river water chemistry due to high hydrological connectivity between lakes and rivers. Because the majority of thermokarst lakes are isolated water bodies without inlets and outlets, this connectivity is achieved via water movement along the permafrost table in the thawed active layer<sup>42</sup>, in the form of so-called suprapermafrost flow between peat bogs and lakes, and further to the rivers. Moreover, given that the water transit time in the northern permafrost-affected WSL rivers is much shorter than those in southern rivers<sup>40,41</sup>, the impact of Se storage and processing in lakes on eventual Se export to large rivers and to the Arctic Ocean will increase northward.

It can be hypothesized that, in addition to direct atmospheric fallout<sup>23</sup>, Se input to the lakes occurs via surface flux over moss and lichen in June (spring) and via suprapermafrost flow in the form of active peat layer water travelling over the permafrost boundary in summer and autumn, as shown schematically in **Fig. 1 B**. In spring, Se may be mobilized directly from melted snow and indirectly from snow water interacting with plant litter and moss/lichen biomass because the underlying peat is frozen. As a result, Se concentrations exhibit very weak or no correlation with UV<sub>254 nm</sub> and DOC. In the end of summer, the active layer boundary is located deeper in the peat layer (30 cm to 100 cm depending on the micro-landscape)<sup>29</sup> and at this time, the soil water actively leaches DOM and Se from peat layers. This is confirmed by

high correlation coefficients of Se with UV<sub>254 nm</sub> and DOC observed in summer and autumn (**Table S2, S3**).

The overwhelming role of humic substances in Se binding in aquatic systems and soils of coniferous forests is well known<sup>43</sup>. Further, a higher DOM aromaticity associated with higher electron donor capacities is known to enhance the binding of halophilic elements such as Hg<sup>44,45</sup> and, by analogy, Se. At the same time, in addition to chromophoric DOM (CDOM), a number of insoluble low-mobile elements (Al, Fe, trivalent (TE<sup>3+</sup>) and tetravalent (TE<sup>4+</sup>) hydrolysates, Pb, U) also demonstrated sizeable correlations with Se (**Table S2**). These correlations may indicate Se presence in the form of organo-ferric, organo-aluminum colloids rather than pure organic complexes with DOM. The existence of such complexes with high molecular weight (> 10-100 kDa) organo-mineral colloids as main carriers of TE<sup>3+</sup>, TE<sup>4+</sup>, Pb<sup>2+</sup>, U<sup>VI</sup> is known from previous size-fractionation studies in surface waters of western Siberia peatlands<sup>28,34</sup>. Se association with Fe/Al oxy-hydroxides and Se incorporation and/or binding to colloidal OM was also demonstrated in soil extracts<sup>46</sup>. Therefore, in organic and Fe-rich soils such as those of WSL peatlands, ternary Se-cationic metal-organic matter complexes<sup>15,47</sup> may play a dominant role. In lake waters, Se may follow these low-soluble, low-mobile elements and coprecipitate with colloidal Fe(III) hydroxides at the redox boundary within the coastal zones of the thermokarst lakes, where partially anoxic soil fluids, or shallow subsurface waters that contain Fe(II), discharge at the active layer – permafrost boundary. Altogether, DOC, CDOM and insoluble TE mark the transport and storage of Se in the form of organic aromatic-rich complexes and organo-mineral colloids, respectively.

In addition to low-mobility elements, some atmosphere originated metalloids (As, Sb) are found to be efficient proxies for Se in lake waters, capable of explaining Se concentration patterns across a large gradient of lake sizes and seasons as shown by PLS analysis (**Fig. S3**). Concomitant enrichment of peat with As and Se was reported in temperate minerotrophic

peatlands<sup>48</sup>, whereas As, Sb, Cd and Pb are strongly enriched in the surface peat layers, indicating an atmospheric supply<sup>49,50</sup>. Therefore, we interpret strong correlation of Se with metalloids and heavy metals as due to a common source, that of atmospheric deposition to surface peat and moss followed by leaching to the lakes.

Further evidence of atmospheric rather than lithological control on Se accumulation in WSL peat stems from data on soluble trace elements such as Sr or Mo which can be used for assessing the degree of groundwater feeding in thermokarst lakes<sup>32</sup> and rivers<sup>51</sup> of this region. This in turn can help to distinguish the source of Se such as surface flow from vegetation debris and upper soil profile, the deep peat horizons, or underlying sedimentary rocks. A lack of correlation between these soluble elements and dissolved Se in lakes indicates a surficial (organic) rather than deep (mineral) source of Se in WSL thermokarst lakes and thaw ponds.

In contrast, strong correlation between Se concentration and UV<sub>254</sub> absorbance suggests that the CDOM can be an important vector of Se transport from soil waters to the lakes. The UV absorbance is used as a proxy for aromatic C; molecular weight and source of DOM and SUVA is known to increase with the increase in aromaticity and hydrophobicity of allochthonous DOM<sup>52,53</sup>. We hypothesize that in discontinuous permafrost zone, where the correlation between Se and CDOM (UV<sub>254</sub>) was strongly pronounced, the maximal thickness of the active layer allows efficient delivery of refractory, highly aromatic carbon from deep peat horizons to lakes via subsurface or deep suprapermafrost flow. As a result, the majority of Se is co-mobilized with aromatic carbon from peat layers to the lakes.

#### *4.3. Consequences of climate warming on pond and lake water Se storage and Se lateral exportation*

A rising issue of concern in the Arctic setting is Hg release by permafrost thaw<sup>12</sup>. The present study demonstrates the importance of frozen peat thaw for delivery of soluble Se to

surface waters (lakes and rivers). It follows that, if Hg and Se are released and bioaccumulate together in the fish food web of surface waters and finally in the Arctic Ocean, the enhanced delivery of Se would eradicate the fish methylmercury toxicity for the Siberian population and future consumers of Arctic fish<sup>54,55</sup>. Further, a decrease in Se atmospheric fallout is expected under future climate change scenarios<sup>56</sup>. Results of this study suggest that, in the permafrost-affected peatlands, the lack of this essential trace element required by humans may be partially compensated for by its enhanced release from thawing peat and subsequent delivery to surface waters via suprapermafrost flow. For this reason, from a long-term perspective, thawing of frozen peatland and release of stored Se may become increasingly beneficial for aquatic biota.

Two main results of this study 1) the lack of effect of lake surface area and 2) the maximal concentration of Se in discontinuous permafrost zones have important biogeochemical consequences on the evolution of Se concentration under climate change scenarios. The first consequence concerns the change in lake size distribution. Scenarios of thermokarst lake evolution under climate warming and permafrost thaw in western Siberia include 1) draining of large thermokarst lakes into the hydrological network, especially pronounced in discontinuous permafrost zones<sup>57,58</sup> and 2) appearance of new depressions, subsidences and small thaw ponds (< 100-1000 m<sup>2</sup>) evidenced across all permafrost zones of this region<sup>28,59</sup>. Regardless of the overall balance between draining of large thermokarst lakes and formation of new small thaw ponds, mean Se concentration in lentic waters of the WSL will remain insensitive to the evolution of the hydrological situation and the overall stock of Se in thermokarst lakes will be determined solely by water volume, similar to that of other trace elements<sup>30</sup>. Thus, drainage of large thermokarst lakes in the discontinuous permafrost zone will bring about a decrease in the Se stock in surface waters, whereas the appearance of new ponds in the continuous permafrost zone will increase the Se aquatic stock in the north. Considering that the aqueous concentration

of Se in the lake water can serve as a proxy for Se emission flux, we expect a sizeable increase in Se emission due to thermokarst lake spreading in continuous permafrost zone.

The 2<sup>nd</sup> consequence deals with prediction of Se behavior under climate warming and permafrost thaw in the WSL. Within the concept of a substituting space for time scenario<sup>29,42</sup>, a permafrost boundary shift northward will bring about the transformation of continuous permafrost zone into discontinuous zones, and discontinuous into sporadic/isolated. This northward boundary shift may double Se concentration in thermokarst lakes of continuous permafrost zone, where the latitudinal ‘thawing front’ will be located. In contrast, disappearance of discontinuous permafrost may decrease Se concentration in thermokarst lakes two-fold. Additionally, in each permafrost zone, increase in active layer thickness may enhance the mobilization of Se in the form of large-size allochthonous organic and organo-mineral colloids rich in aromatic C. Moreover, the increase in the frequency of summer heat waves may strongly increase Se concentration in thaw ponds and thermokarst lakes. Taken together, permafrost thaw and climate warming could increase supply of dissolved Se in thermokarst water bodies of northern part of western Siberia and thereby increase Se delivery from lakes to rivers and further to the Arctic Ocean. Evolution of thermokarst lake areas may proportionally modify fluxes of Se emission to the atmosphere. In discontinuous permafrost zones, the overall supply of dissolved Se may decrease due to large lake drainage and permafrost disappearance. In contrast, the most northern territories of continuous permafrost will likely provide enhanced Se export and emission fluxes as compared to present.

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RSNR-0002) for equipment funding are also acknowledged. Chris Benker is thanked for editing the English of the manuscript.

**SUPPORTING INFORMATION:** Plots of Se concentration in rivers as a function of watershed area and latitude; dependence between Se concentration and SUVA<sub>254 nm</sub>, raw data on Se concentration in lakes and rivers sampled in this study, Pearson correlation coefficients between Se concentration and other major and trace elements for different seasons and territories, results of PLS analysis and regression parameters of Se concentration dependence on DOC, UV<sub>254</sub> and SUVA<sub>254</sub>.

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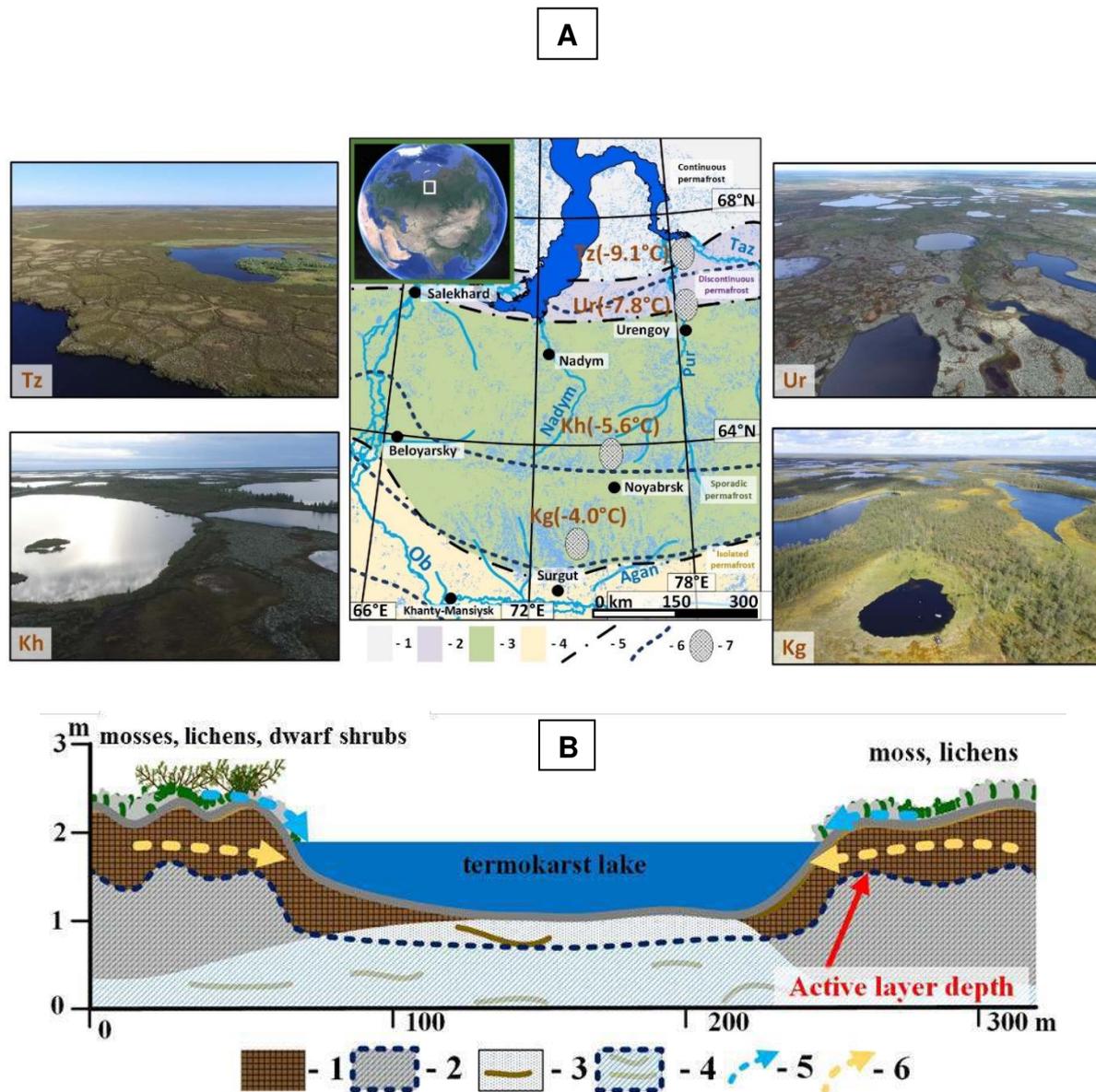
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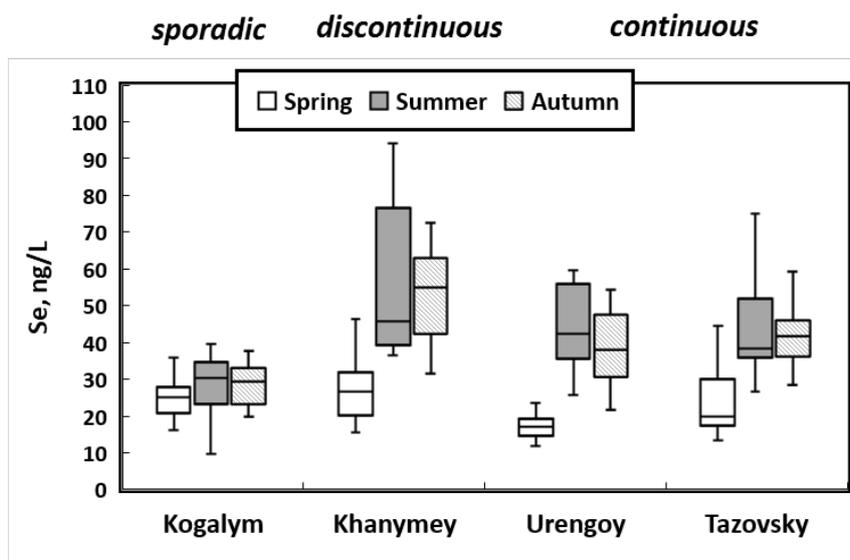


**Figure 1.**

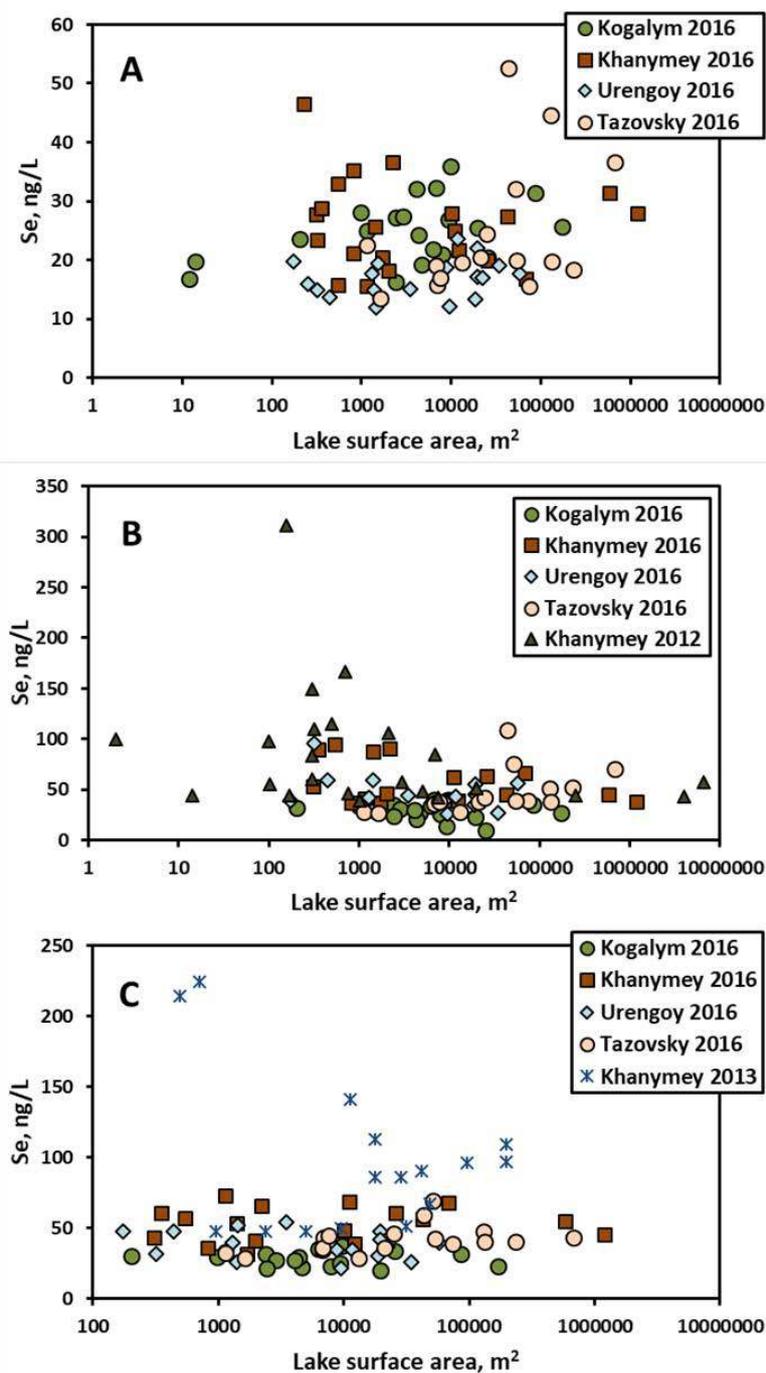
**A:** Sampling sites of thermokarst lakes in the WSL (<http://portal.inter-map.com>, National Snow and Ice Data Center, University of Colorado, Boulder), with four main test sites: Kogalym (Kg), Khanymey (Kh), Urengoy (Ur), and Tazovsky (Tz). The inserts represent aerial photos of main sites (drone-made by authors). The numbers on the legend represent the following: 1, tundra; 2, forest-tundra; 3, northern taiga; 4, middle taiga; 5, borders between natural biomes; 6, borders between permafrost zones; 7, key study sites with mean annual temperature in the parentheses.

**B:** typical environmental context of thermokarst lake in the WSL. Legend:

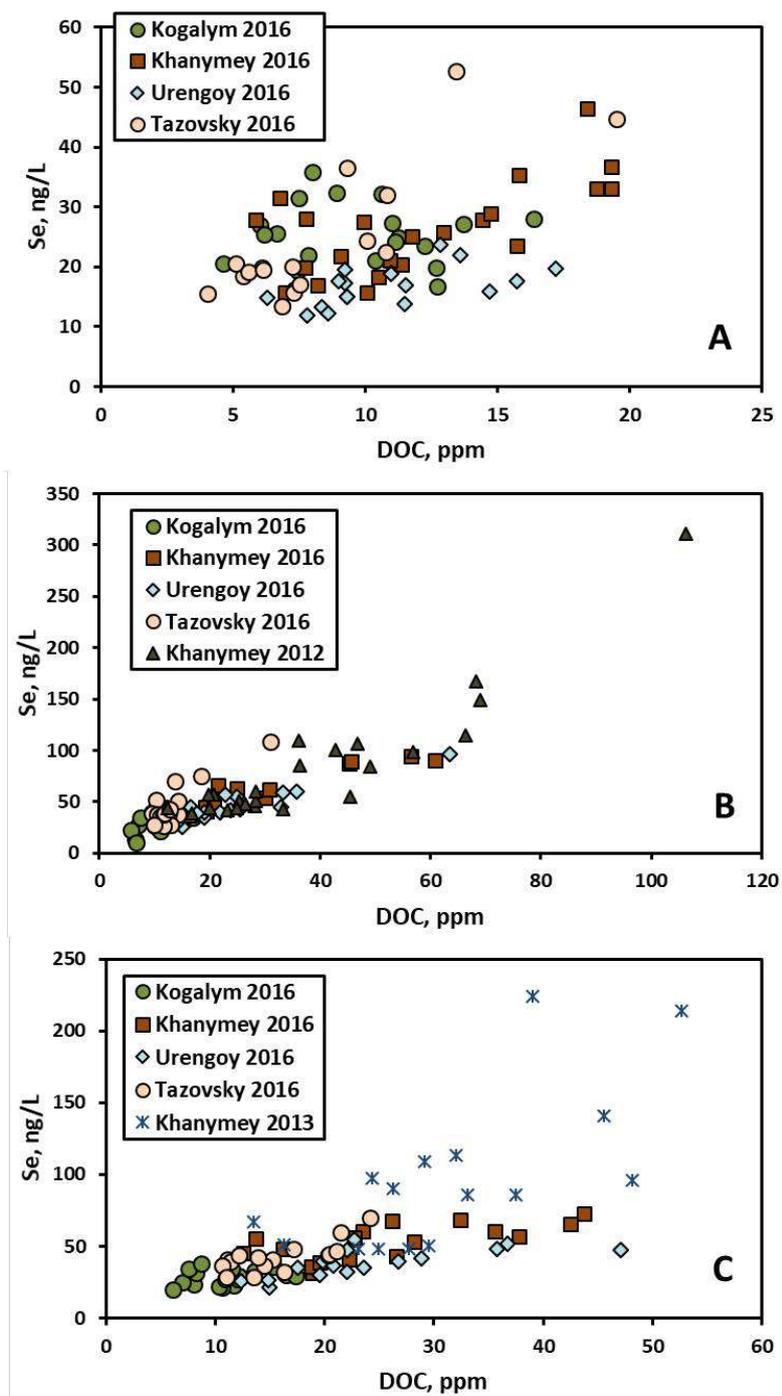
- 1, active (seasonally thawed) layer of the peat deposits;
- 2, permanently frozen peat;
- 3, seasonally thawed layer of sand and clay deposits;
- 4, permanently frozen sands with some clay layers;
- 5, spring-time surface flow;
- 6, summer time suprapermfrost flow.



**Figure 2.** Se concentration (median, 25-75%, min-max) in lakes of 4 study sites, corresponding to latitudinal and permafrost transect from south (Kogalym) to north (Tazovsky) during spring, summer and autumn 2016, shown by white, black and grey rectangles, respectively.



**Figure 3.** Se concentration as a function of lake surface area during three main sampling seasons. A, Spring (May-June); B, Summer (August); C, Autumn (September-October). Note that small thaw ponds were frozen solid in autumn and could not be sampled. Here and in other figures, data of anomalously hot summer in July 2012<sup>31</sup> are shown by triangles in B (Khanymey 2012), and the sampling under ice in October<sup>32</sup> corresponds to “Khanymey 2013” (asterisks) in C.



**Figure 4.** Relationship of Se concentration with DOC in spring (A), summer (B) and autumn (C). Parameters of regressions are listed in **Table S3**.

