



## Lichen, moss and peat control of C, nutrient and trace metal regime in lakes of permafrost peatlands



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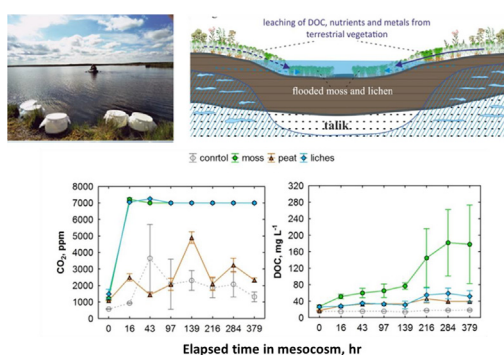
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### HIGHLIGHTS

- Thermokarst development in frozen peatlands enriches surface waters in C, nutrients and metals
- Mesocosm experiments on lake water with addition of moss, lichen and peat
- Dominant role of moss and lichen rather than peat in controlling thermokarst lake chemical composition.
- Under climate warming, a shift in plant community and abundance may be more important than thawing of permafrost peat

### GRAPHICAL ABSTRACT



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### ABSTRACT

Permafrost thaw in continental lowlands produces large number of thermokarst (thaw) lakes, which act as a major regulator of carbon (C) storage in sediments and C emission in the atmosphere. Here we studied thaw lakes of the NE European permafrost peatlands - shallow water bodies located within frozen peat bogs and receiving the majority of their water input from lateral (surface) runoff. We also conducted mesocosm experiments via interacting lake waters with frozen peat and dominant ground vegetation - lichen and moss. There was a systematic decrease in concentrations of dissolved C, CO<sub>2</sub>, nutrients and metals with an increase in lake size, corresponding to temporal evolution of the water body and thermokarst development. We hypothesized that ground vegetation and frozen peat provide the majority of C, nutrients and inorganic solutes in the water column of these lakes, and that microbial processing of terrestrial organic matter controls the pattern of CO<sub>2</sub> and nutrient concentrations in thermokarst lakes. Substrate mass-normalized C, nutrient (N, P, K), major and trace metal release was maximal in moss mesocosms. After first 16 h of reaction, the pCO<sub>2</sub> increased ten-fold in mesocosms with moss and lichen; this increase was much less pronounced in experiments with permafrost peat. Overall, moss and lichen were the dominant factors controlling the enrichment of the lake water in organic C, nutrients, and trace metals and rising the CO<sub>2</sub> concentration. The global significance of obtained results is that the changes in ground vegetation, rather than mere frozen peat thawing, may exert the primary control on C, major and trace element balance in aquatic ecosystems of tundra peatlands under climate warming scenario.

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## 1. Introduction

The surface waters of permafrost peatlands are known to exhibit strong CO<sub>2</sub> oversaturation with respect to atmosphere and thus, yield sizeable CO<sub>2</sub> emissions (Laurion et al., 2010; Lundin et al., 2013; Roiha et al., 2015; Sepulveda-Jauregui et al., 2015; Vonk et al., 2015; Elder et al., 2018; Karlsson et al., 2021). These waters also contain high Dissolved Organic Carbon (DOC) concentrations, rendering them important reservoirs of C and related elements in Northern Hemisphere. Today, C biogeochemical cycles in C-rich peatland waters from the permafrost zone are characterized in Canadian Plane lakes (Negandhi et al., 2013; Bouchard et al., 2014; Matveev et al., 2016, 2019; Arsenault et al., 2018; Wauthy et al., 2018), small bogs of northern Sweden (Roehm et al., 2009; Hodgkins et al., 2014, 2016), and most extensively, in western Siberian lowland (WSL, Frey and Smith, 2005; Frey et al., 2007; Pokrovsky et al., 2011, 2013; Shirokova et al., 2013, 2020; Manasyrov et al., 2014, 2015; Loiko et al., 2017; Serikova et al., 2019).

Among various surface waters of permafrost landscapes, recently formed thermokarst lakes are most interesting because they emit sizeable amount of CO<sub>2</sub> and CH<sub>4</sub> to the atmosphere (Walter et al., 2008; Walter Anthony et al., 2012, 2014; Hodgkins et al., 2014; Ewing et al., 2015; Mann et al., 2015; Natali et al., 2015; Roiha et al., 2015; Schuur et al., 2015; Wik et al., 2016; Serikova et al., 2019). Further, in case of flooding or drainage, these lakes may deliver substantial amount of dissolved nutrients and metals to adjacent hydrological network (Kokelj et al., 2009; Pokrovsky et al., 2011, 2016a, 2016b). The main interest to these shallow surface waters is in their location at the thawing permafrost front, typically in the discontinuous and isolated permafrost zone, where the soil temperature often fluctuates within the highly 'fragile' temperature range (0 to -2 °C) of the permafrost (Romanovsky et al., 2010). As a result, under on-going climate warming and permafrost thaw, these waters may i) spread their surfaces much faster than those in the region with mineral substrates and ii) become highly vulnerable to water heating and heterotrophic respiration of dissolved and particulate organic matter (OM) into CO<sub>2</sub>.

The area coverage of thaw ponds and small depressions in permafrost-affected peatlands of Northern Eurasia is not fully quantified but may range from 5 to 20% of the territory which includes Western Siberia Lowland (WSL), Northern Siberian Lowland, Kolyma and Indigirka Lowland, of overall area > 2 million km<sup>2</sup> (Polishchuk et al., 2020; Zabelina et al., 2021). In Europe, the permafrost peatlands widely occur in the NE part of it, within the Bolshezemelskaya Tundra (200,000 km<sup>2</sup>), although biogeochemical parameters of related thermokarst lakes are quite poorly known.

The main source of DOM in thaw ponds of frozen peatlands is leaching of C from allochthonous reservoirs of solid OM, such as peat and surrounding vegetation (mosses, lichens). The magnitude of this process is not yet quantified, and the relative importance of three main organic 'solid' substrates - moss, lichen and peat - in providing DOC, CO<sub>2</sub> and nutrients to these thaw waters is not known. This, in turn, does not allow predicting the response of these aquatic ecosystems to the change of environmental conditions such as vegetation regime and increasing the active layer thickness (ALT) and the precipitation. The latter will likely bring about a surface drainage through litter layer rather than through underlying mineral soils. To assess the capacity of ground vegetation and peat soil to modify the chemical and gaseous regime of thaw ponds, mere observations of natural environments are not sufficient and ecosystem (mesocosm-level) manipulations are needed.

Indeed, the ecosystem manipulation or mesocosm experiments allow understanding the system behavior under various external impacts (i.e., Hering et al., 2015; de Rozari et al., 2016; Conroy et al., 2016). Although the mesocosm experiments were extensively used for boreal, permafrost- and peat-bearing aquatic landscapes (Bridgham et al., 1999; Judd and Kling, 2002; Blodau and Moore, 2003; Blodau et al., 2004; Basiliko et al., 2006; Balcarczyk et al., 2009; Green et al., 2014; Richardson et al., 2015; Nydahl et al., 2019), only

one study (Manasyrov et al., 2017) dealt with thermokarst lakes of permafrost peatlands. However, in their study, the pCO<sub>2</sub> and dissolved nutrient patterns were not assessed, and two important substrates contributing to the lake water hydrochemical composition – moss and frozen peat – were not tested.

In this work, we performed mesocosm experiments on isolated water volumes of thermokarst thaw ponds and we characterized the change of chemical and gaseous (CO<sub>2</sub>) parameters of pond water in response to the addition of peat, moss and lichen. We hypothesized that peat will be an important source of chromophoric DOM (CDOM) and nutrients, whereas a non-aromatic, bioavailable DOM and nutrients may be released from moss and lichen. To test this hypothesis, we quantified the relative capacity of various organic substrates to change the chemical composition (DOC, nutrients, metals, dissolved CO<sub>2</sub>) of pond water over the time scale (10 to 20 days) comparable to the water residence time in small thaw ponds. Further, we characterized the hydrochemical regime of small thermokarst water bodies of poorly studied Bolshezemelskaya Tundra of NE Europe, and we quantified the C, nutrient, and trace element regime concentration change in natural ponds and lakes depending on their surface area (degree of maturity). We aimed at comparing the pattern of dissolved CO<sub>2</sub>, DOC, nutrients and metals in natural sequence of thermokarst lake evolution to that in the mesocosm manipulation experiments in order to obtain quantitative constraints on future changes of thermokarst lake water chemical composition in response to vegetation change and frozen peat thaw. Based on obtained pattern of dissolved carbon, pCO<sub>2</sub> and elements, we provided first-order predictions of thermokarst lake water hydrochemistry change under various climate warming scenario.

## 2. Study site, experiments and analyses

### 2.1. Physio-geographical context of thaw ponds and thermokarst lakes of the Bolshezemelskaya Tundra

The Bolshezemelskaya Tundra (BZT) peatland is underlaid by permafrost, discontinuous on the eastern part and sporadic to isolated on the western part. The BZT is a hilly moraine lowland located between rivers Pechora and Usa (from the west and south) and the Polar Ural and Pai-Khoi ridge from the east. The dominant altitudes are between 100 and 150 m, created by hills and moraine ridges, composed of sands and silt with boulders. Between the moraines and ridges there are many lakes, mostly of thermokarst origin. The dominant soils are Histosol of peat bogs and podzol-gleys in the south. The mean annual temperature is -3.1 °C and the mean annual precipitation is 503 mm. The dominant vegetation of the tundra zone is mosses, lichens and dwarf shrubs. The peat (1.0–1.5 m thick) overlays Quaternary glacial deposits over Cretaceous sands, clays and silts. The dominant soil catenae are flat-mound bogs along the watershed divides, which comprise the Hemic Cryic Histosols on mounds and Fibric Gelic Histosols on troughs (the soil nomenclature is according to IUSS, 2014). The average thickness of the active layer ranges from 145 ± 20 cm within the depressions to 41 ± 5 cm at the peat mounds.

The thermokarst lakes are shallow (0.5 to 1.5 m) closed basins without distinct inlet and outlets, with watershed surface area smaller or comparable to the lake water area. They receive the surface inflow via lateral drainage of surrounding soil litter and ground vegetation and shallow subsoil water flow over the permafrost table, which is so-called suprapermafrost flow (Manasyrov et al., 2015, 2017; Raudina et al., 2018). The early stage of lake formation includes soil subsidences, lichen and moss submergence, and peat abrasion (Audry et al., 2011; Kirpotin et al., 2011; Shirokova et al., 2013). It follows by lateral spreading of shallow water bodies, when the ratio of the lake circumference to the lake volume diminishes which leads to progressive decrease of allochthonous (terrestrial) organic matter input to the lake.

The leaching of surrounding organic substrates occurs via (1) rain and melt snow that provide a lateral surface input occurring over

moss and lichen cover (Manasypov et al., 2015), (2) direct interaction of the lake water with wave- and thermokarst-abraded peat at the lake shore (Pokrovsky et al., 2011; Shirokova et al., 2013), and finally, (3) suprapermafrost water interaction with frozen peat layer during water travel from elevated points of relief to the lake, over the permafrost table (Raudina et al., 2018). Taking into account these three main

processes supplying the C and inorganic solutes to the thaw lakes, in the present study, we modelled the effect of three main organic substrates – moss, lichen and frozen peat – interacting with thermokarst lake waters at controlled mesocosm conditions.

To assess natural variability of lake solutes as a function of lake size and degree of maturity, between July 14 and July 26 of 2016 and 2017,

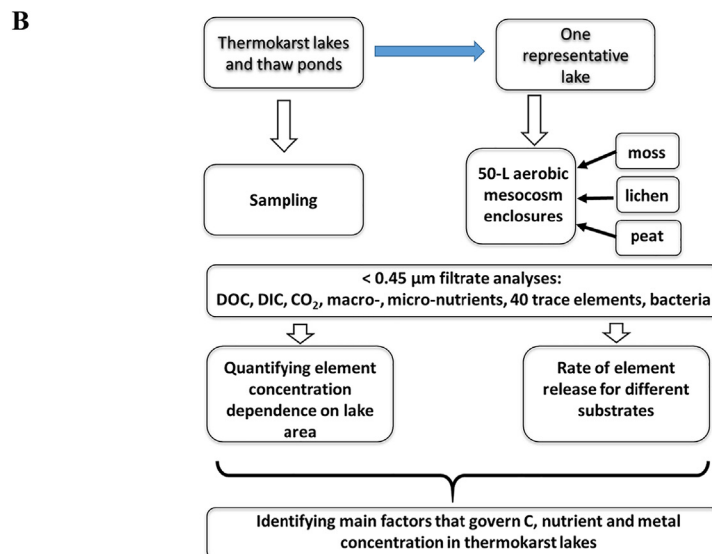
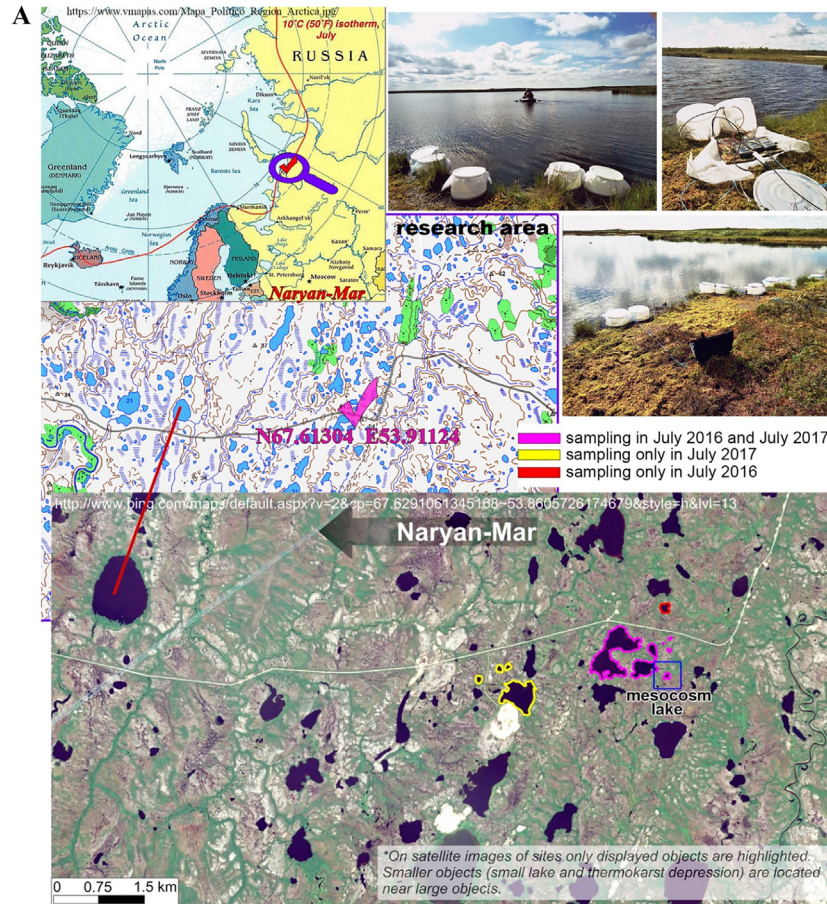


Fig. 1. A: The map of the study site with position of sampled lakes and photos of mesocosm run at the lake shore. B: The work flow chart of the field observations, mesocosm experiments and analyses performed in this study.

we sampled 29 stagnant isolated surface waters located within upland frozen peat bog, including depressions (permafrost subsidence), thaw ponds and thermokarst lakes (Fig. 1A). Depressions in moss and lichen cover are typically filled by water from thawing of ground ice and ranged in size from 0.5 to 2 m<sup>2</sup> with an average depth between 0.1 and 0.3 m. A series of thaw ponds (10 to 1000 m<sup>2</sup> size, 0.3 to 0.5 m depth), and thermokarst lakes (10<sup>3</sup> to 10<sup>6</sup> m<sup>2</sup>, 0.5 to 1.5 m depth) represented several stages of thermokarst water body maturation, from youngest small size ponds to large mature thermokarst lakes (Zabelina et al., 2021). These water bodies are similar to the sequence of thermokarst lakes and ponds described in Northern Europe (Matthews et al., 1997), Alaska (Hinkel et al., 2003) and western Siberia (Audry et al., 2011; Kirpotin et al., 2011).

The surface waters were collected from the shore (depressions) or the PVC boat (thaw ponds and thermokarst lakes). The water samples were filtered on-site using sterile single use Sartorius filters (acetate cellulose, 0.45 µm) for analyses of cations and anions. Unfiltered water samples for nutrient analyses were placed into 250-mL Milli-Q pre-cleaned PVC bottles and kept refrigerated until arrival to the laboratory, within 2–3 h after collection. Conceptual approach of field observations combined with mesocosm experiments in this study is illustrated in Fig. 1B.

## 2.2. Mesocosm experiments

Closed-system mesocosms experiments were performed with thermokarst lake water (pH ~ 5.5) using three organic substrates that are likely to control the hydrochemistry of thermokarst lakes during ecosystem maturation. We selected a typical (6760 m<sup>2</sup>, depth of 1.0 ± 0.5 m) thermokarst lake with moderate DOC (15 mg/L) concentration. The lake was located in the palsa peat bog of Bolshezemelskaya Tundra, 40 km east of the Narian-Mar town (63°46'59" N, 75°39'08" E).

Peat from frozen layer of permafrost (50–70 cm from the surface which is 10 cm below the maximal active layer depth), moss and lichen constituting ca. 30% and 70% of peatland surface vegetation, were collected in the 100 m vicinity of thermokarst lake and dried at 40 °C using Osmofilm® bags during 5 days. The oligotrophic peat was 35% decomposed and contained *Sphagnum angustifolium* (20%), cotton-grass *Eriophorum* (25%), herbs *Scheuchzeria palustris* (15%), bog-sedge (5%), lichens (5%), dwarf shrubs (5%) and some amount of wood debris (pine) and green mosses. The water was collected on 15 July 2017 from the surface (0–20 cm) of the lake and immediately pre-filtered through 100 µm nylon net to remove zooplankton, insects and large organic debris into 50-L PVC tanks. Duplicate tanks with lichen *Cladonia stellaris* (5.9 g<sub>dry</sub>/L), moss *Sphagnum palustris* (9.2 g<sub>dry</sub>/L) and peat (20 g<sub>dry</sub>/L) addition were closed with a 100 µm nylon net and placed directly in the lake ensuring their vertical orientation and no overflow of the lake water (Fig. 1A). Additional aeration of incubated water was achieved through periodic opening of the tank and gentle stirring of the content with pre-cleaned plastic shovel. Control experiments included the same tanks filled with 100 µm-filtered lake water without addition of organic or substrate. The wind-induced wave movement in the lake provided sufficient agitation of the interior of the tank. The experiment lasted 16 days. The CO<sub>2</sub> analyses were run each 2–3 h during first day. The sampling for dissolved major and trace elements was performed after 1, 2, 4, 6, 9, 12 and 16 day of exposure in order to assess both short-term and long-term effect of added substrate on lake water hydrochemistry.

## 2.3. Chemical analyses

The water temperature, pH, dissolved oxygen, and electric conductivity in natural waters and mesocosm experiments were measured directly in the lake water column or inside the tank using Hanna and WTW portable instruments. Dissolved CO<sub>2</sub> concentration was measured using portable submersible Vaissala Carbocap® GM70 Hand-held carbon dioxide meter with GMP222 probes (accuracy 1.5%). Filtered waters of natural thaw ponds and lakes and of mesocosm samplings were processed

using the analytical approaches employed by the GET Laboratory (Toulouse) to analyze low total dissolved solid (TDS), DOM-rich waters from boreal and permafrost-bearing settings (Pokrovsky et al., 2011, 2016a, 2016b; Shirokova et al., 2013). The major anion concentrations (Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were analyzed by ion chromatography (Dionex 2000i), with an uncertainty of 2%. The DOC and Dissolved Inorganic Carbon (DIC) were determined by a Shimadzu TOC-VSCN Analyzer with an uncertainty of 3% and a detection limit of 0.1 mg/L. Specific UV absorbance (SUVA) was measured as absorbance at 254 nm normalized for DOC concentration in L mg<sup>-1</sup> m<sup>-1</sup>. The major and trace elements were measured by quadrupole ICP-MS (7500ce, Agilent Technologies). Indium and rhenium were used as internal standards. The international geostandard SLRS-5 (Riverine Water Reference Material for Trace Metals, certified by the National Research Council of Canada) was used to check the validity and reproducibility of analyses. Good agreement existed between our replicated measurements of SLRS-5 and the certified values (relative difference < 15%).

The nutrient analyses were based on colorimetric assays (Koroleff, 1983a, 1983b). Total dissolved organic nitrogen (DON) was measured from the difference between the total dissolved nitrogen (persulfate oxidation) and the total dissolved inorganic nitrogen (DIN, or the sum of NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>). Uncertainties of DON and DIN analyses were between 10 and 20% and detection limits were between 10 and 50 µg/L. Si concentration was measured by spectrophotometry with molybdate blue with an uncertainty of ±5% and a detection limit of 2 µg/L.

The total bacterial number and dominant cell size morphology were quantified using DAPI fluorescence method (Porter and Feig, 1980). In addition, we performed oligotrophic and eutrophic bacteria (OB and EB, respectively) count in the course of mesocosm experiments, following the standard methodology used in biodegradation experiments of peat waters (i.e., Stutter et al., 2013) as also described previously (Shirokova et al., 2013, 2019; Chupakova et al., 2018).

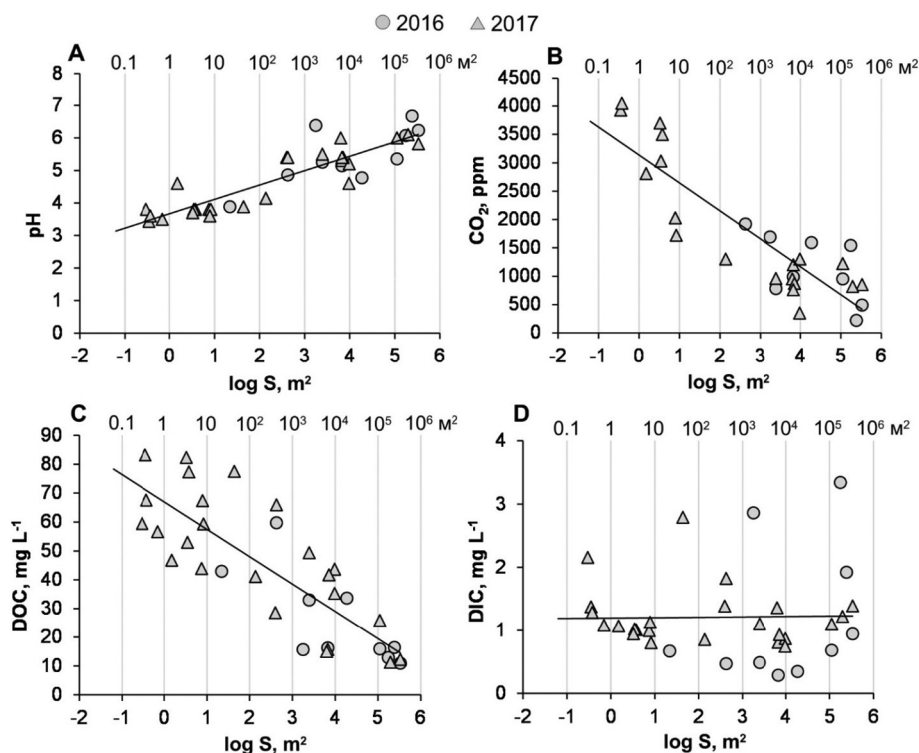
## 2.4. Quantification of element release from organic substrates

In order to calculate the dynamics of element concentration and the amount of element released in the mesocosms, we normalized the difference between element concentration in the experiment and the control (lake water without added substrate) to the concentration of dry substrate in the mesocosm. This allowed tracing the net amount of element ( $i$ , mol L<sup>-1</sup>) released from the substrate (peat, moss or lichen) to the lake water in the course of mesocosm experiment ( $\Delta i$ , mmol kg<sub>dry</sub><sup>-1</sup> substrate). We estimated the maximal rate ( $V_{max}$ , mmol kg<sup>-1</sup> h<sup>-1</sup>) of element release from substrate as a derivative of average maximal change of concentration over the first 24 h. We also quantified the mean rate of element release ( $V_{mean}$ ) over the full duration of experiments, and the maximal effect of concentration increase determined as the average of 2–3 neighboring concentrations, typically after 100 h of reaction. The initial concentration used to trace these dependences was the one measured 5–10 min following the addition of organic substrate. The reason for this choice is that some elements could be present as loosely bound on the surface of organic matter or within the remaining water of humid substrates, notably moss and peat, and quickly released to the aqueous solution, immediately after substrate addition to the reactors. The negative value of  $V_{max}$  rate was indicative of element concentration decrease in the course of experiments; in such case, the rates were not quantified.

## 3. Results

### 3.1. Evolution of element concentration in the natural sequence of lake growth and maturation reflected in the thermokarst lake size

The evolution of major hydrochemical parameters in the course of lake maturation (increase in size) was characterized via a Mann Kendall test of probability at 90 and 95% level of significance (Fig. S1 of the Supplement). It is illustrated as a plot of concentration versus thaw



**Fig. 2.** pH (A), pCO<sub>2</sub> (B), DOC (C) and DIC (D) concentration in depressions, thaw ponds and thermokarst lakes as a function of logarithm of lake surface area (log S). Parameters of linear relationships (Eq. (1)) are listed in Table S1 of the Supplement.

pond and lake area for pH, pCO<sub>2</sub>, DOC and DIC (Fig. 2A–D). There was a systematic increase in pH (ca. 3 units) with lake size increase from 0.1 to 10<sup>5</sup> m<sup>2</sup>, whereas pCO<sub>2</sub> and DOC concentration decreased about ten times with lake growth and maturation, when the lake size increased over 6 orders of magnitude. The lowest pH values and the highest concentrations of DOC and pCO<sub>2</sub> were observed at the very beginning of thermokarst activity - in small soil depressions, subsidences, water puddles and thaw ponds (< 1–10 m<sup>2</sup>). The evolution of nutrient (N, P, Si), major cation (Ca) and metal (Fe, Al) concentrations over the lake maturation was less pronounced (Fig. 3). The change of pH value and element (Ci) concentration with lake area (S<sub>lake</sub>) can be described by a linear function:

$$[C_i] = A \times \log S_{\text{lake}} + B \quad (1)$$

with parameters A and B of the regression listed in Table S1. Considering the trend of element concentration with lake size increase, two main families of solutes were distinguished (Fig. S1). The value of Specific Conductivity (S.C.) and concentrations of eutrophic and oligotrophic bacteria, CO<sub>2</sub>, DOC, nutrients (NO<sub>2</sub>, NO<sub>3</sub>, Si, Fe), and some trace elements (Al, Co, Cd, Pb, Sb, Cs, Tl) decreased with lake size; these components formed the first group of elements. The second group of components demonstrated significant ( $p < 0.05$ ) increase in concentration with lake size: O<sub>2</sub>, Li, Ca, K, Y, REE, As, Hf, U and the pH value. The other elements did not show any significant ( $p > 0.05$ ,  $r < 0.3$ ) correlation with lake size and the probability of their concentration increase or decrease was below 90% (Fig. S1).

### 3.2. Mesocosms of thermokarst lakes from peat palsa plateau

The addition of organic substrates to the lake water caused progressive change of concentration of most dissolved components. The maximal element yield, mean and maximal rates of DOC, nutrient, bacteria, major component (Table 1) and trace element (Table S2) release were normalized to dry weight of organic

substrate and averaged across replicates. These allowed to assess the degree of substrate effect on lake water enrichment (or impoverishment) by each element. For convenience, the element concentration evolution in the mesocosms and in the control enclosures are depicted for several representative major and trace components in Fig. S2 of the Supplement and specified by groups below.

#### 3.2.1. Major parameters of lake water (pH, pCO<sub>2</sub>, carbon and bacteria)

The pH of the lake water strongly decreased by ca. 1.5 units, immediately after addition of all three organic substrates (Fig. 4A). The peat addition produced the lowest pH (ca. 3.75) while the moss and lichen addition yielded similar pH drop at the beginning of experiments; the pH then remained stable for the full duration of exposure. Specific conductivity steadily increased during experiments with mosses but did not evolve in other treatments (Fig. 4B). The DIC was an order of magnitude higher in experiments with moss and lichen compared to peat and lake water control incubation (Table 1). The oxygen regime was similar (80–100% saturation) between lake water control and peat addition, but the O<sub>2</sub> level strongly decreased (ca., by a factor of 5 to 10) after first 50–100 h of experiments with moss and lichen thus producing net negative ΔO<sub>2</sub> values (Fig. 4D).

The pCO<sub>2</sub> pattern in experimental mesocosms demonstrated a 10-fold increase over the first 200 h of lake water reaction with moss and lichen (Figs. 4C; S2B). The degree of pCO<sub>2</sub> increase relative to the control followed the order moss > lichen >> peat. However, when normalized to the amount of biomass used in mesocosm incubation, the moss, lichen, and peat released 19, 34 and 4.7 mmol CO<sub>2</sub> kg<sup>-1</sup>, respectively. The DOC concentration was the highest in experiments with moss addition, rising 8 times, from 20 mg/L to 160 mg/L over 2 weeks of reaction (Figs. 4E; S2C). Lichen and peat addition produced similar, 2–3 fold increase in DOC over first 284 h of reaction. The mass-normalized DOC yield at the end of incubation was equal to 1500, 580, and 89 mmol DOC kg<sup>-1</sup> for moss, lichen and peat, respectively (Table 1).

The UV absorbency and SUVA<sub>254</sub> were drastically different among three substrates and evolved different to that of DOC (Figs. 4F; S2D).

Peat and moss addition produced a 2-fold increase in absorbency whereas lichens did not affect the release of CDOM. The SUVA decreased after 5 days of reaction with moss and lichen but remained essentially constant in experiments with peat addition, when slightly positive rate increase was observed.

The concentration of eutrophic culturable bacteria steadily increased in moss and lichen mesocosms, but decreased after initial rise at 80–100 h in experiments with peat additions (Fig. S3A). The number of oligotrophic bacteria significantly increased with time for all substrates (Fig. S3B) and was ca. 1 to 2 orders of magnitude higher than that in lake water control run. The mesocosms with moss and lichen addition exhibited the highest concentration of cultivable bacteria. Consistent with cultivable (OB and EB) bacterial numbers, the total bacterial (TB) number measured by DAPI was the highest in moss and lichen treatments ( $(20\text{--}40) \times 10^6$  cell mL<sup>-1</sup> without systematic evolution), which was sizably lower in peat treatment ( $(1\text{--}2) \times 10^6$  cell mL<sup>-1</sup>). The latter was comparable with TB in the lake water control ( $5\text{--}6) \times 10^6$  cell mL<sup>-1</sup>.

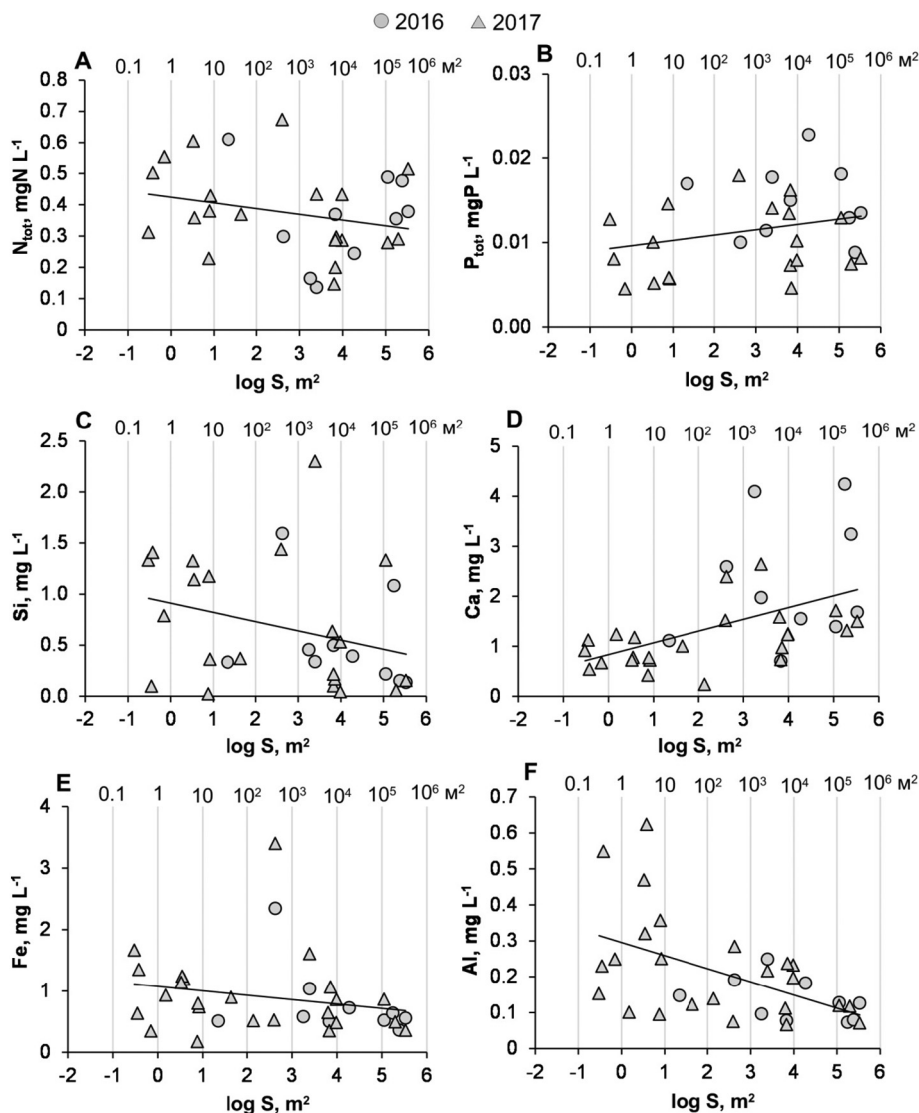
### 3.2.2. Nutrients (Si, P, N)

Dissolved Si exhibited the minimal changes in the course of experiments with stable concentrations achieved over the first day of reaction

(Figs. 5A, S2H). The biomass-normalized Si release was equal to 1.4, 0.97 and 0.26 mmol kg<sup>-1</sup> for moss, lichen and peat treatments (Table 1). Total dissolved P was dominated (> 90%) by PO<sub>4</sub> whose yield was orders of magnitude higher in moss and lichen mesocosms compared to peat addition (Fig. 5B). Total dissolved N was dominated by NO<sub>3</sub> which was generally stable from the very beginning of experiment and did not systematically evolved over 380 h of exposure (Fig. 5C); mosses and lichens released significant amount of nitrate, unlike peat. Addition of moss yielded strong increase in NH<sub>4</sub><sup>+</sup> after 4 days of reaction however the agreement between replicates was quite low (Fig. 5D).

### 3.2.3. Major and trace elements

The final metal yield achieved after ~300 h of reaction for each substrate listed in Table S2 allowed distinguishing two main group of elements, depending on the moss or peat control on their release in the mesocosms. Examples of major and trace elements are shown in Fig. S4. Strong enrichment of the lake water in Li, Na, Mg, K, Fe, Cu, As, Rb, Cs, Ga, Nb and Tl upon the moss addition persisted over full duration of experiments and was significant ( $p < 0.0001$ ) compared to peat and lichen treatments. Therefore, these elements may serve as indicators of the dominance of moss leaching on thermokarst lake water's chemistry. In contrast, high concentrations of lithogenic Be, Al, V, Ni, Y, heavy REEs,



**Fig. 3.** Total dissolved N (A), P (B), Si (C), Ca (D), Fe (E), Al (F), phosphate (G), nitrate (H), ammonia (I), Mg (J), K (K) and Mn (L) concentrations in depressions, thaw ponds and thermokarst lakes as a function of logarithm of lake surface area (log S). Parameters of linear relationships are listed in Table S1.

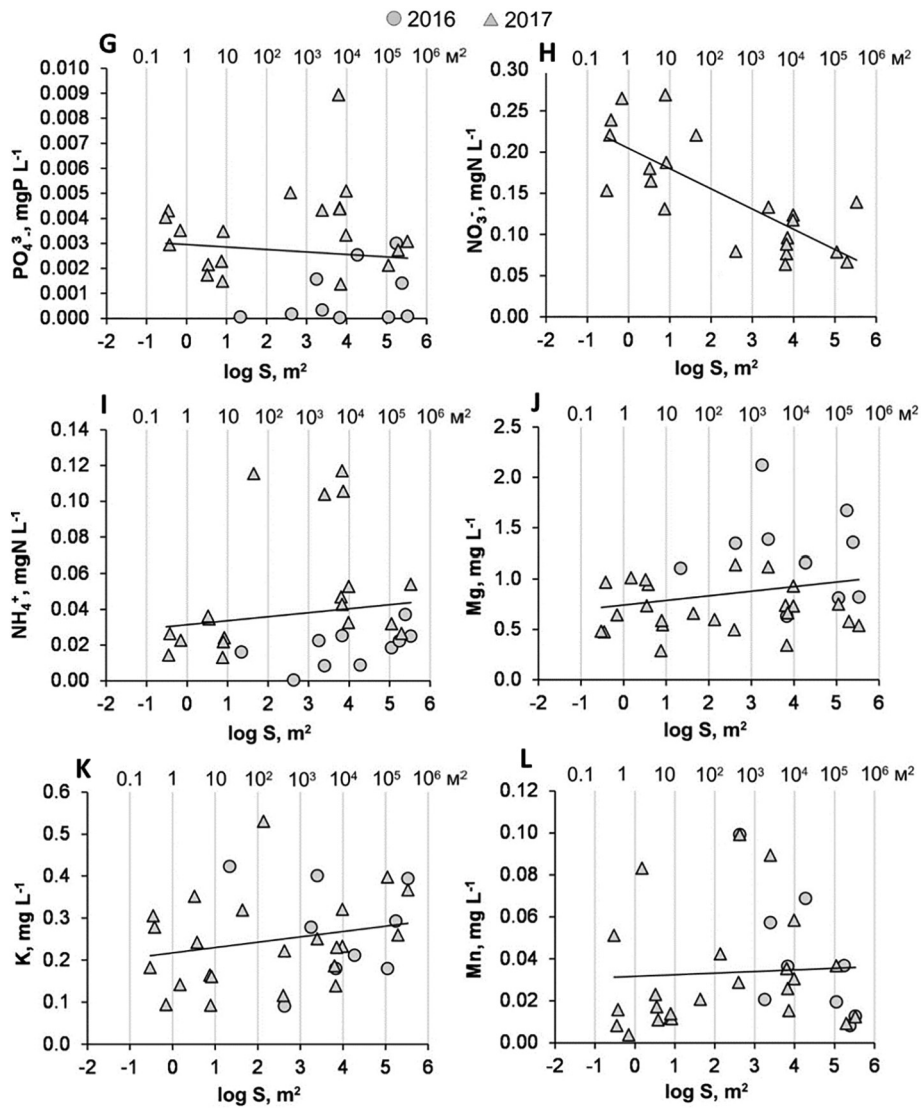


Fig. 3 (continued).

Zr and Hf were observed in mesocosms with peat addition; these elements may be indicative of the influence of peat on thermokarst lake water composition. Addition of lichens enriched aqueous solution in Pb but removed Fe, Al, Ni, Ba, Y, Ga and Zr, as supported by mean and maximal rates of element concentration increase after addition of substrates (see Tables 1 and S2).

#### 4. Discussion

##### 4.1. Lake size control on C, nutrient and metal concentration in natural settings

We observed gradual decrease of S.C.,  $pCO_2$ , DOC, some nutrients (Si,  $NO_3^-$ ), and trace metals (Fe, Al, Zn, Co, Cd, Pb, Cs) from small thaw depressions to thaw ponds and lakes. This is consistent with evolution of water hydrochemistry during thaw pond and thermokarst lake growth and maturation in other frozen peatlands of the world, such as WSL (Pokrovsky et al., 2011; Shirokova et al., 2013; Manasyrov et al., 2014) and palsa peat bog of Canada (Peura et al., 2020). A decrease in concentrations of C, nutrients and metals with lake size may be caused by several parallel mechanisms operating at the lake shore/lake watershed and within the lake water column as depicted in Fig. 6. The leaching of DOC and inorganic solutes occurs from ground vegetation

(mainly moss and lichen) and during peat abrasion at the lake shore (Shirokova et al., 2017; Payandi-Rolland et al., 2020a). The delivery of these substrates decreases with an increase in the ratio of lake circumference and lake watershed area to the lake volume (Manasyrov et al., 2015). Non-negligible amount of C can be delivered via diffusion from lake sediments into the water column (Audry et al., 2011; Shirokova et al., 2020). An increase in the lake volume and associated decrease of solute flux lead to mere dilution of dissolved C, nutrient and metal concentration upon growth of thermokarst lake depth and area. This is reflected by a linear response of DOC concentration to the logarithm of lake water areas (Fig. 2C). In addition to surface vegetation and upper (unfrozen) peat horizons, thawing of ground ice during summer period (Connolly et al., 2020; Lim et al., 2021) may provide sizeable input of DOC and related elements. It can be expected that the role of moss and lichen cover is especially pronounced for small water bodies whereas the suprapermafrost flow-delivered peat leaching products are more important for large lakes. The mineral horizons can be leached by subsoil (shallow underground) waters, especially in large lakes which exhibit deeper drainage basins and higher hydrological connectivity with subsurface reservoirs (Ala-aho et al., 2018).

The mechanisms that are capable removing the solutes via DOM and nutrient processing within the lake water column include heterotrophic bacterial activity (Comte et al., 2015; Deshpande et al., 2016; Roiha

**Table 1**

The mean and maximal release rates and maximal concentration yield of major components normalized to dry weight of substrate in mesocosm experiments. Significant ( $p < 0.05$ ) results are labelled with asterisk (\*).

Index	Substr.	R <sup>2</sup>	F-test ( $p = 0.05$ )	$\bar{c}_{\text{mean}} \pm \text{SE}, \text{X} \cdot \text{hr}^{-1}$	$\bar{c}_{\text{max}} \pm \text{SE}, \text{X} \cdot \text{hr}^{-1}$	$\Delta C_{\text{max}} \pm \text{SE}$	$T_{\Delta C_{\text{max}}}$
EB, CFU · 10 <sup>6</sup> · kg <sup>-1</sup>	Moss	0.64	7.2*	0.05 ± 0.02	0.1 ± 0.4	21 ± 7	379
	Peat	0.74	11.3*	0.022 ± 0.001	0.036 ± 0.004	2.1 ± 0.1	97
	Lichen	0.88	29.2*	0.00074 ± 0.00001	0.33 ± 0.03	58 ± 3	379
OB, CFU · 10 <sup>6</sup> · kg <sup>-1</sup>	Moss	0.92	48.3*	0.044 ± 0.002	0.08 ± 0.02	17.5 ± 0.8	379
	Peat	0.49	3.8*	0.012 ± 0.005	0.05 ± 0.02	5 ± 1	216
	Lichen	0.92	45.0*	0.11 ± 0.02	0.23 ± 0.09	42 ± 6	379
O <sub>2</sub> , mmol · kg <sup>-1</sup> (long)	Moss	0.68	8.62*	-0.128 ± 0.007	-0.98 ± 0.09	-22.9 ± 0.7	379
	Peat	0.52	4.3*	-0.05 ± 0.01	-0.24 ± 0.04	-4 ± 1	97
	Lichen	0.68	8.62*	-0.182 ± 0.008	-1.45 ± 0.02	-37	97
CO <sub>2</sub> , mmol · kg <sup>-1</sup> (short, for peat long)	Moss	0.78	14.4*	6 ± 2	6 ± 2	19 ± 5	3
	Peat	0.10	0.44	0.0026 ± 0.0007	-0.112 ± 0.0064	4.7 ± 0.7	139
	Lichen	0.95	80.5*	4.23 ± 0.04	6.0 ± 0.8	33.8 ± 0.4	8
DIC, mmol · kg <sup>-1</sup>	Moss	0.31	1.78	0.14 ± 0.03	0.7 ± 0.2	14 ± 3	97
	Peat	0.38	2.42	0.006 ± 0.006	0.01 ± 0.02	1 ± 1	216
	Lichen	0.90	37.7*	0.323 ± 0.007	0.54 ± 0.06	31.4 ± 0.7	97
DOC, mmol · kg <sup>-1</sup>	Moss	0.52	4.39*	5 ± 4	8 ± 13	1484 ± 1034	284
	Peat	0.78	14.0*	0.52 ± 0.05	1.5 ± 0.1	89 ± 2	284
	Lichen	0.50	4.01*	2 ± 1	4 ± 5	577 ± 184	284
NH <sub>4</sub> <sup>+</sup> , mmol(N) · kg <sup>-1</sup>	Moss	0.34	2.08	0.02 ± 0.03	0.04 ± 0.12	5 ± 6	216
	Peat	0.36	2.25	-0.0002 ± 0.0001	0.0006 ± 0.0005	-0.04 ± 0.02	284
	Lichen	0.11	0.49	0.0002 ± 0.0002	0.0002 ± 0.0010	0.03 ± 0.08	97
NO <sub>3</sub> <sup>-</sup> , mmol(N) · kg <sup>-1</sup>	Moss	0.81	8.58*	0.05 ± 0.03	0.08 ± 0.06	3.1 ± 0.9	43
	Peat	0.85	11.1*	0.030 ± 0.002	0.050 ± 0.008	1.53 ± 0.02	43
	Lichen	0.80	8.18*	0.01 ± 0.02	0.02 ± 0.04	1.6 ± 0.5	379
NO <sub>2</sub> <sup>-</sup> , μmol(N) · kg <sup>-1</sup>	Moss	0.70	9.44*	0.4 ± 0.6	1 ± 2	15 ± 10	43
	Peat	0.81	17.5*	0.05 ± 0.02	0.10 ± 0.06	9.8 ± 0.5	379
	Lichen	0.09	0.4	0.04 ± 0.06	0.1 ± 0.2	-21 ± 2	16
N <sub>tot</sub> , mmol(N) · kg <sup>-1</sup>	Moss	0.76	6.3*	0.014 ± 0.009	0.04 ± 0.03	8 ± 2	284
	Peat	0.88	14.3*	0.006 ± 0.003	0.04 ± 0.01	3.4 ± 0.5	379
	Lichen	0.75	6.09*	0.03 ± 0.01	0.09 ± 0.08	12 ± 4	379
PO <sub>4</sub> <sup>3-</sup> , μmol(P) · kg <sup>-1</sup>	Moss	0.38	2.46	4 ± 6	7 ± 42	1262 ± 1790	284
	Peat	0.04	0.16	-0.016 ± 0.007	0.01 ± 0.14	0.7 ± 0.4	139
	Lichen	0.43	3.03	5 ± 4	11 ± 7	1234 ± 812	216
P <sub>tot</sub> , μmol(P) · kg <sup>-1</sup>	Moss	0.47	1.79	0.4 ± 0.2	0.7 ± 0.3	1647 ± 2146	379
	Peat	0.19	0.45	-0.02 ± 0.20	0.27 ± 0.05	54 ± 32	0
	Lichen	0.54	2.32	5 ± 4	7 ± 5	1695 ± 1068	284
Si, mmol · kg <sup>-1</sup>	Moss	0.20	0.99	0.003 ± 0.005	0.005 ± 0.007	1.4 ± 0.6	216
	Peat	0.75	11.8*	0.0007 ± 0.0003	0.0024 ± 0.0009	0.26 ± 0.07	379
	Lichen	0.76	12.76*	0.0023 ± 0.0004	0.0035 ± 0.0009	0.97 ± 0.08	379
Na, mmol · kg <sup>-1</sup>	Moss	0.80	15.8*	0.08 ± 0.04	0.11 ± 0.1	32 ± 16	379
	Peat	0.69	8.98*	0.0005 ± 0.0002	0.0036 ± 0.0005	-0.035 ± 0.005	379
	Lichen	0.63	6.67*	0.03 ± 0.02	0.06 ± 0.02	9 ± 1	284
K, mmol · kg <sup>-1</sup>	Moss	0.62	6.53*	0.2 ± 0.2	0.3 ± 0.4	70 ± 49	379
	Peat	0.13	0.6	0.00002 ± 0.00020	-0.0014 ± 0.0004	-0.03 ± 0.05	379
	Lichen	0.34	2.05	0.185 ± 0.005	0.37 ± 0.02	22.5 ± 0.1	97
Ca, mmol · kg <sup>-1</sup>	Moss	0.24	1.27	0.01 ± 0.01	0.01 ± 0.03	3 ± 3	284
	Peat	0.68	8.55*	0.008 ± 0.002	0.019 ± 0.008	0.7 ± 0.2	379
	Lichen	0.85	22.5*	-0.015 ± 0.001	-0.03 ± 0.01	-2.21 ± 0.01	139
Mg, mmol · kg <sup>-1</sup>	Moss	0.34	2.04	0.02 ± 0.02	0.02 ± 0.05	5 ± 7	379
	Peat	0.81	17.2*	0.0005 ± 0.0001	0.002 ± 0.001	-0.45 ± 0.02	379
	Lichen	0.82	18.2*	-0.025 ± 0.003	-0.10 ± 0.02	-1.6 ± 0.1	97
Al, mmol · kg <sup>-1</sup>	Moss	0.48	3.69*	0.0014 ± 0.0005	0.003 ± 0.003	0.14 ± 0.03	97
	Peat	0.91	39.3*	0.00041 ± 0.00003	0.0018 ± 0.0003	0.149 ± 0.007	379
	Lichen	0.99	263*	-0.0014 ± 0.0002	-0.0028 ± 0.0007	-0.223 ± 0.006	379
Fe, mmol · kg <sup>-1</sup>	Moss	0.54	4.63*	0.004 ± 0.002	0.005 ± 0.006	1.4 ± 0.4	284
	Peat	0.91	42.3*	0.00040 ± 0.00004	0.0007 ± 0.0004	0.086 ± 0.009	379
	Lichen	0.85	22.2*	-0.0054 ± 0.0001	-0.0167 ± 0.0005	-0.959 ± 0.007	97

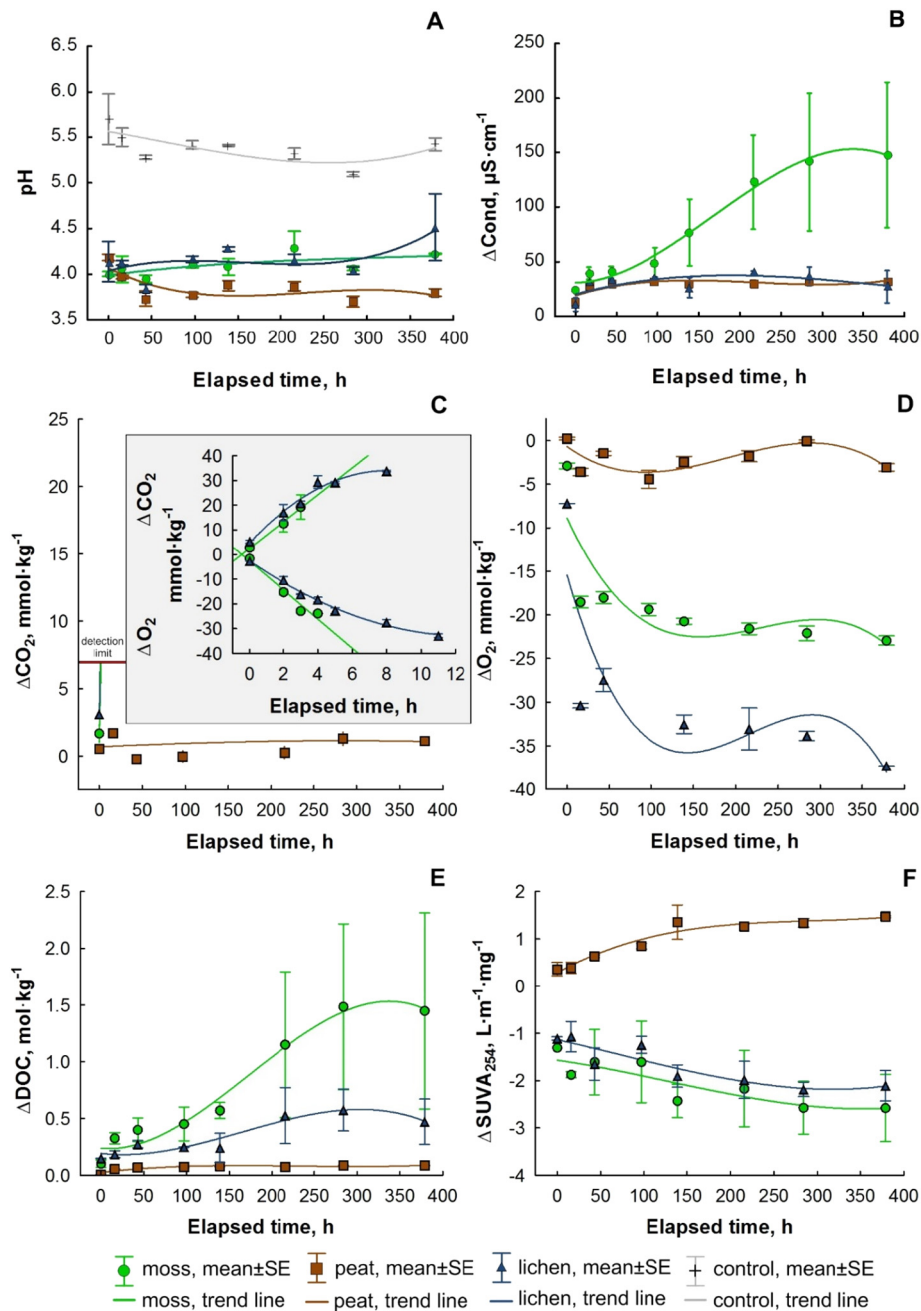
et al., 2015, 2016), photodegradation (although of limited importance, Laurion et al., 2021), and photosynthesis (Tank et al., 2009; Rautio et al., 2011; Przytulska et al., 2016; Bogard et al., 2019; Wauthy and Rautio, 2020). Heterotrophic bacterial and photodegradation of DOM lead to coagulation of Fe, Mn and trace metals and their transfer to lake sediments in the form of particulate OC and metal hydroxides as it is known from laboratory (Oleinikova et al., 2017a, 2017b) and field experiments (Shirokova et al., 2019; Payandi-Rolland et al., 2020b). The second mechanism is nutrient uptake by macrophytes, periphyton, and plankton, whose photosynthesis brings about a pH rise and a pCO<sub>2</sub> decrease in large thermokarst lakes compared to small thaw ponds and depressions as it is known from field observations in thermokarst lakes of the Mackenzie Delta (Squires et al., 2009; Tank et al., 2009). Note here

that the pH increase in the course of lake maturation (Fig. 2A) reflects, from the one hand, the phytoplankton and periphyton photosynthetic activity (Shirokova et al., 2015). From the other hand, lake size increase leads to increasing connectivity with shallow ground water and subsurface waters (Manasypov et al., 2015, 2020). These waters have higher pH due to their reaction with soil mineral horizons and thus can decrease the overall acidity of large thermokarst lakes.

#### 4.2. Behavior of C, nutrient and trace metal in thermokarst lakes after moss, lichen and peat addition in mesocosm experiments

The pattern of aqueous CO<sub>2</sub>, DOC, nutrient and metal concentration in the presence of moss, lichen and peat substrates in the mesocosm

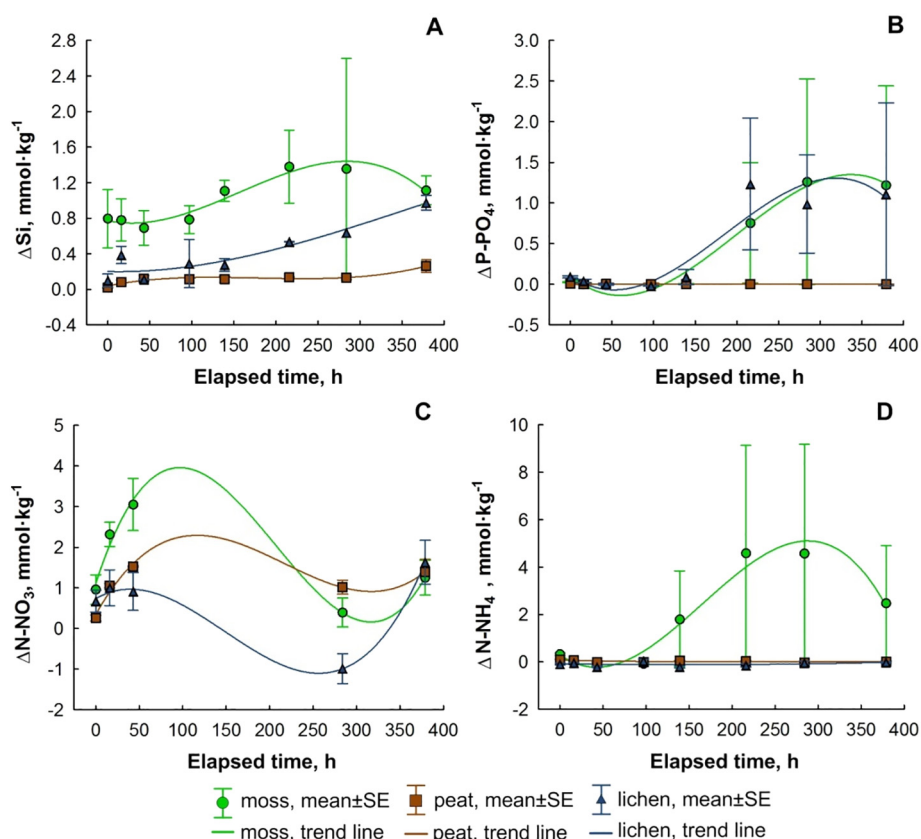




**Fig. 4.** The pH value (A), and the difference between experiment (moss, lichen or peat) and control (lake water without substrate) in Specific Conductivity (B),  $\text{O}_2$  (C),  $\text{pCO}_2$  (D), DOC (E) concentrations and  $\text{SUVA}_{254}$  (F) in mesocosms as a function of exposure time. Here and in other figures below, symbols represent the mean; the error bars correspond to the S.E. of two independent duplicate experiments. Solid lines represent a polynomial fit to the data that was used to calculate the maximal rates and concentration yields.

experiments can serve as an experimental model of thermokarst water body evolution in the natural sequence of peat thawing and lake lateral spreading. The highest  $\text{pCO}_2$  values observed at the very beginning of moss and lichen reaction with lake water (Figs. 4C, S2B, Table 1) are consistent with elevated  $\text{CO}_2$  measured in permafrost thaw subsidence with submerged mosses in this study (i.e., several thousand ppm,  $\times 10$  oversaturated with atmosphere, Fig. 2B). High  $\text{pCO}_2$  in small waterbodies and depressions was also reported in western Siberian (Polishchuk et al., 2018) and NE European (Zabelina et al., 2021) permafrost peatlands. Sizable  $\text{CO}_2$  production by submerged moss and lichen may occur due to both respiration of live bryophytes, fungi and algae and heterotrophic (bacterial) degradation of DOC that was leached from moss and lichen biomass. The response of  $\text{CO}_2$  increase to moss

and lichen addition (1–2 days, Fig. 4C), was much faster than the DOC increase ( $\geq 5$  days, Fig. 4E). This is also reflected in higher values of  $V_{\text{mean}}$  for  $\text{CO}_2$  compared to DOC in the presence of both moss and lichen (Table 1). Such a difference suggests that the respiration of live lichen and moss rather than degradation of biomass is the main driving factor of rapid  $\text{CO}_2$  rise. The  $\text{O}_2$  concentration strongly decreased after first day of reaction with moss and lichen (Figs. 4D; S2A). This indicates that the heterotrophic degradation consuming  $\text{O}_2$  from lake water was the primary cause of partially anoxic conditions in these experiments. It is worth noting that for moss and lichen, the rates of initial (0–24 h)  $\text{O}_2$  decrease ( $7 \pm 1$ ;  $2.7 \pm 0.8 \text{ mmol kg}^{-1}$ ) and  $\text{CO}_2$  increase ( $6 \pm 2$ ;  $4 \pm 1 \text{ mmol kg}^{-1}$ ) were comparable (Fig. 4C, insert). Furthermore, the heterotrophic degradation control on  $\text{O}_2$  level in mesocosms is consistent



**Fig. 5.** Evolution of the difference in Si (A),  $\text{PO}_4$  (B),  $\text{NO}_3$  (C), and  $\text{NH}_4$  (D) concentrations between the mesocosm (moss, lichen or peat) and control in the course of experiments. See Fig. 4 caption for detailed legend.

with higher bacterial number measured in moss and lichen experiment compared to peat experiment (Section 3.2.1). Therefore, results of the present study suggest that the plant-derived “fresh” DOM can be a driven factor of  $\text{CO}_2$  rise, unlike soil refractory DOM. This is consistent with recent mesocosm experiments in a meso-eutrophic lake of the boreal zone (Nydahl et al., 2019). In these experiments, with an addition of colored allochthonous (soil) DOC, there was no relationship between bacterial activities and  $\text{pCO}_2$ .

The sphagnum moss was the most efficient substrate in terms of DOC and  $\text{CO}_2$  production. The reason of higher reactivity of moss compared to lichen is not clear; the higher degradability of moss may be caused by its essentially wet status in natural conditions thus allowing to initiate fast and active heterotrophic bacterial activity, necessary for an enhanced  $\text{CO}_2$  and DOC production. In contrast, in dry lichens and frozen peat, the bacteria were rather dormant and thus not capable to efficiently degrade particulate organic matter at the time scale of mesocosm experiments. Interestingly, that at the end of experiment, corresponding to stable (steady) concentration of aqueous components, the mass-normalized effects of moss exceeded that of lichen and peat by a factor of 2 to 5 (see Tables 1 and S2). In particular, the moss mesocosm yielded the highest level of nutrients, notably  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , K, Fe, Mn, Zn. These nutrients may be potentially limiting for aquatic plankton and periphyton of surface waters from frozen peatlands. Thus, high ammonium concentrations in surface waters derived from decomposition of vegetation are well known for wetland ecosystems (Camargo and Alvaro, 2006). We therefore suggest that, at the beginning of thermokarst development, corresponding to early stages of soil subsidences, the degradation and leaching of mosses rather than that of lichens and peat determine the evolution of C, nutrient and metal concentration in thaw waters of peatlands. In particular, high DOC and  $\text{pCO}_2$  values at the beginning of thermokarst development, observed in the present study of NE European peatlands (Figs. 2B, C; S2B, C) and supported by other observations (Zabelina

et al., 2021 and references therein) are most likely linked to moss, and in a lesser degree, to lichen degradation. Note that the presence of dense *Sphagnum* moss was reported to be the main driver of variation in DOM composition in thermokarst water bodies of the North European permafrost peatlands (Hodgkins et al., 2016).

The finding that frozen peat releases quite low amount of nutrients compared to dominant terrestrial vegetation may have a global significance. It means that in case of permafrost thaw and tundra landscape modification, the primary factor of DOC concentration and  $\text{CO}_2$  emission flux change will be the ground vegetation regime (colonization, flooding, drying), rather than thaw of frozen peat layer and reacting of thawed peat with surface waters. Moreover, given that peat addition is not capable increasing  $\text{pCO}_2$  much higher above that of the control, it is possible that progressive thawing of frozen peat and its reaction with surface fluids might not produce drastic change in  $\text{CO}_2$  emission pattern from inland waters of frozen peatlands. In contrast, the regime of ground vegetation flooding and decay in these wetlands might significantly increase  $\text{CO}_2$  concentration and relevant emission fluxes at the time scale of several days of reaction. The reason for this is that the response of aquatic ecosystem chemical composition and  $\text{CO}_2$  emission to the submerging of mosses is on the order of first hours to first days, which is comparable with the water residence time in local depressions and ephemeral puddles and ponds. This conclusion is at odds with current paradigm that thawing of permafrost will greatly enhance C fluxes in aquatic system, microbial activity, and  $\text{CO}_2$  emission rate (Voigt et al., 2019; Hayes et al., 2014). In case of permafrost peatlands of continental lowlands, the reactivity of frozen peat in aquatic systems will have a subordinate impact on C, nutrient and metal regime in surface waters, compared to lateral expansion or retreat of moss cover and flooding of moss and lichens by surface waters. At the same time, the relative importance of ground vegetation in element delivery to the thermokarst lakes is likely to vary depending on season. Thus, in a recent study of

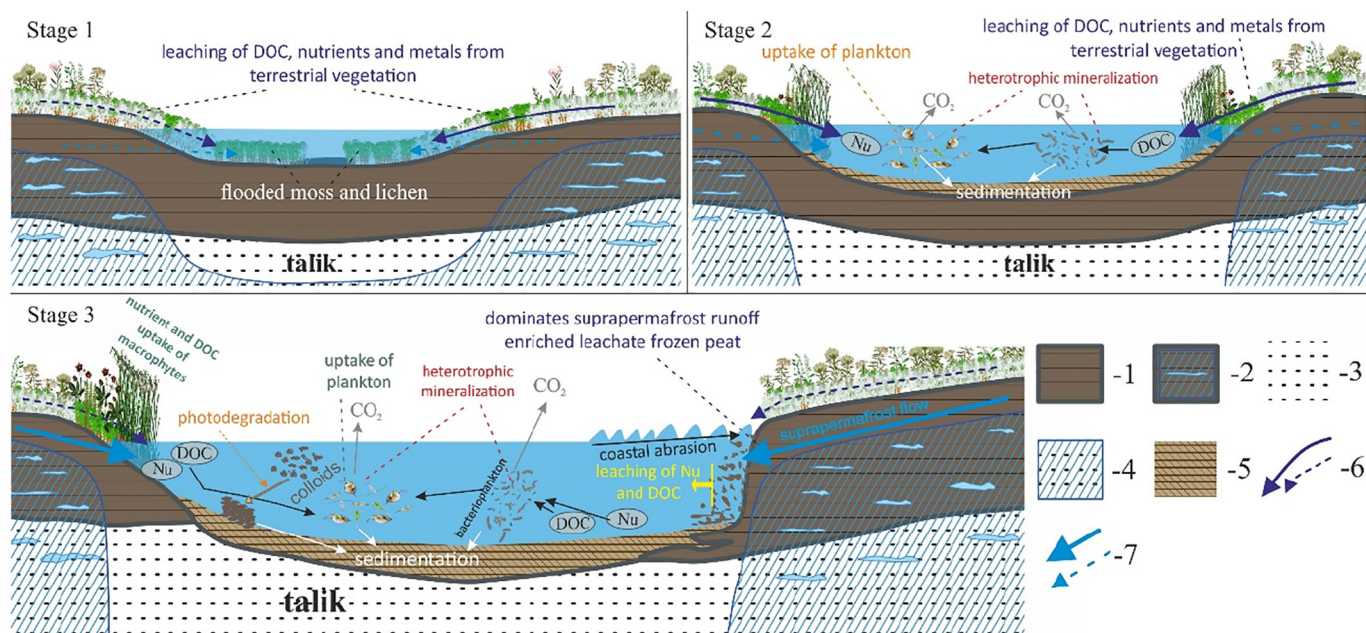
selenium (Se) biogeochemistry in thermokarst lakes of western Siberia (Pokrovsky et al., 2018), we demonstrated that, in addition to direct atmospheric fallout, Se input to the lakes occurs via surface flux over moss and lichen in June (spring) and via supra-permafrost flow in summer and autumn. These mechanisms are fully consistent with those revealed in the present study using mesocosm approach. In particular in spring, Se, together with our trace metals of atmospheric origin, can 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.

The two groups of trace element revealed during addition of various substances to the lake water (Section 3.2.3) can be indicative either of moss (alkalis and alkaline-earth metals, Fe, As, Cu, Ga, Nb, Tl) or peat (Be, V; Ni, Al and trivalent and tetravalent hydrolysates) control on thermokarst lake water chemistry. It is not possible to ascertain specific processes (leaching, adsorption, heterotrophic degradation) controlling these element behavior in the mesocosm experiments without assessing the role of organic and organo-mineral colloids that are likely to control element speciation in surface waters of permafrost peatlands. These mechanisms may include the destabilization of Fe-organic complexes, liberation of ionic Fe (III), its coagulation in the form of Fe oxyhydroxides, and coprecipitation of TE with Fe hydroxides, as it happens in WSL rivers and lakes (Pokrovsky et al., 2016b) and observed in experimental studies of organo-ferric colloids degradation by microbial activity (Oleinikova et al., 2017b). A strong link of trivalent and tetravalent hydrolysates to Fe oxy(hydr)oxides in the form of organo-ferric colloids was already evidenced in the water column and porewater sediments of thermokarst lakes from permafrost peatlands (Pokrovsky et al., 2011; Audry et al., 2011; Shirokova et al., 2013). The elements

exhibiting a concomitant release with DOC are likely to be present as strongly-bound organic species. Typically, these are divalent transition metals ( $Me^{2+}$ ). Their organo-colloidal status is maintained in a wide range of pH and DOC concentrations in thaw ponds and thermokarst lakes of western Siberia (Pokrovsky et al., 2011, 2013, 2016a; Shirokova et al., 2013).

#### 4.3. The role of permafrost thaw and vegetation shift in hydrochemistry of thermokarst lakes subjected to climate warming

Thermokarst development in permafrost peatlands involves lateral spreading of the lake without significant deepening of its basin (Polishchuk et al., 2017; Manasypov et al., 2020). This leads to a decrease of the ratio water volume: border line (perimeter). This was first reported for Arctic tundra by Britton (1957) and later evidenced in western Siberia (Kirpotin et al., 2009, 2011; Audry et al., 2011; Manasypov et al., 2020). Such a decrease yields a concomitant decrease in DOC, conductivity (major cations), Fe, Al, and trace element of the lake water with an increase in the lake size (Pokrovsky et al., 2011, 2013; Shirokova et al., 2013; Manasypov et al., 2014, 2015). Based on results of natural observation in NE Europe and mesocosm experiments, we interpret this trend as due to the dominance of moss and lichen degradation at the beginning of thermokarst lake formation, when small depressions in the moss/lichen cover are filled by water either from thawing of soil ice or of atmospheric origin (stage 1 in Fig. 6). The accumulation of organic and inorganic solutes in the newly-formed depressions triggers DOM, nutrient and metal processing in the water column. This occurs via heterotrophic plankton mineralization and sedimentation to the bottom under the dominance of allochthonous input from



**Fig. 6.** A cartoon of thaw pond and thermokarst lake evolution and the change of sources of DOC and nutrients in the course of evolution, from surface moss and lichen to frozen peat. A three main stage sequence of thermokarst lake formation and development includes: (1) soil depression filled by water which interacted with submerged moss and lichens thus leaching DOM and solutes to the lake; (2) beginning of in-lake processing of DOM via heterotrophic plankton mineralization and sedimentation to the bottom, occurring under the dominance of allochthonous input from vegetation leaching; (3) stage of large mature lake, influenced by nutrients and DOM input from thawed and frozen peat leaching and nutrients and  $CO_2$  uptake by phytoplankton, under on-going DOM, nutrient and metal processing via photo- and biodegradation in the water column.

Legend:

- 1 - Peat of active (unfrozen) layer
- 2 - Frozen peat with ice lenses
- 3 - Unfrozen mineral horizons
- 4 - Frozen mineral horizons
- 5 - Lake sediments
- 6 - Flux of DOC and nutrients that are leached from plant litter
- 7 - Flux of DOC and nutrients that are leached from peat (both active and permafrost layer).

vegetation leaching (stage 2 in Fig. 6). At later stages of lake development, the peat becomes the main supplier of C, nutrient and metal to the water column via suprapermafrost inflow as well as wave abrasion of peat at the lake shore. However, relatively low reactivity of peat (i.e., Payandi-Rolland et al., 2020a and this study) does not allow sufficient accumulation of organic and inorganic components in the lake water column. Instead, mere dilution by atmospheric precipitation and enhanced processing of autochthonous DOM and nutrients (such as photo- and biodegradation and uptake by plankton and periphyton) lead to overall decrease of C, nutrient and metal concentration in large lakes compared to small thaw ponds (stage 3, Fig. 6).

In this study, we hypothesized that peat is an important source of chromophoric DOM (CDOM) and nutrients, whereas a non-aromatic DOM easily available by bacteria may be released from mosses and lichens. As a result, the pattern of CO<sub>2</sub> concentration is determined by a combination of nutrients and DOC delivery from solid source to aqueous phase. This pattern was found to be drastically different between bryophytes (mosses), symbiotic organisms (lichens) and frozen peat. This finding therefore confirms our hypothesis. We further anticipated that progressive change of the ratio of lake water to surrounding organic substrates in the course of lake evolution will produce a systematic change in lake water chemical composition: from moss and lichen degradation control at the beginning of thaw pond formation, at the stage of permafrost subsidence/depression, to coastal peat abrasion and dissolution control at the later stages of lake growth and maturation. At the current state of knowledge, this hypothesis cannot be unambiguously verified, as it requires an estimation of vegetation cover at the small thaw ponds and thermokarst lakes watershed, which is possible only with high-resolution GIS approaches.

According to results of this study, short-term (1–10 years) consequences of climate warming in permafrost peatlands will be mostly pronounced through the change of ground vegetation regime. On a longer perspective (50–100 years), the increase in the active layer depth (currently 1 cm y<sup>-1</sup>, Johansson et al., 2011) will involve much larger amount of peat in water transport within the lake watersheds. This will inevitably increase the relative role of peat in element delivery from the land to the lentic waters of permafrost peatlands. Furthermore, a sizable amount of highly labile C and related elements can be mobilized from currently frozen peat ice into the hydrological network via the suprapermafrost flow (Lim et al., 2021).

Overall, an increase in the active layer thickness, lake water temperature and the duration of unfrozen period due to climate warming should enhance carbon and element leaching from moss, lichen and peat to the thermokarst lakes. However, compared to wave-induced peat abrasion at the lake border, the moss and lichen colonization, submerging and degradation during permafrost thaw and subsidence formation are more important drivers of thermokarst lake water's chemical composition evolution under the on-going environmental changes. Note that this conclusion supports recent findings on very young age of C emitted from permafrost waters which reveals that inland water carbon emissions from permafrost landscapes may be more sensitive to changes in contemporary carbon turnover than the release of pre-aged carbon from thawing permafrost (Dean et al., 2020).

## 5. Concluding remarks

Thawing of frozen peatlands produces depressions, thaw ponds and thermokarst lakes encountered in the NE European discontinuous permafrost zone (Bolshezemelskaya Tundra). There was a systematic decrease in concentrations of dissolved OC, CO<sub>2</sub>, nutrient and metal with an increase in the water body size. In the course of lake maturation (over six order of magnitude increase in the surface area), the pH increased by ca. 3 units while the pCO<sub>2</sub> and DOC concentrations decreased ten-fold. Total P, Ca, Mg increased their concentrations by a factor of 2 to 3, whereas Si, Fe, Al, NO<sub>3</sub> decreased concentrations with lake size

increase. We interpret these changes as due to a combination of external factors (delivery of solutes from lake watershed) and DOM, nutrient and metal processing in the water column.

Mesocosm experiments on thermokarst lake water in the presence of frozen peat, moss and lichen demonstrated that moss and lichen leaching and degradation, rather than peat abrasion, act as a main driver of thermokarst lake water's evolution. The mass-normalized release of DOC, macro nutrients (Si, N, P), major elements (K, Na, Ca, Mg), micronutrients and trace metals (Fe, Mn, Cu, As, Rb, Cs, Tl) was controlled essentially by moss and, in a lesser degree, lichen with almost negligible impact of peat. When comparing to natural sequence of lakes and ponds chemical composition, these mesocosm experiments allowed to characterize the water chemistry during the first step of thaw pond formation, when the moss leaching determines the hydrochemical features of surface water. Upon progressive increase in the lake size, the lichen and moss leaching at the watershed surface become less important than the delivery of peat leaching products by the suprapermafrost flow. This happens due to an increase in the ratio of lake circumference to the lake volume which decreased the delivery of external terrestrial (allochthonous) material. In contrast, when lake water volume increases, the relative role of autochthonous processes of DOM, nutrient and metal transformation, such as photo- and bio-degradation, and phytoplankton/periphyton activity also increase. This leads to gradual removal of DOC, nutrients and metals due to C emission to atmosphere and element deposition to the lake bottom.

Because moss leaching is likely to be most important process controlling hydrochemistry of dissolved elements and CO<sub>2</sub> emission/burial pattern in thermokarst water bodies, the response of the moss coverage regime to permafrost thaw and climate warming in NE European frozen peatlands will chiefly define the DOC and nutrient cycling in lentic waters and CO<sub>2</sub> emission fluxes. Given that the vegetation biomass leaching reactions are very fast, on the order of first hours to days, the hydrological pattern of moss and lichen flooding rather than biogeochemical reactions within the peat soil profile will be controlling short-term response of peat tundra landscapes to permafrost thaw and temperature rise. This contrasts a dominant view that thawing of frozen peat provides the main contribution to the negative feedback of environmental response to the climate change. At least on a short-term scale, the peat thaw may be a subordinate factor of biogeochemical C fluxes compared to the change of wetting and flooding regime of the lake shoreline and moss persistence/growth on the tundra surface.

## CRediT authorship contribution statement

L.S. Shirokova, I.S. Ivanova, S.A. Zabelina and N.S. Shutskiy performed sampling and field mesocosms; A.V. Chupakov performed sampling and data treatment; O. Moreva analyzed and interpreted nutrient concentrations; S.V. Loiko contributed to analytical results and their interpretation, and O. S. Pokrovsky provided supervision and placed this work in the context of current knowledge of DOM in thermokarst lakes. Each co-author has seen and approved the final paper and contributed to writing the manuscript.

## Declaration of competing interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.146737>.

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