



Dispersed ice of permafrost peatlands represents an important source of labile carboxylic acids, nutrients and metals

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ABSTRACT

Thawing of frozen organic and mineral soils and liberation of organic carbon (OC), macro- and micro-nutrients and trace elements from pore ice in high latitude regions represent a potentially important but poorly quantified retroactive linkage to climate warming. This is especially true for permafrost peatlands, occupying a sizable proportion of all permafrost territories and presenting a large and highly vulnerable stock of soil OC which can be subjected to fast thawing at currently circum-zero temperatures. The conventional method of assessing the labile water-soluble fraction of permafrost soils is aqueous extraction from dried soil. However, this technique does not allow collecting native ice present in soil pores and is therefore likely to underestimate or overestimate the pool of labile soil C and nutrients. Here, we present results of direct pore ice analyses performed on native peat cores from the western Siberia Lowland in comparison to the water extraction (10 and 100 g_{dry peat} L⁻¹) of soluble components from the same peat subjected to freeze drying. Aqueous leachates of permafrost peat from both thawed (0–45 cm) and frozen (45–130 cm) layers yielded high concentrations of DOC, nutrients, carboxylic acids and trace metals, comparable or higher to those in peat porewater and dispersed peat ice. We found strong (a factor of 3 to 30) enrichment in the frozen part of the core (below 45 cm, which is active layer depth) in dissolved OC, many carboxylates (acetate, formate, lactate, butyrate, propionate, pyruvate), inorganic nutrients (Si, P, N) and trace elements (Fe, Al, Mn, Zn, Sr and Ba). The dispersed ice which is present in peat below active layer represents highly labile reservoir of organic and inorganic nutrients which should be considered in permafrost thaw scenarios.

1. Introduction

Arctic soils have been the focus of extensive works on C storage and transport due to their role as the largest organic carbon (OC) reservoirs for the terrestrial biosphere (Tarnocai et al., 2009; Schuur et al., 2013). Carbon and nutrient export via lateral pathways, from soils to streams (and ultimately to coastal ocean) is one of the major factors in destabilization of previously sequestered C in permafrost soils (Wieder et al., 2019; Turetsky et al., 2020; O'Donnell et al., 2021). This is especially important for permafrost peatlands located within transitioning sporadic-discontinuous-continuous permafrost zone, such as the western Siberia Lowland (WSL) which includes 1.05 million km² impacted by permafrost. This region exhibits circum-zero temperatures of frozen peat

(Romanovsky et al., 2010; Anisimov and Zimov, 2020) and is highly vulnerable to climate warming (Fewster et al., 2022). The permafrost peatlands acted as important sink for atmospheric CO₂ over millennia timescales but are currently being recognized as a sizable source of C [both CO₂ and CH₄] emissions from inland water surfaces to the atmosphere (Karlssohn et al., 2021) and a riverine exporter of dissolved organic and inorganic carbon (DOC and DIC, respectively) (Frey and Smith, 2005; Frey et al., 2007; Pokrovsky et al., 2020). Although the areal (km²-scale) export of organic carbon and macro- and micro-nutrients from land to ocean in the WSL was measured (Pokrovsky et al., 2015; Pokrovsky et al., 2016; Pokrovsky et al., 2020), the local soil-column scale yield of soluble C and nutrients remains poorly quantified. The importance of seasonal ground ice as a source of water for the

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surrounding landscape is fairly well known from hydrological studies (van Huizen et al., 2020). Thus, Nitzbon et al. (2020) indicated a need to study chemistry of soil ice in ice-rich permafrost of Siberia, which is likely to exhibit fast thaw and which is highly susceptible to thermokarst. However, very few studies have addressed the role of permafrost peat ice as a potential source for organic and inorganic solutes for surrounding freshwaters (Thompson et al., 2015).

Given that more than half the peat deposits in the WSL are currently frozen, and this frozen peat may turn out to be highly reactive upon thawing, there is need to study the capacity of peat soil in delivering solutes to the hydrological network. However, in contrast to a relatively good understanding of the leachability of frozen mineral soils (Fouché et al., 2020 and references therein), experimental assessment of the reactivity of permafrost peat in aqueous solution is only in initial stages (Payandi-Rolland et al., 2020). A significant obstacle in quantifying the capacity of frozen peat solute delivery to surface fluids is the presence of dispersed ice within the pores (Fu et al., 2022). Field measurements across a permafrost gradient in western Siberia demonstrate that, relative to peat porewater from the active (thawed) layer (typically 0–45 cm depth), peat permafrost ice (below 45–60 cm depth) is strongly enriched in DOC, macro-nutrients (Si, P, Ca) and dissolved organic matter (DOM)-bound metals (Lim et al., 2021). These compounds can be readily mobilized to the hydrological network and can provide sizable contributions to riverine export fluxes of chemical elements. In order to up-scale the information obtained from several peat cores to the large territories of permafrost peatlands, field measurements of original peat ice are needed which would prove extremely time and resource consuming. In this regard, there is a clear need for developing a method of assessing the potential of frozen peat in delivery of soluble organic matter, macro- and micro-nutrients upon thawing and contact with surface waters.

Conventional methods of studying soil labile components use aqueous leachates from oven-dried or freeze-dried soils (Jones and Willett, 2006; Shamrikova et al., 2015; Fouché et al., 2020). However, optimal conditions for aqueous extraction (notably the solid:solution ratio) are not well defined and direct verification using field-collected cores is required (Thompson et al., 2015). Here we compared the chemical composition of dissolved (<0.45 μm) components in peat porewater (thawed horizons) and ice (frozen horizons) collected in the discontinuous permafrost zone of the WSL with that of aqueous leachates prepared from freeze-dried peat samples of the same core. As a prerequisite to address the organic compounds in the permafrost ice, we developed methodological aspects of solute extraction from both intact field-frozen peat cores and from freeze-dried material. We further complemented these methods by thorough analysis of inorganic solutes (major and trace elements) to compare with the existing data on elementary composition of permafrost peat fluids and dispersed ice and to develop most optimal procedure for laboratory assessment of leachable stock organic and inorganic macro- and micronutrients in the peat samples from permafrost regions. The novelty of this method, as compared to previous works on peat ice (Lim et al., 2021, 2022a) and peat porewaters (Raudina et al., 2017, 2021), is that it utilizes both native and laboratory-dried peat cores and measurements on previously unassessed carboxylic acids in order to i) characterize the nature of DOM in the peat ice and porewaters, and ii) use this information to assess the capacity of permafrost peatlands to deliver bioavailable organic nutrients to the hydrological network.

2. Study site and methods

2.1. Geographical setting and in-field soil water and ice sampling techniques

Three identical peat cores (0–130 cm, which included only organic layers (>90 % OC) above the mineral horizon) were sampled from the same mound of frozen palsa peatbog in the western Siberia Lowland in

the northern taiga of the sporadic permafrost zone (Khanymey Research station) in mid-August 2018 (Fig. 1). The frozen soil at the peat mound is classified as an Epifibric Endocryic Histosol (IUSS WRB, 2014). Peat thickness is 130 ± 10 cm and it is underlain by a sandy deposit of lacustrine and aeolian origin (Loiko et al., 2019). At this study site, the active layer has maximum thickness of 55–60 cm by early October (Lim et al., 2021), but during the period of sampling, the thawed layer was between 0 and 45 cm. Therefore, throughout this work, we define the thawed layer as 0–45 cm and frozen layer as 45–130 cm. The peat is essentially composed of mosses (*Sphagnum magellanicum*, *Sphagnum angustifolium*, *Sphagnum warnstrorfii* and *Bryidae*) and lichens with smaller amounts of wood and dwarf shrub debris (<10 %) observed at depths of 75 and 125 cm as detailed in Table S1 of the Supplement.

Cores were extracted using a Russian peat borer with a 4 cm diameter following the technique modified according to Shary et al. (2018). Two cores were cut into 13 slices and transported while in the frozen state (-18 °C) to the laboratory for freeze-drying. A third core was processed on-site to collect pore water and ice. For this collection, we followed procedures elaborated in Lim et al. (2021) and Ewing et al. (2015a, Ewing et al., 2015b) for this and similar sites. It should be noted that previous works in permafrost regions of western Siberia demonstrated good agreement between field replicates of the chemical composition of peat porewaters (Rausina et al., 2017, 2021) and permafrost ice (Lim et al., 2021, 2022) when the peat core was sampled at the frozen mound similar to the present study. For peat ice, the frozen peat core was cut into 10-cm layers using a pre-cleaned ceramic blade and thawed at room temperature. Immediately after full thaw of the frozen core, peat water was extracted through 100- μm pre-cleaned Nylon net by applying a local confining pressure (1–5 kg cm^{-2} , dependent on sample humidity). Obtained slurry was immediately centrifuged for 15 min at 3000 g and the supernatant was filtered through a 0.45 μm acetate cellulose filter with the first 10 mL of filtrate discarded. Water from the thawed part of the peat core (native porewater), above the permafrost table, was extracted using the same method immediately after peat sampling. Because the peat in the active layer is highly saturated with water, we could collect sufficient amount of porewater for all samples. The ice content in permafrost peat layers was quantified by measuring the difference between weight of a subsample (126 cm^3) of the frozen core and its weight after fully drying in an oven (for 2 days at 105 °C).

2.2. Leaching of solutes from freeze-dried peat in the laboratory

Peat leachates were prepared using 10-cm slices of thawed (0–45 cm) or frozen (45–130 cm) peat horizon. For this, freeze-dried powder was homogenized via gentle disaggregation and reacted at 10 and 100 $\text{g}_{\text{peat}} \text{L}^{-1}$ with Milli-Q water in a sterile pre-cleaned HDPE bottle under gentle stirring (ping-pong shaker at 150 rpm) over 24 h at 5 °C. The choice of 10 and 100 g L^{-1} peat concentration was a compromise between sufficient amount of water, necessary for analyses, and sufficient concentration of solutes, at rather limited amount of peat available for replicate experiments. Note that the high water uptake by studied dry peat did not allow using a solid:solution ratio of 1:5 which is recommended for mineral soils (Jones and Willett, 2006; Thompson et al., 2015). In fact, complete hygroscopic absorbance of water by dry peat did not allow extraction of a sufficient amount of fluid for analyses. Experimental conditions used in this study (duration of leaching, stirring and temperature regime) were optimized following previous methods for DOC release from the peat of permafrost regions (Payandi-Rolland et al., 2020; Lim et al., 2022b). All leaching experiments were performed in triplicates. For this, the 10-cm slice of each core was divided in two parts, to obtain 10 and 100 $\text{g}_{\text{peat}} \text{L}^{-1}$ suspensions which were placed in three independent vials; after sampling, each vial was entirely sacrificed for analyses. Obtained solution was centrifuged (3000 g during 15 min), filtered through a sterile single-used Sartorius filtration unit (0.22 μm) and stored in the refrigerator or immediately frozen prior to analyses.

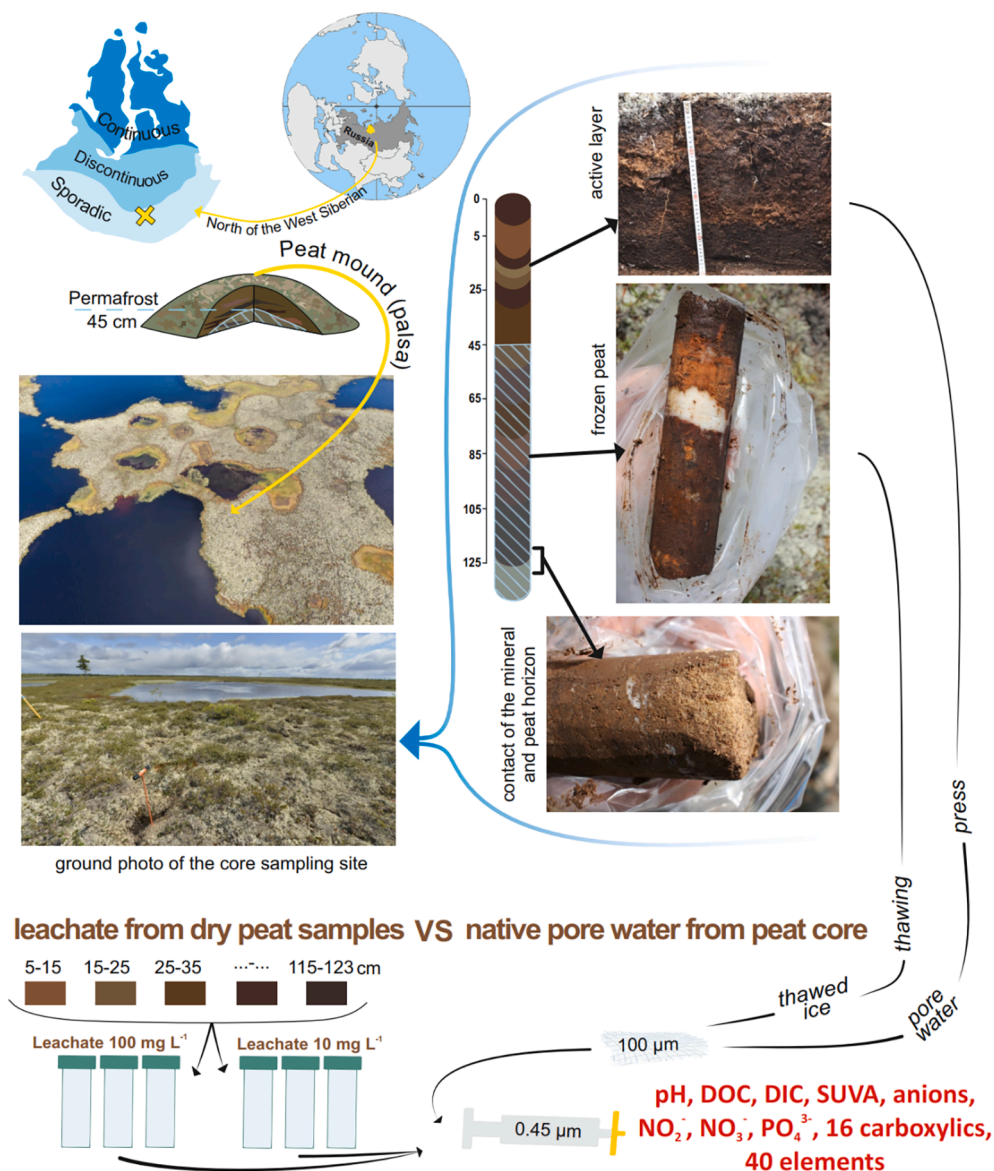


Fig. 1. Map of the studied region, core sampling site, thawed and frozen peat horizons and scheme of experimental and analytical techniques.

2.3. Chemical analyses

Filtered samples were preserved in refrigeration during the month prior to the analysis. Each fraction of filtrate ($<0.45 \mu\text{m}$) was subdivided into two parts: 1) the non-acidified for DOC, DIC and anion analyses, and 1) the acidified (1 % ultrapure double-distilled HNO_3) for trace element analyses. The samples for carboxylic acid analysis were immediately frozen at -20°C . Ultraviolet and visual absorbance of non-acidified filtered and ultrafiltered samples was measured between 200 and 700 nm using a 10-mm quartz cuvette on an Eppendorf BioSpectrometer following the approaches developed in Ilina et al. (2014), Weishaar et al. (2003), and Payandi-Rolland et al. (2021). These allowed for assessment of spectral slopes ($S_{290-350}$, $S_{275-295}$, $S_{350-400}$), the slope ratio (S_R), useful for approximating the molecular weight of DOM and the degree of its aromaticity. The relative amount of aromatic compounds was assessed via specific UV absorbance (SUVA_{254}). The Weight-Average Molecular Weight index of DOM (WAMW), which reflects the degree of polymerization (Helms et al., 2008), was quantified using the absorbance at 280 nm (Chin et al., 1994). Finally, the humification index was characterized using the ratio of absorbance at 250 and 400 nm (the E2:E4 ratio, Park et al., 1999).

The pH was measured with an uncertainty of ± 0.02 pH units. DOC was analyzed using a Carbon Total Analyzer (Shimadzu TOC VSCN) with an uncertainty better than 3 % and detection limit of 0.1 mg L^{-1} . Fifteen carboxylic acids (quininate, lactate, acetate, propionate, formate, butyrate, galacturonate, glutarate, malate, tartrate, maleate, oxalate, fumarate, phthalate and citrate) and main inorganic anions (F^- , Br^- , Cl^- , SO_4^{2-} , NO_3^- , NO_2^- and PO_4^{3-}) were measured by high-performance ionic chromatography (Dionex Ics-5000 +) with an uncertainty of 2 %. We used an in-house standard for organic acid analysis and two ISO standards (ISO 10304-1 and ISO 10304-2) for inorganic anion analysis. The certified reference materials Ion-915 and Ion-964 were used to verify the accuracy of analyses; the reference material measured concentrations were within 10 % of the certified values. Quantification limits were equal to 0.05 mg L^{-1} for Cl^- , 0.001 mg L^{-1} for F^- , Br^- , PO_4^{3-} , 0.01 mg L^{-1} for NO_3^- , SO_4^{2-} and 0.002 mg L^{-1} for quininate, lactate, acetate, propionate, formate, butyrate, galacturonate, glutarate, malate, tartrate, maleate, oxalate, fumarate, phthalate and citrate.

Details of trace element analyses in DOC-rich waters of western Siberia can be found in Lim et al. (2022b). Major (Ca, Mg, Na, K, Si), and ~ 30 trace elements were determined with an Agilent iCap Triple Quad (TQ) ICP MS using both Ar and He modes to diminish the interferences.

About 3 $\mu\text{g/L}$ of In and Re were added as internal standards and we used 3 various external standards. The detection limits for trace elements were determined as 3x blank concentrations. The typical uncertainty for elemental concentration measurements ranged from 5 to 10 % at 1–1000 $\mu\text{g L}^{-1}$ to 10–20 % at 0.001–0.1 $\mu\text{g L}^{-1}$. The MilliQ field blanks were collected and processed to monitor for any potential sample contamination introduced by sampling and/or handling procedures. The SLRS-6 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check accuracy and reproducibility for each analysis (Yeghicheyan et al., 2019). Only those elements that exhibited good agreement between replicated measurements of SLRS-5 and the certified values (relative difference < 15 %) have been reported in this study.

3. Results

3.1. Vertical pattern of pH, specific conductivity, DOC, optical properties and organic acids

The pH values remained quite stable over the full depth of the peat core for both native porewaters and peat ice and experimental leachates. It was close to 4 and virtually indistinguishable for native and 100 g L^{-1} leachate and about one unit higher for 10 g L^{-1} leachate (Fig. 2 A). Specific conductivity slightly increased down the peat core (Fig. 2 B). The DOC concentration was sizably higher in the frozen part of the core compared to the thawed part reaching 1000 mg L^{-1} for native peat ice and 200 mg L^{-1} for laboratory leachates (Fig. 2 C). Among inorganic anions, F^- , Br^- , PO_4^{3-} and NO_2^- exhibited strong enrichment (by a factor of 3 to 20) below the active layer whereas Cl^- , SO_4^{2-} and NO_3^- demonstrated only slight enrichment (<3 times) below the active layer in both native core and experimental leachates (Fig. S1 of the Supplement).

Most organic anions demonstrated strong enrichment in the frozen layer compared to the thawed layer as illustrated in Fig. 3 for acetate, propionate, formate, lactate, butyrate, pyruvate, galacturonate, and glutarate. Overall, in native peat ice core, we observed very high concentrations of butyrate (up to 150 mg L^{-1}), acetate, sulphate, propionate (10–40 mg L^{-1}), phosphate, lactate, citrate, glutarate, pyruvate, formate, and galacturonate (1–8 mg L^{-1}) as illustrated in Fig. S2 of the Supplement. Maleate and oxalate were detected only in the frozen part of the

peat core (Fig. S3 A, B); phthalate exhibited a single maximum (>10 times quantification limit) at the border of the active-frozen layer, at 45 cm depth (Fig. S3 C), and citrate did not exhibit any systematic variations in concentration with depth in experimental leachates but decreased twofold between the thawed and frozen layer (Fig. S3 D of the Supplement).

Although the concentrations of most organic anions gradually or abruptly (below active layer thickness, ALT) increased down the peat core, we noted local maxima at 80–95 cm depths for fluoride, acetate, propionate, formate, butyrate, pyruvate, lactate, galacturonate, glutarate, nitrite, nitrate, phosphate and DOC. This maximum was more strongly pronounced in natural peat cores compared to experimental leachates.

The optical properties of DOM in the peat porewater and ice and in the experimental leachates exhibited a generally similar pattern (Fig. S4 of the Supplement). The SUVA_{254} , normalized molecular weight (WAMW), molar absorptivity, and aromaticity increased from the surface to the bottom of the thawed layer and remained essentially constant in the deep horizons of the frozen layer (65–125 cm), Fig. S4 A–D of the Supplement. Other optical parameters of the fluids (E_{254}/E_{436} , E_{280}/E_{350}) also showed gradual increase from the surface to the bottom of the active layer (5–45 cm) followed by rather constant vertical patterns in the frozen part of the peat core (Fig. S4 E, F of the Supplement). Finally, we measured an increase in spectral slope $S_{290-350}$, $S_{275-295}$ and $S_{350-400}$ values between the thawed and frozen horizons (Fig. S4 G–I of the Supplement).

3.2. Distribution of major and trace elements

According to vertical concentration patterns of major and trace elements, two main groups in peat core fluids and leachates were distinguished. The first group is represented by alkaline (Li, Na, Cs), alkaline-earth metals (Be, Mg, Ca, Sr, Ba), macro- (Si, P) and micro-nutrients (V, Mn, Fe, Co, Ni, Zn, Se), and insoluble lithogenic hydrolysates (Al, Ga). These essentially biogenic (except Li, Be, Al, Ga and Cs) elements exhibited an abrupt increase (by a factor of 3 to 10) in concentration between the thawed and the frozen layers, as illustrated in Fig. 4 A–E. The second group of elements did not show sizable variation in concentrations over the depth of the peat core and included macro- and

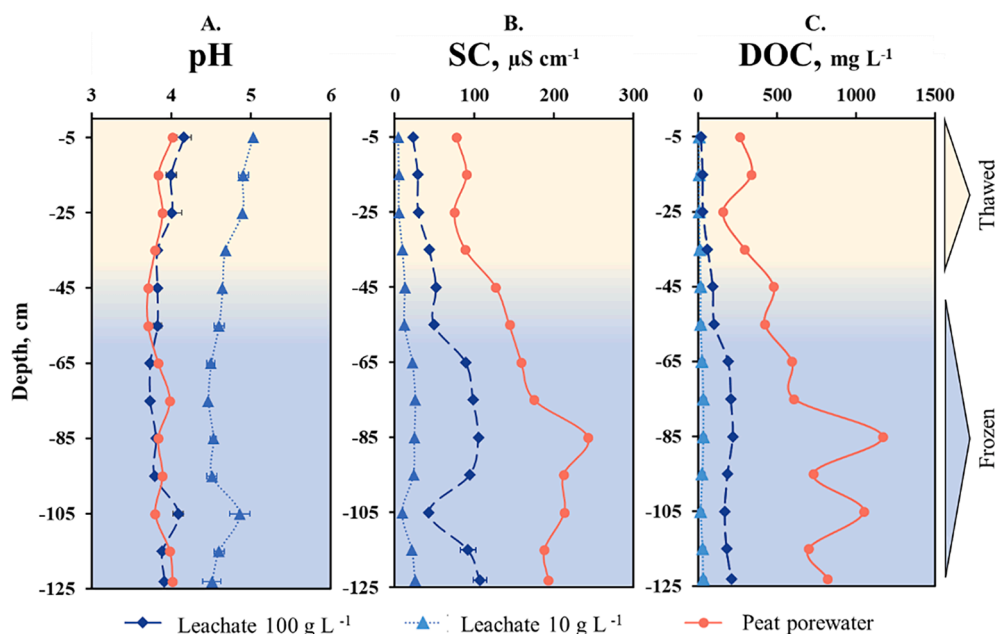


Fig. 2. Major characteristics of native peat porewaters (thawed and frozen layers) and two laboratory aqueous leachates: pH (A), Specific Conductivity (B) and DOC (C). Horizontal error bars correspond to s.d. of triplicates unless within the symbol size.

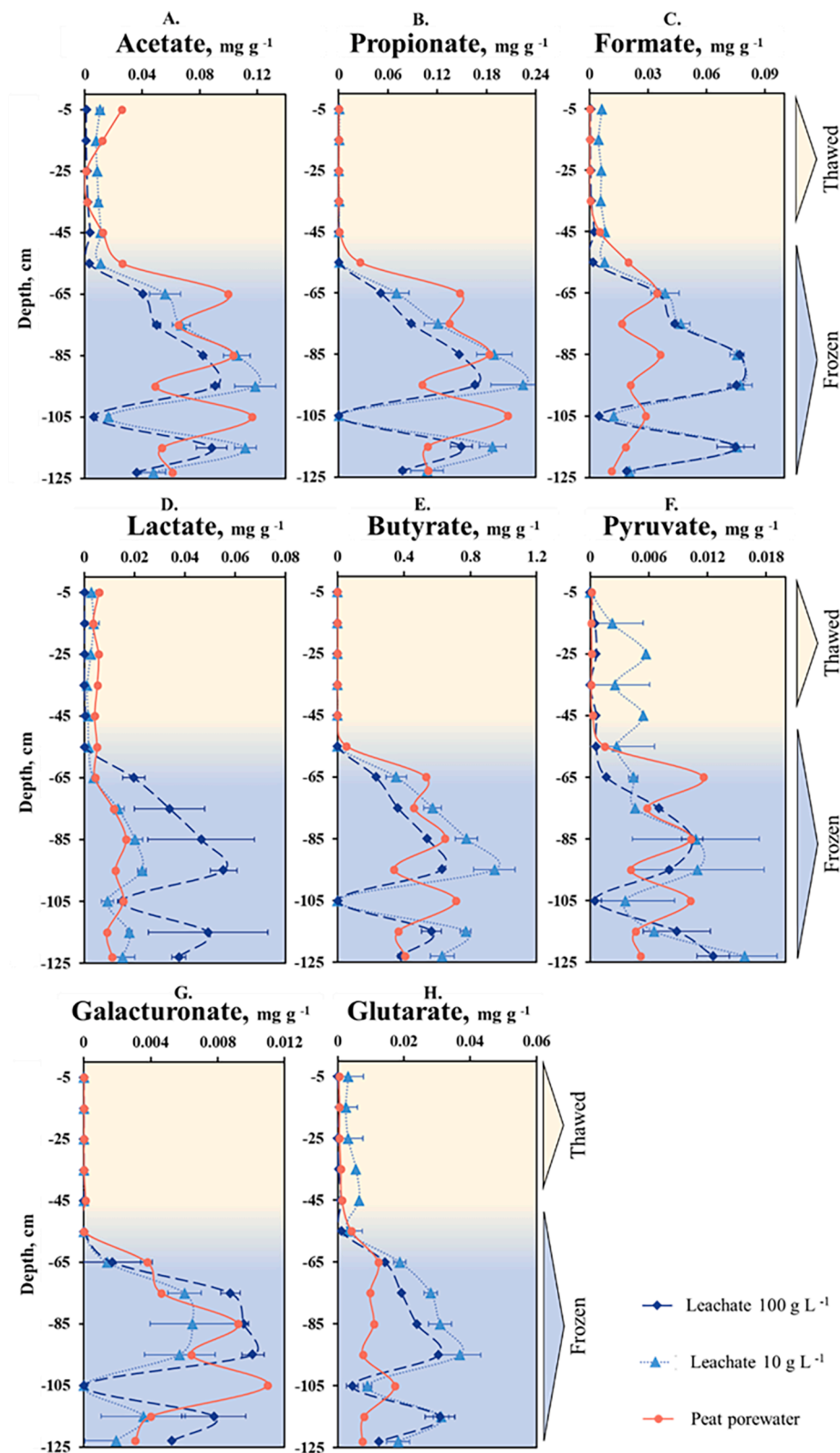


Fig. 3. Peat-mass normalized concentrations of organic ligands in native peat porewaters (thawed and frozen layers) and two laboratory aqueous leachates. Horizontal error bars correspond to s.d. of triplicates unless within the symbol size.

micronutrients (B, K, Rb, Cu, Mo) and essentially lithogenic elements or geochemical traces (Ti, Cr, Y, Zr, Nb, Cd, Sb, REEs, Hf, Tl, W, Th and U), as illustrated in Fig. 5. These two groups were generally similar in stable vertical concentration pattern for both native peat porewater/ice and experimental leachates.

3.3. The difference in solute concentration between frozen and thawed parts of the peat core

The averaged (over several horizons) peat mass-normalized concentrations of solute in thawed (0–45 cm) and frozen (45–130 cm) parts

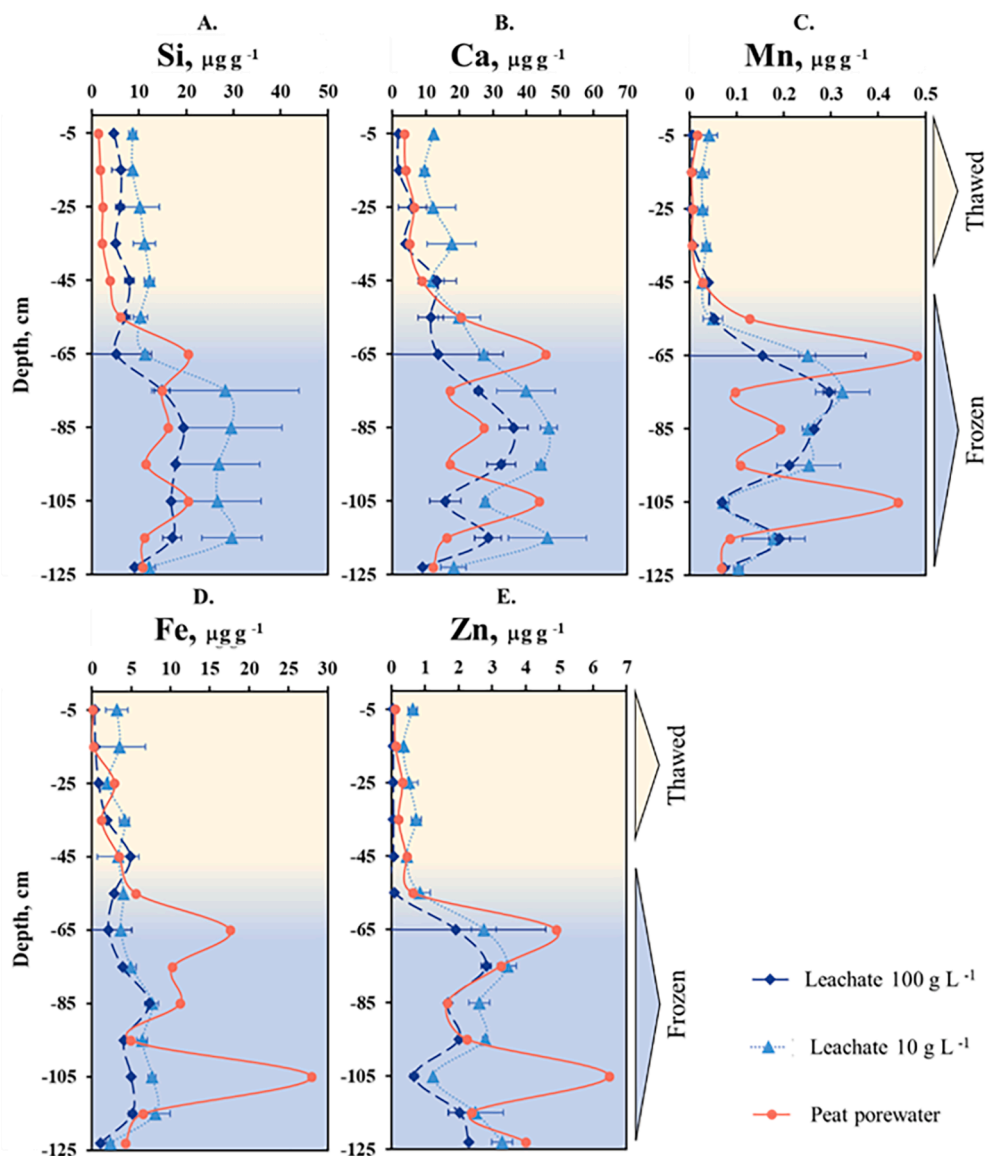


Fig. 4. Peat-mass normalized concentrations of major (Si, A; Ca, B) and trace (Mn, C; Fe, D; Zn, E) element in native peat porewaters (thawed and frozen layers) and two laboratory aqueous leachates. These elements exhibited an abrupt increase in concentration below the thawed layer, detectable in both natural porewaters/ice and aqueous leachates from freeze-dried peat. Horizontal error bars correspond to s.d. of triplicates unless within the symbol size.

of the peat core are listed in [Table S2](#) of the Supplement. Note that the transition frozen/unfrozen zone was the same (± 5 cm) between the three cores. In both native peat core and 100 g/L aqueous leachate, the frozen horizon was sizably enriched (relative to the thawed layer) in alkaline and alkaline-earth metals (Li, Na, Cs, Mg, Ca, Sr, Ba), macronutrients (Si, P), micronutrients (Mn, Co, Fe, Se), and some toxicants (Al, Ga, As, Cd, Tl). The difference between the two layers was much less pronounced or insignificant for K and Rb (essentially surface enrichment), oxyanions and neutral species (B, Cr, V, Sb, Mo, W), DOM-complexed metals (Ni, Cu, and Pb), and low-mobile hydrolysates (Ti, Zr, Hf, Th, Y, REEs, Bi) and U.

To illustrate these differences, we plotted the ratio of mean concentration (normalized to g_{peat}) in the frozen part of the peat core to the mean concentration in the thawed part of the core separately for native samples and laboratory aqueous extracts ([Fig. 6](#)). Despite sizable uncertainties (due to spatial variations in component concentration among several sampled horizons and experimental reproducibility of duplicates), the overwhelming majority of solutes exhibited ratios above 1. Butyrate is enriched by a factor of 1500 to 3000, and propionate – by a factor of 800 in the frozen part of the peat core relative the active layer.

Among organic anions, lactate and glutarate were enriched in the peat leachate by a factor of 180 and 60, respectively, whereas the acetate, formate, pyruvate, galacturonate, exhibited ratios between 5 and 50 for both the field samples and laboratory leachates ([Fig. 6 A](#)). Inorganic anions including nutrients such as PO_4^{3-} , NO_3^- were also enriched in the frozen part of the peat core (between 2 and 8 times in leachates), whereas F- was 40–60 times more concentrated in the peat ice below 45 cm depth compared to the active layer.

Ratios were generally lower for major and trace elements typically ranging between 2 and 10 ([Fig. 6 B](#)) for macro-nutrients (Si, P), cations (Na, Mg, Ca, Sr, Ba), micro-nutrients (Fe, V, Co, Ni, Ba), some oxyanion (As), and ‘light’ lithogenic elements such as Al. Manganese and zinc exhibited the strongest enrichment in the frozen layer (a factor of 15 to 30). This ratio however, was much lower with ranges between 0.5 and 2 for some oxyanions and toxicants (B, Se, Mo, Sb, W, Cu, Pb), alkalis (K, Rb, Cs) as well as lithogenic low mobile elements (Ti, Cr, Y, Zr, Nb, REEs, Hf, Th) and U.

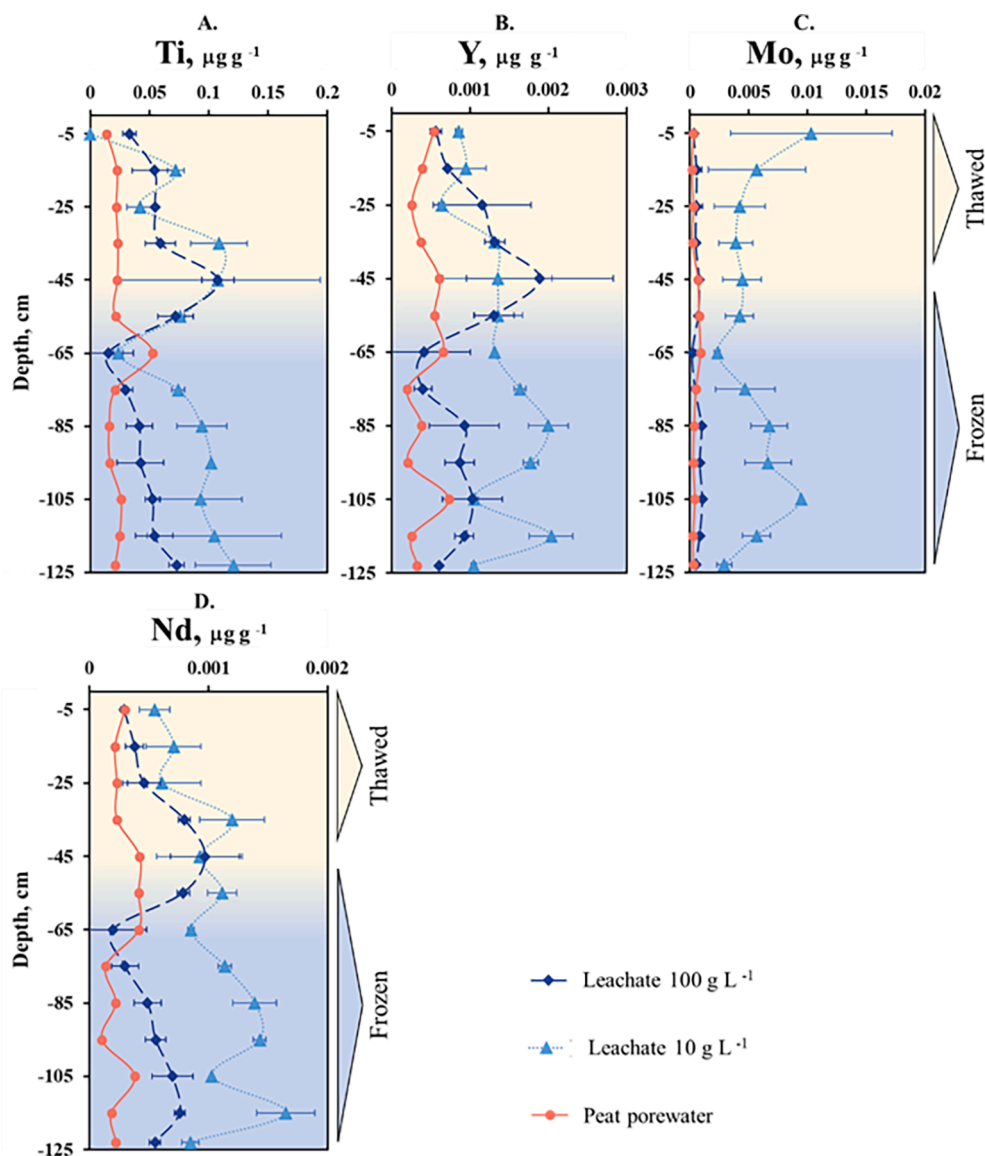


Fig. 5. Examples of peat-mass normalized concentrations of trace element which did not demonstrate sizable differences in concentration between the thawed and the frozen layer, in native peat porewaters and laboratory aqueous leachates. Horizontal error bars correspond to s.d. of triplicates unless within the symbol size.

3.4. Comparison of laboratory leachates with native peat porewaters and ice

The laboratory extractions of 100 g/L demonstrated reasonable agreement (<30 % difference) with native peat porewater and ice in terms of pH, aromaticity, and aqueous concentrations of DOC, F, PO₄, Cl (ice only), SO₄, quinate (ice only), acetate, propionate, formate, butyrate, galacturonate, glutarate, citrate, a number of major (Na, Si, Ca, P_{tot}, Mg, K) and trace (Al, V, Mn, Fe, Zn, Sr, Ni, Ba, REE, Se, Cs, Y, Cd, Rb, Ga, Nb) elements.

However, the analysis of peat mass-normalized yields of solutes in two experimental leachates (10 and 100 g_{peat} L⁻¹) revealed distinct differences in element behavior among different treatments (see Table S2 of the Supplement). The first group of components exhibited similar ($p < 0.01$) yields for both experimental conditions and included acetate, lactate, formate, butyrate, propionate, puryvate, galacturonate, glutarate, fumarate, phthalate, F, DOC, Mg, Al, Si, P, Ca, Ti, V, Mn, Fe, Zn, Ga, As, Sr, Y, Zr, Cs, Ba, medium and heavy REE, Th and U. Presumably, the release of these components was driven by bulk dissolution of peat particles, independent of the pH of aqueous solution. It should be noted that pH was one unit higher in 10 g_{peat} L⁻¹ extracts compared to other

treatments (Fig. 2 A). The elements of the second group were released 2 to 3 times more efficiently in experiments at 10 g_{peat} L⁻¹ compared to those at 100 g_{peat} L⁻¹ and included Cl, SO₄, NO₃, quinate, Li, B, Na, K, Cr, Co, Ni, Cu, Rb, Mo, Cd, Sb, Ce, W and Pb. It is possible that their mobilization to solution from the peat was, at least partially, controlled by desorption processes. The majority of these components are known to be present in the anionic form or as negatively-charged organic complexes (Lim et al., 2022a). Given the difference in pH between the two treatments (4.0 ± 0.1 and 4.95 ± 0.15 for 10 and 100 g_{peat} L⁻¹, respectively), we hypothesize that the higher pH value in the 10 g_{peat} L⁻¹ treatment is responsible for stronger desorption of the anions from the peat surfaces. In fact, it has been documented that a strong increase in negative charge of peat occurs between pH = 4 and 5 (Forsberg and Aldén, 1988).

Regardless of these differences in component yield between different laboratory treatments, the results of the present study demonstrate the highest similarity in the largest number of component yields between native peat porewater/ice and laboratory leachates prepared at 100 g_{peat} L⁻¹. As such, for assessing water-leachable components in the peat, we recommend to perform laboratory extraction from freeze-dried peat samples using MilliQ water at the peat:water mass ratio of 1:10.

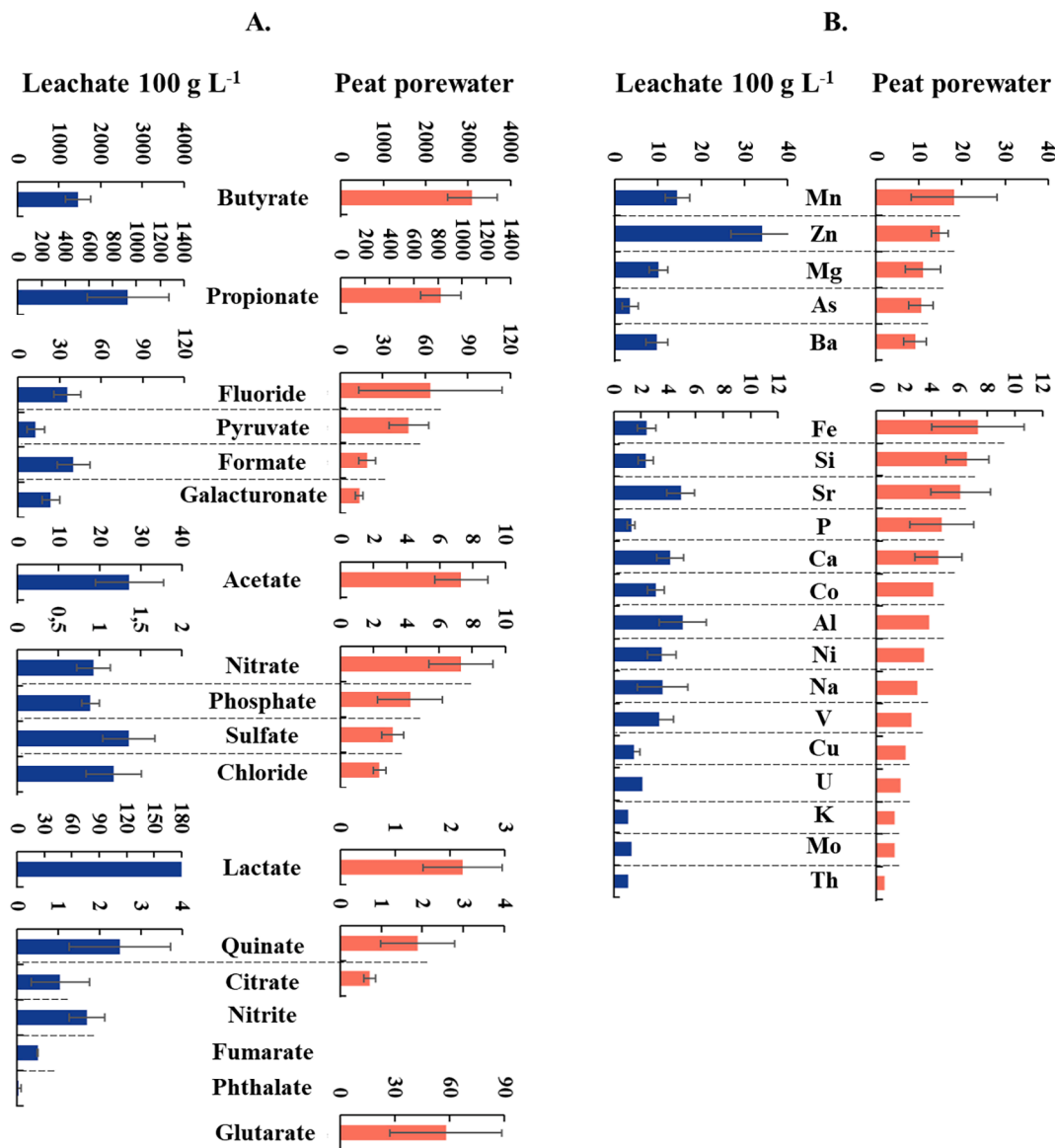


Fig. 6. The ratio of the mean concentration of anions (A) and cations / trace elements (B) normalized to the mass of the peat in the frozen (45–125 cm) part of the peat core to the mean concentration of these solutes in the thawed (0–45 cm) part of the core, for laboratory aqueous leachate performed at $100 \text{ g}_{\text{peat}} \text{ L}^{-1}$ and native peat core.

4. Discussion.

4.1. Spatial pattern of soil porewater and ice solutes

Two main features of the spatial pattern for dissolved organic and inorganic components in the peat porewater and ice from permafrost peatlands are *i*) significantly higher solute concentrations in the frozen layer compared to the active layer, and *ii*) maximal concentration in the horizons located 30 to 40 cm below the active layer boundary. The results of this study are generally consistent with previous findings on DOC, major and trace elements concentration in peat porewater and ice from permafrost peatlands (Raudina et al., 2017, 2021; Lim et al., 2021). These former studies of field peat cores across the WSL demonstrated *i*) generally high concentrations of DOC (60–100 and 300–500 mg L^{-1} in thawed and frozen layer, respectively), *ii*) sizable (≥ 3 times) enrichment of peat ice in alkali and alkaline-earth metals (Ca, Mg, Sr, Ba, Li, Rb and Cs), sulfate, phosphorus, and trace elements (Al, Fe, Mn, Zn, Ni, Co, V, As, Y, REE, Zr, Hf and U) relative to porewaters of the active layer and *iii*) the existence of a solute concentration peak of DOC, P, Ca, Mg, Mn, Fe,

Sr and As (up to factors ranging between 14 and 58 compared to the rest of the peat core) at 85 cm depth, which is 30–40 cm below the active layer.

The main novel results of the present study are that 1) the vertical pattern of element concentration and specific group of elements are also observed for aqueous leachates of freeze-dried peat, and 2) the features of these permafrost peatland cores are also observed for organic nutrients and anions which have not been investigated previously. These include PO_4^{3-} , NO_3^- , NO_2^- and 15 organic acids. Butyrate exhibited by far the highest concentration in the permafrost ice, which corroborates previous results on mineral soils from permafrost regions in Eastern Siberia and Alaska (Drake et al., 2015; Ward and Cory, 2015). The high concentrations of optically-transparent carboxylic acids in peat ice and aqueous leachates from the frozen layer (below 65 cm depth) are consistent with relatively low SUVA_{254} ($< 1\text{--}1.5 \text{ L mg C}^{-1} \text{ m}^{-1} \text{ L}$) in this part of the core. At the same time, most upper layers of the native peat core (5–15 cm) also exhibited low SUVA_{254} and elevated acetate, lactate, quinate and citrate concentrations. This may reflect the presence of plant root exometabolites that are detectable due to low residence time

of water in highly saturated pore waters of the upper part of the peat core (Rezanezhad et al., 2016; Raudina et al., 2017; McCarter et al., 2020). The higher SUVA₂₅₄ and WAMW values at the border of thawed and frozen horizons correspond to accumulation of aromatic polymerized compounds in this layer, probably due to bacterial uptake of bioavailable carboxylates in the overlying active layer. Similarly, an increase in spectral slopes S₂₉₀₋₃₅₀, S₂₇₅₋₂₉₅ and S₃₅₀₋₄₀₀ values (Fig. S4 G-I of the Supplement) between thawed and frozen horizons likely corresponds to a decrease in the molecular weight of DOM (i.e., the degree of polymerization) down the peat core.

Based on the quantitative analysis of 15 carboxylic acids, we estimate that these compounds represent a small fraction of DOM in the permafrost ice. In fact, converting the carboxylate concentration into DOC demonstrates that the majority of these compounds (formate, lactate, glutarate, citrate, pyruvate, galacturonate, quinate, maleate, oxalate, fumarate and phthalate) provide <10 mg C L⁻¹; acetate, formate and propionate contribute from 10 to 20 mg C L⁻¹ while butyrate accounts for approximately 50 mg C L⁻¹ in the permafrost ice. For this study, the total contribution of these carboxylates is <10 % of typical DOC concentrations (500 to 1000 mg L⁻¹) observed in the frozen part of the peat core (Fig. 2 C). Therefore, we hypothesize, following the results on mineral soils from other permafrost regions (Drake et al., 2015; Ward and Cory, 2015), that a sizable part of DOM can be represented by carbohydrates given that *Sphagnum*-derived simple carbohydrates are quite common in porewaters of Arctic peat bogs (i.e., AminiTabrizi et al., 2020). Very low concentrations of aromatic compounds (SUVA₂₅₄ < 1 L mg C⁻¹ m⁻¹) both in the peat ice and aqueous extracts of the permafrost layer are consistent with fresh low polymerized DOM in deep frozen peat horizons. In this regard, this study and its focus on permafrost peatlands validates previous results on mineral permafrost soils in which DOM from deeper horizons exhibits lower SUVA₂₅₄ values compared to DOM from the active layer (Drake et al., 2015; Ward and Cory, 2015; Ward and Cory, 2016; Wickland et al., 2018; Zhang et al., 2017).

The existence of a maximum carboxylate concentration below the active layer, in the so-called transient layer (70–100 cm depth), is also consistent with former observations on inorganic solutes (i.e., Kane et al., 1989; Hinzman et al., 1991; Jessen et al., 2014; Lamhonwah et al., 2017a, 2017b). This transient layer is formed via transfer of solutes from the active layer to the underlying permafrost through successive freeze–thaw cycles and it exhibits distinct concentrations of both inorganic solutes and DOC (Shur et al., 2005).

Quantitative comparison of experimental leachates of freeze-dried peat with natural peat core porewaters and ice demonstrates that the optimal conditions for assessing the water-soluble components is at 100 g_{peat} L⁻¹. The majority of studied solutes, including DOC, macro- and micro-nutrients demonstrated similar (i.e., ±30 %) yield in the laboratory leachates to concentrations in natural porewaters (Table S3 of the Supplement). Therefore, the peat:water ratio of 1:10 is the best trade-off between adequate representation of natural porewater, difficulties in transporting intact peat cores from the field to the laboratory, availability of the solid phase for experiments and analyses, and the peat's specific highly hygroscopic nature preventing use of a high solid:solution ratio (1:5 as recommended for mineral soils). However, use of freeze-dried peat samples instead of native peat from the permafrost zone may overestimate the mass-normalized yield of some carboxylates (lactate, formate, and galacturonate) and a number of trace elements (i.e., Al, V, Cr, Ga, Y, Zr, REEs, Hf, Th, U). It is possible that microbiological consumption of lactate, formate and galacturonate in the pore waters of field peat cores may be responsible for the observed difference with laboratory leachates. A possible cause of enhanced release of low solubility, low mobility trace metals in the laboratory leachates is their co-mobilization with Al in the form of high molecular weight (>30–100 kDa) organo-aluminium colloids (i.e., Pokrovsky et al., 2005). Colloidal Al hydroxides, stabilized by organic matter with coprecipitated trivalent and tetravalent hydrolysates were evidenced by size-fractionation procedure across a 500-km gradient of permafrost peatlands in Western

Siberia (Lim et al., 2022a). Presumably, these organo-Al colloids carrying low solubility trace elements are readily mobilized from peat grains to the aqueous solution in the laboratory leachates. The elements less affected by colloidal transport (alkalis, alkaline earths, oxyanions and neutral molecules) exhibited much smaller differences in concentrations between field porewater/ice and laboratory leachates. In contrast, Fe yield was 3 times lower in the leachates relative to natural porewater. A possible explanation could be Fe(II) oxidation and immobilization as Fe(III) oxy(hydr)oxides in essentially aerobic experimental conditions of this study, whereas in natural settings, sizable (>50 %) fraction of Fe is present in the form of low molecular weight (<3 kDa), presumably ionic, forms such as Fe²⁺ (aq) (Lim et al., 2022a). Therefore, the extraction of native porewaters has to be prioritized relative to laboratory water leaching from dried or freeze-dried peat soil samples.

4.2. Mechanisms of solute enrichment in the frozen layer relative to the thawed layer

Results obtained here allow for an improved understanding of the factors shaping the spatial pattern of organic and inorganic solutes in peat of permafrost regions. It is generally believed that because runoff-associated leaching processes do not operate within the frozen layer, the permafrost contains a high concentration of labile compounds compared to the overlying active layer (Keller et al., 2007). So, as the first and most likely cause of strong enrichment in carboxylic acids in the frozen horizons compared to the upper (thawed) layer, we hypothesize a lack of leaching and microbiological uptake of this labile (bioavailable) OM in the bottom part of the core. As a result of this, simple carboxylic acids that originated from plant litter degradation, root exometabolism and peat leaching could be preserved in the frozen state since the Holocene optimum, when the active layer included full depth of the peat core and the peat was actively forming. In contrast, strong uptake of lactate, acetate, propionate, formate, butyrate in the upper (unfrozen) part of the peat core observed in the present study is most likely linked to contemporary biological activity. A recent study of Canadian permafrost soils demonstrated high microbial lability of low-condensed low-aromatic permafrost DOM given that soil microbes can preferentially mineralize aliphatic proteinaceous organic compounds (Fouché et al., 2020). It is worth noting that after freeze-drying, the mass-normalized release of simple carboxylates (lactate, formate) from peat is 2 to 3 times greater than their concentration in the porewaters in the field (Table S3 of the Supplement). This likely indicates the preservation of this highly labile DOM in small pores and pockets of peat or their retention by peat surfaces.

The second cause for strong enrichment in the permafrost layer's organic C (carboxylates) could be freeze–thaw cycles of peat porewaters. Laboratory experiments on European Arctic peatland waters showed the generation of low molecular weight organic matter and metal-OM complexes after repetitive freezing and thawing of filtered (<0.45 μm) peatland waters (Pokrovsky et al., 2018). Additionally, freeze–thaw cycles of surface waters in NE European permafrost peatlands also produced an increase in aliphatic low molecular weight OM (Payandi-Rolland et al., 2021). Accumulation of organic low molecular weight compounds below the active layer boundary could be attributed to progressive removal from the active layer due to transport along thermal gradients in near-surface permafrost regions as is known for mineral soils (Kokelj and Burn, 2005). Note that about 7 % of the porewater from organic peat soil may remain unfrozen at temperatures as low as –10 °C (Hinzman et al., 1991). Given that capillary peat pores accommodating unfrozen aqueous solution at these subzero temperatures are quite small (<0.01 μm, Ming et al., 2020), one can hypothesize entrapment of small organic molecules rather than highly polymerized large humic and fulvic substances in the pores. Such a mechanism of preservation of labile solutes was first suggested by Gamayunov and Stotland (1988) and could also explain recent observations in permafrost soils from Arctic

Canada that demonstrated permafrost DOM with a greater proportion of low molecular weight organic compounds compared to the active layer (Fouché et al., 2020).

4.3. Implications for permafrost peatlands

Results of the present study demonstrate that on-going thawing of permafrost peat can liberate sizable amount of highly labile carboxylic acids to the surrounding surface waters and thus greatly increase biodegradation potential of river runoff. Considering the minimal thawing rate (active layer thickness increase) in western Siberia [1 cm y^{-1} which is similar to Northern European peatlands as documented by Åkerman and Johansson (2008) and Johansson et al. (2011)], the percentage of ice measured in the peat layer and the proportion of peatlands in WSL river watersheds, the mass balance calculations yield total DOC export increase by $3.7 \pm 2.6 \text{ t km}^{-2} \text{ y}^{-1}$ (Lim et al., 2021). >60 % of this export occur in the form of low molecular weight and potentially bioavailable DOM, which greatly exceeds the current riverine yield in the Western Siberia (Lim et al., 2022a). Given the total dissolved concentration of carboxylic C in permafrost ice ranges from 10 to 50 mg C L^{-1} , results of this study suggest that at least 10 % of this flux could be represented by easily degradable carboxylic acids. These easily degradable carboxylic acids can be entirely converted into CO_2 once it is delivered to the surface waters. On a scale of all frozen peatlands of the WSL (1.05 million km^2), this can non-negligibly add to current inland water C emissions (Karlsson et al., 2021) and greatly enhance biotic metabolism on a short-term scale. A big unknown factor of such increase is the content of organic and inorganic nutrients in the ice from mineral layers (clays and silts) underlying the peat deposits. These mineral layers are capable of both adsorbing and releasing DOM (i.e., Lim et al., 2022b); however, the fate of organic ligands and N- and P-nutrients upon thaw of dispersed ice in these currently frozen mineral horizons remains completely uncertain. Therefore, results of this study point a clear need for the broad-scale assessment of frozen mineral layer reactivity in aqueous solutions, as it may serve as an important governing factor for a terrestrial response to permafrost thaw and hydrological regime change in permafrost peatlands.

5. Conclusions

Comparative study of native peat cores (pore water and ice) and aqueous extracts of dry peat from western Siberia Lowland demonstrated extremely high concentrations of dissolved ($<0.45 \mu\text{m}$) carboxylates (acetate, formate, butyrate, propionate, pyruvate, lactate) in the frozen part of the peat core located below the active layer (10 to 50 mg C L^{-1}). Concentrations of these organic compounds, macro- and micro-nutrients in the frozen peat layer are a factor of 3 to 20 higher than those in the overlying thawed peat. Freeze-dried peat from the frozen horizons reacted with water at various fluid:solid ratios and also demonstrated very high concentrations of labile organic matter and nutrients; this allowed for better definition of the optimal conditions for aqueous *ex-situ* extraction of solutes. Aqueous leachate of $100 \text{ g}_{\text{peat}} \text{ L}^{-1}$ obtained from freeze-dried peat is a suitable surrogate for assessing organic and inorganic solutes that can be released from “native” peat ice and porewater. Possible causes of strong enrichment in carboxylic acids in the frozen peat compared to the thawed layer include but not limited to: (i) a lack of microbiological uptake of bioavailable OM below the active layer, (ii) freeze–thaw cycles of peat porewaters, and (iii) progressive downward removal of DOM from the rooting zone along the thermal gradient, leading to entrapment of small organic molecules rather than large, highly polymerized substances in the peat micropores.

On-going thawing of permafrost peat can liberate sizable amount of highly labile carboxylic acids and inorganic macro- and micro-nutrients to the hydrological network, which can greatly enhance, on a short-term scale, the biotic metabolism and C processing in inland waters of permafrost peatlands. Future studies of dispersed ice within the mineral

horizon, impact of temperature on the leaching of solutes and of biolability of DOM from dispersed ice are needed to better understand the biogeochemical consequences of frozen peat thaw.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2022.116256>.

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