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Abstract

Despite the importance of soil and surface waters freezing in permafrost landscapes, the behaviour of dissolved organic carbon (DOC), nutrients and metals during periodic freeze-thaw cycles (FTC) remains poorly known. The on-going climate warming is likely to increase the frequency of FTC in continental aquatic settings, which could modify the chemical composition of waters. In this study, we conducted 9 repetitive cycles of overnight freezing (-20 °C) and 5 hours thawing (4°C) in the laboratory using representative 0.22 µm-filtered waters from NE European permafrost peatland: leachates of vegetation and soil, and natural surface waters (depression, thermokarst lake and river). Only minor (< 5% - 15%) changes of DOC concentrations, $SUVA_{254}$ and molecular weight were observed in all leachates and the depression water. In contrast, several trace elements (Fe, Al, P, Mn, As, and REE) exhibited sizable variations during FTC (> 10%). The leachates and the depression water were enriched in trace elements, whereas the thermokarst lake and the river demonstrated a decrease in concentration of Fe (-39 and -94 %, respectively), Al (-9 and -85 %), and Mn (-10 and -79 %) during FTC. Overall, the observations demonstrated an increase in aliphatic low molecular weight organic matter (OM), and the precipitation of Fe, Al hydroxides and organo-mineral particles. Therefore, enhanced of frequency of FTC can favour the release of metals and toxicants from acidic OM-rich surface waters and maintain stable OM-metals-colloids in large lakes and rivers, thus regulating aquatic transport of DOC and metals from soils to the Arctic Ocean.

1. Introduction

In Arctic regions, strong permafrost thaw occurs mostly where soil temperature fluctuates around 0 °C (Romanovsky et al., 2010) which corresponds to discontinuous and sporadic permafrost zones. This is especially important in Arctic wetlands such as permafrost peatlands which contain a huge amount of organic carbon (OC) (Hugelius et al., 2014; Schuur et al., 2015). The dissolved OC (DOC) is the main form of terrestrial C exported from soil solutions to rivers and lakes in the wetlands (Chapin et al., 2006; Cole et al., 2007). The transformation of DOC in surface waters involves photo- and bio-degradation which is controlled by light intensity (Selvam et al., 2019), temperature (Boddy et al., 2008), origin of OC and microbial diversity (Young et al., 2005). Transition periods (*i.e.* early spring and late autumn) appeared to be essential times for the export (Manasypov et al., 2015; Pokrovsky et al., 2020) and biodegradation (Payandi-Rolland et al., 2020b) of DOC in rivers and lakes of Arctic wetlands when the majority of DOC originates from leaching of supra-permafrost-soil and vegetation (Ma et al., 2019; Vonk et al., 2015). These periods are dominated by recurrent freeze-thaw cycles (FTC, Henry, 2008). Furthermore, full freezing of thermokarst lake basins in western Siberia was reported to lead to massive coagulation of organo-ferric colloids producing macroscopic, organic- and Fe-rich amorphous particles capable of precipitating to the lake bottom (Manasypov et al., 2015).

Since the 1970s, a lot of attention is given to the impact of freezing and thawing on soil properties (DeLuca et al., 1992; Kim et al., 2017; Larsen et al., 2002; Ren and Vanapalli, 2020; Schimel and Clein, 1996; Xiao et al., 2019). In contrast, studies on the influence of freezing and thawing on dissolved solutes of continental waters are only at their beginning (Chen et al., 2016; Hentschel et al., 2008; Pokrovsky et al., 2018; Savenko et al., 2020; Spencer et al., 2007). Most of them focused on surface water with near circum-neutral pH such as rivers (Chen et al., 2016; Savenko et al., 2020) and ponds (Pokrovsky et al., 2018). The main impact noticed by those studies is the decrease of aromaticity in waters due to FTC (Chen et al., 2016) and the generation of low molecular weight (LMW) organic components (Pokrovsky et al., 2018). The impact of freezing on dissolved organic matter (DOM) in high latitudes is still poorly known. In this study, we conducted freeze-thaw experiments aimed to characterize the impact of FTC on DOC, major and trace elements in waters of one of the largest permafrost peatlands of Europe, the Bolshezemelskaya Tundra (BZT). For this, we used DOM originated from vegetation, soil (peat) and natural water bodies of this peatland. Based on a few available studies dealing with FTC of surface waters (Fellman et al., 2008; Pokrovsky et al., 2018; Xue et al., 2015), we hypothesized that: 1) DOC and trace metals (TM) present in the form of organic and organo-mineral colloids could coagulate under freezing which could favour the transport of mineral under more stable forms (colloids) through lakes and rivers to the Arctic Ocean; 2) OC originated from fresh plant biomass (i.e. leachates not subjected to previous freezing) would be more sensitive to FTC compared to natural waters, as fresh DOC is known to be composed of more labile components, and 3) the FTC could have a more pronounced effect on the degradation of OC from the permafrost compared with active layer OC since the latter has undergone previous seasonal freezing cycles. Overall, we aimed at providing an empirical assessment on the degree of DOC and inorganic solutes concentrations change after repeating freezing and thawing of representative surface waters from permafrost peatlands.

2. Materials and methods

2.1. Substrates origins and use

The DOM used in this study originated from: *i*) natural surface waters of a permafrost peatland, *ii*) aqueous leachates of ground vegetation and *iii*) aqueous leachates of peat soil.

The sampling sites are located in the NE European permafrost peatlands (BZT) within the discontinuous permafrost zone. Natural waters were collected from a small depression, a thermokarst lake and the Pechora River (Supplementary **Table S1**). Waters were filtered on-site through a 0.45 µm sterile filtration unit and re-filtered in the laboratory through a 0.22 µm Nalgene sterile filter before freezing.

The soil and ground vegetation for leachates were collected at the shore of the thermokarst lake (**Table S1 and Figure S1**). The peat core was sampled using a Russian peat corer (see details of sampling and handling in Morgalev et al., 2017). The soils included two subsamples of peat, one collected in the active (unfrozen) layer (20-30 cm below the surface) and the second one in the permafrost zone (> 30-40 cm). Both subsamples represent oligotrophic peat composed of *Sphagnum angustifolium*, cotton-grass *Eriophorum*, *Scheuchzeria palustris*, bog-sedge *Carex* limosa, lichens, dwarf shrubs and some amount of wood debris (pine) and green mosses (Payandi-Rolland et al., 2020b). Ground vegetation contained mosses *(Sphagnum fuscum and Sphagnum augustifolium)* and lichens (*Cladonia* genus), which colonize hollows and mounds of the palsa and are reported to be widely spread species in the tundra (Malmer et al., 2005). Aqueous leachates were prepared by reacting 10 g of organic substrate (10 g_{wet} for frozen peat and 10 g_{dry} for vegetation) with 1 L of sterile MilliQ water under constant agitation (70 rpm) at 25 ± 2 °C in the dark and aerobic conditions (Payandi-Rolland et al., 2020b; Shirokova et al., 2017a, 2017b). After 3 days of reactions, the suspension was centrifuged at 4500 g for 5 minutes and then sterile filtered (< 0.22 µm) using 500 mL Nalgene units and a manual vacuum pump.

2.2. Incubation, freeze-thaw cycles and sampling

A 150 mL aliquot of each leachate and natural waters were placed in pre-cleaned (rinsed 3 times with HCl (1 M) and MQ water and then autoclaved at 121 °C for 20 min) 200 mL polypropylene Nalgene bottles. Experiments with each substrate were performed in duplicate. A cycle of freeze-thaw (adapted from Pokrovsky et al., 2018) started from placing water-filled Nalgene bottles in the freezer (-20 °C) overnight. After the total freeze of the liquid, bottles were transferred into the refrigerator compartment (at 4 °C) and kept there for 5 hours until the ice melted completely. These temperatures can be observed at the permafrost peatlands during the year in winter (Lim et al., 2021), early spring and late autumn ("Climate & Weather Averages in Naryan-Mar, Russia," 2015; Serikova et al., 2019) and are consistent with the range used in previous works (Chen et al., 2016; Pokrovsky et al., 2018; Spencer et al., 2007; Xue et al., 2015). All filtrates have undergone 9 FTC, which corresponds to the average number of annual freeze-thaw cycles observed in high-latitude boreal and Arctic regions (Henry, 2008; Pokrovsky et al., 2018).

After total ice melt in each cycle, we sampled 15 mL of a homogeneous aliquot from the bottle. Before and during the sampling, bottles were vigorously stirred with a magnetic stir bar to provide homogeneous suspension and avoid selective removal of either dissolved or particulate phase. A non-filtered subsample was used to measure pH (uncertainty of ± 0.01 pH units) and specific conductivity (± 0.1 µS.cm^{-1}). The rest of the 15 mL was filtered through a 0.22 µm filter (sterilizing filtration, Minisart® syringe filter). In the filtrates, the DOC was measured with Shimadzu TOC-VSCN with an uncertainty of 2%. The UV-absorbance of water samples was measured using a 10 mm quartz cuvette on a CARY-50 UV-vis spectrophotometer, between 200 and 700 nm. The UV and visible spectra allowed assessment of (*i*) the molecular weight (MW) of DOC *via* the Weight-Average Molecular Weight index

(WAMW, using the absorbance at 280 nm, Chin et al., 1994), (*ii*) the humification index using the ratio of absorbance at 250 and 400 nm (the E2:E4 ratio, Park et al., 1999) and (*iii*) the aromaticity of incubated water *via* specific UV absorbance ($SUVA_{254}$) (Abbt-Braun and Frimmel, 1999). Major cations (Na, Ca, K and Mg), Si, P and trace elements (TE) were measured with a quadrupole ICP-MS (Agilent 7500 ce) using In+Re as an internal standard. The international geo-standard SLRS-5 (Riverine Water Reference Material for Trace Metals) was used to check the validity and reproducibility of analyses.

2.3. Treatment of experimental results

Statistical treatment involved the least square method for regression and the Pearson correlation. All statistical analysis has been accomplished under R-software (version 3.6.2). Boxplot analyses were used to detect outliers. Boxplot values combine the median (Q_2), the first quartile (Q_1), the third quartile (Q_3), and the interquartile range (IQR) which is defined as the difference between Q_3 and Q_1. Outliers are defined as values located outside the first (D_1) and the last (D_9) decile, as “$D_1 = Q_1 - 1.5*IQR$” and “$D_9 = Q_3 + 1.5*IQR$” (Tukey, 1977). Linear regression analyses have been performed using the function “lm” of the package “stats”. The percentage of component gain or loss during FTC ($\Delta FTC_{0\text{-}9}$, %) was calculated as a difference in concentration between the final and initial concentration of a component, normalized to its initial concentration. Trace element complexation with OM and saturation indices of the solution with respect to common solid phases were calculated using the Visual MINTEQ (vMINTEQ) software, following the model specifications for organic-rich waters of permafrost peatlands describe elsewhere (Pokrovsky et al., 2016, 2018). A dataset combining the measured parameters can be found in Payandi-Rolland et al. (2020a).

3. Results and Discussion

3.1 Chemical composition of aquatic substrates

The dissolved (<0.22 µm) concentrations of DOC, major and trace elements of substrates used in this study are reported in **Table 1**. The water samples ranged from acidic (peat and vegetation leachates) to circum-neutral (depression, thermokarst lake, and Pechora River). The DOC of the thermokarst lake and the river was < 10 mg L^{-1}, which is 2 times lower than the leachates of peat and moss, 5 times lower than the lichen leachate, and 10 times lower than the water of depression. Such a wide range is comparable to the one reported for the hydrological continuum (depression → lake → stream → river) of this region (Shirokova et al., 2019). In all substrates, the DIC was below 1.5 mg L^{-1} except for the Pechora River (10.4 mg L^{-1}). The $SUVA_{254}$ ranged from low (< 2 L mgC^{-1} m^{-1}) for the lichen leachate and the depression to near 4 L mgC^{-1} m^{-1} in other natural waters, and finally to values > 5 L mgC^{-1} m^{-1} for leachates of soils and moss. The WAMW of all substrates was lower than 3 kDa and ranged from ≤ 1 kDa in lichen leachate and the depression to near 2-2.5 kDa in other natural waters and in soil and moss leachates. Considering that the MW of fulvic acids (Fa) is approximately 600 to 1000 Da and that the humic acid (Ha) MW is between 1500 and 5000 Da, (Garcia-Mina, 2006; Malcolm, 1990), 3 groups of samples could be distinguished in terms of DOM character: *i*) the humic OM group with a strong influence of Ha (*i.e.* leachates of soils and moss), *ii*) the "mixed" OM group with both influence of humic and fulvic acids (HFa) (*i.e.* the thermokarst lake and the Pechora River) and *iii*) the Fa OM group (*i.e.* lichen leachate and the water from the depression).

The leachate of lichen and the water from depression exhibited the highest DOC concentration (respectively 53 and 107 mg L^{-1}), and lowest WAMW (758 ±1 and 1121 ±7 Da) and $SUVA_{254}$ (0.7 and 1.6 L mgC^{-1} m^{-1}). This indicates that the DOC of these samples is mostly composed of simple OC molecules with the dominance of aliphatic components (Ågren et al., 2008; Tranvik and Jørgensen, 1995; Weishaar et al., 2003). Conversely, other waters exhibited lower DOC concentrations with a high proportion of aromatic compounds (**Table 1**). Considering the observed large difference in concentration of DOC, aromatic/aliphatic composition and the molecular weight of waters, it is anticipated that the effect of FTC could be primarily linked to these parameters. The concentrations of major and trace elements strongly varied among samples with general dominance of alkali and alkaline earth metals such as Ca, Na, Mg and K (**Table 1**). The highest concentrations of metals (Fe, Al, Mn) were observed in the moss leachate and depression waters (**Table 1**). Other trace elements exhibited concentrations lower than 2 µg L^{-1}.

3.2 Visual impact of the freezing process on DOM and removal of outliers

After full freezing of experimental reactors, ice was transparent at the borders and brown in the centre of bottles, similar to other FTC experiments (e.g., Pokrovsky et al., 2018). The concentration of brownish components (chromophoric components) in the centre of the bottle reflects the progressive freezing of water from bottle edges to the centre with a relative accumulation of DOM in the remaining liquid (Petzold et al., 2013; Shafique et al., 2012; Xue et al., 2015; Zaritzky, 2006). Further, it was shown that a high concentration of DOM and low freezing temperatures diminish the proportion of DOM incorporated in the ice phase (Elliott and Henry, 2009; Hentschel et al., 2008; Shafique et al., 2012; Xue et al., 2015). The high concentration of DOC in leachates of soils and moss (around 20 mg L^{-1}), in the leachate of lichen (53 mg L^{-1}) and in the water from the depression (106 mg L^{-1}) associated to the -20 °C temperature used in this study promotes the segregation of DOM in the remaining fluid located at the centre of the bottle during the freezing process. Such a formation of brown coagulates in the ice was interpreted as a change in particles density and diameter that occurs during the freezing (Fellman et al., 2008; Giesy and Briese, 1978), and presumably, leads to the formation of organo-metal aggregates rich in Fe and Al hydroxides (see ***section 3.5***). It is worth noting that after the total thaw of waters, no visual aggregations of OM (brownish area) can be distinguished in liquid. Furthermore, conversely to the FTC experiments on an organic-rich bog and fen waters (Pokrovsky et al., 2018), no brown/yellow precipitates have been observed at the bottom of the containers. From this observation, we hypothesized apparent reversibility of organic colloids and particles aggregation-dissolution during FTC of studied waters.

Preliminary analysis of the DOC concentration evolution during the FTC demonstrated some clear outliers. A boxplot repartition on data revealed that some of the data points can be statistically considered as outliers (see description of outliers given in ***section 2.3***; **Figure 1** and **Table S2**). These outliers are believed to be sampling artefacts. Some samples demonstrated an increase in certain elements concentration during FTC, which is counterintuitive given that all samples were 0.22 µm filtered prior to the incubation and also 0.22 µm filtered at each sampling. Furthermore, these increases were non-systematic and non-reproducible among replicates. We hypothesize that FTC can generate aggregates of DOC and metal hydroxides (see ***section 3.5***) thus producing some "islands" of solute-rich and solute-poor fluids. During the sampling procedure, even under continuous stirring, one can randomly collect some aggregate-enriched aliquots. Because *i)* each sampling are independent and *ii)* the presence of such aggregates, revealed by abnormal DOC concentrations, can biased other measured parameters (absorbance and trace elements concentrations), we have removed the outliers (about 7% of all collected data, see **Table S2**).

In the rest of this study, results and discussions will only deal with the new data set (i.e. without outliers).

3.3. Quantification of freeze-thaw cycles impact on DOC concentration and quality

The evolution of DOC concentration during FTC (**Figure 1**) exhibited variable trends among samples. The DOC concentration slightly increased between the initial stage (prior to the first freezing, *i.e.* FTC0) and after the last freezing (FTC9) in the active layer leachate (5 ± 2%), the thermokarst lake (8%) and the Pechora River (14 ± 4%) (**Figure 2** and **Table S3**). The variations of DOC in other samples were lower than 5%. However, only the increase of thermokarst lake DOC with FTC was superior to 5% and significant (*p_value* < 0.05; **Figure 2** and **Table S4**). Former studies demonstrated generally decreasing DOC concentration in the course of FTC with a range of DOC loss from 7 to 25% (Fellman et al., 2008; Pokrovsky et al., 2018). Fellman et al. (2008) demonstrated that the initial concentration of DOC strongly influenced the removal efficiency, with a loss of 7% when the concentration was < 5 mg L^{-1} and a 20% loss at higher initial DOC concentrations. In the present study, all initial DOC concentrations were superior to 7 mg L^{-1} and waters with the lowest initial concentration (from 7 to 10 mg L^{-1}, **Table 1**) exhibited an increase in DOC (*i.e.* the Pechora River and the thermokarst lake, **Figure 2** and **Table S3Erreur ! Source du renvoi introuvable.**). Therefore, the initial concentration of DOC does not appear to control the DOC removal efficiency in our study. Overall, low variations of DOC (< 5%, at the exception of the thermokarst lake and the Pechora River water) highlight the high stability of DOC when subjected to FTC. This observation is in agreement with the study by Xue et al. (2015) showing that DOC concentrations of lotic waters (which froze on 1 m thick during 3 to 5 months per year in the northern China) were highly stable (from 0.68% increase to 4.3% decrease) through FTC.

The $SUVA_{254}$ values presented in this work do not take into account the iron corrections suggested by Poulin et al. (2014) because the differences between the uncorrected and corrected $SUVA_{254}$ values were below 5% for all incubated substrates at the exception of the depression (maximum 5.9%), see **Table S5**. The $SUVA_{254}$ and WAMW values decreased (from -6.5% to -(17.0 ± 1)%, and from -5.6 % to -(14.1 ± 1)%, respectively) between FTC0 to FTC9 in the thermokarst lake and the Pechora River, whereas in other samples, the variations were below 5% (**Figure 2**, **Figure S2** and **Table S3**). Given that the waters were sterile filtered (< 0.22 µm) before the experiments, the observed decrease of $SUVA_{254}$ and WAMW can be only abiotically driven. This suggests that the FTC can provide an increase in non-aromatic low molecular weight components in waters from moss leachates, thermokarst lake and Pechora River. At the same time, both variations of $SUVA_{254}$ and WAMW in waters of thermokarst lakes and Pechora River were not significantly correlated to the number of FTC (**Table S4**).

The evolution of E2:E4 ratio between the 0 and 9^{th} cycle of freezing was null to positive in all leachates (< 5% increase), clearly positive in the depression (an increase of 8.5%), and negative in the thermokarst lake and the Pechora River (-5.2% and -(5.6 ± 2)%, respectively, **Figure 2** and **Table S3**). In the present study, the relative removal of humic-like aromatic components in waters from the HFa group (see ***section 3.1***, *i.e.* the thermokarst lake and the Pechora River) is corroborated by a decrease of $SUVA_{254}$ and WAMW values through FTC in these samples (**Figure 2** and **Figure S3**). Unlike well-known biotically-driven degradation of humic-like aromatic components in streams and rivers waters demonstrated by the decrease of E2:E4 ratio (Hutchins et al., 2017), in this study the decrease of this ratio is imputed to FTC (abiotic phenomenon) which appear to be also capable of selective removal of humic-like aromatic compounds in the lake and river water. In contrast, in leachates and depression waters, while the E2:E4 ratio slightly (< 10 %) increased with FTC, no evidence of selective removal of LMW components have been detected (the WAMW variations were < 5%).

3.4. Trace element behaviour during FTC

A clear decrease of Fe concentration during FTC in thermokarst lake and the Pechora River (-39.0% and -94.4%; respectively; **Figure 3**, **Figure S4** and **Table S3**) suggests the removal of this element in the form of secondary phases. The saturation index (SI) calculated *via* the vMINTEQ software indicates that Fe can precipitate in the form of akaganeite ($FeO_{0.83}(OH)_{1.17}Cl_{0.17}$, SI: 1.8 to 2.1), goethite ($Fe(OH)_3$, SI: 0.7 to 1.0) and lepidocrocite ($Fe^{3+}O(OH)$, SI: 0.6 to 0.9) in all surface waters. In the case of thermokarst lake and the Pechora River, a significant ($p < 0.05$) increase in (C_{org}/Fe) molar ratio in the course of FTC was observed, which suggested a progressive depletion of Fe relative to C_{org} in the colloidal fraction (**Figure 4A and C**, and **Table S4**).

Aluminium concentration decreased during FTC of moss leachate (-33.4%), thermokarst lake (-9.4%) and Pechora River (-85.1 ±7%) samples (**Figure 4**, **Figure S5** and **Table S3**). The SI calculation did not indicate any supersaturation concerning Al oxyhydroxides. However, the formation of organo-mineral (Fe, Al) coagulates *via* coprecipitation of Fe and Al oxyhydroxides is likely given the sizable correlation ($p < 0.05$) between aqueous concentrations of Fe and Al in the course of the FTC sequence (**Figure S6**) in all waters (with an exception of moss leachate). In the case of the Pechora River, a significant ($p < 0.05$) evolution of the molar ratio $(C_{org}/Al)_{molar}$ with the number of FTC (**Figure 4B** and **Table S4**) suggests the formation of mixed Fe-Al-OM sub-colloidal particles as it is reported in surface waters of permafrost peatlands (Pokrovsky et al., 2016). Other trivalent hydrolysates such as Y and Ga punctually correlated with DOC and Fe during FTC (**Figure S7** and **Table S6**). Light REE

(LREE: La, Ce and Pr) correlated with Fe in the leachate of the active layer and the permafrost, and in waters of the depression and the Pechora River, whereas heavy REE (HREE: Nd, Dy, Yb) significantly correlated with Fe in the Pechora River (**Table S6**).

Phosphate is known to be controlled by dissolved humic substances (Fellman et al., 2008; Francko, 1986; Jones et al., 1988) especially in wetlands where the high concentration of DOM and iron facilitates the complexation of DOC and PO_4 (Dillon and Molot, 1997). However, this was not observed in this study, because there was no correlation between the concentration of PO_4 and DOC, and the molar ratio between organic carbon and phosphate did not systematically vary during the FTC in all samples (**Table S4**). Chromium, vanadium and silicon concentrations decreased in waters of thermokarst lakes and Pechora River (**Figure S8** and **Table S3**), whereas most of the divalent macro- and micro-nutrients (Co and Ni) exhibited a slight increase in concentration through FTC in all waters (**Figure S8** and **Table S3**).

Manganese concentration clearly decreased in thermokarst lake and the Pechora River (respectively -10.4% and -(79.4 ±1) %) but remained stable or increased in other waters (**Figure 3**, **Figure S9** and **Table S3**). The decrease of Mn concentration and the correlation between the molar ratio $(C_{org}/Mn)_{molar}$ and FTC number could indicate a formation of Mn (hydr)oxide particles or Mn coprecipitation with organo-ferric compounds in the water of the Pechora River.

Among tetravalent hydrolysates, Ti and Zr demonstrated an increase in the Pechora River and a decrease in other waters (**Figure S7**). Titanium concentration significantly correlated with Fe in all waters (except the moss leachate). Zirconium correlated with Fe in the leachate of the active layer, permafrost and in the depression. Hafnium and Th correlated with Fe only in water of the depression (**Table S6**). These types of correlation between Fe and insoluble tetravalent hydrolysates have been observed previously in ultrafiltration experiments on boreal forest (Ilina et al., 2016) and permafrost surface waters (Pokrovsky et al., 2016) and indicate the dominance of organo-ferric high molecular weight colloids in TE^{4+} speciation.

Lead concentration increased in the course of FTC in all leachates and decreased in natural waters (**Figure S7** and **Table S3**). Arsenic (As) decreased only in the Pechora River water (**Figure 3**, **Figure S10** and **Table S3**). In riparian wetlands, the presence of As hotspots due to As association with Fe or OM was reported (Guénet et al., 2016). In the present study, linear regressions on As and DOC concentrations were non-significant ($p > 0.05$) in all samples (**Table S6**). In contrast, there was a strong linear regression ($p < 0.03$) between As and Fe concentrations for all studied samples, except the thermokarst lake (**Figure S11** and **Table S6**). It appears then, that the As is bound to the Fe and not to the OM of either vegetations and soils leachates or natural waters. In addition to its control by DOM, As in natural waters can be adsorbed to Fe-oxyhydroxides, such as nano-lepidocrocite (Guénet et al., 2016). Both the correlation between As and Fe concentrations and the supersaturation of solutions with respect to Fe-oxyhydroxides and lepidocrocite secondary phases (***section 3.4***) observed in the present study support this hypothesis.

3.5. Possible mechanisms of DOC and metal transformation during FTC.

Two colloidal pools are responsible for TE speciation in boreal aquatic environments: *i*) small organic-rich colloids and LMW DOM, and *ii*) high molecular weight Fe-rich colloids (Baalousha et al., 2006; Krachler et al., 2012; Stolpe et al., 2013). The LMW colloids dominate metal speciation in acidic thaw pond water and are highly stable during FTC. In contrast, high molecular weights colloids dominated mainly in neutral waters of the permafrost area and are subjected to strong removal during freezing (Pokrovsky et al., 2018). In our study, the MW of

Ha and HFa group can be indicative of LMW colloids (generally ranging between 1 to 50 kDa), while the Fa group (lichen leachate and depression waters) exhibited essentially dissolved fraction ($LMW_{<1\ kDa}$). The $LMW_{1\text{-}50\ kDa}$ colloids are likely to dominate the metals speciation in the thermokarst lake and the Pechora River water. The stronger impact of FTC on the Pechora River and the thermokarst lake water suggests that mixed HFa OM of large terminal water bodies is most vulnerable to the freeze-thaw process. This observation can be attributed to the two binding patterns of metals and OM. These patterns depend on the maximum metal binding capacity of *i*) humic-like component which is reached at neutral to alkaline pH (7 to 9) due to maximal ionization of carboxylate and phenolic acids; and *ii*) fulvic-like component reached at acidic pH (5 to 6) when the majority of carboxylate moieties are dissociated (Garcia-Mina, 2006). Therefore, in contrast to more acidic plant and peat leachates, in the Pechora River, both the presence of humic acids (in HFa) and the neutral pH (7) and in thermokarst lake, the presence of fulvic acids (in HFa) and slightly acidic conditions (pH = 6.3), promote the aggregation of colloidal Fe *via* DOM - metal binding. Considering, based on our experimental observations, a relatively stable concentration of DOC, a decrease of $SUVA_{254}$, WAMW, Fe concentrations, and an increase in C_{org}/Fe ratio in the course of FTC, we suggest preferential degradation of humic-like components in waters from thermokarst lake and Pechora River and formation of aliphatic $LMW_{1\text{-}50kDa}$ colloids. On the contrary, no evidence on the formation of organic and organo-ferric colloids in other waters during FTC has been detected in our study.

3.6. Possible role of FTC in natural environments

Progressive accumulation of DOM and related elements in the remaining fluid due to full freezing of the water column is observed in shallow confined natural water bodies such as thermokarst lakes and ponds of permafrost peatlands (Manasypov et al., 2015). In the present study, the effect of freezing on concentrations of most dissolved components did not generally exceed 10% and was limited to simple physicochemical reactions given that all samples were sterile-filtered before the first freezing. In contrast, in a non-sterile FTC experiment that used various soils from marsh and wet grasslands, a strong DOC production (100 to 300 mg L^{-1}) compared to samples not subjected to FTC was reported (Yu et al., 2011). This increase was believed to be the consequence of microbial cells lysis, physical disruption of soils aggregates, and roots turnover (Bochove et al., 2000; DeLuca et al., 1992; Ivarson and Sowden, 1970; Tierney et al., 2001). In natural permafrost aquatic and soil environments, microbial communities are highly resistant to FTC (Lipson and Monson, 1998; Stres et al., 2010). This suggests that both the capacity of micro-organisms to quickly recover and efficiently biodegrade OM, together with the abiotic transformation of DOC during and after repetitive freezing can become a sizable source of LMW DOC, as also reported in previous studies (Pokrovsky et al., 2018). Further, whereas the freezing process can impact the DOM concentration, the thawing duration (hours or days) has little effect on the DOC aromaticity of leachates (Hentschel et al., 2008; Vestgarden and Austnes, 2009). This implies that the rapid thawing of ice in nature could lead to the production of more easily biodegradable OM components.

The results of the present study demonstrated rather minor (i.e., ≤ 10%) effects of freeze-thaw cycles on DOC quantity and quality in various leachates of soils and vegetation which indicates strong stability of DOM in typical surface waters of boreal peatlands (except large river). As such, the FTC may be of sub-ordinary importance on DOM transformation in surface waters of permafrost peatlands relative to other biotic and abiotic factors such as heterotrophic degradation and photolysis (Payandi-Rolland et al., 2020b; L. S. Shirokova et al., 2019). In contrast, the "mineral" part of organo-mineral colloids present in natural waters was subjected to removal from solution due to freezing as indicated by an increase in C_{org}/Fe and C_{org}/Al molar ratios in the course of FTC of river and lake water. In this regard, the impact of FTC on trace metal can be competitive to bio- and photo-transformation of trace metal colloids (Oleinikova et al., 2018, 2017). Therefore, the first hypothesis of this study was confirmed only for the large river, where both Fe and Al were removed preferentially to DOC. For a thermokarst lake, this hypothesis was only partially confirmed (solely Fe removal). Such a removal of Fe, Al and other metal were not observed in vegetation and soil leachates and in the depression water, thus confirming a subordinary role of freezing on DOM and metal fate in surface waters of permafrost peatlands. This dismisses the second hypothesis of this study on the highest sensitivity of fresh leachates to freezing: regardless of the origin of vegetation leachates (moss and lichen), the change in concentration of DOC and metals during FTC was inferior to that of river and lake waters. In contrast, large water bodies such as the Pechora River or a thermokarst lake meet the ideal conditions for stabilization of OM-mineral colloids. In these settings, the FTC can facilitate aquatic transport of C, nutrients and metals from peatlands surface waters to the Arctic Ocean. However, because the full freezing of large surface water bodies is unlikely compared to small depressions and soil porewaters, the overall impact of FTC on DOC and metal transformations in permafrost peatlands is expected to be low. As such, unlike the bio- and photo-degradation of permafrost DOM in Arctic waters (Cory et al., 2014; Vonk et al., 2015), which has to be considered in models of the future arctic C balance (McGuire et al., 2018), the freeze-thaw cycles are likely to be of secondary importance for C transformation in Arctic continental waters.

Conclusions

This study demonstrated that the pH and OM composition (aromaticity, molecular weight, proportion of humic and fulvic components) are the main factor controlling the DOC (< 0.22 µm) removal from surface waters of permafrost peatlands under freeze-thaw cycles. No quantitative relationship was established between both DOC quantity and quality and the number of FTC in the acidic, DOC-rich aqueous leachates of terrestrial vegetation and various peat horizons. We also observed sizable stability of DOC and metal complexes present in typical surface and soil waters of permafrost peatlands with respect to freeze-thaw cycles. The exceptions are the circumneutral, humic- and fulvic-rich waters of the thermokarst lake and the Pechora River, which likely exhibited formation of Fe- and Al-rich organo-mineral particles. In contrast to DOC concentration which remained rather stable with FTC, trace element variations were pronounced and often exceeded 10%. Thus, in the Pechora River water, concentrations of metal micronutrients and trace elements sizably decreased during FTC. This was also partially pronounced in the thermokarst lake water. As such, large water bodies are most subjected by the FTC impact on OM-mineral colloids transport from lakes and rivers to the Arctic Ocean. This impact can be further accentuated due to enhanced FTC frequency under on-going climate warming in high latitudes.

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Conflicts of interest

The authors declare no conflict of interest.

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Tables and Figures

Tables

Table 1: General physical and chemical dissolved (<0.22 µm) parameters of different aquatic substrates before the first freezing (replicate mean).

		Leachates				Natural waters		
		Frozen peat		Vegetation				
	Abbreviation, units	active layer	permafrost	lichen	moss	depression	thermokarst lake	Pechora River
Acidity	pH, E	4.3	4.6	4.6	5.5	6.4	6.3	7.0
Conductivity, µS cm^{-1}		21.0	17.0	28.0	25.0	141	18.0	77.0
Carbon	DOC, mg L^{-1}	22.5	22.7	52.6	22.6	106	9.40	7.60
	DIC, mg L^{-1}	0.63	0.63	0.66	0.89	0.80	1.40	10.4
	$SUVA_{254}$, L mgC^{-1} m^{-1}	5.3	5.2	0.7	5.2	1.6	4.5	4.0
	E2:E3 ratio	3.50	3.50	3.80	3.90	4.70	3.70	3.50
	E2:E4 ratio	13.4	13.5	11.3	13.5	17.9	10.6	9.50
	E4:E6 ratio	7.00	7.20	3.60	5.50	5.20	4.60	4.00
	WAMW, Da	2525	2489	758	2429	1121	2167	1999
Alkali metals	Na, µg L^{-1}	106	156	701	1171	6787	682	1955
	K, µg L^{-1}	48.9	54.2	2658	223	1483	159	196
	Rb, µg L^{-1}	0.20	0.27	5.08	0.13	28.3	0.19	0.21
Alkaline-earth metals	Mg, µg L^{-1}	50.2	65.8	8.12	440	128	342	1521
	Ca, µg L^{-1}	295.6	419	29.9	922	163	887	7097
	Sr, µg L^{-1}	1.37	1.87	0.08	5.59	0.74	3.69	32.2
	Ba, µg L^{-1}	0.36	0.37	0.13	2.70	0.46	2.06	3.37

Micro- and Macro-nutrients	Si, µg L^{-1}	67.7	64.5	147	1730	271	30.3	1302
	P, µg L^{-1}	6.20	6.91	11.0	703	286	706	652
	Cr, µg L^{-1}	0.14	0.23	0.30	0.53	0.30	0.08	0.07
	V, µg L^{-1}	0.63	0.89	0.03	0.14	0.63	0.10	0.15
	Mn, µg L^{-1}	5.82	8.79	0.70	11.1	5.72	0.35	0.78
	Fe, µg L^{-1}	81.3	123	4.76	476	1327	66.9	180
	Co, µg L^{-1}	0.17	0.23	0.02	0.25	1.26	0.01	0.00
	Ni, µg L^{-1}	0.53	0.72	0.07	0.92	1.54	0.45	0.44
	Mo, µg L^{-1}	0.02	0.03	0.02	0.00	0.27	0.01	0.09
Trivalent hydrolysates	Al, µg L^{-1}	23.7	26.8	11.2	207	93.9	25.9	5.43
	Ga, µg L^{-1}	0.00	0.01	0.00	0.01	0.04	0.00	0.00
	Y, µg L^{-1}	0.01	0.01	0.01	0.20	0.01	0.06	0.07
	La, µg L^{-1}	0.01	0.02	0.02	0.20	0.02	0.05	0.06
	Ce, µg L^{-1}	0.01	0.01	0.04	0.52	0.03	0.11	0.07
	Pr, µg L^{-1}	0.00	0.00	0.00	0.06	0.00	0.01	0.01
	Nd, µg L^{-1}	0.01	0.01	0.01	0.25	0.01	0.06	0.07
	Dy, µg L^{-1}	0.00	0.00	0.00	0.04	0.00	0.01	0.01
	Yb, µg L^{-1}	0.00	0.00	0.00	0.02	0.00	0.01	0.01
Tetravalent hydrolysates	Ti, µg L^{-1}	0.06	0.07	0.27	0.75	0.37	0.13	0.16
	Zr, µg L^{-1}	0.04	0.05	0.02	0.32	0.09	0.06	0.03
	Hf, µg L^{-1}	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	Th, µg L^{-1}	0.00	0.00	0.01	0.06	0.00	0.00	0.00
Toxicants	As, µg L^{-1}	0.83	1.18	0.07	0.19	0.20	0.36	0.76
	Pb, µg L^{-1}	0.03	0.02	0.04	0.20	0.06	0.06	0.69

Figures

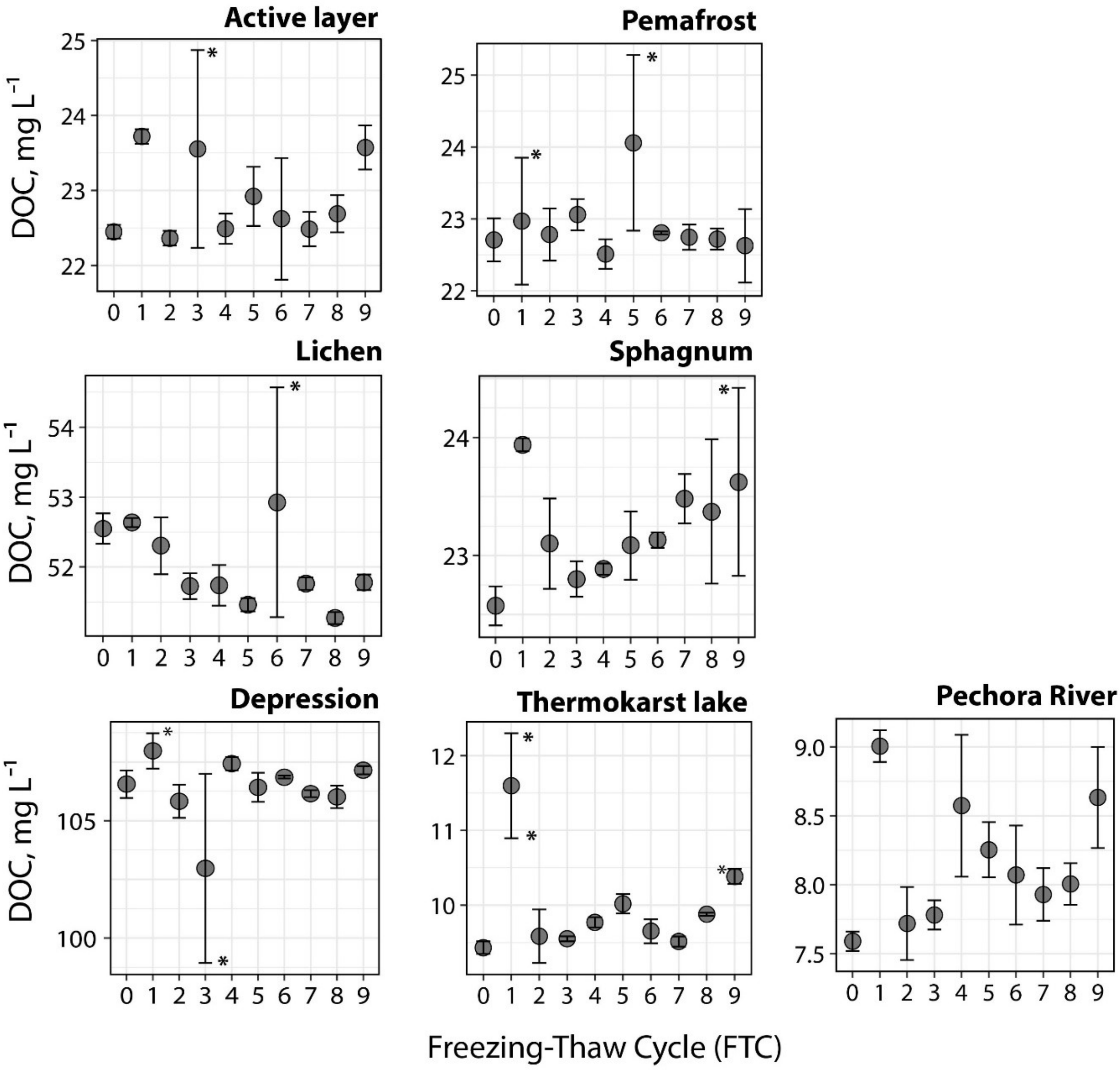

Figure 1: DOC concentration during FTC for each type of waters incubations. "*" indicates the replicate for which data is considered as outliers by boxplots analyses.

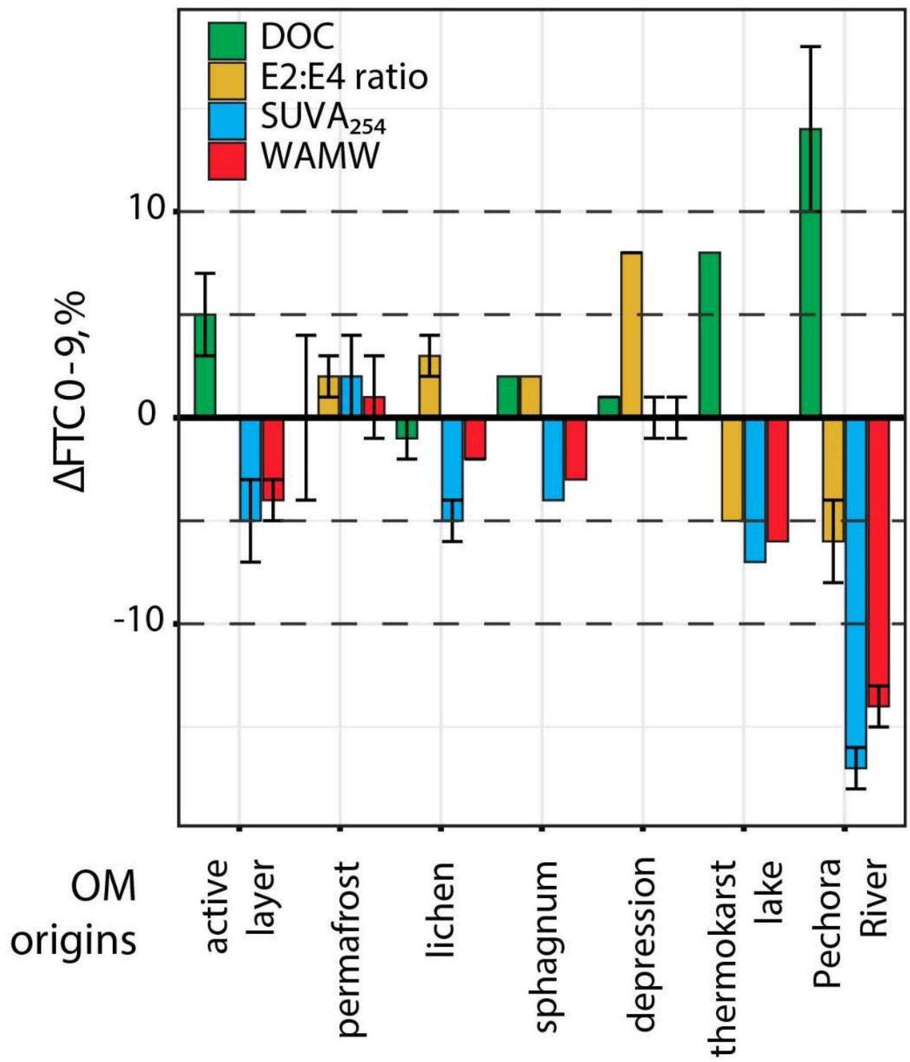

Figure 2: Percent variation (Δ, %) of DOC quantity and quality parameters (DOC concentration, $SUVA_{254}$, E2:E4 ratio and Weight-Average Molecular Weight (WAMW)) between final (FTC 9) and initial (FTC 0) steps of the freezing-thawing experiment. Error bars presented here reflect the standard deviation of replicates.

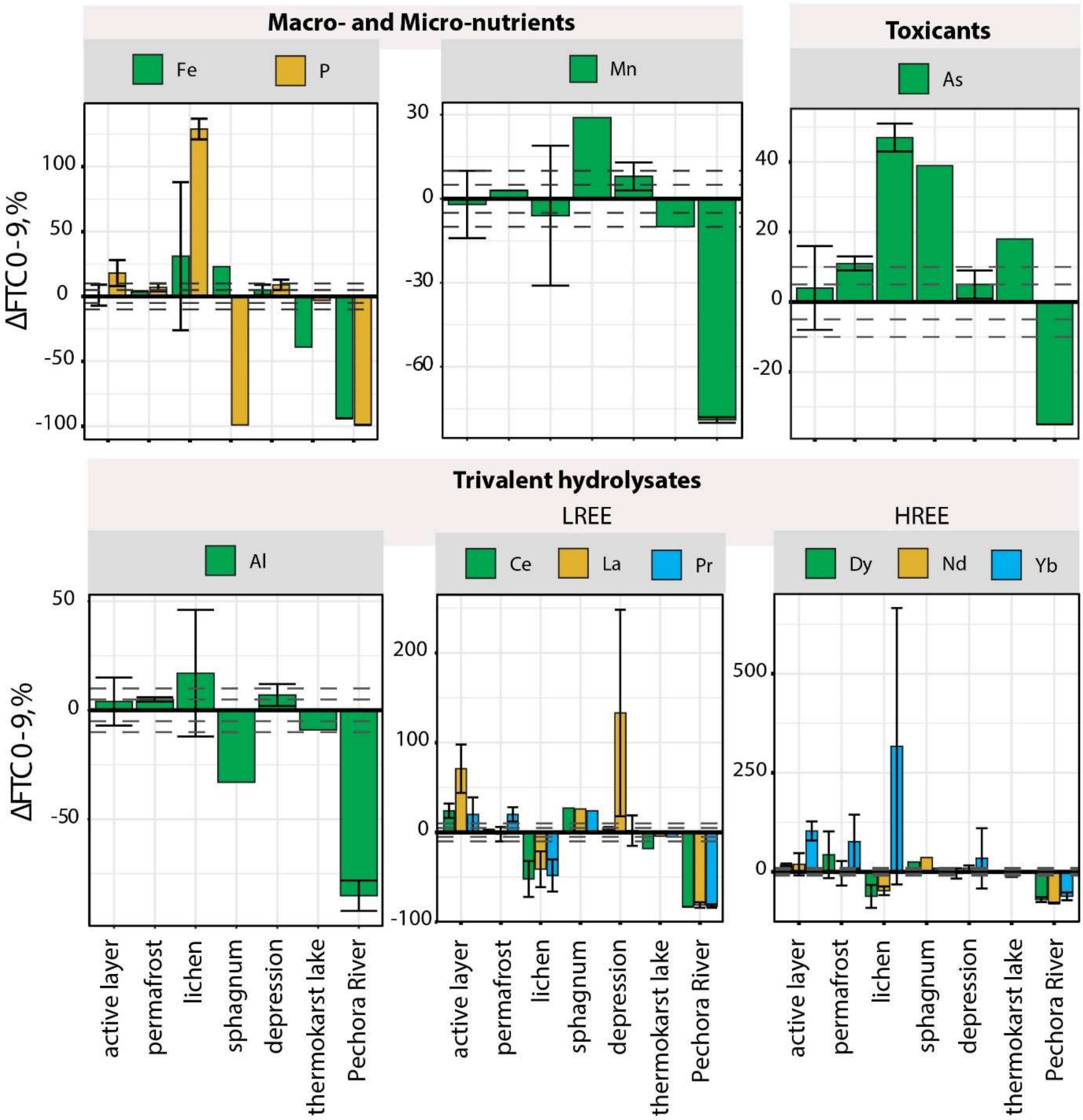

Figure 3: Percent variation of trivalent hydrolysates (Al, Light and Heavy Rare Earth Elements (LREE and HREE)), Macro- and Micro-nutrients (Fe, P, and Mn) and toxicant (As)concentrations between the last and the initial stage of FTC (ΔFTC0-9). Vertical dashed lines indicate variations of 5 and 10% (under and above 0). Errors bars represent the variation between replicates.

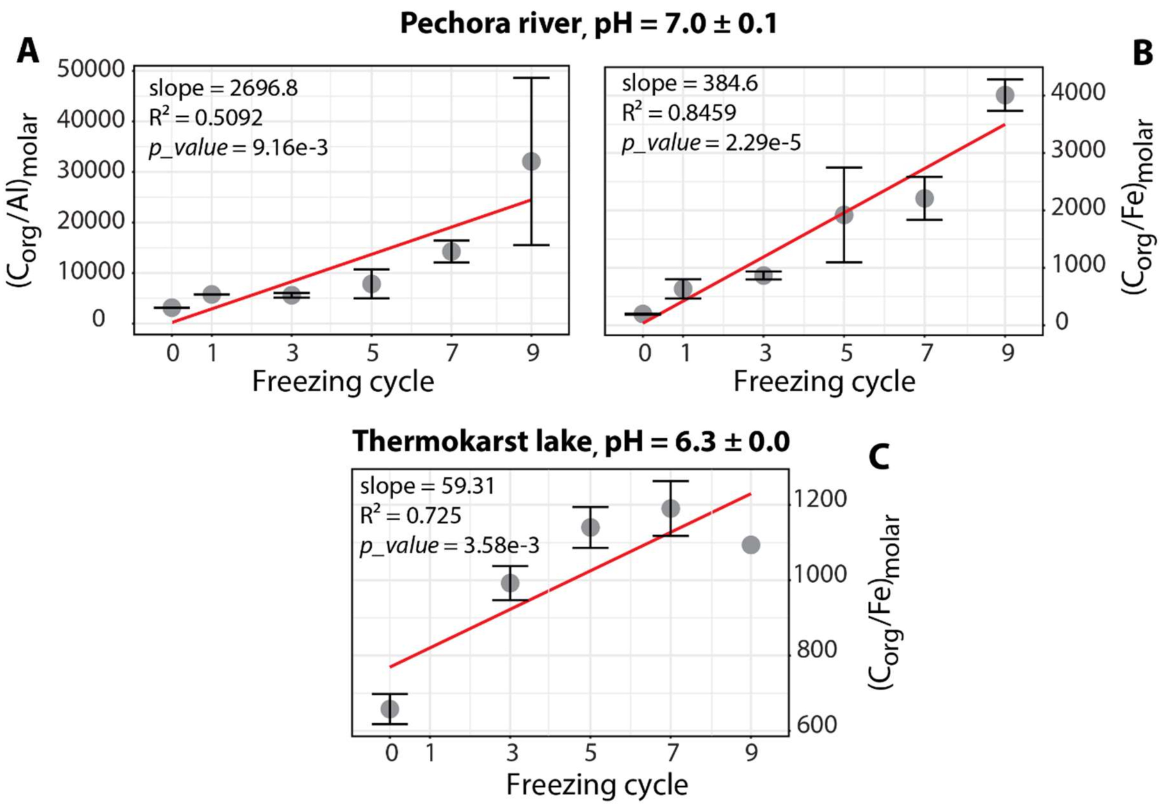

Figure 4: The molar ratio of C_{org} (A) to Al and (B) to Fe for the Pechora River substrate, and the molar ratio of C_{org} (C) to Fe for the thermokarst lake in the course of FTC. The red lines represent the linear regression. Error bars represent the variation between replicates.