Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-528
Manuscript under review for journal Biogeosciences
Discussion started: 14 January 2019


# Humic surface waters of frozen peat bogs (permafrost zone) are highly resistant to bio- and photodegradation

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Key words: depression, stream, river, organic carbon, photolysis, respiration, palsa, permafrost

**Bullet points:**

- Low (< 10%) concentration of bio- and photo-degradable DOM in humic waters from frozen peatlands, discontinuous /continuous permafrost zone
- Low importance of biodegradation and photolysis on DOC processing and $CO_2$ evasion in surface waters of permafrost-affected peatland regions.
- The paradigm of the importance of photolysis and biodegradation in DOC processing in surface waters from permafrost region is challenged for the case of frozen peatlands
- We hypothesize the peat porewater DOM processing and respiration of sediments as main drivers of elevated $pCO_2$ concentration and emission in humic boreal waters of frozen peat bogs.

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**Abstract**

Bio- and photo-degradation of dissolved organic matter (DOM) is identified as dominant vector of C cycle in boreal and high-latitude surface waters. In contrast to large number of studies of humic waters from permafrost-free regions and oligotrophic waters from permafrost-bearing regions, the bio- and photo-lability of DOM from humic surface waters of permafrost-bearing regions has not been thoroughly evaluated. Following standardized methods, we measured biodegradation (low, intermediate, high temperature) and photodegradation (one intermediate temperature) of DOM in surface waters along the hydrological continuum (depression → stream → thermokarst lake → river Pechora) within a European Russian frozen peatland. In all systems, there was no measurable (≥ 10%) bio- or photodegradation of DOM over 1 month of incubation. It is possible that the main cause of the lack of degradation is the dominance of allochthonous refractory (soil, peat) DOM in all studied waters. Yet, all surface waters were supersaturated with $CO_2$. Thus, this study suggest that, rather than bio- and photo-degradation of DOM in the water column, other factors such as peat porewater DOM processing and respiration of sediments are the main drivers of elevated $pCO_2$ and emission in humic boreal waters of frozen peat bogs.

## Introduction

Boreal and subarctic waters contain large amounts of plant, soil, and peat-originated dissolved organic matter (Wilkinson et al., 2013; Kaiser et al., 2017), and the proportion of land-derived organic carbon in waters is likely to increase with ongoing permafrost thaw (Wauthy et al., 2018). Heterotrophic bacteria degrade this DOM (Karlsson, 2007; McCallister and del Georgio, 2008), causing net heterotrophic conditions (Gross Primary Productivity < Respiration) and $CO_2$ emission to the atmosphere from surface waters (Ask et al., 2012; Lapierre et al., 2013). Between 10% and 40% of the dissolved organic carbon (DOC) in lakes,



60 rivers and soil waters of the boreal zone may be available for bacterial uptake over a time frame
61 of several weeks (Berggren et al., 2010; Roehm et al., 2009). The biodegradability of DOM
62 leached from permafrost and non-permafrost soils was recently reviewed by Vonk et al. (2015)
63 who concluded that aquatic DOC is more biodegradable in regions with continuous permafrost
64 compared to regions without permafrost. At the same time, among all Arctic rivers, the highest
65 annual (20%) and winter (ca. 45%) biodegradable DOC (BDOC) was reported for the Ob River,
66 draining through peatlands with minimal influence of permafrost (Wickland et al., 2012).
67 Further, based on 14 studies of BDOC and their own research, Vonk et al. (2015) demonstrated
68 zero BDOC loss in aquatic systems without permafrost, which is contradictory to general
69 understanding of biodegradation of aquatic DOM as major driver of $CO_2$ emission in boreal
70 waters. It is also important to note that all the available bio-degradation studies of inland waters
71 in permafrost regions dealt with either mountain regions with essentially mineral soil substrates
72 in Alaska or Canada (Holmes et al., 2008; Wickland et al., 2012; Ward et al., 2017) or with the
73 yedoma soils of Eastern Siberia (Mann et al., 2014, 2015; Spencer et al., 2015).

74 Similarly, although the photolysis of dissolved organic matter (DOM) in boreal and
75 subarctic aquatic environments contributes to $CO_2$ emission from the inland waters to the
76 atmosphere (Cory et al., 2014), the overwheling majority of photo-degradation studies in the
77 Arctic were conducted on oligotrophic lake waters and streams draining mineral soils of
78 mountain regions (Ward and Cory, 2016; Cory et al., 2013, 2015). The dominance of photolytic
79 processes in DOM processing in arctic waters was reported for N America (Cory et al., 2014;
80 Ward et al., 2017), Canadian surface waters of the temperate zone (Winter et al., 2007; Porcal
81 et al., 2013, 2014, 2015), and small Swedish humic-rich headwater catchments (Köhler et al.,
82 2002). In contrast, several other studies from Scandinavia (Groeneveld et al., 2016; Koehler et
83 al., 2014), Canada (Laurion and Mladenov, 2013; Gareis and Lesack, 2018) and NW Russia
84 (Oleinikova et al., 2017; Chupakova et al., 2018) demonstrated sizeable removal of colored

(chromophoric DOM) but quite small (≤ 10%) impact of sunlight irradiation on bulk DOC concentration in streams, rivers and lakes.

The controversies in both bio-and photo-degradation capacity of surface waters from the arctic regions described above clearly call a need for further studies of these processes, encompassing wider range of aquatic settings. The numerous surface waters located within discontinuous to continuous permafrost zone of Northern Eurasia, where most aquatic systems are drained through frozen peat rather than mineral substrates, are poorly studied regarding bio- and photo-degradability of aquatic DOM. Yet, these regions (NE European Russia or Bolshezemelskaya tundra, Western Siberia Lowland, Northern Siberian Lowland, Kolyma and Yana-Indigirka Lowland) occupy > 2 million km² which is more than 10% of overall permafrost-affected land area and exhibit, in average, ten times higher concentration of soil organic C in the form of 0.5 to 3 m thick peat layer than the rest of the circumpolar regions. As a result of the dominance of histosols, the surface waters draining frozen peatlands are enriched in DOC compared to other permafrost-affected regions (Manasypov et al., 2014; Pokrovsky et al., 2015) and may provide disproportionally high contribution to overall DOM bio- and photo-degradability in the Arctic and subarctic regions.

Numerous experiments in permafrost-bearing and permafrost-free aquatic environments on mineral soil substrates relatively poor in DOC demonstrated that the headwater streams and soil leachate contain most bio-degradable and photo-degradable DOM (Ilina et al., 2014; Mann et al., 2014, 2015; Larouche et al., 2015; Spencer et al., 2015; Vonk et al., 2015). Thus, we hypothesized that, given rather oligotrophic (nutrient-poor) nature of Sphagnum peat from histosols, the bioavailability of essentially recalcitrant DOM in surface waters of frozen peatlands will be low. However, we expected a gradient in the degree of bio- and photo-lability of DOM from permafrost subsidence, head water stream, thermokarst lake and large river, corresponding to the increase in water residence time (Mann et al., 2012).

To test these hypotheses, we used recommended standardized protocol for DOM biodegradation (Vonk et al., 2015) and applied it for 4 main aquatic components of a hydrological continuum 'permafrost subsidence → small stream → large thermokarst lake → large river (Pechora)'. We chose the largest frozen peatlands in Europe, the Bolshezemelskaya Tundra of NE European Russia which is represented by flat-mound (palsa) peat bog (discontinuous and continuous permafrost zone) and belongs to the watershed of the largest European permafrost-affected river, Pechora. Specific questions of this study were (*i*) to asses the difference in BDOC and photodegradable (PDOC) fraction of DOM in surface waters of frozen peat bog along the hydrological continuum, from permafrost depression to large rivers, (*ii*) to relate the BDOC and PDOC concentrations to the snapshot $CO_2$ concentration and emission, and (*iii*) to quantify the impact of temperature on biodegradation potential of surface waters from frozen peatbogs and predict possible impact of warming on DOM biodegradation efficiency. We measured very low bio- and photo-degradability of aquatic DOM from frozen Arctic peatland which may require revisiting the current paradigm of the importance of bio- and photodegradation of DOC in permafrost regions; this should be taken into account for pan-Arctic modeling of C biogeochemical cycle in continental waters.

## 2. Study site and methods

### *2.1. Geographical context and hydrological continuum of the Pechora River basin*

The water samples were collected in the end of July 2017 within the BolsheZemelskaya Tundra (BZT) peatland (continuous to discontinuous permafrost zone), which belongs to the Pechora River watershed (**Fig. S1)**, the largest European Arctic river draining permafrost-bearing terrain (watershed = 322,000 km²; mean annual discharge is 4140 $m^3/s$). The northern part of the Pechora watershed is covered by permafrost: discontinuous on the eastern part and sporadic to isolated on the western part (Brittain et al., 2009). 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 histosols of peat bogs and podzol-gleys in the southern forest-tundra zone. 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.

We sampled surface waters along the typical hydrological continuum, consisting of 1) depression in the moss and lichen cover of upland frozen peat bog, filled by water from thawing of ground ice (permafrost subsidence, 2.5 x 3 m size and 0.3 m depth); 2) small stream (~2 km length) originated from upland peat bog; 3) small thermokarst lake Isino ($S_{area}$ = 0.005 km²) located within the peat bog, and 4) the Pechora River mainstream. Similar principle of the hydrological continuum was considered in the Kolyma River biodegradation experiments (Mann et al., 2012). The list of sampled water objects together with their physical, chemical characteristics and parameters of $CO_2$ system is presented in **Table 1.** The surface waters were collected from the shore (depression and stream) or the PVC boat (r. Pechora and Lake Isino). The water samples were placed into 2-L Milli-Q pre-cleaned PVC jars and kept refrigerated until arrival to the laboratory, within 2-3 h after collection.

*2.2. Experimental set-up*

2.2.1. Biodegradation

For biodegradation assays we followed the standardized protocol for assessing biodegradable DOC of Arctic waters (Vonk et al., 2015). To facilitate the implementation of recommended protocol, we used exactly the same filter towers, inline filter holders, and vacuum devices as depicted in Vonk et al. (2015). Initial samples were filtered through pre-combusted

(4.5 h at 450°C) Whatman GF/F filters of nominal poresize 0.7 µm. All the manipulations were performed in laminar hood box (class A100) under sterile environment; the working space was sterilized by UV light before preparation. Triplicate 30 mL aliquots of 0.7 µm-filtered water were placed into pre-combusted (4.5 h at 450°C) dark borosilicate glass bottles of 40 mL volume, without nutrient amendment and stored at 23±1°C in the dark in thermostat. The bottles were closed with sterilized PVC caps. As recommended, the caps were left loose and the bottles were shaken manually once a day avoiding the liquid touching the cap. The incubated samples were re-filtered through pre-combusted 0.7 µm GF/F filters using sterilized dismountable Sartorius 25 mm filter holder and a cleaned sterile syringe after 0, 2, 7, 14 and 28 days of exposure. Al handling and sampling of bottles was performed in the laminar hood box under sterilized workspace. Filtered samples were acidified with 30 µL of concentrated (8.1 M) double distilled HCl, tightly capped and stored in the refrigerator between 1 and 2 month before DOC analyses. Non-acidified portion of filtrate was used for pH, Specific Conductivity, DIC and $UV_{254\ nm}$ and optical spectra measurement. Control runs were 0.22 µm sterile-filtered water which was incubated in parallel to experiments and re-filtered through 0.7 µm GF/F filters at the day of sampling.

In addition to this 'classic' protocol, we used alternative procedure of biodegradation experiments to test maximally possible DOM removal by bacteria. For this, we replaced initial 0.7 µm GF/F filtration by 3 µm filtration through sterilized Nylon Sartorius membranes, to increase the amount of bacterial cells capable to degrade DOM during incubation. The reason for that is that conventional 0.7 µm (GF/F) filtration might remove too many microbial cells. Besides, re-filtration through the same filter pore size (0.7 µm) recommended in classic protocol may not necessarily remove the newly formed microbial biomass as the cell size of bacteria grown during incubation may not exceed 0.7 µm. In this regard, initial 3 µm-filtration is equivalent of 100% inoculum used by Vonk et al. (2015) and can be considered as maximal

enhancement of DOM biodegradation without addition of nutrients. Further, instead of 0.7 µm refiltration for sampling, we employed 0.22 µm filter pore size for DOC samplings during incubation. This allowed to remove all particulate organic carbon formed via microbial metabolism, as well as some newly grown microbial cells and therefore should enhance the degree of biodegradation calculated as the difference between initial 3 µm-filtration and 0.22 µm filtration at the date of sampling. The control runs were filtered through sterile 0.22 µm filters and incubated parallel to the experiments, following the standard approach for control abiotic experiments in incubation experiments (Köhler et al., 2002). They were re-filtered through 0.22 µm membrane at the day of experimental sampling. To insure the lack of DOC release from sterilized Nylon membrane, we run blank (Milli-Q) filtration through both 0.7 µm GF/F and 0.22 µm Nylon filters; in both cases the DOC blank was below 0.1-0.2 mg/L which is less than 1% of DOC concentration in our samples. The glass bottles were incubated in triplicates at 4±2°C, 22±1°C and 37±3°C using refrigerator and incubators and agitated manually at least once a day over 4 weeks of exposure.

2.2.2. Photodegradation

For photodegradation incubations, water samples of all sites except the river were collected in polypropylene jars and sterile filtered (0.22 µm Nalgene Rapid-Flow Sterile Systems) within 2 h of sampling and refrigerated. Note that the 0.22 µm sterile filtration is the only way of conducting photodegradation experiments, given that the autoclave sterilization of DOM-rich natural water would coagulate humic material and thus is not suitable (Andresson et al., 2018). In this regard, we followed conventional methodology in this field which is exposure of 0.2 µm-sterile filtered samples in quartz reactors in the outdoor pool (Vähätalo et al., 2003; Chupakova et al., 2018; Gareis and Lesack, 2018), solar simulator (Lou and Xie, 2006; Amado et al., 2014) or directly in the lake water (Laurion and Mladenov, 2013; Groeneveld et al., 2016).



The filtrates were transferred under laminar hood box into sterilized, acid-washed quartz tubes (150 mL volume, 20% air headspace) and placed at 3±2 cm depth into outdoor pool which was filled by river water having the light transparency similar to that of the Pechora River (1.5-2.0 m Secchi depth). In-situ measurements of sunlight intensity were conducted using submersible sunlight sensor. The outdoor pools were placed under unshaded area, at the latitude similar to that of the sampling sites. Slight wind movement and regular manual shaking allowed for sufficient mixing of the interior of reactors during exposure. All the experiments were run in triplicates. The water temperature was 19±3°C over 28 days of exposure (18 July - 8 August), with an average magnitude of diurnal water temperature variation of 6°C (recorded every 3 h using EBRO EBI 20 Series loggers). The day light intensity was typically between 5,000 and 20,000 lux (in average 10,000 lux or 14±5 W/m²) which is within the range of solar radiation at the latitude of the polar circle in the end of July - beginning of August. We have chosen 4 weeks exposure time for consistency with biodegradation experiments described above and following the previous studies on photodegradation under sunlight, which is typically from 15 to 70 days (Moran et al., 2000; Vähätalo and Wetzel, 2004; Mostofa et al., 2007; Helms et al., 2008; Chupakova et al., 2018). Dark control experiments were conducted in duplicates, using sterilized glass tubes filled by sterile 0.22 µm-filtered water, wrapped in Al foil and placed in the same outdoor pool as the experiments. The headspace (approx. 20% of total reaction volume) was similar in experimental and control reactors. The individual reactors were sterile sampled at the beginning and at the $2^{nd}$, $7^{th}$, $14^{th}$, $21^{th}$ and $28^{th}$ day of exposure. Each sampling sacrificed the entire reactor. The MilliQ blanks were collected and processed to monitor for any potential sample contamination introduced by our filtration, incubation, handling and sampling procedures. The organic carbon blanks of filtrates never exceeded 0.2 mg/L.

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235 *2.3. Analyses and treatment*

236 The temperature, pH, $O_2$ and specific conductivity in surface waters were measured in
237 the field as described previously (Shirokova et al., 2013b). Dissolved $CO_2$ concentration was
238 measured using portable submersible Vaissala Carbocap® GM70 Hand-held carbon dioxide
239 meter with GMP222 probes (accuracy 1.5%). The diffusional $CO_2$ flux was calculated using
240 wind-based model (Cole and Caraco, 1998) with $k_{600} = 2.07 + 0.215 \times u_{10}^{1.7}$, where $u_{10}$ is the wind
241 speed at 10 m height. In the filtrates, we measured optical density at 254 nm and at selected
242 wavelengths (365, 436 and 470 nm) of the visible spectrum, the concentration of dissolved
243 organic and inorganic carbon (DOC and DIC, respectively). The DOC and DIC were analyzed
244 by high-temperature catalytic oxidation using TOC-VCSN, Shimadzu® (uncertainty ± 2%, 0.1
245 mg $L^{-1}$ detection limit). The DIC was measured after sample acidification with HCl and DOC
246 was analyzed in acidified samples after sparging it with C-free air for 3 min at 100 mL $min^{-1}$ as
247 non-purgable organic carbon (NPOC). Selected quartz reactors in photodegradation
248 experiments were used to measure dissolved $O_2$ using Oxi 197i oximeter with a CellOx® 325
249 galvanic submersible sensor (WTW, Germany; ± 0.5% uncertainty). For this, the $O_2$ galvanic
250 sensor was introduced into the quartz tube immediately after opening of the reactor and allowed
251 to equilibrate for 5-10 min while protecting the open end of the tube from the exchange with
252 atmospheric oxygen via wrapping it in Al foil. All filtered sampled collected from photo-
253 degradation experiments were acidified with ultrapure nitric acid and analyzed for major and
254 trace elements following procedures employed in GET (Toulouse) for analyses of boreal humic
255 waters (Oleinikova et al., 2017, 2018).

256 To account for possible microbial development in biodegradation experiments, we
257 performed oligotrophic and eutrophic bacteria count in the course of incubation, following the
258 standard methodology used in biodegradation experiments of peat waters (Stutter et al., 2013)
259 as also decsribed previously (Shirokova et al., 2017b; Chupakova et al., 2018). In addition, we

measured total bacterial number and quantified the dominant cell size morphology using DAPI fluorescence method (Porter and Feig, 1980). Control experiments did not demonstrate the presence of any countable cells in the observation fields.

The bio- and photodegradable DOC (BDOC and PDOC, respectively) were calculated in percent loss relative to control at each sampling time point *t* (0, 2, 7, 14 and 28 days) according to:

$$BDOC(\%)_t = 100\% \times (DOC_{t,\,control} - DOC_t)/DOC_{t,\,control} \quad (1)$$

Alternatively, the BDOC and PDOC were calculated in percent loss at time point *t* relative to the initial concentration of DOC ($DOC_{t=0}$) following Vonk et al. (2015):

$$BDOC(\%)_t = 100\% \times (DOC_{t=0} - DOC_t)/\ DOC_{t=0} \quad (2)$$

For most treatments and sampled waters, the difference between two methods of bio-/photodegradabale DOC concentration was statistically negligible. Note that in case of negative values provided by Eqn. 2, the BDOC was taken as 0% following the conventional practice in biodegradation experiments (Vonk et al., 2015). The uncertainties of BDOC % numbers were between ±5 and ±10% for experiments, at 4, 23 and 37°C using modified (3 µm and 0.22 µm filtration) protocol. In 'classic' protocol (0.7 µm GF/F filtration) the uncertainties were as high as 15-20% at the end of experiment. We believe that such high uncertainties are linked to high initial DOC concentration, triplicate measurements and simultaneous monitoring of experimental and control runs.

Statistical treatment included the least squares method and the Pearson correlation, because the data were normally distributed. The ANOVA method was used to test the differences in the average DOC concentration versus time in incubation experiments and in the controls and to assess the difference between the light experiments and the dark control for photo-degradation experiments.

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## 3. Results

### *3.1. Assessment of biodegradable DOC*

The waters of hydrological continuum within the Pechora River basin are highly diverse (**Table 1**), with pH range from 3.8 (frozen peat depression) to 6.9 (r. Pechora). The soluble salts concentrations are low as the specific conductivity ranged from 20±10 µS $cm^{-1}$ (stream, thermokarst lake) to ~60 µS $cm^{-1}$ in the peat bog depression and the Pechora River. The DOC concentration decreased from 44 mg/L in frozen peat depression to ~8 mg/L in the Pechora River following the order of water residence time (flow direction) "depression >> stream ≥ thermokarst lake > r. Pechora". The DOC concentration was generally similar (within ± 2%) between 3, 0.7 and 0.22 µm pore size filtration of the initial sample, in agreement with former size fractionation measurement in Arctic and subarctic systems (Vasyukova et al., 2010; Pokrovsky et al., 2012, 2016). All sampled surface waters exhibited $CO_2$ supersaturation with respect to atmosphere (from 440 to 2400 ppm) and net $CO_2$ emission (diffusion) flux ranging from 34 to 74 mmol $CO_2$ $m^{-2}$ $d^{-1}$ (**Table 1**).

In both protocols of biodegradation experiments, two major features were noted: (1) the concentrations of 0.7 µm and 0.22 µm-filtered DOC did not decrease during the exposure and (2) there was no sizable (> 10%) difference between the control run and the incubation experiment (**Fig. 1)**. By 'classic' protocol of biodegradation experiments (0.7 µm GF/F filtration) at 23°C, the BDOC fraction ranged between 0 and 10 % for all surface waters. The modified procedure (3 µm initial filtration and 0.22 µm sampling) did not detect any significant biodegradation for any of the studied waters (average equaled to **5±5%** at 4, 23 and 37°C, **Fig. 2 B, C, D**). The DIC concentrations increased only in stream water incubated at 37°C, where we measured ~10% increase over 28 days of exposure (not shown). This increase was equal to 0.2 mg/L of DIC. Note that equivalent decrease in DOC concentration could not be assessed,



309 presumably due to high DOC concentration (17 mg/L) and the intrinsic uncertainty on NPOC
310 analyses (2%) which did not allow measuring C change smaller than 0.3 mg/L.

311 The $UV_{254\ nm}$ absorbency of samples in the course of dark aerobic exposure
312 demonstrated slight decrease with time (ca., between 5 and 10% over 28 days) in peat bog
313 depression by 'classic' protocol (**Fig. S2** of **Supplement**). However, in all other treatments, the
314 control was indistinguishable from experimental runs and the $SUVA_{254}$ remained constant
315 within the uncertainties of triplicates (ca., ±5 to ±10%).

316 The microbial consortium of all systems was dominated by cocci (0.23 µm median size)
317 and rods (0.96 x 0.20 µm) as revealed from DAPI fluorescent imaging. The number of
318 culturable oligotrophic bacteria increased by a factor of ~ 100 after first 2-7 days of exposure
319 at 23°C both in GF/F-filtered and 3µm-filtered samples, and then remained stable at ca. 10,000
320 to 20,000 CFU $mL^{-1}$ till the end of experiments (**Fig. S3 A, C**). The highest concentration of
321 oligotrophic bacteria was observed in the Pechora River, where as the other samples were not
322 significantly different between each other. The CFU value at 4°C ranged between 1000 and
323 5000 CFU $mL^{-1}$ and did not demonstrate any clear pattern with time of incubation (**Fig. S3 B**).
324 The number of eutrophic bacteria ranged between 1,000 and 15,000 CFU $mL^{-1}$ following the
325 order: r. Pechora > stream ≥ peat bog depression ≥ thermokarst lake. There was no growth of
326 eutrophic or oligotrophic bacteria at 37°C. The total cell number gradually increased in the
327 course of experiment at 23°C with maximal changes observed in peatbog depression and the
328 Pechora River (**Fig. S3 D**). There was a progressive increase of rod-shaped bacillus relative to
329 coccus in the Pechora River and a permafrost stream whereas the thermokarst lake and peatbog
330 depression did no exhibit any systematic change in dominant bacteria morphologies during the
331 biodegradation experiments.

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334 *3.2. Photodegradation of DOM from frozen peatlands*

335 The pH of exposed samples did not exhibit any systematic variation within 0.5 pH unit.
336 The DIC remained fairly stable (within 0.5 mg/L) without any significant ($R^2 < 0.5$; $p > 0.05$)
337 change during incubation, regardless of the type of system, DOC and DIC concentration (not
338 shown). The exposed water remained oxygenated (average $O_2$ saturation close to 90%) with no
339 detectable change (i.e. > 10%) over the course of experiment. Specifc conductivity also
340 remained highly stable over full period of exposure.

341 The bacteria count in photo-degradation reactors at the beginning of exposure and after
342 14 and 28 days of incubation yielded between 1 and 100 CFU $mL^{-1}$. This is a factor of 100 to
343 1000 lower than the number of cells in experiments of bio-degradation run in non-sterilized
344 waters over the same duration of experiments (section 3.1). As such, the microbial degradation
345 was considered negligible at our experimental conditions.

346 There was no sizeable decrease in DOC concentration during 28 d of exposure to
347 sunlight (**Fig. 3 A**). This relative change of DOC concentration ranged from -5 % to +5 % and
348 it did not exceed the non-systematic variability among triplicates. Although the triplicate agreed
349 within less than 2 % (the symbol size in **Fig. 3**), the small change of DOC in peat depression
350 was similar in light experiment and dark control. The % PDOC (relative to starting solution) as
351 a function of exposure time over 28 days of experiment ranged from 0 to 5% in peatbog
352 depression and 0 to 10% in thermokarst lake and permafrost spring (**Fig 3 B**).

353 The $SUVA_{254\ nm}$ in photodegradation experiments decreased much stronger than the
354 DOC. The SUVA decrease relative to control was mostly pronounced in permafrost stream
355 (**Fig. 4**). The optical properties of DOC demonstrated sizeable decrease of $E_{365}/E_{470}$ ratio
356 corresponding to UV/vis absorbing functional groups (**Fig. S4 A),** which was consistent with
357 decreasing $SUVA_{254\ nm}$ during sunlight exposure. The $E_{254}/E_{436}$ ratio, corresponding to

autochthonous vs. terrestrial DOM, did not demonstrate any sizeable change over the course of experiment **(Fig. S4 B).**

Most of major and trace elements did not show any significant (at $p < 0.05$) change in concentration over the photodegradation experiments. Only a few nutrients (P, Fe, Zn, B) and trace metals (Zn, Ti, V, Zr, Nb and Th) demonstrated a decrease in concentration. The decrease of Fe was mostly pronounced in permafrost stream, and did not occur in permafrost depression (**Fig. 5 A**) whereas total dissolved phosphorus systematically decreased, by 20 to 50%, over 28 days of sunlight exposure in permafrost depression, thermokarst lake and permafrost stream (**Fig. 5 B**). A decrease of Ti, Zn, Nb and Th also occurred in thermokarst lake and permafrost stream (not shown). Overall, the magnitude of decrease of P, Fe, Ti, V and Zn in photodegradation experiments followed the order "permafrost stream > thermokarst lake > permafrost depression".

## 4. Discussion

### *4.1. High stability of dissolved organic matter to bio degradation in surface waters from frozen peatland*

The unexpected result of this study was very low BDOC fraction, measured not only in large river (Pechora) but also in small stream, thermokarst lake and peatland depressions formed due to permafrost subsidence. According to compilation of available biodegradation studies, the BDOC fraction (28 days) ranges from 3 to 18% (mean 13%) in waters of continuous permafrost zone and from 5 to 15% (mean 14%) in discontinuous permafrost zone (Vonk et al., 2015). This is higher than the 0 to 10 % of BDOC measured for all water objects from the discontinuous permafrost zone in this study. Note that very few biodegradability studies in aquatic systems dealt with frozen peatlands, and all previous incubation experiments used water

from mountainous regions on mineral soils and rocks in Scandinavia, Alaskan slope and Canada, yedoma regions of Eastern Siberia, or the Yenisey basin. Only one former biodegradation study in peat mire context demonstrated sizable bioavailability of soil aquatic leachate to lake water bacteria (Roehm et al., 2009), but this work did not deal with pure aquatic endmember, unlike this study. Instead, the BDOC of frozen peatlands surface waters measured for the Bolshezemelskaya Tundra inland waters was comparable with the value suggested by Vonk et al (2015) for non-permafrost aquatic DOC (0-1 %).

Another important point revealed in previous work on biodegradation of Arctic waters is that aquatic BDOC in large streams and rivers decreased as the Arctic summer progressed (Vonk et al., 2015), although this pattern was absent for soils and small streams. In our case, thermokarst lake Isino and r. Pechora can be considered as sufficiently large hydrological systems. The sampling was performed in the end of July which is already summer baseflow period and as such 0 to 5 % biodegradable DOC measured for Isino and Pechora in this study is comparable with 0 to 20% BDOC loss reported in large streams and rivers at ~200 Julian day (Vonk et al., 2015). However, small stream and permafrost subsidence remain clearly at the very low edge of BDOC % lost reported for soils and streams in summer. In the estuarine zone of largest European Arctic permafrost-free river, Severnaya Dvina, there was no measurable biodegradation in spring, when the DOM was dominated by allochthonous sources, but a 15 to 20% decrease of DOC occurred during first 300 h in river water collected in August, when sizeable phytoplankton productivity was observed (Shirokova et al., 2017b). In laboratory experiments with individual cultures, moss and peat leachates were also sizably biodegraded over 1-2 days of exposure (Shirokova et al., 2017a), whereas the same bacterial species were not capable degrading DOM from surface waters draining peatland and moss covered bogs (Oleinikova et al., 2018). This is consisted with a priming effect, a possible mechanism by which inputs of biolabile DOC from plant litter enhance the bioavailability of stable DOC

components in aquatic systems, resulting in higher rates of microbial remineralization (Textor et al., 2018).

Mechanistic reasons for extremely low bioavailability of DOC from studied peatlands remain unclear and require in-depth analysis of DOM molecular structure and stoichiometry as well as high resolution microbial approaches. It is known that the DOM released from frozen soils contains high proportions of biologically labile protein-like and photochemically reactive aromatic substances (Gao et al., 2018). Following the pioneering study of Ward et al. (2017), we hypothesize that, similar to DOC from organic (non-permafrost) layer, the concentration of high-lability, aliphatic-like DOC in surface waters of frozen peatlands is too low to sustain microbial population, or that this aquatic DOC, remaining after microbial processing of soil porewater DOC is of low lability for microbes capable to degrade aliphatic-like DOC and inhabiting aerobic zone of permafrost surface waters. The constant pattern of $UV_{254}$ absorbency in biodegradation experiment was consistent with negligible change in BDOC over 28 days of incubation. In comparison, the biodegradation of peat water from European boreal zone was associated with an increase in SUVA by up to 7.4 %, which also implies an increase in the proportion of aromatic compounds (Hulatt et al., 2014). The total bacterial number in studied surface waters $(0.5\text{-}5)\times10^6$ cell $mL^{-1}$ is in excellent agreement with other studies of thermokarst peatland lake waters (Deshpande et al., 2016). Following these researchers, we suggest that the reason of low biodegradability of peatland humic waters is that the majority of active bacteria are associated with particles (> 3 μm) rather than present as free-living cells (< 1 μm) capable to DOC processing. However, further mechanistic studies of model aquatic bacterial communities capable to affect the degradation of DOM from different terrestrial sources are necessary (Logue et al., 2016).

Interestingly, there was no measurable difference in BDOC at 4, 23 and 37°C, as the proportion of BDOC at all temperatures for each system was below 5%. This result allows



433 preliminary prediction of possible consequence of climate change and surface water heating in
434 high latitudes. In a short-term climate warmings scenario, or assuming fast heating of surface
435 waters due to prolonged heat wave of draught occurring both in European, permafrost-free (see
436 Shirokova et al., 2013a) and western Siberian (Pokrovsky et al., 2013) permafrost-bearing
437 peatlands, we do not foresee any measurable change in biodegradability of DOM from the water
438 column. Under even most extreme heating scenario of thermokarst lakes, river and depressions
439 of the frozen peatland territories, the short-term bio-processing of aquatic DOM may remain
440 close to zero.
441
442 *4.2. Negligible impact of photodegradation on DOM transformation in inland waters of*
443 *frozen peatlands*
444 The second main result of this work was high stability of surface waters DOM to
445 sunlight exposure. Over 28 d of incubation in outdoor pools at the conditions corresponding to
446 surface (< 0.05 m depth) water layer of thermokarst lakes and streams from permafrost zone,
447 the change in DOC concentration was less than **5-10%** of the initial value and was not
448 distinguishable from that in the dark control (**Fig. 3 A, B**). Therefore, the DOM of all frozen
449 peatland is quite refractory and not subject to measurable photodegradation over 4 weeks of
450 exposure. This time is comparable with the water residence time in small depressions of the
451 frozen peatland (Novikov et al., 2009) and small thermokarst thaw ponds of frozen palsa
452 peatbog (Manasypov et al., 2015) but much higher than the water travel time in small streams
453 (< 10 km long) and in the lower reaches of Pechora river, from the site of sampling till the
454 Arctic Ocean (ca. several days). This result apparently contradicts the recent paradigm that the
455 photochemical oxidation may account for 70 to 95% of total DOC processed in the water
456 column of arctic lakes, rivers and soils (Cory et al., 2013, 2014; Ward and Cory, 2016; Ward et
457 al., 2017). However, the conclusion of this group of authors is based on study of distilled water



458 leachates of mineral soils, headwater streams, fresh permafrost thaw sites and lakes of N.
459 Alaska slopes, developed on mineral substrates. In contrast, the results of DOM photolysis in
460 polygonal and runnel ponds located in frozen peatlands (2 m peat, 40-60 cm ALT) of continuous
461 permafrost regions of Canada High Arctic demonstrated a relatively fast decay of color and
462 fluorescence, but insignificant losses of DOC over 12 days of exposure time (Laurion and
463 Mladenov, 2013). Recently, no measurable photochemical loss of ancient permafrost DOC has
464 been revealed in the thawing yedoma permafrost sites of the Kolyma River, its tributaries and
465 streams (Stubbins et al., 2017). Another recent study of DOM photodegradation in boreal high-
466 latitude peatland streams of the White Sea watershed demonstrated only 10% decrease in DOC
467 concentration over 10 days of incubation under sunlight (Oleinikova et al., 2017). In the
468 estuarine zone of the largest European Arctic river draining wetland- and forest-dominated
469 permafrost-free territory (Severnaya Dvina), we did not found any measurable photo-
470 degradation of DOM over 1 month of exposure (Chupakova et al., 2018). This comparison
471 clearly demonstrate highly contrasting DOM photolability between the aquatic systems of N.
472 America, draining through mineral soil substrates, and that of boreal and subarctic peatlands.

473 Further, due to high homogeneity of organic substrate surrounding studied waters and
474 similar allochthonous origin of DOM in all surface waters of frozen peatlands, there is no
475 dramatic difference in DOM photodegradability over the hydrological continuum in NE
476 European Arctic, which also contrasts the results obtained in aquatic systems on mineral soils
477 (Cory et al., 2007, 2013; Reader et al., 2014). It is possible that either 1) photochemical
478 degradation of humic peat waters occurs very fast, during first ours to days upon their exposure
479 to sunlight or 2) that the nature of DOM is so refractory that much longer exposure periods, on
480 the order of several months to years (as in the Arctic coast) are necessary to photodegrade the
481 DOM from frozen peatlands. The first explanation is consistent with recent experiments on
482 photodegradation of fresh peat mire water, collected in taiga region of NW Russia, where about



50% of bogwater DOC was photodegraded over 2 days of exposure to sunlight (Oleinikova et al., 2017).

As such, it is possible that all surface waters sampled for experiments in this study, including stagnant water in permafrost depression, were already contacting with sunlight for more than several days and thus became photo-resistant. Assuming the maximal possible DOC loss due to photolysis assessed in our experiments (0.1 mg C $L^{-1}$ $d^{-1}$ corresponding to a loss of 3 mg/L during 28 days) and the light penetration depth of 0.5 m which is comparable with the typical depth of studied water bodies, the photodegradation can supply less than 10 % of total $CO_2$ emission flux from the water surfaces of frozen peatlands (0.4-0.8 g C $m^{-2}$ $d^{-1}$ in this work; 0.8 to 4.4 C $m^{-2}$ $d^{-1}$ in western Siberian rivers and streams, located on very similar context of frozen peat bogs, Serikova et al., 2018). The maximal PDOC value measured in this work is also at the lower end range of DOM photodegradation contribution to C flux in North European boreal and subarctic settings. Thus, DIC annual photo-production contributed between 1 to 8 % of $CO_2$ emissions from a humic lake in south of Sweden (Groeneveld et al., 2016) and globally in the boreal and subarctic zone, sunlight-induced $CO_2$ emissions represent about one tenth to the $CO_2$ emission from lakes and reservoirs (Koehler et al., 2014).

The evolutions of optical properties of DOM as a function of exposure time in different samples were consistent with the mechanisms of photo-sensitive DOM removal during irradiation. The ratio $E_{365}/E_{470}$ is known to correlate with the degree of condensation of DOM aromatic groups and with the degree of humification (Chin et al., 1994; Hur et al., 2006) whereas $UV_{254}$ is used as proxy for aromatic C and source of DOM (Chen et al., 1977; Uyguner and Bekbolet, 2005). The optical properties of DOC were much less conservative under sunlight exposure compared to total dissolved C concentration, as $UV_{254\ nm}$ and $E_{365}/E_{470}$ ratio sizably decreased in the course of experiments. Numerous studies of allochthonous riverine DOM also revealed that photodegradation of colored DOM (CDOM) and $SUVA_{254}$ were much greater

than DOC losses (Spencer et al., 2009; Reche et al., 2000; Vähätalo and Wetzel, 2004; Mostofa et al., 2011; Bittar et al., 2015; Gareis and Lesack, 2018). A decrease of $E_{365}/E_{470}$ corresponded to removal of UV rather than visual light absorbing functional groups, whereas a constant pattern of $E_{254}/E_{436}$ ratio in the hydrological continuum 'depression → stream → lake → river' was consistent with lack of autochthonous DOM in all studied water objects, which were dominated by terrestrial (aromatic) DOM from peat horizons. Overall, our observations confirm the conclusion achieved from a recent compilation of available data across the world that degradation processes act preferentially on CDOM rather than DOC concentration (Massicotte et al., 2017; Oleinikova et al., 2017).

In contrast to DOC, sizeable removal of dissolved P and Fe together with some related trace elements (Ti, V, Zn, Nb) during photolysis of surface waters reflects transformation and coagulation of Fe-rich colloids, that behave independent on organic colloids in humic waters (Vasyukova et al., 2010; Pokrovsky et al., 2016). This precipitation of Fe hydroxides together with P and insoluble trace elements was mostly pronounced in permafrost stream which had the highest pH and thus allowed minimal stability of Fe(III) hydroxides that were coagulated after removal of small amount of DOM that stabilized colloidal Fe (Oleinikova et al., 2017).

*4.3. Lack of bio- and photodegradation in humic surface waters of frozen peat bogs despite sizeable $CO_2$ emission*

The main fundamental result of the present study is that, despite well-known supersaturation of lentic and lotic waters of frozen peatlands to atmospheric $pCO_2$, the surface waters of frozen peatlands exhibit negligible bio- and photo-degradability over time scale (28 days) comparable with water residence time in various reservoirs. This is at odds with the dominant paradigm that bio- and photodegradation control the DOC removal from arctic aquatic ecosystems (Abbot et al., 2014; Cory et al., 2014; Spencer et al., 2015). Given



533 incontestable bio- and photodegradability of peat pore waters and frozen soil extracts reported
534 across the Arctic (Vonk et al., 2015; Selvam et al., 2017), this strongly suggests that the DOM
535 that arrives to small rivers and even permafrost depressions from the soils via lateral soil outflux
536 is already highly degraded. This is consistent with general idea that rates of DOM
537 photochemical alteration and rates of microbial responses to altered DOM are typically rapid,
538 from minutes to days (Cory and Kling, 2018). As such, the majority of elevated $CO_2$ measured
539 in surface waters of permafrost peat landscape originates from degradation of DOM in soil
540 water, not in surface water. We believe that the degradation of soil fluids occurs very fast and
541 completes within first hours or days. This is shorter than the residence time of water in
542 permafrost depressions, thaw ponds and rivers. As a result, we did not detect sizeable bio- and
543 photodegradation of residual DOM in various types of inland waters from permafrost
544 landscapes. In order to explain persistent $CO_2$ supersaturation of inland waters from peatlands,
545 we suggest that benthic respiration of stream, lake and river sediments produce sizeable amount
546 of $CO_2$ thus increasing overall C emission potential of the aquatic systems (MacIntyre et al.,
547 2018; Valle et al., 2018). For example, anaerobic C mineralization of thermokarst lake
548 sediments is fairly well established in discontinuous permafrost zone of peat bogs in western
549 Siberia (Audry et al., 2011) and Canada (Deshpande et al., 2017).

550 The findings of this study and widely reported dominance of non-biodegradable DOC
551 (0-1% BDOC) in large rivers and streams of the non-permafrost zone (Vonk et al., 2015)
552 suggest that 1) the majority of BDOC is degraded before its arrival to large aquatic reservoirs,
553 and 2) the $CO_2$ supersaturation and emission of surface waters from frozen peatlands is due to
554 soil pore water and sediment respiration rather than aerobic bio- and photo-degradation of DOM
555 in the water column. Further, the non-increase in BDOC fraction during temperature rise from
556 4 to 37°C implies that, within the climate warming scenario, the heating of peat surface waters
557 will be a minor factor of overall $CO_2$ balance. Instead, the change of water path and residence

time in pore waters of frozen peatlands, the rate of supra-permafrost water delivery, and magnitude of benthic respiration in large rivers and thermokarst lakes may control the $CO_2$ emission from inland waters.

## Conclusions

This work revealed high resistance of surface waters collected in permafrost peatland to both bio- and photo-degradation. Less than 5-10% of the initial aquatic DOC was removed over 1 month of dark aerobic incubation at 4, 22 and 37°C as well as during sunlight exposure of sterile-filtered waters. In contrast to expected differences in bio- and photo-lability between small permafrost subsidences, streams, large lake and the Pechora River, there was no measurable difference in surface waters BDOC concentration along the hydrological continuum. The contribution of aerobic DOM biodegradation within the water column to observed $CO_2$ supersaturations and net $CO_2$ emission fluxes from bog water, lakes, streams and rivers of peatland territories located within discontinuous permafrost zone is less than 10%. Despite decrease in CDOM during photolysis, this process does not significantly contribute to total DOC degradation and C emission from the surface of inland waters of frozen peatlands.

We hypothesize that refractory nature of DOM from frozen peatlands which is already processed in soil waters before arriving to lentic and lotic surface reservoirs create unfavorable conditions for biodegradation. The reason for high stability of DOM from frozen peatland to photolysis is less clear but can be linked to fast photo-degradation of peat bog and soil shallow underground) waters after their exposure to the surface, occurring within the first hours to days. We conclude on negligible impact of bio- and photo-degradation on DOM processing and $CO_2$ emission in surface waters of frozen peatlands. This calls for future work to quantify bio- and photo-lability of peat pore waters, thawing soil ice, and suprapermafrost flow, which deliver the DOM to the rivers, lakes and depressions.

583 **Acknowledgements**

584 This work was supported by RFFI (RFBR) grants No 17-05-00348_a and 17-05-
585 00342_a, Program FANO No 0409-2015-0140, RFFI No 18-05-01041 and UroRAN No 18-9-
586 5-29. Additional funding from JPI Climate initiative, financially supported by VR (the Swedish
587 Research Council) grant no. 325-2014-6898, is also acknowledged.

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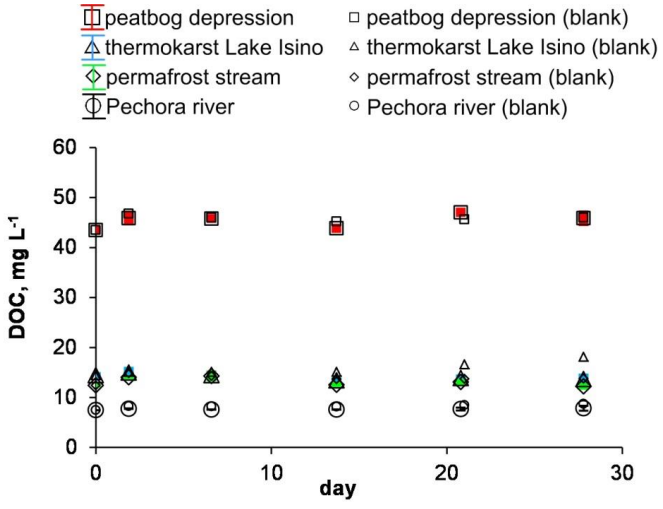


**Fig. 1.** The DOC concentration over time in biodegradation experiments at 23°C. The experiments are shown by solid symbols and the control runs are shown by open symbols: red squares, peatbog depression; green diamonds, permafrost stream; blue triangles, thermokarst Lake Isino, and black circles, the Pechora River. The error bars represent 1 s.d. of three replicates and often within the symbol size.

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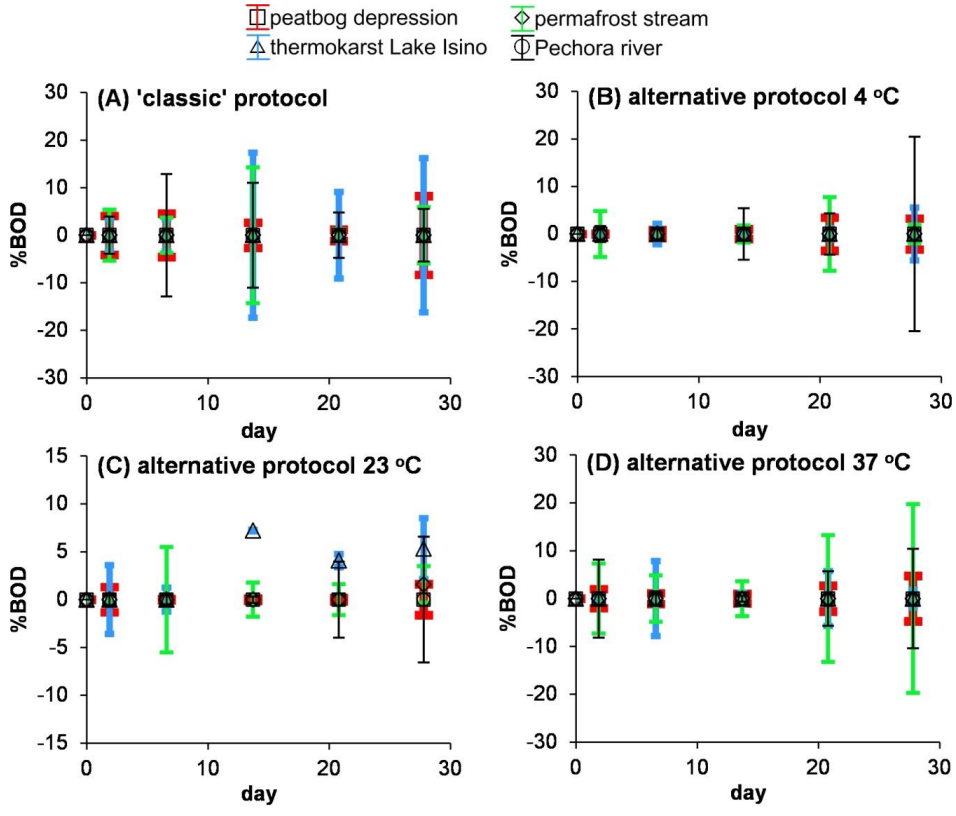


**Fig. 2.** Percentage of biodegradable DOC as a function of time. **A**, 'classic' protocol (0.7 µm GF/F filtration) at 23°C; **B-D**, alternative protocol of 3 µm - filtered solution incubated at 4°C (B), 23°C (**C**) and 37°C (**D**) and filtered through 0.22 µm at each sampling. The error bars are 1 s.d. of triplicates or, in a few cases, duplicates.

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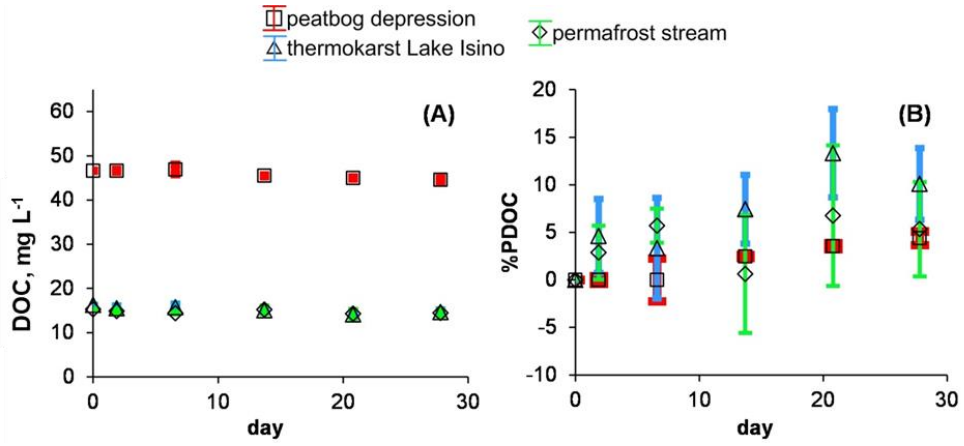


**Fig. 3.** Concentration (A) and percentage of degradable (B) DOC in photo-degradation experiments. The experiments are shown by solid symbols and the control runs are shown by open symbols: red squares, peatbog depression; green diamonds, permafrost stream; and triangles, thermokarst Lake Isino. The error bars are 1 s.d. of triplicates.

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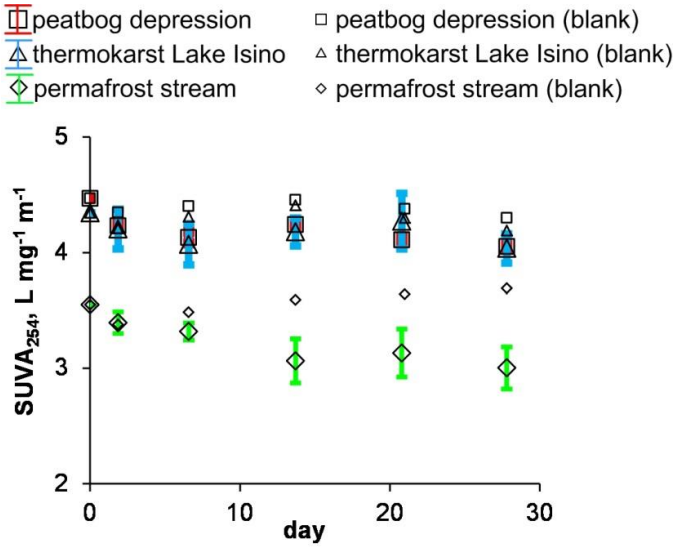


**Fig. 4.** $SUVA_{254\ nm}$ over time in photo-degradation experiments. The error bars are 1 s.d. of triplicates.

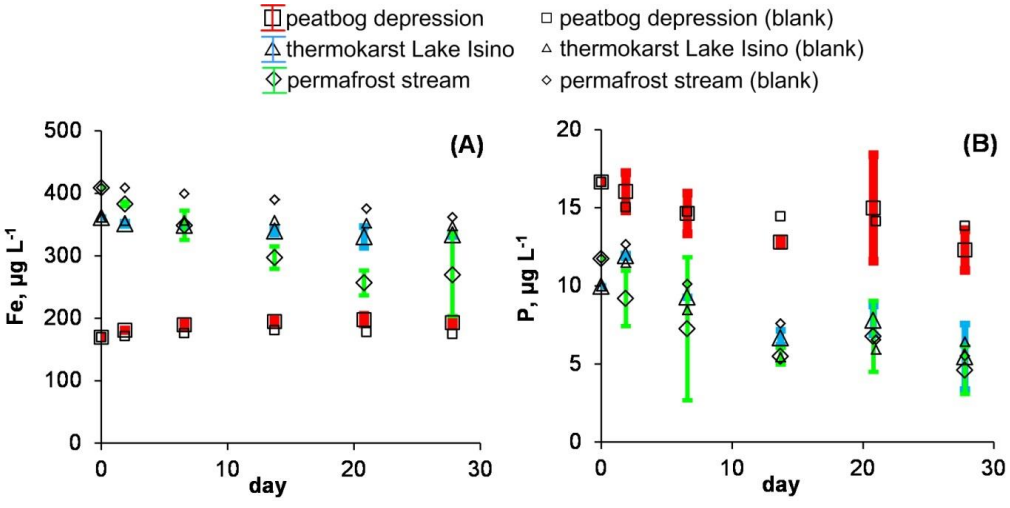


**Fig. 5.** Fe (A) and P (B) concentration over time in photo-degradation experiments. The error bars are 1 s.d. of triplicates.

Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-528
Manuscript under review for journal Biogeosciences
Discussion started: 14 January 2019


960 **Table 1.** Landscape setting, hydrochemical characteristics and $CO_2$ concentration and emission flux of studied waters. S.C. is specific
961 conductivity.
962
963

| Sample I.D. | Description | T,°C | pH | S.C., µS cm$^{-1}$ | DOC, mg L$^{-1}$ | DIC, mg L$^{-1}$ | $SUVA_{254}$ | $pCO_2$, ppm | $CO_2$ flux, mmol m$^{-2}$ d$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| **BZ-2-17** 67º36'48,8"N, 53º54'29,8"E | Depression in peatbog, $S_{area}$ = 7.5 m² | 24 | 3.85 | 59.2 | 43.9 | 0.992 | 4.08 | 440 | 34 |
| **BZ-24-17,** 67°36.53'N 53°50.26'E | Stream in frozen peatland, $S_{watershed}$ = 7.5 km² | 25 | 6.52 | 31.5 | 16.64 | 2.52 | 3.32 | 2370 | 30-300* |
| **BZ-12** 67º36'47,7"N 53º54'38,5"E | Thermokarst lake (Isino), $S_{area}$ = 0.005 km² | 24.1 | 5.30 | 12.9 | 15.65 | 0.808 | 4.10 | 1200 | 74 |
| **P5** 67$^0$40'09,4" 52$^0$39'30,8" | r. Pechora, $S_{watershed}$ = 322,000 km² | 20 | 6.92 | 65.1 | 8.20 | 6.11 | 3.82 | 1860 (night) 780 (day) | 100-130* |

964 Footnote: *, by analogy with small streams of Western Siberian peatlands, of the discontinuous permafrost zone, located in similar
965 environmental context; ** By analogy with Taz and Pur Rivers of western Siberian peatlands (Serikova et al., 2018).
966