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# Diel cycles of carbon, nutrient and metal in humic lakes of permafrost peatlands

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ABSTRACT

Despite the importance of surface waters of permafrost landscapes in carbon (C) emission and dissolved C and metal storage and export, the majority of available observations in high latitude aquatic systems deal with punctual or seasonal sampling without accounting for diurnal variations in temperature and primary productivity-respiration cycles. Towards providing comprehensive understanding of diel variations in $CO_2$ emission, organic C and element concentrations in lakes of frozen peatlands, we monitored, each 2 h over 2 days, the water temperature, pH, $CO_2$ fluxes, $CO_2$, $CH_4$, dissolved organic and inorganic carbon (DOC and DIC, respectively), nutrients, carboxylic acids, bacterial number, and major and trace elements in two acidic (pH = 3.6 and 4.0) and humic (DOC = 15 and 35 mg $L^{-1}$) thermokarst lakes of discontinuous permafrost zone in Western Siberia. We discovered a factor of 2 to 3 higher $CO_2$ concentrations and fluxes during the night compared to daytime in the high-DOC lake. The emission fluxes in the low-DOC lake increased from zero to negative values during the day to highly positive values during the end of night and early morning. The methane concentration varied within a factor of 5 without any link to the diurnal cycle. The bulk of dissolved (< 0.45 µm) hydrochemical parameters remained highly stable with ±10% variation in concentration over 2 days of observation (DOC, DIC, $SUVA_{254\ nm}$, carboxylates (formate, oxalate, puryvate and glutarate), Mn, Fe, Al, other trace elements). Concentrations of Si, P, K, Cu varied within ±20% whereas those of Zn and Ni ranged by a factor of 2 to 4 without any link to diurnal pattern. Overall, the impact of diel cycle on $CH_4$, DOC, nutrient and metal concentration was below 10%. However, neglecting night-time period may underestimate net $CO_2$ emission by ca. 30 to 50% in small organic-rich thaw ponds and switch the $CO_2$ exchange from uptake/zero to net emission in larger thermokarst lakes. Given the dominance of large lakes in permafrost regions, the global underestimation of the emission flux may be quite high. As such, monitoring $CO_2$ concentrations and fluxes in thermokarst lakes during months of extended night time (August to October) is mandatory for assessing the net emissions from lentic waters of frozen peatlands.



## 1. Introduction

The emission of greenhouse gases (GHG), particularly $CO_2$ and $CH_4$, from inland waters at high latitudes is a critical issue of these aquatic system behaviors under on-going climate warming. Due to sizeable amount of GHG and organic carbon (OC) stored in frozen organic-rich soils and produced during soil interaction with surface waters, high-latitude regions, notably peatlands, are at the forefront of environmental research as they can provide crucial information for modeling of terrestrial C cycle modification in response to permafrost thaw, water temperature rise and aquatic biotic community change (Gorham, 1991; Roehm et al., 2009; Peura et al., 2019). A major issue of lake biogeochemistry is the variation of GHG dynamics in response to photosynthesis/respiration cycle of phyto- and bacterioplankton (Szyper et al., 1992; Pollard, 2013; Hanson et al., 2006; Sadro et al., 2014) and benthic macrophytes and periphyton (Yvon-Durocher et al., 2014). The diel $CO_2$ concentration and emission patterns linked to variations in water temperatures and sunlight availability are fairly well documented in temperate rivers and ponds (Baehr and DeGrandpre, 2004; Forget et al., 2009; Lynch et al., 2010; Xiao et al., 2013; Yang et al., 2015; Liu et al., 2016; Spafford and Risk, 2018; DelVecchia et al., 2019). However, due to logistical constraints, the majorities of studies in high latitude, permafrost-affected peatland lakes dealt with one punctual sampling, usually during summer period (e.g., Shirokova et al., 2013; Pokrovsky et al., 2011, 2013), with the exception of several seasonally-rather than daily-resolved measurements (Jonsson et al., 2008; Laurion et al., 2010; Marushchak et al., 2013; Podgrajsek et al., 2014; Manasypov et al., 2015; Serikova et al., 2019). Although the latter studies addressed the seasonality of GHG emission, the diurnal variability of concentration

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and fluxes in these aquatic settings is rarely considered. In fact, there are various factors controlling DOC concentration and gas exchange of the lake with atmosphere and most of these factors are expected to vary diurnally. The 'external' factors are DOC and DIC ($CO_2$) delivery to the lake via shallow surface flow, subsurface (supra-permafrost) flow and possibly underground discharge via taliks (unfrozen water paths through permafrost). The 'internal' factors are determined by metabolism of plankton and periphyton, photo-oxidation of DOC, GHG generation or uptake in sediments, and gas exchange velocity (k) that could vary depending on the wind speed and day/night temperature variation via convective mixing (i.e., Eugster et al., 2003). Because the superposition of these external and internal gas sources likely varies across the systems and the time of the day, their overall impact on net C exchange has to be resolved via diurnal measurements on contrasting but representative lakes of the permafrost zone. Thus, recent in situ observations of $CO_2$ dynamics in tundra and alpine streams indicate net daytime uptake of $CO_2$ by photosynthesis (Peter et al., 2014; Crawford et al., 2017; Rocher-Ros et al., 2019) whereas Arctic lakes showed sizeable diurnal variability in $CO_2$ concentration and fluxes (Lundin et al., 2016).

In addition to GHG gases that are sensitive to diurnal pattern, dissolved organic carbon and trace elements bound to organic complexes are also likely to be affected by variations of light and temperature. However, the majority of trace metal studies in lakes dealt with one sampling during the day (i.e., Hamilton-Taylor and Willis, 1990; Nriagu et al., 1996; Falkner et al., 1997; Viollier et al., 1997; Albéric et al., 2000) and although strong diel variations of solutes were reported in temperate rivers (Brick and Moore, 1996; Neal et al., 2002; Jones et al., 2004; Gammons et al., 2005; Parker et al., 2007; Carling et al., 2011; Nimick et al., 2011; Vorobyev et al., 2019), subarctic organic-rich lakes remained very poorly investigated with the exception of humic lakes in boreal non-permafrost zone (i.e., Shirokova et al., 2010; Pokrovsky and Shirokova, 2013). At the same time, diurnal patterns of trace metals, involved in redox cycles and linked to photo-reduction and photo-oxidation (McMahon, 1969; Barry et al., 1994; Emmenegger et al., 2001), including colloidal forms of trace elements (Pokrovsky and Shirokova, 2013) are fairly well established in temperate lake waters but totally unknown in permafrost-affected humic lakes.

The majority of dystrophic to mesotrophic aquatic systems in frozen peatlands drastically differ from oligotrophic northern rivers and lakes in the sense that the peatland thermokarst lakes and ponds are *i*) highly humic, and typically contain between 10 and 100 $mg\,L^{-1}$ of DOC and *ii*) quite acidic, with pH ranging between 3.5 and 5.5 (Pokrovsky et al., 2014). As a result, the GHG and DOC regime in humic lake may be strongly controlled by a balance between the productivity of plankton, periphyton and macrophytes, and the heterotrophic bacteria mineralization of dissolved and particulate OC in the water column and sediments. Indeed, the heterotrophic bacterioplankton is capable to mineralize dissolved organic matter (DOM) of both allochthonous and autochthonous origin (Tranvik, 1988, 1989; Kritzberg et al., 2004) and thus can potentially liberate or consume associated trace metals. At the same time, limited photic layer and generally small abundance of phytoplankton in thermokarst peatland lakes (Pavlova et al., 2016) might preclude the cycle of $CO_2$ consumption during the day and its production during the night, unlike it is established in oligotrophic lakes of the subarctic (Ask et al., 2012). Further, considering that photo-oxidation of DOM can be the dominant pathway of C processing in arctic waters (Cory et al., 2014), this may increase $CO_2$ concentration from night to day (Bertilsson and Tranvik, 2000) thus counteracting the GPP effect, especially in shallow humic waters.

Therefore, the working hypotheses of this study is that the variability in external factors like temperature and light will exert primary control on DOC and related trace elements, and this will produce a diel cycle in C and elements concentrations and GHG emissions in thermokarst lakes. Further, we anticipate that the higher the DOC in a peatland lake, the smaller will be the response of water column hydrochemistry to diel variations in light and temperature. This response may be essentially controlled by external vs internal sources and thus likely to vary depending on lake size. In order to test these hypotheses, we studied two thaw ponds with different size and DOM content and we quantified (1) the variation of dissolved C and metal concentration between day and night and (2) the degree of diel variation in $CO_2$ flux, in order to reveal the control of hydrochemical parameters by external factors such as temperature and light. For this, we monitored $CO_2$, $CH_4$, organic carbon, major and trace element concentrations and $CO_2$ fluxes in thermokarst lakes during 2 summer days of anticyclone weather. Obtained results allowed to improve monitoring practices and demonstrated the need of revising the existing estimations of $CO_2$ emission from high latitude inland waters, which are mainly based on daytime period.

## 2. Study site, material and methods

We studied typical thermokarst lake (Lake Trisino, N 63°47′09.35″, E 75°38′54.57″, $S_{area} = 16{,}920\,m^2$; $S_{watershed} = 0.108\,km^2$, average depth 0.5 m) and thaw pond (Chernoe, N 63°46′55.72″, E 75°39′11.73″, $S_{area} = 1830\,m^2$; $S_{watershed} \leq 500\,m^2$, average depth 0.3 m) located at the INTERACT Research Station (Khanymey), discontinuous permafrost zone of the Western Siberian Lowland (WSL) as shown in Fig. S1 of Supplement. The permafrost here is abundant within flat-mound peat bogs on the watershed divides. The depth of the active (seasonally unfrozen) layer ranges from 145 ± 20 cm within the depressions to 41 ± 5 cm at the mounds (Raudina et al., 2018). Within the area of the Khanymey Research station, there are numerous thermokarst lakes and thaw ponds formed due to thawing of histosols (0.1 to 1.4 m peat thickness) over mineral (essentially Pleistocene sands) substrates (Shirokova et al., 2013). The feeding of small thaw ponds and large thermokarst lakes occurs either by supra-permafrost flow from adjacent mounds or by surface runoff from the elevated parts of the lake watershed.

The observations were performed during 48 h on July 26-28th 2018, at stable anticyclone conditions without any precipitation event. The July was chosen as the month of maximal surface water temperature and ecosystem productivity. Although the nighttime is much longer in August and September, possible rain events can affect the biotic cycle, thus preventing us from stable and continuous daily measurements. Samples were collected in the middle of the lake, at the depth of 20 cm and 10 cm (Trisino and Chernoe, respectively), from a PVC boat, which was gently moved over the lake surface using a rope held by a person standing on the shore to avoid disturbance of sediments. Every 2 h, the dissolved oxygen (CellOx 325; accuracy of ±5%), specific conductivity (TetraCon 325; ±1.5%), pH (SenTix 41; ±0.02 pH) and water temperature (±0.2 °C) were measured in-situ at 20 cm depth using a WTW 3320 Multimeter. Air temperature and atmospheric pressure were measured using an ADC Summit handheld weather station (Silva). The partial pressure of $CO_2$ ($pCO_2$) in water was measured in-situ using a hand-held infrared gas analyzer (IRGA, GMT222 CARBOCAP 3000 ppm probe, Vaisala; ±1.5%) enclosed within a waterproof and gas-permeable membrane and connected to a logger (MI70, Vaisala; ±0.2%, see details in Serikova et al., 2019).

Water samples for DOC, DIC, and dissolved $CO_2$ and $CH_4$ were collected and analyzed following methods described elsewhere (Manasypov et al., 2015; Polishchuk et al., 2018; Serikova et al., 2018). In brief, for DOC analyses, collected waters were filtered on-site in pre-washed sterile 30-mL polypropylene Nalgene® bottles through single-use Minisart filter units (0.45 μm pore size, Sartorius, acetate cellulose filter). The first 20 mL of the filtrate was always discarded. The DOC and DIC were analyzed using a Carbon Total Analyzer (Shimadzu TOC VSCN) with an uncertainty better than 3% (see Prokushkin et al., 2011 for methodology). For calculating $SUVA_{254}$, we measured ultraviolet absorbance at 254 nm ($UV_{254}$) using a 10-mm quartz cuvette on a Bruker CARY-50 UV-VIS spectrophotometer following Abbt-Braun and Frimmel (1999). Filtered solutions for cations and trace element analyses were acidified (pH = 2) with ultrapure double-distilled $HNO_3$ and stored in HDPE bottles previously washed with 0.1 M HCl and rinsed with ultrapure MilliQ deionized water. The preparation of sampling bottles was performed in a clean bench room class A 10000. Major cations (Ca, Mg, Na, K), Si and trace elements (TE) were determined without pre-concentration by ICP-MS Agilent 7500ce, routinely used in our laboratory for analysis of organic-rich lakes from frozen peatlands (cf. Pokrovsky et al., 2016). We obtained a good agreement between replicated measurements of SLRS-5 (River water reference material for trace metals) and the certified values (relative difference < 10% SD on repeated measurements), for all major and trace elements, except B and P (30%). Chloride, sulfide, fluoride and carboxylic organic ligands (lactate, acetate, propionate, formate, butyrate, pyruvate, galacturonate, glutarate, malate, tartrate, oxalate, phthalate, quinate, and citrate) were measured using a high-performance ion chromatography (Dionex ICS-5000+, analytical column: AS11-HC 4 μm), with an uncertainty of 5% and detection limits of $2\,\mu g\,L^{-1}$. Phosphate was also measured by an IC with an uncertainty of 2% and a detection limit of $1\,\mu g\,L^{-1}$. Total microbial cell concentration was measured after sample fixation in glutaraldehyde, by a flow cytometry (Guava® EasyCyteTM systems, Merck). Cells were stained using 1 μL of a 10 times diluted SYBR GREEN solution (10,000×, Merck), added to 250 μL of each sample before analysis. Particles were identified as cells based on green fluorescence and forward scatter (Marie et al., 1999).

For GHG analyses, unfiltered water was sampled in 25-mL Serum bottles that were closed without air bubbles using vinyl stoppers and aluminum caps and immediately poisoned by adding 0.2 mL of saturated $HgCl_2$ using a two-way needle system. The $CH_4$ concentrations were measured using a Bruker GC-456 gas chromatograph (GC) equipped with flame ionization detector. The $CO_2$ fluxes ($FCO_2$) were measured in both lakes using small (30 cm diameter) floating chambers equipped with non-dispersive infrared $CO_2$ logger (ELG, SenseAir, Bastviken et al., 2015; Alin et al., 2011) and calculated following methods described elsewhere (Vachon et al., 2010; Serikova et al., 2019). The $CO_2$ loggers were calibrated in the lab against pure $N_2$ - $CO_2$ mixtures before each sampling campaign. We placed chambers along a transect from the shore to the center of the lakes, with 6 chambers for the Lake Trisino and 4 chambers for the smaller Chernoe. The $CO_2$ accumulation rate inside each chamber was recorded continuously at 5 min interval. The chambers were ventilated each 2 h and the $CO_2$ accumulation rate inside each chamber was calculated by linear regression for 50 to 100 min accumulation time. Examples of $CO_2$ concentration vs. time in both lakes are shown in Fig. S2. Note that, although linear regression can underestimate $CO_2$ flux in the static floating chamber method (i.e., Xiao et al., 2016), the use of exponential model of Xiao et al. (2016) instead of linear regression yields minor corrections to the final flux values (within ±5–10%) which is below the uncertainty of replicates.

The normality of DOC, major and trace elements, GHG concentration and fluxes was assessed via the Shapiro-Wilk test. Because the data were not normally distributed, we used non-parametric statistics. A non-parameric Mann-Whitney *U* test was taken for treating the data due to the short series of observation, non-normal distribution of number of parameters and some amount of outliers. Regressions were used to examine the relationships between $pCO_2$, $FCO_2$ and water temperature. We used the median, 1st and 3rd quartiles to trace the dependence of all hydrochemical components on the period of observation (day vs. night). Differences in concentrations and fluxes between day and night time and between two lakes were tested using Mann-Whitney *U* test for paired data sets with significance level at 0.05, given the limited number of data (short series of observation and some amount of outliers).

## 3. Results

### 3.1. Lack of diel variations in major lake water parameters, nutrients, trace elements and bacteria

Concentrations of GHG and dissolved components (DOC, DIC, major cations and anions, and 30 trace elements), pH and specific conductivity during the two days observation are provided in the Mendeley Data Repository (Pokrovsky et al., 2019). The two chosen lakes are representative for the region in terms of DOC, GHG and metal concentration as illustrated in plots of lake water hydrochemical parameters as a function of lake surface area (Figs. S3 and S4 of the Supplement). The DOC-rich thaw pond Chernoe had about 2 times higher DOC concentration (significant at $p < 0.001$) than thermokarst lake Trisino and exhibited respectively, 2 to 3 times higher concentrations of divalent metal cations (Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu, Pb, Cd), trivalent and tetravalent TE (Al, Ti, Fe, Zr, REEs, Th), Cr, As, Cs, Nb, and U, which are usually bound to organic colloids in thermokarst waters (Pokrovsky et al., 2016).

The summer-time period of lake sampling corresponds to most stable chemical composition of lake waters (Manasypov et al., 2015 and Fig. S5). This period is often used for C and element pool inventory (Polishchuk et al., 2018) because the lake volume and shoreline are most stable. Moreover, our two day measurements are fully consistent with previous observations under normal summer conditions, as illustrated in Table S1 which lists the mean (± SD) values of pH, DOC, DIC and trace element in both lakes during summer 2013, 2015, 2016 and this study. The Mann-Whitney *U* test did not show significant difference between different years of both lakes.

For convenience, we listed the 48-h median (±IQR) values of all measured parameters at the end of the day and end of the night, corresponding to minimum and maximum of $CO_2$ concentration and emission (see Section 3.2. below) in Table 1. The corresponding median values integrated over two days and nights are given in Table S2. The water temperature of the two lakes followed a similar diurnal cycle with a minimum temperature attained approximately 2 h after sunrise (Fig. 1 A). The difference between day and night was significant, as confirmed by Mann-Whitney U test (p = 0.006 and 0.008 for Trisino and Chernoe, respectively). The pH exhibited rather weak (±0.2 to 0.3 units) fluctuations with generally higher values during the day compared to night time (Fig. 1 B). The water column remained $O_2$-saturated (90%) for both lakes and the $O_2$ concentration increased by ca. 20–30% from the middle of the night until noon, generally following the pattern of pH (not shown). The DOC remained fairly constant with non-systematic variations around the mean value (± SD) of $35.2 \pm 2.0$ and $15.5 \pm 0.9\,mg\,L^{-1}$ in Chernoe and Trisino, respectively

**Table 1**
Median (± IQR) concentration in the Trisino Lake and the Chernoe Pond during the period of low and high emission $CO_2$. The minimum is calculated at the end of the day (late afternoon) and the maximum corresponds to the end of night/early morning.

| Variable | Trisino Lake | | Chernoe Pond | |
|---|---|---|---|---|
| | Day min | Night max | Day min | Night max |
| $T_{water}$, °C | 22.2 ± 1.6 | 18.9 ± 3.4 | 22.1 ± 1 | 18.3 ± 3.05 |
| $T_{air}$, °C | 21.3 ± 3.9 | 15.2 ± 4.5 | 21.3 ± 3.9 | 15 ± 6.2 |
| pH | 3.91 ± 0.03 | 3.81 ± 0.04 | 3.68 ± 0.19 | 3.73 ± 0.04 |
| SC[a], μS cm$^{-1}$ | 19 ± 1 | 19 ± 1 | 28 ± 1 | 29 ± 0.5 |
| flux $CO_2$, g C m$^{-2}$ d$^{-1}$ | −0.03 ± 0.02 | 0.2 ± 0.14 | 0.08 ± 0.06 | 0.22 ± 0.08 |
| $CH_4$, μmol L$^{-1}$ | 0.23 ± 0.06 | 0.42 ± 0.36 | 3.74 ± 2.54 | 4.84 ± 1.51 |
| $CO_2$, ppmv | 360 ± 90 | 740 ± 148 | 580 ± 390 | 1210 ± 155 |
| DIC, mg L$^{-1}$ | 0.6 ± 0.05 | 0.6 ± 0.03 | 0.6 ± 0.11 | 0.7 ± 0.21 |
| DOC, mg L$^{-1}$ | 15.7 ± 1.12 | 14.9 ± 0.44 | 35.9 ± 3.09 | 33.5 ± 4.77 |
| $SUVA_{254}$ | 4.54 ± 0.29 | 4.67 ± 0.06 | 4.92 ± 0.32 | 5.15 ± 0.55 |
| Li, μg L$^{-1}$ | 0.65 ± 0.04 | 0.64 ± 0.01 | 0.61 ± 0.01 | 0.58 ± 0.01 |
| B, μg L$^{-1}$ | 5.62 ± 3.66 | 3.51 ± 1.06 | 8.66 ± 2.69 | 5.37 ± 0.54 |
| Na, μg L$^{-1}$ | 369 ± 13.4 | 367 ± 8.1 | 373 ± 37.1 | 339 ± 24.8 |
| Mg, μg L$^{-1}$ | 243 ± 1.9 | 243 ± 1.3 | 437 ± 2.9 | 431 ± 18.3 |
| Al, μg L$^{-1}$ | 64.1 ± 2.23 | 62.9 ± 3.94 | 137 ± 3 | 136 ± 7.9 |
| Si, μg L$^{-1}$ | 138 ± 19 | 143 ± 31.6 | 227 ± 37.9 | 191 ± 57.2 |
| K, μg L$^{-1}$ | 98.7 ± 26.3 | 85.4 ± 21.9 | 93.5 ± 11.6 | 79.8 ± 32.9 |
| Ca, μg L$^{-1}$ | 44.9 ± 4.24 | 42.5 ± 21.2 | 538 ± 18.7 | 533 ± 77.6 |
| Mn, μg L$^{-1}$ | 8.9 ± 0.06 | 8.99 ± 0.24 | 20.3 ± 0.61 | 20.2 ± 0.61 |
| Fe, μg L$^{-1}$ | 90 ± 2.1 | 88.8 ± 2.71 | 274 ± 27.6 | 272 ± 18 |
| Co, μg L$^{-1}$ | 0.08 ± 0.01 | 0.06 ± 0.01 | 0.12 ± 0.01 | 0.11 ± 0.004 |
| Ni, μg L$^{-1}$ | 0.22 ± 0.04 | 0.24 ± 0.1 | 0.42 ± 0.06 | 0.45 ± 0.3 |
| Cu, μg L$^{-1}$ | 0.16 ± 0.06 | 0.17 ± 0.04 | 0.47 ± 0.01 | 0.45 ± 0.05 |
| Zn, μg L$^{-1}$ | 6.1 ± 8.57 | 3.84 ± 1.73 | 12.2 ± 8.12 | 6.41 ± 0.85 |
| As, μg L$^{-1}$ | 0.32 ± 0.002 | 0.33 ± 0.01 | 0.52 ± 0.01 | 0.52 ± 0.02 |
| Rb, μg L$^{-1}$ | 0.02 ± 0.03 | 0.04 ± 0.03 | 0.07 ± 0.01 | 0.08 ± 0.07 |
| Sr, μg L$^{-1}$ | 1.92 ± 0.06 | 1.93 ± 0.12 | 4.38 ± 0.05 | 4.37 ± 0.38 |
| Y, μg L$^{-1}$ | 0.03 ± 0.002 | 0.03 ± 0.001 | 0.04 ± 0.002 | 0.03 ± 0.002 |
| Pb, μg L$^{-1}$ | 0.11 ± 0.04 | 0.15 ± 0.05 | 0.35 ± 0.02 | 0.36 ± 0.01 |
| Ti, μg L$^{-1}$ | 0.42 ± 0.02 | 0.42 ± 0.02 | 1.4 ± 0.06 | 1.35 ± 0.07 |
| V, μg L$^{-1}$ | 0.92 ± 0.01 | 0.87 ± 0.02 | 1.02 ± 0.05 | 0.98 ± 0.02 |
| Cr, μg L$^{-1}$ | 0.39 ± 0.09 | 0.33 ± 0.05 | 0.71 ± 0.05 | 0.6 ± 0.04 |
| Zr,μg L$^{-1}$ | 0.06 ± 0.002 | 0.05 ± 0.002 | 0.11 ± 0.003 | 0.1 ± 0.01 |
| Mo, μg L$^{-1}$ | 0.004 ± 0.004 | 0.005 ± 0.003 | 0.01 ± 0.002 | 0.01 ± 0.004 |
| Cd, μg L$^{-1}$ | 0.01 ± 0.002 | 0.01 ± 0.001 | 0.03 ± 0.01 | 0.03 ± 0.004 |

**Table 1** (*Continued*)

| Variable | Trisino Lake | | Chernoe Pond | |
|---|---|---|---|---|
| | Day min | Night max | Day min | Night max |
| Sb, μg L$^{-1}$ | 0.04 ± 0.002 | 0.04 ± 0.002 | 0.05 ± 0.003 | 0.04 ± 0.002 |
| Cs, μg L$^{-1}$ | 0.001 ± 0.0001 | 0.001 ± 0.001 | 0.01 ± 0.001 | 0.01 ± 0.002 |
| Ba, μg L$^{-1}$ | 2.14 ± 0.22 | 2.13 ± 0.28 | 4.01 ± 0.21 | 4.06 ± 0.5 |
| La, μg L$^{-1}$ | 0.01 ± 0.001 | 0.01 ± 0.001 | 0.02 ± 0.003 | 0.02 ± 0.001 |
| Ce, μg L$^{-1}$ | 0.02 ± 0.002 | 0.02 ± 0.002 | 0.04 ± 0.004 | 0.05 ± 0.002 |
| Th, μg L$^{-1}$ | 0.01 ± 0.0004 | 0.01 ± 0.001 | 0.02 ± 0.0001 | 0.02 ± 0.001 |
| U, μg L$^{-1}$ | 0.002 ± 0.001 | 0.002 ± 0.0005 | 0.01 ± 0.0003 | 0.01 ± 0.0004 |

[a] SC – specific conductivity.

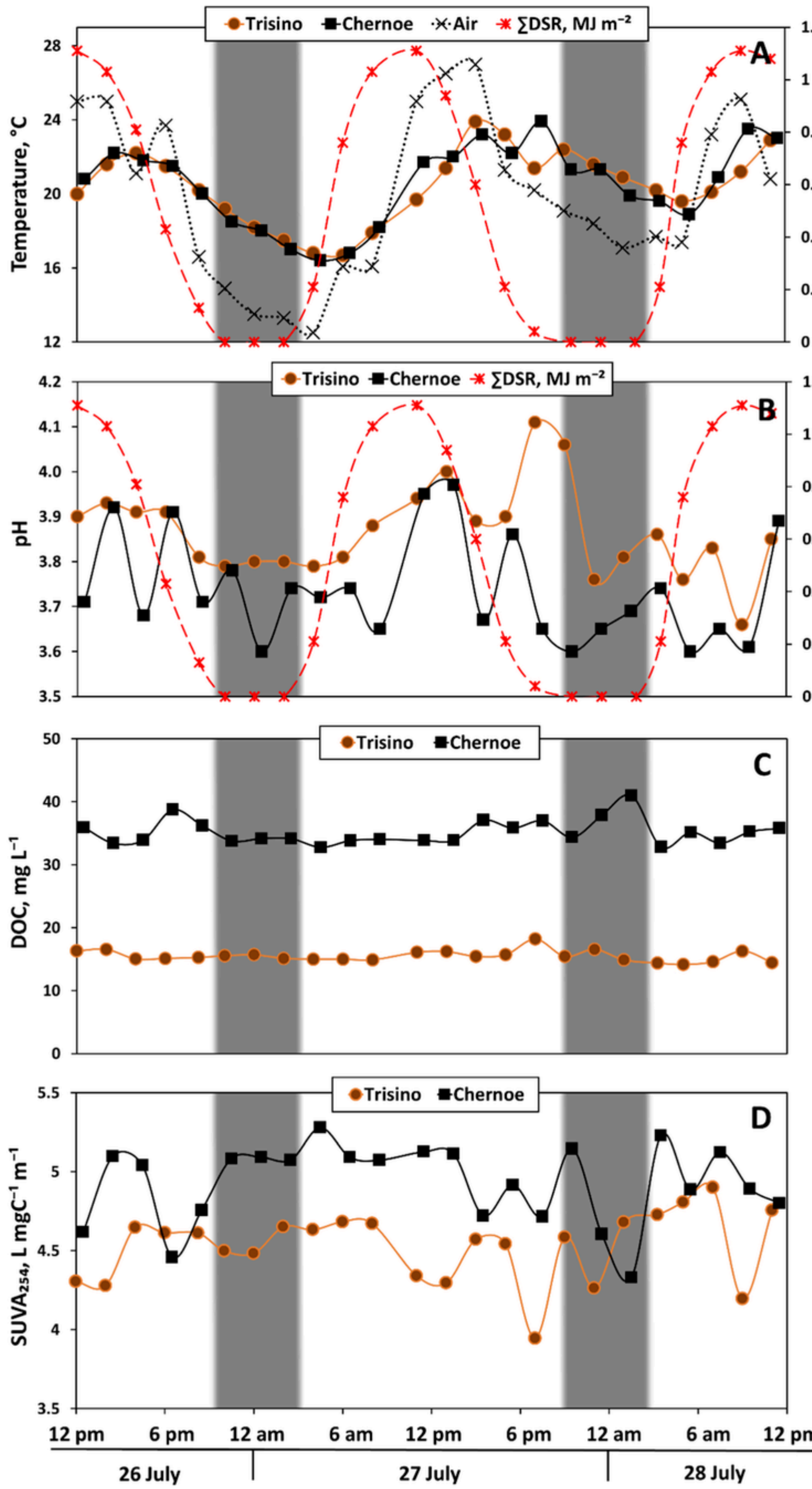
(Fig. 1 C). The $SUVA_{254}$ was also constant and fluctuated non-systematically between 4 and 5 L mg C$^{-1}$ m$^{-1}$ for both lakes (Fig. 1 D).

Phosphate and silica concentrations did not exhibit discernable diel variation in both lakes; $PO_4$ remained essentially constant at 17 to 20 μg P-$PO_4$ L$^{-1}$ (Fig. S6 A), whereas Si fluctuated between 150 and 250 μg L$^{-1}$ without distinct trend (Fig. S6 B). The concentration of carboxylates remained constant (formate, oxalate, pyruvate) or fluctuated without any diel pattern (acetate and lactate) as illustrated in Fig. S7. The concentration of formate and oxalate was ca. 30 to 60% higher in organic-rich Chernoe compared to organic-poor Trisino, and glutarate was detected only in Chernoe, also without diurnal pattern. The total cell number and biomass of bacteria were similar between the two lakes and varied within 10–15% throughout the observations without any systematic difference ($p > 0.05$ of Mann-Whitney *U* test) between the day and the night period (512,000 ± 41,000 cell mL$^{-1}$ in Trisino and 531,000 ± 80,000 cell mL$^{-1}$ in Chernoe).

The DIC in both lakes was very low, 0.6 to 0.7 mg L$^{-1}$ and did not respond to day/night cycle (Fig. S8 A). The major cations (K, Na, Ca, Mg) and anions (Cl, $SO_4$, F) concentrations and specific conductivity (S.C.) also remained constant within ±10% as illustrated in Fig. S8 B for specific conductivity. Most trace elements did not exhibit any sizeable variations over diurnal cycle as their concentrations remained stable within ±10% (Li, B, Al, Ti, V, Cr, Mn, Fe, Co, As, Rb, Sr, Y, Zr, Nb, Cd, Cs, Ba, REEs, Pb, Th, U) as illustrated in Figs. S8–S9. The exceptions were Cu, Zn and Ni whose concentrations varied by a factor of 1.5 to 3.0, respectively, however, without any discernable diel cycle (Fig. S9 D and E). These trace elements did not exhibit significant difference between their day-time and night-time concentrations over 48 h of monitoring as confirmed by Mann-Whitney *U* test ($p > 0.05$ for both lakes).

### *3.2. Dissolved $CO_2$ and $CH_4$ and emission flux of $CO_2$*

The $pCO_2$ ranged from 300 to 800 ppmv in Trisino and from 400 to 1400 ppmv in Chernoe. The $pCO_2$ demonstrated clear diurnal pattern with a factor of 2 to 4 higher concentrations achieved at the end of the night and early morning (Fig. 2 A) compared to the middle of the day. The difference in $CO_2$ concentration between the end of night/early morning peak and the end of day minimum averaged over 48 h of observation was significant for both lakes ($Z = -2.48$, $p = 0.013$ for Trisino; $Z = -2.80$, $p = 0.005$ for Chernoe). The diurnal pattern of $pCO_2$ significantly correlated with water temperature ($T_{water}$): $R_{Spearman} = -0.52$, $p < 0.01$ and $R_{Spearman} = -0.57$, $p < 0.005$


Trisino
Chernoe
Air
∑DSR, MJ m⁻²
A
Temperature, °C
∑DSR, MJ m⁻²
B
pH
C
DOC, mg L⁻¹
D
SUVA254, L mgC⁻¹ m⁻¹
12 pm
6 pm
12 am
6 am
12 pm
6 pm
12 am
6 am
12 pm
26 July
27 July
28 July

for Trisino and Chernoe, respectively (Fig. 2 C). The $FCO_2$ was close to zero or negative during the day time in Trisino (−0.02 ± 0.02 g C $m^{-2}$ $d^{-1}$, mean ± SD) but positive in Chernoe (0.12 ± 0.07 g C $m^{-2}$ $d^{-1}$, mean ± SD). During the night, the $FCO_2$ strongly increased and became positive in Trisino (0.12 ± 0.1 g C $m^{-2}$ $d^{-1}$, mean ± SD), whereas its increase in Chernoe was a factor of 2 to 5 between the day minimum and the night maximum (Fig. 2 B). Similar to $pCO_2$, the $FCO_2$ followed the diurnal pattern which was shifted with respect to solar radiation intensity and significantly ($R_{Spearman} = -0.56$, $p < 0.01$ and $R_{Spearman} = -0.57$, $p < 0.01$ for Trisino and Chernoe, respectively) negatively correlated with water temperature (Fig. 2 D). The difference in $FCO_2$ between early morning maximum and late afternoon minimum was significant ($Z = -2.65$, $p = 0.008$ for Trisino; $Z = -2.19$, $p = 0.028$ for Chernoe). Furthermore, to check the difference in the degree of $pCO_2$ and $FCO_2$ response to diel cycles of temperature and light between two lakes, we used a Mann-Whitney U test. The lakes were significantly different ($Z = -2.00$, $p = 0.045$ for the end of the day minimum; $Z = -2.80$, $p = 0.005$ for the early morning maximum).

The $CH_4$ concentration ranged between 0.15 and 0.5 μmol $L^{-1}$ in DOC-poor Trisino and between 2 and 7 μmol $L^{-1}$ in organic-rich Chernoe (Fig. 3). Possible impact of bubble emissions was taken into account via assessing lateral heterogeneity of $CH_4$ concentrations across the lakes, and reflected in the uncertainty attached to the data at each time of the day. These uncertainties typically ranged from 10 to 20%. There was no systematic trend of $CH_4$ with time and diurnal pattern in large Lake Trisino; however, the $CH_4$ concentrations in small and shallow Chernoe pond increased up to ca. 5-fold after the beginning of sampling without following the diurnal pattern. We therefore cannot exclude sediment disturbance and bubble release due to boat movement, which interfered with methane measurements in the Chernoe Lake given its low depth.

## 4. Discussion

### *4.1. High stability of pH, nutrients, organic acids and dissolved (<0.45 μm) components of thermokarst lakes*

Diurnal variations of major hydrochemical and biological parameters (Eiler et al., 2006) and trace metals, involved in redox cycles (McMahon, 1969; Barry et al., 1994; Emmenegger et al., 2001; Pokrovsky and Shirokova, 2013) in lake waters are fairly well known. The present study adds a novel dimension to the existing knowledge via reporting the chemical composition of previously unknown humic and acidic thermokarst lakes, which are widely distributed in the permafrost zone of Northern Eurasia (Polishchuk et al., 2018). Over 2 days and nights monitoring in the Trisino Lake, the pH decreased by 0.1 to 0.2 unit during the night compared to day time period, presumably reflecting the primary production – mineralization processes (Wright and Mills, 1967; Zirino et al., 1986), as it is known in non-permafrost humic lakes of circum-neutral pH (Shirokova et al., 2010). The low pH of studied lakes (3.86 and 3.71 of Trisino and Chernoe, respectively) stems from a combination of high DOC, acidic nature of surrounding peat and ground and submerged vegetation (mostly mosses). Note that the diel pH variations were much lower (ca., 0.1 ± 0.1 unit) in organic-rich Chernoe which had two times higher DOC concentration. Overall, the obtained results dismiss the hypothesis of temperature and light control on DOC and trace element concentration in lakes and ponds of permafrost peatlands. Moreover, the degree of response in solute concentrations (except pH and $CO_2$) to diel variation in external parameters was not related to the DOC level in humic lakes.

The constant concentration of DOC and lack of discernable diel pattern in SUVA in both lakes suggest that the pool of dissolved organic carbon was not affected, at the diel scale, by the five main processes controlling DOM level in thermokarst lake waters. These are: *i*) soil water input via supra-permafrost flow (Raudina et al., 2018); *ii*) benthic respiration of DOM (Demars, 2019), *iii*) photo-degradation (Cory et al., 2014), *iv*) heterotrophic consumption of DOM in the water column (Kritzberg et al., 2006; Shirokova et al., 2009; Peura et al., 2019) and *v*) phytoplankton and macrophytes exometabolite production (Demarty and Prairie, 2009). First of all, it is possible that the main processes controlling DOC input and removal in the water column, such as phytoplankton metabolite production and photo-oxidation, compensate each other at the diurnal scale. Similarly, the DOC delivery via supra-permafrost flow may accelerate during the day due to enhanced soil heating and ice thaw, but this freshly-delivered allochthonous DOC can be quickly, on the scale of first hours, processed by photolysis (Shirokova et al., 2019). Note that low impact of the phytoplankton and heterotrophs on DOC and SUVA is consistent with lack of diurnal variation in limiting nutrients (Si, $PO_4$), simple organic acids that can be used for heterotrophic metabolism (acetate, lactate, formate, pyruvate, oxalate), and the total bacterial number. A lack of Si concentration change between day and night is also consistent with low abundance of diatoms in thermokarst lakes of Western Siberia, given that the phytoplankton of acidic and humic waters is dominated by cyanobacteria and green algae (Pavlova et al., 2016). Finally, in agreement with results on some temperate rivers (Spencer et al., 2007) and boreal lakes (Shirokova et al., 2010; Pokrovsky and Shirokova, 2013), it is possible that the changes in bulk DOC concentration simply could not be quantified because the biogeochemically-processed fraction of DOC was small and not detectable at overall high DOC level in humic waters. Therefore, the present study corroborates recent results on humic (24 mg DOC $L^{-1}$) and circumneutral (pH = 7.5–9.7) subarctic lake which demonstrated limited variability in DOC and SUVA on a diel scale compared to a seasonal scale (Johnston et al., 2019). The latter was essentially linked to the change in specific organic compounds (decrease of aromatic and polyphenolic classes) and increase in aliphatic compounds, following pulses of allochthonous and autochthonous DOM. Presumably, these pulses are not detectable over hours to daily scale observation, especially in high-DOC aquatic environments. Similar deduction can be applied for the lack of DIC pattern: at the acidic pH of Trisino and Chernoe water, the DIC represents quite small fraction of $CO_2$ and thus the DIC variations linked to photosynthesis cycle could not be resolved due to high $pCO_2$ variations.

For other dissolved (<0.45 μm) components of the water column, we observed quite high stability of concentrations in both lakes, which signifies that the role of diel processes in the water column, the water-sediment exchange and short-term input of supra-permafrost waters were negligible during 2 days of observation. This result is also important from methodological point of view as it suggests that for most dissolved major and trace elements of thermokarst lakes in discontinuous permafrost zone, a single one-time sampling at any pe-

**Fig. 1.** Air and water temperature and direct solar radiation (DSR) (A), pH (B), DOC concentration (C), and SUVA (D) variations in surface water measured in the two lakes of Western Siberia (Trisino and Chernoe). The shadowed area represents night time observations (same for Figs. 2 and 3).

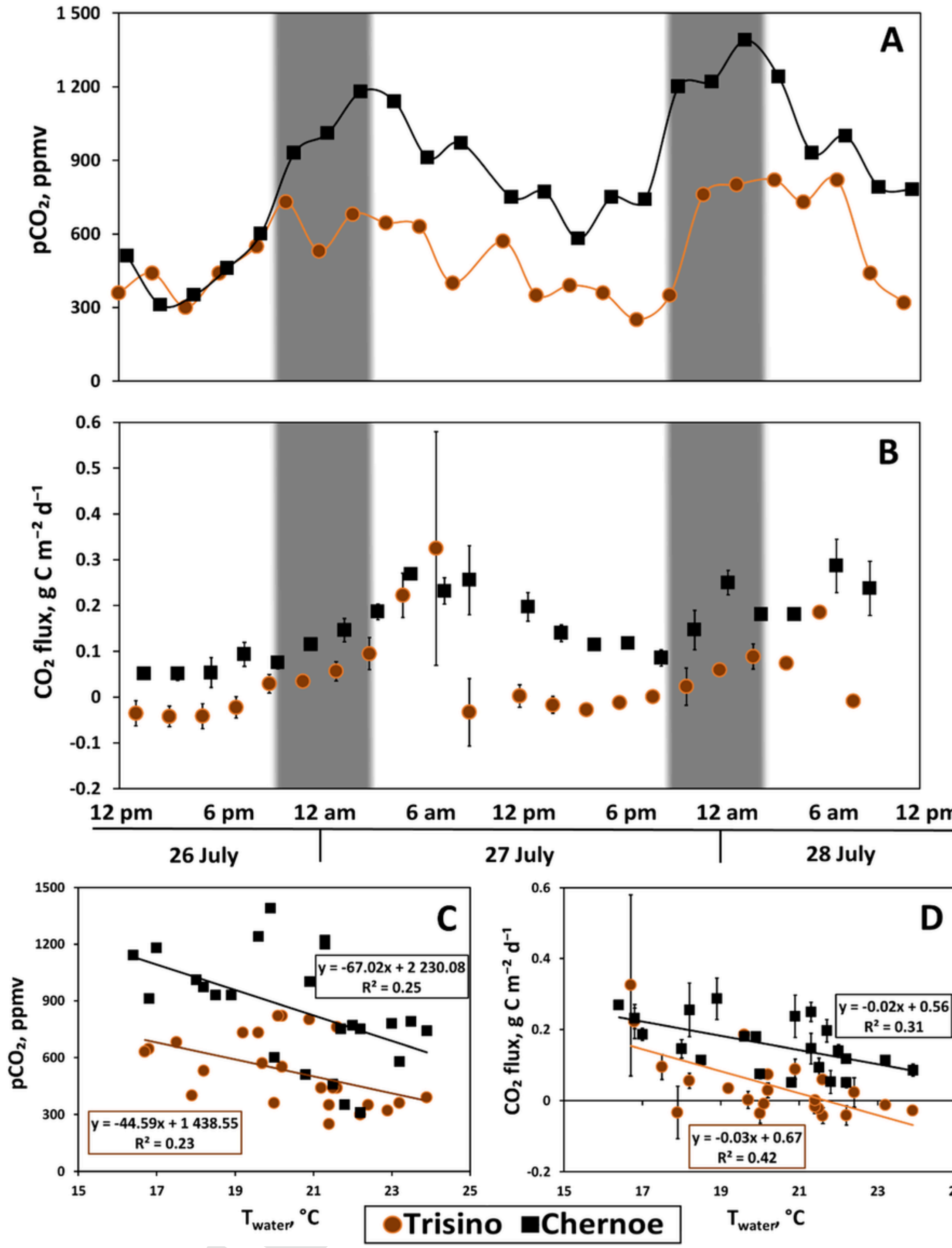



**Fig. 2.** Diurnal pattern of $pCO_2$ (A) and CO2 flux (FCO2) (B) measured in the two lakes of Western Siberia. The negative correlations between $pCO_2$ and water temperature (C) and $FCO_2$ and water temperature (D) are significant at $p<0.01$. The error bars represent the s.d. of six (Trisino) and four (Chernoe) chamber measurements across the lakes.

riod of the day or night is sufficiently representative for a given lake during specific season of the year.

Another important result of our observations is that there was a factor of 2 to 3 higher concentration of DOC and ~30 elements in DOC-rich Chernoe thaw pond compared to the DOC-poor Trisino Lake. It is known that the majority of cations are strongly bound to organic and organo-ferric colloids in thermokarst lakes and ponds of discontinuous permafrost zone of WSL (typically from 80 to 99%, Pokrovsky et al., 2016). Given that both DOC and Fe concentrations are 2 to 3 times higher in the Chernoe Lake compared to the Trisino Lake, the concentration of organo-ferric colloids that bind many trace elements is also higher in the Chernoe Lake. The exceptions are Li, B, Na, K, Si, V, Mo and Sb that are not bound to organic colloids and thus exhibit similar (within ±20%) concentrations in both lakes. Note that while total dissolved phosphorus ($P_{tot}$) was 5 to 10 times lower in the low-DOC Trisino compared to the high-DOC Chernoe, the phos-

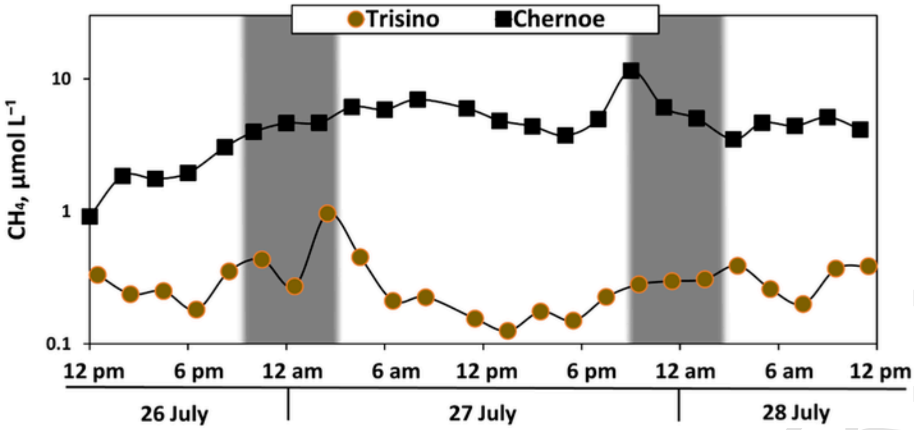



**Fig. 3.** Diurnal pattern concentration of dissolved $CH_4$ measured in the two lakes of Western Siberia. The uncertainties of $CH_4$ concentration are within the symbols size. They stem from 2 to 3 individual measurements in various part of the lake at each time of the day.

phate anion concentrations were rather similar between lakes. As such, the difference in $P_{tot}$ behavior is due to its limitation by organo-ferric colloids rather than due to phytoplankton uptake of P in the Trisino Lake.

### *4.2. Diurnal pattern of $CO_2$ concentration and flux*

Although the present study is probably the first that documents significant diel variations of $pCO_2$ flux using direct chamber measurements in humic thermokarst lakes of permafrost peatlands, our finding are in general agreement with large body of studies in non-permafrost rivers and lakes showing similar pattern of decreased $CO_2$ during daylight hours (Naiman, 1983; Guasch et al., 1998; Bott et al., 2006; Vesala et al., 2006; Parker et al., 2010; Vale et al., 2018; Rocher-Ros et al., 2019) and highest values in the early morning (Dawson et al., 2001; Reiman and Xu, 2019; Yang et al., 2019). The $pCO_2$ and $FCO_2$ diel patterns in permafrost peatland waters confirm the hypothesis that the high-DOC lake exhibits weaker response to temperature and light variations compared to the low-DOC lake.

The diel variabilities of net ecosystem production and related $CO_2$ effluxes are mostly pronounced in oligotrophic lakes (Spafford and Risk, 2018; Liu et al., 2016). In such DOC-poor lakes, the community respiration rates can vary by an order of magnitude, yielding up to $3\,mg\,L^{-1}$ diel changes in DOC concentration and being strongly linked to diel oscillations in water temperature (i.e., Bogard et al., 2019). In other cases, the typical variations of DOC concentrations linked to bacterio-plankton respiration are much lower (for example, 0.1 to $0.3\,mg\,L^{-1}$ over 5 h of night time, Sadro et al., 2011). In contrast, at the high level of DOC in humic thermokarst lakes of peatlands, the 0.1 to $3\,mg\,L^{-1}$ diel variations in DOC cannot be resolved with sufficient precision. Indeed, the $0.3\,g\ C\ m^{-2}\ d^{-1}$ variation in $CO_2$ flux observed in this work (Fig. 2 b) corresponds to a $0.3\,mg\,L^{-1}$ variation in DOC concentration (due to bacterial metabolism or photolysis) in a lake of 1 m depth. In shallower, 30-cm deep thaw ponds like Chernoe, the effect of DOM processing the water column capable to produce the observed $CO_2$ flux is 3 times higher, but still does not exceed $1\,mg\,L^{-1}$ of DOC. Such low effects can be hardly resolved at high DOC level of studied ponds (15 to $35\,mg\,L^{-1}$). At the same time, the role of DOM photolysis as a cause of $CO_2$ emission in subarctic waters (i.e. Cory et al., 2014; Bowen et al., 2019) can be weakly pronounced in permafrost peatlands because the acidic humic waters of thermokarst lakes from frozen peatlands are highly resistant to photo-degradation (Shirokova et al., 2019). This is further confirmed by the fact that the concentrations of photo-sensitive components ($SUVA_{254}$, Fe, Mn) remained conservative with <10% variations during full period of observations (Fig. 1 D, Figs. S9 A and B). It is also possible that the photo-oxidation of DOC to $CO_2$ occurring during the day (Cory et al., 2014; Bertilsson and Tranvik, 2000) is masked by $CO_2$ consumption due to benthic photosynthesis, as it was suggested in some Arctic streams (Rocher-Ros, 2019).

We therefore hypothesize that the respiration of organic matter in sediments (benthic microbial metabolism), rather than DOM processing in the water column are mainly responsible for high $FCO_2$ in general, as it was recently shown in a small catchment on peat soils in boreal zone (Demars, 2019). The $CO_2$ uptake during day time may be linked to macrophytes and submerged mosses that partially colonize the bottom of shallow thermokarst lakes and thaw ponds in this region (Pokrovsky et al., 2014), as it is also known in other Arctic lakes (Squires et al., 2009; Tank et al., 2011; Bouchard et al., 2014). In this regard, the diurnal pattern of $pCO_2$ and $FCO_2$ can be interpreted as a result of a balance between sediment respiration and GPP of periphyton, aquatic plants and submerged mosses. As for the external supply of $CO_2$ from surrounding soils to the lake water (via suprapermafrost flow, Raudina et al., 2018), the variation of this factor counteracts the observed $pCO_2$ pattern because the maximal soil water input due to ice thaw is likely to occur during the highest air temperature (late afternoon) which corresponds to minimal $pCO_2$ level in the lake waters. Similarly, convective mixing is unlikely to contribute to the $CO_2$ emission pattern because, during period of observation at the anticyclonic weather, the $pCO_2$ and $FCO_2$ were strongly correlated ($r^2 = 0.90$, $p < 0.01$) and the wind speed during the anticyclone remained quite low and did not vary between day and night.

### *4.3. Consequences for global $CO_2$ emission, and C and metal pools assessment in thermokarst lakes of Western Siberia lowland*

The observed stability of most dissolved component concentrations in thermokarst lakes of permafrost peatlands has important implication for the evaluation of pools and fluxes of C and related elements. Highly conservative behavior of DOC, DIC, $CH_4$, nutrients, major and trace elements, notably micro-nutrients (except Zn), toxicants and geochemical traces during two days and nights of monitoring demonstrates the representability of one single sampling during the day or night for assessing seasonal (week, month - averaged) behavior of solutes in thermokarst lakes of frozen peatlands. In particular, the pools of DOC and element calculated in thaw ponds and thermokarst lakes of the whole territory of Western Siberia, based on single-point sampling (Polishchuk et al., 2018), provides reasonable approximation for the summer time period. This conclusion corroborates results on diel and seasonal variability of dissolved components in N. American subarctic lake (Johnston et al., 2019).

In contrast, systematically higher $FCO_2$ during the night compared to the day may require some corrections on global estimations of $CO_2$ emissions from lakes and ponds of frozen peatlands. The majority of available measurements on thermokarst lakes and thaw ponds were performed during day-time, without accounting for possible diurnal cycle (see Serikova et al., 2019 and references therein). Considering full duration of unfrozen period on lakes of discontinuous permafrost zone of WSL (mean multi-annual of 137 days, from May 25 to October 7), the night time represents 30% of the ice-free period. The enhanced $FCO_2$ during the night from small thaw ponds (< 2000 $m^2$) such as Lake Chernoe thus increases the average emission from 0.10 to 0.20 g C $m^{-2}$ $d^{-1}$. However, because the contribution of such ponds to overall water area is negligibly small (< 1%, Polishchuk et al., 2018), this does not affect the regional C emission balance. In contrast, medium and large thermokarst lakes (> 1–10 ha) provide the main water surfaces and $CO_2$ aquatic pools in WSL (Polishchuk et al., 2018). In these lakes, the day- time $FCO_2$ in summer could fluctuate around zero (±0.02 g C $m^{-2}$ $d^{-1}$) but rise to 0.25 ± 0.05 g C $m^{-2}$ $d^{-1}$ at the end of the night as it is observed in the Trisino Lake.

The median day-time $CO_2$ flux from lakes of discontinuous permafrost zone of the WSL in summer is 0.74 g C $m^{-2}$ $d^{-1}$ but ranges from −0.3 to 3.13 g C $m^{-2}$ $d^{-1}$ during day time (calculated based on data of 21 lakes in the region, Serikova et al., 2019). Although the variations of $CO_2$ flux between individual lakes may strongly exceed the effect of diurnal cycle, a 0.2 g C $m^{-2}$ $d^{-1}$ increase between day and night may produce sizeable increase in seasonal emission fluxes. Therefore, given the scarcity of diurnal observations on large lakes and the absence of data on night-time emission during ice-off and ice-on periods (when the emission is sizably higher than in summer, Serikova et al., 2019), the quantification of the night-time $CO_2$ emission at the regional level over full open water period of the year is of high priority.

### 5. Conclusions

We observed stable concentrations of pH, DOC, $SUVA_{254}$, $CH_4$, nutrients, carboxylic acids, most major and trace elements in waters of acidic and humic thermokarst lake and thaw pond during a continuous 2-days observation at generally anticyclone weather. In contrast, the $CO_2$ concentration and emission negatively correlated with water temperature and exhibited clear diurnal pattern with a maximum after the sunrise (minimal surface water temperature) and a minimum during late afternoon day-time (maximum surface water temperature). Among major drivers of observed $CO_2$ variation, we exclude photosynthetic/heterotrophic activity of the plankton in the water column and photolysis of DOM. Rather, the balance between benthic respiration of dissolved and particulate organic matter and primary productivity of periphyton, aquatic macrophytes and submerged mosses was responsible for enhanced $CO_2$ emission during the night and $CO_2$ decrease or even uptake during the day. Neglecting night-time $CO_2$ flux, especially in large thermokarst lakes, can sizably underestimate the region-upscaled global C emission. This calls for a need to study diurnal variations in C emission in large (10–500 ha) thermokarst lakes because they mostly contribute to overall inland water surface of the region. These measurements should be focused on late summer and autumn periods when the heterotrophic respiration dominates over primary productivity and the diurnal cycles are most pronounced.

### Uncited reference

Mortimer, 1959

## CRediT authorship contribution statement

**L.S. Shirokova:** Conceptualization, Investigation, Writing - original draft. **D. Payandi-Rolland:** Conceptualization, Investigation, Writing - original draft. **A.G. Lim:** Investigation. **R.M. Manasypov:** Investigation. **J. Allen:** Formal analysis. **J.-L. Rols:** Formal analysis. **P. Benezeth:** Formal analysis. **J. Karlsson:** Formal analysis. **O.S. Pokrovsky:** Conceptualization, Writing - original draft.

### Declaration of competing interest

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

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.139671.

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