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## ► To cite this version:

Tao Wang, Carmen Kalalian, Daniel Fillion, Sébastien Perrier, Jianmin Chen, et al.. Sunlight Induces the Production of Atmospheric Volatile Organic Compounds (VOCs) from Thermokarst Ponds. *Environmental Science and Technology*, 2023, 57 (45), pp.17363-17373. 10.1021/acs.est.3c03303 . hal-04308300

HAL Id: hal-04308300

<https://hal.science/hal-04308300v1>

Submitted on 28 Nov 2023

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1 Sunlight Induces the Production of  
2 Atmospheric Volatile Organic Compounds  
3 (VOCs) from Thermokarst Ponds

4 *Tao Wang<sup>1,2</sup>, Carmen Kalalian<sup>1</sup>, Daniel Fillon<sup>3,4,5</sup>, Sébastien Perrier<sup>1</sup>, Jianmin Chen<sup>2</sup>,*  
5 *Florent Domine<sup>3,4,5\*</sup>, Liwu Zhang<sup>2\*</sup>, Christian George<sup>1\*</sup>*

6 1 Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, 69626,  
7 Villeurbanne, France

8 2 Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention,  
9 Department of Environmental Science & Engineering, Fudan University, Shanghai,  
10 200433, China

11 3 Takuvik Joint International Laboratory, Université Laval (Canada) and CNRS-  
12 INSU (France), Québec, Canada

13 4 Centre d'Études Nordiques, Université Laval, Québec, Canada

14 5 Department of Chemistry, Université Laval, Québec, Canada

15 **KEYWORDS:** permafrost, thermokarst, volatile organic compounds (VOCs), Arctic,  
16 photochemistry

17

18 **SYNOPSIS:** Photoproduction of VOCs from thermokarst ponds water is not directly  
19 correlated to the amount of dissolved organic matter but rather to the availability of  
20 organic matters at the top layers of the liquid phase.

21 **ABSTRACT:** Ground subsidence caused by permafrost thaw causes the formation of  
22 thermokarst ponds, where organic compounds from eroding permafrost accumulate.  
23 We photolyzed water samples from two such ponds in Northern Quebec and discovered  
24 the emission of volatile organic compounds (VOCs) using mass spectrometry. One  
25 pond near peat-covered permafrost mounds was organic-rich, while the other near  
26 sandy mounds was organic-poor. Compounds up to C10 were detected, comprising O,  
27 N, and S atoms. The main compounds were methanol, acetaldehyde, and acetone.  
28 Hourly VOC fluxes under actinic fluxes similar to local solar fluxes might reach up to  
29  $1.7 \text{ nmol C m}^{-2} \text{ s}^{-1}$ . Unexpectedly, the fluxes of VOCs from the organic-poor pond were  
30 greater than those from the organic-rich pond. We suggest that different segregation of  
31 organics at the air/water interface may partly explain this observation. This study  
32 indicates that sunlit thermokarst ponds are a significant source of atmospheric VOCs,  
33 which may affect the environment and climate, via ozone and aerosol formation.  
34 Further work is required for understanding the relationship between pond organic  
35 composition and VOC emission fluxes.

## 36 INTRODUCTION

37 The top 3 m of terrestrial permafrost contains ~ 1000 Pg of carbon in the form of  
38 frozen vegetal debris that has accumulated over the past millennia<sup>1,2</sup>. This is  
39 significantly more than the atmospheric reservoir, 750 Pg<sup>3</sup>, so that the mineralization  
40 of permafrost carbon induced by global warming has the potential to dramatically  
41 accelerate climate change. Projections of CO<sub>2</sub> and CH<sub>4</sub> emissions by thawing  
42 permafrost show a very wide range of values, most of which are between 7 and 100 Pg  
43 C by the year 2100 under the emission scenario RCP4.5<sup>4-7</sup>. However, these estimates  
44 are based on gradual permafrost thaw and ignore numerous processes, including rapid  
45 erosion and abrupt permafrost thaw<sup>8</sup>, increased lightning and fires, and the rapid  
46 northward migration of trees<sup>9</sup>. Much greater emissions are therefore likely<sup>8,10</sup> and  
47 additional process studies are required for more reliable projections.

48 Many model parameterizations of the permafrost contribution to the atmospheric CO<sub>2</sub>  
49 budget rely on field or laboratory warming experiments that observe static  
50 processes<sup>11,12</sup>. Recent experiments however stress that lateral hydrological export could  
51 explain unexpectedly high losses of permafrost carbon<sup>13</sup>. Indeed, ice melting in  
52 permafrost leads to ground subsidence and geomorphological changes with the  
53 formation of erosion gullies and thermokarst ponds<sup>14</sup>. Erosion processes lead to the  
54 accumulation of dissolved and particulate organic carbon (DOC and POC) in  
55 thermokarst ponds<sup>15,16</sup>, where it can be mineralized by microbial respiration and

56 photochemistry<sup>17-19</sup>. These latter processes are seldom included in models of permafrost  
57 carbon and in particular photolytic processes are ignored.

58 Photolysis of DOC and POC leads to the formation of CO<sub>2</sub> and its release to the  
59 atmosphere. However, products of incomplete oxidation are also formed and have been  
60 observed in the liquid phase<sup>20-22</sup>. The more volatile of these products can be released  
61 into the atmosphere and affect climate through several processes. The first one is their  
62 subsequent oxidation to CO<sub>2</sub>. Since gaseous emission measurements from lakes focus  
63 on CO<sub>2</sub> and CH<sub>4</sub><sup>19,23-25</sup>, neglecting this delayed CO<sub>2</sub> source may underestimate the  
64 greenhouse gas (GHG) emissions by lakes. Both field and laboratory studies indicate  
65 that incomplete photo-oxidation may represent up to half the photolysis products in  
66 lakes<sup>22,26</sup>. The second one is through the formation of ozone (O<sub>3</sub>), a potent GHG<sup>27</sup>, as  
67 many of the reactive organic compounds emitted are likely to have a strong O<sub>3</sub>  
68 formation potential<sup>28</sup>. Lastly, the further atmospheric oxidation of emitted compounds  
69 may lead to the formation of less volatile compounds that contribute to aerosol  
70 formation<sup>29</sup>. These aerosols affect climate through light scattering and cloud droplet  
71 formation<sup>30,31</sup>.

72 Here we performed laboratory experiments to explore the release of volatile organic  
73 compounds (VOCs) from the photolysis of waters from thermokarst ponds in palsa and  
74 lithalsa environments. Palsas are peat-covered permafrost mounds whose collapse feeds  
75 large amounts of organic matter into thermokarst ponds. Lithalsas are also permafrost  
76 mounds, but without peat, and the amount and nature of organic matter released to

77 thermokarst ponds are therefore expected to be different. Investigating the contrasted  
78 environments informs us about the variability of VOC emissions from thermokarst  
79 ponds. Below we will demonstrate that both sampled ponds are photochemically active.  
80 We will focus our attention on the different behaviors, and we discuss some aspects of  
81 the mechanisms involved and their underlying atmospheric implications at the sampling  
82 period and sites. The aim of this study is to encourage follow-up investigations to cover  
83 a wider range of conditions and [spatiotemporal](#) coverage.

## 84 MATERIALS AND METHODS

85 **Sample Collection.** The water samples used in this study were sampled in September  
86 2019 from two contrasted thermokarst ponds located within the Canadian subarctic  
87 region at Kuujjuarapik (55°13'11" N, 77°42'52" W) and Umiujaq (56°33'31" N,  
88 76°28'57" W), as shown in Figure 1.

89 The Kuujjuarapik pond was located at the base of a collapsing palsa, and its water  
90 was visibly colored. The Umiujaq pond was surrounded by collapsing lithalsas with  
91 sandy soil, with water less colored than that from the Kuujjuarapik pond. The vegetation  
92 near Umiujaq was mostly lichen (*Cladonia* sp., mostly *C. stellaris*) and dwarf birch  
93 (*Betula glandulosa*) as detailed by Gagnon et al.<sup>32</sup>. The soil organic content is low in  
94 this area, around 4 kg m<sup>-232</sup>. In the sporadic permafrost zone, i.e., where we collected  
95 the water samples, numerous palsas and lithalsas have formed<sup>33</sup>, as carbon reservoirs<sup>34</sup>.

96 To collect the liquid samples, amber glass containers, initially rinsed with  
97 concentrated HNO<sub>3</sub> and then several times with ultrapure water, were then prefilled

98 with ultrapure water (18.2 M $\Omega$ .cm) and emptied at each site, and then filled with pond  
99 water. The triplicate samples were taken from the top 10 cm of the ponds. Blanks were  
100 also collected by opening and closing a bottle filled with ultrapure water at each site.

101 All samples were frozen after collection and kept frozen until the actual photochemical  
102 experiments. The water samples were used for experiments as received i.e., unfiltered.

103 All results given below are blank-corrected, where the signals arising from blanks  
104 were subtracted from those of actual experiments. The VOC production from blanks  
105 was always significantly lower than those from collected samples (see Figure S1).

106 **Experimental Setup.** The approach used here was similar to that in our previous  
107 studies<sup>35,36</sup>. Briefly, a water- and Pyrex-filtered Xenon arc lamp delivered light  
108 irradiation in the actinic region (i.e., at wavelengths longer than  $\sim 280$  nm) to a  
109 cylindrical quartz cell (2 cm diameter and 10 cm length) half-filled with 6 mL of the  
110 unfrozen pond water sample (Figure S2). The headspace of this reactor was then  
111 continuously purged with purified air at a flow rate of 200 mL min<sup>-1</sup>, and its content of  
112 VOCs can be monitored by mass spectrometry (see below). After an initial stabilization  
113 period, the lamp was switched on, simulating solar irradiation for 180 min. The  
114 temperature fluctuations of the reactor were small, i.e., within  $\pm 2^\circ\text{C}$  (Figure S3). The  
115 experimental temperature ( $\sim 25^\circ\text{C}$ ) is comparable to the maximum air temperature  
116 during the warm seasons in northern Quebec<sup>37</sup>. All experiments were performed in  
117 triplicates.

118 Figure S4 gives the spectral profiles of experimental and natural irradiation. Here,  
119 irradiance is calculated for the wavelength range of 280 - 420 nm because only radiation  
120 therein initiates photochemistry, since shorter wavelength may cause photolysis, while  
121 the energy of longer wavelength is not sufficient to induce photochemical reactions.  
122 Laboratory works commonly used this wavelength range to infer the photochemical  
123 production and fluxes of VOCs<sup>38-40</sup>. The experimental irradiance was 8.0 mW cm<sup>-2</sup> as  
124 previously set<sup>41,42</sup>, with an actinic flux of  $1.20 \times 10^{16}$  photon cm<sup>-2</sup> s<sup>-1</sup>. The surface of  
125 irradiated water sample in this laboratory study was several orders of magnitude lower  
126 than in nature, which reduces the flux of products. In order to meet our detection limits,  
127 the experimental irradiance was set to be higher than the natural levels at the sampling  
128 sites, but it still compares to the midday conditions elsewhere and should thus be  
129 regarded as realistic on Earth<sup>43,44</sup>.

130 **Measurement of VOCs.** The VOCs produced upon irradiation were monitored using  
131 a high-resolution proton transfer reaction time-of-flight mass spectrometer (HR-PTR-  
132 ToF-MS, 8000, Ionicon Analytic GmbH, Austria). This technique was previously  
133 described by Müller et al.<sup>45</sup> and uses H<sub>3</sub>O<sup>+</sup> as a soft ionization agent. This MS  
134 continuously sampled 200 mL min<sup>-1</sup> gas flow at the reactor's outlet through a heated  
135 silicon steel tube. Spectra were acquired with a time resolution of 10 s at a mass  
136 resolution of 4500 m/Δm.

137 A calibration standard (TO-14A Aromatic Mix, Restek Corporation, USA)  
138 containing 14 VOCs (100 ppb for each diluted in N<sub>2</sub>) was utilized to calibrate and test



139 the instrument performance. The sensitivity of standard compounds ranged between 15  
140 and 70 cps/ppb, depending on the actual mass. As it was not possible to calibrate the  
141 instruments for each compound detected, the protonation rate constant was assumed to  
142 be  $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , and therefore the mean sensitivity was set to be 30 cps/ppb. The  
143 mass calibration was performed by internal standards: hydronium ion isotope ( $\text{H}_3^{18}\text{O}^+$ ,  
144  $m/z = 21.022$ ) and protonated acetone ( $\text{C}_3\text{H}_7\text{O}^+$ ,  $m/z = 59.049$ ) as commonly selected.  
145 The PTR-MS viewer software (version 3.2.8) was used for the raw spectral analysis,  
146 mass calibration, peak fitting, and area extraction. The mixing ratios of VOCs were  
147 finally determined based on the existing protocols<sup>46</sup>. More details are provided in  
148 Supporting Information (Text S1).

149 **Aqueous Phase Analysis.** For the liquid analysis, the solution before and after the  
150 VOC photochemical measurements were filtered, in contrast to the actual experiments,  
151 by a 0.22  $\mu\text{m}$  polytetrafluoroethylene (PTFE) membrane filter (Pall Corporation, USA).  
152 Each treated sample was analyzed using a Q-Exactive Hybrid Quadrupole-Orbitrap  
153 mass spectrometer (Thermo Scientific, USA) to characterize the liquid molecules  
154 included. In addition, each sample's pH, optical properties, and concentration of non-  
155 purgeable organic carbon (NPOC) were measured. More details are provided in  
156 Supporting Information (Text S2).

157 **Data Processing.** The detected molecules in both phases can be characterized by a  
158 variety of indices, including oxygen-to-carbon ratio (O/C), hydrogen-to-carbon ratio  
159 (H/C), ring and double-bound equivalence (RDBE), aromaticity equivalent (Xc),

160 carbon oxidation state (OSc), and modified aromaticity index ( $AI_{mod}$ ). Kendrick mass  
161 defect (KMD) analysis was performed to identify an array of compounds containing  
162 similar repeated functional groups<sup>47</sup>. Compounds whose elemental compositions only  
163 differ by the number of subunits would possess the same KMD level and line up  
164 horizontally in the KMD plot<sup>48</sup>. In this study, two subunits ( $CH_2$ ,  $COO$ ) were considered  
165 as key to describe the observed photochemistry. The characterization approaches are  
166 detailed in Text S3.

167 Correlation analysis and principal component analysis (PCA) were applied to the  
168 temporal VOC concentration profiles during the second half of light exposure to gain  
169 more insights into the relevant chemistry. Independent samples t-test was used to  
170 compare the experimental results of two different samples, whereas paired samples t-  
171 test compared the scenarios of pre and post irradiation for a specific sample. The  
172 outcome can be characterized by the  $p$  value, which indicates significant discrepancy  
173 or variation, when lower than 0.05. The measurement results from mass spectrometers  
174 are reserved for at least two decimals.

175 **Carbon Flux Calculation.** Following our previous studies on the photochemistry  
176 and VOC production at the air/sea interface<sup>38,39,41,49,50</sup>, we calculated the carbon flux  
177 associated with the emission of a given VOC normalized to the surface of water  
178 available under the simulated sunlight, denoted as  $SF_{VOCs}$  ( $nmol\ C\ m^{-2}\ s^{-1}$ ), according  
179 to:

$$180\ SF_{VOCs} = \sum_{i=1}^m \frac{L \times C_i \times N_i \times 10^{-3}}{V_T \times A} \quad (1)$$

181 where  $L$  is the flow rate of air ( $\sim 3.33 \text{ mL s}^{-1}$ ),  $C_i$  is the concentration of VOC  $i$  (ppb),  
182  $N_i$  is the number of carbon atoms in VOC  $i$  (dimensionless),  $V_T$  is the molar volume of  
183 gas at temperature  $T$  ( $24.4 \text{ L mol}^{-1}$  at  $24.3^\circ\text{C}$ ),  $A$  is the area of surface water exposed to  
184 air ( $17.85 \times 10^{-4} \text{ m}^2$ ),  $m$  is the number of organic species produced over the interface  
185 (38 for Kuujjuarapik and 55 for Umiujaq).

186 Given that the irradiance ( $I$ ) of the natural study site differs from the experimental  
187 setting, we estimated the natural VOC fluxes, denoted as  $NF_{VOCs}$  ( $\text{nmol C m}^{-2} \text{ s}^{-1}$ ), by  
188 using a linear relationship between the photoinduced VOC production and irradiance  
189 as previously reported in other cases<sup>41-43</sup>, as shown by equation (2). This correction  
190 method facilitates the comparison between the VOC emission fluxes derived from the  
191 different laboratory experiments and/or in-field measurements.

$$192 \quad NF_{VOCs} = SF_{VOCs-dark} + (SF_{VOCs-light} - SF_{VOCs-dark}) \times \frac{I_{natural}}{I_{experimental}} \quad (2)$$

193 where  $SF_{VOCs-dark}$  and  $SF_{VOCs-light}$  are respectively the carbon fluxes attributed to the  
194 VOCs emitted before and during irradiation,  $I_{experimental}$  is the experimental irradiance  
195 ( $8.0 \text{ mW cm}^{-2}$ ),  $I_{natural}$  is the natural irradiance. Hourly  $I_{natural}$  during the warm season  
196 of 2019 (1<sup>st</sup> June - 30<sup>th</sup> September) was measured at a meteorological site near the  
197 Umiujaq sampling site<sup>51,52</sup>. Temporal variations of  $I_{natural}$  are given in Figure S5. Solar  
198 irradiance at Kuujjuarapik is very similar to that at Umiujaq (see Figure S4), therefore  
199 we used the Umiujaq data for both sites. Because the experimental irradiance was 22.7  
200 folds of the natural daily mean level, the 180 min of irradiation in the laboratory  
201 simulates  $\sim 3$  days' photochemistry in the field. Similar photoinduced VOC production

202 was previously observed across other water samples under strong and weak irradiation  
203 in a smog chamber system<sup>38</sup>, and therefore no irradiance threshold exists in such type  
204 of investigations. Applying equation 2 (as described above) aims only to underline  
205 some differences in the pattern of emitted VOCs at both sampling sites, without  
206 capturing the full environmental variability of this Arctic region.

207 **Implication Evaluation.** To estimate whether the photochemically produced VOCs  
208 could locally (i.e., at the sampling sites) affect the O<sub>3</sub> budget under a given NO<sub>x</sub>  
209 concentration, O<sub>3</sub> formation potential, *OFP* (μg m<sup>-3</sup>), was calculated according to<sup>28</sup>:

$$210 \quad OFP = \sum_{j=1}^n [X]_j \times MIR_j \quad (3)$$

211 where  $[X]_j$  is the concentration of VOC  $j$  (μg m<sup>-3</sup>),  $MIR_j$  is the maximum incremental  
212 reactivity (MIR) coefficient of VOC  $j$ ,  $n$  is the number of VOC with documented *MIR*  
213 (22 for Kuujjuarapik and 33 for Umiujaq). *MIR* can be taken from the updated research  
214 results (<https://intra.engr.ucr.edu/~carter/SAPRC/>, last access: 10<sup>th</sup>, November 2022).

215 The calculated *OFP* can be normalized by the available air/water interfacial area to  
216 the simulated efflux of O<sub>3</sub>, denoted as  $SF_{O_3}$  (nmol m<sup>-2</sup> s<sup>-1</sup>), which is further corrected  
217 by the outdoor irradiance as that done for carbon flux to the natural  $F_{O_3}$ , denoted as  
218  $NF_{O_3}$  (nmol m<sup>-2</sup> s<sup>-1</sup>), according to:

$$219 \quad SF_{O_3} = \frac{L \times OFP \times 10^{-3}}{M_{O_3} \times A} \quad (4)$$

$$220 \quad NF_{O_3} = SF_{O_3} \times \frac{I_{natural}}{I_{experimental}} \quad (5)$$

221 where  $M_{O_3}$  is the molar mass of O<sub>3</sub> (48.0 g mol<sup>-1</sup>).

## 222      **RESULTS**

223      As soon as the pond water was illuminated in the actinic region, a strong net  
224 photochemical production of a variety of VOCs can be observed (Figure 2a). The  
225 production is sustained and increasing, demonstrating that products are building up as  
226 long as the light was presented. Such production stopped when the light was switched  
227 off, with the concentration decreasing over time. While Figure 2a shows the integrated  
228 signal over all VOCs, more product details are presented in Table S1. The non-  
229 monotonic increases suggest that 2<sup>nd</sup> generation products are formed in both the liquid  
230 and gas phases. The net concentrations of total VOCs produced by photochemistry,  
231 determined by subtracting the background signal of each VOC (i.e., the averaged dark  
232 level before irradiation) by the corresponding maximum signal observed during the 180  
233 min of irradiation, are  $13.83 \pm 2.01$  ppb (mean  $\pm$  standard error [SE]) and  $20.14 \pm 1.93$   
234 ppb for the samples from Kuujjuarapik and Umiujaq, contributed by 38 and 55 species,  
235 respectively. That is, the Umiujaq water exceeds the Kuujjuarapik water in the VOC  
236 photoproduction ( $p < 0.05$ , Figure S6). Thirty volatile products are common to both  
237 sites (Figure 2b).

238      Half of the VOCs emitted from the sunlit Kuujjuarapik sample contain  $\leq 3$  carbons,  
239 and these compounds are responsible for  $\sim 87\%$  of the concentration of the  
240 Kuujjuarapik VOCs (Figure 2c, top half). By contrast, for the Umiujaq VOCs, while  
241 the total concentration is mainly contributed by C1-C3 species, most compounds  
242 contain  $\geq 4$  carbons. The concentration-weighted mean molecular mass of the Umiujaq

243 VOCs (53.26) is slightly greater than that of the Kuujjuarapik VOCs (50.98).  
244 Furthermore, the VOCs are classified into CHO, CH, CHON, CHN, and CHS  
245 subgroups according to their elemental compositions (Figure 2c, bottom half). The  
246 CHO subgroup generally dominates the structure of VOCs observed, and the water  
247 sample from Umiujaq is more efficient than that from Kuujjuarapik in producing all  
248 these subgroups, except for the concentration of CHON and the number of CHS. The  
249 average molecular formulas can be given as  $C_{2.370}H_{4.839}O_{1.026}N_{0.064}S_{0.011}$  for the  
250 Kuujjuarapik VOCs and  $C_{2.651}H_{5.189}O_{0.948}N_{0.065}S_{0.003}$  for the Umiujaq VOCs.

251 Speciation of the observed photoproducted VOCs is given in Figure 2d. As the most  
252 abundant product from the sunlit Kuujjuarapik pond surface water,  $CH_4O$  accounts for  
253 28.3% of the total VOC concentration, followed by  $C_2H_4O$  (20.8%),  $C_3H_6O$  (16.1%),  
254  $C_3H_4O$  (4.6%),  $C_2H_2O$  (3.2%),  $C_2H_4O_2$  (2.2%),  $CH_3NO$  (2.2%),  $C_4H_8O$  (2.1%),  $C_4H_6O$   
255 (1.4%),  $C_2H_5NO$  (1.3%) and other 28 compounds (accounting up to 17.8%). For the  
256 pond water from Umiujaq, the ten most abundant compounds are  $C_2H_4O$  (30.9%),  
257  $CH_4O$  (15.5%),  $C_3H_6O$  (14.8%),  $C_3H_4O$  (5.0%),  $C_2H_4O_2$  (2.4%),  $C_4H_8O$  (2.2%),  $C_3H_5N$   
258 (2.0%),  $C_2H_2O$  (2.0%),  $C_2H_6O$  (1.8%),  $C_4H_8$  (1.7%), followed by the other 45 products  
259 (accounting up to 21.8%). Also, for a given VOC, its relative production is negatively  
260 correlated with its molecular weight (Figure S7).

261 Overall, three dominant species,  $CH_4O$ ,  $C_2H_4O$ , and  $C_3H_6O$  that were normally  
262 identified as methanol, acetaldehyde, and acetone (or possibly propanal or methyl vinyl  
263 ether), are responsible for > 60% of the total VOC concentrations for both samples. A

264 statistical treatment (PCA in Figure S8) further reveals that these three compounds are  
265 not correlated and do originate from distinct processes, depending on the type of  
266 thermokarst pond surface water. Furthermore, positive correlations are common for the  
267 Umiujaq VOCs, whereas more negative correlations are observed among the  
268 Kuujjuarapik VOCs (Figure S9). In general, the Kuujjuarapik VOCs are more  
269 oxygenated, unsaturated, and aromatic than the Umiujaq ones, as reflected by the higher  
270 O/C and OSc, lower H/C and higher RDBE, and higher Xc and AI<sub>mod</sub>, respectively  
271 (Table S2). Such molecular differences are certainly associated with the compositions  
272 of permafrost organic carbon in the two contrasted ponds studied here.

273 The photochemistry of both samples also differs significantly in the filtered liquid  
274 phase. The NPOC levels were  $1320 \pm 16$  and  $1070 \pm 28$   $\mu\text{M}$  for the waters from  
275 Kuujjuarapik and Umiujaq, respectively, before irradiation. After irradiation, as shown  
276 in Figure S10, the NPOC level for Kuujjuarapik significantly increased to  $1823 \pm 170$   
277  $\mu\text{M}$  ( $p < 0.05$ ), whereas that of Umiujaq generally showed no significant change, with  
278 a value of  $1003 \pm 123$   $\mu\text{M}$  ( $p > 0.05$ ). Moreover, as shown in Figure S11, the pH  
279 increased from  $6.9 \pm 0.0$  to  $7.4 \pm 0.1$  for the Umiujaq water ( $p < 0.05$ ), while it decreased  
280 from  $7.1 \pm 0.0$  to  $6.9 \pm 0.0$  for the Kuujjuarapik water ( $p < 0.05$ ). Lastly, the Umiujaq  
281 sample was observed to photobleach with irradiation, while for Kuujjuarapik the  
282 absorbance increased over time for wavelengths below 300 nm (Figure S12).

283 Our observations indicate that the organics contained in the thermokarst ponds are  
284 photochemically active and produce a variety of VOCs. Based on equation (1), under

285 the experimental setting, the integrated  $SF_{VOCs}$  for the Kuujjuarapik and Umiujaq ponds  
286 are 2.83 and 4.61  $\text{nmol C m}^{-2} \text{ s}^{-1}$ , respectively. We further estimated the associated  
287  $NF_{VOCs}$  according to equation (2), and compared the two surface waters. The diel cycle  
288 of hourly  $NF_{VOCs}$  is shown in Figure 3a, and both surface waters produced the highest  
289 carbon fluxes at noon. The average  $NF_{VOCs}$  of the sampling day is estimated to be 0.21  
290  $\text{nmol C m}^{-2} \text{ s}^{-1}$  across the Kuujjuarapik pond and 0.51  $\text{nmol C m}^{-2} \text{ s}^{-1}$  across the Umiujaq  
291 pond. The photoinduced carbon flux across Kuujjuarapik pond primarily consists of  
292  $\text{C}_3\text{H}_6\text{O}$  (20.3%),  $\text{C}_2\text{H}_4\text{O}$  (17.5%), and  $\text{CH}_4\text{O}$  (12.0%), and that across Umiujaq pond is  
293 mostly made of  $\text{C}_2\text{H}_4\text{O}$  (23.4%),  $\text{C}_3\text{H}_6\text{O}$  (16.7%), and  $\text{CH}_4\text{O}$  (5.8%), as shown by  
294 Figure 3b. That is, acetaldehyde, acetone (or possibly propanal or methyl vinyl ether)  
295 and methanol, which account for > 60% of the concentration of photoproducted VOCs  
296 (see Figure 2d), also explain nearly half of the photoinduced VOC-associated carbon  
297 flux over sunlit thermokarst ponds.

298 In order to further reveal the potential importance of the discovered photochemistry,  
299 we speculate that the photoinduced VOC production for a longer time scale can be  
300 estimated by extrapolating the measurement results to the natural irradiance of the warm  
301 season (Figure S13). The highest daily  $NF_{VOCs}$  over the thermokarst ponds would occur  
302 around the summer solstice. As irradiance decreased since then, the  $NF_{VOCs}$  over both  
303 ponds generally decreased. Since  $NF_{VOCs}$  is influenced by temperature, irradiance, and  
304 the properties of water, the atmospheric relevance of this photochemistry should be  
305 accurately evaluated according to the actual situation.



306     **DISCUSSION**

307     To the best of our knowledge, this is the first detection and quantification of  
308 photochemically produced non-methane VOCs from thermokarst ponds. The weak  
309 VOC emissions before irradiation are probably explained by the diffusion to the gas  
310 phase of volatile species photoproducted under natural conditions before sampling. This  
311 is supported by the positive correlation between the individual VOC concentrations  
312 before and during irradiation (Figure S14). Thermokarst ponds are therefore a  
313 photochemical reactor that is able to transform permafrost carbon into atmospheric  
314 VOCs. VOCs have been reported to be also emitted directly by thawing permafrost,  
315 without the intervention of liquid phase photochemistry<sup>53-55</sup>. Current understanding is  
316 that these VOCs were produced by microbial metabolism, mostly anaerobic, and  
317 accumulated over the years before being released by thawing<sup>53-55</sup>. Here, however, we  
318 observed rapid VOC emission which is well correlated to irradiation conditions, so that  
319 production can be ascribed to photochemistry with reasonable certainty, rather than  
320 microbial production. This is in line with the observation of photoproducts over the  
321 liquid phase by others<sup>43</sup>. Given that many photoinduced reactions at the air/water  
322 interface are significantly enhanced in comparison to the corresponding gas- or liquid-  
323 phase bulk processes<sup>56</sup>, and that our experiments were performed in the absence of any  
324 gaseous oxidants (and over very short residence time of the gas phase), the observed  
325 photochemical production of VOCs is mainly related to processes occurring at the  
326 air/water interface, with a possible contribution of aqueous bulk photochemistry.

327 Figure 4 illustrates the generic mechanism summarizing the photochemical  
328 production of VOCs from the surface water in these ponds. Thawing permafrost  
329 releases soil carbon into thermokarst ponds as POC and DOC, which both undergo an  
330 array of photochemical reaction pathways producing secondary DOC (DOCs),  
331 followed by the release of reacted DOC (DOCr) into the atmosphere as VOCs.  
332 Depending on the actual chemistry taking place, partial oxidation or decarboxylation  
333 leads to the formation of DOCr, which is more volatile and therefore more easily  
334 diffuses to the gas phase<sup>20,22,57</sup>. Given that the DOC loading of the Kuujjuarapik pond  
335 water significantly increased after irradiation, photolysis of POC to DOC may be  
336 responsible for the photochemistry in this palsa-affected surface water. In contrast, the  
337 decrease in absorbance of the Umiujaq water after irradiation indicates a decrease in  
338 photoreactive compounds, implying a lower transformation of POC to DOC.

339 Interestingly, the Kuujjuarapik pond water, which is organic-rich because it is  
340 affected by peat, is less efficient in the photochemical production of VOCs than the  
341 Umiujaq one which is organic-poor. Based on our previous research on the  
342 photochemistry of humic acids in multiphase systems similar to the one explored  
343 here<sup>38,41</sup>, we are considering that the photoproduction observed for the thermokarst  
344 pond surface water is strongly impacted by the processes occurring at the air/water  
345 interface, and in particular by the availability of organic matters at the top layers of the  
346 liquid phase. In other words, if more appropriate precursors and oxidants are located at  
347 the sunlit air/water interface, more VOCs should be produced. Such availability is

348 highly pH-dependent, as for example more long-chain organic acids are increasingly  
349 soluble with increasing pH. Herein, the photo-decreased pH of the Kuujjuarapik water  
350 indicates the generation of organic acids derived from the photolysis of POC, during  
351 which the availability of surface acids decreases, whereas the photo-increased pH of  
352 the Umiujaq water implies the higher VOC production efficiency relying on photo-  
353 decarboxylation that can be described as the breakdown of carboxylic acids (R-COOH)  
354 to hydrocarbons (R-H) and CO<sub>2</sub> by sunlight<sup>20,58</sup>:



356 Another indication can be found in the evolution of the optical property of surface  
357 water. The photobleaching of the Umiujaq water implies that large compounds may  
358 photodegrade into smaller fragments with increased volatility. By contrast, the photo-  
359 enhanced absorbance of the Kuujjuarapik water indicates that photochemistry induces  
360 the increase of chemical functionalities, as evidenced by the photo-increased liquid  
361 aromaticity (Table S3). This variation may be attributed to the significant photolysis of  
362 POC, followed by the conversion of non-condensed aromatics to monoaromatics with  
363 higher AI<sub>mod</sub><sup>59</sup>. Overall, the photo-productivity of thermokarst pond water may thus be  
364 better predicted by considering the segregation and processes at the air/water interface  
365 than bulk organic concentration. This is in line with previous research in other aqueous  
366 systems, where the prevalence of interface processes was demonstrated<sup>38,41</sup>.

367 As additionally suggested by the KMD plots for CH<sub>2</sub> (Figure S15) and COO (Figure  
368 S16), most photo-enhanced VOCs would “theoretically” form after the removal of one

369 or more target subunits (e.g., CH<sub>2</sub> or COO) from the photodegraded liquid compounds.  
370 As an example, for both samples, C<sub>4</sub>H<sub>4</sub>O<sub>2</sub> may generate via the photo-dealkylation of  
371 C<sub>5</sub>H<sub>6</sub>O<sub>2</sub> and its homologous series, and the photo-decarboxylation of C<sub>4</sub>H<sub>6</sub>O<sub>3</sub> or  
372 C<sub>5</sub>H<sub>6</sub>O<sub>5</sub> would produce C<sub>3</sub>H<sub>6</sub>O. More suggested “precursor-product” pairs are listed  
373 alongside the KMD plots in the Supporting Information. This points to the fact that, as  
374 expected, we do observe multigeneration products from permafrost carbon conversion,  
375 in agreement with the time profiles seen in Figure 2a. In comparison with the  
376 Kuujjuarapik DOC, the Umiujaq DOC favors the photochemical production of VOCs  
377 via decarboxylation channels. The efficient carboxyl loss follows the photo-increased  
378 pH of the Umiujaq water and may be associated with more significant release of CO<sub>2</sub>.  
379 The relevant mechanisms may be much more complex than expected<sup>60</sup>, depending on  
380 the actual composition of the liquid phase.

381 Uncertainties may exist when reproducing the natural conditions. Firstly, the  
382 production and release of volatile species are obviously changing with temperature<sup>61,62</sup>.  
383 Secondly, the carbons in thermokarst ponds are refreshed because (i) the permafrost is  
384 always thawing by warming<sup>14,63</sup>, rainfall<sup>64</sup>, and wildfire<sup>9</sup>; (ii) wind above the shallow  
385 pond will mix its liquid phase, including the vertical transport from deeper layers to  
386 interface<sup>65</sup>; and (iii) the headwater streams feed the thermokarst ponds by bringing in  
387 soil materials, especially during rain episodes<sup>57,65</sup>. The refresh of thermokarst pond  
388 water will further change its physical properties (e.g., surface tension, liquid viscosity)  
389 that are associated with the performance of air/water interface. Third and perhaps most

390 important, the “chemical history” (e.g., number of diurnal cycles) of permafrost carbons  
391 will also alter the liquid properties<sup>20,22,26</sup>, followed by the variation of sunlight intensity  
392 at various depths and at the aqueous interface<sup>57</sup>. Those effects are certainly to be taken  
393 into account for the following studies.

#### 394 **IMPLICATIONS**

395 It is worthwhile to mention that, the measurements performed by this study are too  
396 limited in space and time to provide a robust assessment of the VOC emission over the  
397 numerous thermokarst landscapes ( $3.6 \times 10^6$  km<sup>2</sup>, ~ 20% of the northern permafrost  
398 region<sup>14</sup>), but given the vast area of this continuously formed natural air/water interface  
399 and the considerable emission fluxes of VOCs under sunlight, there is an urgent need  
400 to take throughout research of this photochemistry over the thermokarst ponds/lakes on  
401 Earth. Besides, temporal difference caused by the variations of carbon compositions,  
402 temperature, and irradiance are warranted in future works, as an attempt to reveal more  
403 characteristics of the photochemistry over thermokarst landscapes.

404 Nevertheless, the photochemical production of atmospheric VOCs may strongly  
405 impact the local air composition by generating significant airborne O<sub>3</sub> in the presence  
406 of NO<sub>x</sub>. Simply based on equations (3) and (4), the  $SFO_3$  is calculated to be 3.83 nmol  
407 m<sup>-2</sup> s<sup>-1</sup> for the Kuujjuarapik sample and 7.34 nmol m<sup>-2</sup> s<sup>-1</sup> for the Umiujaq sample, under  
408 the experimental irradiance. Such results are much higher than the  $SFO_3$  over an  
409 authentic air/sea surface (0.51 nmol m<sup>-2</sup> s<sup>-1</sup>) investigated under the same experimental  
410 condition<sup>42</sup>, suggesting that the photochemistry we discovered might present

411 considerable impacts on the local ozone budget. Corrected by equation (5), the daily  
412 average  $NFO_3$  is  $0.17 \text{ nmol m}^{-2} \text{ s}^{-1}$  for Kuujjuarapik and  $0.32 \text{ nmol m}^{-2} \text{ s}^{-1}$  for Umiujaq,  
413 during the entire warm season. The speciated contribution to  $O_3$  formation is shown in  
414 Figure S17. Among the Kuujjuarapik VOCs,  $C_2H_4O$  (acetaldehyde) is the largest  $O_3$   
415 contributor and accounts for 35.7% of the  $NFO_3$ , followed by  $C_3H_4O$  (acrolein, 11.4%),  
416  $C_3H_4O_2$  (acrylic acid, 5.9%),  $C_4H_6O_2$  (methyl acrylate, 5.5%), and  $C_4H_6O$  (methyl vinyl  
417 ketone, 5.5%). In contrast, the main  $O_3$  contributors among the Umiujaq VOCs are  
418  $C_2H_4O$  (acetaldehyde, 40.5%),  $C_3H_4O$  (acrolein, 9.4%),  $C_4H_8O$  (butanal, 4.4%),  $C_4H_8$   
419 (butene, 4.2%), and  $C_4H_6O$  (methyl vinyl ketone, 4.0%). The ranking of  $NFO_3$  differs  
420 from that of VOC concentrations, implying that the atmospheric impact of this  
421 photochemistry may not be directly determined by the magnitude of VOC emission. In  
422 addition to altering locally the  $O_3$  budget, the emissions of VOCs could also lead to an  
423 increase in secondary organic aerosol formation, similar to what has been observed for  
424 processes involving chromophoric materials at the air/sea interface<sup>66</sup>. This however  
425 needs to be verified by further measurements.

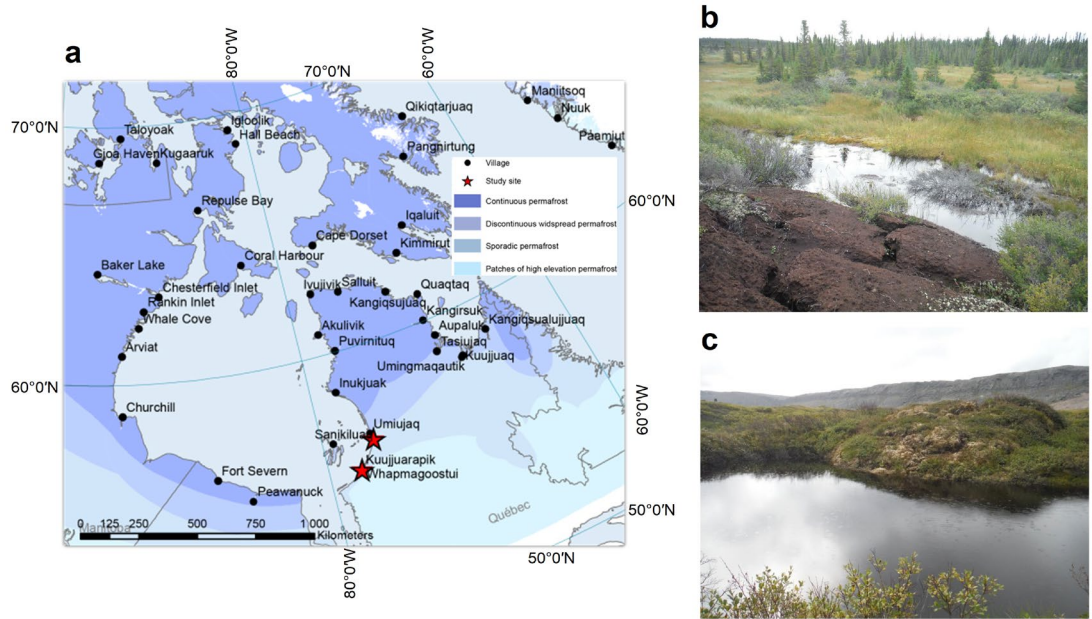
426 Even though the VOC flux data were not reported for typical thermokarst landscapes,  
427 a shallow post-glacial subarctic lake was recently explored for its in-field emission of  
428 six non-methane VOCs<sup>67</sup>, and the comparison results are listed in Table S4. At the end  
429 of subarctic warm season (i.e., September), the lake presented net deposition fluxes of  
430 methanol, acetaldehyde, acetone, and dimethyl sulfide, in contrast to the net emission  
431 fluxes of isoprene and monoterpenes, eventually causing a net deposition flux of total

432 VOCs ( $-0.287 \text{ nmol C m}^{-2} \text{ s}^{-1}$ ). The negative flux measured for the lake demonstrates  
433 that processes other than photochemistry were involved. In this study, both thermokarst  
434 pond waters owned more significant fluxes of methanol, acetaldehyde, and acetone than  
435 other three VOCs, corresponding to the photoinduced VOC emission fluxes of 0.080  
436 and  $0.172 \text{ nmol C m}^{-2} \text{ s}^{-1}$  for Kuujjuarapik and Umiujaq, respectively. While in nature  
437 it is difficult to isolate the contribution of photochemical processes to VOC emissions,  
438 the comparable absolute VOC fluxes obtained in the field and laboratory imply that the  
439 photochemistry reported here may have considerable implications for the budget and  
440 composition of atmospheric VOCs over subarctic water bodies.

441 Another obvious extension of this work is the comparison of the carbon fluxes of  
442 VOCs, which are currently not in-field measured over thermokarst ponds, with those of  
443  $\text{CH}_4$  and  $\text{CO}_2$ , which have been frequently measured over water bodies in the Arctic.  
444 The  $\text{CO}_2$  and  $\text{CH}_4$  fluxes have been measured above ponds close to those we  
445 sampled<sup>19,68</sup>. The average fluxes of  $\text{CO}_2$  and  $\text{CH}_4$  were respectively 143.84 and 5.80  
446  $\text{nmol C m}^{-2} \text{ s}^{-1}$  over a lithalsa-affected thermokarst lake, and 676.28 and 40.60  $\text{nmol C}$   
447  $\text{m}^{-2} \text{ s}^{-1}$  over a palsa-affected thermokarst lake. In comparison, the VOC fluxes we  
448 measured are lower by 1-3 orders of magnitude. However, measurement conditions are  
449 not comparable. Our experiments were performed over samples with a maximal depth  
450 of  $\sim 0.55 \text{ cm}$ , in contrast to the water bodies with depths of typically 2.0 m over which  
451 the gaseous  $\text{CO}_2$  and  $\text{CH}_4$  were produced. Furthermore, one study on a thermokarst lake  
452 near Kuujjuarapik<sup>26</sup> concluded that “only half of the light-associated DOC losses were

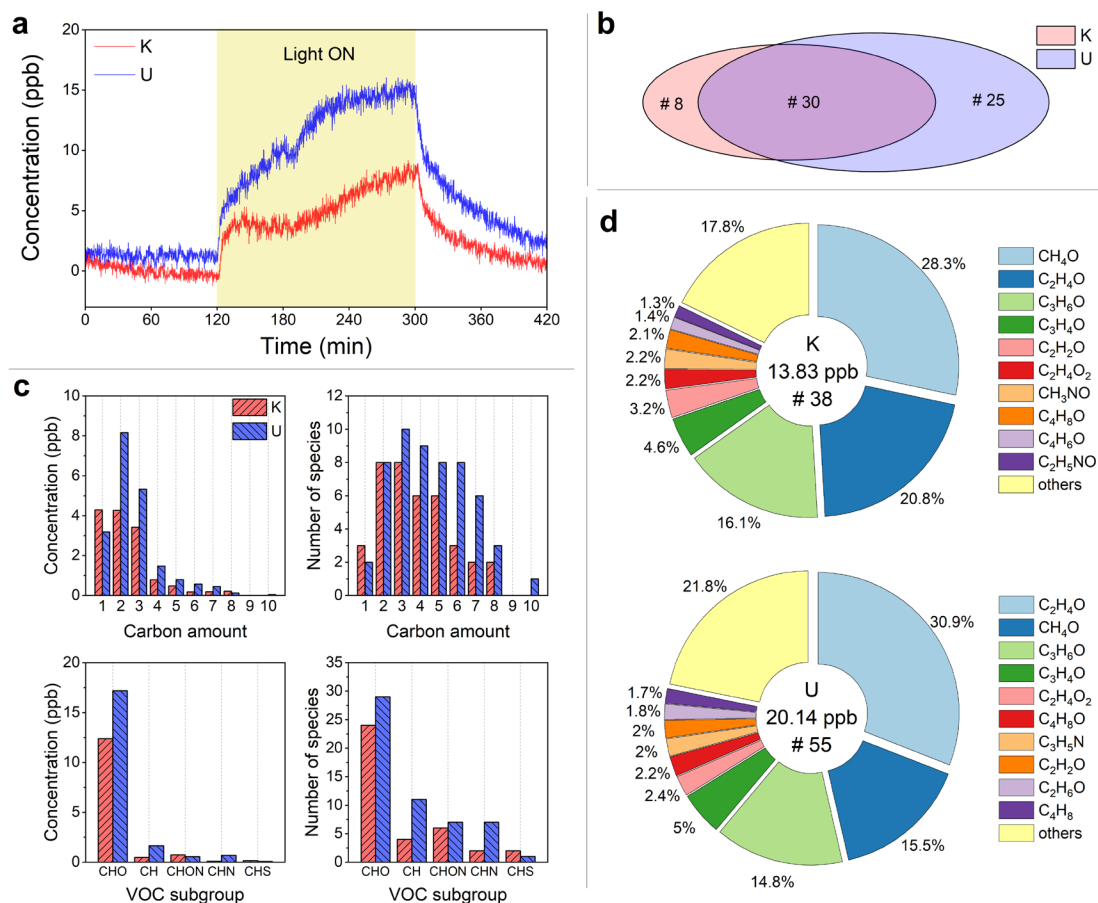
453 converted into CO<sub>2</sub>”, so that the fraction of VOCs produced by pond water photolysis  
454 may actually be significant. Meaningful comparisons would require operating under  
455 similar conditions for CO<sub>2</sub>, CH<sub>4</sub> and VOC measurements. This is an analytical  
456 challenge, left for future research.





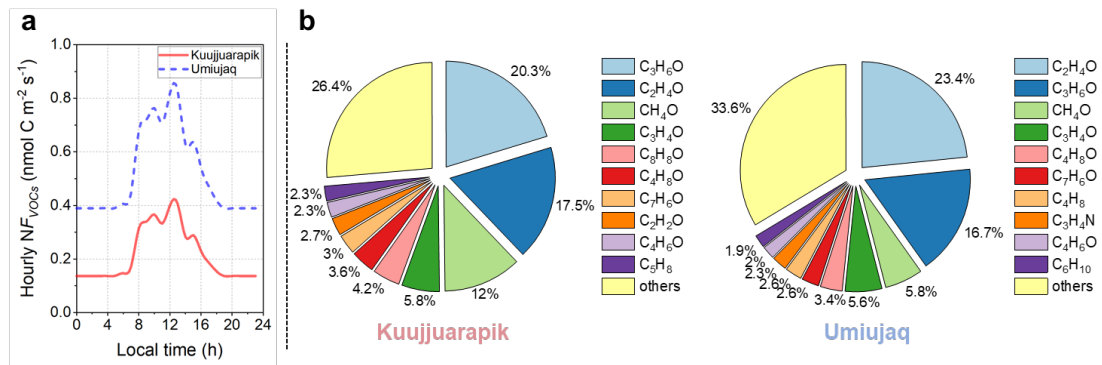
**Figure 1. Overview of the studied thermokarst ponds.**

(a) Geographical location of the sampling sites in Northern Quebec, Canada. The color scale distinguishes the type of permafrost. The study sites are located at the sporadic permafrost zone. Surrounding of the thermokarst ponds located at the (b) Kuujjuarapik and (c) Umiujaq sites.



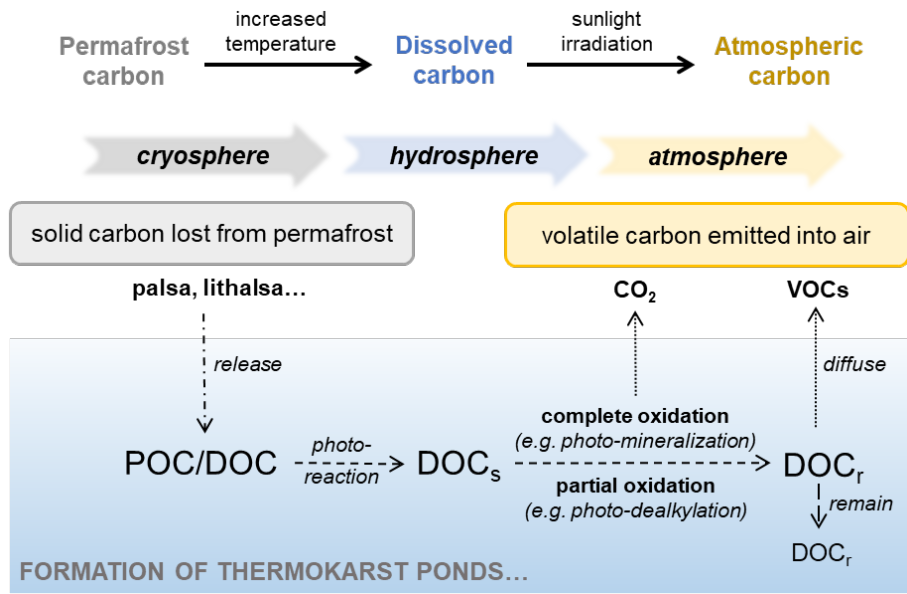
**Figure 2. Characterization of the photoproduction of VOCs.**

(a) Temporal profile of the concentration of VOCs produced from thermokarst pond water. Irradiation is highlighted by the yellow shading. The surface water samples were collected at the Kuujjuarapik (denoted as K) and Umiujaq (denoted as U) sites located in Northern Quebec, Canada. (b) Venn diagram for the numbers of VOCs photoemitted from the different samples. (c) Concentration or number of the photoproduced organic vapors as a function of carbon amount or VOC subgroup, varying with the type of thermokarst pond water sample. (d) Concentration proportions of the photoinduced VOCs. The ten most abundant species are listed for each sample. In total, 38 and 55 photoinduced VOCs, accounting for the measured volume concentrations of 13.83 and 20.14 ppb, were observed for the K and U samples, respectively.



**Figure 3. Evaluation of the photoproduction of VOCs.**

- (a)** Diurnal variation of hourly natural VOC fluxes ( $NF_{VOCs}$ ) over the studied thermokarst ponds. The emission flux of VOC-associated carbon can be calculated by equation (1) and further corrected by equation (2). The radiation data were recorded by a meteorological station near the Umiujaq pond during the sampling day: 4<sup>th</sup> September 2019.
- (b)** Contribution proportions of the photoinduced VOC-associated carbon fluxes (unit:  $\text{nmol m}^{-2} \text{s}^{-1}$ ) over different thermokarst ponds. The ten most abundant species are listed for each site.



**Figure 4. Schematic diagram for the photoinduced VOC production.**

The photochemical production of VOCs can be briefly described as the evolution of soil carbon lost from thawing permafrost to dissolved carbon in thermokarst pond along with the increased temperature, followed by the photo-generation of volatile atmospheric carbon in surface water (solid line arrows). Overall, this photochemistry connects the Earth's cryospheric carbon reservoir to the atmosphere, via the hydrosphere. In detail, it comprises the release of permafrost carbon into thermokarst ponds (dash-dot line arrow), the photo-reaction of particulate organic carbon (POC) and dissolved organic carbon (DOC) in the liquid phase (short-dash line arrow), the further conversion of secondary DOC (DOCs) acting as VOC precursors (short-dash line arrow), the diffusion of volatile reacted DOC (DOC<sub>r</sub>) into the atmosphere as VOCs (dot line arrow), as well as the retention of DOC<sub>r</sub> in the liquid phase (dash line arrow). DOCs can also be completely oxidized to CO<sub>2</sub>.

## ASSOCIATED CONTENT

**Supporting Information.** Description of experimental procedures, methods of data analysis, characteristics (irradiance and actinic flux) of the experimental and natural irradiation; detailed information and molecular characterization of the detected VOCs, photoinduced evolutions of liquid phase, calculation of ozone formation potentials.

## AUTHOR INFORMATION

### Corresponding Author

Liwu Zhang (zhanglw@fudan.edu.cn)

Florent Domine (florent.domine@gmail.com)

Christian George (christian.george@ircelyon.univ-lyon1.fr)

### Author Contributions

T.W., F.D., S.P., and C.G. designed research; T.W., C.K., and S.P. performed research; T.W., C.K., S.P., and C.G. analyzed the data; T.W., D.F., F.D., L.Z., J.C., S.P., and C.G. wrote the paper.

### Notes

The authors declare no competing interest.

## ACKNOWLEDGMENTS

The authors thank Letizia Abis, Xinke Wang, Sophie Tomaz, and Dandan Li (CNRS, IRCELYON) for their help in data analysis. F.D. and D.F. were funded by the French Polar Institute (IPEV, grant 1042) and NSERC discovery grant program. T.W. acknowledges the

National Natural Science Foundation of China (42205099) and the China Postdoctoral Science Foundation (2021M700792). L.W.Z. acknowledges the National Natural Science Foundation of China (22176036, 21976030, 22006020).

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