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1 **Emission of volatile organic compounds to the atmosphere from photochemistry in**  
2 **thermocarst ponds in subarctic Canada**

3 Daniel Fillion<sup>1,2</sup>, Sébastien Perrier<sup>3</sup>, Matthieu Riva<sup>3</sup>, Christian George<sup>3</sup>, Florent Domine<sup>1,2</sup>  
4 and Raoul-Marie Couture<sup>1,2,\*</sup>

5  
6 <sup>1</sup> Centre d'études nordiques and Department of Chemistry, Université Laval, 2325 Rue de  
7 l'Université, Québec, QC, Canada, G1V 0A6

8 <sup>2</sup>Takuvik Joint International Laboratory, Université Laval and CNRS-INSU (France), 2325  
9 Rue de l'Université, Québec, QC, Canada, G1V 0A6

10 <sup>3</sup>Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Ircelyon, 69626, Villeurbanne,  
11 France

12 Correspondance : [raoul.couture@chm.ulaval.ca](mailto:raoul.couture@chm.ulaval.ca)

13 **Keywords** : cold region, permafrost, carbon cycle, dissolved organic matter, VOCs, Vocus  
14 PTR-TOF.

15  
16 **Abstract**

17 Climate warming is accelerating the thawing of permafrost, which contains almost twice  
18 as much carbon as the atmosphere, to a point where a large quantity of dissolved organic  
19 matter (DOM) is being mobilized toward surface waters including thermocarst ponds.

20 DOM can be partially photo-degraded into volatile organic compounds (VOCs) which are  
21 little studied in Arctic environments. The main objective of this work is to identify and  
22 quantify the VOCs emitted to the gas phase by photochemistry from thermocarst water

23 sampled in four ponds from two study sites in northern Quebec. VOC emissions were  
24 characterized by proton-transfer-reaction mass spectrometry. Results show rapid  
25 photoproduction of between 35 and 59 VOCs when dissolved organic matter (DOM) water

26 samples are exposed to radiation. Our results also show that the quality of DOM is a more  
27 important factor to control VOC photoproduction than the quantity of DOM. Depending

28 on the assumptions used in upscaling our laboratory results to the field sites, calculations  
29 yield net carbon fluxes, between 1.93 and 174  $\mu\text{mol C m}^{-2} \text{ d}^{-1}$ . While these values are small  
30 compared to literature values of  $\text{CO}_2$  and  $\text{CH}_4$  fluxes from thermokarst ponds, this process  
31 represents an important flux of reactive molecules that could affect Arctic atmospheric  
32 chemistry.

### 33 **1. Introduction**

34 The Arctic is warming at a rate nearly four times faster than other regions of the globe <sup>1</sup>.  
35 This acceleration affects northern environments in drastic ways, intensifying  
36 geomorphological changes such as permafrost thaw and subsequent formation of  
37 thermokarst ponds <sup>2, 3</sup>. Since permafrost contains almost twice as much carbon as the  
38 atmosphere <sup>4</sup>, its erosion leads to the transfer of organic material to surface waters including  
39 thermokarst ponds. These ponds become important natural bio- and photochemical reactors  
40 where these organic molecules are mineralized, resulting in  $\text{CO}_2$  and  $\text{CH}_4$  emissions to the  
41 atmosphere <sup>5</sup>.

42 Photochemical degradation, which includes photolysis and photosensitization, is a major  
43 pathway of DOM processing in northern inland waters, and photolysis rates are relevant to  
44 the Arctic carbon cycle <sup>6-9</sup>. Terrestrial DOM is rich in chromophoric DOM (CDOM), the  
45 light-absorbing fraction of DOM, which is composed of high molecular weight, aromatic  
46 and colored compounds. Complete and partial photo-oxidation of CDOM produce  $\text{CO}_2$  and  
47 partially oxidized carbon compounds, respectively <sup>10-12</sup>. Product molecules are generally  
48 more aliphatic and, being broken down, have a lower molecular mass than their precursor.  
49 Their fate is generally insufficiently understood in aquatic systems <sup>13</sup>.

50 Here, we test the hypothesis that some partially oxidized photoproducts are sufficiently  
51 volatile to be emitted as volatile organic compounds (VOCs) to the atmosphere. This would  
52 add another pathway for C evasion from thermokarst ponds in addition to those listed  
53 above. While small molecules, such as acetone, formaldehyde, pyruvic acid and  
54 acetaldehyde are photoproducts in the liquid phase<sup>13-15</sup>, their transfer to the gas phase has  
55 not been documented in the Arctic. Given that Brüggemann et al.<sup>16</sup> reported that the  
56 photolysis of humic substances at the sea–air interface could lead to the significant  
57 production of various VOCs, we suggest that similar processes in thermokarst ponds  
58 deserve investigation.

59 VOCs are produced from a wide range of natural and anthropogenic sources and are  
60 ubiquitous in the environment<sup>17</sup>. Yet, their sources in the Arctic have not been studied  
61 extensively. To our knowledge, only a few papers focus on VOC emissions from thawing  
62 permafrost soil<sup>18-22</sup> and marine systems<sup>23,24</sup>. In the atmosphere, VOCs further undergo a  
63 series of oxidative chemical processes leading to the formation of secondary organic  
64 aerosols (SOA)<sup>25</sup>. Since SOA can act as cloud condensation nuclei (CCN)<sup>26</sup>, these  
65 transformations increase water droplet formation within a cloud, which increases cloud  
66 albedo. This process is known as the Twomey effect or the indirect aerosol effect<sup>27</sup>. VOCs  
67 can also contribute to tropospheric ozone (O<sub>3</sub>) and production of radicals (e.g., OH, HO<sub>2</sub>)  
68<sup>28,29</sup>.

69 Thus, VOCs could be a reservoir of C that represents a delayed source of greenhouse gases  
70 (GHGs) CO<sub>2(g)</sub> and O<sub>3(g)</sub> from thermokarst ponds to the atmosphere. This source is not  
71 currently accounted for as studies have focused on direct flux measurements above the  
72 pond<sup>30-33</sup>. Laboratory experiments are necessary to isolate photoproduction since field

73 measurements alone cannot discern the precise origins (cyanobacteria, algae, sunlight) <sup>34</sup>.  
74 This study aims to fill this knowledge gap by examining and quantifying the photolytic  
75 formation of VOCs in thermokarst ponds. To this end, we conducted photo-degradation  
76 experiments on water samples collected in thermokarst ponds from two subarctic regions.  
77 We have estimated VOC emissions using a proton-transfer-reaction time-of-flight mass  
78 spectrometry (Vocus® PTR-ToF-MS). We compare the fluxes of VOCs to literature values  
79 of CO<sub>2</sub> and CH<sub>4</sub> fluxes from subarctic thermokarst ponds. We have also tested the  
80 hypothesis that samples with higher CDOM content might lead to a wider variety and  
81 greater fluxes of photoproducts, due to the observation that DOM photo lability is  
82 related to its chemical composition <sup>12, 35, 36</sup>.

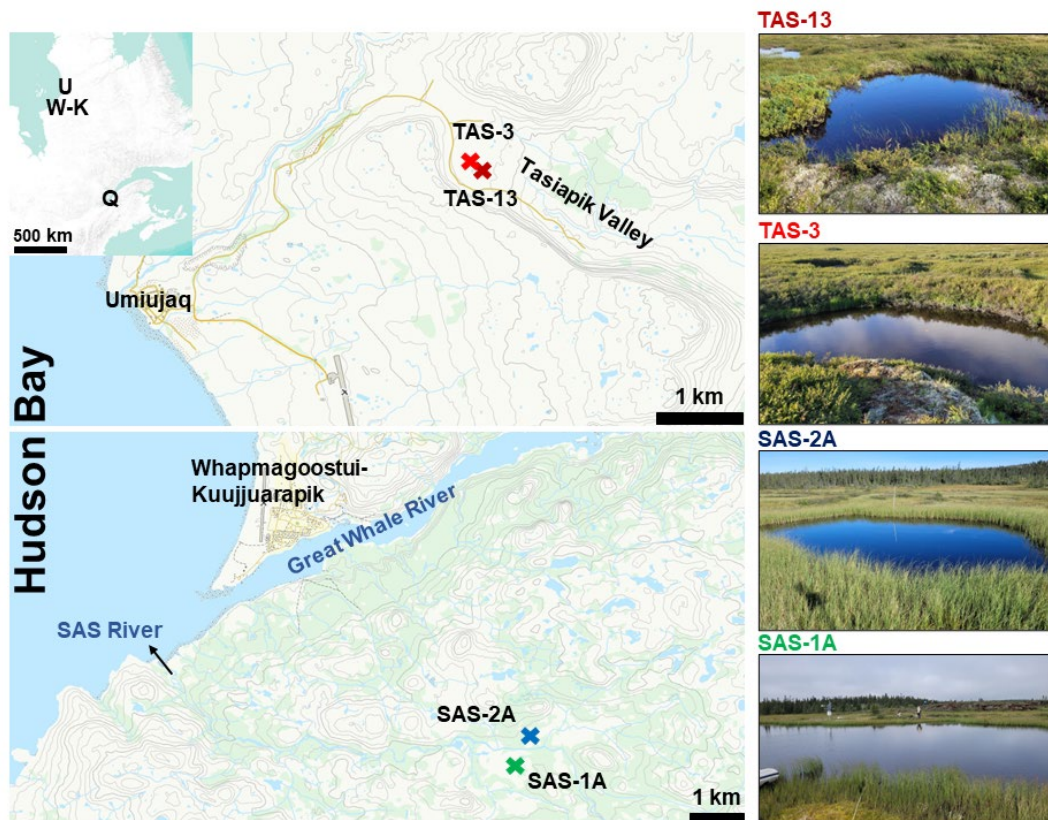
83 We build on our previous preliminary exploration<sup>37</sup> that demonstrated the feasibility of  
84 detecting VOCs from photolysis of natural pond water. Relying on a similar methodology,  
85 we have extended field sampling to four ponds, collecting samples at various depths as  
86 well as riparian water. Furthermore, we filtered (0.2 µm) some samples on site to assess  
87 the impact of particulate matter on photolysis products. Laboratory work was also  
88 expanded to test experimental variables such as dissolved oxygen and exposure time. This  
89 contribution thus provides a clearer basis upon which to evaluate field-relevant VOC  
90 generation in subarctic regions.

## 91 **2. Methodology**

### 92 **2.1. Study sites and selected ponds**

93 The water column was sampled from four ponds located in two locations selected based on  
94 their contrasting organic matter composition and concentrations in the aquatic

95 environment: Tasiapik Valley (TAS; 56.56° N, 76.48° W) and Sasapimakwananistikw  
96 River Valley (SAS; 55.13° N, 77.41° W) (Figure 1). Both locations are on the eastern coast  
97 of the Hudson Bay in Nunavik (northern Quebec, Canada). Thermokarst ponds at TAS are  
98 formed from the collapse of lithalsas, which are small permafrost mounds with an organic-  
99 poor cover <sup>38</sup>. In contrast, thermokarst ponds at SAS are formed following the collapse of  
100 peat-covered permafrost mounds called palsas <sup>39</sup>.



101  
102

103 **Figure 1.** Study sites locations on the Hudson Bay coast in northern Quebec along with  
104 photos of selected ponds. U = Umiujaq, W-K = Whapmagoostui-Kuujuarapik, Q = Quebec  
105 City. Maps adapted with permission from HRDEM - CanElevation Series<sup>40</sup>.

106 The selected ponds at Tasiapik Valley are in the discontinuous permafrost region in the  
107 upper part of the valley, 5 km east of the village of Umiujaq. This area has sandy soils with  
108 low concentrations of soil organic carbon<sup>38</sup>. As a result, thermokarst ponds at this site are  
109 poor in CDOM. To our knowledge, there are no published data on the physicochemistry of  
110 the TAS ponds. The two ponds selected are TAS-3 (56.3336° N, 76.2887° W) and TAS-  
111 13 (56.3346° N, 76.2862° W) (Figure 1). TAS-3 is located at the bottom of a collapsing  
112 lithalsa and has yellow water color while TAS-13 is further away from the lithalsas and has  
113 clearer water. Both ponds were shallow with a maximum depth of 1.9 m for TAS-3 and 0.8  
114 m for TAS-13. Their surface area was not measured but it was less than 100 m<sup>2</sup> for both  
115 ponds. Riparian waters were also sampled at the site, about 30 m upstream from TAS-3  
116 (56.3351° N, 76.2875° W). Also, thermokarst ponds in the Tasiapik Valley have not been  
117 characterized extensively in the literature, thus the thermokarstic origin of TAS-13 cannot  
118 be confirmed (I. Laurion, pers. comm), although its presence near a collapsing lithalsa and  
119 its high DOM concentrations leads us to believe that it is.

120 The SAS valley is located in a peatland, at the northern limit of the sporadic permafrost  
121 zone, 8 km southwest of the village of Whapmagoostui-Kuujjuarapik. Permafrost occupies  
122 only 2% of the surface and is contained in the palsas. Thermal erosion, which started 150  
123 years ago, is responsible for palsa collapse<sup>39</sup>. Consequently, the site contains many dark-  
124 colored thermokarst ponds rich in terrigenous organic matter<sup>41</sup>, leading to strong light  
125 attenuation in the water column<sup>9</sup>. The selected ponds are SAS-1A (55.1301° N, 77.4203°  
126 W) and SAS-2A (55.1304° N, 77.4105° W), located on opposite sides of the SAS river  
127 (Figure 1). Pond SAS-1A has a surface area of 1661 m<sup>2</sup> and a depth of 1.3 m. Pond SAS-  
128 2A is smaller but deeper, with an area of 104 m<sup>2</sup> and a maximum depth of 2.5 m. Again,

129 riparian waters were also sampled, approximately 20 m away from SAS-2A (55,1360° N,  
130 77,4181° W). DOC characterization and CO<sub>2</sub>/CH<sub>4</sub> emissions have been studied at both  
131 ponds<sup>33, 42</sup>.

## 132 **2.2. Sample Collection and in situ Measurements**

133 TAS was visited on August 8–9<sup>th</sup> 2022 and SAS on August 12–13<sup>th</sup> 2022. Prior to water  
134 sampling, vertical profiles of physicochemical properties (temperature, pH, dissolved O<sub>2</sub>  
135 and conductivity) were measured using a RBR Concerto® equipped with the relevant  
136 sensors. At the TAS valley, however, only the surface temperature was measured. Water  
137 samples were retrieved with a 2-L Van Dorn bottle and delivered to amber bottles (60 and  
138 250 mL) that were previously cleaned for 4 hours in HCl (10%), 12–16 hours in NaOH (5  
139 mM) and baked for 3 hours at 450 °C to remove residual organics. The bottles were  
140 thoroughly washed with MilliQ water (18 MΩ) between each of those steps.

141 Before sampling, the bottles were rinsed three times with pond water to saturate sorption  
142 sites at the surface of the glassware. Surface samples for total organic carbon (TOC) and  
143 dissolved organic carbon (DOC) were taken at all sites, with additional bottom samples at  
144 SAS-1A as well as middle and bottom samples at SAS-2A. At TAS, a riparian water sample  
145 was collected by digging a hole ~80 cm deep near the ponds and sampling the water that  
146 filled the hole. At SAS, it was possible to simply open the floating wetland vegetation to  
147 retrieve a riparian sample.

148 Samples for TOC analysis were delivered directly to a 250-mL bottle without filtering,  
149 while samples for DOC analysis were filtered on a 0.2-μm polyethersulfone (PES) syringe  
150 filter into a 60-mL bottle. Field blanks were also taken by applying the same protocol using



151 MilliQ water (18  $\Omega$ ). All bottles were filled to the top to minimize air–water interaction  
152 and kept at 4 °C until analysis. TOC and DOC analysis occurred within two weeks of  
153 sample collection while photolysis experiments occurred four months after sample  
154 collection. They were kept sealed until the analysis. Note that the TOC sample from SAS-  
155 2A (middle) is missing due to it being damaged during transportation back to the  
156 laboratory.

### 157 **2.3. DOM Characterization**

158 TOC and DOC concentrations were measured using a Total Organic Carbon analyzer  
159 (Vario TOC Cube, Elementar) calibrated with potassium hydrogen phthalate (KHP)  
160 standards. Particulate organic carbon (POC) was calculated as the difference between TOC  
161 and DOC.

162 Prior to DOC analysis, a suite of chromophoric properties, collectively referred to as DOC  
163 quality, were assessed. First, CDOM was characterized using absorbance scans acquired  
164 between 200 and 700 nm with a 1 nm increment on a UV–Vis spectrophotometer (Aqualog,  
165 Horiba, USA). A 1-cm path length fused silica UV-transparent cuvette was used. The  
166 samples were allowed to reach room temperature prior to analysis. A blank of MilliQ water  
167 (18 M $\Omega$ ) was done every 10 samples as a reference and subtracted from the sample. The  
168 absorbance values were then converted to absorption coefficients  $a_\lambda$  ( $\text{m}^{-1}$ ) using:

$$169 \quad a_\lambda = \frac{\ln(10) \times A_\lambda}{L} \quad (1)$$

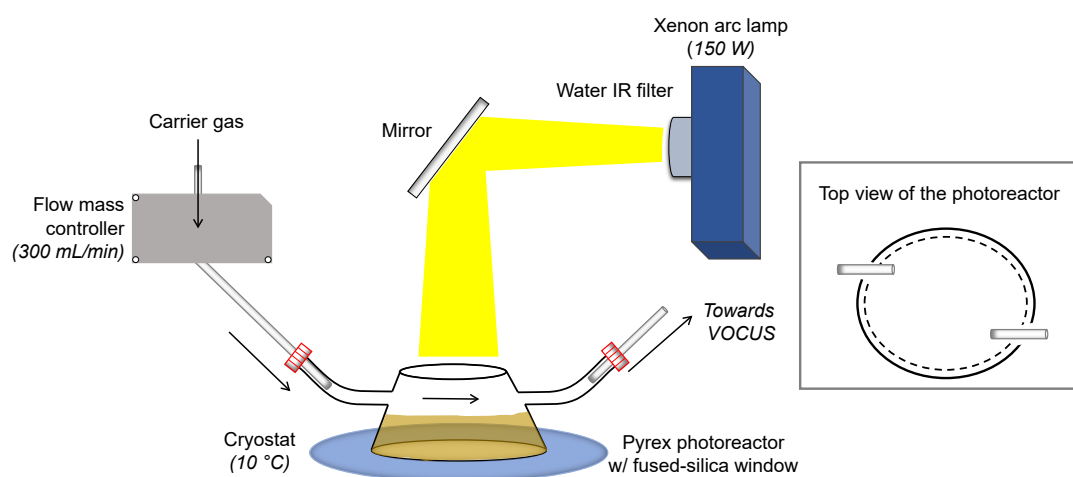
170 where  $A_\lambda$  is the absorbance value at a specific wavelength and L is the optical path length  
171 in meters, here 0.01 m.

172 The indicator  $a_{320}$  was used as a proxy to measure the concentration of CDOM<sup>43</sup>.  $SUVA_{254}$ ,  
173 the specific UV absorbance at 254 nm normalized to DOC concentrations, was calculated  
174 as an indicator of the aromatic content<sup>44</sup>. Finally, the ratio of the slopes between 275–295  
175 nm and 350–400 nm, a metric called the slope ratio (Sr), is inversely proportional to the  
176 molecular size<sup>45</sup> and was obtained using the R package CDOM by Massicotte and  
177 Markager<sup>46</sup>.

## 178 2.4. Photolysis Experiments

179 The experimental set-up for photolysis experiments was adapted from a previously  
180 published design<sup>16,47</sup>. Briefly, a 5-cm high custom Pyrex photoreactor with the axis placed  
181 vertically was equipped with a fused silica window (Figure 2). The reactor had a truncated  
182 conical shape with a diameter of 4 cm at the top and 5 cm at the bottom. It was positioned  
183 under a Xenon arc lamp (150 W, QuantumDesign, France) mounted before a water filter  
184 to simulate solar irradiation ( $\lambda > 280$  nm). This lamp was chosen as it is suitable for aquatic  
185 photodegradation studies<sup>48</sup>. Its irradiance spectrum is shown in Figure S3. A mirror  
186 reflected the incident beam to irradiate the reactor from the top. A constant flow of 300 mL  
187  $\text{min}^{-1}$  of ultrapure  $\text{N}_2$  flowed through the reactor as a carrier gas to bring VOCs to the mass  
188 spectrometer. To ensure anoxia in the photoreactor, the samples were kept under an  $\text{N}_2$   
189 atmosphere for at least 10 minutes before starting an experiment, which is sufficient given  
190 the 10 seconds flush rate. A  $\text{N}_2$  atmosphere was chosen first to investigate photolysis under  
191 anoxic conditions, which are ubiquitous in poorly mixed, and thus strongly stratified,  
192 thermokarst ponds<sup>49,50</sup>. Experiments under oxic conditions were performed with a 20:80  
193 mix of  $\text{O}_2$  and  $\text{N}_2$ . Perfluoralkoxy (PFA) tubing used throughout was rinsed with ethanol  
194 and MilliQ water then baked at 120 °C for 3 hours. The sample temperature was maintained

195 at 10 °C using a cryostat to ensure temperature representative of summer water<sup>51</sup>. Although  
196 we did not test it directly in this study, previous work relying on a similar photochemical  
197 apparatus showed no significant changes in temperatures throughout the experiment (Wang  
198 et al., 2023). A typical experiment contained 15 mL of water sample and began with 30  
199 minutes of stabilization period, after which the lamp was turned on for 90 minutes, and it  
200 ended with another 30 minutes of stabilization without light. Both TOC and DOC water  
201 samples were analyzed using this experimental set-up.



202  
203 **Figure 2** Experimental set-up used for photochemistry experiments. Black arrows indicate  
204 the direction of the carrier gas. The solid and dotted lines on the top view of the  
205 photoreactor show the bottom and top of the reactor, respectively.

## 206 2.5. Mass Spectrometry

207 A Vocus proton-transfer-reaction time-of-flight mass spectrometry (Vocus; ToFwerk AG)  
208 was used to analyze and quantify the VOCs emitted from the photolysis of DOM in  
209 thermokarst samples. Compared with traditional PTR mass spectrometers, the Vocus has a  
210 better mass resolution and detection efficiency due to implemented attributes such as an  
211 improved inlet and source design that minimize contact between analytes and the source  
212 walls<sup>52</sup>. Thus, it can detect chemical species with concentrations in the pptv range with a

213 mass resolving power of 10 000  $m/\Delta m$ <sup>53</sup>. The ionization reagent was hydronium ions  
214 ( $H_3O^+$ ) which allows the detection of a wide range of functional groups<sup>53</sup>.

215 Five sccm of a custom calibration standard were diluted into a 250 sccm flow of clean air  
216 to calibrate the instrument twice a day. The standard was made of the following five VOCs  
217 in  $N_2$ : acetone (240 ppb), benzene (250 ppb), xylene (175 ppb), chlorobenzene (155 ppb)  
218 and  $\alpha$ -pinene (165 ppb). Blank measurements were routinely conducted on the reactor filled  
219 with 15 mL of MilliQ water. Data treatment, mass calibration, peak fitting and time series  
220 plotting was performed using Tofware v.3.2.2 within the IGOR 7.0 environment  
221 (WaveMetrics). A product ion was assigned as a VOC if its blank-subtracted signal  
222 increased at least 3-fold after the lamp was turned on. To simplify chemical formula  
223 assignment, only compounds having C (0–20 atoms), H (0–40), O (0–20), N (0–5), S (0–  
224 2) and P (0–2) were considered. Then, molecular formulae were determined using  
225 Tofware’s high-resolution assignment tool. Methods to extract molecular information from  
226 the PTR-MS masses can be found elsewhere<sup>54, 55</sup>. It is worth noting that such mass  
227 spectrometry technique does not allow us to confirm the structure of the molecules obtained  
228 since different isomers can exist for a given stoichiometry. The chemical composition is  
229 tentatively assigned to compounds but might arise from other compounds fragmenting in  
230 the PTR source<sup>56</sup>. Hence, the term “candidate” is used throughout.

231 To characterize VOCs, five metrics were calculated, namely the H:C and O:C ratios, ring  
232 double-bond equivalent (RDBE), modified aromaticity index ( $AI_{mod}$ ) and the carbon  
233 oxidation state ( $OS_c$ ). A detailed description of these indicators can be found in the SI.

234           **2.6. Flux Calculations**

235 PTR-MS is a method that allows, in principle, the estimation of VOC concentrations  
236 without external calibration, notably when the protonation reaction rate constants ( $k_p$ ) are  
237 known<sup>57,58</sup>. This is due to  $k_p$  being linearly related to the sensitivity (in counts per ppb of  
238 analyte) of the instrument<sup>58</sup>. A method to calculate the concentrations of uncalibrated  
239 compounds based on this relationship is described in Yuan, Koss, Warneke, Coggon,  
240 Sekimoto and de Gouw<sup>59</sup>. Briefly, a calibration curve between the sensitivities and  $k_p$  of  
241 the five calibrants used was constructed (Figure S1 in supplementary information). This  
242 linear equation (sensitivity (cps/ppb) =  $m \times k_p$ , where  $m$  is the slope) was used to estimate  
243 the sensitivity of uncalibrated compounds, which can then be used to estimate  
244 concentrations. The calculated sensitivities have an error range between 50–100 % due to  
245 potential side reactions (e.g., ligand transfer with water cluster) and the ion transmission  
246 efficiency in the ionization source<sup>52</sup>. Because we cannot be certain of the identity of the  
247 compounds, an average value of  $2 \times 10^{-9}$  molecules  $\text{cm}^3 \text{s}^{-1}$  was chosen<sup>57</sup>. The concentration  
248 of a VOC was calculated by taking the maximum signal obtained during the experiment  
249 and subtracting the average background signal 5 minutes before irradiation.

250 Carbon fluxes ( $\text{nmol C m}^{-2} \text{s}^{-1}$ ) associated with VOC formation from the reactor were  
251 calculated using two different approaches. Approach 1 is based on equations 2 and 3 while  
252 Approach 2 is based on Equation 4. First, we converted carbon fluxes into  $\mu\text{mol C m}^{-2} \text{d}^{-1}$   
253 to facilitate comparisons with other studies:

254

$$\text{Flux} = \sum \frac{f \times C_i \times N_i \times 10^{-3}}{A \times V_t} \quad (2)$$

255 where  $f$  = flow rate of the vector gas ( $1.67 \text{ mL s}^{-1}$ ),  $C_i$  = concentration of one VOC (ppb),  
256  $N_i$  = number of C atoms in the VOC chemical formula,  $V_t$  = molar volume of gas ( $24.4 \text{ L}$   
257  $\text{mol}^{-1}$ ),  $A$  = area of surface exposed to irradiation ( $0.00196 \text{ m}^2$ ).

258 Then, to estimate fluxes in the field, we corrected the fluxes ( $\text{Flux}_{\text{corr.}}$ ) to account for the  
259 natural irradiance in the field as follows:

$$260 \quad \text{Flux}_{\text{corr.}} = \text{Flux} \times \frac{E_{\text{field}}}{E_{\text{laboratory}}} \quad (3)$$

261 where  $E_{\text{field}}$  is the average of natural irradiance values obtained in the field in Tasiapik  
262 Valley, near the sampling site, during the warm season of 2021 (May 1<sup>st</sup> to August 30<sup>th</sup>).  
263 They were measured hourly at a meteorological station ( $56.5592^\circ \text{ N}$ ,  $76.4821^\circ \text{ W}$ )  
264 equipped with a radiometer (CNR4; Kipp & Zonen) sensitive to the wavelength range 300–  
265 2800 nm. The spectral distribution was obtained from simulated spectral data (Figure S2)  
266 and the range between 300 and 400 nm was chosen since it is the most relevant for  
267 photochemistry<sup>60</sup>. The dataset was published by Lackner et al.<sup>61</sup>. Since SAS and TAS are  
268 only 167 km apart and can be thought to receive similar seasonal photon fluxes, TAS data  
269 was used for both sites. Moreover,  $E_{\text{laboratory}}$  is the irradiance output from the lamp  
270 normalized to the surface area of the reactor and gives a value of  $5.73 \text{ W/m}^2$  for the range  
271 300-400 nm (Figure S3). Finally, the exact transfer function to link our experimental light  
272 irradiation to the natural light is unknown, we assumed that this relationship was linear.

273 Since flux calculations based on Approach 1 do not account for CDOM absorption or water  
274 column attenuation, we also upscaled VOCs emissions based on a photolysis rate provided  
275 in Cory and Kling (2018), bearing mind the uncertainty in the value of the apparent  
276 quantum yield:

277 
$$\text{Flux} = \int_{300 \text{ nm}}^{400 \text{ nm}} \Phi_{\lambda} E_{\lambda} ((1 - e^{-K_d}) \frac{a_{\text{CDOM},\lambda}}{a_{\text{total},\lambda}}) (4)$$

278 Where  $\Phi_{\lambda}$  is the apparent quantum yield of the gaseous products,  $E_{\lambda}$  is the sunlight  
279 absorption by CDOM,  $K_d$  is the attenuation coefficient (data at SAS and TAS from I.  
280 Laurion, pers. comm.),  $a_{\text{CDOM},\lambda}$  is the absorption coefficient of the CDOM at a specific  
281 wavelength (350 nm) and  $a_{\text{total},\lambda}$  is the total light absorbed.

### 282 **3. Results**

#### 283 **3.1. DOM properties of the selected ponds**

284 DOC concentrations vary among sites and with depth, with bottom samples having higher  
285 DOC concentrations than surface samples (Table 1). The highest values were at the bottom  
286 of SAS-2A. SAS ponds also had a higher TOC content with a lower proportion of POC (0–  
287 8% POC) than the TAS ponds (13–38% POC).

288 CDOM characterization reveals that SAS-2A (bottom) showed high values for the  
289 indicators  $a_{320}$  and  $\text{SUVA}_{254}$ , along with lowest Sr values, establishing that it is likely the  
290 most photo-labile sample. Overall, the values for  $a_{320}$  range between 8.63 and 303  $\text{m}^{-1}$ , with  
291 the highest values measured at SAS.  $\text{SUVA}_{254}$  values at SAS (5.14-6.01  $\text{L mg C}^{-1} \text{m}^{-1}$ ) are  
292 in a similar range than at TAS ( 2.58-7.60  $\text{L mg C}^{-1} \text{m}^{-1}$ ). TAS samples cover a wider range  
293 of Sr values than the samples at SAS, ranging from 0.54, in TAS-13, to 0.97 in TAS-3. Sr  
294 values were grouped between 0.62 and 0.80 at SAS. Finally, riparian samples show  
295 relatively low  $\text{SUVA}_{254}$  (5.93  $\text{L mg C}^{-1} \text{m}^{-1}$ ) and  $a_{320}$  values (8.63–43.6  $\text{m}^{-1}$ ).

296

Site/pond	ID	Depth	[TOC]	[DOC]	[POC]	$a_{320}$	SUVA <sub>254</sub>	Sr
-	-	cm	ppm	ppm	ppm	m <sup>-1</sup>	L mg C <sup>-1</sup> m <sup>-1</sup>	-
SAS-2A	S	25	5.61	5.28	0.33	78.0	5.56	0.76
	M	125	-	13.9	-	162	5.30	0.66
	B	225	28.1	25.8	2.3	303	6.01	0.62
SAS-2A	Rip.	-	19.6	-	-	43.3	-	0.72
SAS-1A	S	25	8.27	7.78	0.49	91.6	5.14	0.80
	B	125	14.9	15.0	<DL	170	5.25	0.69
TAS-3	S	25	14.6	9.14	5.5	49.7	3.457-95	0.84
TAS-13	S	25	6.01	5.19	0.82	63.3	7.60	0.54
TAS	Rip.	-	-	2.89	-	8.63	2.58	0.90

298 **Table 1** Concentrations of TOC, DOC and POC and chromophoric indices calculated from  
 299 UV-Vis spectra obtained for each DOC sample (0.2  $\mu\text{m}$ -filtered sample). (TOC = total  
 300 organic carbon; DOC = dissolved organic carbon; POC = particulate organic carbon;  $a_{320}$   
 301 = absorption coefficient at 320 nm; SUVA<sub>254</sub> = specific ultraviolet absorption at 254 nm;  
 302 Sr = slope ratio; S = surface; M = middle; B = bottom; Rip. = riparian, DL = detection  
 303 limit).

304

### 305 3.2. Photolysis Experiments

306 In all experiments, VOC production started immediately when the lamp was switched on  
 307 (Figure 3). Two kinds of behavior were observed; in the first, the signal reached a  
 308 maximum after a few minutes and then decreased constantly or remained relatively stable  
 309 (i.e., SAS-2A). In the second, the signal continuously increased (i.e., TAS-3 or SAS-2A  
 310 riparian). The photoproduction stopped when the lamp was switched off, with the signal  
 311 decaying and returning to background levels after about 30 minutes. The irradiation of

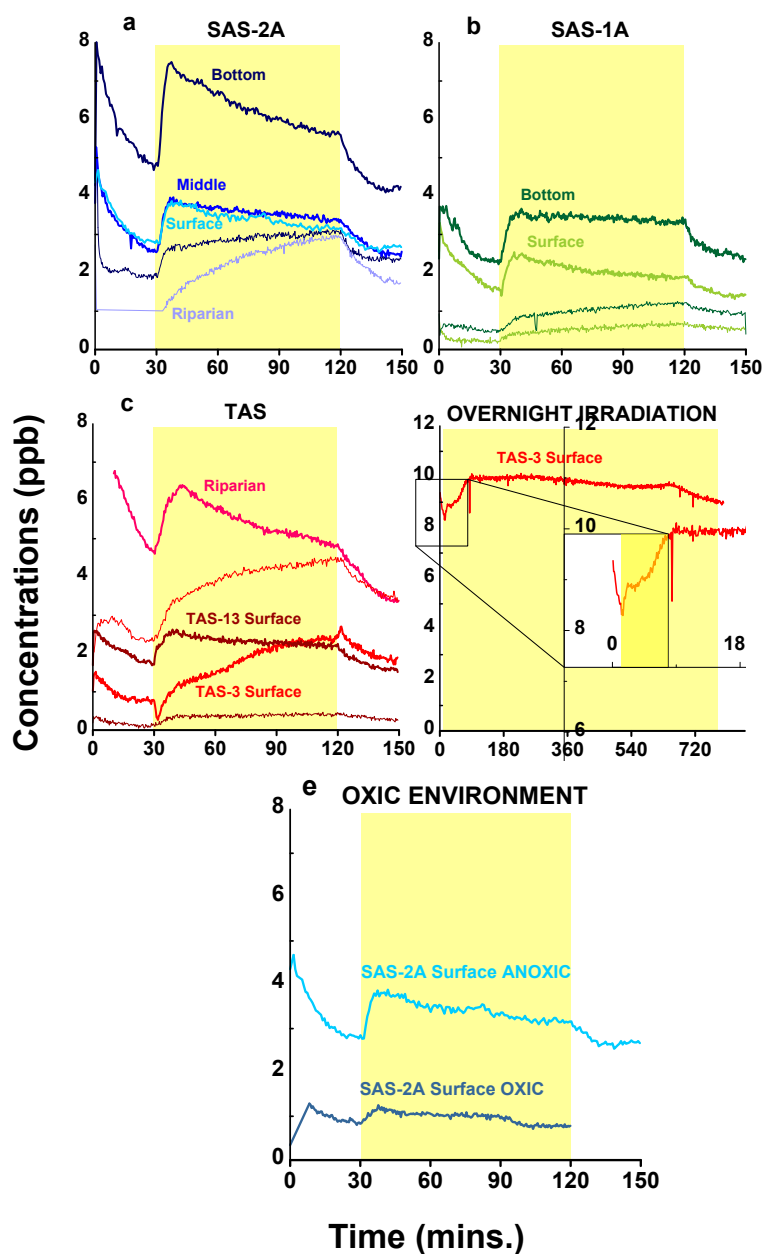


312 MilliQ water also showed some VOC production (Figure S4), which was expected since  
313 the experimental set-up comprises different porous plastic materials and tubing. The  
314 repeatability of the method was assessed by a triplicate done on the SAS-2A bottom sample  
315 (Figure S5).

316 Two additional tests were performed to further investigate the extent of VOC  
317 photoproduction. First, a longer exposure to irradiation demonstrated that about 2–3 hours  
318 were required to deplete all the reactants in the TAS-3 surface sample (Figure 3d). Second,  
319 we evaluated the effects of dissolved oxygen on VOC photoproduction under an oxic  
320 atmosphere (20:80 mix of O<sub>2</sub> and N<sub>2</sub>) for SAS-2A (surface, DOC). The time series obtained  
321 (Figure 3e) shows a pattern similar to that under a N<sub>2</sub> atmosphere, albeit with a weaker  
322 signal.

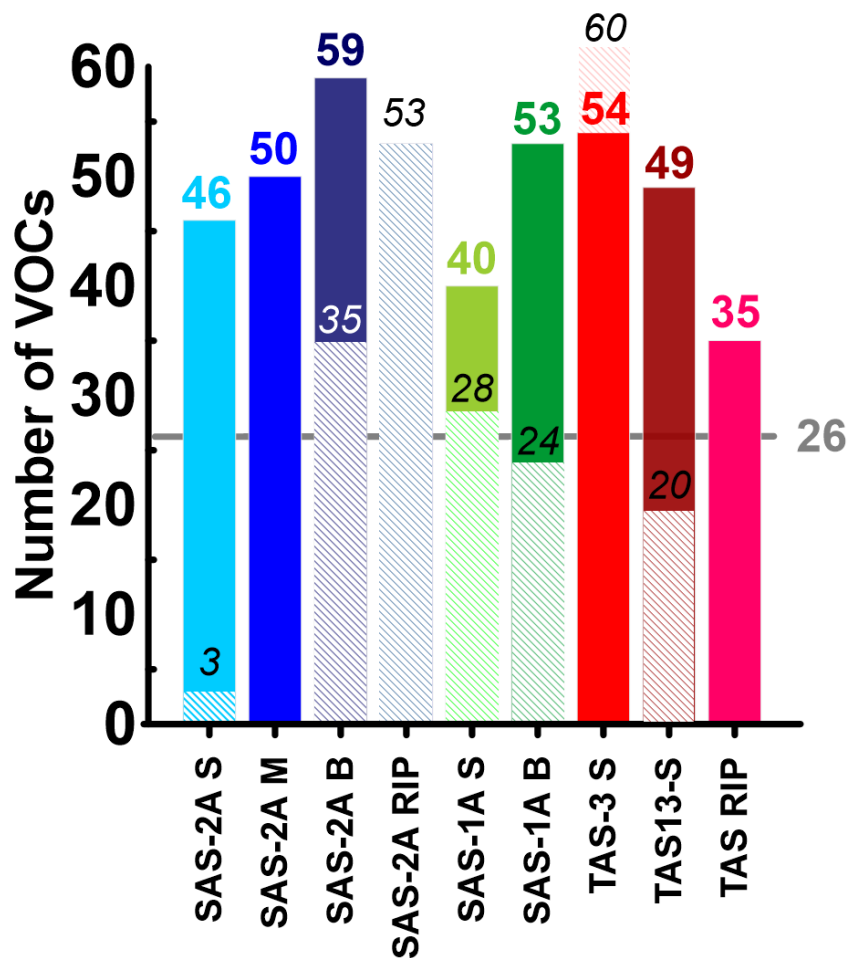
323 After blank subtraction, the total number of VOCs detected by the Vocus from the samples  
324 among all ponds ranged between 35 and 59 species (Figure 4) with 26 molecular masses  
325 being common to all experiments. The TOC samples (non-filtered water) produced fewer  
326 VOCs than the DOC samples (0.2 μm-filtered), except for TAS-3 where 6 additional VOCs  
327 were produced by the TOC sample. Only one S compound (m/Q of 49.011, tentatively  
328 assigned to CH<sub>4</sub>S-H<sup>+</sup>) was detected while no P-containing molecules were detected (Table  
329 S1 and Table S2).

330



332

333 **Figure 3** Blank-subtracted time series of all VOCs produced from each sample at (a) SAS-  
 334 2A (b) SAS-1A, (c) TAS (d) Time-series (not blank subtracted) when TAS-3 (surface) is  
 335 irradiated for 13 hours. The yellow rectangle corresponds to the irradiation window (90  
 336 minutes for anoxic experiments and 60 minutes for the oxalic experiment). The thick line  
 337 corresponds to the DOC samples and the thin line refers to the TOC samples. (e)  
 338 Comparison between oxalic and anoxic environment for the sample SAS-2A (surface).



339

340 **Figure 4** Total number of VOCs detected for each sample at both study sites. The  
 341 horizontal grey line represents the 26 VOCs common to all samples. The dashed boxes  
 342 with italic numbers show the VOCs detected from TOC samples.

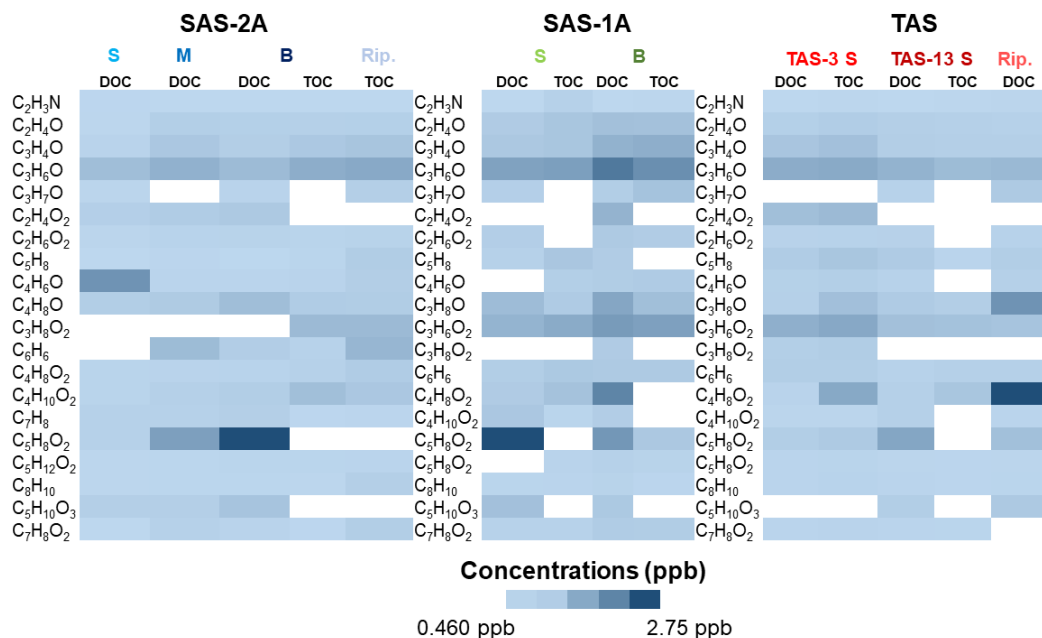
343 The metrics used to characterize VOCs are listed in Table 2. In general, VOCs from SAS  
 344 contained more oxygen atoms than those from TAS, as illustrated by their higher O:C ratio  
 345 and  $OS_c$  values. RDBE and  $AI_{mod}$  values were higher at TAS-3. H:C values ranged between  
 346 1.79 and 1.84 among all ponds.

Site/pond	ID	O:C		H:C		RDBE		AI <sub>mod</sub>		OS <sub>c</sub>	
		DOC	TOC	DOC	TOC	DOC	TOC	DOC	TOC	DOC	TOC
	S	0.27	-	1.81	-	1.93	-	0.25	-	-1.28	-
<b>SAS-2A</b>	M	0.28	-	1.79	-	2.10	-	0.25	-	-1.22	-
	B	0.30	0.28	1.83	1.90	1.87	1.81	0.24	0.20	-1.24	-1.30
<b>SAS-2A</b>	Rip.	-	0.19		1.82		1.91		0.27		-1.45
<b>SAS-1A</b>	S	0.22	0.28	1.81	1.91	1.94	1.80	0.24	0.23	-1.34	-1.31
	B	0.26	0.31	1.84	2.01	1.90	1.35	0.23	0.17	-1.31	-1.39
<b>TAS-3</b>	S	0.19	0.22	1.79	1.80	2.18	1.97	0.31	0.22	-1.35	-1.32
<b>TAS-13</b>	S	0.22	0.29	1.83	2.07	1.97	1.20	0.24	0.16	-1.39	-1.50
<b>TAS</b>	Rip.	0.20	-	1.83	-	1.74	-	0.24	-	-1.37	-

347 **Table 2** Calculated ratios and metrics to characterize the VOCs produced from the  
348 different experiments (O:C = oxygen-to-carbon ratio; H:C = hydrogen-to-carbon ratio,  
349 RDBE = ring double bond equivalent; AI<sub>mod</sub> = modified aromaticity index; OS<sub>c</sub> = carbon  
350 oxidation state).

351 Figure 5 shows the twenty most emitted photoproducts from all DOC and TOC samples.  
352 C<sub>3</sub>H<sub>6</sub>O (acetone or propanal) and C<sub>3</sub>H<sub>8</sub>O<sub>2</sub> (propylene glycol) were the two most abundant  
353 products detected in almost all samples, by concentration. In addition, C<sub>2</sub>H<sub>3</sub>N (acetonitrile),  
354 C<sub>5</sub>H<sub>8</sub> (isoprene or cyclopentene), C<sub>5</sub>H<sub>12</sub>O<sub>2</sub> (1-propanol-3-ethoxy or diethoxymethane),  
355 C<sub>8</sub>H<sub>10</sub> (ethylbenzene or xylene) and C<sub>7</sub>H<sub>8</sub>O<sub>2</sub> (2-methoxyphenol or 4-methylcatechol) were  
356 often detected but in relatively low abundance.

357



358

359 **Figure 5** Concentrations of the twenty most abundant VOCs produced in irradiation  
 360 experiments. White indicating no production (S = surface, M = middle, B = bottom, Rip. =  
 361 riparian).

362 All quantitative results are summarized in Table 3. C fluxes ranged between 1.93 and 9.47  
 363  $\mu\text{mol C m}^{-2} \text{ d}^{-1}$  for SAS and 1.58 and 8.71  $\mu\text{mol C m}^{-2} \text{ d}^{-1}$  for TAS. Both the number of  
 364 VOCs and the fluxes emitted were higher for samples collected from bottom waters. The  
 365 highest fluxes obtained were from SAS-2A (Bottom, DOC sample), which produced 9.47  
 366  $\mu\text{mol C m}^{-2} \text{ d}^{-1}$ . In general, irradiation of DOC samples led to more VOCs emitted as well  
 367 as greater concentrations and fluxes than TOC samples. Finally, in the oxic experiment,  
 368 there were 17 fewer species produced (29 compared to 46) than for its anoxic counterpart.  
 369 Furthermore, oxic conditions reduced the C fluxes almost 3-fold (1.93 compared to 5.06  
 370  $\mu\text{mol C m}^{-2} \text{ d}^{-1}$  under anoxic conditions).

371

372 Fluxes using the second approach (equation 4) are 1 to 2 orders of magnitude higher than  
 373 with the first approach.

374

Site/pond	ID	# of VOCs		Concentrations (ppb)		Fluxes ( $\mu\text{mol C m}^{-2} \text{ d}^{-1}$ )	
		DOC	TOC	DOC	TOC	DOC	TOC
-	-	DOC	TOC	DOC	TOC	DOC	TOC
	S (anoxic)	46	-	0.655	-	5.06 (41.3)	-
	S (oxic)	29	-	0.460	-	1.93 (29.0)	-
<b>SAS-2A</b>	M	50	-	1.39	-	6.78 (87.5)	-
	B	59	35	2.76	1.28	9.47 (174)	4.27 (80.6)
<b>SAS-2A</b>	Rip.	53	-	2.42	-	9.45 (152)	-
<b>SAS-1A</b>	S	40	28	1.01	0.532	4.82 (63.6)	2.11 (33,5)
	B	53	24	1.44	0.856	6.20 (90.7)	2.59 (53.9)
<b>TAS-3</b>	S	54	60	1.79	2.29	6.70 (113)	8.71 (144)
<b>TAS-13</b>	S	49	20	0.932	0.388	4.65 (58.7)	1.58 (24.4)
<b>TAS</b>	Rip.	35	-	1.68	-	6.03 (106)	-

375 **Table 3** Summary of the quantitative results: number of VOCs, concentrations (ppb) and  
 376 fluxes ( $\mu\text{mol C m}^{-2} \text{ d}^{-1}$ ) from laboratory irradiations of water samples. Flux calculations  
 377 using Approach 2 (Equation 4, see text) are in parenthesis.

378

## 379 4. Discussion

### 380 4.1. Photoproduction of VOCs

381 Figure 3a–c suggests that the relatively high signal measured in the first 30-minute  
382 stabilization period prior to irradiation was diffusion of species naturally present at the time  
383 of sampling. However, this phenomenon is also observed for bottom and riparian samples,  
384 which are the least affected by light. It is also possible this is a residual signal from previous  
385 experiments in which semi-volatile compounds may have condensed onto the tubing and  
386 take time to flush. Irradiation of MilliQ water shows a similar pattern with relatively high  
387 signals in the first few minutes (Figure S4), giving support to the latter explanation. The  
388 same mechanism can also explain why the signal did not instantly drop when the lamp was  
389 shut off.

390 Following the onset of irradiation, the signal rose and reached a maximum, after which  
391 most signals started to decline, most likely as reactants were exhausted. However, some  
392 samples exhibited a constant increase in signal throughout the experiment. This may be  
393 due to the different volatilities of VOCs, or a reaction chain, whereby high molecular  
394 weight reactants produce lower molecular weight and more volatile reactants, whose  
395 photolysis in turn produces VOCs. Samples with greater aromaticity (high  $SUVA_{254}$   
396 values, Table 1) are expected to behave this way. To test this hypothesis, the aromatic-rich  
397 surface sample TAS-3 ( $SUVA_{254} = 7.95 \text{ L mg C}^{-1} \text{ m}^{-1}$ ) was irradiated overnight, and a  
398 maximum was eventually reached in the first 3 hours (Figure 3d). Although the experiment  
399 was not blank-subtracted, it was assumed that this would only affect the intensity of the  
400 signal, and not its general behavior (Figure S6). SAS-2A (riparian) is the other example of

401 a sample rich in aromatics that exhibited a constant photoreactivity during irradiation.  
402 Thus, the behavior appeared to be consistent across all samples, with the difference being  
403 the time required to photobleach all DOM.

#### 404 **4.2. Factors that control VOCs photoproduction**

405 Our results point to four factors controlling VOC photoproduction: DOC quality, prior  
406 exposure to sunlight, presence of oxygen and presence of particulate matter.

407 A first factor that controls VOC photoproduction is the quality of the DOC. We observe  
408 that high concentrations of DOC did not lead to a greater diversity of VOCs. On the  
409 contrary, some of the dark-colored, DOC-rich ponds from SAS yielded fewer VOCs than  
410 the TAS ponds. Wang et al.<sup>37</sup> reached similar results and proposed that optical properties  
411 of the water could provide explanatory insights, an assertion we develop in this work. The  
412 three proxies used, namely  $a_{320}$ ,  $SUVA_{254}$  and Sr, give insight into the concentrations,  
413 aromatics and molecular size of CDOM, respectively. The surface water of every pond  
414 exhibited higher  $a_{320}$  values than bottom water, suggesting that CDOM strongly attenuates  
415 light and degrades into smaller moieties. Indeed, we observed that the irradiation of the  
416 DOC sample from TAS-3 (surface) produced the second-highest number of species (54  
417 VOCs, Figure 4) and some of the highest fluxes detected (Table 3). Likewise, despite being  
418 the least concentrated in DOC and TOC, TAS-13's quantitative results were also among  
419 the highest. Since TAS-13 contains high amount of CDOM ( $a_{320}$  of  $63.3 \text{ m}^{-1}$ ) characterized  
420 by large (Sr of 0.54, Table 1) and aromatics ( $SUVA_{254}$  of  $7.60 \text{ L mg C}^{-1} \text{ m}^{-1}$ , Table 1)  
421 molecules, these three proxies collectively point towards high photoreactivity. This  
422 suggests that the aromaticity ( $SUVA_{254}$ ) and chromophoric properties of DOM ( $a_{320}$  and  
423 Sr) were better predictors of the number of VOCs that can be photoproduced than



424 concentration of DOC alone. This is in line with a recent study that reported a strong  
425 relationship between  $SUVA_{254}$  and electron-donating capacity, a property useful to predict  
426 DOM photoreactivity<sup>62</sup>. Other authors found similar correlations that pointed to the  
427 importance of aromatics<sup>63,64</sup> and molecular weight<sup>63</sup> as enablers of photochemistry.

428 A second factor that appeared to govern photoproduction of VOCs in our experiments was  
429 the extent to which the water sample was previously exposed to sunlight. We draw this  
430 conclusion from the observation that the irradiation of riparian waters led to some of the  
431 highest fluxes calculated in this work with values of 9.45 and 6.03  $\mu\text{mol C m}^{-2} \text{d}^{-1}$  for the  
432 riparian zones of SAS-2A and TAS ponds, respectively (Table 3). Likewise, samples  
433 retrieved at the surface were always less productive in terms of the number of VOCs than  
434 samples retrieved from the bottom water, which we ascribe to exposure to sunlight prior to  
435 sampling.

436 A third factor was the presence of dissolved oxygen in the samples. We observed lower  
437 fluxes and a lower number of VOCs produced under oxygenated conditions compared to  
438 anoxic conditions (Table 3). Consequently, the fluxes measured under anoxic conditions  
439 could be upper limits of natural values, since those thermokarst systems may be thoroughly  
440 mixed during turnover events in the spring and fall, thus aerating the water column. The  
441 effects of dissolved oxygen on photochemistry are well documented, as  $\text{O}_2$  allows chemical  
442 pathways that involve reactive oxygen species (ROS, e.g.,  $\text{H}_2\text{O}_2$ , OH)<sup>10</sup>. Specifically, Cory  
443 et al. (2010) highlighted how reactive singlet oxygen ( $^1\text{O}_2$ ) is key in the partial photo-  
444 oxidation of DOM which forms compounds with incorporated O atoms and which have a  
445 lower volatility.

446 Lastly, a fourth factor concerns sample filtration since POC can participate to  
447 photochemistry<sup>65</sup>. Our results showed that, excluding TAS-3 (surface), all DOC samples  
448 produced a higher number of species (Figure 4) along with greater fluxes (Table 3) than  
449 the POC samples. A combination of factors could explain these results. First, light  
450 scattering by particles could minimize light penetration and thus, photodegradation.  
451 Complex particle–organic interactions likely enable adsorption of VOCs onto particles,  
452 hence impeding their emission to the gas phase<sup>66</sup>. Furthermore, other photo-induced  
453 processes, such as POC photo-dissolution into DOC, are possible<sup>65</sup>. These concurrent  
454 reactions could reduce the number of reactants available for photolysis and explain the  
455 observed lower species counts and fluxes. Finally, we cannot rule out that our TOC samples  
456 became partially degraded during their 4-month storage at 4 °C. Since this was not tested  
457 by optical characterization, it cannot be quantified. A more precise evaluation of the role  
458 of POC is needed in future research.

#### 459 **4.3. Significance for the Arctic Environment**

460 Up to now, most studies have focused on emissions of CO<sub>2</sub> and CH<sub>4</sub> from thermokarst  
461 ponds and highlighted their quantitative role in GHG emissions from thawing permafrost  
462 landscapes. At our study sites, Matveev et al.<sup>33</sup> calculated fluxes of CO<sub>2</sub> and CH<sub>4</sub> from  
463 SAS-1A and SAS-2A during the summer. In SAS-1A, their results show values of 1–12.8  
464 mmol C m<sup>-2</sup> d<sup>-1</sup> for CH<sub>4</sub> and 4–55 mmol C m<sup>-2</sup> d<sup>-1</sup> for CO<sub>2</sub>. For SAS-2A, it ranged between  
465 1–10 mmol C m<sup>-2</sup> d<sup>-1</sup> for CH<sub>4</sub> and 20–242 mmol C m<sup>-2</sup> d<sup>-1</sup> for CO<sub>2</sub>. These values are in the  
466 same range as those obtained in a study of 106 ponds in a wetland thermokarst system on  
467 Bylot Island (73°N, Nunavut)<sup>32</sup>. On Bylot Island, CH<sub>4</sub> fluxes varied between 0.03–5.82  
468 mmol C m<sup>-2</sup> d<sup>-1</sup> and CO<sub>2</sub> fluxes between –11.78 (thus representing an uptake from the

469 atmosphere) and  $65.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$ . By comparison, even though the laboratory  
470 experiments conducted here did not perfectly reproduce field conditions, the fluxes of C  
471 from VOCs were generally 3 to 4 orders of magnitude lower than those documented above.  
472 This indicates that VOCs are a small source of carbon in the arctic environment, with fluxes  
473 of  $\text{CO}_2 > \text{CH}_4 \gg \text{VOCs}$ .

474 In this study, we compare two approaches to upscale VOCs fluxes from the experimental  
475 device to those prevailing above the ponds. Results show that considering CDOM  
476 absorption - and not only the total light available - in addition to the water column  
477 attenuation, yield higher fluxes than those obtained by solely extrapolating the absorption  
478 at the air-water interface (Table 3). While the former approximation yields values closer to  
479 the  $\text{CO}_2$  and  $\text{CH}_4$  emissions presented earlier, they remain 2-3 orders of magnitude lower.  
480 As the apparent quantum yield could not be calculated for individual VOC due to the PTR-  
481 MS limitations in molecular assignment, we believe the latter approach provides a more  
482 precise assessment of VOCs photoproduction that should be employed for future research.

483 Other studies measured VOCs released directly from soils in permafrost organic-rich  
484 peatlands and found emission rates ranging between  $88.5$  and  $260.9 \mu\text{g m}^{-2} \text{ h}^{-1}$  <sup>21</sup>. Using an  
485 average VOC molecular mass of  $70 \text{ g mol}^{-1}$  in our experiments and correcting for the  
486 proportion of carbon in each molecular composition, we calculated values of  $7.09$  and  $42.5$   
487  $\mu\text{g m}^{-2} \text{ h}^{-1}$  for the lowest (TAS-13, surface, TOC) and the highest (SAS-2A, bottom, DOC)  
488 emitting samples, respectively. Those results were 1–2 orders of magnitude lower than the  
489 emission fluxes reported by Jiao et al. <sup>21</sup> These comparisons show how the Arctic  
490 landscapes contain important VOCs sources. The results presented here suggest that the  
491 contribution from microbial decomposition of soil organic matter in permafrost is more

492 important than that from CDOM photodegradation in thermokarst ponds. In addition, our  
493 results do not include the contribution of visible light in VOCs photoproduction. While  
494 CDOM absorption of visible light is less important than that of UV light in the water  
495 column (Bowen et al., 2020), it could still account for a non-negligible fraction of VOC  
496 fluxes. This knowledge gap should be addressed in future research.

#### 497 **4.4. Implication for Atmospheric Chemistry and Climate**

498 While our results show that VOC production from thermokarst pond photochemistry makes  
499 a small contribution to C emissions to the atmosphere, they also point to a release of an  
500 array of reactive organic molecules in the atmosphere. The overlooked source of VOCs  
501 presented in this work might contribute to the local formation of atmospheric particles. The  
502 complex role of VOCs as SOA precursors depends on the volatility and solubility of the  
503 oxidation products<sup>26</sup>. For instance, the atmospheric oxidation of aromatic compounds such  
504 as cycloalkanes and cycloalkenes produces molecules containing polar functional groups,  
505 making them an important class of SOA precursor<sup>26</sup>. Based on Table 2, VOCs from SAS-  
506 2A experiments were unsaturated (RDBE between 1.81–2.10,  $AI_{mod}$  between 0.20–0.25)  
507 and the fluxes from aromatics (e.g., benzene, toluene, xylene) are relatively high (Figure  
508 5, Figure S7). The greater fluxes of aromatics and oxygenated VOCs (Figure S7) contrast  
509 with previous similar work using the Vocus<sup>18, 21</sup>. This suggests that VOCs from  
510 thermokarst pond photochemistry could have a greater effect on SOA than other sources  
511 of VOC emissions. Although we did not have the data to quantitatively estimate the albedo  
512 change<sup>67</sup> and the associated radiative forcing, aerosol formation from the VOC emissions  
513 reported here could be high enough to affect the climate.

514 Laboratory and field studies on isoprene (2-methyl-1,3-butadiene, C<sub>5</sub>H<sub>8</sub>) demonstrated its  
515 significant potential to produce both SOAs and O<sub>3</sub> in the presence of acidic particles due  
516 to rapid reactivity with hydroxyl radicals (reaction lifetime of 1.7 hours)<sup>68</sup>. Some authors  
517 have emphasized the importance of monitoring new sources of isoprene in the atmosphere,  
518 especially in unpolluted environments<sup>69, 70</sup>. In this work, a product ion with the formula  
519 C<sub>5</sub>H<sub>9</sub><sup>+</sup>, tentatively assigned to the protonated form of isoprene, was consistently prevalent  
520 among emitted VOCs, especially in TAS samples (Figure 5 and Figure S7). These results  
521 showed that thermokarst ponds photochemistry produced key reactive organic molecules  
522 that may affect ozone production and radical concentrations.

## 523 **5. Conclusions**

524 Continuing permafrost thaw will increase export of terrestrial organic materials, rich in  
525 aromatics and with limited sunlight exposure, to northern inland waters<sup>71</sup>. While the exact  
526 magnitude of DOC photo-processing is debated<sup>8, 72, 73</sup>, some studies have documented an  
527 increased photolability of DOC draining from permafrost<sup>11, 74</sup>. Considering the anticipated  
528 increase in the surface area of water bodies within the permafrost landscape<sup>75</sup>, we argue  
529 that closer monitoring of the emission levels and diversity of VOCs from thermokarst  
530 ponds is needed.

531 We provide evidence for the photo emission of between 35 and 59 compounds to the gas  
532 phase when DOM samples were exposed to actinic irradiation. The quality of the DOM  
533 emerged as a key quantitative factor to control VOC photoproduction. VOC fluxes ranged  
534 between 1.93 and 9.47 μmol C m<sup>-2</sup> d<sup>-1</sup>. This is 3 to 4 orders of magnitude lower than the  
535 fluxes of CO<sub>2</sub> and CH<sub>4</sub> in similar thermokarst systems. It was also 1 to 2 orders of

536 magnitude lower than the VOCs fluxes from organic-rich soils in permafrost environments.  
537 In accordance with our earlier research<sup>37</sup>, we conclude that although VOCs represent a  
538 small contribution to C emissions from surface water to the atmosphere in the Arctic,  
539 sunlight-induced VOCs might disproportionally impact atmospheric chemistry and,  
540 possibly, the climate.

## 541 **6. Supporting information**

542 Details on gas phase analysis, calibration curve, modeled spectral irradiance at the site,  
543 supplemental results on irradiance experiments, fluxes of VOC classes and candidate  
544 molecules detected by PTR-ToF-MS.

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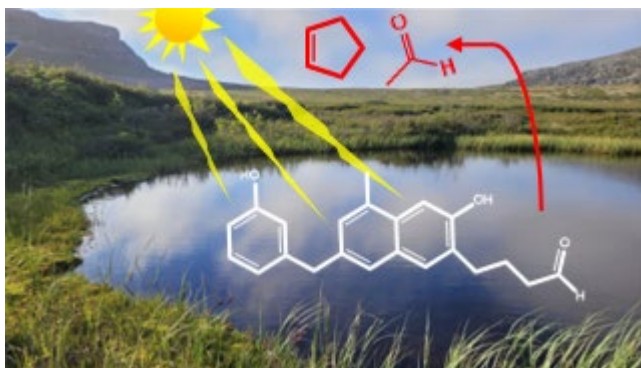
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