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

3 Daniel Fillion^{1,2}, Sébastien Perrier³, Matthieu Riva³, Christian George³, Florent Domine^{1,2}
4 and Raoul-Marie Couture^{1,2,*}

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

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

10 ³Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Ircelyon, 69626, Villeurbanne,
11 France

12 Correspondance : 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 thermokarst 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 thermokarst 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 CO_2 and 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 ¹.
35 This acceleration affects northern environments in drastic ways, intensifying
36 geomorphological changes such as permafrost thaw and subsequent formation of
37 thermokarst ponds ^{2, 3}. Since permafrost contains almost twice as much carbon as the
38 atmosphere ⁴, 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 CO_2 and CH_4 emissions to the
41 atmosphere ⁵.

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 ⁶⁻⁹. 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 CO_2 and
47 partially oxidized carbon compounds, respectively ¹⁰⁻¹². 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 ¹³.

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 phase¹³⁻¹⁵, their transfer to the gas phase has
55 not been documented in the Arctic. Given that Brüggemann et al.¹⁶ 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 environment¹⁷. 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 soil¹⁸⁻²² and marine systems^{23,24}. In the atmosphere, VOCs further undergo a
63 series of oxidative chemical processes leading to the formation of secondary organic
64 aerosols (SOA)²⁵. Since SOA can act as cloud condensation nuclei (CCN)²⁶, 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 effect²⁷. VOCs
67 can also contribute to tropospheric ozone (O₃) and production of radicals (e.g., OH, HO₂)
68^{28,29}.

69 Thus, VOCs could be a reservoir of C that represents a delayed source of greenhouse gases
70 (GHGs) CO_{2(g)} and O_{3(g)} 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 pond³⁰⁻³³. Laboratory experiments are necessary to isolate photoproduction since field

73 measurements alone cannot discern the precise origins (cyanobacteria, algae, sunlight)³⁴.
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 CO₂ and CH₄ 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^{12, 35, 36}.

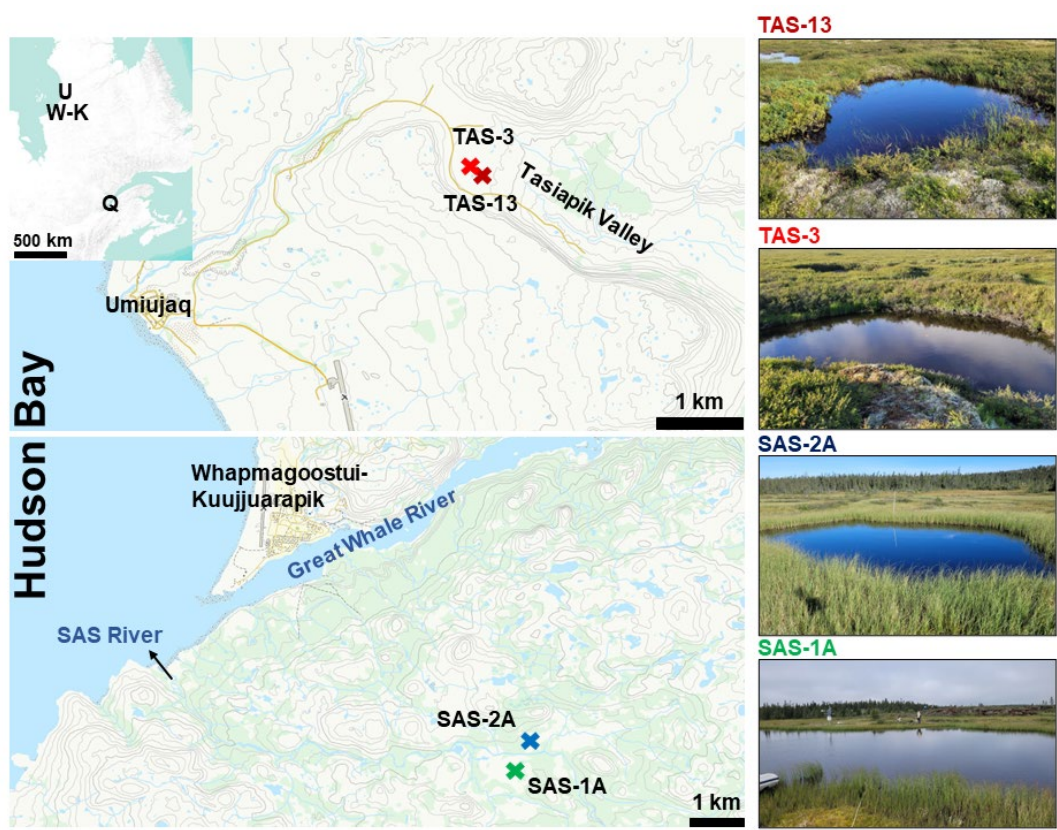
83 We build on our previous preliminary exploration³⁷ that demonstrated the feasibility of
84 detecting VOCs from photolysis of natural pond water. Relying on a similar methodology,
85 we have extended field sampling to four ponds, collecting samples at various depths as
86 well as riparian water. Furthermore, 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 ³⁸. In contrast, thermokarst ponds at SAS are formed following the collapse of
100 peat-covered permafrost mounds called palsas ³⁹.



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 Series⁴⁰.

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 carbon³⁸. 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 m² 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 collapse³⁹. Consequently, the site contains many dark-
124 colored thermokarst ponds rich in terrigenous organic matter⁴¹, leading to strong light
125 attenuation in the water column⁹. 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 m² and a depth of 1.3 m. Pond SAS-
128 2A is smaller but deeper, with an area of 104 m² 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 CO₂/CH₄ emissions have been studied at both
131 ponds^{33, 42}.

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

133 TAS was visited on August 8–9th 2022 and SAS on August 12–13th 2022. Prior to water
134 sampling, vertical profiles of physicochemical properties (temperature, pH, dissolved O₂
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 Ω). 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 Ω) was done every 10 samples as a reference and subtracted from the sample. The
168 absorbance values were then converted to absorption coefficients a_λ (m^{-1}) using:

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

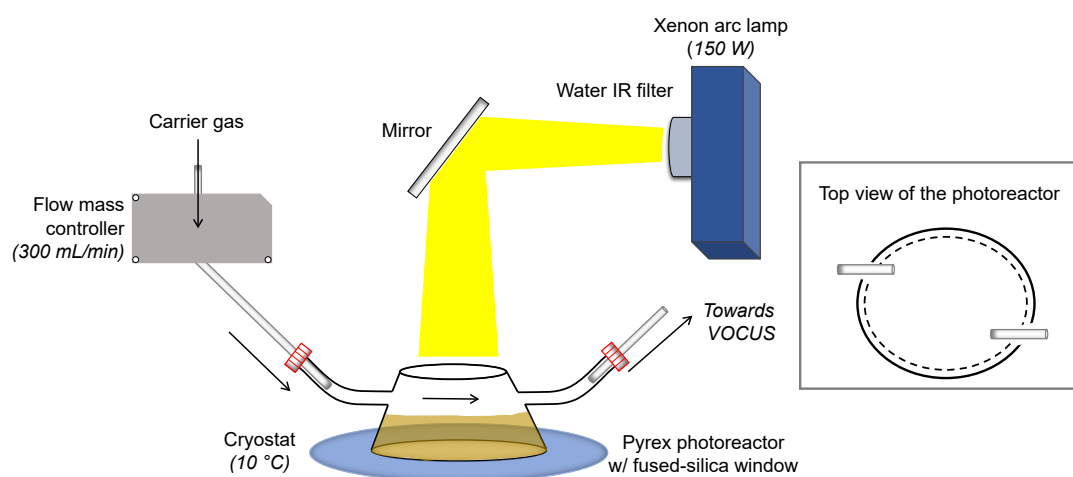
170 where A_λ is the absorbance value at a specific wavelength and L is the optical path length
171 in meters, here 0.01 m.

172 The indicator a_{320} was used as a proxy to measure the concentration of CDOM⁴³. $SUVA_{254}$,
173 the specific UV absorbance at 254 nm normalized to DOC concentrations, was calculated
174 as an indicator of the aromatic content⁴⁴. 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 size⁴⁵ and was obtained using the R package CDOM by Massicotte and
177 Markager⁴⁶.

178 2.4. Photolysis Experiments

179 The experimental set-up for photolysis experiments was adapted from a previously
180 published design^{16,47}. 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 studies⁴⁸. 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 min^{-1} of ultrapure 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 N_2
189 atmosphere for at least 10 minutes before starting an experiment, which is sufficient given
190 the 10 seconds flush rate. A 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^{49,50}. Experiments under oxic conditions were performed with a 20:80
193 mix of O_2 and 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 water⁵¹. 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 walls⁵². Thus, it can detect chemical species with concentrations in the pptv range with a

213 mass resolving power of 10 000 $m/\Delta m$ ⁵³. The ionization reagent was hydronium ions
214 (H_3O^+) which allows the detection of a wide range of functional groups⁵³.

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 α -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^{54, 55}. 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 source⁵⁶. 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.

255 where f = flow rate of the vector gas (1.67 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 L
257 mol^{-1}), A = area of surface exposed to irradiation (0.00196 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_{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 1st to August 30th).
263 They were measured hourly at a meteorological station (56.5592° N , 76.4821° 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 photochemistry⁶⁰. The dataset was published by Lackner et al.⁶¹. 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 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 Φ_{λ} is the apparent quantum yield of the gaseous products, E_{λ} 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 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 m^{-1} , with
291 the highest values measured at SAS. 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 SUVA_{254} (5.93 $\text{L mg C}^{-1} \text{ m}^{-1}$) and a_{320} values (8.63–43.6 m^{-1}).

296

Site/pond	ID	Depth	[TOC]	[DOC]	[POC]	a_{320}	SUVA ₂₅₄	Sr
-	-	cm	ppm	ppm	ppm	m^{-1}	$L\ mg\ C^{-1}\ m^{-1}$	-
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 μ m-filtered sample). (TOC = total
 300 organic carbon; DOC = dissolved organic carbon; POC = particulate organic carbon; a_{320}
 301 = absorption coefficient at 320 nm; SUVA₂₅₄ = 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

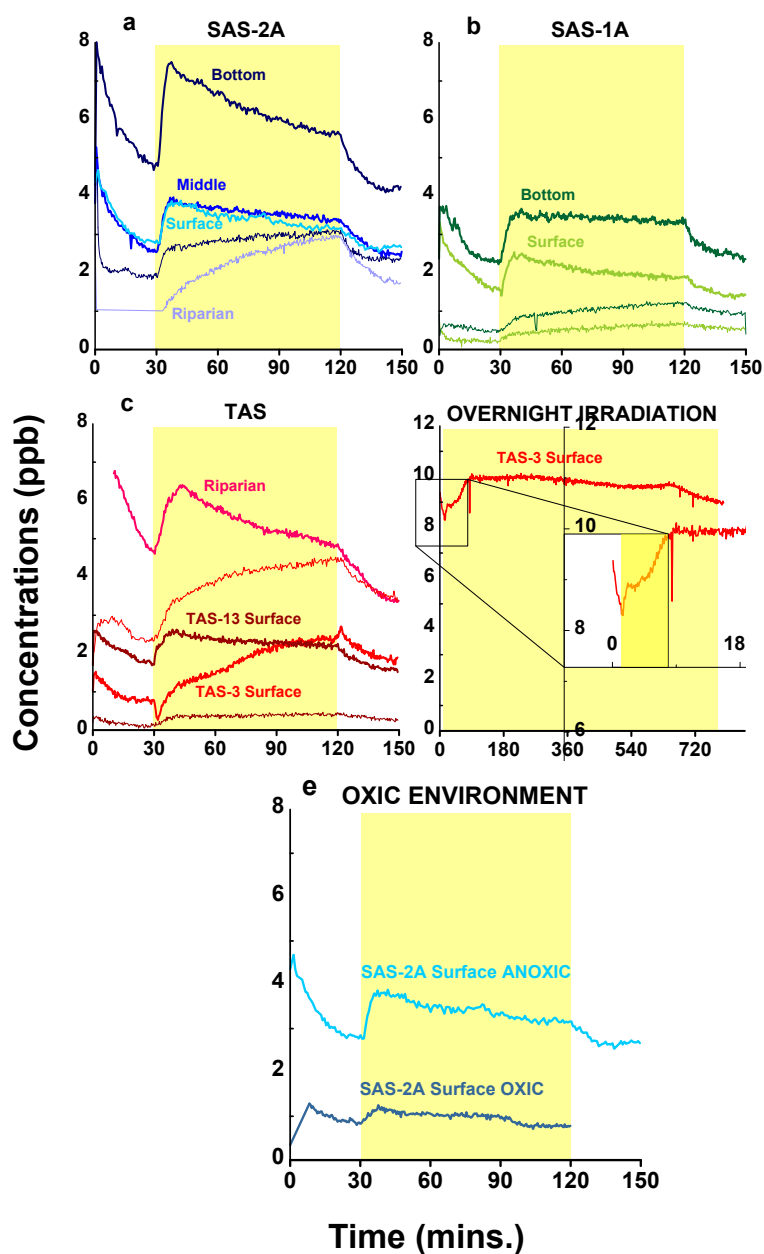
306 In all experiments, VOC production started immediately when the lamp was switched on
 307 (Figure 3). Two kinds of behavior were observed; in the first, the signal reached a
 308 maximum after a few minutes and then decreased constantly or remained relatively stable
 309 (i.e., SAS-2A). In the second, 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 O₂ and N₂) for SAS-2A (surface, DOC). The time series obtained
321 (Figure 3e) shows a pattern similar to that under a N₂ atmosphere, albeit with a weaker
322 signal.

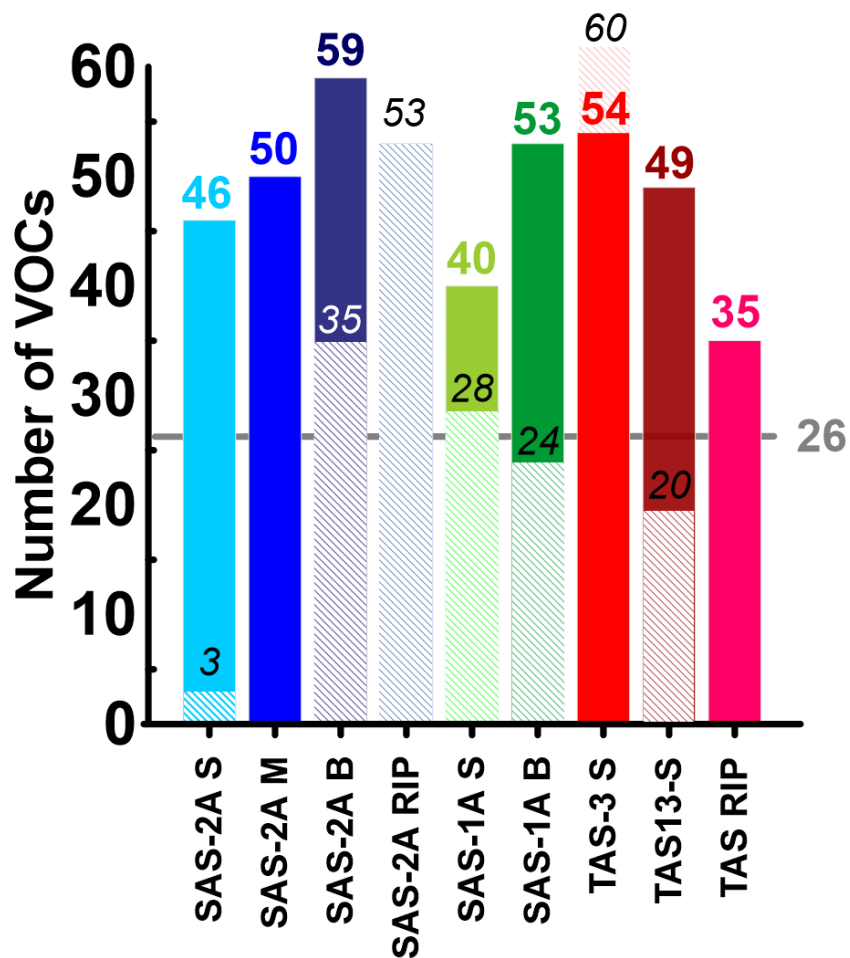
323 After blank subtraction, the total number of VOCs detected by the Vocus from the samples
324 among all ponds ranged between 35 and 59 species (Figure 4) with 26 molecular masses
325 being common to all experiments. The TOC samples (non-filtered water) produced fewer
326 VOCs than the DOC samples (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 CH₄S-H⁺) 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 oxitic experiment). The thick line
 337 corresponds to the DOC samples and the thin line refers to the TOC samples. (e)
 338 Comparison between oxitic 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.

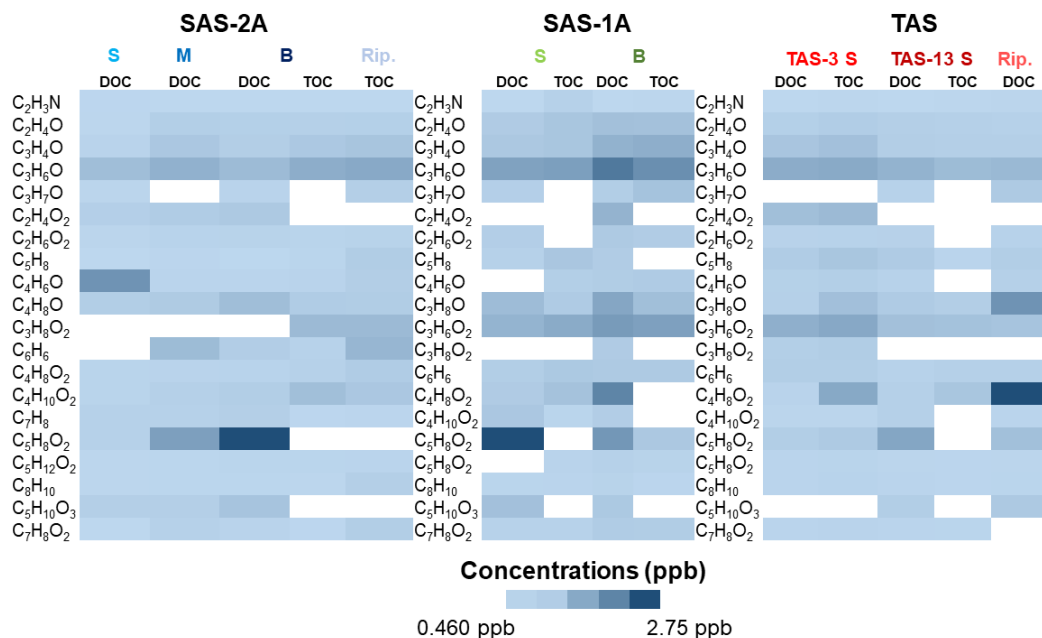
343 The metrics used to characterize VOCs are listed in Table 2. In general, VOCs from SAS
 344 contained more oxygen atoms than those from TAS, as illustrated by their higher O:C ratio
 345 and OS_c values. RDBE and AI_{mod} values were higher at TAS-3. H:C values ranged between
 346 1.79 and 1.84 among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

Site/pond	ID	O:C		H:C		RDBE		AI _{mod}		OS _c	
		DOC	TOC	DOC	TOC	DOC	TOC	DOC	TOC	DOC	TOC
	S	0.27	-	1.81	-	1.93	-	0.25	-	-1.28	-
SAS-2A	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
SAS-2A	Rip.	-	0.19		1.82		1.91		0.27		-1.45
SAS-1A	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
TAS-3	S	0.19	0.22	1.79	1.80	2.18	1.97	0.31	0.22	-1.35	-1.32
TAS-13	S	0.22	0.29	1.83	2.07	1.97	1.20	0.24	0.16	-1.39	-1.50
TAS	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_{mod} = modified aromaticity index; OS_c = carbon
350 oxidation state).

351 Figure 5 shows the twenty most emitted photoproducts from all DOC and TOC samples.
352 C₃H₆O (acetone or propanal) and C₃H₈O₂ (propylene glycol) were the two most abundant
353 products detected in almost all samples, by concentration. In addition, C₂H₃N (acetonitrile),
354 C₅H₈ (isoprene or cyclopentene), C₅H₁₂O₂ (1-propanol-3-ethoxy or diethoxymethane),
355 C₈H₁₀ (ethylbenzene or xylene) and C₇H₈O₂ (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)	-
SAS-2A	M	50	-	1.39	-	6.78 (87.5)	-
	B	59	35	2.76	1.28	9.47 (174)	4.27 (80.6)
SAS-2A	Rip.	53	-	2.42	-	9.45 (152)	-
SAS-1A	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)
TAS-3	S	54	60	1.79	2.29	6.70 (113)	8.71 (144)
TAS-13	S	49	20	0.932	0.388	4.65 (58.7)	1.58 (24.4)
TAS	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.³⁷ 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 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 photoreactivity⁶². Other authors found similar correlations that pointed to the
427 importance of aromatics^{63,64} and molecular weight⁶³ 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 O_2 allows chemical
442 pathways that involve reactive oxygen species (ROS, e.g., H_2O_2 , OH)¹⁰. 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 photochemistry⁶⁵. 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 phase⁶⁶. Furthermore, other photo-induced
453 processes, such as POC photo-dissolution into DOC, are possible⁶⁵. 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 CO₂ and CH₄ from thermokarst
461 ponds and highlighted their quantitative role in GHG emissions from thawing permafrost
462 landscapes. At our study sites, Matveev et al.³³ calculated fluxes of CO₂ and CH₄ 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⁻² d⁻¹ for CH₄ and 4–55 mmol C m⁻² d⁻¹ for CO₂. For SAS-2A, it ranged between
465 1–10 mmol C m⁻² d⁻¹ for CH₄ and 20–242 mmol C m⁻² d⁻¹ for CO₂. 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)³². On Bylot Island, CH₄ fluxes varied between 0.03–5.82
468 mmol C m⁻² d⁻¹ and CO₂ 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 CO_2 and 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 $260.9 \mu\text{g m}^{-2} \text{ h}^{-1}$ ²¹. Using an
485 average VOC molecular mass of 70 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. ²¹ 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 products²⁶. 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 precursor²⁶. 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^{18, 21}. 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 change⁶⁷ 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, C₅H₈) demonstrated its
515 significant potential to produce both SOAs and O₃ in the presence of acidic particles due
516 to rapid reactivity with hydroxyl radicals (reaction lifetime of 1.7 hours)⁶⁸. Some authors
517 have emphasized the importance of monitoring new sources of isoprene in the atmosphere,
518 especially in unpolluted environments^{69, 70}. In this work, a product ion with the formula
519 C₅H₉⁺, 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 waters⁷¹. While the exact
526 magnitude of DOC photo-processing is debated^{8, 72, 73}, some studies have documented an
527 increased photolability of DOC draining from permafrost^{11, 74}. Considering the anticipated
528 increase in the surface area of water bodies within the permafrost landscape⁷⁵, 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⁻² d⁻¹. This is 3 to 4 orders of magnitude lower than the
535 fluxes of CO₂ and CH₄ 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 research³⁷, 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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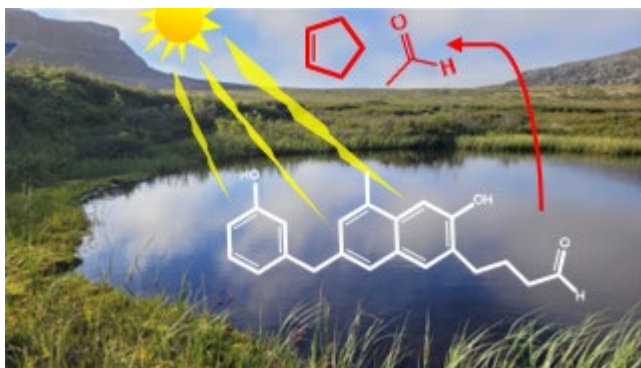
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