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OPTICAL AND PHOTOCHEMICAL CHARACTERIZATION OF CHROMOPHORIC DISSOLVED ORGANIC MATTER FROM LAKES IN TERRA NOVA BAY, ANTARCTICA. EVIDENCE OF CONSIDERABLE PHOTOREACTIVITY IN AN EXTREME ENVIRONMENT

Elisa De Laurentiis,[a] Sandro Buoso,[a] Valter Maurino,[a] Claudio Minero,[a] Davide Vione [a,b]*

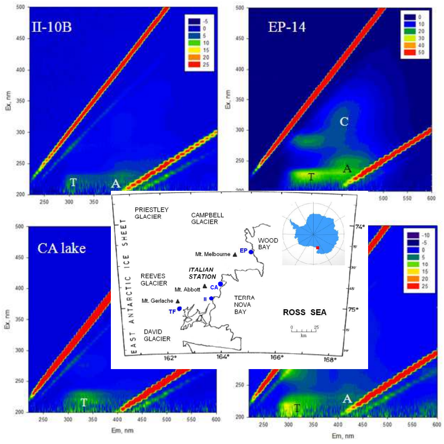
[a] *Università di Torino, Dipartimento di Chimica, Via Pietro Giuria 5, 10125 Torino, Italy.* *http://www.chimicadellambiente.unito.it*

[b] *Università di Torino, Centro Interdipartimentale NatRisk, Via L. Da Vinci 44, 10095 Grugliasco (TO), Italy.* *http://www.natrisk.org*

* Corresponding author. Phone +39-011-6705206 Fax +39-011-6705242.
E-mail: *davide.vione@unito.it*

Abstract

Water samples from shallow lakes located in Terra Nova Bay, Antarctica, were taken in the austral summer season and characterized for chemical composition, optical features, fluorescence excitation-emission matrix (EEM) and photoactivity toward the generation of $^{\bullet}$OH, $^1O_2$ and ^{3}CDOM* (triplet states of chromophoric dissolved organic matter). The optical properties suggested that CDOM would be largely of aquagenic origin and possibly characterized by limited photochemical processing before sampling. Moreover, the studied samples were highly photoactive and the quantum yields for the generation of ^{3}CDOM* and partially of $^1O_2$ and $^{\bullet}$OH were considerably higher compared to water samples from temperate environments. This finding suggests that water in the studied lakes would have considerable ability to photosensitize the degradation of dissolved compounds during the austral summer, possibly including organic pollutants, also considering that the irradiance conditions of the experiments were not far from those observed on the Antarctic coast during the austral summer.



INTRODUCTION

Antarctica is an extreme climatic region and its terrestrial ecosystems are among the most uncontaminated on Earth. Although the seasonally/permanently ice-free regions represent only 2% of the total Antarctic surface, they constitute the largest (and largely unexplored) cold desert on Earth.[1] Antarctic surface lake waters have been less extensively studied than other environmental matrices such as seawater or snow. They are sensitive indicators of environmental changes because modifications in the snow and ice cover can deeply affect water chemistry and biochemistry.[2] Most available data derive from the McMurdo Dry Valleys area in southern Victoria Land.[3-5]

Owing to the unique combination of extreme environmental stresses (*e.g.* low temperature, low photosynthetically active radiation, nutrient limitation, ice cover, limited availability of liquid water, short growth season), the study of Antarctic lakes can provide very interesting information about dissolved compounds such as the Chromophoric Dissolved Organic Matter (CDOM). Among other issues, CDOM is strongly connected with water photoreactivity. Water, soil and sediments from Northern and Southern Victoria Land have been widely studied since 1985, within the framework of the Italian National Research Program in Antarctica (PNRA).[6-8] However, little to nothing is presently known about lake water photochemistry and photoreactivity, in Antarctica in general and in the region of Terra Nova Bay in particular.

The photochemical production of reactive transients is important in surface waters because these species can take part in pollutant degradation, they can induce the transformation of natural occurring molecules (thereby contributing to the geochemical cycling of several major and trace elements), and may also cause oxidative stress to living organisms.[9-13] The most important photogenerated transients are the hydroxyl radical ($^{\bullet}OH$), singlet oxygen ($^1O_2$) and the excited triplet states of CDOM ($^3CDOM^*$).[14,15] These species are produced upon irradiation of photoactive compounds called photosensitizers, among which the main ones in surface waters are CDOM itself, nitrate and nitrite.[16] The production of $^{\bullet}OH$ upon CDOM irradiation is still a matter of debate. On the one hand, there is possibility for H_2O/OH^- to be oxidized to $^{\bullet}OH$ by at least some of $^3CDOM^*$ states.[17] On the other hand, part of $^{\bullet}OH$ photogeneration may be due to photo-Fenton or other H_2O_2-related processes.[18,19] The main reactions involved (or thought to be involved) in $^{\bullet}OH$ generation are the following (note that in the photo-Fenton context CDOM is represented by Fe^{III}-L, where L is an organic ligand that typically undergoes two-electron oxidation; moreover, ISC = inter-system crossing):

$$CDOM + h\nu \rightarrow {}^1CDOM^* \xrightarrow{ISC} {}^3CDOM^* \quad (1)$$
$$^3CDOM^* + H_2O\ (OH^-) \rightarrow CDOM\text{-}H^{\bullet} + {}^{\bullet}OH\ (CDOM^{-\bullet} + {}^{\bullet}OH) \quad (2)$$
$$^3CDOM^* + O_2 \rightarrow CDOM + {}^1O_2 \quad (3)$$
$$Fe^{III}\text{-}L + h\nu \rightarrow Fe^{2+} + L^{+\bullet} \quad (4)$$

$$L^{+\bullet} + O_2 \rightarrow L^{2+} + O_2^{-\bullet} \quad (5)$$

$$2\ O_2^{-\bullet} + 2\ H^+ \rightarrow H_2O_2 + O_2 \quad (6)$$

$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + {}^{\bullet}OH \quad (7)$$

$$NO_3^- + h\nu + H^+ \rightarrow {}^{\bullet}NO_2 + {}^{\bullet}OH \quad (8)$$

$$NO_2^- + h\nu + H^+ \rightarrow {}^{\bullet}NO + {}^{\bullet}OH \quad (9)$$

Also note that $^1O_2$ is produced by $^3CDOM^*$ and O_2 (reaction 3). In this work, the formation of $^{\bullet}OH$, $^3CDOM^*$ and $^1O_2$ was measured upon irradiation of lake water samples from the Terra Nova Bay area, Northern Victoria Land, Antarctica. The rationale is to provide data concerning the photochemical reactivity of environments for which no data are yet available. Furthermore, considering that water-soluble pollutants such as nitrophenols have been detected in some of the studied lake waters (at low concentration values, but suggesting a non-negligible human impact in that remote environment),[20] it is also interesting to assess the intrinsic ability of lake water to photodegrade xenobiotics.

EXPERIMENTAL

Reagents and materials. H_3PO_4 (85%), $NaNO_3$ (99%), $NaNO_2$ (>97.5%), 2,4-dinitrophenylhydrazine (98%), furfuryl alcohol (98%, $^1O_2$ probe), phenol (98.5%) and 2,4,6-trimethylphenol (99%, $^3CDOM^*$ probe) were purchased from Aldrich, $NaNO_3$ (>99.5%), CCl_4 (Uvasol for spectroscopy), benzene (for spectroscopy, $^{\bullet}OH$ probe), and methanol (LiChrosolv gradient grade) from VWR Int., Zero-grade air from SIAD (Bergamo, Italy). Water used was of Milli-Q quality.

Sampling and sample treatment. The present study focused on shallow lakes and ponds located in the Terra Nova Bay area, Northern Victoria Land, Antarctica. The position of the sampling points is shown in Figure 1, while sampling dates and lake features are reported in Table 1. During the austral summer, water samples were taken from the surface layer of the lakes under study and transported under refrigeration to the laboratory (Mario Zucchelli Station, Italian base in the Antarctica). The samples were vacuum-filtered on Millipore MF filter membranes (cellulose acetate, pore diameter 0.45 µm), frozen (-20°C) and stored under freezing till further processing. That included shipping to Italy of the frozen samples, defrosting at 4°C, analysis and irradiation experiments.

To assess the possible effect of freezing on photoreactivity, a sample from Lake Avigliana (NW Italy) was partly irradiated after filtration, and partly frozen (-20°C) and thawed after filtration and before irradiation. Photochemistry experiments (*vide infra* for the set-up description) showed that the difference in photoreaction rates between freezing/thawing and “as is” irradiation of the filtered samples was below 10%, which was also the order of magnitude of experimental repeatability. Therefore, one can assume that the freezing procedure had no significant effect on photoreactivity.

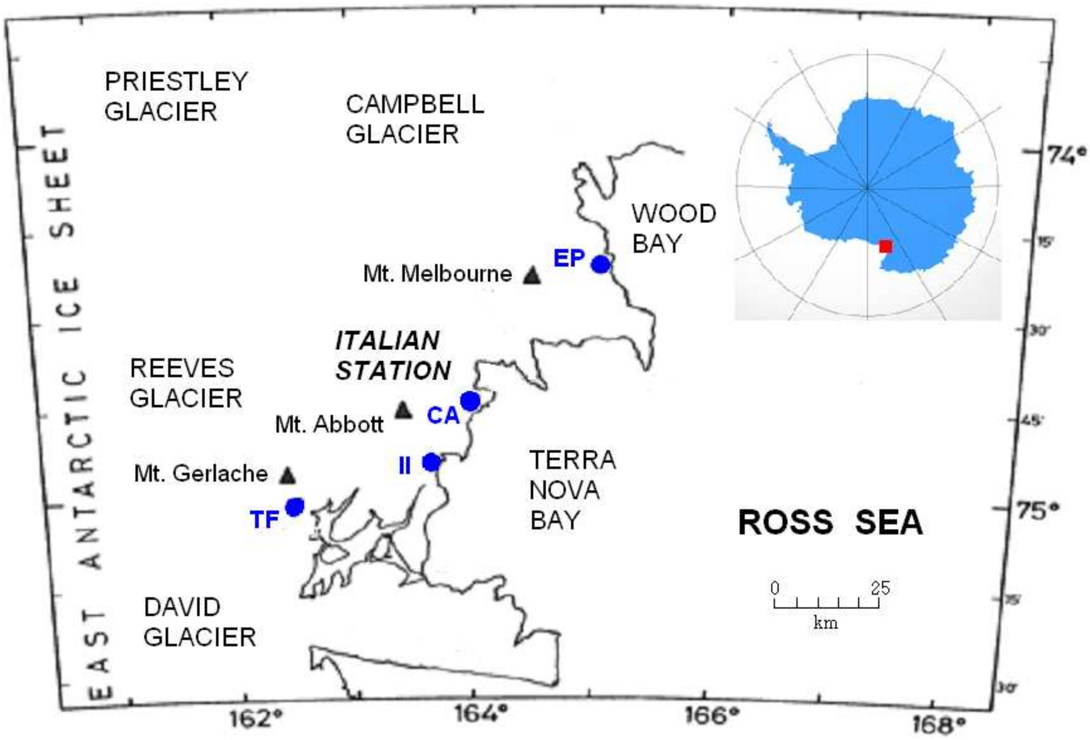


Figure 1. Map of the locations of the investigated lake waters (TF, II, CA, EP, indicated by blue circles; see Table 1 for the acronyms). GW, not indicated on the map for readability issues, is near CA.

Measurement of nitrate, nitrite, DOC and pH. Nitrate was determined by ion chromatography, nitrite by high performance liquid chromatography (HPLC) upon pre-column derivatization with 2,4-dinitrophenylhydrazine (DNPH).[21] DOC was measured as Non-Purgeable Organic Carbon (NPOC) with a Shimadzu TOC-V_{CSH} Total Organic Carbon Analyzer. Sample pH was measured with a Metrohm 602 combined glass electrode, connected to a Metrohm 713 pH meter. Further details on analytical procedures are reported in several previous publications.[16,22-24]

Fluorescence measurements. A Varian Cary Eclipse fluorescence spectrofluorimeter was used, adopting a 10 nm bandpass on both excitation and emission. The bandpass choice was motivated by the low fluorescence intensity of the samples. The fluorescence excitation-emission matrix (EMM) was obtained at 5 nm intervals for excitation wavelengths from 250 to 460 nm and emission ones from 250 to 600 nm. Identification of fluorescent constituents in the water samples was performed on the basis of literature data,[25] using the main fluorescence contours to identify the relevant peaks. Due to relatively low absorbance of the studied samples, fluorescence was not corrected for the inner filter effect.

Table 1. Features of the sampled lakes. [a]

Lake	Site	GPS Coordinates	Sampling Date	Surface (km^2)	Max. Depth (m)	Altitude (m a.s.l)
II-10B	Inexpressible Island	74°52.62’S; 163°43.36’E	7 February 2012	6.8	2.5	30
II-10B_2	Inexpressible Island	74°52.62’S; 163°43.36’E	1 February 2012	6.8	2.5	30
EP-14	Edmonson Point	74°19.74'S; 165°08.03'E	28 January 2012	4	1.5	22
EP-15A	Edmonson Point	74°18.78'S; 165°04.19'E	28 January 2012	4.6	4	0
TF-20_1	Tarn Flat	74°58'11"S; 162°30'52"E	29 January 2012	17.7	3.9	-70
TF-20_2	Tarn Flat	74°58'11"S; 162°30'52"E	8 February 2012	17.7	3.9	-70
GW lake	Gondwana Lake	74°37' S; 164°13' E	31 January 2012	3	2.0	86
CA lake	Carezza lake	74°42'41.8"S;164°02'38.8"E	26 January 2012	7.9	1.5	170

[a] Data from the Scientific Report of Activity of the XXVII Italian Expedition to the Antarctica (2011-2012). Note that Tarn Flat is located in a depression (altitude below sea level).

Irradiation experiments. Lake water samples (20 mL aliquots) were spiked with 1 mM 2,4,6-trimethylphenol (TMP, probe of ^{3}CDOM*), 1 mM furfuryl alcohol (FFA, $^1O_2$ probe) or 2 mM benzene ($^\bullet$OH probe if phenol formation is monitored).[26] Samples were then placed into cylindrical Pyrex glass cells (diameter 4.0 cm, height 2.5 cm), tightly closed with a lateral screw cap. The cells were irradiated from the top under a Solarbox (CO.FO.ME.GRA., Milan, Italy) equipped with a 1500 W Philips xenon lamp and a 310 nm cutoff filter, and they were magnetically stirred during irradiation. Lamp radiation was vertically incident over the solutions and the optical path length was 1.6 cm. Two replicates were made of each irradiation experiment and the results were averaged. Dark runs were carried out by wrapping the cells with aluminum foil and by placing them under the lamp with magnetic stirring. To check for direct photolysis or other processes, the time evolution of TMP and FFA as well as phenol formation from benzene were also monitored upon irradiation in Milli-Q water (blank runs).

The UV irradiance (295-400 nm) reaching the cells was 31.9±2.1 W m^{-2}, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter. The photon flux in solution was actinometrically determined with the ferrioxalate method,[27] taking into account the wavelength-dependent quantum yield of Fe^{2+} photogeneration and the overlap between ferrioxalate absorption and lamp emission.[28] Figure 2 shows the emission spectrum of the lamp, taken with an Ocean Optics USB2000 CCD spectrophotometer (calibrated with an Ocean Optics DH-2000-CAL source) and normalized to the actinometry data. The Figure also reports the absorption spectra of the filtered lake water samples ($A_1(\lambda) = A(\lambda)\, b^{-1}$, where $A(\lambda)$ is the measured absorbance and *b* the optical path length), taken with a V-550 Jasco UV-Vis spectrophotometer with a cylindrical quartz cuvette having $b = 5$ cm. Full absorption spectra were taken from 200 to 800 nm, but Figure 2 only reports part of the measured wavelength ranges.

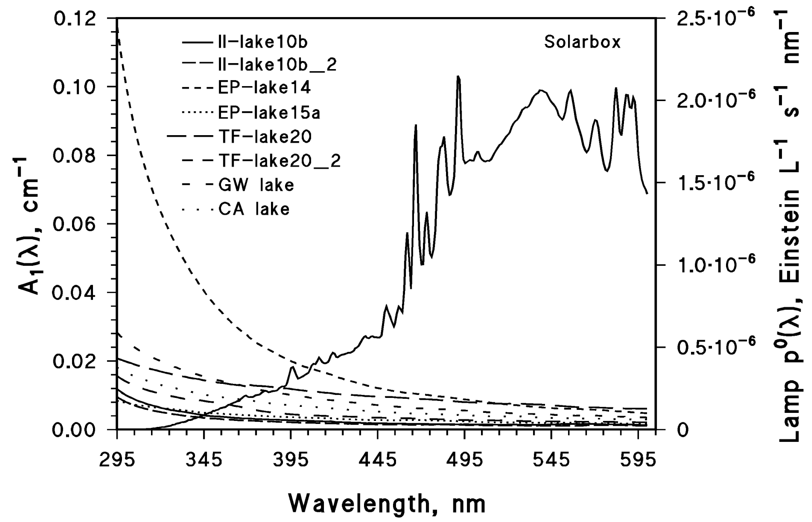


Figure 2. Emission spectrum (spectral photon flux density p°(λ)) of the filtered xenon lamp used in the Solarbox device. Absorption spectra of the studied lake water samples.

The monitoring of TMP, FFA, benzene and phenol after irradiation was carried out by high-performance liquid chromatography with diode array detection (HPLC-DAD, VWR-Hitachi Elite instrument). All samples were eluted with isocratic mixtures of methanol and aqueous H_3PO_4 (pH 2.8) at a flow rate of 1.0 mL min^{-1}. In the case of TMP the eluent used was a mixture of 60:40 (methanol: aqueous H_3PO_4), the TMP retention time was 5.0 min and the detection wavelength 220 nm. For the analysis of FFA the mix ratio was 15:85 (methanol: aqueous H_3PO_4) with detection at 230 nm (FFA retention time 3.7 min). For phenol elution the percentage of methanol was 35% (detection at 210 nm, phenol retention time 4.3 min).

Kinetic data treatment. The time trends of TMP and FFA under irradiation followed pseudo-first order kinetics. The relevant time evolution curves were fitted with equations of the form $C_t\ C_o^{-1} = exp(-k\ t)$, where C_t is the concentration of TMP or FFA at the irradiation time t, C_o the initial concentration, and k the pseudo-first order degradation rate constant. The initial degradation rate is $R = k\ C_o$. The time evolution of phenol formation from benzene was fitted with the equation $P_t = k_P' B_o (k_P'' - k_B)^{-1} (e^{-k_B t} - e^{-k_P'' t})$, where P_t is phenol concentration at the time t, B_o and k_B are the initial concentration and the pseudo-first order degradation rate constant of benzene, respectively, k_P' the first-order rate constant of phenol formation and k_P" the first-order rate constant of phenol transformation. The initial formation rate of phenol is $R_P' = k_P'\ B_o$. The reported errors on the rates ($\pm\sigma$) were derived by curve fitting and depended on the scattering of experimental data around the fit curve, including the variability of replicate experiments.

Measurement of triplet state formation rates. Radiation absorption by chromophoric organic compounds in surface waters yields the excited singlet states, which by inter-system crossing can be transformed into the longer-lived triplet states, ^{3}CDOM*.[29] The states ^{3}CDOM* react with O_2 to give $^1O_2$ or undergo various deactivation reactions. In aerated solution, the lumped first-order deactivation rate constant of ^{3}CDOM* could be $k' \sim 5\cdot10^5$ s^{-1},[30] but a wide variation range of the possible rate constant values is expected. Moreover, ^{3}CDOM* can also react with dissolved organic molecules. TMP is a suitable probe to measure the formation rate of ^{3}CDOM*, $R_{^3CDOM^*}$,[22,31] due to its selectivity toward the triplet states of CDOM. An estimate of the second-order reaction rate constant between TMP and ^{3}CDOM* is $k_{TMP,3CDOM^*} \sim 3\cdot10^9$ M^{-1} s^{-1}.[26] TMP can also react with $^1O_2$, but the $^1O_2$ contribution to the overall TMP transformation would be negligible compared to that of ^{3}CDOM*.[23] The initial concentration value of TMP was set at 1 mM, so that TMP could scavenge a large fraction of photogenerated ^{3}CDOM*. In this way, the calculated value of $R_{^3CDOM^*}$ would be less dependent on the (forcedly approximate) values of k' and $k_{TMP,3CDOM^*}$. At elevated concentration, TMP would mainly scavenge short-lived triplet states and would be poorly sensitive to longer-lived photooxidants.[30] Further details of $R_{^3CDOM^*}$ determination are reported as Supporting Information (hereafter SI).

Measurement of $^1O_2$ formation rates. The formation of $^1O_2$ in surface waters is mainly linked to reaction (3) between ^{3}CDOM* and molecular oxygen. The singlet oxygen thus formed can be deactivated upon collision with the solvent (thermal deactivation), or it can react with dissolved compounds.[32] Furfuryl alcohol (FFA) is a suitable probe molecule to detect and quantify $^1O_2$ formation in aqueous solution, because of its quite selective reaction.[31,33] Further details concerning the determination of the initial formation rate of $^1O_2$, $R_{^1O_2}$, with FFA as probe are reported as SI.

Measurement of $^\bullet$OH formation rates. The formation of phenol from benzene was used as probe reaction for the determination of the formation rate of $^\bullet$OH, $R_{^\bullet OH}$.[34,35] Further details are reported as SI.

Determination of quantum yields. The quantum yields for the formation of ^{3}CDOM*, $^1O_2$ and $^\bullet$OH can be determined by dividing the relevant formation rates by the photon flux P_a absorbed by each sample. Assume $A_1(\lambda)$ as the lake water absorbance, $p°(\lambda)$ as the incident photon flux density of the lamp (see Figure 2 for both $A_1(\lambda)$ and $p°(\lambda)$), and b = 1.6 cm as the optical path length of the irradiated solutions. One has that $P_a = \int_\lambda p°(\lambda)[1-10^{-A_1(\lambda)b}]\,d\lambda$,[36] which would be mostly accounted for by CDOM absorption. Numerical integration was extended over the whole wavelength range. Considering that the initial formation or transformation rates of the probe molecules were used in the calculations, which yielded the initial formation rates of the transient species, the initial lake water absorbance was taken into account to have consistent data in the computation of quantum yields.

RESULTS AND DISCUSSION

Chemical and optical characterization of lake water

Table 2 reports data concerning the physical-chemical and spectral features of the studied lake water samples. Temperature is referred to the time of the sampling, while salinity and conductivity are higher in samples from lakes located near the Ross Sea. Compared to the others, these samples show slightly higher pH that is similar to the saltwater one. The absorption spectra of the studied samples are reported in Figure 2, and the results of spectral calculations (specific absorbance A_1(254nm) DOC^{-1}, spectral slope S, spectral index E2/E3) are reported in Table 2. The lake water $A_1(\lambda)$ spectra in the 280-400 nm range could be approximated with exponential equations of the form $A_1(\lambda) = A_o\, e^{-S\lambda}$, where S

is the spectral slope. Note that nitrate concentration was too low to significantly affect lake-water absorbance at $\lambda \geq 230$ nm.

Samples from lakes located in different sites show some varying chemical features, in particular regarding the concentrations of the anions. Dissolved nitrate was often below the limit of detection of the adopted analytical equipment (ion chromatography, 0.1 µM), except for lakes TF-20_1 and TF-20_2 (Tarn Flat area) as well as CA (Carezza). The former lakes are located between Larsen Glacier and Reeves Glacier and lie in a depression at −70 m below sea level, at 35 km from the Ross Sea. They are surrounded by bare rocks smoothed or modeled in undulating surfaces and are characterized by a noticeable amount of inflowing and out-flowing water.[37] Nitrite levels were in the µM range. Samples from lakes located near the Ross Sea (II-10B, II-10B_2, EP-14) had higher levels of chloride and sulfate, most likely due to contributions from the sea spray.

As far as dissolved organic carbon (DOC) is concerned, the measurements showed values between 2 and 6 mg C L^{-1} with the important exception of EP-14 (Edmonson Point, 26 mg C L^{-1}). This is probably due to the presence of a variety of terrestrial vegetal communities favored by the abundance of water, and to nutrients of bird origin (a penguin rookery is present in the area).[38] Inorganic carbon (IC) is high for almost all the samples, most likely due to inputs of carbonates and bicarbonates from snow/ice-melt and most notably to leaching from local rocks/soil.[37]

The values of the specific absorbance (A_1(254nm) DOC^{-1}) suggest the presence of CDOM that is largely of autochthonous (aquagenic) origin, such as proteinaceous material.[39-41] In contrast, humic lakes that are rich of humic and fulvic substances usually show specific absorbance values above 10 L cm^{-1} $(g\ C)^{-1}$.[41]

It is interesting to compare the values of spectral slope *S* and spectral index E2/E3 of the studied samples with those of alpine lakes, which are located in a rather cold environment at temperate latitudes.[9,23] The data of Table 2 show that E2/E3 < 10 (in many cases it is even E2/E3 < 5) and, most notably, $S \leq 10$ μm^{-1}. The *S* values (and partially also those of E2/E3) are considerably lower when compared to samples from alpine lakes.[9,23] Comparison with boreal lakes from Sweden ($11 < S < 25$ μm^{-1} over 950 samples)[42] also shows considerably lower spectral slope for the studied Antarctic samples. These issues suggest that the spectral properties of CDOM from the studied lakes are different from those observed in other cold environments. The observed differences may have structural implications as there is some evidence that *S* is inversely correlated with size and/or aromaticity of CDOM.[43] The low *S* values in the studied samples could suggest that the relevant CDOM underwent limited exposure to sunlight.[44-47] This issue can be reasonable considering that the lakes under study are frozen for most of the year, although day-long exposure to sunlight would take place in the summer season.

Table 2. Lake chemical features. IC: inorganic carbon (H_2CO_3 + HCO_3^- + CO_3^{2-}).The average depth of the lakes is in the range of 1–2 m. E2/E3 is the ratio between the absorbance values at 250 and 365 nm.[43] The error bounds represent ± σ.

Lake	Salinity, psu	T, °C	Conductivity, µS cm^{-1}	pH	A_1 (254nm)/DOC, cm^{-1} L (g C)$^{-1}$	S, µm^{-1}	E2/E3	DOC, mg C L^{-1}	IC, mg C L^{-1}
II-10B	3.0	1.4	3069	8.0	7.23	10.2 ± 0.3	8.96	3.91 ± 2.82	34.67 ± 1.03
II-10B_2	--	--	--	8.0	5.50	9.9 ± 0.3	9.24	4.29 ± 2.90	30.36 ± 1.26
EP-14	1.0	7.1	1286	7.8	10.65	9.6 ± 0.3	9.93	26.17 ± 2.31	21.11 ± 1.03
EP-15A	0	4.7	29.3	7.1	7.99	5.7 ± 0.1	2.88	1.52 ± 1.03	1.64 ± 0.06
TF-20_1	--	0.3	218	7.6	13.20	4.10 ± 0.04	2.23	2.11 ± 1.61	24.91 ±0.53
TF-20_2	0.2	1.1	248	7.8	8.43	8.4 ± 0.1	4.28	3.24 ± 1.12	11.51 ± 0.45
GW lake	0.1	4.5	126.2	7.2	7.54	7.90± 0.09	3.74	6.22 ± 1.10	3.93 ± 0.58
CA lake	--	--	--	7.7	11.53	6.80 ± 0.08	3.53	2.60 ± 0.37	5.89 ± 0.20

Lake	NO_3^-, µM	NO_2^-, µM	Cl^-, mM	SO_4^{2-}, mM
II-10B	< LOD	4.10	44.16	3.54
II-10B_2	< LOD	3.85	47.95	3.81
EP-14	< LOD	0.397	13.44	0.39
EP-15A	< LOD	1.22	0.21	0.02
TF-20_1	41.8	0.56	1.17	0.14
TF-20_2	58.3	0.62	2.15	0.23
GW lake	< LOD	0.30	0.75	0.12
CA lake	1.40	0.03	1.01	0.07

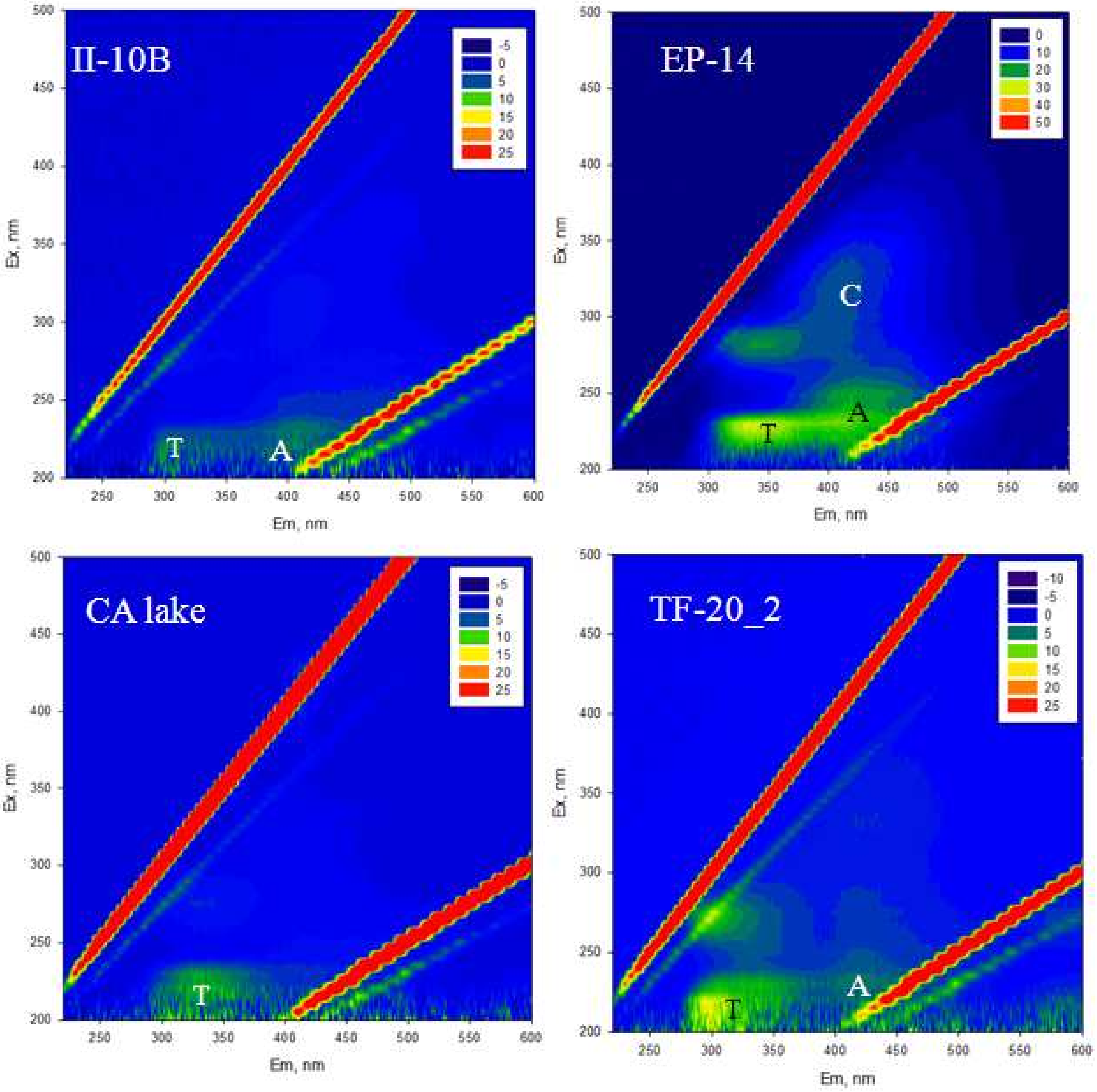


Figure 3. Three-dimensional fluorescence excitation–emission matrices (as contour plots) of Inexpressible Island lake 10B (II-10B), Edmonson Point lake 14 (EP-14), Carezza Lake (CA lake) and Tarn Flat lake 20 (TF-20_2). Fluorescence intensity is scaled from 0 to 25 intensity units for II-10B, CA lake and TF-20_2, and from 0 to 50 for EP-14. A,C: fluorescence peaks of humic substances. T: fluorescence peak of proteinaceous material (tryptophan-like). Ex: excitation wavelength; Em: emission wavelength.

Figure 3 shows representative fluorescence matrix spectra of some of the studied samples (EEM: Excitation Emission Matrix). EEM spectra of the other samples are quite similar. Apart from the linear features that represent the Rayleigh scattering of each sample and the Raman signal of water, plus their second harmonics, fluorescence signals of organic matter suggest some presence of humic or fulvic material (peak A at Ex 200-250 nm/Em 400-450 nm; peak C at Ex 275-350 nm/Em 400-450 nm) as well as of proteinaceous compounds (peak T at Ex 275-300 nm/Em 300-350).[25]

A noticeable feature of the reported EEM spectra is that the fluorescence intensity was quite low. This was particularly true for the signals of humic substances, coherently with previous statements (based on absorption properties) that organic matter in the studied lake water was mainly aquagenic. The fluorescence intensity was lower when compared with lowland lake water samples from temperate regions and approximately comparable to that of samples from alpine lakes.[23,24] Some fluorescence spectra of lake water samples from temperate environments are reported in SI to enable the comparison. In the case of alpine lakes, it should be considered that comparable fluorescence intensity to the studied Antarctic samples was associated to significantly lower values of the DOC (< 1 mg C L^{-1} for alpine lake water).[23]

Photochemical characterization of lake water

The photochemical reactivity of the studied lake water samples was determined by use of probe molecules, and in particular of 1 mM TMP to probe ^{3}CDOM*, of 1 mM FFA to probe $^1O_2$, and of benzene $\rightarrow$ phenol to probe $^\bullet$OH. Figure 4 shows the time evolution of TMP (4a), of FFA (4b) and of phenol from 2 mM benzene (4c), upon irradiation of the studied lake water samples under simulated sunlight. Table 3 shows the parameters that could be derived from the photochemical study: lamp photon flux absorbed by the samples (P_a), initial transformation rates of TMP and FFA (R_{TMP} and R_{FFA}, respectively) and initial formation rate of phenol (R_{Ph}). No transformation of the probe molecules took place in dark experiments with the samples, while some phototransformation was observed in Milli-Q water (blank runs, especially for FFA). The blank rates were subtracted from those measured in the samples, to obtain the formation rates of the transient species (see SI).

Table 3 reports the formation rates of photoreactive transients (R_{3CDOM*}, R_{1O2} and $R_{\bullet OH}$, see SI for calculation details) and the corresponding quantum yields (Φ_{3CDOM*}, Φ_{1O2} and $\Phi_{\bullet OH}$). The use of 1 mM TMP was intended to maximize its reaction with photogenerated ^{3}CDOM*. By so doing, one would reduce the impact of uncertainties associated with the first-order deactivation rate constant(s) of ^{3}CDOM* and with the second-order reaction rate constant(s) between TMP and ^{3}CDOM*. Indeed, the values of R_{TMP} and R_{3CDOM*} reported in Table 3 are not very different and the correction to R_{TMP} to obtain R_{3CDOM*} is not substantial.

As far as hydroxyl radicals are concerned, the reported values of $R_{\bullet\mathrm{OH}}$ and $\Phi_{\bullet\mathrm{OH}}$ include the contributions of nitrate and nitrite in addition to CDOM. Additional runs were carried out to check for ${}^{\bullet}$OH photochemical generation by nitrate and nitrite under the solar simulator.[48,49] Nitrate and nitrite at different initial concentrations were irradiated with 2 mM benzene and the results were compared with the analytical lake water data of Table 2 and the photochemical data of Table 3.

The results of nitrate and nitrite irradiation suggest that ${}^{\bullet}$OH generation in samples II-10B and II-10B_2 would be dominated by nitrite photolysis. In the other cases, CDOM would play an important role in ${}^{\bullet}$OH generation. In Table 3 the values of $\Phi_{{}^{\bullet}OH}^{CDOM}$ represent the contribution of CDOM to ${}^{\bullet}$OH generation, after subtracting the contributions of nitrate and nitrite.

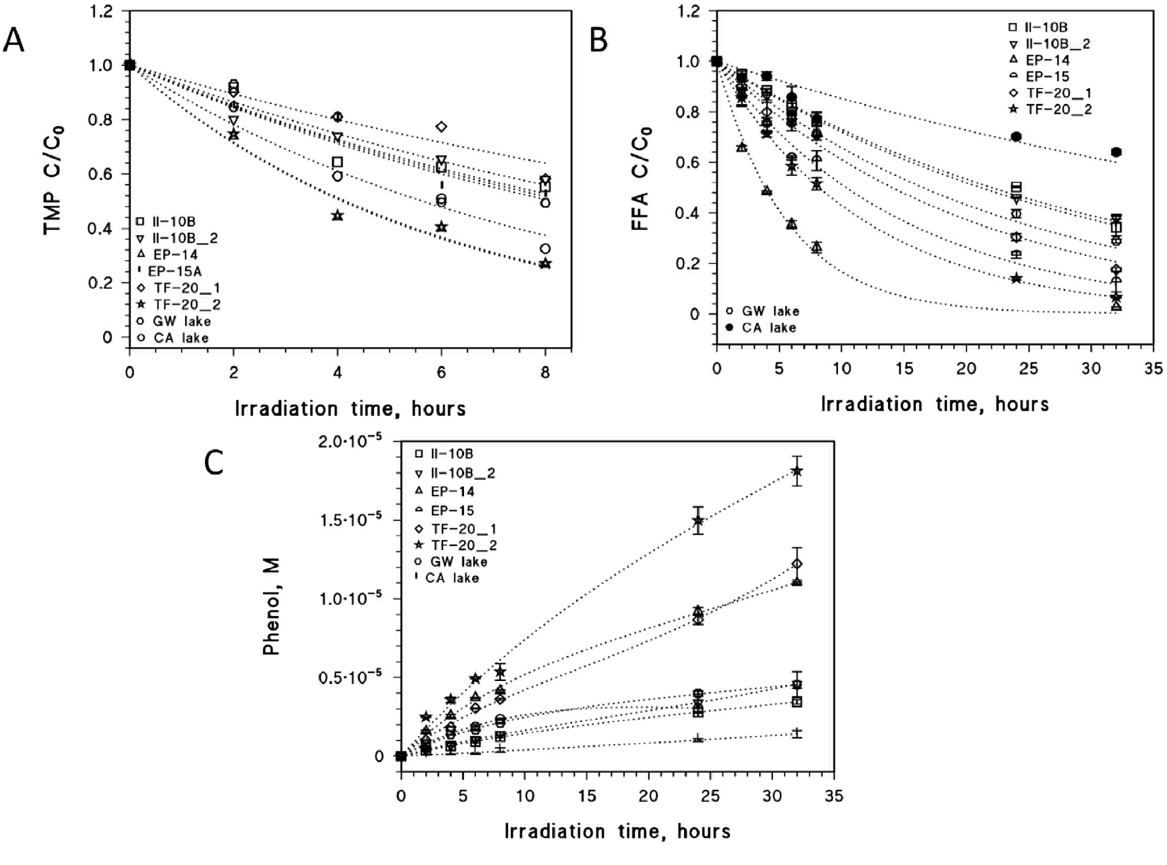


Figure 4. Time evolution of 1 mM TMP (A) and 1 mM FFA (B) spiked to the lake water samples, upon irradiation under simulated sunlight. (C) Time evolution of phenol formation upon irradiation of 2 mM benzene spiked to the samples. The error bars represent the standard error of replicate runs.

Table 3. Lake photochemistry features. The error bounds represent ± σ. Note that R_{3CDOM^*} was determined under the hypotheses that the first-order deactivation rate constant of ^{3}CDOM* is k' = $5 \cdot 10^5$ s^{-1} and that the second-order reaction rate constant between TMP and ^{3}CDOM* is $k_{TMP,3CDOM^*} = 3 \cdot 10^9$ M^{-1} s^{-1}. The generation of $^\bullet$OH would be accounted for by CDOM, nitrate and nitrite.

Lake	**P_a, 10^{-7} Ein L^{-1} s^{-1}**	**R_{TMP}, 10^{-8} M s^{-1}**	**R_{3CDOM^*}, 10^{-8} Ms^{-1}**	**Φ_{3CDOM^*}, 10^{-1}**	**R_{FFA}, 10^{-8} M s^{-1}**	**R_{1O2}, 10^{-8} M s^{-1}**	**Φ_{1O2}, 10^{-2}**
II-10B	1.08	2.43 ± 0.25	2.80 ± 0.29	2.60 ± 0.27	0.87 ± 0.02	Negligible (*)	Negligible
II-10B_2	1.41	2.31 ± 0.16	2.65 ± 0.18	1.90 ± 0.13	0.91 ± 0.02	0.059 ± 0.048	0.42 ± 0.34
EP-14	9.16	5.17 ± 0.32	5.95 ± 0.37	0.65 ± 0.04	4.98 ± 0.33	6.05 ± 0.46	6.60 ± 0.50
EP-15A	2.39	2.28 ± 0.22	2.67 ± 0.25	1.10 ± 0.11	0.97 ± 0.05	1.44 ± 0.68	6.03 ± 2.85
TF-20_1	8.21	1.95 ± 0.19	2.21 ± 0.22	0.27 ± 0.03	1.37 ± 0.32	0.62 ± 0.37	0.76 ± 0.45
TF-20_2	2.95	5.02 ± 0.31	5.80 ± 0.36	2.00 ± 0.12	2.25 ± 0.19	2.07 ± 0.38	7.02 ± 1.29
GW lake	5.62	2.29 ± 0.36	2.68 ± 0.42	0.48 ± 0.08	1.27 ± 0.09	0.40 ± 0.13	0.71 ± 0.23
CA lake	4.28	3.58 ± 0.26	4.15 ± 0.30	0.97 ± 0.07	0.86 ± 0.03	Negligible (*)	Negligible

Lake	**R_{Ph}, 10^{-10} M s^{-1}**	**$R_{\bullet OH}$, 10^{-10} M s^{-1}**	**$\Phi_{\bullet OH}$, 10^{-4}**	**$\Phi_{^\bullet OH}^{CDOM}$, 10^{-4}**
II-10B	0.48 ± 0.02	0.50 ± 0.02	4.64± 0.19	— (°)
II-10B_2	0.52 ± 0.02	0.54 ± 0.02	3.85 ± 0.15	— (°)
EP-14	1.80 ± 0.15	1.89 ± 0.16	2.07 ± 0.17	1.80 ± 0.21
EP-15A	1.19 ± 0.22	1.25 ± 0.23	5.24 ± 0.95	2.07 ± 1.02
TF-20_1	1.44 ± 0.10	1.52 ± 0.11	1.85 ± 0.13	1.30 ± 0.16
TF-20_2	2.22 ± 0.36	2.34 ± 0.38	7.93 ± 0.34	6.13 ± 0.35
GW lake	0.93 ± 0.07	0.98 ± 0.08	1.74 ± 1.29	1.41 ± 1.33
CA lake	0.16 ± 0.04	0.17 ± 0.04	0.39 ± 0.09	0.34 ± 0.10

(*) The degradation of FFA in these samples was equivalent to that of FFA in Milli-Q water (blank run).

(°) The photoproduction of $^\bullet$OH in these samples was dominated by nitrite photolysis.

Hydroxyl radicals could also contribute to the degradation of TMP and FFA. In the former case, however, the values of $R_{\bullet OH}$ were over two orders of magnitude lower compared to those of R_{TMP}. Therefore, $^{\bullet}$OH would not significantly affect TMP degradation even in the hypothesis that TMP scavenges all photogenerated hydroxyl radicals by reacting with them at diffusion-controlled rate (above 10^{10} M^{-1} s^{-1}, [35]). In the case of FFA, with an $^{\bullet}$OH reaction rate constant of $1.5 \cdot 10^{10}$ M^{-1} s^{-1},[35] $^{\bullet}$OH contribution to photoinduced degradation would be negligible for the samples where the measured R_{FFA} was much higher compared to blank experiments of FFA direct phototransformation (EP-14, EP-15A, TF-20_1, TF-20_2, GW). In the other cases $^{\bullet}$OH would account for a minor fraction of R_{FFA}, but for a larger fraction of the difference between the FFA rates in the samples and in the blank. For II-10B_2, $R_{^1O_2}$ had to be decreased by 12% due to the $^{\bullet}$OH contribution to FFA degradation.

When considering the quantum yield data for the generation of ^{3}CDOM*, $^1O_2$ and $^{\bullet}$OH, shown in Table 3, one can make the following observations: *(i)* all the values of Φ_{3CDOM*} and some values of Φ_{1O2} were higher by one order of magnitude or more compared to those reported for lakes and lagoons located in temperate environments (in the case of ^{3}CDOM*, the same values of k' and $k_{TMP,3CDOM*}$ as in this paper have been used to correct R_{TMP});[23,26,50,51] *(ii)* the values of $\Phi_{^{\bullet}OH}^{CDOM}$ were about one order of magnitude higher than those of temperate ecosystems [16,26,52] or organic matter isolates.[53] A caveat is that in the present paper the quantum yields were determined under a solar simulator, while a number of literature works adopted UV irradiation. This difference might reduce the significance of some comparisons, although the maximum absorption of simulated sunlight by lake water took place at $\lambda < 400$ nm. Furthermore, because quantum yields usually decrease with increasing wavelength,[54] a bias connected with the different spectral ranges would mean that our quantum yields are underestimated compared to the literature ones, and that the related differences might be even higher. Overall, one can conclude that CDOM in the studied Antarctic lake water samples was often considerably more photoactive than that found in temperate environments, in particular as far as ^{3}CDOM* generation is concerned. This finding might suggest that photosensitized processes could be important in the studied lakes during the Antarctic summer.

The studied samples showed elevated photoactivity and a fluorescence intensity that was comparable to that of poorly photoactive alpine lakes.[23] This is interesting, because the fluorescence of CDOM is usually reported to be a good proxy of photoactivity.[55-57] From this point of view, the behavior of the studied samples might resemble some triplet sensitizers that are at the same time highly photoactive and poorly fluorescent due to elevated quantum yields of inter-system crossing (ISC).[58] ISC is known to be favored by halide anions,[59] which could play some role in the samples that would be most impacted by sea spray (II-10B, II-10B_2, EP-14). However, the two former samples did not particularly stand out from the others in terms of their photoactivity. Sample EP-14 was characterized by elevated reaction rates of the probe molecules, although this feature would be largely accounted for by its high DOC levels and elevated absorption. Indeed, the quantum yield values of EP-14 for ^{3}CDOM*, $^1O_2$ and $^{\bullet}$OH were not particularly high when compared with the other samples under study. It is interesting to observe that further reactive species such as $Br_2^{-\bullet}$ and $Cl_2^{-\bullet}$ could be formed in irradiated halide-rich samples.[60,61]

The fluorescence of whole CDOM samples might be very different from that of single molecules, because in the case of CDOM a very important role would be played by inter-molecular interactions.[62] For instance, non-fluorescent benzophenones (triplet sensitizers) have been observed to modify the fluorescence of phenolic compounds to produce humic-like fluorescence peaks.[63] Therefore, fluorescence could probe not only the occurrence of photoactive compounds but also their chemical environment, with variable relationships to photoactivity.

As commented above, the studied samples had peculiarly low values of spectral slopes and E2/E3 when compared with lake water from different environments. These values might suggest a low photochemical aging of CDOM, which could be due to low sunlight exposure before sampling.[44-47] Irradiation of the studied samples caused a significant increase of both S and E2/E3 (by 10-50% after 30 h irradiation) and a decrease of the specific absorbance, A_1(254nm) DOC^{-1} (by 25-60% after the same exposure time). The modification of the spectral properties upon irradiation may be consistent with the hypothesis of limited photo-aging. Indeed, CDOM in poorly photoprocessed samples would still contain a significant amount of photolabile compounds that could be effectively degraded under irradiation.[64] Moreover, the increase of S and of E2/E3 would make the relevant values get nearer to those typically observed in photochemically processed lake water.[9,23,42]

Limited pre-exposure of lake water to sunlight might possibly account for elevated photoactivity as, for instance, there is evidence that pre-irradiation of fulvic acids decreases their ability to act as photosensitizers.[65] A possible explanation for this phenomenon is that the most active photosensitizing moieties of CDOM could be quickly transformed by irradiation, while limited photochemical processing would preserve them. To make an example, photoreactive quinones [66] yield hydroxyderivatives upon irradiation,[67] which are considerably less photoactive than the parent compounds.[68] In the studied lake water samples, low photo-aging could be caused by limited exposure to sunlight during the polar winter and the prolonged period of ice cover.

Environmental implications

The CDOM in the studied lakes from Terra Nova Bay, Antarctica had absorption and fluorescence features that suggest a prevailing aquagenic origin. This is reasonable when considering the absence of humic-rich soil in the lake surroundings.[6-8,69-71] The low values of the spectral indexes S and E2/E3 can be consistent with limited CDOM photochemical processing, possibly due to low exposure to sunlight before sampling. This hypothesis would agree with the modifications that S and E2/E3 underwent upon sample irradiation, as photolabile compounds would be preserved in poorly photoprocessed samples. Further characterization of lake-water CDOM (*e.g.* molecular weight determination, functional group elucidation by NMR) will be required to support this hypothesis. The studied samples showed remarkably high photoactivity toward the production of transients such as ^{3}CDOM* and (partially) $^1O_2$ and $^{\bullet}$OH. Data of sunlight irradiance collected on the Antarctic coast, at comparable latitude as Terra Nova Bay, suggest that the maximum UV irradiance reaching the ground (30-40 W m^{-2}) [72] would be comparable to the irradiance of our solar simulator. Of course the maximum irradiance would only be reached near the austral summer solstice, but day-long sunlight irradiation would be operational under those circumstances. This is a further similarity between our experiments and the environmental conditions in the Antarctica, apart from weather-related issues. This consideraton may be important as it suggests that the studied lake water would have an elevated ability to induce photochemical processing of dissolved compounds (including organic pollutants) during the austral summer.

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Supporting Information Available. The Supporting Information contains additional details of the measurements of ^{3}CDOM*, $^1O_2$ and $^{\bullet}$OH, as well as EEM fluorescence spectra of lake water samples from temperate environments. This information is available free of charge via the Internet at http://pubs.acs.org/.

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