

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

A model assessment of the ability of lake water in Terra Nova Bay, Antarctica, to induce the photochemical degradation of emerging contaminants

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1616094> since 2017-01-17T16:59:06Z

Published version:

DOI:10.1016/j.chemosphere.2016.07.049

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and the University of Turin. Changes resulting from the publishing process - such as editing, corrections, structural formatting, and other quality control mechanisms - may not be reflected in this version of the text. The definitive version of the text was subsequently published in CHEMOSPHERE, 162, 2016, 10.1016/j.chemosphere.2016.07.049.

You may download, copy and otherwise use the AAM for non-commercial purposes provided that your license is limited by the following restrictions:

- (1) You may use this AAM for non-commercial purposes only under the terms of the CC-BY-NC-ND license.
- (2) The integrity of the work and identification of the author, copyright owner, and publisher must be preserved in any copy.
- (3) You must attribute this AAM in the following format: Creative Commons BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en>), 10.1016/j.chemosphere.2016.07.049

The publisher's version is available at:

<http://linkinghub.elsevier.com/retrieve/pii/S0045653516309444>

When citing, please refer to the published version.

Link to this full text:

<http://hdl.handle.net/2318/1616094>

A model assessment of the ability of lake water in Terra Nova Bay, Antarctica, to induce the photochemical degradation of emerging contaminants

Marco Minella,^a Valter Maurino,^a Cladio Minero,^a Davide Vione^{a,b,*}

^a *Università degli Studi di Torino, Dipartimento di Chimica, Via P. Giuria 5, 10125 Torino, Italy.*

<http://www.chimicadellambiente.unito.it>

^b *Università degli Studi di Torino, Centro Interdipartimentale NatRisk, Via L. Da Vinci 44, 10095*

Grugliasco (TO), Italy. <http://www.natrisk.org>

* Corresponding author. Tel. +39-011-6705296; Fax +39-011-6705242;

E-mail: *davide.vione@unito.it*

Abstract

The shallow lakes located in Terra Nova Bay, Antarctica, are free from ice for only up to a couple of months (mid December to early/mid February) during the austral summer. In the rest of the year, the ice cover shields the light and inhibits the photochemical processes in the water columns. Previous work has shown that chromophoric dissolved organic matter (CDOM) in these lakes is very reactive photochemically. A model assessment is here provided of lake-water photoreactivity in field conditions, based on experimental data of lake water absorption spectra, chemistry and photochemistry obtained previously, taking into account the water depth and the irradiation conditions of the Antarctic summer. The chosen sample contaminants were the solar filter benzophenone-3 and the antimicrobial agent triclosan, which have very well known photoreactivity and have been found in a variety of environmental matrices in the Antarctic continent. The two compounds would have a half-life time of just a few days or less in the lake water during the

Antarctic summertime, largely due to reaction with CDOM triplet states ($^3\text{CDOM}^*$). In general, pollutants that occur in the ice and could be released to lake water upon ice melting (around or soon after the December solstice) would be quickly photodegraded if they undergo fast reaction with $^3\text{CDOM}^*$. With some compounds, the important $^3\text{CDOM}^*$ reactions might favour the production of harmful secondary pollutants, such as 2,8-dichlorodibenzodioxin from the basic (anionic) form of triclosan.

Keywords: environmental photochemistry; pollutant photodegradation; polar regions; abiotic attenuation processes; emerging pollutants.

Introduction

The Antarctica is the Earth's continent that is least subjected to a direct human impact, and from this point of view it represents a typical example of a remote environment. In spite of this, usually low but sometimes significant contamination levels can be found in several Antarctic matrices (Van de Velde et al., 2005; Fuoco et al., 2009; Vecchiato et al., 2015). The reason is in part the long-range transport of contaminants from other continental areas, which involves most notably the persistent organic pollutants (POPs) (Yogui and Sericano, 2008; Dickhut et al., 2012; Kallenborn et al., 2013; Zhang et al., 2015). Among the POPs, semi-volatile compounds are peculiarly prone to accumulation in cold areas as a consequence of volatilisation/condensation equilibria, according to the well-known global distillation or grasshopper effect (Harner, 1997; Borghini et al., 2005). However, contamination in the Antarctica is not only a consequence of long-range transport, because the limited human activity in the continent has a relatively low but non-negligible environmental impact. It has recently been found that several emerging contaminants (including most notably a range of pharmaceuticals and personal care products) occur in a wide variety of

environmental and biological matrices near scientific bases, as a consequence of the *in situ* release of these xenobiotics (Emnet et al., 2015). The most likely reason is the incomplete elimination of such contaminants from wastes and wastewater (a problem that also affects more sophisticated wastewater treatment plants in temperate areas; Salgado et al., 2012; Luo et al., 2014; Richardson and Ternes, 2014; De Solla et al., 2016), coupled to local transport and biogeochemical cycling.

Surface waters are exposed to several contamination sources, but they have also a self-depollution capability due to both abiotic and biological processes. Among the abiotic decontamination pathways, photochemistry plays an important role for the abatement of biorefractory compounds (Boreen et al., 2003; Pace and Barreca, 2013; Challis et al., 2014; Yan and Song, 2014). The latter can be degraded by direct photolysis, where sunlight absorption by the contaminant triggers its transformation, and/or by indirect photochemistry. In indirect photochemistry, sunlight is absorbed by photosensitisers (e.g. nitrate, nitrite and chromophoric dissolved organic matter, CDOM) that produce reactive transient species, most notably the radicals $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ (the latter mainly produced upon oxidation of inorganic carbon by $\bullet\text{OH}$), singlet oxygen, $^1\text{O}_2$, as well as CDOM triplet states, $^3\text{CDOM}^*$. These transients react with contaminants and cause their transformation. In alternative to reacting with pollutants, the transients can be quenched by reaction with dissolved organic matter, DOM (which scavenges $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$), by reaction with inorganic carbon (carbonate and bicarbonate scavenge $\bullet\text{OH}$), by collision with the solvent (which is the main inactivation process for $^1\text{O}_2$) or, in the case of $^3\text{CDOM}^*$, by a combination of thermal deactivation and reaction with O_2 , the latter yielding $^1\text{O}_2$ (Canonica et al., 2005; Canonica, 2007; Page et al., 2014; Vione et al., 2014; Cawley et al., 2015; Bodhipaksha et al., 2015; Gligorovski et al., 2015). The photoinduced degradation is a major abiotic depollution pathway, but in some cases it can yield secondary pollutants that are more toxic than the parent compounds (Della Greca et al., 2004; Isidori et al., 2009).

The shallow lakes located in Terra Nova Bay, Antarctica, are ice-free for no more than a couple of months every year, during the Antarctic summer (Abollino et al., 2003; Malandrino et al., 2009).

In the rest of the year, the ice cover inhibits photochemistry in lake water. However, the limited time interval in which photoreactions can be operational might be compensated for by an elevated potential of the lake water to trigger photoinduced processes. When irradiated in the laboratory, lake water samples from Terra Nova Bay have actually featured a remarkable CDOM photoreactivity. In particular, by making use of selective probe molecules, the measured quantum yields for the photogeneration of reactive transients ($^3\text{CDOM}^*$, $^1\text{O}_2$, $\bullet\text{OH}$) were one-two orders of magnitude higher compared to lake water at temperate latitudes (De Laurentiis et al., 2013). This peculiarity might be due to the fact that CDOM in the Antarctica is protected from photodegradation during the extensive periods of ice cover, thereby retaining an elevated photoactivity that is partially lost by pre-irradiated CDOM, due to the photodegradation of photoactive moieties (Helms et al., 2008; Stubbins et al., 2012). This finding is potentially very interesting because it could suggest a considerable ability of Antarctic lake waters to induce photochemical self-depollution. However, it is important to assess the significance of such remarkable features in the context of the Antarctic summer irradiation conditions, with whole lake water columns and a short ice-free period (mid December – early/mid February). In this work, such an assessment was carried out with a model approach, applied to the photodegradation of the solar filter benzophenone-3 (hereafter BP3) and the antimicrobial agent triclosan (hereafter TRIC). The rationale for the choice of these sample contaminants is that their photochemical behaviour is very well known and they have actually been detected in several environmental matrices in the Antarctica (Emnet et al., 2015). In particular, both compounds have been detected at tens to hundreds ng L^{-1} levels in wastewater effluents, and BP3 was also found at tens ng L^{-1} levels in seawater, at ng L^{-1} levels in melted sea ice, and at up to tens ng g^{-1} dry weight in biological samples (clams, urchin, fish liver) (Emnet et al., 2015). In the case of TRIC it should be pointed out that its irradiation yields 2,8-dichlorodibenzodioxin as a secondary pollutant of concern (Lores et al., 2005; Latch et al., 2005; Kliegman et al., 2013), thus it is also possible to assess the potential of dioxin formation from irradiated TRIC. The results obtained with

sample molecules of known behaviour allow some generalisations to be made for the phototransformation of other compounds in the lakes under investigation.

Methods

The study lakes are located in the Terra Nova Bay area, Northern Victoria Land, Antarctica, in the surroundings of the Mario Zucchelli Italian Station, between 74-75°S latitude and 162-165°E longitude. A map showing the location of the lakes and the lake acronyms is provided in **Figure 1**.

The model assessment of contaminant phototransformation was carried out with the APEX software (Aqueous Photochemistry of Environmentally-occurring Xenobiotics), available for free download as Electronic Supplementary Information of Bodrato and Vione (2014). APEX predicts photochemical reaction kinetics from photoreactivity parameters (absorption spectra, direct photolysis quantum yields and second-order reaction rate constants with reactive species), and from data of sunlight radiation spectrum, water chemistry and depth (Bodrato and Vione, 2014). APEX is based on a photochemical model, validated by comparison with field data of phototransformation kinetics in surface freshwaters (Maddigapu et al., 2011; De Laurentiis et al., 2012; Marchetti et al., 2013).

In this work, several APEX input data were derived from parameters obtained upon characterisation and irradiation of lake water samples from Terra Nova Bay (De Laurentiis et al., 2013). They include the absorption spectra of the lake water in the 290-800 nm wavelength interval, the dissolved organic carbon (DOC), the concentrations of nitrate and nitrite, as well as the values of inorganic carbon and pH. The latter two parameters allowed the computation of the concentrations levels of carbonate and bicarbonate. Further input data referred to each lake are the water depth and the formation quantum yields of $^3\text{CDOM}^*$, $^1\text{O}_2$ and $\bullet\text{OH}$ from irradiated CDOM

($\Phi_{^3\text{CDOM}^*}^{\text{CDOM}}$, $\Phi_{^1\text{O}_2}^{\text{CDOM}}$ and $\Phi_{\bullet\text{OH}}^{\text{CDOM}}$, respectively). The lifetimes of $^3\text{CDOM}^*$ and $^1\text{O}_2$ were assumed to be similar to those observed in other lake-water environments, and the same assumption was made for the reaction rate constant between $\bullet\text{OH}$ and DOM. The lake-water chemical and photochemical features (De Laurentiis et al., 2013) are reported in **Table SM1** in the Supplementary Material (hereafter SM). The photochemical reactivity parameters of BP3 and TRIC (absorption spectra, direct photolysis quantum yields and second-order reaction rate constants with the photogenerated transients) were derived from the literature (see **Table SM2** (SM)) (Latch et al., 2005; Buth et al., 2009; Vione et al., 2013; Kliegman et al., 2013; Bianco et al., 2015).

The irradiation conditions in the Antarctic summer are peculiar because the sun is always above the horizon with a low (although not constant) elevation angle. The sunlight spectra (photon flux density per unit surface area, expressed as photons $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$) were obtained for fair-weather and no ozone hole conditions with the NCAR-TUV calculator (National Center for Atmospheric Research, 2016) for the region of Terra Nova Bay, in the mid-December to mid-February period at 6 pm local time. This time is half-way between midday and midnight and it represents a reasonable daily average. Midday and midnight appear differently to a bystander in the Antarctic continent during summer (characterized by 24-h daylight) compared to temperate latitudes but, with the exception of the South Pole, they represent the time when the sun is highest and lowest over the horizon, respectively. Because of the low sun elevation angle, sunlight enters the water surface far from the vertical but it is deviated towards the vertical by the refraction phenomenon (Zepp and Cline, 1977). The residual sunlight inclination below the water surface ensures that the light path in water (l) is longer than the water depth d . Assuming that $l = \varphi d$, φ would vary from 1.3 in mid-December to 1.5 in mid-February. The different values of φ at different times were taken into account in calculations.

The absorption of radiation by the photosensitizers (CDOM, nitrate and nitrite) and the studied substrates is computed by APEX taking into account the competition for sunlight irradiance with a

Lambert-Beer approach (Bodrato and Vione, 2014; Braslavsky, 2007). APEX assumes efficient water mixing, which applies reasonably well to the studied Antarctic lakes in the ice-free period due to their limited depths (up to 4 m). The model results are average values over the water column, thus they include the contributions of the well-illuminated surface layer and of darker water at the bottom (Loiselle et al., 2008).

Among the sample contaminants used for photochemical modelling, TRIC is a weak acid with $pK_a = 8$ and its two forms show quite different photochemical reactivity (Latch et al., 2005; Buth et al., 2009; Bianco et al., 2015). Assume k_1 and k_2 as the APEX-computed first-order rate constants for the phototransformation of neutral (acidic) and anionic (basic) TRIC, respectively. Moreover, α_1 and α_2 are the respective molar fractions of the two species, calculated by taking into account their acid-base equilibrium at the lake-water pH values. The overall TRIC rate constant was determined as $k_{TRIC} = k_1 \alpha_1 + k_2 \alpha_2$, and the corresponding half-life time was calculated as $t_{1/2}^{TRIC} = \ln 2 (k_{TRIC})^{-1}$. The fractions of TRIC that undergo degradation as the neutral and anionic form can be expressed as, respectively, $k_1 \alpha_1 (k_{TRIC})^{-1}$ and $k_2 \alpha_2 (k_{TRIC})^{-1}$.

We assume k_{28DCDD} as the pseudo-first order photogeneration rate constant of 2,8-dichlorodibenzodioxin, as computed by APEX by taking into account the first-order transformation rate constants of TRIC (both neutral and anionic forms) in the different photochemical processes and the dioxin formation yields in the same processes. The yields of 28DCDD from anionic TRIC are 4% by direct photolysis (Kliegman et al., 2013) and 14% via $^3CDOM^*$ reactions (Bianco et al., 2015). In contrast, the dioxin is not formed upon reaction of anionic TRIC with $\bullet OH$, or from any phototransformation pathway of neutral TRIC (Kliegman et al., 2013; Bianco et al., 2015). The overall formation yield of 2,8-dichlorodibenzodioxin from TRIC was calculated as $\eta_{28DCDD} = k_{28DCDD} (k_{TRIC})^{-1}$ (Bodrato and Vione, 2014).

Photoreactivity parameters used in APEX have been obtained under laboratory conditions, at temperatures that are certainly higher compared to those of the studied Antarctic lakes. Although

photochemical reactions are among the chemical processes that are least affected by temperature (the energy of sunlight photons excites molecules at states that are often beyond reach for thermal excitation) (Daniels and Alberty, 1955), some overestimation of the reaction kinetics by the model cannot be excluded.

Results and Discussion

Photochemical production and occurrence of reactive transients

The contaminants BP3 and TRIC undergo photodegradation in surface waters at temperate latitudes, mainly by direct photolysis and reaction with $\bullet\text{OH}$ and ${}^3\text{CDOM}^*$ (Vione et al., 2013; Bianco et al., 2015). To model photodegradation in the Terra Nova Bay lakes, first of all the steady-state concentrations of the photoinduced transient species were calculated in the period from half December to half February. The computed concentrations are average values over whole water columns at 6 pm local time under fair-weather conditions, and the levels of $\bullet\text{OH}$ and ${}^3\text{CDOM}^*$ (the most relevant transients for BP3 and TRIC photodegradation) are reported in **Figure 2** throughout the ice-free season. The modelled concentrations of $\bullet\text{OH}$ and ${}^3\text{CDOM}^*$ followed the irradiance of sunlight and were maximum in the solstice day. Moreover, $\bullet\text{OH}$ was highest (some 10^{-16} mol L⁻¹) in lakes TF20 and EP15, and ${}^3\text{CDOM}^*$ was highest (some 10^{-14} mol L⁻¹) in lakes CA, IL10 and EP14.

Apart from the major role of sunlight irradiance, the steady-state concentrations of $\bullet\text{OH}$ and ${}^3\text{CDOM}^*$ ($[\bullet\text{OH}]$ and $[{}^3\text{CDOM}^*]$, respectively) have a complex dependence on lake chemistry and depth, as well as on the respective formation quantum yields from irradiated CDOM ($\Phi_{\bullet\text{OH}}^{\text{CDOM}}$ and $\Phi_{{}^3\text{CDOM}^*}^{\text{CDOM}}$). Correlation bi-plots were drawn by considering the maximum values of $[\bullet\text{OH}]$ and $[{}^3\text{CDOM}^*]$ for each lake (referred to the solstice day) and the photochemically relevant parameters

(water chemistry and depth, transient formation quantum yields). No statistically significant results were obtained for the steady-state [$^3\text{CDOM}^*$], which showed non-significant increases with increasing DOC and $\Phi_{^3\text{CDOM}^*}^{\text{CDOM}}$, and a non-significant decrease with increasing depth (see **Table 1** for the results of the statistical tests). Despite their statistical non-significance, these results are reasonable because $^3\text{CDOM}^*$ is produced by CDOM, which is generally higher at higher DOC, and elevated $\Phi_{^3\text{CDOM}^*}^{\text{CDOM}}$ is favourable to the occurrence of $^3\text{CDOM}^*$. In contrast, high depth is detrimental to all the photochemical processes because the lower depths of deep lakes are poorly illuminated by sunlight. Therefore, the elevated photoreactivity in the well-irradiated surface layer is compensated for by lack of photoreactivity in the dark bottom water. The lack of statistically significant correlations or anti-correlations of [$^3\text{CDOM}^*$] with DOC, $\Phi_{^3\text{CDOM}^*}^{\text{CDOM}}$ and depth is probably explained by the fact that these parameters vary independently of one another in the investigated lakes, and that there is not a single parameter that prevails over the others to significantly influence [$^3\text{CDOM}^*$].

In the case of the steady-state [$\bullet\text{OH}$], a statistically significant correlation was found with the formation quantum yield $\Phi_{\bullet\text{OH}}^{\text{CDOM}}$ ($r = 0.86$, $n = 6$, $p = 0.03$, see **Table 1**), which is reasonable considering that CDOM would be the main $\bullet\text{OH}$ source in most of the investigated lake waters (De Laurentiis et al., 2013). Indeed, coherently with the computed [$\bullet\text{OH}$] data (see **Figure 2b**), it was $\Phi_{\bullet\text{OH}}^{\text{CDOM}} = 3.7 \cdot 10^{-4}$ for TF20 and $2.1 \cdot 10^{-4}$ for EP15, while $\Phi_{\bullet\text{OH}}^{\text{CDOM}}$ was negligible in the case of IL10 (see **Table SM1(SM)**). In contrast, the counter-intuitive significant direct correlation between [$\bullet\text{OH}$] and depth (**Table 1**) is most likely an accidental consequence of the fact that [$\bullet\text{OH}$] itself was highest in the deepest investigated lakes (EP15 and TF20). In spite of depth, the modelled [$\bullet\text{OH}$] was elevated in EP15 and TF20 because of high $\Phi_{\bullet\text{OH}}^{\text{CDOM}}$ and of low DOC, the latter implying the occurrence of little DOM that could scavenge $\bullet\text{OH}$.

Phototransformation of BP3

By considering the levels of the photogenerated transients, as well as the photon flux absorbed by BP3 in each water column, it was possible to compute the pseudo-first order photodegradation rate constants and half-life times of BP3 in the different lakes in the mid-December to mid-February period, assuming fair-weather conditions. The calculated half-life times of BP3 were always lower than 10 days, and they were in the ~day range or below in mid December - early January. Note that in this period the sun is always above the horizon, thus the day unit represents a full day (24 h) of solar irradiation. The photodegradation of BP3 would be dominated by reaction with $^3\text{CDOM}^*$ (>80% of the total), with a secondary role of $\bullet\text{OH}$. The percentage of phototransformation by $\bullet\text{OH}$ ranged from 15-20% of the total in lakes EP15 and TF20, down to <1% in IL10.

In a possible contamination scenario where the pollutant is initially contained in the ice, from which it can reach the lake water upon ice melting, the very fast phototransformation in the water columns of all lakes ($t_{1/2}^{\text{BP3}} \leq 1$ day) after the ice-melting period, which typically takes place around or soon after the solstice (Abollino et al., 2003; Malandrino et al., 2009), would ensure practically complete disappearance of BP3 in a week or less. These results are referred to fair-weather conditions, thus they overestimate the actual phototransformation. Due to actual weather in the Antarctica, and mostly to the effect of clouds, the average UV irradiance might decrease by 20-40%, and the 400-600 nm irradiance by up to 50%, compared to the fair-weather case (Bernhard et al., 2005). Considering that CDOM in lake water is the main sunlight absorber in the 300-500 nm wavelength interval (Loiselle et al., 2008), the phototransformation of BP3 would still be fast enough to ensure its complete elimination soon after the solstice. The modelled BP3 half-life times are higher in mid-February (in the range of 5-10 days under fair weather), but they are referred to ice-free water. They do not apply to all years, because in several cases the lakes would be partially or totally frozen in mid-February. The ice cover highly limits the penetration of light in water (Kepner et al., 2000), thereby decreasing considerably the photodegradation kinetics. Another issue

is that, by mid-February, the lake-water CDOM has been exposed to sunlight for about two months. However, Antarctic lake water sampled in early February still retained considerable photoactivity (De Laurentiis et al., 2013).

Compared to the $^3\text{CDOM}^*$ reactions that would be quite fast in all the lakes, higher differences are expected in the case of $\bullet\text{OH}$ reactions. When taking into account the data of **Figure 2** at the solstice (maxima of the transient steady-state concentrations), $[^3\text{CDOM}^*]$ would be higher by approximately 2.5-fold in lake CA compared to GW (where $[^3\text{CDOM}^*]$ would be the highest and the lowest, respectively). In contrast, $[\bullet\text{OH}]$ would be almost 70 times higher in TF20 than in IL10 (where $[\bullet\text{OH}]$ would be the highest and the lowest, respectively). **Figure 3** reports the BP3 half-life times for the reaction with $\bullet\text{OH}$ alone, for different periods in the various lakes. BP3 photodegradation would be quite fast in lakes EP15 and TF20, and relatively slow in IL10. In the latter case, $\bullet\text{OH}$ would actually play a negligible role in BP3 phototransformation that would be accounted for almost entirely by $^3\text{CDOM}^*$ (>99%).

BP3 reacts with $\bullet\text{OH}$ at diffusion-controlled kinetics (Vione et al., 2013), thus other contaminants are not expected to undergo significantly faster $\bullet\text{OH}$ reaction compared to BP3 (but slower reactions are indeed possible; Buxton et al., 1988). For this reason and for weather-related effects, the results shown in **Figure 3** can be considered as lower limits for the $\bullet\text{OH}$ -induced half-life times of generic pollutants in the given lakes. The $\bullet\text{OH}$ degradation kinetics is particularly relevant for contaminants that do not undergo significant direct photolysis or triplet-sensitised transformation by $^3\text{CDOM}^*$, but that react significantly with $\bullet\text{OH}$. Typically, they are hardly oxidised molecules without chromophoric groups (Buxton et al., 1988). In this case, phototransformation in lake EP14 and, most notably, IL10 might not be fast enough to ensure complete degradation by $\bullet\text{OH}$ during the ice-free season.

Phototransformation of TRIC

TRIC is a weak acid with $pK_a \sim 8$ and its acidic (neutral) and basic (anionic) forms show different photochemical reactivity. For instance, the anionic form undergoes direct photolysis to a higher extent than the neutral one. A further difference from neutral TRIC is that the anionic form yields a dioxin (2,8-dichlorodibenzodioxin, hereafter 28DCDD) upon both direct photolysis and $^3\text{CDOM}^*$ reaction. The reaction with $^3\text{CDOM}^*$ would be the main phototransformation process of TRIC in the water columns of all the Antarctic lakes under examination. It would account for over 96% of the total phototransformation, the remainder being accounted for by direct photolysis and/or reaction with $\bullet\text{OH}$ and $^1\text{O}_2$ (the percentages of the minor processes and their relative importance would vary depending on the lake and the period under examination). The anionic form of TRIC is expected to be a bit more photolabile than the neutral one, and there was a statistically significant correlation ($r = 0.884$, $n = 6$, $p = 0.019$) between the calculated pseudo-first order photodegradation rate constants and the water pH values. The corresponding half-life times of TRIC in the mid-December to mid-February period would be always lower than 5 days, and lower than one day in the period from mid December to late January. Therefore, as already discussed in the case of BP3, and even by taking weather effects into account, any TRIC occurring in the lake water soon after the ice melt would be totally degraded in a relatively short time, in all the lakes under examination.

The direct photolysis is a major phototransformation process for TRIC in aquatic environments at temperate latitudes (Latch et al., 2005; Bianco et al., 2015). In particular, by applying the same model approach as here, but with mid-latitude conditions for sunlight spectrum, irradiance and CDOM photoreactivity, the direct photolysis is predicted to account for up to 50% of the phototransformation of neutral TRIC and for over 70% of the anionic one (Bianco et al., 2015). In Antarctic lake water, the importance of the direct photolysis would be much lower. Moreover, anionic TRIC is more labile by direct photolysis than the neutral form, because it absorbs sunlight to a higher extent and has comparable photolysis quantum yield (Kliegman et al., 2013). The half-

life times for the direct photolysis of TRIC, involving the two forms in equilibrium at the lake-water pH, are reported in **Figure 4a**. The most favourable lakes to the TRIC direct photolysis are IL10 and CA, with pH values of 8 and 7.7, where the anionic form would be an important fraction of the total TRIC. Interestingly, the most unfavourable lake to the TRIC direct photolysis would be EP14 that, despite having pH 7.8, has elevated DOC (above 26 mg C L⁻¹) and optically thick water due to the presence of elevated CDOM. In this case, the direct photolysis of TRIC would be inhibited by competition with CDOM for sunlight irradiance.

Although not so relevant for TRIC phototransformation in the studied lakes, the direct photolysis results provide some insight into the possible behaviour of compounds that, like TRIC, absorb UV radiation and undergo efficient direct phototransformation but that, unlike TRIC, do not react or react poorly with ³CDOM*. In such a case, photochemical attenuation would be operational but is predicted to be considerably slower than the photoinduced removal of compounds that react fast with ³CDOM*.

Figure 4b reports the expected yields (η_{28DCDD}) for the photogeneration of 2,8-dichlorodibenzodioxin (28DCDD) from TRIC in the different lakes. In each case the calculations took into account the fact that anionic TRIC produces 28DCDD with 4% yield by direct photolysis, and with 14% yield upon ³CDOM* reaction, and that neutral TRIC does not yield 28DCDD under irradiation. The acid-base equilibrium between the neutral and anionic forms at the lake water pH was considered as well. The overall 28DCDD yields thus obtained ranged from 2-3% (EP15, GW) to over 8% (IL10). Because 28DCDD is only photogenerated by anionic TRIC, and because the ³CDOM* reaction would be the main TRIC phototransformation pathway in all the cases, there was a non-surprising very significant correlation between the modelled η_{28DCDD} and pH ($r = 0.998$, $n = 6$, $p < 0.001$). Considering that the ³CDOM* processes are those producing 28DCDD with the highest yield, the same lake water conditions that allow for a fast TRIC phototransformation would favour at the same time the production of 28DCDD. The latter compound is more hydrophobic than

TRIC and it could be partitioned to the sediments (Buth et al., 2010; Anger et al., 2013), where it would be partially protected from further phototransformation.

Conclusions

The Terra Nova Bay lakes under consideration are frozen for most of the year, and the ice-free period usually lasts for a couple of months or less. Despite this, the considerable photoreactivity of the lake-water CDOM could compensate for the limited ice-free period and induce an important phototransformation of possible contaminants. The latter was assessed by considering BP3 and TRIC as model pollutants of known photochemical behaviour, and the results obtained with these compounds can allow some general inferences to be drawn for other molecules.

Potential contaminants could reach the lake water by transport during the ice-free period that is, however, rather short. Moreover, pollutants occurring in the ice could be transferred to the water phase upon ice melt. The ice melting often takes place in mid to late December, when the contaminants thus released might undergo effective reaction with photogenerated transients (mainly $^3\text{CDOM}^*$) and be eliminated very quickly from the lake water. The $^3\text{CDOM}^*$ reactions would be key processes for the self-cleaning of lake water from compounds that undergo relatively fast triplet-sensitised transformation, but they might also promote the formation of harmful intermediates as in the case of anionic TRIC. The photochemical production of harmful compounds is strongly substrate-dependent, however, and in several other cases one might observe quick decontamination without production of harmful substances.

The contaminants that do not react with $^3\text{CDOM}^*$ but react with $\bullet\text{OH}$ at near diffusion-controlled kinetics could undergo sufficiently fast phototransformation in some of the lakes (EP15, TF20, CA, GW). However, in lakes EP14 and IL10 the degradation might not be fast enough to ensure photochemical removal before the onset of freezing in the month of February.

Compared to surface waters in temperate environments, the photochemistry in the Terra Nova Bay lakes is strongly shifted towards the ³CDOM* reactions. Therefore, a better understanding of such processes (including the possible formation of harmful intermediates from peculiar contaminants) is essential to assess the fate of pollutants in Antarctic surface waters.

Acknowledgements

Financial support by PNRA - Progetto Antartide is gratefully acknowledged.

References

- Abollino, O., Aceto, M., Buoso, S., Gasparon, M., Green, W. J., Malandrino, M., Mentasti, E., 2003. Distribution of major, minor and trace elements in lake environments of Antarctica. *Antarctic Sci.* 16, 277-291.
- Anger, C. T., Sueper, C., Blumentrit, D. J., McNeill, K., Engstrom, D. R., Arnold, W. A., 2013. Quantification of triclosan, chlorinated triclosan derivatives, and their dioxin photoproducts in lacustrine sediment cores. *Environ. Sci. Technol.* 47, 1833-1843.
- Bernhard, G., Booth, C. R., Ehramjian, J. C., 2005. UV climatology at Palmer Station, Antarctica, based on Version 2 NSF network data. In: Bernhard, G., Slusser, J. R., Herman, J. R., Gao, W. (eds.), *Ultraviolet Ground- and Space-based Measurements, Models, and Effects V*, SPIE, Bellingham, WA.
- Bianco, A., Fabbri, D., Minella, M., Brigante, M., Mailhot, G., Maurino, V., Minero, C., Vione, D., 2015. New insights into the environmental photochemistry of 5-chloro-2-(2,4-dichlorophenoxy)phenol (triclosan): Reconsidering the importance of indirect photoreactions. *Water Res.* 72, 271-280.

- Bodhipaksha, L. C., Sharpless, C. M., Chin, Y. P., Sander, M., Langston, W. K., Mackay, A. A., 2015. Triplet photochemistry of effluent and natural organic matter in whole water and isolates from effluent-receiving rivers. *Environ. Sci. Technol.* 49, 3453-3463.
- Bodrato, M., Vione, D., 2014. APEX (Aqueous Photochemistry of Environmentally occurring Xenobiotics): A free software tool to predict the kinetics of photochemical processes in surface waters. *Environ. Sci.: Processes Impacts* 16, 732-740.
- Boreen, A. L., Arnold, W. A., McNeill, K., 2003. Photodegradation of pharmaceuticals in the aquatic environment: A review. *Aquat. Sci.* 65, 320-341.
- Borghini, F., Grimalt, J. O., Sanchez-Hernandez, J. C., Bargagli, R., 2005. Organochlorine pollutants in soils and mosses from Victoria Land (Antarctica). *Chemosphere* 58, 271-278.
- Braslavsky, S. E., 2007. Glossary of terms used in photochemistry, 3rd edition (IUPAC Recommendations 2006). *Pure Appl. Chem.* 79, 293-465.
- Buth, J. M., Grandbois, M., Vikesland, P. J., McNeill, K., Arnold, W. A., 2009. Aquatic photochemistry of chlorinated triclosan derivatives: potential source of polychlorodibenzo-*p*-dioxins. *Environ. Toxicol. Chem.*, 28, 2555-2563.
- Buth, J. M., Steen, P. O., Sueper, C., Blumentritt, D., Vikesland, P. J., Arnold, W. A., McNeill, K., 2010. Dioxin photoproducts of triclosan and its chlorinated derivatives in sediment cores. *Environ. Sci. Technol.* 44, 4545-4551.
- Buxton, G. V., Greenstock, C. L., Helman, W. P., Ross, A. B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\bullet\text{OH}/\bullet\text{O}^-$) in aqueous solution. *J. Phys. Chem. Ref. Data* 17, 1027-1284.
- Canonica, S., Kohn, T., Mac, M., Real, F. J., Wirz, J., Von Gunten, U., 2005. Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds. *Environ. Sci. Technol.* 39, 9182-9188.
- Canonica, S., 2007. Oxidation of aquatic organic contaminants induced by excited triplet states. *Chimia* 61, 641-644.

- Cawley, K. M., Korak, J. A., Rosario-Ortiz, F. L., 2015. Quantum yields for the formation of reactive intermediates from dissolved organic matter samples from the Suwannee River. *Environ. Eng. Sci.* 32, 31-37.
- Challis, J. K., Hanson, M. L., Friesen, K. J., Wong, C. S., 2014. A critical assessment of the photodegradation of pharmaceuticals in aquatic environments: defining our current understanding and identifying knowledge gaps. *Environ. Sci.: Processes Impacts* 16, 672-696.
- Daniels, F., Alberty, R. A., 1955. *Physical Chemistry*. John Wiley and Sons, New York.
- De Laurentiis, E., Chiron, S., Kouras-Hadef, S., Richard, C., Minella, M., Maurino, V., Minero, C., Vione, D., 2012. Photochemical fate of carbamazepine in surface freshwaters: Laboratory measures and modeling. *Environ. Sci. Technol.* 46, 8164-8173.
- De Laurentiis, E., Buoso, S., Maurino, V., Minero, C., Vione, D., 2013. Optical and photochemical characterization of chromophoric dissolved organic matter from lakes in Terra Nova Bay, Antarctica. Evidence of considerable photoreactivity in an extreme environment. *Environ. Sci. Technol.* 47, 14089-14098.
- De Solla, S. R., Gilroy, E. A. M., Klinck, J. S., King, L. E., McInnis, R., Struger, J., Backus, S. M., Gillis, P. L., 2016. Bioaccumulation of pharmaceuticals and personal care products in the unionid mussel *Lasmigona costata* in a river receiving wastewater effluent. *Chemosphere* 146, 486-496.
- DellaGreca, M., Fiorentino, A., Isidori, M., Lavorgna, M., Previtera, L., Rubino, M., Temussi, F., 2004. Toxicity of prednisolone, dexamethasone and their photochemical derivatives on aquatic organisms. *Chemosphere* 54, 629-637.
- Dickhut, R. M., Cincinelli, A., Cochran, M., Kylin, H., 2012. Aerosol-mediated transport and deposition of brominated diphenyl ethers to Antarctica. *Environ. Sci. Technol.* 46, 3135-3140.

- Emnet, P., Gaw, S., Northcott, G., Storey, B., Graham, L., 2015. Personal care products and steroid hormones in the Antarctic coastal environment associated with two Antarctic research stations, McMurdo Station and Scott Base. *Environ. Res.* 136, 331-342.
- Fuoco, R., Giannarelli, S., Wei, Y., Ceccarini, A., Abete, C., Francesconi, S., Termine, M., 2009. Persistent organic pollutants (POPs) at Ross Sea (Antarctica). *Microchem. J.* 92, 44-48.
- Gligorovski, S., Streckowski, R., Barbati, S., Vione, D., 2015. Environmental implications of hydroxyl radicals ($\bullet\text{OH}$). *Chem. Rev.* 115, 13051-13092.
- Harner, T., 1997. Organochlorine contamination of the Canadian Arctic, and speculation on future trends. *Intern. J. Environ. Pollut.* 8, 51-73.
- Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., Mopper, K., 2008. Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnol. Oceanogr.* 53, 955-969.
- Isidori, M., Parrella, A., Pistillo, P., Temussi, F., 2009. Effects of ranitidine and its photoderivatives in the aquatic environment. *Environ. Int.* 35, 821-825.
- Kallenborn, R., Breivik, K., Eckhardt, S., Lunder, C. R., Mano, S., Schlabach, M., Stohl, A., 2013. Long-term monitoring of persistent organic pollutants (POPs) at the Norwegian Troll station in Dronning Maud Land, Antarctica. *Atmos. Chem. Phys.* 13, 6983-6992.
- Kepner, R. L., Wharton, R. A., Collier, R. D., Cockell, C. S., Jeffrey, W. H., 2000. UV radiation and potential biological effects beneath the perennial ice cover of an Antarctic lake. *Hydrobiologia* 427, 155-165.
- Kliegman, S., Eustis, S. N., Arnold, W. A., McNeill, K., 2013. Experimental and theoretical insights into the involvement of radicals in triclosan phototransformation. *Environ. Sci. Technol.* 47, 6756-6763.
- Latch, D. E., Packer, J. L., Stender, B. L., VanOverbeke, J., Arnold, W. A., McNeill, K., 2005. Aqueous photochemistry of triclosan: Formation of 2,4-dichlorophenol, 2,8-

- dichlorodibenzo-p-dioxin, and oligomerization products. *Environ. Toxicol. Chem.* 24, 517-525.
- Loiselle, S. A., Azza, N., Cozar, A., Bracchini, L., Tognazzi, A., Dattilo, A., Rossi, C., 2008. Variability in factors causing light attenuation in Lake Victoria. *Freshwater Biol.* 53, 535-545.
- Lores, M., Llompart, M., Sanchez-Prado, L., Garcia-Jares, C., Cela, R., 2005. Confirmation of the formation of dichlorodibenzo-p-dioxin in the photodegradation of triclosan by photo-SPME. *Anal. Bioanal. Chem.* 381, 1294-1298.
- Luo, Y. L., Guo, W. S., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., Liang, S., Wang, X. C. C., 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci. Total Environ.* 473, 619-641.
- Maddigapu, P. R., Minella, M., Vione, D., Maurino, V., Minero, C., 2011. Modeling phototransformation reactions in surface water bodies: 2,4-Dichloro-6-nitrophenol as a case study. *Environ. Sci. Technol.* 45, 209-214.
- Malandrino, M., Abollino, O., Buoso, S., Casalino, C. E., Gasparon, M., Giacomino, A., La Gioia, C., Mentasti, E., 2009. Geochemical characterisation of Antarctic soils and lacustrine sediments from Terra Nova Bay. *Microchem. J.* 92, 21-31.
- Marchetti, G., Minella, M., Maurino, V., Minero, C., Vione, D., 2013. Photochemical transformation of atrazine and formation of photointermediates under conditions relevant to sunlit surface waters: Laboratory measures and modelling. *Wat. Res.* 47, 6211-6222.
- National Center for Atmospheric Research, 2016. Quick TUV calculator [WWW Document]. URL http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/ (accessed March 2016).
- Pace, A., Barreca, S., 2013. Environmental organic photochemistry: Advances and perspectives. *Curr. Org. Chem.* 17, 3032-3041.

- Page, S. E., Logan, J. R., Cory, R. M., McNeill, K., 2014. Evidence for dissolved organic matter as the primary source and sink of photochemically produced hydroxyl radical in arctic surface waters. *Environ. Sci.: Processes Impacts* 16, 807-822.
- Richardson, S. D., Ternes, T. A., 2014. Water analysis: Emerging contaminants and current issues. *Anal. Chem.* 86, 2813-2848.
- Stubbins, A., Niggemann, J., Dittmar, T., 2012. Photo-lability of deep ocean dissolved black carbon. *Biogeosciences* 9, 1661-1670.
- Van de Velde, K., Vallelonga, P., Candelone, J. P., Rosman, K. J. R., Gaspari, V., Cozzi, G., Barbante, C., Udisti, R., Cescon, P., Boutron, C. F., 2005. Pb isotope record over one century in snow from Victoria Land, Antarctica. *Earth Planet. Sci. Lett.* 232, 95-108.
- Vecchiato, M., Argiriadis, E., Zambon, S., Barbante, C., Toscano, G., Gambaro, A., Piazza, R., 2015. Persistent Organic Pollutants (POPs) in Antarctica: Occurrence in continental and coastal surface snow. *Microchem. J.* 119, 75-82.
- Vione, D., Caringella, R., De Laurentiis, E., Pazzi, M., Minero, C., 2013. Phototransformation of the sunlight filter benzophenone-3 (2-hydroxy-4-methoxybenzophenone) under conditions relevant to surface waters. *Sci. Total Environ.* 463, 243-251.
- Vione, D., Minella, M., Maurino, V., Minero, C., 2014. Indirect photochemistry in sunlit surface waters: Photoinduced production of reactive transient species. *Chemistry Eur. J.* 20, 10590-10606.
- Yan, S. W., Song, W. H., 2014. Photo-transformation of pharmaceutically active compounds in the aqueous environment: a review. *Environ. Sci.: Processes Impacts* 16, 697-720.
- Yogui, G. T., Sericano, J., 2008. Polybrominated diphenyl ether flame retardants in lichens and mosses from King George Island, maritime Antarctica. *Chemosphere* 73, 1589-1593.
- Zepp, R. G., Cline, D. M., 1977. Rates of direct photolysis in aquatic environment. *Environ. Sci. Technol.* 11, 359-366.

Zhang, Q. H., Chen, Z. J., Li, Y. M., Wang, P., Zhu, C. F., Gao, G. J., Xiao, K., Sun, H. Z., Zheng, S. C., Liang, Y., Jiang, G. B., 2015. Occurrence of organochlorine pesticides in the environmental matrices from King George Island, west Antarctica. *Environ. Pollut.* 206, 142-149.

Table 1. Correlation study involving some of the variables of photochemical significance that characterise the investigated lakes. The cells with correlation coefficients $r > 0$ identify the couples of variables for which there is direct correlation, those with $r < 0$ highlight the anti-correlations. The statistically significant results at the 95% confidence level are shown in bold style.

	$[^3\text{CDOM}^*], \text{ mol L}^{-1}$	$\Phi_{\cdot\text{OH}}$	$\Phi_{^3\text{CDOM}^*}$	$\text{DOC}, \text{ mg C L}^{-1}$	$d, \text{ m}$
$[\cdot\text{OH}], \text{ mol L}^{-1}$	$r = -0.486$ $p = 0.329$	$r = 0.863$ $p = 0.027$	$r = -0.145$ $p = 0.784$	$r = -0.413$ $p = 0.415$	$r = 0.882$ $p = 0.020$
$[^3\text{CDOM}^*], \text{ mol L}^{-1}$		$r = -0.452$ $p = 0.368$	$r = 0.422$ $p = 0.404$	$r = 0.276$ $p = 0.596$	$r = -0.449$ $p = 0.372$
$\Phi_{\cdot\text{OH}}$			$r = -0.384$ $p = 0.452$	$r = 0.038$ $p = 0.942$	$r = 0.639$ $p = 0.172$
$\Phi_{^3\text{CDOM}^*}$				$r = -0.377$ $p = 0.462$	$r = 0.265$ $p = 0.612$
$\text{DOC}, \text{ mg C L}^{-1}$					$r = -0.539$ $p = 0.270$

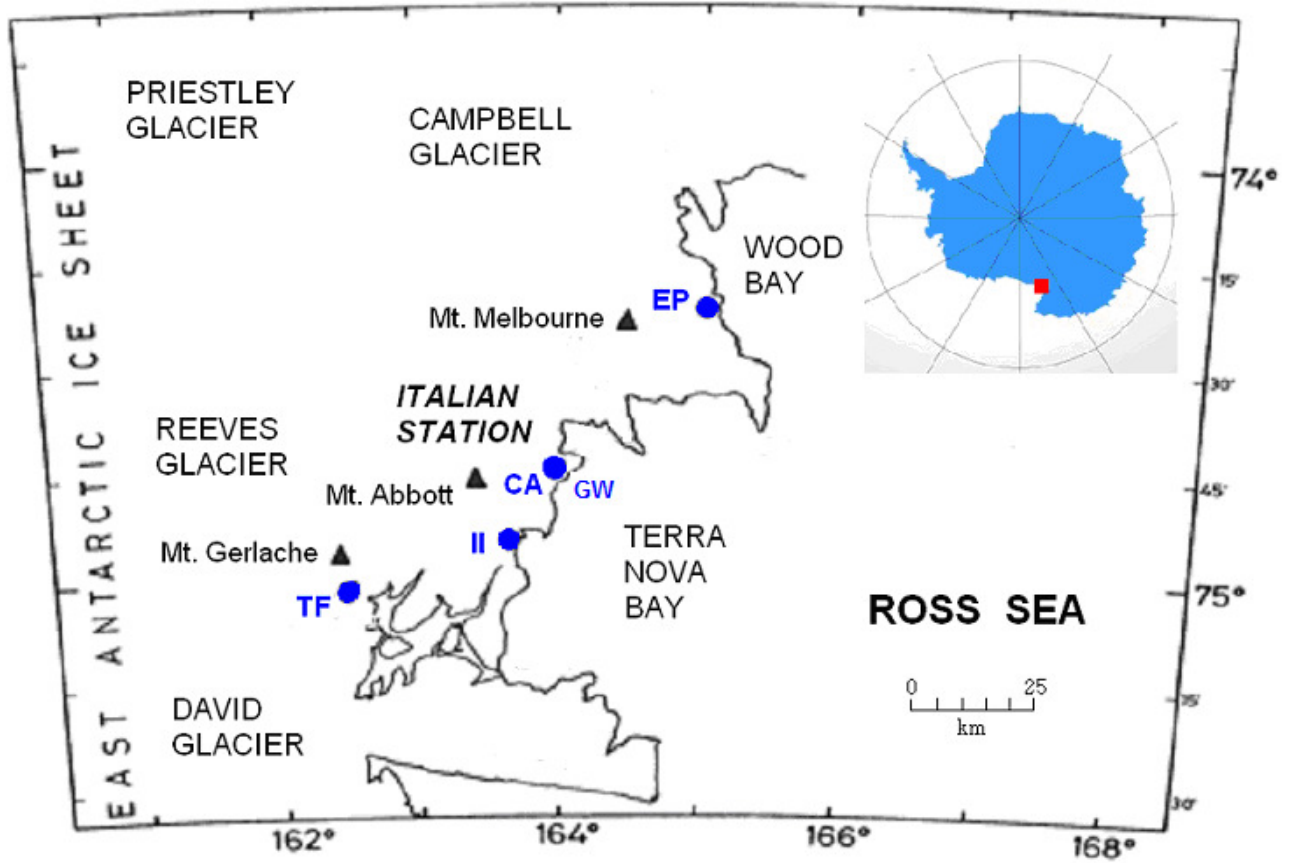


Figure 1. Map showing the location of the study lakes in Northern Victoria Land. Acronyms: EP = Edmonson Point (where lakes EP14 and EP15 are located); IL = Inexpressible Island (location of lake IL10); TF = Tarn Flat (lake TF20); CA = Carezza, and GW = Gondwana. Lakes CA and GW are very near each other.

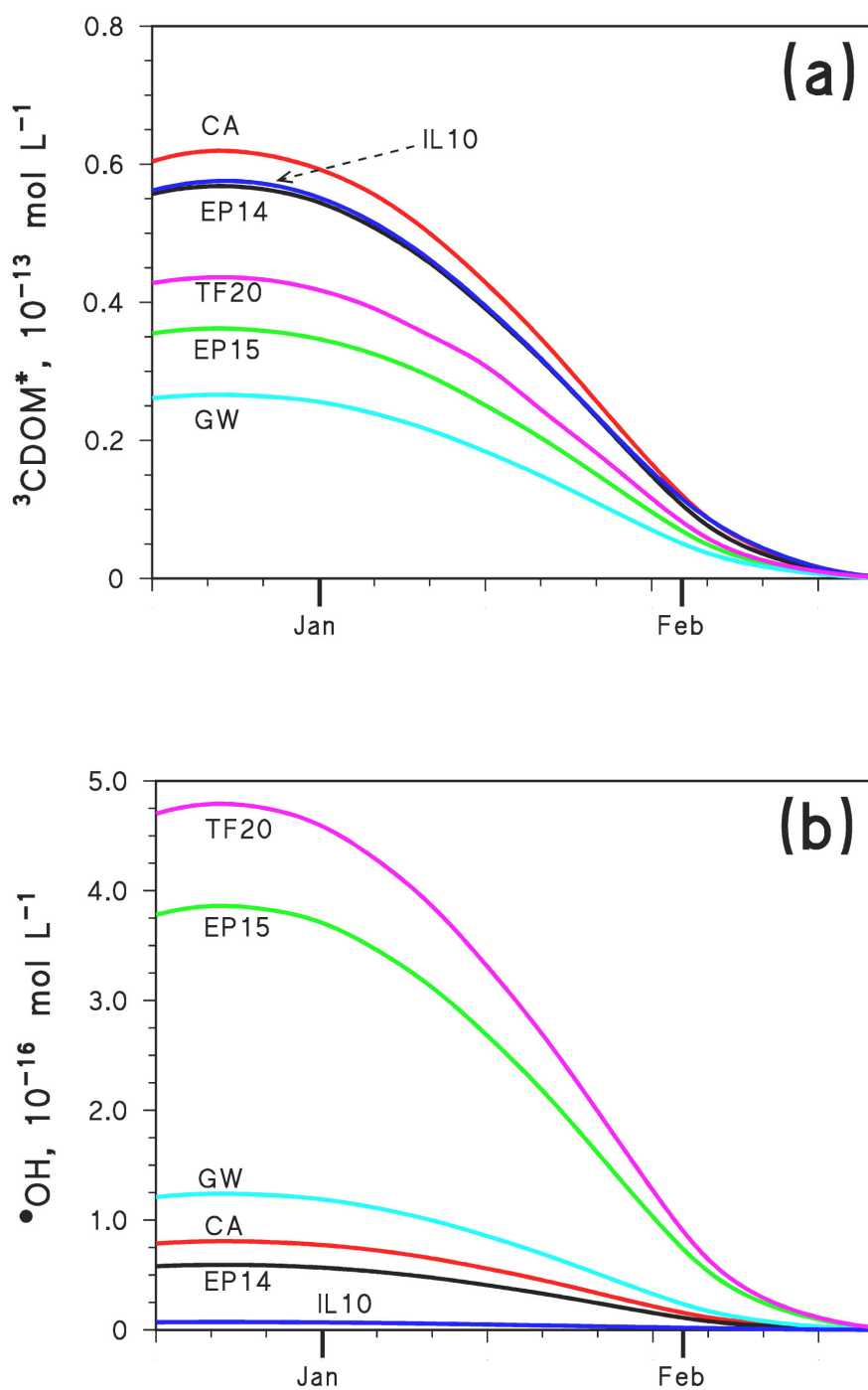


Figure 2. Modelled steady-state concentrations of ${}^3\text{CDOM}^*$ (a) and $\bullet\text{OH}$ (b) in the Terra Nova Bay lakes under study, in the ice-melting/ice-free period. The reported steady-state concentrations are average values over the whole water column, and they take into account the contributions of the well illuminated surface layer and of darker water at the bottom. They are referred to 6 pm local time and fair-weather conditions.

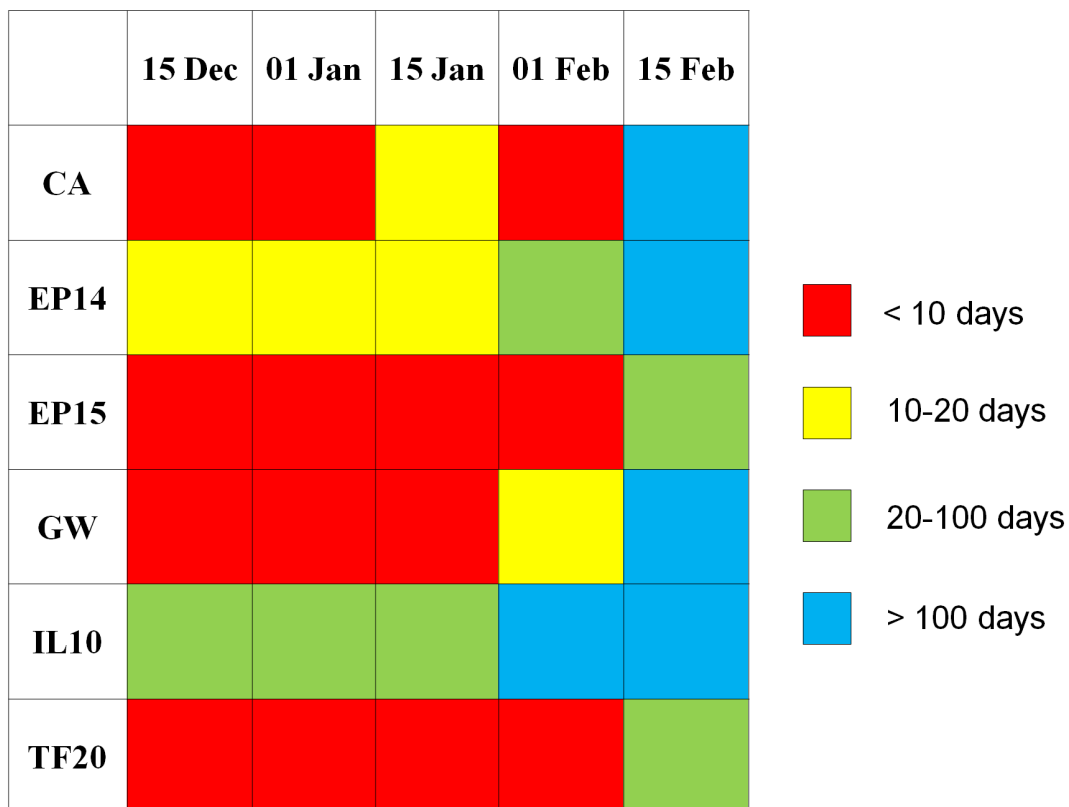


Figure 3. Modelled half-life times of BP3 upon reaction with $\bullet\text{OH}$, in the different Terra Nova Bay lakes and in different periods, under fair-weather irradiation conditions. By comparison, note that the corresponding half-life times for reaction with $^3\text{CDOM}^*$ would be always lower than 10 days, and sometimes even lower than 1 day.

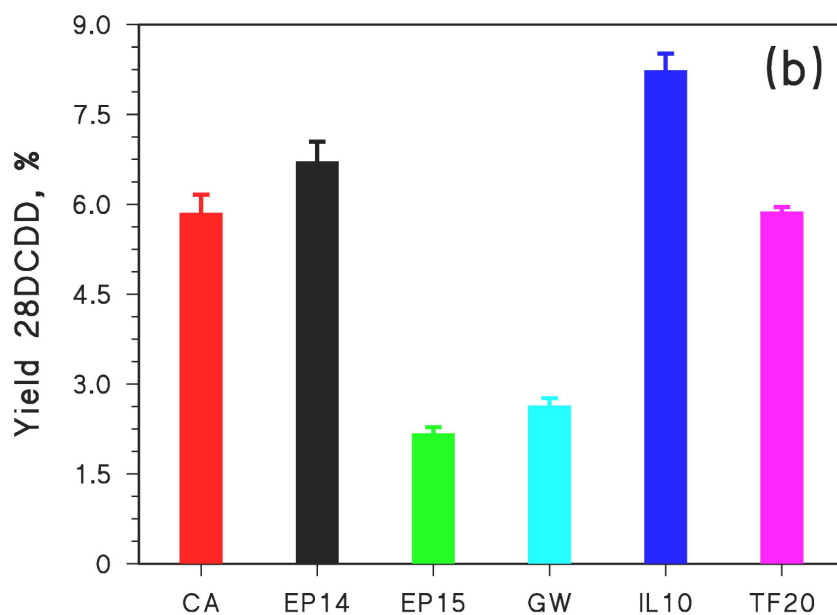
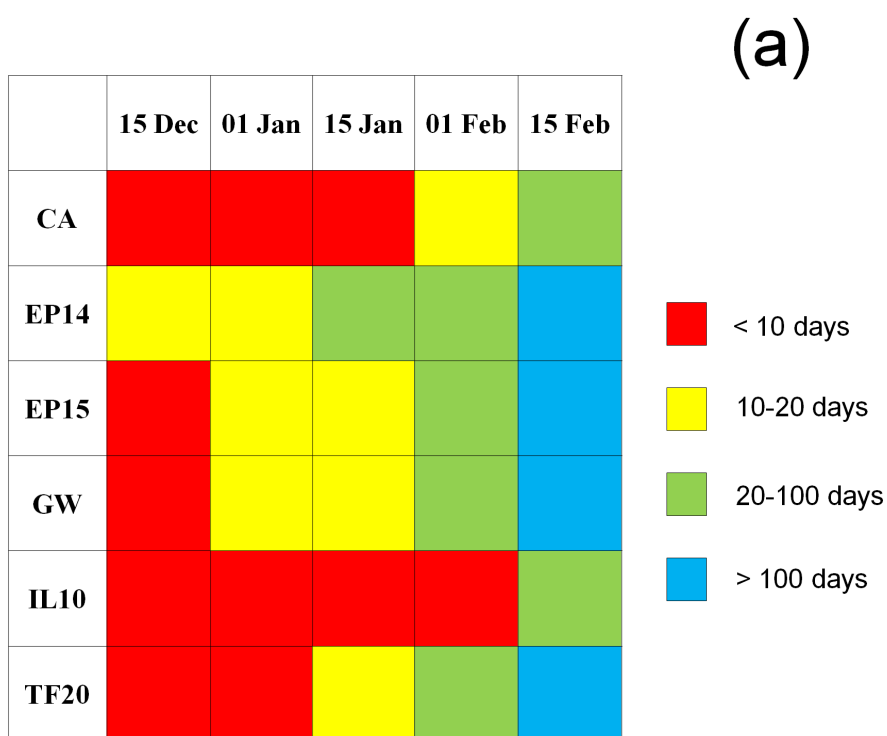


Figure 4. (a) Modelled half-life times of TRIC upon direct photolysis, in the different Terra Nova Bay lakes and in different periods, under fair-weather irradiation conditions. By comparison, note that the corresponding half-life times for reaction with $^3\text{CDOM}^*$ would be always lower than 5 days, and sometimes even lower than 1 day. (b) Modelled formation yields of 28DCDD from anionic TRIC, as average values over the period under consideration (the error bars represent the 95% confidence intervals).