Photochemical consequences of prolonged hydrological drought: A model assessment of the Lower Lakes of the Murray-Darling Basin (Southern Australia)

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Luca Carena,[a] Dario Terrenzio,[a] Luke M. Mosley,[b] Marco Toldo,[c] Marco Minella,[a] Davide Vione [a,*]

[a] *Dipartimento di Chimica, Università di Torino, Via P. Giuria 5, 10125 Torino, Italy.*

[b] *School of Biological Sciences, University of Adelaide, Adelaide, Australia.*

[c] *iMpronta48, Loc. Ciocchini 18, 12060 Novello (CN), Italy.*

* Corresponding author. Tel. +39-011-6705296; E-mail: *davide.vione@unito.it*

Abstract

The prolonged "Millennium" drought affecting Australia in the 2000s had important consequences on surface-water bodies, including the Lower Lakes (Lake Alexandrina and Lake Albert) located at the terminal end of the River Murray system. Shallower water depths, limited solute dilution and altered geochemical processes ensured that the concentration values of several water constituents increased considerably during drought, including the water parameters of photochemical significance (nitrate, bicarbonate, carbonate and the dissolved organic carbon, DOC). The aim of this study was to model the photochemical processes in the Lower Lakes during the drought and post-drought periods, to provide insight into the changes that photoinduced reactions can undergo in

periods of water scarcity. Among the photochemical processes involved in the light-assisted transformation of dissolved compounds, an important role is played by indirect photochemistry where degradation is triggered by photogenerated transient species such as hydroxyl ($^{\bullet}OH$) and carbonate ($CO_3^{\bullet-}$) radicals, and the triplet states of chromophoric dissolved organic matter ($^3CDOM^*$). Results of photochemical modelling suggest that the reactions induced by $^3CDOM^*$ would be enhanced during drought, while the processes triggered by $^{\bullet}OH$ and $CO_3^{\bullet-}$ would be less modified. For compounds undergoing efficient degradation with $^3CDOM^*$, enhanced photochemistry during drought could offset the higher concentration values resulting from lower dilution. In contrast, for compounds mainly degraded by $^{\bullet}OH$ or $CO_3^{\bullet-}$ the drought period could produce a concentration increase not balanced by an increment in the photochemical reactivity of the water body.

Keywords: Indirect photochemistry; photochemical modelling; dissolved organic matter; environmental changes; solute photodegradation; water scarcity.

Introduction

Photoinduced reactions play an important role in the degradation of both natural compounds and anthropogenic pollutants in surface waters (McNeill and Canonica, 2016; Rosario-Ortiz and Canonica, 2016; Parker et al., 2016; Bintou et al., 2015). These reactions are usually divided into direct photolysis, where a molecule absorbs sunlight and gets transformed as a consequence, and indirect photochemistry (Packer et al., 2003; Sanchez-Prado et al., 2012; Remucal, 2014; Hamdache et al., 2018). In the latter case, sunlight is absorbed by the so-called photosensitisers (such as nitrate and the chromophoric dissolved organic matter, CDOM) to produce reactive transient species involved in the degradation of dissolved compounds. In particular, nitrate and CDOM produce hydroxyl radicals ($^{\bullet}OH$) under irradiation, while some irradiated CDOM chromophores (e.g., aromatic carbonyls and quinones) can be promoted to the excited singlet and then triplet states (Vione et al., 2014). The triplet states of CDOM ($^{3}CDOM^{*}$) have enough oxidising power to be involved in the degradation of dissolved compounds (McNeill and Canonica, 2016). Moreover, $^{\bullet}OH$ can oxidise inorganic carbon species (HCO_3^- and CO_3^{2-}) to produce another transient, the carbonate radical ($CO_3^{\bullet-}$), which is also generated upon oxidation of CO_3^{2-} by $^{3}CDOM^{*}$ (Canonica et al., 2005). Direct photolysis and reactions with photogenerated $^{\bullet}OH$, $^{3}CDOM^{*}$ and $CO_3^{\bullet-}$ are among the main photoinduced processes that are responsible for the degradation of dissolved compounds in natural freshwaters (Zeng and Arnold, 2013; Challis et al., 2014; Remucal, 2014; Yan and Song, 2014).

In addition to being photogenerated, the reactive transients are also quenched/scavenged in natural-water environments. In particular, $^{\bullet}OH$ reacts with HCO_3^-, CO_3^{2-}, and most notably with the dissolved organic matter (DOM, not necessarily chromophoric), as well as with Br^- in saltwater. DOM is also the main $CO_3^{\bullet-}$ scavenger, while $^{3}CDOM^{*}$ is mostly quenched by dissolved oxygen (Vione et al., 2014). The photogeneration/consumption budget yields very low steady-state concentrations for the mentioned transient species in sunlit natural waters. Furthermore, the

mentioned processes ensure that indirect photochemical reactions are affected by water chemistry (Zhou et al., 2018). The dissolved organic carbon (DOC, which is a measure of the DOM in natural waters) is a major driver in the selection of the photoreaction pathways, because DOM scavenges $^{\bullet}OH$ and $CO_3^{\bullet-}$ while its chromophoric fraction (CDOM) is involved in the photogeneration of all transient species, in addition to being the main sunlight absorber in natural waters. As a result, the occurrence of $^{\bullet}OH$ and most notably $CO_3^{\bullet-}$ is enhanced in low-DOC waters, while high-DOC environments favour $^{3}CDOM^{*}$ (Vione et al., 2014; Koehler et al., 2018). Furthermore, high nitrate levels enhance the generation of $^{\bullet}OH$ and $CO_3^{\bullet-}$, and $CO_3^{\bullet-}$ itself occurs to a higher extent in waters that are rich in inorganic carbon (most notably, HCO_3^{-} and CO_3^{2-}) (Brezonik and Fulkerson-Brekken, 1998; Mack and Bolton, 1999; Huang and Mabury, 2000).

The occurrence of different transient species may importantly affect phototransformation, primarily because not all the dissolved compounds react fast with all the transients, and some compounds are selectively degraded by one or few of them (Fabbri et al., 2015). Furthermore, different reaction pathways involving the same molecule may produce different transformation intermediates, with peculiar toxicological and environmental effects (Marchetti et al., 2013). Water depth is also very important, because the bottom layers of deep and/or coloured waters are poorly illuminated by sunlight. Therefore, photoreactions are most efficient in shallow and clear water bodies (Vione et al., 2014).

Environmental changes that affect the chemical composition of surface waters (and especially the parameters of photochemical importance) and/or the water column depth have the potential to deeply alter the photoreaction kinetics and pathways. In this context, prolonged drought periods are among the phenomena that could most impact the photoinduced processes (Minella et al., 2013). Drought affects water availability (which is reflected in reductions of water depth), sediment transport, and water chemistry (Mosley, 2015). Unfortunately, at the moment there is very little knowledge about the implications of drought on surface-water photoreactions. Based on simple

hypotheses concerning the mechanisms of water loss (outflow vs. evaporative concentration) in an otherwise closed aquatic compartment, it has been possible to assess possible trends in phototransformation kinetics and pathways (Minella et al., 2013). However, the natural environments are very complex systems where inputs and outputs of photoactive solutes and substrates occur alongside with losses of water. Moreover, chemical and biological processes taking place inside aquatic environments may further modify the chemical composition of water, including the precursors of key photoreactions (Mosley et al., 2014; Mosley, 2015).

It is very important to understand the photoinduced transformation processes that occur in drought-affected water bodies. Periods of water scarcity are increasing worldwide and are often characterised by increased effects of pollution because of lowered dilution (Benotti and Brownawell, 2007; Osorio et al., 2014; Mosley, 2015; Karaouzas et al., 2018). In these cases, photochemical reactions may help degrade biorecalcitrant compounds. However, one should consider actual cases from real environments to see which phenomena may be more important in photodegradation. A very useful example from this point of view is the prolonged drought period affecting Australia in the 2000s, the so-called Millennium Drought (Mosley et al., 2012). While photochemical measurements have unfortunately not been carried out during drought, it has recently become possible to apply photochemical modelling to water chemistry data and obtain insight into the relevant photoinduced reactions (Minella et al., 2016). Photochemical modelling has become reliable enough to derive interesting environmental inferences from data of sunlight irradiance, water chemistry and depth (Marchetti et al., 2013; Bodrato and Vione, 2014). Extended time series of water chemistry data and water column depths, allowing for photochemical modelling, are available for the Lower Lakes of the Murray-Darling Basin, Australia's largest river system, for extreme years of the drought (2007-2010) and the post-drought recovery period (post 2010) (Mosley et al., 2012). The Lower Lakes are at end of this highly regulated arid-semi arid river system with barrages installed and operated since 1940 to prevent seawater ingress due to increased upstream diversion of water. They are designated a wetland of international importance under the

Ramsar convention, and have high environmental, cultural and socio-economic value. The goal of this work is the assessment of the possible impact of drought on photoinduced reactions in the Australian Lower Lakes.

Methods

Study area description and source data

The study area comprises two lakes, Alexandrina and Albert, collectively known as the Lower Lakes (**Figure 1**). The lakes are large (650 and 170 km^2 respectively) and shallow (mean depths of ca. 2.4 m and 1.5 m respectively) (Mosley et al. 2012). The lakes do not have significant submerged (as turbidity high) or riparian vegetation influences on water quality. This area comprises the lowest portion of the Murray-Darling Basin, which has a total catchment area of 1,061,469 km^2. The River Murray enters Lake Alexandrina from the north. The two Lower Lakes are connected via a narrow channel "the Narrung Narrows" with Lake Albert being a terminal lake. Water levels in the lakes are controlled under normal conditions using a series of barrages, gated structures that can be adjusted to regulate outflows to the estuary and Murray Mouth region.

Water quality was measured at three sites (**Figure 1**); two in Lake Alexandrina (Milang and Goolwa) and one in Lake Albert (Meningie) from 2003–2010. These sites were the long term lake monitoring sites in this region (see Mosley et al., 2012). The water quality parameters analysed were salinity/total dissolved solids (TDS), temperature, pH, turbidity, DOC, alkalinity, nutrients (total nitrogen, TN; oxidised nitrogen, NOx; total phosphorus, TP; filterable reactive phosphorus, FRP) and chlorophyll *a*. NOx, measured with the cadmium reduction method (APHA 2005), practically coincides with the concentration of nitrate in samples from shallow lakes.

Samples were taken approximately monthly by grab sampling, using polyethylene plastic bottles in accordance with standard methods (APHA 2005). Subsamples were filtered through 0.45 µm

membrane filters immediately following collection and stored in the dark at 4ºC for determination of dissolved nutrients (NOx, FRP). All analyses were undertaken at the Australian Water Quality Centre, a National Association of Testing Authorities (NATA) accredited laboratory using standard (APHA 2005) methods. For further details see Mosley et al. (2012).

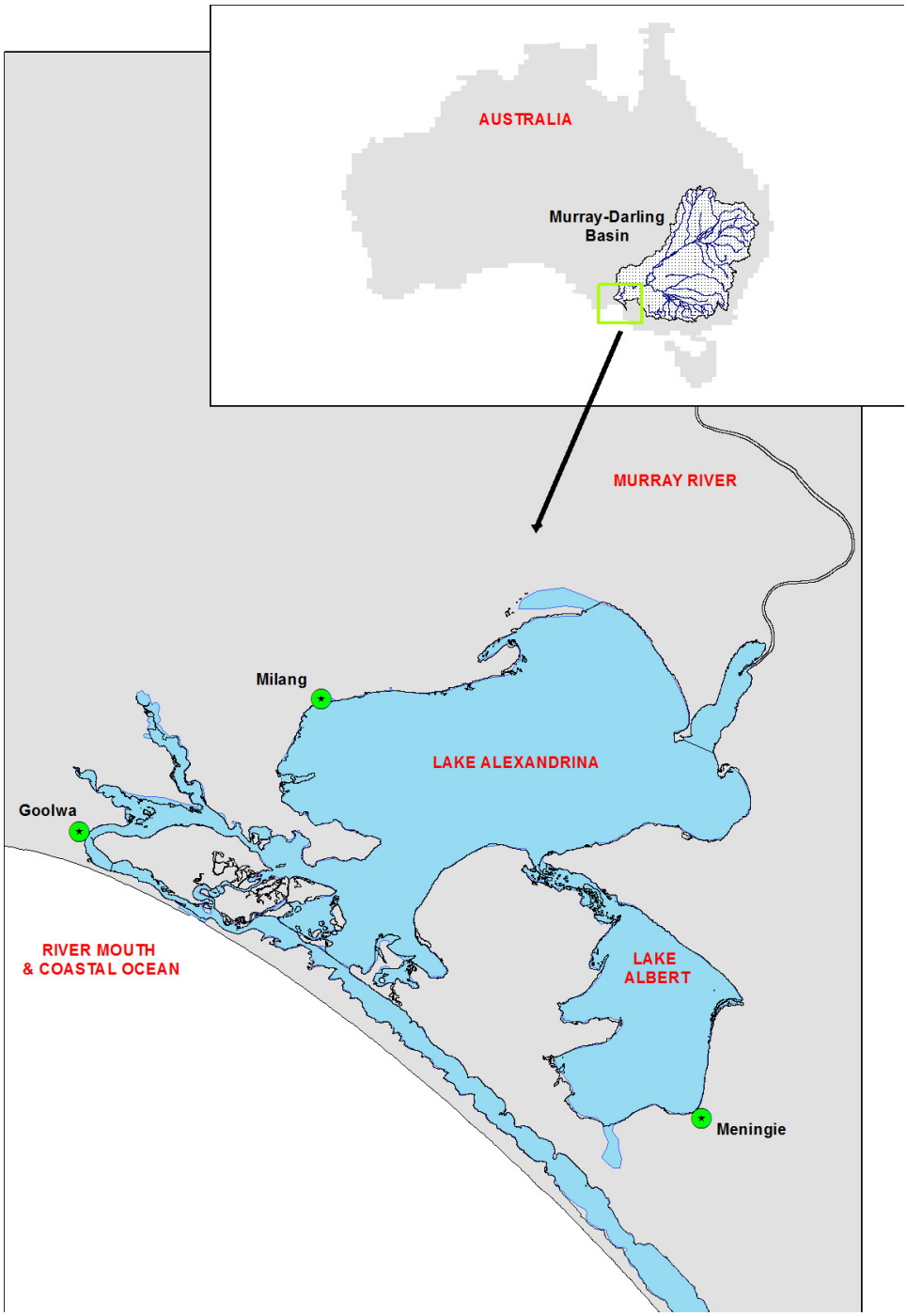

Figure 1 – Map of study area. The green dots highlight the sampling sites.

Photochemical modelling

The modelling of the steady-state concentrations of $^{\bullet}OH$, $CO_3^{\bullet-}$ and $^3CDOM^*$ used the following data: sunlight irradiance and spectrum relevant to the month of the sampling for the Lower Lakes location (35.63° S, 138.28° E; day-averaged data were derived with the *TUV Quick Calculator* software for clear-sky conditions; NCAR, 2015), water depth, as well as the concentration values of chemical constituents of photochemical significance (nitrate, DOC, bicarbonate and carbonate). The water depth values were obtained from the Department for Environment and Water (South Australia) and corrected to the Australian Height Datum (AHD) of the water surface, i.e., the water height relative to the standard seawater level (see **Figure SM1** in the Supplementary Material, hereinafter SM). The concentrations of bicarbonate and carbonate were obtained from the available data of alkalinity and pH, following the calculation procedure provided in the SM.

The DOC datum was used to derive the water absorption spectrum (i.e., the CDOM content) on the basis of known correlations, and was also used as a measure of DOM that is the main scavenger of both $^{\bullet}OH$ and $CO_3^{\bullet-}$ (Bodrato and Vione, 2014). CDOM and nitrate were considered as sources of $^{\bullet}OH$, and CDOM alone as $^3CDOM^*$ source (Vione et al., 2014). Furthermore, the formation of $CO_3^{\bullet-}$ was computed by taking into account the oxidation of HCO_3^- and CO_3^{2-} by $^{\bullet}OH$, and that of CO_3^{2-} by $^3CDOM^*$ (Canonica et al., 2005). As scavenging processes we considered the reactions of $^{\bullet}OH$ with DOM, HCO_3^- and CO_3^{2-}, as well as the consumption of $CO_3^{\bullet-}$ by DOM (Vione et al., 2014). The quenching rate constant of $^3CDOM^*$ used here (5×10^5 s^{-1}) is relevant to air-equilibrated waters because it largely represents the interaction between $^3CDOM^*$ and dissolved O_2 (Canonica and Freiburghaus, 2001). The absorption of sunlight by CDOM and nitrate was calculated by considering that CDOM is the main radiation absorber in natural waters below 500 nm (Loiselle et al., 2008), and by assuming competition for irradiance between the two species with a Lambert-Beer approach (Braslavsky, 2007). While a modelling software based on this computation approach is freely available (APEX: Aqueous Photochemistry of Environmentally-occurring Xenobiotics;

Bodrato and Vione, 2014), APEX has no procedure for reading spreadsheet files and is thus hardly suited to the present task. Suitable software based on the same computation engine was developed by one of us (MT) and used in the present framework, but it is not yet available for public use.

The model calculations, carried out according to the general procedure described above (details are reported as SM), yielded the steady-state concentrations [$^{\bullet}OH$], [$CO_3^{\bullet-}$], and [$^3CDOM^*$]. These data are daily averages referred to the month of the sampling, under the assumption of cloudless sky and perfect mixing of the water column (absence of water stratification). The steady-state concentrations thus obtained can be used to predict the phototransformation kinetics of compounds that are transformed by reaction with $^{\bullet}OH$, $CO_3^{\bullet-}$ and $^3CDOM^*$ (Bodrato and Vione, 2014). The tripeptide glutathione (hereinafter GSH) was chosen to this purpose, because it does not undergo direct photolysis and because its main known photodegradation pathways involve the three transient species examined here (Chu et al., 2017; Vione, 2018). The reaction between GSH and each transient is a second-order process, but the transients have steady-state concentrations unaffected by reaction with GSH. Like all individual solutes in the vast majority of cases, GSH is actually a negligible scavenger of $^{\bullet}OH$, $CO_3^{\bullet-}$, and $^3CDOM^*$ in natural-water conditions because of its much lower concentration in comparison with the naturally occurring scavengers (i.e., DOM for $^{\bullet}OH$ and $CO_3^{\bullet-}$, O_2 for $^3CDOM^*$). GSH degradation can thus be described by a (pseudo) first-order kinetic model, where the overall degradation rate constant (k_{GSH}) is the sum of the contributions of the processes triggered by $^{\bullet}OH$, $CO_3^{\bullet-}$ and $^3CDOM^*$:

$$k_{GSH} = k_{GSH,^{\bullet}OH}[^{\bullet}OH] + k_{GSH,CO_3^{\bullet-}}[CO_3^{\bullet-}] + k_{GSH,^3CDOM^*}[^3CDOM^*] \quad (1)$$

The second-order reaction rate constants used in **Eq. (1)** are $k_{GSH,^{\bullet}OH}$ = 3.5 ×10^9 L mol^{-1} s^{-1}, $k_{GSH,CO_3^{\bullet-}}$ = 5.3 ×10^6 L mol^{-1} s^{-1}, and $k_{GSH,^3CDOM^*}$ = 8 ×10^7 L mol^{-1} s^{-1} (Buxton et al., 1988; Neta et al., 1988; Chu et al., 2017; Vione, 2018).

Results and Discussion

The extreme drought period (2007-2010) in the Lower Lakes had profound effects on water quality with significant increases in salinity, total nitrogen, nitrate, total phosphorus and chlorophyll *a* (Mosley et al. 2012). The post-drought flooding period resulted in input of water rich in dissolved organic carbon derived from rewetting of floodplains and microbial breakdown of organic material (Biswas and Mosley, 2019). These changes provided an ideal opportunity to model photochemical process variations.

Drought and post-drought evolution of photochemically significant parameters

Generally speaking, the concentration values of several parameters of photochemical significance were higher during the drought period in all the sampling stations under study. However, while a simple "less water - more concentrated solutes" relationship may partially explain some of the observed trends (Mosley et al. 2012), in some instances the variations were somewhat different than expected from mere water depth changes. In the case of the Goolwa channel, the maximum concentrations reached by HCO_3^-, NO_3^- and DOC during drought were about twice higher than the corresponding post-drought values (see **Figure 2** for the DOC trend and **Figure SM2** in the SM for all the other parameters). Considering that water depth was halved during drought, increasing concentrations can be explained by a lower degree of solute dilution. For the Milang station (Lake Alexandrina), which also experienced a drought-related halving of the water depth, the concentration values of HCO_3^- and NO_3^- were actually three times higher during drought (see **Figure SM3** in the SM). In this case the water volume reduction only partially explains the concentration difference.

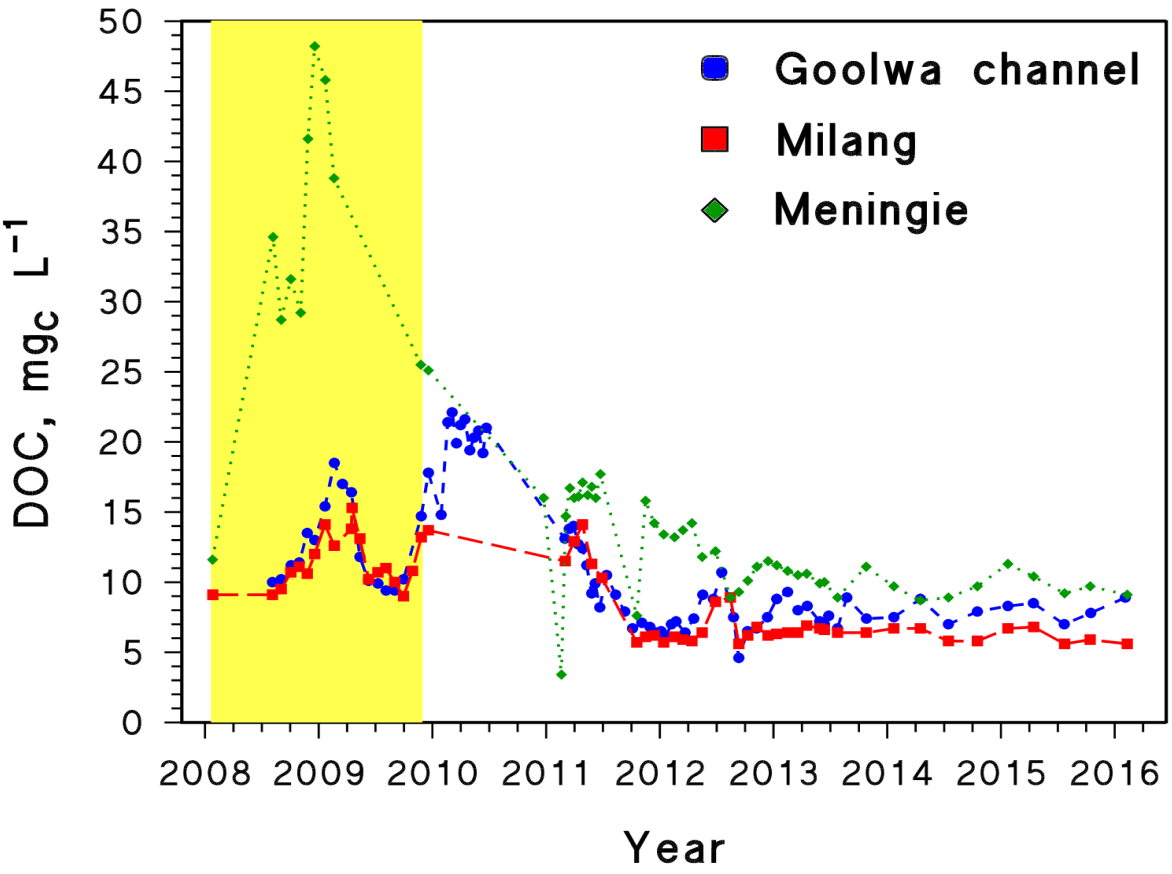

Figure 2 – Time trends of the dissolved organic carbon in the three sampling stations under study (Goolwa channel, Milang, Meningie). The yellow band refers to the extreme drought period (March 2007 – November 2009) as reported in Mosley et al. (2012).

The shallower water during drought resulted in more resuspension (Mosley et al. 2012) that could have caused mobilisation of dissolved nutrients from the sediment or lessened algal uptake. It is interesting to observe that the nitrate concentrations, although highest during drought, never reached really elevated values (they were typically in the 10^{-4} mol L^{-1} range).

Finally, in the case of Lake Albert (Meningie station), the lowest water depth values observed during drought were a factor ~3 lower compared to the post-drought period. While the concentration values of NO_3^- varied accordingly, the DOC during drought was sometimes higher by a factor of 4-5 compared to the post-drought period (**Figure 2**). In contrast, the concentration of HCO_3^- varied very little (see **Figure SM4** in the SM). Higher productivity during drought, which is testified by increased levels of chlorophyll *a* (Mosley et al., 2012), results in increased algal biomass and higher release of water-soluble compounds upon cell lysis (Wetzel, 2001). This could contribute to the DOC enhancement beyond the level expected by lower dilution. The limited variations in HCO_3^- between drought and post-drought periods at Meningie are not dissimilar from observations reported for other environments (Mosley, 2015). This finding is likely accounted for by the terminal Lake Albert system reaching and maintaining saturation with calcium carbonate, which could offset the lower degree of dilution. In support of this, in all the three stations the pH values did not undergo important variations between drought and post-drought (**Figures SM2-4** in the SM). For this reason, the relevant CO_3^{2-} trends did not differ much from those of HCO_3^-. Large pH variations in the Lower Lakes have been reported only in the case of seawater intrusion or oxidation of sulphides in exposed sediments (Mosley et al., 2014).

Expected effects on lake-water photochemistry

The drought and post-drought trends of water depth, NO_3^-, DOC, HCO_3^- and CO_3^{2-} have variable impacts on the lake-water potential to produce photogenerated transients. Moreover, one should

also consider the related seasonal variations in sunlight irradiance (highest in spring/summer and lowest in autumn/winter), which produce comparably oscillating trends in the transient concentrations (Minella et al., 2016). All these factors are taken into account in photochemical modelling, to see which trends can be expected for the steady-state concentrations of $^{\bullet}OH$, $CO_3^{\bullet-}$ and $^3CDOM^*$ that are involved into the photodegradation of natural and anthropogenic compounds.

The time trends of the modelled [$^{\bullet}OH$], [$CO_3^{\bullet-}$] and [$^3CDOM^*$] in the three stations under study for the period 2008-2016, which encompasses the 2008-2010 drought, are reported for Goolwa channel (**Figure 3a**), Milang - Lake Alexandrina (**Figure 3b**) and Meningie - Lake Albert (**Figure 3c**).

Higher [$CO_3^{\bullet-}$] during drought was observed at Milang representing the main lake water body of Lake Alexandrina (**Figure 3b**), and lower [$CO_3^{\bullet-}$] during drought was observed in Lake Albert (**Figure 3c**). In contrast, the limited differences in [$CO_3^{\bullet-}$] at Goolwa might be accounted for by the parallel decrease of both DOC ($^{\bullet}OH$ and $CO_3^{\bullet-}$ scavenger) and nitrate (direct $^{\bullet}OH$ and indirect $CO_3^{\bullet-}$ source) in the post-drought recovery period (**Fig. 2 and SM2**). Indeed, higher nitrate during drought enhanced the formation rates of both $^{\bullet}OH$ and $CO_3^{\bullet-}$, which was offset by higher DOM levels that consume both radical species. When the water depth increased after drought, the dilution decreased the concentrations of both $^{\bullet}OH/CO_3^{\bullet-}$ sources and scavengers, resulting in almost unchanged $^{\bullet}OH$ and $CO_3^{\bullet-}$ steady-state concentrations. However, in the Meningie sampling station (Lake Albert), [$^{\bullet}OH$] and [$CO_3^{\bullet-}$] peaked just after the drought (summer 2011, **Figure 3c**), when a DOC minimum occurred (**Fig. 2**). This DOC minimum is the lowest value recorded in all three water bodies and is connected with the highest levels of both $^{\bullet}OH$ and $CO_3^{\bullet-}$.

The modelled trends of [$^3CDOM^*$] in the three stations show the highest values during drought and a decrease in the post-drought period (**Figure 3**). The rationale of this consistent finding in the model results is linked to the fact that the contents of dissolved organic matter (measured as the DOC and representing the photochemical $^3CDOM^*$ source) were highest in all the stations during drought (see **Figure 2**).

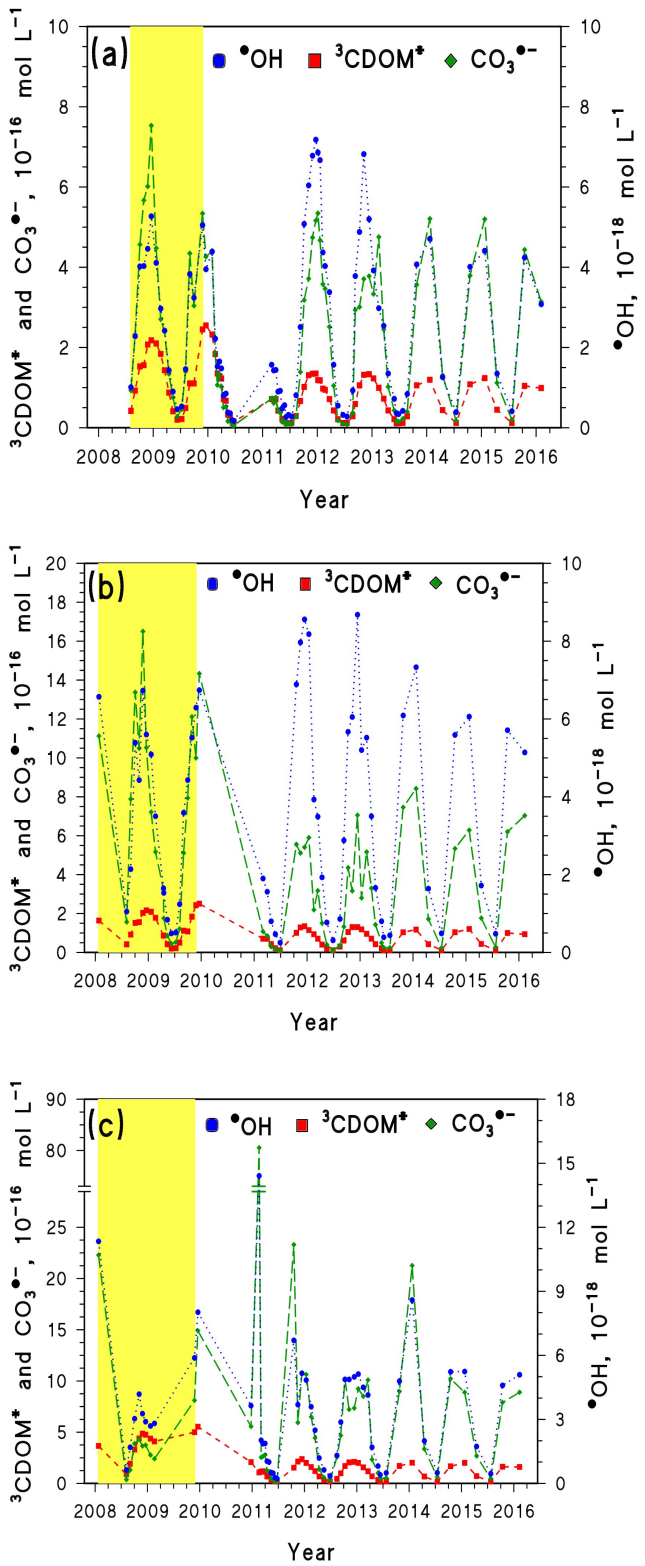

Figure 3 – Model-predicted steady-state concentrations of $^{\bullet}OH$, $CO_3^{\bullet-}$ and $^3CDOM^*$ in: **(a)** Goolwa channel; **(b)** Milang sampling station (Lake Alexandrina), and **(c)** Meningie sampling station (Lake Albert). Water chemistry and depth data refer to the sampling time, and so does the fair-weather sunlight irradiance and spectrum (35.63° S; 138.28° E, 9.00 a.m.) used in model calculations. The yellow band refers to the extreme drought period (up to November 2009) as reported in Mosley et al. (2012).

Increases in organic carbon concentrations in lakes and rivers have been observed globally during droughts (Mosley, 2015), thus the related [^{3}CDOM*] increase might be a key photochemical change that occurs across different systems.

It is interesting to assess what are the possible implications of the reported trends for the photochemical fate of dissolved compounds. The naturally occurring tripeptide glutathione (GSH) is a convenient model molecule to this purpose. GSH is produced by microorganisms for different purposes (detoxification, redox processes, antioxidant action), and it occurs in the photic zone of natural waters upon release in the extracellular environment. Its environmental fate involves both consumption by microorganisms, and photochemical degradation (Chu et al., 2017).

A comparison between experimentally published reaction pathways of GSH photodegradation by irradiated humic substances and photochemical model predictions is provided in the SM, **Figure SM5**. The comparison shows good agreement between the experimental (Chu et al., 2017) and modelled (Vione et al., 2018) roles of $^{\bullet}$OH in GSH degradation. The experimental work did not single out the ^{3}CDOM* process among the phototransformation pathways (Chu et al., 2017), but the absence of direct photolysis, the lack of inorganic carbon in the experiments and the presence of humic substances as photosensitisers strongly suggests that triplet sensitisation could play a key role (Vione et al., 2018). With this assumption, the agreement between experiments and predictions becomes very good.

The pseudo-first order photodegradation rate constants of GSH were here assessed based on the model results for [$^{\bullet}$OH], [$CO_3^{\bullet-}$] and [^{3}CDOM*] (**Eq. 1**), by which one obtains the GSH rate constants accounted for by the three different transient species, as well as the overall rate constant of photodegradation. We used the $^{\bullet}$OH, $CO_3^{\bullet-}$ and ^{3}CDOM* steady-state concentrations obtained for January 2009 (austral summer) to describe the worst drought phase for the three water bodies. In all the cases we took as post-drought conditions an average of the relevant austral summertime concentrations from 2010 onwards. The calculation results are shown in **Figure 4**.

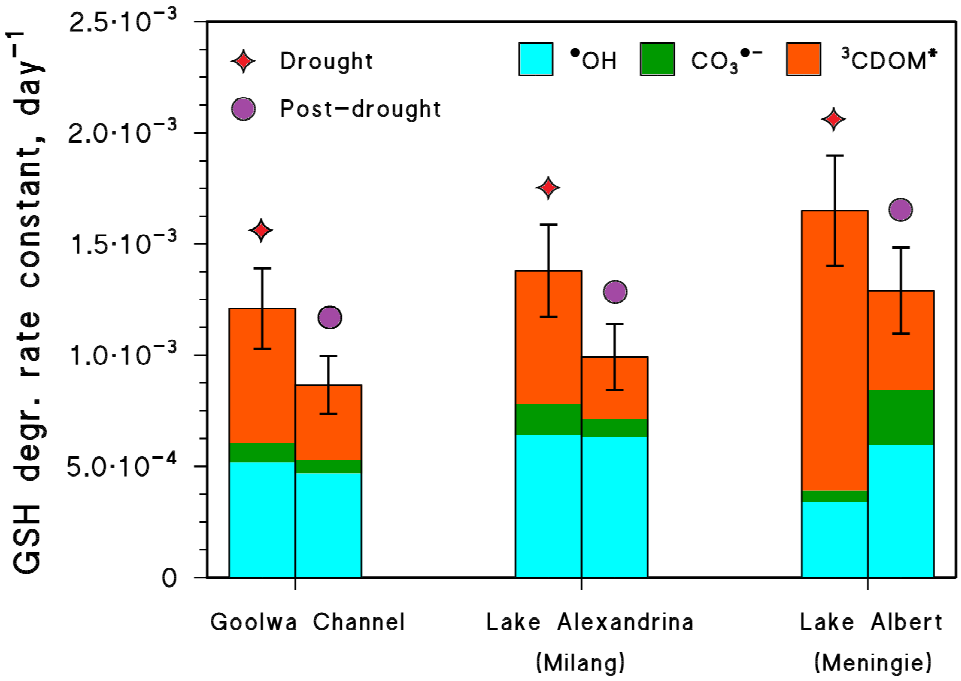

Figure 4 – Predicted first-order degradation rate constants of the tripeptide glutathione (GSH), accounted for by reactions with $^{\bullet}$OH, $CO_3^{\bullet-}$ and ^{3}CDOM*, at the three sampling sites (Goolwa, Milang, Meningie) for extreme drought and average post-drought conditions. The kinetics is relevant to fair-weather, summertime sunlight conditions. The error bars represent the sigma-level uncertainties of model predictions. The different values of [$^{\bullet}$OH], [$CO_3^{\bullet-}$] and [^{3}CDOM*] are reported in **Table 1**.

Table 1. Modelled steady-state concentration values of [$^{\bullet}$OH], [$CO_3^{\bullet-}$] and [^{3}CDOM*] in the three sites under study, used to describe the worst drought phase as well as the post-drought recovery.

	[$^{\bullet}$OH], mol L^{-1}	**[$CO_3^{\bullet-}$], mol L^{-1}**	**[^{3}CDOM*], mol L^{-1}**
Goolwa, drought	4.1×10^{-18}	4.5×10^{-16}	2.1×10^{-16}
Goolwa, post drought	3.7×10^{-18}	3.3×10^{-16}	1.2×10^{-16}
Milang, drought	5.1×10^{-18}	7.2×10^{-16}	2.1×10^{-16}
Milang, post drought	5.0×10^{-18}	4.3×10^{-16}	9.7×10^{-17}
Meningie, drought	2.7×10^{-18}	2.8×10^{-16}	4.4×10^{-16}
Meningie, post drought	4.7×10^{-18}	1.3×10^{-15}	1.6×10^{-16}

Overall, the GSH degradation rate constants decreased when passing from drought to post-drought conditions, which can be largely attributed to the decrease of the ^{3}CDOM* steady-state concentration (see **Table 1** and **Figure SM6**). However, the decrease would be more important in the sites of Goolwa channel and Lake Alexandrina (Milang) than in Lake Albert (Meningie). This prediction could be linked to the water quality recovery timescales (>5 years) for Lake Albert being much longer due to the terminal nature of the lake and its narrow connection with Lake Alexandrina. In contrast, water quality in Lake Alexandrina recovered quickly (<1 year).

Looking at the role of the reactive transient species in the GSH photodegradation, it can be observed that in Goolwa and Milang the decreasing ^{3}CDOM* role is the only important difference between drought and post-drought (**Figure 4**). In contrast, in the case of Lake Albert the decrease in the GSH photodegradation rate by ^{3}CDOM* is partially offset by enhanced $^{\bullet}$OH and $CO_3^{\bullet-}$ phototransformation pathways. This result can be accounted for by the very high (compared to Goolwa channel and Lake Alexandrina, and also in general; Wetzel, 2001) DOC levels in Lake Albert, especially during drought (DOC = 40-50 $mg_C\ L^{-1}$), combined with a considerable decrease in the post-drought period (down to DOC = 10-15 $mg_C\ L^{-1}$; see **Fig. 2**). In these conditions (DOC > 10 $mg_C\ L^{-1}$) the steady-state [$^{\bullet}$OH] and [$CO_3^{\bullet-}$] are dominated by DOM scavenging, and they are inversely proportional to the DOC (Vione et al., 2014; Koehler et al., 2018). In contrast, in both Goolwa channel and Lake Alexandrina the DOC levels were generally lower and they did not undergo a comparably important decrease between the drought and post-drought periods.

It should be underlined that the present results were obtained under the assumption of complete water mixing. This hypothesis is very reasonable in the context of observed monitoring data and the shallow and exposed nature of the Lower Lakes, but it is also interesting to have some insight into the possible photochemical consequences of water stratification. In a stratified lake, the sunlit epilimnion hosts higher photoreactivity than the dark hypolimnion. Therefore, the photodegradation of compounds that mainly reach the lake-water surface is enhanced by stratification, because they

are confined in the photoreactive epilimnion. In contrast, compounds reaching the lake bottom via groundwater remain in the hypolimnion during stratification conditions, and their photodegradation is inhibited as a consequence. Finally, the photodegradation of compounds that are initially distributed evenly in the water column is inhibited by stratification to a variable extent, depending on their photolability. In particular, highly photolabile compounds tend to be totally degraded in the epilimnion, at which point their further photodegradation has to stop. On the other hand, the compound fraction occurring in the hypolimnion is poorly photodegraded, and the outcome is inhibition of phototransformation compared to a well-mixed system. The same effect is much less important for photostable molecules, which are unlikely to be totally photodegraded in the epilimnion during the stratification phase (Vione and Scozzaro, in press).

Implications for drought-affected environments

It is interesting to observe that variable and different conditions, even in nearby environments, might lead to important differences in behaviour as far as the photodegradation processes are concerned. The 2008-2010 drought had an important impact on the water chemistry and depth in the Australian Lower Lakes. From a photochemical point of view, the occurrence of shallower water and the concentration maxima of nitrate and DOC during drought would be most significant. A parallel increase in both nitrate and DOC might potentially produce approximately constant values of [$^{\bullet}OH$] and [$CO_3^{\bullet-}$] (following an increase in both their sources and scavengers) as well as an increase in [$^3CDOM^*$], which is for instance the expected outcome of evaporative water concentration (Minella et al., 2013).

However, the overall trends caused by, e.g., variable water dilution overlap with additional processes that produce short-term variations, and seasonal sunlight irradiance also plays an important role. For instance, in the case of Lake Albert the high peaks of the modelled [$^{\bullet}OH$] and

[$CO_3^{\bullet-}$] during the 2011 summer were the combination of low DOC values, relatively elevated nitrate and (for $CO_3^{\bullet-}$) high inorganic carbon, as well as intense irradiance. Interestingly, if similar phenomena take place during winter, their photochemical effects may be considerably weakened by low irradiance. As far as ^{3}CDOM* is concerned, the high levels that are consistently predicted for all the stations during the drought period are the direct consequence of high DOC concentrations and shallow water.

On these bases one can make some tentative inferences for drought-affected environments, and particularly for the cases where a limited degree of dilution produces high concentration values of the chemical parameters. Elevated DOC is generally favourable to the ^{3}CDOM* processes. Moreover, a further increase in [^{3}CDOM*] beyond the levels predicted in this work may take place if the concentration of dissolved O_2 decreases during drought. Actually, low O_2 leads to slower ^{3}CDOM* quenching (not taken into account in this work) and, as a consequence, to higher [^{3}CDOM*]. The evolution of [$^{\bullet}$OH] and [$CO_3^{\bullet-}$] is much less straightforward, however. A wider range of environmental cases and direct photochemistry measurements will be needed to understand which trends are more typical for [$^{\bullet}$OH] and [$CO_3^{\bullet-}$] during droughts.

Conclusions

The prolonged drought period that affected Australia in the 2000s decade had important consequences on both the depth and chemical composition of water in the Lower Lakes. In particular, a lower degree of solute dilution together with additional processes ensured that the concentration values of several components (and especially of the photochemically significant parameters DOC and nitrate) were higher during drought compared to the post-drought years. Higher DOC levels during drought would favour the ^{3}CDOM* reactions, enhancing the

transformation of ^{3}CDOM*-reactive compounds and partially compensating for low dilution. Actually, the pollution of water environments may increase during drought because human emissions occur within lower water volumes and flushing (Mosley 2015). Examples of pollutants that are mainly degraded by reaction with ^{3}CDOM* are phenylurea herbicides, some sulphonamide antibiotics and several phenolic compounds (Canonica, 2007).

The corresponding drought *vs.* post-drought trends of $^{\bullet}OH$ and $CO_3^{\bullet-}$ were not consistent in all the stations, with Milang showing drought-related $CO_3^{\bullet-}$ peaks and Meningie featuring the opposite behaviour. These inconsistent findings might be caused by the post-drought lowering of both the $^{\bullet}OH/CO_3^{\bullet-}$ sources and scavengers. Overall, compared to the simplified model approaches available in the literature to describe drought photochemistry (Minella et al., 2013), the combination of enhanced ^{3}CDOM* and little modified $^{\bullet}OH$ and $CO_3^{\bullet-}$ makes the Lower Lakes system approximate an evaporative concentration scenario which is consistent with the findings of Mosley et al. (2012).

Although photochemical degradation is a phenomenon that has potential to at least partially offset some environmental consequences of water scarcity, and which could for instance be enhanced by shallower water columns, favourable effects might not take place in all environments and for all involved compounds. A case-by-case assessment is presently needed to better understand the link between variations in environmental factors and photoreaction kinetics. At the present state of knowledge, it is possible to tentatively figure out that drought conditions with the associated (at least partial) evaporative concentration might enhance the ^{3}CDOM* processes as shown in this work. On the other hand, processes induced by $^{\bullet}OH$ and $CO_3^{\bullet-}$ might show specific dependencies on the particular environmental conditions.

A limit of the approach used here is that the formation quantum yields of $^{\bullet}OH$ and ^{3}CDOM* by irradiated CDOM and the scavenging rate constants of $^{\bullet}OH$ and $CO_3^{\bullet-}$ by DOM were assumed to be the same during both the drought and the post-drought periods (see the calculation procedure in the SM). At the moment there are no indications of possible drought-induced variations of these

parameters, but they may be linked to changes in the nature of CDOM (Maizel et al., 2017). Additional research is needed to understand if and to what extent the photoreactivity of CDOM and the scavenging ability of DOM may be affected by water-scarcity conditions.

References

Benotti, M. J., Brownawell, B. J., 2007. Distributions of pharmaceuticals in an urban estuary during both dry- and wet-weather conditions. Environ. Sci. Technol. 41, 5795−5802.

Bintou, A. T., Bianco, A., Mailhot, G., Brigante, M., 2015. A new insight into ethoxyquin fate in surface waters: Stability, direct and indirect photochemical behaviour and the identification of main products. J. Photochem. Photobiol. A: Chem. 311, 118-126.

Biswas, T. K., Mosley, L. M., 2019. From mountain ranges to sweeping plains, in droughts and flooding rains; River Murray water quality over the last four decades. Water Resour. Manag. 33(3), 1087-1101.

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.

Braslavsky, S. E., 2007. Glossary of terms used in photochemistry. third edition. Pure Appl. Chem. 79, 293-465.

Brezonik, P. L., Fulkerson-Brekken, J., 1998. Nitrate-induced photolysis in natural waters: Controls on concentrations of hydroxyl radical photo-intermediates by natural scavenging agents. Environ. Sci. Technol. 32, 3004-3010.

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 ($^{\bullet}OH/O^{-\bullet}$) in aqueous solution. J. Phys. Chem. Ref. Data 17, 513-886.

Canonica, S., Freiburghaus, M., 2001. Electron-rich phenols for probing the photochemical reactivity of freshwaters. Environ. Sci. Technol. 35, 690-695.

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.

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.

Chu, C., Stamatelatos, D., McNeill., K., 2017. Aquatic indirect photochemical transformations of natural peptidic thiols: impact of thiol properties, solution pH, solution salinity and metal ions. Environ. Sci.: Processes Impacts 19, 1518-1527.

Fabbri, D., Minella, M., Maurino, V., Minero, C., Vione, D., 2015. Photochemical transformation of phenylurea herbicides in surface waters: A model assessment of persistence, and implications for the possible generation of hazardous intermediates. Chemosphere 119, 601-607.

Hamdache, S., Sleiman, M., de Sainte-Claire, P., Jaber, F., Richard, C., 2018. Unravelling the reactivity of bifenazate in water and on vegetables: Kinetics and byproducts. Sci. Total Environ. 636, 107-114.

Huang, J. P., Mabury, S. A., 2000. Steady-state concentrations of carbonate radicals in field waters. Environ. Toxicol. Chem. 19, 2181-2188.

Karaouzas, I., Theodoropoulos, C., Vardakas, L., Kalogianni, E., Skoulikidis, N. Th., 2018. A review of the effects of pollution and water scarcity on the stream biota of an intermittent Mediterranean basin. River Res. Appl. 34, 291-299.

Koehler, B., Barsotti, F., Minella, M., Landelius, T., Minero, C., Tranvik, L. J., Vione, D., 2018. Simulation of photoreactive transients and of photochemical transformation of organic pollutants in sunlit boreal lakes across 14 degrees of latitude: a photochemical mapping of Sweden. Water Res. 129, 94-104.

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.

Mack, J., Bolton, J. R., 1999. Photochemistry of nitrite and nitrate in aqueous solution: A review. J. Photochem. Photobiol. Chem. 128, 1-13.

Maizel, A. C., Li, J., Remucal C. K., 2017. Relationships between dissolved organic matter composition and photochemistry in lakes of diverse trophic status. Environ. Sci. Technol. 51, 9624-9632.

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. Water Res. 47, 6211-6222.

McNeill, K., Canonica, S., 2016. Triplet state dissolved organic matter in aquatic photochemistry: Reaction mechanisms, substrate scope, and photophysical properties. Environ. Sci.: Processes Impacts 18, 1381-1399.

Minella, M., Maurino, V., Minero, C., Vione, D., 2013. Modelling photochemical transformation of emerging organic pollutants in surface waters: effect of water level fluctuations following outflow or evaporation, relevant to arid and semi-arid environments. Intern. J. Environ. Anal. Chem. 93, 1698-1717.

Minella, M., Leoni, B., Salmaso, N., Savoye, L., Sommaruga, R., Vione, D., 2016. Long-term trends of chemical and modelled photochemical parameters in four Alpine lakes. Sci. Total Environ. 541, 247-256.

Mosley, L. M., Zammit, B., Leyden, E., Heneker, T. M., Hipsey, M. R., Skinner, D., Aldridge, K. T., 2012. The impact of extreme low flows on the water quality of the Lower Murray River and Lakes (South Australia). Water Res. Manag. 26, 3923-3946.

Mosley, L. M., Zammit, B., Jolley, A., Barnett, L., 2014. Acidification of lake water due to drought. J. Hydrol. 511, 484-493.

Mosley, L. M., 2015. Drought impacts on the water quality of freshwater systems; review and integration. Earth Sci. Rev. 140, 203-214.

NCAR (National Center for Atmospheric Research), 2015. Quick TUV calculator [WWW Document]. URL http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/ (accessed in November 2018).

Neta, P., Huie, R. E., Ross, A. B., 1988. Rate constants for reactions of inorganic radicals in aqueous solution. J. Phys. Chem. Ref. Data 17, 1027-1284.

Osorio, V., Proia, L., Ricart, M., Pérez, S., Ginebreda, A., Cortina, J. L., Sabater, S., Barceló, D., 2014. Hydrological variation modulates pharmaceutical levels and biofilm responses in a Mediterranean river. Sci. Total Environ. 472, 1052-1061.

Packer, J. L., Werner, J. J., Latch, D. E., McNeill, K., Arnold, W. A., 2003. Photochemical fate of pharmaceuticals in the environment: naproxen, diclofenac, clofibric acid, and ibuprofen. Aquat. Sci. 65 (4), 342-351.

Parker, K. M., Reichwaldt, E. S., Ghadouani, A., Mitch, W. A., 2016. Halogen radicals promote the photodegradation of microcystins in estuarine systems. Environ. Sci. Technol. 50, 8505-8513.

Remucal, C. K., 2014. The role of indirect photochemical degradation in the environmental fate of pesticides: A review. Environ. Sci.: Processes Impacts 16, 628-653.

Rosario-Ortiz, F. L., Canonica, S., 2016. Probe compounds to assess the photochemical activity of dissolved organic matter. Environ. Sci. Technol. 50, 12532-12547.

Sanchez-Prado, L., Kalafata, K., Risticevic, S., Pawliszyn, J., Lores, M., Llompart, M., Kalogerakis, N., Psillakis, E., 2012. Ice photolysis of 2,2 ',4,4 ',6-pentabromodiphenyl ether (BDE-100): Laboratory investigations using solid phase microextraction. Anal. Chim. Acta 742, 90-96.

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.

Vione, D., 2018. A model assessment of the role played by the carbonate ($CO_3^{\bullet-}$) and dibromide ($Br_2^{\bullet-}$) radicals in the photodegradation of glutathione in sunlit fresh- and salt-waters. Chemosphere 209, 401-410.

Vione, D., Scozzaro, A., in press. The photochemistry of surface freshwaters in the framework of climate change. Environ. Sci. Technol., DOI: https://doi.org/10.1021/acs.est.9b00968.

Wetzel, R. G. Limnology: Lake and River Ecosystems. Academic Press: Third Edition; 2001.

Yan, S., Song, W., 2014. Photo-transformation of pharmaceutically active compounds in the aqueous environment: A review. Environ. Sci.: Processes Impacts 16, 697-720.

Zeng, T., Arnold, A., 2013. Pesticide photolysis in prairie potholes: probing photosensitized processes. Environ. Sci. Technol. 47, 6735-6745.

Zhou, C., Chen, J., Xie, H., Zhan, Y., Li, Y., Wang, Y., Xie, Q., Zhang, S., 2018. Modeling photodegradation kinetics of organic micropollutants in water bodies: A case of the yellow river estuary. J. Hazard. Mater. 349, 60-67.