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Photochemical reactions and the self-depuration of sunlit freshwaters

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Abstract

Reactions induced by sunlight (direct photolysis and indirect photochemistry) are important ecosystem services that aid freshwater bodies in removing contaminants, although they may also exacerbate pollution in some cases. Without photoinduced reactions, pollution problems would be considerably worse overall. The photochemical reaction rates depend on seasonality, depth, water chemistry (which also significantly affects the reaction pathways), and pollutant photoreactivity. Photochemical reactions are also deeply impacted by less studied factors, including hydrology, water dynamics, and precipitation regimes, which are key to understanding the main impacts of climate change on surface-water photochemistry. Climate change is expected in many cases to both exacerbate freshwater pollution, and enhance photochemical decontamination. Therefore, photochemical knowledge will be essential to understand the future evolution of freshwater environments.

1. Introduction

Surface water bodies, such as rivers and lakes, can contain a number of organic and inorganic pollutants from a range of human activities, including the discharge of industrial and urban wastewater, agriculture and livestock, and even recreational use of water. Some pollutants can act as nutrients (e.g. inorganic nitrogen and phosphorous species), and may be involved in water eutrophication, whereas others are readily biodegradable and transformed by bacteria [1, 2].

Considerable interest has recently been raised by the contaminants of emerging concern (CECs), which differ from nutrients and biodegradable species as they are water-soluble and biorecalcitrant at the same time [3]. These features make CECs elimination from urban wastewater difficult, because biorecalcitrant compounds are poorly degraded by activated sludge, while water-soluble species do not partition to the sludge phase. Not being degraded or otherwise removed by wastewater treatment plants (WWTPs), many CECs remain in the water phase, from which they eventually reach the WWTP outlet, and hence the collecting water bodies [4]. Some CECs do not even need to resist WWTP removal, as they are directly emitted to the water bodies by agriculture (through irrigation water or soil runoff) [5], aquaculture that makes wide use of antibiotics [6], or recreational use of water (e.g. swimming), which causes direct emission into water of sunscreens and fragrances contained in sunbathing lotions [7].

Biorecalcitrant contaminants are understandably resistant to biodegradation in the natural environment, thus photodegradation is potentially very important for the attenuation of these compounds in sunlit waters [8, 9]. Photodegradation involves, first of all, sunlight-absorbing contaminants, i.e. compounds absorbing radiation above 280 nm. Direct photolysis of these compounds occurs if radiation absorption is able to trigger transformation upon bond breaking, bond formation, or ionisation [10, 11]. Indirect photochemistry is operational as well, and in this case the contaminant does not need to absorb sunlight. Sunlight is instead absorbed by naturally-occurring compounds called photosensitisers: the main ones being nitrate, nitrite, and the fraction of natural dissolved organic matter (DOM) that absorbs sunlight, i.e. the chromophoric DOM (CDOM) [12]. Nitrate derives from atmospheric depositions (the air pollutant nitrogen dioxide yields NO_3^- upon hydrolysis in water), agricultural pollution (fertilisers), or enzymatic breakdown of proteins into

amino acids [13], which are deaminated into carboxylic acids and ammonia/ammonium ion (NH_3/NH_4^+)[1]. NH_3/NH_4^+ can then be oxidised to nitrite and, finally, nitrate. Nitrite usually occurs in low concentration, as an intermediate of NH_4^+ oxidation to NO_3^- (which prevails in aerated waters), or NO_3^- reduction to NH_4^+ (more likely in anoxic water). However, higher photoactivity of nitrite compared to nitrate offsets at least in part the lower nitrite concentration [14].

(C)DOM consists of a wide variety of chemical species, such as fatty acids and their hydroxyderivatives, aromatic acids (including humic and fulvic acids), methoxyphenols (lignin derivatives), and ring-condensation compounds. According to its origin, (C)DOM can be allochthonous or autochthonous. The so-called allochthonous organic matter derives from soil (from where it is transported to surface waters by runoff) or atmospheric depositions, the latter usually in quite small amount that is mostly highlighted in organic-poor mountain lakes [15]. In contrast, autochthonous organic matter is produced in the water body as, e.g. microbial exudates or degraded spoils of living organisms [16]. Most of the organic matter is dissolved (hence the acronym DOM), and CDOM is here defined as the DOM fraction that absorbs sunlight [17]. An alternative CDOM definition, not used here, is organic matter that can be detected by typical UV–Vis spectrophotometry: this definition encompasses all compounds absorbing radiation above 190 nm [18]. Here, only dissolved organic compounds absorbing above 280 nm are considered as CDOM.

The absorption of sunlight by nitrate, nitrite, and CDOM yields a number of reactive transient species (photochemically produced reactive intermediates, PPRIs) that include the hydroxyl radical $^\bullet OH$, the carbonate radical $CO_3^{\bullet-}$, singlet oxygen ($^1O_2$), and the triplet states of CDOM ($^3CDOM^*$) [19]. The photolysis of nitrate and nitrite yields $^\bullet OH$, which can in turn produce $CO_3^{\bullet-}$ by oxidising the inorganic carbon species HCO_3^- and CO_3^{2-} [20]. Irradiated CDOM yields all PPRIs: $^3CDOM^*$ and $^1O_2$ directly, $^\bullet OH$ by a number of processes that involve longer reaction chains, and $CO_3^{\bullet-}$ indirectly upon inorganic carbon oxidation [21, 22]. An outline of the main processes following CDOM irradiation is provided in scheme 1. All the mentioned PPRIs can react with the contaminants, and trigger their degradation by indirect photochemistry [19].

Reaction with pollutants is not the main quenching/scavenging process for PPRIs. Although indirect photochemistry may be the main attenuation pathway for several pollutants, scavenging by pollutants is usually a minor process for any PPRI [19].

PPRIs are eliminated from water by reacting with DOM, HCO_3^- and CO_3^{2-} ($^\bullet OH$), or with DOM alone ($CO_3^{\bullet-}$); they may undergo internal conversion, i.e. loss of energy, mostly by collision with the solvent ($^3CDOM^*$ and $^1O_2$), or reaction with dissolved oxygen ($^3CDOM^*$; it is the process that yields $^1O_2$) [19]. The framework is a bit different for $^\bullet OH$ in saltwater and seawater, where $^\bullet OH$ is mainly scavenged by bromide to give the dibromide radical, $Br_2^{\bullet-}$ [24], which is in turn mainly scavenged by DOM. DOM is thus the main $^\bullet OH$ scavenger in freshwater, whereas Br^- plays the same role in saltwater and seawater [19].
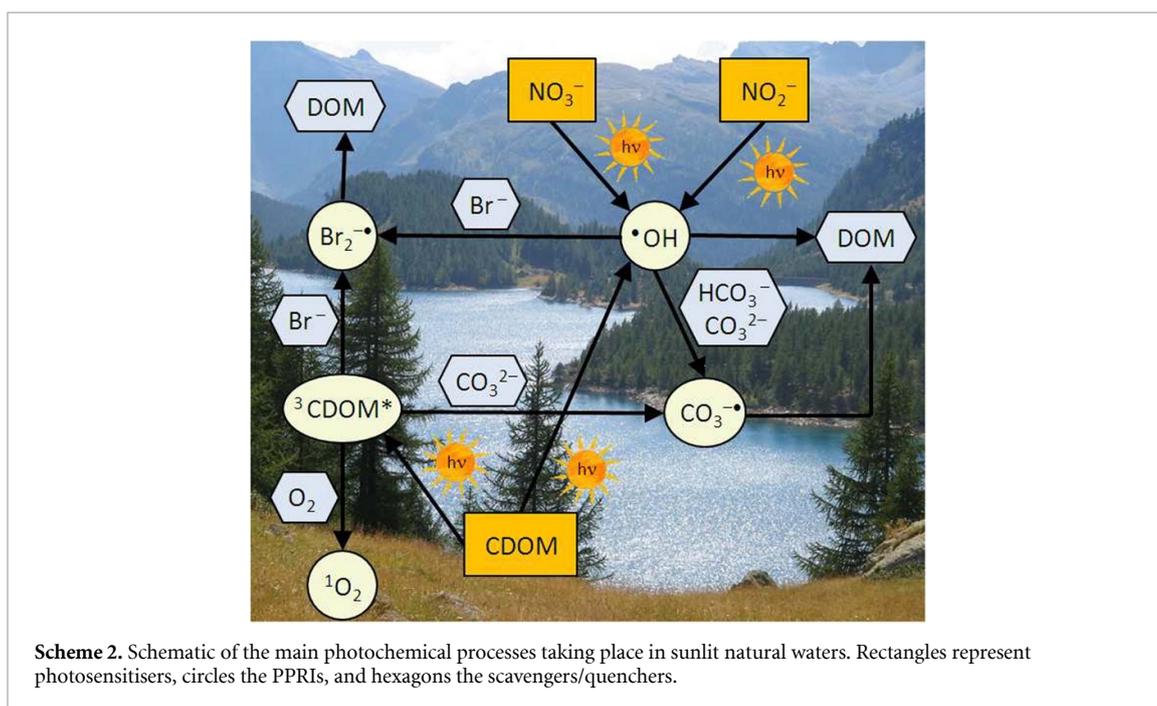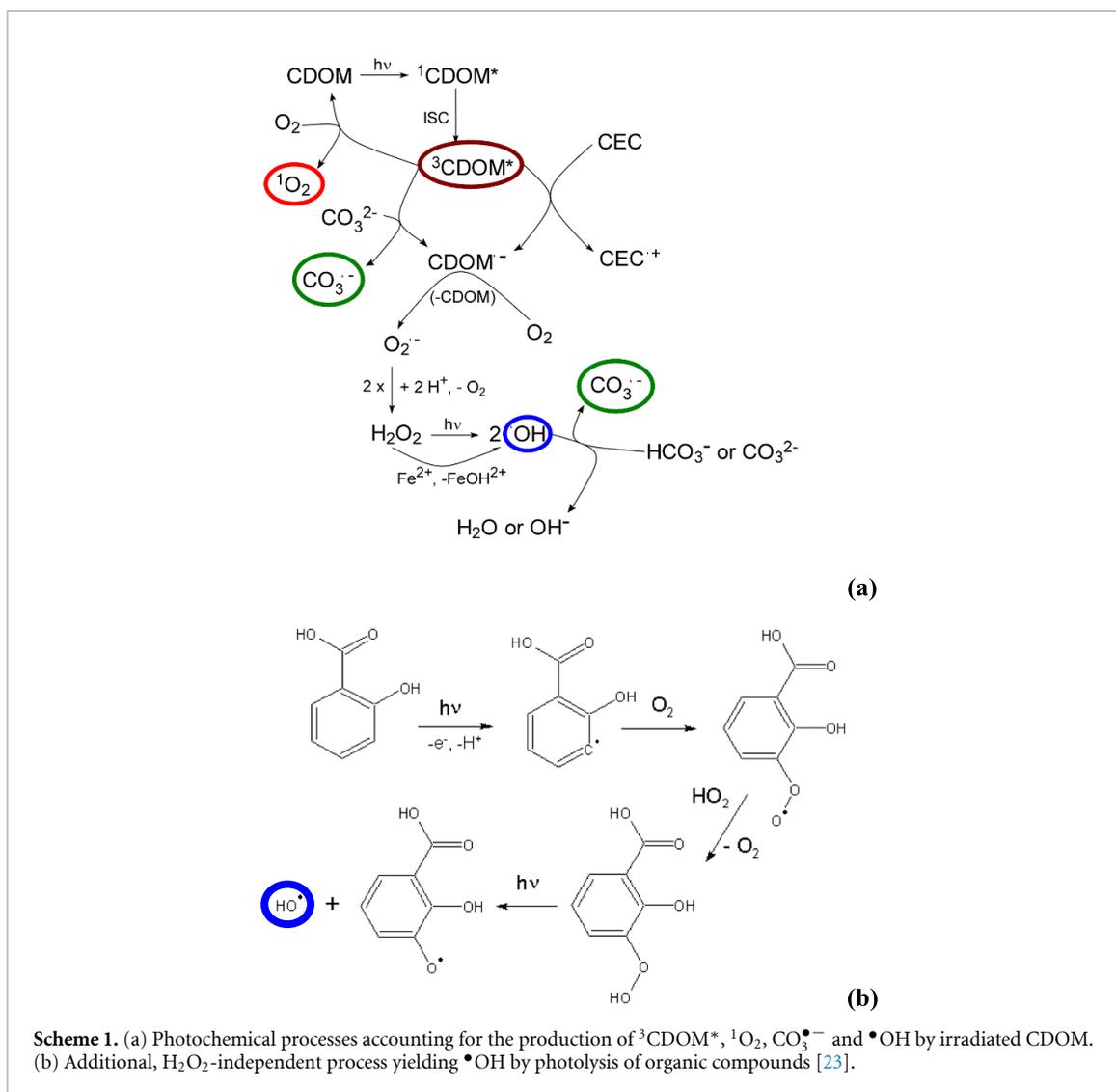
A summary of the main indirect photochemistry processes in surface waters is provided in scheme 2, where rectangles represent photosensitisers, circles are the PPRIs, and hexagons represent scavengers and quenchers. Reaction between PPRIs and pollutants often plays a key role in pollutant attenuation, thus the next sections will extensively deal with pollutant photodegradation.

2. Kinetics of contaminant photodegradation

The main water photosensitisers (nitrate, nitrite, and CDOM) absorb sunlight in different spectral intervals: nitrate absorption is centred in the UVB region, nitrite absorbs both UVB and UVA radiation, while absorption by CDOM decreases exponentially with increasing wavelength (figure 1(a)). CDOM is the main radiation absorber in surface waters, in the 280–500 nm spectral range [19, 25]. The combination between photosensitiser absorption spectra and the spectrum of sunlight ensures that nitrate absorption is almost totally attenuated in the first two meters of the water column, that of nitrite is active until about 4–5 m, while absorption by CDOM is still operational at 10 m and below (figure 1(b)). As suggested by the figure, the decrease of radiation intensity with depth ensures that shallow waters are more thoroughly illuminated by sunlight than deep waters. Photochemical reactions are thus understandably faster in shallow water bodies [19].

Water chemistry highly affects photochemical reaction pathways, due to the interplay between photosensitisers and scavengers. In particular, due to the key roles of CDOM as PPRI source and of DOM as PPRI sink, the water dissolved organic carbon (DOC) acts as a switch between different reaction pathways. As shown in figure 2, the steady-state [$^\bullet OH$] and [$CO_3^{\bullet-}$] decrease with increasing DOC, while [$^3CDOM^*$] and [$^1O_2$] increase with DOC [19]. Figure 2 and most of the following figures were obtained by making

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[1] The carboxylic acids produced by deamination are, for instance, responsible for the smell of old cheese. An alternative decomposition process of amino acids (decarboxylation by loss of CO_2) leads to toxic biogenic amines, such as putrescin, cadaverine, and histamine.

Scheme 1. (a) Photochemical processes accounting for the production of $^3CDOM^*$, $^1O_2$, $CO_3^{\bullet-}$ and $^\bullet OH$ by irradiated CDOM. (b) Additional, H_2O_2-independent process yielding $^\bullet OH$ by photolysis of organic compounds [23].

Scheme 2. Schematic of the main photochemical processes taking place in sunlit natural waters. Rectangles represent photosensitisers, circles the PPRIs, and hexagons the scavengers/quenchers.
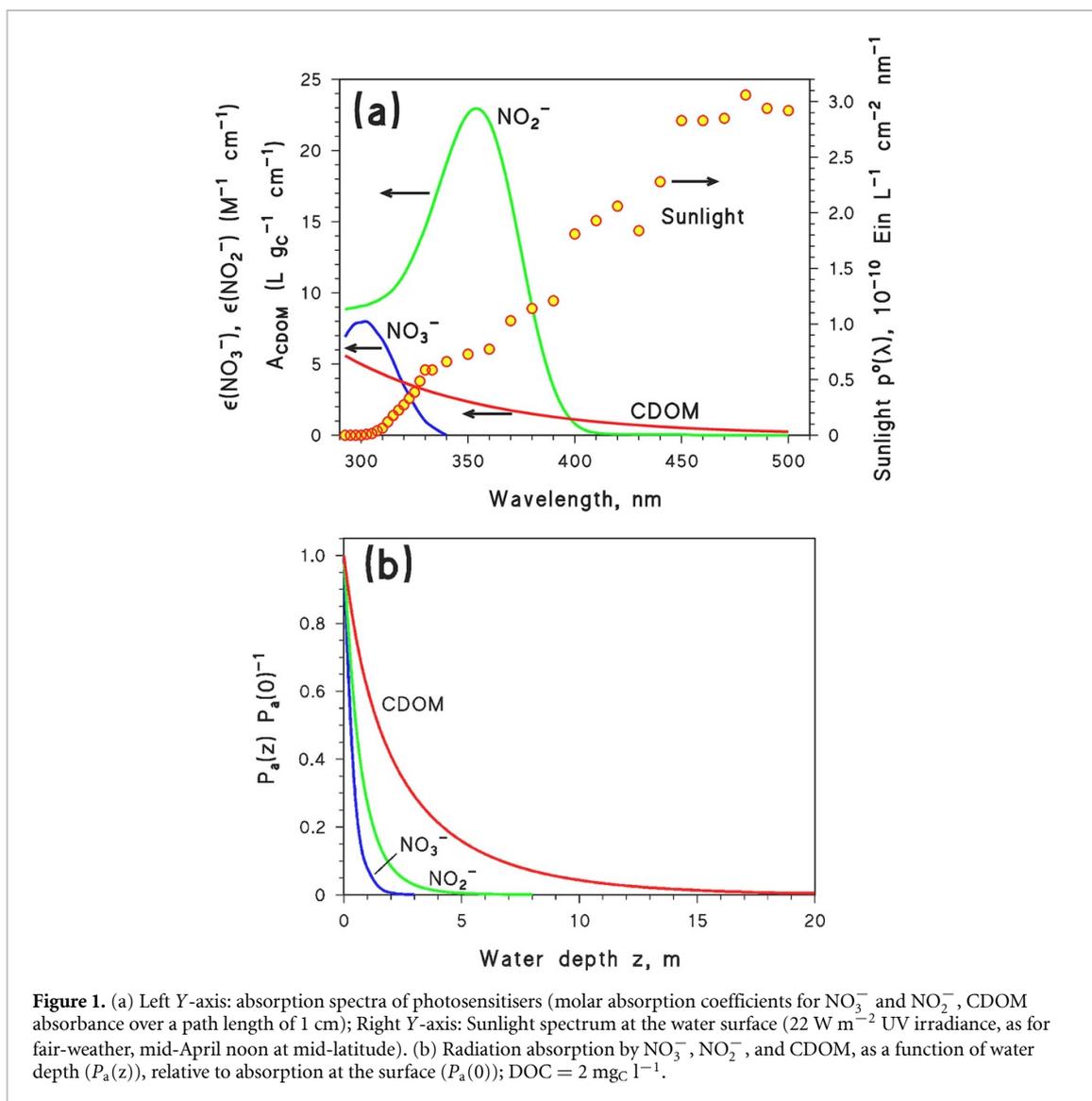
Figure 1. (a) Left Y-axis: absorption spectra of photosensitisers (molar absorption coefficients for NO_3^- and NO_2^-, CDOM absorbance over a path length of 1 cm); Right Y-axis: Sunlight spectrum at the water surface (22 W m^{-2} UV irradiance, as for fair-weather, mid-April noon at mid-latitude). (b) Radiation absorption by NO_3^-, NO_2^-, and CDOM, as a function of water depth ($P_a(z)$), relative to absorption at the surface ($P_a(0)$); DOC = 2 mg$_C$ l^{-1}.

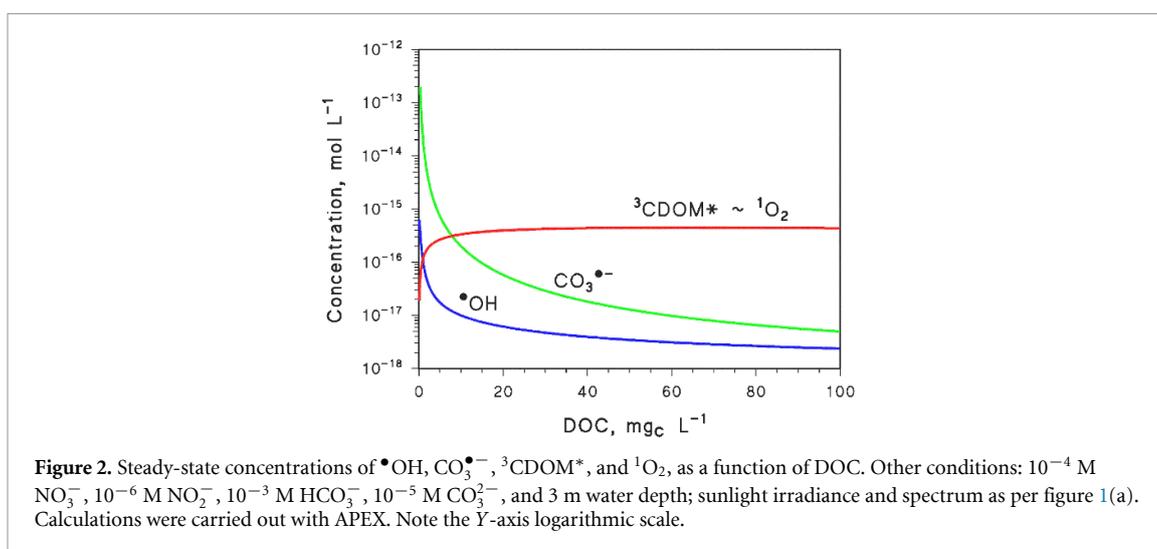**Figure 2.** Steady-state concentrations of $^\bullet OH$, $CO_3^{\bullet -}$, $^3CDOM^*$, and $^1O_2$, as a function of DOC. Other conditions: 10^{-4} M NO_3^-, 10^{-6} M NO_2^-, 10^{-3} M HCO_3^-, 10^{-5} M CO_3^{2-}, and 3 m water depth; sunlight irradiance and spectrum as per figure 1(a). Calculations were carried out with APEX. Note the Y-axis logarithmic scale.

dedicated calculations with the APEX software (Aqueous Photochemistry of Environmentally-occurring Xenobiotics) [26].

The interplay between water depth and DOC is shown in figure 3(a), in the case of carbamazepine (CBZ) as an example. CBZ is a highly biorecalcitrant anti-epileptic drug that, due to poor elimination by WWTPs,

Figure 3. (a) Half-life times ($t1/2$, 24 h sunny summer days at mid-latitude) of the anti-epileptic drug carbamazepine (CBZ), as a function of water depth and DOC. (b) First-order degradation rate constant of CBZ ($k = \ln 2\,(t1/2)^{-1}$) as a function of the DOC, for water depth $d = 3$ m. Other 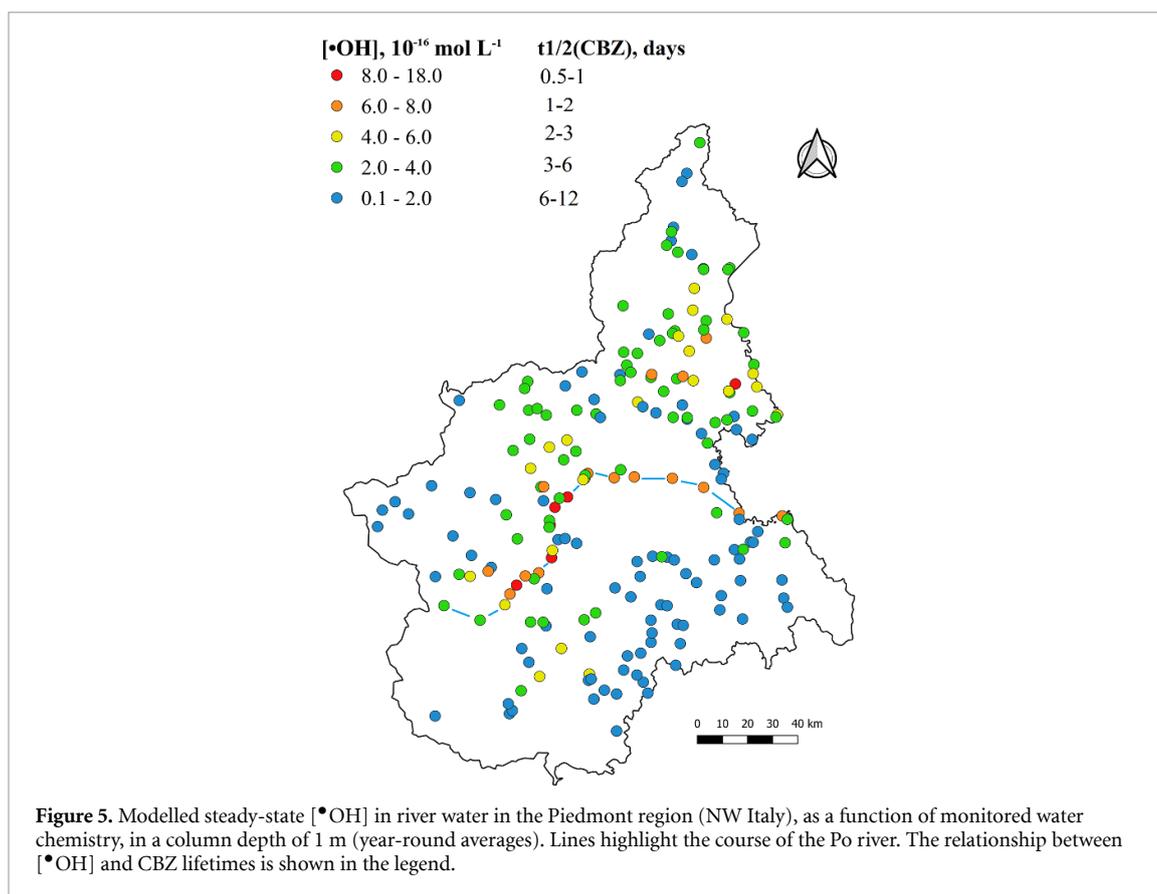conditions: 10^{-4} M NO_3^-, 10^{-6} M NO_2^-, 10^{-3} M HCO_3^-, and 10^{-5} M CO_3^{2-}. Calculations were carried out with the APEX software. Colours highlight the importance of different photodegradation pathways. d.p. = direct photolysis.

Figure 4. CBZ first-order photodegradation rate constants (left Y-axis) and half-life times (right Y-axis), in different months of the year. Water conditions: 3 mg_C l^{-1} DOC, 3 m water depth, 10^{-4} M NO_3^-, 10^{-6} M NO_2^-, 10^{-3} M HCO_3^-, and 10^{-5} M CO_3^{2-}. Fair weather, mid-latitude sunlight. Calculations were carried out with the APEX software. Colours highlight the importance of different photodegradation pathways. d.p. = direct photolysis.

is one of the most widely occurring CECs in freshwater [27]. The lifetime of CBZ is the lowest in shallow waters with low DOC, and the highest in deep waters with high DOC. All the main CBZ photoreaction pathways (direct photolysis, and reaction with $^{\bullet}OH$ and $^3CDOM^*$) are inhibited with increasing depth [28]. On the other hand, increasing DOC inhibits direct photolysis (d.p.) and $^{\bullet}OH$ reaction, while enhancing $^3CDOM^*$ (figure 3(b)). As shown in figure 3(b), $^3CDOM^*$ enhancement at high DOC cannot offset the inhibition of the other photoreaction pathways, which is a typical finding for most CECs [19].

Seasonality is another key factor that controls photoreaction kinetics, because the irradiance of sunlight is much higher in spring/summer than in autumn/winter [29]. Seasonal differences may be considerable, even when taking into account fair-weather days only: as shown in figure 4 as a typical example, CBZ lifetimes increase by almost an order of magnitude between June and December.

Figure 5. Modelled steady-state [$^\bullet$OH] in river water in the Piedmont region (NW Italy), as a function of monitored water chemistry, in a column depth of 1 m (year-round averages). Lines highlight the course of the Po river. The relationship between [$^\bullet$OH] and CBZ lifetimes is shown in the legend.
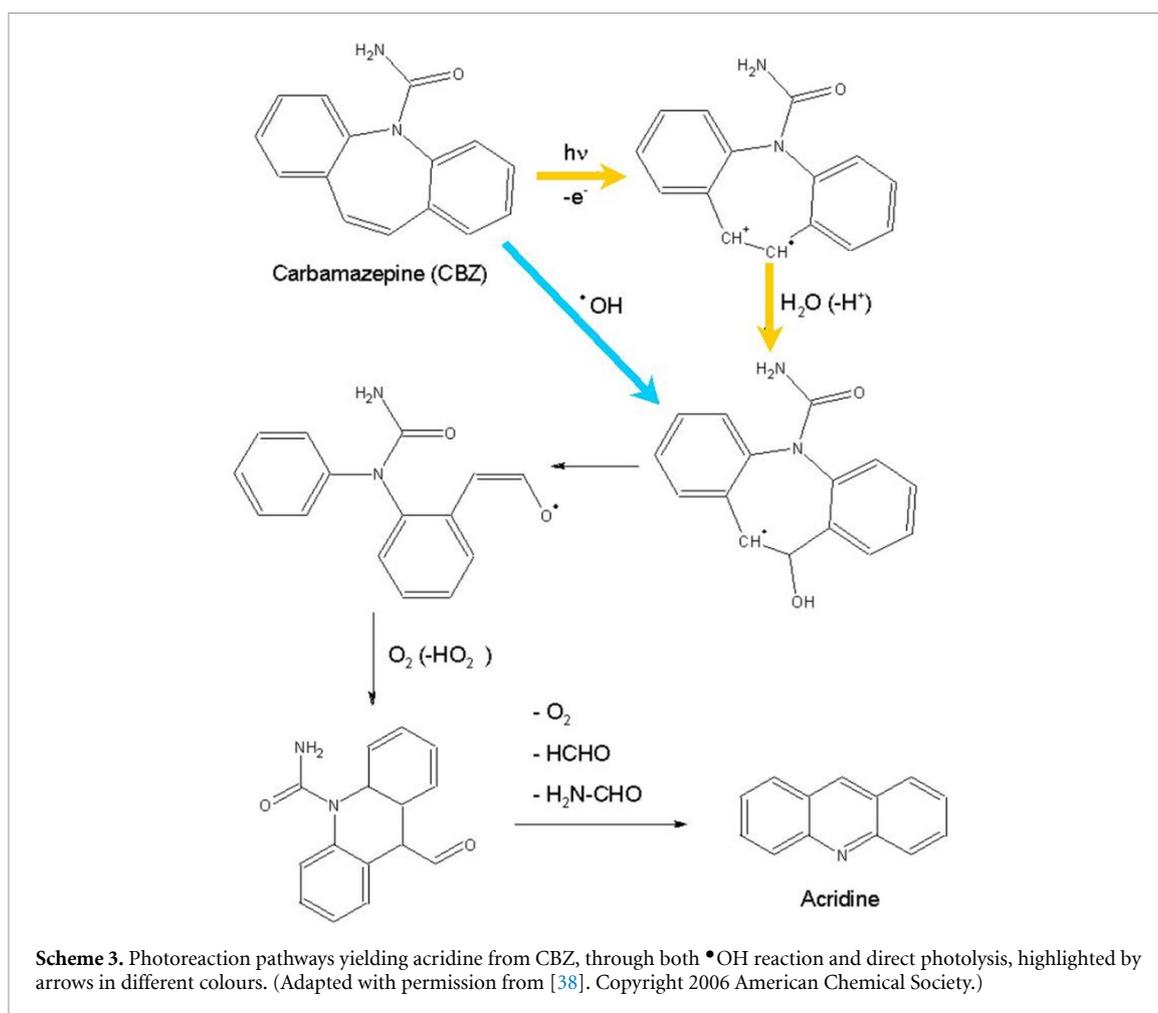
The data shown in figure 4 were obtained with the assumption that water chemistry does not change, when the irradiance of sunlight is modified seasonally. The actual situation is quite different, because the main water parameters with an impact on photochemistry (nitrate, DOC, inorganic carbon) have all peculiar seasonal trends. For instance, nitrate often has winter maxima and summer minima, because it is the main form of inorganic nitrogen, and it is effectively taken up by algae in summer [30]. A further nitrate decrease takes place in summer, because of biological reduction and denitrification processes [31].

The DOC reaches a maximum in late summer, partly as a consequence of algal growth. Algae transform CO_2/H_2CO_3 into organic carbon through photosynthesis, and this organic carbon can be released as DOC upon cell lysis, which starts prevailing over cell growth as summer ends [30]. Another DOC source comes from soil runoff, due to late summer storms [32]. Finally, if $CaCO_3$ is near saturation, it precipitates during summer due to a combination of factors that reduce its solubility, including higher temperatures and higher pH (the latter, as a consequence of CO_2/H_2CO_3 consumption by photosynthetic processes) [33]. Inorganic carbon (HCO_3^- and CO_3^{2-}) is thus often maximum in winter, and minimum in summer, while pH has an opposite trend [30].

Sunlight irradiance is, of course, the main driver of photochemical reactions. Some photosensitisers actually reach their maximum concentrations during winter (e.g. nitrate), but wintertime photochemistry never gains substantial importance. Photochemical reactions are not fully synchronised with irradiance, however, and do not necessarily peak at around the summer solstice [34]. Because of photosensitiser and scavenger trends, processes triggered by $^\bullet$OH/$CO_3^{\bullet-}$ (both generated by nitrate photochemistry, with inorganic carbon contribution in the case of $CO_3^{\bullet-}$, and scavenged by organic matter) tend to peak in late spring. In contrast, processes involving $^3CDOM^*$/$^1O_2$ typically have their maximum importance in late summer. In other words, [$^\bullet$OH] and [$CO_3^{\bullet-}$] in temperate areas tend to reach their yearly maximum *before* the irradiance peak at the summer solstice, while [$^3CDOM^*$] and [$^1O_2$] tend to do the same *after* the solstice [35].

The link between water chemistry and contaminant photodegradation allows for the photo-depuration potential of surface waters to be assessed, as a function of the main photochemically-relevant parameters (DOC, nitrate, nitrite, and inorganic carbon). The latter data are frequently available, because they are routinely monitored by many environmental protection agencies [36]. As an example, figure 5 shows the modelled steady-state [$^\bullet$OH] in river water, in the Piedmont region (NW Italy), together with the associated lifetimes of CBZ. The course of the main river of the region (the river Po, of which all the other rivers are

Scheme 3. Photoreaction pathways yielding acridine from CBZ, through both $^\bullet$OH reaction and direct photolysis, highlighted by arrows in different colours. (Adapted with permission from [38]. Copyright 2006 American Chemical Society.)

tributaries) is highlighted in the figure, showing high [$^\bullet$OH] values due to nitrate inputs from agricultural activities. CBZ initially occurring in another river in Piedmont may not be highly photoprocessed while there, but it would get degraded to a significant extent when water reaches the Po. This is an interesting case of pollution fighting pollution.

As far as CBZ photodegradation is concerned, $^\bullet$OH reaction and direct photolysis are important, because they both transform the toxic (for aquatic organisms) CBZ into less toxic but highly mutagenic acridine, with low but significant acridine yield (around 5%) [37]. The two processes (a direct photolysis and an indirect photochemistry pathway) are in theory very different, but they yield the same transformation intermediate because they have a common path, as shown in scheme 3. Indeed, both photoionisation followed by reaction with water, and $^\bullet$OH attack, tend to produce the same radical species, which then evolves into acridine.

3. Phototransformation intermediates

As mentioned above, photochemical reactions yield intermediates that are often innocuous, but that can sometimes be more harmful than their parent compounds [39]. The interplay between the original CECs and their intermediates has several features:

(a) Interest toward photochemical transformation of CECs usually arises from their being biorecalcitrant. However, transformation intermediates may be more polar, bioavailable, and thus more biodegradable than their parent compounds, thereby enabling bioprocessing to be significant. Actually, photodegradation and biodegradation may operate together along a transformation chain (biodegradation of photostable compounds, photodegradation of biorecalcitrant ones), to finally achieve complete CEC mineralisation [40].

(b) Different photoreaction pathways may yield different intermediates but, frequently, the same intermediate is produced by several pathways (see the case of acridine in scheme 3), often with different yields [41]. A key issue is that many photoprocesses operate through one-electron oxidation (e.g. $CO_3^{\bullet-}$, $^3CDOM^*$, and photoionisation) that is followed by reaction with water, which simulates $^\bullet$OH addition.
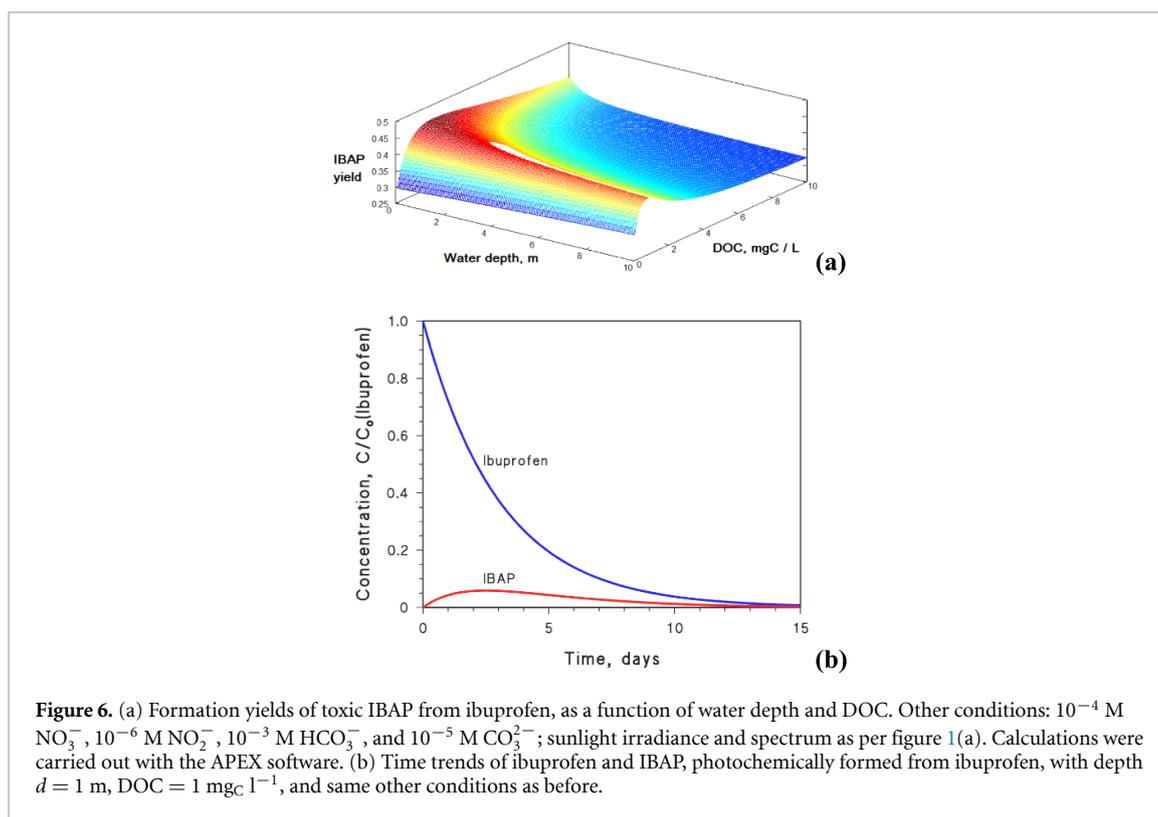
Figure 6. (a) Formation yields of toxic IBAP from ibuprofen, as a function of water depth and DOC. Other conditions: 10^{-4} M NO_3^-, 10^{-6} M NO_2^-, 10^{-3} M HCO_3^-, and 10^{-5} M CO_3^{2-}; sunlight irradiance and spectrum as per figure 1(a). Calculations were carried out with the APEX software. (b) Time trends of ibuprofen and IBAP, photochemically formed from ibuprofen, with depth $d = 1$ m, DOC $= 1$ mg_C l^{-1}, and same other conditions as before.

Environmental conditions such as water chemistry and depth strongly affect the photoreaction pathways, and have considerable impact on the formation of intermediates [42]. For instance, figure 6(a) reports the formation yields of toxic 4-isobutylacetophenone (IBAP) from the non-steroidal anti-inflammatory drug ibuprofen, as a function of DOC and water depth. The peculiar trend is motivated by the fact that ibuprofen transformation yields IBAP through direct photolysis and reaction with $^{\bullet}OH$ and $^3CDOM^*$, with different yields for each process [41]. The $^{\bullet}OH$ reaction prevails in low-DOC conditions (see also figure 2), the direct photolysis has the highest relative importance at intermediate DOC, and $^3CDOM^*$ at high DOC. Further links between CECs and intermediates are the following:

(c) Intermediates can be photochemically degraded, in addition to being formed. As an example, figure 6(b) shows the time trends of ibuprofen and IBAP, following the photochemical reaction scheme *Ibruprofen → IBAP → Other compounds*. As reported in the figure, IBAP is often more photolabile than ibuprofen [41], thus the disappearance of ibuprofen also entails disappearance of toxic IBAP as well.

(d) The relative toxicity of the parent CEC and its identified intermediates can be assessed by experiment, or calculated *in silico* by means of software such as ECOSAR (US-EPA) [43]. ECOSAR allows for predicting acute and chronic toxicity values (reasonably accurate within an order of magnitude), using a quantitative structure-activity relationship. Toxic or otherwise harmful intermediates are usually (and understandably) a focus of attention, and table 1 reports as an example the ECOSAR results for the CEC-intermediate couples CBZ-acridine and ibuprofen-IBAP. It can be seen that IBAP has both acute and chronic toxicity values that are about an order of magnitude lower than those of ibuprofen. Considering the statistical significance threshold of ECOSAR [43], this result suggests that IBAP is likely more toxic than ibuprofen. In contrast, acridine is about as toxic or even less toxic compared to CBZ, but it is a compound of concern for its known mutagenicity [44].

It should be remarked that, in a majority of cases, CEC photodegradation yields intermediates that are actually less toxic than their parent compound. Therefore, photodegradation often results in decreasing pollution. Examples of CECs that are well known to undergo photochemical decontamination are bentazone, tebuconazole, sertraline, dimethomorph, and diclofenac [19]. However, the minority of cases when an intermediate is more harmful than the parent compound is clearly a matter of important concern, and gains plenty of attention [39]. Unfortunately, these cases are very difficult to predict in advance, based on the mere structure of the parent CECs.

Table 1. Acute (LC50, EC50) and chronic (ChV) toxicity values for two CECs, and their transformation intermediates (CBZ, acridine, ibuprofen, and IBAP), towards different freshwater organisms. Calculations were carried out with ECOSAR (US-EPA). The lower the value, the higher the toxicity.

Values in mg l^{-1}		CBZ	Acridine	Ibuprofen	IBAP
Fish	LC50	6.2	9,6	42	5.1
	ChV	0.17	1.1	4.9	0.59
Daphnid	LC50	1.6	6.2	28	3.3
	ChV	0.20	0.84	4.3	0.49
Green algae	EC50	0.10	7.6	41	4.6
	ChV	0.066	2.6	16	1.7

4. Water dynamics in lakes and rivers, and their photochemical implications

Water dynamics have considerable impact on photochemical reactions, and on the ways contaminants are photochemically attenuated [35]. Very important roles in this framework are played by water stratification in lakes, and by the mere fact that water flows in river stretches, which marks an important difference with stationary water bodies.

4.1. Summer stratification in lakes

Lakes that are deep enough can become stratified during summer, because surface water gets heated by summer sunlight, and the warmer surface layer floats over the colder and denser deep water (note that water density decreases with temperature, above 4 °C) [30]. Very shallow lakes can undergo overturn by the mere action of wind, which triggers a series of stratification/mixing events (polymictic lakes) [45]. With deep enough lakes, stratification can last consistently throughout the whole summer season, and beyond. A stratified lake consists of a sunlit surface layer (epilimnion) that is separated from the darker, denser, and cooler bottom water (hypolimnion) by the thermocline, which is defined as the zone of the lake showing the highest temperature gradient with depth [30] (see figure 7).

The epilimnion is in contact with the atmosphere, and hosts extensive photosynthetic activity that is allowed by high irradiance. Epilimnion waters are thus rich in oxygen, and have an oxidizing character. Therefore, many inorganic solutes tend to be found into their highest oxidation states in the epilimnion (e.g. nitrate, sulphate, ferric iron, and Mn(IV) oxides) [46]. By contrast, the hypolimnion is separated from the atmosphere by overlying water, and hosts limited or no photosynthesis because of low irradiance. Lack of water mixing means that oxygen can reach the hypolimnion only by diffusion, which is a slower process than the typical biological processes of oxygen consumption. Oxygen concentration in the hypolimnion thus tends to be relatively low, and hypolimnion waters in some lakes may become anoxic [47].

In the latter scenario, organisms such as fish and crustaceans that cannot live without oxygen have to seek refuge into the epilimnion during summer, thereby experiencing a forcedly small habitat that is delimited by the thermocline [47]. Moreover, inorganic solutes in the hypolimnion tend to occur in their reduced and, sometimes, toxic forms (e.g. ammonium, sulphide, Fe^{2+}, and Mn^{2+}) [46]. As summer ends, or deep into autumn, the epilimnion gets progressively colder, until the whole lake water reaches uniform temperature and stratification is broken, allowing for overturn [30]. Upon overturn, the chemical composition of the lake water gets homogeneous again.

Convective transport phenomena in a mixing lake are usually faster than photochemical reactions. Therefore, although photochemistry is the fastest next to the water surface, reactants and products are quickly distributed within the entire lake volume. Photoinduced processes are thus most easily described as taking place homogeneously in the overturning lake, with rates that average fast reactions at the surface, and slow processes in the lower depths [48].

Compared to a mixing lake (figure 7(a)), the epilimnion is better illuminated by sunlight, while the hypolimnion is much darker. Because photochemical reaction rates are proportional to irradiance, they follow the order epilimnion > whole lake > hypolimnion [48]. Summer stratification thus favours photodegradation of compounds that preferentially reach (and/or are confined into) the epilimnion, such as agrochemicals, which may get into the lake water from surrounding farmland through surface runoff. In contrast, photodegradation of compounds that occur in the hypolimnion (e.g. groundwater contaminants that may reach the lake bottom via aquifer transport and deep springs) is inhibited by stratification. In the case of contaminants that reach (usually large) lakes via (partially) treated wastewater, much depends on the respective position between the wastewater outlet pipe and the thermocline [35].

Stratification also inhibits the photodegradation of pollutants that, when the lake is still well mixed before the onset of stratification, are homogeneously distributed within the entire water column. The most
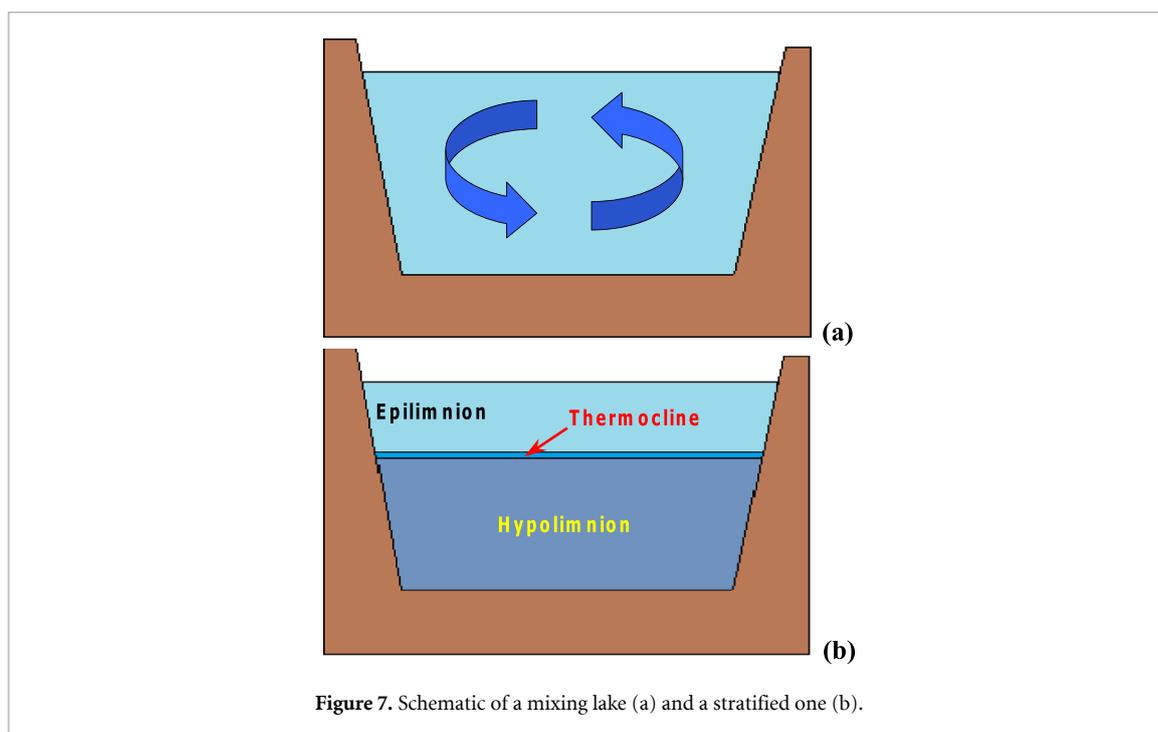
Figure 7. Schematic of a mixing lake (a) and a stratified one (b).

significant inhibition is observed with photolabile contaminants, which may be completely degraded in the epilimnion, well before the end of stratification. In such case, the photochemical processes have to stop due to lack of substrate. At the same time, photodegradation in the hypolimnion is very slow, and transfer of contaminants to the epilimnion, where they would be photodegraded, is extremely slow as well. All these phenomena substantially decrease the photodegradation efficiency of photolabile pollutants in stratified lakes [35].
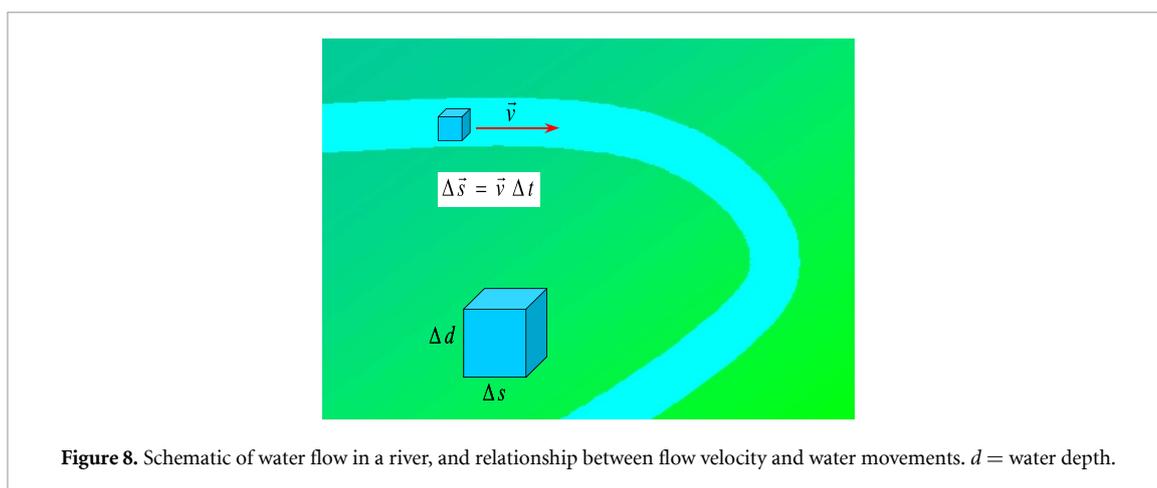
A final remark, is that the depth of the thermocline depends on the ability of sunlight to penetrate into the water column. Clear-water lakes have a deep thermocline, because sunlight can reach relatively deep water and heat it up. In contrast, thermoclines in brownwater lakes are quite shallow, because of the limited penetration depth of sunlight into the water column [49]. If the hypolimnion is anoxic, the communities of fish and other organisms may be subject to important stress in brownwater. These scenarios have significant implications (including photochemical ones) in the framework of climate change (*vide infra*).

4.2. Photochemical implications of water flow in rivers

As far as the behaviour of the water column is concerned, the mathematical treatment of photochemical reaction rates in rivers is the same as that in mixing lakes, and the rates are also the same at equal irradiance, water chemistry, and depth.

The implications of a given reaction rate are, however, not the same in a stationary or a flowing water system [34, 35]. In the case of a river (figure 8), a contaminant is transported by the water flow while it reacts [50, 51]. The main consequence of this scenario, is that the degradation lifetime of the contaminant has to be compared with the in-stream time of river water, before it reaches the sea [34]. For instance, the Po river (northern Italy) is 600 km long and, assuming an average value of the water flow velocity of 1 m s^{-1} [52], around 7 d are needed for river water to reach the sea. A look at figure 5 suggests that CBZ emitted by a WWTP in Piedmont would undergo extensive photodegradation before that time, at least during summer. However, in winter (see figure 4) CBZ could well reach the sea, before undergoing important photodegradation. This means, that the whole river stretch from the WWTP outlet onwards could be affected by CBZ pollution (the only important issue to limit contamination, would be CBZ dilution by the water flow).

An important issue is that the flow velocity $\vec{v}$ of water in a river (a vector quantity with m s^{-1} units) is not constant, not even in module ($|\vec{v}|$). First, water flows faster in narrower points, and more slowly where the river is wider, to maintain a constant flow rate Q, a scalar quantity with m^3 s^{-1} units that is the most informative for river flow. Moreover, $\vec{v}$ also depends on the slope of the terrain: at equal Q, lowland rivers are wider and deeper than highland rivers, where $|\vec{v}|$ is higher to maintain the same Q [53]. Unfortunately, Q is hardly connected with photochemical reactions, while $|\vec{v}|$ is key to them, as shown above. An average value of $|\vec{v}|$ for the relevant river stretch should thus be used.

Figure 8. Schematic of water flow in a river, and relationship between flow velocity and water movements. d = water depth.

There are several instances, when Q is no longer constant. These are typically associated to periods of drought (scarce flow), or important precipitation (flood). Q and the module of $\vec{v}$ are mutually proportional, but the type of proportionality changes with the features of the river course. If river water is constrained by high banks like in natural canyons or artificial channels, one has $|\vec{v}| \propto Q^{1/2}$. In contrast, if the river is allowed to spread or shrink as Q varies, one has $|\vec{v}| \propto Q^{1/3}$ [35].

When Q is low (e.g. droughts), wastewater is poorly diluted, and the contaminants it transports reach high concentration values [54]. At the same time, the water column in the river is shallow, and the river flow is relatively slow. Photochemical reactions are thus quite fast, and there is also longer time for photochemistry to induce contaminant photodegradation in a given river stretch [35]. In this case, higher contamination due to poor wastewater dilution is offset to a variable extent by more efficient photochemical degradation of contaminants, at least if toxic intermediates are not formed: typically, the longer the river stretch, the more extensive the photodegradation [34, 35]. When Q is high (e.g. floods), wastewater may not be a huge issue due to extensive dilution. However, precipitation water can mobilise contaminants from the basin (farmland, industrial areas, polluted town paving) to the river, where deep water and fast flow can make photodegradation quite ineffective. Therefore, photochemistry would not help much with pollution phenomena during floods [35].
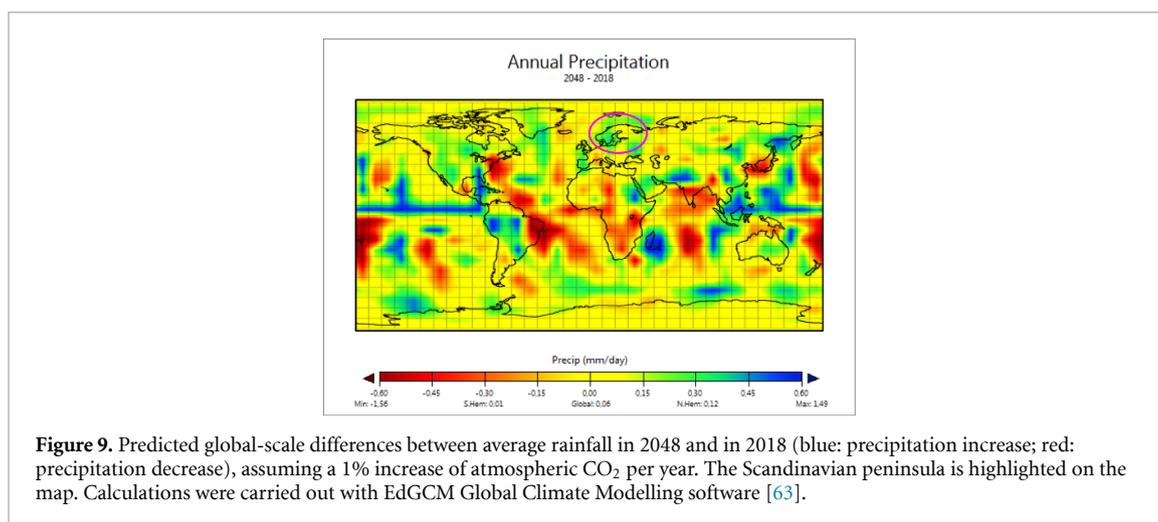
5. A perspective look into the future: water photochemistry and climate change

Climate change has several potential impacts on the photochemistry of surface waters. The rationale is that climatic variations affect chemistry, hydrology, and dynamics of water, and all these factors in turn affect photochemical reactions [35]. The main issues briefly considered here are water browning, lake stratification, winter ice cover, summer water evaporation, and a variable precipitation regime.

5.1. Water browning in boreal environments
In Nordic regions such as, most notably, the Scandinavian peninsula, a combination of recovery from acid rain and increased precipitation (the latter most likely connected with climate change) has increased the transport of organic matter (especially humic and fulvic acids, which are major CDOM components) from soil to surface waters [49, 55]. Acid rain contains sulphuric and nitric acids, derived from atmospheric contaminants such as SO_2 (combustion of S-containing coal) and NO_x (traffic emissions) [56]. When acid rain falls on soil, its low pH keeps humic and fulvic acids in their protonated, and poorly water-soluble, forms. Coal desulfurisation and abatement of NO_x emissions from both petrol and (more recently) diesel vehicles have partially solved the problem of acid rain, which means lower damage to vegetation, but also higher pH values of rain. In such conditions, soil humic and fulvic acids can undergo deprotonation, which increases their water solubility and enhances their transport to the water bodies. The phenomenon is further enhanced by increasing precipitation, over time, in the same regions [57].

Increasing levels of CDOM in water change its colour, from almost transparent (like the majority of surface water samples collected in temperate regions) to yellowish, or even brown/dark brown. For this reason, the phenomenon is termed 'browning' or 'brownification' [49, 55]. The occurrence of water that is more coloured and has higher DOC affects the penetration of sunlight into the water column, with inhibition of photosynthesis and modifications of water dynamics (e.g. lake stratification, *vide infra*) [49]. From a photochemical point of view, browning shifts systems like that depicted in figure 2 towards higher DOC values, thereby inhibiting processes triggered by $^{\bullet}OH$, $CO_3^{\bullet-}$ and the direct photolysis, while

Figure 9. Predicted global-scale differences between average rainfall in 2048 and in 2018 (blue: precipitation increase; red: precipitation decrease), assuming a 1% increase of atmospheric CO_2 per year. The Scandinavian peninsula is highlighted on the map. Calculations were carried out with EdGCM Global Climate Modelling software [63].

enhancing reactions with $^1O_2$ and $^3CDOM^*$ [35, 48, 58]. Moreover, as suggested by figure 3, a DOC increase is likely to slow down the overall rates of photochemical reactions, whereas at the same time modifying the photoreaction pathways.

The future trends of precipitation, as impacted by climate change, predict for instance a further increase of average rainfall in the Scandinavian peninsula (see, e.g. figure 9). This is expected to enhance organic matter transport from soils to surface waters, also because moist soils are richer in organic matter, thereby exacerbating water browning and its consequences [57].

Average precipitation should increase in a warming world, because the evaporation rate will also increase, and water vapour cannot accumulate in the atmosphere beyond a certain extent [59, 60]. However, most of the increase in precipitation would occur over some tropical and equatorial oceans (figure 9), whereas many inland areas might even experience a decrease in average precipitation. Furthermore, even areas with unchanged average precipitation might see an increase in organic matter export from soil, if the same average rainfall is concentrated into fewer rainy days. Extreme rain events are actually more effective in inducing leaching of organic matter from soil, compared to long-lasting, moderate rain [61], even at same or lower total rainfall. Higher leaching by runoff means higher export of organic matter from soil to surface waters, provided that average precipitation is high enough to preserve soil moisture, which is a prerequisite for the long-term occurrence of organic matter in soil. Actually, heavy rain on organic-poor soil cannot leach much organic matter [62].
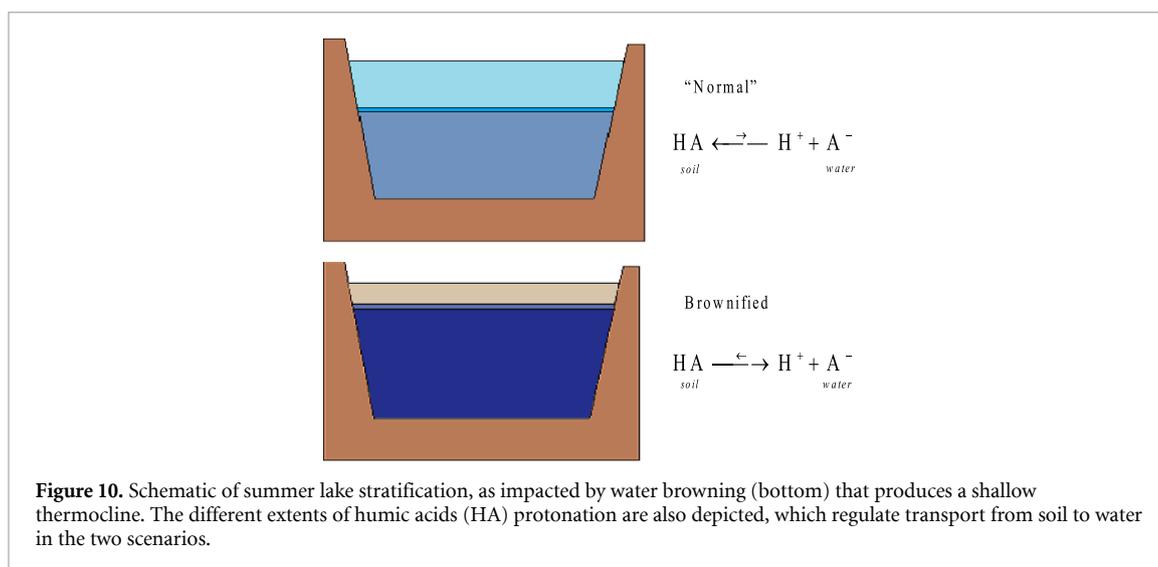
In temperate areas, the phenomenon of browning is much less evident than in Nordic regions: some temperate water bodies have even experienced a DOC decrease, as well as contrasting trends in autochthonous *vs.* allochthonous DOM, where the latter is provided by soil leaching to the water body [64]. In temperate environments, climate change is more likely to induce an increase in both alkalinity and pH of lake water, which results in increasing concentration values of both HCO_3^- and CO_3^{2-}. A possible explanation is enhanced transport of solutes from the catchment to surface waters. If $CaCO_3$ is far from saturation, higher dissolution of $CaSO_4$ in warmer water would occur, alongside with transformation of sulphate into organic sulphur species, with H^+ consumption [65]:

$$SO_4^{2-} + \text{R-H} + 8H^+ + 6e^- \rightarrow \text{R-SH} + 4H_2O.$$
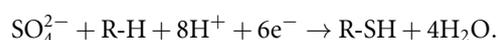
The increase in HCO_3^-, CO_3^{2-}, and pH is favourable to the occurrence of $CO_3^{\bullet-}$, but the latter is not always observed, because $[CO_3^{\bullet-}]$ strongly anticorrelates with DOC (figure 2). Relatively small DOC variations can actually offset even large variations in both inorganic carbon, and pH [66].

5.2. Water stratification in brownified lakes

Water browning reduces the penetration of sunlight into the water column, thereby lowering the extent by which lake water is heated by sunlight. As a consequence, when summer stratification takes place in brownified water, the thermocline is more shallow and the epilimnion accounts for a smaller fraction of the overall lake volume (see figure 10) [49]. Epilimnion photochemistry in a stratified, brownified lake is potentially very interesting, because the epilimnion itself is shallower, but it is also more CDOM- and DOC-rich compared to a non-brownified lake. As suggested by figure 3(a), decreasing depth enhances the photochemical reaction rates, but increasing DOC may lower them, making it intriguing to see where the actual balance stays. Detailed calculations indicate that kinetics of $^\bullet$OH reactions and the direct photolysis

Figure 10. Schematic of summer lake stratification, as impacted by water browning (bottom) that produces a shallow thermocline. The different extents of humic acids (HA) protonation are also depicted, which regulate transport from soil to water in the two scenarios.

are poorly affected in a brownified epilimnion (the opposite effects of depth and DOC more or less offset each other), while $CO_3^{\bullet-}$ reactions are inhibited, and those with $^3CDOM^*/^1O_2$ significantly enhanced. Different contaminants are degraded by these processes to variable extents, but the photodegradation of several compounds would actually become faster in a brownified epilimnion [48].

In temperate areas, in the absence of water browning, summer stratification of lake water will become more stable and will last for longer as a consequence of climate change, because summers will be hotter [67]. Therefore, the photochemical consequences of lake-water stratification, described in section 4.1, will be further exacerbated [68].

5.3. Winter ice cover
Penetration of sunlight into the water column is decreased by an ice layer, and almost totally impeded by snow on ice that reflects sunlight [69]. Therefore, ice melting in late spring as observed in Nordic or mountain areas may have a considerable impact on photochemistry, because of the effect of intense sunlight on ice-free water. Ice reforming in autumn will inhibit photochemistry, but the photochemical reactions in this season are much slower compared to late spring. Therefore, the photochemical implications of ice reforming are much more limited, compared to those of ice melting. Climate change will affect (enhance) photochemistry in these environments, by decreasing the overall duration of the ice cover, delaying autumn ice reforming and, most notably, anticipating spring melting [35].

5.4. Summer water evaporation
As summer temperatures increase as a consequence of climate change, water evaporation will become more important, and will increasingly affect the chemistry of stationary water bodies such as the lakes [70, 71]. When water evaporates, volatile solutes such as O_2 evaporate as well, but non-volatile solutes (e.g. photosensitisers like nitrate, nitrite, and CDOM, and scavengers like DOM) stay in the dissolved phase. Non-volatile solutes thus reach higher concentration values in lesser water; in the case of photosensitisers, this means that the same PPRIs are produced within a smaller water volume. The formation rates of $^\bullet OH$, $CO_3^{\bullet-}$, $^1O_2$ and $^3CDOM^*$ would all increase, proportionally to the water volume lost by evaporation. The concentration of the main scavenger of $^\bullet OH$ and $CO_3^{\bullet-}$ (i.e. DOM) would also increase, however, which means that $[^\bullet OH]$ and $[CO_3^{\bullet-}]$ would not be much modified by evaporation. In contrast, the quenching reactions of $^3CDOM^*$ (involving O_2) and $^1O_2$ (collision with the solvent) would not be much affected by evaporation which, combined with the enhancement of the respective formation rates, would make $[^3CDOM^*]$ and $[^1O_2]$ increase, proportionally to the water volume that is evaporatively lost: for instance, if half the water were lost by evaporation, $[^3CDOM^*]$ and $[^1O_2]$ would be doubled [72].

Overall, evaporative water concentration is expected to enhance photochemical reaction kinetics of those compounds, for which reactions with $^3CDOM^*$ and $^1O_2$ are important attenuation processes (e.g. anilines, phenols, chlorophenolates, thiols, and mercaptans) [19].

5.5. Variable precipitations and river flow velocities
As mentioned before in section 5.1, climate change will likely produce a highly variable precipitation regime. Therefore, even if average rainfall does not change over time, the same rain will likely be distributed over

Table 2. Outline of the main effects of climate change, having an impact on surface-water photochemistry, and their consequences (+: enhancement; o: negligible effect; −: inhibition) on the different photoreaction pathways, represented by the colour scheme.

	+	o	−
Browning	● (red)		● (cyan) ● (yellow) ● (olive)
Brownified epilimnion	● (red)	● (cyan) ● (yellow)	● (olive)
Ice melting	● (cyan) ● (red) ● (yellow) ● (olive)		
Evaporation (lake)	● (red)	● (cyan) ● (yellow) ● (olive)	
Drought (river)	● (cyan) ● (red) ● (yellow) ● (olive)		
Flood (river)			● (cyan) ● (red) ● (yellow) ● (olive)

● $\,^{\bullet}OH$; ● $CO_3^{\bullet -}$; ● $^{3}CDOM^{*}$ & $^{1}O_2$; ● Direct photolysis.

fewer rainy days, and an alternation of drought periods and flood events might become the norm in the future. In the case of rivers during droughts, the combination of shallower water columns and lower water flow velocities will enhance the importance of photochemical reactions, with the key exception of river tracts that dry out, only allowing for underground aquifer flow. Such a slow-flow scenario could become increasingly common, as a consequence of climate change. In contrast, photochemistry will be unimportant during the fewer days characterised by intense precipitation, where deeper and faster-flowing water will decrease the time available for slower photochemical reactions. Photochemical processes will still be enhanced as a whole, because high-flow days will likely become fewer and fewer [34, 35].

A summary of the effects of climate change, and their impact on photochemical reaction pathways, is provided in table 2.
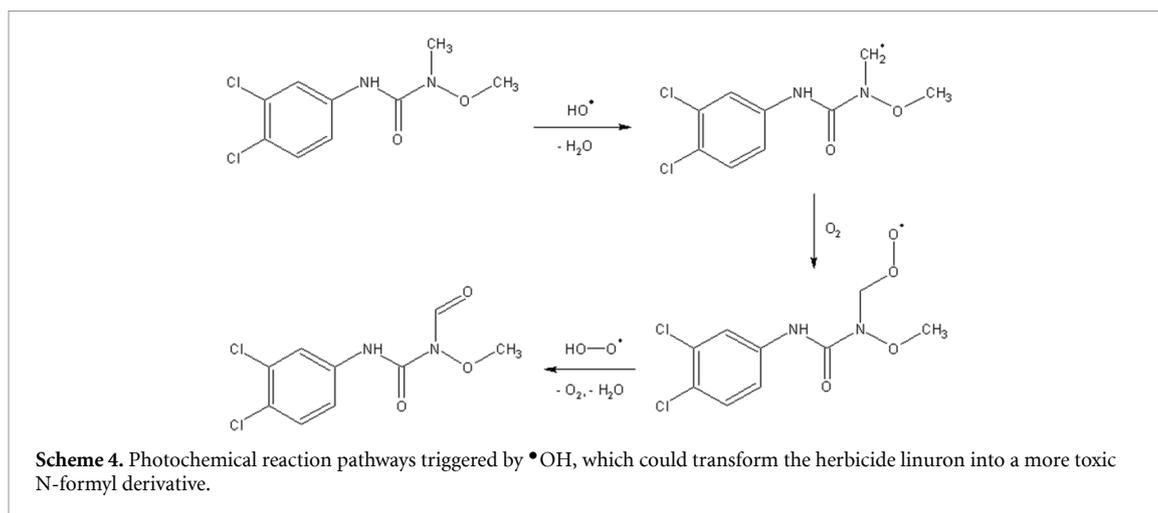
6. Water photochemistry as an ecosystem service

As mentioned above, photochemical reactions in sunlit surface waters may often play a key role in the degradation of recalcitrant contaminants. While it would be highly unrealistic to rely on photochemistry alone to tackle the problem of freshwater pollution, it is evident that things would be much worse, were photochemical reactions not operational. Freshwater photochemistry should thus be regarded as an ecosystem service, provided by surface water bodies and helping against pollution. Like all ecosystem services, however, photochemistry is modified by changes in the natural ecosystems, which may be brought about by either direct human disturbance (e.g. pollution by wastewater), or climate change. The latter acts indirectly on water bodies, because its primary target is the atmosphere. It is extremely important to understand the future evolution of photochemistry as an ecosystem service, which is affected by the starting conditions and the degree of disturbance to avoid, or at the very less predict, service deterioration that would exacerbate pollution issues.

Among possible future evolutions, a foreseen effect of climate change is higher summer temperatures, combined with longer and more stable stratification of lake water. These conditions are favourable to algal growth, including toxic algal blooms that cause emission of cyanobacterial toxins into water [73]. A further condition that could favour the growth of cyanobacteria is the damming of rivers, to provide water reservoirs for hydropower or agriculture and thus face drought events. The problem, however, is that clear lake or basin water is more favourable to photosynthesis, compared to turbid river water, thereby favouring the growth of cyanobacteria [74]. Cyanotoxins can be photodegraded [75] and, given the predicted effects of climate change on surface-water conditions (see section 5), toxins undergoing important reaction with $^{3}CDOM^{*}$, such as microcystin-LR, would undergo enhanced photodegradation, when compared to those that only react with $^{\bullet}OH$, such as cylindrospermopsin [68].

6.1. Limits to the concept of 'pollution fighting pollution'

As a rule of thumb, an ecosystem service can be provided in full only by an intact ecosystem. However, in section 2 above it was mentioned the case of water pollution by agricultural nitrate, which helps photodegradation of organic pesticides, as well as pharmaceuticals and personal care products, originally contained in urban wastewater. The photodegradation process would be particularly effective, if nitrate contaminates the main water body of a region, which collects water from tributary rivers and streams [76]. Nevertheless, such a scenario has it own critical limits, and it should be regarded as an exception rather than the rule. First, photodegradation is very active during the day in summer but not (or very little) during winter, or during the night (note that river water can travel for several dozen kilometres during the night) [19]. Additionally, nitrate pollution by agriculture is usually linked to the occurrence of agrochemicals as further contaminants: it is clearly better not to have contamination in the first stance, rather than having contaminants attenuated by enhanced degradation. Moreover, $^{\bullet}OH$ reactions triggered by irradiated nitrate

Scheme 4. Photochemical reaction pathways triggered by •OH, which could transform the herbicide linuron into a more toxic N-formyl derivative.

often produce real decontamination, but not always. For instance, •OH is able to enhance degradation of phenylurea herbicides, but it does so in part by transforming them into toxic N-formyl compounds, which have higher environmental impact than their parent contaminants (see scheme 4 for the case of linuron) [77–79]. In such and similar cases, one needs a joint consideration of the types of prevailing pollutants, and the features of freshwater ecosystems. By so doing, it can be understood where a certain pollution degree may be tolerated within certain limits, and where urgent remedial measures (e.g. strict limits on the use of given substances) should be taken, to avoid further amplification of an environmental problem. The concept of vulnerability to pollution should thus be introduced, in the assessment of natural ecosystems.

Water pollution is, actually, often detrimental to photochemical decontamination. For instance, following the collapse of the former Soviet Union, enhanced emissions of poorly treated wastewaters into the large but shallow Lake Peipsi (located at the border between present-day Estonia and Russia) have resulted into much higher levels of nutrients occurring in the lake water. In addition to the most evident and pressing environmental concerns (e.g. massive fish kills in windless summer nights, due to lake water being polluted by cyanotoxins, and easily becoming anoxic if not mixed by wind) [80, 81], there is also evidence that long-term DOC increase would hamper the ability of the lake water to trigger degradation of recalcitrant contaminants [82]. In contrast, long-term DOC decrease in Lago Maggiore (NW Italy), due to progressively improving wastewater treatment, has resulted into faster photochemical reactions and, therefore, higher ability of the lake to carry out photochemical water depollution [83].

Therefore, keeping water ecosystems in good environmental health is overall the best way, to ensure that they also carry out the service of ensuring photochemical degradation of recalcitrant contaminants.

7. A photochemistry of water scarcity

A shown several times in section 5, climate change will often bring about a decrease in water availability: two such examples are water evaporation in lakes during summer, and the decrease in water flow and flow rate in rivers during droughts. Both scenarios have the potential to trigger a considerable increase in photochemical reaction rates. It can thus be easily guessed, that the importance of photochemical reactions will mostly increase in the future, and these reactions will have to be considered as important factors in the management of water environments. This is not good news overall, though, because scarce water is frequently affected by considerable pollution problems, which photochemistry only partially helps relieve. This also means, however, that predicting how a given contaminant will photochemically behave in a given environment will take on decisive importance, because much of its environmental impact will likely depend on photochemical reactions.

Hydrology and water dynamics, which are attracting very scarce attention by photochemists at present, are potentially more important than water chemistry in determining photochemical reaction rates, although water chemistry determines the prevailing photoreaction pathways that make up the overall rate.

8. Overview, and research gaps

The main message that is hopefully provided by the present review paper, is that research efforts in the field of surface-water photochemistry are currently focused on chemical process details, and are largely neglecting the correlation between hydrology and photoreaction kinetics. Model calculations suggest that water

Table 3. Summary of the main topics covered in this review paper.

Process/phenomenon	Main implication(s)
• Contaminant photodegradation kinetics	• Kinetics are mostly affected by seasonality, water depth, and the DOC. Water chemistry, and especially the DOC, determine the prevailing photoreaction pathways.
• Phototransformation intermediates	• Intermediates are often less harmful than the parent CECs, with some important exceptions. Water chemistry affects the photointermediate formation yields.
• Summertime lake stratification	• Photoreaction rates follow the order epilimnion > whole lake > hypolimnion, and the photochemical implications of lake stratification depend on where CECs are located.
• Water flow in rivers	• Usually, the slower the flow, the more favoured is photochemistry.
• Water browning	• Browning favours processes triggered by $^3CDOM^*$ and $^1O_2$, to the detriment of $^\bullet OH$, $CO_3^{\bullet-}$, and the direct photolysis.
• Ice cover	• Earlier ice melting in spring has the most favourable effect on photoreactions.
• Water evaporation	• Evaporative concentration enhances $^3CDOM^*$ and $^1O_2$ reactions, while $^\bullet OH$, $CO_3^{\bullet-}$, and the direct photolysis are unaffected.
• Variable precipitations	• Photochemical reactions should be enhanced during droughts.

dynamics have paramount importance in photochemistry, because they largely determine key parameters such as water column depth and flow rate/velocity, which in turn highly affect photoreaction kinetics. The consideration of real-case scenarios, where hydrology and photochemistry are both taken into account, might provide fully new insights into the factors that mostly affect the photochemical fate of pollutants. Furthermore, hydrology and water dynamics are the surface-water features that will be most modified by climate change. Therefore, they will provide the most interesting connections between photochemistry and climate.

The main topics covered here are summarised in table 3.

Concerning the photochemical reaction kinetics and pathways, there are still important knowledge gaps. The main ones are the following:

(a) In addition to the main PPRIs ($^\bullet OH$, $CO_3^{\bullet-}$, $^3CDOM^*$, and $^1O_2$), there are additional transient species that are currently lesser known. Some transients are potentially involved in the formation of toxic by-products (e.g. the brominating agent $Br_2^{\bullet-}$ in saltwater and seawater, and the nitrating agent $^\bullet NO_2$ in waters rich in nitrate and nitrite) [24, 84]. Other species are longer-lived, such as for instance peroxyl and phenoxyl radicals, and may be involved in the degradation of compounds that are peculiarly easy to be oxidised [85]. Very little is currently known about the occurrence of these species, and specific detection techniques are still to be developed.

(b) Key details on the formation pathways of some reactive oxygen species by irradiated CDOM (especially $^\bullet OH$, $O_2^{\bullet-}$, and H_2O_2) are still to be elucidated. The wavelength trends of the respective formation quantum yields also need additional studies [86, 87].

(c) The PPRIs $^\bullet OH$ and $^1O_2$ are known to occur to a much higher concentration in the hydrophobic cores of CDOM, compared to the bulk of the aqueous phase [88, 89]. The environmental implications of this finding for the photodegradation of hydrophobic pollutants are still to be elucidated.

(d) Photochemical models are currently focused on clear-sky scenarios. The photochemical implications of cloudy weather [90], and of atmospheric pollution shielding UV radiation, have full potential to become an active field of research.

(e) Photochemistry modelling software is currently available for free [91–93], and it can be very useful to outline many current and future environmental scenarios. The main limit to a wider use of software is currently represented by user friendliness. Development of more user-friendly packages, provided with, e.g. graphical interfaces, will certainly be very welcome by the environmental photochemistry community.

9. Conclusions

Photochemical processes, including direct photolysis and indirect photochemistry, play a key role in the degradation of recalcitrant contaminants in sunlit surface freshwaters. Photochemistry is a very important ecosystem service provided by water environments, which helps attenuate the problem of pollution, and

which (with few exceptions) is best operated by scarcely polluted water bodies. In a minority of cases, photochemical reactions produce toxic or mutagenic intermediates, and increase the environmental impact of contamination, to a degree that depends on environmental conditions. Understanding the photochemical interplay between contaminants and ecosystems is thus essential to figure out where, and when, photochemistry may be a concern rather than a service.

Photochemical reaction rates depend on water chemistry, depth, seasonality, and pollutant reactivity. In particular, photoreactions are the fastest during summer in shallow water bodies. High DOC values are often detrimental to phototransformation, with the eception of compounds that react peculiarly fast with $^3CDOM^*$ and/or $^1O_2$. Photochemical reactions and their environmental implications are also deeply affected by hydrology and water dynamics, which are at least as significant as the other factors, but have received comparatively lesser attention to date. For instance, summertime lake stratification introduces important differentiation between sunlit epilimnion and dark hypolimnion, with implications for photodegradation that depend on the location of the contaminants in the lake volume. Water scarcity in rivers should be favourable to photodegradation, by ensuring faster photoreaction kinetics because of shallower water, and by providing longer time scales for phoinduced processes (lower flow and flow velocity increase the in-stream residence time of water).

Climate change will impact water chemistry, with interesting implications on photochemistry in some Nordic environments (e.g. water browning, favouring $^3CDOM^*$ and $^1O_2$ reactions, while inhibiting $^{\bullet}OH$, $CO_3^{\bullet-}$, and the direct photolysis). At the same time, climate-related chemical changes are likely to be much less critical in temperate regions. Nevertheless, climate change has the potential to deeply modify photochemical reactions by altering hydrology, water dynamics, and the precipitation pattern (e.g. longer summertime stratification in lakes, shorter periods of ice cover, and altered water flow in rivers during droughts or floods). The photochemical implications of the latter phenomena have been scarcely investigated to date, and they clearly deserve more attention.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the author.

Ethical statement

This paper has not been submitted elsewhere, not even as preprint.

Conflict of interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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