Photochemical reactions in sunlit surface waters: Influence of water parameters, and implications for the phototransformation of xenobiotic compounds

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Photochemical reactions in sunlit surface waters: Influence of water parameters, and implications for the phototransformation of xenobiotic compounds

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Photochemical reactions may be important transformation pathways for biorefractory xenobiotic compounds in surface waters. These reactions can be divided into direct photolysis and indirect photochemistry. In the former, 10 a xenobiotic is transformed upon absorption of sunlight, in the latter sunlight is absorbed by natural photosensitisers (mainly chromophoric dissolved organic matter, nitrate and nitrite), which produce reactive transient species that induce transformation. Direct photolysis and indirect photochemistry are affected by sunlight irradiance, water chemistry and 15 depth, and they can undergo seasonal and long-term changes. This chapter gives an overview of the main photoreactions of significance for surface waters, including their implications for pollutant transformation and the possible generation of harmful intermediates.

1 Introduction

20 Photochemical reactions are potentially important pathways for the removal of biologically refractory xenobiotics from surface waters. The molecules that can undergo photochemical attenuation include several priority and emerging contaminants, such as pesticides, industrial chemicals, pharmaceuticals and personal care products.[1-3] Some of these compounds are directly released into the 25 environment, as in the case of pesticides, which may reach surface waters through different routes including soil runoff and groundwater contamination, followed by transport from ground to surface water.[4-6] In contrast, pharmaceuticals and personal care products (PPCPs) are usually found in wastewater and their release to environmental waters depends on the ability to escape removal by wastewater 30 treatment plants (WWTPs).[7-9]

Technologies used in WWTPs are highly variable depending on location and on the volume to be treated, but most WWTPs were not specifically designed to remove organic microcontaminants.[10] Their main focus is actually the abatement of wastewater organic matter and the control of pathogenic organisms, and a biological 35 treatment step is often employed. The high number of microorganisms in this step and the favourable conditions to biodegradation often ensure a satisfactory abatement of biodegradable chemicals. Moreover, biorefractory but poorly water-soluble compounds can be partitioned to biosolids and removed from the aqueous phase even without biodegradation. Such compounds are found in the sewage 40 sludge, and their possible impact on the environment will depend on the sludge management.[11-14] The most relevant substances to the WWTP-related contamination of surface waters are thus biorefractory and water-soluble chemicals.[15] In some

cases, the concentration of pharmaceuticals at the WWTP outlet can be higher than at the inlet. The rationale is that they undergo metabolism in the human body and are partially excreted in the glucuronidated form (i.e., bound to a molecule of glucuronic acid). The glucuronidated compounds often escape detection at the WWTP inlet, but they can be transformed by bacteria that detach the glucuronic moiety, to be finally released as the pristine molecules that can be detected in the discharged wastewater. While some removal may occur in the WWTP, de-glucuronidation can often more than compensate for this. This issue complicates the exact assessment of the ability of WWTP bacteria to degrade organic microcontaminants.[16-19] Such an ability is often not constant, as it depends on several issues such as seasonality (which affects the PPCP load in addition to the removal efficiency), latitude and operational parameters.[20,21]

A further route to environmental waters is typical of solar filters, a class of PPCPs that is also used in recreational activities such as sunbathing and swimming. In this case, the xenobiotics can directly reach surface waters without entering the WWTPs.[22] Priority and emerging contaminants can thus be emitted to the environment, and environmental waters in particular, by multiple pathways and this issue accounts for their occurrence in a very wide variety of environmental matrices. PPCPs have even been detected in the Antarctica near scientific bases, as a likely consequence of the environmental impact of the however limited human activity in that continent.[23] This is likely a different phenomenon than the significant occurrence of semi-volatile persistent organic pollutants in the polar regions, which is rather a consequence of long-range transport followed by condensation in cold areas (the so-called global distillation or grasshopper effect).[24,25]

The contaminants that are directly emitted into surface waters may undergo different processes, such as transport phenomena (including volatilisation and partitioning to suspended solids and sediments), biodegradation, and photochemical transformation.[26,27] In contrast, WWTP processing tends to select at the outlet the compounds that are most biorefractory and water-soluble, while removing the others. Therefore, it may be assumed that photochemistry is a potentially very important transformation pathway for the xenobiotics that occur in WWTP effluents. Environmental phototransformation is usually divided into direct photolysis and indirect photochemistry. In the case of direct photolysis, sunlight is absorbed by the xenobiotic and the absorption of sunlight triggers degradation. In the case of indirect photochemistry, sunlight is absorbed by naturally occurring molecules called photosensitisers, the main ones being nitrate, nitrite and chromophoric dissolved organic matter (CDOM).[28,29] The latter is the light-absorbing fraction of the natural organic materials that occur in surface waters.[30,31] The irradiation of the photosensitisers produces reactive transient species such as the hydroxyl ($^\bullet$OH) and carbonate radicals ($CO_3^{-\bullet}$), singlet oxygen ($^1O_2$) and CDOM triplet states (^{3}CDOM*). Such transients are reactive and can be involved in the transformation of dissolved xenobiotics. Generally speaking, a compound that absorbs sunlight may potentially undergo both direct photolysis and indirect phototransformation, while compounds that do not absorb sunlight can only be transformed by indirect photoprocesses.[28,29] Phototransformation can be involved in the natural attenuation of several pollutants that occur in surface waters, but it can also produce intermediates that may be more harmful (e.g. toxic or mutagenic) than the parent compound. Therefore, it is important to understand the kinetics and the pathways of the photochemical transformation of xenobiotic molecules, via the main

photoreactions that prevail in surface-water environments.

This report gives an outline of the photochemical reactions occurring in surface waters, and it also provides some examples of harmful intermediates that can be produced by such processes. The links between water chemistry, water depth and photochemistry are also discussed, which allows some tentative inferences to be made on the possible effect that climate change and other stressors can have on the chemistry and, therefore, on the photochemistry of surface waters.

2 Photochemical reactions in surface waters

2.1 Direct photolysis

To be operational in surface waters, the direct photolysis process requires that a xenobiotic compound is able to absorb sunlight. Moreover, the absorption of sunlight has to trigger some kind of transformation. In other words, the direct photolysis process depends on the substrate absorption spectrum (and on the extent by which it overlaps with the spectrum of sunlight) and on its photolysis quantum yield. It also depends on environmental features that will be discussed as well. Typical processes that can follow sunlight absorption are photoionisation, bond breaking, and the formation of excited states (singlet, triplet) that can undergo peculiar reaction pathways.[32] For instance, the direct photolysis of 2-chlorophenol causes ring contraction via the singlet state and dechlorination upon triplet reactivity.[33,34]

Among the environmental features that can affect the direct photolysis process, the main ones are the irradiance and the spectrum of sunlight, water depth and water absorption spectrum. The irradiance of sunlight depends on the time of the day, on seasonality, on latitude and on weather issues. Weather is predictable with difficulty, but the mid-latitude sunlight irradiance would be maximum on midday during fair-weather summertime (specifically, at the summer solstice). Sunlight irradiance typically increases as latitude decreases but, in the tropical belt, the summer solstice is no longer the day of maximum irradiance. For instance, at the equator the irradiance is maximum in the spring and fall equinox under fair-weather conditions. The higher is the total sunlight irradiance, the higher is usually also the UV radiation intensity in both absolute and relative terms. The UV irradiance has key importance for many xenobiotics that absorb sunlight prevalently or exclusively in the UV region.[35,36]

Differently from ultra-pure water, natural waters absorb sunlight and this absorption process interferes with the direct photolysis reactions by decreasing the available irradiance. The absorption spectrum of surface waters, in particular in the environmentally significant wavelength range (i.e. above 300 nm), is largely coincident with the absorption spectrum of CDOM.[31] Only at elevated visible wavelengths (> 500 nm) there may be important contributions from chlorophylls and water itself to absorption. The spectral region above 500 nm, while very important in the determination of the water colour that has implications for e.g. satellite measurements,[37,38] is usually of little importance for the photochemistry of surface waters. Photochemical reactions are mainly linked with radiation in the 300-500 nm wavelength range, where CDOM is by far the main absorber.[39] Nitrate can account for the majority of light absorption around 200-230 nm, but this range is not environmentally significant.[40] CDOM is a very complex mixture of compounds of both allochthonous (soil runoff, atmospheric deposition) and autochthonous origin

(aquagenic processes, mostly biologic), and its absorption spectrum is usually an almost featureless exponential decay of the absorbance with increasing wavelength.[31] Therefore, the absorption spectra of both natural waters and CDOM at 300-500 nm (and often a bit beyond) can be conveniently approximated with an exponential function of the form:
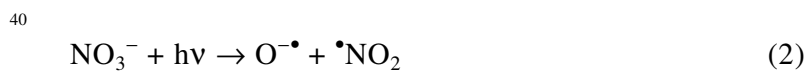
$$A_1(\lambda) = A_o \, e^{-S\lambda} \qquad (1)$$

where λ is the wavelength, $A_1(\lambda)$ is the water absorbance referred to an optical path length of 1 cm, and A_o is a constant that depends on several issues including the amount of organic matter in the water body (measured as the dissolved organic carbon, DOC). The quantity S is the so-called spectral slope, which is usually inversely proportional to the molecular weight of CDOM.[41] This means that high molecular weight CDOM tends to absorb long-wavelength sunlight to a larger extent than the low molecular weight fraction. A closer look at S has suggested that it can undergo small but not negligible variations with wavelength, which may suggest peculiar features connected with CDOM nature and transformation.[42,43]
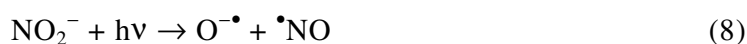
Largely due to the water absorption spectrum, water depth highly affects photochemical reactions because of the attenuation of sunlight as depth increases. The consequence is that the lower depths of water bodies are scarcely illuminated by sunlight, differently from the surface layer where the photoreactions reach the highest rates. Therefore, photochemistry is most effective in shallow water bodies.[44] Because CDOM absorbs short-wavelength sunlight to a higher extent than long-wavelength sunlight (e.g. the UVB more than the UVA and the visible), the penetration depth of sunlight is shorter at shorter wavelengths.[45] Water depth has thus a negative impact on all the photochemical reactions but, most notably, on those that are triggered by short-wavelength radiation.

2.2 Indirect photochemistry

Several photosensitisers occur in surface waters and produce reactive species upon absorption of sunlight. The best known photosensitisers are nitrate, nitrite and CDOM. Nitrate absorbs sunlight in the UVB and (to a lesser extent) UVA regions and light absorption triggers the production of $^\bullet OH$ radicals with quantum yield $\Phi \sim 0.01$. Note that the equilibrium $^\bullet OH \leftrightarrows O^{-\bullet} + H^+$ has $pK_a \sim 12$, thus the production of $^\bullet OH$ via reactions (2,3) in typical surface-water conditions is not really pH-dependent.[46,47] However, a dependence of $^\bullet OH$ photoproduction from pH might arise from the photoisomerisation of nitrate to peroxinitrite ($ONOO^-$, reaction (4)), which is not a $^\bullet OH$ source while its conjugated acid HOONO (peroxynitrous acid, $pK_a \sim 7$) partially is. As a consequence, the production of $^\bullet OH$ upon nitrate photolysis decreases with increasing pH.[48]

$$NO_3^- + h\nu \rightarrow O^{-\bullet} + {}^\bullet NO_2 \qquad (2)$$
$$O^{-\bullet} + H^+ \leftrightarrows {}^\bullet OH \qquad (3)$$
$$NO_3^- + h\nu \rightarrow ONOO^- \qquad (4)$$
$$ONOO^- + H^+ \leftrightarrows HOONO \qquad (5)$$
$$HOONO \rightarrow NO_3^- + H^+ \qquad (6)$$
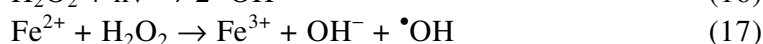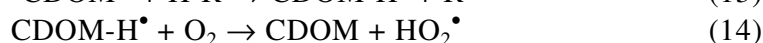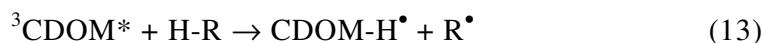$$HOONO \rightarrow {}^\bullet OH + {}^\bullet NO_2 \qquad (7)$$

Nitrite absorbs UVB and, most notably, UVA radiation to a larger extent than nitrate, and radiation absorption by nitrite induces the photogeneration of $O^{-\bullet}/^{\bullet}OH$ as well. Nitrite can also be oxidised by $^{\bullet}OH$ to produce $^{\bullet}NO_2$ (reaction (10)). Due to UVA vs. UVB absorption and higher photolysis quantum yield, the environmental photochemistry of nitrite is more efficient than that of nitrate and often compensates (or even more than compensates) for the lower concentration values that nitrite reaches in surface waters compared to nitrate.[49] Moreover, absorption at higher wavelengths ensures that nitrite photochemistry is operational at lower depths compared to the nitrate one. In addition to $^{\bullet}OH$ photoproduction, nitrate and nitrite both yield $^{\bullet}NO_2$ (reactions (1) and (8-10)) that is a nitrating agent, responsible for instance for the photogeneration of toxic nitroaromatic compounds in particular environments.[50,51]

$$NO_2^- + h\nu \rightarrow O^{-\bullet} + {}^{\bullet}NO \qquad (8)$$
$$O^{-\bullet} + H^+ \leftrightarrows {}^{\bullet}OH \qquad (9)$$
$$NO_2^- + {}^{\bullet}OH \rightarrow {}^{\bullet}NO_2 + OH^- \qquad (10)$$

The photochemistry of CDOM is much more complex compared to that of nitrate and nitrite. Moreover, CDOM is a source of several photoinduced transients and not only of $^{\bullet}OH$. Among CDOM chromophores, there are several groups (e.g. aromatic carbonyl and quinones) that easily undergo inter-system crossing (ISC) to yield the triplet states with elevated quantum yield, which is at the basis of the rather efficient production of $^3CDOM^*$. The transients $^3CDOM^*$ can undergo vibrational deactivation, reaction with dissolved compounds (e.g. the xenobiotics) or with dissolved O_2 to produce singlet oxygen ($^1O_2$).[52]

$$CDOM + h\nu \text{ —(ISC)} \rightarrow {}^3CDOM^* \qquad (11)$$
$$^3CDOM^* + O_2 \rightarrow CDOM + {}^1O_2 \qquad (12)$$
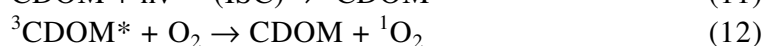
The generation of $^{\bullet}OH$ by irradiated CDOM is much more controversial as far as the actual pathways are concerned. A first issue is that CDOM yields H_2O_2 under irradiation (see e.g. reactions (13-15), where HR is a dissolved organic compound), which can produce $^{\bullet}OH$ by direct photolysis or via the Fenton reaction.[53,54] Moreover, there is also a H_2O_2-independent (and still largely unknown) generation pathway of $^{\bullet}OH$ from irradiated CDOM.[55,56]

$$^3CDOM^* + H\text{-}R \rightarrow CDOM\text{-}H^{\bullet} + R^{\bullet} \qquad (13)$$
$$CDOM\text{-}H^{\bullet} + O_2 \rightarrow CDOM + HO_2^{\bullet} \qquad (14)$$
$$2\ HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (15)$$
$$H_2O_2 + h\nu \rightarrow 2\ {}^{\bullet}OH \qquad (16)$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (17)$$

Finally, the carbonate radical ($CO_3^{-\bullet}$) is produced upon oxidation of carbonate and bicarbonate by $^{\bullet}OH$ and of carbonate by $^3CDOM^*$.[57] In addition to the generation reactions, the scavenging processes of the photoinduced transients are also important for the photochemistry of surface waters. The radical $^{\bullet}OH$ is a strong oxidant and reacts at near diffusion-controlled rates with many dissolved compounds.[58] In surface waters, $^{\bullet}OH$ is mainly produced by irradiation of CDOM, nitrate and nitrite and it is mainly consumed by reaction with dissolved organic matter (DOM, which

also includes the chromophoric fraction CDOM) and inorganic carbon (the latter process yielding $CO_3^{-\bullet}$). In brackish/saline waters, bromide is usually the main $^\bullet OH$ scavenger.[29,59] The reaction with DOM is also the main removal process for $CO_3^{-\bullet}$, while $^1O_2$ mainly undergoes deactivation to O_2 upon collision with the water solvent and $^3CDOM^*$ mainly undergoes vibrational deactivation and reaction with O_2.[29,60] The main processes involving photosensitisers and transients in surface waters are summarised in Figure 1.
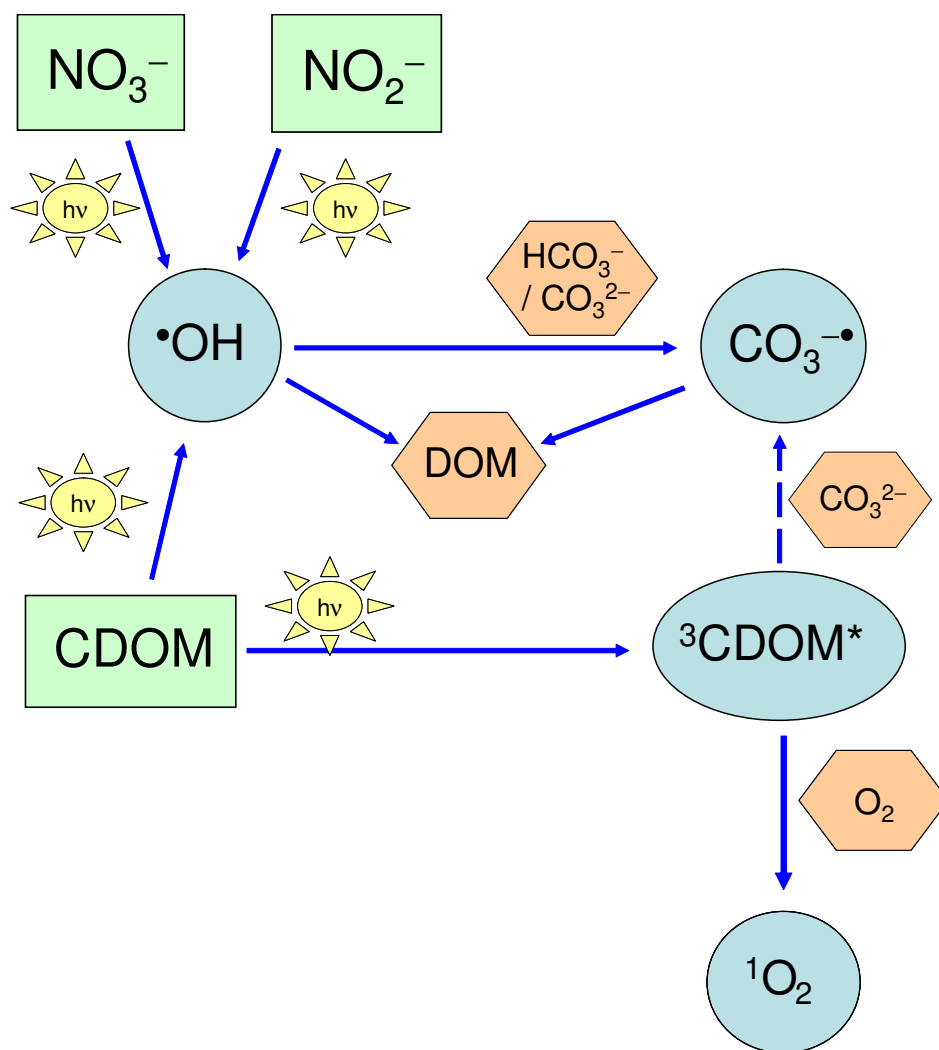
Figure 1. Schematic of the main indirect photochemistry processes taking place in surface waters and involving photosensitisers (represented by rectangles) to produce reactive transient species (circles). The main scavengers are represented by the hexagones.

Due to the budget between photochemical generation and scavenging, the transient species $^\bullet OH$, $CO_3^{-\bullet}$, $^1O_2$ and $^3CDOM^*$ reach relatively low steady-state concentrations in surface waters. Due to its elevated reactivity, $^\bullet OH$ is efficiently scavenged and its typical steady-state concentrations are in the range of 10^{-18}-10^{-16} mol L^{-1}. The other transient species are usually one-two orders of magnitude more concentrated than $^\bullet OH$ but, because they are also less reactive, the interplay between

reactivity and concentration gives different results depending on the actual environment and the dissolved compound that undergoes degradation.[61] The reaction pathways followed by different xenobiotics will be dealt with in the following section. Here it is important to point out that indirect photochemistry processes depend on the sunlight irradiance and, similarly to the direct photolysis, they are favoured in shallow waters during the summer season.

3 Implications for xenobiotic phototransformation

3.1 Reaction pathways followed by different compound classes

The ability of a given compound to undergo direct photolysis and/or one or more of the indirect photochemistry reaction pathways depends on the features of both the compound itself and the surrounding environment. The compound reactivity towards the different photochemical pathways is quantitatively assessed by its direct photolysis quantum yield and the second-order reaction rate constants with the photogenerated transients. For instance, the fungicide dimethomorph would mainly undergo indirect photodegradation by $^\bullet$OH in waters that are poor in organic matter, and by ^{3}CDOM* in DOM-rich waters. In the same water conditions, the solar filter 2-ethylhexyl 4-(dimethylamino)benzoate would mainly undergo direct photolysis independently of the organic matter content.[62,63] This section summarises the available knowledge on the main reaction pathways that tend to be followed by different xenobiotics (on top of which, the environmental features will often decide which is the main phototransformation reaction).

Among PPCPs, the direct photolysis may be irrelevant for β-blockers but it may be important for some β-lactam antibiotics (e.g. amoxicillin and cefazolin), sulfonamides (e.g. sulfamethoxazole and sulfisoxazole), some fluoroquinolones, as well as non-steroidal anti-inflammatory drugs such as diclofenac, ibuprofen and naproxen.[2,3] It may also be an important or even the main phototransformation pathway in the case of solar filters.[63,64] It is unfortunately not easy to make predictions about the importance of direct photolysis, even among compounds that share a related chemical structure. For instance, in the case of phenylurea herbicides, photolysis may be quite important for chlortoluron, fairly important for isoproturon, metoxuron and diuron, and irrelevant for fenuron.[65]

The radical $CO_3^{-\bullet}$ is poorly reactive toward most organic compounds, but there are major exceptions concerning some easily oxidised substrates. Therefore, $CO_3^{-\bullet}$ may be important for the phototransformation of aromatic amines, of sulphur-containing molecules such as organic sulphides and mercaptans, as well as phenolates.[66-68] Singlet oxygen often shows limited reactivity, too, but it is for instance the main environmental reactant for the phototransformation of chlorophenolates.[69] Many knowledge gaps still exist concerning the reactivity of ^{3}CDOM*, which might be an important reactant towards a wide variety of substrates. Anyway, triplet sensitisation (i.e., reaction with ^{3}CDOM*) is thought to play an important role in the degradation of several phenols, phenylurea herbicides and some sulfonamide antibiotics.[52] Finally, $^\bullet$OH is very reactive but its role is partially limited by the very low steady-state concentrations that it reaches in most surface-water environments. Its importance tends to be higher for the degradation of compounds that are poorly reactive toward other phototransformation pathways (e.g. in the cases of toluene or nicotine).[70,71]

3.2 Effects of water chemistry on photochemical reactions

Water chemistry is a major environmental factor that promotes or inhibits particular phototransformation pathways. The direct photolysis processes involving xenobiotic compounds are typically inhibited by the presence of CDOM, which competes with the pollutants for sunlight irradiance.[1,72] Considering that CDOM (similarly to DOM) typically occurs to a higher extent in waters with elevated levels of dissolved organic carbon (DOC), the direct photolysis processes are usually inhibited in high-DOC waters. The radical $^\bullet OH$ is photogenerated by irradiation of nitrate, nitrite and CDOM and it is mainly scavenged by reaction with DOM. Considering that (C)DOM is an important $^\bullet OH$ source but, at the same time, its main scavenger, the steady-state $[^\bullet OH]$ is usually lower as the DOC is higher. Other factors that affect $[^\bullet OH]$, although to a usually lesser extent than the DOC, are the concentration values of nitrate and nitrite ($^\bullet OH$ sources, which positively correlate with $[^\bullet OH]$) and those of carbonate and bicarbonate ($^\bullet OH$ sinks, which negatively correlate with $[^\bullet OH]$).[29]

The DOC trend of $[CO_3^{-\bullet}]$ is even more marked compared to that of $[^\bullet OH]$, because the organic matter both scavenges $CO_3^{-\bullet}$ and inhibits its formation by consuming $^\bullet OH$ (most of $CO_3^{-\bullet}$ is in fact formed by reaction of $^\bullet OH$ with carbonate and bicarbonate). Therefore, the $CO_3^{-\bullet}$ reactions are typical processes that are favoured in low-DOC waters.[73] Another issue is that the formation of $CO_3^{-\bullet}$ from $^\bullet OH$ requires bicarbonate and most notably carbonate, which has a considerably higher reaction rate constant with the hydroxyl radical compared to bicarbonate. As a consequence, $CO_3^{-\bullet}$ is formed to a higher extent as the water pH and the inorganic carbon content are higher.[29,57] For instance, Figure 2 shows the $CO_3^{-\bullet}$ formation rate that results from the oxidation of carbonate and bicarbonate by $^\bullet OH$, based on the acid-base equilibria between the inorganic carbon species and on their reaction rate constants with $^\bullet OH$. The $CO_3^{-\bullet}$ formation rate is plotted relative to the rate at pH 6, which is taken as reference, assuming a constant value of the total inorganic carbon. It can be seen from the figure that the $CO_3^{-\bullet}$ formation rate is very low below pH 5 and becomes quite high above pH 8.5. However, its expected variations are not large in the very common pH interval ranging from 7 to 8.

Usually, there is also a positive correlation between $[^\bullet OH]$ and $[CO_3^{-\bullet}]$, which is understandable when considering that $CO_3^{-\bullet}$ mostly derives from $^\bullet OH$. For this reason, $[CO_3^{-\bullet}]$ is often higher in waters that are rich in nitrate and nitrite.[29,73]

The other two transients species ($^3CDOM^*$ and $^1O_2$) are generated by irradiated CDOM and are scavenged, respectively, by dissolved oxygen (plus internal conversion that hardly depends on solutes) and by collision with the solvent. Therefore, the steady-state $[^3CDOM^*]$ and $[^1O_2]$ are typically higher in high-DOC waters. Furthermore, $[^3CDOM^*]$ is higher in anoxic waters and $[^1O_2]$ in oxygenated ones. Among all water chemistry parameters, the DOC is certainly the most important one to enhance or inhibit the different photochemical reactions.[29] A schematic of the pathways that tend to prevail at different DOC values is provided in Figure 3. Of course, the figure reports a general view of the possible processes. Those that really prevail under definite conditions also depend on the reactivity of a given substrate toward each pathway (for instance, if a xenobiotic does not undergo direct photolysis, the relevant pathway will never be important irrespective of the water DOC value).

With the above-cited limitations, Figure 3 can be read as follows (provided that a given pathway is relevant for a particular xenobiotic): reactions with $CO_3^{-\bullet}$ are most

favoured in low-DOC waters, while intermediate DOC values (e.g. around 2 mg C L^{-1}) may enhance $^\bullet OH$ reactions and the direct photolysis. Direct photolysis and $^\bullet OH$ reactions are actually inhibited at high DOC, but to a lower extent than the $CO_3^{-\bullet}$ processes; moreover, DOM usually inhibits the $^\bullet OH$-induced reactions to a higher extent than CDOM inhibits the direct photolysis. Therefore, if $^\bullet OH$ reaction and direct photolysis are the only operational pathways, $^\bullet OH$ usually predominates at low DOC and direct photolysis at high DOC.[65,74] Finally, high-DOC waters tend to favour the processes induced by $^3CDOM*$ and $^1O_2$.[29,52]

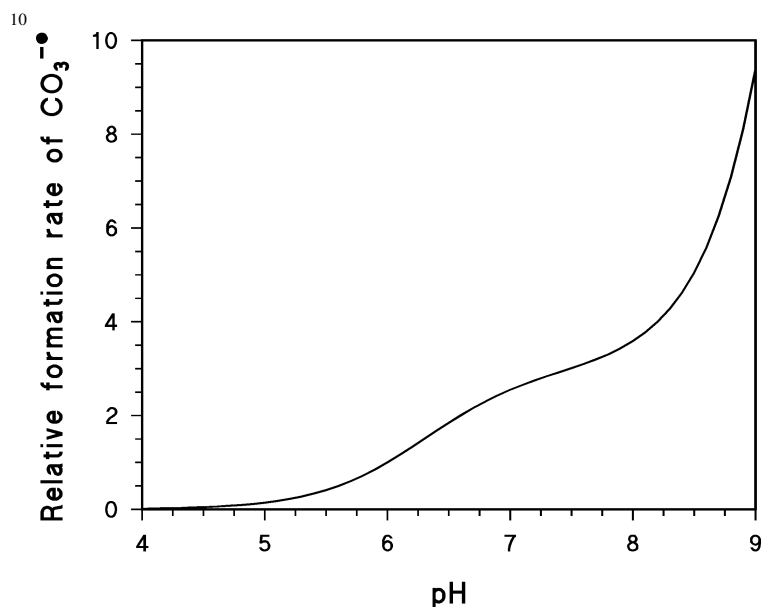**Figure 2.** pH trend of the formation rate of $CO_3^{-\bullet}$ from $^\bullet OH$ oxidation of carbonate and bicarbonate, relative to the value at pH 6 (taken as reference and equal to 1).
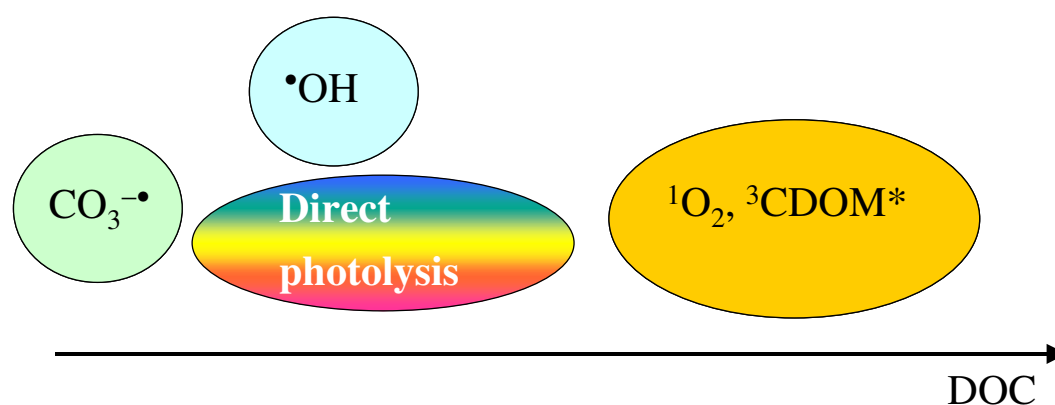

Figure 3. Schematic indication of the different photochemical processes that tend to be favoured for increasing values of the dissolved organic carbon (DOC). The direction of the DOC increase is shown by the arrow.

3.3 Photochemical production of harmful transformation intermediates

As anticipated in the Introduction section, photochemical transformation can lead to the attenuation of xenobiotics but it can also induce the production of harmful compounds. Typically, different photochemical pathways tend to produce different intermediates, and/or the same intermediates with different yields, which has implications for the generation of toxic or mutagenic compounds. For instance, phenylurea herbicides are known to produce toxic N-formyl compounds upon reaction with $^\bullet$OH. Moreover, similarly or equally toxic compounds can also be formed by direct photolysis of the phenylureas metoxuron and diuron. In contrast, the reaction between phenylureas and ^{3}CDOM* should not produce toxic intermediates.[75-78] These considerations, together with the discussion reported in section 3.2, suggests that the photochemical generation of toxic species from phenylureas would be inhibited in high-DOC waters.[65] A similar conclusion is afforded for the toxic intermediate 2-methyl-4-chlorophenol, which is produced from the herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA), in similar yields, by direct photolysis and $^\bullet$OH reaction.[79]

Another example is the formation of toxic isobutylacetophenone (IBAP) from ibuprofen. Production of IBAP with fairly elevated yields (25-30%) takes place upon direct photolysis and ^{3}CDOM* reaction, while the IBAP yield from ibuprofen + $^\bullet$OH is very low. Therefore, toxic IBAP would be typically formed in high-DOC waters.[80] The photochemical formation of mutagenic acridine from carbamazepine occurs with similar yields (3-3.5%) upon both direct photolysis and $^\bullet$OH reaction. The two processes are also the main transformation pathways of carbamazepine in surface waters, which suggests that acridine would be formed photochemically in low but constant yield under varying environmental conditions.[81]

Gemfibrozil is known to produce a strongly mutagenic species upon direct photolysis.[82,83] On the basis of the scheme reported in Figure 2, one could hypothesise that the mutagenic compound would be formed preferentially at intermediate DOC values. A similar prediction could be made for the production of toxic species by direct photolysis of the antibiotic cefazolin.[74,84] The basic form of the antimicrobial agent triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) is known to produce a potentially harmful dioxin by direct photolysis and ^{3}CDOM* reaction, in the latter case with even higher yield. One could hypothesise that dioxin formation is enhanced at high DOC, where the ^{3}CDOM* processes are favoured, but this is little relevant because the direct photolysis is usually the prevailing phototransformation pathway. In this case the key water parameter is actually the solution pH, because protonated triclosan (which prevails at pH < 8) does not yield dioxins upon photochemical transformation.[85,86]

The above examples suggest that water chemistry (most notably, DOC and pH) could be a major factor that directs the photochemical formation of harmful intermediates, with the notable exception of the production of acridine from carbamazepine. The examples were taken from literature papers in which the formation of the intermediates was differentiated on the basis of the actual photochemical pathways. Although the reported cases are only exemplary and not exhaustive, this "phototoxicology" approach is still relatively rare and such details about the photochemical pathways are known so far for a limited number of compounds. A more extended knowledge would be very helpful in elucidating the environmental impact of xenobiotics as a function of the environmental conditions.

4 Possible impacts of long-term changes

In the previous sections it was shown that water chemistry may play a very important role in the phototransformation of xenobiotics and in the production of harmful transformation intermediates. The chemical composition of surface waters can undergo seasonal changes because of biological and chemical processes. For instance, nitrate often has winter maxima because it is consumed by algae during summer, while the consumption of CO_2 because of photosynthesis produces summer maxima of pH in the surface water layer. Calcium and alkalinity often have summer minima because of $CaCO_3$ precipitation in warm water, while the DOC may be high in summer due to the elevated biological productivity.[87] Superposed to the seasonal changes there may be long-term trends that can be directly or indirectly associated with human impact. An example of a direct impact is the discharge of nutrients into water bodies, which causes eutrophication and often increases the values of DOC and possibly those of inorganic nitrogen (e.g. nitrate and nitrite, unless nitrogen is the limiting factor for algal growth). If nutrient inputs change over time, the water chemistry and, as a consequence, its photochemistry may be affected as a consequence. Controls on discharges could for instance decrease the nutrient inputs, often decreasing the water DOC and shifting photochemistry from $^3CDOM^*/^1O_2$ to $CO_3^{-\bullet}/^\bullet OH$ processes.[88]

Another cause of long-term modification is climate change. In the case of lake water, increases in alkalinity and pH are often the main indices that climate change is operating on water chemistry. The rationale is the enhanced dissolution of salts such as $CaSO_4$ in warmer water, where Ca^{2+} can be up-taken but it is not transformed by biota while sulphate is transformed into organic sulphur species with H^+ consumption. A pH increase may lead to higher dissolution of CO_2 into the water, thereby increasing the levels of carbonate and bicarbonate.[89] Higher alkalinity and higher pH would favour the reactions induced by $CO_3^{-\bullet}$, but such changes could be easily offset by variations in the DOC that is a major $CO_3^{-\bullet}$-controlling factor.[73] The DOC is a key water photochemistry parameter and it is affected by climate, but its variations are not easily predictable. In nordic environments, warming would likely produce an increased export of organic matter from soil to surface waters, with consequent "brownification" and DOC increase.[90] In this case, climate change would shift photochemical processes towards $^3CDOM^*/^1O_2$ reactions. In sub-tropical environments, desertification might produce a long-term decrease of organic matter in soil and, as a consequence, in surface waters,[91] which would rather favour $^\bullet OH/CO_3^{-\bullet}$-induced photoprocesses. In temperate areas, climate-related DOC variations are often small and they could be easily offset by other human impacts such as changes in nutrient inputs. It is clear that much additional work is still needed to elucidate the impact of climate on surface-water photochemistry.

5 Conclusions

Direct photolysis and indirect photochemistry (reactions with $^\bullet OH$, $CO_3^{-\bullet}$, $^1O_2$ and $^3CDOM^*$) are potentially important pathways for the transformation of biorefractory xenobiotics in surface waters. Photochemistry is favoured in shallow waters, which can be thoroughly illuminated by sunlight, during fair-weather summertime. The prevailing photochemical reactions that a given compound may undergo in surface waters depend on its reactivity towards the different photochemical pathways and on

the features of the water environment. The latter may favour or inhibit definite photoprocesses depending on chemical parameters such as the DOC, pH, nitrate and nitrite concentration. The DOC is a major photochemical parameter and it can direct the photoreaction pathways by selective enhancement or inhibition. Thus, $CO_3^{-\bullet}$ reactions are favoured at low DOC while $^3CDOM^*/^1O_2$-induced processes are enhanced at high DOC. Moreover, reactions with $^\bullet OH$ and the direct photolysis are usually favoured at intermediate DOC values. The water pH has a considerable impact on $CO_3^{-\bullet}$, the steady-state concentration of which increases with increasing pH. Nitrate and nitrite levels are usually less important than the DOC, but high values of these parameters may lead to elevated steady-state concentrations of $^\bullet OH$ and $CO_3^{-\bullet}$.

The cited photoprocesses can affect the transformation pathways of xenobiotics and, as a consequence, the formation of intermediates. Starting from the same substrate, different photochemical pathways may induce the formation of different intermediates and/or of the same intermediates in different yields. These intermediates can sometimes be more toxic or mutagenic than the parent compound. In this case, the connection between water chemistry, enhanced photoreaction pathways and intermediate formation yields allows the prediction of which environmental conditions are the most or the least favourable to the production of harmful compounds. This issue has a remarkable importance in the assessment of the environmental impact of a xenobiotic substance in different water environments.

Water chemistry can undergo seasonal and long-term changes. As far as the latter are concerned, climate change is a potentially interesting driver because it affects water parameters such as alkalinity, pH and DOC that, in turn, could affect photochemistry. Unfortunately, the DOC variations connected with climate may be different in different environments and they are hardly predictable at temperate latitudes. In this case, it may be very difficult to disentangle the climatic effect from other stressors (e.g. nutrient discharges into water bodies) that could have comparable or even higher effects on the water DOC.

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