Photochemical reactions in sunlit surface waters

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Abstract

Photochemical processes are important pathways for the transformation of biologically refractory organic compounds, including harmful pollutants, in surface waters. They include the direct photolysis of sunlight-absorbing molecules, the transformation photosensitised by the triplet states of chromophoric dissolved organic matter (CDOM), and the reaction with photochemically generated radical transients. Differently from the direct photolysis, the other processes (often indicated as indirect photochemistry) can also induce the phototransformation of compounds that do not absorb sunlight. The excited triplet states of CDOM, ^{3}CDOM*, play a very important role in surface-water photoprocesses, both directly and as sources of singlet oxygen ($^1O_2$). The most important reactive radical species in surface waters are the hydroxyl radical $^\bullet$OH, the carbonate radical $CO_3^{-\bullet}$, and various peroxy radicals that can be produced upon degradation of dissolved organic matter (DOM), either chromophoric or not. Further radical species such as $^\bullet NO_2$, $Cl_2^{-\bullet}$ and $Br_2^{-\bullet}$ can be involved in the generation of harmful degradation intermediates such as aromatic nitro, chloro, and bromoderivatives.

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1. Introduction

The persistence in surface water bodies of dissolved organic compounds, including both natural organic molecules and man-made xenobiotics and pollutants, strongly depends on their transformation kinetics due to abiotic and biological processes. Transformation by micro-organisms can be very important for readily biodegradable molecules, including most notably the nutrients. However, even in the presence of biodegradable compounds, biological processes may produce biorefractory intermediates that undergo further biodegradation with difficulty [1]. In these cases, phototransformation can play an important role for the processing of these dissolved species. It may also happen that biorefractory organic matter becomes bioavailable after some degree of abiotic processing, with the consequence that the combination of abiotic and biological degradation can lead to the complete mineralisation [2]. Furthermore, phototransformation is very important for the removal of a number of emerging pollutants, which hardly undergo biodegradation in either surface waters or wastewater treatment plants [3,4].

The abiotic transformation processes include hydrolysis, oxidation mediated by dissolved oxidising species or by metal oxides, such as Fe(III) and Mn(III,IV) (hydro)oxides, and light-induced reactions [5]. Hydrolysis may produce bond cleavage, implying for instance the loss of a lateral functional chain. Hydrolytic reactions are often acid or base-catalysed, but at the ~neutral pH values typical of surface waters the effects of catalysis may not be very marked [6]. Among the oxidising species dissolved in surface waters, there are a number of reactive transients produced upon sunlight irradiation of photoactive compounds [7]. In the dark, Fe and Mn (hydr)oxides can be involved in charge-transfer processes with compounds that are able to form surface complexes (e.g. salicylate and oxalate). The oxidation of the organic molecule would often occur at the expense of the photoreductive dissolution of the oxide, with formation of water-soluble Fe^{2+} and Mn^{2+} [8,9].

In some cases the removal of a compound from surface waters involves, instead of chemical transformation, the phase transfer from the dissolved phase to suspended solids or sediment, or the volatilisation from the surface water layer [10]. In all these cases the molecule is simply shifted to a different phase, where it can be involved into transformation processes that can be very different from those in water (e.g. atmospheric reactions) [11]. In some cases the original molecule or its transformation intermediates can return back to the water body, as a consequence of dissolution from sediment or of wet and dry deposition from the atmosphere [12].

Many organic pollutants such as polycyclic aromatic hydrocarbons, pesticides, pharmaceuticals and their transformation intermediates are refractory to biological degradation. In such cases the abiotic transformation processes represent major removal pathways from surface waters. Within the abiotic transformation reactions of xenobiotics, those induced by sunlight are receiving increasing attention because of their importance in the removal of the parent molecules and the possible production of harmful secondary pollutants [13,14]. The present chapter will be dedicated to the description of photochemical reactions in sunlit surface waters. They include the direct photolysis of the parent compound upon absorption of sunlight, the transformation sensitised by photoexcited CDOM, and in particular by its humic and fulvic components, and the reaction with photogenerated,

reactive transients that often have the ability of oxidising the organic substrates [15]. It is the case of $^{\bullet}OH$, $CO_3^{-\bullet}$ and $^1O_2$, while other radical transients such as $^{\bullet}NO_2$, $Cl_2^{-\bullet}$ and $Br_2^{-\bullet}$ could produce secondary pollutants [16].

Direct photolysis, although very important in defining the lifetime of many photolabile compounds in surface waters, will seldom lead to complete depollution. It produces instead a number of transformation intermediates that in some cases may be even more harmful than the parent molecule [17,18]. Te complete removal of the xenobiotic species, e.g. by mineralisation, requires the reaction with oxidising transients such as $^{\bullet}OH$, or microbial processing. In many a case the mineralisation is much slower than the primary step of phototransformation of the parent molecule [19].

Finally, while important recent advances have been carried out recently in the modelling of the photochemical fate of pollutants in surface waters [20,21], consideration of the further transformation and phototransformation pathways till complete mineralisation is lagging much behind.

2. Direct photolysis processes

The direct photolysis of a molecule is the consequence of photon absorption. The absorbed spectral photon flux density by a given compound at the wavelength λ, $p_a(\lambda)$, can be expressed in [einstein L^{-1} s^{-1} nm^{-1}], where 1 einstein = 1 mole of photons [22]. The quantity $p_a(\lambda)$ is related to the absorbance $A_\lambda = \varepsilon_\lambda\, b\, c$, where ε_λ is the molar absorption coefficient (decadic), b the optical path length of the solution, and c the concentration of the compound. The quantities b and c are usually expressed in cm and in mol L^{-1}, respectively, in which case the unit of ε_λ is [L mol^{-1} cm^{-1}], and A is dimensionless. Be $i_o(\lambda)$ the spectral photon flux density of incident radiation in solution, expressed in [einstein L^{-1} s^{-1} nm^{-1}]. It is $p_a(\lambda) = i_o(\lambda)\,(1 - 10^{-\varepsilon\lambda\, b\, c})$. In the environment the incident radiation is not monochromatic, and it is interesting to know the absorbed photon flux P_a in a given wavelength interval, say $\lambda_1 \leq \lambda \leq \lambda_2$. The following expression holds for P_a [einstein L^{-1} s^{-1}]:

$$P_a = \int_{\lambda_1}^{\lambda_2} p_a(\lambda)\,d\lambda = \int_{\lambda_1}^{\lambda_2} i_o(\lambda)\cdot\left(1-10^{-\varepsilon_\lambda\cdot b\cdot c}\right)d\lambda \tag{1}$$

Furthermore, in a surface water body the intensity of the incident radiation is not constant over the whole water column. Absorption and scattering phenomena will reduce the radiation intensity as the depth of the water column increases. As a consequence, the spectral photon flux density of incident radiation at the depth x will be a function of both depth and wavelength, as $i_o(\lambda,x)$. Under the simplified assumption that the scattering of radiation is negligible compared to absorption, the Lambert-Beer relationship applies as $i_o(\lambda,x) = i_o(\lambda)\,10^{-\alpha(\lambda)\,x}$, where $i_o(\lambda)$ is the spectral photon flux density of incident radiation on top of the water column and $\alpha(\lambda)$ is the attenuation coefficient [21]. The coefficient $\alpha(\lambda)$ depends on the absorption spectrum of water and is largely accounted for by

CDOM absorption [23]. The measure unit of $\alpha(\lambda)$ is cm^{-1} if x is in cm. In the most general case, for $\lambda_1 \leq \lambda \leq \lambda_2$ and $0 \leq x \leq d$, P_a is given by equation (2), where $2.3 = \ln 10$:

$$P_a = 2.3 \cdot \int_{\lambda_1}^{\lambda_2} \int_0^d i_o(\lambda) \cdot 10^{-\alpha(\lambda)x} \cdot \varepsilon_\lambda \cdot c \, dx \, d\lambda \qquad (2)$$

Figure 1 reports the spectral fluence rate density of sunlight [24] at different values of the water column depth, for a given absorption spectrum $\alpha(\lambda)$ of water. It is apparent the rapid decrease of the fluence rate density within the water column, in particular at the shorter wavelengths.
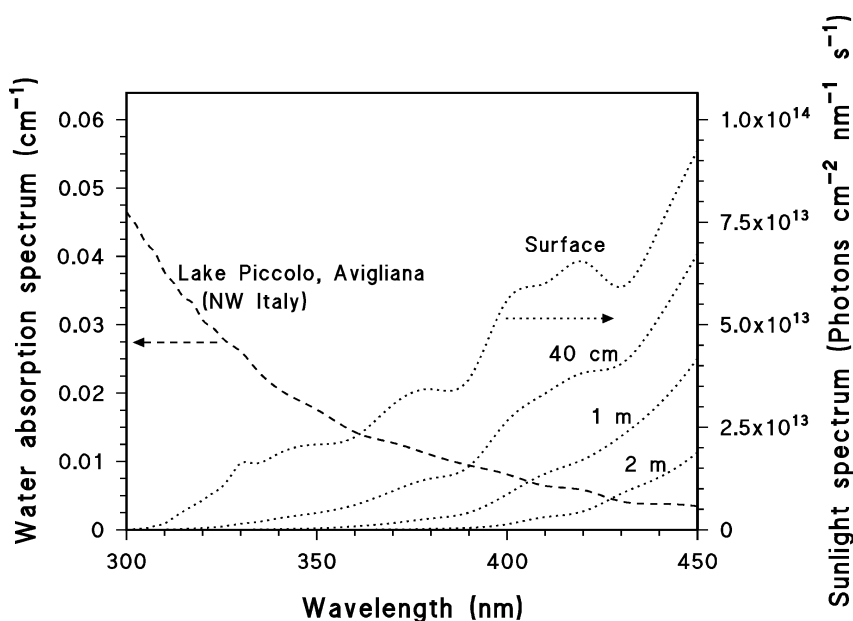
Figure 1. Absorption spectrum $\alpha(\lambda)$ of water from Lake Piccolo in Avigliana (NW Italy), and spectral fluence rate density of sunlight at different depths of the water column, calculated according to the Lambert-Beer approximation. Note that the spectral fluence rate density is the spectral photon flux density times the Avogadro's constant.

The incident spectral photon flux density at a given depth d is a key factor in defining the rate R of direct photolysis, which is directly proportional to absorbed photon flux P_a. However, not all of the absorbed photons are able to induce photolysis to the same extent. This fact is reflected into the photolysis quantum yield Φ, which measures the probability that the absorption of a photon actually induces photolysis. It is $0 \leq \Phi \leq 1$ and, in the most general case, the quantum yield of photolysis is not constant with wavelength [25].
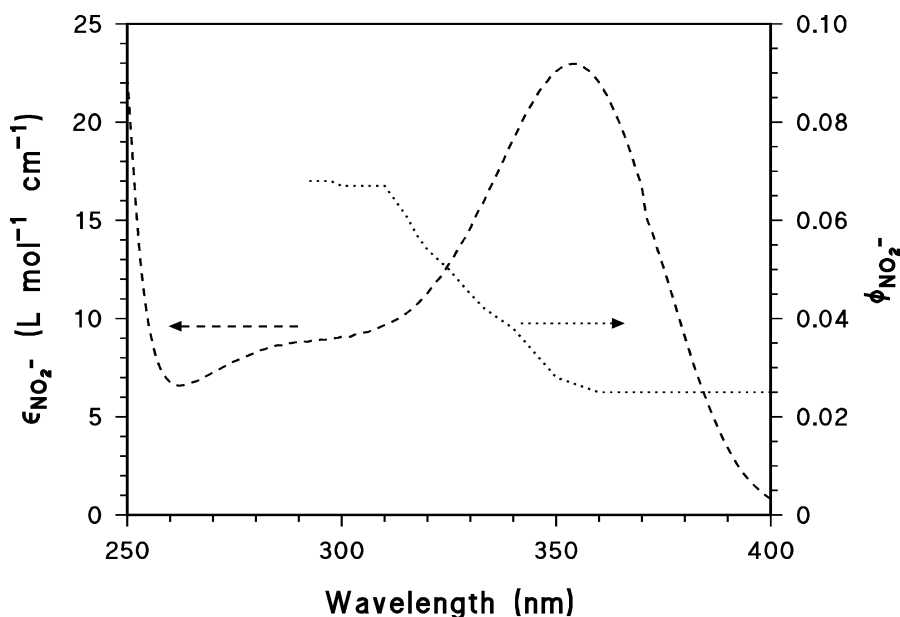
Figure 2. Absorption spectrum and photolysis quantum yield Φ of nitrite in the wavelength interval 250-400 nm. Note the two absorption bands of nitrite at 280 and 365 nm, with different Φ.

Figure 2 shows the case of nitrite, which has an absorption band at around 280 nm with photolysis quantum yield $\Phi = 0.068$, and one at 365 nm with $\Phi = 0.025$ [26]. Nitrite yields $^\bullet OH + {}^\bullet NO$ upon absorption of UV radiation [27]:

$$NO_2^- + h\nu + H^+ \rightarrow {}^\bullet OH + {}^\bullet NO \qquad (3)$$

For irradiation at the wavelength λ the rate of photolysis is $r(\lambda) = \Phi(\lambda)\, p_a(\lambda)$, and the rate R of photolysis for $\lambda_1 \leq \lambda \leq \lambda_2$ and $0 \leq x \leq d$ is [25]:

$$R = 2.3 \cdot \int_{\lambda_1}^{\lambda_2} \int_0^d \Phi(\lambda) \cdot i_o(\lambda) \cdot 10^{-\alpha(\lambda)x} \cdot \varepsilon_\lambda \cdot c \ dx\, d\lambda \qquad (4)$$

Direct photolysis has received much attention concerning the degradation of xenobiotic compounds of high environmental concern, such as polycyclic aromatic hydrocarbons (PAHs), haloaromatics (including some pesticides and their metabolites) and, more recently, pharmaceuticals [13,14].

About PAHs, in the case of naphthalene [28] the direct photolysis proceeds through photoionisation/deprotonation with the net loss of a H atom, followed by either oxidation to naphthoquinone, or ring-opening with formation of monoaromatic carboxylic acids and aldehydes (Figure 3).
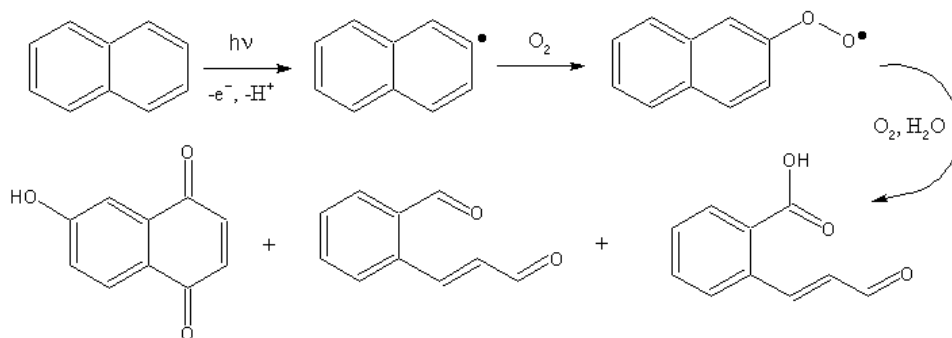
Figure 3. Pathways of the direct photolysis of naphthalene in aqueous solution.

Quite interestingly the quinone derivatives are more photochemically active than the parent PAHs, and could undergo more extensive photoprocessing. For instance, the direct photolysis of anthracene [29] in aerated aqueous solution yields 9,10-anthraquinone that is able to absorb a larger fraction of sunlight compared to anthracene [30], and undergoes photo-oxidation as a consequence (Figure 4).

The photoreactivity of anthracene could be strongly substrate-dependent. Indeed, the direct photolysis of anthracene on silica [31] proceeds via dimerisation in addition to the oxidation to anthraquinone (Figure 5). Furthermore, the semiquinone and hydroquinone derivatives are likely to arise on reduction of irradiated anthraquinone [32]. The surface of silica might significantly enhance photodimerisation processes compared to the homogeneous aqueous solution [33], and SiO_2 might be an interesting model for inorganic colloids in surface waters [34].
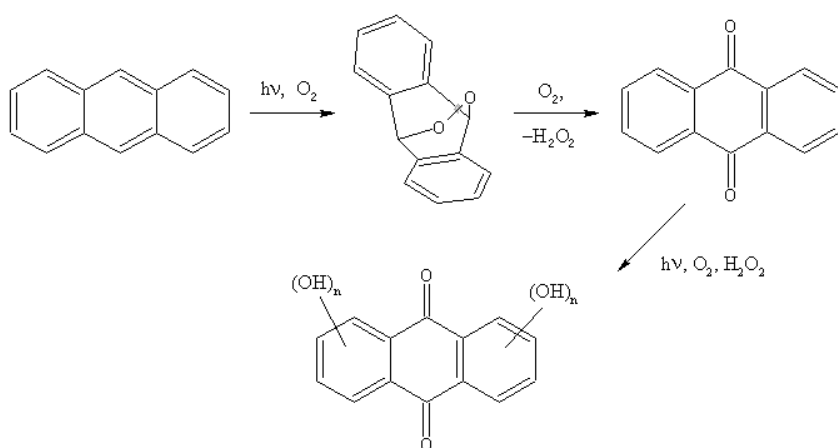
Figure 4. Pathways of the direct photolysis of anthracene in aqueous solution.

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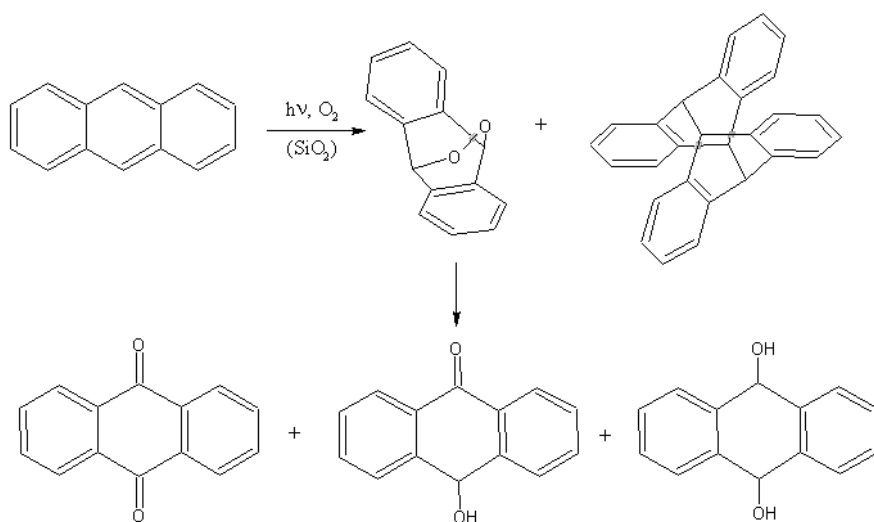
Figure 5. Pathways of the direct photolysis of anthracene on the surface of silica.

Chlorophenols are a class of chlorinated aromatic compounds of considerable environmental concern because they can be released as by-products of various industrial activities [35]. They can also be formed as secondary pollutants upon environmental transformation of various pesticides, mainly the chlorophenoxy-acetic and propionic acids [36,37], and the antimicrobial agent triclosan [38,39]. An important issue in the direct photolysis pathways of chlorophenols is the difference between the *ortho-* and the *para-*substituted ones. In both cases the absorption of radiation leads to the first excited singlet state, which is then transformed into the first excited triplet state by inter-system crossing (ISC) [13]. The main difference is that, in the case of *ortho-*chlorophenols [40], the first excited singlet state is sufficiently long-lived to allow chemical reactivity in alternative to ISC, resulting into ring contraction and loss of HCl to form a cyclopentadienyl carboxyaldehyde (Figure 6). The ring-contraction process would be particularly significant for the phenolate anions [41]. In contrast, the first excited triplet state would mainly react by dechlorination [42], either reductive (with the participation of $HO_2^{\bullet}$) to give the corresponding phenol, or involving oxygen with the final formation of dihydroxyphenols and quinones (Figures 6,7).

Many xenobiotic compounds of environmental concern undergo different photolysis processes in their protonated or deprotonated form, such as 2-methyl-4-chlorophenoxyacetic acid (MCPA). The photolysis pathways are, therefore, strongly dependent on pH. In the case of MCPA the protonated form undergoes molecular rearrangement, while the deprotonated one follows a dechlorination-hydroxylation pathway (Figure 8). Interestingly, due to significant reactions between MCPA excited states and dissolved organic compounds, the direct photolysis quantum yield of MCPA is also linked to the water content of DOM [43].

Dichlorprop, 2-(2,4-dichlorophenoxy)propionic acid, an herbicide that is extensively used in flooded rice farming, is an interesting compound because it acts as a precursor of various chlorinated phenols in the environment, such as 4-chlorocatechol [44] by direct photolysis (Figure 9) as well as 2,4-dichlorophenol and 4-chloro-2-methylphenol upon hydrolysis in aqueous solution

[45]. Another important xenobiotic that can undergo direct photolysis in surface waters is the antimicrobial agent triclosan (Figure 12), which is particularly interesting because its photocyclisation produces a dichlorodibenzodioxin [46]. Interestingly, recent evidence suggests that dioxin formation from triclosan can also take place upon reaction with [3]CDOM* [47].
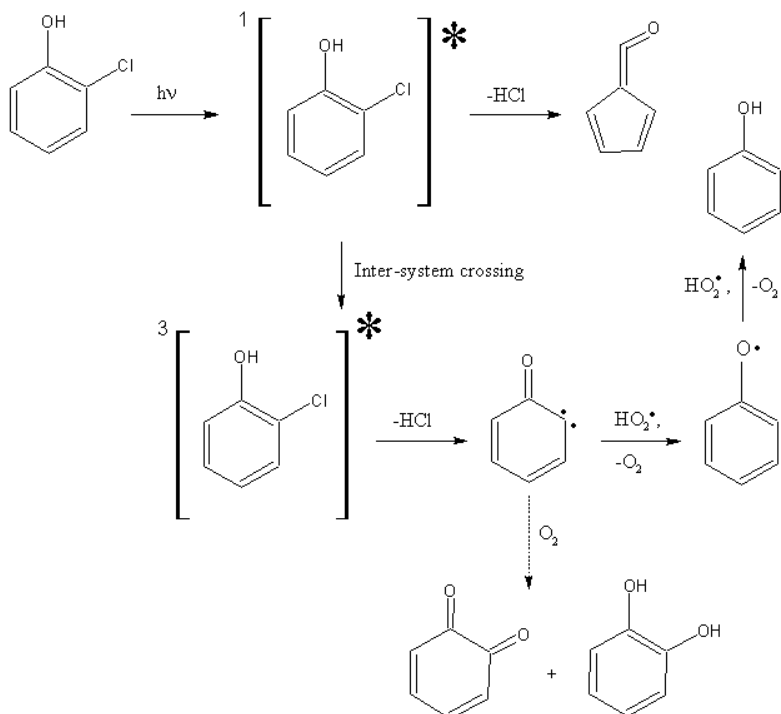
Figure 6. Processes involved in the direct photolysis of 2-chlorophenol in aqueous solution.
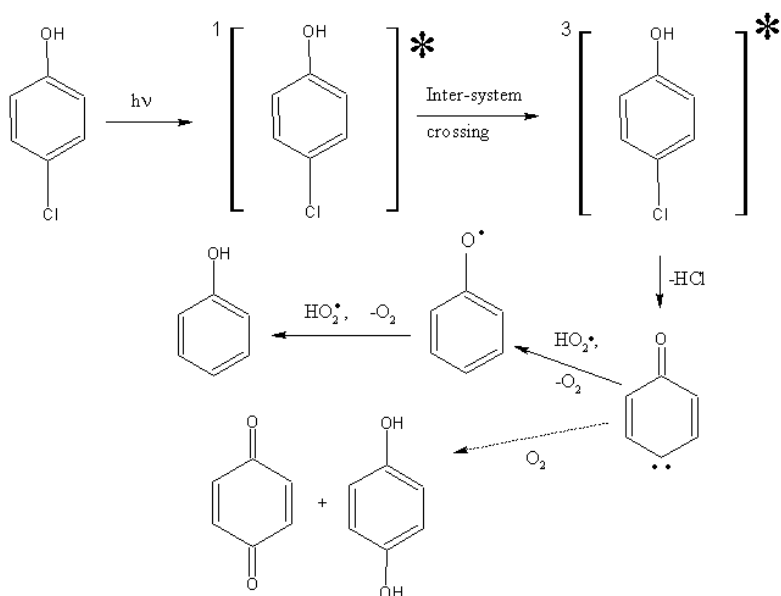
Figure 7. Processes involved in the direct photolysis of 4-chlorophenol in aqueous solution.
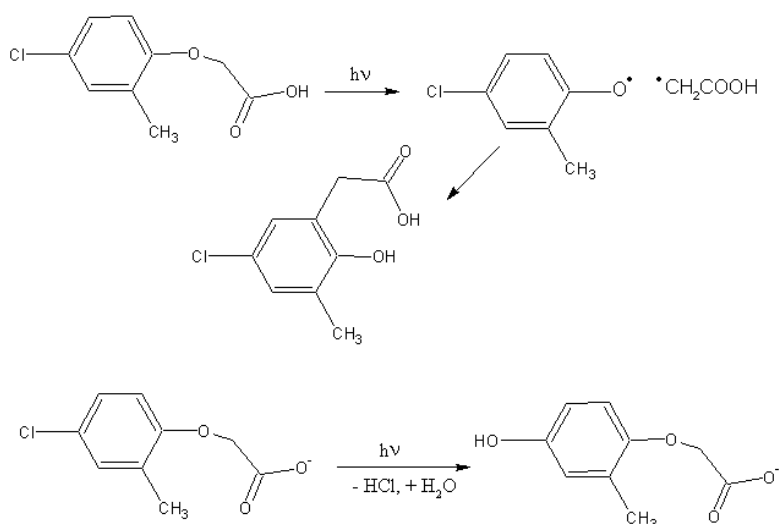
Figure 8. Processes involved in the direct photolysis of MCPA in aqueous solution (both neutral and anionic forms).
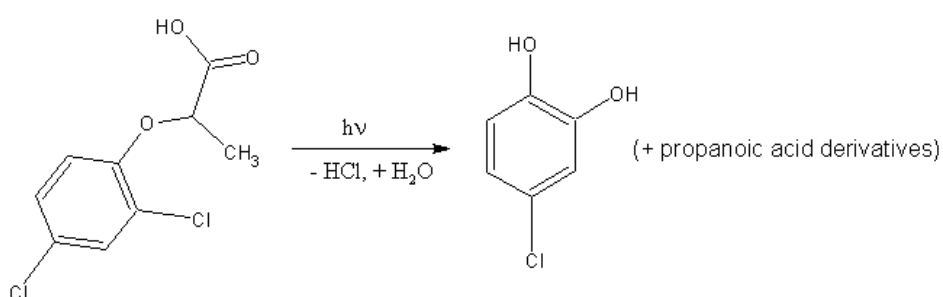
Figure 9. Processes involved in the direct photolysis of dichlorprop in aqueous solution.
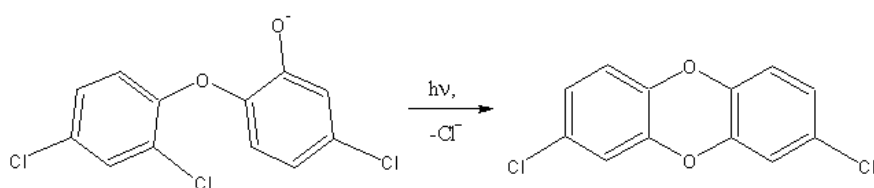
Figure 10. Photocyclisation of triclosan in aqueous solution.

The case of triclosan is a good example of a photolysis process that yields an intermediate that is more harmful than the parent compound. This finding is even more significant because direct photolysis is most likely the main sink of triclosan in surface waters [46,47]. Indeed the photodegradation of a pollutant is not always beneficial to the environment, and the environmental and health impact of the transformation intermediates is to be considered as well [19,48]. Another interesting example is the direct photolysis of the anti-epileptic drug carbamazepine [17,18,49,50] that yields, among the other intermediates, the mutagenic acridine.

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In summary, direct photolysis can be an important process in the degradation of sunlight-absorbing compounds in surface waters, depending on the irradiation intensity (which is maximum in shallow and clear water bodies), the extent of sunlight absorption by the molecule under consideration, and the photolysis quantum yield. The disappearance of the initial molecule is not necessarily the end of the story, however, because transformation intermediates with different properties, and sometimes even more harmful than the parent compound, can be formed due to direct photolysis [51,52].

3. Transformation photosensitised by chromophoric dissolved organic matter (CDOM)

Natural dissolved organic matter in surface waters consists of both autochthonous (aquagenic) material, mainly made up of aliphatic chains that do not absorb radiation (polysaccharides, complex carbohydrates, peptides, proteins), and of allochthonous compounds that derive from soil erosion such as fulvic and humic substances [1]. The latter contain a significant percentage of aromatic groups that absorb sunlight, at such an extent that DOM is the most important radiation absorber in surface waters [23]. A very interesting issue is that sunlight-absorbing DOM (CDOM) is made up of a significant amount of quinonoid substances and aromatic carbonyls, which are known photosensitisers [20]. Therefore, the excitation of CDOM by sunlight can cause the degradation of other dissolved molecules, which do not need to absorb sunlight themselves. The photosensitising ability of CDOM largely depends on the reactions that can be induced by its excited triplet states, $^3CDOM^*$ [53].

As shown in Figure 11, the absorption of radiation by a sensitiser causes the transition from the ground state (which for organic molecules is usually a singlet one, S_o) to a vibrationally excited state of an excited singlet state, S_n (where n = 1, 2…). It usually follows vibrational deactivation to the ground vibrational state of S_1 (also in the cases in which n > 1), at which point various alternatives are possible. A very common one is the thermal loss of energy, e.g. by collision with the solvent, to reach back the ground state S_o. Some molecules lose energy by radiation, emitting fluorescence photons. Rigid systems, such as the condensed rings of PAHs, are more likely to undergo fluorescence emission than the flexible structures. An alternative can be the ISC, in particular when the ground vibrational state of S_1 can have the same or similar energy as an excited vibrational state of the first triplet state (T_1) [25].

Vibrational relaxation will bring the sensitiser from an excited to the ground vibrational state of T_1. The subsequent loss of energy to reach S_o can follow various pathways. A possibility is the thermal energy loss, by a combination of vibration and collision. Solid systems (and some liquid ones) may also emit phosphorescence radiation. An interesting alternative in the present context is the chemical reactivity. The excited triplet states are sufficiently long-lived to allow transfer of energy, electrons or atoms (usually H ones) to or from other molecules.
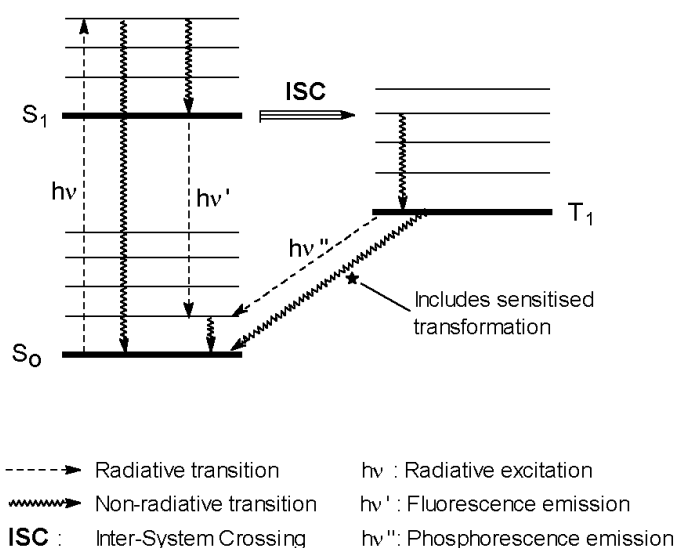
Figure 11. Schematic of the processes that follow the absorption of radiation by a sensitiser.

Be S the sensitiser and M a generic molecule. In the following reactions the superscripts [1] and [3] indicate singlet and triplet states, respectively, and * represents surplus energy [25].

$$^1S + h\nu \rightarrow {}^1S^* \text{ — ISC} \rightarrow {}^3S^* \tag{5}$$
$$^3S^* + M \rightarrow {}^1S + M^* \tag{6}$$
$$M^* \rightarrow \text{Products} \tag{7}$$
$$^3S^* + M \rightarrow S^{-\bullet} + M^{+\bullet} \tag{8}$$
$$^3S^* + M \rightarrow (S+H)^\bullet + (M\text{-}H)^\bullet \tag{9}$$
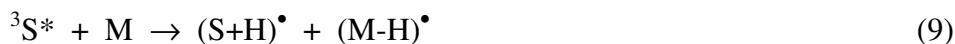
The sensitiser would usually undergo reduction when reacting with M. The reduced sensitiser ($S^{-\bullet}$, $(S+H)^\bullet$) could be further transformed or be recycled back to S by dissolved oxygen (reactions 10,11):

$$S^{-\bullet} + O_2 \rightarrow S + O_2^{-\bullet} \tag{10}$$
$$(S+H)^\bullet + O_2 \rightarrow S + HO_2^\bullet \tag{11}$$

When reactions (10,11) take place, limited or no transformation of S is observed in the process. If S is maintained and M is transformed, the transformation of M photosensitised by S is a photocatalytic process where S is the photocatalyst [32,54]. This does not always happen, however. Different reactions than (10,11) could for instance take place, leading to a net transformation of S [55]. As an alternative, photoexcited S could react with ground-state S [32], the latter behaving as M in reactions (5-9). In such a case, even if $S^{-\bullet}$ or $(S+H)^\bullet$ is recycled back to S by oxygen, the transformation of S would proceed via the oxidised $S^{+\bullet}$ or $(S\text{-}H)^\bullet$.

Reactions (5-9) suggest that photoexcited CDOM can induce the transformation of dissolved organic compounds. The processes involving definite sensitiser molecules are known to a

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considerably better extent than the reactions induced by CDOM as a whole. In particular the transformation reactions of phenols, sensitised by quinones or aromatic carbonyls have been subject to many studies. Figure 12 reports the processes taking place in the presence of phenol and of 3,4-dimethoxybenzaldehyde under irradiation. The photoexcited triplet state of 3,4-dimethoxybenzaldehyde is able to oxidise phenol to the phenoxyl radical, causing its degradation. In contrast, the reduced 3,4-dimethoxybenzaldehyde is re-oxidised by oxygen and no net transformation of the sensitiser is observed in this case. Differently from this ca<se, however, 2- and 3-methoxybenzaldehyde undergo transformation in the presence of phenol under irradiation [54].
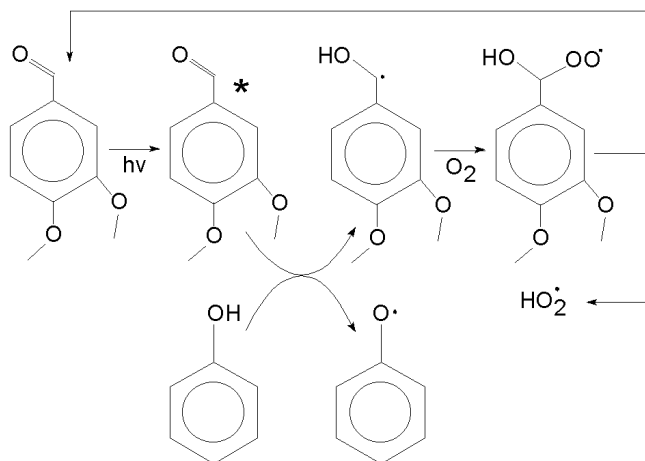
Figure 12. Processes that occur in the presence of phenol and 3,4-dimethoxybenzaldehyde under irradiation.

Another interesting group of sensitisers is represented by the quinonoid compounds, among which the anthraquinones are the most photochemically active species. Due to its water solubility, anthraquinone-2-sulphonate (AQ2S) is the most studied molecule of its class. Radiation-excited AQ2S (which gives ^{3}AQ2S* with fairly elevated ISC yield) is able to oxidise both ground-state AQ2S and phenol, producing hydroxylated AQ2S in the former case (however, AQ2S hydroxyderivatives are also formed via evolution of ^{3}AQ2S*) and phenol dimers via the phenoxyl radical in the second. Reduced AQ2S is recycled back to AQ2S by oxygen, but the net transformation of AQ2S is assured by further reactions that involve ^{3}AQ2S* and/or the oxidised AQ2S intermediates [32,56].

By use of phenol derivatives as probe molecules it has been possible to evaluate as 8×10^{-15} M the steady-state concentration of the ^{3}CDOM* in the surface layer of the Greifensee lake, Switzerland [57]. 2,4,6-Trimethylphenol (TMP) is particularly reactive toward ^{3}CDOM* [58] and the relevant bimolecular reaction rate constant ($k_{TMP} = 1.6 \times 10^9$ M^{-1} s^{-1}) has been measured adopting a competitive model [59], in which the scavenging of ^{3}CDOM* by TMP is able to reduce the production of ^{1}O$_2$ from ^{3}CDOM* itself and ground-state triplet oxygen. The lower generation of ^{1}O$_2$ significantly reduces the transformation of furfuryl alcohol into pyranone, a very sensitive

reaction for the detection of singlet oxygen (see Figure 13). If $[^3CDOM^*] = 8 \times 10^{-15}$ M, the time required for $^3CDOM^*$ to transform 50% TMP would be around 15 hours (note that the half-life time of TMP for reaction with $^3CDOM^*$, in seconds, is given by $t_{1/2} = \ln 2 \, (k_{TMP} \, [^3CDOM^*])^{-1}$).

The transformation processes photosensitised by CDOM have been demonstrated to play a substantial role in the degradation of important classes of pollutants such as phenols, phenylurea herbicides, and sulfonamide antibiotics [20]. In the case of the herbicides isoproturon and diuron, the modelling of $^3CDOM^*$-assisted phototransformation has been able to predict with precision their vertical profiles in the Greifensee lake (Switzerland), thereby confirming the important role of CDOM in the relevant phototransformation [60].
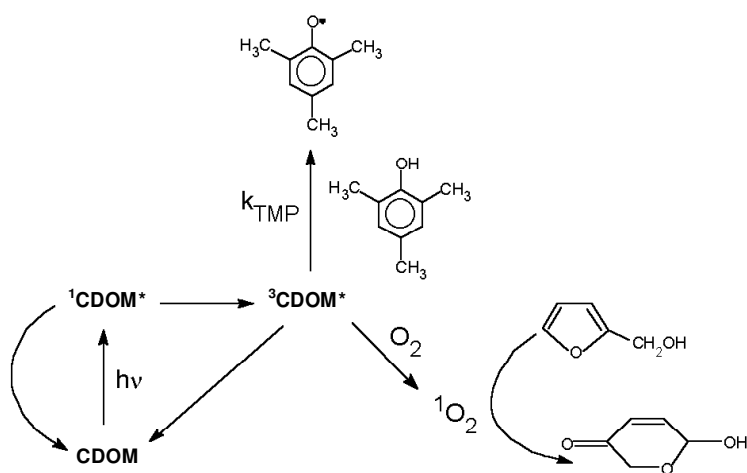
Figure 13. Competitive kinetic model used to measure the rate constant k_{TMP} between $^3DOM^*$ and 2,4,6-trimethylphenol.

Photoexcited $^3CDOM^*$ also induces the oxidation of As(III) to As(V) [61], and of Sb(III) to Sb(V) [62]. Interestingly, some pollutants undergo both direct photolysis upon absorption of sunlight, and transformation photosensitised by $^3CDOM^*$. In this case both CDOM and the substrate compete for radiation absorption, and the effect of CDOM on the phototransformation kinetics can be variable depending on the substrate [53]. If photodegradation in laboratory systems is enhanced in the presence of CDOM, it is a strong indication of an important role played by indirect photolysis processes (among which $^3CDOM^*$ might be significant). If, on the contrary, CDOM inhibits photodegradation, this is often interpreted as an index that $^3CDOM^*$ photoreactions are not important compared to the direct photolysis of the substrate. However, the situation is often more complex because CDOM, as the main sunlight absorber in surface waters, can preserve an active photochemistry even at depths where the direct photolysis is no longer important. For instance, in the case of triclosan, the fact that CDOM inhibits photodegradation in laboratory systems (where direct photolysis predominates due to the shallow water column) is not in contrast with the fact that

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[3]CDOM*-sensitised transformation may be the main photoreaction in deep water [47]. Indeed, it is very possible that [3]CDOM*-induced processes may be important for the transformation of a larger number of compounds than commonly believed [63,64].
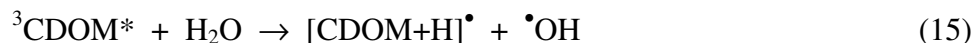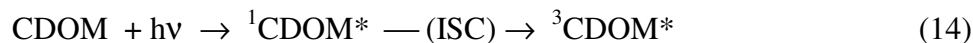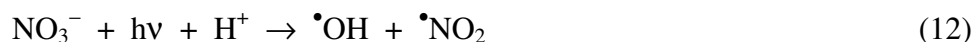
Anyway, it is much more likely for [3]CDOM* to enhance degradation of substrates that undergo direct photolysis at a limited extent. Among the classes of compounds that show faster degradation in the presence of CDOM under irradiation there are sulphur-containing molecules [65-67], phenylurea herbicides [60], Mirex [68], carbaryl [69], and some cyanobacterial toxins [70]. In most of these cases it is very interesting to assess the role of [3]CDOM* versus other reactive transients produced by irradiated CDOM (such as $^\bullet OH$ and $^1O_2$).

4. Reactions induced by the hydroxyl radical, $^\bullet OH$

The hydroxyl radical is one of the most reactive transients that are formed in natural waters. The high reactivity implies that this species can be involved into the degradation of refractory pollutants, some of which (including most notably alkanes, chloroalkanes such as butyl chloride, benzene and toluene) would be almost exclusively degraded by $^\bullet OH$. Quite interestingly, the cited molecules can also be used as probes to quantify $^\bullet OH$ in surface water samples because they would undergo limited direct photolysis or side reactions with $^3CDOM*$ and $^1O_2$ [71]. However, the high reactivity of $^\bullet OH$ is also a drawback for its overall significance as an oxidant in surface waters. The very vast majority of $^\bullet OH$ radicals, which are formed upon irradiation of photoactive precursors, are in fact scavenged by DOM and carbonate/bicarbonate, so that only a small fraction is available for the degradation of xenobiotics [72].

The main photochemical $^\bullet OH$ sources in surface waters are nitrate, nitrite, and CDOM. The former two species produce $^\bullet OH$ upon photolysis [27], while the production of $^\bullet OH$ by irradiated CDOM is a more complex phenomenon [73-75]. First of all, there are at least a H_2O_2-dependent and a H_2O_2-independent pathways. The latter might involve oxidation of water by $^3CDOM*$, which could be supported by some findings concerning model sensitisers [76] but it is not at all a general feature of the excited triplet states [77]. As an alternative, hydroxylated and peroxyl groups in photoprocessed CDOM could undergo photolysis to produce $^\bullet OH$. The H_2O_2-dependent pathway of CDOM is better known, and a possible explanation for it could be the occurrence of photo-Fenton reactions in the presence of Fe traces. They could involve the photolysis of complexes between Fe(III) and natural organic compounds (reactions 16,17, where L is an organic ligand of Fe) [78,79]. Fe(III) could also produce $^\bullet OH$ directly, upon photolysis of its hydroxocomplexes (mainly $FeOH^{2+}$). However, $FeOH^{2+}$ is present at significant levels only under acidic conditions (typically at pH < 5), which are little representative of surface waters [80]. A major exception could be acidic mine drainage water, where Fe(III) photolysis could be a major source of $^\bullet OH$ [81]. Hydroxyl groups on the surface of Fe(III) oxide colloids (=Fe^{III}-OH) would also be able to yield $^\bullet OH$ upon photolysis, but several studies suggest that the efficiency of such an heterogeneous process is very low

[49,80,82]. Accordingly, if Fe plays a significant role in the generation of $^\bullet OH$ radicals under non-acidic conditions, it would mainly be through its possible interaction with DOM (reactions 16,17).

$$NO_3^- + h\nu + H^+ \rightarrow {}^\bullet OH + {}^\bullet NO_2 \tag{12}$$

$$NO_2^- + h\nu + H^+ \rightarrow {}^\bullet OH + {}^\bullet NO \tag{13}$$

$$CDOM + h\nu \rightarrow {}^1CDOM^* —(ISC)\rightarrow {}^3CDOM^* \tag{14}$$

$${}^3CDOM^* + H_2O \rightarrow [CDOM{+}H]^\bullet + {}^\bullet OH \tag{15}$$

$$Fe^{III}\text{-}L + h\nu \rightarrow Fe^{2+} + L^{+\bullet} \tag{16}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \tag{17}$$

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + {}^\bullet OH \tag{18}$$

As far as the relative role of nitrate, nitrite and CDOM as $^\bullet OH$ sources is concerned, on average it is $CDOM > NO_2^- > NO_3^-$ [83]. Such a statement is reinforced by the fact that the maximum absorption of sunlight by nitrate lies in the UVB region (316-320 nm depending on the season), where the absorption by other water components is maximum, while that of nitrite is located in the UVA (360-370 nm). CDOM can produce $^\bullet OH$ radicals even upon absorption of visible radiation (although with lower quantum yields compared to UVB and UVA [84]) and, because the visible is less attenuated by absorption phenomena than for the UV, CDOM photochemistry is still operational in deeper waters compared to nitrite and nitrate [85,86].

The main scavengers of $^\bullet OH$ radicals in surface freshwaters are, in the order, DOM, inorganic carbon (carbonate and bicarbonate), and nitrite [72,86]. In contrast, bromide is the main $^\bullet OH$ scavenger in seawater [4]. From the budget of the $^\bullet OH$ formation and scavenging processes in natural waters one can derive the steady-state [$^\bullet OH$] that, for the surface water layer, usually ranges between 10^{-16} - 10^{-15} M [4,20]. In contrast, the $^\bullet OH$ concentration can be considerably lower in the less illuminated lower depths of a water body [72]. The [$^\bullet OH$] values can now be easily modelled as a function of water chemistry and depth [20], and Figure 14 reports for instance the comparison between the measured and modelled [$^\bullet OH$] in a surface freshwater sample irradiated in the laboratory. Although the significance of the comparison is decreased by the limited water column depth that is allowed by laboratory set-ups, the agreement between model and experiments is more than satisfactory [87].

In addition to [$^\bullet OH$], the other important factor that defines the $^\bullet OH$-related lifetime of an organic compound is its second-order reaction rate constant with $^\bullet OH$ ($k_{\bullet OH}$). Among the different transients present in surface waters, $^\bullet OH$ affords the highest second-order rate constants with organic compounds [71]. One of the reasons of such elevated reactivity is that, while the vast majority of the other radical species (e.g. $CO_3^{-\bullet}$) are mainly involved into electron-capture reactions and less into additional processes, $^\bullet OH$ can abstract electrons, H atoms, or be added to double bonds and aromatic rings. This wide range of possibilities allows $^\bullet OH$ to by-pass many kinetic bottlenecks, simply by reacting in an alternative fashion with a molecule that can be particularly refractory to, e.g., one-electron oxidation [88].
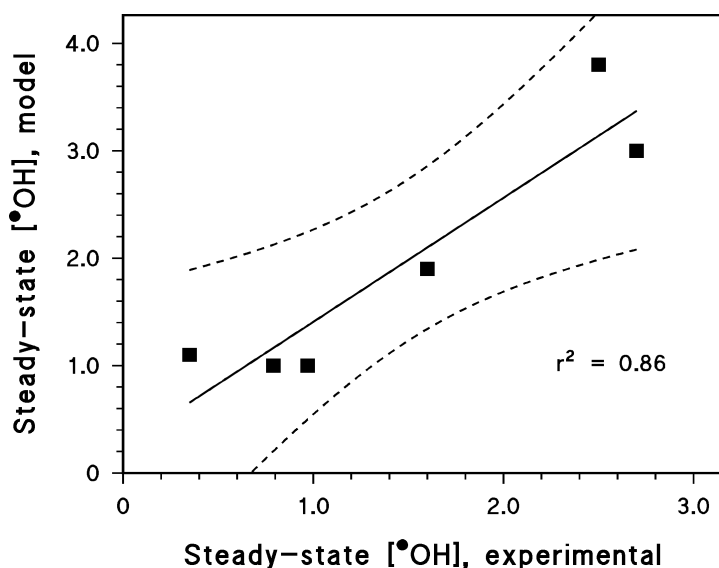
Figure 14. Correlation between the steady-state [$^\bullet$OH] determined experimentally upon irradiation of surface water samples under 22 W m^{-2} simulated sunlight UV irradiance, and the modelled [$^\bullet$OH] concentration. [$^\bullet$OH] units are 10^{-16} M in both cases.

The combination of the steady-state [$^\bullet$OH] with $k_{\bullet OH}$ defines the half-life $t_{1/2}$ of a given compound, due to reaction with $^\bullet$OH. It is $t_{1/2} = \ln 2 \, (k_{\bullet OH} \, [^\bullet OH])^{-1}$, but the value of [$^\bullet$OH] is highly dependent on the irradiation intensity that shows diurnal and seasonal variations. It has been shown that a constant 22 W m^{-2} sunlight irradiance in the UV for 9 hours would deliver the same amount of UV energy as a whole sunny mid-July day at mid latitude [83]. By considering this equivalence, it is possible to correlate the steady-state [$^\bullet$OH], corresponding to 22 W m^{-2} sunlight UV as described by the models, with the lifetime of a given compound expressed in mid-July, mid-latitude days. It is $t_{1/2} \approx 2 \cdot 10^{-5} \cdot (k_{\bullet OH} \, [^\bullet OH])^{-1}$, and Figure 15 reports the plot of $t_{1/2}$ vs. [$^\bullet$OH] for different values of $k_{\bullet OH}$.

To make an example, 2-methylphenol (o-cresol), with $k_{\bullet OH} = 1.1 \times 10^{10}$ M^{-1} s^{-1} [88], under conditions that give 3×10^{-16} M $^\bullet$OH under 22 W m^{-2} sunlight UV, would have $t_{1/2} \approx 6$ days. This is higher than the already-reported 15-h lifetime for the reaction between 2,4,6-trimethylphenol and ^{3}CDOM*, which suggests that transformation photosensitised by CDOM would be a more important sink than $^\bullet$OH for electron-rich phenols. Toluene, with $k_{\bullet OH} = 3 \times 10^9$ M^{-1} s^{-1} [81], under the conditions mentioned above would have $t_{1/2} \approx 22$ days for reaction with $^\bullet$OH. This is higher than for o-cresol, but toluene is not expected to undergo other important photochemical reactions in surface waters [89].
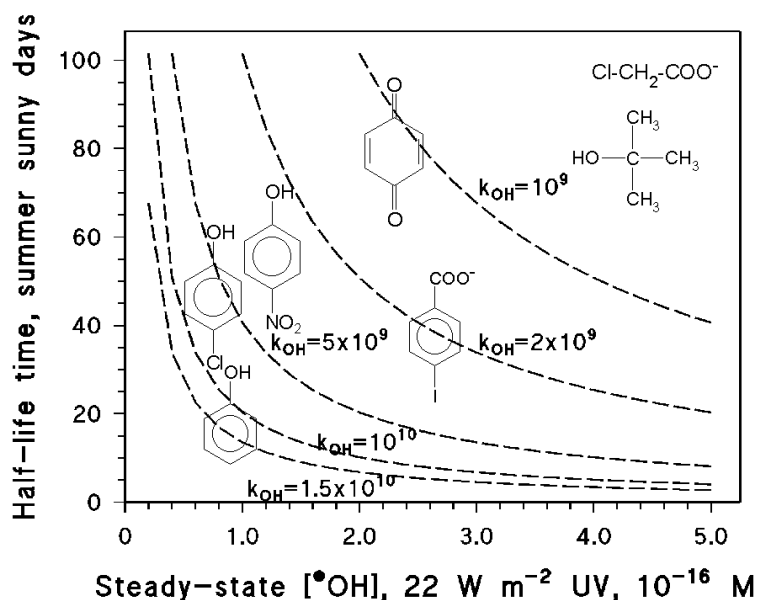
Figure 15. Half-life time (in mid-July, mid latitude sunny days) of a given compound as a function of the steady-state [$^\bullet$OH] (valid for 22 W m^{-2} sunlight UV irradiance) and of its second-order rate constant $k_{\bullet OH}$ (M^{-1} s^{-1} units). Some structures are shown as an example of the different $k_{\bullet OH}$ values.

5. Reactions induced by the carbonate radical, $CO_3^{-\bullet}$

The carbonate radical anion is a fairly reactive transient with relatively elevated reduction potential ($E^0 = 1.59$ V), although its oxidising capability cannot be compared to the hydroxyl radical ($E^0 = 2.59$ V) [90]. The radical $CO_3^{-\bullet}$ is formed in surface waters upon reaction between $^\bullet$OH and CO_3^{2-} or HCO_3^- [91]. An additional pathway for the generation of $CO_3^{-\bullet}$ is the reaction between carbonate and ^{3}CDOM*, but its weight could at most be 10% of the $^\bullet$OH-mediated one [92].

$$^\bullet OH + CO_3^{2-} \rightarrow OH^- + CO_3^{-\bullet} \qquad [k_{19} = 3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}] \qquad (19)$$

$$^\bullet OH + HCO_3^- \rightarrow H_2O + CO_3^{-\bullet} \qquad [k_{20} = 8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}] \qquad (20)$$

$$^3CDOM* + CO_3^{2-} \rightarrow CDOM^{-\bullet} + CO_3^{-\bullet} \qquad [k_{21} = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}] \qquad (21)$$
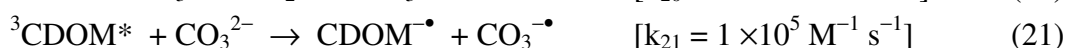
The main sink of the carbonate radical in surface waters is represented by its reaction with DOM. Literature sources do not agree for the rate constant of such a reaction (40 or 280 L (mg C)$^{-1}$ s^{-1}) [91,92], but a value of 100 L (mg C)$^{-1}$ s^{-1} could be not very far from reality. By neglecting for simplicity reaction (21), and by applying the steady-state approximation to [$CO_3^{-\bullet}$], one obtains the following result:

$$\left[CO_3^{-\bullet}\right] = \left[^\bullet OH\right] \cdot \frac{8.5 \cdot 10^6 \cdot \left[HCO_3^-\right] + 3.9 \cdot 10^8 \cdot \left[CO_3^{2-}\right]}{100 \cdot DOC} \qquad (22)$$

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where the DOC (dissolved organic carbon, units of mg C L^{-1}) is a measure of DOM. The main problem with equation (22) is that the concentration values of carbonate and bicarbonate are not always determined together in surface water samples, and the value of the inorganic carbon (IC) is more often available. If one neglects H_2CO_3, it is possible to use the approximation that

IC [mg C L^{-1}] $\approx 1.2 \cdot 10^4$ {[HCO_3^-] + [CO_3^{2-}]}

The pH of the solution allows the separate values of [HCO_3^-] and [CO_3^{2-}] to be derived. In the hypothesis that [HCO_3^-] = 100 [CO_3^{2-}] (pH ~ 8, not unreasonable for surface waters [80]) one gets the following expression for [$CO_3^{-\bullet}$]:

$$[CO_3^{-\bullet}] \approx 10 \cdot [{}^\bullet OH] \cdot \frac{IC}{DOC} \tag{23}$$

Figure 16 shows the modelled trend of [$CO_3^{-\bullet}$] as a function of nitrate and DOC, with IC = 10 mg C L^{-1}. It is apparent that [$CO_3^{-\bullet}$] increases with increasing nitrate (that as an ${}^\bullet OH$ source increases [${}^\bullet OH$]), while it decreases with DOC because organic matter is the major sink of $CO_3^{-\bullet}$. The role of DOM to decrease [$CO_3^{-\bullet}$] would not be substantially modified when taking reaction (21) into account, because the production of $CO_3^{-\bullet}$ by ${}^3CDOM*$ would just be a secondary process [92].
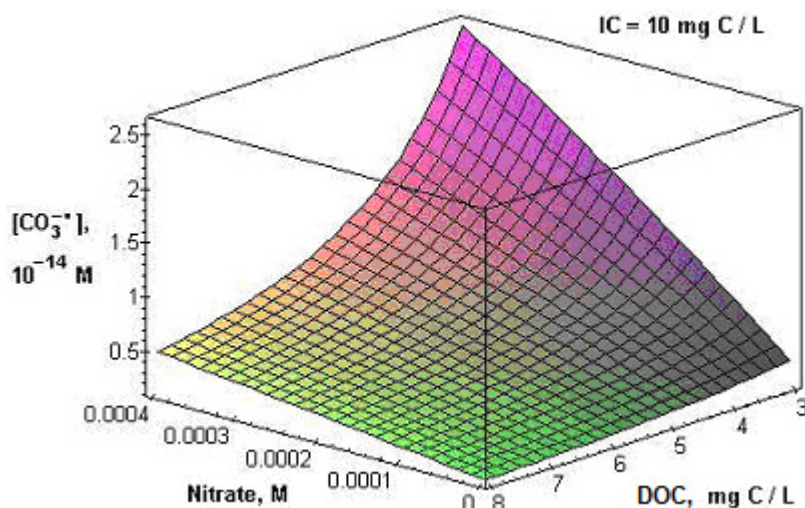
Figure 16. Modelled [$CO_3^{-\bullet}$] in the surface water layer, as a function of nitrate and DOC, in the presence of IC = 10 mg C L^{-1}. Sunlight UV irradiance: 22 W m^{-2}.
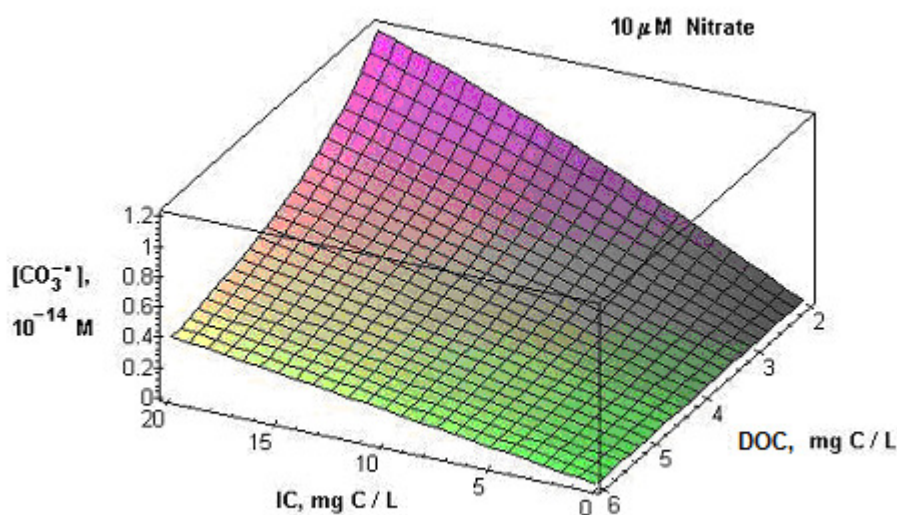
Figure 17. Modelled [$CO_3^{-\bullet}$] in the surface water layer, as a function of IC and DOC, in the presence of [NO_3^-] = 10^{-5} M. Sunlight UV irradiance: 22 W m^{-2}.

Figure 17 shows the trend of [$CO_3^{-\bullet}$] vs. IC and DOC, in the presence of 10^{-5} M nitrate. The concentration of the carbonate radical increases with increasing IC, which is reasonable because carbonate and bicarbonate are the immediate precursors of $CO_3^{-\bullet}$. Moreover, [$CO_3^{-\bullet}$] decreases with DOC because of the role of DOM as sink. Both Figure 16 and 17 indicate that [$CO_3^{-\bullet}$] would reach concentration values up to around 10^{-14} M in the surface water layer, in agreement with laboratory irradiation data of natural samples [93]. This means that $CO_3^{-\bullet}$ would be one-two orders of magnitude more concentrated than $^\bullet OH$, which in some cases could compensate for its lower reactivity. Interestingly, the carbonate radical is mainly formed from $^\bullet OH$ through a pathway (reactions 19,20 with carbonate and bicarbonate) that on average would account for some 10% of hydroxyl scavenging in surface waters [86,87]. The formation rate of $CO_3^{-\bullet}$ would thus be lower than that of $^\bullet OH$ and, as a consequence, the fact that [$CO_3^{-\bullet}$] > [$^\bullet OH$] could only be accounted for by slower $CO_3^{-\bullet}$ scavenging. In fact, the second-order reaction rate constant between $CO_3^{-\bullet}$ and DOM is over two orders of magnitude lower compared to $^\bullet OH$ and DOM [86,91,92].

The rate constants of the reactions that involve $CO_3^{-\bullet}$ and organic compounds are very variable. The upper limit is around 10^9 M^{-1} s^{-1} [94], which is easier to be reached by phenolates, anilines and some sulphur-containing molecules. Considering that bimolecular rate constants in aqueous solution have a diffusion-controlled upper limit of around 2×10^{10} M^{-1} s^{-1}, which is also the upper limit for the reactions that involve $^\bullet OH$ [88], and considering that [$CO_3^{-\bullet}$] ~ 10-100 [$^\bullet OH$], the reaction with $CO_3^{-\bullet}$ can be important for compounds that have a $CO_3^{-\bullet}$ bimolecular reaction rate constant around 10^9 M^{-1} s^{-1}.

Figure 18 shows the half-life times (in mid-July, mid-latitude summer sunny days) of organic compounds, as a function of the steady-state [$CO_3^{-\bullet}$] and of the second-order rate constants for reaction with $CO_3^{-\bullet}$. Some examples of molecular structures are also shown on the Figure, in

connection with the relevant values of the rate constants. The half-life times are calculated as $t_{1/2} = 2 \cdot 10^{-5} \cdot (k_{CO3-\bullet} \, [CO_3^{-\bullet}])^{-1}$. A considerable variability of $k_{CO3-\bullet}$, and of the half-life times as a consequence, is apparent in the figure. This variability is generally much higher than that associated with $k_{\bullet OH}$ and, when $k_{CO3-\bullet}$ is low, $CO_3^{-\bullet}$ is a negligible sink.
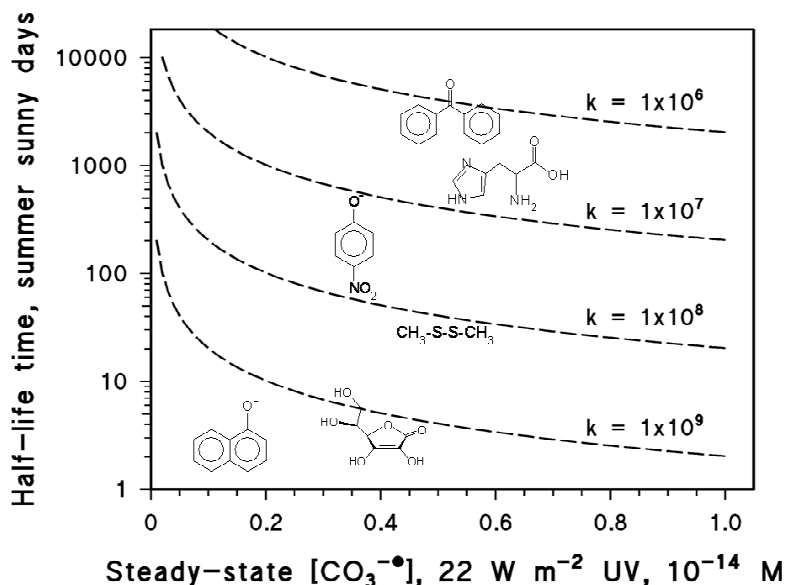
Figure 18. Half-life time (in mid-July, mid latitude sunny days) of a given compound as a function of the steady-state $[CO_3^{-\bullet}]$ (valid for 22 W m^{-2} sunlight UV irradiance) and of its second-order rate constant $k_{CO3-\bullet}$ (M^{-1} s^{-1} units). Some structures are shown as an example of the different $k_{CO3-\bullet}$ values. Note the logarithmic scale of the Y-axis.

6. Reactions induced by singlet oxygen and organic radicals

Singlet oxygen can be formed by activation of ground-state triplet oxygen by $^3CDOM^*$ [53]. It can reach steady-state concentration values in the range $10^{-14} - 10^{-13}$ M in sunlit surface waters, and its formation rate is directly proportional to the amount of radiation absorbed by CDOM. The main removal pathway of $^1O_2$ is the physical quenching upon collision with the water molecules [71].

$$^3CDOM^* + O_2 \rightarrow CDOM + {}^1O_2 \tag{24}$$
$$^1O_2 + H_2O \rightarrow O_2 + H_2O + Energy \tag{25}$$
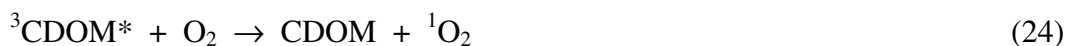
Many molecules show limited reactivity toward $^1O_2$. However, $^1O_2$ can play a significant role in the degradation of compounds such as chlorophenolates and aromatic amino acids [4,45,95]. Furfuryl alcohol is another molecule that reacts fast with $^1O_2$ ($k_{FFA,1O2} = 1.2 \times 10^8$ M^{-1} s^{-1}) [96], and its half-life time due to singlet oxygen (in mid-July, mid-latitude sunny days) would be $t_{1/2} \sim 2 \cdot 10^{-5} \cdot (k_{FFA,1O2} \, [^1O_2])^{-1}$. With $[^1O_2] = 5 \times 10^{-14}$ M one obtains $t_{1/2} \approx 3$ days. Interestingly, $^1O_2$ shows a micro-

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heterogeneous distribution within CDOM and it reaches elevates steady-state levels in the hydrophobic CDOM cores. In this confined environment, it could play an important role toward the degradation of some classes of hydrophobic pollutants [97,98].

The transformation of DOM under irradiation, induced by photolysis or by reaction with radical species such as $^\bullet OH$ and $CO_3^{-\bullet}$, or even the (very limited) scavenging of $^3CDOM^*$ by DOM components can produce various radical species, some of which yield peroxy radicals upon further reaction with oxygen. The radicals thus formed ($R^\bullet$, $ROO^\bullet$, $RO^\bullet$, $R\text{-}H^{+\bullet}$) could be involved in oxidation reactions [99] that are added to the transformation processes mediated by irradiated CDOM. The exact importance of the described radical species in DOM photochemistry is still unclear [53].

$$R\text{-}H + h\nu \rightarrow R^\bullet + H^\bullet \qquad\qquad\qquad (26)$$
$$R\text{-}H + {}^\bullet OH \rightarrow R^\bullet + H_2O \qquad\qquad\qquad (27)$$
$$R\text{-}H + h\nu \rightarrow R\text{-}H^{+\bullet} + e^- \qquad\qquad\qquad (28)$$
$$R^\bullet + O_2 \rightarrow ROO^\bullet \qquad\qquad\qquad (29)$$
$$2\,ROO^\bullet \rightarrow ROO\text{-}OOR \qquad\qquad\qquad (30)$$
$$ROO\text{-}OOR \rightarrow 2\,RO^\bullet + O_2 \qquad\qquad\qquad (31)$$

7. Reactions induced by nitrogen dioxide, $^\bullet NO_2$

Nitrogen dioxide is a nitrating agent that can be formed in surface waters upon nitrate photolysis and nitrite photooxidation [27]:

$$NO_3^- + h\nu + H^+ \rightarrow {}^\bullet OH + {}^\bullet NO_2 \qquad\qquad\qquad (32)$$
$$NO_2^- + h\nu + H^+ \rightarrow {}^\bullet OH + {}^\bullet NO \qquad\qquad\qquad (33)$$
$$NO_2^- + {}^\bullet OH \rightarrow {}^\bullet NO_2 + OH^- \qquad [k_{34} = 1\times 10^{10}\ M^{-1}\ s^{-1}] \qquad (34)$$

The discovery of the involvement of nitrogen dioxide in aromatic photonitration processes induced by the irradiation of nitrate and nitrite ions dates back to the mid '80s [100], but the actual occurrence in the environment of photonitration by $^\bullet NO_2$ has been demonstrated only more recently. Photonitration of 2,4-dichlorophenol [36], 4-chloro-2-methylphenol [37] and 4-chlorophenol [101] is likely to take place in the rice fields of the Rhône river delta, where the primary compounds are formed upon transformation of the herbicides dichlorprop and MCPA. In all the cases the expected time trend of the nitroderivatives, under the hypothesis that $^\bullet NO_2$ is the nitrating agent, is compatible with the available field data.

It is possible to model the steady-state $[^\bullet NO_2]$ in surface waters under the hypothesis that reactions (32) and (34) are the main sources, and hydrolysis (reactions (35,36)) is the main sink [102].

$$2 \, ^\bullet NO_2 \rightleftarrows N_2O_4 \qquad [k_{35} = 4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}; \, k_{-35} = 6.9 \times 10^3 \text{ s}^{-1}] \qquad (35)$$

$$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2 \, H^+ \qquad [k_{36} = 1 \times 10^3 \text{ s}^{-1}] \qquad (36)$$
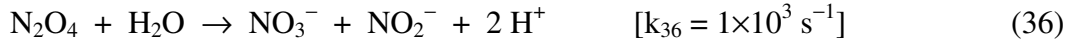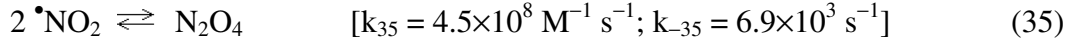
Additional sources and sinks of $^\bullet NO_2$ are possible in surface waters. The oxidation of nitrite by irradiated Fe(III) (hydr)oxides is a very significant pathway leading to aromatic nitration under laboratory conditions [103], but the assessment of its environmental importance is made problematic by the very complex speciation of Fe(III) in surface waters. An important fraction of the total Fe(III) is in fact present in the form of complexes with organic matter [104], the (photo)reactivity of which is poorly known. Indeed, if the average ability of the Fe(III) species to photooxidise nitrite to $^\bullet NO_2$ were comparable to that of hematite, Fe(III) could be a major source of $^\bullet NO_2$ in surface waters containing over 1 mg Fe L^{-1} [102]. However, it is completely unknown to what extent can hematite be considered representative of the photoreactivity of Fe(III) species toward nitrite.

Reaction with DOM, and in particular with its phenolic moieties, could be a significant sink of nitrogen dioxide. However, at the measured [$^\bullet NO_2$] and DOC levels and given the expected rate constants for the reaction between $^\bullet NO_2$ and the phenolic compounds, DOM would be a secondary sink compared to hydrolysis. For DOM to be the main sink, it should be almost completely made up of phenolic moieties [83,102].

From reactions (32,34-36) it is possible to set up an approximate model for the assessment of the steady-state [$^\bullet NO_2$] in surface waters, valid, as the previous ones, for 22 W m^{-2} sunlight UV irradiance. From the cited reactions, and applying the steady-state approximation to [$^\bullet NO_2$], one gets equation (37) [83]:

$$\left[^\bullet NO_2\right] = \sqrt{88.8 \cdot \left[^\bullet OH\right] \cdot \left[NO_2^-\right] + 1.49 \cdot 10^{-15} \cdot \left[NO_3^-\right]} \qquad (37)$$

The steady-state [$^\bullet OH$] can be modelled based on the known sources and sinks. In many cases, unfortunately, the concentration values of nitrite are not available. In this cases one can assume, with reasonable approximation, [NO$_3^-$] $\approx$ 200 [NO$_2^-$] [102] to obtain equation (38):

$$\left[^\bullet NO_2\right] = \sqrt{\left[NO_3^-\right] \cdot \left(0.444 \cdot \left[^\bullet OH\right] + 1.49 \cdot 10^{-15}\right)} \qquad (38)$$

Figure 19 shows the trend of [$^\bullet NO_2$] vs. nitrate and DOC. It is apparent that [$^\bullet NO_2$] increases with increasing nitrate (and nitrite as a consequence, which is correlated with nitrate under the adopted approximation) and decreases with DOC. DOM in the adopted model has mainly the effect of reducing [$^\bullet OH$].
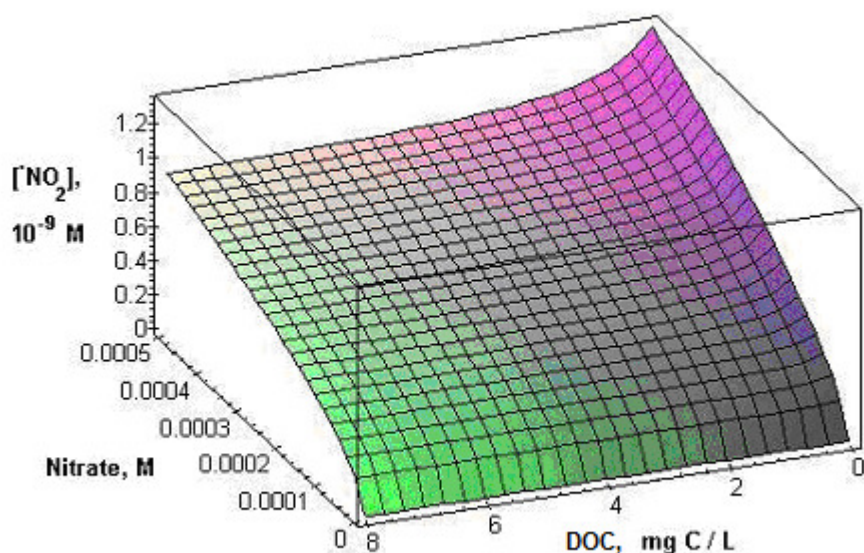
Figure 19. Trend of $[^\bullet NO_2]$ as a function of nitrate and DOC. Sunlight UV irradiance: 22 W m^{-2}.

The relatively elevated steady-state concentration values that $^\bullet NO_2$ can reach in surface waters are compensated for by its low reactivity. Nevertheless, nitrogen dioxide can still be a significant sink for some classes of compounds such as phenols and species containing amino groups [102]. However, transformation processes induced by nitrogen dioxide are very likely to generate secondary pollutants such as nitrophenols and nitrosamines [105], with possibly higher environmental impact than the parent species. For instance the nitration of 2,4-dichlorophenol into 2,4-dichloro-6-nitrophenol transforms a cytotoxic molecule, involved in the oxidative stress of cellular tissues, into a less toxic but potentially mutagenic compound [106].

8. Reactions induced by the dihalogen radicals $Cl_2^{-\bullet}$ and $Br_2^{-\bullet}$

The radicals $Cl_2^{-\bullet}$ and $Br_2^{-\bullet}$ can be generated in surface waters by the oxidation of the chloride and bromide ions. Chloride can be oxidised to $Cl^\bullet/Cl_2^{-\bullet}$ by $^\bullet OH$ in acidic solution, but it is practically non-reactive toward $^\bullet OH$ under neutral conditions. The reason is that the reaction between Cl^- and $^\bullet OH$ is a reversible one, giving back the reactants unless $ClOH^{-\bullet}$ is transformed into $Cl^\bullet$ under acidic conditions [88].

$$Cl^- + {}^\bullet OH \rightleftarrows ClOH^{-\bullet} \tag{39}$$

$$ClOH^{-\bullet} + H^+ \rightleftarrows Cl^\bullet + H_2O \tag{40}$$

$$Cl^\bullet + Cl^- \rightleftarrows Cl_2^{-\bullet} \tag{41}$$

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The oxidation of chloride by $^\bullet OH$ at acidic pH might have some importance in atmospheric waters [107], but it is little likely to affect significantly the chemistry of most surface waters that have pH values in the neutral to basic range [86]. More likely sources of $Cl_2^{-\bullet}$ in surface waters are the oxidation of chloride by semiconductor oxides, such as the Fe(III) (hydr)oxides [49], the photolysis of the complex $FeCl^{2+}$ [108], and the oxidation of chloride by $^3CDOM^*$ [109].

It has been shown that the oxidation of chloride to $Cl_2^{-\bullet}$ by Fe(III) oxide colloids in simulated estuarine water under irradiation could be an importance process in the photodegradation of the anti-epileptic drug carbamazepine [49]. Furthermore, the radical $Cl_2^{-\bullet}$ is an oxidising and chlorinating agent. Phenol chlorination by $Cl_2^{-\bullet}$ has been studied in detail [107] and it involves a primary reaction step where phenol is oxidised to the phenoxyl radical, followed by the reaction between phenoxyl and $Cl_2^{-\bullet}$ to give 2- and 4-chlorophenol (Figure 20).
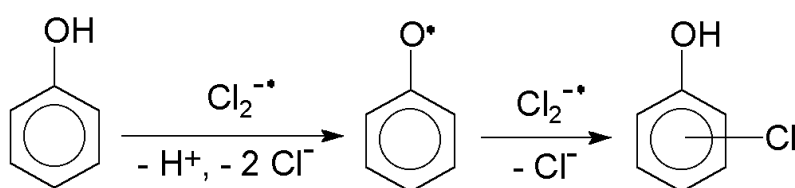
Figure 20. Pathway of phenol chlorination by $Cl_2^{-\bullet}$.

The phenol chlorination yield is relatively low, between 1 and 5%, and the main products of the reaction between phenol and $Cl_2^{-\bullet}$ are phenoxyphenols, dihydroxybiphenyls, and 1,4-benzoquinone [107]. Still, the oxidation of chloride to $Cl_2^{-\bullet}$ is a potentially important pathway for the formation of chloroaromatic compounds in irradiated seawater [110,111].

It is often possible to correlate the second-order rate constants of the reactions between an oxidising agent and whole families of aromatic compounds, with the Hammett σ value given by the different substituent groups on the aromatic ring. One usually obtains a line with a negative slope, because the electron-withdrawing substituents (positive σ) reduce the reactivity of the molecule toward one-electron oxidation. Figure 21 shows the correlation between the second-order rate constants of the reactions involving phenols and benzoates with $Cl_2^{-\bullet}$, and the Hammett σ [94]. The good linearity and the negative slopes confirm that the radical $Cl_2^{-\bullet}$ mainly reacts by one-electron abstraction in the first step of the processes in which it is involved. Chlorination could occur in the second step.
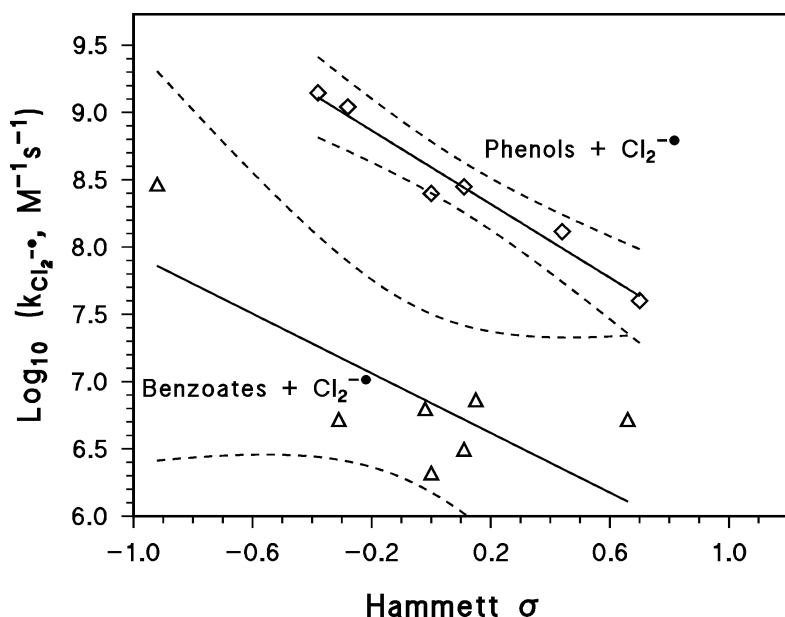
Figure 21. Correlation between the decimal logarithms of the second-order rate constants $k_{Cl2-\bullet}$ and the Hammett σ for substituted phenols and benzoates, for reaction with the radical $Cl_2^{-\bullet}$.

The radical $Br_2^{-\bullet}$ can be formed upon oxidation of bromide by $^\bullet OH$ even in neutral solution [88]. Alternative processes can be the photolysis of the complex $FeBr^{2+}$ and the oxidation of bromide by Fe(III) (hydr)oxides under irradiation [112].
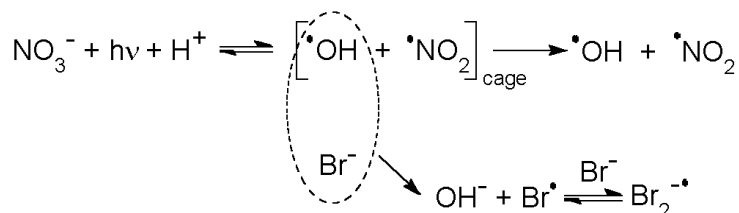
$$Br^- + {}^\bullet OH \rightarrow Br^\bullet + OH^- \qquad [k_{42} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}] \qquad (42)$$

$$Br^\bullet + Br^- \rightleftarrows Br_2^{-\bullet} \qquad (43)$$

$$FeBr^{2+} + h\nu \rightarrow Fe^{2+} + Br^\bullet \qquad (44)$$
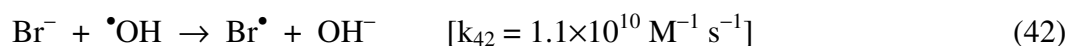
Reaction (42), involving $^\bullet OH$, is potentially the main formation process of $Br^\bullet / Br_2^{-\bullet}$ in surface waters. In keeping with the importance of reaction (42), the bromide ion is the main scavenger of $^\bullet OH$ radicals in seawater [113]. Important scavenging processes by Br^- could also occur in deltas and estuaries, the water of which can be enriched by bromide from seawater. Moreover, bromide can also be found at elevated concentration in some inland brines that are usually associated to temporary water bodies, such as ephemeral rivers and lakes [114].

The bromide ion can also increase the quantum yield of photolysis of some photoactive species, and most notably that of nitrate, because of a solvent-cage effect in the scavenging of photoformed $^\bullet OH$ radicals [115,116]. Nitrate photolysis yields $^\bullet OH + {}^\bullet NO_2$, but the two radical fragments are very likely to recombine before they can exit the surrounding cage of the solvent molecules [117,118]. However, the bromide ion is able to react with $^\bullet OH$ *within the cage* and prevent recombination between $^\bullet OH$ and $^\bullet NO_2$ (see Figure 22). Therefore, the overall generation rate of $^\bullet OH + Br_2^{-\bullet}$ in the presence of bromide is higher than the generation rate of $^\bullet OH$ alone in its absence. This fact, and the reactivity of $Br_2^{-\bullet}$ arising from the process, can have important consequences on the degradation of the compounds that undergo sufficiently fast reaction with $Br_2^{-\bullet}$, such as

phenolates, anilines, and sulphur-containing molecules. For instance, the bromide ion is able to enhance the degradation of dimethyl sulphide and benzophenone-4 upon irradiation of nitrate [113,116].

$$NO_3^- + h\nu + H^+ \rightleftharpoons \left[{}^\bullet OH + {}^\bullet NO_2 \right]_{cage} \longrightarrow {}^\bullet OH + {}^\bullet NO_2$$

$$Br^- \searrow$$

$$OH^- + Br^\bullet \underset{Br^-}{\overset{Br^-}{\rightleftharpoons}} Br_2^{-\bullet}$$

Figure 22. Solvent-cage effect by bromide on the photolysis of nitrate.

The radical $Br_2^{-\bullet}$ is a brominating as well as an oxidising agent with $E^0 = 1.66$ V [90]. Differently from chlorination by $Cl_2^{-\bullet}$, bromination by $Br_2^{-\bullet}$ is very effective and it can be quantitative in the case of phenol [112]. The bromination pathway proceeds in a similar way as the already described chlorination: oxidation of phenol to the phenoxyl radical by $Br_2^{-\bullet}$, followed by reaction between phenoxyl and another $Br_2^{-\bullet}$ to give 2- and 4-bromophenol.

Figure 23 shows the correlation between the rate constants for the reaction of phenolates with $Br_2^{-\bullet}$, and the corresponding Hammett σ [94]. The negative slope suggests the involvement of $Br_2^{-\bullet}$ in one-electron oxidation processes. Moreover, the relatively elevated values of $k_{Br2-\bullet}$ indicate that the radical could be a significant sink of some classes of organic compounds.

It is, unfortunately, not yet possible to directly measure $Cl_2^{-\bullet}$ and $Br_2^{-\bullet}$ in surface waters, However, photochemical modelling has allowed a tentative assessment of $[Cl_2^{-\bullet}]$ and $[Br_2^{-\bullet}]$, which would both be in the 10^{-14}-10^{-12} M range in seawater.
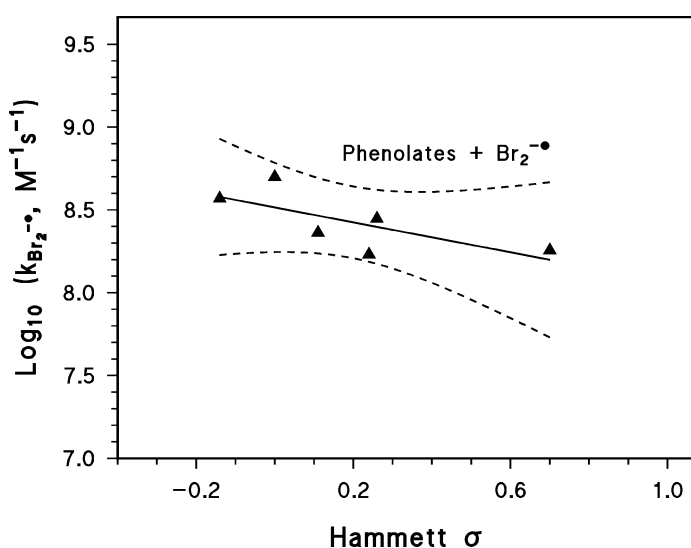
Figure 23. Correlation between the decimal logarithms of the second-order rate constants $k_{Br2-\bullet}$ and the Hammett σ of substituted phenolates, for reaction with the radical $Br_2^{-\bullet}$.

9. Reactions induced by Fe(III) complexes

Fe(III) can be involved in photo-Fenton processes, which under definite circumstances can be important sources of $^\bullet$OH. Moreover, Fe(III) (hydr)oxide colloids under irradiation can produce $^\bullet$NO$_2$ and Cl$_2^{-\bullet}$ radicals upon oxidation of the nitrite and chloride ions. A very important class of photochemical reactions in surface waters involves the complexes between Fe(III) and a very wide variety of organic ligands. This subject will be treated briefly in the present paragraph, but for a more extended account the reader is referred to a review on the subject [119].
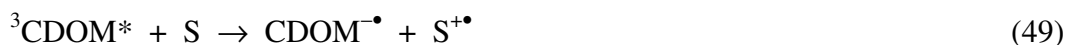
Fe(III) forms photochemically active complexes with a series of carboxylates, and the relevant reactions have been the object of many studies. The photochemistry of ferrioxalate has been studied in depth because of its elevated quantum yield of photolysis and its use as a chemical actinometer. Photolysis proceeds via a ligand-to-metal charge transfer (LMCT) that produces Fe(II) and an oxidised oxalate radical [120]. The latter can undergo mineralisation via decarboxylation, and in fact the photochemistry of Fe(III)-carboxylate complexes can be a significant pathway for the mineralisation of the ligands.

$$Fe^{III}(C_2O_4)_3^{3-} \; + \; h\nu \; \rightarrow Fe^{II}(C_2O_4)_2^{2-} \; + \; C_2O_4^{-\bullet} \tag{45}$$
$$C_2O_4^{-\bullet} \rightarrow CO_2^{-\bullet} + CO_2 \tag{46}$$
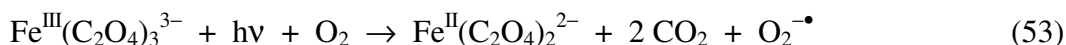$$CO_2^{-\bullet} + O_2 \rightarrow CO_2 + O_2^{-\bullet} \tag{47}$$

LMCT processes are also involved in the degradation of the ligands EDTA and NTA that form complexes with Fe(III). The photochemical transformation of EDTA as complex with Fe(III) is potentially important in surface-water environments because EDTA is refractory to microbial degradation and, for instance, its abatement in wastewater treatment plants is very low [121].

The photoinduced LMCT also involves complexes on the surface of Fe(III) oxides, and most notably those between the surface Fe(III) ions and oxalate [8]. The surface Fe(III)-oxalate complex is able to absorb radiation, which is followed by LMCT with the formation of a transient complex between Fe^{II} and oxidised oxalate (C$_2$O$_4^{-\bullet}$). The complex quickly decomposes with release of C$_2$O$_4^{-\bullet}$ (soon transformed into CO$_2^{-\bullet}$ + CO$_2$) into the solution. A further step is the release of Fe^{2+}. Similar processes of photoreductive dissolution of Fe(III) oxides have been observed in the presence of hydroxycarboxylic acids, most notably the tartaric and gluconic ones [122]. The importance of the cited photochemical processes of Fe(III) photoreduction, where Fe^{2+} is generated upon irradiation of both Fe(III) complexes and Fe(III) (hydr)oxides, is confirmed by field data according to which the concentration of Fe(II) is closely correlated to the sunlight intensity. Such a correlation has been observed under both a monthly and a diurnal scale, in both lake and seawater [123-125]. Indeed, radiation induces the reduction of Fe(III) to Fe(II), and the latter is in turn re-oxidised to Fe(III) in the dark.

An additional pathway that could contribute to the photoreduction of Fe(III) to Fe(II) involves the photoactive components of CDOM (in reaction 49, S is an oxidisable substrate) [119]:

$$CDOM + h\nu \rightarrow {}^3CDOM* \tag{48}$$
$${}^3CDOM* + S \rightarrow CDOM^{-\bullet} + S^{+\bullet} \tag{49}$$
$$Fe(III) + CDOM^{-\bullet} \rightarrow Fe(II) + CDOM \tag{50}$$
$$CDOM^{-\bullet} + O_2 \rightarrow CDOM + O_2^{-\bullet} \tag{51}$$
$$Fe(III) + O_2^{-\bullet} \rightarrow Fe(II) + O_2 \tag{52}$$

In some cases the complexation of Fe(III) by organic ligands enhances the degradation of organic pollutants. For instance, oxalate enhances the degradation of atrazine by irradiated Fe(III). The ligand might have two opposite effects: *(i)* enhancement of Fe(III) photolysis with generation of Fe(II) (reaction 53), which can produce $^\bullet OH$ radicals in the Fenton reaction (56) with H_2O_2. *(ii)* Scavenging of $^\bullet OH$ radicals (reaction 57). Oxalate can enhance degradation if its contribution to the production of $^\bullet OH$ is higher than the scavenging [120].

$$Fe^{III}(C_2O_4)_3{}^{3-} + h\nu + O_2 \rightarrow Fe^{II}(C_2O_4)_2{}^{2-} + 2\,CO_2 + O_2^{-\bullet} \tag{53}$$
$$O_2^{-\bullet} + H^+ \rightleftarrows HO_2^\bullet \tag{54}$$
$$HO_2^\bullet + O_2^{-\bullet} + H^+ \rightarrow H_2O_2 + O_2 \tag{55}$$
$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + {}^\bullet OH \tag{56}$$
$$C_2O_4{}^{2-} + {}^\bullet OH \rightarrow C_2O_4{}^{-\bullet} + OH^- \tag{57}$$

Among the organic ligands of Fe(III), siderophores emitted by bacteria can play a very important role in keeping Fe(III) in its dissolved form. They contain different groups that can bind iron (e.g. hydroxycarboxylates and catecholates, see Figure 24) and in some cases can undergo photolysis with production of Fe(II) [126,127]. These photoprocesses have an important impact on the biogeochemistry of Fe and on its bioavailability, because Fe(II) is much more available to micro-organisms than Fe(III).

The bioavailability of Fe species is usually lowest for Fe(III) (hydr)oxides and highest for dissolved Fe^{2+}. Fe(III) complexes have an intermediate bioavailability. Obviously the photodissolution of Fe(III) (hydr)oxides and the photolysis reactions involving Fe(III) complexes play an important role to increase the bioavailability of iron [128].

Finally, Fe is known to play a significant role in the photobleaching and photomineralisation of (C)DOM in surface waters, that is respectively the decrease of the UV absorbance and of the DOC of surface water samples because of irradiation [23,129].
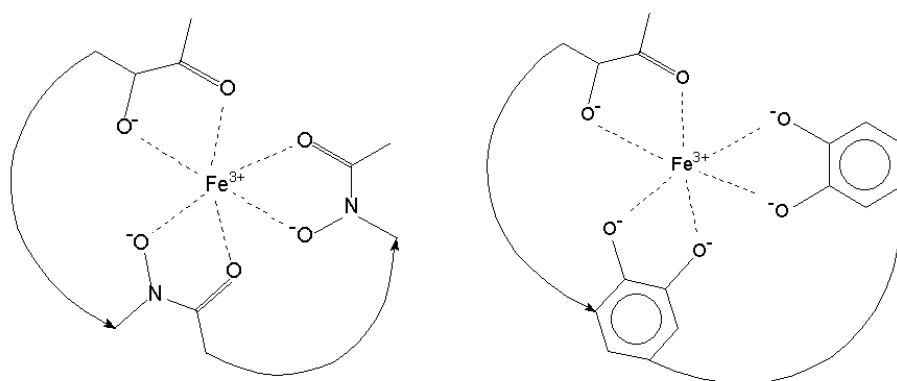
Figure 24. Fe(III)-binding groups in siderophores.

10. Conclusions

Photochemical processes can play an important role in the transformation of biorefractory organic compounds, and most notably of organic pollutants, in surface waters. They include direct photolysis, phototransformation sensitised by CDOM, and reactions with transient species generated by irradiation of dissolved photoactive compounds. The main photoactive compounds in surface waters are CDOM, nitrate, nitrite and Fe(III), but some reactive transients can arise from the interaction of those species with dissolved anions such as carbonate, bicarbonate, nitrite, chloride and bromide. Interestingly, nitrite is both a source and a sink of reactive species in surface waters.

Among the reactive transients, in addition to the excited triplet states of CDOM (^{3}CDOM*), there are $^\bullet$OH, $CO_3^{-\bullet}$, $^1O_2$, DOM-derived radicals, $^\bullet NO_2$, $Cl_2^{-\bullet}$, and $Br_2^{-\bullet}$. They are involved to a variable extent in the degradation of organic compounds, depending both on the conditions of a particular water body and on the structure of the relevant substrate. The radicals $^\bullet NO_2$ and $Br_2^{-\bullet}$ are likely to play a more important role in the generation of secondary pollutants (such as toxic and environmentally persistent aromatic nitro- and bromoderivatives) than in the degradation of the parent molecules. In contrast, ^{3}CDOM*, $^\bullet$OH and $CO_3^{-\bullet}$ as oxidising agents would be more often involved in depollution processes connected with the degradation of the primary compounds. For instance Table 1 reports the reaction rate constants of the phenylurea herbicide diuron with ^{3}CDOM*, $^\bullet$OH and $CO_3^{-\bullet}$, some reasonable values for the steady-state concentrations of the relevant reactive species (valid for 22 W m^{-2} sunlight UV intensity), and the lifetime for the reaction with each species. The lifetime (in mid-July, mid-latitude sunny days) was calculated as $t_{1/2}$ $= 2 \cdot 10^{-5} \cdot (k_i \, [i])^{-1}$, where k_i is the second-order rate constant and [i] the steady-state concentration of the relevant transient.

Table 1. Reaction kinetics of diuron with $^3CDOM^*$, $^{\bullet}OH$ and $CO_3^{-\bullet}$. Note that [i] is valid for 22 W m^{-2} sunlight UV intensity. Note that diuron can also undergo direct photolysis (*vide infra*).

	k_i, M^{-1} s^{-1}	[i], M	$t_{1/2}$, days
$^3CDOM^*$	9×10^6 [130]	8×10^{-15}	280
$^{\bullet}OH$	5×10^9 [88]	1×10^{-16}	40.5
$CO_3^{-\bullet}$	8×10^6 [92]	1×10^{-14}	250

It is apparent in the case of diuron that $^{\bullet}OH$ would prevail as sink over $^3CDOM^*$ and $CO_3^{-\bullet}$, but the situation could be different for other compounds that are more reactive with $^3CDOM^*$ or $CO_3^{-\bullet}$. For instance, in the case of isoproturon, with $k_{3CDOM^*} = 8 \times 10^8$ M^{-1} s^{-1} [130] and $k_{CO3-\bullet} = 3 \times 10^7$ M^{-1} s^{-1} [92], the lifetime for reaction with $^3CDOM^*$ and $CO_3^{-\bullet}$ would be 3 and 68 days, respectively. Assuming $k_{\bullet OH} \approx 10^{10}$ M^{-1} s^{-1} one could obtain a lifetime of around 20 days for reaction with $^{\bullet}OH$, which would make $^3CDOM^*$ the main sink of isoproturon. Lifetimes for the reaction with 10^{-14} M $CO_3^{-\bullet}$ would be lower than 10 days for $k_{CO3-\bullet} > 2 \times 10^8$ M^{-1} s^{-1}, a conditions that is met in the case of anilines and phenoxides, for instance. In the case of the reaction with 8×10^{-15} M $^3CDOM^*$, to obtain $t_{1/2} < 10$ days one would require $k_{3CDOM^*} > 2.5 \times 10^8$ M^{-1} s^{-1}. This condition is met by some phenylurea herbicides and, more markedly, some electron-rich phenols. In the case of 10^{-16} M $^{\bullet}OH$ it would be required $k_{\bullet OH} > 2 \times 10^{10}$ M^{-1} s^{-1} to have $t_{1/2} < 10$ days. This would be a rare event because 2×10^{10} M^{-1} s^{-1} represents the diffusion-control limit for bimolecular rate constants in aqueous solution [88]. Considering that many compounds have $k_{\bullet OH} > 10^9$ M^{-1} s^{-1} [88], the reported data could allow a preliminary assessment of the relative role of $^3CDOM^*$, $^{\bullet}OH$ and $CO_3^{-\bullet}$ as sinks of organic compounds in surface waters under typical conditions.

The relative importance of direct photolysis and of indirect photodegradation is very variable depending on the molecule under consideration and on the composition of water. Direct photolysis is not operational with molecules that do not absorb sunlight, in which case indirect photodegradation has to prevail, but the situation is more complicated for those molecules that absorb sunlight and are reactive toward $^3CDOM^*$, $^{\bullet}OH$, $CO_3^{-\bullet}$ and other transients. The intensity of sunlight absorption and the photolysis quantum yield play a very significant role in defining the rate of the direct photolysis of a given compound. If all the relevant parameters (absorption spectra, quantum yields, second-order reaction rate constants) are known, more precise predictions can be achieved by means of a recently developed photochemical model and software (APEX: Aqueous Photochemistry of Environmentally-occurring Xenobiotics) that determined pollutant photodegradation kinetics as a function of water chemistry and depth [20].

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