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Photochemistry of Surface Fresh Waters in the Framework of Climate Change

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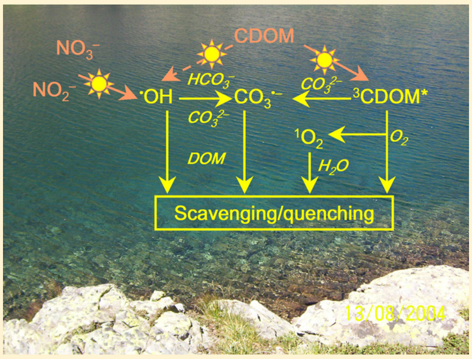
Supporting Information

ABSTRACT: Photochemical processes taking place in surface fresh waters play an important role in the transformation of biorecalcitrant pollutants and some natural compounds and in the inactivation of microorganisms. Such processes are divided into direct photolysis, where a molecule is transformed following sunlight absorption, and indirect photochemistry, where naturally occurring photosensitizers absorb sunlight and produce a range of transient species that can transform dissolved molecules (or inactivate microorganisms). Photochemistry is usually favored in thoroughly illuminated shallow waters, while the dissolved organic carbon (DOC) acts as a switch between different photochemical pathways (direct photolysis, and indirect photochemistry triggered by different transient species). Various phenomena connected with climate change (water browning, changing precipitations) may affect water DOC and water depth, with implications for the kinetics of photoreactions and the associated transformation pathways. The latter are important because they often produce peculiar intermediates, with particular health and environmental impacts. Further climate-induced effects with photochemical implications are shorter ice-cover seasons and enhanced duration of summer stratification in lakes, as well as changes in the flow velocity of rivers that affect the photodegradation time scale. This contribution aims at showing how the different climate-related phenomena can affect photoreactions and which approaches can be followed to quantitatively describe these variations.



1. INTRODUCTION

This contribution considers processes taking place in surface fresh waters due to the action of sunlight. Their occurrence has been acknowledged since at least the late 1970s,[1] and there has been a recent surge of interest into the topic. Photoreactions are involved into the transformation of surface water pollutants,[2] the degradation of natural compounds[3] and the inactivation of micro-organisms.[4]

Many pollutants occur in urban and industrial wastewater, and they are emitted to surface water bodies because of incomplete removal by wastewater treatment plants (WWTPs). Most WWTPs strongly rely on biological processes (activated sludge) to remove the organic load, and in this way, they "select" for biorecalcitrant and hydrophilic compounds that are poorly biodegraded and do not partition on biosolids. These compounds, many of which belong to the class of pharmaceuticals and personal care products (PPCPs),[5,6] are commonly found at the WWTP outlet, as well as in water bodies, such as rivers and lakes.

Many pesticides that are widely used in agriculture are also biorecalcitrant, and their photodegradation can be a very important attenuation pathway in natural surface waters.[7] These compounds enter the water environment via, for example, field runoff or through groundwater. Other pollutants are emitted to surface waters by industries and recreational activities (e.g., solar filters) or may reach the water environment through atmospheric deposition.[8] Natural compounds can be allochthonous and enter aquatic environments via soil runoff or atmospheric deposition, while others are autochthonously produced by aquatic organisms.[9]

Photodegradation tests are commonly used, for example, in the framework of the registration of new chemicals to assess their environmental fate. Such tests are molecule-centered, sometimes only based on direct photolysis, and they tend to classify the substances into photostable and photolabile ones.[10] While not fundamentally wrong (in the same environment, a photostable molecule has longer photochemical lifetime than a photolabile one), this approach underestimates the role of the environment in photodegradation. Different water environments are actually characterized by very different photoreactivity, and the photochemical lifetimes of the same molecule may vary by orders of magnitude in different water bodies.[11] Therefore, a photolabile molecule in a poorly photoactive environment can have comparable (or even longer) lifetime as a photostable molecule in a photoreactive water body.[12] This issue deprives the terms "photostability" and "photolability" of part of their absolute significance.

Photodegradation processes also involve natural compounds, such as proteins, peptides, and amino acids.[13−15] In some

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cases, phototransformation may compete with biodegradation, for example, when a compound upon which microorganisms feed is also photodegraded, which subtracts nutrients or energy to the food chain. The photodegradation of the peptidic thiol glutathione is an instance of competition between photo- and biodegradation.[16,17] In other cases, photodegradation transforms biorecalcitrant forms into biodegradable compounds, thereby providing an additional source of nutrients. When biodegradation processes yield biorecalcitrant species, photodegradation of the latter might open up the way for a further utilization of the related carbon and energy source.[18] Furthermore, the photochemical transformation of heteroatoms, such as N and P, into small inorganic species has the potential to provide an additional source of nutrients that can boost biological processes.[19]

Sunlight can also induce inactivation of microorganisms, such as viruses and bacteria, and is, for instance, exploited in the disinfection of drinking water (SODIS).[20,21] In these cases, sunlight can directly inactivate DNA (or RNA for some viruses), while photogenerated reactive species can damage the virus capsid or the bacterial membrane.[22,23] Interestingly, viruses behave similarly to chemicals under sunlight, and their photodegradation can be described with the same principles used for organic compounds.[24,25] In contrast, the photoinactivation of bacteria is characterized by an initial lag time that has no equivalent with chemicals, and which poses a challenge to a full model description of the photoinactivation kinetics.[26]

While it is increasingly recognized that the environment plays an important role in photoreactions, it should be highlighted that many environmental features are changing over time and that some of these changes have an impact on phototransformation kinetics and pathways.[27] Climate change is one of the main stressors that are progressively modifying the natural aquatic environments[28] and that could affect the photochemistry of surface fresh waters. To date, limited research efforts have been devoted to uncover the link between climate and freshwater photochemistry. However, it is increasingly possible to use models to reliably understand which environmental factors play the most important roles in photoreactions.[27] At the same time, ongoing research is suggesting that several freshwater environmental factors can be affected by climate change in at least some circumstances,[29] thereby allowing for a link to be established between climate effects and their photochemical implications.

It should be anticipated that photochemically interesting modifications induced by climate change are varied and involve at least water chemistry, dynamics, and hydrology. Moreover, not all the described changes are expected to occur in the same climate zones at the same time. To carry out a comprehensive account of the subject, the present contribution includes both literature results and suggestions on new directions. An attempt is made to follow a quantitative approach to the problems, which in some cases requires simplifications and approximations. Predictive calculations are carried out with the APEX code for photochemistry modeling (aqueous photochemistry of environmentally occurring xenobiotics).[30] While other photochemical models are also available,[31,32] they are either limited to the description of the direct photolysis[31] or, while based on the same equations as APEX,[32] require extensive and nonautomatic spreadsheet calculations. Further details concerning photochemical modeling procedures are reported in the Supporting Information (hereafter SI), as well as in previous work.[30] Also refer to the "Glossary of Important Terms" provided at the end of this article.

2. PHOTOCHEMICAL PROCESSES IN SURFACE FRESH WATERS

These processes are usually divided into direct photolysis and indirect photochemistry, but most dissolved compounds undergo both direct photolysis and one or more indirect photoreactions.[10−12] In the case of direct photolysis, the substrate (molecule or microorganism) absorbs sunlight (i.e., radiation with wavelength $\lambda > 290$ nm) and gets transformed as a consequence, which means that its photolysis quantum yield should not be null.[33] Direct photolysis pathways include photoionization and bond breaking, and the latter may proceed through excited singlet or triplet states.[34] A particular instance of direct photolysis is self-sensitized phototransformation, where an excited-state (usually, triplet-state) molecule reacts with the ground state of an identical molecule, and one or both get(s) transformed. Self-sensitized phototransformation becomes faster as the substrate concentration increases because of the bimolecular reaction between excited and ground states.[35] It is different from the other direct photolysis pathways, which slow down with increasing substrate concentration because of absorption saturation.[34]

In the case of indirect photochemistry, sunlight is absorbed by naturally occurring molecules (photosensitizers) to produce reactive transient species, involved in substrate transformation. The main photosensitizers in surface fresh waters are nitrate, nitrite, and the fraction of natural dissolved organic matter that absorbs sunlight (chromophoric dissolved organic matter or CDOM).[11,36] Nitrate absorbs sunlight UV, with absorption maximum at 305 nm (UVB region). At $\lambda > 305$ nm, the absorbance of nitrate decreases while the irradiance of sunlight increases: the solar photon flux absorbed by nitrate is maximum around 320 nm and becomes negligible above 340 nm. The photolysis of nitrate yields $^{\bullet}OH$ (hydroxyl radical) as the main transient.[37,38] Nitrite is another $^{\bullet}OH$ source, with an absorption band peaking at 355 nm (UVA region) and extending into the visible.[39,40]

CDOM is by far the main sunlight absorber in natural waters below 500 nm (above 500 nm, absorption is accounted for by chlorophylls, other pigments, and H_2O itself),[41] and it is often the main photosensitizer. The main transients produced by CDOM are $^{\bullet}OH$, singlet oxygen ($^1O_2$) and CDOM triplet states ($^3CDOM^*$).[11] The radical $^{\bullet}OH$ is very reactive,[42] and is the only transient to effectively degrade recalcitrant compounds such as carbamazepine, acesulfame K and some hydrocarbons.[43] The photochemical generation of $^{\bullet}OH$ by irradiated CDOM is still poorly elucidated, but it partly involves the photoproduction of $O_2^{\bullet-}$ that disproportionates into H_2O_2 and O_2.[44] Photogenerated H_2O_2 can undergo either direct photolysis to $^{\bullet}OH$, or the Fenton reaction in the presence of Fe(II). The H_2O_2 pathway accounts for approximately 50% of $^{\bullet}OH$ photoproduction by CDOM,[45] the other half being accounted for by additional, still unclear processes. Possibly, the photolysis of hydroxylated aromatic compounds might play a role.[46]

The experimental quantification of $^{\bullet}OH$ photoproduction by CDOM takes the Fenton reaction into account, although it does not single out the process importance. Therefore, an important part of Fe photochemistry is implicitly included in the current estimates of CDOM photoreactivity, although it is not explicitly recognized as such.[11] Also note that Fe-based solids are scarcely photoreactive and that, with few exceptions, the photochemistry of surface fresh waters is a photochemistry of dissolved, not suspended, species.[47]

The absorption of sunlight by CDOM chromophores (e.g., aromatic carbonyls and quinones) excites them to the corresponding singlet states (^{1}CDOM*), which can undergo intersystem crossing to ^{3}CDOM*. The triplet states react with dissolved molecules, usually by electron or H atom capture, or by energy transfer. Examples of compounds undergoing efficient degradation by ^{3}CDOM* are phenols, phenylurea herbicides and sulfonamide antibiotics.[48]

The reactive transient species are very quickly consumed in surface fresh waters, which finally gives very low steady-state concentrations (typically, 10^{-18}–10^{-13} mol L^{-1}).[11,49] In particular, $^\bullet$OH is mainly scavenged by natural organic compounds, the DOM (dissolved organic matter, of which CDOM is the sunlight-absorbing fraction).[50] A less important but often significant $^\bullet$OH scavenger is inorganic carbon (HCO_3^- and CO_3^{2-}), which reacts with $^\bullet$OH to produce the carbonate radical ($CO_3^{\bullet-}$) as a further transient form. $CO_3^{\bullet-}$ induces the photodegradation of some phenols, aromatic amines, and sulfur-containing compounds (some amino acids and peptidic thiols, such as glutathione).[51] DOM is the main $CO_3^{\bullet-}$ scavenger.[52]

^{3}CDOM* reacts with dissolved O_2 to produce $^1O_2$.[49] While a generally weaker oxidant than ^{3}CDOM*, $^1O_2$ plays an important role in the environmental photodegradation of chlorophenolates, of some easily oxidized amino acids (histidine, methionine, tyrosine, and tryptophan),[53] and of viruses.[24,25] Singlet oxygen is mainly quenched by collision with water molecules, while the reactions between $^1O_2$ and DOM are usually minor.[54] In aerated water, ^{3}CDOM* is mainly quenched by O_2[55,56] to cause either deactivation, or $^1O_2$ production. The actual $^1O_2$ yield from ^{3}CDOM* depends on the triplet-state nature: on average, approximately half of the overall ^{3}CDOM* + O_2 encounters yields CDOM + $^1O_2$. This means that the $^1O_2$ formation rate would be about twice lower than that of ^{3}CDOM*, but this is offset by a correspondingly slower $^1O_2$ deactivation kinetics. Therefore, one often has [^{3}CDOM*] ~ [$^1O_2$] in aerated water. However, if the levels of dissolved oxygen are low, it is [^{3}CDOM*] > [$^1O_2$].[49] There is some ability of DOM to scavenge ^{3}CDOM*, but the relevant process can be neglected if the water dissolved organic carbon (DOC) is below 20 mg_C L^{-1}.[57]

It is important to distinguish the different photoreaction pathways, for at least two reasons. First of all, effective photochemical modeling can only be carried out by first considering the different processes separately and then summing them up.[30] Second, the photoreaction route deeply affects the nature of the transformation intermediates. Some of the intermediates may be more harmful (e.g., toxic or mutagenic) than the parent compounds,[58] and in some cases photodegradation increases the environmental impact of pollution instead of promoting decontamination. Some pathways that transform pollutants into harmful intermediates or that prevent harmful-intermediates formation are known (see Table S3).[59−71,74]

A schematic of the main indirect photochemistry processes in surface waters is provided in Figure 1, showing the formation of $^\bullet$OH, $CO_3^{\bullet-}$, ^{3}CDOM*, and $^1O_2$. Other transients (e.g., superoxide $O_2^{\bullet-}$, as well as organic oxyl $RO^\bullet$ and peroxyl $ROO^\bullet$ radicals) are also formed by sunlit CDOM.[72] Their role in the photochemistry of organic compounds is still difficult to quantify, but $O_2^{\bullet-}$ (which is also biologically produced) is for instance well-known to play an important role in redox metal cycling.[73]

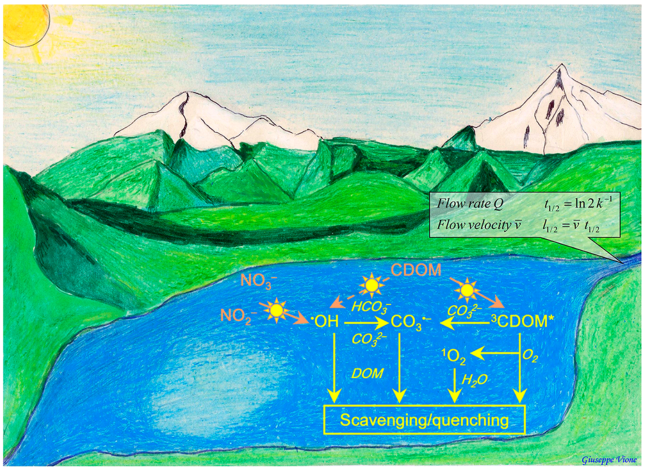

Figure 1. Schematic of the main photochemical processes involving $^\bullet$OH, $CO_3^{\bullet-}$, ^{3}CDOM*, and $^1O_2$ in surface fresh waters. Photosensitizers (nitrate, nitrite, and CDOM) are orange, quenchers/scavengers (inorganic carbon, DOM, oxygen, and water) are in italics. The arrow going from CDOM to $^\bullet$OH is dashed because the process details are still poorly known. The mathematical treatment of photoreactions in rivers is also sketched (vide infra). Drawing reproduced with permission from G. Vione.

The most important environmental factors affecting the photoinduced reactions are sunlight irradiance, water depth and absorption (the latter accounted for by CDOM), the organic matter concentration (DOC), and sometimes also the water pH and temperature.[75−87] In saltwater and seawater, photoprocesses also involve halogen-containing radicals (e.g., $Cl_2^{\bullet-}$, $Br_2^{\bullet-}$, and $ClBr^{\bullet-}$).[88,89] These issues are explained in detail in the SI.

3. KNOWN AND FORESEEABLE IMPACTS OF CLIMATE CHANGE ON PHOTOCHEMICAL REACTIONS IN SURFACE FRESH WATERS

3.1. Water Browning at Elevated Nordic Latitudes (Boreal Lakes). Several (although not all) surface waters in high-latitude Nordic regions (the most lake-rich zones in our planet)[90] are experiencing a gradual increase in both the DOC and the CDOM content, with some exceptions.[29,91] The main reason behind this browning (or brownification) phenomenon is the enhanced export of organic matter from soil to waters due to the combination of (i) more frequent heavy-rain events caused by climate change, which enhance soil runoff and organic-matter transport to the water basins, and (ii) increasing pH of precipitation and atmospheric depositions (i.e., recovery from acidification because of decreasing SO_2 and NO_x emissions), which enhances solubility of soil organic matter such as humic acids.[92,93] Other factors related to browning may include land-use changes and Fe-DOM interactions.[94,95]

Increasing fresh water (C)DOM enhances the photogeneration of ^{3}CDOM* and $^1O_2$, as well as the scavenging of both $^\bullet$OH and $CO_3^{\bullet-}$, thereby shifting indirect photoreactions from $^\bullet$OH/$CO_3^{\bullet-}$ to ^{3}CDOM*/$^1O_2$. Moreover, increasing CDOM inhibits both direct photolysis and the NO_3^-/NO_2^- photochemistry, which is a direct $^\bullet$OH and

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indirect $CO_3^{\bullet-}$ source. Independently of browning, surface waters in boreal regions are already (C)DOM-richer compared to those in temperate areas, which favors $^3CDOM^*/^1O_2$ to the detriment of direct photolysis and $^{\bullet}OH/CO_3^{\bullet-}$.[96] Climate-related browning, which is predicted to go on in several areas, such as the Scandinavian Peninsula,[29] will further exacerbate the photochemical peculiarities of boreal water bodies.[96]

In addition to changing the photoreaction pathways, which affects the reaction intermediates, browning can alter the overall transformation kinetics. The fungicide dimethomorph (Figure 2a) and the antiepileptic drug carbamazepine (Figure 2b), both occurring in lake water in Southern Sweden[97−99] were chosen here to exemplify the photochemical implications of water browning (it was used $A_\lambda = 0.45\ \mathrm{DOC}\ d\ e^{-0.015\lambda}$ as the water absorption spectrum, thus CDOM ∝ DOC).[30] In addition to shifting the photodegradation pathways toward $^3CDOM^*$, the DOC increase would also lower the photodegradation rate constants and increase the photochemical lifetimes.

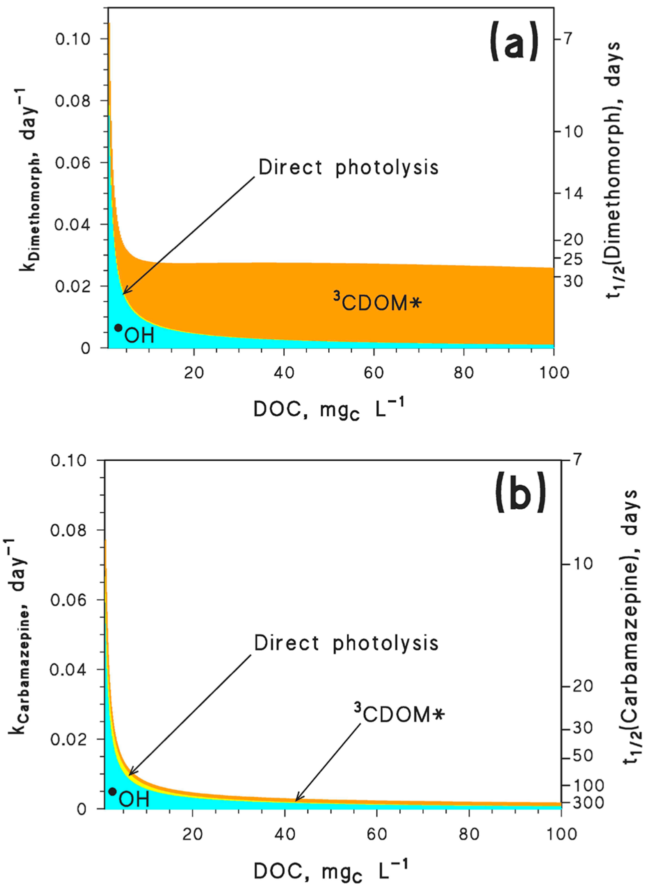

Figure 2. First-order photodegradation rate constants (left *Y*-axis) and corresponding half-life times (right *Y*-axis) of (a) dimethomorph (fungicide) and (b) carbamazepine (antiepileptic drug), as a function of the water DOC. Other water conditions in both cases: 5 m depth, 10^{-4} mol L^{-1} NO_3^-, 10^{-6} mol L^{-1} NO_2^-, 10^{-3} mol L^{-1} HCO_3^-, 10^{-5} mol L^{-1} CO_3^{2-}. The time unit is referred to fair-weather days equivalent to the summer solstice at 60° N latitude. The contributions to photodegradation of $^{\bullet}OH$, $^3CDOM^*$, and direct photolysis are highlighted with different colors.

Browning is not expected to be uniform in a given geographic area. The phenomenon is connected to the water retention times because the longer the water stays in a given basin, the more time it has to get enriched with (C)DOM. Long water retention times (e.g., >6 years in the case of Sweden) are typical of large lakes, where (C)DOM could increase by at least 4-fold in the next decades as a consequence of climate change.[29] Moreover, large lakes in Sweden have usually lower initial (C)DOM content compared to smaller basins. In contrast, small lakes have relatively short water retention times (<3 years), and while they feature already high (C)DOM levels, the relevant (C)DOM increase should be lower in relative terms (around 1.5−2.5 times) than for larger lakes.[29]

It is shown in Figure 2 that the slowdown of photodegradation kinetics with increasing DOC is predicted to be steep when the initial DOC is low, while a plateau trend is observed at high DOC. Therefore, the effect of browning on photochemistry should be more marked in large boreal lakes than in smaller basins because large lakes have lower initial DOC and should undergo a higher relative DOC increase in the future.

Photochemical reactions in boreal environments are also and notably involved in methylmercury (MeHg) degradation.[100,101] Although such a process presently defies modeling, it is highly likely that its kinetics and pathways will be altered in a similar way as for organic pollutants. Therefore, browning should slow down MeHg photodegradation especially in large basins, and shift photoreactions (whichever apply to the MeHg case) from $^{\bullet}OH/CO_3^{\bullet-}$ and direct photolysis to $^3CDOM^*/^1O_2$.

3.2. Photomineralization of Organic Matter.

Photochemical processes are also able to induce (C)DOM transformation and, in particular, its photobleaching (absorbance loss upon irradiation) and photomineralization (photoinduced production of dissolved inorganic carbon, DIC).[102,103] The latter phenomenon also gives a (limited) contribution to the atmospheric CO_2 levels.[104] Although not yet fully understood in its mechanistic details, the photomineralization phenomenon lends itself to photochemical modeling because quantum yields (QYs) are available. In particular, a wavelength-dependent QY expression has been recently reported for photomineralization, which describes DIC photoproduction when coupled with sunlight absorption by CDOM[104]

$$\mathrm{QY}(\lambda) = e^{-(7.16+0.0122(\lambda-290\mathrm{nm}))} \tag{1}$$

where λ is the wavelength [nm]. On this basis, it is for instance possible to assess the amounts of inorganic carbon that can be photochemically produced by a lake unit surface area per unit time [mg_C m^{-2} day^{-1}], as a function of water depth and DOC. Results are provided in Figure 3, and they are in the same range as field observations and previous modeling.[104,105] It is suggested in the figure that browning would enhance DIC photoproduction. The reported trends show a plateau at high DOC because of absorption saturation by CDOM. DIC photoproduction per unit area is higher in deep water because a deeper column is able to absorb sunlight more thoroughly (the depth trend would be quite different when taking into account DIC photoproduction per unit volume). Photomineralization has been widely studied in boreal environments,[103−106] and the data reported here allow for some inferences to be made on the possible effects of browning. The modeled increase of DIC photoproduction with increasing DOC is particularly steep in deep lakes with low initial DOC. This would be the case of large boreal lakes, which are also

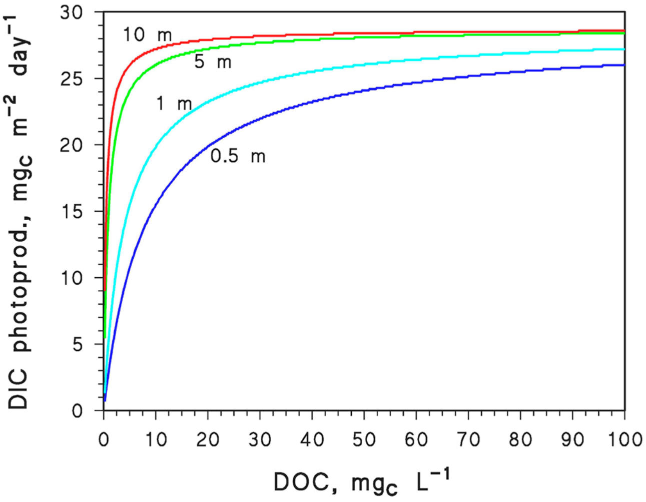

Figure 3. Modeled photomineralization rates (DIC = dissolved inorganic carbon) normalized to lake surface area, as a function of DOC and water depth (reported near each curve). The water absorption spectrum was here approximated with the formula $A_\lambda = 0.45$ DOC $d\, e^{-0.015\lambda}$, where d is depth [units of cm].[30] The time unit is referred to fair-weather days equivalent to the summer solstice at 60° N latitude.

expected to undergo the highest percentage DOC increase because of browning.[29] In contrast, small lakes with high DOC would be located at or near the plateau region, and because they are also expected to undergo limited percentage DOC increases,[29] their DIC photoproduction would not vary much as a consequence of browning. Therefore, the phenomenon of browning-enhanced photomineralization of DOM would mainly involve large lakes.

Enhanced photobleaching, with production of lower molecular weight compounds that absorb sunlight less efficiently, has been reported for some US lakes, several of which underwent a decrease of the DOC over time.[116] These phenomena are exactly opposite to browning, and while browning is expected to enhance ^{3}CDOM* and $^1O_2$ at the expense of $^\bullet$OH, $CO_3^{\bullet -}$, and the direct photolysis, the opposite should happen with lakes where photobleaching prevails. Moreover, a minority of lakes are undergoing photobleaching and DOC increase at the same time.[116] These lakes should experience an inhibition of all indirect photochemistry pathways (including $^\bullet$OH and $CO_3^{\bullet -}$, due to enhanced DOM scavenging), while direct photolysis should be enhanced by photobleaching.

3.3. Alkalinity Changes in Temperate Environments.

In temperate regions, climate effects on water chemistry should be less important than in boreal environments. The implementation (or relaxation) of wastewater legislation to limit nutrient (e.g., N and P) discharge into water bodies has often impacted algal productivity and the temperate-water DOC much more than climate changes.[107,108] However, climate change has the potential to modify alkalinity in temperate water bodies. Freshwater alkalinity has seasonal fluctuations with winter maxima and summer minima, because the precipitation of $CaCO_3$ (and $MgCO_3$ to a lesser extent) in warmer water decreases alkalinity.[109] However, long-term temperature variations due to climate change are presently much smaller than seasonal fluctuations, and the climate-induced precipitation of carbonates, though significant,[110] is much less important than seasonal variations.

In several instances one rather observes a long-term increase of alkalinity, especially in small lakes that have relatively low thermal capacity and respond quickly to temperature variations. The temperature increase may actually enhance the solubilization of salts, such as $CaSO_4$.[111] Of the dissolved ions thus generated, Ca^{2+} is either unchanged or incorporated without modification into living organisms. In contrast, SO_4^{2-} is transformed into organic (reduced) sulfur species according to the following process, where R−H is an organic compound:[112]

$$SO_4^{2-} + R\text{—}H + 6e^- + 8H^+ \rightarrow R\text{—}SH + 4H_2O \qquad (2)$$

The needed electrons are usually provided by living organisms in the form of reduced NAD coenzyme (NADH + H^+), which entails a 1:1 e^-/H^+ exchange. The incorporation of inorganic sulfur into organic molecules is thus equivalent to a net H_2SO_4 loss from lake water, which increases both alkalinity and pH. These effects are potentially favorable to $CO_3^{\bullet -}$-induced processes as explained below, but increases in alkalinity and pH are not necessarily climate-related. They might also take place because of recovery from acid rains and acid depositions, in which case one should observe that both NO_3^- and SO_4^{2-} undergo a long-term decrease.[113]

Figure 4a reports a modeled trend of $[CO_3^{\bullet -}]$ when pH increases at constant $[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$. $[CO_3^{\bullet -}]$ initially increases with pH up to pH 7, because HCO_3^- replaces H_2CO_3 that does not react with $^\bullet$OH.[114] The $[CO_3^{\bullet -}]$ value is then approximately constant in the pH interval 7−8, where HCO_3^- is the main $CO_3^{\bullet -}$ source and $[HCO_3^-]$ does not vary much. $[CO_3^{\bullet -}]$ increases again above pH 8−8.3, where CO_3^{2-} starts playing a significant role as $CO_3^{\bullet -}$ source (CO_3^{2-} reacts with $^\bullet$OH ∼ 50 times faster than HCO_3^-).[114] Depending on the conditions, $[CO_3^{\bullet -}]$ could be increased by 2−3 times from pH 6 to 9. However, the figure also shows that $[CO_3^{\bullet -}]$ is very sensitive to the DOC and that the pH effect can be easily offset by DOC variations. For instance, one needs pH 9 with DOC = 1.3 $mg_C\ L^{-1}$ to have the same $[CO_3^{\bullet -}]$ value that occurs at pH 7 with DOC = 1 $mg_C\ L^{-1}$. Considering that long-term pH changes do not usually exceed 0.2−0.3 pH units,[27,107,108] one needs a very stable DOC for $[CO_3^{\bullet -}]$ to be controlled by pH.

Figure 4b depicts the $[CO_3^{\bullet -}]$ changes when alkalinity varies at constant pH. $[CO_3^{\bullet -}]$ increases with alkalinity, but its sensitivity to the DOC is always important. To maintain the steady-state $[CO_3^{\bullet -}]$ constant after a DOC increase from 1 to 1.3 $mg_C\ L^{-1}$, alkalinity should for instance double from 1 to 2 mequiv L^{-1}, which is far beyond any expected climate effect.[27]

As a result, whether alkalinity decreases due to $CaCO_3$ ($MgCO_3$) precipitation or increases due to $CaSO_4$ dissolution, these changes are not necessarily reflected into a corresponding $[CO_3^{\bullet -}]$ variation.[27] Much depends on the DOC trend because the strong inverse relationship between $[CO_3^{\bullet -}]$ and DOC may easily prevail over the direct relationship between $[CO_3^{\bullet -}]$ and alkalinity.

3.4. Hotter Summers and Warmer Winters: Photochemical Implications of Lake Water Stratification and of Ice-Cover Duration.

One of the consequences of climate change is that summer temperatures will increase in many locations. During summer, lake water often undergoes stratification because the warmer and less dense surface water (epilimnion) floats over the colder and denser bottom water (hypolimnion). Epilimnion and hypolimnion are separated by the thermocline, a usually thin zone that is

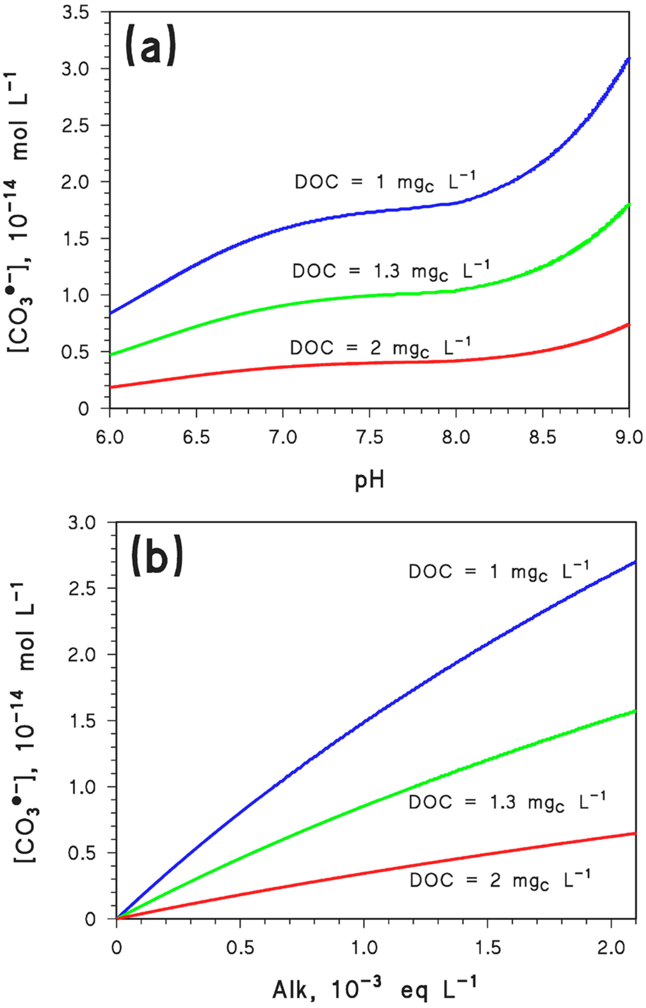

Figure 4. (a) Modeled steady-state $[CO_3^{\bullet -}]$ as a function of water pH, for different values of the DOC. Overall conditions: 22 W m^{-2} sunlight UV irradiance, 5 m depth, 0.1 mmol L^{-1} nitrate, 1 μmol L^{-1} nitrite, 1 mmol L^{-1} of H_2CO_3 + HCO_3^- + CO_3^{2-} (the concentration value of each of the three species depends on pH). (b) Modeled steady-state $[CO_3^{\bullet -}]$ as a function of alkalinity (Alk), for different values of the DOC. Overall conditions: 22 W m^{-2} sunlight UV irradiance, 5 m depth, 0.1 mmol L^{-1} nitrate, 1 μmol L^{-1} nitrite, $[CO_3^{2-}] = 10^{-3}$ $[HCO_3^-]$ (pH 7.3).

characterized by a sharp temperature drop.[109] Stratification may cause difficulties to higher life forms because the hypolimnion may become anoxic in highly productive environments,[115] although this does not always happen.[116] Summer stratification usually ends with lake overturn, which typically takes place in autumn when the water column becomes isothermal.[109] Higher temperatures will usually increase the stratified water stability and produce longer stratification periods, although the exact effects strongly depend on the environment.[117−119]

From a photochemical point of view, the surface water layer is thoroughly illuminated by sunlight and photodegradation processes are most efficient there. In contrast, the bottom water is much darker and photochemistry is inhibited as a consequence. When the lake is stratified, photochemistry proceeds faster in the sunlit epilimnion compared to the darker hypolimnion. The two compartments evolve differently, producing a depth gradient in the concentration of photodegradable compounds.[120] In contrast, during the mixing phase, the water transport processes are usually faster than photodegradation, and they ensure a fairly homogeneous chemical composition throughout the water column. Therefore, although most photodegradation takes place in the surface layer, the mixed system can be more easily described by considering average photodegradation kinetics in the whole water column.[30]

It is interesting to compare a mixed and a stratified system as far as the photodegradation efficiency is concerned. Time is a reasonable variable to be considered because summer stratification is expected to get longer because of climate change.[121] For simplicity, it is assumed here that the compound at time zero is evenly distributed in the whole water column, and that no emission occurs afterward. Then, in the one case, it is additionally assumed that the lake is stratified: therefore, the photochemical evolution of the compound is modeled separately in the epilimnion and the hypolimnion. At the end of the stratification period, it is hypothesized that the lake undergoes instantaneous mixing to achieve homogeneous concentration of the residual compound in the whole water column. The whole-column concentration is obtained as the average of the concentration values in the epilimnion and hypolimnion, weighted for the respective volumes (V_{epi} and V_{hypo}). The alternative scenario consists in thorough water mixing from the very start, so that the photochemical evolution of the compound is modeled in the whole water column. The modeled time trends will be labeled “epilimnion”, “hypolimnion”, “stratification + mix”, and “mix”, where the latter is referred to thorough water mixing. The stratification + mix case at a given time t assumes lake water stratification before t and complete mixing at t. Photodegradation is expected to be fastest in the epilimnion and slowest in the hypolimnion, but it is interesting to compare the stratification + mix and mix scenarios. This comparison is carried out in the framework of two different (simplified) lake geometries: a parallelepiped, swimming-pool-like shape (Figure 5a) and a conical geometry with 90° aperture angle (Figure 5b). Water chemistry is assumed to be the same in the two cases (see figure caption for details). Further information concerning modeling is provided as SI. The model results are here shown for dimethomorph (fungicide) and paracetamol (antipyretic).

In the case of the parallelepiped geometry, photodegradation of both compounds in the epilimnion is obviously faster than in the hypolimnion (Figure 5a1 and 5a2). The mix case is intermediate because here photodegradation takes place in the whole water column, which is deeper than the epilimnion but better illuminated than the hypolimnion. The comparison between the mix and stratification + mix scenarios suggests that photodegradation is faster in the mix case and that the differences between mix and stratification + mix are higher in the case of paracetamol. The reason is that paracetamol is more photolabile than dimethomorph.[83,122] A photolabile compound can undergo complete or almost complete degradation in the epilimnion during the stratification phase (see Figure 5a2). Degradation in the epilimnion has then to slow down or even stop due to lack of the substrate, despite elevated sunlight irradiance. At the same time, the fraction of pollutant that occurs in the hypolimnion cannot reach the water surface to be degraded, at least not until overturn (mixing). In contrast, photodegradation does not stop in the mix scenario because the compound does not reach complete degradation in the whole water column. Therefore, if the

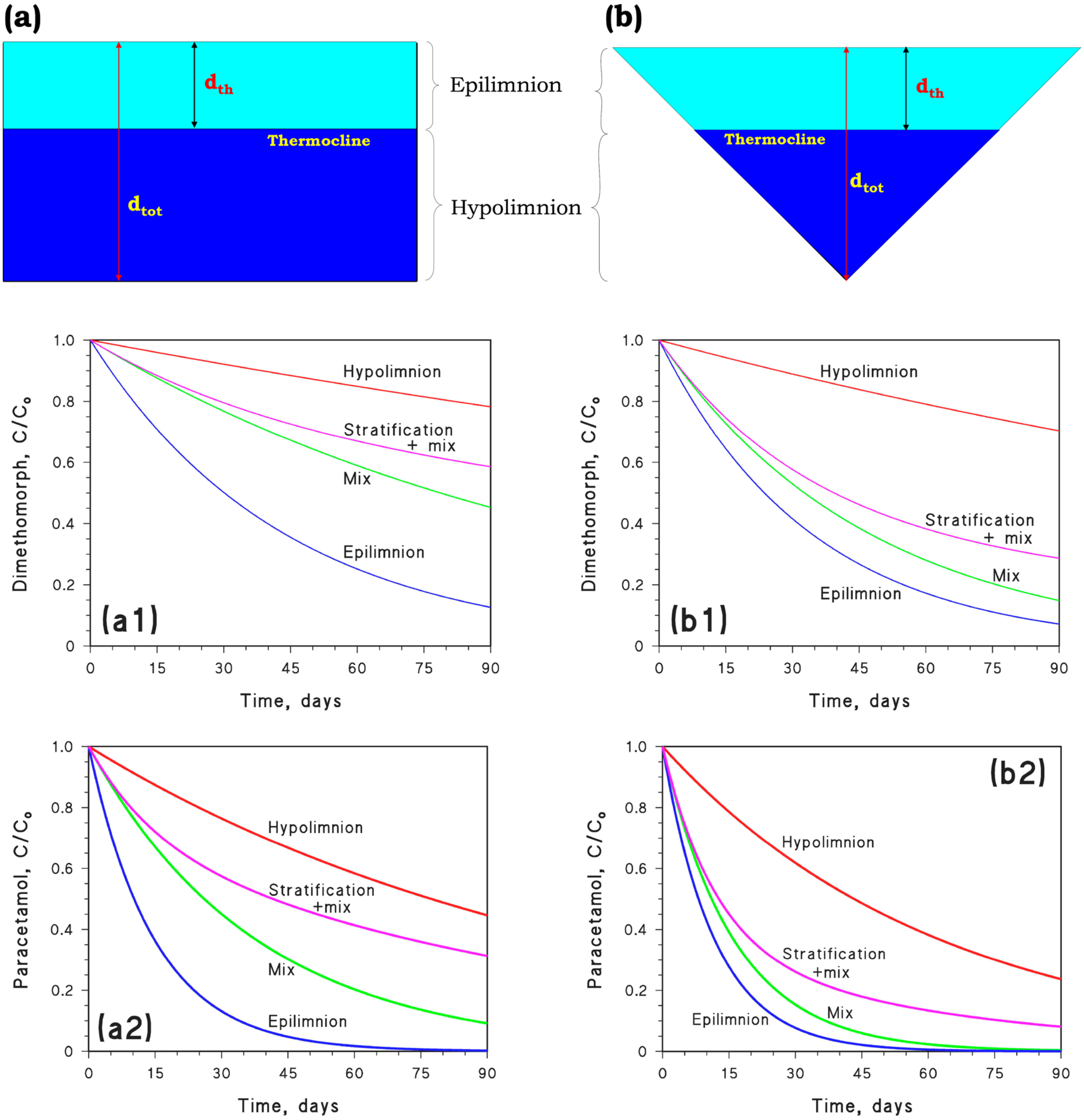

Figure 5. Comparison of phototransformation kinetics in lake water under stratification versus mixing conditions, in the case of a lake with parallelepiped shape (a) and with conical shape (b). Phototransformation in a thoroughly mixed water column is represented by the mix curves. In the case of stratification conditions, the evolution of pollutants in the epilimnion and hypolimnion was computed separately. The stratification + mix curves represent the pollutant concentration in the whole water column, following stratification for the given time period (e.g., 45 or 60 days) and sudden mix thereafter. The modeled pollutants are dimethomorph (a1 and b1) and paracetamol (a2 and b2). Water conditions: maximum lake depth d_{tot} = 50 m, depth of the thermocline d_{th} = 15 m (which gives a maximum hypolimnion depth of 35 m), 2 mg$_C$ L^{-1} DOC, 10^{-4} mol L^{-1} NO_3^-, 10^{-6} mol L^{-1} NO_2^-, 10^{-3} mol L^{-1} HCO_3^-, and 10^{-5} mol L^{-1} CO_3^{2-}.

compound is labile enough to be completely (or almost completely) photodegraded in the epilimnion, the stratification phase considerably slows down its overall degradation kinetics. Coherently, similar trends as those reported for paracetamol are also observed with the photolabile basic form of glutathione (GS$^-$) and with the MS2 virus (see Figure S7). To further support this interpretation, one can note that differences between mix and stratification + mix are very small in the case of carbamazepine, which is still less photoactive than dimethomorph (see Figure S8). If the difference between mix and stratification + mix is quite small, it can be offset by a deepening thermocline that might occur in some (but not all) environments as a consequence of higher temperatures.[123] A deeper thermocline would increase V_{epi} at the expense of V_{hypo}, slowing down the photodegradation kinetics in a deeper epilimnion.

In the case of the conical geometry, the time trends obtained by photochemical modeling are reported in Figure 5b1 (dimethomorph) and Figure 5b2 (paracetamol). Apart from the slightly different kinetics that depends on the different values of the average depths, the behavior of a conical lake would be very similar to that of a parallelepiped one. Again, differences between the mix and stratification + mix scenarios are expected to be smaller for dimethomorph than for paracetamol.

The reported results suggest that differences in photochemical behavior between mixed and stratified lake water do not depend much on the lake geometry. If the compounds occur in the lake water from the start and no emission takes place thereafter, a longer summer stratification period induced by climate change is expected to slow down the photodegradation kinetics. The effect is more important as the compounds are more photolabile.

On the other hand, if it is assumed that continuous emission takes place at the water surface, stratification is favorable to photodegradation because it is better for photodegradable solutes to be confined in the epilimnion, where photoreactions are faster. In a well-mixed water column, the compounds are in fact distributed in an environment that is less illuminated than the epilimnion. Finally, if continuous emission takes place at the lake bottom, stratification hinders photodegradation because the relevant compounds are confined in the dark hypolimnion.

Lakes located in mountain areas or lowland lakes in high-latitude regions may be ice-covered for a significant fraction of the year. When an ice sheet covers the lake surface, sunlight can hardly reach the underlying water and photochemical processes are stopped as a consequence. Therefore, it can be safely assumed that photochemistry in mountain lakes is operational from ice melting in late spring until ice reforming in autumn.[77,124] To make an instance, lakes located in the European Alps (midlatitude zone) at 2000−3000 m altitude are typically covered by ice from October−November until May−July.[125]

Global warming is expected to reduce the ice-cover duration because of increasing average temperatures, which will anticipate ice melting and delay ice reforming.[126] As a consequence of a longer ice-free period, photochemical processes will have more time to be operational. The seasonal trends of the steady-state [$^{\bullet}$OH], [$CO_3^{\bullet -}$], and [^{3}CDOM*] (~[$^1O_2$]) at midlatitudes in ice-free water are reported in Figure 6a, and they obviously show summer maxima and winter minima. To make an instance on possible implications, the corresponding seasonal trends of the pseudo-first-order degradation/inactivation rate constants and half-life times of GS^- (the basic form of glutathione) and the bacteriophage virus MS2 are reported in Figure 6b, which also gives insight into the model uncertainties.

It is noteworthy that the transient steady-state concentrations are quite higher in May−July (ice-melting time) than in October−November (ice-reforming time, see the arrows on the figure). Indeed, the photoreaction rates are directly proportional to the irradiance, while ice melting and ice reforming are delayed compared to the spring and fall equinox, respectively. The plot of Figure 6a clearly suggests that earlier ice-melting in spring, when transients steady-state levels in ice-free water would be high, has more important photochemical implications than delayed ice reforming in autumn.

Higher winter temperatures could also affect the vegetation cover. On a mountain slope the tree line defines the highest altitude at which trees can grow. Warming climate causes trees to grow at progressively higher altitudes, thereby colonizing environments where their presence was not possible just a few decades ago (however, a further reason for trees to grow in new areas is the abandonment of mountain villages).[127−129] An interesting implication of expanding forests is the changing nature of soil, because the forest soil is richer in organic matter compared to the soil of alpine meadows (or to a landscape that is made up of bare rocks, where soil is virtually absent).[130] These phenomena have implications for lake water photochemistry, because the photoactivity of lake water CDOM in mountain environments is largely affected by the surrounding vegetation, following the order: forests > meadows > bare rocks.[131] The rationale is that forest-soil CDOM is richer in humic substances, which can reach lake water via runoff and generate reactive species ($^{\bullet}$OH, ^{3}CDOM*, $^1O_2$) upon sunlight exposure. In contrast, in a lake surrounded by meadows or bare rocks the organic matter will mainly consist of autochthonous material produced by algae, such as proteins and oligopeptides, or of allochthonous compounds from atmospheric deposition, which absorb less sunlight and are less photoactive compared to humic substances.[132,133]

Increased CDOM photoreactivity together with a longer ice-free season will likely enhance photoreactions in mountain lakes, thereby increasing the lake water potential to photodegrade natural compounds, damage microorganisms, and

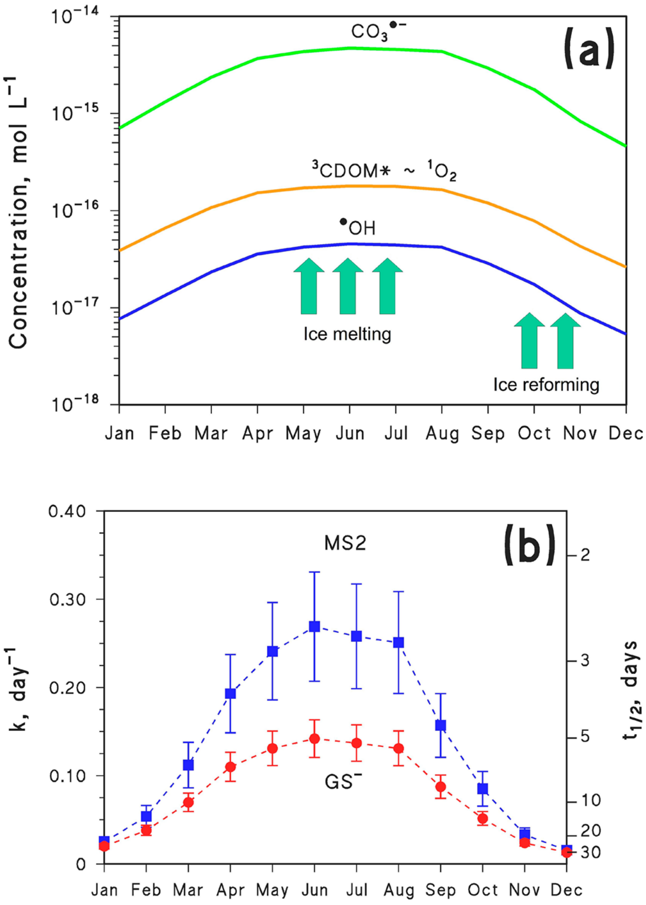

Figure 6. (a) Modeled steady-state concentrations of the main photogenerated transient species in different months of the year (Northern hemisphere). The vertical arrows highlight the periods of ice melting in May−July and ice reforming in October−November, which is for instance typical of lakes located in the European Alps at 2000−3000 m altitude. (b) Modeled first-order photodegradation rate constants (left *Y*-axis) and photochemical half-life times (right *Y*-axis) for the virus MS2 and the basic form of glutathione (GS^-). In both cases the irradiation conditions correspond to fair-weather days in mid latitude, without ice cover on the lake surface. Water conditions: 5 m depth, 2 mg_C L^{-1} DOC, 10^{-4} mol L^{-1} NO_3^-, 10^{-6} mol L^{-1} NO_2^-, 10^{-3} mol L^{-1} HCO_3^-, and 10^{-5} mol L^{-1} CO_3^{2-}. The error bounds represent the sigma-level uncertainty of model predictions.

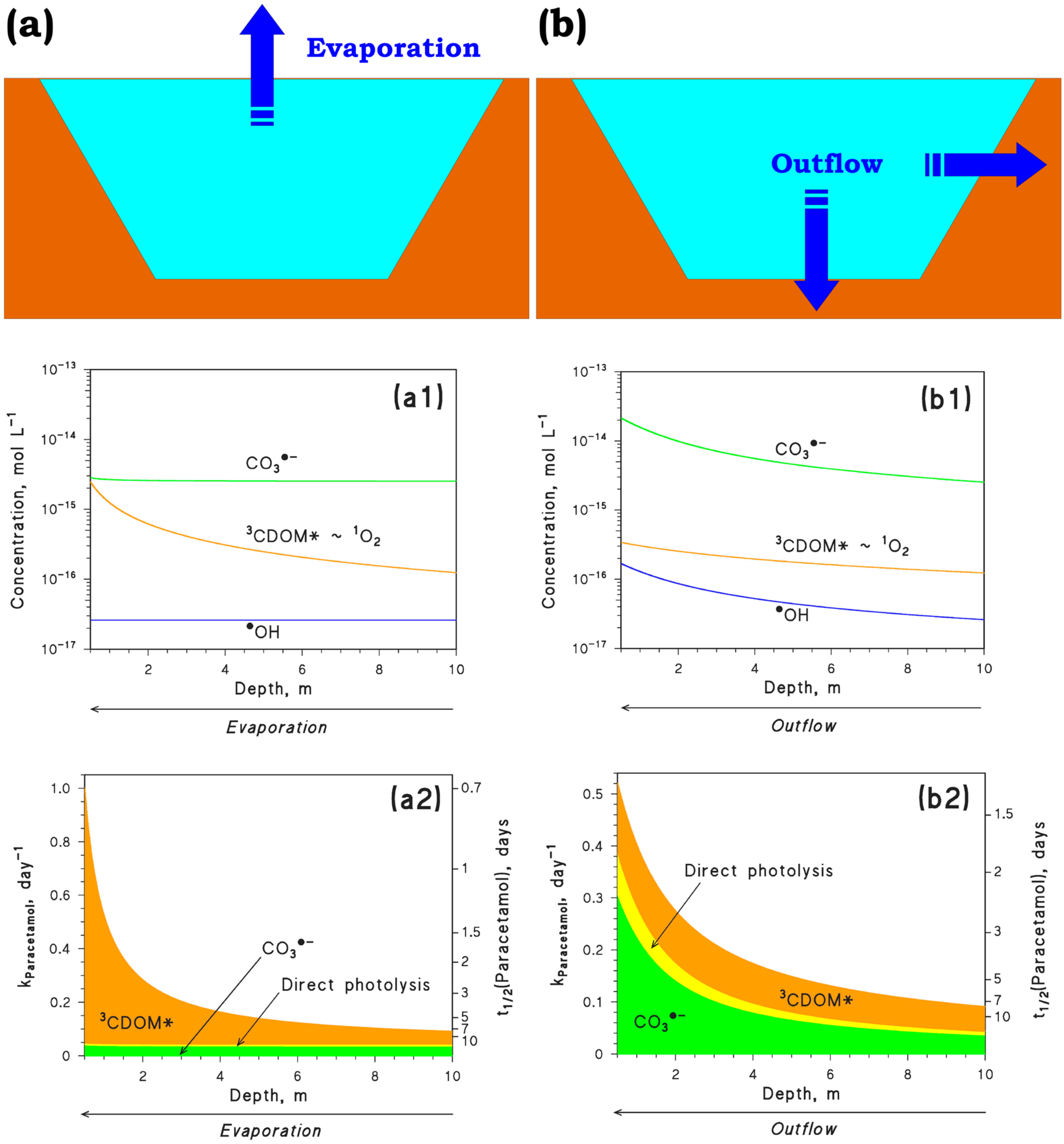

Figure 7. Trends of the main photogenerated transient species in lake water (steady-state concentrations) following evaporation (a, a1) and outflow (which includes seepage into sediments) (b, b1). Note the logarithmic scale in the *Y*-axis of (a1, b1). Modeled phototransformation kinetics of paracetamol because of evaporation (a2) and outflow (b2). The left *Y*-axis of (a2, b2) reports the photodegradation rate constants: the corresponding half-life times are shown in the right *Y*-axis. The contributions of the different photoinduced processes to photodegradation are highlighted with different colors. Initial water conditions in all cases: 2 mg_C L^{-1} DOC, 10^{-4} mol L^{-1} nitrate, 10^{-6} mol L^{-1} nitrite, 10^{-3} mol L^{-1} bicarbonate, 10^{-5} mol L^{-1} carbonate.

attenuate pollutants deriving from atmospheric depositions. Indeed, in scarcely populated mountain environments atmospheric depositions often prevail as pollution sources compared to agricultural activities and wastewater discharge.[133] Interestingly, the combination of a longer ice-free season with enhanced CDOM levels that increase water absorbance would have contrasting effects on the UVB stress to living organisms, with the former enhancing UVB exposure and the latter carrying out a protective effect.[77,134] However, tree growth is expected to be slower than changes in ice dynamics.[135]

3.5. Changes in Water Availability.

3.5.1. Water-Depth Fluctuations in Lakes. Climate change is expected to modify the amount and distribution of global precipitation. Water evaporation will increase in a warmer world, and globally the rate of precipitation equals the evaporation rate. However, precipitation rates are (and will be) unevenly distributed around the planet.[136,137] Figure S9 shows tentative predictive scenarios of future global precipitation (average differences between 2048 and 2018) for given global trends of atmospheric CO_2: a 1% increase per year (scenario 1, extrapolation of the present trend to the future), as well as two more optimistic projections (scenario 2, 0.5% increase per year; scenario 3, 0.2% increase per year).

The maps show that the precipitation increases will likely be concentrated in limited parts of the globe, and in several cases they will occur over the oceans. In some continental areas average precipitations might well decrease over time, despite the global precipitation increase. The different scenarios do not agree as to where these areas are located, but some continental zones of Africa, Asia, Central, and South America (and possibly Europe) might be affected. Moreover, even with constant average precipitations, increasing temperatures will produce enhanced evaporation and higher water demand for human activities, thereby increasing water-shortage probability.[138,139] Finally, the seasonal distribution of precipitation is also important. More refined climate models actually suggest that even in the case of constant average precipitation, one might expect an increasing alternation of heavy-rain periods with drought events.[140,141] Therefore, large fluctuations in water availability might occur in several areas around the world.

In the case of lakes, changing water availability modifies the water-column depth. Constant depth implies compensation between water inflow (from precipitation, ingoing rivers, deep sources) and outflow (through evaporation, seepage into sediments and outgoing rivers). Heavy-rain events usually provide a water surplus that causes the column depth to increase. In contrast, during prolonged droughts the water losses overcome the inflows, and water depth decreases as a result. In some arid environments, water loss may proceed up to complete lake desiccation.[142−144]

Water depth is a key variable for photochemical reactions, thus its fluctuations play an important photochemical role. In principle, photoinduced processes are faster in shallower environments and water photochemistry should be enhanced by drought events.[11] However, the level of enhancement of the different photoreaction pathways depends on the prevailing mechanism of water loss.[145]

First of all, water can simply flow away (e.g., in the sediments or along an out-going river) and not be restored by precipitation.[146] In this case, neglecting for simplicity chemical and biological processes occurring in shallow water and other solute sources/sinks, one may observe decreasing depth at constant water chemistry.[145] Water can also be lost by evaporation, which plays a major role in case of elevated dry-season temperatures, if the lake bottom is impermeable and in the absence of important out-flowing rivers.[147] Evaporation causes loss of water and of volatile solutes (e.g., dissolved gases), but photosensitizers and scavengers (except for O_2) are usually nonvolatile and remain in solution.[145] Evaporative concentration of nonvolatile solutes can sometimes give rise to high-salinity environments (brines) or even salt crusts after complete water evaporation.[148,149]

It is assumed here that decreasing water depth (and volume) following evaporation produces a proportional increase in the concentration values of NO_3^-, NO_2^-, HCO_3^-, CO_3^{2-}, and the DOM, expressed as DOC. In this context (simplified case of solute mass conservation), the same amounts of photosensitizers will absorb the same number of sunlight photons in a smaller water volume. Because transient formation rates are measured by formed amounts per unit volume and time, they will be higher in a smaller volume. Evaporation will also increase the concentration of scavengers, such as DOM, HCO_3^-, and CO_3^{2-}, but not of O_2 that is the main ^{3}CDOM* quencher. Moreover, inactivation of $^1O_2$ by collision with the solvent is unlikely to be affected by evaporation.[145]

The predicted trends of the steady-state [$^\bullet$OH], [$CO_3^{\bullet-}$], and [^{3}CDOM*] (∼[$^1O_2$]) as a consequence of pure evaporation are reported in Figure 7a1. Evaporation is not expected to modify [$^\bullet$OH] and [$CO_3^{\bullet-}$], because higher formation rates are compensated for by enhanced scavenging by DOM (for both $^\bullet$OH and $CO_3^{\bullet-}$), and by HCO_3^-/CO_3^{2-} (only for $^\bullet$OH). In contrast, [^{3}CDOM*] and [$^1O_2$] will increase because of enhanced formation rates and scarcely modified quenching kinetics.

The concentration trends caused by outflow (decreasing depth at constant water chemistry) are reported in Figure 7b1. In this case all the transient steady-state concentrations are predicted to increase with decreasing water depth, but the increase should be higher for $^\bullet$OH and $CO_3^{\bullet-}$ compared to ^{3}CDOM* and $^1O_2$. The rationale is that ^{3}CDOM* and $^1O_2$ are produced by irradiated CDOM, which absorbs UV−visible radiation. In contrast, $^\bullet$OH is also directly (and $CO_3^{\bullet-}$ indirectly) generated by nitrate and nitrite. Nitrate mostly absorbs UVB radiation that poorly penetrates in the water columns, while nitrite absorption largely occurs in the UVA that has intermediate behavior between UVB and visible light.[150] All photoreactions are thus enhanced in shallower water, but particularly the processes triggered by UV-only absorbing species such as nitrate and nitrite.

The different impacts of evaporative concentration and outflow on the phototransformation kinetics of paracetamol are reported in Figure 7a2 (evaporation) and Figure 7b2 (outflow). First of all, phototransformation always gets faster as the water depth decreases. However, the reasons for this acceleration are scenario-dependent. In the case of evaporation, faster degradation is caused by the enhanced ^{3}CDOM* process. In contrast, during outflow the photodegradation is enhanced by $CO_3^{\bullet-}$. Moreover, direct photolysis is enhanced by outflow because paracetamol absorbs sunlight UV, which penetrates poorly in deep water columns. In contrast, direct photolysis is not much modified by evaporation, because the effect of a shallower water column is offset by higher CDOM levels. Similar behavior as for paracetamol is predicted for GS$^-$ and MS2 (Figure S10).

Dissolved O_2 was here assumed not to vary for simplicity, but in the dry season, it could be either decreased by high temperatures that inhibit its solubilization in water, or increased by photosynthetic activity.[151] Because O_2 scavenges ^{3}CDOM* to produce $^1O_2$, lower O_2 levels would decrease [$^1O_2$] and increase [^{3}CDOM*] (and vice versa for higher O_2 levels). Therefore, the behavior of [^{3}CDOM*] with decreasing depth may be somewhat different from that shown in Figure 7. Moreover, the $CO_3^{\bullet-}$ role could be reduced by $CaCO_3$ precipitation.[109]

3.5.2. The Case of Rivers. The importance of photochemical reactions in rivers largely depends on the water flow and particularly on the flow velocity.[152] Note that the flow rate Q (units of m^3 s^{-1}) is the water volume flowing per unit time, while the flow velocity $\overline{v}$ (units of m s^{-1}) indicates how fast the water travels along the watercourse. The value of $\overline{v}$ is more variable than that of Q along a river stretch, but the average $\overline{v}$ in a river combined with the river length provides the time scale within which photoreactions can take place.[153] In the case of a river eventually discharging into the sea, one can assume that photochemistry in river water is important only if it induces significant transformation of (at least some) solutes before seawater mixing.[152]

In the framework of a variable precipitation regime, one can expect a widely changing river flow rate. The flow rate is actually one of the most common variables to describe river water availability because it represents the water volume delivered per unit time. According to the schematic in Figure 8, the flow rate Q can be expressed as $Q = \Delta y \Delta z \overline{v}$.[154] In the framework of pollutant photodegradation, it is very important to derive the average flow velocity (which might not be trivial, as conditions change along the watercourse[153,154]) because $\overline{v}$ transforms a half-life time into a half-life length. By so doing, one can ascertain whether the river is long enough to ensure sufficient pollutant transformation due to photochemical processes.[152]

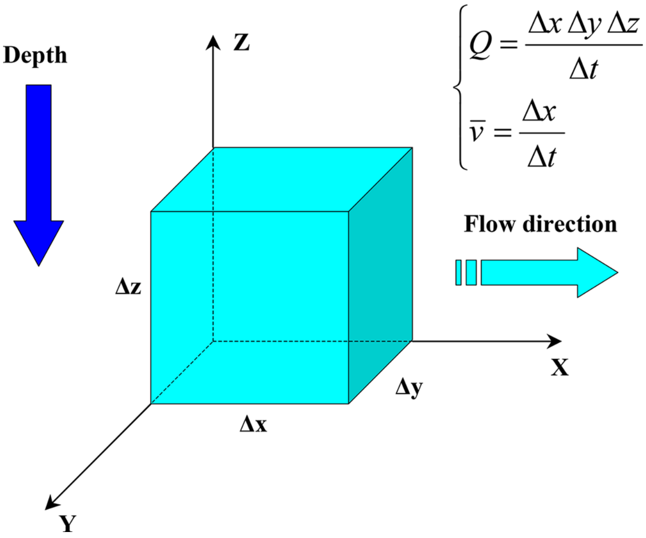

Figure 8. Schematic of river flow based on a small volume cell. The relationship between flow rate Q and flow velocity $\overline{v}$ is also given.

Assume a river with flow rate $Q = 100$ m^3 s^{-1} and an average flow velocity $\overline{v} = 1$ m s^{-1} under normal flow conditions. The assumed flow rate can for instance be obtained with an average water depth of 4 m and an average width of 25 m. Then, assume that a prolonged drought period causes Q to decrease down to 1/100 of the initial value. Under the simplified hypothesis that the decrease in Q is evenly distributed along the three axes, one obtains that water depth, river width, and flow velocity are each decreased by a factor of $\sqrt[3]{Q/Q_o} \sim 4.6$ times. Note that decreasing width has negligible impact on photochemical reactions. Considering flow rate Q, flow velocity $\overline{v}$, and depth d one has $\overline{v}/\overline{v}_o = d/d_o = \sqrt[3]{Q/Q_o}$, where "o" refers to normal flow conditions ($Q_o = 100$ m^3 s^{-1}, $\overline{v}_o = 1$ m s^{-1}, $d_o = 4$ m).

In rivers, outflow strongly overcomes evaporation and it can be assumed for simplicity that the flow-rate decrease takes place at constant water chemistry. By knowing the variations in water depth d one can model the photodegradation rate constants k, and the usual relationship applies between k and the half-life time ($t_{1/2} = \ln 2 \; k^{-1}$). Then, the relationship between half-life time ($t_{1/2}$) and half-life length ($l_{1/2}$, which is the river length needed to halve the initial substrate concentration) should take into account the river flow velocity ($l_{1/2} = \overline{v} \; t_{1/2}$).[152]

Model results are reported in Figure 9 for dimethomorph (**9a**), paracetamol (**9b**), GS$^-$ (**9c**), and MS2 (**9d**) as a function of the flow rate Q. The phototransformation rate constants increase as the water flow decreases because of decreasing water depth. The increase in k is largely accounted for by $^\bullet$OH for dimethomorph, $CO_3^{\bullet -}$ for paracetamol and GS$^-$, and direct photoinactivation for MS2. Moreover, the changing water depth and rate constant combine with the varying flow velocity $\overline{v}$ to affect the half-life length $l_{1/2}$: for dimethomorph, a $t_{1/2}$ doubling from 5 to 10 days causes a 6.5-times increase of $l_{1/2}$. For paracetamol, doubling $t_{1/2}$ from 2 to 4 days increases $l_{1/2}$ by 6 times, and a 5-fold $l_{1/2}$ increase is produced when doubling the MS2 lifetime from 1 to 2 days.

The more photolabile species paracetamol and MS2 have clearly higher chances to undergo significant photodegradation in river water: low-flow conditions may produce $l_{1/2} = 10-50$ km, and in many circumstances extensive phototransformation could occur between the outlet of a given WWTP and the next. In this case, enhanced photodegradation could partially offset the higher level of contamination produced by lesser wastewater dilution, caused by low river water flow.[155,156] In contrast, the $l_{1/2}$ values for dimethomorph easily reach the hundred-kilometer range, and not all rivers are long enough to ensure sufficient photodegradation of this compound. A similar issue happens with refractory carbamazepine (see Figure S11); thus, it is not surprising if carbamazepine is usually considered as a conservative compound in river water.[157,158] Indeed, photodegradation of refractory compounds in rivers might require very low flow conditions caused by prolonged drought to become important.

3.7. Drought-Flood Scenarios. A likely future evolution that may be observed in many world regions is an intermittent level of precipitations, even at constant or nearly constant average amounts, with long rainless periods, followed by intense precipitation events.[140] During droughts, a major pollution problem is represented by low wastewater dilution.[155] In this case, enhanced photochemical processes may partially compensate for increased pollution.[152] In contrast, during heavy-rain events the main pollution source to surface waters is the mobilization of pollutants from the watershed (e.g., soil, ponds, urban areas).[159] In this case, photochemistry may contribute little to decontamination because of the combination of high water depths and (for rivers) high water flow velocities. Therefore, if a drought-flood scenario becomes the norm in a water basin, photochemistry may help decontaminate enhanced pollution by wastewater during droughts, but it may be less effective against pollution by watershed runoff during floods.

4. RESEARCH NEEDS

An attempt was made here to provide quantitative predictions of the foreseeable impacts of climate change on photochemical processes in surface fresh waters. However, in several cases, the quantitative approach was enabled by assumptions and approximations that may hide important knowledge gaps. Modifications in the trophic status of water bodies brought about by climate change, with possible events of eutrophication or oligotrophication depending on features, such as location, latitude, and environmental conditions, have a potentially foreseeable but still poorly known impact on photochemistry. It will also be important to better understand the impact of climate change on the (C)DOM quantity, quality, and photoreactivity (here assumed not to vary with

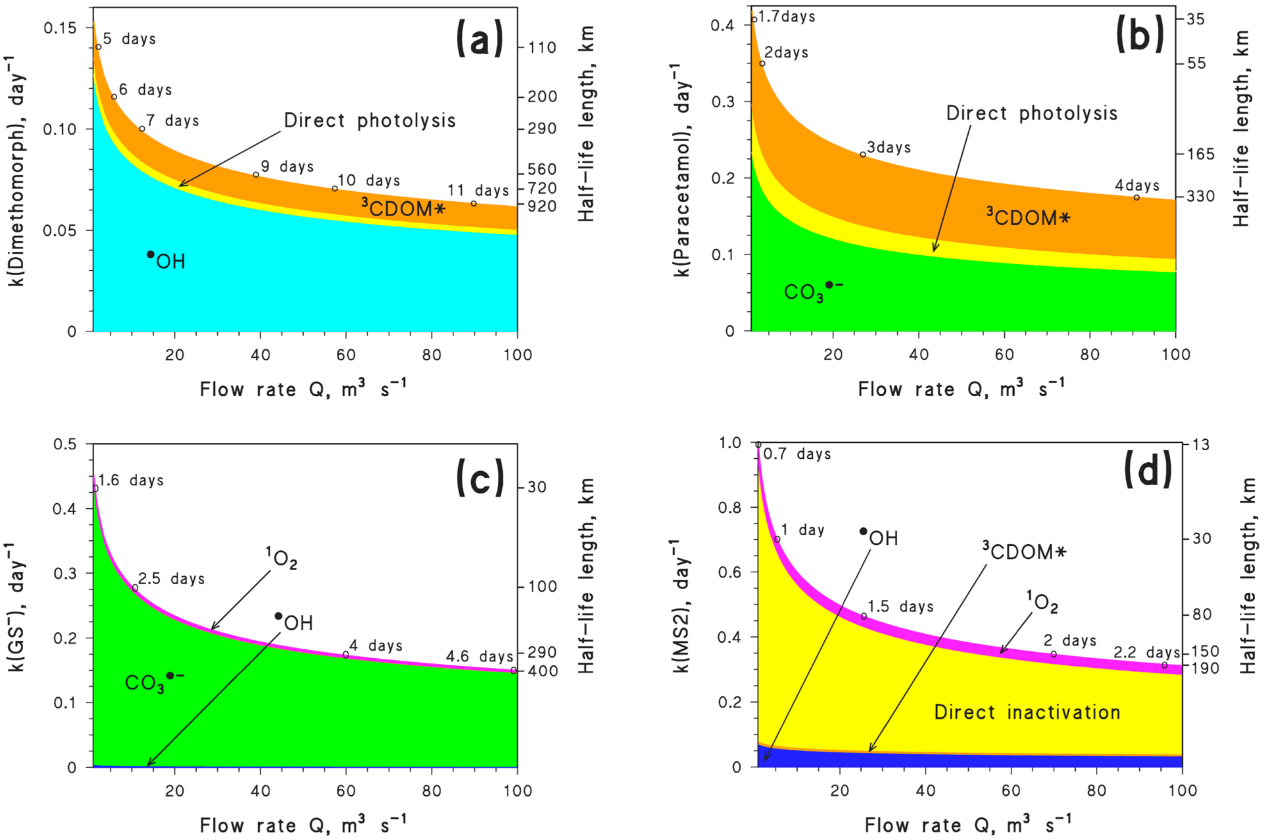

Figure 9. Variations of the photodegradation kinetics of dimethomorph (a), paracetamol (b), GS$^-$ (c), and MS2 (d) as a function of the river flow rate Q. The left-Y axis reports the modeled photodegradation rate constants k. The circles show sample half-life times that correspond to given values of the photodegradation rate constant ($t_{1/2} = \ln 2\ k^{-1}$). The half-life lengths reported on the right Y-axis were calculated on the basis of the half-life times reported as circles ($l_{1/2} = \bar{v} t_{1/2} = \bar{v}_o t_{1/2} \sqrt[3]{Q/Q_o}$). Other water conditions in both cases: 2 mg$_C$ L^{-1} DOC, 10^{-4} mol L^{-1} nitrate, 10^{-6} mol L^{-1} nitrite, 10^{-3} mol L^{-1} bicarbonate, 10^{-5} mol L^{-1} carbonate. The water depth was d_o = 4 m, when Q_o = 100 m^3 s^{-1}, and it varied as $d = d_o \sqrt[3]{Q/Q_o}$.

varying DOC, see SI), where opposite effects may possibly take place in different kinds of environments. Moreover, the role of ^{3}CDOM* in pollutant photodegradation will certainly benefit from more accurate measurements of the relevant reaction rate constants.[160,161]

It should be underlined that the quantity and quality of photosensitizers and scavengers in water is only one of the factors involved in photochemical reactions that are potentially affected by climate change. In temperate environments, modifications in hydrological features, such as water depth, flow rate, and summer lake water stratification, will likely be much more important. First of all, more straightforward ways are needed to determine the average flow velocity in rivers.[153,154] Furthermore, the quantitative approach followed here did not consider parallel variations of hydrological features and water chemistry, except for the case of evaporative concentration in lakes. Changes in hydrology may actually take place together with additional processes, which could introduce further chemistry variations and modify the predicted trends.[162,163] There is a clear need to study real-world cases, to understand how phenomena such as prolonged drought may affect the photochemical parameters. For instance, conditions of oxygen scarcity may be caused by a temperature increase,[164] depleting ^{1}O$_2$ and enhancing ^{3}CDOM*. This phenomenon has the potential to speed up the photodegradation of pollutants that react with ^{3}CDOM* rather than ^{1}O$_2$. The reverse may take place during algal blooms because of enhanced photosynthesis.[165] The assessment of cases drawn from actual environments will help corroborate or negate these speculations.

Changes in phototransformation pathways, in addition to the phototransformation kinetics, may induce modification in the toxicity profile of the intermediates. The study of the hazards connected with intermediates formed via different photoreaction pathways is a research topic that has attracted very little attention thus far. Indeed, there should be wide room for introducing a new discipline (environmental phototoxicology of pollutants) that is presently almost a blank sheet.

5. IMPLICATIONS FOR CLIMATE-AFFECTED ENVIRONMENTS

Climate change has the potential to alter many features of water bodies, and some of them may affect considerably the photoinduced processes. In some cases the modifications will alter all photochemical pathways, while in other cases the photoreactions will be shifted from, for example, ^{3}CDOM*/^{1}O$_2$ to •OH/CO$_3^{•-}$/direct photolysis or vice versa. In the latter scenarios, different classes of pollutants will undergo a varying degree of photodegradation. Indeed, •OH is involved in the photodegradation of recalcitrant compounds (e.g., carbamazepine and acesulfame K) and

Table 1. (Top) Summary of the Main Foreseeable Effects of Climate Change on Photochemical Processes in Surface Fresh Waters and (Bottom) Pollutant Classes That Are Preferentially Degraded by the Different Photogenerated Transient Species ($^{\bullet}OH$, $CO_3^{\bullet -}$, $^3CDOM^*$, $^1O_2$)

phenomenon	enhanced pathways	inhibited pathways
browning	$^3CDOM^*$, $^1O_2$	$^{\bullet}OH$, $CO_3^{\bullet -}$, direct photolysis
photobleaching/DOC decrease	$^{\bullet}OH$, $CO_3^{\bullet -}$, direct photolysis	$^3CDOM^*$, $^1O_2$
photobleaching/DOC increase	direct photolysis	$^3CDOM^*$, $^1O_2$, $^{\bullet}OH$, $CO_3^{\bullet -}$
alkalinity increase	$CO_3^{\bullet -}$ (but rarely stands out)	$^{\bullet}OH$
longer summer stratification in lakes	all if compounds occur in the epilimnion	all if compounds occur in the hypolimnion or if they are photolabile and evenly distributed in the water column
shorter period of ice cover	all	
evaporative concentration	$^3CDOM^*$, $^1O_2$	
non-offset water outflow	$^{\bullet}OH$, $CO_3^{\bullet -}$, direct photolysis	
lower flow velocity in rivers	all	
higher flow velocity in rivers		all

transient species	pollutant classes preferentially degraded by the given transient
$^{\bullet}OH$	recalcitrant pollutants, hydrocarbons
$CO_3^{\bullet -}$	phenols, anilines, sulfur-containing compounds
$^3CDOM^*$	phenols, phenylurea herbicides, sulfonamide antibiotics
$^1O_2$	chlorophenolates, natural compounds, viruses

hydrocarbons, $CO_3^{\bullet -}$ reacts preferentially with aromatic amines, phenols, and sulfur-containing molecules, while $^3CDOM^*$ is for instance involved in the photodegradation of phenols, phenylurea herbicides, and sulfonamide antibiotics. Interestingly, phenols can be photodegraded by both $CO_3^{\bullet -}$ at low (C)DOM and $^3CDOM^*$ at high (C)DOM, and the pathway shift may not affect much phototransformation. As far as the reaction routes are concerned, both $CO_3^{\bullet -}$ and $^3CDOM^*$ can transform phenols into the corresponding phenoxy radicals, with possible formation of dimeric species or even dibenzofurans, which may be of particular concern in the case of chlorophenols.[166,167] Differently from pollutants, natural compounds and viruses can undergo efficient degradation/inactivation by $^1O_2$. For some viruses, photoinactivation could involve a direct process at low (C)DOM and $^1O_2$ reaction at high (C)DOM.

Climate effects on water chemistry may be very important in several lakes located at elevated latitudes in the boreal hemisphere and, especially, in the Scandinavian peninsula because of the phenomenon of water browning associated with (C)DOM increases.[168] The most likely photochemical consequence of browning is an enhancement of $^3CDOM^*/^1O_2$ reactions at the expense of $^{\bullet}OH$, $CO_3^{\bullet -}$, and direct photolysis.[96] However, other lakes might undergo both DOC decrease and photobleaching,[116] which is the opposite phenomenon and would shift photoreactions in the opposite direction. Moreover, some lakes undergoing photobleaching and DOM increase at the same time,[116] would experience inhibition both of $^3CDOM^*/^1O_2$ due to the CDOM decrease (photobleaching), and of $^{\bullet}OH/CO_3^{\bullet -}$ due to enhanced scavenging (DOM increase). All the main indirect photochemistry pathways will thus be inhibited, but direct photolysis will be enhanced by photobleaching, which increases the underwater irradiance available for direct photoreactions.

Compared to boreal environments, temperate water bodies will probably undergo less important changes in water chemistry. Alkalinity and pH affect the $CO_3^{\bullet -}$ reactions, but the steady-state $[CO_3^{\bullet -}]$ is very sensitive to the DOC, and small DOC fluctuations could overcome most alkalinity variations.[27]

While changes in water chemistry and especially (C)DOM features are scientifically very intriguing, photochemical modeling suggests that the most important photochemistry modifications are to be looked for in the realm of hydrology and, especially, the changes in water dynamics and availability. Warmer summers may produce longer lake stratification,[119] thereby enhancing the separate photochemical evolution of the sunlit epilimnion and the dark hypolimnion. The expected effect on the degradation kinetics is strongly dependent on substrate photoreactivity, distribution, and mode of emission, while the shape of the lake might play a less important role. In this case, all photochemical reactions will be either enhanced or inhibited.

All photoreactions in high-mountain lakes may be enhanced by a shorter period of ice cover,[77] because all photoprocesses are virtually extinguished in ice-covered water. Given the monthly trend of sunlight irradiance, anticipated ice melting in late spring might have higher impact on photoreactions than delayed ice reforming in late autumn. On a longer term, these processes will occur together with changes connected with a progressively more elevated treeline.[131]

Climate effects may also induce considerable fluctuations in water availability, with important changes in the water-column depth of lakes, as well as in the depth and flow velocity of rivers. In both cases, conditions of water shortage might enhance the kinetics of photoinduced reactions. In the case of lakes, the water-loss mechanism is very important, because evaporation favors $^3CDOM^*/^1O_2$, while outflow/seepage mostly enhances $^{\bullet}OH/CO_3^{\bullet -}$.[145] Further issues that might be important are seasonal irradiance changes as the water is lost, in-water reactions, and inputs/outputs of solutes that further modify the water chemical composition.[163] In the case of rivers much depends on the average water flow velocity, which sets the time frame for (all) photoreactions to occur. Wastewater pollutants become a problem with water scarcity because of lesser wastewater dilution, but photochemical reactions might in part compensate for this through enhanced kinetics and longer time scales allowed for degradation.[152] In contrast, watershed pollutants reaching surface waters during floods are much less likely to undergo effective photodegradation.

See Table 1 for a summary of all these implications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b00968.

> Photochemical model details, effect of environmental factors on aquatic photoreactions, modeling of stratified lake water, global precipitation map, and model results for glutathione, MS2, and carbamazepine in rivers (PDF)

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■ GLOSSARY OF IMPORTANT TERMS

- **Chromophoric dissolved organic matter (CDOM)**: the fraction of dissolved organic matter that absorbs sunlight and induces photochemical reactions.
- **CDOM triplet states (^{3}CDOM*)**: excited states of CDOM that are formed from excited singlets (^{1}CDOM*) upon light absorption and intersystem crossing
- **Dissolved inorganic carbon (DIC, $\mathrm{mg_C\ L^{-1}}$)**: the sum of the concentrations of dissolved H_2CO_3, HCO_3^-, and CO_3^{2-}
- **Dissolved organic carbon (DOC, $\mathrm{mg_C\ L^{-1}}$)**: the concentration of organic carbon that is dissolved in natural waters; it is the most straightforward way to quantify DOM
- **Dissolved organic matter (DOM)**: the pool of (mostly natural) compounds that are dissolved in environmental waters and act as scavengers of $^\bullet$OH and $CO_3^{\bullet-}$
- **Photobleaching**: the loss of absorbance by CDOM upon exposure to sunlight due to the degradation of chromophoric species.
- **Quantum yield**: the ratio between the transformation rate of a photochemical reaction and the photon flux absorbed by the species that triggers the process (directly or indirectly)
- **Steady-state concentration**: the concentration of a transient species T, constant with time, which results from the budget of formation and very fast transformation; if S is a sensitizer and P a product, with R_T as the formation rate of T and k as the first-order transformation rate constant of T into P, then $\begin{cases} \mathrm{S} \xrightarrow{h\nu} \mathrm{T} & \dfrac{d[\mathrm{T}]}{dt} = 0 = R_\mathrm{T} - k[\mathrm{T}] \Rightarrow [\mathrm{T}] = \dfrac{R_\mathrm{T}}{k} \\ \mathrm{T} \xrightarrow{k} \mathrm{P} & \end{cases}$ applies

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