



Long-term trends of chemical and modelled photochemical parameters in four Alpine lakes



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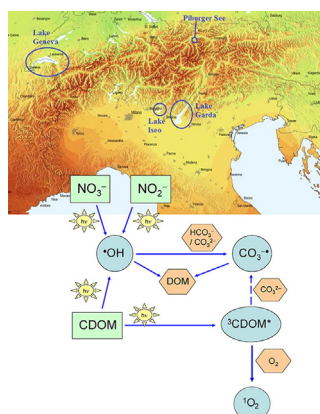
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HIGHLIGHTS

- Photoinduced species ($\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$, $^3\text{CDOM}^*$) were modelled in four Alpine lakes.
- Photochemical modelling was based on long-term series of water chemistry.
- Chemical stability implied stability of photochemical parameters.
- In Piburgersee, large chemistry variations still yielded photochemical stability.
- There is evidence of “photochemical buffering” effects in some lake ecosystems.

GRAPHICAL ABSTRACT



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ABSTRACT

Based on long-term trends of water chemistry parameters of photochemical significance from four lakes located in the Alps (Iseo, Garda, Piburgersee, Geneva), we calculated the corresponding steady-state concentrations of photoinduced transient species with an *ad-hoc* photochemical model. Such transients were the hydroxyl ($\cdot\text{OH}$) and carbonate ($\text{CO}_3^{\cdot-}$) radicals, singlet oxygen ($^1\text{O}_2$), and the triplet states of chromophoric dissolved organic matter ($^3\text{CDOM}^*$). Among the investigated lakes, Lake Iseo, for example, showed a long-term near-stability in chemical parameters that resulted in a photochemical stability. By contrast, Piburgersee underwent important chemical modifications, but the interplay of compensation (parallel increase of both inorganic and organic carbon) and near-saturation effects (organic matter as main $\cdot\text{OH}$ source and sink) prevented the modelled photochemistry to undergo significant shifts over time. This result suggests the occurrence of a sort of “photochemical buffering” in some lake ecosystems, which would dampen modifications of the steady-state concentration of the photochemically-formed reactive transients, even in the case of significant changes in water chemistry. Finally, in lakes Garda and Geneva, long-term changes in water chemistry had an effect on photochemistry. While in Lake Garda the small increase in DOM was associated to a small increase in $^1\text{O}_2$ and $^3\text{CDOM}^*$, in Lake Geneva, the increases in pH and bicarbonate and the decrease in nitrite resulted in an $\cdot\text{OH}$ decrease. Overall, our results

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predict very different lake photochemistry patterns in relation to alterations in water chemistry parameters caused by climate change, such as changes in water alkalinity and dissolved organic carbon concentration.

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1. Introduction

The chemical composition of lake water has important effects on (and it is in turn affected by) biological and abiotic processes, including those induced by exposure to sunlight. Water chemical composition has typically seasonal fluctuations, such as for example, the summer minima of nitrate (consumed by algal growth) and alkalinity (due to CaCO_3 precipitation), as well as the summer maxima of pH (because of CO_2 consumption by photosynthesis) and, sometimes, of the dissolved organic carbon (DOC; organic compounds may be released in summer by algal growth and lysis or be introduced from the catchment) (Wetzel, 2001). Water chemical composition is also affected on the long-term by direct human disturbance (e.g., eutrophication) and climate change (Rogora et al., 2003; Adrian et al., 2009; Lu et al., 2013). Lakes are good sentinels of diverse environmental changes due to their ability to quickly modify their chemical, physical and biological characteristics as a consequence of alterations in their surrounding landscape and atmosphere (Bertoni et al., 1998; Carpenter et al., 2007; Pham et al., 2008; Williamson et al., 2008; Adrian et al., 2009; Williamson et al., 2009).

The effects of climate change may be observed on a range of chemical parameters of lake water. However, the effects can be variable depending for example, on latitude, catchment characteristics and multiple climate-related phenomena (Porcal et al., 2009; Sucker and Krause, 2010; Rogora et al., 2013; Mosley, 2015), as well as on alkalinity (Sommaruga-Wögrath et al., 1997; Skjelkvåle et al., 2005). The associated changes impact the biota and can also modify the way the lake responds to sunlight exposure, including most notably several photochemical reactions (De Laurentiis et al., 2014).

Alkalinity is largely affected by climate change, particularly in soft-water lakes (Schindler, 1997; Sommaruga-Wögrath et al., 1997; Koinig et al., 1998). Changes in alkalinity may involve the temperature-enhanced dissolution of CaSO_4 , where Ca^{2+} can be up-taken, but it is not transformed by biota, while SO_4^{2-} is biologically transformed into organic sulphur compounds with consumption of H^+ . The latter induces, for example, enhanced dissolution of carbon dioxide into the surface lake water layer (Schindler, 1997). For example, in reaction (1), R-H is an organic compound and R-SH is a mercaptan, and several H^+ ions are consumed in the relevant transformation.

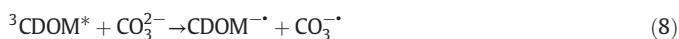
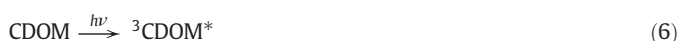


The DOC content of lake water is largely influenced by runoff, which in turn may be affected by climate change (Hudson et al., 2003; Zhang et al., 2010). Changes in DOC concentration are important because they affect the penetration of sunlight (and most notably of UV radiation) into the water column (Laurion et al., 2000), as well as several other processes including photochemical reactions (Schindler, 1997).

In lake water, the absorption of light by photosensitizers, which include chromophoric dissolved organic matter (CDOM), nitrate and nitrite is one of the key steps of the aqueous photochemical reactivity. The irradiation of the photosensitizers induces the production of transient species, such as the hydroxyl ($\cdot\text{OH}$) and carbonate ($\text{CO}_3^{\cdot-}$) radicals, singlet oxygen ($^1\text{O}_2$), and CDOM triplet states ($^3\text{CDOM}^*$) (Pace and Barreca, 2013; Vione et al., 2014). These transient species are reactive and they can be involved in the photochemical transformation of many biorefractory pollutants (industrial chemicals, some pesticides, pharmaceuticals and personal care products) and of naturally occurring DOM (dissolved organic matter; Medeiros et al., 2015; Minella et al., 2015). Therefore, they contribute strongly not only to

the photochemical self-depuration potential of surface water bodies (Peng et al., 2006; Fenner et al., 2013; Zeng and Arnold, 2013), but also to the biogeochemical transformation of key nutrients (C, N, P).

The $\cdot\text{OH}$ radical is formed upon photolysis of nitrate and nitrite (reactions 1, 2). The hydroxyl radical is also formed by irradiation of CDOM, the latter through pathways that are not yet completely elucidated (Page et al., 2011; Glover and Rosario-Ortiz, 2013; Mostafa et al., 2014) and that could also involve iron-based species in Fenton/photo-Fenton processes. The radical $\text{CO}_3^{\cdot-}$ is formed upon oxidation of carbonate and bicarbonate by $\cdot\text{OH}$ (reactions 3, 4) and, to a lesser extent, upon carbonate oxidation by $^3\text{CDOM}^*$ (Canonica et al., 2005). Singlet oxygen and $^3\text{CDOM}^*$ are produced by CDOM irradiation according to reactions (6, 7, 8) (Coelho et al., 2011; Mostafa and Rosario-Ortiz, 2013; Marchisio et al., 2015).



Lake-water components can also scavenge the reactive transients. For instance, DOM is the main sink of both $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$, while $\cdot\text{OH}$ is also significantly scavenged by carbonate and bicarbonate (reactions 4, 5) and, to a lesser extent, by nitrite. In brackish water and saltwater, bromide is the main $\cdot\text{OH}$ sink. The transients $^3\text{CDOM}^*$ and $^1\text{O}_2$ can react with organic matter, but DOM plays a minor role as their scavenger (Cory et al., 2010; Wenk et al., 2013). In contrast, the main $^1\text{O}_2$ sink is the thermal deactivation upon collision with water, while $^3\text{CDOM}^*$ is mostly scavenged by O_2 (reaction 7) and it can also be thermally deactivated (Vione et al., 2014; Page et al., 2014).

Interestingly, CDOM is an important photosensitizer and DOM is a sink for several transient species, but DOM-rich waters (characterized by elevated levels of the dissolved organic carbon, DOC) usually contain high CDOM as well. The combination of formation and scavenging accounts for the typical correlations that are observed between transient species and water components (Vione et al., 2014). Because CDOM is an important $\cdot\text{OH}$ source, but DOM is by far its main sink, the $\cdot\text{OH}$ levels can be negatively related with DOC. An even stronger negative relationship is often observed between DOC and $\text{CO}_3^{\cdot-}$, because DOM both scavenges $\text{CO}_3^{\cdot-}$ and inhibits its formation by consuming $\cdot\text{OH}$ (Canonica et al., 2005; Vione et al., 2014). In contrast, $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$ often positively correlate with nitrate and nitrite, and $\text{CO}_3^{\cdot-}$ with inorganic carbon species as well (Minella et al., 2011). The transients $^3\text{CDOM}^*$ and $^1\text{O}_2$ are produced by CDOM irradiation and they are poorly scavenged by DOM, thus they positively correlate with DOC. However, the correlation may be weak because CDOM is a major radiation absorber (Bracchini et al., 2005) and it can easily become saturated (Vione et al., 2014). If this is the case (which is more common at elevated DOC levels), CDOM variations may have a limited impact on the photon flux absorbed by CDOM itself (Minella et al., 2013; Bianco et al., 2015),

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