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

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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 ($^{\bullet}$OH) and carbonate ($CO_3^{-\bullet}$) radicals, singlet oxygen ($^1O_2$), and the triplet states of chromophoric dissolved organic matter (^{3}CDOM*). Among the investigated lakes, Iseo showed a long-term near-stability of the chemical parameters that was reflected into a corresponding stability of the photochemical ones. 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 $^{\bullet}$OH source and sink) prevented the modelled photochemistry to undergo significant drifts 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 impact on photochemistry. While in L. Garda the increase in DOM was associated to the increase in $^1O_2$ and ^{3}CDOM*, in L. Geneva, the increases in pH and bicarbonate and the decrease in nitrite resulted in an $^{\bullet}$OH decrease. Overall, our results predict very different lake photochemistry behaviours in relation to alterations in water chemistry parameters caused by climate change (most notably, changes in water alkalinity and organic carbon).

Keywords: environmental photochemistry; long-term trends; seasonal trends; indirect photochemistry; climate change.

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 chemistry has seasonal fluctuations, such as 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 (as organic compounds may be released by algal growth and lysis) (Wetzel, 2001). Water chemistry is also affected on the long-term by direct human disturbance (*e.g.*, wastewater discharge) and climate change (Lu et al., 2013; Adrian et al., 2009). Lakes are good sentinels of change due to their ability to quickly modify their chemical, physical and biological features as a consequence of changes in their surrounding landscape and atmosphere (Bertoni et al., 1998; Carpenter et al. 2007; Pham et al. 2008; Williamson et al. 2008; Williamson et al. 2009; Adrian et al., 2009). The effects of climate may be observed on a range of chemical parameters of lake water, including most notably the DOC (however, such an effect can be variable depending on *e.g.*, latitude, catchment characteristics and multiple climate-related phenomena; Porcal et al., 2009; Sucker and Krause, 2010; Mosley, 2015; Rogora et al., 2013) and the alkalinity (Sommaruga-Wögrath et al. 1997; Skjelkvåle et al. 2005). The associated changes impact the biota and they can also modify the way lake water responds to sunlight exposure, including most notably the photochemical reactions (De Laurentiis et al., 2014).

Alkalinity is probably the water chemistry parameter that is affected by climate change in the most straightforward fashion (Sommaruga-Wögrath et al. 1997). A possible explanation for this effect involves the temperature-enhanced dissolution of $CaSO_4$, where Ca^{2+} is biologically stable but SO_4^{2-} is transformed into organic sulphur compounds by biota, with consumption of H^+ that induces *e.g.* enhanced dissolution of carbon dioxide into lake water (Schindler 1997). In reaction (1), R-H is an organic compound and R-SH a mercaptan. Moreover, the increase in temperature would also affect the concentration of dissolved inorganic nitrogen due to higher phytoplankton productivity (Sommaruga-Wögrath et al. 1997; Rogora et al. 2003).

$$SO_4^{2-} + \text{R-H} + 8\ H^+ + 6\ e^- \rightarrow \text{R-SH} + 4\ H_2O \qquad (1)$$

In lake water, the absorption of light from photoactive compounds called 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 ($^{\bullet}OH$) and carbonate ($CO_3^{-\bullet}$) radicals, singlet oxygen ($^1O_2$) and CDOM triplet states ($^3CDOM^*$) (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 (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 $^{\bullet}OH$ radical is formed upon photolysis of nitrate and nitrite (reactions 1,2) with quantum yields Φ that are respectively wavelength-independent and decreasing with wavelength. 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 $CO_3^{-\bullet}$ is formed upon oxidation of carbonate and bicarbonate by $^{\bullet}OH$ (reactions 3,4) and, to a lesser extent, upon carbonate oxidation by $^3CDOM^*$ (Canonica et al., 2005). Singlet oxygen and $^3CDOM^*$ are produced by CDOM irradiation according to reactions (5-7) (ISC = inter-system crossing) (Coelho et al., 2011; Mostafa and Rosario-Ortiz, 2013; Marchisio et al., 2015).

$$NO_3^- + h\nu + H^+ \rightarrow {}^{\bullet}NO_2 + {}^{\bullet}OH \quad [\Phi_2 = 0.01] \qquad (2)$$
$$NO_2^- + h\nu + H^+ \rightarrow {}^{\bullet}NO + {}^{\bullet}OH \quad [\Phi_3 = 0.065\text{-}0.025] \qquad (3)$$
$${}^{\bullet}OH + HCO_3^- \rightarrow OH^- + CO_3^{-\bullet} \quad [k_4 = 8.2\cdot 10^6\ M^{-1}\ s^{-1}] \qquad (4)$$
$${}^{\bullet}OH + CO_3^{2-} \rightarrow H_2O + CO_3^{-\bullet} \quad [k_5 = 3.9\cdot 10^8\ M^{-1}\ s^{-1}] \qquad (5)$$
$$CDOM \xrightarrow{h\nu,\ ISC} {}^3CDOM^* \qquad (6)$$
$${}^3CDOM^* + O_2 \rightarrow CDOM + {}^1O_2 \qquad (7)$$
$${}^3CDOM^* + CO_3^{2-} \rightarrow CDOM^{-\bullet} + CO_3^{-\bullet} \qquad (8)$$

Lake-water components can also scavenge the reactive transients. For instance, DOM is the main sink of both $^{\bullet}OH$ and $CO_3^{-\bullet}$, while $^{\bullet}OH$ 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 $^{\bullet}OH$ sink. The transients $^3CDOM^*$ and $^1O_2$ 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 $^1O_2$ sink is the thermal deactivation upon collision with water, while $^3CDOM^*$ 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 (characterised 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 $^{\bullet}OH$ source, but DOM is by far its main sink, the $^{\bullet}OH$ levels can be negatively correlated with DOC. An even stronger negative correlation is often observed between DOC and $CO_3^{-\bullet}$, because DOM both scavenges $CO_3^{-\bullet}$ and inhibits its formation by consuming $^{\bullet}OH$ (Canonica et al., 2005; Vione et al., 2014). In contrast, $^{\bullet}OH$ and $CO_3^{-\bullet}$ often positively correlate with nitrate and nitrite, and $CO_3^{-\bullet}$ with inorganic carbon species as well (Minella et al., 2011). The transients $^3CDOM^*$ and $^1O_2$ 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), which is the driving force for the photochemical production of ^{3}CDOM* and $^1O_2$.

The chemical parameters of lake water that have photochemical significance (most notably, DOC, nitrate, nitrite, carbonate and bicarbonate) can undergo complex seasonal fluctuations and long-term drifts, because of the combination of e.g. abiotic and biological processes, direct human impact, and climate change. These variations combine in a complex way with sunlight irradiance to modify photochemical reactions and the levels of photoinduced transients, which depend on both irradiance and water chemistry. While long-term series of photochemical variables (e.g., transient concentrations) are usually not available, chemical parameters are routinely monitored in several lake environments and they constitute an important data set from which photochemistry can be assessed by modelling (Minella et al., 2011; Minella et al., 2013). Thus, our objective was to model the long-term evolution of photochemically-formed transient species in lakes having different water chemistry.

2. Study sites

This study considered four lakes located in the Alps, namely Iseo and Garda (Italy), Piburgersee (Austria) and Lake Geneva (Switzerland/France). Their location is shown in the map reported as **Figure S1** in the Supplementary Material (hereafter SM), together with their main geographical and morphological features (see **Table S1** of SM). The watersheds of the lakes Iseo and Garda are mainly composed of sedimentary rocks. Crystalline formations (including both igneous and metamorphic rocks) are present only in their most northern sections.

Lake Iseo is a deep Italian lake located in the prealpine area of east-central Lombardy at 185 m a.s.l. The lake covers a surface area of 60.9 km^2, has a maximum depth of 256 m and is characterized by steep banks and a large island that separates the central plateau from the eastern 100 m deep channel. The theoretical renewal time of the lake is approximately 4.2 years. At the southwest extreme, the Oglio River exits the basin and in the northern end two main inflows enter, the Oglio River and the ‘‘Italsider (or Industrial) Canal’’. The Oglio River drains a wide mountain catchment and the Industrial Canal is diverted from the Oglio River 10 km upstream from its mouth. On the south, the Lake is open to a plain, while high mountains and several lateral valleys are present on both the eastern and western sides, strongly influencing the thermally driven wind field. Lake Iseo is classified as oligo-monomictic, as only two complete overturns have occurred in the last 20 years (March 2005 and 2006; Leoni et al. 2014). The reduction in the frequency of full winter circulation episodes in the lake might be linked both to the increased chemical stability of the water column (Ambrosetti and Barbanti, 2005) and to climate change (Valerio et al. 2015). The lake underwent a relatively rapid eutrophication in the seventies, the main reason being the large nutrient loading from the inflows. Since 1992, many studies have been conducted in Lake Iseo; water samples taken continuously over the last decades at the deepest point of the basin form the basis for a description of its trophic evolution (see Salmaso et al, 2012, and references therein; Salmaso et al., 2014, and references therein).

Compared with Iseo and the other large lakes south of the Alps, the long theoretical water renewal time of Lake Garda (27 years) is due to its low catchment/lake surface ratio and to minor annual rainfall. The main inflow is from River Sarca, at the northern edge of the lake. Other tributaries are of minor importance and mainly flow towards the west and north shores. The outflow, with an average discharge of 58 m^3 sec^{-1}, is via River Mincio, at the southern edge of the lake. Details of the catchment and the lake are reported in IRSA (1974). Lake Garda is divided into two basins, separated by an underwater ridge connecting Punta S. Vigilio with the Sirmione Peninsula. The west basin is large and deep (z_{max}=350 m), whereas the east basin (z_{max}=80 m) represents a small portion of the lake's overall volume (less than 7%). The Garda water parameters relevant to this study were obtained from the sampling station located at the deepest point of the lake (45.69 N, 10.72 E) in the west basin.

Lake Geneva is located in the western part of the Alps as represented in **Figure S1(SM)**. It is a large and deep carbonated peri-alpine lake, which never freezes over and is thermally stratified during most of the year. Moreover, Lake Geneva does not undergo complete water mixing every winter. The lake is sampled at a reference station located at the deepest point in the basin. The monitoring of Lake Geneva was established in the 1970s. Sampling was initially carried out once a month, but since 1981 there is a bimonthly campaign in spring, summer and autumn (SOERE, 2014).

Piburgersee is a small meromictic and dimictic mountain lake located in Tyrol, Austria with a catchment area composed of forest (60%), meadows and bare rocks (35%) and agriculture (5%). The lake water retention time is ca. 2 years. The ice-cover typically lasts from early December until April. Further information on lake characteristics and seasonality can be found elsewhere (Sommaruga and Psenner 1995).

For all the lakes, only the chemical composition of samples taken near the surface (where sunlight irradiance is the highest) was taken into account for photochemical modelling.

3. Methods

The modelling of lake water photochemistry used APEX software (Aqueous Photochemistry of Environmentally-occurring Xenobiotics) that is freely available as Electronic Supplementary Information of Bodrato and Vione (2014). APEX is based on a photochemical model that predicts steady-state concentrations of transient species ($^{\bullet}OH$, $CO_3^{-\bullet}$, $^1O_2$, $^3CDOM^*$) as a function of the seasonally variable sunlight spectrum, water chemistry and depth (Vione, 2014; Bodrato and Vione, 2014). APEX allows for instance for the prediction of the phototransformation kinetics of xenobiotics, on which basis the photochemical model was validated upon comparison with available field data (Maddigapu et al., 2011; De Laurentiis et al., 2012; Marchetti et al., 2013).

The absorption of radiation by photosensitisers (CDOM, nitrate and nitrite) and xenobiotics is computed by taking into account competition for sunlight irradiance in a Lambert-Beer approach (Braslavsky, 2007; Bodrato and Vione, 2014). Data obtained with APEX are averages over the water column (in the present case, computations were run for the upper 1 m depth), and they include the contributions of the sunlit surface layer and of darker water at the bottom. Therefore, results apply to well-mixed water bodies, including the epilimnion of stratified lakes.

The sunlight spectrum data (spectral photon flux density at mid-latitude for different months of the year, based on a cloudless sky) are reported in **Figure S2(SM)**. Their use was based on the month of each sampling event. Sunlight is not vertically incident over the water surface, but refraction at the interface deviates the light path into the water towards the vertical. Under mid-latitude conditions, the daily-averaged ratio between the path length l of sunlight in water and the depth d varies from $l/d = 1.45$ in winter to 1.15 in summer (Bodrato and Vione, 2014).

A final issue is that the model predicts very similar trends of ^{3}CDOM* and $^1O_2$ as a function of water chemistry. Here only the modelling results for $^1O_2$ are presented, but the same conclusions can be drawn for ^{3}CDOM*.

The available and modelled data for each lake underwent Principal Component Analysis (PCA) with the free chemometric software V-Parvus 2008 (Forina et al., 2008) on the column autoscaled data. The statistical significance of the long-term trends was tested by using both Pearson correlation and the nonparametric Mann-Kendall test on the yearly averaged data. The Mann-Kendall test is applicable to the detection of a monotonic trend of a time series with no seasonal or other cycle (which accounts for operating on year averages). The test was carried out with the Excel template MAKESENS, specifically developed for the analysis of annual atmospheric and precipitation concentrations (Salmi et al., 2002). The threshold for statistical significance was placed at $\alpha = 0.15$.

An important issue in photochemical modelling is the fact that the DOC is probably the most important chemical parameter of photochemical significance, because it is involved in the assessment of the contributions of both DOM and CDOM to photochemistry. The DOC is in fact essential for the modelling of $^{\bullet}$OH (of which CDOM is a major source and DOM the main sink), $CO_3^{-\bullet}$ (scavenged by DOM and produced by CDOM, indirectly through $^{\bullet}$OH and directly *via* ^{3}CDOM* + CO_3^{2-}), and $^1O_2$/^{3}CDOM* (photochemically generated by CDOM irradiation). DOC values were available for Piburgersee and Lake Geneva but, unfortunately, they were unavailable for Garda and only a partial set was present for Iseo. It was thus necessary to find a DOC proxy, which correlates sufficiently well with DOC to allow its indirect assessment when data was missing.

4. Results and discussion

4.1. Assessment of the dissolved organic carbon

Several authors have reported an inverse correlation between DOC values and Secchi disk depths (Sugiyama et al., 2004; Aguilera et al., 2013), based on the reasonable assumption that high-DOC waters show elevated absorption of sunlight (Morris et al., 1995). In fact, the combination of absorbing material and suspended particles in high concentration would decrease the penetration of sunlight in the water column (Wetzel, 2001; Salmaso et al., 2007). A correlation study, carried out in this work with the available data sets (lake water samples for which both parameters were available), suggested that the Secchi depth can be useful to distinguish between lakes having DOC values varying in different ranges. In this case, data points from different lakes occupy separate regions of the Secchi depth *vs*. DOC plot. However, the Secchi depth was not suitable to detect DOC variations within the same lake, because the relevant correlations were not statistically significant.

An interesting correlation could be found, in Lake Iseo, between the DOC and some biological parameters, most notably the sum of phytoplankton and crustaceans biomass (expressed as biovolume, mm^3 m^{-3}). The correlation obtained was very significant ($r^2 = 0.72$, $p < 0.01$, $n=30$). This relationship was applied to the Iseo samples, whenever the DOC was not available, and to the Garda samples, to get an estimate of the DOC values and their variations. The application of the model to Lake Garda and Iseo is justifiable because of the common limnological features of the two water bodies. Although lakes also receive DOC from soils in their catchments through underwater flow, rivers and direct surface runoff, the contributions from these sources are of little importance in the upper pelagic layers of the large and deep lakes, such as Iseo and Garda. These lakes are characterized by the presence of a large pelagic zone, which is scarcely affected by the direct influx of tributaries or by meteorological events. Indeed, in both lakes, the sampling stations are located in the centre of the water basins and in deepest zones, which are more than 12 km (Iseo) and 20 km (Garda) distant from the main inflows. The temporal fluctuations of DOC concentrations in these two lakes can, therefore, be assumed to be controlled primarily by the seasonal cyclic pattern in autochthonous sources.

The balance among different DOC sources depends on a suite of lake morphology, hydrology and, furthermore, on physical, chemical, and biological processes within the lake. The concentration of autochthonous DOC is in principle related to lake productivity, *i.e.*, high concentration for eutrophic lakes, but it also depends on the location of the sampling station (Bertilsson and Jones, 2003; Rodriguez-Murillo and Filella, 2015). In Lake Iseo, the horizontal length scale of the inlets water intrusions (Oglio River and Italsider Canal) is important from a biological perspective because it is the length scale over which the inflow potential energy transports nutrients and allochthonous compounds. This length scale was of the order of 4 km, supported by both the salinity measurements and calculations based on the intrusion dynamics (Hogg et al., 2013).

4.2. Correlations and time trends

The lake water data are referred to periods of 12-14 to 20 years (1998/1999-2010/2012 for Iseo, Garda and Piburgersee; 1992-2012 for Lake Geneva). The first two principal components accounted for 65.5% of the total variance for Lake Iseo (1A), 54.7% for Garda (1B), 59.6% for Piburgersee (1C), and 66.8% for Geneva (1D).

Similar loadings in the PCA analysis of two or more variables suggest a correlation among them (**Figure 1**). This is for instance, the case of the photochemical variables ($^{\bullet}OH$, $CO_3^{-\bullet}$, $^3CDOM^*$, $^1O_2$) and the sunlight irradiance ("Sun"), or of pH and carbonate. Variables such as for example, pH and nitrate showed a well-known negative correlation (Wetzel, 2001) in the PCA plots. Non-correlated variables have loadings that tend to be orthogonally directed, such as for instance alkalinity and sunlight irradiance in Lake Iseo (**Figure 1A**).

Typically the investigated chemical and modelled photochemical parameters fluctuated seasonally. Samples belonging to the same season are highlighted in **Figure 1**. As expected for lake waters, some variables had higher values during the summer or spring-summer months and they included photochemical parameters ($^{\bullet}OH$, $CO_3^{-\bullet}$, $^3CDOM^*$, $^1O_2$), sunlight irradiance, pH, carbonate, and often the DOC concentration. In contrast, alkalinity and bicarbonate often had peaks in spring or winter-spring, while nitrate usually showed winter maxima (Wetzel, 2001; Salmaso et al., 1997).

Superposed on the seasonal variations there may be long-term changes. Lake Iseo showed a general long-term stability in water chemistry, apart from the already mentioned seasonal fluctuations and a slight increase of pH and carbonate (see **Figure 2** and **Table S2(SM)**). Therefore, the modelled photochemical parameters ($^{\bullet}OH$, $CO_3^{-\bullet}$, $^1O_2$ and $^3CDOM^*$) did not undergo significant long-term variations.

Lake Garda underwent a small increase (+ 0.5% in 12 years) in DOC concentration, and there was some indication of a parallel small increase in the modelled steady-state concentrations of $^1O_2$ and $^3CDOM^*$ (see **Figure 3** and **Table S3(SM)**). Here, the connection of the chemical and photochemical parameters was rather straightforward, because higher DOC means higher CDOM that is a source of both $^3CDOM^*$ and $^1O_2$.

The Piburgersee (**Figure 4** and **Table S4(SM)**) underwent statistically significant long-term changes in several chemical parameters (alkalinity and bicarbonate as well as, to a lesser degree, pH, DOC, and carbonate). These important changes are reasonable when considering the smaller volume of Piburgersee in comparison with the other lakes under investigation. Unexpectedly, despite these significant or very significant changes in water chemistry, the modelled photochemical transients ($^{\bullet}OH$, $CO_3^{-\bullet}$, $^1O_2$, $^3CDOM^*$) did not undergo statistically significant variations on the long-term. This issue makes Piburgersee a quite interesting case study. As far as $^{\bullet}OH$ is concerned, its steady-state concentration would depend on the levels of its sources (CDOM and nitrate) and of its sinks (DOM and, usually to a lesser extent, carbonate and bicarbonate). The very significant increase in alkalinity and bicarbonate concentration in Piburgersee could decrease $^\bullet$OH and increase $CO_3^{-\bullet}$, because inorganic carbon consumes $^\bullet$OH to produce $CO_3^{-\bullet}$. However, the Piburgersee water has DOC ~ 2 mg C L^{-1} (~ 170 μM C), nitrate below 10^{-5} M, bicarbonate ~0.5 mM and carbonate at μM levels. Under these conditions, CDOM would be the main $^\bullet$OH source (~80% of the total $^\bullet$OH production) and DOM its main sink (over 90% of scavenging). Due to the contemporary role of organic matter as the main $^\bullet$OH source and sink (Page et al., 2014), the steady-state [$^\bullet$OH] would show a very limited dependence on the inorganic carbon (despite the very significant variations of the latter) and would also be poorly influenced by the DOC levels, which showed some increase.

In the case of $CO_3^{-\bullet}$, we assume that in addition to the non-significant trend of $^\bullet$OH (with which the carbonate radical is usually correlated), the parallel increase of inorganic and organic carbon ($CO_3^{-\bullet}$ source and sink, respectively) would produce mutual compensation.

All the above-described effects (saturation trends, like in the case of $^\bullet$OH sources and sinks, as well as compensation for $CO_3^{-\bullet}$) would be able to buffer the possible long-term variations in photochemistry.

In the case of Lake Geneva (**Figure 5** and **Table S5(SM)**) there was a significant increase in pH and in bicarbonate and a decrease in nitrite. Because nitrite yields $^\bullet$OH while bicarbonate consumes it, the reasonable outcome was a decrease over time of the steady-state [$^\bullet$OH].

Overall, the four lakes showed a range of different behaviours in the long-term trends of both chemical and photochemical parameters. They featured long-term stability of the parameters set (Iseo), statistically significant long-term changes of some chemical parameters without changes in photochemical ones (Piburgersee), and some long-term changes in both chemical and photochemical parameters (Geneva and, to a lesser extent, Garda).

5. Conclusions

Our results illustrate four case studies with different long-term trends of photochemical parameters in lake water. Previous studies (Minella et al., 2011 and 2013) have suggested that long-term changes of water chemistry would be reflected in modifications of the lake-water photochemistry. However, the present study supports the idea that a changing photochemistry requires not only changes in water chemistry, but the right changes as well. On the one hand, stability in water chemistry will imply stability of photochemistry as in the case of Iseo. In contrast, even large modifications of water chemistry (Piburgersee) could still produce photochemical stability, provided that compensation or near-saturation effects are operational. For instance, a DOC increase could offset an increase of alkalinity and yield stable $CO_3^{-\bullet}$ levels, while increasing alkalinity is not expected to strongly influence the $^\bullet$OH levels if organic carbon is the predominant $^\bullet$OH sink. In the case of Piburgersee it will be interesting to carry out model calculations in about a decade, to see whether the compensation effects can go on for a long time or if they break down at some point.

These issues may have important implications in the context of the changes that are connected with climate, because they might suggest the occurrence of "photochemical buffering" phenomena in some environments. It will be extremely interesting to further widen the scope of the present study, by taking into account similar databases in other regions of the world that report time series of chemical parameters of photochemical significance (organic matter, inorganic nitrogen and most notably nitrate, as well as inorganic carbon).

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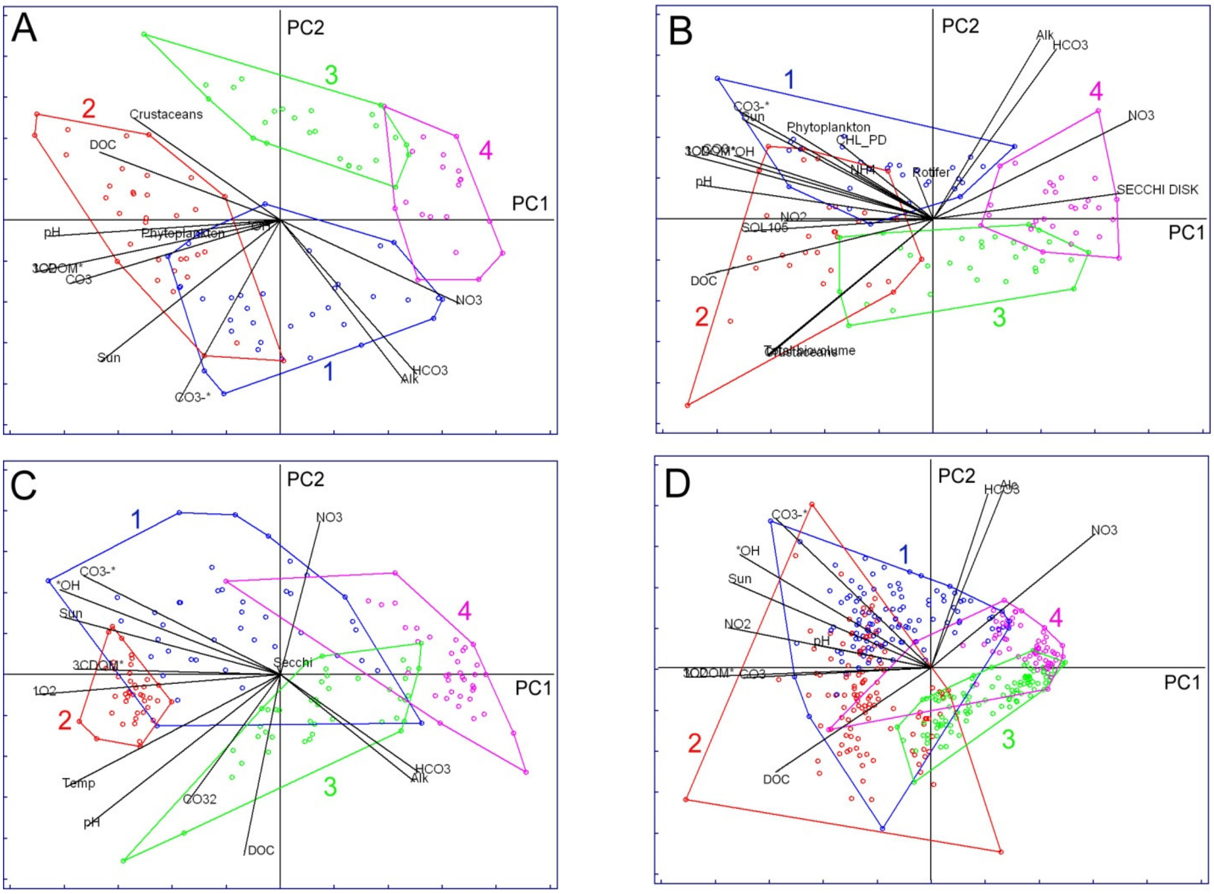

Figure 1. Principal Components Analysis (PC2 *vs*. PC1) for A) Lake Iseo; B) Lake Garda; C) Piburgersee and D) Lake Geneva. Each graph reports both variable loadings and sample scores; in the latter case, samples are grouped by season and each season is highlighted with a different colour/number: (1, blue) spring; (2, red) summer; (3, green) fall and (4, purple) winter.

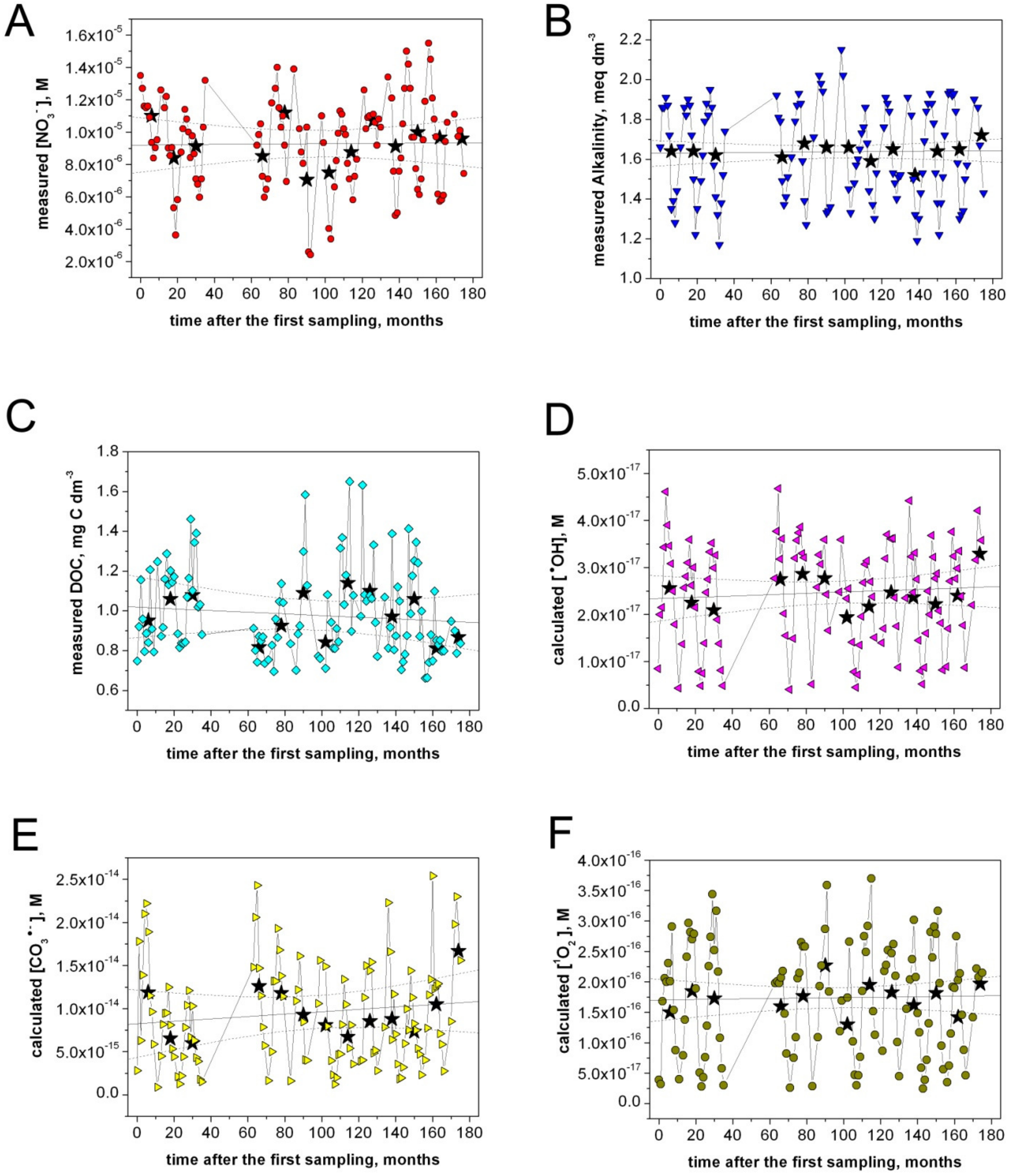

Figure 2. Time trends of NO_3^- (A), alkalinity (B), DOC (C) and of the modelled steady-state concentration of $^{\bullet}OH$ (D), $CO_3^{\bullet-}$ (E) and $^1O_2$ (F) for Lake Iseo. The black stars represent the year averages of each relevant parameter, based on which the regression lines (solid) and the 95% confidence bounds (dashed) were calculated.

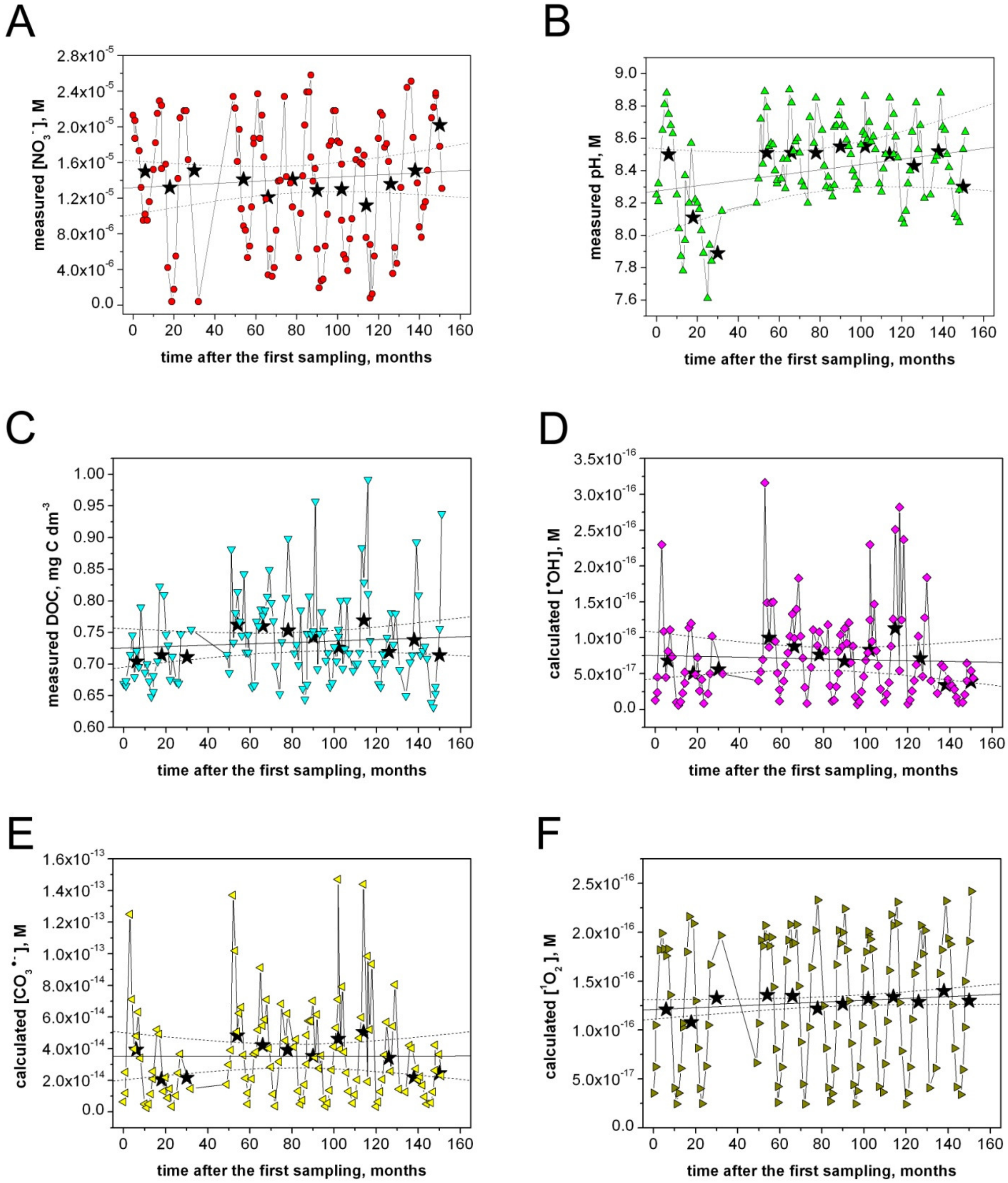

Figure 3. Time trends of NO_3^- (A), pH (B), DOC (C) and of the modelled steady-state concentration of $^{\bullet}OH$ (D), $CO_3^{\bullet-}$ (E) and $^1O_2$ (F) for Lake Garda. The black stars represent the year averages of each relevant parameter, based on which the regression lines (solid) and the 95% confidence bounds (dashed) were calculated.

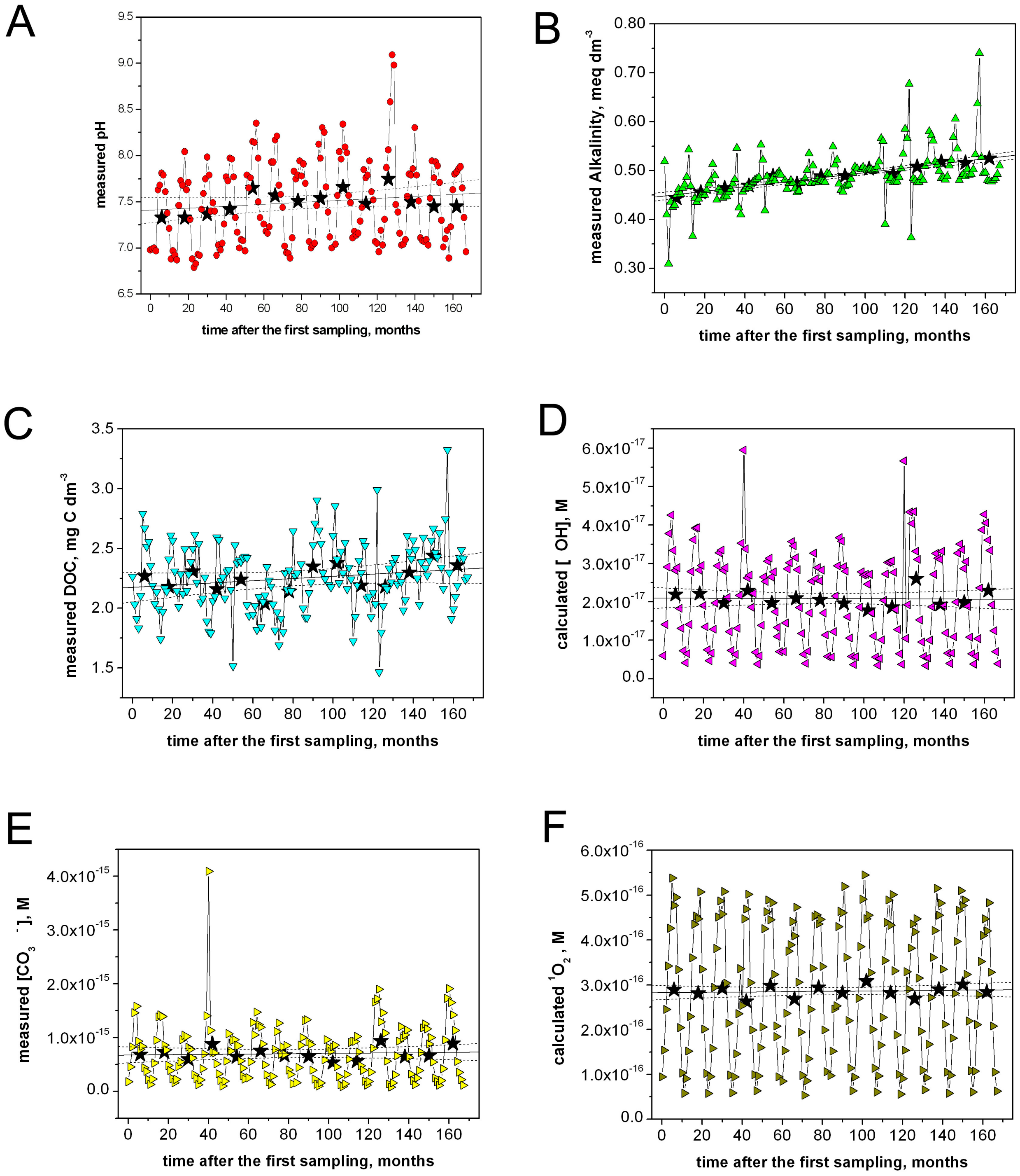

Figure 4. Time trends of pH (A), alkalinity (B), DOC (C) and of the modelled steady-state concentration of $^{\bullet}$OH (D), $CO_3^{\bullet-}$ (E) and $^1O_2$ (F) for Piburgersee. The black stars represent the year averages of each relevant parameter, based on which the regression lines (solid) and the 95% confidence bounds (dashed) were calculated.

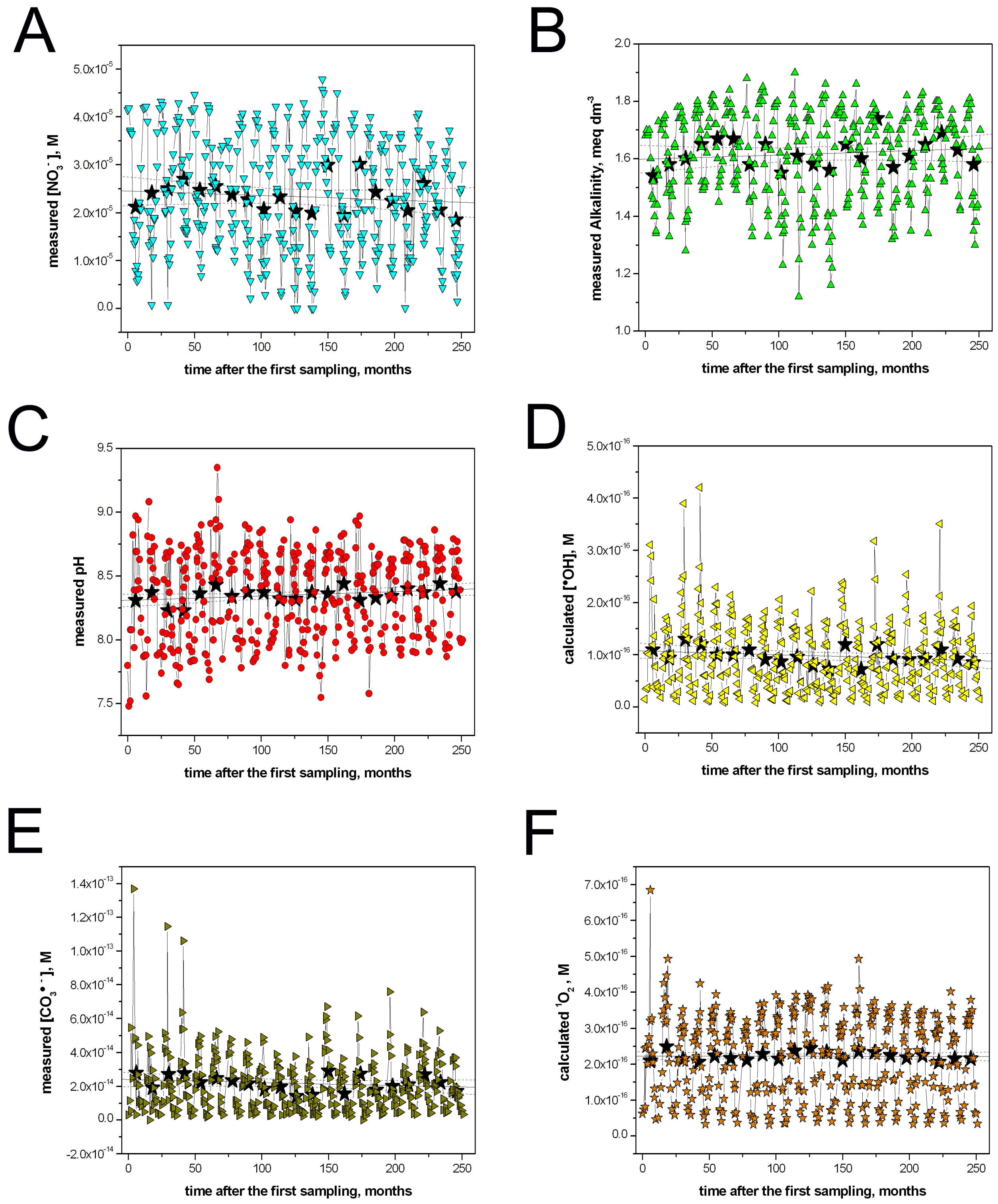

Figure 5. Time trends of NO_3^- (A), alkalinity (B), pH (C) and of the modelled steady-state concentration of $^\bullet OH$ (D), $CO_3^{\bullet-}$ (E) and $^1O_2$ (F) for Lake Geneva. The black stars represent the year averages of each relevant parameter, based on which the regression lines (solid) and the 95% confidence bounds (dashed) were calculated.

SUPPLEMENTARY MATERIAL

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

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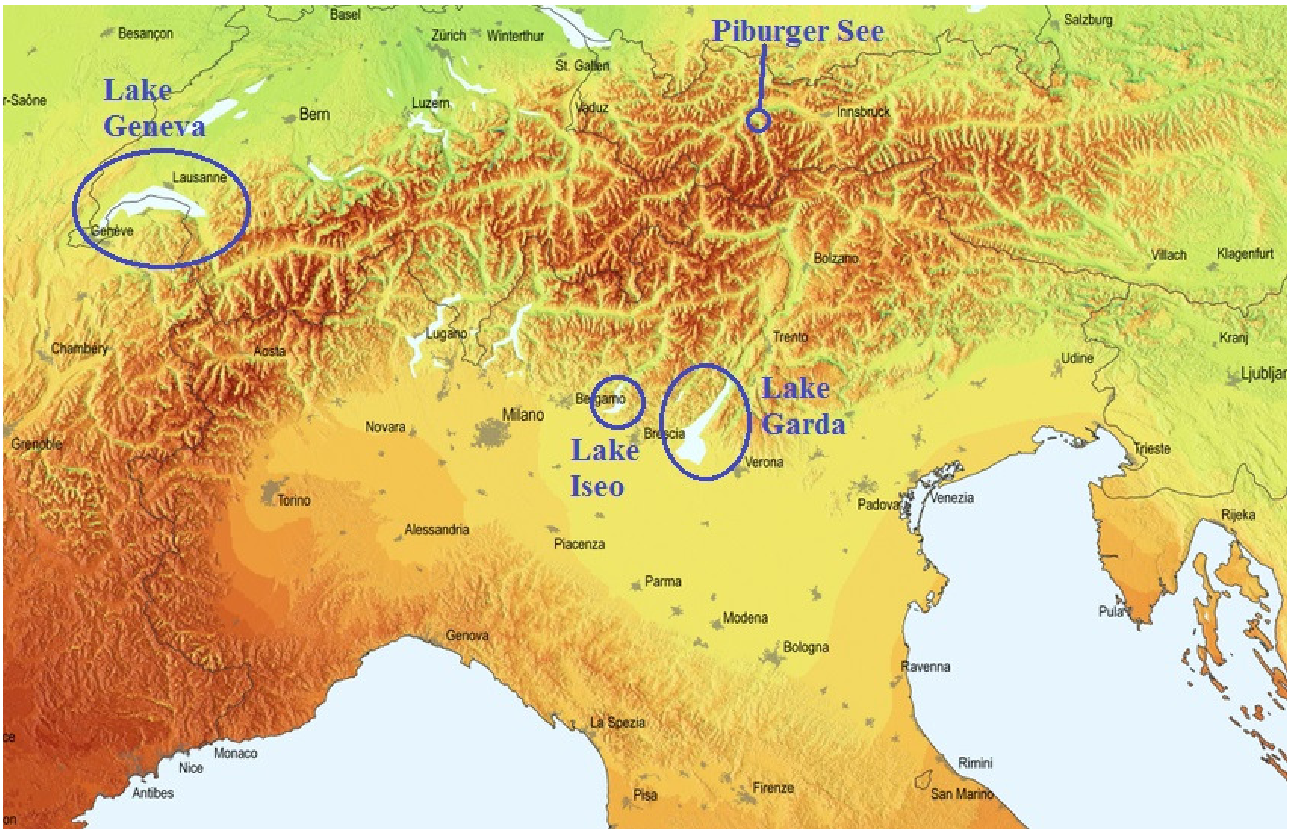

Figure S1. Map showing the locations of the studied lakes.

Table S1. Geographical location of the sampling point and morphological characteristics of the investigated lakes.

Lake	Latitude	Longitude	Maximum length (km)	Maximum width (km)	Surface area (km^2)	Altitude (m)	Maximum depth (m)	Mean depth (m)	Total volume (km^3)	Watershed area (km^2)	Water time residence (year)
Garda	45°41'N	10°43' E	52	16	368	65	350	133	49	2260	26.6
Iseo	45°43'N	10°03' E	20.2	3	61	186	256	124	7.6	1736	4.2
Geneva	46°27’N	6°32’ E	72.3	13.8	580.1	372	309	152.7	89	7975	11.5
Piburgersee	47°11’N	10°53 E	0.81	0.25	0.137	913	24.6	13.7	0.00183	2.65	~2.0

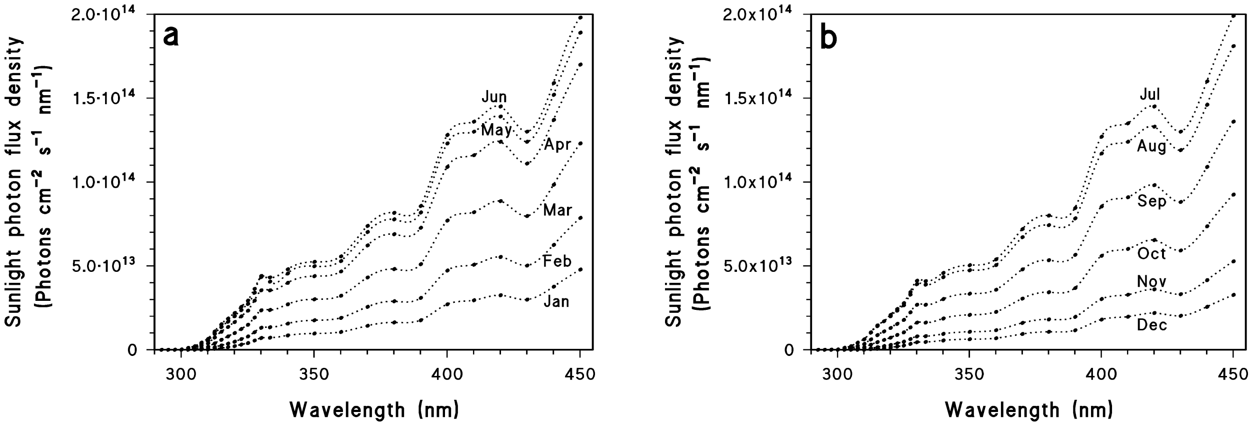

Figure S2. Spectra of sunlight (incident photon flux density) at mid latitude in different months of the year (Bodrato and Vione, 2014). They are referred to the 15th of the relevant month and are 8-h averages, from 8 a.m. to 4 p.m. solar time.

Table S2. Summary of the time trends parameters measured (NO_3^-, pH, alkalinity, phytoplankton, crustaceous and DOC), calculated (HCO_3^- , CO_3^- and Sun irradiance) and modeled (steady-state concentration of $^{\bullet}OH$, $CO_3^{\bullet -}$, $^1O_2$ and $^3CDOM^*$) for the Lake Iseo from 1998 to 2012. *R*: linear correlation coefficient; *S*: slope of the linear fit; *I*: intercept of the linear fit. For the significance level of the statistical tests the following symbol are used: *** if trend at α = 0.001, ** if trend at α = 0.01, * if trend at α = 0.05, + if trend at α = 0.1, +/– if trend at α = 0.15 and if the cell is blank the significance level is greater than 0.15.

	NO_3^-, M	**pH**	**Alk, eq/L**	**Phytoplankton, mm^3/m^3**	**Crustaceans, mm^3/m^3**	**HCO_3^-, M**	**CO_3^{2-}, M**	**DOC, mg C/L**	**$^{\bullet}OH$, M**	**$CO_3^{-\bullet}$, M**	**$^1O_2$, M**	**$^3CDOM^*$, M**	**Sun, Einstein cm^{-2} s^{-1}**
Average value	9.39×10^{-6}	8.42	1.63×10^{-3}	2.65×10^3	4.26×10^3	1.60×10^{-3}	2.68×10^{-5}	9.86×10^{-1}	2.42×10^{-17}	9.18×10^{-15}	1.72×10^{-16}	8.79×10^{-17}	1.31×10^{-8}
Number of points	115	115	115	115	115	115	115	115	114	115	115	115	115
R	–0.0134	0.1109	–0.0350	0.0202	–0.1311	–0.0418	0.1067	–0.0878	0.0112	0.0407	0.0015	0.0020	0.0223
R^2	0.0002	0.0123	0.0012	0.0004	0.0172	0.0017	0.0114	0.0077	0.0001	0.0017	2×10^{-6}	4×10^{-6}	0.0005
S	-6.6×10^{-10}	0.0007	-2×10^{-7}	0.8073	–7.4	-1.9×10^{-7}	3.4×10^{-8}	–0.0003	2.2×10^{-21}	4.3×10^{-18}	2.5×10^{-21}	1.7×10^{-21}	2.9×10^{-12}
I	9.4×10^{-6}	8.35	1.64×10^{-3}	2.57×10^3	4.93×10^3	1.60×10^{-3}	2.38×10^{-5}	1.02	2.40×10^{-17}	8.78×10^{-15}	1.72×10^{-16}	8.78×10^{-17}	1.28×10^{-8}
Pearson test (yearly average)		+/– (p=0.11)					+						
Mann Kendall test													

Table S3. Summary of the time trends parameters measured (NO_2^-, NO_3^-, pH, NH_4^+, alkalinity, phytoplankton, crustaceous, rotifer, chlorophyll, total biovolume, Secchi disk depth, Suspended Solid (Dry weight at 105°C) and DOC), calculated (HCO_3^- , CO_3^- and Sun irradiance) and modeled (steady-state concentration of $^{\bullet}OH$, $CO_3^{\bullet-}$, $^1O_2$ and $^3CDOM^*$) for the Lake Garda from 1998 to 2010. *R*: linear correlation coefficient; *S*: slope of the linear fit; *I*: intercept of the linear fit. For the significance level of the statistical tests the following symbol are used: *** if trend at $\alpha = 0.001$, ** if trend at $\alpha = 0.01$, * if trend at $\alpha = 0.05$, + if trend at $\alpha = 0.1$, +/– if trend at $\alpha = 0.15$ and if the cell is blank the significance level is greater than 0.15.

	NO_2^-, M	**NO_3^-, M**	**pH**	**NH_4^+, M**	**Alkalinity, eq/L**	**Phytoplankton, mm^3/m^3**	**Crustaceans, mm^3/m^3**	**Rotifer, mm^3/m^3**	**CHL_PD, µg L^{-1}**	**Total biovolume, mm^3/m^3**	**Secchi disk, m**	**SOL 105, Dry weight mg/l**	**HCO_3^-, M**	**CO_3^{2-}, M**	**DOC, mg C/L**	**$^{\bullet}OH$, M**	**$CO_3^{-\bullet}$, M**	**$^1O_2$, M**	**$^3CDOM^*$, M**
Average value	1.97×10^{-7}	1.38×10^{-5}	8.44	5.71×10^{-7}	2.04×10^{-3}	9.70×10^{2}	1.26×10^{3}	19.4	2.76	1.28×10^{3}	9.49	0.859	1.99×10^{-3}	3.24×10^{-5}	0.74	7.36×10^{-17}	3.69×10^{-14}	1.29×10^{-16}	6.59×10^{-17}
Number of points	118	118	118	108	118	118	118	118	118	118	115	118	118	118	118	118	118	118	118
R	0.0166	-0.0061	0.2315	-0.0664	0.0758	0.1335	0.0236	-0.0914	-0.0931	0.0206	-0.1663	0.0634	0.0951	0.130	0.1072	-0.0167	0.0025	0.0709	0.0709
R^2	0.0003	3.7×10^{-5}	0.0536	0.0044	0.0057	0.0178	0.0006	0.0083	0.0086	0.0004	0.0276	0.0040	0.0091	0.0167	0.0115	0.0003	6.4×10^{-6}	0.0050	0.0050
slope	9.2×10^{-11}	-9.6×10^{-10}	0.0014	-7.8×10^{-10}	1.6×10^{-7}	2.6	0.57	-0.07	-0.004	0.50	-0.018	0.0007	1.9×10^{-7}	5.2×10^{-8}	0.0002	-2.3×10^{-20}	1.7×10^{-18}	1.1×10^{-19}	5.5×10^{-20}
intercept	1.90×10^{-7}	1.38×10^{-5}	8.33	6.29×10^{-7}	2.02×10^{-3}	7.67×10^{2}	122×10^{3}	25.0	3.05	1.24×10^{3}	10.94	0.800	1.97×10^{3}	2.82×10^{-5}	0.72	7.54×10^{-17}	3.68×10^{-14}	1.20×10^{-16}	6.15×10^{-17}
Pearson test (yearly average)						*												+	+
Mann Kendall test						+													

Table S4. Summary of the time trends parameters measured (temperature, NO_3^-, pH, alkalinity, DOC and Secchi disk depth), calculated (HCO_3^- , $CO_3^-$and Sun irradiance) and modeled (steady-state concentration of $^{\bullet}OH$, $CO_3^{\bullet-}$, $^1O_2$ and $^3CDOM^*$) for the Lake Piburgersee from 1999 to 2012. *R*: linear correlation coefficient; *S*: slope of the linear fit. For the significance level of the statistical tests the following symbol are used: *** if trend at α = 0.001, ** if trend at α = 0.01, * if trend at α = 0.05, + if trend at α = 0.1, +/– if trend at α = 0.15 and if the cell is blank the significance level is greater than 0.15.

	Temp, °C	**pH**	**Alkalinity eq/L**	**Secchi disk, m**	**NO_3^-, M**	**DOC, mg C /L**	**HCO_3^-, M**	**CO_3^{2-}, M**	**$^{\bullet}OH$, M**	**$CO_3^{\bullet-}$, M**	**$^1O_2$, M**	**$^3CDOM^*$, M**
Average value	11.1	7.50	4.88×10^{-4}	8.11	1.06×10^{-5}	2.25	4.87×10^{-4}	1.43×10^{-6}	2.09×10^{-17}	7.02×10^{-16}	2.86×10^{-16}	1.53×10^{-16}
Number of points	165	166	166	152	166	166	166	166	166	166	166	166
R	0.0396	0.1391	0.4744	–0.0004	–0.1124	0.1717	0.4634	0.1394	–0.0274	0.0096	0.0061	–0.0981
R^2	0.0016	0.0193	0.2251	1.72×10^{-7}	0.0126	0.0295	0.2148	0.0194	0.0008	9.2×10^{-5}	3.7×10^{-5}	0.0096
slope	0.0061	0.0013	4.62×10^{-7}	-1.51×10^{-5}	-1.23×10^{-8}	0.0010	4.53×10^{-7}	8.29×10^{-9}	-6.82×10^{-21}	1.02×10^{-19}	1.89×10^{-20}	-1.93×10^{-19}
intercept	10.5	7.39	4.50×10^{-4}	8.12	1.17×10^{-5}	2.17	4.49×10^{-4}	7.36×10^{-6}	2.14×10^{-17}	6.93×10^{-16}	2.84×10^{-16}	1.69×10^{-16}
Pearson test (yearly average)		+/– (p=0.13)	***			+/– (p=0.14)	***					
Mann Kendall test			***				***	+				

Table S5. Summary of the time trends parameters measured (NO_2^-, NO_3^-, pH and alkalinity), calculated (HCO_3^- , $CO_3^-$and Sun irradiance) and modeled (steady-state concentration of $^{\bullet}OH$, $CO_3^{\bullet -}$, $^1O_2$ and $^3CDOM^*$) for the Lake Geneva from 1992 to 2012. *R*: linear correlation coefficient; *S*: slope of the linear fit; *I*: intercept of the linear fit. For the significance level of the statistical tests the following symbol are used: *** if trend at $\alpha = 0.001$, ** if trend at $\alpha = 0.01$, * if trend at $\alpha = 0.05$, + if trend at $\alpha = 0.1$, +/– if trend at $\alpha = 0.15$ and if the cell is blank the significance level is greater than 0.15.

	pH	**Alkalinity, eq/L**	**NO_2^-, M**	**NO_3^-, M**	**NPOC, mg C/L**	**HCO_3^-, M**	**CO_3^{-2}, M**	**$^{\bullet}OH$, M**	**$CO_3^{-\bullet}$, M**	**$^1O_2$, M**	**$^3CDOM^*$, M**
Average value	8.36	1.61×10^{-3}	3.81×10^{-7}	2.30×10^{-5}	1.35	1.56×10^{-3}	2.30×10^{-5}	9.70×10^{-17}	2.14×10^{-14}	2.22×10^{-16}	1.14×10^{-16}
Number of points	400	402	402	402	402	402	402	402	402	402	402
R	0.0851	0.0142	–0.0733	–0.0990	–0.0367	0.0418	0.0102	–0.0965	–0.1003	–0.0131	–0.0132
R^2	0.00725	0.0002	0.0054	0.0098	0.0013	0.0017	0.0001	0.0093	0.0101	0.0002	0.0002
slope	0.0004	3.00×10^{-8}	-2.43×10^{-10}	-1.57×10^{-8}	-0.0002	1.07×10^{-7}	2.40×10^{-9}	-8.88×10^{-20}	-2.38×10^{-17}	-2.09×10^{-20}	-1.07×10^{-20}
intercept	8.31	1.61×10^{-3}	4.11×10^{-7}	2.50×10^{-5}	1.37	1.55×10^{-3}	2.27×10^{-5}	1.08×10^{-16}	2.44×10^{-14}	2.24×10^{-16}	1.15×10^{-16}
Pearson test (yearly average)	+		+/– (p=0.15)			+/– (p=0.14)					
Mann Kendall test	+							+			