



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

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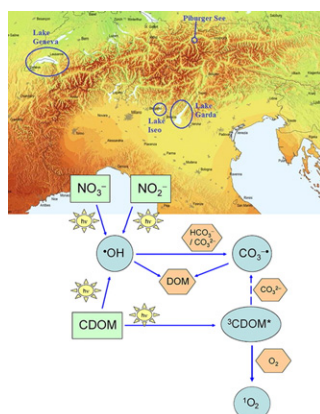
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HIGHLIGHTS

- 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.

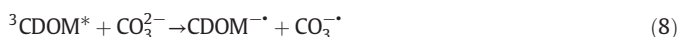


The DOC content of lake water is largely influenced by runoff, which in turn may be affected by climate change (Hudson et al., 2003; Zhang et al., 2010). Changes in DOC concentration are important because they affect the penetration of sunlight (and most notably of UV radiation) into the water column (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),

which is the driving force for the photochemical production of $^3\text{CDOM}^*$ and $^1\text{O}_2$.

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 shifts, because of the combination of for example, 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 photochemical processes can be modelled (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 characteristics. By doing so, it is possible to get insight into the long-term trends of chemical parameters of photochemical significance, and to understand which parameter changes may have the largest impact on lake-water photochemistry. Further, our study constitutes a basis to understand the potential influence and importance of climate change on photochemical processes in lake water.

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 Fig. 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 km², 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 Sarca River, 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 m³ sec⁻¹, is via Mincio River, 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 ($z_{\text{max}} = 350$ m), whereas the east basin ($z_{\text{max}} = 80$ 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 Fig. 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 (^1OH , $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$, $^3\text{CDOM}^*$) 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 Fig. 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 $^3\text{CDOM}^*$ and $^1\text{O}_2$ as a function of water chemistry. Here only the modelling results for $^1\text{O}_2$ are presented, but the same conclusions can be drawn for $^3\text{CDOM}^*$.

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 $^{\bullet}\text{OH}$ (of which CDOM is an important source and DOM the main sink), $\text{CO}_3^{\bullet-}$ (scavenged by DOM and produced by CDOM, indirectly through $^{\bullet}\text{OH}$ and directly via $^3\text{CDOM}^* + \text{CO}_3^{2-}$), and $^1\text{O}_2/^3\text{CDOM}^*$ (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. Proxies for dissolved organic carbon concentration in lakes Iseo and Garda

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; Salmasso et al., 2007). Our correlation analysis, using lake data sets 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. However, the Secchi depth was not suitable to detect DOC variations within the same lake, because the relevant correlations were not statistically significant (data not shown). In contrast, a very significant correlation between the DOC concentration and the sum of phytoplankton and crustaceans biomass (expressed as biovolume, $\text{mm}^3 \text{m}^{-3}$) was found for Lake Iseo ($r^2 = 0.72$, $p < 0.01$, $n = 30$). This relationship was applied to the Iseo samples, whenever the DOC was not available (for a total of $n = 85$ data points), and also to the Garda samples ($n = 126$), to get an estimate of the DOC values and their variations. The application of this relationship to Lake Garda and Lake Iseo is justifiable because of the common limnological and morphometrical (Table S1) features of the two water bodies, as well as of the common geological composition of the watersheds (Salmasso et al., 2007).

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 to the upper pelagic layers of the large and deep lakes Iseo and Garda. These lakes are characterized by the presence of a large pelagic zone, which is little affected by the direct influx of tributaries. Indeed, in both lakes, the sampling stations are located in the centre of the water basins 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 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,

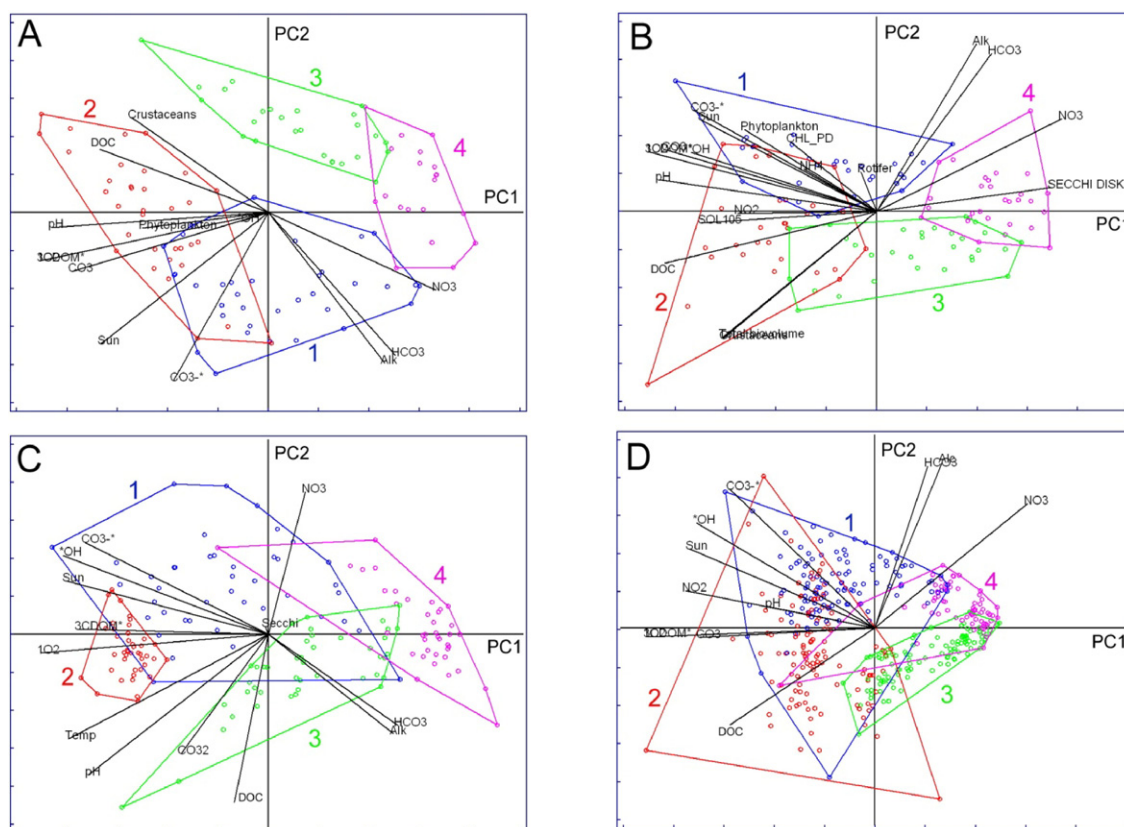


Fig. 1. Principal Components Analysis (PC2 vs. PC1) for A) Lake Iseo; B) Lake Garda; C) Piburgersee and D) Lake Geneva. Each graph reports both variable loadings and sample scores; in the latter case, samples are grouped by season and each season is highlighted with a different colour/number: (1, blue)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

that is, high concentrations for eutrophic lakes. Nevertheless, in large lakes it also depends on the location of the sampling station (Bertilsson and Jones, 2003; Rodríguez-Murillo and Filella, 2015). In Lake Iseo, the horizontal length scale of the inlet water intrusions (Oglio River and Italsider Canal) is important from a biological perspective because it is the length scale over which the inflow's potential energy transports nutrients and allochthonous DOC. This length scale is of the order of 4 km as supported by both, conductivity 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 (Fig. 1A), 54.7% for Garda (Fig. 1B), 59.6% for Piburgersee (Fig. 1C), and 66.8% for Geneva (Fig. 1D).

Similar loadings in the PCA analysis of two or more variables suggest a correlation among them (Fig. 1). This is for instance, the case of the photochemical variables ($^{\bullet}\text{OH}$, $\text{CO}_3^{\bullet-}$, $^3\text{CDOM}^*$, $^1\text{O}_2$) 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 tended to be orthogonally directed, such as for instance alkalinity and sunlight irradiance in Lake Iseo (Fig. 1A).

Typically the investigated chemical and modelled photochemical parameters fluctuated seasonally. Samples belonging to the same season are highlighted in Fig. 1. As expected for lake waters, some variables had higher values during the summer or spring–summer months and they included photochemical parameters ($^{\bullet}\text{OH}$, $\text{CO}_3^{\bullet-}$, $^3\text{CDOM}^*$, $^1\text{O}_2$), 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).

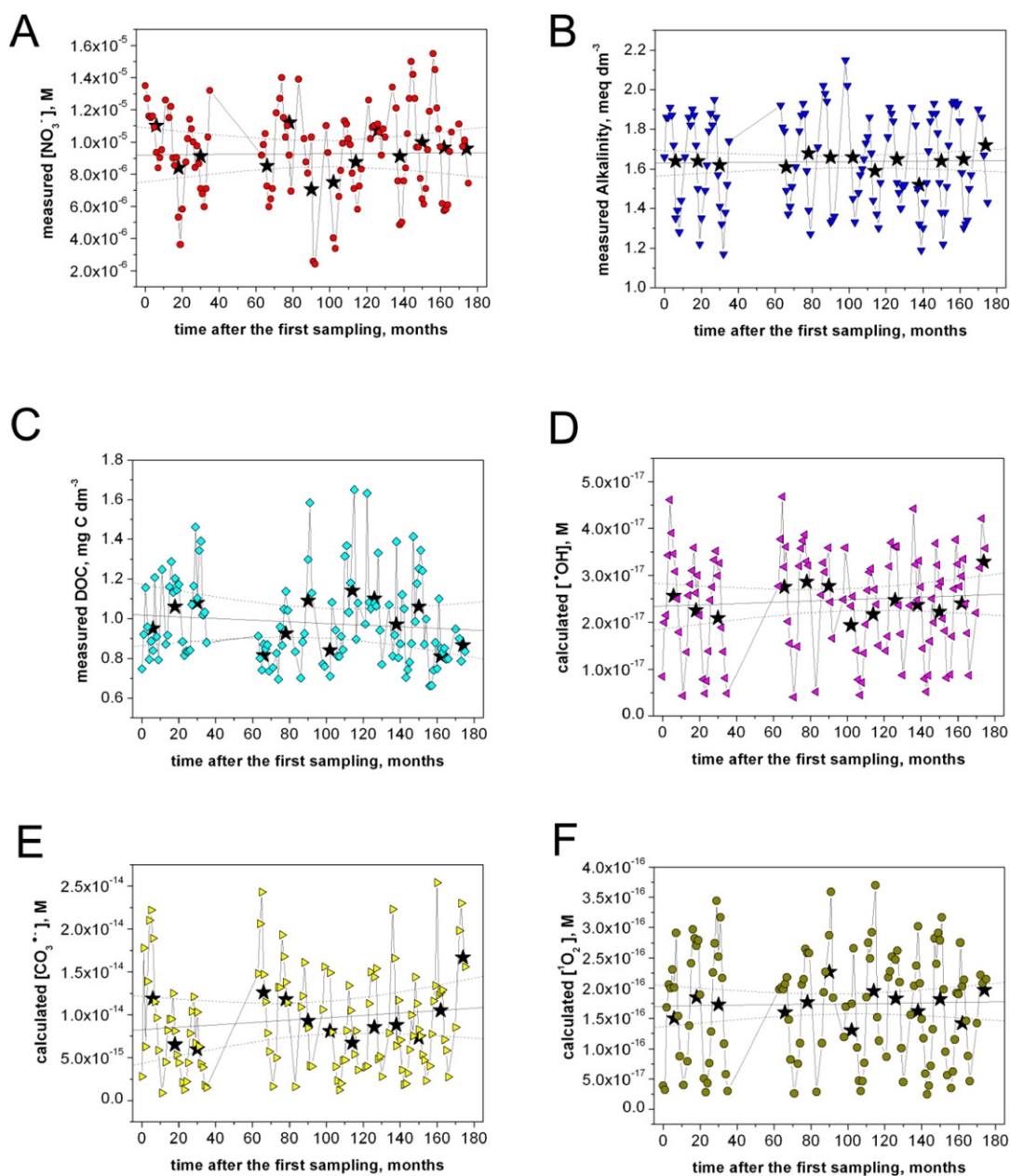


Fig. 2. Time trends of NO_3^- (A), alkalinity (B), DOC (C) and of the modelled steady-state concentration of $^{\bullet}\text{OH}$ (D), $\text{CO}_3^{\bullet-}$ (E) and $^1\text{O}_2$ (F) for Lake Iseo. The black stars represent the year averages of each relevant parameter, based on which the regression lines (solid) and the 95% confidence bounds (dashed) were calculated.

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 Fig. 2 and Table S2 (SM)). Therefore, the modelled photochemical parameters ($^{\bullet}\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$) did not undergo significant long-term variations.

Lake Garda underwent a small increase (+0.5% in 13 years) in DOC concentration, and there was some indication of a small increase in the modelled steady-state concentrations of $^1\text{O}_2$ and $^3\text{CDOM}^*$ (see Fig. 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 $^3\text{CDOM}^*$ and $^1\text{O}_2$.

The Piburgersee (Fig. 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 ($^{\bullet}\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$, $^3\text{CDOM}^*$) did not undergo statistically significant variations on the long-term. This issue makes Piburgersee a quite interesting case study. As far as $^{\bullet}\text{OH}$ 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 $^{\bullet}\text{OH}$ and increase $\text{CO}_3^{\bullet-}$, because inorganic carbon consumes $^{\bullet}\text{OH}$ to produce $\text{CO}_3^{\bullet-}$. However, the Piburgersee water has DOC $\sim 2 \text{ mg C L}^{-1}$ ($\sim 170 \mu\text{M C}$), nitrate below 10^{-5} M , bicarbonate $\sim 0.5 \text{ mM}$ and carbonate at μM levels. Under these conditions, CDOM would be the main $^{\bullet}\text{OH}$ source ($\sim 80\%$ of the total $^{\bullet}\text{OH}$ production) and DOM its main sink (over 90% of scavenging). Due to the contemporary role of organic matter as the main

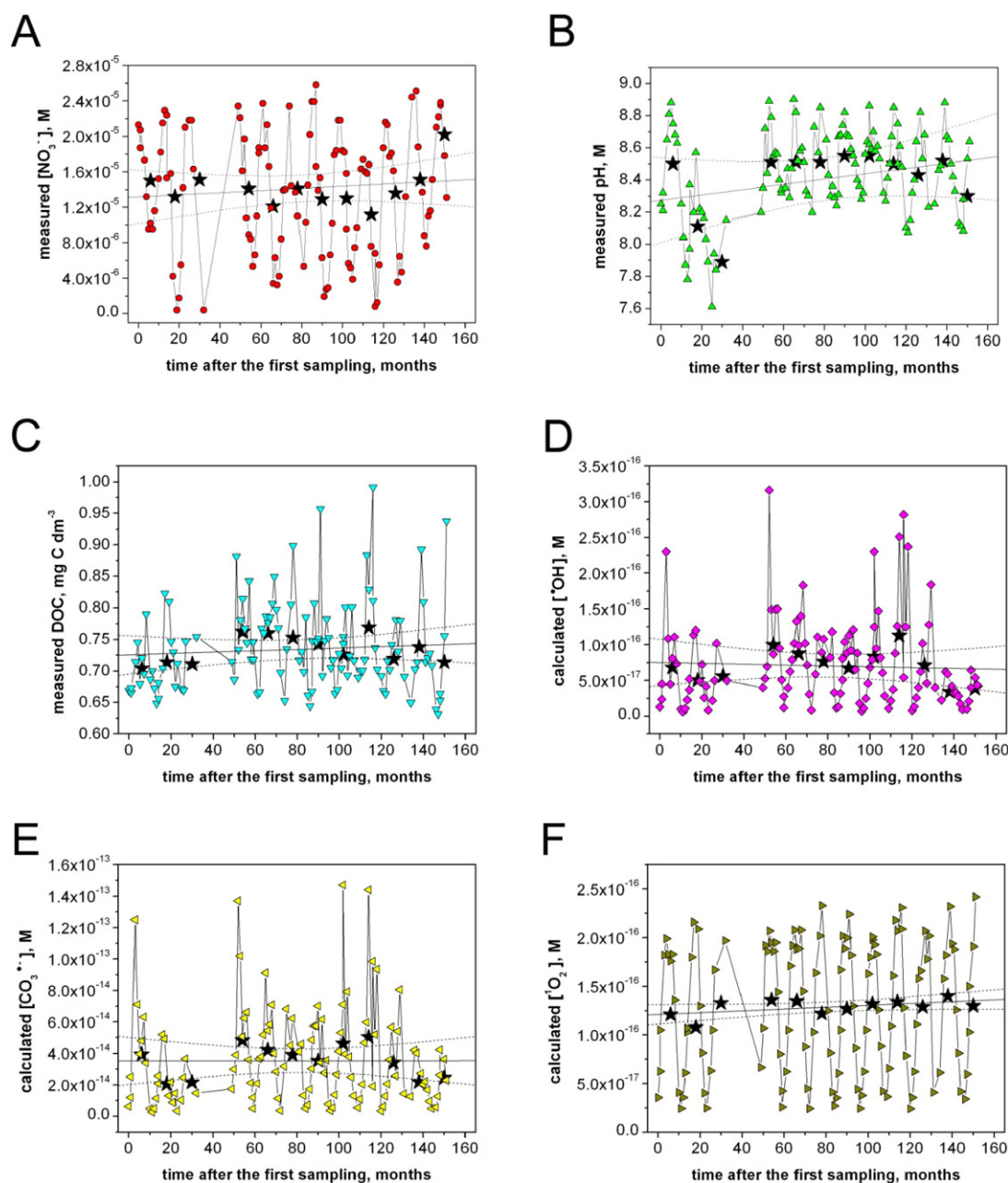


Fig. 3. Time trends of NO_3^- (A), pH (B), DOC (C) and of the modelled steady-state concentration of $^{\bullet}\text{OH}$ (D), $\text{CO}_3^{\bullet-}$ (E) and $^1\text{O}_2$ (F) for Lake Garda. The black stars represent the year averages of each relevant parameter, based on which the regression lines (solid) and the 95% confidence bounds (dashed) were calculated.

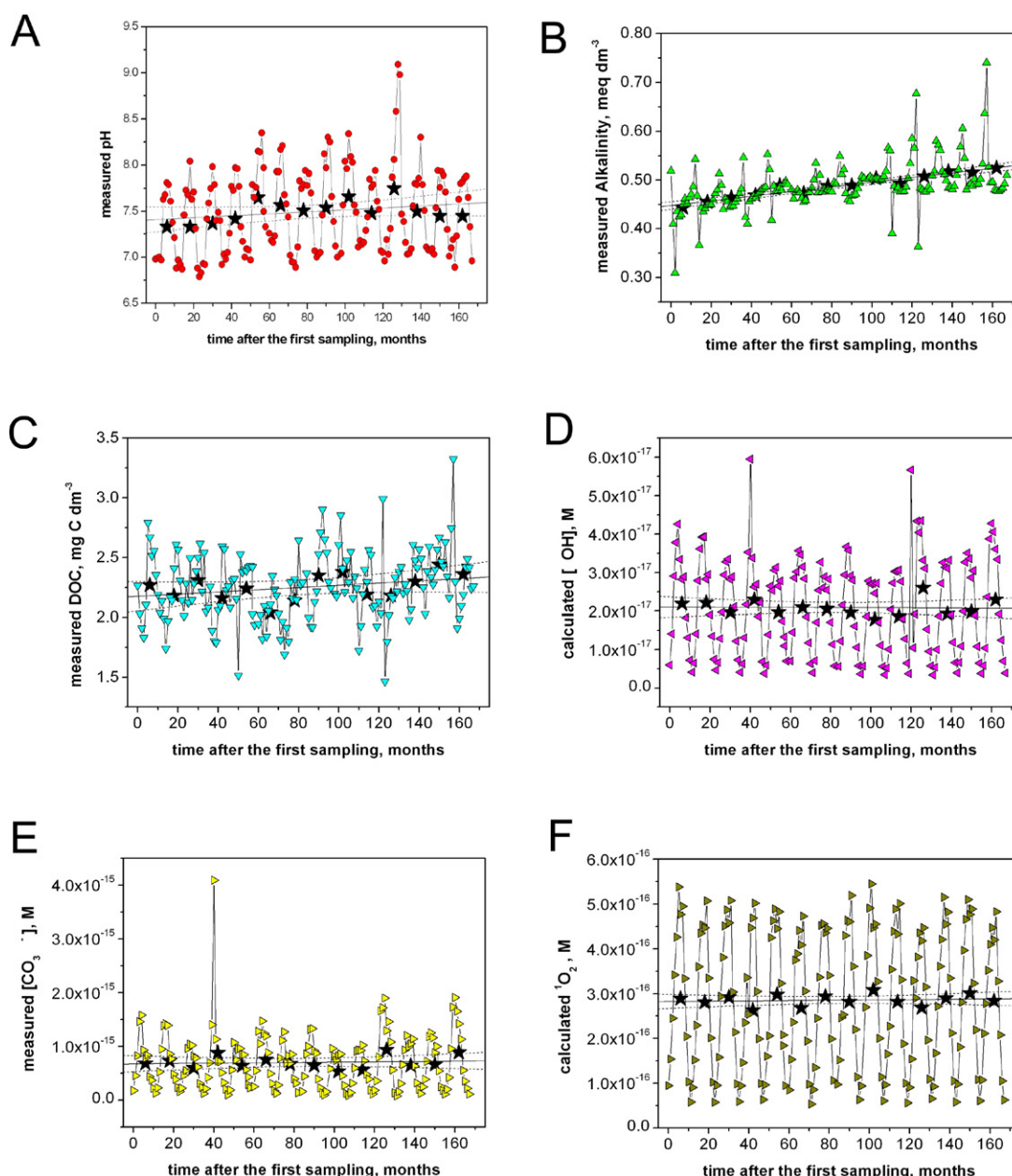


Fig. 4. Time trends of pH (A), alkalinity (B), DOC (C) and of the modelled steady-state concentration of $\cdot\text{OH}$ (D), $\text{CO}_3^{\cdot-}$ (E) and $^1\text{O}_2$ (F) for Piburgersee. The black stars represent the year averages of each relevant parameter, based on which the regression lines (solid) and the 95% confidence bounds (dashed) were calculated.

$\cdot\text{OH}$ source and sink (Page et al., 2014), the steady-state $[\cdot\text{OH}]$ 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 $\text{CO}_3^{\cdot-}$, we assume that in addition to the non-significant trend of $\cdot\text{OH}$ (with which the carbonate radical is usually correlated), the parallel increase of inorganic and organic carbon ($\text{CO}_3^{\cdot-}$ source and sink, respectively) would produce mutual compensation.

All the above-described effects (saturation trends, like in the case of $\cdot\text{OH}$ sources and sinks, as well as compensation for $\text{CO}_3^{\cdot-}$) would be able to buffer the possible long-term variations in photochemistry.

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

Overall, the four lakes showed a range of different patterns 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).

The significant increase in DOC concentration in surface waters of both Piburgersee and Lake Garda could be due to changes in precipitation and sunlight exposure. Variations in exposure of surface waters to sunlight may be due to changes in the duration of the ice-cover period that, however, do not apply to Garda which never freezes over. Moreover, a decrease of the ice-cover duration due to climate warming should increase sunlight exposure and might cause a DOC decrease through photomineralisation of organic matter (Hudson et al., 2003; Zhang et al., 2010). In contrast, the observed increase in DOC concentration in both lakes could be linked to higher runoff. In the case of Lake Garda the increase of DOC concentration, significant but amounting to only <1% over 13 years, possibly due to enhanced runoff (Fig. 3),

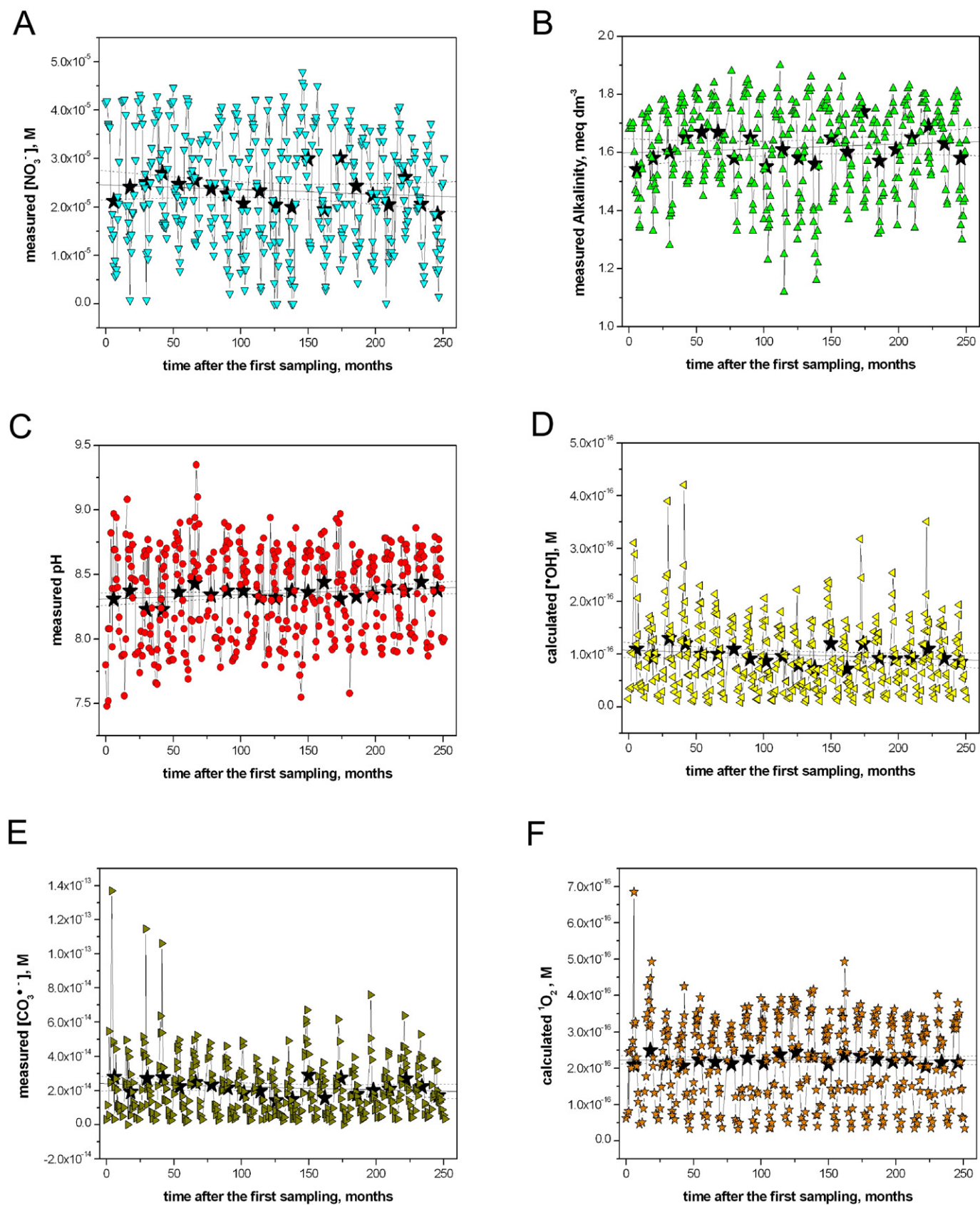


Fig. 5. Time trends of NO_3^- (A), alkalinity (B), pH (C) and of the modelled steady-state concentration of $^1\text{OH}^-$ (D), CO_3^{*-} (E) and $^1\text{O}_2$ (F) for Lake Geneva. The black stars represent the year averages of each relevant parameter, based on which the regression lines (solid) and the 95% confidence bounds (dashed) were calculated.

would not be in contrast with the fact that the DOM in the lake pelagic environment would be mainly of autochthonous origin. Interestingly, increased runoff due to precipitation would be connected to a decrease in the residence time of water in the lakes, which would reduce the time in which photochemical reactions could take place.

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, 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 accompanying 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 result in 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^{2-} levels, while increasing alkalinity is not expected to strongly influence the $^{\bullet}\text{OH}$ levels, if organic carbon is the predominant $^{\bullet}\text{OH}$ sink. In the case of Piburgersee, it would 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 climate change because they might suggest the occurrence of “photochemical buffering” phenomena in some environments. It will also be 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 (DOC, inorganic nitrogen, inorganic carbon).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.08.149>.

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