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A MODEL APPROACH TO ASSESS THE LONG-TERM TRENDS OF INDIRECT PHOTOCHEMISTRY IN LAKE WATER. THE CASE OF LAKE MAGGIORE (NW ITALY)

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Abstract

A model-based approach is here developed and applied to predict the long-term trends of indirect photochemical processes in the surface layer (5 m water depth) of Lake Maggiore, NW Italy. For this lake, time series of the main parameters of photochemical importance that cover almost two decades are available. As a way to assess the relevant photochemical reactions, the modelled steady-state concentrations of important photogenerated transients ($^\bullet OH$, $^3CDOM^*$ and $CO_3^{-\bullet}$) were taken into account. A multivariate analysis approach was adopted to have an overview of the system, to emphasise relationships among chemical, photochemical and seasonal variables, and to highlight annual and long-term trends. Over the considered time period, because of the decrease of the dissolved organic carbon (DOC) content of water and of the increase of alkalinity, a significant increase is predicted for the steady-state concentrations of the radicals $^\bullet OH$ and $CO_3^{-\bullet}$. Therefore, the photochemical degradation processes that involve the two radical species would be enhanced. Another issue of potential photochemical importance is related to the winter maxima of nitrate (a photochemical $^\bullet OH$ source) and the summer maxima of DOC ($^\bullet OH$ sink and $^3CDOM^*$ source) in the lake water under consideration. From the combination of sunlight irradiance and chemical composition data, one predicts that the processes involving $^\bullet OH$ and $CO_3^{-\bullet}$ would be most important in spring, while the reactions involving $^3CDOM^*$ would be most important in summer.

1. Introduction

Sunlight-driven processes are important pathways for the transformation of organic compounds, including xenobiotics in surface waters and for the possible formation of secondary pollutants (Patel-Sorrentino et al., 2004; Vulliet et al., 2010; Ge et al., 2010; Buth et al., 2010). Photochemical transformation can involve molecules that absorb sunlight (direct photolysis), in which case the process is driven by photon absorption by the substrate. However, solar radiation is also able to induce the indirect transformation of compounds that do not absorb sunlight. In this case (indirect or sensitised photolysis), sunlight is absorbed by photoactive molecules (photosensitisers, *e.g.* Chromophoric Dissolved Organic Matter, CDOM, and nitrate) and induces the generation of reactive transients, most notably the radicals $^\bullet OH$ and $CO_3^{-\bullet}$, singlet oxygen, $^1O_2$, and the triplet states, $^3CDOM^*$. These transients can induce the transformation of many compounds, including those that do not absorb sunlight (Hoigné, 1990).

The rates and the importance of photochemical transformation processes depend on both molecular and environmental features. In the case of direct photolysis, key parameters at a molecular level are the absorption spectrum and the photolysis quantum yield (Boule et al., 2005). The penetration of radiation into the water column is the main environmental feature that controls the direct photolysis (Loiselle et al., 2009). As far as indirect photochemical processes are concerned, they depend as molecular features, on the reactivity between the target molecule and the various photogenerated transients, and on water chemical composition and light penetration as environmental features (Hoigné, 1990).

In the case of the sensitised reactions involving $^\bullet OH$ and $CO_3^{-\bullet}$, the role of the environmental features can be as important as, or even more important than that of molecular reactivity (Vione et al., 2009a and 2010a). Therefore, it is suggested that environment-dependent parameters such as water chemical composition and column depth can play a major role in indirect photochemistry.

Possible modifications of water chemistry can affect the role and the kinetics of the indirect photochemical processes and, therefore, the fate of xenobiotics in surface water. However, to the best of our knowledge, the long-term assessment of sensitised photochemical processes in freshwater is an issue that has seldom been addressed.

A number of factors may affect the chemical composition of lake water, both in the short (*e.g.* seasonality) and in the long term (interannual variability and trends). Variation of the trophic level of the lake, due to eutrophication/oligotrophication processes, is a major driver of change for chemical variables, including major ions, nutrients (phosphorus and nitrogen compounds, silica) and dissolved organic matter (DOM). Beside eutrophication, also meteorology and climate play a role in the temporal variation of lake chemistry, both directly (*e.g.* temperature effect on chemical reactions in lake water) and indirectly through the effects on lake catchment, hydrology, and physical and biological processes in lake water (Schindler, 2009; Adrian et al., 2009). Changes to watersheds caused by climate warming can in turn affect the properties of lakes to which they drain.

Examples include changes of nutrient inputs, balance between base cations and strong acid anions, carbon cycles, and mercury (Schindler, 2009).

DOM in aquatic systems includes organic molecules of variable origin and composition. It is usually defined as the organic carbon fraction that can pass through a 0.45 μm filter, although such a definition might not be entirely appropriate (Minella et al., 2011). The main sources of DOM to freshwater systems can be the leaching of decomposed organic matter from soil or from fresh and dried leaf material (Robertson et al., 1999; Glazebrook and Robertson, 1999; Pace et al., 2004; Howitt et al., 2007). The parameter DOC integrates multiple responses within a lake, such as water transparency, heat absorption and lake metabolism. DOC levels in lake water also respond to changes in the catchment (Evans et al., 2002), atmospheric deposition (Monteith et al., 2007) and increased CO_2 concentration (Freeman et al., 2004). Changes in air temperature may directly influence DOC export from soil to surface water, by affecting soil moisture and temperature and by altering decomposition and mineralisation of organic matter (Evans et al., 2002). Increased precipitation and discharge would also lead to higher DOC export from the catchment into lake waters (Hongve et al., 2004). Several driving factors have been proposed to explain DOC trends in water bodies, the most realistic one being a complex interaction of changing atmospheric deposition and rising temperature (Monteith et al., 2007).

Nitrate is usually the dominant form of N in lake water and shows high seasonal variability in response to chemical and biological processes. Nitrate concentrations usually highly exceed the nitrite ones (Wetzel, 2001), in particular in the well-oxygenated epilimnion. Nitrogen compounds are subjected to temporal variations in lake water, which are strongly dependent on climatic factors (*e.g.* Hessen et al., 2009; Weyhenmeyer, 2008; Mitchell et al., 1996; Murdoch et al., 1998). Increasing temperature and change in precipitation regime affect biological processes in soil and water, which are involved into the retention and release of N (Windolf et al., 1996; Khalili and Weyhenmeyer, 2009). Seasonal and long-term variations of N compounds in lake water are influenced by biological processes, among which uptake by phytoplanktonic algae and denitrification in bottom water play a major role (Seitzinger et al., 2006). These processes are in turn affected by water temperature, thus climate parameters may exert a major control on nitrogen variability in lake water. In the case of the epilimnion of Lake Maggiore, the nitrite/nitrate ratio is significantly lower compared to shallower lakes in NW Italy (Vione et al., 2009c and 2010a).

The purpose of the present study is to assess the possible impacts that seasonal and, most notably, long-term changes of the water chemical composition may have on sensitised (indirect) photochemical processes in lake water. As indicator of sensitised photochemistry, we have adopted the steady-state concentration of reactive transient species ($^{\bullet}OH$, $CO_3^{-\bullet}$, $^3CDOM^*$) in the first 5 m of the water column. Indeed, the upper water layer is the one receiving the most elevated sunlight irradiance, and it is where the photochemical reactions usually reach the highest rates. To link chemical composition and photochemistry, we adopted a modelling approach originally conceived to predict the photochemical degradation kinetics of organic pollutants in surface waters. We modified the model to obtain the desired steady-state concentrations of the reactive transients. The

original model was able to predict with very good accuracy the experimental and field data concerning the photochemical lifetime of organic xenobiotics (Albinet et al., 2010; Maddigapu et al., 2011; Vione et al., 2009a and 2010a).

Lake Maggiore was chosen as a case study because of the availability of long-term series of water chemical data (Mosello et al., 2001; Salmaso et al., 2007; Bertoni et al., 2010).

The assessment of photochemistry starts from 1992, because it is limited by data concerning a major parameter of photochemical importance, the DOC. An assessment is provided of the long-term trend of the modelled photochemical parameters ($^{\bullet}OH$, $CO_3^{-\bullet}$, $^3CDOM^*$) and of the main factors affecting them.

2. Methods, theory and calculations

2.1. Lake water chemical composition

Lake Maggiore (see map in Figure 1) is a large, deep subalpine lake located in Northern Italy. The catchment (6600 km^2) lies half in Italy (Piedmont and Lombardy) and half in Switzerland (Canton Ticino). The northernmost part of the area is occupied by the Alps, with the highest peak (Monte Rosa) reaching 4633 m a.s.l.; most of the population (634,000) lives in the subalpine area in the southern part of the catchment, where the main industrial activities are also located. The morphological characteristics of the area do not permit extensive agriculture (Mosello et al., 2001). Almost 80% of the total population is connected to wastewater treatment plants. The percentage of treated wastewater from factories and industrial activities in general is 77% for the area surrounding the lake and 100% for the rest of the catchment. Presently, the total phosphorus load to the lake is around 200 t P y^{-1}, which can be considered acceptable for the maintenance of the present oligotrophic status of the lake (Rogora, 2007).

The water chemistry of Lake Maggiore has been monitored since the 1950s, and the available data have put in evidence the typical pattern of eutrophication/re-oligotrophication (Mosello and Ruggiu, 1985). The lake underwent eutrophication in the 1960s due to the nutrient load from its watershed, it then experienced a complete recovery after the 1990s and reached mean values of total phosphorus close to the pristine conditions ($< 10\,\mu g\,P\,L^{-1}$) (Salmaso et al., 2007).

Since 1991, monitoring of Lake Maggiore has been regularly performed under the International Commission for Protection of Italian-Swiss Waters (CIPAIS, reports available at http://www.cipais.org/laghi/verbano_pubblicazioni.html). The lake is sampled monthly at the deepest point (360 m, see sampling point position in Figure 1), with several samples taken at different depths along the column, and the water samples are analysed for the main chemical variables at the chemistry laboratory of the CNR ISE. Temperature profiles are also performed during each sampling.

In this study we focused on the data series of pH and alkalinity (determined by potentiometric methods) and nitrate (ion chromatography) in the surface layer. Details of the analytical methods

used and the quality controls performed in the laboratory can be found in Mosello et al. (1998 and 2001). DOC data were also collected in the framework of the research funded by the CIPAIS, and were made available for this study by R. Bertoni of the CNR ISE. Details on sampling and analytical determination of DOC can be found in Bertoni et al. (2010).

For pH, alkalinity and nitrate, the data are referred to the lake surface (between 0 and 5 meter depth). DOC data are representative of the euphotic zone, *i.e.* from the surface to the thermocline depth, which includes the 5-m surface layer. The depth of the lake thermocline to be used in the model was determined from the vertical temperature profiles of the lake water. It was defined as the depth where the ratio $\Delta T / \Delta d$ (where T is the temperature and d is the water column depth) was maximum.

2.2. Model for the description of surface-water photochemistry

In this work, we are mainly interested into the modelling of indirect photochemical reactions in the surface layer of lake water. The modelled transients are the radicals $^{\bullet}OH$ and $CO_3^{-\bullet}$ and the excited triplet states $^3CDOM^*$. Figure 2 depicts the different sources and sinks of the relevant transients in lake water.

2.2.1. Surface-water absorption spectrum

A correlation has been found between the absorption spectra of lake water samples and their content of dissolved organic matter (DOM), expressed as DOC (units of mg C L^{-1}). The following equation holds for the water spectrum, with a σ-level incertitude of approximately 20% (Vione et al., 2010a):

$$A_1(\lambda) = 0.45 \cdot DOC \cdot e^{-0.015 \cdot \lambda} \qquad (1)$$

$A_1(\lambda)$ is the specific absorbance of lake water, namely the absorbance over an optical path length b = 1 cm, and has units of cm^{-1}. Equation (1) was adopted to model the radiation absorption of water from Lake Maggiore, based on the time series of DOC.

2.2.2. Hydroxyl radicals, $^{\bullet}OH$

From the water chemistry data of Lake Maggiore, it can be inferred that the main $^{\bullet}OH$ sources are CDOM and nitrate (equation 2). The exact pathway(s) for the $^{\bullet}OH$ production by CDOM is/are still under debate, but they should involve $^3CDOM^*$ at some level (Mostofa and Sakugawa, 2009).

$$NO_3^- + h\nu + H^+ \rightarrow {}^{\bullet}OH + NO_2 \qquad (2)$$

The very low concentration of nitrite in the surface water of Lake Maggiore (Mosello et al., 2001; Vione et al., 2009c) would make this source a secondary one. Various studies have yielded useful correlation between the formation rate of $^{\bullet}OH$ by nitrate ($R_{\bullet OH}^{NO3-}$) and CDOM ($R_{\bullet OH}^{CDOM}$) and the

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respective absorbed photon fluxes of sunlight (P_a^{CDOM} and P_a^{NO3-}, expressed in einstein L^{-1} s^{-1}) (Vione et al., 2009b and 2010a):

$$R_{\bullet OH}^{CDOM} = (3.0 \pm 0.4) \cdot 10^{-5} \cdot P_a^{CDOM} \qquad (3)$$

$$R_{\bullet OH}^{NO3-} = (4.3 \pm 0.2) \cdot 10^{-2} \cdot \frac{[DIC] + 0.0075}{2.25\,[DIC] + 0.0075} \cdot P_a^{NO3-} \qquad (4)$$

where $[DIC] = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$ is the total amount of inorganic carbon. CDOM and nitrates are expected to generate $^\bullet OH$ independently, thus the total formation rate of $^\bullet OH$ ($R_{\bullet OH}^{tot}$) would simply be the sum of their contributions: $R_{\bullet OH}^{tot} = R_{\bullet OH}^{CDOM} + R_{\bullet OH}^{NO3-}$.

The calculation of the photon fluxes absorbed by CDOM and nitrate requires taking into account the mutual competition for sunlight irradiance. In a Lambert-Beer approximation at a given wavelength λ, the ratio of the photon flux densities absorbed by two different species i and j ($p_a^i(\lambda)$ $p_a^j(\lambda)^{-1}$) is equal to the ratio of the respective absorbances ($A_i(\lambda)\,A_j(\lambda)^{-1}$). The same is also true for the ratio of the photon flux density absorbed by a species to the total photon flux density absorbed by the solution, $p_a^{tot}(\lambda)$ (Braslavsky, 2007). We assume d as the water column depth in cm (in this study, $d = 500$ cm), $A_{tot}(\lambda) = A_1(\lambda)\,d$ as the total absorbance of the water column, and $p°(\lambda)$ as the incident spectral photon flux density of sunlight. The sunlight $p°(\lambda)$ shows a seasonal variation (see Figure 1 in the Supplementary Material, hereafter SM) (Frank and Klöpffer, 1988). CDOM is by far the main radiation absorber between 280 and 450 nm (Bracchini et al., 2010), thus $A_{tot}(\lambda) \approx A_{CDOM}(\lambda)$.

$$A_{tot}(\lambda) = A_1(\lambda) \cdot d \approx A_{CDOM}(\lambda) \qquad (5)$$

$$A_{NO3-}(\lambda) = \varepsilon_{NO3-}(\lambda) \cdot d \cdot [NO_3^-] \qquad (6)$$

$$p_a^{tot}(\lambda) = p°(\lambda) \cdot (1 - 10^{-A_{tot}(\lambda)}) \approx p°(\lambda) \cdot (1 - 10^{-A_{CDOM}(\lambda)}) = p_a^{CDOM}(\lambda) \qquad (7)$$

$$p_a^{NO3-}(\lambda) = p_a^{tot}(\lambda) \cdot A_{NO3-}(\lambda) \cdot [A_{tot}(\lambda)]^{-1} \qquad (8)$$

An important issue is that $p°(\lambda)$ is usually reported in units of einstein cm^{-2} s^{-1} nm^{-1} (see for instance Figure 1-SM), thus the absorbed photon flux densities are expressed in the same units. To express the formation rates of $^\bullet OH$ in M s^{-1}, the absorbed photon fluxes P_a^i should be expressed in einstein L^{-1} s^{-1}. Integration of $p_a^i(\lambda)$ over wavelength would give units of einstein cm^{-2} s^{-1} that represent the moles of photons absorbed per unit surface area and unit time. Assuming a cylindrical volume of unit surface area (1 cm^2) and depth $d = 500$ cm, the absorbed photon fluxes in einstein L^{-1} s^{-1} units would be expressed as follows (note that 1 L = 10^3 cm^3):
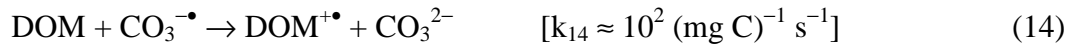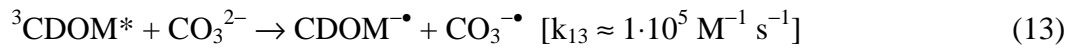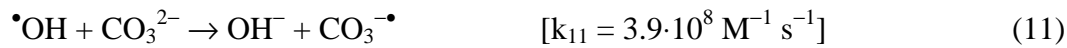
$$P_a^{CDOM} = 10^3 \, d^{-1} \int_\lambda p_a^{CDOM}(\lambda)\,d\lambda \qquad (9)$$

$$P_a^{NO3-} = 10^3 \, d^{-1} \int_\lambda p_a^{NO3-}(\lambda)\,d\lambda \qquad (10)$$

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The photogenerated $^\bullet$OH radicals are consumed by the natural scavengers present in surface water (mainly DOM, bicarbonate and carbonate). The natural scavengers have a $^\bullet$OH scavenging rate constant (units of s^{-1}) equal to the sum of their single contributions: $\Sigma_i\ k_{Si}\ [S_i] \approx 2\cdot10^4\ DOC + 8.5\cdot10^6\ [HCO_3^-] + 3.9\cdot10^8\ [CO_3^{2-}]$ (DOC is expressed in mg C L^{-1}, the other concentration values are in molarity) (Buxton et al., 1988; Hoigné et al., 1990). The steady-state [$^\bullet$OH] in the first 5 m of the water column can be expressed as $[^\bullet OH] = R_{\bullet OH}{}^{tot}\ (\Sigma_i\ k_{Si}\ [S_i])^{-1}$, where $R_{\bullet OH}^{tot} = R_{\bullet OH}^{CDOM} + R_{\bullet OH}^{NO3-}$, and $R_{\bullet OH}^{CDOM}$, $R_{\bullet OH}^{NO3-}$ are given by equations (3, 4).

2.2.3. Carbonate radicals, $CO_3^{-\bullet}$

The radical $CO_3^{-\bullet}$ is mainly produced upon oxidation of carbonate and bicarbonate by $^\bullet$OH and upon carbonate oxidation by ^{3}CDOM*. The main $CO_3^{-\bullet}$ sink in surface waters is the reaction with DOM (Buxton et al., 1988; Canonica et al., 2005).

$$^\bullet OH + CO_3^{2-} \rightarrow OH^- + CO_3^{-\bullet} \qquad [k_{11} = 3.9\cdot10^8\ M^{-1}\ s^{-1}] \qquad (11)$$

$$^\bullet OH + HCO_3^- \rightarrow H_2O + CO_3^{-\bullet} \qquad [k_{12} = 8.5\cdot10^6\ M^{-1}\ s^{-1}] \qquad (12)$$

$$^3CDOM* + CO_3^{2-} \rightarrow CDOM^{-\bullet} + CO_3^{-\bullet} \qquad [k_{13} \approx 1\cdot10^5\ M^{-1}\ s^{-1}] \qquad (13)$$

$$DOM + CO_3^{-\bullet} \rightarrow DOM^{+\bullet} + CO_3^{2-} \qquad [k_{14} \approx 10^2\ (mg\ C)^{-1}\ s^{-1}] \qquad (14)$$

The formation rate of $CO_3^{-\bullet}$ in reactions (11, 12) is given by the formation rate of $^\bullet$OH times the fraction of $^\bullet$OH that reacts with carbonate and bicarbonate, as follows:

$$R_{CO3-\bullet(\bullet OH)} = R_{\bullet OH}^{tot} \cdot \frac{8.5\cdot10^6\cdot[HCO_3^-] + 3.9\cdot10^8\cdot[CO_3^{2-}]}{\sum_i k_{Si}[S_i]} \qquad (15)$$

The formation rate of $CO_3^{-\bullet}$ in reaction (13) is given by (Canonica et al., 2005; Vione et al., 2009a):

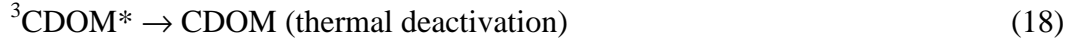$$R_{CO3-\bullet(CDOM)} = 6.5\cdot10^{-3}\cdot[CO_3^{2-}]\cdot P_a^{CDOM} \qquad (16)$$

The total formation rate of $CO_3^{-\bullet}$ is $R_{CO3-\bullet}{}^{tot} = R_{CO3-\bullet(\bullet OH)} + R_{CO3-\bullet(CDOM)}$. In the present case, $R_{\bullet OH}{}^{tot}$, P_a^{CDOM}, and $R_{CO3-\bullet}{}^{tot}$ as a consequence were referred to the first 5 m of the water column. The steady-state concentration of $CO_3^{-\bullet}$ can be expressed as $[CO_3^{-\bullet}] = R_{CO3-\bullet}{}^{tot}\ (k_{14}\ DOC)^{-1}$.

2.2.4. CDOM triplet states, ^{3}CDOM*

The formation of the excited triplet states of CDOM (^{3}CDOM*) in surface waters is a direct consequence of radiation absorption by CDOM. In aerated solution, ^{3}CDOM* could undergo thermal deactivation or reaction with O_2, and a lumped pseudo-first order quenching rate constant $k_{3CDOM*} \approx 5\cdot10^5\ s^{-1}$ has been observed in aerated solution for reactions (18, 19) (Canonica and Freiburghaus, 2001).

$$CDOM + h\nu \rightarrow {}^{3}CDOM* \tag{17}$$

$$^{3}CDOM* \rightarrow CDOM \text{ (thermal deactivation)} \tag{18}$$

$$^{3}CDOM* + O_2 \rightarrow CDOM + {}^{1}O_2 \tag{19}$$

In the Rhône delta waters it has been found that the formation rate of $^{3}CDOM*$ is $R_{3CDOM*} = 1.28 \cdot 10^{-3} \, P_a{}^{CDOM}$ (Al-Housari et al., 2010). $P_a{}^{CDOM}$ is here referred to the first 5 m of the water column (see equation (9) with $d = 500$ cm), and the steady-state concentration of $^{3}CDOM*$ can be expressed as $[^{3}CDOM*] = R_{3CDOM*} (k_{3CDOM*})^{-1} = 1.28 \cdot 10^{-3} \, P_a{}^{CDOM} (k_{3CDOM*})^{-1}$.

Reaction (19) yields $^{1}O_2$ that is reactive and can be successfully modelled (Maddigapu et al., 2011). However, also $[^{1}O_2]$ would be directly proportional to $P_a{}^{CDOM}$, and the conclusions that can be drawn for $^{3}CDOM*$ by the present modelling approach are also valid for $^{1}O_2$. For this reason, only $^{3}CDOM*$ will be discussed hereafter.

The photochemical model was applied to the case of Lake Maggiore. The model results (concentration of the main photogenerated reactive species) are a function of: *(i)* the water chemical composition (nitrate, DOC, bicarbonate and carbonate, the latter two derived from alkalinity and pH; Martell et al., 1997) determined in the surface water layer for each relevant sampling date; and *(ii)* the sunlight $p°(\lambda)$ that was referred to the month of the sampling (see Figure 1-SM). It represents a 8-h average from 8 am to 4 pm and is valid for cloudless sky.

2.3. Multivariate Analysis

The adopted photochemical model fixes a number of foreseeable relationships between sunlight irradiance, water composition data and the modelled photochemical parameters. However, irradiance and most notably the water chemical composition undergo complex changes, with some parameters showing opposite seasonal trends and/or statistically significant or insignificant long-term variations. All such trends are reflected in a non-predictable way into the model results. For this reason, a simple mono- or bivariate description of the system under consideration could lead to loss of information.

In this study the measured chemical variables (pH, alkalinity, nitrate, DOC), the computed concentrations of the photogenerated transients ($^{\bullet}OH$, $CO_3^{-\bullet}$, $^{3}CDOM$), the seasonal contribution of the sun (quantified as the integral over wavelength of the spectral photon flux density, $P_o = \int_{\lambda} p°(\lambda)\,d\lambda$, where $p°(\lambda)$ is reported in Figure 1-SM and λ varies from 280 to 450 nm) and the depth of the lake thermocline were considered simultaneously by using Principal Components Analysis (PCA). By the analysis of the loadings it was possible to emphasise the nature of the interrelationships among variables. Correlations, anti-correlations and non-correlations correspond to parallel, anti-parallel and perpendicular loadings, respectively. Furthermore, the scores analysis highlighted the seasonal and long-term trends of the relevant parameters in the surface layer of Lake Maggiore in the period under consideration.

The PCA calculations were carried out with the free chemometric software V-Parvus 2008 (Forina et al., 2008).

3. Results and discussion

3.1. Time trend of the monitored chemical parameters

A total of 157 water samplings were considered over the period 1992-2008. The chemical parameters under consideration are pH, alkalinity, DOC and nitrate (see Figure 2-SM). These parameters undergo seasonal variations: pH, alkalinity and DOC are higher in spring-summer and lower in autumn-winter, while nitrate follows the opposite trend. Seasonal variation is particularly evident for pH and nitrate, which are also anticorrelated in a statistically significant way (see Figure 3): it is $R^2 = 0.54$, while the Pearson test at 95% confidence level for 157 data points foresees that (anti)correlation is statistically significant if $R^2 > 0.024$.

The anticorrelation between pH and nitrate is related to biological processes taking place in surface water in summer: the nitrogen uptake by planktonic algae reduces the NO_3^- levels and the photosynthetic consumption of CO_2 increases the pH values (Wetzel, 2001).

Alkalinity usually reaches maxima in spring or early summer. Afterwards the uptake of CO_2 in the surface layer, coupled with increasing water temperature, induces $CaCO_3$ precipitation that causes a rapid decrease of alkalinity (Figure 2B-SM). This process is regularly observed in Lake Maggiore, although it shows different timing and amplitude in different years (Rogora, 2007). DOC maxima in summer are likely caused by a combination of factors (*e.g.* biological activity, leaching from soil, precipitation), among which autochthonous production might play a significant role. For instance, fluorescence studies indicated that fulvic acids undergo photodegradation and protein-like components are produced by microbial activity during the summer months in Lake Biwa, Japan (Mostofa et al., 2005).

In the case of alkalinity and DOC there is a statistically significant long-term variation, with alkalinity increasing over all the period and DOC decreasing from 1997 onwards. In the case of alkalinity it is $R^2 = 0.23$, for DOC it is $R^2 = 0.20$.

The DOC decline has been linked to the oligotrophication of the lake (decrease of total P concentrations) occurred since the 1980s due to the diversion of the P load from the lake watershed (Bertoni et al., 2004). This oligotrophication process also led to a decrease of the in-lake productivity (Bertoni et al., 1998) and to a decrease of the chlorophyll-a concentration. An analysis of the driving factors for the DOC long-term evolution revealed that in Lake Maggiore the temporal change in the anthropogenic pressure (namely the reduction of the phosphorus load) is more important than meteorological or climatic factors in driving the DOC trends (Bertoni et al., 2010).

The increase of alkalinity is most evident in the latest period, from 2003 onwards. An increase of the solute export from the catchment due to climate warming has been proposed as a possible

explanation for such a positive trend. Beside alkalinity, also conductivity and the main base cations (calcium, magnesium, potassium) showed a tendency to increase in the last few years, confirming an increasing solute content of the lake water (Rogora, 2007). However, this hypothesis warrants further investigations considering the high number of factors controlling the inorganic carbon content of lake water.

3.2. Expected time trend of the modelled photochemical parameters

Figure 4 shows the modelled time trends of the steady-state concentrations of $^\bullet OH$ (2A), $CO_3^{-\bullet}$ (2B) and $^3CDOM^*$ (2C). In all the cases one can observe a clear seasonal variation, with maxima in spring-summer and minima in autumn-winter. This is reasonable considering that $^\bullet OH$, $CO_3^{-\bullet}$ and $^3CDOM^*$ are all produced by photochemical reactions. A statistically significant increase with time is observed for both $^\bullet OH$ ($R^2 = 0.11$) and $CO_3^{-\bullet}$ ($R^2 = 0.14$), but not for $^3CDOM^*$. In the case of $[^\bullet OH]$, the average values calculated with the model show an increase by about three fold from 1992 to 2008. The corresponding increase of $[CO_3^{-\bullet}]$ would be of almost one order of magnitude. As a consequence, the indirect photochemical transformation processes involving $^\bullet OH$ and $CO_3^{-\bullet}$ are expected to considerably grow in importance in the time period under consideration.

Figure 4 shows that $[^\bullet OH]$ is in the 10^{-17} - 10^{-16} M range, $[CO_3^{-\bullet}]$ is around 10^{-14} M, and $[^3CDOM^*]$ around 10^{-15} M. These values are very reasonable for surface lake water (Canonica et al., 2005). The ratio $[CO_3^{-\bullet}]$ $[^\bullet OH]^{-1}$ calculated for Lake Maggiore is usually included in the range of 100-300. This means that $CO_3^{-\bullet}$ would be more important than $^\bullet OH$ in the degradation of compounds, for which the ratio of the respective second-order rate constants for reaction with $CO_3^{-\bullet}$ and $^\bullet OH$ is higher than 0.01. To make an example, the reaction rate constants of aniline with $^\bullet OH$ and $CO_3^{-\bullet}$ are $k_{\bullet OH} = 1.4 \cdot 10^{10}$ M^{-1} s^{-1} (Buxton et al., 1988) and $k_{CO3-\bullet} = 5.0 \cdot 10^8$ M^{-1} s^{-1} (Neta et al., 1988), with $k_{CO3-\bullet}$ $(k_{\bullet OH})^{-1} = 0.036$. With $[CO_3^{-\bullet}] = 1.0 \cdot 10^{-14}$ M, one obtains a pseudo-first order degradation rate constant $k_{An} = k_{CO3-\bullet}$ $[CO_3^{-\bullet}] = 5.0 \cdot 10^{-6}$ s^{-1} for reaction of aniline with $CO_3^{-\bullet}$, which would correspond to a half-life time $t_{1/2} = \ln 2$ $(k_{An})^{-1} = 1.4 \cdot 10^5$ s = 39 h. In the case of $[^\bullet OH] = 1.0 \cdot 10^{-16}$ M, one gets $k_{An} = k_{\bullet OH}$ $[^\bullet OH] = 1.4 \cdot 10^{-6}$ s^{-1} and $t_{1/2} = 5.0 \cdot 10^5$ s = 138 h. Transformation of aniline by $1.0 \cdot 10^{-14}$ M $CO_3^{-\bullet}$ would thus be significantly faster compared to $1.0 \cdot 10^{-16}$ M $^\bullet OH$. Note that in a real-case scenario the half-life times would be higher, because the values of $[^\bullet OH]$ and $[CO_3^{-\bullet}]$ are here referred to a 8-h averaged intensity of sunlight (8 am – 4 pm; Figure 1-SM) that does not take the night into account. Therefore, the $[^\bullet OH]$ and $[CO_3^{-\bullet}]$ values calculated here are higher than the daily (24 h) averages.

3.3. Principal Components Analysis results

The results of the Principal Components Analysis on the (previously autoscaled) experimental and computed data are reported in Figure 5. Only the first and the second principal component (PC1,

PC2) are significant as determined by the average variance criterion, Malinowski indicator (Malinowski, 2002). PC1 and PC2 explain together 72% of the total variance.

Figure 5 shows the scores and loadings plot for PC1 *vs.* PC2. It can be seen that the photochemical parameters ($^\bullet$OH, $CO_3^{-\bullet}$, ^{3}CDOM*) are all positively correlated with sunlight, as expected. The correlation is strongest in the case of ^{3}CDOM*. Interestingly, nitrate would be a significant source of both $^\bullet$OH and $CO_3^{-\bullet}$, the latter upon reactions (11, 12) of $^\bullet$OH with carbonate and bicarbonate. Nitrate is also anticorrelated with sunlight, because it shows sharp maxima in autumn-winter (see Figure 2D-SM). Therefore, it is understandable that the contribution of nitrate to $^\bullet$OH and $CO_3^{-\bullet}$ decreases the correlation between the two transients and sunlight. The steady-state concentration $[CO_3^{-\bullet}]$ is also correlated with $[^\bullet$OH$]$ and alkalinity, the latter being largely accounted for by HCO_3^-. This is very reasonable when considering that reactions (11, 12) yield $CO_3^{-\bullet}$ from $^\bullet$OH + HCO_3^- / CO_3^{2-}.

A clear anticorrelation is also evident, as expected, between the position of the thermocline and the sunlight intensity. The depth of the epilimnion in Lake Maggiore, and in general in the deep subalpine lakes in Northern Italy reaches the maximum at the end of the winter (Ambrosetti et al., 2010), a period characterised by low sunlight intensity.

Correlation can also be observed between ^{3}CDOM* and DOC. Indeed, radiation absorption by CDOM and formation of ^{3}CDOM* are expected to occur to a higher extent when the DOC is more elevated (Al Housari et al., 2010). In contrast, an anticorrelation would be observed between DOC and both $[^\bullet$OH$]$ and $[CO_3^{-\bullet}]$ (see also Figure 6A,B). DOM is the main sink of both $^\bullet$OH and $CO_3^{-\bullet}$. In the latter case, the scavenging of $^\bullet$OH by DOM would also inhibit the reactions between $^\bullet$OH and HCO_3^- / CO_3^{2-} to yield $CO_3^{-\bullet}$. Note that anticorrelation between $[^\bullet$OH$]$ and DOC can be observed in water bodies like Lake Maggiore, characterised by rather elevated nitrate concentration (around $5\cdot10^{-5}$ M) and relatively low DOC (often 1 mg C L^{-1}, see Figure 2C-SM). In such a case nitrate would be a competitive $^\bullet$OH source compared to CDOM, and DOM would be the main $^\bullet$OH sink. Overall, dissolved organic compounds in Lake Maggiore would play a more important role as $^\bullet$OH sinks than as $^\bullet$OH sources. In different environments, where the much higher content of DOM makes CDOM the major $^\bullet$OH source and DOM the main sink, anticorrelation between $[^\bullet$OH$]$ and DOC might not be observed (Al Housari et al., 2010).

A very interesting issue arises from the anticorrelation between $^\bullet$OH / $CO_3^{-\bullet}$ and DOC, coupled with the correlation between $CO_3^{-\bullet}$ and alkalinity (see Figure 5). Indeed, the significant decrease of DOC and the increase of alkalinity over the considered time period (Figures 2B-SM and 2C-SM) account for the significant increase with time of the modelled $[^\bullet$OH$]$ and $[CO_3^{-\bullet}]$ (see Figure 4A,B). This means that, in Lake Maggiore, the long-term trends of $[^\bullet$OH$]$ and $[CO_3^{-\bullet}]$ as derived from the model are dominated by the variations of DOC and alkalinity.

A further photochemistry issue is that the decrease of DOC is expected to enhance as well the direct photolysis of organic compounds. Indeed, the chromophoric portion of DOM competes with other dissolved molecules for radiation absorption (Lam et al., 2003; Latch et al., 2003) and, in

some cases, DOM can decrease the direct photolysis quantum yields of other substrates (Vione et al., 2010b).

Figure 7 shows the PCA analysis (PC1 *vs.* PC2) of the data, grouped by season. The position of the sunlight loading reflects the fact that, as far as sunny days are considered, the average irradiance is the same in spring and in summer. The same applies to autumn and winter, with lower irradiance values. Interestingly, $^{\bullet}OH$ and $CO_3^{-\bullet}$ appear to be maximum in spring while $^3CDOM^*$ would be maximum in summer. At equal sunlight irradiance between spring and summer, two main reasons could account for the difference. The first is that DOC is maximum in late summer – early autumn, which shifts into summer the maximum of $^3CDOM^*$ because of the correlation between $^3CDOM^*$ and DOC. In contrast, because of the anticorrelation between DOC and $^{\bullet}OH$ / $CO_3^{-\bullet}$, the latter species reach the maximum concentration in spring when the DOC is relatively far from the highest values. A further reason is connected with the winter maximum and summer minimum of nitrate, which significantly contributes to $^{\bullet}OH$ formation (reaction 2) and, via reactions (11, 12), to that of $CO_3^{-\bullet}$. Therefore, at equal sunlight irradiance, the contribution of nitrate to $^{\bullet}OH$ / $CO_3^{-\bullet}$ is expected to be higher in spring than in summer.

4. Conclusions

By modelling the indirect photochemistry in the surface water layer of Lake Maggiore (NW Italy, layer depth $d = 5$ m), a considerable and statistically significant increase of both [$^{\bullet}OH$] and [$CO_3^{-\bullet}$] was obtained between 1992 and 2008. By applying mono- and multivariate statistical analysis to water composition data and model results, we derived that the long-term increase would be dominated by the trends of both DOC and alkalinity. The former underwent a statistically significant decrease and the latter an increase over the considered period. Both [$^{\bullet}OH$] and [$CO_3^{-\bullet}$] are anticorrelated with DOC, and [$CO_3^{-\bullet}$] is correlated with alkalinity. The cited correlations / anticorrelations have the following reasons: *(i)* DOM is a major sink of both $^{\bullet}OH$ and $CO_3^{-\bullet}$, which is a typical issue in nitrate-rich and DOM-poor environments such as Lake Maggiore; and *(ii)* the formation of $CO_3^{-\bullet}$ takes place upon reaction between $^{\bullet}OH$ and HCO_3^- / CO_3^{2-}.

Interestingly, [$^{\bullet}OH$] is expected to undergo a three-fold increase and [$CO_3^{-\bullet}$] to increase by almost one order of magnitude from 1992 to 2008. The rates of photochemical transformation of organic compounds and pollutants by $^{\bullet}OH$ and $CO_3^{-\bullet}$ are expected to increase correspondingly, which means that the surface layer of lake water could become more and more effective in inducing indirect photochemical degradation. This tendency could be enhanced in the future by an eventual further increase of the alkalinity values: under the hypothesis of a correlation between alkalinity export from the lake watershed and climate warming, alkalinity could continue increasing in the next decades due to the temperature increase, as predicted by most climate scenarios (Solomon et al., 2007). Moreover, the significant decrease of the DOC is expected to favour the direct photolysis processes, which would further contribute increasing the photochemical reactivity of the lake water.

The expected seasonal trend of photochemistry is also interesting. Obviously, higher occurrence of $^\bullet$OH, $CO_3^{-\bullet}$ and ^{3}CDOM* would take place in spring-summer, when sunlight is more intense compared to autumn-winter. However, because of the summer maximum of DOC (which is a source of ^{3}CDOM* and a sink of $^\bullet$OH/$CO_3^{-\bullet}$) and the winter maximum of nitrate (which is a source of $^\bullet$OH and, as a consequence, of $CO_3^{-\bullet}$), [$^\bullet$OH] and [$CO_3^{-\bullet}$] are expected to be maximum in spring while [^{3}CDOM*] would be maximum in summer.

Nitrate levels in Lake Maggiore, as in water bodies in general, are expected to be modified by climate change. In Lake Maggiore, an overall trend of NO_3^- increase is expected as a consequence of the high fluxes of N compounds from atmospheric deposition, which is the main vehicle of N for this lake (Mosello et al., 2001; Rogora et al., 2007). Nitrate levels could also be enhanced by the indirect effects of climate warming, because of the relationships between temperature/precipitation and N dynamics in soil and water (Adrian et al., 2009; Schindler et al., 2009).

This work shows that it is possible to model the expected long-term trends of $^\bullet$OH, $CO_3^{-\bullet}$ and ^{3}CDOM* if the data series of DOC, nitrate, alkalinity and pH (and/or carbonate and bicarbonate) are available. That would be of help to elucidate the possible consequences of the long-term anthropic and climatic changes on lake-water photochemistry, as well as to include photochemistry in climate prediction models. This is potentially important because climate change may affect the long-term evolution of lake photochemistry, trough its effects on the environmental features.

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Captions to the Figures.

Figure 1. Map showing the location of Lake Maggiore in NW Italy. The triangle shows the sampling point for chemical analysis (corresponding to the point of maximum depth of the Lake, 360 m).

Figure 2. Conceptual scheme depicting the main photochemical processes that produce and consume the modelled transients. Circles represent the transient species, rectangles their photochemical sources, hexagons their sinks; hν = sunlight.

Figure 3. Relationship between nitrate concentration and pH. Note the evident anticorrelation between the two variables. The linear regression line is reported (solid line), together with its confidence bands for $\alpha = 95\%$ (dashed curves).

Figure 4. Modelled time trends of the steady-state [$^\bullet$OH] (A), [$CO_3^{-\bullet}$] (B) and [^{3}CDOM*] (C) in the surface layer ($d = 5$ m) of Lake Maggiore, over the period under consideration. The spectral photon flux density of sunlight ($p°(\lambda)$) was referred to the month of the sampling (see Figure 1-SM). It considers cloudless sky and is a daily 8-h average (8 am – 4 pm). The solid line is the regression line, the dashed curves represent the 95% confidence bounds.

Figure 5. Principal Components Analysis (PC1 vs. PC2 plot) of the data.

Figure 6. Relationship between $^\bullet$OH and DOC (A) and between $CO_3^{-\bullet}$ and DOC (B). Note the evident anticorrelation due to the scavenging effect of dissolved organic matter towards $^\bullet$OH and $CO_3^{\bullet-}$.

Figure 7. Principal Components Analysis (PC1 vs. PC2 plot) of the data: seasonal grouping. The scores of the samples belonging to the same season are identified with equal indexes: (1) winter; (2) spring; (3) summer; (4) autumn.
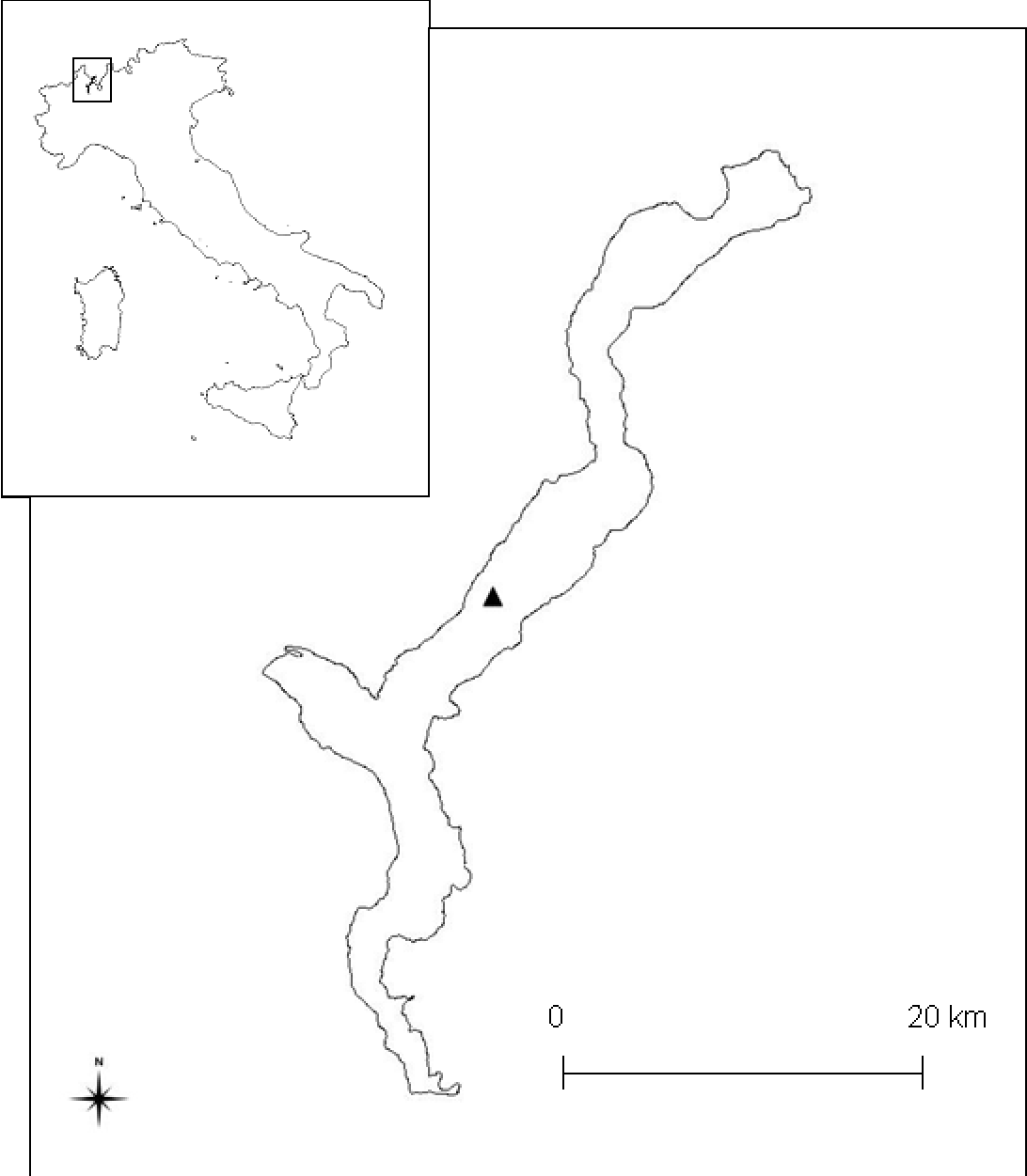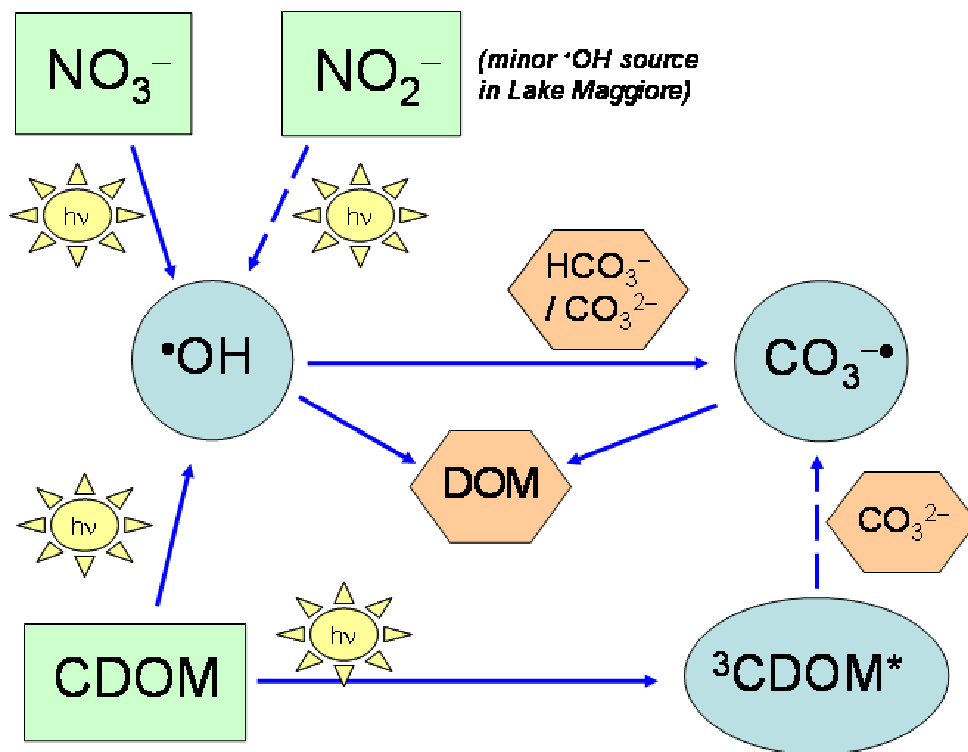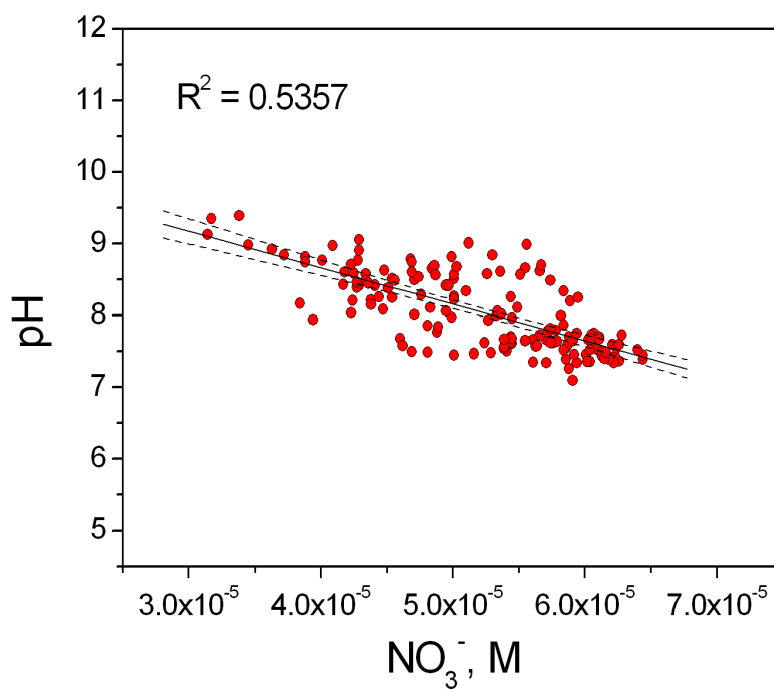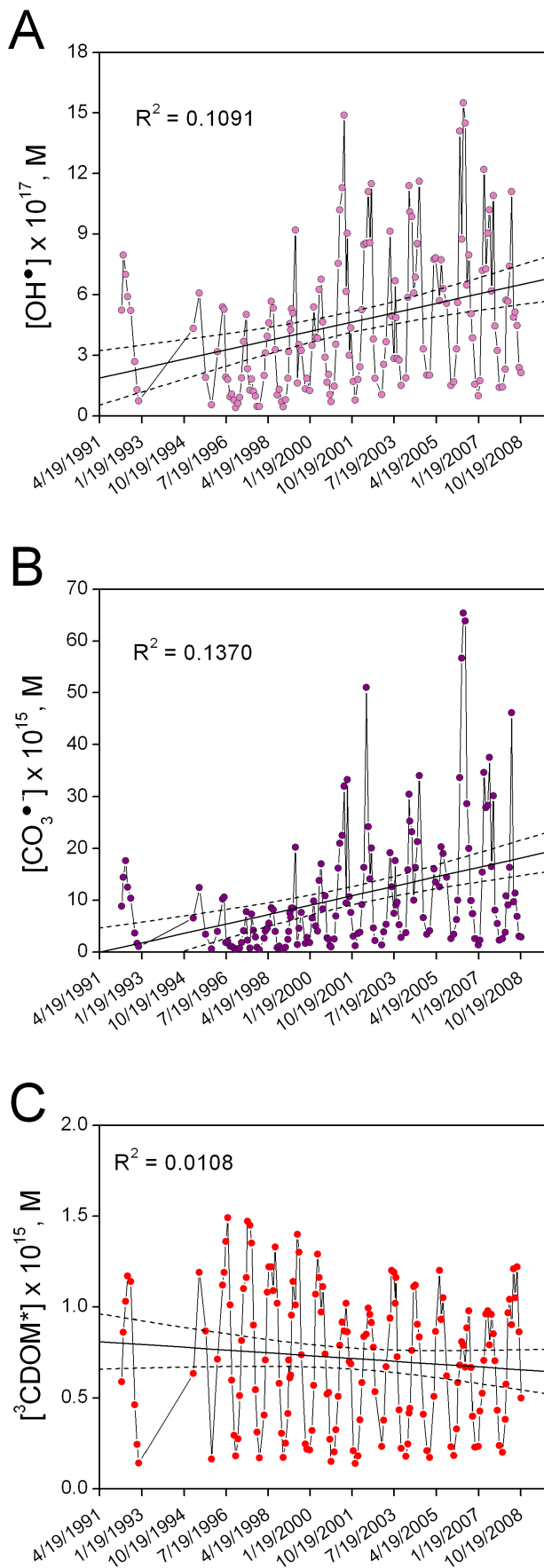
Figure 1

Figure 2

Figure 3

Figure 4

A

R^2 = 0.1091

[OH$^\bullet$] x 10^{17}, M

B

R^2 = 0.1370

[CO$_3^\bullet{}^-$] x 10^{15}, M

C

R^2 = 0.0108

[^{3}CDOM*] x 10^{15}, M

Figure 5

Figure 6

Figure 7