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Modelling lake-water photochemistry: Three-decade assessment of the steady-state concentration of photoreactive transients ($\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$ and ${}^3\text{CDOM}^*$) in the surface water of polymictic Lake Peipsi (Estonia/Russia)

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Abstract

Over the last 3-4 decades, Lake Peipsi water (sampling site A, middle part of the lake, and site B, northern part) has experienced a statistically significant increase of bicarbonate, pH, chemical oxygen demand, nitrate (and nitrite in site B), due to combination of climate change and eutrophication. By photochemical modelling, we predicted a statistically significant decrease of radicals $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ (site A, by 45% and 35%, respectively) and an increase of triplet states of chromophoric dissolved organic matter (${}^3\text{CDOM}^*$; site B, by ~25%). These species are involved in pollutant degradation, but formation of harmful by-products is more likely with ${}^3\text{CDOM}^*$ than with $\bullet\text{OH}$. Therefore, the photochemical self-cleansing ability of Lake Peipsi probably decreased with time, due to combined effects of climate change and eutrophication. In different environments, ecosystem restoration policies had the additional advantage of enhancing sunlight-driven detoxification, suggesting that photochemical self-cleansing would positively correlate with lake water quality.

Keywords: Surface-water photochemistry; Lake Peipsi; Long-term trends; Sensitised photolysis.

1. Introduction

Direct and indirect photochemical reactions are important processes in sunlit surface waters and can induce transformation of dissolved compounds, including xenobiotics (Boreen et al., 2003; Remucal and McNeill, 2011). In direct photolysis, a molecule absorbs sunlight and undergoes transformation that depends on irradiance, photolysis quantum yield, water depth, and light absorption by molecule and water (Niu et al., 2005). The photolysis quantum yield is sometimes affected by water composition (Vione et al., 2010). Indirect or sensitised photolysis involves transients ($\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$, $^3\text{CDOM}^*$) produced by photosensitisers, such as nitrite (NO_2^-), nitrate (NO_3^-) and CDOM (Richard et al., 2007; Canonica et al., 2007). Sensitised photolysis depends on substrate reactivity, irradiance, depth and water chemistry, which affects both photosensitisers and scavengers (e.g. DOM that scavenges $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$; Kelly and Arnold, 2012). CDOM is also the main radiation absorber between 290 and 500 nm, which impacts all photochemical processes (Bracchini et al., 2010).

Sensitised photolysis is more affected by water chemistry than direct photolysis (Maddigapu et al., 2011) and can undergo seasonal and long-term trends due to biological processes, human disturbance or climate change. Photochemical parameters are much more difficult, costly and longer to be measured than chemical ones, which accounts for the non-existence of long-term data of water photochemistry. This knowledge gap can be partially offset by modelling. Some of us have developed a model to link water chemistry and photochemistry (Albinet et al., 2010). Conceived and validated for pollutant phototransformation (Hatipoglu et al., 2010; Vione et al., 2011), the model can assess the impact of several disturbance factors on photosensitised processes (Minella et al., 2011). In the present work, the model predicted long-term changes in photogenerated transients in Lake Peipsi, based on available water chemistry data.

Lake Peipsi ($57^\circ 51' - 59^\circ 01' \text{ N}$; $26^\circ 57' - 28^\circ 10' \text{ E}$, 30 m a.s.l., see Figure 1), situated on the Estonian/Russian border, has 3,555 km² surface area (volume = 25 km³). It is polymictic and shallow, with 7.1 m mean depth, 15.3 m maximum depth, and hydraulic retention time of ~2 years. Catchment area (lake included) is 47,800 km². It is elongated in the north-south direction and consists of three limnologically different parts: Lake Peipsi *sensu stricto* (*s.s.*), the largest and deepest northern part; Lake Lämmijärv, the middle strait-like part; and Lake Pihkva, the southern and most shallow part. Water level is not regulated but undergoes considerable natural fluctuations: 3.04 m range over the last 80 years, and 1.15 m annual average (Jaani, 2001). Located in the northern temperate region, Lake Peipsi is normally covered with ice from December till April. It is eutrophic, with mean total phosphorus (TP) and total nitrogen (TN) at 48 mg P m⁻³ and 784 mg N m⁻³ during ice-free periods from 2006 to 2010 (Kangur et al., 2012). Nutrients are significantly lower in the northern and deepest part, Lake Peipsi *s.s.*, than in the southern part, Lake Pihkva. Moreover, P input in the southern part is increasing (Kangur and Möls, 2008).

2. Methods

2.1. Time series

Consistent time series of photochemically significant data for Lake Peipsi are available since 1972. The present study is based on data collected in the middle of Lake Lämmijärv (A) and in the northern part of Lake Peipsi *s.s.* (B, see Figure 1). Details are reported as Supplementary Material (hereafter SM), which also describes the photochemical model used to determine steady-state concentrations ($[\bullet\text{OH}]$, $[\text{CO}_3^{\bullet-}]$ and $[\text{}^3\text{CDOM}^*]$) in the water surface layer (1 m optical path length of sunlight). The model predicts transient concentrations as a function of water chemistry and seasonally-variable irradiance (Figure SM1; Frank and Klöpffer, 1988). Photochemistry mainly depends on NO_3^- , NO_2^- , dissolved organic carbon (DOC), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}), the latter determined from HCO_3^- and pH. DOC was approximately estimated from available Chemical Oxygen Demand (COD). Although DOC and COD measure different things, we adopted the useful correlation $\text{DOC} = 0.18 \pm 0.02 \text{ COD}$ reported for lake water ($R^2 = 0.95$; Chang et al., 1998). Exponentially decreasing water absorption spectrum was modelled from DOC (see SM). The used spectral slope (0.015 nm^{-1} ; Bracchini et al., 2010; Maddigapu et al., 2011) is fully compatible with available Lake Peipsi data (Reinart et al., 2004). Concerning absorbance values, our approach might underestimate absorption by highly humic (C)DOM in nordic lake environments (Freeman et al., 2001). However, elevated COD/DOC in Lake Peipsi would ensure that almost all incident irradiance below 500 nm is absorbed over a 1 m path length (Reinart, 2008). This would reduce errors on absorbed photon flux calculations, derived from incertitude on absorbance (see SM). Photoproduction of $\bullet\text{OH}$ by nitrate *via* photolysis and photoisomerisation/homolysis would be affected by pH and inorganic carbon (Vione et al., 2009), but nitrite and CDOM would prevail in Lake Peipsi as $\bullet\text{OH}$ sources. Furthermore, an optical path length of 1 m would correspond to different depths (0.65-0.9 m), depending on seasonal-variable solar zenith angle (see Figure SM3 and related discussion; Zepp and Cline, 1977; Montenbruck and Pflieger, 1994).

2.2. Multivariate analysis: Principal Component Analysis (PCA)

Due to complex relationships among monitored chemical variables and modelled $[\bullet\text{OH}]$, $[\text{CO}_3^{\bullet-}]$ and $[\text{}^3\text{CDOM}^*]$, PCA was used. Loadings analysis emphasises interrelationships among variables, because correlations, anti-correlations and non-correlations correspond to parallel, anti-parallel and perpendicular loadings, respectively. The position and grouping of each sample on PC plane (Scores Analysis) can highlight seasonal or long-term trends. PCA calculations were carried out on column-autoscaled data, with the free chemometric software V-Parvus (Forina et al., 2008).

3. Results and Discussion

3.1. Trends by season

Interesting seasonal trends could be seen in site A. Figure 2 reports scores and loadings plot (PC1 vs. PC2, which explain 52% variance), with seasonally-grouped scores (1: winter; 2: spring; 3: summer; 4: fall). Nitrate has winter maxima, because algal uptake reduces its level in other seasons (Black et al., 1993). Anticorrelation between nitrate and pH is accounted for by algal growth in summer, which consumes nitrate as well as CO₂ by photosynthesis, thereby increasing pH (Wetzel, 2001). Nitrite is highest in spring and fall, possibly because of recirculation phenomena (reported water data are referred to the surface layer).

Transients $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$ are anticorrelated with COD. DOM would consume both radicals, and $\cdot\text{OH}$ scavenging also inhibits oxidation of HCO_3^- and CO_3^{2-} to $\text{CO}_3^{\cdot-}$. Although most $\cdot\text{OH}$ in Lake Peipsi would be photogenerated by CDOM, $\cdot\text{OH}/\text{COD}$ anticorrelation suggests that DOM as $\cdot\text{OH}$ scavenger would be more important than CDOM as source. Formation of $\text{CO}_3^{\cdot-}$ from $\cdot\text{OH}$ would account for the correlation between $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$. Radicals $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$ correlate with nitrite, thus elevated $[\text{NO}_2^-]$ is required for $[\cdot\text{OH}]$ and $[\text{CO}_3^{\cdot-}]$ to be high. Indeed, NO_2^- is much more important as $\cdot\text{OH}$ source than as scavenger (Vione et al., 2011).

Levels of $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$ are maximal during spring. Sunlight irradiance would be exactly the same (on average) in spring and summer if meteorology issues are not considered. Higher $[\cdot\text{OH}]$ and $[\text{CO}_3^{\cdot-}]$ in spring than in summer are probably due to: (i) higher COD levels in summer, causing considerable $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$ scavenging; and/or (ii) higher spring levels of NO_2^- , yielding $\cdot\text{OH}$ and, as a consequence, $\text{CO}_3^{\cdot-}$. In contrast, elevated summer (C)DOM and irradiance account for the summer maximum of $[\text{CDOM}^*]$.

Seasonal trends and correlations are practically the same in eutrophic Lake Peipsi (sampling site A) and in oligotrophic Lake Maggiore (NW Italy; Bertoni et al., 2010; Minella et al., 2011), despite considerable differences in water depth, trophicity, climate zone and surrounding environment. However, this statement is partially offset by the lack of clear seasonal trends in sampling site B (PCA data not shown). Apart from partial differentiation between fall/winter and spring/summer, no clear differences could be highlighted in site B between fall and winter and between spring and summer. The different seasonal effects on sites A and B could depend on morphology: Lake Lämmijärv (site A) is on average smaller and shallower than Lake Peipsi *s.s.* (site B). Therefore, site A could have a more pronounced seasonality in chemical parameters. Site A actually corresponds to the deepest point (15.3 m) of the whole lake, but this study considered the mixed surface layer that could receive contributions from nearby shallow environments.

3.2. Long-term trends

3.2.1. Site A, monitored chemical parameters

Figure 3(A-E) reports the time trends of HCO_3^- (determined from alkalinity and pH), pH, NO_3^- , NO_2^- and COD for site A, from May 1972 to October 2010. Table 1 reports results of Pearson correlation test for the relevant time series. Qualitative trends (increase or decrease) did not vary much when considering whole data or seasonal groups (spring/summer and fall/winter separately), but population size reduction in the latter case somewhat changed statistical significance (see SM).

For whole data, there is statistically significant time increase of HCO_3^- , pH, CO_3^{2-} (not reported), NO_3^- and COD. The increase of HCO_3^- and pH is probably connected to alkalinity increase. Such variables would be associated in water systems at equilibrium (see SM; note, however, that carbonate and bicarbonate were determined from measured values of alkalinity and pH and not from air/water equilibria). The lack of point-by-point correlation between HCO_3^- and pH (Figure 2) suggests that equilibrium between water and atmosphere is not reached in any single moment, but an equilibrium-like behaviour might appear over time. Alkalinity increase might be caused by enhanced transport of ionic solutes from catchment area to the lake. Although not making univocal evidence, this is an expected effect of climate change (Schindler, 2009). Significant increase of alkalinity and pH was reported for lakes located in Southern Nordic Europe (Skjelkvåle et al., 2005), experiencing similar climate conditions as Lake Peipsi.

Although seasonally uncorrelated (see Figure 2), the long-term increases of NO_3^- and COD are an index of ongoing lake eutrophication (Senga et al., 2011). In Lake Peipsi the increase of phosphorus delayed recovery of water quality (Haberman et al., 2010; Kangur and Möls, 2008). Persistent eutrophication phenomena have been observed, including massive cyanobacteria blooms and night-time oxygen depletion, causing severe oxygen deficit in lake bottom and fish kills during still, warm summer nights. Additional effects are cyanotoxins in water, low water transparency and lake-bottom siltation (Kangur et al., 2005; Kangur et al., 2007). Independently of eutrophication, a slight COD increase was reported for lakes in Southern Nordic Europe because of warmer climate (Freeman et al., 2001), including elevated summer temperatures combined to declining acid deposition (Evans et al., 2005).

3.2.2. Site A, modelled photochemical parameters

Figure 3(F-H) reports the time trends of $[\bullet\text{OH}]$, $[\text{CO}_3^{\bullet-}]$ and $[\text{}^3\text{CDOM}^*]$. The increase of $\text{}^3\text{CDOM}^*$ is statistically insignificant, while decrease of both $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ is significant. These trends are probably dominated by COD increase, with different impacts and consequences. CDOM increase is expected to enhance $\text{}^3\text{CDOM}^*$ (Al-Housari et al., 2010), but CDOM is the main sunlight absorber below 500 nm (Bracchini et al., 2010). High CDOM in Lake Peipsi could saturate absorption even in the surface layer. Therefore, CDOM absorbed photon flux would respond very little to organic matter changes, reducing $[\text{}^3\text{CDOM}^*]$ variations.

On the other hand, $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ are scavenged by DOM and the scavenging rate constant shows no saturation (see SM). Therefore, DOM increase would proportionally decrease both $[\bullet\text{OH}]$ and $[\text{CO}_3^{\bullet-}]$. The significant NO_3^- increase would hardly affect $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$, because nitrite and most notably CDOM would prevail as $\bullet\text{OH}$ sources in Lake Peipsi.

Transients $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$ and ${}^3\text{CDOM}^*$ are involved in pollutant photodegradation (Hoigné, 1990), which is part of the self-depollution ability of a water body. Significant decrease of $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ and insignificant ${}^3\text{CDOM}^*$ variation indicate a decrease of photochemical self-cleansing potential in site A.

3.2.3. Sampling site B, monitored chemical parameters

Figure 4(A-E) reports the time trends of HCO_3^- , pH, NO_3^- , NO_2^- and COD for site B, from February 1980 to October 2010. According to Pearson test results (Table 1), there is a statistically significant increase for all plotted parameters and CO_3^{2-} (data not shown). Such trends have presumably the same explanation as for site A. Furthermore, the statistically significant increase of nitrite over time could be a further sign of eutrophication. In addition to increasing nitrogen, eutrophication could favour the scarce oxygenation of near-bottom water during summer (Wetzel, 2001; Kangur et al., 2012), increasing bottom $[\text{NO}_2^-]$ and its surface levels during mixing.

3.2.4. Sampling site B, modelled photochemical parameters

Figure 4(F-H) reports the time trends of $[\bullet\text{OH}]$, $[\text{CO}_3^{\bullet-}]$ and $[{}^3\text{CDOM}^*]$. The increase of ${}^3\text{CDOM}^*$ is statistically significant, while variations of $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ are insignificant. The significant ${}^3\text{CDOM}^*$ trend can be explained because COD in site B (28 mg L^{-1} on average) was lower than in site A (36 mg L^{-1} on average). Lower COD would mean lower DOM and lower CDOM, which lowers the degree of absorption saturation and makes ${}^3\text{CDOM}^*$ respond more promptly to DOM variations.

The pretty stable $[\bullet\text{OH}]$ and $[\text{CO}_3^{\bullet-}]$ values are produced by compensation of opposite effects. Significant time increase of nitrate and most notably nitrite is offset by increasing COD, which enhances $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ scavenging.

3.3. Implications for pollutant phototransformation

Statistically significant decrease of $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ is predicted in site A, and significant increase of ${}^3\text{CDOM}^*$ in site B. In site A, 2010 average values of $[\bullet\text{OH}]$ and $[\text{CO}_3^{\bullet-}]$ would be, respectively, 55% and 65% of the 1972 ones ($[\bullet\text{OH}]$ would decrease from $3.0 \cdot 10^{-17}$ to $1.6 \cdot 10^{-17} \text{ M}$, $[\text{CO}_3^{\bullet-}]$ from $2.0 \cdot 10^{-15}$ to $1.3 \cdot 10^{-15} \text{ M}$). Such variations are higher than the $\sim 10\%$ statistical incertitude in conversion between COD and DOC (Chang et al., 1998). By comparison, $[{}^3\text{CDOM}^*]$ would vary from $4.5 \cdot 10^{-15}$ to $5 \cdot 10^{-15} \text{ M}$. To assess associated changes in pollutant transformation kinetics, one can take the example of aniline that has second-order reaction rate constants, $k_{\text{Aniline}, \bullet\text{OH}} = 1.4 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{Aniline}, \text{CO}_3^{\bullet-}} = 5 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988; Neta et al., 1988).

The pseudo-first order rate constants can be expressed as $k_{Aniline}^{\bullet OH} = k_{Aniline, \bullet OH} \cdot [\bullet OH]$ and $k_{Aniline}^{CO_3^{\bullet -}} = k_{Aniline, CO_3^{\bullet -}} \cdot [CO_3^{\bullet -}]$. The associated half-life times are $\tau_{Aniline}^i = \ln 2 (k_{Aniline}^i)^{-1}$, with $i = \bullet OH$ or $CO_3^{\bullet -}$. With average 1972 and 2010 data reported above, one gets that: (i) the reaction of aniline with $CO_3^{\bullet -}$ in Lake Peipsi would be twice faster than $\bullet OH$ reaction; (ii) it is $(k_{Aniline}^{tot})_{1972} = (k_{Aniline}^{\bullet OH})_{1972} + (k_{Aniline}^{CO_3^{\bullet -}})_{1972} = 1.4 \cdot 10^{-6} \text{ s}^{-1}$ and $(k_{Aniline}^{tot})_{2010} = 8.7 \cdot 10^{-7} \text{ s}^{-1}$. Therefore, the average transformation rate of aniline in 2010 would be 40% lower than in 1972. In terms of half-life times, $(\tau_{Aniline}^{tot})_{year} = \ln 2 [(k_{Aniline}^{tot})_{year}]^{-1}$, expressed as outdoor summer days (Albinet et al., 2010), one gets $(\tau_{Aniline}^{tot})_{1972} \sim 14$ days and $(\tau_{Aniline}^{tot})_{2010} \sim 22$ days. During winter, solar irradiance can be reduced to one-fifth (Frank and Klöpffer, 1988) or even less due to partial ice cover, and $(\tau_{Aniline}^{tot})$ can be considerably higher.

$[^3CDOM^*]$ would increase by $\sim 25\%$ in site B, from $4 \cdot 10^{-15} \text{ M}$ in 1980 to $5 \cdot 10^{-15} \text{ M}$ in 2010. In the same period, $[\bullet OH]$ and $[CO_3^{\bullet -}]$ were almost unchanged in the $2 \cdot 10^{-17}$ and $(1.7-1.8) \cdot 10^{-15} \text{ M}$ ranges, respectively. Considering the phenylurea herbicide metoxuron, with $k_{Metoxuron, ^3CDOM^*} = 2.5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Canonica et al., 2006), one gets $(k_{Metoxuron}^{^3CDOM^*})_{1972} = k_{Metoxuron, ^3CDOM^*} \cdot [^3CDOM^*] = 1.0 \cdot 10^{-5} \text{ s}^{-1}$ and $(k_{Metoxuron}^{^3CDOM^*})_{2010} = 1.2 \cdot 10^{-5} \text{ s}^{-1}$. This would mean $(\tau_{Metoxuron}^{^3CDOM^*})_{1972} \sim 1.9$ days and $(\tau_{Metoxuron}^{^3CDOM^*})_{2010} \sim 1.6$ days in summer, but $^3CDOM^*$ -induced degradation processes could be inhibited in DOM-rich waters (Wenk and Canonica, 2012).

Interestingly, seasonal variations of $[\bullet OH]$, $[CO_3^{\bullet -}]$ and $[^3CDOM^*]$ in both sites A and B are much higher than differences between 1972 (or 1980) and 2010 averages (Figures 3F-H and 4F-H).

4. Conclusions

Water chemistry in Lake Peipsi over the last 3-4 decades showed a statistically significant increase of HCO_3^- , CO_3^{2-} , NO_3^- , COD, pH (sites A and B) and NO_2^- (only site B). These trends are likely caused by combination of climate change and increased eutrophication. Although the latter is mostly due to human activities (Kangur and Möls, 2008; Haberman et al., 2010), climate warming may also favour eutrophication phenomena (Paerl and Paul, 2012; Kangur et al. 2012).

Water chemistry has different effects on modelled photochemical parameters. In site A, the model predicts significant decrease with time of $[\bullet OH]$ and $[CO_3^{\bullet -}]$ (by 45 and 35%, respectively), because of stable NO_2^- and increasing DOM. Site B has qualitatively similar but quantitatively different trends, which produce stable $[\bullet OH]$ and $[CO_3^{\bullet -}]$ and increasing $[^3CDOM^*]$ (by $\sim 25\%$). Eutrophication is active in both sites (Kangur and Möls, 2008; Haberman et al., 2010; Kangur et al., 2012), thus lakes undergoing eutrophication could experience significant decrease of $[\bullet OH]$ and $[CO_3^{\bullet -}]$ (or no change) and significant but less important increase of $^3CDOM^*$ (or no change). The species $\bullet OH$, $CO_3^{\bullet -}$ and $^3CDOM^*$ are involved in pollutant phototransformation, but $\bullet OH$ is less likely to produce harmful intermediates (Legrini et al., 1993; Zertal et al., 2001). In terms of depollution, therefore, $^3CDOM^*$ increase would not compensate for $\bullet OH$ decrease. By comparison,

Lake Maggiore (a deep lake located in the southern alpine region) is quickly recovering from past eutrophication and shows significant increase with time of both $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$ (Bertoni et al., 1998; Minella et al., 2011). The comparison suggests that environmental recovery policies would also restore the photochemical self-depollution capacity of lake waters. In contrast, worsening water quality could damage the natural capacity of lake water to photodegrade harmful compounds.

Water chemistry data in Lake Peipsi were obviously not collected to assess photochemistry. Luckily, chemical parameters that characterise water ecology also allow photochemical modelling. Because similar data sets have likely been obtained worldwide, the model approach outlined here could enable large-scale photochemistry assessment, highlighting modifications due to long-term human disturbance and climate change.

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Table 1. Correlation coefficients of the time trend of monitored chemical and modelled photochemical parameters for water in Lake Peipsi, in the two sampling sites. In the “*Trend*” column, “+” means a positive slope of the regression line (increase of parameter with time), “-” a negative slope (decrease with time). In the “*Test result*” column, statistically significant correlations ($p < 0.05$) are highlighted in bold. Note that the Pearson test at 95% significance level foresees statistically significant correlation if $R^2 > 0.020$ for 160 data points, and if $R^2 > 0.031$ for 125 data points.

<i>Parameter</i>	<i>Sampling site A</i>			<i>Sampling site B</i>		
	R^2 (<i>exp.</i>)	<i>Trend</i>	<i>Test result</i>	R^2 (<i>exp.</i>)	<i>Trend</i>	<i>Test result</i>
HCO_3^-	0.083	+	$p < 0.001$	0.338	+	$p < 0.0005$
CO_3^{2-}	0.049	+	$p < 0.01$ ^(a)	0.248	+	$p < 0.0005$
NO_3^-	0.084	+	$p < 0.001$ ^(b)	0.198	+	$p < 0.0005$
NO_2^-	0.014	+	$p > 0.05$	0.099	+	$p < 0.0005$
<i>COD</i>	0.078	+	$p < 0.001$ ^(c)	0.045	+	$p < 0.005$ ^(h)
<i>pH</i>	0.077	+	$p \sim 0.001$ ^(d)	0.334	+	$p < 0.0005$
$\bullet OH$	0.057	-	$p < 0.005$ ^(e)	$4 \cdot 10^{-5}$	+	$p > 0.1$
$CO_3^{\bullet -}$	0.038	-	$p < 0.025$ ^(f)	0.010	+	$p \sim 0.1$
${}^3CDOM^*$	0.013	+	$p > 0.1$ ^(g)	0.033	+	$p < 0.01$

^(a) The CO_3^{2-} increase in site A was statistically not significant in the separated spring+summer and fall+winter data sets (see Table SM1).

^(b) The NO_3^- increase in site A was statistically not significant in the fall+winter data, when separately analysed (see Table SM1).

^(c) The *COD* increase in site A was statistically not significant in the spring+summer data, when separately analysed (see Table SM1).

^(d) The *pH* increase in site A was statistically not significant in the fall+winter data, when separately analysed (see Table SM1).

^(e) The $\bullet OH$ increase in site A was statistically not significant in the fall+winter data, when separately analysed (see Table SM1).

^(f) The $CO_3^{\bullet -}$ increase in site A was statistically not significant in the separated spring+summer and fall+winter data sets (see Table SM1).

^(g) The ${}^3CDOM^*$ increase in site A was statistically significant in the fall+winter data, when separately analysed (see Table SM1).

^(h) The *COD* increase in site B was statistically not significant in the fall+winter data, when separately analysed (see Table SM1).

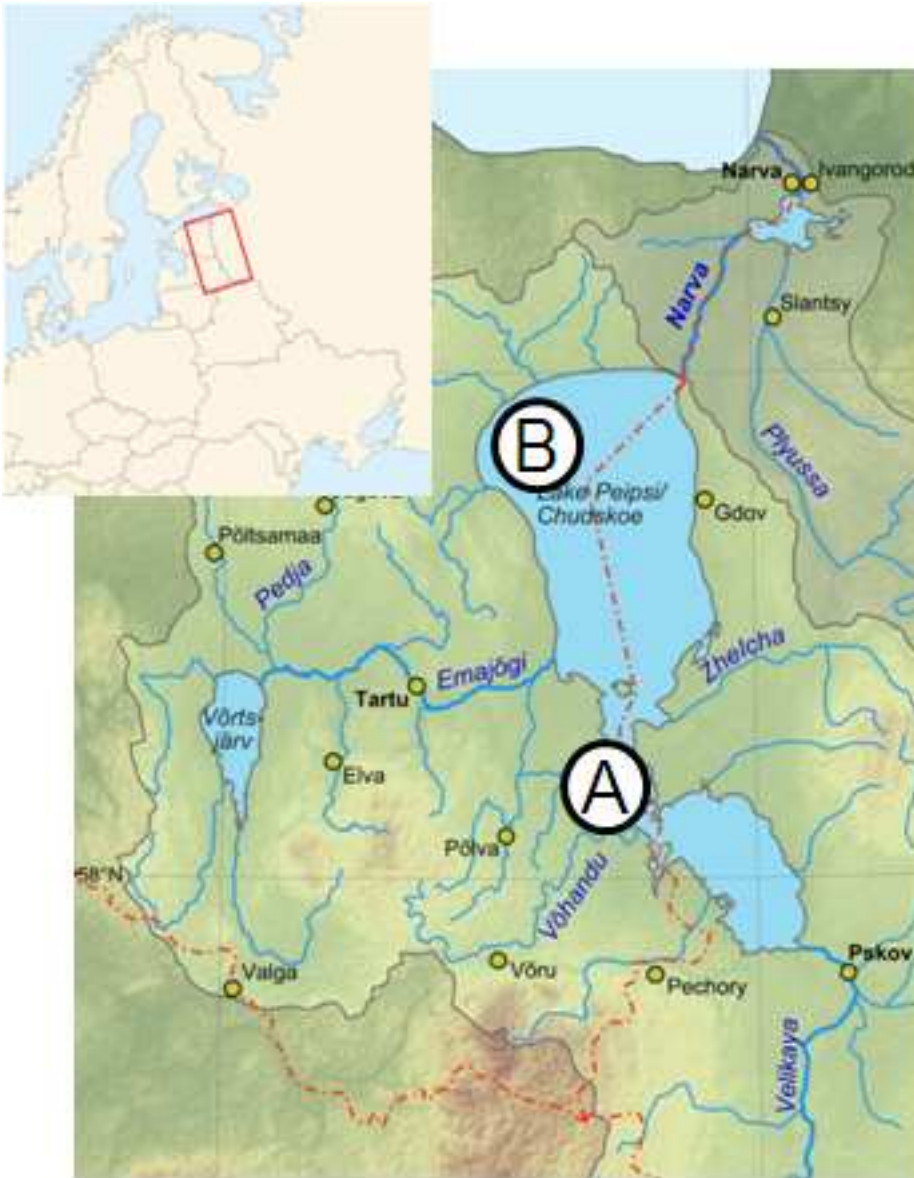


Figure 1. Map showing the location of Lake Peipsi. The circles show the two sampling sites (A and B).

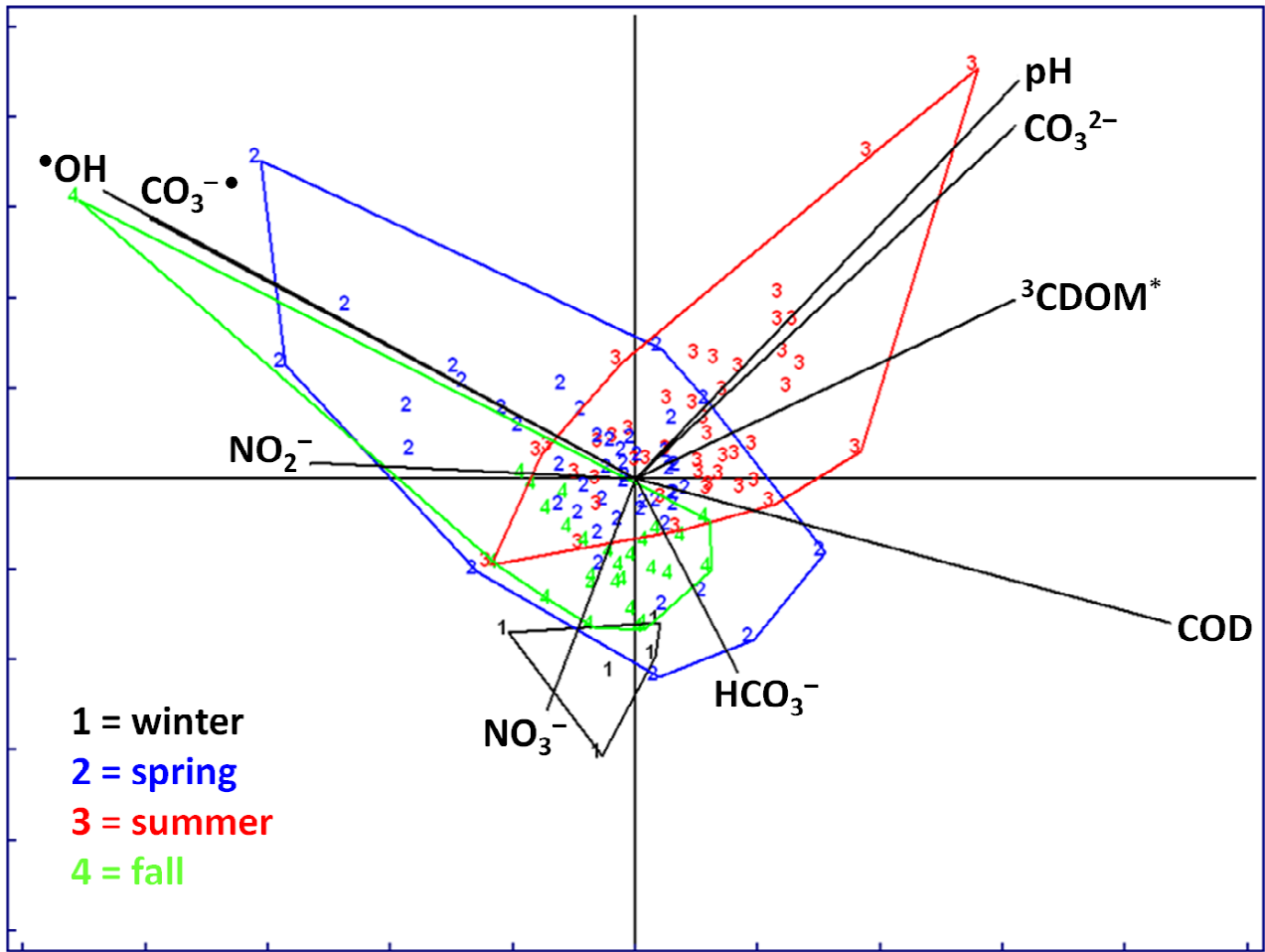


Figure 2. Principal Components Analysis (PC1 vs. PC2) for site A. The sample scores belonging to the same season are identified with equal indexes: (1) winter; (2) spring; (3) summer, and (4) fall.

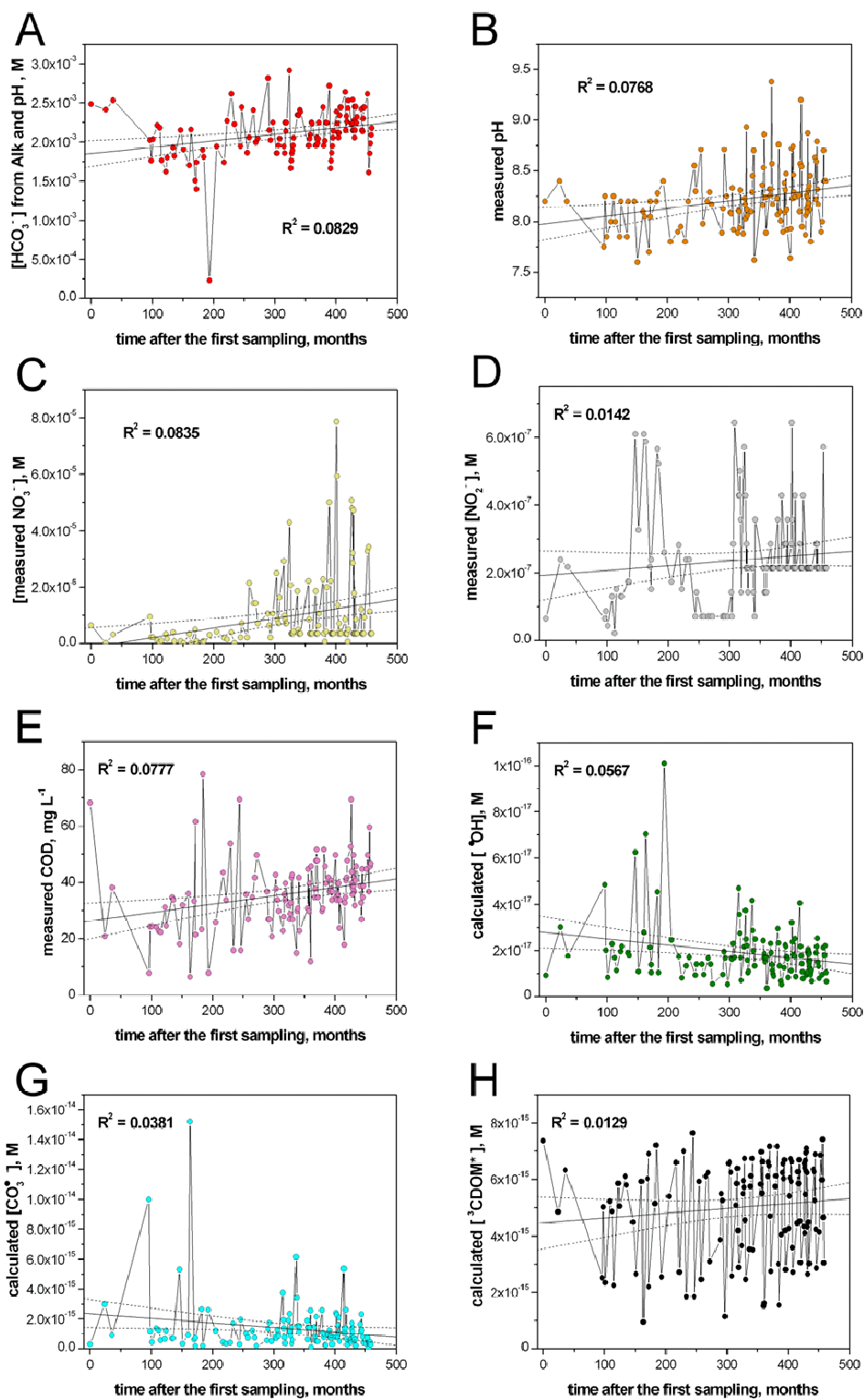


Figure 3. Time series of measured chemical and modelled photochemical variables in Lake Peipsi (1 m sunlight optical path length, site A, May 1972 – October 2010). The linear regression of experimental data with its confidence bands ($\alpha = 95\%$) and the R^2 value are reported on each plot. The spectral photon flux density of sunlight ($p^\circ(\lambda)$) was referred to the month of sampling (see Fig. SM1).

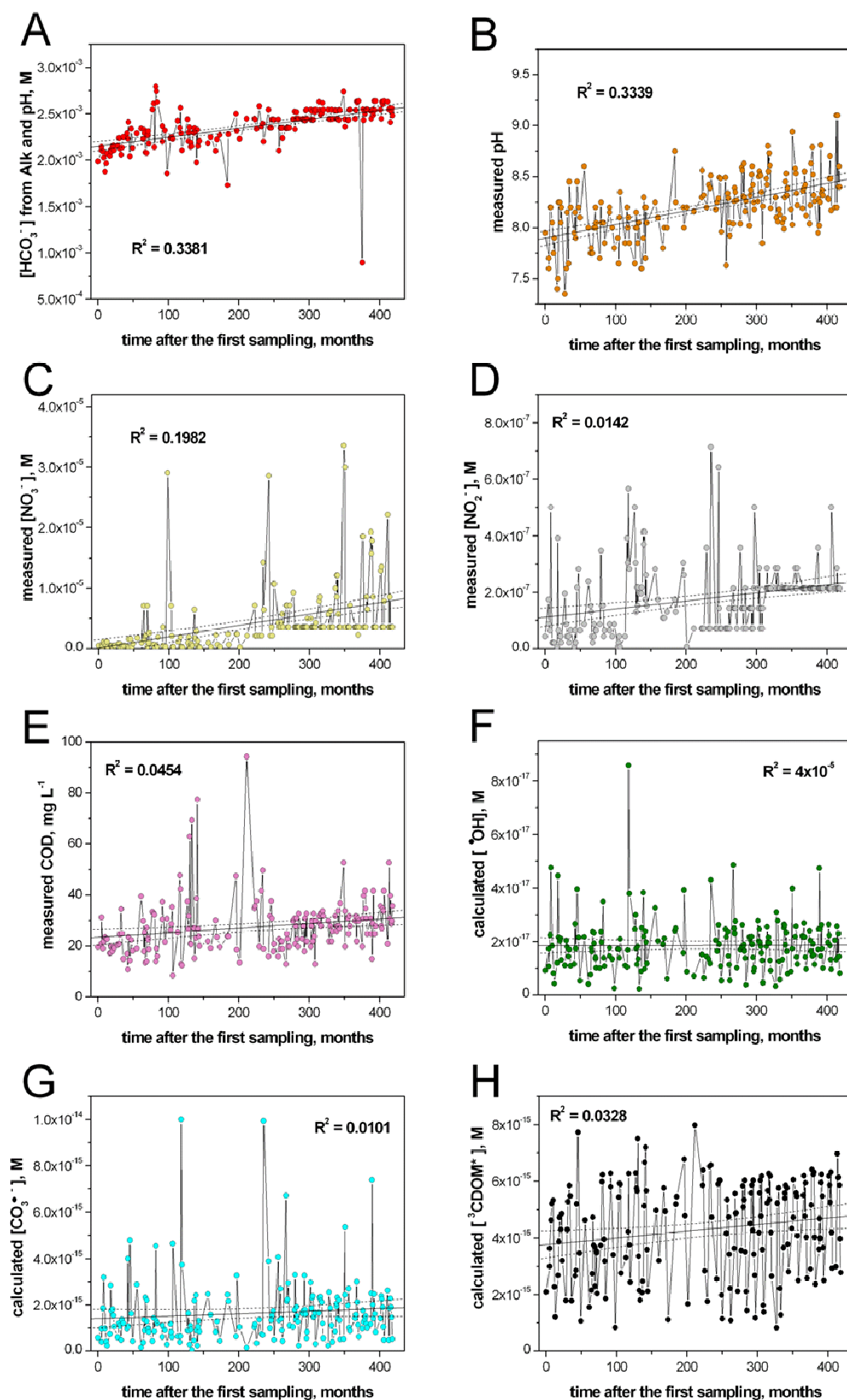


Figure 4. Time series of measured chemical and modelled photochemical variables in Lake Peipsi (1 m sunlight optical path length, site B, February 1980 – October 2010). Other issues as for Fig. 3.