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Assessing the phototransformation of diclofenac, clofibric acid and naproxen in surface waters: Model predictions and comparison with field data

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Abstract

Phototransformation is important for the fate in surface waters of the pharmaceuticals diclofenac (DIC) and naproxen (NAP) and for clofibric acid (CLO), a metabolite of the drug clofibrate. The goal of this paper is to provide an overview of the prevailing photochemical processes, which these compounds undergo in the different conditions found in freshwater environments. The modelled photochemical half-life times of NAP and DIC range from a few days to some months, depending

on water conditions (chemistry and depth) and on the season. The model indicates that direct photolysis is the dominant degradation pathway of DIC and NAP in sunlit surface waters, and potentially toxic cyclic amides were detected as intermediates of DIC direct phototransformation. With modelled half-life times in the month-year range, CLO is predicted to be more photostable than DIC or NAP and to be degraded mainly by reaction with the $\bullet\text{OH}$ radical and with the triplet states of chromophoric dissolved organic matter (${}^3\text{CDOM}^*$). The CLO intermediates arising from these processes and detected in this study (hydroquinone and 4-chlorophenol) are, respectively, a chronic toxicant to aquatic organisms and a possible carcinogen for humans. Hydroquinone is formed with only ~5% yield upon CLO triplet-sensitised transformation, but it is highly toxic for algae and crustaceans. In contrast, the formation yield of 4-chlorophenol reaches ~50% upon triplet sensitisation and ~10% by $\bullet\text{OH}$ reaction. The comparison of model predictions with field data from a previous study yielded a very good agreement in the case of DIC and, when using 4-carboxybenzophenone as proxy for triplet sensitisation by CDOM, a good agreement was found for CLO as well. In the case of NAP, the comparison with field data suggests that its direct photolysis quantum yield approaches or even falls below the lower range of literature values.

Keywords: Diclofenac; Naproxen; Clofibric Acid; Environmental Photochemistry; Photolysis; Pollutant fate.

1. Introduction

In recent years a growing interest has arisen for the emerging pollutants or contaminants of emerging concern. They belong to diverse chemical and commodity classes or sub-classes and are often found in wastewater. The effluents of wastewater treatment plants (WWTPs) are major routes

of emerging contaminants to surface water bodies, because these compounds are often polar and biorefractory and undergo partial or poor removal by traditional WWTP technologies (Richardson and Ternes, 2014). Pharmaceuticals and personal care products (PPCPs) are an important class of emerging contaminants, which could cause adverse effects (directly or through their metabolites) on aquatic environments, the food webs and possibly also human health (Fatta-Kassinos et al., 2011; Bu et al., 2013; Prasse et al., 2015).

Among PPCPs, diclofenac (DIC) and naproxen (NAP) are two very widespread non-steroidal anti-inflammatory drugs. The sales volumes of DIC are quite high, and in the years from 2010 to 2013 its average world annual consumption was 1443 ± 58 t (Acuña et al., 2015; Azuma et al., 2015). In addition to possible concerns for human health by direct use (Moore et al., 2014), DIC is potentially ecotoxic for surface-water environments (Escher et al., 2011; Diniz et al., 2015) where it can reach $\mu\text{g L}^{-1}$ levels (Patrolecco et al., 2015). These issues have prompted the inclusion of DIC in the list of substances to be monitored in the latest European Water Framework Directive (Ribeiro et al., 2015). Moreover, the use of DIC in veterinary medicine causes adverse effects to the populations of vultures (Oaks et al., 2004; Camina et al., 2014).

NAP was found to occur at tens to hundreds ng L^{-1} levels in surface waters (Patrolecco et al., 2015; Arlos et al., 2015), and it has even been detected in drinking water (Benotti et al., 2009). Although its concentration levels are too low to cause acute toxicity, the frequent detection of fairly elevated concentrations might cause chronic effects on aquatic organisms such as crustaceans and algae (Fernandez et al., 2010). Moreover, NAP transformation intermediates should also be considered for a complete ecotoxicological assessment of this compound in surface waters (Isidori et al., 2005).

Clofibric acid (CLO) is another interesting compound because it is a metabolite of the cholesterol-lowering pharmaceutical drug clofibrate and a structural isomer of the herbicide mecoprop (Santos

et al., 2000). CLO occurs in surface waters at tens ng L⁻¹ levels (Patrolecco et al., 2015), and chronic exposure can cause harmful effects to fish (Corcoran et al., 2015; Coimbra et al., 2015) and possibly crustaceans (Gonzales-Ortegon et al., 2015).

Photochemistry is a potentially important transformation pathway for the investigated compounds (Boreen et al., 2003; Bartels and von Tümpling, 2007; Bonvin et al., 2013; Yan and Song, 2014; Duran-Alvarez et al., 2015), and its significance is increased by the fact that the irradiation of pharmaceuticals mixtures may increase their toxicity (Li and Lin, 2015). Generally speaking, phototransformation in surface waters can be divided into direct photolysis (a xenobiotic absorbs sunlight, which triggers its degradation) and indirect photochemistry. In the latter, sunlight is absorbed by naturally-occurring photosensitisers (most notably nitrate, nitrite and chromophoric dissolved organic matter, CDOM) to produce reactive transient species ($\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and CDOM triplet states, $^3\text{CDOM}^*$) (Dong et al., 2015). More precisely, nitrate and nitrite yield $\bullet\text{OH}$, while irradiated CDOM produces $^3\text{CDOM}^*$ (which can form $^1\text{O}_2$ by reaction with oxygen) and $\bullet\text{OH}$ as well. The carbonate radical is produced upon oxidation of carbonate and bicarbonate by $\bullet\text{OH}$ and of carbonate by $^3\text{CDOM}^*$ (Canonica et al., 2005; De Laurentiis et al., 2013; Bahnmuller et al., 2014; Janssen et al., 2014; Trivella et al., 2015; Bintou et al., 2015). Dissolved organic matter (DOM, not necessarily chromophoric), which is usually quantified as dissolved organic carbon (DOC), is the main sink of both $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$. This issue, combined with the fact that CDOM is a major photosensitiser, explains why $\bullet\text{OH}$ and $\text{CO}_3^{\bullet-}$ are usually more concentrated in low-DOC waters. In contrast, the highest levels of $^3\text{CDOM}^*$ and $^1\text{O}_2$ usually occur in high-DOC environments (Vione et al., 2014).

The photodegradation of DIC, NAP and CLO (see **Table 1** for their structures) has been studied in the laboratory, indicating that the direct photolysis should be an important pathway in the

environmental phototransformation of DIC and NAP (Packer et al., 2003; Abdelmelek et al., 2011; Yu et al., 2013). However, to our knowledge few attempts (and only for DIC) have been made to compare predictions based on laboratory studies with field results concerning the persistence of these compounds (Buser et al., 1998; Bonvin et al., 2013). A field study that includes estimates of photoreaction kinetics is for instance available for the sunlit epilimnion of Lake Greifensee, Switzerland (Tixier et al., 2003). It could be very conveniently exploited to validate and verify the results of laboratory simulations, because it is one of the very few examples to our knowledge where the phototransformation kinetics was disentangled from the overall field attenuation. Comparison between laboratory and field results requires a complete set of photoreactivity data. However, although the direct photolysis quantum yields and the reaction rate constants with $\bullet\text{OH}$ are available for the three compounds, the reaction rate constant with $^1\text{O}_2$ is only known for NAP and there is no indication of the reactivity of the investigated substrates with $\text{CO}_3^{\bullet-}$ and, most notably, $^3\text{CDOM}^*$ (Yu et al., 2014). A photochemical model is also needed to link the laboratory results with the processes occurring in the actual environment, for instance to simulate the decrease of photodegradation with increasing water column depth.

The goal of the present work was, first of all, to fill in the gaps in the photoreactivity data, providing the missing rate constants with $^1\text{O}_2$ and assessing the reactivity of DIC, NAP and CLO with $\text{CO}_3^{\bullet-}$ and $^3\text{CDOM}^*$. The data already available and those provided in the framework of this work were then used as input for a photochemical model (APEX: Aqueous Photochemistry of Environmentally-occurring Xenobiotics; Bodrato and Vione, 2014), to compare model predictions with field data of photochemical persistence. This approach allows a check on and a calibration of the model, and it provides a very useful discussion step about the significance of the input photoreactivity data. On this basis, the photochemical persistence of DIC, NAP and CLO was assessed as a function of environmental variables (water chemistry, depth, seasonality), and the

prevailing phototransformation pathways were identified. Insight was also obtained into the intermediates that may be formed via the main phototransformation reactions.

2. Materials and methods

2.1. Chemicals. The chemical reagents used in this work were of at least analytical grade and used as received, without further purification. Eluents used in liquid chromatography were of gradient-grade quality, and water was of Milli-Q quality.

2.2. Steady state irradiation experiments. Reaction rate constants that have not previously been reported required the choice of particular irradiation conditions with the use of different lamps. The reactivity with $\text{CO}_3^{\bullet-}$ was studied by irradiating the relevant substrates in the presence of nitrate and bicarbonate, using a Philips TL 20W/01 lamp with emission maximum at 313 nm. The reactivity with $^1\text{O}_2$ was studied by irradiating the substrates with Rose Bengal as $^1\text{O}_2$ source, under a yellow Philips TL D 18W/16 lamp with emission maximum at 545 nm. Finally, anthraquinone-2-sulphonate (AQ2S) was used as CDOM proxy in steady state irradiation experiments to study the reactivity with $^3\text{CDOM}^*$. The rationale for the focus on $^3\text{CDOM}^*$ is that triplet-sensitised processes are often more important than additional reactions induced by other species formed by irradiated CDOM (e.g. superoxide and oxygen-containing organic radicals; Canonica and Freiburghaus, 2001). The relevant systems were irradiated under a Philips TL-D 18W BLB lamp, with emission maximum at 368 nm.

The use of CDOM proxies like AQ2S to obtain reaction rate constants is motivated by the fact that it is difficult to obtain precise and widely representative kinetic data when working with natural CDOM samples, also because CDOM chemistry and its variations in different environments is still

incompletely understood (Golanoski et al., 2012). Anyway, an assessment of the reaction rate constants of several xenobiotics with $^3\text{CDOM}^*$ from prairie potholes has been provided by Zeng and Arnold (2013). Atrazine is the only compound for which the reaction rate constants with $^3\text{CDOM}^*$ ($(1.2\pm 0.2)\cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$; Zeng and Arnold, 2013) and with $^3\text{AQ2S}^*$ ($(1.4\pm 0.1)\cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$; Marchetti et al., 2013) are both available, with a remarkably good agreement. Moreover, the choice of AQ2S was motivated by experimental convenience, because this compound reacts almost exclusively *via* its triplet state without producing additional transients (e.g. $\cdot\text{OH}$ or $^1\text{O}_2$), which could interfere with the assessment of $^3\text{AQ2S}^*$ reactivity. The AQ2S photochemistry is also well known (Bedini et al., 2012), which enables the assessment of reaction rate constants with $^3\text{AQ2S}^*$ by using steady irradiation alone. A disadvantage is represented by the fact that $^3\text{AQ2S}^*$ may be more reactive than average $^3\text{CDOM}^*$ (De Laurentiis et al., 2014). The $^3\text{AQ2S}^*$ rate constant data were thus checked by using additional photosensitisers (4-carboxybenzophenone, riboflavin), which required laser flash photolysis experiments (*vide infra*). Also note that there are environmental differences in CDOM chemical composition and, consequently, in the reactivity of $^3\text{CDOM}^*$ itself (De Laurentiis et al., 2012; De Laurentiis et al., 2013; Cawley et al., 2015; Bodhipaksha et al., 2015), which would be an issue for the choice of any CDOM proxy. In this work, these problems were minimised through a comparison between model predictions and field data.

The spectral photon flux densities of the TL 01 and TL-D BLB lamps in the irradiated solutions were determined by combining measurements of lamp spectra (using a calibrated Ocean Optics USB 2000 CCD spectrophotometer, taking into account the transmittance of the Pyrex window of the irradiation cells) with actinometry based on 2-nitrobenzaldehyde (2NBA) (Galbavy et al., 2010). The 2NBA actinometer could not be used with the yellow lamp (TL D 16), in which case the photon flux density was roughly assessed by spectrophotometric data alone. However, this important approximation had no effect on the $^1\text{O}_2$ reactivity determination, which did not make use of spectral photon flux densities and was rather based on the measurement of the $^1\text{O}_2$ production

rate by Rose Bengal (R_{1O_2}), using furfuryl alcohol as a probe (see further details in the Supplementary Material, hereafter SM). The spectral photon flux densities of the lamps are reported in SM, **Figure SM1**, together with the absorption spectra of the used photosensitisers (nitrate, AQ2S, Rose Bengal). The absorption spectra were measured with a Varian Cary 100 Scan double-beam UV-vis spectrophotometer, using Hellma quartz cuvettes (1.000 cm optical path length). The absorption spectra of DIC and NAP are reported in **Figure 1**, while CLO does not absorb radiation above 290 nm. The absorption spectra of DIC and NAP were also measured as a function of pH, in the interval 6.5 - 8.5, adjusted by addition of a phosphate buffer at 10 mM total concentration. These spectra, showing no variation with pH, are reported in SM, **Figures SM2 - SM3**. The direct photolysis of DIC and NAP was studied in the pH interval 6.5 - 8.5, again adjusted with a 10 mM phosphate buffer, upon irradiation under the Philips TL 01 lamp described above.

Solutions to be irradiated (5 mL) were inserted in cylindrical Pyrex glass cells (having a lateral neck for sample transfer, and tightly closed with a screw cap), and placed under the chosen lamp for irradiation under magnetic stirring. The solutions were irradiated mainly from the top. In each series of experiments, the light-absorbing photoactive compound had the same concentration to ensure that possible inner-filter effects (however limited, due to the low solution depth of 0.4 cm) were the same in all the cases. After the scheduled irradiation time, the Pyrex cells were withdrawn from the lamp and the solutions underwent analysis to monitor the time evolution of the substrates. The standard initial concentration of each substrate (NAP, DIC or CLO) was 20 μ M, or less when required by the kinetic determinations. In the experiments aimed at the identification of the transformation intermediates, a larger solution volume (20 mL) at higher substrate concentration (0.5 mM) was irradiated to facilitate the detection/identification procedure.

2.3. Analytical determinations. The time trends of NAP, DIC and CLO were monitored by High Performance Liquid Chromatography with Diode Array Detection (HPLC-DAD). The identification

of the transformation intermediates was carried out by gas chromatography coupled with mass spectrometry (GC-MS), after extraction with dichloromethane and derivatisation with BSTFA (N,O bis(trimethylsilyl)trifluoroacetamide). This derivatisation procedure transforms polar compounds, with hydroxyl and carboxyl groups, into the corresponding trimethylsilyl derivatives thereby making them more amenable to CH₂Cl₂ extraction and GC analysis (Lin et al., 2008). Apolar compounds, which could be formed as well under irradiation, do not react with BSTFA but they are normally extracted by CH₂Cl₂. This approach may offer complementary and additional results compared to the liquid chromatographic techniques used in previous studies to detect the transformation intermediates of DIC, NAP and CLO (Doll and Frimmel, 2003; DellaGreca et al., 2004; Bartels and von Tümpling, 2007; Li et al., 2012; Salgado et al., 2013). Details on instruments and procedures are reported as SM. The mass spectra of the parent compounds and the identified intermediates, together with the proposed structures, are reported as SM.

2.4. Laser flash photolysis experiments. To determine the reactivity of the excited states of 4-carboxybenzophenone (CBP) and riboflavin (RIB), a Nd:YAG laser system instrument (Quanta Ray GCR 130-01) operated at 355 nm (third harmonic) with typical energies of 45 mJ (single pulse of ~9 ns duration) was used. Individual cuvette samples (3 mL volume) were used for only one measurement in order to avoid problems with photodegradation processes. A detailed technical description of the LFP apparatus has been reported elsewhere (Brigante et al., 2010). Stock solutions of photosensitisers (CBP and RIB) and quenchers (CLO, DIC and NAP) were prepared in Milli-Q water, and pH was fixed at 7.0 ± 0.5 by using NaOH. The decay of the CBP and RIB triplet states was monitored at 550 and 640 nm, respectively, to avoid spectral interferences from radical species produced by photosensitisers and/or quenchers upon laser excitation. The pseudo-first order decay constants were obtained by fitting the absorbance vs. time data with a single exponential decay equation. The error was calculated as 3σ from the fit of the experimental data. All the experiments were performed at ambient temperature (293 ± 2 K) in aerated solutions.

2.5. Photochemical modelling. The model assessment of NAP, DIC and CLO photodegradation was carried out with the APEX software (Aqueous Photochemistry of Environmentally-occurring Xenobiotics), available for free as Electronic Supplementary Information of Bodrato and Vione (2014). APEX predicts photochemical reaction kinetics from photoreactivity parameters (absorption spectra, direct photolysis quantum yields and second-order reaction rate constants with transient species) and from data of water chemistry and depth (Bodrato and Vione, 2014; Vione, 2014). APEX predictions have been validated by comparison with field data of pollutant phototransformation kinetics in surface freshwaters (Maddigapu et al., 2011; Marchetti et al., 2013).

The standard solar spectrum used in APEX is referred to fair-weather conditions during summertime at mid latitude (see **Figure 1**) (Frank and Klöpffer, 1988). Sunlight irradiance is not constant in the natural environment due to fluctuations in meteorological conditions (not included in APEX) and of diurnal and seasonal cycles. To allow easier comparison between model results and environmental conditions, APEX uses a summer sunny day (SSD) as time unit, equivalent to fair-weather 15 July at 45° N latitude. An exception is represented by the *APEX_Season* function, which computes monthly trends of photoreaction kinetics and uses as time unit the days of the relevant month. The absorption of radiation by the photosensitisers (CDOM, nitrate and nitrite) and the studied substrates is calculated based on competition for sunlight irradiance in a Lambert-Beer approach (Bodrato and Vione, 2014; Braslavsky, 2007). APEX applies to well-mixed waters and gives average values over the water column, which includes the contributions of the well-illuminated surface layer and of darker water in the lower depths, where irradiance is very low (Loiselle et al., 2008). The uncertainties associated to the modelled parameters are determined by error propagation, using the *APEX_Errors* function. The reported uncertainties on model predictions represent $\pm\sigma$.

APEX also predicts kinetics and yields of intermediates formation. Assume that in each photochemical process p the intermediate i is formed with yield η_i^p , experimentally determined as the ratio between the initial formation rate of i and the initial transformation rate of the parent substrate s (note that i can be formed from s via different photochemical processes with different yields). Denote k_s^p as the pseudo-first order degradation rate constant of s in each process p , as predicted by the model under environmental conditions. Under the same conditions, the overall formation yield of i from s can be calculated as $\eta_i = \sum_p (\eta_i^p k_s^p) \left(\sum_p k_s^p \right)^{-1}$ (Bodrato and Vione, 2014).

3. Results and Discussion

3.1. Substrate photoreactivity

The detailed results of the irradiation experiments are shown in the SM. **Table 1** reports a summary of the photoreactivity data of the investigated substrates. Some data are from the literature, and the missing rate constants were assessed in this study following the experimental procedures reported in the SM. A significant reactivity between the three substrates and $\text{CO}_3^{\bullet-}$ could be excluded because bicarbonate addition to an $\bullet\text{OH}$ -based system (irradiated nitrate) inhibited instead of enhancing the substrate phototransformation (De Laurentiis et al., 2014; also see SM). The direct photolysis quantum yield of CLO has been determined as ~ 0.005 (Andreozzi et al., 2003), but from the measured UV-Vis absorption spectra of CLO we could exclude a significant absorption of sunlight. Therefore, we assume that the CLO direct photolysis is not important in the natural environment. This assumption is consistent with an assessment carried out by Tixier et al. (2003) of the possible attenuation pathways of CLO in surface waters. A check was also made of the direct photolysis

kinetics of DIC and NAP as a function of pH, in the interval 6.5 - 8.5 that encompasses most of the conditions found in surface waters (Polesello et al., 2006). The absorption spectra of DIC and NAP do not vary in the considered pH range (see **SM, Figures SM2-SM3**), and the kinetics of the direct photolysis of both compounds was also independent of pH (see **SM, Figures SM4-SM5**). Therefore, no changes in the direct photolysis behaviour of DIC and NAP are expected at the typical pH values of surface waters.

In the case of NAP and CLO, the second-order reaction rate constants with $^3\text{AQ2S}^*$ were higher than $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and, most notably, higher than the corresponding reaction rate constants with $\bullet\text{OH}$ (**Table 1**). Considering that the $^3\text{CDOM}^*$ states in surface waters (apart from a very few exceptions) are not expected to be more powerful oxidants than $\bullet\text{OH}$ (Zeng and Arnold, 2013), the $^3\text{AQ2S}^*$ reactivity with NAP and CLO is unlikely to be representative of the behaviour of natural CDOM. For this reason, the second-order reaction rate constants of the three studied xenobiotics were also measured in the presence of additional triplet sensitisers such as 4-carboxybenzophenone (CBP) and riboflavin (RIB) (Canonica et al., 2005; Kouras-Hadef et al., 2012), which required laser flash photolysis experiments. The laser excitation of CBP produced two transient peaks centred at 350 and 550 nm, attributed to the triplet state ($^3\text{CBP}^*$; Canonica et al., 2005), as shown in **SM, Figure SM10**. The CBP^* signal disappeared after 10 μs following a pseudo-first order decay with rate constant $k' = (5.28 \pm 0.06) \cdot 10^5 \text{ s}^{-1}$. The laser excitation of RIB yielded two main transient peaks at $\sim 300 \text{ nm}$ and $\sim 640 \text{ nm}$ (see **SM, Figure SM10**). The absorption band at 300 nm has been previously attributed to the presence of the RIB triplet state ($^3\text{RIB}^*$) and of a radical (RIB^\bullet), which has an absorption maximum around 337 nm (Land and Swallow, 1969). The transient signal at 640 nm, where only the triplet state absorbs radiation, decayed with a pseudo-first order rate constant of $(3.40 \pm 0.05) \cdot 10^5 \text{ s}^{-1}$. To avoid the occurrence of known spectral interferences and to minimise the likelihood of additional interferences (less likely as wavelength increases), the decay of $^3\text{CBP}^*$ and $^3\text{RIB}^*$ in the presence of DIC, NAP and CLO was monitored at 550 and 640 nm, respectively. In a

Stern-Volmer approach, the pseudo-first order decay constants of $^3\text{CBP}^*$ and $^3\text{RIB}^*$ were plotted as a function of the substrates (DIC, NAP, CLO) concentration, and the corresponding second-order reaction rate constants were obtained as the slopes of the resulting lines. The Stern-Volmer plots are reported in **Figure 2**, and the second-order reaction rate constants are shown in **Table 1**. The reaction rate constant between DIC and $^3\text{CBP}^*$ was comparable to that of $^3\text{AQ2S}^*$, and the reaction rate constants with $^3\text{RIB}^*$ were always higher than those with $^3\text{CBP}^*$. The degree by which these values are representative of the $^3\text{CDOM}^*$ reactivity was assessed by considering attenuation data obtained in the field.

3.2. Comparison between model predictions and field data

A field assessment of the attenuation kinetics of NAP, DIC and CLO is available for the epilimnion of Lake Greifensee (Switzerland) in late summer (Tixier et al., 2003). Possible photoinduced processes have been considered in the cited study, together with other removal pathways that include sorption, transport and volatilisation. Therefore, it is one of the very few cases where phototransformation of NAP, DIC and CLO could be singled out from the field data. To compare field results with APEX predictions, we used Greifensee water chemistry data (0.1 mM nitrate, 3.5 mg C L⁻¹ DOC, 2 mM bicarbonate, 10 µM carbonate), a water column depth of 5 m that is representative of the lake epilimnion (Canonica et al., 2005), and we corrected the model results for typical mid-latitude irradiance conditions that are ~1.5 times lower compared to those of constant fair weather (Frank and Klöpffer, 1988). The reactivity between the studied substrates and $^3\text{CDOM}^*$ was assessed by considering AQ2S, CBP and RIB as proxy sensitiser, with the second-order reaction rate constants for triplet sensitisation reported in **Table 1**.

In the case of DIC phototransformation, Tixier et al. (2003) reported $k_{DIC}^{photo} = (8.3 \pm 1.2) \cdot 10^{-2} \text{ day}^{-1}$. APEX modelling gave the following results: with $k_{DIC,^3CDOM^*} = k_{DIC,^3AQ2S^*}$, $k_{DIC} = (9.0 \pm 0.9) \cdot 10^{-2} \text{ day}^{-1}$; with $k_{DIC,^3CDOM^*} = k_{DIC,^3CBP^*}$, $k_{DIC} = (8.9 \pm 1.0) \cdot 10^{-2} \text{ day}^{-1}$; with $k_{DIC,^3CDOM^*} = k_{DIC,^3RIB^*}$, $k_{DIC} = (9.8 \pm 1.2) \cdot 10^{-2} \text{ day}^{-1}$. In all the cases there was a good or very good agreement between model predictions and field data (all the uncertainty intervals already overlapped at the $1-\sigma$ level), most likely because over 85% of the modelled DIC phototransformation was accounted for by direct photolysis. The direct phototransformation may allow for more accurate modelling compared to indirect photochemistry, which is subject to uncertainties connected with the behaviour of irradiated CDOM that is a major direct or indirect source of reactive transient species (Vione et al., 2014). Based on these results, the value of $k_{DIC,^3CDOM^*} = (1.0 \pm 0.3) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ assumed hereafter was the average of $k_{DIC,^3AQ2S^*}$, $k_{DIC,^3CBP^*}$ and $k_{DIC,^3RIB^*}$.

The measured field attenuation rate constant of CLO was not higher than 0.01 day^{-1} (Tixier et al., 2003). Here it is assumed that it is totally accounted for by photochemical processes. APEX modelling returned the following: with $k_{CLO,^3CDOM^*} = k_{CLO,^3AQ2S^*}$, $k_{CLO} = 0.10 \pm 0.03 \text{ day}^{-1}$; with $k_{CLO,^3CDOM^*} = k_{CLO,^3CBP^*}$, $k_{CLO} = 0.0087 \pm 0.0029 \text{ day}^{-1}$; with $k_{CLO,^3CDOM^*} = k_{CLO,^3RIB^*}$, $k_{CLO} = 0.049 \pm 0.015 \text{ day}^{-1}$. The field results are compatible with $k_{CLO,^3CDOM^*} = k_{CLO,^3CBP^*} = (4.7 \pm 0.6) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$, which will be assumed hereafter as the reaction rate constant between CLO and $^3\text{CDOM}^*$.

In the case of NAP, the part of the field attenuation rate constant that could not be accounted for by phase partitioning or transport processes was equal to $k_{NAP} \sim 0.05 \text{ day}^{-1}$ (Tixier et al., 2003). A major issue with NAP photochemistry is the direct photolysis quantum yield Φ_{NAP} , for which there is wide variation in the literature data (see **Table 1**). A model assessment of k_{NAP} under Greifensee

water conditions as a function of a variable Φ_{NAP} was carried out by considering the absorption spectrum of NAP, the reaction rate constants with $\cdot\text{OH}$ and $^1\text{O}_2$, and the measured reaction rate constants with $^3\text{AQ2S}^*$, $^3\text{CBP}^*$ or $^3\text{RIB}^*$. The results are reported in **SM - Figure SM11**. It is suggested that the field data cannot be reproduced with $k_{NAP,^3CDOM^*} = k_{NAP,^3AQ2S^*}$ at any Φ_{NAP} . In contrast, by using either $k_{NAP,^3CDOM^*} = k_{NAP,^3CBP^*}$ or $k_{NAP,^3CDOM^*} = k_{NAP,^3RIB^*}$, one gets that the field data can be reproduced with $\Phi_{NAP} \sim 0.005$, which is about half of the lower end of the literature values (Packer et al., 2003; Pereira et al., 2007; Marotta et al., 2013). Marotta et al. (2013) have recently reported that the photolysis of NAP in aerated solution partially takes place by self-photosensitisation, which is not likely to occur at the low concentration values typical of the natural environment. This observation justifies the use of a low value of Φ_{NAP} , but the lowest one that can be found in the literature is $\Phi_{NAP} = 0.01$ (Marotta et al., 2013). While a difference by a factor 2 can be deemed acceptable when comparing model predictions with field data, it is possible that the disagreement is partially due to the fact that Marotta et al. (2013) used UVC irradiation. Moreover, one cannot exclude that the NAP photolysis quantum yield is affected by environmental conditions such as the content of DOC in the lake water. A decrease of the direct photolysis quantum yield in the presence of non-absorbing organic compounds, possibly connected with the triplet-state reactivity of the substrate, has already been reported for the herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) (Vione et al., 2010). Furthermore, antioxidant moieties occurring in DOM have been reported to favour the reduction of partially oxidised compounds back to the parent molecule (Wenk and Canonica, 2012). If the direct photolysis of NAP occurs at least partially by photoionisation, this could be an additional process by which DOM could decrease Φ_{NAP} . Hereafter, we will assume that Φ_{NAP} is included in the range of 0.005-0.01, and we will take $k_{NAP,^3CDOM^*} = (1.0 \pm 0.2) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ as the average of $k_{NAP,^3CBP^*}$ and $k_{NAP,^3RIB^*}$.

3.3. Modelling the photoreactivity of DIC, NAP and CLO in surface waters

The photoreactivity data reported in **Table 1** (direct photolysis quantum yields and reaction rate constants with $\bullet\text{OH}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$) were used as input for APEX modelling. In the case of NAP direct photolysis, two different scenarios ($\Phi_{\text{NAP}} = 0.01$ and 0.005) were considered based on the previous comparison with field data. **Figure 3** shows the APEX-modelled half-life times of DIC (**3a**), CLO (**3b**) and NAP (**3c,d**) as a function of the water depth d and the dissolved organic carbon (DOC), using $\Phi_{\text{NAP}} = 0.01$ (**3c**) and $\Phi_{\text{NAP}} = 0.005$ (**3d**) as per the above discussion. Larger differences in the NAP half-life times in the two scenarios are expected at low DOC, where the contributions of photochemical processes other than the direct photolysis are more limited than at high DOC (*vide infra*).

Figure 3 shows that NAP and DIC are expected to be more photolabile than CLO, and that the modelled half-life times increase with increasing depth and DOC. The rationale for the increase with depth is that the bottom layers of deep water bodies are poorly illuminated by sunlight, which limits the rates of photochemical reactions. Because APEX calculates average values for a water column of given depth, the importance of the poorly photoactive deep water increases with increasing depth and leads to longer half-life times. The trend with DOC is accounted for by the fact that waters rich in organic matter have also elevated CDOM, which competes with xenobiotics for sunlight irradiance and inhibits their direct photolysis. Moreover, high DOM levels cause important $\bullet\text{OH}$ scavenging, which is insufficiently compensated for by the increased importance of $^3\text{CDOM}^*$ or by the $\bullet\text{OH}$ production from irradiated CDOM. The reason for this behaviour is that, differently from $\bullet\text{OH}$ scavenging by DOM, CDOM photochemistry is affected by absorption saturation (Minella et al., 2013). The modelled steady-state concentrations of $\bullet\text{OH}$ and $^3\text{CDOM}^*$ are reported in **SM**, **Figure SM12**, as a function of water depth and DOC. Both $[\bullet\text{OH}]$ and $[^3\text{CDOM}^*]$ decreased

with increasing depth, due to poor irradiation of the bottom layers of deep water bodies, while an increase of the DOC caused [$\bullet\text{OH}$] to decrease and [${}^3\text{CDOM}^*$] to increase. The modelled $\bullet\text{OH}$ levels around or below 10^{-16} M and the ${}^3\text{CDOM}^*$ levels around 10^{-15} M are typical of surface-water conditions (Zeng and Arnold, 2013; Page et al., 2014).

Interestingly, the predicted photochemical half-life times of DIC are quite comparable to those reported for two south-Sweden lakes (Boren and Norra Bergundasjön), which ranged between a week and a month in late spring (Zou et al., 2015a,b). A more precise comparison is unfortunately not possible because Zou and co-workers reported the average water depth for the two lakes, but not key water chemistry parameters such as the DOC.

APEX assesses the overall transformation of a compound by first considering each photochemical pathway separately and by then summing up the results. The availability of these data makes it easy to compute the relative role of each single pathway in the whole phototransformation process (Bodrato and Vione, 2014). **Figure 4** reports the modelled percentages of DIC (**4a**), CLO (**4b**) and NAP (**4c,d**) phototransformation accounted for by the different photochemical processes, as a function of the DOC. The NAP data are referred to $\Phi_{\text{NAP}} = 0.01$ (**4c**) and $\Phi_{\text{NAP}} = 0.005$ (**4d**). It is noticeable that the direct photolysis plays a very important role in the photochemical attenuation of DIC and NAP. In the case of NAP, the assumed value of Φ_{NAP} had a reasonably limited impact on the percentage of the substrate that undergoes direct photolysis. As to the other processes, the relative importance of ${}^3\text{CDOM}^*$ increases and that of $\bullet\text{OH}$ decreases with increasing DOC. Increasing DOC inhibits the $\bullet\text{OH}$ process to a higher extent than the direct photolysis, which accounts for the maximum in the direct photolysis percentages of DIC and NAP at $\text{DOC} = 0.5\text{-}1.5$ mg C L^{-1} . The $\bullet\text{OH}$ and ${}^3\text{CDOM}^*$ processes predominate in the case of CLO, for which the DOC is

the key parameter that defines the prevalent photodegradation pathway. Finally, reaction with $^1\text{O}_2$ is expected to be minor in all the cases.

The model results reported so far are referred to summertime irradiation. **Figure 5** shows the predicted seasonal trend of the first-order photodegradation rate constants of NAP, DIC and CLO in Greifensee-like environmental conditions. In the case of NAP, both $\Phi_{\text{NAP}} = 0.01$ and $\Phi_{\text{NAP}} = 0.005$ scenarios are reported. The right Y-axis scale also reports some half-life times ($t_{1/2}$), which correspond to the given rate constant (k) values according to the relationship: $t_{1/2} = \ln 2 k^{-1}$. It is confirmed that CLO, with half-life times higher than 50 days in any season, is considerably more photostable than the other two compounds. The half-life time of NAP understandably depends on the chosen value of the photolysis quantum yield, but a roughly comparable photolability is anyway predicted for DIC and NAP. The half-lives of NAP and DIC could be as short as 1-2 weeks during summertime but considerably longer in different seasons, and DIC showed a slightly more pronounced seasonal variation than NAP. The rationale is that DIC absorbs sunlight only in the UVB region, the irradiance of which has a considerable winter deficit compared to summertime (Frank and Klöpffer, 1988), while NAP also absorbs in the UVA.

3.4. Transformation intermediates

The detection and identification of the transformation intermediates produced by the main surface-water photoreaction pathways ($\bullet\text{OH}$, triplet sensitisation and, where relevant, direct photolysis) was carried out by dichloromethane extraction, BSTFA derivatisation and GC-MS analysis. The identified compounds are listed in **Table 2**, and their mass spectra are reported as SM. Intermediate **I** was formed upon NAP direct photolysis (the main phototransformation pathway of NAP in surface waters, see section 3.3), most likely via ring opening and fragmentation. DellaGreca et al. (2004) have irradiated NAP under simulated sunlight, and they detected intermediates arising from

the transformation of the lateral chain bearing the carboxylic function. Such a difference is probably due to the fact that the used detection techniques (MALDI-TOF for DellaGreca et al. vs. GC-EI-MS in the present work) differ for sensitivity, for the ability to detect volatile vs. non-volatile compounds, as well as for the ionisation mechanism. The intermediates detected by DellaGreca et al. (2004) were often more toxic than the parent NAP (Isidori et al, 2005). In contrast, **I** is not expected to exhibit a much different ecotoxicological behaviour than NAP and, being more polar, it could even be less toxic (Mayo-Bean et al., 2012).

DIC was found to produce **II** and **III** by direct photolysis (the main photoreaction pathway in environmental conditions), plus **IV** by triplet sensitisation (experimentally achieved by irradiation in the presence of AQ2S). The production of **II** requires a cyclisation process, likely involving the carboxylic lateral chain of DIC and the amino group. The compound **III** might derive from **II** by elimination of HCl. The amido group present in both **II** and **III** could make these compounds more acutely and chronically toxic than the parent DIC, toward several freshwater organisms (fish, algae and daphnid) (Mayo-Bean et al., 2012). Bartels and von Tümpling (2007) have also identified **II** as a major intermediate arising from the sunlight-induced photodegradation of DIC. Salgado et al. (2013) have studied the intermediates arising from DIC UVC irradiation. They, too, have identified compounds produced by a cyclisation process (HCl elimination between the two aromatic rings), while some structural dissimilarities with the present work might be motivated by the different irradiation wavelengths. For instance, Salgado et al. (2013) did not detect cyclic amido compounds, but they found some of their potential precursors. As an aromatic amine, the formation of **IV** (2,6-dichloroaniline) by triplet-sensitised degradation of DIC might raise some concern, although **IV** is not classified among potentially carcinogenic molecules (Acros, 2016). Both DIC and **IV** have relatively low toxicity towards mammals (the LD50 values for mice and rats are in the ranges of hundreds and tens mg/kg, respectively). Also the toxicity to bacteria, algae and daphnid, although higher in the case of **IV** (the relevant EC50 values of **IV** are in the (sub)mg L⁻¹ range, compared to

tens-hundreds mg L⁻¹ for DIC; Santos et al., 2010; Acros, 2016), is of limited concern for aquatic environments. Acute toxicity to fish, higher for **IV** compared to DIC, is also of limited environmental concern (the respective LD50 values are of some mg L⁻¹ and over one hundred mg L⁻¹; Acros, 2016; Praskova et al., 2011). However, DIC is also known to cause chronic effects to fish at µg L⁻¹ levels (Santos et al., 2010), thus the transformation of DIC into **IV** might even be beneficial to the aquatic environments.

We have detected 4-chlorophenol (**V**) and hydroquinone (**VI**) as CLO phototransformation intermediates, by [•]OH reaction (**V**) and triplet sensitisation (**V** + **VI**). The formation of **V** follows cleavage of the lateral chain, while **VI** also requires a hydrolytic dehalogenation. Both compounds have been detected as CLO intermediates upon phototransformation and advanced oxidation (Doll and Frimmel, 2003; Li et al., 2012), and **V** is also a microbial metabolite of CLO (Kosjek et al., 2009). CLO, **V** and **VI** are moderately and comparably toxic for mammals (for all compounds, LD50 values for mice and rats are of the order of some hundreds mg/kg), but **V** is also classified as possibly carcinogenic for humans (Acros, 2016). The acute toxicity of these compounds towards aquatic organisms is of limited concern (the EC50 of **V** towards *Daphnia magna* is 6 mg L⁻¹, while that of CLO is over 100 mg L⁻¹; Han et al., 2006; Merck-Millipore, 2016), but **VI** shows chronic toxicity to daphnid and algae in aquatic environments at levels above a few µg L⁻¹ (Eastman, 2016). For comparison, CLO requires levels > 40 mg L⁻¹ to show chronic toxicity to daphnid (Han et al., 2006). The transformation of CLO into **VI** could thus be harmful to aquatic organisms, while the transformation into **V** has human health concerns due to possible carcinogenicity.

The formation of **V** and **VI** from CLO, upon triplet sensitisation and [•]OH reaction, was quantitatively assessed using HPLC-DAD (see **SM**, **Figures SM13**, **SM14** and the relevant description). In agreement with the GC-MS results, no **VI** was detected from CLO + [•]OH while **V**

was quantified in both cases. The yield of **VI** upon triplet sensitisation of CLO was rather low (~5%), but it can be compensated for by the fact that **VI** shows much higher chronic toxicity than CLO towards aquatic organisms. In contrast, **V** is a key intermediate of CLO phototransformation: its yield ranged from ~10% for the $\bullet\text{OH}$ reaction to ~50% for the triplet-sensitised process. With these data, it is possible to model the overall formation yield of **V** from CLO (η_V^{CLO}) under varying environmental conditions, as shown in **Figure 6** as a function of depth and DOC. Coherently with the important role of triplet sensitisation in the formation of **V**, the modelled η_V^{CLO} was relatively low (~10%) at low DOC and quite high (~40%) at high DOC.

3.5. Challenges associated with photochemical modelling

This paper shows that modelling is suitable to predict the photochemical fate of xenobiotics in sunlit surface waters, but key difficulties still persist that are prevalently associated with a correct choice of the input data rather than with the model calculations. The following challenges can be highlighted in photochemical modelling:

(i) Determination of the second-order reaction rate constants with $^3\text{CDOM}^*$. When using model sensitiser, it should be considered that several of them may be more reactive than average CDOM. This work suggests that 4-carboxybenzophenone (CBP) can give reasonable results, but the measurement of the second-order reaction rate constants between $^3\text{CBP}^*$ and xenobiotics requires the use of the laser flash photolysis technique. Clearly, a steady-state irradiation method to determine the $^3\text{CBP}^*$ reaction kinetics needs to be developed to overcome this limitation. When using anthraquinone-2-sulphonate (AQ2S) as model triplet sensitiser, which allows steady-state irradiation to be employed, one will sometimes obtain only an upper limit for the $^3\text{CDOM}^*$ reaction rate constant. The reaction rate constants with $^3\text{AQ2S}^*$ should be dealt with particular care if they are too close to the diffusion-control limit ($10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$) and/or if they are higher than the $\bullet\text{OH}$

reaction rate constants. In such cases, allowance should be made for the $^3\text{CDOM}^*$ rate constants to be at least one order of magnitude lower than the $^3\text{AQ2S}^*$ ones. This allowance would likely be needed anyway to take into account the variable photoreactivity of $^3\text{CDOM}^*$ in different environments, as well as the possible inhibition of $^3\text{CDOM}^*$ -induced transformation by antioxidants occurring in DOM.

(ii) Dependence of the direct photolysis quantum yields on environmental conditions. For different reasons (scavenging of excited states, antioxidant activity), the natural DOM operates an intrinsic inhibition effect on the direct photolysis process, which adds to the competition for irradiance carried out by CDOM. Therefore, the direct photolysis quantum yields determined in ultra-pure water in the laboratory may not be representative of those found in all environmental conditions.

(iii) Field data against which to validate the model. As shown in this paper, field data of photoattenuation kinetics can be very useful to check the model predictions and, even more critically, to validate the input data. Unfortunately most studies only report point concentrations of pollutants and other works, while computing the environmental persistence, do not distinguish between photochemistry and other processes. Therefore, it is quite common not to find adequate field data in the literature. In this work, we were lucky to find a suitable field study published in 2003. Unfortunately, more recent studies did not provide equally useful pieces of information for our purposes.

One might think that some of the above difficulties could be circumvented by irradiation of xenobiotics in natural water samples. In this case, however, in addition to solving problems in the choice of representative sample(s), one should determine direct photolysis quantum yields and second-order reaction rate constants by irradiation of a sample where all the processes are operational at the same time. One possibility is to add selective scavengers to block some photochemical pathways and allow the study of one process at a time, but it is far from certain that scavengers which are selective enough do really exist. It has been shown for instance that popular $\bullet\text{OH}$ and $^1\text{O}_2$ scavengers are also able to inhibit some triplet-sensitised processes (Maddigapu et al.,

2010), which would introduce a considerable measurement bias with a natural water sample under irradiation.

4. Conclusions

- On the basis of photoreactivity parameters and photochemical modelling, the light-induced degradation of DIC in Lake Greifensee was very successfully predicted. DIC would mainly undergo phototransformation by direct photolysis, while $^3\text{CDOM}^*$ and $\cdot\text{OH}$ would play a secondary role.
- The comparison between model predictions and Greifensee field results suggests that the direct photolysis quantum yield of NAP (Φ_{NAP}) would approach or even fall below the lower end of the literature data. Under surface-water conditions, reasonable Φ_{NAP} values are around 0.005-0.01.
- It is predicted that CLO is considerably more photostable compared to NAP and DIC. The latter two compounds would mainly be degraded by direct photolysis, with very similar lifetimes. The direct photolysis would not be operational for CLO, which would be degraded mainly by $\cdot\text{OH}$ and $^3\text{CDOM}^*$. 4-Carboxybenzophenone was the most suitable CDOM proxy to assess the reactivity of CLO with $^3\text{CDOM}^*$.
- The reactions of DIC, NAP and CLO with $\text{CO}_3^{\cdot-}$ or $^1\text{O}_2$ would not be important degradation pathways in environmental waters.
- Among the detected phototransformation intermediates, due to the potential or known toxicity for aquatic organisms or possible carcinogenicity, concern may be raised by the formation of (i) 4-chlorophenol and hydroquinone from CLO, especially in CDOM-rich waters, and (ii) 2,6-dichloroaniline and cyclic amides from DIC.

- The main challenges connected to photochemical modelling are the assessment of the reaction rate constants between xenobiotics and ³CDOM*, the possible variations of the direct photolysis quantum yields as a function of environmental conditions, and the scarce availability of suitable field data against which to check the model predictions.

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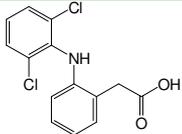
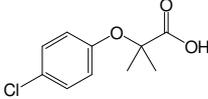
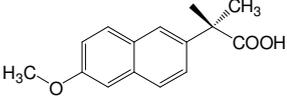
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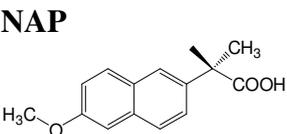
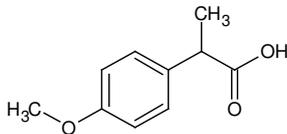
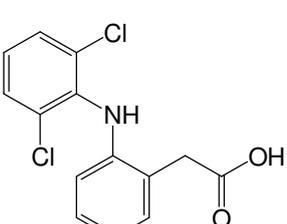
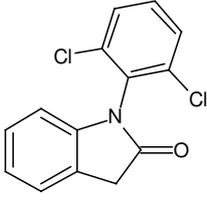
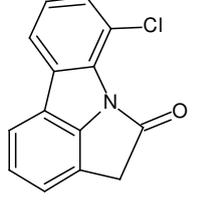
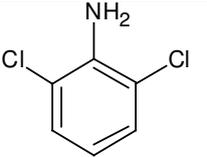
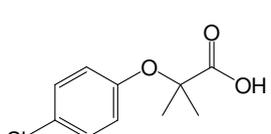
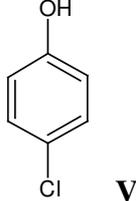
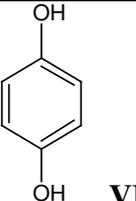
Table 1. Photochemical reactivity parameters of S = DIC, CLO or NAP, obtained either from the literature or experimentally in this work. Model photosensitisers: AQ2S = anthraquinone-2-sulphonate; CBP = 4-carboxybenzophenone; RIB = riboflavin. The reported values of $k_{S,^3CDOM^*}$ are those assumed in this work on the basis of the results obtained with the model photosensitisers, after comparison with field data. In the case of DIC, $k_{DIC,^3CDOM^*}$ was the average of $k_{DIC,^3CBP^*}$, $k_{DIC,^3RIB^*}$ and $k_{DIC,^3AQ2S^*}$; in the case of CLO, it was assumed $k_{CLO,^3CDOM^*} = k_{CLO,^3CBP^*}$; finally, $k_{NAP,^3CDOM^*}$ was the average of $k_{NAP,^3CBP^*}$ and $k_{NAP,^3RIB^*}$.

	Diclofenac (DIC)	Clofibric acid (CLO)	Naproxen (NAP)
			
$\Phi_{S,Phot}$ (unitless)	$9.4 \cdot 10^{-2}$	$5.5 \cdot 10^{-3}$	$(1-3.6) \cdot 10^{-2}$
Ref.	1	6	1-3
$k_{S,^3OH}$ ($M^{-1} s^{-1}$)	$(9.3 \pm 0.1) \cdot 10^9$	$7 \cdot 10^9$	$8 \cdot 10^9$
Ref.	5	7	4
$k_{S,^1O_2}$ ($M^{-1} s^{-1}$)	$(1.3 \pm 0.2) \cdot 10^7$	$(6.0 \pm 1.9) \cdot 10^5$	$(1.1 \pm 0.1) \cdot 10^5$
Ref.	This work	This work	1
$k_{S,^3AQ2S^*}$ ($M^{-1} s^{-1}$)	$(7.6 \pm 0.2) \cdot 10^8$	$(1.2 \pm 0.1) \cdot 10^{10}$	$(3.2 \pm 0.1) \cdot 10^{10}$
Ref.	This work	This work	This work
$k_{S,^3CBP^*}$ ($M^{-1} s^{-1}$)	$(6.4 \pm 1.6) \cdot 10^8$	$(4.7 \pm 0.6) \cdot 10^8$	$(7.5 \pm 1.2) \cdot 10^8$
Ref.	This work	This work	This work
$k_{S,^3RIB^*}$ ($M^{-1} s^{-1}$)	$(1.7 \pm 0.1) \cdot 10^9$	$(5.5 \pm 1.0) \cdot 10^9$	$(1.3 \pm 0.2) \cdot 10^9$
Ref.	This work	This work	This work
$k_{S,^3CDOM^*}$ ($M^{-1} s^{-1}$)	$(1.0 \pm 0.3) \cdot 10^9$	$(4.7 \pm 0.6) \cdot 10^8$	$(1.0 \pm 0.2) \cdot 10^9$
Ref.	This work	This work	This work

Legend for the references (Ref.)

1. Packer et al. (2003)
2. Pereira et al. (2007)
3. Marotta et al. (2013)
4. Ben Abdelmelek et al. (2011)
5. Yu et al. (2013)
6. Andreozzi et al. (2003)
7. Razavi et al. (2009)

Table 2. Proposed structures for the detected transformation intermediates of the studied compounds. The GC retention time (t_R) and the Kovats retention index (I_K , within square brackets) of each intermediate are also reported, together with the relevant photochemical process(es) involved in formation. By comparison, it was $I_K = 1600.7$, 1800.9 and 1001.0 for NAP, DIC and CLO, respectively.

Parent compound	Process (conditions)	Intermediate structure/identifier	t_R , min [I_K , unitless]
NAP 	Direct photolysis	 I	11.55 [1201.2]
DIC 	Direct photolysis	 II	14.44 [1601.7]
	Direct photolysis	 III	13.31 [1401.8]
	Triplet sensitisation (AQ2S+hv)	 IV	7.33 [600.7]
CLO 	$\cdot\text{OH}$ ($\text{H}_2\text{O}_2+\text{h}\nu$) & triplet sensitisation (AQ2S+hv)	 V	7.22 [600.4]
	Triplet sensitisation (AQ2S+hv)	 VI	8.69 [800.5]

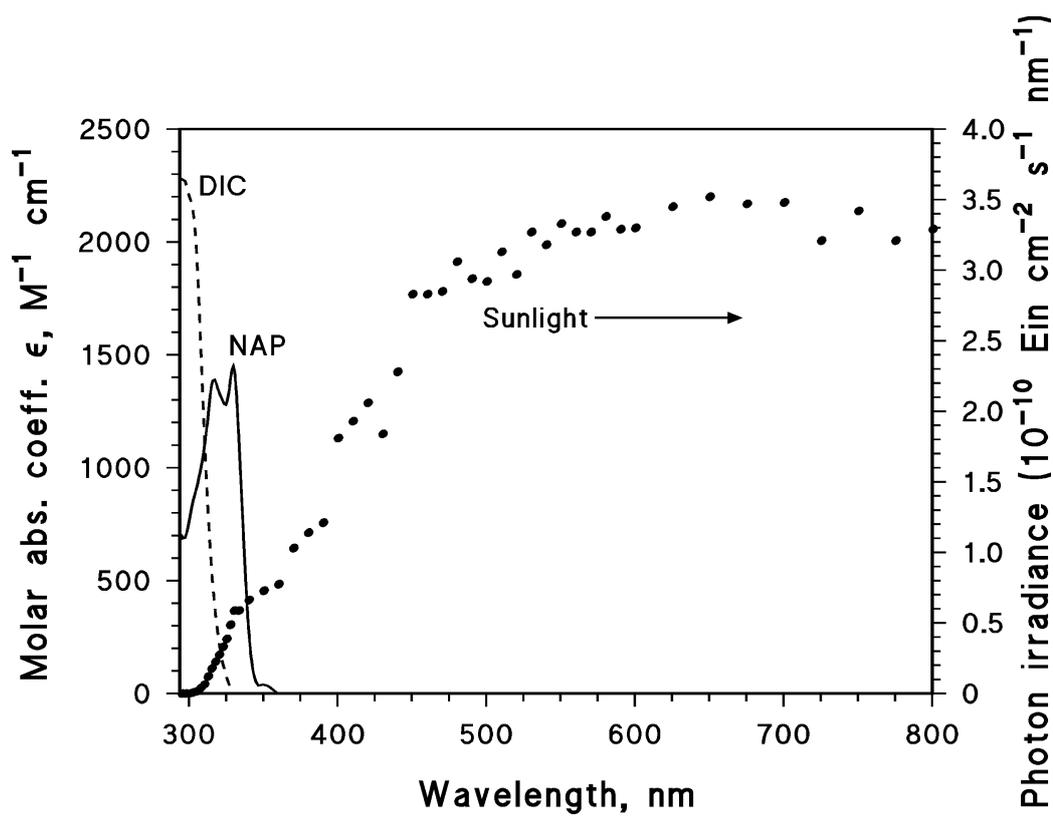


Figure 1. Absorption spectra (molar absorption coefficients) of DIC and NAP. Sunlight spectrum at the ground (spectral photon flux density; Frank and Klöppfer, 1988), used as input for photochemical modelling.

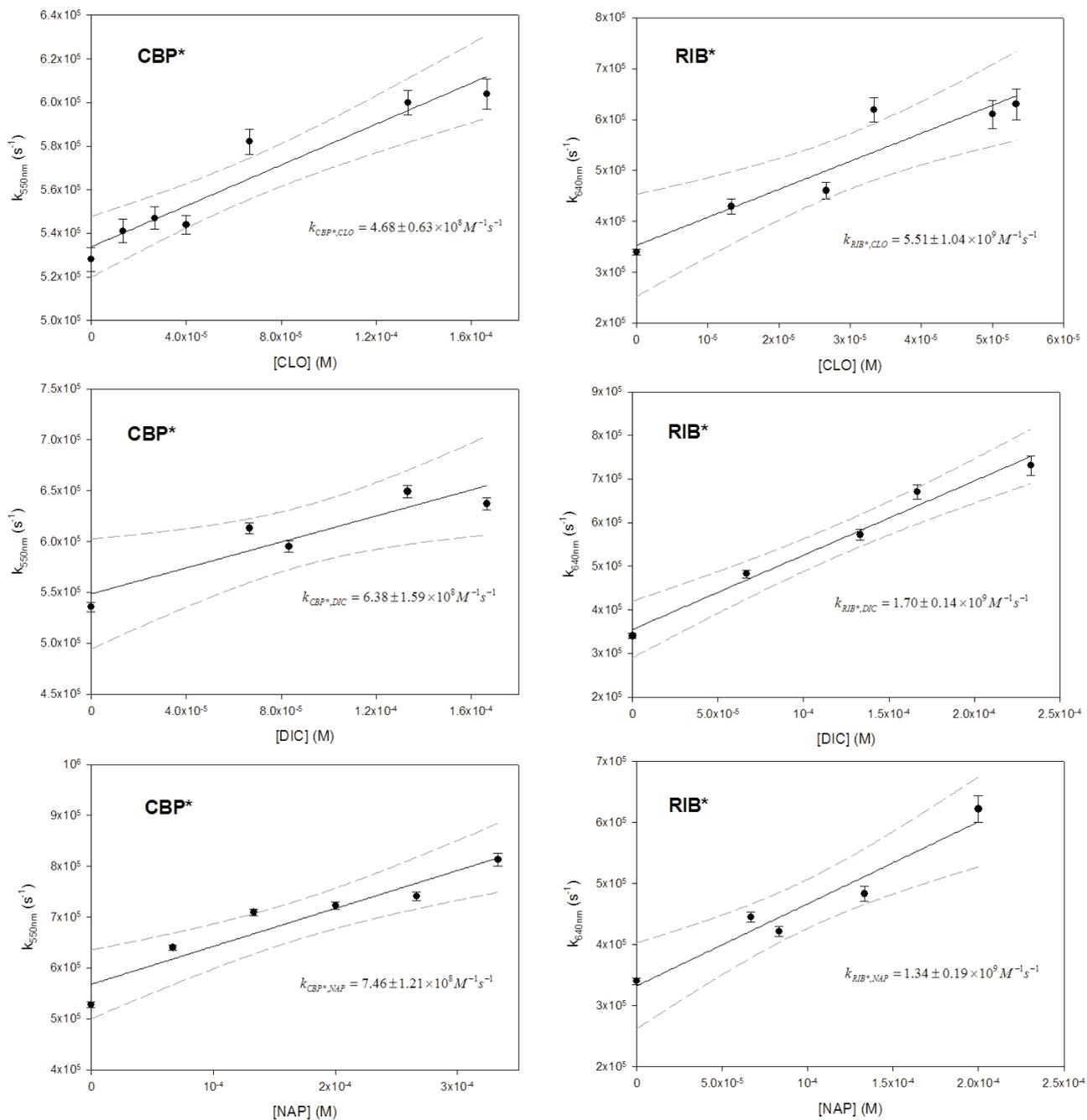


Figure 2. Stern-Volmer plots of the first-order decay constants of the triplet state of 4-carboxybenzophenone (CBP*), detected at 550 nm (left column plots), and of the triplet state of riboflavin (RIB*), detected at 640 nm (right column plots), as a function of the concentrations values of CLO, DIC and NAP. Laser irradiation at 355 nm, 45 mJ pulse⁻¹.

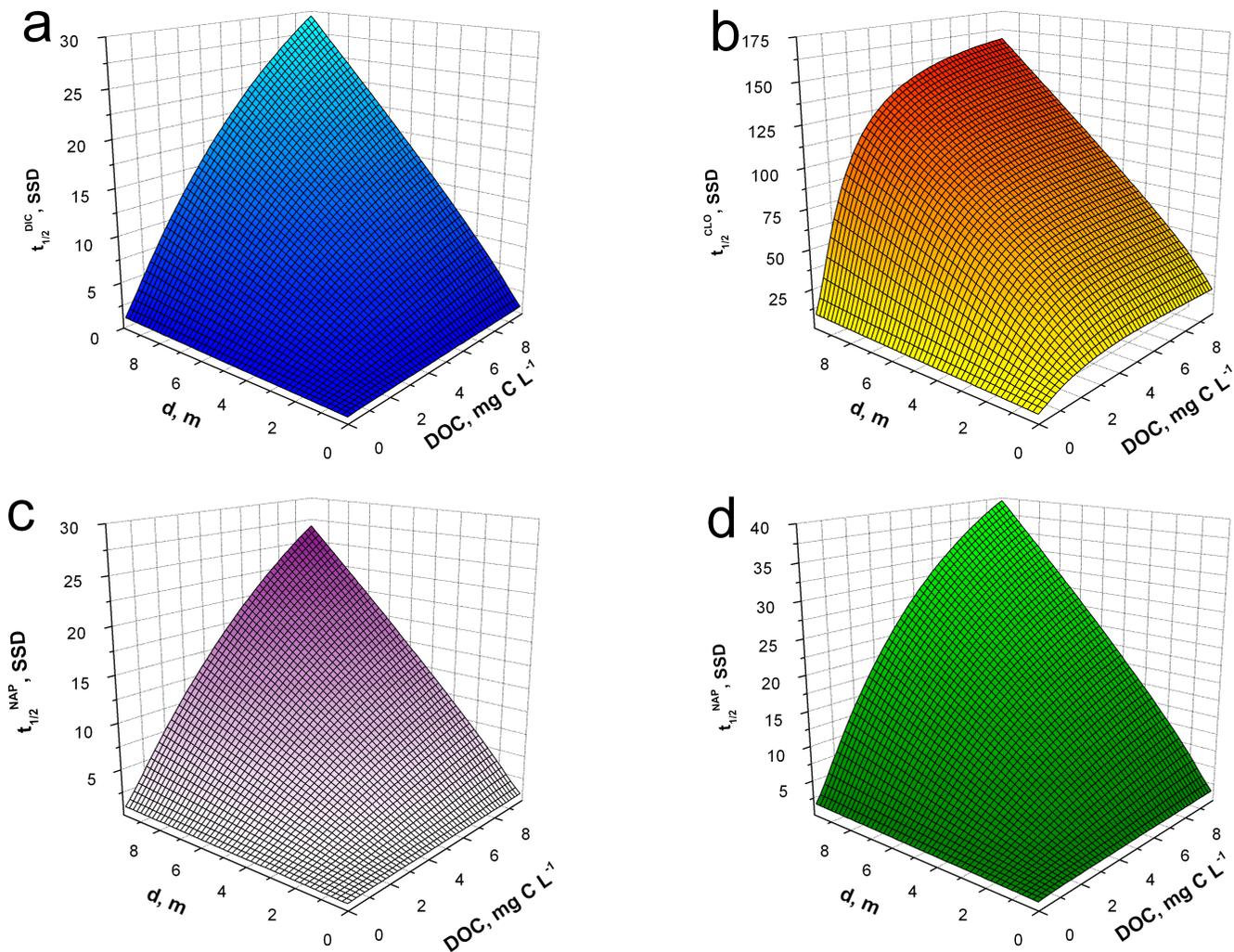


Figure 3. Modelled half-life times of DIC (**a**), CLO (**b**) and NAP (**c**: $\Phi_{\text{NAP}} = 0.01$; **d**: $\Phi_{\text{NAP}} = 0.005$) as a function of water depth (d) and dissolved organic carbon (DOC), under summertime fair-weather irradiation. Other water parameters: 0.1 mM nitrate, 2 mM bicarbonate, 10 μM carbonate. Summertime irradiation conditions at mid-latitude were used for modelling.

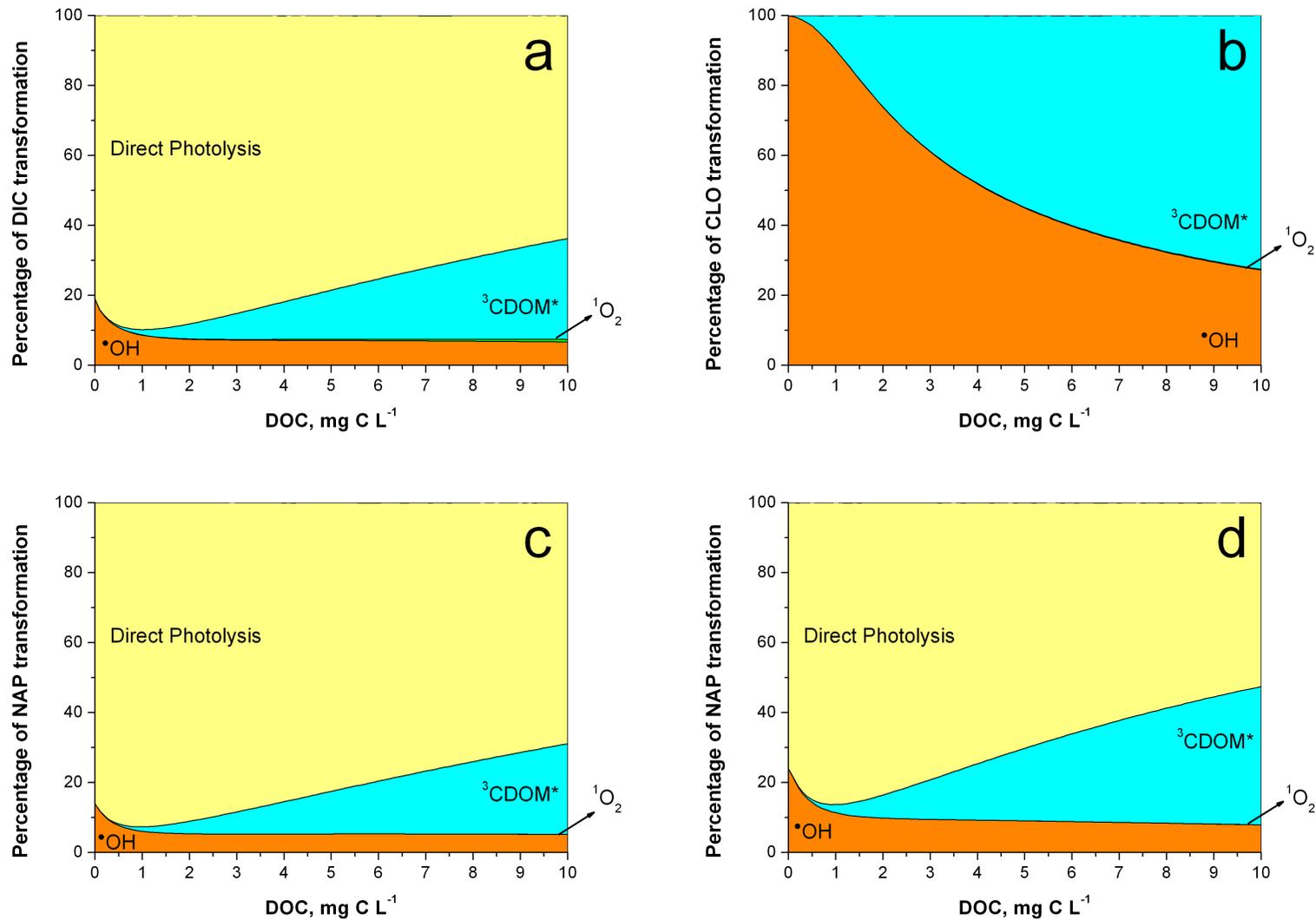


Figure 4. Modelled percentage of substrate phototransformation (a: DIC; b: CLO; c: NAP with $\Phi_{\text{NAP}} = 0.01$; d: NAP with $\Phi_{\text{NAP}} = 0.005$) accounted for by the different photochemical pathways, as a function of the DOC. Other water parameters: 5 m depth, 0.1 mM nitrate, 2 mM bicarbonate, 10 μM carbonate. Summertime irradiation conditions at mid-latitude and with fair weather were used for modelling.

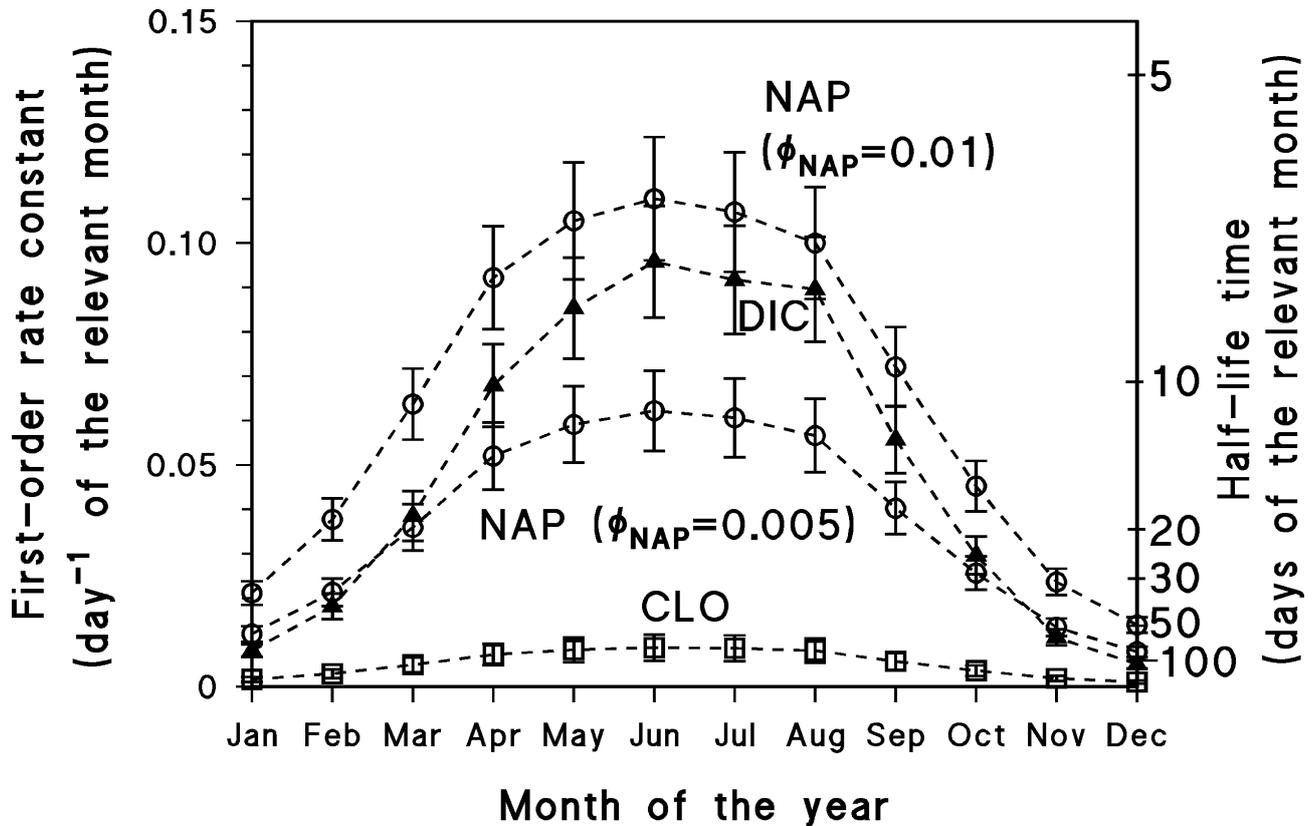


Figure 5. Seasonal variations of the modelled first-order rate constants (left Y-axis) and of the corresponding half-life times (right Y-axis) of NAP, DIC and CLO, for mid-latitude and fair-weather conditions. In the case of NAP, the two scenarios with $\Phi_{\text{NAP}} = 0.01$ and $\Phi_{\text{NAP}} = 0.005$ are reported. Water parameters: 3.5 mg C L⁻¹ DOC, 5 m depth, 0.1 mM nitrate, 2 mM bicarbonate and 10 μ M carbonate. The first-order rate constants were predicted by using the *Apex_season* function, the associated error bounds ($\pm\sigma$) were obtained with the *Apex_error* function.

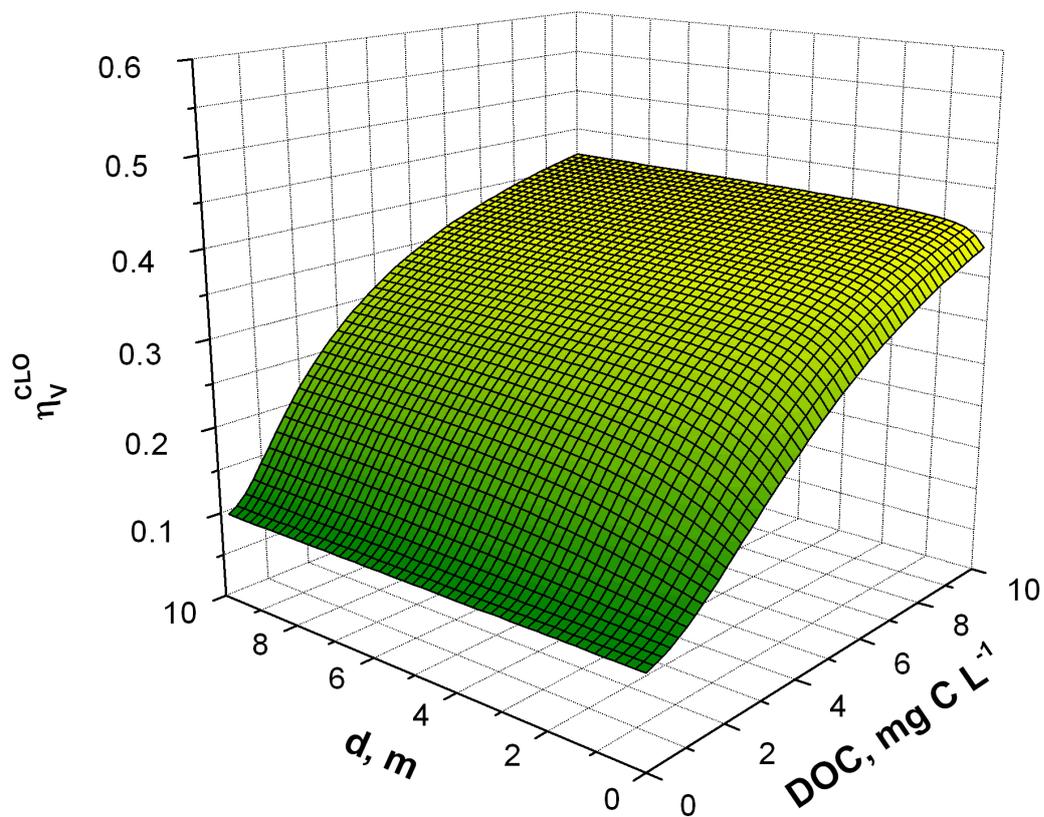


Figure 6. Formation yield of 4-chlorophenol (**V**) upon CLO phototransformation, as a function of the water depth d and the dissolved organic carbon (DOC). Other water parameters: 0.1 mM nitrate, 2 mM bicarbonate, 10 μM carbonate. Summertime irradiation conditions at mid-latitude under fair weather were used for modelling.