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# **Phototransformation of Acesulfame K in surface waters: Comparison of two techniques for the measurement of the second-order rate constants of indirect photodegradation, and modelling of photoreaction kinetics**

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## ***Abstract***

By use of photochemical modelling we show that acesulfame K (ACE) can undergo photodegradation in surface waters, mainly by reaction with  $\bullet\text{OH}$  and possibly  $^3\text{CDOM}^*$  (the triplet states of chromophoric dissolved organic matter). With the possible exception of shallow water bodies containing low dissolved organic carbon, we predict ACE to be a refractory compound in environmental waters which agrees well with many literature reports. We used two methods to measure the photoreactivity parameters of ACE, of which one is based on the monitoring of the time evolution of ACE alone and the other is based on the monitoring of both ACE and a reference compound (hereafter, they are referred to as substrate-only and substrate + reference method, respectively). The substrate + reference method can be time-saving, but it is potentially prone to

interferences. In this work, ibuprofen and atrazine were used as reference compounds of known behaviour to study the photoreactivity of ACE by competition kinetics in the substrate + reference method. The two methods gave overall comparable results, partially because two different reference compounds instead of only one were used in the substrate + reference method. By so doing, however, one loses part of the time-saving advantage of the substrate + reference method.

**Keywords:** *photochemical modelling; reactive transient species; competition kinetics; organic contaminants; indirect degradation pathways; Acesulfame K.*

## **Introduction**

Acesulfame K (potassium salt of 6-methyl-1,2,3-oxathiazine-4(3H)-one-2,2-dioxide, hereafter ACE) is an artificial sweetener that is around 200 times sweeter than sucrose, about as sweet as aspartame, but less than saccharine. ACE is resistant to pH and heat conditions, which accounts for its use in pastries and drinks (Kutyla-Kupidura et al., 2016). The use of artificial sweeteners is gradually increasing in food and drink manufacturing, with the purpose of meeting special dietary requirements. Artificial sweeteners are either not metabolised in the human body (such as ACE), or are metabolised via different pathways than sugars (Kroger et al., 2006). There are some indications that ACE may be recalcitrant to microbial metabolism as well, despite recently described exceptions (see, e.g., Castronovo et al., 2017). Together with sucralose, ACE appears to be among the most stable artificial sweeteners (Sang et al., 2014). For this reason, after human excretion ACE may not be efficiently removed by wastewater treatment plants (Subedi and Kannan, 2014). ACE is a refractory xenobiotic in water bodies, and it has been detected in surface and drinking water at levels ranging from  $\text{ng L}^{-1}$  to even  $\text{sub-mg L}^{-1}$  (Gan et al., 2013; Sang et al., 2014). For this reason, together with other artificial sweeteners, ACE is a contaminant of emerging concern (Kokotou et

al., 2012). The refractory nature also accounts for the use of ACE as a wastewater tracer (Harwood, 2014).

Biorecalcitrant and water-soluble compounds such as ACE can undergo photoinduced degradation in sunlit environments (Gan et al., 2014; Perkola et al., 2016). Photoinduced processes are usually divided into direct photolysis and indirect photochemistry. In the case of direct photolysis, degradation is triggered by sunlight absorption by the pollutant itself. In the case of indirect photochemistry, sunlight is absorbed by photoactive compounds called photosensitisers such as Chromophoric Dissolved Organic Matter (CDOM), nitrate and nitrite. Light-excited photosensitisers produce reactive transient species that are involved in pollutant degradation. For instance, CDOM, nitrate and nitrite produce hydroxyl radicals ( $\bullet\text{OH}$ ), and CDOM also yields reactive triplet states ( $^3\text{CDOM}^*$ ) and singlet oxygen ( $^1\text{O}_2$ ) (Rosario-Ortiz and Canonica, 2016; McNeill and Canonica, 2016). Moreover, the oxidation of carbonate and bicarbonate by  $\bullet\text{OH}$ , and of carbonate by  $^3\text{CDOM}^*$  produces the carbonate radical,  $\text{CO}_3^{\bullet-}$  (Canonica et al., 2005). These transient species have very short lifetimes in surface waters, where they quickly reach steady-state concentrations. In addition to reaction with pollutants, the transients are quickly scavenged by water components such as dissolved organic matter (DOM, as in the case of  $\bullet\text{OH}$  and  $\text{CO}_3^{\bullet-}$ ), dissolved oxygen (accounting for  $^1\text{O}_2$  generation from  $^3\text{CDOM}^*$ ), or upon collision with the water solvent (the main  $^1\text{O}_2$  inactivation pathway) (Vione et al., 2014).

The direct and indirect photoreactivity of dissolved xenobiotics can be assessed by measuring their photolysis quantum yields and the second-order reaction rate constants with the main photoreactive transient species, and by using these data as the basis for photochemical modelling (De Laurentiis et al., 2014; Avetta et al., 2016). The modelling of photochemical reactions in surface waters is based on the computation of light absorption by substrates and photosensitisers and on the consideration of the photochemical reactivity of these compounds in terms of direct photolysis quantum yields

and photogeneration of reactive transient species (Vähätalo and Wetzel, 2004; Bodrato and Vione, 2014; Koehler et al., 2014).

One of the methods to measure the photoreactivity of dissolved compounds makes use of scavengers or probe molecules under definite irradiation conditions (De Laurentiis et al., 2014; Avetta et al., 2016). An alternative approach uses competition kinetics with reference compounds of known reactivity (Ervens et al., 2003). The main difference is that the first method requires the monitoring of the time trend of the studied compound alone (substrate-only approach), while in the other case both the study compound and the reference one are monitored at the same time (substrate + reference approach). In the latter case the study and reference compound are mixed together in the same solution and thus exposed to the same conditions. Therefore, one derives the second-order reaction rate constant between the studied substrate and the reactive transient species from the experimental degradation kinetics of substrate and reference, because the reaction rate constant between the reference compound and the transient is known (Ervens et al., 2003; Gligorovski et al., 2015). An advantage of the substrate + reference method is that just one irradiation experiment may be enough to assess reactivity towards a particular transient, while the substrate-only method is more time consuming as it requires around 4-6 experiments to obtain the same result (De Laurentiis et al., 2014). In some cases only the substrate + reference method can be used (e.g., in the assessment of virus photoinactivation; Mattle et al., 2015), but this method is sensitive to interferences from additional photodegradation pathways that may be operational at the same time. Therefore, it is important that the degradation of both substrate and reference mostly involves the reaction with a single transient species (Gligorovski et al., 2015). For the above reasons, it is interesting to compare the two methods for the assessment of ACE photoinduced reactivity.

Previous studies have dealt with the photodegradation of ACE in the laboratory (Gan et al., 2014; Perkola et al., 2016), but the reported data do not translate easily into the behaviour of this compound in a variety of natural environments and do not allow for a straightforward comparison

with field data. Therefore, this work has two main goals: (i) to assess the photoreactivity of ACE in surface waters, combining kinetic measurements and photochemical modelling and comparing the model predictions with available field data, and (ii) to compare the substrate-only and substrate + reference methods for the measurement of ACE reactivity in different photoreactions.

## Experimental Section

**Reagents, Materials, and Compound Acronyms.** Acesulfame K (ACE, purity grade 99%), NaNO<sub>3</sub> (99%), NaHCO<sub>3</sub> (99.7%), Na<sub>2</sub>HPO<sub>4</sub>×2H<sub>2</sub>O (>99.5%), 2-propanol (98%), tetrabutylammonium hydrogen sulfate (>99%), methanol (>99.9%), furfuryl alcohol (98%), anthraquinone-2-sulfonic acid, sodium salt (AQ2S, 97%), and 2-nitrobenzaldehyde (98%) were purchased from Aldrich, Rose Bengal from Alfa Aesar, H<sub>3</sub>PO<sub>4</sub> (85%) from Carlo Erba.

**Irradiation Experiments.** Absorption measurements were carried out with a Varian Cary 100 Scan UV-Vis spectrophotometer, using 1 cm Hellma quartz cuvettes. Based on the absorption spectra of reasonably concentrated solutions, ACE did not appear to absorb radiation significantly above 300 nm (see Figure SM1 in the Supplementary Material, hereafter SM), in agreement with previous reports (Perkola et al., 2016). The lamps we used all emitted radiation above 300 nm (see Figure SM2 in SM for the lamp spectra), thus ACE is not expected to undergo direct photolysis under our experimental set-ups. The lamps used in the irradiation experiments (*vide infra*) were chosen to ensure selective excitation of the photosensitisers (nitrate, Rose Bengal and AQ2S) and to limit additional (unwanted) photoreactions. The goal here is to obtain reliable photochemical reactivity parameters, which are then used as input data for a photochemical model to get insight into the environmental significance of ACE photodegradation.

In a first series of experiments, the indirect photoreactivity of ACE was studied following an established protocol (De Laurentiis et al., 2014) that is based on the substrate-only method. Briefly, the  $\bullet\text{OH}$  reactivity (second-order reaction rate constant between ACE and  $\bullet\text{OH}$ ) was studied by irradiating  $20\ \mu\text{mol L}^{-1}$  ACE with nitrate ( $10\ \text{mmol L}^{-1}$   $\text{NaNO}_3$  as  $\bullet\text{OH}$  source; Mack and Bolton, 1999) under a 20 W Philips TL 01 UVB lamp with emission maximum at 313 nm. The lamp produced a UV irradiance of  $5.1\pm 0.2\ \text{W m}^{-2}$  over the irradiated solutions, measured with a CO.FO.ME.GRA. irradiance meter equipped with a 290-400 nm probe. The spectrum of the TL 01 lamp (incident spectral photon flux density in solution as a function of wavelength) is reported in the SM. The photon flux density was obtained by spectral measurements with a calibrated Ocean Optics USB 2000 CCD spectrophotometer, combined with 2-nitrobenzaldehyde chemical actinometry (see Marchisio et al., 2015, for the details of the procedure). The alcohol 2-propanol at  $0.05\text{-}1.0\ \text{mmol L}^{-1}$  concentration was used as  $\bullet\text{OH}$  scavenger of known reactivity ( $k_{2\text{-Propanol},\bullet\text{OH}} = 1.9\times 10^9\ \text{L mol}^{-1}\ \text{s}^{-1}$ ; Buxton et al., 1988). The irradiation of nitrate yields  $\bullet\text{NO}_2 + \bullet\text{OH}$  and  $\text{NO}_2^- + \text{O}$  (Svoboda and Slavíček, 2014), where  $\bullet\text{NO}_2$  may show limited reactivity towards easily oxidisable compounds such as phenols (Nissenson et al., 2010), and O atoms are additional  $\bullet\text{OH}$  sources via reaction with water (Mack and Bolton, 1999).

Significant reactivity between ACE and  $\text{CO}_3^{\bullet-}$  was excluded by UVB irradiation of  $20\ \mu\text{mol L}^{-1}$  ACE in the presence of  $10\ \text{mmol L}^{-1}$   $\text{NaNO}_3$  and variable  $\text{NaHCO}_3$  concentrations ( $0\text{-}20\ \text{mmol L}^{-1}$ ). See Vione et al. (2009) for the rationale of these experiments, and Figure SM4 in SM plus related discussion for further details. The reactivity between ACE and  $^1\text{O}_2$  was studied by irradiation of  $10\ \mu\text{mol L}^{-1}$  ACE and  $10\ \mu\text{mol L}^{-1}$  Rose Bengal ( $^1\text{O}_2$  source) under a yellow lamp (Philips TL D 18W/16 Yellow). The lamp had an irradiance of  $11\pm 1\ \text{W m}^{-2}$  over the irradiated solutions, measured with the above CO.FO.ME.GRA. irradiance meter equipped with a broadband probe. The used yellow lamp is not suitable for chemical actinometry, thus only indicative data were obtained for the incident photon flux density from spectral measurements, irradiance values

and photon energy. For this reason, lamp spectral data were not used for calculations. Instead, the generation rate of  $^1\text{O}_2$  under the yellow lamp was measured with  $0.1 \text{ mmol L}^{-1}$  furfuryl alcohol (FFA) as probe compound of known reactivity ( $k_{\text{FFA},^1\text{O}_2} = 1.0 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ ; Appiani et al., 2017).

Finally, the reactivity with the AQ2S triplet state ( $^3\text{AQ2S}^*$ ) was studied by irradiating ACE ( $5\text{-}15 \mu\text{mol L}^{-1}$ ) and AQ2S ( $0.1 \text{ mmol L}^{-1}$ ) under a UVA lamp Philips TL-D 18W BLB with emission maximum at 368 nm, producing a UV irradiance of  $18.0 \pm 0.4 \text{ W m}^{-2}$  over the irradiated solutions.

In all of the above experiments ACE followed a first-order decay kinetics that allowed the determination of the first-order rate constant  $k_{\text{ACE}}$ . The ACE degradation rate was calculated as  $R_{\text{ACE}} = k_{\text{ACE}} C_o$ , where  $C_o$  is the initial ACE concentration.

Some words should be spent about the use of AQ2S as CDOM proxy. On the one side, AQ2S is a proxy molecule with which photoreactivity measurements can be carried out by steady-state irradiation alone (other proxies require use of the laser flash photolysis technique). Moreover, AQ2S does not yield  $\bullet\text{OH}$  or  $^1\text{O}_2$  under irradiation (Maddigapu et al., 2010). However,  $^3\text{AQ2S}^*$  is often more reactive compared to the triplet states of other proxies or of CDOM itself. Although in some cases excellent agreement has been found between the reactivity of  $^3\text{AQ2S}^*$  and  $^3\text{CDOM}^*$  (Zeng and Arnold, 2013; Marchetti et al., 2013), in other cases the use of AQ2S leads to overestimations that should be taken into account (Avetta et al., 2016). In the absence of a better option, AQ2S was used here but its potential limitations were considered.

In a second series of experiments, the reactions of ACE with  $\bullet\text{OH}$ ,  $^1\text{O}_2$  and  $^3\text{AQ2S}^*$  were studied by the substrate + reference method. Two reference compounds were chosen here, namely ibuprofen (IBU) and atrazine (ATZ). The rationale for the choice is that the two compounds undergo limited direct photolysis and that they have known reaction rate constants with  $\bullet\text{OH}$ ,  $^1\text{O}_2$  and  $^3\text{AQ2S}^*$ . IBU is more reactive than ATZ towards all three transients (Ruggeri et al., 2013; Marchetti et al., 2013), thus the combination of the two compounds spans a reasonable reactivity range. In these

experiments, mixtures of 20  $\mu\text{mol L}^{-1}$  ACE + 20  $\mu\text{mol L}^{-1}$  IBU (or ATZ) were irradiated in the presence of 10  $\text{mmol L}^{-1}$  nitrate under UVB ( $\bullet\text{OH}$  reactivity), 10  $\mu\text{mol L}^{-1}$  Rose Bengal under yellow light ( $^1\text{O}_2$  reactivity), and 0.1  $\text{mmol L}^{-1}$  AQ2S under UVA ( $^3\text{AQ2S}^*$  reactivity). Each experiment was carried out in duplicate, and the relevant standard errors are reported together with the experimental data. In each case the degradation followed a pseudo-first order kinetics, which allowed the determination of the first-order transformation constants  $k_{\text{ACE}}$ ,  $k_{\text{IBU}}$  and  $k_{\text{ATZ}}$ . Because in each experiment two compounds occurred in the same mixture (ACE + IBU or ACE + ATZ), both experienced the same steady-state concentration of the reactive transient [X], where X =  $\bullet\text{OH}$ ,  $^1\text{O}_2$  or  $^3\text{AQ2S}^*$ . The concentration [X] is in steady-state because the transient species X is deactivated very quickly after formation. For this reason, the second-order reaction between S and X (with second-order rate constant  $k_{\text{S+X}}$ , where S = ACE, IBU or ATZ) phenomenologically behaves as a first-order process with rate constant  $k_{\text{S}} = k_{\text{S+X}} [\text{X}]$ . For mixtures of ACE + IBU and ACE + ATZ, the following equations hold (Ervens et al., 2003; Gligorovski et al., 2015):

*(ACE + IBU mixture)*

$$k_{\text{ACE}} = k_{\text{ACE+X}} [\text{X}] \quad (1)$$

$$k_{\text{IBU}} = k_{\text{IBU+X}} [\text{X}] \quad (2)$$

$$k_{\text{ACE+X}} = k_{\text{ACE}} (k_{\text{IBU}})^{-1} k_{\text{IBU+X}} \quad (3)$$

*(ACE + ATZ mixture)*

$$k_{\text{ACE}} = k_{\text{ACE+X}} [\text{X}] \quad (4)$$

$$k_{\text{ATZ}} = k_{\text{ATZ+X}} [\text{X}] \quad (5)$$

$$k_{\text{ACE+X}} = k_{\text{ACE}} (k_{\text{ATZ}})^{-1} k_{\text{ATZ+X}} \quad (6)$$

Based on the measured values of  $k_{\text{ACE}}$ ,  $k_{\text{IBU}}$  and  $k_{\text{ATZ}}$  and on the known values of  $k_{\text{IBU+X}}$  and  $k_{\text{ATZ+X}}$ , the second-order rate constants  $k_{\text{ACE+X}}$  with X =  $\bullet\text{OH}$ ,  $^1\text{O}_2$  and  $^3\text{AQ2S}^*$  were determined with

equations (3) and (6). Note that  $[X]$  may differ in the ACE + IBU system compared to the ACE + ATZ one, thus it is not surprising to find a  $k_{ACE}$  value in the presence of ACE + IBU that is different from  $k_{ACE}$  in the presence of ACE + ATZ.

**Experimental Procedures and Analytical Determinations.** For the irradiation experiments, aqueous samples (20 mL total volume) were placed in cylindrical Pyrex glass cells having 4.0 cm diameter and 2.3 cm height. The cells, equipped with a lateral neck for liquid handling, were tightly closed with a screw cap and irradiated with magnetic stirring. After the scheduled irradiation time each cell was withdrawn from the lamp, its content transferred into a vial and kept refrigerated till analysis within the same day. The concentration of ACE, IBU and/or ATZ in solution was determined by high-performance liquid chromatography coupled with UV detection (HPLC-UV). A Merck-Hitachi liquid chromatograph was used, equipped with AS-2000A autosampler (100  $\mu$ L injection volume), L-6200 and L-6200A pumps for high-pressure gradients, L-4200 UV-Vis detector and a reverse-phase column VWR LiChroCART 125-4 (125 mm  $\times$  4 mm  $\times$  5  $\mu$ m) packed with LiChrospher 100 RP 18. Samples were eluted with a mixture of A = 5 mM tetrabutylammonium hydrogen sulphate in water and B = acetonitrile, with the following gradient: 30% B for 4 min, then up to 60% B in 15 min and hold for 1 min, down to 30% B in 1 min and hold for 5 min (post-run equilibration). The eluent flow rate was 1.0 mL min<sup>-1</sup>, under which conditions the retention times were 3.9 min for ACE, 10.3 min for ATZ, and 19.1 min for IBU. The detection wavelength was set at 220 nm. The pH values of the solutions to be irradiated, measured with a combined glass electrode connected to a Metrohm 602 pH meter, were around 6 and they typically varied by no more than 0.2-0.5 units during irradiation.

**Photochemical Modelling.** The model assessment of ACE 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 based on photoreactivity parameters of given compounds (absorption spectra, direct photolysis quantum yields and second-order reaction rate constants with transient species) and on data of water chemistry and depth (Bodrato and Vione, 2014). APEX predictions have been validated by comparison with field data of pollutant phototransformation kinetics in surface freshwaters (Marchetti et al., 2013; Avetta et al., 2016). The standard solar spectrum used in APEX is referred to fair-weather conditions during summertime at mid latitude (see Figure SM1 in SM) (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. 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 low (Loiselle et al., 2008). An additional issue is that sunlight is not vertically incident over the water surface, although refraction deviates the light path in water towards the vertical. The path length  $l$  of light in water is longer than the water depth  $d$  (Bodrato and Vione, 2014), and on 15 July at 45°N one has for instance  $l = 1.05 d$  at noon, and  $l = 1.17 d$  at  $\pm 3$  h from noon that is a reasonable daily average.

## Results and Discussion

### *Measurement of ACE Reaction Rate Constants*

The direct photolysis of ACE under sunlight at ~neutral pH is reported to be very slow (Perkola et al., 2016) or negligible (Gan et al., 2014). The most likely reason is the fact that ACE does not absorb radiation above 300 nm, while the sunlight irradiance below 300 nm is extremely limited (Frank and Klöpffer, 1988). Moreover, when the direct photolysis kinetics is very slow (e.g.,  $t_{1/2}$  above 1 month of continuous irradiation in the laboratory; Perkola et al., 2016) a number of confounding factors may come into play including photosensitising impurities in the solutions and glassware, hydrolysis and other processes. For these reasons, the direct photolysis of ACE is not discussed here. We could also exclude significant reactivity with  $\text{CO}_3^{\bullet-}$  by means of irradiation experiments carried out with  $\text{NaNO}_3 + \text{NaHCO}_3$  (see Figure SM4 in SM and related discussion).

Our first series of experiments was carried out according to the substrate-only method. The reaction with  $\bullet\text{OH}$  was studied by irradiation of ACE and nitrate, assessing the inhibition of ACE phototransformation upon addition of 2-propanol as  $\bullet\text{OH}$  scavenger. Rose Bengal was used as  $^1\text{O}_2$  source, and the formation rate of  $^1\text{O}_2$  was quantified using furfuryl alcohol as probe compound. The degradation of ACE by  $^1\text{O}_2$  was studied at low ACE concentration ( $10 \mu\text{mol L}^{-1}$ ), obtaining a very low reaction rate  $R_{\text{ACE}}$ . The reactivity between ACE and  $^3\text{AQ2S}^*$  was studied upon irradiation of mixtures of ACE and AQ2S at low ACE concentration, so as to obtain a linear trend of  $R_{\text{ACE}}$  vs. [ACE]. Although experimentally quite heavy, this methodology is reasonably robust in face of potential interferences. The substrate-only method followed in fact a well-established protocol that has been extensively used in previous studies (Marchetti et al, 2013; Ruggeri et al., 2013; De Laurentiis et al., 2014; Avetta et al., 2016). The methodology being well established, the details of the experiments are reported as SM (see Figures SM3-SM6 and related discussion). The obtained

second-order reaction rate constants are provided in **Table 1**. In the case of  $^1\text{O}_2$ , poor reactivity just allowed the calculation of an upper limit for the reaction rate constant with ACE,  $k_{ACE,^1\text{O}_2}$ .

The second series of experiments followed the substrate + reference method. The results of the irradiation of a mixture of ACE and IBU in the presence of  $\text{NaNO}_3$  are reported in **Figure 1a**. IBU underwent faster degradation compared to ACE, suggesting faster reaction with  $\bullet\text{OH}$ . IBU also underwent a limited but non-negligible direct photolysis, as shown by irradiation of IBU alone in the same figure. Negligible direct photolysis was observed for ACE, coherently with the fact that this compound does not absorb radiation significantly above 300 nm. With an optical path length of 1.6 cm in the irradiation cells, the absorbance of  $0.01 \text{ mol L}^{-1} \text{ NO}_3^-$  at 313 nm (lamp emission maximum) is  $A_{\text{NO}_3^-} = 0.1$ , while  $20 \text{ }\mu\text{mol L}^{-1}$  IBU has  $A_{\text{IBU}} = 1.5 \times 10^{-5}$ . These absorbance values are low enough to exclude an important shadowing effect between nitrate and IBU (Braslavsky, 2007). Therefore, the  $\bullet\text{OH}$ -induced degradation of IBU in the presence of nitrate could be obtained by subtracting the direct photolysis rate observed without nitrate from the degradation rate observed with nitrate.

**Figure 1b** shows the time trends of ACE and ATZ in mixture, with and without  $\text{NaNO}_3$ . The different degradation kinetics of ACE compared to the previous case is likely due to different  $[\bullet\text{OH}]$  values in the two systems. To account for the limited direct photolysis of ATZ under UVB irradiation, the ATZ degradation rate without nitrate (direct photolysis) was subtracted from the rate obtained with nitrate. This simple operation was again allowed by the low absorbance values at 313 nm ( $A_{\text{NO}_3^-} = 0.1$ ,  $A_{\text{ATZ}} = 4 \times 10^{-4}$ ). The faster degradation of ACE compared to ATZ suggests a higher  $\bullet\text{OH}$  reaction rate constant for ACE.

The values of  $k_{ACE,\bullet\text{OH}}$  assessed by using IBU and ATZ as reference compounds are reported in **Table 1**. The rate constants obtained with the substrate-only, the substrate + IBU reference and the substrate + ATZ reference methods show reasonable agreement. Note that variations of a factor  $\sim 2$

often occur in the  $\bullet\text{OH}$  rate constants measured by different methods (Buxton et al., 1988). Our  $k_{ACE;\bullet\text{OH}}$  values are also not very far from the literature data of  $(4\text{-}5)\times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  (Toth et al., 2012; Kaiser et al., 2013).

**Figure 1c** shows the time trends of ACE + IBU and of ACE + ATZ upon UVA irradiation with AQ2S. Direct photolysis was not operational on our irradiation time scale (data not shown). The  $^3\text{AQ2S}^*$  rate constants of ACE ( $k_{ACE,^3\text{AQ2S}^*}$ ), obtained by using IBU and ATZ as reference compounds are reported in **Table 1**, together with the rate constant derived with the alternative procedure. The value of  $k_{ACE,^3\text{AQ2S}^*}$  (substrate-only method) depends on the  $^3\text{AQ2S}^*$  inactivation kinetics that proceeds by reaction with water (see equation (19) in the SM), with  $k_{^3\text{AQ2S}^*} = 5\times 10^6 \text{ s}^{-1}$  as per a recent estimate (Bedini et al., 2012). A previous study reported  $k_{^3\text{AQ2S}^*} = 1.1\times 10^7 \text{ s}^{-1}$  (Loeff et al., 1983), and the literature values of  $k_{IBU,^3\text{AQ2S}^*}$  and  $k_{ATZ,^3\text{AQ2S}^*}$  were based on the older datum. To obtain comparable values of  $k_{ACE,^3\text{AQ2S}^*}$  with the different methods, the literature values of  $k_{IBU,^3\text{AQ2S}^*}$  and  $k_{ATZ,^3\text{AQ2S}^*}$  were recalculated by assuming  $k_{^3\text{AQ2S}^*} = 5\times 10^6 \text{ s}^{-1}$ . If the older value of  $k_{^3\text{AQ2S}^*}$  is used instead of the more recent one, the  $k_{ACE,^3\text{AQ2S}^*}$  values reported in **Table 1** should be all multiplied by 2.2.

The reported values of  $k_{ACE,^3\text{AQ2S}^*}$  show a reasonable agreement. The datum most departing from the others was obtained by using IBU as reference compound, in which case the degradation of ACE was quite slow as compared to that of IBU (see **Figure 1c**). If the second-order reaction rate constants of the study and reference compound are very different (in the case of IBU and ACE they differ by an order of magnitude), the methodology based on the rate constant ratios (see equations 3 and 6) may lose in accuracy. In fact, it is difficult to compare different reaction kinetics at different time scales, where the assumption of constant  $[\text{X}]$  may no longer be valid. Fortunately, ATZ was also used as reference compound and it showed comparable degradation kinetics as ACE.

**Figure 1d** shows the time trends of ACE + IBU and of ACE + ATZ upon irradiation with Rose Bengal under the yellow lamp. Very limited degradation was observed in all the cases, although a relatively long irradiation time (up to 26 h) was applied. The considerable uncertainties associated to the data fit with a pseudo-first order kinetics may account for the difference of a factor  $\sim 2$  between the  $k_{ACE,^1O_2}$  values obtained with IBU and ATZ as reference compounds (see **Table 1**). However, these values are coherent with the upper-limit estimate obtained with the substrate-only method.

Averages of the measured rate constants (see **Table 1**) were used in the following section devoted to photochemical modelling. The  $^1O_2$  upper-limit estimate was not taken into account in the  $k_{ACE,^1O_2}$  average, which was thus based on two values only.

### ***Photochemical Modelling***

The ACE reaction rate constants measured in the previous section can be used to obtain an estimate of the photochemical fate of this compound in surface waters, by use of photochemical modelling with the APEX software. First of all, it is interesting to compare model predictions with available field data of ACE persistence. ACE is often suggested to behave conservatively in surface waters, which implies slow degradation (Storck et al., 2016). For instance, data from the Swedish lake Norra Bergundasjön in spring suggest that ACE and carbamazepine (both biorecalcitrant compounds; Gasser et al., 2011; Liu et al., 2014) were among the most refractory pollutants, with similar behaviour within experimental uncertainty and slightly higher persistence in the case of ACE (Zou et al., 2015a). The water residence time in the lake was around 120 days, while ACE and carbamazepine appeared to be considerably more persistent than that. Zou et al. assumed ACE to be conservative and calculated carbamazepine to have a half-life time of 1200-1400 days in the lake water. However, from the uncertainties in the field measurements one cannot exclude that the two

compounds underwent dissipation with similar kinetics. In the case of Norra Bergundasjön in spring it is estimated  $[\bullet\text{OH}] = (1-2) \times 10^{-18} \text{ mol L}^{-1}$  (Koehler, personal communication) which, combined with the average  $k_{ACE,\bullet\text{OH}}$  value reported in **Table 1**, gives a ACE half-life time of 700-1400 days. Considering that the  $\bullet\text{OH}$  reaction rate constant of carbamazepine may be some 1.3 times higher than that of ACE (Wols and Hofman-Caris, 2012), one can predict that ACE is slightly more persistent than carbamazepine if both compounds are mainly degraded by  $\bullet\text{OH}$ . The comparison between model predictions and field data suggests some overestimation of the dissipation kinetics by the photochemical model, but there are many uncertainties in both field persistence data (the reported half-life times are at least one order of magnitude longer than the water residence time) and photoreactivity estimates. Anyway, it is unlikely that additional photoreaction pathways such as those with  $^1\text{O}_2$  and  $^3\text{CDOM}^*$  play a very important role in the transformation of ACE in Norra Bergundasjön, because they would further decrease the modelled half-life times. A negligible reaction with  $^1\text{O}_2$  is reasonable given the low reaction rate constant with ACE (see **Table 1**). In the case of  $^3\text{CDOM}^*$ , considering that  $k_{ACE,^3\text{AQ2S}^*}$  is one order of magnitude lower than  $k_{ACE,\bullet\text{OH}}$ , one needs  $[^3\text{CDOM}^*] \sim [\bullet\text{OH}]$  or lower to have a reasonably limited contribution of  $^3\text{CDOM}^*$  to ACE photodegradation. However, this is unlikely because  $[^3\text{CDOM}^*] \gg [\bullet\text{OH}]$  is a common finding in natural waters (Vione et al., 2014). Therefore,  $k_{ACE,^3\text{AQ2S}^*}$  probably overestimates the  $^3\text{CDOM}^*$  reactivity in Norra Bergundasjön. In the modelling part that follows, the ACE half-life times will be assessed under the following alternative assumptions: (i)  $k_{ACE,^3\text{CDOM}^*} = k_{ACE,^3\text{AQ2S}^*}$ ; (ii) neglecting the reaction between ACE and  $^3\text{CDOM}^*$ .

The model results of ACE phototransformation in the two scenarios are reported in **Figure 2**, as half-life times ( $t_{1/2}$ ) as a function of water depth and of the dissolved organic carbon (DOC). The DOC is a measure of the dissolved organic matter (DOM) occurring in surface waters (Wetzel, 2001). **Figure 2a** reports the model predictions for  $k_{ACE,^3\text{CDOM}^*} = k_{ACE,^3\text{AQ2S}^*}$ . The almost linear

increase of the half-life time with increasing depth is a consequence of the fact that deep water bodies are poorly illuminated by sunlight (Loiselle et al., 2008). Therefore, the elevated photoactivity of the water surface layer is offset by the low to nil photoactivity in the lower depths, to a larger extent as the water body is deeper. The half-life time is also predicted to increase as a function of the DOC, up to a plateau trend. The increase of the DOC would inhibit the  $\bullet\text{OH}$  reaction and enhance the  ${}^3\text{CDOM}^*$  one, with overall compensation in the plateau region (see **Figure 2b** for the fractions of ACE phototransformation accounted for by  $\bullet\text{OH}$  and  ${}^3\text{CDOM}^*$ , as a function of the DOC, for a water depth  $d = 5$  m).

The obtained half-life times, of up to a few months, may be long enough to account for the observed conservative behaviour in rivers (Spoelstra et al., 2013; Liu et al., 2014), where the water flow prevents the precise determination of slow attenuation kinetics. In the case of lakes, it is easier to identify slow degradation processes and to differentiate them from a purely conservative behaviour. Therefore, the predicted half-life times are not really consistent with the observed persistence of ACE in lake water (Zou et al., 2015a/b).

Longer half-life times are reported in **Figure 2c**. Compared to the previous case (**Figure 2a**), the  ${}^3\text{CDOM}^*$  process was neglected and only degradation by  $\bullet\text{OH}$  was considered. With this assumption, a considerable degree of persistence is predicted for ACE in deep water bodies with high DOC, in general agreement with the reported behaviour in the field (Spoelstra et al., 2013; Liu et al., 2014; Zou et al., 2015a/b). The framework could be different for shallow and DOM-poor environments, for which ACE field data are unfortunately hardly available. For instance, a half-life time of  $\sim 3$  weeks is predicted for 1 m depth and  $\text{DOC} = 1 \text{ mgC L}^{-1}$ . This result is independent of the occurrence of the  ${}^3\text{CDOM}^*$  process, because the  $\bullet\text{OH}$  reaction would prevail anyway in shallow waters with low DOC. In the  $\bullet\text{OH}$ -only scenario, the ACE half-life time has also a significant dependence on nitrate concentration. The decrease of  $t_{1/2}$  with increasing  $[\text{NO}_3^-]$  is more important as the water DOC is lower (see **Figure 2d**) because the role of nitrate as  $\bullet\text{OH}$  source is more

important in low-DOC as compared to high-DOC conditions, where most  $\bullet\text{OH}$  is generated by CDOM (Vione et al., 2014).

## Conclusions

The two methods used here to calculate the second-order reaction rate constants of ACE with photoreactive transient species occurring in surface waters gave reasonably comparable results. This is interesting because the substrate + reference method may lead to time savings. However, it may provide less accurate data than the substrate-only method if the degradation rates of the studied and reference compound are very different (e.g., an order of magnitude or above) and if multiple photoreaction pathways are operational at the same time. Fortunately, ACE did not undergo direct photolysis that was also limited for the reference compounds we used. Considering the other problem, because of the highly variable reactivity of different substrates in different processes, it is recommended to use more than one reference compound to reduce the experimental uncertainty, as done here with ibuprofen and atrazine. Unfortunately, with more reference compounds one increases the number of the required experiments, which reduces the main competitive advantage (rapidity) of the substrate + reference method over the substrate-only one.

In the case of ACE we found that the prevailing photochemical reaction in sunlit surface waters would involve  $\bullet\text{OH}$ , with possibly some contribution by  $^3\text{CDOM}^*$ . By assuming that the  $\bullet\text{OH}$  process only is important, one gets an ACE persistence that is compatible with field data from lake environments. Field data from rivers are less conclusive. When found in deep and DOM-rich environments, ACE approximates a conservative behaviour with limited degradation. However, there might be exceptions in shallow water bodies with low DOC, particularly under summertime irradiation conditions, where the photodegradation of ACE might not be negligible.

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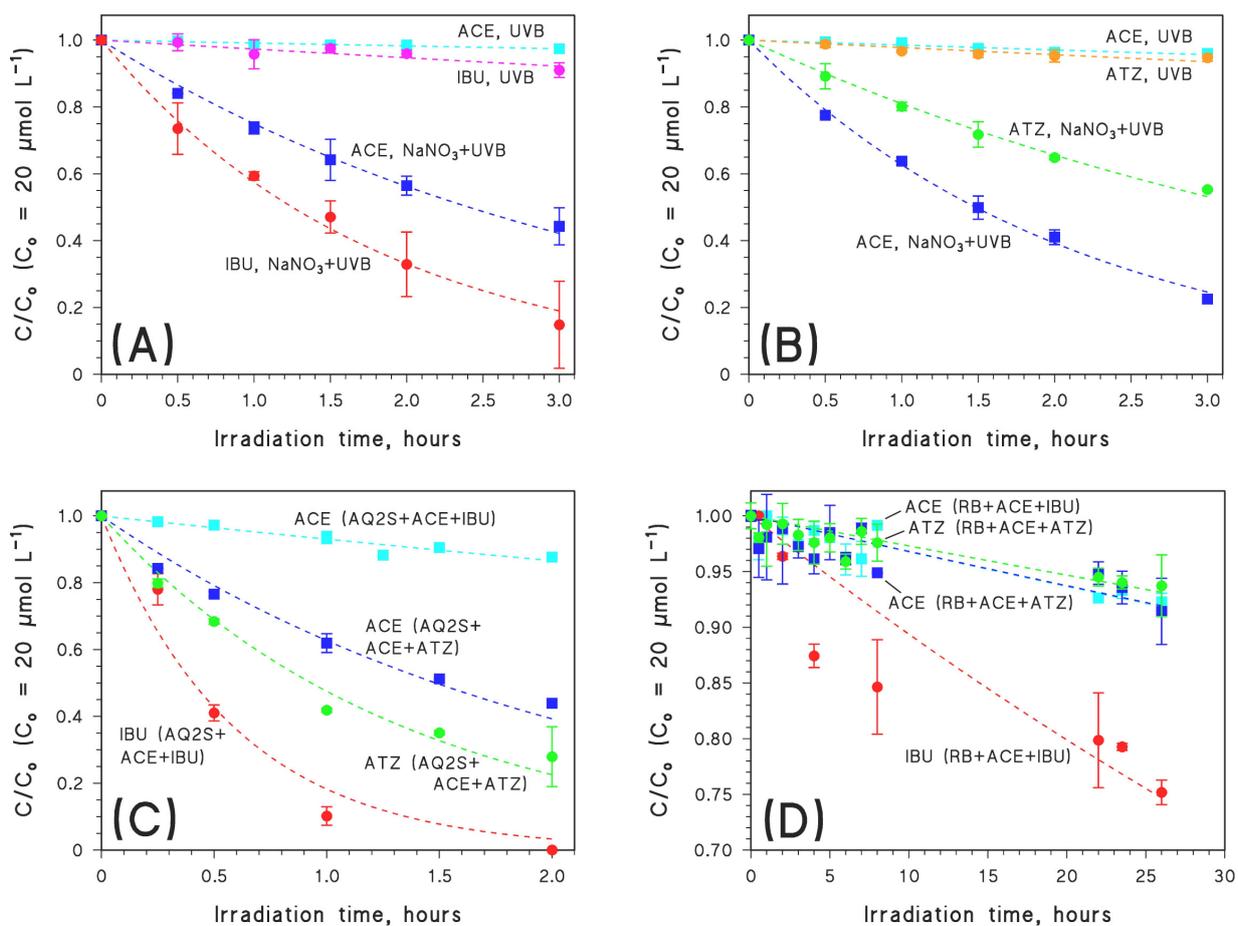
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**Table 1.** Measured second-order reaction rate constants of ACE with different transient species ( $\bullet\text{OH}$ ,  $^3\text{CDOM}^*$  and  $^1\text{O}_2$ ), using different methods. The first is the substrate-only method that uses scavengers and probe molecules. The details of the experimental results obtained with this method are discussed in SM. The second method is the substrate + reference one, where IBU and ATZ were used as reference compounds in two different sets of experiments. The substrate + reference method used literature values for the rate constants of IBU and ATZ:  $k_{\text{IBU},\bullet\text{OH}} = (1.0\pm 0.3)\times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{\text{ATZ},\bullet\text{OH}} = (2.7\pm 0.3)\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{\text{IBU},^1\text{O}_2} = (6.0\pm 0.6)\times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_{\text{ATZ},^1\text{O}_2} = (4.0\pm 0.4)\times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (Ruggeri et al., 2013; Marchetti et al., 2013). In the case of the  $^3\text{AQ2S}^*$  rate constants, the literature data (Ruggeri et al., 2013; Marchetti et al., 2013) were corrected by considering the same value of the pseudo-first order decay constant of  $^3\text{AQ2S}^*$  used here in the substrate-only method ( $k_{^3\text{AQ2S}^*} = 5\times 10^6 \text{ s}^{-1}$ ), in place of the value used in the literature references ( $k_{^3\text{AQ2S}^*} = 1.1\times 10^7 \text{ s}^{-1}$ ). Therefore, here we used  $k_{\text{IBU},^3\text{AQ2S}^*} = (4.4\pm 0.1)\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{ATZ},^3\text{AQ2S}^*} = (6.5\pm 0.3)\times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  as reference values for the  $^3\text{AQ2S}^*$  reaction rate constants. The error bounds in the table represent the standard errors.

	<b>X = <math>\bullet\text{OH}</math></b>	<b>X = <math>^3\text{AQ2S}^*</math></b>	<b>X = <math>^1\text{O}_2</math></b>	<b>Notes</b>
$k_{\text{ACE},X}, \text{M}^{-1} \text{ s}^{-1}$	$(4.3\pm 0.5)\times 10^9$	$(4.4\pm 0.3)\times 10^8$	$< 2.5\times 10^5$	Substrate-only method
$k_{\text{ACE},X}, \text{M}^{-1} \text{ s}^{-1}$	$(8.1\pm 3.1)\times 10^9$	$(8.0\pm 0.8)\times 10^8$	$(1.7\pm 0.6)\times 10^4$	Substrate + reference (IBU)
$k_{\text{ACE},X}, \text{M}^{-1} \text{ s}^{-1}$	$(5.3\pm 0.6)\times 10^9$	$(4.0\pm 0.2)\times 10^8$	$(4.0\pm 1.1)\times 10^4$	Substrate + reference (ATZ)
$k_{\text{ACE},X}, \text{M}^{-1} \text{ s}^{-1}$	<b><math>(5.9\pm 2.0)\times 10^9</math></b>	<b><math>(5.5\pm 2.2)\times 10^8</math></b>	<b><math>(2.8\pm 1.1)\times 10^4</math></b>	<b>Average of above values</b>



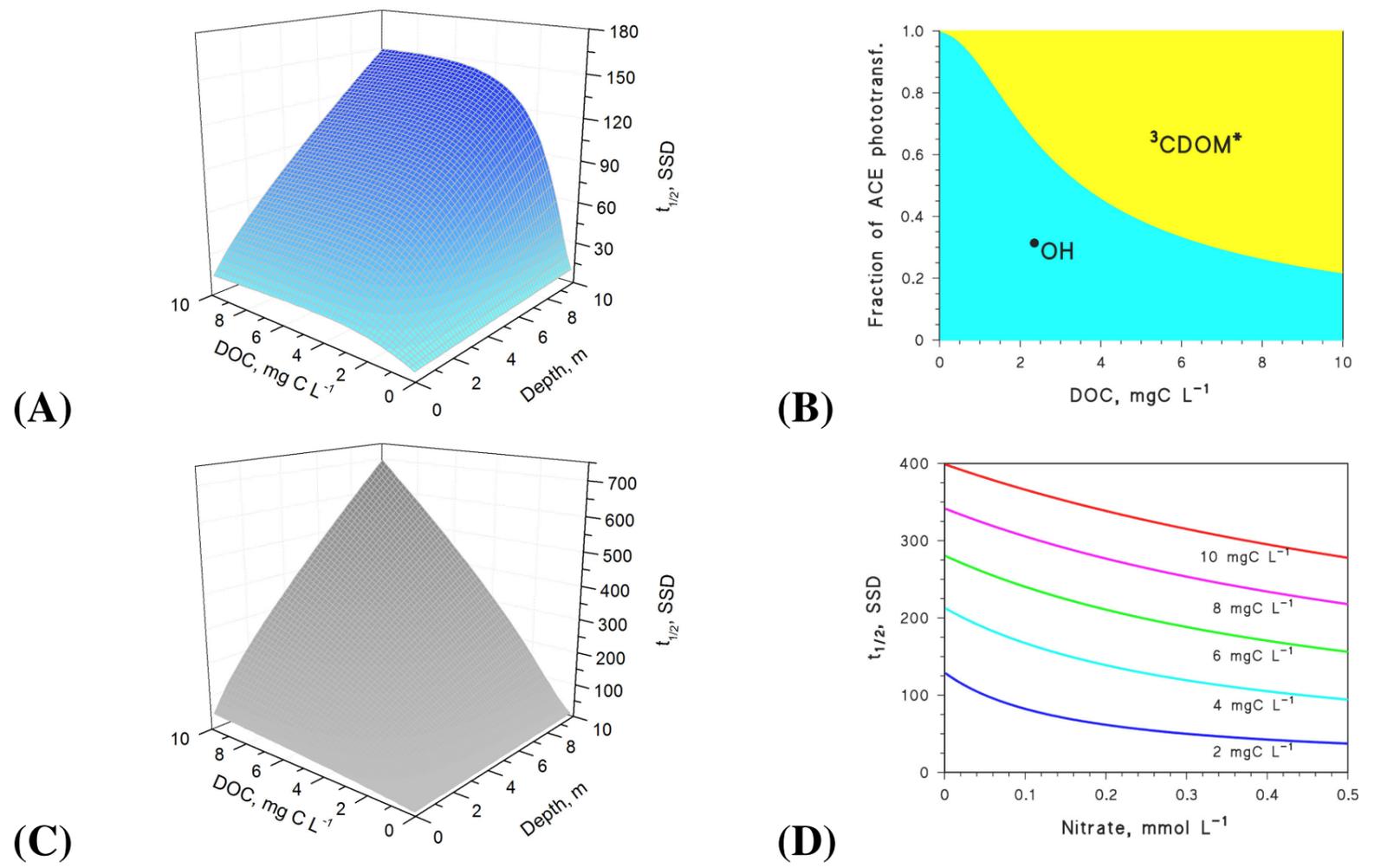
**Figure 1.** (A) Time evolution of  $20 \mu\text{mol L}^{-1}$  ACE (light blue squares) and of  $20 \mu\text{mol L}^{-1}$  IBU (purple circles) in mixture under UVB irradiation alone. Time evolution of  $20 \mu\text{mol L}^{-1}$  ACE (blue squares) and of  $20 \mu\text{mol L}^{-1}$  IBU (red circles) in mixture under UVB irradiation in the presence of  $0.01 \text{ mol L}^{-1}$   $\text{NaNO}_3$ .

(B) Time evolution of  $20 \mu\text{mol L}^{-1}$  ACE (light blue squares) and of  $20 \mu\text{mol L}^{-1}$  ATZ (brown circles) in mixture under UVB irradiation alone. Time evolution of  $20 \mu\text{mol L}^{-1}$  ACE (blue squares) and of  $20 \mu\text{mol L}^{-1}$  ATZ (green circles) in mixture under UVB irradiation in the presence of  $0.01 \text{ mol L}^{-1}$   $\text{NaNO}_3$ .

(C) Time evolution of  $20 \mu\text{mol L}^{-1}$  ACE (light blue squares) and of  $20 \mu\text{mol L}^{-1}$  IBU (red circles) in mixture under UVA irradiation in the presence of  $0.1 \text{ mmol L}^{-1}$  AQ2S. Time evolution of  $20 \mu\text{mol L}^{-1}$  ACE (blue squares) and of  $20 \mu\text{mol L}^{-1}$  ATZ (green circles) in mixture under UVA irradiation in the presence of  $0.1 \text{ mmol L}^{-1}$  AQ2S.

(D) Time evolution of  $20 \mu\text{mol L}^{-1}$  ACE (light blue squares) and of  $20 \mu\text{mol L}^{-1}$  IBU (red circles) in mixture under yellow-lamp irradiation in the presence of  $10 \mu\text{mol L}^{-1}$  RB. Time evolution of  $20 \mu\text{mol L}^{-1}$  ACE (blue squares) and of  $20 \mu\text{mol L}^{-1}$  ATZ (green circles) in mixture under yellow-lamp irradiation in the presence of  $10 \mu\text{mol L}^{-1}$  RB.

In all the cases, the error bars represent the standard error of replicate experiments.



**Figure 2.** (A) Modelled half-life times (SSD units) of ACE as a function of the DOC and of water depth, with  $k_{ACE,{}^3\text{CDOM}^*} = k_{ACE,{}^3\text{AQ2S}^*}$ .

Other water conditions: 0.1 mM nitrate, 1  $\mu$ M nitrite, 2 mM bicarbonate, 10  $\mu$ M carbonate.

(B) Fractions of ACE phototransformation accounted for by  $\bullet$ OH and  ${}^3\text{CDOM}^*$  as a function of the DOC, for a water depth  $d = 5$  m and with  $k_{ACE,{}^3\text{CDOM}^*} = k_{ACE,{}^3\text{AQ2S}^*}$ . Other water conditions as before.

(C) Modelled half-life times of ACE as a function of the DOC and of water depth, neglecting the  ${}^3\text{CDOM}^*$  reaction. Other water conditions as before.

(D) ACE half-life times as a function of nitrate concentration, neglecting the  ${}^3\text{CDOM}^*$  reaction. The legend near each curve gives the value of the water DOC. Other conditions: 5 m depth, 1  $\mu$ M nitrite, 2 mM bicarbonate, 10  $\mu$ M carbonate.