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# **A model assessment of the potential of river water to induce the photochemical attenuation of pharmaceuticals downstream of a wastewater treatment plant (Guadiana River, Badajoz, Spain)**

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## ***Abstract***

We predicted the possible direct and indirect phototransformation kinetics of carbamazepine (CBZ), ibuprofen (IBU) and diclofenac (DIC) in river water, based on data of water chemistry obtained for the Guadiana River near Badajoz (Southwestern Spain) during a year-round sampling campaign. The three compounds were chosen, (i) because they occurred at the outlet of the wastewater treatment plant (WWTP) in Badajoz, as well as in river water sampled 1 km downstream of the WWTP, and (ii) because their photochemical fate in surface waters is known well enough to be modelled. The modelled phototransformation kinetics would be negligible in winter and fastest in April-August, with comparable rate constants in April through August despite differences in sunlight irradiance. Favourable water chemistry would in fact offset the lower irradiance, and vice versa. Half-life times of at least three weeks - one month are predicted for CBZ and IBU.

Photodegradation may be an important attenuation pathway for biorecalcitrant CBZ, while IBU photochemistry is unlikely to be competitive with other processes including biodegradation. The predicted DIC photochemical half-life times of 7-10 days in April-August would be comparable with the biodegradation kinetics data reported in the literature. Photochemistry might not induce extensive phototransformation of xenobiotics in the Guadiana River under normal flow conditions, but it could become important in the case of low flow produced by water scarcity.

**Keywords:** Phototransformation; River water; Carbamazepine; Diclofenac; Ibuprofen.

## 1. Introduction

Wastewater treatment plants (WWTPs) are important sources of several emerging contaminants, including pharmaceuticals and personal care products (PPCPs) to surface waters (Petrovic et al., 2003; Richardsdon and Ternes, 2014; Ebele et al., 2017). The reason is that most WWTPs have been designed to eliminate nutrients and pathogens from wastewater and they largely rely on solid removal, biological processes and disinfection. Unfortunately, many emerging contaminants are biorecalcitrant and resist degradation in biological treatment steps (Fatta-Kassinos et al., 2010). Hydrophobic biorecalcitrant molecules partitioning to biosolids could still be removed from the aqueous phase during the solid separation step, while the water-soluble compounds tend to remain dissolved (Kosjek and Heath, 2010). The polar contaminants will thus occur in the wastewater effluent, unless an important reaction takes place with the disinfectant in the final treatment stage. In some cases, however, disinfection can produce secondary contaminants such as the chloroderivatives (Buth et al., 2011). Moreover, some pharmaceuticals are excreted by the human body in metabolised forms such as the glucuronide conjugates, which may mask the occurrence of the parent xenobiotics at the WWTP inlet. The bacteria that operate in the biological treatment step

often detach the sugar moiety and set free the original drug which, if sufficiently biorecalcitrant, can be found in higher concentration at the WWTP outlet than at the inlet (Radjenovic et al., 2007). This back-transformation of drug metabolites definitely complicates the assessment of the PPCP biodegradation potential in WWTPs (Ternes, 1998). New treatment technologies including advanced oxidation processes will be needed to carry out a technological update of WWTPs, and to enable effective PPCP removal (Huber et al., 2003; Wang et al., 2017; Wang et al., 2018).

Once they reach natural water (often, river water), the contaminants may undergo a range of transformation pathways that make up the self-depuration potential of the water body, but that would sometimes produce harmful secondary pollutants (Kümmerer 2009a/b). Attenuation may take place biologically, but the most biodegradable compounds undergo complete or almost complete abatement at the WWTP level and, from this point of view, WWTPs tend to select rather biorecalcitrant molecules at their outlet. A caveat to this line of reasoning is that the biodegradation behaviour in a WWTP may not be representative of the biological processes taking place in river water in contact with sediment (Fono et al., 2006; Kunkel and Radke, 2011). Therefore, PPCP biodegradation in surface waters cannot be excluded. Abiotic degradation involves hydrolysis, dark redox processes and, most notably, photochemical reactions (Dunnivant and Anders, 2006). The latter are induced by sunlight and are usually divided into direct photolysis and indirect photochemistry (Vione et al., 2014). In the direct photolysis, the pollutant absorbs sunlight and undergoes transformation as a consequence (Fenner et al., 2013). In the case of indirect photochemistry, sunlight is absorbed by naturally occurring compounds called photosensitisers that include nitrate, nitrite and chromophoric dissolved organic matter (CDOM) (Pace and Barreca, 2014). Irradiated photosensitisers generate reactive transient species that are involved in pollutant degradation. In particular, the sunlight irradiation of nitrate, nitrite and CDOM yields the hydroxyl radical ( $\bullet\text{OH}$ ), while irradiated CDOM also produces singlet oxygen ( $^1\text{O}_2$ ) and reactive triplet states ( $^3\text{CDOM}^*$ ) (Vione et al., 2014; Rosario-Ortiz and Canonica, 2016; McNeill and Canonica, 2016).

Moreover, the carbonate radical ( $\text{CO}_3^{\bullet-}$ ) is produced by oxidation of carbonate and bicarbonate by  $\bullet\text{OH}$ , and of carbonate by  $^3\text{CDOM}^*$  (Canonica et al., 2005). In addition to being produced, the transients are also quenched in natural waters. Dissolved organic matter (DOM), which can be quantified as the dissolved organic carbon (DOC), is the main scavenger of  $\bullet\text{OH}$  and  $\text{CO}_3^{\bullet-}$  (Vione et al., 2014; Gligorovski et al., 2015). In contrast,  $^3\text{CDOM}^*$  are quenched by reaction with  $\text{O}_2$  to yield  $^1\text{O}_2$  and, to a lesser extent, by internal conversion (Rosario-Ortiz and Canonica, 2016; McNeill and Canonica, 2016). Finally,  $^1\text{O}_2$  is quenched by collisions with the water solvent (Rodgers and Snowden, 1982). The direct photolysis and the reactions with  $\bullet\text{OH}$ ,  $\text{CO}_3^{\bullet-}$ ,  $^1\text{O}_2$  and  $^3\text{CDOM}^*$  usually account for the majority of the photochemical transformation of xenobiotics in sunlit surface waters (Boreen et al., 2003; Vione et al., 2014). The phototransformation kinetics depend on several issues including the intrinsic photoreactivity of the xenobiotic by direct photolysis and indirect photochemistry, the chemical composition and depth of the natural water, and the irradiance of sunlight. The irradiance may vary depending on location, weather, time of the day and season. The water chemistry has seasonal trends as well, because of the combination of biological and chemical processes (Vione, 2017). While most attention has been focused on the impact of seasonal sunlight irradiance on photochemistry, the simultaneous variations in the occurrence of key photosensitisers (chromophoric organic compounds, nitrate and nitrite) and scavengers (DOM and inorganic carbon) have been largely overlooked.

To our knowledge, relatively few works have directly addressed the attenuation of xenobiotics in rivers (Schwientek et al., 2016), although several data from laboratory studies are available concerning biotic and abiotic transformation in river water or water/sediment systems (e.g., Löffler et al., 2005; Kunkel and Radke, 2008). The main difficulty is linked with important transport phenomena in rivers, which act as a confounding factor in the detection and quantification of transformation processes to a much larger extent than for, e.g., lake water (Yu-Chen Lin et al., 2006; Radke et al., 2010; Kunkel and Radke, 2011). To our knowledge, naproxen is the only

xenobiotic for which there is some (but non univocal) field evidence of photodegradation in rivers (Yu-Chen Lin et al., 2006; Fono et al., 2006; Radke et al., 2010). To overcome some of the above-cited difficulties, the present work uses photochemical modelling to assess the potential of sunlit river water to induce the photodegradation of xenobiotics. The model predictions are based on known photoreactivity data, on clear-sky sunlight irradiance, and on data of water chemistry collected during a one-year sampling campaign carried out at the Guadiana River near the town of Badajoz, Southwestern Spain. The target pollutants (carbamazepine, ibuprofen and diclofenac) were chosen among the emerging contaminants detected at the outlet of the Badajoz WWTP, located 1 km upstream of the river sampling site. The rationale for the choice of the three pollutants is that their environmental (photo)fate has been extensively studied (Tixier et al., 2003; Bonvin et al., 2013), and their photodegradation is already known to proceed mainly by direct photolysis and reactions with  $\bullet\text{OH}$  and  $^3\text{CDOM}^*$ . The relevant quantum yields and reaction rate constants have already been determined (Vione et al., 2011; De Laurentiis et al., 2012; Avetta et al., 2016).

## 2. Experimental

### 2.1. Water sampling

The Rincón de Caya WWTP is located in the city of Badajoz (Spain) and it is operated by FCC Aqualia. The plant is described in **Figure 1** and it is designed to treat an average flow of  $66,000 \text{ m}^3 \text{ day}^{-1}$ , to deliver services to a population equivalent of 385,000 inhabitants. However, it is currently treating an average flow of  $35,000 \text{ m}^3 \text{ day}^{-1}$ . Samples were taken from the Badajoz WWTP outlet and from Guadiana River, in a point 1 km downstream of the WWTP. A bucket was dipped, respectively, into the treated water tank placed at the end of the plant waterline and in the river, as

far as possible from the bank, at 0.5 m depth. The bucket was then brought out at the surface, and water samples were collected in polyethylene containers (or in glass bottles for emerging contaminants determination), which were filled to the very top to avoid headspace. Samples were preserved at 4°C immediately after the collection. The collected water samples were then brought to the laboratory to be analysed.



**Figure 1.** Sampling sites (top) and Badajoz WWTP process scheme (bottom).

## ***2.2. Analytical procedures***

The pH and temperature of the samples were measured by means of a portable pH-meter (pH25, CRISON; accuracy: 0.12%; precision: 0.37%). Nitrates and nitrites were measured using a Hach Lange DR 3900 spectrophotometer (Hach Lange, Berlin, Germany) using the nitrate kits LCK 339 (Hach Lange, 1–60 mg/L NO<sub>3</sub>, accuracy 1% and precision 5%) and the nitrite kits LCK 341 (Hach Lange, 0.05–2 mg/L NO<sub>2</sub>, accuracy 1% and precision 4%).

For the determination of Chemical Oxygen Demand (COD), LCK 314 cuvette tests were used (15 to 150 mgO<sub>2</sub> L<sup>-1</sup>; Hach Lange) and the samples were measured with the Hach Lange spectrophotometer described above (accuracy: 1%; precision: 11%). In order to assess the degree of mineralisation, dissolved organic carbon (DOC) and inorganic carbon (IC) were determined by a Shimadzu TOC-VCSH/CSN analyser (accuracy: 0.2%; precision: 0.8%), by injecting the aqueous solutions obtained after filtration with 0.45 µm filters.

In order to determine alkalinity, samples were titrated with sulphuric acid to pH 4, and total alkalinity was calculated based on the volume of the acid used for the titration. Dissolved oxygen was determined by a portable oximeter with a polarographic oxygen electrode (OXI 45, CRISON). Conductivity was measured by a portable conductivity-meter (CM35, CRISON; accuracy: 1.24%; precision: 1%).

The analytical methodology carried out for the quantification of emerging contaminants is based on conventional solid phase extraction (C18 SPE cartridges) followed by liquid chromatography (LC) of the extract with detection by triple quadrupole mass spectrometry (Agilent 6460 Triple Quadrupole LC/MS System; mass accuracy: 0.1 Da from 5–1,000 m/z; 0.01% from 1,000–2,000 m/z; 0.02% from 2,000–3,000 m/z). The chromatographic program was based on the method

developed by Petrovic et al. (2014) for the measurement of pharmaceuticals in both wastewater and surface water.

### ***2.3. Photochemical modelling***

The direct and indirect photochemistry processes were modelled with the APEX software (Aquatic 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 of xenobiotics, sunlight irradiance, and data of water chemistry and depth (Bodrato and Vione, 2014). The data of xenobiotics photoreactivity were derived from the literature (Vione et al., 2011; De Laurentiis et al., 2012; Avetta et al., 2016). The solar spectrum used in model calculations was obtained for fair-weather conditions and for the geographic coordinates of Badajoz with the UCAR-TUV calculator by the National Center for Atmospheric Research (NCAR, 2017), and it was referred to the actual sampling months (exactly, the 15<sup>th</sup> day of each relevant month). A 24-hour averaged spectrum was obtained in each case and used for calculations, thus the predicted first-order rate constants  $k$  are expressed in time units ( $\text{day}^{-1}$ ) that represent 24-h days of the each month. In addition to the first-order rate constants, in this work we also report the more intuitive half-life times, calculated as  $t_{1/2} = \ln 2 k^{-1}$  and expressed in the same day units.

Water chemistry data needed by the model were obtained from the river water sampling campaign. In particular, the values of nitrate, nitrite and dissolved oxygen (the latter to assess the <sup>3</sup>CDOM\* decay kinetics) were converted into molar units, the DOC was used as such, and the concentration values of bicarbonate and carbonate were derived from the inorganic carbon (IC) data and from the pH values. It was used a standard depth  $d = 3$  m that is reasonably representative of the Guadiana river at the sampling site. The content of both DOM and CDOM in river water was derived from the

DOC values following the procedure reported by Bodrato and Vione (2014). APEX calculates the absorption of radiation by the photosensitisers (CDOM, nitrate and nitrite) and the target xenobiotics on the basis of competition for sunlight irradiance, in a Lambert-Beer approach (Bodrato and Vione, 2014; Braslavsky, 2007). The model results apply to well-mixed waters and provide average values over the water column, with contributions from the well-illuminated surface layer and from darker water in the lower depths, where irradiance is very low (Loiselle et al., 2008).

### 3. Results and Discussion

The wastewater discharged by the Badajoz WWTP into the Guadiana River contained several emerging contaminants at detectable ( $\sim \text{ng L}^{-1}$ ) levels, which were also detected at a river sampling site located 1 km downstream of the WWTP. The detected contaminants included pharmaceuticals (trimethoprim, primidone, sulfamethoxazole, diphenylhydramine, diltiazem, fluoxetine, carbamazepine, norgestrel, diclofenac, gemfibrozil, ibuprofen, naproxen), personal care products (N,N-Diethyl-meta-toluamide, triclosan), diet-related compounds (caffeine, sucralose), as well as tris(2-chloroethyl) phosphate (flame retardant and plasticiser), benzophenone (UV filter) and perfluorooctanoate (derived from the degradation of fluorotelomer-based polymers). Such compounds are typically found in WWTP effluents from all over the world (Deblonde et al., 2011).

For three of the detected contaminants, namely carbamazepine (CBZ), ibuprofen (IBU) and diclofenac (DIC), the photochemical reactivity is known in sufficient detail to allow for the modelling of photochemical degradation. Moreover, model predictions for these three compounds have been previously validated by comparison with field attenuation data available for surface-water environments (Vione et al., 2011; De Laurentiis et al., 2012; Avetta et al., 2016). There is thus some evidence that photochemical modelling can give insight into the environmental behaviour of CBZ, IBU and DIC. The photochemical degradation kinetics of a given compound depends both on its intrinsic photoreactivity and on environmental features such as sunlight irradiance, water chemistry and depth (Boreen et al., 2003; Vione et al., 2014). The photoreactivity parameters of CBZ, IBU and DIC are shown in **Table 1**. The main monitored chemical data of the Guadiana River water, referred to monthly samplings carried out in the year 2016 (plus an additional sampling in March 2017) are provided in **Table 2**.

The three investigated compounds are all potentially hazardous for aquatic organisms (Ferrari et al., 2003; Letzel et al., 2009; Gamarra Jr. et al., 2014). In our March 2017 sample, DIC had the nearest level to the predicted no-effect concentration, PNEC (24 ng L<sup>-1</sup> in river water, compared to PNEC values ranging from 115 ng L<sup>-1</sup> to over 10 µg L<sup>-1</sup> depending on the literature source; Ferrari et al., 2004; Grung et al., 2006). The concentration of CBZ was 6 ng L<sup>-1</sup> (PNEC = 500 ng L<sup>-1</sup>), while that of IBU was 49 ng L<sup>-1</sup> (PNEC = 20 µg L<sup>-1</sup>) (Ferrari et al., 2004; Grung et al., 2006). The consistent finding of concentration values below the PNECs is, unfortunately, of limited significance for the state of the environment because it refers to a single grab sample that is hardly representative of the variable occurrence over time of xenobiotics in wastewater (Majewsky et al., 2011). Anyway, the occurrence of CBZ, IBU and DIC in wastewater and river water accounts for the importance of addressing their photochemical attenuation kinetics and pathways.

At least some of the seasonal trends of the water chemistry parameters reported in **Table 2** can be explained by known processes. For instance, nitrate undergoes important fluctuations that are expected for a nutrient that is consumed by algal growth. The low nitrate values in the period from June to August can be explained by its transformation into organic nitrogen by microorganisms, which are more abundant in summertime because of enhanced photosynthesis (Mulholland and Hill, 1997). The growth of algae also enhances the transformation of inorganic into organic carbon, and algal death/lysis is an important supply of water-soluble organic compounds to freshwater during the summer season (Oliver et al., 2016; Wunsch et al., 2016). This issue might explain why the dissolved organic carbon (DOC) was higher in the period from May to July compared to the preceding months (February to April). Another phenomenon taking place in the warm seasons, characterised by higher water temperature, is the precipitation of CaCO<sub>3</sub> that decreases the water alkalinity (Effler et al., 1987). Coherently, in our case the measured alkalinity was generally lower in spring-summer than in the other months of the year.

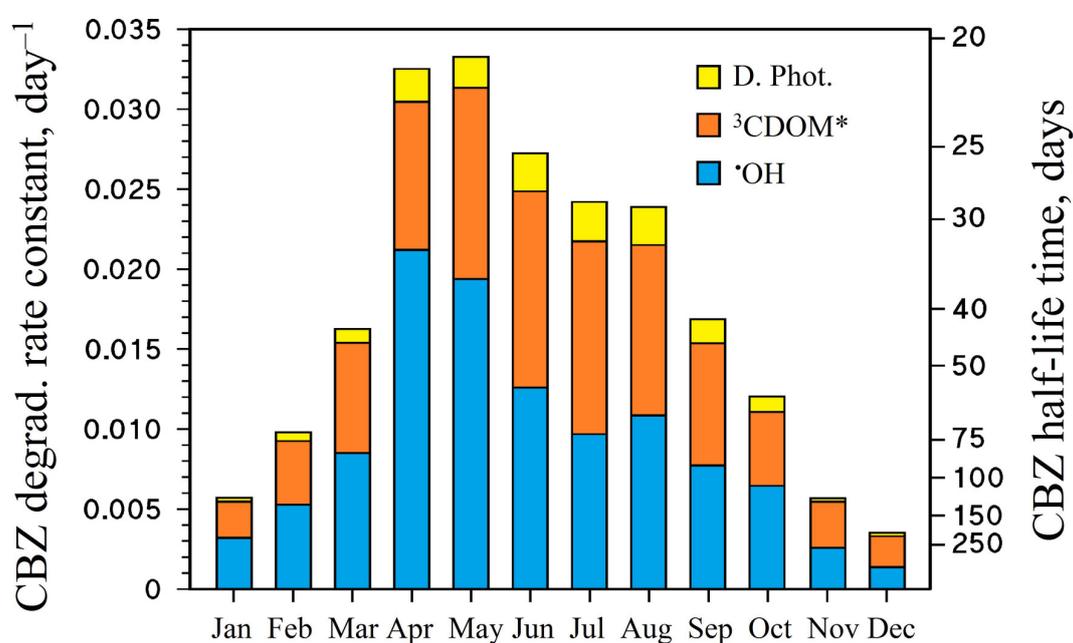
The seasonal trends and fluctuations of the chemical parameters, together with the irradiance of sunlight, all affect the photochemical processes and, therefore, the overall kinetics of xenobiotics phototransformation. For instance, considering that nitrate is a  $\bullet\text{OH}$  source while DOM (measured as the DOC) is a  $\bullet\text{OH}$  sink (Vione et al., 2014), the summer minima of nitrate and the maxima of DOC (the latter are little pronounced in the Guadiana River) would partially offset the high sunlight irradiance in the summer months, as far as the  $\bullet\text{OH}$  processes are concerned. A similar consideration holds for  $\text{CO}_3^{\bullet-}$  as well. Moreover, reactions induced by  ${}^3\text{CDOM}^*$  and  ${}^1\text{O}_2$  tend to be favoured, and the direct photolysis inhibited, in high-DOC waters. The three considered xenobiotics (CBZ, IBU and DIC) are mainly photodegraded by direct photolysis and reactions with  $\bullet\text{OH}$  and  ${}^3\text{CDOM}^*$ , while degradation by  ${}^1\text{O}_2$  and  $\text{CO}_3^{\bullet-}$  plays a minor to negligible role (Vione et al., 2011; De Laurentiis et al., 2012; Avetta et al., 2016). Of the relevant reactions, those involving  ${}^3\text{CDOM}^*$  are the most uncertain to be modelled because of the largely undefined nature of CDOM, which is expected to vary in different environments. Such variations have implications both for the CDOM ability to induce the formation of  ${}^3\text{CDOM}^*$  under illumination, and for the reactivity of  ${}^3\text{CDOM}^*$  toward a particular xenobiotic. Indeed, the overall behaviour of CDOM/ ${}^3\text{CDOM}^*$  in irradiated natural waters likely depends on the aggregate properties of a large number of generally unknown photosensitisers, which might occur at different extents in different conditions (McNeill and Canonica, 2016).

The modelled phototransformation rate constants of CBZ in the different months are shown in **Figure 2**. It can be inferred that CBZ would mainly be photodegraded by  $\bullet\text{OH}$  and  ${}^3\text{CDOM}^*$  (with the above-reported caveat for the latter), with a secondary role of the direct photolysis. As expected, the predicted phototransformation is faster during the warmer seasons and, when considering an intrinsic uncertainty in these predictions of at least 20-30% (Bodrato and Vione, 2014), the whole period from April to August looks as the most favourable to the photoinduced reactions. Although

the difference is hardly significant given the model uncertainties, one can notice that the predicted phototransformation rate constants were somewhat higher in April and May compared to June, despite the generally more intense sunlight irradiance in June. The reason is that in April and May the levels of nitrate and nitrite ( $\bullet\text{OH}$  sources) were higher, and at the same time the levels of DOM ( $\bullet\text{OH}$  sink) were lower compared to June (see **Table 2**). **Figure 2** coherently suggests that the phototransformation of CBZ in April and May would be strongly linked to the  $\bullet\text{OH}$  reactions. Interestingly, the predicted CBZ transformation rate constant was lower by less than 10% in March 2017 (not shown) compared to March 2016, which is far below the model uncertainty.

The predicted CBZ phototransformation kinetics would produce half-life times of at least three weeks - one month. Because of the considerably biorecalcitrant nature of CBZ (Zuccato et al., 2005), photochemical transformation with half-life times below one month has the potential to be the main attenuation process for this compound in the warm season. To get some insight into the significance of this finding, one should take into account the in-stream time spent by water in the river basin. The in-stream time is different from the residence time or age of water in the catchment, which strongly depends on exchanges with aquifers and can be determined with tracer methods based on stable isotopes (McGuire and McDonnell, 2006). In contrast, the in-stream time largely depends on the flow velocity. Under low-flow conditions, the flow velocity in a river can be as low as  $0.1 \text{ m s}^{-1}$  (Worrall et al., 2014). With the half-life values predicted for CBZ in April-August, this means a travel distance of around 200 km that is not far from the  $\sim 240$  km length of the Guadiana River from Badajoz to the sea. It should be underlined that the occurrence of variable environmental conditions, including the presence of several dams on the Guadiana River downstream of Badajoz, makes the present calculation just a very rough assessment. Still, it can be inferred that significant CBZ photodegradation could take place under very low flow velocity conditions, which in a river environment are usually associated with water scarcity and with a decreasing water depth (Worrall et al., 2014). Because the photoreaction rates are higher in shallow water (Boreen et al., 2003;

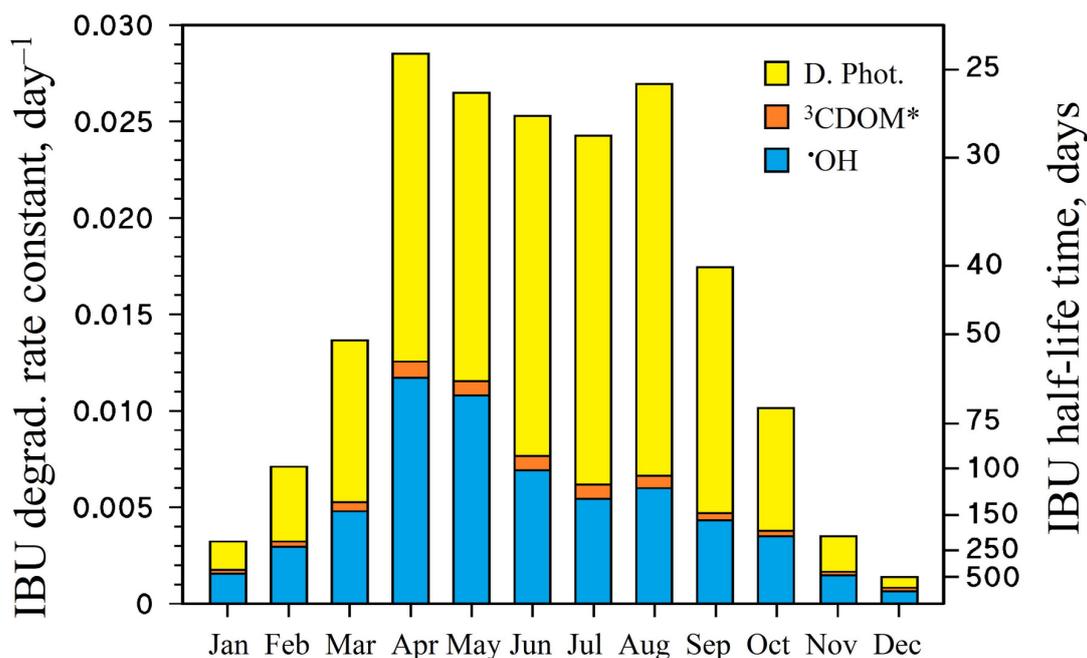
Avetta et al., 2016), water scarcity could enhance photochemistry by the combined action of faster processes in shallow water and longer in-stream water residence times (*vide infra*). In contrast, in the presence of a  $1 \text{ m s}^{-1}$  flow velocity that has been observed under non-scarcity conditions in the Guadiana and similar river systems in the Iberian Peninsula (Godinho et al., 2000; Kilsby et al., 2007; Barbosa et al., 2010), one might expect a <10% photodegradation potential for CBZ before the river discharge into the sea. The latter estimate is consistent with the approximately conservative behaviour that is usually reported for CBZ in river water (Schwientek et al., 2016).



**Figure 2.** Predicted rate constants of CBZ photodegradation in the Guadiana River, induced by the main photochemical processes ( $\cdot\text{OH}$ ,  ${}^3\text{CDOM}^*$  and direct photolysis) in the different months of the year. Here and in the following graphs it was assumed a water depth of 3 m. The right Y-axis reports the half-life times  $t_{1/2}$  corresponding to the rate constants  $k$  ( $t_{1/2} = \ln 2 \ k^{-1}$ ). D.Phot. = direct photolysis. When comparing the different values, consider a model prediction uncertainty of at least 20-30%. Time units are days of each relevant month.

Among the CBZ phototransformation intermediates, acridine is a compound of concern because of its mutagenicity. Acridine is formed with relatively low yields (3.6% of transformed CBZ by direct photolysis, 3.1% by  $\bullet$ OH reaction, no formation by  $^3$ CDOM\*; De Laurentiis et al., 2012) that are, however, offset by its potential impact on the environment. In the case of the Guadiana River, where CBZ direct photolysis is hardly important (see **Figure 2**), it is suggested that most of acridine would be photogenerated by the  $\bullet$ OH process.

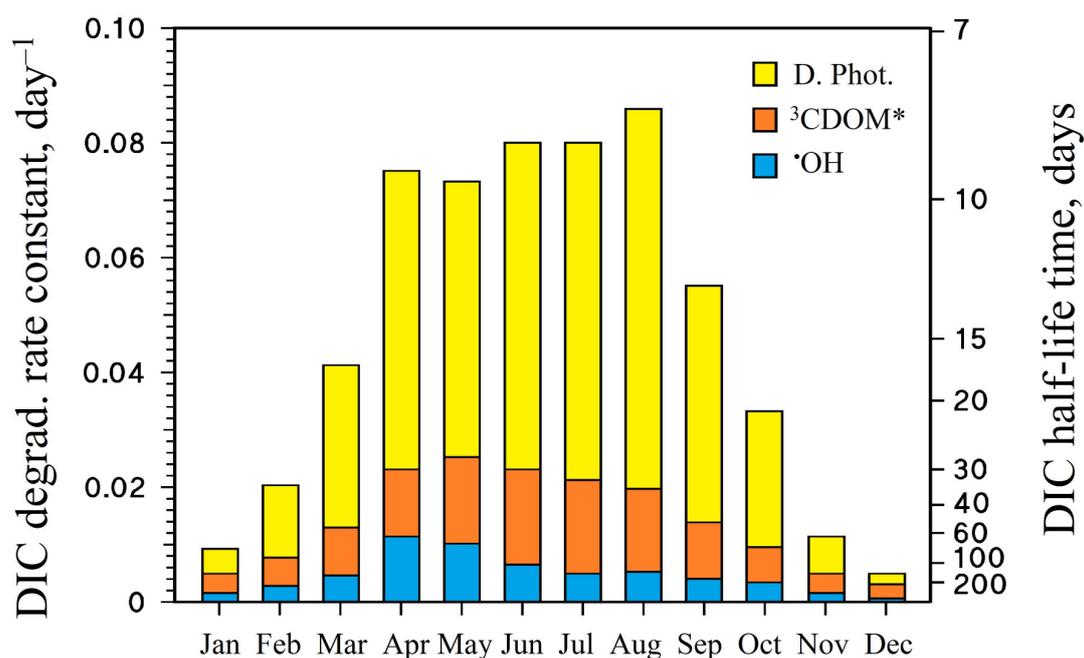
The modelled phototransformation kinetics of IBU are reported in **Figure 3**. One can notice limited degradation by  $^3$ CDOM\*, while the direct photolysis and the  $\bullet$ OH reaction would predominate. The direct photolysis would be on average the main process, especially in the summer months when the overall photodegradation of IBU is expected to be most significant. The plot suggests that, similarly to the case of CBZ, the period from April to August would be the most favourable to IBU photodegradation, with photochemical half-life times longer than 25 days. As in the case of CBZ, a <10% difference in the modelled IBU photodegradation rate constants was obtained between March 2016 and March 2017. The IBU photochemical half-lives obtained here are comparable to those of CBZ, and they are significantly longer than the few days usually reported for the attenuation of IBU in river water, presumably due to biological processes (Kunkel and Radke, 2008 & 2011; Radke et al., 2010). Therefore, photochemistry is likely to play a secondary role in the attenuation of IBU downstream of the Badajoz WWTP. Among the IBU phototransformation intermediates, 4-isobutylacetophenone (IBAP) is known to be more toxic than the parent compound. IBAP is formed at ~25% yield of reacted IBU upon direct photolysis, ~2% yield upon  $\bullet$ OH reaction, and ~31% yield by  $^3$ CDOM\* (Ruggeri et al., 2013). In the context of the Guadiana River water, the direct photolysis is expected to be the photochemical process that would account for most of IBAP production. However, despite the important yield by direct photolysis, the actual formation of IBAP would be limited by the low IBU fraction that is expected to react photochemically.



**Figure 3.** Predicted photodegradation rate constants (left Y-axis) and half-life times (right Y-axis) of IBU in the Guadiana River, involving the main photochemical processes ( $\cdot\text{OH}$ ,  $^3\text{CDOM}^*$  and direct photolysis, D.Phot.) in the different months of the year. When comparing the different values, consider a model prediction uncertainty of at least 20-30%. Time units are days of each relevant month.

The modelled phototransformation kinetics of DIC are reported in **Figure 4**. Once again the April-August period appears to be the most favourable to phototransformation, with differences in the degradation rate constants that are considerably lower than the model uncertainties. The direct photolysis is expected to dominate the photochemical transformation of DIC, especially in spring-summer, with secondary contributions from the reactions triggered by  $\cdot\text{OH}$  and  $^3\text{CDOM}^*$ . Transformation half-lives ranging from a week to ten days are foreseen for DIC in river water from April to August, thereby suggesting that DIC would be significantly more photolabile than CBZ or IBU. Under very low-flow conditions ( $0.1 \text{ m s}^{-1}$  flow velocity), one can roughly assess that up to 90% DIC could be photodegraded in the Guadiana River. That percentage might decrease to 20%

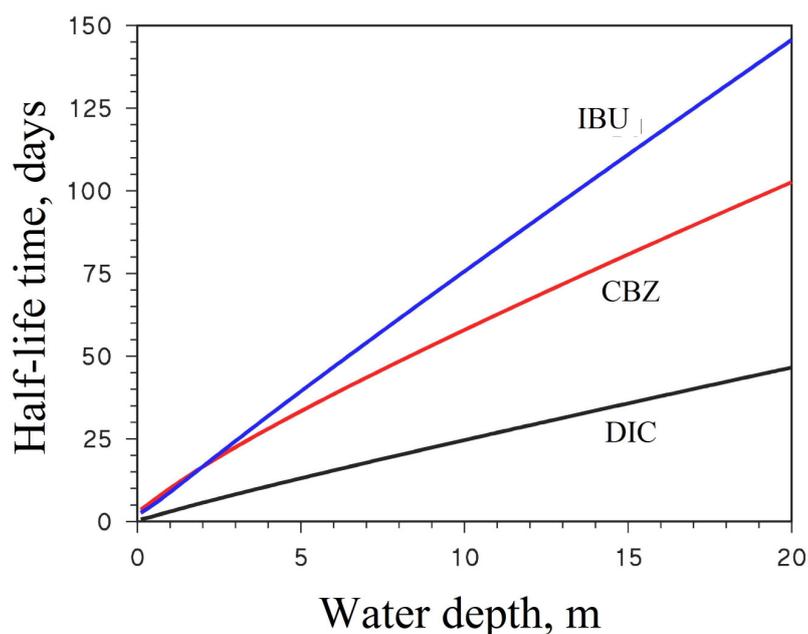
with  $1 \text{ m s}^{-1}$  flow velocity. The modelled half-life times are comparable to those reported for DIC biological attenuation in river water (Kunkel and Radke, 2008 & 2011; Radke et al., 2010), thereby suggesting that photo- and biodegradation may play roughly comparable roles in the removal of this compound. Significant phototransformation in river water has for instance been proven in the case of naproxen, which has comparable photolability as DIC (Avetta et al., 2016). The direct photolysis of DIC, which is its main predicted phototransformation pathway, is known to proceed at least partially by photocyclisation with production of transformation intermediates that could be more toxic than DIC itself towards aquatic organisms (Avetta et al., 2016). The intermediate formation yields are unfortunately not available due to lack of standards, which prevents the assessment of the toxicity budget between transformed DIC and the photogenerated compounds.



**Figure 4.** Predicted photodegradation rate constants (left Y-axis) and half-life times (right Y-axis) of DIC in the Guadiana River, induced by the main photochemical processes ( $\cdot\text{OH}$ ,  $^3\text{CDOM}^*$  and direct photolysis, D.Phot.) in the different months of the year. When comparing the different values, consider a model prediction uncertainty of at least 20-30%. Time units are days of each relevant month.

The potential of sunlit river water to induce the photodegradation of emerging contaminants is thus expected to be higher under low-flow conditions, which are favoured by water scarcity. Water scarcity is also connected with low water column depths, and photochemical reactions are known to be enhanced in shallow water (Minella et al., 2013). The impact of water depth on the photochemical half-life times of the compounds under consideration is reported in **Figure 5**, which shows that the half-life times scale almost linearly with depth. IBU and CBZ have similar half-lives in shallow water, but the IBU lifetime increases faster than the CBZ one as the depth increases. The reason is the importance of the direct photolysis in the case of UVB-absorbing IBU, because UVB radiation shows limited penetration inside the water columns compared to longer-wavelength radiation. In contrast, CBZ is mainly degraded by  $\bullet\text{OH}$  and  $^3\text{CDOM}^*$  that are photochemically produced by nitrate and, most notably, nitrite and CDOM. The latter species absorb UVA and (for CDOM) also visible radiation, which reach deeper layers in the water columns compared to UVB radiation (Loiselle et al., 2008).

Our results suggest a potentially important link between water scarcity conditions and photochemical reactions in river water. Ongoing climate change in the Mediterranean region is expected to affect overall precipitation, and the current projections for the Iberian peninsula foresee a significant precipitation decrease in the next decades, although with quite variable annual average figures (from -5% to even -30-40%) (Giorgi and Lionello, 2008; Gualdi et al., 2013). Moreover, independently of the overall precipitation amount, in the next years it is very likely that long water scarcity periods in the warm seasons will be alternated with strong precipitation events (Trenberth et al., 2003). Lengthy drought periods could favour photochemical reactions in river water, provided that they do not lead to complete river bed desiccation. Moreover, during low-flow conditions the dilution of wastewater is less effective and the concentration of xenobiotics in river water can become quite high (Petrovic et al., 2011).



**Figure 5.** Predicted half-life times of CBZ, IBU and DIC as a function of the water depth. The model calculations used average NCAR sunlight irradiance data, as well as average concentration values of photosensitisers and scavengers detected in the Guadiana River in the period from April to August, when the phototransformation kinetics were comparable. In particular, we used  $8.8 \text{ mgNO}_3^- \text{ L}^{-1}$  nitrate,  $0.64 \text{ mgNO}_2^- \text{ L}^{-1}$  nitrite,  $7.6 \text{ mg}_c \text{ L}^{-1}$  DOC,  $27 \text{ mg}_c \text{ L}^{-1}$  inorganic carbon, pH 7.6, and  $5.1 \text{ mg L}^{-1}$  dissolved  $\text{O}_2$ .

Based on our approximate assessment concerning the Guadiana River, the phototransformation of CBZ and DIC might be relatively limited (10-20%) under typical flow conditions, but it could become quite important (>50%) in the case of prolonged droughts.

## 4. Conclusions

Among the xenobiotics detected at the outlet of the Badajoz WWTP, as well as in the Guadiana River 1 km downstream of the WWTP, photochemical modelling can be carried out for CBZ, IBU and DIC. Photoreactivity parameters are in fact available for these compounds, and photodegradation predictions have been validated previously against field results. Based on clear-sky sunlight irradiance, and on water chemistry data obtained in a year-round sampling campaign in the Guadiana River, our photochemical model suggests that photodegradation would be most important in the months from April to August, and quite slow in winter. Interestingly, in the months that are characterised by the highest clear-sky sunlight irradiance (June and July) the river water showed low nitrate concentrations and elevated DOC levels, which are detrimental to  $\bullet\text{OH}$  reactions and direct photolysis. Therefore, the predicted photodegradation kinetics in June and July did not differ much from those calculated for April, May and August, despite differences in irradiance. Considering that summer minima of nitrate and maxima of DOC commonly occur in several surface-water environments, this photochemical behaviour could be quite typical of surface water bodies. According to the model, DIC would be more photolabile than CBZ and IBU and, for the latter compound, photodegradation is likely to be slower than biotransformation. Comparable photodegradation and biotransformation kinetics are expected to occur for DIC, while in the case of biorefractory CBZ the photodegradation could well be the main attenuation pathway in river water during the warm seasons.

The extent of pollutant attenuation induced by photochemical reactions would depend much on the flow velocity, which affects the in-stream water residence time. In the case of CBZ and DIC, significant (although possibly not complete) phototransformation might take place in the presence of low flow velocity, which typically occurs during droughts and provides more time for the photoinduced reactions to operate in river water. Water scarcity could become more common in the

Mediterranean region in the next decades, at least during the warm seasons. These conditions may exacerbate the pollution of river water, inducing a lesser degree of wastewater dilution that may result into high concentrations of xenobiotics. However, water scarcity would also enhance photochemical attenuation processes by decreasing both the flow velocity and the water depth, inducing faster photoreactions in shallow water.

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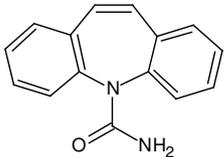
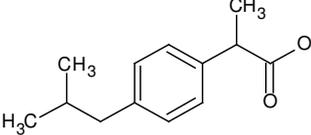
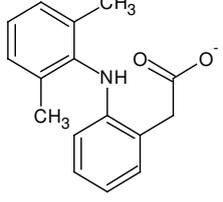
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**Table 1.** Photoreactivity parameters (direct photolysis quantum yields and second-order reaction rate constants with  $\bullet\text{OH}$ ,  $^1\text{O}_2$  and  $^3\text{CDOM}^*$ ) of the xenobiotics under consideration, where S = CBZ, IBU or DIC (IBU: Vione et al., 2011; CBZ: De Laurentiis et al., 2012; DIC: Avetta et al., 2016). The absorption spectra of these xenobiotics were taken from the same sources. There is evidence that the reaction with  $\text{CO}_3^{\bullet-}$  would not be important in the phototransformation of these compounds. The reaction rate constants with  $^3\text{CDOM}^*$  have been derived in the literature sources using several triplet sensitizers as CDOM proxies. By comparing the predicted phototransformation kinetics with those actually observed in natural surface waters, it has been possible to select which proxy rate constants were most representative of those with  $^3\text{CDOM}^*$ . Such selected rate constants are here reported.

	<b>CBZ</b> 	<b>IBU</b> 	<b>DIC</b> 
$\Phi_s$ , unitless	$7.8 \times 10^{-4}$	0.33	0.094
$k_{S,\bullet\text{OH}}$ , $\text{M}^{-1} \text{s}^{-1}$	$1.8 \times 10^{10}$	$1.0 \times 10^{10}$	$9.3 \times 10^9$
$k_{S,^1\text{O}_2}$ , $\text{M}^{-1} \text{s}^{-1}$	$1.9 \times 10^5$	$6.0 \times 10^4$	$1.3 \times 10^7$
$k_{S,^3\text{CDOM}^*}$ , $\text{M}^{-1} \text{s}^{-1}$	$7.6 \times 10^8$	$4.5 \times 10^7$	$1.0 \times 10^9$

**Table 2.** Chemical composition of the Guadiana River water, sampled 1 km downstream of the Badajoz WWTP at 0.5 m depth, in the various months of the 2016 sampling campaign. The data relative to the March 2017 sampling are also reported.

	pH	T, °C	Nitrate, mgNO <sub>3</sub> <sup>-</sup> L <sup>-1</sup>	Nitrite, mgNO <sub>2</sub> <sup>-</sup> L <sup>-1</sup>	DOC, mg <sub>C</sub> L <sup>-1</sup>	COD, mg L <sup>-1</sup>	IC, mg <sub>C</sub> L <sup>-1</sup>	Alkalinity, mg CaCO <sub>3</sub> L <sup>-1</sup>	Dissolved O <sub>2</sub> , mg L <sup>-1</sup>	Conductivity, μS cm <sup>-1</sup>
<b>Jan 2016</b>	7.5 ± 0.1	12.7 ± 0.2	11.1 ± 1.3	0.62 ± 0.14	7.75 ± 0.24	10 ± 2	31.49 ± 0.62	155 ± 11	7.2 ± 0.5	580 ± 4
<b>Feb 2016</b>	7.6 ± 0.1	16.4 ± 0.3	11.5 ± 1.1	0.18 ± 0.07	6.10 ± 0.03	23 ± 3	34.18 ± 0.23	155 ± 15	8.6 ± 0.6	690 ± 6
<b>Mar 2016</b>	7.8 ± 0.2	17.6 ± 0.2	4.9 ± 0.7	0.26 ± 0.02	6.43 ± 0.03	24 ± 3	26.41 ± 0.22	125 ± 9	6.9 ± 0.4	530 ± 2
<b>Apr 2016</b>	7.5 ± 0.1	19.1 ± 0.1	13.3 ± 1.0	1.02 ± 0.18	6.15 ± 0.10	23 ± 2	26.56 ± 0.28	130 ± 12	5.5 ± 0.3	480 ± 3
<b>May 2016</b>	7.6 ± 0.2	19.5 ± 0.1	21.7 ± 1.5	1.58 ± 0.15	8.47 ± 0.05	27 ± 3	20.33 ± 0.35	130 ± 11	5.3 ± 0.3	450 ± 4
<b>Jun 2016</b>	7.6 ± 0.1	22.2 ± 0.1	5.3 ± 0.8	0.36 ± 0.03	8.41 ± 0.04	25 ± 2	29.68 ± 0.14	125 ± 10	4.7 ± 0.2	540 ± 5
<b>Jul 2016</b>	7.8 ± 0.1	23.0 ± 0.1	1.1 ± 0.3	0.11 ± 0.02	7.82 ± 0.31	35 ± 4	28.84 ± 0.16	125 ± 7	5.0 ± 0.4	510 ± 4
<b>Aug 2016</b>	7.5 ± 0.1	25.7 ± 0.1	2.5 ± 0.5	0.13 ± 0.03	6.85 ± 0.11	24 ± 3	28.59 ± 0.24	120 ± 10	4.8 ± 0.2	470 ± 3
<b>Sep 2016</b>	8.4 ± 0.2	23.8 ± 0.1	2.5 ± 0.6	0.14 ± 0.02	6.65 ± 0.07	42 ± 6	30.25 ± 0.56	150 ± 13	7.6 ± 0.6	530 ± 2
<b>Oct 2016</b>	7.7 ± 0.1	19.2 ± 0.2	5.1 ± 0.9	0.21 ± 0.03	5.88 ± 0.09	30 ± 2	33.94 ± 0.45	155 ± 11	7.3 ± 0.4	620 ± 4
<b>Nov 2016</b>	7.7 ± 0.1	18.0 ± 0.2	0.3 ± 0.1	0.19 ± 0.02	7.55 ± 0.11	112 ± 9	26.39 ± 0.66	150 ± 9	6.7 ± 0.4	520 ± 2
<b>Dec 2016</b>	7.6 ± 0.2	14.0 ± 0.3	17.0 ± 1.4	0.15 ± 0.01	10.29 ± 0.05	23 ± 3	26.33 ± 0.07	155 ± 11	7.8 ± 0.5	640 ± 3
<b>Mar 2017</b>	8.8 ± 0.1	19.1 ± 0.2	2.5 ± 1.2	0.17 ± 0.01	6.21 ± 0.07	30 ± 5	24.42 ± 0.54	125 ± 6	8.2 ± 0.5	520 ± 2