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# Photochemical transformation of phenylurea herbicides in surface waters: A model assessment of persistence, and implications for the possible generation of hazardous intermediates

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## Abstract

This work models the phototransformation kinetics in surface waters of five phenylurea herbicides (diuron, fenuron, isoproturon, metoxuron and chlortoluron), for which important photochemical parameters are available in the literature (direct photolysis quantum yields and reaction rate constants with  $\bullet\text{OH}$ ,  $\text{CO}_3^{\bullet-}$  and the triplet states of chromophoric dissolved organic matter,  $^3\text{CDOM}^*$ ). Model calculations suggest that isoproturon and metoxuron would be the least photochemically persistent and diuron the most persistent compound. Reactions with  $\bullet\text{OH}$  and  $^3\text{CDOM}^*$  would be the main phototransformation pathways for all compounds in the majority of environmental conditions. Reaction with  $\text{CO}_3^{\bullet-}$  could be important in waters with low dissolved organic carbon (DOC), while direct photolysis would be negligible for fenuron, quite important for chlortoluron, and somewhat significant for the other compounds. The direct photolysis of metoxuron and diuron is known to increase toxicity, and such a photoreaction pathway would be enhanced at intermediate DOC values (1-4 mg C L<sup>-1</sup>). The reaction between phenylureas and  $\bullet\text{OH}$  is known to produce toxic intermediates, differently from  $^3\text{CDOM}^*$ . Therefore, the shift of reactivity from  $\bullet\text{OH}$  to  $^3\text{CDOM}^*$  with increasing DOC could reduce the environmental impact of photochemical transformation.

**Keywords:** Phenylurea herbicides; direct and indirect photolysis; environmental photochemistry; environmental chemodynamics.

## 1. Introduction

The worldwide diffusion of intensive agriculture has caused an increasing contamination of water resources by pesticides, which can reach the aquatic environment *via* runoff or leaching. Phenylurea herbicides (PUHs) are employed in large amount to control different weeds and grasses in crops. For instance, isoproturon and chlortoluron are used for cereals and fluometuron in cotton fields, while diuron also finds application as algicide in paints and coatings (Tomlin, 2009).

PUHs are quite mobile in soil because of high water solubility and low adsorption on solids. Some PUHs are also frequently detected in surface, ground and even drinking water (Kaur et al., 2012). Under environmental conditions, phenylureas can persist in groundwater for periods ranging from days to weeks depending on temperature and pH (Sanchis-Mallols et al., 1998).

In the case of surface waters, PUHs removal by sedimentation or gas exchange can be excluded based on physical-chemical properties and reactivity. Degradation occurs through a combination of biotic and abiotic processes (Nélieu et al., 2009), including direct and indirect photochemical reactions (Gerecke et al., 2001). Direct photolysis of PUHs is limited by weak sunlight absorption and moderate quantum yields. Still, it could be a significant transformation pathway under spring or summertime conditions (Boulkamh et al., 2001).

Indirect photochemistry is linked to the occurrence of reactive transients such as the radicals  $\bullet\text{OH}$  and  $\text{CO}_3^{\bullet-}$ , singlet oxygen ( $^1\text{O}_2$ ) and the excited triplet states of chromophoric dissolved organic matter ( $^3\text{CDOM}^*$ ). These species are produced by irradiation of photoactive compounds called photosensitisers, such as CDOM, nitrate and nitrite (Richard et al., 2007; Canonica, 2007; Fenner et al., 2013). Nitrate, nitrite and CDOM are all photochemical sources of  $\bullet\text{OH}$  (Page et al., 2011; Dong and Rosario-Ortiz, 2012), and irradiated CDOM also yields  $^3\text{CDOM}^*$  and  $^1\text{O}_2$ , the latter upon reaction between  $^3\text{CDOM}^*$  and  $\text{O}_2$  (Canonica and Freiburghaus, 2001; Golanoski et al., 2012). The radical  $\text{CO}_3^{\bullet-}$  is produced upon oxidation of carbonate and bicarbonate by  $\bullet\text{OH}$  and, to a lesser extent, upon carbonate oxidation by  $^3\text{CDOM}^*$  (Canonica et al., 2005). The environmental role of the cited transients depends on substrate reactivity (expressed as second-order reaction rate constants), on water chemistry and depth (Felicyn et al., 2012).

PUHs photochemistry has been the object of several studies, and a wide range of reaction rate constants and photolysis quantum yields is available for diuron (DIU), fenuron (FEN), isoproturon (IPT), metoxuron (MTX) and chlortoluron (CTL) (the chemical structures of these PUHs are reported in Figure 1-SM of the Supplementary Material, hereafter SM). Photoreactivity data allow the model assessment of photochemical persistence as a function of environmental conditions (Maddigapu et al., 2011; Vione et al., 2011; De Laurentiis et al., 2012). The goal of the present paper is to determine photochemical half-life times of the above-mentioned PUHs and the relative roles of each phototransformation pathway. The latter issue is important because peculiar photoreactions may produce harmful intermediates (Donner et al., 2013), which is often observed in the case of PUHs (Galichet et al., 2002; Bonnemoy et al., 2004; Amine-Khodja et al., 2004).

Despite the importance of assessing the environmental significance of photoreactions that could increase the PUHs impact, to our knowledge no comprehensive assessment or comparison of the different pathways involving PUHs has been carried out to date.

## 2. Methods

### 2.1. Source data

Direct photolysis quantum yields and reaction rate constants of target PUHs with  $\cdot\text{OH}$ ,  $\text{CO}_3^{\cdot-}$  and  $^3\text{CDOM}^*$  were derived from the literature (see Table 1). No data are available for the reaction of PUHs with  $^1\text{O}_2$ , which is probably negligible (Gerecke et al., 2001). Because PUHs are poor radiation absorbers in the UVB and most notably the UVA region, many photolysis quantum yields have been determined by UVC irradiation. This is unlikely to be a problem in the present context, because the quantum yields of complex molecules in solution are often independent of wavelength (Turro et al., 1978). When direct photolysis involves reactions of singlet or triplet excited states, the quantum yield does not change despite excitation of different absorption bands. Independently of the excitation wavelength and the excited state reached by absorption, radiationless deactivation causes the first excited singlet state to be reached (Tchaikovskaya et al., 2002), from which chemical transformation or inter-system crossing to the triplet state occurs (Turro et al., 1978). Excitation of different absorption bands can produce wavelength-dependent quantum yields if photoreactions are faster than deactivation, but this usually occurs with small molecules and/or in the gas phase (Young et al., 2013). Therefore, UVC quantum yields are sufficiently appropriate to assess PUHs direct photochemistry under natural sunlight.

### 2.2. Photochemical modelling

The assessment of phototransformation kinetics was carried out with the APEX software (Aqueous Photochemistry of Environmentally-occurring Xenobiotics), which predicts photochemical half-life times as a function of water chemistry and depth (Vione, 2014; Bodrato and Vione, 2014). APEX is based on a photochemical model, validated by comparison with phototransformation kinetics in surface freshwaters (Maddigapu et al., 2011; De Laurentiis et al., 2012; Marchetti et al., 2013).

Results apply to well-mixed water bodies, including the epilimnion of stratified lakes. The absorption of radiation by photosensitisers (CDOM, nitrate and nitrite) and xenobiotics is computed by taking into account competition for sunlight irradiance in a Lambert-Beer approach (Braslavsky, 2007; Bodrato and Vione, 2014). In the case of PUHs, the availability of photolysis quantum yields and second-order reaction rate constants with transients ( $\cdot\text{OH}$ ,  $\text{CO}_3^{\cdot-}$ ,  $^3\text{CDOM}^*$ ) allows the assessment of transformation kinetics. Data obtained with APEX are averages over the water column and include the contributions of the well-illuminated surface layer and of darker water at the bottom (Loiselle et al., 2008).

Sunlight irradiance is not constant in the natural environment, because of meteorological issues (not included in APEX) and of diurnal and seasonal cycles. To allow easier comparison between model results and environmental conditions, APEX uses as time unit a summer sunny day (SSD), equivalent to fair-weather 15 July at 45° N latitude. Sunlight is not vertically incident over the water surface, but refraction at the interface deviates the light path in water towards the vertical. The light path length  $l$  depends on the depth  $d$ : on 15 July at 45°N it is  $l = 1.05 d$  at noon, and  $l = 1.17 d$  at  $\pm 3$  h from noon that is a reasonable daily average (Bodrato and Vione, 2014).

### 3. Results and discussion

A major issue in the assessment of PUHs phototransformation is the reaction rate constant(s) with  $^3\text{CDOM}^*$ . A common approach consists in the use of CDOM proxies such as aromatic carbonyls or quinones (Ma et al., 2010; Golanoski et al., 2012). Table 1 reports literature reaction rate constants between PUHs and  $^3\text{CDOM}^*$ , which have been assessed by use of benzophenone (BP) and 3'-methoxyacetophenone (MAP) as proxies. With the exceptions of MTX and partially IPT, the reaction rate constants with  $^3\text{BP}^*$  are 1-2 orders of magnitude higher than those with  $^3\text{MAP}^*$ , which is a non-negligible difference as far as photochemical modelling is concerned. Gerecke et al. (2001) have studied the transformation of DIU under real sunlight, in the presence of water from the Greifensee lake (Switzerland). Irradiation of small volumes (optical path length of sunlight in the cm range) yielded a pseudo-first order rate constant  $k_{\text{DIU}} = (2.6 \pm 0.4) \cdot 10^{-4} \text{ min}^{-1} (\mu \pm \sigma)$ , which under the adopted irradiation conditions (fair-weather sunlight in July, from 10 am to 4 pm) would correspond to  $k_{\text{DIU}} = 0.09 \pm 0.01 \text{ day}^{-1}$ . With dissolved organic carbon (DOC) at 3.5 mg C L<sup>-1</sup> and 0.1 mM nitrate (as per the typical Greifensee conditions; Gerecke et al., 2001; Canonica et al., 2005), and with the reaction rate constant with  $^3\text{BP}^*$  taken as representative of  $^3\text{CDOM}^*$ , our model gives  $k_{\text{DIU}}^{\text{APEX}} = 0.08 \pm 0.02 \text{ SSD}^{-1}$ . The agreement is very good if one takes 1 SSD = 1 outdoor day of Gerecke et al. (2001), which is reasonable considering that irradiation was carried out under fair-weather summertime sunlight. The agreement between model and experiments gets worse by using the  $^3\text{MAP}^*$  rate constant. Furthermore, with the  $^3\text{MAP}^*$  data one would conclude that the reaction with  $^3\text{CDOM}^*$  plays a minor role in DIU photodegradation, which is in sharp contrast with the results obtained by Gerecke et al. (2001). Therefore, better agreement between model predictions and experimental data is obtained by using the DIU reaction rate constant with  $^3\text{BP}^*$ . There is also independent evidence that triplet-sensitised reactions play an important role in the phototransformation of PUHs (Halladja et al., 2007). For these reasons, the following discussion will be based on the  $^3\text{BP}^*$  rate constants. By using the  $^3\text{MAP}^*$  data, one gets lower importance of the  $^3\text{CDOM}^*$  transformation pathway and higher PUH persistence, particularly in DOM-rich water. The difference is more marked for DIU, FEN and CTL compared to MTX and IPT.

### 3.1. Modelled photochemical half-life times

The photochemical persistence of the PUHs under study was modelled by assuming variable water depth and DOC, and by fixing the other parameters of photochemical significance at values that may be commonly found in surface waters (0.1 mM nitrate, 1  $\mu$ M nitrite, 2 mM bicarbonate and 10  $\mu$ M carbonate; Gerecke et al., 2001; Polesello et al., 2006). The bicarbonate/carbonate ratio would correspond to pH  $\sim$  7.5 (Martell et al., 1997). The same water conditions were chosen for all the substrates, to facilitate comparisons.

Figure 1 shows that the half-life times follow the order IPT  $\sim$  MTX < CTL < FEN < DIU. Therefore, IPT and MTX would be the least photochemically persistent and DIU the most persistent compound. The half-life times increase with sunlight path length (*i.e.*, with depth), because in a deep water body only the surface is thoroughly illuminated by sunlight. The reported average result combines considerable photoreactivity in the upper layer with poor or even absent photoreactivity at the bottom.

The increase of the half-life time with DOC (which measures both DOM and CDOM in the model) is a consequence of several factors. Reaction with  $\bullet$ OH is usually inhibited in high-DOC waters because, although CDOM is an important  $\bullet$ OH source, DOM is usually a more important scavenger and the steady-state [ $\bullet$ OH] is often anticorrelated with DOC (Brezonik and Fulkerson-Brekken, 1998). A similar consideration holds for  $\text{CO}_3^{\bullet-}$ , which is mainly produced upon oxidation of carbonate and bicarbonate by  $\bullet$ OH. In fact, scavenging of  $\bullet$ OH by DOM inhibits the  $\bullet$ OH reaction with inorganic carbon that yields  $\text{CO}_3^{\bullet-}$ , which is additionally consumed by DOM itself (Canonica et al., 2005). Direct photolysis processes are inhibited in high-DOC waters because of competition for sunlight irradiance between the substrate and CDOM, which is the main sunlight absorber in surface waters below 500 nm (Galgani et al., 2011). In contrast,  $^3\text{CDOM}^*$  reactions would be enhanced by a DOC increase (and the  $^1\text{O}_2$  ones as well, but singlet oxygen is poorly reactive towards PUHs; Gerecke et al., 2001). The increase of half-life times with DOC suggests that the enhancement of  $^3\text{CDOM}^*$  would not offset the inhibition of the other photoprocesses. The likely reason is that CDOM easily saturates radiation absorption if the optical path length is in the metre range. Increasing DOC would thus produce a limited increase of the photon flux absorbed by CDOM and, as a consequence, of the  $^3\text{CDOM}^*$  formation rate (Maloney et al., 2005), thereby levelling off the steady-state [ $^3\text{CDOM}^*$ ] (see Figure 2-SM). In contrast, [ $\bullet$ OH] and [ $\text{CO}_3^{\bullet-}$ ] would steadily decrease with increasing DOC (Brezonik and Fulkerson-Brekken, 1998). The absorption saturation effect by CDOM may not be evident in laboratory experiments (Gerecke et al., 2001), where the adopted optical path length is much shorter compared to typical environmental conditions.

An issue that is not included in our model is that DOM contains antioxidant moieties that could inhibit the transformation of pollutants by  $^3\text{CDOM}^*$ . The inhibition is a consequence of the reduction, by DOM antioxidants, of the radical species arising from the oxidation of substrates by  $^3\text{CDOM}^*$ , giving back the starting compounds and slowing down transformation (Wenk et al.,

2011). Such an effect is not particularly important in the case of PUHs (Canonica and Lubscher, 2008), probably because the related radical species are not easily reduced to the original compounds.

### 3.2. Relative role of different photoprocesses in PUHs transformation

Figure 2 reports the modelled fractions of IPT degradation that are accounted for by  $\bullet\text{OH}$ ,  ${}^3\text{CDOM}^*$ ,  $\text{CO}_3^{\bullet-}$  and the direct photolysis, as a function of DOC and the sunlight path length, for constant values of the other water parameters (same as for Figure 1). IPT is the most photolabile among the studied PUHs (see Figure 1), and its transformation would be mostly accounted for by  $\bullet\text{OH}$  and  $\text{CO}_3^{\bullet-}$  at low DOC and by  ${}^3\text{CDOM}^*$  at high DOC. The relative importance of direct photolysis would be  $\sim 10\%$  under the most favourable conditions ( $\text{DOC} = 1\text{-}3 \text{ mg C L}^{-1}$ ).

The fractions of IPT transformation by both  $\bullet\text{OH}$  and the direct photolysis have a maximum with increasing DOC, because photodegradation follows four different pathways. Of these,  $\bullet\text{OH}$ ,  $\text{CO}_3^{\bullet-}$  and the direct photolysis are inhibited by DOC, while  ${}^3\text{CDOM}^*$  is enhanced. The inhibition by increasing DOC (and, therefore, increasing DOM and CDOM) of the  $\text{CO}_3^{\bullet-}$  pathway is much larger compared to  $\bullet\text{OH}$  and the direct photolysis, because of a double negative effect: DOM both scavenges  $\text{CO}_3^{\bullet-}$  and inhibits its formation by consuming  $\bullet\text{OH}$  (Canonica et al., 2005). Therefore, at low DOC the main effect of increasing organic matter would be the inhibition of  $\text{CO}_3^{\bullet-}$  reactions to the initial advantage of direct photolysis and  $\bullet\text{OH}$ , while the importance of  ${}^3\text{CDOM}^*$  would still be limited. A further increase of DOC is expected to enhance significantly  ${}^3\text{CDOM}^*$  at the expense of the other processes. Coherently, Figure 2 shows that the fraction of IPT transformation by  $\text{CO}_3^{\bullet-}$  monotonically decreases and that of  ${}^3\text{CDOM}^*$  monotonically increases with increasing DOC.

The fraction of IPT transformation accounted for by direct photolysis decreases as the water depth increases, because IPT mainly absorbs sunlight in the UVB region. The shorter wavelengths penetrate little in the water column, because they are most effectively absorbed by CDOM (Del Vecchio and Blough, 2004). In contrast, CDOM also absorbs visible radiation that penetrates more deeply in water and induces  ${}^3\text{CDOM}^*$  generation. Therefore, the relative role of  ${}^3\text{CDOM}^*$  increases if the water column gets deeper. The depth effect is less important for  $\bullet\text{OH}$ , which is produced by both UV-absorbing compounds (nitrate and nitrite) and CDOM. A similar issue holds for  $\text{CO}_3^{\bullet-}$ , which is mainly produced by  $\bullet\text{OH}$ .

Many of the trends highlighted in the case of IPT are also valid for the other compounds, and most notably for CTL (see Figure 3-SM) and FEN (see Figure 4-SM). CTL is the studied substrate for which direct photolysis would be most important (up to 40% of total photodegradation), while the case of FEN is the opposite as photolysis would account for less than 1% transformation.

Among the studied PUHs, MTX is the most reactive towards  $\text{CO}_3^{\bullet-}$  and the relevant pathway accounts for most of MTX degradation at low DOC (up to 80% of total transformation). However, the  $\text{CO}_3^{\bullet-}$  importance quickly decreases as DOC increases (see Figure 5-SM). Because of the strong inhibition of  $\text{CO}_3^{\bullet-}$  reactions carried out by DOM, the degradation of PUHs by  $\text{CO}_3^{\bullet-}$  would be



important in low-DOC waters only. Moreover, the modelled conditions (and in particular the bicarbonate/carbonate ratio) are referred to pH ~ 7.5. Such conditions would also be relevant to the pH interval 7-8, where the steady-state  $[\text{CO}_3^{\bullet-}]$  is expected to undergo rather limited variations (De Laurentiis et al., 2014). Reactions induced by  $\text{CO}_3^{\bullet-}$  would become less significant than shown in the plots at pH < 7, and more important at pH > 8.

DIU is the studied PUH with the highest ratio of  $k_{\bullet\text{OH}}(k_{\text{CDOM}^*})^{-1}$  (second-order rate constants, see Table 1). Therefore,  $\bullet\text{OH}$  would play a more important role in DIU photodegradation compared to the other compounds (up to 70% of the total, see Figure 6-SM).

### 3.3. Possible photochemical production of harmful PUHs intermediates

Photochemical PUHs transformation may produce intermediates that are more toxic than the parent compounds (Farran and Ruiz, 2004). For instance, the toxicity of MTX and DIU is known to be increased by direct photolysis (Bonnemoy et al., 2004), possibly because of the formation of toxic formylated and demethylated intermediates (Tixier et al., 2001). Direct photolysis would account for up to 7% of the overall photochemical transformation of DIU (see Figure 6-SM), and for up to 16% of that of MTX (Figure 5-SM). The associated increase of toxicity could thus be environmentally significant.

The reaction of IPT with  $\bullet\text{OH}$  is known to produce, in addition to ring-hydroxylated derivatives, toxic N-formyl compounds in which the  $-\text{N(R)CHO}$  functions (where R may be H or  $\text{CH}_3$ ) derive from oxidation, and demethylation if applicable, of  $-\text{N}(\text{CH}_3)_2$ . These intermediates could account for increased toxicity upon IPT indirect phototransformation (Galichet et al., 2002), because they are among the most toxic PUHs derivatives (Tixier et al., 2001). The  $\bullet\text{OH}$  pathway can account for up to 30-35% of the overall photoreaction kinetics of IPT under favourable conditions (see Figure 2), thus the production of harmful compounds by IPT +  $\bullet\text{OH}$  cannot be neglected. In surface waters the process would be particularly significant at 1-2 mg C L<sup>-1</sup> DOC, where the importance of the  $\bullet\text{OH}$  reactions would be higher. The formation of N-formyl intermediates has also been observed in the degradation of other PUHs by  $\bullet\text{OH}$  (Poulain et al., 2003; Halladja et al., 2007; Shankar et al., 2008).

The transformation of PUHs by irradiated humic and fulvic acids (important CDOM components) has been shown to produce dimeric species as well as ring-hydroxylated compounds. The latter largely overlap with those produced by  $\bullet\text{OH}$  (Amine-Khodja et al., 2004; Halladja et al., 2007). A first reason could be that humic substances (HS) produce some  $\bullet\text{OH}$  under irradiation (Coelho et al., 2011; Jacobs et al., 2011). Moreover, the excited triplet states  $^3\text{HS}^*$  could also act as low-level hydroxylating species, which simulate  $\bullet\text{OH}$  reactivity in some conditions but not under all circumstances (Page et al., 2011). For instance, irradiated HS do not produce N-formyl compounds to a significant extent (Amine-Khodja et al., 2004; Halladja et al., 2007). In this case, the reactivity shift from  $\bullet\text{OH}$  to  $^3\text{CDOM}^*$  that occurs in surface waters with increasing DOC could reduce the formation of toxic intermediates from PUHs.

## 4. Conclusions

The persistence of the considered phenylurea herbicides in surface waters, as far as photochemical reactions are concerned, would be in the following order (from the least to the most persistent): IPT ~ MTX < CTL < FEN < DIU. PUHs would undergo photochemical transformation *via* a variety of pathways, including reactions with  $\cdot\text{OH}$ ,  ${}^3\text{CDOM}^*$  and  $\text{CO}_3^{\cdot-}$ , as well as direct photolysis. Reactions with  ${}^3\text{CDOM}^*$  and  $\cdot\text{OH}$  would be the main photochemical pathways in most environments. By considering PUHs reactivity with  ${}^3\text{BP}^*$  (BP as CDOM proxy), it is predicted that  ${}^3\text{CDOM}^*$  would play the most important role in the transformation of IPT, FEN and CTL under the majority of environmental conditions. Overall,  ${}^3\text{CDOM}^*$ -mediated processes would predominate in deep waters with high DOC.

The reaction with  $\text{CO}_3^{\cdot-}$  could be important in low-DOC waters, where it would account for instance for a very considerable fraction of MTX transformation (even 80% at pH ~ 7.5). The water pH values would play a substantial role on  $\text{CO}_3^{\cdot-}$ -mediated processes: the steady-state  $[\text{CO}_3^{\cdot-}]$  would undergo limited variations in the 7-8 pH interval, but it would rapidly decrease at pH < 7 and rapidly increase at pH > 8. Direct photolysis could be quite important for CTL (up to 40% of overall transformation), and would be negligible for FEN (always below 1%).

The phototransformation of several PUHs is known to produce intermediates that are more toxic than the parent compounds, which happens for instance in the photolysis of both MTX and DIU. Because photolysis accounts for up to 16% of MTX and up to 7% of DIU transformation at intermediate DOC values in shallow waters, the process could be of environmental concern.

Reaction between IPT and  $\cdot\text{OH}$  is known to yield toxic N-formyl intermediates. The process could be environmentally important, because  $\cdot\text{OH}$  would cause up to 30-35% of IPT phototransformation. The production of potentially toxic N-formylated compounds has been described for other PUHs in the presence of  $\cdot\text{OH}$ , while reaction with  ${}^3\text{CDOM}^*$  seems not to yield such species. The reactivity shift in surface-water photochemistry, from  $\cdot\text{OH}$  to  ${}^3\text{CDOM}^*$  with increasing DOC, could thus decrease the potential of photochemical reactions to produce toxic species upon PUH transformation.

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**Table 1.** Photolysis quantum yields ( $\Phi_{\text{phot}}$ ) of the investigated PUHs (DIU, FEN, MTX, IPT and CTL) and their second-order rate constants for the reaction with the main photoinduced transients ( $\text{CO}_3^{\cdot-}$ ,  $\cdot\text{OH}$ ,  $^3\text{BP}^*$  and  $^3\text{MAP}^*$  as  $^3\text{CDOM}^*$  proxies).

		DIURON (DIU)	FENURON (FEN)	METOXURON (MTX)	ISOPROTURON (IPT)	CHLORTOLURON (CTL)
$\Phi_{\text{Phot}}$		$1.25 \cdot 10^{-2}$ [a]	$6 \cdot 10^{-3}$ [e]	$2 \cdot 10^{-2}$ [b]	$2 \cdot 10^{-3}$ [g]	$3 \cdot 10^{-2}$ [g]
Second-order reaction rate constants with photoinduced transients ( $\text{M}^{-1} \text{s}^{-1}$ )	$\text{CO}_3^{\cdot-}$	$8.3 \cdot 10^6$ [c]	$6.0 \cdot 10^6$ [c]	$1.1 \cdot 10^8$ [c]	$3.0 \cdot 10^7$ [c]	$1.7 \cdot 10^7$ [c]
	$\cdot\text{OH}$	$9.45 \cdot 10^9$ [d]	$7 \cdot 10^9$ [e]	$5.8 \cdot 10^9$ [f]	$7.9 \cdot 10^9$ [g]	$6.9 \cdot 10^9$ [g]
	$^3\text{BP}^*$	$5.2 \cdot 10^8$ [h]	$2.0 \cdot 10^9$ [h]	$3.1 \cdot 10^9$ [h]	$3.2 \cdot 10^9$ [h]	$2.7 \cdot 10^9$ [h]
	$^3\text{MAP}^*$	$9 \cdot 10^6$ [h]	$8.1 \cdot 10^7$ [h]	$2 \cdot 10^9$ [h]	$8.2 \cdot 10^8$ [h]	$2.7 \cdot 10^8$ [h]

[a] Djebbar et al., 2003.

[b] Boulkamh et al., 2001.

[c] Canonica et al., 2005.

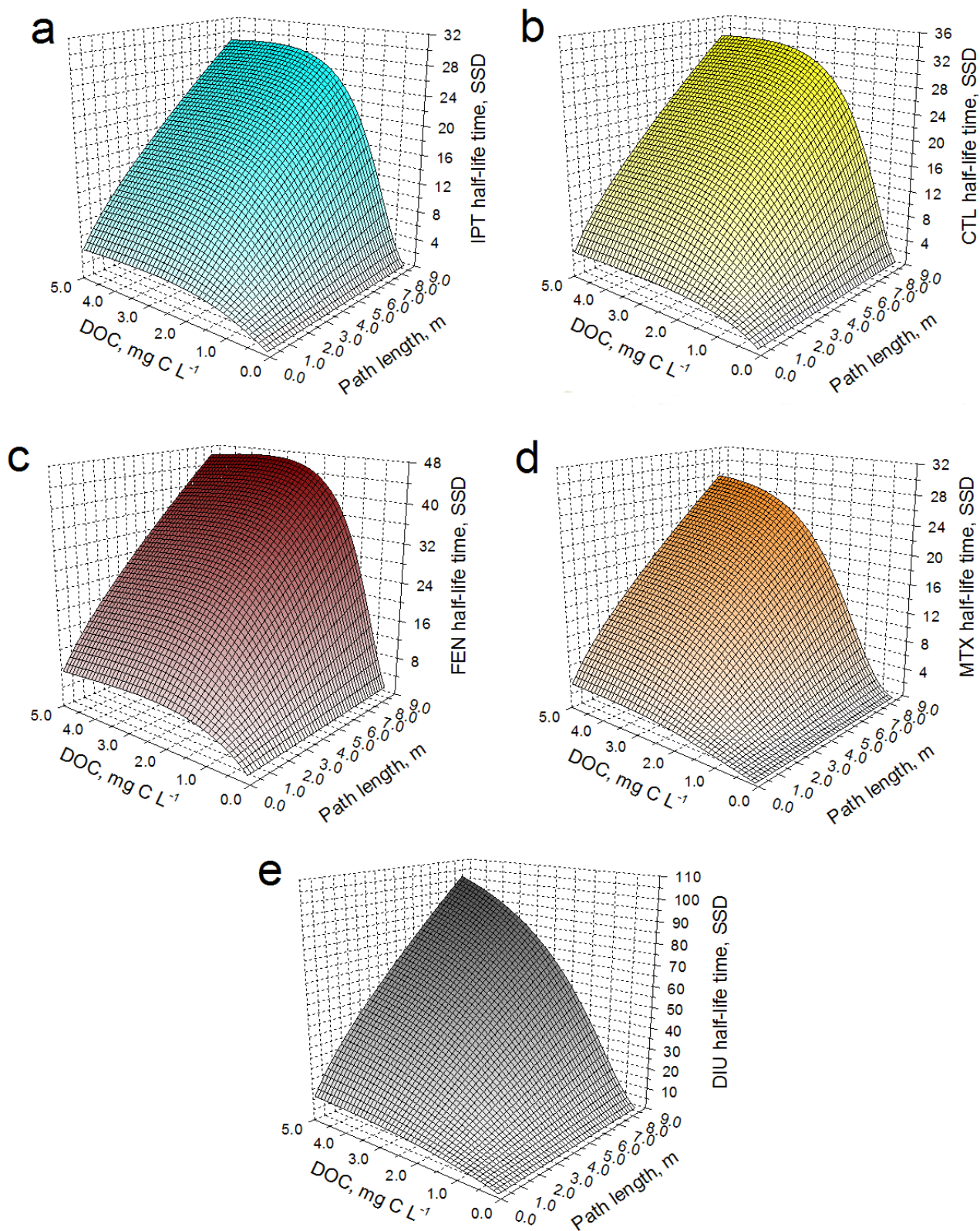
[d] Olasehinde et al., 2013.

[e] Mazellier et al., 2007.

[f] Lester et al., 2013.

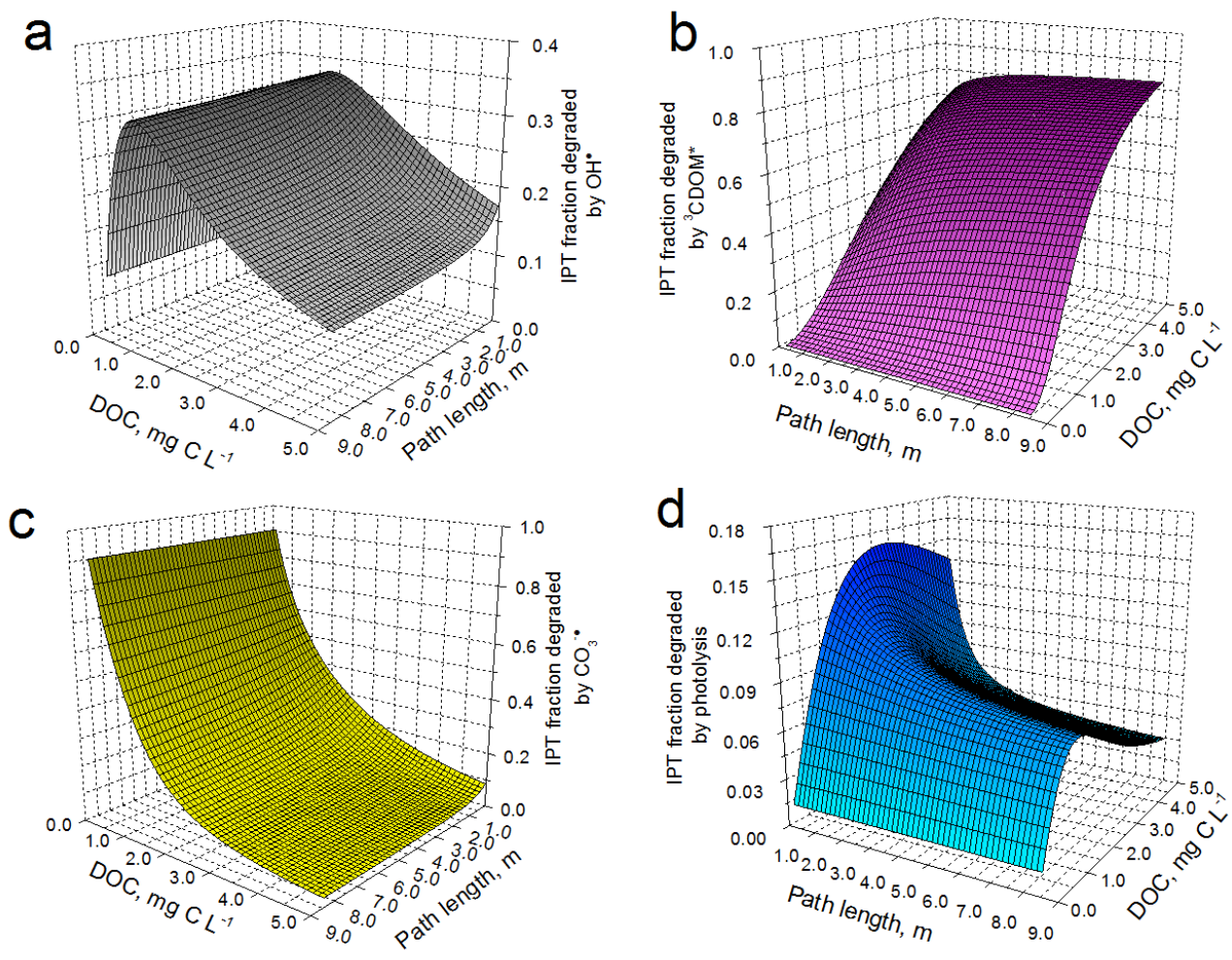
[g] Benitez et al., 2007.

[h] Canonica et al., 2006.



**Figure 1.** Modelled half-life times, as a function of DOC and the optical path length of sunlight, for the investigated PUHs: (a) IPT; (b) CTL; (c) FEN; (d) MTX; (e) DIU. Other water conditions: 0.1 mM  $\text{NO}_3^-$ , 1  $\mu\text{M}$   $\text{NO}_2^-$ , 2 mM  $\text{HCO}_3^-$ , 10  $\mu\text{M}$   $\text{CO}_3^{2-}$ .





**Figure 2.** Modelled fraction of IPT that is degraded by  $\bullet\text{OH}$  (a),  ${}^3\text{CDOM}^*$  (b),  $\text{CO}_3^{\bullet-}$  (c) and the direct photolysis (d), as a function of DOC and the sunlight path length. Other water conditions:  $0.1 \text{ mM NO}_3^-$ ,  $1 \text{ }\mu\text{M NO}_2^-$ ,  $2 \text{ mM HCO}_3^-$ ,  $10 \text{ }\mu\text{M CO}_3^{2-}$ .