Modelling the Photochemistry of Imazethapyr in Rice Paddy Water

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Abstract

In this work the photochemistry of imazethapyr, an imidazolinone herbicide used in rice crops, was modelled in rice paddy water. The photochemical half-life time of the herbicide was assessed by means of the APEX software (*Aqueous Photochemistry of Environmentally occurring Xenobiotics*) taking into account the direct photolysis, the reactions with hydroxyl radicals ($HO^{\bullet}$) and, in some cases, the reactions with the excited triplet states of chromophoric dissolved organic matter (^{3}CDOM*). We found that direct photolysis and $HO^{\bullet}$ reaction can account for a half-life time ranging between 5 and 11 days in May, which is in quite good agreement with the half-life times measured in the field and reported in the literature. These findings suggest that direct photolysis and reaction with $HO^{\bullet}$ are important degradation pathways for imazethapyr in paddy water. Dissolved organic matter (DOM) has been reported in the literature to decrease the imazethapyr photodegradation rate. Our model computations confirm this finding but, upon comparison of model predictions with experimental data from the literature, we provide evidence of a non-negligible role of DOM-photosensitised processes in imazethapyr degradation, particularly in DOM-rich waters. We also assess an upper limit (1×10^8 L mol^{-1} s^{-1}) for the second-order rate constant of the reaction between imazethapyr and ^{3}CDOM*. Furthermore, on the basis of literature-

reported photodegradation pathways and by using both APEX and the US-EPA ECOSAR V2.0 software, we assess that the direct photolysis by-products of imazethapyr could pose a potential ecotoxicological threat to aquatic systems.

Keywords

Imidazolinone herbicides; Photochemical fate; Rice-field water; APEX; Photochemical model.

1. Introduction

Imidazolinone herbicides are pesticides that control a broad spectrum of weeds in different crops, such as rice, wheat and maize (Tan et al., 2005). They inhibit the acetolactate synthase (ALS) enzyme, also called acetohydroxyacid synthase (AHAS), which is a central enzyme in the synthesis of branched-chain amino acids in plants (Lonhienne et al., 2018; Xie et al., 2018). Other ALS-inhibiting herbicides are those belonging to the families of triazolopyrimidines, pyrimidinyl-thiobenzoates, sulfonylamino-carbonyltriazolinones and sulfonylureas. Imazethapyr, imazapic, imazamox, imazaquin and imazapyr are examples of imidazolinone herbicides (Tan et al., 2005).

The use of pesticides has become indispensable in rice-fields (Wei et al., 2015), and it could increase in the future because of climate change (Rodenburg et al., 2011). The worldwide use of imidazolinone herbicides in paddies is usually associated to the cultivation of imidazolinone-tolerant rice varieties (Sudianto et al., 2013). By applying these herbicides in imidazolinone-tolerant rice crops, it is possible to control the growth of the red rice that causes significant yield losses in rice production (Shivrain et al., 2009). Despite the effectiveness of these herbicides, several works have described the growth of imidazolinone-resistant red rice plants in paddies (Scarabel et al., 2012; Kaloumenos et al., 2013).

The persistence of pesticides in paddies is a problem of environmental concern, because the pesticides occurring in the floodwater can contaminate the surface water bodies connected with the rice fields (Trinh et al., 2014). Previous works have reported the presence of imidazolinone herbicides in the outlet water of rice fields and in surface waters (Battaglin et al., 2000; Milan et al., 2017). The persistence of pesticides is linked to the different degradation pathways that these compounds can undergo in surface waters, including paddy water, such as microbial degradation, chemical hydrolysis and photochemical reactions (Fenner et al., 2013). The latter can be divided into direct photolysis and indirect photochemistry. Direct photolysis occurs when a compound absorbs sunlight and undergoes subsequent transformations, such as bond cleavage or ionisation. In contrast, the indirect phototransformation of a xenobiotic is triggered by reaction with reactive transients species that are usually called Photochemically Produced Reactive Intermediates (PPRIs). The main PPRIs are hydroxyl radicals ($HO^{\bullet}$), carbonate radicals ($CO_3^{\bullet-}$), the excited triplet states of chromophoric dissolved organic matter (^{3}CDOM*) and singlet oxygen ($^1O_2$). They are formed upon sunlight absorption by photosensitisers (CDOM, nitrate and nitrite) that occur naturally in surface water bodies. All of the mentioned photosensitisers are directly involved in the formation of $HO^{\bullet}$ radicals, and they also indirectly produce $CO_3^{\bullet-}$ through the oxidation of bicarbonate and carbonate by photogenerated $HO^{\bullet}$ (to a lesser extent, $CO_3^{\bullet-}$ is also produced upon carbonate oxidation by ^{3}CDOM*) (Buxton et al., 1988; Mack and Bolton, 1999; Canonica et al., 2005). DOM is the main scavenger of $HO^{\bullet}$ and $CO_3^{\bullet-}$ and, therefore, the associated photoprocesses are usually enhanced in DOM-poor waters (Vione et al., 2014). CDOM under irradiation is also the source of ^{3}CDOM* and $^1O_2$, where the latter is formed by energy transfer processes between ^{3}CDOM* and ground-state molecular oxygen (Haag and Hoigné, 1986; Appiani and McNeill, 2015; McNeill and Canonica, 2016). The processes triggered by ^{3}CDOM* and $^1O_2$ are usually favoured in DOM-rich waters (Vione et al., 2014).

Photochemical reactions can be important degradation pathways for many pesticides in surface waters, including the imidazolinone herbicides (Mabury and Crosby, 1996; Armbrust, 2000;

Burrows et al., 2002; Remucal, 2014). Specifically, in the case of imazethapyr, [5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-4,5-dihydroimidazol-1H-2-yl)nicotinic acid], the photochemical transformations prevail over chemical hydrolysis (Ramezani et al., 2008). Imazethapyr has been found to degrade by direct photolysis and with $HO^{\bullet}$ radicals (Avila et al., 2006). The presence of DOM has been reported to decrease the imazethapyr degradation rate because of light screening (Elazzouzi et al., 2002; Ramezani et al., 2008; Espy et al., 2011). In this work, the photochemical fate of imazethapyr (half-life times, role of direct photolysis and PPRIs in photodegradation) was modelled in rice-field water by using a suitable photochemistry-modelling software (APEX; Bodrato and Vione, 2014), on the basis of herbicide photochemical parameters from the literature and of data from a previous study into the photoreactivity of paddy-field CDOM (Carena et al., 2017). Furthermore, a rough assessment of the reactivity of imazethapyr toward $^{3}CDOM^{*}$ was carried out in this work by comparing literature data with our model predictions. Finally, some toxicological features of the imazethapyr phototransformation products were assessed based on literature-reported degradation pathways and by using Structure-Activity Relationships software (ECOSAR V2.0), developed by US-EPA.

2. Materials and Methods

2.1 *Photochemical Modelling*

The photochemical modelling was carried out with the APEX software (*Aqueous Photochemistry of Environmentally occurring Xenobiotics*) (Bodrato and Vione, 2014). APEX is a suitable modelling tool that has been used in several previous works to assess the photochemical fate of xenobiotics in well mixed surface-waters, in which the chemical composition profile can be considered constant with the water depth (see, e.g., Vione, 2014). A detailed description of the APEX mathematical model is explained in the software User's Guide, which is freely available as supporting information in Bodrato and Vione (2014). Briefly, APEX requires input data concerning the

photoreactivity of both the studied xenobiotic (namely, the direct photolysis quantum yield and the second-order rate constants for reaction with the PPRIs) and the surface-water environment. The imazethapyr photolysis quantum yield and its second-order rate constant for reaction with $HO^{\bullet}$ have been measured by Avila et al. (2006) as 0.023 and 2.8×10^{13} L mol^{-1} h^{-1} (i.e., 7.8×10^{9} L mol^{-1} s^{-1}), respectively. We used these values to model the photochemical fate of imazethapyr. The cited authors have performed irradiation experiments with a simulated sunlight equipment and have measured the imazethapyr direct photolysis quantum yield and the $HO^{\bullet}$-reaction rate constant by comparing the herbicide photodegradation with that of a chemical actinometer and of reference compounds, respectively.

The water chemical composition is a key environmental feature for phototransformation, because water chemistry and photochemistry are closely connected. In particular, the concentrations of DOM (expressed as dissolved organic carbon, DOC), nitrate, nitrite, bicarbonate and carbonate are key input data to assess the photochemical fate of a xenobiotic by using APEX. Other very important environmental parameters are the depth of the water body, the sunlight spectrum and the absorption spectrum of the water itself (which is mainly accounted for by CDOM and is modelled by APEX based on the DOC value). Because the photochemical processes are enhanced in clear and shallow water bodies, the photochemical half-life times can be highly affected by the water depth (Beretvas et al., 2000). The standard spectral photon flux densities used in APEX are referred to a sunlight spectrum reaching the water surface in a cloudless 15th July at 45°N latitude, at 9 am or 3 pm solar time, with a UV-irradiance of 22 W m^{-2}. The total amount of sunlight energy reaching the ground in one such day defines the Summer Sunny Day (SSD) time unit used in the model, which is equivalent to a mid-latitude, fair-weather 15 July and corresponds to 10 h of continuous irradiation at steady 22 W m^{-2} UV irradiance. Finally, the formation quantum yields of the PPRIs $HO^{\bullet}$, ^{3}CDOM* and $^{1}O_2$ by irradiated CDOM (respectively, $\Phi_{HO^{\bullet}}^{CDOM}$, $\Phi_{^{3}CDOM*}^{CDOM}$ and $\Phi_{^{1}O_2}^{CDOM}$) are key input parameters of the model, and they depend upon the considered environment. Several previous

works have photochemically characterised sunlit aquatic environments such as, for instance, lakes and paddy floodwater (Canonica et al., 2005; Al Housari et al., 2010; Timko et al., 2014; Carena et al., 2017). Paddy-water photoreactivity parameters are available from Carena et al. (2017), who report $\Phi_{HO^\bullet}^{CDOM} = 2.3\times10^{-5}$, $\Phi_{^3CDOM^*}^{CDOM} = 2.9\times10^{-2}$, and $\Phi_{^1O_2}^{CDOM} = 9.0\times10^{-3}$.

In this work, the photochemical fate of imazethapyr was modelled in a typical environment (water depth = 5 cm) of a paddy field located at northern mid-latitude during the first half of May, at the beginning of the rice growing season. This is a period when the rice-fields are flooded, their water depth can range between 5 and 15 cm and the rice plants are still in their early growth stages (Roger, 1996), thus the sunlight shadowing by the rice-plant canopy can be neglected (Carena and Vione, 2017). We fixed the water depth equal to 5 cm without considering fluctuations due to dynamic hydrological events such as irrigation, rainfall, evapotranspiration and percolation. Although water depth can highly affect the photochemical processes (Beretvas et al., 2000), rice-field water is a shallow aquatic system where absorption saturation is unlikely to occur. Therefore, one expects little variations of the model results when changing the depth between 5 and 15 cm and by taking constant the water chemical composition. The dissolved organic carbon (DOC) and nitrate content were used as master variables to assess the photochemical fate of imazethapyr, because direct photolysis and the reactivity with $HO^\bullet$ radicals are generally influenced by these two parameters (Vione et al., 2014). Based on literature reports (Quesada et al., 1997; Barreiros et al., 2011; Carena et al., 2017), DOC values between 4 and 10 mgC L^{-1} and nitrate concentrations between 1.5 and 100 μmol L^{-1} are reasonable for paddy floodwater. The used bicarbonate and carbonate concentrations were computed by taking into account an air-equilibrated aqueous system at pH 8 (25 °C, 3 mmol L^{-1} ionic strength), and they were $[HCO_3^-] = 6.8\times10^{-4}$ mol L^{-1} and $[CO_3^{2-}] = 4.0\times10^{-6}$ mol L^{-1}, respectively. However, bicarbonate and carbonate concentrations could be quite far from these values because the paddy-field system can undergo both diurnal and longer-term pH fluctuations due to the photosynthetic processes taking place in the floodwater (Roger, 1996) and to

the exchange of CO_2 between air, water and soil (Saito and Watanabe, 1978). Although inorganic carbon can affect the photochemistry of $CO_3^{\bullet-}$-reactive compounds (Huang and Mabury, 2000; Liu et al., 2016), to our knowledge this is not the case of imazethapyr.

The July-based APEX output data were converted into May-based ones by means of the *APEX_season* function, which basically makes a correction for the incident solar irradiance. Furthermore, the optical depth of the floodwater (6 cm) was computed by correcting the actual depth (5 cm) for a 1.2 factor that takes into account both the solar zenith angle and the refraction of light at the air-water interface (Bodrato and Vione, 2014; Carena and Vione, 2017).

2.2 ***Toxicological modelling***

Acute-toxicity parameters (LC_{50} and EC_{50}) and chronic toxicity values (ChV) to aquatic organisms were assessed by using the ECOSAR V2.0 software [Ecological Structure Activity Relationships (ECOSAR) Class Program], developed by the U.S. Environmental Protection Agency (EPA) and freely available (https://www.epa.gov/tsca-screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model; Mayo-Bean et al., 2012). Several previous studies have used U.S. EPA ECOSAR to predict aquatic toxicity of chemicals (Reuschenbach et al., 2008; Frank et al., 2010; Ortiz de García et al., 2014). The software can assess also other chemical properties, such as the water solubility. Here, the LC_{50} and EC_{50} values higher than the predicted water solubility of the relevant compounds were neglected.

3. Results and Discussion

3.1. *Photodegradation by direct photolysis and HO• reaction*

Fig.1 shows the computed photochemical half-life times ($t_{1/2}$) of imazethapyr in rice-field water as a result of direct photolysis and HO• reaction, as a function of the DOC that measures DOM. We find that DOM affects the photodegradation of imazethapyr by increasing its $t_{1/2}$ value, in agreement with reports from the literature (Elazzouzi et al., 2002; Ramezani et al., 2008; Espy et al., 2011). At DOC ~ 5 mgC L^{-1}, the modelled pesticide $t_{1/2}$ in May ranges between 8 and 11 days but faster photodegradation can occur at lower DOC. These results are in reasonable agreement with the reported lifetime of 3-7 days for imazethapyr in the field (Santos et al., 2008; Zanella et al., 2011; Martini et al., 2013; Reimche et al., 2015). Furthermore, Reimche et al. (2015) have measured $t_{1/2}$ ~ 5 days in subtropical rice-field water, suggesting that photodecomposition is the main imazethapyr breakdown process in such an environment. Similar results have been found by Santos et al. (2008).

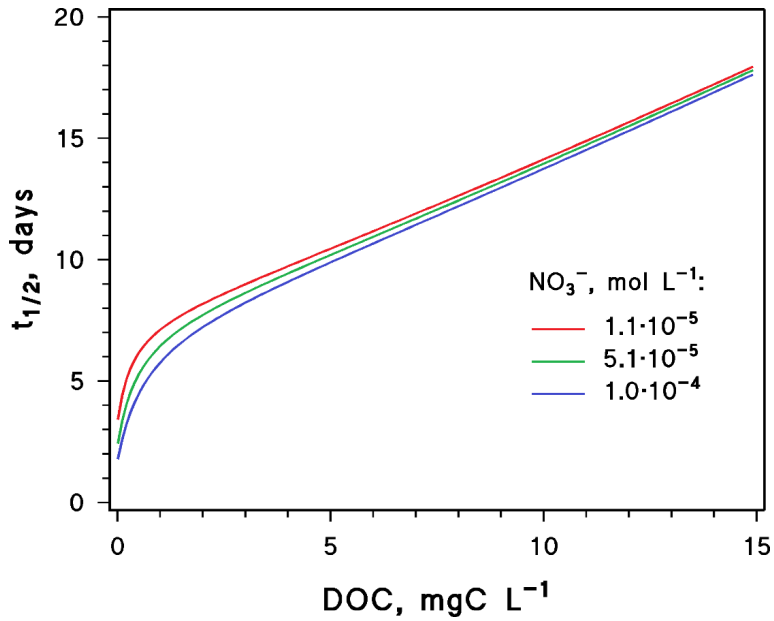


Fig. 1. Photochemical half-life times of imazethapyr in paddy-field water computed with APEX, as a function of water DOC and for different nitrate levels. Direct photolysis and reactions with hydroxyl radicals account for the pesticide photodegradation. Other APEX input data were as follows: 1.5×10^{-6} mol L^{-1} NO_2^-, 6.8×10^{-4} mol L^{-1} HCO_3^-, 4.0×10^{-6} mol L^{-1} CO_3^{2-} and 6 cm optical depth.

Nitrate affects the half-life time of the pesticide, especially at low DOC values where the $HO^{\bullet}$ radicals play an important role in the overall photodegradation (see Fig.2 for the DOC trend of the imazethapyr photoreaction pathways). Actually, nitrate is a $HO^{\bullet}$ source (and the main one at low DOC, together with nitrite) while DOM is the main scavenger (Vione et al., 2014), which accounts for the favourable role of nitrate towards photodegradation (the role of $HO^{\bullet}$ at low DOC is more important if nitrate is more concentrated, see Fig.2). The scavenging of $HO^{\bullet}$ by DOM is one of the reasons why the photoreaction kinetics of imazethapyr get slower as the DOC increases (see Fig.1).

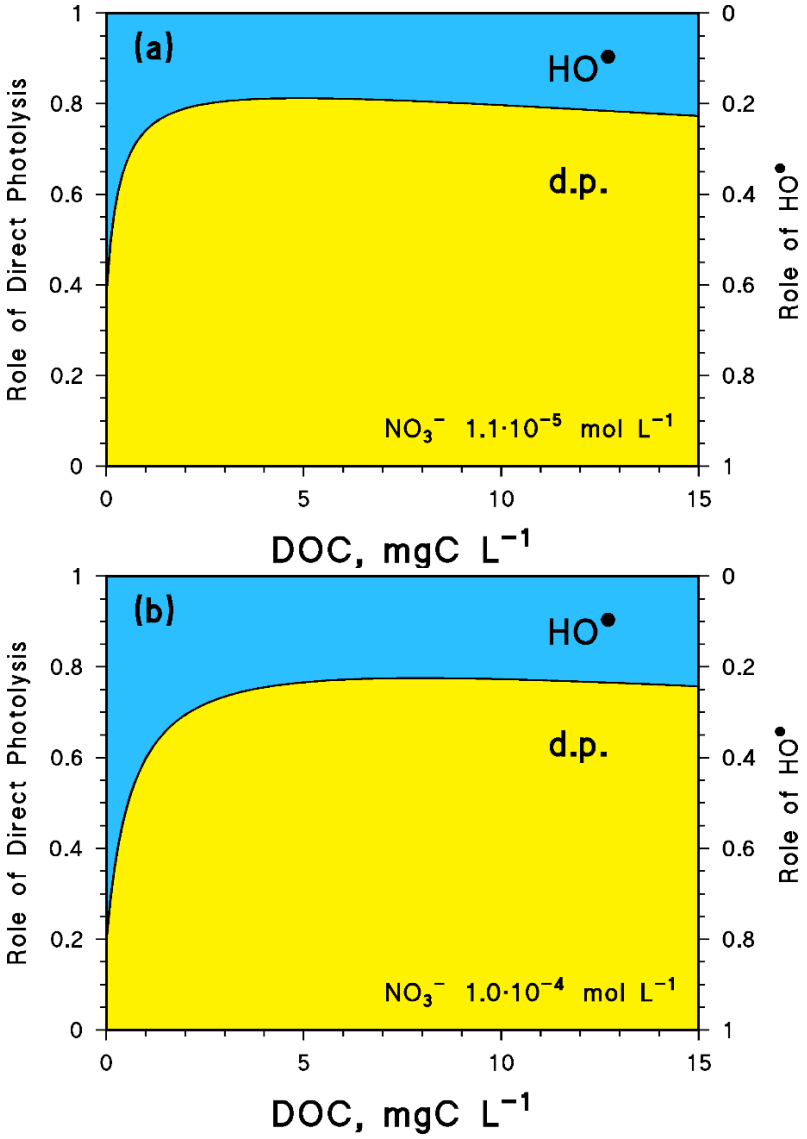


Fig. 2. Role of direct photolysis and hydroxyl radicals reactions in the overall photodegradation of imazethapyr in paddy water, at different nitrate concentrations. The curves were computed with the APEX software. Other APEX input data were as follows: 1.5×10^{-6} mol L^{-1} NO_2^-, 6.8×10^{-4} mol L^{-1} HCO_3^-, 4.0×10^{-6} mol L^{-1} CO_3^{2-} and 6 cm optical depth.

In contrast, the role of nitrate on pesticide photodegradation and the effect of its concentration become very small at relatively high DOC levels (> 5 mgC L^{-1}), where there is little difference in the $t_{1/2}$ values with varying nitrate (see Fig.1). At high DOC the DOM is an efficient $HO^{\bullet}$ scavenger (which favours imazethapyr phototransformation by direct photolysis, see Fig.2) and CDOM becomes the main $HO^{\bullet}$ source, thus an increase in the nitrate content cannot affect much the photoreaction kinetics.

3.2. *An assessment of the role of ^{3}CDOM* in imazethapyr photodegradation*

The DOC is a key variable affecting the half-life of imazethapyr, which becomes longer as the DOC increases (Fig.1). There are two main reasons for this finding, namely: (i) the screening effect of CDOM, which absorbs sunlight and inhibits the imazethapyr direct photolysis, and (ii) the $HO^{\bullet}$ radicals scavenging (note that both direct photolysis and $HO^{\bullet}$ reactions are inhibited as the DOC increases, but the $HO^{\bullet}$ processes are inhibited to a higher extent; Vione et al., 2014). Coherently, previous works have shown that natural organic matter (NOM) decreases the photodegradation rate of imazethapyr (Elazzouzi et al., 2002; Ramezani et al., 2008; Espy et al., 2011). However, in spite of these experimental evidences corroborated by model calculations, CDOM could still act as a photosensitiser for the degradation of imazethapyr at high DOC values. Such a result has for instance been reported in the case of triclosan (Bianco et al., 2015), where phototransformation is slowed down upon addition of CDOM but is dominated by ^{3}CDOM* at high DOC. It is thus interesting to assess a possible reactivity of imazethapyr toward ^{3}CDOM*, also because paddy fields are photochemical reactors where ^{3}CDOM* potentially play an important role (Carena et al., 2017). Espy et al. (2011) have assessed the effect of natural organic matter (NOM) on imazethapyr photodegradation with outdoor photolysis experiments (July, ~44°N latitude). In that study, imazethapyr has been irradiated in phosphate-buffered (pH 7) ultrapure-water solutions in the presence of Suwannee River NOM (52.5% C by mass). The (pseudo-first order) rate constant of imazethapyr photodegradation (k') has been shown to decrease, compared to that in buffered ultra-

pure water, by ~20% at both 1.6 and 5.0 mg L^{-1} NOM, and by ~33% at 9.2 mg L^{-1} NOM (corresponding to ~0.84, 2.60 and 4.83 mgC L^{-1} DOC, respectively). By using APEX, we roughly assessed the second-order reaction rate constant between imazethapyr and ^{3}CDOM* (k_I^{T*}), by reproducing the DOC trend of the ratio $k'_{DOCj}\,(k'_{DOC0})^{-1}$ obtained from the data reported by Espy et al. (2011). Here, k'_{DOCj} is the pseudo-first order transformation rate constant of imazethapyr in the presence of j mgC L^{-1} DOC, whereas k'_{DOC0} refers to low to nil DOC content.

To better simulate the experimental conditions of Espy et al. (2011), we adopted low concentration of nitrate and negligible (1×10^{-10} mol L^{-1}) nitrite levels. The bicarbonate and carbonate concentrations were computed by taking into account an air-equilibrated water system at pH 7. Note that these water conditions are completely different from those used to model the imazethapyr photochemical fate in paddy-water, because in this case was had to model the photochemical behaviour of synthetic solutions. Furthermore, we used physical-chemical features of typical (C)DOM that occur in rivers and lakes (Bodrato and Vione, 2014), rather than the (C)DOM of the paddy-water environment. For instance, we used PPRIs formation quantum yields $\Phi_{HO^\bullet}^{CDOM} = 3\times10^{-5}$, $\Phi_{^3CDOM*}^{CDOM} = 1.3\times10^{-3}$ and $\Phi_{^1O_2}^{CDOM} = 1.2\times10^{-3}$. Fig.3 shows the literature experimental data, superposed to the $k'_{DOCj}\,(k'_{DOC0})^{-1}$ curves modelled with APEX for different values of k_I^{T*}. A good fit of the experimental data of Espy et al. (2011) was achieved by assuming 3×10^{-7} mol L^{-1} NO_3^- and $k_I^{T*} = 1\times10^8$ L mol^{-1} s^{-1}. The literature data could be reproduced reasonably well also by assuming $k_I^{T*} = 10^6$-10^7 L mol^{-1} s^{-1}. In contrast, $k_I^{T*} > 10^8$ L mol^{-1} s^{-1} produced a notable increase of $k'_{DOCj}\,(k'_{DOC0})^{-1}$ with increasing DOC, especially above 1 mgC L^{-1}, because of a considerable reactivity between imazethapyr and ^{3}CDOM*. Note that $^1O_2$, which is formed as a consequence of ^{3}CDOM* production, was not taken into account because it is often poorly reactive toward xenobiotic compounds (Vione et al., 2014). For the above reasons, $k_I^{T*} = 10^8$ L mol^{-1} s^{-1} could be considered as an upper limit for the reaction rate constant between imazethapyr and ^{3}CDOM*.

However, further experimental studies should be carried out to better understand the reactivity between imazethapyr and ^{3}CDOM*, by using, for instance, CDOM-proxy compounds such as anthraquinone-2-sulphonate (AQ2S) or 4-carboxybenzophenone (CBBP) (Minella et al., 2018).

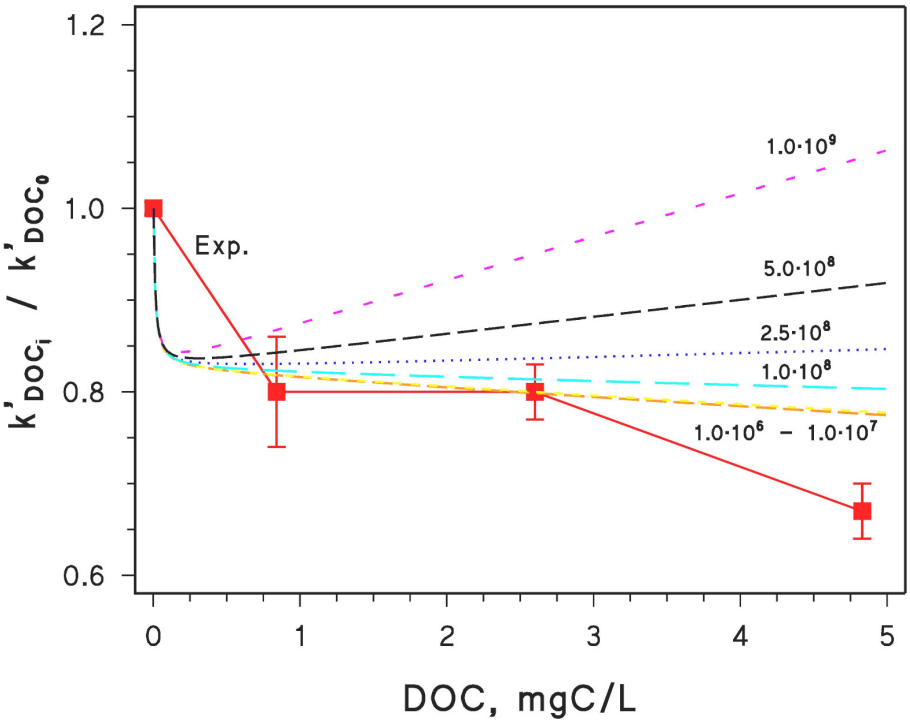
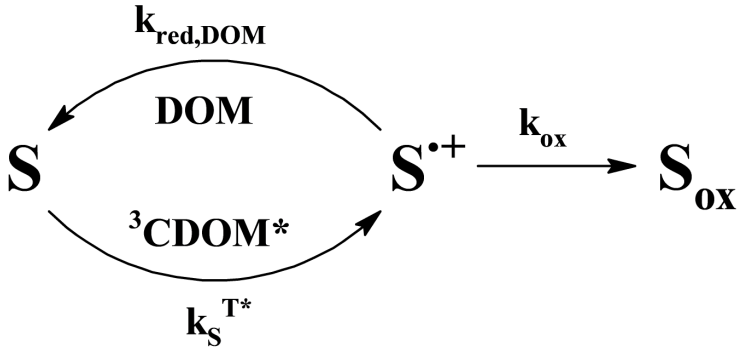


Fig. 3. Model reproduction of the experimental data (■) reported by Espy et al. (2011), with the associated error bounds (± σ). The curves were computed at different values of k_I^{T*} by using the APEX software. Other APEX input data were as follows: 3×10^{-7} mol L^{-1} NO_3^-, 1×10^{-10} mol L^{-1} NO_2^-, 5.6×10^{-5} mol L^{-1} HCO_3^-, 3.7×10^{-8} mol L^{-1} CO_3^{2-} and 3 cm optical path length.

The partial mismatch between model predictions and experimental data at DOC around 5 mgC L^{-1} (see Fig.3) could be accounted for in part by the (shown) uncertainty in the experimental data, and in part by the model relative error of about 10-20%. Moreover, differences between the photochemical features of the experimental CDOM and those assumed in the model could account for different photoreaction kinetics. Finally, it must be pointed out that our model did not include the possible back-reduction effects that can be operational in the case of several xenobiotics

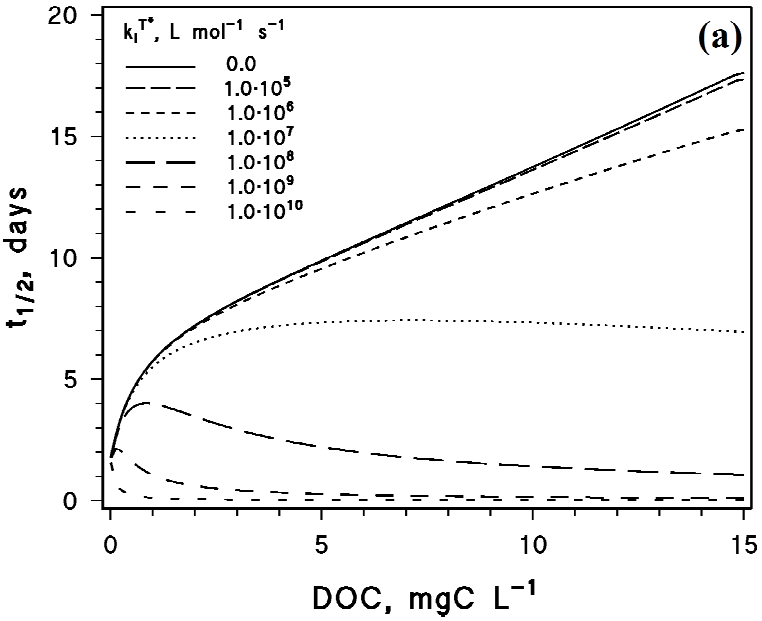
(Canonica and Laubscher, 2008), where the DOM phenolic moieties reduce back to the initial compound the radical species produced by oxidation of the substrate by ^{3}CDOM* (Scheme 1; Wenk et al., 2011; Wenk and Canonica, 2012; Yuan et al., 2016). Such an effect could account for the photoreactivity decrease at high DOC.



Scheme 1. Back-reduction effect leading to the inhibition of the oxidation of the substrate S by ^{3}CDOM* (adapted from Wenk et al., 2011).

The reaction between imazethapyr and ^{3}CDOM* could modify the predicted herbicide half-lives in paddy water. To take the ^{3}CDOM* role into account, Fig.4a shows the herbicide half-life times for different values of k_I^{T*} (the values of k_I^{T*} > 10^8 L mol^{-1} s^{-1} are only included as examples). The model conditions are here referred to paddy water and not to ultra-pure water. Note that, if $k_I^{T*} \leq$ 10^6 L mol^{-1} s^{-1}, $t_{1/2}$ would not change significantly as compared to the scenario reported in Fig.1. In such a case, the reactions with ^{3}CDOM* have unimportant role in the overall degradation of the herbicide, which is dominated by direct photolysis and HO$^\bullet$ reaction (see Fig.5a for the main pathways of imazethapyr photodegradation with k_I^{T*} = 10^6 L mol^{-1} s^{-1}). However, by increasing k_I^{T*} by an order of magnitude (k_I^{T*} = 10^7 L mol^{-1} s^{-1}), one has a significant role of the ^{3}CDOM*

process for DOC > 3 mgC L^{-1} (see Fig.5b). The $t_{1/2}$ vs. DOC curve gets modified as a consequence (see the relevant curve in Fig.4a, and compare it with the corresponding curve in Fig.1). The pseudo-plateau (actually, a broad maximum) observed for $t_{1/2}$ as a function of the DOC, for k_I^{T*} = 10^7 L mol^{-1} s^{-1} and DOC > 3 mgC L^{-1}, is accounted for by the fact that the inhibition of the direct photolysis and of the $HO^{\bullet}$-induced degradation of imazethapyr is counterbalanced by the reaction with ^{3}CDOM* (Fig.5b).



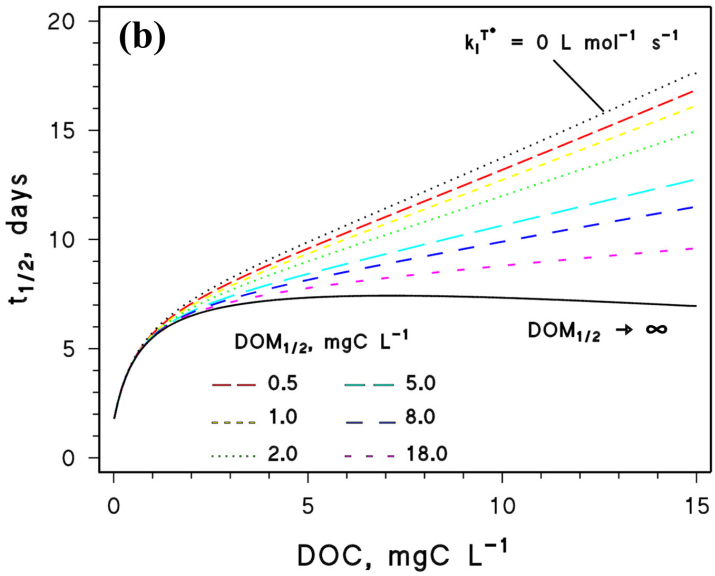


Fig. 4. Half-life times of imazethapyr in paddy floodwater, for (a) different values of k_I^{T*} and (b) different values of $DOM_{1/2}$ ($k_I^{T*} = 1.0\times10^7$ L mol^{-1} s^{-1}). Other APEX input data were as follows: 1.0×10^{-4} mol L^{-1} NO_3^-, 1.5×10^{-6} mol L^{-1} NO_2^-, 6.8×10^{-4} mol L^{-1} HCO_3^-, 4.0×10^{-6} mol L^{-1} CO_3^{2-} and 6 cm optical depth.

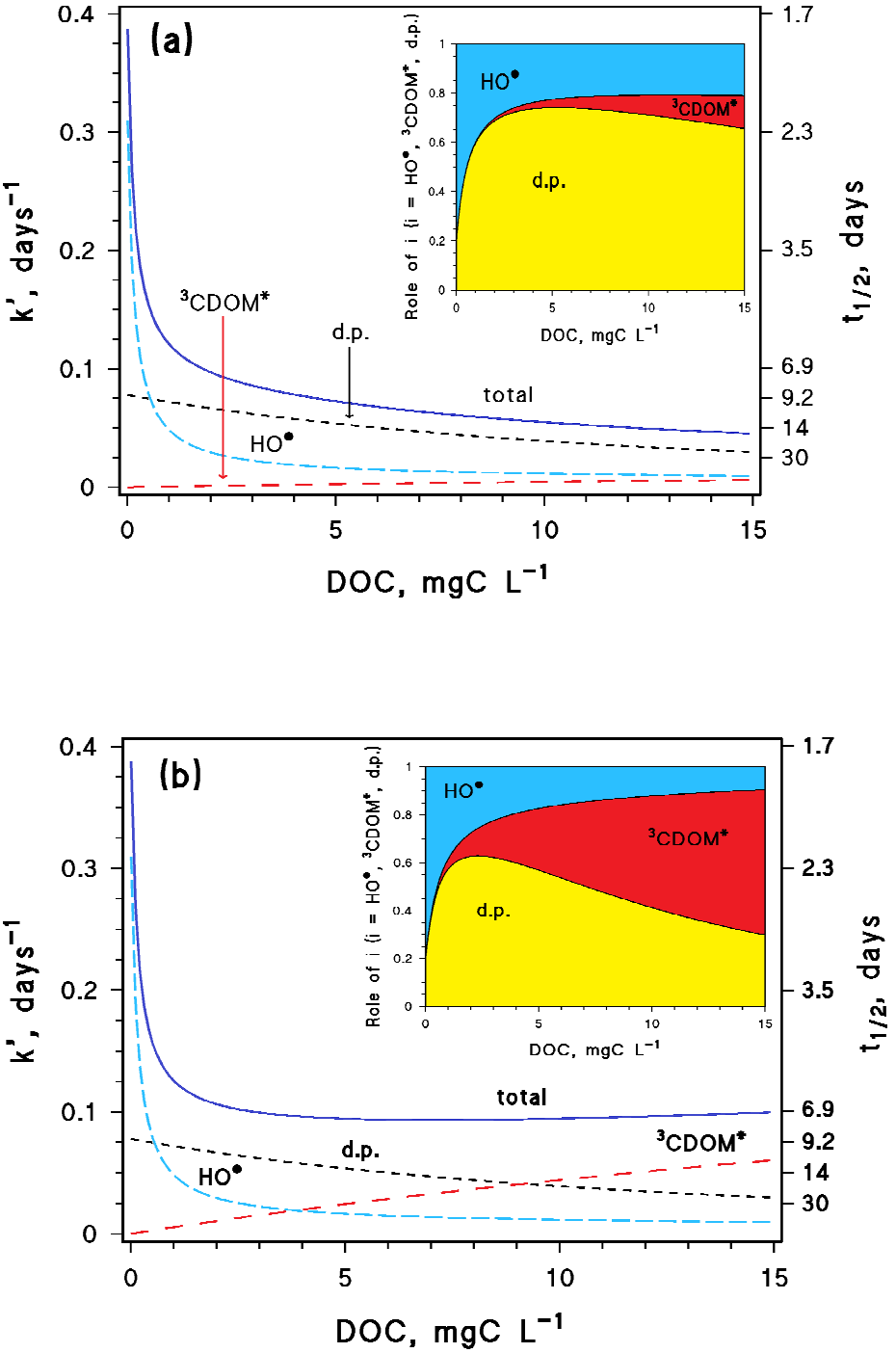


Fig. 5. Pseudo-first order rate constants ($k'_{d.p.}$, k'_{HO°, k'_{3CDOM*}, *and* $k'_{total} = k'_{d.p.} + k'_{HO^\circ} + k'_{3CDOM*}$) of imazethapyr photodegradation in paddy floodwater. The used k_I^{T*} values were (a) 1.0×10^6 L mol^{-1} s^{-1} and (b) 1.0×10^7 L mol^{-1} s^{-1}. Other APEX input data were as follows: 1.0×10^{-4} mol L^{-1} NO_3^-, 1.5×10^{-6} mol L^{-1} NO_2^-, 6.8×10^{-4} mol L^{-1} HCO_3^-, 4.0×10^{-6} mol L^{-1} CO_3^{2-} and 6 cm optical depth. The inserts show the fractions of imazethapyr photodegradation accounted for by the different photoreaction pathways.

The predicted half-lives for $k_I^{T*} = 10^7$ L mol^{-1} s^{-1} and DOC around 5 mgC L^{-1} (about one week) are still compatible with the literature reports (Santos et al., 2008; Zanella et al., 2011; Reimche et al., 2015), and the agreement is even better than for the case when the ^{3}CDOM* reactions were neglected. While not making conclusive evidence in favour of a significant ^{3}CDOM* reaction, this means anyway that the literature data suggest $k_I^{T*} \leq 10^8$ L mol^{-1} s^{-1} and, possibly, $k_I^{T*} \sim 10^7$ L mol^{-1} s^{-1}.

Although to our knowledge a possible back-reduction effect on imazethapyr oxidation by ^{3}CDOM* has not yet been investigated, we tried to include it into the model. Of course this operation implies a certain degree of speculation, but it can show how the back-reduction process might affect the imazethapyr photodegradation if it were operational. Furthermore, paddy-water DOM is mainly composed by soil-derived humic substances (Carena et al., 2017) that can act as effective anti-oxidants (Wenk et al., 2011; Vione et al., 2018). Fig.4b shows the photochemical lifetimes for different values of $DOM_{1/2}$, which measures the back-reduction effect. $DOM_{1/2} = k_{ox} (k_{red,DOM})^{-1}$ does in fact represent the DOC value that halves the photodegradation rate constant by ^{3}CDOM*, compared to the case when the back-reduction is not operational (Canonica and Laubscher, 2008). The lower is $DOM_{1/2}$, the more important are the back-reduction reactions. In general, $DOM_{1/2}$ depends upon the type of DOM and the xenobiotic and previous studies have shown that it can vary between 0.7 and 17 mgC L^{-1} (Canonica and Laubscher, 2008; Vione et al., 2018). By assuming $k_I^{T*} = 10^7$ L mol^{-1} s^{-1}, one can take into account the inhibition of the xenobiotic oxidation by ^{3}CDOM*

by using an apparent reaction rate constant that is expressed as the product ψk_I^{T*}. Here, ψ = [1 + DOC·$(DOM_{1/2})^{-1}$]$^{-1}$ takes into account the back-reduction effect (Vione et al, 2018). Indeed, by assuming $DOM_{1/2}$ = 0.5 mgC L^{-1} (i.e., important back reactions), the half-life times approach those computed without including the reactivity of imazethapyr with ^{3}CDOM* (that is, k_I^{T*} = 0 L mol^{-1} s^{-1}). In contrast, by assuming higher $DOM_{1/2}$ values that imply a lower importance of the back reduction, the half-lives become increasingly similar to those observed in the case of no back-reduction.

3.3. *Assessment of the possible toxicity of the known direct-photolysis intermediates of imazethapyr, and of the conditions that would enhance their occurrence in the environment*

As shown in Fig.5, direct photolysis is a non-negligible transformation pathway for imazethapyr, even at quite high DOC levels. Espy et al. (2011) have proposed mechanistic pathways for the direct photolysis of imazethapyr at ~254 nm. Although this wavelength is not environmentally significant, it has been suggested that the mechanism could be similar in the environment. Actually, Kasha's rule for the fate of the excited states suggests that relatively complex organic molecules may have direct photolysis quantum yields and pathways that poorly depend on the irradiation wavelengths (Turro et al., 1978).

Moreover, previous works have reported similar degradation pathways for the direct photolysis at wavelengths > 290 nm of other imidazolinone herbicides, with comparable molecular structure as imazethapyr (Quivet et al., 2004; Quivet et al., 2006; Harir et al., 2007; Christiansen et al., 2015). It is thus possible and interesting to assess the possible impacts on the aquatic environment of the known imazethapyr phototransformation products. By using the ECOSAR V2.0 software, we estimated both short-term and chronic aquatic toxicology data. Fig.6 shows the acute toxicity to aquatic organisms (fish, daphnid and algae) of the direct photolysis by-products of imazethapyr,

identified by Espy et al. (2011) and here indicated with the same acronyms used in the original paper (P1 to P6). The compounds P4, P3, P5b and P5a are directly formed upon imazethapyr direct photolysis, while P2 and P1 derive from P4 and P3, respectively, and P6 derives from P5a. The predicted toxicological data suggest that the compounds P1 to P4 could produce an increase of the acute toxicity to aquatic organisms (with ECOSAR, two compounds can be said to have different toxicity if the predicted values differ by at least one order of magnitude, i.e., one logarithmic unit in the plot of Fig.6; Mayo-Bean et al., 2012). The toxicity of the other by-products (P5a, P5b, P6) would be comparable to or lower than that of imazethapyr. A similar trend was found for the chronic toxicity (data not shown) as assessed by means of the Chronic Value (ChV) parameter, which is the geometric mean of the NOEC and LOEC values (No/Lowest Observed Effect Concentration, respectively; Mayo-Bean et al., 2012).

Because of the potential formation of more toxic compounds, the direct photolysis of imazethapyr could be of environmental concern. It is thus important to assess the conditions where the direct photolysis is an important degradation pathway for imazethapyr, and where its kinetics is fast enough. Fig.7a shows that direct photolysis would be the fastest at low DOC. However, under such conditions the $HO^{\bullet}$ reaction would be an important competing pathway. As shown in Fig.7b, the role of the imazethapyr direct photolysis would be enhanced when DOC ~ 2 mgC L^{-1}, and it would be important even above that value if $k_I^{T*} < 10^7$ L mol^{-1} s^{-1}. In the other cases, the relative importance of the direct photolysis would be decreased by the competition of $HO^{\bullet}$ and ^{3}CDOM* reactions. Overall, one could expect significant photoproduction of toxic direct photolysis by-products at intermediate DOC levels (e.g., 2-5 mgC L^{-1}). However, a more precise estimate of the impact of imazethapyr direct photolysis on aquatic organisms requires the knowledge of the formation yields of the toxic by-products, which are presently unavailable.

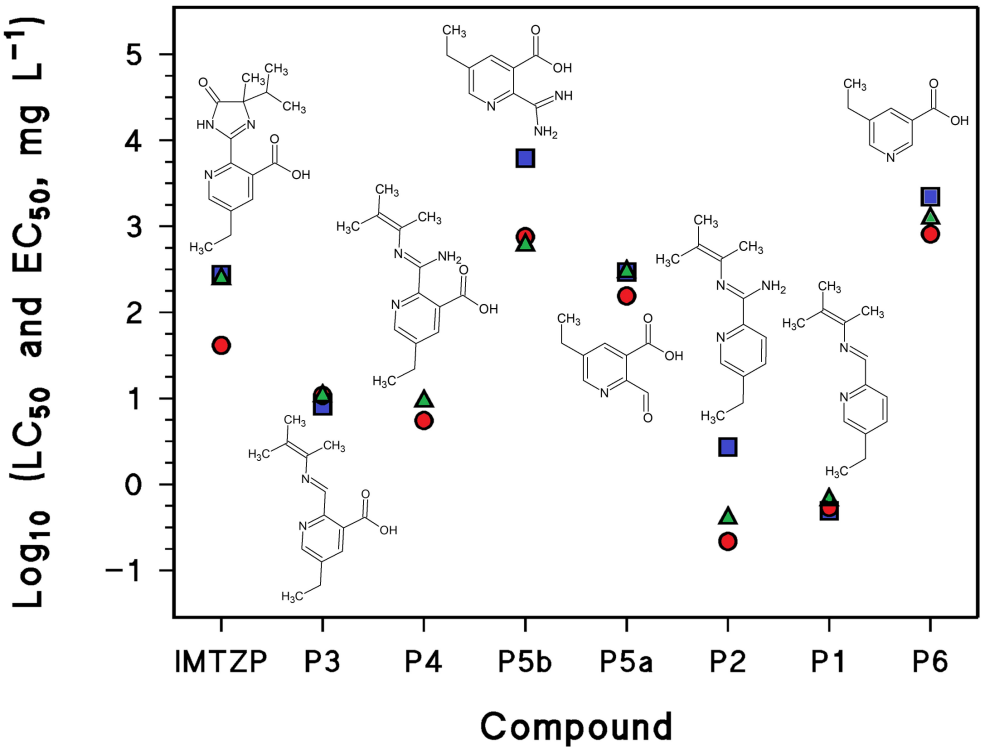


Fig. 6. Acute-toxicity data computed with the ECOSAR V2.0 software (US-EPA) for the compounds formed upon imazethapyr direct photolysis (Espy et al., 2011). Note the logarithmic scale on the Y-axis. Also note that LC_{50} refers to fish (96 h, ■) and daphnid (48 h, ▲), while EC_{50} refers to green algae (96 h, ●). IMTZP = imazethapyr.

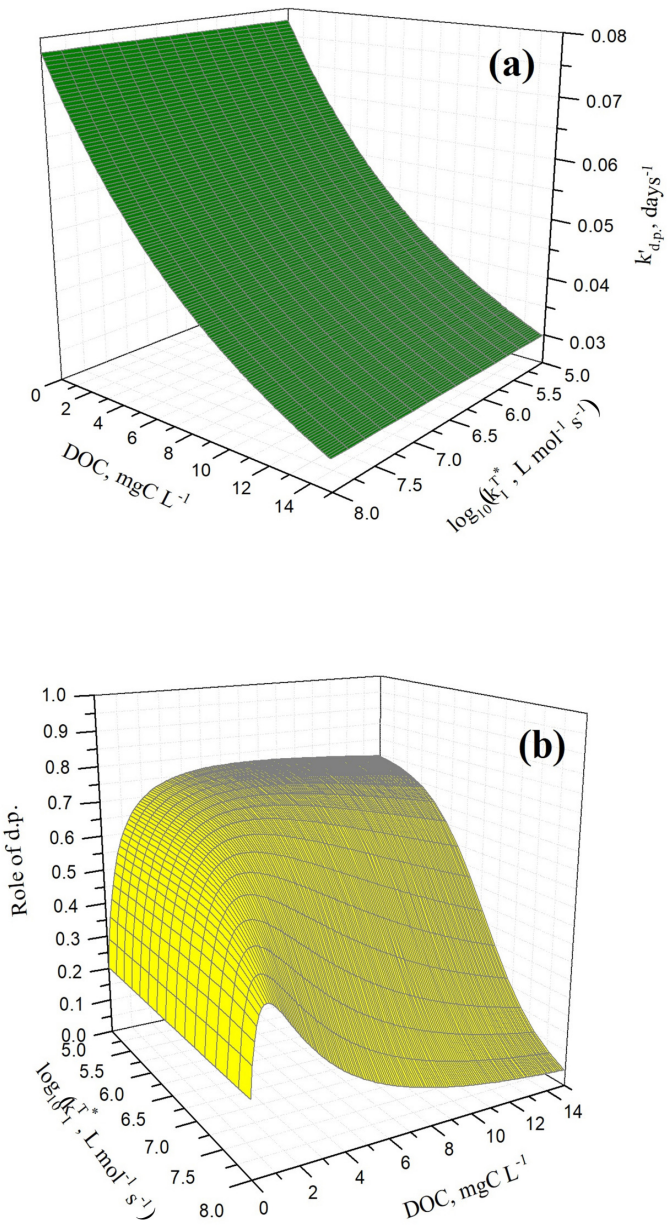


Fig. 7. (a) Imazethapyr direct photolysis pseudo-first order rate constant and (b) role of direct photolysis in the overall herbicide photodegradation in paddy water (May), as a function of the DOC and of the decimal logarithm of the second-order reaction rate constant between imazethapyr and ^{3}CDOM*. The curves were computed with the APEX software. Relevant APEX input data were as follows: 1.0×10^{-4} mol L^{-1} NO_3^-, 1.5×10^{-6} mol L^{-1} NO_2^-, 6.8×10^{-4} mol L^{-1} HCO_3^-, 4.0×10^{-6} mol L^{-1} CO_3^{2-} and 6 cm optical depth.

4. **Conclusions**

Previous works have demonstrated that (i) imazethapyr undergoes relatively fast phototransformation in aqueous solution by direct photolysis and $HO^{\bullet}$ reaction (Avila et al., 2006), and (ii) it has a half-life time in paddy water ranging between 3 and 7 days (Santos et al., 2008; Zanella et al., 2011; Martini et al, 2013; Reimche et al., 2015). In this study, the photochemical fate of imazethapyr was modelled in paddy floodwater by using the APEX software. The half-life time was first computed by taking into account the direct photolysis and the reaction with $HO^{\bullet}$ radicals, obtaining a quite good agreement between model predictions and field data. Therefore, direct photolysis and $HO^{\bullet}$ reaction can be important degradation pathways for imazethapyr in paddy water. DOM inhibits the phototransformation of imazethapyr because of $HO^{\bullet}$ scavenging and of the screening of incident sunlight, which reduces the $HO^{\bullet}$ formation rate from nitrate and nitrite and prevents light absorption by the herbicide. A similar behaviour has been found in previous works (Elazzouzi et al., 2002; Ramezani et al., 2008; Espy et al., 2011). However, by trying to model the inhibition effect of DOM reported by Espy et al. (2011), we found evidence that ^{3}CDOM* could possibly sensitise the photodegradation of imazethapyr, and that 10^8 L mol^{-1} s^{-1} could be a reasonable upper limit for the second-order rate constant of the reaction between the herbicide and ^{3}CDOM* (a likely value could be around 10^7 L mol^{-1} s^{-1}). The consideration of the ^{3}CDOM* reaction even slightly improved the agreement between the modelled imazethapyr lifetime in paddy water and the literature findings.

Although the $HO^{\bullet}$ and ^{3}CDOM* reactions can have a non-negligible role in imazethapyr photodegradation, respectively at low and high DOC levels, direct photolysis is a key degradation pathway. Furthermore, by assessing the toxicity of the transformation by-products by means of the ECOSAR V2.0 software, we found that the direct photolysis could be of environmental concern because it yields toxic intermediates. However, to better understand the imazethapyr photochemical

fate in paddy water, further studies should be carried out to experimentally assess: (i) the reactivity of imazethapyr toward ^{3}CDOM*, singlet oxygen (a photoreactive intermediate that could also be important in the DOM-rich rice-field waters) and the carbonate radicals; (ii) the actual toxicity of the direct-photolysis by-products, as well as of those arising from indirect photochemistry, and (iii) their formation yields.

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Conflict of interest

None

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