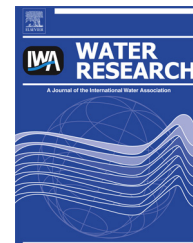




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Assessing the photochemical transformation pathways of acetaminophen relevant to surface waters: Transformation kinetics, intermediates, and modelling

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ABSTRACT

This work shows that the main photochemical pathways of acetaminophen (APAP) transformation in surface waters would be direct photolysis (with quantum yield of $(4.57 \pm 0.17) \cdot 10^{-2}$), reaction with CO_3^{2-} (most significant at $\text{pH} > 7$, with second-order rate constant of $(3.8 \pm 1.1) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and possibly, for dissolved organic carbon higher than 5 mg C L^{-1} , reaction with the triplet states of chromophoric dissolved organic matter ($^3\text{CDOM}^*$). The modelled photochemical half-life time of APAP in environmental waters would range from days to few weeks in summertime, which suggests that the importance of phototransformation might be comparable to biodegradation. APAP transformation by the main photochemical pathways yields hydroxylated derivatives, ring-opening compounds as well as dimers and trimers (at elevated concentration levels). In the case of $^3\text{CDOM}^*$ (for which the triplet state of anthraquinone-2-sulphonate was used as proxy), ring rearrangement is also hypothesised. Photochemistry would produce different transformation products (TPs) of APAP than microbial biodegradation or human metabolism, thus the relevant TPs might be used as markers of APAP photochemical reaction pathways in environmental waters.

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1. Introduction

The anti-inflammatory and antipyretic drug acetaminophen (N-(4-hydroxyphenyl)ethanamide) is one of the most widely sold over-the-counter drugs worldwide (Newson et al., 2000; McBride, 2011), and it ranks #1 in the list of pharmaceuticals marketed in many European countries (EFPIA, 2006). Its worldwide use is perhaps best exemplified by the multitude of names it has been given, among which are paracetamol, acetaminophen and acetyl-*para*-aminophenol, from which its most common acronym (APAP) has been derived. In this paper as well, APAP will be used for acetaminophen.

Like other popular pharmaceuticals, APAP and its metabolites are released into wastewater by excretion and probably because of incorrect disposal via the toilet, which causes a relevant load at the inlet of wastewater treatment plants (WWTPs) (Del Rio et al., 2013). APAP is rather effectively degraded by biological processes, but appreciable concentrations can still be found at WWTP effluents or in surface waters (Stamatis and Konstantinou, 2013). The large use of APAP ensures that quite elevated loads reach the natural environment despite degradation in WWTPs (Morasch et al., 2010; Chiron et al., 2010; Gros et al., 2010). For this reason, it is very important to investigate the fate of APAP in surface waters, where it is potentially toxic to *e.g.* aquatic invertebrates (Jones et al., 2002).

APAP biodegradation would take place in a time scale from days to months (Hari et al., 2005; Jones et al., 2005; Yamamoto et al., 2005), and sequestration contributes to its removal from water in contact with sediment (Loeffler et al., 2005). Recent research has highlighted that APAP is also transformed by photochemical processes that can be competitive with biodegradation (Yamamoto et al., 2009; Peuravuori, 2012). Photochemical reactions are an important class of abiotic pathways for dissolved pollutants in surface waters (Tixier et al., 2003). They are usually divided into direct photolysis, where absorption of sunlight by the pollutant causes its transformation, and indirect photodegradation. In the latter case, photoactive compounds called photosensitisers (such as nitrate, nitrite and chromophoric dissolved organic matter, CDOM) absorb sunlight and produce reactive species such as $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$ and CDOM triplet states, $^3\text{CDOM}^*$ (Gerecke et al., 2001; Boreen et al., 2003; Canonica et al., 2005; Page et al., 2011). In the case of APAP, photodegradation has been investigated in the presence of nitrate and CDOM, although the role of the possible photoreactive transients (*e.g.* $\cdot\text{OH}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$) was not differentiated (Peuravuori, 2012). However, as it will be demonstrated in the present paper, one of the most important pathways of APAP phototransformation (reaction with $\text{CO}_3^{\cdot-}$) has not been taken into account so far. Therefore, the importance of photochemistry in the environmental fate of APAP might have been underestimated.

This work studies the kinetics of APAP photo-transformation pathways of potential environmental significance, by determining the direct photolysis quantum yield and the reaction rate constants with $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$. These data allow for the modelling of APAP lifetime, as a function of environmental conditions such as water chemistry and depth. The study of transformation

intermediates (also called transformation products, TPs) can be very important in the environmental (photo)chemistry of xenobiotics, because sometimes TPs are of higher concern than the parent molecule. Examples are the cases of triclosan (Kliegman et al., 2013) and carbamazepine (Donner et al., 2013). Therefore, the TPs of APAP formed via the main photochemical reaction pathways were identified to get insight into the environmental conditions that would favour their photoassisted occurrence.

2. Experimental section

2.1. Reagents and materials

Acetaminophen (APAP, purity grade 98%), anthraquinone-2-sulphonic acid, sodium salt (AQ2S, 97%), hydroquinone (HQ, 98%), 1-nitronaphthalene (1NN, 99%), furfuryl alcohol (98%), NaNO_3 (>99%), NaHCO_3 (98%), $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (98%), $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (98%), HClO_4 (70%) and H_3PO_4 (85%) were purchased from Aldrich, NaOH (99%), H_2O_2 (35%) and 2-propanol (LiChrosolv gradient grade) from VWR Int., methanol (gradient grade) from Carlo Erba, Rose Bengal (RB) from Alfa Aesar.

2.2. Irradiation experiments

The kinetic parameters relevant to the main photochemical processes that would involve APAP in surface waters (direct photolysis and reaction with $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$) were determined by laboratory measurements. These results allow for the modelling of the lifetime of pollutants as a function of environmental variables (Vione et al., 2011; De Laurentis et al., 2012a). AQ2S was used as CDOM proxy to assess reactivity between APAP and $^3\text{CDOM}^*$. Reasons for this choice are the widespread occurrence of quinones in CDOM (Cory and McKnight, 2005) and the fact that irradiation of AQ2S, unlike other triplet sensitisers, does not yield interfering transients such as $\cdot\text{OH}$ or $^1\text{O}_2$. The triplet state $^3\text{AQ2S}^*$ is not quenched by oxygen because it quickly reacts with H_2O to form two water adducts, which evolve into hydroxyderivatives without producing $\cdot\text{OH}$ (Maddigapu et al., 2010). AQ2S initial concentration was 0.1 mM, to limit the additional complication represented by reaction between the excited and ground states of AQ2S (Bedini et al., 2012).

Solutions (5 mL) were irradiated in Pyrex glass cells (4.0 cm diameter, 2.3 cm height, 295 nm cut-off wavelength) and magnetically stirred during irradiation. Irradiation of APAP alone to study direct photolysis, of APAP + nitrate or APAP + H_2O_2 to study reaction with $\cdot\text{OH}$, and of APAP + nitrate + bicarbonate to study reaction with $\text{CO}_3^{\cdot-}$ was carried out under a 20 W Philips TL 01 UVB lamp, with emission maximum at 313 nm. The lamp had $3.0 \pm 0.2 \text{ W m}^{-2}$ UV irradiance in the 300–400 nm range, measured with a power meter by CO.FO.ME.GRA. (Milan, Italy) equipped with a UV-sensitive probe. The incident photon flux in solution was actinometrically determined using the ferrioxalate method (Kuhn et al., 2004). By knowing, as a function of wavelength, the fraction of radiation absorbed by $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$, the quantum yield of Fe^{2+} photoproduction and the shape of the lamp

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