



A model assessment of the importance of direct photolysis in the photo-fate of cephalosporins in surface waters: Possible formation of toxic intermediates



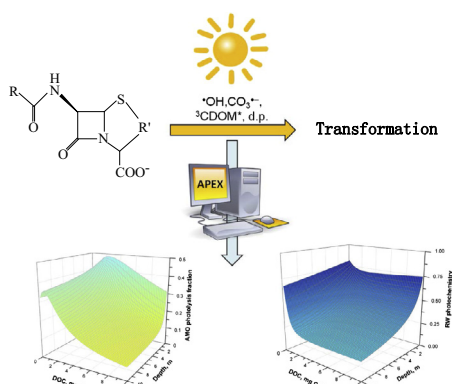
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HIGHLIGHTS

- Cephalosporins are transformed in surface waters by hydrolysis and photochemistry.
- Photochemistry would prevail in waters with low depth and/or low DOC.
- Important direct photolysis for cefazolin, negligible for cefradine and cefalexin.
- Direct photolysis is favoured in shallow waters with intermediate/high DOC values.
- Such conditions favour the formation of toxic intermediates.

GRAPHICAL ABSTRACT



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ABSTRACT

The direct and indirect photodegradation of six cephalosporins was predicted using a photochemical model, on the basis of literature values of photochemical reactivity. Environmental photodegradation would be important in surface water bodies with depth $\leq 2-3$ m, and/or in deeper waters with low values of the dissolved organic carbon ($\text{DOC} \leq 1 \text{ mg C L}^{-1}$). The half-life times would range from a few days to a couple of weeks in summertime. In deeper and higher-DOC waters and/or in different seasons, hydrolysis could prevail over photodegradation. The direct photolysis of cephalosporins is environmentally concerning because it is known to produce toxic intermediates. It would be a major pathway for cefazolin, an important one for amoxicillin and cefotaxime and, at $\text{pH} < 6.5$, for cefapirin as well. In contrast, direct photolysis would be negligible for cefradine and cefalexin. The DOC values would influence the fraction of photodegradation accounted for by direct photolysis in shallow water, to a different extent depending on the role of sensitisation by the triplet states of chromophoric dissolved organic matter.

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1. Introduction

The occurrence of pharmaceuticals in surface waters is a matter of concern, because of their adverse effects on living organisms and

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drinking water supplies. Many pharmaceuticals are only partially degraded in wastewater treatment plants (WWTPs), the outlets of which are thus important point sources of these xenobiotics (Kümmerer, 2009; Pal et al., 2010; Kosjek and Heath, 2011). In particular, antibiotics have been detected in the ng L^{-1} to $\mu\text{g L}^{-1}$ range in surface waters, where the possible bioaccumulation and the induction of drug resistance in bacteria may affect environmental

and human safety (Corvaglia et al., 2008; Xu et al., 2011; Manzetti and Ghisi, 2014; Lee et al., 2014; Iliiev et al., 2015; Jahne et al., 2015).

Cephalosporins are a widely used class of β -lactam antibiotics in human and veterinary medicine (Ball, 1999), and they are detected at significant concentration at the inlet and outlet of WWTPs (Rossmann et al., 2014). Their degradation in surface waters mainly occurs through abiotic pathways (hydrolysis and photochemistry), while biodegradation may be important in sediment (Jiang et al., 2010). The kinetics of cephalosporin hydrolysis is minimum under \sim neutral conditions (Yamana and Tsuj, 1976), thus photodegradation can be a competitive pathway in surface waters (Wang and Lin, 2012).

Photodegradation is usually divided into direct photolysis and indirect photochemistry. The involvement of both processes in surface-water conditions has been shown for cephalosporins (Xu et al., 2011; Wang and Lin, 2012) and other antibiotics (Li et al., 2011, 2014; Lian et al., 2015; Niu et al., 2013). In direct photolysis, a xenobiotic undergoes transformation triggered by sunlight absorption (Pace and Barreca, 2013). In indirect photochemistry, sunlight is absorbed by naturally-occurring photosensitisers such as chromophoric dissolved organic matter (CDOM), nitrate and nitrite (Tai et al., 2012). Photosensitisers produce reactive transients including HO^\cdot , $^1\text{O}_2$ and CDOM triplet states ($^3\text{CDOM}^*$). The radicals HO^\cdot are produced by photolysis of nitrate and nitrite, and through different processes that may or may not involve H_2O_2 upon CDOM irradiation (Page and McNeill, 2011). The transients $^3\text{CDOM}^*$ and $^1\text{O}_2$ are produced by CDOM photochemistry, while the carbonate radicals ($\text{CO}_3^{\cdot-}$) are formed upon oxidation of carbonate and bicarbonate by HO^\cdot and of carbonate by $^3\text{CDOM}^*$ (Canonica et al., 2005).

Wang and Lin (2012) have observed that cephalosporin direct photolysis produces intermediates that are more toxic than the parent compounds. It is thus very important to assess the significance of direct photolysis in surface-water environments and to identify the conditions where it may be favoured. To our knowledge, the photodegradation of cephalosporins has been studied in the laboratory (Jiang et al., 2010; Xu et al., 2011; Wang and Lin, 2012) but not in the field, and a direct extrapolation of laboratory results to surface-water conditions may be problematic because of e.g. very different water column depths (Vione, 2014). To tackle this problem, we used a model approach to describe phototransformation. Model calculations are based on literature photoreactivity parameters for each compound (direct photolysis quantum yields and second-order reaction rate constants with transients), and on environmental conditions such as water chemistry and depth. The environmental conditions are thus predicted where (i) cephalosporin phototransformation can be important compared to e.g. hydrolysis, and (ii) direct photolysis accounts for an important fraction of the photochemical transformation.

2. Methods

2.1. Source data

Table 1 reports the available photoreactivity parameters of the cephalosporins under investigation. The direct photolysis quantum yield was measured under real sunlight for amoxicillin (AMO; Andreozzi et al., 2004), and using a solar simulator for the other compounds (Wang and Lin, 2012). The availability of photolysis quantum yields and second-order reaction rate constants with HO^\cdot is important for photochemical modelling because, differently from the first-order rate constants, second-order ones and quantum yields can be extended over a much wider range of conditions that go far beyond the laboratory ones. Pulse radiolysis of water

Table 1

Direct photolysis quantum yields (Φ_{DP}) and second-order reaction rate constants with HO^\cdot of the cephalosporins under investigation. The structures of the investigated compounds are reported in Scheme S1 of the Supplementary Material (SM). CFP data are reported for two pH values, because CFP undergoes an acid–base equilibrium with $\text{pK}_a = 5.44$ (Wang and Lin, 2012). In this case, modelling took into account the fractions of the two forms which occurred at both pH values. n/a: not available.

| Compound | Φ_{DP} | $k_{\text{Compound,HO}^\cdot}$ ($\text{M}^{-1} \text{s}^{-1}$) |
|-------------------|--|--|
| Amoxicillin (AMO) | $6 \cdot 10^{-3}$ ^a | $6.9 \cdot 10^9$ ^c |
| Cefalexin (CFX) | $9.1 \cdot 10^{-2}$ ^b | $7.1 \cdot 10^9$ ^b |
| Cefradine (CFD) | $7.6 \cdot 10^{-2}$ ^b | $1.1 \cdot 10^{10}$ ^b |
| Cefotaxime (CTX) | $1 \cdot 10^{-3}$ ^b | $8.1 \cdot 10^9$ ^b |
| Cefazolin (CFZ) | $6.0 \cdot 10^{-2}$ ^b | $6.5 \cdot 10^9$ ^d |
| Cefapirin (CFP) | $7 \cdot 10^{-3}$ (pH 7) ^b $1.6 \cdot 10^{-2}$ (pH 5) ^b | n/a |

^a Andreozzi et al. (2004).

^b Wang and Lin (2012).

^c Song et al. (2008).

^d Dail and Mezyk (2010).

plus competition kinetics with SCN^- has been used to derive the HO^\cdot second-order reaction rate constants of AMO (Song et al., 2008) and cefazolin (CFZ; Dail and Mezyk, 2010). Comparable results were obtained for AMO by Andreozzi et al. (2005), upon UV irradiation of H_2O_2 and competition kinetics with benzoic acid. The rate constants of cefalexin (CFX), cefradine (CFD) and cefotaxime (CTX) with HO^\cdot have been measured by Wang and Lin (2012) with the Fenton reaction, using acetophenone as model compound.

2.2. Photochemical modelling and toxicity predictions

The assessment of the phototransformation kinetics was carried out with the APEX software (Aqueous Photochemistry of Environmentally-occurring Xenobiotics). It predicts photochemical half-life times as a function of water chemistry and depth, for compounds with known direct photolysis quantum yields and second-order reaction rate constants with transient species (Vione, 2014; Bodrato and Vione, 2014). APEX is based on a photochemical model, validated by comparison with field data of phototransformation kinetics in surface freshwaters (Maddigapu et al., 2011; De Laurentiis et al., 2012; Marchetti et al., 2013). Its time unit is a summer sunny day (SSD), corresponding to fair-weather 15 July at 45°N latitude. Further information is reported in the Supplementary Material (hereafter SM).

Insight into acute and chronic toxicity was obtained with the software ECOSAR (Ecological Structure Activity Relationship, <http://www.epa.gov/oppt/newchems/tools/21ecosar.htm>, last accessed April 2015), which gives a standard toxicity profile based on acute and chronic endpoints for fish, daphnid and algae (acute: median lethal concentrations for fish and daphnid, median effective concentrations for algae; chronic: geometric mean of the no observed effect concentration and of the lowest observed effect concentration for all organisms).

3. Results and discussion

The data reported in Table 1 show that the direct photolysis quantum yield is available for all the investigated compounds (two values are reported for cefapirin, CFP, which undergoes an acid–base equilibrium with $\text{pK}_a = 5.44$; Wang and Lin, 2012). Unfortunately, the reaction rate constant with HO^\cdot is not available for CFP. Because the known HO^\cdot rate constants for the compounds of interest are all higher than $5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$, in a conservative approach this value was taken as a reasonable lower limit for the reaction rate constant(s) between CFP (both forms) and HO^\cdot .

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