Water Research 105 (2016) 383–394

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Assessing the phototransformation of diclofenac, clofibric acid and naproxen in surface waters: Model predictions and comparison with field data

Paola Avetta [a], Debora Fabbri [a], Marco Minella [a], Marcello Brigante [b, c], Valter Maurino [a], Claudio Minero [a], Marco Pazzi [a], Davide Vione [a, d, *]

[a] Università degli Studi di Torino, Dipartimento di Chimica, Via P. Giuria 5, 10125 Torino, Italy[1]
[b] Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France
[c] CNRS, UMR 6296, ICCF, BP 80026, F-63177 Aubière, France
[d] Università degli Studi di Torino, Centro Interdipartimentale NatRisk, Via L. Da Vinci 44, 10095 Grugliasco (TO), Italy[2]

ARTICLE INFO

Article history:
Received 10 February 2016
Received in revised form
24 August 2016
Accepted 27 August 2016
Available online 30 August 2016

Keywords:
Diclofenac
Naproxen
Clofibric acid
Environmental photochemistry
Photolysis
Pollutant fate

ABSTRACT

Phototransformation is important for the fate in surface waters of the pharmaceuticals diclofenac (DIC) and naproxen (NAP) and for clofibric acid (CLO), a metabolite of the drug clofibrate. The goal of this paper is to provide an overview of the prevailing photochemical processes, which these compounds undergo in the different conditions found in freshwater environments. The modelled photochemical half-life times of NAP and DIC range from a few days to some months, depending on water conditions (chemistry and depth) and on the season. The model indicates that direct photolysis is the dominant degradation pathway of DIC and NAP in sunlit surface waters, and potentially toxic cyclic amides were detected as intermediates of DIC direct phototransformation. With modelled half-life times in the month-year range, CLO is predicted to be more photostable than DIC or NAP and to be degraded mainly by reaction with the $^{\bullet}OH$ radical and with the triplet states of chromophoric dissolved organic matter ($^{3}CDOM^{*}$). The CLO intermediates arising from these processes and detected in this study (hydroquinone and 4-chlorophenol) are, respectively, a chronic toxicant to aquatic organisms and a possible carcinogen for humans. Hydroquinone is formed with only ~5% yield upon CLO triplet-sensitised transformation, but it is highly toxic for algae and crustaceans. In contrast, the formation yield of 4-chlorophenol reaches ~50% upon triplet sensitisation and ~10% by $^{\bullet}OH$ reaction. The comparison of model predictions with field data from a previous study yielded a very good agreement in the case of DIC and, when using 4-carboxybenzophenone as proxy for triplet sensitisation by CDOM, a good agreement was found for CLO as well. In the case of NAP, the comparison with field data suggests that its direct photolysis quantum yield approaches or even falls below the lower range of literature values.

1. Introduction

In recent years a growing interest has arisen for the emerging pollutants or contaminants of emerging concern. They belong to diverse chemical and commodity classes or sub-classes and are often found in wastewater. The effluents of wastewater treatment plants (WWTPs) are major routes of emerging contaminants to surface water bodies, because these compounds are often polar and biorefractory and undergo partial or poor removal by traditional WWTP technologies (Richardson and Ternes, 2014). Pharmaceuticals and personal care products (PPCPs) are an important class of emerging contaminants, which could cause adverse effects (directly or through their metabolites) on aquatic environments, the food webs and possibly also human health (Fatta-Kassinos et al., 2011; Bu et al., 2013; Prasse et al., 2015).

Among PPCPs, diclofenac (DIC) and naproxen (NAP) are two very widespread non-steroidal anti-inflammatory drugs. The sales volumes of DIC are quite high, and in the years from 2010 to 2013 its

* Corresponding author. Università degli Studi di Torino, Dipartimento di Chimica, Via P. Giuria 5, 10125 Torino, Italy.
E-mail address: davide.vione@unito.it (D. Vione).
[1] http://www.chimicadellambiente.unito.it
[2] http://www.natrisk.org,davide.vione@unito.it

http://dx.doi.org/10.1016/j.watres.2016.08.058
0043-1354/

average world annual consumption was 1443 ± 58 t (Acuña et al., 2015; Azuma et al., 2015). In addition to possible concerns for human health by direct use (Moore et al., 2014), DIC is potentially ecotoxic for surface-water environments (Escher et al., 2011; Diniz et al., 2015) where it can reach μg L^{-1} levels (Patrolecco et al., 2015). These issues have prompted the inclusion of DIC in the list of substances to be monitored in the latest European Water Framework Directive (Ribeiro et al., 2015). Moreover, the use of DIC in veterinary medicine causes adverse effects to the populations of vultures (Oaks et al., 2004; Camina et al., 2014).

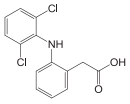
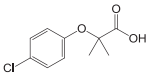
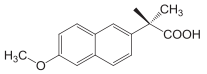
NAP was found to occur at tens to hundreds ng L^{-1} levels in surface waters (Patrolecco et al., 2015; Arlos et al., 2015), and it has even been detected in drinking water (Benotti et al., 2009). Although its concentration levels are too low to cause acute toxicity, the frequent detection of fairly elevated concentrations might cause chronic effects on aquatic organisms such as crustaceans and algae (Fernandez et al., 2010). Moreover, NAP transformation intermediates should also be considered for a complete ecotoxicological assessment of this compound in surface waters (Isidori et al., 2005).

Clofibric acid (CLO) is another interesting compound because it is a metabolite of the cholesterol-lowering pharmaceutical drug clofibrate and a structural isomer of the herbicide mecoprop (Santos et al., 2000). CLO occurs in surface waters at tens ng L^{-1} levels (Patrolecco et al., 2015), and chronic exposure can cause harmful effects to fish (Corcoran et al., 2015; Coimbra et al., 2015) and possibly crustaceans (Gonzalez-Ortegon et al., 2015).

Photochemistry is a potentially important transformation pathway for the investigated compounds (Boreen et al., 2003; Bartels and von Tümpling, 2007; Bonvin et al., 2013; Yan and Song, 2014; Duran-Alvarez et al., 2015), and its significance is increased by the fact that the irradiation of pharmaceuticals mixtures may increase their toxicity (Li and Lin, 2015). Generally speaking, phototransformation in surface waters can be divided into direct photolysis (a xenobiotic absorbs sunlight, which triggers its degradation) and indirect photochemistry. In the latter, sunlight is absorbed by naturally-occurring photosensitisers (most notably nitrate, nitrite and chromophoric dissolved organic matter, CDOM) to produce reactive transient species ($^{\cdot}OH$, $CO_3^{-\cdot}$, $^1O_2$ and CDOM triplet states, ^{3}CDOM*) (Dong et al., 2015). More precisely, nitrate and nitrite yield $^{\cdot}OH$, while irradiated CDOM produces ^{3}CDOM* (which can form $^1O_2$ by reaction with oxygen) and $^{\cdot}OH$ as well. The carbonate radical is produced upon oxidation of carbonate and bicarbonate by $^{\cdot}OH$ and of carbonate by ^{3}CDOM* (Canonica et al., 2005; Canonica et al., 2006; De Laurentiis et al., 2013; Bahnmueller et al., 2014; Janssen et al., 2014; Trivella et al., 2015; Bintou et al., 2015). Dissolved organic matter (DOM, not necessarily chromophoric), which is usually quantified as dissolved organic carbon (DOC), is the main sink of both $^{\cdot}OH$ and $CO_3^{-\cdot}$. This issue, combined with the fact that CDOM is a major photosensitiser, explains why $^{\cdot}OH$ and $CO_3^{-\cdot}$ are usually more concentrated in low-DOC waters. In contrast, the highest levels of ^{3}CDOM* and $^1O_2$ usually occur in high-DOC environments (Vione et al., 2014).

The photodegradation of DIC, NAP and CLO (see Table 1 for their structures) has been studied in the laboratory, indicating that the direct photolysis should be an important pathway in the environmental phototransformation of DIC and NAP (Packer et al., 2003; Abdelmelek et al., 2011; Yu et al., 2013). However, to our knowledge few attempts (and only for DIC) have been made to compare predictions based on laboratory studies with field results concerning the persistence of these compounds (Buser et al., 1998; Bonvin et al., 2013). A field study that includes estimates of photoreaction kinetics is for instance available for the sunlit epilimnion of Lake Greifensee, Switzerland (Tixier et al., 2003). It could be very conveniently exploited to validate and verify the results of laboratory simulations, because it is one of the very few examples to our knowledge where the phototransformation kinetics was disentangled from the overall field attenuation.

Table 1
Photochemical reactivity parameters of S = DIC, CLO or NAP, obtained either from the literature or experimentally in this work. Model photosensitisers: AQ2S = anthraquinone-2-sulphonate; CBP = 4-carboxybenzophenone; RIB = riboflavin. The reported values of $k_{S,^3CDOM*}$ are those assumed in this work on the basis of the results obtained with the model photosensitisers, after comparison with field data. In the case of DIC, $k_{DIC,^3CDOM*}$ was the average of $k_{DIC,^3CBP*}$, $k_{DIC,^3RIB*}$ and $k_{DIC,^3AQ2S*}$; in the case of CLO, it was assumed $k_{CLO,^3CDOM*} = k_{CLO,^3CBP*}$; finally, $k_{NAP,^3CDOM*}$ was the average of $k_{NAP,^3CBP*}$ and $k_{NAP,^3RIB*}$.

	Diclofenac (DIC)	Clofibric acid (CLO)	Naproxen (NAP)
			
$\Phi_{S,Phot}$ (unitless)	9.4×10^{-2}	5.5×10^{-3}	$(1–3.6) \times 10^{-2}$
Ref.	1	6	1–3
$k_{S,^{\cdot}OH}$ (M^{-1} s^{-1})	$(9.3 \pm 0.1) \times 10^9$	7×10^9	8×10^9
Ref.	5	7	4
$k_{S,^1O_2}$ (M^{-1} s^{-1})	$(1.3 \pm 0.2) \times 10^7$	$(6.0 \pm 1.9) \times 10^5$	$(1.1 \pm 0.1) \times 10^5$
Ref.	This work	This work	1
$k_{S,^3AQ2S*}$ (M^{-1} s^{-1})	$(7.6 \pm 0.2) \times 10^8$	$(1.2 \pm 0.1) \times 10^{10}$	$(3.2 \pm 0.1) \times 10^{10}$
Ref.	This work	This work	This work
$k_{S,^3CBP*}$ (M^{-1} s^{-1})	$(6.4 \pm 1.6) \times 10^8$	$(4.7 \pm 0.6) \times 10^8$	$(7.5 \pm 1.2) \times 10^8$
Ref.	This work	This work	This work
$k_{S,^3RIB*}$ (M^{-1} s^{-1})	$(1.7 \pm 0.1) \times 10^9$	$(5.5 \pm 1.0) \times 10^9$	$(1.3 \pm 0.2) \times 10^9$
Ref.	This work	This work	This work
$k_{S,^3CDOM*}$ (M^{-1} s^{-1})	$(1.0 \pm 0.3) \times 10^9$	$(4.7 \pm 0.6) \times 10^8$	$(1.0 \pm 0.2) \times 10^9$
Ref.	This work	This work	This work

Legend for the references (Refs.).
1. Packer et al. (2003)
2. Pereira et al. (2007)
3. Marotta et al. (2013)
4. Ben Abdelmelek et al. (2011)
5. Yu et al. (2013)
6. Andreozzi et al. (2003)
7. Razavi et al. (2009).