A model assessment of the potential of river water to induce the photochemical attenuation of pharmaceuticals downstream of a wastewater treatment plant (Guadiana River, Badajoz, Spain)

Davide Vione [a, b, *], Angel Encinas [c], Debora Fabbri [a], Paola Calza [a]

[a] Università di Torino, Dipartimento di Chimica, Via Pietro Giuria 5, 10125 Torino, Italy
[b] Università di Torino, Centro Interdipartimentale NatRisk, Largo Paolo Braccini 2, 10095 Grugliasco TO, Italy
[c] FCC Aqualia S.A., C/ Montesinos 28, 06002, Badajoz, Spain

HIGHLIGHTS

- Phototransformation kinetics was modelled for CBZ, IBU and DIC.
- CBZ phototransformation would prevail over biodegradation.
- For IBU, biodegradation would likely be more important than photochemistry.
- Phototransformation and biodegradation would be comparable for DIC.
- Phototransformation would be enhanced under water scarcity (low flow) conditions.

GRAPHICAL ABSTRACT
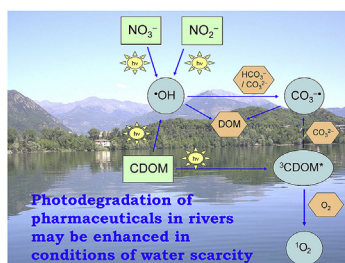
ARTICLE INFO

ABSTRACT

We predicted the possible direct and indirect phototransformation kinetics of carbamazepine (CBZ), ibuprofen (IBU) and diclofenac (DIC) in river water, based on data of water chemistry obtained for the Guadiana River near Badajoz (Southwestern Spain) during a year-round sampling campaign. The three compounds were chosen, (i) because they occurred at the outlet of the wastewater treatment plant (WWTP) in Badajoz, as well as in river water sampled 1 km downstream of the WWTP, and (ii) because their photochemical fate in surface waters is known well enough to be modelled. The predicted phototransformation kinetics would be negligible in winter and fastest in April–August, with comparable rate constants in April through August despite differences in sunlight irradiance. Favourable water chemistry would in fact offset the lower irradiance, and vice versa. Half-life times of at least three weeks - one month are predicted for CBZ and IBU. Photodegradation may be an important attenuation pathway for biorecalcitrant CBZ, while IBU photochemistry is unlikely to be competitive with other processes including biodegradation. The predicted DIC photochemical half-life times of 7–10 days in April–August would be comparable with the biodegradation kinetics data reported in the literature. Photochemistry might not induce extensive phototransformation of xenobiotics in the Guadiana River under normal flow conditions, but it could become important in the case of low flow produced by water scarcity.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Wastewater treatment plants (WWTPs) are important sources of several emerging contaminants, including pharmaceuticals and

* Corresponding author. Università di Torino, Dipartimento di Chimica, Via Pietro Giuria 5, 10125 Torino, Italy.
E-mail address: davide.vione@unito.it (D. Vione).

personal care products (PPCPs) to surface waters (Petrovic et al., 2003; Richardson and Ternes, 2014; Ebele et al., 2017). The reason is that most WWTPs have been designed to eliminate nutrients and pathogens from wastewater and they largely rely on solid removal, biological processes and disinfection. Unfortunately, many emerging contaminants are biorecalcitrant and resist degradation in biological treatment steps (Fatta-Kassinos et al., 2010). Hydrophobic biorecalcitrant molecules partitioning to biosolids could still be removed from the aqueous phase during the solid separation step, while the water-soluble compounds tend to remain dissolved (Kosjek and Heath, 2010). The polar contaminants will thus occur in the wastewater effluent, unless an important reaction takes place with the disinfectant in the final treatment stage. In some cases, however, disinfection can produce secondary contaminants such as the chloro derivatives (Buth et al., 2011). Moreover, some pharmaceuticals are excreted by the human body in metabolised forms such as the glucuronide conjugates, which may mask the occurrence of the parent xenobiotics at the WWTP inlet. The bacteria that operate in the biological treatment step often detach the sugar moiety and set free the original drug which, if sufficiently biorecalcitrant, can be found in higher concentration at the WWTP outlet than at the inlet (Radjenovic et al., 2007). This back-transformation of drug metabolites definitely complicates the assessment of the PPCP biodegradation potential in WWTPs (Ternes, 1998). New treatment technologies including advanced oxidation processes will be needed to carry out a technological update of WWTPs, and to enable effective PPCP removal (Huber et al., 2003; Wang et al., 2017, 2018).

Once they reach natural water (often, river water), the contaminants may undergo a range of transformation pathways that make up the self-depuration potential of the water body, but that would sometimes produce harmful secondary pollutants (Kümmerer, 2009a, b). Attenuation may take place biologically, but the most biodegradable compounds undergo complete or almost complete abatement at the WWTP level and, from this point of view, WWTPs tend to select rather biorecalcitrant molecules at their outlet. A caveat to this line of reasoning is that the biodegradation behaviour in a WWTP may not be representative of the biological processes taking place in river water in contact with sediment (Fono et al., 2006; Kunkel and Radke, 2011). Therefore, PPCP biodegradation in surface waters cannot be excluded. Abiotic degradation involves hydrolysis, dark redox processes and, most notably, photochemical reactions (Dunnivant and Anders, 2006). The latter are induced by sunlight and are usually divided into direct photolysis and indirect photochemistry (Vione et al., 2014). In the direct photolysis, the pollutant absorbs sunlight and undergoes transformation as a consequence (Fenner et al., 2013). In the case of indirect photochemistry, sunlight is absorbed by naturally occurring compounds called photosensitisers that include nitrate, nitrite and chromophoric dissolved organic matter (CDOM) (Pace and Barreca, 2014). Irradiated photosensitisers generate reactive transient species that are involved in pollutant degradation. In particular, the sunlight irradiation of nitrate, nitrite and CDOM yields the hydroxyl radical ($^\bullet$OH), while irradiated CDOM also produces singlet oxygen ($^1O_2$) and reactive triplet states ($^3CDOM^*$) (Vione et al., 2014; Rosario-Ortiz and Canonica, 2016; McNeill and Canonica, 2016). Moreover, the carbonate radical ($CO_3^{\bullet-}$) is produced by oxidation of carbonate and bicarbonate by $^\bullet$OH, and of carbonate by $^3CDOM^*$ (Canonica et al., 2005). In addition to being produced, the transients are also quenched in natural waters. Dissolved organic matter (DOM), which can be quantified as the dissolved organic carbon (DOC), is the main scavenger of $^\bullet$OH and $CO_3^{\bullet-}$ (Vione et al., 2014; Gligorovski et al., 2015). In contrast, $^3CDOM^*$ are quenched by reaction with O_2 to yield $^1O_2$ and, to a lesser extent, by internal conversion (Rosario-Ortiz and Canonica,

2016; McNeill and Canonica, 2016). Finally, $^1O_2$ is mainly quenched by collisions with the water solvent (Rodgers and Snowden, 1982). The direct photolysis and the reactions with $^\bullet$OH, $CO_3^{\bullet-}$, $^1O_2$ and $^3CDOM^*$ usually account for the majority of the photochemical transformation of xenobiotics in sunlit surface waters (Boreen et al., 2003; Vione et al., 2014). The photo-transformation kinetics depend on several issues including the intrinsic photoreactivity of the xenobiotic by direct photolysis and indirect photochemistry, the chemical composition and depth of the natural water, and the irradiance of sunlight. The irradiance may vary depending on location, weather, time of the day and season. The water chemistry has seasonal trends as well, because of the combination of biological and chemical processes (Vione, 2017). While most attention has been focused on the impact of seasonal sunlight irradiance on photochemistry, the simultaneous variations in the occurrence of key photosensitisers (chromophoric organic compounds, nitrate and nitrite) and scavengers (DOM and inorganic carbon) have been largely overlooked.

To our knowledge, relatively few works have directly addressed the attenuation of xenobiotics in rivers (Schwientek et al., 2016), although several data from laboratory studies are available concerning biotic and abiotic transformation in river water or water/sediment systems (e.g., Löffler et al., 2005; Kunkel and Radke, 2008). The main difficulty is linked with important transport phenomena in rivers, which act as a confounding factor in the detection and quantification of transformation processes to a much larger extent than for, e.g., lake water (Yu-Chen Lin et al., 2006; Radke et al., 2010; Kunkel and Radke, 2011). To our knowledge, naproxen is the only xenobiotic for which there is some (but non univocal) field evidence of photodegradation in rivers (Yu-Chen Lin et al., 2006; Fono et al., 2006; Radke et al., 2010). To overcome some of the above-cited difficulties, the present work uses photochemical modelling to assess the potential of sunlit river water to induce the photodegradation of xenobiotics. The model predictions are based on known photoreactivity data, on clear-sky sunlight irradiance, and on data of water chemistry collected during a one-year sampling campaign carried out at the Guadiana River near the town of Badajoz, Southwestern Spain. The target pollutants (carbamazepine, ibuprofen and diclofenac) were chosen among the emerging contaminants detected at the outlet of the Badajoz WWTP, located 1 km upstream of the river sampling site. The rationale for the choice of the three pollutants is that their environmental (photo) fate has been extensively studied (Tixier et al., 2003; Bonvin et al., 2013), and their photodegradation is already known to proceed mainly by direct photolysis and reactions with $^\bullet$OH and $^3CDOM^*$. The relevant quantum yields and reaction rate constants have already been determined (Vione et al., 2011; De Laurentiis et al., 2012; Avetta et al., 2016).

2. Experimental

2.1. Water sampling

The Rincón de Caya WWTP is located in the city of Badajoz (Spain) and it is operated by FCC Aqualia. The plant is described in Fig. 1 and it is designed to treat an average flow of 66.000 m^3 day^{-1}, to deliver services to a population equivalent of 385,000 inhabitants. However, it is currently treating an average flow of 35,000 m^3 day^{-1}. Samples were taken from the Badajoz WWTP outlet and from Guadiana River, in a point 1 km downstream of the WWTP. A bucket was dipped, respectively, into the treated water tank placed at the end of the plant waterline and in the river, as far as possible from the bank, at 0.5 m depth. The bucket was then brought out at the surface, and water samples were collected in