Science of the Total Environment xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

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

Environmental photochemical fate of selected pharmaceutical compounds in natural and reconstituted Suwannee River water: Role of reactive species in indirect photolysis

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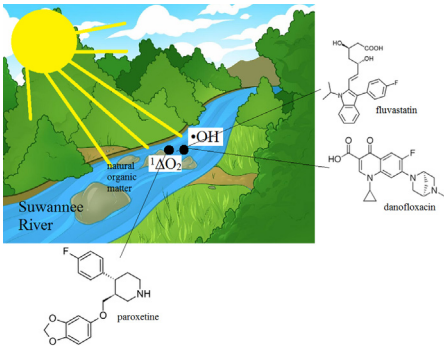
HIGHLIGHTS

- Danofloxacin, fluvastatin and paroxetine degrade in natural water to various extents due to direct and indirect photolysis
- Hydroxyl radical and singlet oxygen contribute to the degradation (indirect photolysis)
- Second order rate constants for the pharmaceuticals with these reactive species vary from 10^4 to 10^9 $M^{-1}s^{-1}$

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 October 2016
Received in revised form 1 December 2016
Accepted 2 December 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Danofloxacin
Paroxetine
Fluvastatin
Hydroxyl radical
Singlet oxygen
Kinetics

ABSTRACT

This study reports the impact of two reactive species, hydroxyl radical and singlet oxygen, on the photochemical degradation of three selected pharmaceutical compounds in natural and reconstituted solutions of Suwannee River water. Absolute bimolecular rate constants ($M^{-1}s^{-1}$) were determined for the reaction of hydroxyl radical and singlet oxygen with danofloxacin ($(6.15 \pm 0.11) \times 10^9$; $(7.50 \pm 0.13) \times 10^4$), fluvastatin ($(6.96 \pm 0.16) \times 10^9$; $(1.64 \pm 0.18) \times 10^8$), and paroxetine ($(8.65 \pm 0.12) \times 10^9$, $(1.18 \pm 0.13) \times 10^8$), respectively. For all three pharmaceutical compounds, the rate constants for reactions with the hydroxyl radical were similar; however, those for singlet oxygen varied by three orders of magnitude. In the waters studied, the steady-state concentration of the hydroxyl radical was on the order of 10^{-17}–10^{-18} M, and for singlet oxygen, 10^{-12}–10^{-14} M. The percent contribution of each species to the degradation of each pharmaceutical in each water matrix was calculated, and several trends were identified enabling a better understanding of the role of these reactive species.

1. Introduction

Pharmaceutical compounds have been widely detected in the environment in recent years. These emerging pollutants of concern, despite their ubiquitous presence, remain poorly understood in terms of their

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http://dx.doi.org/10.1016/j.scitotenv.2016.12.008
0048-9697/

environmental fate and their effects on human and ecosystem health (Kolpin et al., 2002; Boreen et al., 2003). Pharmaceuticals enter the environment through several pathways: they may be excreted partially unmetabolized by human patients (Kummerer, 2004) and enter the environment through wastewater, or they may simply be dumped "down the drain" by consumers or medical facilities (Halling-Sorensen et al., 1998; Song et al., 2008). Once in the environment, they have unknown, and potentially serious, consequences to aquatic ecosystems, including toxicity to algae (Johnson et al., 2007) and aquatic organisms (Robinson et al., 2005).

Three representative pharmaceutical compounds were chosen from three different families. The first, danofloxacin, is a member of the fluoroquinolone family. Fluoroquinolones are one of the most widely used antibiotics for both humans and animals (Leal et al., 2012), and have been detected in treated wastewater at multiple locations around the world (Zhang and Huang, 2005; Yasojima et al., 2006; Gros et al., 2007). The second, fluvastatin, is a member of the statin family, designed to lower cholesterol levels and prevent heart disease. Fluvastatin is a second-generation statin that is widely prescribed, and prior work has been done on its photo-degradation (Mielcarek et al., 2005; Razavi et al., 2011b). Finally, paroxetine is an antidepressant compound that has been detected in the environment (Schultz and Furlong, 2008). Antidepressants are used to treat not just depression but a wide variety of medical conditions including sleep and eating disorders, alcohol and drug abuse, panic, chronic pain and post-traumatic stress disorder (Mejo, 1990). These compounds were chosen because they represent three different classes of pharmaceuticals, have high sales volume, and little is known about their fate in the natural environment.

Currently utilized treatment technologies are often ineffective in removing pharmaceutical compounds from wastewater (Hartig et al., 2001; Heberer, 2002; Nghiem et al., 2005), resulting in their presence in surface waters (Fono et al., 2006). While in rivers and lakes, pharmaceutical compounds are exposed to sunlight in the presence of natural organic matter that is ubiquitous in the environment. Photochemical degradation is likely to be an important loss mechanism for many pharmaceutical pollutants in surface waters (Boreen et al., 2003), and photochemistry in natural waters is more complex than in pure water due to the presence of DOM and other photoactive dissolved and particulate constituents and inorganic ions (Lam et al., 2003; Grandbois et al., 2008). Therefore, an understanding of photochemical fate is useful when designing treatment technologies such as constructed wetlands that are capable of removing pharmaceuticals from wastewater.

The purpose of this study was to understand the photochemical degradation of three pharmaceuticals in the Suwannee River. While the Suwannee River was chosen due to the commercial availability of organic matter isolates, the results are broadly relevant to the degradation of pharmaceuticals in sunlit bodies of water. Studies were conducted on reconstituted waters consisting of individual organic matter isolates dissolved in distilled water as well as on water samples from the river itself. The role of two reactive species, hydroxyl radical and singlet oxygen, was quantified using absolute reaction rate constants.

2. Methods and materials

2.1. Materials

Danofloxacin was obtained from Sigma Aldrich, and fluvastatin and paroxetine from Shanghai FWD Chemicals Limited. The structures of these pharmaceuticals are shown in Fig. 1. Suwannee River humic acid, fulvic acid and natural organic matter were obtained from the International Humic Substance Society (1991 Upper Buford Cir. Rm 439, St. Paul, MN 55108). Solutions of these isolates were prepared at a concentration of 25 mg L^{-1} in water filtered with a Millipore Milli-Q® system, which includes constant illumination by a xenon arc lamp at 172 nm to keep total organic carbon concentrations below 13 μg L^{-1}.

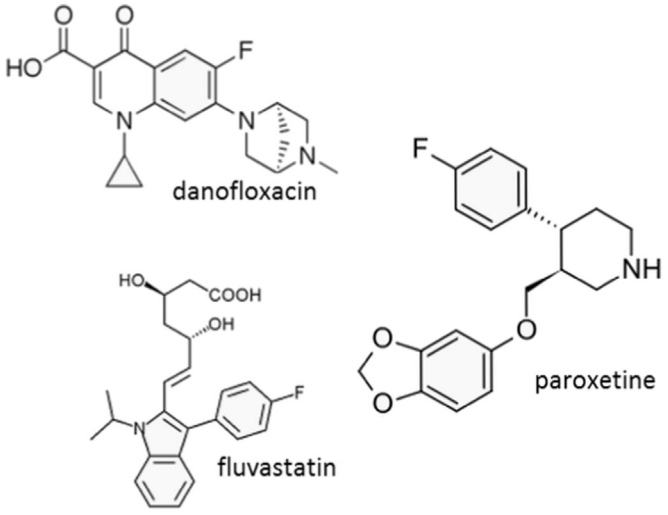

Fig. 1. Structures of target compounds.

The Suwannee River water sample was obtained April 18, 2013 in brown bottles, chilled over ice and sent overnight to the laboratory, and extracted as described elsewhere (Cottrell et al., 2013). Chemical characterization of the natural and reconstituted waters samples were determined by the Southeast Environmental Research Center at Florida International University, and are shown in Table S1. Furfuryl alcohol, furfural, Rose Bengal, and terephthalic acid were purchased from Sigma Aldrich.

The water matrices used in this study were selected to help understand the degradation of pharmaceuticals in the Suwannee River. The first consisted simply of the pharmaceutical dissolved in Milli-Q® water to assess the direct photolysis of each compound in the experimental setup. The next three water matrices were prepared using different isolates of Suwannee River organic matter (humic acid, fulvic acid, and natural organic matter) at 25 mg L^{-1}. Lastly, raw filtered surface water (RFSW) from the Suwannee River was studied. Because of the optical density of the water as collected, samples were diluted 1 to 5 with Milli-Q® water. This ratio was chosen in order to approximate the UV–visible absorbance of the three isolate solutions as closely as possible (Fig. 2). The behavior of the compounds in undiluted RFSW was also studied and the results are presented for reference, although this sample was too concentrated for the light to reach the majority of the volume, as is likely the case in the Suwannee River itself.

To simulate sunlight, a Luzchem solar simulator with a 300 W ceramic xenon lamp (XE300BF) was used with a 1/800 Esco optical glass filter and dimmer to best match the AM 1.5 solar spectrum with

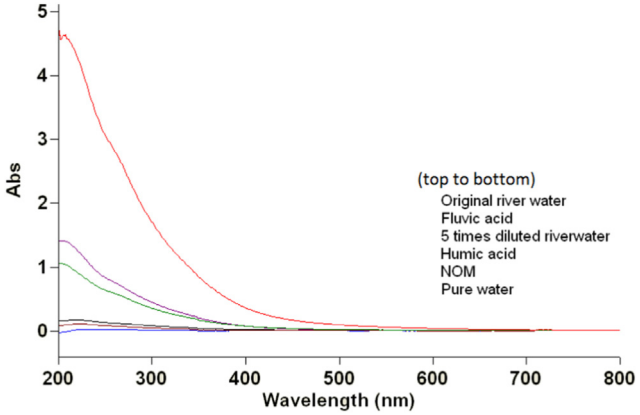

Fig. 2. Absorption spectra of water samples used in this study.

Please cite this article as: Santoke, H., Cooper, W.J., Environmental photochemical fate of selected pharmaceutical compounds in natural and reconstituted Suwannee River water: Role of r..., Sci Total Environ (2016), http://dx.doi.org/10.1016/j.scitotenv.2016.12.008