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Degradation of the pharmaceuticals diclofenac and sulfamethoxazole and their transformation products under controlled environmental conditions

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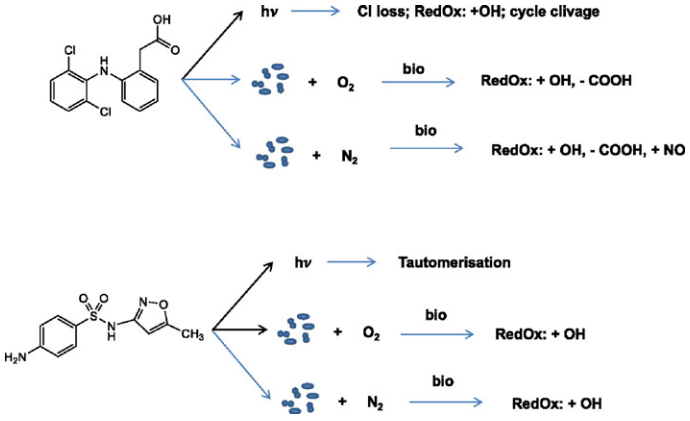
HIGHLIGHTS

- Degradation products vary depending on the process involved.
- Kinetics of degradation depend on media physicochemical characteristics.
- Some products of degradation are not persistent.

GRAPHICAL ABSTRACT



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ABSTRACT

Contamination of the aquatic environment by pharmaceuticals via urban effluents is well known. Several classes of drugs have been identified in waterways surrounding these effluents in the last 15 years. To better understand the fate of pharmaceuticals in ecosystems, degradation processes need to be investigated and transformation products must be identified. Thus, this study presents the first comparative study between three different natural environmental conditions: photolysis and biodegradation in aerobic and anaerobic conditions both in the dark of diclofenac and sulfamethoxazole, two common drugs present in significant amounts in impacted surface waters. Results indicated that degradation kinetics differed depending on the process and the type of drug and the observed transformation products also differed among these exposure conditions. Diclofenac was nearly degraded by photolysis after 4 days, while its concentration only decreased by 42% after 57 days of exposure to bacteria in aerobic media and barely 1% in anaerobic media. For sulfamethoxazole, 84% of the initial concentration was still present after 11 days of exposure to light, while biodegradation decreased its concentration by 33% after 58 days of exposure under aerobic conditions and 5% after 70 days of anaerobic exposure. In addition, several transformation products were observed and persisted over time while others degraded in turn. For diclofenac, chlorine atoms were lost primarily in the photolysis, while a redox reaction was promoted by biodegradation under aerobic conditions. For sulfamethoxazole, isomerization was favored by photolysis while a redox reaction was also favored by the biodegradation under aerobic conditions. To summarize this study points out the occurrence of

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different transformation products under variable degradation conditions and demonstrates that specific functional groups are involved in the tested natural attenuation processes. Given the complexity of environmental samples more analytical effort is needed to fully identify new products of potential toxicity.

1. Introduction

The presence of pharmaceuticals in urban discharges is an emerging concern for the disruption of aquatic ecosystems and human health. Numerous studies have been conducted on the presence of pharmaceuticals in the aquatic environment (Aminot, 2013; Fatta-Kassinos et al., 2011a; Hernández et al., 2007; Segura et al., 2009; Ziylan and Ince, 2011). These studies show that a vast amount of various drugs from urban effluents end up in waterways at concentrations of potential concern. The degradation of these pharmaceuticals in the environment also needs to be considered, thus studies on their environmental fate to understand degradation mechanisms and transformation products arising therefrom are required to assess their toxicity. Unfortunately, compared to the presence of parent compounds, the occurrence of pharmaceutical transformation products in the aquatic environment is much less known. Several studies have identified transformation products of key pharmaceuticals in laboratory and wastewater treatment plants but few studies have investigated them in the aquatic environment.

The natural degradation of several pharmaceutical classes such as antibiotics, non-steroidal anti-inflammatory drugs, anti-psychotics, β-blockers, cholesterol-lowering drugs, hormones and analgesics have been studied (Challis et al., 2014). Different experimental degradation conditions were previously investigated, such as photo-transformation (Boreen et al., 2003; Challis et al., 2014; Yan and Song, 2014), including the photolysis (Batchu et al., 2014; Gonzalez et al., 2009; Huguet et al., 2013; Salgado et al., 2013; Schulze et al., 2010) and photocatalysis (Nasuhoglu et al., 2011), the oxidative decarboxylation (Huguet et al., 2013), biodegradation (Langenhoff et al., 2013; Zhang et al., 2008), degradation by ultrasound (Hartmann et al., 2008; Ziylan et al., 2014) and the influence of the degree of sun exposure (Bartels and von Tümpling Jr, 2007). However, few studies have focused on all aspects of the degradation of pharmaceuticals in environmental media. A variety of degradation processes may occur in the environment: photo-transformation by sunlight and biodegradation by bacteria under aerobic and anaerobic conditions. Several factors can also influence environmental degradation such as physico-chemical water conditions (pH, oxygen, temperature, turbidity), and the weather (sun brightness).

There are several indications that photochemical degradation is one of the most significant processes with regard to the environmental fate of pharmaceuticals. This type of degradation depends on several factors including physico-chemical characteristics of pharmaceuticals and their specific structure such as presence of aromatic rings, conjugated π systems, diverse functional groups and heteroatoms, which facilitate direct absorption of solar radiation (Challis et al., 2014; Fatta-Kassinos et al., 2011b). In streams, it can be generally assumed that pharmaceuticals are exposed to solar radiation composed of photons of UV, infrared and visible wavelengths, which are mostly above 290 nm, as well as bacteria in aerobic and anaerobic media. Additionally, photosensitizing species such as photolytically excited natural organic matter (NOM), nitrates, carbonates and iron in the water column may lead to indirect photolysis at temperatures ranging from 0 to 20 °C and a fairly stable pH around 8 (Challis et al., 2014; Fatta-Kassinos et al., 2011b). All these factors play an important role in the photodegradation of pharmaceuticals in the environment as shown by a previous study on the degradation of antibiotics, which demonstrated that the fate of these compounds was dependent on media pH, organic and chlorine contents, as well as the irradiation source (Batchu et al., 2014). Therefore, two pharmaceuticals with different physico-chemical properties were chosen to experiment diverse degradation processes: the anti-inflammatory drug diclofenac (DCF) and the antibiotic sulfamethoxazole (SMX).

Photo-transformation pathways of DCF in a reconstructed standard freshwater have been studied in controlled hydrolysis and photolysis experiments (Agüera et al., 2005). Identification of photo-products generated by sunlight in aerobic condition was done by gas chromatography mass spectrometry and liquid chromatography coupled to time-of-flight mass spectrometry (LC-TOFMS). This latter technique has proven to be one of the most powerful approaches currently existing to investigate suspected or unknown transformation products. Various degradation products can be proposed following the analysis by GC–MS spectra (mass and fragments) and LC-TOFMS (exact mass), that suggest loss of chlorine, hydroxylation, cyclisation, loss of CO_2, oxidation and reduction.

Photo-transformation pathways of SMX in water matrices with enriched environmental components have been studied for a better understanding of the effects of multi-factors on the drug (Niu et al., 2013). They concluded that biodegradation and hydrolysis are negligible in dark. Also, photodegradation is influenced by the concentration of SMX and the solution pH: the photodegradation decreased with an increase in drug concentration and higher pH as well. Based on LC-MS/MS triple quadrupole analysis, a photo-transformation mechanism in pure water was proposed which included three main pathways: hydroxylation of the phenyl, fragmentation of the isoxazole ring and cleavage of the sulfoxide bond. Moreover, increasing concentration of fulvic acids led to a decrease in the photodegradation of SMX and the same phenomenon was observed with increase in concentration of suspended sediments.

Analysis of pharmaceuticals and their degradation products in water samples is typically done by solid phase extraction (SPE) prior to LC-MS/MS and GC–MS (Baker and Kasprzyk-Hordern, 2011; Fatta et al., 2007; Hollender et al., 2010; Kosjek and Heath, 2008). Accurate mass and high resolution mass spectrometers, such as time-of-flight (TOF) or hybrid quadrupole-time-of-flight (QqTOF), are particularly useful to confirm the exact mass of unknown (Agüera et al., 2005) and associate a chemical formula to a compound. By performing tandem mass experiments, further molecular fragmentation can be performed and compared to the original drug's fragmentation pattern to identify similar fragments, find modifications and suggest probable molecular structures. The development of a method to determine the degradation products has, however, its challenges: the formation of several unknown products with different physicochemical properties makes difficult the development of a single effective extraction method for all compounds along with a single chromatography method for their separation. Furthermore, not all degradation products have available commercial analytical standard to confirm the identity of the transformation products which implies that molecular structures were proposed to explain potential degradation pathways.

The aim of this study was to determine individually the influence of controlled natural environmental factors on the degradation of DCF, which rapidly degrades in the environment (Jiskra, 2008), and SMX, which is rather likely much more persistent (Niu et al., 2013) and then compare the degradation products obtained from different natural degradation processes. These pharmaceuticals were chosen for the present study because of their ubiquity and high concentrations in receiving waters of municipal wastewater