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Sunlight-induced degradation of fluoroquinolones in wastewater effluent: Photoproducts identification and toxicity

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HIGHLIGHTS

- The sunlight degradation of five fluoroquinolones was studied in WWTPs effluent.
- The photodegradation was studied at environmentally significant concentrations.
- Photoproducts were identified and their distribution profiles were monitored.
- The toxicity of the photoproducts was studied by long-term *V. fischeri* assay.
- Photoproducts contribution to the overall biotoxic effect ($\mu g\ L^{-1}$ level) was proved.

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ABSTRACT

The photodegradation of Ciprofloxacin (CIP), Enrofloxacin (ENR), Danofloxacin (DAN), Marbofloxacin (MAR) and Levofloxacin (LEV), five widely used fluoroquinolones (FQs), was studied in urban WWTP secondary effluent, under solar light. The degradation profiles and the kinetic constants were determined at the micrograms per litre levels (20–50 $\mu g\ L^{-1}$). The photo-generated products were identified by high-pressure liquid chromatography coupled to electrospray ionization tandem mass spectrometry (HPLC–ESI-MS/MS). The toxicity of the photoproducts was assessed by *Vibrio fischeri* light emission inhibition assay performed on irradiated and not-irradiated FQs solutions, at environmentally significant concentrations. Attention was focused on the evaluation of the photoproducts contribution to the overall biotoxic effect of these emerging pollutants. Data from chronic exposure experiments (24–48 h) were primarily considered. Results confirmed the major usefulness of chronic toxicity data with respect to the acute assay ones and proved the not negligible biotoxicity of the FQs photodegradation products.

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1. Introduction

In the last decades increasing attention has been paid to the occurrence, behaviour, and fate of pharmaceutically active compounds introduced in the environment. Despite this, the still limited knowledge about the environmental fate and effect of pharmaceuticals requires intensive and further investigations (Babić et al., 2013). Fluoroquinolones (FQs) represent an important class of emerging pollutants in water and soil environmental systems (Andreu et al., 2007; Speltini et al., 2010, 2011). These drugs are the most frequently detected in water, followed by sulphonamides, tetracycline, and macrolides (Kusari et al., 2009). FQs are amphoteric molecules obtained by modification of the quinolone core structure by insertion of a fluorine atom in C-6 position and a piperazinyl – or piperazine derivative – group at C-7. They act through inhibition of bacterial DNA gyrase and topoisomerase IV enzymes. The fluorine atom at C-6 position of the ring provides a more than 10-fold increase in gyrase inhibition and up to 100-fold improvement in minimum inhibitory concentrations, while substituent groups at position C-7 play a key role in determining the antibacterial spectrum and bioavailability. These synthetic antibiotics are widely employed both in human and veterinary medicine due to their high potency, broad activity spectrum, good bioavailability, high serum levels, and a potentially low incidence of side-effects (Andersson and MacGowan, 2003). After administration, FQs are only partially metabolized, thus large part of the ingested dose (>50%), excreted with no structural modification (Van

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Doorslaer et al., 2011; Reemtsma and Jekel, 2006), reaches the wastewater treatment plants (WWTPs) (Andreozzi et al., 2003). These are not capable of a quantitative abatement, therefore FQs enter environmental waters where are detected at concentrations ranging from ng L^{-1} to μg L^{-1} (Speltini et al., 2010). In spite of the continuous release of FQs, the accumulation to high concentrations is hampered by FQs photosensitivity. Indeed, photochemistry represents the main transformation path of these compounds resistant to hydrolysis, thermal decomposition, and biodegradation (Andreozzi et al., 2003; Speltini et al., 2010; Sturini et al., 2012a, 2014). Nevertheless, complete mineralization is hard to achieve in water systems under the most common environmental conditions (Kusari et al., 2009), leading to the persistence of various photoproducts together with residual parent drugs (Babić et al., 2013; Prabhakaran et al., 2009; Sturini et al., 2010, 2014). The degradation kinetics is influenced by the organic and inorganic matrix constituents and by adsorption on suspended particulate, both having large effects on the degradation rates (Andreozzi et al., 2003; Schmitt-Kopplin et al., 1999; Sturini et al., 2010, 2014).

The formation of photo-generated products has to be considered to realistically value the overall environmental impact of FQs pollution. In this context, recent works showed that beside the parent drugs also their photoproducts exert antimicrobial activity, contributing to stimulate bacterial resistance (De Bel et al., 2009; Kusari et al., 2009; Sturini et al., 2012b; Sukul et al., 2009).

More recently, different studies have been focused to assess the ecotoxicity of photolyzed aqueous FQs solutions (Li et al., 2011; Sirtori et al., 2012; Vasconcelos et al., 2009; Vasquez et al., 2013). The results currently available indicate that despite the degradation of the parent drugs, the solutions preserved significant toxicity after photolysis, reasonably due to the formation of bioactive products (Li et al., 2011; Sirtori et al., 2012; Vasconcelos et al., 2009). However, as underlined by Vasconcelos et al. (2009), the concentrations used in those studies (Li et al., 2011; Sirtori et al., 2012) were higher than those normally measured in the environment, and only data from short-time assays are available up to now (Li et al., 2011; Sirtori et al., 2012; Vasconcelos et al., 2009). With regard to this, it should be considered that in the case of the bioluminescence inhibition assay, long-term assays (e.g. 24 h) are required to obtain more realistic results, because short-term assays underestimate or even fail to detect toxicity (Backhaus et al., 1997).

The photolytic degradation of FQs in untreated urban WWTP effluents under solar light, at the low micrograms *per* litre levels, has not been reported as yet. Indeed, Babić et al. (2013) investigated the photolytic degradation of Ciprofloxacin (CIP), Enrofloxacin (ENR) and Norfloxacin (NOR) in simulated pharmaceutical industry wastewater. Other studies focused on the photocatalytic abatement of Ofloxacin (OFL) in secondary treated effluents (Michael et al., 2010), or on UV-A irradiation of 15–50 mg L^{-1} Moxifloxacin (MOX) solutions in deionized water (Van Doorslaer et al., 2013) or in hospital effluent (Van Doorslaer et al., 2015), as well as on 2 mg L^{-1} CIP in wastewater effluent under UV (Keen and Linden, 2013).

To the authors' best knowledge, only one paper (Vasquez et al., 2013) reported the chronic effects (24 h) of photolyzed OFL solutions at the low μg L^{-1} concentration levels on *Vibrio fischeri* light emission, proving that UV degradation processes create genotoxic byproducts.

The first goal of this work was the study of the photodegradation of five widely employed FQs – CIP, ENR, Danofloxacin (DAN), Marbofloxacin (MAR), Levofloxacin (LEV) – in urban WWTP secondary effluent, under solar light, at the micrograms per litre levels. The degradation profiles have been determined for each drug and the kinetic constants were calculated. The photoproducts were identified by high-pressure liquid chromatography coupled to electrospray ionization tandem mass spectrometry (HPLC–ESI-MS/MS) and the photochemical pathways have been elucidated. The second goal was the evaluation of the ecotoxicity of the photoproducts derived from each FQ under the above mentioned realistic conditions by long-term *V. fischeri* assay. With respect to the data from the current literature, biotoxicity experiments were conducted at micrograms *per* litre levels (1–90 μg L^{-1}) following a completely different approach which allowed us to discern the contribute of the photoproducts to the toxicity of the samples from that of residual FQs.

2. Experimental section

2.1. Reagents and materials

All chemicals employed were reagent grade or higher in quality and were used without any further purification. Analytical grade CIP, DAN, ENR, LEV and MAR were supplied by Fluka (Sigma–Aldrich). HPLC gradient grade acetonitrile (ACN) and methanol (MeOH) were from VWR, and H_3PO_4 (85%, w/w) from Carlo Erba Reagents; HCOOH (98–100%, w/w) was obtained from Merck. Ultra-pure water (resistivity 18.2 MΩ cm^{-1} at 25 °C) was produced in laboratory by means of a Millipore (Milan, Italy) Milli-Q system. FQs stock solutions were prepared in pure water and stored in the dark at 4 °C until use. Working solutions were renewed daily.

The luminescent bacteria *V. fischeri* were employed as lyophilized aliquots, which were prepared from fresh cultures maintained at the laboratory starting from an original batch supplied by the Pasteur Institute (Paris, France). The 96-wells "Black Cliniplate" microplates were supplied by Thermo Scientific (Vantaa, Finland). Nutrient broth components were obtained from Sigma–Aldrich.

2.2. Analytical determinations

The HPLC system consisted of a pump Series 200 (Perkin Elmer) equipped with vacuum degasser and a programmable fluorescence detector (FD). The FD excitation/emission wavelengths selected were 297/507 nm for MAR, 280/500 for LEV and 280/450 nm for CIP, DAN and ENR. After an equilibration period of 10 min, 50 μL of each sample were injected into a 250 × 4.6 mm, 5 μm Ascentis RP-Amide (Supelco) coupled with a similar guard-column. The mobile phase was 25 mM H_3PO_4–ACN (85:15) for 30 min at a flow rate of 1 mL min^{-1}. Instrumental quantification limits: 0.81 μg L^{-1} for CIP, 0.51 μg L^{-1} for DAN, 0.37 μg L^{-1} for ENR, 0.43 μg L^{-1} for LEV, 0.69 μg L^{-1} for MAR.

The HPLC-UV system consisted of a Shimadzu (Milan, Italy) LC-20AT solvent delivery module equipped with a DGU-20A3 degasser and interfaced with a SPD-20A UV detector. The injection volume was 20 μL. The analysis wavelength selected was 275 nm. 20 μL of each sample was injected into a 250 × 4.6 mm, 5 μm Analytical Ascentis C18 (Supelco) coupled with a similar guard-column. The mobile phase was 25 mM H_3PO_4–ACN (85:15), at a flow rate of 1 mL min^{-1}. Instrumental quantification limits: 0.35 mg L^{-1} for CIP, 0.42 mg L^{-1} for DAN, 0.17 mg L^{-1} for ENR, 0.06 mg L^{-1} for LEV, 0.1 mg L^{-1} for MAR.

The HPLC–ESI-MS/MS analyses for photoproducts identification were performed by using an Agilent 1100 HPLC with a Luna C18 (150 × 4.6 mm, 5 μm) column, maintained at 30 °C. The mobile phase was HCOOH 0.5% (v/v) in ultrapure water-ACN (90:10), at a flow rate of 1.2 mL min^{-1}, and the injection volume was 5 μL.

The samples from WWTPs were analysed on a Poroshell column (2.1 × 50 mm, 2.7 μm), with MeOH/water–0.1% HCOOH (22:78) as the mobile phase (flow rate 0.5 mL min^{-1}), allowing a better

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