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Environmental fate of non-steroidal anti-inflammatory drugs in river water/sediment systems

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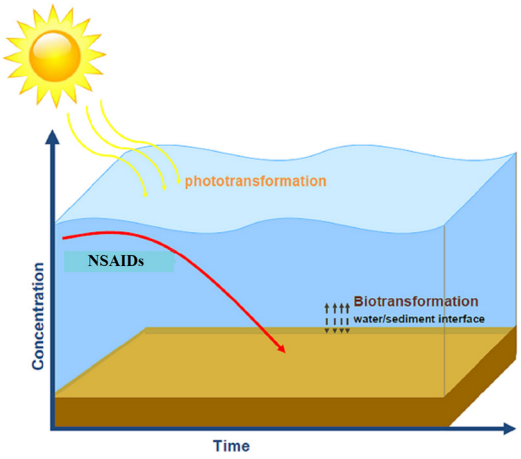
HIGHLIGHTS

- Biodegradation rates of NSAIDs in river/sediment systems depend on redox conditions.
- Biodegradation rate of NSAIDs are faster under aerobic than anaerobic conditions.
- Sorption is a rather insignificant process for removing NSAIDs from river water.
- Ibuprofen is removed from river water through biodegradation rather than sorption.
- Ibuprofen biodegraded faster than Naproxen, Diclofenac and Ketoprofen.

GRAPHICAL ABSTRACT



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ABSTRACT

Laboratory tests were conducted with four non-steroidal anti-inflammatory drugs (naproxen, ibuprofen, diclofenac and ketoprofen) under different redox conditions (aerobic, anoxic, anaerobic and sulfate-reducing conditions) in order to assess abiotic and biotic degradation in a river water/sediment system. The river water was sampled from Sperchios River and the sediment was collected from the banks of a rural stream where the discharge point of a wastewater treatment plant is located. To quantitatively describe degradation kinetics of the selected compounds, pseudo first-order kinetics were adopted. According to the results, it can be stated that the concentration of the substances remained constant or decreased only marginally ($p \geq 0.05$) in the sterile experiments and this excludes abiotic processes such as hydrolysis or sorption as major removal mechanisms of the target compounds from the water phase and assign their removal to microbial action. Results showed that the removal rate of the compounds decreases as dissolved oxygen concentration in the river water/sediment system decreases. All compounds were found to be biodegradable under aerobic conditions at dissipation half-lives between 1.6 and 20.1 days, while dissipation half-lives for naproxen and ketoprofen increase by a factor of 2 under all tested conditions in the absence of oxygen.

1. Introduction

Non-steroidal anti-inflammatory drugs (NSAIDs) is a category of analgesic medication that reduces pain, fever and inflamma-

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tion [1]. NSAIDs are pharmaceuticals used in large quantities by humans and animals. The widespread presence of pharmaceuticals in the aquatic environment and more specifically in surface waters, groundwater, wastewater and in some cases in the drinking water has been well documented during the last years [2–5]. Wastewater treatment plants (WWTPs) are a well known source and one of the most significant pathways for their transfer to the environment [6]. It is well evidenced that most of these chemicals are only partially removed through wastewater treatment and therefore are detected in secondary effluents [7,8].

The main elimination processes of such chemicals following their disposal in surface waters are photodegradation, sorption and biodegradation. However, it should be underlined that the elimination of the compounds is rather a transformation, which leads to the formation of several by-products, than mineralization [9–13]. Most pharmaceuticals have been reported to be photoactive [14,15] while their sorption depends on both compound's physicochemical properties and sediment's nature [16]. Biodegradation, through the activity of microorganisms presented in water/sediment system, has been shown to be an efficient attenuation process for many emerging contaminants [17–22]. Although the effectiveness of biodegradation has been demonstrated, few data are available for the degradability of NSAIDs in the aquatic environment after treated wastewater being disposed to surface waters. Furthermore most of the studies were performed either with synthetic water and not with river water or with microorganisms inoculated from activated sludge or digested sludge samples and not with autochthonous biomass from river sediments [23,24].

Therefore, the objective of this study was to assess the environmental transformation of four NSAIDs in river systems and more specifically to evaluate the role of sorption and biodegradation on their transformation under different redox conditions. In order to closely simulate the natural river system, we used in our experiments, sediment collected in the proximity of the point of disposal of the treated effluent of a WWTP. Thus the microbial community used, had been acclimatized in real conditions (presence of pharmaceuticals due to wastewater disposal) and with a realistic density.

The compounds selected in this study as representatives of the NSAIDs are naproxen (NPX), ketoprofen (KTP), diclofenac (DCF) and ibuprofen (IBU). The target compounds have been selected due to their frequent detection in surface water [25] and their estrogenic activity [26–28]. According to Directive 2013/39/EC (article 8b) [29], diclofenac has been included in the watch list of substances for which EU-wide monitoring data are to be gathered for the purpose of supporting future prioritization exercises in accordance with Directive 2000/60/EC [30]. The physicochemical properties of the target compounds are presented in Table 1.

2. Experimental methods

2.1. Materials and reagents

Methanol (MeOH) and ethyl acetate were of high performance liquid chromatography (HPLC) grade (Merck, Darmstadt, Germany) and were used as received. Bis(trimethylsilyl) trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS) and pyridine, used for silylation, were purchased by Supelco (Bellefonte, PA, USA) and Carlo Erba-SDS (Peypin, France), respectively. Analytical standards of IBU, NPX, KTP, DCF, and meclofenamic acid (MCF) were supplied by Dr. Ehrenstorfer (Germany). All compounds were used without further purification (minimum purity > 99%). Stock solutions of individual compounds were prepared in methanol at 1000 mg L^{-1} and kept at −18 °C. HPLC grade water was prepared in the laboratory using a MilliQ/Milli-RO Millipore system (Millipore, Billerica, Massachusetts USA). Ultra-pure HCl (32%) was used for acidification of the samples (Merck, Germany).

2.2. Sediment and river water collection

River water samples were collected from the Spercheios River water system, which is located in the Central-Eastern Greece. More specifically, the river water was sampled from a point along the river that received minimal pollution due to anthropogenic activities. The sediment samples were collected from the banks of a tributary of the Spercheios river. The sampling point of the sediment was close to the discharge point of the Lamia urban WWTP so that the microbial community to be acclimated to the presence of the target compounds. This stream after a distance of few kilomemter flows into Spercheios River downstream from the point of collection of the river water samples. Sediment was collected at the entire surface of the sediment layer (0–5 cm depth). Temperature, pH, dissolved oxygen and conductivity measurements performed during sample collection. Water and sediment were collected separately in glass bottles. Additionally, sediment was sieved to <2 mm and water was filtered under suction through 0.45 μm membranes to remove particulate and algal materials, while all samples were stored at 4 °C until used and for no longer than 1 day. Sediment and water samples were characterized for organic and inorganic nutrients, while the background concentration of the target compounds were also determined (Table S1 in Supplementary Material).

2.3. Lab-scale experiments

Lab-scale experiments were conducted according to a modification of the guidelines of the Organization for Economic Co-Operation and Development (OECD): OECD 308 Aerobic and Anaerobic Transformation in Aquatic Sediment Systems [33] and OECD 309 Aerobic Mineralisation in Surface Water – Simulation Biodegradation Test [34]. All experiments were performed simultaneously for all conditions (aerobic, anaerobic, anoxic, sulfate reducing) without further acclimation of the microbial community in the presence of the selected pharmaceuticals. Only a period of few days were needed to reach reasonable stability of the systems (as reflected by dissolved oxygen concentration, redox potential of the sediment and water, pH, zero concentrations of nitrate and sulfate where necessary and macroscopic separation of phases).

2.3.1. Aerobic experiments

Aerobic degradation experiments were carried out in 1 L glass bottles with a sediment: water volume ratio of 1:3 (200 g of wet sediment and 600 mL of river water), while the thickness of the sediment layer was 2.5 cm. The amount of the sediment (dry weight basis) per incubation vessel was around 110 g. The scope of the aerobic experiments was to simulate a natural aquatic sediment system, which is often aerobic in the upper water phase, while the surface layer of sediment can be either aerobic or anaerobic, whereas the deeper sediment is usually anaerobic. For the purpose of this test, the water phase was continuously aerated with pressurized air. The oxygen concentration was always close to saturation level and therefore was not a limiting factor. All experiments were carried out without shaking, in darkness in order to exclude the effect of photolysis. The measured pH in the water phase remained relatively constant at 8.0 ± 0.3, during the course of the tests. The nominal concentration of each compound in the added water was around 40 μg L^{-1}. All compounds were incubated as a mixture. The concentration used in these experiments was low enough to ensure that the biodegradation kinetics obtained in the test, reflect those expected in the environment. Samples for analysis were taken after being spiked (t = 0) and in regular intervals over a period of up

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