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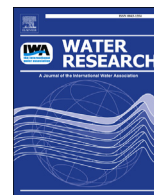

Abiotic degradation and environmental toxicity of ibuprofen: Roles of mineral particles and solar radiation

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ABSTRACT

The growing medical and personal needs of human populations have escalated release of pharmaceuticals and personal care products into our natural environment. This work investigates abiotic degradation pathways of a particular PPCP, ibuprofen, in the presence of a major mineral component of soil (kaolinite clay), as well as the health effects of the primary compound and its degradation products. Results from these studies showed that the rate and extent of ibuprofen degradation is greatly influenced by the presence of clay particles and solar radiation. In the absence of solar radiation, the dominant reaction mechanism was observed to be the adsorption of ibuprofen onto clay surface where surface silanol groups play a key role. In contrast, under solar radiation and in the presence of clay particles, ibuprofen breaks down to several fractions. The decay rates were at least 6-fold higher for irradiated samples compared to those of dark conditions. Toxicity of primary ibuprofen and its secondary residues were tested on three microorganisms: *Bacillus megaterium*, *Pseudoaltermonas atlantica*; and algae from the *Chlorella* genus. The results from the biological assays show that primary PPCP is more toxic than the mixture of secondary products. Overall, however, biological assays carried out using only 4-acetylbenzoic acid, the most abundant secondary product, show a higher toxic effect on algae compared to its parent compound.

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1. Introduction

Pharmaceuticals and personal care products (PPCPs) are, in general, any product used for personal health or cosmetic reasons or used by agribusiness to enhance growth or health of livestock (Boxall et al., 2012). Majority of the PPCPs emerge in the environment via medication residues that pass out of the body, used or expired medications placed in the trash, or personal care products washed down the shower drain (Overturf et al., 2015). Hundreds of individual PPCPs have been detected at parts-per-billion and parts-per-trillion concentrations in wastewater and surface water (Deo, 2014). In recent studies, active pharmaceutical compounds (PhACs), i.e. clofibric acid, ibuprofen, diclofenac, and bisphenol A, have been identified at concentrations up to 1 g/L in affluent and effluent waters (Blair et al., 2013). These studies also highlight the occurrence of PhACs in drinking water at concentrations of ng/L (Khan and Nicell, 2015). Many of these compounds are not removed by wastewater treatment; this has become a particular concern if drinking-water sources include a substantial fraction of treated wastewater effluent (Kolpin et al., 2002).

Pharmaceuticals, as well as several chemicals used in personal care products, are biologically active compounds which are designed to interact with particular biological pathways in target humans and animals at prescribed doses. Consequently, some PPCPs are well-known endocrine disruptors and cause adverse effects in the reproductive system of humans and wildlife (Kortenkamp et al., 2009; Overturf et al., 2015). In the environment, some PPCPs are quickly metabolized or degraded quickly while others persist and may also be mobile. Xu et al. and others have reported limited breakdown of selected PPCPs in the presence of agricultural soil and have attributed the differences in degradation to the differences in the indigenous microbial population of the soil (Xu et al., 2009). However, Ternes and co-workers have shown that biodegradation pathways of PPCPs appear to be slow and persistent against bacterial degradation (Ternes et al., 2004). Yet, secondary products of PPCPs, resulting from environmental processes, have

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been found in water and soil (Li, 2014). In a recent study, Jacobs et al. highlights that breakdown of ibuprofen is 6-fold faster in the presence of organic matter, e.g.: fulvic acid (Jacobs et al., 2011). However, little is known about exact molecular level processes and the influence of environmental conditions on above degradation pathways. Perhaps even more importantly, the toxicity of the secondary residues is unknown. Thus, the current work attempts to fill this knowledge gap by a detail study to gain molecular level insights of fate, transformation and log-term health effects of PPCPs and their secondary residues.

PPCPs released to the environment are in constant interaction with soil particles, a complex mixture of metals, metal oxides and clay particles. Thus, soil particles provide a reactive surface for heterogeneous chemical and photochemical reactions to occur. The current study focuses on abiotic degradation pathways of a particular PPCP, ibuprofen, in the presence of a major mineral component of soil, kaolinite clay. Ibuprofen was selected as a proxy for PPCPs due to its high environmental abundance, inherent toxicity and structural features similar to many PPCP compounds. Chemical and photochemical reactions of ibuprofen were also studied under light and dark conditions so as to simulate and differentiate between daytime and nighttime processing of PPCPs. The results of this study, for the first time, propose a detailed reaction mechanism for the abiotic degradation of ibuprofen, starting from surface adsorption to the formation of particular secondary products. Further, the current work evaluates the toxicity of ibuprofen and its degraded products on three microorganisms. Thus, we provide a detailed report on potential toxic effects of degraded secondary residues - a heretofore-unexamined process. The information will be used to interpret field observations of PPCP residues and their toxic effects on aquatic life and human health as they are transformed under various environmental conditions. This work therefore contributes to our understanding of pharmaceutical mobilization in water bodies.

2. Materials and methods

2.1. Chemicals and reagents

Ibuprofen (≥99.5%, Sigma-Aldrich) and 4-acetylbenzoic acid (≥98%, Sigma-Aldrich) were used as reference material. During solution preparation, double DI Milli-Q water (Res > 18.2 MΩ, Millipore Advance A10) was used. Kaolinite, KGa-1b, from the Source Clay Repository in Washington County, Georgia, was used as a proxy soil mineral. In toxicological studies, dimethyl sulfoxide (certified ACS, Fisher Scientific) was used to prepare standard solution. Phenylarsine oxide (≥97%, Sigma-Aldrich) was used as the "complete kill" control. Nutrient broth (BD Difco™) and Marine broth (BD Difco™) served the bacterial growth media. Algal cells were grown using Alga-Gro® Freshwater medium (Carolina). MTT reagent (3-(4,5-Dimethylthiazol-2-yl)-2,5-Diphenyltetrazolium Bromide; Fisher) was used to prepare 5 mg/mL stock solution in PBS and added to a final concentration of 0.5 mg/mL.

2.2. Particle characterization

Clay (kaolinite) was characterized using powder X-ray diffraction (XRD) performed on a Bruker D-5000 diffractometer with a Cu K_α source. FTIR spectra of kaolinite particles were obtained using a Thermo.

Scientific IS50 spectrophotometer equipped with a Ge internal reflective element (IRE). Surface areas were determined from a seven-point N_2-BET isotherm using a Quantachrome Autosorb1 surface area analyzer. Particle dimensions were obtained from single particle analysis with Scanning Electron Microscopy (SEM). Particle size was determined from the analysis of approximately 300 particles.

2.3. Degradation studies

2.3.1. Batch reactor studies

The experiments were carried out in a custom-built glass reactor using 10 mM ibuprofen solutions. Given the low sensitivity of current toxicological assays, high initial concentrations of ibuprofen were used. These experiments were conducted in the absence and the presence of solar simulator (150 W xenon lamp, New Port) with an Air Mass 0 filter. The temperature was kept constant through use of a water jacket. The particle loading was maintained 0.2 g/L of kaolinite in solutions of 10 mM ibuprofen. pH of the ibuprofen solution increased from 3.7 to 4.5 upon addition of kaolinite particles. Over time, samples were periodically removed from the reactor using a disposable syringe that was connected to 12 cm of Teflon tubing. Aliquots (1 mL) were collected into HPLC vials after passing through a 0.2 μm PTFE filter (Expertek). Analysis of filtered extracts was performed by reverse phase HPLC (Agilent 1100). HPLC conditions are described in Supporting Information.

2.3.2. Liquid chromatography-mass spectroscopy (LC-MS)

Filtered samples collected at the end of batch reactor studies were analyzed using LC-MS to identify secondary products in the mixture. Here, the degraded solutions were concentrated and then analyzed using nano-flow liquid chromatography (Thermo Fisher Ultimate 3000RLS Nano) coupled with an Orbitrap Fusion Tribred mass spectrometer (Thermo Fisher) that provided high resolution, accurate mass measurement and multiple fragmentation mechanisms for molecular structural elucidation. Details of LC-MS experimental conditions are described in Supporting Information.

2.4. Biological studies

2.4.1. Experimental setup

Stock solutions of ibuprofen and 4-acetylbenzoic acid were prepared in DMSO at concentration of 100 mM. A 96 well-plate experimental setup is illustrated in Supporting Information (SI Fig. 1). Briefly, each of the wells was filled with 150 μL of bacterial or algal cell suspension. 3.0 μL of 100 mM ibuprofen stock solution was pipetted to the first well to attain the final drug concentration of 1 mM. 150 μL was then transferred from the first well to the second well. This 1:2 serial dilution process was repeated until the lowest test concentration (15.6 μM) was obtained. The effect of two solvents, water and DMSO, was also studied to evaluate any effect on the growth of organisms. Additionally, phenylarsine oxide (PAO) was used as a positive control, "complete-dead" or "complete-killed", and was tested at final concentration of about 67 μM. The well-plates containing *B. megaterium* and *P. atlantica* were incubated at 30 °C with gentle shaking. Alternately, the plate with *Chlorella* cells was placed on a rotary shaker (72 rpm) at room temperature underneath a 17 W fluorescent light on a 12 h light and dark cycle.

2.4.2. Toxicological assays

Cell densities for *B. megaterium*, *P. atlantica* and *Chlorella* cells were monitored through OD measurements at 595 nm using Microplate Reader (Molecular Devices). Viability of bacterial cells was further measured using standard MTT assay. At 24 h, 30 μL of 5 mg/mL of MTT reagent was added to each well of the 96 well-plate and incubated for 1 h at 30 °C. After the period of incubation, they were solubilized in 200 μL of DMSO. OD measurements were taken at 490 nm. BD FACSCalibur flow cytometer was used to assess the comparative toxic effects between ibuprofen and its secondary products on algal cell size, granularity/shape, and

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