Science of the Total Environment 447 (2013) 267–273

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

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

Multi-phase partitioning, ecological risk and fate of acidic pharmaceuticals in a wastewater receiving river: The role of colloids

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HIGHLIGHTS

- WWTP is the main source of pharmaceuticals to the receiving river in Shanghai.
- The colloids contribute 9–36% to the total pharmaceutical concentration in water.
- Truly dissolved diclofenac poses a potential risk to aquatic organisms.
- Clofibric acid and diclofenac tend to accumulate in water compartment.

ARTICLE INFO

Article history:
Received 12 October 2012
Received in revised form 4 January 2013
Accepted 4 January 2013
Available online 4 February 2013

Keywords:
Pharmaceuticals
Partitioning
Ecological risk
Fate
Level III fugacity model

ABSTRACT

The occurrence and multi-phase distribution of five pharmaceutical compounds were investigated in an urban wastewater treatment plant (WWTP) receiving river by analysis of pharmaceuticals in sediment, particulate matter, conventional dissolved phase (>0.7 μm), colloidal phase (5 kDa to 0.7 μm), and truly dissolved phase (<5 kDa) water. Diclofenac was found in all samples, followed by clofibric acid, ibuprofen, ketoprofen, and naproxen with the decreasing detection frequency. All targets in WWTP outfall site were higher than those in the upstream and downstream, indicating that the WWTP is an important input source of pharmaceuticals in the river. The colloidal phase contributed 10–14% of ketoprofen, 8–26% of naproxen, 17–36% of clofibric acid, 22–33% of diclofenac, and 9–28% of ibuprofen in the aquatic system, suggesting the colloids will play an important role as carrier to contaminants in the aquatic environment. Based on truly dissolved concentrations of pharmaceuticals in water, only the risk quotient (*RQ*) value for diclofenac towards fish was higher than 1, indicating it poses a potential risk to aquatic organisms. Finally, a Level III fugacity model was used to further assess the environmental fate of the selected pharmaceuticals (exemplified for clofibric acid and diclofenac). Both clofibric acid and diclofenac tend to accumulate in water compartment with the percentage of 99.7% and 60.6%, respectively. Advection in river is a significant loss process for clofibric acid (56.4%) and diclofenac (54.4%).

1. Introduction

Recently, pharmaceuticals released into the environment have received a lot of attention. Pharmaceuticals are a large and diverse group of compounds designed to prevent, cure and treat diseases and improve health. Once administered, most of pharmaceutical compounds can be excreted with feces and urine and enter into natural aquatic bodies. Pharmaceutical compounds can be partly removed through deposition and degradation processes of wastewater treatment plants (WWTPs) before discharging into receiving waters. Some pharmaceuticals may persist for several meters or kilometers downstream of WWTP point sources (Lindqvist et al., 2005; Spongberg and Witter, 2008). Thus, WWTP effluent discharge was regarded as one of the most important sources of pharmaceutical residues in the aquatic environment (Lindqvist et al., 2005). This creates the potential to produce a loading of pharmaceuticals over the course of a large river system containing multiple wastewater discharge points. Therefore, a good understanding of the occurrence and distribution of pharmaceuticals in river receiving wastewater is necessary to improve the knowledge of their risk and fate in the environment.

The behavior and fate of pharmaceutical in WWTPs and surface waters were documented in numerous studies (Falås et al., 2012; Gao et al., 2012; Gracia-Lor et al., 2012; Gros et al., 2010; Jelic et al., 2011; Santos et al., 2009; Wang et al., 2010; Zhao et al., 2010; Zhou et al., 2011). In our previous study, we investigated five acidic pharmaceuticals in a typical tertiary-level WWTP of Shanghai to explore their behavior and fate during typical wastewater treatment, and estimated the potential releases of pharmaceuticals through wastewater from Shanghai into the Yangtze River (Duan et al., 2013).

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http://dx.doi.org/10.1016/j.scitotenv.2013.01.017

However, most of these studies focused on the aqueous phase, and concentrations of the pharmaceuticals in solid fraction were rarely determined partly because of the analysis challenge in these matrices and the presumption that pharmaceuticals are highly water-soluble. In addition, pharmaceutical residues were traditionally subdivided into dissolved and particulate fractions in natural waters according to an operationally defined limit (e.g., 0.7 μm) (Baker et al., 2012). However, this so-called dissolved fraction clearly does not represent the truly dissolved fraction and can be further divided into colloidal and truly dissolved fractions. Colloids are ubiquitous in the aquatic environment and have received more and more attention because of their small size and large specific surface area, and thus their high reactivity toward contaminants as well as high mobility (Graham et al., 2008). Recent studies reported that colloids can interact strongly with many organic pollutants such as pharmaceuticals and estrogenic chemicals, indicating that aquatic colloids may play a significant role in regulating the environmental behavior of pharmaceuticals (Maskaoui and Zhou, 2010; Zhou et al., 2007). Therefore, the occurrence and distribution of pharmaceuticals in multi-phase in aqueous environment should be further addressed considering the long-term fate and impact of pharmaceuticals in the aquatic systems.

In this study, we aim to investigate the occurrence and multi-phase distribution of five acidic pharmaceuticals in an urban WWTP receiving river in Shanghai. The binding of the selected pharmaceuticals to particulate (>0.7 μm), colloidal (5 kDa to 0.7 μm), and truly dissolved (<5 kDa) phases in the water was further assessed. Potential risks of pharmaceuticals on the aquatic organisms in the WWTP receiving river were also evaluated using pharmaceutical concentrations in the truly dissolved phase. Finally, we established the fate of clofibric acid and diclofenac in the river receiving wastewater based on the Level III fugacity model by Mackay and Paterson (1991) with a slight modification.

2. Materials and methods

2.1. Chemicals

Ibuprofen, naproxen, ketoprofen, diclofenac, and clofibric acid were obtained from Sigma-Aldrich (St. Louis, MO, USA). HPLC grade methanol, acetone, as well as formic acid were purchased from Tedia Company, Inc (USA), and ultra-pure water was produced by a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Standard stock solutions of individual pharmaceuticals (50 mg/L) were prepared in methanol and renewed every three months, respectively. Working solutions of mixture standards with different concentrations were prepared by diluting the stock solutions before each analytical run. All the solutions were stored at 4 °C in the dark.

2.2. Sample collection

Surface water and sediment samples were collected from a river receiving a WWTP effluent in Shanghai, China. Sampling sites were selected at a WWTP effluent outfall, the upstream (200 m) and downstream (200 m, 500 m, 800 m, 1.6 km, and 3.2 km) of the WWTP effluent outfall, respectively. Four sampling events were conducted on December 22nd, 2010, January 4th, 8th, 2011, and March12th, 2011, respectively. Grab water samples were collected in 4 L clean amber glass bottle from 0.5 to 1 m below the surface. Before sample collection, each bottle was pre-rinsed with river water for three times. Then the collected water samples were transported in an ice-packed cooler to the laboratory. Water was collected from 0.5 to 1 m below the surface and transported in a cooler to the laboratory. Surface sediments (0–5 cm) were collected in prewashed jars and kept in a cooler during transport to the laboratory.

Water samples were filtered through pre-baked (4 h; 450 °C) 0.7 μm glass fiber filters (GF/F, Whatman, Mainstone, England). The filtrate was stored at 4 °C to avoid any degradation until extraction. The suspended particles collected on 0.7 μm glass fiber filters and sediments were wrapped with pre-baked (450 °C) aluminum foil, sealed in Ziplock bags, and stored at −18 °C until further treatment.

2.3. Colloidal phase isolation

Colloidal phase was isolated by cross-flow ultrafiltration (CFUF) system, following the method reported by Wilding et al. (2004). Briefly, using a Millipore 5 kDa regenerated cellulose Pellicon 2 PLAC ultrafiltration membrane, the CFUF operation was carried out in a sampling mode in which the retentate flow (colloidal phase) was directed back to the feed container, while the permeate flow as soluble phase was directed to a separate container. At the end of isolation, all samples including filtrate (conventional dissolved phase), colloidal phase, and soluble phase (truly dissolved phase) were separated to triplicate sub-samples before extraction. Colloids are defined as particles between 5 kDa and 0.7 μm.

2.4. Sample extraction and instrumental analysis

The method for the extraction and analysis of pharmaceuticals in aqueous samples was described elsewhere (Kimura et al., 2007). Briefly, all of the aqueous samples (filtrate, colloidal phase, and soluble phase) were extracted using a solid-phase extraction (SPE) system. The pH of the samples was adjusted to 4.0 with 2 mol/L HCl. A known amount (200 ng) of fenoprop was added as surrogate standard. After the cartridges (ENVI-18, 500 mg, 3 mL) were conditioned by applying 2 mL of methanol and 2 mL of Milli-Q water (pH = 2), the water samples were introduced to the cartridges by means of PTFE tubes at a flow rate of approximately 5–8 mL/min. After washing by 5 mL of 5.0% methanol solution, the cartridges were dried under vacuum for 2 h and eluted with 3 mL of acetone. The extracts were then evaporated to approximately 500 μL under a gentle nitrogen stream and 500 μL of methanol was added. Evaporation continued until the final volume of the extracts was 500 μL.

Suspended particles and sediment samples were extracted by the ultrasonic solvent extraction method reported by Ternes et al. (2005) with a slight modification here. Suspended particles and sediments were freeze-dried and accurately weighed before extraction. Then they were extracted with 6 mL and 2 mL of methanol in series and twice with 2 mL acetone. 200 ng of surrogate standard (fenoprop) was spiked into the slurry in the first extraction step. In all extraction steps, the slurry was ultrasonicated for 10 min and then centrifuged at 5000 rpm for 5 min. Supernatants from all of the extraction steps were combined and evaporated to 1 mL under a stream of nitrogen. This concentrates were redissolved in 100 mL of distilled water (pH = 4), and the SPE was carried out in the same manner as that described above.

All samples were analyzed by TSQ Quantum high performance liquid chromatography coupled with mass spectrometry (Thermo Fisher Scientific, San Jose, CA, USA). The separation was performed on an Agilent Eclipse XDB C18 reversed phase column (150 mm × 2.1 mm, 5 μm), with the flow rate of 350 μL/min. Methanol and water with 0.1% (v/v) acetic acid were used for the separation. The injection volume was 10 μL, and the column temperature was 30 °C. The gradient was held at 75% of methanol for 5 min, and increased to 90% of methanol within 5 min and held for 5 min, and then reset to initial conditions of 75% of methanol in 5 min. The mass spectrometer detections of pharmaceuticals were operated in selected reaction monitoring (SRM) mode.

2.5. Fugacity model

Fugacity model is a well established model and has been applied to study the fate of pollutants in various environments. Fugacity