Journal of Environmental Chemical Engineering 2 (2014) 495–502

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Seasonal occurrence and removal of pharmaceutical products in municipal wastewaters

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ARTICLE INFO

Article history:
Received 11 November 2013
Accepted 30 January 2014

Keywords:
Seasonal
Wastewater
PPCPs
Treatment
WWTP

ABSTRACT

The occurrence in municipal wastewaters of six pharmaceutical products, paracetamol, ibuprofen, naproxen, diclofenac, caffeine and carbamazepine, which belong to different therapeutic classes (analgesic drugs, anti-inflammatory, antiepileptic and stimulant compounds), have been investigated. Influent and effluent water samples from two conventional wastewater treatment plants (WWTPs) of the North of Spain were collected at different seasons and analyzed. Ranges of PPCPs concentrations were similar to levels reported in other studies worldwide. Influent concentrations ranges were 2.3–42 μg/L for ibuprofen and naproxen, 0.04–7.8 μg/L for caffeine and paracetamol, and 0.03–0.4 μg/L for carbamazepine and diclofenac. The highest concentrations were found for ibuprofen in the untreated municipal wastewaters. Effluent concentrations were always below 5.7 μg/L. Diclofenac and carbamazepine persisted in WWTP effluents, whereas paracetamol, ibuprofen, naproxen and caffeine showed removal efficiencies between 75% and 99%. Considering first-order kinetics for the biodegradation of these compounds, apparent kinetic constants were calculated and similar values were obtained for both WWTPs, although one of them resulted to be more sensitive to temperature changes.

Introduction

Pharmaceutical and personal care products (PPCPs) and their metabolites are contaminants extensively found in the aquatic environment [1]. These emerging environmental pollutants deserve special attention due to the fact that some of them may cause ecological and health harm [2–4]. Increasing numbers of water samples obtained from lakes, streams, aquifers and municipal supplies across the world have been found to be contaminated by trace quantities of such residues [5]. These compounds might be excreted by patients or be improperly disposed by users and end up in municipal wastewaters. One of the major sources of PPCPs in the aquatic environment is the effluent discharge from wastewater treatment plants (WWTPs) [1,6]. Current municipal wastewater treatment processes are insufficient at degrading many PPCPs and removal rates vary depending on the treatment technology used and the compound considered. Hence, variable amounts of PPCPs are continuously released into surface, ground and coastal waters [7].

The concentration of pollutants in influents and effluents of WWTPs are routinely monitored in many countries [5]. Despite of the fact that little attention has been paid to seasonal variation of PPCPs, results of different studies showed that the concentrations of PPCPs in municipal wastewater and their treated effluents may vary along the year [8–11]. Furthermore, diurnal variation patters in specific PPCPs that correlates with daily drug administration have also been identified in some cases [12].

The goal of this work was to assess the occurrence and removal of selected pharmaceutical products from municipal wastewaters in the North of Spain. As far as we know, this is the first study of this kind carried out in this region. With this aim, samples from two WWTPs were collected and analyzed along the four seasons in one year. Additionally, local hospital effluents were also analyzed. Moreover the seasonal variability in PPCPs occurrence and removal was also investigated.

Materials and methods

Selected PPCPs

The PPCPs considered in this study include: paracetamol, ibuprofen, naproxen, diclofenac, caffeine and carbamazepine.

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http://dx.doi.org/10.1016/j.jece.2014.01.023

Table 1
Sampling details.

Date	Week day	Sampling time	Average day temperature (°C)	Average day precipitations (mm)
20/12/2010	Monday	~8:30 (WWTP1) ~10:00 (WWTP2) ~11:00 (Hospital)	~9	0.2
22/02/2011	Tuesday	~8:30 (WWTP1) ~10:00 (WWTP2) ~11:00 (Hospital)	~12	3.6
19/05/2011	Thursday	~8:30 (WWTP1) ~10:00 (WWTP2) ~11:00 (Hospital)	~15	0.6
25/07/2011	Monday	~8:30 (WWTP1) ~10:00 (WWTP2) ~11:00 (Hospital)	~19	0.4

These compounds were chosen to represent different groups of pharmaceutical products widely reported to occur in aquatic systems, specifically: analgesic, anti-inflammatory, antiepileptic and stimulant drugs. Caffeine is among the 30 most frequently detected organic wastewater pollutants and carbamazepine, diclofenac and ibuprofen are among the top 10 high priority pharmaceuticals identified in a European assessment of PPCPs due to their high consumption [4,7].

Sample collection

Wastewater was sampled from influent and effluent flows of two local water utilities (WWTP1 and WWTP2) and effluents from the University Central Hospital of Asturias (HUCA). This hospital has 1324 beds and the wastewater is directly discharged into the public sewage system. All facilities were located in Asturias, a region sited in the North of Spain. Grab samples were collected in autumn, winter, spring and summer (see Table 1) using a sample device consisting in a plastic bottle attached to a stick. After collection, samples were transferred to 2.5 L glass bottles and transported to laboratory. The same day of collection, samples were adjusted to pH 2.00 ± 0.10 using hydrochloric acid 3.5 M and stored at 4 °C in the dark until extraction (maximum 12 h).

Description of treatment plants

The treatment in WWTP1 consists of screening, grit and grease removal, primary clarification, activated sludge treatment to achieve removal of biochemical oxygen demanding organic compounds (BOD), nitrogen and phosphorus and, finally, a secondary clarification (Fig. 1). The biological degradation takes place in a "channel type" bioreactor with anaerobic/anoxic/aerobic zones and an average retention time of 8 h. The influent samples were taken after screening and the effluent samples were taken after secondary clarification.

The treatment in WWTP2 consists of screening, grit and grease removal, activated sludge treatment to achieve removal of BOD and nitrogen and, finally, secondary clarification (Fig. 1). The biological degradation takes place in a "carrousel type" bioreactor with anoxic/aerobic zones and an average retention time of 10 h. In this case, the influent samples were taken after sand and grease removal and the effluent samples were taken after secondary clarification.

Both facilities receive a day contaminant charge between 1 and 2 kgCOD/m^3d, being the BOD_5/COD relationship upon 0.4–0.9, so these are middle or easily biodegradable wastewaters. However, WWTP1 receives a 25% of industrial wastewater and 75% municipal wastewater, whereas WWTP2 receives only municipal wastewater that includes several hospital effluents (around 3% of the total wastewater that arrives to WWTP2 comes from hospitals). WWTP1 and WWTP2 serve a population equivalent of 260,000 and 20,000 respectively.

Removal of micropollutants within activated sludge systems can be associated to three main mechanisms: volatilization to air, sorption to the sludge and biological conversion. Models referring to pharmaceutical compounds usually did not include volatilization because it is not considered a significant removal mechanism for this family. Additionally, sorption mechanism is complex and still remains not sufficiently documented [13]. In this work, only degradation in the biological reactors was considered to determine apparent kinetic constants. Large municipal wastewater treatment plants could be represented as plug flow or ideally mixed tank in series [14]. Equations for biodegradation modeling usually consider the degradation of dissolved micropollutant concentration following a first-order kinetic [13]. Plug flow and first-order transformation kinetics were assumed in this case:

$$\ln\frac{C_i}{C_e} = k\theta \quad (1)$$

where C_i is the pollutant influent concentration, C_e the pollutant effluent concentration, k is the apparent kinetic constant for contaminant removal and θ is the hydraulic retention time of the biological reactor.

In order to calculate apparent activation energy, an Arrhenius type equation was employed:

$$k = k_0 e^{-E_a/RT} \quad (2)$$

where k_0 is the pre-exponential factor, E_a is the apparent activation energy, T is the absolute temperature and R is the universal gas constant.

Analytical methodology

As first step, wastewater samples underwent vacuum filtration twice (20–25 μm Whatman filter paper and 0.45 μm Albet Labscience nitrocellulose filter). Solid-phase extraction (SPE) method was employed to concentrate the analytes from the aqueous samples; MCX 3cc/60 mg, 60 μm (Waters Oasis) cartridges were used and 0.5 L of influent samples and 1 L of effluent samples were loaded. Recovery values for MCX extraction are reported in Table 2. The volumes of sample to be filtered were selected considering previous works [15,16] and the cartridge manufacturer's instructions. After SPE, cartridges were dried for 1 h, the analytes were eluted (3 mL of ethyl acetate, 3 mL of 50/50 ethyl acetate/acetone and 3 mL of 48/48/2 ethyl acetate/acetone/ammonium hydroxide) and extracts were evaporated to dryness under a nitrogen stream. Ethyl acetate (≥99.8%, Sigma–Aldrich) (1.5 mL) was used for reconstitution and the reconstituted samples were filtered (0.20 μm Whatman nylon filter) [15]. All compounds, except caffeine, were analyzed after a derivatization step with N-Methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) (Sigma–Aldrich). For this purpose, 100 μL of MSTFA were added to 100 μL of the reconstituted sample and this mixture was kept for 35 min in an oven at 65 °C. Amber autosampler vials were employed.

Finally, samples were injected onto a GC/MS (Agilent Technologies; 6890 N Network GC System, 5975 inert Mass Selective Detector, 7683B Series injector, 7683 series Autosampler) fitted with a column HP-5MS (30 m × 0.25 mm id × 0.25 μm, 19091S-433, Agilent Technologies). The carrier gas was ultrapure helium at a constant flow of 1.3 mL/min. The oven temperature was held at 50 °C for 30 s, and then programmed at 10 °C/min to 250 °C with the final temperature being held for 5 min A sample volume of 1 μL was injected in the splitless mode. The transfer line and ion source were set at 280 °C and 230 °C, respectively. Each compound