Chemosphere 111 (2014) 418–426

Contents lists available at ScienceDirect

Chemosphere

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

Seasonal changes in antibiotics, antidepressants/psychiatric drugs, antihistamines and lipid regulators in a wastewater treatment plant

Oksana Golovko *, Vimal Kumar, Ganna Fedorova, Tomas Randak, Roman Grabic

University of South Bohemia in Ceske Budejovice, Faculty of Fisheries and Protection of Waters, South Bohemian Research Center of Aquaculture and Biodiversity of Hydrocenoses, Zatisi 728/II, 389 25 Vodnany, Czech Republic

HIGHLIGHTS

- 272 WWTP influent and effluent samples were analyzed within 12 months.
- Significant seasonal differences in influent concentration were observed.
- Both influent and effluent concentrations were higher in winter season.

ARTICLE INFO

Article history:
Received 6 September 2013
Received in revised form 28 March 2014
Accepted 31 March 2014

Handling Editor: I. Cousins

Keywords:
Personal care products
Wastewater samples
Seasonal variation
Removal efficiency
Influent
Effluent

ABSTRACT

Seasonal changes in the concentration of 21 pharmaceuticals in a wastewater treatment plant (WWTP) in České Budějovice were investigated over 12 months. The target compounds were 10 antibiotics, 4 antidepressants, 3 psychiatric drugs, 2 antihistamines and 2 lipid regulators. 272 Wastewater samples (136 influents and 136 effluents) were collected from March 2011 to February 2012 and analyzed using two-dimensional liquid chromatography coupled with tandem mass spectrometry. All studied pharmaceuticals were frequently detected in both the influent and the effluent wastewater samples, except for meclozine, which was only found in the influent. The mean concentration of pharmaceuticals varied from 0.006 μg L^{-1} to 1.48 μg L^{-1} in the influent and from 0.003 μg L^{-1} to 0.93 μg L^{-1} in the effluent. The concentration of most pharmaceuticals was higher during winter.

1. Introduction

Detection of pharmaceuticals in the environment has raised concerns in recent years (Halling-Sorensen et al., 1998; Jorgensen and Halling-Sorensen, 2000; Jones et al., 2001; Heberer, 2002; Nakada et al., 2007; Calisto and Esteves, 2009). Despite a growing number of studies pertaining to this subject, there is still little information available regarding environmental transformations, seasonal variations in concentration, and the fate and effects of these compounds in aquatic media (Brain et al., 2004; Calisto and Esteves, 2009; Sui et al., 2011). A large variety of pharmaceuticals have been found in the environment, including analgesics, antibiotics, β-blockers, lipid regulators, antidepressants, and contraceptives (Halling-Sorensen et al., 1998; Jones et al., 2006; Calisto and Esteves, 2009). Following administration, pharmaceuticals are generally excreted either unchanged or in the form of metabolites (active and inactive), resulting in their emission to wastewater treatment plants (WWTPs) (Heberer, 2002). If not removed during treatment, the compound may then be released into local aquatic systems via the effluent of WWTPs (Halling-Sorensen et al., 1998). Treated effluents may also be reused for irrigation, and produced biosolids can be used in agriculture as soil amendments or disposed to landfill, which could lead to further water contamination by pharmaceuticals (Jelic et al., 2011).

The concentrations of pharmaceuticals in the influent and the effluent of WWTPs are routinely monitored in many countries (Lindberg et al., 2005; Vieno et al., 2005; Gobel et al., 2007; Xu et al., 2007; Nakada et al., 2007; Kasprzyk-Hordern et al., 2009; Gros et al., 2010; Jelic et al., 2011; Sui et al., 2011; Bueno et al., 2012; Gracia-Lor et al., 2012; Lajeunesse et al., 2012; Senta et al., 2013; Yu et al., 2013b). Several studies have recently demonstrated

* Corresponding author. Tel.: +420 608828076.
E-mail addresses: ogolovko@frov.jcu.cz (O. Golovko), vkumar@frov.jcu.cz (V. Kumar), fedorg00@frov.jcu.cz (G. Fedorova), randak@vurh.jcu.cz (T. Randak), rgrabic@frov.jcu.cz (R. Grabic).

http://dx.doi.org/10.1016/j.chemosphere.2014.03.132
0045-6535/

that the concentrations of pharmaceuticals and personal care products (PPCPs) in municipal wastewater and its treated effluents are subject to considerable seasonal variations (Valcarcel et al., 2013; Yu et al., 2013b). For example, higher concentrations of some target pharmaceuticals (trimethoprim and venlafaxine) were detected in winter than in summer in Spain (Valcarcel et al., 2013), and a similar trend was observed in five WWTPs in the United States (carbamazepine) (Yu et al., 2013b). However, seasonal variations and their effects on removal of many of pharmaceuticals are poorly understood (Verlicchi et al., 2012).

Seasonal variation may depend upon either societal factors (production, consumption, excretion) or environmental factors (solar irradiance, precipitation, temperature, etc.) (Vieno et al., 2005; Bueno et al., 2012; Yu et al., 2013b). Some of the targeted PPCPs in this study (trimethoprim, sulfamethoxazole, erythromycin, carbamazepine) are frequently detected in WWTP (Kasprzyk-Hordern et al., 2009; Bueno et al., 2012; Verlicchi et al., 2012), however, little is known about the concentration changes of these compounds in wastewater during the year. Likewise, seasonal concentration changes of norfloxacin, ciprofloxacin, levofloxacin, oxazepam, mirtazapine, sertraline, memantine, fexofenadine, meclozine, rosuvastatin and atorvastatin in wastewater have nor been evaluated to date.

Therefore, in this study, we investigated the occurrence and removal of 21 selected PPCPs in the influent and effluent wastewater of a WWTP in České Budějovice, Czech Republic over 1 year.

2. Materials and methods

2.1. Chemicals

Liquid chromatography–mass spectrometry (LC–MS) grade methanol and acetonitrile (Li Chrosolv Hypergrade) were purchased from Merck (Darmstadt, Germany). Formic acid to acidify the mobile phases was acquired from Labicom (Olomouc, Czech Republic). Ultra pure water was produced using an Aqua-MAX-Ultra System (Younglin, Kyounggi-do, Korea). All analytical standards were of high purity (mostly 98%). Native standards: azithromycin, carbamazepine, ciprofloxacin, citalopram, clarithromycin, erythromycin, fexofenadine, levofloxacin, memantine, mirtazapine, norfloxacin, oxazepam, sertraline, sulfasalazine, sulfamethoxazole, sulfapyridine, trimethoprim, venlafaxine, rosuvastatin, atorvastatin, meclozine were kindly donated by the Laboratory of Environmental Chemistry, Umea University (Umea, Sweden) (Table 1).

Internal standards (IS): trimethoprim ($^{13}C_3$) was purchased from Cambridge Isotope Laboratories Inc. (Andover, MA, USA), while carbamazepine (D_{10}) and amitriptyline (D_6) were acquired from CDN Isotopes (Pointe-Claire, Quebec, Canada). Stock solutions of all pharmaceuticals were prepared in methanol at a concentration of 1 mg mL^{-1} and stored at −20 °C. A spiking mixture was prepared for each compound by diluting stocks in methanol to a final concentration of 1 μg mL^{-1} and stored at −20 °C.

2.2. Sampling

Sampling was conducted from March 2011 to February 2012 in a WWTP in České Budějovice, Czech Republic. In total 272 samples were collected (136 samples from the influent and 136 samples from the effluent) (Table SM-1). To avoid misinterpretation (errors) we did not include concentrations data when day flow of wastewater effluent was higher than 60 000 m^3 day^{-1} (abnormal conditions) (Table 2). This WWTP utilizes a biological activated sludge process with partial nitrification and thermophile anaerobic sludge stabilization. The capacity of this WWTP is 90 000 m^3 day^{-1} and it serves 112 000 inhabitants. The main input consists of wastewater from communal use, while industrial use accounts for less than 5% of the input water. In České Budějovice, there is one regional hospital (České Budějovice Regional Hospital). Time proportional (15 min) composite samples of influent and effluent were collected over a 24-h period by an automated sampler (ASP-STATION 2000 sampler, manufactured by E + H). All samples were collected into high density polyethylene bottles, immediately frozen and stored until analyses. For the two-dimensional liquid chromatography method (LC/LC method), thawed water samples were filtered through a syringe filter (0.45 μm, regenerated cellulose, Labicom, Olomouc, Czech Republic), after which 10 ng of internal standards were added to 10 mL of sample. Each sample was prepared and analyzed in triplicate.

Table 1
PPCPs selected for this study, limit of quantification (LOQ) of target pharmaceuticals measured in wastewater.

Compounds	LOQ (μg L^{-1})	Frequency of detection (%)	
		Influent	Effluent
Antibiotics (ATB)			
Norfloxacin	0.003	100	100
Levofloxacin	0.003	99	64
Ciprofloxacin	0.003	100	91
Azithromycin	0.007	99	75
Erythromycin	0.006	100	100
Clarithromycin	0.003	100	100
Trimethoprim	0.003	100	100
Sulfapyridine	0.003	100	100
Sulfamethoxazole	0.005	100	100
Sulfasalazine	0.001	100	99
Psychiatric drugs			
Carbamazepine	0.008	100	100
Oxazepam	0.004	100	100
Memantine	0.003	54	78
Antidepressants			
Mirtazapine	0.002	100	100
Citalopram	0.005	100	100
Sertraline	0.003	70	37
Venlafaxine	0.007	100	100
Antihistamine			
Fexofenadine	0.005	100	100
Meclozine	0.002	96	0
Lipid regulators			
Rosuvastatin	0.002	100	100
Atorvastatin	0.003	100	59

2.3. LC–MS/MS analysis

A triple stage quadrupole MS/MS TSQ Quantum Ultra mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) coupled with Accela 1250 LC and Accela 600 LC pumps (Thermo Fisher Scientific) and an HTS XT-CTC autosampler (CTC Analytics AG, Zwingen, Switzerland) was used for analysis. The system was wired and connected for in-line SPE automated extraction and tandem mass spectrometric detection.

A Hypersil Gold (20 mm × 2.1 mm i.d., 12 μm particles) column from Thermo Fisher Scientific (San Jose, CA, USA) was used as the extraction column. For PPCPs analysis, two analytical columns were used in two separate runs. A Cogent Bidentate C18 column (50 mm × 2.1 mm i.d., 4 μm particle sizes from MicroSolv Technology Corporation Eatontown, NJ, USA) was used for determination of trimethoprim, sulfapyridine, sulfasalazine, citalopram, sertraline, venlafaxine, memantine sulfamethoxazole, rosuvastatin and atorvastatin. Hypersil Gold column (50 mm × 2.1 mm i.d. 3 μm particles) was used for determination of norfloxacin, levofloxacin, ciprofloxacin, azithromycin,