Chemosphere 99 (2014) 160–170

Contents lists available at ScienceDirect

Chemosphere

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

Occurrence and fate of pharmaceutically active compounds in the largest municipal wastewater treatment plant in Southwest China: Mass balance analysis and consumption back-calculated model

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HIGHLIGHTS

- 21 and 18 Target PhACs were detected in the wastewater and sludge.
- Mass loads of PhACs per person were calculated and compared with other countries.
- Biotransformation/biodegradation was the main removal mechanism for the PhACs.
- Construct the back-calculated PhAC consumption model based on influent concentration.

ARTICLE INFO

Article history:
Received 12 June 2013
Received in revised form 16 October 2013
Accepted 22 October 2013
Available online 21 November 2013

Keywords:
Pharmaceutically active compound
Wastewater
Sludge
Mass balance analysis
Pharmaceutical consumption back-calculated model
China

ABSTRACT

The occurrence and fate of twenty-one pharmaceutically active compounds (PhACs) were investigated in different steps of the largest wastewater treatment plant (WWTP) in Southwest China. Concentrations of these PhACs were determined in both wastewater and sludge phases by a high-performance liquid chromatography coupled with electrospray ionization tandem mass spectrometry. Results showed that 21 target PhACs were present in wastewater and 18 in sludge. The calculated total mass load of PhACs per capita to the influent, the receiving water and sludge were 4.95 mg d^{-1} $person^{-1}$, 889.94 μg d^{-1} $person^{-1}$ and 78.57 μg d^{-1} $person^{-1}$, respectively. The overall removal efficiency of the individual PhACs ranged from "negative removal" to almost complete removal. Mass balance analysis revealed that biodegradation is believed to be the predominant removal mechanism, and sorption onto sludge was a relevant removal pathway for quinolone antibiotics, azithromycin and simvastatin, accounting for 9.35–26.96% of the initial loadings. However, the sorption of the other selected PhACs was negligible. The overall pharmaceutical consumption in Chongqing, China, was back-calculated based on influent concentration by considering the pharmacokinetics of PhACs in humans. The back-estimated usage was in good agreement with usage of ofloxacin (agreement ratio: 72.5%). However, the back-estimated usage of PhACs requires further verification. Generally, the average influent mass loads and back-calculated annual per capita consumption of the selected antibiotics were comparable to or higher than those reported in developed countries, while the case of other target PhACs was opposite.

1. Introduction

Recently, overwhelming interest about the presence of pharmaceutically active compounds (PhACs) as "pseudopersistent" contaminants in the environment have been shown due to their potential negative effects on aquatic ecosystems and terrestrial wildlife (Pomati et al., 2007; Martinez, 2008; Dirany et al., 2011). A significant fraction of parent PhACs are excreted either as unmetabolized or as transformation products, via urine and feces of human body or veterinary, and are introduced into the sewer systems, which have become the principal entry pathway of PhACs residues into the aquatic environment (Leung et al., 2012).

Municipal wastewater treatment plants (WWTPs) are regarded as major barriers that can prevent contaminants in wastewater

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http://dx.doi.org/10.1016/j.chemosphere.2013.10.062

from entering the receiving environment. However, WWTPs were not originally designed to deal with complex PhACs. These substances and their metabolites enter into WWTPs where some of them may not be completely removed or transformed during the treatment process leading them into the receiving environment. Even higher concentrations were found in effluent than in influent for some recalcitrant PhACs. In the last decade, numerous published literatures have investigated and documented the behavior and fate of PhACs from various therapeutic classes in the WWTPs in North American, Europe and Australia (Verlicchi et al., 2012). However, only a few papers were concerned with the situation in China, perhaps because of the difficulties of analysis and the expensive trial costs. To date, main one specific therapeutic class, antibiotics, has been investigated by limited previous studied in China (Xu et al., 2007; Gulkowska et al., 2008; Gao et al., 2012a; Zhou et al., 2013).

Extensive literatures on the concentration levels of PhACs in aqueous phases such as wastewater or surface water is available (Li and Zhang, 2011; Leung et al., 2012; Aydin and Talinli, 2013); however, the presence of PhACs is much less explored in sewage sludge than in wastewater or surface water because of the great effort required in analyzing this difficult matrix. An aqueous phase removal percentage, which is based on the concentrations of PhACs in the influent and the effluent of WWTPs, is often used as the only parameter available for calculating the PhAC removal efficiency in WWTPs (Leung et al., 2012). The sorption onto sludge is a relevant removal pathway for certain PhACs (Jelic et al., 2011, 2012; Jia et al., 2012; Zhou et al., 2013). Thus, an aqueous phase removal percentage cannot comprehensively assess the removal of PhACs in WWTPs accurately. Mass balance analysis approach would be an effective way to understand the fate of PhACs in WWTPs and their mass loading to the receiving environments.

The level of PhACs in the influent depends on their consumption. Scheurer et al. (2009) reported the occurrence of the widely used metformin in surface waters in German and concluded that the high concentrations of metformin in aquatic environment were in agreement with the consumption data. ter Laak et al. (2010) stressed the potential of using pharmaceutical sales data for the prediction of concentrations in the aqueous environment. Kasprzyk-Hordern et al. (2009) estimated the pharmaceutical usage in local communities based on their concentrations in wastewater influent. Besse et al. (2008) calculated the predicted environmental concentrations (PECs) of PhACs using drug consumption data and found that the calculated PECs were consistent with the field measurements. Rowney et al. (2009) predicted the concentrations of cytotoxic drugs in the catchment area of the Thames River by considering the consumption data. Sum up above mentioned studies, we can come to the conclusion that there is a good correlation between PhAC consumption and the residual loads in the influent for different therapeutic classes and that the analysis of post-therapeutic residual concentrations in the influent after human administration can be an alternative method to back-calculate PhAC usage by considering the pharmacokinetics of the target PhACs in humans.

To date, a few studies reported the occurrence and behavior of the antibiotics in WWTPs in the fastest developing cities of China such as Beijing, Guangzhou and Hong Kong (Xu et al., 2007; Gulkowska et al., 2008; Sui et al., 2010; Gao et al., 2012a; Zhou et al., 2013), and the results of these studies indicated that the contamination level of antibiotics varied among cities in China. However, no information was available in other wide areas in China. During the past two decades, the Chongqing region in the southwestern China, having a population of 3.3 million inhabitants, has become one of the fastest growing economies and most densely urbanized areas in the world. The pharmaceutical consumption in hospitals in the region is about 1.361 billion RMB. It is supposed that the occurrence of PhACs in the aquatic environment of Chongqing is of particular interest and may be higher concentrations than other regions. All the WWTPs in Chongqing, which include only two treatments steps (physical and biological) and do not use tertiary treatment or an advanced sewage treatment (e.g. ultrafiltration, flocculation, ozonation, advanced oxidation, or osmosis), were not originally designed for removal of the PhACs. Therefore, it is imperative to obtain accurate information on the elimination of PhACs in these WWTPs to supply the scientific data for the WWTP upgrades and also to provide treatment alternatives for those PhACs refractory to elimination.

Probably due to the lack of regulations of all kinds of drugs, the PhACs, especially the antibiotics, were misused seriously in China. According to statistics, the annual per capita consumption of antibiotics is 138 g in China and the figure is 10 times as much as that of the United States. However, the information on annual pharmaceutical consumption in various cities in China is unavailable because establishing a collective record system for all practitioners, public and private hospitals, as well as over-the-counter PhACs is complicated and costly.

Here, based on measured pharmaceutical concentrations in influent of the WWTP and the pharmacokinetics of PhACs in humans, we tried to create a back-calculated model for the prediction of the loads of PhACs to provide a reference for improving current statutory regulation on pharmaceutical consumption. In addition, the average mass loads of PhACs per person reported in developed countries and in this study were calculated and a comparison analysis was made to have a better understanding of pharmaceutical occurrence and mass inputs into the environment. Lastly, dewatered sludge was collected to determine the concentrations and to assess the sorption of target PhACs onto sludge. Based on the data obtained, mass balance analysis was used to explore their potential removal mechanisms.

2. Materials and methods

2.1. Chemicals and reagents

Eight classes of 21 PhACs were selected for this study: analgesics, sulfonamide antibiotics (SAs), macrolide antibiotics (MAs), quinolone antibiotics (QAs), antiepileptics, cholesterol lowering statin drugs, lipid regulators and antihypersensitives. The 21 target PhACs were ibuprofen (IBP), diclofenac (DCF), clofibric acid (CA), bezafibrate (BZB), simvastatin (SVT), atorvastatin (ATT), carbamazepine (CBZ), erythromycin-H_2O (ERY), roxithromycin (ROX), azithromycin (AZM), Amlodipine (ALP), moxifloxacin (MOX), Acetaminophen (ACM), gemfibrozil (GFB), metoprolol (MTP), sulfamethoxazole (SMZ), sulfadiazine (SDZ), sulfamethazine (SM1), trimethoprim (TMP), ofloxacin (OFX) and norfloxacin (NOR). These compounds were selected because of their high consumption in Chongqing and their being frequently detected in surface and wastewater. Chemical structures, CAS numbers and physicochemical properties of the 21 target PhACs are shown in Supplementary Information. Internal standards simatone (SMT), dihydrocarbamazepine (DCBZ), caffeine-$^{13}C3$ (CF-^{13}C) and mecoprop-D^3 were purchased from Accustandard (New Haven, CT, USA), Sigma–Aldrich, C/D/N Isotopes (Quebec, Canada) and Dr. Ehrenstoefer (Augsburg, Germany), respectively. Oasis hydrophilic–lipophilic balanced (HLB, 6 cc, 200 mg) cartridges were purchased from Waters (Milford, MA, USA). Syringe filters with 0.45 mm pore size were purchased from Pall Corp., United States. Milli-Q water was used throughout the study. HPLC-grade methanol was provided by Merck (Germany).

The individual and internal standard solutions were prepared at concentrations of 500 mg L^{-1} by dissolving appropriate amounts of