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Occurrence, fate and ecotoxicological assessment of pharmaceutically active compounds in wastewater and sludge from wastewater treatment plants in Chongqing, the Three Gorges Reservoir Area

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HIGHLIGHTS

- All the 21 analyzed PhACs were detected in wastewater and 18 in sludge.
- The removal of PhACs was insignificant in primary and disinfection processes.
- Contribution of sorption to sludge was only 1.5% for the target PhACs.
- Five antibiotics and a mixture of 21 detected PhACs may pose a risk to algae.

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ABSTRACT

The occurrence, removal and ecotoxicological assessment of 21 pharmaceutically active compounds (PhACs) including antibiotics, analgesics, antiepileptics, antilipidemics and antihypersensitives, were studied at four municipal wastewater treatment plants (WWTP) in Chongqing, the Three Gorges Reservoir Area. Individual treatment unit effluents, as well as primary and secondary sludge, were sampled and analyzed for the selected PhACs to evaluate their biodegradation, persistence and partitioning behaviors. PhACs were identified and quantified using high performance liquid chromatography/tandem mass spectrometry after solid-phase extraction. All the 21 analyzed PhACs were detected in wastewater and the target PhACs except acetaminophen, ibuprofen and gemfibrozil, were also found in sludge. The concentrations of the antibiotics and SVT were comparable to or even higher than those reported in developed countries, while the case of other target PhACs was opposite. The elimination of PhACs except acetaminophen was incomplete and a wide range of elimination efficiencies during the treatment were observed, i.e. from "negative removal" to 99.5%. The removal of PhACs was insignificant in primary and disinfection processes, and was mainly achieved during the biological treatment. Based on the mass balance analysis, biodegradation is believed to be the primary removal mechanism, whereas only about 1.5% of the total mass load of the target PhACs was removed by sorption. Experimentally estimated distribution coefficients (<500 L/kg, with a few exceptions) also indicate that biodegradation/transformation was responsible for the removal of the target PhACs. Ecotoxicological assessment indicated that the environment concentrations of single compounds (including sulfadiazine, sulfamethoxazole, ofloxacin, azithromycin and erythromycin-H_2O) in effluent and sludge, as well as the mixture of the 21 detected PhACs in effluent, sludge and receiving water had a significant ecotoxicological risk to algae. Therefore, further control of PhACs in effluent and sludge is required before their discharge and application to prevent their introduction into the environment.

1. Introduction

Pharmaceutically active compounds (PhACs), which are primarily designed to elicit a specific biological response for human and veterinary use, are regarded as "pseudopersistent" contaminants due to their continual input into the ecosystem and permanent presence (Daughton

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and Ternes, 1999; Hernando et al., 2006). The environmental pollution from PhACs has therefore provoked considerable scientific attention around the world over the past decade not only because of their potential adverse effects on various organisms (Pomati et al., 2006; Quinn et al., 2009; Santos et al., 2010; Wilson et al., 2003), but also due to their role in the development/maintenance/transfer/spread of antibiotic-resistant bacteria and antibiotic-resistant genes in the long term in the environment (P. Gao et al., 2012; Huang et al., 2011; Martinez, 2008; Zhu et al., 2013). Besides, the presence of PhACs could also endanger the reuse of treated wastewater, escalating human exposure to PhACs (Kim and Aga, 2007). Significant fractions of PhACs are excreted in the unmetabolized or metabolized form, via urine and feces of humans or animals. These PhACs are delivered into raw sewage systems and eventually reach the municipal wastewater treatment plants (WWTPs). WWTPs were not originally designed to deal with pharmaceutical contaminants, and they were built and upgraded with the principal aim of removing biodegradable carbon, nitrogen and phosphorus compounds and microbiological organisms. Therefore, WWTPs have limited capability of removing PhACs from wastewater. Even higher concentrations were found in effluent than in influent for some recalcitrant PhACs such as carbamazepine (CBZ), diclofenac (DCF) and metoprolol (MTP) (L. Gao et al., 2012; Jelic et al., 2011). As a result, treated wastewater containing PhACs is discharged into water bodies or reused for irrigation and recreation, and PhACs can end up onto soil when biosolids produced during wastewater treatment are reused as soil amendment. Given the poor elimination, WWTP discharges (sludge and effluent) are frequently identified as the principal pathway for the entry of PhAC residues into the environment (Jelic et al., 2012, 2011). Other sources may include the disposal of unwanted PhACs and waste from pharmaceutical manufacturing processes, as well as direct discharges from untreated domestic, agricultural and aquaculture wastewater.

With the continual improvements of advanced analytical technology and methodologies, PhACs have been widely identified and their concentration can be detected at ng/L levels in various environmental matrices (Huerta-Fontela et al., 2011). Today, the occurrence and fate of PhACs in urban centers in developed countries, such as Europe, North American and Australia, have been extensively investigated and well documented (Jelic et al., 2011; Kasprzyk-Hordern et al., 2009; Rosal et al., 2010; Verlicchi et al., 2012). PhACs have been detected in WWTP effluents, groundwater, surface water, river water and even drinking water at concentrations ranging from ng/L to μg/L level (Huerta-Fontela et al., 2011). Their concentrations in biosolids can range from μg/kg to mg/kg level (Gobel et al., 2005; Golet et al., 2003; Jelic et al., 2011; Martin et al., 2012). Due to inappropriate uses, uncontrolled disposal of PhACs and lack of regulations, the risk of exposure to PhACs is probably greater in the developing world. For example, China, a developing country, has considerable PhAC production and consumption (approximately 1.9 million tons consumption in 2009). The extensive use of PhACs may imply that PhACs are present in the environment at higher concentrations, and possibly with wider distributions, than those found in western countries. However, only a few studies about the situation in China have been reported (Chang et al., 2010; Gulkowska et al., 2008; Li and Zhang, 2011; Lin et al., 2008; Xu et al., 2007). Furthermore, most of studies simply focused on the determination of PhACs in the aqueous phase, and considered WWTPs as "black boxes", and calculated their overall removal efficiencies based on the concentrations of PhACs in raw influent and final effluent. The concentrations of PhACs in sludge were rarely determined mainly due to the demanding efforts required in the analysis of challenging matrices. Few studies considered the fate and distribution of PhACs in individual treatment processes, such as primary treatment, biological treatment and chlorination. To date, no studies in China have focused on the concentration of multiple therapeutic classes of pharmaceuticals except antibiotic in sludge and on the potential environmental risks from pharmaceutical residuals on ecosystems. Such information is important and urgently needed as many urban areas of China have increasingly large populations, huge annual pharmaceutical consumption and inadequacy of sewage treatment facilities.

The major objective of this study was to verify the occurrence and behavior of 21 target PhACs, including several antibiotics, analgesics, antiepileptics, antilipidemics and antihypersensitives, at four WWTPs with different treatment technologies in Chongqing, the Three Gorges Reservoir Area. Individual treatment unit effluents along activated sludge treatment process, as well as primary and secondary sludge, were sampled and studied in order to evaluate the biodegradation, persistence and partitioning behaviors of the target PhACs in both aqueous and solid phases. PhACs were chosen to represent a wide range of physicochemical properties. Mass balance analysis was performed to estimate fate of PhACs in the WWTPs and to explore their potential removal mechanisms. Furthermore, K_d values were calculated, from the measured concentrations of PhACs in the collected wastewater and sludge samples, to further identify the contribution of sorption onto sludge during the removal. We also assessed the potential ecological risks caused by the target PhACs on aquatic species based on calculated risk quotients (RQs). To the best of our knowledge, this is the first report on the occurrence of PhACs from multiple therapeutic classes except antibiotics in sludge in China to estimate adsorption of the target PhACs onto sludge.

2. Materials and methods

2.1. Chemicals and reagents

All the analytical standards for the studied PhACs were of high purity grade (>90%). Amlodipine (as besilate, ALP) and moxifloxacin (as hydrochloride, MOX) were obtained from European Pharmacopeia. Ibuprofen (IBP), DCF, clofibric acid (CA), bezafibrate (BZB), simvastatin (SVT), atorvastatin (as calcium salt, ATT), CBZ, erythromycin (as hydrate, ERY), roxithromycin (ROX) and azithromycin (as dehydrate, AZM) were purchased from Sigma-Aldrich, USA. Acetaminophen (ACM), gemfibrozil (GFB), MTP (as tartrate), sulfamethoxazole (SMZ), sulfadiazine (SDZ), sulfamethazine (SM1), trimethoprim (TMP), ofloxacin (OFX) and norfloxacin (NOR) were provided by Dr. Ehrenstorfer from Germany. Internal standards, namely, simatone (SMT), dihydrocarbamazepine (DCBZ), caffeine-$^{13}C_3$ (CF-^{13}C) and mecoprop-D_3 were purchased from Accustandard (New Haven, CT), Sigma-Aldrich, C/D/N Isotopes (Quebec, Canada) and Dr. Ehrenstorfer (Augsburg, Germany), respectively. Oasis hydrophilic–lipophilic balanced (HLB, 6 cc^3, 200 mg) cartridges were purchased from Waters Corporation (Milford, MA, USA). Syringe filters with 0.45 mm pore size were purchased from Pall Corp (USA). Milli-Q water was used throughout the study. High-performance liquid chromatography (HPLC)-grade methanol was provided by Merck (Germany).

The individual standard solutions as well as internal standard solutions were prepared at concentrations of 500 mg/L by dissolving appropriate amounts of PhACs in methanol. The dehydrated form of ERY (ERY-H_2O) is most frequently detected in the environment and therefore ERY-H_2O was measured in this study. A standard solution of ERY-H_2O was obtained by adjusting the pH of an ERY solution to 3.0 using 3 M H_2SO_4. After 4 h of stirring at room temperature complete conversion to ERY-H_2O was achieved. The completeness of the reaction was verified by checking for leftover ERY and possible metabolites using mass spectrometry. All stock solutions were stored in the dark at −20 °C, and new stock solutions were prepared every three months. A mixture of all PhACs was prepared by appropriate dilution of individual stock solutions in methanol–water (30:70, v/v) and it was renewed before each analytical run. A separate mixture of internal standards, used for internal standard quantification, was prepared in methanol and subsequently diluted in methanol–water (30:70, v/v) mixture.