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Occurrence, fate, and mass balance of different classes of pharmaceuticals and personal care products in an anaerobic-anoxic-oxic wastewater treatment plant in Xiamen, China

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ABSTRACT

In this study, the occurrence and fate of 49 pharmaceuticals and personal care products (PPCPs) were investigated in an anaerobic-anoxic-oxic (A2/O) wastewater treatment plant (WWTP) for seven consecutive days using 24-h composite sampling technique. Special emphasis was placed to understand the distribution of PPCPs in dissolved and adsorbed phase, and to evaluate PPCP fate in different treatment units. Among the 49 PPCPs, 40 PPCPs in influent, 36 in effluent, 29 in sludge and 23 in suspended solids were detected at least once during sampling. Non-steroidal anti-inflammatory drugs (NSAIDs) and a stimulant were predominant PPCPs in influent whereas antibiotics were predominant in sludge, effluent and suspended solids. Removal efficiencies from the aqueous phase based on the dissolved PPCPs showed variable contribution in removing different PPCPs under screen and grit chamber, anaerobic treatment, anoxic treatment, oxic treatment and sedimentation-UV treatments, with the highest removal percentage by anaerobic process in terms of both individual and overall treatment. Mass load analysis showed that 352 g PPCPs enter the WWTP daily while 14.5 g and 58.1 g were discharged through effluent and excess sludge to the receiving sea water and soil applications, respectively. Mass balance analysis based on both aqueous and suspended PPCPs showed 280 g (79.4%) mass of influent PPCPs was lost along the wastewater treatment processes, mainly due to degradation/transformation.

1. Introduction

During the last decade, the attention of the environmental researchers has been shifted from conventional pollutants (for examples, pesticides, heavy metals, polybrominated biphenyls, polycyclic aromatic hydrocarbons) to the emerging pollutants (EPs), because they pose adverse health effects to human beings and terrestrial life (Bu et al., 2013). Pharmaceuticals and personal care products (PPCPs) are regarded as a class of EPs (Repice et al., 2013), which enter the environment, mainly through the effluent of municipal wastewater treatment plants (WWTPs) and livestock activities (de García et al., 2013; Besse et al., 2012; Lv et al., 2014). Several studies have reported the occurrence and fate of PPCPs in wastewater (dissolved form) and in sludge (adsorbed form) with concentrations in the range of ng/L-μg/L and μg/kg-mg/kg, respectively (Azzouz and Ballesteros, 2013; Sun et al., 2014, 2016; Lapworth et al., 2012), whereas, only few studies have reported the occurrence and distribution of PPCPs on suspended solids (SS). Most of these studies either focused on few PPCPs or involved the suspended sludge particles only, but the role of SS of different treatment units remained unaccounted (Gao et al., 2012; Jia et al., 2012; Petrie et al., 2014).

Municipal wastewater treatment system is usually considered as an effective process to restrict PPCPs from entering the receiving environment (Al-Rifai et al., 2011; Li et al., 2013). Several studies

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have investigated the removal efficiencies of PPCPs from the aqueous phase based on their dissolved concentrations in the influent and effluent (Sun et al., 2016, 2014; Luo et al., 2014; Ratola et al., 2012; Clara et al., 2004). Results showed that wastewater treatment processes could partly or completely remove PPCPs with the removal efficiencies from negative values (carbamazepine, metoprolol, and so on) to 100% (caffeine, acetaminophen, and so on) (Sun et al., 2016, 2014; Luo et al., 2014; Ratola et al., 2012; Clara et al., 2004). Previous studies have provided fundamental information about the overall removal efficiency of municipal wastewater treatment system. However, there is a knowledge gap about the reasons for the negative removal values of some PPCPs (high concentration in effluent than the influent) during municipal wastewater treatment (Ort et al., 2010; Rodayan et al., 2014; Lindberg et al., 2005). Thus, an investigation about the removal efficiency of PPCPs across different treatment processes (e.g. anaerobic treatment, aerobic treatment, sedimentation, or disinfection) may reveal better understanding about the negative values in the overall removal efficiencies (Li et al., 2013; Wang et al., 2014).

Apart from the removal efficiencies, mass balance assessment reveals information about the fate and pathways of each PPCP (Petrie et al., 2014). This assessment shares the information not only about the removal of PPCPs from aqueous phase but it also reveals the removal mechanism whether sorption or degradation/transformation. In addition, the mass load analysis provides information about the mass flux of PPCPs to the receiving environment (Liu et al., 2012; Salgado et al., 2011). For mass balance and mass load studies, few researchers have considered the total loads of PPCPs in aqueous as well as in suspended phase (Alvarino et al., 2014; Blair et al., 2015). Without accounting for PPCPs in the SS, the mass balance and mass load studies would be underestimated.

In the present study, 24-h composite samples were collected for consecutive seven days from a WWTP equipped with anaerobic-anoxic/oxic (A2/O) process. Samples were collected along the different treatment processes, including the initial influent, influent A2/O, between two A (A-A), between A and O (A-O), effluent A2/O, final effluent, and return sludge. The purpose of the present study was therefore to (1) determine the occurrence of selected 49 PPCPs in wastewater, SS, and sludge, (2) evaluate the contribution of each treatment process on the PPCP removal, and (3) investigate the mass load and fate of PPCPs by assessing the mass loads and mass balance.

2. Experimental

2.1. Chemicals and reagents

All the 49 target PPCPs and the isotopic standards were purchased from Fluka (USA), Sigma-Aldrich (USA), Dr. Ehrenstorfer GmbH (Germany), Accu Standard (USA) or Cambridge Isotope Laboratories (USA). Table S1 of Supplementary information (SI) presents the detailed information of these chemicals. Oasis HLB solid phase extraction (SPE) cartridges (500 mg, 6 mL) were purchased from Waters Corp. (Millford, MA). All the solvents were purchased from Tedia (USA) and possessed either HPLC grade quality or analytical grades of highest purity. Purified reagent water was prepared using Milli-Q water purification system (Millipore, USA). Individual stock standard solutions of all PPCPs were prepared in methanol and were refrigerated at −20 °C in dark.

2.2. Sampling site and sample collection

The WWTP investigated in this study is in Xiamen located in the southeast of China (117°53′-118°25′E and 24°25′-24°54′N). The WWTP receives predominantly domestic wastewater with little industrial wastewater. The overall treatment process involves screen, grit chamber, anaerobic/anoxic/oxic (A2/O), sedimentation, and UV disinfection as shown in Fig. 1.

Twenty-four hour composite samples of wastewater (WW) from six locations of WWTP and the returned sludge (RS) were collected for consecutive seven days from 29th February 2016 to 6th March 2016. The wastewater samples were collected from initial influent, influent A2/O, wastewater after anaerobic (A-A), wastewater after anoxic (A-O), effluent of A2/O and the final effluent (Fig. 1). The SS samples were collected by filtering the wastewater samples (500 mL) using pre-weighed filters and then freeze-drying these filters. Table S2 of SI presents WW parameters like total organic carbon (TOC), total nitrogen (TN), orthophosphate (PO_4), ammonium ions (NH_4^+), nitrite ions (NO_2^-), nitrate ions (NO_3^-), total phosphorous (TP) and total nitrogen (TN).

2.3. Sample preparation and analysis

All types of samples (WW, RS and SS) were extracted using USEPA SPE method 1694 (Englert, 2007). The details about sample preparation/extraction are provided in SI. Sample extraction was carried out using 500 mL WW, 0.1 g RS and 0.1 g filtered and freeze-dried SS, where sufficient quantity of SS sample was available (A-A, A-O and effluent A2/O). In case of influent and influent A2/O, the quantity of SS sample was less than 0.1 g, therefore the whole GF/F filters including SS were processed for sample preparation. The SS of the final effluents were not processed due to its trace amounts and minor contribution to the mass loads (Liu et al., 2012).

All the extracted samples were analyzed by liquid chromatography triple quadrupole mass spectrometry (LC-QqQ MS) method using multiple reaction monitoring (MRM) mode in both positive and negative ionization as used in our previous studies (Lv et al.,

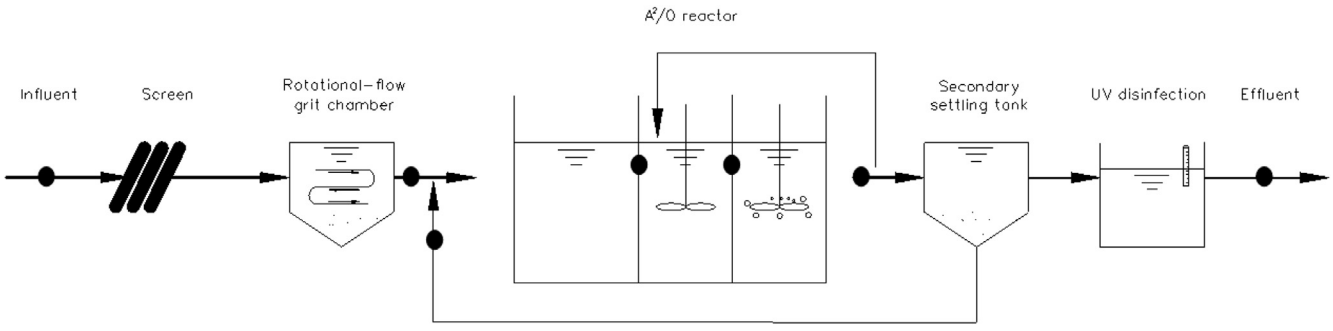

Fig. 1. Schematic diagram showing the treatment in the WWTP and the sampling points (●).