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Fate and mass balance of bisphenol analogues in wastewater treatment plants in Xiamen City, China☆

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ABSTRACT

Due to the well-known endocrine disrupting ability of bisphenol A (BPA), its production and usage have been regulated. Consequently, other bisphenol analogues (BPs) have been used as the replacement of BPA. Despite their widespread use, few studies have investigated the occurrence and fate of BPs in wastewater treatment plants (WWTPs). In this study, we conducted a city-wide monitoring survey and collected the wastewater and sludge samples from seven WWTPs in Xiamen, China over seven days. The concentrations of dissolved and adsorbed BPs in the influent and effluent, together with the BP concentrations in the sludge were determined. Five BPs, including BPA, BPAF, BPE, BPF, and BPS, were widely detected. The medium concentrations of BPA, BPAF, BPE, BPF, and BPS were 1318, 0.282, 3.70, 50.0, and 48.0 ng/L in the influent, 177, 0.714, 3.64, BLD, and BLD in the effluent, and 343, 3.09, BLD, 56.5, 1.01 μg/kg in the sludge. Spatial variations were observed, which implied the industrial origin of BPA. The efficiencies of BP removal from aqueous phase were evaluated, and results showed that BPA, BPF, and BPS were highly removed with removal efficiencies higher than 78%, while BPAF and BPE were resistant in WWTPs. Mass load calculations showed that 2075 g BPs entered into the WWTPs in Xiamen City each day, while 246 g and 63 g were discharged via effluent and excess sludge, respectively. Mass balance analysis showed that BPS and BPA were mainly biodegraded, BPF were mainly adsorbed and biodegraded, BPAF was resistant to biodegradation, while BPE was resistant to both biodegradation and adsorption.

1. Introduction

Bisphenol analogues (BPs) are a class of organic chemicals with two hydroxyphenyl functional group, including bisphenol A (BPA), bisphenol AF (BPAF), bisphenol B (BPB), bisphenol E (BPE), bisphenol F (BPF), bisphenol S (BPS), bisphenol Z (BPZ), and so on. BPs have a variety of industrial usage; for example, BPA is widely used to manufacture polycarbonate plastics and epoxy resins, BPAF is used to produce membranes and optical fibers, BPS is used in the thermal paper, and BPF, BPS, and BPAF are the main substitutes of BPA in the manufacturing of polycarbonate plastics and epoxy resins (Delfosse et al., 2012; Chen et al., 2016). Due to the well-known endocrine disrupting activity of BPA and other BPs (Delfosse et al., 2012; Rochester and Bolden, 2015), great concerns have been raised on adverse effects of BPs on the human health and ecological safety.

Quite a few studies have investigated the occurrence and fate of BPA in the wastewater treatment plants (WWTPs) (Huang et al., 2012; Jiang et al., 2013; Mohapatra et al., 2010; Luo et al., 2014; Qiang et al., 2013; Carvalho et al., 2016; Belhaj et al., 2015). Results showed that BPA have been widely detected in the wastewater and sludge, with the concentrations of ng/L-mg/L and μg/kg-mg/kg, respectively (Huang et al., 2012; Jiang et al., 2013; Luo et al., 2014;

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Sun et al., 2014, 2016a). However, the knowledge on the occurrence of BPs other than BPA in the wastewater and sludge is limited. Researchers investigated sludge samples in Korea (Lee et al., 2015), US (Yu et al., 2015), and China (Song et al., 2014), respectively, which have provided fundamental data for the understanding of BP occurrence in the sludge (Chen et al., 2016). However, the information on the occurrence of BPs (other than BPA) in the wastewater either in the dissolved form or adsorbed onto the suspended solids (SS), and the integrated information of BPs in both wastewater and sludge, is limited.

WWTPs could partially remove BPA with the removal efficiencies of 62.5–99.6% (Luo et al., 2014). The aqueous phase removal percentage is often used to evaluate the removal efficiencies of BPA during the treatment process (Luo et al., 2014). However, the removal percentage based on the dissolved phase cannot comprehensively show the fate of organic pollutants in the WWTPs (Zhou et al., 2013), because BPs might adsorb onto the sludge/suspended particles due to their high values of log K_{ow} (Table S1, in the Supplemental Information, SI). As an alternative, mass balance assessment is a valuable way for understanding the fate of organic micropollutants and their mass loads to the receiving environments (Zhou et al., 2013; Supowit et al., 2016). So far, limited studies, including Bertanza et al., (2011), Guerra et al., (2015), and Boni et al., (2012) have investigated the mass balance of BPA and provided useful information. However, the studies of the fate of BPs other than BPA, including their removal efficiencies during wastewater treatment processes and their mass loads via effluent and sludge, was not yet available.

In this study, we collected the influent, effluent, and sludge samples from seven WWTPs in Xiamen, which is the major city in Southeast China. Seven BP concentrations in the wastewater, suspended solids (SS), and sludge were determined. The spatial and temporal variations of BP occurrence and removal were investigated. Special emphasis was placed on the mass balance assessment and mass load analysis of BPs during the wastewater treatment processes. The focus of this paper is to fill the knowledge gap of the fates of BPs in the WWTPs.

2. Materials and methods

2.1. Chemicals

BP compounds and bisphenol A isotope standards were purchased from Dr. Ehrenstorfer GmbH (Germany) and CNW (China). Physicochemical properties, including the molecular structure and log K_{ow} are given in Table S1 of SI. Methanol, acetonitrile and acetone (HPLC grade) were provided by Tedia (USA), $Na_4EDTA{\cdot}2H_2O$ (analytical grade) was provided by Sinopharm (China). The reagent water was prepared with a Milli-Q water purification system (Millipore, USA). Stock solutions of individual BPs were prepared in methanol and stored at −20 °C in the dark.

2.2. Sampling campaign

Xiamen is a major city in the southeast of China (117°53′-118°25′ E and 24°25′-24°54′ N). The land area is 1573 km^2, and the population is 3.86 million in 2015, which showed a very high population density. There are seven steadily running WWTPs which receive both domestic wastewater and industrial wastewater, and another two small scale WWTPs which are under test run. Samples were collected from all the seven steadily running WWTPs (W1–W7) on February 28th to March 4th and March 6th, 2016. Automatic samplers were deployed at the influent, effluent, and return sludge (activated sludge in W1) to collect 24 h composite samples (0:00–24:00). The treatment processes, average daily processing capacity, average dry sludge production, and the ratio of domestic wastewater to industrial wastewater over the 7 sampling days are shown in Table 1. Detail performance of WWTPs on each sampling day is shown in Table S2 in SI. To further understand the contribution of individual treatment process on the BP removals, composite samples across the treatment processes in W3 were collected manually by taking 200 mL sample after every 2 h from 10:00 a.m. to 10:00 a.m. the next day. Samples included the initial influent, the influent of anaerobic-anoxic-oxic (A2O) process, wastewater between the anaerobic and anoxic processes, wastewater between anoxic and oxic processes, wastewater after oxic process, final effluent, and return sludge on February 29th to March 6th, 2016. After everyday sample collection, all the samples were immediately transferred to lab in the pre-cleaned glass bottles in the dark ice cooler, and the aqueous sample preparations were performed within 48 h.

2.3. Sample analysis

Wastewater samples were prepared using solid phase extraction (SPE) (Sun et al., 2014). Briefly, samples were filtered (GF/F glass fiber filters, 0.7 μm, Whatman), acidified to pH 2 using hydrochloric acid, added with 125 mg $Na_4EDTA{\cdot}2H_2O$, and spiked with 50 μL isotope labelled standards as surrogate (500 μg/L). Oasis HLB cartridge (500 mg 6 mL, Waters) were preconditioned sequentially with 20 mL methanol, 6 mL water, and 6 mL water with pH 2.0, and then loaded by 500 mL samples at 5 mL/min. After the cartridges drying, analytes were eluted with 12 mL of methanol and 6 mL of mixture (acetone: methanol = 1:1). The eluates were evaporated to dryness with nitrogen stream and reconstituted to 1.00 mL with methanol. The samples were stored at 4 °C in the dark until the sample preparation was performed, which was within 48 h after sample collection.

Sludge and SS samples were prepared following the US EPA method 1694 (USEPA). Briefly, lyophilized samples (up to 0.100 g) were first extracted twice using mixture of 15.0 mL phosphate buffer (pH = 2.0) and 20 mL acetonitrile followed by extraction with 15.0 mL acetonitrile. The combined extract was then concentrated to 20–30 mL by rotary evaporation, and diluted with 200 mL of reagent water. Samples were then cleaned up via the SPE method used for liquid samples.

Instrumental analysis was performed by liquid chromatography-tandem mass spectrometry (LC-MS/MS). Chromatographic separation of analytes was performed using a Kinetex C18 column (100 mm × 4.6 mm, 2.6 μm, Phenomenex, USA) by a Shimadzu LC system (Shimadzu, Japan). A binary gradient (Table S3) with a flow rate of 0.80 mL/min was used. Mobile phase A contained 5 mmol/L ammonium acetate in water, while mobile phase B was methanol. The mass spectrometric measurements were carried out on an ABI triple quadrupole (QqQ) MS in the negative mode. The multiple reaction monitoring (MRM) mode was applied with the monitored target, reference ions, and other detail MS parameters shown in SI Table S1. The quantification was achieved via standard calibrations as shown in Table S4.

2.4. Quality assurance and quality control (QA/QC)

QA/QC was conducted to ensure the identification and quantification of the BPs. Identification of each BP was performed by LC-MS/MS with MRM, using the 2 highest characteristic precursor ion/product ion transition pairs (SI Table S1). The ratios of product transitions were calculated to ensure correct identification. Method quantification limits (MQLs), which were evaluated based on instrument quantification limits and analyte recovery (Li et al., 2016), were in the range of 0.043–2.43 ng/L for wastewater and