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Occurrence and fate of bisphenol A transformation products, bisphenol A monomethyl ether and bisphenol A dimethyl ether, in wastewater treatment plants and surface water

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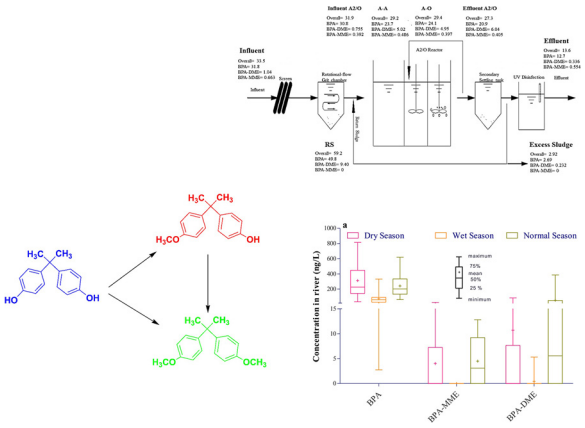
GRAPHICAL ABSTRACT



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ABSTRACT

Due to the wide use, bisphenol A (BPA) has been detected frequently in the aquatic environment. However, the information on the distribution of BPA transformation products is limited. In this study, we investigated two BPA transformation products, namely bisphenol A monomethyl ether (BPA-MME) and bisphenol A dimethyl ether (BPA-DME). This study revealed that both transformation products were widely detected in the wastewater treatment plants (WWTPs) as well as in surface water of Jiulong River and its estuary with higher detected concentrations and detection frequencies for BPA-DME. Temporal variations were observed in a WWTP based on a five-year sampling campaign. Mass load of BPA and its transformation products was evaluated and results indicated the generation of BPA-MME and BPA-DME during the wastewater treatment processes, which contributed for 1.95% BPA removal. BPA and its transformation products were also widely detected in the surface water of Jiulong River and its estuary. Results indicated their additional generation in the surface water, since

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BPA-MME and BPA-DME in the surface river water were with similar level or even higher than effluent in WWTPs.

1. Introduction

Bisphenol A (BPA), chemically designated as 2,2-bis(4-hydroxyphenyl) propane is a very common synthetic organic compound, used as intermediate in variety of consumer products like polycarbonate plastics and epoxy resins [1]. It is one of the highest production chemicals in the world manufactured in bulk with a global market share of 15 billion pounds in 2013 [2] and is predicted to increase with annual growth rate of 4.7% from 2014 to 2020 [3]. In China, it is also increasing continuously due to the fast development of the polymer industry [4,5]. Because of its well-known endocrine disrupting activity, BPA has been considered as a concern for human health as well as for the environment [6], and many adverse health effects have been associated with BPA exposure that include diabetes, reproductive disorders, obesity, birth defects, cardiovascular diseases and breast cancer [7,8].

After release during production and usage, BPA can be transformed or degraded via abiotic and biological processes in the aquatic system [9]. The abiotic processes, including photo degradation and advanced oxidation can effectively remove BPA with the major transformation products of 4-isopropenylphenol and 4-hydroxycumyl alcohol [3,10]. In addition, our previous study showed that BPA can be transformed to nitro- and dinitro-BPA via abiotic nitration in the presence of nitrite [11]. For the biological processes, bacteria [12,13], fungi [10,14] and algae [15,16] have been reported to be capable of BPA degradation and transformation. Oxidative skeletal rearrangement is one of the major metabolic routes, in which the transformation products mainly 4-isopropenylphenol, 4-hydroxybenzaldenhyde, 4-hydroxybenzoate, 4-hydroxycumyl alcohol and hydroquinone are formed [9]. In addition, bacterial cometabolism is also a major way for BPA transformation. For examples, McCormick et al. [17] showed that *Mycobacterium* sp. could catalyze *O*-methylation of BPA, with the major transformation products of BPA monomethyl ether (BPA-MME) and dimethyl ether (BPA-DME). Generally, the transformation products showed less toxicity or less endocrine disrupting activity compared to BPA [11,18,19]. However, BPA-MME and BPA-DME were more toxic to the developing zebrafish embryo than the parent compound [17], indicating their higher risk to the aquatic environment.

Large number of studies have investigated the BPA occurrence in various environmental compartments [20]. BPA has been widely detected in the influent as well as effluent of wastewater treatment plants (WWTPs) at concentrations in the range of ng/L ~ mg/L [21,22]. Wastewater treatment processes partly removed BPA from aqueous phase with the removal efficiencies of 62.5–99.6% [23]. In addition, BPA has been detected widely throughout the world in surface waters, with the concentration ranged from below detection limits (BLDs) to 56 μg/L [21,22]. Previous studies have provided fundamental information on the occurrence and fate of BPA. However, the information on the transformation products, especially the potentially more toxic BPA-MME and BPA-DME, is limited.

Our previous studies suggested that 85% of BPA was removed during wastewater treatment processes mainly via biodegradation or biotransformation, based on the mass balance analysis of BPA in seven WWTPs [24]. Keeping in view the possible transformation of BPA into BPA-MME and BPA-DME, together with the higher toxicity of transformation products, we designed this study to investigate the occurrence and fate of BPA, BPA-MME and BPA-DME in WWTPs and surface river water. Special emphasis was placed on the (1) temporal variations over five years (2012–2016), (2) spatial variations in different WWTPs and along different treatment units, (3) mass balance analysis during wastewater treatment processes, and (4) their distribution in the river and estuary water. This is the first ever study that report the occurrence and fate of BPA-MME and BPA-DME in WWTPs as well as in the surface river water.

2. Experimental

2.1. Chemicals and reagents

BPA and BPA-DME with purity greater than 98.0% were purchased from Sigma-Aldrich (USA). BPA-MME was not commercially available so it was synthesized in our laboratory with detail of synthesis in supplementary information (SI). The structure of synthesized BPA-MME was characterized by gas chromatography mass spectrometry (GC–MS) and nuclear magnetic resonance (NMR) as shown in Fig. S1 and Fig. S2 in SI. Physicochemical properties along with toxicity level of these compounds have been listed in Table S1 in SI. HPLC grade acetone, *n*-hexane and analytical reagent grade methyl iodide and potassium carbonate were supplied by Sigma-Aldrich and Sinopharm. Stock solutions of BPA, BPA-MME and BPA-DME were prepared in acetone (1.00 g/L). Derivatizing agent N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) and pyridine were purchased from Sigma–Aldrich and Alfa Aesar respectively. Water used in all these experiments was of Milli-Q (USA) grade and all other reagents and glassware were of highest grade available.

2.2. Sampling details

Xiamen is a major city in the southeast of China (117°53′–118°25′ E and 24°25′–24°54′ N) with the population of 3.92 million in 2016. There are seven steadily running WWTPs in Xiamen City, with detailed

Table 1
Sample type, sampling dates, sample strategy and sampling location.

Sampling Location	Sample Type	Sampling dates	Sampling strategy
W1 (1st Serial)	Wastewater (influent and effluent)	August 28th and December 3rd, 2012, March 6th and May 30th 2013	Grab
W1 (2nd Serial)	Wastewater (influent and effluent)	February 20th, May 8th, August 11th, and November 12th, 2014	Grab
W1 (3rd Serial)	Wastewater and suspended solid (influent, influent A2/O, A-A, A-O, Effluent A2/O, effluent), and sludge	February 29th to March 6th, 2016	24 h Composite
W1-W7	Wastewater and suspended solids (influent, effluent), sludge	February 28th to March 1st, 2016	24 h Composite
Jiulong River and estuary	Surface water	September 5-6, 2012, January 15-17, 2013 and June 7-9, 2013	Grab

W1-W7 represents each of the seven wastewater treatment plants.