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Occurrence and profiles of halogenated phenols, polybrominated diphenyl ethers and hydroxylated polybrominated diphenyl ethers in the effluents of waste water treatment plants around Huang-Bo Sea, North China

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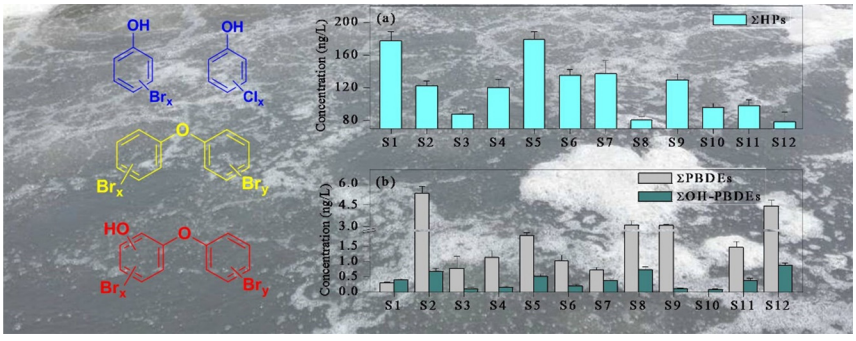
HIGHLIGHTS

- HOPs were detected in all effluents of twelve WWTPs near Huang-Bo Sea.
- The levels of ΣHPs, ΣPBDEs and ΣOH-PBDEs were 77.2–168.5, nd-5.3 and 0.08–0.88 ng/L.
- PCP, BDE47 and 6-OH-BDE-47 had the highest detection frequencies.
- Positive correlations were found between BDE-47 and its metabolites 6-OH-BDE-47.
- Release of HOPs via waste water effluents is necessary to be considered.

GRAPHICAL ABSTRACT



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ABSTRACT

Halogenated organic pollutants (HOPs), as ubiquitous environment contaminants, have attracted increasing concerns due to the potential adverse health impacts on organisms and even humans. Waste water treatment plants (WWTPs) are one source of HOPs to the environment through their discharge of treated effluent. In this study, the presence and profiles of 6 halogenated phenols (HP), 17 polybrominated diphenyl ethers (PBDE) and 11 hydroxylated polybrominated diphenyl ethers (OH-PBDE) were investigated in 12 WWTP effluent samples collected near Huang-Bo Sea in Dalian, China. These targeted organohalogen pollutants were found in all the effluent samples with the total concentrations of ΣHPs, ΣPBDEs and ΣOH-PBDEs ranging from 77.2 to 168.5 ng/L, from not-detected to 5.3 ng/L and from 0.08 to 0.88 ng/L, respectively. The most abundant congeners of HPs and PBDEs in the effluents were pentachlorophenol (PCP), BDE-47 and BDE-99, while for OH-PBDEs, 6-OH-BDE-47 and 5-OH-BDE-47 were the most abundant. In addition, the statistical analysis showed that a significant ($p < 0.05$) positive correlation was observed between BDE-47 and its metabolite 6-OH-BDE-47, indicating that PBDEs may be a source of OH-PBDEs detected in the effluents.

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1. Introduction

Halogenated phenols (HPs, such as bromophenols, chlorophenols) and polybrominated diphenyl ethers (PBDEs) are a large group of anthropogenic chemicals that are of great concern due to their ubiquitous distribution, persistence, bioaccumulation potential and toxicity (de Wit, 2002; Hites, 2004; Sim et al., 2009). The production volume of pentaBDE mixture, which is composed of the congeners of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), 2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99), 2,2′,4,4′,6-pentabromodiphenyl ether (BDE-100), 2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE-153), and 2,2′,4,4′,5,6′-hexabromodiphenyl ether (BDE-154), was estimated at 7500 metric tons in 2001 in North America (Hites, 2004). These chemicals are widely used as polymer intermediates, and flame retardants in varieties of products including textiles, furniture, electronic equipment, dyes, pulp, paints, herbicides and wood preservatives (WHO, 1989; WHO, 2005; de Wit, 2002; Sim et al., 2009).

In most cases, bromophenols or PBDEs are simply mixed into polymer products and not chemically bound to the products, thus they may leach out from products during the period of production, usage and disposal (de Wit, 2002). Owing to the massive and continuous usage, they are being discharged into the environment and can still be detected in air, water, sediment, fish and even human serum (Chen et al., 2006; Meng et al., 2008; Qiu et al., 2010; Sim et al., 2009 and Zhu et al., 2009). HPs and PBDEs are of high toxicity and have possible harmful effects on human health and aquatic ecosystems (Hites, 2004; Yang and Zhang, 2013). Furthermore, bromophenols and PBDEs have been demonstrated to be precursor compounds of a class of even more toxic chemicals, hydroxylated polybrominated diphenyl ethers (OH-PBDE), in abiotic and biotic media under certain conditions. For example, 6-OH-BDE-47 can be formed from BDE-47 in aqueous solution under simulated solar light irradiation (Zhao et al., 2015). In the study of Routii et al. (2009), 3-OH-BDE47 and 4′-OH-BDE49 were formed through oxidative biotransformation of BDE47 in the Baltic ringed seals. There is increasing evidence that OH-PBDEs are ubiquitous in environments such as rain and snow (Ueno et al., 2008), and aquatic organisms, including algae (Malmvarn et al., 2005) and fish (Valters et al., 2005), as well as human blood (Chang et al., 2010; Yu et al., 2010). The concern over OH-PBDEs has risen steadily since they elicit various adverse effects in exposed organisms, including neurotoxicity, thyroid disruptions and endocrine disruptions (Harju et al., 2007; Meerts et al., 2001; Zheng et al., 2012). As a result, there is a need to investigate and assess the sources of all these halogenated organic pollutants (HOPs) in the environment.

Waste water treatment plants (WWTPs) are likely to receive a significant amount of HPs and PBDEs along with municipal and industrial waste water, and then become a source of them to the receiving water bodies and regional environments surrounding such discharge sources (Wang et al., 2007). Thus, occurrence of these HOPs in the effluents from both industrial and municipal waste waters into natural water bodies is an ongoing and serious threat to human health and natural water quality. Previous studies have detected high levels of these HOPs in the WWTP effluents. For example, the total concentrations of 6 HPs and 8 PBDEs were as high as 410 ng/L and 900 ng/L in the effluents from WWTPs in Seville, Spain and Marine, USA, respectively (Padilla-Sanchez et al., 2011; Anderson and MacRae, 2006). Hua et al. (2005) found only one tribromo-OH-PBDE congener in both WWTP effluents located on the Detroit River and nearby surface water. There has been no extensive description of all these HOPs in these studies, and the relationships among them are still not fully understood. Overall, relatively few measurements of these HOPs in effluents samples from WWTPs have been reported, especially for OH-PBDEs.

Therefore, the goal of the present study was to give a comprehensive characterization of the occurrence and levels of 6 HPs, 17 PBDEs congeners, as well as 11 OH-PBDEs (Figs. S1 and S2), in 12 conventional WWTPs from Dalian, North China. Dalian is a coastal city located near the Bohai Sea and the Huang Sea. The effluents from most of the WWTPs in Dalian were discharged into those two seas. Identification and quantification of these HOPs in the effluents of WWTPs are of great importance to an assessment of their ecological risks in the Huang-Bo sea basin. The congener profiles of these HPs, PBDEs and OH-PBDEs in the effluents were also analyzed. The relationships between the PBDEs and OH-PBDEs in these effluents were also evaluated. This study presents the first characterization of occurrence and profiles of HOPs in WWTP effluents, which can help us guide the risk assessment of HOPs.

2. Methods and materials

2.1. Standards and reagents

Six halogenated phenols (>99% purity), namely, 2,4-dibromophenol (2,4-DBP), 2,6-dibromophenol (2,6-DBP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-tribromophenol (2,4,6-TBP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP), were purchased from Acros Organics (New Jersey, USA). Eleven OH-PBDEs and seventeen PBDEs were selected in this study, namely, 4′-hydroxy-2,2′,4-tribromodiphenyl ether (4′-OH-BDE-17), 3′-hydroxy-2,4,4′-tribromodiphenyl ether (3′-OH-BDE-28), 4-hydroxy-2,2′,3,4′-tetrabromodiphenyl ether (4-OH-BDE-42), 3-hydroxy-2,2′,4,4′-tetrabromodiphenyl ether (3-OH-BDE-47), 5-hydroxy-2,2′,4,4′-tetrabromodiphenyl ether (5-OH-BDE-47), 6-hydroxy-2,2′,4,4′-tetrabromodiphenyl ether (6-OH-BDE-47), 4′-hydroxy-2,2′,4,5′-tetrabromodiphenyl ether (4′-OH-BDE-49), 6-hydroxy-2,2′,3,3′,4-pentabromodiphenyl ether (6-OH-BDE-82), 4-hydroxy-2,2′,3,4′,5-pentabromodiphenyl ether (4-OH-BDE-90), 5′-hydroxy-2,2′,4,4′,5-pentabromodiphenyl ether (5′-OH-BDE-99) and 3-hydroxy-2,2′,4,4′,5′,6-hexabromodiphenyl ether (3-OH-BDE-154), 2,2′,4, -tribromodiphenyl ether (BDE-17), 2,4,4′-tribromodiphenyl ether (BDE-28), 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), 2,3′,4,6′-tetrabromodiphenyl ether (BDE-71), 2,3′,4,4′-tetrabromodiphenyl ether (BDE-66), 2,2′,3,4,4′-tetrabromodiphenyl ether (BDE-85) 2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99), 2,2′,4,4′,6-pentabromodiphenyl ether (BDE-100), 2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE-153), 2,2′,4,4′,5,6′-hexabromodiphenyl ether (BDE-154), 2,2′,3,4,4′,5-heptabromodiphenyl ether (BDE-138), and 2,2′,3,4,4′,5,6′-heptabromodiphenyl ether (BDE-183), 2,3,3′,4,4′,5,6-heptabromodiphenyl ether (BDE-190), 2,2′,3,3′,4,4′5,5′,6-heptabromodiphenyl ether (BDE-206), 2,2′,3,3′,4,4′,5,6,6′-heptabromodiphenyl ether (BDE-207), 2,2′,3,3′,4,5,5′,6,6′-heptabromodiphenyl ether (BDE-208), and 2,2′,3,3′,4,4′,5,5′,6,6′-heptabromodiphenyl ether (BDE-209). These PBDEs and OH-PBDEs standards were all purchased from Sigma-Aldrich (USA). The structures of 11 OH-PBDE congeners and 17 PBDEs are shown in Fig. S1. The surrogate standards, decachlorobiphenyl (PCB-209) and 2-hydroxy-5-chlorobiphenyl (2-OH-5-Cl-PCB), were obtained from Sigma-Aldrich (USA), while the internal standard, 3,3′,4,4′-tetrabromodiphenyl ether (BDE-77), was purchased from Accustandard (USA). The derivatization reagent, pentafluorobenzoyl chloride (PFBCl), of analytical grade, was acquired from Acros Organics (Geel, Belgium). Diazomethane was synthesized in acetonitrile using *N*-nitroso-*N*-methylurea (Sigma-Aldrich, USA). 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from Sigma Chemical Co. (St. Louis, MO, USA). Hexane, acetonitrile, methanol, ethanol, acetone and dichloromethane (DCM) were all of HPLC grade and were acquired from Tedia Chemical (USA). Other chemicals used for the analysis included potassium hydroxide, potassium chloride, sodium chloride and concentrated hydrochloric acid (36.5%); all were of analytical grade and obtained from Kermel Chemical (China). Deionized water was produced by a HealForce system (HealForce, China). Stock solutions (40 ng/mL for OH-PBDEs and 25 ng/mL for PBDEs) were prepared in acetonitrile and stored at −20 °C.