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Mass loading and removal of benzotriazoles, benzothiazoles, benzophenones, and bisphenols in Indian sewage treatment plants

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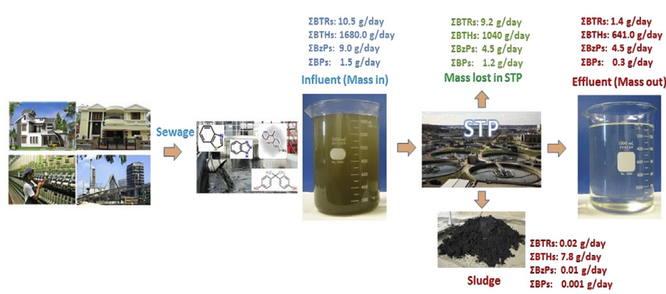
HIGHLIGHTS

- Mass loading and removal of 21 emerging contaminants were determined in Indian STPs.
- BTHs were found at the highest concentration, at 49,400 ng L^{-1} in influents and 50,200 ng g^{-1}, dry wt in sludge.
- Select benzophenone derivatives were measured in STPs for the first time.
- Removal efficiencies of the emerging chemicals in STPs ranged from 23.4 to 97%.

GRAPHICAL ABSTRACT



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ABSTRACT

Little is known about the occurrence of emerging environmental contaminants, such as benzotriazoles (BTRs), benzothiazoles (BTHs), benzophenones (BzPs), and bisphenol analogues (BPs) in India. In this study, we determined the occurrence and removal of BTRs, BTHs, BzPs, and BPs in five Indian sewage treatment plants (STPs). The respective measured mean concentrations ($N = 5$) in influents and effluents were 370 and 57.4 ng L^{-1} for BTRs, 50800 and 20200 ng L^{-1} for BTHs, 351 and 163 ng L^{-1} for BzPs, and 98.0 and 9.6 ng L^{-1} for BPs. Among the target chemicals analyzed, BTHs were found at elevated levels, and the measured levels were some of the highest ever reported in the literature. The mean concentrations ($N = 5$) of BTRs, BTHs, BzPs, and BPs in sludge were 44.2, 51200, 124, and 200 ng g^{-1} dry wt, respectively. The removal efficiencies for BTRs, BTHs, BzPs, and BPs ranged as follows: 54.2–85.6%, 23.4–85.0%, 51.8–71%, and 76.0–97.0%, respectively, and were comparable to those reported for other countries. Elevated concentrations of BTHs in Indian STPs can be related to consumption of these chemicals in a wide range of products including paper, textile and rubber materials.

1. Introduction

Studies on the occurrence and fate of chemicals of emerging concern, including pharmaceuticals, flame retardants, plasticizers, food additives, and preservatives, have received considerable

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attention in recent years. Following use, these chemicals are subsequently washed down the drain and reach municipal sewer systems. Monitoring of these chemicals in sewage treatment plants (STPs) provides valuable information on the chemicals' usage and discharge rates in a community. The use of STPs as chemical observatories to identify the chemicals of emerging concern has been proposed (Venkatesan and Halden, 2014). Among various chemicals of concern, attention has been paid to endocrine-disrupting chemicals (EDCs), such as bisphenols (BPs), benzophenones (BzPs), benzotriazoles (BTRs), benzothiazoles (BTHs), and phthalates (Froehner et al., 2011; Gago-Ferrero et al., 2011; Gani et al., 2016; Wang and Kannan, 2016; Zhang et al., 2011).

BTRs and BTHs are xenobiotics, widely used as corrosion inhibitors, photostabilizers, de-icing fluids, and vulcanizing agents in rubber production (Asimakopoulos et al., 2013; Fiehn et al., 1994; Kloepfer et al., 2005; Stasinakis et al., 2013; Wang et al., 2016). Studies have shown that BTHs are genotoxic (Yan et al., 2014; Hornung et al., 2015). A laboratory in vitro study showed that BTRs possess anti-estrogenic activity (Harris et al., 2007). BzPs are commonly used in personal care products (PCPs) to protect skin and hair from UV radiation, and 2-hydroxy-4-methoxybenzophenone (BP-3, or oxybenzone) is the major benzophenone used in PCPs. The derivatives/metabolites of BP-3, such as BP-1, BP-2, BP-3, BP-8, and 4OH-BP, have been reported to occur in the environment and human specimens (Kunisue et al., 2012; Louis et al., 2014; Negreira et al., 2009). BP-3 and their metabolites exhibit strong estrogenic potentials (Kim and Choi, 2014). BPs are widely used in the production of polycarbonate plastics and epoxy resins (Chen et al., 2016). The concern over widespread human exposure and associated health effects has led to regulations on the use of BPA in the USA and several European countries (Chen et al., 2016). The regulations on BPA promulgated the development of alternative substances, such as bisphenol S (BPS) and bisphenol F (BPF) (Liao et al., 2012; Rochester and Bolden, 2015). Very few studies, however, have documented the occurrence of BTHs, BTRs, BzPs, and BPs in STPs (Ekpeghere et al., 2016; Froehner et al., 2011; Gago-Ferrero et al., 2011; Liu et al., 2012; Song et al., 2014; Zhang et al., 2011). Further, studies on the occurrence and distribution of chemicals of emerging concern in India are scarce. Few studies have reported on the occurrence of antibiotics and other pharmaceuticals (Subedi et al., 2017; Mutiyar and Mittal, 2014; Singh et al., 2014), parabens (Karthikraj et al., 2017), and phthalate esters (Gani et al., 2016; Selvaraj et al., 2015) in Indian STPs. However, to the best of our knowledge, no earlier studies have reported on the occurrence and removal of BTRs, BTHs, BzPs, and BPs in STPs in India. In this study, we describe mass loading and removal of 21 chemicals that belong to four classes, namely, BTRs, BTHs, BzPs, and BPs, in five STPs from India.

2. Materials and methods

2.1. Chemicals and reagents

Four BTRs [benzotriazole, BTR; methyl benzotriazole, Me-BTR; 5,6-dimethyl benzotriazole, 5,6-DiMe BTR; and 5-chloro benzotriazole, 5-Cl BTR], three BTHs [benzothiazole, BTH; 2-hydroxybenzothiazole, 2-OH-BTH; and 2-(methylthio)benzothiazole, 2-MeS BTH], six BzPs [benzophenone, BzP; 2,4-dihydroxy benzophenone, BP1; 2,2,4,4′-tetra-hydroxybenzophenone, BP2; 2,2′-dihydroxy-4-methoxybenzophenone, BP8; 4-hydroxybenzo phenone, 4-OHBP; and 4-methyl benzophenone, 4-MeBP], and eight BPs, [2,2-bis(4-hydroxyphenyl) propane, BPA; 4,4′-sulfonyldiphenol, BPS; 4,4′-di-hydroxydiphenylmethane, BPF; 4,4′-(hexafluoroisopropylidene)-diphenol, BPAF; 4,4′-(1-phenylethylidene) bisphenol, BPAP; 4,4′-(1,4-phenylenediisopropylidene) bisphenol, BPP; 4,4′-cyclo-hexylidenebisphenol, BPZ; and 2,2-bis(4-hydroxyphenyl)butane, BPB] were analyzed in this study. The analytical standards of 5-Cl BTR, 2-MeS-BTH, BzPs, BPs, and D_4-BTR were purchased from Sigma Aldrich (St. Louis, MO, USA). BTR, BTH, and 2-OH-BTH were purchased from Alfa Aesar GmbH & Co., KG (Karlsruhe, Germany). Me-BTR and 5,6-DiMe-BTR were purchased from Acros Organics (Morris Plains, NJ, USA). D_4-BTH and D_6-Me-BTR were purchased from Toronto Research Chemicals (Toronto, Ontario, Canada) and Santa Cruz Biotechnology, Inc (Dallas, TX, USA), respectively. ^{13}C-labeled oxybenzone (2-OH-4-MeO-BP, ring $^{13}C_6$-BP3; 99%), $^{13}C_{12}$-BPA (99%), and $^{13}C_{12}$-BPS (98%) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Formic acid (98% v/v) and hydrochloric acid (HCl) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Ultra-pure water was obtained by a Milli-Q water purification system (Barnstead International; Dubuque, IA, USA).

2.2. Sample collection and extraction

Fifteen samples (five each of influent, effluent, and sludge) from five STPs and five raw sewage samples collected from sewerage channels (at the point of discharge from homes, before reaching STPs) at five locations in India were analyzed. Further details on the sampling locations and STPs are presented in Table S1. Grab samples (~250 mL each) were collected in summer (July through August 2012). All five STPs (Saidpur, SP_{STP}; Beur, BE_{STP}; Coimbatore, CO_{STP}; Udupi, UP_{STP}; and Manipal, MP_{STP}) mainly treated domestic discharges and used activated biological treatment processes. The combined sludge produced after primary and secondary treatments was collected from all STPs. Population served by each STP, wastewater inflow rate (MLD) and sludge production rate (tons/year, wet wt) were: 350,000, 19, 60.7 for SP_{STP}; 275,000, 20.9, 67 for BE_{STP}; 350,000, 22.5, 12 for CO_{STP}; 10,000, 2, not available for UP_{STP}; and 12,000, 2, not available for MP_{STP}. All samples were collected in certified, pre-cleaned 250 mL polypropylene bottles, shipped to the laboratory in Albany, New York, and stored in a freezer at −20 °C until extraction.

All four classes of target chemicals (BTRs, BTHs, BzPs, and BPs) were extracted by a solid-phase extraction (SPE) method with an Oasis MCX cartridge, as described earlier, with slight modifications (Wang and Kannan, 2016). Further details of sample extraction are provided in the supporting information.

2.3. Instrumental analysis

2.3.1. LC-ESI(+)MS/MS analysis of BTRs and BTHs

An electrospray triple quadrupole mass spectrometer (ESI-MS/MS; Applied Biosystems API 2000, Foster City, CA, USA) interfaced with an Agilent 1100 Series HPLC (Agilent Technologies Inc., Santa Clara, CA, USA) was used for the analysis of BTRs and BTHs in the positive ionization mode. An Agilent Zorbax SB-Aq column (2.1 mm × 150 mm, 3.5 μm; Santa Clara, CA, USA) was used for chromatographic separation of the target chemicals. The mobile phase gradient (A: acetonitrile and B: water that contains 0.4% acetic acid) was eluted at a flow rate of 300 μL min^{-1} and the detailed HPLC parameters have been described elsewhere (Asimakopoulos et al., 2013). The multiple reaction monitoring (MRM) transitions were optimized by the infusion of native and internal standards by use of a built-in Harvard syringe pump (Table S2). The ionization voltage was 4.5 kV. The curtain and collision gas (nitrogen) flow rates were 20 and 7 psi, respectively, and the source heater was set at 600 °C. The nebulizer gas (ion source gas 1) and the heater gas (ion source gas 2) were set at 45 and 60 psi, respectively. The data acquisition was set at a scan speed of 60 ms and at a resolving power of 0.70 FWHM.