



Occurrence and fate of parabens and their metabolites in five sewage treatment plants in India



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HIGHLIGHTS

- The mass loading and fate of parabens were studied in Indian sewage treatment plants.
- Parabens and their metabolites were found at elevated levels in Indian STPs.
- >80% of parabens and >28% of their metabolites were removed in Indian STPs.
- Sorption to particulates was a minor removal mechanism and degradation occurs in STPs.

GRAPHICAL ABSTRACT



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ABSTRACT

Parabens (*p*-hydroxy benzoic acid esters) are antimicrobial agents, used widely as preservatives in personal care products (PCPs), pharmaceuticals, foods, and beverages. PCPs that contain parabens are a major source of these chemicals in sewage treatment plants (STPs). Very few studies have demonstrated the occurrence of parabens in wastewater. In this study, the occurrence and fate of six parabens, methyl-(MeP), ethyl-(EtP), propyl-(PrP), butyl-(BuP), heptyl-(HpP) and benzyl-(BzP) parabens, and five of their metabolites (4-HB, 3,4-DHB, OH-MeP, OH-EtP and BA) were studied in five STPs in India. The concentrations of parent parabens (\sum_6 parent parabens) in five STPs ranged between 131 and 920 ng/L in influent; 16 and 67 ng/L in effluent; and 104 and 1090 ng/g, dry weight, in sludge samples. The sum concentrations of five paraben metabolites (\sum_5 paraben metabolites) in five STPs ranged between 4110 and 34,600 ng/L in influent; 2560 and 3800 ng/L in effluent; and 1220 and 35,900 ng/g, dry weight, in sludge samples. These values were higher than those reported for many industrialized countries. We calculated the mass loadings, removal efficiencies, and environmental emissions of parabens based on the measured concentrations in influents, effluents, and sludge. The mean removal efficiencies of parent parabens and their metabolites ranged from 80% to 100% and 28% to 76%, respectively.

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1. Introduction

Humans are exposed to several chemicals from the use of consumer products on a daily basis. Although the chemicals used in consumer products are intended for a desired purpose, some of them produce undesirable health effects following chronic, long-term exposures.

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Chemicals such as parabens are widely used in personal care products (PCPs) as antimicrobial preservatives (Liao et al., 2013b; Smarr et al., 2016; Sun et al., 2016). Parabens have been shown to possess estrogenic activities *in vitro* and *in vivo* (Darbre and Harvey, 2008; Smarr et al., 2016). Although the use and allowable concentrations of parabens in PCPs (0.4% by weight for individual parabens or 0.8% by weight for a mixture of parabens) are regulated, over 22,000 consumer products have been reported to contain these weakly estrogenic compounds (CIR, 2012). As a consequence, parabens are widely distributed in water, sediment, and soil as well as in human matrices, such as urine, blood, and adipose tissue (Bledzka et al., 2014; Brausch and Rand, 2011; CIR, 2012; Liao et al., 2013a; Moreta et al., 2015; Perez et al., 2012; Wang et al., 2015). Studies from Canada (Lee et al., 2005), the UK (Kasprzyk-Hordern et al., 2009), France (Gasperi et al., 2014), Hong Kong (Yu et al., 2012), and China (Sun et al., 2016) have demonstrated the occurrence of parabens in wastewater. A few studies have suggested that conventional sewage treatment plants (STPs) do not completely remove these chemicals from the water cycle (Garcia et al., 2014; Gonzalez-Marino et al., 2011; Li et al., 2015). Nevertheless, little is known about the fate of parabens in STPs, and earlier studies have not measured degradation products of parabens in wastewater and/or sludge, except for a recent study from the USA (Wang and Kannan, 2016). A report by the European Business and Technology Center indicated that only <20% of domestic and <60% of industrial wastewater are treated in India (http://ebtc.eu/pdf/111031_SNA_Snapshot_Water-and-waste-water-in-India.pdf). Another study reported that 38,354 million liters of sewage are produced in major cities in India daily, but the available capacity for treatment is only 11,786 million liters per day (http://www.ais.unwater.org/ais/pluginfile.php/356/mod_page/content/111/CountryReport_India.pdf). Thus, only 30% of the sewage produced in India is treated. Further, the operational efficiency of existing STPs to treat emerging environmental chemicals is not well understood. Studies have shown that populations in India are exposed to elevated concentrations of several toxic environmental chemicals (Guo et al., 2011; Liao et al., 2012; Xue et al., 2015). Evaluation of the sources and pathways of such chemicals in the environment is needed. In this study, we examined the occurrence and fate of parabens and their metabolites in samples collected from five STPs in India.

2. Materials and methods

2.1. Reagents and standards

The target analytes, methyl paraben (MeP), ethyl paraben (EtP), propyl paraben (PrP), butyl paraben (BuP), heptyl paraben (HpP), benzyl paraben (BzP), and 4-hydroxy benzoic acid (4-HB) were purchased from AccuStandard, Inc (New Haven, CT, USA). Methyl protocatechuate (OH-MeP), ethyl protocatechuate (OH-EtP), 3,4-dihydroxy benzoic acid (3,4-DHB), and benzoic acid (BA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). $^{13}\text{C}_{12}$ -MeP, $^{13}\text{C}_{12}$ -EtP, $^{13}\text{C}_{12}$ -PrP, $^{13}\text{C}_{12}$ -BuP, $^{13}\text{C}_{12}$ -HpP, $^{13}\text{C}_{12}$ -BzP, and $^{13}\text{C}_{12}$ -4-HB were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) for use as labeled internal standards (ISs). Formic acid (98.2%) was purchased from Sigma-Aldrich, and HPLC-grade methanol was purchased from Mallinckrodt Baker (Phillipsburg, NJ, USA). Milli-Q water was obtained by an ultrapure water system (Barnstead International; Dubuque, IA, USA).

2.2. Sample collection

Wastewater influent and effluent samples were collected from five STPs in India, Saidpur (SP_{STP}), Beur (BE_{STP}), Coimbatore (CO_{STP}), Udipi (UP_{STP}), and Manipal (MP_{STP}), during July and August 2012. SP_{STP} and BE_{STP} are located in northeastern India, whereas CO_{STP}, UP_{STP}, and MP_{STP} are located in southern India (Fig. S1). All STPs treat domestic waste and employ activated sludge treatment. The combined

aerobically digested sludge produced after primary and secondary treatments was collected from all STPs. Information with regard to the daily wastewater inflow, treatment capacity, population served by the STPs, and sludge production rate are given in Table 1. Grab samples were collected from these STPs. In addition to STP samples, raw sewage samples from open sewerage channels (prior to reaching STPs) near residential areas also were collected. All samples were collected in pre-cleaned 250 mL polypropylene (PP) bottles, shipped frozen to the laboratory in Albany, New York, USA, and stored in a freezer at $-20\text{ }^{\circ}\text{C}$ until analysis.

2.3. Sample preparation/extraction

All wastewater and raw sewage samples (50 mL) were centrifuged at $5000 \times g$ for 10 min, and the supernatant was filtered through a glass fiber filter (37 mm, pore size $1\ \mu\text{m}$; GE Osmonics, Inc., Minnetonka, MN, USA) to separate suspended particulate matter (SPM) from the aqueous fraction. A known concentration of a mixture of labeled ISs (20 to 40 ng/mL) was spiked and allowed to equilibrate for 30 min at room temperature. The SPM was transferred into a pre-weighed PP tube and spiked with the labeled IS mixture. The samples were extracted by solid-phase extraction with Oasis MCX $6\ \text{cm}^3$ (60 mg; Waters, Milford, MA, USA) cartridges. The cartridges were conditioned with 5 mL of methanol and 5 mL of Milli-Q water, and then the samples were loaded at a rate of $\sim 1\ \text{mL}/\text{min}$ and allowed to dry at room temperature for $\sim 30\ \text{min}$ under vacuum. After that, the cartridges were eluted with 10 mL of methanol. The eluents were concentrated to 1 mL under a gentle stream of nitrogen, using a TurboVap 110 evaporator (Zymark, Inc., Hopkinton, MA, USA). The concentrated sample extracts were transferred into glass vials, and $10\ \mu\text{L}$ was injected into high-performance liquid chromatography-tandem mass spectrometry.

All sludge samples were freeze-dried, and $\sim 100\ \text{mg}$ of the samples were spiked with 20 ng of labeled IS mixture, vortex mixed, and allowed to equilibrate for 30 min at room temperature. The sludge samples were extracted with 5 mL of methanol/water mixture (5:3 V/V) by shaking for 60 min in an orbital shaker and then centrifuged at $4500 \times g$ for 5 min (Eppendorf Centrifuge 5804; Hamburg, Germany). The extraction was repeated twice, and the supernatants were combined in a PP tube and concentrated to $\sim 3\ \text{mL}$ under a gentle stream of nitrogen. The final volume was adjusted to 10 mL with Milli-Q water that contained 0.2% formic acid (pH 2.5). The extract was passed through Oasis MCX $6\ \text{cm}^3$ cartridges as described above. For SPM, the pre-weighed glass fiber filter (obtained after centrifugation and filtration of 50 mL of influents, effluents, or raw sewage samples) was freeze-dried and spiked with labeled ISs. The further extraction procedure was similar to that described for the sludge samples above.

2.4. Instrumental analysis

The target analytes were determined by a Shimadzu Prominence™ Modular HPLC system (Shimadzu Corporation, Kyoto, Japan) coupled with an Applied Biosystems API 3200™ electrospray triple quadrupole mass spectrometer (ESI-MS/MS; Applied Biosystems) under the negative ion multiple reaction monitoring (MRM) mode. The MS/MS parameters were optimized by the infusion of individual compounds into the

Table 1
Characteristics of five Indian sewage treatment plants (STPs) studied.

STP	Inflow (capacity) MLD	Population served	Sludge production (tons/year, wet wt)
Saidpur (SP _{STP})	19 (45)	350,000	60.7
Beur (BE _{STP})	20.9 (35)	275,000	67.0
Manipal (MP _{STP})	2.0	12,000	NA
Udipi (UP _{STP})	2.0	10,000	NA
Coimbatore (CO _{STP})	22.5 (50)	350,000	12.0

NA = Information not available.

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