Science of the Total Environment 644 (2018) 754–761

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Concentrations and fate of parabens and their metabolites in two typical wastewater treatment plants in northeastern China

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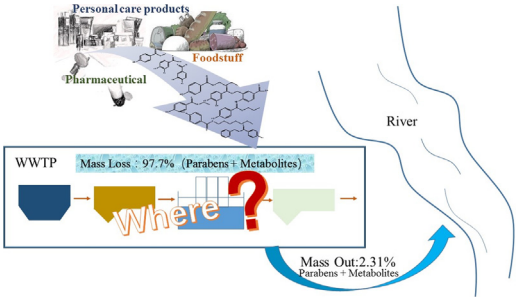
HIGHLIGHTS

- 6 parabens and 4 metabolites were studied in two typical sewage systems.
- Parabens and metabolites were frequently present in wastewater and sludge.
- The A/O and CAST treatment processes are both effective at removing parabens.
- Significant environmental emissions were observed in both effluent and sludge.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 April 2018
Received in revised form 28 June 2018
Accepted 28 June 2018
Available online xxxx

Editor: Jay Gan

Keywords:
Parabens
Metabolites
Wastewater treatment plant
Occurrence
Fate

ABSTRACT

Parabens are widely used in food, pharmaceuticals, and personal care products because they are excellent preservatives. Recently, the environmental fate of parabens has attracted attention owing to their similarity to some endocrine disrupters. Wastewater treatment plants (WWTPs) are both important sinks of parabens discharged from our daily activities and key pollution sources for the environment if the parabens are not completely removed. However, research in this area is scarce, especially in Asia. In this study, 6 commonly used parabens and 4 metabolites were analyzed in wastewater and sludge samples from two typical WWTPs with different treatment processes (the anaerobic-oxic (A/O) and cyclic activated sludge technology (CAST) treatment processes). The average concentrations of parabens in the A/O and CAST treatment processes were 1510 ng/L and 2180 ng/L, respectively, in the influent, and 70.5 ng/L and 19.7 ng/L, respectively, in the effluent. The paraben removal efficiencies in the A/O treatment process were between 56.8% and 100%, which is lower than the efficiencies for the CAST treatment process (97.7% to 100%). The average concentrations of metabolites in the A/O treatment process, which were much higher than paraben concentrations, were 35,200 ng/L in the influent, 334 ng/L in the effluent, and 146 ng/g in the sludge samples. The removal efficiencies for the 4 metabolites were >92% for the A/O treatment process. In total, for the A/O treatment process, 5.07 kg and 16.8 kg of parabens, and 24.4 kg and 16.0 kg of metabolites, were discharged into the environment annually via effluent and sludge, respectively. Overall, the results of this study indicate that the A/O and CAST treatment processes are both effective at removing parabens and their metabolites.

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https://doi.org/10.1016/j.scitotenv.2018.06.358
0048-9697/

1. Introduction

The alkyl esters of *p*-hydroxybenzoic (parabens) are widely used as preservatives in food, pharmaceuticals, and cosmetics/personal care products (Alan, 2008; Dodge et al., 2015; Liao et al., 2013a). Methyl- (MeP), ethyl- (EtP), propyl- (PrP), butyl- (BuP), benzyl- (BzP), and heptyl-parabens (HepP) are used in common day-to-day products. Owing to their antimicrobial properties and high stability, paraben use has a long and global history. For example, fifty years ago, the USA Food and Drug Administration allowed the use of parabens as preservatives in foodstuffs and cosmetics. In China, the use of parabens in food and cosmetic products is also permitted. According to the Chinese Standard for the Use of Food Additives (GB2760-2014), the use of sodium methyl *p*-hydroxybenzoate, EtP, and sodium ethyl *p*-hydroxybenzoate in food is permitted. According to the Chinese Safety and Technical Standards for Cosmetics (Version 2015), MeP, EtP, PrP, BuP, and their salts may be used in cosmetic production. In production, two and/or several parabens are often used together to enhance the antibacterial effect (Chen et al., 2008).

However, recently both in vitro and in vivo studies have shown that parabens have estrogenic effects (Byford et al., 2002; Darbre et al., 2004; Darbre et al., 2003; Darbre et al., 2002; Lemini et al., 2003; Okubo et al., 2001; Pugazhendhi et al., 2005), and the safety of their use in day-to-day products and in the environment has become a public concern (Boberg et al., 2010). Parabens can degrade into their metabolites under certain conditions. Methyl protocatechuate (OH-MeP) and ethyl protocatechuate (OH-EtP) are metabolites of the corresponding parabens produced via hydroxylation processes (Guengerich, 2001; Tay et al., 2010). 4-hydroxybenzoic acid (4-HB) is the major common metabolite of all parabens (Abbas et al., 2010; Boberg et al., 2010; Lin et al., 2011; Tay et al., 2010; Wang et al., 2013), but 4-HB has estrogenic properties, which may have toxicity and autotoxicity effects on plant growth and development (Cecchi et al., 2004). In addition, hydroxylation of 4-HB to 3,4-dihydroxybenzoic acid (3,4-DHB) has also been reported in studies of laboratory animals (Abbas et al., 2010; Boberg et al., 2010; Guengerich, 2001; Liu et al., 2002; Ste-Marie et al., 1999). Furthermore, a study has shown that 3,4-DHB is associated with obesity (Xue et al., 2015).

Parabens and their metabolites are widely found in our day-to-day products (e.g., food, pharmaceuticals, and cosmetics) (Guo et al., 2014; Liao et al., 2013c; Ma et al., 2016), environmental matrix (e.g., indoor dust, sewage, sludge, and river water) (Lee et al., 2005; Li et al., 2015; Liao et al., 2013b; Peng et al., 2008; Tran et al., 2016), and human fluids and tissues (e.g., urine, serum, fat, placental tissue, and breast tumors) (Alan, 2008; Calafat et al., 2010; Frederiksen et al., 2011; Ma et al., 2013; Sandanger et al., 2011; Wang et al., 2015; Xue et al., 2015). Generally, parabens and their metabolites are eventually collected at wastewater treatment plants (WWTPs), which are considered an important sink for these compounds. Furthermore, if parabens are not completely removed in WWTPs, the outflowing effluent and sludge should be considered important point sources for the environment. The fate and removal characteristics of parabens and their metabolites in WWTPs have recently attracted increasing attention. A few studies have investigated parabens in WWTPs (Karthikraj et al., 2017; Kasprzyk-Hordern et al., 2009; Lee et al., 2005; Li et al., 2015; Sun et al., 2016; Wang and Kannan, 2016; Yu et al., 2011), but only two studies from the USA (Wang and Kannan, 2016) and India (Karthikraj et al., 2017) have reported on the occurrence and fate of both parabens and their metabolites. Little is known about the fate of parabens and their metabolites in individual treatment units, which is crucial to understanding the detailed pathway of parabens in WWTPs.

In this study, 6 parabens and 4 metabolites were analyzed in wastewater and sludge samples collected from two typical WWTPs (an industrial and a domestic wastewater treatment plant) in Harbin City, northeastern China. The objectives of this study were (1) to investigate the occurrence and removal efficiency of parabens and their metabolites in typical WWTPs; (2) to compare results for two typical wastewater treatment processes; and (3) to study the fate of parabens and their metabolites in WWTPs based on mass loading and environmental emissions.

2. Experimental methods

2.1. Reagents and standards

Standard solutions (100 μg/mL, purity >99%) of 6 parabens and 4 metabolites, including MeP, EtP, PrP, BuP, BzP, HepP, 4-HB, OH-MeP, OH-EtP, and 3,4-DHB, were purchased from AccuStandard (New Haven, CT, USA). Internal standard solutions (100 μg/mL, purity >99%), including $^{13}C_6$-MeP, $^{13}C_6$-EtP, $^{13}C_6$-PrP, and $^{13}C_6$-BuP, were also purchased from AccuStandard. The physicochemical properties and molecular structure of the target compounds are presented in Table S1 (Supporting Information). HPLC-grade methanol, dichloromethane, and other organic solvents were all purchased from JT Baker (Phillisburg, NJ, USA). Ultrapure water was prepared using a Milli-Q ultrapure system (Thermo Scientific, USA). All the standards and stock solutions were stored at −20 °C before analysis.

2.2. Sample collection

Detailed information on the two WWTPs used in this study is presented in Table S2. The two plants are denoted as WWTP 1 and WWTP 2 in this paper. An anaerobic-oxic treatment process (A/O, primary + secondary biological treatment by an activated sludge process) and a cyclic activated sludge technology–hydrolytic acidification treatment process (CAST, hydrolytic acidification + cyclic activated sludge technology + ultraviolet disinfection) were applied in WWTP 1 and WWTP 2, respectively. The locations of the wastewater sampling sites are presented in Fig. S1. To obtain the representative data for parabens, wastewater samples were collected from the two WWTPs for two programs, one in October 2016 and one in January 2017. The average concentration of the two sampling programs was used to interpret the results of Section 3.1. Wastewater samples from each treatment unit were collected based on hydraulic retention time (HRT). Briefly, the four wastewater samples were collected using 1 L brown glass bottles in the HRT period; these samples were then uniformly mixed to provide one sample for each treatment process unit. To study the fate of the parabens and metabolites (Sections 3.2 and 3.3), wastewater samples from the influent, aerobic tank, and secondary tank in the A/O treatment process were collected, based on the HRT, in March 2017. The sampling method for the wastewater samples was same as that described above. Concurrently, sludge samples were also collected. Sludge samples were collected from the sludge dewatering tank, the final endpoint for all the WWTP sludge, using a stainless steel jar. All the collected wastewater samples were stored in a refrigerator at 4 °C until extraction. Sludge samples were sealed in aluminum bottles and kept at −20 °C until extraction.

2.3. Sample treatment

The wastewater samples (100 mL for effluent, 20 mL for other wastewater samples) were diluted to 800 mL with ultrapure water, spiked with internal standards (50 ng for each compound) prior to extraction, and allowed to equilibrate for 30 min at room temperature. For parabens, the samples were extracted using a solid-phase extraction method with Oasis HLB cartridges (6 cm^3, 500 mg; Waters, Milford, MA, USA). The cartridges were preconditioned with 6 mL dichloromethane, 6 mL methanol, and 6 mL ultrapure water under gravity (c. 1 mL/min), and the samples were the passed through the cartridge at c. 1 mL/min. Cartridges were allowed to dry for 40 min under a vacuum and then eluted with 7 mL methanol and 7 mL dichloromethane. For metabolites, the samples were extracted using a solid-phase extraction method with