Science of the Total Environment 593–594 (2017) 368–374

Contents lists available at ScienceDirect

Science of the Total Environment

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

Occurrence, temporal variation, and estrogenic burden of five parabens in sewage sludge collected across the United States

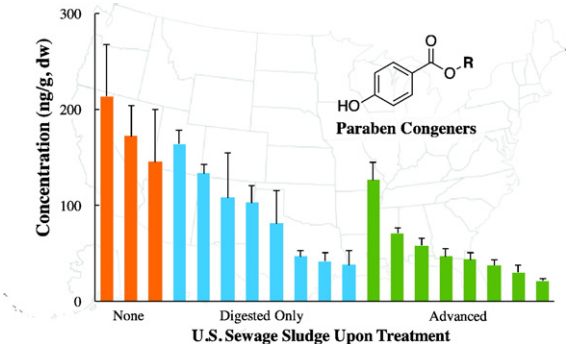
Jing Chen [a], Benny F.G. Pycke [a], Bruce J. Brownawell [b], Chad A. Kinney [c], Edward T. Furlong [d], Dana W. Kolpin [e], Rolf U. Halden [a,*]

[a] Biodesign Center for Environmental Security, Biodesign Institute, School of Sustainable Engineering and the Built Environment, Arizona State University, 781 E. Terrace Mall, Tempe, AZ 85287, United States
[b] School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, NY 11794-5000, United States
[c] Chemistry Department, Colorado State University-Pueblo, 2200 Bonforte Blvd., Pueblo, CO 81001, United States
[d] U.S. Geological Survey, Denver Federal Center, P.O. Box 25585, Denver, CO 80225, United States
[e] U.S. Geological Survey, 400 S. Clinton Street, Iowa City, IA 52240, United States

HIGHLIGHTS

- First multi-state survey of U.S. sludges indicates ubiquity of parabens.
- Paraben levels in U.S. sewage sludge differ by treatment and season.
- Estrogenic burden posed by parabens in U.S. sludge is low.
- Natural estrogens in sludge pose >10,000× higher risk than parabens.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 January 2017
Received in revised form 16 March 2017
Accepted 18 March 2017
Available online 27 March 2017

Editor: D. Barcelo

Keywords:
Paraben
Wastewater treatment plants (WWTPs)
Estrogenic potential
Sludge

ABSTRACT

Five parabens used as preservatives in pharmaceuticals and personal care products (PPCPs) were measured in sewage sludges collected at 14 U.S. wastewater treatment plants (WWTPs) located in nine states. Detected concentration ranges (ng/g, dry weight) and frequencies were as follows: methyl paraben (15.9 to 203.0; 100%), propyl paraben (0.5 to 7.7; 100%), ethyl paraben (<0.6 to 2.6; 63%), butyl paraben (<0.4 to 4.3; 42%) and benzyl paraben (<0.4 to 3.3; 26%). The estrogenicity inherent to the sum of parabens detected in sewage sludge (ranging from 10.1 to 500.1 pg/kg 17β-estradiol equivalents) was insignificant when compared to the 10^6-times higher value calculated for natural estrogens reported in the literature to occur in sewage sludge. Temporal monitoring at one WWTP provided insights into temporal and seasonal variations in paraben concentrations. This is the first report on the occurrence of five parabens in sewage sludges from across the U.S., and internationally, the first on temporal variations of paraben levels in sewage sludge. Study results will help to inform the risk assessment of sewage sludge destined for land application (biosolids).

* Corresponding author at: 781 E. Terrace Mall, Tempe, AZ 85287-5904, United States.
E-mail address: rolf.halden@asu.edu (R.U. Halden).

http://dx.doi.org/10.1016/j.scitotenv.2017.03.162
0048-9697/

1. Introduction

Parabens are a group of compounds that have been extensively used as preservatives in pharmaceutical and personal care products (PPCPs), food, beverages, and industrial products, due to their broad spectrum of antimicrobial activity, good stability over a wide pH range, and moderate solubility (Bledzka et al., 2014). Recently there has been an increase in the concern over the potential risks of parabens on human and animal health (Soni et al., 2005). Parabens are considered to represent a group of emerging endocrine disruptors that cause immune dysfunctions and affect human reproductive outcomes (Tavares et al., 2009; Routledge et al., 1998; Boberg et al., 2010; Smith et al., 2013). Potential links have been suggested between parabens and breast cancer etiology (Darbre et al., 2004; Darbre and Harvey, 2014; Charles and Darbre, 2013). Furthermore, studies have shown parabens to be toxic to aquatic organisms, such as algae, fish and invertebrate (Brausch and Rand, 2011; Terasaki et al., 2015; Yamamoto et al., 2011; Madsen et al., 2001). With the continuing debate and ongoing study on the safety of parabens, monitoring of parabens in the environment is important for effective assessment and management of ecological risks.

Widespread use of parabens has led to their ubiquitous presence in various environmental matrices, including wastewater, surface water, soil, sediments, sewage sludge and indoor dust (Fan et al., 2010; Gonzalez-Marino et al., 2011; Wang et al., 2012; Liao et al., 2013; Hartmann et al., 2016; Sun et al., 2016) as well as biological matrices including human urine (Calafat et al., 2010), serum, cord blood (Pycke et al., 2015), breast tissues (Shanmugam et al., 2010), placenta (Jimenez-Diaz et al., 2011) and amniotic fluid (Philippat et al., 2013). The most commonly used parabens in commercial products include methyl paraben (MePB), ethyl paraben (EtPB), propyl paraben (PrPB), butyl paraben (BuPB) and benzyl paraben (BePB). As parabens are mainly used in PPCPs, they are continuously released into domestic and industrial wastewater and conveyed through the sewer system to wastewater treatment plants (WWTPs) (Haman et al., 2015). Although over 90% of parabens can be effectively removed during conventional wastewater treatment in which biodegradation plays a significant role, ng/L levels of parabens are known to remain detectable in treated wastewater (Bledzka et al., 2014). One study reported the total concentration of six parabens including MePB, EtPB, PrPB, BuPB, BePB and HePB (heptyl paraben) to range from 1.08 to 7.93 ng/L in the final effluent from two WWTPs in Albany, NY, representing 1.57–8.03% of the mass loading (Wang and Kannan, 2016). During conventional treatment, a fraction of the paraben load can be removed by sorption to sewage sludge. In an advanced WWTP, 91.8% of initial parabens mass loading was lost mainly due to degradation, while the contribution of sorption and output of primary and excess sludge was about 7.5% (Li et al., 2015). Since environmental monitoring studies have focused mainly on the aqueous phase (dissolved parabens), only a limited number of studies are available on the presence of parabens in sewage sludge. However, monitoring of parabens in sludge is important for both ecological and human health risk assessments (Venkatesan and Halden, 2014). Treated sewage sludge is being recycled in many countries via application on land, and current sludge disposal practices can lead to contamination of soil, groundwater and surface water in susceptible settings (Venkatesan and Halden, 2013). Thus, the potential effect of such practices on soil and water from paraben contamination needs to be evaluated. There have been few studies worldwide on the occurrence of parabens in sewage sludge (Li et al., 2015; Albero et al., 2012; Viglino et al., 2011; Yu et al., 2011), and only one such study in the U.S. from two WWTPs in the Albany area of New York State (Wang and Kannan, 2016). Thus, additional studies are necessary to understand the temporal and spatial variations of parabens in sewage sludge.

The goal of the present study was to address this knowledge gap by determining: 1) the variation of parabens in U.S. sewage sludge from 14 WWTPs located in nine U.S. states; 2) the temporal variations in paraben concentrations in sewage sludge over the course of a year at one WWTP; and 3) the estrogenic potency contributed by parabens in sewage sludge relative to levels of co-occurring estrogens.

2. Methods

2.1. Chemicals and reagents

Methylparaben (MePB) was purchased from Aldrich (Sigma-Aldrich, St. Louis, MO), and $^{13}C_6$-MePB (99%) were obtained from Cambridge Isotope Laboratories (Andover, MA). Ethylparaben (EtPB), propylparaben (PrPB), butylparaben (BuPB), and benzylparaben (BePB) were purchased from RT Corp (Laramie, WY) (Supporting Information, SI, Table S1), and their deuterated standards (d_5-EtPB, d_4-PrPB, d_4-BuPB) were purchased from C/D/N Isotopes (Quebec, Canada). LC-MS-grade (99%) methanol, water, and acetic acid were obtained from Fluka and LC-MS-grade acetone was obtained from Sigma-Aldrich (St. Louis, MO). Individual stock solutions of the native and isotopically-labeled compounds were prepared in methanol. The working standards were prepared by serial dilution of stock solutions with methanol prior to use. All stock solutions were stored in glass vials with polytetrafluoroethylene septa at −20 °C. All glassware was washed with detergent, rinsed with ultrapure water and heated at 550 °C for 4 h prior to use.

2.2. Sewage sludge samples

Sludge samples were collected at 14 sludge-processing facilities located in nine states (Arizona, Indiana, Florida, Maryland, Montana, New York, Texas, Wisconsin, and Vermont), with an additional commercially available product (A3) from another plant purchased at a nationwide retail store. We relied on cooperation with WWTPs and U.S. Geological Survey (USGS) employees to provide the samples studied, which were provided based on condition of nondisclosure of their identity and exact geographic location. Basic information about the WWTP operations is provided in SI (Table S2). Locations of WWTPs were named from A to N, and each sample was named using the same ID as the plant, except where multiple samples were taken, then numbers were assigned after plant ID.

The facilities sampled in this study treated a broad range of wastewater flows (<10 to >150 million L of wastewater per day) and employed a variety of sludge treatment strategies. In the U.S., treated sewage sludge destined for application on land is categorized into Class A and Class B biosolids based on the pathogen reduction criteria described by the United States Environmental Protection Agency (USEPA) (40 CFR Part 503). Class A biosolids contain no detectible levels of pathogens and can be sold or given away in a bag, or to be applied to land, lawn, and home gardens, whereas Class B biosolids are highly treated but may still contain low levels of pathogens (Walker et al., 1994). Samples in this study included untreated sludge, Class B biosolids with many of them being subjected to anaerobic digestion, and Class A biosolids prepared using one or two additional treatments (dewatering, extended storage and composting) after digestion. One or two types of sludge from each site were sampled once between March and June of 2009, with additional samples collected ($n = 18$) in plant A between March 25, 2009 and April 7, 2010 for the temporal study. The samples were collected as discrete units, then frozen after sampling, thawed, subsampled, shipped to Arizona State University on dry ice in glass jars with polytetrafluoroethylene septa, stored at −80 °C, and homogenized prior to extraction.

2.3. Sample preparation

Sludge samples were oven dried at 60 °C for 24 h, and then about 100 mg dried sewage sludge was weighed and transferred into a 15-mL polypropylene conical tube. Ten nanograms of $^{13}C_6$-MePB, d_5-EtPB, d_4-PrPB, and d_4-BuPB were spiked as internal standard. The sludge