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Occurrence and estrogenic potency of eight bisphenol analogs in sewage sludge from the U.S. EPA targeted national sewage sludge survey

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HIGHLIGHTS

- BPA, BPS and BPF were determined in 76 sewage sludge from the USA.
- Bisphenols were found at concentrations ranging from 12.8 to 4730 ng/g dw in sludge.
- Only 0.02% of the total BPA production volume was emitted through sludge disposal.
- The estrogenic activity of BPA was lower than that of natural estrogens in sludge.

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ABSTRACT

As health concerns over bisphenol A (BPA) in consumer products are mounting, this weak estrogen mimicking compound is gradually being replaced with structural analogs, whose environmental occurrence and estrogen risks are not well understood yet. We used high performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) to determine the concentrations of eight bisphenol analogs in 76 sewage sludge samples collected by the U.S. Environmental Protection Agency (EPA) in 2006/2007 from 74 wastewater treatment plants (WWTPs) in 35 states. Bisphenols were detected at the following concentration ranges (ng/g dry weight) and detection frequencies: BPA (6.5–4700; 100%); bisphenol S (BPS; <1.79–1480; 84%); bisphenol F (BPF; <1.79–242; 68%); bisphenol AF (BPAF; <1.79–72.2; 46%); bisphenol P (BPP; <1.79–6.42; <5%), bisphenol B (BPB; <1.79–5.60; <5%), and bisphenol Z (BPZ; <1.79––66.7; <5%). Bisphenol AP (BPAP) was not detected in any of the samples (<1.79 ng/g dw). Concentrations of BPA in sewage sludge were an order of magnitude higher than those reported in China but similar to those in Germany. The calculated 17β-estradiol equivalents (E_2EQ) of bisphenols present in sludge samples were 7.74 (0.26–90.5) pg/g dw, which were three orders of magnitude lower than the estrogenic activity contributed by natural estrogens present in the sludge. The calculated mass loading of bisphenols through the disposal of sludge and wastewater was <0.02% of the total U.S. production. As the usage of BPA is expected to decline further, environmental emissions of BPS, BPF, and BPAF are likely to increase in the future. This study establishes baseline levels and estrogenic activity of diverse bisphenol analogs in sewage sludge.

1. Introduction

Bisphenol analogs (hereafter 'bisphenols') are a class of chemicals with two para-hydroxyphenyl functional groups, with bisphenol A (BPA) as the prototype compound. Bisphenols are

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widely used in industrial and commercial applications including inner coating of food cans, dental sealants, electronic equipment, thermal papers, and polycarbonate plastics [1,2]. As the concern over the safety of BPA continues to grow, this compound is gradually replaced with other analogs, such as bisphenol F (BPF) and bisphenol S (BPS), which are structurally similar to BPA [3], in many applications. BPA, BPS, and BPF have been shown to be toxic in many laboratory animal studies, and most notably, these compounds elicit weak estrogenic activities [4–9]. Human exposure to BPA has been linked to endocrine disorders and obesity [10,11].

Bisphenols have been frequently found in consumer products such as thermal receipt papers [3], currency bills [3,12], personal care products [13], foodstuffs, and polycarbonate plastic bottles [5,14–16]. Sources and pathways of human exposure to BPA have been widely studied. The occurrence of BPA in blood, urine, breast milk, placenta, and hair has been reported in many countries [5,17–21]. Studies have also reported the occurrence of BPA in environmental matrices such as air, water, soil, sediment, sewage sludge (SS) and indoor dust [18,22,23]. However, very few studies have reported the occurrence of bisphenols other than BPA in environmental matrices [23,24].

Several studies have reported the occurrence and fate of BPA in wastewater treatment processes. The removal efficiency of BPA in wastewater treatment varies widely, from 1% to 77%, and a considerable fraction of BPA is sorbed to sludge and the sorption is influenced by the degree of nitrification and hydraulic retention time [25]. Sewage sludge can be a good matrix for monitoring environmental contaminants, as this can reflect the usage pattern of many chemicals derived from domestic and industrial activities [26]. Sewage sludge, as defined by the U.S. Environmental Protection Agency (EPA), is nutrient-rich organic residuals that when treated and processed, may be recycled and applied as fertilizer [27]. Land-application of SS is an inexpensive option for disposal and can provide valuable nutrients to the soil, which may enhance soil properties and plant yield [28]. In 2004, approximately 50–60% of 6.5 million tons (dry weight) of municipal SS produced in the U.S. was land-applied [29]. While land-applied SS offers a source of rich nutrients, they can also release pollutants that become sequestered into the terrestrial food chain or leached into groundwater [30,31]. A few studies have reported the occurrence of artificial sweeteners, pharmaceuticals, and illicit drugs in agricultural soils following the land application of SS [32–34]. The EPA initiated the Targeted National Sewage Sludge Survey (TNSSS) in the mid-2000s to characterize pollutants that may be present in SS generated by the nation's publicly owned treatment works (POTWs) to develop regulations on the use or disposal of SS [35]. In that study, SS samples were collected from 74 POTWs that employ secondary treatment or better in 2006/2007 [35]. Several pollutants have been analyzed in these samples and the results have been published [29,36–39]. However, no earlier study has reported the occurrence of bisphenols in SS from nationally representative samples. The aims of the present study were to investigate the occurrence and profiles of bisphenols in SS samples, and to estimate the mass loading of bisphenols through the application of SS to land. The estrogenic activity contributed by several bisphenols in SS was calculated using the reported estrogenic potency values. We analyzed eight bisphenols, including BPA, BPF, BPS, 4,4-(hexafluoroisopropylidene)-diphenol (BPAF), 2,2-bis(4-hydroxyphenyl) butane (BPB), 4,4′-cyclo-hexylidenebisphenol (BPZ), 4,4′-(1,4-phenylenediisopropylidene) bisphenol (BPP), and 4,4-(1-phenylethylidene) bisphenol (BPAP) in 76 archived SS samples collected by the EPA in 2006/2007 using high performance liquid chromatography-tandem mass spectrometry (HPLC–MS/MS).

2. Materials and methods

2.1. Standards and reagents

Analytical standards of 2,2-bis(4-hydroxyphenyl) propane (BPA; purity ≥97%), BPAF (∼97%), BPAP (∼99%), 4,4-sulfonyldiphenol (BPS; ∼98%), BPP (∼99%), BPZ (∼98%), and 4,4′-dihydroxydiphenylmethane (BPF; ∼98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Analytical standard of BPB (∼98%) was obtained from TCI America (Portland, OR, USA). $^{13}C_{12}$-BPA was purchased from Cambridge Isotope Laboratories (≥99%; Andover, MA, USA). Formic acid (98.2%) was from Sigma–Aldrich, and HPLC-grade methanol was from Mallinckrodt Baker (Phillipsburg, NJ, USA). Milli-Q water (18.2 MΩ) was prepared from an ultrapure water purification system (Barnstead International, Dubuque, IA, USA). Stock solutions of bisphenols and $^{13}C_{12}$-BPA were prepared at 1 mg/mL in methanol and stored at −20 °C.

2.2. Sample collection

A total of 76 sewage sludge samples were collected by the EPA from 74 POTWs in 35 states that are representative of the nation's 3337 POTWs during August 2006 and March 2007. The selection criteria for POTWs and sampling procedure were provided in detail in the sampling and analysis technical report [35]. Briefly, each POTW in full operation in 2002 and/or 2004, and treated more than 1 million gallons per day (MGD), with secondary or better treatment was selected. Two samples were collected at ten POTWs, either because the facility had more than one treatment system and produced two types of final SS, or for quality assurance purposes, as well as one single grab sample at the remaining 64 facilities (Table S1). After the completion of TNSSS, the samples were acquired by the Halden Laboratory and archived at −20 °C as part of the Human Health Observatory (H2O) and national sewage sludge repository (NSSR) at Arizona State University [36]. Eight samples were either missing or broken during shipment and handling. A total of 76 samples were shipped in glass jars to Wadsworth Center, New York State Department of Health, Albany, New York, and were stored at −20 °C until chemical analysis.

2.3. Sample preparation

Sewage sludge samples were freeze-dried using a freeze drier (Labconco, Kansas City, MO, USA). Sludge extraction and cleanup procedures were similar to those previously reported, with minor modifications [23]. Briefly, freeze–dried sample (0.1–0.2 g) was spiked with 20 ng of $^{13}C_{12}$-BPA and extracted with 5 mL of methanol/water mixture (5:3, v/v) by shaking in an orbital shaker (Eberbach, Ann Arbor, MI, USA) at 250 oscillations/min for 30 min. After centrifugation at 4800 × *g* for 5 min (Eppendorf Centrifuge 5804, Hamburg, Germany), the supernatant was transferred into a 15 mL glass tube. The extraction was repeated twice, and the extracts were combined and concentrated to ∼4 mL under a gentle stream of nitrogen. After dilution to 10 mL with 0.2% formic acid (pH 2.5), the extract was purified with an Oasis MCX cartridge (60 mg/3 cm^3; Waters, Milford, MA, USA). The cartridge was preconditioned with 5 mL of methanol and 5 mL of water. After loading the sample, the cartridge was washed with 15 mL of 25% methanol in water and 5 mL of water, and then eluted with 5 mL of methanol. The eluate was transferred into a vial and vortex mixed before HPLC-MS/MS analysis.