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House crickets can accumulate polybrominated diphenyl ethers (PBDEs) directly from polyurethane foam common in consumer products

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ABSTRACT

Polybrominated diphenyl ether (PBDE) flame retardants are added at percent levels to many polymers and textiles abundant in human spaces and vehicles, wherein they have been long assumed to be tightly sequestered. However, the mg kg^{-1} burdens recently detected in indoor dust testify to substantial releases. The bulk of released PBDEs remain in the terrestrial environment, yet comparatively little research focuses on this compartment. There, insects/arthropods, such as crickets, are the most abundant invertebrate organisms and facilitate the trophic transfer of contaminants by breaking down complex organic matter (including discarded polymers) and serving as food for other organisms. Our experiments revealed that house crickets (*Acheta domesticus*) provided uncontaminated food and free access to PUF containing Penta-BDE (8.7% dry wt) for 28 d accumulated substantial PBDE body burdens. Crickets allowed to depurate gut contents exhibited whole body burdens of up to 13.4 mg kg^{-1} lipid ΣPenta-BDE, 1000-fold higher than typically reported in humans. Non-depurated crickets and molted exoskeletons incurred even higher ΣPenta-BDE, up to 80.6 and 63.3 mg kg^{-1} lipid, respectively. Congener patterns of whole crickets and molts resembled those of PUF and the commercial Penta-BDE formulation, DE-71, indicative of minimal discrimination or biotransformation. Accumulation factor (AF) calculations were hampered by uncertainties in determining actual PUF ingestion. However, estimated AFs were low, in the range of 10^{-4}–10^{-3}, suggesting that polymer–PBDE interactions limited uptake. Nonetheless, results indicate that substantial PBDE burdens may be incurred by insects in contact with current-use and derelict treated polymers within human spaces and solid waste disposal sites (e.g. landfills, automotive dumps, etc.). Once ingested, even burdens not absorbed across the gut wall may be dispersed within proximate terrestrial food webs via the insect's movements and/or predation.

1. Introduction

Concerns have increased about the accumulation of plastics in the environment. In 2009 alone, 28 million tons of plastics entered the US environment via municipal solid waste (US EPA, http://www.epa.gov/osw/nonhaz/municipal/msw99.htm). In addition, immense "garbage patches" have been discovered in the major oceanic gyres (Rios et al., 2010). With respect to biological impacts, greatest attention has focused on physical entanglement or digestive blockages due to ingestion of discarded plastics by mammals and birds (Ryan et al., 1988). Hydrophobic plastics can also concentrate persistent organic pollutants (POPs) from ambient air and water and the toxicological implications of these sorbed residues have received recent scrutiny (Teuten et al., 2007, 2009; Rios et al., 2010). However, their levels are orders of magnitude lower than those of intentional polymer additives.

Polybrominated diphenyl ethers (PBDEs) have been widely used to flame retard consumer plastics. Of the three commercial PBDE mixtures, Penta-BDE is the most bioaccumulative and toxic and has been listed as a POP under the Stockholm Convention (http://chm.pops.int/default.aspx). Penta-BDE has been used primarily to flame retard polyurethane foam (PUF) products. About 5.5×10^8 kg of PUF is produced annually for furniture cushioning in the US (Alliance for Flexible Polyurethane Foam, 2011). Another 2.3×10^8 kg is used for carpet underlayment in the automotive sector and in other applications (Alcock et al., 2003; Polyurethane Foam Association, 2011). After usage, most PUF products end up in landfills and automotive dumpsites, etc. PUF products are also illegally discarded alongside roads and highways in some rural environments (Matthews County, VA Board of Supervisors Personal Communication). Soil insect abundance and activity is typically high in such waste disposal environments (Robinson, 2005) increasing opportunities for interaction with derelict consumer products and exposure to chemical additives therein. US manufacturers have added percent levels of Penta-BDE to PUF to meet state-mandated

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flame retardancy standards. As PBDEs were not chemically reacted with the polymer, some escaped over the product's lifetime. The observation of mg kg^{-1} levels of PBDEs in indoor dust and increasing levels in humans and wildlife underscore the need for a better understanding of the role of polymer products in exposure. In the face of increasing environmental and human health concerns, The European Union officially banned Penta-BDE in 2004, although some member states had already terminated usage and US production ceased at the end of that same year (Frederiksen et al., 2009). Nonetheless, vast amounts persist in current-use and discarded products.

While viewed as persistent in the environment, plastics eventually weather and disintegrate (Browne et al., 2008; Barnes et al., 2009). Some PUF formulations are especially vulnerable, crumbling after only a few weeks of exposure to outdoor conditions (Hale et al., 2001). As particle size decreases, surface area increases and so to does the potential for additive PBDE release and dispersal. The importance of finished products rather than manufacturing as a source of PBDEs to the environment was highlighted in a recent Antarctic study (Hale et al., 2008). While no BFR or plastics manufacturing occurs on that continent, substantial PBDE concentrations were discovered in indoor dust within buildings, wastewater treatment sewage sludge and nearby aquatic organisms and sediments.

Legacy POPs (e.g. PCBs) were historically released primarily through industrial or heavy commercial processes. Human exposure to such POPs has since occurred predominantly via consumption of contaminated fish, rather than direct contact with PCB-containing products (Harrad and Diamond, 2006). In contrast, the dominant pathway for human PBDE exposure appears to be ingestion of dust originating from PBDE-treated polymer products in homes, vehicles and the workplace (Harrad and Diamond, 2006; Allen et al., 2008; Frederiksen et al., 2009). Some of the PBDEs within such dust are still contained within polymer fragments (Webster et al., 2009) and this may control their bioavailability and future dispersal and persistence. Owing to extensive usage in polymer products and their ubiquity within human living spaces, losses from in-use and discarded products will remain important PBDE sources to the global environment well into the future (Frederiksen et al., 2009). Alcock et al. (2003) estimated that the total reservoir of BDE 47 alone available for redistribution from finished PUF products to the US and UK environments was about 2620 and 520 metric tons, respectively. This congener constitutes only about 40% of Penta-BDE commercial mixtures (La Guardia et al., 2006). Hence, the total amount of Penta-BDE in play would be more than double these estimates.

Fugacity modeling indicates that most polymer products and associated PBDEs will be discharged to, and remain in, the terrestrial environment (Palm et al., 2002). In addition, many insects (e.g. crickets, carpet beetles, silverfish, termites, ants and moth larvae) are prodigious shredders and degraders of natural and synthetic polymers (Robinson, 2005). Many of these are also prolific within solid waste disposal sites and are frequent invaders of human habitations wherein they may cause substantial damage. Nonetheless, most insect-related POP studies to date have focused on aquatic rather than terrestrial species. Recent studies of the role of spiders in transferring aquatic-derived mercury and PCB burdens to birds highlight the potential importance of terrestrial invertebrate transport pathways (Cristol et al., 2008; Walters et al., 2010). Findings of substantial burdens of highly brominated PBDEs in terrestrial-feeding birds of prey (Chen and Hale, 2010) also support the need for further investigation of such exposure routes. Insects constitute a significant fraction of the total species and biomass present in soil-associated ecosystems. Yet we are aware of only three publications addressing PBDE burdens in terrestrial insects (Hale et al., 2002; Wu et al., 2009; Yu et al., 2011). In these studies, PBDE measurements were ancillary to the major study foci.

Impacts of soil-associated PCBs on the house cricket, *A. domesticus* (Paine et al., 1993), as well as the utility of this species to serve as a bioindicator of POP contamination in general (Walton, 1989; Paine et al., 1993), have been demonstrated. Such studies indicate that crickets can accumulate and transfer POPs within food webs. Yet, the extent to which such insects may assimilate PBDEs directly from treated polymers has remained virtually uninvestigated. We therefore examined the potential for uptake of Penta-BDE by house crickets allowed access to a commercially treated PUF polymer product.

2. Materials and methods

2.1. Cricket-PUF bioassay

The ASTM soil toxicity/bioaccumulation bioassay (ASTM E-1676, 1997) was used as a model to assess the accumulation and bioavailability of Penta-BDE contained in commercial PUF to house crickets (*A. domesticus*). Briefly, 21-d nymphs (Fluker Farms; Port Allen, LA) were acclimated to laboratory conditions for 48 h prior to exposure. Nymphs ($n = 10$) were randomly assigned to 2 L beakers ($N = 4$ treatments and $N = 4$ controls). Food and water (Fluker Farms Cricket Quencher© and Cricket Feed©) were provided *ad libitum*. Cylindrical PUF cores (0.5 g; 6 cm × 2 cm o.d.) were cut from a large piece of stock furniture foam (~1 m^2) purchased new from a local upholstery retail shop. Cores and cardboard shelters were placed in the test beakers. Cores were weighed before and after exposure to estimate PUF ingestion. Crickets in control beakers were treated identically, except with no access to PUF. The bioassay was conducted at 26 ± 3 °C, relative humidity of 45 ± 5%, with a 12:12 light:dark photoperiod. Control and PUF-exposed crickets were collected at day 14 and 28 of the experiment. Crickets were depurated by removing the PUF from treatment beakers, while maintaining access to fortified food and water *ad libitum* for an additional 96 h. Cricket body lengths were measured.

Exoskeleton molts were collected as discovered from 14 d- and 28 d-exposed crickets. Owing to the small size of the sheds (<0.1 g), only a single composite sample ($n = 1$) was attainable from each treatment. To conserve sample for PBDE analysis, lipid content determinations were conducted on molts ($n = 3$) collected from non-exposed crickets of the same age cohort from the stock population reared along with exposed and control crickets. To estimate growth and minimize stress to test crickets, individuals ($n = 60$) were randomly selected from the stock culture for length measurements at the start of the bioassay (i.e. "$t = 0$" crickets). These were not used in the subsequent exposure assay. Crickets and molts were rinsed of adhering material with deionized water, lyophilized and homogenized prior to analysis.

2.2. Chemical analysis

PUF total organic carbon content (TOC) was determined using an Exeter CHN Model 440 CE Elemental Analyzer (North Chelmsford, MA). The PBDE analytical methodology generally followed that of Chen et al. (2008). Briefly, freeze-dried samples were spiked with a surrogate standard (PCB 204) to monitor analyte recoveries and then subjected to enhanced solvent extraction (Dionex ASE 200; Sunnyvale, CA) using methylene chloride at 100 °C and 1000 psi. The lowest concentration PBDE standard (16 ng mL^{-1}) yielding a S/N ratio of $\geqslant 3$ was used to establish quantitation limits (QLs). Thus, QLs varied by sample weight available for extraction: 23–81 μg kg^{-1} dw (213–870 μg kg^{-1} lipid) for whole cricket samples, 128 μg kg^{-1} dw (1280 μg kg^{-1} lipid) for molts and