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Polybrominated Diphenyl Ether Accumulation in an Agricultural Soil Ecosystem Receiving Wastewater Sludge Amendments

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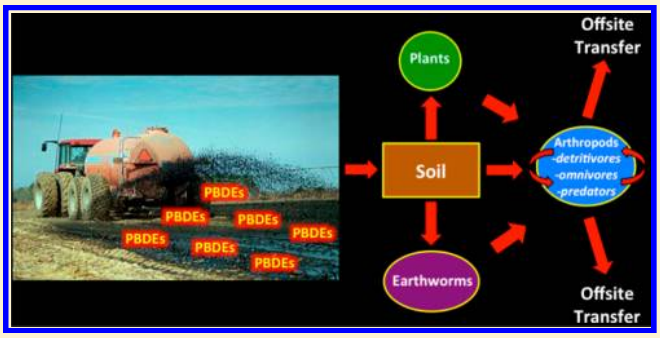
Supporting Information



ABSTRACT: Few studies have addressed bioaccumulation of organic pollutants associated with land-application of biosolids. We thus examined PBDE burdens within a soil ecosystem receiving long-term sludge amendments and a reference soil ecosystem receiving only manure inputs. No PBDEs were detected in reference site samples, but sludge-amended soils contained 17 600 ± 2330 μg/kg $\sum_{3-7}$PBDE (total organic carbon (TOC) basis). $\sum_{3-7}$PBDE burdens were highest in soil invertebrates with the greatest contact with sludge-amended soil (e.g., $\sum_{3-7}$PBDE of 10 300 ± 2670 and 3000 ± 200 μg/kg lipid for earthworms and detritivorous woodlice, respectively). PBDEs were below quantitation limits in vegetation from the sludge-amended site. Surprisingly, we measured quantifiable PBDE burdens in only a single sample of predaceous ground spiders from the sludge-amended site. BDE-209 burdens in sludge-amended soil and earthworms were 7500 ± 2800 μg/kg TOC and 6500 ± 4100 μg/kg lipid, respectively. BDE 209 was detected in fewer taxa, but the burden in a detritivorous millipede composite was high (86 000 μg/kg lipid). PBDE congener patterns differed among species, with worms and ground beetles exhibiting Penta-BDE-like patterns. Penta-BDE biota-soil accumulation factors (BSAFs) ranged from 0.006 to 1.2, while BDE-209 BSAFs ranged from 0.07 to 10.5. δ^{13}C and δ^{15}N isotope signatures were poorly correlated with PBDE burdens, but sludge-amended samples were significantly δ^{15}N enriched.

■ INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) have been widely used to flame retard polymer and textile-containing consumer products and are now widely dispersed in the global environment. Manufacture of the Penta-BDE formulation was phased out in the U.S. and European Union (EU) in 2004 due to constituent persistence and bioaccumulation potentials. Historically, the dominant PBDE formulation in global use has been Deca-BDE, but it has been presumed to possess negligible bioaccumulation potential.[1] However, surprising concentrations of Deca-BDE constituents have been detected in some terrestrial-feeding birds of prey.[2,3] Also, its major constituent, BDE-209, may debrominate to more bioaccumulative, less brominated congeners in the environment.[4,5] Hence, U.S. Deca-BDE manufacture was to be phased out after 2013, and further restrictions are contemplated in the EU. Despite these regulatory actions, constituents of both formulations persist in the environment, and inputs will continue from in-use and discarded products.

Unlike legacy POPs (e.g., PCBs), released primarily via industrial activities, PBDEs have been intentionally incorporated at percent levels in common consumer products, such as furniture cushioning, carpet underlayment, textiles, and thermoplastics.[6,7] These high concentrations and the abundance of PBDE-containing products within homes, workplaces, and vehicles have resulted in substantial human exposure. Once believed safely sequestered in polymers, PBDEs may migrate from treated products throughout their life cycles and accumulate in humans, wildlife, soils, sediments, and sewage sludges. Though product degradation and dust generation are emerging as prominent PBDE exposure pathways in indoor environments,[8,9] increasing reports of PBDEs in sewage sludges suggest that land application of these materials may be a significant pathway by which PBDEs are introduced into terrestrial soil ecosystems.[10−15]

About 8 × 10^6 metric tons of sewage sludge are generated in the U.S. annually, more than half of which is now applied to agricultural and other lands as soil amendments known euphemistically as *biosolids*.[13,14,16,17] While supplying nutrients, sludge also contains a plethora of toxic microcontaminants.[18−20,10,12−15,17] Research and regulatory attention to these materials has focused primarily on metals, while organic pollutants have been presumed to either be labile or below levels of concern. However, reports of burdens in U.S. sludges and sludge-amended soils have increased.[10−15,17,19] Nonetheless,

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organic pollutants remain unregulated in U.S. biosolids. North American demand for Penta-BDE historically represented 90% of global usage, and PBDE burdens in U.S. biosolids have been found to be proportionately high.[10,12−15,17]

Inadequate research has examined the fate of PBDEs in soil ecosystems from sewage sludge amendments. Indeed, we are aware of only two published field studies of soil invertebrates (in both cases, earthworms) exposed to sludge-associated PBDEs, both of which examined only earthworms and were conducted by the same group within the same sludge-amended agricultural fields in Sweden (wherein PBDE usage has been historically lower).[21,22] We are also unaware of any published studies examining PBDE accumulation in arthropods inhabiting sludge-amended soils. We thus investigated PBDE accumulation in two soil ecosystems, one receiving long-term (~25 yr) sludge amendments and one receiving only manure amendments. Enrichment of ^{15}N and ^{13}C in soil and biota from the two sites was also examined to characterize trophic interactions and distribution of sludge-associated constituents within the soil invertebrate food web.

EXPERIMENTAL SECTION

Study Sites. We studied an untilled hay field (~60 000 m^2) adjacent to the Chesapeake Bay within the Mid-Atlantic region of the U.S. The dominant vegetation was eastern gamagrass (*Tripsacum dactyloides*), a native forage species related to corn (*Zea mays*). Though precise estimates of sludge tonnage applied to the system were unavailable, landowners confirmed sludge application to the field at agronomic nitrogen rates at 2−3 year intervals since the mid-1980s. We also studied a comparable reference field (~6000 m^2) 160 km south of the sludge-amended field. This site had been cleared of trees two years prior to sampling and had received only animal manure inputs since. The dominant vegetation was orchard grass (*Dactylis glomerata L.*).

Paired Soil−Earthworm, Vegetation, and Sludge Sampling. Paired soil and earthworm samples were collected from randomly selected quadrats by excavating the upper 15 cm of soil and hand sorting worms and soils. Worms (~10 g) and collocated soil (~1 kg) were pooled to yield paired earthworm−soil composite samples. Earthworms were identified as mixtures of *Lumbricus terrestris* and *L. rubellus*, *Apporectodea caliginosa*, *Apporectodea* spp., and *Allolobophora* spp. Grass shoots were collected just above the root crown. At the sludge-amended site, weathered biosolid material was also collected as discovered and pooled to create sample composites. Biosolids are typically applied with a tractor and attached mechanical spreader, potentially resulting in heterogeneous distribution on the soil surface. Samples were stored on ice for transport back to the laboratory. There, earthworms were rinsed with deionized water, depurated on moistened KimWipes for 24 h, and rinsed again with deionized water prior to freezing at −10 °C. Soil was sieved to <2000 μm and stored at −10 °C. All samples were freeze-dried prior to analysis (see Supporting Information).

Arthropod Sampling. Arthropods were collected at or near the soil surface by hand and included wolf spiders (Araneae: Lycosidae: *Hogna* spp., *Schizocosa* spp., and *Rabidosa* spp.), millipedes (Polydesmida: Paradoxosomatidae), woodlice (Isopoda: Porcellionidae), grasshoppers (Orthoptera: Acrididae), field crickets (Orthoptera: Gryllidae), ground beetles (Coleoptera: Carabidae), firefly larvae (Coleoptera: Lampyridae), and June beetle larvae and adults (Coleoptera: Scarabidae). Web spiders were also collected and composited, including mixtures of garden spiders (Araneae: Araneidae: *Argiope* spp.), crab spiders (Araneae: Thomisidae), black widows (Araneae: Theridiidae), and other orb-weavers (e.g., Araneae: Araneidae: *Mangora* spp.). Arthropods were allowed to purge their gut contents for 24 h and then were stored at −10 °C. Individual wolf spiders (sludge-amended n = 347; reference site n = 245) were sorted into fresh weight size classes (i.e., < 0.1 g, 0.1−0.2 g, 0.2−0.3 g, 0.3−0.4 g, > 0.4 g). Samples were cleaned of obvious soil and vegetation and identified to at least Family.

Chemical Analysis. Lyophilized 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) as previously described,[4,5,12,23] followed by size exclusion and silica gel purification. Sample lipids were estimated by evaporating 10% of the extract to constant weight. Following addition of a quantitation standard, decachlorodiphenyl ether (DCDE; Ultra Scientific, Kingston, RI), Penta- and Octa-BDE constituents were separated on a gas chromatograph (GC) (Varian 3400; Sugar Land, TX) equipped with a 15 m DB-5 column (J&W Scientific; Folsom, CA; 0.25 μm film, 0.32 mm ID) and Varian 8200 CX autosampler. The GC carrier gas was helium, and injections were made in the splitless mode. PBDEs were detected using mass spectrometry (MS) (Varian 4D GC-MS/MS) with selected ion monitoring and quantified with eight-point calibration curves generated using the summed areas of the three major ions of each PBDE congener relative to DCDE. Analysis of Deca-BDE constituents was performed using methods reported previously[4,5,24] (see Supporting Information).

Statistical Analysis. Statistical evaluations were performed using StatPlus:Mac (AnalystSoft Inc.; Vancouver, BC, Canada). Statistical significance was determined at the α = 0.05 level using two-tailed testing. PBDE BSAFs were computed as the ratio of lipid-normalized whole body tissue to total organic carbon (TOC)-normalized soil concentrations. One-way analysis of variance (ANOVA) with Tukey's honestly significant difference (HSD) posthoc testing was used to determine significant differences among PBDE burdens, BSAFs, and stable isotope enrichment (see Supporting Information for details).

RESULTS AND DISCUSSION

PBDEs in Soil and Vegetation. PBDEs are lipophilic and are enriched in high organic solids during wastewater treatment. Sludge application to land will transfer associated burdens to soils, resulting in their accumulation over time.[10,13−15] However, to date, few studies have examined this phenomenon, and fewer still have considered PBDE accumulation in soil biota. Mean Penta-BDE and Deca-BDE concentrations in the U.S. EPA Targeted National Sewage Sludge Survey[17] were 2030 and 2180 μg/kg dw, respectively, in sludges collected from 74 publicly own treatment works (POTWs) across the U.S. in 2006−2007. In our sludge-amended soils, all targeted congeners (BDE 28, 47, 99, 100, 153, 154, 183, 206, 207, 208, and 209) were detected, but BDE 28, 183, 206, 207, and 208 were below established QLs. None of the targeted PBDEs were detectable in reference site soil samples (Table S1; see Supporting Information for details). Mean BDE 209 burdens in the sludge-applied soil (7500 μg/kg TOC; 86 μg/kg dry weight (dw)) were 2- to 3-fold lower than the sum of tri- to octa-brominated congeners ($\sum_{3-7}$PBDE = 17 600 μg/kg TOC; 260 μg/kg dw). Andrade et al.[10] reported $\sum$PBDE (BDE 47 + 99 + 209) burdens of 53 μg/kg dw in U.S. (Mid-Atlantic) sludge-amended soils, and Xia et al.[15] reported ∑PBDE (BDE 47 + 99 + 100 + 153 + 154) burdens of 658 μg/kg dw in experimental soils receiving PBDE-contaminated sludge from a major U.S. (Midwestern) POTW. For comparison, ∑Penta-BDE burdens in soils receiving only atmospheric inputs are typically in the range of 1−12 μg/kg dw.[7]

Ratios of ∑Penta-BDE to BDE 209 in sludge and sludge-amended soils appear to be generally decreasing over time commensurate with diminished use and release of Penta-BDE.[14] However, quantifying such trends is challenging due to the notorious complexity of sludge residues and originating wastewater streams.[14] For example, Hale et al.[13] reported ∑Penta-BDE and BDE 209 burden ranges of 1100−2290 and 85−4890 μg/kg, respectively, in U.S. biosolids collected from multiple states prior to cessation of Penta-BDE production in the U.S. (2004). More recently, the same group reported ∑Penta-BDE and ∑Deca-BDE constituent burdens of 1080 and 6630 μg/kg, respectively, in biosolids derived from the major Midwestern POTW referenced above.[14] Comparable ratios of Penta- to Deca-BDE constituents were also observed in soils amended with these biosolids.[14] Andrade et al.[10] reported BDE 209 burdens about 3-fold in excess of ∑Penta-BDE (BDE 47 + 99) burdens in biosolids collected from the U.S. Mid-Atlantic region between 2005 and 2008. However, they also reported lower relative BDE 209 burdens in soils receiving repeat treatments with those biosolids,[10] consistent with our measured soil burdens. In contrast, as earlier noted, the U.S. EPA TNSSS[17] reported comparable mean ∑Penta-BDE and BDE 209 burdens in U.S. sludges, consistent with our weathered sludge samples (Table 1).

Our soil $\sum_{3-7}$PBDE burdens were consistent throughout the sludge-amended site (RSD = 13%; N = 10), indicating uniform distribution. This was surprising, as mechanized application typically yields heterogeneous sludge dispersal. Such uniformity may be related to recent application (two years prior to sampling) and/or consistently recurring application over time. Mean soil burdens (TOC basis) were also consistent with those reported for the most heavily sludge-amended Swedish field (19900 μg/kg; loss on ignition basis) reported by Sellström et al.[22] PBDE burdens in U.S. sludge-amended soils typically exceed those in other countries, presumably due to more intensive PBDE usage here.[14] The anomalously high Swedish site had received sludge from a wastewater facility serving textile plants. There, soil Penta-BDE congener burdens were incurred in the order BDE 99 > 47 > 100 > 153 ≈ 154,[22] consistent with commercial Penta-BDE mixtures.[24] By comparison, congeners were incurred in our sludge-amended soil in the order BDE 47 ≈ 99 > 100 > 154 > 153, with BDE 154 burdens being about 4-fold higher than BDE 153. This was an intriguing finding, as burdens of this congener were not similarly disproportionate in our weathered sludge or earthworm samples (Table 1). Moreover, perhaps not unexpectedly after two years of weathering, burdens of all PBDEs were significantly lower in weathered sludge. It is not clear what might account for such disproportionate BDE 154 soil burdens. Evidence of BDE 209 debromination in soil samples was not apparent.

Plants are essential components of terrestrial ecosystems, thus the extent of PBDE accumulation in vegetation is critical. Uptake of lipophilic contaminants by plants has been previously reported to be limited, although partitioning from air to leaf surfaces may be significant for some compounds.[25] In our gamagrass samples, PBDEs were < QL (Table 1), consistent with previous reports of negligible PBDE accumulation in sludge-amended corn.[14,15] In contrast, Huang et al.[26] found that shoots contained 490 μg/kg dw BDE-209 after exposure of several plant species to soil spiked with BDE 209 (3613 μg/kg dw), while Vrkoslavová et al.[27] reported ∑Penta-BDE uptake in the range 15.4−76.6 μg/kg in nightshade and tobacco grown in undiluted biosolids (∑Penta-BDE = 568 μg/kg). Mueller et al.[28] reported that solvent extraction recovered <10% of PBDEs from aged soil (spiked with DE-71 at 75 μg/kg dw) except where mixed species plantings were examined. However, they observed minimal PBDE uptake by plants (i.e., < 5 μg/kg dw). Such reported differences in accumulation by plants may be related to species differences and exposure mode (i.e., spiked vs aged PBDEs).

PBDEs in Earthworms. Earthworm $\sum_{3-7}$PBDE concentrations were significantly higher ($p < 0.001$) than in any of the arthropods, comparable to PCB uptake in worms and soil arthropods from field-contaminated soils.[29] With the exception of BDE 28, we detected the targeted Penta-BDE constituents in virtually all biota from the sludge-amended site. However, only BDE 47 and 99 were consistently quantifiable in most samples. Mean earthworm $\sum_{3-7}$PBDE burdens were 10 300 μg/kg lipid and, like soil burdens, were consistent across the sludge-amended study site (RSD = 26%; N = 10).

Ingestion of soil containing PBDEs is likely the dominant exposure route for earthworms, with accumulation tending to decrease with increasing soil organic matter and log Kow.[22,30] Extended contaminant−soil interaction or aging may further reduce bioavailability.[31] Likewise, PBDEs associated with polymer fragments produced by weathering or abrasion may exhibit low bioavailability.[32] But such fragments may be important as PBDE levels within may be at percent levels. Hence, given the same bulk soil PBDE concentrations, one might expect reduced uptake from soils containing biosolids and polymer constituents relative to solvent-delivered contaminants. However, we recently reported similar PBDE accumulation by worms exposed to soils amended with composted and anaerobically digested biosolids, as well as PBDE-treated foam microparticles and solvent-delivered DE-71.[12] Anaerobically digested sludges are the most commonly land-applied and were applied to our study site every 2−3 years since the mid-1980s. There, we found that the mean BDE-209 burden in worms was 6500 (±4100) μg/kg lipid, consistent with worm burdens (5200 μg/kg lipid) at the most heavily contaminated sludge-amended field site in the Swedish study by Sellström et al.[22] However, in their study, BDE-209 soil burdens (33 600 μg/kg; loss on ignition basis) were about 4.5-fold higher at their most contaminated site than mean soil burdens measured here (attributable to sludge derived from textile effluents).

Though our worm BSAFs were lower than those reported for worms from Swedish sludge-amended fields[22] (Table S2), we observed comparable trends of decreasing BSAF with increasing log Kow (Figure 1). We reported similar trends in biosolids-exposed worms in the lab.[12] However, our lab-generated BSAFs[12] were 5- to 20-fold higher than field-exposed BSAFs reported here and 2- to 4-fold higher than field-exposed worms in the Sellström et al.[22] study. Aging of the soil/biosolids/PBDEs, or heterogeneity of biosolids distribution, may have contributed to the lower field-derived BSAFs we observed. Confinement of worms to relatively small volumes of biosolids-amended soil under lab conditions likely also contributed. Our lab BSAFs decreased with increasing biosolids

Table 1. Summary of Mean (±S.D.) PBDE Burdens and Quantitation Limit (QL) Ranges (μg/kg) for Soil and Weathered Sludge (TOC basis) and Biota (Lipid Basis) Samples from the Sludge-Amended Site[a]

sample matrix	N	47	100	99	154	153	Σ_{3-7}PBDEs	209	Σ_{9-10}PBDEs	lipid (%)[b]	PCB-204 (%)	Σ_{3-7}PBDE QL[b]	Σ_{9-10}PBDE QL[b]	trophic status
soil[c]	10	6700 ± 1100	1600 ± 260	6600 ± 800	690 ± 120	150 ± 23	17600 ± 2330	7500 ± 2800	7500 ± 2800	1.5–1.9[d]	82–103	53–76[d]	830–1300[d]	
weathered sludge[c]	3	910 ± 160	180 ± 25	730 ± 140	78 ± 16	81 ± 19	2000 ± 500	950 ± 240	950 ± 240	2.7–3.9[d]	84–97	47–69[d]	770–1200[d]	
vegetation	3	<QL	<QL	<QL	<QL	<QL		<QL		40.1–42.7[d]	78–86	16-31[d]	150–340[d]	
earthworms[c]	10	4500 ± 1700	1800 ± 770	4000 ± 1000	210 ± 91	210 ± 81	10300 ± 2670	6500 ± 4100	6500 ± 4100	7.8–11.1	52–92	132–221	1700–6600	detritivore
millipedes	1	390	<QL	200	<QL	<QL	590	65 000	87 000	8.7–9.6	79–96	170–180	1500–2800	detritivore
woodlice	3	2200 ± 96	290 ± 51	530 ± 87	<QL	<QL	3000 ± 200	<QL		7.5–10.6	81–90	150–210	1100–1600	detritivore
June beetle larvae	3	400 ± 200	<QL	260 ± 110	<QL	<QL	670 ± 280	60 000	60 000	2.2–22.1	68–72	180–210	722–1310	herbivore
June beetle adults	2	1400–1800	<QL	390–440	<QL	<QL	1760–2220	<QL		9.5–10.1	89–93	357–381	3210–3970	herbivore
grasshoppers	3	<QL	<QL	<QL	<QL	<QL		<QL		9.1–12	57–71	51–64	440–850	herbivore
crickets[e]	3	53–55	<QL	150–320	<QL	<QL	200–400	1440	1440	13.3–18.6	70–84	51–83	770–1260	omnivore
firefly larvae	2	1400–1900	<QL	540–770	<QL	<QL	1890–2660	<QL		5.3–5.9	90–93	344–431	2320–2520	predator
ground beetles	3	800 ± 200	320 ± 120	740 ± 270	40 ± 10	40 ± 10	1980 ± 560	5800 ± 3800	5800 ± 3800	13.8–16.7	52–62	38–40	540–590	predator
web spiders[f]	2	<QL	<QL	<QL	<QL	<QL		<QL		12.3–14.7	90–93	130–150	720–810	predator
wolf spiders[g]														
wolf1	2	<QL	<QL	<QL	<QL	<QL		<QL		7.7–9	67–87	150–220	620–1700	predator
wolf2	2	<QL	<QL	82	<QL	<QL	82	1690	1690	7.3–11.5	65–82	72–85	1200–1700	predator
wolf3	2	<QL	<QL	<QL	<QL	<QL		<QL		8.1–10.6	69–84	140–150	530–1400	predator
wolf4	2	<QL	<QL	<QL	<QL	<QL		<QL		9.2–13.8	82–83	190–300	580–1300	predator
wolf5	2	<QL	<QL	<QL	<QL	<QL		<QL		11.2–15.5	65–79	69–100	1700–2700	predator

[a]Where sample $N < 3$, PBDE burdens are reported as a range. [b]Lipid values and lipid-normalized QLs calculated on a dry weight basis and reported as a range for each sample type. [c]Only $N = 8$ soil composites analyzed for Octa- and Deca-BDE constituents, as two samples were lost during processing for Penta-BDE analysis. BDE-209 was >QL in only $N = 6$ soil and $N = 6$ worm samples. BDE-206, -207, and -208 detected in all soil, weathered sludge and worm composites but < QL in all. Weathered sludge samples are composites of identifiable sludge fragments collected as discovered on the soil surface. [d]TOC reported for soil, weathered sludge and vegetation; QLs reported on TOC basis. [e]BDE-47 was > QL in only $N = 2$ composites, but BDE-99 > QL in all. [f]Composites of black widows, garden spiders, spiny and long-jawed orb weavers, and tangle web spiders (see Experimental Section). [g]12–70 individuals composited according to masses: wolf1 < 0.1 g; wolf2 = 0.1–0.2 g; wolf3 = 0.2–0.3 g; wolf4 = 0.3–0.4; wolf5 > 0.4 g.

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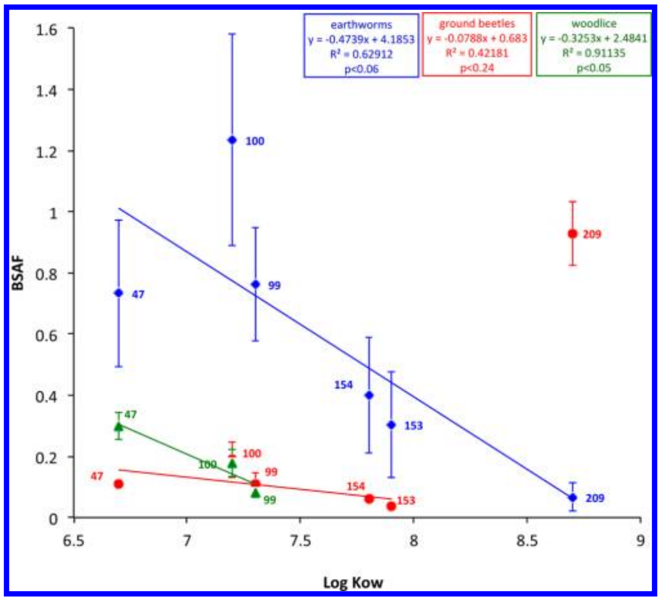

Figure 1. Least squares regression of mean PBDE BSAFs and log Kow values for earthworms, ground beetles, and woodlice from the sludge-amended site. Ground beetle BDE-209 burdens were determined to be statistical outliers (Dixon's Q-test) and were thus omitted from regressions. Error bars are standard deviations from the mean, and those not visible are small enough to be obscured by the data point. Penta-BDE constituent log Kow data from ref 57; BDE-209 log Kow data from ref 58.

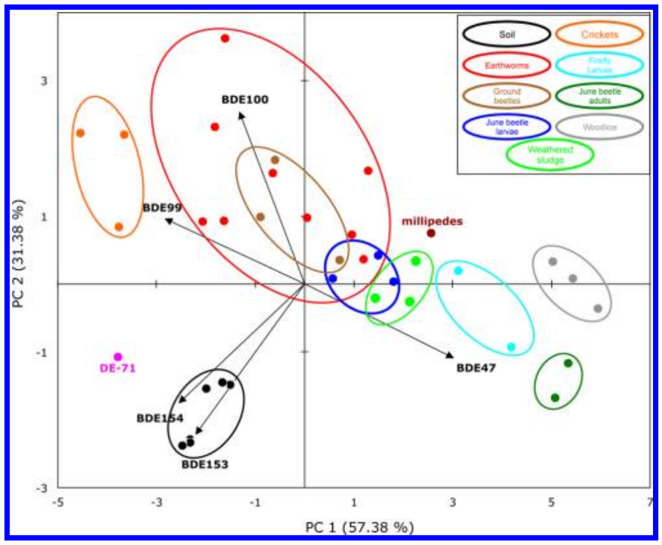

Figure 2. PCA results for lipid- and TOC-normalized Penta-BDE constituents in biota, soil, and weathered sludge from the sludge-amended site (expressed as a percent of total PBDEs). Sample types are grouped with colored ovals to highlight relationships (except for the single millipede composite and DE-71). Some worm ($N = 10$) and soil ($N = 10$) data points are obscured due to overlap of points. DE-71 constituent data from ref 24.

dosage as well, similar to patterns reported for worms exposed to solvent-delivered PBDEs.[33] Lab BSAFs for Penta-BDE constituents in the range of 0.9−5.8 have also been reported for worms exposed to Penta-BDE-spiked natural soil.[34] More consistent with our results, however, Blankenship et al.[29] reported PCB BSAFs in the range 0.48−0.66 for field-exposed worms.

PBDEs in Arthropods. We are aware of only three reports of PBDE accumulation in terrestrial insects,[6,32,35] only one of which was specifically designed to assess PBDE accumulation in insects.[32] There, house crickets (*Acheta domesticus*) reared with PBDE-treated polyurethane foam (PUF) accumulated mg/kg burdens of Penta-BDE constituents. Hale et al.[6] had previously serendipitously observed that house crickets reared with treated PUF as food for experimental frogs accumulated mg/kg burdens (209 000 μg/kg lipid) of Penta-BDE. Wu et al.[35] reported that Penta-BDE constituents dominated in insect composites examined during a frog monitoring study near a Chinese e-waste recycling site. The mean BDE 47/99 ratio calculated from their reported composite insect burdens was 0.83, consistent with that of the DE-71 mixture (0.79),[24] but lower than nearly all of our soil biota (1.1−4.3; Table S2).

We used principal components analysis (PCA) to visualize Penta-BDE congener contributions within our collected sample types. A biplot of scores and loadings showed that PC1 and PC2 explained 88.8% of the variation in the data set (Figure 2). Congener patterns for crickets, firefly larvae, June beetle adults, woodlice, millipedes, and soil are well separated in the PCA plot, while ground beetles, June beetle larvae, earthworms, and weathered sludge are more intimately associated. Such patterns suggest a kind of *weathering* of Penta-BDE constituents as they migrate from soil into the invertebrate food web, similar to trends reported by Blankenship et al.[29] for PCB congeners in a contaminated soil food web. The overlapping weathered sludge pattern appears consistent with this view. The PCA plot also revealed that the biota were deficient in BDE 154 and 153 relative to our sludge-amended soil samples, while woodlice, June beetles (adults and larvae), firefly larvae, and millipedes were more enriched in BDE-47 (presumably indicative of its increased bioavailability). Overlap of congener pattern variance among worms, June beetle larvae, and ground beetles may also be indicative of the latter's preference for soft-bodied prey. Overlap of June beetle larvae and weathered sludge congener patterns may also reflect direct contact of larvae with surficial weathered sludge. The proximity of weathered sludge congener patterns to those of the worms and ground beetles is also noteworthy.

BDE 47 typically dominates in wildlife samples. However, it was near the QL in our cricket composites, while BDE 99 dominated in excess of its proportion in soil and weathered sludge samples. Except for crickets, BDE 47 burdens were generally greater than other Penta-BDE constituents in all sampled arthropods (Table 1). In contrast, BDE-99 burdens were substantial in earthworms and soil, consistent with its predominance in the commercial Penta-BDE formulation and some biosolids.[12,13] Interestingly, BDE 100 was quantifiable only in soil, weathered sludge, earthworm, woodlice, and ground beetle composites. Though the major Octa-BDE constituent (BDE-183) was detected in all samples, it was never above sample QLs. The nona-brominated constituents (BDE-206, 207, and 208) of the commercial Deca-BDE mixture were also detected in several sample types but were quantifiable only in the single millipede composite (8500, 9300, and 4000 μg/kg lipid, respectively). The major Deca-BDE constituent (BDE-209) was quantifiable only in soil, weathered sludge, worms, millipedes, crickets, ground beetles, June beetle larvae, and a single wolf spider composite (size class 2). Descriptive statistics for this congener were thus computed accordingly.

Among sampled arthropods, woodlice exhibited the highest $\sum_{3-7}$PBDE burdens, but their BDE 209 levels were < QL (Table 1). The BDE 47/99 ratio in woodlice exceeded 4, compared to 1.1 in worms and collocated soil (Table S2).

The lower relative BDE 99 burden may be due to this isopod's preference for ingesting weathered organic matter. As woodlice possess some capacity for biotransforming PAHs,[36] this may also indicate a greater capacity for BDE 99 elimination. Millipedes, like woodlice, consume weathered organic matter preferentially. However, $\sum_{3-7}$PBDE burdens in millipedes were appreciably lower than in woodlice or earthworms (Table 1), and the BDE 47/99 ratio was intermediate (2.0) between that of soil, earthworms, and woodlice (Table S2), perhaps indicative of distinct biotransformation capacities. Surprisingly, BDE 209 was detected at 65 000 μg/kg lipid in the millipede composite. We thus initially believed this to be an analytical artifact. However, BDE 209 was not detected in any lab or field blanks, or in any reference site samples (Table S1). Unfortunately, due to limited sample mass, the sample was extracted in its entirety, so repeat analysis was not possible. BDE 206, 207, and 208 were also detected in millipedes, but in ratios generally consistent with commercial Deca-BDE.

Firefly larvae are robust predators of the upper soil strata, where they preferentially consume soft-bodied invertebrates (e.g., worms, slugs, and snails). Firefly $\sum_{3-7}$PBDE burdens were appreciably higher than those observed in millipedes but comparable to those in the detritivorous woodlice (Table 1). Interestingly, firefly BDE 47/99 ratios (2.5−3.0) were also comparable to those of woodlice, indicating similar enrichment relative to soil and weathered sludge. These findings are reminiscent of those of Xia et al.[37] who reported that median Penta-BDE burdens were similar in both carnivorous and herbivorous aquatic insects from the Hudson River (USA).

June beetle larvae were present in larger numbers at the reference site where only manure was applied, consistent with the preference of adult beetles for organic matter enriched egg deposition sites. At the sludge-amended site, June beetle larvae $\sum_{3-7}$PBDE burdens and BDE 47/99 ratios (1.5) were similar to those of the detritivorous millipedes (Table 1; Table S2). As seen in the millipedes, BDE 209 burdens in June beetle larvae were also comparably high (60,000 μg/kg lipid). However, this congener was quantifiable in only one sample composite. June beetle adults were also collected from the sludge-amended field site and exhibited $\sum_{3-7}$PBDE burdens about 3-fold higher than the larvae. Their BDE 47/99 ratio (3.5) exceeded that of the larvae as well (Table 1; Table S2). As adults feed primarily on foliage, rather than on detritus or soil, and because PBDEs were < QL in the gamagrass, this may reflect enrichment of body burdens during metamorphosis, as has been observed for PBDE burdens in some aquatic insects.[38] Blankenship et al.[29] reported similar results for PCBs. There, they measured $\sum$PCBs of 340 μg/kg wet weight (ww) in composite samples of adult June and Japanese beetles from field-contaminated soil (soil $\sum$PCBs = 6500 μg/kg ww). June beetles are formidable fliers and thus may represent a significant pathway for off-site transport of such contaminants. To explore this, we normalized $\sum_{3-7}$PBDE lipid burdens to the number of individuals per composite sample and estimated an impressive burden range of 590−740 μg $\sum_{3-7}$PBDE per individual.

In contrast to June beetles, ground beetles (like firefly larvae) preferentially consume soft-bodied invertebrates. $\sum_{3-7}$PBDE burdens in ground beetles were surprisingly similar to those in June beetles, but also similar to those in the predaceous fireflies, as one might expect. However, the ground beetle BDE47/99 ratio (1.2) was more consistent with that of the soil and worms (Table S2). Their BDE 209 burdens were also substantial (5800 μg/kg lipid; Table 1), consistent with those observed in worms, a preferred prey item.

Crickets are opportunistic scavengers that consume diverse biotic and abiotic materials, including polymers.[32] $\sum_{3-7}$PBDE burdens in crickets from the sludge-amended site were among the lowest of all invertebrates sampled, with the lowest corresponding BDE 47/99 ratio (Table 1; Table S2). This may indicate a capacity for efficient BDE 47 elimination. However, such congener patterns were not apparent in previous studies of PBDE uptake in closely related house crickets.[6,32] Though rapid uptake and elimination of PCBs[39] and PAHs[40] by house crickets has been reported, these differences may also relate to field-exposed crickets consuming weathered Penta-BDE residues in decaying materials, in contrast to lab-exposed crickets consuming non-weathered residues associated with PUF. While closely related to crickets, grasshoppers are strict herbivores. Consistent with undetectable burdens in gamagrass, PBDEs were < QL in grasshoppers from the sludge-amended site. See the Supporting Information for additional discussion of PBDE accumulation in arthropods, as well as biomagnification estimates for putative trophic relationships.

As spiders are top macroinvertebrate predators in soil ecosystems,[41] we hypothesized that wolf spiders would incur appreciable sludge-associated PBDE burdens. Surprisingly, PBDEs were < QL in all but a single wolf spider composite (size class 2) from the sludge-amended site (Table 1). We are aware of no published reports of PBDE accumulation in spiders. However, PCB accumulation in riparian web-building (Araneidae, Tetragnathidae) and closely related ground-dwelling spiders (Pisauridae: *Dolomedes* spp.) has been reported.[42,43] As ground-feeding spiders are thought to have evolved more sophisticated digestive and detoxification enzyme systems in response to increased intake of diverse xenobiotics,[44] these species may have evolved a unique capacity for PBDE elimination.

Evaluating Equilibrium Partitioning (EPT). EPT predicts that relative burdens of hydrophobic contaminants in soil and resident organisms will be governed by fugacity.[45,46] Under these conditions, regression of lipid and TOC-normalized PBDE burdens should yield an approximately isometric fitted line with zero intercept. Complicating this simplistic scenario are factors such as protracted mass transfer from slowly reversible soil organic carbon pools, short organismal life spans, biotransformation, equivalency of lipid and TOC partitioning, and food digestion effects. Thus, because worms are in intimate contact with (and ingest copious) soil, we hypothesized that equilibrium partitioning would drive PBDE accumulation, whereas uptake by arthropods would be complicated by additional mechanisms. To explore this, we evaluated the relationship between tissue lipid and soil TOC PBDE burdens for dissimilar taxa using least-squares regression (Figure 3). For earthworms and ground beetles, lipid and soil TOC burdens were significantly correlated ($r^2 = 0.95$; $p < 0.001$), whereas the woodlice data (though borderline) were not ($r^2 = 0.37$; $p < 0.06$). These results support our hypothesis regarding PBDE accumulation in worms and at least a representative arthropod. The significant positive correlation for ground beetles was more surprising, however. But, this too may be explained in part by their preference for earthworm prey.

Trophic Interactions. At our sludge-amended and reference sites, soil, vegetation, and grasshoppers occupied lower positions with respect to δ^{15}N, while δ^{15}N enrichment in sludge-amended samples was considerably higher overall (Figure 4A,B). The reference site was densely mixed deciduous

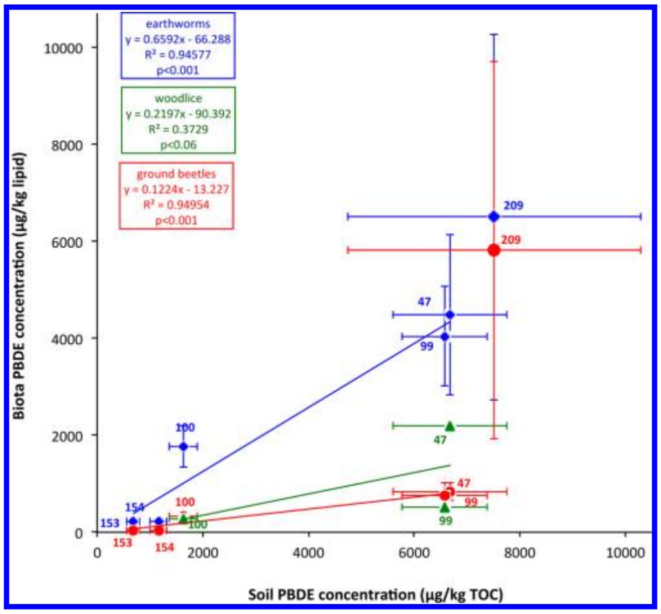

Figure 3. Least squares regression analysis of mean tissue (lipid basis) and soil (TOC basis) PBDE burdens for earthworms ($N = 10$), ground beetles ($N = 3$), and woodlice ($N = 3$) from the sludge-amended site. BDE-209 data points were omitted from the worm ($N = 6$) and ground beetle ($N = 3$) regressions. Error bars are standard deviations from the means.

forest prior to being cleared two years prior to our study. Hence, periodic manure inputs over such a short period may not have been sufficient to similarly impact δ^{15}N values. For comparison, Choi et al.[47] reported δ^{15}N enrichment values of 2.2−2.8 for soil from a similar Mid-Atlantic forest. Studies of C and N stable isotope enrichment in sludge-amended soil systems are limited. However, mean δ^{15}N enrichment in weathered sludge samples from our sludge-amended site was comparable to that reported for sludge-amended forests,[48,49] sewage sludge used as combustion feedstock,[50] sewage-impacted coastal zones,[51] terrestrial arthropods inhabiting a sewage-influenced wetland,[52] and benthic biota inhabiting a deep-sea sludge dumpsite.[53] In the Wang et al.[48,49] studies, δ^{15}N enrichment in sampled vegetation also reflected that of the applied biosolids, as seen here (Figure 4A).

Here, reference site ground beetles were unusual in that their δ^{15}N signature was significantly lower than that of woodlice and June beetle larvae but comparable to that of worms, again perhaps indicative of their dietary preference for worms. This may also reflect greater omnivory among ground beetles more generally.[54] Relatively lower overall δ^{13}C enrichment may also be explained by differences in C3 (temperate forest influences) versus C4 (gamagrass) photosynthetic pathways at work in the dominant vegetation at the two sites. Reference site trophic relationships were more consistent with temperate agricultural soil ecosystems[54,55] than those in the sludge-amended system. For example, wolf spiders from the reference site were significantly enriched in δ^{15}N relative to all other biota, indicative of their predatory status. We originally hypothesized that wolf spiders would feed at the top of these soil food webs. However, at the sludge-amended site, several soil, detritus, and plant consumers exhibited greater δ^{15}N enrichment than wolf spiders in size classes 1, 3, and 4. There, wolf spiders in size classes 2 and 5 (and web spiders) occupied the highest trophic positions (Figure 4A). Wolf spiders in size class 4 were also

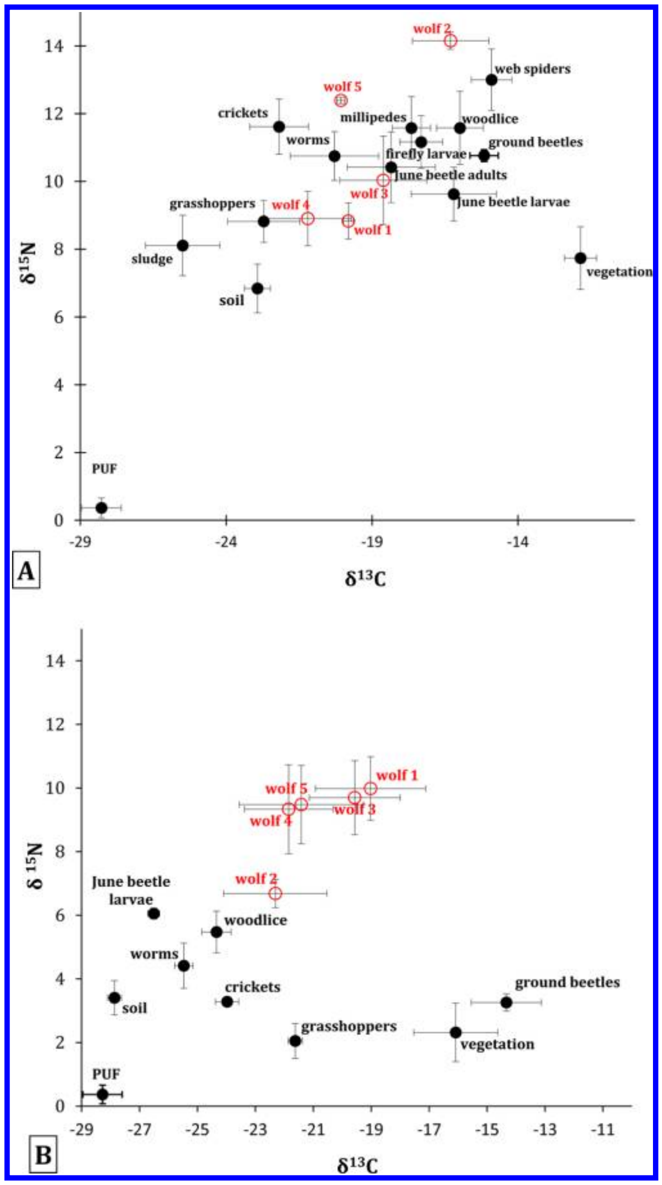

Figure 4. Mean carbon (δ^{13}C) and nitrogen (δ^{15}N) stable isotope signatures for samples collected from the sludge-amended (A) and manure-amended reference (B) sites. See main text for sample collection details. For wolf spiders: wolf 1 < 0.1 g; wolf 2 = 0.1−0.2 g; wolf 3 = 0.2−0.3 g; wolf 4 = 0.3−0.4 g; wolf 5 > 0.4 g (Table 1). The PUF data point is the mean of polyurethane foam subsamples collected from furniture cushioning and carpet underlayment samples from multiple locations throughout the U.S. ($N = 10$). Error bars are standard deviations from the means.

unusual in appearing to feed at least one trophic level below wolf spiders in the smaller size class 2. Smaller wolf spiders typically feed within detrital food webs,[55] so we were surprised to find the larger wolf spiders (size classes 3 and 4) appearing to feed within this level. Increased feeding by larger wolf spiders within detrital food webs may indicate a lack of larger prey items in this system.[55] This is consistent with the relative scarcity of some of our targeted sample types (e.g., millipedes). Alternatively, increased organic matter inputs associated with sludge applications may increase detritivore biomass and commensurate predation by larger spiders within the detrital food web.[55] Interestingly, sludge-amended wolf spiders were also significantly smaller relative to reference site spiders ($p < 0.05$; fresh weight). This may be due in part to decreased availability of higher quality prey within the sludge-amended site, which can increase intraguild predation and cannibalism, thereby stressing the entire community.[54,56] Such stresses may also account for our observed isotopic relationships (and minimal PBDE burdens detected) in our wolf spider composites.

McNabb et al.[54] measured $\delta^{13}C$ and $\delta^{15}N$ enrichment in wolf spider (*Pardosa* spp.) size classes within a similar (but not sludge-amended) temperate agroecosystem and found no changes in $\delta^{15}N$ signatures as juveniles matured to adulthood. However, increased $\delta^{13}C$ enrichment with growth was observed in that study. We observed comparable changes in $\delta^{13}C$ enrichment with size in wolf spiders at our sludge-amended site. They also noted $\delta^{13}C$ and $\delta^{15}N$ enrichment in ground beetles comparable to wolf spiders, reflective of shared predaceous feeding habits. Here, $\delta^{15}N$ enrichment in sludge-amended ground beetles was not significantly different from that in the wolf spiders in size class 3, but $\delta^{13}C$ enrichment was higher, suggesting some overlap of trophic status. $\delta^{15}N$ enrichment in woodlice, millipedes, and crickets was similar, but $\delta^{13}C$ enrichment among these taxa varied. Interestingly, $\delta^{15}N$ enrichment was similar in firefly larvae, ground beetles, June beetle adults, crickets, and worms. Though comparable enrichment among predaceous taxa is consistent with their ecology, similar $\delta^{15}N$ enrichment in crickets and earthworms is more difficult to explain.

$\delta^{13}C$ and $\delta^{15}N$ are increasingly measured in bioaccumulation studies to assess impacts of trophic status on uptake. For example, Walters et al.[42] found that total PCB burdens were significantly correlated with $\delta^{15}N$ (positively) and $\delta^{13}C$ (negatively) in spiders from a contaminated riparian ecosystem. In a related study of a contaminated riparian system, $\delta^{15}N$ enrichment in upland web building spiders (Araneidae) and terrestrial insects was more consistent with our reference site arthropods.[43] In contrast to the Walters et al.[42] findings, however, our arthropod $\sum_{3-7}$PBDE burdens were poorly correlated with $\delta^{13}C$ and $\delta^{15}N$ ($\delta^{13}C$ r^2 = 0.35, $p < 0.17$; $\delta^{15}N$ $r^2 = 0.0018$, $p < 0.93$) (Figures S1, S2), as were our computed BSAFs (data not shown). However, it is interesting to note that the PBDE burdens (82 and 1690 μg/kg lipid for $\sum_{3-7}$PBDE and BDE-209, respectively) in our single wolf spider composite (size class 2) exhibited maximum $\delta^{15}N$ enrichment, consistent with the positive correlations between total PCB and $\delta^{15}N$ in spiders (including the closely related *Dolomedes* spp.) reported by Walters et al.[42]

Our findings indicate that soil contact is likely more important than trophic status in determining PBDE accumulation in soil invertebrates inhabiting this sludge-applied site, and that sludge-associated PBDEs are entering this soil food web. However, because of the difficulty in sampling some targeted arthropod taxa and the minimal PBDE burdens exhibited by wolf spiders, we are unable to draw definitive conclusions regarding the extent to which trophic transfer of sludge-associated PBDEs may be occurring therein. Additional studies of the wolf spider population at this site are clearly needed to reconcile our anomalous observations of minimal PBDE accumulation in these top macroinvertebrate predators.

ASSOCIATED CONTENT

Supporting Information

Additional details on analytical methodologies; quality assurance/quality control (QA/QC); and supplemental experimental details, results, discussion, and references, as well as supporting Tables S1−S3 and Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interests.

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