

DETERMINATION OF POLYBROMINATED DIPHENYL ETHER SOIL LEVELS AT A FIRE FIGHTER TRAINING STATION AND ALONG RAILROAD TRACKS

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Abstract

Analysis of the PBDE content of soils from remote rural areas along railroad tracks and from a fire fighter training site demonstrated contamination of the soil, particularly at the latter site where BDE-47, -99, -100, -153, and -154, were found at considerable levels. The remote sites, along old railway tracks, showed minimum contamination (highest congener, BDE-47 ~1,600 pg/g) when compared with the burn site (highest congener BDE-99 ~90,000 pg/g). The remote sites had a slightly different congener distribution with BDE-47 present in the highest concentration resembling the reports for air samples. The surface sample at the training site (0-5 cm) showed more than ~5 times higher concentration levels than the subsurface samples (5-15 cm). The PBDE levels decreased as distance from the burn site increased, with the rate of decrease being nearly the same for all congeners. The presence of BDE-183, a marker for the octa formulation, was detected, but the concentrations were low and highly variable indicating a different source from the penta formulation.

Introduction

Polybrominated diphenyl ethers (PBDEs) are utilized as flame retardants and have been demonstrated to be ubiquitous environmental contaminants. The three major formulations of PBDEs used are pentaBDEs, octaBDEs, and decaBDEs. Because of their physical-chemical similarity to other persistent organic chemicals and similarities to various biologically toxic compounds (ie dioxins and PCBs), their accumulation in the environment is of concern. The usual pollution sources are industrial enterprises either manufacturing the PBDEs or when PBDEs are incorporated into various manufactured goods, ie electronics, textiles or various foams used in furniture manufacture. The manufactured goods form a secondary but significant point of contamination as they are degraded or disposed of. A significant portion of the pollution is carried by air and airborne particles with which the highly lipophilic PBDEs are combined and deposited in soil worldwide. Early uses primarily involved the penta formulation, but as its mobility in the environment became known its use declined both from voluntary discontinuances and statutory regulation. However, because of the large amounts of PBDEs incorporated into manufactured goods, any decline in environmental levels will occur slowly. Significantly large amounts of PBDEs have been utilized in North America then in Europe and as consequence reported body burdens in the US are 20 times higher than the European burdens¹, the monitoring of these compounds is of special interest.

Congener specific assays provide information concerning the source of the PBDEs as well as any changes in the composition produced by processes which show differences between the congeners. The congener patterns present are quite different for the different formulations enabling certain congener or congener pattern to be used as biomarkers to identify sources of pollution.² Minor congener differences do occur in the material from the air filters relative to the floor dust collected from vacuuming where the air filters were enriched in the more volatile congeners (ie BDE-47).³

The purpose of this study was to analyze potential contamination from burning objects at a fire fighter training station. By sampling soil at different directions and distances from the burn site, a measure of the localization or delocalization of the pollution could be obtained.

Materials and Methods

Soil collections. A facility where furniture and other combustibles were burned for training firefighters was chosen as the soil sampling site. Soil samples (0-15 cm) from different directions at different distances (ie 0, 3, 6, 9, or 12 ft) from the burning site were collected in July 2005. In May 2006, top soils (0-5 cm) as well as 5-15 cm soils were collected at the same facility with collection distance extended to 34 ft from the burning site. In addition, 4 different sites along old railroad tracks where pentachlorophenol treated wood was used and dioxins levels were elevated were used as comparison sites. The soil samples were dried, ground, and sieved

through a 2 mm screen and stored in the dark at room temperature until analyzed.

Soil sample cleanup. Into a 20 mL glass scintillation vial with Teflon lining cap, 1g (or 0.1 g if levels were high) of soil was weighed and 10 μL of ^{13}C labeled internal standards were added at the following concentrations: 200 $\text{pg}/\mu\text{L}$ for BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183; 400 $\text{pg}/\mu\text{L}$ for BDE-197 and BDE-207, and 2000 $\text{pg}/\mu\text{L}$ for BDE-209. To each vial 10 mL of toluene:acetone (70:30) was added and the slurry was sonicated for 1 hr. The solvent was decanted through funnels containing 20g of pre-wetted sodium sulfate/glass fiber filters. The soil samples were extracted 2 more times using 5 mL fresh toluene:acetone (70:30) and sonicated for 30 minutes each time. The filtrates were combined and concentrated to about 0.5 mL. After addition of 5 mL of hexane to each tube the sample was filtered through a high density polyethylene filter and loaded onto columns (an acid/neutral/basic silica column followed by an alumina column) for an automated cleanup procedure (Fluid Management System Waltham, MA). To the concentrated eluant (~ 0.5 mL), injection standards (1.5 ng of $^{13}\text{C}_{12}$ BDE-77 and BDE-139, and 3 ng of $^{13}\text{C}_{12}$ BDE-205) were added and the sample concentrated in dodecane to a volume of 20 μL , with 2 μL samples being injected into the GC.

GC-MS analysis. A Hewlett Packard 5890 gas chromatograph coupled to a VF Autospec mass spectrometer was used to analyze the soil samples. The isotope-dilution GC-MS method for PBDE congeners' quantitation was similar to the publication described by Huwe et al⁴ with the following changes: 1). The GC temperature program was 120-330 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$ ramp with an initial 2 min hold and a final 25 min hold.; 2). A 6 points standard calibration curve with expanded range of concentration was used. The range of mono- to tetra-BDEs was 2–500 $\text{pg}/\mu\text{L}$; penta & hexa BDEs 3-750 $\text{pg}/\mu\text{L}$, hexa BDEs 4-1000 $\text{pg}/\mu\text{L}$, hepta BDEs 5-1250 $\text{pg}/\mu\text{L}$, octa- and nona BDEs 8-2000 $\text{pg}/\mu\text{L}$, and deca-BDEs 80-20,000 $\text{pg}/\mu\text{L}$. 3). Relative response factors were calculated based on $^{13}\text{C}_{12}$ –BDE-77 for mono- to tetra- BDEs, $^{13}\text{C}_{12}$ –BDE-139 for penta- to hepta- BDEs, and $^{13}\text{C}_{12}$ –BDE-205 for octa- to deca- BDEs., and 4) The mass units resolution was set at 5000. The amounts of each congener were obtained by automatic calculation using the instrument software OPUSquan version 3.6.

Results and Discussion

A substantial amount of pentaBDEs used as flame retardants are found in polyurethane foam in furniture and car seats as well as various textiles while octa-BDEs are found in the polystyrenes used in televisions and computers⁵. The soils near a facility where furniture and other combustibles were burned for training firefighters was selected as the soil sampling site because BDE contamination could be expected. The purpose of this study was to find out how depth and distance affect the distribution of PBDE congeners from their origin.

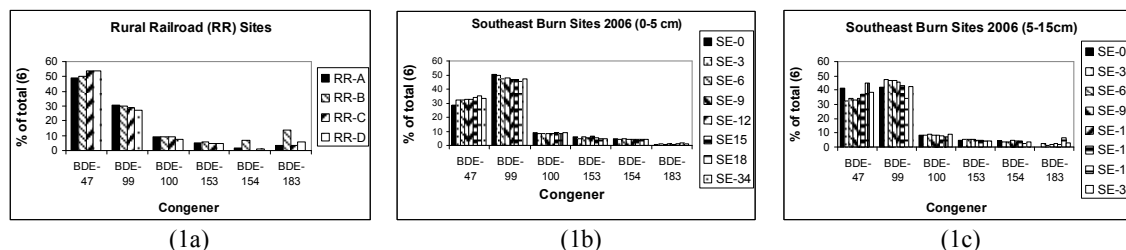
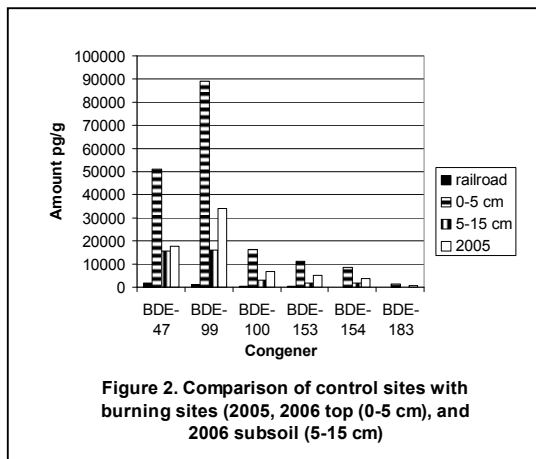


Figure 1. Percent of the total BDE-47, -99, -100, -153, -154 and -183 from railroad sites (1a), the 2006 top soil (0-5cm) from burn site (1b), and the 2006 sub-surface soil (5-15cm) from the burn site to the south east (SE) from the burn site.

Figure 1 shows the results of the study expressed as percent of the total of six congeners prevalent in environmental samples. Figure 1a is from various railroad sites that were remote from major cities along railway tracks that we utilized as a comparison because no obvious source close to the sampling site was releasing PBDEs. Figure 1b and c are the results of samples taken in a south eastern direction from the burn site at distances ranging from 0 to 34 ft from the concrete burning site. It is apparent the percent composition for the burn site differs from the remote sites. The different composition with the much higher amounts (Figure



rural sites showed a lower ratio that is more typical of air sampling, although more work is needed to establish the origin of these sites' contamination.

Figure 2 shows the amounts in the surface sample (0-5 cm.) were much higher than the subsurface sample (5-15 cm). In addition, both samples from the burn site were considerably higher than the railroad site. The difference in composition, particularly the much higher composition of the more volatile BDE-47 strongly implies quite different sources of pollution of the railroad site and the burn sites. The presence of higher concentrations of the more volatile component could indicate the source of pollution being air carried. Indeed the distribution is similar to that in a previous study.⁷ The values found in 2005 are lower than the surface samples obtained in 2006 principally because the 2005 samples included some subsurface material. The weighed average demonstrated the 2006 data showed higher amounts for BDE-47 with the other congeners slightly higher (within 20%) than the theoretical ratio of 1.0 indicating minimal change.

The burning site was a concrete slab and the most likely method of distribution would be through the air or through washing of the concrete slab either by rain or cleanup operations. Because the area surrounding the slab is flat, the water drainage would be somewhat random and could result in high levels of pollution away from the zero distance site. This is evident in figure 3. However, the falloff with distance is also evident and when modeled by an exponential function shows a reasonable fit. The consistency between congeners is also evident in figure 3.

The measurements for BDE-183 demonstrated small amounts for all but one sample. The surface sample at the burn site showed values ranging from 285 to 1287 pg/g, the deeper sample at the burn site showed values ranging from 53 to 250 pg/g, and the railroad sites were from 17 to 297 pg/g. The decrease with distance from the burn site could be qualitatively observed, but showed difference in the five congeners from the penta formulation (figure 3). The subsurface soil samples at the burn site showed more randomness and the values were close to those at the rural (railroad) sites. This data is difficult to interpret, but it appears BDE-183 does not significantly migrate downward as much as the congeners from the penta formulation, at least at the concentrations found at the burn site.

2) present at the burn sites makes it clear that latter sites were being contaminated by the burning objects or chemicals released from the burning; also, the congener pattern remains consistent with distance from burn site. Comparison of the surface soils (0-5 cm) and the subsurface soils (5-15 cm) indicate the subsurface samples were more variable but very similar to the surface samples with a small decrease in the more volatile BDE-47. The BDE-47, -99, 100, 153, and 154 are the five major congeners found in the pentaBDE formulation and Hassanin et al⁶ reported that because the relative abundance found in soils is similar to the pentaBDE formulation, this formulation is responsible for the soil contamination. The abundance of BDE-47 to BDE-99 ratio was ca 1: 1.8; similar to our observation, (1: 1.46 for 0-5 cm and 1:1.20 for the 5-15 cm). The

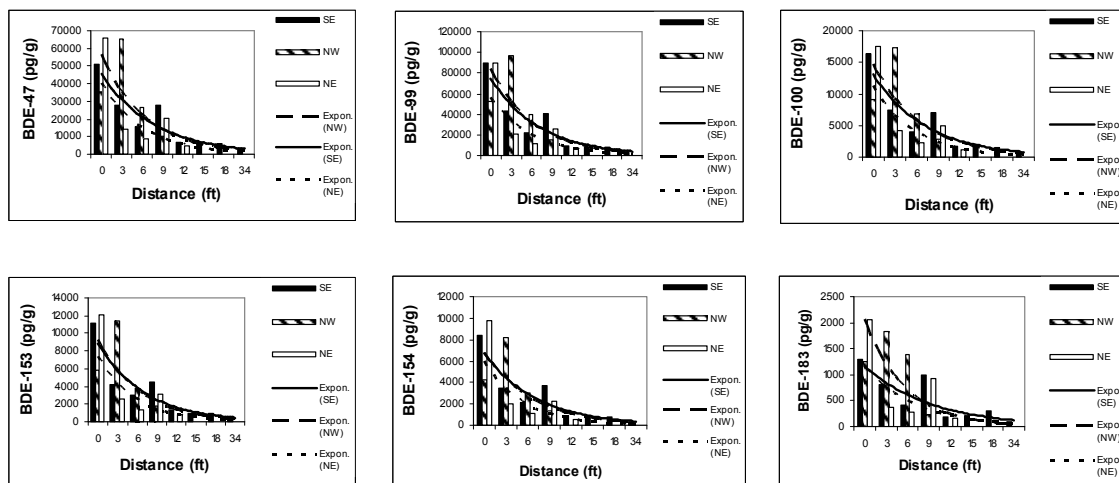


Figure 3. The amounts shown as a function of sampling distance for all three directions and for congeners BDE-47, 99, 100, 153, 154, and 183. The lines represent the fit of an exponential decay function for each of the three sites.

In conclusion, congener specific analysis has demonstrated pollution at a site where PBDE containing objects are burned. The contamination decreases rapidly with distance and the rate of decrease is essentially the same for all congeners used as markers for the penta formulation of BDEs. Some differences occur for BDE-183, a marker for the octa formulation. Although BDE-183 was found at both the rural sites and the burn site, the amounts are smaller than congeners from the penta formulations, probably because the current sites are not major deposits of electronic waste. Even in sites remote from urban areas, PBDE contamination can easily be measured although the composition is clearly different from our burn site and the amounts much lower.

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Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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