Polybrominated Diphenyl Ethers in US soils.

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Introduction

In 2004, Hites summarized concentrations of polybrominated diphenyl ethers (PBDEs) in various environmental media and reported that over the past thirty years total PBDE concentrations in human milk, blood and tissue have increased by a factor of approximately 100 [1]. Furthermore, PBDE concentrations in human serum, adipose tissue, and breast milk have shown that PBDE levels are nearly 20 times higher in North American individuals than those from individuals in Europe[1]. Recent work on North American indoor environments has suggested that dietary exposure of household dusts may constitute a significant route of exposure, especially to children[2, 3].

In addition to indoor dusts, surface soils may also present an opportunity for assessing the environmental concentrations of PBDEs. Concentrations of PBDEs in various surface soils have only been reported in one study of UK and Norwegian soils[4]. Other than a single report of concentrations in two soil samples outside a former polyurethane foam manufacturing facility, no concentrations of PBDES in US soils have been reported[5].

The objective in this study was to measure for PBDE concentrations in surface soils of the United States. In this study, we analyze 33 soil samples from fifteen states across the United States for PBDEs. These are the first reported concentrations of PBDES in US soils from a broad range of geographic locations.

Materials and Methods

Concentrations of thirty polybrominated diphenyl ethers were measured in more than thirty soil sample from across the United States. Samples of convenience were collected between January 2004 and December 2005, and were received from the various sources sealed in airtight polyethylene bags. Debris was removed, and soils were sieved to 2 millimeter sieve size. The soil samples were extracted and analyzed following the method developed by Stapleton et al. [2] for analysis of PBDEs in dust samples.

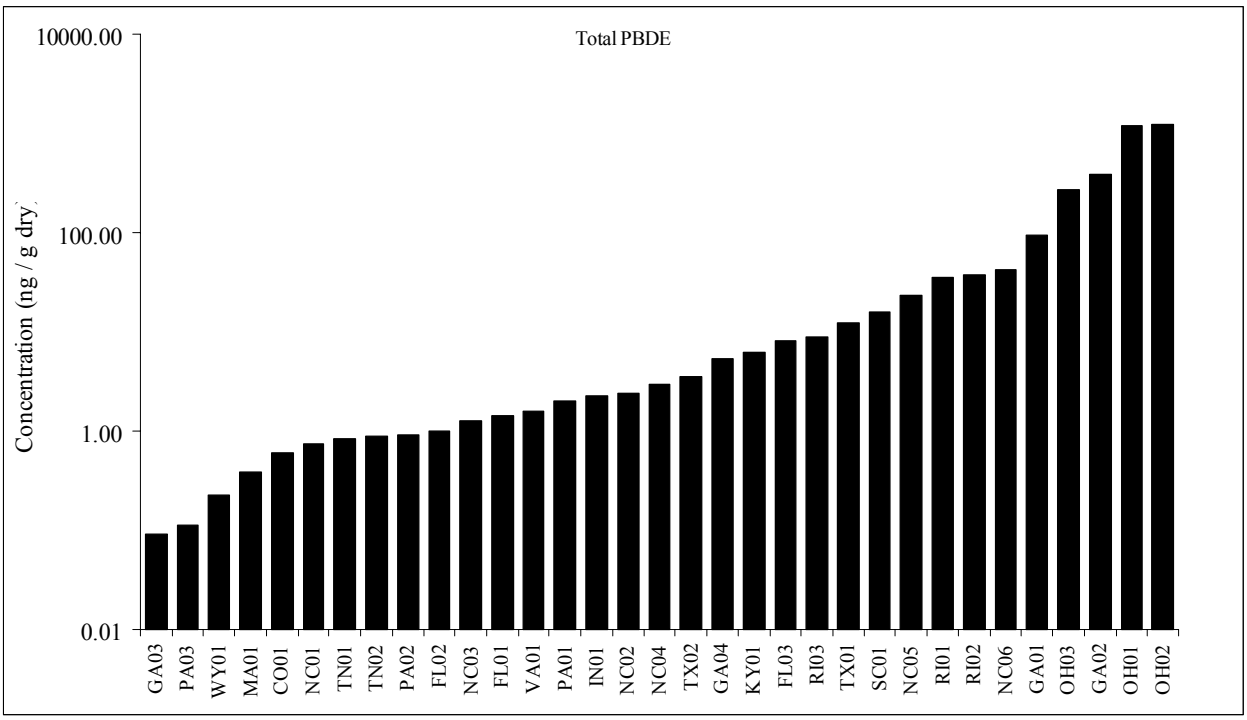
Briefly, approximately 1 to 2 grams wet weight of soil was extracted in DCM and after clean-up, soils were analyzed using an Agilent 6890 series gas chromatograph coupled to an Agilent 5975 mass spectrometer. Prior to extraction, a 13C-labeled BDE 209 (Wellington Laboratories, Guelph, Ontario) and a monofluorinated brominated diphenyl ether, FDE160 (Chiron A.S., Trondheim, Norway), were added to each sample as internal standards. Quantification of BDE congeners was performed using negative chemical ionization and was operated in the selected ion monitoring mode. All BDEs were quantified using ions 79 and 81 (bromide ions) except BDE 209, which was monitored with ions 487 and 409. The 30 BDE congeners quantified are as follows: 17, 25, 28, 30, 33, 47, 49, 66, 71, 75, 85, 99, 100, 116, 119, 138, 153, 154, 155, 156, 183, 196, 197, 201, 202, 203, 206, 207, 208 and 209. A 15m, 0.25mm (i.d.) 5% phenyl-methylpolysiloxane capillary column (0.25-µm film thickness; J & W Scientific) was used for the separation of the BDE congeners, and all injections were performed by on-column injection. The inlet was programmed to follow the oven temperature program which was 80 °C for 2 min, then increased at a rate of 15 °C/min to 230 °C, then 7 °C/min from 230 °C to 290 °C followed by a hold at 290 °C for 25 min. The ion source was held at a constant temperature of 200 °C, the quadrupole was held at 100 °C, and the transfer line was held at 290 °C. The method detection limit (MDL)

for the PBDE congeners ranged from 0.058 ng/g dry mass (for BDE 153) to 0.21 ng/g dry mass (for BDE 209). Only concentrations greater than the method detection limits are reported here.

Results

Concentrations of total PBDEs in thirty three soil samples ranged from 0.09 to 1200 ng /g dry weight. PBDEs were observed in every soil sample. Total concentrations of PBDEs are shown in **Figure 1**. Concentrations of total PBDEs averaged 103 ± 296 ng / g dry (± 1 standard deviation), with a geometric mean concentration of 5.3 ng /g dry.

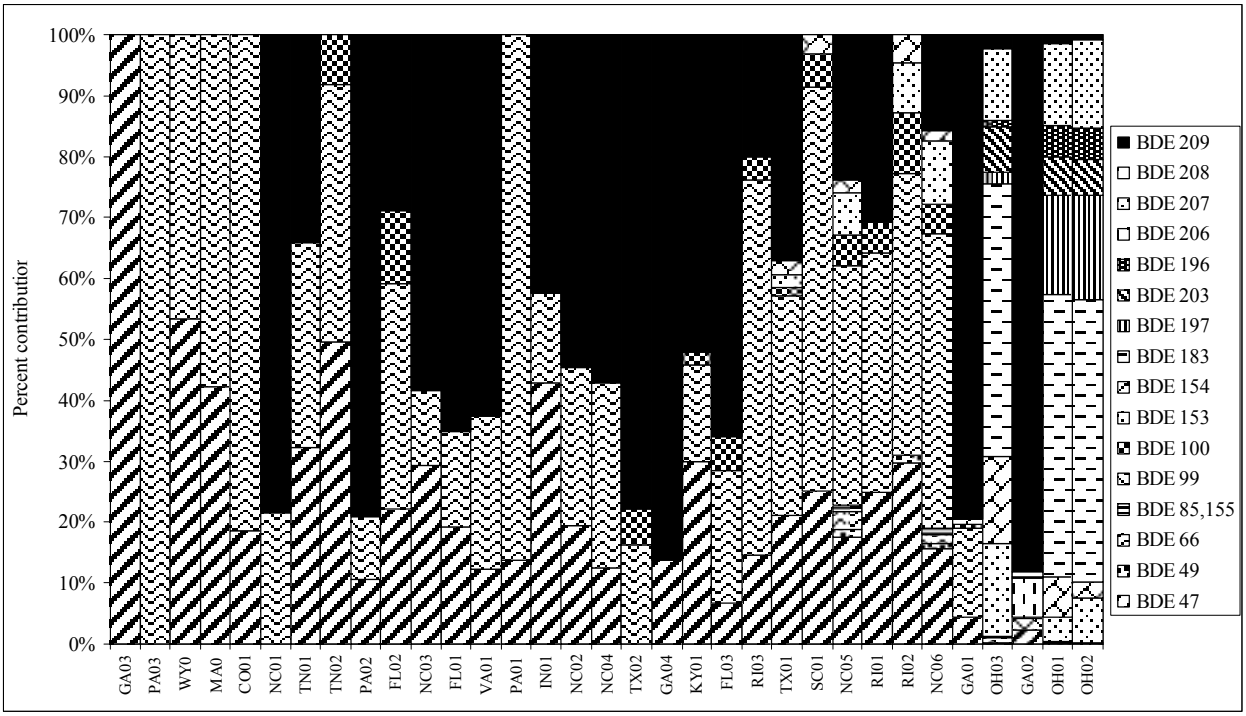
Figure 1. Concentrations of total PBDEs in thirty-three US soil samples, arranged in order of increasing concentration (ng / g dry).



BDE47 was the most frequently observed congener, measured in 31 of 33 samples, followed by BDE99, which was observed in 30 samples. The concentrations of these two congeners averaged 2.1, and 3.9 ng / g dry.

BDE209 was measured in 24 of the samples. The concentration of BDE 209 averaged 21.1 ng / g dry. Concentrations of BDE209 ranged from 0.3 to 342 ng / g dry, and had a geometric mean concentration of 3.2 ng / g dry. Across all samples, BDE 209 was the congener measured at the second highest concentration, and was observed in 73 % of the samples analyzed. The congener measured in the highest concentration across all samples was BDE 183, for which concentrations ranged from 121 to 562 ng / g dry, but was only observed in three samples. For congener distributions in these thirty-three samples see **Figure 2**. Seventeen of the 30 congeners analyzed were observed in these US soil samples, with 13 congeners not observed in any sample. Congeners that were not observed in any sample include BDE numbers: 17, 25, 28, 33, 71, 75, 116, 119, 138, 156, 201, and 202.

Figure 2. Fractional contributions of PBDE congeners to measured concentrations for thirty three US soil samples.



For comparison, PBDE concentrations in surface soils across a latitudinal transect of across the United Kingdom and Norway ranged from 0.065 to 12 ng / g dry for the twenty two congeners analyzed by Hassanin, et al.[4]. Norwegian soils ranged from 0.13 to 3.0 ng / g dry and averaged 0.97 ng / g dry. UK woodland soils ranged from 0.11 to 12 ng /g dry and averaged 2.5 ng / g dry. The highest concentration of PBDEs measured in these US soils is a factor of one hundred times higher than the highest concentration measured in UK, of 12 ng / g dry.

One prior report of PBDE concentrations in US soils outside a polyurethane foam manufacturing facility reported total PBDE concentrations of 13600 ng / g dry. Another soil sample from the same location contained less than 300 ng / g dry [5].

Omitting the five highest concentration US soil samples, PBDE concentrations in the remaining 28 samples analyzed in this work averaged 7.9 ± 12.2 ng / g dry, with a maximum value of 43.1 ng / g dry. These twenty-eight samples had a geometric mean concentration of 2.4 ng / g dry. The average concentrations of PBDEs in these twenty-eight US soil samples is a factor of three times higher than UK soils, and a factor of 8 times higher than Norwegian soils.

Acknowledgements

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

References

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