PBDE CONTAMINATION OF SOIL FROM WEATHERED OUTDOOR COMPUTER SCRAP

Orazio CE[1], Peterman PH[1], Feltz KP[1], Menneke MH[2]

[1]U.S. Geological Survey, Columbia Environmental Research Center, 4200 New Haven Road, Columbia, MO USA 65201; [2]Missouri Department of Natural Resources, Hazardous Waste Program, P.O. Box 176, Jefferson City, MO USA 65102

Introduction

Flame retardants are incorporated into the polymeric materials of electrical and electronic equipment (EEE) to reduce the risk of fire. Tetrabromobisphenol-A (TBBPA) and polybrominated diphenylethers (PBDEs) are major brominated flame retardants used in EEE, constituting about 1% of the EEE plastics. The three commercial PBDE mixtures, Penta, Octa and Deca have been added to numerous polymers since the 1970's[1]. There are 209 possible PBDE congeners but due to factors driving the bromination of diphenyl, few actually comprise the commercial mixtures. Deca is about 98% congener 209 (fully brominated), while Octa contains mostly hexa-nona brominated PBDEs and Penta contains primarily tetra-hexa brominated PBDEs. TBBPA is typically chemically reacted with the polymer during manufacture, whereas the PBDEs are blended in (additive) and thus are not covalently bound. TBBPA is used in circuit boards while PBDEs are in various plastics. Penta has been added to polyurethane foam and other polymers, while uses of Octa include ABS plastic housing of EEE. Deca PBDE is used in high impact polystyrene housings for EEE, including TV sets and computers. PBDEs can bleed and volatilize from the polymer product[2]. Rising levels of PBDEs have been reported in sediments, soils, indoor air, dust, foods, human tissues, fish and wildlife[3].

Management of waste EEE is a growing international issue. Each year in the United States alone, approximately 30 million computers are discarded, dumped in landfill, recycled or incinerated. Recycling operations typically store the computer scrap indoors prior to dismantling, however in some cases, storage occurs in the outdoors. In such cases, exposure to direct sunlight, rain and elevated temperatures may accelerate the release and transport of PBDEs into the air, soil and nearby aquatic environments. We conducted a study to determine if PBDEs were leaching from computer scrap stored outdoors. We measured PBDE congener concentrations in soil and sediments of a field stacked with 15,000 scrap computer systems that had been exposed to the outdoor elements four to five years.

Materials and Methods

The field of computer scrap, located in rural central Missouri farmland, USA contained various ages of computers, printers, CRT monitors, and electronic typewriters ranging from late 1970's to late 1990's models. The closely stacked computer scrap piles ranged in height from 1-2 meters and stretched a distance of approximately half a kilometer in length, with a width of 10-100 meters. The 3 acre computer scrap field was strewn along a bordering stream which receives runoff from the entire computer scrap field. The edge of the piles was as close as 5 meters from the stream. See diagram of the site in Figure 1. The annual rainfall in the area is about 90 cm. Sunny summer temperatures typically range from 30-40 degrees C.

Samples of soil and sediment were collected in July 2003 using clean, solvent washed stainless steel spoons. Five subsamples were taken of soil from an area and a composite made. Stream sediments were collected from a cross section of the stream and from five sites along the stream and compositied on site. Samples were homogenized by mixing for several minutes with the spoons. Special care was taken to eliminate contamination of the samples with PBDE containing plastics and dust that may be PBDE contaminated.

Sampling equipment was thoroughly cleaned between sites to avoid cross contamination. Sample jars with Teflon lined lids were kept sealed, airtight and in the dark prior to analysis.

The following samples were taken on the downhill edge of one area of the computer scrap field:

1. Soil wiped with dry glass fiber filter from monitor casing (unexposed to sun)
2. Soil 0-5 cm deep at end of computer field, underneath monitor (unexposed to sun)
3. Soil (0-5 cm deep) from sun-exposed area one meter from the edge of the scrap field.
4. Sediment composite of five areas of creek receiving runoff from scrap field.
5. Dry wipes of 6 sun-exposed monitors with glass fiber filter paper

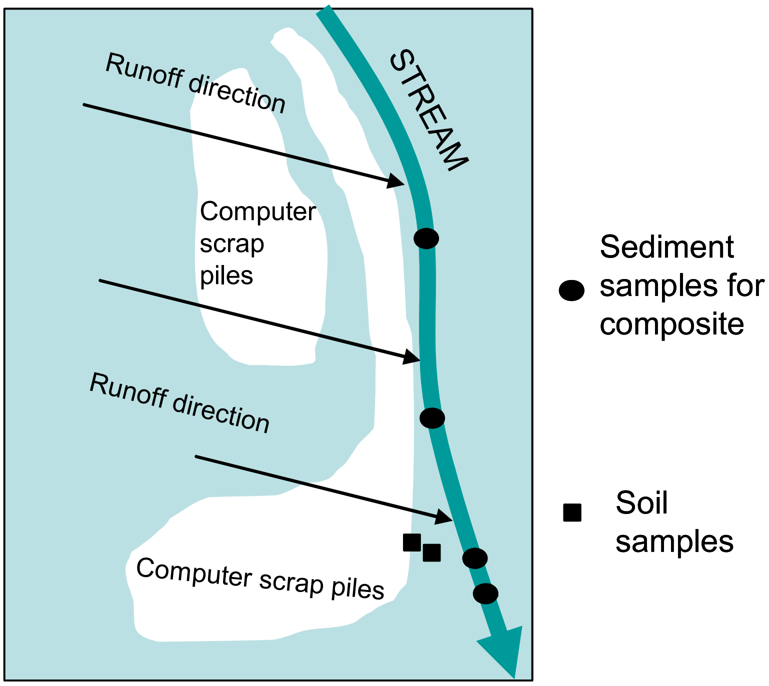

Figure 1. Diagram of computer scrap field sampling locations. Area of computer scrap piles is approximately 3 acres. Runoff (arrows) from field drains into stream. Stream is within 5-50 meters of scrap piles. This diagrammatic representation of piles shows computer scrap pile as white areas.

Quality control samples including blank solvents, sediment control blanks and filter blanks were carried along with the sample analysis. Samples were processed under reduced light or under gold lamps to reduce photolysis of the PBDEs[4]. In the lab, samples were dried with anhydrous sodium sulfate, spiked with isotope dilution ^{13}C-PBDEs standards, and extracted with dichloromethane in Soxhlet apparatus for 8 hours. Filter wipes of the computer surfaces were analyzed in the same manner. Extracts were concentrated and then cleaned up with low pressure GPC (Biobeads S-X3), high pressure GPC (Phenogel), and low pressure (0.5 bar) flash (40-63 µm, 3-g) silica gel column chromatography. After an initial 4-mL cyclopentane dump fraction, all PBDEs were collected in one eluate (15% MTBE in cyclopentane). Eluates at final volume were in nonane.

Gas chromatography with high resolution mass spectrometry (GC/HRMS) was used to measure PBDE congeners ranging from mono-deca brominated. All 40 PBDEs were resolved or nearly resolved (33 from 28) using a 45 m x 0.20 mm x 0.1 µm DB-5MS column (Agilent Corp) set at 400 kPa (55 psi). Five-µL injections (nonane) were made through a septumless Merlin Microseal into a heated (285 ºC) Siltek-treated (Restek Corp) Spiral Uniliner that was connected to a 2.5 m x 0.32 mm Siltek-treated retention gap to the capillary column. Temperature program was 155 ºC (1 min hold) to 175 ºC at 10 ºC/min to 340 ºC at 2 ºC/min (2 min final hold). An Agilent 5890A GC/Micromass 70S HRMS was calibrated with tris(pentadecafluoroheptyl)-s-triazine and acquired a total of seven groups of selected ions. Both molecular and $(M\text{-}Br_2)^+$ fragment ions for PBDEs and ^{13}C-PBDEs were measured. The PBDE $(M\text{-}Br_2)^+$ ions are exact molecular ions for brominated dibenzofurans (PBDFs), therefore possible PBDF photolysis products eluting within an ion group could be differentiated from higher brominated PBDEs by any absent PBDE molecular ions.

Results and Discussion

PBDEs were found in the soil samples taken at the down slope edge of the computer scrap field. Table 1 shows the concentrations (ng/g dry weight) of the PBDEs detected. The highest congener concentrations were found in soil underneath a last pile of computer scrap (soil, end of pile) at the downhill edge of the piles in the field. The soil layer scraped from the underside of a computer monitor contained different relative concentrations of PBDE congeners as seen in Figure 1. Deca-PBDE 209 was detected in the soil taken directly from the computer housing. The soil just one-meter from the edge of the piles of computers had lower concentrations and different patterns of PBDEs than the other two soil samples, indicating some movement of the PBDEs from the pile. Only PBDE 183 was detected (3 ng/g) in the composite of the stream sediments. This suggests limited movement of PBDEs from the field of computer scrap to the stream. The dry wipe of the six sun-exposed computer monitors contained no detectable PBDEs.

Table 1. Concentration (ng/g dry wt) PBDEs in Soils & Sediment, Computer Scrap Site

bromination	4	5	5	6	6	6	7	8	8	9	10
congener #	47	100	99	154	153	138	183	196/7	203	207	209
Soil on monitor case	6	2	7	11	62	2.5	340	300	47	220	60
Soil, end of pile	22	6.6	30	55	270	12	1,500	300	52	320	<10
Soil meter from pile	16	6.4	30	5	12	0.7	55	5	0.6	2	<10
Stream sediment	<2	<0.4	<1.5	<0.3	0.7	<0.2	3	<0.2	<0.2	<0.5	<10

PBDE 183 was very high (1500 ng/g) in the soil from underneath the last of the scrap computers at the downhill edge of the scrap field but much lower in the soil that was adhering to the bottom casing of the monitor. The high concentration of PBDE 183 and smaller equal levels of PBDEs 153 and 207 generally matches the relative composition pattern in the technical Octa PBDE mixture. The detection of deca-PBDE 209 in the other soil sample suggests both Octa and Deca mixture sources. In the stream sediment composite, PBDE 183, a major component of the Octa formulation, was the only detectable PBDE.

Although the extent of this sampling of the computer scrap field was somewhat limited, the soils and sediments sampled indicate that PBDEs in the computer scrap have leached PBDEs from the computers into the soil beneath them. Movement of the PBDE contamination from the computer area via soil erosion (particle bound transport) seems to be limited. The lush growth of field grass likely reduces erosion of the contaminated soil and limits contamination of the nearby stream sediment (bank and streambed). Transport of PBDEs in the dissolved phase is likely to be limited, based on the very low water solubilities of the PBDEs.

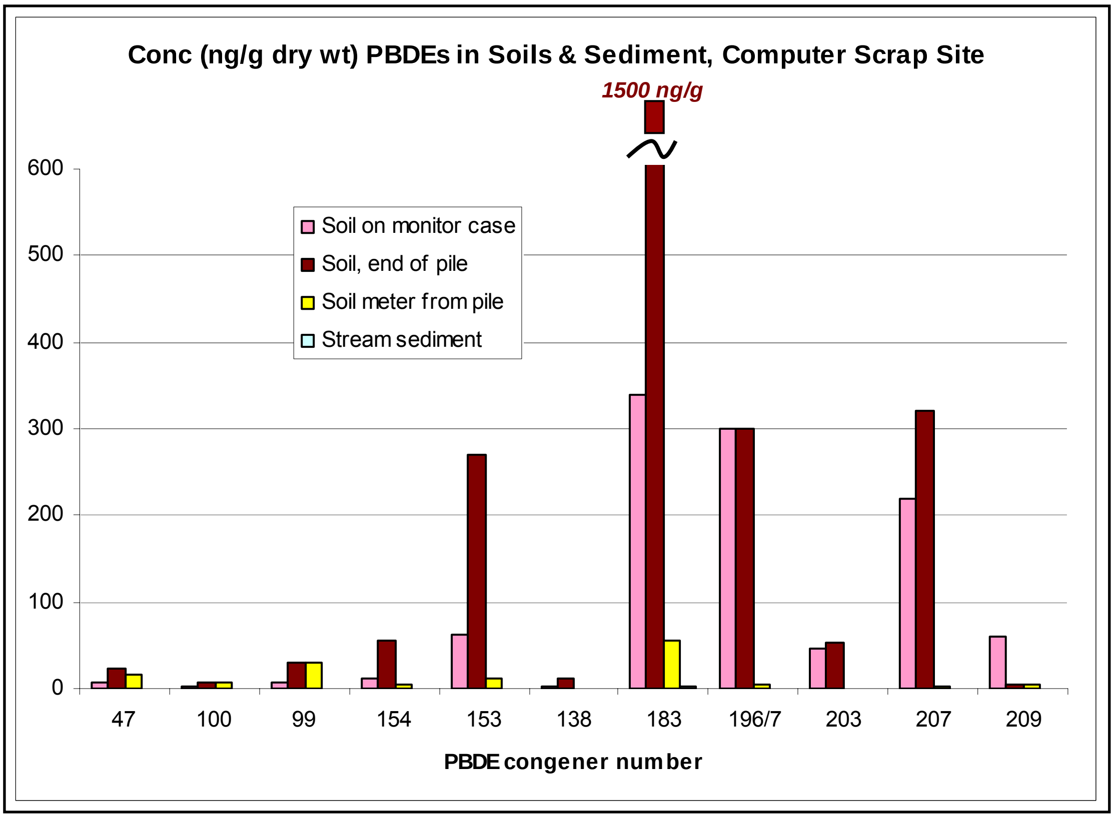

Figure 2. Concentrations of PBDEs (ng/g dry wt) in soils and sediments sampled from the computer scrap site in central Missouri, USA July 2003.

Release of the PBDEs from the computer scrap polymers is likely the result of outdoor heating of the computer plastics, oxidation and aging of the plastic from sun exposure of the top layer of the piles, and rain wash-off to the soil below. In addition, dust from the computer captured during use indoors may contribute, to an unknown extent, to the PBDE soil contamination. PBDEs volatilized into the air from the heated surfaces of the computer scrap cases are a likely release of PBDEs into the environment however this transport mechanism was not measured in this study.

Acknowledgements
We appreciate the support of this study by USGS and DNR personnel.

References

1. Alaee M, Arias P, Sjödin A, Bergman Å. *Environ Intl* 2003;29:683-689.
2. Watanabe I, Sakai S. *Environ Intl* 2003;29:665-682.
3. De Wit CA. *Chemosphere* 2002;46:583-624.
4. Peterman PH, Orazio CE, Feltz KP. *Organohalogen Compounds* 2003;63:357-360.