Assessment of PBDEs in spruce needles and air surrounding the Trail Waste Facility in Ottawa, Ontario, Canada

Annick D. ST-Amand[1], Paul M. Mayer[1] and Jules Blais[2]

[1]Department of Chemistry, University of Ottawa, Ottawa, ON, K2C 1N5
[2]Department of Biology, University of Ottawa, Ottawa, ON, K2C 1N5

Polybrominated diphenyl ethers (PBDEs) are flame retardants used during the manufacturing process of a variety of electronic devices, plastics and fabrics in order to increase their fire resistance. Three commercial formulations are available: PentaBDE (mainly BDE-47, BDE-99 and BDE-100), OctaBDE (BDE-153 and BDE-183) and DecaBDE (BDE-209) [(1,2)]. Several studies have shown that PBDEs are present in areas as far away as the arctic, and that their concentration is increasing rapidly [(3,4)]. A recent model showed that vegetation likely plays an important role in the long-range atmospheric transport of PBDEs [(5)]. However, few long-term atmospheric studies have been done, and data for PBDEs in vegetation are sparse [(5,6)].

The objectives of this study are to develop an efficient method for the extraction of PBDEs from spruce needles, assess PBDEs concentrations in spruce needles and air (volatile and particulate-bound) near the Trail Waste Facility in Ottawa, Canada and eventually evaluate surface (needles) – air exchange during the course of a year.

Sampling was done at the Trail Waste Facility in Nepean, ON in February and March 2004. Norway spruce (*Picea Abies*) needles were collected regularly along with air samples. A modified high volume air sampler was run for approximately 24h, resulting in sample air volumes of about 1000m^3. Particulates were trapped on a Whatman glass microfiber filter (GMF) and volatile species were collected with two polyurethane foam plugs (PUFs) to assess breakthrough.

Two procedures were considered for the extractions of PBDEs in spruce needles: Sonication/Liquid-Liquid extraction and Accelerated Solvent Extraction (ASE). Extracts collected were then concentrated to approximately 1mL and subjected to a clean-up step with deactivated silica. Fractions collected with hexane were concentrated to 0.5mL. PUFs and filters were Soxhlet extracted for 16-18h with hexane and extracts were also concentrated to 0.5mL. All analyses were done with a GC-MS/NCI. The following PBDE congeners were quantified: BDE 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, and 190.

Although both extraction techniques did yield good recoveries for spiked material (usually better than 80%), efficiency of the sonication process to extract PBDEs from the waxy residue of the needles was questioned. ASE was chosen for this study because

several parameters could be optimized: solvent, pressure, temperature, and number and duration of static cycles. Preliminary investigations were done with a standard mixture of studied congeners and maximum recoveries of 80-95% were obtained for all congeners (except for BDE 17) with dichloromethane: hexane (1:1) at 1500psi with two 10min extraction cycles. An extraction temperature of 140°C was chosen because needles extracted at or above this temperature, were completely stripped of waxy residue, and temperature otherwise had little impact on PBDEs. Needle samples collected in February 2004 showed an average total PBDE concentration of 0.75ng/g dry weight or 35ng/g lipid. Not surprisingly, BDE 47 and 99 were present in highest concentrations.

Air samples collected in the same month show little concentration of volatile PBDEs. In fact, only BDE 28, 47 and 99 were present in the extract for a total volatile PBDE concentration of less than 1pg/m^3. Particulate-bound PBDE were found in much higher concentrations and almost all congeners could be quantified. Total particulate-bound PBDE concentration was from 3 to 24 pg/m^3. This could be due to a number of meteorological factors, including temperature and wind direction. At low temperatures, most PBDEs are bound to particulates. In general, the congener profiles were very similar between samples showing that presence of PBDEs at the Trail Waste Facility is due to commercial formulations.

1. de Wit, C.A., Chemosphere, 2002, **46**, 583-624.
2. Alaee, M. *et al*., Environ. Int., 2003, **29**, 683-689.
3. Hale, R.C. *et al*., Environ. Int., 2003, **29**, 771-779.
4. Ikonomou, M.G. *et al*., Environ. Sci. Tech., 2002, **36**, 1886-1892.
5. Gouin, T. and Harner, T., Environ. Int., 2003, **29**, 717-724.
6. Alaee, M., Environ. Monit. Ass., 2003, **88**, 327-341.