



# Dispersal patterns of polybrominated diphenyl ethers (PBDEs) in the vicinity of an automotive shredding and metal recycling facility

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## ABSTRACT

Concentrations of polybrominated diphenyl ethers (PBDEs) were determined in air samples from near a large outdoor automotive shredding and metal recycling facility and the surrounding local area. This was done using a combination of active air samplers (AAS) measuring particle-associated and vapor-phase compounds, and, for the first time, passive air samplers (PAS) consisting of polyurethane foam (PUF) deployed at high spatial resolution around the facility. AAS data showed average levels of  $\Sigma_{11}$ PBDE in the adjacent commercial precinct ( $439 \pm 222 \text{ pg m}^{-3}$ ) were on average a factor of 50 times higher than those in the residential area 1.5 km away ( $8.5 \pm 3.6 \text{ pg m}^{-3}$ ). In addition, the PBDE composition in air was different between the commercial and residential areas with quantifiable concentrations for eleven PBDEs (BDE-28, -47, -100, -99, -153, -183, -197, -196, -206, -207 and -209) in the commercial area. In contrast, only five of these congeners were detected in the residential area. Congener BDE-209 dominated the profile in air at both active air monitoring sites (i.e. commercial and residential) and was entirely associated with the particulate-phase, contributing on average 63% of the  $\Sigma_{11}$ PBDE mass in samples. Congener composition in PAS deployed across the field study area (16 km<sup>2</sup>) were also dominated by BDE-209 with this congener representing 75% of the  $\Sigma_{11}$ PBDE mass in samples, a proportion similar to that observed in active samples. The attenuation of  $\Sigma_{11}$ PBDEs in PAS vs. distance from the recycling facility was best fitted using an empirical exponential decay model ( $r^2=0.89$ ). Model results indicated the major wind direction plays only a minor role in determining the observed spatial distribution of PBDEs.

## Keywords:

Polybrominated diphenyl ethers  
Automotive shredding and metal recycling facility  
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## 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of persistent organic pollutant (POP) commonly employed as flame retardants. They are incorporated in many polymers and foams that are used in consumer furniture, automobiles and electronic products (Alaee et al., 2003; Schechter et al., 2005). There are concerns that PBDEs may pose a hazard to humans (Chao et al., 2007; Main et al., 2007) and the environment in general due to their toxicity (WHO, 1994). The listing of commercial pentabromodiphenyl ether (penta-BDE) and octabromodiphenyl ether (octa-BDE) as POPs under the Stockholm Convention has led to their gradual phasing-out of production and reduction in use in many countries. For example, Australia ceased importations of the penta-BDE and octa-BDE in mid 2000 (NICNAS, 2005). Despite these PBDE phase-outs the recycling industry, particularly electronic (E)-waste and automobiles represent substantial ongoing reservoirs for human and environmental exposure.

It has recently been reported that the global automotive industry produces approximately 50 million tons of waste each year (Guo et al., 2012). In Australia alone, it is estimated that over 500 000 end-of-life vehicles (ELVs) currently enter the waste stream in Australia each year (Environment Australia, 2002). Following the dismantling process to salvage any parts of economic value, the gutted vehicles (hulks) are either flattened by crushing, or sent directly (uncrushed) to a shredder facility. The shredding process separates the materials into three fractions: ferrous,

nonferrous, and automotive shredder residue (ASR). ASR comprises glass, rubber, plastics, fibers, dirt, and fines and is classified as a hazardous waste in Europe (Vermeulen et al., 2011). It typically contains relatively high concentrations of heavy metals (Nourreddine, 2007; Gonzalez-Fernandez et al., 2008) and POPs including, polychlorinated biphenyls (PCBs) (US EPA, 1991) and PBDEs (Sakai et al., 2006; Petreas and Oros, 2009). The relatively high PBDE levels in ASR of between 50 ppm (Petreas and Oros, 2009) and 300 ppm (Sakai et al., 2006) are a consequence of PBDEs being used extensively for flame retardation purposes during vehicle manufacture (BSEF, 2006).

While ASR is a key area of environmental concern in relation to ELVs, few studies have focused on POP emissions to the atmosphere during the actual shredding process of automobiles (Francois et al., 2004; Cahill et al., 2007). During the highly energetic shredding process PBDEs entrained in ASR may be released to the air, potentially contaminating the local area and broader atmosphere. In addition, such recycling processes may co-release aerosols providing the necessary transport mechanism for PBDEs restricted to the particulate-phase.

Although active air samplers (AAS) are a conventional tool for sampling POPs such as PBDEs in air, they are impractical for sampling at high spatial resolution as they require electricity and are not cost effective. In contrast, passive air samplers (PAS) are simple tools that provide time-integrated estimates of concentrations in air (Shoeb and Harner, 2002; Bartkow et al.,

2005). Because PAS are usable at many sites simultaneously and require no maintenance during deployment, they are useful for spatial surveys and related modeling. Several studies have used PAS on a meso-scale identifying PBDE urban-rural gradients (Gouin et al., 2005; Harner et al., 2006; Harrad and Hunter, 2006; Hearn et al., 2012). More recently, studies have used PAS to identify the source-receptor relationships in urban and industrial areas (Baek et al., 2008; Choi et al., 2008).

In this study active air samples were collected in commercial and residential areas in the vicinity of a large automotive shredding and metal recycling facility. In addition, PAS were deployed around the perimeter of the recycling facility and along transects extending approximately 2 km east, south, west and north of the site to investigate the spatial distributions in the local area. Levels of PBDEs accumulated in PAS were assessed on the basis of their distance from the recycling facility and associations with meteorological conditions.

## 2. Experimental

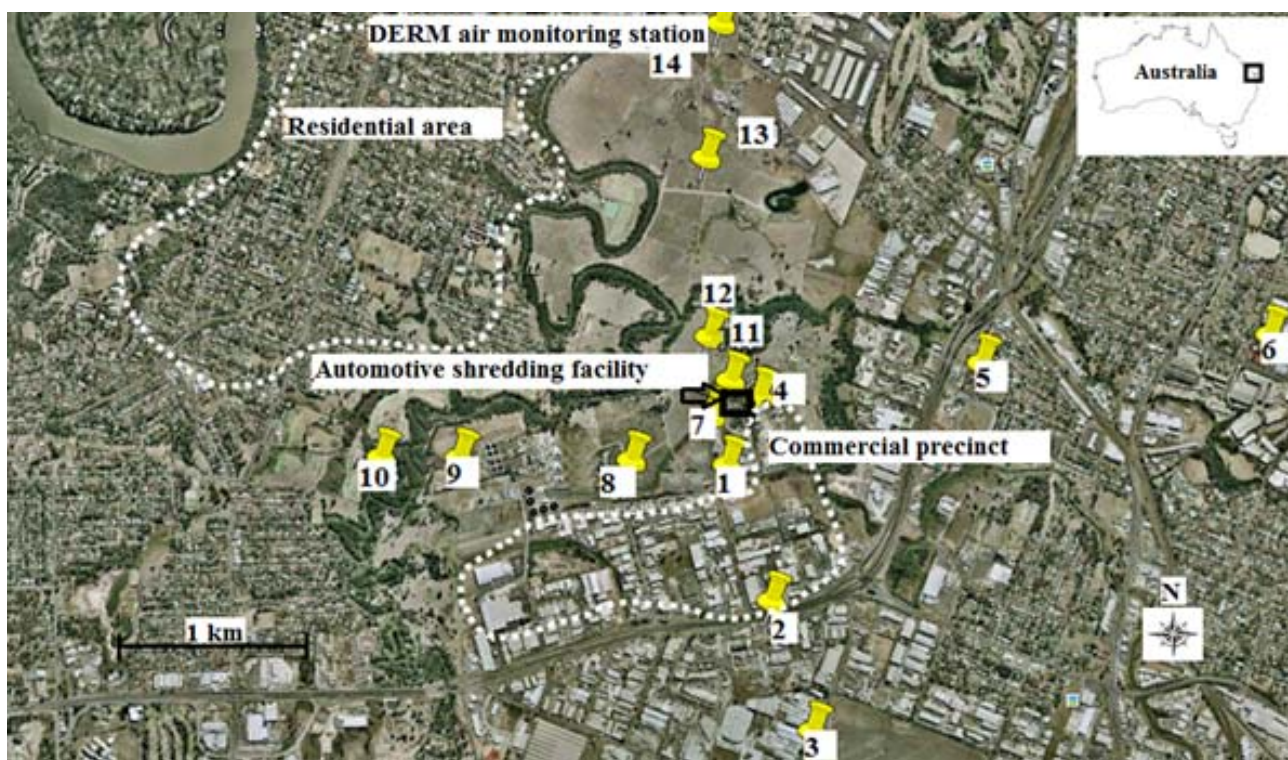
### 2.1. Sampling sites

The automobile shredding and metal recycling facility investigated in this study is the largest of its type in Brisbane, Australia. The entire operation is conducted outdoors and the facility is located in a main industrial region of Brisbane approximately 7 km SW of the central business district that contains a combination of light, general, heavy and extractive industries and covers an area of about 30 km<sup>2</sup>. A relatively large commercial precinct is located directly alongside the recycling facility on the southern perimeter and the nearest residential area is approximately 1.5 km WNW of the site (Figure 1).

Active air samples in the commercial precinct were collected from the yard of a business adjacent to the recycling facility. The sampler was within ~100 m of the actual shredder and is denoted as site 4 in Figure 1. In the residential area samples were collected from an existing air monitoring station which forms part of the citywide Department of Environment and Resource Management (DERM) air-monitoring network (denoted as site 14 in Figure 1). Additional meteorological data was also obtained from this air monitoring site. Also shown in Figure 1 are the additional 12 PAS sites which were located along 4 transects extending approximately 2 km east, south, west and north of the recycling facility and covered an area of approximately 16 km<sup>2</sup>. Geographic coordinates of all monitoring sites together with distance from the source are found in Supporting Material, SM (Table S1).

### 2.2. AAS

Low-volume active air samplers were deployed alongside PAS at site 4 in the commercial area and site 14 in the residential area during the main summer (2009–2010) sampling period. Air samples were collected using a filter-adsorbent active sampling system consisting of glass microfiber filters (GMF) (Whatman 90 mm (GF/A, 1.6 μm)) to collect particle-associated PBDEs and a glass cartridge filled with two PUF plugs (length 4.0 cm, diameter 3.5 cm, density 0.026 g cm<sup>-3</sup>) to collect vapor phase PBDEs. The two PUF plugs placed within the glass cartridge were in series with the second PUF plug used to assess any breakthrough of vapor-phase PBDEs. This cartridge was attached to a low volume pump (Gardner Denver V-VTE) and a gas meter was employed to determine the volume of air sampled. The sampler inlet (~1.5 m high) was oriented vertically with all particle sizes able to be sampled. No bias in particle size collected and by association, POPs associated with different particle size ranges is therefore expected.



**Figure 1.** Location of all air monitoring sites ( $n = 14$ ) in the field study area and the commercial and residential areas in relation to the automotive shredding and metal recycling facility. Map sourced and site locations identified using Google Maps.

In the commercial area, three active air samples were collected: 11–18 January, 2010 (742 m<sup>3</sup>); 28 Jan–05 Feb, 2010 (887 m<sup>3</sup>) and 16–23 February, 2010 (604 m<sup>3</sup>). The average sampling rate was approximately 4 m<sup>3</sup> h<sup>-1</sup>. In the residential area two active air samples were collected between 15–29 January, 2010 (748 m<sup>3</sup>) and 6–19 February, 2010 (712 m<sup>3</sup>). Because a lower volume vacuum pump was used at the residential site, samples were collected over a longer time period (*i.e.* 14 days) with an average sampling rate of approximately 2.2 m<sup>3</sup> h<sup>-1</sup>.

Prior to sampling, the GMFs were rinsed with acetone and placed in a furnace at 450°C for 24 h. Once removed, they were placed in foil envelopes that were previously rinsed with acetone. PUF plugs were pre-extracted using accelerated solvent extraction (ASE) (Dionex, 300) with acetone and hexane (20/80 v/v). They were dried under a stream of nitrogen and stored in cleaned amber glass jars prior to field deployment. All glassware was pre-cleaned, rinsed with acetone and wrapped in foil for transport to the sampling site.

### 2.3. PAS

PAS consisting of polyurethane foam (PUF) disks were deployed over two periods: spring (2008) between 22 September–4 November (43 days) and summer (2009–2010) between 10 December–28 February (81 days). PUF disks (Tisch, Environmental TE-1014; Area=3.62×10<sup>-2</sup> m<sup>2</sup>; Volume=1.95×10<sup>-4</sup> m<sup>3</sup>; Density=2.36×10<sup>4</sup> g m<sup>-3</sup>) were installed in a stainless steel sampling chamber (“flying saucer” design). In the preliminary spring (2008) PAS deployment, two PUF disks were installed in a single chamber at a limited number of sites (*i.e.* sites 4, 7 and 12) (see Figure 1) to assess reproducibility and the analytical error associated with the PAS method. During the more extensive PAS deployment in the summer (2009–2010) sampling period coinciding with AAS deployment, PAS were deployed at all 14 air monitoring sites (see Figure 1). Because results from the first PAS deployment for PAS reproducibility were considered satisfactory, only single PUF disks were installed in each chamber during the summer (2009–2010) sampling period. PUF disks were pre-extracted using the same method described above for PUF plugs and stored in cleaned amber glass jars prior to field deployment. At the time of sampling PUF disks were transferred from sample jars to the sampling chamber using gloves. After sampling the PUF disks were placed in their original containers and stored at temperatures below 5 °C until extraction.

### 2.4. Analytical methods

All samples were spiked with internal standards (<sup>13</sup>C<sub>12</sub>BDE–28, –47, –99, –153, –154, –183, –197, –207 and –209; Wellington Isotope Laboratories, Canada) prior to extraction. The GMFs, PUF plugs and PUF disks were then extracted by ASE using hexane/toluene (80/20 v/v) and the extracts purified using acidic silica (40% w/w) columns, topped with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Labeled BDE–138 was added to samples as the recovery standard immediately prior to analysis by HRGC–HRMS (HP 5890 II GC coupled to a VG AutoSpec mass spectrometer; splitless injection; injector temperature 320 °C). The lighter congeners (BDE–17, –28, –47, –49, –66, –71, –77, –85, –99, –100, –119, –126, –138, –153, –154, –156, –184, –183 and –191) were separated on a Rxi<sup>®</sup>–1ms column (20 m × 0.18 mm id, 0.18 mm film thickness) with ultra-high purity helium carrier gas; flow rate 1.0 mL min<sup>-1</sup>; temperature program 100 °C for 1 min, 30 °C min<sup>-1</sup> to 200 °C, 30 °C min<sup>-1</sup> to 350 °C and 350 °C for 1 min; total run–time 16 min. The mass spectrometer operating conditions were as follows: ion source and transfer line temperatures 340 °C and 360 °C respectively;

ionization energy 38 eV; electron multiplier voltage set to produce a gain of 10<sup>6</sup>. Resolution was maintained at 5 000 (10% valley definition) throughout the sample sequence. Selective Ion Monitoring (SIM) experiments were performed in the electron impact mode with monitoring of the exact masses of appropriate ions for native and labeled compounds.

### 2.5. Quality control

Field and method blanks (*i.e.* solvent blanks) were collected for both the active and passive air samples. PBDE levels in the method and field blanks were similar, indicating contamination was negligible during transport and storage. Contamination of sampling media was restricted to congeners BDE–47 and BDE–209 and the average level (ng PUF<sup>-1</sup>) in blanks ranged between 0.2–4.8% of the average concentration in various types of air sampling media (*i.e.* PUF plugs, GMFs and PUF disks). For active air sampling media the blank PUF plug and GMF values were combined to calculate the average level in blanks, with contamination in GMFs<LOD. The mean and standard deviation for the blank values, calculated from both the field and method blanks are reported in Tables 1, 2 and 3 also include the limit of detection (LOD), defined as the mean blank value plus 3 × standard deviation (ng PUF<sup>-1</sup>). Sample concentrations of PBDEs were not blank corrected. The recovery rates for the labeled PBDEs (*i.e.* surrogates) in all sampling media ranged between 42.8% and 80.7 % (see Tables 1, 2 and 3). Additional tests for determining surrogate recovery rates were assessed by spiking blank PUF disks (*n*=2). To elaborate, two PUF disks were spiked with 20 µl of the <sup>13</sup>C<sub>12</sub> surrogate mixture and PUF disks were then treated exactly as samples (see the SM, Table S2). Non-extracted surrogate spikes were also performed by spiking 10 µl of the PBDE calibration mixture and 20 µl of the <sup>13</sup>C<sub>12</sub> surrogate mixture into 0.5 ml toluene and run through the analytical method.

### 2.6. Meteorological data

The DERM air monitoring station (denoted as site 14 in Figure 1) in the residential area was employed to measure wind velocities using an anemometer (~4.0 m in height) and direction was determined with a wind vane. A wind rose for the summer (2009–2010) sampling campaign was drawn to indicate the overall frequency of wind directions and speeds by summing 10 minute average measurements. Wind velocities were categorized into the following ranges: 0 to 2; 2 to 4; 4 to 6 and 6 to 8 m s<sup>-1</sup>. Temperatures during the spring (2008) and summer (2009–2010) sampling periods, also monitored at the DERM air monitoring station, were 20 °C (range 10.6–35.1 °C) and 26 °C (range 17.1–35.1 °C) respectively. The full range of temperatures during both PAS sampling periods and collection of all active air samples is provided in the SM (Table S3).

### 2.7. Model development

GraphPad Prism Version 5.0 (GraphPad Software, San Diego, USA) was used to develop an empirical exponential decay model (amount accumulated in PAS vs. distance from the automotive shredding facility). PAS data was weighted (1/Y<sup>2</sup>) to minimize their relative distances and fitted using least squares (ordinary) approach. The default GraphPad Prism ROUT coefficient (Q=1) was used to detect outliers (Motulsky and Brown, 2006). Model performance was assessed in terms of the coefficient of determination (*r*<sup>2</sup>), the standard deviation of the residuals (*S*<sub>*y*,*x*</sub>) and 95% confidence intervals. Comparison of attenuation coefficients was performed using a sum of squares *F*–test.

**Table 1.** Range of  $\Sigma_{11}$ PBDE concentrations ( $\text{pg m}^{-3}$ ) in air collected at the commercial site (site 4), during the summer 2009 – 2010 sampling period. PBDE partitioning behavior is represented by concentrations ( $\text{ng PUF}^{-1}/\text{ng GMF}^{-1}$ )

PBDE congeners	28	47	100	99	153	183	197	196	207	206	209	$\Sigma_{11}$
<b>Collection period (11–18 January, 2010)</b>												
(Air volume sampled=742 $\text{m}^3$ )												
PUF plug ( $\text{ng PUF}^{-1}$ )	2.9	20.0	8.2	1.7	0.10	1.1	nd	nd	nd	nd	nd	
Vapor-phase ( $\text{pg m}^{-3}$ )	3.9	27.0	11.1	2.3	0.13	1.5	na	na	na	na	na	
GMF ( $\text{ng GMF}^{-1}$ )	nd	8.8	21.2	2.4	nd	24.2	5.6	1.2	14.4	9.0	378.8	
Particulate-phase ( $\text{pg m}^{-3}$ )	na	11.9	3.2	28.6	na	32.6	7.5	1.6	19.4	12.1	510.0	
Bulk ( $\text{pg m}^{-3}$ )	3.9	38.9	14.3	30.9	0.1	34.1	7.5	1.6	19.4	12.1	510.0	672.8
<b>Collection period (28 January–05 February, 2010)</b>												
(Air volume sampled=887 $\text{m}^3$ )												
PUF plug ( $\text{ng PUF}^{-1}$ )	3.1	23.8	2.7	11.5	0.2	1.2	nd	nd	nd	nd	nd	
Vapor-phase ( $\text{pg m}^{-3}$ )	3.5	26.8	3.0	13.0	0.23	1.4	na	na	na	na	na	
GMF ( $\text{ng GMF}^{-1}$ )	nd	2.6	nd	5.6	nd	5.4	nd	nd	2.6	0.2	148.2	
Particulate-phase ( $\text{pg m}^{-3}$ )	na	2.9	na	6.3	na	6.1	na	na	2.9	0.2	167.0	
Bulk ( $\text{pg m}^{-3}$ )	3.5	29.7	3.0	19.3	0.2	7.5	na	na	2.9	0.2	167.0	233.3
<b>Collection period (16–23 February, 2010)</b>												
(Air volume sampled=604 $\text{m}^3$ )												
PUF plug ( $\text{ng PUF}^{-1}$ )	0.9	16.2	1.8	7.9	0.2	1.0	nd	nd	nd	nd	nd	
Vapor-phase ( $\text{pg m}^{-3}$ )	1.5	26.8	3.0	13.0	0.3	1.7	na	na	na	na	na	
GMF ( $\text{ng GMF}^{-1}$ )	nd	3.0	nd	7.6	nd	13.6	2.0	nd	5.2	2.6	181.8	
Particulate-phase ( $\text{pg m}^{-3}$ )	na	5.0	na	12.6	na	22.5	3.3	na	8.6	4.3	301.0	
Bulk ( $\text{pg m}^{-3}$ )	1.5	31.8	3.0	25.6	0.3	24.2	3.3	na	8.6	4.3	301.0	403.6
Median bulk ( $\text{pg m}^{-3}$ )	3.5	31.8	3.0	25.6	0.2	24.2	5.4	1.6	8.6	4.3	301.0	409.2
Mean bulk ( $\text{pg m}^{-3}$ )	3.0	33.5	6.8	25.3	0.2	21.9	5.4	1.6	10.3	5.5	326.0	439.4
SD	1.3	4.8	6.5	5.8	0.1	13.4	3.0	na	8.4	6.0	172.9	221.6
Blank values ( $n=6$ )												
Mean $\pm$ SD		0.2 $\pm$ 0.1									0.2 $\pm$ 0.2	
LOD ( $\text{ng PUF}^{-1}$ )	0.08	0.5	0.08	0.08	0.08	0.1	0.1	0.1	0.1	0.1	0.8	
Mean recovery (%) <sup>13</sup> C <sub>12</sub>	69.3	85.0	na	55.2	56.1	50.7	46.4	na	40.9	na	33.4	

na: Not applicable.

nd: Not detected.

LOD: Method detection limit, defined as the mean blank value plus 3  $\times$  SD.**Table 2.** Range of  $\Sigma_{11}$ PBDE concentrations ( $\text{pg m}^{-3}$ ) in air collected at the residential site (site 14), during the summer 2009 – 2010 sampling period. PBDE partitioning behavior is represented by concentrations ( $\text{ng PUF}^{-1}/\text{ng GMF}^{-1}$ )

PBDE congeners	28	47	100	99	209	$\Sigma_5$
<b>Collection period (15–29 January, 2010)</b>						
(Air volume sampled=748 $\text{m}^3$ )						
PUF plug ( $\text{ng PUF}^{-1}$ )	0.4	1.8	0.1	0.8	nd	
Vapor-phase ( $\text{pg m}^{-3}$ )	0.5	2.4	0.1	1.1	na	
GMF ( $\text{ng GMF}^{-1}$ )	nd	nd	nd	0.4	4.8	
Particulate-phase ( $\text{pg m}^{-3}$ )	na	na	na	0.5	6.4	
Bulk ( $\text{pg m}^{-3}$ )	<b>0.5</b>	<b>2.4</b>	<b>0.1</b>	<b>1.6</b>	<b>6.4</b>	<b>11.0</b>
<b>Collection period (6–19 February, 2010)</b>						
(Air volume sampled=712 $\text{m}^3$ )						
PUF plug ( $\text{ng PUF}^{-1}$ )	0.3	1.3	0.1	0.6	nd	
Vapor-phase ( $\text{pg m}^{-3}$ )	0.4	1.8	0.1	0.8	na	
GMF ( $\text{ng GMF}^{-1}$ )	nd	nd	nd	0.4	1.6	
Particulate-phase ( $\text{pg m}^{-3}$ )	na	na	na	0.6	2.2	
Bulk ( $\text{pg m}^{-3}$ )	<b>0.4</b>	<b>1.8</b>	<b>0.1</b>	<b>1.4</b>	<b>2.2</b>	<b>5.9</b>
Median (bulk) $\text{pg m}^{-3}$	0.5	2.1	0.1	1.5	4.3	8.5
Mean (bulk) $\text{pg m}^{-3}$	0.5	2.1	0.1	1.5	4.3	8.5
SD	0.1	0.4	0.0	0.1	3.0	3.6
Blank values ( $n=2$ )						
Mean $\pm$ SD		0.1				
LOD ( $\text{ng PUF}^{-1}$ )	0.08	0.1	0.08	0.08	0.08	
Mean recovery (%) <sup>13</sup> C <sub>12</sub>	78	85.2	na	81.15	76.45	

na: Not applicable.

nd: Not detected.

LOD: Method detection limit, defined as the mean blank value plus 3  $\times$  SD.

**Table 3.** Levels (ng PUF<sup>-1</sup>) of  $\Sigma_{11}$ PBDEs accumulated in PAS along four transects during the summer (2009–2010) sampling campaign

PBDE congener	28	47	100	99	153	183	197	196	207	206	209	$\Sigma_{11}$	
PAS Site (km) <sup>a</sup>													
4	0.1	1.8	22.0	3.5	17.5	8.2	11.7	5.4	4.3	20.0	20.8	307.9	423.1
11	0.1	2.3	48.7	11.8	66.2	7.6	22.4	20.5	12.0	12.5	16.5	1012.0	1232.0
1	0.2	0.8	9.9	0.9	5.0	1.1	5.4	4.2	3.4	10.3	8.3	160.9	210.2
7	0.2	0.5	7.5	0.7	3.2	0.7	1.6	1.0	0.5	nd	3.5	66.3	85.5
12	0.3	1.6	28.0	3.4	19.3	7.1	11.3	9.1	10.0	20.2	17.9	343.4	471.3
8	0.7	0.4	5.4	0.9	5.4	1.1	2.3	1.0	0.2	nd	1.2	50.2	68.1
2	0.8	0.2	3.8	0.3	1.3	0.9	nd	nd	nd	0.9	1.8	70.3	79.5
5	1.0	0.1	1.1	0.1	0.3	nd	nd	nd	nd	nd	nd	16.1	17.7
13	1.0	0.1	1.7	0.1	0.3	1.0	nd	nd	nd	nd	nd	5.7	8.9
9	1.3	0.2	1.9	0.1	0.7	0.7	nd	nd	nd	nd	nd	12.1	15.7
3	1.5	0.4	4.5	0.6	3.0	1.0	nd	nd	nd	nd	nd	13.2	22.7
10	1.7	0.1	1.4	0.1	0.2	0.5	nd	nd	nd	nd	nd	<LOD	2.3
14	1.8	0.1	1.8	0.1	0.7	nd	nd	nd	nd	nd	nd	10.1	12.8
6	2.2	0.2	1.9	0.2	0.7	0.6	nd	nd	nd	nd	nd	6.9	10.5
Median	0.9	0.3	4.2	0.5	2.2	1.0	8.4	4.8	3.9	12.5	8.3	50.2	45.4
Mean	0.9	0.6	10.0	1.6	8.8	2.5	9.1	6.9	5.1	12.8	10.0	159.6	190.0
SD	0.7	0.7	13.8	3.1	17.6	3.1	7.8	7.3	4.9	8.0	8.3	280.4	337.1
Blank values (n=4)													
Mean blank (ng PUF <sup>-1</sup> )		0.4										1.0	
LOD (ng PUF <sup>-1</sup> )		0.5										2.5	
Mean recovery (%) <sup>13</sup> C <sub>12</sub>	55.8	63.1	na	53.3	53.8	49.5	43.1	na	46.6	na	34.9		

<sup>a</sup> PAS distance (km) from source.

nd–Non detected, na–not available.

LOD–Method detection limit, defined as the mean blank value plus 3 × SD.

### 3. Results and Discussion

#### 3.1. AAS data

Although 24 PBDEs were analyzed for, only congeners BDE–28, –47, –100, –99, –153, –183, –197, –196, –207, –206 and –209 were detected in both the AAS and PAS samples. Therefore, consideration of PBDE levels for the remainder of this work is in terms of the sum of levels of these 11 congeners ( $\Sigma_{11}$ PBDEs). Levels of PBDEs in air samples collected at the commercial site (site 4) ranged between 233 and 673 pg m<sup>-3</sup> (see Table 1) and were on average a factor of 50 times higher than levels measured at the residential air monitoring site (see Table 2). BDE–209 dominated congener composition in air at the commercial and residential air monitoring sites and represented 74 and 51% of the  $\Sigma_{11}$ PBDE mass in samples respectively. Based on AAS sampling data, all PBDEs with six or more bromines were effectively only detected in the particulate–phase (*i.e.* associated with the GMF in active samples). The larger molecular weight congeners, due to their larger octanol–air partition coefficients ( $K_{OA}$ ) and lower vapor pressures, are restricted in their atmospheric transport to primarily the particulate–phase (Harner and Shoeib, 2002). Although hepta–, octa–, and nona–BDE congeners were routinely detected at the commercial air monitoring site, the only congeners associated with the particulate phase in air at the residential site were BDE–99 and BDE–209 (see Table 2).

Cahill et al. (2007) reported similar PBDE levels and profile in air near an automotive and shredding facility in the US. In that study, BDE–209 also dominated emissions and was entirely associated with the particulate phase with concentrations up to 1 900 pg m<sup>-3</sup> at the downwind fence–line. Results from that study also indicated PBDE air concentrations over time (*i.e.* 24 hrs) were highly variable. This was primarily attributed to the time when the facility was not in operation, suggesting aerosol generation from shredding activity was an important source for these heavier PBDEs at the site.

The PBDE levels in air at the residential site (site 14) are comparable to those found in the only previous Australian study

(Toms et al., 2009) also undertaken in Brisbane, which reported PBDE levels using a similar low–volume active air sampling technique. In that study levels of  $\Sigma_{26}$ PBDEs in Brisbane's ambient air ranged between 1.7 and 6.8 pg m<sup>-3</sup> with congener composition also dominated by BDE–209.

#### 3.2. PAS data–determining reproducibility and variability

In terms of PAS data in this study we focus on mass (ng PUF<sup>-1</sup>) to exclude any uncertainty in the sampled air volume from the discussion. The congener composition in PAS for both sampling periods was dominated by BDE–209 and on average contributed 75% to the  $\Sigma_{11}$ PBDEs levels in PAS, a proportion similar to that observed in active samples. Full detail of the congener composition in PAS for each sampling period is presented in the SM (Figure S1).

In the preliminary (spring 2008) PAS deployment a limited number of sites (4, 7 and 12) were used to investigate reproducibility of PAS data collected around the perimeter of the automotive shredding facility by installing two PUF disks in a single chamber. The percent relative standard deviation (%RSD) between  $\Sigma_{11}$ PBDE levels accumulated in replicate PUF disks ranged between 7.8–10.8%. In comparison, the %RSD between the mean  $\Sigma_{11}$ PBDE level determined at each air monitoring site (4, 7 and 12) was 34% (see the SM, Table S4). Variability in PBDE levels was also detected between these three sites in the following summer (2009–2010) sampling period with a %RSD of 63%. The increased %RSD in the latter sampling period was contributed to by PAS being deployed for approximately double the length of time (*i.e.* 81 days). These results indicate that concentrations of PBDEs immediately outside of the recycling facility were highly dependent on the location of the sampler relative to the facility. The variability between the sampling periods (spring vs. summer) suggest additional factors such as prevailing wind direction and variability in source release rates during different times of the year may produce "hotspots". For the purposes of this study results indicate that PAS are suitable for capturing high resolution spatial differences in PBDE levels in such dynamic environments.

### 3.3. PAS transect data

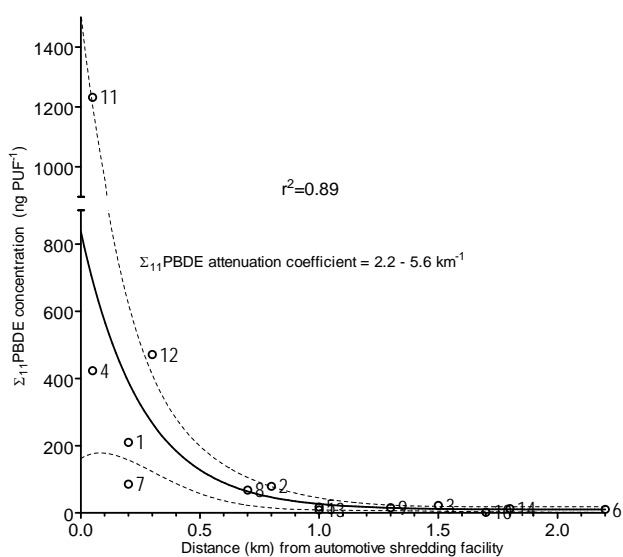
PAS deployed along transects generally demonstrated a decreasing  $\Sigma_{11}$ PBDE level with increasing distance from the facility, indicating this source dominated PBDE emissions in the study area (see Table 3). The levels of  $\Sigma_{11}$ PBDEs accumulated in PAS along transects varied by more than two orders of magnitude (1 232 to 2.3 ng PUF<sup>-1</sup>, median 45.4 ng PUF<sup>-1</sup>).

Also shown in Table 3 is a clear change in the congener patterns occurring within transects, with congeners BDE-183, -197, -196, -206 and -207 not detected in PAS deployed >1 km in radius from the recycling facility.

### 3.4. Modeling PAS data

PAS transect data was best fitted to an exponential decay model using a least squares (ordinary) approach ( $r^2=0.69$ ). A large standard deviation of the residuals was associated with the model ( $S_{y,x} = 209$ ) and GraphPad Prism recognized 2 sites (sites 11 and 12) as being different or “outliers” due to a high residual variance (data not shown). The poor performance of the model was a consequence of the large variability in levels of  $\Sigma_{11}$ PBDEs in PAS close to the recycling facility (*i.e.* within 300 m). To reduce the influence of these sites PAS data was weighted ( $1/Y^2$ ) which significantly reduced the standard deviation of the residuals ( $S_{y,x}=0.65$ ) and meant no outliers were detected by the model (see the SM, Table S5). As shown in Figure 2, at 95% confidence intervals the weighted model estimates the attenuation coefficient ( $k$ ) for  $\Sigma_{11}$ PBDE to be between 2.2–5.6 km<sup>-1</sup> and predicts the distance for PBDE levels in emissions to fall to half initial values occurs between 120–320 m from the recycling facility.

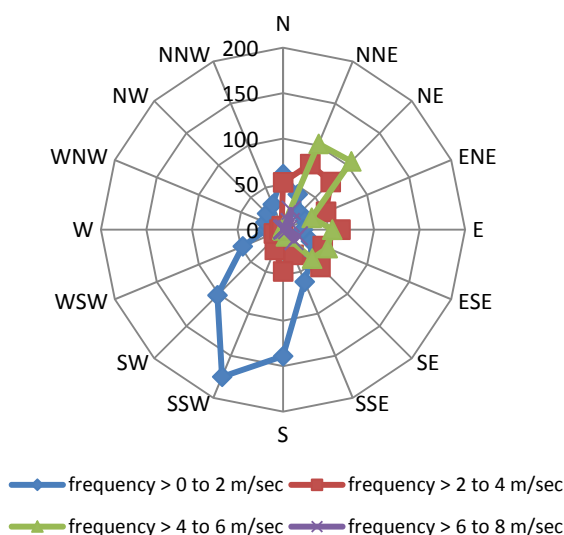
We also developed models for congeners BDE-209, BDE-99 and BDE-47 to compare individual attenuation coefficients (see the SM, Table S6). These congeners were selected because they were detected in virtually all PAS (*i.e.* 98%) and were representative of the different PBDE partitioning behavior predicted by gas-particle partitioning models (Harner and Shoeib, 2002). A sum of squares  $F$ -test indicated no significant difference ( $p=0.88$ ) between congener attenuation coefficients.



**Figure 2.** Decrease in  $\Sigma_{11}$ PBDE levels (ng PUF<sup>-1</sup>) accumulated in PAS versus PAS distance (km) from the automotive shredding facility. Data is fitted to an empirical exponential decay model (solid line). The 95% confidence bands are represented by the dotted lines either side of the curve.

### 3.5. Identifying possible reasons for outliers

Since wind direction is highly variable on a local scale, it was particularly important that wind data in this study was obtained as close to the automotive shredding facility as possible. Measured wind velocities from the DERM air monitoring station were categorized into the following ranges: >0 to 2; 2 to 4; 4 to 6 and 6 to 8 m s<sup>-1</sup>. Linear regression analysis of wind velocity (plotted as the midpoint of these ranges) and frequency of occurrence of these velocities for each month during the summer (2009–2010) sampling campaign affords no significant difference in slopes ( $p=0.31$ ) (see the SM, Figure S2 and Table S7). This indicates no major differences in wind velocities or their frequency between months. The wind rose presented in Figure 3 shows the frequency of different wind strengths and directions over the entire summer (2009–2010) sampling period. It shows the majority of winds in the study area were from an arc between the NNE and SSW. Low wind flows between >0 to 2 m s<sup>-1</sup> dominated the sum of wind strengths (~46%) and are consistent with the outlier data along the northern transect (sites 11 and 12).



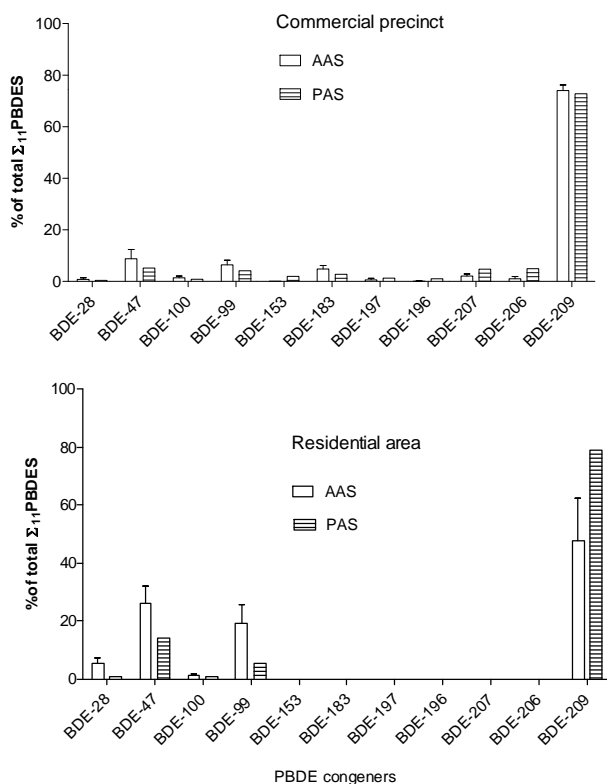
**Figure 3.** Wind rose (24 hr) showing the frequency of different wind velocity categories and directions over the whole summer (2009–2010) sampling period, derived by summing the frequency of each wind direction and velocity range measured over 10-minute periods.

These outliers identified by the model may only be examples of the increased variability in PAS near the source. However, the fact both outliers were along the same transect suggest a common factor, such as the major wind direction. It is worth noting that while outlier data from PAS deployed along the northern transect (sites 11 and 12) tended to be elevated compared to those from other transects, PAS installed further along the northern transect were not similarly affected.

### 3.6. Comparing PAS and AAS data

While AAS results are consistent with PAS data they do not represent a time-weighted result for PAS data. The inherent variability in the PBDE composition in air over time (*i.e.* different air masses) at both sites is indicated in both Tables 1 and 2. In this study, active air samples were deliberately collected over longer time periods (*i.e.* approximately 1–2 weeks) and at low sampling rates because of the expected increased variability of PBDE levels in air. Previous studies have also identified in any comparison of AAS and PAS derived data there is uncertainty in the proportion of particles in air which is sampled by the PAS (Klanova et al., 2008; Chaemfa et al., 2009a; Chaemfa et al., 2009b). In this work a comparison of both the PAS and AAS samples collected in the

commercial and residential areas indicates BDE-209 dominated sample congener composition during the summer (2009–2010) sampling period (see Figure 4). In addition, both AAS and PAS methods identified PBDE composition in air was different between commercial and residential areas (see Figure 4). Linear regression analysis of the congener distributions obtained using either AAS and PAS samplers provided positive correlations at both the commercial area ( $r^2=0.99$ ) and the residential area ( $r^2=0.85$ ) (see the SM, Tables S8–S11).



**Figure 4.** Comparison of the PBDE congener distributions in PAS and AAS samples collected in the commercial and residential areas during the summer (2009–2010) sampling period.

#### 4. Conclusions

Typical congener patterns of PBDEs for the commercial and residential areas as measured by both AAS and PAS were significantly different, suggesting that the commercial precinct is predominantly influenced by the recycling facility. In contrast, the profile from air of the residential area is more characteristic of that in the city's ambient air (Hearn et al., 2012) and mostly influenced by the broader urban "plume". The dominance of BDE-209 in emissions which was entirely associated with the particulate-phase, means relatively simple dust suppression measures may reduce the emission rates from such recycling facilities. Model results suggest contamination of the local environment is restricted to within approximately a 300 m radius. Future studies should focus on nearby workers' and residents' blood levels of PBDEs near such facilities (i.e. within 300 m) to investigate if body burdens and congener patterns are influenced by chronic exposure to such industrial sources.

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#### Supporting Material Available

Percent composition of PBDE congeners accumulated in PAS at air monitoring sites during both PAS sampling periods (Figure S1), Linear regression analysis of wind velocity (plotted as the midpoint of these ranges) and frequency of occurrence of these velocities for each month during the summer (2009 – 2010) (Figure S2), Co-ordinates of air monitoring sites in field study area and their respective distance from the automotive shredding facility (Table S1), Recovery rates of spiked surrogates ( $^{13}\text{C}_{12}$ -PBDEs) from blank PUF disks ( $n=2$ ) (Table S2), Mean temperature ranges during collection of PAS and AAS samples. Data accessed from the DERM air monitoring station (site 14) (Tables S3), Levels ( $\text{ng PUF}^{-1}$ ) of  $\Sigma_{11}$ PBDEs accumulated in replicate PAS deployed at three sites (4,7 and 12) in the vicinity (i.e. within 300 m) of the automotive shredding facility during the preliminary spring (2008) PAS sampling period (Table S4), Exponential decay model results for weighted ( $1/Y^2$ )  $\Sigma_{11}$ PBDE data ( $\text{ng PUF}^{-1}$ ). Fitted using least squares (ordinary) fit (Q value=1.0%) Only PAS data collected during summer (2009–2010) have been used for model development (Table S5), Exponential decay model results for weighted ( $1/Y^2$ ) BDE-47, BDE-99, BDE-209 data ( $\text{ng PUF}^{-1}$ ). Fitted using least squares (ordinary) fit (Q value = 1.0%) Only PAS data collected during summer (2009–2010) have been used for model development (Table S6), Results for linear regression analysis of wind velocity (plotted as the midpoint of these ranges) and frequency of occurrence of these velocities for each month during the summer (2009–2010) (Table S7), Linear regression statistics of the AAS and PAS congener distribution data obtained at the automotive shredding facility (site 4) during the summer (2009–2010) sampling period (Table S8), Comparison of the congener distribution data for both the AAS and PAS samples collected at the automotive shredding facility (site 4). All 11 targeted congeners were detected by both sampling methods at site 4 during the summer (2009–2010) sampling period (Table S9), Linear regression statistics of the AAS and PAS congener distribution data obtained at the reference site (site 14) during the summer (2009–2010) sampling period (Table S10), Comparison of the congener distribution data for both the AAS and PAS samples collected at the reference site (site 14) (Table S11). This information is available free of charge via the Internet at <http://www.atmospolres.com>.

#### References

- Alaee, M., Arias, P., Sjodin, A., Bergman, A., 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environment International* 29, 683-689.
- Baek, S.-Y., Choi, S.-D., Lee, S.-J., Chang, Y.-S., 2008. Assessment of the spatial distribution of coplanar PCBs, PCNs, and PBDEs in a multi-industry region of South Korea using passive air samplers. *Environmental Science and Technology* 42, 7336-7340.
- Bartkow, M.E., Booij, K., Kennedy, K.E., Muller, J.F., Hawker, D.W., 2005. Passive air sampling theory for semivolatile organic compounds. *Chemosphere* 60, 170-176.
- BSEF, 2006. Brominated Science and Environmental Forum. <http://www.bsef.com/uploads/library/vehicule%20fire%20safety.pdf>. Accessed on 11/11/2011.
- Cahill, T.M., Groskova, D., Charles, M.J., Sanborn, J.R., Denison, M.S., Baker, L., 2007. Atmospheric concentrations of polybrominated diphenyl ethers at near-source sites. *Environmental Science and Technology* 41, 6370-6377.

- Chaemfa, C., Barber, J.L., Moeckel, C., Gocht, T., Harner, T., Holoubek, I., Klanova, J., Jones, K.C., 2009a. Field calibration of polyurethane foam disk passive air samplers for PBDEs. *Journal of Environmental Monitoring* 11, 1859-1865.
- Chaemfa, C., Wild, E., Davison, B., Barber, J.L., Jones, K.C., 2009b. A study of aerosol entrapment and the influence of wind speed, chamber design and foam density on polyurethane foam passive air samplers used for persistent organic pollutants. *Journal of Environmental Monitoring* 11, 1135-1139.
- Chao, H.R., Wang, S.L., Lee, W.J., Wang, Y.F., Papke, O., 2007. Levels of polybrominated diphenyl ethers (PBDEs) in breast milk from central Taiwan and their relation to infant birth outcome and maternal menstruation effects. *Environment International* 33, 239-245.
- Choi, S.D., Baek, S.Y., Chang, Y.S., 2008. Atmospheric levels and distribution of dioxin-like polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in the vicinity of an iron and steel making plant. *Atmospheric Environment* 42, 2479-2488.
- Environment Australia, 2002. Environmental Impact of End-of-Life Vehicles: An Information Paper. <http://www.environment.gov.au/archive/settlements/publications/waste/elv/impact-2002/index.html>. Accessed on 15/07/10.
- Francois, F., Blondeel, M., Bernaert, P., Baert, R., 2004. Diffuse emissions of PCDD/F and dioxin like PCB from industrial sources in the Flemish Region (BELGIUM). *Organohalogen Compounds* 66, 906-912.
- Gonzalez-Fernandez, O., Hidalgo, M., Margui, E., Carvalho, M.L., Queral, I., 2008. Heavy metals' content of automotive shredder residues (ASR): evaluation of environmental risk. *Environmental Pollution* 153, 476-482.
- Gouin, T., Harner, T., Daly, G.L., Wania, F., Mackay, D., Jones, K.C., 2005. Variability of concentrations of polybrominated diphenyl ethers and polychlorinated biphenyls in air: implications for monitoring, modeling and control. *Atmospheric Environment* 39, 151-166.
- Guo, Q.J., Zhang, X., Li, C., Liu, X.M., Li, J.H., 2012. TG-MS study of the thermo-oxidative behavior of plastic automobile shredder residues. *Journal of Hazardous Materials* 209, 443-448.
- Harner, T., Shoeib, M., Diamond, M., Ikononou, M., Stern, G., 2006. Passive sampler derived air concentrations of PBDEs along an urban-rural transect: spatial and temporal trends. *Chemosphere* 64, 262-267.
- Harner, T., Shoeib, M., 2002. Measurements of octanol-air partition coefficients ( $K_{oa}$ ) for polybrominated diphenyl ethers (PBDEs): predicting partitioning in the environment. *Journal of Chemical and Engineering Data* 47, 228-232.
- Harrad, S., Hunter, S., 2006. Concentrations of polybrominated diphenyl ethers in air and soil on a rural-urban transect across a major UK conurbation. *Environmental Science and Technology* 40, 4548-4553.
- Hearn, L.K., Kennedy, K., Hawker, D.W., Toms, L.M.L., Alberts, V., Mueller, J.F., 2012. Spatial mapping of city wide PBDE levels using an exponential decay model. *Journal of Environmental Monitoring* 14, 643-650.
- Klanova, J., Eupr, P., Kohoutek, J., Harner, T., 2008. Assessing the influence of meteorological parameters on the performance of polyurethane foam based passive air samplers. *Environmental Science and Technology* 42, 550-555.
- Main, K.M., Kiviranta, H., Virtanen, H.E., Sundqvist, E., Tuomisto, J.T., Tuomisto, J., Vartiainen, T., Skakkebaek, N.K., Toppari, J., 2007. Flame retardants in placenta and breast milk and cryptorchidism in newborn boys. *Environmental Health Perspectives* 115, 1519-1526.
- Motulsky, H.J., Brown, R.E., 2006. Detecting outliers when fitting data with nonlinear regression - a new method based on robust nonlinear regression and the false discovery rate. *BMC Bioinformatics* 7, 123.
- NICNAS, 2005. Summary of information on polybrominated flame retardants. Chemical Gazette; No. C 5. [http://www.nicnas.gov.au/publications/chemical\\_gazette/pdf/2005may\\_whole.pdf](http://www.nicnas.gov.au/publications/chemical_gazette/pdf/2005may_whole.pdf), accessed on June 2012.
- Nourredine, M., 2007. Recycling of auto shredder residue. *Journal of Hazardous Materials* 139, 481-490.
- Petreas, M., Oros, D., 2009. Polybrominated diphenyl ethers in California wastestreams. *Chemosphere* 74, 996-1001.
- Sakai, S., Takahashi, S., Osada, M., Miyazaki, T., 2006. Dioxin-related compounds, brominated flame retardants and heavy metals in automobile shredder residue (ASR) and their behavior in high-temperature melting process. *Organohalogen Compounds* 68, 1824-1827.
- Schechter, A., Papke, O., Joseph, J.E., Tung, K.C., 2005. Polybrominated diphenyl ethers (PBDEs) in US computers and domestic carpet vacuuming: possible sources of human exposure. *Journal of Toxicology and Environmental Health-Part A* 68, 501-513.
- Shoeib, M., Harner, T., 2002. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environmental Science and Technology* 36, 4142-4151.
- Toms, L.M.L., Bartkow, M.E., Symons, R., Paepke, O., Mueller, J.F., 2009. Assessment of polybrominated diphenyl ethers (PBDEs) in samples collected from indoor environments in South East Queensland, Australia. *Chemosphere* 76, 173-178.
- US EPA, 1991. PCB, Lead and Cadmium Levels in Shredder Waste Materials: A Pilot Study, EPA 560/5-90-00BA, Washington, 474 pp.
- Vermeulen, I., Van Caneghem, J., Block, C., Baeyens, J., Vandecasteele, C., 2011. Automotive shredder residue (ASR): reviewing its production from end-of-life vehicles (ELVs) and its recycling, energy or chemicals' valorisation. *Journal of Hazardous Materials* 190, 8-27.
- World Health Organization, 1994. Environmental Health Criteria 162: Brominated Diphenyl Ethers, Geneva.