

## AMBIENT ATMOSPHERIC LEVELS OF PBDES ACROSS URBAN AND RURAL CENTRES IN AUSTRALIA DETERMINED USING POLYURETHANE FOAM (PUF) PASSIVE AIR SAMPLING

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### Introduction

Polybrominated diphenyl ethers (PBDEs), a class of brominated flame retardants are persistent, lipophilic compounds with a tendency to bioaccumulate<sup>1</sup>. In Australia, PBDEs have been evaluated primarily in human samples such as breast milk and blood sera which have shown that the human body burden appears to be higher than many countries in Europe and Asia but lower than the USA and Canada<sup>2</sup>. To date there is very limited exposure data available on sources, fate and exposure pathways of PBDEs in the Australian population although a comparison of human body burden from intake and chemical half life as well as various age specific factors suggest that current intake data underestimate the human body burden<sup>2</sup>. Exposure through dust, indoor air and to a lesser extent ambient air, are being assessed as exposure pathways in this context. The focus on indoor air was prompted by overseas studies which simultaneously compared indoor and outdoor levels to find that PBDE exposures via indoor air are greater than outdoor air by factors ranging from 15 to 50<sup>3,4,5</sup>. A preliminary study of indoor-outdoor exposure in Australia has provided initial confirmation of this finding with sum of PBDE concentrations in domestic indoor air 10 times that of outdoor air for two sites in Brisbane, Queensland (Toms unpublished data).

The atmosphere is considered an important pathway for the dispersion and transformation of semivolatile organic chemicals such as the PBDEs. To our knowledge no published data are available on the concentration of PBDEs in air from other regions in Australia. In this study we aimed to systematically evaluate the concentration of PBDEs at outdoor sites around Australia. Passive sampling has been applied successfully in the monitoring of PBDEs for urban-rural transects, indoor-outdoor exposure studies and over continental scales overseas. In this study, passive samplers were deployed across multiple sites within capital cities, rural/regional centres and a rural background site in three states of Australia. An assessment of current ambient exposure was derived using sampling rates for each site obtained from the use of performance reference compounds (PRCs). The ambient concentrations observed are compared with data from other studies around the world.

### Materials and Methods

Polyurethane foam (PUF) passive samplers (certified PBDE free) were co-deployed at eight sites (Table 1) within the states of Queensland (QLD), Western Australia (WA) and South Australia (SA) during winter (June/July 2007). Two PUF discs were deployed in two separate chambers at each site in a configuration validated previously<sup>6</sup> in order to double the sampling rate/increase detection for each replicate sample. PUF were pre-extracted/extracted using accelerated solvent extraction with dichloromethane. Each PUF was loaded with performance reference compound (PRC) PCBs (#s 21, 30 & 204) prior to deployment in order to determine an in-situ ambient temperature corrected estimate of the sampling rate ( $R_s \text{ m}^3 \cdot \text{day}^{-1}$ ) for each site. QA/QC samples included replicate solvent and PUF field blanks. All samples were spiked with internal standard (<sup>13</sup>C<sub>12</sub> BDEs-28, 47, 99, 153, 154, 183, 197, 207 and 209; Wellington Isotope Laboratories) prior to extraction and purified using gel permeation chromatography and Na<sub>2</sub>SO<sub>4</sub>/Florisil columns. The clean-up procedure was optimized for the recovery of PAHs (analysed post-GPC), PCBs and organochlorine pesticides which were the initial focus of the monitoring campaign.

Samples were analysed by HRGC/HRMS (HP 5890 II GC coupled to a VG AutoSpec mass spectrometer; splitless injection; injector temperature 280 °C). Twenty-two PBDE congeners (BDE-17, 28, 47, 49, 66, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, 209) were separated using He as a

carrier gas on a Zebron ZB-5MS column (10m × 0.18mm id., 0.18mm film thickness). Resolution was maintained at 5,000 (10% valley definition) throughout the sample sequence. Multiple ion detection experiments were performed in the electron impact mode with monitoring of the exact masses of appropriate ions for native and labelled compounds. Criteria used for positive identification and quantification were: (i) retention time within 1 second of the retention time of corresponding  $^{13}\text{C}_{12}$  internal standard; (ii) ion ratio  $\pm 20\%$  of the theoretical ion ratio; (iii) signal to noise ratio  $>$  than 3:1 (iv) limit of detection (LOD) - the average level in field blanks + 3 SD (BDE-47,-99,-100,-206,-207,-209) or if not detected in field blanks was determined from calibration curves (intercept/slope) of native compounds to internal standard. Average field blank values where detected were subtracted from the amount accumulated to estimate ambient concentration and LOD ambient concentration limits adjusted accordingly for these PBDEs.

## Results and Discussion

PBDEs (Table 1) were detected in the samples from all sites. The average coefficient of variation (CV) in the determination of sum of PBDEs ( $\Sigma$ PBDEs) for each site was 13 % which is indicative of the applicability of this form of sampling for screening for relative differences across multiple locations. The in-situ PRC (PCB 30) based sampling rates ranged from 1.6 – 5.2  $\text{m}^3\cdot\text{day}^{-1}\cdot\text{PUF}^{-1}$  and averaged 3.1  $\text{m}^3\cdot\text{day}^{-1}\cdot\text{PUF}^{-1}$ . The average sampling rate was consistent with previous calibration work for SOCs<sup>7</sup>, with 3 - 4  $\text{m}^3\cdot\text{day}^{-1}$  typically assumed where PRCs are not used. The volume of air sampled ( $V_A$ ) during the deployment period (Table 1) ranged from 143 – 430  $\text{m}^3$ .

The average ambient concentration estimates ( $\text{pg}\cdot\text{m}^{-3}$ ) for individual congeners at each site are provided in Table 1. The average  $\Sigma$ PBDEs ( $\text{pg}\cdot\text{m}^{-3}$ ) both inclusive ( $\Sigma_{15}$ ) and exclusive of deca BDE-209 ( $\Sigma_{15} - 209$ ) and BDE-47:99 ratios are also determined for each site. The  $\Sigma_{15}$  concentration estimates ranged from  $8.7 \pm 0.17$  to  $223 \pm 24$   $\text{pg}\cdot\text{m}^{-3}$  for Gladstone-QLD and Perth-WA respectively. The  $\Sigma_{15} - 209$  concentration estimates ranged from  $2.3 \pm 0.84$  to  $59 \pm 0.37$  for Gladstone-QLD and Mount Gambier-SA. Notably the rural corridor site Mutdapilly-QLD did not have the lowest ambient estimates for either parameter with levels of  $24 \pm 0.87$  and  $4.5 \pm 2.9$   $\text{pg}\cdot\text{m}^{-3}$  respectively. While Mutdapilly is a rural location where neighbouring properties are kilometers apart from each other (low density), it is located 55 km South West of the capital of QLD, Brisbane. Wind directions during the sampling period switch between North Easterlies and South Westerlies for that site. The highest  $\Sigma_{15}$  measured within each state of Australia have been observed for urban capital cities. The relative levels of  $\Sigma_{15}$  ( $\text{pg}\cdot\text{m}^{-3}$ ) for these cities were: Perth-WA (223)  $>$  Adelaide-SA (178)  $>$  Brisbane-QLD (79). However, levels in the regional centre of Mount Gambier in SA are higher (107) than urban levels in Brisbane-QLD. An “urban pulse” in spatial assessments of PBDE loads has been demonstrated previously in overseas studies<sup>8,9,10,11</sup>.

The average  $\Sigma$ PBDEs measured in Australia are consistent with overseas studies. For example, where BDE-209 is included overseas measurements (2002 – 2003) for an American mid-west transect ranged from: 13 – 980 (Chicago); 6.4 – 44 (Indiana); 2.7 – 165 (Arkansas); and 5.0 – 42 (Louisiana). The range for Chicago, while higher than the other sites on average, was exaggerated by a single measurement of 956  $\text{pg}\cdot\text{m}^{-3}$ , for deca BDE-209<sup>12</sup>. Similarly, values have been obtained for Kyoto, Japan<sup>13</sup> ranging from 1.5 – 58  $\text{pg}\cdot\text{m}^{-3}$  and 0.4 – 78.5 for an island in the Baltic Sea<sup>14</sup>. Elevated levels for ambient air have been reported for Guangzhou in China<sup>14-16</sup> in 2004 and 2004-2005 which reported contributions from BDE-209 ranging from 1082 – 49937  $\text{pg}\cdot\text{m}^{-3}$ . Ranges of concentration estimates not including BDE-209 reported for Europe [(2.8 -21)<sup>11</sup>, (0.06 – 43)<sup>8</sup>, (0.22 – 37)<sup>17</sup>], Asia [( $<$ 0.13-340), (10 – 29), (5 – 71) and (2 – 21)<sup>18</sup>] and Canada [(3 – 30)<sup>10</sup>, (6 – 85)<sup>9</sup>], are similarly comparable to the range observed in Australia of 2.3 – 59.

BDEs-47,-99 and -209 dominate the ambient concentration profiles for each site. Deca BDE-209 was typically the dominant PBDE for Australian sites present at between 37 - 80 % of  $\Sigma_{15}$ . BDE-47 and 99 ranged from 5 – 36 and 7 – 21 % of  $\Sigma_{15}$  respectively. The ratio of BDE-47:-99 have been used as a marker for the influence of technical “penta” mixes in ambient measurements, with ratios of approximately 0.7 - 1 considered typical. In this study 7 out of the 8 sites have BDE-47:99 ratios which approximate this range. “Deca” technical mixes typically

contain < 3 % nona BDE and 97 – 98 % deca BDE<sup>1</sup> which again appears consistent with the relative abundance of nona BDEs-206, and -207 to deca BDE-209 in ambient air in Australia. Congeners from both of these technical mixes dominate the ambient concentration profiles in Australia. Deca BDE-209 dominance of ambient concentration has been found previously at Gotska Sandon Island<sup>14</sup> (Baltic Sea), Guangzhou (China)<sup>16</sup>, and Kyoto (Japan)<sup>13</sup> and in exterior window films in Southern Ontario (Canada)<sup>19</sup>. Interestingly in America where BDE-209 was previously only detected at 1 out of 5 sites in the period 1997 – 1999<sup>20</sup> follow up monitoring in 2002 - 2003 consistently detected BDE-209 at all sites which included several sites from the previous period.<sup>12</sup>. Notably it was BDE-47 which dominated these American congener profiles not BDE-209.

This current Australian study represents the first ambient air PBDE estimates across multiple states and sites. The levels are comparable with measured levels overseas. Given the observed variation in levels in overseas studies with season and the demonstrated dominance of BDE-209 in most Australian samples it is apparent that there is a need for long term monitoring, across wider spatial scales and including remote sites to adequately assess exposure. The phasing out of the use of “penta” and “octa” technical mixtures in Australia from 2005 may have led to the substitution of commercial “deca” mixes and account in part for the current BDE-209 dominance. The relative levels of the dominant congeners in Australia appear consistent with the use of both these technical mixes. Given the urban dominance of PBDEs and an observed urban rural gradient it is likely that urban areas are a source of PBDEs to their respective regions.

Deca BDE-209 has been found mostly within the particulate phase in ambient air when both vapour and particulate phases have been sampled using conventional high volume samplers<sup>14,15</sup>. Passive air samplers deployed in suitable chambers protected from depositional particulate matter should sample predominantly vapour phase compounds and fine particulate matter capable of diffusive transport. Further work calibrating the sampling rate for PBDEs in PUF passive samplers against high volume samples which can distinguish between vapour and particulate phase PBDEs are required to validate these estimates. Comparisons of PUF passive sampler estimates of PBDE concentration with high volume estimates have however shown good agreement<sup>8,9,11</sup> although BDE-209 was not assessed. Unlike with most passive air sampling studies BDE-209 has been detected in Australia and an ambient concentration estimate made, whether this is a result of higher levels in Australia due to BDE-209 dominance of ambient profiles or increasing levels generally overtime is unclear.

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**Table 1: Summary of PBDE concentrations in ambient air,  $\Sigma$ PBDE (pg.m<sup>-3</sup>) and BDE-47:99 ratios measured at 8 sites in Australia using PUF passive air samplers**

Sites	Ambient Concentration Estimates pg.m <sup>-3</sup>														$\Sigma$ PBDE pg.m <sup>-3 a</sup>		47:99	
	tri		tetra			penta			hexa			octa	nona		deca	$\Sigma_{15}^b$		$\Sigma_{15} - 209^c$
	17	28	47	66	71	85	99	100	153	154	156	196	206	207	209			
Perth-WA [ $V_A^d = 237$ ] urban, capital of WA	1.9	0.5	11.7	<0.084	0.7	1.0	16	3.1	1.0	<0.84	<0.42	1.1	5.1	5.4	176	223±24	47±13	0.73
Bunbury-WA [ $V_A = 201$ ] regional centre	0.20	0.30	6.8	<0.010	0.60	1.4	7.7	0.52	<0.050	<1.0	<0.50	<0.50	1.8	<0.72	47	64±2.3	17±5.9	0.88
Brisbane-QLD [ $V_A = 430$ ] urban, capital of QLD	0.49	1.4	28	0.51	1.1	0.81	12	0.98	0.41	0.58	0.26	<0.23	1.7	1.3	29	79±17	50±8.9	2.3
Gladstone-QLD [ $V_A = 427$ ] regional centre	0.16	0.18	1.1	<0.047	<0.14	<0.094	1.2	0.27	<0.023	<0.47	<0.23	<0.23	<0.64	<0.34	6.4	8.7±0.17	2.3±0.84	0.88
MtDapilly-QLD [ $V_A = 332$ ] rural corridor	<0.090	<0.030	1.7	<0.060	<0.18	<0.12	2.7	0.3	<0.030	<0.60	<0.30	<0.30	1.1	1.0	19	24±0.87	4.5±2.9	0.63
Adelaide-SA [ $V_A = 208$ ] urban, capital of SA	0.34	0.94	22	0.72	1.2	1.7	21.8	3.5	1.7	1.7	4.0	<0.48	3.1	3.2	115	178±41	63±34	1.0
Gawler-SA [ $V_A = 250$ ] regional centre	1.0	0.88	4.8	<0.080	0.54	0.76	4.1	0.40	<0.040	<0.80	0.56	<0.40	<1.1	0.70	23	36±13	13±6.1	1.2
Mount Gambier-SA [ $V_A = 143$ ] regional centre	0.70	0.88	23	0.14	1.5	2.0	22.1	2.7	1.2	<1.4	3.9	<0.70	2.3	0.95	48	107±7.7	59±0.37	1.0

<LOD values indicated in italics; <sup>a</sup> average from sum of each replicate for each site ± standard deviation not including LOD values; <sup>b</sup> potentially 15 if detected; <sup>c</sup> sum of all congeners excluding 209; <sup>d</sup>  $V_A$  is the PRC derived in-situ estimate of volume of air sampled (m<sup>3</sup>)