

POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN DUST FROM PRIMARY SCHOOLS IN SOUTH EAST QUEENSLAND, AUSTRALIA

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Introduction

Polybrominated diphenyl ethers (PBDEs) are used to reduce the flammability of commercial and household items. PBDEs may leach or volatilize from products and enter the environment, resulting in potential human exposure to these persistent, lipophilic chemicals. Health outcomes associated with exposure include alteration in thyroid function, diabetes, neurobehavioral, developmental and reproductive disorders [1]. Due to the relatively long turn-over times of the products treated with PBDEs, and the potential for emissions once such products enter the waste stream, there is likely to be ongoing exposure. [2].

Human exposure to these chemicals is thought to occur via dust ingestion, inhalation [3] and dietary intake [4]. PBDEs have been detected in household dust samples from many countries [5-7] and in different building types including offices [8], classrooms in the UK [9] and Korea [10], and daycare centres in Sweden [11]. Some studies show that concentrations of PBDEs in dust can be correlated with PBDE concentrations in human milk or blood serum [6, 12].

Measurement of human body burdens of PBDEs in Australia [13] and elsewhere [14, 15] have shown that PBDE concentrations are higher in children than in adults. The mean Σ PBDE concentration in serum from Australian children aged 6-9 (n=180) and 9-12 (n=240) years are 32 and 21 ng/g lipid, respectively, compared to adults > 16 years where the mean Σ PBDE concentration is 12 ng/g lipid [13]. While the reasons for higher levels in children require further investigation, one source may be exposure to dust containing high PBDE concentrations. Given the length of time that children spend in the school classroom, this may be a source of PBDE exposure and potential contributor to the higher body burden.

The objectives of this project were to: determine concentrations of PBDEs in dust from primary schools; estimate intake of PBDEs via dust ingestion for these school age (8-11 years) children; and investigate any relationship between PBDE concentrations in classroom dust and putative sources within the classroom.

Materials and methods

This project was conducted as part of a large multidisciplinary epidemiological project, titled "Ultrafine Particles from Traffic Emissions and Children's Health (UPTECH)". State schools in the Brisbane Metropolitan Area (South East Queensland), Australia that were not in close proximity to any major local air pollution sources other than vehicular traffic, did not use central air-conditioning system in the classrooms, and had at least two classrooms used by 8-11 year old children were included in the UPTECH project (<http://www.qut.edu.au/research/research-projects/uptech>). The dust collection occurred between August 2011 and May 2012 using techniques described previously [16]. Four with four samples were collected from each classroom. The sample collection for PBDE assessment was conducted in two participating classrooms in a random selection of 10 of the 25 UPTECH schools (coded as S7, S11, S12, S14, S15, S16, S17, S18, S19 and

S21. Classrooms in South East Queensland were remarkably similar from school to school with respect to contents and occupancy levels. Approximately 24 students and 1 teacher used the classroom for around 5 hours per day (excluding lunch breaks), 5 days per week, 40 weeks per year. Each classroom occupied an area of around 70 m², with 24 desks and 24 hard plastic chairs, 1 foam office chair for the teacher, around 5 computers, an interactive whiteboard, and a combination of carpet and vinyl floor covering. Some also had soft pillows/cushions for sitting on the floor. Overall, 16 classrooms were sampled from 10 schools, yielding a total of 28 dust samples for analysis. Due to the low dust mass collected, in most cases the four sampled sections were combined into one or two samples of dust.

The PBDEs targeted for analysis were BDE-17, -28, -47, -49, -66, -85, -99, -100, -154, -183, and -209 using a method modified slightly from that described previously [17]. After GC analysis solvent was exchanged to methanol and extracts run on LC-MS/MS for higher brominated PBDEs as described previously [18]. No PBDEs were detected in blank samples, which consisted of pre-cleaned sodium sulfate, sieved through mesh and treated like a sample. Standard Reference Material (SRM) 2585 was analysed with every batch as an additional control and found to be within 10% of the certified levels. Σ PBDEs included all BDEs targeted for analysis. A handheld Niton XL3t X-ray Fluorescence device (XRF device) was used to analyse items for bromine content within the classrooms from two schools using a method which is similar to one described elsewhere [19]. Statistical analysis was carried out using Bayesian hierarchical linear modeling.

Results and discussion

PBDEs were detected in all 28 dust samples. Σ PBDEs ranged from 11–2163 ng/g dust; with an arithmetic mean of 600 ng/g dust. BDE-209 ranged from <10 – 2035 ng/g dust with a mean of 402 ng/g dust; BDE-99 ranged from <0.83 – 247 ng/g dust with a mean of 102 ng/g dust; and BDE-47 ranged from <0.5 – 122 ng/g dust with a mean of 48 ng/g dust (Table 1).

Table 1. Range, mean and standard error PBDE concentrations (ng/g dust) in dust collected from state primary schools in South East Queensland, Australia

Congener	Minimum	Maximum	Mean	Standard Error
BDE 17	n.d. (0.36)	2.0	0.4	0.1
BDE 28	n.d. (0.38)	4.4	1.0	0.2
BDE 49	n.d. (0.42)	6.0	1.7	0.3
BDE 47	n.d. (0.5)	122	48	5.9
BDE 66	n.d. (0.75)	4.6	1.6	0.2
BDE 100	n.d. (0.75)	114	10	4.2
BDE 99	n.d. (0.83)	247	102	14
BDE 85	n.d. (1.3)	63	5.1	2.9
BDE 154	n.d. (1.5)	19	6.6	1.1
BDE 153	n.d. (1.9)	41	14	2.3
BDE 183	n.d. (2.5)	103	8.3	3.6
BDE 209	n.d. (10)	2035	402	94
ΣPBDEs	11.3	2163	600	100

Assessment of congener profiles revealed a large degree of variation in the proportions of each congener across the schools (Figure 1). The dominant congener in the dust samples was BDE-209, followed by BDE-99 and BDE-47, contributing between 24–78%, 3.7–45%, and 0.8–34%, respectively to the Σ PBDE concentration. The presence of the BDE-209 in dust is likely due to a greater use of the deca-BDE commercial product that is mainly used in plastics and textiles compared to the penta- and octa-BDE flame retardant products that were used in furniture foam and plastics prior to phase out around 2005 [20].

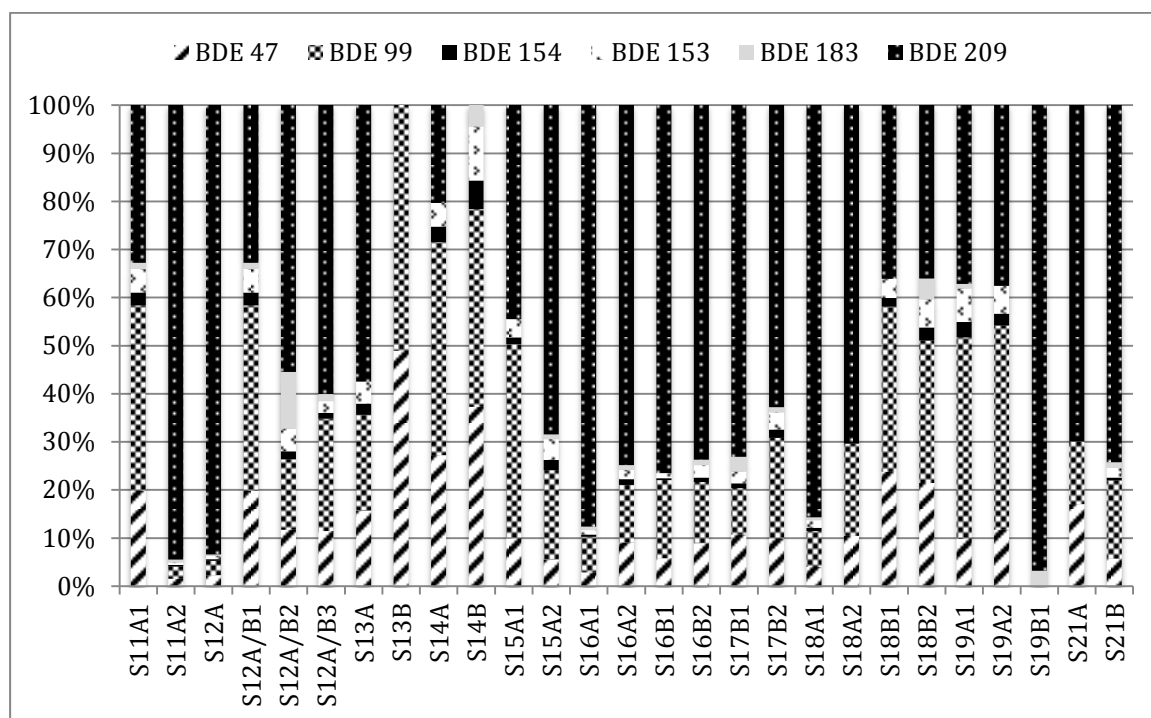


Figure 1. Mean congener profile distribution (percent) for all dust samples (n=26) from Brisbane metropolitan primary schools (n=10). (BDEs 17, 28, 49, 66, 85 and 100 contributed less than 5% to the sum PBDE concentrations and are not represented in this Figure)

In homes, relationships between PBDE concentrations in dust and indices of putative source items within a room such as number of electronics [21] or presence of crumbling foam furniture [22] have been reported. However, due to the similarities in classrooms from this study, it is not possible to differentiate between schools based on potential PBDE treated products. In addition, all schools were located in metropolitan Brisbane and therefore no comparison between urban/ rural differences could be made. Seasonal variations were considered but could not be determined due to the small number of observations and the small number of replicates of schools in each season.

XRF investigation in two schools found bromine was detected at 5873, 28 and 488 ppm, in a computer keyboard, a computer monitor and in a room divider from one school and at 677 and 123 ppm in a foam chair and pillow, respectively at the other school. These results fall into the ranges reported from homes in the USA [23]. No other items in the classrooms were shown to have detectable bromine. It is therefore not possible to attribute the PBDE content detected in the dust to any specific item in the classrooms on the basis of XRF analysis.

When compared to other indoor environment, the mean concentration of BDE-209 was 402 ng/g dust in the classrooms; higher than that found in homes but lower than that found in offices in Australia [24]. From the 97.5th percentile dose of BDE-209 a child will receive as a result of ingestion of classroom dust was calculated to be 0.8 ng/day, based on 3 mg/day dust ingestion [25]. These concentrations were higher than in homes in Australia [24] and while they may contribute to some of the higher body burden, they do not fully explain the higher levels of PBDEs measured in Australian children. Further investigation of actual dust ingestion rates in children as well as dietary exposure of school children is required to accurately calculate paediatric PBDE exposure.

References:

1. Kim, Y., F. Harden, L. Toms, and R. Norman (2014) *Chemosphere*. 106: p. 1-19
2. Harrad, S. and M. Diamond (2006) *Atmospheric Environment*. 40: p. 1187-1188
3. Harrad, S., S. Hazrati, and C. Ibarra (2006) *Environ Sci Technol*. 40(15): p. 4633-8
4. Gomara, B., L. Herrero, and M.J. Gonzalez (2006) *Environ Sci Technol*. 40(24): p. 7541-7
5. Sjodin, A., O. Papke, E. McGahee, J.F. Focant, R.S. Jones, T. Pless-Mullooli, L.M. Toms, T. Herrmann, J. Muller, L.L. Needham, and D.G. Patterson, Jr. (2008) *Chemosphere*. 73(1 Suppl): p. S131-6
6. Coakley, J., S. Harrad, Goosey E, Ali N, Dirtu AC, N. Van den Eede, A. Covaci, J. Douwes, and A. Mannelje (2013) *Environment International*. 59C: p. 255-261
7. Toms, L.M., M.E. Bartkow, R. Symons, O. Paepke, and J.F. Mueller (2009a) *Chemosphere*. 76(2): p. 173-8
8. Watkins, D., M. McClean, A. Fraser, J. Weinberg, H. Stapleton, and T. Webster (2013) *Environment International*. 59C: p. 124-132
9. Harrad, S., E. Goosey, J. Desborough, M. Abdallah, L. Roosens, and A. Covaci (2010) *Environmental Science & Technology*. 44(11): p. 4198-4202
10. Wu, Q., S.Y. Baek, M. Fang, and Y.S. Chang (2010) *Indoor air*. 20(3): p. 263-70
11. Thuresson, K., J.A. Bjorklund, and C. de Wit (2012) *Sci Total Environ*. 414: p. 713-721
12. Stapleton, H.M., S. Eagle, A. Sjodin, and T.F. Webster (2012) *Environmental Health Perspectives*. 120(7): p. 1049-54
13. Toms, L.M.L., A. Sjodin, F. Harden, P. Hobson, R. Jones, E. Edenfield, and J.F. Mueller (2009) *Environmental Health Perspectives*. 117: p. 1461-1465
14. Eskenazi, B., J. Chevrier, S.A. Rauch, K. Kogut, K.G. Harley, C. Johnson, C. Trujillo, A. Sjodin, and A. Bradman (2013) *Environmental Health Perspectives*. 121(2): p. 257-62
15. Ali, N., S. Eqani, R. Malik, H. Neels, and A. Covaci (2013) *Science of the total environment*. 461-462: p. 655-662
16. Harrad, S., C. Ibarra, M. Diamond, L. Melymuk, M. Robson, J. Douwes, L. Roosens, A.C. Dirtu, and A. Covaci (2008) *Environ Int*. 34(2): p. 232-8
17. Brommer, S., S. Harrad, N. Van den Eede, and A. Covaci (2012) *Journal of environmental monitoring*. 14: p. 2482-2487
18. Abdallah, M., S. Harrad, and A. Covaci (2009) *Analytical Chemistry*. 81: p. 7460-7467
19. Gallen, C., A. Bank, S. Brandsma, C. Baduel, P. Thai, G. Eaglesham, Heffernan A., Leonards., P. Bainton, and Mueller J.F. (2014) *Science of the total environment*. accepted 20 Jan 2014
20. U.S. Environmental Protection Agency (2013) <http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/pbde.html>. accessed (22 July 2013)
21. Allen, J.G., M.D. McClean, H.M. Stapleton, and T. Webster (2008) *Environmental Science and Technology*. 42: p. 4222-4228
22. Whitehead, T.P., F.R. Brown, C. Metayer, J.-S. Park, M. Does, M. Petreas, P.A. Buffler, and S. Rappaport (2013) *Environment International*. 57-58: p. 11-24
23. Imm, P., L. Knobeloch, C. Buelow, and H. Anderson (2009) *Environ Health Perspect*.
24. Toms, L.M., M.E. Bartkow, R. Symons, O. Paepke, and J.F. Mueller (2009) *Chemosphere*. 76(2): p. 173-8
25. U.S. Environmental Protection Agency, *Exposure Factors Handbook, General Exposures*. EPA/600/P-95/002Fa. Vol. 1. 1997, Washington DC: Office of Research and Development National Center for Environmental Assessment.