CONTINUING SOURCES OF PCBS: THE SIGNIFICANCE OF BUILDING SEALANTS

Melymuk, Lisa[1], Robson, Matthew[2], Csiszar, Susan[1], Diamond, Miriam[1, 2], Helm, Paul[3], Blanchard, Pierrette[4] and Backus, Sean[5]

[1] Department of Chemical Engineering & Applied Chemistry, University of Toronto, Toronto, Canada, M5S 3E5
[2] Department of Geography, University of Toronto, Toronto, Canada, M5S 3G3
[3] Environmental Monitoring & Reporting Branch, Ontario Ministry of Environment, Toronto, Canada, M9P 3V6
[4]Air Quality Research, Environment Canada, Toronto, Canada M3H 5T4
[5] Ontario Water Quality Monitoring, Environment Canada, Burlington, Canada, L7R 4A6

Introduction

The polychlorinated biphenyls (PCBs) are a group of persistent organic chemicals that were very widely used in the 1950s, 60s and 70s for a broad range of applications. During this time it is estimated that over 1.3 million tonnes of PCBs were produced worldwide[1], with 635,000 tonnes being produced in North America alone[2].

Due to growing public and scientific concerns about their toxicity, long term persistence and global distribution, PCBs were gradually phased out of production throughout most of the industrialized world by the late 1970s. Concentrations worldwide dropped over the next decade in response to decreased production, but the rate of decline now appears to have either slowed considerably or stopped entirely in many areas of the world[3]. PCBs remain a ubiquitous environmental contaminant.

One of the key reasons for this continued prevalence is the presence of large reservoirs of PCBs in materials and equipment still in use in some jurisdictions; as although the manufacture of PCBs was largely banned, their continued use in existing materials was not. One of the most important of these is probably the use in elastic building sealants constructed in the 1950-70s.

Building sealants are particularly important as not only do they represent a considerable percentage of the remaining PCB stocks (10-18%)[1,4], but by the very nature of this use, they are classically open sources i.e. applied superficially to the outside of buildings, and therefore permanently exposed to a wide variety of uncontrollable loss process, such as volatilization, wash off and erosion. All of these processes contribute to the overall burden of PCBs in urban areas and beyond.

The importance of PCB-containing sealants as a continuing emission source is supported by a range of studies that have found elevated concentrations of PCBs in urban areas[5,6,7] that cannot be accounted for in terms of environmental cycling[6].

To investigate the significance of these sealants as a remaining source of PCBs a combined small scale screening campaign and GIS based stock estimation was undertaken for the city of Toronto, Canada. Toronto is Canada's largest city, covering approximately 635 km^2 on the northwest shore of Lake Ontario.

Methods

Sampling

26 buildings were selected from a small urban area of Toronto for investigation, 20 that were built between 1950 and 1980, when PCBs were used in building sealants, and 3 before and after these dates to check for temporal variations. From each building a small (approximately 50 mg) sample of sealant was removed and placed into a clean pre-weighed test tube. The tube was then sealed, transported back to the laboratory and refrigerated (4°C) until analysis. All samples were collected within one week in December 2007.

The tubes were then reweighed and the exact sample mass calculated. 1 mL of hexane added and the sample sonicated for 25 minutes, the hexane removed and placed into a clean glass vial. This was then repeated twice more. The combined extracts were then washed with 2 mL of concentrated H_2SO_4. The top solvent layer was then removed and eluted through a 1 g Florisil SPE tube (Supelclean, ENVI-Florisil , Supelco) with 10 mL of hexane. The resulting sample was then adjusted to 12 mL. A 500 µL aliquot was transferred to a GC vial and spiked with a known amount of internal standard (PCB 119).

All samples were analyzed using an Agilent 6890N gas chromatograph coupled to an Agilent 5975 Mass Selective Detector. Chromatographic separation was achieved with a 60m DB-5 column (25 µm i.d., 0.25 µm film thickness) running a temperature program of 140°C for 2 min, then 5°C min^{-1} to 215°C held for 5 min, followed by 10°C min^{-1} to 280°C held for 10 minutes. 1 µL of analyte was injected in splitless mode, with the interface and injector held at 280°C. 83 PCB congeners were quantified with a method detection limit of 52 µg/g Σ_{83}PCBs.

This relatively high method detection limit was chosen, as PCBs were typically added to sealants at levels in excess of 10 mg/g in order to act as a plasticizer[8]. Therefore samples containing PCBs that were not at sufficient concentrations to act as a plasticizer were excluded.

One blank was run for every 5 samples. No target congeners were detected.

Results and Discussion

Congener and Aroclor Data

Of the 26 buildings selected for analysis, 6 had detectable concentrations of PCBs in sealants, with concentrations ranging over two orders of magnitude, from 0.57 mg/g to 82.09 mg/g, with a mean concentration of 22.10 mg/g detected (Table 1). No PCBs were detected in those building outside of the target age range (i.e. pre 1950, post 1980).

From these samples it appears that only one third of buildings constructed between 1950 and 1980 are likely to have been constructed with PCB containing sealants. These data also confirm the relatively brief time frame (30 yrs) during which these chemical were used. These findings are in very close agreement to those of previous studies elsewhere such as in Boston[9] and Switzerland[8] where similar amounts of PCBs, rates of detection and construction dates have been recorded.

Further examination of the data indicate that four of these buildings (bldgs 11, 13, 23, 25) have congener profiles that closely match Aroclor 1254, one (bldg 9) that matches Aroclor 1260, and one (bldg 20) that appears to be a mixture of both Aroclors 1248 and 1254 (Figure 1). This also closely agrees with the work of Herrick[6] in Boston, who concluded that these two Aroclors were the predominate mixtures used for this purpose in North America.

Comparison of the concentration of PCBs in these 6 samples with our calculated lowest possible functional concentration (10 mg/g), suggests shows that for 4 of the buildings (bldgs, 9,20 and 25) considerable amounts of PCBs (on average 66%) must have been lost in some way.

Further analysis suggests that there has been a greater loss of lower chlorinated congeners from these samples than of the more chlorinated congeners, with almost no trichlorobiphenyls being detected despite their presence in significant quantities in all of the original technical PCB mixtures that were used (Fig 1). This suggests that a major loss process for PCBs from these sealants is probably direct volatilization from the sealant surface, with the process being of greater importance for the lower chlorinated congeners. This is important as (a) it indicates that these sealants may act as a source to areas considerable distances away, due to direct atmospheric transport of these more volatile congeners, and (b) that these sealants may also account for the strong temperature dependence seen in urban gas phase PCB concentrations that has historically been ascribed to the revolatilization of previously deposited material[10].

This hypothesis of sealants as a source of PCBs to urban air through volatilization is further supported by the fact that there is also an appreciable increase in the relative proportion of the higher chlorinated congeners in these samples relative to the original Aroclor mixtures. This shift in congener distribution would not occur if a less temperature dependent mechanism was at work such as, for example, direct erosion of the sealants.

Wider significance of PCB sealants

To estimate the significance of these sealants as a source of PCBs from the city of Toronto as a whole, we constructed a GIS database, containing all of the structural volumes for buildings within the target age range, their locations, the estimated amount of sealant present, and the 0.3 proportion of buildings expected to contain PCBs.

Using the concentrations determined in our screening campaign, we then calculated the expected range (upper and lower bound) of PCBs still present in sealants in the city. We estimated that there are from 3 to 496 tonnes of Σ_{83} PCBs still present in sealants in the city (Table 2), with the most likely estimate being 133 tonnes.

The usage of PCB sealants has important implications for the geographic distribution of PCBs in cities that expanded significantly in the 1950s and 1960s. This is supported by the work of Gingrich *et al*[13] who found similar trends in PCB levels in surface films in Toronto. Secondly, these results have implications for PCB exposure via inhalation of indoor and outdoor air and dust. This is important as it indicates that a person's exposure to chemicals via the atmosphere (both indoor and outdoor), which has been estimated to be between 6 and 64% of overall human exposure to these chemicals[11], is likely to be very heterogeneous. Exposure will depend on when and where an individual's residence and workplace were built.

Conclusions

This study shows that PCB-impregnated building sealants is a current reservoir of PCBs in cities, with upwards of 133 tonnes of PCBs potentially remaining in building sealants in Toronto alone. This stock appears to be depleted of the lower chlorinated congeners which is consistent with their loss by volatilization. This has considerable implications for the stock and flows of PCBs in urban areas. For example, if only 0.1% of the total PCB burden in sealants in Toronto escaped each year this would equate to a continued yearly input of 3.0 to 500 kg of fresh PCBs to the environment surrounding Toronto.

Acknowledgements:

Funding was provided by Great Lakes Atmospheric Deposition grant to Diamond, Helm, Blanchard and Backus, Ontario Ministry of the Environment, Environment Canada, Toronto and Region Conservation Authority, and the Natural Sciences and Engineering Research Council of Canada.

References:

1. Breivik, K., Sweetman, A., Pacyna, J. M., Jones, K. C. 2002. *The Science of the Total Environment* 290 (1-3): 199.
2. Commission for Environmental Cooperation. 1996. *Status of PCB management in North America*. Ottawa: Prospectus Inc.,
3. Bhavsar, S. P., Jackson, D. A., Hayton, A., Reiner, E. J., Chen, T., Bodnar, J. 2007. *Journal of Great Lakes Research* 33 (3): 592.
4. Andersson, M., Ottesen, R., Volden, I.. 2004. *The Science of the Total Environment* 325 (1-3): 139.
5. Gingrich, S.E., Diamond, M.L., Stern, G.A., McCarry, B.E., 2001. *Environmental Science & Technology* 35 (20): 4031.
6. Robson, M., Harrad, S. 2004. *Environmental Science & Technology* 38 (6): 1662.
7. Hsu, Y.K., Holsen, T.M., Hopke, P.K. 2003. *Environmental Science & Technology* 37 (4): 681.
8. Kohler, M., Tremp, J., Zennegg, M., Seiler, C., Miner-Kohler, S., Beck, M., Lienemann, P., Wegmann, L., Schmid, P. 2005. *Environmental Science & Technology* 39 (7): 1967.

9. Herrick, R. F., McClean, M. D., Meeker, J. D., Baxter, L. K., Weymouth, G. A. 2004. *Environmental Health Perspectives* 112 (10): 1051.
10. Harrad, S.J., Sewart, A.P., Alcock, R., Boumphrey, R., Burnett, V., Duarte-Davidson, R., Halsall, C., Sanders, G., Waterhouse, K., Wild, S.R., Jones, K.C. 1994. *Environmental Pollution* 85: 131.
11. Currado, G.M., Harrad, S.J. 1998. *Environmental Science & Technology* 32 (20): 3043.
12. Frame, G. M., Cochran, J. W., Boewadt, S.S. 1996. *J. High Res. Chromatogr.* 19: 657.
13. Gingrich, S.E., Diamond, M.L. 2001. *Environmental Science & Technology* 35 (20): 4031.

Figure 1: Percentage distribution of PCB homologue groups in building sealants and Aroclors 1248, 1254 and 1260 (Aroclor data taken from 12)

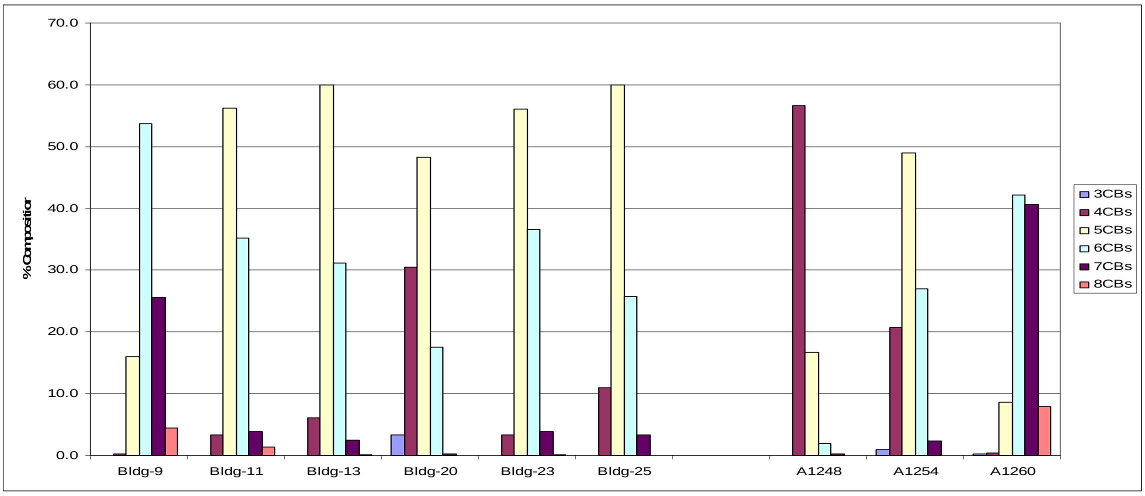

Table 1: PCB concentrations in building sealants

Building Number	Year of Construction	Concentration of Σ_{83}PCBs (mg/g)
9	1963	8.66
11	1958	11.47
13	1967	28.94
20	1973	0.57
23	1950	82.09
25	1965	0.88

Table 2: Calculated PCB burdens (tonnes of Σ_{83}PCBs) in building sealants in Toronto, Canada

Best Estimate (Tonnes Σ_{83}PCBs)	Low Estimate (Tonnes Σ_{83}PCBs)	High Estimate (Tonnes Σ_{83}PCBs)
133	3	496