

THE RELATIVE CONTRIBUTIONS OF PRIMARY AND SECONDARY SOURCES OF ATMOSPHERIC PCB IN BIRMINGHAM, U.K.

Jianzhang Ren and Stuart Harrad*

Institute of Public & Environmental Health, University of Birmingham, Birmingham B15 2TT, U.K.

Introduction

For PCBs, the atmosphere is the key point of entry into the air-to-cattle-to-human food chain, which is responsible for the majority of human exposure (1). Atmospheric source apportionment of PCBs thus has a pivotal rôle in controlling such exposure. In line with EC Council Directive 96/59/EC, the U.K. government has formulated an action plan to phase out and destroy PCBs still remaining in use (2). It is important that the influence on human exposure of such a programme is evaluated, and to do so, the relative contribution of leaks from PCB-filled equipment to the overall atmospheric source flux must be determined. A review of recent literature (3-5) suggests that whilst PCB volatilisation from soil (*i.e.* secondary releases) is likely to constitute the most significant source; primary sources - principally leaks from capacitors sited indoors - may still make appreciable contributions in urban areas. In particular, Halsall *et al* (4) used a simple box model of PCB fate within the atmosphere above Manchester, U.K., which - albeit based on a single indoor air sample - *inter alia* illustrated the *potential* significance of indoor air ventilation as a source of PCB # 52 in outdoor air. Support for this hypothesis comes from the fact that PCB concentrations in indoor air in the West Midlands are *ca* 30 times greater than those outdoors (6).

This paper uses a simple box model approach to make a preliminary estimate of the relative contribution of primary (indoor air ventilation) and secondary (volatilisation from soil) sources to concentrations of individual PCB congeners in the atmosphere of the West Midlands conurbation, with the specific intention of assessing the potential impact on atmospheric concentrations of PCBs of the U.K. government's action plan. Although the complexity of such a dynamic system and the need for a more detailed study is fully recognised, we consider that this study provides a useful indication of the potential significance of indoor air ventilation as a source of PCBs in the West Midlands area.

As an additional means of source apportionment, we have measured the enantiomeric ratio (ER) of PCB 149 in soil and outdoor air. In commercial PCB formulations, the 19 chiral PCBs are present as racemates - *i.e.* ER = 1. By comparison, due to enantiomeric differences in resistance to biodegradative processes, the ERs of chiral organochlorines found in soils - and which are preserved upon volatilisation - deviate from 1 (7). It is therefore hypothesised that a knowledge of ERs in samples of outdoor air, commercial PCB formulations, and soil may indicate the extent to which the contemporary ambient atmospheric burden is due to revolatilised material, and how much arises from fresh emissions from remaining PCB stocks.

To illustrate, if the ER for a given chiral congener in soil (ER_{soil}) is known, and it is assumed that this ER would be preserved on volatilisation, the percentage contribution of racemic sources (*e.g.*

indoor air ventilation) to outdoor air levels of that PCB ($PC_{RACEMIC}$) may be calculated using the equation below.

$$PC_{RACEMIC} = \frac{ER_{OA} - ER_{SOIL}}{ER_{RACEMIC} - ER_{SOIL}} \times 100\%$$

Where ER_{OA} = ER in outdoor air and $ER_{RACEMIC} = 1$

Methods

Where data on PCB concentrations have not been reported previously, they were obtained via GC/MS methodology reported elsewhere (8). ERs of PCB 149 were determined in sample extracts prepared as for conventional PCB analysis, using a Fisons' MD800 GC/MS operated in EI/SIM mode, fitted with a Chirasil-Dex CB column (25 m, 0.25 mm, 0.25 μ m). The oven program was 140 C for 2 min, then 5 C min^{-1} to 180 C, and held for 60 min. ERs were measured in 10 outdoor air samples taken at our campus monitoring station (identical to that reported elsewhere (9)), and in 9 surface soils at various locations on our campus. Samples for ER measurements were taken in March and April 1999. The algorithms and the sources of input values used to estimate the magnitude of the sources considered by the box model (dimensions are 20 km wide, by 20 km long, by 2 km high) are described below.

Source

S_{vol} (volatilisation from soil)

Algorithm

$M_0 [1 - e^{-k_v \times t}]$ where $M_0 = C_{soil} \times$ surface area of "box" covered by soil \times topsoil depth \times soil density
 t = time interval over which model is run, 1 day

S_{vent} (ventilation of building air)

$C_{IA} \times VOL_{BA}$

M_0 = total mass of individual PCB congener associated with "box" topsoil; C_{soil} = arithmetic mean level in soil to 5 cm depth (taken from a study of 14 soils sampled at 7 sites in the West Midlands in early 1999 – this study). Surface area of "box" covered by soil = 20% total surface area (4); topsoil depth assumed to be 5 cm; soil density = 1000 kg m^{-3}

k_v = 1st order rate constant for PCB loss from soil (measured for PCBs 28, 52, 101, 138, and 180 (10)). We have conservatively assumed that all loss is due to volatilisation. Where congener-specific data are unavailable, we have assumed k_v to equal that for the congener of the same homologue group.

C_{IA} = arithmetic mean indoor air PCB concentration (mean of samples from 14 different indoor microenvironments between 2/97 and 2/98 (6))

VOL_{BA} = volume of building air \times daily ventilation rate

Ventilation rate assumed to be 50% h^{-1} ; building air volume to be 0.05 % of total "box" volume (4)

Results and Discussion

The box model estimates of the relative contribution of volatilisation from soil and ventilation of indoor air to outdoor air levels of 10 individual tri- through heptachlorinated PCBs, together with congener-specific input values for C_{soil} , k_v , and C_{IA} - are shown in Table 1. ER_{SOIL} values were in the range 0.86-1.03 (arithmetic mean = 0.92, $\sigma = 0.07$), while ER_{OA} values were between 0.99 and 1.08 (arithmetic mean = 1.02, $\sigma = 0.03$).

Primary versus Secondary Sources

Box Model Estimates The column “% Primary” in Table 1 shows the estimated contribution of indoor air ventilation to atmospheric PCB concentrations in the West Midlands. Clearly, indoor air ventilation appears particularly significant for the tri- and tetrachlorinated congeners due to their predominance in indoor air. Furthermore, this approach suggests that for the sum of congeners considered here, ventilation of building air and volatilisation from soil represent roughly equal sources of atmospheric PCB in the West Midlands.

Estimates based on ERs Clearly, the fact that ER_{OA} is essentially racemic, and ER_{SOIL} is appreciably <1, indicates that racemic sources constitute easily the most significant source of atmospheric concentrations of PCB 149 at our urban background monitoring site. This estimate of $PC_{RACEMIC}$ may be extrapolated to other PCBs where it can be demonstrated that their concentrations in outdoor air are highly correlated with PCB 149. Linear regression of atmospheric concentrations of PCB 149 against those of ΣPCB in 41 samples taken at our campus site between July 1997 and July 1998 (11), revealed a highly significant (>99.9%) positive linear correlation ($\Sigma PCB = 41.9 \times PCB\ 149 + 37$; $R = 0.85$). However, correlation does not in itself necessarily imply that the contribution of racemic sources to concentrations of ΣPCB (or of other individual PCBs) is identical to that of PCB 149. Our estimate of the contribution of racemic sources to atmospheric concentrations of PCB 149 at our site is 100%. Therefore, the concentration of PCB 149 in the absence of racemic sources = 0. Substituting $PCB\ 149 = 0$ into the regression equation gives a concentration of ΣPCB in the absence of racemic sources of $37\ \text{pg m}^{-3}$. Given that the arithmetic mean atmospheric concentration of ΣPCB at our site = $290\ \text{pg m}^{-3}$ (9), the percentage contribution of racemic sources to atmospheric concentrations of $\Sigma PCB = 100 \times [(290-37)/290] = 87\%$. An important caveat, is that our measurements of ER_{OA} were made in March and April, when lower soil temperatures would be expected to reduce the extent of PCB volatilisation from soil. Further monitoring of *inter alia* seasonal and diurnal variations in ER_{OA} for PCB 149 and other chiral PCBs will be conducted and their implications for source apportionment evaluated for both ΣPCB and individual congeners.

Although the uncertainties associated with both source apportionment approaches used are acknowledged, together they provide good evidence to suggest that a comprehensive decommissioning of PCB-contaminated equipment remaining in use - as envisaged in the U.K. government's action plan - may have a significant effect on reducing PCB levels in U.K. urban atmospheres.

References

1. Duarte-Davidson, R., Jones, K. C. *Sci. Tot. Environ.* **1994**, *151*, 131.

2. Department of the Environment, United Kingdom action plan for the phasing out and destruction of polychlorinated biphenyls (PCBs) and dangerous PCB substitutes, Department of the Environment, London, **1997**.
3. Harrad, S. J. et al *Environ. Poll.* **1994**, *85*, 131.
4. Halsall, C. J. et al *Environ. Sci. Technol.* **1995**, *29*, 2368.
5. Dyke, P. H., Stratford, J. *Organohalogen Compds.* **1998**, *36*, 365.
6. Currado, G. M.; Harrad, S. J. *Environ. Sci. Technol.* **1998**, *32*, 3043.
7. Bidleman, T. F., Falconer, R. L. *Environ. Sci. Technol.*, **1999**, *33*, 206A.
8. Ayris, S. et al *Chemosphere*, **1997**, *35*, 905.
9. Currado, G. M.; Harrad, S. *ibid.*
10. Ayris, S. PhD Thesis, University of Birmingham **1998**.
11. Currado, G. M. PhD Thesis, University of Birmingham **1999**.

Table 1: Box Model Output

Congener	k_v (d ⁻¹)	C_{SOIL} (ng kg ⁻¹)	C_{IA} (ng m ⁻³)	S_{VOL} (ng d ⁻¹)	S_{VENT} (ng d ⁻¹)	% Primary
28/31	2.60E-03	2.35E+02	6.30E-01	2.44E+09	3.02E+09	55.34
52	1.90E-03	3.11E+02	1.51E+00	2.36E+09	7.25E+09	75.43
49	1.90E-03	1.79E+02	2.95E-01	1.36E+09	1.42E+09	51.03
101	1.00E-03	9.28E+02	6.58E-01	3.71E+09	3.16E+09	45.98
99	1.00E-03	4.18E+02	1.84E-01	1.67E+09	8.83E+08	34.58
118	1.00E-03	1.29E+03	2.28E-01	5.16E+09	1.09E+09	17.51
149	6.00E-04	1.10E+03	1.41E-01	2.64E+09	6.77E+08	20.41
153	6.00E-04	1.78E+03	1.13E-01	4.27E+09	5.42E+08	11.27
138	6.00E-04	2.30E+03	1.26E-01	5.52E+09	6.05E+08	9.88
180	4.00E-05	8.61E+02	2.50E-02	1.38E+08	1.20E+08	46.56
ΣPCB ^a				2.93E+10	1.88E+10	39.07

^aSum of congeners reported here