

# ENVIRONMENTAL TRANSPORT AND FATE

## FURTHER STUDIES OF AIR-TO-GRASS TRANSFER OF POLYCHLORINATED BIPHENYLS (PCBs)

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### Background and Objectives

With respect to vapour-phase depositional air-to-plant transfer of persistent organic pollutants (POPs), recent research has highlighted the need to differentiate between equilibrium partitioning and kinetically limited gaseous deposition. The most satisfactory explanation to date of air-to-plant transfer of PCBs, is that presented by McLachlan<sup>1</sup>, and evaluated in the field by Böhme *et al*<sup>2</sup>. Summarised, the framework states that plant uptake of PCBs from the atmosphere essentially occurs by one of the following two processes:

- i) equilibrium partitioning between the vapour phase and pasture, and
- ii) kinetically-limited gaseous deposition

#### *Equilibrium partitioning*

$$C_v/C_G = mK_{OA}^n \text{ (equation 1)}$$

Where  $C_v$  = PCB concentration in the plant/pasture ( $\text{mol m}^{-3}$ );  $C_G$  = atmospheric PCB concentration in the gas phase ( $\text{mol m}^{-3}$ ), and  $m$  and  $n$  are constants depending on factors like the plant species

Hence, where equilibrium partitioning is appropriate, plotting  $\log(C_v/C_G)$  versus  $\log K_{OA}$  should be linear with a slope of  $n$  and a y-intercept of  $\log m$ . According to the framework, such equilibrium partitioning governs air-to-plant transfer of trichlorinated PCBs, and under certain conditions (primarily air temperature) that of tetra, penta, and even hexachlorinated PCBs. In contrast, for congeners not reaching equilibrium, such plots would become non-linear. This is only partly consistent with the experimental observations of Thomas *et al* who claimed that equilibrium partitioning governed air-to-pasture transfer of *all* PCBs<sup>3</sup>. The framework's authors accounted for this apparent discrepancy by pointing out that studies such as that of Thomas *et al* studied compounds covering a range of  $K_{OA}$  values that were insufficient to detect the relatively subtle transition between equilibrium partitioning and kinetically limited gaseous deposition. This is supported by the fact that - using a non-parametric curve fitting technique - we were able to detect curvilinearity (*i.e.* evidence of non-equilibrium behaviour for penta through hepta-PCBs) in plots of  $\log(C_v/C_G)$  versus  $\log K_{OA}$  at grass exposure times up to 8 weeks.

#### *Kinetically limited gaseous deposition*

For those PCBs not governed by equilibrium gas-phase partitioning, transfer is expected to occur *via* kinetically limited gaseous deposition, described by equation (2)

$$C_v / C_G = A \gamma_{GG} t / V \text{ (equation 2)}$$

# ENVIRONMENTAL TRANSPORT AND FATE

where  $A$  is the surface area of the vegetation ( $\text{m}^2$ );  $g_{\text{GG}}$  is the mass transfer coefficient describing transport from the atmosphere to the vegetation surface ( $\text{m h}^{-1}$ );  $t$  = exposure time (h);  $V$  = volume of vegetation ( $\text{m}^3$ )

It is important to note that  $C_v/C_g (= K_{\text{VG}})$  is independent of  $K_{\text{OA}}$  in this instance, and furthermore that plots of  $C_v$  versus  $C_g$  would be linear for PCBs for which uptake was *via* kinetically limited gaseous deposition. This has been experimentally confirmed<sup>4</sup>.

In an earlier paper<sup>4</sup>, we identified an important issue concerning equation (2). In essence, providing that there was minimal variation of  $A$ ,  $V$ , and  $g_{\text{GG}}$  with exposure time for the same pasture sward, if one plotted  $C_v$  versus  $C_g$  for the same sward for different exposure times ( $t$ ), one would expect to see an increase in the slope of this plot that was directly proportional to  $t$ . In short, the slope for an experiment where the exposure time was 4 weeks would be twice that for an equivalent experiment where exposure time was 2 weeks. Our previous work<sup>4</sup> revealed a broad increase in slopes of  $C_v$  versus  $C_g$  plots with exposure time, but insufficient measurements were made to evaluate the significance of this increase; and as measurement of  $A$  and  $V$  were not made, the impact of temporal variation in these parameters (which could influence slopes of  $C_v$  versus  $C_g$  plots) were not assessed.

## Experimental

A plot of pasture grass was “fenced-off” within 2 m of the background urban site where air monitoring was conducted. The plot was cut back on 5<sup>th</sup> May 2000 and sampled every 2 weeks until 27<sup>th</sup> July 2000. The species composition of the mixed sward was typical of U.K. pasture grassland. PCB concentrations in air were measured over a single 24 h period every week during the experiment. For studying air-to-pasture transfer, atmospheric PCB concentrations were taken to be the mean of the 2 measurements made during each pasture sampling period. Automatic monitoring of air temperature was conducted during all sampling events. PCB concentrations in both the atmospheric vapour phase ( $C_g$ ) and pasture samples ( $C_v$ ) were determined using well-validated containment-enrichment, GC/MS procedures. Measurements of grass surface area and volume were conducted *via* a digitised imaging protocol.

## Results and Discussion

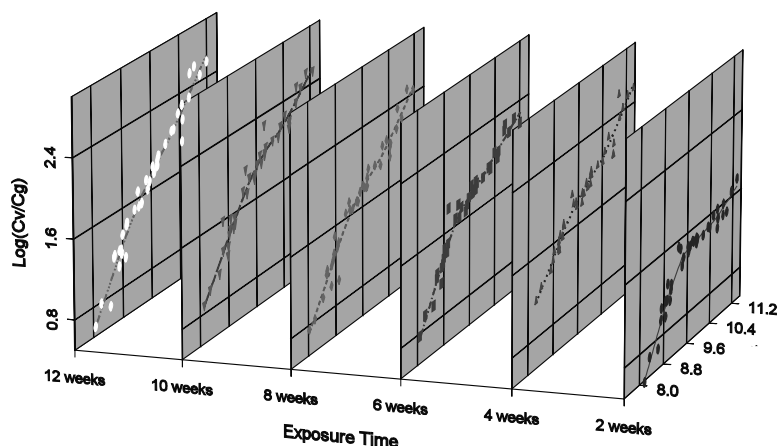
Figure 1 shows plots of  $\text{Log}(C_v/C_g)$  versus  $\text{Log } K_{\text{OA}}$  (corrected for the mean air temperature over the sampling period) for pasture samples taken after 2, 4, 6, 8, 10 and 12 weeks exposure. To aid detection of the point at which the mechanism of uptake changes from equilibrium partitioning to kinetically limited gaseous deposition, we have used a locally weighted least-squares method – the Cleveland-Devlin noise-reduction smoothing algorithm<sup>4</sup> – for non-parametric curve fitting. Using this technique, it is apparent that the plots display curvilinearity at high  $\text{Log } K_{\text{OA}}$  ( $>9.6$ ) at up to 10 weeks exposure, with a fully linear plot denoting the attainment of equilibrium not achieved until 12 weeks.

An alternative means of detecting whether equilibrium has been attained is to observe whether  $C_v$  values increase with exposure time. While Thomas *et al* observed no variation in  $C_v$  with exposure time for PCBs, Currado and Harrad<sup>5</sup> found an appreciable increase with exposure time in concentrations of 6 out of the 8 hexa- and heptachlorinated PCBs. A problem with this approach is that  $C_v$  is dependent on  $C_g$  and also on  $K_{\text{OA}}$  (equation 1). There will be appreciable variations in both  $C_g$  and  $K_{\text{OA}}$  (due to temperature variations) between different sampling periods, which could mask any temporal changes in  $C_v$  values due to non-equilibrium behaviour. In an attempt to factor out the impact of variations in temperature and  $C_g$ , we have instead plotted  $K_{\text{VG}}/K_{\text{OA}}$  against exposure time, where  $K_{\text{VG}} = C_v/C_g$  and  $K_{\text{OA}}$  is temperature-corrected. In summary, we observed equilibrium to be reached by 4 weeks for tri and tetra-PCBs, but that equilibrium was not clearly attained for hexa and hepta-PCBs until at least 8 weeks. Figures 2 and 3 are illustrative plots for congener # 31/28 and #153 respectively.

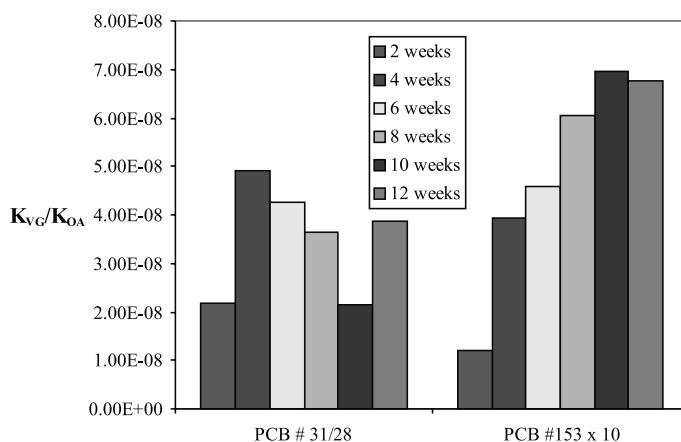
# ENVIRONMENTAL TRANSPORT AND FATE

**Table 1.** Variation in Slope of  $C_V$  versus  $C_G$  Plots for Penta, Hexa and Heptachlorobiphenyls with Exposure Time

| Exposure Time (weeks) | Slope | p      |
|-----------------------|-------|--------|
| 2                     | 26.3  | <0.001 |
| 4                     | 74.5  | <0.001 |
| 6                     | 62.5  | <0.001 |
| 8                     | 96.7  | <0.001 |
| 10                    | 82.2  | <0.001 |



**Figure 1.** Plots of  $\text{Log}(C_V/C_G)$  versus  $\text{Log}K_{OA}$  at Different Exposure Times



**Figure 2.** Illustrative Examples of Variation of  $K_{VG}/K_{OA}$  with Exposure Time

# ENVIRONMENTAL TRANSPORT AND FATE

We then plotted  $C_v$  versus  $C_g$  for all penta, hexa and heptachlorobiphenyls (*i.e.* those PCBs lying on the curvilinear portion of the plots in Fig. 1) at exposure times of 2, 4, 6, 8, and 10 weeks (the 12 week sample was omitted as the evidence presented above suggested equilibrium to have been attained by this time). Table 1 shows that there is a statistically significant positive linear relationship ( $p < 0.001$ ) between  $C_v$  and  $C_g$  at each exposure time. Furthermore, there is a statistically significant increase in the magnitude of the slopes with exposure time ( $P = 0.1$ ). In an attempt to factor out the influence of changes with exposure time of the ratio of grass surface area to volume ( $A/V$ ), we normalised the slopes of  $C_v$  versus  $C_g$  plots by dividing by  $A/V$  and plotting versus exposure time. Interestingly, as our data revealed an increase of  $A/V$  with exposure time, such normalisation rendered the relationship between slopes and exposure time statistically insignificant ( $p > 0.1$ ).

## References

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4. Mao, H. and Harrad, S. (2000), *Organohalogen Compds*, 45, 276
5. Currado, G.M and Harrad, S. (1999). Air-to-Grass Transfer of PCBs. Poster presented at Dioxin '99, 19<sup>th</sup> International Symposium on Halogenated Environmental Organic Pollutants and POPs, 12-17/9/99, Venice, Italy.