

AIR-TO-PASTURE TRANSFER OF POLYCHLORINATED BIPHENYLS (PCBs): EQUILIBRIUM PARTITIONING OR KINETICALLY-LIMITED GASEOUS DEPOSITION?

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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. In the former, the compound has reached equilibrium between the atmospheric vapour-phase and the leaf surface. In the latter, the storage capacity of the compound in the plant lipid is so great, that transfer from the atmospheric vapour-phase occurs too slowly to reach equilibrium within the time span of a "normal" growing period. This has only recently received serious consideration, as previous work had almost exclusively regarded vapour-phase transfer as an equilibrium process. The most satisfactory explanation to date of air-to-plant transfer of PCBs, is that presented by McLachlan¹, and evaluated in the field by Böhme *et al*². 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

The algorithms describing PCB behaviour in each case are as follows:

Equilibrium partitioning

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

Where C_V = PCB concentration in the plant/pasture (mol m^{-3})
 C_G = atmospheric PCB concentration in the gas phase (mol m^{-3})
 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. 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* PCBs³. The framework's authors

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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 conflicting findings of Currado and Harrad^{4,5}). These authors obtained an apparently linear relationship when they plotted $\log(C_V/C_G)$ versus $\log K_{OA}$ for tri- through heptachlorinated PCBs⁴). However, in contrast to Thomas *et al* - who observed no variation in concentrations of any PCBs in pasture with exposure time - Currado and Harrad⁵) found that - while concentrations of 20 out of 23 tri- through pentachlorinated PCBs in pasture did not change with exposure time (varied between 2, 4, and 6 weeks); there was an appreciable increase with exposure time (*i.e.* over and above the combined sampling and analytical variability) in concentrations of 6 out of the 8 hexa- and heptachlorinated PCBs. The inference of these findings is that while tri- through pentachlorinated PCBs had reached equilibrium within 2 weeks; the hexa- and heptachlorinated congeners had not reached equilibrium after 6 weeks - *i.e.* for these congeners, the assumption of equilibrium partitioning was inappropriate.

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)

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

where A is the surface area of the vegetation (m^2)

γ_{GG} is the mass transfer coefficient describing transport from the atmosphere to the vegetation surface ($m \text{ h}^{-1}$)

t = time of exposure (h)

V = volume of vegetation (m^3)

It is important to note that C_V/C_G is independent of K_{OA} in this instance, and furthermore that plots of C_V versus C_G would be linear for POPs for which uptake was *via* kinetically limited gaseous deposition. This is consistent with the observations of both McLachlan⁶), and Jones and Duarte-Davidson⁷), who noted that pasture uptake of PCDD/Fs was independent of K_{OA} or any other PCDD/F physicochemical property. In a similar vein, Currado and Harrad⁸) noted that a linear relationship existed between C_V and C_G for penta and hexachlorinated PCBs, but not the tri and tetrachlorinated congeners.

Another important issue raised by the framework concerns equation (2). It is evident that γ_{GG} would remain constant for a given congener, and both A and V would remain essentially constant with time for the same pasture sward. As a result, 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 the increase in 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. Such increases in the slope have potentially important implications, as it implies that for constant vapour phase PCB concentrations, concentrations in pasture will increase with exposure time, albeit moderated to an unknown extent by the anticipated decrease in surface area per unit volume of vegetation (as grass grows longer over a typical growing period, it also grows thicker/coarser).

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Against this backdrop, we set out to:

1. Ascertain which uptake process governed air-to-pasture transfer of a range of tri through heptachlorobiphenyls, and
2. Investigate whether for those PCBs governed by kinetically limited gaseous deposition, the slope of C_V versus C_G plots increased proportionally to exposure time

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 11th May 1999 (sample discarded) and sampled every 2 weeks until 5th July 1999, giving a total of 4 samples. The species composition of the mixed sward was typical of U.K. pasture grassland⁴). 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 reported elsewhere⁹).

Results and Discussion

Figure 1 shows plots of $\text{Log}(C_G/C_V)$ versus $\text{Log} K_{OA}$ (corrected for the mean air temperature over the sampling period) for pasture samples taken after 2, 4, 6, and 8 weeks exposure. In order to assist 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 algorithm¹⁰) – for non-parametric curve fitting. Using this technique, it is apparent that the plots become curvilinear at high $\text{Log} K_{OA}$ (>10.5) even after 8 weeks exposure. This is evidence that congeners for which $\text{Log} K_{OA} > 10.5$ have still not seen enough air to reach equilibrium *i.e.* that plant uptake is kinetically limited.

Having identified those PCB congeners governed by kinetically limited gaseous deposition, we plotted C_V versus C_G for 7 individual hexa and heptachlorobiphenyls (*i.e.* those PCBs for which temperature-corrected $\text{Log} K_{OA}$ exceeded 10.5) at exposure times of 2, 4, 6, and 8 weeks. The slopes and intercepts summarised in Table 1 (all plots revealed highly significant – $p < 0.001$ – linear relationships between C_V and C_G), are – while not unequivocal evidence – not inconsistent with the hypothesis that slopes of such plots will increase proportionally with exposure time, moderated by variations in A/V . We were unable to obtain satisfactorily precise measurements of A/V in this experiment, and obtaining such measurements, together with studying a wider range of compounds is needed to confirm or disprove this potentially important idea.

References

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

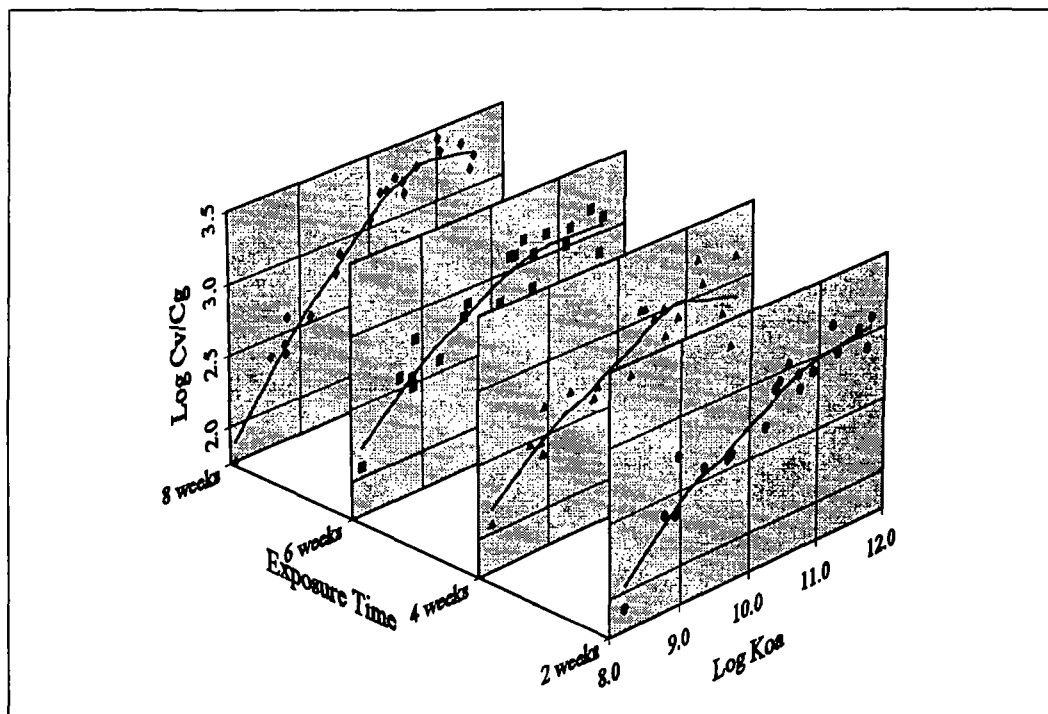


Table 1: Increase in Slope of C_V versus C_G Plots for Hexa and Heptachlorobiphenyls with Sampling Duration

Exposure Time (weeks)	Slope	Intercept
2	30.2	3.5
4	36.7	-2.3
6	50.4	2.1
8	59.7	0.7