Air-Pasture Transfers of PCBs

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Abstract
A field experiment was conducted to study the air to pasture transfer of PCBs at a rural coastal site in north-west England. Data are presented which suggest that freshly grown grass approached or attained equilibrium with the gas phase component of PCB in air rather rapidly, within about two weeks of exposure time. High molecular weight congeners partitioned onto the vegetation to a greater extent than lighter congeners, an effect which was more marked during the winter than in the summer.

Introduction

PCBs and other semi-volatile organic contaminants (SVOCs) can reach terrestrial systems following emission to the atmosphere, atmospheric transport and deposition processes. There is considerable interest at present in the processes of air-vegetation transfer/exchange of SVOCs, both as a source of these compounds to terrestrial foodchains and because of the role plant biomass may play in scavenging compounds from the atmosphere or potentially re-releasing them for continued global cycling. However, there is still a need to improve our understanding of the 'dynamics' of these processes.

In this paper we present data from a field experiment where the air-grass transfer of PCBs has been quantified over a number of months under three different simulated pasture grassland management scenarios.

Experimental section

A field plot was fenced off on an established sward of unimproved upland pasture at a field station site owned by Lancaster University, in the north-west of England. The sward comprised *Lolium perenne* (~30%), *Holcus lanatus* (~30%), *Agrostis capillaris* (~10%), *Poa pratensis* (~10%) and *Cynosurus cristatus*(~10%) and a range of other grasses and forbs. A meteorological site and ambient PCB monitoring equipment have been based at the site for a number of years and PCB air data reported previously (1). The field plot was established in early April 1996 into a series of 1 m^2 sub-plots. Three management regimes were established; 'simulated grazing', in which triplicate sub-plots were harvested every 2 weeks through the growing season between April and October 1996; 'simulated silage production', in which triplicate sub-plots were harvested at 6 week intervals (i.e. late May, late-July and mid-September); 'long-term growth', in which triplicate sub-plots were harvested every 3 months (i.e. in July, September and January). Air samples (gas + particle phase) were also taken every 1 or 2 weeks and coincided with grass harvesting. Grass yields (g m^{-2}) were always recorded.

Great care was taken to avoid contamination of the vegetation during sample handling. Samples were placed into sealed bags in the field and frozen until required. The sample for analysis (30 g wet weight) was frozen with liquid nitrogen, ground with powdered sodium sulphate (50 g), spiked with labelled recovery standards and soxhlet extracted for 8 hours with 250 ml 4:1 hexane:acetone.

The extract was firstly cleaned up on a silica/acidified silica double-layered column and eluted with hexane and secondly on a Biobeads SX-3 GPC column and eluted with 1:1 DCM:hexane mixture. Internal standards and keeper solvent were then added and the final sample taken down to 50 µl. Air filter and PUF samples were extracted separately with hexane and fractionated on a silica column. Quantification was achieved by GC-MS on a Fisons MD-800 with separation on a CPSil-8 50 m column. Grass lipid contents were estimated by hexane extraction on the dry, ground grass.

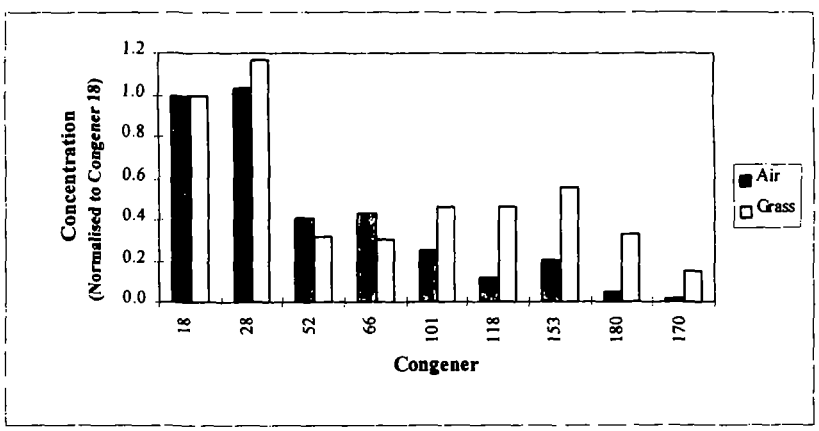
Results and Discussion

Air and grass concentrations

Air concentrations (Σ of 52 congeners) varied between 54 and 288 pg m^{-3}, with values in the summer (late-May to late-September) being generally higher. The lighter congeners (e.g. 18, 31, 28 and 33) were the most abundant; virtually all of the atmospheric burden of the PCBs was associated with the PUF plugs (≥93%).

Grass concentrations in the samples taken every 2 weeks varied between 890 and 2300 pg ΣPCB/g DW (equivalent to ~ 35 - 130 ng ΣPCB/g plant lipid), with no clear seasonal trend. The heavier congeners were relatively abundant in the grass compared to the air (see Figure 1). This reflects congener differences in the air:vegetation partitioning behaviour.

Figure 1: Normalised congener patterns averaged for air and vegetation



Comparisons of concentrations with exposure time

Given the dominance of the gas phase component of PCBs in air at this site, the key air-vegetation transfer pathway is envisaged as being partitioning onto the plant leaf wax/cuticle surfaces. Presumably, therefore, the concentrations of PCBs on grass will be influenced by the time of exposure (i.e. the amount of air which comes into contact with the leaf surface), various environmental factors (e.g. temperature, wind speed) and features of the vegetation (e.g. growth rate, leaf surface properties).

In this experiment at certain sampling times the 'simulated grazing', 'simulated silaging' and 'long-term growth' plots were sampled simultaneously (e.g. on the 8 July). It is instructive to compare the concentrations and compound mixtures for these samples (see Figure 2). This shows that the

concentrations of PCBs after essentially different exposure times are comparable. This suggests that the vegetation has approached or reached equilibrium with the air rather rapidly, within the two weeks exposure time of the 'simulated grazing' sward.

Seasonal differences in the air:vegetation partitioning process were also noted in the study, which may be related to ambient temperature. For example, Figure 3 shows the relative abundance of several congeners in the 3-monthly samples harvested in July, September and January. The heavier congeners have greater relative abundance in the January sample.

Figure 2: PCB concentrations in vegetation exposed for 2 weeks, 6 weeks or 3 months and harvested together in July 1996

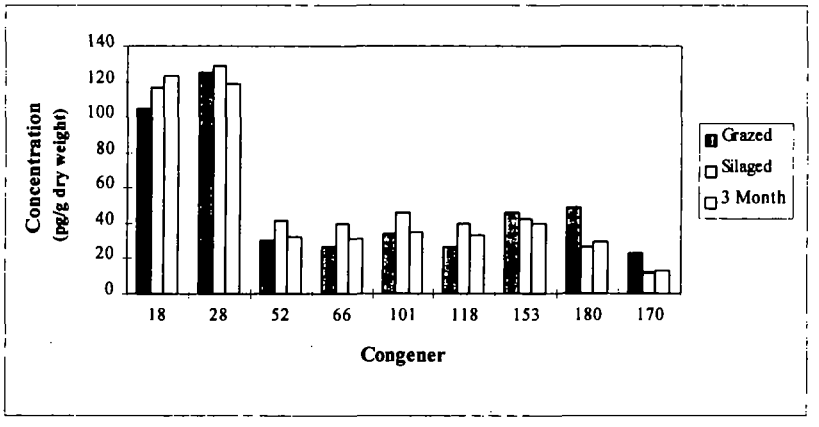
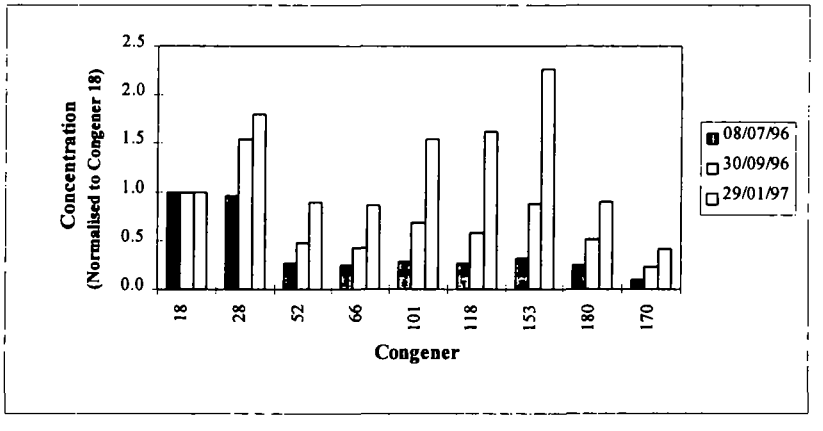


Figure 3: Normalised congener patterns for the long-term exposure samples

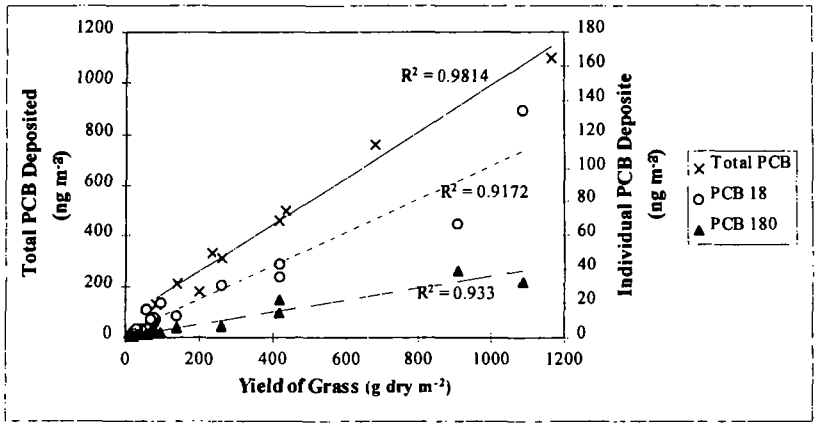


PCB scavenging by vegetation

Because the PCB concentrations in the vegetation seem to approach/reach equilibrium within two weeks, the amounts of PCBs scavenged from the air shows an excellent linear correlation with plant yield, as shown in Figure 4. Consequently the removal of PCBs from air by pasture is greater

during periods in the spring and summer when there is active plant growth. During this study weeks in late July and August gave little yield and hence small offtake/removal.

Figure 4: The amounts of PCBs scavenged by the pasture as a function of yield



Partitioning into plant lipids

Given the air concentrations (pg/m^3) and the grass concentrations (pg/g dry or lipid weight), it is possible to derive a value for the volume of air 'represented' per g of plant tissue (m^3/g). This calculation was performed for a range of congeners in the nine 2 weekly samples and the data are presented in Table 1. It can be seen that the heavier congeners partition appreciably more to the grass than the lighter congeners.

Table 1: Volumes of air represented per unit weight of vegetation

Congener	C_G/C_A m^3/g dry weight (range)	C_L/C_A m^3/g lipid weight	Log K_{OA}*
18	8.5 (3.7-19)	390	7.83
28	8.9 (4.4-16)	420	8.30
52	7.1 (2.4-10)	330	8.73
66	10 (1.1-19)	510	9.26
101	15 (5.7-21)	710	9.60
118	26 (11-51)	1300	10.19
153	22 (7.3-42)	1100	10.51
180	55(19-86)	2700	11.43
170	69 (11-160)	3600	11.68

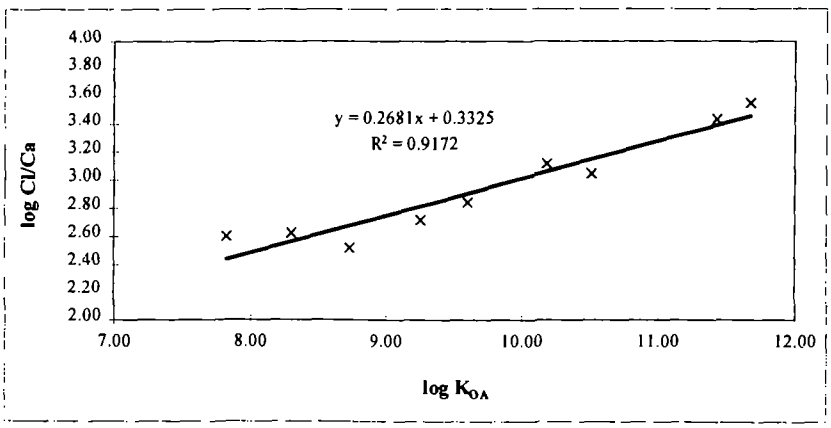
* Data derived from ref. 3 and estimated at 20 °C.

The field site is on a windy, exposed westerly sea facing hillside. Measurements of windspeed over the period April-October 1996 averaged 8 m/s, suggesting that the vegetation will have 'seen' a large volume of air relative to a sheltered site. Clearly the amounts of air in direct contact with

the vegetation would have been a function of windspeed and sward characteristics, which would affect the boundary layer thickness of air over the leaf surfaces.

Several workers have proposed the use of the octanol:air partition coefficient in helping to model the gas phase:leaf transfer of SVOCs (2). Table 1 presents estimates of the log K_{OA} values derived from Harner and Bidleman (3). Figure 5 presents a plot of log(m^3 air/g lipid) against log K_{OA}, which is linear with a correlation coefficient (r^2) of 0.901. This implies that K_{OA} can be used to describe the air-plant partitioning of these compounds.

Figure 5: Log(m^3 air/g lipid) against octanol-air partition coefficients



Acknowledgements

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Literature cited

1.Lee, R. G. M. and Jones, K. C., Proc. of this Dioxin '97 conference.
2.Tolls, J. and McLachlan, M.S., Environ Sci Technol, 1994, **28**, 159-166.
3.Harner, T. and Bidleman, T., J Chem Eng Data, 1996, **41**, 895-899.