PCBs IN GRASS ARE DUE TO VOLATILISATION FROM SOIL

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Introduction

Although there is a substantial body of research that has *indirectly* suggested that PCBs enter grass predominantly *via* uptake from air, rather than from soil (either *via* root-to-foliage translocation, or foliar contamination with either soil particles or PCBs volatilising from soil)[1], *direct* evidence has hitherto been lacking. A "proof-of-concept" study by our group, compared chiral signatures of PCB 95 in soil, with those in air (sampled at 150 cm height above ground) and grass from the same location (within the same 10 m x 10 m square area)[2]. Results indicated that while signatures in air were racemic, those in grass displayed a strong similarity to those in soil in many cases, that was especially marked in the warmer sampling periods. This is surprising given our earlier finding that while chiral signatures of PCB 95 in outdoor air sampled at ~1.5 m height are racemic, those in co-located soil samples are not[3]. Combined, this implies that the PCBs in grass arise principally *via* vapour phase foliar uptake of PCBs that have volatilised from soil. The current study tests this hypothesis by comparing chiral signatures of PCB 95 in spatially and temporally consistent samples of soil, grass, and air collected at various heights on a vertical transect.

Materials and methods

Sampling strategy Sampling was conducted at the Elms Road Observatory Site (EROS) location on the University of Birmingham campus. Two campaigns were conducted in both spring/summer 2009 and 2010. In 2009, sampling commenced on 3rd June, with samples of soil, grass and air taken at t = 15, 29, 44, 58, 72, 85, 100, and 114 days. Sampling in 2010 began on 26th March, with samples taken at t = 14, 28, 42, 56, 70, and 84 days. Soil was sampled to 5 cm depth using a stainless steel soil corer, with four cores collected over a 1 m^2 area, pooled and homogenised for analysis. Grass was harvested from the same 1 m^2 area, washed carefully with distilled deionised water to remove any adhering soil particles, freeze dried and homogenised for analysis. Air was sampled on a vertical transect using PUF disk passive air samplers situated such that the PUF disk was positioned at heights of 3, 10, 40, 90, and 130 cm above the soil surface. While the four highest samplers were of a standard fully-sheltered design, the lowest sampler was not fitted with the bottom stainless steel shelter in order to be positioned as close as possible to the surface. In order to prevent contamination of the PUF disk in this sampler with soil particles, a filter paper on a wire mesh support was placed inside the sampler between the soil surface and the PUF disk.

Analytical procedures PUF disks were extracted directly in a soxhlet apparatus, while soil samples (30 g "wet" weight) were mixed with anhydrous sodium sulfate, and grass samples (50-200 g wet weight) were dried in a freeze dryer and homogenised prior to pressurised liquid extraction (ASE-350, Dionex). Before extraction, samples were spiked with appropriate quantities of PCBs 34, 62, 119, 131, and 173 as internal standards. The extraction solvent for all samples was hexane. Crude sample extracts were purified by a combination of partitioning with concentrated sulfuric acid, DMSO extraction and elution through a florisil microcolumn. Purified extracts were concentrated to 50 μL nonane prior to GC-MS analysis on an Agilent 5975 MSD operated in EI/SIM mode. One μL of the purified extract was injected for analysis. Concentrations of PCBs 28/31, 52, 101, 118, 138, 153, and 180 were determined on a HP-5MS column (30 m x 0.25 mm x 0.25 μm film thickness), while chiral signatures (enantiomer fractions – EFs) of PCB 95 were determined in samples using a ChiraSil-Dex column (25 m x 0.25 mm x 0.25 μm film thickness). GC oven temperature programmes and ions monitored were as reported previously by our group[3].

Results and discussion:

Concentrations in soil and grass are expressed on a dry weight basis; the moisture content of the soil was determined by oven drying a separate aliquot to constant weight. Concentrations in air samples taken at 10, 40,

90, and 130 cm were derived using air sampling rates derived from a 50 day calibration exercise conducted specifically for this sampling configuration when deployed outdoors. Air sampling rates for the specially-adapted sampler configuration used at the lowest height were not determined as linear uptake of PCBs over the calibration exercise was not observed with the sampler in this configuration. However, it was still possible to determine the masses of PCBs present in air samples taken at this height. Moreover, as air sampling rates are assumed to be non-enantioselective; it was possible to compare EFs of PCB 95 in all air samples.

PCB Concentrations Table 1 shows the average concentrations of ΣPCB in air at 10, 40, 90, and 130 cm, in grass, and in soil during both the 2009 and 2010 campaigns. Concentrations in air are a little higher than those detected previously at the EROS location using active high volume samplers in 1999-2000 (74 pg ΣPCB m^{-3})[4] and passive air samplers in 2003-2004 (43 pg ΣPCB m^{-3})[5]. One plausible explanation for the higher concentrations recorded in this study is that while this study only sampled during warmer periods when concentrations are known to be higher[4]; the previous studies have sampled year-round. The higher atmospheric concentrations in 2009 (June-September inclusive) compared to those recorded in the 2010 campaign (March-June inclusive) are also consistent with previous observations of higher concentrations in air during warmer periods[4]. Concentrations in grass and soil are consistent with those recorded previously in soil at EROS in 2003-2004[5] and those detected in grass at a rural site in Northwest England in 1996[6]. Interestingly, concentrations in air increase with increasing height above the soil surface. Using repeated measures ANOVA reveals the concentration increase with height to be significant at each height in the 2009 campaign ($p<0.05$). A similar observation is made for the 2010 campaign data, with the exception that concentrations at 90 and 130 cm heights are statistically indistinguishable ($p>0.05$). This increase in concentration with increasing height presumably reflects the increasing influence with height of emissions from the built environment at EROS, which has been shown previously to exert a far stronger influence on PCB concentrations in air at 1.5 m height than volatilisation from soil[5]. It is in contrast to the findings of Krauss et al[7], who found atmospheric PCB concentrations to *decrease* with increasing height on passing from 25 through 80, up to 160 cm. However, the PCB concentrations in soil in this earlier study[6] were much higher (1.1 – 160 mg ΣPCB kg^{-1}) than in our study. Hence, the influence of volatilisation from soil at such higher soil concentrations would likely be much greater; moreover, at the lowest soil concentration, concentrations in air were not discernibly different at the three heights studied[7].

Table 1: Average concentrations of ΣPCBs in air (pg m^{-3}), soil (pg g^{-1} dry weight), and grass (pg g^{-1} dry weight)

Year/Concentrations in…	Air (10 cm)	Air (40 cm)	Air (90 cm)	Air (130 cm)	Soil	Grass
2009	88	150	170	190	310	1300
2010	60	80	130	150	1030	2600

Chiral Signatures of PCBs Figures 1 and 2 show the average ± 1 standard deviation of the EFs of PCB 95 detected in samples of soil, grass, and air at different heights in the 2009 and 2010 campaigns. The EF values recorded in soil and grass in both campaigns are consistent with the average values recorded previously at EROS (0.453±0.023)[5] for soil and 0.4755±0.0175 for grass[2]. Likewise, the racemic or near-racemic EFs recorded in air at all except the lowest height samples concur with our previous findings[3,5]. In both campaigns however, there is a clear deviation from racemic in air samples collected at the lowest height towards the signature displayed in soil. A t-test confirms that the EFs in air sampled at 3 cm height differ significantly ($p<0.05$) from those at the other heights sampled in both 2009 and 2010. This is consistent with our hypothesis that at the urban background soil concentrations present at EROS, PCBs volatilise from soil to an extent that is discernible only at the soil:air interface. The greater disparity between EFs in soil and those in the 3 cm height air samples collected in 2010 compared to 2009 seems likely attributable to the fact that the 2010 samples were collected during spring rather than summer with concomitant lower soil temperatures. Also of significance are the non-racemic EFs observed in grass samples, particularly in the 2009 campaign. This supports our hypothesis that the origin of PCBs in grass stems from dry gaseous foliar uptake of PCBs volatilised from soil. While great care was taken to remove any adhered soil from grass samples prior to analysis, we also compared the congener profiles in soil with those detected in grass and air samples. This revealed that while profiles were dominated by PCBs 28/31 and 52 (~60-80% of ΣPCB in air; ~30-50% ΣPCB in grass); these congeners constituted only ~5-15% ΣPCB in soil.

Figure 1: Chiral Signatures (Average ± σ_n) of PCB 95 in Samples of Air, Soil, and Grass taken in 2009

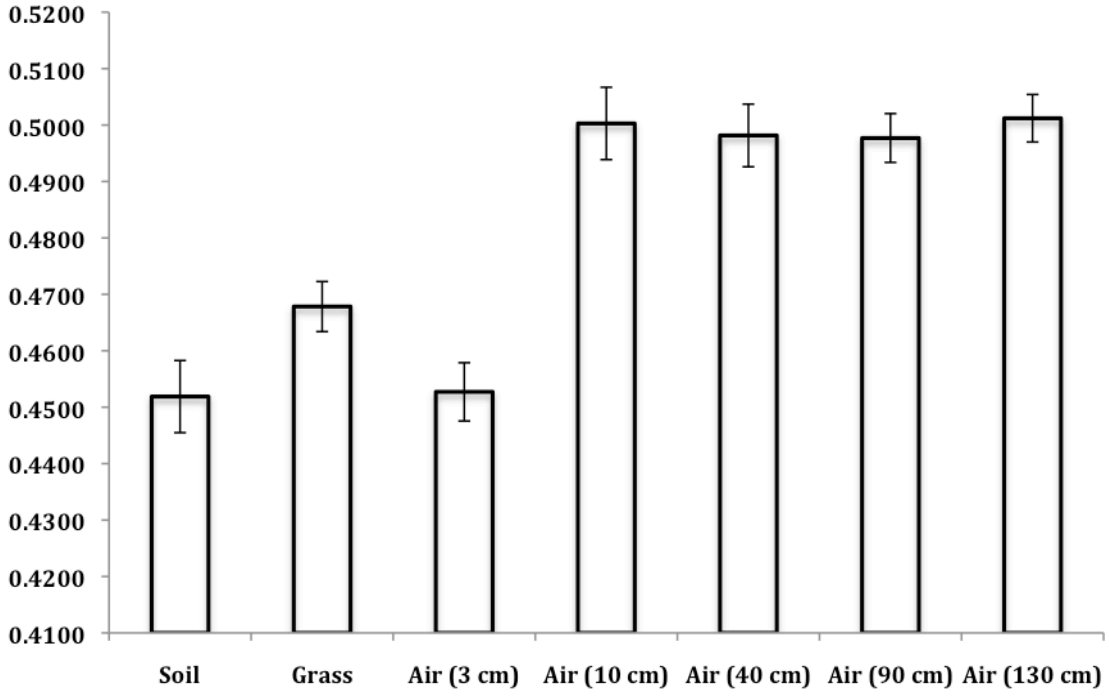
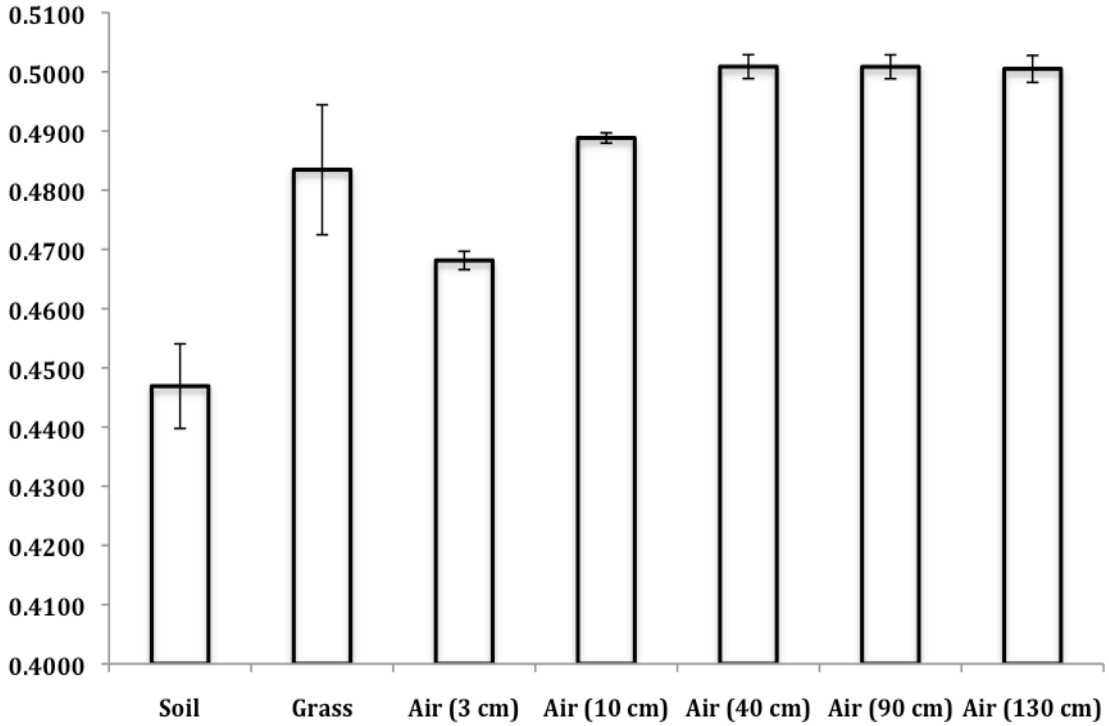


Figure 2: Chiral Signatures (Average ± σ_n) of PCB 95 in Samples of Air, Soil, and Grass taken in 2010



The findings of this study have important implications for the biogeochemical cycling of PCBs, as it highlights an important mechanism via which the substantial reservoir of PCBs associated with topsoil may be mobilised and transferred into the terrestrial food chain.

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