Concentrations and Chiral Signatures of Polychlorinated Biphenyls in Outdoor and Indoor Air and Soil in a Major U.K. Conurbation

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Concentrations and chiral signatures of polychlorinated biphenyls (PCBs) were measured in outdoor air (using polyurethane foam (PUF) − disk passive samplers) and surface soil samples taken at approximately monthly intervals over 1 year at 10 locations on a rural−urban transect across the West Midlands of the U.K. In both air and soil, concentrations clearly decrease with increasing distance from the city center, supporting the existence of an urban "pulse", that indicate the West Midlands conurbation to be a source of PCBs to the wider environment. Concentrations of PCBs in outdoor air samples in this study are well below those reported previously for indoor air in the West Midlands. This, combined with comparison of chiral signatures in outdoor air and soil with those in samples of indoor air taken in the West Midlands, suggest strongly that the principal contemporary source of PCBs in this conurbation is ventilation of indoor air and not volatilization from soil. Future reductions in PCB concentrations in outdoor air and ultimately human exposure appear best achieved by action to remove remaining sources of PCBs from existing structures.

Introduction

Polychlorinated biphenyls (PCBs) have found widespread use in a diverse range of applications, with around 1.2 million tonnes produced worldwide (*1*). Approximately 67 000 and 40 000 t were produced and used, respectively, in the U.K. (*1*). Owing to concerns about their adverse effects on humans and wildlife, their production—but not use—ceased in the U.K. and most of the industrialized world in the late 1970s. Although U.K. human exposure to dioxin-like PCBs via the diet has fallen in recent years in response to cessation of their production (*2*, *3*), human health concerns remain—currently a substantial proportion of U.K. schoolchildren and toddlers are exposed via the diet at levels that exceed the U.K. government's recommended tolerable daily intake to dioxins and dioxin-like PCBs (*3*). Furthermore, we reported recently that concentrations of PCBs in indoor air in the U.K.'s West Midlands displayed no significant change over the past decade, remaining on average around 30 times above that outdoors and contributing an average of 30% of combined human exposure to ΣPCB via the diet and air (*4*).

In addition to direct impacts on human exposure, elevated concentrations of PCBs in indoor air have been hypothesized to help maintain contemporary outdoor air concentrations via ventilation (*5*). This is consistent with our recent comparison of chiral signatures of PCBs in bulk outdoor air and soil at one urban and one rural West Midlands location (*6*). While signatures in outdoor air were racemic, matching those in commercial PCB formulations, those in soil displayed appreciable enantioselective degradation. These data led us to hypothesize that volatilization from soil is not an important source of PCBs to bulk outdoor air at the two sites monitored (*6*). Given the policy implications of this hypothesis, it is important that it is tested elsewhere.

We reported recently spatial trends in concentrations of polybrominated diphenyl ethers (PBDEs) in outdoor air and soil at ten locations along an urban:rural transect in Birmingham (*7*). These data revealed an "urban pulse" with concentrations increasing with proximity to the urban center. Similar findings have been reported for both PBDEs and PCBs in the Greater Toronto conurbation (*8*). We attributed such "urban pulses" for PBDEs to the widespread indoor contamination by PBDE-treated goods that subsequently ventilate outdoors (*7*). Owing to the ongoing contamination of indoor environments with PCBs (*4*), we hypothesize a similar "urban pulse" will be observed along the same West Midlands urban−rural transect for PCBs.

Outdoor air and soil are important matrices to monitor. Air is important because atmospheric transport is the most efficient means of dispersing contaminants away from locations in which they were originally used, and soil is important because it constitutes the major terrestrial sink for PCBs in the U.K. (*1*). Furthermore, comparison of chiral signatures in air, soil, and grass suggests that although volatilization from soil does not influence bulk air, it does impact on air concentrations at the soil:air interface, therefore supplying PCBs to grass foliage (*9*), with consequent impacts on human exposure via foodstuffs derived from grazing animals.

This study reports concentrations of PCBs in outdoor air and surface soil taken on an approximately monthly basis from 10 locations on a 79 km urban−rural transect across the West Midlands. We also report chiral signatures of three atropisomeric PCBs, viz. congeners 95, 136, and 149 in the same samples. The direction of the transect corresponds with the prevailing wind direction—i.e. from the southwest (upwind) to the northeast (downwind)—affording a potential insight into the role of the heavily urbanized center as a source of PCBs to the wider environment. By covering distances from Birmingham city center of 48 km southwest to 31 km northeast with intersite distances of 3−17 km, spatial variation between a range of rural, suburban, and urban locations was studied.

Furthermore, we observed previously racemic or near-racemic signatures for PCB #s 95 and 149 in 20 samples of indoor air that match closely those in outdoor air, but not those in soil (*9*). This—combined with concentrations of PCBs in indoor air that exceed substantially those in outdoor air (*4*)—suggests that ventilation of indoor air is a far more significant contributor to outdoor air concentrations than volatilization of PCBs from soil. To further examine this, we report chiral signatures of PCB #s 95, 136, and 149 in a further set of 11 samples of indoor air taken within the West Midlands for which concentrations of PCBs have been previously reported (*4*).

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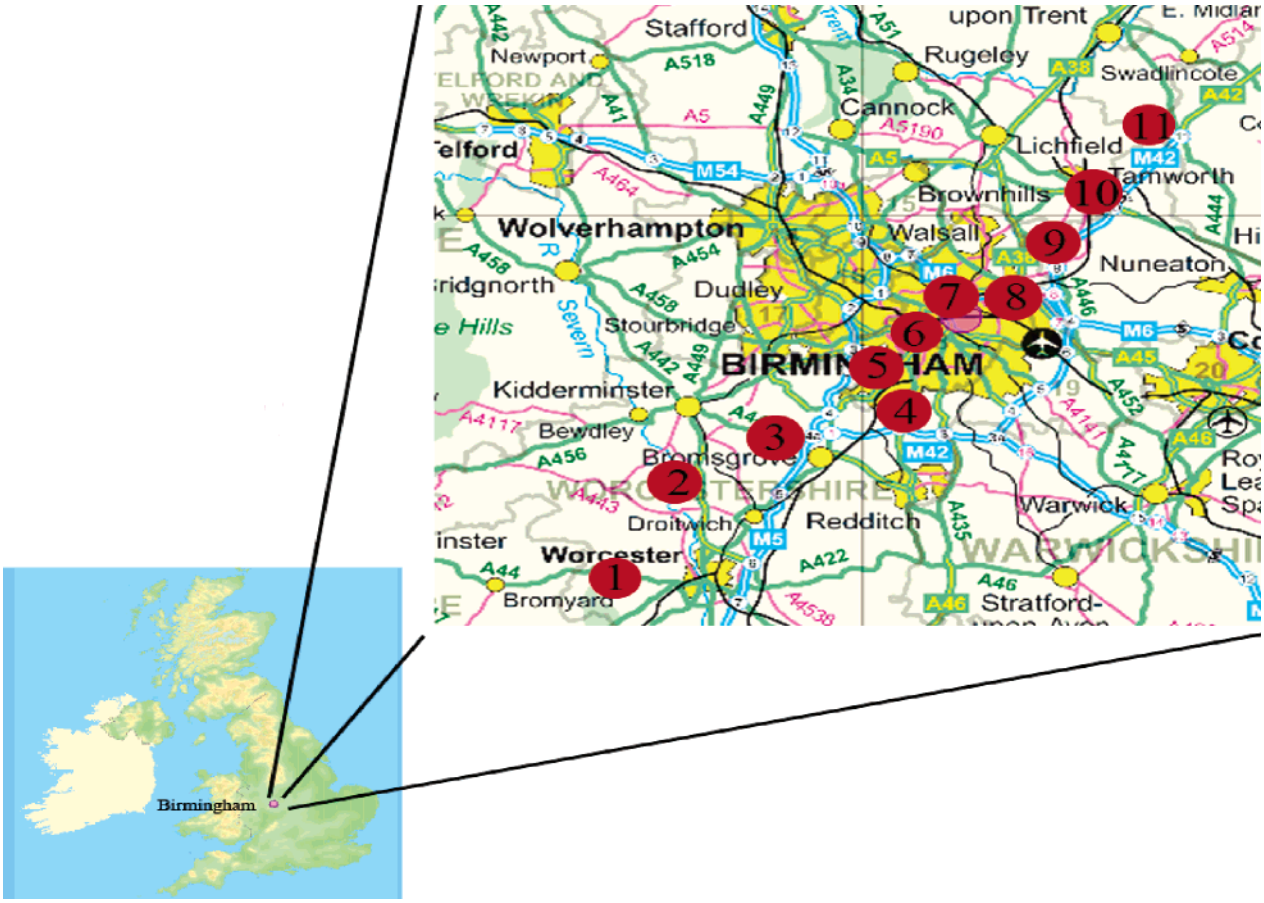

FIGURE 1. Sampling locations.

Our principal objectives were as follows: (a) to assess the spatial variation of concentrations of PCBs in outdoor air and topsoil within the West Midlands; (b) by comparison of chiral signatures of PCBs in air and soil at ten locations as well as in samples of indoor air to further test the hypothesis that volatilization from soil is not currently an important source of PCBs to bulk outdoor air and that a more important source is ventilation of PCB-contaminated indoor air; and (c) to use these data to understand the environmental sources and fate of PCBs—in particular the significance of urban areas as source regions.

Experimental Section

Sampling Strategy. Outdoor air and soil samples were collected from 10 sites within the West Midlands. The duration of each sampling period varied between 4 and 7 weeks. Sampling sites were located on a southwest (upwind) to northeast (downwind) transect with a mix of rural, suburban, and urban locations. Figure 1 shows the location of each outdoor sampling location, with each number relating to a specific location. Further details on the geographic location of each site and exact dates of each sampling period are reported elsewhere (*7*). In summary, sites 1, 2, 3, 4, 5, and 6 are located respectively 48, 31, 21, 11, 6, and 3 km upwind of the city center site 7; while sites 8, 9, and 11 are respectively 6, 18, and 31 km downwind of site 7. For operational reasons, monitoring at site 10 ceased after 2 months, and no data are reported for this location. At each location, 11 paired air and soil samples were taken. Chiral signatures were also determined in samples of indoor air. The indoor microenvironments for which data are reported consist of 21 offices, 9 homes, and 2 public environments—a post office and a coffee shop. Sampling protocols in indoor environments are reported elsewhere (*4*).

Air Sampling. Passive air samplers (i.e., PUF disks) were employed to provide a time-integrated sample over each sampling period. Full details of those employed in this study in both outdoor and indoor locations have been reported previously (*4*, *7*).

Conversion of contaminant masses per sample into concentrations requires knowledge of the air sampling rate of the PUF disk samplers employed and sampler deployment time. Examination of the literature relating to sampling rates of similar PUF disk sampler configurations employed outdoors led us to select a sampling rate of 3.5 m^3 day^{-1} for PCBs (*8*). There is a degree of uncertainty associated with extrapolation of sampling rates derived for one sampler configuration to another and use of a uniform rate independent of sampling temperature and congener. However, given the close correlation between concentrations derived at site 6 via both active high-volume samplers (average concentration = 252 ± 156 pg ΣPCB m^{-3} (*10*)) and in this study (average concentration = 253 ± 57 pg ΣPCB m^{-3}) we believe that the selected sampling rate is appropriate for this study. It is assumed that sampling rates are not enantioselective.

Soil Sampling and Determination of Soil Organic Carbon Content. Soil samples were collected at the same locations as the air samples, at the end of each air sampling period. Details of the sampling procedure are reported elsewhere (*7*). Aliquots of soil sampled at each site during sampling period 7 (March−April 2004) were subjected to determination of their organic carbon content using a Leco RC-412 instrument (*7*).

Analytical Protocols. The methods employed to determine concentrations and chiral signatures of PCBs have been reported in detail elsewhere (*4*−*6*, *9*, *10*). Target PCBs are consistent with those reported previously by our research

group (*4*, *5*, *10*). In summary, samples were treated with known quantities of internal standards (PCB #s 34, 62, 119, 131, and 173), prior to Soxhlet extraction for 12 h with hexane (air samples) and hexane:acetone (2:3 v/v) (soil samples). Concentrated crude extracts were washed with water (soil samples only) and then concentrated H_2SO_4, prior to further purification via elution through a Florisil column (10 g) with dichloromethane (50 mL) (soil samples only), solvent exchange to hexane followed by lipid removal via solvent exchange between dimethyl sulfoxide and hexane, and Florisil chromatography (2 g, eluted with 20 mL hexane). After concentration and solvent exchange to nonane, GC/MS analysis was conducted on a Fisons MD-800 instrument fitted with (a) for determination of PCB concentrations, a Varian Factor 4 VF-5ms column (60 m × 0.25 mm i.d., 0.25 μm film thickness), and (b) for determination of chiral signatures of PCB #s 95, 136, and 149, a Chirasil-Dex (10% permethylated 2,3,6-tri-O-methyl β-cyclodextrin as chiral selector on a polysiloxane backbone, 25 m × 0.25 mm × 0.25 μm, Chrompack) column.

When determining concentrations of PCBs, peaks were accepted only if the following criteria were met: (i) signal-to-noise ratios for the least abundant ion exceeded 3:1; (ii) peaks eluted within 5 s of standards injected on the same day; and (iii) isotope ratios for peaks were within 20% of those obtained for standards run on the same day.

Quantification criteria for the determination of chiral signatures were as follows: (1) signal-to-noise ratios for the least intense ion exceeded 10:1; (2) peaks eluted within 5 s of standards injected on the same day; (3) isotope ratios for the 2 monitored ions agreed within ±5% of standards run on the same day; (4) there were no obvious coelutions from other PCBs that would not be discernible via calculation of isotope ratios; and (5) chiral signatures calculated for the least intense ion of each pair agreed within ±5% of those calculated for the other monitored ion.

Field blanks consisting of a PUF disk (treated in identical fashion to those used for sampling, except that no air was aspirated through them) for air samples ($n = 11$), and method blanks (i.e., as field blanks with the exception that PUF disks were not transported to/from sampling site) ($n = 5$) were analyzed and found to contain concentrations of target PCBs that were no greater than 3% of the concentrations found in the corresponding samples. Our data are thus not corrected for blank concentrations. Average recoveries of internal standards for all samples ranged from 40% (PCB # 62) to 68% (PCB # 119). Similarly, average recoveries of QA/QC standards (PCB #s 19 and 147) added to PUF disks prior to sampling to provide an indication of contaminant loss during sampling *and* analysis combined were 95 and 75%, respectively. Air sample concentrations were not corrected for such losses. The repeatability of our passive sampling and analytical procedures combined was evaluated by deploying simultaneously 4 passive samplers at site 6. The low relative standard deviations observed for concentrations of the target PCB congeners (average = 4.6%; range 0.5−6.5%) demonstrate good repeatability for our sampling and analytical method. Method detection limits for individual PCBs were typically 0.03 pg m^{-3} and 0.25 pg g^{-1} dry weight for air and soil samples, respectively. To evaluate the accuracy of our methods for the determination of both PCB concentrations and of chiral signatures, we analyzed five aliquots of a Canadian National Water Research Institute sediment reference material (EC-5). The results obtained (see Tables S1 and S2) reveal our measurements to agree closely with those certified for concentrations and with those reported previously by our research group (*6*) and others (*11*) for chiral signatures. In this paper, we express chiral signatures as enantiomer fractions (EFs). For PCB # 95, the elution order of the two enantiomers is unknown—and the EF is defined as the ratio of the concentration of the first eluting enantiomer to the sum of the concentrations of both enantiomers (*12*). By comparison, for PCB #s 136 and 149, for which elution orders on the Chirasil-Dex GC column used in this study are known, EFs were calculated as the ratio of the (+) enantiomer to the sum of both enantiomers (*13*). Figure S1 shows the baseline resolution of enantiomers of the target PCBs in a soil extract from site 6.

Results and Discussion

PCB Concentrations in Air. Table 1 summarizes concentrations of PCB #s 28/31, 52, 101, 138, 153, 180, and ΣPCB in air samples. A full data set containing concentrations in each sample is provided as Supporting Information (Table S3). It is instructive to compare concentrations recorded in this study at site 6 (average 253 ± 57 pg ΣPCB m^{-3}), with those recorded previously at the same location (*5*, *10*). Given the sample sets were taken 2−4 years apart, using different sampling equipment and sampling durations (earlier studies used high volume active air samplers over 24−48 h periods), we found strong similarities between the data sets as evidenced by the fact that average concentrations of ΣPCB in 1997−1998 and 1999−2000 were 290 ± 178 and 252 ± 156 pg m^{-3}, respectively (*5*, *10*). As discussed previously, concentrations in the West Midlands are at the lower end of those for urban areas elsewhere in the U.K. and North America (*5*).

Figure 2 (top) reveals an "urban pulse", whereby concentrations peak in Birmingham city center (site 7) and decrease with distance from the center. We expressed the magnitude of this pulse as the ratio of the average concentration detected at the city center to the average concentration for all sites. For ΣPCB in air, it is 3.62. This compares with the corresponding value for ΣBDE in the same air samples of 2.2 (*7*) and may suggest that urban centers are currently more significant sources of PCBs than PBDEs. Furthermore, higher concentrations to the northeast of the city center (sites 9 and 11) cf. those to the southwest (sites 1, 2, and 3) are consistent with the city center being a source of PCBs to downwind locations. However, we cannot exclude the possible existence of point sources of PCBs that may have influenced concentrations at sites 9 and 11. These findings are consistent with those recently reported for an urban−rural transect in Toronto (8 locations, simultaneously sampled over 3 periods), that revealed a strong urban−rural gradient for PCB concentrations in outdoor air (*8*), and other studies (e.g., for Lake Michigan), which conclude urban/industrial areas like Chicago constitute large sources of PCBs (*14*).

PCB Concentrations in Soil. Table 2 summarizes concentrations (pg g^{-1} dry weight) of target PCBs in soil samples in this study. Concentrations of PCB #s 95 and 149 at site 6 are consistent with those at this location in 2001−2002, while those of PCB # 136 exceed slightly those reported previously (*6*). There are no other data on PCB concentrations in soil in the West Midlands with which this study can be compared. However, our data are consistent with a recent survey of soil from 200 rural U.K. locations, in which ΣPCB concentrations ranged between 274 and 80 600 with a median of 2520 pg g^{-1} dry weight (*15*). As concentrations of POPs in soil are strongly influenced by the organic carbon/matter content of the soil, Figure 2 (bottom) summarizes the organic carbon-normalized concentrations of PCBs in soils. A full data set containing concentrations of ΣPCB and PCB #s 28/31, 52, 101, 138, 153, and 180 (both dry weight and organic carbon basis) in each sample is provided as Supporting Information (Table S4). As for air samples, an "urban pulse" is apparent (4.72 for ΣPCB; Figure 2 - bottom), whereby organic carbon-normalized concentrations peak in Birmingham city center (site 7). As for air, there is a strong decline in organic carbon-normalized concentrations of ΣPCB and distance from the city center.

TABLE 1. Summary of Average (σ_{n-1} in Parentheses) Concentrations (pg m^{-3}) and Enantiomer Fractions (EFs) of Selected PCBs in Air Samples in This Study

congener/ site #	1	2	3	4	5	6	7	8	9	11	indoor air[a]	EROS[b]	Crete[c]
28	2.86 (0.95)	2.34 (1.08)	2.24 (0.75)	4.78 (1.74)	6.12 (1.97)	12.1 (4.55)	13.0 (2.80)	10.4 (3.39)	3.65 (1.22)	3.70 (1.87)		19 (10)	
52	3.03 (1.27)	2.67 (1.79)	2.11 (0.73)	4.87 (1.40)	5.58 (2.43)	11.1 (5.23)	21.3 (9.77)	10.8 (3.15)	4.38 (1.36)	3.92 (1.64)		22 (15)	
101	2.20 (1.19)	1.39 (0.96)	1.16 (0.42)	2.99 (1.61)	2.83 (0.82)	7.54 (3.75)	24.9 (9.92)	7.83 (6.38)	2.57 (1.13)	2.20 (0.95)		15 (11)	
138	0.61 (0.28)	0.63 (0.31)	0.67 (0.31)	2.06 (1.09)	1.56 (1.15)	5.09 (1.13)	16.4 (8.35)	4.74 (2.32)	1.35 (0.88)	1.08 (0.47)		3.5 (2.5)	
153	1.10 (0.27)	1.16 (0.59)	0.49 (0.23)	1.41 (0.96)	1.38 (0.89)	3.88 (1.61)	14.0 (6.88)	3.54 (1.95)	1.09 (0.70)	0.79 (0.41)		3.5 (2.2)	
180	0.72 (0.73)	0.48 (0.24)	0.65 (0.31)	1.45 (0.88)	1.53 (0.75)	2.61 (1.18)	6.81 (3.80)	3.07 (2.08)	1.78 (1.66)	1.24 (0.99)		1.0 (0.59)	
95	1.55 (0.98)	1.08 (0.69)	0.79 (0.41)	0.45 (0.19)	2.14 (1.00)	5.08 (2.09)	20.5 (6.67)	6.13 (3.65)	1.81 (0.91)	1.55 (0.66)		13 (10)	
136	0.31 (0.15)	0.23 (0.12)	0.20 (0.07)	0.59 (0.38)	0.42 (0.28)	1.21 (0.43)	4.20 (2.72)	1.32 (0.75)	0.45 (0.32)	0.29 (0.14)		1.2 (0.80)	
149	1.49 (0.65)	1.29 (0.72)	0.83 (0.34)	2.26 (1.76)	2.28 (1.37)	6.95 (2.67)	26.3 (9.83)	7.02 (3.74)	2.08 (1.96)	1.36 (0.48)		4.5 (3.4)	
ΣPCB	66.0 (18.5)	53.8 (18.8)	46.5 (11.2)	101 (29.5)	116 (30.4)	253 (57.0)	588 (150)	231 (63.0)	88.1 (22.5)	80.2 (23.8)		252 (156)	
EF (95)	0.492 (0.005)	0.488 (0.016)	0.492 (0.005)	0.495 (0.002)	0.495 (0.003)	0.497 (0.003)	0.499 (0.002)	0.497 (0.003)	0.491 (0.006)	0.492 (0.004)	0.496 (0.003)	0.497 (0.004)	0.49–0.51
EF (136)	0.497 (0.003)	0.495 (0.006)	0.503 (0.020)	0.502 (0.005)	0.499 (0.003)	0.499 (0.003)	0.499 (0.002)	0.500 (0.004)	0.495 (0.005)	0.498 (0.003)	0.500 (0.003)	0.501 (0.004)	
EF (149)	0.498 (0.003)	0.497 (0.006)	0.492 (0.010)	0.498 (0.002)	0.499 (0.003)	0.499 (0.003)	0.499 (0.002)	0.497 (0.002)	0.499 (0.004)	0.495 (0.006)	0.500 (0.004)	0.502 (0.003)	0.48–0.50

[a] Data reported for 32 samples; EF values for some congeners have previously been reported for 20 samples (*9*). [b] EROS (Elms Road Observatory Site) — equivalent to site 6 in this study. Data for EFs and concentrations of PCB # 136 are from ref *6*; data for all other congeners and ΣPCB are from ref *10*. All EROS data obtained using high volume air samplers and are the sum of both particle and gas phase. [c] Data reported for 13 samples; range of values is cited (*16*).

FIGURE 2. (top) Spatial variation of average concentrations (pg m^{-3}) of ΣPCB in air samples and (bottom) spatial variation of average concentrations (ng g^{-1} OC) of ΣPCB in soil samples (error bars are ±1 σ).

Similar declines in concentration with distance from city center exist for all target congeners.

Chiral Signatures of PCBs. The average and standard deviation of EF values for PCB #s 95, 136, and 149 in outdoor air and soil at each site are reported in Tables 1 and 2, respectively. Corresponding values for indoor air samples (including those reported previously (*9*)) are included in Table 1. EF values for each congener in all outdoor air and soil samples are reported in Tables S3 and S4, respectively, with those in each indoor air sample reported in Table S5. While signatures for each congener in all air samples are racemic or near-racemic, those in soil display—particularly for PCB # 95—far greater variation (as illustrated by σ_{n-1} values and reversal of direction of enantioselective degradation) and deviation from racemic. Tables 1 and 2 show our data are consistent with the only other two studies to have reported chiral signatures of PCB #s 95 and 149 in air and soil (*6*, *16*).

Chiral Signatures of PCBs in Soil. We have reported previously chiral signatures of PCB #s 95, 136, and 149 in soils from one urban (EROS = site 6 in this study) and one semirural location (*6*). Based on these earlier data, we concluded appreciable enantioselective degradation of the monitored PCBs was occurring in topsoil as a result of aerobic microbial degradation, albeit at a slow rate discernible only by chiral techniques. For PCB # 95, the first eluting enantiomer was preferentially degraded, while for PCB #s 136 and 149, preferential degradation of the (+) enantiomer occurred. The present study is largely consistent with our earlier findings as it confirms appreciable edaphic enantioselective degradation of all target congeners occurs, that this is most marked for PCB # 95, and that—with rare exceptions—it is the first eluting enantiomer of PCB # 95 that is preferentially degraded. However, while the occurrence of edaphic enantioselective degradation of PCB #s 136 and 149 is confirmed by this study, its magnitude is less, and the direction at some sites is different from that observed previously. As our QA/QC procedures show our measurements in the two studies to be comparable, we are unsure as to the cause of these differ-

TABLE 2. Summary of Average (σ_{n-1} in Parentheses) Concentrations (pg g^{-1} Dry Weight) and Enantiomer Fractions (EFs) of Selected PCBs in Soil Samples in This Study

congener/ site #	1	2	3	4	5	6	7	8	9	11	EROS[a]	Switzerland[b]	Czech Republic[c]
28	8.1 (5.8)	3.6 (2.3)	8.9 (8.9)	21.8 (16.0)	11.0 (7.4)	18.8 (13.0)	178 (121)	22.2 (9.0)	6.6 (4.1)	6.0 (5.0)			
52	13.9 (7.4)	6.9 (4.7)	19.1 (13.1)	36.0 (20.9)	37.4 (27.0)	37.7 (19.2)	297 (202)	69.4 (23.2)	16.2 (15.7)	12.0 (12.1)			
101	18.8 (7.2)	11.9 (8.5)	43.6 (37.7)	42.2 (20.6)	40.5 (17.9)	68.8 (30.5)	388 (207)	142 (56.7)	22.3 (8.9)	20.3 (11.4)			
138	13.3 (7.4)	12.7 (7.1)	66.6 (51.9)	45.4 (21.1)	49.4 (27.7)	95.8 (57.1)	636 (290)	189 (67.2)	42.0 (24.7)	30.0 (18.3)			
153	28.2 (10.8)	19.8 (13.0)	39.3 (31.7)	34.3 (16.1)	33.6 (16.6)	54.3 (35.9)	357 (139)	129 (37.8)	25.0 (16.9)	20.5 (13.3)			
180	12.0 (4.2)	8.8 (6.7)	19.0 (14.2)	26.0 (13.8)	23.5 (11.7)	29.6 (18.1)	297 (101)	69.8 (27.5)	17.5 (13.8)	10.5 (6.0)			
95	13.6 (7.0)	8.0 (4.9)	31.5 (30.9)	31.5 (12.1)	30.7 (11.9)	49.8 (20.8)	359 (160)	141 (46.8)	24.1 (15.1)	15.4 (9.6)	51 (26)		
136	7.8 (3.1)	6.4 (4.2)	18.7 (15.6)	18.4 (7.9)	17.7 (7.7)	34.8 (18.8)	221 (89.7)	67.6 (27.4)	13.0 (7.1)	9.1 (5.6)	13 (6.3)		
149	34.4 (21.3)	27.1 (18.0)	87.4 (61.3)	73.8 (33.0)	75.3 (40.8)	149 (64.2)	991 (340)	276 (78.1)	62.6 (44.4)	45.0 (27.7)	107 (58)		
							13300						
ΣPCB	574 (171)	357 (190)	1050 (675)	1240 (359)	1150 (492)	1820 (733)	(4140)	3820 (653)	763 (388)	580 (326)		0.45–0.55	0.36–0.51
	0.446	0.477	0.496	0.475	0.444	0.472	0.496	0.452	0.453	0.449	0.453		
EF (95)	(0.014)	(0.024)	(0.021)	(0.015)	(0.022)	(0.009)	(0.001)	(0.009)	(0.019)	(0.055)	(0.023)		
	0.506	0.472	0.496	0.496	0.502	0.496	0.497	0.490	0.495	0.490	0.522		
EF (136)	(0.010)	(0.016)	(0.007)	(0.011)	(0.006)	(0.006)	(0.001)	(0.014)	(0.015)	(0.011)	(0.012)		
	0.498	0.490	0.529	0.504	0.495	0.494	0.498	0.500	0.513	0.492	0.544	0.44–0.56	0.42–0.51
EF (149)	(0.020)	(0.038)	(0.014)	(0.016)	(0.009)	(0.006)	(0.001)	(0.007)	(0.023)	(0.027)	(0.017)		

[a] EROS (Elms Road Observatory Site) – equivalent to site 6 in this study. Data from ref 6. [b] Data reported for 105 samples; range of values is cited (*16*). [c] Data reported for 12 samples; range of values is cited (*16*).

TABLE 3. Significance Values for Paired t-Test Comparison of Chiral Signatures in Matched Outdoor Air and Soil Samples at Each Transect Location

site #/ parameter	*P* value for PCB # 95[a]	*P* value for PCB # 136	*P* value for PCB # 149
1	<0.001	>0.05	>0.05
2	>0.05	0.006	>0.05
3	>0.05 (0.004)	>0.05	<0.001
4	0.004	>0.05	>0.05 (0.023)
5	<0.001	>0.05	<0.001
6	<0.001	>0.05	0.030
7	0.01	0.024	>0.05
8	<0.001	>0.05 (0.004)	>0.05
9	<0.001	>0.05	>0.05 (0.004)
11	0.04	>0.05 (0.003)	>0.05

[a] Based on comparison of EF values (values in parentheses where shown are based on comparison of DFR values where different – see text).

ences, and further study of the enantioselective edaphic behavior of PCBs is warranted.

Comparison of Chiral Signatures in Air and Soil and Implications for Atmospheric Source Apportionment. We have used previously a paired t-test to show that EFs in matched soil and outdoor air samples from two locations are statistically different and that volatilization from soil was not a significant source of PCBs in bulk outdoor air at those sites (*6*). We have repeated this exercise for each location in this study, with the results (expressed as *p* values) reported in Table 3. More detailed consideration reveals simple t-test comparison of signatures in paired air and soil samples, to be misleading in instances where the direction of enantioselective degradation in one or both of the matrices varies (i.e., EF values both exceed and fall below 0.500). To illustrate, take a hypothetical case where EF values in air samples are all 0.500, but those in matching soil samples are clearly different from those in air but that vary in direction: 0.444, 0.490, 0.495, 0.513, 0.505, 0.492, 0.506, 0.518, 0.509, 0.512, and 0.495. A paired t-test on these EF values fails to detect any difference between the two data sets ($p = 0.76$). In such cases, we believe it is more meaningful to express chiral signatures as "deviation from racemic" (DFR) values, where DFR is defined as the modulus of (0.500-EF) (*17*). When the hypothetical data set above is compared using DFR values, a significant difference ($p = 0.033$) is detected. Hence, Table 3 also gives *p* values for paired t-test comparisons of chiral signatures in outdoor air and soil that are calculated using DFR values—these are only reported if different to the *p* values calculated using EFs. Table 3 shows for PCB # 95, for which nonracemic signatures in soil are observed at all sites except the most urbanized location (site 7), there is a statistically significant difference between EFs in soil with those in outdoor air at eight sites (nine if DFR values are used). In contrast, edaphic enantioselective degradation of PCB #s 136 and 149 is far less extensive than for PCB # 95, and for PCB # 136 only two sites (four if DFR is the metric), and for PCB # 149 only three sites (five if DFR values employed) display statistically distinguishable chiral signatures in outdoor air and soil.

We have reported previously that chiral signatures of PCB #s 95 and 149 in 20 samples of indoor air taken within the West Midlands match closely those in outdoor air but not those in soil (*9*). As shown in Table 1 and Table S3, EF values for all congeners in all 32 indoor air samples reported here are—where detected—similar to those in outdoor air, i.e., racemic or near-racemic—and display average and standard deviation values for each congener within the range for outdoor air. This similarity between chiral signatures in indoor and outdoor air, coupled with the disparity between

those in outdoor air and soil for many cases, suggests strongly that ventilation of indoor air is a far more significant source of PCBs to the West Midlands atmosphere than volatilization from soil. This is supported by the fact that current PCB concentrations in indoor air in the West Midlands exceed substantially those in outdoor air at any of the sites in this study (*4*). We hypothesize the high density of indoor environments contaminated with PCBs results in significant emissions when these environments exchange air with outdoors, accounting for the "urban pulses" observed for concentrations of PCBs in both outdoor air and soil in this study, and results in the West Midlands acting as an area source of PCBs. This has significant policy implications, as if replicated elsewhere it suggests future reductions in PCB concentrations in outdoor air and ultimately human exposure are best achieved by action to remove remaining sources of PCBs in use in the built environment.

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Supporting Information Available

Summary of concentrations and chiral signatures of PCBs detected in the EC-5 reference material (Tables S1 and S2), listings of chiral signatures of PCB #s 95, 136, and 149 and concentrations of PCB #s 28/31, 52, 101, 138, 153, and 180 in each air (Table S3) and soil sample (Table S4 − both (a) dry weight and (b) normalized to organic carbon content) as well as chiral signatures in all indoor air samples Table (S5), and mass chromatograms showing the resolution of enantiomers of PCB #s 95, 136, and 149 in a soil extract from site 6 (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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