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A STUDY OF THE SPATIAL DISTRIBUTION OF PCBs IN THE UK ATMOSPHERE USING PINE NEEDLES

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ABSTRACT

Past and current polychlorinated biphenyl (PCB) inputs to the environment, mainly in industrialized countries, continue to determine a global re-distribution of these contaminants. In order to better understand PCB transport and distribution phenomena, a number of large-scale distribution studies have been recently published in the literature. In this paper a nationwide survey of 28 pine needle samples taken across the UK is presented. Mean PCB concentrations of a number of latitudinal bands (transects) revealed the presence of a decreasing concentration gradient from southern England to northern Scotland of a factor of ~7. The pine needle data also provide evidence to suggest: 1) that there has been a decrease in the PCB concentration of the atmosphere in the southern UK; and 2) there is a relationship between regional mean needle PCB concentrations and population densities. Calculated air concentrations from the pine needle results were compared with measured literature data of a similar area to test the possibility of using bioconcentration factors (BCF) based on n-octanol:air partition coefficients (Koa) to predict air-leaf equilibrium of semivolatile organic compounds. A more detailed analysis, in accordance with some literature data, has revealed that uncertainties arise when leaf-air uptake of molecules with high Koa values (Log Koa > 8-9) is modelled. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Despite regulations and restrictions on the use and disposal of PCBs in many industrialized countries, PCBs continue to be detected in environmental samples and attract interest because of their global distribution and re-

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cycling, propensity to accumulate in foodchains and possible adverse health effects. A topic of particular interest is the re-mobilisation of previously emitted and deposited PCBs, long range transport and possible accumulation in polar regions (Wania and Mackay, 1993; Lead et al., 1996). Under this scenario, industrialized temperate countries in Europe and North America are envisaged as constituting important global source regions. Models of the transport and distribution of chlorinated hydrocarbons on regional and global scales require input data on spatial distribution (Harner et al., 1995) to aid validation and prediction. For these reasons and to better understand distribution and transport mechanisms, studies on PCBs in the environment are likely to continue in the future.

This paper presents a study of diffuse PCB contamination in the UK troposphere based on the use of pine needles as "passive samplers". A companion paper on PAHs (Tremolada et al., 1996) details the benefits and limitations of using vegetation instead of direct measurements of the air concentrations.

The UK was our study area. Data on the production, use, and environmental contamination of PCBs in the UK have been published in recent years. Harrad et al. (1994) estimated that of the 66000 t produced in the UK between 1954 and 1977, 40000 t were used within the country. Of these 40000 t released or in use in the UK, only 400 t are estimated to be present in the UK surface environment now, the bulk of it in soil (93 %). Analyses of dated sediment and peat cores (Sanders et al., 1992; Sanders et al., 1995) and archived samples of soil, vegetation and air filters (Jones et al., 1992; Alcock et al., 1993; Jones et al., 1995) from the UK all indicate that PCB levels in the UK environment rose after their commercial production, peaked in the 1960/70s and have declined significantly. Harner et al. (1995) have modelled the trends in soil concentrations, arguing that in the past the soil was a net sink for atmospherically deposited PCBs but that there is currently a net "degassing" of PCBs back to the atmosphere. Congeners with different degrees of chlorination exhibit rather different behaviour or rates of change in their re-cycling and re-mobilisation between air-soil and air-plant. Inventory estimates suggest that contemporary primary emission of PCBs to the UK atmosphere are swamped by inputs resulting for secondary emissions and environmental re-cycling (Harrad et al., 1994).

A basic assumption of this large scale distribution study is that pine needle samples for different locations reflect regional differences in PCB (diffuse) contamination of the atmosphere. We present and discuss the spatial and temporal distribution trends of PCBs in the UK as reflected currently in the pine needles and discuss the relationship and process of air-needle transfer in the context of the physicochemical properties of the compounds.

MATERIALS AND METHODS

Sampling: The samples were collected in rural sites, selected to be as far as possible away from main cities, principal roads and industrial plants. A series of 9 latitudinal transects nationwide in the UK were sampled in two periods in May-June and August 1994, to give a total of 28 samples. Details of the sample locations are reported in Table 1 and Figure 1.

Table 1. Transect number, sample location and grid reference number of the 28 pine needle samples collected in UK.

transect	Sample	locality	grid reference
9	9a	Loch Stack	NC 29 41
	9b	Mereckland	NC 39 29
	9c	Schinness	NC 51 17
	9d	Rogart	NC 73 03
8	8a	Lair	NH 03 48
	8b	Achnasheen	NH 15 58
	8c	Garve	NH 37 64
7	7a	Loch Cluanie	NH 04 12
	7b	Invergarry	NH 28 01
	7c	Loch Laggan	NN 54 89
6	6a	Bridge of Balgie	NN 57 46
	6b	Invervar	NN 66 48
	6c	Tummel bridge	NN 74 61
5	5a	Muirkirk	NS 69 28
	5b	Crawfordjohn	NS 87 23
	5c	St. Mary's Loch	NT 25 22
	5d	Traquair	NT 32 33
4	4a	Ingleton	SD 71 74
	4b	Hawes	SD 83 88
	4c	West Witton	SE 05 88
3	3a	Oakmoor	SJ 95 44
	3b	Ilam Park	SK 14 52
2	2a	Hailes Abbey	SP 06 30
	2b	Hidcote	SP 17 42
	2c	Upton House	SP 38 45
1	1a	Somerton	ST 49 28
	1b	Stourhead	ST 76 35
	1c	Heale Garden	SU 10 32

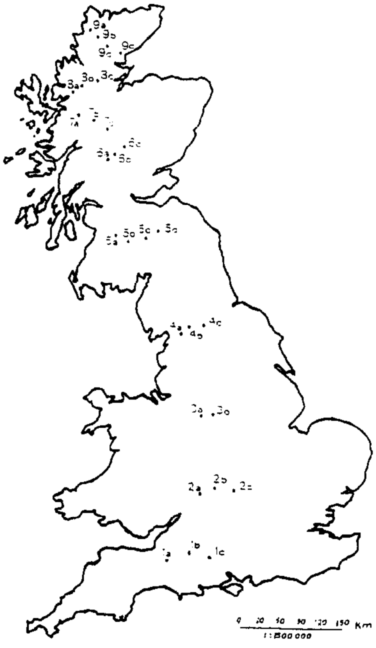

Figure 1. Sample location on the UK map. Codes are those of Table 1.

Pinus sylvestris was chosen as the species from which needles were collected for two main reasons: because it has been used previously in studies of this type (Eriksson et al., 1989; Strachan et al., 1994; Kylin et al., 1994) and because it is widely distributed across the country. Freshly shed pine needle samples (about of 10 g each) were collected from the ground at the end of their life cycle, wrapped in aluminium foil and closed in glass jars. The foil and glass jars had both been rinsed twice previously in n-hexane. Samples were stored at -20 °C until analysis was performed.

Chemical analysis: Sample pre treatment: samples were homogenised and the water content was measured on sub-samples by weighing after 12 *h* in the oven at 105 °C.

Extraction: a pre-extraction was performed with n-hexane to clean the 6-place Soxhtec extraction apparatus and the thimbles (2 *h* hot extraction and 2 *h* rinsing). Samples (3-4 g) were then weighed into the extraction thimbles and the extraction was performed using *n*-hexane (2 *h* hot extraction and 2 *h* rinsing). One blank extraction was run in each batch of five samples.

Clean-up: because this method was developed for the analysis of a spectrum of persistent organic pollutants in pine needles, among which PCB and PAH compounds, a number of purification steps was performed on the extracts before sulphuric acid clean up. The following chromatographic phases were used: alumina (Aluminium Oxide Active, BDH, Poole, England), Florisil (Florisil about 60-100 u.s. mesh, BDH, Poole, England) and silica (Silica gel 60, particle size 0.063-0.200 mm, Merck, Darmstadt, Germany). Sample extracts were concentrated to a few ml under a stream of nitrogen, loaded onto a alumina column (3 g of alumina deactivated 4% + 0.2 g of anhydrous sodium sulphate on the top in 7 mm I.D. glass column). The sample was eluted with 6 ml of DCM and this step repeated, after reduction of the sample to about 1 ml by a nitrogen stream. Florisil column chromatography (1 g of Florisil in pasteur pipette) was repeated twice, loading the sample concentrated to about 1 ml and eluting it with 10 ml of DCM. The sample was gently dried under a nitrogen stream, re-suspended with n-hexane and loaded on a silica-gel column (2.5 g of silica-gel activated at 130 °C for 3 *h* + 0.2 g of anhydrous sodium sulphate on the top in 7 mm I.D. glass column). PCBs were eluted from the silica gel column with 34 ml of n-hexane. After the concentration of the sample by rotary evaporation to 10 ml, 5 ml of concentrated sulphuric acid was added and left to react overnight. The acid was removed and the sample concentrated to about 1 ml for Florisil column chromatography (1 g of Florisil in pasteur pipette). The sample was eluted with 15 ml of n-hexane and gently dried under a stream of nitrogen. A known amount of dodecane (50 ul or 100 ul) was added to the sample before reducing the extract down to the dodecane volume only.

Analysis: GC analyses were performed using a Hewlett Packard 5890A with an electron capture detector (ECD) and a CP-Sil8 CB Chrompack capillary column (50 m, 0.2 mm ID, 0.11 μm film thickness). Helium was used as the carrier gas (at 0.32 ml/min, 30 psi) and nitrogen as the make up gas (at 60 ml/min). Injector and detector temperatures were 280 °C and 350 °C respectively. The temperature programme was as follows: 100 °C for 2 min, increase at 20 °C/min to 140 °C, increase at 4 °C/min to 200 °C for 13 min, and increase at 4 °C/min to 280 °C for 8 minutes.

The following IUPAC congener numbers in elution order were screened: 30, 54, 28, 52, 104, 40, 61/74, 66, 155, 101, 119, 110/77, 82/151, 149, 118, 188, 153, 138, 187, 183, 202/156, 180, 169, 170, 198, 201, 194, 205, and 209. Congener 209 was used as a retention time marker and added to each extract prior to the GC-ECD analysis. Relative retention times of unknown peaks were identified and quantified with respect to congener 209 and an external-standard calibration, using a VG Minichrom data handling system. The calibration curve was performed using five solutions containing from 2.5 to 100 pg/μl, injecting 1 μl.

The procedure described above has been checked for recoveries and reproducibility. Recovery was investigated by spiking pine needle sub samples with three increasing amounts of standard. For all the compounds analysed results were in the range of 80 and 100%. Reproducibility was calculated on replicate analyses giving an error of about 20-30%.

Concentration data are reported here on a dry weight basis as reported by some other authors (e.g. Reischl et al., 1987; Jensen et al., 1992), although Simonich and Hites (1994) advocated expressing concentrations on a lipid weight basis. However the lipid contents of some of the samples analysed here were between 8 and 11%.

Statistical treatment of data: Geometric means were calculated from the concentration data of each transect. The geometric mean was chosen to avoid biassing the results because of a few highly contaminated samples. Correspondence Factor Analysis (CFA) was used for the treatment of the data, after converting the mass units of the contaminants in the concentration values from nanograms to picomoles. The analysis was performed according to a statistical computer program STAT-ITCF version 3.0, 1987 originally produced by ECOSOFT and translated and corrected by the "Institut Technique des Céréales et des Fourrages", Paris. This multivariate approach has been previously used for the analysis of data of this type (Calamari et al., 1994).

RESULTS AND DISCUSSION

Pine needle PCB levels in UK. Table 2 presents the analytical results of the 28 pine needle samples from the UK. Generally very low concentrations were present, especially in the Scottish samples (transects 9, 8, 7 and 6), where the concentrations of many congeners were below the detection limit (ΣPCB typically < 1 ng/g d.w.). In the southern transects more congeners were measured than in the north and slightly higher concentrations detected (several ng/g d.w. of ΣPCB concentration). Among the 32 congeners screened, congeners 101, 110/77, 149, 118, 153, 138 and 180 were nearly always detected and were present at the highest concentrations (together with congeners 28 and 52 when they were measured above the detection limit). Almost the same group of congeners (namely 28, 52, 77, 101, 118, 153, 138 and 180) were taken as major congeners by Halsall et al., (1995) in the air of four UK urban centres (London, Manchester, Cardiff and Stevenage).

The relative differences in the congener composition are highlighted by the graphical CFA representation of the 27 samples shown in Figure 2. Sample 6b was not included because all congener concentrations measured in this sample were below the detection limit. Sixteen variables (congeners) detected in at least one sample were used to prepare the plot.

Table 2. PCBs in pine needle samples from the UK. Sample codes are as shown in Figure 1. Concentrations are expressed in ng/g dry weight. Congeners for which data are not reported were below the detection limit of 0.02 ng/g d.w., except for congener 66 whose detection limit was 0.4 ng/g d.w. due to the presence of an interferring peak.

Samples	9a	9b	9c	9d	8a	8b	8c	7a	7b	7c	6a	6b	6c	5a	5b	5c	5d	4a	4b	4c	3a	3b	2a	2b	2c	1a	1b	1c
PCB congeners														ng/g d.w.														
30																												
54																												
28	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.41	<0.4	<0.4	<0.4	0.55	0.41	<0.4	<0.4	<0.4	<0.4	<0.4
52	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.42	0.47	0.41	0.68
104																												
40																												
61/74	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	0.14	<0.1	0.28	0.1	0.12	0.19	0.23	0.13	0.12	<0.1	0.14	<0.1	0.3
66																												
155																												
101	0.06	0.05	0.08	0.09	0.14	0.1	0.08	0.11	0.13	0.11	0.32	<0.04	0.2	0.18	0.11	0.12	0.15	0.51	0.17	0.28	0.41	0.37	0.34	0.33	0.36	0.41	0.28	0.55
119																												
110/77	0.1	0.08	0.11	0.14	0.17	0.13	0.09	0.11	0.14	0.13	0.34	<0.04	0.18	0.14	0.15	0.18	0.17	0.9	0.21	0.19	0.42	0.35	0.32	0.53	0.52	0.54	0.37	0.80
82/151	0.05	0.06	0.06	0.07	0.13	0.08	0.04	0.08	0.09	0.07	0.1	<0.04	0.09	<0.04	0.05	0.06	0.07	0.29	0.07	0.05	0.05	0.05	0.06	0.1	0.08	0.13	0.45	0.19
149	0.12	0.05	0.13	0.16	0.14	0.15	0.05	0.11	0.14	0.09	0.23	<0.04	<0.04	0.11	0.15	0.11	0.19	0.52	0.19	0.28	0.43	0.32	0.33	0.32	0.3	0.43	0.26	0.53
118	0.03	0.02	0.02	0.08	0.07	0.03	0.03	0.05	0.04	0.04	0.18	<0.02	<0.02	0.09	0.09	0.11	0.11	0.67	0.12	0.07	0.21	0.17	0.18	0.22	0.19	0.21	0.12	0.44
188																												
153	0.04	0.05	0.04	0.13	0.16	0.08	0.09	0.09	0.06	0.08	0.24	<0.04	0.17	0.19	0.18	0.13	0.22	0.69	0.13	0.19	0.44	0.22	0.32	0.24	0.24	0.4	<0.04	0.46
138	<0.04	<0.04	<0.04	0.08	0.14	0.05	0.04	0.1	0.04	0.05	0.28	<0.04	0.21	0.25	0.15	0.14	0.18	0.68	0.15	0.18	0.44	0.31	0.36	0.34	0.32	0.4	0.23	0.67
187	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.07	0.05	0.07	0.19	0.07	0.03	0.07	0.04	0.09	0.1	0.1	0.14	0.09	0.2
183	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	<0.02	0.08	<0.02	<0.02	<0.02	<0.02	0.1	<0.02	<0.02	0.05	<0.02	0.06
202/156	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.06	0.18	0.08	0.45	0.19	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
180	0.02	<0.02	0.03	0.03	0.04	0.03	0.04	0.02	0.02	0.04	0.79	<0.02	0.26	0.53	0.13	0.59	0.17	2.81	0.81	0.94	0.39	0.85	0.58	0.61	0.51	0.4	0.25	0.44
169																												
170	<0.02	<0.02	<0.02	0.02	0.03	<0.02	0.02	0.02	0.02	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.04	0.15	<0.02	<0.02	0.05	<0.02	0.06	0.07	0.07	0.07	0.03	0.09
198																												
201	0.04	0.03	0.02	0.03	0.05	0.05	0.06	0.02	<0.02	0.08	<0.02	<0.02	<0.02	<0.02	0.03	0.03	0.05	0.08	0.06	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.03
194																												
205																												
ΣPCB	**0.46**	**0.34**	**0.49**	**0.83**	**1.1**	**0.70**	**0.54**	**0.71**	**0.68**	**0.71**	**2.5**	**<0.28**	**1.1**	**1.7**	**1.2**	**1.9**	**1.5**	**8.7**	**2.3**	**2.3**	**3.1**	**3.5**	**3.3**	**3.0**	**3.1**	**3.8**	**2.5**	**5.4**

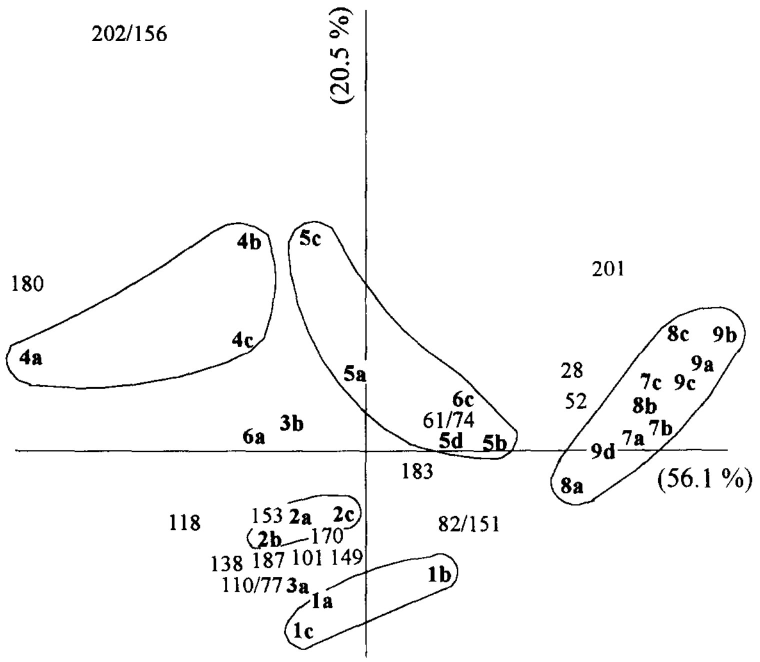

Figure 2. CFA of 27 single data concentrations of 16 PCBs in the 9 UK transects. The graphical display is obtained by the projection of the points on the first and second axes. The variability explained by each axis is reported in parentheses. PCB compounds are identified by the IUPAC congener number, while the samples are identified by the same codes of Table 2.

The samples appear to be grouped by the different transect areas, based on differences in the congener composition. The most northern transect samples (9, 8, and 7) lie together on Figure 2. The four samples from transect 5 are dispersed on Figure 2 and placed in between the northern-most transect samples and those from transect 4. The samples from transects 1 and 2 are also grouped together, but away from the other locations. The samples from transect 3 are quite scattered and lie between the transect 1 and 4 samples; the same can be said for the transect 6 samples which lie between the north and middle transect samples.

In summary, Figure 2 indicates an homogeneity in the congener composition for the samples coming from the same transect and the same area. Four main groups can be derived: one composed of the samples of the northern transects (9, 8, 7), one that groups the samples from the southern transects (1, 2), and the two groups of transect 4 and 5 samples. The congener composition is slightly changing from the southern transects to northern ones with a higher proportion of congeners 101, 118, 180, 149, 153, and 138 toward the south. Presumably this reflects differences in the source PCB mixtures and usage patterns and/or their environmental fate/behaviour.

Spatial distribution of PCB in the UK environment. The mean concentrations (geometric mean) of the ΣPCBs for each transect versus the north-south distance are shown in Fig. 3. Differences among the 9 transects in the ΣPCB content were statistically significant ($p>0.0001$, $n=9$). The mean ΣPCB concentrations range by a factor of ~7 from 0.5 ng/g d.w. to a maximum of 4 ng/g d.w.

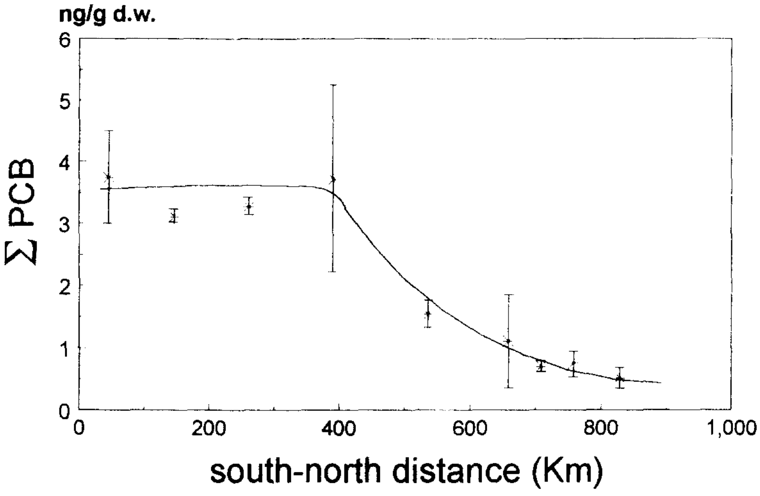

Figure 3. Spatial trend of ΣPCB in UK. Distance is referred to the mean distance of each transect from the south coast of UK.

Concentrations were quite constant in the four southern-most transects, then sharply decrease between the fourth and the fifth transect and then gradually decrease northwards through Scotland. It should be noted that mean annual ambient temperatures are lower in northern Scotland (~4 °C) than southern England (~10 °C). This is likely to have at least three important effects: a) slow the rate of volatilisation/re-mobilisation of previously deposited PCBs in the north relative to the south, thereby reducing air concentrations; b) increase the proportion of airborne PCB on the particulate phase in northern air relative to southern air; c) increase the partitioning of gas phase PCB from air onto needle surfaces. Interestingly, despite the presence of populated and industrialized cities (Glasgow and Edinburgh) in southern Scotland, the regional effects in England seem much stronger sources of PCBs. Bracewell et al. (1993) presented data for four transects of peat samples from the north to the south of Scotland; their work also showed a concentration gradient of a factor of 3.7 between the south and the north of Scotland, very similar to that found in this study (factor 3.05 between transect 5 and 9 results). Generally, therefore, the data of this study suggest that the regional (national) picture in the UK is of higher air concentrations in the south.

No other spatial distribution study using vegetation as the sampling matrix has been performed in the UK, although several studies have reported on PCB distribution in surface soils (Bracewell et al., 1993; Alcock et al., 1993; Creaser and Fernandes, 1986; Eduljee et al., 1987; Jones et al., 1989). These have generally shown higher concentrations in urban/industrial centres, with values up to several hundred ng ΣPCB/g (Eduljee et al., 1987; Alcock et al., 1993) near source regions and as low as a few ng/g in remote locations (Alcock et al., 1993; Jones et al., 1989).

The ΣPCB concentration gradient from the north to the south of the UK (Figure 3) seems to have a very similar trend in relation to those found for the higher molecular weight PAH compounds (Tremolada et al., 1996). Because a contamination gradient for PCB has been quantified between the south more densely populated and with an higher concentration of industrial activities and the north less impacted by man, a correlation between the ΣPCB contamination levels and the population density is attempted in Figure 4 giving an R^2 of 0.92. Population density has been chosen as crude index related to potential PCB-source-man activities.

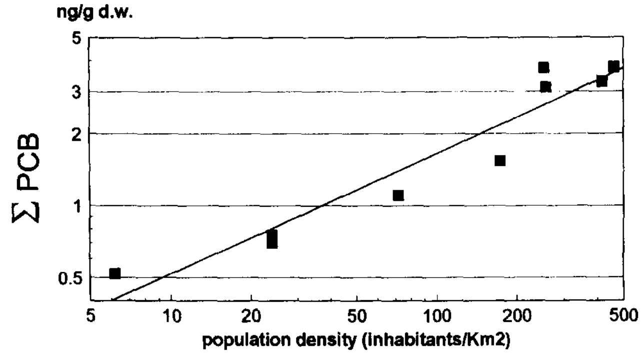

Figure 4. ΣPCB of the pine needle mean concentrations (geometric means) of the 9 transects versus density of population in the same transect areas in UK.

Comments on possible time trend information: As noted in the introduction, there is interest at present in the changing environmental levels of PCBs. In this context, the data of the present work can usefully be compared with a limited series of measurements of archived herbage samples from Rothamsted Experimental Station, UK, analysed in the same laboratory (Jones et al., 1992). These authors reported mean ΣPCB concentrations of 28 ng/g d.w. for herbage sampled each year but bulked for the period 1985-1989. Rothamsted lies close to the transect 2 samples taken for this study, with the corresponding value for pine needles analysed here of 3.5 ng/g d.w.. Obviously sites and species differences are likely to be important, but the needle data does seen to correspond well with the earlier herbage results. The measurements of archived herbage samples cover a time interval from 1965 to 1989. These data indicate that air concentrations of ΣPCBs at one site in rural England have decreased by a factor of 50 over this period. The needles were sampled in 1994. Figure 5 plots data for selected congeners in the Rothamsted herbage, together with that from needles (transect 2 geometric means) versus time.

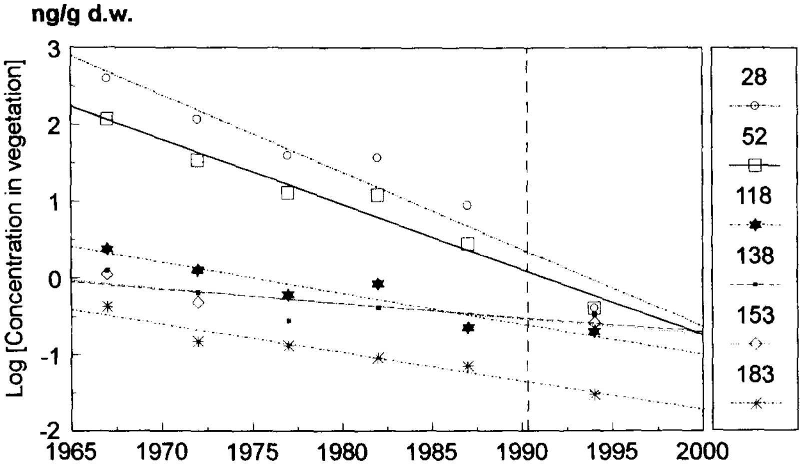

Figure 5. Temporal trend of different PCB congeners (data are reported as Log of the concentration in ng/g d.w.). Results before 1990 are those of Jones et al., (1992) of PCB content of Rothamsted herbage; results of 1994 are mean concentrations (geometric mean) of transect 2 pine needle content (this work).

Although the vegetation type differs, the single congener pine needles results for 1994 agree very well with the corresponding congener trends drawn for 1965-1989 period. R^2 values are: 0.93, 0.96, 0.89, 0.54, 0.83, 0.94 for congeners 28, 52, 118, 138, 153, and 183 respectively, showing the high correlation between the decreasing trend and the current pine needle results. The slopes of the different congeners are: -0.10, -0.085, -0.040, -0.018, -0.020, and -0.037 for congeners 28, 52, 118, 138, 153, and 183 respectively. The slopes of the decreasing trends indicate higher decreases for the low molecular weight congeners (congeners 28 and 52, slope of -0.1 in average) than high molecular weight congeners that show slope values of -0.04 or less. This observation may be explained by the higher tendency of the low molecular weight congeners to volatilize to the atmosphere and be advected elsewhere and/or degraded by photoreactions. Low molecular weight congeners (congeners 15, 18, 28, 40, 52) account for most of the reduction in herbage (Jones et al., 1992); with higher molecular weight congeners decreasing only from 1-2 ng/g d.w. in 1965-69 to ~0.2 or less in 1985-1989 (congeners 118, 138 153, 183).

Calculated versus measured PCB concentrations: Mean concentrations in vegetation were used for a quantitative evaluation of the mean levels in air through the use of bioconcentration factors (BCFs) theoretically calculated from the physicochemical properties. Table 3 presents selected physicochemical properties and calculated Koa and BCF values for the analysed congeners for which concentration were measured above the detection limit.

Table 3. Selected physicochemical properties of PCB congeners (n-octanol/water partition coefficient, Kow and Henry's Law constant, H) and calculated Log Koa and Log BCF values (n-octanol/air partition coefficient, Koa and bioconcentration factor in vegetation, BCF)

PCB congener	Log Kow *	H ** (25 °C) Pa*m^3/mol	Log Koa 25 °C	Log BCF 25 °C	Log BCF 8 °C
28	5.67	28.44	7.61	5.95	6.35
52	5.84	32.50	7.72	6.06	6.46
61	6.04	23.81	8.06	6.40	6.80
74	6.20	21.75	8.26	6.60	7.00
101	6.38	24.00	8.39	6.74	7.13
77	6.36	10.00	8.75	7.10	7.49
110	6.48	20.00	8.57	6.92	7.31
82	6.20	14.80	8.42	6.77	7.16
151	6.64	28.50	8.58	6.92	7.32
149	6.67	23.08	8.70	7.04	7.44
118	6.74	12.70	9.03	7.37	7.77
153	6.92	16.50	9.10	7.44	7.84
138	6.83	13.20	9.10	7.45	7.84
187	7.17	20.00	9.26	7.61	8.00
183	7.20	20.25	9.29	7.63	8.03
202	7.24	22.80	9.28	7.62	8.02
156	7.18	9.00	9.62	7.96	8.36
180	7.36	10.63	9.73	8.07	8.47
170	7.27	8.80	9.72	8.06	8.46
201	7.62	13.00	9.90	8.24	8.64
ΣPCB				**7.58**	**7.98**

* Values estimated by Hawker and Connell (1988)

** Values estimated by Dunnivant et al. (1992)

BCF values were calculated for two temperatures, the temperature at which physicochemical properties are given and the mean temperature estimated for transect 4 band for which comparable rural air data as been measured in both vapour and particulate phases by Halsall (1995) over a year period. BCFs were calculated as reported in Bacci et al. (1990), using a temperature-dependence correction in accordance with that given by Mackay et al. (1986).

As reported in Table 3, BCF values of the different congeners range, as expected on the basis of the differences in their physicochemical properties, over two orders of magnitude from a Log value of 6, e.g. 6.35 at 8 °C for congener 28 (trichlorobiphenyl) to Log values of 8, e.g. 8.64 at 8 °C for congener 201 (octachlorobiphenyl). Because many experimental BCF values are given for mixtures of PCBs, the mean of the Log values of the calculated BCFs has been reported for comparative purpose. Table 4 presents a series of BCF values for PCBs as given by Morosini et al. (1993) and a good agreement between the calculated·and the experimental values is derived, confirming the predictive capability of Koa-based theoretic BCFs, as reported in the literature (Bacci et al., 1990; Paterson et al., 1991; Schramm et al., 1987; Muller et al., 1994; Tolls and McLachlan, 1994; McLachlan et al., 1995).

Table 4. Calculated and measured bioconcentration factors for foliage (BCF) for different congeners and for the ΣPCB from Morosini et al. (1993).

PCB congeners	Log BCF				
	Calculated this work (8 °C) [1]	Calculated by Morosini et al. (1993)[2]	Environmental measurements (Ulm) [3]	Environmental measurements (France) [4]	Laboratory measurements (Italy) [5]
28	6.35	5.94			
52	6.46	6.24	6.89		
101	7.13	7.17	7.05		
118	7.77	7.74	7.59		
138	7.84	7.78	7.44		
153	7.84	7.74	7.51		
180	8.47	7.88	7.81		
ΣPCB	7.98		7.25	7.35	7.28

[1] Calculated through the equation BCF = 0.022 Kow/Kaw (Bacci et al., 1990) with data from Table 3. Vapour pressure and water solubility have been recalculated for a temperature of 8 °C.

[2] Calculated through the equation BCF = 0.022 Kow/Kaw (Bacci et al., 1990) by Morosini et al. (1993).

[3] Morosini et al. (1993).

[4] Villeneuve et al. (1988).

[5] Bacci et al. (1990).

Table 5 reports the calculated and measured (vapour phase only) concentrations of a number of PCB congeners. The calculated ones are derived from transect 4 pine needle sample results and the measured ones from a rural area near the city of Lancaster, north west of England (Halsall, 1995). At least for certain chemicals, gaseous dry deposition has been seen to be the key process of bioaccumulation of SOC in vegetation via air-leaf uptake (Umlauf et al., 1994; McLachlan et al., 1995). In Table 5 a relatively good agreement was found, especially for the lightest congeners, for which calculated values were within or very near the 95% confidence limits of the Log-probit distribution of the measured data. A good agreement was also obtained for the ΣPCBs of the calculated data and the measured ones (71 and 90 pg/m^3 respectively). The prediction of the air concentrations of many congeners is within ± a factor of 2 in respect to the measured concentrations, while the others generally do not exceed a factor of ± 5. Figure 6 again shows a generally good agreement between calculated and measured values.

Table 5. Calculated PCB concentrations in air (Ca calculated) from concentrations in vegetation from transect 4, C50 of the Log-probit analysis and 95% Confidence Limits (Ca measured (C50) and 95% C.L.) of the vapour concentration of the same PCB congeners in a rural area near Lancaster UK (Halsall, 1995), and factor of difference between calculated and measured values (Difference Factor).

PCB congener	Ca calculated pg/m^3	Ca measured (C50) and 95% C.L. pg/m^3	Ratio of Ca(cal.) / Ca(meas.)
28	48	35 (31-39)	+1.4
52	<37	18 (16-20)	
61/74	4.9 *	4.4 (2.4-6.3)	+1.1
101	5.7	3.7 (2.6-4.9)	+1.5
110/77	3.4 *	4.8 (1.9-7.5)	-1.4
82/151	1.5 *	1.1 (0.7-1.4)	+1.4
149	2.9	6.1 (3.6-8.7)	-2.1
118	0.81	4.1 (3.2-5.1)	-5.1
153	1.0	5.0 (4.5-5.6)	-5.0
138	0.99	0.43 (0.15-0.79)	+2.3
187	0.19	2.8 (2.2-3.4)	-15.0
183	0.08	0.01 (0.00001-0.06)	+8.0
202/156	0.19 *		
180	1.2	4.2 (3.3-5.3)	-3.5
170	0.04	0.02 (0.0001-0.08)	+2.0
201	0.03	0.14 (0.02-0.31)	-4.7
ΣPCB	**71**	**90**	**-1.3**

* Concentrations in air have been calculated with the mean of the BCF values of the two congeners.

** Insufficient values above the detection limit to allow calculation of Confidence Limit.

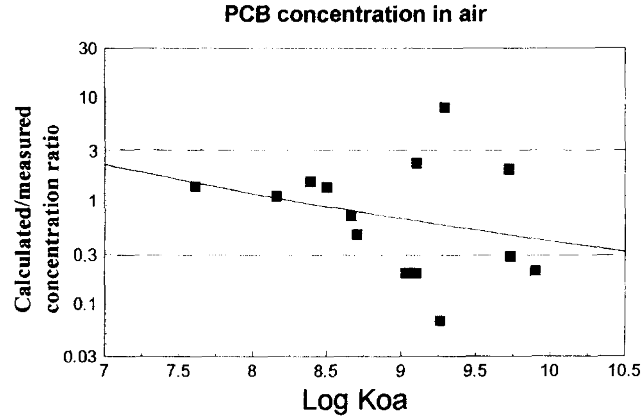

Figure 6. Octanol-air partition coefficient (Koa) versus the ratio between PCB concentrations in air calculated from the pine needle results (transect 4, this work) and PCB median concentration measured in air from a similar area (Halsall, 1995).

Almost all the calculated/measured ratios were within one order of magnitude with the majority of them near the ratio of 1. Generally, when the log Koa value is < 8.5 predictions seem to be very accurate; however, they become less reliable above this value. A similar trend was noted for the PAH data (Tremolada et al., 1996) with increasingly poor agreement between measured and predicted air concentrations for compounds of increasing Log Koa (above ~ 8.5). McLachlan et al. (1995) have noted previously that for more volatile compounds (Log Koa < 8) air-grass leaf equilibrium is approached more rapidly than for compounds with high Koa values. Compounds with Log Koa values < 8 approach equilibrium, allowing the prediction of air:leaf equilibrium using the BCF approach, while compounds with a Log Koa between 8 and 11 did not approach equilibrium and their uptake was independent of their physicochemical properties. Data of this work do not allow to distinguish whether "non-equilibrium" conditions or alternative pathways are involved in the bioaccumulation of these compounds in vegetation taking into account that uncertainties in physicochemical property data, analytical difficulties and site specificity can interfere with this type of validation. However, it is suggested that bioaccumulation of highly hydrophobic chemicals by vegetation warrants further research, since it is unclear which is the key process in the air-leaf uptake for compounds with high Koa values.

CONCLUSION

Evidence for low-level diffuse PCB contamination in the UK environment is provided through the use of pine needles as passive air samplers. A relatively uniform PCB distribution was found in the rural/remote sites monitored nationwide in the UK. Both the spatial distribution and the congener composition change slightly from south to north; mean ΣPCB concentrations decrease northward, with a difference between the south and the north of a factor of ~7. A relationship was found between the mean ΣPCB concentration of each transect and population density of the same area.

The comparison between calculated and measured concentrations in air provides useful evidence of generally good predictions of the mean air concentrations from the pine needle data through the use of Koa-based BCFs. However, a more detailed analysis of calculated and measured values suggests that better predictions are obtained for congeners with Log Koa values < 8.5, while more uncertainties appear for those congeners with higher Koa values (Log Koa > 8.5). These data and findings from the literature, seem to suggest that for low Koa values (Log Koa < 8-9) Koa-based partitioning and near-equilibrium conditions determine the leaf-air uptake process, while for high Koa values (Log Koa > 9) "non equilibrium" and/or alternative processes may be present.

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