

Evidence that diffuse domestic burning is an important source of PCDD/Fs and co-PCBs

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Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are formed during incomplete combustion and released as unwanted by-products of industrial processes (1). The role of domestic burning as a source of atmospheric PCDD/Fs in national PCDD/F emission inventories (e.g. 2) is minor. On the other hand, elevated concentrations of PCDD/Fs during the winter in pre-dominantly rural areas have been ascribed to domestic burning (3), although elevated levels of POPs during colder months could be influenced by reduced atmospheric mixing (e.g. inversion layers). We undertook this sampling campaign in winter 1998 at four sites in northern England, two of them in small villages, to elucidate the importance of domestic burning on the local air quality. PCBs are re-cycled in the environment from soil, vegetation and released from buildings (4), so their atmospheric concentrations are little influenced by domestic burning. Consequently PCBs were used as a reference group of compounds for the importance or otherwise of meteorological parameters for atmospheric POP concentrations.

Materials and Methods

Sampling sites: Samples (ca. 800 m³) were taken over 3 or 4 days in January and February 1998 in i) Manchester, an urban centre (site A); ii) in Clapham and Austwick, small villages in the Yorkshire Dales (sites B&C) and iii) in Lancaster, in a semi-rural area (site D).

Analytical procedure: The method employed has been described elsewhere (5). Briefly, air samples were taken with PS-1 air samplers (Graseby Andersen) equipped with a glass fibre filter (GFF) and 2 polyurethane foam plugs (PUF). The PUF plugs were spiked with all ¹³C₁₂-2,3,7,8-substituted congeners prior to sampling. ¹³C₁₂-PCBs were added prior to extraction. PUFs and GFFs were combined, extracted in toluene for 16 hours, cleaned-up on a mixed silica column and fractionated on a basic alumina column. Fraction I (7%DCM-heptane) contained the PCBs, fraction II (toluene) the co-PCBs and the final fraction III (50%DCM-heptane) the PCDD/Fs. Our method seeks to quantify the full range of mono- to octa-CDD/Fs. PCDD/Fs and PCBs 77, 126 & 169 were analysed by HRGC-HRMS using an HP6890 GC connected to a Micromass Autospec Ultima high resolution mass spectrometer at 10,000 resolving power. Total homologues were quantified on a 30m DB5-MS, and the 2,3,7,8-substituted congeners on a 60m SP2331. PCB-quantification was achieved by GC-MS (EI-mode) on a Fisons MD-800 in SIM mode with separation on a CP-Sil-8 50 m column (for more detail see 6)

Quality Control: Method detection limits were 0.5 fg/m³ for the 2,3,7,8-substituted tetra- to hepta CDD/Fs, 25 fg/m³ for HpCDD, 10 fg/m³ for OCDF and 170 fg/m³ for OCDD. Mean recoveries for the tetra- to octa-2,3,7,8-substituted CDD/Fs were between 64% and 97%, 48% for 2,8-DiCDF, 47% for 2,7-DiCDD and 55% for 2,3,7-TriCDD. Mean blank levels for PCBs were ~ 1.5pg/m³ for PCBs 18, 28, 31& 52 and ~ 0.5 pg/m³ for all other PCBs. Mean recoveries of ¹³C₁₂-PCBs (# 28, 52, 101, 153, 138, 180 & 209) were between 52-67%.

Results and discussion

Formation and Sources I

PCDD/Fs: Σ TEQ (I-TEQ) concentrations varied from 18 to 460 fg TEQ/m³ at site A, and from <10 to 100 fg TEQ/m³ at the other sites. Mean concentrations of Σ TEQ and of Σ P₄₋₈CDD/Fs were on average 3 times higher at site A than at the rural sites (see Table 1). Σ P₃₋₈CDD/Fs were dominated by tri-CDFs and OCCD; the general homologue profile follows the 'average' one as described in the literature (7). Mono- & di-CDFs were an order of magnitude higher than tri- to octa-CDD/Fs.

Table 1: Minimum, maximum and average PCDD/F and PCB concentrations at the four sites

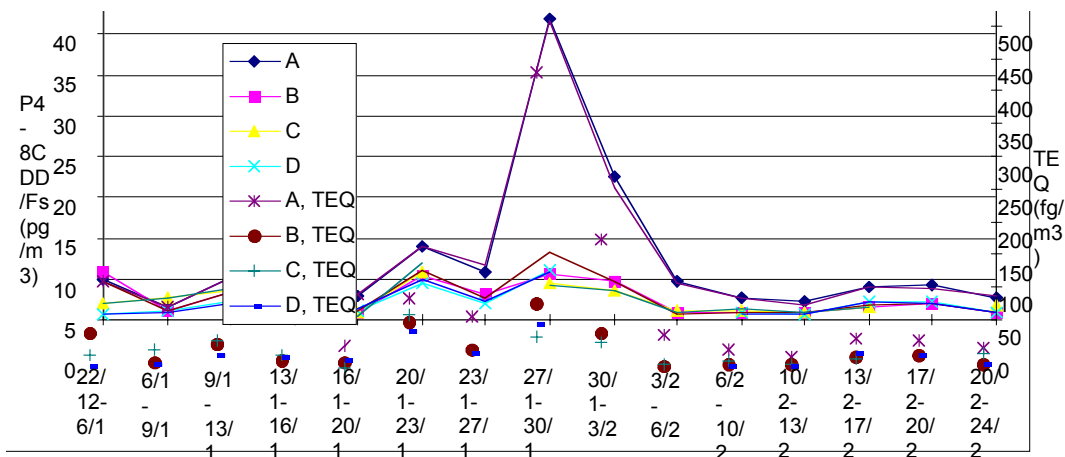
site	P ₄₋₈ CDD/Fs (pg/m ³)	P ₁₋₈ CDD/Fs (pg/m ³)	Σ TEQ (fg/m ³)	Σ PCBs (pg/m ³)	#77 (pg/m ³)	#169 (fg/m ³)
A	1.5-37 (7.6)	9.8-130 (32)	18-460 (95)	190-750 (500)	0.5-2.3 (1.0)	3.8-63 (15)
B	0.8-5.8 (2.6)	15-42 (28)	9-100 (34)	35-140 (67)	0.1-0.3 (0.2)	1.0-51 (7.5)
C	0.8-5.8 (2.4)	15-44 (30)	6-87 (32)	57-100 (73)	0.2-0.6 (0.3)	1.6-47 (8.4)
D	0.8-6.0 (2.3)	15-130 (54)	8-73 (28)	26-110 (60)	0.1-1.0 (0.3)	1.3-9.2 (4.8)

PCBs: PCB concentrations showed a smaller range of concentrations, differences between minimum and maximum concentrations did not exceed a factor of 4 at any site. Site A had the highest concentrations, with 500 pg/m³ on average, roughly 7 times higher than at the rural sites. The town-countryside difference was less pronounced for the co-planar PCBs (see Table 1). PCBs # 77 and 169 were still higher at site A, but levels exceeded those at the rural sites only by factors of 4 and 2, respectively.

Temporal and spatial variation at the 4 sites: As can be seen in Figure 1, Σ TEQ and Σ P₄₋₈CDD/Fs varied similarly at the four sites. Levels increased during the colder sampling events at all sites. The simultaneous changes of PCDD/F concentrations at all sites suggest common causes, either due to a reduced dilution of PCDD/Fs in the atmosphere (i.e. regional meteorology) and/or due to increased emissions during the coldest sampling events. Domestic burning is the only likely seasonally-dependent source.

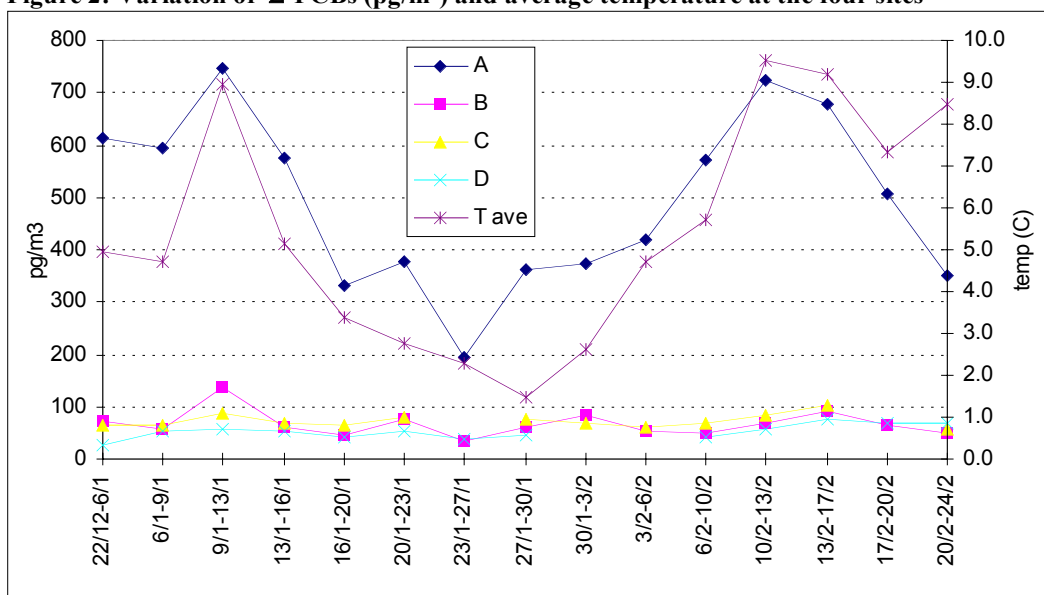
Figure 1: Variation of Σ P₄₋₈CDD/Fs (pg/m³) and Σ TEQ at the four sites

Formation and Sources I



As expected, concentrations of PCBs followed the increase or decrease of the average temperature, most noticeably at site A (see Figure 2). PCB concentrations at the rural sites were higher during warmer sampling events, but the temperature-dependency was less pronounced.

Figure 2: Variation of Σ PCBs (pg/m^3) and average temperature at the four sites



Correlation with meteorological parameters: Atmospheric PCDD/F, co-PCB and PCB concentrations were correlated with meteorological parameters, namely average, minimum and maximum temperature, wind direction and speed (see Table 2).

Formation and Sources I

PCDD/Fs: At site A, all PCDD/Fs were significantly inversely correlated with wind speed and average temperature (T_{ave}) at $P \leq 0.05$. Wind direction was not significantly correlated with PCDD/Fs. Wind speed was similarly correlated at $P \leq 0.05$ to PCDD/Fs at site B & C; only di-CDD/Fs, tri- and tetra-CDDs and hepta-CDDs were not significantly correlated at site B. T_{min} showed a significant correlation ($P \leq 0.05$) with mono-CDD/Fs and tri- to hexa-CDFs at site B, whereas at site C tetra-CDDs were inversely correlated to T_{ave} at $P \leq 0.05$. Wind direction was significantly inversely correlated to tri- to hexa-CDFs at site C ($P \leq 0.05$). At site D, T_{ave} was not significantly correlated to PCDD/Fs ($P \leq 0.05$), but wind direction was inversely significantly correlated to all PCDD/Fs except mono- & di-CDD/Fs ($P \leq 0.05$). At site D, wind speed was significantly correlated to OCDD and penta-CDDs at $P \leq 0.05$ (see Table 2).

PCBs: At site A, T_{ave} was significantly correlated to most PCBs; few PCBs had negative, but not significant, correlations with T_{ave} , namely # 206, #209 & #126; #169 was significantly negatively correlated to T_{ave} ($P \leq 0.05$). Wind speed was significantly correlated to PCBs #101 and higher ($P \leq 0.05$), whereas few PCBs were significantly negatively correlated, namely # 206, 126 and 169. There were fewer significant correlations with T_{ave} at sites B,C & D. Wind speed was not significantly correlated to any PCBs except negatively to PCB # 126 at sites B and C ($P \leq 0.05$). Wind direction was significantly inversely correlated with PCB # 126 at site C and positively with PCB #77 at site B ($P \leq 0.05$).

Table 2: Correlation coefficients between minimum temperature (T_{min}), wind speed (WS), wind direction (WD) and selected PCBs and PCDD/Fs (significant at * $P \leq 0.05$, ** $P \leq 0.01$)

	Manchester			Clapham			Lancaster		
	T_{ave}	WS	WD	T_{min}	WS	WD	T_{ave}	WS	WD
# 28	+0.23	+0.08	+0.39	+0.22	-0.26	+0.21	+0.43	-0.04	+0.12
# 44	+0.61**	+0.34	+0.45	+0.52*	-0.05	+0.29	+0.37	-0.15	+0.14
# 110	+0.63**	+0.47*	+0.31	+0.50	+0.08	+0.09	+0.22	-0.21	-0.11
# 118	+0.55*	+0.39	+0.25	+0.48	-0.01	+0.02	+0.01	-0.19	-0.22
# 138	+0.48*	+0.51*	+0.18	+0.41	+0.03	+0.01	+0.26	+0.01	-0.11
# 153	+0.44	+0.49*	+0.15	+0.38	+0.17	-0.04	+0.30	+0.18	-0.03
# 180	+0.48*	+0.62**	+0.34	+0.43	-0.16	+0.16	+0.25	+0.00	-0.15
# 77	+0.07	-0.31	+0.03	+0.32	-0.06	+0.54*	+0.15	+0.36	+0.13
# 126	-0.44	-0.70**	-0.25	-0.56*	-0.56*	-0.08	+0.21	+0.35	+0.05
# 169	-0.52*	-0.79**	-0.32	-0.20	-0.27	+0.23	-0.36	-0.09	-0.52
MCDFs	-0.56*	-0.75**	-0.37	-0.61*	-0.62*	-0.05	-0.24	-0.26	-0.49
DiCDFs	-0.57*	-0.74**	-0.17	+0.16	+0.18	+0.68**	+0.40	+0.32	+0.56*
TriCDFs	-0.52*	-0.76**	-0.32	-0.68**	-0.54*	-0.09	-0.28	-0.28	-0.59*
TCDFs	-0.52*	-0.78**	-0.31	-0.67**	-0.61**	-0.17	-0.40	-0.42	-0.72**
PeCDFs	-0.56*	-0.82**	-0.29	-0.61*	-0.65**	-0.20	-0.48	-0.48*	-0.76**
HxCDFs	-0.52*	-0.80**	-0.29	-0.55*	-0.66**	-0.22	-0.45	-0.46*	-0.70*
HpCDFs	-0.54*	-0.79**	-0.28	-0.50	-0.70**	-0.18	-0.36	-0.44	-0.68**
OCDF	-0.46	-0.75**	-0.27	-0.43	-0.75**	-0.29	-0.25	-0.31	-0.52

Evidence for diffuse domestic burning: Two key meteorological parameters become evident from the initial presentation of results, namely temperature and wind speed. Only PCDD/Fs were

inversely affected by these 2 parameters, not PCBs, suggestive of different sources for these compound groups. Co-planar PCBs 126 and 169 do not follow the trend of the other PCBs, i.e. increasing concentrations with increasing temperature, but rather the inverse trend together with PCDD/Fs. Strong correlations with wind speed at sites A-C point towards ground-level sources of PCDD/Fs, #126 & #169. Tri- to hexa-CDFs are separated out as indicators of the rural samples.

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