Gas-particle partitioning of PCDD/Fs in daily air samples

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Introduction

The fate of PCDD/Fs in the atmosphere is primarily governed by their gas-particle partitioning. The extent by which PCDD/Fs are particle-bound determines their atmospheric lifetime due to wet and dry deposition, photolysis and reaction with OH radicals.
As there are few reported PCDD/F gas-particle distribution studies to date, we have studied the partitioning of di- to octa-CDD/Fs with a series of short-term (24 or 48 hrs) samples at Lancaster, UK, in winter 1997. PCDD/F partitioning coefficients are derived for all the measured congeners and homologue groups and correlated with the subcooled-liquid vapour pressure and good correlations are obtained. For 2 samples taken in December, a strong increase in ΣTEQ was found together with a different gas-particle distribution.

Experimental Section

Eight air samples (800 - 1200 m^3) to study gas-particle partitioning were taken at Lancaster University's field station (54°2'N, 2°45'W) on the north west coast of the UK during November and December 1997. Samples were taken with a view to minimising the temperature fluctuation during the sampling interval. Each sample code (A-H) consists of PUFs/GFFs combined from 3 hi-vols (except samples A and E - 2 hi-vols) employed concurrently; the combined polyurethane foam plugs and combined glass fibre filters were analysed separately. PUF plugs were extracted with DCM for 16 hrs, GFFs were extracted with toluene for 16 hrs and cleaned up by acid silica refluxing followed by fractionation on basic alumina. The particulate fraction was put through an additional carbon column clean-up step. The PUF plugs were spiked with all $^{13}C_{12}$-2,3,7,8-substituted congeners prior to sampling, the GFFs were spiked prior to extraction. Analysis was performed on a Micromass Autospec Ultima, operated at a resolution of at least 10,000. Homologue groups were quantified together on a DB5-column and congener-specific data was obtained using an SP-2331 column. Average recoveries for the 2,3,7,8-substituted congeners ranged from 70 - 95%; recoveries for $^{13}C_{12}$-2,8-DiCDF, $^{13}C_{12}$-2,7-DiCDD and $^{13}C_{12}$-2,3,7-TrCDD were between 45 and 60%.
Combined daily samples B+C and G+H were compared to simultaneously sampled two-day samples; differences for 2,3,7,8-substituted congeners and Σ P_{2-8}CDD/Fs averaged 10%.

The total suspended particulate matter (TSP) was measured with an additional air sampler; GFF sheets were equilibrated in controlled humidity 24 hrs before and after sampling and weighed. Sampling dates, air volumes, meteorological parameters, TSP-levels, air mass origins and ΣTEQ-values are given in Table 1.

Table 1: Sampling dates, meteorological parameters, TSP-levels, air mass origins and the ΣTEQ of the gas-particle distribution study at Lancaster, UK

Sample code	A	B	C	D	E	F	G	H
Sampling date	17.-19.11.	19.-20.11	20.-21.11	21.-22.11	22.-24.11	2.-3.12	3.-4.12	4.-5.12.
air volume (m^3)	1184	885	1127	971	1252	830	808	775
temperature (°C)	12.5±3	10.5±1.5	7.3±2.5	7±3.5	7±2.5	-0.3±2.5	1.5±2.5	2.5±1.5
rel. humidity	87%	82%	78%	89%	90%	100%	88%	88%
rain (mm)	2.5	6.3	-	-	3.8	0.3	-	0.2
TSP (μg/m^3)	22	40	30	33	22	29	26	31
air mass origin	France - S-Engl.	France - S-Engl.	Ireland-Germ.	S-Engl.	France - S-Engl.	Scotl.	Scotl. - Scand.	Scotl. - Ireland
TEQ (fg/m^3)	15	18	33	44	44	32	320	100

Results and Discussion

Air concentrations - 2,3,7,8-substituted PCDD/F and homologue groups

The PCDD/F concentrations found in the 16 samples are summarised in Table 2, together with the particle-bound fraction, the $\Sigma_{(4-8)}$PCDD/Fs, the ΣTEQ and contribution of the particle-bound fraction to the ΣTEQ. Di- and tri-chlorinated congeners which are included in our analytical method are also shown in Table 2. Samples A-F showed low ΣTEQ concentrations, typical for a rural site, with 15-44 fg TEQ/m^3. Samples G and H had a strong increase in ΣTEQ, with 320 fg TEQ/m^3 and 100 fg TEQ/m^3 respectively.
The contribution of the different congeners to the ΣTEQ was quite consistent; 2,3,4,7,8-PeCDF was the main contributor, at ~25% of the ΣTEQ. 1,2,3,7,8-PeCDD was the only other congener contributing more than 10%. Sample G was different to the others, with a much higher PCDF contribution. The homologue patterns are typical of the UK background (1).

Gas-particle partitioning of 2,3,7,8-substituted PCDD/Fs and homologue groups

A partitioning coefficient, K_p=(F/A)/TSP, was calculated for all the 2,3,7,8-substituted congeners and the homologue groups and log K_p was plotted against the temperature corrected logarithm of the subcooled liquid vapour pressure, $p_L°$,: $\log K_p = m_r \bullet \log p_L + b_r$ with m_r the slope and b_r the y-intercept of the trendline (2). The $p_L°$ data were taken from Mackay *et al.* (3) and Ballschmiter and Bacher (4). We calculated mean values of m_r= -0.63 and b_r= -4.6; all correlations were highly significant (99%). Other studies reported similar slopes of the trendlines but different y-intercepts:

Eitzer and Hites found $m_r = -0.775$ and $b_r = -5.72$ at a site in urban Bloomington, Indianapolis (5) and values of $m_r = -0.70$ and $b_r = -5.5$ have been reported for rural Germany (see in 6).

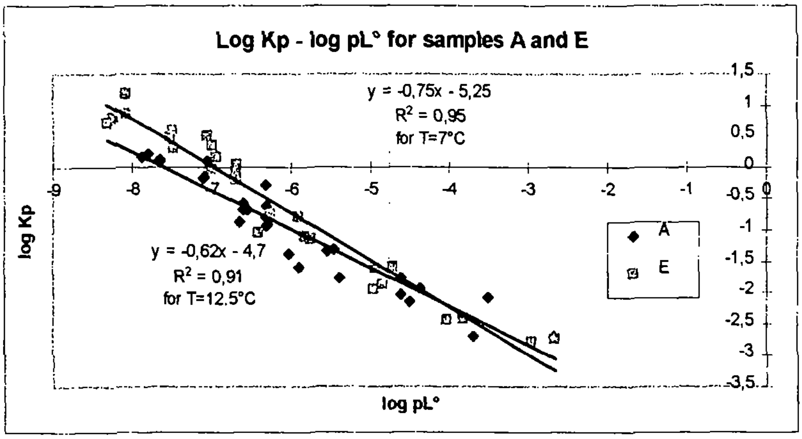
Table 2: Air concentrations (fg/m^3) of the 2,3,7,8-substituted congeners and the homologue groups measured at Lancaster and the fraction which was particle -bound (in brackets)

Sample	A	B	C	D	E	F	G	H
PCDFs								
2,3,7,8-	6.5 (0.21)	9.3 (0.19)	9.1 (0.54)	18 (0.51)	18 (0.36)	12 (0.62)	95 (0.90)	33 (0.62)
1,2,3,7,8-	8.4 (0.28)	12 (0.43)	22 (0.74)	31 (0.74)	28 (0.61)	20 (0.91)	280 (0.97)	75 (0.93)
2,3,4,7,8-	7.1 (0.51)	12 (0.68)	15 (0.79)	26 (0.87)	25 (0.78)	16 (0.94)	230 (0.99)	58 (0.95)
1,2,3,4,7,8-	10 (0.72)	12 (0.82)	52 (0.97)	40 (0.94)	27 (0.94)	17 (0.95)	360 (0.98)	85 (0.98)
1,2,3,6,7,8-	7.7 (0.73)	9.3 (0.86)	27 (0.95)	29 (0.95)	26 (0.93)	14 (0.96)	280 (0.99)	69 (0.98)
1,2,3,7,8,9-	2.6 (0.92)	4.6 (0.81)	3.7 *(0.94)*	4.4 *(0.94)*	3.4 *(0.94)*	3.0 *(0.80)*	26 (0.95)	6.9 *(0.91)*
2,3,4,6,7,8-	11 (0.84)	13 (0.89)	22 (0.96)	34 (0.95)	28 (0.96)	18 *(0.93)*	300 (0.98)	79 (0.97)
1,2,3,4,6,7,8	35 (0.94)	31 (0.94)	170 (0.99)	98 (0.98)	72 (0.99)	38 (0.97)	880 (0.99)	260 (0.99)
1,2,3,4,7,8,9	6.0 *(0.96)*	6.4 *(0.96)*	35 *(0.99)*	16 *(0.98)*	9.2 *(0.98)*	7 (0.69)	120 (0.99)	33 *(0.99)*
OCDF	37 (0.97)	42 (0.97)	260 (1.00)	82 (0.98)	45 *(0.99)*	23 (0.95)	460 (0.99)	230 (0.99)
PCDDs								
2,3,7,8-	0.7 (0.17)	1.2 (0.58)	1.6 (0.55)	2.0 (0.49)	1.9 (0.35)	2.1 (0.58)	14 (0.88)	4.8 (0.58)
1,2,3,7,8-	3.7 (0.36)	4.1 (0.63)	7.3 (0.81)	9.5 (0.89)	15 (0.80)	12 (0.96)	59 (0.96)	26 (0.96)
1,2,3,4,7,8-	3.3 (0.75)	3.8 *(0.93)*	7.7 (0.94)	12 *(0.98)*	14 *(0.99)*	12 *(0.95)*	48 (0.97)	28 *(0.98)*
1,2,3,6,7,8-	10 (0.82)	8.6 (0.89)	16 (0.96)	24 (0.98)	30 (0.97)	22 (0.93)	80 (0.95)	54 (0.98)
1,2,3,7,8,9-	8.1 (0.85)	6.7 (0.92)	14 *(0.98)*	18 *(0.99)*	24 (0.98)	22 (0.95)	67 (0.97)	45 (0.98)
1,2,3,4,6,7,8	120 (0.97)	75 (0.96)	160 (0.99)	220 (0.99)	260 (0.99)	220 (0.97)	530 (0.97)	560 (0.98)
OCDD	400 (0.97)	270 (0.97)	520 *(0.99)*	670 (0.98)	690 *(0.99)*	590 (0.95)	1200 (0.98)	1900 (0.98)
ΣPCDFs								
P_2CDF	3800 (.00)	3100 (.01)	77000 (.01)	5400 (.01)	4400 (.04)	3000 (.03)	19000 (.14)	25000 (.03)
P_3CDF	410 (0.16)	320 (0.05)	380 (0.09)	550 (0.12)	800 (0.08)	490 (0.15)	3200 (0.29)	1200 (0.10)
P_4CDF	200 (0.13)	180 (0.14)	220 (0.28)	400 (0.34)	520 (0.23)	330 (0.47)	4000 (0.85)	1100 (0.45)
P_5CDF	110 (0.51)	100 (0.47)	180 (0.71)	330 (0.8)	320 (0.63)	200 (0.90)	3400 (0.97)	850 (0.92)
P_6CDF	86 (0.77)	84 (0.91)	280 (0.98)	310 (0.97)	260 (0.95)	140 (0.99)	3000 (0.99)	700 (0.99)
P_7CDF	62 (0.94)	63 (0.97)	360 (1.00)	190 (0.98)	140 (0.99)	66 (0.95)	1600 (0.99)	450 (0.99)
ΣPCDDs								
P_2CDD	160 (0.04)	150 (0.03)	330 (0.42)	180 (0.05)	180 (0.04)	120 (0.06)	350 (0.06)	780 (0.02)
P_3CDD	50 (0.04)	44 (0.06)	46 (0.17)	71 (0.11)	99 (0.07)	55 (0.18)	490 (0.34)	190 (0.10)
P_4CDD	92 (0.28)	72 (0.22)	130 (0.41)	170 (0.36)	270 (0.20)	100 (0.61)	1300 (0.81)	370 (0.45)
P_5CDD	68 (0.47)	48 (0.44)	100 (0.69)	210 (0.84)	320 (0.67)	160 (0.95)	1200 (0.95)	510 (0.95)
P_6CDD	110 (0.82)	94 (0.89)	190 (0.93)	310 (0.97)	560 (0.95)	220 (0.96)	1000 (0.96)	620 (0.97)
P_7CDD	220 (0.97)	140 (0.96)	310 (0.99)	450 (0.99)	530 (1.00)	400 (0.97)	1100 (0.97)	1100 (0.98)
$\Sigma_{(4-8)}$ PCDD/Fs	1390	1100	2550	3130	3640	2230	18100	7880
ΣTEQ	15 (62%)	18 (72%)	33 (87%)	44 (88%)	44 (82%)	32 (91%)	320 (97%)	100 (93%)
log K_p-log p_L trendline data								
intercept	**-4.7**	**-5.1**	**-4.9**	**-5.0**	**-5.3**	**-4.0**	**-3.3**	**-4.9**
slope	**-0.62**	**-0.65**	**-0.69**	**-0.69**	**-0.75**	**-0.49**	**-0.47**	**-0.68**
regression	**0.91**	**0.95**	**0.88**	**0.95**	**0.95**	**0.78**	**0.77**	**0.91**

(values in *italics* were calculated assuming non-detects as half the detection limit)

The PCDD/Fs show a big range in their gas-particle distribution, with 1-40% of P_2CDD/Fs and 95-100% of OCDD/F particulate-bound in these wintertime samples. A temperature effect is most pronounced for the tetra- and penta-CDD/Fs, which are > 90% particle-bound for samples F-H (mean temperatures <3°C), but generally ≤ 50% for samples A and B (mean temperatures >10°C). This trend is illustrated in Figure 1, with sample A (T=12.5°C) having lower K_p-values than sample E (T=7°C) for similar TSP concentrations.
Samples G and H have a highly significant (99%) different slope from the other samples suggesting that gas and particulate phase were not in equilibrium when sampled.

Figure 1: log K_p - log p_L plot for samples A and E with regression lines



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