Atmospheric Transport of PCDD/Fs along a Global North-South Transect

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Introduction

Samples for the determination of PCDD/Fs were taken in October -December 1998 on board the *RRS Bransfield* on a cruise from Grimsby, in the UK, to several British Antarctic Survey bases in the southern hemisphere, ultimately reaching Halley (75 °S, 20 °W).

Materials and Methods

Air sampling Air samples were taken with a GPS-1 PUF air sampler (Graseby Andersen), equipped with a Whatman glass fibre filter (GFF, 10cm diameter) and 2 polyurethane foam plugs (PUF, 6.5cm diameter, 5cm length). The air sampling and analytical procedure has been described elsewhere (1).

Quality Control Field blanks (1 in 5) and laboratory blanks (1 in 10) were routinely incorporated in the analytical procedure and used to derive detection limits as three times the standard deviation of the mean concentration in the blanks. Detection limits for the 2,3,7,8-substituted PCDD/Fs were ~0.5-1 pg/sample and ~ 1-2 pg/sample for the homologue groups (except Cl_2DFs - 25 pg/sample and OCDD - 5 pg/sample). Mean recoveries for the $^{13}C_{12}$-PCDD/Fs were between 57-85%.

Interference of stack emissions The three stack samples taken exhibited no consistent profiles; in two of the samples, only $Cl_{1\text{-}4}$DFs were detected, while the third one displayed a full range of PCDD/Fs. The samples for which an interference was noticed did not show higher concentrations of $Cl_{1\text{-}4}$DD/Fs than the samples taken before or after it.

Results and discussion

General Comments on Ambient Air Concentrations Ambient PCDD/Fs were higher over the North Atlantic than over the South Atlantic. Highest concentrations of $Cl_{1\text{-}8}$DFs and $Cl_{2\text{-}8}$DDs all occurred between 25 and 52 °N. Concentrations were lowest from ~60 °S and southwards. Table 1 compares ambient air concentrations of $Cl_{2\text{-}8}$DDs and the ΣTEQ from different locations and seasons around the world. Included from this sample set are results from Montevideo (MV), the Falkland Islands (FI), Bird Island (BI) and near Halley (HA).

Evidence for PCDD/F releases in the southern hemisphere PCDD/F concentrations at Montevideo were comparatively high and reached levels detected in UK winter samples from Lancaster and Manchester (UK), providing evidence for current PCDD/F emission sources in South America. Further evidence was the detection of PCDD/Fs in the remote southern hemisphere. On average it takes ~ 1 year for the air of the northern to reach the southern hemisphere (6). Half-lives of gaseous PCDD/Fs (with respect to OH-radical attack) are in the order of days to tens of days (7), making any exchange of PCDD/Fs released in one hemisphere to the other unlikely and

insignificant compared to local releases. The Falkland Islands exhibited PCDDF concentrations ~ similar to measurements from the western Irish coast. Concentrations of PCDD/Fs at the Falkland Islands, although low, were still higher by factors of 2-5 than measured south of 40 °S.

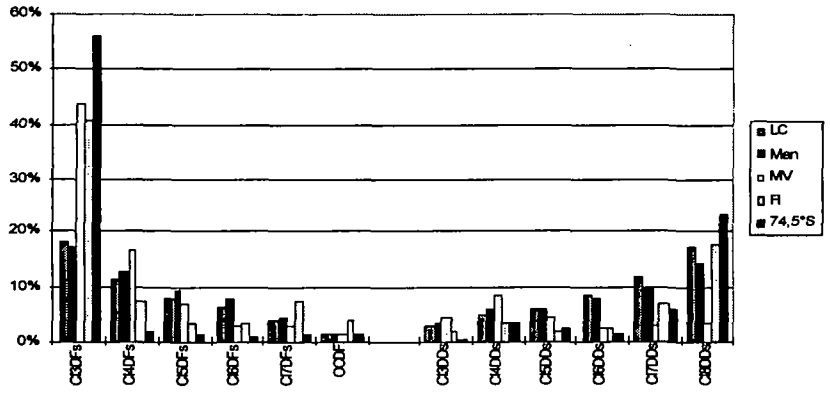
Table 1: Comparison of PCDD/Fs in ambient air (fg/m^3)

in fg/m^3	Manchester[a] 1-3'98	Irish coast[b] 5'97	Sandy Hook[c] 7'98	MV[d] 11'98[e]	FI[d] 11'98	Bi[d] 11'98[f]	HA[d] 12'98
Cl_2DDs	2,000	86	2,000	780	99	14	12
Cl_3DDs	290	41	28	260	10	5.4	0.66
Cl_4DDs	560	36	17	510	19	10	5.3
Cl_5DDs	560	30	15	270	12	4.1	3.9
Cl_6DDs	720	42	38	150	14	4.8	2.3
Cl_7DDs	900	52	130	180	42	10	8.6
OCDD	1,300	80	340	210	110	35	36
Σ TEQ	100[g]	3.6[h]	6.6[g]	40[g]	2.6[g]	0.87[g]	0.50[g]

[a] Ref. 2; [b] Ref. 1; [c] Ref. 3; [d] this study [e] recovery-problems in gaseous phase; [f] interference by *ship's emissions possible*; [g] Ref. 4; [h] Ref. 5

Relative Homologue Profiles. Figure 1 shows the relative contribution of the tri- to octa-chlorinated homologue groups to $\Sigma Cl_{3-8}DD/Fs$ for selected air measurements from the northern and southern hemisphere. The average profile from Lancaster and Manchester mirror the 'general' ambient air profile as described in the literature (see in 8). However, the samples from Montevideo, the Falkland Islands and near Halley were all dominated by Cl_3DFs, contributing > 40 % of the total (as compared to < 20 % for Lancaster and Manchester). At Montevideo, any of the PCDDs contributed < 10 % of the total; Cl_4DDs are in higher abundance than OCDD.

Figure 1: Relative contribution of $Cl_{3-8}DD/Fs$ to $\Sigma Cl_{3-8}DD/Fs$ for selected locations in the northern* and southern hemisphere**



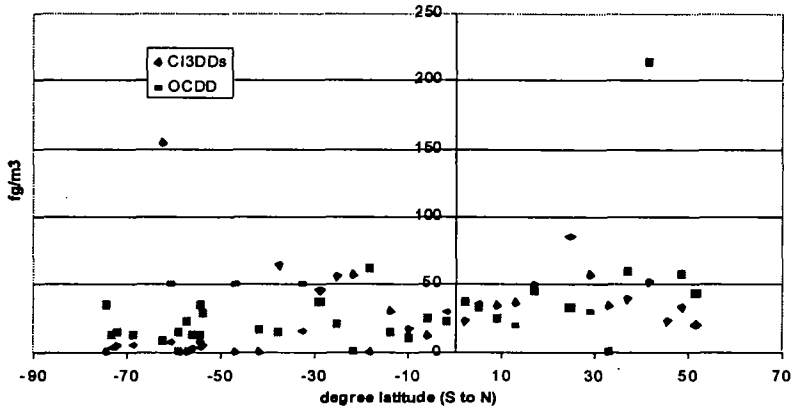
* LC - Lancaster, Man - Manchester: mean values for winter 1998 (Ref. 2);
** *MV, FI* and sample 53 (near Halley) from this study

Samples from the Falkland Islands and near Halley were dominated by Cl_3DFs (~ 40 % of the total) and OCDD (~ 20 % of the total), the most persistent PCDD/Fs in the gaseous and particulate-bound phase, respectively.

PCDD/Fs in the gaseous phase

Concentrations of $Cl_{2/3}DD/Fs$ were highest in the northern hemisphere; concentrations decreased around the equator and, with few exceptions, decreased strongly at 40 °S (see Figure 2 for Cl_3DD concentrations). Concentrations of $Cl_{4-6}DD/Fs$ in the gaseous phase followed the trend outlined for $Cl_{2/3}DD/Fs$ which is interesting as their relative proportion in the gaseous phase increased markedly around the equator.

Figure 2: Ambient Cl_3DD and OCDD-concentrations (fg/m^3) along a north-south transect



PCDD/Fs in the particulate phase

Concentrations of PCDD/Fs in the particulate phase were generally low, with most homologue groups rarely exceeding 50 fg/m^3. Figure 2 shows concentrations of OCDD as a function of degrees latitude. The fairly constant concentrations of $Cl_{7/8}DD/Fs$ in the particulate phase suggest a fairly consistent background concentration of, most likely, accumulation mode particles above the Atlantic ocean. Accumulation mode particle are small enough not to be deposited close to emission sources.

Conclusions

PCDD/Fs are global pollutants: Ambient PCDD/Fs occur in the remote south. We found evidence for significant PCDD/F releases in the southern hemisphere.

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References

1. Lohmann, R.; Green, N.J.L.; Jones, K.C. **1999** *Environmental Science and Technology* 33, 2872-2878.
2. Lohmann, R.; Northcott, G.L.; Jones, K.C. **2000** Assessing the Contribution of Diffuse Domestic Burning as a Source of PCDD/Fs, PCBs and PAHs to the UK Atmosphere *Environmental Science and Technology*, in press.
3. Lohmann, R., Brunciak, P.L.; Gigliotti, C.L.; Nelson, E.; Van Ry, D.; Glenn, T.; Eisenreich, S.J., Jones, J.L., Jones, K.C.: **2000** Spatial and Temporal Distribution of Atmospheric PCDD/Fs in New Jersey. Submitted to *Environmental Science and Technology*.
4. Van den Berg, M.; Birnbaum, L.; Bosveld, A.T.C.; Brunström, B.; Cook, P.; Feeley, M.; Gisey, P.; Hanberg, A.; Hasegawa, R.; Kennedy, S.W.; Kubiak, T.; Larsen, J.C.; van Leeuwen, R.F.X.; Liem, A.K.D.; Nolt, C.; Peterson, R.E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillit, D.; Tysklind, M.; Younes, M.; Waern, F.; Zacharewski, T. (**1998**) *Environmental Health Perspectives* 106, 775-792.
5. Kutz, F.W.; Barnes, D.G.; Bottimore, D.P.; Greim, H,; Bretthauer, E.W. **1990** *Chemosphere* 20, 751-757.
6. Seinfeld, J.H.; Pandis, S.N. Atmospheric Chemistry and Physics, **1998**, Wiley, 1326p, ISBN 0471178152.
7. Kwok, E.S.C.; Arey, J.; Atkinson , R. **1995** *Environmental Science and Technology* 29, 1591-1598.
8. Lohmann, R.; Jones, K.C. **1998** *The Science of the Total Environment* 219, 53-81.