Polychlorinated Dibenzo-*p*-dioxins, Dibenzofurans, Co-planar PCBs and Mono-*ortho* PCBs in Urban Air.

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) have 75 and 135 congeners. Some of the congeners with chlorine substitution at 2, 3, 7 and 8 positions in their molecules are extremely toxic. It is considered that the sources of the dioxins are municipal waste incinerators[1,2] and these compounds extend widespreadly via atmosphere. PCBs have theoretically 209 congeners containing with four non-*ortho* chlorine substitution congeners(co-planar PCBs) and eight mono-*ortho* chlorine substitution congeners(mono-*ortho* PCBs). The co-planar and mono-*ortho* PCBs are approximate isostereomers of the most toxic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin with planar structure and are known to be one of the toxic substances. The toxic equivalently factors (TEFs)[3] are recommended for the 2,3,7,8-substituted PCDDs and PCDFs and co-planar and mono-*ortho* PCBs. Since toxicities vary with positions of chlorine substitution, we must identify and determine these congeners with HRGC/HRMS. In this study, we determined PCDDs, PCDFs, co-planar PCBs and mono-*ortho* PCBs in urban air and assessed toxicity of these compounds in ambient air.

Experimental

Sampling

Samples of ambient air were collected from urban area by high volume air sampler with filter and polyurethane foam plugs (PUF)[4,5] in 1992. Flow rate was about 1 m^3/min.

Extraction and Clean-up

Filter and PUF samples were extracted respectively with toluene and acetone using Soxhlet extractors for 18 hours. Both extracts were combined and concentrated to volume

of 100ml. The sample was separated four samples and analysed for dioxins and PCBs respectively. Both aliquot were spiked with ^{13}C-labelled internal standards for each degree of chlorination. Samples for dioxin analysis were washed with conc. H_2SO_4 and water, and the retained organic phase was concentrated, purified on silica-gel column and separated by alumina column. The elute was concentrated to ca.100ul for GC/MS analysis. For PCB analysis the sample was saponified with 1N KOH in ethanol and extracted 2 times with hexane. The extract was purified by silica-gel column and alumina column. The successive procedures were the same as for dioxins. This method is shown in Fig. 1.

GC/MS analysis

Determinations were performed with a HP 5890A-J gas chromatograph (Hewlett Packard), and JMS-SX102 mass spectrometer (JEOL) at a resolution of ca. 10000 using SP-2331 (60m) or HP-5 (25m) column for dioxin analysis and a DB-5 column (50m) for PCBs. The GC temperature programs are shown in Table 1. The results were corrected for the recovery of internal standards.

Resuls and Discussion

The results are shown in Tables 2 and 3. In these results shown that concentrations of PCDDs and PCDFs in winter were higher than in summer. Results for PCBs were different from PCDDs and PCDFs. The main components of PCDDs and PCDFs were hepta and octa chlorinated congener, these of co-planar PCBs were 3,3',4,4'-T4CB and these of mono-*ortho* PCBs were 2',3,4,4',5- and 2,3',4,4',5-P5CB, 2,3,3',4,4'-P5CB and 2,3,3',4,4',5-H6CB.

Comparison the concentrations of 2,3,7,8-substituted PCDDs and PCDFs with co-planar and mono-*ortho* PCBs, showed that PCBs were about ten times higher (Tables 2,3). But the ratio accounting for PCDFs were 70% of the total toxic equivalents (TEqs)(Table 4, Fig.2). PCDDs were 20%, sum of both PCBs were 10%. It seems that PCDFs mainly contributed to the toxicity in ambient air.

Referances

1) Olie,K., Vermeulen,P.L., Hutzinger,O. *Chemosphere* 6, 455-459, 1977.
2) Hiraoka,M *Waste Management Research* 1, 20-37, 1990.
3) Safe,S. *C.R.C. Crit.Rev.Toxicol.* 21, 51-88, 1990.
4) Nakano,T., Tsuji,M., Okuno,T *J.Environ.Chem.* 1, 325-332, 1991.
5) Kuwata,K., Yamashi,Y. *J.Environ.Chem.* 1, 359-370, 1991.

Table 1. GC/MS analytical conditions

GC	HP 5890A-J (Hewlet Packerd)			
Column	SP-2331 60m × 0.32mm ID × 0.17um FT (for dioxin analysis)			
	HP-5 25m × 0.32mm ID × 0.17um FT (for dioxin analysis)			
	DB-5 50m × 0.25mm ID × 0.25um FT (for PCB analysis)			
MS	JMS-SX102 (JEOL)			
	Resolution ca. 10000			
	Trap current 1000uA			
Temperature programs				
	Column	SP-2331	HP-5	DB-5
	Injection Temp. (℃)	260	290	260
	Initial Temp. (℃)	100	100	100
	Initial Time (min.)	1.5	1.5	1.5
	Rate 1 (℃/min.)	20	20	15
	Final Temp. 1 (℃)	180	180	160
	Rate 2 (℃/min.)	3	10	4
	Final Temp. (c)	260	290	260
	Final Time (min.)	20	1	20

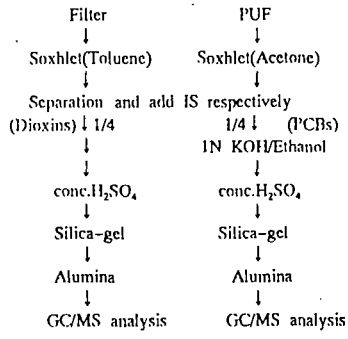

Fig.1 Clean-up procedures for Dioxin and PCB.

Table 2. Concentrations Levels of 2,3,7,8-substituted PCDDs and PCDFs in urban air. (pg/m³)

	Summer			Winter		
	Ave.	Max.	Min.	Ave.	Max.	Min.
Dioxins						
2,3,7,8-T4CDD	0.007	0.026	-	0.040	0.060	-
1,2,3,7,8-P5CDD	0.087	0.123	0.058	0.193	0.515	-
1,2,3,4,7,8-H6CDD	0.180	0.340	0.061	0.376	0.815	0.060
1,2,3,6,7,8-H6CDD	0.274	0.415	0.176	0.683	1.749	0.220
1,2,3,7,8,9-H6CDD	0.191	0.252	0.134	0.555	1.394	0.048
1,2,3,4,6,7,8-H7CDD	2.375	3.651	1.240	4.213	8.385	0.581
O8CDD	4.624	6.259	2.751	10.358	29.054	1.388
Dibenzofuran						
2,3,7,8-T4CDF	0.173	0.246	0.127	0.308	0.565	0.049
1,2,3,7,8-P5CDF	0.401	0.558	0.250	0.868	1.994	0.179
2,3,4,7,8-P5CDF	0.484	0.807	0.256	0.898	1.589	0.178
1,2,3,4,7,8-H6CDF	0.687	1.073	0.360	1.317	2.651	0.246
1,2,3,6,7,8-H6CDF	0.714	1.262	0.332	1.308	2.508	0.267
1,2,3,7,8,9-H6CDF	0.261	0.362	0.142	0.233	0.678	-
2,3,4,6,7,8-H6CDF	1.381	2.507	0.527	2.321	4.380	0.514
1,2,3,4,6,7,8-H7CDF	5.020	8.427	2.314	5.948	11.569	1.303
1,2,3,4,7,8,9-H7CDF	0.630	1.128	0.201	0.771	1.579	0.138
O8CDF	5.338	8.996	1.838	5.588	10.788	1.021

- : ND (Detection limit is 0.01pg/m³)

Table 3. Concentrations Levels of co-planar and mono-*ortho* PCBs in urban air. (pg/m³)

	Summer			Winter		
	Ave.	Max.	Min.	Ave.	Max.	Min.
Co-planar PCBs						
3,3',4,4'	3.506	4.595	2.484	1.741	2.463	1.277
3,3',4,4',5	0.312	0.508	-	0.361	0.707	0.131
3,3',4,4',5,5'	0.118	0.263	-	0.181	0.395	-
Mono-*ortho* PCBs						
2',3,4,4',5	*	*	*	*	*	*
2,3',4,4',5	12.776	18.075	9.165	4.581	6.376	3.239
2,3,4,4',5	0.508	1.055	-	0.443	0.606	0.280
2,3,3',4,4'	7.496	12.708	5.159	4.824	7.240	2.053
2,3,4,4',5,5'	1.790	3.208	0.962	0.762	1.205	0.449
2,3,3',4,4',5	2.754	7.391	0.727	4.558	8.845	0.717
2,3,3',4,4',5'	0.373	0.833	-	0.333	0.550	0.097
2,3,3',4,4',5,5'	0.261	0.479	-	0.345	0.603	0.189

- : ND (Detection limit is 0.02pg/m³)
* : 2',3,4,4',5-P5CB is not separate to 2,3',4,4',5-P5CB

Table 4. TEQs Levels of PCDDs and PCDFs and co-planar and mono-*ortho* PCBsin urban air. (pg-TEQ/m³)

	Summer			Winter		
	Ave.	Max.	Min.	Ave.	Max.	Min.
PCDDs	0.143	0.204	0.093	0.350	0.814	0.040
PCDFs	0.645	1.069	0.333	1.114	2.047	0.221
Co-planar	0.072	0.110	0.025	0.063	0.115	0.026
Mono-*ortho*	0.026	0.044	0.018	0.016	0.021	0.007
Total	0.886	1.427	0.469	1.543	2.990	0.294

Fig.2 TEQ concentrations in urban air.