DEVELOPMENT OF AIR EMISSION FACTORS AND SOURCE INVENTORIES OF HCB AND PCB

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Introduction

Dioxins, HCB and PCB are listed in the Stockholm convention on persistent organic pollutants as unintentionally produced POPs and the convention calls for the understanding of the status of emission and for the implementation of emission reduction measures using BAT/BEP guidelines. In Japan, "law concerning special measures against Dioxins" was enacted in 2001, which has effectively regulated emission of dioxins. Further, a national surveys of HCB and PCB emissions has been conducted since 2001, and the national inventory of these 2 POPs has been published in the national implementation plan, aiming at the improvement in the precision of the inventory. Internationally, very little information is available regarding the emissions of HCB and PCB as compared to Dioxins and additional information is being sought. This paper presents a summary of the on-going research in Japan on the air emission factors used and the results of air emission source inventories of HCB and PCB.

Materials and Methods

Fig. 1 shows the overview of the calculation method of air emission factors and the inventory of atmospheric emission. Priorities for the facility types subject to the present investigation have been given to; 1) Part II source categories in Annex C of the Stockholm Convention, 2) Emission sources for which relatively large amount of emissions have been identified in the register of dioxin emissions[1] that has been developed by a separate national project, and, 3) those emission sources among the Part III source categories in Annex C of Stockholm Convention, which are expected to be widely prevalent in Japan in the future[2].

Measured values were obtained from the following sources; 1) results from the survey by the Ministry of the Environment on the current status of HCB and PCB emissions, 2) results from a survey conducted by the Ministry of Economy, Trade and Industry, 3) Results of voluntary surveys conducted by companies and reported through the Ministry of Economy, Trade and Industry. The number of data collected, as of the end of fiscal year 2007, amounts to a total of 404 individual data on 351 facilities under 27 categories. During the survey on the current status of HCB and PCB emissions, measurement of the data was carried out under normal operation condition. In accordance with Japan Industrial Standards (JIS), the samples were purified and fractionated on a multilayer silica gel column/ alumina column, and the analysis was done using high resolution gas chromatography-mass spectrometry (GC/MS) with a resolution of over 10,000[3]. Values for PCB were assumed to be the sum of the concentrations of all the congener having mono to deca chlorine atoms[4].

Based on the measured values, emission factor was calculated by using the formula shown in Fig. 1. For multiple data for the same facility, mean value of the data was used as the representative value. Additionally, confirmation was also done to see if the sample size was sufficient for calculation and whether any data with exceptionally high or low values were present. The total annual emission for HCB and PCB was calculated as follows;
Total annual emission = Emission factor × National activity rate indicator (1)

Results and discussion:

Emission factors

Table 1 summarizes the emission factors for HCB, PCB, PCDD/F and dlPCB. Emission factor values of HCB are 0.11-79,000 μg/t. Those of PCB are 0.29-92,000 μg/t (with exceptions of certain values with different units).
It should be noted that in Japan according to the stipulations under the "Air Pollution Control Law", emission standards been set for soot/dust (0.04-0.4 g/m^{3}N) and NOx (70-1200 ppm) restricting emissions from most of the facilities surveyed. Further, Dioxins emission standard of 0.1-10 ng-TEQ/m^3 has been set for waste incineration

facilities, steel sintering furnaces, steel-making electric furnaces, secondary manufacturing facilities for zinc and aluminum. The emission factor for PCDD/F and dlPCB for the incineration plants (either municipal or industrial) in Japan is within the values for "Controlled combustion, good APCS：30 μgTEQ/t MSN Burned" and "High technology combustion, sophisticated APCS：0.5 μgTEQ/t MSN Burned" in the PCDD/PCDF Toolkit2005[5], as set out in the PCDD/PCDF Toolkit2005[5]. For manufacturing sectors like the cement production facilities of Japan, the value is similar to the smallest value in the "Dry kilns preheater/ precalciner, T<200℃：0.05 μgTEQ/t of Cement ", as set out in the abovementioned toolkit. Regarding other categories, the values are also similar to cases where some kind of control measures has been applied. Hence, it can be said that the emission factors for HCB and PCB obtained corresponds to the emission factors for facilities in the BAT/BEP guideline where some sort of emission reduction measure has been implemented.

Emission factors of HCB, PCB, PCDD/F and dlPCB for secondary zinc production facilities, rare precious metal recovery facilities and alumina fiber manufacturing facilities are relatively large in all cases. Some categories have relatively large emission factors of HCB or PCB although the emission factor of PCDD/F and dlPCB are comparatively smaller. These include cement kilns, lead primary/secondary smelting facilities, and copper primary smelting facilities. To facilitate measures for HCB/PCB emission reduction, we therefore suggest that efforts should be made to decrease emissions from the categories of facilities with large emission factors and those with a large amount of emissions.

Uncertainty

Sufficient amount of data have been obtained for the categories of cement kilns and metallurgy industries, and it can be said that the accuracy of emission factors for these categories is reliable for application in Japan. However, for municipal solid waste incineration facilities, industrial waste incineration facilities, small-scale incinerators, and sewage sludge incinerators, as the number of these facilities in Japan is quite large, it is highly probably that there is a margin of uncertainly in the data obtained and used to calculated the emission factor. The accuracy of emission factors for specific chemical production facilities including KP boilers used in pulp production and chlorobenzene production plant and roof tile production facilities is considered to be sufficient for the development of air emission inventories in Japan since the total emission from these facilities is small although the number of samples used for calculating the emission factors is little. A few sets of data recorded for sewage sludge incineration facilities and secondary zinc production facilities were significantly larger compared to other data from same or similar facilities.

Release to air

For the year 2006, the total emission of HCB and PCB in Japan was estimated to be 179 kg and 654 kg respectively. We will be continuing to increase the number of measured data and hence increase the accuracy of emission factors in the future too. It is our intention to use the knowledge for proper emission reduction measures.

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Table 1: HCB and PCB emission factor [EF] and uncertainty factor [UF]

	Emission source			Total number of facilities	Number	Activity rate	Unit (#)	HCB [EF] (ug/#)	PCB [EF] (ug/#)	[UF]	PCDD/F and dlPCB [EF] (ug-TEQ/t)
Part II source categories	Waste incinerators	Municipal solid waste incinerator		1,214	25	A	t	380	72	(*1)	1.6
		Industrial waste incinerator		2,112	21	A	t	420	200	(*1)	3.3
		Small-scale incinerator		64,341	4	A	t	810	570	(*4)	14 - 18
		Sewage sludge incinerator		296	8	A	t	21	360	(*5)	
	Cement kilns			56	56	B	t	180	6400	+	0.064
	Metallurgic industries	Iron ore sintering		25	20	C	t	150	430	+	0.27
		Secondary aluminium production	Drying furnace	258	7	D	t	1,700	3,400		2.7
			Roasting furnace		2	E	t	25	99		7.4
			Melting furnace		17	E	t	1800	7200	+	8.5
			Melting furnace using chlorides		3	F	t	1,100	23		0.45
			Scrap metal melting for metal rolling	109	8	G	t	39	130		0.65
		Secondary zinc production		16	15	H	t	42,000	89,000	(*3)	7.1
Part III source categories	Thermal process in metallurgic industry not included in Part II	Lead recovery plant		3	3	I	t	990	92,000	+	0.060
		Electric furnace for steel		91	25		t	2,100	2,600	+	1.7
		Copper primary smelting		6	11	I	t	11,000	96	+	0.43
		Lead primary smelting		2	2	I	t	340	11,000	+	0.38
		Zinc primary smelting		7	10	I	t	1,000	920	+	0.11
		Brass and bronze products production		183	16	G	t	9,400	2,500	+	1.7
	Fosil fuel-fired plant	Fossil fuel power plant		193	10	J	kWh	0.00044	0.0013	+	coal: $7.1\text{^}10^{-6}$ crude/heavy oil: $6.7\text{^}10^{-6}$ LNG: $7.6\text{^}10^{-7}$
	Biomass power plant	Black liquor boiler used in pulp and paper production		15	8	K	t	2.4	19	(*2)	0.006
		Woody biomass power plant and heat utilization plant			6	L	t	310	34	+	2.0
		Bio methane power plant and heat utilization plant			1	M	m^3	0	0.003	(*2)	$1.7\text{^}10^{7}$
	Specific chemical production process	Vinyl chloride monomer production		7	14	G	t	72	8.9	+	0.072
		Caprolactam production plant		4	2	G	t	3.2	8.1	(*2)	0.00035
		Chlorobenzene production plant		2	1	G	t	0.11	0.290	(*2)	$2.8\text{^}10^{-4}$
		Carbon tetrachloride production plant		3	1	G	t	0.46	400	(*2)	19
		Tetrachloroethylene production plant		3	1	G	t	1,800	5.7	(*2)	0.001
	Crematorium			4,899	10	N	Body	150	410	+	2.2 - 4.8
	Copper cable roasting furnace				6	G	t	580	110	+	shaft furnace: 0.85 reverberatory: 0.24 DIP furnace: $5.4\text{^}10^{-4}$
	Vehicle	Diesel engine (light fuel)			1	O	L	0.00091	0.011	(*2)	$3.2\text{^}10^{-5}$
		Gasoline engine (Gasoline)			1	O	L	0.00046	0.014	(*2)	$2.9\text{^}10^{-6}$
Other sources	Roof tile production			301	2	G	Leaf	0.038	0.065	(*2)	$5.5\text{^}10^{-6}$
	Lime production			136	7	G	t	8.2	110	(*1)	0.12
	Cast and forged steel production			1,316	11	P	t	210	2,000	+	0.34
	Rare precious metal recovery production			3	3	I	t	79,000	44,000	+	3.7
	Almina fiber production			4	4	G	t	26,000	29,000	+	9.3
	Aluminum casting			532	10	G	t	300	140	+	reverberatory: 0.13 crucible furnace: 0.31

Regarding PCDD/F and dlPCB, data is obtained from "Register of dioxins emissions[1]". The data used for estimating the emission factors of HCB and PCB are not from same facilities and measurements also have not been carried out during the same time period.
A; Annual incineration amount, B; Annual cement clinker production amount, C; Annual iron ore sinter production amount, D; Annual can scrap treatment amount, E; Annual scrap treatment / melting scrap amount, F; Annual chlorine treatment amount, G; Annual production amount, H; Annual electric furnace dust treatment amount, I; Annual raw material input amount, J; Annual amount of electric generation, K; Annual black liquor treatment amount, L; Annual wood chip utilization amount, M; Annual bio methane generation amount (estimated), N; Annual cremation number, O; Annual amount of vehicle fuel consumption, P; Annual scrap melting input amount.
(See legend on next page)

Table 1: (See previous page)

+ Estimation based on sufficient measured data with no exceptionally large data present
(*1) Insufficient measured data, additional measurements planned
(*2) Sample size is small, but as the total emission amount is not large, it is considered to be of a sufficient accuracy
(*3) Few facilities with above-normal data emission factors possibly included.
(*4) Insufficient measured data, additional measurements planned. Emission factor of PCB is considered to be of a sufficient level of accuracy because of the small value of PCB emission
(*5) Insufficient measured data pending, additional measurements planned. Emission factor of HCB is considered to be of a sufficient degree of accuracy because of the small value of HCB emission. Further, for PCB, data from a facility with a above-normal emission factor is possibly included.

Table 2: POPs release to air（2006, Japan）

Source of emission	Emission		
	HCB (kg/yr)	PCB (kg/yr)	PCDD/F, dlPCB (g-TEQ/yr)
Part II source categories	**86**	**565**	**237-262**
Waste incineration	25	14	192-217
Cement kilns	12	424	4.5
Pulp manufacturing facilities	0	0	0
Metallurgic industries	49	120	41
Secondary copper production	-	-	-
Sinter plants in iron and steel industries	16	45	21
Secondary aluminium production	3.2	11	11
Secondary zinc production	30	64	8.2
Part III source categories	**92**	**95**	**49**
Thermal process in the metallurgical industry not mentioned in Part II	91	94	42
Fossil fuel-fired utility and industrial boilers	0.23	0.69	2.0
Firing fuel-fired utility and industrial boilers	0.2	0.29	0.09
Specific chemical production processes	0.28	0.04	0.28
Crematoria	0.17	0.46	2.5-5.4
Vehicle	0.06	1.2	1.2
Smoldering of copper cables	0.44	0.09	0.6
Other Sources	**1.3**	**5.9**	**4.8-4.9**
Total	179	654	289-317

The numbers in each category have been rounded off and hence their sum does not exactly match the total. All the PCB congeners have been counted.

Figure 1: A flowchart for development of air emission factors and source inventories of HCB and PCB