AIR EMISSION FACTORS AND EMISSION INVENTORY OF HCB, PCB AND PENTACHLOROBENZENE

Yamamoto M[1], Kokeguchi K[1], Yamamoto G[1], Yamaguchi N[2], Ohtsuka K[2], Sakai S[3]

[1]Ministry of the Environment, Kasumigaseki, Tokyo, Japan; [2]EX Research Institute Ltd, 2-17-22 Takada, Toshima-ku, Tokyo 171-0033, Japan; [3]Kyoto University, Environment Preservation Research Center, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Introduction

Stockholm convention, which was adopted in 2001 and came into force in May 2005, aims to reduce the emission and eliminate the usage of Persistent Organic Pollutants (POPs) through a legally binding international framework. Unintentionally produced POPs in the convention include PCDD, PCDF, HCB and PCB (included when the convention came into force), and Pentacholorobenzene (added in August 2010). Understanding the state of emission of these unintentionally produced POPs and measures to counter emission through the implementation of BAT/BEP guidelines is desired.

The situation of the understanding of the state of emission of PCDD/F from 61 countries, PCBs from 30 countries and HCB from 33 countries has been made public in the homepage of the secretariat of Stockholm Convention[1]. There are a lot of countries which have not determined their amount of HCB and PCB emission. In 2008, Emission from European community (EC), United Kingdom of Great Britain and Northern Ireland (UK) and Japan are comparatively larger than amounts disclosed by other countries.

Emission factor of Japan has been calculated using data obtained from actual measurement. Air emission factors for HCB and PCB has already been reported in 2008[2] and 2009[3]. This paper reports the air emission factor of PeCB and revisions of the air emission factors of HCB and PCB caused due to existence of facilities which have changed their equipments, raw materials or operation methods hence impacting the emission factors.

Materials and methods

The sources where revisions of emission factors have been carried out include Municipal solid waste incineration, Cement kilns, Secondary zinc production and Electric furnace for steel production. The data and outline of the facilities where actual measurement was carried out is summarized in table 2. As the number of facilities categorized as “Municipal solid waste incineration” and “Electric furnace for steel production” is very large in Japan, facilities from 30 locations in Japan were randomly selected. There are also instances where multiple measurements have been carried out from the same facility.

For the actual measurement, sampling was carried out during normal operation of the facilities. In accordance with Japan Industrial Standards (JIS), samples were purified and fractionated on a multilayer silica gel column / alumina column and analyzed by high-resolution gas chromatography-mass spectrometry (HRGC/HRMS) with a resolution of over 10,000. Values for PCBs were taken as the sum of the concentrations of all congeners having one to ten chlorine atoms.

Air emission factors were calculated from the following equations:

$$K_{HCB_i}=\frac{\sum C_{HCB_i}\times E_i}{A_i} \quad \cdots\cdots (1)$$

$$K_{PCB_i}=\frac{\sum C_{PCB_i}\times E_i}{A_i} \quad \cdots\cdots (2)$$

C; Concentration, A; Activity rate, E; Gas emission, K; Emission factor

“C; Concentration” represents the actual measured values, uncorrected for oxygen concentration.

The total annual emissions for HCB and PCBs were calculated as follows:

Total annual emissions = Emission factor × National activity rate indicator・・・・・(3)

Results and discussion:

Municipal solid waste incinerations

As compared to previous reporting, data from two facilities that closed down were deleted while actual measurement data of 2 stoker furnaces (the most common type of furnace in Japan) were added to ensure that the distribution of furnaces in the sample represented the actual national distribution. Further, additional measurements were carried out at 4 facilities that had managed to reduce POPs emission through measures like optimization of CO concentration, combustion temperature, supplementary fuel amount or method of blowing activated carbon. Old data for HCB and PCB were replaced by the new data hence obtained. As a result, the emission factor for HCB was estimated as 140µg/t-MSW as compared to the previously reported value of 380µg/t-MSW. The emission factor for PeCB is 400µg/t but it should be noted that the number of samples is limited. The emission factor of PCDD/F for Municipal solid waste incinerations is similar to the reported values in CORINAIR[4], NAEI[5] and the Toolkit[6]. The emission factor of HCB and PCB is smaller than that of NAEI by a single order of magnitude.

Cement kilns

In Japan, from the viewpoint of effective usage of waste and by-products, the amount of intake in cement kilns is increasing year by year and hence maintaining the stable operation of the plant (CO concentration of the furnace, oxygen concentration and management of combustion temperature) has become an important issue. Hence, additional measurements were carried out at 10 facilities and using the latest data, the emission factors for total HCB and PCB were revised. As a result, the emission factor of PCB increased slightly to 7,400µg/t from the previously reported value of 6,400µg/ton. The data for PCB is the summation of data for concentrations of all congeners having one to ten chlorine atoms and it is estimated that congeners with mono or di-chlorine atoms account for about 90% of total emission of PCB from cement kilns. The emission factor for PeCB is 1,200 µg/ton but it should be noted that the number of actual measurement data is limited.

Cement kilns in Japan use dry furnaces with suspension pre-heaters or new-suspension pre-heaters and in majority of cases EPs are used for the treatment of flue gas. Further, the amount of waste and by products used as alternative feedstock, thermal energy, or admixture as a national average equals 451kg/ton(cement production) in fiscal year 2009[7]. Comparisons for HCB and PCB of cement kilns cannot be made, but for PCDD/F, the emission factor for Japan is 0.053µg-TEQ/ton, which is comparable with the Toolkit value of 0.05 – 0.6µg-TEQ/ton.

Secondary zinc production

After the previous reporting, a single facility has been closed down, and flue gas treatment facilities or raw material management systems have changed in a lot of other facilities. Hence additional measurements were done and the old data were replaced by new ones. As a result, emission factor for HCB changed from 42,000µg//ton (electric furnace dust treatment amount) to 8700µg/ton, the emission factor for PCB changed from 89,000µg/ton to 81,000µg/ton, showing a decrease in values from previous reporting. The emission factor for PeCB was estimated as 13,000µg/ton. The majority of facilities where measurements were carried out this time were using electric furnace dust as raw material to produce zinc oxide using reduction volatility method. Comparison of emission factor of HCB in secondary zinc production cannot be made, but the emission factor of PCB is larger than that of CORINAIR by a single order magnitude and the emission factor of PCDD/F is smaller by a single order magnitude than that of CORINAIR and the Toolkit.

Electric furnace for steel production

After the previous reporting, actual measurement data from 5 facilities were added. Data from 5 other facilities which had installed gas coolers were also measured and the emission factor was recalculated using 36 data from 29 facilities. As a result, the emission factor of HCB changed from 2,100µg /ton to 1,900µg /ton, that of PCB from 2,600µg/ton to 2,900µg /ton.

Emission factor of PeCB is 1,200µg/ton, but it needs to be noted that the number of samples of measured data is very low. The emission factor of PCB and PCDD/F in Japan is of a similar level to that of CORINAIR and NAEI.

Total emission

In Japan the first estimation of emission amount of HCB and PCB was carried out in 2002. Since that period to 2009, revisions were made on emission factors for waste incineration and ferrous and non ferrous metal

productions due to installation of new facilities and promotion of emission reduction measures. The activity amount also changed and hence the total emission of HCB was estimated as 110kg/year in 2009 as compared to 190kg/year in 2002. Emission amount of PCB was estimated as 560kg/year in 2009, which is the same amount estimated for 2002.
The emission factors of four sources were revised in this report. However, it can be concluded that emission reduction measures have been implemented for other sources too. Further, the majority of data being used are old data collected during 2001, 2002. Hence, it is being planned to carry out further measurements and make appropriate revisions of the emission factors and continue the discussion on the changes of emission amounts.

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Table 1 POPs release to Air (Japan)

Source of emission	2002 (kg/year : HCB, PeCB, PCB, g-TEQ/year : PCDD/F & dl-PCB)				2009 (kg/year : HCB, PeCB, PCB, g-TEQ/year : PCDD/F & dl-PCB)			
	HCB	PeCB	PCB	PCDD/F, dl-PCB	HCB	PeCB	PCB	PCDD/F, dl-PCB
Waste incineration	43	NE	15	759	18	14	18	103
Ferrous and non-ferrous metal production	130	NE	190	183	79	7	170	49.9
Heat and power generation	0.6	NE	1.1	1.86	0.44	NE	0.9	1.18
Production of mineral products	11	NE	350	1.81	10	61	370	1.66
Transportation	NE	NE	NE	1.4	0.053	NE	1.1	1.0
Production of chemicals and comsumer goods	0.24	NE	0.03	1.07	0.26	NE	0.03	0.46
Miscellaneous	0.19	NE	0.53	3.85	0.19	NE	045	2.06
Waste dispowal	NO	NO	NO	NO	NO	NO	NO	NO
Open burning processes	NO	NO	NO	NO	NO	NO	NO	NO
Total	190	NE	560	986	110	110	560	193

NO: Not Occurring, NE: Not Estimated
The numbers in each category have been rounded off, so their sum does not exactly match the total. All PCB congeners have been counted, The PCDD/F and dl-PCB data is taken from The Register of Dioxins Emissions. The data used for estimating the emission factors of HCB and PCBs are not from the same facilities, and the measurements were not taken during the same time period.

Table2 Comparison of Emission Factors

	Chemicals	Emission Factor								Reported data (Japan, 2009)						
		Unit	Japan		CORINAIR	NAEI	Toolkit	Note		Facility Type	Capacity	Air pollution control system (number)	data	Concentration (ng, ng-TEQ/m³N)		
			Previous report	This report	2009	2008	2005							Max	Mid	Min
(1) Municipal solid waste incinerators	HCB	µg/t-*2	380	140	0.2~60*7	2000	-	*8		Rotary kiln, fluidized bed furnace, Stoker gasification melting furnace	0.002 ~ 0.079 Mt/a	FF (22) ESP (4)	26	570	9.4	ND
	PeCB	µg/t-*2	-	400	-	-	-						4	160	41	2.9
	PCB	µg/t-*2	72	63	0.53~160*7	506	-						26	280	3.6	ND
	PCDD/F*1	µg-TEQ/t-*2	1.6	1.0	0.35~110*6	1.1	0.5~30						26	3.0	0.023	ND
(2) Cement kilns	HCB	µg/t-*3	180	190	NE	-	-	*9		Dry type rotary kiln	0.62 ~ 2.8 Mt/a	FF (1) ESP (55)	70	1600	10	ND
	PeCB	µg/t-*3	-	1200	-	-	-						7	1600	100	2
	PCB	µg/t-*3	6400	7400	NA	-	-						70	35000	970	7.1
	PCDD/F*1	µg-TEQ/t-*3	0.064	0.053	NE	-	0.05~0.6						70	0.13	0.0040	ND
(3) Secondary zinc production	HCB	µg/t-*4	42000	8700	-	-	-	*10		Rotary kiln, Electric furnace	0003 ~ 0.16 Mt/a	FF (8) FF and activated carbon (7) wet ESP (6) unknown (2)	17	10000	140	0.96
	PeCB	µg/t-*4	-	13000	-	-	-						9	16000	760	5.6
	PCB	µg/t-*4	89000	81000	3100	-	-						17	31000	400	4.1
	PCDD/F*1	µg-TEQ/t-*4	8.5	3.9	100	-	5~100						17	5.7	0.72	0.000026
(4) Electric furnace for steel production	HCB	µg/t-*5	2100	1900	-	NA	-	*11		Electric furnace	0.23 ~ 1.1 Mt/a	FF (29)	36	1100	89	3.2
	PeCB	µg/t-*5	-	1200	-	-	-						5	710	150	23
	PCB	µg/t-*5	2600	2900	1900~3600	4700	-						36	3800	320	ND
	PCDD/F*1	µg-TEQ/t-*5	1.7	0.97	0.8~2	1.3	0.1~10						36	1.5	0.037	ND

ND= 0.6 (ng-HCB/m³), 0.6 (ng-PeCB/m³), 0.0006~0.4(ng-PCB/m³), 0.0003~0.002(ng-PCDD/F/m³)

*1: PCDD/F and dl-PCBs (Japan). Reported data were obtained during actual measurement of HCB, PeCB, and PCB.

*2: Municipal solid waste

*3: Cement clinker production (Japan), cement (CORINAIR 2009 and Toolkit 2005)

*4: Electric Furnace dust treatment (Japan), Zinc production (CORINAIR 2009 and Toolkit 2005)

*5: Iron and steel production (Japan, CORINAIR 2009, NAEI), liquid steel (Toolkit 2005)

*6: EF=(1-Abetment efficiencies default value)×EF technology, unabated. Abetment efficiencies=97%～99.99%

*7: As the abatement efficiencies of HCB, PCB was not written, it is assumed to be the same value as that of PCDD/F.

*8: Controlled combustion; good APC system, or High technology combustion; sophisticated APC system

*9: 0.6 = Rotary kilns ESP/FF, T<200℃, 0.05 = Dry kilns pre-heater/pre-calciner T<200℃ (Toolkit 2005)

*10: 100 = Hot briquetting/rotary furnaces, basic dust control; e.g. FF, ESP, 5 = comprehensive pollution controls, e.g. FF with active carbon/DeDiox technology (Toolkit 2005)

*11: 0.1 = Clean scrap, virgin iron, EAF designed for low PCDD/PCDF emission, 3 = Clean scrap, virgin iron, afterburner and FF, 10 = Dirty scrap (cutting oils, general contamination), scrap preheating, limited controls (Toolkit 2005)