SOURCE INVENTORIES OF HCB AND PCB AND UNCERTAINTY OF THEIR AIR EMISSION FACTORS

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Abstract

Air emission factors of hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) were analyzed and the total emissions of HCB and PCBs were estimated in Japan compared with other documented values. The emission factors of sintering furnaces in the iron and steel industry are comparable to other reported values. We have identified cement kilns and the secondary metals production as emission sources with relatively large emission factors. The emission of HCB and PCBs in Japan in 2006 is estimated to be 179 and 654 kg, respectively.

Introduction

Dioxins, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) are listed in the Stockholm Convention on Persistent Organic Pollutants as unintentionally produced POPs, and the Convention calls for an understanding of the status of their emission and the implementation of emission reduction measures based on Best Available Techniques / Best Environmental Practices (BAT/BEP) guidelines. In Japan, the Law Concerning Special Measures Against Dioxins was enacted in 2001, and it has led to effective regulation of dioxin emissions. Furthermore, national surveys of HCB and PCB emissions have been conducted since 2001, and the national inventory of these two classes of POPs has been published in the National Implementation Plan. Compared to dioxins, very little information is available internationally regarding the emissions of HCB and PCBs. Here, we analyze the values of air emission factors of HCB and PCBs presented in 2008, compare them with other documented values, and estimate the total emissions of HCB and PCBs in Japan.

Materials and Methods

The method of estimating air emission factors and the inventory of air emissions have already been presented[1]. Measured values were obtained from the following sources: 1) a survey by the Ministry of the Environment, Japan, on the current status of HCB and PCB emissions, 2) a survey by the Ministry of Economy, Trade and Industry, Japan, and 3) voluntary surveys by companies and reported through the Ministry of Economy, Trade and Industry. As of the end of fiscal year 2007, the data collected amounted to a total of 405 measurements at 352 facilities under 27 categories. During the survey on the current status of HCB and PCB emissions, measurements were carried out under normal operating conditions. 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 (GC/MS) 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[2]. Air emission factors were calculated from the following equations:

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

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

where K is the emission factor, C is concentration, A is activity rate, and E is gas emission. The concentrations represent the actual measured values, uncorrected for oxygen. When multiple measurements were obtained from the same facility, the mean value was used. 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

Comparison of Emission Factors

The emission factors of major emitters of HCB and PCBs in Japan were compared with the corresponding values for HCB and PCBs reported in the UNEP Standardized Toolkit[3] and the values for HCB, PCBs and polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) reported in the Core Inventory of Air Emission in Europe (CORINAIR) 2007 (Table 1). CORINAIR[4] has compiled data presented to the National Experts in the National Reference Centers by various countries, and it also includes information on the sources of the data.

a. Waste Incinerators

The emission factor of PCDD/F and dioxin-like PCBs (dl-PCBs) for the incineration of municipal solid waste (MSW) in Japan is 1.6 µg-TEQ/t of incinerated waste, a value that lies between those of 0.5 µg-TEQ/t-MSW (high-technology combustion, sophisticated APCS) and 30 µg-TEQ/t-MSW (controlled combustion, good APCS) reported in the UNEP Toolkit[3]. The emission factor of PCDD/F presented in CORINAIR 2007[4] is comparable to the value of 0.5 µg-TEQ/t-MSW (high-technology combustion, sophisticated APCS). The emission factor for PCBs is based on a survey of facilities equipped with one or two step cleaning (alkaline venturi washer, injection of lime and bag filter). For these facilities, although the method of flue gas treatment is similar to that used in Japan, the emission factor is two orders of magnitude larger. Although the details of the incinerators and the material incinerated are not available, the emission factor of HCB in CORINAIR 2007 is comparable to that found for Japan. The emission factors of HCB and PCBs for waste incinerators in Japan were estimated by using measurements from 25 facilities, though these represent only a small fraction of the total number of facilities in Japan.

b. Cement kilns

The emission factor for dioxins in Japan is 0.064 μg-TEQ/t-cement clinker produced, which is comparable with the Toolkit value of 0.05 – 0.6 μg-TEQ/t-cement (wet kilns, electrostatic precipitator / fabric filter (ESP/FF) T<200℃; dry kilns and preheater/precalciner kilns, T<200℃). Although the type of incinerator and flue gas treatment facility used for calculating the emission factor for PCDD/F in CORINAIR 2007 are not stated, the value is similar to the values of Japan and Toolkit.

The emission factors of PCBs and HCB presented in CORINAIR 2007 is three order and an order of magnitude smaller than that found for Japan. A representative example of congener distribution for cement kilns is shown in Figure 1. Of 56 facilities targeted for direct measurement in Japan, 54 showed a congener distribution similar to that of Figure 1, from which it can be estimated that about 90% of PCBs emitted from cement kilns in Japan are mono- or di-chlorinated. In principle, the total PCB concentration is calculated by summing the concentrations of all homologues. However, there is also a method of representing total PCBs by summing seven indicator congeners with 3 to 7 chlorine atoms known as the Dutch 7 (PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, and PCB-180). The total concentration for the facility in Figure 1 ranges from 49 ng/m^3N (∑Dutch 7 + TeCB-68) to 4900 ng/m^3N (total of 209 congeners). (During GC/MS, the mass spectra of TeCB-68 overlapped that of TeCB-52, so the sum of TeCB-52 and TeCB-58 was used. The value of 49 ng/m^3N is therefore the sum of the concentrations of eight isomers, the Dutch 7 + TeCB-68.)

Cement kilns in Japan are normally rotary kilns with suspension preheaters or so-called new suspension preheaters installed, and the dust collected mainly by the electric dust collector is reused as part of the feedstock. Industrial bodies in Japan have compared the mass balance of PCBs and PCDD/F/dl-PCBs by using data from operating kilns and report that PCBs are formed at around 600℃ at the preheater and, although they break down near the top cyclone, reformation is seen at the ESP, as well as the feed process, at around 100℃[5]. Furthermore, regarding the difference in the emission behavior of PCBs and PCDD/F/dl-PCBs from the ESP, they conclude that in the ESP temperature range, because adsorption to dust due to the vapor pressure is lower for PCBs with lower numbers of chlorine atoms, PCBs can be emitted to the atmosphere more easily than PCDD/F/dl-PCBs. In addition to the operational control and management of dust at the ESP outlet, it was reported that the management and reduction of chlorine concentrations by means of a chlorine bypass system helps reduce PCB formation and that the direct input of ESP/BF dust into the kiln helps reduce the circulation of PCBs in the dust.

c. Sintering Furnaces in the Iron and Steel Industry

The emission factor for dioxins in Japan is 0.27 µg-TEQ/t-sinter produced, which is comparable to the value of 0.3 – 5 µg-TEQ/t-sinter produced (high technology emission reduction) reported in the Toolkit. In most facilities in Japan, flue gas is treated with an electric dust collector. The emission factor of 15 µg-TEQ/t-sinter produced given in CORINAIR 2007 is similar to the Toolkit value of 20 µg-TEQ/t-sinter produced (high waste recycling oil contaminated materials) and is two orders of magnitude greater than the emission factor of PCDD/F/dl-PCBs for Japan. The emission factor of HCB is one order of magnitude lower than that found for Japan, but that of PCBs is similar. The emission factors of HCB and PCBs presented here are estimated from direct measurements from 20 of a total of 25 facilities in Japan, and we believe that the measurements are precise enough to represent the air emission factor in Japan.

d. Other emission sources

Apart from the three major emission sources discussed above, we are now carrying out a detailed comparative analysis of the secondary production of aluminum (melting furnace) and zinc, as well as electric furnaces for steel production. For other emission sources such as biomass fuel combustion facilities, chemical manufacturing facilities, and automobiles, there are not enough direct measurements, but the total emissions are comparatively small, so that the value of the emission factor for the sources we have described[1] is sufficiently accurate to estimate the inventory of atmospheric emissions in Japan.

Release to air

The emission of HCB and PCBs in Japan in 2006 is estimated to be 179 and 654 kg, respectively (Table 2). In this project, we have identified cement kilns and the secondary metals production as emission sources with relatively large emission factors. We intend to continue collecting measurements for these emission sources, to analyze the emission behavior of HCB and PCBs, and to use the results to identify effective control measures for these chemicals.

Acknowledgments

This work was financially supported by the Ministry of the Environment, Japan, through the Unintentionally Produced POP Emission Control Measures Project. We gratefully acknowledge the members of the advisory committee of this project, namely, Drs. Yasuyuki Shibata, Kiyoshi Tanabe, Takeshi Nakano, and Shigeki Masunaga for their input. We also express our appreciation to the Ministry of Economy, Trade and Industry, Japan, and the private companies that provided data for the surveys.

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Table 1 Comparison of Emission Factors

	Chemicals	Units	Emission factor				Notes
			Japan (this study)	CORINAIR 2007	CORINAIR *2	Toolkit 2005	
(1) Waste incineration (municipal solid waste incinerator)	HCB	µg/t-MSW	380	—	100-10000	—	Good combustion with good abatement system
	PCB	µg/t-MSW	72	6300	—	—	
	PCDD/F *1	µg-TEQ/t-MSW	1.6	0.5	—	0.5 -30	
(2) Cement kilns	HCB	µg/t-*3	180	—	11	—	Well controlled plant, ESP
	PCB	µg/t-*3	6400	—	1	—	
	PCDD/F *1	µg-TEQ/t-*3	0.064	—	<0.2-1	0.05-0.6	
(3) Iron ore sintering	HCB	µg/t-sinter produced	150	—	32	-	Well controlled plant
	PCB	µg/t-sinter produced	430	—	200	-	
	PCDD/F *1	µg-TEQ/t-sinter produced	0.27	—	15	0.3-5 20*4	
(4) Secondary aluminum production (melting furnace)	HCB	µg/t-*5	1800	5,000,000 *6	-	-	Well controlled plant
	PCB	µg/t-*5	7200	—	-	-	
	PCDD/F *1	µg-TEQ/t-*5	8.5	- *7	-	0.3-5	
(5) Secondary zinc production	HCB	µg/t-*8	42000	-	-	-	Well controlled plants
	PCB	µg/t-*8	89000*9	-	-	-	
	PCDD/F *1	µg-TEQ/t-*8	7.1	63.1-379	-	5-100	
(6) Electric furnace for steel production	HCB	µg/t-*10	2100	-	-	-	Well controlled plants
	PCB	µg/t-*10	2600	-	3600	-	
	PCDD/F *1	µg-TEQ/t-*10	1.7	-	0.15-1.8	0.1-10	

*1: PCDD/F and dl-PCBs (Japan) , *2: Abatement type and plant type are not specified, *3: Cement clinker production (Japan), cement (CORINAIR 2007 and Toolkit 2005), *4: High waste recycling including oil contaminated materials, *5: melting scrap (Japan), Aluminum (CORINAIR 2007 and Toolkit 2005, *6: use of hexachloroethane, *7: 0.01-13.7 ng-TEQ/m^3, *8: Electric Furnace dust treatment (Japan), Zinc production (CORINAIR 2007 and Toolkit 2005), *9: A few facilities with above-normal data emission factors are possibly included, *10: Iron and steel production (Japan, CORINAIR 2007), liquid steel (Toolkit 2005).

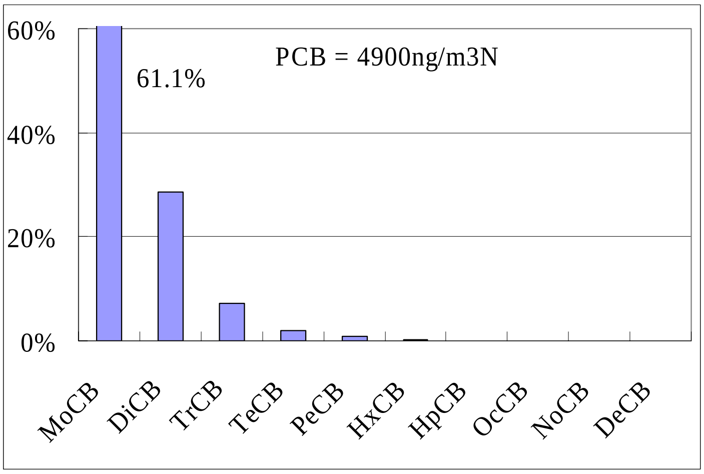

Figure 1 Typical Homologue Pattern of Cement Production Facility

Table 2 POP Release to Air (2006, Japan)

Source of emission	Emission		
	HCB (kg/year)	PCB (kg/year)	PCDD/F, dl-PCB (g-TEQ/year)
Part 2 Source categories	**85**	**553**	**238-262**
Waste incineration	24	9.1	192-217
Cement kilns	12	424	4.5
Pulp manufacturing facilities	0	0	0
Metallurgic Industries	49	120	42
Secondary copper production	—	—	-
Sinter plants in the iron and steel industry	16	45	21
Secondary aluminum production	3.2	11	12.5
Secondary zinc production	30	64	8.2
Part 3 Source categories	**92**	**96**	**49**
Thermal process in the metallurgical industry not mentioned in part 2	91	94	42
Fossil fuel-fired utility and industrial boilers	0.23	0.69	2.0
Firing fuel-fired utility and industrial boilers	0.22	0.29	0.09
Specific chemical production processes	0.28	0.04	0.28
Crematoria	0.17	0.46	2.5-5.4
Vehicles	0.06	1.2	1.2
Smoldering of copper cables	0.44	0.09	0.6
Other sources	**1.3**	**4.7**	**3.7-3.8**
Total	179	654	289-317

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.