# IDENTIFICATION OF PCB CONGENERS BY UNINTENTIONAL FORMATION

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**Introduction**

PCBs are persistent in the environment and show a common property of long-range transport. The two main sources of PCBs are: Commercial production such as technical grade (Arochlor, Kanechlor, Clophen etc.) and by-product in combustion processes during the incineration of industrial and municipal waste as thermodynamically stable compounds. Technical PCBs are produced by chlorination of biphenyl that have been used extensively since 1930 in a variety of industrial uses, including as dielectrics in transformers and large capacitors, as heat exchange fluids, as paint additives, in carbonless copy paper and in plastics. Further environmental contamination may occur from the disposal of old electrical equipment containing PCBs.
The total amount produced world-wide is estimated at 1.5 million tons.
On the other hand, there are a number of industrial processes in the organic pigment, pesticide, chemical and aluminum refining industries that inadvertently produce PCB-laden materials. PCB can be produced when chlorine, hydrocarbon and elevated temperatures (or catalysts) are present together.
Unintentional formation of PCB from chemical manufacturing process[1,2)] such as organic pigment have been known since 2000[3)]. Recently since the fact which some organic pigment contained PCB unintentionally formed in the manufacturing process was reported by industrial association, the Ministry of Economy, Trade and Industry Japan stopped manufacture, import, and trade the organic pigment that an international standard was exceeded by administrative guidance, and is much concerned about PCB level in organic pigment[4)].
POPs monitoring including PCBs have been conducted since 2002 using GC-HRMS with high sensitive analysis in air, sediment, water and biological matrices by Ministry of the Environment, Japan (MOEJ)[5)]. Additional PCBs survey in unintentional formation also conducted in combustion processes[6)] and organic pigment[1)].
PCBs volatilize from water or solid surfaces in spite of their low vapour pressure, and partly as a result of their hydrophobicity; atmospheric transport may therefore be a significant pathway for the distribution of PCBs in the environment.
This report summarized the identification of PCB congeners by unintentional formation such as combustion processes and organic pigment, and finally evaluated PCB congeners in ambient air monitoring data.

**Materials and methods**

Ambient air sampling and analytical methods for the POPs monitoring are designed carefully to assure the quality of the data as well having high sensitivity to cope with probable further decreases in environmental levels of POPs during long-term monitoring by MOEJ.
Following 21 chemicals (groups), out of 23 POP chemicals, with the exception of dioxins and furans, the analytical methods were established and evaluated as POPs monitoring techniques in ambient air at several site of Japan. Data on their short-term spatial variations will contribute to a clarification and understanding of environmental transport and background levels in ambient air.
Sampling; 3 days continuous sampling or 1 week sampling by high volume air ampler 1,000 $m^3$ under 700 L/min, 24hrs or 100 L/min, 1 weeks using quarts fiber filter, Poly urethane foam (PUF) and active carbon fiber felt (ACF).
Fortified $^{13}C$ surrogate $^{13}C_{12}$- PCBs mix $^{13}C$-POPs mix and $^{13}C$-New POPs Mix before sampling.
Method validation are evaluated under POPs monitoring project by MOEJ.
GC-HRMS: Autospec-Ultima (Waters/Micromass), MS resolution > 10,000 (10% Valley), HT8-PCB (SGE) GC column for all congener specific analysis of PCBs, DB-17HT column used for 24 POPs with 13grouping.
All congener specific PCB data using GC-HRMS were evaluated in detail by our laboratory.

**Results and discussion**

Fig. 1 shows typical PentaCBs chromatograms of technical PCB (KC-300) and incineration sample by GC-HRMS. PCB congeners pattern from thermal processes seems completely different from technical PCBs. PCBs without ortho chlorine substitution, coplanar (Dioxin-like) PCBs are predominant in thermal processes sample. Fig.2 shows PCBs homologue profile in thermal processes exhaust gas such as cement kiln, steel sintering furnace, secondary production of zinc and waste incineration with the comparison of ambient air sample. Generally thermal process sample are predominant monoCBs especially for cement kiln sample. On the other hand ambient air PCB homologue profile indicates predominant triCBs > tetraCBs, DiCBs. But the homologue profile shift to lower chlorination patter in winter season.

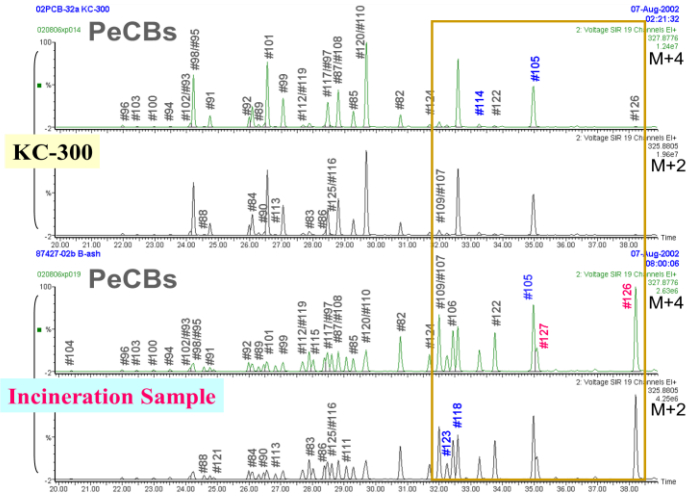


Fig.1 typical PentaCBs chromatograms of technical PCB (KC-300) and incineration sample by GC-HRMS.

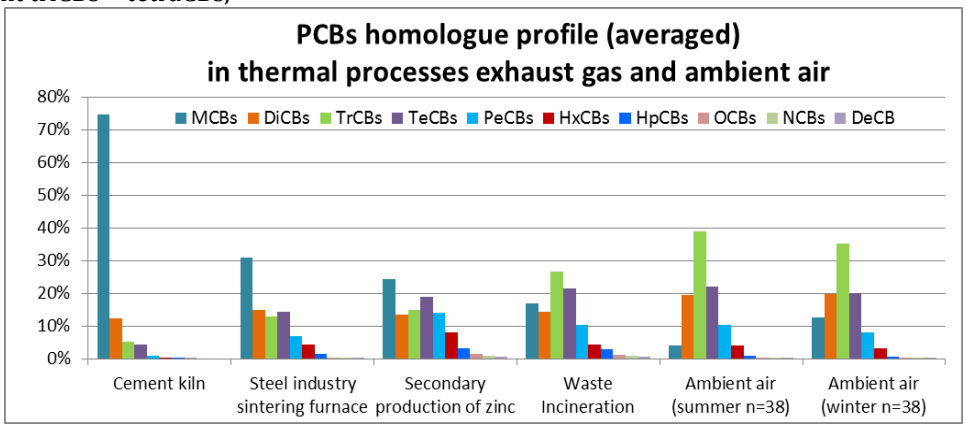


Fig. 2 PCBs homologue profile (averaged) in thermal processes and ambient air.

PCBs have been reported in ambient air at all 35 site of Japan with the concentrations 27 to 840 (averaged 130) pg/m$^3$ in warm season, tr(16) to 280 (averaged 54) pg/m$^3$ in cold season in 2013[5]. These indicated lower levels at cold season and reported relatively higher levels in industrialized areas.

Fig. 3 shows PCB congeners profile in ambient air, technical PCB and thermal processes (fly ash and cement kiln exhaust gas). These data indicates that PCB congeners profiles in ambient air samples are stable both in summer and winter season although homologue profiles shift to lower chlorination. Additionally PCB congeners profile in ambient air samples are relatively similar to technical PCBs for triCBs, tetraCBs(data not shown), on the other hand monoCBs and DiCBs are basically different to technical PCBs. Especially 3,3'-dichlorobiphenyl (#11) is most predominant DiCBs congener in ambient air sample although minor congeners in technical PCB and thermal processes, which might be suggest the another source such as organic pigment. DiCB(#11) is one of the highest PCB (>1000 ppm) impurities detected in the dichlorobenzidine type PY12 in Japan as well as imported organic pigment[4]. MonoCBs profile in ambient air seems partly similar profile to thermal processes. Fig. 4 shows averaged PCB congeners (mono, di, tri and tetraCBs) level in ambient air. DiCB(#11) is one of the highest PCB congener and shows same trends in all 35 site of Japan since 2002.

Table 1 summarizes predominant PCB congeners in ambient air, technical PCB, thermal processes and organic pigment investigated these data.

In the atmosphere, the vapor-phase reaction of PCBs with hydroxyl radicals (which are photo chemically formed by sunlight) may be the dominant transformation process. The degradation of PCBs in the environment depends largely on the degree of chlorination of the biphenyl, with persistence increasing as the degree of chlorination

increases. Half-lives for PCBs undergoing photodegradation range from approximately 10 days for a monoCBs to 1.5 years for a heptaCBs. The persistence of PCBs, combined with the high partition coefficients of various isomers (log KOW ranging from 4.3 to 8.26), vapor pressure, Henry's constant and physicochemical stability in the atmosphere provide the necessary conditions for PCBs to bioaccumulate in organisms.
Further investigation recommended for the identification of PCB congeners from various sources with atmospheric transport in the environment.

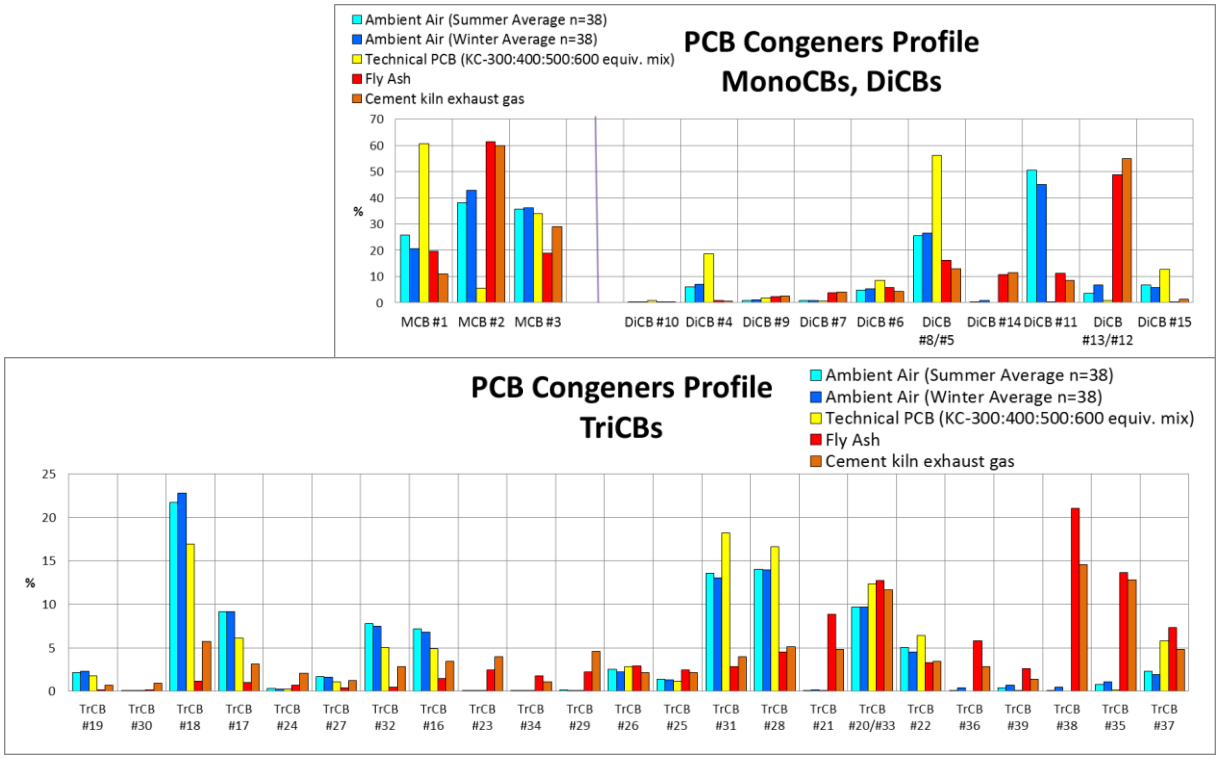

Fig.3 PCB congeners profile (mono, di and triCBs) in ambient air, technical PCB and thermal processes.

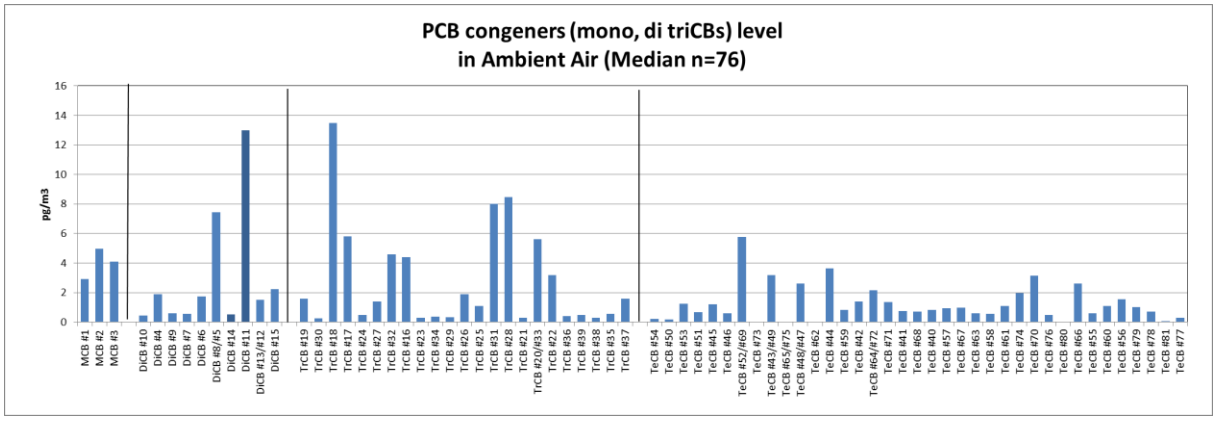

Fig4 PCB congeners (mono, di, tri and tetraCBs) level in ambient air.

Table1 Predpminant PCB congeners in ambient air, technical PCB, thermal processes and organic pigment.

| | Ambient Air | Technical PCBs 9) | Thermal processes 7,8) | Organic Pigment |
|---|---|---|---|---|
| **MCBs** | **#2 #3 > #1** | **#1 (2-), #3 (4-)** | **#2 (3-), #3 (4-)** | **#3 (PY12 dichlorobenzidine)** |
| **DiCBs** | **#11 > #8/5 >> #4, #6, #13/12, #15** | **#8 (24'-)/ #5 (23-), #4 (22'-), #15 (44'-)** | **#12 (33'-)/ #13 (34'-), #14 (35-), #11 (33'-), #15 (44'-)** | **#11 (PY12 dichlorobenzidine) #9 (PR2 dichloroaniline) #5 (PV23 dioxazine)** |
| **TriCBs** | **#18 > #31, #28 > #20/33, #17, #32, #16 > #22** | **#31 (24'5-), #28-(244'), #18-(22'5), #33 (2'34-) #37-(344')** | **#38 (345-), #35 (33'4-), #20 (233'-)/#33 (2'34-), #21 (234-), #37 (344'-)** | **#31 (PR2 dichloroaniline, PY81 tetrachlorobenzidine) #35(PY12 dichlorobenzidine)** |
| **TeCBs** | **#52 > #44, #70 > #66, #43/49, #48/47,** | **#52 (22'55'-) #44 (22'35'-) #70 (23'4'5-) #66 (23'44'-)** | **#77 (33'44'-) #78 (33'45-) #79 (33'45'-) #81 (344'5-)** | **#52 (PR2etc dichloroaniline, PY81 tetrachlorobenzidine) #77(PY12 dichlorobenzidine)** |
| **PeCBs** | **#98/#95, #101 > #110/120 > #99, #87/115** | **#95 (23'35'6-) #101 (22'455'-) #110 (233'4'6-) #118 (23'44'5-) #105 (233'44'-)** | **#126 (33'44'5-) #105 (233'44'-) #127 (33'455'-) #118 (23'44'5-) #107 (233'4'5-) #108 (233'45'-) #114 (2344'5-) #122 (2'33'45-)** | **#101, #118 (PR112 trichloroaniline)** |
| **HxCBs** | **#149/139 > #153 > #138, #136 > #154, #131, #133** | **#149 (22'344'55'-) #138 (22'344'5'-) #153 (22'34'55'6-)** | **#169 (33'44'55'-) #156 (233'44'5-) #157 (233'44'5'-) #167 (23'44'55'-) #129 (22'3345-)** | **2,2',3,4',5,5'-(#146), #153, #149 (PR-112 trichloroaniline)** |
| **HpCBs** | **#182/187, #180, #179, #174, #190** | **#180, 170, 187 174** | **#189, #170, #172** | - |
| **OCBs** | **#199, #203, #194** | **#194, #199 > #203, #196** | **#194 > #195, #196, #205** | - |
| **NCB DeCB** | **#206** | **#206** | **#206** | **#209, 206 (PG7 phthalocyanine)** |

**Acknowledgements**
These POPs monitoring are organized by Ministry of the Environment, Japan.

**References:**

1. Anezaki, K, Takahashi, G, Tawara, K, Nakano, T (2012): Organohalogen Compounds. 74: 1433-1436.
2. Takasuga T, Nakano T, Shibata Y.(2012); Organohalogen Compounds. 74: 1437–1440
3. Litten S.(2000); Organohalogen Compounds. 46: 369-372
4. http://www.meti.go.jp/english/press/2013/0510_02.html Compiled Results of Reanalysis of the Presence of Polychlorinated Biphenyls (PCBs) as By-products in Organic Pigmentsoint. Joint Press Release with the Ministry of Health, Labour and Welfare and the Ministry of the Environment, May 10, 2013
5. Chemicals in the environment 2013. Environmental health and safety division, Environmental Health Department, Ministry of the Environment, Japan.
6. Emission control measures for unintentional formation POPs 2011(in Japanese); Contract work report for MOEJ, EX Research Institute.
7. Takasuga, T, Inoue, T, Ohi, E, Umetsu, N, Ireland, P, Takeda, N (1994);Organohalogen Compounds. 19: 173–176.
8. Takasuga, T., Inoue, T., Ohi, E. and Senthilkumar, K. (2004); *Arch. Environ. Contam. Toxicol*., 46, 419–431.
9. Takasuga, T., Senthilkumar, K., Noma, Y. and Sakai, S. (2005); *Arch. Environ. Contam. Toxicol*., 49(3), 385–395.