PCB #11 (3, 3'-DICHLOROBIPHENYL) AS A PREDOMINANT PCB CONGENERS IN AMBIENT AIR FROM UNINTENTIONAL FORMATION

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Introduction

PCBs are persistent in the environment and show a common property of long-range transport. The main sources of PCBs are commercial production such as technical grade (Arochlor, Kanechlor, Clophen etc.) and the total amount produced world-wide is estimated at 1.5 million tons. Technical PCBs are synthesized 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.

On the other hand, another sources of PCBs are by-product from unintentional formation such as combustion processes during the incineration of industrial and municipal waste, cement kiln, steel industry sintering furnace, secondary production of zinc etc. as well as 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)].

In Japan POPs monitoring including PCBs in ambient air have been conducted since 2002 with high sensitive analysis using GC-HRMS 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 vapor 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 as well having high sensitivity to assure the quality of the data and trends during long-term monitoring by MOEJ.

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 38 site of Japan.

Sampling; 700 L/min X 24hrs, 3 days continuous sampling or 100 L/min X 1 week sampling by high volume air ampler using quarts fiber filter, Poly urethane foam (PUF) and active carbon fiber felt (ACF).

The ^{13}C surrogate fortified $^{13}C_{12}$- PCBs mix ^{13}C-POPs mix and ^{13}C-New POPs mix before sampling.

Method validations 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.

Results and discussion

Fig.1 shows PCBs homologue profile in ambient air sample with the comparison of thermal processes exhaust gas such as cement kiln, steel sintering furnace, secondary production of zinc and waste incineration. Generally thermal process sample are predominant lower PCBs congeners especially for monoCBs in 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. Total PCBs levels have been reported in ambient air at all 36 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 Japan[5)]. These indicated PCBs are lower levels at cold season and reported relatively higher levels at industrialized areas.

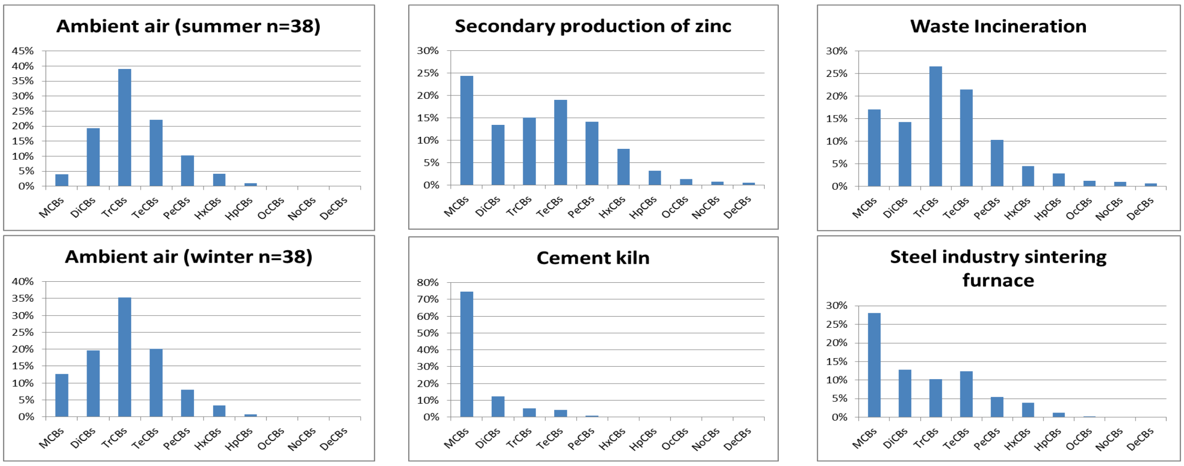

Fig. 1 PCB homologue profile in ambient air in summer and winter season

Fig. 2 shows averaged PCB congeners (mono, di and triCBs) level in ambient air. These data indicates that PCB congener profiles in ambient air samples are stable both in summer and winter season although homologue profiles shift to lower chlorination. 3,3'-dichlorobiphenyl (#11) is one of the highest PCB congener and shows same trends in most site of Japan with exception of technical PCB stockpile area since 2002.

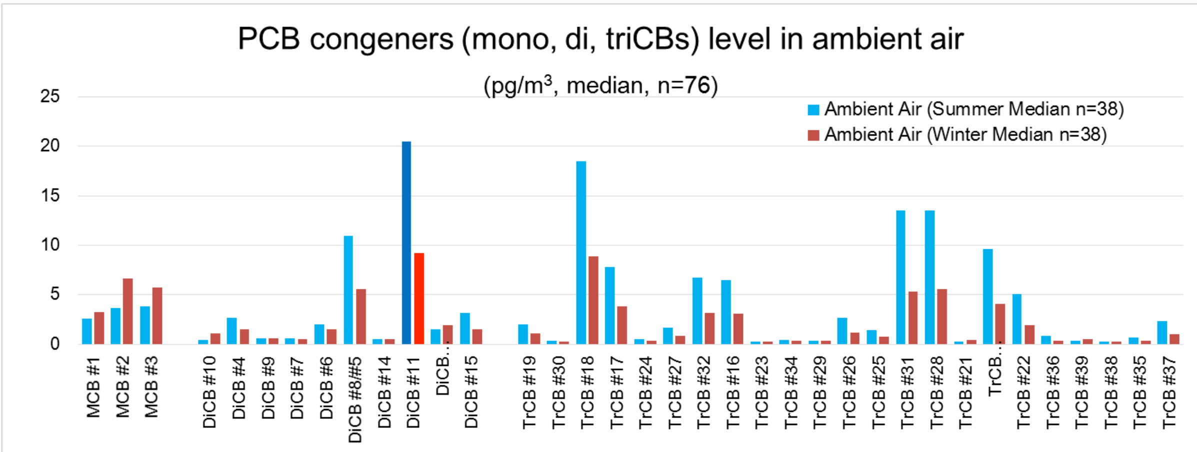

Fig. 2 PCB congeners (moni, di, triCBs) profile in ambient air in summer and winter season

Fig. 3 shows PCB congeners profile in ambient air, technical PCB and thermal processes (fly ash and cement kiln exhaust gas). Additionally PCB congeners profile in ambient air samples are relatively similar to technical PCBs for triCBs, tetraCBs(data not shown), But monoCBs and DiCBs are basically different to technical PCBs. Especially DiCB (#11) is most predominant DiCBs congener in ambient air sample although minor congeners in technical PCB and thermal processes, which suggest the another source such as organic pigment. DiCB (#11) is detected one of the highest PCB (>1000 ppm) impurities in the dichlorobenzidine type Pigment Yellow (PY12) in Japan as well as imported organic pigment[4)]. On the other hand MonoCBs profile in ambient air seems mixture of technical PCB and thermal processes.

PCB congeners pattern from thermal processes are completely different from technical PCBs. PCB congeners without ortho chlorine substitution, such as coplanar (Dioxin-like) PCBs are predominant in thermal processes sample [7,8].

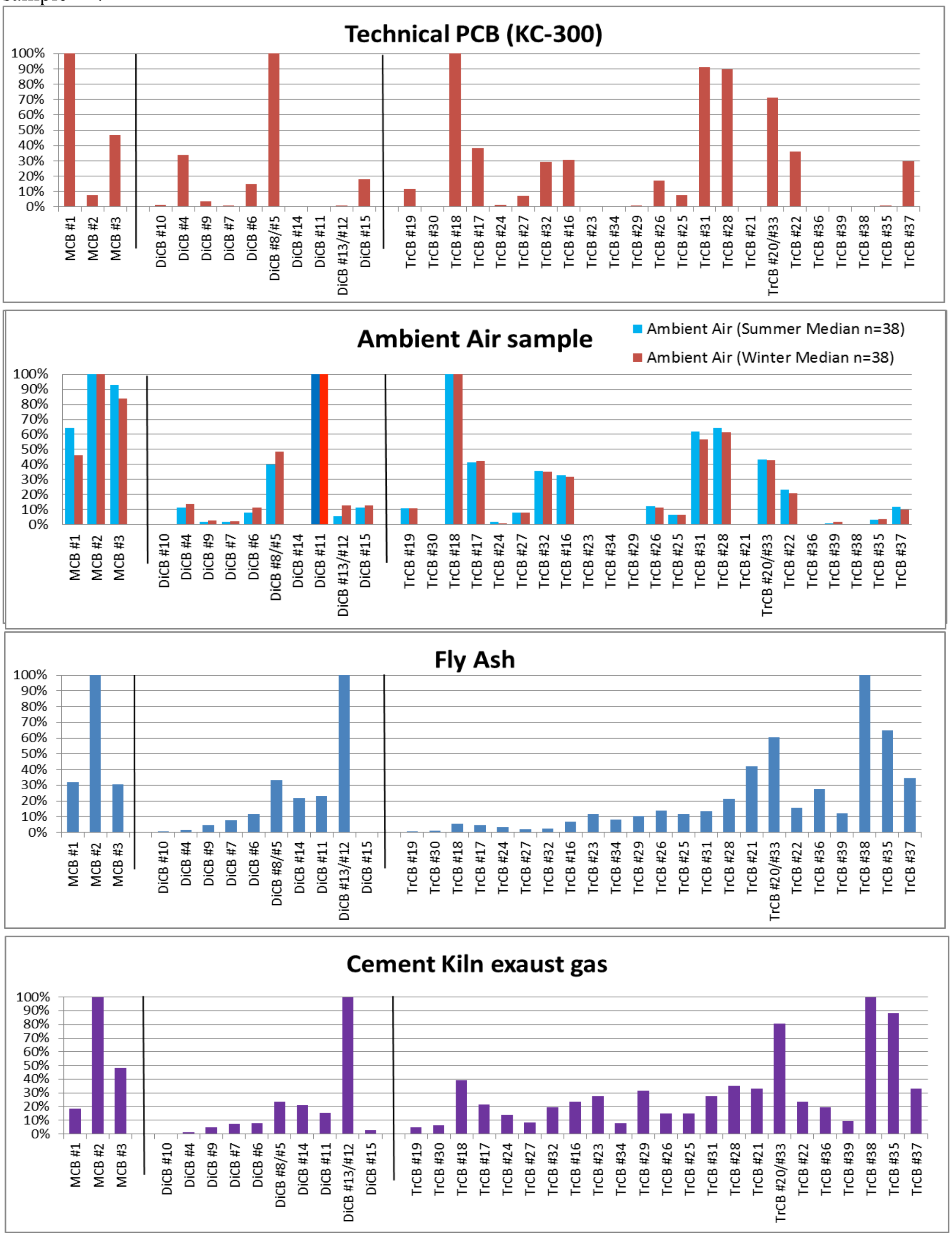

Fig. 3 Relative PCB congeners (in each chline degree ; moni, di, triCBs) profile in ambient air, technical PCB and thermal processes

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 range from approximately 10 days for a monoCBs to 1.5 years for a heptaCBs with undergoing photo degradation. The presence of PCB #11 (3, 3'-Dichlorobiphenyl) as a predominant PCB congeners in ambient air may suggest continuous supply from unintentional formation combined with the high vapor pressure, Henry's constant and physicochemical stability in the atmosphere.
Further investigation recommended for the identification of PCB congeners from various sources with atmospheric transport in the environment.

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

	Ambient Air	Technical PCBs 8)	Thermal processes 7)	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 (34-)/ #13 (34'-), #14 (35-), #11 (33'-)	#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 to NonaCBs in ambient air sample ; Basically similar to Technical PCB congeners pattern				

Acknowledgements
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