

CONCENTRATIONS AND CONGENER PROFILES OF POLYCHLORINATED BIPHENYLS, PENTACHLOROBENZENE, AND HEXACHLOROBENZENE IN COMMERCIAL PIGMENTS

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Introduction

Some persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs), pentachlorobenzene (PeCBz) and hexachlorobenzene (HCB), have been used worldwide in transformers and condensers, or as agricultural chemicals. However, owing to their adverse effects on organisms and their environmental persistence, the manufacture and use of POPs have been banned: at present, these POPs are formed as an unintentional by-product of combustion process such as waste incinerator. It has been observed that some organic pigments contain high concentrations of PCBs as a by-product¹. This observation has been gaining attention, as the PCBs congeners in these pigments are significantly different from industrial PCBs product, such as Aroclor and Kaneclor, and in particular, 3,3'-dichlorobiphenyl (#11) have been found in these pigments and have also been found as the primary congeners in the environment²⁻⁵.

Commercially available azo and phthalocyanine pigments in Japan were investigated, the concentrations of PCBs congeners, PeCBz, and HCB were determined for analyzing congener patterns. Oil paints manufactured using these pigments as a component were also analysed. These pigments contains PCB substructure as starting material such as 3,3'-dichloro-4,4'-diaminobiphenyl and 2,2',5,5'-tetrachloro-4,4'-diaminobiphenyl, and chlorobenzenes and/or PCBs were formed as by-products in the manufacturing process of these pigments¹.

Materials and Methods

The pigments were obtained from 2 companies within Japan. Each pigment was accurately weighed to the mg-order, and placed in a separating funnel with a small amount of hexane. After adding 10 to 20 mL of concentrated sulfuric acid, the sample was shaken vigorously, and this process was repeated until the hexane layer lost all color. The hexane layer was washed with purified water, and then dehydrated with sodium sulfate. Then, a surrogate (Table 1) was added to the liquid extract and a rotary evaporator was used to concentrate it, after which it was added to a multilayer silica-gel column and eluted with 200 mL of hexane. The elution was added to a Supelclean sulfoxide SPE tube, and 9 mL of hexane was used to remove impurities. Next, a Discovery Ag-ION SPE tube was attached to the bottom of the Supelclean sulfoxide SPE tube, and the sample was eluted with 50 mL of 5% dichloromethane/hexane. This new elution was concentrated and internal standard substances (Table 1) were added to make a 50 μ L nonane solution.

The quantification of the PCBs, PeCBz and HCB was performed by high resolution gas chromatography (HP6890 Agilent Technologies, USA)- high resolution mass spectrometer

(JMS700D, JEOL, Japan). HT8-PCB capillary column(60m, 0.25mm i.d., Kanto Kagaku, Japan) was used for determination of PCB all congeners. The limits of detection were 0.0001–0.0006 mg kg⁻¹ for PCBs, and 0.0006–0.001 mg kg⁻¹ for PeCBz and HCB.

Table 1 List of PCBs, PeCBz and HCBz standards

Homologue	Congener IUPAC #	
	Surrogate ¹⁾	Recovery standards ¹⁾
PCBs		
MoCBs	#3	
DiCBs	#15	#8
TrCBs	#28	#32
TeCBs	#60	#70
PeCBs	#101	#97
HxCBs	#141	#153
HpCBs	#178	#180
OcCBs	#194	#205
NoCBs	#208	#206
DeCB	#209	
Chlorobenzenes		
	PeCBz	#32
	HCBz	#32

1) denote ¹³C₁₂ labeled standards

Results and Discussion

Concentration Levels and Congener Patterns

The pigments examined included 15 azo-type and 5 phthalocyanine-type pigments. The results are shown in Table 2. Figs. 1 and 2 show the congener patterns for PCBs in azo and phthalocyanine pigments, respectively. For azo pigments, the concentration levels were as follows: PCBs, 0.16 to 740 mg kg⁻¹; PeCBz, ND to 0.018 mg kg⁻¹; and HCB, ND to 0.019 mg kg⁻¹; and for phthalocyanine pigments: PCBs, ND to 0.43 mg kg⁻¹; PeCBz, 0.0057 to 8.5 mg kg⁻¹; and HCB, 0.020 to 19 mg kg⁻¹. The Stockholm Convention restricts the movement of substances with concentrations exceeding 50 ppm (mg kg⁻¹), and the EU has measures in place to ban their use. In Japan, waste products with over 0.5 ppm are supposed to be specially disposed of as PCB-containing waste. Of these pigments examined in this study, there were 12 kinds that included more than 0.5 ppm, one of which exceeded 50 ppm. Although the level of PeCBz and HCB in all azo pigments were less than 0.02 mg kg⁻¹, the range of PeCBz and HCB in the phthalocyanine pigments (except PB15) was 3.2–19 mg kg⁻¹. For PCBs in the azo pigments, in Company B's PY14, #52 was the dominant congener, accounting for 99% of all PCBs, but in the others, only #11, #35, and #77 were found, with #11 accounting for over 80% of the total PCBs. For the phthalocyanine pigments except PB15, #209 was the dominant congener, accounting for 95% of all PCBs, with highly chlorinated compounds such as #202, #206, #207, and #208 also accounting for a few percent of all PCBs. #77, which is found in the azo pigments, is a dioxin-like PCB (DLPCB). The dioxin concentration level for azo pigments calculated using the toxic equivalency factor (TEF) for this congener was 0 to 49 pg-TEQ/g.

Table 2 Concentration of PCBs, PCBz and HCBz in commercial pigment

Sample #	C.I. name	maker	Total PCBs	Total TEQ*	PCBz	HCBz	dominant PCB	Chemical class
			mg/kg	pg-TEQ/g	mg/kg	mg/kg	congeners	
a1	PO13	A	9.6	3.6	ND	ND	#11, #35, #77	pyrazolone
a2	PO16	A	0.34	3.0			#11, #35, #77	disazoorange
a3	PY12	A	0.69	0.9	0.0016	0.0021	#11, #35, #77	disazoyellow
a4	PY13_1	A	0.87	3.0	0.0024	0.0030	#11, #35, #77	disazoyellow
a5	PY13_2	A	1.2	1.6	ND	ND	#11, #35, #77	disazoyellow
a6	PY14	A	1.4	1.9	0.0016	0.0038	#11, #35, #77	disazoyellow
a7	PY17_1	A	0.34	2.4	0.0024	0.0039	#11, #35, #77	disazoyellow
a8	PY17_2	A	0.83	0.84	0.0027	0.0060	#11, #35, #77	disazoyellow
a9	PY55	A	0.73	0.41	0.0014	0.0032	#11, #35, #77	disazoyellow
a10	PY83_1	A	1.5	0.21	0.0010	0.0026	#11, #35, #77	disazoyellow
a11	PY83_2	A	3.0	2.4	0.0016	0.0028	#11, #35, #77	disazoyellow
a12	PY83_3	A	4.1	1.8	ND	ND	#11, #35, #77	disazoyellow
a13	PY83_4	A	0.33	0	0.0013	0.0063	#11, #35, #77	disazoyellow
p1	PG7_1	A	0.43	0	8.5	19	#209	phthalocyanine
p2	PG7_2	A	0.16	0	3.8	9.6	#209	phthalocyanine
p3	PG7_3	A	0.20	0	4.0	7.9	#209	phthalocyanine
p4	PG7_4	A	0.27	0	3.2	10	#209	phthalocyanine
a14	PY14	B	17	49	0.018	0.019	#52	disazoyellow
a15	PO13	B	740	0	0.0098	0.0031	#11, #35, #77	pyrazolone
p5	PB15	B	ND	0	0.0057	0.020	-	phthalocyanine

* DLPCBs- based TEQ

** ND: Not detected (<LOD)

PCBs in Oil Paints

A compositional analysis for PCBs was carried out on commercially available oil paints from 3 companies that use azo pigments as an ingredient. The results are shown in Table 3. Other than in Company c's Permanent Yellow Light, PCBs were found in all paints, with #11, #35, #52, and #77 being the most prevalent. The paints were separated into two categories, whose primary congeners are either #35 and #77 or #52, #101, and #153.

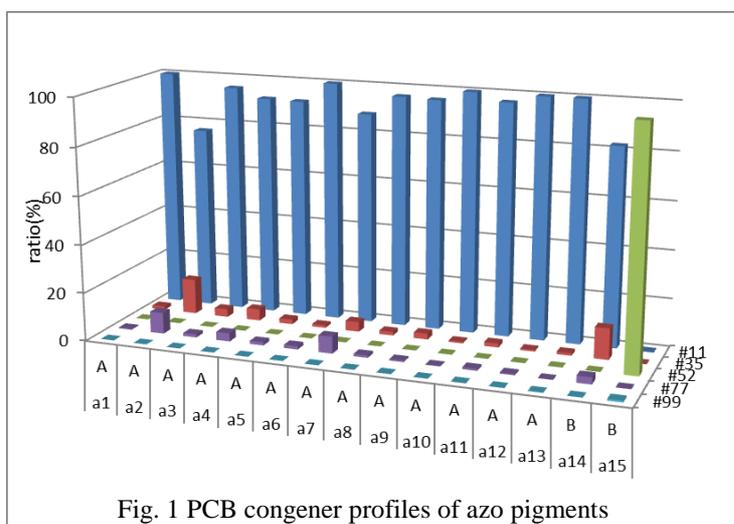


Fig. 1 PCB congener profiles of azo pigments

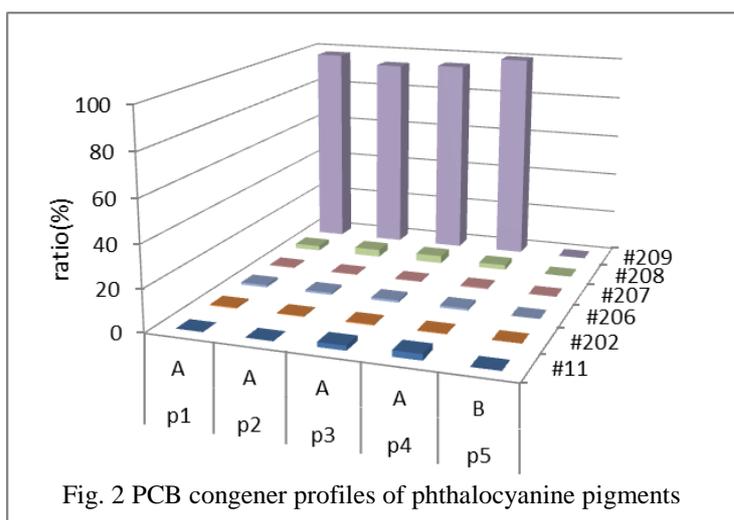


Fig. 2 PCB congener profiles of phthalocyanine pigments

Table 3 Dominant PCB congeners in commercial oil-based paint

brand name	maker	C.I. name	dominant congener
Permanent Yellow light	a	PY14	#11, #35, #77
Permanent Yellow deep	a	PY152	#11, #35, #77
Permanent Yellow lemon	a	PY81	#11, #52, #101, #153
Permanent Yellow Orange	a	PO14	#11, #35, #77
Permanent Yellow deep	b	PY83	#11, #35, #77
Permanent Yellow lemon	b	PY81	#52
Permanent Yellow deep	c	-	#11, #35
Permanent Yellow light	c	-	-

the tetrazo forms, in which diazonium salts are formed.

Phthalocyanine green is manufactured by first producing copper phthalocyanine crude blue (pigment blue 15) and then chlorinating it. Methods for creating copper phthalocyanine crude blue include the reaction of phthalic anhydride with urea and copper chloride or the reaction of phthalodinitrile with copper chloride. The latter process tends to produce phthalocyanine pigments of higher purity and quality, and has also been confirmed to generate less HCB as a by-product. This is thought to be due to the quantity and types of impurities in copper phthalocyanine crude blue and the difference in temperature during chlorination. Formation of HCB as a by-

Congener Patterns for 3,3'-Dichlorobenzidine PCBs

An analysis was performed on 3,3'-dichlorobenzidine PCBs, an ingredient in azo pigments. The total concentration was 1.7 mg kg⁻¹, and consisted of #206 (34%), #128 (17%), #157 (12%), #77 (11%), #35 (9%), and less than 5% of others. The concentration of #11 was found to be 0.6%.

Characteristics of PCBs, PeCBz and HCB in Pigments

Generally, azo pigments are made from 3,3'-dichlorobenzidine or 2,2',5,5'-tetrachlorobenzidine, which are then made into a tetrazo form with sodium nitrite or hydrochloric acid, coupled with acetoacetanilide or 3-methyl-1-phenyl-5-pyrazolin. 3,3'-dichlorobenzidine has a similar structure to #11, and 2,2',5,5'-tetrachlorobenzidine is similar to #52, so it is plausible that pigments containing mainly #11 are made using the former, and those containing mainly #52 are made using the latter. #35 and #77 were found as dominant congeners in the Permanent Yellow Deep, Light, and Orange oil paints, but since these congeners are also characteristically found in 3,3'-dichlorobenzidine, the pigments were also likely to have been made using 3,3'-dichlorobenzidine. Similarly, #52 is present at noticeably high levels in Pigment Yellow Lemon, so it is most likely been made using 2,2',5,5'-tetrachlorobenzidine. The congeners present in 3,3'-dichlorobenzidine all share chlorine at the 3,3' positions in their structures, but their congener patterns are significantly different from that of 3,3'-dichlorobenzidine. This is probably due to #11, #35, and #77 being present as a by-product of the refining process, after being produced during the synthesis of

product is also related to highly chlorinated PCB by-products, and it has been suggested as the reason why compounds containing 9 or 10 chlorine atoms have been found as the dominant congeners in phthalocyanine green.

Seasonal Variations in Atmospheric PCB Levels in Sapporo and Environmental Behavior of PCBs from Pigments

A low-volume air sampler (20 to 30 L min⁻¹) was used in Sapporo to perform monthly sampling of the atmosphere from April 2005 to March 2011. Quartz fiber filter paper and polyurethane foam with activated carbon felt were used as the material for air collection⁶. The results are shown in Fig. 3. The PCB concentration varies from 69 to 1200 pg m⁻³, with an average of 361 pg m⁻³ over 6 years. The concentration of #11 was 2.4-37 pg m⁻³, with an average of 11.4 pg m⁻³ over 6 years. There are noticeable trends that both increase in summer and decrease in winter, showing a strong temperature dependence. #11 accounted for 10% or less of all PCBs, similar to results found in a study in Chicago³. This proportion was also found to decrease during the summer. It is thought that this is due to the increase in temperature, which causes more highly chlorinated PCBs to be vaporized from the soil, leading to a relative decrease in the proportion. In addition, #11 accounted for 35-70% of all dichloric types, with a noticeable tendency to increase during the summer. This is thought to be due to Kaneclor being a more common source of PCBs than pigments around the sampling area. Of the congeners containing in these pigments, #35 and #209 were detected as 0.4 and 0.05% of the total PCBs respectively.

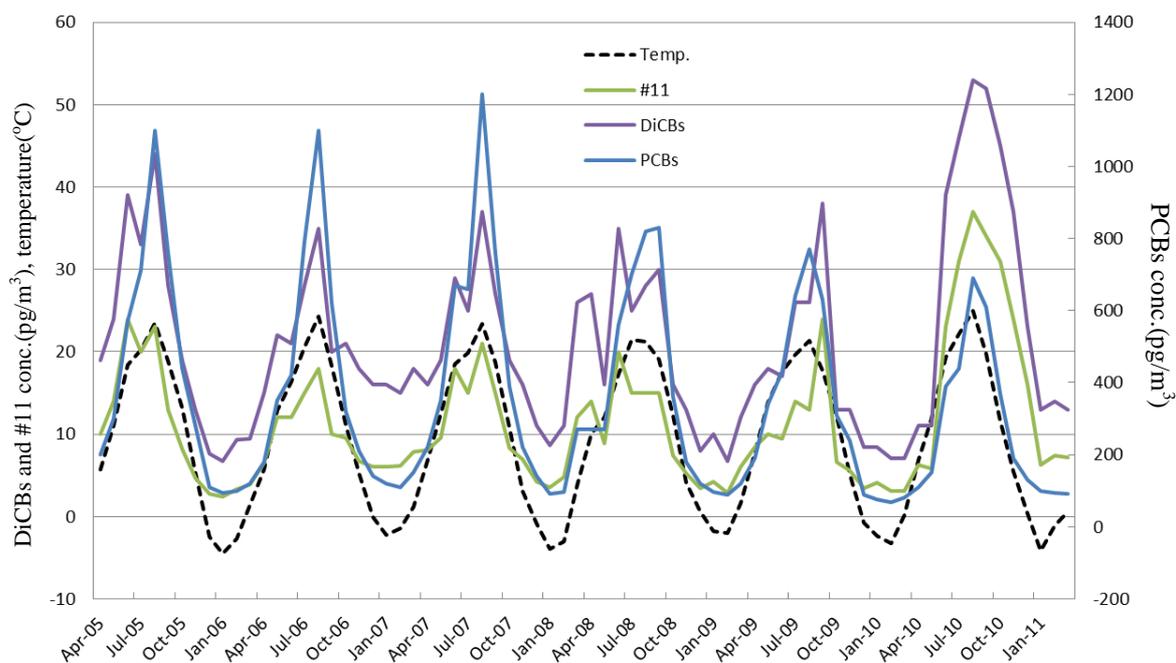


Fig. 3 Seasonal variations of PCBs, DiCBs and #11 congener in Sapporo city

References

1. Hu D, Hornbuckle K C. (2010); *Environ Sci Technol.* 44: 2822–2827
2. Rodenburg L A, Guo J, Du S, Cavallo G J. (2010); *Environ Sci Technol.* 44: 2816–2821
3. Hu D, Martinez A, Hornbuckle K C. (2008); *Environ Sci Technol.* 42: 7873–7877
4. Li YM, Geng DW, Hu YB, Wang P, Zhang QH, Jiang GB.(2012); *Chin Sci Bull.* 57: 1499–1503
5. Basu I, Arnold K A, Venier M, Hites R A. (2009); *Environ Sci Technol.* 43: 6488–6492
6. Anezaki K, Yamaguchi K. (2012); *J. Environ Chem.* 21: 303-311(in Japanese)