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RESEARCH ARTICLE

Concentration levels and congener profiles of polychlorinated biphenyls, pentachlorobenzene, and hexachlorobenzene in commercial pigments

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Abstract The concentration levels and congener profiles of polychlorinated biphenyls (PCBs), pentachlorobenzene (PeCBz), and hexachlorobenzene (HxCBz) were assessed in commercially available organic pigments. Among the azo-type pigments tested, PCB-11, which is synthesized from 3,3′-dichlorobendizine, and PCB-52, which is synthesized from 2,2′,5,5′-tetrachlorobendizine, were the major congeners detected. It is speculated that these were byproducts of chlorobendizine, which has a very similar structure. The total PCB concentrations in this type of pigment ranged from 0.0070 to 740 mg/kg. Among the phthalocyanine-type pigments, highly chlorinated PCBs, mainly composed of PCB-209, PeCBz, and HxCBz were detected. Their concentration levels ranged from 0.011 to 2.5 mg/kg, 0.0035 to 8.4 mg/kg, and 0.027 to 75 mg/kg, respectively. It is suggested that PeCBz and HxCBz were formed as byproducts and converted into PCBs at the time of synthesizing the phthalocyanine green. For the polycyclic-type pigments that were assessed, a distinctive PCB congener profile was detected that suggested an impact of their raw materials and the organic solvent used in the pigment synthesis. PCB pollution from PCB-11, PCB-52, and PCB-209 pigments is of particular concern; therefore, the monthly variations in atmospheric concentrations of these pollutants were measured in an urban area (Sapporo city) and an industrial area (Muroran city). The study detected a certain level of PCB-11, which is not included in PCB technical mixtures, and revealed continuing PCB pollution originating from pigments in the ambient air.

Keywords Polychlorinated biphenyls · Congeners · Hexachlorobenzene · Pentachlorobenzene · Pigments · Ambient air · Byproduct

Introduction

Owing to their physical and chemical stability, polychlorinated biphenyls (PCB) were widely used until the mid-1970s under product names such as aroclor and kanechlor (PCB technical mixtures) (Abramowicz 1990). They were used in a great range of products such as transformers, capacitors, and non-carbon paper. However, many countries now prohibit their manufacturing and use as they were designated as persistent organic pollutants (POPs) on discovery of their high toxicity, residual effects, and accumulative properties in living organisms (Çok and Şatiroğlu 2004). In spite of it being over 30 years since discontinuation of their production, PCBs can still be detected in various media owing to their accumulation in sediments and wildlife such as fish (Davis et al. 2007).

It is well known that PCB technical mixtures and the byproducts of incinerated waste materials are the main causes of PCB pollution (Ishikawa et al. 2007; Takasuga et al. 2006). There are 209 congeners of PCBs, and the compositional pattern of PCB technical mixtures and that of incinerated waste materials are different (Kim et al. 2004). In general, PCBs detected in the air have a highly similar compositional pattern to that of PCB technical mixtures (Anezaki et al. 2007; Gedik et al. 2010; Honda et al. 2008; Ilyas et al. 2011; Ishaq et al. 2003; Martinez et al. 2012; Rachdawong and Christensen 1997; Wethington and Hornbuckle 2005). However, in recent years, there have been a

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number of reports of PCB-11 (3,3′-dichlorobiphenyl), which does not exist in PCB technical mixtures (Frame et al. 1996; Schulz et al. 1989), specifically detected in ambient air (Basu et al. 2009; Nakano et al. 2008; Hu et al. 2008; Li et al. 2012a), water (Du et al. 2008; Litten et al. 2002; Rodenburg et al. 2010) and mussels (King et al. 2002). Hu and Hornbuckle (2010) suggested that PCB-11 could be unintentionally formed as a byproduct in the production of azo-type yellow pigment from 3,3′-dichlorobenzidine and reported the detection of this PCB on the order of ng/g in several azo-type pigments. Rodenburg et al. (2010) detected PCB-11 at similar levels in printed newspapers, magazines, and plastic products and implied that these were the major pollution sources of PCB-11 in ambient air. In addition to PCB-11, other PCBs present as impurities in pigments have been reported. For example, PCB-52 (2,2′,5,5′-tetrachlorobiphenyl) was detected in an azo-type pigment made from 2,2′,5,5′-tetrachlorobenzene and PCB-209 and POPs such as hexachlorobenzene (HxCBz) and pentachlorobenzene (PeCBz) were detected in phthalocyanine green (Hu and Hornbuckle 2010). In addition, it has been indicated that highly chlorinated PCBs can be inadvertently produced during the refinement of titanium dioxide, leading to concerns of PCB contamination from white pigments that include titanium dioxide (Rowe et al. 2007; Praipipat et al. 2013). As such, the evidence for the presence of POPs within pigments is clear; however, there are few studies that have assessed the congener patterns of PCBs, their toxicity, and the relative concentration characteristics in detail for each type of pigment, in addition to their correlation with HxCBz and PeCBz. It is extremely important to gain an accurate understanding of PCB concentration levels in pigments, especially from the risk communication standpoint, as the international transfer of PCBs in a concentration of 50 mg/kg or over is prohibited by the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention 2001).

In this study, we examined the concentration levels and congener patterns of PCBs, as well as the concentration levels of PeCBz and HxCBz, in organic pigments (oil paint) that are manufactured by five companies and are available on the Japanese market. When dioxin-like PCBs (DL-PCBs) were detected, their dioxin concentration levels (toxic equivalent, TEQ) were also calculated. The study included a wide range of azo-type and phthalocyanine-type pigments, in addition to a small number of polycyclic-type.

The isotope dilution method using surrogate materials was used for analysis in conjunction with high resolution gas chromatography–high resolution mass spectrometry (HRGC–HRMS). The monthly variations in atmospheric concentration levels of major congeners in pigments (i.e., PCB-11, PCB-52, and PCB-209) were measured over a 5-year period in the urban area of Sapporo and the industrial area of Muroran, Japan, and the trend in quantities of PCBs originating from pigments in ambient air was examined.

Materials and methods

Reagents and chemicals

A total of 46 organic pigments that are available in Japan and are manufactured by five different companies (A–E) were examined (azo-type pigments (29), phthalocyanine-type pigments (13), and polycyclic-type pigments (4)). The samples acquired from Companies C, D, and E were obtained as oil paint. Standards of PCBs, PeCBz, and HxCBz were purchased from Cambridge Isotope Laboratories Inc. (MA, USA) (Table 1). The organic solvent and silica gel designed for dioxin analysis and concentrated H_2SO_4 (super special grade) were obtained from Wako Pure Chemical Industries, Ltd. (Japan). Supelclean sulfoxide SPE tubes (Numata et al. 2008) and Discovery Ag-ION SPE tubes were obtained from Supelco.

Sample analysis

Pigment analysis

Each pigment was accurately weighed on the order of milligrams and placed in a separating funnel with a small amount of concentrated H_2SO_4 followed by the addition of 100 to 150 mL of hexane. The mixture was then 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 Na_2SO_4. An isotope-labeled surrogate (Table 1) was subsequently added to the liquid extract, and it was concentrated by rotary evaporation. It was then added to a multilayer silica gel column (6 g of 22 % H_2SO_4 silica gel, 4.5 g of 44 % H_2SO_4 silica gel, 4.5 g of 55 % H_2SO_4 silica gel, and 3 g of 2 % KOH silica gel) and eluted with 200 mL of hexane. The eluent was added to a Supelclean sulfoxide SPE tube, and the impurities were removed using 9 mL of hexane. A Discovery Ag-ION SPE tube was then attached to the bottom of the Supelclean sulfoxide SPE tube, and the sample was eluted with 50 mL of 5 % dichloromethane/hexane. This eluent was subsequently concentrated and syringe spike substances (Table 1) were added to make a 50-μL nonane solution.

Analysis of ambient air samples

The ambient air samples were collected in the urban area of Sapporo and the industrial area of Muroran, both of which are located on the Japanese northern island, Hokkaido. Sapporo has a population of 1.9 million and is the central city of Hokkaido. Muroran is located approximately 100 km south of Sapporo and has a population of 0.1 million. It is an industrial area with steel plants, oil refineries, shipyards, and PCB waste treatment facilities.

Table 1 List of PCB and chlorobenzene standards

Homolog/chlorobenzene	Native[b]	Surrogate[ab]	Syringe spike[ab]
MoCBs	#1, #3	#3	
DiCBs	#8, #9, #10, #12, #15	#15	#9
TrCBs	#18, #19, #33, #35, #37, #38	#28	#32
TeCBs	#44, #52, #54, #57, #74, #77, #78, #79, #80	#60	#70
PeCBs	#99, #104, #114, #118, #123, #126	#101	#97
HxCBs	#153, #155, #156, #157, #162, #167, #169	#141	#153
HpCBs	#188, #189	#178	#180
OcCBs	#194, #195, #202, #205	#194	#205
NoCBs	#206, #208	#208	#206
DeCB	#209	#209	
PeCBz	PeCBz	PeCBz	#9
HxCBz	HxCBz	HxCBz	#32

The calibration standards were prepared by mixing native, surrogate, and syringe spike standards

[a] Denotes $^{13}C_{12}$ labeled standards

[b] Denotes PCB congeners represented by IUPAC number

Ambient air samples were collected using a low volume air sampler equipped with a quartz fiber filter (QFF), two polyurethane foam plugs (PUF), and an activated carbon fiber felt (ACF) for 1 month, with a flow rate of 30 L/min and a sampling volume of approximately 1,000 m^3 (Anezaki and Yamaguchi 2011). Thereafter, the QFF and PUFs were extracted using pressurized liquid extraction (PLE) with toluene and acetone, respectively. The ACF was extracted by ultrasonic agitation with acetone, and then PLE with toluene. These extracts were combined and an isotope-labeled surrogate (Table 1) was added. The resulting sample was applied to a multilayer silica gel column (3 g of 10 % $AgNO_3$ silica gel, 6 g of 22 % H_2SO_4 silica gel, 4.5 g of 44 % H_2SO_4 silica gel, 4.5 g of 55 % H_2SO_4 silica gel, and 3 g of 2 % KOH silica gel) and eluted with 200 mL of hexane. The eluted sample was further purified by a fractional activated carbon column combined with high performance liquid chromatography. The eluent was then concentrated and syringe spike substances (Table 1) were added to make a 20-μL nonane solution.

HRGC–HRMS analysis

The quantification of the PCBs, PeCBz, and HxCBz was performed by HRGC (HP6890 Agilent Technologies, USA) in combination with HRMS (JMS700D, JEOL, Japan). The samples were analyzed with an HT8-PCB capillary column (Matsumura et al. 2002) (60 m, 0.25 mm i.d., Kanto Kagaku, Japan) with the following temperature program: 120 °C for 1 min, 20 °C/min to 180 °C, 2 °C/min to 260 °C, 5 °C/min to 300 °C, and held at 300 °C for 8 min. This method resulted in the separation of the 209 congeners into 193 peaks. In particular, PCB-11 was completely separated from the other congeners, with no interferences. The HRMS was operated in selected ion monitoring mode for each congener group and chlorobenzene. For the concentrations of PCB congeners, it was assumed that the HRGC–HRMS relative sensitivity for PCB congeners with the same chlorine count would be the same; the concentrations were then calculated for each congener. The assignments for each congener in the chromatogram were checked against literature values (Matsumura et al. 2002) and analysis of fly ash samples.

Quality control and quality assurance

The limits of quantification (LOQ) varied depending on congener and sample size. The LOQ values for pigment samples were found to be 0.0001–0.0006 mg/kg for each PCB congener, and 0.0004–0.001 mg/kg for PeCBz and HxCBz. The LOQ for ambient air samples was found to be 0.002–0.01 pg/m^3 for each PCB congener. The concentrations for the peaks were determined by isotope dilution quantification using surrogates. The surrogate recovery rates (calculated using syringe spike) of PCBs were within the range of 50–120 %, and those of monochlorinated biphenyl, PeCBz, and HxCBz were within the range of 40–80 %. Laboratory blanks and field blanks were also checked regularly. The lab blank values were found to be extremely low. Meanwhile, the field blank values for the PCBs in ambient air samples were present (~1.0 pg/m^3) and consistent. Therefore, the mean field blank value was used for subtraction. An extract of reference material (reference sea sediment for PCB analysis, JSAC0452, KTYH0452) was analyzed using the same analysis procedure for quality assurance, and results were found to be within the range of certified values. Code "BY" from Company B was analyzed three times, and the quantitative values were compared to determine precision (RSD=9.8 %).

Results and discussion

Concentration levels and congener profiles

Tables 2, 3, and 4 show the color index (C.I.) names and the concentrations of each PCB congener, PeCBz, and HxCBz

Table 2 Concentrations of PCB congeners, PeCBz, and HxCBz in azo-type paint pigments (unit, milligram per kilogram)

PCB		Code	FY3	FY6	ZAY	FY2	FY4	FY4B	FY5	FY7	FYM	FY7B	CFY	9SA	FOGR	PO
		Company	A	A	A	A	A	A	A	A	A	A	A	A	A	B
Congener	Chlorine	C.I. name	PY12	PY13	PY13	PY14	PY17	PY17	PY55	PY83	PY83	PY83	PY83	PO13	PO16	PO13
IUPAC#	positions															
#2	3-MoCB															
#11	3,3′-DiCB		0.66	0.80	1.1	1.4	0.30	0.80	0.70	1.5	2.9	4.1	0.33	9.4	0.26	14
#35	3,3′,4-TrCB		0.023	0.042	0.023	0.015	0.014	0.013	0.018	0.010	0.050	0.025	0.0035	0.13	0.050	2.2
#52	2,2′,5,5′-TeCB															
#77	3,3′,4,4′-TeCB		0.0090	0.030	0.016	0.019	0.024	0.0084	0.0041	0.0021	0.024	0.018		0.036	0.030	0.49
#101	2,2′,4,5,5′-PeCB															
#153	2,2′,4,4′,5,5′-HxCB															
ΣPCBs			0.69	0.87	1.2	1.4	0.34	0.83	0.73	1.5	3.0	4.1	0.33	9.6	0.34	17
WHO-TEQ(pg-TEQ/g)[a]			0.90	3.0	1.6	1.9	2.4	0.84	0.41	0.21	2.4	1.8		3.6	3.0	49
Chlorobenzene																
PeCBz			0.0016	0.0024		0.0016	0.0024	0.0027	0.0014	0.0010	0.0012		0.0013			0.0090
HxCBz			0.0021	0.0030	0.0008	0.0038	0.0039	0.0060	0.0032	0.0026	0.0014		0.0063			

PCB	BY	125	123	179	180	S-1419	S-1418	PYLi	PYL	PYD	IY	PYO	IO	NR	BH
	B	C	C	C	C	D	D	E	E	E	E	E	E	E	E
Congener	PY81	PY81	PY83	PR170	PR170	PY74	PY83	PY14	PY81	PY152	PY154	PO13	PO36	PR22	PR188
IUPAC#															PO69
#2												0.022			
#11	0.53	0.016	7.6				2.3	0.85	0.39	1.4	0.0070	6.9	0.0096		
#35		0.019	0.15				0.060	0.10		0.011		1.3	0.014		
#52	730	8.2							57						
#77			0.15					0.20		0.012		1.1	0.10		
#101	0.019	0.038							0.063						
#153	0.0072	0.024							0.079						
ΣPCBs	740	8.3	7.9				2.4	1.2	58	1.4	0.0070	9.2	0.13		
WHO-TEQ(pg-TEQ/g)[a]			15					20		1.2		110	10		
Chlorobenzene															
PeCBz	0.017		0.0060						0.0024		0.0029				
HxCBz	0.016		0.032	0.0062		0.0049		0.0056			0.0018		0.0021		

[a] WHO-TEQ is calculated for dioxin-like PCB congener(#77) using WHO-TEF. Blank spaces indicate that none of that component was detected

Table 3 Concentrations of PCB congeners, PeCBz, and HxCBz in phthalocyanine-type paint pigments (unit, milligram per kilogram)

PCB congener IUPAC#	Chlorine positions	Code	GO	GN	G550	5310	PB	035	083	S-1319	S-1208	OB	PGL	PGD	OG
		Company	A	A	A	A	B	C	C	D	D	E	E	E	E
		C.I. name	PG7	PG7	PG7	PG7	PB15	PB15:1	PG7	PG7	PB15	PB15:3	PY3 PG7	PG7	PG36
#2	3-MoCB														0.0030
#4	2,2′-DiCB														0.017
#5/8	2,3-DiCB 2,4′-DiCB														0.048
#6	2,3′-DiCB														0.14
#11	3,3′-DiCB				0.0045	0.0078							0.0089		0.049
#12/13	3,4–DiCB 3,4′–DiCB														0.057
#15	4,4′-DiCB														0.012
#93/95/98	2,2′,3,5,6–PeCB 2,2′,3,5′,6–PeCB 2,2′,3′,4,6–PeCB								0.0023						
#101	2,2′,4,5,5′-PeCB								0.023						
#194	2,2′,3,3′,4,4′,5,5′-OcCB									0.012					
#196	2,2′,3,3′,4,4′,5,6′-OcCB								0.0006						
#198	2,2′,3,3′,4,5,5′,6-OcCB								0.0027						
#199	2,2′,3,3′,4,5,5′,6′-OcCB								0.0007	0.0024					
#202	2,2′,3,3′,5,5′,6,6′-OcCB		0.0025	0.0005	0.0010	0.0009			0.0006						
#203	2,2′,3,4,4′,5,5′,6-OcCB								0.0017						
#205	2,3,3′,4,4′,5,5′,6-OcCB								0.0007						
#206	2,2′,3,3′,4,4′,5,5′,6-NoCB		0.0048	0.0016	0.0022	0.0027			0.025	0.0022				0.0008	
#207	2,2′,3,3′,4,4′,5,6,6′-NoCB		0.0020	0.0006	0.0007	0.0015			0.025	0.0065				0.0014	
#208	2,2′,3,3′,4,5,5′,6,6′-NoCB		0.010	0.0057	0.0073	0.0064			0.066	0.0017				0.0041	
#209	DeCB		0.42	0.15	0.19	0.25			2.3	0.56			0.0019	0.16	0.029
ΣPCBs			0.43	0.16	0.20	0.27			2.5	0.57			0.011	0.16	0.36
Chlorobenzene															
PeCBz			8.4	3.7	3.9	3.1	0.0054	0.0037	2.5	0.14	0.0069	0.0094	0.0035	1.4	0.18
HxCBz			19	9.4	7.6	9.8	0.019	0.010	75	7.8	0.0060	0.017	0.027	5.9	1.5

Cluster congeners that co-elute on HT8-PCB column are expressed by “/”. Blank spaces indicate that none of that component was detected

Table 4 Concentrations of PCB congeners, PeCBz, and HxCBz in polycyclic-type paint pigments (unit, milligram per kilogram)

PCB congener IUPAC#	Chlorine positions	Code	012	S-1312	S-1314	PV
		Company	C	D	D	E
		C.I. name	PR254	PG8 etc.	PG8	PV23
#1	2-MoCB					0.016
#2	3-MoCB		0.016			
#3	4-MoCB		0.053			
#4	2,2′-DiCB		0.036			
#5	2,3-DiCB					0.74
#6	2,3′-DiCB		0.067			
#7	2,4-DiCB					0.0033
#8	2,4′-DiCB		0.68			
#9	2,5-DiCB					0.0074
#11	3,3′-DiCB		0.025			
#12	3,4-DiCB					0.44
#13	3,4′-DiCB		0.69			
#15	4,4′-DiCB		0.74			
#16	2,2′,3-TrCB					0.0053
#20/33	2,3,3′-TrCB 2′,3,4-TrCB					0.0099
#40	2,2′,3,3′-TeCB					0.031
#56	2,3,3′,4′-TeCB					0.14
#77	3,3′,4,4′-TeCB					0.062
ΣPCBs			2.3			1.5
WHO-TEQ [a](pg-TEQ/g)						6.2
Chlorobenzene						
PeCBz			0.0022			
HxCBz			0.0035			

Cluster congeners that co-elute on HT8-PCB column are expressed by "/". Blank spaces indicate that none of that component was detected

[a] WHO-TEQ is calculated for dioxin-like PCB congener (#77) using WHO-TEF

in azo-type, phthalocyanine-type, and polycyclic-type pigments, respectively. The TEQ of the pigments from which DL-PCBs were detected is also included.

Among the azo-type pigments, PCBs were detected in 24 out of the 29 tested. The concentration levels ranged from 0.0070 to 740 mg/kg, with two samples giving values over 50 mg/kg, the level at which transfer is restricted by the POP convention. Furthermore, 19 pigment types contained PCB concentrations above 0.5 mg/kg, the level at which a substance is considered to be PCB-containing in Japan. Either PeCBz or HxCBz were identified in 19 of the samples, but the concentrations were below 0.032 mg/kg in all cases.

PCB-11 was identified as being the major congener present in all of the azo-type pigments that contained PCBs, except for pigment yellow (PY)81 and pigment orange (PO)36. This substance accounted for more than 70 % of the total PCB concentration (over 90 % in 15 types), followed by PCB-35 and PCB-77, which each accounted for just over 10 %. PCB-11, PCB-35, and PCB-77 were detected in company E's IO (PO36), and PCB-77 made the largest contribution, accounting for 77 % of the total PCB concentration. PCB-77 is one of the DL-PCBs, and the TEQ ranged from 0–110 pg-TEQ/g, with PO13 having a particularly high value. In contrast, for PY81, PCB-52 was detected as the major congener, accounting for more than 98 % of the total PCB concentration, followed by PCB-11, PCB-101, and PCB-153, which constituted less than 1 %. Among the pigments whose major congener was PCB-11, the total PCB concentration was in the range 0.0070–17 mg/kg, whereas for those whose major congener was PCB-52, it was 8.3–740 mg/kg. Thus, in general, the pigments whose major congener was PCB-52 had higher overall PCB concentration levels.

Among the phthalocyanine-type pigments, PCBs were detected in nine out of the 13 tested. The concentration levels ranged from 0.011 to 2.5 mg/kg, with none exceeding 50 mg/kg; however, two were above the 0.5 mg/kg level specified by the Japanese government as being PCB-containing. PeCBz and HxCBz were detected in pigment green (PG)7 and PG36, at concentration levels of 0.0035–8.4 mg/kg and 0.027–75 mg/kg, respectively. On the other hand, no PCBs were detected in pigment blue (PB)15 and the concentration levels of both PeCBz and HxCBz were all below 0.02 mg/kg. In the different PG7 samples, except for company E's PGL, which is mixed with PY3, PCB-209 (a decachlorinated substance) accounted for more than 92 % of the total PCB concentration, followed by PCB-208, PCB-206, and PCB-207 (all nonachlorinated substances), as well as a part of congener of octachlorinated substance which occupied less than several percent. Among the nonachlorinated substances, PCB-208 was present in the highest concentration, apart from in company D's S-1319. Furthermore, in the PG7 samples, high concentrations of PeCBz and HxCBz were also detected. In contrast, the concentration levels of PCB, PeCBz, and HxCBz were low in PG36, with dichlorinated substances detected as the major congeners.

Among the polycyclic-type pigments, PCB was detected in two out of four types, with pigment red (PR)254 and pigment violet (PV)23 having concentrations of 2.3 and 1.5 mg/kg, respectively, which were above the 0.5 mg/kg level. In the PR254 sample, PeCBz and HxCBz were also detected, but at levels below 0.004 mg/kg. The major congeners detected in this pigment type were dichlorinated PCB-8, PCB-13, and PCB15. These, in combination with PCB-4, PCB-6, and PCB-11, meant that 97 % of the total PCB content of PR254 was made up of dichlorinated congeners. The major congeners found in PV23 were the dichlorinated substances PCB-5 and PCB-12 as well as some tetrachlorinated substances such as PCB-56, PCB-77, and PCB-40. Although there was a small portion of mono and trichlorinated substances detected, the di- and tetra-substituted congeners accounted for 94 % of the total PCBs. The TEQ of PCB-77 was found to be 6.2 pg-TEQ/g. For the HT8-PCB column, it is slightly difficult to separate PCB-5 from PCB-8 and PCB-12 from PCB-13 because their relative retention times (RRT) is similar. However, the high concentrations of PCB-8 and PCB-13 in PR254 and those of PB-5 and PCB-12 in PV23 were identified from the single peaks by comparing the RRT of PR254 and PV23 based on chromatograms and values from literature (Matsumura et al. 2002) and comparing PCB-8 and PCB-12 with the relevant standards.

In 2010, Hu and Hornbuckle analyzed 33 pigments collected in Iowa, USA. PCBs were found in 15 of these, with concentration levels in the range 0.002–0.1983 mg/kg. Rodenburg et al. (2010) studied the amounts of PCB-11 contained in 20 colored consumer goods (newspapers, magazines, plastic products, etc.). PCB-11 was found in 15 of these, with concentration levels in the range 0.00011–0.038 mg/kg. The PCB concentrations found in the pigments examined in this study were found to be at similar or higher levels.

Byproduct of POPs in pigments

Azo-type paint 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 $NaNO_2$ or HCl and coupled with acetoacetanilide or 3-methyl-1-phenyl-5-pyrazoline. 3,3′-Dichlorobenzidine has a similar structure to PCB-11, and 2,2′,5,5′-tetrachlorobenzidine is similar to PCB-52. Therefore, it is plausible that pigments containing mainly PCB-11 are made from the former, and those containing mainly PCB-52 are made from the latter.

Meanwhile, PCB-35 and PCB-77 were also detected in the pigments whose major congener was PCB-11. The structures of PCB-35 and PCB-77 are the same as PCB-11, apart from additional chlorines at the *p*-position. Such structures would be the same as those resulting from the substitution of two amino groups of 3,3′-dichlorobenzidine with chlorine. This indicates that the diazonium salt, which is produced as a result

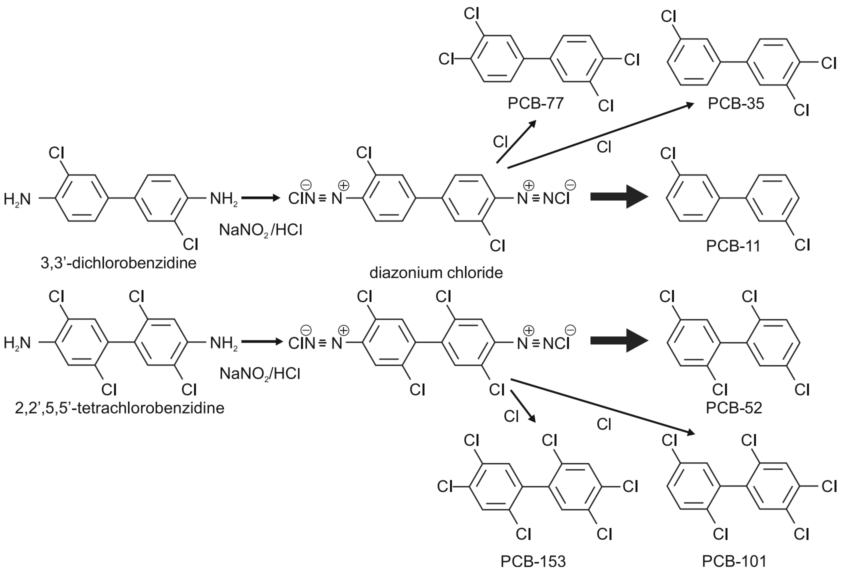

Fig. 1 Byproduct of PCBs in the manufacture process of azo-type pigments

of diazotizing 3,3′-dichlorobenzidine, would be reduced, and a diazonium radical would form. Nitrogen released from the diazonium radical would produce an aryl radical to which chorine would then be added, forming the byproducts PCB-35 and PCB-77 (Fig. 1). The progress of the radical reaction largely depends on temperature, pH, and the status of the catalyst, e.g., copper. It is speculated that this is why most of the byproduct consisted of PCB-11, with PCB-35 and PCB-77 only contributing slightly. Similarly, it is likely that PCB-101 and PCB-153 were detected in the pigments whose major congener was PCB-52 because substitution of the amino group of 2,2′,5,5′-tetrachlorobenzidine with chlorine by a similar mechanism would result in such byproducts (Fig. 1).

Phthalocyanine-type paint pigments

PG7 is manufactured by first producing copper phthalocyanine crude blue (PB15) and then chlorinating it. Methods for creating PB15 include the reaction of phthalic anhydride with urea and $CuCl_2$ and the reaction of phthalodinitrile with $CuCl_2$. The latter process tends to produce phthalocyanine pigments of higher purity and quality. This is thought to be due to the quantity and types of impurities in the PB15 and the difference in temperature during its chlorination.

Four different types of PB15 from four companies were tested, with no PCBs identified in any of the samples. In addition, the concentrations of PeCBz and HxCBz were all below 0.02 mg/kg, which were lower than those of PG7. These results suggest that the formation of POP byproducts does not occur during the PB15 development process, but rather in the subsequent chlorination step. Furthermore, all tested PG7 samples exhibited concentrations with the trends PeCBz < HxCBz and nonachlorinated biphenyls < decachlorinated biphenyl (PCB-209) and there was a tendency for highly chlorinated compounds to be predominant, with hardly any PCBs below octachlorinated substances detected. These results indicate that chlorination occurs first with dichlorobenzene and trichlorobenzene, which are the organic solvents used in the synthesis of PB15. PeCBz and HxCBz are subsequently formed by hyperchlorination of the chlorobenzenes, and finally, highly chlorinated PCBs are formed (Fig. 2). It is known that these chains of reactions progress as a result of radical reactions (Hu and Hornbuckle 2010; Liu et al. 2001). Thus, it is suspected that the quantities of POPs would be influenced by the amount of impurities, reaction temperature, and time.

Meanwhile, for PG36, of which only one sample was tested, the concentrations of PCB-209, PeCBz, and HxCBz were found to be much smaller than that of PG7, with dichlorinated congeners dominantly detected. This is thought to be because PG36 and PB15 are formed by halogenations with chlorine and bromine, and thus, the amounts of PeCBz and HxCBz were small owing to the low amount of chlorine, in addition to competition between bromination and chlorination.

Polycyclic-type paint pigments

PR254 is one of the diketopyrrolopyrrole pigments and is synthesized by heating and curing *p*-chlorobenzonitrile and succinate ester (e.g., diethyl succinate) (Faulkner and Schwartz 2009; Shamekhi and Nourmohammadian 2012). Most of the detected PCB congeners were dichlorinated substances, all of which had a single chlorine substituent on either aryl group of the biphenyl backbone. No congener with two chlorine substituents on the same aryl group was detected. These results of the congener pattern analysis indicate a strong influence of the biphenyl formation mechanism as a result of the radical reaction of *p*-chlorobenzonitrile.

PV23, also called dioxazine violet, is synthesized by the warming and ring-closing reaction of 3-amino-9-ethylcarbazole and 2,3,5,6-tetrachlorobenzoquinone in *o*-dichlorobenzene (Faulkner and Schwartz 2009). Almost all PCBs found in these samples were dichlorinated or tetrachlorinated substances, and their major congeners (PCB-5, PCB-12, PCB-56, PCB-77, PCB-40) all had two adjacent chlorine atoms on one of the aryl groups of the biphenyl backbone. This strongly suggests that there is an influence of biphenyl formation as a result of the radical reaction of *o*-dichlorobenzene. The congener concentrations of the tetrachlorinated substances were found to be in the order PCB-56 > PCB-77 > PCB-40. This indicates that there is also an influence due to the steric structure. Furthermore, because no PeCBz or HxCBz were detected, it is speculated that chlorination of *o*-dichlorobenzene did not occur.

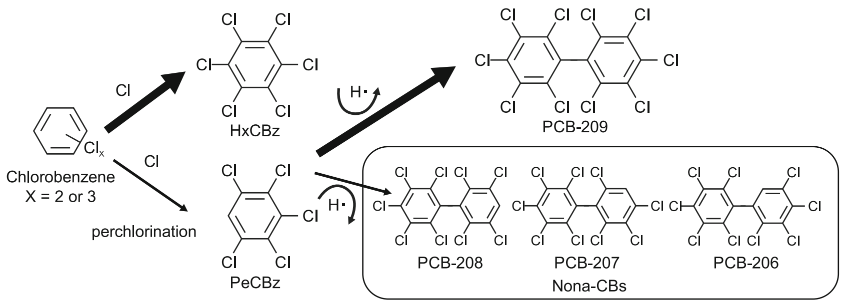

Fig. 2 Byproduct of PCBs in the manufacture process of phthalocyanine-type pigments

However, this study only tested one sample each for PV23 and PR254 and there are still many points regarding formation of PCBs as byproducts that need to be elucidated by further investigation.

Seasonal variation in PCB levels in ambient air

The monthly variations in ambient air concentration levels of PCB-11, PCB-52, and PCB-209, which were characteristically high in azo-type and phthalocyanine-type pigments, were measured. Figure 3 shows the results for the urban area of Sapporo (April 2005 to March 2011) and the industrial area of Muroran (April 2006 to March 2011). The total PCB levels for the 6 years in Sapporo were in the range of 69–1,200 pg/m^3, with a mean level of 360 pg/m^3. The mean levels of PCB-11 and PCB-52 were 11 and 25 pg/m^3, respectively. PCB-52 tended to be higher; however, after July 2010, PCB-11 showed higher levels. For the 5 years of testing in Muroran, the total PCB levels were found to be in the range 33–190 pg/m^3, with a the mean level of 83 pg/m^3, which was much lower than for the urban area of Sapporo. The mean levels of PCB-11 and PCB-52 were 8.0 and 2.9 pg/m^3, respectively. The level of PCB-11 was similar in both cities ($p<0.001$), whereas the concentration of PCB-52 measured in Muroran was 10 to 50 % that of Sapporo. Furthermore, the concentrations of total PCBs, PCB-11, and PCB-52 tended to be higher in the summer months in both cities, demonstrating the impact of elevated temperature on volatilization of PCBs in ambient air (Wania et al. 1998). The concentration of PCB-209 was less than 0.1 pg/m^3 in both cities, with no seasonal variation evident. In both cities, the other congeners present were mainly PCB-28, 52, 101, 110, 118, 138, and 153, with indications that the PCBs in the air were strongly linked to PCB technical mixtures. In Table 5, the levels of PCB-11, PCB-52, and total PCBs in ambient air recorded in the present study were compared with those of other locations. The ranges in both cities were similar to or slightly higher than those reported for Chile (Pozo et al. 2012), Azerbaijan (Aliyeva et al. 2012), Turkey (Cindoruk and Tasdemir 2010), northern South China Sea (Li et al. 2012b), and a nationwide survey conducted by the Ministry of the Environment in Japan (2013). While the PCB levels were lower than those in the USA (Basu et al. 2009; Hu et al. 2008), the levels were higher than those in clean areas such as Antarctica (Piazza et al. 2013; Li et al. 2012a) and the background area of China (Wu et al. 2011).

Figure 4 shows the ratio of PCB-11 to dichlorinated substances (PCB-11/DiCBs), PCB-52 to tetrachlorinated substances (PCB-52/TeCBs), and PCB-209 to total PCBs (PCB-209/Total PCB). During the sampling period, the

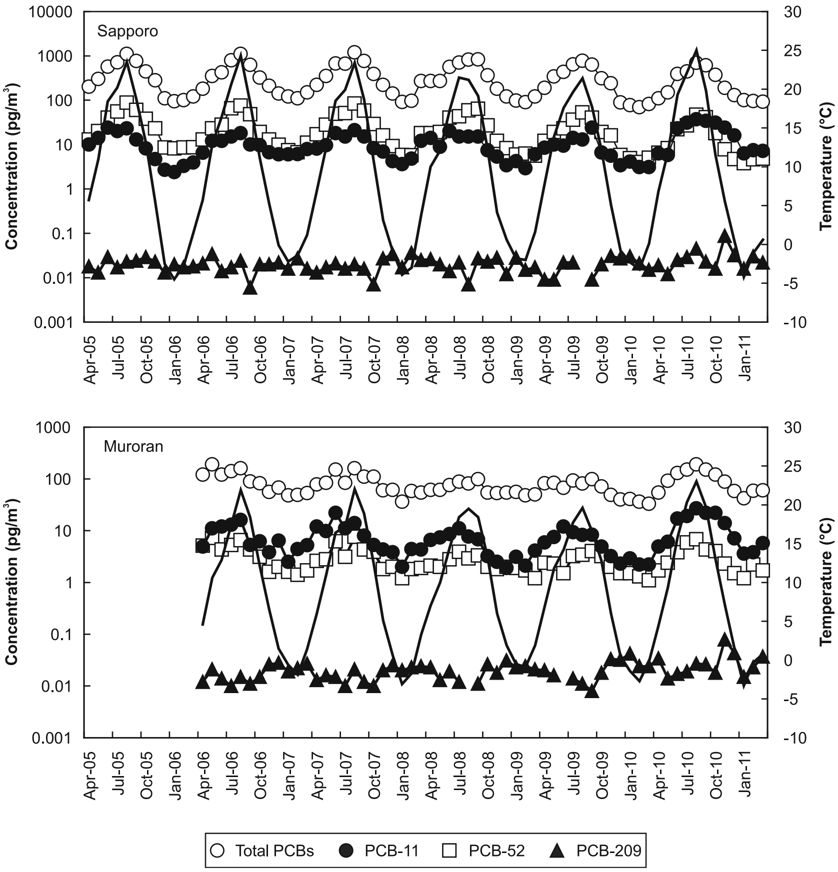

Fig. 3 Monthly variations of total PCBs (*white circle*), PCB-11 (*black circle*), PCB-52 (*white square*), and PCB-209 (*black up-pointing triangle*) congeners in ambient air samples and mean air temperature during sampling (*solid line*). PCB-209 was not detected in August 2009 in Sapporo and in June 2009 and August 2008 in Muroran

Table 5 Comparison of PCB-11, PCB-52, and total PCB concentrations (picogram per cubic meter) in ambient air from various locations in the world

Location	Year	PCB-11	PCB-52	ΣPCB	References
Sapporo, Japan	2005–2011	2.4–37	3.8–88	69–1,200 (Σ^{209}PCBs)	Present study
Muroran, Japan	2006–2011	1.9–27	1.1–7.6	33–190 (Σ^{209}PCBs)	Present study
Great Lake, USA	2004–2007	n.d.–306.91	NA	6.81–7,264.88 ($\Sigma^{107\text{-}124}$PCBs)	Basu et al. 2009
northern South China Sea	2005	NA	7.47–28.5	32.3–167 (Σ^{12}PCBs)	Li et al. 2012b
Chicago, USA	2006–2007	n.d.–140	NA	75–5,500 (Σ^{209}PCBs)	Hu et al. 2008
Concepción, Chile	2007	NA	NA	40–350 (Σ^{48}PCBs)	Pozo et al. 2012
China(background)	2007–2008	NA	0.6–6.3	4.0–27.5 (Σ^{7}PCBs)	Wu et al. 2011
Azerbaijan	2008	NA	2–44	11–209 (Σ^{7}PCBs)	Aliyeva et al. 2012
Bursa, Turkey	2008–2009	NA	22.01–33.11	316–570 (Σ^{83}PCBs)	Cindoruk and Tasdemir 2010
Terra Nova Bay, Antarctica	2009–2010	NA	0.061–0.451	1.199–15.230 (Σ^{126}PCBs)	Piazza et al. 2013
King George Island, Antarctica	2009–2010	0.96–1.59	0.056–0.21	26.74–45.08 (Σ^{205}PCBs)	Li et al. 2012a
Japan	2011	NA	NA	17–660 (Σ^{209}PCBs)	Ministry of the Environment 2013

NA not available, *n.d.* not detected

PCB-52/TeCBs ratio was 18–30 % (mean, 26 %) in Sapporo and 13–20 % (mean, 16 %) in Muroran. In both cities, the ratio remained fairly constant throughout the year. The PCB-52 contribution was larger in the urban area of Sapporo. Meanwhile, the PCB-11/DiCBs ratio was 36–70 % (mean, 50 %) in Sapporo and 28–79 % (mean, 52 %) in Muroran. In both cities, the ratio showed similar seasonal variations, in particular, the PCB-11 contribution tended to be higher in the summer. The value for PCB-209/Total PCBs was 0–0.05 % in Sapporo and 0–0.1 % in Muroran, with contributions becoming particularly high in winter. PCB-52 is contained within PCB technical mixtures at a certain concentration, and it makes up 11–39 % of the tetrachlorinated substances in kanechlor, 9.5–34 % in aroclor, 9.2–51 % in clophen, and 25 % in sovol (Takasuga et al. 2006). As it is generally believed that the PCB pollution in environmental samples is largely due to PCB technical mixtures, the stable PCB-52/TeCB ratio during the sampling period in both cities indicates that PCB-52 in ambient air originates from such mixtures. It is also considered that the higher contribution of PCB-52 in Sapporo, compared to Muroran, is further evidence of the strong influence of PCB technical mixtures,

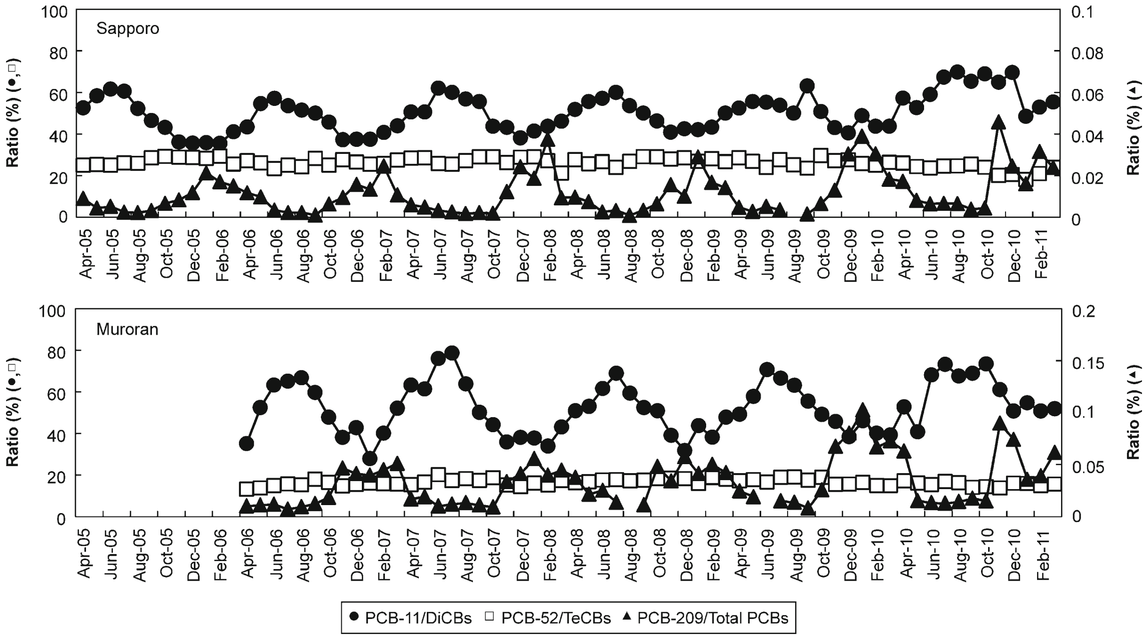

Fig. 4 Monthly variations in the ratio of PCB-11/DiCBs (*black circle*), PCB-52/TeCBs (*white square*), and PCB-209/Total PCBs (*black up-pointing triangle*)

which are mainly composed of highly chlorinated substances such as KC500. On the other hand, the large variations in PCB-11/DiCB ratio confirm that the detected PCB-11 did not originate from PCB technical mixtures, suggesting a contribution from azo-type pigments. The likely reason for PCB-209/Total PCBs increasing in winter, while PCB-11/DiCBs decreased, is the higher volatility of PCB-11. It is unlikely that PCB-209 would be volatilized from the soil into the air even in the warmer months, and so a relatively stable concentration is maintained all year round. On the other hand, the concentration of total PCBs (most of which are thought to come from PCB technical mixtures) decreased in winter, resulting in the observed increase in PCB-209/Total PCBs. With PCB technical mixtures consisting of only a small amount of PCB-209 (~0.11 %, Takasuga et al. 2006), the seasonal change in PCB-209/Total PCBs demonstrates the possibility that PCB-209 is derived from sources other than PCB technical mixtures. However, the concentration of PCB-209 found was extremely low and it is unclear whether it was derived from pigments or combustion sources.

Conclusion

In this study, we investigated the concentrations and congener patterns of PCBs, PeCBz, and HxCBz included in various pigments. The congeners of the PCBs included in each of the pigments were found to be significantly different from those of PCB technical mixtures, with the number of congeners detected being less than 20. PeCBz and HxCBz were also detected in phthalocyanine-type pigments. Pollution by these POPs was shown to be strongly related to the ingredients of pigments, as well as the organic solvents used in their production. The total PCB concentrations in pigments were generally only a few milligrams per kilogram, but some were also found to have levels over the 50 mg/kg level that was restricted by the POP convention. Some also included DL-PCBs, which had toxicity levels similar to dioxin itself. PCBs in the air were monitored over 5 years in two cities, with the concentrations of PCB-11 found confirming that PCBs likely derived from pigments were entering the atmosphere.

In Japan in 2010, approximately 29,000 tons of organic pigments were produced or imported, with an estimated 7,000- tons being azo or phthalocyanine-type pigments that included PCBs. Industrial production of PCB technical mixtures and chlorobenzenes has already ended, with countries now working to abolish them in accordance with the POP convention. However, significant amounts of PCBs, PeCBz, and HxCBz inadvertently produced along with pigments are used throughout the world and subsequently released into the environment. The particular PCB congeners contained in pigments are unique, with much unknown about their toxicity, persistence, and dynamic state in the environment. Therefore, in addition to reducing the levels of these materials included in pigments, it is also desirable to promote monitoring and evaluation of the toxicity of PCB congeners derived from pigments.

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