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Investigation of Isomer Specific Polychlorinated Biphenyls in Printing Inks

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Polychlorinated biphenyls (PCBs) are wellknown persistent environmental pollutants. They can bioaccumulate and cause toxic biological effects. Applications of PCBs, in both closed and open systems, have been forbidden in many countries for about 15 years. Furthermore, PCBs have not been produced commercially for several years. However, an incidental production of PCB, as by-product, may take place during the synthesis of chlorinated solvents, chlorinated benzene, glycerol, pigments and so on (Hanneman 1982; DCMA 1982; Hodges et al. 1983; Erickson 1986; De Voogt and Brinkman 1989; Sistovaris et al. 1990).

Since heavy metals have been recognized to pollute the environment, many of the metal based inorganic pigments in chemical products have been substituted by organic synthetic pigments. A number of such pigments have been shown to contain small amounts of PCBs (DCMA 1982; Sistovaris et al. 1990). Organic synthetic pigments are used in various types of chemical products: printing inks, paints, cosmetics, etc. Printing inks are widely used in many industries, for example, for serigarphy on paper, paperboard, glass, metal, ceramics, and electric as well as electronic articles. The information about the pigments present in printing inks is generally not available. Moreover, PCB impurities present in the pigments may be unknown. Thus, to estimate emission of PCBs through the uses of printing inks, a knowledge of levels of PCBs in these products is required. In a pilot study, 11 printing inks, which are used in bulk in Denmark, were analysed for the contents of isomer specific PCBs. The results of the above mentioned study are reported in the present paper.

MATERIALS AND METHODS

4,4′-dichlorobiphenyl (PCB 15), 2,4′,5′-trichlorobiphenyl (PCB 31), 2,5,2′,5′-tetrachlorobiphenyl (PCB 52),

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2,4,5,2',5'-pentachlorobiphenyl (PCB 101), and 2,4,5,2',4',5'- hexachlorobiphenyl (PCB 153) were from Cambridge Isotope Laboratory, USA. p,p'-DDE was from Aldrich, Germany. Eleven serigraphy printing inks, randomly chosen from a group of 29 printing inks which were previously investigated for organic solvent content (Rastogi 1991), were analysed for isomer specific PCBs (Table 1) in the present study.

Table 1. Identification of the serigraphy printing inks analysed.

Sample No.	Colour	Field of application	Manufacturing Co.
695	Yellow	Electric and electronic articles	1
742	Red	Paper and paperboard	2
744	Green	Paper and paperboard	2
746	Yellow	Paper and paperboard	3
750	Green	Paper and paperboard	4
757	Yellow	Paper and paperboard	5
758	Green	Electric and electronic articles	5
769	Black	Paper, paperboard, metal, glass and plastic	6
770	Yellow	Paper and paperboard	6
771	Brown	Paper, paperboard,electric and electronic articles	7
772	Black	Serigraphy on paper and paperboard	7

PCBs from approximately 10 g printing ink samples were extracted using an earlier described method (Storr-Hansen and Rastogi 1988). p,p'-DDE (final concentration 30 ppb) was used as an internal standard (IS). The final volume of PCB extract, including IS, was 1 ml.

The analysis of isomer specific PCBs in the sample extracts was performed by GC-mass spectrometry (MS). The GC conditions were as follows. Column: DB-5, 50 m x 0.25 mm (i.d.), 0.1 μm (df). Temprature program: 1 min at 90°C, 25°C/min to 180°C, 2 min at 180°C, 1.5°C/min to 225°C, 3°C/min to 280°C, 5 min at 280°C. Carrier gas: He, total flow 50ml/min, column headpressure 175 kPa. Injector: on column, 250°C. Injection volume: 2 μl.

Selective ion monitoring (SIM) by MS was performed for the identification of dichloro-, trichloro-, tetrachloro-, pentachloro- and hexachlorobiphenyls. The masses and their relative abundance used for the identification of respective PCB isomers were as described by Erickson (1986). The mass with 100% relative abundance was used for the quantitation of respective PCB isomer. The MS instrument used was Finnigan INCOS 50, in positive ion mode. Each mass was scanned for 0.091 second. All the samples were analysed in duplicate. To prepare Calibration curves for the quantitation of PCB isomers, standards of PCB 15, PCB 31, PCB 52, PCB 101 and PCB 153 in concentrations 10-200 ppb were analysed. Only linear range of the calibration curves were used for the quantitation of PCBs.

RESULTS AND DISCUSSION

The analysis of PCBs in printing ink extracts by GC-MS employing SIM revealed that 7/11 printing inks contained isomers of dichloro-/tetrachloro-/pentachloro-/hexachlorobephenyl (Table 2). The detection limits of PCB standards were shown to be approximately 5 ppb. Four of the samples analysed were shown to contain dichlorobiphenyl, none of the samples contained trichlorobiphenyl, 4 samples contained tetrachlorobiphenyl, 3 samples contained pentachlorobiphenyl, and 1 sample contained hexachlorobiphenyl. Two isomers of dichlorobiphenyl, only one isomer of tetrachlorobiphenyl, 7 isomers of pentachlorobiphenyl, and 3 isomers of hexachlorobiphenyl were identified in the printing inks (Table 2). On the basis of the retention times of the PCB standards used in the present study, it was confirmed that the tetrachloro- biphenyl isomer identified in the printing inks was PCB 52, one of the identified pentachlorobiphenyl isomer was PCB 101, and one of the hexachlorobiphenyl isomers identified was PCB 153. No PCBs were detected in sample nos. 742, 757, 769 and 770.

Quantitation of PCB isomers was performed by using peak areas of ions with 100% relative abundance. Calibration curves for all PCB standards were shown to be linear in the concentration range 10-100 ppb. The relative standard deviation as well as day to day variation of PCB quantitation was found to be $< \pm 8\%$. The recovery of PCBs from a sample (no. 744), spiked with 25 ppb of the PCB standards, was shown to be >76%. The PCB contents of the printing inks analysed are described in Table 2. The results are not corrected for recovery. As described in Table 2, the printing inks contained 1-180 ppb of various PCB isomers. Total PCB content in the printing inks was found to be 1-184 ppb.

Sistovaris et al (1990) have demonstrated impurities of dichloro-, trichloro-, tetrachloro-, pentachloro- and hexachlorobiphenyls in dioxazine type pigments as well as

Table 2. Contents of isomer specific of PCBs in printing inks.

Sample No.	PCB content ng/g (ppb) Di-chloro-	Tetra-chloro-	Penta-chloro-	Hexa-chloro-	Total
695	0.8 (1)	n.d.	4.5 (1)	n.d.	5.3
744	n.d.	1.7 (1)	30.3 (7)	37.1 (3)	69.1
746	15.5 (1)	n.d.	n.d.	n.d.	15.5
750	n.d.	11.1 (1)	n.d.	n.d.	11.1
758	1.0 (1)	180.4 (1)	2.8 (3)	n.d.	184.2
771	78.9 (1)	n.d.	n.d.	n.d.	78.9
772	n.d.	1.0 (1)	n.d	n.d.	1.0

Number of PCB congeners identified are described in parenthesis. n.d. = not detected.

in azo-pigments prepared from chloroanilines and chlorobenzidines. Furthermore, Dry Color Manufacturing Association (1982) has described the impurity of 3,3'-biphenyl in phthalocyanine green, phthalocyanine blue and in diarylide yellow. Thus, it may be argued that the pigments present in the printing inks were the sources of PCBs in these products.

Printing inks may be considered as diffuse sources of new PCB release into the environment, because these products are used in various industries. The PCBs from the printing inks may be emitted during the printing processes as well as through the waste from the industries, which use printing inks. Printed paper and paperboard may be significant sources of release of PCBs into the environment, because PCBs may be emitted not only during the printing processes, but also during the recycling of printed paper and paperboard. Furthermore, PCBs from printed material may be transferred and accumulate in recycled paper. It has been suggested that recycling of PCB containing selfcopying paper was the source of PCB in recycled paper and paperboard (De Voogt et al. 1984; Storr-Hansen and Rastogi 1988). The use of PCB in selfcopying paper has been forbidden for several years. Therefore, it is presumed that the load of PCBs in recycled paper may not increase anymore. To ensure that recyled paper and paperboard do not contain unreasonable high amounts of PCBs, due to printed material as a new source of PCB, a regular monitoring of PCB in these products may be important.

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