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Polychlorinated Biphenyls and Heavy Metal Levels in Recycled Paper for Household Use

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The interest in the use of recycled products has been growing for the past many years. Thus, the dangerous chemicals once in use, now forbidden, may persist in the recycled products. This may pose a problem of bioaccumulation of poisonous chemicals as well as a threat to the philosophy of the use of recycled products.

The non-carbon copying paper containing 2-6% polychlorinated biphenyls (PCB's) by weight (Kuratsune and Masuda 1972, Van Esche et al. 1972) has been commonly used in the nineteen sixtees. Although the use of non-carbon copypaper has been forbidden for the past 15 years, De Voogt et al. (1984) demonstrated that recycled papers contained small amounts of PCB's similar to those used for the production of non-carbon copypaper. Thus the old discarded archives may be one of the sources of PCB's in the recycled papers.

Besides PCB's cadmium (Cd), mercury (Hg), lead (Pb) and other heavy metals from the print-inks (colours) may also be introduced to the recycled paper. The aim of the present study was to evaluate, on behalf of Danish Environmental Protection Agency, the levels of PCB's, Cd, Hg and Pb in the recycled paper for the household use. For this purpose we undertook a pilot study for the determination of the contents of PCB's, Cd, Hg and Pb in recycled papers that were available in the Danish market.

MATERIALS AND METHODS

The non-recycled and recycled papers analysed in the present study are described in Table 1. The Danish EPA, after the market survey, selected the paper samples and obtained them directly from the manufacturer/importer to avoid contamination from other sources.

One of the recycled paper samples was produced in Denmark and others were imported to Denmark from various other European Countries (Table 1).

All the glasware used for PCB-analysis were cleaned with chromic acid. The glasware used for heavy metal analysis were cleaned with

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Table 1. Non-recycled and recycled papers analysed.

Sample no.	Produced in	Sample description
6-0813	W. Germany	Papertowels, white-red checks (1)
6-0814	Sweden	Papertowels, white (1)
6-0815	Denmark	Toiletpaper, light gray (1)
6-0816	Netherland	Toiletpaper, white (1)
6-0817	Finland	Toiletpaper, light yellow (1)
6-0818	Denmark	Toiletpaper, white (2)
6-1003	Yugoslavia	Toiletpaper, white (1)

(1) - Recycled. (2) - Non-recycled.

nitric acid. The chemicals used were of the purest quality available. Each sample was analysed in duplicate. For the PCB-analysis, five grams of paper was soxhlet extracted with 100 ml n-hexane for 12 hours. The extract was dried over anhydrous Na_2SO_4 and concentrated to 2 ml by distillation. The concentrated extract was loaded on a 2x33 cm column packed with 19 g florisil which was preactivated 12 hours at 420°C followed by deactivation with 1% (w/w) redistilled water. The top 1 cm of the column packing was anhydrous Na_2SO_4. The PCB's were eluted with 200 ml n-hexane of which the last 150 ml were collected and concentrated to approximately 1 ml by distillation. The eluate was then further concentrated to dryness under a gentle nitrogen stream at room temperature. The dried material was redissolved in 1 ml n-hexane containing 50 ng/ml hexachlorobenzen as internal standard. Gaschromatography of 1 ul of the redissolved eluate was then performed on a Hewlett-Packard 5880A gas chromatograph equipped with a ^{63}Ni electron capture detector, under the following conditions:

Column: 25 m fused silica capillary column, 0.32 mm i.d., coated with 0.52 um 5% phenylmethylsilicon.
Temperature: 60°C-150°C at a rate of 15°C/min, 150°C-190°C at 4°C/min and 190°C-280°C at 8°C/min, and finally 20 min. at 280°C.
Carrier gas: N_2, flow 3 ml/min.
Injector: On column.
Detector: ECD, 300°C.
Make-up gas: N_2, 35 ml/min.

The gas chromatogram of PCB's in the recycled papers were found to be similar to those obtained by De Voogt et al. (1984) for PCB's in the household papers and for the standard Aroclor 1242 (Figures 1 and 2).

Therefore quantitation of PCB's in the paper samples was performed according to the method of De Voogt et al. (1984) by integrating areas of 27 peaks of standard Archlor 1242.

The above mentioned method used for the analysis of PCB's revealed a recovery of 79% of the 100 ppb Aroclor 1242 added to the non-

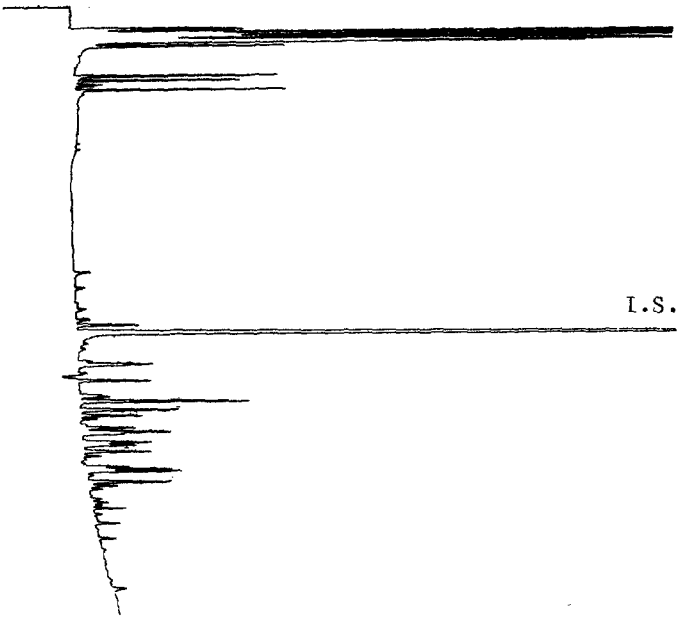

Figure 1. Capillary chromatogram of PCB standard Aroclor 1242. I.S. is internal standard hexachlorobenzene.

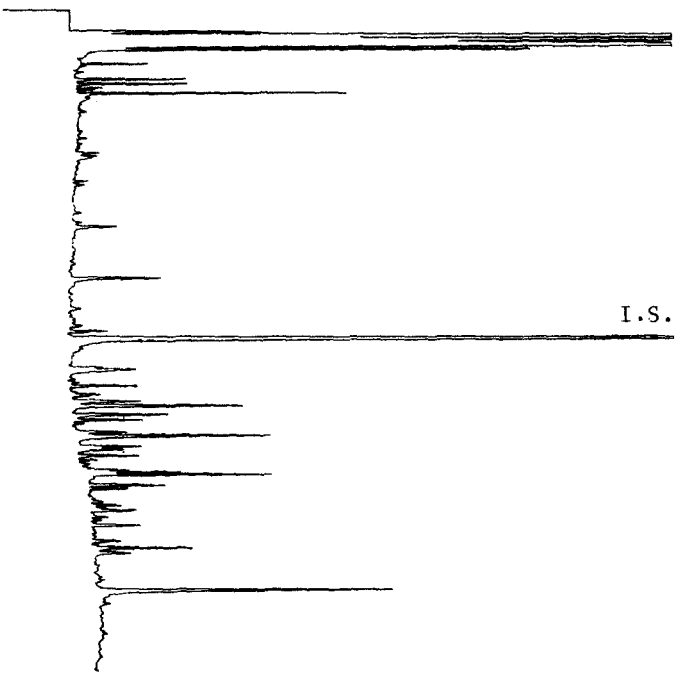

Figure 2. Capillary chromatogram of sample no. 6-0814. I.S. is internal standard hexachlorobenzene.

recycled paper. The relative standard deviation of the method was found to be below 10%. The detection limit of the method was approximately 20 ppb. The EC-detector showed a linearity in the range of 99 ng/ml - 990 ng/ml Aroclor 1242. Therefore, the sample extracts were either diluted or concentrated before quantitation to fit the linear curve.

For the heavy metals analyses one gram of the paper was divided in small pieces and dry ashed for 2 hours at 420°C in a porcelain crucible. After cooling down to room temperature, the sample was carefully transferred to a Kjeldahl-flask. The crucible was rinsed 3 times with 6M HCl (total 15 ml) and the washings mixed with the ashed sample. The sample in 6M HCl was then refluxed for 20 min. at 180°C. This was filtered through a Whatman No. 1 filterpaper, prewashed with 6M HCl, and the filter was then washed with 25 ml redistilled water. The filtrate and washing were combined and made up to 50 ml with redistilled water.

The content of Pb and Cd in the 6M HCl extracts of papers were determined by the use of graphite furnace-atom absorption spectrophotometry, and Hg was determined by the use of mercury hydride system with atom absorption spectrophotometer. The detection limits of Cd, Hg and Pb were 10 ppb, 50 ppb and 100 ppb respectively. The standard deviation of the method was <5%. The recovery of Cd, Hg and Pb from the non-recycled paper spiked with these metals were 98%, 88% and 89% respectively.

All the recovery studies were made in duplicate.

RESULTS AND DISCUSSION

The contents of PCB's and heavy metals in the investigated samples as a mean of double determinations are described in Table 2. The results are not corrected for the recoveries. All the recycled papers analysed in the present study were found to contain PCB's (mean 135 ppb), but no PCB's were traced in the non-recycled paper analysed.

The chromatographic patterns of PCB's in the recycled papers were found to be similar to those obtained by De Voogt et al. (1984) for the recycled papers and paperboard samples. However, quantitative analysis revealed that the content of PCB's in the samples under the present study were 10 - 100 times lower than those obtained by De Voogt et al. (1984). The PCB level in the recycled papers analysed in the present study were comparable with the levels of PCB's in the household paper products (Williams et al. 1979). Thus, the results of the present study may indicate that the PCB's level in the recycled paper has been constant or they were declining in the past 8 years. In any case, it may be desirable to follow the concentrations of PCB's in these products, in order to evaluate the contribution of PCB's from recycled paper to the environment.

The analysis of heavy metals revealed that 2/6 recycled papers

Table 2. The contents of PCB's and heavy metals in the non-recycled and recycled papers analysed (6-0818 non-recycled).

Sample no.	PCB's (ppb)	Cd (ppb)	Hg (ppb)	Pb (ppb)
6-0818	n.d.	66	n.d.	118
6-0813	113	32	98	189
6-0814	52	n.d.	n.d.	453
6-0815	93	n.d., 18 20, 13	n.d.	7730, 16730, 10800, 15300
6-0816	212	34	386	568
6-0817	75	n.d.	n.d.	322
6-1003	262	14	n.d.	857

contained Hg and 4/6 recycled papers contained Cd. Pb was found to be present in all the investigated samples. The results of double determinations of heavy metals in the sample 6-0815 were significantly different from each other (Table 2). Therefore, the sample was subjected to reanalysis of heavy metals. All the four results are shown in the Table 2. It seems that the paper sample 6-0815 is not homogeneous with respect to heavy metals content. However, it can not be ruled out that the sample 6-0815 contains some substances which interfere in the analysis of heavy metals.

To our knowledge there is no report available on the analysis of heavy metals in recycled papers. Moreover, our study included only one reference sample (non-recycled paper). Therefore, the evaluation of the significance of heavy metal content in the recycled paper compared to that in the non-recycled paper must be done with great caution. The results of the present study indicate that the Pb content in the recycled papers is much higher than that in the non-recycled paper. Since Pb is toxic, and can be absorbed through the skin (Rastogi and Clausen 1976), the regulation of Pb content in recycled paper for household use must be considered.

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