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Pivnenko, Kostyantyn; Eriksson, Eva; Astrup, Thomas Fruergaard

POLYCHLORINATED BIPHENYLS (PCBs) IN WASTE PAPER FROM DANISH HOUSEHOLD WASTE

K. PIVNENKO[1], E. ERIKSSON[1] and T. F. ASTRUP[1]
[1] Department of Environmental Engineering, Technical University of Denmark, Miljøvej Building 113, DK-2800 Kgs. Lyngby, Denmark
*Corresponding author: kosp@env.dtu.dk, tel. 45251602, fax. 45932850

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Abstract

Between 1930 and 1993 Polychlorinated Biphenyls (PCBs) were extensively used in a variety of applications throughout the world. The applications were generally divided between closed (e.g. electrical transformers) and open. One of the most important open applications was as a solvent in carbonless copy paper. Although production and use of PCBs is heavily restricted in most of the countries, prolonged use of products containing PCBs as well as their physical-chemical characteristics and persistent nature allowed them to remain in the environment. The aim of the present paper was to provide an estimation of PCB concentrations in the waste paper samples from Danish household waste. Additionally, the goal was to estimate total amount of PCBs present in European paper and discuss implications it may have on paper recycling. Paper samples coming from Danish household waste were sorted into more detailed fractions to provide the composition of the waste flow. PCBs were quantified by means of gas chromatography coupled with mass spectrometry (GC-MS) in all of the samples collected. Total concentrations of PCBs in paper and board ranged from 18 to 31 μg/kg. Results extrapolated to the total of European paper show that PCBs in paper represent relatively small amount when compared to other open type applications. Contamination of food with PCBs could potentially be of concern and should be assessed in more details.

1- INTRODUCTION

Polychlorinated biphenyls (PCBs) is a group of organic chemicals in which chlorine is attached to a biphenyl molecule composed of two benzene rings (Figure 1). PCBs may contain from 1 to 10 chlorine atoms in the molecule. Apart from the degree of chlorination (i.e. total number of chlorine present) of a PCB, the PCBs will vary depending on the position of the chlorine atom(s). Taking into account the number of chlorines and their position on the biphenyl ring(s) in a PCB molecule a total of 209 congeners of PCBs exist. Mixtures of PCBs are also known by their trade names, among which Aroclor is the most common [1]. It has been shown that Aroclor may contain up to 157 PCB congeners [2], which are expected to be found in the environment. After the first commercial manufacturing of PCBs their use spread throughout industrial sector and commercial products. In the period between 1930 and 1993 more than 1.3 million tonnes of PCBs were produced worldwide, with the USA being the largest single producer accounting for almost half of the figure by weight [3]. PCBs applications can be divided in closed and open applications. Closed would signify applications where environment or users are not directly exposed to PCBs (e.g. electric transformers, capacitors, hydraulic compressors, etc.) in contrast to open applications (e.g. paint, building insulation, carbonless copy paper, flame retardants, etc.). Most of the PCB mixtures were used in closed applications, accounting for approx. 79% of the global production [4]. It has been estimated that between 13% and 16% of the original PCBs still remain in use – mainly in closed systems [5]. Release of PCBs is associated with their production and consumption or the direct emissions from thermal processes (e.g. electricity production through combustion). Main source of direct emissions is waste incineration, although in Europe levels of PCBs release decreased dramatically (approx. 80%) to 3 tonnes per annum in the period 1990-2011 [6].

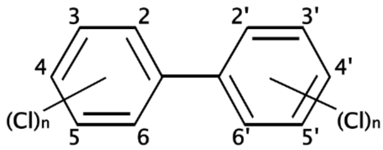

Figure 1: Chemical structure of PCBs.

PCBs have been characterized as Persistent Organic Pollutants (POPs) and their production was banned in the USA in 1979. Following the trend, worldwide production was gradually decreased until it was almost ceased at the beginning of the 1990 [3]. Nevertheless, equipment and products containing PCBs are still in use worldwide. According to the Stockholm Convention on POPs, signed by 152 countries, complete environmentally sound management of PCBs should be achieved by the year 2028. The terms of the convention state that articles with PCB content above 0.005% are regarded as PCB containing articles and should be managed accordingly [5]. Due to analytical challenges associated with identification and potential quantification of all 209 PCBs, lists of indicator congeners have been proposed. Commonly used list of six indicator PCBs (CB28, 52, 101, 138, 153 and 180) – PCB6, was initially proposed by the German Standardization Organization (DIN 51527-1). This list covers PCBs with high concentrations in technical mixtures and wide range of chlorine atoms (3 to 7 chlorine atoms per molecule). The list, expanded to include CB118, is generally used in EU for analysis of PCBs in environmental and food samples [7]. Since by measuring only the seven congeners (PCB7) not all of the PCBs potentially present in a sample are accounted for a correction factor had to be proposed. Commonly used approach for a correction factor calculations would be calculating the relative presence of PCB7 in the most commonly used technical mixtures of PCBs [7]. This approach shows that by multiplying the PCB7 concentration found in any environmental sample by a factor ranging from 2.5 to 8.1 (mean 4.6), the total concentration of PCBs in a sample can be estimated. Alternatively, the share of PCB7 in the global PCBs production may be taken into account [3], which would result in a correction factor of 5.6.

Commercial PCBs mixtures with approx. 42% of chlorine (Aroclor 1242) were widely used in the manufacture of mechanical copy paper [8]. PCBs mixture was used as solvent in the microcapsules used in carbonless copy paper (Figure 2). During recycled paper reprocessing burst microcapsules would release PCB-carrying ink which would attach to pulp and particulate matter. The largest portion of PCBs would remain in the final paper product, while significantly smaller amounts would be released into wastewater or would vaporize at paper drying step [9]. Release of PCBs through wastewater and their accumulation in the receiving water bodies has received certain attention, e.g. the case of Fox River, Wisconsin, USA [10,11]. In this case high number of paper mills that produced or recycled carbonless copy paper in period 1954-1971 without proper PCB monitoring of their effluents resulted in extensive contamination of the river sediment. The remediation of sediment is part of the US EPA Superfund project and is still in the active phase [12].

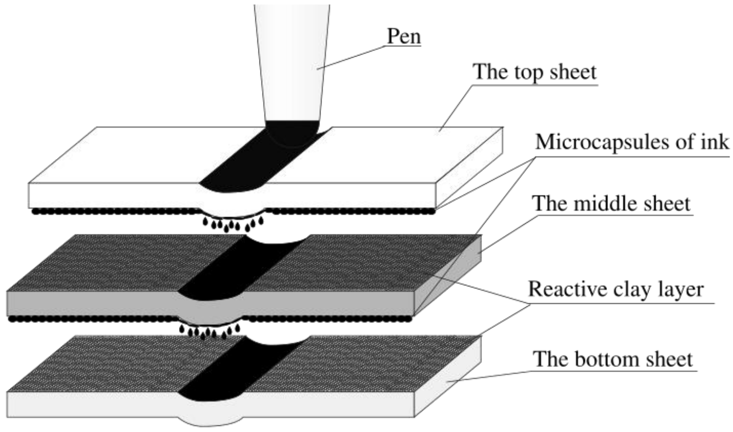

Figure 2: Basic principles of carbonless copy paper operation [13].

The aim of the present work was to estimate the PCB quantities in paper and board derived from Danish household waste. Based on the results, preliminary estimations regarding the total amounts of PCBs present in paper in Europe should be drawn. Additionally, the goal was to evaluate the potential implications presence of PCBs may have on the recycling of waste paper and board.

2- MATERIALS AND METHODS

2.1 Paper samples

Paper and board samples derived from Danish household solid waste. Initial samples were manually sorted into more detailed fractions based on the function of paper (e.g. advertisements) or its physical characteristics (i.e. board). Sorted samples of paper and board were shredded to particle size < 4 mm. For each of the fractions a representative subsample of shredded paper and board would be taken, lyophilized (CoolSafe 100-9 Pro, Labogene, Denmark) and stored in sealed glass containers at -20°C for before being analysed.

2.2 Quantification of PCBs

A sub-sample of 2 g of dry paper or board was extracted using Microwave-Assisted Extraction (MAE) performed on an Multiwave 3000 SOLV Microwave Platform System (Anton-Paar). The sample was extracted in n-hexane as a solvent at 120 °C for 40 min. After procedure, the extraction vessel was cooled down and the extracts passed through a Solid Phase Extraction (SPE) step to assure a clean-up of the solution. The chromatographic separation was achieved on an Agilent 6890 gas chromatographer with splitless mode injection. Helium was used as carrier gas with a 1 ml/min constant flow. Detection was achieved on an Agilent 5975C triple-axis mass-selective detector operated in SIM mode. The achieved detection limit was 0.33 μg/kg DW.

3- RESULTS AND DISCUSSION

The physical composition of the waste paper samples collected and the concentration of PCB7 in the respective fractions are reported in Table 1. The household paper contained mainly printed advertisements, newspapers and magazines (83%). Concentrations of PCB7 in the samples ranged from 1.9 to 10.4 μg/kg for "Newspapers & Magazines" and "Office paper & Books", respectively. These figures came mainly from PCB6 congeners (data not shown), which represented 83-95% of the PCB7 concentration. For comparison, European legislation allows concentrations of PCB6 in foodstuffs to be as high as 300 μg/kg, while food fed to infants and young children should not contain more than 1 μg/kg of PCB6 [14]. The highest concentration of PCBs in fraction "Office paper & Books" could indicate potential presence of paper products with longer life-spans (e.g. archives, books) than the rest of the paper fractions. Relatively higher levels of PCBs in board when compared to paper could be the result of accumulation of PCBs due to recycling, as board could reach average recycling rates as high as 94% [15]. These concentrations show tremendous decrease when compared to concentrations in paper during the active use of PCBs in paper production, e.g. recycled paperboard at the beginning of 1970 contained 15300 μg/kg [16]. The contribution of each of the fractions to total presence of PCB7 is evident from the last column of the Table 1. Summed up, the total concentration of PCB7 in the paper and board was 3.9 μg/kg. Similarly Butera et al. found 3.4 μg/kg as the average concentration of PCB7 in Danish construction and demolition waste [17]. Calculation of the PCBs intake could be done though derivation of the total amount of PCBs potentially migrated into foodstuff. Taking into account the general assumption that an average European citizen with an average body weight of 60 kg has a total lifetime intake of 1 kg packed foodstuff per day. This amount of foodstuff is usually assumed to be contained in 6 dm^2 of packaging with total content being migrated from packaging into enclosed food [18]. Daily Intake (DI) of PCBs through consumption of packed food can be calculated as follows:

$$DI = \frac{C_p\left[\frac{\mu g}{Kg_p}\right]*CF*G_p\left[\frac{Kg_p}{dm^2}\right]*6\left[dm^2\right]}{1\left[\frac{Kg_f}{day}\right]*60\left[\frac{Kg_{bw}}{Kg_f}\right]} \quad (1)$$

C_p: Concentration of PCB7 in paper

CF: Correction factor

G_p: Grammage of paper

Assuming a relatively high grammage of paper board of 0.004 kg/dm^2, the DI would be calculated as 0.03 µg/kg$_{bw}$/day if "Office paper & Books" fraction was recycled into food packaging and 100% of PCBs that it contains were transferred into the newly made packaging. This value is 50% higher than the Tolerable Daily Intake (TDI) 0.02 µg/kg of body weight as derived by World Health Organization [19]. However, it should be pointed out that the calculation of DI represent the "worst-case scenario" and involves a substantial number of assumptions.

	Fraction name	**Composition [% wet weight]**	**PCB7 [µg/kg$_{fraction}$]**	**PCB7 [µg/kg$_{total}$]**
Paper	Advertisements	56	3.3	1.9
	Newspapers & Magazines	27	1.9	0.5
	Office paper & Books	4	10.4	0.4
	Other paper	1	3.5	<0.1
Board	-	13	8.5	1.1
	Total	100		3.9

Table 1: Physical and chemical (PCB7) characterization of household waste paper and board.

As explained in the Introduction PCB7 does not account for all the PCBs potentially present in a sample. A correction factor to be used can range from 4.6 to 8.1 depending whether the mean of the composition of most common PCBs mixtures or the mixture most commonly applied in carbonless paper production are used. These assumptions would result in the range of total concentration of PCBs in paper between 18 and 31 µg/kg. As mentioned in the introduction of the work, only waste with PCB content higher than 50,000 µg/kg (i.e. 0.005% by weight) can be characterized as PCB waste. Waste paper collected in the EU for recycling in 2012 was 46.81 million tonnes [15]. Assuming composition of European waste paper similar to the one resulting from the samples discussed here would result in 833 to 1470 kg of total PCBs present in waste paper collected for recycling in Europe. If paper not reaching a paper mill for recycling but being alternatively managed with the rest of the municipal waste (though e.g. incineration, landfilling, etc.) would be accounted for, these figures would increase to 1157-2041 kg of pure PCBs. It has been estimated that in the city of Toronto, Canada (population of approx. 2.5 million) alone sealants in buildings contain 13000 kg of pure PCBs [20].

4- CONCLUSIONS

All samples of paper and board collected from Danish household waste contained PCBs in measurable quantities. Presence of PCBs could indicate paper with long life span or could be attributed to recycling. The estimated total amount of PCBs in European paper was relatively small when compared to other open applications. Calculated daily intake, based on the highest concentration found, was higher than tolerable limits proposed by WHO. The calculation represents a "worse-case scenario" and is based on a number of assumptions. Whether recycling of paper and board containing PCBs and their migration into foodstuff could pose a threat to consumer health should be looked into in more details.

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