

## THE FORMATION OF PCB DURING A 'DE NOVO' TEST ON DUST FROM VARIOUS ORIGINS

Daniel Schroyens<sup>2</sup>, Kathleen Schoyens<sup>1</sup>, Nadezhda Zyaykina<sup>1</sup>, Alfons Buekens<sup>1</sup>

<sup>1</sup>Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel, Belgium, E-mail: [abuekens@vub.ac.be](mailto:abuekens@vub.ac.be)

<sup>2</sup>Laborelec, Rodestraat 125, B-1630 Linkebeek, Belgium

### Introduction

Polychlorobiphenyls, PCB, is a generic name for a range of complex mixtures with 209 different possible congeners and 10 homolog groups, ranging from mono- to decachlorobiphenyl. They were first commercially produced in 1929, and their use became quite important in the sixties, with main applications as insulating materials in electrical equipment, thermal oil, and plasticizers in plastic and building products. In the seventies they were associated with animal procreation problems, and their use was at first restricted to closed systems and eventually banished. PCB are lipophilic, low volatility, oily or fatty chemicals. Their chemical and thermal stability, once a major technical advantage, is now responsible for their extreme persistence and ubiquity in the environment, and their presence in the food chain. Neither soil microbes nor animals are able to break down effectively the highly chlorinated PCB, what causes a very slow elimination.<sup>1</sup> Most of the PCB in the environment is due to its former use. However, Stieglitz et al.<sup>3,4</sup> have shown that fly ash from municipal incinerator plants acts as a source of a wide variety of halogenated aromatic compounds, generated by gasification of residual carbon in a temperature range 300-400 °C. The process is based on a metal-ion catalysed transfer of chloride to the carbon lattice, with formation of carbon chloride bonds and subsequent oxidation, also metal catalysed, of the carbon lattice and release of PCDD, PCDF, as well as PCB. Once formed PCB may also act as precursors for PCDF, not, however, for PCDD.

PCB-analyses can be represented various ways, the following methods being most in use:

- 1) the total amount of PCBs is evaluated by quantifying the 6 (in Belgium 7) marker PCB. The result is then multiplied by a conventional factor, based on experience values,
- 2) the congeners with a WHO toxicity equivalent are estimated and the TE-value reported,
- 3) a complete analysis is produced, and the congeners are grouped into homolog classes.

In the E.U.-Programme MINIDIP the results from FZ-Karlsruhe have been extended to other industrial processes. The purpose of this contribution was to investigate: a) the amount of PCB formed, b) its homolog and congener distribution, and d) its relation to the other families of chloroaromatics. The results are important for two purposes: to identify the origin of a PCB-contamination and to assess the potential relevance of particular industrial processes with respect to WHO-TE toxicity. This work is ongoing, and more complete results will be presented in Korea.

### Materials and Methods

A number of samples of industrial origin were investigated, mainly dust collected at various positions in a sintering plant and Waelz process units, as well as samples collected at different locations of a MSWI (boiler, E-filter, semi-wet scrubber baghouse, wet scrubber), in a hospital waste incinerator, and a wood waste fired boiler (Table 1). All analyses were performed by

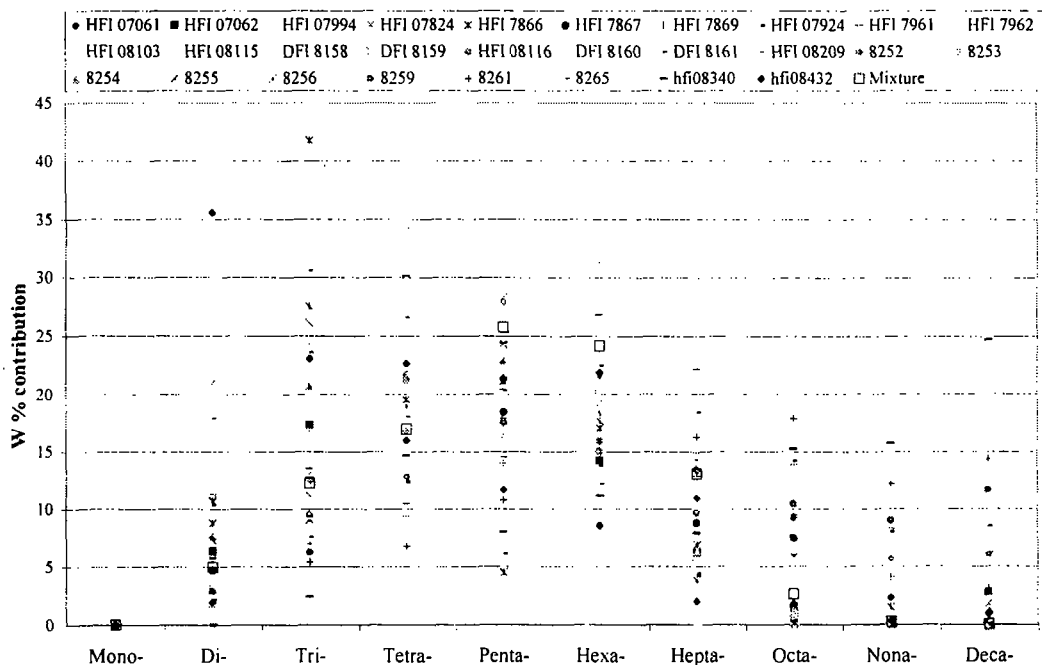
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Forschungszentrum Karlsruhe. The PCPh, PCBz, PCB and PCDD/F were quantified by the use of <sup>13</sup>C-internal standards. The PCPh, PCBz and PCB were analysed by HRGC/LRMS with a 60 m DB-5 column and the PCDD/F by HRGC/HRMS (HP5890 - Fisons Autospec) with a 60 m DB-Dioxin column.

**Table 1: Origins of the hitherto analysed samples.**

| Origin   | Samples  |
|--|--|
| dust samples from a sintering plant  | HFI 07061 / HFI 07062 / HFI 07994  |
| dust samples from 2 Waelz process units  | HFI 07824 / HFI 7866 / HFI 7867 / HFI 7869 / HFI 08115 / DFI 8158 / DFI 8159 / HFI 08116 / DFI 8160 / DFI 8161 |
| dust collected at different locations in a Municipal Solid Waste Incinerator plant | 8252 / 8253 / 8254 / 8255 / 8256 / 8259 / 8261 / 8265 / HFI 07924 / HFI 7961 / HFI 7962 / HFI 08209            |
| Wood Fired Boiler  | hfi08432   |
| medical waste Incinerator plant  | HFI 08103 / hfi08340   |

**Results: Total Load of individual Samples.** For the total concentration of PCB in the relevant samples values from 10 to almost 300,000 ng PCB/g were observed.



**Figure 1: A comparison of the homolog contribution of the analysed samples with a mixture of commercial PCB.**

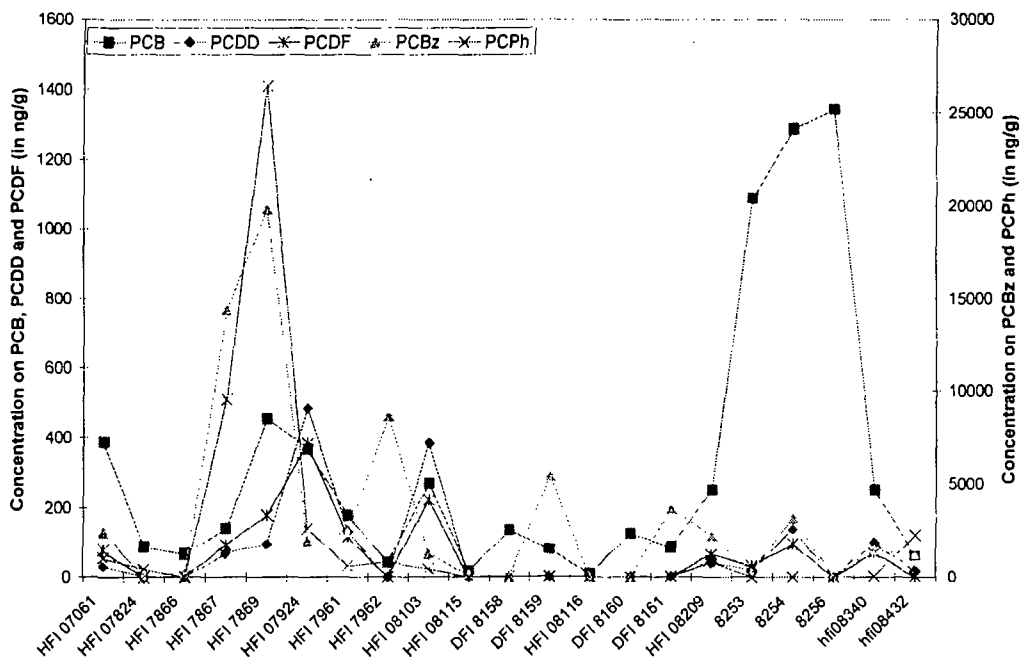
**Homolog Classes.** This representation allows subdividing the homolog fingerprints of the individual samples according to two criteria: average level of chlorination, and spread around this value. The average level of chlorination of thermally formed PCBs in most cases amounts to 4 or 5, but some samples are lower chlorinated, whereas some others even feature sizeable amounts of decachlorobiphenyl! Highly chlorinated samples were identified in hospital waste incineration, an

**ORGANOHALOGEN COMPOUNDS**

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ESP-fly-ash of a MSW-incinerator plant, and a fly ash of a fluid bed unit firing plastics rich waste. Low chlorinated samples were found in wood combustion, a Waelz process sample, the quench and a basic scrubber column of a MSW-incinerator, and the salt rich (!) dust sample from the E-Filter of a sintering plant. It is difficult to derive a clear rule from the data, and the effect of the quality of the catalytic system, or of the availability of chlorine requires further investigation. Figure 1 shows the homolog distribution for the different analysed samples, as compared to a mixture of commercial PCB (AROCOR 1242, 1254 and 1260 in equal parts). Most of the analysed samples show homolog fingerprints in analogy with the mixture of commercial PCB, with exception of three samples that contain an almost equal concentration of tetra- up to decachlorobiphenyl.

Figure 2 and 3 show the relation between the PCB and some other chlorinated compounds (PCDD/F, PCBz and PCPh). Figure 2 shows the correlation for low-level concentrations of PCB and Figure 3 shows the correlation for high-level concentrations of PCB. From this representation the quality of the correlation between the various chloroaromatic families can be derived. Moreover, it allows a rapid screening of origins that may be richer in PCB than average.



**Figure 2: Correlation between PCB, PCDD, PCDF, PCBz and PCPh.**

The relationship between PCB and other generic groups was investigated statistically, with the following result: (the correlation with PCPh is very weak and even negative !)

**Table 2: correlations between various classes of compounds:**

| Compounds      | PCDF | PCDD | PCBz | PCPh |
|----------------|------|------|------|------|
| R <sup>2</sup> | 0.70 | 0.66 | 0.51 | 0.06 |

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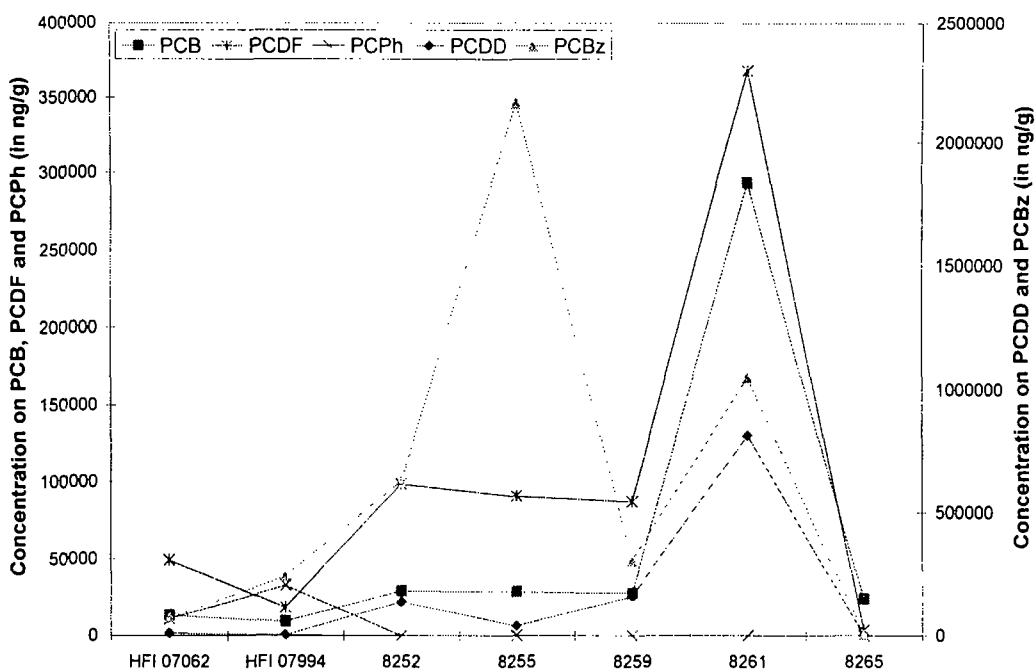


Figure 3: Correlation between PCB, PCDD, PCDF, PCBz and PCPh, for high-level PCB

## Conclusions

This paper relates to an ongoing study on the formation of PCB in various metallurgical and incineration processes, conducted with the aims of providing information that may help in source discrimination and of a further identification of relevant new sources of WHO-TE. In most cases the homolog distribution resembles that of commercial PCB qualities, but some samples contain highly and even fully chlorinated PCB. The reason for such differences in profile is still unknown.

## Acknowledgements

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