

SCREENING OF POLYCHLORINATED DIBENZOTHIOPHENES IN THE SWEDISH ENVIRONMENT

Haglund P, Andersson R, Aurell J, Bergek S, Karlsson S, Liljelind P, Olofsson U, Spinnel E, Sundqvist K

Department of Chemistry, Environmental Chemistry, Umeå University, SE-90187 Umeå, Sweden

Introduction

This report summarized the findings of a Swedish screening project focusing on the sources and environmental levels of polychlorinated dibenzothiophenes (PCDBTs), Figure 1.

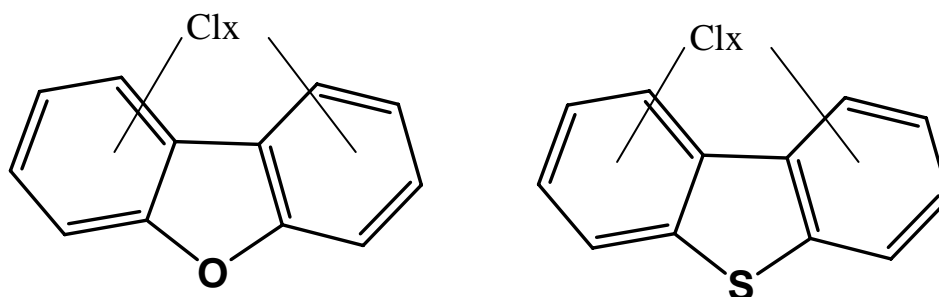


Figure 1. Structural formulas of polychlorinated dibenzofurans (left) and dibenzothiophenes (right).

PCDBTs are the sulphur analogues of the polychlorinated dibenzofurans (PCDFs) and have been shown to be formed simultaneously in high temperature processes, e.g. incineration¹ and metal reclamation², or during pulp bleaching³. Unfortunately, they also exhibit the same environmental properties as the PCDFs and are, thus, persistent, bioaccumulating, and toxic. The potency does however appear to be lower than the corresponding PCDFs or polychlorinated dibenzo-p-dioxins (PCDDs)^{4,5,6,7}. Within the current project the environmental occurrence was investigated in order to find out how the levels compare to the PCDD/F, and to obtain a rough risk ranking of the two classes of compounds.

Material and methods

Most of the samples analysed have previously been analysed for PCDD/Fs and have then been archived. The samples were stored dark and at low temperature and there should not be any risk for substantial analyte losses or transformations. The remaining samples were analysed as soon as possible after the sampling.

All samples were extracted and cleaned up using the procedures normally used for PCDD/Fs. In short, the analytes were extracted using organic solvents; bulk co-extracted material were removed using multi-layer columns filled with KOH-silica, silica, H₂SO₄ silica, silica and (if the samples contain sulphur) copper powder; and planar compounds, including PCDD/Fs and PCDBTs, were isolated using activated carbon fractionation. Due to the structural similarity of PCDBTs and PCDFs the two classes of compounds behave similarly during sample extraction and clean up.

Carbon-13 labelled PCDD/Fs were added as internal and recovery standards and were used in the quantification of both PCDBTs and PCDD/Fs using gas chromatography – high resolution mass spectrometry (GC-HRMS). The MS was tuned to >20,000 resolution to discriminate between PCDBTs and PCDDs. The PCDBT elution windows were established using a synthetic mixture of mono- through octa-CDBT and purified fly ash extracts. Selected ion recording (SIR) and time segmenting (one segment per homologue level) were used in order to maximize sensitivity in the GC-HRMS determination. The quantification was based on peak areas comparison of PCDBTs in samples and PCDDs in standards assuming equal molar responses of the two compound classes, as well as among all isomers of each homologue level.

Results and discussion

An overview of the PCDBT levels, as compared to PCDD/Fs, in various sample types is given in **Table 1**. The comparisons are made on total level basis whenever possible. Otherwise, the comparisons are made between the total level of PCDBT and the total PCDD/F-TEQ, which will naturally overemphasize the levels of the PCDBTs. Generally, the levels of PCDBTs were about two orders of magnitude lower than the corresponding PCDD/F levels.

Table 1. Relative levels of PCDBTs och PCDD/Fs in selected samples.

Sample type (number)	Σ PCDBT / Σ PCDD/F (interval)	Σ PCDBT / PCDD/F-TEQ (interval)	Σ PCDBT / PCDD/F-TEQ (median)
MSW (3)	0.003 – 0.009	0.13 – 0.15	0.14
Steel mill (2)	0.25 – 0.48	35 – 50	>35
Snow, deposition (3)	0.03 – 0.04	1.8 – 2.0	1.8
Sediment (5)	–	0.5 – 3.5	1.5
Soil (6)	–	0.01 – 2.0	0.4
Sewage sludge (7)	–	1.7 – 3.2	2.8
Biota, food, feed (18)	0.003 – 0.034	0.01 – 24	0.13

For the incineration samples a dependency was observed between the temperature at the sampling point and the PCDBT levels (**Figure 2**). Much higher levels were observed at ~300°C than at 830°C, which is consistent with what is normally observed for PCDD/Fs. Elevated levels were also found when fuels enriched in sulphur were incinerated; and when SO₂ was added to the flue gas. Moreover, tests performed in a full-scale MSW indicate that the ration between PCDBTs and PCDD/Fs are influenced by the sulphur/chlorine ratio. A high ratio results in more PCDBTs. Consequently, more PCDBTs were formed when fuels amended with tyres were incinerated, and less PCDBTs (and more PCDD/Fs) were formed when a fuel amended with PVC was incinerated. Low levels of PCDBTs were also formed during steel production. Notably, however, the PCDBT/ PCDD/F ratio was rather high (**Table 1**).

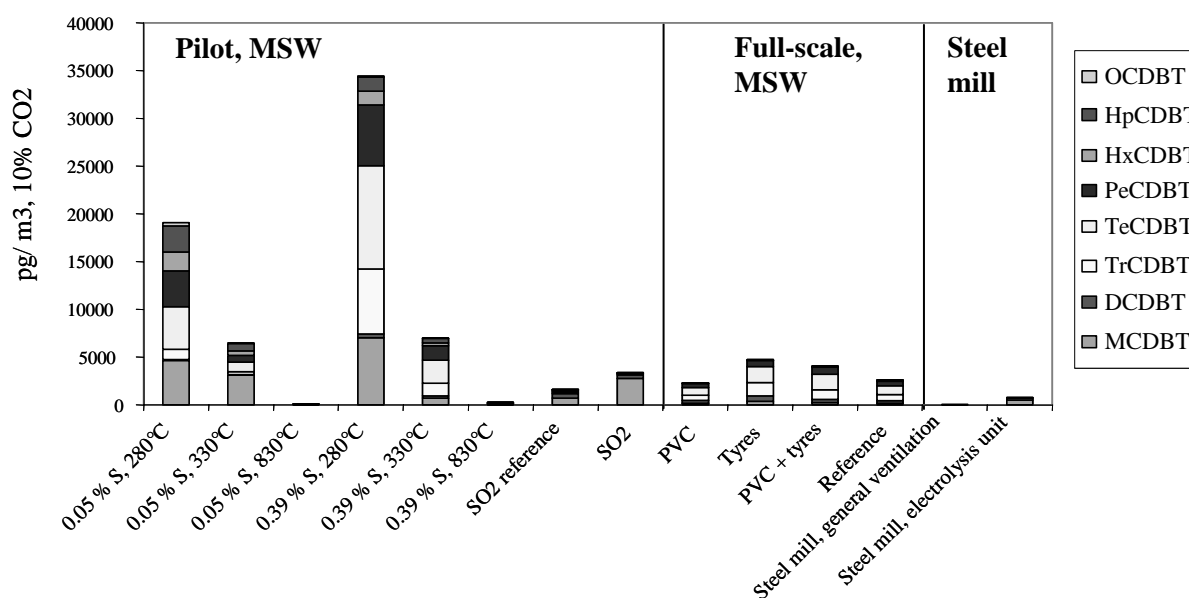


Figure 2. Levels of PCDBT in flue gas samples of a pilot municipal solid waste (MSW) incinerator, a full-scale MSW, and a steel mill. The sulphur content and flue gas temperature at the sampling point are indicated for the pilot MSW. The full-scale MSW fuel had been amended with chlorine and sulphur containing materials (as indicated).

Ambient levels and trends

The levels and patterns of PCDBT in snow collected in the vicinity of an incineration plant clearly indicate that PCDBTs are emitted from the plant. The levels decrease with distance from the plant and the pattern in the sample closest to the plant resembles that of PCDBTs in flue gas from a full-scale MSW incinerators.

A similar comparison of PCDBT levels and patterns in sediment samples collected close to other potential PCDBT sources and source regions were also made (Figure 3). It revealed that samples collected close to pulp and paper mills in Skutskär, Norrundet and Vallvik were elevated in some specific PCDBT congeners; although similar total levels were found in some background areas. It also showed that the sediments close to major cities (Malmö and Stockholm) contained relatively high PCDBT levels. In the Stockholm area the levels decreased with distance from central Stockholm (Värtahamnen > Lake Mälaren > Södertälje kanal > Södertälje reference). No reason could be found for the high levels of PCDBT detected in sediment collected close to the remote island Gotska Sandön, located in central Baltic Proper.

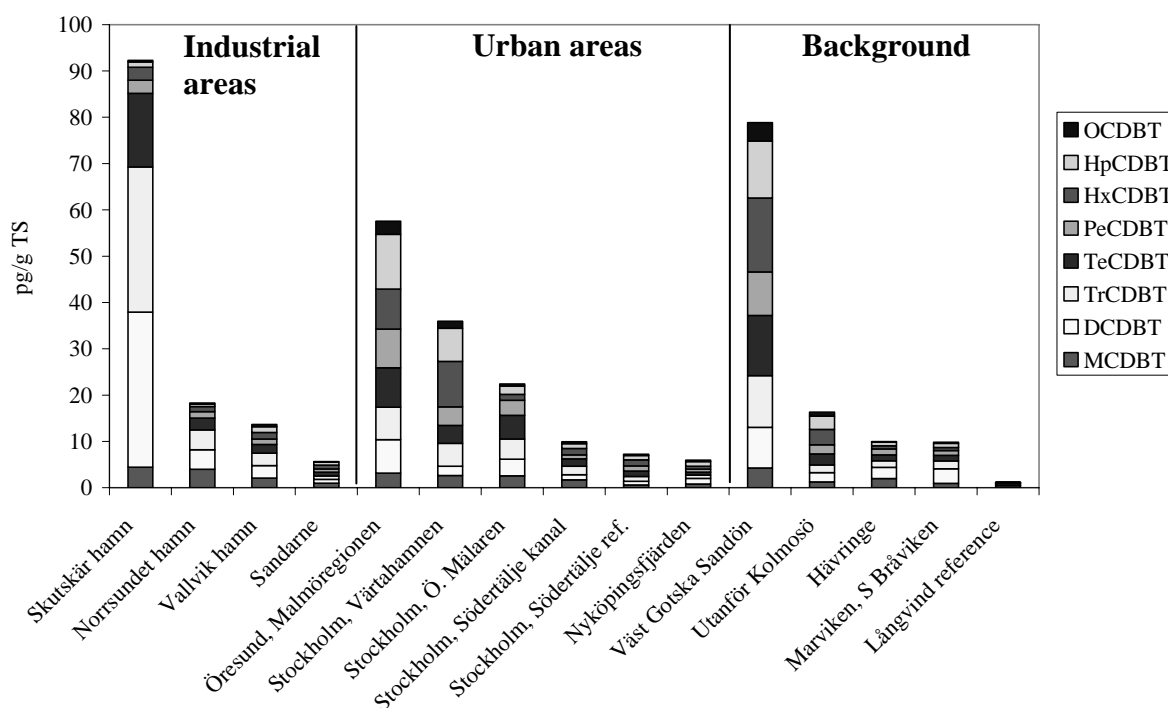


Figure 3. Levels (pg/g dry matter; TS) of PCDBT in sediment samples.

Analysis of soil samples from a chlor-alkali plant, former pentachlorophenol (PCP) wood impregnation facilities and a few sites in South America where cables have been burned to reclaim the copper indicates that all these activities may lead to soil pollution.

Highest total PCDBT levels were found in the South American soil samples (up to 1,600 pg/g dry soil) followed by the chlor-alkali soil (450 pg/g). Notably, the PCDBT pattern in the chlor-alkali soil was very similar to the sediment pattern found outside the pulp and paper mills. Soil from the PCP sites contained much higher PCDD/F (up to 15,000 pg/g) than PCDBT levels (up to 180 pg/g). Thus, PCP does not seem to be highly contaminated with PCDBTs.

Analysis of digested sludge from municipal sewage treatment plants exhibited rather constant PCDBT levels, with total PCDBT levels ranging from 4.4 to 15 pg/g dry weight, which is about two orders of magnitude less than normally found of total PCDD/Fs. Thus, the PCDD/Fs seem to affect the sludge quality more than the PCDBTs.

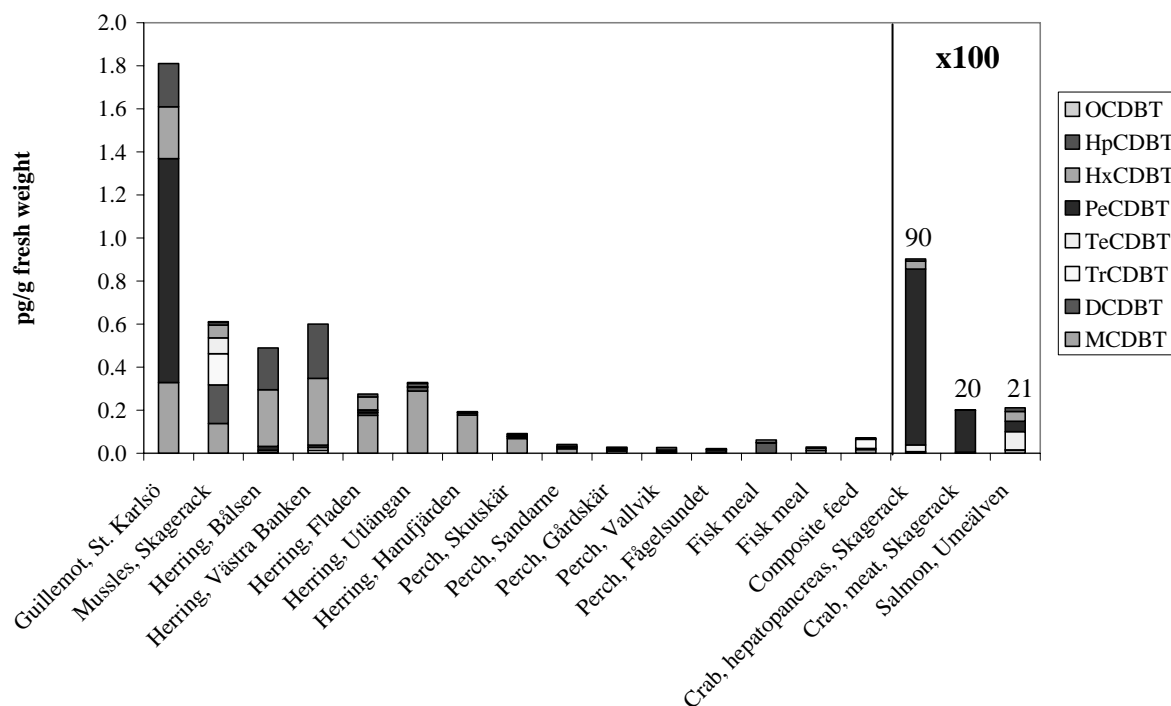


Figure 4: Levels of PCDBT in biological samples.

All biological (and related) samples analysed contained PCDBTs at levels ranging from 0.02 to 90 pg/g fresh weight (**Figure 4**). Highest levels were found in samples of crab hepatopancreas and meat, and in an old salmon sample (from the 1980s). These were also high in PCDD/Fs. The reasons for the particular high levels in these samples are likely related to the low metabolic activity of crabs and generally high biomagnification of POPs in salmon. The remaining samples were all below 2 pg/g fresh weight. Considering the lower biological potency of PCDBTs as compared to PCDD/Fs it seems like the PCDBTs does not constitute a major threat to biota, including humans.

Acknowledgements

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