

# Polychlorinated Dioxins (PCDDs), Dibenzofurans (PCDFs) and Other Polynuclear Aromatics (PCPNAs) Formed During PCB Fires

Dedicated to Professor Arne Fredg on his 80th birthday

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## Abstract

Soot samples and wipe tests from PCB fires were analyzed by HPLC-MS. In an accidental PCB fire, where oil-filled capacitors burned with PCB-filled capacitors, PCDFs were the major polychlorinated products formed. In another capacitor fire, probably caused by electrical malfunction, polychlorinated biphenyls (PCBPs) were the major products, but smaller amount of PCDFs and polychlorinated pyrenes (PCPYs) were also formed. This is the first report where PCBPs and PCPYs have been identified in incineration products. Thermal destruction of PCB in a rotary cement kiln gave no indication of formation of PCDFs or other polychlorinated products.

## Introduction

The polychlorinated dioxins (PCDDs) and dibenzofurans (PCDFs) are two series of tricyclic aromatic compounds with similar chemical, physical, biological and toxicological properties. The basic structures and numbering are given in Fig. 1. The number of chlorine atoms can vary between one and eight, and the number of positional isomers is quite large. In all there are 75 PCDDs and 135 PCDFs and the number of isomers for a given number of chlorine atoms are given in Table I.

Some of the compounds have extraordinarily toxic properties and have been the subject of much concern. They are known as highly stable contaminants in chlorinated phenols, phenoxy acids and in PCBs. They have also been involved in accidents and massive intoxications like the Yusho accidents in Japan in 1968 and in Taiwan in 1979, the accident near Seveso, Italy in 1976 and in the Love Canal controversy in U.S.A. in 1978. There is a pronounced difference in biological effects between different PCDD and PCDF isomers. A factor of  $10^3$ - $10^4$  can be found for so closely related isomers as 2,3,7,8- and 1,2,3,8-tetra-CDD. The isomers with the highest acute toxicity are 2,3,7,8-tetra-CDD, 1,2,3,7,8-penta-CDD, 1,2,3,4,7,8-, 1,2,3,6,7,8- and 1,2,3,7,8,9-hexa-CDD, 2,3,7,8-tetra-CDF, 1,2,3,7,8- and 2,3,4,7,8-penta-CDF and 1,2,3,4,7,8- and 2,3,4,6,7,8-hexa-CDF, see Fig. 2. All these isomers have their four lateral positions substituted for chlorine, and they all have LD<sub>50</sub>-values in the range 1-100 µg/kg<sup>-1</sup> for the most sensitive animal species. The same isomers have been reported to have the highest biological potency.

The polychlorinated biphenyls (PCBPs) is another series of compounds closely related to the PCDDs and PCDFs, see Fig. 1. The number of PCBP isomers is 75, and one of these, the 2,3,6,7-tetra-CBP has been investigated by Poland. The biological activity of this compound was in the same region as 2,3,7,8-tetra-CDD [1].

Emissions from municipal waste incinerators, heating facilities

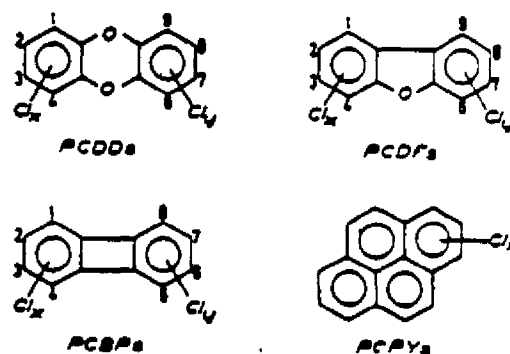


Fig. 1. Structure and numbering of the polychlorinated dioxins (PCDDs) dibenzofurans (PCDFs) and biphenyls (PCBPs)

and thermal power plants have long been the subject of public concern. Whereas previously the emission of dust, smoke, toxic metals and noxious gases was of prime concern, the presence of potentially hazardous organic compounds has only recently been reported. The polynuclear aromatic hydrocarbons (PNAHs) was the first group of compounds to be discussed.

In 1977 Lahanatis *et al.*, reported on the finding of chlorinated organic compounds in the fly ash of a municipal incinerator. The compounds detected were chlorinated aliphatics and benzenes, pesticides and PCBs [2]. Also in 1977 Olie *et al.*, reported on the occurrence of PCDDs and PCDFs in the fly ash of three municipal incinerators in the Netherlands. Their results indicated the presence of up to 17 PCDD isomers, but no quantification or isomer identification was given [3].

Table I. Number of PCDD and PCDF isomers for a certain number of chlorine atoms

|        | PCDDs | PCDFs |
|--------|-------|-------|
| Mono-  | 2     | 4     |
| Di-    | 10    | 16    |
| Tri-   | 14    | 33    |
| Tetra- | 22    | 38    |
| Penta- | 14    | 28    |
| Hexa-  | 10    | 16    |
| Hepta- | 2     | 4     |
| Octa-  | 1     | 1     |
| Total  | 75    | 135   |

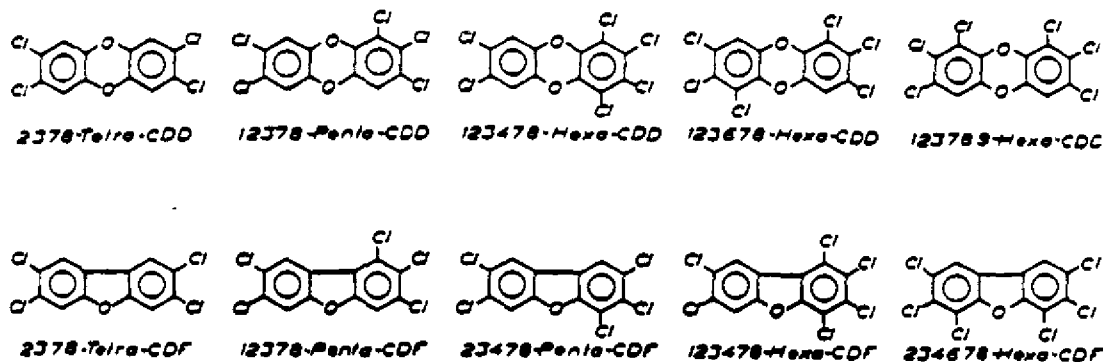


Fig. 2. The most toxic PCDD and PCDF isomers.

At about the same time, we were engaged in an investigation on the occurrence of PCDDs, PCDFs and other chlorinated compounds in fly ash and soot of an industrial heating facility in Switzerland. Later the study was expanded to include fly ash of a larger municipal incinerator. The analyses were carried out by high resolution GC mass spectroscopy allowing identification and quantification of the major PCDD and PCDF components [4-6]. In recent years emission from incinerators have been analyzed in the Netherlands, Italy, Canada, U.S.A., Germany, Switzerland and Sweden [7]. Due to sampling difficulties, fly ash samples have been much more frequently analyzed than flue gas, particulate and other products from the incinerator. The quantitative results are normally given in terms of levels of groups of isomers with the same number of chlorine atoms. The total levels of PCDDs and PCDFs are in the range of  $1-5 \mu\text{g g}^{-1}$  [7].

A detailed investigation of the specific isomers present in fly ash samples shows that in general the known toxic PCDD isomers were present only as minor constituents. On the contrary, the most toxic PCDF isomers were present as major constituents in these samples [4, 5]. The results in these investigations also indicate that commercial chlorophenols are the main precursors to the PCDDs found, see Fig. 3. On the other hand the PCBs are the main precursors to the PCDFs found in the fly ash samples and also in the Yusho rice oil [4, 5].

A possible contamination of PCBs in the Yusho rice oil, in used PCBs and in pyrolyzed PCBs has been investigated by Buser *et al.* [8]. The PCBs could conceivably be formed from PCBs at high temperatures under exclusion of oxygen, see Fig. 3. However, no definite proof for the presence of PCBs at any significant level ( $> 5\%$  relative to the level of PCDFs) could be found [8]. The presence of other chlorinated polynuclear aromatics (PCPNAs) in samples from incineration processes has never been discussed or demonstrated.

We have previously studied the pyrolysis of PCBs. When commercial mixtures or well defined isomers are heated in air in a sealed ampoule, the yields of PCDFs are normally in the 1-5% range, and this method has successfully been used for the preparation of PCDF standards [5, 9, 10]. These observations indicated that any burning of PCBs can be an important environmental source of the hazardous PCDFs, and already in 1978 we declared that all degradation and disposal of PCBs should be carefully controlled in order to avoid accidental formation of hazardous PCDFs [9].

This statement has later been confirmed by two accidental PCB fires in transformer stations, one in downtown Toronto, Canada [11] and the other 70 km N Stockholm, Sweden [12]. In the Swedish study a 30-100 fold increase in the levels of PCDFs was observed, but the analytical technique used did not allow the identification of individual PCDF isomers.

In the present study, we report on the analysis of soot samples and wipe tests from two PCB fires and from a study of the thermal destruction of PCBs.

#### *Analysis of trace levels of PCDDs and PCDFs*

Due to the extreme toxicity of some of the PCDD and PCDF isomers, very sensitive and highly specific analytical techniques are required. Detection levels in biological and environmental samples should be orders of magnitude below the usual detection limits obtained in pesticide analysis. A sensitivity of 1 pg ( $10^{-12}$  g) might be required to detect the most toxic isomers (see Fig. 2) in a 1 g sample (1 pg/g = 0.001 ppb). The different isomers of PCDDs and PCDFs is known to vary greatly in their biological and toxicological properties and therefore the separation, identification and quantification of the most toxic isomers becomes important.

In recent years a number of analytical methods have been developed for the trace analyses of PCDDs and PCDFs in a variety of matrices including soot and other products from incineration and accidental fires. The most specific and selective of these methods are utilizing mass spectroscopy MS [13, 14]. The purified extracts from the clean-up were used for the final

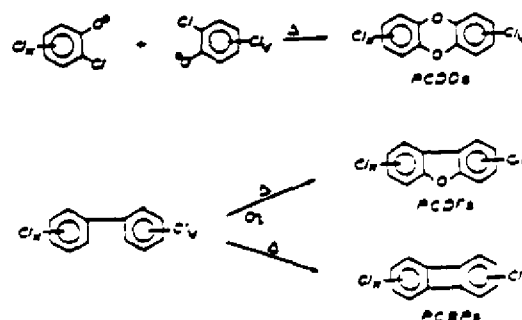


Fig. 3. Formation of PCDDs, PCDFs, and PCBs by pyrolytic processes.

analysis using high-resolution gas chromatography-mass spectrometry. Mass selective detection (mass fragmentography) was used to detect PCDDs and PCDFs by selective monitoring of  $M - 2$  and/or  $M + 4$ . The MS-instrument is operating in the electron impact (EI) or the negative chemical ionization (NCI) mode. The quantification is based on peak area measurements and comparison either with internal standards or calibration curves of authentic standards (external standards).

#### Experimental

##### Extraction and clean-up

The sample (soot sample or Kleenex tissue from wipe tests) was spiked with 1 ppb of  $2,3,7,8\text{-}^{13}\text{C}_{12}$ -tetra-CDD,  $2,3,7,8\text{-}^{37}\text{Cl}_4$ -tetra-CDF and  $^{37}\text{Cl}_4$ -octa-CDD. Thereafter the sample is treated with 10 ml of 1 M hydrochloric acid for one hour (shaking). The slurry was filtered by suction of a Buchner funnel, washed with water, and dried in the air.

The dried material was transferred to a Soxhlet extractor and extracted with toluene (about 100 ml) for 48 h at a speed of 1–2 ml min<sup>-1</sup>. The toluene was evaporated until 100 µl on a rotavapor with some external heating, the rest of the solvent was eliminated by a purified N<sub>2</sub> flush without external heating. The residues were dissolved in 2 ml of *n*-hexane and added to a Silica gel column prepared from 0.5 g of Kieselgel 60, 70–230 mesh (Merck) eluted with 5 ml of *n*-hexane. The hexane was evaporated until 100 µl using a stream of nitrogen and 2 µl of this solution was used for the analysis of PCBs. The PCDDs and PCDFs were separated from other polychlorinated impurities using an Alox-column (1.0 g basic Alox aktiv. 1, Woelm, ICN West Germany). The first fraction, 10 ml-hexane, methylene chloride (98:2) was discharged. The second fraction, 10 ml *n*-hexane, methylene chloride (1:1) was collected and evaporated until dryness in a stream of nitrogen. The residue was dissolved in a known amount of solvent (100 µl) and 2 µl was used for the GC/MS analyses.

##### High-resolution gas chromatography-mass spectrometry

We have used two glass capillary columns, one 25 m SE 54 (I.d. 0.34 mm) and one 55 m Silur 10 c (I.d. 0.26 mm). The GC conditions are summarized in Table II. The columns were attached via an open split and 0.5 m of a fused silica column directly into the ion source of the MS. A Finnigan Model 4021 mass spectrometer was used operating in the EI or NCI mode (CH<sub>3</sub>), see Table III.

##### Standards and reference compounds

The PCDD and PCDF standards used (tetra- to octachloro) have

Table II Gas chromatography conditions used in the study

|                   | SE 54                                                              | Silur 10 c                                                         |
|-------------------|--------------------------------------------------------------------|--------------------------------------------------------------------|
| Column, length    | 25 m                                                               | 55 m                                                               |
| Column, i.d.      | 0.34 mm                                                            | 0.26 mm                                                            |
| Interface length  | 0.5 m                                                              | 0.5 m                                                              |
| Interface, i.d.   | 0.16 mm                                                            | 0.11 mm                                                            |
| Pressure (helium) | 21 psi                                                             | 55 psi                                                             |
| Injector temp.    | 230°C                                                              | 230°C                                                              |
| Temp. program     | 80°C–2 min<br>80–160°C 20°/min<br>160–260°C 2°/min<br>260°C–10 min | 80°C–2 min<br>80–160°C 20°/min<br>160–240°C 2°/min<br>240°C–10 min |

Table III Mass spectroscopy conditions used in the study

|                        | EI                                  | NCI                                 |
|------------------------|-------------------------------------|-------------------------------------|
| Electron energy        | 70 eV                               | 120 eV                              |
| Emission current       | 4 mA                                | 34 mA                               |
| Electron multiplier    | 1.5 kV                              | 1.5 kV                              |
| Sensitivity            | 10 <sup>-16</sup> A V <sup>-1</sup> | 10 <sup>-16</sup> A V <sup>-1</sup> |
| High vacuum            | 5 × 10 <sup>-11</sup> torr          | 5 × 10 <sup>-11</sup> torr          |
| Forepressure ionizer   | 0.01 torr                           | 0.30 torr                           |
| Ionizer temp.          | 270°C                               | 180°C                               |
| Manifold temp.         | 130°C                               | 130°C                               |
| Transmitter line temp. | 270°C                               | 270°C                               |
| Interface line temp.   | 250°C                               | 250°C                               |

been described elsewhere [13, 15, 16]. No standards were available for mono-, di and tri-CDFs. A solution of 2,3,6,7-tetra-CBP was obtained from David Stalling, Columbia, MO U.S.A. No other qualitative or quantitative PCBY or PCPY standards are available.

Individual MS-response factors have been determined for 28 different PCDFs [16], and were used for the quantification of these isomers. For unidentified isomers the response factors for 2,3,7,8-tetra- and 2,3,4,7,8-penta-CDF was used.

#### Results

##### Accidental PCB fire, Skövde, Sweden

In March 1982 a fire broke out in a capacitor battery (400 V) serving a high frequency oven in a casting line of a metal treatment factory in Skövde, Sweden. The dielectricum in the capacitors consisted of mineral oil or PCB and the two types of capacitors were mixed at random. The fire started in a capacitor containing mineral oil, and about 2 h elapsed until the fire was completely extinguished. The capacitor room situated in the basement of the foundry was burned out, the copper bars for electricity in the ceiling was partly melted (m.p. 1080°C). The smoke spread in the building in an area of 60 × 30 m.

The capacitor battery contained 21 capacitors filled with PCB (5 kg each). An inspector after the fire showed 12 of these capacitors had been opened and 9 of them were still sealed.

The following samples were analyzed (wipe tests, Kleenex tissue, 1 dm<sup>2</sup>).

- (1) On the floor, in the capacitor battery.
- (2) On the floor, close to the capacitor battery.
- (3) On the wall in the capacitor room, 2 m from the capacitor battery, 3 m above the floor.

Table IV Levels of PCDFs (ng m<sup>-2</sup>) for samples from the Skövde fire

| PCDF              | Sample number |     |      |                 |
|-------------------|---------------|-----|------|-----------------|
|                   | 1             | 2   | 3    | 4               |
| 2,3,7,8-Tetra-CDF | 20            | 100 | < 1  | n.d.            |
| Total Tetra-CDFs  | 100           | 600 | < 1  | 10 <sup>a</sup> |
| Total Penta-CDFs  | 40            | 100 | n.d. | n.d.            |
| Total Hexa-CDFs   | 40            | 60  | n.d. | n.d.            |
| Total Hepta-CDFs  | 8             | 8   | n.d. | n.d.            |
| Octa-CDF          | 5             | 5   | n.d. | n.d.            |

n.d. = Not detected.

<sup>a</sup> Different isomers than those found in samples 1 and 2.

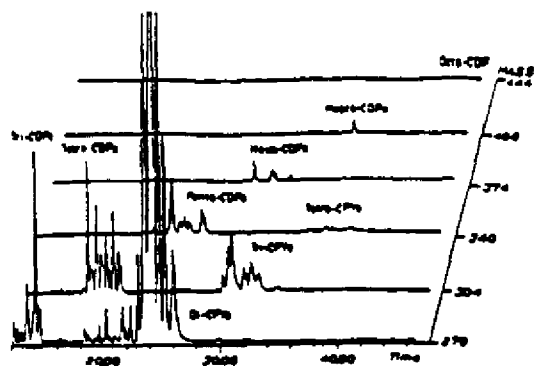


Fig. 4. Mass fragmentogram of extract from accidental PCF fire, Skövde, Sweden.

(4) On a bench 10 m from the oven.

The results are collected in Table IV. The results show that high levels of PCDFs ( $> 0.1 \mu\text{g m}^{-3}$ ) could only be found in an area close to the fire. At a distance of 10 m the levels were about 100 times lower. The low levels in sample number 3 can be explained by the high temperature at this sampling location (the copper bar was partly melted here).

The fragmentogram of the PCDFs (tri-CDFs to octa-CDF) is shown in Fig. 4. Making the assumption of an equal response for tri- and tetra-CDFs, the levels of tri-CDFs is about the same as tetra-CDFs. The highly toxic 2,3,7,8-tetra-CDF is one of the major tetra-CDF isomers.

In addition to the PCDFs Fig. 4 shows the presence of another series of chlorinated compounds. The molecular weights and number of chlorine atoms indicate that this series is the polychlorinated pyrenes, the PCPy's, see Fig. 1. Especially the di-CPy's are the dominating compounds at mass 270. However, the final proof cannot be obtained due to lack of synthetic standards. It can be noted that no PCDDs and no PCBs could be identified in the samples from this fire.

#### Accidental PCB fire, Stockholm, Sweden

In August 1981 a fire broke out in a capacitor battery (10 KV) in an electrical power station in Stockholm, Sweden. The fire was probably caused by malfunction in the electrical system.

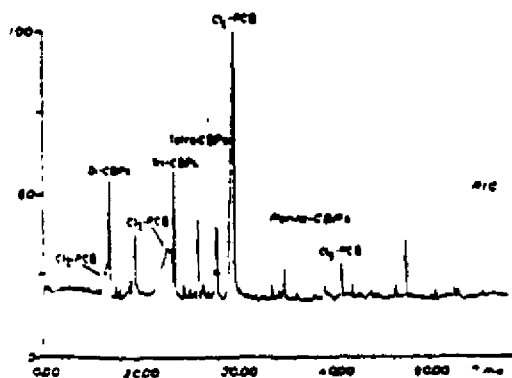


Fig. 5. Mass fragmentogram (total ion current) of extract from accidental PCF fire, Stockholm, Sweden.

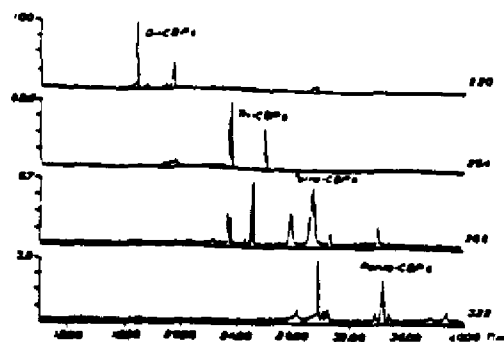


Fig. 6. Mass fragmentogram (PCBPs) of extract from accidental PCB fire, Stockholm, Sweden.

We have analyzed a wipe test from this fire taken about 1 m from the capacitor. First we analyzed the extract after the silica gel step, see Fig. 5. In addition to the PCBs, which were not totally removed from the sample, the chromatogram contained several other peaks. Inspection of the complete mass spectra revealed these peaks to be a series of compounds with a molecular weight corresponding to di-, tri-, tetra- and penta-CBPs. This series is probably formed by a direct cyclization of PCBs, see Fig. 3.

In Fig. 6 we have collected the fragmentograms of the ions corresponding to di- to penta-CBPs. Several isomers could be found within each group. The absence of synthetic standards creates a problem for the identification, but the presence of PCBs (or the isomeric polychlorinated acenaphylenes) could be checked by following the M and M + 2 traces. For most of peaks in Fig. 6 we found the expected ratio between the M and M + 2 ions.

The new MS/MS technique [17] provides another possibility to check for the presence of PCBPs. We have used this method to analyze for the tetra-CBPs. We have used this method to analyze for the tetra-CBPs ( $m/z = 288$ ) where high levels of tetrachloro PCB ( $m/z = 290$ ) could interfere. We selected  $288^+$  as the parent ion scanning for daughter ions. From the synthetic standard 2,3,6,7-tetra-CBP we found  $253^+$  and  $218^+$  to be the major daughter ions. The MS/MS experiment is shown in Fig. 7. All the major peaks in the extract had the expected daughter ions, the number of tetra-CBP isomers found in this sample was about 10.

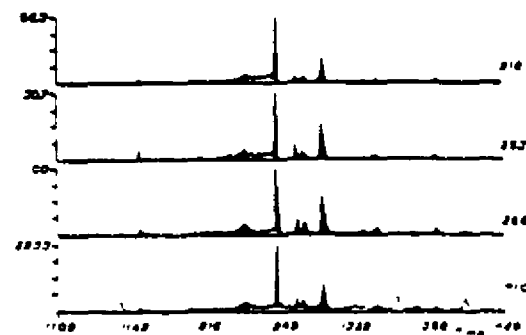


Fig. 7. Mass fragmentogram (MS/MS) of tetra-CBPs from accidental PCB fire, Stockholm, Sweden.

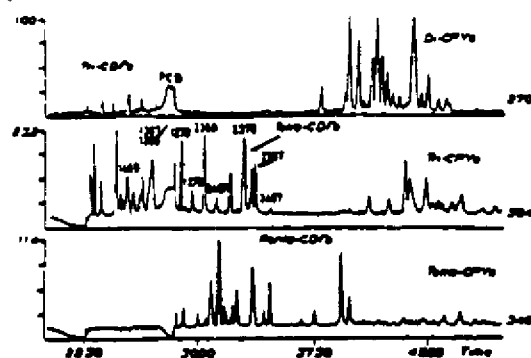


Fig. 8. Mass fragmentograms (PCDFs and PCPYs) of extract from accidental PCB fire, Stockholm, Sweden.

The extract from the Alon step was analyzed for PCDFs (and PCDDs) in the usual way, and the quantitative data is given in Table V. The level of PCDFs was found to be  $1.4 \mu\text{g m}^{-3}$  which is approximately two times higher than in the Skövde fire. However, it should be kept in mind that in the Stockholm fire we should also consider the PCBs present. A rough estimation gave the levels of PCBs to be about  $25\text{--}30 \mu\text{g m}^{-3}$ .

Figure 8 is the fragmentograms for the ions 270 (tri-CDFs and di-CPYs) 304 (tetra-CDFs and tri-CPYs) and 340 (penta-CDFs and tetra-CPYs). The highest levels were found for the tetra-CDFs and the tri-CPYs.

Among the PCDFs we can identify a number of isomers. The highly toxic 2,3,7,8-tetra-CDF and 2,3,4,7,8-penta-CDF could both be identified as major peaks. It should be noted that individual response factors [16] have been used to calculate the levels given in Table V.

#### Thermal PCB destruction, rotary cement kiln, Norway

We have analyzed a series of samples taken during a test study of thermal destruction of PCB in a rotary cement kiln in Norway. The kiln is 150 m long with a diameter of 3.5 m. It has a so called "wet" oven operating at  $1450^\circ\text{C}$  in the solid material and  $2000^\circ\text{C}$  in the flames. During the test period  $4 \text{ m}^3$  of PCB was burned at a feeding rate of  $50 \text{ kg h}^{-1}$ . The results are collected in Table VI.

Table VI. Amounts of PCDFs and PCDDs found in PCB destruction

|            | Condensate<br>$\text{ng l}^{-1}$ | XAD-1<br>Filter 1<br>$\text{ng g}^{-1}$ | XAD-2<br>Filter 2<br>$\text{ng g}^{-1}$ | Filter<br>1<br>$\text{ng}$ | Filter<br>2<br>$\text{ng}$ | Electro<br>filter<br>$\text{ng g}^{-1}$ | Sintered<br>cement<br>$\text{ng g}^{-1}$ |
|------------|----------------------------------|-----------------------------------------|-----------------------------------------|----------------------------|----------------------------|-----------------------------------------|------------------------------------------|
| Tri-CDFs   | <0.04                            | <0.2                                    | <0.08                                   | <0.6                       | <0.2                       | <25                                     | <300                                     |
| Tri-CDDs   | <0.1                             | <0.2                                    | <0.05                                   | <1.9                       | <0.2                       | <12                                     | <300                                     |
| Tetra-CDFs | <0.2                             | <0.1                                    | <0.2                                    | <6.3                       | <0.1                       | <1.2                                    | <50                                      |
| Tetra-CDDs | <0.2                             | <0.1                                    | <0.05                                   | <3.0                       | <0.1                       | <1.0                                    | <50                                      |
| Penta-CDFs | <0.04                            | <0.05                                   | <0.05                                   | <6.3                       | <0.2                       | <1.5                                    | <50                                      |
| Penta-CDDs | <0.1                             | <0.05                                   | <0.05                                   | <6.3                       | <0.2                       | <1.5                                    | <50                                      |
| Hexa-CDFs  | <2.4                             | <0.7                                    | <0.3                                    | <6.3                       | <0.9                       | <2.5                                    | <150                                     |
| Hexa-CDDs  | <0.6                             | <0.7                                    | <0.2                                    | <6.3                       | <0.9                       | <2.5                                    | <150                                     |
| Hepta-CDFs | <4.6                             | <1.4                                    | <3                                      | <6.3                       | <0.2                       | <5.0                                    | <50                                      |
| Hepta-CDDs | <0.2                             | <0.1                                    | <0.05                                   | <0.3                       | <0.1                       | <0.3                                    | <5                                       |
| Octa-CDF   | <1.0                             | <0.3                                    | <0.3                                    | <1.3                       | <0.4                       | <0.5                                    | <250                                     |
| Octa-CDD   | <0.4                             | <0.2                                    | <0.1                                    | <0.6                       | <0.4                       | <0.5                                    | <250                                     |

Table V. Amounts of PCDFs found in samples from accidental PCB fire, Stockholm, Sweden

| PCDF                    | Amount<br>$\text{ng m}^{-3}$ |
|-------------------------|------------------------------|
| 2,3,7,8-Tetra-CDF       | 150                          |
| 1,2,3,7-Tetra-CDF       | 150                          |
| 2,3,6,8-Tetra-CDF       | 125                          |
| 1,4,6,8-Tetra-CDF       | 75                           |
| 2,4,6,7-Tetra-CDF       | 37                           |
| 3,4,6,7-Tetra-CDF       | 7.5                          |
| 1,2,5,7+1,3,5,9-CDF     | 100                          |
| Other Tetra-CDFs        | 750                          |
| Total Tetra-CDFs        | 1200                         |
| 2,3,4,7,8-Penta-CDF     | 45                           |
| 1,2,4,7,8-Penta-CDF     | 38                           |
| 1,2,3,6,7-Penta-CDF     | 15                           |
| 1,3,4,7,8-Penta-CDF     | 11                           |
| 2,3,4,6,7-Penta-CDF     | 7.5                          |
| 1,2,4,6,8-Penta-CDF     | 3.8                          |
| 1,2,4,7,8-Penta-CDF     | 3.8                          |
| 1,2,3,6,7-Penta-CDF     | 3.8                          |
| 1,2,4,6,8-Penta-CDF     | 3.8                          |
| 2,3,4,6,8-Penta-CDF     | 2                            |
| 1,2,3,7,8+1,2,3,4,8-CDF | 15                           |
| Other Penta-CDFs        | 19                           |
| Total Penta-CDFs        | 175                          |
| Total Hexa-CDFs         | <0.5                         |

No PCDFs or PCDDs could be found in any of the samples, but in three of the samples we found traces of tetrachlorinated biphenyls.

#### Conclusions

A comparison of the Skövde fire with the Stockholm fire shows that these two PCB fires produced quite different products. The Skövde fire is a "normal" fire where mineral oil generated the heat. The major products formed here are PCDFs and PCPYs, while no PCBs could be identified.

The Stockholm fire was caused by an electrical malfunction. The temperature in this fire was probably much higher than in Skövde. In this fire the PCBs were the major products while PCDFs and PCPYs were minor constituents.

Another PCB fire occurred in the State Office Building in Binghamton, New York, U.S.A. Analyses of soot samples formed in this fire showed the presence of 2,3,7,8-tetra-CDD and other tetra-CDDs [18]. However, no dioxins have been found in the soot from the Swedish PCB fires. This difference can be explained by the presence of polychlorinated benzenes in the transformer oil in Binghamton. It has been shown by Buser that PCDDs and PCDFs are formed during the pyrolysis of polychlorinated benzenes [19].

Two new classes, the PCBPs and PCPYs were reported for the first time in these samples.

The data from the PCB test burning indicate that this might be a safe method for the destruction of the PCB, now in use in capacitors and transformers.

#### Acknowledgements

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#### References

1. Poland, A., Glover, E. and Korte, A. S., *J. Biol. Chem.* 251, 4936 (1976).
2. Lahavita, E. S., Perles, H. and Korte, F., *Chemosphere* 6, 11 (1977).

3. Olla, K., Vermoulen, P. L. and Hutzinger, O., *Chemosphere* 6, 4 (1977).
4. Buser, H. R., Besshardt, H. P. and Rappe, C., *Chemosphere* 7, 11 (1978).
5. Buser, H. R., Besshardt, H. P., Rappe, C. and Lindahl, R., *Chemosphere* 7, 419 (1978).
6. Buser, H. R. and Besshardt, H. P., *Mitt. Geb. Lebensmittelsicherh. u. Hyg.* 69, 191 (1978).
7. Lutenhauer, J. W. A., Olla, K. and Hutzinger, O., *Chemosphere* 9, 301 (1980).
8. Buser, H. R., Rappe, C. and Garb, A., *Chemosphere* 7, 419 (1978).
9. Buser, H. R., Besshardt, H. P. and Rappe, C., *Chemosphere* 7, 109 (1978).
10. Buser, H. R. and Rappe, C., *Chemosphere* 8, 157 (1979).
11. Ministry of the Environment, Ontario, Canada New Release February 13 (1979).
12. Jonsson, J. and Sandström, G., in *Chlorinated Dioxins and Related Compounds* (Edited by O. Hutzinger, R. W. Frei, E. Meroni, and F. Pocchiari), p. 201. Pergamon Press, Oxford (1982).
13. Buser, H. R., *Polychlorinated Dibenzop-dioxins and Dibenzofurans Formation, Occurrence and Analysis of Environmentally Hazardous Compounds*. Thesis, University of Umeå (1978).
14. Rappe, C. and Buser, H. R., in *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Compounds* (Edited by R. Kimbrough), p. 41. Elsevier, Amsterdam (1980).
15. Buser, H. R. and Rappe, C., *C. Anal. Chem.* 52, 2257 (1980).
16. Garb, A., *Studies of Polychlorinated Dibenzofurans Thesis*, University of Umeå, (1982).
17. Cooks, R. G. and Gluk, G. L., *Chem. Eng. News*, p. 40 Nov. 30 (1981).
18. Rappe, C., *Report on the Analysis of Binghamton Soot*, May 4 (1981).
19. Buser, H. R., *Chemosphere* 8, 251 (1979).