Formation, Occurrence and Analysis of Polychlorinated Dibenzofurans, Dioxins and Related Compounds

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In several accidents (fires, explosions) involving electrical systems containing polychlorinated biphenyls (PCBs) or benzenes (PCBZs), the formation of polychlorinated tricyclic aromatic compounds such as polychlorinated dibenzofurans (PCDFs), dibenzo-p-dioxins (PCDDs) and biphenylenes (PCBP) was observed. These findings were not surprising in light of our previous studies on the formation of PCDFs and PCDDs from the thermolysis (500–750°C in presence of air) of PCBs or PCBZs. In these experiments we identified three main and a fourth minor reaction pathway leading to PCDFs from PCBs. The three main reactions involved the loss of ortho-Cl, and the losses of ortho-HCl with and without a 2,3-chlorine shift. The fourth, minor reaction route found with some PCBs, involved the loss of ortho-H2. These reaction pathways were intramolecular cyclizations via oxidation to phenolic compounds. Thermolysis of commercial PCBs (Aroclor 1254 and 1260) yielded the same PCDF isomers as expected from the main PCB components via these four reaction pathways; the isomers formed included the toxic 2,3,7,8-substituted tetra-, penta- and hexa-CDFs. Thermolysis of PCBZs involved complex condensation reactions with multiple rearrangements leading to PCDFs as well as PCDDs. Again oxidation to phenolic products was involved but the reaction routes are not yet fully elucidated.

The results of samples from transformer and capacitor accident sites showed very complex PCDF mixtures with 2,3,7,8-substituted isomers as main components and originating from the PCBs in the transformer liquid. The unusual presence of PCDDs in samples from the Binghamton accident originates from PCBZs present in transformer fluid of that specific installation, thus confirming our previous thermolysis findings. The source of PCBP's and their route of formation have not yet been fully elucidated. The application of high-resolution gas chromatography in combination with mass spectrometry is documented and the need for isomer-specific analyses discussed.

Introduction

Polychlorinated tricyclic aromatic compounds have been identified in several accidents involving transformers and capacitors with polychlorinated biphenyls (PCBs) and benzenes (PCBZs) (1,2). This group of compounds includes some of the most toxic synthetic chemicals known. The formations and possible release of these compounds in accidents from electrical system failures (fires, explosions, overheating) with involvement of PCBs and PCBZs constitutes a new, previously unrecognized health hazard and environmental contaminations as well as occupational exposures with these chemicals have to be prevented.

The group of tricyclic aromatic compounds of concern here is consisting of three series, namely the polychlorinated dibenzo furans (PCDFs), dibenzo-p-dioxins (PCDDs) and biphenylenes (PCBP). Substitution by chlorine of these ring systems leads to a number of chloro homologs and isomers ranging from the mono to the fully chlorinated octachloro compounds. There is a total of 135 PCDF, 75 PCDD and 75 PCBP isomers (see Table 1). The largest number of isomers in all three series is found for the tetrachloro compounds, namely 38 tetrachlorodibenzo furans (tetra-CDFs), 22 tetrachlorodibenzo-p-dioxins (tetra-PCDDs) and 22 tetrachloro-

| Chlorine substitution | Number of isomers |
|-----------------------|-------------------|
|                       | PCDFs | PCDDs | PCBP |
| Mono                  | 4     | 2     | 2    |
| Di                    | 16    | 10    | 10   |
| Tri                   | 28    | 14    | 14   |
| Tetra                 | 38    | 22    | 22   |
| Penta                 | 28    | 14    | 14   |
| Hexa                  | 16    | 10    | 10   |
| Hepta                 | 4     | 2     | 2    |
| Octa                  | 1     | 1     | 1    |
| Total                 | 135   | 75    | 75   |

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robiphenylenes (tetra-CBP). The large number of isomers is one of the reasons for the complexity and difficulty of the analyses.

Some of these compounds proved extremely toxic and hazardous (3-7). LD_50-values range from 1 to 100 μg/kg for the most sensitive laboratory animal species. There is a great deal of toxicity data on PCDDs, especially on 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-tetra-CDD), and some on PCDFs, but comparatively little on PCBPs. However, from structural considerations and from the biological activity of some congeners, the PCDFs and PCBPs have to be considered as in similar toxicity as the PCDDs (6,7).

Toxicity seems to depend on the number and the position of the chlorine substituents of a congener (4,5). It is highest for the tetra-, penta- and hexachloro compounds. Pronounced differences in toxicity are found between isomers. Toxicity apparently is highest for isomers fully chlorinated at the lateral (2-, 3-, 7- and 8- in PCDFs and PCDDs, 2-, 3-, 6- and 7-in PCBPs) positions (5,7). The most hazardous compounds are thus the so-called 2,3,7,8 (2,3,6,7)-substituted isomers. There are seven such isomers in the PCDF series, and five each in the series of the PCDDs and PCBPs. The structures of the 2,3,7,8-substituted PCDFs and PCDDs are shown in Figure 1a and 1b, respectively. The most toxic isomer appears to be 2,3,7,8-tetra-CDD that also has a high cocarcinogenic potential (8). The most toxic members of the other two series are expected to be 2,3,7,8-tetra-CDF and 2,3,6,7-tetra-CBP; both compounds are isosteric to 2,3,7,8-tetra-CDD. PCDDs and PCDFs have caused environmental contaminations (Seveso, Vietnam, Love Canal, Missouri) and human intoxications (Yusho in Japan and Taiwan); they have received wide public attention. Comparatively little is known about the PCBPs.

PCDDs and PCDFs are found as undesired trace contaminants in certain industrial chemicals such as the chlorophenols and their derivatives (2,3,7,8-tetra-CDD is a contaminant of 2,4,5-trichlorophenol and 2,4,5-T herbicides) and PCBs (9). The levels of PCDDs and PCDFs are usually in the ppm or sub-ppm range, nevertheless the presence of these contaminants proved to be responsible for some of the toxic properties of these industrial chemicals. Of special interest here is the presence of PCDFs in PCBs. These industrial chemicals were used in very large quantities (world production above 1 million tons) in many applications. Due to their good electrical properties, their nonflammability and chemical stability they were used in electrical systems as transformer and capacitor fluids. Among the many commercial products were Aroclors, Clophenes, Phencloors, Phenalenelnes, Pyranols, Kanecloors and many others. Aroclor 1254 and 1260 were preferred products in the U.S.; they had an average composition containing 54 and 60% chlorine, respectively. The unrestricted industrial use of PCBs caused a large scale environmental contamination. At least one manufacturer restricted production and sales of PCBs in the 1970s to closed systems (capacitors and transformers). Chlorobenzenes apparently were added sometimes to these products in specific applications (2).

Commercial PCBs were shown to contain PCDFs as impurities (9,10). The toxicity of some PCB formulations was responsible for the search and the finding of PCDFs as toxic agents (10). The levels of PCDFs in some commercial PCBs surveyed are listed in Table 2; other tricyclic compounds (PCDDs and PCBPs) were not present in these samples (Buser and Rappe, unpublished, 1979). The samples analyzed showed rather complex isomeric mixtures of PCDFs. Among the isomers identified were 2,3,7,8-substituted congeners such as 2,3,7,8-tetra-, 1,2,3,7,8- and 2,3,4,7,8-penta-, and 1,2,3,4,7,8-hexa-CDF. Additional isomers found were 2,3,6,8- and 2,3,6,7-tetra-, 1,2,4,7,8-, and 2,3,4,6,8,9-hepta-CDF. A sample of used PCB showed increased

| Sample            | Tri | Tetra | Penta | Hexa | Hepta | Total |
|-------------------|-----|-------|-------|------|-------|-------|
| Aroclor 1254      | 0.10| 0.25  | 0.70  | 0.81 |       | 1.9   |
| Aroclor 1254      |     | 0.05  | 0.10  | 0.02 |       | 0.2   |
| Aroclor 1250      | 0.06| 0.30  | 1.00  | 1.10 | 1.35  | 3.8   |
| Clophen T94       | 0.10| 0.30  | 1.78  | 2.54 | 0.82  | 5.4   |
| Prodelec 3010     | 0.41| 1.08  | 0.38  | 0.07 |       | 2.0   |
| Mitsubishi (used) | 2.13| 4.00  | 3.30  | 0.55 |       | 10.0  |
levels of PCDFs (Table 2). Significantly increased levels of PCDFs were calculated for the PCB causing the Yu-
sho poisoning in Japan (11). In that incident, PCB used as a heat transfer liquid was oxidized and contaminated 
rice oil for human consumption via a faulty heating 
system.

PCDFs and PCDDs are known to be formed in ther-
mal reactions from suitable precursors such as from 
chlorophenols, PCBs and PCBZs (12–14). They have 
also been detected in emissions and fly ash from mu-
icipal and industrial incinerators (15,16). PCDDs and 
PCDFs are also suspected to be formed, although in 
extremely low yields, from more common substances 
like lignin by chlorination reactions under incineration 
conditions (17). Of special interest here is their forma-
tion by thermal reactions from PCBs and PCBZs.

Formation of PCDFs from the 
Thermolysis of PCBs

In 1978, we reported the conversion of PCBs into 
PCDFs via thermolytic reactions in laboratory experi-
ments (13). Although this reaction was anticipated, 
surprisingly, no experimental evidence had been previously 
reported. Up to that time little attention was actually 
paid to the possible formation of PCDFs from inciner-
ation or combustion of PCBs.

In our laboratory experiments, we demonstrated the 
conversion to PCDFs from small quantities (100 µg) of 
commercial PCBs (Aroclor 1254 and 1260) at tempera-
tures from 500 to 750°C in the presence of air (reaction 
times ca. 5 sec). The reactions were found to be intra-
molecular cyclizations of the type shown in Eq. (1). 
Conversion rates were 1 to 25% based on the PCB reacted. 
This formation of PCDFs was judged to be of significant 
environmental significance in case of accidental burning 
or incineration of PCBs (13). The experiments resulted 
in complex isomeric mixtures of PCDFs. The reactions 
apparently led easily and exclusively to PCDFs; neither 
PCDDs nor PCBPs were observed.

In further model experiments using individual, spe-
cially synthesized PCB isomers, we identified three main 
and fourth, minor reaction route leading to PCDFs 
(Eq. (2)) (18). These reactions involved the loss of ortho-
Cl₄, the loss of ortho-HCl with and without 2,3-chlorine 
shift, and finally the loss of ortho-H₂. The last reaction 
was only of some importance for a few specific PCB 
isomers; the formation of PCDFs from PCBs was found 
to proceed mainly via reaction pathways 1–3. The PCDFs 
formed predominantly contained thus one or two chlor-
ines fewer than the PCB precursors. Eighteen different 
PCB isomers were investigated and more than 40 PCDFs 
were observed. These reactions leading to very specific 
PCDF isomers were also used for the preparation of small quantities of PCDF reference compounds. More 
recently all 38 tetra-CDF isomers were prepared via 
these reaction routes (19).

Conversion rates were in the per cent range at op-
timal temperatures of 500–600°C. At 700°C, the deg-
radation rates were faster than the rates of formation; 
at temperatures above 800°C, PCBZs were the only 
identifiable products beside CO₂, HCl and carbon.

The same reactions were also found to occur with the 
bromo analogs. Firemaster BF-6, a flame retardant with 
2,4,5,2′,4′,5′-hexabromobiphenyl as a main component, 
was converted into toxic 2,3,7,8-tetra-bromodibenzo-
furan (13,20). The thermal conversion of polybromi-
nated biphenyls (PBBs), and of polychlorinated 
and polybrominated diphenyl ethers (PCDPEs), used as 
flame retardants and in electrical appliances (TV cov-
ers), into toxic products (21) raises serious concern, and 
the use of these products in these applications should 
be carefully reconsidered.

From the four reaction pathways it is possible to de-
duce the structure of the PCDF isomers expected from 
the thermolysis of the various PCB isomers present in 
commercial formulations. Two commercial PCBs (Ar-
oclor 1254 and 1260) were analyzed for individual PCB 
isomers by using high-resolution gas chromatography 
(HRGC) and mass spectrometry in comparison to au-
thentic reference compounds. In Table 3 we list the 
major PCB components found in these formulations and 
the PCDFs expected by the four reaction pathways. 
Aroclor 1254, consisting primarily of tetra-, penta-, hexa-
and heptachlorobiphenyls and small amounts of tri- and 
octachlorobiphenyls, is expected to yield di-, tri-, tetra-, 
penta- and hexa-CDFs; Aroclor 1260 consisting 
primarily of penta-, hexa-, hepta- and octachlorobiphenyls 
is expected to yield tri-, tetra-, penta-, hexa- and hepta-
CDFs. It is seen from Table 3 that the PCDFs expected 
include the toxic 2,3,7,8-substituted isomers.

Analysis of the thermolysis products of Aroclor 1254 
and 1260 in fact confirmed these predictions. From these 
pyrolyses, about 30 major and more than 30 minor PCDF 
isomers were observed, with total yields in the range
Table 3. Main PCB components in commercial PCB formulations (Aroclor 1254 and 1260) and PCDF isomers expected from their thermolysis.

| PCB isomers founda | PCDF isomers expected by various reaction routesb |
|--------------------|-----------------------------------------------|
| In Aroclor 1254    | Route (1) Route (2) Route (3) Route (4) |
| 2,5,2',5'          | 2,8      2,4,8 1,4,8 1,4,6,9 |
| 2,3,2',5'          | 2,6      2,4,6 1,4,6; 1,2,8 1,2,6,9 |
| 2,5,3',4'          | —        —      2,6,7; 2,3,8 1,4,7,8 |
| 2,3,6,2',5'        | 1,4,8; 1,2,8 1,4,6,8; 1,2,6,8; 1,2,4,8 1,2,6,9; 1,4,6,9 — |
| 2,4,5,2',5'        | 2,3,8     2,3,5,6; 2,3,4,8 1,4,7,8; 1,3,4,8 1,3,4,6,9 |
| 2,3,4,2',5'        | 2,6,7     2,4,6; 1,2,3,8; 1,4,6,71,2,3,6,9 1,2,4,7,8 |
| 2,3,6,3',4'        | —        —      —      1,2,6,7 1,2,6,7 1,2,6,7 |
| 2,4,5,3',4'        | —        —      —      1,4,7,8; 1,4,6,7; 1,2,7,8; 1,2,6,7 |
| 2,3,4,3',4'        | —        —      —      1,2,6,7 1,2,6,7 1,2,6,7 |
| 2,3,6,2',4',5'     | 1,4,7,8; 1,2,7,8 2,3,4,6,9; 2,3,4,8,9; 1,3,4,8,9; 1,3,4,6,9 — |
| 2,4,5,2',5',6'     | 2,3,8     2,3,4,7,8 1,2,3,8; 1,2,3,6,9 1,3,4,6,9 |
| 2,3,4,2',3',6'     | 1,4,6,7; 1,2,6,7 1,2,4,6,7; 1,3,4,6,7 1,3,4,6,9 |
| 2,3,6,2',4',5'     | 2,3,6,7   2,3,4,5,6,7 1,2,3,4,6,9 |
| 2,3,5,6,2',4',5'   | 2,3,4,6,7; 1,2,3,6,9 1,2,3,4,6,9; 1,2,3,4,8,9 — |
| 2,3,5,6,2',3',6'   | 1,2,4,7,8 1,2,4,6,7; 1,2,4,6,8 |
| 2,3,5,6,2',4',5'   | 1,2,4,6,7 1,2,3,4,6,8; 1,2,3,4,8,9; 1,2,3,4,6,9 |
| 2,3,5,6,2',3',4',5'| 1,2,4,6,7 1,2,3,4,6,8; 1,2,3,4,8,9; 1,2,3,4,6,9 |

*Analysis by HRGC and mass spectrometry, major components in italics, subscripts tetra-to octa- omitted.

*Subscripts di-, tri- etc. omitted; 2,3,7,8-substituted tetra-, penta- and hexa-CDF isomers in italics.

![Figure 2](image-url)

**Formation of PCDFs and PCDDs from the Thermolysis of PCBZs**

In subsequent experiments, we observed the formation of tricyclic aromatic compounds in thermolytic reactions from PCBZs (14). The main products were PCDFs in yields of up to 1%, and PCDDs in somewhat smaller yields. Because chlorophenols were also observed, the reactions presumably start with oxidation of PCBZs followed by condensation to PCDFs and...
PCDDs, possibly by way of PCDPEs as shown in the tentative reaction scheme in Eq. (3). These condensations are bimolecular and require the presence of higher concentrations of PCBZs to proceed efficiently. PCBZs can be formed from other chlorinated organic compounds including PVC (22) and possibly even from inorganic chloride and organic materials under pyrolytic conditions; however, the amounts of PCBZs and the concentrations reached by these routes are probably too low to represent an untenable risk for the formation of PCDFs and PCDDs. The situation, however, may be different, if attempts were made to dispose of larger quantities of PCBZs such as wastes and residues from industrial chemical processes by incineration. Strict controls have to be implemented for such processes in order to ensure safe disposal and to prevent environmental contaminations and occupational exposures to PCDFs and PCDDs (24).

The actual reaction mechanisms have not been elucidated in these experiments. They seem rather complex involving multiple rearrangements, as indicated from the pyrolysis of 1,2,4-trichlorobenzene that gave a complex mixture of PCDFs (at least 10 tetra-, 18 penta-, 14 hexa-, and all 4 hepta-CDFs were observed) as well as tetra-, penta- and hexa-CDDs. Pyrolysis of 1,2,4,5-tetrachlorobenzene similarly gave a complex mixture of penta-, hexa-, hepta- and octa-CDF, and smaller amounts of hexa-, hepta- and octa-CDD, again indicating extensive rearrangements. No PCBP were observed in these experiments.

**Analysis of Polychlorinated Tricyclic Aromatic Compounds**

The analysis of polychlorinated tricyclic aromatic compounds is complicated by the extremely low detection levels required (due to the high toxicity of some of the compounds), the many additional, co-extracted, very often chlorinated compounds present, and the large numbers of isomers involved. Very sensitive, selective and specific analytical techniques are required. There have been great efforts undertaken and a wealth of information is available on analytical methods; several international conferences and workshops were devoted to PCDDs and PCDFs. The most specific methods described use mass spectrometry for detection, quantification and confirmation of these compounds. A more detailed description of the analysis of these compounds in environmental samples is given elsewhere (23). In that article, we emphasize the importance of isomer identifications and of isomer-specific analyses, especially of 2,3,7,8-substituted isomers. Extraction and cleanup procedures are required that recover most or all of the PCDFs, PCDDs and possibly PCBP as a group. HRGC analysis is used for the separation of isomers; electron-impact (EI) and negative chemical ionization (NCI) mass spectrometry are used for detection and identification. Combined mass spectrometry-mass spectrometry (MS-MS) is potentially useful but has not yet been investigated here. The identification of PCDFs and PCDDs is usually easily accomplished by mass spectrometry, but that of PCBP is more complicated because of interference from PCBs (23).

All PCDFs and PCDDs containing four or more chlor-
ine substituents are available as qualitative standards; a few are available in larger quantities as weigh-in standards for quantitative analyses. In our analyses, calibration of the mass spectrometer response (single or multiple ion detection, SID, MID) was made by using 2,3,7,8-tetra-, 1,2,3,6,8,9-hexa- and octa-CDD, and 2,3,7,8-tetra-, 1,2,3,4,7,8-hexa- and octa-CDF. The same response was assumed for other isomers, and those of the penta- and heptachloro compounds were interpolated from the neighboring chloro homologs.

**Occurrence of Polychlorinated Tricyclic Aromatic Compounds after Accidents in Electrical Systems**

Several incidents resulting in the formation of polychlorinated tricyclic aromatic compounds from fires and explosions of malfunctioning electrical systems containing PCBs and PCBZs have been reported from North America and Scandinavia (1,2). A fire of a transformer in the basement of the 19-story state office building in Binghamton, NY was probably the first occasion of a serious contamination of a non-industrial building (2). In this incident, PCDFs and to a lesser degree PCDDs and PCBPs were observed. Additional incidents in Sweden involving capacitors with PCBs were discussed by Rappe et al. (1). In one of these accidents (capacitor battery fire in Skövde), significant quantities of PCDFs as well as some PCPYs were formed (tetra-, penta- and hexa-CDFs including 2,3,7,8-tetra-CDF at a combined level of up to 1 µg/m²), but apparently no PCDDs or PCBPs were observed. In another of these accidents (light-arching in capacitors, Stockholm), however, significant amounts of PCBPs (25–30 µg/m²) were observed in addition to PCDFs (combined level of up to 1.4 µg/m²) and some PCPYs. The formation of these additional products was ascribed to the different conditions of this fire (presumably much higher temperatures). In none of these accidents, PCDDs were observed. The occurrence of PCDDs in samples from the Binghamton accident is not surprising due to the presence of PCBZs (35% tri- and tetrachlorobenzene, 65% PCBs) in the transformer fluid of that installation.

We have analyzed in detail soot samples from two accident sites. A soot sample of the Binghamton accident (courtesy D. Stalling and A. Schecter) was analyzed by HRGC and EI mass spectrometry for PCDFs and PCDDs. The sample was previously extracted with toluene and purified by carbon chromatography at the Columbia National Fisheries Research Laboratory, Columbia, MO. In Figure 3 we show a chromatogram of the PCDF analysis. The levels of the various PCDF isomers were quantified and are reported in Table 4. They were 28, 670, 965, 460 and 40 ppm for tetra-, penta-, hexa-, hepta- and octa-CDF, respectively. The maximum level was found for the hexa-CDF; the combined level of all PCDFs was more than 2000 ppm. Taking into account PCB levels in soot of up to 20%, conversion rates for the formation of PCDFs in the per cent range are indicated. A 55-1 m Silar 10c HRGC column was used for the isomer-specific analysis reported in Figure 3. As major isomers, 2,3,7,8-tetra-, 1,2,3,7,8-penta-, and 1,2,3,4,7,8- and 1,2,3,6,7,8-hexa-CDF were present. Apparently, this accident produced significant quantities of 2,3,7,8-substituted isomers. In Table 4, we also indicate the various PCDF isomers formed in the pyrolysis of commercial PCBs (Aroclor 1254 and 1260).
indicated, the major PCDFs observed in this soot sample were those produced from these pyrolyses, suggesting PCBs as primary precursors of the PCDFs, although some contribution of PCDFs from PCBZs may also be present.

In Figure 4 we show a chromatogram of the PCDD analysis of the same Binghamton soot sample. The results are quantified in Table 5. As indicated, the combined level of PCDDs is around 20 ppm, about 100 times lower than the level of PCDFs, indicating the contamination to be primarily due to the latter compounds. Maximum level was found for the hepta-CDDs, somewhat smaller levels of tetra-, penta-, hexa- and octa-CDD were observed. Again, 2,3,7,8-substituted isomers were present, including 2,3,7,8-tetra-, 1,2,3,7,8-penta- and to a lesser degree all three toxic hexa-CDDs. The sources of these PCDDs are very likely PCBZs present in the transformer fluid (23% tri- and 12% tetrachlorobenzene); we previously reported the formation of tetra- to octa-CDDS from tri- and tetrachlorobenzenes in our thermolysis experiments (14). In addition to PCDFs and PCDDs, the presence of some PCBPs was reported (2); however, isomers were not identified.

Table 4. PCDF isomers found in soot from transformer accident in Binghamton, NY and in PCB pyrolyzates.

| PCDF isomer           | Level of PCDF isomers observed in soot, ppm | Isomers in PCB pyrolyzates |
|-----------------------|---------------------------------------------|-----------------------------|
| 2,3,7,8-Tetra-CDF     | 12                                          | ***                         |
| 1,3,7,9-Tetra-CDF     | 1                                           | *                           |
| Others                | 15 (4)                                      |                             |
| 1,2,3,7,8-Penta-CDF   | 310                                         | ***                         |
| 2,3,4,7,8-Penta-CDF   | 48                                          | ***                         |
| 1,2,4,7,8-Penta-CDF   | 25                                          | ***                         |
| 1,2,4,7,9-Penta-CDF   | 22                                          | *                           |
| 1,3,4,7,8-Penta-CDF   | 65                                          | ***                         |
| 2,3,4,8,9-Penta-CDF   | 25                                          | *                           |
| 1,2,3,6,7-Penta-CDF   | 60                                          | *                           |
| 2,3,4,6,7-Penta-CDF   | 12                                          | *                           |
| Others                | 110 (12)                                    |                             |
| 1,2,3,4,7,8-Hexa-CDF  | 310                                         | ***                         |
| 1,2,3,4,6,7-Hexa-CDF  | 150                                         | ***                         |
| 1,2,3,4,6,7-Hexa-CDF  | 10                                          | *                           |
| 1,2,3,6,8,9-Hexa-CDF  | 30                                          | *                           |
| 1,2,3,6,8,9-Hexa-CDF  | 38                                          | *                           |
| 1,2,4,6,7,8-Hexa-CDF  | 50                                          | ***                         |
| 1,3,4,6,7,8-Hexa-CDF  | 125                                         | ***                         |
| Others                | 250 (8)                                     |                             |
| 1,2,3,4,6,7,9-Hepta-CDF| 230                                         | ***                         |
| 1,2,3,4,6,7,9-Hepta-CDF| 120                                         | ***                         |
| 1,2,3,4,6,7,9-Hepta-CDF| 55                                          | *                           |
| 1,2,3,4,7,8,9-Hepta-CDF| 55                                          | *                           |
| Octa-CDF              | 40                                          | *                           |

*Approximate number of additional isomers given in parentheses. bLaboratory experiments using Aroclor 1254 and 1260; major isomers found denoted by ***; others by *.

Table 5. PCDD isomers found in soot from transformer accident in Binghamton, NY.

| PCDD isomer     | Level of PCDDs observed in soot, ppm |
|-----------------|--------------------------------------|
| 2,3,7,8-Tetra-CDD | 0.6                         |
| Others          | 0.6 (4)                             |
| 1,2,3,7,8-Penta-CDD | 2.5                        |
| Others          | 2.5 (7)                             |
| 1,2,3,4,7,8-Hexa-CDD | 0.7                           |
| 1,2,3,4,6,7-Hexa-CDD | 0.6                           |
| 1,2,3,7,8,9-Hexa-CDD | 0.4                           |
| 1,2,3,4,6,7,9/1,2,4,6,8,9-Hexa-CDD | 1.2                          |
| 1,2,3,6,8,9/1,2,3,6,7,9-Hexa-CDD | 1.3                          |
| 1,2,3,4,6,7-Hexa-CDD | 0.5                           |
| 1,2,3,4,6,7,9-Hepta-CDD | 4                             |
| 1,2,3,4,6,7,8-Hepta-CDD | 3                             |
| Octa-CDD        | 2                                   |

*Number of other isomers given in parentheses.

Figure 4. Chromatogram (SID mass spectral analysis, EI, m/z 320, 354, 388, 424 and 458) showing elution of tetra-, penta-, hexa-, hepta- and octa-CDDs in soot sample (see Fig. 5).
Table 6. PCDF isomers found in soot from capacitor accident in Finland (1982).

| PCDF isomer          | Level of PCDFs observed in soot, ppm* |
|----------------------|--------------------------------------|
| Tri-CDFs             | 270 (19)                             |
| 2,3,7,8-Tetra-CDF    | 3                                    |
| 1,3,6,8-Tetra-CDF    | 1                                    |
| 1,3,7,9-Tetra-CDF    | 10                                   |
| 1,3,6,7-Tetra-CDF    | 7                                    |
| 2,3,6,8-Tetra-CDF    | 2                                    |
| 2,3,6,7-Tetra-CDF    | 4                                    |
| 3,4,6,7-Tetra-CDF    | 1                                    |
| 1,2,3,7,8-Penta-CDF  | 24 (13)                              |
| 2,3,4,7,8-Penta-CDF  | 1-2                                  |
| 1,2,4,7,9-Penta-CDF  |                                      |
| 1,2,3,6,7-Penta-CDF  |                                      |
| 1,2,6,7,8-Penta-CDF  |                                      |
| 2,3,4,6,7-Penta-CDF  |                                      |

*Number of other isomers given in parentheses.

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