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POLYCHLORINATED DIOXINS AND DIBENZOFURANS

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JAN 1 1984

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INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two series of tricyclic almost planar aromatic compounds which exhibit similar physical, chemical and biological properties and have been the subject of much concern in recent years. They have been involved in accidents like that in Seveso, Italy in 1976, the fire in the Binghamton State Office Building in 1981, the Love Canal incident in Niagara Falls in 1979, the intoxications at horse arenas in Missouri in 1971 and Times Beach, Missouri in 1982-83, the Yusho accidents in Japan in 1968 and in Taiwan in 1979 and also in the herbicide spraying program in Vietnam in the late 1960s.

The chemical structures and numbering of these hazardous compounds are given in Figure 1. The number of chlorine atoms in these compounds can vary between one and eight producing up to 75 PCDD and 135 PCDF positional isomers as shown in Table 1.

Animal studies and in vitro experiments have indicated that there is a pronounced difference in toxic and biologic effects among different PCDD and PCDF isomers. A factor of 1 000 - 10 000 in difference can be found for so closely related isomers as 2,3,7,8- and 1,2,3,8-tetra-CDD and 1,2,3,7,8- and 1,2,4,7,8-penta-CDD (Bradlaw and Casterline, 1976; Poland et al., 1976). The isomers with the highest activity and the highest acute toxicity are

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those having 4-6 chlorine atoms and all lateral (2,3,7 and 8) positions substituted for chlorine, see Table 2. The LD₅₀-values for guinea pigs for 2,3,7,8-tetra-CDD, 1,2,3,7,8-penta-CDD, 2,3,7,8-tetra-CDF and 2,3,4,7,8-penta-CDF are all below 10 µg/kg (Mc Connell et al., 1978; Moore et al., 1979; Huff et al., 1980).

ANALYTICAL PROCEDURES

Because of the extreme toxicity of some of the isomers of PCDDs and PCDFs, highly sensitive and specific analytical techniques are required for the measurements. Detection levels in human and ecological samples should be orders of magnitude below the usual detection levels obtained in pesticide analysis. A detection level of 1 pg (10^{-12} g) or less might be required to detect 2,3,7,8-tetra-CDD and the other isomers listed in Table 2 in 1 g sample (1 ppt or sub ppt). Any analysis at such low levels are complicated by the presence of a multitude of other interfering compounds.

Another complication is the large number of isomers (Table 1) and the large variation in toxicity and biological potency between closely related isomers. A risk evaluation should be based on the levels of the highly toxic isomers found in isomer specific analyses.

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In recent years a great number of analytical methods have been developed for the analysis of trace amounts of PCDDs and PCDFs and especially for the most toxic 2,3,7,8-tetra-CDD in environmental samples. The most specific of these methods are based on mass spectrometry (MS). Prerequisites for a good analysis are: representative sampling, good storage, efficient extraction and sample purification (clean-up, containment enrichment) followed by good isomer separation, ultra sensitive detection and useful confirmatory information. Several review articles incorporating the analytical methods of

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PCDDs and PCDFs have appeared recently: McKinney (1978), Rappe and Buser (1981), Esposito et al., (1980), Karasek (1982), Tiernan (1983) and Tosine (1983). Most of the older methods have been critically reviewed by a panel of experts in the National Research Council of Canada (1981).

Sample Clean-up

Two different procedural trends can be recognized:

- a) all PCDD and PCDF isomers can be analyzed in one single fraction by the containment enrichment procedure (Stalling et al., 1983; Norstrom et al., 1982; and Tiernan, 1983).
- b) specific isomers are analyzed in different fractions mainly after reverse phase and normal phase High Pressure Liquid Chromatography (HPLC) separation (Lamparski et al., 1979).

The latter method allows the identification of only a few PCDD isomers, mainly 2,3,7,8-tetra-CDD. However, for a monitoring program a broad and general method is preferred.

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A series of PCDDs and PCDFs have now been identified in technical formulations and in various environmental samples such as human blood and adipose tissue, fish tissue, seal fat, bird eggs, beef fat and deer tissue, sediments, soil, fly ash and other products from incineration or combustion processes. The clean-up methods vary for the different matrices. As one example, the method for the extraction and containment enrichment of a fish tissue sample is discussed in detail by Stalling et al. (1983). This method has also been

used for other samples such as sediments and human tissue samples. In this method fish tissue (up to 100 g) is ground with Na_2SO_4 and applied to a first chromatographic system containing a segment of potassium silicate and another segment of silica gel. This system is followed by a column containing cesium silicate and silica gel followed by a column of carbon dispersed on glass fibers. Before elution the fish-salt mixture was spiked with $^{13}\text{C}_{12}$ -2,3,7,8-tetra-CDD, $^{13}\text{C}_{12}$ - or $^{37}\text{Cl}_4$ -2,3,7,8-tetra-CDF and $^{37}\text{Cl}_8$ -octa-CDD or $^{13}\text{C}_{12}$ -octa-CDD.

The carbon adsorbs most planar chlorinated (and unchlorinated) polynuclear aromatic compounds and the major portion of biological co-extractives is not retained. The PCDDs and PCDFs along with similar chemicals are then removed from the carbon by reverse elution with toluene. The toluene is evaporated slowly, O'Keefe et al. (1982), and the sample is re-dissolved in hexane and applied to two columns in tandem. The first column contains both sulfuric acid dispersed on silica gel and cesium silicate. The eluate from this column passes directly into the second column containing alumina.

Gas Chromatographic (GC) Separation and Isomer Identification

The purified extracts are used directly for the final analyses using a Gas Chromatograph - Mass Spectrometer (GC/MS) equipped with a glass capillary column coated with either of Silar 10 C, SP 2330, OV-17 or OV-101 or a fused silica column coated with either SP 2330, SP 2340, SILOV, SE 54 or DB-5. The column leads directly into the ion source of the MS instrument, which is operating either in the electron impact (EI) or the negative chemical ionization (NCI) mode.

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In view of the large variation in toxicological and biological effects of the PCDD and PCDF isomers, it is imperative that the isomers, particularly those having the highest toxicity, ^{b/c} identified. For an unambiguous isomer identification it is necessary to have access to all isomeric standards within a specific group of congeners, e.g. all the the 22 tetra-CDDs and all the 38 tetra-CDFs. All the 22 tetra-CDD have been prepared, and using a Silar 10 C glass capillary column the highly toxic 2,3,7,8-tetra-CDD can be separated from all the other 21 tetra isomers (Buser and Rappe, 1980). Recently all the 14 penta-CDDs and the 10 hexa-CDDs have been prepared. Using the Silar 10 C column the toxic 2,3,7,8-substituted isomers can be separated from all the other isomers (Buser and Rappe, 1983). The SP 2330 fused silica column can also be used for this separation (Rappe et al, 1984) and Figure 2 illustrates the separation of tetra-, penta- and hexa-CDDs.

In the PCDF series Mazer et al. (1983) have synthesized all the 38 positional tetra-CDF isomers. The products were mixtures of isomers, and each of these isomers could be identified using both a SP 2330 and a SE 54 capillary column. Later, Bell and Gará (1983) have isolated and characterized all tetra-, penta- and hexa-CDFs. The SP 2330 column can separate most of these isomers (Rappe et al., 1984) see also Figure 3. The toxic 1,2,3,7,8-penta-CDF co-elutes with the 1,2,3,4,8-isomer and the toxic 1,2,3,4,7,8-hexa-CDF with the 1,2,3,4,7,9-isomer, but these isomers can be separated on less polar columns like OV-17 and DB-5.

A very limited number of investigations have been performed using these complete sets of synthetic standards.

Quantification

Mass specific detection (mass fragmentography) has been used to quantify PCDDs and PCDFs in the samples by selective monitoring M, M+2 and/or M+4 ions. The quantification is based on the peak area measurements and comparison of these areas using either isotopically labelled internal standards (^{13}C or ^{37}Cl) or calibration curves of external standards. At a first approach it has been generally assumed that all isomers of a particular congener of PCDD or PCDF (e.g. the tetrachloro isomers) have the same response factors using the MS quantification technique. However, an investigation using 13 well defined tetra-CDF isomers have shown a 3-fold variation in the response factors using the EI mode and up to a 20-fold variation using the NCI mode. For the higher chlorinated homologues (Cl_5 , Cl_6) the difference was found to be smaller (Rappe et al., 1983 a).

LEVELS OF PCDDs and PCDFs IN COMMERCIAL PRODUCTS

Phenoxy herbicides

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The dioxin problem was first recognized in connection with teratogenic effects found for the phenoxy herbicide 2,4,5-T. These effects were shown to be caused by 30 $\mu\text{g/g}$ of 2,3,7,8-tetra-CDD present in this particular sample (Courtney and Moore, 1971). The levels of 2,3,7,8-tetra-CDD in drums of the herbicide "Agent Orange" placed in storage in the USA or in the Pacific before 1970 have been found to vary between 0.02 to 54 $\mu\text{g/g}$. More than 450 samples have been analyzed in this study (Firestone, 1978; Esposito et al., 1980). Since "Agent Orange" was formulated as a 1:1 mixture of the butyl esters of 2,4,5-T and 2,4-D, the levels of 2,3,7,8-tetra-CDD in individual 2,4,5-T preparations that were manufactured and used in the 1960's could be as high as 100 $\mu\text{g/g}$.

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As a result of governmental regulations, efforts were made during the 1970's to control and minimize the formation of 2,3,7,8-tetra-CDD during the 2,4,5-T production, and now all producers claim that their products contain less than 0.1 µg/g of 2,3,7,8-tetra-CDD.

The analytical methods used in these studies of phenoxy herbicides are not isomer specific, however more recent studies using isomer specific methods have confirmed that the 2,3,7,8-isomer is the major isomer in 2,4,5-T formulations (Buser and Rappe, 1980).

Sixteen samples of 2,4-D esters and amine salts from Canada have been analyzed for the presence of PCDDs. Eight out of nine esters and four out of seven amine salts were found to be contaminated, the esters showed significantly higher levels than the salts. The tetra-CDD observed was the 1,3,6,8-isomer as verified by synthetically prepared authentic standard (Cochrane et al., 1982). In other studies it has been found that no other tetra-CDD than the 1,3,6,8-isomer elutes in this window.

Hexachlorophene

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The bactericide hexachlorophene is prepared from the same starting material as used for the manufacture of 2,4,5-T, but there are very few data available in the literature on the levels of contaminants in this product. Three samples analyzed by Baughman (1974) showed 0.2-0.5 ng/g of 2,3,7,8-tetra-CDD. However, hexachlorophene also contains 100 µg/g of a hexachloroxanthene, the 1,2,4,6,8,9-isomer (Göthe and Wachtmeister, 1972). In this connection it could also be pointed out that a purification step (distillation, or recrystallization) results in a remarkable increase of impurities in the residues.

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Chlorophenols

Chlorophenols has been used extensively since the 1930s as fungicides, mold inhibitors, antiseptics, disinfectants and insecticides. The annual world production volume is estimated to be in the order of 150 000 tons. The most important use of 2,4,6-tri-, 2,3,4,6-tetra- and pentachlorophenol (or their Na or K salts) is for wood perservation. Pentachlorophenol or salts are also used for slime control in the manufacture of pulp or in synthetic cutting fluids, for tanning leather, in paint, glues and outdoor textiles.

Chlorophenols may contain a variety of contaminants, including PCDDs and PCDFs. Table 3 collects a number of relevant analyses of these products. The levels of PCDDs and PCDFs are much higher for these products than for the phenoxy herbicides.

It has also been reported that several positional isomers of PCDDs and PCDFs are present in the chlorophenols. However, a complete set of isomeric standards has not been used in these investigations, and more research is necessary to identify all the isomers present for a risk evaluation of these products.

Polychlorinated Biphenyls

Vos et al. (1970) were able to identify PCDFs (tetra- and penta-CDFs) in samples of European PCBs (Phenoclor DP-6 and Clophen A 60) but not in a sample of Aroclor 1260. They found the toxic effects of these PCB products to be parallel to the levels of PCDFs present in the products. Bowes et al.

(1975) examined a series of Aroclors as well as the samples of Aroclor 1260, Phenoclor DP-6 and Clophen A-60, that had previously been analyzed by Vos et al. (1970). They used packed columns and very few standard compounds and they reported that the most abundant PCDFs had the same chromatographic retention time as that of 2,3,7,8-tetra-CDF and 2,3,4,7,8-penta-CDF. The quantitative results of their investigation are summarized in Table 4. More research is needed to prove the existence of these toxic isomers.

Diphenyl Ether Herbicides

In 1980 Yamagishi et al. reported on the occurrence of PCDDs and PCDFs in the commercial diphenyl ether herbicides CNP, NIP and X-52. The values are collected in Table 5. Very few synthetic standards were used, but the major tetra-CDDs were identified as the 1,3,6,8- and 1,3,7,9-isomers, the expected impurities in the starting material 2,4,6-trichlorophenol. No 2,3,7,8-tetra-CDD was found in these samples.

FORMATION BY PHOTOCHEMICAL REACTIONS

The photochemical formation of 2,3,7,8-tetra-CDD under laboratory conditions by dimerization or cyclization reactions has been studied by Akermarck (1978). Although it was possible to detect very small amounts of 2,3,7,8-tetra-CDD, it could be expected that if this compound was formed under environmental conditions, it should be efficiently photo-dechlorinated to much less toxic products, especially in the presence of potent hydrogen donors like the phenoxy herbicide esters. (Akermarck, 1978; see also Sundström et al., 1979). However, within the soil photochemical reaction are not very likely to occur.

Another photochemical process of potential environmental importance is the dechlorination of higher chlorinated PCDDs, by which process a tetra-CDD can be formed by dechlorination of the octa-CDD. This reaction was studied by Crosby et al., (1971). The tetra-CDD isomer formed in this reaction has later been identified as the 1,4,6,9-isomer (Buser and Rappe, 1978) a tetra-CDD expected to be substantially less toxic than the 2,3,7,8-isomer.

Crosby and Moilanen (1973) studied the photolysis of a series of PCBs dispersed in water. For two isomers, 2,5-dichloro- and 2,2',5,5'-tetra-chlorobiphenyls, small amounts (0.2%) of 2-mono-CDF was found among the products.

FORMATION BY THERMAL REACTIONS

The formation of 2,3,7,8-tetra-CDD as a result of thermal reactions of 2,4,5-T and 2,4,5-T derivatives has been the subject of controversy. Heating 2,4,5-T salts at 400-450°C for 30 minutes or longer yields approximately 1 g of 2,3,7,8-tetra-CDD per kg of 2,4,5-T salt, while no dioxin was identified from the same treatment of 2,4,5-T acid or esters (Langer et al., 1973; Baughman, 1974). Using a more sensitive analytical method Ahling et al. (1977) reported that 0.2-3 mg of 2,3,7,8-tetra-CDD was formed per kg of 2,4,5-T esters during combustion at 500-850°C. Two reports (Stehl and Lamparski, 1977; Andersson et al., 1978) have shown that 2,3,7,8-tetra-CDD could not be found on burning samples of spiked or sprayed vegetation at 600°C. The combustion gases, soot, particles and ashes were analyzed and the detection limit was 4 mg/kg 2,4,5-T burned, or less.

Rappe et al. (1978) have studied the burning of material impregnated with various salts of chlorophenols. Very carefully purified 2,4,6-tri- and pentachlorophenate were studied in addition to a commercial formulation of 2,3,4,6-tetrachlorophenate. The analytical method used in this study was not isomer specific, but the following conclusions could be drawn concerning the formation of PCDDs by thermal reactions:

- the expected dimerization products and products formed in the "Smiles rearrangement" are the major PCDDs,
- no other thermal isomerization of the PCDDs formed can be observed;
- no formation of higher chlorinated PCDDs can be observed,
- octa-CDD and other higher chlorinated PCDDs yield lower chlorinated dioxins in a nonspecific dechlorination reaction. This is also a major reaction pathway,
- a series of PCDFs was also observed

It has been found that PCBs can be converted to PCDFs under pyrolytic conditions. The pyrolysis of commercial PCBs in sealed quartz ampoules in the presence of air yielded about 30 major and more than 30 minor PCDFs. The optimal yield of PCDFs was about 10% calculated on the amount of PCB decomposed. Thus uncontrolled burning of PCBs can be an important environmental source of hazardous PCDFs. Therefore, it was recommended (Buser et al., 1978 a; Buser et al., 1978 b) that all destruction of PCB contaminated waste using incinerators must be carefully controlled. In the temperature range 300-400°C, the yield of conversion seems to be in the part-per-million range (Morita et al., 1978), but Nagayama et al. (1981) have reported a dramatic increase of PCDFs at these temperatures in the presence of stainless steel and nickel.

Buser and Rappe (1979) studied the pyrolysis of 15 individual synthetic PCB isomers. This study showed that the formation of PCDFs can follow several competing reaction pathways, as seen in Figure 5. In another study, where a series of chlorobenzenes were pyrolyzed in the same way, Buser (1979) found that significant amounts (~ 1%) of PCDDs and PCDFs were formed. A complex mixture of isomers of PCDDs and PCDFs found suggesting several reaction routes.

Using the same technique as above Lindahl et al., (1980) studied the thermal decomposition of polychlorinated diphenyl ethers. Both PCDDs and PCDFs were formed involving several pathways. The temperature range was 500-600°C and the yields varied from 0.1% to 4.5%. It has also been reported that pyrolysis of PVC yields higher chlorinated benzenes (Ahling et al., 1978).

The data discussed in this section is summarized in Table 6.

OCCURRENCE IN FLY ASH AND INCINERATION PRODUCTS

Emissions from municipal incinerators, heating facilities and thermal power plants have for long time been the subject of much concern. Whereas previously, the emission of dust, smoke, toxic metals and noxious gases were of prime concern, the presence of potentially hazardous organic compounds from these emissions has been recognized only recently. In 1977 Lahaniatis et al. reported on the finding of chlorinated organic compounds in fly ash of a municipal incinerator. The compounds detected were chlorinated aliphatics, benzenes, PCBs and pesticides.

Also in 1977 Olie et al. reported on the occurrence of PCDDs and PCDFs in fly ash from three municipal incinerators in the Netherlands. Their results indicated the presence of up to 17 PCDD peaks, but not quantification or isomer identification was possible due to lack of synthetic standards. Buser and Bosshardt (1978) studied fly ash from a municipal incinerator and an industrial heating facility, both in Switzerland. In the former the levels of PCDDs was 0.2 $\mu\text{g/g}$ and of PCDFs 0.1 $\mu\text{g/g}$. In the industrial incinerator the levels were 0.6 $\mu\text{g/g}$ and 0.3 $\mu\text{g/g}$, respectively.

During the period 1978-1982 a series of papers, reports and reviews have been published confirming the original findings of Buser and Bosshardt. Up to now less data have been reported on the levels of PCDDs and PCDFs in other incineration products such as particulates and flue gas condensate, which are the true emissions.

As mentioned earlier a risk evaluation should be based on the levels of the highly toxic isomers found in isomer specific analyses. However, in most studies of fly ash the results are given in terms of total levels of tetra-, penta-, hexa-, hepta- and octa-CDDs and CDFs. The value of such studies is limited, especially in this case where the number of isomers is quite large. More than 30 PCDDs and 60 PCDFs have been found in fly ash samples. Other authors make the assumption of an equal distribution among the isomers. This seems to be an erroneous approach. Using the isomer specific analytical method

described above, two samples from municipal waste incinerators were analyzed, the two upper curves Figure 4. The Swedish incinerator was operating by the fluidized bed technique, the Canadian by conventional technique.

In both samples we could identify a series of PCDDs and PCDFs. Of special interest is the observation that all tetra-CDDs found in these two samples co-elutes with the isomers present in a mixture of all the 22 tetra-CDDs (Figure 4, lower curve). A variation in the levels of the highly toxic 2,3,7,8-tetra-CDD was also observed. In the Swedish sample this isomer constitutes about 3% of the total level of tetra-CDDs while in the Canadian sample this isomer is less than 0.3%. This is a tenfold variation of this interesting isomer. Moreover, in these samples the ratio between the largest and the smallest peak is more than 100:1 (C. Rappe, S. Marklund, unpublished).

Another interesting parameter to investigate for various incinerators is the PCDF/PCDD ratio. At the Cl₄ and Cl₅ levels, the PCDFs are in general much more abundant than the PCDDs, while the situation is reversed at the Cl₇ and Cl₈ levels (Rappe et al., 1983 b).

In a report in 1978 it was proposed by scientists from Dow Chemical Company that PCDDs and especially 2,3,7,8-tetra-CDD are ubiquitous and formed as trace level byproducts of any normal combustion (Dow, 1978; Bumb et al., 1980). Consequently dioxins should have been present in the environment since the advent of fire ("The Trace Chemistries of Fire"). A recent survey of PCDD levels in particulate from residential wood combustion units is quoted in support of the above (Nestrick and Lamparski, 1982). The survey showed PCDD levels in the ppt-range. The major constituent was octa-CDD, but tetra-CDDs (including the 2,3,7,8-isomer) was also found. The occurrence of PCDFs is not discussed in these reports.

However, this hypothesis has been criticized (Anonymous, 1979, 1982). One of the main arguments is that coal-fired power plants are ruled out as a possible source of 2,3,7,8-tetra-CDD (Kimble and Gross, 1980; Junk and Richard, 1981). Another argument is that data are completely lacking in the Dow studies on levels of dioxin precursors (see Table 5) in the material being burned, including the air in the flames.

LEVELS OF PCDDs and PCDFs IN PCB FIRES

In February 1981 a fire in the State Office Building in Binghamton, NY, USA caused a transformer to rupture, releasing soot in the whole building. The dielectric fluid in the transformer consisted of a mixture of PCB (65%) and chlorinated benzenes (35%).

The soot was found to be highly contaminated by PCDFs, the total level of PCDFs was more than 2000 µg/g. The results of the analysis are compiled in

Table 7. The most toxic isomers (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 1,2,3,6,7,8-hexa-CDF) were found to be the major constituent within each group of congeners. In addition a series of PCDDs could also be identified including a large amount of the highly toxic 2,3,7,8-tetra-CDD and 1,2,3,7,8-penta-CDD. (Rappe et al. 1983 b; Buser and Rappe, 1983.) It is assumed that the chlorinated benzenes were the dioxin precursors.

During 1981-1983 a series of capacitor accidents have occurred in Scandinavia. The accidents were of two kinds: capacitor explosions or capacitor fires where mineral oil filled capacitors were also involved. In all cases the accident sites were contaminated by PCDFs (see Table 7).

In the soot from the Binghamton building polychlorinated biphenylenes (PCBPs, Figure 1) have also been observed (D. Stalling, CNFRL, Columbia, MO, personal communication). Using the MS/MS technique Rappe et al. (1982) found high levels of these compounds in the wipes from a capacitor explosion in Stockholm, Sweden. The 2,3,6,7-tetra-CBP is closely related in structure to the most toxic PCDDs and PCDFs, and this compound has also been found to have a strong biological activity (Poland et al. 1977).

LEVELS OF PCDDs and PCDFs IN ENVIRONMENTAL SAMPLES

Soil, sediments and vegetation

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Samples of soil and vegetation from Seveso, Italy have been analyzed. In 1976, immediately after the accident in the chemical plant producing 2,4,5-chlorophenol, the levels of 2,3,7,8-tetra-CDD in vegetation were

found to be up to 50 $\mu\text{g/g}$ (Firestone, 1978). In the following years, when there was no direct contact of the newly grown vegetation with the aerosol cloud, the levels of dioxin in plants dropped by several orders of magnitude (Wipf et al., 1982). Studies by Young (1983) indicate that the half-life for 2,3,7,8-tetra-CDD in soil is 10-12 years. In 1977 one year after the accident in Seveso no traces of TCDD were found in the flesh of apples, pears and peaches, nor in corn cobs and kernels grown near the factory. The detection limit for the analysis was reported as 1 pg/g . At the same time about 100 pg/g of dioxin was detected in the peels of fruits. This strongly suggests that the contamination is due to dust and not from plant uptake. The dioxin level in the soil was found to be in the order of 10 ppb, about 1000 $\mu\text{g/m}^2$ (Wipf et al., 1982).

In 1973 it was found that three horse arenas in Missouri were contaminated by high levels of 2,3,7,8-tetra-CDD, the highest value was about 30 ppm (Kimbrough et al., 1977). This contamination resulted from the application in 1971 of waste oil to control dusting at these locations. The dioxin had originated at a hexachlorophene producing factory in Verona, MO. Additional tri- and tetra-CDDs have also been found, but the major component was 1,2,4,6,8,9-hexachloroxanthene (Buser, 1978) a compound which apparently can serve as a marker for this type of contamination. The xanthene is a normal by-product in the hexachlorophene production and has never been associated with the production of 2,4,5-trichlorophenol or 2,4,5-T derivatives.

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In 1982, numerous sites of potential 2,3,7,8-tetra-CDD contamination were discovered in Eastern Missouri. The contamination originated from the same waste oil from the factory in Verona, MO. In the town of Times Beach, MO, the streets of the entire town had been sprayed. Now, more than 52 00 soil samples have been analyzed from Times Beach. The dioxin levels were higher than 1 ppb in 22% of the samples and higher than 100 ppb in 2.2%, the highest value was 350 ppb (Personal communication R.D. Kloepper, US EPA Region VII, Kansas City, Kansas).

Another location of great concern is Love Canal, Niagara Falls, NY. Here Smith et al. (1983) also found high levels of 2,3,7,8-tetra-CDD in storm sewer sediments taken from around the Love Canal waste disposal site, the highest value was 312 ppb.

In a recent study Czuczwa and Hites (1983) have found a series of PCDDs and PCDFs in sediment samples from several locations in Saginaw River and Bay and southern Lake Huron. The levels ranged from 100 ppb in urban areas to 100 ppt at remote sites. Although no isomers were identified, the analytical profiles in the sediments were reported to follow closely to those found in combustion samples, suggesting that combustion is the major source of PCDDs and PCDFs found in the sediments. Analyses of sediment cores showed a dramatic increase in the levels at a depth corresponding to approximately 1940 and remaining high up to now. There is no good correlation between the trend in these levels and the trend for coal burning in the United States, which can be predicted from the hypothesis of "Trace Chemistries of Fire". However, the levels in the sediments agree well with the production of chlorinated aromatic compounds.

Very few analyses of sprayed vegetation has been reported. A rough estimate of 2,3,7,8-tetra-CDD contamination of 20-1000 pg/g can be made on the basis of the level of 2,4,5-T found in newly sprayed vegetation and the level of 2,3,7,8-tetra-CDD in the spray formulation used, even higher values could be obtained if Agent Orange is used. Sundström et al. (1979) reported on data in agreement with this estimation. However the analytical technique used in this study was not isomer specific. Vegetation was sprayed with 2,4,5-T ester contaminated by only 0.06 µg/g of 2,3,7,8-tetra-CDD. A sample of leaves collected 42-45 days after the spraying was found to have 170 pg/g of TCDD, somewhat lower than the expected value (600 pg/g) indicating a slow photochemical breakdown.

Aquatic organisms

Fish and shellfish taken from areas in South Vietnam, that were heavily exposed to "Agent Orange" during military defoliation operations in the 1960s have been reported to contain 18-810 pg/g of TCDD. (Baughman and Meselson, 1973). The analytical technique of direct inlet-high resolution MS used in this study is not considered isomer specific. It did not include any GC separation at all.

Rappe et al. (1981) identified a series of tetra to octa-CDFs in fat samples of a snapping turtle from Hudson River and gray seal from Baltic Sea. The total levels of PCDFs in these samples were 3 ppb and 40 ppt, respectively. In both samples the major PCDFs consisted of the most toxic isomers (2,3,7,8-tetra-, 2,3,4,7,8-penta- and 1,2,3,4,7,8- and 1,2,3,6,7,8-hexa-CDF).

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Norstrom et al. (1982) have analyzed pooled samples of herring gull eggs collected in 1982 from various parts of the Great Lakes. In all samples 2,3,7,8-tetra-CDD was found in levels ranging from 9 to 90 pg/g. The identity of the 2,3,7,8-isomer was confirmed by retention times on three capillary columns. In another study Stalling et al. (1983) were not able to identify measurable levels of tetra-CDDs and other PCDDs in fish samples from Lake Superior (the detection level was 2-5 ppt). The difference could be explained by the migration of the herring gulls during the winter. On the contrary a series of PCDFs could be identified in the Lake Superior fish samples, indicating a more widespread background levels for the PCDFs than for the PCDDs. Stalling et al. (1983) also reported on the analysis of fish samples from Lakes Michigan, Huron and Ontario. The toxic 2,3,7,8-substituted PCDDs and PCDFs (Table 2) were present in all samples, the highest levels being found in samples from Lake Huron, Lake Ontario and Tittabawasee River. The residue pattern found in the fish and locally high levels suggest a strong influence by point source discharges. The recent data by O'Keefe et al. (1983) is also in agreement with this statement.

LEVELS IN HUMAN SAMPLES

Occupational Exposure

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Occupational exposure to 2,3,7,8-tetra-CDD can occur during the production of 2,4,5-trichlorophenol and the subsequent production and use of 2,4,5-T acid and esters. The 2,4,5-T was first produced commercially in 1944 in United States and the use of 2,4,5-T as herbicide increased in the 1940's

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and 1950's. However, the problem of dioxin contamination in 2,4,5-T was not recognized until 1957 (Kimmig and Schulz, 1957).

The most heavy exposure after a normal production is during a purification step as the residues are by far more contaminated than the purified products. Only limited information is available on the levels of dioxin contamination of products prepared prior to the 1970's, and absolutely no information is available on the dioxin levels in the corresponding residues. Consequently it is a difficult task to estimate the levels of occupational and general exposure during this period.

The dioxin exposure of soldiers and the general population during the military use of phenoxy herbicides during the Vietnam war has been the subject of much concern both among the Veterans in the United States and Australia as for the people in Vietnam. Shepard and Young (1983) discuss a study where very low levels of tetra-CDD, believed to be the 2,3,7,8-isomer, was detected in adipose tissue from many of the Vietnam Veterans, although the levels are not considered to correlate well with known exposure data or with health status. No experimental conditions are given in this report.

In order to evaluate any study of trace amounts of 2,3,7,8-tetra-CDD in samples from exposed people it is of fundamental importance to know the background levels of this compound in different part of the world.

Ryan and Williams (1983) recently reported on the levels of 2,3,7,8-tetra-CDD in 23 autopsy samples of adipose tissue from the Great Lakes area in Canada. The analytical method used was capable of separating the 2,3,7,8-isomer with a possible 1-3 other co-eluting isomers. The 2,3,7,8-tetra-CDD

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was found in 22 of the 23 samples and values ranged from 4.1 to 130 ppt. Excluding the outlying high sample the average value was 10.7 ± 5.4 ppt.

Preliminary data from the analyses of human adipose tissue both from Canada (personal communication J. Ryan, Health Protection Branch, Ottawa, Canada) and from Sweden (C. Rappe and M. Nygren, manuscript in preparation) seem to indicate background levels (1-600 ppt) in the general population for both PCDDs and PCDFs ranging from tetrachloro through octachloro compounds. The levels have a tendency to increase with increasing number of chlorine atoms, although the octa-CDF was always at very low levels. The highly toxic 2,3,7,8-substituted isomers were the dominating isomer within each group of congeners, indicating a correlation between the isomers found in human tissue and those found in fish samples, see above.

This rather complicated situation generates special problems in order to evaluate a certain exposure; in Vietnam, occupational or dietary. The best solution seems to analyze for all PCDDs and PCDFs using a clean-up technique that results in one single fraction, which can be used to analyze for all PCDDs and PCDFs. The data should be analyzed using pattern recognition methodology.

Analysis of blood plasma can be used to evaluate occupational exposure to PCDDs and PCDFs, which can occur during the production or use of 2,4,6-tri-, 2,3,4,6-tetra- and pentachlorophenol. Rappe et al. (1983 c) have investigated such exposure through the analyses of blood plasma of exposed workers and unexposed controls. Good correlation was found between the plasma levels and

- 1) the nature of exposure
- 2) the duration of exposure
- 3) the isomers present in the commercial formulation

Yusho Episodes

In 1968 more than 1500 persons in southwest Japan were intoxicated by consumption of a commercial rice oil accidentally contaminated by PCBs, PCDFs and polychlorinated quaterphenyls (Masuda et al. 1982, Miyata et al., 1978). In 1979 a similar episode occurred in central Taiwan, the number of persons involved here approaching 2000 (Chen et al. 1980). Both these accidents have been referred to as Yusho episodes, but recently the Taiwanese episode is renamed Yu-cheng.

The Japanese rice oil contained more than 40 PCDF isomers, tri- to hexa-CDFs. Analyses of liver samples taken from the Japanese patients about 18 months after the exposure showed a dramatic decrease in the number of PCDF isomers. Apparently most of the PCDF isomers have been metabolized or excreted during the period between exposure and sampling (Rappe et al. 1979).

A comparison between the PCDF isomers found in the Yusho oil and in the liver samples revealed an interesting relationship. Most of the isomers retained had all lateral positions (2-, 3-, 7- and 8-) substituted for chlorine, these isomers have the highest toxicity (see Table 2).

The rate of excretion of these toxic dibenzofuran isomers is very slow, as studied by the Japanese and Taiwanese Yusho patients.

A 15-20% reduction in the blood levels was found in one year, and PCDFs

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could still be found 11 years after the exposure in Japan (Rappe et al., 1983 c). This indicates a dramatic difference in the rate of excretion between man and rodents, where the half life of 2,3,7,8-tetra-CDD is reported to be only a few weeks.

CARCINOGENICITY AND CANCER EPIDEMIOLOGY

The carcinogenic effects of dioxins have been studied in a series of animal experiments. The 2,3,7,8-tetra-CDD, 1,2,3,6,7,8- and 1,2,3,7,8,9-hexa-CDD are reported to have carcinogenic or co-carcinogenic effects. In man the carcinogenic effects are related to the exposure to phenoxy herbicides and chlorophenols. It is difficult to separate the effects of the parent compounds from the effects of the dioxin and dibenzofuran contaminants (IARC, 1982, NTP, 1980 a and b).

Two Swedish case-control studies have shown an increased risk of soft-tissue sarcomas in men exposed to phenoxy herbicides and chlorophenols (Hardell and Sandström, 1979; Eriksson et al., 1981). A high incidence of soft-tissue sarcomas has also been observed among workers employed in the manufacture of these products in the United States (Honchar, 1981). Three cases of thoracic soft-tissue sarcomas have been reported for persons, who served in Vietnam and were exposed to "Agent Orange" (Sarma and Jacobs, 1982). Other studies have failed to demonstrate the relation between soft-tissue sarcomas and exposure to phenoxy herbicides and chlorophenols, and the safe diagnosis of soft tissue sarcomas has been discussed (Smith, 1983; Fingerhut, 1983).

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Another case control study in Sweden suggests a correlation between

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and non-Hodgkin's lymphomas (Hardell et al., 1981) but further research is needed to confirm this. It has also been pointed out that exposure to chlorophenols (and their impurities) could be an exposure in common for different groups with increased risk of nasal cancer for people occupied with wood products, leather, textile and cutting fluids (Hardell et al., 1983).

CONCLUSIONS

Using the analytical standards now available it has recently been shown that isomer specific analyses can be performed for all toxic PCDD and PCDF isomers. Only very few laboratories have now access to these standards and collected experience to work with them (about 5 laboratories in the whole world). Due to the possibility of false positive results, all PCDD and PCDF analyses should be performed using a methodology which has been proven to be isomer specific.

The amount detected in these procedures is in the pg range or lower and containment enrichment methods have been developed to inject an aliquot corresponding to 1 g of the sample or more. Thus the detection level is in the ppt range or lower.

Using this analytical technique background levels of tetrachloro through octachloro PCDDs and PCDFs have been found in ecological samples as well as in human adipose tissue in America and Scandinavia.

This sensitive and selective analytical technique is associated with laboratory problems like cross contamination and poor recoveries of internal standards. More research is needed to specify each step in the complicated analytical procedure. The available standards should be used to optimize the methods of sample purification for all isomers of PCDDs and PCDFs.

There is also a great need for more monitoring data, especially in soil, sediments, air, water, aquatic organisms and in the general human population in the industrialized part of the world as well as in developing countries.

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Table 1. Number of positional PCDD and PCDF isomers

Level of chlorine substitution	Number of isomers	
	PCDDs	PCDFs
Cl ₁ (Mono)	2	4
Cl ₂ (di)	10	16
Cl ₃ (tri)	14	28
Cl ₄ (tetra)	22	38
Cl ₅ (penta)	14	28
Cl ₆ (hexa)	10	16
Cl ₇ (hepta)	2	4
Cl ₈ (octa)	1	1
	75	135

Table 2. The most toxic PCDD and PCDF isomers

PCDDs	PCDFs
2,3,7,8-Tetra-CDD	2,3,7,8-Tetra-CDF
1,2,3,7,8-Penta-CDD	1,2,3,7,8-Penta-CDF
1,2,3,6,7,8-Hexa-CDD	2,3,4,7,8-Penta-CDF
1,2,3,7,8,9-Hexa-CDD	1,2,3,6,7,8-Hexa-CDF
1,2,3,4,7,8-Hexa-CDD	1,2,3,7,8,9-Hexa-CDF
	1,2,3,4,7,8-Hexa-CDF
	2,3,4,6,7,8-Hexa-CDF

Table 3. Levels of PCDDs and PCDFs in commercial chlorophenols (ug/g)
(From Rappe et al., 1979)

	2,4,6-Cl ₃	2,3,4,6-Cl ₄	PCP	PCP
Tetra-CDDs	< 0.1	< 0.1	< 0.1	< 0.1
Penta-CDDs	< 0.1	< 0.1	< 0.1	< 0.1
Hexa-CDDs	< 1	< 1	< 1	2.5
Hepta-CDDs	< 1	10	0.5	175
Octa-CDD	< 1	2	4.3	500
Tetra-CDFs	1.5	0.5	< 0.1	< 0.1
Penta-CDFs	17.5	10	< 0.1	< 0.1
Hexa-CDFs	36	70	0.03	< 0.3
Hepta-CDFs	4.8	70	0.5	19
Octa-CDF	< 1	10	1.1	25

Table 4. Levels of PCDFs in commercial PCBs ($\mu\text{g/g}$)
(From Bowes et al., 1975)

Sample	Tetra	Penta	Hexa	Total
Aroclor 1248 (1969)	0.5	1.2	0.3	2.0
Aroclor 1254 (1969)	0.1	0.2	1.4	1.7
Aroclor 1254 (1970)	0.2	0.4	0.9	1.5
Aroclor 1260 (1969)	0.1	0.4	0.5	1.0
Aroclor 1260 (Tot AK3)	0.2	0.3	0.3	0.8
Aroclor 1016 (1972)	ND	ND	ND	-
Clophen A 60	1.4	5.0	2.2	8.4
Phenoclor DP-6	0.7	10.0	2.9	13.6

ND = Not Detectable

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Table 5. Levels of PCDDs and PCDFs in commercial diphenyl ether herbicides (µg/g). (From Yamagishi et al., 1981)

	CNP	NIP	X-52
Tri-CDDs	ND	0.15	0.03
Tetra-CDDs	14.0	0.38	0.03
Penta-CDDs	37	0.05	0.01
Hexa-CDDs	0.8	ND	ND
Mono-CDFs	ND	0.34	0.48
Di-CDFs	0.35	0.12	0.21
Tri-CDFs	0.41	0.47	0.45
Tetra-CDFs	0.4	0.29	0.32
Penta-CDFs	1.0	ND	0.08
Hexa-CDFs	0.2	ND	ND

ND = Not Detected

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Table 6. Formation of PCDDs and PCDFs by thermal processes

Precursor	Conditions	Products
2,4,5-T salt	Pyrolysis	2,3,7,8-TCDD
2,4,5-T (vegetation)	Pyrolysis	No TCDD
	Burning	—
Chloro phenate	Burning	PCDDs ^x + PCDFs
PCBs	Pyrolysis	PCDFs ^{xx}
Polychloro benzenes	Pyrolysis	PCDFs + PCDDs ^{xxx}
Chloro Diphenyl ethers	Pyrolysis	PCDFs + PCDDs
PVC	Pyrolysis	Polychlorobenzenes

x = PCDD formed by dimerization and a non-specific dechlorination

xx = other products: hexa- and penta-chlorobenzenes

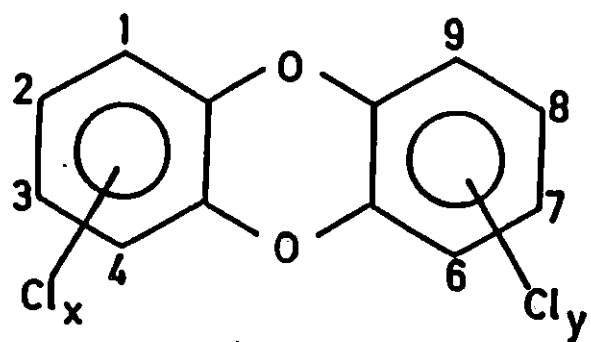
xxx = other products: PCBs, polychlorinated naphthalenes

Table 7. Levels of PCDFs in samples from PCB fires

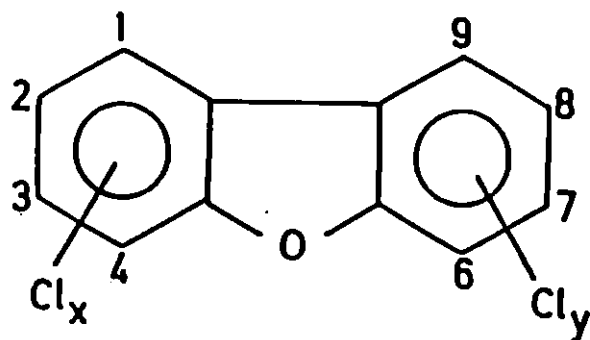
	ΣCl_4	2378-	ΣCl_5	ΣCl_6	ΣCl_7	Cl_8	$\Sigma PCDDs$	PCBPs ^x
Binghamton ($\mu g/g$)	20	12	670	965	460	40	20	+
Stockholm ($\mu g/m^2$)	1.2	0.15	0.175	-	-	-	-	+++
Skövde ($\mu g/m^2$)	0.6	0.1	0.1	0.06	0.008	0.006	-	-
Surahammar ($\mu g/m^2$) (before cleaning)	1.2	0.3	0.3	0.15	0.07	0.01	-	-
Surahammar ($\mu g/m^2$) (after cleaning)	< 0.02	< 0.004	< 0.01	< 0.01	< 0.015	< 0.002	-	-
allstahammar ($\mu g/m^2$) (before cleaning)	1.6	0.54	0.36	0.60	0.80	1.34	-	-
allstahammar ($\mu g/m^2$) (after cleaning)	0.002	0.0002	0.0005	0.0003	0.0007	0.0011	-	-
Electrical locomotive ($\mu g/m^2$)	4.9	1.2	1.5	0.4	0.17	0.04	-	-

x polychlorinated biphenylenes +++ high levels, + low levels

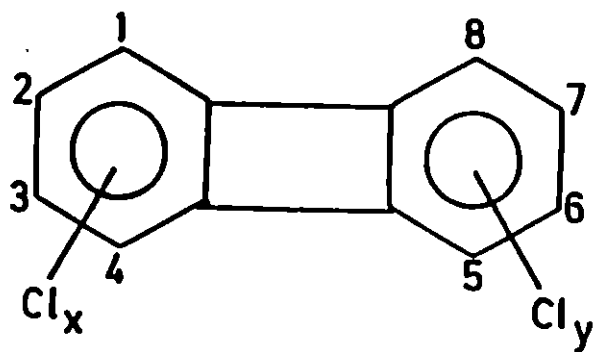
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PCDDs



PCDFs



PCBPs

$$x + y = 1 - 8$$

Figure 1. Formulas for the compounds discussed.

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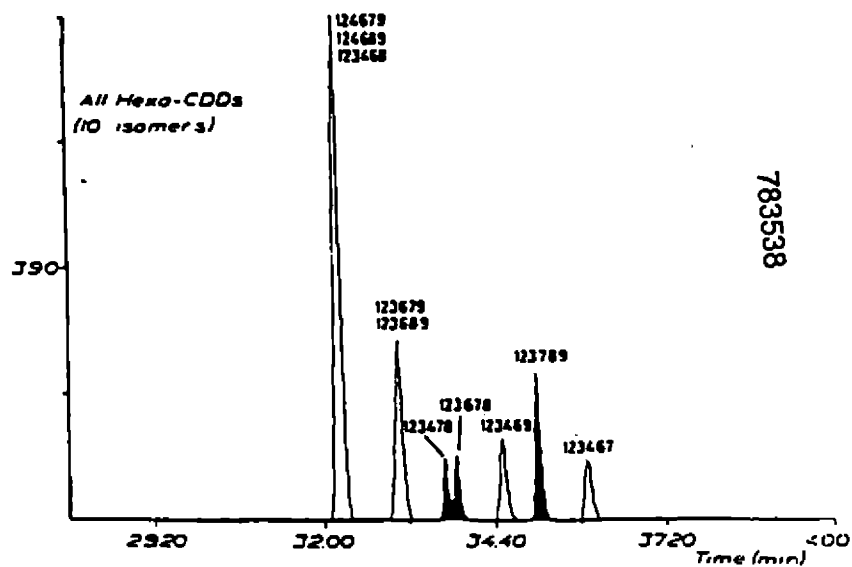
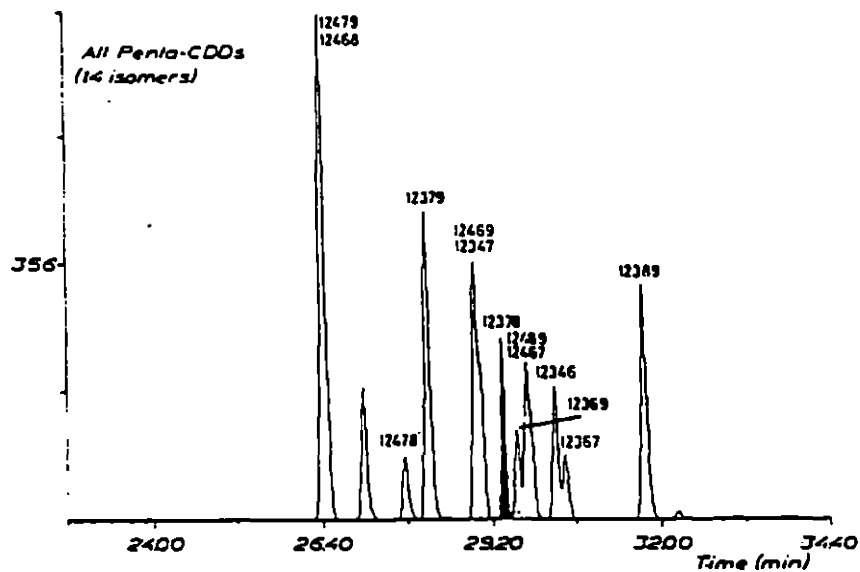
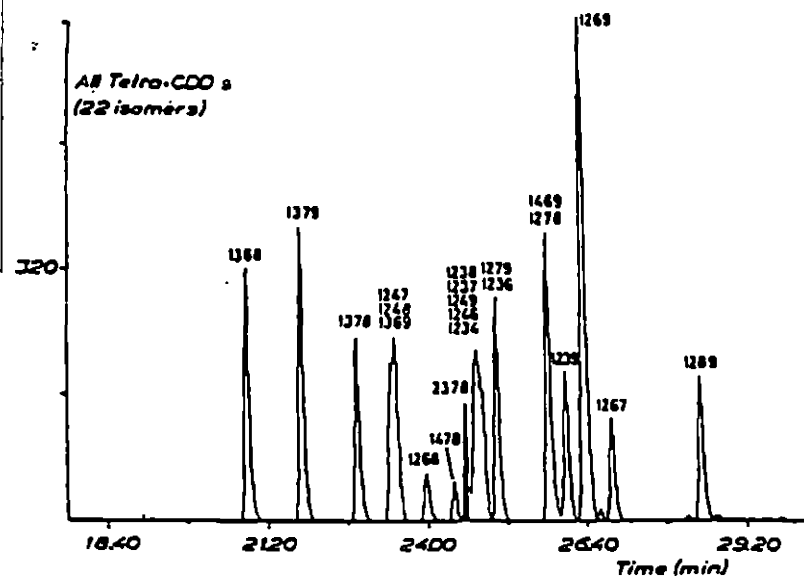
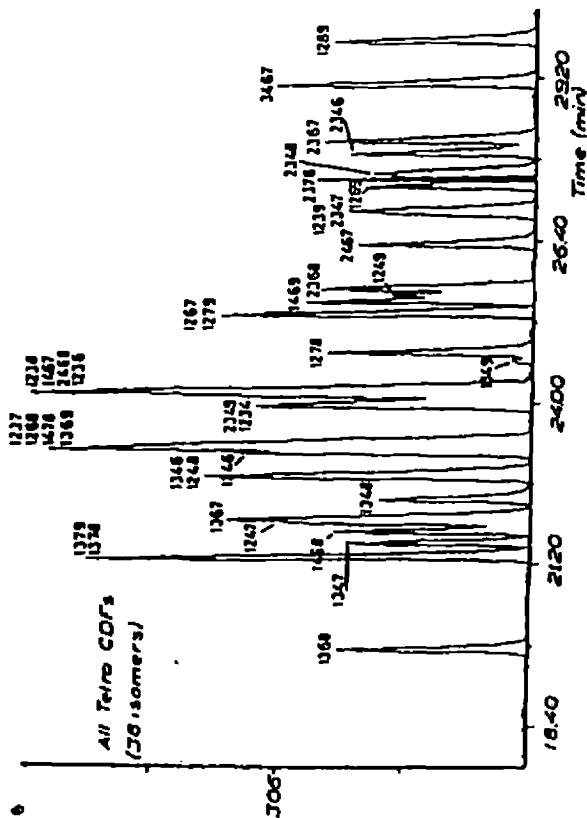
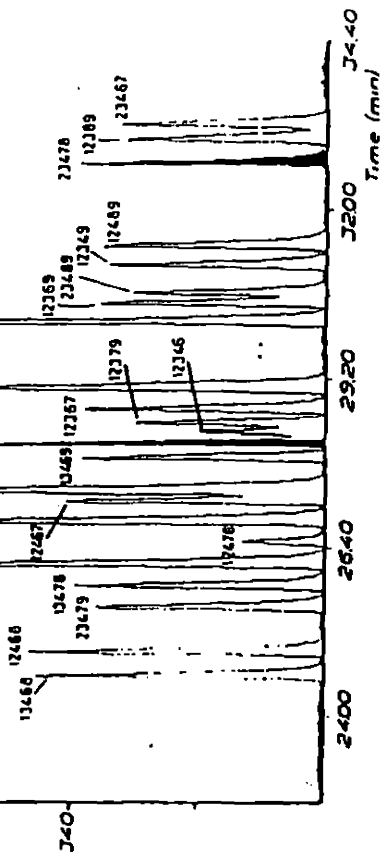


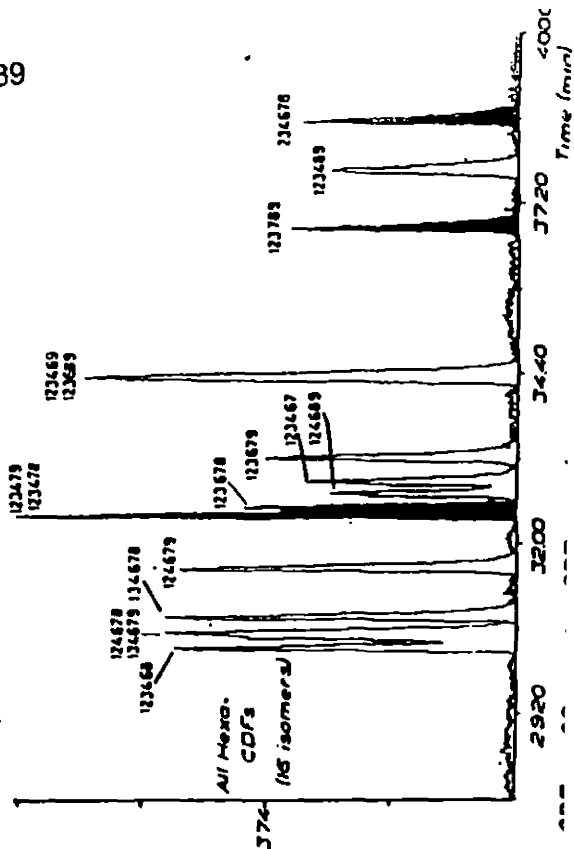
Figure 2. Separation of 22 tetra-CDDs, 14 penta-CDDs and

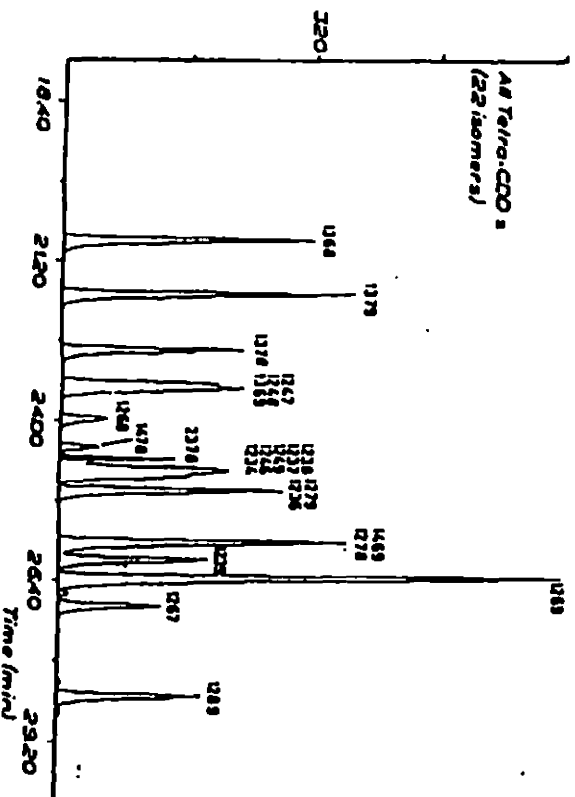
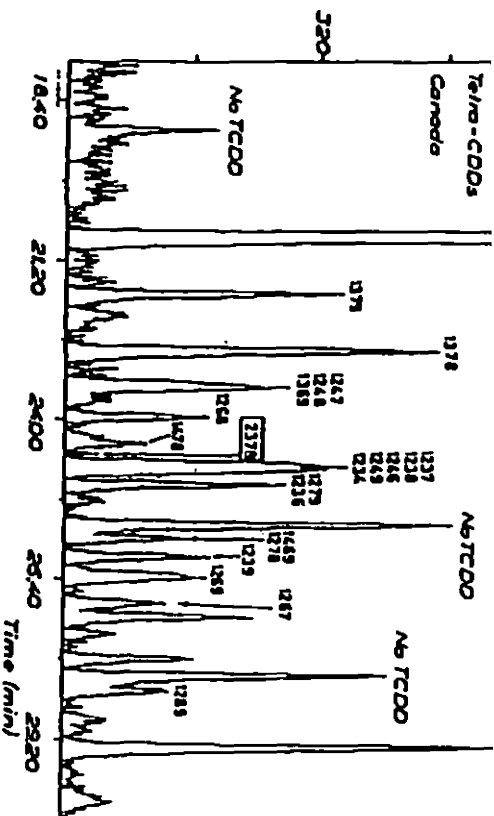


783539



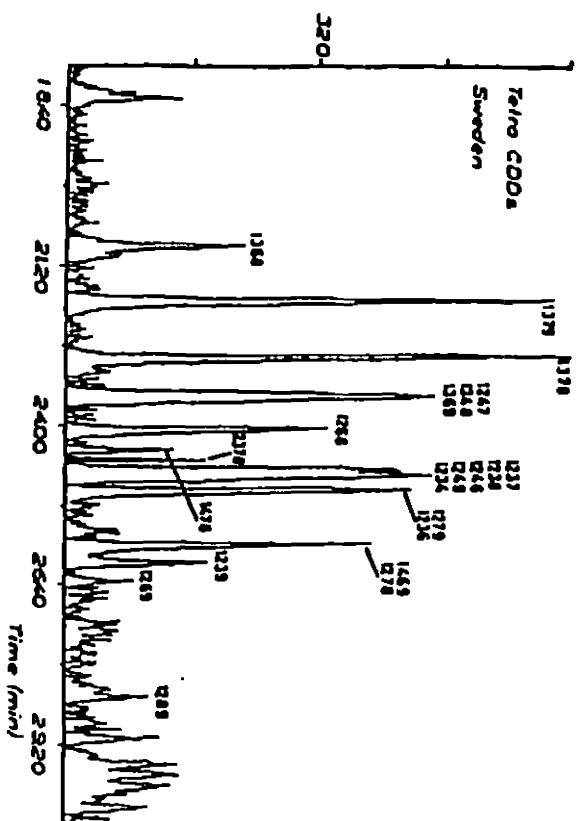
GENP 010728



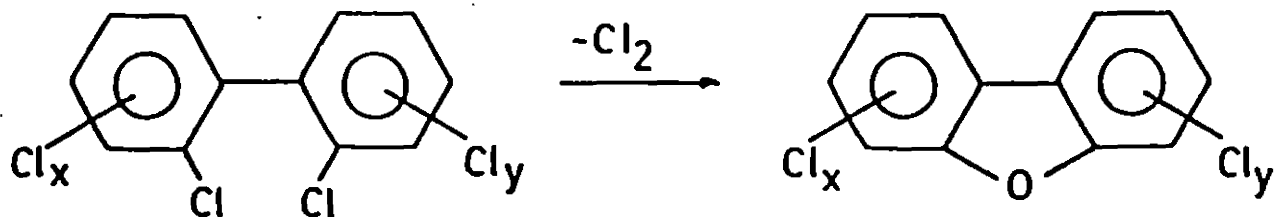


GENP 010729

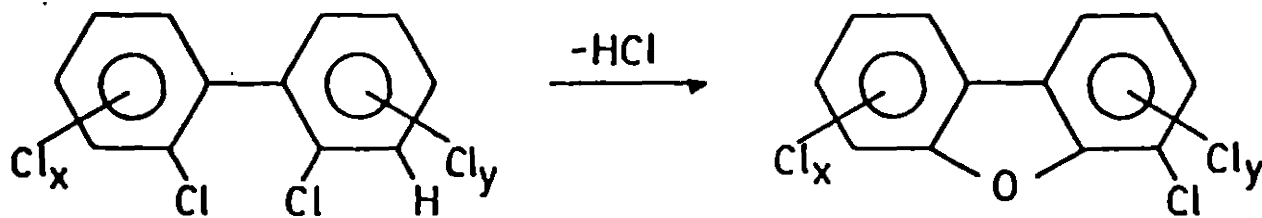
783540



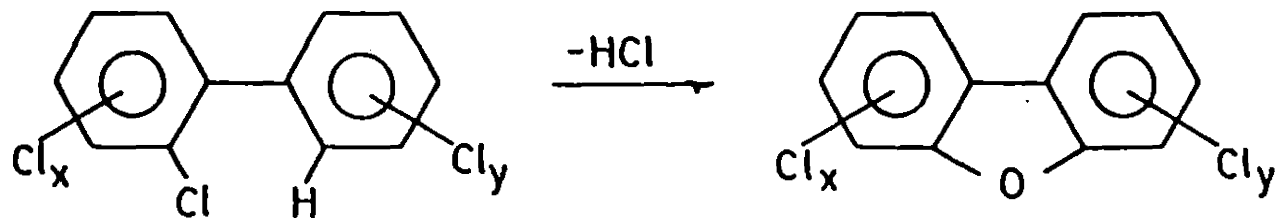
reaction route 1
(loss of ortho-Cl₂)



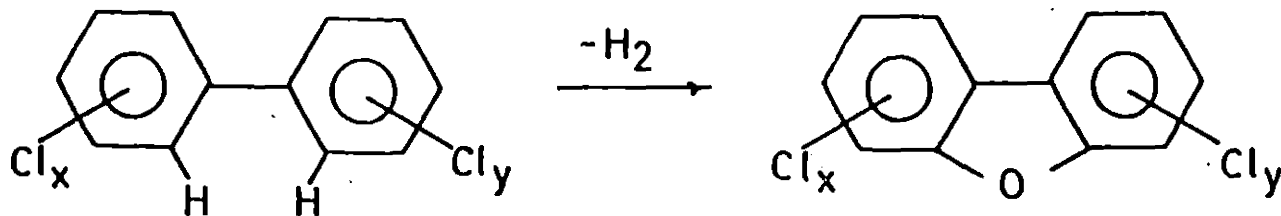
reaction route 2
(loss of HCl involving
a 2,3-chlorine shift)



reaction route 3
(loss of ortho-HCl)



reaction route 4
(loss of ortho-H₂)



783541

GENP 010730

Figure 5. Reaction pathways for the thermal formation of PCDFs from PCBs.