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Sources And Fate of Polychlorinated Dibenzodioxins, Dibenzofurans and Related Compounds in Human Environments

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Several of the major incidents resulting in potential human exposures to polychlorinated dibenzodioxins (PCDDs) and/or polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and related compounds which have occurred in the U.S. in recent periods have resulted from improper disposal of hazardous chemical wastes. Prominent examples of such environmental contamination episodes are the Love Canal, into which ton quantities of chlorinated organic compounds containing substantial concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) were deposited; numerous sites in the State of Missouri which were contaminated by the dumping of chlorinated organic wastes containing various PCDDs and possibly PCDFs, and PCBs; and the environs of a 2,4-D/2,4,5-T manufacturing plant site in Arkansas, which were contaminated with PCDDs. Environmental assessments of such sites have revealed extensive contamination of soils, waterways, fish and other biological species with these toxic compounds, which in turn could lead to human exposures. Other recently identified sources of PCDDs, PCDFs and related compounds in human environments include stack effluents from municipal refuse incineration, and fires and explosions involving electrical devices containing PCBs and polychlorinated benzenes. Data obtained in assessments of such incidents are presented, and the implications of these findings with respect to the distribution and persistence of PCDDs, PCDFs and related chemicals in the environment and possible effects on humans are discussed.

Introduction

There is increasing recognition in the United States that polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are accumulating in the environment, largely as a consequence of several major contamination incidents which have received widespread publicity. However, the U.S. has not experienced episodes of human exposure and toxic response to such compounds which are comparable in severity or magnitude to the Yusho incident, which occurred in Japan, or the similar Yu-Cheng incident which occurred in Taiwan, and which are discussed in much detail in other papers in this volume. Accidental oral ingestion by humans of such compounds in substantial quantities, as occurred in the latter incidents, has not been experienced in the U.S., and human exposures to PCDDs, PCDFs and PCBs in this country have generally been much more subtle, and consequently, possible effects have been much more difficult to diagnose. U.S. investigators have therefore obtained very little information about the persistence and effects of toxic PCDDs, and PCDFs in human tissues and organs. Somewhat more information has been obtained with respect to residues of PCBs in human tissues, but the health effects of such residues are still uncertain. As a result of the generally lower exposures of humans in the U.S. to the PCDDs and PCDFs, even in cases of substantial environmental contamination, as compared to the Yusho and Yu-Cheng incidents, the levels of these compounds that have been detected in human tissues are extremely small, and detection requires highly sophisticated analytical procedures. The

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only PCDDs which have been detected thus far in humans are TCDDs (*1*), and the presence of other PCDDs and PCDFs has either not been sought or has not been reported. In cases where TCDDs were detected, the concentrations were in the low parts-per-trillion range. Quantitative measurement of such concentrations of PCDDs with reliability typically requires 5 to 10 g of the tissue being analyzed, even with the state-of-the-art analytical procedures.

Interpretation of the finding of TCDDs (or of any PCDDs, PCDFs or PCBs, for that matter) in human tissues is difficult to interpret in terms of any particular exposure episode or accident which has occurred in the U.S. because the residual levels of these compounds which may be present in the "unexposed" population have not been established. Some evidence has been obtained, however, which suggests that there is a background level of TCDDs in some segments of the general population (*2*), but the principal mechanisms of human exposure and absorption of these compounds are largely unknown. Thus, the dangers to humans which are posed by the presence of these compounds in air, water, soils and sediments, and food (fish, for example) are still uncertain.

In spite of our limited knowledge of the human toxicity of compounds such as the PCDDs, PCDFs and PCBs, there is still widespread interest in the U.S. in the contamination of the environment with these compounds, and potential human health effects resulting therefrom, as clearly indicated by the presentations of other U.S. participants in this conference. It is accurate to say that, in the U.S., we are still primarily in an assessment mode, in which we are attempting to define the major sources and extent of contamination of human environments with such compounds. In this respect, much more attention has been given thus far in the U.S. to the PCDDs than to the PCDFs. This has been largely due to the fact that U.S. regulatory agencies, such as the U.S. Environmental Protection Agency and the U.S. Food and Drug Administration have focused their concerns almost entirely on TCDDs, and even on the 2,3,7,8-TCDD. This focus originated with the initial belief that certain chlorophenols and their derivatives were the major sources of TCDD contamination in the environment. More recent studies by our laboratory (*3–5*) and by a few other groups (*6–10*) have shown that various combustion processes, for example, municipal refuse incinerators, can be significant sources of a broad spectrum of PCDDs and PCDFs, as well as other related chlorinated organic compounds (chlorophenols, cholorobenzenes) which may be involved in formation of the former. Other events which have called increasing attention to the PCDFs in the U.S. recently are the occurrences of fires and breakdowns in PCB-filled electrical devices (transformers and capacitors), with resultant environmental contamination and, in some cases, human exposures to toxic PCDFs produced in these combustion processes. It seems likely that significant numbers of such accidents have occurred in the U.S. over the past several years, but the magnitude of the potential hazard from such events has only recently been recognized. The experiences of Japanese and Chinese scientists with the Yusho and Yu-Cheng incidents should be particularly relevant in attempting to assess the U.S. episodes with PCB-electrical device failure, and possible human health consequences.

The present paper describes recent work of the Brehm Laboratory on several major environmental assessments in the U.S. which have been concerned with PCDDs/PCDFs contamination. Also briefly described are on-going collaborative efforts with medical scientists to diagnose and understand human toxic effects resulting from exposure to these compounds. Prior to presenting data obtained in these investigations, the analytical procedures utilized in determining PCDDs/PCDFs and related compounds in various environmental and biological sample matrices will be briefly summarized.

Methodology for Analysis of PCDDs/PCDFs and Related Compounds

PCDDs/PCDFs

The analytical procedures applied to determine quantitatively the concentrations of PCDDs and PCDFs in environmental and biological media involve a sequence of three operations: (a) destruction and/or extraction of PCDDs/PCDFs from the sample matrix and partitioning of these into an organic solvent; (b) preliminary separation of PCDDs/PCDFs from other matrix constituents using aqueous–organic partitioning techniques and liquid chromatography; (c) detection of PCDDs/PCDFs in the cleaned-up extract using coupled gas chromatography–mass spectrometry (GC–MS). These steps are described in more detail in the following and in a recent review. (*11*)

Addition of Isotopically Labeled Internal Standards. Isotopically labeled PCDDs are added in known quantities to each sample prior to analysis. These provide a basis for the quantitative determination of the native PCDDs in the sample, and any losses of the latter incurred in sample processing are then automatically taken into account. The recovery of the internal standards which is achieved also provides an indication of the overall efficacy of the analytical procedure. Depending upon the PCDD analytes which are being determined, the internal standards added to the sample may include any or all of the following: $^{37}Cl_4$-2,3,7,8-tetra-CDD; $^{13}C_{12}$-2,3,7,8-tetra-CDD; $^{37}Cl_4$-1,2,3,4,6,7,8-hepta-CDD; $^{37}Cl_8$-octa-CDD; $^{13}C_{12}$-octa-CDD. The labeled tetra-CDDs are used as the reference for tetra- and penta-CDDs and CDFs, the labeled hepta-CDD is used as the reference for hexa- and hepta-CDDs and CDFs and the labeled octa-CDDs are used as the reference for octa-CDDs and CDFs, since only a limited number of isotopically labeled standards are available.

Digestion and/or Extraction of Samples. Solid samples which cannot readily be digested or completely dissolved, such as soils, sediments, particulates from combustion and other sources, are extracted, following addition of the internal standards, either in a Soxhlet apparatus or by agitating the sample with solvent in a sealed bottle, typically for a period up to 16 hr. Benzene or toluene is the solvent usually utilized in Soxhlet extractions. Bottle extractions are generally accomplished with hexane–methanol as the solvent.

Solid samples which can be completely dissolved, such as human and other animal tissues, are initially digested, following addition of the internal standards using 40% KOH and ethanol, with mild heating and agitation of the mixture in a sealed bottle. The digested mixture is then extracted with petroleum ether or hexane. Alternatively, some tissues samples, such as fish, are digested with concentrated HCl, followed by extraction with hexane.

Liquid samples, such as water, solvents and other liquids from combustion trains and other sources, chemical wastes, and blood, are extracted following addition of internal standards, by agitating the sample with a solvent in a sealed bottle for periods ranging from 3 to 16 hr. Petroleum ether, hexane or methylene chloride is generally used as the solvent with such samples.

Preliminary Fractionation and Cleanup of Extracts. Extracts resulting from the foregoing procedures are usually treated by a sequence of washings

Table 1. Sequence of operations in GC–MS (MS-25) analyses of PCDD and PCDF in sample extract.

Elapsed time, min	Event	GC column temperature, °C	Temperature program rate, °C/min	Ions monitored by mass spectrometer (*m/z*)	Compounds monitored
0.00	Injection, splitless	190			
1.50	Turn on split valve	190			
2.00	Begin temperature program to 220°C	190	5		
5.00	Open column flow to mass spectrometer	205	5		
6.50	Start PROGRAM 2; sweep = 200 ppm; time on each mass = 0.12 sec	220		235.980	Di-CDF
				237.977	Di-CDF
				251.974	Di-CDD
				253.972	Di-CDD
10.50	Stop PROGRAM 2	220			
11.00	Start PROGRAM 3; sweep = 200 ppm; time on each mass = 0.15 sec	220		269.941	Tri-CDF
				271.938	Tri-CDF
				285.935	Tri-CDD
				287.932	Tri-CDD
15.00	Stop PROGRAM 3	220			
15.50	Start PROGRAM 4; sweep = 100 ppm; time on each mass = 0.15 sec	220		258.930	Tetra-CDD
				303.902	Tetra-CDF
				305.899	Tetra-CDF
				319.897	Tetra-CDD
				321.894	Tetra-CDD
				327.885	$^{37}Cl_4$-Tetra-CDD
23.50	Stop PROGRAM 4	220			
24.00	Start PROGRAM 5; sweep = 750 ppm; time on each mass = 0.2 sec	220		337.863	Penta-CDF
				339.860	Penta-CDF
				353.858	Penta-CDD
				355.855	Penta-CDD
25.00	Begin temperature program to 230°C	220	5		
34.50	Stop PROGRAM 5				
35.00	Start PROGRAM 6; sweep = 150 ppm; time on each mass = 0.25 sec	230		373.821	Hexa-CDF
				375.818	Hexa-CDF
				389.816	Hexa-CDD
				391.813	Hexa-CDD
50.00	Begin temperature program to 235°C		5		
53.50	Stop PROGRAM 6	235			
54.00	Start PROGRAM 7; sweep = 750 ppm; time on each mass = 0.35 sec	235		407.782	Hepta-CDF
				409.779	Hepta-CDF
				423.777	Hepta-CDD
				425.774	Hepta-CDD
				431.765	$^{37}Cl_4$-Hepta-CDD
70.00	Stop PROGRAM 7				
85.00	Start PROGRAM 8; sweep = 750 ppm; time on each mass = 0.50 sec	235		441.732	Octa-CDF
				443.740	Octa-CDF
				457.738	Octa-CDD
				459.735	Octa-CDD
				471.717	$^{37}Cl_8$-Octa-CDD
95.00	Stop PROGRAM 8				
130.00	Return to initial temperature				

with 0.1 N KOH, concentrated H_2SO_4 and distilled water, the aqueous phase from the base (KOH) washing being retained for analysis for chlorophenols and other polar compounds of interest, and the acid and water washings in each case being discarded. The extracts are then concentrated and passed through a combination liquid chromatography column packed with silica, 33% NaOH modified silica, and 44% H_2SO_4 modified silica, eluting with hexane. The effluent from this column is again concentrated and passed through a column of Woelm basic alumina (activated for 16 hr. at 600°C), 3% methylene chloride in hexane being used as the initial eluting solvent (this eluent fraction is either discarded or retained for PCB and/or chlorobenzene analyses) and finally, the PCDDs/PCDF being eluted with 50% methylene chloride in hexane. The latter fraction is concentrated to dryness, and then reconstituted with an appropriate solvent just prior to GC–MS analysis.

GC-MS Analysis of Extracts for PCDDs/PCDFs. Appropriate aliquots of the sample extracts are injected into the coupled GC–MS for quantitative determination of the PCDDs/PCDFs. The mass spectrometer is operated in the selected ion monitoring mode (SIM), with at least two different ion masses (and sometimes as many as four) being monitored for each chlorinated class of PCDDs/PCDFs. The capillary gas chromatographic column is temperature programmed and data acquisition and operation of the mass spectrometer (selection of ions monitored at various GC retention times) is accomplished with an on-line computer. Several different capillary GC columns are used, depending upon the scope of the analyses. Either high resolution mass spectrometry (static resolution of 10,000) or low resolution mass spectrometry (static resolution of 1000) is used, depending upon the degree of specificity desired for the analysis. Typical gas chromatographic and mass spectrometric parameters applicable for these analyses are summarized below, and a typical sequence of GC–MS operations for an analysis of the entire series of PCDDs/PCDFs (di- through octachlorinated) is shown in Table 1.

Typical gas chromatographic conditions for PCDDs/PCDFs analyses were: chromatograph: Varian 3700; column: 50 or 60-m WCOT fused silica or glass capillary, coated with OV-101, SP-2340, SP-2330, DB-5, Silar-10C or OV-17/Silar-10C phases; carrier gas: hydrogen, 30 lb head pressure; column temperature: programmed (see Table 1); interface temperature: 250°C; injection mode: split at 50:1.

Typical mass spectrometric conditions for PCDDs/PCDFs analyses are: mass spectrometer: Kratos MS-25 or MS-30; ionization mode: electron impact (ionizing voltage 70 eV); mass resolution: 1000, 7500, or 10,000; source temperature: 250°C; accelerating voltage: 4 kV; operating mode: selected ion monitoring (see Table 1 for ion masses monitored); data system: Kratos DS55SM.

The criteria which GC–MS data must satisfy in order to be attributed to PCDDs/PCDFs present in the sample extracts are as follows.

(1) The mass chromatographic peaks produced by the unknown component must exhibit appropriate GC retention times; that is, they must fall within a retention time "window" established for a particular class of PCDD or PCDF (e.g., tetra-CDD). These "windows" are established by injecting representative standards for each class of PCDD and PCDF.

(2) Mass chromatographic peaks produced by the component must exhibit the appropriate response for at least two major ions characteristic (that is, known to appear in the mass spectrum) of the particular PCDD or PCDF class being monitored. The ratio of relative intensities of the two ions monitored as indicators must correspond to that resulting from injection of a corresponding calibration standard within ± 30%.

(3) In cases where the sample matrix causes shifts in the GC retention times of the components of interest, as compared to the retention times of the corresponding standards determined from a separate injection of standards, and as indicated by analogous shifts in the retention times for the internal standards added to the sample, the identification of a specific PCDD and/or PCDF must be confirmed by coinjection of the sample with an added quantity of the PCDD or PCDF isomer in question. Enhancement of a given mass chromatographic peak upon such coinjection leads to tentative assignment of the unknown peak as a specific PCDD or PCDF isomer.

There are 210 separate isomers of the PCDDs and PCDFs (75 PCDDs, 135 PCDFs), as shown in Table 2. Since pure standards corresponding to all of these isomers are available in few if any laboratories, the approach currently utilized for calibration of the GC–MS instrumentation and quantitation of the compounds of interest in analyses such as those described here is to utilize selected standards representative of each chlorinated class of the PCDDs/PCDFs and to assume that the data obtained for these is representative of all isomers in each chlorinated group (for example, monochlorinated, dichlorinated, etc.). The procedures employed here entail obtaining a mass spectrum for each of

Table 2. Number and type of chlorinated isomers of the polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), chlorinated phenols (CPs), chlorinated benzens (CBzs) and polychlorinated biphenyls (PCBs).

Number of chlorine atoms per molecule	Number of isomers				
	PCDDs	PCDFs	CPs	CBzs	PCBs
1	2	4	3	1	3
2	10	16	6	3	12
3	14	28	6	3	24
4	22	38	3	3	42
5	14	28	1	1	46
6	10	16	–	1	42
7	2	4	–	–	24
8	1	1	–	–	12
9	–	–	–	–	3
10	–	–	–	–	1
Total	75	135	19	12	209

the representative isomers injected into the GC–MS, noting in particular the relative abundances of the m^+ and $(m + 2)^+$ peaks (m indicates the molecular ion here); determining gas chromatographic retention times for each isomer standard injected; and based on the above data, select the ion masses appropriate for detecting and quantifying the isomers in the class of interest, and select the gas chromatographic retention time window appropriate for all isomers in the class (that is, the time interval during which the earliest-eluting and latest-eluting isomers of a particular class elute from the gas chromatographic column and enter the mass spectrometer source; this must be estimated in cases where not all isomers of a given class are available). This retention time window must also include the retention time for the internal standard employed in quantifying the isomers of a particular class.

PCDDs/PCDFs in the sample extract are quantified by obtaining the ratios of the mass spectral responses obtained for the ions characteristic of the native PCDDs/PCDFs to those of the appropriate internal standards (listed earlier in this section) added to the sample in known concentrations. The concentrations of the native PCDD/PCDF are then determined by comparing the above data with calibration curves, prepared by plotting the analytical results obtained for a series of standards, each of which contains a fixed concentration of internal standard, but varying concentrations of representative PCDD and/or PCDF. More specifically, the ratio of the ion intensity recorded for the native PCDD/PCDF to the ion intensity obtained for the appropriate labeled internal standard is plotted as a function of the ion intensity obtained for the labeled internal standard. Since the labeled internal standard is added at the beginning of the sample preparation/analysis scheme, and, since the internal standard is quantified at the same time as the native analyte(s), it is clear that the quantitative result obtained for the internal standard reflects losses of PCDD/PCDF incurred during the course of sample handling and analysis.

The PCDDs/PCDFs calibration standards used in the analyses reported herein include the following: (1) for PCDDs: all 22 tetra-CDDs; 1,2,3,7,8-penta-CDD; 1,2,3,4,6,7-hexa-CDD; 1,2,3,4,6,7,8-hepta-CDD; octa-CDD; $^{37}Cl_4$-2,3,7,8-tetra-CDD; $^{13}C_{12}$-2,3,7,8-tetra-CDD; (2) for PCDFs: 1,2,4,8-tetra-CDF; 2,3,6,8-tetra-CDF; 2,3,7,8-tetra-CDF; 1,2,4,7,8-penta-CDF; 1,2,4,6,7,9-hexa-CDF; 1,2,3,4,6,8,9-hepta-CDF; octa-CDF.

Polychlorinated Biphenyls

The sample extract fraction from the liquid chromatographic separation procedure which contains the PCBs (as identified earlier) is analyzed using the same general GC–MS approach as that described above for PCDDs/PCDFs. In this case, however, the internal standard utilized is D_6-3,3',4,4'-tetra-CB. The GC and MS parameters are essentially the same as described for the PCDDs/PCDFs except that the DB-5 capillary GC column is used exclusively in this case, and the GC temperature programming and the MS ions monitored in the SIM mode are different, as shown in Table 3. The chlorinated biphenyls used for calibration in these analyses are 4-CB; 3,3'-diCB, 2,4',5-triCB; 3,3',4,4'-tetraCB; 2,2',6,6'-tetraCB; 2,3,4,5,6-pentaCB; 2,2',4,5,5'-pentaCB; 2,2',4,4',5,5'-hexaCB; 2,2',3,4,4',5,5'-octaCB; 2,2'3,3',4,4',5,6,6'-nonaCB; and 2,2',3,3',4,4',5,5',6,6'-decaCB.

Chlorobenzenes

The sample extract fraction containing chlorobenzenes (as noted in the earlier section) is analyzed by using the same procedures as described above for the PCDDs/ PCDFs, except that the internal standard used in this case is $^{13}C_6$-hexachlorobenzene, and the GC temperature program and the mass spectral ions monitored are those appropriate for the chlorobenzenes (see Table 3).

Chlorophenols

The aqueous sample extract fraction containing the sodium chlorophenates (as noted in the previous section on sample cleanup procedures) is acidified and the chlorophenols are partitioned into benzene. This solution is concentrated and treated with acetonitrile, pyridine, isooctane and acetic anhydride, in order to acetylate the chlorophenols. The derivatized chlorophenols are then subjected to GC–MS analyses by essentially the same procedures described above for the other compounds monitored in these studies, except that, again, the GC program and the mass spectral ions monitored are those appropriate to the chlorophenols as shown in Table 3. Also, for the chlorophenol analyses, the internal standard used is $^{13}C_6$-pentachlorophenol.

Sources of PCDDs/PCDFs and Related Compounds Detected as Environmental Contaminants in Recent Episodes Occurring in the U.S.

Some prominent sources of PCDDs/PCDFs which have been identified in recent environmental assessments in the U.S. are discussed in the following sections.

Improper Disposal of Chlorinated Chemical Wastes

Several instances of extensive environmental contamination by the PCDDs and related compounds which have been recognized in the U.S. in the past ten years have originated from the improper disposal of hazardous chemical wastes associated with the manufacture of

Table 3. Sequence of operations in GC-MS-25-DS analyses of sample extracts for chlorinated benzenes, chlorinated phenols and poly chlorinated biphenyls.

Elapsed time, min	Event	GC column temperature, °C	Temperature program rate, °C/min	Loss monitored by mass spectrometer (*mz*)	Compounds monitored
Chlorinated benzenes					
0.00	Injection, splitless	60	–		
1.50	Split valve on	60	–		
2.00	Begin GC temperature program to 250		8		
7.00	Start SIM program	100	8	145.969, 147.966	Cl_2 benzenes
	Sweep width = 500 ppm			179.930, 181.927	Cl_3 benzenes
	Time on ion-masses = 0.1 sec			213.891, 215.888	Cl_4 benzenes
	Time on $^{13}C_6$-hexachlorobenzene ion			247.852, 249.848	Cl_5 benzene
	masses = 0.1 sec			283.810, 285.807	Cl_6 benzene
				283.831, 191.828	$^{13}C_6$-Cl_6-benzene
22.00	Stop program	220			
26.00	Final temperature	250			
28.00	Cool column to initial temperature				
Chlorinated phenols					
0.00	Injection, splitless	60	–		
1.50	Split valve on	60	–		
2.00	Begin GC temperature program to 250°C		12	195.887, 197.884	Cl_3 phenols
	Start SIM program	156	12	229.867, 231.864	Cl_4 phenols
	Sweep width = 500 ppm			263.847, 265.844	Cl_5 phenol
	Time on ion masses = 0.1 sec			273.861	$^{13}C_6$-Cl_5-phenol
	Time on $^{13}C_6$-PCP ion mass = 0.1 sec				
18.00	Column temperature on hold	252			
20.00	Stop program				
25.00	Cool column to initial temperature				
Polychlorinated biphenyls					
0.00	Injection, splitless	190	–	–	–
1.50	Split valve on	190	–	–	–
7.00	Open column flow to mass spectrometer	190	–	–	–
	Begin GC temperature program to 270°C		5	–	–
	Start SIM program			188,039, 190.036	Cl_1 PCBs
	Sweep width = 100 ppm			222.000, 223.997	Cl_2 PCBs
	Time on ion masses = 0.1 sec			255.961, 257.958	Cl_3 PCBs
	Time on D_6-tetrachlorobiphenyl ion			289.922, 291.919	Cl_4 PCBs
	masses = 0.1 sec			325.880, 327.877	Cl_5 PCBs
				359.841, 362.839	Cl_6 PCBs
				393.802, 395.800	Cl_7 PCBs
				427.763, 429.761	Cl_8 PCBs
				463.722, 465.719	Cl_9 PCBs
				497.683, 499.680	Cl_{10} PCBs
				295.922, 297.919	D_6-Cl_4-labeled PCB
23.00	Hold column temperature	270	–		
35.00	Stop SIM program	270	–		
40.00	Cool column to initial temperature				

certain chlorinated organic compounds. In particular, the commercial production of trichlorophenol, as well as various derivative products, such as 2,4,5-T and other herbicides and germicides, can yield large quantities of waste products containing substantial concentrations of PCDDs. Three areas of the U.S. which have been or are still being intensely investigated by the U.S. Environmental Protection Agency for PCDDs contamination from such sources, and in which the work of the Brehm Laboratory has played a major role, are described below.

Love Canal. The Love Canal, located in Niagara Falls, NY, was originally conceived in the 1890s as a source of hydroelectric power that was to be generated by water diverted from the Niagara River. This plan proved to be impractical, and this fact, coupled with financial problems, led to abandonment of the partially dug canal. The site apparently remained unused until the 1940s, when the Hooker Chemicals and Plastics Corporation acquired the property and began to use it for disposal of chemical wastes. By 1953, when chemical waste burial at the site apparently terminated, some 21,800 tons of various wastes had been deposited in the canal, including an estimated 200 tons of trichlorophenol and 2,000 tons of chlorobenzenes (*12*). Shortly after Hooker terminated disposal activities at the site, the property was sold to the Niagara Falls Board of

Education, which subsequently installed a drain system in the former canal area and built a school on the site. Between the 1950s and the early 1970s, houses were built completely surrounding the former canal, roads were constructed around and over the canal area, and sanitary and storm sewers were constructed to service the area. In 1975 and 1976, heavy rainfall caused a marked groundwater level elevation and portions of the landfill in the former canal area subsided and drums of waste began to surface. Ponds of surface water, heavily contaminated with chemicals, developed, and residents of adjacent houses complained of the migration of this water into their yards and of heavy chemical odors. Evidence that the chemicals had also migrated in the subsurface strata was observed by the fact that noxious, oily chemical residues appeared in basement sumps of houses around the former canal area, and foundations of some houses exhibited chemical seepage. Chemical fumes were also observed to emanate from storm sewer openings at about this period. As a consequence of these events, and complaints about health effects resulting from these wastes, preliminary environmental sampling was conducted at the site by the State of New York, and in 1978 the NY State Department of Health declared the site to be a health threat, and ordered that the area nearest the landfill be fenced and restricted to public access. This led to the closing of the school, the evacuation of residents from the first ring of houses surrounding the landfill and the purchases of these houses by New York State. Both the State and Federal governments declared that a state of emergency existed in the canal area. In late 1978 and early 1979, the City of Niagara Falls designed and constructed a barrier drain system parallel to, and on both sides of the southern portion of the Love Canal. A permanent leachate treatment facility (equipped with activated-carbon filters) to collect contaminants collected by the drain system was also installed near the site at this time. The remainder of the barrier drain system around the canal was completed by New York State in late 1979, and a clay cap was installed over the former canal. After some preliminary cytogentic screening of selected residents from the Love Canal area in early 1980, the Federal government again declared a state of emergency and the U.S. EPA initiated a comprehensive environmental monitoring program at the site, which was concluded in October 1980.

The U.S. EPA-sponsored environmental monitoring program at the Love Canal involved collection of some 6853 field samples. These samples included soil cores, water from groundwater monitoring wells installed at the site, drinking water, water and sediments from sanitary and storm sewers and from sumps, surface water and sediments from area creeks and rivers, sediments from the Leachate Treatment Facility, and air samples from residences in the area. Selected biota from the site, including crayfish, domestic dog hair, maple leaves, field mice, and earthworms were also collected. Some of these samples were analyzed for as many as some 130 organic compounds and for 16 inorganic compounds. The environmental sampling and chemical analysis investigations were accompanied by extensive geophysical and hydrogeological studies to define the geology and strata of the area, in order to understand groundwater transport of contaminants from the former canal. All analyses of environmental samples from the Love Canal site for 2,3,7,8-TCDD (the major PCDD contaminant expected in the Love Canal waste) were accomplished by the Brehm Laboratory, of Wright State University and validating analyses were accomplished on some samples by the U.S. EPA's Research Triangle Park laboratory (HERL). The results obtained for all samples for which the Brehm Laboratory reported a positive finding of TCDD were confirmed by the EPA/HERL (RTP) analyses of portions of the same sample extracts. High resolution mass spectrometric measurements (as described in the earlier section on methodology) were employed by both laboratories for these determinations. Quality assurance was further maintained by periodic analyses by the Brehm Laboratory of performance evaluation samples which had been prepared by EPA to contain known quantities of 2,3,7,8-TCDD (no analyte added, 60 ppt of 2,3,7,8-TCDD, or 120 ppt of 2,3,7,8-TCDD). These samples were submitted to the Brehm Laboratory along with normal samples and were analyzed by the laboratory without prior knowledge of the TCDD content. Performance on these samples was quite acceptable,

Table 4. Concentrations of 2,3,7,8-TCDD detected in storm sewer sediments collected at the Love Canal site.

Sample	Location	Measured concentration of 2,3,7,8-TCDD, ppb
A-21	97th St. and Read Avenue	329
A-13	97th St. and Colvin Blvd.[a]	672,638[b]
A-10	96th St. and Colvin Blvd.[a]	5.39
A-11	96th St. and Greenwald Ave.[a]	170
A-12	97th St. and Greenwald Ave.	ND[c]
A-22	96th St., near Apt. 620 in Court 2	ND[c]
A-20	97th St. and Wheatfield Ave.[a]	199,224[b]
A-4	97th St. and Frontier Ave.[a]	393,303[b]
A-3	100th St. and Frontier Ave.[a]	0.2
A-2	102nd St. and Frontier Ave.[a]	ND[c] ND[b,c]
A-1	Buffalo Avenue, near 10108 Buffalo	ND[c]
A-19	99th St. and Wheatfield Ave.[a]	0.2
A-17	101st St. and Wheatfield Ave.[a]	0.4
A-18	102nd St. and Wheatfield Ave.[a]	ND[c]
A-15	100th St. and Colvin Blvd.[a]	0.054
A-16	101st St. and Colvin Blvd.[a]	ND[c]
A-5	Frontier Ave. between 93rd and 96th St.	ND[c] ND[b,c]
A-6	93rd St. and Frontier Ave.	ND[c]
A-7	Frontier Ave. between 92nd and 93rd St.	ND[c] ND[b,c]
A-8	93rd St. and Read Ave.	ND[c]
A-9	93rd St. and Colvin Blvd.	0.165, 0.419

[a]Turning point or junction of the storm sewer line occurs at this location.

[b]Duplicate analysis of a second sample aliquot from this site.

[c]Indicates not detected; minimum detectable concentrations for these samples were generally in the 10–100 ppt range.

recovery of the added TCDD typically being on the order of 70% or better.

Of the several types of samples from the Love Canal area which were analyzed for TCDD, the air samples, soil samples from the vicinity of homes around the former canal, surface water samples, and water samples from the groundwater monitoring wells were found to contain no TCDD (with detection limits in the ppt range).

As shown by the data presented in Table 4, 2,3,7,8-TCDD was detected in many of the storm sewer sediment samples collected from the canal area. The data shown in this table are grouped by sampling site to reflect the observed concentrations in the sewer lines along the direction of waterflow extending from the former canal location itself to the sewer outfalls in nearby creeks or the Niagara River. Thus, the samples, A-21, A-13, A-10 and A-11, in that order, are from one such sewer line segment which discharges into Black Creek near Berzholtz Creek, while the samples A-20, A-4 and A-3, in that order, are a group from a second sewer line segment which discharges into the Niagara River. Similarly, samples A-15 and A-16 are from still another storm sewer line segment extending from the former canal area and discharging into Black Creek. Samples A-19 and A-17 are from parallel storm sewer line segments which discharge into the Niagara River. In general, these results show patterns of decreasing concentrations of 2,3,7,8-TCDD in the storm sewer lines as the distance from the former canal increases. Other sediment samples for which data are reported in Table 4, which were collected at storm sewer locations other than those along the sewer lines draining the immediate former canal area, (for example, A-2, A-5 through A-8 and A-18, and A-22) showed nondetectable levels of 2,3,7,8-TCDD. These results provide strong evidence that 2,3,7,8-TCDD from the canal area was sorbed on soil particulates and transported by water flow through the storm sewers. The tendency for TCDD to accumulate in sediments has been observed previously, and the generally low concentrations of TCDD observed in water reflect the low aqueous solubility of these compounds.

The hypothesis regarding migration of the 2,3,7,8-TCDD from the canal area is further supported by the findings of these compounds in stream sediments collected from Black and Bergholtz Creeks and from the Niagara River near the storm sewer outfall points. These data are shown in Table 5.

Table 5 also shows the 2,3,7,8-TCDD concentrations detected in samples collected from basement sumps of houses located in the former canal area. All of the sump samples in which TCDD was detected (those results reported in Table 5) originated from houses located in the immediate periphery (the so-called "ring 1") of the former canal. One such sample (S5033) exhibited a concentration of 9570 ppb. This site was coincident with a known sand lens on the western side of the Love Canal, where leakage from the canal was apparently enhanced. Sump samples from houses outside ring 1 showed no detectable levels of 2,3,7,8-TCDD.

Table 5. Concentrations of 2,3,7,8-TCDD in various samples collected from the Love Canal area.

Sample	Location	Measured concentration of 2,3,7,8-TCDD, ppb
W22251	Leachate treatment plant, influent, liquid phase	1.56
W22253	Leachate treatment plant, effluent, liquid phase	ND (0.006)[a]
S50331	Sump sediment, residence, 703 97th St.	9570
W20068	Sump water, residence, 476 99th St.	0.592[b]
W20072	Sump water, residence, 476 99th St.	0.492[b]
S50188	Sediment, Black Creek near 98th St.	0.075
S50179	Sediment, Black Creek near storm sewer outfall	37.4
S50130	Sediment, Bergholtz Creek at junction with Black Creek	1.32
S50196	Sediment, Niagara River near 102nd St. storm sewer outfall	0.061[c]
S50197	Sediment, Niagara River near 102nd St. storm sewer outfall	0.012[c]
S50198	Sediment, Niagara River near 102nd St. storm sewer outfall	0.023[c]

[a]Indicates not detected; value given in parentheses is the minimum detectable concentration.
[b]Samples were obtained from two different sumps at this residence.
[c]Samples were three different aliquots of the same sample and are probably not homogeneous.

Finally, the presence of 2,3,7,8-TCDD in the former canal and the fact that it was being transported in leachate from the canal were established by the finding of this compound in the influent to the leachate treatment facility (see Table 5). Effluent from the leachate treatment facility contained no measurable concentration of TCDD.

The observed results with respect to 2,3,7,8-TCDD environmental contamination in the Love Canal area are generally consistent with the patterns for other organic contamination which were revealed by the EPA study and the earlier New York State investigations. These results are also understandable in terms of the geology and hydrology of the site and verify the anticipated contaminant transport mechanisms. The fact that 2,3,7,8-TCDD is still present in the Love Canal area nearly twenty years after chemical waste disposal at the site was terminated suggests that this compound may have a substantial half-life in the environment.

Sites in the State of Missouri. Extensive contamination of the environment with 2,3,7,8-TCDD occurred in the State of Missouri in the early 1970s as a result of the spraying of horse arenas, roads and parking lots with mixtures of used oil and chemical waste, or in some cases undiluted chemical waste products. The history of these episodes has been documented in some detail in a recent comprehensive newspaper publication. (*13*) The problem first became apparent at several horse arenas, and led to the deaths of some 90 horses, as well as dogs, cats, chickens, birds and other animals and insects. Several people, including a few children, suffered health

effects which were reported to include chloracne, kidney, bladder and gastrointestinal problems, severe headaches, nausea, nosebleeds and nervous and psychological disorders. The source of the chemical waste was ultimately traced to a defunct manufacturing company, the Northeastern Pharmaceutical and Chemical Company (NEPACCO), which had manufactured hexachlorophene from 2,4,5-trichlorophenol (TCP) which was contaminated with the 2,3,7,8-TCDD impurity. The manufacturing process involved distillation of the TCP, which yielded a still bottom waste containing several hundred parts per million of 2,3,7,8-TCDD. Several thousand gallons of this waste were dispersed by a chemical and waste oil salvage company over a sizable area of southwestern and eastern Missouri during the 1970s.

It was not until 1974, some three years after the first application of the NEPACCO wastes to a horse arena and the resultant adverse animal and human health effects, that the Center for Disease Control (CDC) identified 2,3,7,8-TCDD as the chemical responsible for the problems. CDC advised the State of Missouri of this fact, but the source of the TCDD was not immediately realized since the waste hauler handled chemicals from many sources and virtually no records were maintained. After a long series of investigations by private citizens who had been affected by the chemical wastes, and by the State of Missouri, the source of the TCDD was identified, but the extent to which these wastes had been dispersed were still not apparent. While some minor remedial efforts were attempted at various affected horse arenas during the following three to five year period (mostly by the owners of these arenas) which consisted of removing some of the top layers of soil from these sites and transferring it to landfills, there was little concerted action by either the State of Missouri or the Federal government to fully assess and remedy the problem. Ironically, this was largely due to the erroneous belief that TCDD had a half-life in soil of less than a year, the basis for this being an Air Force report by Young et al.(*14*). More recent measurements, described below, clearly suggest that this estimate of TCDD half-life in soils is grossly in error.

In 1980 and 1981, attention was focused on the site of the former NEPACCO manufacturing operation, since acquired by Syntex, because it was discovered that a large tank containing chemical wastes which included 2,3,7,8-TCDD had been left at the site when NEPACCO terminated operations. It was also discovered that wastes from the original operation had been improperly buried at various sites around the area and that contamination of the nearby Spring River had occurred. As more information was revealed about these and other sites at which the waste containing TCDD had been dispersed, it became apparent that more extensive environmental assessment was necessary. In 1982, the U.S. EPA initiated a new round of sampling at several of the originally sprayed horse arenas and at several other sites known to have been sprayed by the waste salvage company which collected the NEPACCO still bottoms. Most of these initial samples were analyzed for 2,3,7,8-TCDD by the Brehm Laboratory of Wright State University. The first such samples, taken from the Shenandoah Stables showed levels of 2,3,7,8-TCDD in the soil as high as 1750 parts per billion. Representative data for soil samples from the stables and from other suspected sites of contamination are presented in Table 6. The initial results obtained in these analyses were announced by EPA on August 18, 1982, and it was immediately apparent that, at least under the conditions prevailing at the Missouri sites, 2,3,7,8-TCDD exhibits a much longer half-life in soils than the one year which had previously been estimated. These results prompted one of the largest environmental assessments yet undertaken in the U.S. Literally thousands of soil, water and biological samples have been collected from some 33 suspected sites throughout the State of Missouri during 1983 and analyzed for 2,3,7,8-TCDD by EPA and ten contract laboratories. The Brehm Laboratory has continued to play a key role in assessing the Missouri problem, and provided much of the data which ultimately led to evacuation of an entire Missouri town, Times Beach, Missouri, which had been heavily contaminated with 2,3,7,8-TCDD (see Table 7). The U.S. government subsequently purchased all property in this town and relocated the residents.

Long-term health effects on the population of Missouri which was exposed to 2,3,7,8-TCDD are not yet apparent, but several medical surveys are in progress or are planned. Hopefully, these will include chemical measurements aimed at detection of TCDD in human tissue samples.

Table 6. Selected results of the analyses of environmental samples from the State of Missouri for 2,3,7,8-TCDD

Sample	Sample description	Concentration of 2,3,7,8-TCDD detected, ppb
107G- 1	Shenandoah Stables, composite of 0–6 in. soil core from area where contaminated soil removed from arena had been placed in 1972	113
107G- 2	Composite of 6–30 in. soil core from same site as sample 170G-1	1750
170G- 5	Shenandoah Stables, composite of 0–6 in. soil core from perimeter of arena	127
170G- 7	Shenandoah Stables, composite of 6–12 in. soil core from perimeter of arena	101
211G- 5	Timberline Stables, composite of 6–12 in. soil core from perimeter of arena	30
211G- 7	Timberline Stables, composite of 12–18 in. soil core from perimeter of arena	42
211G-25	Bliss Farm, composite of 0–6 in. soil core from farm road	382
211G-33	Bubbling Springs Ranch, composite of 0–6 in. soil core from perimeter of arena	76
211G-35	Bubbling Springs Arena, composite of 6–12 in. soil core from perimeter of arena	95
288G-69	Minker residential area, soil	50

Table 7. Concentrations of 2,3,7,8-TCDD in selected soil samples from Times Beach, MO.

	Sampling site and identification	Concentration of 2,3,7,8-TCDD detected, ppb or ng TCDD/g sample
KBA-1	Times Beach, Dogwood, Beach-Park Road	30
KBA-2	Times Beach, Dogwood, Orchard-Dahlia Road	72
KBA-3	Times Beach, Dogwood, Lincoln-Woodland, Shoulder	11
KBA-18	Times Beach, Dogwood, Dahlia-Beach	52
KBA-6	Times Beach, Juniper, Beach-Park Road, 0–6 in.	317
KBA-23	Times Beach, Juniper, Dahlia-Beach	38
KBA-10	Times Beach, Laurel, Dahlia-Beach, Shoulder, 0–6 in.	74
KES-10	Times Beach, Laurel, Orchid-Dahlia	121
KES-24	Times Beach, Laurel, Dahlia-Beach	110
KES-11	Times Beach, Ivy, Orchid-Dahlia	24
KES-22	Times Beach, Ivy, Dahlia-Beach	28
KBA-4	Times Beach, Ivy, Dahlia-Beach, Ditch, 0–6 in.	4.4
KES-28	Times Beach, Oak, Dahlia-Beach	6.3
KBA-5	Times Beach, Oak, Dahlia-Beach Ditch, 6–12 in.	9.2

Combustion Processes as Sources of PCDDs/PCDFs

In the late 1970s several European investigators reported the detection of PCDDs/PCDFs in fly ash and other combustion products from the incineration of municipal refuse. These findings have been summarized in a review by Lustenhouwer et al. (*15*). Concerns raised by these observations prompted the U.S. EPA to support investigations by the Brehm Laboratory of municipal refuse incinerator effluents to determine whether or not toxic compounds such as these were being generated. This led to the first report of PCDDs/PCDFs in such effluents in the U.S. by our laboratory in 1979, based on measurements on the effluents from a waste-fueled boiler in Nassau County, NY (*3*). Subsequently, more elaborate investigations were accomplished by the Brehm Laboratory on several other municipal incinerators. In addition to analyzing the effluents from these plants for PCDDs/PCDFs, other related chlorinated hydrocarbons, including chlorophenols, chlorobenzenes and PCBs, were also determined in an effort to obtain insight into the mechanism of information of PCDDs/PCDFs in such combustion environments. Some of the data obtained in these studies have been reported previously (*4,5*), and the stack sampling and analytical procedures applied have been described in some detail. The analytical methodology applied is essentially that presented earlier in this paper.

Results of the analyses of stack effluents from two different incinerators, one located in Virginia and the other located in Ohio, are presented and compared here. The Virginia plant sampled is a refuse-fired steam boiler which burns ordinary "as-received" municipal refuse on a grate. The Ohio plant was burning a compacted pelletized fuel prepared by processing municipal refuse at the time the stack samples reported here were collected. The latter plant is also a steam-generating facility but is equipped with superior effluent control devices and generally operates with higher combustion efficiency than the Virginia plant. The Virginia plant average combustion temperature was in the neighborhood of 700 to 800°F, while that of the Ohio plant was typically 900 to 1000°F. In both of the plants sampled, stack effluents were collected after the control

Table 8. Concentrations of selected chlorinated hydrocarbons determined in flue gas effluents from refuse incineration.

Compound	Concentration of flue gas: Municipal refuse-fired steam boiler, Virginia, $\mu g/m^3$	Refuse-derived-fuel fired power plant, Ohio, ng/m^3
Chlorodibenzo-*p*-dioxins		
Tetra-	0.38	0.65
Penta-	0.53	0.43
Hexa-	0.85	1.2
Hepta-	2.0	20
Octa-	0.49	12
Total	4.3	34
Chlorodibenzofurans		
Tetra-	2.6	11
Penta-	1.6	3.0
Hexa-	1.8	6.5
Hepta-	2.2	23
Octa-	0.17	7.1
Total	8.3	51
Chlorobenzenes		
Di-	4.4	7.8
Tri-	19	56
Tetra-	29	57
Penta-	39	0
Hexa-	11	9.5
Total	103	130
Chlorophenols		
Tri-	129	3435
Tetra-	64	3074
Penta-	41	2914
Total	234	9423

devices and are therefore indicative of the actual air emissions to the environment.

In Table 8, the measured concentrations of PCDDs/PCDFs, chlorobenzenes and chlorophenols in the effluents from the two plants mentioned above are summarized. In both cases, the concentrations of PCBs in the effluents were negligible by comparison with the other compounds listed. As can be seen from the data in Table 8, the concentrations of PCDDs/PCDFs and related compounds in the combustion effluents from the Virginia plant are substantially larger (by factors ranging from about 30 to 800) than the corresponding products from the Ohio plant. Probably, this reflects, in part, the greater combustion efficiency achieved at the Ohio plant, but these differences may also be due to substantial differences in the municipal refuse fuel incinerated by the two plants. Of the several types of chlorinated hydrocarbons determined, the chlorophenols are present in the largest concentrations in the effluents from both incinerators, although substantial quantities of the chlorobenzenes are also observed. It is seen that the total PCDFs are more abundant than the total PCDDs by about a factor of two in both cases. The two incinerators show some differences in the relative concentrations of the various chlorinated classes (for example, tetra-, penta-, etc.) of the several compounds detected, as indicated in Table 9. This is particularly evident for the chlorophenols. Trichlorophenol is the major chlorophenol in the effluents from the Virginia incinerator, whereas pentachlorophenol is dominant in the Ohio incinerator effluents. Similarly, tetra-CDFs are the dominant CDFs from the Virginia plant, while hepta-CDFs are the principal PCDFs from the Ohio plant. Tetra-CDDs are also present in larger concentrations relative to the other PCDDs in the Virginia effluents than in the Ohio effluents.

Table 9 also shows the relative concentrations of the various chlorinated hydrocarbons determined in several different incinerator tests at each of the two sites. Since the composition of municipal refuse undoubtedly varies considerably over a period of time, it would be expected that the quantities of the chlorinated hydrocarbon effluents would vary considerably from test to test. Such variations would also be expected to be greater for the Virginia plant which burned ordinary "as-received" refuse than for the Ohio plant which utilized a preprocessed moderately uniform refuse-derived fuel. In general, the data are consistent with these expectations, but the variations from test-to-test do not seem to be as great as might have been anticipated, with the exception, perhaps, of the chlorobenzenes.

It is interesting that the tetra-CDDs, which are currently of greatest concern from a toxicity viewpoint, are generally the least abundant of the PCDDs in the effluents from both incinerators. In the case of the tetra-CDDs, the isomeric composition of these compounds in the effluents was determined. As shown in Table 10, the highly toxic 2,3,7,8-TCDD is a very minor component of the tetra-CDDs (about 1% of the total TCDDs). The pattern and abundance of tetra-CDD isomers was remarkably similar in the effluents from both incinerators discussed here.

The implications of the present findings with respect to the mechanism of formation of PCDDs/PCDFs in combustion processes has been discussed elsewhere (*4*), but it seems likely that both the chlorobenzenes and the chlorophenols are precursors and/or intermediates in the formation of the PCDDs/PCDFs.

Table 9. Relative concentrations of selected chlorinated hydrocarbons in flue gas effluents from refuse incineration as indicated by stack sampling tests on different operating days.

	% of total compounds of each type					
	Municipal refuse-fired boiler, Virginia			RDF-fired power plant, Ohio		
Compound	Test #3	Test #5	Test #7	Test #1	Test #2	Tests #3&4 (composite)
PCDDs						
Tetra-	20	17	9	2	5	6
Penta-	18	22	12	1	5	5
Hexa-	20	37	20	3	11	9
Hepta-	29	19	48	58	42	53
Octa-	12	5	11	35	37	27
PCDFs						
Tetra-	35	65	31	21	22	18
Penta-	14	23	19	6	9	9
Hexa-	22	28	21	13	12	14
Hepta-	28	12	26	46	23	55
Octa-	2	1	2	14	4	4
Chlorobenzenes						
Di-	0	6	4	6	0	2
Tri-	4	11	19	43	6	8
Tetra-	23	14	28	44	9	7
Penta-	56	51	38	0	56	28
Hexa-	17	19	11	7	29	55
Chlorophenols						
Tri-	67	64	55	36	28	6
Tetra-	20	28	28	33	38	19
Penta-	12	8	17	31	34	50

Table 10. Specific TCDD isomers identified in the extract of particulates present in flue gas effluents collected from municipal refuse incineration.

TCDD isomer[a]	% of total TCDDs in Virginia plant effluents
1,3,6,8-	20.97
1.3,7,9-	13.29
1,3,6,9-	5.17
1,3,7,8-/1,4,6,9-/1,2,4,8-	10.64
1,2,4,6-/1,2,4,9-	14.77
1,2,6,8-	7.09
1,4,7,8-	6.65
1,2,7,9-	2.07
1,2,3,4-/1,2,3,6-/1,2,6,9-	11.08
1,2,3,7-/1,2,3,8-/2,3,7,8-[b]	3.84
1,2,7,8-	4.43

[a]Based on gas chromatographic separation with a 60-m OV-101 WCOT glass capillary column.

[b]Analysis of the same sample extract with a 60-m SP-2340 capillary GC column, which resolves the 2,3,7,8-TCDD from the other 21 TCDD isomers, indicates that 2,3,7,8-TCDD constitutes about 1% of the total TCDDs.

impact of the observations reported here on pal incinerator effluents for human health effects have not yet been determined. An earlier preliminary assessment of other incinerators by the U.S. EPA, in which only TCDD was measured in the effluents, and in which the health risks were asserted to be negligible must obviously be reevaluated in light of the present findings. It is also clear that additional assessments of various types of incinerators, both in the U.S. and elsewhere, are needed in order to reliably estimate the contribution of such sources to the overall environmental burden of PCDDs/PCDFs and related compounds, and to more realistically estimate resultant human health effects.

Fires and Malfunctions in PCB-Filled Transformers as Sources of PCDDs/PCDFs

Laboratory studies have established that the pyrolysis of chlorobenzenes at temperatures of about 600°C yields both PCDDs and PCDFs (*15*). Similarly, laboratory pyrolyses of PCBs (600–800°C) have been shown to produce PCDFs (*16,17*). These observations suggest that pyrolysis of fluids such as the Askarels, whch have been widely used as transformer dielectrics and heat-transfer fluids, could be a significant mechanism for pollution of the environment with PCDDs/PCDFs. This has been confirmed by accidental fires in transformers containing such fluids which have occurred in Canada (*18*), Sweden (*19,20*), the U.S. and elsewhere. A recent fire of this type which occurred in Binghamton, NY in February 1981 in a New York State Office Building resulted in contamination of the entire building and the possible exposure of firemen and workers involved in cleaning the building to PCDDs/PCDFs (*21*). After initial chemical analyses to determine preliminarily the nature and extent of PCDDs/PCDFs contamination, and when it became apparent that this contamination was extensive, the building was closed and all use of the facility was terminated (*22*). Attempts to clean and detoxify the building are still in progress. In this paper, we describe the results of some of the analytical measurements by the Brehm Laboratory which were aimed at assessing the PCDDs/PCDFs contaminants resulting from the Binghamton fire. Some preliminary studies of human tissue samples from persons who were possibly exposed to PCDDs/PCDFs in this fire were also undertaken in collaboration with Dr. Arnold Schecter of the State University of New York, Binghamton, NY. All chemical analyses were accomplished by the Brehm Laboratory, while Dr. Schecter was responsible for medical surveillance and testing of these subjects. The latter results are described elsewhere in this volume (*23*). It is hoped that it will be possible to correlate observations of PCDDs/PCDFs in the human tissue samples with the levels of exposure and with symptoms of adverse health effects reported by the victims and confirmed by medical tests and microscopic examination of tissues. These studies are still in a preliminary stage, however, and it is premature to draw conclusions at this point (*23*).

Presented here are some of the data obtained in assessing the PCDDs/PCDFs contamination in the New York State Office Building in Binghamton and in an adjacent garage. The fire occurred in the basement of the building and generated copious quantities of soot, which entered the main air distribution of the building and was dispersed throughout the 18-story building. The transformer originally contained about 1000 gal of a fluid consisting of 65% PCBs (Aroclor 1254) and 35% tri- and tetrachlorinated benzenes. Samples of soot were collected at various points in the building and analyzed for PCDDs/PCDFs. Typical results of such analyses are shown in Table 11, and clearly show that substantial quantities of PCDDs/PCDFs were sorbed on the soot. The PCDFs were present in the soot in markedly higher concentrations than the PCDDs and included approximately 220 ppm of the 2,3,7,8-TCDF, as well as quantities of other penta- and hexa-CDFs which are thought to be toxic.

Wipe samples of surfaces from the Broome County garage adjacent to the Binghamton State Office Building were also analyzed and revealed that the garage surfaces were contaminated with PCDDs/PCDFs (Table 12). Comparison of the latter data with corresponding analytical results obtained for a wipe of a control garage not exposed to the State Office Building fire (Table 13) clearly indicate that the PCDDs/PCDFs in the Broome County garage originated from the PCB transformer fire.

The levels of PCDDs/PCDFs generated by the fire in the Binghamton State Office Building are obviously of concern in terms of possible human exposures of firemen, who were in the building at the time of the fire

Table 11. Concentrations of CDDs/CDFs in soot samples from PCB transformer fire in Binghamton, NY.[a]

	Concentration of CDDs/CDFs, ppm	
	Wright State	Buser[b]
Chlorodibenzo-*p*-dioxins (CDDs)		
Tetra-	<3.0	1.2
Penta-	<2.0	5.0
Hexa-	<3.0	4.7
Hepta-	7.0	7.0
Octa-	5.0	2.0
Chlorodibenzofurans (CDFs)		
Tetra-	1920	28
Penta-	1200	670
Hexa-	1160	965
Hepta-	405	460
Octa-	66	40

[a]Different soot samples, collected at different times and from different locations within the building, were analyzed by the two laboratories for which data is shown.
[b]Data of Buser (*24*).

and afterward, and of workers who were in the building to initiate cleaning following the fire and prior to recognition of the potential chemical hazard. As noted above, chemical analyses of tissues from some of these personnel for PCDDs/PCDFs are being accomplished in conjunction with medical surveillance and testing. Preliminary results of the latter are discussed briefly in other papers in this volume (*23*).

Table 12. Results of HRGC/LRMS analysis of wipe sample from Broome County garage adjacent to Bingamton State Office Building for tetra- through octachlorinated dibenzo-*p*dioxins and dibenzofurans.

CDD/CDF[a]	Apparent isomers	Quantity of CDD/CDF detected, ng/wipe	Minimum detectable quantity, ng/isomer	Recovery of ^{37}Cl-labeled internal standards, %
TCDD	ND	ND	0.10	100
PCDD	ND	ND	0.10	
HxCDD	ND	ND	0.20	
HpCDD	1,2,3,4,6,7,8-	0.65	0.20	
	1,2,3,4,6,7,9-	0.45	0.20	
	Total HpCDD	1.1	0.20	100
OCDD	1,2,3,4,6,7,8,9-	1.0	0.20	100
TCDF	1,2,4,8-	2.0	0.10	
	2,3,6,8-	3.1	0.10	
	2,3,7,8-	9.6	0.10	
	Other isomers (8)	35.8	0.10	
	Total TCDF	50.4	0.10	
PCDF	1,2,4,7,8-	5.2	0.10	
	Other isomers (13)	11.8	0.10	
	Total PCDF	17.0	0.10	
HxCDF	1,2,4,6,7,9-	1.6	0.20	
	Other isomers (12)	43.6	0.20	
	Total HxCDF	45.2	0.20	
HpCDF	1,2,3,4,6,8,9-	2.7	0.20	
	Other isomers (4)	4.6	0.20	
	Total HpCDF	7.3	0.20	
OCDF	1,2,3,4,6,7,8,9-	7.3	0.20	

[a]Prefix designations are: T- = tetra; P- = penta-; Hx- = hexa-; Hp- = hepta-; O- = octa-.

Table 13. Results of HRGC/LRMS analysis of wipe sample from another garage not contaminated by Binghamton State Office Buidling fire for tetra- through octa-chlorinated dibenzo-*p*-dioxins and dibenzofurans.

CDD/CDF	Apparent isomers	Quantity of CDD/CDF detected, ng/wipe	Minimum detectable quantity, ng/isomer	Recovery of ^{37}Cl-labeled internal standards, %
TCDD	ND	ND	0.10	100
PCDD	ND	ND	0.05	
HxCDD	ND	ND	0.20	
HpCDD	1,2,3,4,6,7,8-	ND	0.20	
	1,2,3,4,6,7,9-	ND	0.20	
	Total HpCDD	ND	0.20	100
OCDD	1,2,3,4,6,7,8,9-	0.50	0.30	100
TCDF	1,2,4,8-	ND	0.05	
	2,3,6,8-	ND	0.5	
	2,3,7,8-	ND	0.5	
	Other isomers (ND)	ND	0.05	
	Total TCDF	ND	0.05	
PCDF	1,2,4,7,8-	ND	0.05	
	Other isomers (ND)	ND	0.05	
	Total PCDF	ND	0.05	
HxCDF	1,2,4,6,7,9-	ND	0.20	
	Other isomers (ND)	ND	0.20	
	Total HxCDF	ND	0.20	
HpCDF	1,2,3,4,6,8,9-	ND	0.20	
	Other isomers (ND)	ND	0.20	
	Total HpCDF	ND	0.20	
OCDF	1,2,3,4,6,7,8,9-	ND	0.30	

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