Chemosphere, Vol.15, Nos.9-12, pp 1265-1271, 1986 0045-6535/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

PYROLYSIS AND COMBUSTION OF AROCLOR 1254 CONTAMINATED DIELECTRIC FLUIDS

Gilbert Addis
Electric Power Research Institute

DIOXIN 85-5th International Symposium on Chlorinated Dioxins and Related Compounds

ABSTRACT Pyrolysis and combustion products were determined for several levels of PCB contamination in mineral oil and other dielectric fluids. Yields of PCDFs were roughly proportional to the quantity of PCB in the feed.

BACKGROUND

The electric utility industry as a major purchaser of PCBs in the past has been left with a legacy of PCB problems of two different dimensions. Although the reality of PCB as a problem is still being debated and evaluated, the industry is retrofilling or replacing its PCB equipment at a steady pace. A short time ago, there were about 40,000 (1) PCB transformers in utility hands with perhaps an equal or larger number owned by nonutility entities. Several well publicized PCB fires (2,3) in the United States have accelerated the effort toward removal of the askarel (generic term for PCB or PCB/tri-/tetrachlorobenzene) equipment.

Two options are open for elimination of PCBs in transformers. The first is retrofilling and the second is replacement of the transformer. Each method has its adherents and its detractors. Retrofilling, in the absence of further improvement of the technology, takes more than a year before a transformer can be reclassified as uncontaminated (in the United States, below 50 ppm PCB). During most of this time, PCB concentration in the transformer fluid is still above 500 ppm because even if one uses the best available technology, between 2 and 5% of the old liquid remains behind after draining a transformer as thoroughly as possible. It is estimated that this residual takes approximately 3 months to come to equilibrium with the replacement fluid. The dilution process must therefore be repeated several times before an appropriately low PCB level is reached. We understand that there is considerable research presently underway to speed up the removal of this trapped material; however, the work has not yet come to fruition.

Where physically possible, complete replacement of the transformer appears to be the easy way out. However, disposal of the transformer requires draining of the PCB followed by flushing with a solvent. The liquids must then be destroyed in a licensed incinerator while the transformer carcass must go to a certified landfill. Certified landfills in the USA are rapidly disappearing and it is also considered possible that these may become the next generation of problem cleanup sites.

A second area of concern is the roughly 2,000,000 (1) mineral oil transformers, which over the years have inadvertently become contaminated with PCBs at the 50 ppm level or higher. About 10% of these are contaminated above 500 ppm and must be treated as PCB transformers.

This pair of problems has fostered a need to learn more about the pyrolysis and combustion of PCB, both in its concentrated state, and at various levels of contamination in retrofill fluids, such as silicone and mineral oil. PCB is also of interest as a contaminant in tetrachloroethylene, because it is a potential retrofill fluid, although it is more likely to be used as a replacement fluid.

WORK PLAN

A project has been sponsored and partially funded by the Electric Power Research Institute (EPRI) for the New York State Department of Health to study pyrolysis and combustion

products of PCBs, both as a concentrated fluid and as a contaminant in mineral oil and several replacement fluids. In this project we define pyrolysis as the high-temperature decomposition of a fluid in an oxygen-depleted atmosphere. Combustion is defined as oxidation in the presence of an open flame and an excess of air. The work plan includes the investigation of Aroclor 1254, "neat," as well as at a 50, 500, and 5000 ppm impurity level in mineral oil, silicone and tetrachloroethylene. Since a mixture of tri- and tetrachlorobenzene is frequently found as diluent in askarels, these two compounds, both separately and as a blend, also are being investigated.

EQUIPMENT & PROCESS

Pyrolysis

Pyrolysis trials as described by Eadon (4) were conducted using a simple thermostatically controlled apparatus, capable of accommodating a 6-cm diameter metal block within its 9-cm-long heated region. In order to minimize hazards and disposal problems, yet permit sufficient product formation to facilitate detection of PCDDs and PCDFs, pyrolyses were performed on 100 µl samples. In an attempt to differentiate this work from other earlier and ongoing investigations, as well as to simulate more accurately certain catastrophic incidents, pyrolyses were conducted at atmospheric pressure. The necessity of containing the starting materials and nongaseous pyrolysis products in an open system led to the use of an 8 mm ID x 0.5 m glass tube, sealed at one end, and mounted vertically. The material to be pyrolyzed was deposited at the sealed end, then inserted into a tight-fitting hole in the preheated metal block in the heating apparatus. Typically, the liquid refluxed up the inner walls of the tube; the length of the tube and its comparatively large unheated volume kept the reflux level well below the open end in all experiments. To assure containment, the topmost 5 cm of the tube was chilled in dry ice and the end of the tube was connected to a charcoal trap. No visible material was trapped in the chilled region, and excellent mass balances were generally observed.

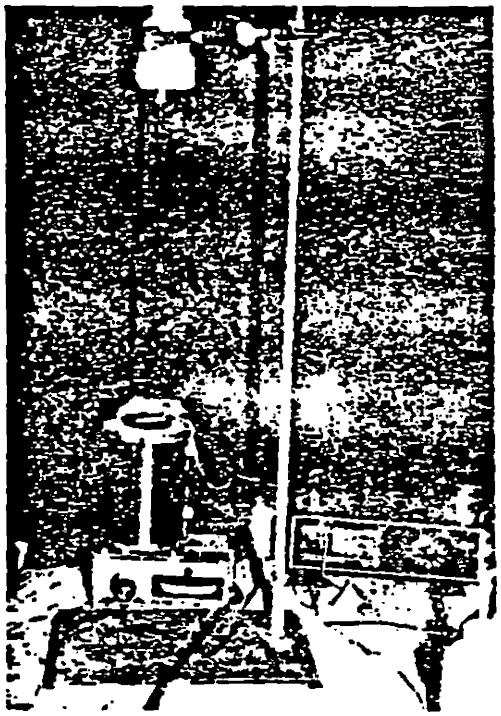

Figure 1: Pyrolysis Equipment

Combustion

The design of the combustion apparatus was also constrained by the necessity of assuring that all discharged gases pass through a trapping system capable of efficient removal of PCBs and any potentially toxic products. The combustion chamber consists of a 1 m quartz tube with a 22-mm ID. One end of the chamber accommodates a modified blast burner and inlet tube through which the end of a 1/16" x 24" (1.6 x 635 mm) syringe needle is introduced via airtight connections. The inlet tube and needle are mounted to allow sample introduction into the flame of the blast burner. Sample addition is accomplished using a 10-ml syringe mounted in a worm syringe drive. The combustion chamber is mounted in a furnace capable of maintaining temperatures of 100-1000°C in three independently controlled zones. The effluent of the combustion chamber is passed through a water filled impinger, then through an XAD-2 packed adsorbent tube which in turn is attached through an orifice to a vacuum line. XAD-2 has been shown here and elsewhere to be an efficient trapping agent for polychlorinated dibenzofurans (PCDFs) and dibenzo-p-dioxins (PCDDs).

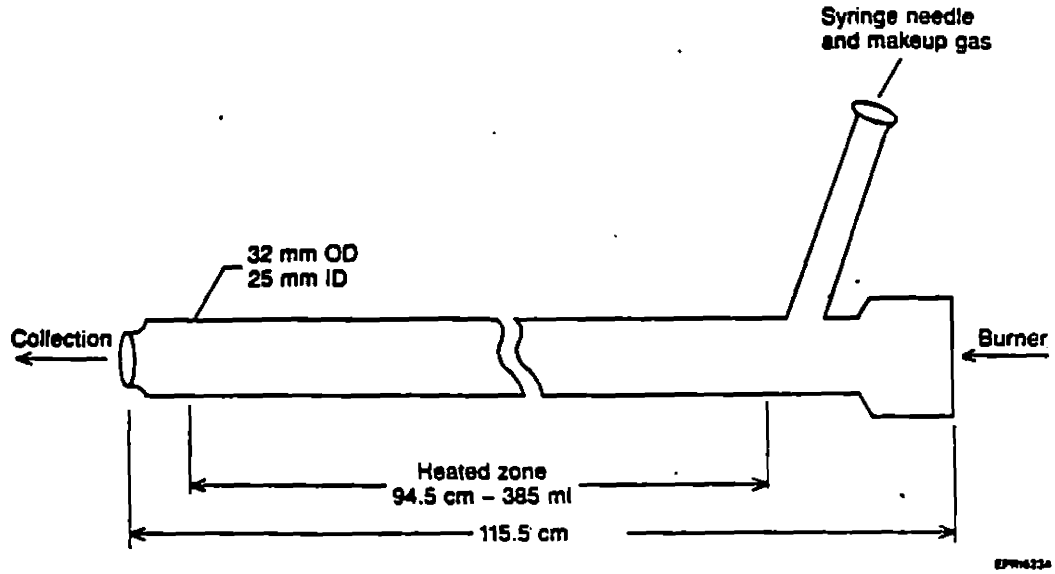

Figure 2: Combustion Tube

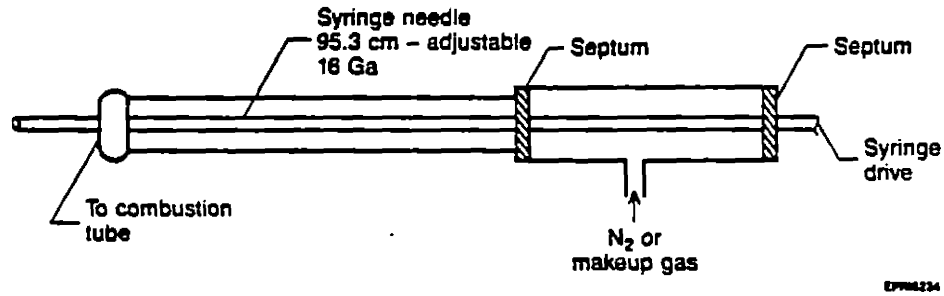

Figure 3: Feed Syringe

ANALYSIS

Because of the hazardous nature of the compounds to be prepared and to check out equipment expeditiously using rapid analytical techniques, the trials were approached stepwise. Initial runs in each case were made with unchlorinated biphenyl to determine the suitability of the equipment and to find a first approximation of proper operating conditions. These runs were followed by trials using individual PCB congeners known to form specific PCDF mixtures. It was anticipated that the relatively simple products formed could be analyzed by capillary GC/EC or GC/FID after chromatographic cleanup. This technique was successful, except in the pyrolysis of contaminated mineral oil. The mineral oil itself produced a complex mixture, and it was necessary, after appropriate up-front cleanup, to resort to the use of GC/MS from the start. Having thus optimized as far as possible operating conditions and analytical procedures, runs were finally made using Aroclor 1254 as the test fluid.

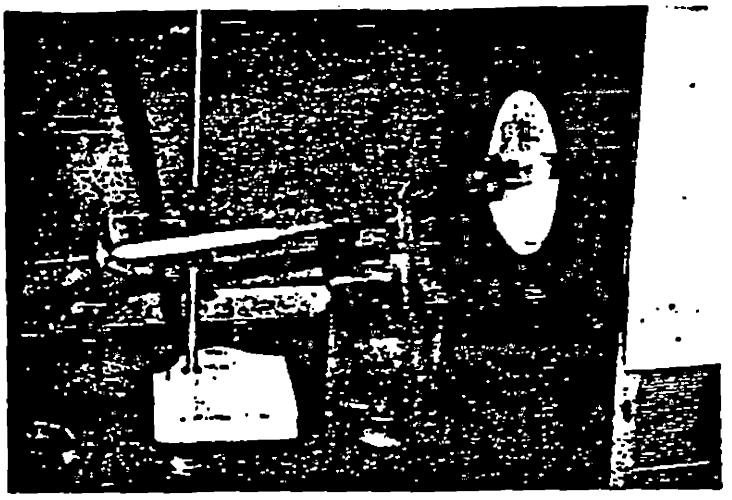

Figure 4: Combustion Product Trap

RESULTS

Pyrolysis of Aroclor 1254 in Mineral Oil, Silicone, and C_2Cl_4

Under the conditions chosen for this project, conversion of PCBs to PCDFs in the trial runs reached an approximate maximum around 550°C. Most of the subsequent runs with Aroclor 1254 were then made at this temperature setting. Where other temperatures were used, they have been noted in the text or tables. All runs were of 15 minutes duration.

To minimize run-to-run experimental variations found in the preliminary work, and to produce larger samples for analysis, a series of six runs was made at each set of conditions. The six runs of each set were always made during a single day and combined randomly (prior to cleanup) into two composites for analysis. Results are tabulated in Tables 1 and 2. Note

TABLE 1: PCDF Formed (ng)/Gram of "Mixture" pyrolyzed: Aroclor 1254 in Insulating Fluids

Sample	Description	2378[2] TCDF	Total TCDF	12378[2] PeCDF	Base Peak PeCDF	Total PeCDF	Base Peak HxCDF	Total HxCDF	Total HpCDF	OCDF
42582	100% Aroclor 1254	1,300	8,200	-	-	16,000	8,000	8,000	60	-
42583	100% Aroclor 1254	965	5,500	-	-	10,000	5,100	5,100	-	-
50854	5,000 ppm[1] in mineral oil	15.0	49.0	17.0	62.0	165	87.0	162	24.0	< 2
50855	5,000 ppm in mineral oil	11.8	33.0	17.2	55.0	171	60.0	205	14.0	0.23
50856	500 ppm in mineral oil	1.6	-	1.8	6.7	17.2	6.3	16.8	< 10	-
50857	500 ppm in mineral oil	1.1	3.1	1.9	5.8	18.2	6.8	18.1	2.2	-
50858	50 ppm in mineral oil	-	-	0.4	1.1	3.1	1.5	3.5	-	-
50859	50 ppm in mineral oil	-	-	0.9	1.7	3.4	1.3	-	-	-
45298	5,000 ppm[3,4] in silicone	9.9	107.0	4.5	-	70.0	2.2	6.9	0.15	-
44295	5,000 ppm[5] in tetrachloroethylene	1.2	2.9	4.6	-	28.0	5.5	12.5	0.9	-
42571	Native mix[6] in mineral oil									
	Added	9.3	-	17.2 (23478)	-	32.4 (234678)				56 (OCDD)
	Found	9.1	-	17.5	-	23.0			47	

(1) Each mineral oil sample represents a composite of three separate pyrolyses which were combined prior to analysis to minimize run-to-run variation. All pyrolyses at 550°C for 15 minutes.
(2) Includes coeluters on DB-5 column.
(3) 650°C.
(4) Chlorinated fluorenes(?) at 10x higher level.
(5) 600°C.
(6) Mineral oil spiked with PCDFs to test method.

TABLE 2: PCDF Formed (ng) per Gram of 'Aroclor 1254 Pyrolyzed in Insulating Fluid

Sample	Description	2378[2] TCDF	Total TCDF	12378[2] PeCDF	Base Peak PeCDF	Total PeCDF	Base Peak HxCDF	Total HxCDF	Total HeCDF	OCDF
42582	100% Aroclor 1254	1,300	8,200	-	-	16,000	8,000	8,000	60	-
42583	100% Aroclor 1254	965	5,500	-	-	10,000	5,100	5,100	-	-
50854	5,000 ppm[1] in mineral oil	3,000	9,000	3,400	12,400	33,000	17,400	32,400	4,800	64
50855	5,000 ppm in mineral oil	2,360	6,600	3,440	11,000	34,200	12,000	41,000	2,800	46
50856	500 ppm in mineral oil	3,200	-	3,600	13,400	34,400	12,600	33,600	-	-
50857	500 ppm in mineral oil	2,200	6,200	3,800	11,600	36,400	13,600	36,200	4,400	-
50858	50 ppm in mineral oil	-	-	8,000	22,000	62,000	30,000	70,000	-	-
50859	50 ppm in mineral oil	-	-	18,000	34,000	68,000	26,000	-	-	-
45298	5,000 ppm[3] in silicone	1,980	21,400	900	-	14,000	440	1,380	30	-
44295	5,000 ppm[4] in tetrachloroethylene	240	580	960	-	5,600	1,100	2,500	180	-

(1) Each mineral oil sample represents a composite of three separate pyrolyses. These were combined prior to analysis to minimize run-to-run variation. All pyrolyses at 550°C for 15 minutes.
(2) Includes coeluters on DB-5 column.
(3) 650°C.
(4) 600°C.

that Tables 1 and 2 report the same data but expressed in different form. Table 1 shows ng PCDF formed per gram of total mixture pyrolyzed, while Table 2 shows ng PCDF per gram of Aroclor 1254.

It may be seen that conversions of PCBs to PCDFs are substantially identical for all congeners and chlorination groups measured for 5000 and 500 ppm, and are less than an order of magnitude different for 100% PCB. Conversion appears to increase slightly at 50 ppm, but this may be the result of measuring error due to analytical difficulties at this level.

Pyrolyses in silicone and tetrachloroethylene show conversion efficiencies qualitatively similar to mineral oil for tetra- and penta-CDF, but are apparently dropping off for higher chlorination levels. Added work must be done to confirm these levels.

Analysis of the pyrolysis products of PCBs in both silicone and tetrachloroethylene yielded qualitative indications of several products related to PCDF/PCDD. In silicone, compounds tentatively identified as chlorinated fluorenes were found in the MS scans. Also, in pyrolyzing 1,2,3,4,5 pentachlorobiphenyl in silicone, a series of compounds (which may be methylated chlorinated fluorene) was found. Chlorine atoms plus methyl-groups total four in each case (Figure 5).

Pyrolysis of 2-chlorobiphenyl in silicone has fluorene as a major product. This has been compared with an authentic standard. Other compounds listed above as products in the silicone and discussed in the tetrachloroethylene work below will be compared with authentic standards before their presence is considered confirmed.

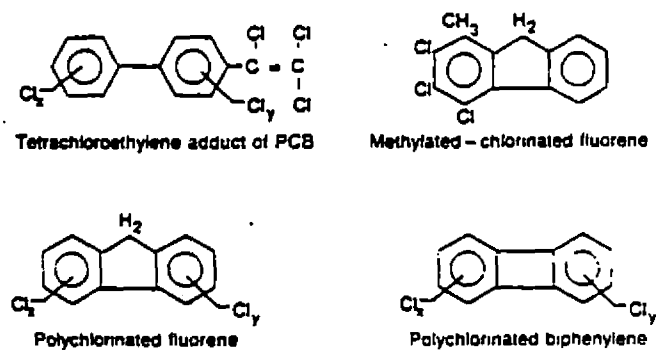

Figure 5: Compounds Related to PCDF/PCDD

In the combustion and pyrolysis of 1254 in tetrachloroethylene, preliminary work shows that some different tetra- and penta-CDFs are being formed, compared to "neat" 1254 or 1254 in mineral oils. Chlorinated fluorene may also be forming. In addition, a compound that may be a reaction product of PCB and tetrachloroethylene is possible.

Combustion of Aroclor 1254 in Mineral Oil, Silicone and C_2Cl_4

Conversion for the isomer groups studied (Table 3) was near optimum for a combustion wall temperature of 550°C and a 3-second residence time. With feed solutions of mineral oil containing Aroclor 1254 at 50, 500, and 5,000 ppm, tri-, tetra-, and penta-CDF conversion in ng/g PCB fed fell within a narrow range for each of the isomer groups. Under all conditions, hexa- and hepta-CDF formation was not detectable.

Combustion trials with PCBs in silicone were not completed successfully. Large quantities of SiO_2 formed. The finely divided SiO_2 tended to plug the equipment, particularly the feed needle and the sample collection train.

In C_2Cl_4 solution, combustion yields were similar to those found with mineral oil for the $-Cl_3$ isomers. There were substantially greater yields for the more highly chlorinated isomers, reflecting chlorination of lower chlorinated CDFs. Combustion in C_2Cl_4 under oxygen depletion provides a substantial yield of biphenylenes.

TABLE 3: Combustion of Aroclor 1254 in Insulating Fluids at 550°C - 3 Seconds

Solvent	1254 in sol. Combusted ug/ml	PCB's Destroyed %	% PCDFs Formed(1) Cl_3	Cl_4	Cl_5	Cl_6	Cl_7
Mineral Oil	5000	82-88	0.72	0.58	0.17	-(2)	-(2)
Mineral Oil	500	87-92	0.4	0.33	0.084	-(2)	-(2)
Mineral Oil	50	88-90	0.3	0.3	0.056	-(2)	-(2)
C_2Cl_4	5000	68	0.44	1.50	1.35	0.33	0.50
C_2Cl_4	500	92	0.24	0.7	0.66	0.23	0.70
C_2Cl_4	50	72	0.44	1.32	1.0	0.38	0.16
Silicone(3)	-	-	-	-	-	-	-

(1) Based on PCB in feed.
(2) None detected.
(3) Runs unsuccessful. Equipment plugged with SiO_2.

OTHER WORK IN PROGRESS

Pyrolysis and combustion of tri- and tetrachlorobenzene are underway in the laboratory. These results will be of value in assessing the potential fire products from askarels where the PCB is diluted with these solvents.

Preparation of certain synthetic chemicals such as substituted fluorenes is being undertaken. These will be used to confirm the structure of several of the unknowns that appeared during the GC/MS analysis.

DISCUSSION

Part of the original impetus in this project was to determine whether formation of partial oxidation products of PCB was linear with increasing dilution in a solvent. This question appears to be answered. Within the constraints of variations in analytical conditions and recoveries during cleanup and analyses of extremely small quantities of material, the linearity should be considered good; in most cases, there was no more than a factor of 10 variation in a range of concentrations from 50 ppm to 100% of the askarel tested. Improvements in the pyrolysis and combustion schemes during the course of the project provided this degree of resolution. No doubt, this can be improved upon with further sophistication in the work.

The results of these laboratory trials are found to be significantly different from those of other workers in the field (5-9). This fact brings with it a word of caution in applying any of these results to real-world PCB fires except for use as guiding principles because each real PCB fire, under completely random conditions, is different from all others. Even

within a given fire, there will be an infinite range of competing reactions. It can be assumed that only a small portion of the combustion process has optimum conditions, and that the combustion process varies with time, leading to the partial destruction of the various combustion by-products. Thus, all of the research being done must be considered as setting a boundary or worst-case condition that gives a general direction to the investigation of the real world.

A number of new avenues for exploration have been seen here and in the work of others. Among the more significant ones are the finding of relatively large quantities of other chlorinated polycyclic aromatic compounds (PCAs). A second is the need for a more rapid method of analysis. A bioassay designated the Flat-Cell Assay (10), based on a change in in vitro growth and morphology of a line of skin cells has been shown to be very sensitive and relatively specific for the more toxic of the PCDF and PCDD compounds. The biological mechanism of this effect is considered to be related to the development of chloracne in humans after 2,3,7,8-TCDF exposure and is thus, a relevant end point. This method is already applicable to certain products of combustion. It is being modified to detect and assay these products in the presence of solvents such as mineral oil, which currently interfere with the test. Calibration against a range of chlorinated PCAs would follow.

ACKNOWLEDGMENTS

The help of K. Aldous, R. Briggs, G. Eadon, D. Hilker, K. Kidd, A. Narang, R. Narang, P. O'Keefe, and R. Smith are gratefully acknowledged.

REFERENCES

1. RPC. Volume III - Report of the Study of PCBs in Equipment Owned by the Electric Utility Industry. Prepared for the Edison Electric Institute, Washington, D.C., February 1982.

2. N. C. Kim and G. Eadon. The Binghamton State Office Building. Workshop Proceedings: PCB By-product Formation, EPRI CS/EL-4104, July 1985, p. 5-1.

3. R. L. Wade. Utilization of Quantitative Risk Assessment Techniques in the Development of Decontamination Standards (A Case Study - San Francisco, California). Ibid, p. 5-16.

4. G. Eadon. Pyrolysis and Combustion of Mineral Oil, Tetrachloroethylene and Silicone Oil Mixtures Containing Aroclor 1254. Ibid., p. 3-24.

5. S. E. Swanson, M. D. Erickson, and L. Moody. Products of Thermal Degradation of Dielectric Fluids. Prepared for the U.S. Environmental Protection Agency, Washington, DC. Interim Report No. 2, May 1985.

6. H. R. Buser, H-P. Bosshardt, and C. Rappe. Formation of Polychlorinated Dibenzofurans (PCDFs) from the Pyrolysis of PCBs. Chemosphere 7(1), 1978, pp. 109-119.

7. H. R. Buser and C. Rappe. Formation of Polychlorinated Dibenzofurans (PCDFs) from the Pyrolysis of Individual Isomers. Chemosphere 8(3), 1979, pp. 157-174.

8. B. Dellinger, W. Rubey, D. L. Hall, and S. L. Mazer. Laborary Investigation of the High-Temperature Formation and Destruction of PCDFs. Workshop Proceedings: PCB By-product Formation, EPRI CS/EL-4104, July 1985, p. 3-17.

9. C. Rappe, S. Marklund, and L-O. Kjeller. Formation of PCDFs from PCBs. Ibid., p. 3-28.

10. J. F. Gierthy and D. Crane. In Vitro Bioassy for Dioxin-Like Activity Based on Alterations in Epithelial Cell Proliferation and Morphology. Fundamentals in Applied Toxicology, Vol. V, 1975, in press.