

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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SUBJECT: Status Report* 8EHQ-1178-0209
(Supplement)

Approved _____

FROM: Frank D. Kover
Assessment Division, OTE/OTS

Revision _____
Needed _____

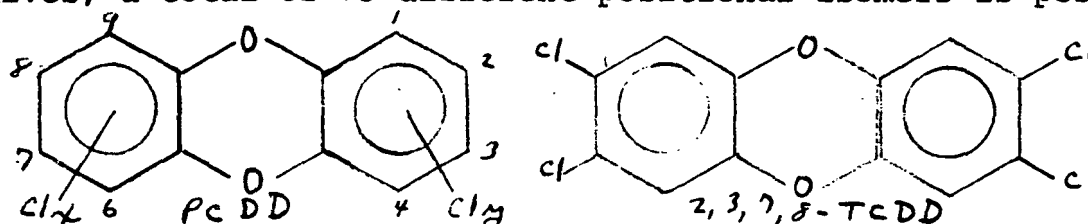
TO: Joseph J. Merenda, Director
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Submission Description

The submission was made as a followup to Dow Chemical Company's two earlier submissions on the detection of chlorinated dioxins and other chlorinated organics in various environmental samples. In a press release (attached), Dow concluded that "its research ... has verified the following sources for chlorinated dioxins: refuse incinerators, fossil-fueled powerhouses, gasoline and diesel powered automobiles and trucks, fireplaces, charcoal grills and cigarettes." On the basis of this work, Dow concluded that "dioxins occur everywhere as a result of normal combustion processes." The submission consists of the press release and related material, a report presenting Dow's data and conclusions, and several appendices describing sampling and analytical methodologies.

Background

The polychlorinated dibenzo-p-dioxins (PCDDs) are a series of tricyclic aromatic compounds which exhibit similar chemical and physical properties. The basic structure of PCDDs (as shown below) has eight possible points of chlorine substitution. From the monochloro to the octachloro derivatives, a total of 75 different positional isomers is possible.



*NOTE: This status report is the result of a preliminary staff evaluation of information submitted to EPA. Statements made herein are not to be regarded as expressing final Agency policy or intent with respect to this particular chemical. Any review of the status report should take into consideration the fact that it may be based on incomplete

tion.

The most extensively studied isomer of the PCDDs is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), one of the most potent toxicants presently known. The toxic effects induced by other TCDD isomers are less well characterized; however, they appear to exhibit a lesser degree of toxicity (both quantitatively and qualitatively) than 2,3,7,8-TCDD. For these reasons, the PCDD isomer attracting the greatest amount of Agency interest and activity is the 2,3,7,8-TCDD.

Submission Evaluation (An overall evaluation of the submitted information will be presented in this section of the status report; a detailed technical evaluation of the submission can be found in the attached appendix.)

The information contained in the present submission was received as a followup to the Dow Chemical Company's earlier submissions of June 28, 1978 (8EHQ-0678-0209) and October 11, 1978 (8EHQ-1078-0209 [Followup]) which concerned the presence of chlorinated dioxins in Tittabawassee River fish collected near Dow's Midland, MI chemical plant. A detailed description and evaluation of the June, 1978 submission can be found in the status report prepared for that submission. The following listing summarizes the most important points from that initial Dow submission.

a) Tetrachloro dibenzo-p-dioxins (TCDDs, isomers not identified) appear to be widespread contaminants of the Tittabawassee and Saginaw Rivers (and possibly Saginaw Bay) downstream from Midland. Octachloro dibenzo-p-dioxin (OCDD) also appears to be widely distributed downstream of Dow. TCDD was not detected in 3 fish taken upstream of the Dow Midland facility, although OCDD was apparently detected in one of these fish.

b) Five of six caged rainbow trout held in a mixture of Dow's tertiary waste treatment effluent under flowing conditions for 7 days accumulated traces of TCDD (ppt).

c) Caged rainbow trout held in flowing waters approximately six miles downstream from Dow's plant accumulated detectable amounts (ppt) of TCDD (whole fish analysis) after 30 days of exposure. This indicates downstream movement of TCDD.

Based on the above, it appeared that Dow's discharge represented the major, if not the only, source of the chlorinated dioxin contamination found in the Tittabawassee and Saginaw Rivers and Saginaw Bay in Michigan.

The latest submission represents the output of a Task Force established by Dow's Michigan Division "to identify the

potential sources of the chlorinated dioxins" found in the Tittabawassee River. This report advances as "strongly supported" a number of conclusions that, on careful evaluation, have no documented support in the information submitted by Dow. A detailed evaluation of Dow's report is provided in the attached appendix; the main points resulting from the Agency's evaluation have been condensed as follows:

a) No information, other than purely circumstantial evidence, has been submitted by Dow to support the premise that polychlorinated dibenzo-p-dioxins (PCDDs) and especially the TCDDs are typical by-products of combustion. Other investigators have demonstrated under laboratory conditions that PCDDs can be formed during the pyrolysis of polychlorophenates or polychlorophenoxy-containing materials. However, there is no experimental evidence (either submitted by Dow or present in the literature) indicating that combustion in the absence of PCDD precursors normally results in PCDD synthesis.

b) Much of the analytical work reported by Dow in this submission used methods that have "not always been validated and not yet corroborated by other scientists." Because of this, little or no analytical significance can be derived from the results reported by Dow. In order to derive significant and valid analytical meaning and/or conclusions from the results of part per billion (ppb) and part per trillion (ppt) analysis for PCDDs, the results must be accompanied by (1) appropriate quality control results and (2) a complete description of the criteria used to identify and confirm the presence of PCDD residues.

c) Many of the PCDD residue values relied on by Dow when formulating its conclusions as to the "ubiquity" of PCDDs were identical or approximately equal to the analytical method's level of detection. Such numbers have uncertain analytical significance especially in situations when non-validated analytical methods are employed.

d) Dow claims (p.21 of its report) that the results of its analysis of soil and dust samples "strongly support the conclusion that chlorinated dioxins are produced in incinerators and fossil fueled powerhouses as a consequence of combustion." In point of fact, the results presented by Dow offer no scientific documentation (other than weakly circumstantial evidence) relating its observations on PCDD contamination of soil and dust to the synthesis of PCDDs as a by-product of incineration or power generation. There is some circumstantial evidence that the hexachloro dibenzo-p-dioxins (HxCDDs), heptachloro dibenzo-p-dioxins (HpCDDs), and octachloro dibenzo-p-dioxins (OCDDs) identified in the soil samples from the urban and the metropolitan areas may be

associated with the operation of a powerplant and an incinerator, respectively. This, however, does not demonstrate that the presence of these substances results from their synthesis as a normal combustion by-product. EPA's evaluation of these data indicates that the following conclusions, contrasting Dow's claims, can be supported:

- (1) Midland, MI, and especially the area around the Dow plant, exhibits the greatest evidence for gross PCDD contamination among the various locations sampled. This is true both in terms of the proportion of samples in which PCDDs were detected and the degree of contamination evident in individual samples. In the latter case, the levels of PCDDs found in Midland are 2-4 orders of magnitude greater than those reported at other locations. The fact that much higher levels of PCDDs were found in soil and dust around the Dow chemical plant as compared to urban, metropolitan, and rural areas suggests that polychlorophenol production or some other activity at the Dow plant may be the source of the observed PCDD contamination.
- (2) To the extent that TCDDs, especially 2,3,7,8-TCDD, are the PCDDs of greatest Agency concern, the levels of TCDDs identified in Midland soil and dust samples indicate that this area represents a definite TCDD "hot spot." In comparison, there are very few instances where TCDDs were reported at other sites.

e) In part V of its report, Dow cites several European authors who have reported the presence of PCDDs in fly ash from municipal incinerators and in fly ash from an industrial heating facility. Dow notes (p.22 of its report) that one of the authors postulates that the PCDDs are formed as a result of the thermal condensation of chlorophenols, although mention is made in the article that a thermal synthesis reaction involving inorganic chloride and organic material "was considered to be entirely possible." Dow, however, fails to discuss several other studies which indicate that the pattern of PCDD isomers identified in fly ash (from incinerators and heating facilities) was almost identical to that found when a mixture of polychlorophenates was pyrolyzed under controlled conditions. One of these papers goes on to state that available evidence indicates that commercial chlorophenols cannot be excluded as the precursor to PCDDs in fly ash. The information submitted by Dow appears to offer some degree of support for this statement. In general,

fly ash from Dow's chemical waste incinerators show higher levels of PCDDs than does fly ash from its fossil fueled powerhouse. The difference may be related to the nature of the material being burned in each operation. One possible explanation is that the chemical wastes being burned in Dow's incinerators already contain PCDDs or PCDD precursors (polychlorophenoxy material) (i.e., wastes from Dow's chlorophenol production processes) and that these substances are the sources of the observed PCDDs.

f) Dow claims (on p.30 of its report) that "wipe testing and air monitoring data are strong evidence that (Dow) manufacturing plants do not emit levels of chlorinated dioxins sufficient to explain the finding of these compounds in the soil samples reported earlier." No scientific basis for this conclusion is provided in the data presented by Dow.

g) Dow reports (pp.33-35) trace quantities of PCDDs in scrapings taken from the inside of car and diesel truck mufflers. Does this necessarily mean, as Dow advances, that PCDDs are formed during combustion in the engine? If the car or truck was driven primarily in an industrial area or near sources that might be considered contaminated with PCDDs or PCDD precursors, airborne particulates containing these substances could be drawn into the air intake of the engine. Any PCDDs not decomposed in passage through the engine might then be deposited in the muffler. The statement (p.35) that PCDDs "are in particulate emissions from internal combustion engines" cannot be supported because vehicles' exhaust gases were not analyzed. The only conclusions that can be supported by the observations presented in this section are that (1) PCDDs have been identified in some muffler scrapings, however, (2) the source of the PCDDs is unknown.

h) Dow claims (pp.35-36) that soot collected from 2 fireplaces contains PCDDs; however, Dow offers no documentation of its claim that none of the wood burned in the fireplace "had been treated with any wood preservatives." Without such evidence, these results can not support Dow's thesis concerning the synthesis of PCDDs as a normal combustion by-product.

i) The geographic locations of the homes where fireplace soot and home electrostatic precipitator particulates were sampled may be important. This is of interest because the dust collected in the electrostatic precipitator (electronic air cleaner) had a higher concentration of PCDDs than the soot samples from the fireplaces (acknowledged sources of typical combustion by-products). A home electrostatic precipitator functions to a certain extent as a "high volume

air sampler." In the case cited by Dow, the electrostatic precipitator was operated over a period of 6 spring and summer months. Thus, the precipitator particulates analyzed by Dow represent airborne material collected over a 6 month period which does not coincide with the months generally associated with heavy space heating-related combustion or home fireplace usage. Therefore, the PCDD values for the home electrostatic precipitator-collected particulates may, to a certain extent, represent the results of incidental ambient air "sampling" conducted at the site of the house.

j) Dow claims to have verified charcoal grills and cigarettes as sources of PCDDs. No evidence is presented to indicate that charcoal grills per se produce PCDDs, although an attempt is made to show that steaks cooked on charcoal grills contain newly synthesized PCDDs. The reported PCDD residue values, however, are identical or approximately equal to the analytical method's level of detection such that the reported values have limited analytical significance. In its cigarette assays, Dow reports finding picogram (10-12g) concentrations of PCDDs per cigarette (in trapped cigarette smoke particulates). However, several questions remain concerning the significance of this assay (e.g., results of unburned cigarette [control] analysis; geographic location of the conducted studies, etc.).

k) Dow reports that it identified polychlorinated dibenzofurans (PCDFs) in a number of the analyzed environmental samples. This finding should be investigated in more detail in light of the high toxicity of several PCDF isomers.

Overview

In summary, Dow's efforts "to identify the potential sources of the chlorinated dioxins" found in the Tittabawassee River indicate that it is possible that some portion, likely quite small, of the PCDDs identified in Tittabawassee River fish may have originally been formed and released to the environment as a combustion by-product rather than as a direct water effluent release as suggested by the information in the original submission. An important consideration, however, is that (with the exception of some OCDD) PCDDs were not detected in fish collected upstream from Dow's Midland, MI plant. Therefore, the available information (especially point (d) above) continues to suggest that the Dow Chemical Company's Midland, MI plant represents the major, if not the only, source of the TCDD contamination found in the Tittabawassee and Saginaw Rivers and Saginaw Bay in Michigan.

Current Production and Use

polychlorinated dibenzo-p-dioxins are impurities that may be formed as unwanted contaminants under certain conditions during the production of chlorophenols. For example, 2,3,7,8-TCDD has been identified as a contaminant produced during the manufacture of 2,4,5,-trichlorophenol (2,4,5,-TCP) by current production methods. Because of this, 2,4,5-trichlorophenoxy acetic acid (2,4,5,-T), a registered pesticide derived from 2,4,5-TCP, is also potentially contaminated with 2,3,7,8-TCDD from the TCP intermediate.

Comments/Recommendations

a) This submission and status report should be transmitted to OPP, SAD, CAD, PID, LTAT (AD), OE, OWWM, OGC, OAQPS, ORD, OMSAPC, Region V, Michigan Department of Natural Resources, CPSC, USDA, FDA, OSHA, NIEHS, and NIOSH.

b) The submitter should be asked to provide the clarifications outlined in the status report and appendix. The submitter should be asked to prepare a written response to the questions; in addition, a meeting between Dow and EPA is suggested to provide a full discussion of the scientific aspects of the submission.

c) The development of a Sources/Effects Report (Phase I document) on PCDDs is recommended. This activity should also include consideration of the polychlorinated dibenzofurans (PCDFs).

d) Controlled combustion studies are needed to evaluate Dow's hypothesis that PCDD synthesis occurs in most combustion processes as well as to indicate the scope of any future monitoring effort.

e) SAD (OPII) should initiate consideration of an appropriate monitoring program to determine the degree and extent of PCDD contamination in Midland, MI, as well as other current or historical sites of possible PCDD contamination (e.g., chlorophenol manufacturing, processing, or disposal sites). Environmental monitoring for PCDFs should also be considered. These efforts should be closely coordinated with ongoing or contemplated activities in other EPA offices (e.g., OPP, IERL/Cinn., OWWM, OAQPS, Region V, etc.).

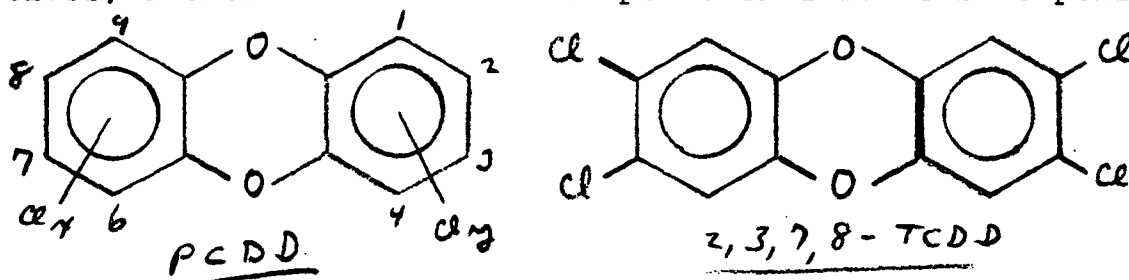
f) OTS efforts to assess the sources and extent of PCDD and PCDF contamination as well as possible control needs should be closely coordinated with the efforts of other EPA offices and federal agencies by PID (OPII), possibly through intra-agency work groups and the Regulatory Development Work Group of IRLG, respectively. All of these efforts should be

coordinated with the designated Headquarters Coordinator for all dioxin-related activities.

g) An 8(d) rule to collect health and safety studies on PCDDs and PCDFs should be considered.

APPENDIX (8EHQ-1178-0209) (Supplement)

The polychlorinated dibenzo-p-dioxins (PCDDs) are a series of tricyclic aromatic compounds which exhibit similar chemical and physical properties. The basic structure of PCDDs (as shown below) has eight possible points of chlorine substitution. From the monochloro to the octachloro derivatives, a total of 75 different positional isomers is possible.



The most extensively studied isomer of the PCDDs is 2,3,7,8-tetrachloro dibenzo-p-dioxin (2,3,7,8-TCDD), one of the most potent toxins presently known. The toxic effects induced by other TCDD isomers are less well characterized; however, they appear to exhibit a lesser degree of toxicity (both quantitatively and qualitatively) than 2,3,7,8-TCDD. For these reasons, the PCDD isomer attracting the greatest amount of Agency interest and activity is 2,3,7,8-TCDD.

Submission Evaluation (The following sections refer to subheadings in Dow's report.)

I. Building Blocks for Chlorinated Dioxins

The report's conclusions state that "conditions in a flame favor the occurrence of every conceivable type of chemical reaction" (p. 5), so that PCDDs may be formed in trace quantities wherever combustion occurs. The formation of polycyclic organic compounds during combustion is not a new finding. During coal combustion, the initial pyrolytic reaction can result in fragmentation, ring closures, condensation, and aromatization. The main products tend to be polynuclear ring compounds, occasionally containing nitrogen, oxygen, or sulfur, and simple compounds like H_2 , H_2S , NH_3 , CH_4 , CO_2 , etc.

Dow opens the discussion in Part I by establishing that inorganic chloride, gaseous products (SO_2 , NO_x , CO , etc.), metals (V, Fe, Ni, etc.), and a wide variety of aliphatic and aromatic hydrocarbons are present during refuse- or fossil-fueled combustion reactions. The submitter then postulates that "at ultratrace levels, parts per billion, the number of compounds which may possibly form on particulate matter approaches or exceeds that presently known to

man." While this statement may be true, it is never linked experimentally in Dow's submission to a demonstration that PCDDs will typically form during combustion reactions. Several authors (e.g., Buser et al. [Chemosphere, 7(2), 165, 1978]; Rappe et al. [Chemosphere, 7(3), 269, 1978], Stehl and Lamparski [Science, 196, 1008, 1977]; Ahling et al. [Chemosphere, 6(8), 461, 1977]; Buser and Rappe [Chemosphere, 7(2), 199, 1978]), on the other hand, have demonstrated in a laboratory setting that PCDDs can be formed during the pyrolysis of polychlorophenates (sodium salt) or polychlorophenoxy-containing materials (e.g., polychlorophenate-impregnated leaves, wood shavings, plywood, or waste oil). Rappe et al. (1978) stated that the concentration of PCDDs in the combusted samples represented a sizeable increase over the levels detected in the original polychlorophenate samples.

IV. Airborne Particulate Matter

Soil samples were collected from "13 different locations inside and outside (Dow's) Midland Plant" and analyzed for tetrachlorodibenzo-p-dioxin (TCDD), hexachlorodibenzo-p-dioxin (HxCDD), heptachlorodibenzo-p-dioxin (HpCDD), and octachlorodibenzo-p-dioxin (OCDD). Dow does not further identify the sites with respect to individual locations or distances from the plant or specific plant operations. The analytical results are presented in Table 1. Dow notes that the analytical method was not validated and, therefore, the results are qualitative only.

Table 1. PCDDs in 13 Midland Soil Samples^a
(taken from p.17 of Dow's report)

<u>TCDD</u>	<u>HxCDD</u>	<u>HpCDD</u>	<u>OCDD</u>
4/13	9/13	13/13	13/13

a) Collected from "inside and outside the Midland plant."

A second set of soil samples was collected in the same manner; 5 of these, "including the ones corresponding to those that previously gave positive TCDD results, were analyzed by a newly developed and validated analytical method." Dow goes on to state that this new method permitted the separation of the 2,3,7,8-TCDD from "almost all of its other 21 isomers." These results are summarized in Table 2. The specific sample selection sites represented by Table 2 should be clearly identified as to their placement with respect to the Dow plant.

Dow's claim at this juncture and at subsequent points in the submission that its analytical method permitted separation of TCDD isomers is not adequately supported by any of the figures shown in the submission or the attached appendices. Dow should be asked to provide a detailed description of the methods of extraction and analysis as well as the criteria utilized in the identification of TCDD isomers; e.g., (a) GC/HRMS (gas chromatography/high resolution mass spectroscopy) detection method, (b) elemental composition of molecular masses m/e 320, m/e 322, and m/e 324, (c) molecular ion Cl ratio, 0.8/1.0, (d) GC/HRMS retention time of test samples and confirmatory samples fortified with specific TCDD isomers, (e) m - COCl loss, m/e 257, (f) use of and techniques for GC/HRMS double ion monitoring, (g) a description of the capillary column GC resolution measured in theoretical and/or effective plates, and (h) a description of the degree of GC resolution of specific TCDD isomers (Dow's tables should be more specific and indicate identified isomers and their contribution to the total value shown). In addition, Dow should clarify if the quantified values of TCDD isomers shown in its report are based on the response of specific isomers or if the values are normalized to the response of 2,3,7,8-TCDD. Finally, there is some question that the harsh (acid) conditions used for sample extractions may have resulted in PCDD formation from precursors or by dechlorination of higher PCDD isomers. Dow should be asked to confirm its findings by providing comparative results from neutral extraction procedures, if available.

The information needs outlined in the preceding paragraph concerning TCDD isomer values also apply in all cases to HxCDD, HpCDD, and OCDD isomer values reported in the Dow submission. Any available data on the presence of pentachloro dibenzo-p-dioxin isomers in environmental samples should also be requested.

Dow states on p.2 of its report that the "analytical methodology is so very new that it has not always been validated and not yet corroborated by other scientists." Limited analytical significance can be derived from results generated using nonvalidated procedures. In order to derive significant and valid analytical meaning and/or conclusions from the results of part per billion (ppb) and part per trillion (ppt) analysis for PCDDs, the results must be accompanied by (1) appropriate quality control results and (2) a complete description of the criteria utilized to identify and confirm the presence of PCDD residues. Furthermore, in cases where the reported PCDD residue levels and the limit of detection are of identical or approximately equal value, such numbers have uncertain analytical significance especially in situations when nonvalidated analytical methods are employed. PCDD values which are not greater than ten times (10X) the noise

have been identified with an asterisk (*) in this status report. (When analyzing for trace levels of PCDDs, a signal to noise ratio of 2.5:1 is considered to be the level of detection; values below this ratio are reported as non-detected [ND]. When a sufficient amount of the sample and time are available to the analytical chemist, samples having a signal to noise ratio between 2.5:1 and 10:1 should be rerun a second time to verify the result. If the second analysis falls between 2.5:1 and 10:1, the two separate results and the average should be reported. Values resulting from a single analysis are not contested if the signal to noise ratio is at least 10:1 and the ratio of peak heights m/e 322:m/e 320 is in the proper isotopic proportion.)

Table 2. PCDDs in 5 Midland Soil Samples^a (ppb)
(taken from Dow's Table III)

Sample	TCDD isomers other than 2,3,7,8-TCDD	2,3,7,8-TCDD ^b	HxCDD	HpCDD	OCDD
1	17	16	280	3200	20500
2	9	6	40	470	2500
3	18	100	120	650	6300
4	13	16	280	240	11700
5	0.8	0.3	7	70	490

a) Taken from "inside and outside the Midland plant."

b) Values are reportedly based on the "separation of the 2,3,7,8-TCDD from almost all of its 21 other isomers" (see discussion in the text).

Next, dust samples were collected at various locations in a "Dow research building" and subsequently extracted and analyzed using a method reportedly separating "the 2,3,7,8-TCDD from all but about 11 of its isomers". (As discussed earlier, this statement should be supported by documentation indicating that eleven TCDD isomers plus the 2,3,7,8-TCDD equals one fraction. Dow's statement to that effect is not sufficient.) The results of this work are presented in Table 3. Dow should be asked to clearly describe what it means by the term "air intake." Does the PCDD contamination of this air intake dust result from the handling of "inside" or "outside" air?

Table 3. Dust Samples from a Dow Research Building (ppb)
(taken from Dow's Table IV)

<u>Sample</u>	TCDD isomers other than <u>2,3,7,8-TCDD</u>		<u>HxCDD</u>	<u>HpCDD</u>	<u>OCDD</u>
	<u>2,3,7,8-TCDD</u>	<u>2,3,7,8-TCDD^a</u>			
1st floor	0.5	1.0	18*	240*	960
1st floor	2.3	2.3	28	520	3800
2nd floor	1.3	2.6	11*	140	650
2nd floor	-	0.7	9*	250	2600
2nd floor (2 weeks after cleaning)	1.5	1.2	20*	320	2000
air intake	2.3	2.3	35*	1200	7500

a) Values are reportedly based on the "separation of the 2,3,7,8-TCDD from all but about eleven of its isomers" (see discussion in the text).

*Value is close to the detection limit for the analytical method employed (signal is less than 10X noise).

Additional dust samples from Midland and an unspecified "metropolitan area" were collected and analyzed for control purposes. These samples did not satisfy this need, therefore, dust and soil samples were collected from additional, vaguely characterized ("rural," "urban," and "major metro") sites. Table 4 represents a composite presentation of these results.

Dow concludes (p.21) that these data (Tables 1-4) "strongly support the conclusion that chlorinated dioxins are produced in incinerators and fossil fueled powerhouses as a consequence of combustion. These results indicate that chlorinated dioxins are more widespread than previously anticipated and are perhaps ubiquitous". In point of fact, the results presented offer no scientific documentation (other than weakly circumstantial evidence) relating Dow's observations on PCDD contamination of soil and dust to the synthesis of PCDDs as a by-product of incineration or power generation. There is some circumstantial evidence that the HxCDD, HpCDD, and OCDD identified in the soil samples from the urban and the metropolitan areas may be associated with the operation of a powerplant and an incinerator, respectively. This, however, does not demonstrate that the presence of these substances results from their synthesis as a normal combustion by-product. Table 5 presents a comparison of the

total number of PCDD-positive samples collected from the Midland, MI area with those collected from other locations. From Table 5, the following observations, contrasting Dow's claims, can be supported:

- (a) Midland, MI, and especially the area around the Dow plant, exhibits the greatest evidence for gross PCDD contamination among the various locations sampled. This is true both in terms of the proportion of samples in which PCDDs were detected and the degree of contamination evident in individual samples. In the latter case, the levels of PCDDs found in Midland are 2-4 orders of magnitude greater than those reported at other locations. The fact that much higher levels of PCDDs were found in the soil and dust around the Dow chemical plant as compared to urban, metropolitan, and rural areas suggests that polychlorophenol production or some other activity (spills, plant emissions, combustion of chemical wastes, etc.) at the Dow plant may be the source of the observed PCDD contamination.
- (b) To the extent that TCDDs, especially 2,3,7,8-TCDD, are the PCDDs of greatest Agency concern, the levels of TCDDs identified in Midland soil and dust samples indicate that this area represents a definite TCDD "hot spot." In comparison, there are very few instances where TCDDs were reported at other sites.

V. Incineration

In its introduction to this section, Dow cites several European authors who have reported the presence of PCDDs in fly ash and flue gas from municipal incinerators (Olie et al., Chemosphere, 6(8), 455, 1977), in fly ash alone from a municipal incinerator, and in fly ash from an industrial heating facility (Buser et al., Chemosphere, 7(2), 163, 1973). Dow notes (p.22) that Olie et al. postulate that the PCDDs are formed as a result of the thermal condensation of chlorophenols, although mention is made in the article that a thermal synthesis reaction involving inorganic chloride and organic material (especially hexachlorobenzene and other highly chlorinated benzene) "was considered to be entirely possible." Dow, however, fails to discuss aspects of the Buser et al. (1973) study as well as a Rappe et al. (Chemosphere, 7(3), 269, 1978) study which indicate that the pattern of PCDD isomers identified in fly ash (from incinerators and heating facilities) was almost identical to that found when a mixture of polychlorophenates was pyrolyzed under controlled conditions. Buser et al. go on to state

Table 4. PCDDs in Soil and Dust Samples (ppb)
(taken from Dow's Tables III, IV, V, and VI)

<u>Sample</u>	<u>TCDD</u>	<u>HxCDD</u>	<u>HpCDD</u>	<u>OCDD</u>
Midland				
(1)	0.03*	0.2	2.3	19
(2)	0.04*	0.4	3.9	31
(3)	See Tables 2 and 3 for other Midland values.			
Rural				
(1)	ND	ND	ND	ND
(2)	ND	ND	ND	0.1*
(3)	ND	ND	ND	ND
(4)	ND	ND	0.3*	0.10
(5)	ND	ND	0.05*	0.17
(6)	ND	ND	0.02*	0.16
(7)	ND	ND	ND	ND
(8)	ND	ND	0.03*	0.11*
Urban ^a				
(1)	ND	1.2	1.6	2.0
(2)	ND	ND	0.23	0.96
(3)	ND	0.03*	0.30	2.0
(4)	ND	ND	ND	0.05*
(5)	ND	ND	0.035*	0.20
Major Metro ^b				
(1)	ND	ND	0.14	0.41
(2)	ND	0.03*	0.24	1.0*
(3)	0.03	0.31	3.3	22.0
(4)	ND	0.12*	1.4	8.5
(5)	0.006*	0.14	0.85	3.2
(6)	0.005*	0.04*	0.36	1.4
(7)	0.005*	0.09*	0.96	6.0
(8)	ND	0.02*	0.10	0.35
(9)	ND	ND	0.64	2.6
(10)	0.04*	0.34*	3.2	8.2
(11)	ND	0.09	0.8	3.5
(12)	ND	0.1	0.3	0.4
(13)	ND	ND	ND	ND
(14)	ND	0.3	1.0	3.8

a) Samples collected from between 300-1500 feet from a "powerhouse."

b) Samples collected from between 100-3300 feet from an "incinerator" (except for (14) which was collected at a "metro river shoreline").

*Value is close to the detection limit for the analytical method employed (signal is less than 10X noise).

ND) Signal not detected at 2.5X noise.

Table 5. A Comparison of PCDD-Positive Soil and Dust Samples/
Total Analyzed from Different Locations

<u>Location</u>	<u>TCDD Isomers</u>	<u>2,3,7,8-TCDD</u>	<u>HxCDD</u>	<u>HpCDD</u>	<u>OCDD</u>
Midland, MI	16/25 ^a (64%) ^b (0.03-18) ^c	11/11 ^d (100%) (0.3-100)	22/26 (88%) (0.2-280)	26/26 (100%) (2.3-3200)	26/26 (100%) (19-20500)
Other Locations (total)	5/23 (22%) (0.005-0.04)		10/23 (43%) (0.02-1.2)	18/23 (78%) (0.02-3.3)	20/23 (87%) (0.05-22.0)
Rural	0/8 (0%)		0/8 (0%)	4/8 (50%)	5/8 (63%)
Urban	0/5 (0%)		2/5 (40%) (0.03-1.2)	4/5 (80%) (0.035-1.6)	5/5 (100%) (0.05-2.0)
Major Metro	5/10 (50%) (0.005-0.04)		8/10 (80%) (0.02-0.34)	10/10 (100%) (0.10-3.3)	10/10 (100%) (0.35-22.0)

- a) This entry reportedly represents TCDD isomers other than 2,3,7,8-TCDD; i.e., the analytical method is claimed to have achieved some degree of TCDD isomer separation. All other entries in this column apparently represent aggregate totals for all TCDD isomers.
- b) Percent (PCDD-positive samples/location). Note that for purposes of this table, asterisked (*) values taken from Tables 3 and 4 were considered "positive" despite questions as to the analytical significance of some of these values.
- c) Range of detected levels in ppb.
- d) This entry reportedly represents some degree of separation of the 2,3,7,8-TCDD from other TCDD isomers.

that available evidence indicates that commercial chlorophenols cannot be excluded as the precursor to PCDDs in fly ash. As noted briefly in the discussion of part I, Rappe et al. (among others) have also shown that the combustion of leaves, wood shavings, plywood, or waste oil containing chlorophenates can yield a variety of PCDD isomers in the ash. Dow reports that it operates two major chemical waste incinerators at Midland, MI. The first is a large stationary tar burner and the second is a rotary kiln incinerator. Samples of particulate matter were removed from the stacks and analyzed for PCDDs. The resulting data are summarized in Table 6. Particulates from the stationary tar burner and the rotary kiln incinerator show no detectable TCDD when operated with supplementary fuel. (The levels of the other PCDD isomers are, nonetheless, still relatively high.) However, when the rotary kiln incinerator is operated without supplemental fuel, extremely high levels of TCDDs (and other PCDDs as well) are detected. Several important questions immediately arise. Does Dow generally operate the rotary kiln incinerator with supplemental fuel when using it for chemical waste incineration? Dow should specify the types and conditions of operation of air pollution control devices (including scrubbers) used to control particulate emissions from these incinerators? It is also important to know whether the particulate samples were collected from the stacks "upstream" or "downstream" from the scrub water inlet (i.e., before or after scrubbing) (see part VII below). In addition, were the particulates scraped from the walls of the stacks or were they collected from the gas phase or an electrostatic precipitator (or some other pollution control device).

VI. Powerhouses

Particulates from a Dow Midland powerhouse stack were collected and analyzed. Fuel oil and coal are burned in the powerhouse. The results of the PCDD analyses are presented in Table 7.

It is not clear why the TCDD isomers (other than 2,3,7,8-TCDD which was not detected) are so high (compared to other PCDDs) in the powerhouse particulate. Likewise, if Dow's thesis concerning the synthesis of PCDDs as a normal combustion by-product is correct, why do the incinerators as opposed to the powerhouse, in general, show higher levels of PCDDs in the fly ash? The difference may be related to the nature of the material being burned in each operation. One possible explanation is that the chemical wastes being burned in the incinerators already contain PCDDs or PCDD precursors (polychlorophenoxy material); that is, the wastes

Table 6. PCDDs in Particulate Matter from Dow Incinerators (ppb)
(taken from Dow's Tables VIII and IX)

	TCDD isomers other than				
<u>Sample</u>	<u>2,3,7,8-TCDD</u>	<u>2,3,7,8-TCDD^a</u>	<u>HxCDD</u>	<u>HpCDD</u>	<u>OCDD</u>
<u>Stationary tar burner</u> (with supplemental fuel)					
(1)	ND	ND	20	90	330
(2)	ND	ND	7	125	440
(3)	ND	ND	6	60	190
(4)	ND	ND	4	160	320
(5)	ND	ND	1	27	250
<u>Rotary kiln incinerator</u> (without supplemental fuel)					
(1)	1,800	2,300 ^b	13,000	110,000	180,000
(2)	5,000	8,200 ^b	65,000	510,000	310,000
(3)	3,300	110	1,300	2,000	3,000
(4)	12,000	ND	5,600	37,000	59,000
<u>Rotary kiln incinerator</u> (with supplemental fuel)					
(1)	ND	ND	1.4	13.0	30.0
(2)	ND	ND	ND	4.0	9.0
(3)	ND	ND	ND	6.0	15.0
(4)	ND	ND	5.0	27.0	170.0
(5)	ND	ND	4.0	110.0	950.0

a) Dow's report does not specify the number of TCDD isomers represented by values in this column.

b) These values may be high; see Dow's comment on p.24.

Table 7. PCDDs in Particulates from a Powerhouse Stack (ppb)
(taken from Dow's Table X)

<u>TCDD isomers other than 2,3,7,8-TCDD</u>	<u>2,3,7,8-TCDD^a</u>	<u>HxCDD</u>	<u>HpCDD</u>	<u>OCDD</u>
38*	ND	2	4	24

a) Dow's report does not specify the number of TCDD isomers represented by this value.

*Value is close to the detection limit for the analytical method employed (signal is less than 10X noise).

result from Dow's chlorophenol production processes. Rappe et al. (1978) offer several different mechanisms for the formation of PCDDs given the presence of pre-formed PCDDs or PCDD precursors. The 3 proposed mechanisms are:

- a) by dimerization of chlorophenates,
- b) by dechlorination of higher chlorinated PCDDs, and
- c) by cyclization of PCDD precursors.

VII. Waterborne Particulates

Composite scrubber water samples were taken from the rotary kiln incinerator during the same sampling reported in part V of the report. Particulates were filtered from the scrubber water and both the particulates and the water filtrate were analyzed for PCDDs. (Note that Dow's analytical method ML-AM-78-63 [Dow's Appendix B3] [specific for soil, dust, and particulate samples] was used to analyze the scrubber water particulates. Dow, however, does not specify the analytical method used to examine the water filtrate. This should be clarified.) Table 8 presents the results of these analyses and also compares the scrubber water PCDD values with those reported for rotary kiln fly ash (previously reported in Table 6). When comparing the PCDD levels reported in the different samples, it should be noted that there is no indication whether all the samples were taken within a short time of each other or days apart. In addition, it is not clear if the same wastes were being burned or if similar incineration conditions existed when the respective samples were taken. Dow should be asked to provide a complete description of the operating conditions (normally and during sampling), nature of the wastes burned normally and during sampling, and use of air pollution control devices on the rotary kiln incinerator. Dow should also describe the method of disposal used for scrubber water particulates and any other solid wastes resulting from these incineration procedures.

In addition, Dow should provide the same information for its stationary tar burner.

VIII. Combustion of Dioxins

The U.S. EPA report entitled "At-Sea Incineration of Herbicide Orange Onboard the M/T Vulcanus" (EPA-600/2-78-086) was published in April, 1978. A copy of this publication should be transmitted to Dow in any followup to this submission.

Table 8. PCDDs in Rotary Kiln Scrubber Water and Stack
Fly Ash (ppb)
(taken from Dow's Tables IX, XI, and XII)

Without supplemental fuel

<u>Sample</u>	TCDD isomers other than <u>2,3,7,8-TCDD</u>	<u>2,3,7,8-TCDD</u>	<u>HxCDD</u>	<u>HpCDD</u>	<u>OCDD</u>
A) scrubber water particulates	300	2,200 ^a	3,400	26,000	42,000
B) scrubber water filtrate	0.0018*	0.001 ^{a*}	0.005	0.24	0.026
C) fly ash particulates ^b	(1) 1,800 (2) 5,000 (3) 3,300 (4) 12,000	2,800 8,200 110 ND	13,000 65,000 1,300 5,600	110,000 510,000 2,000 37,000	180,000 810,000 3,000 59,000

With supplemental fuel

D) scrubber water particulates	14	32 ^a	200	970	1,200
E) fly ash particulates ^b	(1) ND (2) ND (3) ND (4) ND (5) ND	ND ND ND ND ND	1.4 ND ND 5.0 4.0	13.0 4.0 6.0 27.0 110.0	30.0 9.0 15.0 170.0 950.0

a) The analytical method reportedly did not separate the 2,3,7,8-TCDD from 11 other isomers.

b) The high results reported for 2,3,7,8-TCDD "are probably due to analysis by the non-specific GC-MS packed column method" (see p.24 of Dow's report). In addition, Dow's report does not specify the number of TCDD isomers represented by the values in the 2,3,7,8-TCDD column.

*Value is close to the detection limit for the analytical method employed (signal is less than 10X noise).

IX. Michigan Division Manufacturing Plants as Potential Sources of Trace Levels of Chlorinated Dioxins in the Environment

A. Wipe testing

The fact that 8 out of 230 wipe tests gave positive results for TCDD merits consideration. The wipe test area, 100 cm², is roughly equivalent to the area of a human hand and 1 ug TCDD may be approaching a toxic level (LD₅₀ male guinea pig, 0.6 ug/kg). The text indicates that the analyses were conducted by gas chromatography with a detection limit of 1 ug/wipe; however, Appendix B4 states that analyses were carried out by GC-MS with a level of detection of 0.1 ug/sample. These points should be clarified. In addition, information as to the suitability of the wipe test methodology to actual conditions which might be encountered in the Michigan Division manufacturing plants should be provided by Dow.

B. Air monitoring

The method of sample collection is not described in sufficient detail in Dow's report. Are particulates sampled during this procedure? Also, note that part of the report appears to have been omitted at the top of page 30. This omission should be clarified.

A statement made on p.30 could be misleading. "The few molecules that take this path (vaporization) will be destroyed by photodegradation within a few hours even when the day is cloudy (23)." This statement could lead one to believe that if PCDDs are released to the atmosphere they will be destroyed. If these compounds are really volatilized then they could possibly be decomposed; however, if they are adsorbed onto fly ash or other particulate matter they would probably not be destroyed photolytically or to only a limited extent. In addition, the applicability of Dow's reference 23 (Nash and Beall, 1977) to the above quotation is not clear; clarification is required.

Dow claims on page 30 that the "wipe testing and air monitoring data are strong evidence that (Dow) manufacturing plants do not emit levels of chlorinated dioxins sufficient to explain the finding of these compounds in the soil samples reported earlier." No scientific basis for this conclusion is provided in the data presented by Dow. In the first place, there is no way to compare the ppb levels of TCDD found in soil and dust with the "1 ug/wipe" values reported for the wipe testing. To support its conclusion, Dow would either have to "wipe test" soil samples or, preferably, analyze pesticide plant wipes on a ng/g (ppb) basis. Handled in any other way, one is left to compare apples with oranges. Similarly,

there is no way to compare Dow's plant air monitoring data with the PCDD values reported for soil and dust samples collected outside the plant. Furthermore, there is no indication as to the location of each wipe test or air sampling site in relation to the various operations involved with polychlorophenol production or handling. Dow should present a grid of its polychlorophenol production and handling sites and identify the sampling points for the 230 wipe tests and 35 air monitoring assays. Any available monitoring data (wipe tests, air sampling, etc.) regarding Dow laboratory facilities as potential sources of PCDD contamination should also be provided.

C. Aqueous streams

Further information on the "tests" for primary organics reported in this section should be provided by Dow.

D. Cooling waters

The results of Dow's analyses of cooling tower "residues" for PCDDs are shown in Table 9. It is important to know if these towers cool steam or other effluent streams from the polychlorophenol facilities, the power plants, or the incinerators discussed earlier. Dow should provide a map of its plant site showing the location and relationship of each cooling tower, incinerator, powerhouse, and production facility (especially those producing or handling polychlorophenols or derivatives). In addition, Dow should further describe what it means by "cooling tower residue"; is this a water or sediment sample? Dow should also support with analytical results its statement on page 30 that "product leaks to cooling towers" do not occur.

Table 9. PCDDs in Cooling Tower Residues
(taken from Dow's Table XIII)

<u>Location</u>	<u>TCDD</u>	<u>HxCDD</u>	<u>HpCDD</u>	<u>OCDD</u>
Northwest	ND (L.O.D. _a 0.05)	ND	25	119
East	ND (L.O.D. 0.05)	ND	12	56
Central #1	1.6*	10	20	107
Central #2	6.0	-	-	-

a) Level of detection was 0.05 ppb.

*Value is close to the detection limit for the analytical method employed (signal is less than 10X noise).

Dow states in this section (p.30) that "(it) was assumed that cooling tower residues would be positive for chlorinated dioxins." Dow should be asked to provide the basis for this assumption. On page 31, Dow states that "(from) these data (see Table 9), we conclude that the presence of chlorinated dioxins in cooling tower residues confirms the airborne route." Dow should be asked to explain the term "airborne route" and specify the sources of the PCDDs found in cooling tower residues.

Central to this discussion of cooling towers is the assumption that Dow does not use 2,4,5-trichlorophenol in its cooling tower waters as a biocide. Dow should be asked to clarify this point. In the event that Dow does use 2,4,5-trichlorophenol, then the PCDDs found in the cooling tower residues may not be from airborne particulates.

E. Various aqueous streams

For this part of the report, Dow sampled various aqueous streams in its Midland plant. The samples were collected from sewer lines before they entered the waste treatment plant. The samples were selected on the basis of "the stream source and its rate of flow." This vague description of the samples is inadequate. Do any of the sampled aqueous streams come directly from chlorophenol production or handling operations? Do these samples include particulates? If not, these analyses have limited value. Dow indicates it employed analytical method ML-AM-73-97 (Appendix B2) for the analyses reported in this section. The method is specified for the analysis of fish and soil samples; its applicability to aqueous stream analysis should be demonstrated.

On page 32, Dow states that in the case of sewer water analyses, "the source of the chlorinated dioxins cannot be reliably determined by the ratio of the various species." However, in immediate juxtaposition to this statement is Dow's remark (p.33) that "(with) the exception of sewer water samples 2 and 4 and cooling tower central #1, the data indicate that the chlorinated dioxins are from the same source as those on soil and dust. The exceptions have species whose ratios are similar to those found on particulates from the powerhouse." Dow should clarify the meaning and significance of these remarks. Insofar as Dow states in the Introduction (p.2) that "(samples) were not taken by statistical design and results are not intended to represent anything other than the sample analyzed," how can Dow proceed to compare the PCDD ratios from one sample with those from another? Moreover, how can Dow draw conclusions from such a comparison? Furthermore, how can the submitter state in one paragraph that a comparison of PCDD ratios will not yield a

"reliable" determination of the source, but then in the next paragraph draw 2 separate and distinct conclusions from these same ratios.

Another statement on page 33 deserves comment: "The (PCDD) ratios (found in the cooling tower or sewer waters) do not fit those normally found in any manufactured product." The meaning of the phrase "normally found in any manufactured product" is not clear because no known polychlorophenol product or derivative contains both TCDD and OCDD. In general, trichlorophenol contains TCDD, while pentachlorophenol contains HxCDD, HpCDD, and OCDD but no TCDD. If Dow is aware that any of its products contain both TCDD and OCDD (or for that matter, both trichlorophenol and pentachlorophenol), it should so inform the Agency. Dow should describe the spatial relationship of its trichlorophenol production facility to the location of its pentachlorophenol production site. Are any waste water lines common to both? What is the composition of the chlorophenol wastes incinerated by Dow? Do these wastes represent a composite of both trichlorophenol and pentachlorophenol wastes? Or are wastes from the two chlorophenol production processes burned sequentially in the same incinerator?

X. Chlorinated-dioxin Containing Particulate Matter from Mufflers

Dow reports trace quantities of PCDDs in scrapings taken from the inside of car and diesel truck mufflers. The cars sampled were equipped with and without catalytic converters. Does this necessarily mean, as Dow advances, that PCDDs are formed during combustion in the engine? If the car or truck was driven primarily in an industrial area or near sources that might be considered contaminated with PCDDs or PCDD precursors, airborne particulates containing these substances could be drawn into the air intake of the engine. Any PCDDs not decomposed in passage through the engine might then be deposited in the muffler. The statement (p.35) that PCDDs "are in particulate emissions from internal combustion engines" cannot be supported because vehicles' exhaust gases were not analyzed. The only conclusions that can be supported by the observations presented in this section are that (1) PCDDs have been identified in some muffler scrapings, however, (2) the source of the PCDDs is unknown.

The analytical method (GC-EC vs. GC-MS) used to detect TCDD isomers was not specified in Dow's Table XV; this information should be provided.

XI. Commonplace Sources

1. Soot from fireplaces

Dow reports that soot collected from 2 fireplaces contains PCDDs. The results are presented in Table 10. Dow states (pp. 35 and 36) that none of the wood burned in the fireplaces "had been treated with any wood preservatives." Dow should be asked to document this statement.

2. Particulate matter from a home electrostatic precipitator

The results of PCDD analysis performed on this sample are presented in Table 10.

Table 10. PCDDs in Fireplace Soot and Particulates from a Home Electrostatic Precipitator (ppb)
(taken from Dow's Table XVI)

<u>Source</u>	TCDD isomers other than <u>2,3,7,8-TCDD</u>	<u>2,3,7,8-TCDD^a</u>	<u>HxCDD</u>	<u>HpCDD</u>	<u>OCDD</u>
fireplace A	0.27	0.1*	3.4	16	25
fireplace B	ND	ND	0.23	0.67	0.89
electrostatic precipitator	0.40*	0.6*	34	430	1300

a) Dow's report does not specify the number of TCDD isomers represented by values in this column.

*Value is close to the detection limit for the analytical method employed (signal is less than 10X noise).

The geographic location of each house sampled in Table 9 should be provided by Dow. Were these houses in the Midland, MI area, and if so were they near Dow's plant? This is of some interest because the particulate collected in the electrostatic precipitator (electronic air cleaner) have a higher concentration of PCDDs than the soot samples from the fireplaces (acknowledged sources of typical combustion by-products). A home electrostatic precipitator functions to a certain extent as a "high volume air sampler." In the case cited by Dow, the electrostatic precipitator was operated over a period of 6 spring and summer months. Thus, the precipitator particulates analyzed by Dow represent airborne

material collected over a 6 month period which does not coincide with the months generally associated with heavy space heating-related combustion or home fireplace usage. Therefore, the PCDD values for the home electrostatic precipitator-collected particulates may, to a certain extent, represent the results of incidental ambient air "sampling" conducted at the site of the house. For this reason, the location of this particular house may be important.

3. Charcoal broiled steaks

The results of this assay are presented in Table 11. As can be seen, all samples were negative for TCDD and HxCDD and in only one case (that being an "over-done" steak) did the GC-MS (gas chromatography-mass spectrometry) method of analysis "support" the GC-EC (gas chromatography-electron capture) result. However, even in that case (as in all other instances reported in the table), the reported OCDD residues and the level of detection are of identical or approximately equal value such that the number has limited analytical significance. Furthermore, the blank sample (uncooked steak?) had a concentration of 6 ppt of OCDD (determined by GC-EC, although the value is so close to its level of detection as to have limited analytical significance). Was this blank (uncooked steak?) contaminated with pentachlorophenol, a widespread environmental contaminant?

Table 11. PCDD Content of Charcoal Grilled Steak (ppb)
(taken from Dow's Table XVII)

<u>Sample</u>	TCDD isomers other than <u>2,3,7,8-TCDD</u>		<u>2,3,7,8- TCDD</u>	<u>HxCDD</u>	<u>HpCDD</u>		<u>OCDD</u>	
					<u>GC-MS</u>	<u>EC</u>	<u>GC-MS</u>	<u>EC</u>
blank	ND		ND	ND	ND	0.004*	ND	0.006*
medium-rare	ND		ND	ND	ND	0.003*	ND	0.005*
well-done	ND		ND	ND	ND	0.006*	ND	0.012*
over-done	ND		ND	ND	ND	0.007*	0.029*	0.016*

*Value is close to the detection limit for the analytical method employed (signal is less than 10X noise).

XII. Cigarette Smoke

Cigarette smoke particulates were also analyzed for PCDDs; the results are presented in Table 12.

Table 12. PCDDs in Cigarette Smoke Particulates
(10^{-12} g/cigarette)
(taken from Dow's Table XVIII)

<u>Location of purchase and test</u>	<u>TCDD isomers other than 2,3,7,8-TCDD</u>	<u>2,3,7,8- TCDD^a</u>	<u>HxCDD</u>	<u>HpCDD</u>	<u>OCDD</u>
urban 1	ND	ND	8.0	8.5	50
urban 2	ND	ND	4.2	9.0	13

- a) Dow's report does not specify the number of TCDD isomers represented by values in this column.

Several questions arise concerning this assay. Are PCDDs or PCDD precursors present in unburned cigarettes (possibly due to pesticide use of polychlorophenols, or derivatives)? How does 10^{-12} g/cigarette relate to 10^{-12} g/g (or ppt)? The cigarettes were smoked in two unidentified "urban locations"; why was this method chosen over a controlled study conducted in a lab? Were the cigarettes "smoked" near Midland, MI or some other industrial site; in other words, how would the results of ambient air sampling at the two locations compare with the reported cigarette-PCDD values? Do the individual results in Dow's Table XVIII represent GC-EC or GC-MS analysis? Are the methods confirmatory in their results?

XIII. Other Chlorinated Compounds Identified

The polychlorinated dibenzofuran (PCDF) findings reported in this section should be investigated further. Several investigators (Buser et al., Chemosphere, 7(5), 419, 1973a; Rappe et al., Chemosphere, 7(5), 431, 1978; Buser et al., Chemosphere, 7(5), 439, 1978b; Rappe et al., Chemosphere, 6(5), 231, 1977; Buser et al., Chemosphere, 7(1), 109, 1973c; etc.) have identified PCDFs in polychlorophenol pesticides, saw dust from polychlorophenol-treated wood, fly ash, PCB mixtures, and as a by-product of the combustion of PCBs. Of significance are the Buser et al. (1973a) findings that the major PCDF constituents (in fly ash as well as in PCB pyrolyzates) tended to be the most toxic PCDF isomers (2,3,7,8-tetra-CDF; 1,2,3,7,8-penta-CDF; and 2,3,4,7,8-penta-CDF). This contrasts

with the Buser et al. (1978a) findings on the distribution of PCDD isomers in polychlorophenate pyrolyzates where the less toxic isomers were in greatest concentration.