POINT SOURCES AND ENVIRONMENTAL LEVELS OF 2378-TCDD (2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN) ON THE MIDLAND PLANT SITE OF THE DOW CHEMICAL COMPANY AND IN THE CITY OF MIDLAND, MICHIGAN

11/5/84

EXECUTIVE SUMMARY

Background

This report summarizes The Dow Chemical Company investigation of point sources and environmental levels of 2378-TCDD* on the Dow Midland Plant Site and in the City of Midland, Michigan. It is part of the research initiatives program announced by Dow in June 1983 to address public concerns about the trace presence of dioxins in the environment, and the potential health impact of TCDD levels in the Midland community.

This study was a comprehensive search for all critical point sources of TCDD to the air, soil and water in the Midland area. Nearly 240 environmental samples were collected and tested by Dow analytical scientists during this research. About 6,000 data points were gathered on the samples.

Using the most advanced analytical technology available, the scientists searched for sources by measuring the concentration of TCDD in each sample and the amount of the source effluent from which the samples were taken. A unique "fingerprinting" technique helped the researchers to identify the most significant sources of TCDD. Finally, the research team studied how TCDD is transported in the environment and how it can be removed from circulation.

Dr. Henry Freiser, professor of Analytical Chemistry at the University of Arizona, served as an independent auditor and monitor for this study. Dr. Freiser is a respected researcher in the field of environmental analytical methodology and trace analysis. The reliability of the analytical procedures used in gathering the data and the validity of the conclusions have also been reviewed by an independent panel of world-recognized authorities on various aspects of data collection and interpretation. This panel, chaired by Professor Freiser, consisted of Professor R. Graham Cooks, Department of Chemistry, Purdue University, Professor Dr. Otto Hutzinger, Chair of Ecological Chemistry and Geochemistry, University of Bayreuth, Federal Republic of Germany, and Professor Peter C. Jurs, Department of Chemistry, Pennsylvania State University.

Point source identification provides the basis on which Dow will continue to pursue research, and develop site-specific controls to further reduce the movement of trace quantities of TCDD into the Midland environment. The results of this study have been submitted to local, state and federal government regulatory agencies.

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*The specific isomer 2378-TCDD will be referred to as TCDD or dioxin.

Results Summary

1. Surface soil TCDD levels in the City of Midland are significantly below the 1 part per billion (ppb) concern level for residential areas established by the U.S. Public Health Service Centers for Disease Control (CDC).

2. Dioxin levels in more than 99 percent of the surface soils examined on the Midland Plant Site also are below that 1 ppb level. Two well-defined areas covering less than one-half percent of the Midland Plant Site have been identified where TCDD levels in soil are 5-50 ppb. These two areas are being contained. These two areas are directly associated with the historical manufacture and handling of chlorophenolic compounds. These findings are consistent with available scientific data about the formation and distribution of TCDD: It is known to be a trace contaminant in certain chlorophenolic manufacturing process and a low-level byproduct from the combustion of organic materials in the presence of chlorine-containing compounds.

3. Following a comprehensive study of Midland Plant Site power generating, chemical manufacturing and waste management operations, the largest point source of dioxin emissions to the air environment was found to be the Waste Incinerator. Other identified point sources were shown to be small in comparison to this source and, therefore, were not considered dominant sources. As currently operated, the Waste Incinerator releases approximately one-third gram of TCDD to the atmosphere per year. The concentration of TCDD in the vent from the Waste Incinerator is comparable to, if not lower than, that emitted by several municipal incinerators investigated by the U.S. Environmental Protection Agency.

4. This low-level emission rate cannot account for the TCDD levels known to be accumulated in the surface soils of the Midland Plant Site and in the City of Midland. Detailed analyses of past incineration practices, along with studies on the soils and airborne dust particles in the Midland area, show that historical dispersion of ashes and vent stack particulates from historical incineration operations are the probable source of the trace TCDD levels now found in the local environment.

5. The Waste Incinerator is also the most probable source of the 0.6 gram per year of TCDD which enters the Tittabawassee River from the Midland Plant Site. Exhaust gas wash waters from the Waste Incinerator appear to be the major source of the TCDD leaving the Dow Waste Water Treatment Plant. A comprehensive survey of all other sources of TCDD to Midland Plant Site wastewater (described in more detail later in this summary) has identified three historical sources that release TCDD intermittently to the Midland Plant Site Waste Water Treatment Plant. The current outfall to the Tittabawasee River from the entire plant contains about 25 parts per quadrillion TCDD carried by fine suspended solids.

DIOXIN POINT SOURCE RESEARCH STUDY RESULTS: SOIL SAMPLING

I. CITY OF MIDLAND SOIL SAMPLING

Analyses for TCDD in soil samples taken in the City of Midland and in samples taken just outside the Plant indicate that TCDD soil levels are significantly below the 1 part per billion (ppb) concern level established by the U.S. Public Health Service Centers for Disease Control (CDC) for exposure in residential areas. Levels between 0.0006-0.45 ppb were observed; the levels decrease with increasing distance from the Midland Plant Site suggesting that trace levels in area soils may be associated with current or former Midland Plant Site operations.

II. NON-MIDLAND SOIL SAMPLING

In order to assess the above findings, soil samples were also taken in industrialized areas of 16 other Midwestern and Midatlantic cities. Samples were taken near major steel, automotive or chemical manufacturing facilities, and near municipal solid waste incinerators. According to the data collected, soil levels of TCDD were below 0.01 ppb. Comparison of these data with those on the City of Midland soil samples suggests that:

1. While soil levels close to the Midland Plant Site are below 1 ppb, the levels are higher than those found in other industrialized urban areas. This suggests that the Dow Midland Plant Site is a primary source of the trace levels of TCDD in the immediate environment.

2. Soil levels found in the City of Midland further from the Plant Site are within the range measured in industrialized areas of other U.S. cities.

3. The widespread presence of TCDD in U.S. urban soils up to 0.01 ppb suggests that local combustion sources are probable sources of trace dioxin at those locations, including both industrial and municipal waste incinerators.

III. DOW MIDLAND PLANT SITE SOIL SAMPLING

The Midland Plant Site has been involved in manufacturing chlorophenolic compounds since the 1930's. Of 24 commercially significant compounds produced at one time or another, only two are still manufactured at the Site. Chlorophenolic production site studies were important in investigating potential

TCDD sources since TCDD is a known trace contaminant in certain chlorophenolic production processes. For this segment of the study, repeated soil samples were gathered from locations where relatively high TCDD levels were expected or found. Samples were also taken where low levels were predicted, to verify the predictions.

Data were categorized in three groups:

Group 1--samples from three areas known to be directly associated with current or historic chlorophenolic production and handling;

Group 2--samples from locations known to be associated with incineration of chemical and conventional wastes, and ash storage;

Group 3--samples from a variety of on-site locations away from potential TCDD sources, believed to represent a general TCDD surface soil background level within the Midland Plant Site fenceline.

Group 1 TCDD soil levels generally were below 1 ppb with two exceptions. Two areas with localized elevated levels of TCDD up to 50 ppb were identified. These two locations total less than six acres and comprise less than one-half percent of the total 1500-acre Midland Plant Site. These areas are located where chlorophenols were manufactured historically. Group 2 soils were also below 1 ppb except for two samples with levels of 2 and 4 ppb, values typical of those seen in incinerator ash and particulates. Group 3 soils were all well-below 1 ppb.

In summary, with the exception of two localized areas, surface soil TCDD levels in the majority of the Midland Plant Site were below 1 ppb. In areas away from known potential TCDD sources, surface soil levels generally were less than one-half ppb.

IV. DIOXIN POINT SOURCES TO MIDLAND SOILS

The purpose of this portion of the study was to identify primary TCDD sources. The mere presence of TCDD in a stream or sample does not confirm this as a source. Before an effluent or stream can be considered a primary TCDD source it must meet the following criteria:

1. The concentration must be high enough to significantly contribute to the levels observed in the environment.

2. The quantity, or mass of TCDD being emitted must be sufficiently large to account for the observed quantities of TCDD in the environment.

3. There must be a plausible dispersal mechanism.

4. The source must have a "fingerprint" corresponding to that observed in the environment.

Using these criteria several potential TCDD sources were investigated:

1. Midland Plant Site Powerhouse--This 60-megawatt, two-million-pound-per-hour steam cogeneration plant was evaluated as a potential TCDD source; samples were taken of powerhouse cinders, flyash, stack dust and exhaust gases. Although minute traces of TCDD are present in the ash and stack particulates, none were concentrated enough to be significant sources of TCDD to the area environment.

2. Combustion Unit and Process Vent Stack Effluents--The Midland Plant Site operates four combustion units which incinerate chlorinated wastes. Several process vents with potential TCDD emissions were also analyzed. The largest of these units is the rotary kiln Waste Incinerator. Trace levels of TCDD were found in exhaust streams of each of these units.

   Not including the Waste Incinerator, the combined TCDD output of all these other units was only 0.001 gram per year. The Waste Incinerator releases about 0.3 gram per year. Therefore, attention was focused on the Midland Plant Site Waste Incinerator as the most likely TCDD source into the environment.

3. Midland Plant Site Waste Incinerator--This unit typically burns more than 200 tons of solid and liquid waste combustible trash and waste daily. To minimize particulate emissions, kiln ashes are quenched in a water slurry, and combustion gases are scrubbed with water in an extensive emission control system. The ash is sent to a licensed Class I landfill. The water from the ash quench and emission control system is routed to the Midland Plant Site Waste Water Treatment Plant.

   It should be noted that the Waste Incinerator exhaust TCDD concentrations were significantly lower than those from municipal waste incinerators measured and reported by the U.S. Environmental Protection Agency. Municipal incinerators were found to be emitting exhaust gases with TCDD concentrations up to 70 times greater than the Midland Plant Site Incinerator.

   In samples taken for this part of the study, the quantity of TCDD currently being emitted to the atmosphere was not enough to account for levels being found in the environment. The impact of the Waste Incinerator on the area environment will be discussed later in this summary.

4. Transport--TCDD surface soil levels inside the Midland Plant Site were higher than in City of Midland residential soils. This suggests that an airborne transport mechanism is dispersing the dioxin.

   To confirm the point source for this airborne TCDD, researchers analyzed dust particulates from various sources. It was noted that the concentrations generally were within the range that would be expected for stack particulates dispersed from the Waste Incinerator.

V. DIOXIN POINT SOURCE RESEARCH STUDY RESULTS: WASTE WATER STREAM SAMPLING, TRANSPORT AND CONTROL

This study segment identified possible TCDD sources flowing into the wastewater system, distinguishing current from historical sources. Water, sediment and sludge samples were collected and analyzed. Water flow rates were approximated for the streams that were sampled.

The Midland Plant Site wastewater system handles about 19 million gallons of water daily. All sources that flow into this network were sampled: sewers, the riverbank revetment system, incinerator scrubber waste and landfill dewatering systems.

The findings indicate:

1. The Waste Incinerator is a current point source of TCDD to the wastewater system. TCDD was found in all exhaust scrubber water streams from the Incinerator.

2. Samples taken from dewatering wells located on a closed on-site landfill showed TCDD levels between 1.8 and 3.4 ppb. These wells are an important historical source of TCDD. These wells have been deactivated. The landfill is clay-capped and is surrounded by a clay wall extending to the natural clay bottom to prevent leakage and rainwater infiltration.

3. A shallow sump near former chlorophenol production sites produced samples containing about 1 ppb TCDD. This sump formerly flowed into the sewer system, but has been deactivated.

4. Sludge samples from the general sewer showed concentrations of 1-80 ppb TCDD. Organic material containing TCDD was found to be entering the sewer from an historical deposit.

5. An extensive analysis was made of the Midland Plant Site sewer system which serves current manufacturing units. No currently operating manufacturing facility discharges a significant quantity of TCDD into the sewer system.

6. Samples indicate that 0.08 gram per year TCDD enters the wastewater system from the underground revetment system which protects the Tittabawasee River from possible contamination.

VI. TCDD Wastewater Transport

The solubility of TCDD in water is very low, yet it travels quickly in moving water. An unexpected and significant finding of this study is that TCDD appears to be transported on suspended silt and other particulate matter moved by flowing streams. Unfiltered water effluents containing suspended silt show

TCDD levels in the parts per quadrillion range. Solids filtered off from these samples and analyzed separately show TCDD levels in the parts per billion range. In fact, TCDD concentrations on these particulates are similar to those that would be expected on Waste Incinerator ash.

The Midland Plant Site Waste Water Treatment facility processes almost 7 billion gallons of wastewater every year, and yet only 0.6 gram TCDD are discharged annually into the Tittabawassee River. A steady reduction of TCDD content in the wastewaters is achieved as the waters are processed through primary, secondary and tertiary treatment.

Since TCDD is transported via suspended silts and particulates, the efficiency of TCDD removal is proportional to the efficiency of suspended solids removal. For example, primary treatment settles out large particulate solids. During this treatment stage, TCDD concentrations were found to drop from 1500 ppq to 150 ppq. Levels drop to 50-75 ppq in secondary treatment as biomass micro-organisms engulf TCDD-carrying particles. When the biomass is filtered off, the entrapped particles also are removed. Following tertiary treatment, involving further bioentrapment and settling, only 25 ppq TCDD is ultimately discharged to the river. These final carrier particulates are extremely small and generally are resistant to settling, coventional filtration and engulfment by micro-organisms.

In another major finding of this study, Dow pilot-plant research has confirmed that the TCDD being carried out in effluent via suspended particulates can be further reduced by two to five times through efficient sand filtration.

VII. FURTHER STUDY OF THE MIDLAND PLANT SITE WASTE MANAGEMENT SYSTEM AND THE ULTIMATE FATE OF TCDD

Having determined that the Midland Plant Site Waste Incinerator is a primary current contributor to TCDD levels in the soils and wastewater of the Site, further research was conducted to define the formation and fate of TCDD in the Waste Incinerator.

Three sample sets were collected from exhaust stack and exhaust scrubbing operations. From the analyses it was determined that the amount of TCDD in the ash and particulates captured in the exhaust purification system ranged up to about 13 grams per year.

This calculation takes into account the average concentration of TCDD in the samples, and the total amount being released from the Incinerator to the environment in a year. About one half of the TCDD is in the incinerator ash, formed during rotary kiln combustion of rubbish and organic materials in the presence of available chlorine. The other half, created in the afterburner unit, is 95 percent captured by the exhaust scrubber equipment, allowing only 0.3 gram per year to escape to the atmosphere.

These current levels being vented from the Incinerator stack do not account for the levels of TCDD accumulated at the Midland Plant Site and in the City of Midland. Further investigation was done to identify the source of those levels. One of the possible sources identified was historical low-temperature burning of liquid wastes at the Midland Plant Site which began as early as 1930; solid wastes were burned in a rotary kiln beginning in 1948. Combustion gases were vented directly to the atmosphere until 1968. High temperature incineration - a method used to minimize the formation of dioxin and maximize its destruction - was not fully implemented until 1978, when research indicated that dioxin was formed by low-temperature combustion.

From these and other data, it is reasonable to conclude that historical incineration operations on the Midland Plant Site have formed and emitted quantities of TCDD sufficient to account for the surface soil levels now observed.

VIII. SUMMARY

Waterborne outflow from the Waste Water Treatment Plant and airborne particulate from the Waste Incinerator are the largest apparent point sources of TCDD to the environment. (Current TCDD discharge from the Midland Plant Site to the Tittabawasee River is approximately 0.6 gram per year, while the Waste Incinerator currently emits about 0.3 gram of TCDD per year from the stack to the atmosphere.) These sources, however, do not account for currently observed levels of TCDD measured in soils of the Midland Plant Site or the City of Midland. Previous manufacturing and incineration operations are believed to be the key sources.

Dow's waste management practices play an important role in minimizing the environmental impact of TCDD generated on the Midland Plant Site. The first step is incineration of solid and liquid wastes using sophisticated water scrubbing of vent gases. This removes 98 percent of the TCDD, either as ash going to Class I landfill or waterborne particulates to the Waste Water Treatment Plant.

The next step is removing particulate from the wastewater by using the Waste Water Treatment Plant. This treatment system yields a 50 fold reduction in TCDD because the compound is carried via suspended silts and particulates in the water streams which the Treatment Plant is designed to remove.

The final phase of minimizing environmental impact is containment of the primary and secondary Waste Water Treatment Plant residues in secure landfill on Dow property.

In the search for critical point sources of TCDD to the Midland Plant wastewater system, four important sources have been identified. Three are historical deposits that release TCDD intermittently into the sewer system.

The fourth is the Waste Incinerator. It is the only major currently generating source identified on the Midland Plant Site. However, the relative size or significance of these four sources cannot be clearly established by flow data alone.

IX. USE OF PATTERN RECOGNITION TECHNIQUES TO HELP IDENTIFY TCDD POINT SOURCES

"Fingerprinting"

Chemical fingerprinting is a technique for learning where a chemical compound has been produced. Like a person, each sample containing dioxins has its own "fingerprint;" its own chemical makeup determined by what percentage of each tetrachloro dioxin isomer is present. Each fingerprint is different, depending on the means by which it was created. For example, the combination of TCDD isomers formed during incineration is different from the concentration of TCDD isomers formed during chemical production.

Isomer percentages are determined for a compound and recorded on a chart, or chemical profile. Each chart creates a "fingerprint" pattern peculiar to that sample. This fingerprint can then be compared to other fingerprints for known sources. If the fingerprint patterns match, this suggests that the suspected source may be responsible for the observed levels. This visual fingerprinting method can also be carried out using mathematical pattern recognition techniques.

The value of pattern recognition techniques in helping to identify the dominant point sources of TCDD into the surface soils of the Midland area is illustrated by the following conclusions which can be drawn from these data when used in conjunction with the facts shown in previous sections:

1. TCDD isomer patterns of Midland area soil were distinctly different from TCDD patterns of samples gathered from Powerhouse ash and from Plant Site areas with localized elevated levels of TCDD. It is therefore unlikely that these sources have contributed significantly to the TCDD levels observed in the Midland area.

2. The TCDD isomer pattern of Midland area soil was similar, though not identical, to that of both the Waste Incinerator ash and Waste Incinerator stack particulates. These materials have been historically accessible to the environment, and airborne transport appears to be a TCDD dispersal method. Therefore, although the possibility of contributions from additional TCDD sources cannot be excluded, the Waste Incinerator, or other historical waste incineration operations, are indicated as the most probable dominant point source of TCDD currently found on the Midland Plant Site. This is in accord with the conclusion reached earlier considering current and historical waste incinerator operating conditions and emission controls.

A modification of the same "fingerprinting" technology was also used to help identify the most important TCDD point sources to the Midland Plant Site wastewater system. Because the TCDD levels in the wastewater stream leaving the Midland Plant Site are so low, the TCDD "fingerprints" are very faint. In fact, only four TCDD isomers can be used for pattern comparison. This weakens the use of the comparison technique. Nonetheless, the four-isomer comparison which can be made does show that:

1. The TCDD isomer pattern of the Waste Incinerator exhaust scrubber effluent is very similar to the pattern of particulates found leaving the Waste Water Treatment Plant.

2. No combination of the TCDD isomer patterns from the other three (historical) sources matches at all closely the Waste Water Treatment Plant particulate TCDD pattern.

Therefore, within the limitations of this pattern comparison technique, the exhaust gas scrubbing system of the Midland Plant Site Waste Incinerator appears to be the most likely point source of the TCDD passing through the Waste Water Treatment Plant.

CONCLUSIONS

It is this intent of this report to provide a basis from which to further reduce the trace levels of dioxin moving into the area environment. This study has indicated that:

1. TCDD levels in the Midland community are primarily the result of previous incineration operations. Current Waste Incinerator technology has been improved to the point where this unit compares favorably with municipal solid waste incinerators.

2. Two small areas with localized elevated levels of TCDD have been identified on the Midland Plant Site. Those areas are being contained, and permanent containment is being developed in a cooperative plan with the Environmental Protection Agency.

3. The primary TCDD source to the Tittabawassee River appears to be the Waste Incinerator. Although more that 98% of the TCDD is already removed by the Waste Water Treatment Plant, a special filtration system is being designed and constructed to further reduce TCDD discharge to the river. Additionally, it should be empahsized that research is already proceeding to individually address each of the other three sources to the wastewater system that have been identified.