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DOW CHEMICAL COMPANY - MIDLAND PLANT
WASTEWATER CHARACTERIZATION STUDY

PRELIMINARY
SUMMARY OF RESULTS

MARCH 28, 1983

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
ENVIRONMENTAL SERVICES DIVISION
EASTERN DISTRICT OFFICE

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
REGION V
230 SOUTH DEARBORN ST.
CHICAGO, ILLINOIS 60604

REPLY TO ATTENTION OF

March 31, 1983

Re: DOW CHEMICAL COMPANY - MIDLAND PLANT:
WASTEWATER CHARACTERIZATION STUDY

The attached preliminary report presents the results of a study of toxicant contamination in discharges of the Dow Chemical Company at Midland, Michigan, and in the waters of the Tittabawassee River near the Dow plant. The study was performed to assist the State of Michigan in the development of effluent limitations to be included in a revised NPDES wastewater discharge permit for Dow. The final report of the study will be completed this summer.*

Samples of Dow's Midland plant wastewater effluents were collected and analyzed for a wide range of pollutants. In addition, fish were held in cages for 28 days in the Tittabawassee River at the point where Dow's effluent is discharged as well as upstream and downstream of the plant. The exposed fish were analyzed to determine the concentrations of toxicants that had accumulated in their tissues. Of the pollutants examined in both wastewater and fish, dioxins were given particular emphasis.

Field work for the study, including all sample collection, was completed in September 1981. Because of the complexity of the analysis and the need to perfect methods to analyze samples in the sub-parts per trillion range, the completion of this report was delayed until now.

More than 40 toxic organic chemicals were identified and quantified in the main process wastewater outfall, most in the low part per billion range. Discharge of toxic organic pollutants from the plant is estimated to exceed 6 tons per year. More than 30 organic chemicals were found in whole fish exposed to the main outfall plume at levels ranging from a few parts per billion to over 1 part per million. These chemicals include chlorinated benzenes and phenols, and certain pesticides.

A number of dioxin isomers were found in the discharges and the caged fish. The most toxic dioxin isomer, 2,3,7,8-tetrachloro dibenzo-p-dioxin, was found at a level of 50 parts per quadrillion in the main process effluent and at 100 parts per trillion in whole fish exposed to the effluent plume. The complete results from the fish bio-accumulation study are not yet available. The remaining analyses will be completed this summer.

Valdas V. Adamkus
Regional Administrator

* [illegible]

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A. Sediment Survey Data

B. Conventional Water Sampling Data

C. PCDDs and PCDFs - Methodology and Quality Control Large Volume Sampling Study

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E. Bioaccumulation Study Results

F. PCDDs and PCDFs - Methodology and Quality Control Bioaccumulation Study

I. INTRODUCTION

In the spring and summer of 1981, the Michigan Department of Natural Resources (MDNR) and Region V of the U.S. Environmental Protection Agency cooperated in development of a wastewater characterization study for the Midland Plant of the Dow Chemical Company USA, Michigan Division. The plant is located in Midland, Michigan, on the Tittabawassee River in Midland County, (Figure 1). The MDNR and EPA-Region V conducted this study because of the nature of the process operations at Dow Chemical, concern over actual and potential discharges of toxic substances from the Midland Plant, and lack of cooperation from Dow Chemical to provide requested wastewater discharge and production process information. The study results, along with other information being sought from Dow Chemical, will be used to develop a Best Available Technology (BAT) NPDES permit for the Midland Plant which will effectively regulate the discharge of toxic pollutants.

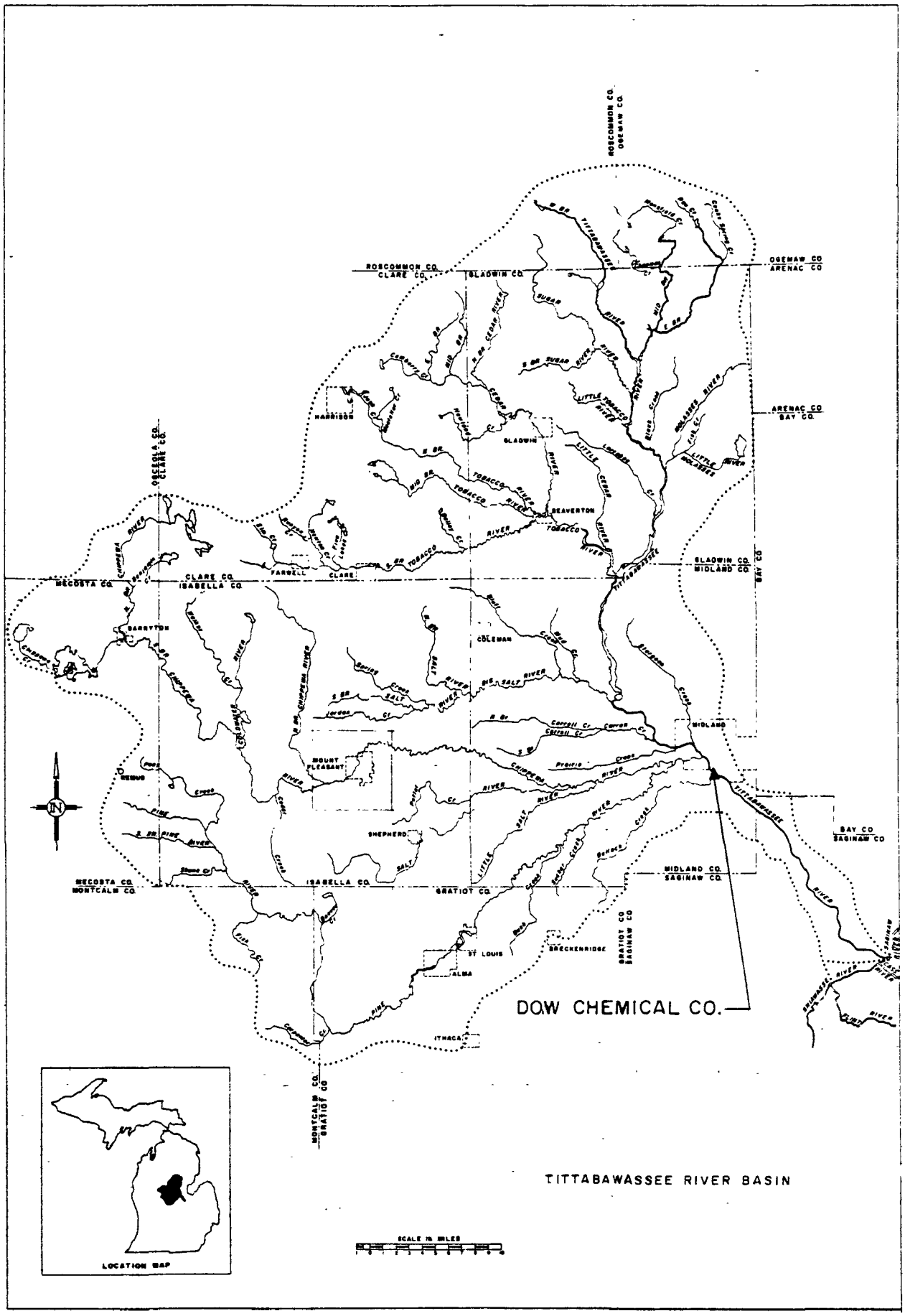
The purposes of this summary report are to present a compilation of currently available data from the study and to present preliminary findings and conclusions regarding the character of the Dow Chemical discharge. The final report on this study will include all of the raw data and quality assurance for the data as well as the sampling and analytical protocols used in this study. The final report will present comparisons of the available discharge data from this study with historical discharge data, and, comparisons of the bioaccumulation study results with results from other bioaccumulation studies and native fish data. The final report will also identify, at least in part, those operations and production processes at the Midland Plant recommended for evaluation and further study and assess compliance with current NPDES permit conditions. The final report will not assess the potential human health impacts of the discharges from Dow Chemical as that is beyond the scope of this study. In conducting the study, EPA and MDNR provided split or duplicate samples to Dow Chemical for its analyses. Dow Chemical data for these split and duplicate samples will be evaluated by EPA and MDNR upon receipt.

A major problem with complex field studies is the time required to obtain the final results. This continues to be a particular problem with this study as a substantial number of organic chemical analyses of complex sample matrices and

the development of new sampling and analytical methods were required. The initial planning for this survey was based, in part, upon the availability of EPA laboratory resources, specifically for analyses of the large-volume water samples and bioaccumulation samples for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). EPA laboratory resources were not available at the time the field studies were to begin. As a result, Region V was compelled to secure analytical contractors for virtually the entire project. The difficulty in obtaining numerous contracts and contract amendments with the required detection levels and analytical quality assurance; the financial resources required; and the complexity of the analyses contributed to the delay in obtaining results. At this writing, not all of the data are available. This report was prepared in the interest of providing the currently available data.

The planning for this study was completed by the EPA Region V Eastern District Office in consultation with the then Region V Enforcement Division; the Region V Central Regional Laboratory; the MDNR Office of Toxic Materials Control (now the Toxic Chemicals Evaluation Section); the Great Lakes National Program Office; and, the then Region V Air and Hazardous Materials Division. The water sampling field work was conducted by the Eastern District Office and the bioaccumulation study was conducted by the MDNR and Central Regional Laboratory. The Region V Quality Assurance Office reviewed and approved all analytical protocols. The Central Regional Laboratory managed all laboratory contracts and provided quality assurance audits of the analytical contractors.

The term "dioxin" is often used to describe 2,3,7,8-tetrachloro dibenzo-p-dioxin (2,3,7,8-TCDD). The isomer 2,3,7,8-TCDD is the most toxic of the dioxin isomers. In this report, the term "PCDDs" means all polychlorinated dibenzo-p-dioxin isomers and "PCDFs" means all polychlorinated dibenzofuran isomers.


ROSCOMMON CO.
OGEMAW CO.
ROSCOMMON CO.
CLARE CO.
GLADWIN CO.
OGEMAW CO
ARENAC CO
ARENAC CO
BAY CO.
OSCEOLA CO.
CLARE CO.
HARRISON
GLADWIN
BEAVERTON
GLADWIN CO.
MIDLAND CO.
BAY CO
MECOSTA CO.
CLARE CO.
ISABELLA CO.
FARWELL
CLARE
BARRYTON
COLEMAN
MIDLAND
MOUNT PLEASANT
REMUS
SHEPHERD
BAY CO
SAGINAW CO
MECOSTA CO.
MONTCALM CO.
ISABELLA CO.
GRATIOT CO.
MIDLAND CO.
SAGINAW CO.
GRATIOT CO
SAGINAW CO
ST. LOUIS
BRECKENRIDGE
ALMA
ITHACA
MONTCALM CO.
GRATIOT CO
DOW CHEMICAL CO.
LOCATION MAP
SCALE IN MILES
TITTABAWASSEE RIVER BASIN

II. OBJECTIVES

The primary objective of this study is to quantify the conventional, non-conventional, toxic organic and toxic inorganic pollutant discharges from the Dow Chemical - Midland Plant. This information and data will be used to develop a Best Available Technology (BAT) NPDES permit for Dow Chemical. The permit conditions are likely to include specific effluent limitations for certain organic pollutants; the regulation of others through the use of indicator pollutants; a compliance schedule for additional in-process controls and end-of-pipe treatment; and, conventional and special monitoring requirements.

Secondary objectives include: (1) a determination of the types and the extent of bioaccumulation of pollutants discharged by Dow Chemical in fish; (2) sub-part per trillion analyses of effluent samples for PCDDs and PCDFs; (3) development of information on contamination of fish, sediment, and water in the Tittabawassee River; and (4) analyses of native fish from the Grand River for PCDDs and PCDFs.

III. SCOPE OF WORK

To accomplish the study objectives, a multi-phased field program was planned in the spring and summer of 1981 and executed in late summer and early fall of 1981. Field programs included the following: (1) a sediment survey of the Tittabawassee River to determine whether significant toxic pollutant contamination of the sediments has occurred; (2) four 24-hour composite samples of Dow Chemical water intakes and effluent discharges to determine pollutant discharges at the low parts per billion range; (3) one large-volume 24-hour composite sample of Dow Chemical water intakes, certain effluent discharges, and the receiving water to determine discharge rates of dioxin and furan compounds in the sub-part per trillion range; (4) a static daphnia bioassay and an algal assay to determine whether or not the Dow Chemical main process wastewater effluent exhibits acute toxic effects or stimulatory effects on algal growth; (5) an Ames test of the main process wastewater discharge to determine whether the effluent exhibits mutagenic properties; (6) a fish bioaccumulation study to determine the level and rate of bioaccumulation of pollutants discharged by Dow Chemical; and, (7) analyses of native fish from the Grand River for organic compounds.

IV. FINDINGS AND CONCLUSIONS

A. Based upon the results of this study, the Dow Chemical - Midland Plant contributes the following discharges to the Tittabawassee River:

	Net Annual Discharge in Excess of
Total Dissolved Solids	125,000 Tons
Chlorides	60,000 Tons
Sulfates	10,000 Tons
Chemical Oxygen Demand	5,000 Tons
Total Organic Carbon	700 Tons
Total Kjeldahl Nitrogen	275 Tons
Ammonia-Nitrogen	250 Tons
Phosphorus (as P)	40 Tons
Toxic Organic Pollutants	6 Tons
Toxic Metal Pollutants	4 Tons
Phenols (4AAP)	1 Ton

More than 40 toxic organic chemicals were identified and quantified in the main process wastewater discharge from Outfall 031. Most were found in the low parts per billion range. A number of organic chemicals were identified but not quantified. Thus, the total discharge of organic pollutants is probably considerably higher than the amount listed above. The effluent does not contain a significant amount of readily biodegradable carbonaceous material. The toxic metals analyzed were found in the low parts per billion range, generally at concentrations below most ambient water quality criteria. Dow Chemical did not report any abnormal operations of the wastewater treatment facilities or process-related spills during the surveys.

B. The results of the large-volume water sampling for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans and the bioaccumulation study demonstrate that the discharge from Dow Chemical is a source of

PCDDs and PCDFs in the Tittabawassee River/Saginaw Bay system. The isomer 2,3,7,8-TCDD was positively identified in the discharge from Outfall 031 at a concentration of 50 parts per quadrillion (ppq) and in the plume of Outfall 031 in the Tittabawassee River at a concentration of 45 ppq. Four tetrachloro dioxin isomers were found in Outfall 005 at a total concentration of 2300 ppq and two tetrachloro dioxin isomers were found in Outfall 031 at a total concentration of 80 ppq. The isomer 2,3,7,8-TCDD and other PCDDs detected in both Outfalls 031 and 005 were not detected in the Tittabawassee River and Lake Huron water intakes to the Dow Chemical plant. Outfall 031 is the main process wastewater discharge from the plant and Outfall 005 contains the discharge from the power house fly ash pond. The isomer 2,3,7,8-TCDF and other PCDFs were also found in the discharges from Outfalls 005 and 031. The concentrations of all PCDFs found in both outfalls exceeded 9000 ppq. The specific sources of these compounds at the Dow Chemical - Midland Plant have not been identified.

If these data represent typical discharge rates, about 1/3 pound of a pound of PCDDs and 10 pounds of PCDFs are released directly to the Tittabawassee River on an annual basis by Dow Chemical. The discharges of PCDDs, PCDFs, and other organic pollutants measured during this survey are probably less than would have been found in the past owing to process and production changes made by Dow Chemical prior to this survey.

C. The complete results from the caged fish bioaccumulation study are not available at this writing. Herbicide analyses for all sampling stations are not complete, and data for PCDDs and PCDFs are not available for certain stations.

The available data for PCDDs and PCDFs demonstrate that PCDDs and PCDFs discharged by Dow Chemical concentrate in fish held in a mixture of the discharge from Outfall 031 and the Tittabawassee River at the point of discharge. Levels of 2,3,7,8-TCDD reached 100 ppt (0.1 ppb) in whole fish, while the concentration of all PCDD isomers ranged from 820 to 1280 ppt (0.82 to 1.28 ppb). The FDA guideline for 2,3,7,8-TCDD is 50 ppt in edible portions of fish. There are, as yet, no guidelines for other PCDD isomers. PCDDs were not found in fish held at various points upstream of the Dow Chemical plant or in unexposed fish at concentrations greater than 8 ppt. Data are not yet available for fish held downstream of the plant. PCDFs were found in the fish exposed to

the discharge of Outfall 031 at levels ranging from 6480 to 17,200 ppt (6.48 to 17.2 ppb). Upstream control fish showed relatively little contamination by PCDFs (8 to 290 ppt).

More than 30 other organic chemicals were also found in fish exposed to the plume of Outfall 031 at levels ranging from a few ppb to over 1 ppm. These chemicals include chlorinated benzenes and phenols, and certain pesticides.

D. The discharge from Outfall 031 was found not be acutely toxic to Daphnia magna over one 48-hour static bioassay testing period; and, not acutely toxic to catfish held continuously for 28 days in a mixture of the discharge and the Tittabawassee River at the point of discharge. Native fish often have been observed in the plume of the discharge. The discharge did not exhibit mutagenic properties in one series of Ames tests (direct test and RLEA test). Based upon one algal assay, the discharge from Outfall 031 has a higher stimulatory effect on algal growth than the river intake water. Although the discharge was found not to be acutely toxic, given the number and type of compounds discharged, the potential chronic or long term effects of the discharge are still of concern.

E. The current practice at Dow Chemical is to mix and treat large volumes of cooling water with the process wastewaters, thus diluting the concentrations of pollutants found in the process wastewaters. Because of the relatively low concentrations of most of the organic chemicals discharged by Dow Chemical, the most effective method to achieve further reduction in the mass discharge of these pollutants is to isolate the contributing sources at the production process unit and provide, where appropriate, additional process-specific pretreatment facilities. At this writing, Dow Chemical has not provided sufficient information and data to EPA and the MDNR for evaluation of alternate pollution control measures.

V. RECOMMENDATIONS

A. The sources of PCDDs, PCDFs, and the other organic chemicals found in Outfall 031 should be identified. Likewise, the source of PCDDs and PCDFs found in Outfall 005 should be determined. Additional testing for PCDDs and

PCDFs at similar and different industrial and municipal facilities should be conducted to determine the potential for widespread low-level discharge of these compounds from other sources. Comprehensive multi-media investigations covering atmosphere emissions, deposition on soil, solid wastes, and untreated and treated wastewater should be conducted at selected industrial sites, including Dow Chemical, to determine the pathways to the environment for PCDDs and PCDFs.

B. The feasibility of additional in-process, end-of-process, and end-of-pipe treatment at Dow Chemical should be established where appropriate.

C. The remaining fish data for herbicides, PCDDs, and PCDFs should be obtained as soon as possible.

D. EPA and MDNR should obtain and evaluate Dow Chemical data for split samples provided to Dow Chemical from this survey.

E. Dow Chemical should document the effect on the discharge of any changes in production operations, air pollution control, or wastewater treatment operations that have occurred since this study was completed.

VI. DOW CHEMICAL - MIDLAND PLANT

A. General Plant Description

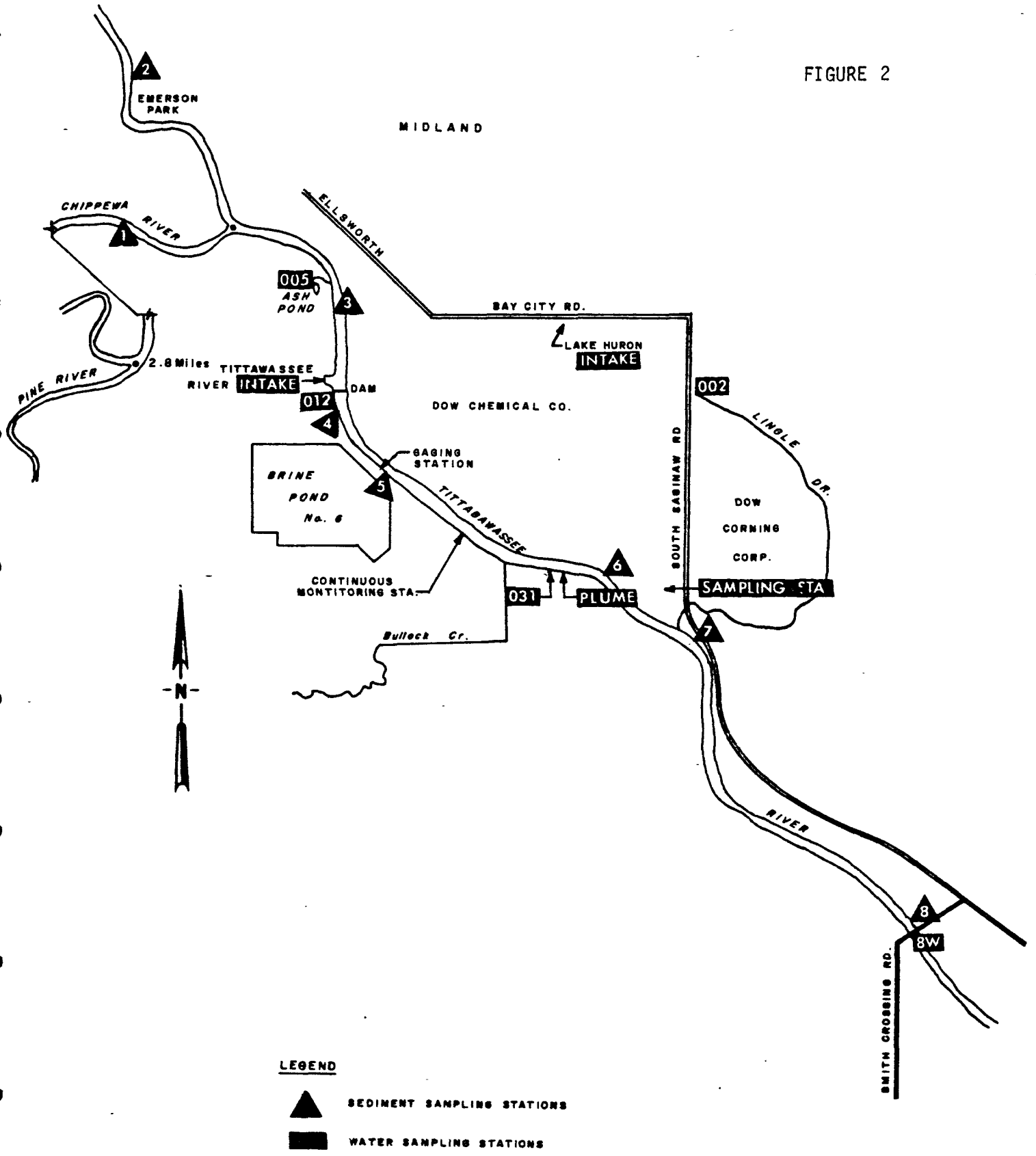
The Dow Chemical - Midland Plant is an operating unit of the Michigan Division of Dow Chemical USA. The facility is located in Midland, Michigan, and extends along both banks of the Tittabawassee River (see Figure 2). The Midland Plant is one of the largest chemical manufacturing complexes in the United States and is operated continuously. About 5000 people are employed at the plant. The following types of chemicals are produced:

1. Alkalies and Chlorine
2. Cyclic Intermediates
3. Industrial Organic Chemicals
4. Industrial Inorganic Chemicals
5. Plastic Materials, Synthetic Resins, and Non-Vulcanizable Elastomers
6. Medicinal Chemicals and Botanical Products
7. Surface Active Agents, Finishing Agents, and Sulfonated Oils
8. Pesticides and Agricultural Chemicals

Dow Chemical discharges contact and non-contact cooling waters, storm water runoff, and treated process and sanitary wastewaters to the Tittabawassee River through five outfalls. In addition to the wastewaters generated at the Midland Plant, the company also treats wastewater from other industries. These include about 1.7 MGD of process wastewaters from the nearby Dow Corning silicone products facility; about 0.18 MGD of sanitary and laboratory wastewaters from the Consumers Power Midland Nuclear Plant; about 0.02 MGD of truck washing wastewaters from the Chemical Leaman and Coastal Trucking Line at Midland; and, about 500 gallons per day of leachate from the Dow Chemical Salzburg Road landfill.

According to Dow Chemical's most recent NPDES permit application, the average daily wastewater flows from these outfalls are as follows:

FIGURE 2


EMERSON PARK
MIDLAND
CHIPPEWA RIVER
ELLSWORTH
005
ASH POND
BAY CITY RD.
LAKE HURON
INTAKE
2.8 Miles
TITTAWASSEE RIVER
INTAKE
DAM
PINE RIVER
012
DOW CHEMICAL CO.
002
LINGLE DR.
GAGING STATION
BRINE POND No. 6
TITTABAWASSEE
SOUTH SAGINAW RD
DOW CORNING CORP.
CONTINUOUS MONITORING STA.
031
PLUME
SAMPLING STA
Bullock Cr.
N
RIVER
8
8W
SMITH CROSSING RD.
LEGEND
SEDIMENT SAMPLING STATIONS
WATER SAMPLING STATIONS

Outfall 005	-	3.9	MGD
Outfall 012	-	30.0	MGD
Outfall 014	-	0.7	MGD
Outfall 015	-	0.3	MGD
Outfall 031	-	26.5	MGD
Total	-	61.4	MGD

The average discharge for Outfall 031 on the sampling dates for this survey was 35.4 MGD. Most of the discharge is comprised of Tittabawassee River water diverted at the Dow Dam into the plant for process and cooling purposes. Other intake water sources include the city of Midland (1.4 MGD) and Lake Huron (10.5 MGD). Lake Huron water is chlorinated and demineralized prior to use in various processes. The other intake waters are generally not treated prior to use.

A description of the sources of effluent discharged through the outfalls active during the EPA-MDNR survey is presented below:

Outfall 002 - At the time of the survey, the discharge was about 5 MGD to the Tittabawassee River via Lingle Drain. The discharge has since been diverted to the wastewater treatment facilities tributary to Outfall 031. The discharge consisted of untreated non-contact cooling water from coolers and heat exchangers in the monomer and polymer plastic production area and various hydrocarbon production processes.

Outfall 005 - The discharge from this outfall is overflow from an ash pond serving the power house. Cooling water, general use water, and boiler blowdown are also diverted to the ash pond. The discharge is to the Tittabawassee River via Ashby Drain.

Outfall 012 - Dow Chemical refers to this outfall as the "H" flume. Non-contact cooling water from the west power house condensers and excess river water are discharged directly to the Tittabawassee River.

Outfall 031 - This discharge consists of treated process wastewaters, cooling water, water softener backwash, cooling tower blowdown, incinerator scrubber water, sanitary wastewaters, surface water runoff, and landfill leachate. Treatment is provided in an end-of-pipe biological

treatment facility followed by a large settling pond called the tertiary pond. The discharge is from the tertiary pond to the Tittabawassee River. Dow Chemical has also installed numerous in-process product and by-product recovery systems and pollution control systems. However, the company has provided only limited information to EPA and MDNR about the processes and the treatment systems. According to MDNR records, Dow Chemical made several process modifications in the period 1978 to 1981 which were designed to improve the discharge from Outfall 031.

Other active Dow Chemical outfalls not described above include Outfalls 001, 014, and 015. Outfall 001 serves as a standby for Outfall 031. Outfalls 014 and 015 convey air conditioner cooling water from the plant administration building directly to the Tittabawassee River. These outfalls were not sampled during the EPA-MDNR survey.

B. Waste Management at the Dow Chemical - Midland Plant

Solid and liquid wastes generated at Dow Chemical and wastewaters received from outside sources are disposed of by one of four methods: (1) concentrated liquids and burnable solid wastes are incinerated; (2) "biodegradable" dilute liquids and a substantial volume of cooling water are processed in the wastewater treatment facilities tributary to Outfall 031; (3) non-biodegradable dilute liquids are injected in one of several deep-wells; and, (4) non-burnable solid wastes are landfilled.

Wastewater Treatment Plant - "Biodegradable" dilute liquids (process and sanitary wastewaters) are separated into two categories - phenolic wastewaters and other organic wastewaters. Figure 3 is a schematic diagram of the biological treatment systems used to treat these wastewaters. Wastewaters from the phenolic processes are pumped to the phenolics pretreatment system, where suspended solids are removed by primary clarification. The wastewaters are then processed in trickling filters and an activated sludge system operated in series. After final clarification, the phenolic plant effluent is directed to the larger biological treatment facility for further treatment with all of the remaining wastewaters described above.

The wastewaters are collected and directed to primary settling tanks where suspended solids are removed. Wastewaters high in BOD and toxic wastewaters can be diverted to a "shot" pond during spills or emergencies and metered into the treatment system at a controlled rate. The overflow from the primary tanks is combined with the effluent from the phenolics treatment plant prior to entering activated sludge aeration basins for biological treatment. From the aeration basins, the wastewater is fed to secondary clarifiers. Settled activated sludge is recycled to the aeration basins. Effluent from the secondary clarifier is pumped to the teritiary pond, which is about 200 acres in area and has a maximum capacity of about 600 million gallons. The retention time in the pond provides for temperature equalization and continued biological action. The effluent from the tertiary pond is discharged to the Tittabawassee River through Outfall 031.

Primary sludge from the biological treatment facility is pumped to clay pits located near the intersection of Saginaw and Salzburg Roads and dewatered. The dewatered sludge is ultimately disposed of at Dow Chemical's Salzburg Road landfill. The supernatant from the clay pits is returned to the wastewater treatment plant. Sludge from the phenolic treatment system is either recycled or processed in the other biological treatment system. Secondary sludge from the biological treatment system is thickened, filtered and incinerated.

Incineration - The incineration area includes a rotary kiln (refuse burner) and a tar burner (thermal oxidizer). The tar burner is a standby unit for the rotary kiln. The tar burner operates at 1000°C in a single combustion chamber with a retention time of about 2 seconds. Only liquids or gases are incinerated in this unit. The liquid feed rate is 7.5 gpm. The refuse burner is fed solid and liquid wastes. The rotary kiln or primary combustion chamber provides about 45 minutes retention at 600-800°C. Exit gases are routed to a secondary combustion area where they are subjected to 1000°C at a retention time of about 2 seconds. The refuse burner is fired with tars or natural gas. Both units have qualified for interim status under RCRA.

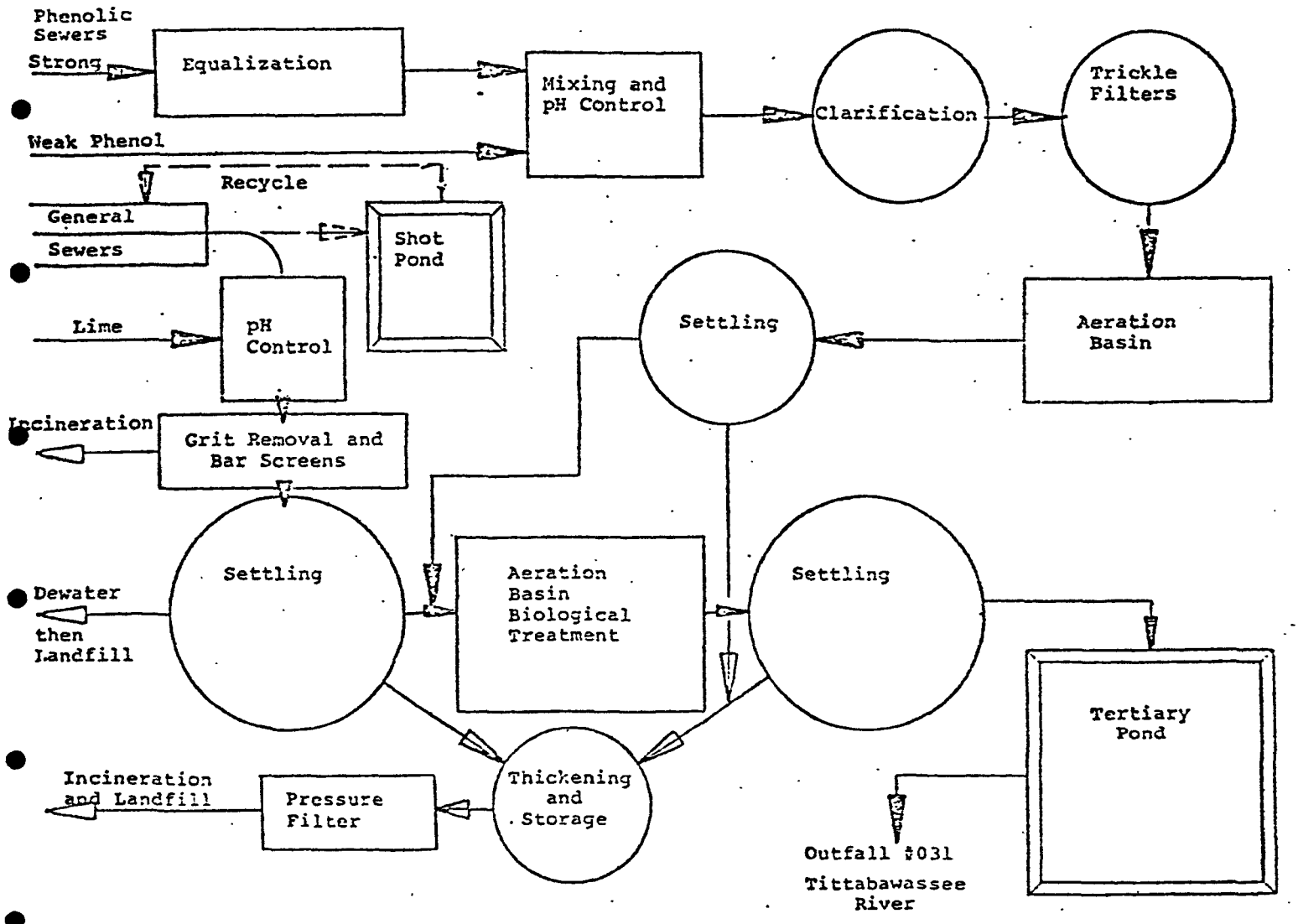
Incinerator ash is landfilled at the Salzburg Road landfill. Incinerator stack gases are scrubbed with effluent from the wastewater treatment system. The scrubber effluent is then returned to the wastewater treatment system.

Landfill - Dow Chemical has been operating a landfill located on Salzburg Road since January 1981. The landfill was approved by MDNR for hazardous waste disposal on February 10, 1982, and has qualified for interim status under RCRA. As noted above, incinerator ash, wastewater treatment sludges, contaminated soil, and demolition material are currently landfilled at this site. Leachate collected from the landfill is diverted to the wastewater treatment plant.

Disposal Wells - Dow Chemical disposes of a small volume of process wastewaters by deep well injection. These wastewaters cannot be readily treated by other means. About 18 gpm are passed through sand filters and then pumped into the receiving underground formation. Dow Chemical had operated as many as seven deep disposal wells and had disposed of as much as 120 gpm in this fashion in the past. Wastewaters disposed of by deep well injection contain several organic compounds and are typically high in dissolved salts. According to the MDNR critical materials list for the disposal wells submitted by Dow Chemical, some of the compounds injected are benzenes, dioxins, phenols, metals, PCBs, styrene, chloroform and others.

FIGURE 3

MICHIGAN DIVISION
WASTE TREATMENT PLANT (WTP)



MIDLAND WASTE WATER TREATMENT PLANT
THE DOW CHEMICAL COMPANY U.S.A., MICHIGAN DIVISION

VII. FIELD STUDIES

A. Sediment Sampling

A sediment survey of the Tittabawassee River from 0.5 miles upstream of State Route M-20 downstream to Smith's Crossing Road was conducted on March 18-19, 1981. River sediment grab samples were obtained for analysis at eight locations shown on Figure 2. The locations of the sampling sites for the water sampling survey described below are also presented in Figure 2. Each sediment sampling site is described in Table 1. Because the stream bottom is mostly sand and gravel, an attempt was made to select sites which appeared to have accumulations of organic material. For this reason, the samples do not represent average or typical Tittabawassee River sediment quality. However, the data obtained do provide an indication of the types of compounds discharged in the area that accumulate in sediments. The results presented in Appendix A show that more than 40% of the compounds positively identified and quantified were either benzenes or benzene derivatives. Also, more than 90% of the compounds detected were found in samples obtained at sampling stations which are near or downstream of Dow Chemical - Midland Plant discharges. Only one compound, di-n-octylphthalate, was identified upstream of the Dow Dam. Several unidentified compounds were detected in some of the sediment samples. Given the nature of the sediments and anticipated discharge levels of PCDDs and PCDFs from Dow Chemical, the sediment samples were not analyzed for PCDDs or PCDFs.

B. Conventional Water Sampling Program

During September 1981, four 24-hour composite sampling programs were conducted at the Dow Chemical - Midland Plant. The sampling dates, the water intakes, and selected effluent discharges sampled are listed below:

Survey Number	Date	Sampling Stations: Intakes	Sampling Stations: Outfalls, Other
1	September 1-2, 1981	LH, TR*	002, 005, 012, 031, 031P**, DC***
2	September 9-10, 1981	LH, TR	005, 031, 031P, TRSC****
3	September 15-16, 1981	LH, TR	031, 031P, DC
4	September 29-30, 1981	LH, TR	031, 031P

* TR - Tittabawassee River Intake
LH - Lake Huron Intake
** 031P - Plume of Outfall 031 in the Tittabawassee River
*** DC - Untreated Wastewater From Dow Corning
**** TRSC - Tittabawassee River at Smith's Crossing Road

TABLE 1

SEDIMENT SAMPLING LOCATIONS
TITTABAWASSEE AND CHIPPEWA RIVERS: M-20 to Smith's Crossing
MARCH 18-19, 1981

Station Number	Sample Number	Stream	River Mile Point	Location and Site Specific Collection Method
1*	81EH03S01	Chippewa	0.6	The sample was collected with a large metal spoon in about 1 foot of water near north shore approximately 0.6 miles above the Tittabawassee River confluence.
2*	81EH03S08	Tittabawassee	24.0	The sample was collected with a large metal spoon at Emerson Park just below Snake Creek near east bank.
3	81EH03S02	Tittabawassee	23.5	The sample was obtained with a Petersen dredge above the Dow dam near the west bank and opposite Dow building #73.
4	81EH03S03	Tittabawassee	22.5	The sample was collected near the west bank immediately below Dow Chemical's H-flume discharge which is below the Dow dam. The sample was obtained with a Petersen dredge.
5	81EH03S04	Tittabawassee	22.0	The sample was collected near west bank opposite brine pond #6. The sample was obtained with a Petersen dredge.
6	81EH03S05	Tittabawassee	20.5	The sample was obtained near the east bank about ½ mile below Bullock Creek. The sample was collected with a Petersen dredge.
7	81EH03S06	Tittabawassee	20.0	The sample was obtained near the east bank about 500 feet below the Lingle drain confluence. The sample was collected with a Petersen dredge.
8	81EH03S07	Tittabawassee	19.0	The sample was obtained near the east bank about 200 feet about Smith's Crossing Road bridge. A Petersen dredge was used to collect the sample.

* These samples were not analyzed.

Outfalls 014 and 015 were not sampled since the discharge from these outfalls is office building air conditioning water. The samples obtained from each of the above listed sites were analyzed for conventional pollutants, non-conventional pollutants, toxic metal pollutants, and toxic organic pollutants. Various physical measurements were also made during each 24-hour sampling period. The gross discharges from Outfall 031 are summarized below. The complete data will be included in the final report. A summary of the gross pollutant loadings at each point sampled is presented in Appendix B.

1. Conventional and Non-Conventional Pollutants, Nutrients, Dissolved Salts

Outfall 031
(Gross Discharge in Pounds/Day)

Survey	1	2	3	4
Pollutants				
Total Dissolved Solids	810,000	790,000	676,000	960,000
Chloride	340,000	358,000	303,000	428,000
Fluoride	200	200	160	190
Sulfate	87,000	81,000	64,000	75,000
Total Suspended Solids	1,450	2,600	3,640	7,130
Chemical Oxygen Demand	34,500	29,200	38,500	41,300
Total Organic Carbon	4,640	6,060	5,460	7,880
BOD_5	---	1,450	1,370	1,500
Total Kjeldahl Nitrogen	1,860	2,070	1,700	1,630
Ammonia-N	1,640	1,750	1,310	1,180
NO_2 and NO_3-N	115	104	11	41
Phosphorus (P)	130	320	420	146

The discharge from Outfall 031 carries high loadings of dissolved salts to the Tittabawassee River (total dissolved solids concentrations ranging from about 2,800 to 3,000 mg/l; chloride concentrations ranging from about 1,200 mg/l to 1,300 mg/l; sulfate concentrations ranging from about 280 to 300 mg/l). The discharge contains relatively low

levels of suspended solids and readily biodegradable material. As noted in Section C, the discharge of nutrients can have a stimulatory effect on algal growth.

2. Toxic Metal Pollutants

Outfall 031
(Gross Discharge in Pounds/Day)

Survey	1	2	3	4
Total Metals				
Arsenic	---	0.87	---	---
Cadmium	---	---	---	---
Chromium	2.30	3.60	3.20	3.75
Copper	0.58	1.40	---	1.13
Lead	---	---	---	---
Zinc	18.0	26.8	23.2	39.4

Based upon these data, the discharge of the above toxic metals from Outfall 031 does not appear to be of concern from a water quality standpoint. Typical effluent concentrations are as follows: arsenic (ND to 3 ppb); cadmium (ND); chromium (8 to 14 ppb); copper (ND to 5 ppb); lead (ND); and zinc (60 to 100 ppb).

3. Toxic Organic Pollutants

Outfall 031
(Gross Discharge in Pounds/Day)

Survey	1*	2	3	4
a. Volatile Compounds				
(B-1,3,4) Methylene chloride	26.12	No Sample	1.30	45.00
1,1-Dichloroethylene	0.87	"	0.70	5.25
1,1-Dichloroethane	1.31	"	1.00	1.80

Survey		1*	2	3	4
(B-1,3,4)	Chloroform	2.87	No Sample	3.00	9.38
(B-1,3,4)	1,2-Dichloroethane	2.41	"	2.00	3.75
	1,1,1-Trichloroethane	0.92	"	1.02	4.13
	Carbon Tetrachloride	3.78	"	2.10	18.77
(B-4)	Bromodichloromethane	0.83	"	---	1.24
	1,2-Dichloropropane	0.55	"	0.90	1.91
	Trichloroethylene	0.35	"	0.60	1.39
	Dibromochloromethane	1.04	"	---	4.88
	1,1,2,2-Tetrachloroethane	1.13	"	0.80	7.51
	Chlorobenzene	---	"	1.00	---
	Bromoform	---	"	---	4.50

* Average of two grab samples for volatile compounds.
(B-1,3,4) Blank Contamination - Surveys 1,3,4
(B-4) Blank Contamination - Survey 4

b. Base/Neutral Compounds

	Pyrene	---	---	0.27	---
	2-Chloronaphthalene	0.26	---	---	---
	1,2-Dichlorobenzene	Trace	Trace	Trace	---
	1,3-Dichlorobenzene	0.41	0.41	0.13	0.71
	1,4-Dichlorobenzene	0.64	0.29	0.19	0.75
	1,2,4-Trichlorobenzene	1.19	0.58	0.32	1.39
(B-1,4)	Di-n-butyl phthalate	0.21	---	---	0.21
	Butyl benzyl phthalate	---	---	---	Trace
(B-2,3)	Bis(2-ethylhexyl) phthalate	21.2	60.6	7.1	3.42
	Bis(2-chloroethyl) ether	0.04	0.28	0.25	1.28
(B-4)	Isophorone	---	Trace	Trace	---
	Dioctyl phthalate	---	2.05	---	---
	Acenaphthene	---	---	---	0.17

(B-1,4) Blank Contamination - Surveys 1 and 4
(B-2,3) Blank Contamination - Surveys 2 and 3
(B-4) Blank Contamination - Survey 4

Survey	1	2	3	4
c. Acid Compounds				
2-Chlorophenol	0.28	Trace	Trace	Trace
Phenol	0.28	---	Trace	Trace
2,4-Dichlorophenol	0.35	---	---	0.26
2,4,6-Trichlorophenol	1.25	---	---	Trace
Pentachlorophenol	4.35	0.55	---	0.94
d. Herbicides				
Dichloroprop	---	---	0.02	0.22
2,4-D	0.01	---	0.30	---
Silvex	---	0.03	1.60	2.14
2,4,5-T	---	---	0.40	0.18
e. Pesticides, PCBs				
(B-1) Aldrin	0.06	0.06	---	0.21
(B-1) 4-4'-DDD	0.01*	---	---	0.01*
Endosulfan I	0.03*	---	---	---
Endrin aldehyde	0.01*	0.02*	---	0.01*
Heptachlor epoxide	0.01	0.01*	---	0.02**
β -BHC	---	0.01	---	---
γ -BHC	---	---	---	0.01*
PCB-1242	---	---	1.10	---
PCB-1254	---	---	0.09	---
PCB-1260	---	---	0.20	---

* Not confirmed on second column GC/ECD.

** Not confirmed on second column GC/ECD due to interference.

(B-1) Blank Contamination - Survey 1

f. Other Organic Compounds

The concentrations of the compounds listed below were determined by the analyst by selecting the best fit from a computerized library search program to the mass spectra obtained for each sample. The quantitation of these compounds was not accomplished using a pure standard of each compound, but was calculated against the response of an internal standard. Thus, the pollutant loading data and identification of each compound presented below are considered tentative.

1) Volatile Compounds

Survey	1*	2	3	4
Methane, dimethoxy	3.77	No Sample	21.90	45.04
Ethane, 1,1'-oxy bis	43.52	"	6.60	13.14
Methane, oxy bis	25.63	"	---	4.13

* Average of two grab samples for volatile compounds.

2) Extractable Compounds

2-Propanol, 1(2-methoxy-1 methylethoxy), or isomers	4.10	2.20	3.40	19.89
2,5-Cyclohexadiene-1,4-dione, 2,6-Bis(1,1-dimethylethyl) isomers	0.90	---	---	---
Pentanone, hydroxy methyl	---	---	1.30	---
2-Propanol, 1-(2-methoxy, propoxy)	---	---	---	101.30
1-Propanol, 2-(2-hydroxy, propoxy)	---	---	---	60.05
Benzamide, N-butyl	---	---	---	2.70
Oxy bis propanol	---	---	---	33.03

The discharge from Outfall 031 contains more than 50 organic chemicals including volatile compounds, base/neutral compounds, acid compounds, pesticides, PCBs, and herbicides. Most of the compounds were detected at concentrations in the low and sub-ppb range. If lower levels of detection were available, it is likely more chemicals would have been found, particularly those found in the untreated wastewaters (such as the Dow Corning effluent). While the effluent is not acutely toxic (see Section C), the continued net discharge of more than 35 lbs/day of toxic organic chemicals to the environment is of concern. Methylene chloride and discharges of those chemicals listed in item f above were not included in this estimate. On an annual basis, 35 lbs/day is equivalent to over 6 tons/year.

C. Static Daphnia Bioassay, Algal Assay, Ames Test

1. Static Bioassay

Static bioassays, using Daphnia magna, were completed on samples obtained during the third conventional water survey, September 15-16, 1981. The samples were obtained from the Dow Chemical Lake Huron and Tittabawassee River Intakes, Outfall 031, and a field blank. The bioassay was begun on September 22, 1981, and conducted according to the protocol outlined in "Standard Operating Procedure for Static Bioassay Screening Test," EPA Region V - Central Regional Laboratory. The results of the bioassay are presented in Table 2.

The Lake Huron Intake sample produced 100% mortality in both aliquots. The mortalities are due to the presence of chlorine in the sample which was not removed prior to testing. The Lake Huron water supply is chlorinated by Dow Chemical at its lake pumping station. The mortalities observed in the other samples, including the blank and controls are not considered significant. The discharge from Outfall 031 on September 15-16, 1981, did not exhibit acute toxic effects to Daphnia magna.

2. Algal Assay

A static algal assay was conducted on the same samples collected for the daphnia bioassay. The algal assay followed the procedure, "Standard Operating Procedure for Screening Algal Assay for Determination of Inhibiting or Stimulating Effects of Effluents," EPA Region V - Central Regional Laboratory. The results, which are based on a comparison to a control population, are presented below in Table 3.

Table 2

Static Daphnia Bioassay

(Number of Survivors and Percent Mortality in Duplicate Test Aliquots)

	Aliquot	No. of Survivors			Percent Mortality		
Time (Hours)		0	24	48	0	24	48
Control	a.	10	9	9	0	10	10
	b.	10	9	9	0	10	10
Lake Huron Intake	a.	10	0	0	0	100	100
	b.	10	0	0	0	100	100
Outfall 031	a.	10	10	10	0	0	0
	b.	10	10	10	0	0	0
Tittabawassee River Intake	a.	10	9	9	0	10	10
	b.	10	10	10	0	0	0
Field Blank	a.	10	8	8	0	20	20
	b.	10	7	0	0	30	100

Table 3

Static Algal Assay

Sample	Effect	
Lake Huron Intake	Inhibition	51.3%
Tittabawassee River Intake	Stimulation	63.9%
Outfall 031	Stimulation	191.6%
Field Blank	Stimulation	102.8%

The Lake Huron sample inhibited algal growth because of the chlorine present in the sample. The discharge from Outfall 031 and the field blank showed high stimulatory effects on algal growth. The effect produced by the discharge from Outfall 031 is about twice that of the field blank and three times higher than the Tittabawassee River upstream of Outfall 031. This is due to the level of nutrients in the discharge. The observed stimulatory effect in the field blank is believed to be a result of low level nutrient concentrations present in the sample, possibly the result of the bottle preparation or the distilled water used to make up the blank.

3. Ames Test

The Ames Test was used for the purpose of determining whether the discharge from Outfall 031 exhibits mutagenic properties. This test was conducted on the samples described above. For each sample, a concentrated sample extract (100X) was used to conduct a direct test and a rat liver enzyme activation (RLEA) test for five bacteria test strains. No mutagenic activity was found in either the direct or the RLEA test.

D. Large Volume Water Sampling for PCDDs and PCDFs

A pilot study was conducted for EPA-Region V by Wright State University to develop a sampling and analytical method to determine PCDDs and PCDFs in aqueous samples in the sub-part per trillion range. In short, this method consists of obtaining a large volume water sample; performing an extraction with a suitable solvent for an extended period; solvent exchange and clean-up; and HRGC-HRMS analyses of the extract for the desired

compounds. After completion of the pilot study, actual effluent and river samples were obtained. Based upon the quality control completed with the pilot study and with the analyses of the field samples, all of the data for PCDDs and PCDFs presented below are considered to be of acceptable quality. Reference is made to Appendix C for a summary of the analytical methodology and quality control for the large volume sampling study.

One 24-hour composite water sample was taken at each of the following points and extracted and analyzed for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo furans in accordance with the protocols summarized in Appendix C. Dow Chemical was provided split samples for its analysis along with the extraction and analytical protocols.

Dow Chemical - Midland Plant

- Lake Huron Water Intake
- Tittabawassee River Intake
- Outfall 005 (Power House Fly Ash Pond)
- Outfall 031 (Main Process Wastewater Discharge)

Tittabawassee River

- Outfall 031 Plume
- At Smith's Crossing

The results from this study are presented graphically in Figures 4 and 5 for dioxins, and Figures 6 and 7 for furans. The data are presented in Appendix D.

1. Dioxins

Neither 2,3,7,8-TCDD nor any other dioxin isomers were found in the water intakes to the Dow Chemical Plant at the 10 parts per quadrillion (ppq) level. 2,3,7,8-TCDD was not detected, but may have been present in Outfall 005. The high levels of other tetrachloro isomers may have obscured the response of the 2,3,7,8 isomer in that sample. The combined concentration of five other tetrachloro isomers found in the discharge from Outfall 005 exceeded 2000 ppq (the mass discharge to the Tittabawassee River was about 7×10^{-5} lbs/day). None of the penta-, hexa-, hepta-, or octachloro isomers were detected in Outfall 005.

2,3,7,8-TCDD was positively identified in the discharge from Outfall 031 at a level of 50 parts per quadrillion (mass discharge of between 1 and 2×10^{-5} lbs/day). The total

mass discharge of the two tetrachloro isomers found in Outfall 031 was in excess of 2×10^{-5} lbs/day. 2,3,7,8-TCDD, an additional tetrachloro isomer, and one pentachloro dioxin isomer were found in the discharge plume of Outfall 031 in the Tittabawassee River in the range of 35 to 50 parts per quadrillion. Three tetrachloro isomers, not including 2,3,7,8-TCDD, were found downstream in the Tittabawassee River at Smith's Crossing Road at a total concentration of 40 parts per quadrillion.

2. Furans

The results for polychlorinated dibenzo furans are similar to those for dioxins although furans were detected at higher levels. Both the Lake Huron and Tittabawassee River water intakes contained detectable quantities of 2,3,7,8-TCDF and a few other isomers at less than 100 ppq, while the discharges from Outfalls 005 and 031 contained significantly higher concentrations of 2,3,7,8-TCDF (about 1700 ppq and 800 ppq, respectively) and other tetra- and penta- chloro isomers (several thousand ppq for both outfalls). The discharge from Outfall 005 may have influenced the results for the Tittabawassee River intake sample as the outfall empties into the river upstream of the intake. The mass discharge of all furan isomers from Outfall 005 was about 33×10^{-5} lbs/day, and nearly 300×10^{-5} lbs/day from Outfall 031. PCDFs were also found in the Outfall 031 plume and downstream in the Tittabawassee River at Smith's Crossing.

FIGURE 4

DOW CHEMICAL-TITTABAWASSEE RIVER STUDY
LARGE VOLUME WATER SAMPLES
POLYCHLORINATED DIBENZO-P-DIOXINS

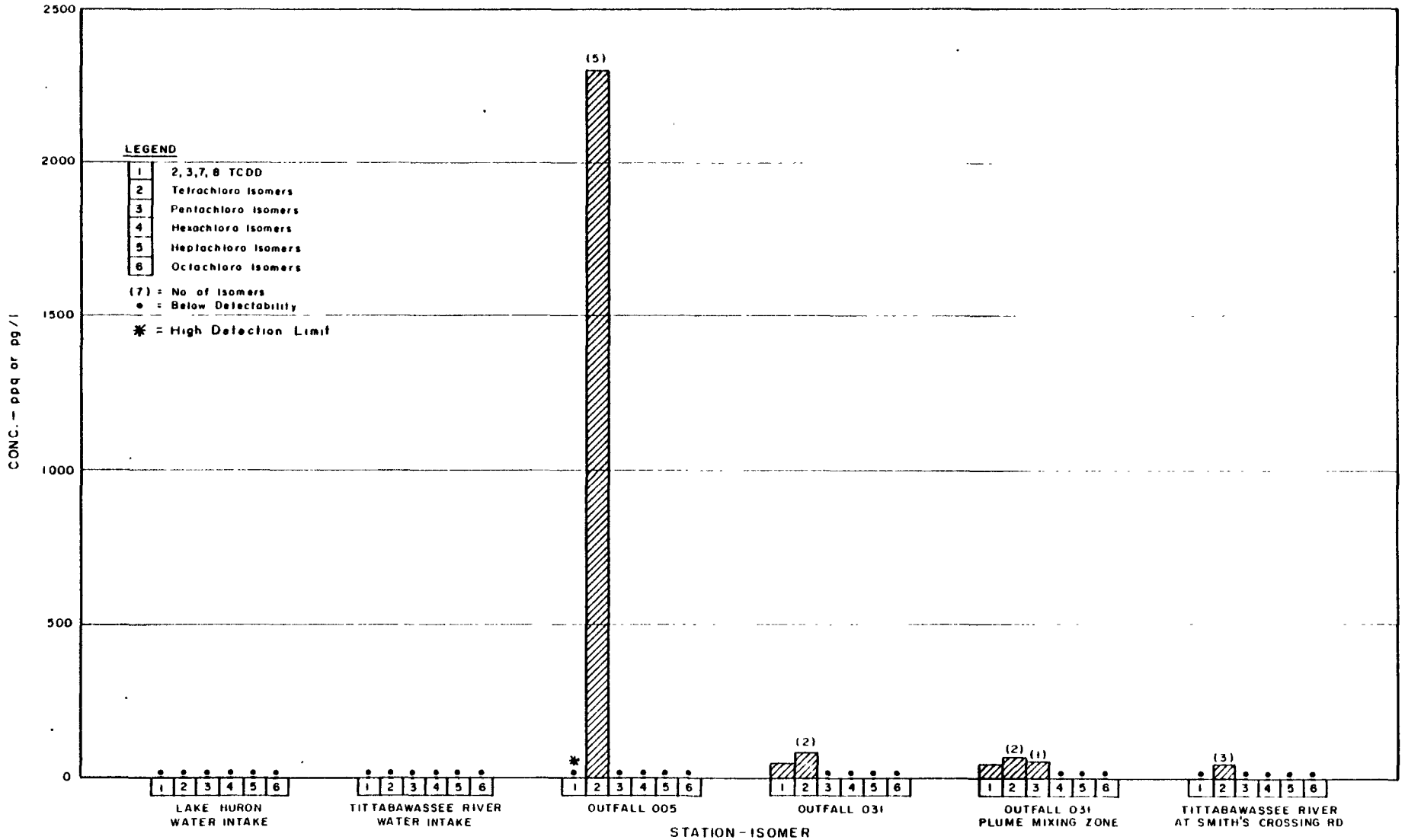


FIGURE 5

DOW CHEMICAL-TITTABAWASSEE RIVER STUDY
LARGE VOLUME WATER SAMPLES
POLYCHLORINATED DIBENZO-P-DIOXINS

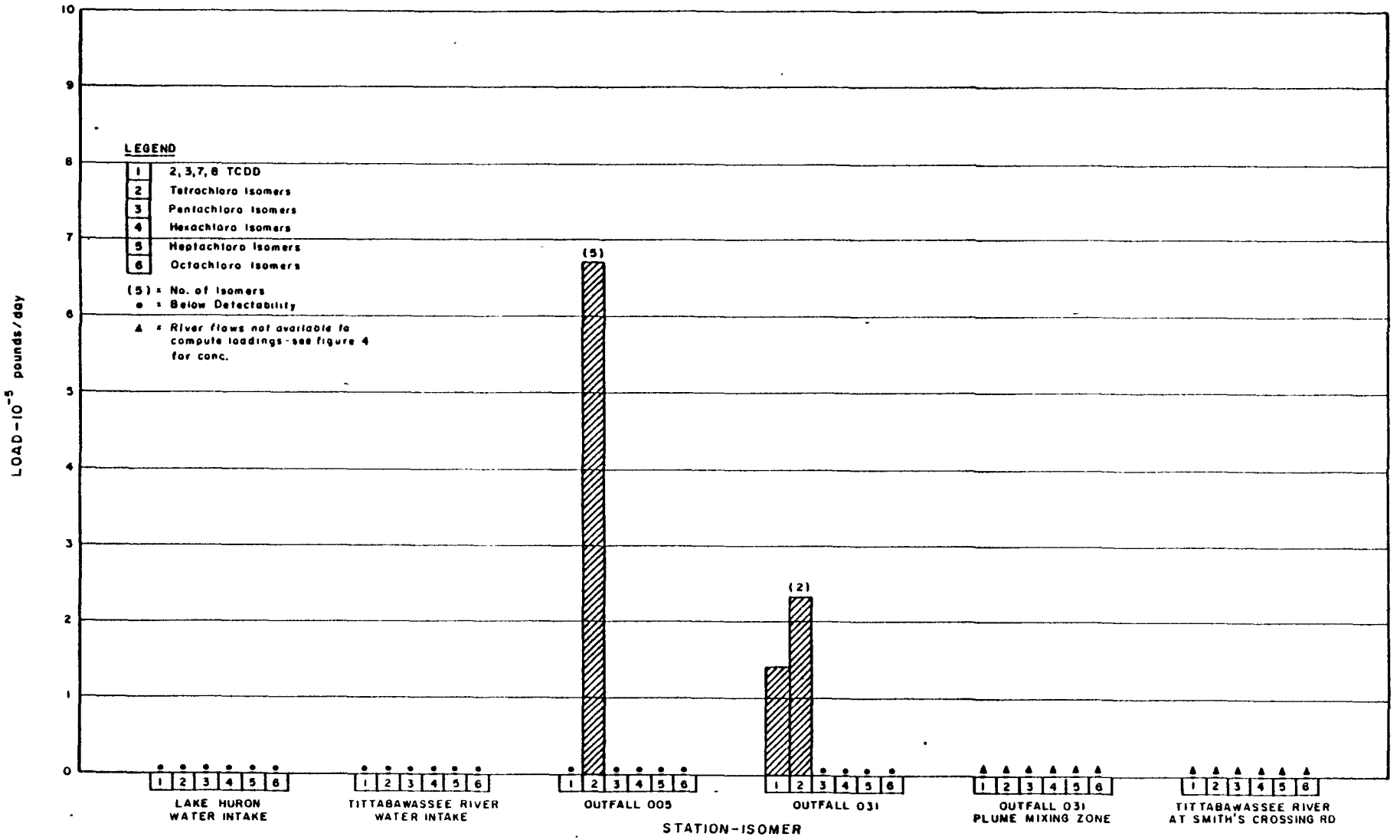


FIGURE 6

DOW CHEMICAL-TITTABAWASSEE RIVER STUDY
LARGE VOLUME WATER SAMPLES
POLYCHLORINATED DIBENZOFURANS

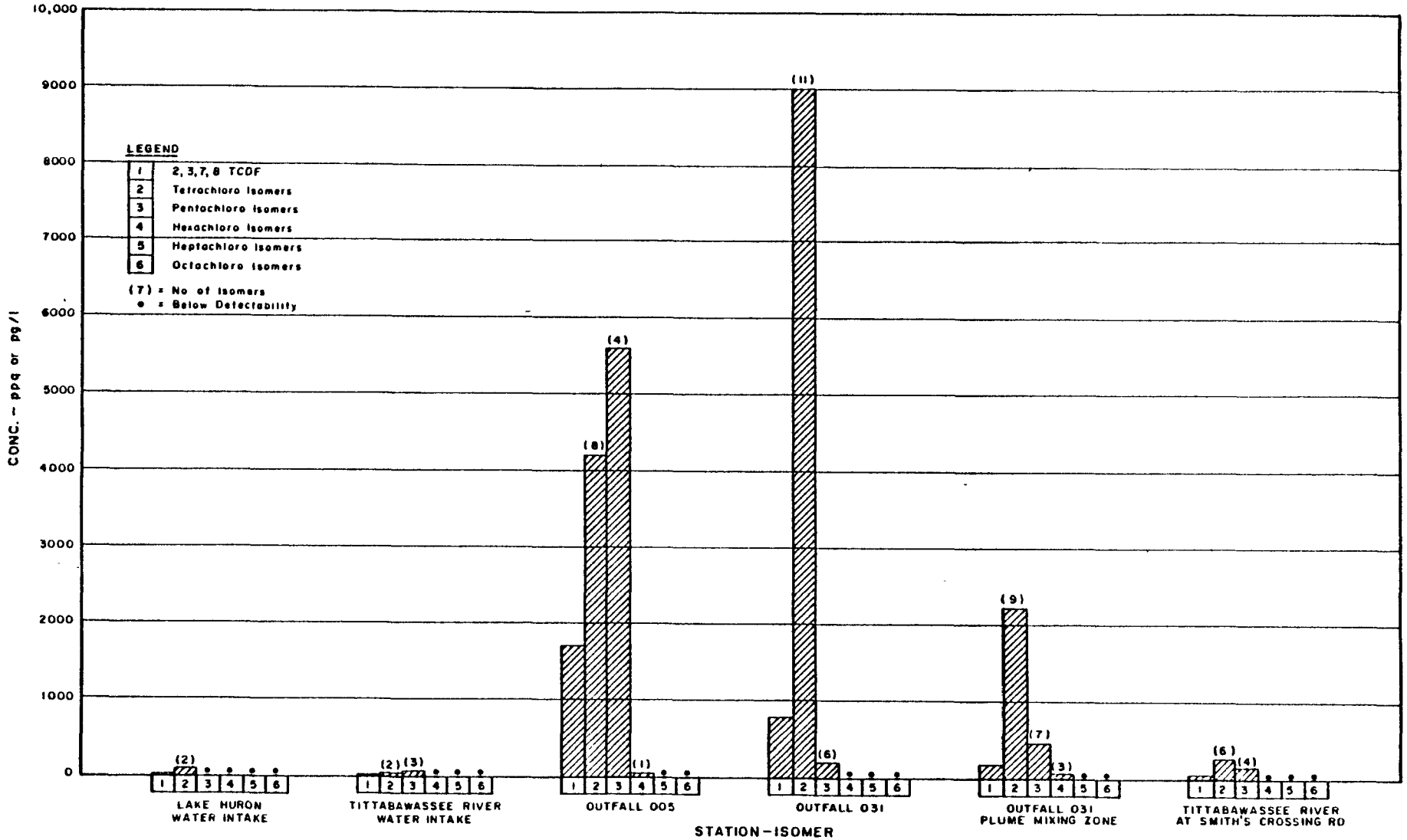
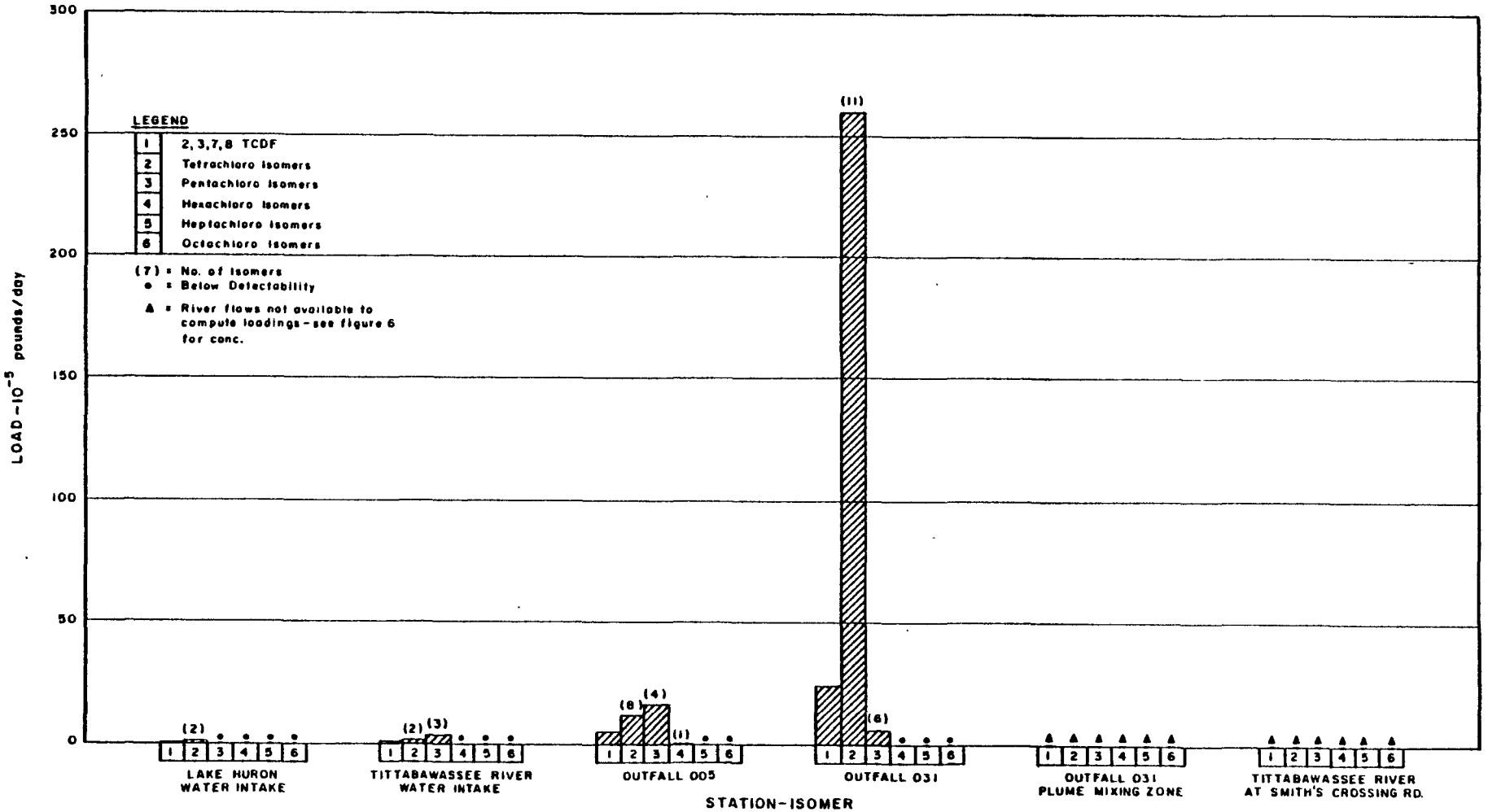


FIGURE 7

DOW CHEMICAL-TITTABAWASSEE RIVER STUDY
LARGE VOLUME WATER SAMPLES
POLYCHLORINATED DIBENZOFURANS



E. Bioaccumulation Study

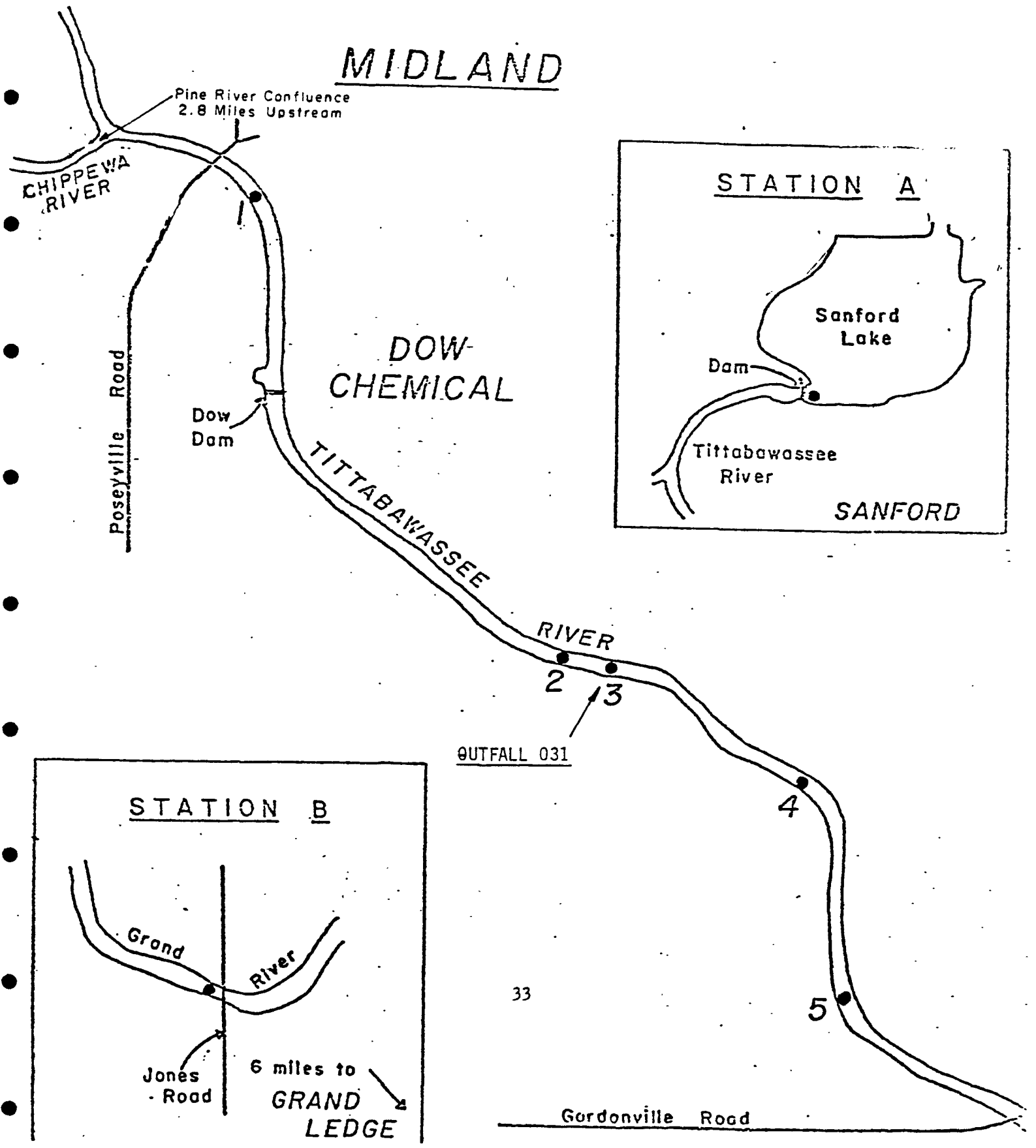
A bioaccumulation study was conducted in the Tittabawassee River around the Dow Chemical - Midland Plant to determine which toxic organic chemicals discharged by Dow Chemical bioaccumulate in fish exposed to the effluent. Caged catfish were exposed to the plume of Dow Chemical's process wastewater effluent (Outfall 031) in the Tittabawassee River for a period of 28 days. Whole fish were analyzed after various periods of exposure for PCDDs, PCDFs, and other organic compounds. The caged fish were fed during the experiment to maintain their body weight and general health. All of the fish were acclimated in a laboratory prior to the study. Caged fish were also exposed to the Tittabawassee River both upstream and downstream of Dow Chemical to establish appropriate controls and reference points. At the request of the MDNR, caged fish were placed in the Grand River at Jones Road near Grand Ledge, Michigan and analyzed with native fish from the Grand River.

The original study plan called for exposing the fish directly to Dow Chemical's process wastewater effluent at the outlet of the tertiary pond just upstream from Outfall 031 and also analyzing native fish from the tertiary pond. However, Dow Chemical objected, contending that EPA's legal authority under Section 308 of the Clean Water Act does not extend to such activities. Rather than engage in lengthy arguments, and possibly litigation, over this matter, the study plan was modified to place the caged fish in the plume of Outfall 031 in the Tittabawassee River rather than in the outlet of the tertiary pond. Based upon conductivity and dissolved solids measurements of the discharge from Outfall 031 and the plume, the fish in the plume were exposed to the outfall discharge diluted at or less than 1:1 by river water.

The locations at which caged fish were exposed are listed below and shown on Figure 8.

Station Number	Location
--	Control - Central Regional Laboratory
A	Tittabawassee River Upstream of Sanford Dam
1	Tittabawassee River at Poseyville Road
2	Tittabawassee River Downstream of Dow Dam but Upstream of Outfall 031

Figure 8


MIDLAND
Pine River Confluence
2.8 Miles Upstream
CHIPPEWA RIVER
1
Posey-ville Road
Dow Dam
DOW CHEMICAL
TITTABAWASSEE RIVER
2
3
OUTFALL 031
4
5
Gordonville Road
STATION A
Sanford Lake
Dam
Tittabawassee River
SANFORD
STATION B
Grand River
Jones Road
6 miles to GRAND LEDGE

3	Tittabawassee River in Outfall 031 Mixing Zone (Plume)
4	Tittabawassee River Outside of the Outfall 031 Mixing Zone (About 1.98 Miles Downstream from the Dow Dam)
5	Tittabawassee River About 2.65 Miles Downstream from the Dow Dam
B	Grand River at Jones Road near Grand Ledge, Michigan

The final report of this study will present a detailed account of the bioaccumulation study, including the field and analytical protocols followed. The results available at this writing are summarized in Figures 9 to 15. Because of the high cost for contract analyses for PCDDs and PCDFs, Region V limited the initial set of analyses to selected samples. These included the fish food, control fish, and caged fish exposed for 28 days at Stations A, B, 1, and 3. Based upon the results presented here, analyses for selected samples at Stations 2, 3, 4, and 5 for dioxins and furans are now being completed. Analyses for other toxic organic chemicals except herbicides have been completed. The herbicide analyses should be available in the near future. Except as noted, the data presented below are considered by EPA to be valid data based upon the quality control work completed. Reference is made to Appendix E for all of the data available at this writing from the bioaccumulation study. Reference is made to Appendix F for a summary of the analytical protocols and quality control for the analyses of PCDDs and PCDFs in fish.

All of the results presented below are based upon analyses of the whole fish. Separate analyses of fish filets or fatty tissue were not completed. Dow Chemical was provided with split samples of the ground fish for its analyses.

1. Dioxins and Furans

Figure 9 illustrates that 2,3,7,8-TCDD was found in fish exposed for 28 days in the plume of Outfall 031 at levels of about 100 parts per trillion (ppt). The total concentration of tetrachloro PCDD isomers found was about 800 ppt. Also, three pentachloro PCDD isomers were found in a duplicate sample (second fish) at a total

concentration of about 500 ppt. 2,3,7,8-TCDD was found at 7 ppt (near the detectable level of 5 ppt) in the control fish and at 8 ppt in the fish held for 28 days at Station 1 upstream from Dow Chemical. No PCDD's were found in the fish food, a duplicate Day 28 sample from Station 1, and at Station B (Grand River). These data and those from the large volume sampling study demonstrate that Dow Chemical discharges 2,3,7,8-TCDD and other dioxin isomers to the Tittabawassee River and that these compounds can concentrate in fish to levels in excess of the FDA guideline for 2,3,7,8-TCDD of 50 ppt.

The results for furans are similar in that relatively little or no furans were found except in the fish exposed to the Outfall 031 plume (see Figure 10). The levels of furans found were about an order of magnitude higher than the levels of dioxins. It is noteworthy that the caged fish in this study were not exposed to bottom sediments at any station. Thus, the fish were not able to feed from the bottom as do certain species of native fish. This should be considered when comparing these data to data obtained from native fish which may be exposed to dioxins, furans, and other compounds in bottom sediments.

Figures 11 and 12 present PCDDs and PCDFs for native fish obtained from the Grand River at Jones Road and Francis Road by the MDNR. These data show 2,3,7,8-TCDD was found in the Jones Road fish at a concentration of 20 ppt and one pentachloro isomer was found at a concentration of 25 ppt. PCDDs were not found in the fish sample from Francis Road. 2,3,7,8-TCDF was found at 40 ppt in the Jones Road fish. In all, seven tetrachloro dibenzo furan isomers were found at a total concentration of 230 ppt; four pentachloro isomers at 140 ppt; and, two hexachloro isomers at 30 ppt. For the fish obtained at Francis Road, one tetrachloro isomer other than 2,3,7,8-TCDF was found at a concentration of 20 ppt.

2. Base Neutral Compounds

Figure 13 summarizes the results for base neutral compounds. These data show that fish exposed to Outfall 031 readily accumulated several base neutral compounds, principally chlorinated benzenes (dichloro, trichloro and hexachloro). Aside from contamination by phthalate compounds and naphthalene and phenanthrene, the control fish did not contain the same base neutral compounds as found in the fish exposed to Outfall 031. 1,2,4–Trichlorobenzene was found in fish from Station 1 upstream of Dow Chemical at a level 15 to 20 times lower than found in fish exposed to Outfall 031. The downstream Tittabawassee River fish showed lower levels of most of the chlorinated

benzene compounds accumulated in fish exposed to the plume from Outfall 031. The Day 28 fish and duplicate Day 28 fish from the Grand River showed highly variable levels of naphthalene. Chlorinated benzenes were not found in the Grand River fish.

3. Acid Compounds

The control fish showed no accumulation of acid compounds (Figure 14). However, phenol was detected but not confirmed in fish exposed at Station A - Sanford Dam and Station 1 - Poseyville Road. 2,4,6-Trichlorophenol and pentachlorophenol were found in caged fish exposed at Poseyville Road for 28 days at levels of 160 and 630 ppb, respectively. These results may be due to the influence of the Pine River which empties into the Tittabawassee River via the Chippewa River upstream of Poseyville Road. The Pine River is known to have contaminated sediments and receives industrial discharges. Pentachlorophenol was found in fish exposed to the Outfall 031 plume at levels up to 1300 ppb. Phenolic compounds were not found in fish exposed at Stations 4 and 5, downstream from Dow Chemical.

4. Pesticides, PCBs

The data summarized in Figure 15 illustrate that the greatest number and highest levels of pesticides were found in the fish exposed to the plume of Outfall 031. The total weight of accumulated pesticides generally increased with time of exposure. It is important to note that some of the pesticides were detected but not confirmed on a second GC/ECD column (see Appendix D). While all of the compounds may not have been confirmed, most probably due to the complex sample matrix of the Outfall 031 discharge, the data clearly show the discharge from the outfall results in bioaccumulation of more compounds at higher levels than do background river stations. Some of the pesticides were also detected but not confirmed at the background stations. Confirmation consists of analyzing the sample on a second instrument column to positively verify the compound identification. For purposes of the summary report, the results presented in Figure 15 should be viewed accordingly.

The control fish contained Aldrin; DDD; DDE; Dieldrin; Endosulfan I; Endosulfan sulfate; and Heptachlor at values ranging from 5 to 34 ppb. DDD, Dieldrin, and Endosulfan I values were confirmed. Fish exposed at Station A - Sanford Dam contained most of the same compounds at similar levels and also α-BHC at about 6 ppb. α-BHC, DDD, DDE, and Dieldrin were confirmed at this site. Slightly higher levels of most of the

same compounds were detected in fish from Station 1 - Poseyville Road in addition to α-BHC (5 to 15 ppb), Endosulfan II (21 ppb), and PCB-1248 (46 ppb). α-BHC, DDD, DDE, and Endosulfan I were confirmed at Stations 1 and 2. The influence of the Pine River may account for the higher levels and additional compounds. The data obtained at Station 2 (downstream of the Dow Dam but upstream of Outfall 031) show similar levels of most of the same compounds found at Station 1 in addition to Endrin aldehyde and Heptachlor.

The fish exposed to Outfall 031 contained unconfirmed levels of Aldrin in excess of 200 ppb; α-BHC in excess of 200 ppb; β-BHC in excess of 20 ppb; γ-BHC at 16 ppb; Endosulfan sulfate in excess of 200 ppb; and Endrin at 63 ppb. Confirmed levels of DDD (as high as 42 ppb); DDE (as high as 65 ppb); DDT (as high as 37 ppb); Dieldrin (as high as 12 ppb); Endrin aldehyde (as high as 26 ppb); and, Heptachlor epoxide (as high as 46 ppb) were also found in fish exposed to the plume of Outfall 031. Data obtained from fish exposed at Stations 4 and 5 show lower levels of pesticide accumulation than did the fish exposed in the plume of Outfall 031. Aldrin, DDD, Dieldrin, and Heptachlor epoxide were confirmed in fish from Station 4, while α-BHC, DDD, DDE, Dieldrin, Heptachlor epoxide, and Heptachlor were confirmed at Station 5. PCBs were not detected in any of the caged fish held in the Tittabawassee River.

The caged fish at Station B (Grand River at Jones Road) contained confirmed levels of α-BHC, γ-BHC, and DDD at less than 20 ppb, and unconfirmed levels of DDE, Endosulfan I, Endrin aldehyde, Endosulfan sulfate, and Endosulfan II at less than 23 ppb. The Grand River native fish contained much higher confirmed levels of pesticides than the caged fish from the Tittabawassee and Grand Rivers, particularly DDD (18-300 ppb); DDE (37-330 ppb); and DDT (48-230 ppb). The native Grand River fish also contained PCBs at confirmed levels ranging from 160 to 1020 ppb (PCB-1254) and 160-1360 ppb (PCB-1260).

5. Other Extractable Compounds

The fish samples from the bioaccumulation study were also analyzed for extractable organic compounds not included in the toxic (priority) pollutant list. These compounds were determined by the analyst by selecting the best fit from a computerized library search program to the mass spectra obtained for each sample. The quantitation of these compounds was not accomplished using a pure standard of each compound, but was calculated against the response of an internal standard. Thus, the concentrations presented are considered estimates. Many of these compounds were found at levels significantly higher than those noted above. The data are also presented in Appendix E.

FIGURE 9

DOW CHEMICAL-TITTABAWASSEE RIVER
BIOACCUMULATION STUDY
POLYCHLORINATED DIBENZO-P-DIOXINS

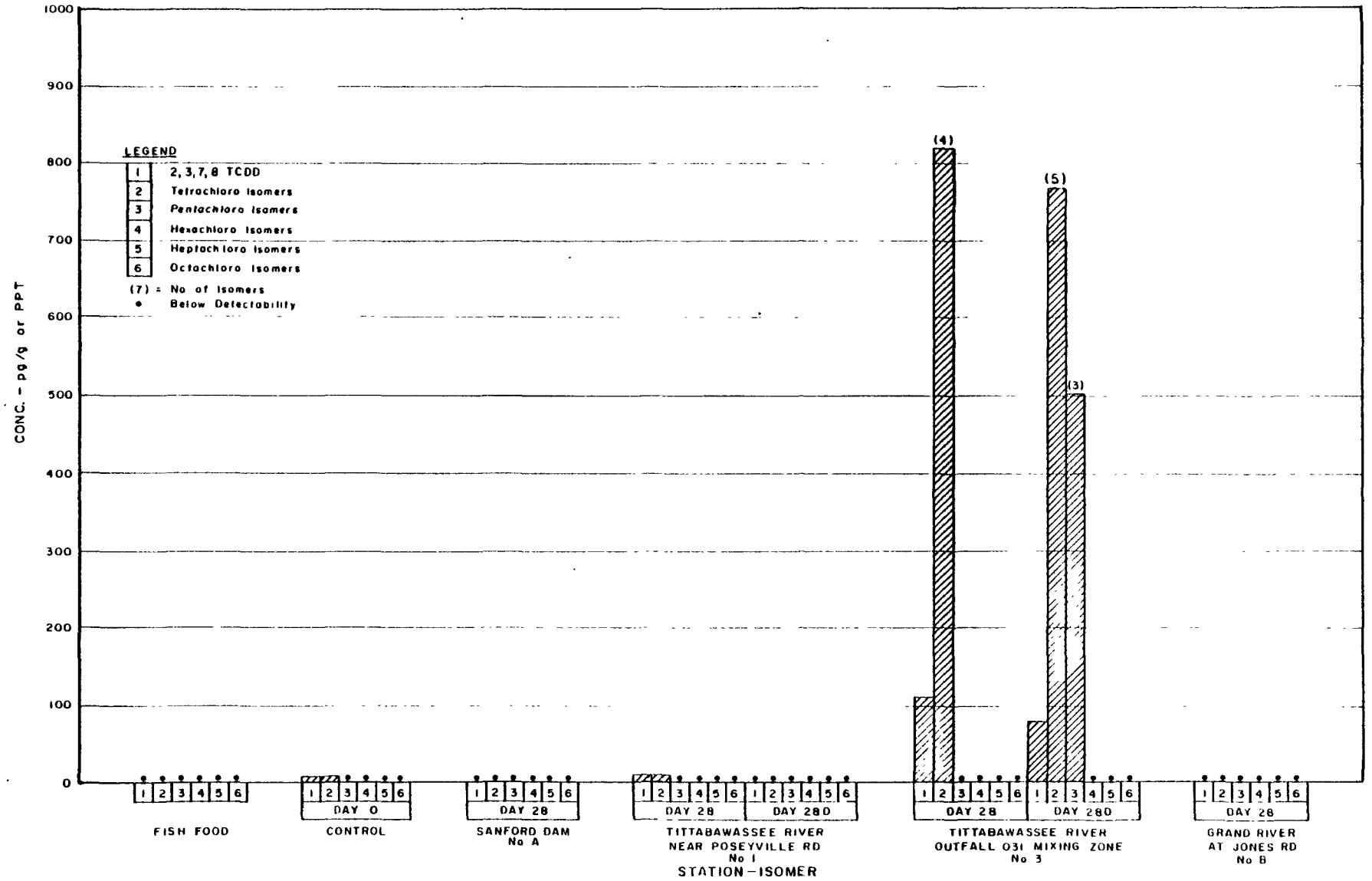


FIGURE 10

DOW CHEMICAL–TITTABAWASSEE RIVER
BIOACCUMULATION STUDY
POLYCHLORINATED DIBENZOFURANS

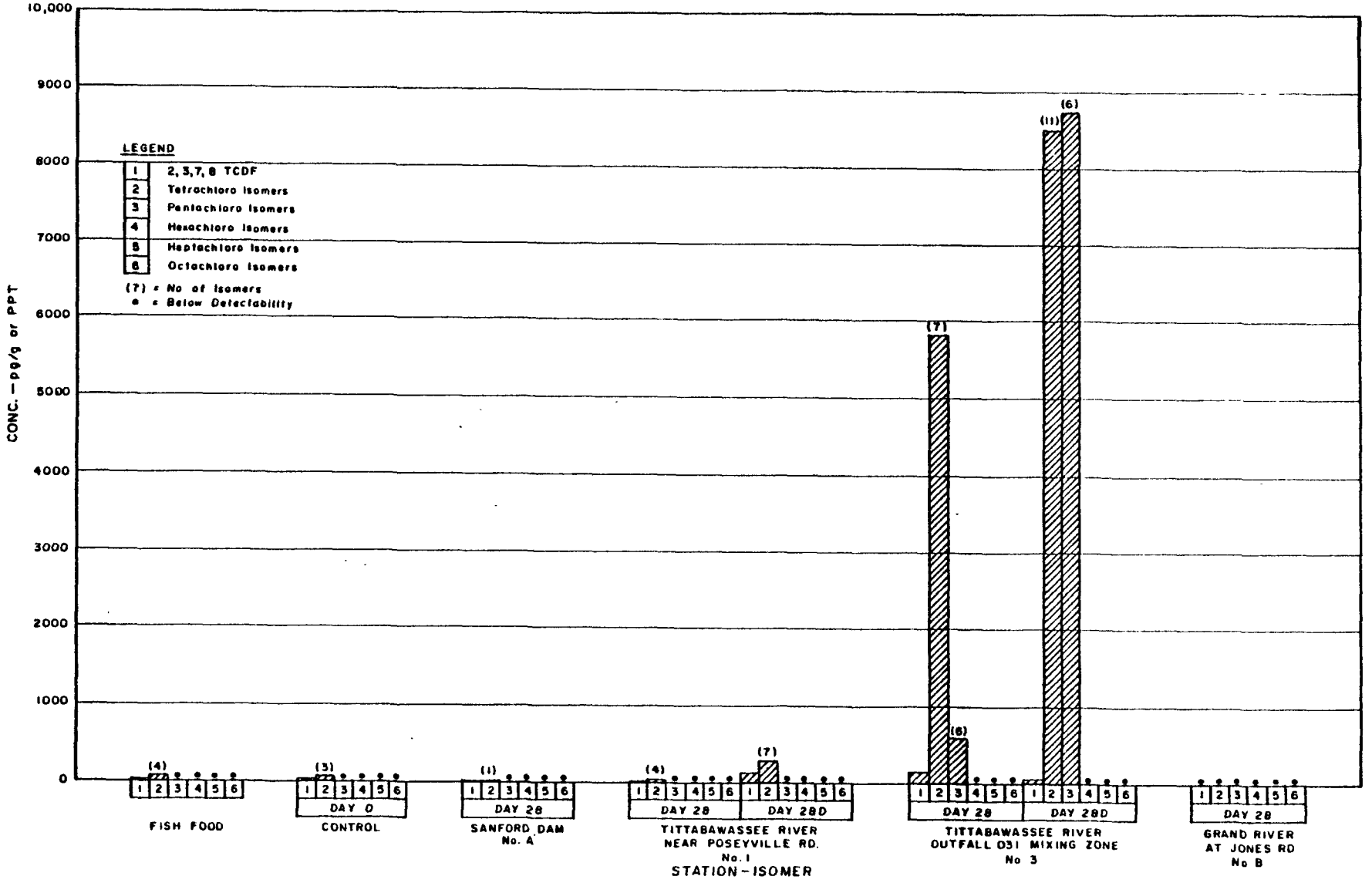


FIGURE 11

GRAND RIVER

POLYCHLORINATED DIBENZO-P-DIOXINS
NATIVE FISH

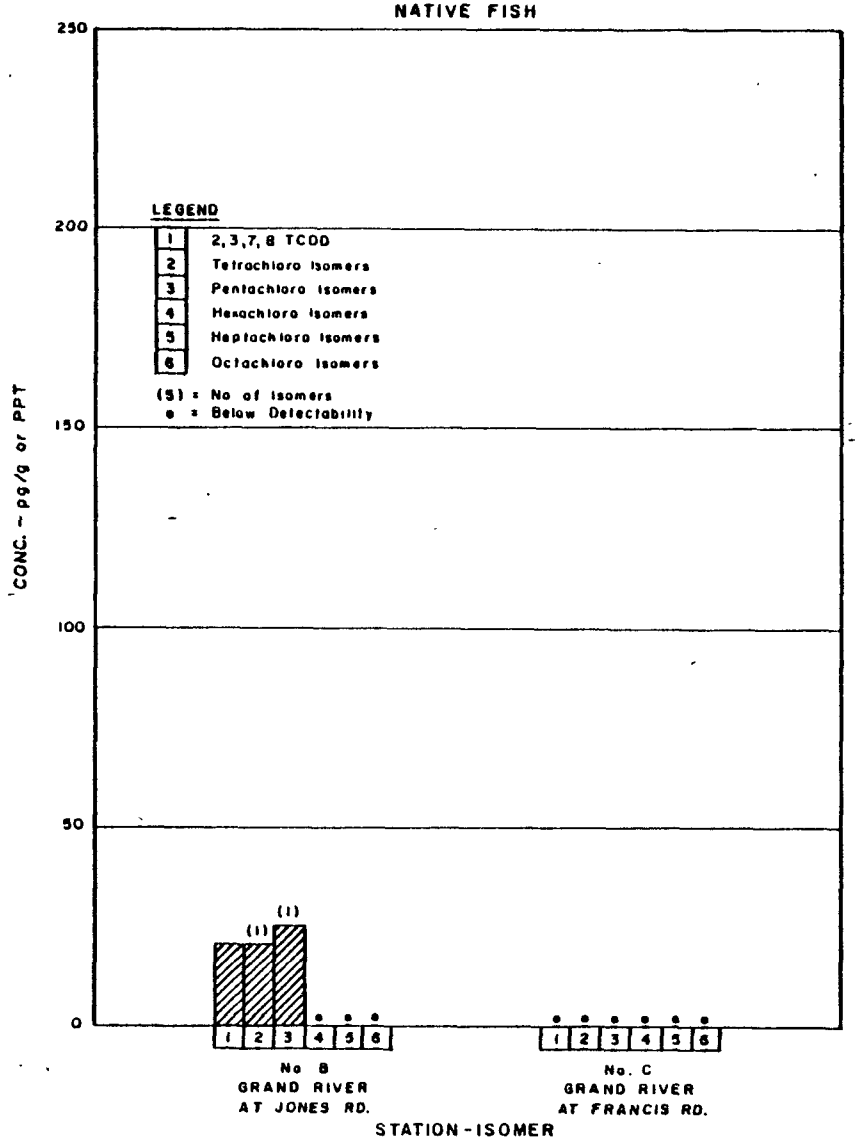


FIGURE 12

GRAND RIVER

POLYCHLORINATED DIBENZOFURANS
NATIVE FISH

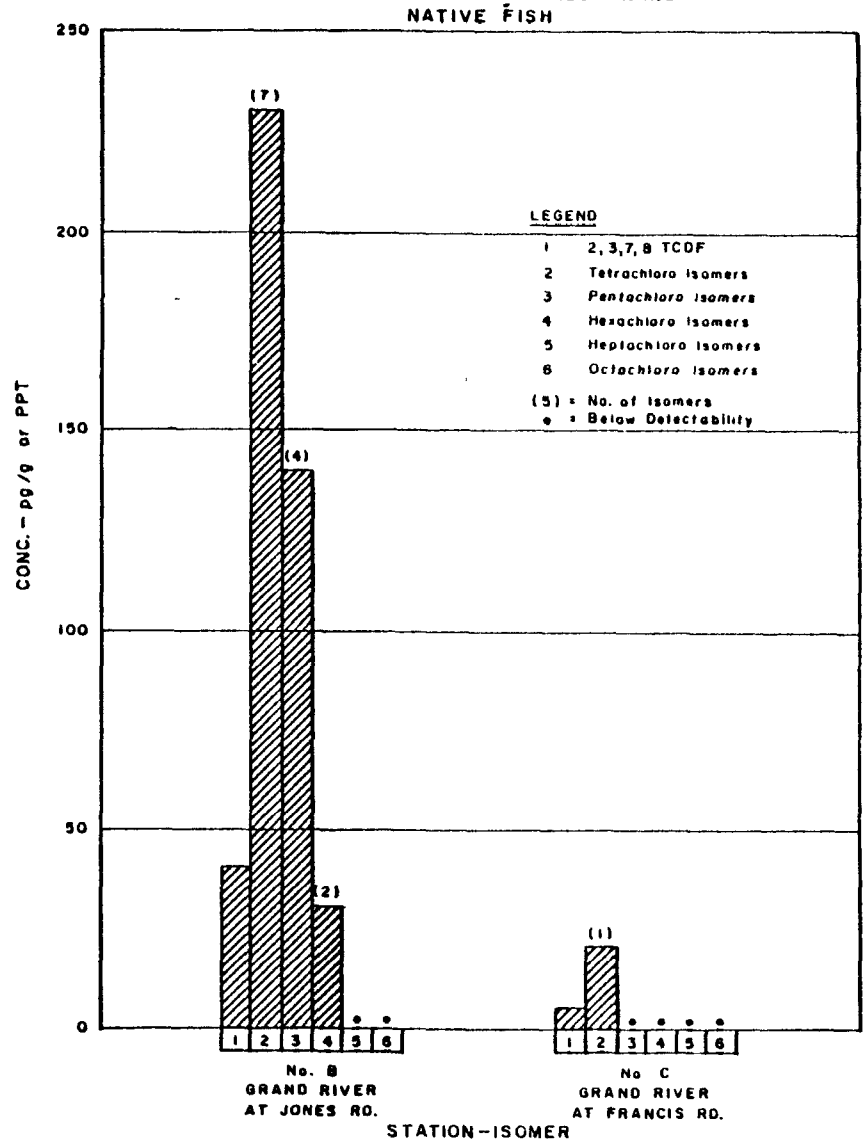


FIGURE 13

DOW CHEMICAL-TITTABAWASSEE RIVER
BIOACCUMULATION STUDY
BASE/NEUTRAL COMPOUNDS

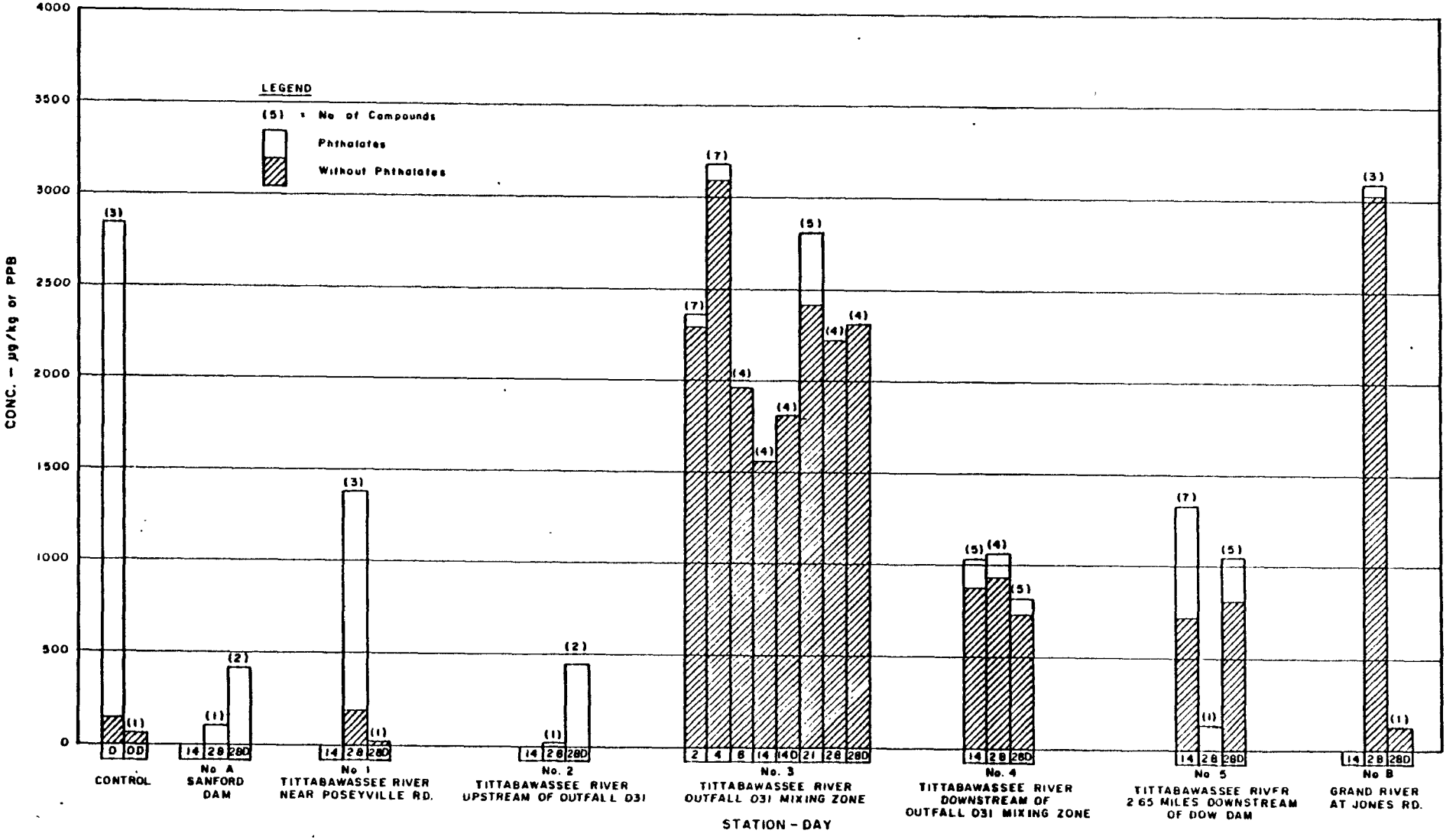


FIGURE 14

DOW CHEMICAL–TITTABAWASSEE RIVER
BIOACCUMULATION STUDY
ACID EXTRACTABLES

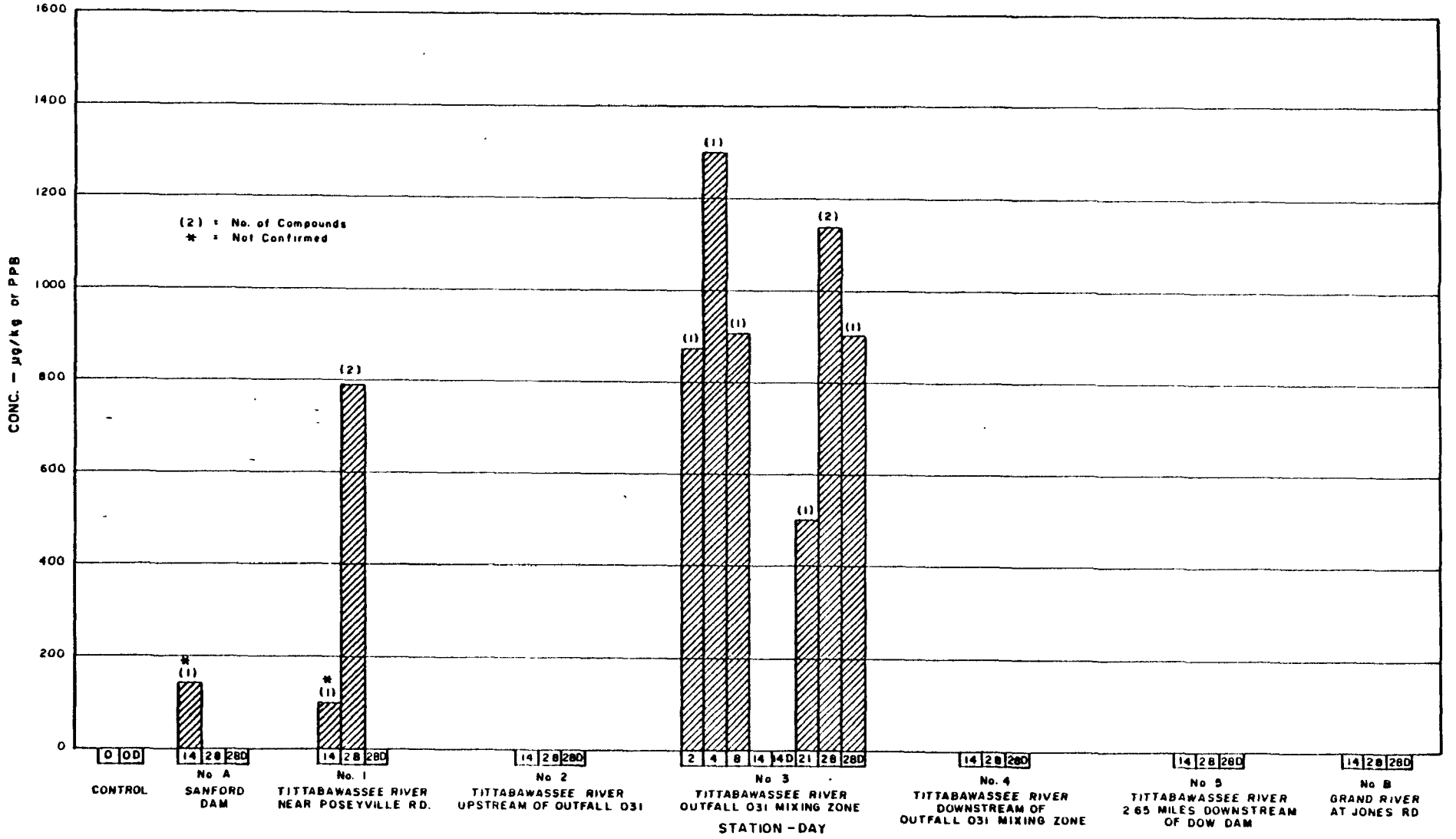
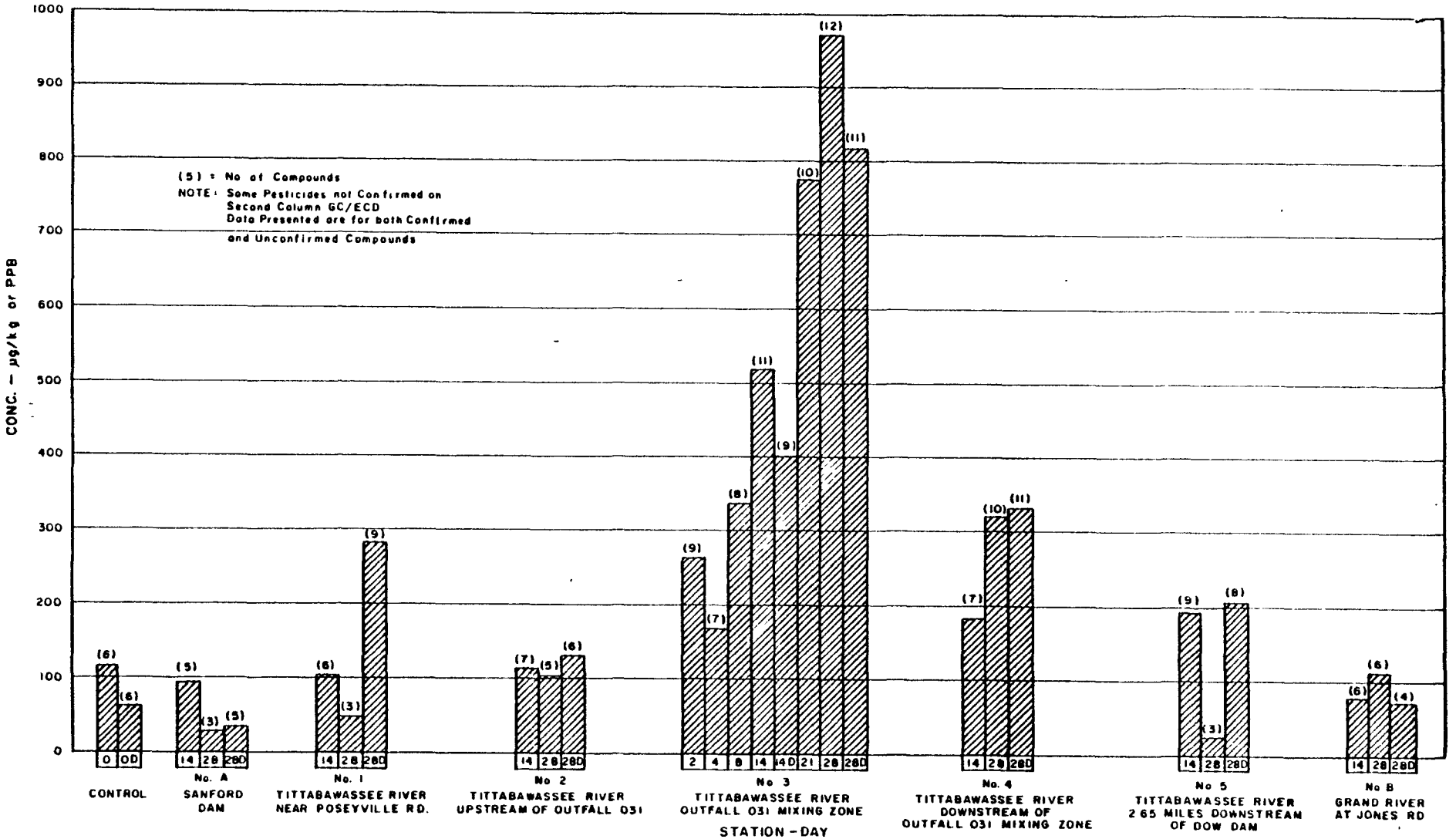


FIGURE 15

DOW CHEMICAL-TITTABAWASSEE RIVER
BIOACCUMULATION STUDY
PCB - PESTICIDE



APPENDIX A

SEDIMENT SURVEY DATA

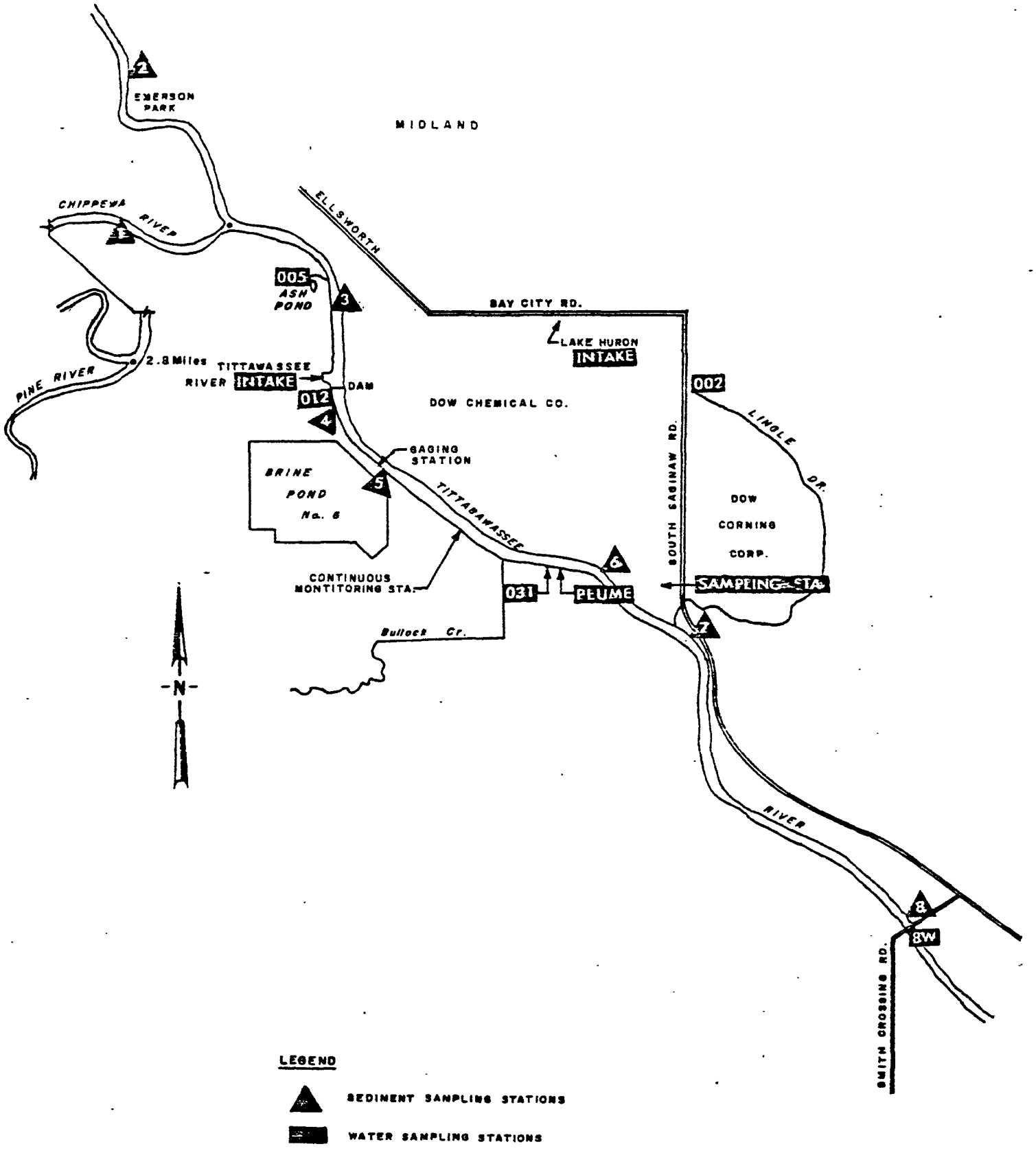

EMERSON PARK
MIDLAND
CHIPPEWA RIVER
ELLSWORTH
005
ASH POND
BAY CITY RD.
LAKE HURON
INTAKE
2.8 Miles
TITTAWASSEE RIVER
INTAKE
DAM
012
PINE RIVER
DOW CHEMICAL CO.
002
LINDLE DR.
GAGING STATION
BRINE POND No. 6
TITTABAWASSEE
SOUTH SAGINAW RD.
DOW CORNING CORP.
CONTINUOUS MONITORING STA.
031
PEUME
SAMPLING STA.
Bullock Cr.
N
RIVER
8
8W
SMITH CROSSING RD.
LEGEND
SEDIMENT SAMPLING STATIONS
WATER SAMPLING STATIONS

TABLE 1

SEDIMENT SAMPLING LOCATIONS
TITTABAWASSEE AND CHIPPEWA RIVERS: M-20 to Smith's Crossing
MARCH 18-19, 1981

Station Number	Sample Number	Stream	River Mile Point	Location and Site Specific Collection Method
1*	81EH03S01	Chippewa	0.6	The sample was collected with a large metal spoon in about 1 foot of water near north shore approximately 0.6 miles above the Tittabawassee River confluence.
2*	81EH03S08	Tittabawassee	24.0	The sample was collected with a large metal spoon at Emerson Park just below Snake Creek near east bank.
3	81EH03S02	Tittabawassee	23.5	The sample was obtained with a Petersen dredge above the Dow dam near the west bank and opposite Dow building #73.
4	81EH03S03	Tittabawassee	22.5	The sample was collected near the west bank immediately below Dow Chemical's H-flume discharge which is below the Dow dam. The sample was obtained with a Petersen dredge.
5	81EH03S04	Tittabawassee	22.0	The sample was collected near west bank opposite brine pond #6. The sample was obtained with a Petersen dredge.
6	81EH03S05	Tittabawassee	20.5	The sample was obtained near the east bank about ½ mile below Bullock Creek. The sample was collected with a Petersen dredge.
7	81EH03S06	Tittabawassee	20.0	The sample was obtained near the east bank about 500 feet below the Lingle drain confluence. The sample was collected with a Petersen dredge.
8	81EH03S07	Tittabawassee	19.0	The sample was obtained near the east bank about 200 feet about Smith's Crossing Road bridge. A Petersen dredge was used to collect the sample.

* These samples were not analyzed.

Discharger: Tittabawassee River

Sample Date: March 18-19, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office
Sediment Results

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

			Titt. River Above Dow Dam EH03S02		Titt. River Below H Flume EH03S03		Titt. River Near #6 Brine Pond EH03S04		Titt. River Below Bullock Creek EH03S05		Titt. River Below Lingle Drain EH03S06		Titt. River Above Smith's Crossing EH03S07					
SAMPLE TYPE			G		G		G		G		G		G					
TIME			1505		0935		0945		1005		1025		1045					
DATE			3/18/81		3/19/81		3/19/81		3/19/81		3/19/81		3/19/81					
DEPTH FEET (Water)			3.0		2.0		2.0		1.5		1.0		2.5					
PARAMETER	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day
I. ORGANICS																		
A. Base/Neutral & Acid Compounds																		
1,3-dichlorobenzene			<0.1	--	<1.3	--	<1.5	--	0.4	--	0.6	--	0.4	--				
1,4-dichlorobenzene			<0.1	--	<1.2	--	<1.3	--	0.4	--	0.5	--	0.3	--				
hexachloroethane			<0.0	--	<0.5	--	<0.6	--	<0.4	--	<0.0	--	<0.1	--				
bis(2-chloroethyl)ether			<0.0	--	<0.2	--	<0.2	--	<0.1	--	<0.0	--	<0.0	--				
n-nitrosodipropylamine			<0.0	--	<0.3	--	<0.3	--	<0.2	--	<0.0	--	<0.1	--				
nitrobenzene			<0.2	--	<2.5	--	<2.7	--	<1.8	--	<0.2	--	<0.6	--				
isophorone			<0.3	--	<4.4	--	<4.8	--	<3.2	--	<0.3	--	<1.1	--				
bis(2-chloroethoxy)methane			<0.0	--	<0.2	--	<0.2	--	<0.1	--	<0.0	--	<0.0	--				
1,2-dichlorobenzene			<0.1	--	<1.2	--	<1.3	--	0.4	--	0.5	--	0.3	--				
1,2,4-trichlorobenzene			<0.0	--	<0.2	--	<0.3	--	<0.2	--	<0.0	--	<0.1	--				
naphthalene			<0.0	--	<0.1	--	<0.1	--	<0.1	--	<0.0	--	<0.0	--				
hexachlorobutadiene			<0.0	--	<0.4	--	<0.5	--	<0.3	--	<0.0	--	<0.1	--				
2-chloronaphthalene			<0.0	--	<0.4	--	<0.4	--	<0.3	--	<0.0	--	<0.1	--				
acenaphthylene			<0.1	--	<1.1	--	<1.2	--	<0.8	--	<0.1	--	<0.3	--				
dimethylphthalate			<0.4	--	<5.6	--	<6.2	--	<4.1	--	<0.4	--	<1.4	--				
2,6-dinitrotoluene			<0.0	--	<0.6	--	<0.6	--	<0.4	--	<0.0	--	<0.1	--				
acenaphthene			<0.1	--	<1.1	--	<1.2	--	<0.8	--	<0.1	--	<0.3	--				
2,4-dinitrotoluene			<0.1	--	<1.0	--	<1.1	--	<0.7	--	<0.1	--	<1.9	--				
fluorene			<0.1	--	<1.9	--	<2.1	--	<1.4	--	<0.1	--	<0.5	--				
diethylphthalate			<0.4	--	<5.9	--	<6.5	--	<4.3	--	<0.4	--	<1.4	--				
1,2-diphenylhydrazine			<0.1	--	<1.9	--	<2.0	--	<1.4	--	<0.1	--	<0.4	--				
n-nitrosodiphenylamine			<0.2	--	<2.2	--	<2.4	-	<1.6	--	<0.1	--	<0.5	--				

Discharger: Tittabawassee River

Sample Date: March 18-19, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

Sediment Results

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

			Titt. River Above Dow Dam EH03S02		Titt. River Below H Flume EH03S03		Titt. River Near #6 Brine Pond EH03S04		Titt. River Below Bullock Creek EH03S05		Titt. River Below Lingle Drain EH03S06		Titt. River Above Smith's Crossing EH03S07					
SAMPLE TYPE			G		G		G		G		G		G					
TIME			1505		0935		0945		1005		1025		1045					
DATE			3/18/81		3/19/81		3/19/81		3/19/81		3/19/81		3/19/81					
DEPTH FEET (Water)			3.0		2.0		2.0		1.5		1.0		2.5					
PARAMETER	mg/kg	**Gross #/Day**	mg/kg	**Gross #/Day**	mg/kg	**Gross #/Day**	mg/kg	**Gross #/Day**	mg/kg	**Gross #/Day**	mg/kg	**Gross #/Day**	mg/kg	**Gross #/Day**	mg/kg	**Gross #/Day**	mg/kg	**Gross #/Day**
A. Base/Neutral & Acid Compounds																		
4-bromophenylphenyl ether			<0.2	--	<3.3	--	<3.6	--	2.4	--	<0.2	--	<0.8	--				
hexachlorobenzene			<0.0	--	<0.4	--	<0.5	--	0.1	--	<0.1	--	<0.1	--				
1-chloronaphthalene			<0.0	--	<0.4	--	<0.4	--	<0.3	--	<0.0	--	<0.1	--				
phenanthrene/anthracene			<0.1	--	<0.8	--	<0.8	--	<0.6	--	<0.0	--	<0.2	--				
fluoranthene			<0.6	--	<8.9	--	<9.7	--	<6.5	--			<2.1	--				
pyrene			<0.6	--	<8.9	--	<9.7	--	<6.5	--	11.2	--	<2.1	--				
di-n-butylphthalate			<0.5	--	<7.3	--	6.6	--	<5.3	--	< 0.5	--	<1.8	--				
butylbenzylphthalate			<0.0	--	<0.4	--	<0.4	--	<0.3	--	<0.0	--	<0.1	--				
chrysene			<0.0	--	<0.3	--	<0.3	--	<0.2	--	<0.0	--	<0.1	--				
benzo(A)anthracene			<0.0	--	<0.3	--	<0.3	--	<0.2	--	<0.0	--	<0.1	--				
bis(2-ethylhexyl)phthalate			<0.0	--	<0.4	--	<0.4	--	<0.3	--	<0.0	--	<0.1	--				
di-n-octylphthalate			2.1	--	2.0	--	8.4	--	5.3	--	9.2	--	23.0	--				
benzo(B)fluoranthene			<0.0	--	<0.5	--	<0.5	--	<0.4	--	<0.0	--	<0.1	--				
benzo(A)pyrene			<0.1	--	<1.0	--	<1.1	--	<0.7	--	<0.1	--	<0.2	--				
indeno(1,2,3-C,D)pyrene			<0.0	--	<0.4	--	<0.5	--	<0.3	--	<0.0	--	<0.1	--				
benzo(G,H,I)perylene			<0.3	--	<3.9	--	<4.2	--	<2.8	--	<0.2	--	<0.9	--				
dibromobiphenyl(ISTD)			<0.5	--	<6.5	--	1.6	--	<4.8	--	<0.4	--	<1.6	--				
2-nitrophenol			<0.0	--	<0.3	--	<0.3	--	<0.2	--	<0.0	--	<0.1	--				
2-chlorophenol			<0.0	--	<0.2	--	<0.2	--	<0.1	--	<0.0	--	<0.0	--				
phenol			<0.0	--	<0.2	--	<0.2	--	<0.1	--	<0.0	--	<0.0	--				
2,4-dimethylphenol			<0.0	--	<0.2	--	<0.2	--	<0.1	--	<0.0	--	<0.0	--				
2,4-dichlorophenol			<0.0	--	<0.3	--	<0.3	--	<0.2	--	<0.0	--	<0.1	--				
p-t-butylphenol			<0.2	--	<3.2	--	<3.5	--	<2.3	--	<0.2	--	<0.8	--				

Discharger: Tittabawassee River

Sample Date: March 18-19, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office
Sediment Results

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

			Titt. River Above Dow Dam EH03S02		Titt. River Below H Flume EH03S03		Titt. River Near #6 Brine Pond EH03S04		Titt. River Below Bullock Creek EH03S05		Titt. River Below Lingle Drain EH03S06		Titt. River Above Smith's Crossing EH03S07					
SAMPLE TYPE			G		G		G		G		G		G					
TIME			1505		0935		0945		1005		1025		1045					
DATE			3/18/81		3/19/81		3/19/81		3/19/81		3/19/81		3/19/81					
DEPTH FEET (Water)			3.0		2.0		2.0		1.5		1.0		2.5					
PARAMETER	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day
A. Base/Neutral & Acid Compounds																		
p-chloro-m-cresol			<0.4	--	<5.2	--	<5.6	--	<3.8	--	<0.3	--	<1.3	--				
2,4,6-trichlorophenol			<0.5	--	<6.9	--	<7.5	--	<5.0	--	<0.4	--	<1.7	--				
pentachlorophenol			<0.0	--	<0.5	--	<0.5	--	<0.1	--	<0.0	--	<0.1	--				
4-nitrophenol			<0.1	--	<1.4	--	<1.5	--	<1.0	--	<0.1	--	<0.3	--				
B. PCB's & PBB's																		
PCB 1242			< 13	--	< 6	--	<0.7	--	< 2	--	< 1	--	< 6	--				
PCB 1248			< 3	--	< 2	--	<0.2	--	<0.5	--	<0.3	--	< 2	--				
PCB 1254			< 1	--	<0.6	--	<0.1	--	<0.2	--	<0.1	--	<0.6	--				
PCB 1260			< 1	--	<0.6	--	<0.1	--	<0.2	--	<0.1	--	<0.6	--				
hexabromo-biphenyl			<1.7	--	<1.7	--	<1.7	--	<1.7	--	<1.7	--	<1.7	--				
dibromo-biphenyl			<0.05	--	<0.05	--	<0.05	--	<0.05	--	<0.05	--	<0.05	--				
C. Purgeables*																		
chlorobenzene			--	--	--	--	--	--	--	--	--	--	0.0038	--				
D. Other Compounds																		
hydrocarbons (9)			1.0	--	--	--	--	--	--	--	--	--	--	--				
sulfur (S8)			1.4	--	--	--	--	--	--	--	1.5	--	--	--				
1,7,7-trimethyl-bicyclo [2.2.1] heptan-2-one			--	--	--	--	0.2	--	--	--	--	--	--	--				

*Purgeables were detected in only one sample, EH03S07. None of the other samples were found to contain any purgeable compound above the detection limit (approx. 2 ppb).

Discharger: Tittabawassee River

Sample Date: March 18-19, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

			Titt. River Above Dow Dam EH03S02		Titt. River Below H Flume EH03S03		Titt. River Near #6 Brine Pond EH03S04		Titt. River Below Bullock Creek EH03S05		Titt. River Below Lingle Drain EH03S06		Titt. River Above Smith's Crossing EH03S07					
SAMPLE TYPE			G		G		G		G		G		G					
TIME			1505		0935		0945		1005		1025		1045					
DATE			3/18/81		3/19/81		3/19/81		3/19/81		3/19/81		3/19/81					
DEPTH FEET (Water)			3.0		2.0		2.0		1.5		1.0		2.5					
PARAMETER	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day
D. Other Compounds																		
octanoic acid			--	--	--	--	0.8	--	--	--	--	--	--	--				
beta-gurjunene			--	--	--	--	0.3	--	--	--	--	--	--	--				
alpha-fornesene			--	--	--	--	0.3	--	--	--	--	--	--	--				
1-methoxy-4-(phenylethynyl)benzene			--	--	--	--	1.1	--	--	--	--	--	--	--				
unidentified compounds (Spectrum 340)			--	--	--	--	0.2	--	--	--	--	--	--	--				
unidentified compounds (Spectrum 395)			--	--	--	--	0.4	--	--	--	--	--	--	--				
unidentified compounds (Spectrum 406)			--	--	--	--	0.9	--	--	--	--	--	--	--				
unidentified compounds (Spectrum 467)			--	--	--	--	1.7	--	--	--	--	--	--	--				
unidentified compounds (Spectrum 517)			--	--	--	--	0.9	--	--	--	--	--	--	--				
unidentified compounds (Spectrum 520)			--	--	--	--	1.6	--	--	--	--	--	--	--				
unidentified compounds (Spectrum 560)			--	--	--	--	0.8	--	--	--	--	--	--	--				
unidentified compounds (Spectrum 591)			--	--	--	--	2.8	--	--	--	--	--	--	--				
hydrocarbons (2)			--	--	--	--	0.5	--	--	--	0.5	--	--	--				
sec-butylethylbenzene			--	--	--	--	--	--	0.3	--	--	--	--	--				
3,5-dimethyl-2-cyclohexen-1-one			--	--	--	--	--	--	0.1	--	0.1	--	--	--				
1,3,5-tris(1-methylethyl)benzene			--	--	--	--	--	--	0.1	--	--	--	--	--				
1,1'oxybisbenzene			--	--	--	--	--	--	0.1	--	0.8	--	3.0	--				
2-phenoxy-1,1'biphenyl			--	--	--	--	--	--	0.8	--	--	--	5.3	--				
terphenyl			--	--	--	--	--	--	0.1	--	--	--	--	--				
1,1':3',1-terphenyl			--	--	--	--	--	--	0.3	--	--	--	--	--				
hydrocarbons (11)			--	--	--	--	--	--	2.2	--	--	--	--	--				
sulfur molecule (S8)			--	--	--	--	--	--	4.0	--	--	--	7.7	--				
1,1'biphenyl			--	--	--	--	--	--	--	--	0.1	--	--	--				

Discharger: Tittabawassee River

Sample Date: March 18-19, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office
Sediment Results

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

			Titt. River Above Dow Dam EH03S02		Titt. River Below H Flume EH03S03		Titt. River Near #6 Brine Pond EH03S04		Titt. River Below Bullock Creek EH03S05		Titt. River Below Lingle Drain EH03S06		Titt. River Above Smith's Crossing EH03S07					
SAMPLE TYPE			G		G		G		G		G		G					
TIME			1505		0935		0945		1005		1025		1045					
DATE			3/18/81		3/19/81		3/19/81		3/19/81		3/19/81		3/19/81					
DEPTH FEET (Water)			3.0		2.0		2.0		1.5		1.0		2.5					
PARAMETER	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day	mg/kg	Gross #/Day
D. Other Compounds																		
unidentified silicon compounds (10)			--	--	--	--	--	--	--	--	3.3	--	--	--				
hexaethylbenzene			--	--	--	--	--	--	--	--	--	--	4.7	--				
4-phenoxy-1,1'-biphenyl			--	--	--	--	--	--	--	--	--	--	2.3	--				
tetraethylbenzene (1 isomer)			--	--	--	--	--	--	--	--	--	--	1.4	--				
1,2,4,5-tetrakis (1-methylethyl)-benzene			--	--	--	--	--	--	--	--	--	--	0.9	--				
unidentified silicon compounds (4)			--	--	--	--	--	--	--	--	--	--	4.4	--				
hydrocarbons (1)			--	--	--	--	--	--	--	--	--	--	4.0	--				
unidentified compounds (Spectrum 448)			--	--	--	--	--	--	--	--	--	--	2.5	--				
unidentified compounds (Spectrum 973)			--	--	--	--	--	--	--	--	--	--	2.1	--				

APPENDIX B

CONVENTIONAL WATER SAMPLING DATA

Discharger: Dow Chemical Co. Midland Plant

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

Conventional Water Samples

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

	SURVEY #1							SURVEY #2			SURVEY #3				SURVEY #4			
	L.H. Intake	Tit.R. Intake	002	005	012	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	L.H. Intake	Tit.R. Intake	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	
SAMPLE TYPE	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	
TIME	0808-0923	0735-0830	0844-0906	0737-0650	0955-0840	0950-0730	0925-0920	1108-0550	0720-0435	0900-0635	1002-0521	0735-0450	0900-0542	1020-0640	0917-0518	0800-0504	0948-0555	
FLOW, MGD	12.4*	65.0*	5.5*	5.2*	34.6*	34.8*	1.87*	12.4*	65.2*	34.6*	12.4*	55.0*	27.3*	1.87*	12.4*	65.7*	45.0*	
TEMPERATURE °C	19-21	22-24	32-34	22-27	25-27	21-26	25-30	18-20	18-20	18-20	14-16	16-18	17-20	20-23	12-16	10-15	11-17	
PH (S.U.)	7.7-8.0	7.9-8.3	6.0-7.4	7.7-8.3	8.1-8.2	6.7-7.2	—	7.1-7.6	7.1-8.2	6.7-7.0	7.1-7.5	6.9-8.3	6.8-7.4	—	7.0-7.3	7.0-8.0	6.5-7.4	
CONDUCTIVITY µmho/cm	210-230	380-510	—	700-900	—	3700-3800	—	220-240	500-650	4000-5000	230-260	500-680	4800-5400	—	210-280	450-700	2400-4000	
PARAMETER	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day
I. ORGANICS																		
A. Base/Neutral																		
Anthracene	—	—	0.02	—	—	—	0.02	—	—	—	—	—	—	—	—	—	—	
Phenanthrene	—	—	—	Trace	—	—	0.02	—	—	—	—	—	—	0.01	—	—	—	
Fluoranthene	—	—	—	—	—	—	0.15	—	—	—	—	—	—	—	—	—	—	
Pyrene	—	—	0.02	—	—	—	—	—	—	0.27	—	—	—	—	—	—	—	
Naphthalene	—	—	0.20	—	—	—	0.03	—	—	—	—	—	—	0.13	—	—	—	
2-Chloronaphthalene	—	—	—	—	—	0.26	—	—	—	—	—	—	—	—	—	—	—	
1,2-Dichlorobenzene	—	—	0.17	—	—	Trace	—	—	—	Trace	—	—	Trace	—	—	—	—	
1,3-Dichlorobenzene	—	—	—	—	—	0.41	—	—	—	0.14	—	—	0.13	—	—	—	0.71	
1,4-Dichlorobenzene	—	—	—	—	—	0.64	—	—	—	0.29	—	—	0.19	—	—	—	0.75	
1,2,4-Trichlorobenzene	—	—	—	—	—	1.19	—	—	—	0.58	—	—	0.32	—	—	—	1.39	
Di-n-butyl phthalate **	0.12	—	0.02	0.08	0.19	0.21	0.05	—	0.32	—	—	—	—	—	—	—	0.21	
Butyl benzyl phthalate	1.65	2.70	0.13	1.08	2.74	—	—	0.17	2.28	—	—	—	—	—	—	—	Trace	
Bis(2-ethylhexyl)phthalate***	—	46.62	1.24	—	0.29	21.2	0.27	—	—	60.6	1.96	78	7.1	—	45.50	7.12	3.42	
Bis(2-chloroethyl)ether	—	—	—	—	—	0.04	—	—	—	0.28	—	—	0.25	—	—	—	1.28	
Diethyl phthalate	—	—	—	Trace	Trace	—	—	—	Trace	—	—	—	—	—	0.55	—	—	
Isophorone****	—	—	—	—	—	—	0.01	—	—	Trace	—	—	Trace	0.02	—	—	—	
Dioctyl phthalate	—	—	—	—	—	—	—	—	—	2.05	—	—	—	—	—	—	—	
Acenaphtene	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.17	

*Dow Est. **Blank Contamination Survey #1 & #4 ***Blank Contamination Survey #2 & 3 ****Blank Contamination Survey #4

-- Less than detection

Discharger: Dow Chemical Co. Midland Plant

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

Conventional Water Samples

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

	SURVEY #1							SURVEY #2			SURVEY #3				SURVEY #4			
	L.H. Intake	Tit.R. Intake	002	005	012	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	L.H. Intake	Tit.R. Intake	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	
SAMPLE TYPE	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	
TIME	0808-0923	0735-0830	0844-0906	0737-0650	0955-0840	0950-0730	0925-0920	1108-0550	0720-0435	0900-0634	1002-0521	0735-0450	0900-0542	1020-0640	0917-0518	0800-0504	0948-0555	
FLOW, MGD	12.4*	65.0*	5.5*	5.2*	34.6*	34.8*	1.87*	12.4*	65.2*	34.6*	12.4*	55.0*	27.3*	1.87*	12.4*	65.7*	45.0*	
TEMPERATURE °C	19-21	22-24	32-34	22-27	25-27	21-26	25-30	18-20	18-20	18-20	14-16	16-18	17-20	20-23	12-16	10-15	11-17	
PH (S.U.)	7.7-8.0	7.9-8.3	6.0-7.4	7.7-8.3	8.1-8.2	6.7-7.2	—	7.1-7.6	7.1-8.2	6.7-7.0	7.1-7.5	6.9-8.3	6.8-7.4	—	7.0-7.3	7.0-8.0	6.5-7.4	
CONDUCTIVITY µmho/cm	210-230	380-510	—	700-900	—	3700-3800	—	220-240	500-650	4000-5000	230-260	500-680	4800-5400	—	210-280	450-700	2400-4000	
PARAMETER	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day
I. ORGANICS (Continued)																		
B. Pesticides/PCBs																		
Aldrin (1[a])	—	—	—	—	0.01[b]	0.06[a]	—	—	0.02[b]	0.06[a]	0.001[b]	—	—	0.004	—	—	0.21[a]	
α-BHC (1[c])	—	—	0.01[c]	—	0.01[b]	—	—	—	—	—	0.001[b]	0.01[b]	—	—	—	0.01[c]	—	
4,4'-DDD (1a)	—	—	—	—	0.01[a]	0.01[b]	—	—	—	—	—	—	—	—	—	0.02[b]	0.01[b]	
4,4'-DDE (1c)	—	—	0.01[c]	0.01[c]	—	—	—	—	—	—	0.002[a]	—	—	—	—	0.02[b]	—	
4,4'-DDT (2[a])	—	—	—	—	0.01[b]	—	—	—	—	—	—	—	—	0.0003[b]	—	0.02[b]	—	
Dieldrin (1[a])	—	—	—	—	0.01[a]	—	—	—	—	—	0.004[b]	—	—	—	—	—	—	
Endosulfan I	—	—	—	—	—	0.03[b]	—	—	—	—	—	—	—	—	—	—	—	
Endrin aldehyde	—	0.01[c]	—	—	—	0.01[b]	—	—	—	0.02[b]	0.003[b]	—	—	0.001[b]	—	—	0.01[b]	
Heptachlor	—	0.01[a]	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Heptachlor epoxide	—	—	—	—	—	0.01[a]	—	—	—	0.01[b]	—	—	—	0.0004[a]	—	—	0.02[c]	
PCB-1242	—	—	—	—	—	—	0.07	—	—	—	—	—	1.10	—	—	—	—	
PCB-1254	—	—	—	—	—	—	0.01	—	—	—	—	—	0.09	—	—	—	—	
β-BHC	—	—	—	—	—	—	—	—	—	0.01[a]	—	—	—	—	—	—	—	
Endrin	—	—	—	—	—	—	—	—	—	—	0.001[a]	—	—	—	—	—	—	
PCB-1260	—	—	—	—	—	—	—	—	—	—	—	—	0.2	—	—	—	—	
γ-BHC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.01[b]	

a = Confirmed on second column GC/ECD
b = Not confirmed on second column GC/ECD
c = Not confirmed on second column CG/ECD due to interference
— = Less than detection

* Dow Est.
(1) Blank contamination during first survey
(2) Blank contamination during third survey

Discharger: Dow Chemical Co. Midland Plant

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

Conventional Water Samples

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

	SURVEY #1							SURVEY #2			SURVEY #3				SURVEY #4			
	L.H. Intake	Tit.R. Intake	002	005	012	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	L.H. Intake	Tit.R. Intake	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	
SAMPLE TYPE	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	
TIME	0808-0923	0735-0830	0844-0906	0737-0650	0955-0840	0950-0730	0925-0920	1108-0550	0720-0435	0900-0635	1002-0521	0735-0450	0900-0542	1020-0640	0917-0518	0800-0504	0948-0555	
FLOW, MGD	12.4*	65.0*	5.5*	5.2*	34.6*	34.8*	1.87*	12.4*	65.2*	34.6*	12.4*	55.0*	27.3*	1.87*	12.4*	65.7*	45.0*	
TEMPERATURE °C	19-21	22-24	32-34	22-27	25-27	21-26	25-30	18-20	18-20	18-20	14-16	16-18	17-20	20-23	12-16	10-15	11-17	
PH (S.U.)	7.7-8.0	7.9-8.3	6.0-7.4	7.7-8.3	8.1-8.2	6.7-7.2	—	7.1-7.6	7.1-8.2	6.7-7.0	7.1-7.5	6.9-8.3	6.8-7.4	—	7.0-7.3	7.0-8.0	6.5-7.4	
CONDUCTIVITY µmho/cm	210-230	380-510	—	700-900	—	3700-3800	—	220-240	500-650	4000-5000	230-260	500-680	4800-5400	—	210-280	450-700	2400-4000	
PARAMETER	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day
I. ORGANICS (Continued)																		
C. Herbicides																		
Dichloroprop	—	—	—	—	0.32	—	0.001	—	—	—	—	—	0.02	—	—	0.04	0.22	
2,4-D	—	0.08	—	0.001	0.03	0.01	0.001	—	—	—	0.01	—	0.30	0.002	0.01	0.08	—	
Silvex	—	0.03	—	—	0.02	—	0.001	—	—	0.03	—	—	1.60	0.004	—	0.01	2.14	
2,4,5-T	—	0.02	—	—	—	—	—	—	—	—	—	—	0.40	—	—	—	0.18	
D. Acid Extractables																		
2-Chlorophenol	—	—	—	—	—	0.28	—	—	—	Trace	—	—	Trace	—	—	—	Trace	
Phenol	Trace	—	0.07	Trace	Trace	0.28	Trace	—	—	—	—	—	Trace	Trace	—	—	Trace	
2,4-Dimethylphenol	—	—	0.02	—	—	—	—	—	—	—	—	—	—	0.2	—	—	—	
2,4-Dichlorophenol	—	—	—	—	—	0.35	—	—	—	—	—	—	—	—	—	—	0.26	
2,4,6-Trichlorophenol	—	—	0.03	—	—	1.25	—	—	—	—	—	—	—	—	—	—	Trace	
P-Chloro-m-cresol	—	—	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Pentachlorophenol	—	—	0.02	—	—	4.35	—	—	—	0.55	—	—	—	—	—	—	0.94	
E. Other Extractables (1)																		
Cyclohexene, chloro	1.60	1.50	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Cyclohexane, dichloro (B_1)	2.50	12.50	—	1.10	—	—	—	—	—	—	0.07	—	—	—	—	—	—	
2-Propanol,1(2-methoxy-1 methylethoxy) or isomers	—	—	—	—	—	4.10	—	—	—	2.20	—	—	3.40	—	—	—	19.89	
2,5 Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl) isomers	—	—	—	—	—	0.90	—	—	—	—	—	—	—	—	—	—	—	

*Dow Est. B_1 = Blank contamination Survey #1 (1) = Conc. based on a comparison of the total ion area of the compound with that of an internal std.

— = Less than detection

Discharger: Dow Chemical Co. Midland Plant

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office
Conventional Water Samples

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

	SURVEY #1							SURVEY #2			SURVEY #3				SURVEY #4			
	L.H. Intake	Tit.R. Intake	002	005	012	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	L.H. Intake	Tit.R. Intake	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	
SAMPLE TYPE	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	
TIME	0808-0923	0735-0830	0844-0906	0737-0650	0955-0840	0950-0730	0925-0920	1108-0550	0720-0435	0900-0635	1002-0521	0735-0450	0900-0542	1020-0640	0917-0518	0800-0504	0948-0555	
FLOW, MGD	12.4*	65.0*	5.5*	5.2*	34.6*	34.8*	1.87*	12.4*	65.2*	34.6*	12.4*	55.0*	27.3*	1.87*	12.4*	65.7*	45.0*	
TEMPERATURE °C	19-21	22-24	32-34	22-27	25-27	21-26	25-30	18-20	18-20	18-20	14-16	16-18	17-20	20-23	12-16	10-15	11-17	
PH (S.U.)	7.7-8.0	7.9-8.3	6.0-7.4	7.7-8.3	8.1-8.2	6.7-7.2	—	7.1-7.6	7.1-8.2	6.7-7.0	7.1-7.5	6.9-8.3	6.8-7.4	—	7.0-7.3	7.0-8.0	6.5-7.4	
CONDUCTIVITY μmho/cm	210-230	380-510	—	700-900	—	3700-3800	—	220-240	500-650	4000-5000	230-260	500-680	4800-5400	—	210-280	450-700	2400-4000	
PARAMETER	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day
I. ORGANICS (Continued)																		
E. Other Extractables(1)																		
Benzene acetic acid, hydroxy ester of	--	--	--	--	--	11.90	--	--	--	6.30	--	--	9.80	--	--	--	45.04	
Tetrachloro phenol	--	--	--	--	--	0.80	--	--	--	--	--	--	--	--	--	--	--	
Dichlorocyclopentalen, isomers	--	--	--	--	--	1.20	--	--	--	--	--	--	--	--	--	--	--	
Tetrachloroethane	--	--	4.10	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
Ethylbenzene	--	--	0.70	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
Xylene	--	--	0.90	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
Ethyl methy benzene	--	--	6.90	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
Dichloroethyl benzene	--	--	0.50	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
Tetradecanoic acid	--	--	--	0.30	--	--	--	--	--	--	--	--	--	--	--	--	--	
Hexadecanoic acid	--	--	--	0.30	--	--	--	--	--	0.09	--	--	--	--	--	--	--	
Formamide, N-N-dimethyl	--	--	--	--	2.60	--	--	--	--	--	--	--	--	--	--	--	--	
Alkyl benzene $C_{13}H_{20}$	--	--	--	--	--	--	1.30	--	--	--	--	--	--	--	--	--	--	
Biphenyl	--	--	--	--	--	--	12.50	--	--	--	--	--	--	--	--	--	--	
Benzene, 1,1-oxybis	--	--	--	--	--	--	10.90	--	--	--	--	--	--	--	--	--	--	
Biphenyl, ethyl	--	--	--	--	--	--	1.60	--	--	--	--	--	--	--	--	--	--	
Benzoic acid	--	--	--	--	--	--	3.90	--	--	--	--	--	--	--	--	--	--	
Dimethyl phenol, isomer of	--	--	--	--	--	--	6.90											
Dioctyl adipate (B_{23})	--	--	--	--	--	--	--	0.88	--	17.0	3.10	1.00	0.59	--	186	41	30	
Methane, sulfonyl bis	--	--	--	--	--	--	--	--	--	0.95	--	--	0.89	--	--	--	--	
Ethane, 1,1'Oxybis(2-methoxy)	--	--	--	--	--	--	--	--	--	0.38	--	--	--	--	--	--	--	
Tetrachloro benzene	--	--	--	--	--	--	--	--	--	0.78	--	--	0.43	--	--	--	9.38	

*Dow Est. B_{23} = Blank contamination Survey #2 & 3

-- = Less than detection

(1) = Conc. based on a comparison of the total ion area of the compound with that of an internal std.

Discharger: Dow Chemical Co. Midland Plant

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office
Conventional Water Samples

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

	SURVEY #1							SURVEY #2			SURVEY #3				SURVEY #4			
	L.H. Intake	Tit.R. Intake	002	005	012	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	L.H. Intake	Tit.R. Intake	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	
SAMPLE TYPE	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	
TIME	0808-0923	0735-0830	0844-0906	0737-0650	0955-0840	0950-0730	0925-0920	1108-0550	0720-0435	0900-0635	1002-0521	0735-0450	0900-0542	1020-0640	0917-0518	0800-0504	0948-0555	
FLOW, MGD	12.4*	65.0*	5.5*	5.2*	34.6*	34.8*	1.87*	12.4*	65.2*	34.6*	12.4*	55.0*	27.3*	1.87*	12.4*	65.7*	45.0*	
TEMPERATURE °C	19-21	22-24	32-34	22-27	25-27	21-26	25-30	18-20	18-20	18-20	14-16	16-18	17-20	20-23	12-16	10-15	11-17	
PH (S.U.)	7.7-8.0	7.9-8.3	6.0-7.4	7.7-8.3	8.1-8.2	6.7-7.2	—	7.1-7.6	7.1-8.2	6.7-7.0	7.1-7.5	6.9-8.3	6.8-7.4	—	7.0-7.3	7.0-8.0	6.5-7.4	
CONDUCTIVITY μmho/cm	210-230	380-510	—	700-900	—	3700-3800	—	220-240	500-650	4000-5000	230-260	500-680	4800-5400	—	210-280	450-700	2400-4000	
PARAMETER	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day
I. ORGANICS (Continued)																		
E. Other Extractables (1) (Continued)																		
Pentanone, hydroxy methyl	—	—	—	—	—	—	—	—	—	—	1.30	—	1.30	—	—	6.58	—	
Benzaldehyde	—	—	—	—	—	—	—	—	—	—	0.16	—	—	—	—	—	—	
1,1'Biphenyl,2-phenoxy	—	—	—	—	—	—	—	—	—	—	—	—	—	0.15	—	—	—	
1,1'Biphenyl,4-phenoxy	—	—	—	—	—	—	—	—	—	—	—	—	—	0.04	—	—	—	
1,1 Biphenyl	—	—	—	—	—	—	—	—	—	—	—	—	—	2.20	—	—	—	
Alkyl benzene, C_8H_{10}	—	—	—	—	—	—	—	—	—	—	—	—	—	3.00	—	—	—	
Alkyl benzene, C_9H_{12}	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
2-Cyclohexen-1-ol (B_4)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.08	—	
2-Cyclohexen-1-one	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.59	—	
1,2-Cyclohexandiol	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.45	—	—	
Cyclohexone	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.33	—	—	
2-Propanol,1-(2-methoxy,propoxy)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	101.30	
1-Propanol,2-(2-hydroxy,propoxy)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	60.05	
Benzamide,N-butyl	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.70	
Oxybis propanol	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	33.03	

*Dow Est.

B_4 = Blank contamination Survey #4

(1) = Conc. based on a comparison of the total ion area of the compound with that of an internal std.

— = Less than detection

Discharger: Dow Chemical Co. Midland Plant

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office
Conventional Water Samples

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

	SURVEY #1							SURVEY #2			SURVEY #3				SURVEY #4			
	L.H. Intake	Tit.R. Intake	002	005	012	031	Dow Corn.	L.H. Intake	Tit.R. Intake	(1) 031	L.H. Intake	Tit.R. Intake	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	
SAMPLE TYPE	G	G	G	G	G	G	G	G	G		G	G	G	G	G	G	G	
TIME	2238	2130	2355	1751	0043	1220 / 1750	2310	2225	2020		2140	2000	2045	2205	1735	1710	1810	
FLOW, MGD	12.4*	65.0*	5.5*	5.2*	34.6*	34.8*	1.87*	12.4*	65.2*		12.4*	55.0*	27.3*	1.87*	12.4*	65.7*	45.0*	
TEMPERATURE °C	20.0	24.0	33.0	27.0	27.0		27.5	19.5	20.0		16.0	16.0	19.0	23.0	12.0	10.0	12.0	
PH (S.U.)	7.8	8.2	7.4	8.1	8.15	6.8/6.7	--	7.4	7.1		7.4	8.0	7.2	--	7.0	8.0	7.3	
CONDUCTIVITY µhmo/cm	220	380	--	850	--	3800/3700	--	220	510		260	500	4900	--	210	520	4000	
PARAMETER	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day
I. ORGANICS (Continued)																		
F. Volatiles																		
Chloromethane	--	--	--	--	--	--	57.7	--	--		--	--	--	4.50	--	--	--	
Methylene chloride (B134)	--	--	1.6	0.2	--	52.24	1.9	--	--		0.30	--	1.30	0.14	--	--	45.00	
Trichlorofluoromethane	--	--	2.6	--	--	--	--	--	--		--	--	--	--	--	--	--	
1,1-Dichloroethylene	--	--	0.9	--	--	0.87	--	--	--		--	--	0.70	0.50	--	--	5.25	
1,1-Dichloroethane	--	--	--	--	--	1.31	--	--	--		--	--	1.00	0.30	--	--	1.80	
Chloroform (^{B}134)	3.6	--	0.20	--	--	2.90 / 2.84	5.90	3.62	--		3.10	--	3.00	--	3.62	--	9.38	
1,2-Dichloroethane (^{B}134)	--	--	4.50	--	--	2.41	--	--	--		--	--	2.00	1.09	--	--	3.75	
1,1,1-Trichloroethane	--	--	0.20	--	--	0.70 / 1.13	8.10	--	--		--	--	1.02	296	--	--	4.13	
Carbon Tetrachloride	--	--	--	--	--	3.50 / 4.06	3.10	--	--		--	--	2.10	--	--	--	18.77	
Bromodichloromethane (^{B}4)	0.78	--	--	--	--	0.70 / 0.96	--	1.24	--		0.90	--	--	--	0.85	--	1.24	
1,2-Dichloropropane	--	--	--	--	--	1.10	--	--	--		--	--	0.90	--	--	--	1.91	
Trichloroethylene	--	--	0.10	--	--	0.70	0.90	--	--		--	--	0.60	0.40	--	--	1.39	
Dibromochloromethane	0.95	--	--	--	--	2.00	--	0.92	--		--	--	--	--	--	--	4.88	
Benzene	--	--	1.10	--	--	--	18.70	--	--		--	--	--	6.70	--	--	--	
1,1,2,2-Tetrachloroethane	--	--	0.11	--	--	1.10 / 1.16	6.10	--	--		--	--	0.80	2.80	--	--	7.51	
Toluene	--	--	1.30	--	--	--	390	--	--		--	--	--	733	--	--	--	
Chlorobenzene	--	--	--	--	--	--	7.30	--	--		--	--	1.0	7.20	--	--	--	
Ethylbenzene	--	--	3.10	--	--	--	28.10	--	--		--	--	--	17.2	--	--	--	
Chloroethane	--	--	--	--	--	--	--	--	--		--	--	--	4.20	--	--	--	
Trans-1,2-Dichloroethylene	--	--	--	--	--	--	--	--	--		--	--	--	0.20	--	--	--	
Bromoform	--	--	--	--	--	--	--	--	--		--	--	--	--	--	--	4.50	

*Dow Est. (1) No volatile samples obtained B134 - Blank contamination Surveys 1, 3 & 4 B4 - Blank contamination Survey 4

-- = Less than detection

Discharger: Dow Chemical Co. Midland Plant

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

Conventional Water Samples

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

	SURVEY #1							SURVEY #2			SURVEY #3				SURVEY #4			
	L.H. Intake	Tit.R. Intake	002	005	012	031	Dow Corn.	L.H. Intake	Tit.R. Intake	(1) 031	L.H. Intake	Tit.R. Intake	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	
SAMPLE TYPE	G	G	G	G	G	G	G	G	G		G	G	G	G	G	G	G	
TIME	2238	2130	2355	1751	0043	1220 / 1750	2310	2225	2020		2140	2000	2045	2205	1735	1710	1820	
FLOW, MGD	12.4*	65.0*	5.5*	5.2*	34.6*	34.8*	1.87*	12.4*	65.2*		12.4*	55.0*	27.3*	1.87*	12.4*	65.7*	45.0*	
TEMPERATURE °C	20.0	24.0	33.0	27.0	27.0		27.5	19.5	20.0		16.0	16.0	19.0	23.0	12.0	10.0	12.0	
PH (S.U.)	7.8	8.2	7.4	8.1	8.15	6.8/6.7	--	7.4	7.1		7.4	8.0	7.2	--	7.0	8.0	7.3	
CONDUCTIVITY µhmo/cm	220	380	--	850	--	3800/ 3700	--	220	510		260	500	4900	--	210	520	4000	
PARAMETER	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day
I. ORGANICS (Continued)																		
G. Other Volatiles (2)																		
Methane, dimethoxy	--	--	--	--	--	49 33 / 37 70	--	--	--		--	--	21.90	--	--	--	45.04	
Ethane, 1,1'Oxybis	--	--	--	--	--	25 25 / 20 00	--	--	--		--	--	6.60	153	--	--	13.14	
Ethane, 1,1,1,2-Tetrachloro	--	--	10.60	--	--	--	--	--	--		--	--	--	--	--	--	--	
Benzene, ethenyl	--	--	28.40	--	--	--	--	--	--		--	--	--	--	--	--	--	
Benzene, dimethyl-isomers	--	--	3.10	--	--	--	608	--	--		--	--	--	452	--	--	--	
Benzene, alkyl-isomers (C_9H_{12})	--	--	44.00	--	--	--	--	--	--		--	--	--	--	--	--	--	
2-Propanone	--	--	--	--	--	--	0.70	--	--		--	--	--	--	--	--	--	
Cyclohexane, methyl	--	--	--	--	--	--	17.20	--	--		--	--	--	--	--	--	--	
Methane, trimethoxy	--	--	--	--	--	3 77	--	--	--		--	--	--	1.03	--	--	--	
2-Propanol	--	--	--	--	--	--	35.9	--	--		--	--	--	--	--	--	--	
2-Chloropropane	--	--	--	--	--	--	--	--	--		--	--	--	53	--	--	--	
Propane, 2,2'-Oxybis	--	--	--	--	--	--	--	--	--		--	--	--	10	--	--	--	
Propane, 1,1,1-Trichloro	--	--	--	--	--	--	--	--	--		--	--	--	0.97	--	--	--	
2-Butanol, 2-Methyl	--	--	--	--	--	--	--	--	--		--	--	--	0.47	--	--	--	
Methane, Oxybis	--	--	--	--	--	--	--	--	--		--	--	--	0.28	--	--	--	
														--	--	--	4.13	

*Dow Est. (1) No volatile samples obtained (2) Conc. based on a comparison of the total ion area of the compound with that of an internal std.

-- = Less than detection

Discharger: Dow Chemical Co. Midland Plant

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office
Conventional Water Samples

Sample Type: 8 C-8 hour flow proportioned composite
24C-24 hour flow proportioned composite
EVC-Equal Volume Composite
G-Grab

	SURVEY #1							SURVEY #2			SURVEY #3				SURVEY #4			
	L.H. Intake	Tit.R. Intake	002	005	012	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	L.H. Intake	Tit.R. Intake	031	Dow Corn.	L.H. Intake	Tit.R. Intake	031	
SAMPLE TYPE	24 EVC	24 EVC	24 EVC	24EVC	24EVC	24EVC	24EVC	24EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	
TIME	0808-0923	0735-0830	0844-0906	0737-0650	0955-0840	0950-0730	0925-0920	1108-0550	0720-0435	0900-0635	1002-0521	0735-0450	0900-0542	1020-0640	0917-0518	0800-0504	0948-0555	
FLOW, MGD	12.4*	65.0*	5.5*	5.2*	34.6*	34.8*	1.87*	12.4*	65.2*	34.6*	12.4*	55.0*	27.3*	1.87*	12.4*	65.7*	45.0*	
TEMPERATURE °C	19-21	22-24	32-34	22-27	25-27	21-26	25-30	18-20	18-20	18-20	14-16	16-18	17-20	20-23	12-16	10-15	11-17	
PH (S.U.)	7.7-8.0	7.9-8.3	6.0-7.4	7.7-8.3	8.1-8.2	6.7-7.2	—	7.1-7.6	7.1-8.2	6.7-7.0	7.1-7.5	6.9-8.3	6.8-7.4	—	7.0-7.3	7.0-8.0	6.5-7.4	
CONDUCTIVITY µmho/cm	210-230	380-510	—	700-900	—	3700-3800	—	220-240	500-650	4000-5000	230-260	500-680	4800-5400	—	210-280	450-700	2400-4000	
PARAMETER	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day	Gross #/Day
II. METALS																		
Arsenic	—	—	—	0.26	—	—	—	—	—	0.87	—	—	—	—	—	—	—	
Cadmium	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Chromium	—	—	21.30	0.43	0.58	2.30	12.50	—	1.10	3.60	—	0.90	3.20	—	—	1.64	3.75	
Copper	8.70	3.80	0.30	0.35	—	0.58	6.20	5.07	—	1.40	5.10	1.80	—	—	5.70	2.19	1.13	
Lead	0.21	—	—	—	—	—	—	—	—	—	0.50	—	—	—	—	—	—	
Zinc	5.0	4.9	1.10	0.48	2.90	18.0	1.70	2.69	4.90	26.8	1.20	1.40	23.2	—	2.30	4.38	39.4	
III. CONVENTIONAL																		
TDS	14170	178890	14910	20820	86280	810000	74720	14170	174000	789500	11790	135320	676440	—	12410	206030	961520	
TSS	520	4880	1060	610	7790	1450	1840	620	14140	2600	—	6880	3640	—	1450	12603	7130	
BOD-5	620	1080	275	130	—	—	2680	105	1090	1445	206	1380	1370	2640	—	—	1500	
COD	620	11930	2060	1520	5190	34540	9680	—	8700	29150	413	9630	38480	9980	—	8770	41283	
TOC	—	3790	460	390	1730	4640	1450	—	4350	6060	—	3670	5460	1110	—	5480	7880	
NH_3-N	—	—	—	—	—	1640	835	—	—	1750	—	—	1310	770	—	—	1180	
TKN	17.5	360	30	30	200	1860	880	13	375	2070	6.2	270	1700	740	11.4	430	1630	
$NO_2 + NO_3$	34.1	330	30	10	180	115	16	34	375	104	19.6	73.3	11.4	2.8	17.6	1430	413	
Total Phorphorus	—	27	2	3	20	130	5	—	27	320	—	—	420	4.7	—	27.4	146	
Chloride	930	21690	2890	6030	11540	340000	42110	830	19030	357865	827	18810	302820	37430	930	25750	427840	
Fluoride	—	108	4	8	57	203	12	10	108	202	31.0	91.7	160	9.4	—	54.8	188	
Sulfate	1760	22230	1610	1990	11250	87070	—	1655	22840	80810	1655	20180	63750	—	1550	25750	75060	
Phenol (4AAP)	—	—	1	—	—	8	4	—	—	6.3	—	—	2.5	—	—	—	751	
Cyanide	—	—	—	—	—	—	—	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	

*Dow Est. (1) Not analyzed
— = Less than detection

APPENDIX C

PCDDs and PCDFs
Methodology and Quality Control

Large Volume Sampling Study

I. DIOXIN METHODOLOGY - WATER

The objective of this study was to analyze selected polychlorinated dibenzofurans (PCDF) and polychlorinated dibenzo-p-dioxins (PCDD) in water. The detection limits specified for these compounds were parts-per-quadrillion (1 part in 10^{15} or ppq). Specific compounds which were selected for identification included: 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF), 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), and all tetra through octa chloro furan and dioxin isomers. High resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) was used to identify and quantify these materials at the indicated trace level. The exact masses used for each isomer class and the expected isotope ratio used in part for identifying individual compounds, as well as limits of detection for the water are presented in Table 1. 2,3,7,8-tetrachlorodibenzo-p-dioxin-$^{13}C_{12}$ was used as an internal standard for quantification and recovery determinations. These recovery determinations are found in Table 2 and were used to estimate the influence of the matrices on the analytical measurements.

Preparation of Water Samples

The water samples were extracted and cleaned-up using the following procedure. A ten liter aliquot of water was transferred from the original sample bottle to a 19 liter glass bottle, and spiked with 2 ng of 2,3,7,8-tetrachlorodibenzo-p-dioxin-$^{13}C_{12}$ (2,3,7,8-TCDD-$^{13}C_{12}$). The water aliquot and internal standard were mixed for 30 minutes using a magnetic stirring bar. After the initial mixing, the stirring was discontinued and one liter of hexane was added to the aliquot for extraction of organics. The stirring was resumed and the aliquot extracted for 16 hours. After the extraction process, the aliquot and hexane were allowed to equilibrate for two hours. The hexane was transferred to a 1000 ml Kuderna-Danish (K-D) flask using a 100 ml volumetric pipet. Distilled water was added to the bottle to force the last 100 ml or less of hexane into the neck of the bottle which facilitated its transfer. The K-D flasks were placed in a hot water bath and the extracts were concentrated to a volume of 20 ml. The extracts were transferred to 250 ml separatory funnels, using three 5 ml hexane rinses of the K-D flask. The hexane extracts were washed three times each in the following sequence: 50 ml of 1M NaOH, 50 ml of distilled water, 50 ml of concentrated H_2SO_4, and finally 50 ml of distilled water. All base, acid and water washes were collected, neutralized and discarded. The hexane extracts were transferred to 125 ml K-D flasks, using three 5 ml hexane rinses of 250 separatory funnels, and concentrated to a volume of 5 ml. The extracts were introduced onto alumina columns to isolate the furan and dioxin compound classes. The columns were eluted sequentially with 25 ml of hexane, 25 ml of 1:1 (V:V) hexane:carbon tetrachloride, and 20 ml of 1:1 (V:V) hexane:methylene chloride. Decane (20 ul) was added to the hexane:methylene chloride fraction containing the furans and dioxins, and the fraction concentrated to 20 ul prior to analyses.

The extracts were analyzed by high resolution gas chromatography/ high resolution mass spectrometry (HRGC/HRMS) at a mass resolution of 8000-12000 ($M/\Delta M$, 10 percent valley). A VG Model 7070H mass spectrometer interfaced to a Carlo Erba Model 4160 gas chromatograph was used. The chromatographic column was a 30M DB-5 fused silica column with helium carrier gas. All HRGC/HRMS data were acquired in the multiple ion detection mode using a VG Model 2035 Data System and will be archived on magnetic tape for a period of five years.

II. QUALITY CONTROL

A. Internal Audits

The following quality assurance procedures were employed. Perfluorokerosene was introduced through a heated inlet for tuning, mass calibration and establishing mass resolution. A 2 ul injection of a test mixture containing 20 pg/ul of 2,3,7,8-TCDD and 95 pg/ul of 2,3,7,8-TCDD-$^{13}C_{12}$ was analyzed. The analysis of this test mixture provided the following information:

- Information concerning sensitivity (absolute response of 2,3,7,8-TCDD-$^{13}C_{12}$)
- Accuracy of quantification (native response as compared to that of its C-13 analogue)
- Elution within a specific retention time window
- Chromatographic peak shape symmetry.

Decane was analyzed to check for dioxin carry over. This information is used to access performance of the instrument before the measurement of PCDF and PCDD at trace levels is conducted in actual samples.

The actual sample analyses were by the following procedure: four to six samples, a duplicate or spike, an extraction blank, a test mixture, a decane blank, then the cycle was repeated.

B. External Audits

1. On-site Visit

During September 20-21, 1982, Marcia A. Kuehl, QC Coordinator for the Central Regional Laboratory, toured the Battelle Columbus dioxin facilities and audited the chain-of-custody documentation. She spent a large portion of the time observing the acquisition and reduction of the dixoin/furan data by HRGC/HRMS.

The objective of this audit was to inspect whether the analysis of Dow Study samples was conducted according to Contract #68-01-6421, (Amendment to Work Assignment Specifications #003) and to present and resolve any anomalous results reported by Battelle for the blind QC samples that CRL submitted along with the actual samples.

Document Control Study

When the Dow samples arrived at Battelle, the secured shipping and receiving area contacted the team responsible for the project. An authorized person signed for the samples and transported them to the Dioxin Extraction Laboratory. There the samples were unpacked and checked against the packing list. They were then recorded in the GCA Project File logbook along with a Battelle number. All logbook entries were of the form XXYYZZ where XX indicates the logbook number, YY the page of entry and ZZ the line number of the page.

Only three people had keys to the Dioxin Extraction Laboratory and sample storage area. As the extraction of the samples proceeded, all extraction notes were entered in the GCA Project File logbook according to the format above. When the extracts were ready for HRGC/HRMS, they were picked up by Dan Aichele, and all HRGC/HRMS work pertaining to the samples was entered in the HRGC/HRMS logbook, with cross-references to the extract numbers obtained from the GCA Project File logbook kept in the locked Dioxin Extraction Laboratory. All computer outputs and raw HRGC/HRMS data was filed by CRL sample number designation in a file box kept in the HRGC/HRMS laboratory. The discs containing Dow sample HRGC/HRMS data were also stored there.

The entire Battelle facility is a security area. In order for visitors to gain entry, they must fill out a visitors card indicating their affiliation and Battelle employee to be contacted. A visitor's badge is typed which indicates that a Battelle escort is required at all times. Employees wear identification badges and can only gain entry by a coded keycard or by showing their ID card to a receptionist. Battelle personnel were careful to not divulge the exact nature of the analytical work being done on other projects, nor to name any other clients.

All of the GCA Project File logbook information, relating HRGC/HRMS logbook information, and raw computer printouts was photocopied and submitted with the final draft of the report on 12/30/82. The final report was peer reviewed at Battelle and was sent to GCA (prime Contractor) as required by the contract. The photocopied logbook and raw data was sent directly to the CRL on 12/30/82 along with a copy of the final report.

Battelle QA/QC Protocols

A decane solvent blank and 2,3,7,8-TCDD-$^{13}C_{12}$ standard was run at least once a day. The area response of the 2,3,7,8-TCDD-$^{13}C_{12}$ standard must be approximately 4000 and no less than 2000. The ion peak ratio at m/z of 320 to 322 and 332 to 334 must be 0.77 $\pm$ 10%. This ion peak ratio for the native 2,3,7,8-TCDD to 2,3,7,8-TCDD-$^{13}C_{12}$ must be within 10% of the expected ratio for the analysis to be acceptable.

A seven-point calibration curve of 2,3,7,8-TCDD is run every 6 months. Each day, the samples are injected to insure that they are within the linear range before actual data reduction/quantitation is done. Two injections of each extract were made to monitor precision of the 2,3,7,8-TCDD-C^{13} recovery. For all of the Dow Samples, 2,3,7,8-TCDD-C^{13} was used as the internal standard. No historically based control limits for 2,3,7,8-TCDD-$^{13}C_{12}$ recovery from water and fish have been set by Battelle. Recovery information is found in Table 2.

No splitting of Dow Samples into lab-prepared duplicates was done. No lab spiking of actual Dow Samples to serve as a matrix spike was done either. The blind QC samples submitted by CRL served in these functions.

Quantification Procedure

Before any samples, standards or blanks are injected into the Carlo Erba HRGC and VG 7070H HRMS system, the instrument is tuned by the perfluorokerosene lock mass of 319. The response of the MS to this compound must meet the mass criteria specified before samples are injected. The VG 7070H electronics were modified by Battelle personnel to allow more rapid scans over the acquisition time, and thus give greater resolution and lower detection levels.

All quantitation is done on the basis of a one-point calibration standard of 2,3,7,8-TCDD-C^{13}. Qualitative identification is done on the basis of retention time. The correct mass ratio ($\pm$ 10%) of the isomer's two largest peaks is also used for verification of identity.

The simplified formulas used are given below:

$$\text{CONC pg/g} = \frac{2000 \text{ pg } 2,3,7,8\text{-TCDD-}C^{13} \times \dfrac{\text{area of analyte in sample}}{\text{area of } 2,3,7,8\text{-TCDD-}C^{13} \text{ in sample}}}{\text{weight of sample (g)}}$$

$$\text{detection limit} = \frac{2.5 \times \dfrac{\text{area of analyte in sample} \times 2000 \text{ pg}}{\text{area of } 2,3,7,8\text{-TCDD-}C^{13} \text{ in sample}}}{\text{sample weight}}$$

2. Blind QC Water Sample Results

QC samples were prepared and originally analyzed by Dr. Robert Harless, EPA-RTP. They were sent to Curtis Ross, Director CRL, EPA Region V to use as part of the Quality Assurance program audit of Battelle Columbus Laboratories for this study. The water QC samples were received in sealed ampules with benzene as the solvent. These ampules were opened by CRL personnel at Argonne National Laboratory and mixed with approximately 25 liters of organic free water to form the blind QC samples. CRL sample numbers were assigned to the blind QC samples to further aid in disguising them.

Before any analytical data was generated, a comparison of EPA 2,3,7,8-TCDD standard (82LS10R05) was made with the Battelle prepared quantitation standard. The EPA standard was previously round robin-tested and found to contain 10 pg/ul (600 pg in the 60 ul ampule). A variation of only + 10% was allowed between Battelle and this EPA standard. Four additional standards in benzene were then analyzed for 2,3,7,8-TCDD; 1,3,6,8-TCDD; 1,3,7,9-TCDD; 2,3,7,8-TCDF; OCDD and OCDF.

After these standards were judged acceptable by Dr. Harless, a blind QC spike (81EH07S09) was analyzed and reported next. After acceptance of this data, actual sample and other blind analysis began. Results of all blind standards and samples are given in Table 3.

Recovery Comments

1) 81EH07S23(Spike QC) - OCDF was reported at a much higher level than the spike. The data was re-reduced and the result of 230 ppt was verified. The problems in OCDD and OCDF recoveries appear to stem from the lack of a OCDD-C^{13} standard to check the actual response against the internal standard.

2) 81EH07S24(Blank QC) - OCDF at a level of 180 ppq was reported. No OCDF was present in the QC ampule used to mix this sample. The data was recalled from disc and the result reverified at 230 ppq. If this QC sample was mixed after the 81EH07S23 and/or 81EH07S25 QC Samples, carryover may have occurred to account for this value.

3) 81EH07S25(Spike QC) - Recovery of OCDF was high (750 ppq recovered vs 160 ppq spiked). Due to the lack of a C^{13} labelled OCDD standard to judge the relative response against 2,3,7,8-TCDD-C^{13}, quantitation was, at best, an estimate. The data was recalled from disc and reverified at 430 ppq using peak height rather than area.

CONCLUSION:

Due to the imprecise and inaccurate OCDF results discovered by the three blind audits, any positive OCDF data for water samples should not be considered usable. All other dioxin/furan sample data should be considered of an acceptable level of quality.

TABLE 1. SELECTED DATA FOR THE POLYCHLORINATED DIBENZOFURANS AND POLYCHLORINATED DIBENZO-P-DIOXINS OF INTEREST

Compounds	Accurate mass		Theoretical Isotope Ratio	Limit of Detection	
	Low Mass	High Mass		Water	Fish
Tetrachlorodibenzofuran	303.9016	305.8987*	.77	10 ppq	5 ppt
Tetrachlorodibenzo-p-dioxin	319.8965	321.8936*	.77	10 ppq	5 ppt
Pentachlorodibenzofuran	339.8597*	341.8567	1.54	20 ppq	20 ppt
Pentachlorodibenzo-p-dioxin	355.8546*	357.8517	1.54	20 ppq	20 ppt
Hexachlorodibenzofuran	373.8207*	375.8178	1.23	40 ppq	40 ppt
Hexachlorodibenzo-p-dioxin	389.8156*	391.8127	1.23	40 ppq	40 ppt
Heptachlorodibenzofuran	407.7817*	409.7788	1.03	80 ppq	80 ppt
Heptachlorodibenzo-p-dioxin	423.7766*	425.7737	1.03	80 ppq	80 ppt
Octachlorodibenzofuran	441.7428	443.7398*	0.88	100 ppq	100 ppt
Octachlorodibenzo-p-dioxin	457.7377	459.7347*	0.88	100 ppq	100 ppt

* Quantitation Mass

TABLE 2. INTERNAL STANDARD RECOVERIES OF 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN-$^{13}C_{12}$ IN WATER

Water Recoveries

Sample Name	Internal Standard Recovery (%)
81EH07S10	90
81EH07S12	71
81EH07S22	81
81EH07S23	89
81EH07S23	87
81EH07S24	94
81EH07S13	71
81EH07S26	91
81EH07S39	83
81EH07S53	85
81EH07S66	84
81EH07S88	83

TABLE 3. BLIND WATER SAMPLE RESULTS
UNITS = pg/l

		2,3,7,8-TCDD			2,3,7,8-TCDF			1,3,6,8-TCDD			1,3,7,9-TCDD			OCDD			OCDF		
RFP #	CRL #	Reported	True	% Recovery	Reported	True	% Recovery	Reported	True	% Recovery	Reported	True	% Recovery	Reported	True	% Recovery	Reported	True	% Recovery
EPA-V-1		0	0	-	0	0	-	0	0	-	0	0	-	-	0	-	0	0	-
EPA-V-2		190	200	95	0	0	-	116	200	58	44	60	73	-	0	-	0	0	-
EPA-V-3		48	40	120	0	0	-	70	100	70	30	30	100	-	0	-	0	0	-
EPA-V-4		36	40	90	0	0	-	63	100	63	22	30	73	-	0	-	0	0	-
EPA-V-26	81EH07S09	10	16	63	25	24	104	5	16	31	2	*5	40	45	80	45	21	80	26
Blank	81EH07S10-B	<3	0	-	<3	0	-	<3	0	-	<3	0	-	-	0	-	<1	0	-
Blank	81EH07S12	<15	0	-	<3	0	-	<15	0	-	<15	0	-	-	0	-	<25	0	-
Blank	81EH07S22-A	<3	0	-	<5	0	-	<3	0	-	<3	0	-	-	0	-	8	0	-
EPA-V-25	81EH07S23	5	*8	62	17	12	142	8**	*8	100	8**	*2	-	-	0	-	230	*40	>400
EPA-V-24	81EH07S24	<1	0	-	3	0	-	<1	0	-	<1	0	-	-	0	-	180	0	-
EPA-V-27	81EH07S25	17	32	53	41	48	85	27**	32	65	27**	*10	-	60	160	60	750	160	>400

* - below contract required detection limit
** - reported as total of 2 isomers
A - 54-77 pg/l pentachlorinated dibenzofurans also reported
B - 11 pg/l pentachlorinated dibenzofurans also reported

APPENDIX D

Large Volume Sampling Study Results

Discharger: Dow Chemical Co. Midland, MI

Sample Date: September 9-10, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

Large Volume Water Samples

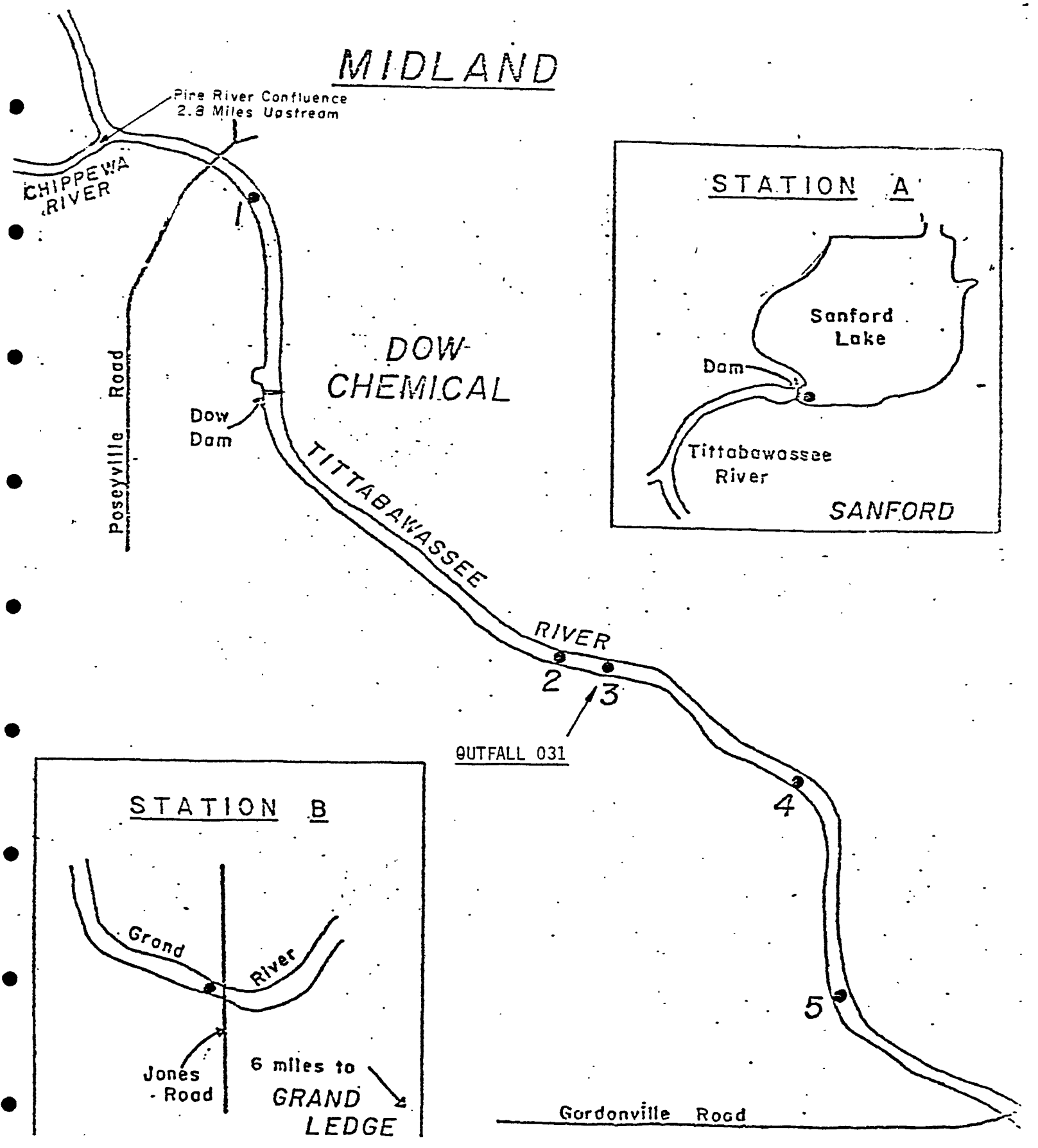
	Lake Huron Water Intake		Tittabawassee River Water Intake		Outfall 005		Outfall 031		Outfall 031 Plume Mixing Zone		Tittabawassee River at Smith's Crossing Road	
SAMPLE TYPE TIME	24 EVC 1108-0550		24 EVC 0720-0435		24 EVC 0755-0450		24 EVC 0900-0630		24 EVC 0935-0645		24 EVC 1105-0525	
FLOW MGD TEMPERATURE °C PH (S.U.) CONDUCTIVITY µmho/cm	12.4 18-20 7.1-7.6 220-240		65.2 18-20 7.1-8.2 500-650		3.5 17.5-21.5 7.2-7.5 570-770		34.6 18-20 6.7-7 0 4000-5500		18-20 7.1-7.5 2200-4500		18-20 7.6-8.2 600-730	
PARAMETER	ppq/ (# isomers)	Gross 10^{-5} lbs/da	ppq/ (# isomers)	Gross 10^{-5} lbs/da	ppq/ (# isomers)	Gross 10^{-5} lbs/da	ppq/ (# isomers)	Gross 10^{-5} lbs/da	ppq/ (# isomers)	Gross 10^{-5} lbs/da	ppq/ (# isomers)	Gross 10^{-5} lbs/da
I. Polychlorinated Dibenzo-P-Dioxin												
2,3,7,8 TCDD	< 10	--	< 10	--	< 120*	--	50	1.44	45	--	< 10	--
Tetrachloro isomers	< 10	--	< 10	--	2300/(5)	6.71	80/(2)	2.31	70/(2)	--	40/(3)	--
Pentachloro isomers	< 20	--	< 20	--	< 20	--	< 20	--	50/(1)	--	< 20	--
Hexachloro isomers	< 40	--	< 40	--	< 40	--	< 40	--	< 40'	--	< 40	--
Heptachloro isomers	< 80	--	< 80'	--	< 80	--	< 80	--	< 80'	--	< 80	--
Octachloro isomers	< 100'	--	< 100'	--	< 100	--	<100	--	<100'	--	< 100	--
II. Polychlorinated Dibenzofurans												
2,3,7,8 TCDF	40	0.41	15	0.82	1700	4.96	790	22.80	190	--	50	
Tetrachloro isomers	100/(2)	1.03	30/(2)	1.63	4200/(8)	12.26	9000/(11)	259.71	2200/(9)	--	280/(6)	--
Pentachloro isomers	< 20	--	70/(3)	3.81	5600/(4)	16.35	190/(6)	5.48	450/(7)	--	170/(4)	--
Hexachloro isomers	< 40	--	< 40'	--	50/(1)	0.15	< 40	--	55/(3)	--	< 40'	--
Heptachloro isomers	< 80	--	< 80	--	< 80	--	< 80	--	< 80	--	< 80	--
Octachloro isomers	< 100'	--	< 100'	--	< 100	--	< 100	--	< 100'	--	< 100	--

<100' = A finite value was reported by Battelle at a level below the contract detection limit

* Elevated detection limit. High levels of other tetrachloro isomers may have obscured the response of the 2,3,7,8 isomer.

APPENDIX E

Bioaccumulation Study Results


MIDLAND
Pine River Confluence
2.8 Miles Upstream
CHIPPEWA RIVER
1
DOW CHEMICAL
Dow Dam
Poseyville Road
TITTABAWASSEE RIVER
2
3
OUTFALL 031
4
5
Gordonville Road
STATION A
Sanford Lake
Dam
Tittabawassee River
SANFORD
STATION B
Grand River
Jones Road
6 miles to GRAND LEDGE

Discharger: Dow Chemical Co. Midland, MI

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

	Fish Food	Control	#A Sanford Dam	#1 Tittabawassee River Near Poseyville Road		#3 Tittabawassee River Outfall 031 Mixing Zone		#B Grand River @ Jones Road	#B Grand River @ Jones Road	#C Grand River @ Francis Rd.
SAMPLE TYPE	Fish Food	Caged Fish	Caged Fish	Caged Fish		Caged Fish		Caged Fish	Native Fish	Native Fish
		Day 0	Day 28	Day 28	Day 28 Dup	Day 28	Day 28 Dup	Day 28	Native Fish	Native Fish
PARAMETER	pg/g/ (# isomers)	pg/g/ (# isomers)	pg/g/ (# isomers)	pg/g/ (# isomers)	pg/g/ (#isomers)	pg/g/ #isomers)	pg/g/ (# isomers)	pg/g/ (# isomers)	pg/g/ (# isomers)	pg/g/ (# isomers)
I. ORGANICS										
E. Polychlorinated Dibenzo-P-Dioxins										
2.3.7.8 TCDD	< 5	7	< 5	8	<13*	110	80	< 5	20	< 5
Tetrachloro isomers	< 6	7	< 5	8	<13*	820/(4)	770/(5)	< 7	20/(1)	< 11
Pentachloro isomers	< 10	< 10	< 10	<10	<10	< 10	510/(3)	<10	25/(1)	< 10
Hexachloro isomers	< 20	< 20	< 20	<20	<20	< 20	< 20	<20	< 20	< 20
Heptachloro isomers	< 40	< 40	< 40	<40	<40	< 40	< 40	<40	< 40	< 40
Octachloro isomers	< 90	< 90	< 90	<90*	<90	< 90	< 90	<90	< 90	< 90
F. Polychlorinated Dibenzofurans										
2.3.7.7 TCDF	20	30	8	15	120	140	51	< 5	40	< 5
Tetrachloro isome-s	70/(4)	60/(3)	8/(1)	40/(4)	290/(7)	5800/(7)	8500/(11)	< 7	230/(7)	20/(1)
Pentachloro isomers	< 10	< 10	< 10	< 10	<10	590/(6)	8700/(6)	<10	140/(4)	< 10
Hexachloro isomers	< 20	< 20	< 20	< 20	<20	< 20	< 20	<20	30/(2)	< 20
Heptachloro isomers	< 40	< 40	< 40	< 40	<40	< 40	< 40	<40	< 40	< 40
Octachloro isomers	< 90	< 90	< 90	< 90	<90	< 90	< 90	<90	< 90	< 90

* - Elevated detection limit due to poor internal std. recovery

Discharger: Dow Chemical, Midland, MI
Bio Study

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

	Control		#A Sanford Dam			#1 Tittabawassee River Near Poseyville Road			#2 Tittabawassee River Upstream of Outfall 031			#3 Tittabawassee River Outfall 031 Mixing Zone							
SAMPLE TYPE	Fish		Caged Fish			Caged Fish			Caged Fish			Caged Fish							
	Day 0	Day 0 Dup	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	Day 2	Day 4	Day 8	Day 14	Day 14 Dup.	Day 21	Day 28	Day 28 Dup
PARAMETER	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
I. ORGANICS																			
A. Base/Neutral																			
Phenanthrene	60	--	--	--	--	--	72	--	--	--	--	34	--	--	--	--	--	--	--
Naphthalene	84	62	--	--	--	--	--	22	--	--	--	60	28	--	--	--	--	--	--
Bis(2-ethylhexyl) phthalate	2700	--	--	95	260	--	1200	--	--	21	360	--	--	--	--	--	390	--	--
Di-n-Butyl phthalate	--	--	--	--	150	--	--	--	--	--	78	70	84	--	--	--	--	--	--
1,2-Dichlorobenzene	--	--	--	--	--	--	--	--	--	--	--	260	140	26	48	62	--	--	--
1,3-Dichlorobenzene	--	--	--	--	--	--	--	--	--	--	--	170	220	120	150	130	250	90	120
1,4-Dichlorobenzene	--	--	--	--	--	--	--	--	--	--	--	160	260	120	160	210	280	110	140
1,2,4-Trichlorobenzene	--	--	--	--	--	--	110	--	--	--	--	1600	2400	1700	1200	1400	1800	1900	1900
Hexachlorobenzene	--	--	--	--	--	--	--	--	--	--	--	--	46	--	--	--	84	120	150
B. Acid Extractables																			
2,4,6-Trichlorophenol	--	--	--	--	--	--	160	--	--	--	--	--	--	--	--	--	--	140	--
Pentachlorophenol	--	--	--	--	--	--	630	--	--	--	--	870	1300	900	--	--	500	1000	900
Phenol	--	--	140[a]	--	--	100[a]	--	--	--	--	--	--	--	--	--	--	--	--	--

-- = Less than detection

a = Sample matrix caused reduced resolution between native phenol and the d_5 phenol surrogate spike. As a result, the presence of phenol is not confirmed in this sample.

Discharger: Dow Chemical, Midland, MI
Bio Study

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

	#4 Tittabawassee River D/S of Outfall 031 Mixing Zone			#5 Tittabawassee River 2.65 Mi Downstream of Dow Dam			#B Grand River at Jones Road			#B Grand River at Jones Road					Grand River
SAMPLE TYPE	Caged Fish			Caged Fish			Caged Fish			Native Fish					Native Fish
	Day 14	Day 28	Day 28 Dup	Day 14	Day 28	Day 28 Dup	Day 14	Day 28	Day 28 Dup	82LS07 S01	82LS07 S02	82LS07 S03	82LS07 S04	82LS07 S05	82LS07 S06
PARAMETER	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
I. ORGANICS															
A. Base/Neutral															
1,3-Dichlorobenzene	86	72	52	66	--	62	--	--	--	--	--	--	--	--	--
1,4-Dichlorobenzene	110	70	50	80	--	60	--	--	--	--	--	--	--	--	--
1,2,4-Trichlorobenzene	650	790	570	440	--	690	--	--	--	--	--	--	--	--	--
Di-n-Butyl phthalate	--	--	56	500	130	62	--	--	--	--	--	52	--	--	--
Bis(2-Ethylhexyl)phthalate	150	130	78	110	--	180	--	62	--	--	--	320	100	78	--
Naphthalene	--	--	--	--	--	Trace	--	3000	120	--	--	22	1700	660	--
Phenanthrene	--	--	--	--	--	--	--	24	--	--	--	--	--	--	--
1,2-Dichlorobenzene	34	--	--	26	--	--	--	--	--	--	--	--	--	--	--
Diethyl phthalate	--	--	--	100	--	--	--	--	--	--	--	--	--	--	--
B. Acid Extractables	None	None	None	None	None	None	--	--	--	--	--	--	--	--	--

-- = Less than detection

Discharger: Dow Chemical Co., Midland, MI Bio Study

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

	Control		#A Sanford Dam			#1 Tittabawassee River Near Poseyville Road			#2 Tittabawassee River Upstream of Outfall 031			#3 Tittabawassee River Outfall 031 Mixing Zone							
SAMPLE TYPE	Caged Fish		Caged Fish			Caged Fish			Caged Fish			Caged Fish							
	Day 0	Day 0 Dup.	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	Day 2	Day 4	Day 8	Day 14	Day 14 Dup.	Day 21	Day 28	Day 28 Dup.
	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/k
C. Extractables Qualitative Analysis (1)																			
1,3-Dioxolane-4-Methanol 2,2-dimethyl	3400	11000			64000	500	31000	4000	27000	34000	33000	4900		8300	1900	17000	13000	20000	15000
Benzaldehyde	840					--	--		780					--	--	400	380	--	
Furan, 2-pentyl	1400				11000	2700	5700	960	3100	7800		2900		--	6200	2900	3700	4700	
3-Octen-2-One						--	--		810					--	--	740	--	--	
3,5-Heptadien-2-One,6-methyl					1200	1200	3900				2500		3800	--	--	3100	1900	--	
3-Nonen-2-One						--	2800		3800		1300		8000	--	--	4500	2400	--	
Trichlorobenzene isomers						--	--					2400		740	720	1000	1000	730	
Tetrachlorobenzene,isomers						--	1700						8900	4000	7300	9400	7400	15000	
2-Octenal,2-butyl						--	--		1900					--	--	1500	--	--	
Benzene acetic acid, alpha-methoxy esters of						--	--							--	--	830	670	--	
Pentachloro benzene						--	--							--	--	680	830	1800	
Benzene acetic acid					4800	--	2100				2100			--	--	--	--	--	
3-Penten-2-One,5 phenyl						--	--							--	--	--	1000	--	
1,1' Bi phenyl, 2-phenoxy						--	--							--	--	--	250	--	
2-cyclohexen-1-one, 3,5-dimethyl	1000																		
2,4-Nonadienal	300												1000						
Cyclohexanone		22000			3700				4900		2900								1300
3-Buten-2-One,4-Phenyl																			
Cyclohexanol								20000	3300	9000	1400		1000						

(1) Concentration based on a comparison of the total ion area of the compound with that of the internal standard
-- = Less than detection

Discharger: Dow Chemical Co., Midland, MI Bio Study

Sample Date: September 1-30, 1981

U. S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

	#4 Tittabawassee River D/S of Outfall 031 Mixing Zone			#5 Tittabawassee River 2.65 Mi Downstream of Dow Dam			#8 Grand River at Jones Road			#8 Grand River at Jones Road					Grand River
SAMPLE TYPE	Caged Fish			Caged Fish			Caged Fish			Native Fish					Native Fish
	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	82LS07 S01	82LS07 S02	82LS07 S03	82LS07 S04	82LS07 S05	82LS07 S06
PARAMETERS	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
C. Extractables Qualitative Analysis (1)															
1,3-Dioxolane-4-Methanol 2,2-dimethyl	9800	2500	40000	19000	15000	23000	8000	3700	2100	22000	3100			3400	--
Benzaldehyde	700	--		420	740									--	--
Furan, 2-pentyl	4000	1500		2000			3400			3500	2900			5100	--
3-Octen-2-One	2500	--								840				--	--
3,5-Heptadien-2-One,6-methyl	3000	--	3400	3100	4500	2000	5800	3100	2000	13000	4900	5900		--	--
3-Nonen-2-One	3600	--								4000				--	--
Trichlorobenzene isomers	--	--	450				830							--	--
Tetrachlorobenzene isomers	1600	--	3400	3700		4200	13000							--	--
2-Octenal, 2-butyl	--	--												--	--
Benzene acetic acid, alpha-methoxy esters of	--	--												--	--
Pentachloro benzene	--	--												--	--
Benzene, ethenyl	--	--												7200	--
Nitrous acid, cyclohexyl ester	--	--												17000	--
3-Penten-2-One,3-methyl	--	--												7000	--
Cyclohexanol				2000		1800	3400	1500	3500						
Cyclohexanone				890							13000				
2-cyclohexen-1-one,3,6,-dimethyl-6-(1-methylethyl				2500											
Benzeneacetic Acid				6300				920				3200			

(1) Concentration based on a comparison of the total ion area of the compound with that of the internal standard.
-- = Less than detection

Discharger: Dow Chemical Co., Midland, MI Bio Study

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

	#4 Tittabawassee River D/S of Outfall 031 Mixing Zone			#5 Tittabawassee River 2.65 Mi Downstream of Dow Dam			#B Grand River at Jones Road			#B Grand River at Jones Road					Grand River
SAMPLE TYPE	Caged Fish			Caged Fish			Caged Fish			Native Fish					Native Fish
	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	82LS07 S01	82LS07 S02	82LS07 S03	82LS07 S04	82LS07 S05	82LS07 S06
PARAMETERS	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
C. EXTRACTABLES QUALITATIVE ANALYSIS (1) Continued															
Benzene Ethanol	--	--	--	--	--	--	--	--	730	--	--	--	--	--	--
Benzene Acetic Acid	--	--	2700	--	3100	--	810	--	--	--	--	--	--	--	--
2-Cyclohexen-1-One-,3,5-Dimethyl	--	--	--	--	--	--	--	--	--	1400	--	1100	--	--	--
3-Buten-2-One,4-Phenyl	--	--	--	--	--	--	--	--	--	3000	--	--	--	--	--
Decanoic Acid,2,4,6-Trimethyl-Methylester	--	--	--	--	--	--	--	--	--	7200	--	--	--	--	--
3-Hepten-2-One	--	--	--	--	--	--	--	--	--	--	1500	--	--	--	--
Benzene Ethanol	--	--	--	--	--	--	--	--	--	--	--	720	--	--	--
Benzene Propanoic Acid	--	--	--	--	--	--	--	--	--	--	--	840	--	--	--

Discharger: Dow Chemical Co, Midland, MI, Bio Study

Sample Date: September 1-30, 1981

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

	Control		#A Sanford Dam			#1 Tittabawassee River Near Poseyville Road			#2 Tittabawassee River Upstream of Outfall 031			#3 Tittabawassee River Outfall 031 Mixing Zone							
SAMPLE TYPE	Caged Fish		Caged Fish			Caged Fish			Caged Fish			Caged Fish							
	Day 0	Day 0 Dup.	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	Day 2	Day 4	Day 8	Day 14	Day 14 Dup.	Day 21	Day 28	Day 28 Dup.
PARAMETER	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/k
I. ORGANICS																			
D. PCB/Pesticide																			
Aldrin	8.7[b]	5.2[b]	--	--	--	--	25[b]	--	--	5.9[b]	--	70[b]	49[b]	27[b]	180[b]	121[b]	260[b]	250[c]	260[c]
α-BHC	--	--	7.0[b]	--	5.9[a]	5.4[a]	15[b]	9.1[a]	10[a]	--	5.4[b]	47[b]	57[b]	31[b]	100[b]	99[b]	160[b]	220[b]	110[b]
β-BHC	--	--	--	--	--	--	--	--	--	--	--	6.1[b]	8.1[b]	6.2[b]	20[b]	--	--	24[b]	13[b]
δ-BHC	--	--	--	--	--	--	--	5.3[c]	--	--	--	--	--	--	--	--	--	--	--
γ-BHC	--	--	--	--	--	--	--	--	--	--	--	--	--	--	5.5[b]	--	--	16[b]	--
4,4'-DDD	21[a]	7.8[b]	40[b]	--	8.0[a]	21[a]	--	44[a]	9.1[b]	37[a]	42[a]	12[a]	12[b]	9.9[b]	42[a]	26[c]	6.5[b]	75[b]	37[a]
4,4-DDE	26[b]	17[b]	18[b]	11[b]	10a	17[b]	--	32a	17[b]	20a	18[a]	26[b]	15[b]	--	40[b]	65a	160[b]	52[b]	--
4,4-DDT	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	22[a]	37a	23[c]
Dieldrin	12[a]	13[a]	17[b]	9.2[b]	5.1[a]	15[a]	--	39[b]	23[b]	--	33[b]	12[a]	14[a]	7.5[a]	7.1[a]	9.6[a]	12[a]	7.8[a]	29[b]
Endosulfan I	15[a]	19[b]	13[b]	8.5[b]	5.2[c]	15[b]	8.4[a]	15c	17[a]	18a	14c	70b	--	12b	46[a]	29[a]	51[b]	180[b]	260[b]
Endrin Aldehyde	--	--	--	--	--	--	--	--	9.5[b]	--	--	7.4[b]	--	--	--	12[b]	26[a]	--	13[b]
Heptachlor epoxide	--	--	--	--	--	--	--	--	--	--	--	13[b]	16[b]	10[b]	46[a]	36[b]	--	65[b]	37[b]
Endosulfan sulfate	34[b]	--	--	--	--	30[b]	--	69[b]	29[b]	--	--	--	--	230[b]	23[b]	--	--	22[b]	--
Heptachlor	--	5.1[b]	--	--	--	--	--	--	--	--	--	--	--	--	11b	7.4[b]	14[b]	22[b]	10[b]
Endrin	--	--	--	--	--	--	--	--	--	21[b]	18[b]	--	--	--	--	--	63[b]	--	25[c]
Endosulfan II	--	--	--	--	--	--	--	21[b]	--	--	--	--	--	--	--	--	--	--	--
PCB-1248	--	--	--	--	--	--	--	46[b]	--	--	--	--	--	--	--	--	--	--	--

a = Confirmed on second column GC/ECD
b = Not confirmed on second column GC/ECD
c = Not confirmed on second column due to interference

-- = Less than detection

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Eastern District Office

Discharger: Dow Chemical, Midland, MI Bio Study

Sample Date: September 1-30, 1981

SAMPLE TYPE	#4 Tittabawassee River D/S of Outfall 031 Mixing Zone Caged Fish			#5 Tittabawassee River 2.65 Mi Downstream of Dow Dam Caged Fish			#8 Grand River at Jones Road Caged Fish			#8 Grand River at Jones Road Native Fish					Grand River Native Fish
	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	Day 14	Day 28	Day 28 Dup.	82LS07 S01	82LS07 S02	82LS07 S03	82LS07 S04	82LS07 S05	82LS07 S06
PARAMETER	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
I. ORGANICS															
D. PCB/Pesticide															
Aldrin	34[a]	67[b]	88[c]	53[b]	--	56[c]	--	--	--	--	--	--	--	--	--
α-BHC	43[b]	58[b]	57[b]	54[b]	5.6[a]	39[b]	9.7[b]	5.2	--	13[b]	--	--	13[b]	12[b]	--
β-BHC	--	--	--	6.6[b]	--	--	--	--	--	--	--	--	--	--	--
δ-BHC	--	--	--	--	--	--	--	--	--	7.5[c]	9.0[c]	--	11[c]	7.6[b]	--
γ-BHC	--	--	7.6[b]	--	--	5.3[b]	6.1[a]	--	--	--	--	--	--	6.1[b]	--
4-4'-DDD	28[a]	36[b]	36[a]	34[b]	--	36[a]	19[a]	16[a]	16[a]	130[a]	18[b]	42[a]	240[a]	300[a]	71[b]
4,4'-DDE	18[b]	28[b]	16[c]	21[b]	11[a]	--	--	19[b]	14[b]	140[a]	190[a]	37[a]	240[a]	330[a]	160[a]
4,4'-DDT	--	--	--	--	--	--	--	--	--	110[c]	150[c]	48[c]	180[c]	230[c]	79[c]
Dieldrin	11[a]	5.7[a]	13[b]	13[a]	--	15[a]	--	34[b]	--	9.5[a]	8.9[b]	--	10[a]	17[a]	7.2[c]
Endosulfan I	33[b]	40[b]	45[c]	39[b]	9.3[b]	27[c]	23[b]	18[c]	20[c]	68[a]	94[b]	23[a]	110[b]	150[b]	62[c]
Endrin aldehyde	--	9.0[b]	5.1[c]	7.7[b]	--	--	9.0[b]	--	--	14[b]	--	--	6.8[b]	--	14
Heptachlor epoxide	16[a]	13[b]	20[b]	20[a]	--	--	--	--	--	--	--	--	6.5[c]	7.6[c]	--
Endosulfan sulfate	--	--	--	--	--	--	--	--	23[b]	--	--	--	24[b]	--	--
Heptachlor	--	--	--	5.6[a]	--	--	--	--	--	--	--	--	--	--	--
Endrin	--	37[b]	27[c]	--	--	18[c]	--	--	--	14[c]	27[c]	--	25[c]	37[c]	55
Endosulfan II	--	--	16[b]	--	--	13[b]	11[b]	21[b]	--	22[b]	19[b]	--	--	17[b]	--
PCB-1254	--	--	--	--	--	--	--	--	--	380[a]	550[a]	160[a]	640[a]	1020[a]	370[a]
PCB-1260	--	--	--	--	--	--	--	--	--	540[a]	1010[a]	160[a]	950[a]	1360[a]	260[a]

a = Confirmed on second column GC/ECD
b = Not confirmed on second column GC/ECD
c = Not confirmed on second column GC/ECD due to interference

-- = Less than detection

APPENDIX F

PCDDs and PCDFs
Methodology and Quality Control

Bioaccumulation Study

III. DIOXIN METHODOLOGY AND QUALITY CONTROL

A. Method for Fish Analyses

Battelle Columbus Laboratories, under subcontract 1-453-003-222-01 to GCA; performed the dioxin analyses. The objective of this study was to analyze selected polychlorinated dibenzofurans (PCDF) and polychlorinated dibenzo-p-dioxins (PCDD) in fish. The detection limits specified for these compounds were parts-per-trillion (1 part in 10^{12}, or ppt) in fish. Specific compounds which were selected for identification included: 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF), 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), and all tetra through octa chloro furan and dioxin isomer classes. High resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) was used to identify and quantify these materials at the indicated trace level. The exact masses used for each isomer class and the expected isotope ratio used in part for identifying individual compounds, as well as limits of detection for the fish are presented in Table 1. 2,3,7,8-tetrachlorodibenzo-p-dioxin-$^{13}C_{12}$ was used as an internal standard for quantification and recovery determinations. These recovery determinations are found in Table 2 and were used to estimate the influence of the matrices on the analytical measurements.

Preparation of Fish Samples

The fish samples were extracted and cleaned up using the following procedure. Approximately 5 g portions of fish were placed in 125 ml round bottom flasks. The fish samples were spiked with 2 ng of 2,3,7,8-TCDD-$^{13}C_{12}$ internal standard followed by the addition of 20 ml of ethanol and 20 ml of 40 percent KOH. The samples were digested for one hour at 80°C. After cooling, they were extracted three times each with 10 ml volumes of hexane. The combined hexane extracts weree transferred to 125 ml separatory funnels and washed three times each with 10 ml of distilled water. The hexane extracts were concentrated to 5 ml using K-D apparatus. Each concentrate was transferred to a multilayered silica column containing the following materials oriented top to bottom:

- Activated silica
- Silica containing 44 percent concentrated sulfuric acid
- Activated silica
- Silica containing 33 percent 1M sodium hydroxide
- Activated silica

These columns were eluted with 30 ml of 1:1 (V:V) benzene:hexane. The benzene:hexane fraction was exchanged into 5 ml of hexane and transferred to alumina columns. The alumina column was eluted sequentially with 25 ml of hexane, 25 ml of 1:1 (V:V) hexane:carbon tetrachloride, and 20 ml of 1:1 (V:V) hexane:methylene chloride. Decane (20 ul) was added to the hexane:methylene chloride fraction, and these mixtures were concentrated to 20 ul prior to their analyses.

The extracts were analyzed by high resolution gas chromatography/ high resolution mass spectrometry (HRGC/HRMS) at a mass resolution of 8000-12000 (M/ M, 10 percent valley). A VG Model 7070H mass spectrometer interfaced to a Carlo Erba Model 4160 gas chromatograph was used. The chromatographic column was a 30M DB-5 fused silica column with helium carrier gas. All HRGC/HRMS data were acquired in the multiple ion detection mode using a VG Model 2035 Data System and will be archived on magnetic tape for a period of five years.

B. Quality Control

1. Internal Audits

The following quality assurance procedures were employed. Perfluorokerosene was introduced through a heated inlet for tuning, mass calibration and establishing mass resolution. A 2 ul injection of a test mixture containing 20 pg/ul of 2,3,7,8-TCDD and 95 pg/ul of 2,3,7,8-TCDD-$^{13}C_{12}$ was analyzed. The analysis of this test mixture provided the following information:

- Information concerning sensitivity (absolute response of 2,3,7,8-TCDD-$^{13}C_{12}$)
- Accuracy of quantification (native response as compared to that of its C-13 analogue)
- Elution within a specific retention time window
- Chromatographic peak shape symmetry.

Decane was analyzed to check for dioxin carry over. This information is used to access performance of the instrument before the measurement of PCDF and PCDD at trace levels is conducted in actual samples.

The actual sample analyses were by the following procedure: four to six samples, a duplicate or spike, an extraction blank, a test mixture, a decane blank, then the cycle was repeated.

2. External Audits

A. On-site Visit

See Part 2, B.1.

B. Blind QC Fish Sample Results

Blanks

Along with the actual fish samples two grinding blanks and two dioxin-free fish filet samples were analyzed. Battelle also extracted and analyzed a solvent blank. The only reported levels of furans in any blank were 10 pg in the grinding blank (dry ice) prepared before fish sample grinding and 95 ppt in the blank perch filet EPA-V-17. The source of the 10 pg tetrachlorinated dibenzofuran in the grinding blank is not known. The concentration of 10 pg per sample jar rinse cannot be converted to ppt, so data is uncorrected.

1) 82LS10R02

Originally, only five grams of the filet was taken for analysis. 95 ppt 2,3,7,8-TCDF was reported for this first run. A suppression at the prefluorokerosene lock mass appeared, creating an artifically low 2,3,7,8-TCDD-C^{13} signal. This suppression caused all quantitation to be biased high. The remaining 5 grams of filet were extracted and put through an additional florisil clean-up and the suppression disappeared. No 2,3,7,8-TCDF was reported for this aliquot.

Spikes

Four spiked fish filets were obtained from Dr. Harless at RTP and sent as "blinds" to Battelle for analysis. However, since the appearance of the samples EPA-V-21-2, EPA-V-20, EPA-V-21, and EPA-V-22 differed from the actual sample catfish pastes, they were not actually "blinds". Battelle, however, did not know which filets, if any, were blanks and they did not know the isomers or levels used in spiking.

A nearly consistent lack of recovery of OCDF and OCDD at levels of 100-200 ppt occurred. This may be due to the fact that the spike levels used were near or at the detection limit. In conversations with Battelle, it was discovered that OCDD and OCDF have varying response factors relative to C^{13}-TCDD. These results are therefore estimated against 2,3,7,8-TCDD-C^{13} as no pure certified OCDD and OCDF standards were available. Such quantitation may be biased low for the sample results. No OCDD or OCDF was reported above the contract detection limit of 90 ppt in any of the samples.

820IS22 (EPA-V-22)

This spiked filet QC sample yielded high (277%) recovery of 2,3,7,8-TCDF and low 2,3,7,8-TCDD recovery (54%). The spectral data was recalled off of the disc and the results recalculated. A suppression of the 2,3,7,8-C^{13} signal occurred. The usual Battelle procedure is to go back and rerun the extract through an additional florisil column. This was done and the unsuppressed signals yielded 168% recovery for 2,3,7,8-TCDF and 92% recovery 2,3,7,8-TCDD. The recovery for 2,3,7,8-TCDF was still high due to reappearing mass interference at mass 304 of TCDF.

CONCLUSION

Due to the imprecise and low biased OCDD and OCDF recovery discovered in blind spike audits, any positive OCDD and OCDF data for fish samples should not be considered valid. All other dioxin/furan sample data should be considered of an acceptable level of quality.

TABLE 1. SELECTED DATA FOR THE POLYCHLORINATED DIBENZOFURANS AND POLYCHLORINATED DIBENZO-P-DIOXINS OF INTEREST

Compounds	Accurate mass		Theoretical Isotope Ratio	Limit of Detection	
	Low Mass	High Mass		Water	Fish
Tetrachlorodibenzofuran	303.9016	305.8987*	.77	10 ppq	5 ppt
Tetrachlorodibenzo-p-dioxin	319.8965	321.8936*	.77	10 ppq	5 ppt
Pentachlorodibenzofuran	339.8597*	341.8567	1.54	20 ppq	20 ppt
Pentachlorodibenzo-p-dioxin	355.8546*	357.8517	1.54	20 ppq	20 ppt
Hexachlorodibenzofuran	373.8207*	375.8178	1.23	40 ppq	40 ppt
Hexachlorodibenzo-p-dioxin	389.8156*	391.8127	1.23	40 ppq	40 ppt
Heptachlorodibenzofuran	407.7817*	409.7788	1.03	80 ppq	80 ppt
Heptachlorodibenzo-p-dioxin	423.7766*	425.7737	1.03	80 ppq	80 ppt
Octachlorodibenzofuran	441.7428	443.7398*	0.88	100 ppq	100 ppt
Octachlorodibenzo-p-dioxin	457.7377	459.7347*	0.88	100 ppq	100 ppt

* Quantitation Mass

TABLE 2. INTERNAL STANDARD RECOVERIES OF 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN-$^{13}C_{12}$ IN FISH

Fish Recoveries	
Sample Name	Internal Standard Recovery (%)
82LS10R04	52
82LS10R02	50
82LS10R01	56
82LS05S01	93
82LS05S02	89
81LS15S08	56
81LS11S01	59
81LS17S01	86
81LS17S03	57
81LS17S06	72
81LS17S07	47
82LS07S05	49
82LS07S06	51

TABLE 3. DOW FISH BLANK RESULTS

UNITS: ppt

ISOMER	Battelle Solvent Blank	Dry Ice** Before 82L205S02	Dry Ice** After 82L505S02	82L510R02 EPA-V-17 Run 1	82L510R02 EPA-V-17 Run 2	820I07R15
2,3,7,8-TCDF	<(7)	< 5	< 5	95	< 7	< 5
2,3,7,8-TCDD	<(4)	< 5	< 5	< 7	< 7	< 5
Tetra CDF	<(4)	10	< (4)	95/(1)	< 7	< 5
Tetra CDD	<(4)	< (2)	< (2)	< 7	< 7	< 5
Penta CDF	<(1)	<(11)	<(19)	<20	<20	<10
Penta CDD	<(1)	<(20)	<(37)	<10	<14	<10
Hexa CDF	<(2)	< (7)	<(19)	<20	<20	<20
Hexa CDD	<(5)	<(12)	< (9)	<20	<20	<20
Hepta CDF	<(1)	<(17)	<(12)	<40	<40	<40
Hepta CDD	<(2)	< (6)	< (4)	<40	<40	<40
Octa CDF	<(4)	<(25)	<(16)	<90	<90	<90
Octa CDD	<(3)	<(11)	< (4)	<90	<90	<90

** Units = total pg per sample jar rinse.
(X) = (detection limit Battelle); other < values are based on contract detection limits.

TABLE 4. DOW FISH SPIKE RESULTS

UNITS: % recovery

ISOMER	EPA-V-21-2 82LS10R04	EPA-V-20 82LS10R01	EPA-V-21 820I07S20	EPA-V-22 820I07S22	Spike (ppt) Levels
2,3,7,8-TCDD	173	80	103	54	10- 30
2,3,7,8-TCDF	70	125	154	277	20- 40
1,3,6,8-TCDD	105*	92*	60	88	10- 33
1,3,7,9-TCDD	105*	92*	115	130	3- 10
OCDD	0	75	0	0	100-200
OCDF	0	64	0	0	100-200

*Isomers not quantified spearately.

[illegible] Agency