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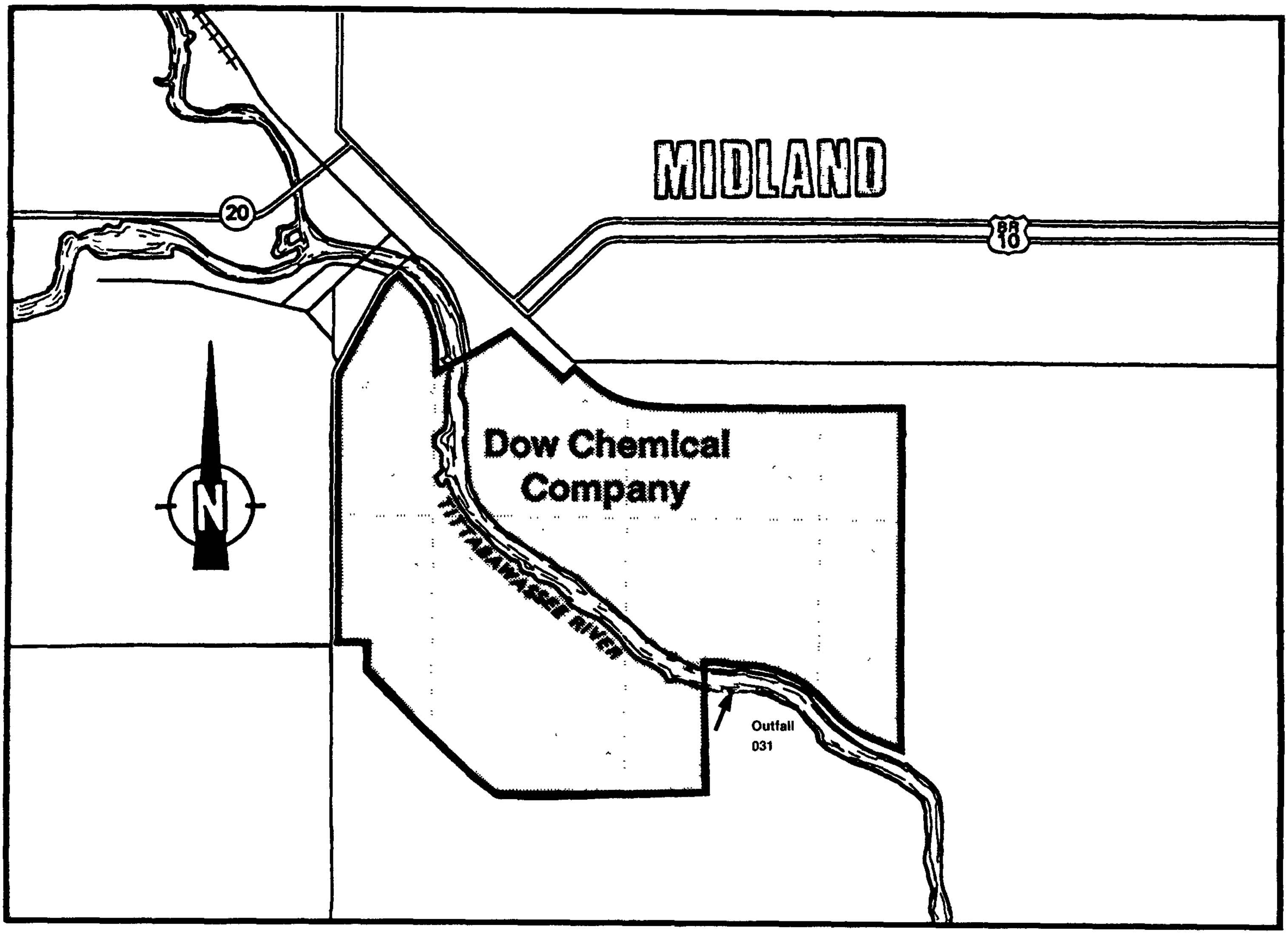
Michigan Dioxin Studies

Dow Chemical Wastewater Characterization Study

Tittabawassee River Sediments and Native Fish



DOW CHEMICAL WASTEWATER CHARACTERIZATION STUDY

TITTABAWASSEE RIVER SEDIMENTS AND NATIVE FISH

JULY 1986

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ACKNOWLEDGMENTS

This report presents results of environmental studies at the Dow Chemical - Midland Plant and in the Tittabawassee River spanning the period 1978 to 1985. The combined efforts of many dedicated people from the Michigan Department of Natural Resources (MDNR), the United States Environmental Protection Agency, and contract laboratories were required to complete this work.

The 1978 Dow Chemical, river sediment, and activated carbon studies were planned by Mr. Karl Bremer and Mr. Gary Amendola of Region V in consultation with Mr. Richard Powers and Mr. Thomas Rohrer of the MDNR Toxic Chemical Evaluation Section. The field sampling was conducted by Mr. Willie Harris and Mr. Philip Gehring with members of the Region V Eastern District Office field crew. Mr. Linn Duling of the MDNR directed the collection of Tittabawassee River fish in 1978. Environmental samples were processed and analyzed by USEPA's Pesticide Monitoring Laboratory, Bay St. Louis, Mississippi, under the direction of Dr. Aubry DuPuy and by Mr. Robert Harless at USEPA's Environmental Monitoring and Support Laboratory at Research Triangle Park, North Carolina, or, by the University of Nebraska.

The 1981 Dow Chemical wastewater characterization and bioaccumulation studies were planned by Mr. Richard Powers and Mr. Linn Duling of the MDNR; Mr. Jonathan Barney, Mr. Howard Zar of the Region V Water Division; and Mr. Charles Stiener and Mr. Gary Amendola of the Region V Environmental Services Division. The wastewater sampling was directed by Mr. Willie Harris and Mr. Philip Gehring of the Region V Eastern District Office. Mr. Linn Duling, Mr. Charles Stiener and members of the MDNR Toxic Chemical Evaluation Section conducted the bioaccumulation study. Analytical work associated with the 1981 studies was coordinated by Mrs. Marcia Kuehl of the Region V Central Regional Laboratory under direction of Mr. Curtis Ross, laboratory director. Analytical contractors included GCA Corporation and Battelle Memorial Institute, Columbus, Ohio. Special note is made of the contribution of Mr. Robert Harless who conducted supplemental quality assurance analyses of water and fish for PCDDs and PCDFs and who provided invaluable assistance in evaluating and interpreting data.

Native fish from the Tittabawassee River were collected in 1983 by the MDNR Toxic Chemical Evaluation Section under the direction of Mr. Linn Duling. The fish were analyzed for dioxin by USEPA's Environmental Research Laboratory in Duluth, Minnesota under the direction of Dr. Douglas Kuehl.

The 1984 Dow Chemical in-plant and effluent and Tittabawassee River studies were planned by Mr. David Barna and Mr. Gary Amendola of the Region V Eastern District Office and Mr. Jonathan Barney of the Region V Water Division in consultation with Mr. Richard Powers, Mr. James Grant, and Mr. Thomas Rohrer of the MDNR Toxic Chemical Evaluation Section and Region V's Dioxin Task Force under the direction of Mr. David Stringham. Mr. Philip Gehring directed the

Eastern District Office field crew and Region V Water Division personnel in the conduct of the field sampling. Mrs. Marcia Kuehl and Mr. Frank Thomas under the direction of Mr. Curtis Ross of the Region V Central Regional Laboratory coordinated the analytical work and provided quality assurance reviews of the data developed by the following contract laboratories: the Brehm Laboratory of Wright State University; Midwest Research Institute; Battelle Memorial Institute; Compuchem; West Coast Technical/IT Corporation; Versar; California Analytical Labs, Inc.; U.S. Testing Company; Rocky Mountain Analytical; and Science Applications, Inc. Mr. Brian Buckham of the Eastern District Office compiled and reduced much of the data presented in this report. The summary of supplemental studies of the Tittabawassee and Saginaw Rivers and Saginaw Bay was prepared by Larry Fink of USEPA's Great Lakes National Program Office.

The authors also wish to acknowledge the cooperation of the Dow Chemical Company for the completion of the 1984 Midland Plant wastewater sampling program.

This report was typed by Ms. Carol Kopcak and Mrs. Ellen Harrison of the Eastern District Office. The figures and graphs were prepared by Belinda Robinson of the Region V Graphic Arts Department.

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I. INTRODUCTION

In June 1978 the Michigan Division of Dow Chemical Company in Midland, Michigan, (Dow Chemical) informed the Michigan Department of Natural Resources (MDNR) and the Michigan Department of Public Health (MDPH) that rainbow trout exposed to a mixture of Dow Chemical's treated effluent prior to discharge from outfall 031 to the Tittabawassee River at Midland accumulated up to 50 parts per trillion (ppt) 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) in edible portions, and up to 70 ppt in whole fish. Supplemental analyses of edible portions (skin-off filet) of Tittabawassee River native catfish previously collected in 1976 downstream of Dow Chemical's discharge ranged from 70 to 230 ppt of 2378-TCDD. Fish collected upstream of the Dow Dam did not contain detectable levels. The company also reported that 2378-TCDD concentrations in Tittabawassee River native fish collected in 1977 ranged from not detected (ND) to 240 ppt for various species. Most species tested yielded positive findings from 20 to 170 ppt.

The results of these and related Dow Chemical studies prompted the MDPH to issue a fish consumption advisory in June 1978 for any fish collected from the Tittabawassee River downstream of the Dow Dam. (The advisory remained in effect until March 1986, when it was modified to include only catfish and carp.) In September 1978 the United States Environmental Protection Agency (USEPA) made a preliminary determination that concentrations of 2378-TCDD in Tittabawassee River fish represented a substantial risk to the public health pursuant to Section 8(e) of the Toxic Substances Control Act of 1976.

In November 1978 Dow Chemical released a report on "The Trace Chemistries of Fire ..." which discusses sources of dioxins in the environment. Dow Chemical concluded that dioxins, including 2378-TCDD, are ubiquitous as a result of a wide variety of combustion processes, that dioxins detected in Michigan Division air, dust, soils and wastewater come from power house, rotary kiln and tar burner combustion, but that Michigan Division chemical manufacturing processes could not be ruled out as a source of dioxins detected in one sample of wastewater collected from a Dow Chemical process sewer.

Follow-up studies conducted by USEPA and the U.S. Food and Drug Administration (USFDA) in 1979 and 1980 determined that 2378-TCDD persisted at levels of concern in Tittabawassee River, Saginaw River and Saginaw Bay native fish, despite closing of Dow Chemical production facilities for manufacture of 2,4,5-trichlorophenol and the derivative 2,4,5-T herbicide.

Dow Chemical's first wastewater discharge permit under the Clean Water Act's National Pollutant Discharge Elimination System (NPDES) expired in September 1979. As part of the development of a second round NPDES permit, the MDNR and USEPA Region V cooperated in development of a wastewater characterization study for the Dow Chemical - Midland Plant during the spring and summer of 1981. The MDNR and USEPA-Region V conducted the 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, at that time, the unavailability of production process information. Preliminary results from that study were released in March 1983. 1/ The study results documented the discharge of 2378-TCDD from Dow Chemical and quantified the release of other toxic, nonconventional, and conventional pollutants to the Tittabawassee River. Recommendations for further study of dioxins presented in the 1983 report were subsequently incorporated into USEPA's Dioxin Strategy and National Dioxin Study. 2/

In the summer of 1983, USEPA-Region V initiated a series of comprehensive studies of dioxins and other toxic pollutants at the Dow Chemical - Midland Plant and in and around the city of Midland. Those studies were conducted in response to a request from the Michigan Department of Natural Resources to follow-up the 1983 report and were consistent in objectives with the then-evolving USEPA Dioxin Strategy. In 1984, the MDNR issued to Dow Chemical an interim NPDES permit which includes water quality-based effluent limitations for several toxic pollutants and an associated administrative order which sets out interim effluent limitations for the discharge of 2378-TCDD. Also, in 1984, the USEPA and Dow Chemical settled litigation regarding USEPA's access to in-plant information necessary for the development of Best Available Technology (BAT) NPDES permit conditions for the Midland plant. 3/ As a result of these regulatory actions, wastewater discharge issues at Dow Chemical have become better defined and substantial progress has been made toward reducing the discharge of toxic pollutants.

This report presents final results associated with the 1983 report; compares those results with recent monitoring from Region V's comprehensive studies of dioxins and other toxic pollutants and recent monitoring by Dow Chemical; reviews recent data for PCDDs and PCDFs in Tittabawassee River sediments and fish; compares the wastewater treatment systems installed at the Dow Chemical - Midland Plant to model wastewater treatment technologies considered by USEPA during development of national effluent limitations guidelines (Best Available Technology effluent limitations); and presents a preliminary assessment of additional wastewater treatment technologies and Best Management Practices that may be necessary to attain Best Available Technology effluent limitations for the Midland plant. Also, presented in Appendix E is a summary of supplemental studies of the Tittabawassee and Saginaw Rivers and Saginaw Bay conducted by state and federal agencies.

The term "dioxin" is often used to describe 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD). The isomer 2378-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.

II. OBJECTIVES

The primary objectives of this work are to quantify the conventional, nonconventional, toxic organic and toxic inorganic pollutant discharges from the Dow Chemical - Midland Plant and to assess the need for additional wastewater treatment and best management practices necessary to achieve Best Available Treatment Economically Achievable (BAT) as defined by the Clean Water Act. The information and data contained in this report are being used by the Michigan Department of Natural Resources and USEPA-Region V to develop a proposed BAT NPDES permit for Dow Chemical.

Secondary objectives include: (1) characterization of untreated wastewaters and in-plant sludges and sediments; (2) determination of the types and the extent of bioaccumulation of pollutants discharged by Dow Chemical in fish; (3) sub-part per trillion analyses of effluent samples for PCDDs and PCDFs; and (4) development of information about contamination of native fish and sediments in the Tittabawassee River.

III. SCOPE OF WORK

Major field surveys were conducted by Region V and MDNR in 1981 and by Region V in 1984. 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 PCDDs and PCDFs 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.

As part of USEPA's comprehensive study of dioxins and other toxic pollutants, sampling was conducted in 1984 at the major process wastewater sewers at Dow Chemical; at other nonprocess wastewaters, including incinerator wastewaters, ground water collection systems, and landfill dewatering systems; at the treated discharge to the Tittabawassee River; and for Tittabawassee River sediments. Data obtained from USEPA's 1981 and 1984 surveys are compared with Dow Chemical monitoring data and other available data from preliminary dioxin investigations conducted by Region V in 1978.

IV. MAJOR FINDINGS AND CONCLUSIONS

A. Dow Chemical - Midland Plant

1. Untreated Wastewaters and Sewer Sludges

Untreated wastewaters from process and nonprocess operations at the Dow Chemical - Midland Plant contain high levels of numerous chemical compounds. Raw waste loadings of volatile compounds determined during the 1984 USEPA survey [carbon tetrachloride (940 lbs/day); methylene chloride (920 lbs/day); styrene (570 lbs/day); chloromethane (410 lbs/day); toluene (350 lbs/day); benzene (160 lbs/day); and ethylbenzene (122 lbs/day)] were greater than raw waste loadings of semi-volatile compounds [phenol (520 lbs/day); 2,4-dichlorophenol (45 lbs/day); 1,2-dichlorobenzene (20 lbs/day); pentachlorophenol (16 lbs/day); 2,4,6-trichlorophenol (13 lbs/day); and naphthalene (13 lbs/day)]. The high levels of volatile compounds are significant from an air pollution standpoint. Emission of one-sixth of the volatile compounds from the sewerage and wastewater treatment systems would be sufficient to classify the plant as a major source of volatile organic carbon (VOC). The findings of chlorinated benzenes and pentachlorophenol in untreated wastewaters long after termination of production of these compounds suggests continued leaching of the compounds from sewer system sludges and plant soils.

Most of the untreated wastewater loading of PCDDs and PCDFs can be attributed to contributions from various process sewers and the hazardous waste incinerator. The raw waste loading of TCDDs was estimated to be about 6.9×10^{-4} lbs/day (3.1×10^{-4} kg/day) and about 1.3×10^{-2} lbs/day (6.1×10^{-3} kg/day) for TCDFs. Although 2378-TCDD was not detected in untreated wastewaters from the process sewers or the hazardous waste incinerator, other tetra-octa CDDs and CDFs were found in the 1984 USEPA study.

2. Tertiary Pond Sediments

Sediments from the tertiary pond system were found to be contaminated with several organic chemicals. Surface sediments from the primary (pentagonal) and secondary (rectangular) ponds were found to contain larger numbers and higher levels of pollutants than found in tertiary pond sediments. These data suggest the pond system has been at least partially effective in removing settleable pollutants not removed in the biological treatment facility. Chlorinated benzenes were found at relatively high levels in primary and secondary pond sediments (13-67 ppm) compared to tertiary pond sediments (ND-1.5 mg/l). Surface sediments in the ponds were generally found to be more heavily contaminated than bottom pond sediments.

The gradient of PCDDs and PCDFs across the pond system was substantially less than for other pollutants. These data suggest that PCDDs and PCDFs entering the pond system are attached to finer particles that tend to settle over a wider area than other semi-volatile pollutants which may be associated with heavier particles. 2378-TCDD was detected at 1.7 ppb in primary pond surface sediments, 3.8 ppb in secondary pond surface sediments, and from 0.10 to 0.93 ppb in tertiary pond surface sediments.

B. Dow Chemical - Outfall 031 Discharge

1. Wastewater Characterization

Process changes at the Midland plant and water conservation measures have resulted in a gradual reduction in the average discharge flow from outfall 031 from over 50 MGD in the mid 1970s to less than 20 MGD today. Recent monitoring by USEPA and Dow Chemical suggest that discharges of toxic organic pollutants and certain nonconventional pollutants have been reduced since 1981. The apparent increase in the discharge of toxic metals is attributed to chromium discharges which are higher than measured by USEPA in 1981. A summary of annualized effluent discharge loadings is presented below:

	Estimated Annualized Discharge in Tons		
	1981 USEPA Survey	1984 USEPA Survey	1984-1985 Dow Chemical Monitoring
Total dissolved solids	148,000	150,000	129,000 (net)
Total suspended solids	680	1,040 [180]	420 (net)
Total kjeldahl nitrogen	330	87	--
Ammonia-N	270	27	23 (net)
Total phosphorus	46	14 [5]	11
Toxic organic pollutants	15.5	1.9	4.9
Toxic metal pollutants	5.7	6.9	16.7

Note: [ ] Estimated current annual full-scale discharge loading based upon pilot plant filter data. Effluent phosphorus data from the full-scale filter system installed in November 1985 are not available at this writing.

The estimated annual discharge of phosphorus from outfall 031 is 5 tons/year based upon limited pilot plant studies, about 90% less than loadings determined in 1981.

2. PCDDs and PCDFs

Based upon six months of full-scale operation of the effluent filtration system, Dow Chemical has achieved a 67% reduction in the discharge loading of 2378-TCDD (9.9×10^{-7} kg/day to 3.3×10^{-7} kg/day). The current estimated annual discharge is 1.20×10^{-4} kg/year. TCDD analyses by Dow Chemical indicate that 2378-TCDD comprises less than 3% of the total TCDDs present. The predominant TCDD isomers, both before and after pilot filtration, are 1368-TCDD, 1379-TCDD, and 1237+1238-TCDD. Based upon limited data, the unfiltered outfall 031 discharge appears to contain higher levels of TCDFs than TCDDs and higher levels of other PCDFs than corresponding PCDDs. Pilot plant filter data suggest the full-scale filter may be achieving more than 90% removal of TCDDs, 2378-TCDF, and HxCDDs, HpCDFs and OCDD. Only data for 2378-TCDD have been reported for the full-scale filter system at this writing.

3. Biomonitoring

Static bioassays (Daphnia magna) conducted by USEPA in 1981 for the outfall 031 discharge indicated the discharge exhibited no acute toxicity to test organisms. The discharge exhibited a stimulatory effect on algal growth and caused no mutagenicity in the Ames test (direct and rat liver enzyme activated test procedures). The 1981 USEPA studies were completed at a time when the average effluent discharge was about 34 MGD. Biomonitoring conducted by Dow Chemical in 1985 as required by NPDES permit MI0000868 yielded the following results for flow-through studies:

	Daphnia Magna	Pimephelas Promelas (fathead minnow)
Acute toxicity		
48-Hour LC_{50}	40% effluent	No toxicity
Chronic toxicity		
MATC (geometric mean)	35.8% effluent	21.7% effluent*

*embryo-larval test

At the time of the Dow Chemical studies, the discharge flow was about 20 MGD. Dow Chemical attributed acute toxicity to daphnia to the salinity of the effluent. The mass discharge of salts was about the same as that encountered during the 1981 USEPA studies. However, the concentration of dissolved solids was about 40% higher due to the reduction in discharge flow. Dow Chemical also reports that for the minnow study (embryo-larval test), there were no observed concentration related effects at hatch and a normal hatch occurred, yet no organisms survived beyond 13 days. No cause for the chronic toxicity observed was suggested by Dow Chemical. Test water for the Dow Chemical bioassays was prefiltered through a 25-micron sock. Since chemical analyses of the wastewater before and after filtration were not reported, the effects of this procedure are not known.

4. Bioaccumulation Studies

Final results from the 1981 USEPA-MDNR bioaccumulation study confirmed preliminary results with respect to the discharge of 2378-TCDD from outfall 031 and the accumulation of 2378-TCDD and other TCDDs in caged catfish exposed to the plume of outfall 031 in the Tittabawassee River. The preliminary contract laboratory results for PCDFs could not be confirmed. A unique finding is that 1368-TCDD accumulated in caged fish exposed to the outfall/river water mixture at higher levels than 2378-TCDD. After 28 days of exposure, 2378-TCDD reached nearly 40 ppt and 1368-TCDD to about 160 ppt. Penta-CDDs (140 ppt), hexa-CDDs (43 ppt), and TCDFs (454 ppt) were found in these fish by USEPA analysts. There was no indication that an equilibrium level of 2378-TCDD had been reached after

28 days of exposure. The fish exposed to the plume of the discharge accumulated greater numbers and higher levels of other organic chemicals, including polynuclear aromatic compounds, chlorinated phenols, and pesticides, than did fish exposed at control sites.

A recent biouptake study conducted by Dow Chemical did not demonstrate significant uptake of 2378-TCDD or 2378-TCDF in catfish exposed for 28 days to a mixture of 15% effluent and 85% river water. Hexachlorobenzene uptake reached 3.7 ppm (whole fish sample) in the Dow Chemical study. Most other organic chemicals included in the study protocol did not exhibit significant accumulation over the test period. As with other biomonitoring by Dow Chemical, the test water was prefiltered using a 25-micron sock prior to exposing the organisms. The effect of that procedure on the test results is not known.

5. Pollutants of Concern

From a wastewater treatment technology standpoint, the principal toxic pollutants of concern are listed below. The evaluation of appropriate Best Available Technology effluent limitations and Best Management Practices programs will focus primarily on these toxic pollutants.

Volatile Organic Pollutants

- Benzene
- Carbon tetrachloride
- Ethylbenzene
- Methylene chloride
- Toluene
- Styrene

Semi-Volatile Organic Pollutants

- 2,4-Dichlorophenol
- 2,4,5-Trichlorophenol
- 2,4,6-Trichlorophenol
- Pentachlorophenol
- 1,2-Dichlorobenzene
- 1,3-Dichlorobenzene
- 1,4-Dichlorobenzene
- 1,2,4-Trichlorobenzene
- 1,2,4,5-Tetrachlorobenzene
- Hexachlorobenzene
- 2,4-D
- 2,6-D
- 2,4,5-T
- Dinoseb
- Bis(chlorobutyl) ether
- 2,3,7,8-TCDD (PCDDs and PCDFs)

Toxic Metal Pollutants

- Antimony
- Chromium
- Nickel
- Zinc

C. Tittabawassee River

1. River Sediments

Tittabawassee River sediments are composed principally of sand and gravel with few pockets of distinctly organic material. Low ppm levels of several pollutants including substituted benzenes and their derivatives were identified in 1981 by Region V. Relatively few compounds were found in similar samples obtained in 1984. The 1984 data indicate that pesticide contamination of river sediments originates upstream from Dow Chemical.

2378-TCDD was not detected at 10 to 30 ppt in Tittabawassee River sediments or flood plain samples obtained in 1984. Other PCDDs and PCDFs were found in river sediments. The highest levels were found near Smith's Crossing Road, located just downstream from Dow Chemical. TCDDs ranged from not detected to 0.15 ppb in sediments obtained near the Dow plant; PeCDDs from not detected to 0.03 ppb; HxCDDs from not detected to 0.11 ppb; HpCDDs from 0.03 to 1.1 ppb; and OCDD from 0.25 to 6.8 ppb. PCDFs were found at similar levels. 2378-TCDF was identified in river sediments obtained near Dow Chemical. HpCDDs, OCDD, HpCDFs, and OCDF were found at concentrations less than 0.5 ppb in sediments collected upstream and well downstream of Dow Chemical. Other PCDDs and PCDFs were not detected in these samples. These data indicate the measurable extent of river sediment contamination by PCDDs and PCDFs attributable to Dow Chemical operations extends downstream to the Gratiot Road/Center Road reach of the river (about 17.1 to 19.5 miles). Limited data for flood plain samples collected within 100 yards of the river indicate these samples are contaminated at higher levels than nearby river sediments.

The distribution of TCDDs in Dow Chemical tertiary pond sediments, outfall 031 wastewater solids, and Tittabawassee River sediments and flood plain samples is consistent, establishing another direct linkage between the discharge and contamination of the river.

2. Native Fish

Bottom feeding fish (carp and catfish) collected downstream of the Dow Chemical - Midland Plant exhibit 2378-TCDD contamination about an order of magnitude greater than game fish when edible portions of fish are compared. Typical levels of 2378-TCDD in skin-off filet samples of catfish are 39 to 75 parts per trillion (ppt). Average levels in skin-off carp filets may range from 30 to 50 ppt, with maximum values greater than 500 ppt. The variability of 2378-TCDD in skin-on filet samples of game fish (walleye, smallmouth bass, white bass, crappie, and northern pike) is more limited with average values by species in the range of 3 to 10 ppt. Maximum single fish values recorded in crappie, walleye, and northern pike are 5 ppt, 14 ppt and 15 ppt, respectively. The level of 2378-TCDF in walleye (skin-on filet) collected downstream of Dow Chemical is about 12 times greater than the levels of 2378-TCDD. Other TCDDs, HxCDDs, HpCDDs and OCDD were also found in walleye at levels exceeding those of 2378-TCDD.

While lower levels of 2378-TCDD were detected in catfish collected in 1985 than in those collected in 1978 (limited number of samples analyzed), available data do not suggest a significant decrease in 2378-TCDD concentrations in carp from 1978 to 1985, or in walleye or smallmouth bass from 1983 to 1985. Given the persistence of PCDDs and PCDFs in the environment, the contamination of Tittabawasee River sediments, the widespread presence of PCDDs and PCDFs in Midland area soils, and continued low-level releases from the Dow Chemical - Midland Plant, it is highly probable that native fish in the Tittabawassee River will remain contaminated with 2378-TCDD and other PCDDs and PCDFs at or near current levels for several years.

Data available for skin-on filet samples of game fish for other toxic organic pollutants show that white bass and northern pike contain higher levels of pollutants than do walleye. Smallmouth bass samples had the lowest lipid content and the lowest levels of organic contamination.

D. Best Available Technology

1. To a large extent, the wastewater treatment facilities installed by Dow Chemical at the Midland plant are consistent with model wastewater treatment systems considered by USEPA during development of national effluent limitations guidelines. Treatment of volatile toxic organic pollutants is either deficient or lacking at certain Dow Chemical processes.

2. Most of the process operations at the Midland plant fall within the following major industrial categories for which EPA has either promulgated or proposed national effluent limitations guidelines:

Organic Chemicals and Plastics and Synthetic Fibers
Inorganic Chemicals
Pesticides
Pharmaceuticals

Final effluent limitations guidelines have not been promulgated for the Organic Chemicals and Plastics and Synthetic Fibers Category which accounts for about 70% of the process operations at the Midland Plant. Wastewaters from categorical processes account for about one-third of the discharge from outfall 031. The balance is distributed among noncategorical process wastewaters, nonprocess wastewaters, storm water, and noncontact cooling water. In the absence of final effluent limitations guidelines for most of the process and nonprocess operations, proposed NPDES permit BAT effluent limitations and best management practices control programs must be developed on a best professional judgment basis pursuant to Section 402(a)(1) of the Clean Water Act.

3. Proposed BAT effluent limitations for toxic pollutants will likely be developed at the process level for certain pesticide processes, and on a plant-wide basis for other process and nonprocess operations. Volatile organic pollutants may be limited at the process level in certain circumstances. Effluent limitations for conventional and nonconventional pollutants will likely be proposed as plant-wide limitations. Best management practices programs may be proposed for specific pollutants and areas of the plant.

V. DOW CHEMICAL - MIDLAND PLANT

A. Production Operations

The Dow Chemical Midland plant is a large chemical manufacturing complex encompassing about 1500 acres along both banks of the Tittabawassee River at Midland, Michigan (Figure 1). Throughout its history, Dow Chemical has manufactured over 1000 different inorganic and organic chemicals at Midland including cyclical intermediates; industrial organic and inorganic chemicals; plastic materials; synthetic resins; nonvulcanized elastomers; medicinal chemicals; surface active agents; finishing agents; sulfonated oils; insecticides; herbicides; and formulated pesticides.

The manufacture of chlorinated phenols for use in herbicide, pesticide, and other products has been a significant operation at the Midland plant. According to Dow Chemical, commercial production of chlorinated phenols began in the 1930s and continued at substantial levels into the 1970s. 4/ Dow reports that only two chlorinated phenolic products are currently manufactured:

- 2,4-dichlorophenol
- 2,4-dichlorophenoxyacetic acid (2,4-D).

Production of all other chlorinated phenolic intermediates and products was terminated in the late 1970s. A complete list of chlorinated phenolic compounds produced at the Dow site is presented in Table 1.

The Dow Chemical Midland plant falls within Tiers 1, 2, 3, 4, and 6 of the USEPA Dioxin Strategy 2/: 2,4,5-trichlorophenol (2,4,5-TCP) was produced (Tier 1); 2,4,5-TCP was used to make pesticide products (Tier 2); and 2,4,5-TCP and derivatives were formulated into pesticide products (Tier 3). The plant is a combustion source (Tier 4), and Dow Chemical operates processes for other organic chemicals or pesticides that are considered to have a low potential for dioxin formation (Tier 6).

B. Dow Chemical Brine Operations and Chemical Disposal Wells

The Dow Chemical Company was founded in Midland in 1897 as a producer of brine chemicals. Dow Chemical mined naturally occurring brine from the Sylvania aquifer, a dense sandstone formation with interbedded limestone about 5000 feet deep, ranging in thickness from about 200 to about 500 feet. The raw calcium chloride brine was conveyed through a network of underground piping and ancillary equipment to the Dow Chemical complex in Midland. After removal of salts and minerals, the spent brine was sent to Brine Pond #6 on-site for holding prior to filtration and pressure injection to the same formation through return wells.

The brine system, as permitted by Michigan DNR, consists of the following:

Figure 1

**Location Map
Tittabawassee River Basin
Dow Chemical - Midland Plant**

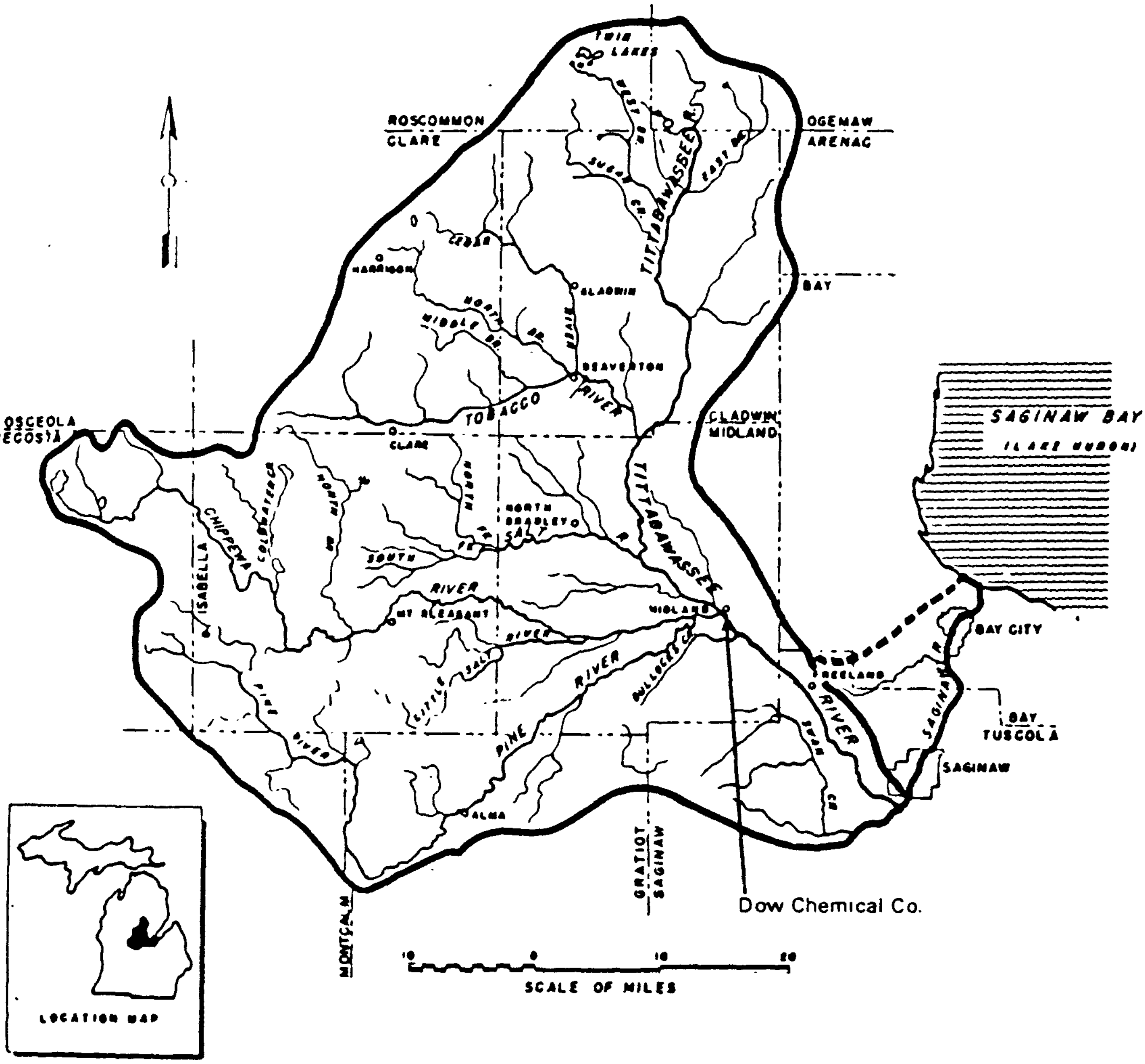

Table 1

A Compilation of the Commercially Significant Chlorophenolic Compounds Manufactured on the Midland Plant Site of the Dow Chemical Company

Chlorophenols

- 2-chlorophenol
- 4-chlorophenol
- *2,4-dichlorophenol
- 2,4,5-trichlorophenol
- Sodium 2,4,5-trichlorophenate
- Zinc 2,4,5-trichlorophenate
- 2,4,6-trichlorophenol
- Sodium tetrachlorophenate
- 2,3,4,6-tetrachlorophenol
- Pentachlorophenol
- Sodium pentachlorophenate

Chlorophenoxy Derivatives[1]

- *2,4-dichlorophenoxyacetic acid (2,4-D)
- 2-(2,4-dichlorophenoxy) propanoic acid
- 2-methyl-4-chlorophenoxyacetic acid
- 2,4,5-trichlorophenoxyacetic acid (2,4,5-T)
- 2-(2,4,5-trichlorophenoxy) propanoic acid

Other Chlorophenol Derivatives

- 2-(2,4,5-trichlorophenoxy) ethanol
- 2-(2,4,5-trichlorophenoxy) ethyl 2,2-dichloropropanoate
- O,O-dimethyl-O-(2,3,5-trichlorophenyl) phosphorothioate
- 2-cyclopentyl-4-chlorophenol
- 4-t-butyl-2-chlorophenol
- 4-t-butyl-2-chlorophenyl methyl N-methyl-phosphoramidate
- Chlorinated phenyl phenols
- Chlorinated diphenyl oxide derivatives

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*2,4-dichlorophenol and 2,4-D are the only compounds from this list that are currently being manufactured on the Midland plant site.

[1]These chlorophenoxy acid derivatives have also been converted into various water soluble salts.

Source: Point Sources and Environmental Levels of 2378-TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin) on the Midland Plant Site of the Dow Chemical Company and in the City of Midland, Michigan, Dow Chemical Company, Midland, Michigan, November 1984.

- 70 brine production wells
- 35 brine injection wells
- 7 solution mining wells
- about 150 miles of pipelines, 25-30 years old.

The brine system occupies portions of three counties:

- Midland County (Midland, Ingersoll, Homer, Lee, Larkin, Greendale, Porter, and Mt. Haley Townships)
- Bay County (Williams Township)
- Saginaw County (Richland, Freemont, Bryant, Thomas, St. Charles, and Swan Creek Townships)

The areal extent of the Dow Chemical brine operation is illustrated by Figure 2.

The physical make-up of the calcium chloride brine mined by Dow is as follows:

- 70% water
- approximately 20% calcium chloride
- approximately 5% sodium chloride
- approximately 5% other inorganic salts

Brine processing in the Dow Chemical complex removed iodine, bromine, and calcium. USEPA has previously reported the chemical composition of Dow Chemical brines and compared the Dow Chemical brines to other Michigan brines and oil and gas brines from other parts of the country. 5/ In May 1985, Dow Chemical entered into a consent order with Michigan DNR calling for a phased shutdown of the Dow brine system. The consent order requires shutdown of the entire brine system by December 31, 1986. 6/ At this writing, Dow Chemical has ceased brine mining operations and is in the process of closing the system. 6a/

The Dow Chemical brines are similar in composition to other oil and gas brines in Michigan and from elsewhere in the United States, including low levels of benzene, toluene, phenol, and various polynuclear aromatic hydrocarbons. The Dow Chemical spent brines may also contain trace levels of PCDDs and PCDFs.

Dow Chemical has also operated chemical disposal wells, injecting process chemical wastes into the Sylvania and Dundee formations. 7/ Michigan DNR data for Dow Chemical underground industrial waste disposal systems have been reviewed. According to these data, phenolic compounds were reported to have been injected into the Sylvania formation. Other chemical process wastes, including copper, butyl alcohol, chlorinated benzene compounds, phenolic compounds, pyridines, and the pesticides 2,4,5-T and tordan were also injected into the Dundee formation. Table 2 summarizes chemical disposal well location, receiving formation, interval of receiving aquifer, and injected fluid characteristics obtained from the MDNR data. According to Dow Chemical, use of chemical disposal wells was discontinued in December 1982. 8/

Figure 2

Location Map
Dow Chemical - Midland Plant
Brine System

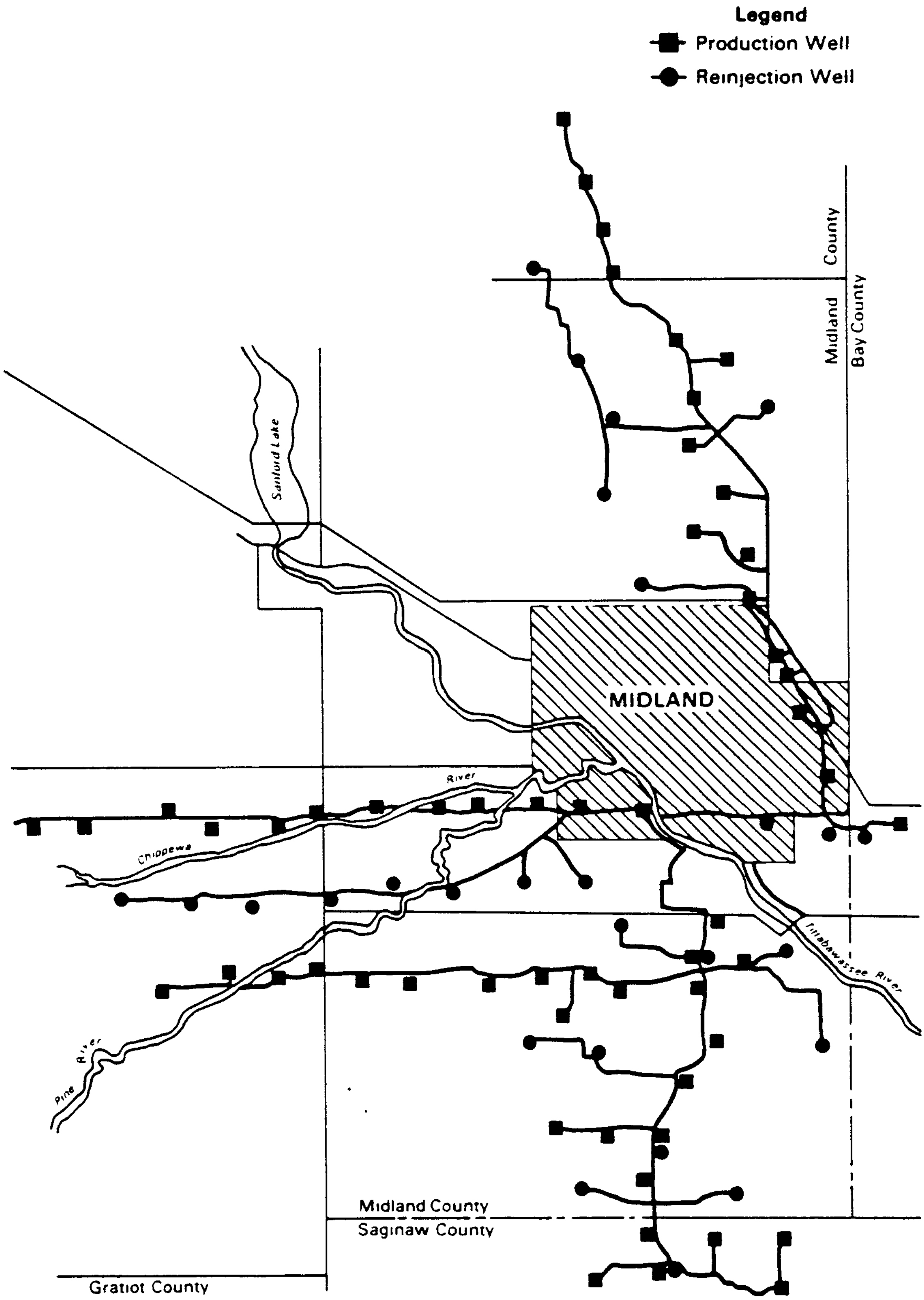


Table 2

Dow Chemical
Disposal Well Data

Chemical Disposal Well No.	Location (Midland County)	Receiving Formation	Interval of Receiving Aquifer	Injected Fluid Characteristics
W.D. #1	NE 1/4, NE 1/4, SE 1/4; Sec. 27, T14N; R2E	Dundee	3606'-3985'	Activated sludge.
W.D. #2	SE 1/4, SW 1/4, SE 1/4; Sec. 22, T14N; R2E	Dundee	3645'-3984'	Copper, butyl alcohol, chlorinated benzene compounds, phenolic compounds, tordan, pyridenes, 2,4,5-T.
W.D. #3	SW 1/4, NW 1/4, SW 1/4; Sec. 21, T14N; R2E	Dundee	3645'-3900'	Copper, butyl alcohol, chlorinated benzene compounds, phenolic compounds, tordan, pyridenes, 2,4,5-T.
#4CD	SW 1/4, SW 1/4, SW 1/4; Sec. 22, T14N; R2E	Sylvania	4986'-5117'	Phenolic compounds.
W.D. #5	NW 1/4, NW 1/4, NW 1/4; Sec. 28, T14N; R2E	Dundee	3645'-3888'	Copper, butyl alcohol, chlorinated benzene compounds, phenolic compounds, tordan, pyridenes, 2,4,5-T.
W.D. #8	SE 1/4, SW 1/4, NE 1/4; Sec. 27, T14N; R2E	Sylvania	4925'-5150'	Phenolic compounds.
W.D. #9	SE 1/4, SE 1/4, NE 1/4; Sec. 26, T14N; R2E	Sylvania	4917'-5182'	Phenolic compounds.

Source: Michigan Department of Natural Resources Geological Survey Division
Well and Reservoir Data on Underground Industrial Waste Disposal Systems.

C. Riverbank Revetment System

Dow Chemical has installed a revetment ground water interception system (RGIS) for about 11,700 feet along the northeast bank of the Tittabawassee River at the Midland plant. 4/ The RGIS consists of sheet piling to stabilize the riverbank and minimize the inflow of river water to the collection system; a trench containing drain tile for collection of ground water; a clay cap; and a series of sumps for accumulation and removal of ground water. Six sumps on the northeast bank inside the sheet piling collect ground water from the site to prevent mixing with river water or ground water beneath the river. At this writing, Dow Chemical is evaluating the effectiveness of the RGIS pursuant to RCRA 40 CFR Part 265. Depending upon the results of that evaluation, additional corrective actions may be required to address ground water contamination at the site. The company has recently applied for state permits to extend the revetment system along the riverbanks. The RGIS results in about 1 MGD of discharge to the Midland plant wastewater treatment system. The locations of the existing drainage system and sumps are shown in Figure 3.

The company also operates a drain tile collection system along the opposite bank of the Tittabawassee River at brine pond No. 6 and the tertiary pond to collect wastewaters leaking from those ponds.

D. Dow Chemical Sewerage and Wastewater Treatment System

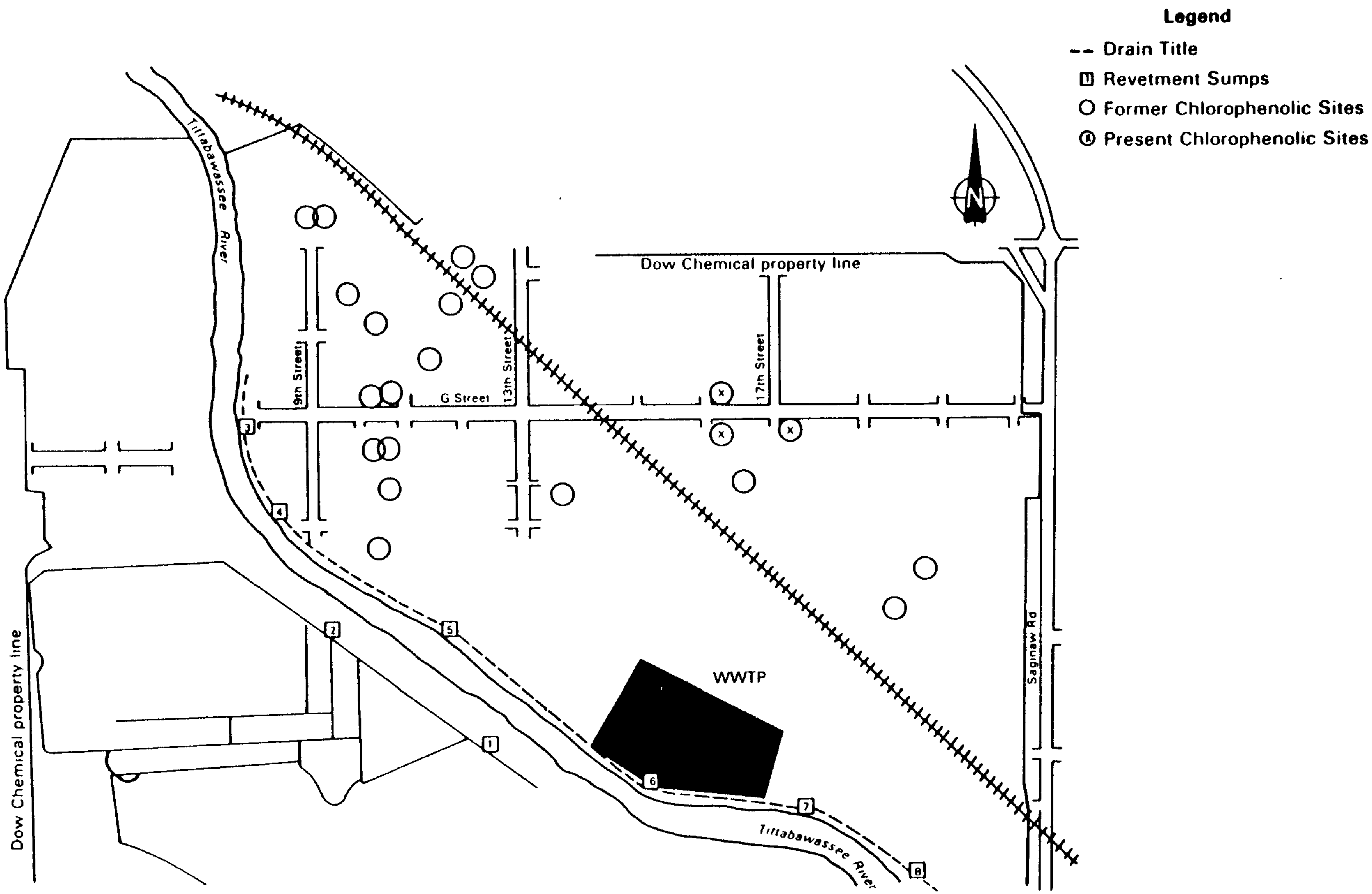
Solid and liquid wastes generated at Dow Chemical and wastewaters received from outside sources are disposed of by one of three methods: (1) concentrated liquids and burnable solid wastes are incinerated; (2) "biodegradable" dilute liquids and a substantial volume of cooling water are processed in the wastewater treatment facilities tributary to outfall 031; and (3) nonburnable solid wastes are landfilled.

Dow Chemical discharges contact and noncontact cooling waters, storm water runoff, and treated process and sanitary wastewaters to the Tittabawassee River through five outfalls. 9/ In addition to the wastewaters generated at the Midland plant, the company also treats wastewater from other sources. 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 (when construction was in process); about 0.02 MGD of truck washing wastewaters from the Chemical Leaman and Coastal Trucking Line at Midland; about 1 MGD of ground water collected in the revetment system sumps noted above; about 0.01 MGD of leachate from the Dow Chemical Salzburg Road landfill; and roughly 0.002 MGD of collected leachate from the Rockwell landfill. Dow Chemical also collects and treats about 0.05 MGD of leachate and intercepted ground water from the Poseyville Road landfill to limit migration of contaminated ground waters away from the site.

According to Dow Chemical's most recent NPDES permit application (1982), the average daily wastewater flows from these outfalls are as follows:

Figure 3

Location Map
Dow Chemical
Riverbank Revetment System



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 the 1981 USEPA survey was 35.4 MGD. When the 1984 USEPA surveys were conducted, the average flow had been reduced to about 20 MGD. Most of the discharge orginates as 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 and Lake Huron. Lake Huron water is chlorinated and demineralized prior to use in various processes. The other intake waters are generally not treated prior to use.

Descriptions of the sources of effluent discharged through the outfalls active during the various surveys are presented below:

Outfall 002 - At the time of the 1981 survey, the discharge from outfall 002 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 noncontact 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. Noncontact 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, other noncontact cooling water, incinerator scrubber water, sanitary wastewaters, surface water runoff, landfill leachate, and ground water collected in the RGIS. Treatment is provided in an end-of-pipe biological treatment facility followed by three settling ponds, the largest of which is called the tertiary pond. The tertiary pond effluent is pumped through mixed-media sand filters prior to discharge to the Tittabawassee River. Dow Chemical has also installed numerous in-process product and by-product recovery systems and pollution control systems. Recent data indicate the flow from outfall 031 has been reduced to less than 20 MGD.

Other active Dow Chemical outfalls not described above include outfalls 001, 014, and 015. Outfall 001 serves as an emergency standby for outfall 031 and would convey wastewater from the biological treatment plant directly to the river. 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 1981 or 1984 surveys.

Wastewater Treatment Plant - "Biodegradable" dilute liquids (process and sanitary wastewaters) are separated into two categories - phenolic wastewaters and other organic wastewaters. Figure 4 is a schematic diagram of the wastewater treatment plant. Wastewaters from the phenolic processes are pumped through enclosed and open conduits to the phenolics pretreatment system, where suspended solids are removed by primary clarification. The phenolic 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 process wastewaters, nonprocess wastewaters, noncontact cooling waters, landfill leachates, collected ground water, and surface runoff from the site. There are several sections of the major sewer system where wastewaters are conveyed through open conduits or ditches as opposed to enclosed conduits.

The wastewaters from the remainder of the plant 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 diversion basin during spills or emergencies and metered into the treatment system at controlled rates. 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 clarifiers is pumped to the tertiary ponds, which are about 200 acres in area and have a maximum capacity of about 600 million gallons. The retention time in the ponds provides for temperature equalization and continued biological action. The effluent from the tertiary ponds is discharged to the Tittabawassee River through outfall 031 after filtration through recently installed mixed-media filters.

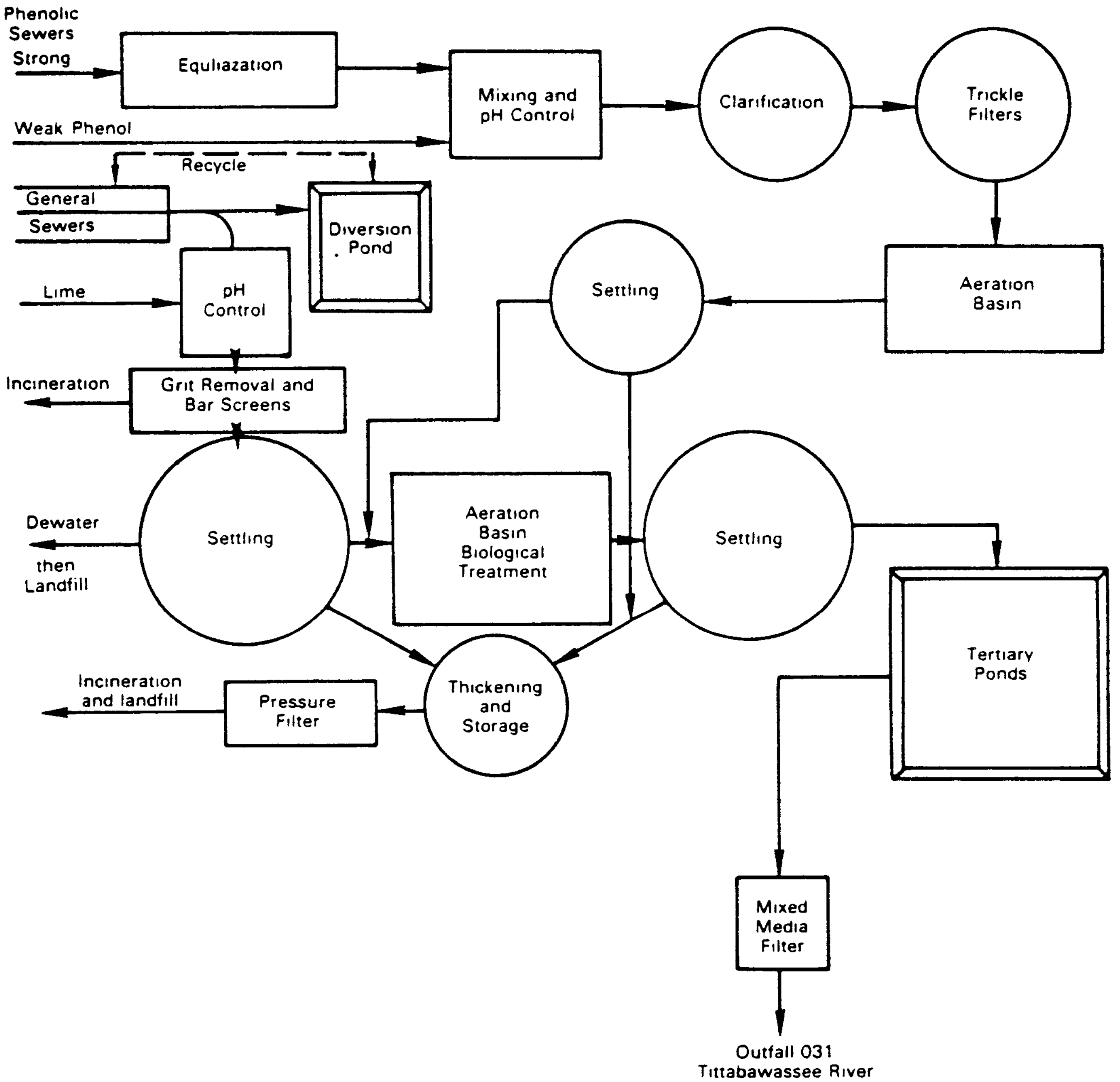
Primary sludge from the biological treatment facility was pumped to clay-lined sludge dewatering pits located near the intersection of Saginaw and Salzburg Roads. Recently, Dow Chemical installed additional mechanical sludge dewatering equipment at the wastewater treatment facility. The sludge dewater pits are maintained for emergency use. The dewatered sludge is ultimately disposed of at Dow Chemical's Salzburg Road landfill. Supernatant from the sludge dewatering pits was returned to the wastewater treatment plant. Sludge from the phenolic treatment system is either recycled or processed in the other biological treatment system. Sludge from the biological treatment system is thickened, filtered, stored on-site, and landfilled.

E. Dow Chemical Waste Incinerators

The incineration area includes a rotary kiln (refuse burner) and a tar burner (thermal oxidizer). 4/ 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 with solid and liquid

Figure 4

Schematic Diagram
Dow Chemical
Wastewater Treatment Facilities



wastes at rates of approximately 5 to 6 tons per hour, and 2 to 4 tons per hour, respectively. The rotary kiln, or primary combustion chamber, provides about 45 minutes of solid waste retention at a design combustion temperature of 650° to 950°C. Exit gases are routed to an afterburner section, in which a retention time of 1.5 to 1.8 seconds at 1000° to 1100°C is provided.

Solid wastes are fed to the refuse burner in loose form and, in the case of specialized wastes from process and laboratory areas, in individual containers weighing a maximum of 200 pounds. The containers are introduced to the rotary kiln every five to six minutes. Concentrated liquid wastes enter the rotary kiln through two air-atomized nozzles, along with a third nozzle firing low-BTU liquid wastes composed of dilute contaminated water from processes or surface runoff. Another concentrated liquid waste nozzle is located in the afterburner section; this nozzle is steam-atomized. Combustion may be supplemented with natural gas at all three nozzles. 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.

Studies by Dow Chemical identified a number of PCDDs and 2378-TCDF in incinerator stack gases, stack gas particulates, and scrubber waters. 4/ Incinerator scrubber waters are quantitatively characterized in Section VII.A.1. Region V also characterized incinerator emissions, incinerator feeds, ash, and scrubber waters (report in preparation).

F. Dow Chemical Landfills

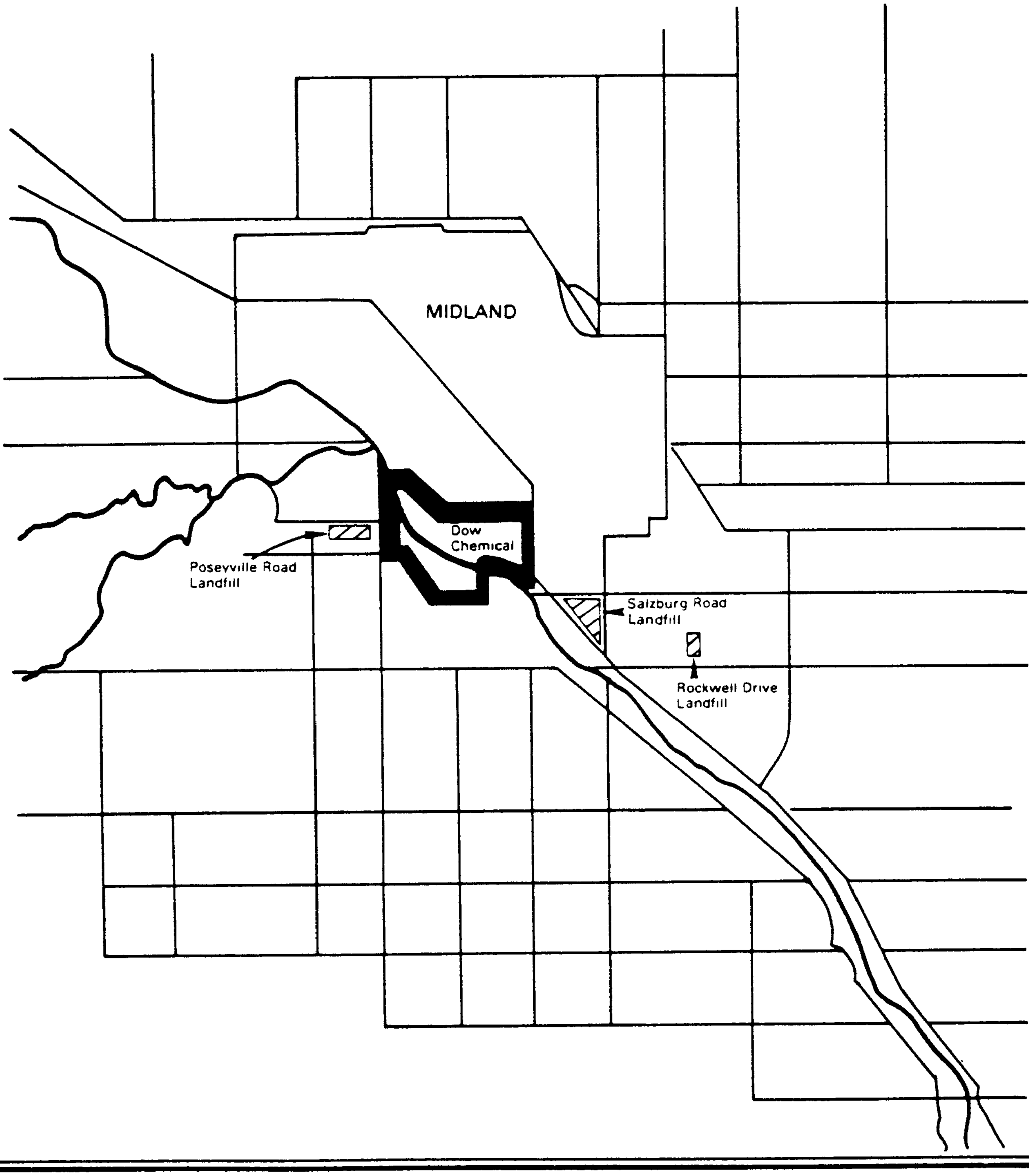
Dow Chemical has been operating a landfill located on Salzburg Road since January 1981. The landfill was approved by MDNR for hazardous waste disposal on February 10, 1982, and has qualified for interim status under RCRA. As noted above, incinerator ash, wastewater treatment sludges, contaminated soil,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

Dow Chemical used two off-site landfill sites, near Poseyville Road and Rockwell Drive, which are now closed. Dow activity at these sites includes leachate collection, site dewatering, and ground water monitoring. At the Poseyville Road landfill, Dow Chemical also operates ground water intercepting wells to collect contaminated ground water leaving the site. Figure 5 presents the location of the off-site landfills. The company also disposed of chemical manufacturing wastes and other solid waste on the plant site at several locations.

Several modifications to Dow Chemical's solid waste, wastewater collection, and wastewater treatment facilities will be completed as Dow Chemical comes into compliance with the implementing regulations of the Resource Conservation and Recovery Act (RCRA) and the Hazardous and Solid Waste Amendments of 1984. It is likely that the open sewers at the plant will be enclosed or replaced and modifications will be made to the diversion basin and other treatment facilities.

Figure 5

**Location Map
Dow Chemical Landfills**



VI. FIELD STUDY RESULTS

The results of USEPA field studies conducted from 1978 to 1984 at the Dow Chemical - Midland plant and in the Tittabawassee River are reported here along with recent monitoring data obtained by Dow Chemical. The USEPA surveys include Midland plant untreated wastewater and in-plant sludge sampling (1978, 1984); treated wastewater effluent sampling (1978, 1981, 1984); treated effluent biomonitoring (1981); a bioaccumulation study (1981); and Tittabawassee River sediment sampling (1978, 1981, 1984). Summaries of the data and major findings are presented below. The complete field and laboratory data are presented in the respective appendices noted for each aspect of the studies. Also presented in the appendices for each study where such analyses were completed are tentatively identified compounds from broad scan analyses. For the most part the tentatively identified compounds are not reviewed in this section.

A. Dow Chemical Untreated Wastewaters and In-Plant Sludges

1. Untreated Wastewaters (Appendices A-1, A-2)

Figure 6 presents a sewer system schematic diagram for the Midland plant. Water samples were obtained at or near the confluence of each major sewer system with the main inteceptor sewers tributary to the wastewater treatment facilities. Samples of incinerator wastewater streams, landfill leachate collection systems, and the riverbank revetment system were also obtained. The sampling locations are designated on Figure 6 for the major process sewers. The principal purposes of sampling the major process wastewater sewers and other nonprocess wastewaters were to identify the toxic, conventional, and nonconventional pollutants present in each major sewer system and to determine whether these pollutants are effectively treated or removed as the wastewaters are processed in the wastewater treatment facilities. Also, the data have been used to target areas of the Midland plant where additional in-process or end-of-process controls might be necessary to attain BAT.

Table 3 presents a summary of the mass discharges of volatile pollutants from the major process wastewater sewers and nonprocess sources. These data represent the conditions present at the time of the sampling event and may or may not be representative of conditions experienced over the longer term. Nonetheless, the data present an order of magnitude estimate of the mass discharge of volatile pollutants to the wastewater treatment system. As shown, the total discharge on the sampling dates was in excess of 3700 lbs/day (1700 kg/day). Carbon tetrachloride, methylene chloride, styrene, chloromethane, toluene, benzene, and ethylbenzene were present at levels in excess of 100 lbs/day (45.4 kg/day). As shown elsewhere, the current mass discharge of volatile pollutants to the Tittabawassee River from outfall 031 is about 10 lbs/day (4.5 kg/day).

Figure 6

Location Map
USEPA Sampling Locations
Dow Chemical Process Sewers
August 1984

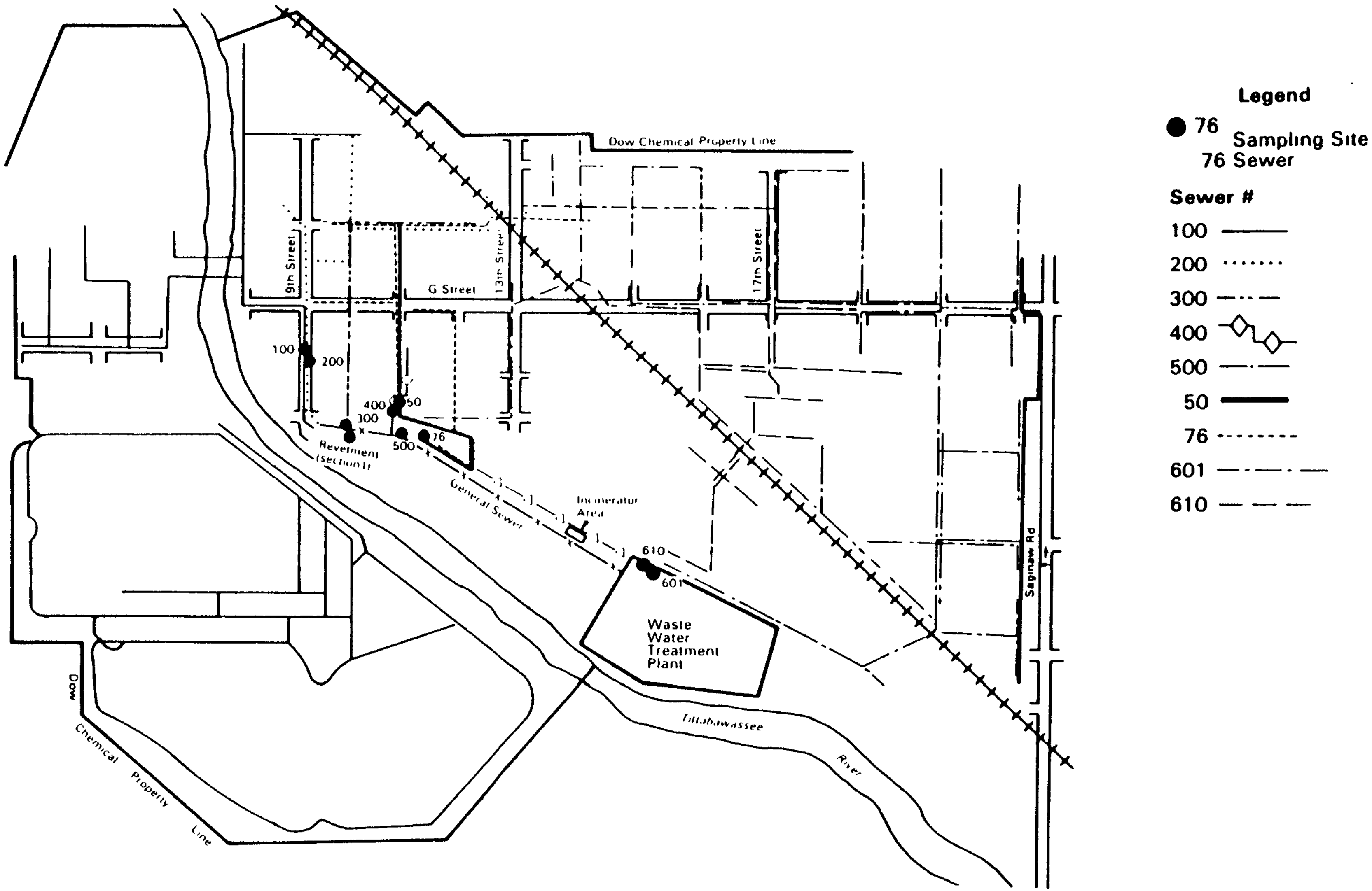


Table 3

Volatile Pollutant Summary
Untreated Wastewaters
Dow Chemical - Midland Plant
August 29, 1984; October 23, 1984

Volatile Pollutant	Mass Discharge to Wastewater Treatment lbs/day	kg/day
acrylonitrile	38.7	17.6
benzene	158.6	72.1
carbon tetrachloride	942.4	427.5
chlorobenzene	72.1	32.8
1,2-dichloroethane	3.9	1.8
1,1,1-trichloroethane	58.5	26.5
1,1-dichloroethane	<0.1	<0.1
chloroform	8.3	3.8
trans-1,2-dichloroethane	1.1	0.5
1,2-dichloropropane	0.7	0.3
ethylbenzene	122.1	55.5
methylene chloride*	922	419.1
chloromethane	407.6	184.9
tetrachloroethene	28.8	13.1
toluene	347.3	157.9
trichloroethene	1.4	0.6
acetone*	11.2	5.1
2-butanone*	4.1	1.9
styrene	572.1	259.5
xylenes (total)	55.0	25.0
bromomethane	0.1	<0.1
bromoform	1.1	0.5
carbon disulfide	<0.1	<0.1
1,1-dichloroethene	1.2	0.5
vinyl chloride	0.9	0.4
chloroethane	0.2	<0.1
4-methyl-2-pentanone	0.1	<0.1
Total	3759.7 lbs/day	1707.4 kg/day

*Detected in field blank samples. Data corrected for field blank contamination.

The mass discharge of volatile pollutants in untreated wastewaters at these levels is significant from an air pollution standpoint. Volatilization in open sumps, sewers, and tanks and air stripping from biological reactors and other wastewater treatment plant vessels can be highly efficient. Air stripping of only 15% of the raw waste loading of volatile pollutants would exceed the 100 ton/year criterion necessary for qualification as a major air pollution source of hydrocarbon emissions. 10/ Estimated current annualized emissions of volatile pollutants from process sources at the plant are about 3600 tons/year. 10a/

Best Available Technology (BAT) for volatile pollutants is reviewed in Section VII. The model BAT treatment systems under consideration by USEPA include in-process steam stripping systems to remove and recover volatile pollutants. Because of the high raw waste loadings of volatile pollutants, additional in-process or end-of-process controls for certain Dow Chemical process areas will be evaluated for BAT.

Table 4 is a similar table for semi-volatile pollutants. Semi-volatile pollutants are defined as those determined with EPA Method 625 by GC/MS (gas chromatography/mass spectrometry) for acid and base/neutral organic fractions. Phenol accounted for nearly 80% of the 670 lbs/day (304 kg/day) raw waste loading of semi-volatile pollutants. Several chlorinated phenols including 2-chlorophenol; 2,4-dichlorophenol; 2,4,5-trichlorophenol; 2,4,6-trichlorophenol; and pentachlorophenol accounted for about 83 lbs/day (37.6 kg/day), or about 12% of the raw waste loading. The balance is principally comprised of lesser amounts of chlorinated benzenes and polynuclear aromatic hydrocarbons. The changes in chlorinated phenols production in the late 1970s by Dow Chemical have most likely resulted in substantially lower raw waste discharges of chlorinated phenols and chlorinated benzenes to the treatment systems. A substantial portion of the current raw waste loading of these pollutants is likely due to sludges and sediments deposited in the sewerage system. As shown later in this report, semi-volatile pollutants are efficiently removed in the existing end-of-pipe wastewater treatment facilities.

Table 5 presents data for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) for the major process sewers, the incinerator streams, landfills, and revetment system (RGIS). These data indicate that the incinerator streams and the process sewers generally account for nearly all of the PCDDs and PCDFs reaching the wastewater treatment facility. 2378-TCDD was identified in one sample of Salzburg Landfill leachate (11 ppq). The Rockwell Landfill dewatering sample was found to contain 2378-TCDD at a concentration of 270 ppq (parts per quadrillion). However, the data are suspect. The laboratory completing the analyses did not meet quality assurance objectives for other PCDDs and PCDFs. Although 2378-TCDD was not detected in incinerator wastewaters, data obtained by Dow Chemical indicate that the incinerator streams are the most significant wastewater source of 2378-TCDD and other PCDDs and that much of the 2378-TCDD discharged to the Tittabawassee River originates from the incinerator. 4/ Dow Chemical is currently installing a pretreatment system for incinerator wastewaters to reduce dioxin discharges to the biological wastewater treatment plant. Dow Chemical has also isolated three other wastewater sources of 2378-TCDD -- (1) a dewatering sump in the abandoned

Table 4

Semi-Volatile Pollutant Summary
Untreated Wastewaters
Dow Chemical - Midland Plant
August 28-29, 1984; October 23, 1984

Semi-Volatile Pollutant	Mass Discharge to Wastewater Treatment lbs/day	kg/day
2,4,6-trichlorophenol	12.8	5.8
2-chlorophenol	6.9	3.1
2,4-dichlorophenol	44.8	20.3
pentachlorophenol	16.4	7.4
phenol	520.3	236.0
benzoic acid	5.2	2.4
4-methylphenol	11.9	5.4
2,4,5-trichlorophenol	2.1	1.0
1,2,4-trichlorobenzene	1.7	0.8
hexachlorobenzene	<0.1	<0.1
bis(2-chloroethyl)ether	0.8	0.4
1,2-dichlorobenzene	20.0	9.1
1,3-dichlorobenzene	0.4	.2
1,4-dichlorobenzene	8.1	3.7
fluoranthene	<0.1	<0.1
bis(2-chloroisopropyl)ether	0.1	<0.1
naphthalene	12.9	5.9
phenanthrene	<0.1	<0.1
4-chlorophenylphenylether	0.2	0.1
n-nitrosodiphenyl amine	<0.1	<0.1
bis(2-ethylhexyl)phthalate	0.4	0.2
dimethyl phthalate	0.4	0.2
benzyl alcohol	1.2	0.5
2,4-dimethylphenol	<0.1	<0.1
2-methylphenol	<0.1	<0.1
acenaphthene	<0.1	<0.1
di-n-butylphthalate	<0.1	<0.1
diethylphthalate	<0.1	<0.1
acenaphthalene	<0.1	<0.1
anthracene	<0.1	<0.1
fluorene	<0.1	<0.1
2-methylnaphthalene	<0.1	<0.1
Total	667.9 lbs/day	303.9 kg/day

Table 5

PCDD and PCDF Summary
Untreated Wastewaters
Dow Chemical - Midland Plant
August 28-29, 1984; October 23, 1984; December 4, 1984

Mass Discharge to Wastewater Treatment Facility
(lbs/day)

	Process Sewers	Incinerator Streams	Landfill(1)	Revetment System	Total lbs/day	Total kg/day
2378-TCDD	--	--	5.0×10^{-9}	--	--	--
Total Tetra CDDs	3.9×10^{-4}	3.0×10^{-4}	--	1.2×10^{-6}	6.9×10^{-4}	3.1×10^{-4}
Total Penta CDDs	--	2.7×10^{-6}	--	--	2.7×10^{-6}	1.2×10^{-6}
Total Hexa CDDs	1.0×10^{-7}	--	--	--	1.0×10^{-7}	4.5×10^{-8}
Total Hepta CDDs	1.2×10^{-4}	7.3×10^{-5}	--	5.9×10^{-7}	1.9×10^{-4}	8.6×10^{-5}
OCDD	1.7×10^{-3}	4.5×10^{-4}	--	2.9×10^{-6}	2.2×10^{-3}	1.0×10^{-3}
2378-TCDF	7.8×10^{-6}	4.2×10^{-6}	--	4.6×10^{-8}	1.2×10^{-5}	5.4×10^{-6}
Total Tetra CDFs	7.6×10^{-3}	5.8×10^{-3}	--	8.0×10^{-8}	1.34×10^{-2}	6.1×10^{-3}
Total Penta CDFs	6.1×10^{-5}	3.4×10^{-5}	--	--	9.5×10^{-5}	4.31×10^{-5}
Total Hexa CDFs	6.2×10^{-5}	6.5×10^{-5}	--	--	12.7×10^{-5}	5.8×10^{-5}
Total Hepta CDFs	6.6×10^{-4}	1.4×10^{-4}	--	--	8.0×10^{-4}	3.6×10^{-4}
OCDF	1.0×10^{-2}	1.9×10^{-4}	--	--	1.0×10^{-2}	4.5×10^{-3}

Note: (1) Positive findings of 2378-TCDD in the Rockwell Landfill dewatering sample are qualified. Data for other PCDDs and PCDFs are not valid for this sample.

trichlorophenol production area; (2) a dewatering sump in the abandoned strong phenolic wastewater treatment facilities; and (3) sludges in a section of the major sewer system. 4/ At this writing, Dow Chemical has ceased pumping the two dewatering sumps and is studying remedial measures for the sludges, which must be disposed of in accordance with RCRA and HSWA requirements.

Table 6 presents untreated wastewater loadings of toxic and nonconventional metal pollutants. Iron and aluminum comprise about 87% of the 3500 lbs/day (1600 kg/day) loading with lesser amounts of zinc, copper, manganese, chromium, lead, nickel, and barium accounting for over 12%. Effluent data for outfall 031 indicate that metal pollutants are effectively treated in the wastewater treatment facilities.

Raw waste data for conventional and other nonconventional pollutants are presented in Table 7.

2. In-Plant Sludges (Appendix A-3)

Tables 8, 9, 10, and 11 present the range of concentrations of volatile, semi-volatile, metal, and PCDD and PCDF compounds found in sludges from major sewer systems in the Midland plant. Sludge samples were obtained to determine whether the sludges could be significant wastewater sources of PCDDs and PCDFs or other toxic pollutants. Figure 7 shows the sample locations. Sampling was limited to those sites at or near the mouth of each major sewer where representative samples could be obtained in a reasonable and safe manner. A sediment sample was also taken from a sump serving a major section of the underground revetment system (RGIS). Data for the revetment system sump are presented in Table 12.

The general sewer is an open ditch which conveys wastewaters to the main wastewater treatment area. Most plant sewers are tributary to the general sewer with the exception of the strong phenolic wastewaters (50 sewer, 76 sewer) and half of the incinerator water streams (venturi/demister). Dow Chemical reports that accumulation of solids in the general sewer requires cleaning about every two years with the last cleaning occurring in 1984. 4/ Proper removal of these contaminated solids will be addressed by future in-plant remedial actions conducted pursuant to RCRA regulations.

The highest concentrations of organic compounds were found in the incinerator area samples taken from the general sewer. Chlorinated benzene concentrations ranged from 2,200-110,000 ppm for the incinerator area #2 sample. The 50 sewer also exhibited chlorinated benzenes at lesser concentrations (20-1410 ppm). The 50 sewer carried wastewater from chlorophenol manufacturing operations that are now shut down and from a shallow dewatering sump located in that area. Relatively lower levels of chlorinated phenols were found in certain sewers.

A review of the PCDD and PCDF data show that 2378-TCDD was identified in four of the samples: 300 sewer (0.5 ppb), 500 sewer (0.4 ppb), 50 sewer (11 ppb), and the general sewer-incinerator area #1 (9.2 ppb). The latter sample was also characterized by elevated concentrations (14-35,000 ppb) of

Table 6

Metal Pollutant Summary
Untreated Wastewaters
Dow Chemical - Midland Plant
August 28-29, 1984; October 23, 1984

Metal	Mass Discharge to Wastewater Treatment	
	lbs/day	kg/day
Aluminum	400	181.4
Antimony	4.5	2.0
Arsenic	3.3	1.5
Barium	15.3	6.9
Beryllium	<0.1	<0.1
Cadmium	0.6	0.3
Chromium	58.0	26.3
Cobalt	0.8	0.4
Copper	87.7	39.8
Iron	2705	1230
Lead	24.7	11.2
Manganese	70.9	32.2
Mercury	0.1	<0.1
Nickel	17.1	7.8
Selenium	0.2	0.1
Silver	0.1	<0.1
Thallium	<0.1	<0.1
Tin	<0.1	<0.1
Vanadium	1.3	0.6
Zinc	181	82.1
Total	3570.9 lbs/day	1623.1 kg/day

Table 7

Conventional and Nonconventional Pollutant Summary
Untreated Wastewaters
Dow Chemical - Midland Plant
August 28-29, 1984; October 23, 1984

Pollutant	Mass Discharge to Wastewater Treatment	
	lbs/day	kg/day
Total dissolved solids	678,500	308,400
Total suspended solids	68,800	31,300
Biochemical oxygen demand (5-day)	17,700	8,030
Total kjeldahl nitrogen	1,000	455
Ammonia-nitrogen	560	253
Total phosphorus	1,080	490
Phenols (4AAP)	2,420	1,100

Table 8

Volatile Organic Pollutant Summary
In-Plant Sludges
Dow Chemical - Midland Plant
October 1984

Volatile Compound	Range of Concentrations (ppm)
Benzene	0.01-738
Carbon tetrachloride	ND-520
Chlorobenzene	0.04-24,000
Chloroform	ND-<10
Ethylbenzene	ND-590
Methylene chloride	ND-440B
Tetrachloroethene	0.03-6300
Toluene	ND-178
Trichloroethene	ND-26
Acetone	ND-0.6B
Carbon disulfide	ND-0.03
Styrene	ND-670
Total xylenes	ND-96

B = Blank contamination.

Table 9

Acid and Base Neutral Pollutant Summary
In-Plant Sludges
Dow Chemical - Midland Plant
October 1984

Acid and Base Neutral Compound	Range of Concentrations (ppm)
2,4,6-trichlorophenol	ND-<0.33
2-chlorophenol	ND-<0.33
2,4-dichlorophenol	ND-1.6
Pentachlorophenol	ND-1.8
Phenol	ND-130
2,4,5-trichlorophenol	ND-<1.6
1,2,4-trichlorobenzene	ND-80,000
Hexachlorobenzene	ND-2200
1,2-dichlorobenzene	ND-110,000
1,3-dichlorobenzene	ND-8100
1,4-dichlorobenzene	ND-100,000
4-chlorophenyl phenyl ether	ND-43
Hexachlorobutadiene	ND-<20
Naphthalene	ND-9300
Phenanthrene	ND-<0.33

Table 10

Metal Summary
In-Plant Sludges
Dow Chemical - Midland Plant
October 1984

Metal	Range of Concentrations (ppm)
Aluminum	771-7220
Antimony	ND-464
Arsenic	ND-65
Barium	13-125
Beryllium	ND-10
Cadmium	ND-4
Calcium	ND-180,000
Chromium	43-667
Cobalt	ND-7
Copper	21-238
Iron	4160-20,100
Lead	ND-13
Magnesium	494-87,100
Manganese	33-561
Mercury	ND-1.8
Nickel	13-96
Potassium	1280-14,600
Selenium	ND
Silver	ND-17
Sodium	249-1,400
Thallium	ND
Tin	ND-44
Vanadium	6-59
Zinc	31-556

Table 11

PCDDs and PCDFs
In-Plant Sludges
Dow Chemical - Midland Plant
October 1984

(Concentrations in ppb.)

	50 Sewer	100/200 Sewer	300 Sewer	500 Sewer	General Sewer Incinerator Area #1	General Sewer Incinerat Area #2
2378-TCDD	11	ND	0.5	0.4	9.2	ND
Total tetra CDDs	21	ND	2.6	0.4	139	0.03
Total penta CDDs	11	0.2	7.0	ND	189	0.07
Total hexa CDDs	25	13	43	3.3	870	0.4
Total hepta CDDs	14	34	39,000	85	30,000	1.3
OCDD	ND	72	ND	134	ND	0.7
2378-TCDF	8.8	4.6	1.1	0.8	14	ND
Total tetra CDFs	11	6.7	3.9	0.8	304	0.05
Total penta CDFs	12	8.8	14	ND	293	0.02
Total hexa CDFs	6.2	ND	40	0.2	988	0.1
Total hepta CDFs	38	24	29,000	68	4300	4.0
OCDF	102	12	1700	377	35,000	5.8

Figure 7

Location Map
USEPA Sampling Locations
Dow Chemical Process Sewer Sludge
October 1984

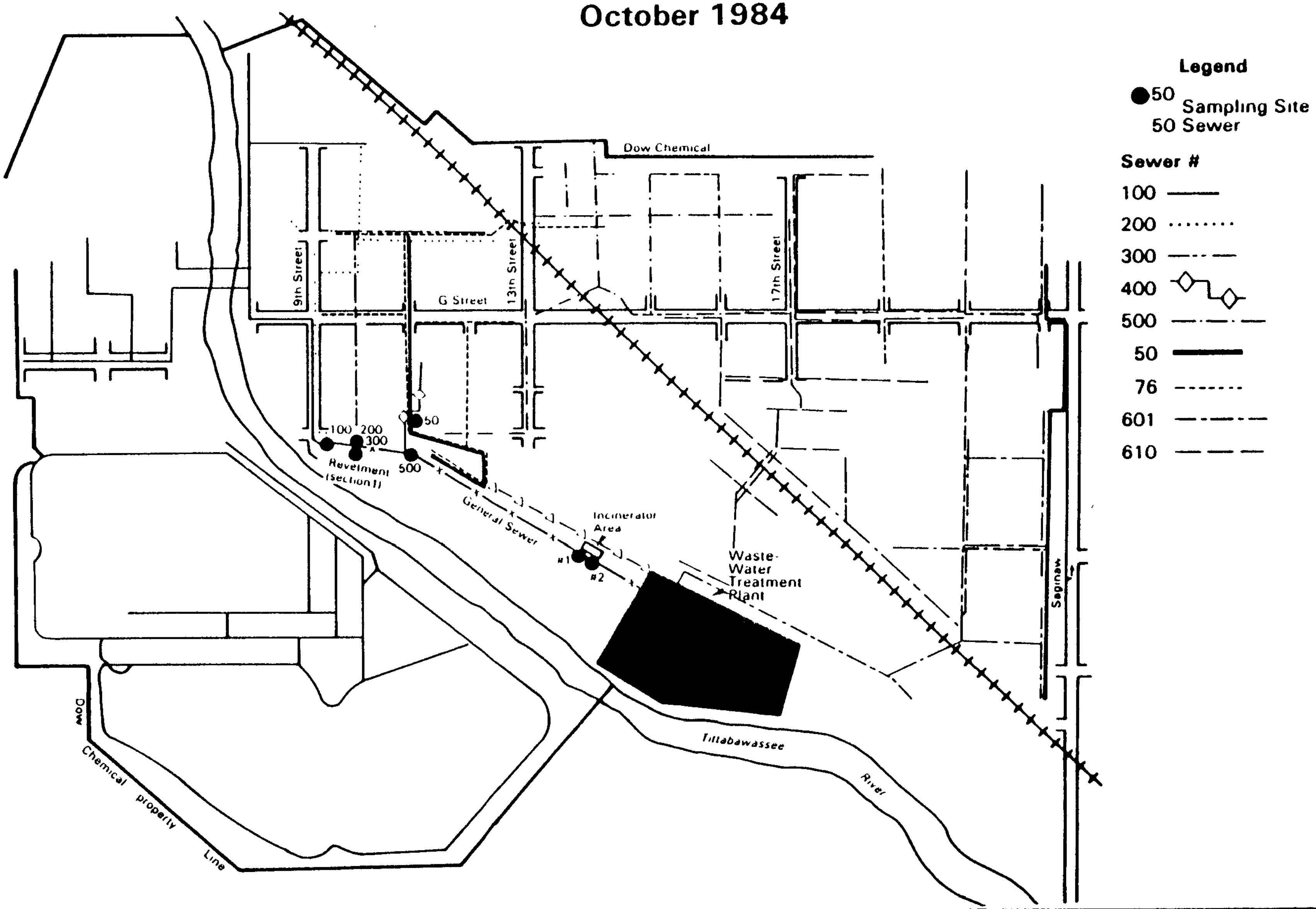


Table 12

Pollutant Summary
Riverbank Revetment Section #1 Sediment
Dow Chemical - Midland Plant
October 1984

Pollutant	Concentration (ppm)
Volatiles	
Benzene	24
Chlorobenzene	184
Chloroform	22
Tetrachloroethene	6300
Trichloroethene	38
Acid and Base Neutral	
2,4-dichlorophenol	42
Phenol	25
1,2,4-trichlorobenzene	940
Hexachlorobenzene	1730
Hexachloroethane	150
1,2-dichlorobenzene	1180
1,3-dichlorobenzene	250
1,4-dichlorobenzene	960
Fluoranthene	<20
Hexachlorobutadiene	5300
Hexachlorocyclopentadiene	5300
Naphthalene	<20
Phenanthrene	<20
Pyrene	<20
Metals	
Aluminum	4570
Antimony	50
Arsenic	113
Barium	125
Beryllium	ND
Cadmium	ND
Chromium	15
Cobalt	ND
Copper	114
Iron	120,000
Lead	ND
Manganese	253
Nickel	52
Selenium	ND
Silver	20
Thallium	ND
Tin	ND
Vanadium	48
Zinc	178

Table 12 (continued)

Pollutant	Concentration (ppb)
PCDDs and PCDFs	
2378-TCDD	4
Total tetra CDDs	146
Total penta CDDs	111
Total hexa CDDs	180
Total hepta CDDs	365
OCDD	916
2378-TCDF	64
Total tetra CDFs	249
Total penta CDFs	127
Total hexa CDFs	109
Total hepta CDFs	853
OCDF	2739

other PCDDs and PCDFs. This area is impacted by discharges from the sludge dewatering building, the incinerator, and contaminated sludges upstream in the sewer system.

The sludge sample from the revetment system sump contain relatively high ppm levels of several toxic organic pollutants including tetrachloroethene (6300 ppm); hexachlorobutadiene (5300 ppm); hexachlorocyclopentadiene (5300 ppm); hexachlobenzene (1730 ppm); and other chlorinated benzenes and phenols at levels up to about 1000 ppm. 2378-TCDD and 2378-TCDF were found at 4 ppb and 64 ppb, respectively, with levels of other PCDDs and PCDFs in the high ppb to low ppm range. These data suggest ground water at the site is highly contaminated at certain locations and that the RGIS has been at least partially effective in intercepting contaminated ground water.

In 1978, after Dow Chemical notified the Michigan Department of Public Health that it had found dioxin in native fish from the Tittabawassee River, Region V conducted wastewater treatment system sludge and river sediment sampling programs. The in-plant sludges and river sediments were analyzed for total TCDDs. At that time, USEPA's analytical contractor (University of Nebraska) could not conduct isomer-specific analyses for 2378-TCDD. The TCDD results for the wastewater sludges are presented in Table 13. Phenol treatment system sludges ranged from not quantifiable to 160 ppt (0.16 ppb) in the waste activated sludge. TCDDs in the general treatment system sludges ranged from 283-5800 ppt (0.28-5.8 ppb).

The highest concentration (5800 ppt) was found in the waste primary sludge from the main plant wastewater treatment system, with lesser amounts in other wastewater treatment system solids. Also, 0.38 ppt (380 ppq) of TCDD was found in the untreated phenolic wastewater prior to treatment. TCDDs were not detected at 0.25 ppt (250 ppq) in 2,4-D process waste then being disposed of by deep well injection. At the time, Dow Chemical was disposing of wastewater treatment plant sludges by incineration or landfilling.

An experimental wastewater and river water sampling program using activated carbon to determine whether the wastewater discharge from Dow Chemical was a dioxin source was also conducted in 1978. The results of that study are reviewed in Section VI.B.2.

3. Tertiary Pond Sediments (Appendix A-4)

As noted earlier, Dow Chemical discharges the effluent from the biological treatment facilities to a series of three ponds for additional treatment prior to discharge to the Tittabawassee River via outfall 031. The flow is routed first through a relatively small pentagon-shaped pond, then through a narrow rectangular pond, followed by a large final polishing pond, called the tertiary pond. The three ponds cover about 220 acres and average about 3-4 feet in depth, resulting in a volumetric capacity of about 600 million gallons. The estimated retention time is about 30 days for typical effluent flows in the range of 20 million gallons per day.

Table 13

TCDDs In Dow Chemical - Midland Plant Samples
October 1978

USEPA-Region V Sample Number	UNL Number	Sample Site	TCDDs (ppt)	DL	Analyst's Notes
EA06S18A	UN166	Phenol Treatment System - Waste Primary Sludge	NQ	(8)	Small positive signals detected near detection limit.
EA06S18B	UN167	Phenol Treatment System - Waste Primary Sludge	NQ	(8)	
EA06S19	UN168	Phenol Treatment System - Waste Activated Sludge	160	(12)	
EA06S24	UN169	General Treatment System - Waste Primary Sludge	5800	(56)	
EA06S25	UN170	General Treatment System - Primary Skimmings	470	(10)	
EA06S26	UN171	General Treatment System - Waste Activated Sludge	283	(48)	
EA06S28	UN172	2,4-D Process Waste to Deep Well	ND	(0.25)	Peak observed at M/Z 320 and 322, but isotope ratio incorrect for positive identification.
EA06S29	UN173	Raw Phenol Wastewaters after Equalization	0.38	(0.20)	

Note: (1) UNL - University of Nebraska - Analytical Contractor
(2) DL - Analytical detection level
(3) ND - Not detected at stated detection level
(4) NQ - Detected at or near detection level, but not quantified

In July 1984, Region V collected unconsolidated sediment samples at five locations in the ponds, one each in the primary (pentagonal) and secondary (rectangular) ponds and three in the larger tertiary pond. Figure 8 presents the approximate sampling locations. At each site, surface sediments (approximately 0-3") and bottom pond sediments (bottom 3") were collected and analyzed for metals, volatile pollutants, and semi-volatile pollutants, including PCBs, pesticides, and PCDDs and PCDFs. At the time samples were collected, the unconsolidated sediment layers above the clay layers in the primary and secondary ponds were found to be about twelve to fifteen inches, while sediments in the tertiary pond averaged about six inches in thickness. Dow Chemical reports that sediments have not been dredged from the ponds since they were put into service. Table 14 presents a summary of the positive findings for volatile and semi-volatile pollutants. Data for PCDDs and PCDFs are presented in Table 15. Metals data are presented in Appendix A-4. Because the sediment layer in each pond was not compacted, the bottom sediment samples may have contained some of the pond bottom clay layer as opposed to only sediments. The results reviewed below should be viewed accordingly.

Volatile pollutants, including benzene, chlorobenzene, ethylbenzene, toluene, acetone, and xylenes were found at the highest levels in the surface sediments from the primary pond. Concentrations ranged from 310 ppb (xylenes) to 4000 ppb (chlorobenzene). Lower levels of the same pollutants found in surface sediments (10 to 190 ppb) were also found in primary pond bottom sediments. The secondary pond surface sediments were contaminated by the same pollutants to a lesser extent (<10 to 230 ppb) than the primary pond surface sediments. In similar fashion, the secondary pond bottom sediments were not as highly contaminated (<10 to 50 ppb) as the secondary pond surface sediments. Relatively few volatile pollutants were found in the tertiary pond surface sediments and virtually none at low ppb levels in the bottom sediments.

On a gross basis, the semi-volatile organic pollutants were distributed in roughly the same manner as were the volatile pollutants. However, the secondary pond surface sediments contained relatively high levels of a few pollutants (4-methyl phenol-17,000 ppb; 1,2,4-trichlorobenzene-35,000 ppb; 1,2-dichlorobenzene-2700 ppb; and heptachlor-12,000 ppb) not found in primary pond surface sediments. 1,3-Dichlorobenzene and 1,4-dichlorobenzene were found in primary pond sediments at 13,000 ppb and 67,000 ppb, respectively. The tertiary pond surface sediments contained pentachlorophenol (3950 ppb) and pyrene (2300 ppb) which were not found in surface or bottom sediments from the other ponds. The tertiary pond surface sediments also contained relatively low ppb levels (27 to 61 ppb) of four pesticide products.

Without long-term data on the effluent characteristics from Dow Chemical's biological treatment facility and some notion of sediment deposition rates, it is difficult to determine what the significance of these findings might be. However, pollutants associated with the production of chlorinated phenols, notably the chlorinated benzenes, appear to be the principal organic pollutants found in the sediments. Inasmuch as most of the chlorinated phenols production at the Midland plant was terminated in the late 1970s, the contribution of these pollutants from process wastewaters in the future should be considerably less than in the past. The current raw wastewater loadings of chlorinated

Figure 8

Location Map
USEPA Sampling Locations
Dow Chemical Tertiary Pond Sediments
July 1984

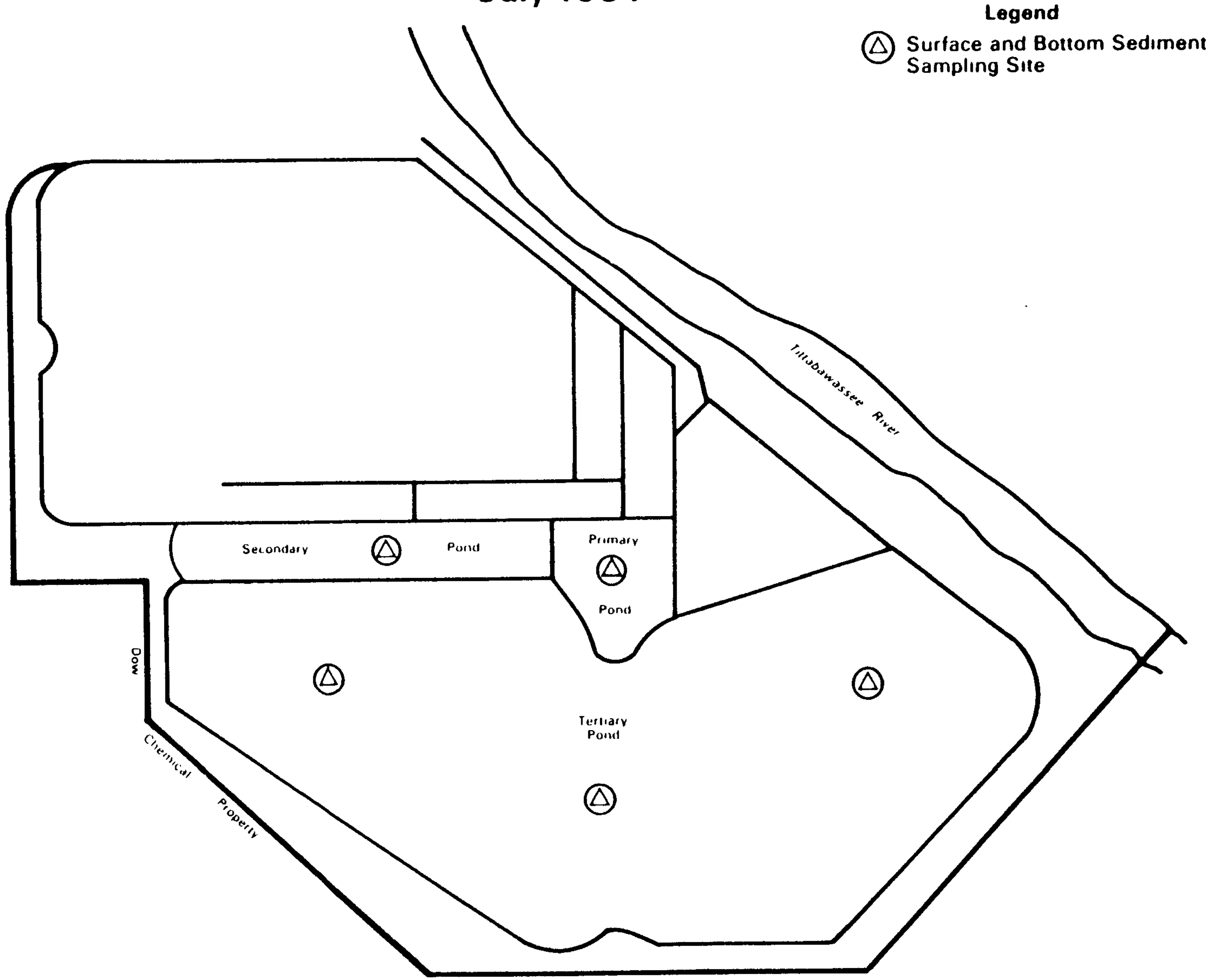


Table 14

Toxic Organic Pollutant Summary
Dow Chemical Treatment Pond Sediments
July 1984

ug/kg (parts per billion (ppb))

Volatile Pollutants	Primary Pond Surface	Primary Pond Bottom	Secondary Pond Surface	Secondary Pond Bottom	Tertiary Pond Surface	Tertiary Pond Bott
Benzene	500	20	30	<2.5	--	--
Chlorobenzene	4000	78	160	23	10.2	--
Ethylbenzene	2800	190	230	25	6.2	--
Methylene chloride	1900B	1100B	98B	50 B	160 B	367
Chloroform	--	--	--	<2.5	--	--
Bromoform	--	--	--	9.8	--	--
Tetrachloroethane	--	--	16	12	--	--
Toluene	340	9.4	110	26	<1.7	--
Trichloroethene	--	--	<2.5	<2.5	--	--
Acetone	1300	<50	<50	--	<17 B	--
Styrene	--	--	<2.5	--	--	--
Total xylenes	310	9.7	39	15	--	--
Acid and Base Neutral Pollutants**						
4-nitrophenol	--	--	--	--	<50	--
Pentachlorophenol	--	--	--	--	3950	--
Phenol	--	--	--	--	<5	--
4-methylphenol	--	--	17,000	--	--	--
1,2,4-trichlorobenzene	--	--	35,000	<10	1460	--
Hexachlorobenzene	--	--	<10	--	--	--
1,2-dichlorobenzene	--	--	2700	--	--	--
1,3-dichlorobenzene	13,000	2000	<10	--	--	--
1,4-dichlorobenzene	67,000	10,000	8500	--	<1800	--
Naphthalene	<10	--	--	--	--	--
Bis(2-ethylhexyl)phthalate	9500	--	2300	--	1600	--
Di-n-butyl phthalate	<10	--	<10	1700	<5	--
Di-n-octyl phthalate	--	--	--	--	--	<[illegible]
Chrysene	<10	--	--	--	--	--
Pyrene	--	--	--	--	2300	--
PCB/Pesticide Pollutants						
4,4'-DDT	--	--	480	--	39	--
Endrin	--	--	330	--	61	--
Endrin aldehyde	--	--	--	--	40	--
Heptachlor	--	--	12,000	--	27	--

Notes: (1) -- = Not detected.
(2) B = Blank contamination.
(3) *Average of three (3) tertiary pond samples.
(4) **Tertiary pond surface based on average of two (2) samples.

Table 15

PCDD and PCDF Summary
Dow Chemical Treatment Pond Sediments
July 1984

ng/g (parts per billion (ppb))

	Primary Pond		Secondary Pond		Teritary Pond					
					Upper		Mid		Lower	
PCDDs and PCDFs	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
2378-TCDD	1.7	0.87	3.8	--	0.14	0.05	0.93	0.02	0.10	0.03
Total tetra CDDs	18	10	26	0.25	1.5	0.41	9.2	0.23	2.0	0.11
Total penta CDDs	10	5.9	23	--	0.81	0.26	6.3	0.08	0.67	--
Total hexa CDDs	14	17	38	--	2.6	0.49	26	0.75	1.7	--
Total hepta CDDs	125	64	840	6.0	17	2.0	201	6.4	11	1.0
OCDD	482	168	920	16	72	12	324	23	44	4.4
2378-TCDF	--	0.25	1.8	0.10	0.09	0.04	0.90	0.06	0.15	0.02
Total tetra CDFs	95	19	93	1.5	15	3.6	44	1.5	22	0.49
Total penta CDFs	26	6.5	14	--	2.5	0.43	3.4	0.26	2.0	0.09
Total hexa CDFs	20	7.0	16	--	1.8	0.29	8.0	0.20	1.4	0.06
Total hepta CDFs	84	18	320	1.3	4.5	0.50	31	0.80	5.1	0.20
OCDF	117	22	256	2.8	7.3	0.94	33	1.7	5.6	0.35

Notes: (1) -- = Not detected.
(2) Data reported on wet weight basis with the exception of tertiary pond-lower-bottom sample.

benzene as depicted in Table 4 is relatively low (about 30 lbs/day, 13.6 kg/day). The presence of semi-volatile compounds in pond sediments should not be of great concern from an effluent discharge standpoint since operation of the recently installed effluent filter should effectively minimize any slug discharges of pollutants that might have occurred during periods of turbulent conditions in the ponds. The filter system affords little or no protection for volatile pollutants that may be released from pond sediments. The distribution of these pollutants in the three ponds suggest that slug discharges at outfall 031 resulting from disturbing the sediments in the primary or secondary ponds, are not likely. Continued low-level releases of the compounds over time can be expected.

PCDDs and PCDFs are more evenly distributed throughout the pond system than other semi-volatile pollutants (Table 15). This is probably due to the relative particle size distribution of the suspended solids to which the PCDDs and PCDFs are attached. Dow Chemical reports that much of the discharge of 2378-TCDD from outfall 031 can be attributed to wastewaters from the hazardous waste incinerator. 4/ Fine particulates scrubbed from the exhaust gases are believed to pass through the biological treatment facility. If this is the case, one would expect 2378-TCDD, as well as other PCDDs and PCDFs, to be distributed over the large surface area of the pond system. The data presented in Table 15 support this hypothesis. Note that higher levels of PCDDs and PCDFs were found in primary and secondary pond sediments than in tertiary pond sediments; also, the lowest levels of PCDDs and PCDFs were found in tertiary pond surface sediments closest to the discharge from the pond to outfall 031. Based upon recent soil study results for the Midland area, Region V has concluded that atmospheric deposition of 2378-TCDD from Dow Chemical incinerator emissions and other process and fugitive sources have resulted in widespread low-level 2378-TCDD contamination of city soils. 10b/ If atmospheric deposition was the primary transport mechanism for PCDDs and PCDFs to pond sediment, one would expect a fairly uniform distribution across the system. The data presented here indicate the principal source of PCDDs and PCDFs in pond sediments is the biological treatment plant effluent as opposed to atmpspheric deposition.

As with the other semi-volatile pollutants, operation of Dow Chemical's effluent filter should minimize any slug discharges of PCDDs and PCDFs from outfall 031 during turbulent pond conditions. These data suggest the pond system has provided a measure of effluent reduction benefit not otherwise available until installation of the final effluent filter system. Tittabawassee River sediments are compared with treatment pond sediments elsewhere in this report.

B. Wastewater Effluent Sampling - Outfall 031 (1978-1985)

Over the past several years, Dow Chemical has significantly reduced the wastewater discharge flow to the Tittabawassee River from the Midland plant. In the early 1970's, wastewater discharge flows in excess of 50 MGD were common. During the 1981 survey, the average discharge was about 34 MGD, and at the time of the August 1984 survey, the average discharge was about 20 MGD. At this writing (February 1986), the discharge from outfall 031 is averaging about 18 MGD. The reduction of flow is largely accounted for by changes in production operations at the Midland plant and installation of cooling water recycle systems and other water conservation measures.

Trends in the discharge loadings of conventional, nonconventional, and toxic pollutants from outfall 031 are reviewed below. Data for PCDDs and PCDFs and available biomonitoring data are reviewed separately. At the time of the last USEPA sampling program (December 1984), Dow Chemical had not completed construction of the final effluent mixed-media filtration system for the discharge from outfall 031. Region V initiated a short-term grab sampling program of a pilot filter system to estimate the likely effects of the full-scale filter on effluent quality. Tables 16-26 present summaries of the effluent data from the Region V September 1981 and August 1984 surveys, recent Dow Chemical monitoring data, and the December 1984 USEPA sampling program for the filtration pilot plant.

The USEPA effluent data presented in Tables 16-26 are gross discharge loadings or concentrations as opposed to net loadings or concentrations. Gross discharge loadings and concentrations are presented because most pollutants were either not detected or not detected at significant levels in the Tittabawassee River. Also, the retention time of the water in the Midland plant is so long (up to 30 days) that adjusting effluent concentrations for intake concentrations for intake and effluent samples collected simultaneously would not be meaningful. Water intake data are presented in the appendices with effluent data collected during the same surveys. The Dow Chemical data for total dissolved solids, total suspended solids, BOD_5, and ammonia-N are net discharge loadings reported in accordance with the terms of NPDES permit MI0000868.

1. <u>Conventional, Non-Conventional, and Toxic Pollutants</u>
<u>(Appendices B-1 (1981 data); B-2 (1984 data); B-3 (</u>Dow Chemical data)

Table 16 presents data for conventional and nonconventional pollutants. Despite a reduction in flow of more than 40%, the discharge of total dissolved solids monitored by USEPA has remained within a narrow range of 809,000 to 830,000 lbs/day. More frequent monitoring by Dow Chemical confirm the magnitude of the total dissolved solids discharge. About 75% of the total suspended solids contained in the tertiary pond effluent and more than half of the influent total phosphorus loading were removed by the pilot filter. Recent NPDES permit self-monitoring data by Dow Chemical with the full-scale filtration system on line confirm the expected performance for suspended solids removal. Based upon the 1981 survey, Region V characterized the discharge for outfall 031 as the largest point source of phosphorus to the Saginaw Bay drainage basin. The annual discharge was estimated to be about 40 tons. The August 1984 sampling data indicate the annual discharge before filtration may have been reduced to about 16 tons. The pilot plant data indicate the current annual discharge may be in the range of 5 to 6 tons. Phosphorus data for the full-scale filtration system are not available at this writing.

Table 17 summarizes volatile pollutant data. The more recent data indicate that the discharge of volatile pollutants has been significantly reduced from 1981. Fewer compounds were detected by Region V in 1984, and those detected were generally found at lower levels. The discharge loadings of chloroform, carbon tetrachloride, and methylene chloride were in the range of 1 to 3 lbs/day, with lesser amounts of 1,2-dichloroethane and 1,1,1-trichloroethane. Methylene chloride, carbon tetrachloride, and chloroform were found at the highest levels

Table 16

Conventional and Non-Conventional Pollutants Summary
Dow Chemical - Midland Plant
Outfall 031

(Gross Discharge Loadings in lbs/day
except as noted - See Note 1)

Conventional and Other Pollutants	USEPA - September 1981			USEPA - Aug. 1984	Dow Chemical - July 1984-December 1985			USEPA - December 1984	
	Max.	Min.	Avg.		Max.	Min.	Avg.	Pilot Plant Influent (031)	Pilot Plant Effluent
Total dissolved solids	960,000	676,000	809,000	815,000	960,000	454,000	705,000	830,000	828,000
Chloride	428,000	303,000	357,000						
Fluoride	200	160	190						
Sulfate	87,000	64,000	77,000						
Total suspended solids	7130	1450	3700	7485	4778	663	2308	3905	976
Chemical oxygen demand	41,300	29,200	35,900						
Total organic carbon	7880	4640	6010						
BOD_5	1500	1370	1440	1338	893	18	423		
Total kjeldahl nitrogen	2070	1630	1820	355				602	391
Ammonia-N	1750	1180	1470	134	508	0	124	163	162
NO_2 and NO_3-N	115	11	68						
Total phosphorus	420	130	254	90	140	24	62	68	30

Notes (1) Dow Chemical phosphorus data are monthly averages based upon average flow and phosphorus data from monthly operating reports (MORs) submitted to Michigan DNR. Dow Chemical data for total dissolved solids, total suspended solids, BOD_5, and ammonia-N are net discharge loadings.

(2) USEPA September 1982 average data are based upon four 24-hour composite samples taken at weekly invervals.

(3) USEPA August 1984 data are for one 24-hour composite sample.

(4) USEPA December 1984 pilot plant filter data are for one grab sample.

Table 17

Volatile Organic Summary
Dow Chemical - Midland Plant
Outfall 031

(Gross Discharge Loadings in lbs/day)

Volatile Toxic Organic Pollutants	USEPA - September 1981			USEPA - Aug. 1984	Dow Chemical - July 1984-December 1985			USEPA - December 1984	
	Max.	Min.	Avg.	Avg.	Max.	Min.	Avg.	Pilot Plant Influent (031)	Pilot Plant Effluent
Methylene chloride	45.00B	1.30B	24.14B	1.71B	8.8	--	2.5	2.93B	3.42B
1,1-dichloroethylene	5.25	0.70	2.27	--	--	--	--*	--	--
1,1-dichloroethane	1.80	1.00	1.37	--	--	--	--*	--	--
Chloroform	9.38B	2.87B	5.08B	3.25	5.5	--	2.2	--	1.79
1,2-dichloroethane	3.75B	2.00B	2.72B	0.98	--	--	--*	--	--
1,1,1-trichloroethane	4.13	0.92	2.02	0.80	5.2	--	1.2	--	--
Carbon tetrachloride	18.77	2.10	8.22	2.76	14.4	--	4.1	--	--
Bromodichloromethane	1.24B	--	0.69	--	--	--	--*	--	--
1,2-dichloropropane	1.91	0.55	1.12	--	--	--	--*	--	--
Trichloroethylene	1.39	0.35	0.78	--	--	--	--*	--	--
Dibromochloromethane	4.88	--	1.97	--	--	--	--*	--	--
1,1,2,2-tetrachloroethane	7.51	0.80	3.15	--	3.5	--	0.5	--	--
Chlorobenzene	1.00	--	0.33	--	--	--	0.05	--	--
Bromoform	4.50	--	1.50	--	31.4	--	2.9	--	--
Tetrachloroethene	--	--	--	<0.81	5.1	--	0.9	0.81	0.81
1,2-dibromoethane	--	--	--						
1,1,2-trichloroethane				--	--	--	--	--	--

Notes (1) -- = Not detected.
(2) B = Blank contamination.
(3) * = One sample only.
(4) Dow Chemical data are monthly averages based on monthly operating reports (MORs) submitted to Michigan DNR for the period of July 1984-December 1985 unless otherwise noted.

in the untreated wastewaters (Table 7). Dow Chemical monitoring data for the period July 1984 to December 1985 indicate the average discharges of carbon tetrachloride, methylene chloride, bromoform, and chloroform are in the 2 to 4 lbs/day range. Other volatile pollutants routinely found in the outfall 031 discharge by Dow Chemical include 1,1,1-trichloroethane, tetrachloroethene, and 1,1,2,2-tetrachloroethane. Limited data for the filtration pilot plant suggest the full-scale filtration system will have little or no impact on the discharge of volatile pollutants from the Midland plant. The physical and chemical properties of the volatile compounds are such that filtration is not an effective removal mechanism.

Data for semi-volatile compounds are presented in Table 18. During the 1984 USEPA survey, semi-volatile compounds were not detected in the discharge from outfall 031, while in 1981, several compounds, including chlorinated phenols and chlorinated benzenes, were discharged in the 0.1 to 2.0 lbs/day range. It is likely that some semi-volatile compounds were present in 1984 but not detected. Detection levels at the USEPA contract laboratory were in the 10 to 100 ppb range. Recent monitoring by Dow Chemical also detected chlorinated benzenes in the same range as the 1981 data, and bischlorobutyl ether as high as 10.7 lbs/day. Other compounds detected by Dow Chemical include chlorinated benzenes (average discharge in the range of 0.5 lbs/day); chlorinated phenols, including 2,4-dichlorophenol; 2,4,6-trichlorophenol and pentachlorophenol; and bis (2-ethylhexyl) phthalate. The USEPA pilot plant sampling suggests that traces of 2,4,6-trichlorophenol and pentachlorophenol may remain in the discharge after filtration. Table 19 presents data for herbicides, pesticides, and PCBs. The more recent USEPA and Dow Chemical data suggest no detectable discharge of pesticides and PCBs, but continued discharge of silvex, 2,4-D, 2,6-D, and Dinoseb. Many semi-volatile organic compounds including herbicides, pesticides, and PCBs tend to associate with suspended particulates in aqueous systems. Thus, operation of the full-scale filtration system is expected to result in lower discharge levels of these pollutants than would otherwise occur.

Metals data are presented in Table 20. Most toxic metals were found at relatively low concentrations in both the 1981 and more recent sampling programs (i.e., less than 50 ppb). Zinc is the only toxic metal detected in the pilot plant effluent (about 100 ppb); a projected full-scale discharge loading is about 21 lbs/day. Dow Chemical reported discharges of chromium and zinc without the final effluent filter in place of 33 and 50 lbs/day, respectively. Lower discharge levels are expected with the full-scale filtration system in place.

2. PCDDs and PCDFs
(Appendix B-4 (1978 data); B-5 (1981 data); B-6 (1984 data); B-7 (Dow Chemical data))

As noted earlier, Region V conducted an experimental monitoring study at the Dow Chemical - Midland Plant during September 1978 to determine if the presence of dioxin in fish from the Tittabawassee River was attributable to the discharge from outfall 031. At that time, USEPA did not have the capability to analyze for 2378-TCDD in water samples at concentrations in the sub-part per trillion range. In an attempt to concentrate 2378-TCDD that may have been present, Region V developed a granular activated carbon canister sampling

Table 18

Acid and Base Neutral Pollutant Summary
Dow Chemical - Midland Plant
Outfall 031

(Gross Discharge Loadings in lbs/day)

Acid and Base Neutral Pollutants	USEPA - September 1981			USEPA - Aug. 1984	Dow Chemical - July 1984-December 1985			USEPA - December 1984	
	Max.	Min.	Avg.		Max.	Min.	Avg.	Pilot Plant Influent (031)	Pilot Plant Effluent
2-chlorophenol	0.28	trace	0.07	--	0.2	--	0.01	--	--
Phenol	0.28	--	0.07	--	0.7	--	0.3	--	--
2,4-dichlorophenol	0.35	--	0.15	--	0.7	--	0.1	--	--
2,4,6-trichlorophenol	1.25	--	0.31	--	1.0	--	0.1	--	<0.33
Pentachlorophenol	4.35	--	1.46	--	4.6	--	1.5	--	<0.33
Pyrene	0.27	--	0.07	--	--	--	--*	--	--
2-chloronaphthalene	0.26	--	0.07	--	--	--	--*	--	--
1,2-dichlorobenzene	trace	--	trace	--	3.7	--	0.5	--	--
1,3-dichlorobenzene	0.71	0.18	0.42	--	0.9	--	0.2	--	--
1,4-dichlorobenzene	0.75	0.19	0.47	--	1.8	--	0.3	--	--
1,2,4-trichlorobenzene	1.39	0.32	0.87	--	1.9	--	0.5	--	<0.33
Di-n-butyl phthalate	0.21B	--	0.05B	--	--	--	--	<0.16B	--
Butylbenzyl phthalate	trace	--	trace	--	--	--	--*	--	--
Bis(2-ethylhexyl) phthalate	60.6B	3.42	23.08B	--	--	--	0.67*	--	--
Bis(2-chloroethyl) ether	1.28	0.04	0.46	--	0.7	--	0.3	<0.49	<0.49
Isophorone	trace	-- B	trace	--	--	--	--*	--	--
Dioctyl phthalate	2.05	--	0.51	--	--	--	--*	--	--
Acenaphthene	0.17	--	0.04	--	--	--	--*	--	--
Bis(2-chloroisopropyl) ether	--	--	--	--	--	--	--**	<0.49	<0.49
1,2,3-trichlorobenzene	--	--	--		0.25	--	0.08**		
1,2,4,5-tetrachlorobenzene	--	--	--		1.59	0.53	1.00**		
Bis(chlorobutyl) ether	--	--	--		10.73	0.37	4.26**		
Aniline	--	--	--	--	0.08	0.02	0.03**	--	--
Naphthalene				--	.1	--	0.04	--	--

Notes (1) -- = Not detected.
(2) B = Blank contamination.
(3) * = One sample only.
(4) ** = Average of three samples.
(5) < = Compound present but at less than stated value
(6) Dow Chemical data are monthly averages based on monthly operating reports (MORs) submitted to Michigan DNR for the period of July 1984-December 1985 unless otherwise noted.

Table 19

Herbicides/PCB/Pesticides Summary
Dow Chemical - Midland Plant
Outfall 031

(Gross Discharge Loadings in lbs/day)

Herbicides/ PCB/Pesticides Pollutants	USEPA - September 1981			USEPA - Aug. 1984	Dow Chemical - July 1984-December 1985			USEPA - December 1984	
	Max.	Min.	Avg.		Max.	Min.	Avg.	Pilot Plant Influent (031)	Pilot Plant Effluent
Herbicides									
Dichloroprop	0.22	--	0.06						
2,4-D	0.30	--	0.08		0.058	0.004	0.015*		
Silvex	2.14	--	0.94		1.44	0.45	1.01**		
2,4,5-T	0.40	--	0.15		--	--	-- **		
2,6-D	--	--	--		0.84	0.44	0.59**		
Dinoseb	--	--	--		1.95	--	1.22**		
PCB/Pesticides									
Aldrin	0.21	--	0.08 B	--	--	--	--	--	--
4,4'-DDD	0.01B[1]	--	0.005	--	--	--	--	--	--
Endosulfan I	0.03	--	0.008	--	--	--	--	--	--
Endrin aldehyde	0.02[1]	--	0.01[1]	--	--	--	--	--	--
Heptachlor epoxide	0.02[2]	--	0.01[1,2]	--	--	--	-- **	--	--
Beta-BHC	0.01	--	0.003	--	--	--	--	--	--
Gamma-BHC	0.01	--	0.003	--	--	--	--	--	--
PCB-1242	1.10	--	0.28	--	--	--	--	--	--
PCB-1254	0.09	--	0.02	--	--	--	--	--	--
PCB-1260	0.20	--	0.05	--	--	--	--	--	--

Notes (1) -- = Not detected.
(2) B = Blank contamination.
(3) [1]Not confirmed on second column GC/ECD.
(4) [2]Not confirmed on second column GC/ECD due to interference.
(5) * = Dow Chemical monthly average MOR data.
(6) ** = Average of three samples; other Dow Chemical data - one sample.

Table 20

Metals Summary
Dow Chemical - Midland Plant
Outfall 031

(Discharge Loadings in lbs/day)

Metal Pollutants	USEPA - September 1981 Max.	USEPA - September 1981 Min.	USEPA - September 1981 Avg.	USEPA - Aug. 1984	Dow Chemical - December 1985 Max.	Dow Chemical - December 1985 Min.	Dow Chemical - December 1985 Avg.	USEPA - December 1984 Pilot Plant Influent (031)	USEPA - December 1984 Pilot Plant Effluent
Aluminum				-- B				21.6	--
Antimony				1.35	--	--	8.34	--	--
Arsenic	0.87	--	0.22	--	--	--	--	--	--
Barium				6.67				8.95	9.27
Beryllium				--	--	--	--	0.21	0.39
Cadmium	--	--	--	--	--	--	--	--	2.1
Chromium	3.75	2.30	3.21	--	--	--	33.36	--	--
Cobalt				--				--	--
Copper	1.40	--	0.78	1.3	--	--	--	6.8	3.7
Iron				5.86				66.7	17.4
Lead	--	--	--	--	--	--	--	--	--
Manganese				31.9				48.2	45.6
Mercury				--	--	--	--	--	--
Nickel				4.39	--	--	--	2.76	2.44
Selenium				--	--	--	--	--	--
Silver				--	--	--	--	--	--
Thallium				--				--	--
Tin				5.21				--	--
Vanadium				--				--	--
Zinc	39.4	18.0	26.9	4.07	--	--	50.0	39.2	21.2

Notes (1) B = Blank contamination.
(2) -- = Not detected.
(3) Dow Chemical metals data based on one-time sampling event.

system to sample large volumes of water over time. The study design called for suspending three sampler assemblies in the discharge from outfall 031 (tertiary pond overflow) and two assemblies at each of the following locations in the Tittabawassee River: upstream of the Dow Dam; downstream of outfall 031 near Smith's Crossing Road; and at Freeland Road (Appendix B-4). Figure 9 shows the approximate sampling locations. The plan was to operate the samplers for up to one week, until 10,000 liters of water were filtered, or until the filters became clogged with sediment. The volumetric flow through the filters ranged from 1100 liters to 5800 liters after several days of operation in the field. The results are presented in Table 21.

Only filters from Dow Chemical outfall 031 and from the Tittabawassee River upstream of the Dow Dam were extracted by EPA's Pesticides Monitoring Laboratory at Bay St. Louis, Mississippi, and analyzed by EPA's Environmental Monitoring Systems Laboratory at Research Triangle Park, North Carolina. 2378-TCDD was not detected in the extract from either sample. However, three other TCDD isomers were detected in the extract from the outfall 031 sample; none were detected in the Tittabawassee River upstream sample. Because neither the collection efficiency of the activated carbon sampling systems for 2378-TCDD and other PCDDs, nor the efficiency of extracting those compounds from the carbon were known, the results must be characterized as only qualitative. Nonetheless, the limited results from this study indicated that Dow Chemical was discharging TCDDs to the Tittabawassee River.

In September 1981, Region V conducted additional dioxin studies at the Dow Chemical- Midland Plant. 1/ As part of that work, an experimental large volume effluent sampling scheme was developed to allow the detection of 2378-TCDD and other PCDDs and PCDFs in the sub-part per trillion range. A method validation pilot study was conducted by the Brehm Laboratory at Wright State University under contract to Region V. 11/ In short, this method consists of obtaining a large volume water sample; performing an extraction with a suitable solvent for an extended period; performing solvent exchange and clean up; and, analyses of the extract for the desired compounds by HRGC-HRMS. After completion of the pilot study, actual effluent and river samples were obtained at the following locations:

Dow Chemical - Midland Plant

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

Tittabawassee River

- Outfall 031 Plume
- Smith's Crossing Road

Because of the large volume of sample required for analysis, the 24-hour composite sample for each site was collected as two separate 12-hour composite samples in separate containers. The analytical contractor, Battelle Columbus Laboratories, Columbus, Ohio (formerly Battelle Memorial Institute), was to

Figure 9

Location Map
1978 USEPA Dioxin Study
Tittabawassee River
Dow Chemical - Midland Plant

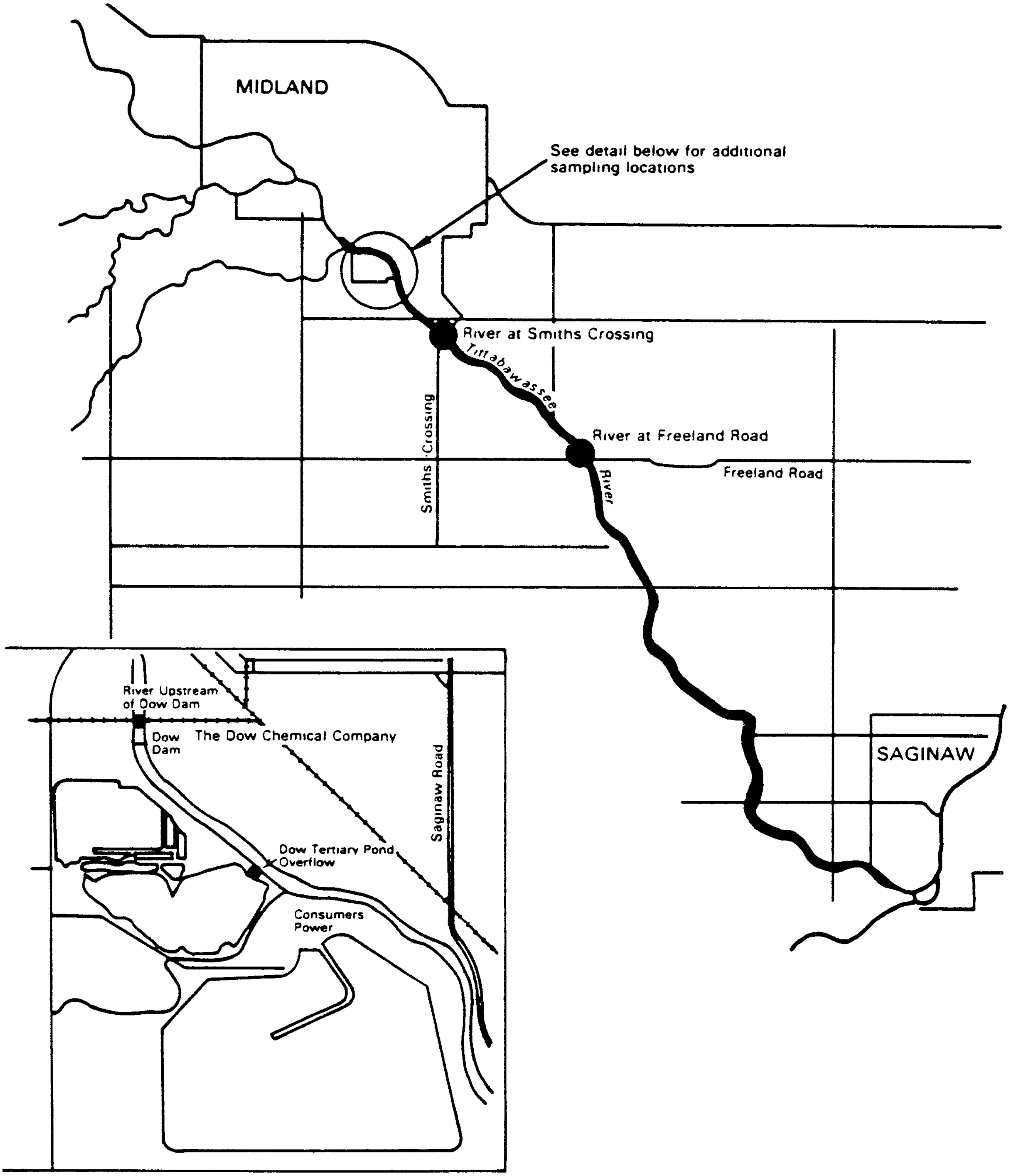


Table 21

1978 USEPA Dioxin Study
Tittabawassee River - Dow Chemical - Midland Plant
Large Volume Activated Carbon Samples

Sample No.	Sample Site	Volume of Water Sampled	Analytical Results 2378-TCDD	
EA06S01	Dow Chemical-Outfall 031	3900 liters	--	Note 1
EA06S02		3100	NA	Note 2
EA06S03		4600	ND	Notes 3 and 4
EA06S04	Tittabawassee River upstream	5800	ND	Note 3
EA06S05	of Dow Dam at Dow Bridge	3100	NA	
EA06S06	Tittabawassee River near	1400	NA	
EA06S07	Smith's Crossing Road	1100	NA	
EA06S08	Tittabawassee River at	5000	NA	
EA06S09	Freeland Road	4300	NA	
EA06S10	Blank Carbon No. 1	--	--	Note 1
EA06S11	Blank Carbon No. 2	--	NA	

<u>Notes</u>:

(1) Samples EA06S01 (Dow Chemical-Outfall 031) and EA06S10 (Blank Carbon No. 1) were provided to Dow Chemical for comparative analyses. Analytical results were not received from Dow Chemical for these samples.

(2) NA - Not analyzed.

(3) ND - Not detected; detection levels of ^{35}Cl-TCDD reported as 2.0 parts per quadrillion (10^{15}) for sample EA06S03 and 50 parts per quintillion for sample EA06S04. The detection limits are based upon theoretical 100% collection and extraction efficiency.

(4) Three TCDD isomers were detected in sample EA06S03 (Dow Chemical effluent).

(5) The collection and analytical extraction efficiencies of the carbon filters for 2378-TCDD had not been determined at the time of the 1978 study.

conduct solvent extraction on the entire volume of sample collected at each site and perform HRGC/HRMS analyses on each extract. However, Battelle extracted only one portion of the 24-hour composite sample. After the results were reported, Region V could not arrange for confirmatory analyses on the same samples analyzed by Battelle because of insufficient extract volume remaining from the Battelle analyses. Consequently, Region V made arrangements for extraction of the remaining sample at USEPA's Pesticide Monitoring Laboratory at Bay St. Louis, Mississippi, and analyses of the extracts by USEPA's Environmental Monitoring Systems Laboratoy (EMSL) at Research Triangle Park, North Carolina. Unfortunately, because Battelle did not extract the entire volume of sample obtained at each site, subsequent analyses by USEPA-EMSL were not conducted on the same samples analyzed by Battelle. Thus, the Battelle and USEPA-EMSL data presented in Table 22 are not fully comparable.

Based upon the quality control work completed for the Battelle analyses, including the USEPA-EMSL analyses, the data reported at Battelle for PCDDs are considered tentative. Due to the presence of chlorinated diphenyl ethers, as determined by USEPA-EMSL in the remaining sample volumes, the Battelle results for PCDFs are not considered valid and have not been reported in Table 22. Based upon the quality control work completed for the USEPA-EMSL analyses, those results for PCDDs are considered valid. EMSL qualified the PCDF data as tentative without confirmation by a second laboratory. Dow Chemical was provided split samples for this study along with the extraction and analytical protocols. Analytical results for the split samples were not received from Dow Chemical.

Although the data presented in Table 22 have limitations as described above, they do provide a clear indication that Dow Chemical was discharging PCDDs and PCDFs to the Tittabawassee River. The Lake Huron and Tittabawassee River water intakes had no detectable PCDDs or PCDFs, while the discharge from outfall 031 was found to contain 2378-TCDD at 50 ppq (Battelle's analysis), and 1368-TCDD (144 ppq) and 1379-TCDD (29 ppq) by EMSL. HxCDDs, OCDDs, TCDFs, HpCDFs, and OCDFs were also found in the discharge by EMSL. The Tittabawasee River downstream from outfall 031 was also found to be contaminated with PCDDS and PCDFs. 2378-TCDD was identified at 39 ppq by USEPA, along with higher levels of higher chlorinated PCDDs and PCDFs than found in outfall 031. OCDD was found in the discharge from outfall 005 at 228 ppq, most likely the result of ash handling operations from the powerhouse. The 1981 data reported for outfall 031 from EMSL are consistent with data reported by USEPA for samples obtained in 1984 and subsequent analyses reported by Dow Chemical.

Table 23 presents a summary of data for PCDDs and PCDFs at Dow Chemical water intakes, outfall 031, and the pilot effluent filter discussed earlier. These samples were obtained by USEPA during August and December 1984. The Tittabawassee River intake, located downstream of outfall 005-Powerhouse Ash Pond, did not contain any 2378-TCDD or 2378-TCDF but was found to contain 43 ppq of other TCDFs and nearly 200 ppq of OCDD. The ash pond discharge is the suspected source of this contamination, although other upstream sources cannot be ruled out with these data. Other PCDDs and PCDFs were not found to be present at stated detection levels. The Lake Huron intake was found to be free of all PCDDs and PCDFs at stated detection levels except OCDD which was detected at

Table 22

Large Volume Water Sampling for PCDDs and PCDFs
Dow Chemical - Midland Plant
September 9-10, 1981

Results in parts per quadrillion (ppq)

Sample Location	Lake Huron Water Intake		Tittabawasse River Intake		Outfall 005		Outfall 031		Outfall 031 Plume Mixing Zone		Tittabawassee River Smith's Crossing Road	
Sample Number	81EH07S26		81EH07S13		81EH07S88		81EH07S39		81EH07S53		81EH07S66	
Laboratory	BMI-C	EPA	BMI-C	EPA	BMI-C	EPA	BMI-C	EPA	BMI-C	EPA	BMI-C	EPA
PCDDs												
1368-TCDD	NA	ND (8)	NA	ND (7)	NA	ND (23)	NA	144 (8)	NA	108 (33)	NA	68 (8)
1379-TCDD	NA	ND (8)	NA	ND (7)	NA	ND (8)	NA	29 (8)	NA	33 (8)	NA	ND (8)
2378-TCDD	<10	ND (8)	<10	ND (7)	<120[a]	ND (23)	50	ND (8)	45	ND (9)	<10	39 (8)
Total TCDDs	<10	NA	<10	NA	2300	NA	80	NA	70	NA	40	NA
Total PeCDDs	<20	ND(18)	<20	ND(32)	<20	ND(108)	<20	NA	50	NA	<20	NA
Total HxCDDs	<40	ND(18)	<40	ND(32)	<40	ND(108)	<40	143(21)	<40[a]	ND (32)	<40	ND (20)
Total HpCDDs	<80	ND(37)	<80[a]	ND(60)	<80	ND (62)	<80	ND(99)	<80[a]	ND (72)	<80	504(102)
OCDD	<100[a]	ND(72)	<100[a]	ND(60)	<100	228 (62)	<100	543(99)	<100[a]	300(154)	<100	2700(102)
PCDFs												
2378-TCDF	NV	ND (3)	NV	ND (8)	NV	ND (20)	NV	ND(11)	NV	ND (20)	NV	ND (16)
Total TCDFs	NV	ND (7)	NV	NA	NV	NA	NV	50 to 2000[c]	NV	50 to 2000[c]	NV	50 to 2000[c]
Total PeCDFs	NV	NA	NV	NA	NV	NA	NV	NA	NV	NA	NV	NA
Total HxCDFs	NV	NA	NV	NA	NV	NA	NV	NA	NV	NA	NV	NA
Total HpCDFs	NV	ND(43)	NV	ND(54)	NV	ND (55)	NV	453(55)	NV	ND (55)	NV	937 (47)
OCDF	NV	ND(53)	NV	ND(54)	NV	ND (53)	NV	254(55)	NV	ND (55)	NV	814 (47)

Notes: (1) Laboratories - BMI-C - Battelle Columbus Laboratories, Columbus, Ohio (formerly Battelle Memorial Institute).
EPA - Environmental Protection Agency EMSL, Research Triangle Park, North Carolina.

(2) a - BMI-C reported a positive response below the contract detection level.
b - Elevated detection level for 2378-TCDD ascribed by BMI-C to high levels of other TCDDs.
c - Presence and concentration of TCDF isomers considered tentative by EMSL without confirmation by second analytical laboratory.

(3) ND - Not detected at stated detection levels, ( ).
NA - Not analyzed
NV - BMI-C data for PCDFs not valid due to presence of chlorinated diphenylethers.

(4) BMI-C and EMSL analyzed different portions of 24-hour composite samples. The analytical results presented in this table are not split sample results. See text for discussion.

Table 23

PCDDs And PCDFs
Water Intakes, Outfall 031, Pilot Plant Filter
Dow Chemical - Midland Plant

Results in parts per quadrillion (ppq)

	Water Intakes August 28-29, 1984		Outfall 031		Pilot Plant Effluent	%
	Tittabawassee River	Lake Huron	August 28-29, 1984	December 4, 1984	December 4, 1984	Removal
2378-TCDD	ND (22)	ND (45)	ND (50)	ND (9)[a]	ND (8)[a]	--
Total Tetra CDDS	ND (12)	ND (15)	ND (35)	2000	69	97
Total Penta CDDs	ND(120)	ND(150)	ND(126)	350	ND(17)	100
Total Hexa CDDs	ND (46)	ND (57)	ND (82)	180	180[b]	--
Total Hepta CDDs	ND (81)	ND(158)	ND(191)	1400	280[b]	--
OCDD	188	305	ND(333)	5400	790[b]	--
2378-TCDF	ND (22)	ND (29)	ND (56)	ND (9)[a]	ND (7)	--
Total Tetra CDFs	43	ND (13)	3940	12000	1500	88
Total Penta CDFs	ND (51)	ND (51)	ND (46)	1700	ND(33)	100
Total Hexa CDFs	ND (36)	ND (43)	ND (79)	1500	ND(15)	100
Total Hepta CDFs	ND (54)	ND(104)	ND (84)	7400	86	99
OCDF	ND(175)	ND(126)	ND(209)	6600	440[b]	--

Notes: (1) Samples obtained on August 28-29, 1984, were 24-hour composite samples.
(2) Samples obtained on December 4, 1984, were grab samples.
(3) a = Data for 2378-TCDD and 2378-TCDF were generated 3/1/85 using a Gometer SP 2330 column.
(4) b = Possible carryover from previous injection of analytical standard.
(5) ( ) = Detection level.

about 300 ppq. This level would not be of concern from a public health standpoint. OCDD is relatively nontoxic compared to 2378-TCDD and other PCDDs. The presence of OCDD in this sample may be due to laboratory-induced contamination since OCDD is particularly difficult to clean from laboratory apparatus. 2378-TCDD and other PCDDs were not detected in the discharge from outfall 031 during the August sampling study at detection levels ranging from 35 ppq (TCDDs) to 333 ppq (OCDD). (Dow Chemical measured 2378-TCDD during August 1984 at 3.1 and 3.7 ppq). TCDFs were found at 3900 ppq. 2378-TCDF and other PCDFs were not detected at detection levels ranging from 46 ppq (PeCDF) to 209 ppq (OCDF).

In December 1984, Region V obtained grab samples at the influent and effluent of the pilot filter plant operated by Dow Chemical on the discharge from outfall 031. These samples were obtained to further characterize the discharge from outfall 031 for PCDDs and PCDFs and to obtain a rough assessment of the expected performance for the full-scale filter system. The pilot plant influent sample is listed as the December 4, 1984, outfall 031 effluent sample in Table 23. 2378-TCDD and 2378-TCDF were not detected in the influent or effluent samples at detection levels ranging from 7 to 9 ppq. (Dow Chemical reported the 2378-TCDD concentration in outfall 031 as 5 ppq for a sample obtained on December 4, 1984). The outfall 031 sample was found to contain relatively high levels of other PCDDs and PCDFs. Despite some analytical interferences for the pilot plant effluent sample, these limited data and the data presented in Table 25 indicate the filter system should remove about 90% of the PCDDs and PCDFs present in the outfall 031 discharge. The rate of removal for PeCDDs, TCDFs, PeCDFs, HxCDFs, HpCDFs, and OCDF as determined by the USEPA monitoring is about the same as that determined from the USEPA and Dow data for TCDDs. Dow Chemical does not routinely report data for any PeCDDs nor TCDFs (other than 2378-TCDF) or HxCDFs, HpCDFs, or OCDF. Further characterization of the full-scale filter system now in operation should be conducted to assess the residual loadings of PCDDs and PCDFs to the Tittabawassee River. As shown below, Dow Chemical has characterized the full-scale filter operation for 2378-TCDD for the brief period of time the filter has been operated.

As part of its point source study of dioxin at the Midland plant 4/, Dow Chemical conducted several measurements of PCDDs for outfall 031. Table 24 presents isomer-specific analyses of TCDDs for two samples conducted in 1983 and 2378-TCDD data for a third sample collected in early 1984. These samples were obtained at outfall 031 prior to installation of the full-scale filter system. Although the concentration of the sum of all TCDDs in each sample varied (about 600 ppq vs 1600 ppq), the distribution of TCDDs remained about the same. 1368-TCDD and 1379-TCDD were predominant. This is also true of other data obtained at outfall 031 by Dow Chemical during pilot filtration studies in March 1984. These data are presented in Table 25 along with data for 2378-TCDF and higher chlorinated PCDDs. The 1368-TCDD and 1379-TCDD isomers were the predominant TCDDs found in all of the effluent samples. These isomers are often associated with combustion operations and the manufacture of 2,4-D. 12/ The sum of the TCDDs in these sample generally exceeds the sum of the higher chlorinated HxCDDs, HpCDDs, and even OCDD. This is not the case in most environmental samples where HpCDDs and OCDD are generally found at much higher levels than TCDDs. The tertiary pond sediments exhibited the latter, more common environmental pattern.

Table 24

Dow Chemical Effluent Monitoring
Tetrachloro Dibenzo-p-Dioxins

Outfall 031

Sample Date:	April 4, 1983			May 13, 1983		
Species Monitored	Concentration			Concentration		
	ppq	(LOD)	Relative %	ppq	(LOD)	Relative %
1469.TCDD	N	(6.0)	N	N	(3.0)	N
1269.TCDD	N	(6.0)	N	N	(3.0)	N
1267.TCDD	N	(6.0)	N	N	(3.0)	N
1289.TCDD	N	(6.0)	N	N	(3.0)	N
1369.TCDD	11.0	(6.0)	0.7	4.0	(2.0)	0.7
1247+1248.TCDD	67.0	(_)	4.2	22.0	(_)	3.7
1278.TCDD	12.0	(6.0)	0.8	N	(3.0)	N
1268.TCDD	11.0	(6.0)	0.7	3.0	(2.0)	0.5
1237+1238.TCDD	360.0	(_)	22.6	94.0	(_)	15.9
1279.TCDD	9.0	(6.0)	0.6	N	(2.0)	N
1246.TCDD	N	(5.0)	N	3.0	(2.0)	0.5
1478.TCDD	7.0	(5.0)	0.4	N	(2.0)	N
1236.TCDD	7.0	(5.0)	0.4	N	(2.0)	N
1239.TCDD	N	(5.0)	N	N	(2.0)	N
1249.TCDD	8.0	(5.0)	0.5	2.0	(2.0)	0.3
1368.TCDD	750.0	(_)	47.1	345.0	(_)	58.3
1379.TCDD	270.0	(_)	17.0	97.0	(_)	16.4
1378.TCDD	34.0	(5.0)	2.1	11.0	(3.0)	1.9
1234.TCDD	5.0	(5.0)	0.3	N	(3.0)	N
Total ISO-TCDDS	1551.0		97.5	581.0		98.1
2378.TCDD	40.0	(_)	2.5	11.0	(2.0)	1.9
13C.2378.TCDD Recovery		85%			87%	

Notes: (1) N = Not detected at LOD i.e. 2.5 X peak-to-valley noise.
(2) (_) = Signifies response > = 25 X peak-to-valley noise.
(3) 2378-TCDD was detected at 31 ppq on January 30, 1984.
(4) Analyses completed by Dow Chemical Company.

Table 25

Pilot Plant Filtration Studies
Dow Chemical - Midland Plant
March 1984
PCDDs and 2378-TCDFs

Parts per quadrillion (ppq)

	Outfall 031 Discharge		Pilot Filter Effluent		
Species Monitored	Range	Average	Range	Average	Percent Removal
1469.TCDD	--	ND	--	ND	--
1269.TCDD	ND-3	1	--	ND	--
1267.TCDD	--	ND	--	ND	--
1289.TCDD	--	ND	--	ND	--
1369.TCDD	6-35	16	--	ND	100
1247+1248.TCDD	62-750	337	12-45	29	91
1278.TCDD	5-40	22	ND-4	2	91
1268.TCDD	6-80	36	2-5	4	89
1237+1238.TCDD	1200-14000	6100	200-630	460	92
1279.TCDD	--	ND	--	ND	--
1246.TCDD	ND-8	3	ND-1	ND	--
1478.TCDD	--	--	--	--	--
1236.TCDD	--	ND	--	ND	--
1239.TCDD	ND-21	8	--	ND	100
1249.TCDD	3-12	6	--	ND	100
1368.TCDD	2000-30000	12000	360-1100	853	93
1379.TCDD	1200-18000	7267	220-790	577	92
1378.TCDD	78-1000	416	16-46	34	92
1234.TCDD	2-9	5	--	ND	100
Total ISO-TCDDs	4564-63958	26219	810-2619	1959	93
2378.TCDD	13-76	35	2-5	3	91
2378.TCDF	16-120	54	4-8	6	89
124679+124689.HCDDS	87-580	272	15-40	27	90
123468.HCDD	52-700	307	8-40	23	93
123679+123689.HCDDs	150-1300	577	28-75	48	92
123469.HCDD	--	--	--	--	--
123478.HCDD	35-390	172	ND-15	9	95
123678.HCDD	--	--	--	--	--
123467+123789.HCDDs	19-150	70	ND-10	6	91
Total HCDDs	343-3120	1398	51-180	114	92
1234679.HC7DD	770-4100	1943	96-160	125	94
1234678.HC7DD	690-4800	2150	83-160	118	95
Total H7CDDs	1460-8900	4093	179-320	243	94
OCDD	7800-60000	25633	690-1300	930	96

Note: (1) Analyses completed by Dow Chemical Company.

The above data indicate that the TCDDs, including 2378-TCDD, may be bound to smaller (and lighter) particles that do not settle out as readily in the pond system. Of interest is that the relative distribution of the PCDDs in the filtered and unfiltered samples remains about the same, although the absolute levels in the filtered samples are generally 90 to 95% less than in the unfiltered samples. This suggests that the filter system may not preferentially remove dioxin-containing suspended solids of any given size (or weight) classes. As noted earlier, Dow Chemical reports that much of the dioxins in the outfall 031 discharge prior to filtration can be attributed to fine particulates from the hazardous waste incinerator which pass through the wastewater treatment facilities. 4/ In order to further control the discharge, the company is installing a clarifier for incinerator wastewaters prior to discharge to the biological treatment facility.

Under the terms of NPDES permit MI0000868, Dow Chemical is required to monitor the discharge from outfall 031 for 2378-TCDD twice monthly. 13/ Table 26 presents a summary of Dow Chemical effluent monitoring data for 2378-TCDD for the period July 1984 to March 1986. The monthly average discharge loadings to the Tittabawassee River are displayed in Figure 10 for the period July 1984 to October 1985, which was prior to installation of the final effluent filter. The monthly average discharge ranged from 4.1 to 49.2 x 10^{-7} lbs/day (1.9 to 22.3 x x 10^{-7} kg/day) and averaged 21.9 x 10^{-7} lbs/day (9.9 x 10^{-7} kg/day). There are no apparent seasonal or cyclical trends in the discharge. Limited data obtained after installation of the filter (November 1985-April 1986) indicate the long-term average discharge may be on the order of 7.2 x 10^{-7} lbs/day (3.3 x 10^{-7} kg/day), suggesting a 67% reduction in the discharge loading. The reported 2378-TCDD concentrations for the outfall 031 discharge ranged from 2 to 8 ppq during this period. The final effluent limitation is currently set at 10 ppq. Longer-term dioxin data, including at least one summer and fall season, are necessary to fully characterize the performance of the filter system and a pretreatment system for incinerator wastewaters now being installed by Dow Chemical.

3. Biomonitoring

a. 1981 USEPA Survey

(1) Static Bioassay

Static bioassays, using *Daphnia magna*, were completed on samples obtained on September 15-16, 1981. Samples were obtained from the Dow Chemical Lake Huron and Tittabawassee River intakes and outfall 031. A field blank was also prepared. The bioassay was begun on September 22, 1981, and conducted by the Region V Central Regional Laboratory 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 27.

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

Table 26

2378-TCDD Discharge Loadings
Outfall 031
Dow Chemical - Midland Plant

Month	Average Discharge Flow (MGD)	Average 2378-TCDD Concentration (ppq)	2378-TCDD Discharge Loading (lbs/day)	(kg/day)
Prior to filter installation			x 10^{-7}	
1984 July	19.2	10.5	16.8	7.6
August	13.5	4.5	5.1	2.3
September	21.8	3.4	6.2	2.8
October	22.9	6.2	11.8	5.4
November	17.8	12.5	18.6	8.4
December	19.4	12.5	20.2	9.2
1985 January	22.1	19.0	35.0	15.9
February	17.9	12.5	18.7	8.5
March	21.0	28.0	49.1	22.3
April	24.7	18.5	38.1	17.3
May	16.7	3.0	4.2	1.9
June	21.0	16.5	28.9	13.1
July	16.7	32.0	44.6	20.2
August	21.1	17.0	29.9	13.6
September	27.8	4.5	8.6	3.9
October	20.3	8.9	15.1	6.8
Mean	20.2	13.1	21.9	9.9
After filter installation				
November	17.3	2.0	2.9	1.3
December	26.2	3.5	7.7	3.5
1986 January	19.4	5.5	8.9	4.0
February	18.0	8.0	12.0	5.5
March	19.5	3.5	5.7	2.6
April	19.4	4.0	6.5	2.9
Mean	19.8	4.4	7.3	3.3

Notes: (1) Average monthly discharge flow based upon daily measurements.
(2) Average 2378-TCDD concentration based upon two measurements per month.

Figure 10

Dow Chemical - Midland Plant
2378-TCDD Discharges
July 1984 - April 1986

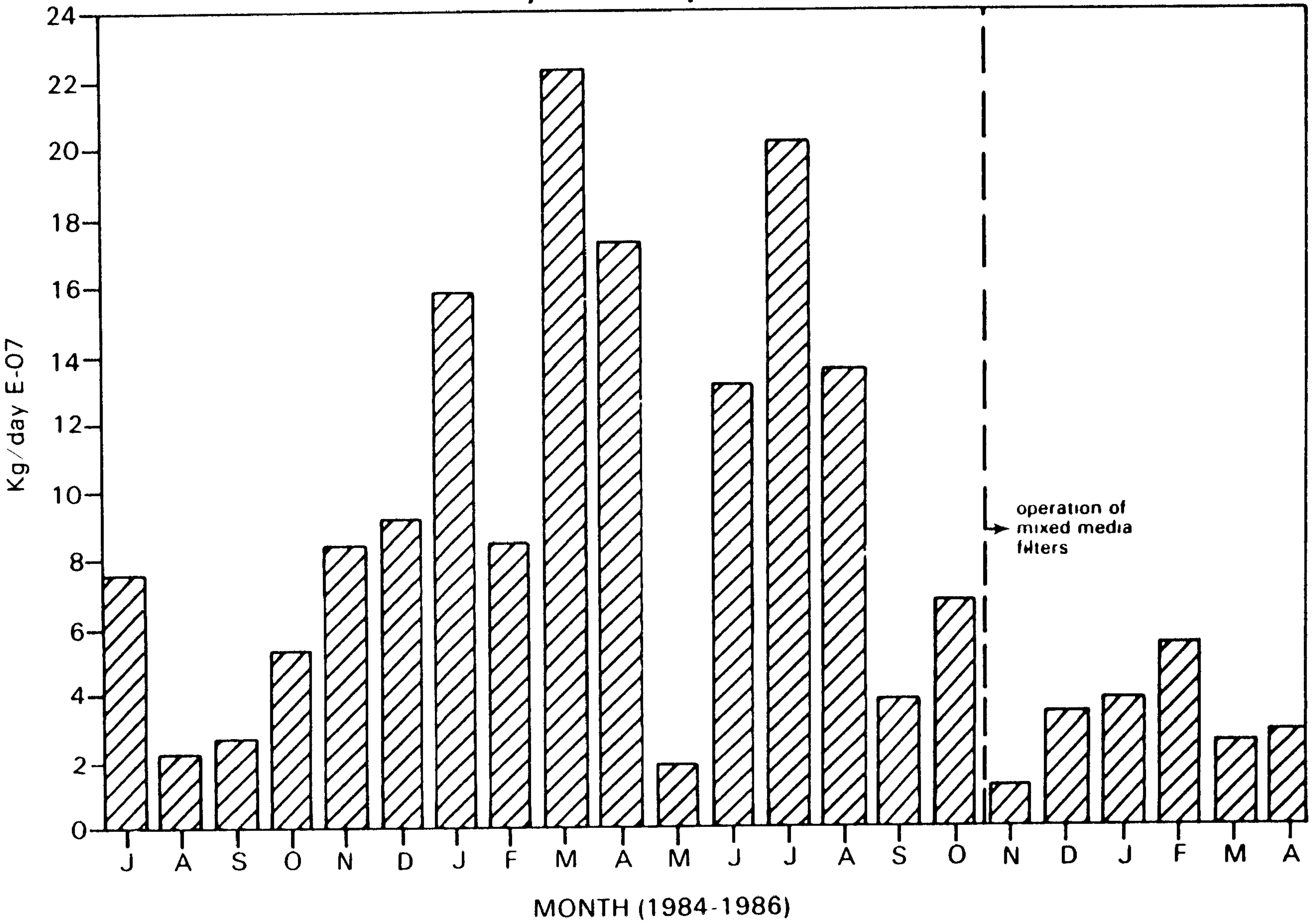


Table 27

Dow Chemical - Midland Plant
Static Daphnia Bioassays
September 15-16, 1981

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

by Dow Chemical at its lake pumping station. This result would be common for testing of public water supplies where chlorine was not removed. 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 28.

Table 28
Dow Chemical - Midland Plant
Static Algal Assay

September 15-16, 1981

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 effect is attributed to the levels 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 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 activated (RLEA) test for five bacteria test strains. No mutagenic activity was found in either the direct or the RLEA test.

b. Dow Chemical NPDES Monitoring

Special Condition 10 of NPDES permit MI0000868 required that Dow Chemical determine chronic toxicity of the effluent from outfall 031 to Daphnia magna and rainbow trout or the fathead minnow. 13/ Dow Chemical conducted acute and chronic flow through studies with Daphnia magna and fathead minnows under a protocol approved by the MDNR as provided for in NPDES permit MI0000868. The 48-hour acute and 21-day chronic flow-through Daphnia magna studies and the 96-hour acute and 31-day embryo-larval fathead minnow tests were conducted in January 1986 using outfall 031 effluent. The test water was again filtered in the laboratory through a 25 micron filter prior to contact with the test organisims. 14/ Note that as of January 1986, the full-scale final effluent filtration system was in operation. Thus, the test water was filtered twice-once in the field and once in the laboratory. The extent to which the test organisms in either test were exposed to chemical components typically present in the discharge is not known. Chemical characterizations of the outfall 031 effluent and the test waters were not presented with either test report. 15,16/

The results of the acute and chronic toxicity studies, as reported by Dow Chemical, are presented below:

Daphnia magna

1. Acute toxicity	
48-hour LC50 (95% C.I.)	40% (33.3-46.7%) tertiary effluent
2. Chronic toxicity	
MATC	24.3%<MATC<52.8% tertiary effluent
MATC (geometric mean)	35.8% tertiary effluent

The MATC is the hypothetical toxic threshold concentration falling between the highest test concentration (concentration of outfall 031 effluent) showing no effect and the next higher test concentration exhibiting an effect when compared to controls. Dow Chemical reported that mortality was the most sensitive endpoint during the chronic test and that all mortality occurred during the first 48 hours of exposure. The company attributes observed mortality to salinity concentrations in the test waters. The total salinity for a 100% effluent sample was estimated to be about 4000 mg/l. Note that no mortality was observed in Region V's 1981 static Daphnia bioassay for the outfall 031 effluent. At that time, the salinity (total dissolved solids) loading of the discharge was about the same as it is now in terms of mass discharge, but about 40% less in terms of concentration due to a substantially higher effluent flow at the time of the 1981 USEPA study.

Dow Chemical conducted a 96-hour acute toxicity test using fathead minnows (Pimephelas Promelas Rafinesque) as well as a 31-day embro-larval chronic test. The company reported that the effluent was not acutely toxic to the fathead minnow (no mortality in 100% test water) and that no concentration related effects on hatchability of embryos and normal larvae at hatch were observed. However, survival was reported to drop precipitously after six days of exposure, with no survival beyond 13 days. The results are summarized below:

Pimepheleas Promelas

1. Acute toxicity
   48-hour LC50 — no toxicity

2. Chronic toxicity (embryo-larval test)
   MATC — 15.9%<MATC<29.6% tertiary effluent
   MATC (geometric mean) — 21.7% tertiary effluent

Dow Chemical did not explain the chronic toxicity observed in this test. At this writing, the Michigan Department of Natural Resources, is reviewing the test results to determine whether whole effluent toxicity effluent limitations or additional water quality-based effluent limitations for outfall 031 are appropriate. 17/

C. River Sediment Surveys

USEPA Region V conducted river sediment surveys in 1978, 1981, and 1984. Figures 11 and 12 presents the approximate locations of the sampling stations for each survey. The 1978 survey included analyses for TCDDs; the 1981 survey focused on toxic organic pollutants other than dioxins and furans; and the 1984 survey included analyses of river sediments and a limited number of Tittabawassee River flood plain samples for PCDDs, PCDFs, and other toxic organic pollutants.

1. 1978 USEPA Sediment Survey (Appendix C-1)

The first USEPA river sediment survey was conducted in October 1978 after Dow Chemical notified the Michigan Department of Public Health that it had found dioxin in native fish from the Tittabawassee River. The goals of that survey were to determine whether dioxins had concentrated in Tittabawassee and Saginaw River sediments and whether the Dow Chemical - Midland Plant was a likely source of the contamination. Sediment grab samples were obtained from the Tittabawassee River upstream of the Dow dam, downstream to the Saginaw River near Bay City. At the same time samples of Dow Chemical wastewater treatment sludges and wastewaters were also obtained. Those data were reviewed in Section B. The 1978 sediment data are presented in Table 29. Note that the results are for total tetrachlorodibenzo-p-dioxins (TCDDs). At the time the study was conducted USEPA's analytical consultant, Department of Chemistry at the University of Nebraska-Lincoln, could not conduct isomer-specific analyses for 2378-TCDD or other TCDDs using then available analytical methods.

The data show no detectable TCDDs in Tittabawassee and Saginaw River sediments at detection limits generally less than 50 parts per trillion (ppt). However, for four of six Tittabawassee and Saginaw River sediment samples collected downstream of Dow Chemical, instrument signals characteristic of TCDDs were observed, but not in correct ratios for confirmation of TCDDs. Dow Chemical

Figure 11

Location Map
USEPA River Sediment Sampling Surveys
1978 - 1984

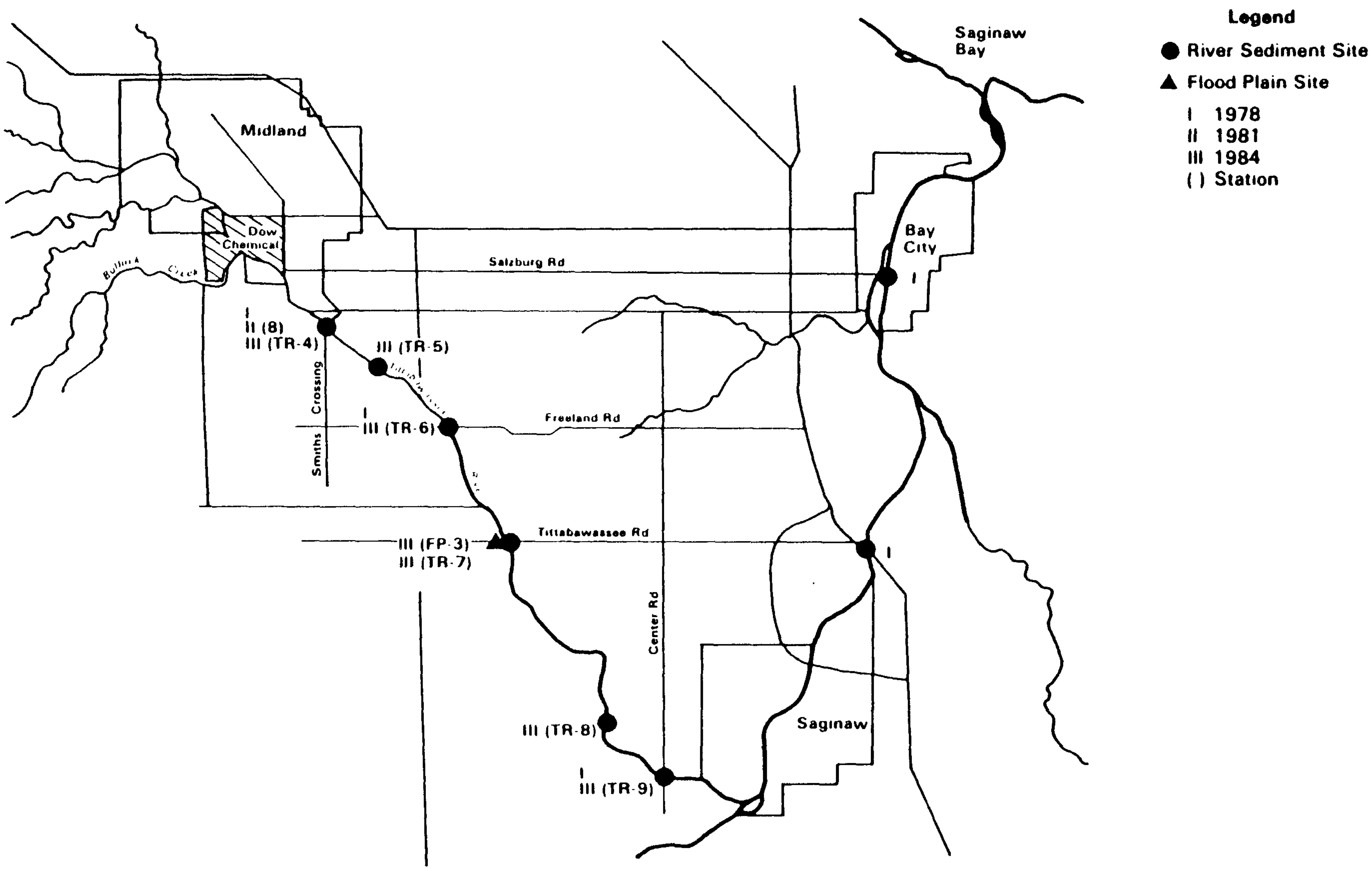


Figure 12

Location Map
USEPA River Sediment Sampling Surveys
1978 - 1984
(Dow Chemical - Midland Plant Area)

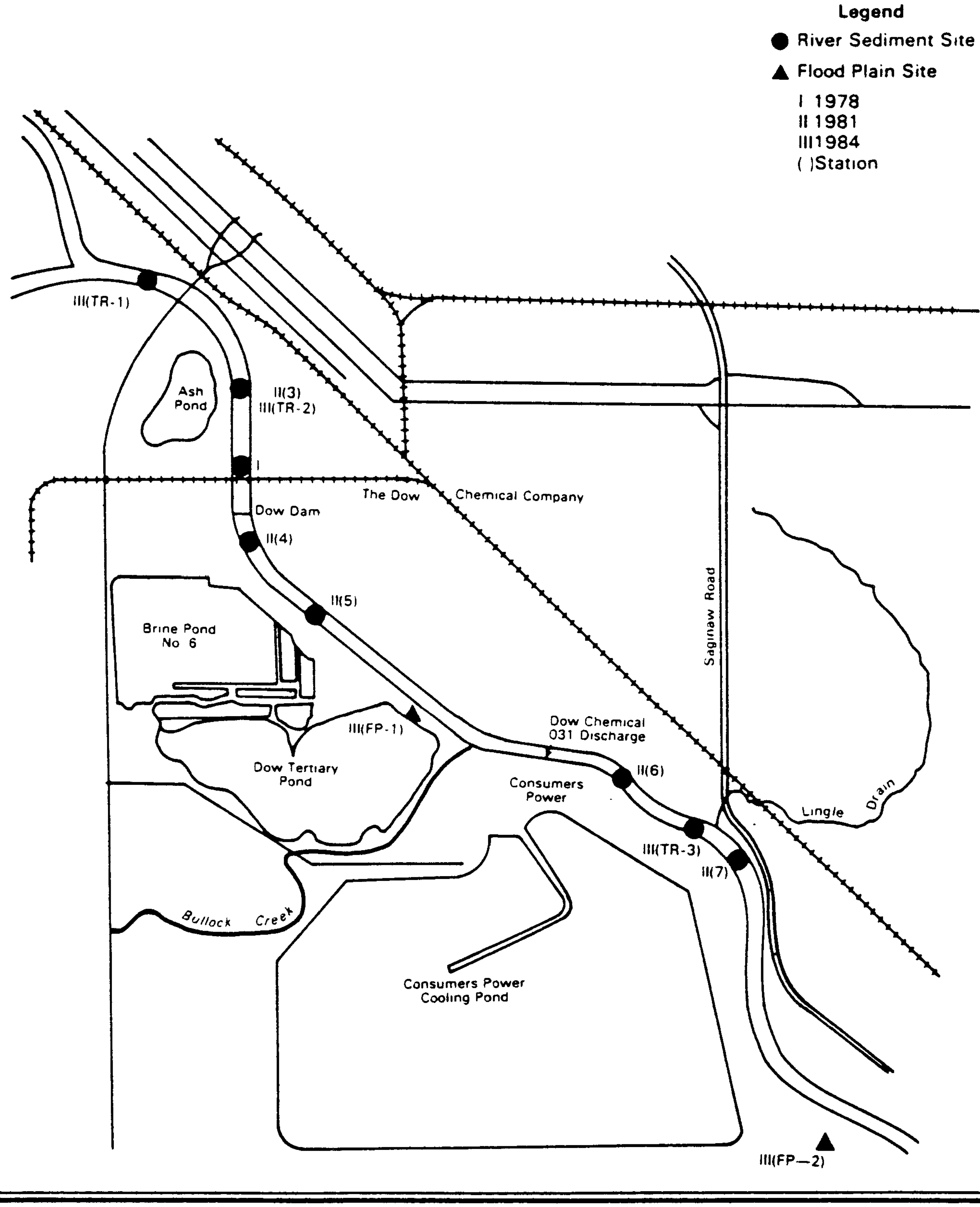


TABLE 29

1978 USEPA SEDIMENT SURVEY
TITTABAWASSEE AND SAGINAW RIVERS
OCTOBER 1978

USEPA-Region V Sample Number	UNL Number	Sample Site	TCDDs (ppt)	DL	Analyst Notes
EA06S12	UN159	Tittabawassee River - Dow Chemical Bridge Upstream of Dow Dam	ND	(19)	
EA06S13A	UN160	Tittabawassee River - near Smith's Crossing Road	ND	(8)	
EA06S13B	UN161	Tittabawassee River - near Smith's Crossing Road	ND	(41)	
EA06S14	UN162	Tittabawassee River - at Freeland Road	ND	(12)	Peak observed at M/Z 320 and 322, but isotope ratio incorrect for positive identification.
EA06S15	UN163	Tittabawassee River - at Center Road Upstream from Saginaw	ND	(680)	" " " " " " "
EA06S16	UN164	Saginaw River - I-75 at Zilwaukee	ND	(48)	" " " " " " "
EA06S17	UN165	Saginaw River - Salzburg Road at Bay City	ND	(10)	" " " " " " "

NOTES: (1) Samples were analyzed by Department of Chemistry, University of Nebraska-Lincoln.
(2) Analyses are for total tetrachlorodibenzo-p-dioxins.

wastewater treatment system sludges were found to contain TCDDs at concentrations ranging from barely detected at 8 ppt to 5800 ppt (Table 13). One internal plant untreated wastewater was found to contain TCDDs at 0.38 ppt. While TCDDs were found in untreated wastewaters and treatment plant sludges inside the Dow Chemical - Midland Plant, TCDDs could not be confirmed in river sediments downstream from the plant at that time.

2. 1981 USEPA Sediment Survey (Appendix C-2)

The 1981 sediment survey encompassed an area of the Tittabawassee River from 0.5 miles upstream of State Route M-20 downstream to Smith's Crossing Road. River sediment grab samples were obtained on March 18-19, 1981, for analysis at eight locations shown on Figures 11 and 12. Each sediment sampling site is described in Appendix C-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 positive findings presented in Table 30 show that many of the compounds either positively or tentatively identified were substituted benzenes or their 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. Most of the compounds detected were found at concentrations in the low or sub parts per million range (mg/kg). Only one compound, di-n-octylphthalate, was identified upstream of the Dow dam. Several unidentified compounds were detected in some of the sediment samples. As noted above, the sediment samples were not analyzed for PCDDs or PCDFs.

3. 1984 USEPA Sediment Survey (Appendix C-3)

The primary objectives of the 1984 sediment survey were to determine ambient levels of PCDDs, PCDFs, and other toxic organic pollutants at selected Tittabawassee River and flood plain sites; to determine the extent of PCDD and PCDF contamination in Tittabawassee River sediments; and to determine whether the distribution of PCDDs and PCDFs in river sediments and flood plain samples matched the distribution in Dow Chemical tertiary pond sediments and wastewater samples. Nine Tittabawassee River sediment samples and three flood plain samples were collected on July 25 and 27, 1984. The samples were collected from about 0.2 miles downstream from the confluence of the Chippewa River with the Tittabawassee River, to Center Road near the city of Saginaw. Approximate sampling locations are shown on Figures 11 and 12. Descriptions of the sampling sites and sampling methods are presented in Appendix C-2 along with the complete analytical results. Toxic metals data for these samples are also presented in Appendix C-3. Positive findings are reviewed below.

The data for toxic organic pollutants are summarized in Table 31. The findings are consistent with data collected in 1981. Relatively few toxic organic pollutants were found in any of the sediment or flood plain samples collected. The presence of methylene chloride at low levels in most of the samples may be attributable to field or laboratory operations. Methylene

TABLE 30

1981 USEPA SEDIMENT SURVEY
TITTABAWASSEE RIVER
MARCH 1981

mg/kg (parts per million)

Station:	3	4	5	6	7	8
Location:	Titt. River Above Dow Dam	Titt. River Below H Flume	Titt. River Near #6 Brine Pond	Titt. River Below Bullock Creek	Titt. River Below Lingle Drain	Titt. River Above Smith's Crossing
Sample Number:	EH03S02	EH03S03	EH03S04	EH03S05	EH03S06	EH03S07
Base/Neutral & Acid Pollutants						
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
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
Di-n-octylphthalate	2.1	2.0	8.4	5.3	9.2	23.0
Volatile Pollutants						
Chlorobenzene	-	-	-	-	-	0.0038
Tentatively Identified Pollutants						
Hydrocarbons (9)	1.0	-	-	-	-	-
Sulfur (S8)	1.4	-	-	-	1.5	-
1,7,7-trimethyl-bicyclo [2.2.1] heptan-2-one	-	-	0.2	-	-	-

NOTES: (1) < = Not detected at specified detection limit.

TABLE 30 (continued)

mg/kg (parts per million)

Station:	3	4	5	6	7	8
Location:	Titt. River Above Dow Dam	Titt. River Below H Flume	Titt. River Near #6 Brine Pond	Titt. River Below Bullock Creek	Titt. River Below Lingle Drain	Titt. River Above Smith's Crossing
Sample Number:	EH03S02	EH03S03	EH03S04	EH03S05	EH03S06	EH03S07
Tentatively Identified Pollutants						
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	-
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

TABLE 31

1984 USEPA SEDIMENT SURVEY
TITTABAWASSEE RIVER SEDIMENTS AND FLOOD PLAIN
TOXIC ORGANIC POLLUTANTS
JULY 1984
ppb (ug/kg)

Station Number:	TR-1	TR-2	TR-3	FP-1	TR-4	FP-2	TR-5	TR-6	TR-7	FP-3	TR-8	TR-9
Location:	Above Ash Pond	Below Ash Pond	Above Lingle Drain	Flood Plain @ T. Pond	Smith's Crossing Bridge	Flood Plain @ White & Debolt	Upstream of Brown Mills	Free-land	Titta. Road	Flood Plain @ Titta. Road	Gratiot Road	Center Road
Benzene	--	--	--	--	--	--	--	--	--	<5	--	--
Methylene chloride*	2400	32	29	85	17	--	46	16	57	9500	40	99
Toluene	5.2	--	--	--	--	--	--	--	--	--	--	--
Xylenes	--	--	--	--	--	--	--	--	--	<5	--	--
Bis(2-ethylhexyl)phthalate*	870	--	--	--	--	--	--	--	--	<10	--	<10
Di-n-butyl phthalate*	<10	--	--	--	--	--	--	--	--	--	--	--
Di-n-octyl phthalate*	--	--	840	450	--	3100	--	--	--	--	--	--
Diethyl phthalate*	--	--	--	--	--	--	--	--	<10	--	--	<10
4,4'-DDT	14	17	8.3	6.6	--	--	--	--	--	31	--	--
4,4'-DDE	20	19	19	--	12	88	--	--	--	43	--	--
4,4'-DDD	15	14	--	7.3	--	--	--	--	--	13	--	--

Notes: 1. -- = Not detected. (Refer to Appendix C-2 for detection limits.)
2. All other organic priority pollutants not detected.
3. * = Presence may be due to laboratory or field contamination.

chloride is used as a cleaning solvent. The high levels in two samples (2400 ppb above Dow Chemical ash pond, and 9500 ppb flood plain at Tittabawassee Road) are much greater than expected from field or laboratory operations. Findings of methylene chloride at these levels in environmental samples would not be expected. Three pesticide compounds (4,4'-DDT; 4,4'-DDE; and 4,4'-DDD) were found in four river sediment samples and each of the three flood plain samples. The data suggest contributions upstream of the Dow Chemical - Midland Plant as all three compounds were found in samples collected upstream of outfall 031 as well as in the downstream sediments.

Table 32 presents PCDD and PCDF data for the sediment and flood plain samples. The data are graphically displayed in Figures 13 and 14. Sediment results clearly distinguish the Dow Chemical - Midland Plant as the primary source of PCDDs and PCDFs to the Tittabawassee River system. Upstream of the Dow dam only low levels of HpCDDs (0.02-0.11 ppb); OCDD (0.08-0.47 ppb); HpCDFs (0.01-0.06 ppb); and OCDF (0.02-0.17 ppb) were found. Other PCDDs and PCDFs were not detected in these samples at detection levels ranging from 0.01 to 0.03 ppb. The highest levels of PCDDs and PCDFs were found in the sediment and flood plain samples collected near and immediately downstream of the outfall 031 discharge. Concentrations generally decrease with travel downstream. Concentrations of OCDD at Gratiot and Center Roads are about the same as those found in sediments immediately upstream of the Midland plant. HpCDDs were not found in these samples. The levels of HpCDFs and OCDF exhibit the same trend. However, the concentration of TCDFs in the Gratiot Road sample (1.4 ppb) is much higher than in most of the upstream samples. Also, the levels of PCDDs and more notably PCDFs, in the flood plain sample obtained near Tittabawassee Road suggest either a heavy deposition of PCDDs and PCDFs at that point from the Dow Chemical discharge or possibly another point source of PCDFs in that area. Other significant point sources could not be identified in the vicinity of the sampling station. Examination of the distribution of PCDFs in Dow Chemical tertiary pond sediments suggest outfall 031 is the source. Based upon the production history of chlorinated phenols at the Midland plant, it is likely that past discharges may account for these findings.

The sediment and flood plain data indicate that sediment contamination extends from Dow Chemical wastewater discharges downstream to the Gratiot Road to Center Road reach of the river (17.1 to 19.5 miles). Although 2378-TCDD was not detected in any of the river sediment or flood plain samples, based upon Dow Chemical discharge data and historical and current findings in native fish, it is undoubtedly present at levels less than analytical detection levels for this survey (0.01 to 0.03 ppb or 10 to 30 ppt). The river sediment data are not sufficient to determine whether there are highly contaminated areas that may warrant removal.

Table 33 presents a comparison of the distribution of TCDDs in Dow Chemical treatment pond surface sediments, wastewater discharges, and river and flood plain sediments. The data plainly demonstrate a clear pattern. The percent contribution of the 1368- and 1379-TCDD isomers present in treatment pond sediments is mirrored in river and flood plain sediments for the reach of the river most heavily impacted by the Dow Chemical discharge.

TABLE 32

1984 USEPA SEDIMENT SURVEY
TITTABAWASSEE RIVER SEDIMENTS AND FLOOD PLAIN SAMPLES
PCDDs and PCDFs
JULY 1984

Concentrations in parts per billion (ppb).

Station Number:	TR-1	TR-2	TR-3	TR-4	TR-5	TR-6	TR-7	TR-8	TR-9	FP-1	FP-2	FP-3
Location:	Above Ash Pond	Below Ash Pond	Above Lingle Drain	At Smith's Crossing	Upstream of Brown Mill's Run	At Freeland Road	At Titta. Road	At Gratiot Road	At Center Road	At Dow Tertiary Pond	At Waite & Debolt Drain	At Titta. Road
2378-TCDD	ND/0.03	ND/0.01	ND/0.01	ND/0.01	ND/0.01	ND/0.01	ND/0.01	ND/0.02	ND/0.01	ND/.01	ND/.01	ND/.03
Total Tetra CDDs	ND/0.01	ND/0.01	0.15	0.08	0.01	0.02	0.01	ND/0.02	ND/0.01	0.11	0.13	0.36
Total Penta CDDs	ND/0.03	ND/0.01	ND/0.01	0.03	ND/0.01	ND/0.01	ND/0.01	ND/0.05	ND/0.03	0.09	ND/.01	0.12
Total Hexa CDDs	ND/0.03	ND/0.01	0.02	0.11	ND/0.01	0.01	ND/0.01	ND/0.07	ND/0.03	0.14	ND/.01	0.20
Total Hepta CDDs	0.11	0.02	0.29	1.1	0.03	0.05	0.05	ND/0.04	ND/0.04	2.1	0.53	1.3
OCDD	0.47	0.08	1.6	6.8	0.26	0.25	0.46	0.33	0.30	16	3.9	7.8
2378-TCDF	ND/0.03	ND/0.01	0.01	0.10	0.02	0.03	0.02	0.03	ND/0.02	0.02	0.11	2.18
Total Tetra CDFs	ND/0.03	ND/0.01	2.7	0.43	0.19	0.20	0.13	1.4	0.09	1.0	1.5	7.6
Total Penta CDFs	ND/0.03	ND/0.01	0.02	0.20	ND/0.01	0.02	ND/0.01	ND/0.03	ND/0.03	0.10	0.09	4.1
Total Hexa CDFs	ND/0.03	ND/0.01	0.03	0.37	ND/0.01	0.05	0.02	ND/0.03	ND/0.03	0.15	0.04	1.7
Total Hepta CDFs	0.06	0.01	0.16	1.3	0.04	0.07	0.05	ND/0.04	0.03	0.65	0.65	1.9
OCDF	0.17	0.02	0.30	3.0	0.10	0.07	0.12	0.08	0.10	1.3	1.5	2.3

NOTES: (1) Sample analyzed by Brehm Laboratory, Wright State University.
(2) ND - Not detected at stated detection level.
(3) See Figures 11 and 12 for approximate sample locations.
(4) Data for TR-4, TR-5, TR-6 reported on wet weight basis.

Figure 13

PCDDs in Tittabawassee River Sediment and Flood Plain Samples July 1984 USEPA Survey (parts per billion - ppb)

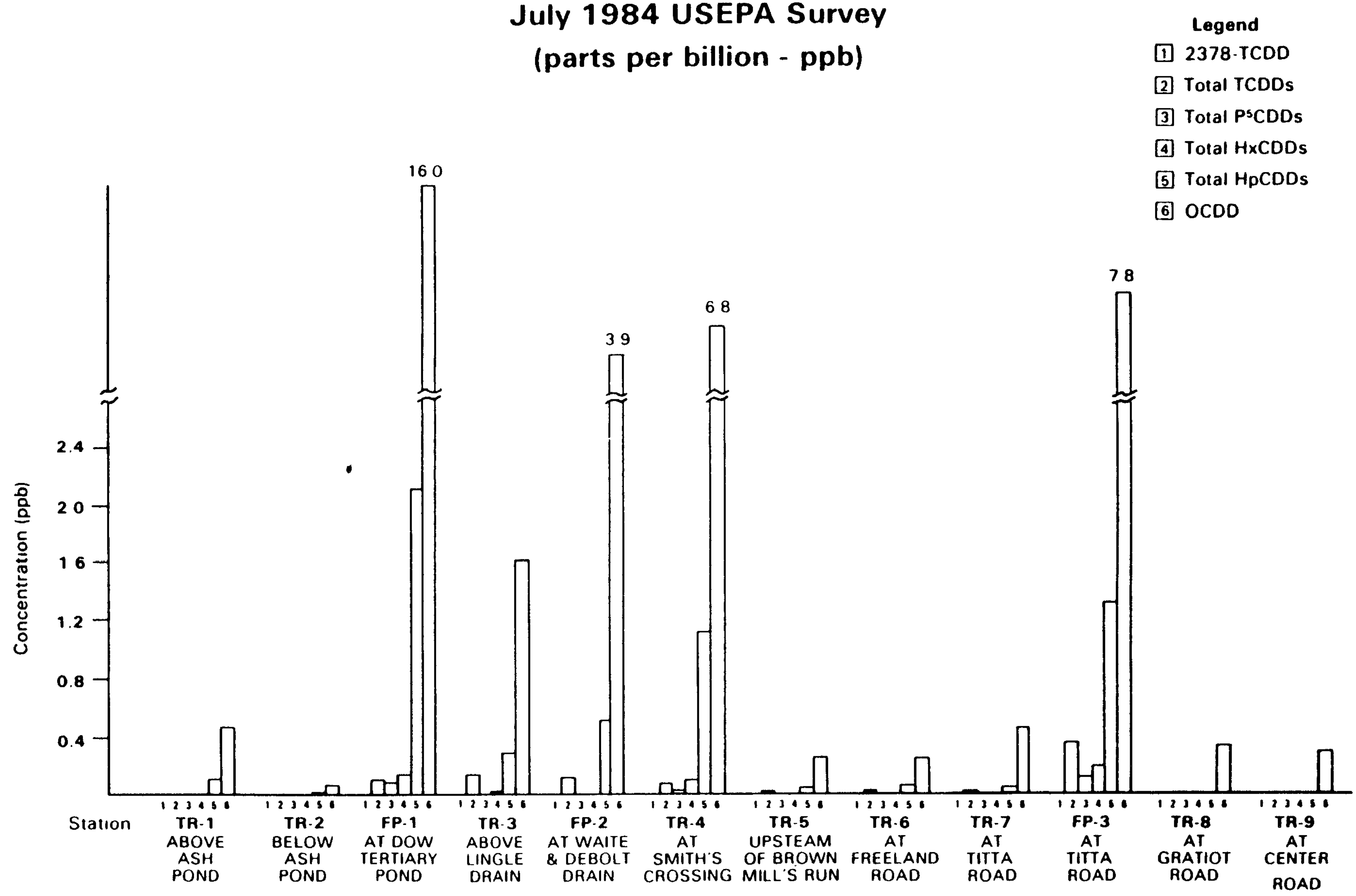


Figure 14

PCDFs in Tittabawassee River Sediment and Flood Plain Samples July 1984 USEPA Survey

(parts per billion - ppb)

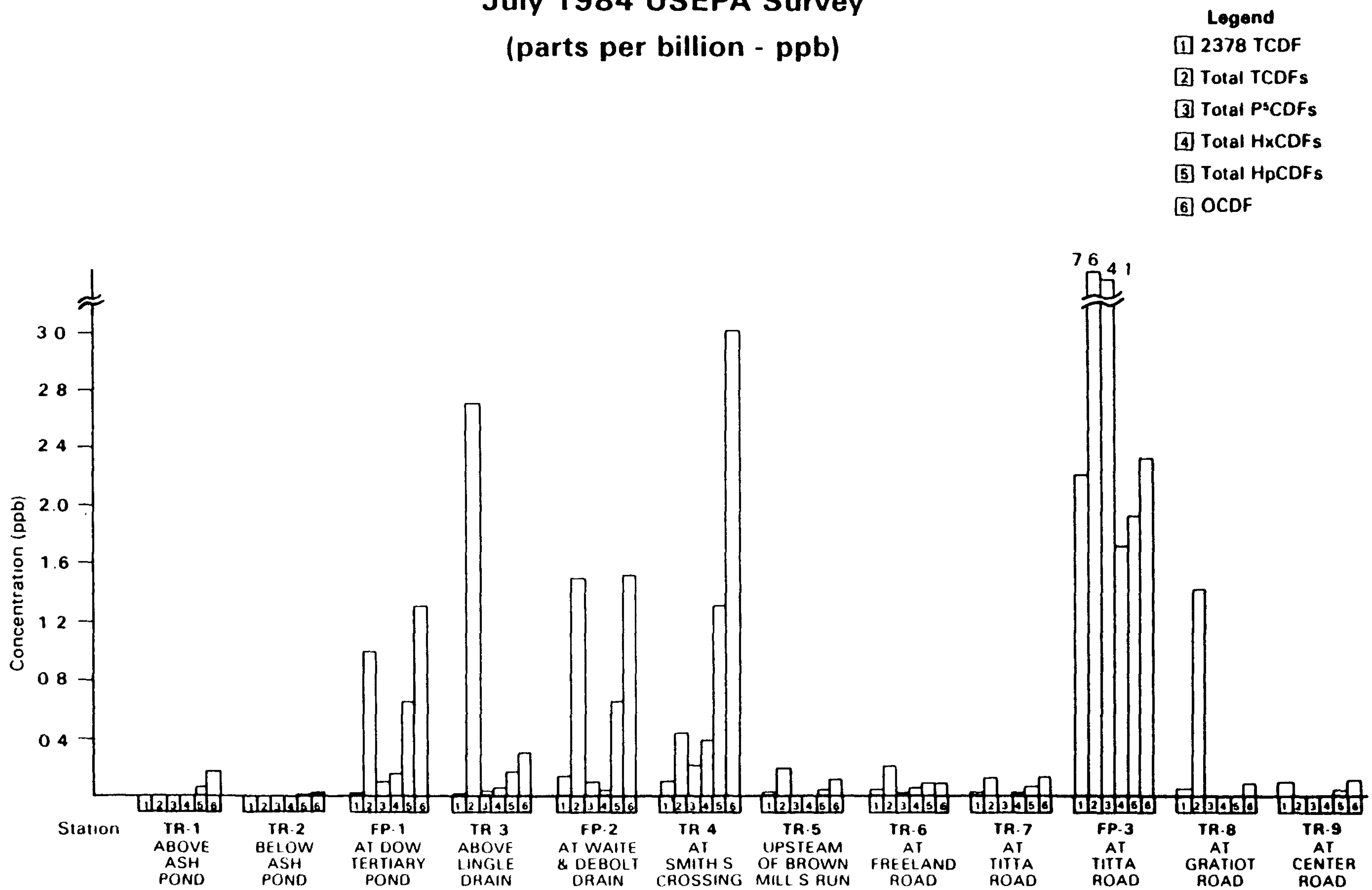


TABLE 33

DISTRIBUTION OF TCDDs
DOW CHEMICAL TREATMENT POND and WASTEWATERS
TITTABAWASSEE RIVER SEDIMENTS and FLOOD PLAIN SAMPLES

	TCDD Isomers (% of Total)				
Treatment Pond Surface Sediments	1368	1379	1237 1238	2378	Other
Primary	51	22	10	9	8
Secondary	44	21	10	14	11
Tertiary	54	19	10	9	8
Wastewater Discharges	49	23	22	1	6
River Sediments					
Upstream of Dow Dam (TR-1, 2)	ND	ND	ND	ND	ND
Dow Dam to Smith's Crossing (TR-3, 4)	58	26	12	ND	4
Smith's Crossing - Tittabawassee Road (TR-5,6,7)	59	20	6	ND	15
Gratiot Road - Center Road (TR-8, 9)	ND	ND	ND	ND	ND
Flood Plain					
Dow Tertiary Pond (FP-1)	49	25	20	ND	7
Waite and Debolt Drain (FP-2)	54	27	19	ND	ND
Tittabawassee Road (FP-3)	57	23	14	ND	6

NOTES: (1) Tertiary pond data are averages for three samples.
(2) Wastewater discharge data are averages for five Dow Chemical samples (see Tables 24 and 25).
(3) River sediment data are averages for listed stations.
(4) ND = Not detected.

The river sediment data for metals presented in Appendix C-2 do not indicate any significant contributions from Dow Chemical operations. Generally, there are no significant differences in concentrations of detected metals between sediments collected upstream and downstream of the Midland plant. Concentrations of several toxic metals (arsenic, beryllium, cadmium, chromium, cobalt, nickel, and zinc) found in flood plain sediments were generally about twice as high as levels found in river sediments. This finding is most likely due to the method and pattern of deposition of these pollutants under high river stage.

D. Bioaccumulation Studies

1. 1981 USEPA-MDNR Study (Appendix D-1)

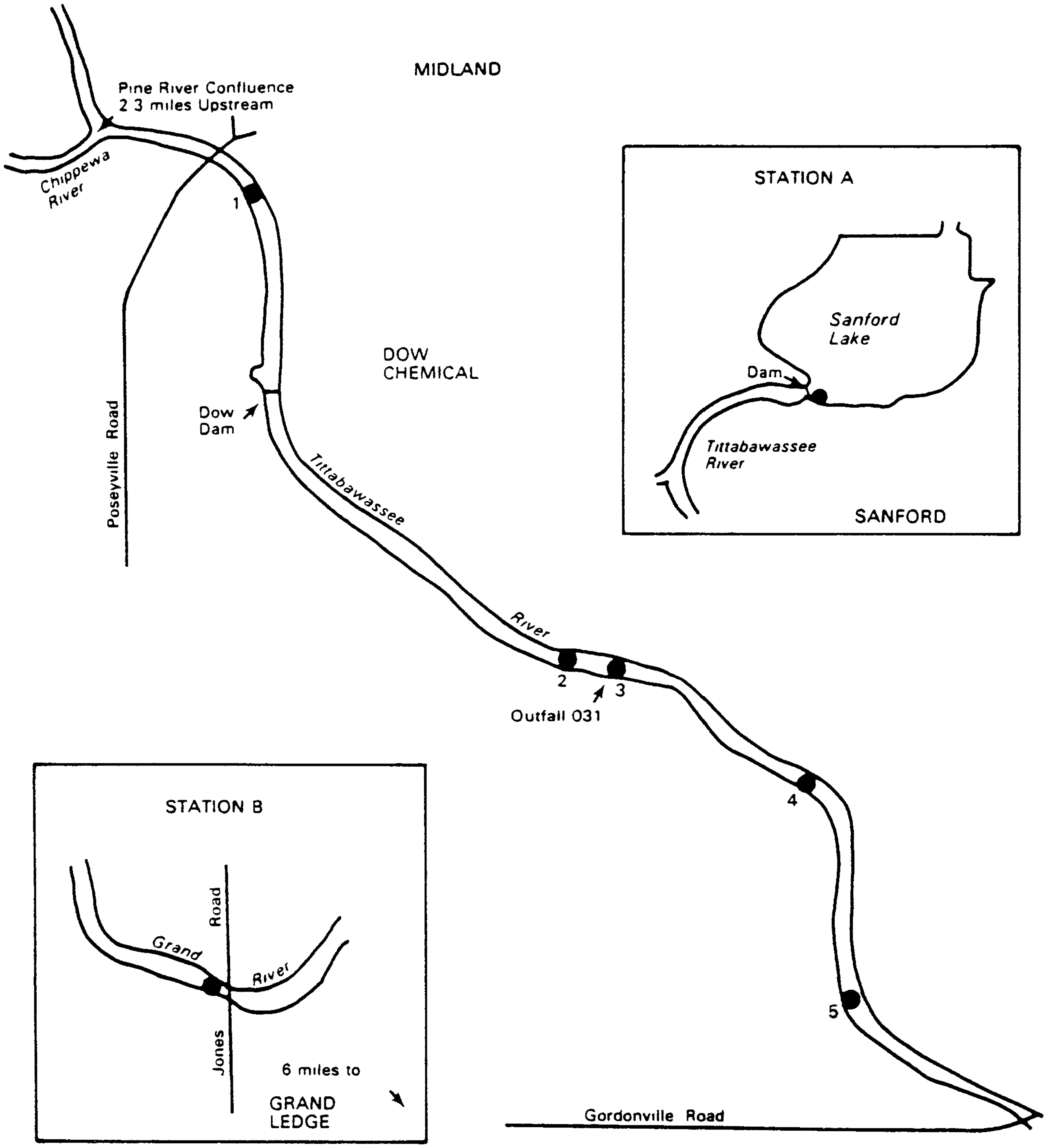
Region V and the Michigan Department of Natural Resources conducted a bioaccumulation study in the Tittabawassee River around the Dow Chemical - Midland Plant during September 1981. The study was conducted to determine which toxic organic pollutants discharged by Dow Chemical bioaccumulate in fish exposed 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 toxic organic compounds. The caged fish were fed during the experiment to maintain body weight and general health. All of the fish were acclimated in a laboratory prior to the study. Caged fish were 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 also placed in the Grand River at Jones Road near Grand Ledge, Michigan, and analyzed along with native fish from the Grand River. The cages were suspended in the water column at each site. Thus, the fish were not exposed to bottom sediments, but were exposed to suspended matter in the water column.

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 prior to discharge from outfall 031, and also analyzing native fish from the tertiary pond. However, Dow Chemical objected, contending that USEPA's legal authority under Section 308 of the Clean Water Act did not extend to such activities. Rather than engage in lengthy arguments, and possibly litigation, over the matter at that time, Region V and MDNR modified the study plan 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 conducted during the study, the fish in the plume were exposed to the outfall discharge diluted at or less than 1:1 by river water. Preliminary results from the study were reported previously. 1/

The locations at which caged fish were exposed are listed below and shown on Figure 15.

Figure 15

USEPA-MDNR
1981 Bioaccumulation Study
Caged Fish Sites



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
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 complete study results are presented in Appendix D. Significant findings are presented below:

a. PCDDs and PCDFs (Appendix D-1)

The analytical requirements for the study included isomer specific analyses for 2378-TCDD, 1368-TCDD, and 2378-TCDF as well as analyses for total penta through hepta-CDDs and CDFs, OCDD, and OCDF. Unfortunately, not all of the analytical objectives were achieved by the analytical contractor. Quality control reviews and reanalyses of sample extracts by USEPA indicate that the PCDF data produced were not valid due to interferences by hexa through deca chlorinated diphenyl ethers; quantitation of penta through hepta CDDs is questionable due to lack of internal standards; and the digestion procedure used used may have destroyed native OCDD present. 18/ Notwithstanding these problems, the valid data confirmed by EPA duplicate analyses and split sample analyses by Dow Chemical 19/ demonstrate that the outfall 031 discharge contained 2378-TCDD and other TCDDs found in Tittabawassee River native fish. In an attempt to determine the rate at which PCDDs and PCDFs may accumulate in fish, specimens were analyzed after 2, 4, 8, 14, 21, and 28 days of exposure to the outfall 031 plume. Specimens were analyzed after 14 and 28 days of exposure at other sites. Duplicate (separate) fish samples were obtained at selected sites after 14 and 28 days of exposure. Split samples (homogenate of whole fish composite samples) were provided to Dow Chemical for analyses for the fish food, control fish, Grand River native fish, and caged fish from Stations 2, 3, 4, 5, and B. Table 34 presents the results generated by Region V's analytical contractor, Battelle Memorial Institute, Columbus, Ohio. Table 35 presents split sample results from the Region V contractor, Dow Chemical and USEPA-EMSL. Table 36 presents the complete USEPA analytical results for Day 28 fish at outfall 031. These analyses were conducted on an extract prepared by the Region V analytical contractor.

Table 34

1981 USEPA-MDNR Bioaccumulation Study
Dow Chemical - Midland Plant
Contract Laboratory Results - Battelle Memorial Institute

(analyses in parts per trillion)

	Fish Food	Control Fish		Station A Sanford Dam		Station 1 Upstream Poseyville Road			Station 2 Upstream of Outfall 031		
		Day 0	Day 0	Day 14	Day 28	Day 14	Day 28	Day 28	Day 14	Day 28	Day 28
Sample Number: 81LS	15S08	11S01	11D01	15S06	17S06	15S01	17S01	17D01	15S02	17S02	17D02
2378-TCDD	<6	<7	<3	<4	<3	2	8	<13	<3	<3	<3
1368-TCDD	<5	<5	<3	<4	<5	<3	<5	<13	<3	<3	<3
Total TCDD	<6	7	<3	<2	4	2	8	<13	<3	<3	<3
Penta CDD	<4	<4	<4	<3	<3	<5	<6	<3	<6	<2	<3
Hexa CDD	<2	<1	<7	<3	<1	<3	<2	<1	<4	<3	<2
Hepta CDD	<1	<3	<1	<7	<2	<4	<1	<5	<4	<2	<2
OCDD	<1	<6	<4	<4	<3	<4	<7	<2	<3	<3	<3

Notes: (1) OCDD data for fish are not valid; ethanolic KOH digestion procedure may have destroyed OCDD.
(2) Quantitation of penta-octa CDDs questionable due to lack of $^{13}C_{12}$-OCDD internal standard.
(3) Tetra-octa CDF data not valid due to interference by hexa-deca chlorinated diphenyl ethers.

Table 34 (continued)

1981 USEPA-MDNR Bioaccumulation Study
Dow Chemical - Midland Plant
Contract Laboratory Results - Battelle Memorial Institute

(analyses in parts per trillion)

	Station 3								Station 4		
	Outfall 031 Plume								Downstream of Outfall 031 -1.98 miles		
	Day 2	Day 4	Day 8	Day 14	Day 14	Day 21	Day 28	Day 28	Day 14	Day 28	Day 28
Sample Number: 81LS	12S01	13S01	14S01	15S03	15D03	16S01	17S03	17D03	15S04	17S04	17D04
2378-TCDD	<4	64	7	12	<4	17	110	80	<3	2	<3
1368-TCDD	<4	NR	NR	<3	<4	NR	590	NR	<3	NR	NR
Total TCDD	<4	140	84	12	<4	50	820	770	<3	11	110
Penta CDD	<5	<8	<3	<4	<7	<7	<6	510	<3	<4	<4
Hexa CDD	<3	<7	<4	<5	<4	<4	<6	<1	<7	<4	<7
Hepta CDD	<2	<9	<8	<6	<3	<3	<4	<1	<1	<3	<4
OCDD	<4	<10	<4	<6	<2	<3	<5	<1	<2	<8	<3

Notes: (1) OCDD data for fish are not valid; ethanolic KOH digestion procedure may have destroyed OCDD.
(2) Quantitation of penta-octa CDDs questionable due to lack of $^{13}C_{12}$-OCDD internal standard.
(3) Tetra-octa CDF data not valid due to interference by hexa-deca chlorinated diphenyl ethers.
NR Data not valid; poor recovery of internal standards.

Table 34 (continued)

1981 USEPA-MDNR Bioaccumulation Study
Dow Chemical - Midland Plant
Contract Laboratory Results - Battelle Memorial Institute

(analyses in parts per trillion)

	Station 5			Station B	
	Downstream of Outfall 031 -2.65 miles			Grand River	
	Day 14	Day 28	Day 28	Day 14	Day 28
Sample Number: 81LS	15S05	17S05	17D05	15S07	17S07
2378-TCDD	NR	8	<3	<3	<7
1368-TCDD	NR	NR	<3	<3	<7
Total TCDD	NR	39	<3	<3	<7
Penta CDD	NR	<2	<4	<2	<1
Hexa CDD	NR	<2	<4	<6	<3
Hepta CDD	NR	10	<5	<1	<2
OCDD	NR	<1	130	<4	<4

	Grand River Native Fish					
Sample Number: 82LS	07S01	07S02	07S03	07S04	07S05	07S06
2378-TCDD	<3	NR	<3	NR	23	<5
1368-TCDD	<3	NR	<3	NR	<5	<11
Total TCDD	<3	NR	<3	NR	20	<11
Penta CDD	<3	NR	<3	NR	25	<3
Hexa CDD	<4	NR	<4	NR	<3	<1
Hepta CDD	<4	NR	<3	NR	<4	<5
OCDD	<3	NR	<7	NR	<6	<3

Notes: (1) OCDD data for fish are not valid; ethanolic KOH digestion procedure may have destroyed OCDD.
(2) Quantitation of penta-octa CDDs questionable due to lack of $^{13}C_{12}$-OCDD internal standard.
(3) Tetra-octa CDF data not valid due to interference by hexa-deca chlorinated diphenyl ethers.
NR Data not valid; poor recovery of internal standards.

Table 35

1981 USEPA-MDNR Bioaccumulation Study
Dow Chemical - Midland Plant
Between-Lab Comparison for 2378-TCDD

(analyses in parts per trillion)

	Fish Food	Control Fish		Station 2 Upstream of Outfall 031		Station 3 Outfall 031 Plume					
		Day 0	Day 0	Day 28	Day 28	Day 4	Day 8	Day 14	Day 14	Day 28(1)	Day 28
Sample Number: 81LS	15S08	11S01	11D01	17S02	17D02	13S01	14S01	15S01	15D03	17S03	17D03
Battelle Memorial Institute	ND (6)	ND (7)	ND (3)	ND (3)	ND (3)	64	7	12	ND (4)	110	80
Dow Chemical	ND (0.3)	6.4	7.1	6.1	7.1	11	13	21	19	38	41

Notes: NA = Not analyzed.
NR = Not reported.
ND = Not detected (detection limit).
(1) = USEPA-EMSL results in triplicate for Station 3 outfall 031 plume, Day 28 (sample 81LS17S03) are 35, 31, and 46 ppt, respectively.

Table 36

1981 USEPA-MDNR Bioaccumulation Study
Dow Chemical - Midland Plant
USEPA-EMSL Split Sample Analyses

Sample Identification	Outfall 031 Plume Station 3 - Day 28		
Field Sample Number:	81LS17S03		
Laboratory Sample Number:	D-654	D-678-A	D-678
1368-TCDD	160 (34)	158 (12)	--
1379-TCDD	ND (34)	ND (12)	--
2378-TCDD	35 (34)	31 (12) 46	--
Penta CDDs	ND (78)		140 (32)
Hexa CDDs	628 (78)		438 (32)
Hepta CDDs	--		ND (100)
OCDD	--		ND (100)
2378-TCDF	--	ND (6)	--
Tetra CDFs	--	454 (6)	--
Hepta CDFs	--	--	Interfences
OCDF	--	--	ND (77)

Notes: (1) Analytical results in parts per trillion (ppt).

(2) Method Efficiency

D-654 -- 9% Recovery $^{37}Cl_4$-TCDD

D-678-A -- 102% Recovery $^{37}Cl_4$-TCDD

D-678 -- 82% Recovery $^{37}Cl_4$-OCDD

(3) Seven TCDF isomers were tentatively identified in sample D-678-A.

Data for 2378-TCDD and total TCDDs for the control fish (Day 0) and Day 14 and Day 28 fish from each caged fish site are graphically displayed in Figure 16. The fish food, control fish (laboratory) and upstream caged fish and Grand River caged fish contained little or no TCDDs initially or after 28 days of exposure. After 28 days fish exposed to the outfall 031 plume accumulated from 80 to 110 ppt of 2378-TCDD (Battelle analyses). Duplicate analyses by EPA and split sample analyses by Dow Chemical indicate the actual 2378-TCDD levels in Day 28 fish for the outfall 031 plume site may be in the range of 35 to 46 ppt. Caged fish exposed in the Tittabawassee River at Station 4 and 5 (about 2 and 2.7 miles downstream from outfall 031, respectively) contained lower ppt levels of (ND-30 ppt) of 2378-TCDD after 28 days of exposure based upon Battelle and Dow Chemical analyses. The data for total TCDDs exhibit the same trend. The finding of TCDDs other than 2378-TCDD at levels well in excess of 2378-TCDD is believed to be unique to this study. Most studies indicate that 2378-TCDD is the only TCDD encountered in native fish. 20/ For this study the data presented in Table 36 indicate that 1368-TCDD accounted for most of the TCDDs found. While unique, these data are consistent with the wastewater characterizations for outfall 031 (Tables 24 and 25).

Since the caged fish were not exposed to bottom sediments, which may have contained historical deposits of 2378-TCDD, the study results clearly indicate the outfall 031 discharge at that time was contributing 2378-TCDD and other TCDDs to the Tittabawassee River system. It is considered likely that fine suspended sediments in the discharge containing dioxin were ingested by the test organisms over the exposure period.

Figure 17 presents a comparison of Battelle and Dow Chemical 2378-TCDD split sample analyses of caged fish exposed to the outfall 031 plume throughout the study. USEPA-EMSL duplicate analytical results for the Day 28 fish are also presented. The high concentration measured by Battelle for Day 4 (64 ppt 2378-TCDD) does not follow the trends established by the remaining Battelle data or the Dow Chemical data. This value may be the result of analytical error or possibly a nonhomogenous sample caused by a test organism ingesting an unusually high level of dioxin from the outfall. Aside from the one anomalous data point for Day 4, both the Battelle and Dow data exhibit a fairly uniform increase in concentration through 21 days of exposure, with divergence in the analyses at Day 28. The duplicate sample results by USEPA-EMSL confirm the Dow Chemical data and distinguish the Battelle data as not representative. Discounting the Battelle Day 4 and Day 28 data, the remaining data approximate a straight line as illustrated in Figure 17 ($Y = Ax + b$, where $A = 1.132$, and $b = 0.312$; $r = 0.908$ indicating a reasonably good fit of the data to the straight line depicted by the coefficients A and b). The results do not indicate a steady state concentration was achieved after 28 days of exposure.

Based upon Battelle analyses, the Grand River caged fish (Station B) did not contain 2378-TCDD after 28 days of exposure (detection level of 7 ppt). However, Dow Chemical's analyses of the duplicate field sample for 28 days of exposure was 4.4 ppt. Grand River native fish (whole carp) were found to contain up to 23 ppt of 2378-TCDD. A Tier 3 (Dioxin Strategy) facility located near the fish collection site is the likely source of the dioxin contamination in native fish. 21/

Figure 16

USEPA-MDNR
1981 Bioaccumulation Study
TCDD Results

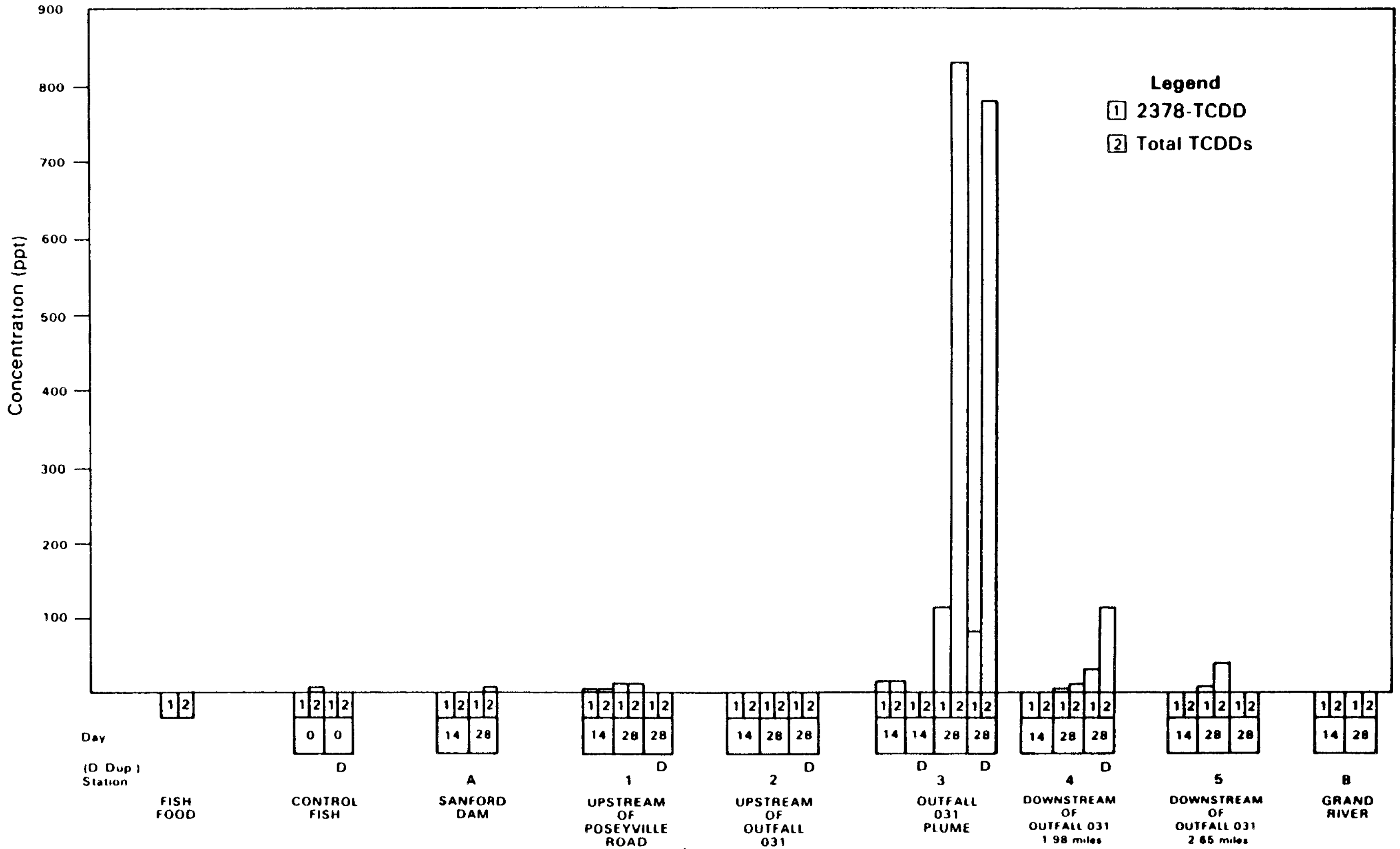
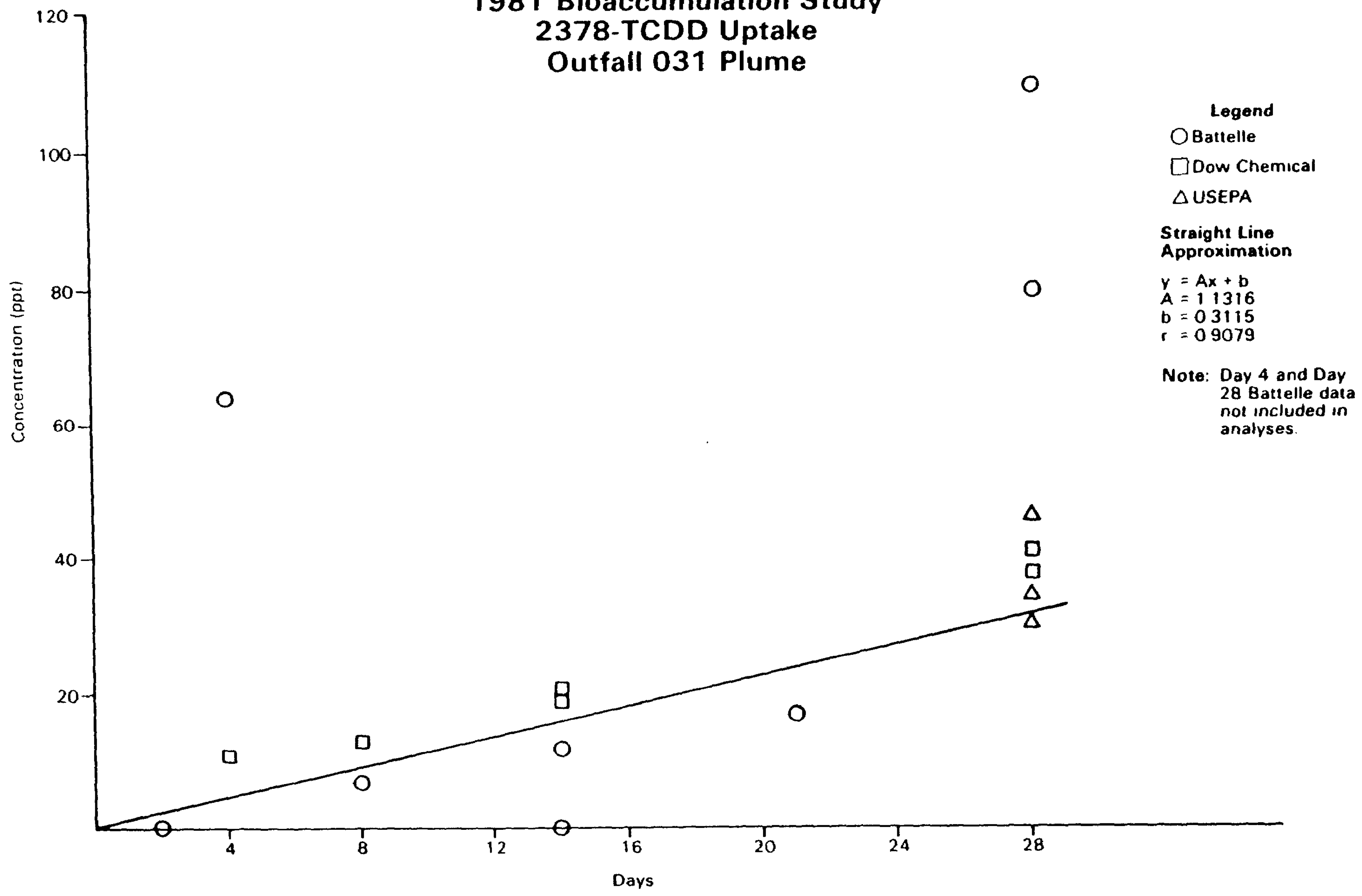


Figure 17

USEPA-MDNR
1981 Bioaccumulation Study
2378-TCDD Uptake
Outfall 031 Plume



b. Base Neutral Compounds (Appendix D-2)

Figure 18 summarizes the results for base neutral compounds. These analyses and those for other organic compounds reviewed below were completed by GCA Corporation under contract to Region V. 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 the outfall 031 plume. 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 the outfall 031 plume. The downstream Tittabawassee River fish exhibited 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.

c. Acid Compounds (Appendix D-2)

The control fish showed no accumulation of acid compounds (Figure 19). 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.

d. Pesticides, PCBs (Appendix D-2)

The data summarized in Figure 20 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 increase 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-2). While analyses of compounds could not be confirmed due to the complex sample matrix of the fish exposed to 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. The results presented in Figure 19 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

Figure 18

USEPA-MDNR
1981 Bioaccumulation Study
Base Neutral Compounds

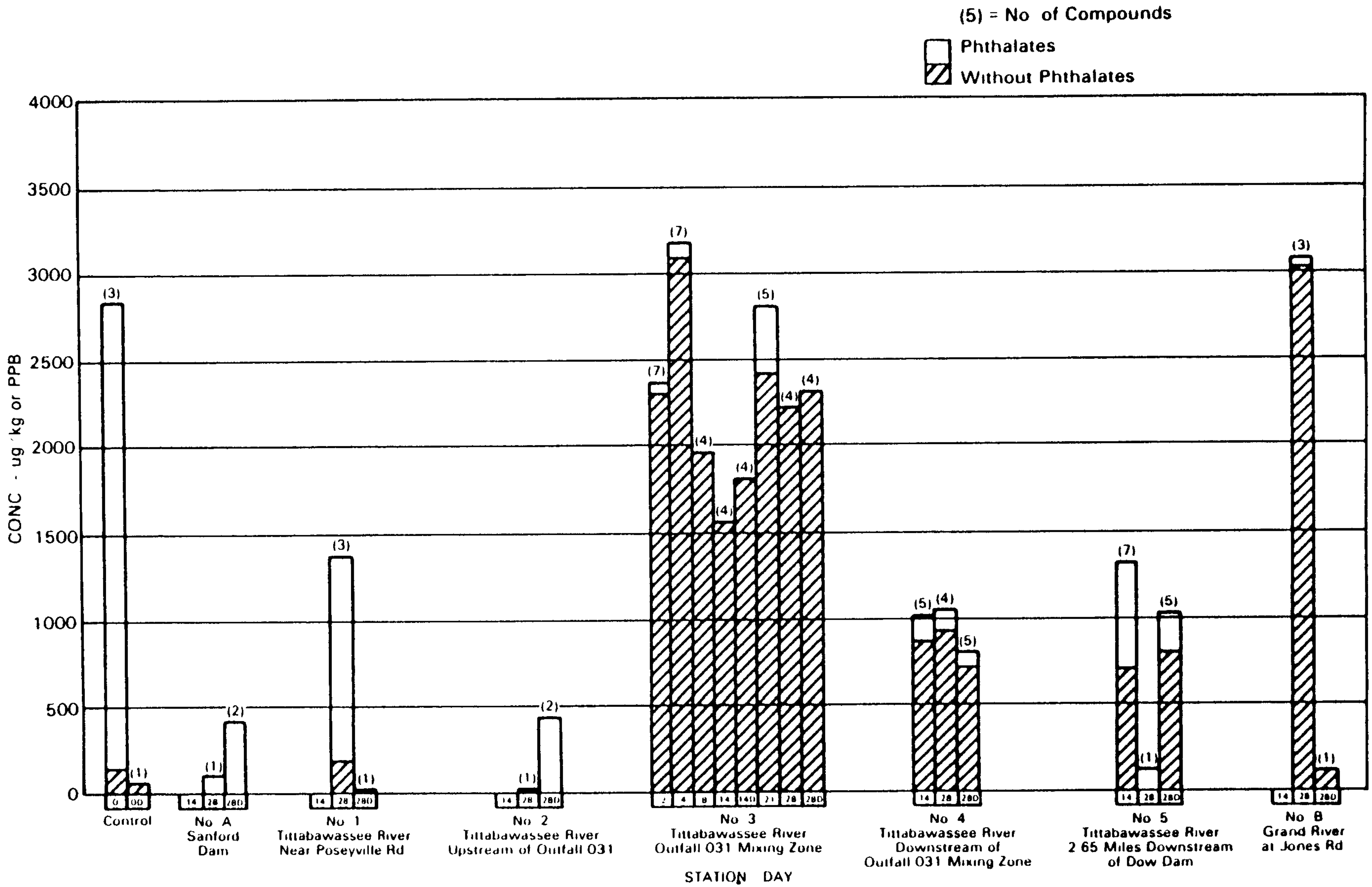


Figure 19

USEPA-MDNR
1981 Bioaccumulation Study
Acid Compounds

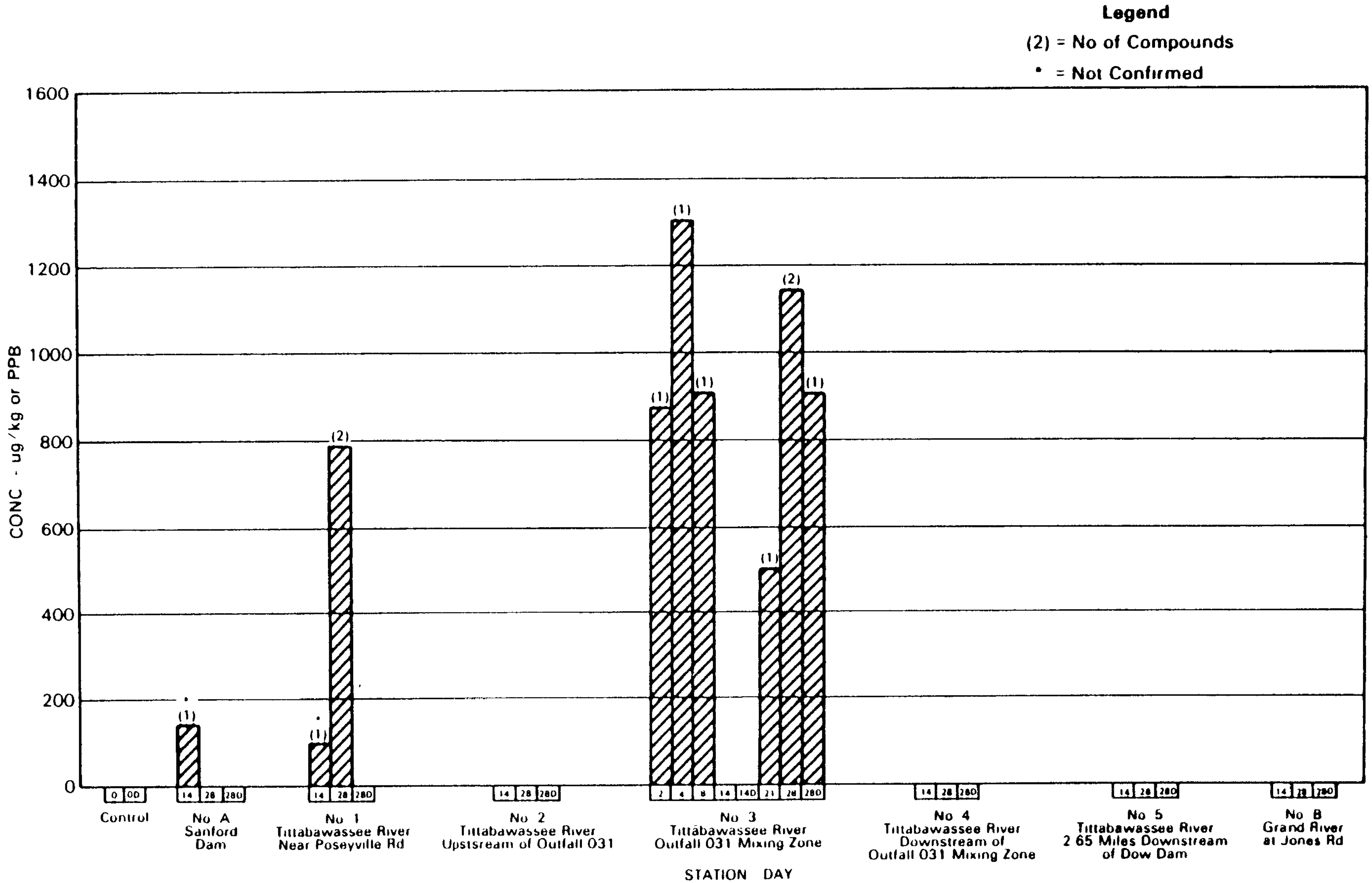


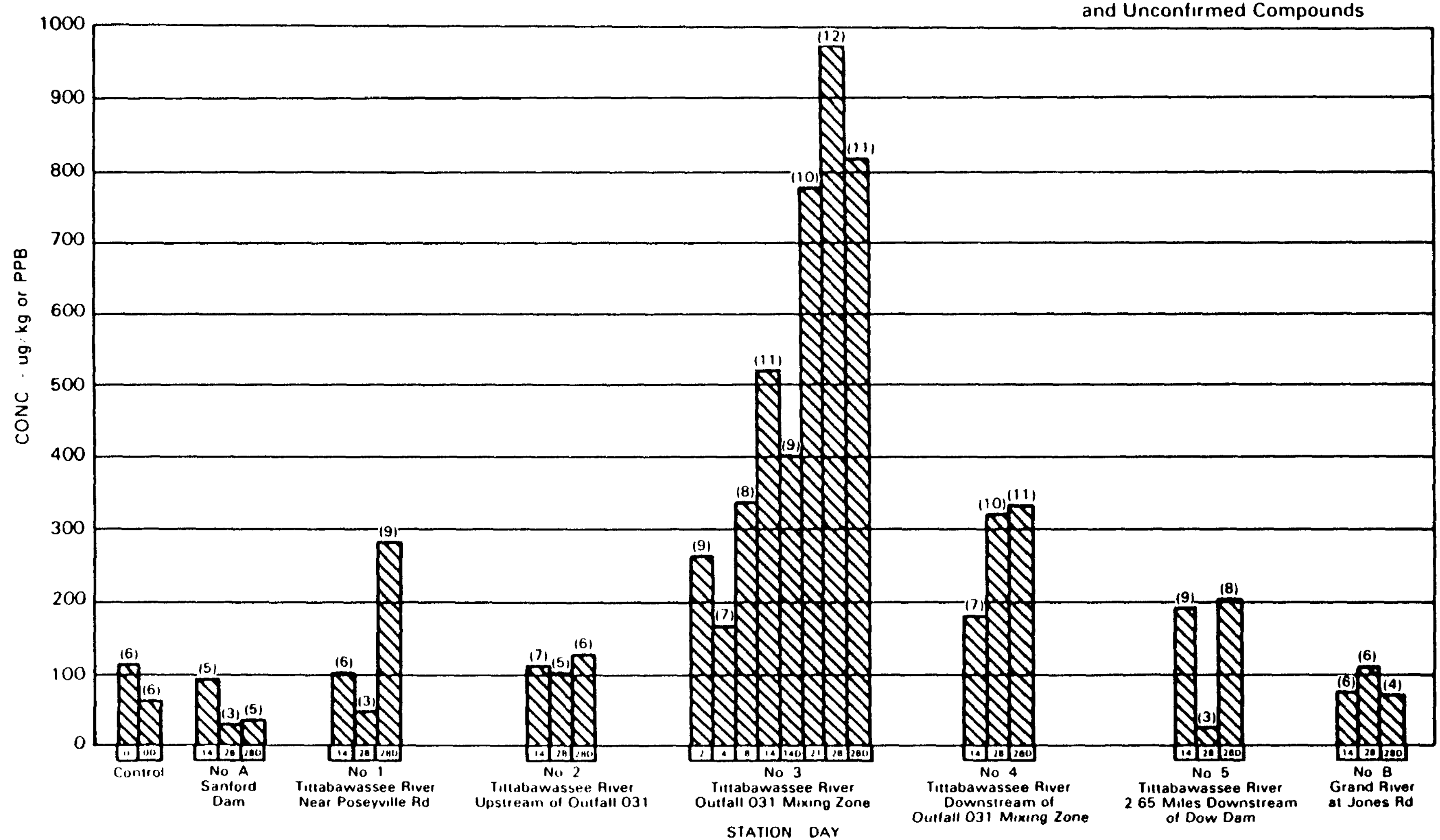
Figure 20

USEPA-MDNR
1981 Bioaccumulation Study
Pesticides and PCBs

Legend

(5) = No of Compounds

Note Some Pesticides not Confirmed on Second Column GC/ECD Data Presented are for both Confirmed and Unconfirmed Compounds



alpha-BHC at about 6 ppb. Alpha-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 alpha-BHC (5 to 15 ppb), endosulfan II (21 ppb), and PCB-1248 (46 ppb). Alpha-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 the outfall 031 plume contained unconfirmed levels of aldrin in excess of 200 ppb; alpha-BHC in excess of 200 ppb; beta-BHC in excess of 20 ppb; gamma-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 alpha-BHC, DDD, DDE, dieldrin, heptachlor epoxide, and heptachlor were confirmed in fish at Station 5.

The caged fish at Station B (Grand River at Jones Road) contained confirmed levels of alpha-BHC, gamma-BHC, and DDD at less than 20 ppb, and unconfirmed levels of DDE, endosulfan I, endrin aldehyde, endosulfan sulfate, and endosulfan II, all 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).

e. Other Extractable Compounds (Appendix D-2)

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 compound were found at levels significantly higher than those noted above. The data are also presented in Appendix D-2.

Attempts were also made to develop analytical methods for analyses of herbicide compounds in fish, but these efforts were abandoned due to the complexity of the task and resource constraints. Frozen homogenate of the fish samples from this study have been archived at the USEPA National Water Quality Laboratory at Duluth, Minnesota.

2. Dow Chemical Biouptake Study - October 1985 (Appendix D-3)

As required by Special Condition 9 of NPDES permit MI0000868, Dow Chemical conducted a 28-day flow-through biouptake study to simulate the effects of outfall 031 on Tittabawassee River native fish. Catfish were used as the test organism. For control purposes unexposed whole and gutted fish and whole and gutted fish exposed to Tittabawassee River water taken from upstream from outfall 031 were analyzed. To simulate the dilution of the outfall 031 discharge by the river, test organisms were exposed to a mixture of 15% outfall 031 discharge and 85% river water. The study was conducted in aquaria. According to Dow Chemical, both river water and the outfall 031 discharge were filtered through a 25-micron sock to protect test apparatus flow control valves from being fouled by particulate matter present in the test waters. 22/ The study results reported to date by Dow Chemical to the MDNR are presented in Table 37. The chemical composition of the test water was not reported by Dow Chemical. In marked contrast to the USEPA-MDNR study results from the 1981 in-situ study reviewed above, the test organisms in Dow's study did not exhibit measurable bioaccumulation of 2378-TCDD or most other organic compounds analyzed. The analytical detection limits reported by Dow Chemical were in the range of 0.6 to 3.6 ppm for heptachlor epoxide; 2,4-dichlorophenol; aldrin; pentachlorophenol; 1,2,3-trichlorobenzene; aniline; and alpha-BHC. None of these compounds were found in control or exposed fish. Detection levels for the other compounds listed in Table 34 were less than 11 ppb. Because of the relatively high analytical detection levels reported by Dow Chemical for the above-listed compounds, the results from this study cannot be compared directly with results from the 1981 USEPA-MDNR study where analytical methods with low ppb detection levels were used.

The levels of 2378-TCDD and 2378-TCDF found in fish exposed to the 15/85 mixture of outfall 031 and the Tittabawassee River were about the same as that found in the control fish and fish exposed to the Tittabawassee River water taken upstream from outfall 031. Hexachlorobenzene accumulated to 3.7 ppm in whole fish exposed to the outfall/river mixture vs. no detectable levels and 22 ppb in the unexposed fish and fish exposed to the upstream river water, respectively. Levels of 1,2,4,5-tetrachlorobenzene were higher in whole fish exposed to the outfall/river mixture than in fish exposed to the river (4.9 ppm vs. 1.5 ppm). 1,2,4-Trichlorobenzene and pentachlorobenzene were found in the 0.2 to 0.5 ppm range in fish exposed to the outfall/river mixture. The results for the chlorinated benzenes are consistent with the findings from the 1981 USEPA-MDNR study.

As part of its point source investigation of 2378-TCDD contamination at the Midland plant, Dow Chemical conducted particle size analyses of the particulate matter in the outfall 031 discharge. 4/ These data indicate that the particle size range for the outfall 031 discharge prior to filtration is about 2 to 100 microns, with over 90% of the particles less than 25 microns in diameter. A pilot plant filter effluent contained about 90% fewer particles by volume, but the distribution of the particles present was about the same as that of the particles in the unfiltered water. These results indicate that the 25-micron sock used to protect flow control devices during the biouptake study would be

TABLE 37

DOW CHEMICAL BIOUPTAKE STUDY
OCTOBER 1985

	Day 0 Fish		Day 28 Fish 100% River Water		Day 28 Fish 15% 031 Effluent/85% River Water	
	Whole Fish	Gutted Fish	Whole Fish	Gutted Fish	Whole Fish	Gutted Fish
Acrylonitrile	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)
Aldrin	NQ(1.8)	NQ(1.8)	NQ(1.8)	NQ(1.8)	NQ(1.8)	NQ(1.8)
alpha-BHC	NQ(3.6)	NQ(3.6)	NQ(3.6)	NQ(3.6)	NQ(3.6)	NQ(3.6)
Aniline	NQ(2.6)	NQ(2.6)	NQ(2.6)	NQ(2.6)	NQ(2.6)	NQ(2.6)
1,2-Dichlorobenzene	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)
1,3-Dichlorobenzene	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)
1,4-Dichlorobenzene	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)	NQ(0.004)
2,4-Dichlorophenol	NQ(0.8)	NQ(0.8)	NQ(0.8)	NQ(0.8)	NQ(0.8)	NQ(0.8)
Heptachlor epoxide	NQ(0.6)	NQ(0.6)	NQ(0.6)	NQ(0.6)	NQ(0.6)	NQ(0.6)
Hexachlorobenzene	NQ(0.04)	NQ(0.04)	0.022	0.017	3.7	0.2
PCB Isomers						
Dichloro-	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)
Trichloro-	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)
Tetrachloro-	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)
Pentachloro-	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)
Hexachloro-	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)	NQ(2.3)
Pentachlorobenzene	NQ(0.011)	NQ(0.011)	NQ(0.011)	0.2	0.5	NQ(0.011)
Pentachlorophenol	NQ(1.9)	NQ(1.9)	NQ(1.9)	NQ(1.9)	NQ(1.9)	NQ(1.9)
1,2,3,4-Tetrachlorobenzene	NQ(0.007)	NQ(0.007)	1.1	2.3	1.0	NQ(0.007)
1,2,4,5-Tetrachlorobenzene	NQ(0.006)	NQ(0.006)	1.5	0.5	4.9	NQ(0.006)
2,3,7,8-TCDD	0.7 ppt	0.7 ppt	0.9 ppt	0.9 ppt	1.2 ppt	1.2 ppt
2,3,7,8-TCDF*	2.4 ppt	2.1 ppt	2.4 ppt	2.4 ppt	2.5 ppt	2.3 ppt
1,2,3-Trichlorobenzene	NQ(2.1)	NQ(2.1)	NQ(2.1)	NQ(2.1)	NQ(2.1)	NQ(2.1)
1,2,4-Trichlorobenzene	NQ(0.0001)	NQ(0.0001)	NQ(0.0001)	NQ(0.0001)	0.29	0.5
2,4,5-Trichlorophenol	NQ(0.011)	NQ(0.011)	NQ(0.011)	NQ(0.011)	NQ(0.011)	NQ(0.011)
2,4,6-Trichlorophenol	NQ(0.011)	NQ(0.011)	NQ(0.011)	NQ(0.011)	NQ(0.011)	NQ(0.011)

Notes: (1) All results in parts per million (ppm), unless otherwise noted.
(2) * Qualified: isomer specificity cannot be proven.
(3) Dow Chemical completed a 28-day fish biouptake study pursuant to Special Condition #9, NPDES permit MI0000868 using catfish as the test organisms.
(4) Analyses by Dow Chemical Company.

expected to remove a portion of the suspended solids present in the wastewaters. The amount of suspended solids removed has not been reported but would probably include particles with diameters less than 25 microns as the filter media became loaded with larger particles. Thus, the test organisms would not be exposed to any bioaccumulative pollutants associated with the suspended solids removed. Without chemical characterization of the filtered water used in this study and the unfiltered water from the effluent, it is not possible to fully assess the study results.

The accumulation of hexachlorobenzene and other chlorinated benzenes in fish after 28 days of exposure is noted. These data and the untreated wastewater and sewer sludge data presented earlier suggest a residual loading of chlorinated benzenes in the Midland plant sewerage system despite termination of chlorinated benzene production in the early 1980s. The results also suggest that the chlorinated benzenes discharged are either dissolved or attached to fine particles.

E. Tittabawassee River Native Fish Collections

Table 38 presents a summary of 2378-TCDD analyses of native fish collected from the Tittabawassee River during the period 1978 to 1985. 23,24,25,26,27/ The data are displayed by collection event, species, and type of sample (whole fish, skin-on filet, or skin-off filet). Because of limited data, it is difficult to discern statistically significant trends or patterns in the levels of 2378-TCDD in fish over time. However, it is clear that bottom feeding fish such as carp and catfish contain consistently higher levels of 2378-TCDD than other species which may not forage on the stream bottom to the same extent as carp and catfish. Also, the concentrations found in bottom-feeding fish are not normally distributed. For the 1978 and 1983 surveys the range of concentrations found was large. The 1983 MDNR-USEPA study included analyses of 25 individual carp filets. Most of the detected concentrations were well below the mean value of 50 ppt, with a few samples in the 100-200 ppt range and a maximum of 530 ppt. Concentrations in walleyes are much more uniform. This may be due to the fact that many walleye are transitory as opposed to carp and catfish. Figure 21 presents the results of the 1983 and 1985 fish collections. Comparable data by species, location, and sample type from the different surveys are reviewed in Table 39.

TABLE 38

Tittabawassee River Native Fish Collections
2378-TCDD
1978-1985

(parts per trillion)

Study	Location/Species	Whole Fish No.	Whole Fish Range	Whole Fish Average	Filet - Skin On No.	Filet - Skin On Range	Filet - Skin On Average	Filet - Skin Off No.	Filet - Skin Off Range	Filet - Skin Off Average
1978 USEPA	Dow Dam to Center Road									
	Carp							6	ND-93	41
	Channel Catfish							3	42-695	337
	Yellow Perch							3[a]	ND-20	10
	Dublin Road									
	Carp							1		ND
1980 MDNR/ USEPA	Dow Dam to Center Road									
	Carp	5	33-142	89.6						
	White Sucker	3	3-10	7.0						
	Emerson Park									
	Carp	3	7-62	40.7						
1983 MDNR/ USEPA	Smiths Crossing Road									
	Carp	1[b]		190				25	12-530	50
	Catfish							1[b]		75
	Smallmouth Bass				1[b]		5.1			
	Walleye				5	2.8-5.1	3.9			

Notes: (1) a - includes two, 2-fish composites
(2) b - five-fish composite
(3) ND - not detected
(4) The Dublin Road sampling site is located upstream of the Dow Chemical - Midland Plant.
(5) The Emerson Park sampling site is located upstream of the Dow Chemical - Midland Plant.

TABLE 38 (continued)

Tittabawassee River Native Fish Collections
2378-TCDD
1978-1985

(parts per trillion)

Study	Location/Species	Whole Fish			Filet - Skin On			Filet - Skin Off		
		No.	Range	Average	No.	Range	Average	No.	Range	Average
1985 MDNR/ MDPH/FDA/Dow Chemical	Dow Dam to Smith's Crossing Road									
	Walleye-Spring Run				8	2.5- 7.6	4.4			
	Walleye-Summer Resident				6	2.6-14.0	6.5			
	Crappie				3[c]	2.8- 4.5	3.9			
	Northern Pike				3	6.1-15.0	9.5			
	White Bass				4[d]	5.7-15.0	8.2			
	Smallmouth Bass				3	2.8- 6.4	5.0			
1985 Dow Chemical	Smith's Crossing Road									
	Carp							2	3.8-54	28.9
	Catfish							1		39
	Walleye				5	ND-3.6	2.3			
	Dublin Road									
	Carp							3	ND-24	8.6

Notes: (1) c - three-fish composite for each measurement
(2) d - includes three 3-fish composite and one 4-fish composite
(3) ND - not detected
(4) The Dublin Road sampling site is located upstream of the Dow Chemical - Midland Plant.

Figure 21

Tittabawassee River Native Fish
1983 and 1985 Collections
2378-TCDD

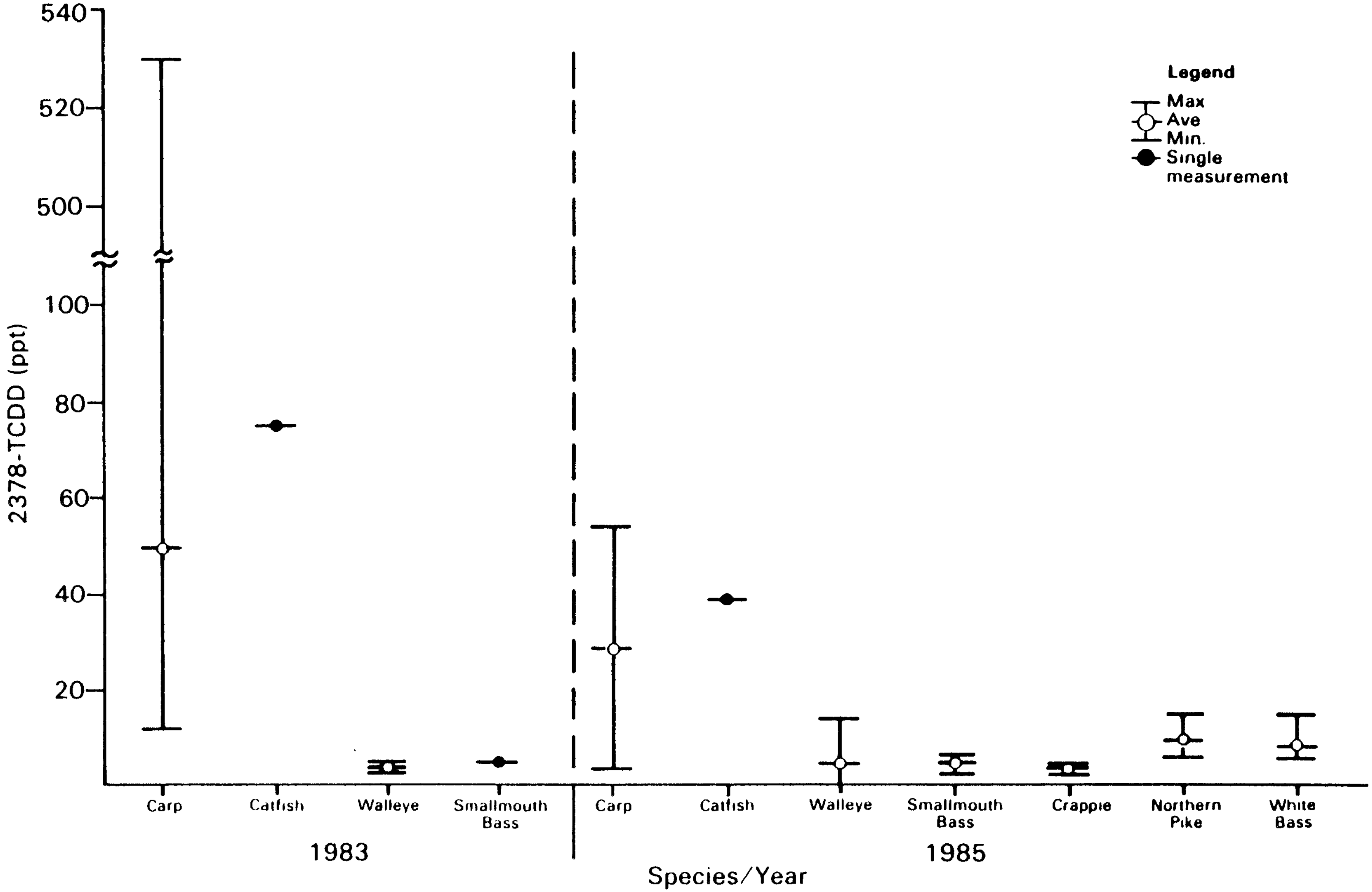


TABLE 39

Tittabawassee River Native Fish Collections
Trends in 2378-TCDD Concentrations

2378-TCDD (ppt)			
Year	Number	Range	Average
Carp - Whole Fish			
1980	5	33-142	89.6
1983	5 (comp)	--	190
Carp - Skin-off Filet			
1978	6	ND-93	41
1983	25	12-530	50
1985	2	3.8-54	28.9
Catfish - Skin-off Filet			
1978	3	42-695	337
1983	5 (comp)	--	75
1985	1	--	39
Walleye - Skin-on Filet			
1983-summer	5	2.8-5.1	3.9
1985-spring	8	2.5-7.6	4.4
-summer	6	2.6-14.0	6.5
-fall	5	ND-3.6	2.3
Smallmouth Bass - Skin-on Filet			
1983	5 (comp)	--	5.1
1985	3	2.8-6.4	5.0

These data do not suggest any significant changes in the levels of 2378-TCDD in carp over time. Based upon limited data, it would appear that levels of 2378-TCDD in catfish have decreased from 1978 to 1985. Sufficient data are not available to make this conclusion with any degree of confidence. There is virtually no change in average 2378-TCDD levels in walleye or smallmouth bass from 1983. Typical levels for both species tend to center on about 5.0 ppt.

Because of the distribution of 2378-TCDD in Midland area soils and the persistence of 2378-TCDD in the environment, bottom feeding fish and other game fish from the Tittabawassee River may not exhibit significantly lower levels of 2378-TCDD in the near future. Runoff from the city, the wastewater discharge from Dow Chemical, and atmospheric deposition from Dow Chemical operations will continue to contribute 2378-TCDD to the river system. Although Dow Chemical has initiated measures which should reduce the wastewater discharge and atmospheric emissions, continued low-level releases from the Midland plant are expected over the foreseeable future. Currently, there does not appear to be any feasible means of controlling contributions from area runoff outside the Dow plant. A river bottom improvement program without an area-wide runoff control or soil management program would not yield measureable benefits. Thus, while the concentrations of 2378-TCDD in Tittabawassee River fish should decrease slowly over time, residual levels in the low ppt range for walleye, bass, and other game fish, and somewhat higher levels in carp and catfish can be expected for at least several years. This discussion is presented to indicate that measurable progress in reducing dioxin levels in Tittabawassee River fish will probably occur slowly overtime and not immediately after control measures are implemented. This is not to suggest that further efforts to improve the river system not be undertaken or that in-place control measures be abandoned.

Under the terms of a consent order with USEPA, Dow Chemical is required to monitor native fish in the Tittabawassee River every two years through 1991. 3/ Table 40 presents the 1985 results for 2378-TCDD, 2378-TCDF, and total TCDDs, HxCDDs, HpCDDs, and OCDD. The 2378-TCDD data are consistent with prior findings presented in Table 38. The results for walleyes are of interest. 2378-TCDF concentrations are roughly 12 times higher than 2378-TCDD in skin-on filet samples. The concentrations of other TCDDs were much more variable in the same samples. The levels of 2378-TCDD and 2378-TCDF were about 10 times higher in a walleye viscera composite than in filet samples. The relatively high levels of 2378-TCDF and other PCDDs suggest that the presence of other PCDDs and PCDFs in addition to 2378-TCDD should be considered when evaluating health risks from consumption of fish from the Tittabawassee River. 28/ USEPA's evaluation of the potential health risks associated with consumption of fish taken from the Tittabawassee River will be presented separately.

Table 41 presents analytical results for a number of toxic organic pollutants selected by the Michigan Department of Public Health for fish collected as part of the 1985 cooperative study by MDPH, MDNR, FDA, and Dow Chemical. The fish were collected in the vicinity of Smith's Crossing Road. Individual fish skin-on filet samples or composite skin-on filet samples of the following species were analyzed: crappie, white bass, smallmouth bass, walleye, and northern pike. As with 2378-TCDD, the limited data do not allow for much statistical analysis. Nonetheless, species to species comparisons of average fish flesh concentrations indicate that white bass and northern pike contained the highest levels of contaminants while smallmouth bass contained the lowest levels. Highest contaminant levels were generally found in those samples with higher lipid (% fat) content. The lipid content of the white bass samples averaged 3.5%, while that of the northern pike samples averaged 1.2%. Although the average lipid content of the walleye samples was 2.1%, the levels of most pollutants were below those for northern pike. The lipid content of the smallmouth bass samples was about 0.1%, the lowest encountered in this study.

The native fish all exhibited substantially lower levels of hexachlorobenzene (0.008 to 0.038 ppm) than did catfish exposed to a filtered mixture of 15% outfall 031 effluent and 85% Tittabawassee River water from Dow Chemical's 1985 biouptake study (Table 37). Those fish accumulated hexachlorobenzene to 3.7 ppm while control fish exposed to filtered Tittabawassee River water only contained 0.022 ppm, which is in the range of values found in five species of native fish.

TABLE 40

PCDDs and PCDFs
NATIVE FISH COLLECTION
TITTABAWASSEE RIVER, 1985

(parts per trillion)

Species	Date Taken	Location Taken	2378-TCDD	2378-TCDF	Total Tetrachloro Dioxin Isomers	Total Hexachloro Dioxin Isomers	Total Heptachloro Dioxin Isomers	Octachloro Dioxin
Walleye	8/22/85	Smith's Crossing	2.5	34	2.8	36	34	95
Walleye	8/22/85	Smith's Crossing	2.6	24	1.9	19	26	55
Walleye	8/22/85	Smith's Crossing	3.0	28	17	5.6	6.2	16
Walleye	8/22/85	Smith's Crossing	3.6	40	ND(1.4)	ND(2.7)	ND(11)	15
Walleye(a)	8/22/85	Smith's Crossing	ND(1.8)	11	ND(1.5)	ND(2.5)	ND(2.8)	6.4
Composite of Walleye Viscera (b)			22	300	36	ND(5.3)	ND(3.9)	29
Carp(c)	8/22/85	Smith's Crossing	3.8	8.7	7.8	6.8	9.3	15
Carp	8/22/86	Smith's Crossing	54	94	59	ND(9.1)	26	26
Catfish(d)	8/30/85	Smith's Crossing	39	28	92	23	27	43
Carp	10/21/85	Dublin Road	ND(1.7)	ND(4.4)	ND(2.3)	ND(2.0)	ND(3.7)	3.8
Carp	10/21/85	Dublin Road	1.9	3.3	ND(8.8)	ND(3.8)	5.1	8.5
Carp	10/21/85	Dublin Road	24	83	ND(1.6)	15	15	14

Notes: (1) Walleye - Skin-on filet.
(2) Carp and catfish - skin-off filet.
(3) Total tetrachlorodioxin isomers do not include 2378-TCDD.
(4) Samples collected and analyzed by Dow Chemical Company pursuant to settlement agreement in Civil Action No. 83-CV7011BC (United States vs The Dow Chemical Company).
(5) The Dublin Road sampling site is located upstream of the Dow Chemical - Midland Plant.
(6) Percent lipid content for selected samples are as follows (average of 10 replicate 2 gm samples):
(a) Walleye filet - 1.9% ± 0.4%
(b) Walleye viscera composite - 14.6% ± 0.8%
(c) Carp filet - 3.0% ± 0.4%
(d) Catfish filet - 9.1% ± 2.7%

TABLE 41

TOXIC ORGANIC POLLUTANTS
NATIVE FISH COLLECTION
MDPH/MDNR/FDA/DOW CHEMICAL
TITTABAWASSEE RIVER 1985

mg/kg (parts per million)

	Crappie			White Bass			Small Mouth Bass		
	No. of Analyses	Range	Average	No. of Analyses	Range	Average	No. of Analyses	Range	Average
% Fat (hexane extractables)	3	0.3-0.6	0.5	4	2.3-4.9	3.5	3	0.1-0.15	0.11
Terphenyls (5432, 5442)	3	ND-0.050	0.017	4	0.200-0.330	0.232	3	ND-0.050	0.017
PCB (1254)	3	0.087-0.185	0.130	4	1.076-1.650	1.328	3	0.024-0.085	0.045
alpha-Chlordane	3	0.003-0.004	0.004	4	0.012-0.021	0.017	3	ND-0.002	<0.001
gamma-Chlordane	3	0.001-0.002	0.002	4	0.004-0.006	0.005	3	ND-0.001	<0.001
Oxychlordane	3	0.004-0.008	0.006	4	0.010-0.018	0.014	3	ND-0.002	<0.001
Cis-nonachlor	3	0.002-0.007	0.004	4	0.006-0.016	0.010	3	ND-0.003	0.001
Trans-nonachlor	3	0.003-0.003	0.003	4	0.010-0.024	0.018	3	ND-0.002	<0.001
p,p'-DDD	3	0.036-0.068	0.052	4	0.085-0.316	0.155	3	0.010-0.053	0.028
p,p'-DDE	3	0.027-0.039	0.033	4	0.099-0.260	0.160	3	0.009-0.033	0.018
p,p'-DDT	3	0.002-0.003	0.003	4	0.003-0.020	0.009	3	0.001-0.005	0.002
Dieldrin	3	0.001-0.003	0.002	4	0.007-0.023	0.013	3	ND-0.001	<0.001
Hexachlorobenzene	3	0.008-0.013	0.010	4	0.014-0.020	0.017	3	ND-0.004	0.002
Toxaphene	3	0.020-0.025	0.023	4	0.048-0.137	0.089	3	ND-0.025	0.008
Octachlorostyrene	2	0.001-0.001	0.001	3	0.001-0.003	0.002	2		ND
Heptachlor epoxide	1	---	ND	1	---	0.004	3	ND-0.001	<0.001

NOTES: (1) Fish collected from the Tittabawassee River between the Dow Dam in Midland and the vicinity of Smith's Crossing Road.
(2) Crappie analyses conducted on 3-fish composites; white bass analyses conducted on one 4-fish composite and three 3-fish composites; other analyses conducted on individual fish.
(3) All samples are skin-on filets.

TABLE 41 (continued)

mg/kg (parts per million)

	Walleye			Northern Pike		
	No. of Analyses	Range	Average	No. of Analyses	Range	Average
% Fat (hexane extractables)	14	0.70-3.2	2.1	3	1.1-1.3	1.2
Terphenyls (5432, 5442)	14	ND-0.500	0.093	3	ND-0.125	0.042
PCB (1254)	14	0.197-1.658	0.588	3	0.230-0.685	0.382
alpha-Chlordane	14	ND-0.014	0.010	3	0.005-0.118	0.044
gamma-Chlordane	14	ND-0.011	0.004	3	0.002-0.034	0.014
Oxychlordane	14	ND-0.012	0.005	3	0.009-0.018	0.014
Cis-nonachlor	14	ND-0.018	0.010	3	0.006-0.051	0.022
Trans-nonachlor	14	ND-0.036	0.015	3	0.006-0.149	0.057
p,p'-DDD	14	ND-0.098	0.051	3	0.061-0.606	0.270
p,p'-DDE	14	0.034-0.212	0.100	3	0.066-0.131	0.105
p,p'-DDT	14	ND-0.026	0.012	3	0.009-0.020	0.013
Dieldrin	14	ND-0.007	0.001	3	ND-0.007	0.002
Hexachlorobenzene	14	0.002-0.038	0.009	3	0.006-0.017	0.012
Toxaphene	14	ND-0.222	0.097	3	0.038-0.107	0.068
Octachlorostyrene	10	ND-0.003	0.001	2	0.002-0.005	0.004
Heptachlor epoxide	14	ND-0.005	0.002	3	0.001-0.009	0.004

NOTES: (1) Fish collected from the Tittabawassee River between the Dow Dam in Midland and the vicinity of Smith's Crossing Road.
(2) Crappie analyses conducted on 3-fish composites; white bass analyses conducted on one 4-fish composite and three 3-fish composites; other analyses conducted on individual fish.
(3) All samples are skin-on filets.

VII. NPDES PERMIT - BEST AVAILABLE TECHNOLOGY

A. Clean Water Act Requirements

Section 402 of the Clean Water Act (CWA) establishes a National Pollutant Discharge Elimination System (NPDES) permit program. The NPDES program is designed to limit the discharge of pollutants into navigable waters of the United States from point sources through a combination of various requirements including technology-based and water quality-based effluent limitations. The Act provides that the Administrator of USEPA can delegate the permit program to state pollution control agencies and that the Administrator or his designee, must concur with permits issued by delegated state agencies. The NPDES permit program for Michigan was delegated to the Michigan Department of Natural Resources by USEPA on October 17, 1973. 29/

Sections 301, 304, 306, and 307 of the Act also provide that USEPA must promulgate national effluent limitations guidelines and standards of performance for major industrial categories for three major classes of pollutants: (1) conventional pollutants (total suspended solids, biochemical oxygen demand, oil and grease, and pH); (2) toxic pollutants (e.g., toxic metal and toxic organic pollutants); and (3) nonconventional pollutants (e.g., ammonia, fluoride, phenols (4AAP)). Six types of national effluent limitations guidelines and standards must be promulgated for each industrial category:

Abbreviation	Type of Effluent Limitations Guideline or Standard
BPT	Best Practical Control Technology Currently Available
BAT	Best Available Technology Economically Achievable
BCT	Best Conventional Pollutant Control Technology
NSPS	New Source Performance Standards
PSES	Pretreatment Standards for Existing Sources
PSNS	Pretreatment Standards for New Sources

The pretreatment standards are applicable to industrial facilities with wastewater discharges to publicly owned treatment works (POTWs) which generally are municipal wastewater treatment plants. The effluent limitations guidelines and new source performance standards are applicable to industrial facilities with direct discharges to navigable waters. Thus, only the first four types of guidelines are applicable to the Dow Chemical - Midland Plant.

Section 301 of the CWA requires that BPT limitations were to have been achieved by July 1, 1977; BAT effluent limitations for toxic pollutants by July 1, 1984; BAT effluent limitations for nonconventional pollutants within three years from date of promulgation but no later than July 1, 1987. BCT effluent limitations were to have been achieved by July 1, 1984. Section 402(a)(1) of the Act provides that in the absence of promulgated effluent limitations guidelines and standards, the Administrator or his designee may establish limitations for specific dischargers on a case-by-case basis. USEPA regulations provide that these limits may be established using "best professional judgment" taking into account proposed effluent limitations guidelines and standards and other relevant scientific, technical, and economic information.

B. NPDES Permit MI0000868

As part of the NPDES permit program, the Michigan Water Resources Commission issued NPDES permit MI0000868 to Dow Chemical on May 17, 1984. In accordance with EPA's NPDES permit regulations (40 CFR §123.44), Region V commented on and concurred with issuance of the permit by the state. 30,31/ The permit has a four-year term and expires on June 30, 1988. An administrative order was issued by the Water Resources Commission concurrently with the NPDES permit, ordering Dow Chemical to install an end-of-pipe treatment facility (mixed media filter) for control of 2378-TCDD and to initiate other dioxin control measures. The NPDES permit contains water quality-based effluent limitations for several toxic organic pollutants developed by the Michigan Department of Natural Resources and effluent limitations for conventional, nonconventional, and other toxic pollutants. The permit also contains several special conditions that require Dow Chemical to conduct chemical wastewater characterizations, a fish biouptake study, acute and chronic bioassays and toxicity studies, and a phosphorus minimization study. The results of the chemical wastewater characterization and biomonitoring studies were reviewed earlier in this report.

As a condition of its concurrence in the issuance of NPDES permit MI0000868, USEPA Region V stated that the permit could not be considered to be a BAT permit, since it did not fully implement the requirements of the Clean Water Act with respect to BAT. 31/ Accordingly, the MDNR and Region V agreed that the next NPDES permit issued to Dow Chemical would contain appropriate water quality-based effluent limitations, and technology-based effluent limitations and control programs to meet the requirements of the Clean Water Act. Region V has agreed to provide technical assistance to MDNR for developing the proposed technology-based effluent limitations and control programs.

The remainder of this section presents a brief review of the status of those effluent limitations guidelines applicable to the Dow Chemical - Midland Plant; a comparison of wastewater treatment technologies installed by Dow Chemical with technologies considered by EPA for developing national effluent limitations guidelines; and a preliminary assessment of the types of treatment technologies and control programs Region V believes will be necessary for Dow Chemical to comply with Section 402 of the Clean Water Act. To protect confidential business information, only general information and data are presented in this report. A separate document that includes development of specific BAT effluent limitations will be prepared to support the proposed BAT NPDES permit for the Midland plant.

C. Applicable Effluent Limitations Guidelines and Standards

Most of the current process operations at the Dow Chemical - Midland Plant fall within the following industrial categories for which USEPA has either proposed or promulgated effluent limitations guidelines and standards:

Organic Chemicals	40 CFR Part 414
Inorganic Chemicals	40 CFR Part 415
Plastics and Synthetic Fibers	40 CFR Part 416
Pharmaceuticals	40 CFR Part 439
Pesticides	40 CFR Part 455

In addition, there are numerous nonprocess sources at the Midland plant that contribute significant volumes of contaminated wastewaters that must be treated. These sources include hazardous waste incinerator wastewaters, landfill leachates, utilities, tank car washings, the riverbank ground water collection system, and sanitary wastewaters. Dow Chemical also treats wastewaters from the nearby Dow Corning silicone chemicals plant. Aside from the Dow Corning wastewaters, none of the nonprocess wastewaters at the Midland plant are limited by categorical effluent limitations or standards.

At this writing, USEPA has promulgated final effluent limitations guidelines and standards for the Inorganic Chemicals, Pesticides, and Pharmaceuticals Categories 32/ and has proposed effluent limitations guidelines and standards for the Organic Chemicals, Plastics and Synthetic Fibers Categories, which have been combined into one category. The Agency's latest proposal of effluent limitations guidelines and standards for the Organic Chemicals, Plastics and Synthetic Fibers Category was published on March 21, 1983. 33/ That proposal included effluent limitations for several volatile and semi-volatile toxic organic pollutants. About 70% of the operations at the Midland plant fall within the Organic Chemicals, Plastics and Synthetic Fibers Category. In the absence of promulgated effluent limitations guidelines and standards for most of the process operations at the plant, the development of best available technology and best conventional technology effluent limitations and control programs must be developed largely on a best professional judgment (BPJ) basis pursuant to Section 402(a)(1) of the Clean Water Act and 40 CFR §125.3(c)(2). None of the final or proposed effluent limitations guidelines address 2378-TCDD or other PCDDs and PCDFs.

The model wastewater treatment technologies considered by USEPA in developing proposed or final BAT effluent limitations guidelines for the industrial categories relavent to production operations at Dow Chemical are summarized in Table 42.

D. Comparison of Dow Chemical Wastewater Treatment Technologies with EPA Model Wastewater Treatment Technologies

As noted in Section V, the Dow Chemical - Midland Plant is a large chemical manufacturing complex comprised of numerous separate production facilities covering about 1500 acres. Chemical manufacturing at the site began prior to 1900. The plant has undergone continual rebuilding over the years as the product mix was changed in response to market developments. For most of its recent history, the Midland plant has had a central sewerage and wastewater treatment system. As shown in Figure 4, the existing wastewater treatment facilities are comprised of equalization, primary settling, biological treatment (completely mixed activated sludge and trickling filters), secondary settling, a three-pond system for additional suspended materials removal, and a final

TABLE 42

National Effluent Limitations Guidelines
Model BAT Wastewater Treatment Technologies

Category	Summary of Model Treatment
Final ELGs	
Inorganic Chemicals	No discharge; return of spent brines to mined formation
Pesticides	In-process recovery and control; biological treatment
Pharmaceuticals	In-process recovery and control; biological treatment
Proposed ELGs	
Organic Chemicals, Plastics, and Synthetic Fibers	In-process recovery and control; biological treatment

Sources:
1. USEPA Final Development Document for Effluent Limitations Guidelines and Standards for the Inorganic Point Source Category, EPA 440/1-82/007, June 1982.
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3. USEPA Final Development Document for Effluent Limitations Guidelines and Standards for the Pesticides Chemicals Category, EPA 440/1-85/079, September 1985.
4. USEPA Final Development Document for Effluent Limitations Guidelines and Standards for the Pharmaceutical Manufacturing Point Source Category, EPA 440/1-83/084, September 1983.
5. USEPA Proposed Development Document for Effluent Limitations Guidelines and Standards for the Organic Chemicals and Plastics and Synthetic Fibers Point Source Category, EPA 440/1-83/009b, February 1983.

effluent polishing filter. In addition, there are varying levels of pretreatment installed at the production processes. The sewerage system at the Midland plant is constructed to collect all process wastewaters, nonprocess wastewaters, noncontact cooling waters, sanitary wastewaters, and surface runoff from the plant site. Most of the sewer system is enclosed underground piping; however, there are several sections of open ditches or conduits which are considered by Region V to be regulated surface impoundments for purposes of RCRA.

Table 43 presents a summary of wastewater flows at the Dow Chemical - Midland Plant. These data are based upon information developed by Dow Chemical and supplied to Region V and MDNR in accordance with the terms of a consent order for Civil Action No. 83-CV7011BC. 3/ The data were current as of August 1984. Current year (1986) data will be used to develop proposed BAT effluent limitations for the next NPDES permit for the Midland plant. These data indicate that only about one-third of the total discharge from outfall 031 is process wastewater from production operations potentially regulated by USEPA categorical effluent limitations guidelines; about one-third of the accounted for discharge is comprised of noncontact cooling; and the balance is attributed to noncategorical sources.

The central (main plant) wastewater treatment system installed by Dow Chemical includes all of the unit operations considered as part of the model wastewater treatment facilities by USEPA for treatment of wastewaters from organic chemicals, plastics, and pharmaceutical processes. The pond system and final effluent polishing filter installed by Dow Chemical are additional treatment facilities not included in USEPA's model treatment facilities. While the "end-of-pipe" treatment facilities installed at the Midland plant are equivalent to or exceed those facilities considered as best available technology (BAT) by USEPA, data presented in this report suggest that in-process controls for several organic chemical processes are not equivalent to BAT, even when considered with superior end-of-pipe treatment. This is particularly true of certain volatile organic chemical pollutants (see Table 3). Also, data presented herein indicate the continued presence of residual levels of toxic semi-volatile organic pollutants (e.g., pentachlorophenol, chlorinated benzenes), despite termination of both production and substantial usage of these materials at the Midland plant. These data suggest that scattered or diffuse sources throughout the plant (sewer sludges, contaminated soils, pond sediments) may be contributing residual discharge loadings to the outfall.

USEPA promulgated effluent limitations guidelines requiring zero discharge for many inorganic chemical production processes including some of those at the Midland plant. The model technology for these processes includes reinjection of spent brines to underground formations and reuse and recovery of process materials. According to Dow Chemical records, zero discharge of pollutants had not been achieved at certain inorganic chemical processes at the Midland plant. The status of these processes will be reviewed in light of the recent termination of brine mining operations by Dow Chemical.

Dow Chemical has installed process-specific treatment systems for certain pesticide processes consistent with those considered by USEPA when developing the pesticide effluent limitations guidelines. The current NPDES permit includes process-specific limits for the 2,4-D process. 13/

TABLE 43

Dow Chemical Wastewater Flow Summary

	Typical Wastewater Flow		
	Gal/Min	MGD	m^3/Day
Categorical Processes			
Organic Chemicals	697	1.00	3785
Plastics	1343	1.93	7305
Inorganic Chemicals	156	0.22	833
Pesticides	47	0.07	265
Pharmaceuticals	22	0.03	114
SUBTOTAL	2265	3.25	12302
Dow Corning	1200	1.73	6548
Noncategorical Process Wastewaters			
Incinerator	1880	2.71	10257
Landfill Leachates	43	0.06	227
Tank Car Washings	35	0.05	189
River Bank Collection	180	0.26	984
R & D Services	350	0.50	1893
General Plant Services	320	0.46	1741
Other (including sanitary)	116	0.17	643
SUBTOTAL	2924	4.21	15934
Other Wastewaters	674	0.97	3671
Storm Water	910	1.31	4958
Noncontact Cooling Water	3727	5.37	20325
TOTAL	11700	16.84	63738

Source: Dow Chemical Company, August 24, 1984.

E. Best Available Technology Considerations

As noted above, the wastewater treatment facilities installed by Dow Chemical are, to a large extent, consistent with process control and wastewater treatment technologies considered by USEPA during development of final and proposed national effluent limitations guidelines and standards. However, several factors preclude a relatively simple application of categorical effluent limitations and guidelines to develop BAT permit conditions. These include the size and complexity of the site; the historical development of central sewerage and wastewater treatment facilities; the volume of wastewater from noncategorical sources; the presence of certain toxic pollutants not regulated by effluent limitations guidelines (e.g., PCDDs, PCDFs); and, lack of final effluent limitations guidelines for the organic chemicals and plastics operations, comprising about 70% of the current chemical production facilities at the plant. Thus, the proposed BAT permit conditions will be largely based upon best professional judgment.

Based upon information developed as part of this study, the following factors will be considered in developing the proposed BAT effluent limitations:

1. Final Effluent Limitations Guidelines for the Pesticide Category

It is likely that process-specific effluent limitations for pesticide chemicals will be developed for each pesticide operation with a wastewater discharge. These limitations will be applied at the process discharge prior to mixing with noncontact cooling waters or wastewaters from other operations. Effluent limitations for conventional pollutants (total suspended solids, BOD_5, pH) will be considered as part of the plant-wide limitations applicable to outfall 031.

2. Final Effluent Limitations Guidelines for the Inorganic Chemicals Category

Each inorganic chemical process will be evaluated for conformance with promulgated guidelines. Where appropriate, process specific limitations (no discharge) will be applied. Inorganic chemical processes not regulated by the effluent limitations guidelines probably will be controlled by the plant-wide effluent limitations.

3. Final Effluent Limitations Guidelines for the Pharmaceutical Category

Since the central wastewater treatment system includes treatment operations beyond those considered in the development of the national effluent limitations guidelines, the plant-wide limitation for conventional pollutants will be used to regulate pharmaceutical operations.

4. Proposed Effluent Limitations Guidelines for the Organic Chemicals, Plastics and Synthetic Fibers Category

The proposed effluent limitations guidelines will be considered for the organic chemicals and plastics operations. Emphasis is expected to be placed on controls for volatile pollutants at certain processes. Semi-volatile pollutants will largely be controlled by plant-wide limitations for specific toxic organic pollutants and conventional pollutants. If final effluent limitations guidelines for organic chemicals and plastics operations are promulgated prior to issuance of the next NPDES permit for the Midland plant, the final guidelines will be considered in development the final NPDES permit limits.

5. Nonprocess Wastewaters

Wastewaters from nonprocess operations (contaminated ground water, utilities, landfill leachates, tank car washings, R & D services, sanitary wastewater) will be controlled by plant-wide limitations and best management practices programs (see below).

6. Noncontact Cooling Water

In the development of plant-wide BAT effluent limitations, no allowance or effluent limitations credits will be proposed for noncontact cooling waters tributary to outfall 031. Noncontact cooling waters generally dilute process and nonprocess wastewaters.

7. Plant-Wide Effluent Limitations

Proposed BCT effluent limitations for outfall 031 for total suspended solids will be based upon performance standards for the final effluent filtration system, taking into account normal process variability. Proposed effluent limitations for toxic organic pollutants will be developed considering the proposed effluent limitations guidelines and process and nonprocess wastewater flow rates from appropriate sources. The current plant-wide effluent limitation of 10 ppq for 2378-TCDD will be reviewed in the context of BAT.

8. Best Management Practices (BMPs)

The proposed BAT NPDES permit will likely include best management practices programs developed under Section 304(e) dealing with: (1) specific chemicals that continue to be found in the effluent despite no production or substantial usage at the plant; (2) specific chemicals that are of concern from a water quality or human health standpoint as identified by MDNR; and (3) elimination of open sewers and possibly cleaning certain sections of sewers to remove accumulations of toxic chemicals.

Final NPDES permit effluent limitations for conventional, toxic, and nonconventional pollutants determined to be present at significant levels will be set either through the technology-based approach described above, or through an independent assessment of the discharge levels necessary to assure compliance with state water quality standards. The more stringent effluent limitations developed from these assessments will be governing.

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31. Sutfin, Charles H., Director, Water Division, Region V, U.S. Environmental Protection Agency, Chicago, Illinois, to (Paul Zugger, Chief, Water Quality Division, Michigan Department of Natural Resources, Lansing, Michigan) May 14, 1984, ALS, 3 pp.

32. Code of Federal Regulations (July 1985) 40 CFR Parts 415, 439 and 455.

33. Federal Register, 48 FR 11828, March 21, 1983.

34. Stringham, David A., Chief, Solid Waste Branch, Waste Management Division, Region V, U.S. Environmental Protection Agency to (J. M. Rio, Manager Environmental Services, Michigan Division, Dow Chemical U.S.A., Midland, Michigan) March 26, 1986, ALS, 3 pp. with attachments.