Polychlorinated Biphenyl Survey of the Kalamazoo River and Portage Creek in the Vicinity of the City of Kalamazoo 1972

State of Michigan
Water Resources Commission
Bureau of Water Management
Department of Natural Resources
January, 1973

DSW 029690

STLCOPCB4013652

SUMMARY

1. Significant concentrations of PCB's were found in fish from the Kalamazoo River in the vicinity of Kalamazoo during a July-August 1971 survey (Hesse and Willson, 1972).

2. Sampling of water, industrial and municipal effluents, settleable solids, and bottom sediments within the Kalamazoo area was conducted during 1972 in an attempt to isolate sources of the PCB contamination.

3. Portage Creek is a major contributor of PCB's as Aroclor 1242 to the Kalamazoo River in the City of Kalamazoo vicinity. The source of PCB's, with the possible exception of intermittent discharges from the Reed Street storm sewers, arises from the Bryant Mill Ponds' sediments and from an Allied Paper Corporation settling basin discharge between Alcott and Cork Streets.

4. The sediments in the Bryant Mill Ponds contained PCB levels up to 368 ppm. PCB's in these sediments are available for leaching to the water of Portage Creek. When the ponds were drained in July 1972, many sediments from it were washed downstream, contributing to the PCB enrichment of Portage Creek by exposing these sediments to additional water surface, erosion and decomposition.

5. The discharge from an Allied Paper Corporation settling basin contained extremely high levels of PCB's, up to 65 ppb as Aroclor 1242.

6. Another significant source of PCB contribution to the Kalamazoo River is the discharge from the Kalamazoo WWTP. Sampling is currently being conducted in the sanitary interceptor system to isolate and identify point sources.

STLCOPCB4013653

Polychlorinated Biphenyl Survey of the Kalamazoo River and Portage Creek in the Vicinity of the City of Kalamazoo 1972

INTRODUCTION

Polychlorinated biphenyls (PCB's) have recently received considerable attention as an environmental contaminant because of their persistence and chronic toxicity in an aquatic ecosystem (Risebrough and de Lappe, 1972). PCB's have been commonly used as plasticizers, flame retardants, insulating and heat exchange fluids, hydraulic fluids, and as ingredients in carbonless paper and printing inks (Reynolds, 1969; Broadhurst, 1972).

Structurally related to DDT, PCB's behave similar to DDT chemically in being relatively insoluble in water, but very soluble in lipids (Nimmo, et al, 1971). Consequently, low levels of PCB's in water from industrial sources accumulate in fish and other aquatic animals to levels that may be unsafe for human consumption (Stalling and Mayer, 1972).

The Water Resources Commission (WRC) July-August, 1971 Kalamazoo River biological survey pointed to the presence of very significant levels of PCB's in fish collected from certain sections of the Kalamazoo River (Hesse and Willson, 1972). The report indicated that the primary sources of PCB input into the Kalamazoo River system were from the cities of Kalamazoo and Battle Creek.

In 1972, further sampling was conducted in the vicinity of the City of Kalamazoo to identify possible sources of PCB loss to the environment. This report covers the 1972 investigation.

DSW 029692

STLCOPCB4013654

METHODS

Three types of samples were collected for PCB analysis in connection with this report: settleable solids, sediment (grab and core) and water (grab and composite).

Settleable solids were collected in 200 ml glass stoppered, wide mouth (4 cm dia.) bottles. The bottles were suspended approximately one foot below the water surface and left in the stream eight days before collection.

Soft bottom sediments composed of organic matter, silt and clays, were collected in bottles identical to those used for settleable solids. Core sediment samples were collected by driving a length of one inch diameter electrical conduit into soft sediments, corking the end open to the atmosphere and removing the conduit from the sediments. The core was then extracted from the conduit, with the use of a plunger-like apparatus, measured, sectioned and the individual sections placed in glass stoppered bottles. Care was taken to reduce cross contamination between sampling sites with the sampler by rinsing the conduit between core samples and by pretaking several core samples at a site before keeping one for analysis.

Water samples were collected in one gallon glass jugs with teflon lined caps. One hundred milliliters of hexane was added to the jug prior to collecting the sample to act as a PCB extractant. Stream and industrial sampling was accomplished by Water Resources Commission personnel from either the District 3 (Grand Rapids) Office or the Water Quality Appraisal Section (Lansing) as indicated on each appropriate table.

All samples were analyzed by the Water Resources Commission Pesticide Laboratory in Lansing by gas chromatography. Both Aroclor 1242 and 1254 were used as analytical standards for each sample.

SAMPLING AND RESULTS

On April 20, 1972, water samples were collected from the discharges of several industries in the Kalamazoo area considered to be possible PCB users. In addition, samples were collected from Portage Creek at Michigan Avenue and from the final effluent of the Parchment Wastewater Treatment Plant (WWTP). Portage Creek receives effluents from several industries including two paper mills in the vicinity of the Bryant Mill Ponds (Figure 1). The results of the analyses show that the PCB concentrations were below the limit of detectability for all locations except Portage Creek which contained 0.47 parts per billion (ppb) as Aroclor* 1242 (Table 1). (*Aroclor is a registered trademark of the Monsanto Company).

To determine comparative PCB concentrations over a period of time, settleable solids samplers were placed on May 17, 1972, at four locations in Portage Creek and six in the Kalamazoo River in the vicinity of the City of Kalamazoo (Figure 2). After eight days exposure the settleable solids were collected and analyzed. Significant concentrations of PCB's, ranging from 0.23 to 2.63 parts per million (ppm), occurred at all the sample sites except two upstream from the Bryant Mill Ponds in Portage Creek (Table 2). The PCB's present appeared to be largely Aroclor 1254 in the Kalamazoo River above Portage Creek, Aroclor 1242 in Portage Creek and an equal mixture of both downstream from the confluence of Portage Creek and the Kalamazoo River. This data corresponds well with the results of PCB analyses conducted on fish collected from the Kalamazoo River in 1971 (Hesse and Willson, 1971). The results also tend to verify the suspicion that the Bryant Paper Mill Ponds between Cork and Alcott Streets were holding PCB containing wastes in their sediments from previous paper recycling operations involving carbonless

DSW 029693

STLCOPCB4013655

paper and printing inks (Chester Harvey, Personal Communication).

On July 1, 1972 the City of Kalamazoo opened the gates of the Bryant Dam at Alcott Street to drain the Bryant Ponds in connection with a municipal project. Shortly after the ponds had been drained, several water and sediment samples were collected from Portage Creek and other suspect discharges to the Kalamazoo River. Although significant PCB levels were present in sediment samples from the lower Bryant Pond, 6.53 ppm, the Lake Street site which is farther downstream was much higher, 25.45 ppm (Figure 1 and Table 3). This may be explained in part by the previous draining of the Bryant Ponds and possible subsequent downstream transport of the more highly contaminated sediments. Water samples taken from Portage Creek at the face of the Alcott Street Dam (the gates had been closed on July 6 and the Bryant Ponds refilled by July 12, 1972) and at Michigan Avenue displayed a low upstream (0.16 ppb) and high downstream (3.60 ppb) PCB concentration similar to the sediment samples (Table 3). This twenty fold increase in concentration could be explained by the PCB contaminated water flowing in slugs received from an intermittent discharge, by the water accumulating PCB's in proportion to the distance it flowed over contaminated sediments, or by another source of PCB's entering Portage Creek downstream from Alcott Street. The level of PCB's in all the remaining water samples collected on July 12, 1972 were below the limit of detectability (Table 3).

In an effort to check on possible points of PCB input to Portage Creek between Alcott Street and Michigan Avenue, storm sewers on five streets were selected, with the assistance of Kalamazoo WWTP personnel, and sampled on July 25, 1972. At only one street, Alcott, were the storm sewers visibly discharging into Portage Creek. The PCB concentrations in the Alcott Street storm sewer waters were below the limit of detectability (Table 4). Both of the Reed Street storm sewer samples had high concentrations of PCB's. However, since both were partially submerged and a discharge was not discernible, it is quite probable that the water collected was largely Portage Creek water. A similar situation existed for the Bryant Street storm sewer due to broken walls that allowed Portage Creek water to flow into the sewer. Water samples collected from Portage Creek at four other street locations from Stockbridge Street downstream to the Kalamazoo River contained consistently high concentrations of PCB's ranging from 0.9 ppb to 1.3 ppb (Table 4).

Sediment collected from the east side of the lower Bryant Mill Pond contained very high levels of PCB's, 50.28 ppm, as did sites downstream at Alcott, Bryant, Reed and Stockbridge streets which ranged from 11.64 to 26.30 ppm (Table 4). A very small discharge was observed from one storm sewer that opened to Portage Creek from the West side of Lake Street. Sediments collected from the sewer contained high levels of PCB's (Table 4), but it is probable that the sediments were deposited in the sewer from previously high water levels in Portage Creek. Subsequent investigation indicated the sewer drains only a short section of a residential street.

The storm sewer outfalls investigated on July 25 were reexamined on August 31, but since the discharge conditions had not changed from the previous sampling, none of the sewers were resampled.

Water samples were collected again on August 31 from sites in Portage Creek and the Kalamazoo River in Kalamazoo. The results of the Portage Creek samples indicate that high PCB levels from 0.15 to 0.59 ppb were present from the Alcott Street Dam to the Kalmazoo River (Table 5). The PCB level in the Kalmazoo River at Michigan Avenue, upstream from the confluence with Portage Creek, was below the limit of detectability, but two downstream sites near Mosel Street had high levels, 0.28 and 0.45 ppb, indicating the influence of Portage Creek and possibly

020694 MSD

STLCOPCB4013656

the Kalamazoo WWTP on PCB contamination of the river (Figure 2 and Table 5).

Previous eight hour composite sampling of the Kalamazoo WWTP final effluent on March 28, June 6 and June 7, 1972 indicated high levels of Aroclor 1242 (1.70*, 1.92 and 1.00 ppb respectively) were being discharged to the Kalamazoo River via the WWTP outfall. (*Aroclor 1254 was also present in this sample. This would result in a slight overestimation of the Aroclor 1242 value).

Two outfalls to Portage Creek above the upper Bryant Mill Pond were also sampled on August 31. A 30-inch sewer entering the east side of the creek from the Norton Drive area had considerable discharge but no detectable PCB's. Slightly upstream and across the creek a 2-inch (polyvinylchloride pipe) discharge was sampled as an outfall of a diked Allied Paper Corporation settling basin. Although it was not a large discharge, the PCB concentration was extremely high, 56 ppb, indicating a possible significant source of PCB input to Portage Creek (Table 5).

Sediment core samples were taken from four locations in the Bryant Mill Ponds. High concentrations of PCB's, up to 368.7 ppm, appeared in specific layers in the profile of each core sample (Table 6). At three of the locations the PCB rich layer was at the top of the profile, but at the fourth location near the Alcott Street Dam, the rich layer was at the six to eight inch depth.

On November 20, 1972 the outfall from the Allied settling basin was resampled. The two inch plastic pipe had been replaced with an eight inch steel pipe, but the PCB concentration remained extremely high, 65.0 ppb as Aroclor 1242.

The Kalamazoo WWTP interceptor sewer system was sampled on December 6, 1972, to locate sources of PCB input. Eight hour composite samples from five of the main interceptor trunks plus the WWTP's raw intake and final effluent were collected. The results indicate that Aroclor 1254 was the predominant PCB form present (Table 7) unlike the previous results from the March and June effluent samples. Sampling is being continued on the interceptor trunk lines to further isolate sources.

DISCUSSION

A comparison of the results of the April 20, July 12, July 25 and August 31 sampling indicate a definite pattern to the PCB levels in Portage Creek. The PCB concentration in the water at Cork Street upstream from the Bryant Mill Pond on July 12 and August 31 (<0.1 and <0.1 ppb, respectively) and at the Alcott Street dam face on the same dates (0.16 and 0.15 ppb respectively) indicate that the PCB input from the Bryant Mill Pond sediments and the Allied Paper Corporation settling basin discharge is fairly constant (Tables 3 and 5) except when the contaminated sediments are washed from the ponds.

The bottom sediments in the upper and lower Bryant Mill Ponds appear to act as a significant reservoir of PCB's for the Portage Creek system. A layer of highly contaminated sediment probably exists throughout the ponds. The highest concentration found in a core sample is over six times higher than one of the highest concentrations reported in the literature, 61.0 ppm in Escambia River, Florida (Nimmo, et al., 1971).

The sites downstream from Alcott Street appear to have the highest levels of PCB's in the water at the time of the drawing down of Bryant Mill Ponds, and then recede to pre-drawdown levels as the sediments in the stream were leached of PCB's. This is best exemplified by the water samples collected from the Michigan Avenue site which contained 0.47, 3.60, 1.30 and 0.59 ppb PCB's on April 20, July 12 (following drawdown), July 25 and on August 31, 1972, respectively.

DSW 029695

STLCOPCB4013657

Since there was no known PCB input from storm sewers downstream from Alcott Street to Lake Street, it is probable that the increase in concentration with distance is a factor of the contaminated sediments releasing PCB's to the water.

Nisbet and Sarofim (1972) utilize the similarity between the properties of DDT and PCB's to formulate the conclusion that most PCB's released into fresh waters are adsorbed onto bottom sediments. A possible mechanism for the release of the adsorbed PCB's from sediments is indicated by Hamelink, et al. (1971). They state that the amount adsorbed (DDT and metabolites) is largely dependent on the organic matter content of the sediments. Therefore, a reduction in organic matter content of the sediments by increased decomposition in the stream would tend to release adsorbed hydrocarbons, such as PCB's to the water. The mechanism for PCB uptake by the water is probably equilibrium diffusion.

The impact of Portage Creek's PCB discharge on the Kalamazoo River is masked somewhat by the close proximity of the Kalamazoo WWTP discharge, an additional source of PCB input. However, the PCB concentrations discharged from Portage Creek are so high that the contribution to the Kalamazoo River must be considered significant.

Field work by; Jon Lauer, Aquatic Biologist
Roger Przybysz, Water Quality Investigator
Dennis Swanson, Aquatic Biologist

Chemical Analysis by: James Bedford, Chemist

Report by: Jon Lauer, Aquatic Biologist
Water Quality Appraisal Section
Michigan Water Resources Commission
Bureau of Water Management
Department of Natural Resources

January, 1973

Dist.
Portage Creek, kalamazoo River, Kalamazoo County
Toxic Materials: Polychlorinated Biphenyls

BIBLIOGRAPHY

Broadhurst, Martin G. 1972. Use and replaceability of polychlorinated biphenyls. Envir. Health Perspectives 2:81-102.

Hamelink, J. L., R. C. Waybrant, and R. C. Ball. 1971 A proposal: exchange equilibria control the degree chlorinated hydrocarbons are biologically magnified in lentic environments. Trans. Amer. Fish. Soc. 100 (2):207-214.

Hesse, John and Ronald Willson, 1972. Biological survey of the Kalamazoo River, June-August 1971. Michigan Water Resources Commission, 87 pg.

Nimmo, D. R., P. D. Wilson, R. R. Blackman and A. J. Wilson, June 1971. Polychlorinated biphenyls adsorbed from sediments by fiddler crabs and pink shrimp. Nature 231:50-52.

Nisbet, I. C. T. and A. F. Sarofim. 1972. Rates and transport of PCB's in the environment. Envir. Health. Perspectives 1: 21-38.

DSW 029696

STLCOPCB4013658

Reynolds, L. M. 1969. Polychlorinated biphenyls and their interference with pesticide residue analysis. Bull. Envir. Contam. and Toxical. 4 (3): 128-143.

Risebrough, Robert W. and Brock de Lappe. 1972. Accumulations of polychlorinated biphenyls in ecosystems. Envir. Health Perspectives 1:39-46.

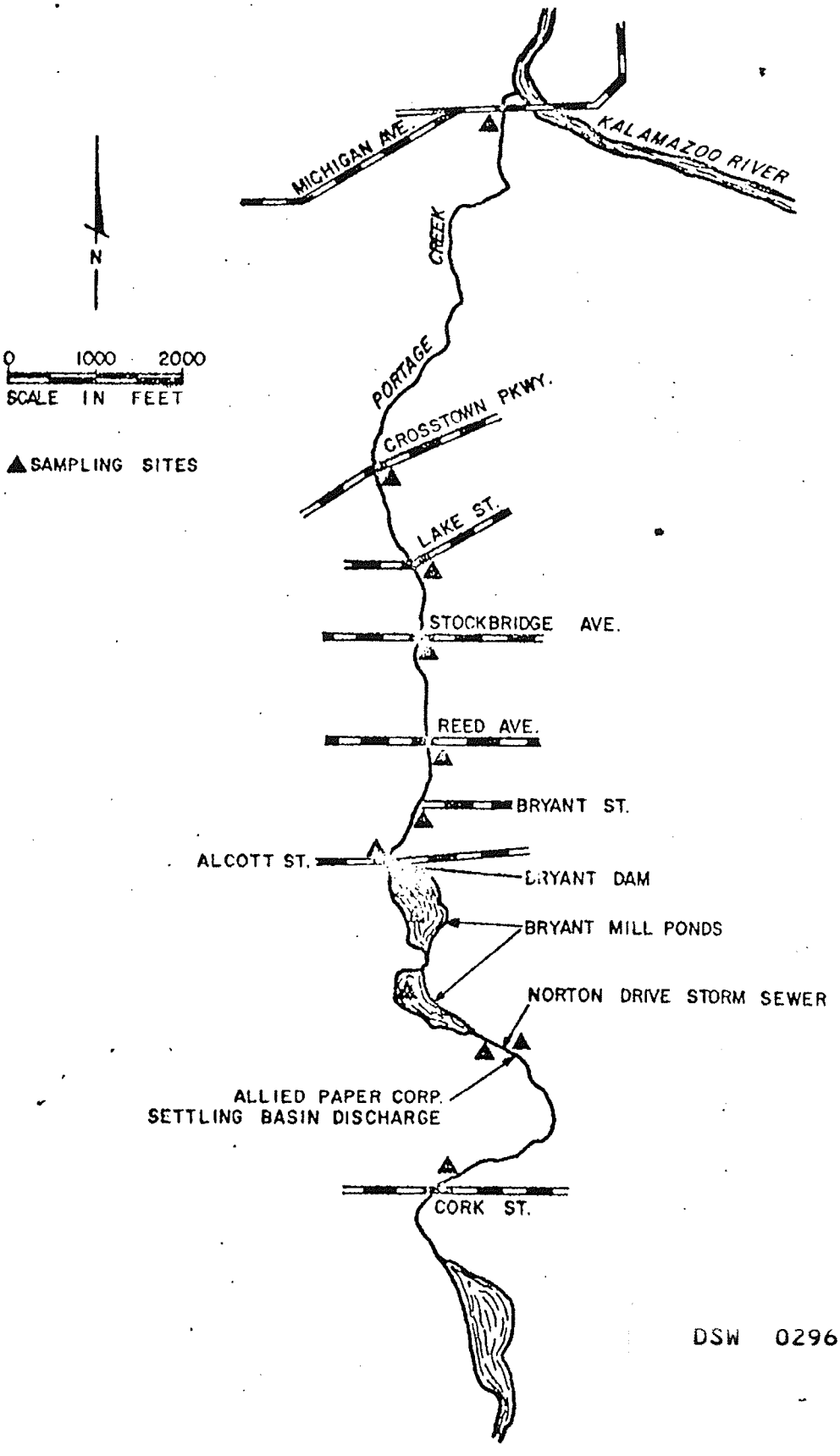
Stalling, David L. and Foster L. Mayer, Jr. 1972. Toxicities of PCB's to fish and environmental residues. Envir. Health Perspectives 1:159-164.

DSW 029697

STLCOPCB4013659

FIGURE 1

SAMPLING SITE LOCATIONS ON PORTAGE CREEK IN KALAMAZOO

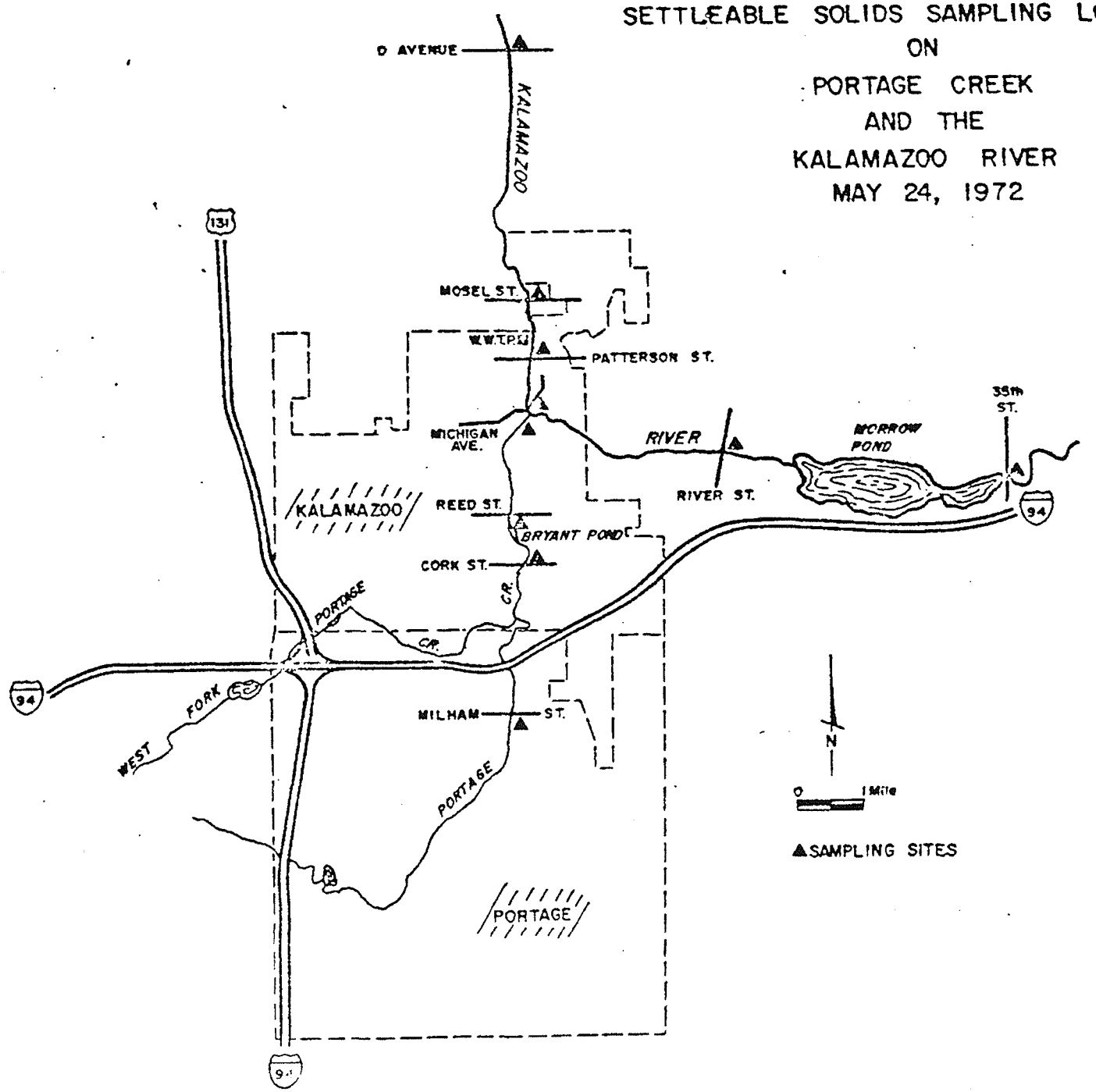


DSW 029698

STLCOPCB4013660

FIGURE 2

SETTLEABLE SOLIDS SAMPLING LOCATIONS ON PORTAGE CREEK AND THE KALAMAZOO RIVER MAY 24, 1972



DSW 029699

STLCOPCB4013661

Table 1. PCB concentrations in water grab samples collected in the City of Kalamazoo and vicinity of WRC District 3 personnel, April 20, 1972.

Location	PCB concentration in ppb, Aroclor 1242 Standard
Brown Paper Company	
White Water Discharge	
Parchment Mill #1	< 0.10
Parchment Mill #2	< 0.10
Storm Sewer Discharge	< 0.10
Checker Cab Company Discharge	< 0.10
Consumers Power Company Discharge, Kalamazoo	< 0.10
Edward Street Storm Sewer, Kalamazoo	< 0.10
Portage Creek at Michigan Avenue, Kalamazoo	0.47

DSW 029700

STLCOPCB4013662

Table 2. PCB concentrations in settleable solids collected in the City of Kalamazoo and vicinity by WRC Water Quality Appraisal personnel, May 17 - 24, 1972.

Location	Wet Weight Grams	PCB concentration in ppm Aroclor Standard 1242	1254
Kalamazoo River			
35th Street Galesburg	32.0	----	0.44
River Street Comstock	16.0	----	0.23
Michigan Avenue Kalamazoo	11.4	----	0.56
Patterson Avenue Kalamazoo	16.9	1.09*	0.42*
Mosel Street Parchment	23.5	0.89*	0.36*
D Avenue Kalamazoo Twp.	6.0	1.08*	0.40*
Portage Creek			
Milham Rd., Portage	10.9	----	0.03
Cork Street, Kalamazoo	20.5	----	0.05
Reed Street, Kalamazoo	28.0	1.33	----
Michigan Avenue, Kalamazoo	17.5	2.63	----

*The presence of both Aroclor 1242 and 1254 in these samples would result in a slight overestimation of the values.

DSW 029701

Table 3. PCB concentrations in water and sediment grab samples collected from various locations in the City of Kalamazoo and vicinity by WRC District 3 personnel, July 12, 1972.

Location	PCB concentration Aroclor 1242 Standard (ppb)
The Upjohn Company Cooling Water Discharge to Portage Creek	< 0.10
Allied Paper Corporation Monarch Discharge to Portage Creek	< 0.10
Hydreco Discharge to Kalamazoo River	< 0.10
Consumers Power Company Morrow Plant Cooling Water Discharge to Kalamazoo River	< 0.10
Portage Creek	
Cork Street	< 0.10
Alcott Street (from face of Bryant Dam)	0.16
Michigan Avenue	3.60
Davis Creek	
Lake Street	< 0.10
Sediment from Portage Creek	(ppm wet weight)
Lower Bryant Mill Pond	6.53
Lake Street	25.45

DSW 029702

STLCOPCB4013664

Table 4. PCB concentrations in water and sediment grab samples collected from Portage Creek by WRC Water Quality Appraisal personnel, July 25, 1972.

Location	PCB concentration Aroclor 1242 Standard (ppb)
Portage Creek Water Samples	
Alcott Street	
West Sewer	< 0.10
East Sewer	< 0.10
Bryant Street	
*East Sewer	0.59
Reed Street	
*West Sewer	0.42
*East Sewer	1.20
Stockbridge Street	0.90
Lake Street	1.00
Crosstown Parkway	1.00
Michigan Avenue	1.30
Portage Creek Sediment Samples	(ppm wet weight)
Lower Bryant Mill Pond	50.28**
Alcott Street	26.30
Bryant Street	11.64
Reed Street	24.85
Stockbridge Street	18.78
*Lake Street (West Sewer)	12.05

*Portage Creek water and sediment probable source of PCB contamination. See text for details.

**Aroclor 1254 was also present in this sample. This would result in a slight overestimation of the Aroclor 1242 value.

DSW 029703

Table 5. PCB concentrations in water samples collected from various locations in the City of Kalamazoo and vicinity by WRC Water Quality Appraisal personnel, August 31, 1972.

Location	PCB concentration Aroclor 1242 Standard (ppb)
Portage Creek	
Cork Street	< 0.10
Upper Bryant Mill Pond (upstream end)	< 0.10
Alcott Street (from face of Bryant Dam)	0.15
Bryant Street	0.42
Reed Street	0.48
Stockbridge Street	0.22
Michigan Avenue	0.59
Kalamazoo River	
Michigan Avenue	< 0.10
Mosel Street (Upstream 300 m.)	0.28
(Downstream 300 m.)	0.45
Discharges to Portage Creek	
30" storm sewer from Norton Drive Area	< 0.10
2" discharge from Allied Paper Corp. settling basin	56.0

*Aroclor 1254 was present in all the samples. This would result in a slight overestimation of the Aroclor 1242 value.

DSW 029704

STLCOPCB4013666

Table 6. PCB concentrations in sediment core samples collected from four locations in the Bryant Mill Ponds on Portage Creek by WRC Water Quality Appraisal personnel, August 31, 1972.

Location	PCB Concentrations ppm Dry Weight-1242 Aroclor Standard-Wet Weight	
Bryant Mill Ponds		
West Side, Upper Pond-14" core		
0-2" depth interval	368.7	106.7
6-8" depth interval	10.0	3.4
12-18" depth interval	< 0.5	< 0.2
Northeast Side, Lower Pond-10" core		
0-2.5" depth interval	107.5	32.4
2.5-5.0" depth interval	79.6	25.8
5.0-7.5" depth interval	61.0	27.3
7.5-10.0"depth interval	65.6	25.7
Northwest Side, Lower Pond-14" Core		
0-3.5" depth interval	88.0	38.6
3.5-7.0" depth interval	5.1	2.7
7.0-10.5" depth interval	5.0	1.7
10.5-14.0" depth interval	6.6	2.5
Southwest Side, Lower Pond-14" Core		
0-2.5" depth interval	8.5	2.6
2.5-5.0" depth interval	28.3	9.5
5.0-8.0" depth interval	6.4	2.8
8.0-11.0" depth interval	75.6	22.1
11.0-14.0" depth interval	13.4	6.6

DSW 029705

STLCOPCB4013667

Table 7. PCB concentrations in eight hour composite samples of sewage collected from the Kalamazoo WWTP interceptor sewer system and plant site by Kalamazoo Public Works personnel, December 6, 1972.

Location	PCB Concentration ppb Arcolor 1254 Standard
Patterson Street Sewer (West) serving near N. W. city	0.34
Red Arrow Interceptor serving Galesburg, Portage, S. E. City	0.87
Spring Valley Interceptor serving N. E. City	0.34
North Limits Sewer serving N. City and Kalamazoo Twp.	0.21
Industrial Sewer serving Three Paper Companies	0.86*
Raw Intake, Kalamazoo WWTP	0.49*
Final Effluent, Kalamazoo WWTP	0.19*

*Hexane was lost from the samples, reducing the PCB concentration actually present.

DSW 029706

STLCOPCB4013668