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WATER POLLUTION ASPECTS OF POLYBROMINATED BIPHENYL PRODUCTION: RESULTS
OF SURVEYS IN THE PINE RIVER IN THE VICINITY OF ST. LOUIS,
MICHIGAN

by

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ABSTRACT

A study was conducted to evaluate the extent of water contamination by a flame retardant chemical downstream from its major production site at St. Louis, Michigan. PBB's were measured in the plant effluent, river water, fish and duck tissue, and sediments of the Pine River. Fish uptake rates and bioconcentration factors were estimated. Concentrations in local fish populations were sufficiently high that a health warning against consumption has been issued.

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INTRODUCTION

A recent incident in Michigan involving accidental contamination of animal feeds has triggered considerable environmental and human health concern over a chemical belonging to the class of compounds called polybrominated biphenyls (PBB).

During mid-1973 a polybrominated biphenyl flame retardant product called FireMaster BP-6 was apparently accidentally substituted for a magnesium-oxide based feed additive called NutriMaster produced by the same company. Abnormal animal response to the contaminated feed concentrate led to extensive studies on the affected animals. Symptoms included hair loss and roughening, abnormal hoof growth, losses in weight and milk production, excessive abortions and stillbirths, loss of vitality of adults and offspring and finally death in some cases. The cause of the problem was not discovered until April, 1974. By that time, thousands of farm animals had become contaminated.

U. S. Food and Drug Administration guidelines have been set at 0.3 ppm for meat and milk, and 0.05 ppm for eggs on a fat basis. Through April, 1975, 15,942 cattle, 3,469 swine, 394 sheep, over 1 million chickens and tons of eggs, milk, butter, feed and other products have been destroyed because of PBB contamination.

Epidemiological studies of humans exposed to PBB's through consumption of contaminated foods are currently being conducted by the Michigan Department of Public Health.

Detailed reports of the contamination incident and epidemiological studies are to be presented at the 9th Annual Conference on Trace Substances in

Environmental Health in June (Isleib and Whitehead; Humphrey, Hayner and Budd, 1975).

The toxicity and persistence of PBB's, as exhibited in the agriculturally related incident described above, stimulated Michigan's Department of Natural Resources, Bureau of Water Management staff to evaluate the potential for water contamination and related environmental problems from the commercial production of this class of compounds.

Michigan Chemical Corporation, St. Louis, Michigan is the major manufacturer of polybrominated biphenyls in the United States. Production of their polybrominated biphenyl flame retardant, FireMaster BP-6, began in 1970 and totals approximately 4 million pounds annually. The company buys and markets the FireMaster BP-6 as a raw product to be used as a component of thermoplastics in a variety of applications (Table 1).

Chemically, many people have likened PBB's to the more commonly known contaminant polychlorinated biphenyls (PCB's). The main structural difference is the attachment of the halogen bromine rather than chlorine on the basic biphenyl molecule. Figure 1 shows the general structure. BP-6 is actually a mixture of brominated biphenyls with an average bromine content equivalent to about six bromine atoms per molecule. It is somewhat less soluble in water than PCB's. Michigan Chemical Corporation data lists a solubility in water of 11 parts per billion at 25°C. Unlike PCB's, FireMaster BP-6 is a solid at room temperature. It decomposes at temperatures of 300-400°C.

The fact that PBB's are not used as liquids makes them much less susceptible to general environmental contamination than PCB's. They are reportedly not easily leached from the thermoplastics in which they have been incorporated.

The potential for water pollution appears to be primarily related to production and formulation processes rather than through usage. The remainder

of this paper deals with the evaluation of contamination of the Pine River downstream from the Michigan Chemical Corporation plant where the major U.S. production of PBB's is centered. Other potential sites yet unevaluated would be receiving waters of industries who use the raw material in formulation and manufacture of thermoplastic products. Reported in this paper are results of surveys which determined concentrations of PBB's in Michigan Chemical Corporation discharges to the Pine River, river water, sediments, and resident fish and duck populations. Also included is a study of PBB uptake by introduced fish held captive in the Pine River at various locations.

MATERIALS AND METHODS

Effluent and River Water Sampling

Samples of company effluent discharges were obtained on different occasions by either grab sampling or compositing over a 48-hour period into one gallon glass containers equipped with teflon-lined caps and containing 100 milliliters (ml) of redistilled hexane as preservative.

River water samples were collected August 19-20, 1974 by a 30-hour glass composite sampler described by Zillich *et al.* (1973) and on other occasions by grab sampling into one-gallon glass containers containing 100 ml of hexane preservative.

Effluent and river water samples were analyzed at the Michigan Bureau of Water Management Water Quality Laboratory in Lansing. These were extracted with redistilled hexane (85%) and ethyl ether (15%) and analyzed with a Varian Aerograph gas chromatograph equipped with a 1/8" X 6' column packed with 5% OV-210. A tritium detector was used and operated at 225°C with an oven temperature of 210°C.

Sediments

Sediments collected on July 22, 1974, were collected with an Ekman dredge. The surface layer was skimmed off and transported to the laboratory in Whirlpak bags. Those sediment samples collected on February 20, 1975 and April 15, 1975 were hand-scooped from the river bottom into wide-mouth 250 ml glass bottles and transported to the laboratory in the collection bottles.

Sediments were analyzed at the Michigan Bureau of Water Management Laboratory using the same methods as described above for water. Extractions, however, were made using a hexane:acetone mixture at a 2:1 ratio.

Fish

Resident fish populations were sampled on June 19, 1974 by angling and were analyzed by the Food and Drug Administration, Division of Chemical Technology Laboratory in Washington, D.C. Fish sampled on July 23, 1974 were captured by gillnetting and were analyzed by the Michigan Department of Agriculture Laboratory, East Lansing, Michigan. All resident fish samples were filleted and analyzed on a wet weight basis.

A study was conducted to determine the rate of PBB uptake utilizing introduced fish placed in cages in the Pine River. Fathead minnows (Pimephales promelas) with an approximate average weight of 2 grams each were used. The minnows were obtained from the Department of Natural Resources Wolf Lake Fish Hatchery. The fish cages were constructed of 3/4 inch plywood, one-foot square and one-foot deep. Screened openings on two sides provided water circulation. Fifteen to eighteen minnows were placed in each cage.

Two cages, anchored offshore to a steel fence post, were used at each of four stations. The fish were conditioned to the ambient river water temperature for 15 to 20 minutes prior to being placed in the cages.

Station 1 was 1 1/2 miles upriver of the Michigan Chemical Corporation plant near the U.S. 27 expressway bridge. The cages were placed about 30 meters downriver of the bridge. Station 2 was located in the St. Louis Reservoir approximately 5 meters offshore of the Michigan Chemical Corporation discharge 006. Station 3 was also in the St. Louis reservoir, about 5 meters from the south shore and 50 meters east of the Michigan Chemical Corporation fence. Station 4 was approximately 1/4 mile downstream from the reservoir, 10 meters downriver of the municipal power plant dam in St. Louis.

The upstream station served as a control, while the two stations in the reservoir were in the immediate area of process water discharges. Station 4 allows for dilution with all the reservoir water and mixing as the river flows over the dam.

Samples of minnows were collected at the time of introduction and after one-week and two-week periods of exposure. Each sample consisted of a composite of 10-15 whole minnows. The minnows were individually wiped with dry paper towels to remove the slime layer. One-gallon grab water samples were also collected from each station at the time of introduction and at the one- and two-week sampling times. Analysis of both water and fish samples were performed in the Michigan Bureau of Water Management Chemical Laboratory in Lansing using methods comparable to those used for sediment analyses.

Ducks

Ducks killed on the Pine River below St. Louis during the first week of Michigan's 1974 duck season (October 9-16) were obtained from local hunters on January 8, 1975 to determine possible contamination of local waterfowl. The hunters had skinned, eviscerated and frozen the ducks soon after shooting them. The ducks were returned to Lansing and thawed. Breast muscle was removed,

packaged in tin foil and refrozen. The duck tissue was then analyzed by Gas Liquid Chromatography at the Michigan Department of Agriculture Laboratory, East Lansing.

RESULTS

Michigan Chemical Corporation Discharges

Figure 2 shows the locations of the various Michigan Chemical Corporation discharges to the impoundment on the Pine River at St. Louis. Eight of these outfalls have been sampled for polybrominated biphenyl (as BP-6) contamination (Table 2).

The highest concentrations found in any of the discharges were detected by company sampling of outfall 005 in 1972 prior to any knowledge of the hazards of this chemical. Values ranged from 98 to 503 $\mu\text{g/l}$. The source of contamination was within the BP-6 production area where particles of the material were getting into the cooling water during the flaking operation. To solve the problem additional shielding was added to the flaker and a brine chiller was installed to recirculate the flaker cooling water. Condenser cooling water was recycled to outfall 006. Outfall 005 was then abandoned. By having taken these actions the company officials believed all losses to the river had been eliminated.

No further monitoring of outfalls for PBB's was conducted until the Michigan Bureau of Water Management investigation began in June, 1974 following the discovery of this chemical's effects on the accidentally contaminated farm animals. Our initial sampling was directed at outfall 006 since this was the only outfall from the BP-6 production area. The highest concentration detected in this outfall was 10.6 $\mu\text{g/l}$.

It was not until September, 1974 that additional outfalls not directly associated with BP-6 production were tested. Six additional outfalls (002,

003, 004, 008, 013 and 014) were found to contain measurable PBB concentrations with some far exceeding concentrations detected in outfall 006. Investigations that followed showed hydrobromic acid, produced as a by-product in the BP-6 operation, and utilized in several other production areas to be the probable source of contamination in five of the six other contaminated outfalls. The only explanation of the slight contamination in outfall 008 was that that process received intake water from the impoundment a short distance from contaminated outfalls 013 and 014.

Based upon average flow rates and concentrations found for the seven contaminated outfalls, the quantity of PBB being discharged to the river was estimated to be approximately 0.25 pounds per day.

River Water

The Pine River is part of the Saginaw River system which flows into Saginaw Bay of Lake Huron. The Pine River flows through portions of Isabella, Gratiot and Midland Counties and joins the Chippewa River 2 miles upstream from its confluence with the Tittabawassee River at Midland. Michigan Chemical Corporation, St. Louis, is located on the Pine River approximately 25 river miles upstream from the Pine's confluence with the Chippewa. The Pine River at St. Louis has a once in ten years, seven day low flow of about 27 cfs.

Water sampling in the Pine River downstream from the Michigan Chemical Corporation plant has shown detectable concentrations as far as 8 miles below St. Louis at Magruder Road. Concentrations ranged from 3.2 µg/l in the impoundment 75 yards downstream from the plant to 0.01 µg/l at Magruder Road. Concentrations at stations 12 and 20 miles downstream (Meridian Road and Prairie Road, respectively) were below the sensitivity limit of 0.01 µg/l. None was detected at two stations in the Tittabawassee River downstream from the confluence of the Pine and Chippewa Rivers.

Stream Sediments

Concentrations of PBB's in stream sediments collected throughout the Pine River from 7 miles upstream of the Michigan Chemical Corporation plant and downstream to its confluence with the Chippewa River and from two sites on the Tittabawassee River are presented in Table 4.

Concentrations upstream from the Michigan Chemical Corporation plant were all less than the sensitivity limit of 30 µg/kg with the exception of one sample which contained 60 µg/kg collected near the M-46 highway bridge approximately 1/4 mile upstream of the plant. Upstream currents during periods of water level regulation at the St. Louis dam could possibly account for the slight contamination upstream from the plant.

PBB concentrations in nearshore sediments in the area of plant outfalls were as high as 77,000 µg/kg.

Downstream from the St. Louis Reservoir the sediment concentrations showed a gradual decline from 6,200 µg/kg 1/4 mile downstream to 100 µg/kg 24 miles downstream. Two samples from the Tittabawassee River at Midland showed the presence of PBB's but at extremely low levels (16 µg/kg and trace).

Resident Fish Tissue Analyses

Elevated PBB levels (Table 3) have been found in Pine River fish ranging up to a maximum of 1.33 mg/kg in carp (whole fillets; wet weight) captured in the reservoir in the vicinity of Michigan Chemical Corporation. Downstream sampling showed a continued high concentration of 1.25 mg/kg in carp from Bagley Road, three miles downstream, and measurable concentrations (0.09 mg/kg) in carp captured eight miles downstream (Magruder Road). Concentrations of PBB's in bullheads were low at all stations. Samples of carp and drum from the Tittabawassee River did not have detectable concentrations. The extent of fish contamination, therefore, appears to be limited to the Pine River.

Caged Fish Uptake Study

Uptake of PBB's by fathead minnows (Pimephales promelas) occurred at 2 of the test stations (Table 6). No PBB's were detected in either the fish or the water at Station 1. This station was about three miles upstream of the Michigan Chemical plant. At Station 3, all the fish died from undetermined causes before one week had passed. Thus, there were not fish to be analyzed. However, PBB residues were measured in the water at this site and ranged from 0.4 to 1.3 $\mu\text{g}/\text{l}$.

At Station 2, a mean of 3.9 $\mu\text{g}/\text{l}$ was measured in the water. The range of three measurements was from 0.9 to 9.8 $\mu\text{g}/\text{l}$. After one week the fish accumulated 0.81 mg/kg measured on a wet weight basis. After two weeks the fish had retained 1.0 mg/kg PBB.

At Station 4, below the dam in St. Louis, the levels of PBB in the water were below the level of analytical sensitivity (0.1 $\mu\text{g}/\text{l}$). After one week the fish accumulated 0.2 mg/kg and after two weeks had accumulated 1.0 mg/kg.

Ducks

Concentrations of PBB's in the flesh of 3 duck species (Mallards, Teal and Wood Duck) collected within 2 miles of the Michigan Chemical plant ranged from 5.3 to 29 mg/kg (fat basis) and are presented in Table 7.

DISCUSSION

It was not known immediately whether PBB concentrations detected in the river water were a significant environmental hazard. Concentrations found in resident fish were sufficiently high to indicate a problem, however. The U.S. Food and Drug Administration (FDA) has not established a guideline for allowable

PBB concentrations in fish intended for human consumption. Considering the 0.3 mg/kg (ppm) FDA limit for meat on a fat basis, fish with 1.33 mg/kg (whole fillet basis) appear extremely high. Converting the 1.33 to a fat basis would increase it to approximately 30 mg/kg. On November 21, 1974 Michigan Department of Public Health officials issued a warning against consumption of fish from the contaminated zone of the Pine River.

The PBB uptake study using introduced fish held in cages indicated that extremely low levels of PBB in the water are sufficient to cause unacceptable concentrations in fish flesh in a very short period of time. At Station 4, where water concentrations remained consistently less than 0.1 $\mu\text{g}/\text{l}$, the caged fish accumulated 1,000 $\mu\text{g}/\text{kg}$ in their tissue. This represents a concentration factor of greater than 10,000 fold with just two weeks of exposure. Bioaccumulation of PBB's, therefore, appears comparable to polychlorinated biphenyls (PCB's). Hansen, et al., (1971) reported PCB concentration factors in two fish species to be 10,000 to 50,000 times the exposure levels in water.

Ducks apparently also have a high capacity for accumulating PBB's in their tissue. All duck samples analyzed from the Pine River had PBB concentrations exceeding the FDA guideline of 0.3 mg/kg.

On November 20, 1974, the Michigan Chemical Corporation temporarily suspended all production of polybrominated biphenyls pending alterations of wastewater disposal. This action was taken voluntarily by the company upon verbal request by the Michigan Bureau of Water Management. Even with all production and utilization of by-products halted, concentrations of PBB's in the discharges to the Pine River continue to be high on occasions. Although erratic, concentrations as high as 150 $\mu\text{g}/\text{l}$ have been detected following shutdown. Explanations for continued losses include release of PBB's accumulated in the discharge pipes and infiltration of surface water which accumulates PBB's

from contact with contaminated soils. Soil samples collected from the bagging and loading areas were found to have 3,500 and 2,500 mg/kg PBB's respectively. Studies to determine possible corrective measures are currently underway.

While this paper has dealt solely with water contamination from a source of commercial production of PBB's, contamination may also occur at industrial sites using the raw material. Investigations should be initiated at these sites.

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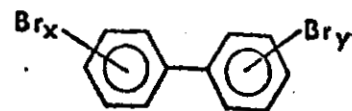


Figure 1. Generalized drawing of a Polybrominated Biphenyl molecule where x and y represent 1 to 5 attached Bromine atoms.

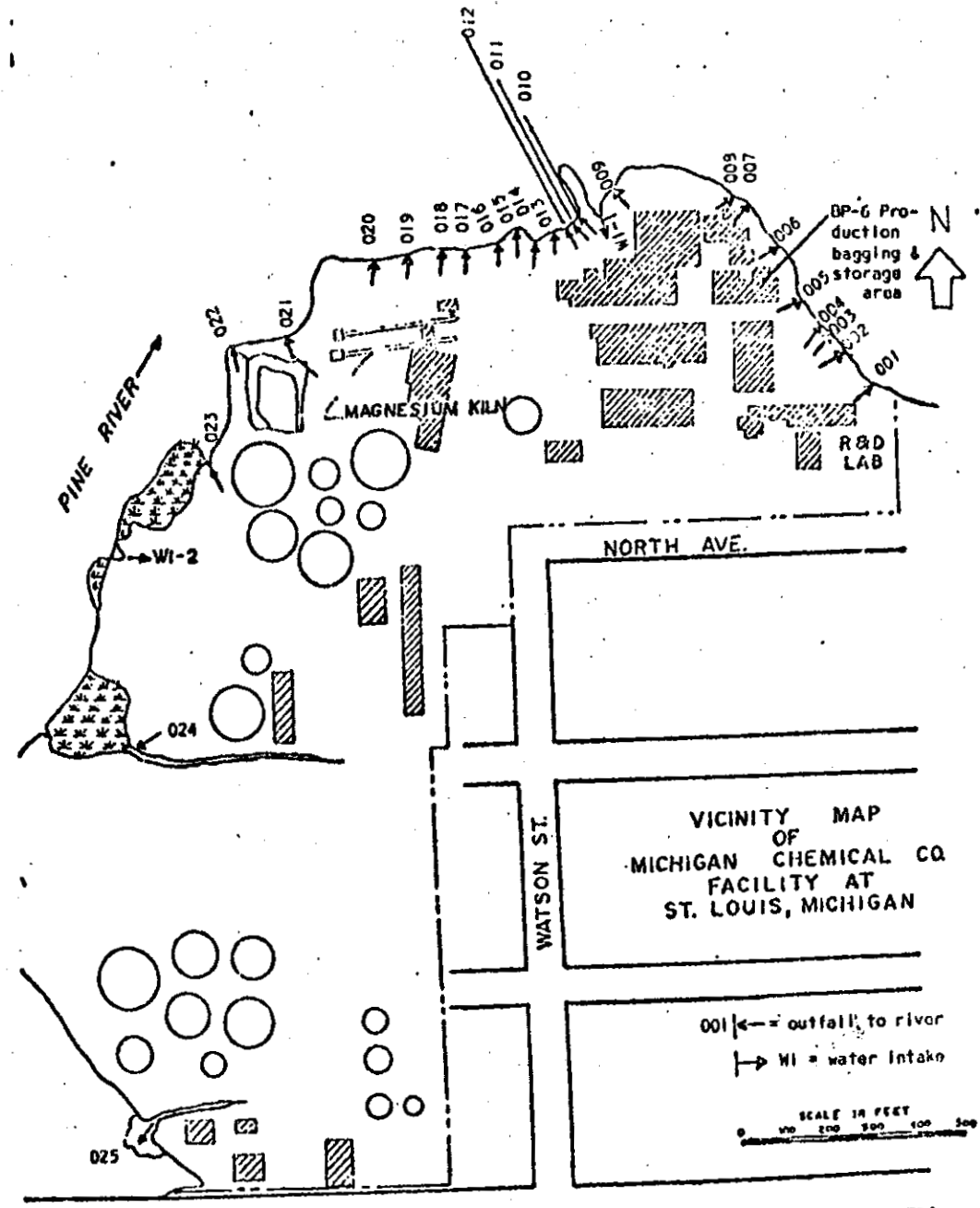


Figure 2. Michigan Chemical Corporation outfalls (NPDES No.) to the St. Louis Reservoir on the Pine River at St. Louis, Michigan.

Table 1. Industrial uses^a of FireMaster BP-6.

Industry Type	Products	Percent of Total Production
Business Machines and Industrial Equipment	Typewriter, calculator and micro-film reader housings	48
Electrical	Radio and TV parts, thermostats, shaver and hand tool housings	35
Fabricated Products	Projector housings, movie equipment cases	12
Transportation	Miscellaneous small automotive parts, i.e. electrical wire connectors, switch connectors, speaker grills	1
Miscellaneous	Components for industrial equipment	4

^a As presented by A. Fred Korst, Vice President of Research and Development, Michigan Chemical Corporation to the Michigan Environmental Review Board, September 23, 1974.

Table 2. Polybrominated Biphenyls in Michigan Chemical Corporation discharges to the Pine River, August 2, 1972 to February 20, 1975. Numbers in parentheses () represent sampling after temporary shutdown, November 20, 1974.

NPDES Discharge #	MBM ¹ Sampling		MCC ² Sampling	
	No. of Samples	Concentration Range (g/l)	No. of Samples	Concentration Range (g/l)
001	---	---	(1)	(1.2)
002	1 (5)	104.0 (0.6-150.0)	7 (17)	<1.0-74.1 (<1.0-25.8)
003	1 (1)	1.6 (34.0)	4 (14)	19.0-97.0 (<1.0-131.0)
004	1 (2)	<0.1 (1.8-38.0)	1 (13)	<1.0-0.4 (<1.0-41.8)
005 ^a	---	---	5 (---)	98.0-503.0 (---)
006 ^{a*}	4 (---)	0.1-3.6 (---)	6 (---)	<1.0-10.6 (---)
006 ^{a**}	1 (6)	6.6 (<0.1-4.3)	12 (20)	<1.0-10.2 (<1.0-1.0)
008	1 (---)	0.7 (---)	3 (13)	<1.0- 1.0 (<1.0-3.8)
013	1 (2)	10.0 (<0.1-<0.1)	10 (15)	<1.0-15.8 (<1.0-4.5)
014	1 (14)	36.0 (0.5-1.6)	9 (16)	<1.0-13.3 (<1.0-4.2)

¹ Michigan Bureau of Water Management

² Michigan Chemical Corporation

^a Outfall Abandoned July, 1973

^{a*} Cooling Water from BP-6 Production; No discharge after 11-20-74

^{a**} Combined Refrigeration and BP-6 Cooling Water

Table 5. Concentrations of Polychlorinated Biphenyls (PBB) in fish tissue (whole fillet; wet weight basis).

Sampling Date	Species	Location	% Fat	Concentration (ppm)
6/19/74	carp ¹	Pine R. (Reservoir below Mich. Chem.)		0.85
6/19/74	bullhead ¹	Pine R. (Reservoir below Mich. Chem.)		Trace (<0.05)
6/19/74	drum ¹	Tittabawassee R. (Riverside Blvd.)		Not detected
6/19/74	carp ¹	Tittabawassee R. (Riverside Blvd.)		Not detected
7/23/74	carp ² (3 fish composite)	Pine R. (Vicinity of Leonard Refinery)		Not detected
7/23/74	carp ² (2 fish composite)	Pine R. (Reservoir below Mich. Chem.)		1.33
7/23/74	carp ² (3 fish composite)	Pine R. (Below Main St. bridge)		0.18
7/23/74	bullhead ²	Pine R. (Vicinity of Leonard Refinery)	0.31	0.20
7/23/74	bullhead ²	Pine R. (Reservoir below Mich. Chem.)	0.21	0.03
7/23/74	carp ² (3 fish composite)	Pine R. (Below Main St. bridge)	3.1	1.15
7/23/74	carp ² (3 fish composite)	Pine R. (Bagley Road)	4.27	1.26
7/23/74	carp ² (2 fish composite)	Pine R. (Hagrudder Rd.)	0.9	0.09

¹ Analysis by U. S. Food and Drug Administration laboratory, Washington, D.C.
² Analysis by Michigan Department of Agriculture laboratory, East Lansing, Michigan.

Table 6. Water concentrations and caged fish^a uptake levels of PBB in the Pine River, near St. Louis, Michigan.

Station	Date	PBB in Water (µg/l)	PBB in Fish mg/kg
1. Pine River at U.S. 27	10-4-74	<0.1	<0.1
	10-11-74	<0.1	<0.1
	10-18-74	<0.1	<0.1
2. St. Louis reservoir at Michigan Chemical discharge 006	10-4-74	0.9	<0.1
	10-11-74	9.8	0.8
	10-18-74	1.1	1.0
3. St. Louis reservoir east of Michigan Chemical	10-4-74	0.4	100% mortality
	10-11-74	0.5	
	10-18-74	1.3	
4. Pine River below dam in St. Louis	10-4-74	<0.1	<0.1
	10-11-74	<0.1	0.2
	10-18-74	<0.1	1.0

^afathead minnows (*Pimephales promelas*)

Table 7. PBB concentrations in ducks shot on the Pine River, St. Louis, Michigan, 1974.

Species	No. in composite	Distance below St. Louis (miles)	Percent Crude Fat	PBB (mg/kg)	
				Whole Weight Basis	Fat Basis
Mallard	1	0 - 1	2.76	0.64	23
Mallard	2	1 - 2	1.13	0.06	5.3
Teal	3	0 - 1	6.14	1.8	29
Wood Duck	3	1 - 2	1.36	0.29	21

Table 3. Concentrations of polybrominated biphenyls (PBB) in river water samples.

Date	River	Location	PBB Concentration ($\mu\text{g/l}$)
6/6/74	Pine	Reservoir below Michigan Chemical Company	3.2
8/20/74	Pine	Cheesman Rd.	0.01
8/20/74	Pine	Main St., St. Louis	0.04
8/20/74	Pine	McGregor Rd.	0.07
8/20/74	Pine	Bagley Rd.	0.02
8/20/74	Pine	Magruder Rd.	0.01
8/20/74	Pine	Meridian Rd.	<0.01
8/20/74	Pine	Prairie Rd.	<0.01
8/19/74	Tittabawassee	Bridge at Dow plant	<0.01
8/19/74	Tittabawassee	Washington Rd., Freeland	<0.01

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Table 4. Polybrominated biphenyls in sediments of the Pine River and Tittabawassee River, July, 1974 - April, 1975. Concentrations in $\mu\text{g/kg}$ dry weight.

Station Description	Sampling Date	PBB's ($\mu\text{g/kg}$)
Pine River & Harrison Rd. Bridge, 7 miles upstream from St. Louis Launching Site	7-22-74	<30
Alma Reservoir at Alma Boat Launching Site	7-22-74	<30
Pine River & Republic St. below Alma Ship	7-22-74	<30
St. Louis Reservoir near trailer park & U.S. 27, 1 1/2 miles upstream from Michigan Chemical	7-22-74	<30
St. Louis Reservoir & H-46, 1/4 mile upstream of Michigan Chemical	7-22-74	60
Pine River Reservoir near outfall 023 (truck wash area)	2-20-75	37,000
Pine Reservoir near outfall 020	2-20-75	1,100
Pine River Reservoir near outfall 008	2-20-75	77,000
Pine River Reservoir near outfall 002	2-20-75	14,000
St. Louis Reservoir 75 yds downstream from plant boundary, 30 yds off south shore	7-22-74	9,000
St. Louis Reservoir 75 yds downstream from plant boundary, 50 yds off north shore	7-22-74	4,800
Pine River below St. Louis Reservoir at Main St. Bridge, 1/2 mile downstream of Michigan Chemical	7-22-74	6,200
Pine River & McGregor Rd. Bridge, 2 miles downstream from St. Louis Reservoir	7-22-74	1,600
Pine River & Bagley Road Bridge, 3 miles downstream	7-22-74	430
Pine River & North County Line Rd. Bridge, 4 miles downstream	7-22-74	440
Pine River & Magruder Rd. Bridge, 6 miles downstream	7-22-74	270
Pine River & Porter Rd. Bridge, 11 miles downstream	7-22-74	300
Pine River & Meridian Rd. Bridge, 17 miles downstream	7-22-74	90
Pine River & Prairie Rd. Bridge, 24 miles downstream	7-22-74	100
Tittabawassee River 1/4 mile downstream from Chippewa confluence	4-15-74	16
Tittabawassee River 1/2 mile downstream from Chippewa confluence	4-15-74	Tr.

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