

# Polybrominated Biphenyl (PBB) Contamination of the Pine River, Gratiot, and Midland Counties, Michigan

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Michigan Chemical Corporation, St. Louis, Michigan manufactured PBB from 1970 until November 20, 1974. Studies in 1974 showed significant quantities of PBB in effluent discharged from the facility and in water, fish, ducks, and sediments from the Pine River. Fish uptake rates and bioconcentration factors were estimated. Followup surveys over the three year period since the termination of PBB production indicate a decline in PBB loadings to the river but no significant corresponding decline of PBB levels in sediments, fish and duck tissue. A Michigan Department of Public Health warning against consumption of Pine River fish from St. Louis downstream to its confluence with Chippewa River remains in effect.

## Introduction

Michigan Chemical Corporation, St. Louis, Michigan was the major manufacturer of polybrominated biphenyls (PBB) in the United States. Production of their PBB flame retardants, FireMaster BP-6 and FireMaster FF-1, totalled approximately 11,323,000 lb between 1971 and 1974 (Table 1). The company produced, bagged, and marketed the raw products to be used as a component of thermoplastics in a variety of applications. Production of PBB by Michigan Chemical Corporation was voluntarily stopped on November 20, 1977 upon request by the Michigan Department of Natural Resources (DNR).

Chemically, PBB is similar to the more commonly known contaminant polychlorinated biphenyl (PCB). The main structural difference is the attachment of bromine rather than chlorine on the biphenyl molecule. FireMaster BP-6 and FF-1 are mixtures of brominated biphenyls with an average bromine content equivalent to six bromine atoms per molecule. They are somewhat less soluble in water (11 ppb at 25°C) than PCB. Unlike PCB, FireMaster BP-6 and FF-1 are solids at room temperature.

Table 1. Annual production of polybrominated biphenyl (PBB) by Michigan Chemical Corporation, St. Louis, Michigan.

	Annual production, lb	
	FireMaster BP-6	FireMaster FF-1
1971	185,000	15,000
1972	2,221,000	131,000
1973	3,889,000	0
1974	4,882,000	0
Total	11,177,000	146,000

Since PBB is not used as a liquid, it is much less likely to contaminate the environment than is PCB. PBB is also reportedly not easily leached from the thermoplastics in which it has been incorporated. Therefore the potential for contamination of the aquatic environment by PBB appears to be primarily related to production and formulation processes rather than to usage.

This report evaluates the contamination of the Pine River in Gratiot and Midland counties downstream from the Michigan Chemical Corporation plant. 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 29 river miles upstream from the Pine's confluence with the

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Chippewa. The Pine River at St. Louis has a once-in-ten years, seven-day drought flow of about 27 ft 3/sec.

Surveys were conducted from 1974 through 1977 to determine PBB concentrations in Michigan Chemical Corporation effluent discharged to the Pine River, river water and sediments, and resident fish and duck populations. PBB uptake by introduced fish held captive in the Pine River at various locations during active PBB production was also measured.

## Methods

Samples of company effluent were obtained by either grab sampling or collection of a composite sample over a 24-hr period into 1-gal glass containers equipped with Teflon-lined caps and containing 100 ml of redistilled hexane as a solvent. River water samples were collected August 19-20, 1974 by a 30 hr glass composite sampler described by Zillich et al. (1) and on other occasions by grab sampling into 1-liter glass containers.

Sediments collected on July 22, 1974, were collected with an Ekman dredge. The surface layer was removed and transported to the laboratory in Whirlpak bags. Grab samples of the surface layer of sediment were hand collected into wide-mouth 250 ml glass bottles on all other sampling dates.

Resident fish populations were collected by angling, gillnetting, or chemical treatment of the river with rotenone. All fish samples were skinless fillets. Fathead minnows (*Pimephales promelas*) with an approximate average weight of 2 g each were used in the caged fish uptake study conducted October 4-18, 1974. The minnows were obtained from the Department of Natural Resources Wolf Lake Fish Hatchery. The fish cages were constructed of 3/4-in. plywood, 1 ft square and 1 ft deep. Screened openings on two sides allowed 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 min prior to being placed in the cages. Samples of minnows (composites of 10-15 whole minnows) were collected at the time of introduction and after one-week and two-week periods of exposure. The minnows were individually wiped with dry paper towels to remove the slime layer. The fish were then wrapped in aluminum foil and frozen, until analysis. 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.

Ducks killed on the Pine River below St. Louis during October 9-16 were obtained from local hunters on January 8, 1974. 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 aluminum foil, and refrozen. On September 28, 1976 ducks were collected by Department of Natural Resources staff from Section 18, T12N, R2W downstream from St. Louis. One side of the breast (muscle and skin only) of each duck was removed after all feathers had been plucked. The other side of the breast was removed after it had been skinned. The breast portions were then grouped into composite samples according to species and whether they were plucked or skinned. In 1977, ducks were again collected by Department of Natural Resources staff from Sections 17, 18, and 19, T12N, R2W. Paired samples of skinned and plucked breast tissue were analyzed.

Company effluent and river water and sediment samples were analyzed at the Michigan Bureau of Environmental Protection Laboratory in Lansing. Effluent and river water samples were extracted with redistilled hexane:ethyl ether (85:15) and analyzed for polybrominated biphenyl residues via electron-capture gas chromatography. The instrument used was a Varian Aerograph equipped with a Nickel-63 detector. A glass column, 1/8 in. x 6 ft packed with 5% OV-210 liquid phase on QF-1 (100-120 mesh) solid support was used for all analyses. Carrier gas was purified nitrogen at a flow rate of 28.0 ml/min. Column temperature was kept isothermal at 225°C and the detector was maintained at 315°C. Peak response was measured by a Varian millivolt recorder with a 0.1 mV signal producing full scale detection. The minimal detectable level using these conditions was 0.1  $\mu\text{g/l}$ . for a 1.0 liter water sample. Spiked samples gave an average recovery of 90.0%. Sediments were analyzed, as described above for water. Sediment extractions, however, were made using a hexane:acetone mixture at 2:1 ratio.

Resident fish samples obtained on June 19, 1974 were analyzed by the Food and Drug Administration, Division of Chemical Technology Laboratory in Washington, D. C. Resident fish sampled on all subsequent dates and all duck samples were analyzed by the Michigan Department of Agriculture Laboratory, East Lansing, Michigan. Analysis of both water and fish samples in the caged fish uptake study were performed in the Michigan DNR Bureau of Environmental Protection Laboratory in Lansing using methods comparable to those used for sediment analyses.

## Results and Discussion

### Michigan Chemical Corporation Discharges

Eight Michigan Chemical Corporation outfalls to the impoundment on the Pine River at St. Louis have been sampled for polybrominated biphenyl (as BP-6). The highest concentrations found in any outfall were detected by company sampling of outfall 005 in 1972. Values ranged from 98 to 503  $\mu\text{g/l}$ . The source of contamination was within the BP-6 production area where particles of PBB were lost to the cooling water during the flaking operation. To alleviate this problem, additional shielding was added to the flaker and a brine chiller was installed to recirculate the flaker cooling water. Condenser cooling water was repiped to outfall 006. Outfall 005 was then abandoned. Company officials believed all PBB losses to the river had been eliminated by these actions.

The Michigan Bureau of Environmental Protection began an investigation in June, 1974 following the disclosure that farm animals had been accidentally contaminated and poisoned by PBB (2). Outfall 006 was sampled first, since it was the only outfall from the BP-6 production area. The highest PBB concentration detected in the effluent from 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 sampled. 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. Hydrobromic acid, produced as a by-product in the BP-6 operation and utilized in several other production areas, was thought to be the source of contamination in five of the six other contaminated outfalls. The low level PBB contamination in outfall 008 was thought to originate in intake water drawn from the impoundment a short distance from contaminated outfalls 013 and 014. Based upon flow rates and concentrations found for the seven contaminated outfalls, the quantity of PBB being discharged to the river during the September 4-5, 1974 survey was calculated to be 167 g/day (Table 2).

Even with all PBB production and utilization of by-products halted, concentrations of PBB in the effluent discharged to the Pine River continued to be high on occasions. Although erratic, concentrations as high as 150  $\mu\text{g/l}$ . were detected following shutdown. Explanations for continued losses include release of PBB accumulated in the discharge pipes and infiltration of surface water which might accumulate PBB from contact with contaminated soils. Soil samples collected from the bagging and

loading areas were found to contain 3500 and 2500  $\text{mg/kg}$  PBB, respectively. These highly contaminated soils were removed upon order of the DNR and lesser contaminated areas were sealed with asphalt to protect against further infiltration of precipitation. Most recent effluent samples show negligible PBB levels. Calculated daily loadings decreased to less than 1 g/day by August 1977 (Table 2).

### River Water

Water sampling in the Pine River downstream from the Michigan Chemical Corporation plant in August 1974 showed detectable concentrations (range 0.01-0.07  $\mu\text{g/l}$ ) as far as 12 miles below St. Louis at Magruder Road. PBB concentrations at Meridian and Prairie Roads (25 and 29 miles downstream, respectively) were less than 0.01  $\mu\text{g/l}$ . PBB, the analytical limit of detectability obtained by using 1-liter grab samples rather than larger composite samples as in 1974. Because of the reduction of analytical sensitivity, little can be said about changes in river water PBB concentrations since 1974.

### Stream Sediments

Concentrations of PBB's in stream sediments collected in 1974, 1976, and 1977 in the Pine River from 3.3 miles upstream of the Michigan Chemical Corporation plant downstream to its confluence with the Chippewa River are presented in Table 3.

Concentrations upstream from the Michigan Chemical Corporation plant were all less than the analytical sensitivity limit of 100  $\mu\text{g/kg}$  with one exception. A sample collected near the M-46 highway bridge approximately 1/4 mile upstream of the plant contained 350  $\mu\text{g/kg}$ . Upstream currents during periods of water level regulation at the St. Louis dam could account for this slight contamination upstream from the plant.

Downstream from the St. Louis Reservoir the 1974 sediment concentrations showed a gradual decline from 6200  $\mu\text{g/kg}$  immediately below the St. Louis Dam to 100  $\mu\text{g/kg}$  29 miles downstream. The results of 1976 and 1977 sediment analyses showed that PBB distributions and concentrations in the sediments have not greatly changed since 1974. In a more localized sampling of sediments near Michigan Chemical Corporation plant outfalls on January 20, 1975 PBB concentrations in nearshore sediments were as high as 77,000  $\mu\text{g/kg}$ .

Table 2. PBB concentrations and loadings discharged to the Pine River by Michigan Chemical Corporation, St. Louis, Michigan.

NPDES permit outfall number	Date	Concn, $\mu\text{g/l}$ .	Flow, MGD <sup>b</sup>	Loading, lb/day
001	September 4-5, 1974 <sup>a</sup>	< 0.1	0.022	—
002		100.0	0.096	0.080115
003		1.6	0.075	0.001001
004		< 0.1	0.104	—
006		5.6	0.410	0.019161
008		0.73	7.4	0.045081
013		10.0	0.363	0.030293
014		36.0	0.642	0.192876
Total				<u>0.368527</u> (167.3 g/day)
001	January 8, 1975	—	0.274	—
002		150.0	0.019	0.023784
003		34.0	0.770	0.218480
004		1.8	0.104 <sup>c</sup>	0.001562
006		3.3	0.455	0.012530
008		0.22	6.336	0.011633
013		< 0.1	0.190	—
014		1.6	0.490	<u>0.006543</u> 0.274532 (124.6 g/day)
001	February 20, 1975	—	0.22	—
002		4.4	0.060	0.002203
003		19.0	0.770	0.122092
004		38.0	0.104 <sup>c</sup>	0.032980
006		1.7	0.448	0.006356
008		—	6.336	—
013		< 0.1	0.188	—
014			0.455	—
Total				<u>0.163631</u> (74.3 g/day)
001	September 25, 1975	0.27	0.009	0.000020
002		2.1	0.034	0.000596
003		1.6	0.285	0.003805
004		—	—	—
006		0.22	0.476	0.000874
008		< 0.1	4.740	—
013		0.61	0.193	0.000982
014		0.17	0.376	<u>0.000533</u> 0.00681 (3.1 g/day)
Total				
001	October 6-7, 1975 <sup>a</sup>	0.31	0.013	0.000034
002		1.0	0.016	0.000134
003		2.4	0.230	0.004607
004		—	—	—
006		0.11	0.360	0.000330
008		0.11	6.800	0.006242
013		< 0.10	0.303	—
014		0.11	0.408	<u>0.000374</u> 0.011721 (5.3 g/day)
Total				
001	September 3, 1976	0.10	0.025	0.000021
002		< 0.10	0.018	—
003		0.31	0.320	0.000828
004		—	—	—
006		0.21	0.489	0.000857
008		< 0.1	5.489	—
013		0.62	0.181	0.000936
014		0.16	0.345	<u>0.000461</u> 0.003103 (1.4 g/day)
Total				

Table 2 (Continued)

NPDES permit outfall number	Date	Concn. $\mu\text{g/l}$ .	Flow, MGD <sup>b</sup>	Loading, lb/day
001	August 16, 1977	<sup>c</sup>	—	—
002		<sup>c</sup>	—	—
003		0.3	0.633	0.0016
004		—	—	—
006		<sup>c</sup>	—	—
008		< 0.1	5.458	—
013		< 0.1	0.107	—
014		< 0.1	0.397	—
Total				0.0016 (0.7 g/day)

<sup>a</sup> Industrial Wastewater Surveys (24 hr composite samples and flow calculations).<sup>b</sup> Average flow from company monthly operating report for month of sample.<sup>c</sup> October, 1974 average flow.<sup>d</sup> Discharges combined into outfall number 003.

Table 3. PBB in Pine River sediments.

Sampling station	Distance below St. Louis dam, miles	Concentration, $\mu\text{g/kg}$ (dry weight)		
		7/22/74	9/3/76	8/16/77
Republic Street downstream from Alma Reservoir	—	<100	<100	—
M-46 1/4 mile upstream from Michigan Chemical Corporation	—	<100	<100	350
St. Louis Reservoir immediately downstream from Michigan Chemical Corporation	—	4800	1100	7100
Immediately downstream from St. Louis Reservoir	—	9200	1200	500
McGregor Road	4	1600	200	400
Bagley Road	6	430	<100 (trace)	260
Magruder Road	12	270	<100	130
Meridian Road	25	<100	<100	<100
Prairie Road	29	100	<100	150

### Resident Fish Tissue Analyses

Elevated PBB levels were found in several Pine River fish species ranging up to a maximum of 1.33 mg/kg in carp (skinless fillets; wet weight) captured in the reservoir in the vicinity of Michigan Chemical Corporation (Table 4). Significant levels of PBB were present in fish from each station sampled during 1974 and 1976. No PBB was detected in fish from the Alma Reservoir which is upstream from Michigan Chemical Corporation and above a dam which prevents upstream fish movement. Samples of carp (*Cyprinus carpio*) and freshwater drum (*Aplodinotus grunniens*) collected and analyzed from the Tittabawassee River in 1974 did not have detectable concentrations of PBB. The extent of fish contamination appears to be limited to the Pine River downstream from St. Louis. There was no apparent change in PBB concentrations in fish between 1974 and 1976.

The U. S. Food and Drug Administration (FDA) has not established a tolerance limit for human consumption for PBB in fish. The tolerance limit for beef was originally established at 1.0 mg/kg (fat weight basis) and later lowered to 0.3 mg/kg. Fish with 1.33 mg/kg (wet weight basis) would contain

approximately 30 mg/kg PBB on a fat weight basis. This is obviously greatly in excess of the FDA tolerance limit for beef. On November 21, 1974 the Michigan Department of Public Health issued a warning against consumption of fish from the contaminated zone of the Pine River. This warning was renewed following a review of the 1976 fish data.

### Caged Fish Uptake Study

Uptake of PBB's by fathead minnows (*Pimephales promelas*) occurred at two of the test stations (Table 5). 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. PBB residues in the water at this site ranged from 0.4 to 1.3  $\mu\text{g/l}$ .

At Station 2, a mean of 3.9  $\mu\text{g/l}$  PBB was measured in the water. The range of three measurements was from 0.9 to 9.8  $\mu\text{g/l}$ . Seven days after introduction, the fish accumulated 800  $\mu\text{g/kg}$  measured on a wet weight basis. After two weeks exposure the fish had accumulated 1000  $\mu\text{g/kg}$  PBB.

At Station 4, below the dam in St. Louis, the

Table 4. PBB In Pine River fish, 1974 and 1976.

Year	Species	PBB concn, mg/kg <sup>a</sup>				
		Alma Reservoir	St. Louis Reservoir	Bagley Road	Magruder Road	Prairie Road
1974	Carp	ND <sup>b</sup>	ND 1.33 0.85	0.87 1.26	0.19 0.09	0.26
	White sucker	ND			0.67	
	Northern pike	ND		0.54		
	Bullhead	ND		0.45	0.78	
1976	Carp	ND	0.75	0.40	0.22 0.68	0.06 0.10
	Northern pike	ND	0.18		0.23	
	Largemouth bass	ND		0.74	0.19	ND
	Smallmouth bass					0.13
	Rockbass			0.70	0.50	0.32

<sup>a</sup> Wet weight, skinless fillets, composite samples.<sup>b</sup> None detected.Table 5. PBB uptake from the Pine River by introduced, caged fathead minnows (*Pimephales promelas*).

Station		PBB concentration, ppb <sup>a</sup>		
		10/4/74	10/11/74	10/18/74
1 Control—U.S. 27 approximately 1½ miles upstream from Michigan Chemical Corporation	Fish	<100	<100	<100
	Water	< 0.1	< 0.1	< 0.1
2 St. Louis Reservoir at Michigan Chemical Corporation approximately 5 m off outfall 006	Fish	<100	800	1000
	Water	0.9	9.8	1.1
3 St. Louis Reservoir approximately 50 m east of Michigan Chemical Corporation	Fish	100% Mortality (cause unknown)		
	Water	0.4	0.5	1.3
4 Immediately below St. Louis dam	Fish	<100	200	1000
	Water	< 0.1	< 0.1	< 0.1

<sup>a</sup> Fish µg/kg wet weight basis; water µg/l.

levels of PBB in the water were below the level of analytical sensitivity (0.1 µg/l.). After 1 week the fish accumulated 200 µg/kg, and after 2 weeks had accumulated 1000 µg/kg.

The PBB uptake by fish held in cages indicates 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 µg/l., the caged fish accumulated 1000 µg/kg in their tissue. This represents a concentration factor of greater than 10,000-fold in just two weeks of exposure. Bioaccumulation of PBB's, therefore, appears comparable to polychlorinated biphenyls (PCB's). Hansen et al. (3) reported PCB concentration factors in two fish species to be 10,000 to 50,000 times the exposure levels in water. Other estimates of PCB accumulation ratios by fish vary from 26,000 to 200,000 times the exposure levels in water (4).

## Ducks

Concentrations of PBB in the flesh of three wild duck species (mallards, teal, and wood duck) col-

Table 6. PBB in ducks collected from the Pine River within 2 miles downstream from St. Louis during 1974, 1976, and 1977<sup>a</sup>

Species	Year	Number in sample	PBB in breast tissue (whole weight), mg/kg	
			With skin	Skinless
Mallard	1974	3	—	0.25
	1976	3	2.00	0.24
	1977	—	—	—
Wood duck	1974	3	—	0.29
	1976	4	2.70	0.17
	1977	4	0.23	0.08
Teal	1974	3	—	1.8
	1976	—	—	—
	1977	1	ND	ND

lected within two miles of the Michigan Chemical Corporation plant in 1974, 1976 and 1977 are presented in Table 6. PBB in skinless breast tissue from composite samples of mallards, wood ducks, and teal in 1974 was 0.25, 0.29, and 1.8 mg/kg, respectively, on a whole weight basis. Samples were either not available for all species from year to year or not equal in number. Concentrations of PBB in samples with skin left on are considerably higher than in skinless samples indicating much of the PBB is associated with the skin or fat layer between the skin and muscle. Interpretation of residue data for wild ducks is complicated because of their migratory habits. Nevertheless, the majority of ducks analyzed from the Pine River contained measurable concentrations of PBB.

This study has been possible through the cooperative efforts of many individuals and agencies. Employees of the Environmental Service, Fisheries, Law, Water Quality, and Wildlife Divisions of the Michigan DNR were responsible for planning, collection of samples and analysis of data.

The following laboratories performed analyses of samples: Michigan Department of Agriculture; U. S. Food and Drug Administration, Division of Chemical Technology (Washington, D. C.); and the Michigan Bureau of Environmental Protection laboratory.

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