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RESEARCH REPORT 74

MERCURY CONTENT OF VARIOUS BOTTOM SEDIMENTS, SEWAGE TREATMENT PLANT EFFLUENTS AND WATER SUPPLIES IN WISCONSIN

A Preliminary Report

By

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ABSTRACT

All bottom sediments were found to contain background mercury concentrations of from <0.01 to 0.35 ppm, depending on the texture of the sediment. High mercury deposits were found below the discharges of the Wyandotte Chemicals Company at Port Edwards on the Wisconsin River and below several pulp and paper mills on the Wisconsin, Chippewa, Flambeau, Wolf, Menominee and Fox Rivers. Accumulations in fish were found to occur where the alkalinities and pH of the waters were below 50 ppm and 7.5, respectively. Significant amounts of mercury were found below several sewage treatment plants which accept mercury-containing wastes. All public surface water supplies sampled contained less than 0.2 ppb mercury.

CONTENTS

INTRODUCTION

In late March, 1970, the Canadian government announced that mercury residues had been found in fish from the St. Clair River, Lake St. Clair, the Detroit River and Lake Erie. This report was followed in late April by the finding of mercury in fish taken from the Petenwell and Castle Rock flowages of the Wisconsin River. Subsequently, high mercury levels have been found in fish from a section of the Flambeau-Chippewa River. The mercury residue in fish from these areas has raised many questions concerning the sources of mercury and its compounds and the extent to which these materials have accumulated in the environment.

There have been two occurrences, both in Japan, of mercury poisoning in humans from eating fish which were contaminated with mercury. The first of these occurred in Minamata beginning in 1953. Between 1953 and 1960, 110 people were either severely disabled or died after eating fish and shellfish caught in Minamata Bay. The second incident occurred in 1965 in Niigata. Methyl mercury discharged from two plastic plants was found to be responsible for the poisonings and deaths.

In Sweden, concern over the increasing mercury residues in birds was traced to mercury seed dressings and resulted in a ban on the use of these compounds in 1965. A more complete discussion of the mercury problem in Japan and Sweden is presented in Konrad (1970).

The mercury problem was first investigated in North America by Norvald Fimreite, a Norwegian graduate student at the University of Western Ontario. Fimreite initiated a study into the uses of mercury in Canada for the purpose of evaluating the possible sources of environmental contamination. Fish taken from Lake St. Clair in early March, 1970, contained mercury concentrations as high as 5 ppm. On March 24, the Canadian Department of Fisheries and Forestry banned the sale and export of fish caught commercially within the Canadian boundaries of Lake St. Clair.

The major sources of mercury contamination in Wisconsin have been associated with the mercury cell process for the production of chlorine and caustic soda and the use of phenyl mercuric acetate as a slimicide by the paper industry. In May, 1970, a letter was sent by the Department of Natural Resources to each pulp and paper mill in Wisconsin advising that the use of mercury compounds be discontinued.

Since high levels of mercury had been found in the bottom sediments and fish below the outfalls from mercury cell chlorine plants in Canada and Michigan, the initial phases of a statewide survey of fish, game birds and animals was concentrated on a section of the Wisconsin River in the vicinity of a chlor-alkali plant at Port Edwards operated by Wyandotte Chemicals Corporation. Analyses of the plant effluent and the sediments 125 feet below the outfall in April, 1970, revealed 0.15 and 800 ppm mercury, respectively. Fish samples collected below the plant outfall exceeded the 0.5 ppm "action level" established by the Food and Drug Administration (FDA).

From May to October, 1970, the Department of Natural Resources surveyed water and bottom sediments from major drainage basins in the state, public surface-water supplies and municipal sewage treatment plants for mercury. These investigations were conducted to determine the location of mercury deposits and to establish natural background levels in bottom sediments. Mercury deposits in bottom sediments reflect past and present discharges of mercury and have been found to be responsible for the long-term mercury contamination of the aquatic environment in Sweden due to the conversion of inorganic mercury to monomethyl mercury in the bottom sediments (Jensen and Jernelov, 1969). This report will discuss the results of this initial survey. Fish and wildlife samples were also collected from drainage basins throughout the state and have been discussed by Kleinert (1970, a and b).

METHODS AND MATERIALS

Analyses for total mercury content of bottom sediments and sewage treatment plant sludges were conducted on the wet (not previously dried) sample as follows: The sample (10 g) was digested in a mixture of $H_2SO_4 \cdot HNO_3$ by the method of the Association of Official Analytical Chemists (1965). The digestate was oxidized with 5 percent $KMnO_4$ (drop-wise to a persistent color) prior to reduction with $SnCl_2$ and analysis by the flameless atomic absorption procedure of Rathje (1969). Moisture content of the sample was determined separately and mercury content expressed as a function of the dry weight. Water samples (25 ml) were analyzed in a like manner except for the omission of the digestion step. A perkin-Elmer Model 303 atomic absorption spectrometer, equipped with a 10 cm x 2 cm flow cell and rapid response recorder, was used for all analyses.

Alkalinity and pH were determined by the procedures described in Standard Methods (Amer. Pub. Health Ass. et al., 1965).

Sediment samples were obtained with either an Ekman or Petersen Dredge and transported to the laboratory in 200 ml bottles. Public water supply and sewage treatment plant samples were collected with the assistance of the plants involved.

RESULTS AND DISCUSSIONS

Bottom Sediments and Water Samples

Samples were taken from 168 locations in 30 river and stream systems. The locations of bottom sediment and water samples are shown on Figures 1-7, and the mercury contained at each of these locations is shown in Tables 1-7. Sample locations were chosen to reflect the contribution, if any, of discharges from industrial and municipal sewage treatment plants and to assess background levels due to natural sources of mercury in the environment.

Wisconsin River and Environs

Locations on the Wisconsin River were selected to show the influence of pulp and paper operations and the mercury cell chlorine-caustic soda plant operated by Wyandotte Chemicals Corporation at Port Edwards. There are 16 pulp and paper mills between Rhinelander and Nekoosa. Phenyl mercuric acetate (PMA) was likely at one time used in all mills for slime control. This usage has generally decreased since 1958 when the FDA banned the presence of mercury in paper used for food wraps. However, PMA was used in several mills for slime control and in coated papers until May, 1970.

Mercury deposits were found at locations 5, 6, 7 and 8 in the Rhinelander-Tomahawk area (Fig. 1a and Table 1). Mercury content at these four locations averaged 1.30 ppm and covered a section about 20 miles in length. No increased mercury contents in the bottom sediments were found in the Tomahawk-Stevens Point stretch of the Wisconsin River. In the Stevens Point-Wisconsin Rapids area, Samples 24, 26, 27, 30 and 32 show increased levels of mercury. This deposit is most likely due to the heavy concentration of paper mills in this area (six mills in 19 miles). The third area of mercury deposits

on the Wisconsin River is below the Wyandotte Chemicals Corporation at Port Edwards (Samples 35, 36, 37, 38, Fig. 1b). This deposit is the largest, in terms of concentration found in any state river. A concentration of 684 ppm was found directly below the plant outfall. One mile downstream the concentration dropped to 9.6 ppm. The bottom sediment at location 35 is largely sand and evidently does not have a high capacity to retain mercury (the higher concentrations in this area were associated with sediments containing clay and organic matter). The mercury content of Sample 39, taken below the paper mill at Nekoosa, likely reflects past mercury usage by the paper mill and is not a result of Wyandotte operations. Minor mercury deposits were found above the Wisconsin Dells dam (Sample 44, Fig. 1b) and in the outfall ditch of the Badger Ordnance Works near Prairie du Sac (this deposit is not in the river) (Sample 47, Fig. 1b). These four areas of mercury deposits are believed to be responsible for the high concentration of mercury reported in fish from the Wisconsin River by Kleinert (1970a).

The mercury contents of water samples were below the 0.5 ppb sensitivity of the analytical method used for the entire length of the Wisconsin River, with the exception of several samples obtained in May and June, 1970. These samples were taken from the Rhinelander and Wisconsin Rapids-Nekoosa areas. Several samples below Rhinelander were 3 ppb while one above the Boom Lake Dam was 1.5 ppb. Cross sectional samples taken at the bridges in Wisconsin Rapids and Nekoosa were 0.8 ppb. When these areas were resampled in July and August, 1970, the mercury levels had decreased to <0.5 ppb. The decrease may be due to flow characteristics of the river or to seasonal variations in the chemical and biological properties of the waters and bottom sediments.

Small deposits of mercury were also found in the sediments of the Brule River below its junction with the Iron River (Sample 54, Figure 1a) and in the Baraboo River below Wonewoc (Sample 57, Figure 1b). This latter deposit was located below the Wonewoc sewage treatment plant outfall.

The natural background levels for the Wisconsin River area appear to be <0.05 to 0.1 ppm in sandy sediments and 0.1 to 0.35 in sediments with high organic matter and clay contents.

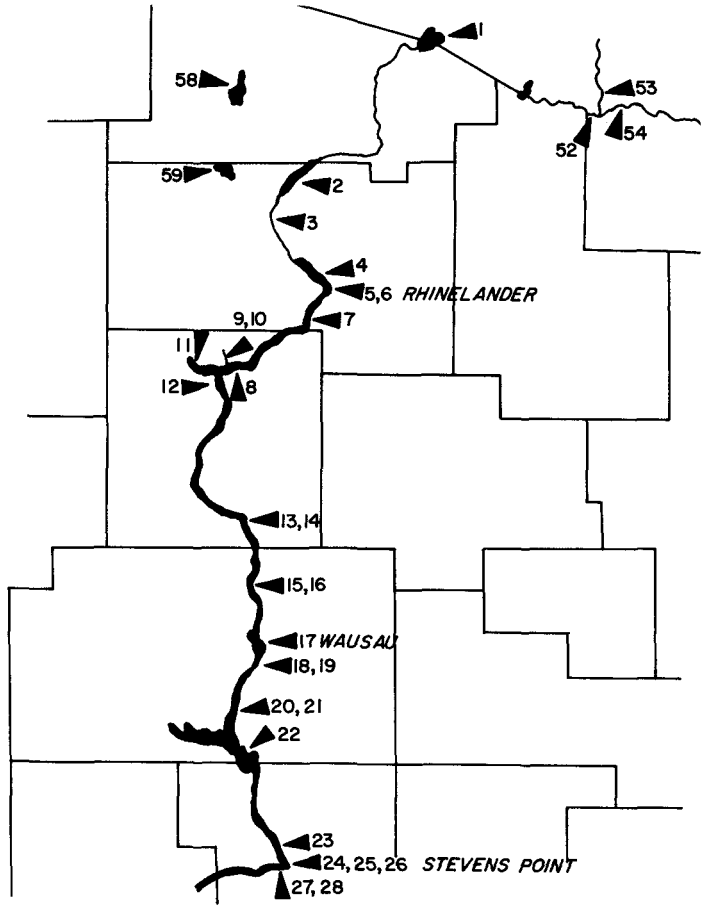

FIGURE 1a. Upper Wisconsin River

FIGURE 1b. Lower Wisconsin River

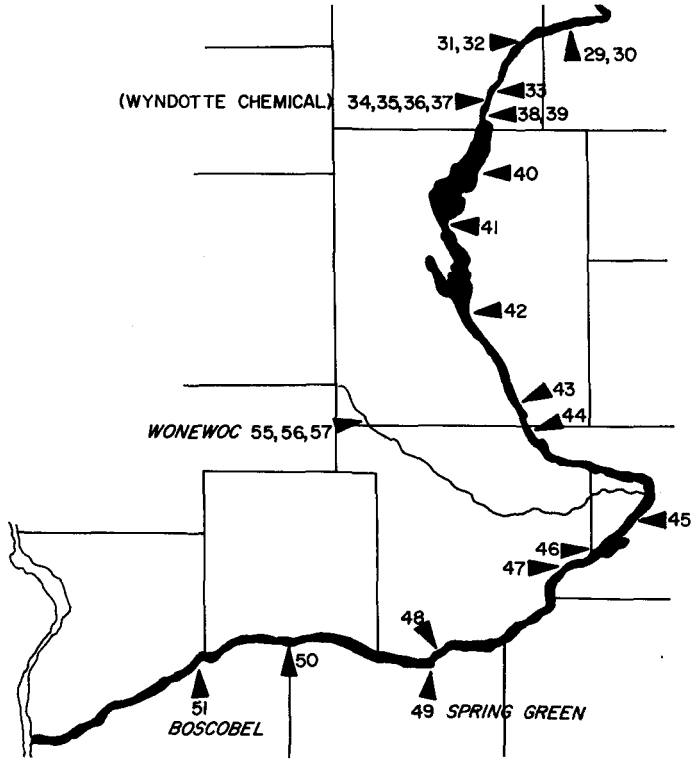

TABLE 1

Mercury Content of Sediments and Waters From the Wisconsin, Brule and Baraboo Rivers and Trout and Minocqua Lakes

*Sample No.	Miles	Location	Mercury Content, ppm Sediment	Water
		Wisconsin River		
1	414.5	Lac Vieux Desert	<0.10	<0.0005
2	367	Rainbow Flowage	0.10	<0.0005
3	357	Above McNaughton	<0.10	<0.0005
4	350	0.25 miles above Boom Lake Dam	0.20	<0.0005
5	349	Davenport St. Bridge - Rhinelander	0.70	<0.0005
6	348.5	Above Pelican River Entrance	1.35	<0.0005
7	343	Above Hat Rapids Dam	1.65	<0.0005
8	328.5	Lake Alice	1.50	<0.0005
	322.6	Tomahawk River		
9		(a) 300 ft. above Georgia Pacific	<0.05	<0.0005
10		(b) 300 ft. below Georgia Pacific	0.30	<0.0005
11	322	0.25 miles above Hwy. 86 Bridge - Lake Mohawksin	0.13	<0.0005
12	320.5	200 ft. below Wisconsin Dam - Owens Illinois Glass	0.05	<0.0005
13	294	100 ft. above Ward Paper - Merrill	<0.05	<0.0005
14	293.5	150 yds. below Ward Paper - Merrill	0.06	<0.0005
15	279	Above Wausau Paper Mill - Brokaw	<0.05	<0.0005
16	278.5	Below Wausau Paper Mill - Brokaw	<0.05	<0.0005
17	271.6	Lake Wausau - Below Rib River	<0.05	<0.0005
18	267.5	0.25 miles above American Can Company - Rothschild	<0.05	<0.0005
19	267.0	0.25 miles below American Can Company - Rothschild	0.05	<0.0005
20	257.8	0.25 miles above Mosinee Paper Mills - Mosinee	0.10	<0.0005
21	257.3	0.25 miles below Mosinee Paper Mills - Mosinee	0.10	<0.0005
22	248.1	Hwy. 34 Bridge - Lake DuBay	0.18	<0.0005
23	230.8	Hwy. 10 Bridge above Consolidated Papers - Stevens Point Division	0.05	<0.0005
24	230.4	300 ft. below Consolidated Papers - Stevens Point Division	6.00	<0.0005
25	228.2	0.25 miles above Consolidated Papers - Wisconsin River Division	0.25	<0.0005
26	227.6	0.25 miles below Consolidated Papers - Wisconsin River Division	0.90	<0.0005
27	227.4	100 yds. below Whiting Plover Paper	1.30	<0.0005
28	227.3	300 yds. below Whiting Plover Paper	0.75	<0.0005
29	216.3	Above Biron Dam	0.31	------
30	216.0	150 yds. below Consolidated Paper - Biron Division	1.60	<0.0005
31	212.6	Green Bay & Western Railroad Bridge below Consolidated Papers - Kraft Div.	0.35	<0.0005
32	211.6	Main St. Bridge below Consolidated Papers - Wisconsin Rapids Division	3.70	<0.0005
33	206.0	Below Nekoosa-Edwards - Port Edwards	0.25	<0.0005
34	204.6	Above Wyandotte Outfall	0.47	<0.0005
35	204.4	125 ft. below Wyandotte Outfall	684	------
36	204.4	150 ft. below Wyandotte Outfall	25	<0.0005
37	204.0	0.25 miles below Wyandotte Outfall	0.25	------
38	203.5	Hwy. 73 Bridge - Nekoosa	9.6	<0.0005
39	203.3	Below Nekoosa-Edwards - Nekoosa	1.4	<0.0005
40	183	Kieffer's Point - Petenwell Flowage	0.32	------
41	173	Below Petenwell Dam	0.37	------
42	156.7	Below Castle Rock Dam	<0.05	<0.0005
43	143.1	At Plainville	0.25	<0.0005
44	137.4	Above Wisconsin Dells Dam	0.80	<0.0005
	110.4	Baraboo River	----	------
45	106.0	I-94 Bridge	----	<0.0005
46	97.3	Railroad Bridge - Merrimac	----	<0.0005
47	94.6	Badger Ordinance Outfall	3.1	<0.0005
48	66	Above Spring Green	<0.05	------
49	64	Below Spring Green	0.11	------
50	42.1	Muscoda	<0.05	------
51	27	Boscobel	----	<0.0005
	0	Mississippi River		
		Brule River		
52	40	0.25 miles above the Iron River	<0.05	<0.0005
53	40	200 ft. above mouth in Iron River	8.7	<0.0005
54	38.5	1.5 miles below the Iron River	1.2	<0.0005
	0	Menominee River		
		Baraboo River		
55	78.1	Above Wonewoc	0.38	<0.0005
56	77.7	Hwy FF Bridge - Wonewoc	.30	------
57	77.0	Wonewoc Sewage Treatment Plant	0.90	<0.0005
	0	Wisconsin River		
		Lakes		
58		Trout	<0.10	<0.0005
59		Minocqua (1)	0.10	<0.0005
		(2)	<0.10	<0.0005

Northeastern Lake Michigan Tributaries

Figure 2 and Table 2 represent the mercury content of bottom sediments in various rivers of northeastern Wisconsin. The Lower Fox River, represented by Samples 14-27, reflects the high concentration of pulp and paper mills (19 mills in 40 miles). The average mercury content of samples from Appleton to the mouth is 1.43 ppm. The usage of mercuric slimicides by paper mills on the Fox River was similar to that on the Wisconsin River and likely accounts for the high mercury concentrations in this 40-mile length of river. Mercury was also found in the effluent of the Appleton sewage treatment plant. There is little evidence of mercury accumulation in fish in the Fox River or near the mouth in Green Bay (mercury levels in deposits in Green Bay average 1.5 ppm while levels in fish were below 0.5 ppm). This is possibly due to the alkaline waters of the river (pH 8), and is consistent with the finding in Sweden that formation of monomethyl mercury is inhibited at higher pH's (Jernelov, A., pers. comm.).

Small mercury deposits were found in the Wolf River below a paper mill at Shawano and at Marinette, also below a paper mill. Fish were not significantly affected at either location.

All other locations on the Peshtigo, Oconto, Kewaunee, East and West Twin and Manitowoc Rivers generally reflected only background levels in the bottom sediments and waters. Sample 31 (Fig. 2) at Fremont on the Wolf River showed a level of mercury in the water somewhat higher than what could be attributed to natural sources. It is possible that this level is due to the influence of the sediment deposits at Shawano; however, additional investigations will be made to determine the actual source.

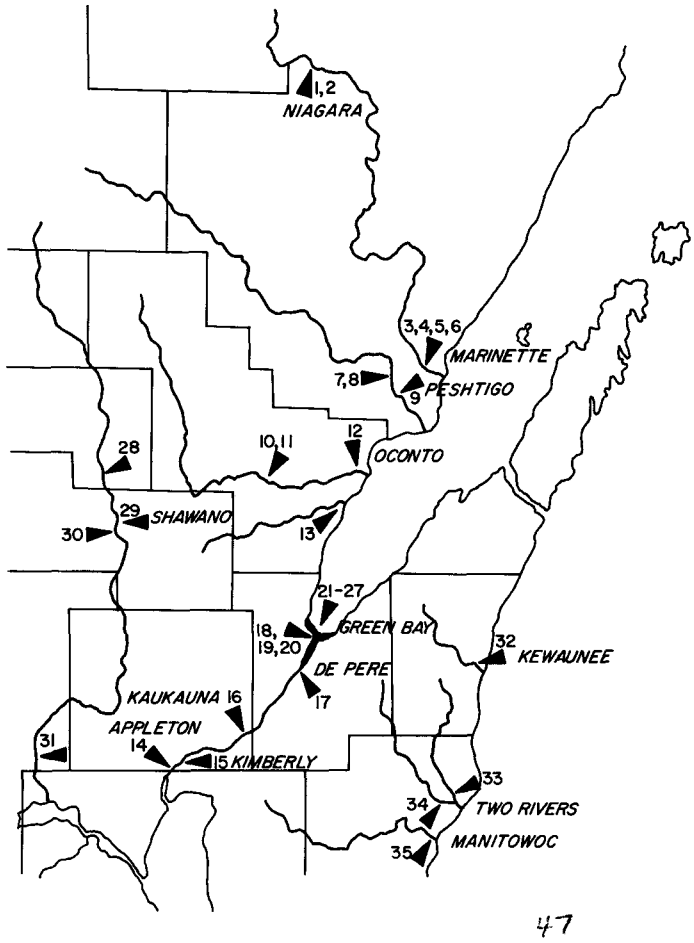

FIGURE 2. Northeastern Lake Michigan Tributaries

TABLE 2

Mercury Content of Sediments and Water From the Menominee, Peshtigo, Oconto, Pensaukee, Lower Fox, Wolf, Kewaunee, East Twin, West Twin and Manitowoc Rivers

*Sample No.	Miles	Location	Mercury Content, ppm Sediment	Water
		Menominee River		
	114	Mouth of Brule River		
1		0.25 miles below Niagara Paper Mill	0.28	------
2		1 miles below Niagara Paper Mill	0.14	------
3	3.5	200 yds. above Upper Dam - Marinette	<0.10	<0.0005
4	3.4	Upper Dam - Marinette	----	<0.0005
5	2.3	300 ft. below Scott Paper - Marinette	1.15	<0.0005
6	1.0	100 ft. below Ansul Chemical	0.30	<0.0005
	0	Lake Michigan		
		Peshtigo River		
7	10.5	200 yds. above Dam - Peshtigo	<0.10	<0.0005
8	9.8	Hwy. "41" Bridge - Peshtigo	----	<0.0005
9	7.0	3.5 miles below Badger Paper	<0.10	<0.0005
	0	Green Bay		
		Oconto River		
10	19.8	300 yds. above Upper Dam - Oconto Falls	0.10	<0.0005
11	15.1	1.5 miles above Stiles Dam	0.23	<0.0005
12	3.1	U.S. "41" Bridge - Oconto	----	<0.0005
	0	Green Bay		
		Pensaukee River		
13	0.8	Hwy. "S" Bridge - Pensaukee	----	<0.0005
	0	Green Bay		
		Lower Fox River		
	39.9	Lake Winnebago		
14	31.9	0.25 miles above Hwy. "47" Bridge-Appleton	0.34	0.0008
15	27.4	Below Kimberly-Clark - Kimberly	0.97	------
16	24.4	0.4 miles above Kaukauna Dam	3.3	------
17	7.5	0.25 miles above DePere Dam	3.6	------
18	2.3	Mason St. Bridge - Green Bay	2.5	0.0045
19	1.4	East River	2.0	<0.0005
20	0	Mouth of Fox River - Green Bay	1.25	<0.0005
		Lower Green Bay		
21		(a) ½ mile West of Grassy Island	1.80	<0.0005
22		(b) 2 miles East and 1.5 miles North of Fox River Mouth	1.70	------
23		(c) 2 miles out in Ship Channel	1.35	------
24		(d) Off Long Tail Point	0.25	------
25		(e) 0.4 miles West of Sable Point	0.14	------
26		(f) 2 miles SW of Red Banks	0.60	------
27		(g) 400 yds. NE of Red Banks	0.25	------
		Wolf River		
28	111.7	Hwy. "M" Bridge - Keshena	----	0.001
29	103.5	Hwy. "29" Bridge 0.4 miles above Shawano Paper Mills	0.14	<0.0005
30	103.0	Hwy. "M" Bridge 0.25 miles below Shawano Paper Mills (1)	0.85	<0.0005
		(2)	0.05	------
31	16.4	Hwy. "10" Bridge - Fremont	----	0.0035
	8.6	Lake Poygan	----	------
	0	Fox River		
		Kewaunee River		
32	3.1	Hwy. "E" Bridge - Kewaunee	----	0.0009
	0	Lake Michigan		
		East Twin River		
33	0.2	17th St. Bridge - Two Rivers	----	0.0008
	0	Lake Michigan		
		West Twin River		
34	0.4	Madison St. Bridge - Two Rivers	----	0.001
	0	Lake Michigan		
		Manitowoc River		
35	1.8	Hwy. "10" Bridge - Manitowoc	----	0.0008
	0	Lake Michigan		

*Sample numbers correspond to sample locations on Figure 2.

Flambeau-Chippewa River System

Mercury deposits were found below Park Falls (Sample 15) and in the Ladysmith area (Samples 16 and 17) on the Flambeau River (Fig. 3 and Table 3). These deposits are the result of paper mills located in each of these cities. The bottom sediments of the Lower Chippewa River in the Chippewa Falls-Eau Claire areas contained elevated mercury levels. The mercury found in these samples probably resulted from paper production in these areas. However, since samples taken below sewage treatment plant effluents at Chippewa Falls and Eau Claire also contained mercury, there could possibly be additional sources in this area. Only background levels of mercury were present in the Chippewa and Flambeau flowages and the Red Cedar River headwaters.

The pH and alkalinity of the Flambeau-Chippewa River system is similar to that of the Wisconsin River, and possibly results in mercury in the bottom sediments accumulating in fish at levels in excess of 0.5 ppm.

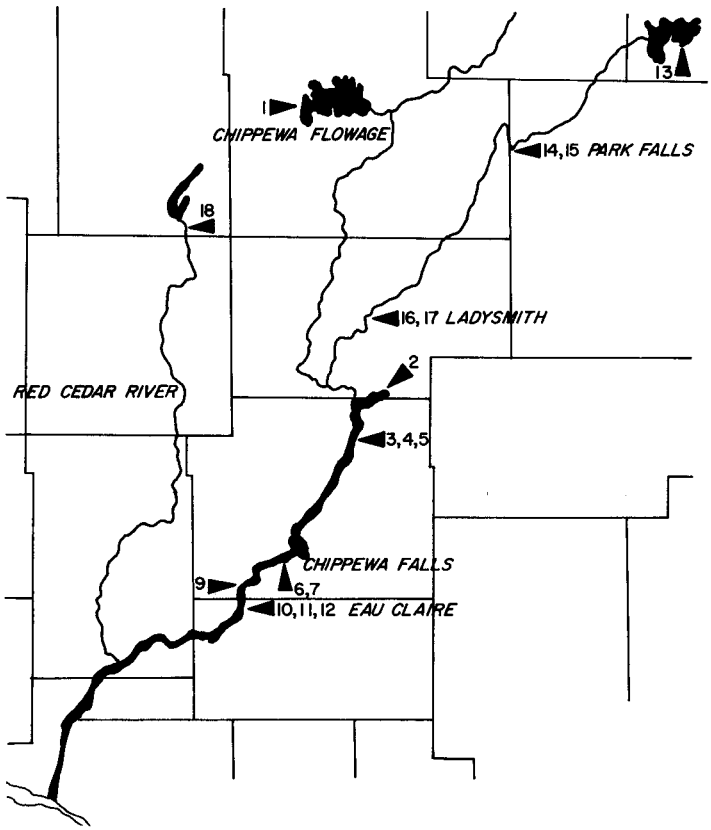

FIGURE 3. Flambeau-Chippewa River System

Rock-Yahara River System

A small increase in mercury content was found in the Rock River below Afton (Sample 3, Fig. 4 and Table 4). The source of this small deposit is presently unknown. The discharge of mercury containing effluent from the Madison sewage treatment plant has resulted in a relatively large buildup in the sediments of their outfall ditch (Sample 11, Fig. 4). The relatively high pH of waters in this area evidently limits the availability of mercury in the sediment deposit and fish are not affected in these waters.

FIGURE 4. Rock-Yahara River System

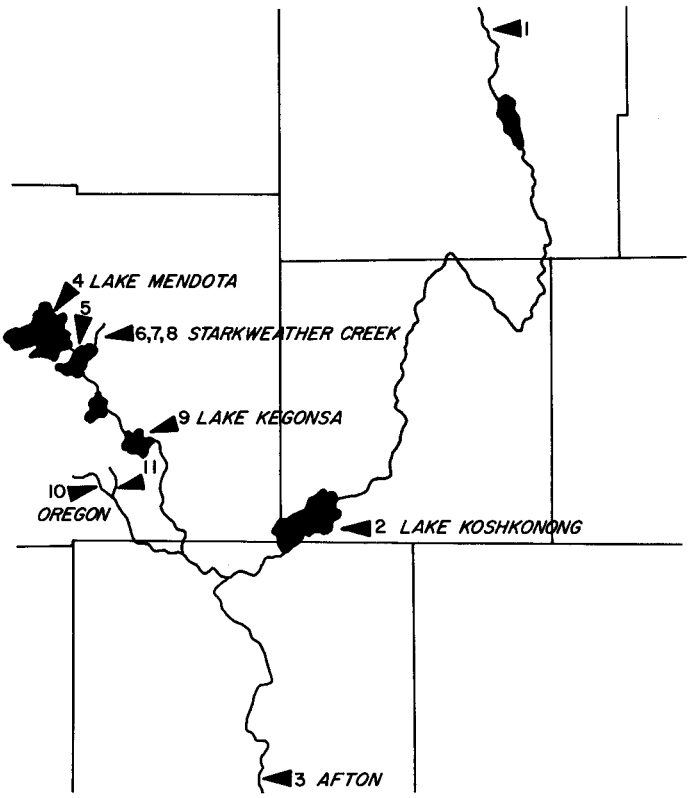

TABLE 3

Mercury Content of Sediments and Waters From the Chippewa, Flambeau and Red Cedar Rivers

*Sample No.	Miles	Location	Mercury Content, ppm Sediment	Water
		Chippewa River		
1	175.2	Chippewa Flowage	<0.05	<0.0005
	117.1	Flambeau River		
2	110.0	Junction with Holcombe River	<0.05	
3	100.8	Above Cornell Paperboard	----	<0.0005
4	99.5	0.75 miles below Cornell Paperboard	<0.05	<0.0005
5	99.2	1.0 mile below Cornell Paperboard	<0.05	------
6.	73.1	100 yds. below Chippewa Falls STP	0.45	------
7.	72.8	500 yds. below Chippewa Falls STP	0.25	------
8.	64.0	4 miles above Sterling Paper	<0.05	------
9.	59.9	Below Sterling Paper	0.30	------
10.	59.1	Madison St. Bridge - Eau Claire	<0.05	------
11.	54.5	Below Eau Claire STP	<0.05	------
12.	54.2	0.25 miles below Eau Claire STP	0.13	------
	26.8	Red Cedar River		
	0	Mississippi River		
		Flambeau River		
13.	110	Flambeau Flowage	<0.05	<0.0005
14.	94	0.5 mile above Flambeau Paper Co.-Park Falls	<0.05	------
15.	92	0.5 mile below Flambeau Paper Co.-Park Falls	0.60	------
16.	19.8	Hwy. 8 Bridge above Peavey Paper - Ladysmith	0.17	------
17.	18.0	Hwy. 27 Bridge below Peavey Paper - Ladysmith	<0.05	<0.0005
	0	Chippewa River		
		Red Cedar River		
18.	101	0.25 mile below Birch Lake Dam	<0.05	------
	0	Chippewa River		

*Sample numbers correspond to sample locations on Figure 3.

TABLE 4

Mercury Content of the Sediments and Waters From the Rock, Yahara and Badfish Rivers

*Sample No.	Miles	Location	Mercury Content, ppm Sediment	Water
		Rock River		
1	132	Horicon Marsh	<0.05	<0.0005
2	40	Lake Koshkonong	0.07	<0.0005
	27.3	Yahara River		
3	10.1	Afton	0.40	<0.0005
	0	Illinois State Line		
		Yahara River		
4	38.8	Lake Mendota - Average 3 samples	0.10	<0.0005
5	33.8	E. Washington Ave. Bridge - Madison	----	<0.0005
	33.0	Starkweather Creek		
6		(a) Above Ray-O-Vac	0.25	<0.0005
7		(b) At Ray-O-Vac	0.85	------
8		(c) Below Ray-O-Vac	0.50	<0.0005
9	21	Lake Kegonsa	0.10	<0.0005
	6.6	Badfish Creek		
	0	Rock River		
		Badfish Creek		
10	16.0	Below Oregon Sewage Treatment Plant	----	<0.0005
11	15.0	In Madison STP Outfal Ditch	11.5	<0.0005
	0	Yahara River		

*Sample numbers correspond to sample locations on Figure 4.

Southeastern Lake Michigan Tributaries

The discharge of mercury containing effluent from the Portage sewage treatment plant has resulted in elevated mercury levels in the Upper Fox River below Portage (Fig. 5 and Table 5). No additional deposits were found on the Upper Fox River or in Lake Winnebago, and a small sample of fish thus far analyzed has not shown any buildup of mercury. Mercury deposits are found in the lower portions of the Milwaukee River and in Milwaukee harbor. However, the chemistry of these deposits is such that fish are not affected.

Other Areas

No significant mercury deposits were found in the St. Louis or Brule Rivers (Fig. 6 and Table 6) or the Namekagon, St. Croix, Mississippi and Galena Rivers (Figures 7a and 7b and Table 7).

The location of mercury deposits in the bottom sediments of Wisconsin rivers is summarized in Figure 8. Locations 2, 3, 4, 6, 7, 8, 12, 13 and 15 on the Chippewa, Flambeau, Fox, Wisconsin and Wolf Rivers reflect the influence of paper and pulp operations. Sewage treatment plant effluents have resulted in deposits at locations 1, 5 and 11 on the Baraboo, Fox and Rock Rivers. The deposit at 10 is the result of industrial effluents. The sources of the deposits at 9 and 10 have not been identified.

A comparison of mercury content in sediments and fish with the alkalinity and pH of the waters is shown in Table 8. Mercury accumulation in fish was found in waters which had an alkalinity of less than 50 ppm and a pH less than 7.5. Much additional research is required along these lines before any conclusions regarding the parameters controlling release of mercury from sediment deposits can be made.

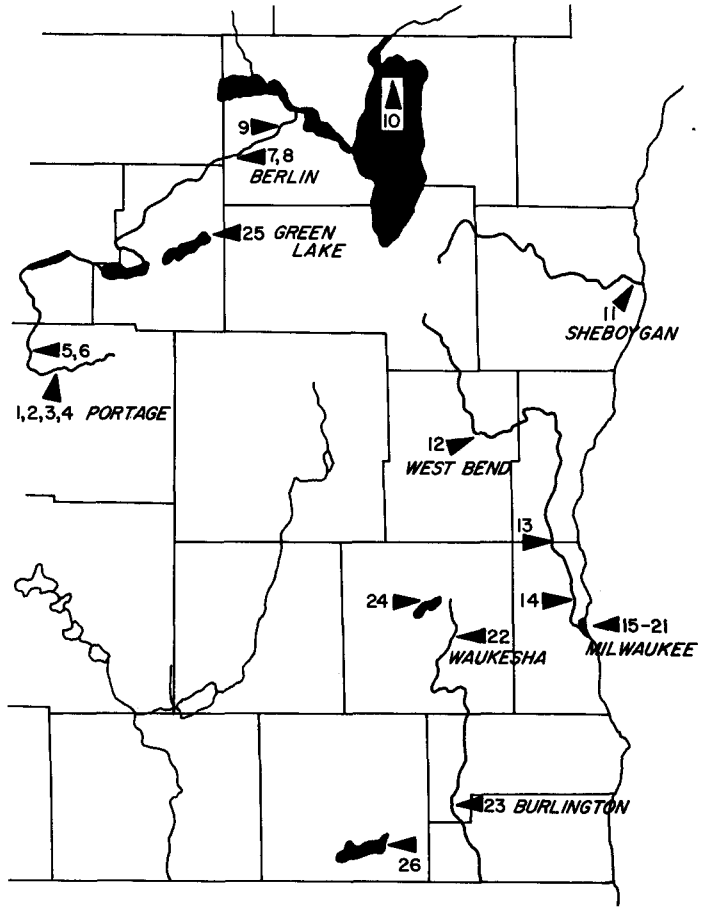

FIGURE 5. Southeastern Lake Michigan Tributaries

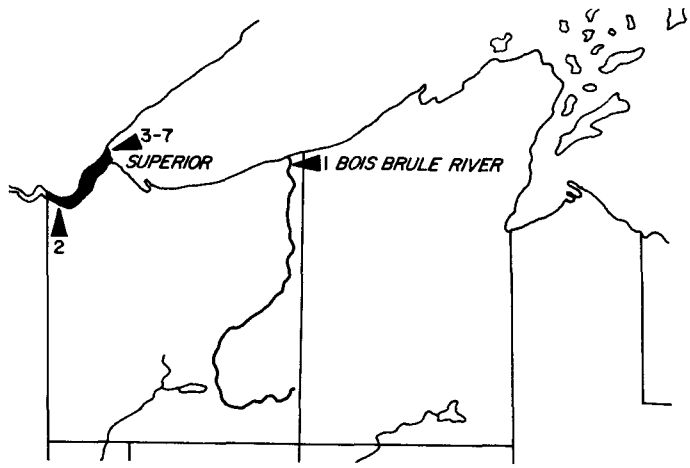

FIGURE 6. Lake Superior Tributaries

TABLE 5

Mercury Content of Sediments and Waters From the Upper Fox, Sheboygan, Milwaukee and Fox (Illinois) Rivers and Pewaukee, Big Green and Geneva Lakes

*Sample No.	Miles	Location	Mercury Content, ppm Sediment	Water
		Upper Fox River		
1	160.9	Above Portage STP	<0.05	------
2	160.7	Portage STP	----	0.006
3	160.3	Hwy. "33" Bridge - Average 3 samples	3.7	<0.0005
4	160	Above Portage Canal	4.8	<0.0005
5	159.6	In Portage Canal	0.2	<0.0005
6	159	Below Portage Canal	6.8	<0.0005
7	90.7	100 yds. below Berlin STP	<0.05	<0.0005
8	90.6	200 yds. below Berlin STP	<0.05	<0.0005
9	76.1	Hwy. "21" Bridge - Omro	----	0.003
	69.9	Wolf River	----	------
10	49	Lake Winnebago - North End	0.25	------
	0	Green Bay		
		Sheboygan River		
11	1.5	8th St. Bridge - Sheboygan	----	<0.0005
	0	Lake Michigan		
		Milwaukee River		
12	51.8	Hwy. "MY" Bridge below West Bend	0.35	<0.0005
13	18.8	Above Thiensville Dam	0.20	<0.0005
14	3.1	Above North Avenue Dam	0.60	<0.0005
	0	Inner Milwaukee Harbor		
15		(a) Milwaukee River - Interstate Br.	0.85	<0.0005
16		(b) Menominee River - Union Station	0.30	<0.0005
17		(c) Kinnickinnic River - Kinnickinnic Br.	0.30	<0.0005
18		(d) Turning Basin	1.70	<0.0005
	0	Outer Milwaukee Harbor		
19		(a) 500 ft. East of Jones Island	3.8	<0.0005
20		(b) 300 ft. North of South Shore Harbor	----	<0.0005
21		(c) 500 ft. East of McKinley Beach	----	<0.0005
		Fox (Illinois) River		
22	56.5	Hwy. "D" Bridge below Waukesha	0.75	<0.0005
23	11.8	Hwy. "JB" Bridge below Burlington	<0.05	<0.0005
	0	Illinois State Line		
		Lakes		
24		Pewaukee	<0.05	<0.0005
25		Big Green (1)	0.20	------
		(2)	<0.05	------
26		Geneva	0.1	<0.0005

*Sample numbers correspond to sample locations on Figure 5

TABLE 6

Mercury Content of Sediments and Waters From the Brule (Douglas County) and St. Louis Rivers

*Sample No.	Miles	Location	Mercury Content, ppm Sediment	Water
		Brule (Douglas County) River		
1	0.5	800 yds. above Mouth	<0.05	<0.0005
	0	Lake Superior		
		St. Louis River		
2	10	Hwy "23" Bridge - State Line	<0.05	<0.0005
	0	Superior Harbor		
3		(a) 75 yds. below Fiber Products	0.22	<0.0005
4		(b) 0.25 miles South Belknap Street	0.20	<0.0005
5		(c) 800 yds. SW of Conners Point	0.38	<0.0005
6		(d) 0.7 miles West of Entry	0.10	<0.0005
7		(e) Superior Sewage Treatment Plant	0.80	<0.0005

*Sample numbers correspond to sample locations on Figure 6.

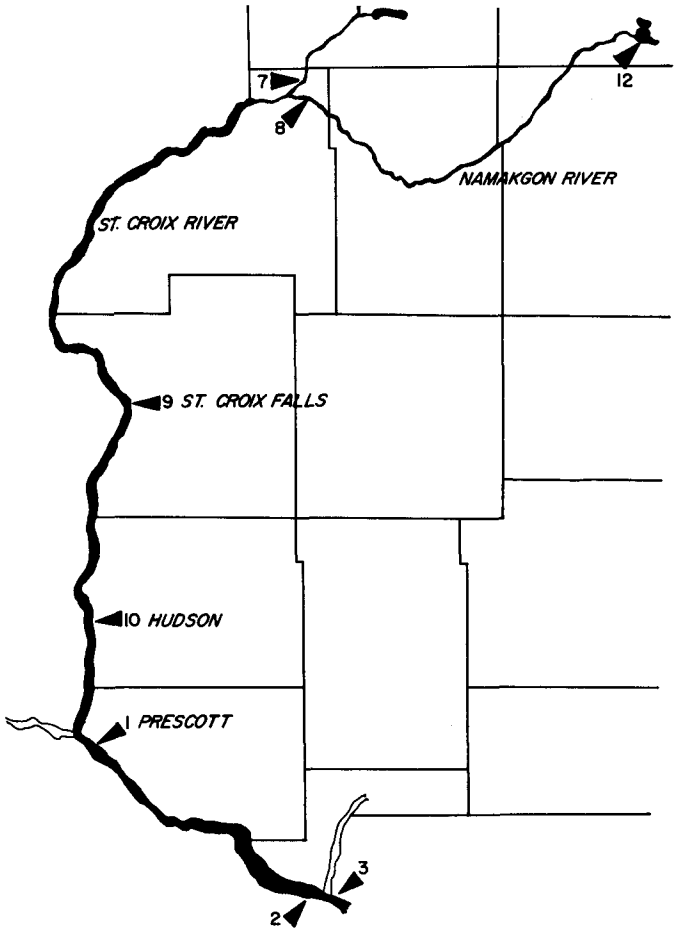

FIGURE 7a. Upper Mississippi River

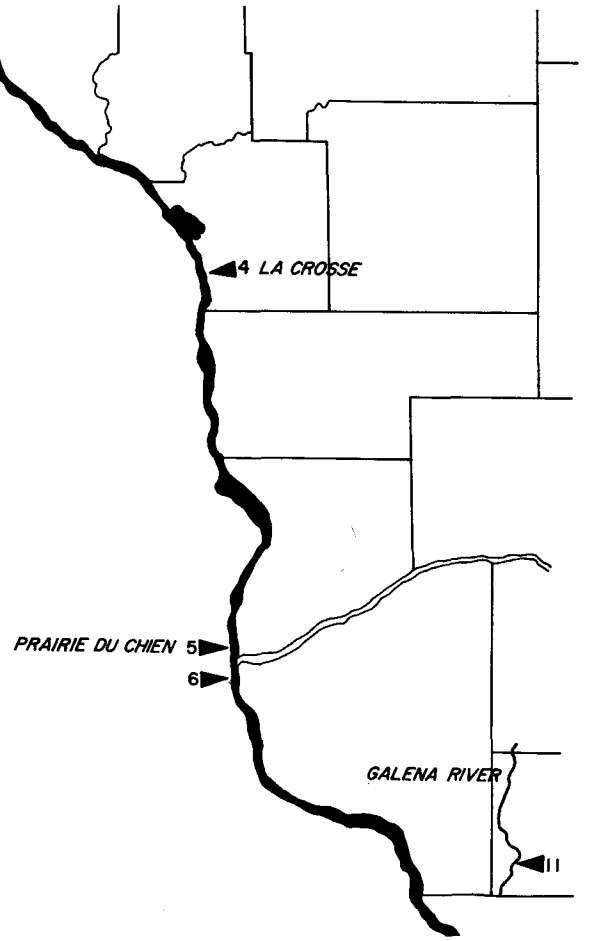

FIGURE 7b. Lower Mississippi River

TABLE 7

Mercury Content of Sediments and Waters From the Mississippi, St. Croix and Galena Rivers and Lake Namekagon

*Sample No.	Miles	Location	Mercury Content, ppm Sediments	Water
		Mississippi River		
	230.8	St. Croix River		
1	224.5	0.5 mile below St. Croix River - Prescott	0.20	------
2	185	Lake Pepin - Southern End	0.08	------
	182.8	Chippewa River		
3	179	Below Chippewa River	----	------
4	110	Below LaCrosse - Goose Island	<0.05	<0.0005
5	53.9	Above Wisconsin River - Prairie du Chien	0.05	<0.0005
	50.3	Wisconsin River		
6	50.0	Below Wisconsin River - Wyalusing State Park	----	<0.0005
	0	Illinois State Line		
		St. Croix River		
7	138.0	Above Namekagon River	0.09	<0.0005
8	137.7	Namekagon River	<0.05	<0.0005
9	54.0	St. Croix Falls	----	<0.0005
10	16.1	I-94 Bridge - Hudson	0.12	------
	0	Mississippi River		
		Galena River		
11	6.3	Hwy. "W" West of New Diggings	< 0.05	<0.0005
	0	Illinois State Line		
		Lakes		
12		Namekagon	0.08	------

*Sample numbers correspond to sample locations on Figures 7a and 7b.

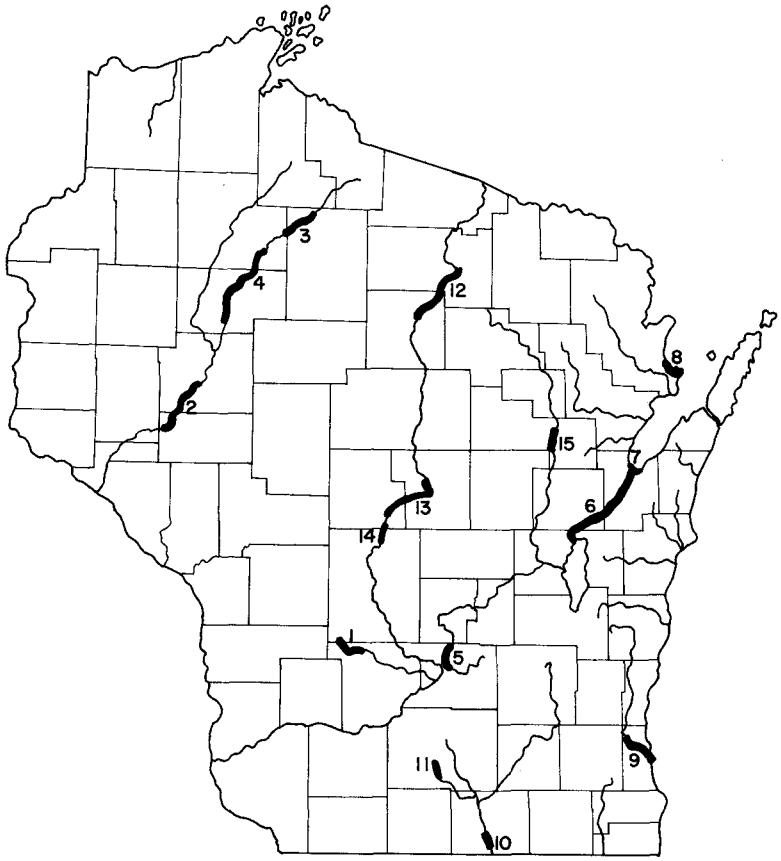

FIGURE 8. Location of Mercury Deposits in Bottom Sediments of Wisconsin Rivers

TABLE 8. LOCATION OF MERCURY DEPOSITS IN BOTTOM SEDIMENTS OF WISCONSIN RIVERS

River	Location of Deposit (No. Corresponds to Sample Location on Figure 8)		Source of Deposit	Average Mercury Content (ppm)	Average Alkalinity (ppm)	Average pH	Fish Accumulation (ppm)
Baraboo	1.	Below Wonewoc	Sewage Treatment Plant Effluent	0.5	-	7.6	N.A.
Chippewa	2.	Chippewa Falls-Eau Claire	Paper Mill	1.2	33	7.1	0.60
Flambeau	3.	Below Park Falls	Paper Mill	0.6	20	6.9	0.41
	4.	Ladysmith Area	Paper Mill	1.4	25	7.2	1.07
Fox	5.	Below Portage	Sewage Treatment Plant Effluent	0.8	-	7.6	N.A.
	6.	Neenah-Menasha to Mouth	Paper Mills and Sew. Trt. Plt. Eff.	2.0	139	7.8	0.36
	7.	Lower Green Bay	Paper Mills	1.5	-	7.2	0.21
Menominee	8.	Marinette Area	Paper Mills	1.2	81	7.6	0.45
Milwaukee	9.	Above Mouth and Milwaukee Harbor	Unknown	1.5	168	7.8	0.13
Rock	10.	Below Janesville	Unknown	0.4	225	8.3	0.11
	11.	Below Madison Sewage Outfall - Badfish Cr.	Sewage Treatment Plant Effluent	11.5	-	7.5	N.A.
Wisconsin	12.	Rhinelander - Tomahawk	Paper Mills	1.5	20	6.7	0.95
	13.	Stevens Point-Wis. Rapids	Paper Mills	2.7	30	6.8	0.51
	14.	Port Edwards-Nekoosa	Chlorine Plant	684	36	6.8	1.24
Wolf	15.	Below Shawano	Paper Mills	0.8	92	7.8	N.A.

Sewage Treatment Plant Effluent

To determine the effect of municipal sewage treatment effluents on the accumulation of mercury in sediments and on the quality of surface water supplies, samples were obtained from 25 sewage treatment plants, and 17 public surface water supplies (Tables 9 and 10). Sewage treatment plants which accept sewage containing mercury were found to have elevated mercury levels in the sludge and in several cases in the final effluents. Sludges from Kaukauna, Portage, Green Bay, Kimberly, Madison and Appleton contained 3.7, 5, 6, 16, 20 and 29 ppm mercury, respectively (Table 9). Of these, however, only Madison, Appleton and Portage were found to discharge mercury containing effluents. As a consequence of these discharges, deposits of mercury have been found in the sediments of the Madison outfall ditch (Table 4) and the Fox River below Portage (Table 5) and Appleton (Table 2). Sources of mercury in the Madison area may include chemical laboratories (university and private), hospitals, and the plants manufacturing batteries. The relative amounts of mercury discharged to the sewer from these sources is at present unknown.

Public Surface Water Supplies

All public surface water supplies sampled contained less than 0.2 ppb mercury in raw and finished waters (Table 10). This is well below the 5 ppb level adopted by the Public Health Service as its standard. These represent all the water supplies from Lake Michigan and Lake Winnebago. Surface waters associated with mercury deposits in the bottom sediments were also generally less than 0.5 ppb or below the sensitivity of the analytical method used.

MISCELLANEOUS STUDIES AND FUTURE PLANS

In the course of the mercury study program, the Department has conducted several special investigations to evaluate and monitor sources of mercury. The following section will briefly describe these studies.

Departmental staff from the Environmental Protection District Office in Wisconsin Rapids has sampled the influent and effluent waters at the Wyandotte plant daily on a random schedule. These samples are split with the company and sent to Madison for analysis.

Samples have been taken from waste streams at Ray-O-Vac battery plants in Madison, Portage and Wonewoc. These consisted of samples of waste discharged to surface waters and to the sanitary sewer system.

The Department has instructed Ray-O-Vac to decrease the amount of mercury discharged to the sewage system to less than 0.1 ppm and to completely eliminate storm sewer discharges to Starkweather Creek in Madison. Currently, the Wonewoc, Portage and new Fennimore plants have attained this level. The Madison plant has significantly decreased the concentration of mercury in its production waste waters. This mercury containing water is discharged directly to the sanitary sewer system every 7 to 10 days from a 10,000 gallon holding tank. Solid waste is no longer allowed to reach Starkweather Creek and complete compliance with the Department's instructions is expected in early 1971.

Several pulp and paper mill effluents have been sampled and the mercury content determined. No significant levels of mercury were detected in any effluents sampled ($\ll$0.0005 ppm).

Samples of paper pulps produced in Wisconsin and elsewhere were obtained from several paper mills to determine the levels of mercury used for slime control in paper pulps. Samples ranged from $<$ 0.05 to 0.55 ppm mercury. Most pulp samples, however, contained $<$0.1 ppm.

The use of mercury was investigated in the manufacture of mercury switches, paint and waxes, in hospital and chemical laboratories, in agricultural operations, and in mold control on golf course greens.

TABLE 9

Mercury Content of Various Sewage Treatment Plants in Wisconsin

Date Sampled	Location	Discharged To	Mercury Content ppm
6/11/70	Appleton - Raw		0.016
6/11/70	Appleton - Final	Fox River	0.001
6/11/70	Appleton - Sludge		29
8/17/70	Appleton - Raw		0.004
8/17/70	Appleton - Final	Fox River	0.0015
8/12/70	Berlin - Raw		0.0015
8/12/70	Berlin - Final	Fox River	0.0005
6/11/70	DePere - Raw		<0.001
6/11/70	DePere - Final	Fox River	<0.001
7/13/70	Eagle River Hospital - Sewer	Eagle River STP	<0.0005
7/14/70	Eagle River - Final	Wisconsin River	0.001
7/29/70	Francis Creek - Final	West Twin River	<0.0005
6/11/70	Green Bay - Raw		0.0008
6/11/70	Green Bay - Final	Fox River	<0.0005
6/11/70	Green Bay - Sludge		6
6/11/70	Kaukauna - Raw		<0.001
6/11/70	Kaukauna - Final	Fox River	<0.001
6/11/70	Kaukauna - Sludge		3.7
5/21/70	Kenosha - Raw		0.001
5/21/70	Kenosha - Final	Lake Michigan	0.001
8/5/70	Kewaunee - Raw		<0.001
8/5/70	Kewaunee - Final	Lake Michigan	<0.001
6/11/70	Kimberly - Raw		<0.001
6/11/70	Kimberly - Final	Fox River	<0.001
6/11/70	Kimberly - Sludge		16
5/22/70	LaCrosse - Raw		0.002
5/22/70	LaCrosse - Final	Mississippi River	<0.001
5/22/70	LaCrosse - Sludge		2.15
6/11/70	Little Chute - Raw		<0.001
6/11/70	Little Chute - Final	Fox River	<0.001
6/11/70	Little Chute - Sludge		0.016
7/27/70	Madison - Raw		0.008
7/27/70	Madison - Final	Badfish Creek	0.0025
2/29/70	Madison - Sludge		20
5/21/70	Milwaukee Jones Island - Raw		0.003
5/22/70	Milwaukee Jones Island - Final	Lake Michigan	<0.0005
5/21/70	Milwaukee South Shore - Raw		0.0015
5/21/70	Milwaukee South Shore - Final	Lake Michigan	0.002
7/15/70	Mishicot - Raw		0.0006
7/15/70	Mishicot - Final	East Twin River	0.0007
6/11/70	Neenah-Menasha - Raw		<0.001
6/11/70	Neenah-Menasha - Final	Fox River	<0.0005
6/11/70	Neenah-Menasha - Sludge		1.4
7/16/70	New Berlin Hospital - Final	Root River	0.0006
7/28/70	Oconomowoc - Final	Oconomowoc River	<0.0005
6/11/70	Portage - Raw		0.011
6/11/70	Portage - Final	Fox River	0.002
6/11/70	Portage - Sludge		5
6/16/70	Portage - Raw		0.027
6/16/70	Portage - Final	Fox River	0.005
7/27/70	Portage - Final	Fox River	0.003
8/3/70	Pulaski - Raw		<0.0005
8/3/70	Pulaski - Final	Duck Creek	<0.0005
5/21/70	Racine - Raw		0.002
5/21/70	Racine - Final	Lake Michigan	0.002
5/22/70	South Milwaukee - Raw		0.003
5/22/70	South Milwaukee - Final	Lake Michigan	0.0005
7/27/70	Sturgeon Bay - Raw		<0.0005
7/27/70	Sturgeon Bay - Final	Lake Michigan	<0.0005
7/28/70	Sussex - Final	Pewaukee River	<0.001
7/22/70	Two Rivers - Raw		<0.0005
7/22/70	Two Rivers - Final	Lake Michigan	<0.0005

TABLE 10

Mercury Content of Surface Water Supplies in Wisconsin

Date Sampled	Location	Source	Mercury Content ppm
6/8/70	Appleton - Raw	Fox River	<0.0001
6/12/70	Cudahy - Raw	Lake Michigan	<0.0002
6/12/70	Cudahy - Finished		<0.0002
6/9/70	Grand Army Home - Raw	Rainbow Lake	<0.0001
6/9/70	Green Bay - Raw	Lake Michigan	<0.0001
6/12/70	Kenosha - Raw	Lake Michigan	<0.0002
6/12/70	Kenosha - Finished		<0.0002
6/10/70	Manitowoc - Raw	Lake Michigan	<0.0001
6/7/70	Marinette - Raw	Green Bay	<0.0001
6/8/70	Menasha - Raw	Lake Winnebago	<0.0001
6/10/70	Neopit - Raw	Wolf River - W. Branch	0.00015
6/10/70	Milwaukee-Howard Avenue - Raw	Lake Michigan	<0.0002
6/10/70	Milwaukee-Howard Avenue - Finished		<0.0002
6/10/70	Milwaukee-Linwood Station - Raw	Lake Michigan	<0.0002
6/10/70	Milwaukee-Linwood Station - Finished		<0.0002
6/8/70	Milwaukee-North Shore - Raw	Lake Michigan	<0.0002
6/8/70	Milwaukee-North Shore - Finished		<0.0002
6/9/70	Neenah - Raw	Lake Winnebago	<0.0001
8/4/70	Oshkosh - Raw	Lake Winnebago	<0.0001
6/8/70	Port Washington - Raw	Lake Michigan	<0.0002
6/8/70	Port Washington - Finished		<0.0002
6/12/70	Racine - Raw	Lake Michigan	<0.0002
6/12/70	Racine - Finished		<0.0002
6/10/70	Sheboygan - Raw	Lake Michigan	<0.0001
6/12/70	South Milwaukee - Raw	Lake Michigan	<0.0002
6/12/70	South Milwaukee - Finished		<0.0002
6/8/70	Two Rivers - Raw	Lake Michigan	<0.0001

An extensive resampling of bottom sediments from the Upper Wisconsin, Lower Fox and the Flambeau-Chippewa Rivers has been initiated. These samples will be used to determine the extent of mercury deposits in these rivers and to evaluate the parameters which may control the release of mercury from these deposits.

Samples of coal have been obtained from major power plants in the state to determine the amount of mercury which may be released to the atmosphere by the combustion of coal. Preliminary analyses indicate that that the mercury content of coal is <0.1 ppm. Approximately 60% of this mercury is released upon combustion.

Surface soil samples have been collected from the vicinity of the Wyandotte plant to determine the extent of any airborne mercury from the plant's hydrogen venting system. Increased levels were found downwind of the plant, indicating that gravitational fallout of particulate mercury is occurring.

SUMMARY AND CONCLUSIONS

In general, it can be concluded that all bottom sediments contain at least trace amounts of mercury. Background levels ranged from <0.05 to 0.35 ppm with an average of about 0.15 ppm. The highest mercury deposits were found below industrial discharges (chlorine-caustic soda and pulp and paper production).

Significant amounts of mercury were found below several sewage treatment plants. Alkalinity and pH may have an important role in the release of mercury from bottom sediments and the subsequent accumulation in fish. Through research currently conducted by the Department and cooperative research programs with the University of Wisconsin, the mechanism and pathways of this release will be elucidated.

Lake and river waters and public surface water supplies were found to contain extremely low concentrations of mercury. Except for the consumption of fish from the Wisconsin and Flambeau-Chippewa Rivers, the normal uses of these waters is not affected.

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