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SURVEYS OF TOXIC METALS IN WISCONSIN

REMOVAL OF METALS FROM WASTE WATERS BY MUNICIPAL SEWAGE TREATMENT PLANTS

CONCENTRATION OF METALS IN FISH

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ABSTRACT

REMOVAL OF METALS FROM WASTE WATERS BY MUNICIPAL SEWAGE TREATMENT PLANTS

The Department of Natural Resources conducted a questionnaire survey of Wisconsin industries utilizing and/or consuming metals in 1971 and a field survey of municipal sewage treatment plants for metal content in 1972. Metals included in the survey were arsenic, cadmium, copper, chromium, lead, mercury, nickel, selenium and zinc. The southeastern corner of Wisconsin accounted for more than 65 percent (440,998 pounds) of the total metals use reported for the state. In general, high concentrations of metals in sewage treatment plants were associated with areas of high metal use and the average metal removal efficiency for all plants investigated was approximately 50 percent.

CONCENTRATION OF METALS IN FISH

Concentrations of metals found in fillets of fish sampled from Wisconsin waters were less than 0.05 ppm for cadmium, 0 to 0.42 ppm for chromium, 2.7 to 18.3 for zinc, 0 to 4.31 for lead and 0 to 0.35 for arsenic. Based upon the fish tested in this survey, we do not believe these metals are present in sufficient amounts to create any hazards to consumers.

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SURVEYS OF TOXIC METALS IN WISCONSIN

Removal of Metals From Waste Waters by Municipal Sewage Treatment Plants

By
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Concentration of Metals in Fish

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INTRODUCTION

The Department of Natural Resources is continuing programs to investigate the magnitude and environmental significance of discharges of arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium and zinc. In 1971 the Department conducted a survey of the state's major metal-working and metal-consuming industries to pinpoint locations where metals are discharged. In 1972 the Department conducted surveys of municipal sewage treatment plant influents, effluents, and sludges to detect concentrations of most of these metals and to determine the effectiveness of primary and secondary treatment for metals removal. This report will present the results of both the 1971 and 1972 surveys.

SOURCES OF METAL DISCHARGE

Sources of metal discharge to the environment include losses from mining or metal-working industries, losses from processing and burning coal, petroleum and other fuels containing metals as impurities or additives, discharges from municipal sewerage systems, leaching from solid waste disposal sites, and losses from a variety of consumer uses. Metals and metal compounds may be discharged to waters via waste effluents or may enter the water from airborne fallout. In addition, soils, sediments, and rock contain metals which leach into surface and ground waters by natural processes.

Waste waters from the following industrial groups are most likely to contain metals in varying concentrations: primary metals industries, fabricated metal products, machinery, transportation equipment, chemicals and allied products, leather and leather products. This group of industries is well represented in Wisconsin as shown in Table 1. The major portion of Wisconsin's manufactured goods for several decades has come from the metal-working industries. These industries in Wisconsin, for example, paid out about 60 percent of the state's total manufacturing payroll in 1960 and about 3.3 percent of the national payroll in metal-working industries (Austin 1964).

INDUSTRY SURVEY

A toxic substance survey questionnaire was prepared by the Department and mailed to 278 industrial facilities in Wisconsin in March, 1971. The survey questionnaire primarily concerned the use and discharge of various metals and metal compounds. The industrial facilities included in the survey were selected from the classified directory of the Wisconsin Manufacturer's Association (Wisconsin Manufacturer's Association 1971). Selection of facilities to be included in the survey was based on two criteria: (1) those facilities known or believed to be using metals or metal compounds in manufacturing processes, and (2) large facilities with 50 or more employees. Some smaller facilities such as electroplating plants were also included because of their high consumption of metals.

The questionnaires were completed and returned by 98 percent of the facilities contacted. Information reported included annual estimates of the loss of metals to the air, water, and soil from each facility. The survey did not include all possible sources of metal discharge, and was based upon voluntary estimates by the reporting industries. Because of these limitations the survey findings should be regarded as minimal estimates of the actual quantities of metals being discharged in the state.

The survey summary of metal discharges to the air, water, and soil of the state is presented in Table 2. Discharges to the water include both direct discharges to surface waters and discharges to a water effluent sent to a municipal or private waste water treatment plant. Reported discharges of chromium, lead, and zinc each totaled more than 100,000 pounds annually, while reported discharges of copper exceeded 80,000 pounds and nickel 40,000 pounds annually. Lead is discharged chiefly as solid waste, while the largest copper, chromium, nickel, and zinc discharges are made to the water. Reported arsenic, cadmium and selenium discharges were each below 6,000 pounds annually. Reported discharges of beryllium and mercury were less than 300 pounds annually.

Total metals discharge to the air, water, and soil by specific area is summarized in Table 3. The most industrialized areas of the state account for the largest metals discharge, as expected. The southeastern corner of Wisconsin which includes the Milwaukee, Racine, and Kenosha metropolitan areas account for 440,998 pounds of metal discharges annually, which is more than 65 percent of the total reported for the state. The central Wisconsin area, including Merrill, Wausau, Mosinee and Port Edwards, is second with a reported discharge of 71,632 pounds or more than 10 percent of the total.

High concentrations of metals in sewage treatment plant samples were most often found in plants serving metal discharging industries identified in the mail survey. Additional industrial sources of metal discharges were identified when concentrations of metals were found in sewage treatment plants serving industries which the mail survey did not include.

SEWAGE TREATMENT PLANT SURVEY

A survey of sewage treatment plants for heavy metals was conducted in the winter and spring of 1972. The objectives of the survey were to determine natural background levels and to measure the levels which occurred in municipalities where known metal discharges were present. Thus, to obtain a cross-section of the sewered population, all municipalities of greater than 10,000 population were sampled along with smaller communities where inputs of heavy metals were suspected. A total of 35 treatment plants was sampled. The samples consisted of 24-hour composites of the influent and effluent and a grab sample of the final sludge. Chromium, copper, zinc, lead, mercury, cadmium and nickel were determined on each sample by atomic absorption spectrometry. The treatment plants included serve

2,336,000 people or approximately 75 percent of the total Wisconsin sewered population. Of this total about 80 percent are served by 28 secondary facilities (16 activated sludge and 12 trickling filters) and the remainder by primary treatment plants.

The ranges and mean metal concentrations of influents to the 35 treatment plants sampled are represented in Table 4. A wide range of values was observed for each of the metals with the widest variation observed for mercury and chromium and narrowest for zinc and cadmium. In order to obtain a more representative mean and standard deviation, the two highest values were rejected in the case of mercury and chromium. This procedure is justified since these values were an order of magnitude greater than the next nearest value. Background or "normal" concentrations were determined by rejecting all values greater than one standard deviation above the mean. The sum of the mean and the standard deviation also gave a useful "upper limit" for the "normal" concentration range. Treatment plants in which this value was exceeded were deemed to have sources of the metal in question other than background or diffuse sources. These plants are listed in Table 4. Although complete agreement with the metals survey was not obtained, some similarity in geographic regions could be identified.

The relationship of the influent and effluent concentrations was determined using various analyses of

TABLE 1. Ranking of Wisconsin Industries*

Standard Industrial Code Classification		Total Number of Establishments in Wisconsin	Percent of Total Industrial Employment in Wisconsin
SIC 35;	Machinery, except electrical	130	31
SIC 26;	Paper and allied products	80	13
SIC 20;	Food and kindred products	75	8
SIC 33;	Primary metals industries	54	9
SIC 37;	Transportation equipment	38	18
SIC 34;	Fabricated metal products	30	8
SIC 28;	Chemicals and allied products	20	2
SIC 30;	Rubber and miscellaneous plastic products	20	2
SIC 36;	Electrical machinery	12	4
SIC 31;	Leather and leather products	10	1
SIC 22;	Textile mill products	9	1

*From Weston (1971).

TABLE 2. Industrial Discharges of Metals to the Air, Water, and Soil of Wisconsin

Metal	No. of Reported Discharges To			Annual Poundage Discharged To			
	Air	Water	Soil	Air	Water	Soil	Total
Arsenic	5	10	4	–	1,800	530	2,330
Beryllium	1	1	1	50	–	–	50
Cadmium	5	20	6	–	5,557	26	5,583
Chromium	27	54	18	971	63,294	44,751	109,016
Copper	12	47	19	8,449	75,865	2,564	86,878
Lead	20	29	13	4,078	4,693	115,392	124,163
Mercury	6	15	11	–	90	141	231
Nickel	16	39	12	894	41,040	2,475	44,409
Selenium	4	7	3	–	5,907	–	5,907
Zinc	19	44	16	67,315	97,231	85,585	250,131
Total	115	266	103	81,757	295,477	251,464	628,698

TABLE 3. Annual Poundage of Metal Wastes Discharged to the Air, Water and Soil in Selected Areas

Metal	Annual Poundage Discharged to the Air, Water, and Soil							
	Milwaukee Area	Racine Kenosha Area	Fox River Valley Marinette Peshtigo	Central Wisconsin Area	Grafton Mayville Horicon Beaver Dam Hartford Ripon Fond du Lac	Madison Janesville Beloit Lake Mills	Sheboygan Kohler Manitowoc Two Rivers	La Crosse Sparta
Arsenic	–	–	1,800	530	–	–	–	–
Beryllium	50	–	–	–	–	–	–	–
Cadmium	754	–	30	–	4,743	30	–	–
Chromium	19,460	31,777	3,360	1,591	3,516	3,680	8,430	17,000
Copper	6,688	74,099	3,820	2,150	870	197	405	2,210
Lead	2,500	117,965	–	380	–	–	861	345
Mercury	–	–	–	29	–	–	–	90
Nickel	22,933	3,214	50	3,038	615	435	–	8,450
Selenium	–	–	–	5,907	–	–	–	–
Zinc	64,443	97,115	55	58,007	8,875	610	10,145	81
Total	116,828	324,170	9,115	71,632	18,619	4,952	19,841	28,176

correlation (Table 5). Copper, zinc, cadmium, mercury and nickel followed a linear correlation, while it was necessary to apply a nonlinear power correlation to chromium and lead. The amount of each metal in the effluent was significantly correlated with the amount in the influent (probability level less than .01). The average removal efficiency for all plants was approximately 50 percent. Little difference was observed between primary and secondary treatment for chromium removal. However, for the metals on which sufficient data were available, the higher degree of treatment was more effective in removing the metals.

The distribution of influent and effluent concentrations in all plants sampled is shown in Figure 1. In general, the treatment plant is an effective, although not necessarily an efficient, means of removing metals present in the influent sewages. This is evidenced by the general shift of the distribution to the left following treatment.

The removal of metals as the waste water passes through the plant results in an accumulation of metal in the sludge. Analyses of grab samples of sludge from the various treatment plants is presented in Table 6. In general, the plants which have expressively high concentrations in the raw sewage also have high values in the sludge. By using the influent-effluent correlation equation it is possible to calculate the amount of metal which can be expected to be found in the sludge. This sludge loading rate will be valuable in evaluating sludge disposal procedures.

The data collected in the study do not allow a direct evaluation of the above hypothesis, since sludge production rates corresponding to the influent and effluent sampling periods were not determined.

Also, the heterogenity of the sludges would necessitate more than one grab sample in order to obtain representative concentration values. Even though the values in Table 6 are not necessarily the same as those which might be predicted, they do serve to illustrate the magnitude of the sludge disposal problem which must be faced if agricultural land disposal of sludge is contemplated.

It is evident from the results of this survey that heavy metal contaminaiton of surface waters is possible below the outfalls of sewage treatment plants which accept wastes high in heavy metals. To evaluate this possibility, additional sampling for metals above and below sewage treatment plants with known or suspected metals accumulation will be included in future drainage basin surveys.

Application of sludge to agricultural lands must be preceded by an evaluation of the heavy metal content in order to control residue build-up.

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TABLE 4. Heavy Metal Characteristics of Influents to Treatment Plants Sampled*

	Chromium	Copper	Lead	Zinc	Mercury	Nickel	Cadmium
Observed range	< 0.05-14.0	<0.02-1.4	0.006-0.68	0.10-1.4	<0.0005-0.24	< 0.04-3.0	< 0.002-0.09
Mean	0.65**	0.18	0.17	0.50	0.002**	0.20	0.02
Standard deviation	1.25	0.24	0.14	0.35	0.0026	0.25	0.018
Background							
Average	0.22	0.11	0.14	0.34	0.001	0.073	0.016
Upper limit	1.90	0.42	0.31	0.85	0.0046	0.45	0.038
Plants exceeding upper limit	1. Fond du Lac 2. Milw. Jones Island 3. Milw. South Shore 4. North Fond du Lac 5. Sheboygan 6. S. Milwaukee	1. Chippewa Falls 2. Eau Claire 3. Milw. South Shore	1. Chippewa Falls 2. Kenosha 3. West Bend	1. Appleton 2. Chippewa Falls 3. Eau Claire 4. Kenosha 5. La Crosse 6. Manitowoc 7. Milw. Jones Island 8. Sheboygan 9. Watertown	1. Kaukauna 2. Madison 3. Menomonie 4. Milw. Jones Island 5. North Fond du Lac 6. Racine 7. West Bend	1. North Fond du Lac 2. Ripon 3. Wisconsin Rapids	1. Fond du Lac 2. Milw. Jones Island 3. Ripon

* mg/l

** The two highest values were excluded in calculation of mean and standard deviation for chromium and mercury because of the wide range of variation.

TABLE 5. Relation Between Influent Concentration and Effluent Concentration for the Treatment Plants Investigated, and Percent Removal of Metals

Metal	Regression Equation	Correlation Coefficient	Percent Removal		
			Primary	Secondary	All Plants
Chromium	$y = 0.38x^{0.84}$	0.836[1]	52	50	50
Copper	$y = 0.41x^{+0.02}$	0.796	37	55	51
Lead	$y = 0.25x^{0.57}$	0.703	38	51	48
Zinc	$y = 0.37x^{+0.08}$	0.588	36	51	48
Cadmium	$y = 0.32x^{+0.007}$	0.813	0	41	34
Mercury	$y = 0.68x^{-0.0002}$*	0.790	14	69	59
	$y = 0.002x^{-0.0004}$**	0.958			
Nickel	$y = 0.87x^{-0.027}$	0.995	50[2]	18	20

*x < 0.01 mg/l
**x > 0.01 mg/l
[1]All correlations significant to the 1% level of probability.
[2]Obtained for only one plant.

TABLE 6. Concentrations of Metals in the Influent, Effluent and Final Digested Sludge from Selected Wisconsin Sewage Treatment Plants.

	Chromium			Copper			Lead			Zinc			Cadmium			Mercury			Nickel		
Plant	I*	E*	S*	I	E	S	I	E	S	I	E	S	I	E	S	I	E	S	I	E	S
Appleton	0.32	1.4	5,400	0.13	0.056	1,200	0.28	<0.08	3,300	0.88	<0.08	3,600	0.008	0.016	13	<0.0005	<0.0005	11.5	0.04	0.08	15
Beaver Dam	0.1	0.02	690	0.04	0.02	370	0.1	<0.05	440	0.2	<0.04	1,500	<0.02	<0.02	15	<0.0005	<0.0005	2.7	0.28	0.2	950
Beloit	0.04	<0.02	260	0.11	<0.02	700	0.08	<0.08	350	0.35	0.65	2,400	<0.01	<0.01	20	0.0016	0.0005	10	<0.08	<0.08	40
Chippewa Falls	0.04	0.05	500	0.9	0.06	1,500	0.5	<0.08	530	1.0	0.1	1,750	0.015	<0.01	10	0.0028	<0.0005	5	<0.08	<0.08	25
DePere	0.12	0.08	1,250	0.012	0.028	490	0.08	0.08	700	0.8	0.34	4,100	0.008	<0.008	37	0.0008	0.0003	5.9	<0.04	<0.04	20
Eau Claire	0.2	0.2	6,400	1.4	0.8	10,000	0.2	<0.2	730	1.0	0.8	6,000	<0.02	<0.02	15	0.0009	0.0008	7	<0.04	<0.04	85
Fond du Lac	14.0	1.8	32,000	0.13	0.04	350	0.3	0.1	990	0.42	0.08	1,550	0.09	0.03	40	0.0013	<0.0005	5.8	0.12	0.12	90
Green Bay MSD	0.20	0.12	290	0.06	0.044	440	0.20	0.16	300	0.38	0.18	1,920	0.016	<0.008	13	<0.0007	<0.0005	2.4	0.14	0.12	140
Janesville	0.20	0.4	2,000	0.1	0.1	1,400	<0.08	0.08	220	0.15	0.2	2,300	<0.02	<0.02	65	<0.0005	<0.0005	2.2	0.15	0.2	520
Kaukauna	0.08	0.03	640	0.056	0.02	1,300	0.2	<0.08	2,200	0.18	0.09	1,400	0.02	0.008	10	0.08	<0.0005	3.6	0.08	<0.04	20
Kenosha	0.28	<0.05	2,000	0.04	<0.05	2,900	0.4	<0.08	550	1.40	0.48	5,500	0.02	<0.02	110	0.001	<0.0005	0.6	0.08	0.1	220
La Crosse	0.4	0.4	1,270	0.17	0.15	1,050	0.3	0.2	530	1.40	0.8	2,280	0.03	0.03	30	0.0008	0.0005	5.4	<0.04	<0.04	50
Madison MSD	0.08	0.06	350	0.08	0.025	670	0.08	0.08	410	0.37	0.12	4,200	0.008	0.008	22	0.013	<0.0005	17.5	0.04	0.04	55
Manitowoc	0.6	0.3	2,300	0.2	0.1	1,300	0.1	0.08	740	1.0	0.5	5,300	0.03	<0.02	100	0.0006	<0.0005	7.1	0.3	0.2	900
Marshfield	0.32	<0.05	800	0.3	0.06	1,500	<0.08	<0.08	300	0.26	0.04	1,800	<0.02	<0.02	13	0.0025	0.0015	22	0.24	<0.05	200
Menomonie	<0.04	0.04	90	0.04	0.04	390	<0.08	<0.08	450	0.22	0.38	1,800	<0.008	0.008	14	0.008	0.008	13.3	<0.04	<0.04	50
Milwaukee MSD																					
1. Jones Is.	2.1	0.1	7,400	0.07	<0.05	500	0.16	<0.08	850	1.0	0.16	3,400	0.06	<0.02	185	0.006	0.0008	—	0.12	<0.05	140
2. S. Shore	5.6	1.5	16,000	0.48	0.36	270	0.3	<0.08	1,350	0.68	0.2	2,900	<0.02	<0.02	15	0.001	0.0008	2.6	0.2	0.1	340
Neenah-Menasha	0.16	0.05	70	0.11	0.15	140	0.2	0.1	200	0.32	0.2	490	<0.01	<0.01	12	0.0015	0.001	7.3	<0.05	<0.05	25
N. Fond du Lac	3.6	2.9	8,500	0.11	0.10	1,780	0.006	0.004	680	0.56	0.48	4,200	<0.002	<0.002	30	0.005	0.004	18	3.0	2.6	7,500
Oshkosh	0.2	0.06	310	0.04	0.02	176	0.1	<0.1	190	0.2	0.08	1,200	0.01	0.01	7	<0.0005	<0.0005	2.4	<0.04	<0.04	15
Portage	<0.05	<0.05	120	<0.05	<0.05	350	<0.1	0.1	500	0.1	0.1	1,800	<0.01	<0.01	12	0.0015	0.001	7.3	<0.05	<0.05	25
Racine	0.24	0.16	3,500	0.14	0.08	2,850	0.2	0.2	4,600	0.44	0.38	8,000	<0.02	<0.02	170	0.24	0.001	8	<0.05	0.07	250
Rhinelander	0.25	0.07	500	0.1	0.1	950	0.2	0.1	1,100	0.35	0.3	2,450	<0.01	0.01	18	0.0006	0.0006	4.4	<0.08	<0.08	220
Ripon	0.6	0.2	1,800	0.12	0.06	470	0.16	0.08	490	0.64	0.38	2,800	0.08	0.04	270	0.0007	0.0006	1.8	0.5	0.32	1,600
Sheboygan	7.4	3.2	13,600	0.08	0.2	165	0.08	0.08	230	1.2	1.0	3,400	0.02	<0.02	20	0.0011	0.0006	2.4	0.08	0.06	75
S. Milwaukee	3.6	2.6	22,500	0.05	<0.05	280	<0.08	<0.08	270	0.14	0.12	620	<0.02	<0.02	<10	<0.0005	<0.0005	1.5	<0.05	<0.05	20
Stevens Point	<0.05	<0.05	50	<0.02	<0.05	290	<0.08	<0.08	100	0.34	0.08	650	<0.02	<0.02	210	0.003	0.002	3.9	<0.05	<0.05	<10
Superior	<0.05	<0.05	220	0.25	0.1	850	<0.08	<0.08	860	0.24	0.28	1,350	<0.02	<0.02	10	0.001	0.001	31	<0.05	<0.05	30
Two Rivers	0.2	0.1	450	0.1	0.07	520	0.15	0.2	850	0.5	0.5	4,300	<0.02	0.02	170	0.0007	<0.0005	2.7	0.28	0.2	950
Watertown	0.35	0.1	1,100	0.4	0.06	1,030	0.08	<0.08	400	1.2	0.25	1,130	0.01	0.01	13	<0.0005	<0.0005	4	0.15	0.15	250
Waukesha	<0.05	<0.05	2,070	0.07	<0.05	2,680	<0.08	<0.08	980	0.24	0.16	12,200	<0.02	<0.02	18	0.0008	<0.0005	11	<0.05	<0.05	170
West Bend	0.17	<0.05	800	0.07	0.06	580	0.68	0.08	1,400	0.28	0.12	3,500	0.02	<0.02	400	0.004	0.001	8.5	<0.05	<0.05	135
Whitewater	0.15	<0.05	215	0.15	<0.05	420	<0.08	<0.08	245	0.4	0.08	1,370	<0.02	<0.02	<10	<0.0005	0.001	—	<0.05	<0.05	20
Wisconsin Rapids	0.6	0.22	2,650	<0.05	<0.05	300	<0.08	<0.08	400	0.12	0.04	1,220	<0.02	<0.02	150	0.002	<0.0005	5	0.64	0.5	1,700

*I = Influent (concentration expressed as mg/l)
E = Effluent (concentration expressed as mg/l)
S = Sludge (concentration expressed as mg/kg dry weight)

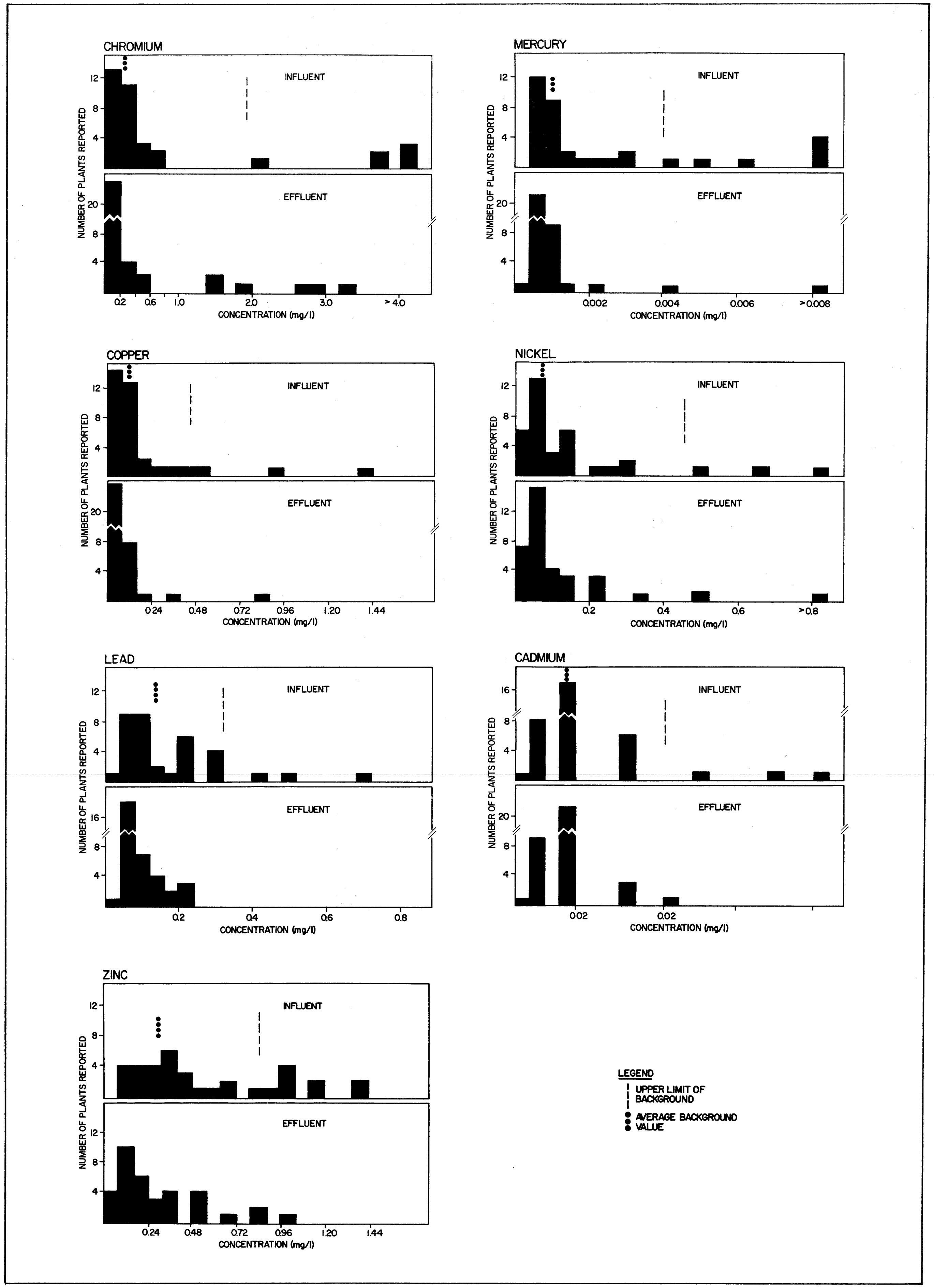


FIGURE 1. *Distribution of influent and effluent concentrations in sewage treatment plants.*

CONCENTRATION OF METALS IN FISH

INTRODUCTION

The Department of Natural Resources began a survey program in April, 1970 to determine levels of toxic metals in Wisconsin fish. The survey followed Swedish and Canadian reports of mercury contamination of fish. The fish were sampled in a variety of Wisconsin waters throughout the state, including waters receiving industrial and municipal wastes, waters draining agricultural areas, lakes and streams removed from the urban population centers, and waters situated in the various soil and bedrock provinces of the state.

The first priority was to analyze the samples for mercury, and these findings have been published (Kleinert and Degurse 1972). Plans were also made to analyze the samples for other toxic metals at a later date when the laboratory would have sufficient time to do the work. Selected fish fillet samples were subsequently analyzed for arsenic, cadmium, chromium, lead and zinc, and the results reported here.

FISH COLLECTIONS

Fish collections were made by field personnel of the Wisconsin Department of Natural Resources from April through November, 1970. Fish were most commonly collected by either trap nets or electrofishing gear with some collections furnished by sport and commercial fishermen.

Fish samples consisted of 1 to 20 fish of the same species. Almost all samples contained medium or larger fish of sufficient size for use as human food or commercial processing. Field personnel were instructed to wrap each sample in separate plastic bags and freeze until delivery could be made to the laboratory. The laboratory conducted a total of 505 metals determinations on 224 fish samples.

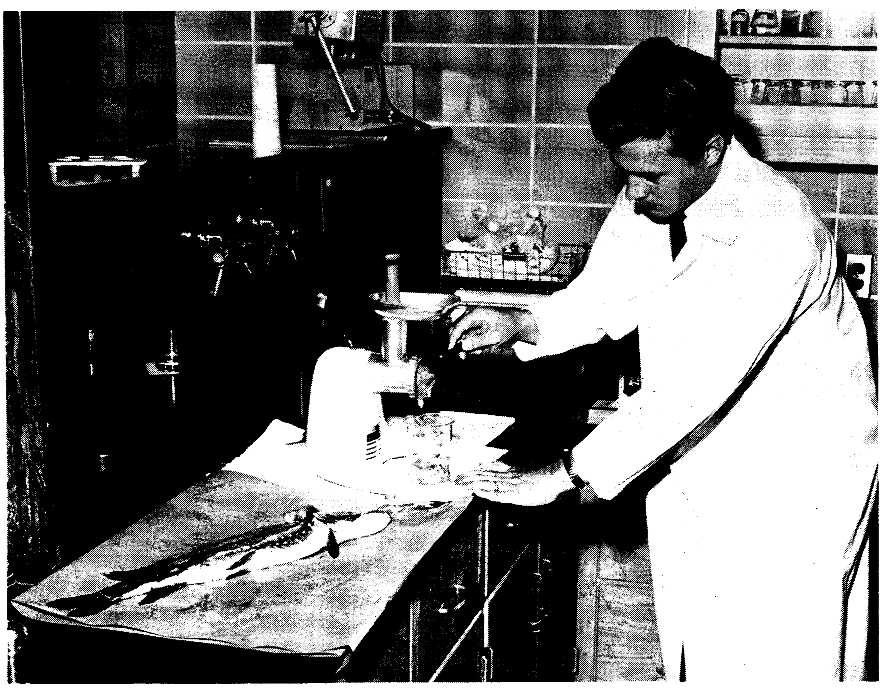
LABORATORY ANALYSIS

Fish fillets, or more specifically fish muscle tissue excluding bone, were processed for analysis. The wet, not previously dried sample was digested prior to analysis. The digestion procedure used for cadmium, chromium and zinc analysis is a modification of the acid digestion procedure described in Standard Methods (American Public Health Association 1971: 418-427).

Cadmium, Chromium and Zinc: Ten grams of sample were placed in a 100 ml Kjeldahl Flask containing two glass beads. Ten milliliters of concentrated HNO_3 was added and the mixture was heated with a flame until half of the volume was left and most of the tissue was in solution. At this time, 1.5 ml of concentrated H_2SO_4 was added and the digestion was continued until charring began. Concentrated nitric acid was added dropwise until the char disappeared. The addition of nitric acid was repeated as necessary until no more charring occurred and the solution was straw colored. The heat was then removed and the solution allowed to cool. After addition of 1.5 ml of 3 to 1 concentrated HNO_3 and $HClO_4$, the solution was reheated until the solution cleared and fumes of SO_3 reached the neck of the flask.

For chromium and zinc the solution was transferred to a 10 ml volumetric flask, diluted to volume with distilled water and read by direct aspiration into the flame of a Perkin Model Elmer Model 403 spectrophotometer employing direct read out capacity and an air-acetylene flame. The wavelengths used for zinc and chromium were 213.8 and 357.9 mμ, respectively. Appropriate standards for zinc and chromium were prepared by diluting volumes of stock solutions with 10 percent concentrated H_2SO_4 in distilled water. Ten samples fortified with chromium and zinc yielded 76 percent recovery for zinc and 95 percent recovery for chromium.

For cadmium another 10 g sample was digested by the above procedure and transferred to a 100 ml volumetric flask for chelation and extraction as described in Standard Methods (American Public Health Association 1971: 210-215). The solution in the flask was diluted to 50 ml total volume with distilled water. Two drops bromophenol blue (0.1 g in 100 ml 50 percent ethanol water solution) were added and the pH was adjusted by adding 2.5 M NaOH by drops until a



Chemist prepares northern pike fillets for metal analysis in the laboratory.

blue color persisted. HCl (0.3 M) was added by drops until the blue color disappeared, then 1 ml 0.3 M HCl was added in excess, followed by 1.5 ml of 1 percent ammonium pyrrolidine dithiocarbamate in water solution; the solution was mixed. Five milliliters methyl isobutyl ketone was added and the mixture was shaken for one minute. The layers were allowed to separate and distilled water was added until the ketone layer was in the neck of the flask. The ketone layer was aspirated into the flame of a Beckman Model DU spectrophotometer equipped with a laminar flow burner and atomic absorption accessory employing an air-acetylene flame. The wavelength used for cadmium was 228.8 mμ. A standard curve was prepared by running 0.0, 0.5, 1.0, 2.5, and 5.0 μg quantities of cadmium through the chelation-extraction procedure. In the samples checked none contained greater than 0.05 ppm cadmium. Seven samples fortified with 0.2-0.3 ppm cadmium gave an average of 90 percent recovery by the procedure.

Lead: Ten milliliters of 5 to 1 concentrated HNO_3 and concentrated $HClO_3$ were added to a 50 ml beaker containing 3 g of sample. The beaker was covered with a watch glass and digested on a hot plate until the solution cleared. The flask was removed from the hot plate, 10 ml distilled water was added and the flask heated again until all but a small amount of acid and water remained (Brown, Skougstad, and Fishman 1970). This was transferred to a 25 ml volumetric flask with 10 ml of distilled water and extracted as for cadmium. The Beckman Model DU spectrophotometer was used for analysis with wavelength set at 217.0 mμ. Fortified samples yielded 90 to 95 percent recovery.

Arsenic: The procedures used for arsenic analysis are described in Morrison and George (1969) and Hundley and Underwood (1970). Ten grams of sample, 3 g MgO, one beakerfull (10 ml) of whatman CF 11 cellulose powder and distilled water were stirred to a homogenous slurry, placed in a coors No. 2 crucible, dried in an air draft oven overnight at 95° C. The dried material was then charred over an open flame until the evolution of smoke ceased. The crucible was allowed to cool. The charred material was covered with 3 g of $Mg(NO_3)_2.6H_2O$, placed in a cold muffle furnace and heated to 550-600° C for 2½ hours. The ashed sample was removed from the furnace, allowed to cool and transferred to a 125 ml Erlenmeyer flask equipped with a 24 & 40 joint using 45 ml of 6N HCl. The crucible was rinsed with 40 ml of distilled water adding the rinse to the sample flask. Two milliliters of 15 percent KI was mixed with the sample, followed by the addition and mixing of 1 ml of 40 percent $SnCl_2.2H_2O$ in concentrated HCl.

Arsenic was evolved from the sample using a Fisher apparatus (Analytical Chemistry 1972). Three milliliters of 0.5 percent silver diethyldithiocarbamate in pyradine was used in the absorber tube as the chelating solution. Three grams of zinc were used to evolve the arsenic. Samples and standards were read against the silver diethyl-dithiocarbamate solution using the Beckman Model DU spectrophotometer set at 540 mμ. A standard curve was prepared using 0.0, 1.0, 2.5, 5.0, and 10.0 μg arsenic per flask. Fifteen fortified samples resulted in an average recovery of 99 percent.

FINDINGS

Table 1 lists the data on the fish collected at each location together with the amounts of the various metals found in the fish fillets. Table 2 lists the species of fish collected in the survey. Locations of waters where the fish were collected are shown in Figure 1. The data are discussed and compared with similar data from other regions and existing standards for metals concentrations in foods for each of the metals as follows:

Cadmium

The detection limit for cadmium in the fish fillets tested was 0.05 ppm. There was no detectable cadmium in the 101 samples from Wisconsin waters. Fish collected in Michigan waters are reported to contain up to 0.3 ppm cadmium (Hesse and Evans 1972) and fish collected in New York State waters are reported to contain 0.04 to 0.17 ppm cadmium (Tong et al. 1972). The U. S. Food and Drug Administration has no standard for cadmium levels in fish but does have a guideline of 0.5 ppm cadmium in leaching solutions added to enamelware and pottery (Food and Drug Administration 1973b).

Chromium

The detection limit for chromium in the fish fillets tested was 0.03 ppm. Measurable amounts of chromium were found in 61 of 97 samples tested. The highest chromium concentrations detected in fish from Wisconsin waters were 0.42 ppm (sucker from Milwaukee Harbor), 0.27 ppm (carp off mouth of the Fox River in Green Bay), and 0.18 ppm (smallmouth bass from the Wisconsin River below the Prairie du Sac Dam). Fish collected in Michigan waters are reported to contain up to 0.5 ppm chromium (Hesse and Evans 1972). The U. S. Food and Drug Administration has no standards for chromium levels in fish or other foods (Potter 1973).

Zinc

The detection limit for zinc in the fish fillets tested was 0.05 ppm. Zinc was found in measurable amounts in all of the 97 fish samples tested. The highest zinc concentrations detected in fish from Wisconsin waters were 18.3 ppm (goldfish from the lower Milwaukee River), 17.6 ppm (bluegill from Trout Lake in Vilas County), 17.0 ppm (pumpkinseed from the Gordon and St. Croix Flowages). Fish collected in Michigan waters are reported to contain from 6 to 45 ppm zinc (Hesse and Evans 1972) and fish collected in New York State waters are reported to contain 1.2 to 38 ppm zinc (Tong et al. 1972). The U. S. Food and Drug Administration has no standards for zinc in foods (Potter 1973). The Canadian Food and Drug Directorate set a standard of 100 ppm zinc in marine and fresh water animal products (Mount et al. 1970).

Lead

The detection limit for lead in the fish fillets tested was 0.05 ppm. Lead was found in measurable amounts in 103 of 115 samples tested. The highest lead concentrations detected in fish from Wisconsin waters were 4.31 ppm (northern pike from the Flambeau Flowage), 2.87 ppm (sucker from the Galena River), and 1.12 ppm (channel catfish from the Wisconsin River near Boscobel). Fish collected in Michigan waters are reported to contain from 0.1 to 0.9 ppm lead (Hesse and Evans 1972). The U. S. Food and Drug Administration has not established standards for lead in fishery products (Potter 1973). The Canadian Food and Drug Directorate set a standard of 10

TABLE 1. Arsenic, Cadmium, Chromium, Lead and Zinc Levels in Fish From Wisconsin Waters

Water	County	Site	Date	Sample Number	Species	Length (Inches)	Metal Levels in ppm				
							Cr	Zn	Cd	As	Pb
Brule River	Douglas	T49N, R10W, S10	21 Jul 1970	464	Sucker	15.0	–	–	0	–	0.27
				463	Sucker	16.0	0	4.3	–	0	–
				450	6 Sucker	10.0	–	–	0	–	0
				461	Walleye	13.0	0	3.7	–	0.13	–
				459	Walleye	13.0	–	–	0	–	0
				456	Brown Trout	10.0	–	–	0	–	0.30
				448	Brown Trout	10.2	0.08	5.7	–	–	–
				454	2 Rainbow Trout	8.0-10.0	0	4.0	–	0	–
Chippewa River	Sawyer	Chippewa Flowage	3 Aug 1970	494	Sucker	15.0	–	–	0	–	0.25
				495	Sucker	15.0	–	–	0	–	0.14
				493	Sucker	17.0	0.03	3.3	–	0	–
				439	Walleye	10.0	–	–	0	–	0.12
				441	Walleye	10.0	–	–	0	–	0.30
				444	Walleye	10.0	0.14	3.4	–	0.10	–
				443	Walleye	10.0	0	3.9	–	0	–
				492	Walleye	17.0	0.04	3.7	–	0	–
Chippewa River	Pepin	Below Durand	11 Sep 1970	983	Sucker	16.0	0.08	10.4	–	0.13	–
				997	Sucker	17.0	–	–	0	–	0.75
				998	Sucker	18.0	–	–	0	–	0.35
				996	Sucker	18.5	0.06	3.8	–	0.10	–
				982	Carp	15.0	–	–	0	–	0.52
				984	Carp	15.0	–	–	0	–	0.67
				986	Carp	15.0	0.05	14.3	–	0.10	–
				970	Walleye	18.0	–	–	0	–	0.44
				971	Walleye	19.0	–	–	0	–	0.45
				972	Walleye	20.0	–	–	–	0.16	–
				995	Walleye	20.0	0.07	3.8	–	0.10	–
				973	Walleye	21.0	0.03	2.9	–	0.13	–
Flambeau River	Iron	Flambeau Flowage	29 Jul 1970	747	Redhorse	16.4	0.04	3.4	–	0.10	–
				728	Redhorse	16.8	–	–	0	–	0.41
				727	Redhorse	17.0	–	–	0	–	0.38
				738	Rock Bass	6.0-7.0	0.04	5.9	–	0.12	–
				748	Northern Pike	14.6	–	–	0	–	0.21
				749	Northern Pike	18.3	–	–	0	–	4.31
				746	Northern Pike	18.3	0.05	3.5	–	0.10	–
				734	Walleye	13.9	0.05	3.5	–	0.10	–
				730	Walleye	17.5	–	–	0	–	0.25
Fox River	Racine	Below Burlington	5 Aug 1970	548	Sucker	14.6	–	–	0	–	0.28
				480	Sucker	16.0	–	–	0	–	0.75
				481	Redhorse	16.0	0	5.7	–	0	–
				483	Carp	–	–	–	–	–	0.32
				485	Carp	–	–	–	0	–	0.22
				488	2 Crappie	–	–	–	0	–	–
				484	White Bass	14.0	0.03	4.0	–	0	–
				476	Smallmouth Bass	17.3	–	4.7	–	0	–
				551	Channel Catfish	12.0	–	–	0	–	–
				552	Channel Catfish	12.0	–	–	0	–	0.35
Galena River	Lafayette	T2N, R1E, S27	6 Aug 1970	501	2 Sucker	9.1-9.9	–	–	0	–	2.87
				502	3 Sucker	10.0-11.0	0.04	5.0	–	0	–
				498	2 Smallmouth Bass	9.6	–	–	0	–	0.27
				496	Smallmouth Bass	11.8	0.03	3.7	–	0	–
Green Bay	Brown	E. of Fox River Mouth	5 Aug 1970	1,193	Carp	16.0	–	–	0	–	0.44
				1,194	Carp	16.0	–	–	0	–	0.46
				1,195	Carp	16.0	–	–	0	–	0.27
				1,191	Carp	18.0	0.07	8.8	–	–	–
				1,190	Carp	30.0	0.27	7.1	–	–	–
Green Bay	Door	N. of Sturgeon Bay Canal	5 Jun 1970	358	5 Sucker	14.7-18.5	–	–	–	–	0.12
				360	Lake Alewife	6.7-9.5	–	–	0	–	0.12
				363	Cisco	16.0	0	3.7	–	0.10	–
				359	3 Burbot	20.0-28.8	0	5.1	–	0.10	–
				356	Lake Trout	26.0	–	–	–	–	0.11
				355	Lake Trout	28.5	–	–	–	0.35	–
Lake Geneva	Walworth	Lake Geneva	13 Oct 1970	1,401	Carp	25.8	–	–	–	–	0.35
				1,400	Carp	30.4	–	–	–	–	0.27
				1,378	Northern Pike	21.6	–	–	–	–	0.26
				1,368	Largemouth Bass	12.8	0.07	4.7	–	0.10	–
				1,384	Smallmouth Bass	10.5	–	–	–	–	0.26
				1,381	Smallmouth Bass	12.5	0.07	4.5	–	0	–
				1,380	Smallmouth Bass	12.7	0.05	4.4	–	0.10	–
				1,369	Smallmouth Bass	13.0	0.06	6.1	–	0	–

Water	County	Site	Date	Sample Number	Species	Length (Inches)	Metal Levels in ppm				
							Cr	Zn	Cd	As	Pb
Lake Mendota	Dane	Lake Mendota	23 Jul 1970	1,187	Sucker	16.1	–	–	0	–	0.32
			and	1,175	Sucker	17.2	–	–	0	–	0.53
			29 Sep 1970	1,186	Sucker	18.6	0.07	3.5	–	0	–
				1,185	Sucker	18.8	0.09	3.6	–	0.10	–
				612	Carp	15.0	–	–	0	–	–
				617	White Bass	12.2	–	–	–	–	0.32
				616	White Bass	12.5	–	–	0	–	0.39
				608	White Bass	13.5	0	3.5	–	0.11	–
				607	Northern Pike	15.0	0.05	3.4	–	0	–
				1,212	Walleye	16.0	–	–	–	–	0.59
				1,180	2 Bluegills	6.4-8.1	–	–	0	–	0.22
Lake Michigan	Kewaunee	E. of Kewaunee	1 Jun 1970	323	10 Alewife	5.6-8.0	–	–	–	–	0
				335	Rainbow Trout	17.7	–	–	0	–	0.25
				332	Brown Trout	18.5	–	–	0	–	0.25
				336	Brook Trout	17.3	0	3.2	–	0	–
				334	Coho Salmon	19.3	0	4.1	–	0.14	–
Lake Superior	Bayfield	Apostle Island	12 Aug 1970	778	Sucker	14.0	–	–	0	–	0.25
				777	Sucker	16.2	–	–	0	–	0.21
				776	Sucker	18.8	0.20	4.0	–	0.12	–
				772	Brown Trout	17.7	–	–	0	–	0.21
				771	Brown Trout	17.7	0.09	4.2	–	0	–
				782	Lake Trout	20.6	–	–	0	–	0.34
				781	Lake Trout	20.7	0.07	3.4	–	0.12	–
Lake Waubesa	Dane	Lake Waubesa	28 Jul 1970	520	Carp	21.0	–	–	0	–	0.50
				521	Carp	21.0	–	–	0	–	0.50
				836	Northern Pike	21.5	–	–	0	–	0.30
				815	Northern Pike	22.0	0.07	4.2	–	0	–
				596	Largemouth Bass	–	0.05	7.2	–	0	–
				595	Largemouth Bass	8.1	0.04	5.7	–	0.10	–
				594	Largemouth Bass	11.6	–	–	0	–	0.26
Lake Winnebago	Winnebago	Asylum Bay	23 Apr 1970	232	Freshwater Drum	13.5	–	–	0	–	0.05
				228	Freshwater Drum	14.0	–	–	0	–	0.05
				229	Freshwater Drum	17.0	0	4.1	–	0	–
				231	Freshwater Drum	17.0	–	–	–	0	–
				238	2 Crappie	11.0	–	–	0	–	0.05
				236	Crappie	11.0	–	–	0	–	0.05
				234	Crappie	11.0	0	4.6	–	0	–
				237	Northern Pike	12.0	0	4.8	–	0	–
				239	Northern Pike	20.0	–	–	0	–	0.94
Menominee River	Marinette	River Mouth	20 May 1970	182	2 Sucker	14.0-18.0	–	–	0	–	0.07
			and	66	2 Sucker	20.0	–	–	0	–	0.18
			15 Jun 1970	181	3 Bullheads	8.8-9.1	–	–	0	–	0.05
				69	3 Bullheads	8.5-10.0	–	–	0	–	0.05
				214	2 Sunfish	7.0	0.04	5.7	–	0	–
				176	Sunfish	7.5	0	4.8	–	–	–
				215	Largemouth Bass	14.5	0	3.7	–	0	–
				185	Largemouth Bass	16.0	0	4.1	–	0.12	–
Milwaukee River	Milwaukee	Above North Ave.	9 Jul 1970	418	8 Goldfish	10.0	0	18.3	–	0.10	–
				417	3 Carp	10.0-13.0	–	–	0	–	0.30
				416	Carp	14.0	–	–	0	–	0.27
				415	Carp	16.0	–	–	–	0	–
Milwaukee River	Milwaukee	Milwaukee Harbor	20 May 1970	18	Sucker	–	0.42	6.9	–	0	–
			and	22	3 Sucker	–	–	–	0	–	–
			25 May 1970	17	2 Coho Salmon	18.0-20.0	0	4.6	–	0	–
Milwaukee River	Ozaukee	Above Thiensville	8 Jul 1970	407	4 Sucker	10.0-14.0	0	4.8	–	0	–
				408	4 Sucker	11.0-12.0	0	4.7	–	0	–
				409	Carp	15.0	–	–	0	–	0.05
				410	Carp	17.0	–	–	0	–	0.30
				411	Carp	18.0	0	10.6	–	0	–
				414	Northern Pike	15.0	–	–	0	–	0.06
				412	Northern Pike	17.0	0	4.2	–	0	–
				413	Northern Pike	17.0	–	–	0	–	0.05
Mississippi River	Pepin	Lake Pepin	15 Jun 1970	301	5 Sucker	10.0-16.0	–	–	0	–	0.0
				266	Crappie	10.0	0	4.4	–	0	–
				263	Crappie	11.0	–	–	0	–	0.05
				264	Crappie	11.0	–	–	0	–	0.05
				221	Channel Catfish	18.0	0	5.7	–	0	–
				277	Northern Pike	18.0	0	3.8	–	0	–
				270	Largemouth Bass	17.0	–	–	0	–	0.0
				272	Largemouth Bass	17.0	0	3.9	–	0	–

Water	County	Site	Date	Sample Number	Species	Length (Inches)	Metal Levels in ppm				
							Cr	Zn	Cd	As	Pb
Mississippi River	Vernon	Below Stoddard	18 May 1970	1	4 Sucker	15.0-17.0	–	–	0	–	0.18
				4	5 Crappie	9.5-11.0	0	5.9	–	–	–
				2	3 Walleye	10.0-12.0	–	–	0	–	0.05
				5	3 Largemouth Bass	10.0-14.0	–	–	0	–	0.18
				3	2 Channel Catfish	18.0-20.5	0	4.7	–	–	–
				6	6 Northern Pike	26.0	0.04	3.8	–	–	–
Nevin Hatchery	Dane	Hatchery Ponds	17 Sep 1970	1,010	Rainbow Trout	–	–	–	0	–	–
				1,011	Rainbow Trout	–	–	–	0	–	–
				1,016	Rainbow Trout	–	0.09	3.9	–	0.10	–
				1,017	Rainbow Trout	–	0.06	3.0	–	0.14	–
Rock River	Dodge	Horicon	15 May 1970	353	Northern Pike	25.0	–	–	0	–	0.10
				351	Northern Pike	26.0	–	–	0	–	0.10
				350	Northern Pike	28.0	0.09	5.1	–	0	–
				349	Northern Pike	30.0	0	5.8	–	0	–
Rock River	Jefferson	Lk. Koshkonong	16 Jul 1970	388	Carp	23.0	–	–	0	–	0.0
				387	Carp	24.0	–	–	0	–	0.30
				386	Carp	24.5	0	6.6	–	0.10	–
				385	Carp	25.0	0	8.4	–	0	–
				400	Channel Catfish	12.5	–	–	0	–	0.0
				401	Channel Catfish	16.0	–	–	0	–	0.0
Rock River	Rock	Below Janesville	16 Jul 1970	379	3 Carp	13.5-15.0	–	–	0	–	0.12
				378	Carp	17.5	–	–	0	–	0.12
				380	2 Crappie	8.0	–	–	0	–	0.12
				381	2 Yellow Bass	–	0.04	5.8	–	–	–
				376	Channel Catfish	17.7	0.03	5.7	–	0	–
				377	Northern Pike	16.0	0	4.7	–	0	–
St. Croix River	Douglas	Gordon and St. Croix Flowage	20 Oct 1970	1,448	White Sucker	12.5	–	–	–	–	0.25
				1,447	White Sucker	17.5	–	–	–	–	0.76
				1,480	2 Crappie	8.0-9.0	0.10	14.2	–	0.10	–
				1,475	7 Pumpkinseed	4.5-6.2	0.08	17.0	–	0.17	–
				1,466	Largemouth Bass	15.0	–	–	–	–	0.25
				1,464	Largemouth Bass	18.0	0.05	3.5	–	0.10	–
				1,457	Northern Pike	16.0	0.05	5.1	–	0.10	–
				1,453	Northern Pike	24.0	–	–	–	–	0.58
				1,452	Northern Pike	28.0	–	–	–	–	0.36
St. Louis River	Douglas	River Mouth	5 May 1970 and 11 Aug 1970	834	Sucker	13.5	–	–	0	–	0.33
				833	Sucker	14.0	–	–	0	–	0.45
				832	Sucker	14.0	0.06	3.5	–	0.10	–
				831	Sucker	16.5	0.05	3.8	–	0	–
				164	Walleye	22.5	–	–	0	–	0.05
				162	Walleye	23.7	0.04	3.9	–	0.10	–
Trout Lake	Vilas	Trout Lake	21 Jul 1970 and 23 Jul 1970	882	Sucker	18.2	–	–	0	–	0.73
				873	Redhorse	25.3	–	–	0	–	0.28
				1,269	5 Bluegill	6.2-7.5	0.12	17.6	–	0.10	–
				1,272	5 Bluegill	6.4-7.2	0.13	17.6	–	0.11	–
				1,268	5 Rock Bass	6.9-8.1	–	–	–	0.10	–
				1,263	5 Yellow Perch	7.9-8.0	–	–	–	0.11	–
				1,262	5 Yellow Perch	8.9-10.1	–	–	0	–	0.66
				875	Walleye	16.9	–	–	0	–	0.28
Wisconsin River	Vilas	Lac Vieux Desert	30 Jun 1970	278	4 Sucker	13.0-20.0	–	–	0	–	0.0
				286	3 Yellow Perch	3.0-7.0	–	–	0	–	0.0
				284	Yellow Perch	10.0	0.03	5.7	–	0	–
				283	Northern Pike	23.0	–	–	0	–	0.0
				281	Walleye	14.0	–	–	0	–	0.0
				282	Walleye	14.0	0	3.7	–	0	–
				280	Walleye	16.0	0	4.2	–	0	–
Wisconsin River	Marathon	Lake Wausau	13 Oct 1970	1,341	Carp	13.7	0.13	4.2	–	0.10	–
				1,347	Sucker	18.0	–	–	–	–	0.27
				1,348	Sucker	18.0	–	–	–	–	0.22
				1,335	Bowfin	20.0	0.09	2.7	–	0	–
				1,362	5 Bluegills	4.0-8.0	–	–	–	–	0.48
				1,364	5 Sunfish	5.3-6.9	0.09	16.6	–	0.13	–
				1,367	5 Yellow Perch	5.5-9.0	0.10	15.0	–	0	–
				1,339	Northern Pike	22.0	–	–	–	–	0.22
				1,338	Northern Pike	22.6	–	–	–	–	0.41
Wisconsin River	Adams-Juneau	Upper Petenwell Flowage	11 May 1970	347	Carp	18.0	0	3.0	0	–	0.12
				346	Carp	25.0	–	–	0	–	0.19
				328	Crappie	12.0	0.04	4.5	–	0	–
				342	Northern Pike	17.0	–	–	0	–	0.15
				343	Northern Pike	18.0	–	–	0	–	0.19
				341	Walleye	13.0	–	–	–	0	–
Wisconsin River	Dane-Sauk	Below Prairie du Sac Dam	15 May 1970	26	Carp	17.0	–	–	0	–	0.25
				27	White Bass	16.5	0.04	7.6	0	0	–
				30	3 Largemouth Bass	10.5-14.0	–	–	0	–	0.07
				28	2 Smallmouth Bass	10.0-11.0	0.18	10.5	–	0	–
				29	Walleye	16.0	0.14	5.0	–	0	–

Water	County	Site	Date	Sample Number	Species	Length (Inches)	Metal Levels in ppm Cr	Zn	Cd	As	Pb
Wisconsin River	Grant-Crawford	Boscobel	29 Jun 1970	1,286	Carp	21.9	0.05	6.0		0	
				126	Redhorse	16.0	0.03	3.8		0	
				127	Quillback	16.0					0.05
				121	Freshwater Drum	12.0			0		0.05
				120	Freshwater Drum	16.0	0.04	3.6		0	
				1,291	Channel Catfish	18.3			0		1.12
				1,290	Channel Catfish	19.0			0		0.70
				1,304	Smallmouth Bass	15.2	0.08	3.7		0.12	

*0 = sample tested and the metal not present in detectable concentrations.
– = sample not tested for the metal indicated.

ppm lead in marine and fresh water animal products (Mount et al. 1970).

Arsenic

The detection limit for arsenic in the fish fillets tested was 0.1 ppm. Arsenic was found in measurable amounts in 29 of 95 samples tested. The highest arsenic concentration detected in fish from Wisconsin waters was 0.35 ppm (lake trout from Green Bay), 0.17 ppm (pumpkinseed from the Gordon and St. Croix Flowages) and 0.16 ppm (walleye from the Chippewa River below Durand). Fish collected in Michigan waters are reported to contain up to 0.40 ppm arsenic. The U. S. Food and Drug Administration has no standards for arsenic in fish, but has established a tolerance level of 2 ppm for arsenic in chicken and turkey livers, gizzards, kidneys, and hearts and in similar meat for swine (Food and Drug Administration 1973a).

DISCUSSION AND CONCLUSION

Cadmium was not found in detectable amounts in the fish samples tested. Chromium, arsenic and lead were present in quantities less than 1 ppm with the exception of three samples which exceeded 1 ppm lead. Zinc levels were present in greater amounts, ranging between 3.0 and 18.3 ppm. These data compare with the results obtained for similar surveys conducted in Michigan by Hesse and Evans (1972) and in New York State by Tong et al. (1972).

Although certain samples showed higher concentrations of one or more of the metals analyzed, no general trends were apparent in the data which would indicate fish from areas of higher metal use had significantly higher metal concentrations. An exception was that the highest chromium levels were found in fish samples taken from Milwaukee Harbor and at the mouth of the Fox River in Green Bay which are industrial areas. Bluegill from Trout Lake in Vilas County contained nearly as much zinc as goldfish from the lower Milwaukee River. A much larger sample size would be required before meaningful statistical comparisons of the metals' levels in fish from various locations in the state could be made. Hesse and Evans (1972) report that fish from locations of metal discharge in Michigan have higher concentrations of zinc, chromium, and copper.

Species differences have been noted in the levels of metals present in fish. Previous studies of mercury in fish indicate the larger fish of the same species often contain higher mercury concentrations, as do certain species such as walleye and northern pike (Kleinert and Degurse 1972). The sample sizes in the present study are too small to allow similar comparisons. Hesse and Evans (1972) report that mercury is concentrated most by predatory species while zinc, chromium, copper, manganese and nickel tend to be highest in bottom feeding species including carp, suckers, and redhorse.

All foods, including meat and fish, normally contain small amounts of most of the metals, some of which are necessary nutrients. Studies of metals in the total diets of children showed cadmium concentrations from 0.027 to 0.062 ppm, chromium concentrations from 0.175 to 0.472 ppm, and zinc concentrations from 2.67 to 6.36 ppm (Murthy et al. 1971). Mercury concentrations in fish have reached levels that are dangerous to consumers at two locations in Japan as a consequence of industrial pollution (Takeuchi 1970). Although no harmful incidents have been reported, fishermen have been advised to limit their consumption of fish from sections of the Wisconsin, Chippewa, and Flambeau Rivers because fish from these waters commonly exceed the Food and Drug Administration tolerance level of 0.5 ppm mercury in fish (Kleinert and Degurse 1972).

Metal levels in the fish tested in this survey are below standards established by the U. S. Food and Drug Administration and/or the Canadian Food and Drug Directorate for zinc, arsenic, and lead in foods. There are no standards for comparison for cadmium and chromium. However, levels of cadmium and chromium in fish tested less than 0.5 ppm, which is the tolerance level for mercury (a more toxic metal than cadmium and chromium) in fish. Based upon the fish tested in this survey, we do not believe arsenic, lead, zinc, cadmium, and chromium are present in sufficient amounts to create any hazard to consumers.

Although much remains to be learned, it is evident that the concentration of metals in fish tissue is a complex phenomenon, dependent upon many factors, which involve the chemistry of metal compounds in water as well as physiological processes within the fish. Studies should be conducted to determine the extent to

TABLE 2. Fish Species Collected in the Survey

Common Name	Scientific Name
Rough Fish and Minnows	
Sucker	*Catostomus* spp.
Redhorse	*Moxostoma* spp.
Quillback	*Carpiodes cyprinus*
Freshwater drum	*Aplodinotus grunniens*
Carp	*Cyprinus carpio*
Goldfish	*Carassius auratus*
Bowfin	*Amia calva*
Alewife	*Alosa pseudoharengus*
Game Fish and Panfish	
Largemouth bass	*Micropterus salmoides*
Smallmouth bass	*Micropterus dolomieui*
Bluegill	*Lepomis macrochirus*
Crappie	*Pomoxis* spp.
Pumpkinseed	*Lepomis gibbosus*
Rockbass	*Ambloplites rupestris*
Northern pike	*Esox Lucius*
Catfish	*Ictalurus* spp.
Yellow perch	*Perca flavescens*
Walleye	*Stizostedion vitreum*
Cisco	*Coregus artedii*
Brook trout	*Salvelinus fontinalis*
Brown trout	*Salmo Trutta*
Rainbow trout	*Salmo gairdneri*
Lake trout	*Salvelinus namaycush*
Coho salmon	*Oncorhynchus kisutch*
White bass	*Roccus chrysops*
Yellow bass	*Roccus mississippiensis*
Burbot	*Lota lota*

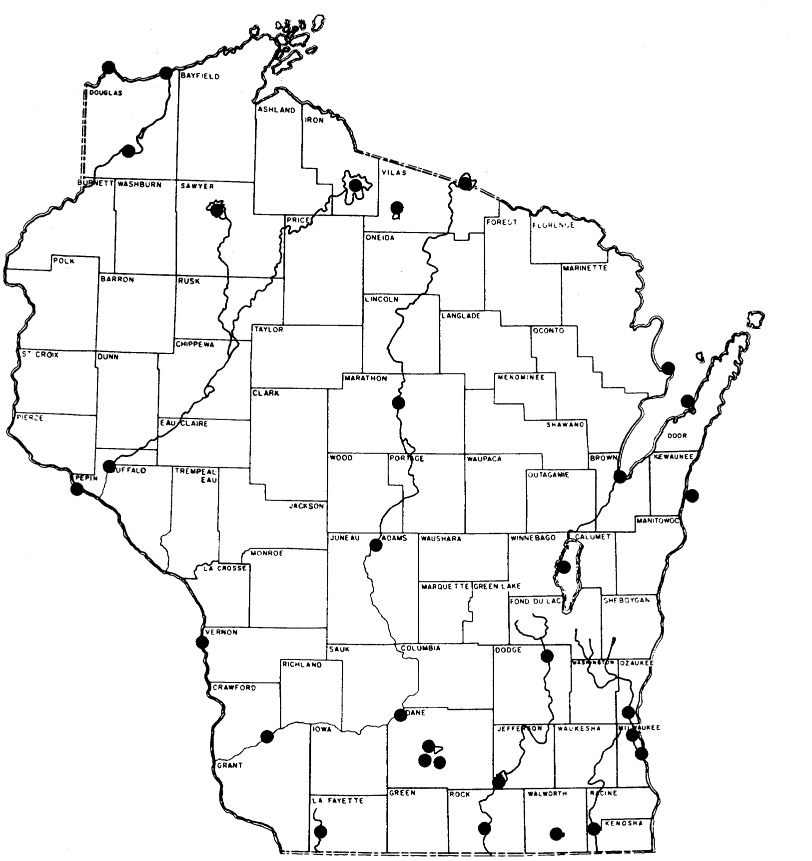


FIGURE 1. *Collection locations of fish sampled in the survey.*

which various metals accumulate in fish under experimental conditions. Unidentified pollution sources will be identified under new surveillance programs authorized by s. 144.54 of the Wisconsin Statutes. This law requires facilities discharging industrial wastes and toxic substances to report annually to the Department the concentration and quantity of the pollutants, including toxic metals, which are discharged. The first reports under this program are due on March 1, 1974. The reports can be used as a basis to identify new locations where fish samples should be taken for metal analysis.

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