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Concentration and Distribution of Selected Trace Elements In The Maumee River Basin, Ohio, Indiana and Michigan

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State of Ohio
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ABSTRACT

During the period August, 1971 to April, 1973, water and stream-bottom sediment samples were collected from 225 sites distributed throughout the Maumee River basin in northwestern Ohio, southeastern Michigan and northeastern Indiana. Split sediment samples were treated with a weak and a strong extractant before being examined by an atomic absorption spectrophotometer. Water samples were analyzed without specific preparation. The water and sediment samples were analyzed in order to determine the concentration of Ag, Al, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sn, Sr, and Zn.

The concentration of these elements in both water and sediment included a wide range, but in most cases, the concentrations in water are very small while in sediment it may be very large.

Seven municipalities within the basin are characterized by large concentrations of one or more elements in water or sediment. These localities include Fort Wayne and Butler, Indiana; Hudson, Michigan; and Maumee, Findlay, Defiance, and Decatur, Ohio. The high concentrations are probably the result of industrial and municipal waste disposal.

Not all anomolous concentrations are restricted to industrial centers. A large number of samples from small streams in rural areas contained high concentrations of arsenic, mercury, lead, zinc and nickel. These may be related to the agricultural use of pesticides. A natural source, however, may be related to the discharge of mineralized ground water, which reflects the chemical composition of the strata through which the water has migrated.

Some high concentrations may be more apparent than real, particularly for those elements characterized by a low wave length. This is due to instrument error, and analytical techniques. In particular, these elelemts include arsenic, mercury and tin.

INTRODUCTION

In recent years, and particularly since the discovery of mercury in Lake St. Clair and Lake Erie, the general population has become increasingly aware of the role of heavy metals in relation to health. Unfortunately, an adequate data bank, relating to concentrations of trace elements in the environment, is not presently available, although the acquisition of knowledge is progressing at an enormous rate. In view of the general lack of specific data, particularly background information, it is exceedingly difficult to determine when a chemical parameter in water or sediment is anomalous. Consequently, it is equally difficult to establish realistic limits of certain trace elements in consumable items.

Depending on their chemical state, metals such as arsenic, lead, cadmium, and mercury may be very toxic in small concentrations. Others, such as copper, cobalt, zinc, chromium, and possibly nickel and tin, are essential to life in trace amounts (Lee, 1972). Although little is known about the effects of aluminum, silver, and strontium on health, their ingestion in excessive amounts may be dangerous. While it is possible that low levels may not harm adults, they may have adverse long-term effects on children. The toxic effect of a trace metal in water is determined by the intrinsic toxicity of the metal itself as well as by its possible occurrence in other parts of the physical environmental, such as the atmosphere, foods, and soils. Consequently, the physiological significance of each trace element must be evaluated in terms of total human environment.

Relatively abundant, the average concentration in the earth's crust of aluminum, strontium, chromium, nickel, zinc, copper, cobalt, and lead are respectively, 82,300 mg/kg (milligram per kilogram), 375 mg/kg, 100 mg/kg, 75 mg/kg, 70 mg/kg, 55 mg/kg, 25 mg/kg, and 13 mg/kg. On the other hand, arsenic, tin, cadmium, mercury, and silver are relatively rare with average concentrations, respectively, of 2 mg/kg, 2 mg/kg, 0.2 mg/kg, 0.08 mg/kg, and 0.07 mg/kg, (Mason and Verry, 1968).

Trace metals, however, tend to concentrate in anomalous areas and the background concentrations of any one of these metals may be much less or much more than these average values. For example, high concentrations of lead, mercury, and cadmium may be present in various ores, coal, lignite, petroleum, phosphate-bearing rocks and limestone. Some sea organisms may concentrate lead, silver, and cadmium in their tissues 1000 to 200,000 times the average concentration found in the oceans (Thompson, 1971).

Trace elements may also be concentrated by the activities of man. Industrial waste and municipal sewage, which may contain relatively high concentrations of a few trace metals, are dumped into streams, rivers, lakes, and oceans. Particulate and gaseous matter is allowed to contaminate the atmosphere with thousands of tons of pollutants containing high concentrations of, among other things, cadmium, arsenic, mercury, and lead, which, in turn, covers the soil with chemically rich substances. Even public water-supply systems may be concentrating potentially toxic trace metals. Lead, cadmium, silver, zinc, and copper may be found in finished waters as a result of plumbing, while lead chromate paints used in steel water storage tanks may be a source of lead and chromium. The use of aluminum sulfide at the treatment plant may increase the aluminum concentration in the finished water by a factor of five. Windhock, capital of South West Africa and the first city to recycle waste water directly into drinking water, may be concentrating trace metals in the process (Hafen, 1972).

The Ohio Department of Health (1953) indicated that, although there is evidence of metallic wastes being generated within the Maumee River basin, few investigations comparing trace metal concentrations in water and sediment have been undertaken. Considering the possible toxic effects of some trace metals, a quantitative study of this type should be of benefit to all basin residents, and to those involved in resource management, public health, and industry.

Samples of water collected from a flowing stream represent the chemical conditions that existed only during the instant that the water sample was collected--a single instant in time. A waste discharged into a stream might be reflected in a water sample, but, if the injection is intermittant, the sample more likely, would show nothing significant.

A standard method of geochemical prospecting in many parts of the world includes the collection and chemical analysis of stream deposits. Stream deposits provide clues to the geochemistry of a drainage basin because many chemical substances are continuously incorporated as a part of the deposit. Consequently, the deposits serve as a storehouse of information concerning the history of the area upstream from the sampling site.

Purpose and Scope of the Investigation

The purpose of this study was to determine the concentration and distribution of selected trace elements in surface water and stream sediments in the Maumee River basin, which lies prinicpally in northwestern Ohio (Figure 1). The trace elements (those that generally occur in concentrations of less than one mg/l in solution) examined during the study were aluminum, arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, silver, strontium, tin, and zinc. It was suspected that a survey of this type could provide sufficient information to determine both the background concentration of each element and range of concentration in sediment and water.

Because of the size of the basin (6586 square miles) and the time involved in collecting and analyzing samples, the study was restricted to a broad regional approach. No single area was studied in detail and repetitive samples were not taken from sites that showed anomalously high values for various metals.

A few sites that contain unusually high concentrations of a few heavy metals were detected. These should be examined in greater detail.

Previous Investigations

During the summer and fall of 1950 and 1951, the Ohio Department of Health and the Indiana Stream Pollution Control Board conducted a pollution survey in the Maumee River basin (Ohio Department of Health, 1953). They found many water courses grossly contaminated and indicated concern over the discharge of copper and zinc at St. Marys, chromium, cadmium and copper in plating wastes at Bluffton, nickel and chromium in the vicinity of Defiance and chemical and metallic wastes at Fort Wayne. In addition, phenolic compounds were being discharged at Lima, Waterville, Toledo, Findlay, Fort Wayne and Auburn.

Kopp and Kroner (1968), as a part of their national study in 1962-1967, collected several water samples from the Maumee River at Toledo. The samples were analyzed for aluminum, arsenic, cadmium, chromium, copper, nickel, lead, and silver. The results of these analyses are presented in Table 1.

Losee and Adkins (1971) investigated the relationship between selected trace elements and the formation of dental caries. Their study included part

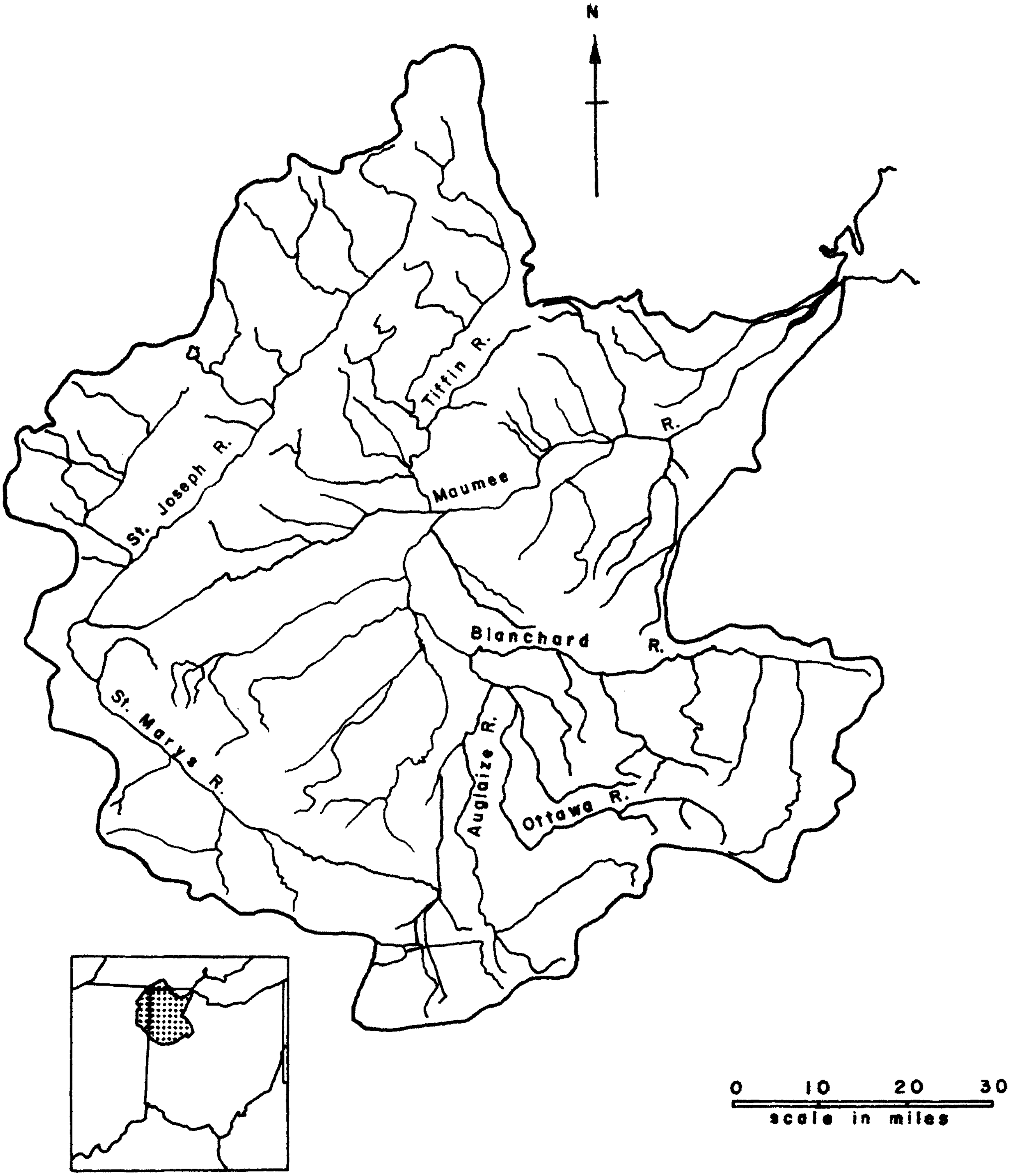

Figure 1. Index map showing the major streams in the Maumee River basin.

Element	Number of Positive Occurrences	Frequency of Detection, %	Positive Observed Values, mg/l		
			Min.	Max.	Mean
Ag	3	12.5	.001	.009	.0053
Al	7	29.1	.025	.138	.069
As	2	8.3	.281	.336	.309
Cd	1	4.1	--	--	.009[1]
Cr	7	29.1	.006	.015	.011
Cu	19	79.2	.005	.039	.010
Ni	8	33.3	.009	.058	.024
Pb	9	37.5	.016	.090	.036

[1] Single value

Table 1. Trace-metal concentrations in water samples collected from the Maumee River at Toledo, Ohio (Data from Kopp and Kroner, 1968).

of northwestern Ohio. They found that "the residences of 62 percent of the caries-resistant men were on high-lime Wisconsin Till soils associated with rocks that contain extensive celestite deposits. The water supplies had significantly more boron, lithium, molybdenum, and strontum than the finished water supplies for the seven largest cities in Ohio" (p. 203). Losee and Adkins reported that the water in the Ohio part of the study area, which was used for cooking and drinking, was highly mineralized ground water and that a very high percentage of the foodstuffs consumed were locally grown. Additionally, they reported that during cooking, strontium, molybdenum, and lithium were transferred from the cooking water to the foodstuff (beans). One can only conclude from their report that strontium, lithium, molybdenum, and boron in the diet may have a significant effect on the reduction of dental caries.

Birsa (1972) analyzed 17 limestone and dolomite samples from quarries in northwestern Ohio for copper, chromium, cadmium, nickel, and lead. He reported anomalously high values of nickel and higher than average concentrations of lead. Birsa's results are compared with world average values in limestone and dolomite, as provided by Rankama (1950), in Table 2.

	Rankama (1950)		Birsa (1972)
Copper	Average for limestone	20.2 ppm	8.01 ppm
	Average for dolomite	12.6 ppm	1.
Chromium	Carbonate from Lapland	2.0 ppm	1.96 ppm
Cadmium			1.86 ppm
Nickel	Limestone from Sweden	3.0 to 10.0 ppm	178.44 ppm
Lead	Average of several samples	5.0 to 32.6 ppm	33.31 ppm

Table 2. Average concentration of selected heavy metals in carbonate rocks in the Maumee River Basin and world averages.

Welsh (1972) examined 46 aquatic and streamside plants, collected in the vicinity of Defiance, Findlay, and Lima, Ohio, for calcium, cadmium, chromium, copper, lead, nickel, and strontium. In some cases, he found lead concentrations in the plants to be 10 to 20 times greater than that in the subjacent alluvium. Statistical data outlined by Welsh (1972, p. 36) are shown in Table 3.

Four trace metals (copper, lead, mercury, and zinc) were examined in eight water and sediment samples collected from the Ottawa River in the vicinity of Lima by Webb (1972). Although concentrations of lead and mercury in water were too small to be detected, copper and zinc reached a maximum of 0.011 and 0.113 mg/l, respectively. Using an extracting agent consisting of hydrochloric and sulfuric acid, sediment samples when found to contain as much as 200.98 mg/l of lead, 163.51 mg/l of mercury, 1345.55 mg/l of zinc, and 4.18 mg/l of copper. Webb concluded that anomalous concentrations in sediment samples were possibly due to agricultural chemicals and waste disposal.

A study similar to Webbs was conducted by Bowen (1972) along the Blanchard River. Bowen collected eight water and eight sediment samples representing an equal number of rural and urban areas, and determined their concentration of copper, mercury, lead, and zinc. Mercury and lead were not detected in any water sample, copper was present in only two, but zinc reached a maximum of 0.018 mg/l and was present, at least in trace amounts, in all of them. Using an acid extracting agent for the sediment, he found concentrations of copper to range from a trace to 7.078 mg/l, mercury to range from undetectable to a maximum 79.063 mg/l, lead to range from undetected to 22.088 mg/l, and zinc to range from 0.511 to a maximum of 21.468 mg/l. Bowen pointed out that, with one exception, high concentrations of mercury were present only in agricultural areas. The exception was collected about 600 yards downstream from a large medical complex.

Schultz (1972) analyzed 85 water and 82 sediment samples collected throughout the Maumee River basin. He looked for 10 metals (aluminum, arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver and tin). The results of Schultz'a study are summarized in Table 4. The study was continued by Hayes (1973), who examined 140 water and 113 sediment samples. Hayes not only looked for the 10 metals that Schultz analyzed, but added cobalt, strontium and zinc. His collections increased the density of sampling sites throughout the basin. The investigations by Hayes and Schultz were funded by the Office of Water Resources Research (Project Numbers 417X and 396X) through the Water Resources Center at The Ohio State University. This report is the final project report and summarizes the work conducted by Schultz and Hayes.

Element		Concentration (ug/g)	Sample Number
Cu	Max.	863.912	0-39, grass
	Mean	55.082	
	Min.	0.000	M-34, weeds
Ni	Max.	390.082	B-12,aquatic plant
	Mean	27.307	
	Min.	0.000	M-30, M-34, M-36 0-38, B-42
Pb	Max.	231.836	M-34, weeds
	Mean	23.881	
	Min.	0.000	0-36, 0-38, 0-41
Cd	Max.	125.494	0-37, tree roots
	Mean	4.672	
	Min.	0.000	M-36, 0-36, 0-38, B-42
Cr	Max.	417.883	0-39, grass
	Mean	29.864	
	Min.	Trace	M-33$_b$, M-34, 0-36 0-41, B-42
Sr	Max.	893.484	0-38, weed
	Mean	91.501	
	Min.	0.561	M-33$_a$, grass
Ca	Max.	10,871.010	0-38, weed
	Mean	889.020	
	Min.	4.028	0-35, weed

Table 3. Concentration of selected element in plants from the vicinity of Defiance, Findlay, and Lima (from Welsh, 1972).

Element	Number of Positive Occurrences	Frequency of Detection, %	Positive Observed Values, mg/l Min.	Max.	Mean	No. of Samples above P.H.S. Limit
Ag	12	15.2	0.001	0.010	0.005	0
Al	19	22.3	0.036	5.32	2.12	-[1]
As	6	7.0	1.54	2.30	1.93	6
Cd	15	17.6	0.004	0.035	0.015	5
Cr	27	35.2	0.002	0.121	0.019	2
Cu	20	23.5	0.013	0.082	0.036	0
Hg	17	20.0	0.207	0.944	0.555	17[2]
Ni	13	15.2	0.005	0.531	0.130	0[2]
Pb	15	17.6	0.016	0.134	0.079	13
Sn	10	12.9	0.109	1.20	0.474	-[1]

Water Analyses

Element	Number of Positive Occurrences	Frequency of Detection, %	Positive Observed Values, mg/l Min.	Max.	Mean	No. of Samples Above Mean
Ag	56	79.3	0.026	1.50	0.323	14
Al	66	80.5	1.05	1430	194	20
As	14	17.1	3.51	180	42.6	3
Cd	30	37.8	0.024	0.564	0.180	13
Cr	55	68.3	0.003	18.1	0.995	10
Cu	31	51.2	0.052	8.74	1.02	6
Hg	75	91.5	2.55	174	30.3	27
Ni	65	97.6	0.029	21.9	3.12	20
Pb	38	46.3	0.145	16.7	2.15	11
Sn	17	20.7	1.79	84.4	19.3	5

Sediment Analyses-Extractable

Ag	50	62.2	0.028	1.96	0.375	11
Al	37	45.1	0.314	82.7	12.5	11
As	5	6.1	7.81	110	22.1	3
Cd	19	29.3	0.041	2.04	0.435	5
Cr	37	48.8	0.019	0.728	0.231	11
Cu	42	51.2	0.072	3.751	1.30	16
Hg	48	58.3	0.759	55.7	18.2	20
Ni	63	76.8	0.076	5.41	1.33	18
Pb	26	31.7	0.070	6.40	1.93	11
Sn	10	12.2	2.38	35.0	10.1	3

Sediment Analyses-Exchangeable

1. No limit presently established.
2. Number of samples exceeding U.S.S.R. limit.

Table 4. Results of water and sediment analyses of samples from the Maumee River basin (from Schultz, 1972).

GENERAL FEATURES OF THE MAUMEE RIVER BASIN

Location and Principal Geographic Features

The Maumee River Basin is centrally located between the major metropolitan and industrial centers of the Great Lakes-Ohio River region. The basin, which is nearly flat, covers 6,586 square miles. Of this area, 4,856 square miles are in northwestern Ohio, 1,260 are in northeastern Indiana, and 470 lie in southern Michigan (Figure 1). The basin is divided into 12 sub-drainage basins (Table 5) that contain 271 named streams with a total length of 2,118 miles and many small unnamed water courses, which account for another 700 miles (Ohio Division of Water, 1960).

The southwestward flowing St. Joseph River, rising in south-central Michigan, flows about a hundred miles through Ohio into Indiana, joining the St. Marys River at Fort Wayne. The St. Marys River originates in Shelby County, Ohio, and flows about a hundred miles northwest to Fort Wayne (Figure 1). The Maumee River, originating at the confluence of these two rivers, flows northeastward nearly 150 miles before emptying into Lake Erie at Toledo. Other major tributaries to the Maumee River include the Auglaize, Tiffin, and Blanchard Rivers.

The topography of the basin is a result of glacial action. A low ridge, left by the retreating glacier, separates the Maumee from the surrounding Wabash, Miami, and Scioto River basins. Glacial Lake Maumee, now represented by deposits of clay and silt, covered the east-central part of the basin. This swampy area, called the Great Black Swamp by early settlers, was turned into productive farmland through intensive ditching and tiling in the late 1800's and early 1900's.

Population, Economy, and Landuse

Although a precise figure cannot be readily determined, the basin is estimated to contain a population well over a million. Deutsch (unpublished) gives the population distribution as 74, 23, and 3 percent for Ohio, Indiana, and Michigan, respectively. There are 17 municipalities in the basin with populations exceeding 5,000 (World Atlas, 1960). About two-thirds of the

	Sub-basin	Area (Square miles)
1.	Saint Marys	817
2.	Little Auglaize	408
3.	Upper Auglaize	378
4.	Ottawa	373
5.	Lower Blanchard	255
6.	Upper Blanchard	507
7.	Upper Maumee and Lower Auglaize	908
8.	Tiffin	804
9.	Saint Joseph	1060
10.	Middle Maumee	397
11.	Lower Maumee	426
12.	Part of Lower Maumee and Tenmile Creek	253

Table 5. Area of sub-drainage basins in the Maumee River Basin (Data from Ohio Division of Water, 1957, 1960).

population is concentrated in the Fort Wayne and Toledo metropolitan areas.

Industry requires ready availability to large sources of water. Toledo has an unlimited supply in Lake Erie, and Fort Wayne utilizes the St. Marys and St. Joseph Rivers in addition to wells that provide large quantities of ground water. As a result, industry and population are concentrated in the Toledo and Fort Wayne areas. The value of manufacturing in the basin exceeds a billion dollars annually. Some of the important industries in the basin include the manufacture of machinery, transportation equipment, glass, clay and stone products, metals, rubber, chemical paper, and textiles (Table 6). Petroleum and coal refining and processing are major enterprises in Toledo, Lima, and Findlay. The processing of locally produced food is another important source of income.

With the exception of Lucas and Allen Counties, Ohio, and Allen County, Indiana, more than 93 percent of every county is devoted to agricultural use.

Municipality	Industries
Toledo, Ohio	Serves as a transhipment point for coal, iron, ore, grain, and steel; manufactures glass products, machinery, auto parts, and refined oil.
Fort Wayne, Indiana	Manufactures electrical equipment, meat products, hosiery, tools, truck bodies, farm implements, pumps and gasoline station equipment, and paints.
Lima, Ohio	Manufactures construction machinery, petroleum products, chemicals, aircraft parts and equipment, steel castings, and cigars.
Findlay, Ohio	Manufactures rubber tires and tubes, washing machines, porcelain goods, and electronic parts; processes beet sugar, limestone and fertilizer; produces natural gas and oil.
Defiance, Ohio	Manufactures machinery, household appliances, metal products, communications equipment, hardware, auto parts, and processed food and dairy products.
Bowling Green, Ohio	Located in a grain and dairy farming region; processes tomato and meat products; manufactures cut glass, machinery and burial vaults.
Maumee, Ohio	Manufactures food coloring, kitchen cabinets, plastics, and machine tools.
Van Wert, Ohio	Processing center for grain, livestock, poultry, and cheese; manufactures canned foods, textiles, and metal products.
Decatur, Indiana	Manufactures cement, tile, dairy and wood products, soybean products, castings, and electrical machinery.
St. Marys, Ohio	Summer resort center; manufactures rubber products, steel products, boxes, wool textiles, and cigars.
Celina, Ohio	Supply center for sportsmen; produces furniture, chemicals, metal products, canned goods, and lithographs.
Bryan, Ohio	Manufactures condensed milk, lubricating equipment, auto parts, furnaces, furniture, toys, candy, and pharmaceuticals.
Wapakoneta, Ohio	Trade center for agricultural goods; produces furniture, steel toys, cigars, machine tools, dairy products, and canned goods.
Napolean, Ohio	Agriculture marketing center; manufactures bricks, tiles, farm machinery and metal products.

Table 6. The 15 largest municipalities in the Maumee River Basin and their industries.

GEOLOGY AND HYDROLOGY OF THE AREA

Geology

Regional Geological Setting

The stratigraphic sequence within the basin consists chiefly of shale, limestone, dolomite, and, in the northern extremity of the basin, some sandstone. These bedrock formations generally are covered with a few feet to a few hundred feet of glacial drift. The Mississippian, Devonian, and Silurian formations are quite dissimilar in their physical and hydrological characteristics. The north-plunging Cincinnati Arch, separating the Appalachian basin in the east from the Indiana, Illinois, and Michigan basins in the west and northwest, further complicated the environment of deposition of these formations.

Bedrock Geology

Silurian, Devonian, and Mississippian rocks subcrop beneath the drift or crop out along many stream valleys in the Maumee basin. The rocks become progressively younger toward the north. In the southern part of the basin carbonate rocks of Middle (Niagara) Silurian age form the bedrock surface. The uppermost unit is the Lockport Dolomite.

The Lockport is overlain by the Bass Islands Group of Late (Cayuga) Silurian age, which ranges from zero thickness to at least 500 feet. The Bass Islands Group includes, in ascending order, the Greenfield Dolomite, Tymochtee Formation, Put-in-Bay Dolomite, and the Raisen River Dolomite. In the eastern and northwestern parts of the basin the Bass Islands Group is overlain by progressively younger strata of Devonian and Mississippian ages that consist chiefly of dolomite interbedded with relatively thin shale.

Unconformably overlying the Bass Islands Group are Devonian strata consisting in ascending order, of the Sylvania Sandstone, Helderberg Limestone, and Detroit River Dolomite. Overlying the Detroit River Dolomite (or Group, depending on regional usage), is the Dundee Limestone and the Traverse Group. The strata extending from the base of the Lockport to the top of the Traverse

Group are commonly known as the Big Lime.

The Antrim (Ohio) Shale arcs in a broad band across the west central part of the basin, unconformably overlying the Traverse Group. The Antrim is Mississippian or possibly uppermost Devonian in age.

Lower Mississippian rocks are characterized in ascending order, by the Bedford Shale, Berea Sandstone, and Sunbury and Coldwater Shales. The youngest formation, the Marshall Sandstone of Mississippian age, is present in only two relatively small areas in the northern part of the basin.

In general the Silurian and Lower Devonian strata in certain areas, have relatively high secondary permeability and may provide significant yields to wells. The Marshall Sandstone is also quite permeable. Those strata ranging from the base of the Dundee to the top of the Coldwater Shale have relatively low values of permeability, and generally are not major sources of water supply.

Glacial Geology

Most of the basin is covered with glacial deposits consisting of gravel, sand, alluvium, fine silt, and clay. In many places the drift is very thin and bedrock crops out along the stream channels. Prior to glaciation, drainage patterns were being developed on the bedrock surface, and crevices and solution channels were being formed. The retreat of the ice left these features filled and covered with glacial sediments. In these areas the drift is commonly thick.

Glacial deposits can be grouped into three types: (1) outwash deposits consisting of washed and sorted sand and gravel; (2) till deposits composed of unsorted mixtures of sand and gravel in a clay and silt matrix; and (3) glacial-lake deposits of fine silt and clay.

The first type, generally, has good permeability and is an excellent source of water, while the others have very low permeabilities and are poor sources of water. For a detailed discussion of the glacial geology of this area refer to Forsyth (1965), Forsyth (1966), Goldthwait and others (1961), Indiana Geological Survey (1956), Wayne (1958), Wayne and Zumberge (1965), and Zumberge (1960).

Hydrology

Precipitation

The climate of the basin is largely controlled by the extensive, flat land mass to the west and southwest (Ohio Division of Water, 1960). Prevailing winds from the south and southwest, resulting from low pressure centers originating in the Gulf area, are responsible for lower rainfall and less severe storms in the Maumee Basin as compared to other regions in Ohio and Michigan. The mean annual precipitation for the basin is about 34 inches, which is 4 inches less than the Ohio average. The distribution of the average annual precipitation in the Maumee River Basin is shown in Figure 2.

Water losses in the basin, resulting from evapotranspiration, average about 24 inches annually. As can be seen in Figure 3, the greatest loss is in the southern half of the basin and corresponds roughly to the areas of higher average annual precipitation (Figure 2) and higher average annual streamflow (Figure 4). It should be noted, however, that part of the water loss, the difference between precipitation and surface runoff, reflects infiltration, but since the water table maintains a relatively constant level due to groundwater discharge to streams, the infiltrated quantity appears as streamflow.

More than 75 percent of the Maumee River basin in cropland (Ohio Division of Water, 1960), the water table is very close to the ground surface, precipitation is usually associated with storms of moderate intensity, and relatively dry southwesterly winds pass over the basin. Consequently, the basin has a fairly high evapotranspiration rate.

Surface Water

The Maumee River basin is characterized by low relief. Consequently, streams have relatively low gradients and long lengths. The Maumee has a gradient of only 1.3 feet per mile over a length of almost 150 miles. The St. Joseph, St. Marys, Auglaize, and Blanchard Rivers, all about 100 miles long, have gradients of 3.1, 2.5, 3.2, and 0.9 feet per mile, respectively (Ohio Division of Water, 1960). The Tiffin River, 60 miles long, has a gradient of only 1.2 feet per mile.

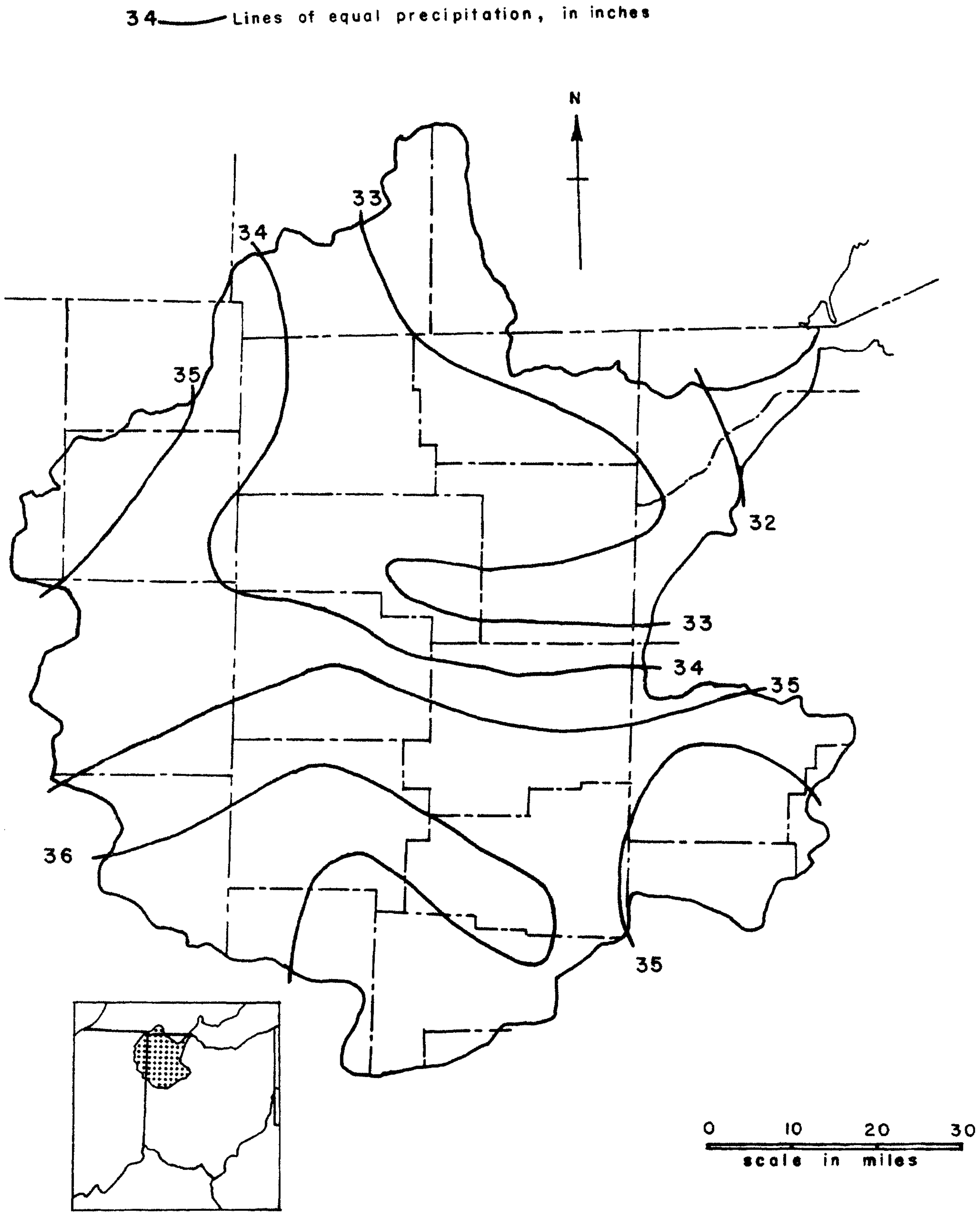

Figure 2. Distribution of precipitation on the Maumee River basin.

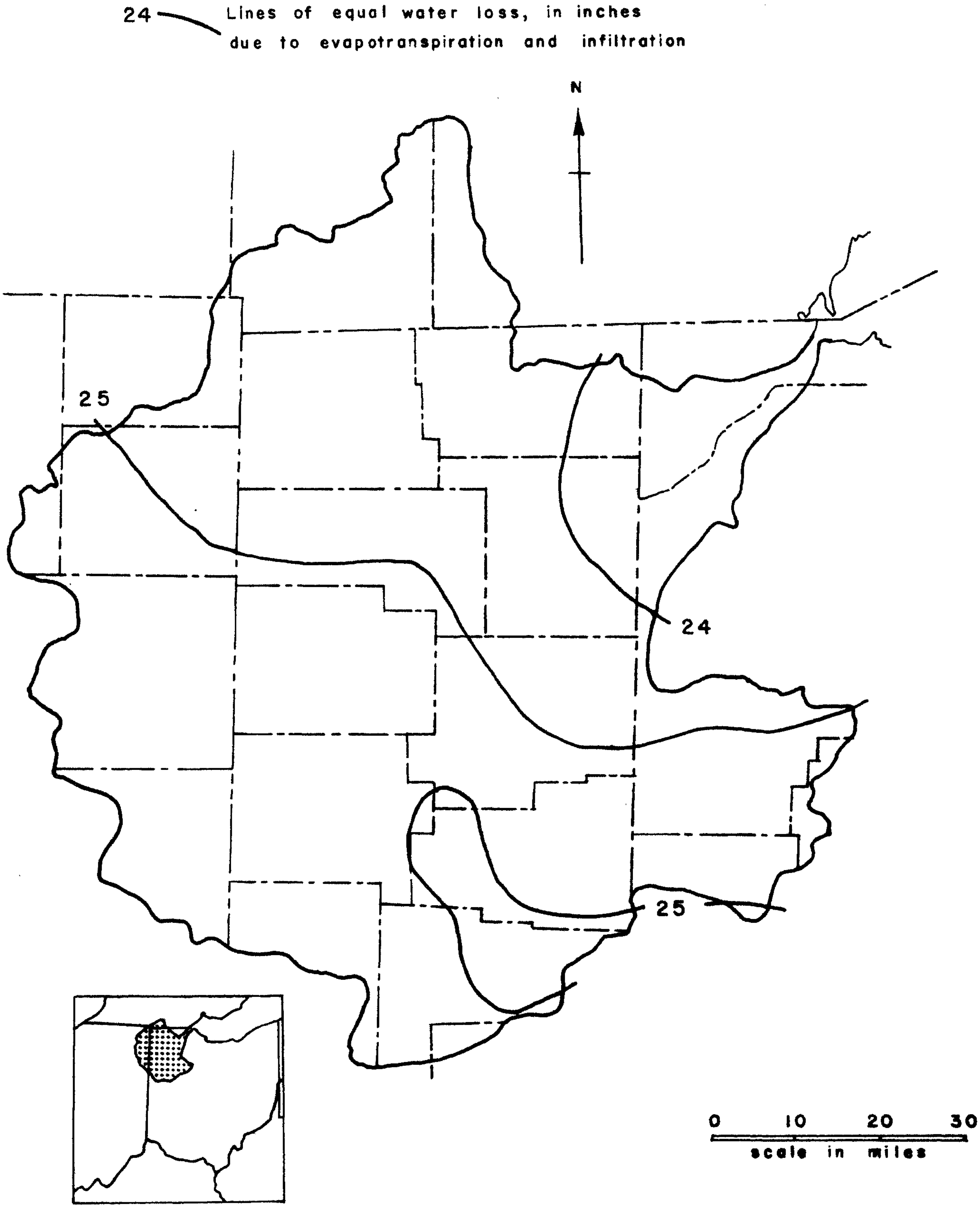

Figure 3. Distribution of water loss in the Maumee River basin due to evaportranspiration and infiltration.

With the exception of the Maumee River, the drainage patterns of the major streams are predominately controlled by morainal glacial deposits. Almost the entire length of the St. Joseph River, the St. Marys River below Menden, Ohio, and the upper reaches of the Auglaize River above Wapakoneta, Ohio, lies along the distal margin of the Fort Wayne Moraine. The Ottawa River between Ada and Lima, also flows along the Fort Wayne Moraine. Bean Creek, a tributary of the Tiffin River, meanders along the distal margins of parts of the Fort Wayne, Wabash, and Defiance Moraines. The Blanchard River flows adjacent to the distal edge of the Defiance Moraine between Findlay and Glandorf, Ohio. The only major watercourse that does not show a direct relationship to end moraines is the Maumee River. This river and most of its smaller tributaries drain the Maumee Lake Plain.

The average annual streamflow at various locations in the Maumee Basin ranges from 8 to 11 inches (Figure 4). The area of greatest average annual streamflow (more than 10 inches) roughly corresponds to the area of highest average annual precipitation and to areas of higher ground-water yield from glacial and bedrock sources.

Runoff, which includes all the water flowing in a stream channel past a given section at any instant in time, has four main sources: (1) precipitation falling directly on the surface of the stream, (2) surface runoff, (3) interflow or subsurface flow, and (4) ground-water discharge. Thus, areas having relatively high precipitation, permeable surface soils and large, effluent ground-water bodies show sustained high flow throughout the year, with a relatively small ratio between flood flow and mean flow. Areas having lower precipitation, less permeable surface soils and smaller effluent ground-water bodies have smaller base flows and higher ratios of peak to average flows.

The drainage area and discharge of nine major streams within the basin are listed in Table 7. The effects of significant ground-water discharge can be seen in the St. Joseph River, St. Marys River, Maumee River, Bean Creek, and the Tiffin River by inspection of their hydrographs. The St. Joseph and St. Marys Rivers receive recharge from sand and gravel deposits along their entire length as does the headwater regions of the Tiffin River and Bean Creek. The upper reach of the Maumee River receives recharge from the Fort Wayne Moraine and the lower reach from the Defiance Moraine. The ratios of peak to average flow for the St. Joseph, St. Marys, Maumee and Tiffin Rivers, and Bean Creek, are, respectively, 5.4, 7.8, 6.8, 6.4, and 8.5.

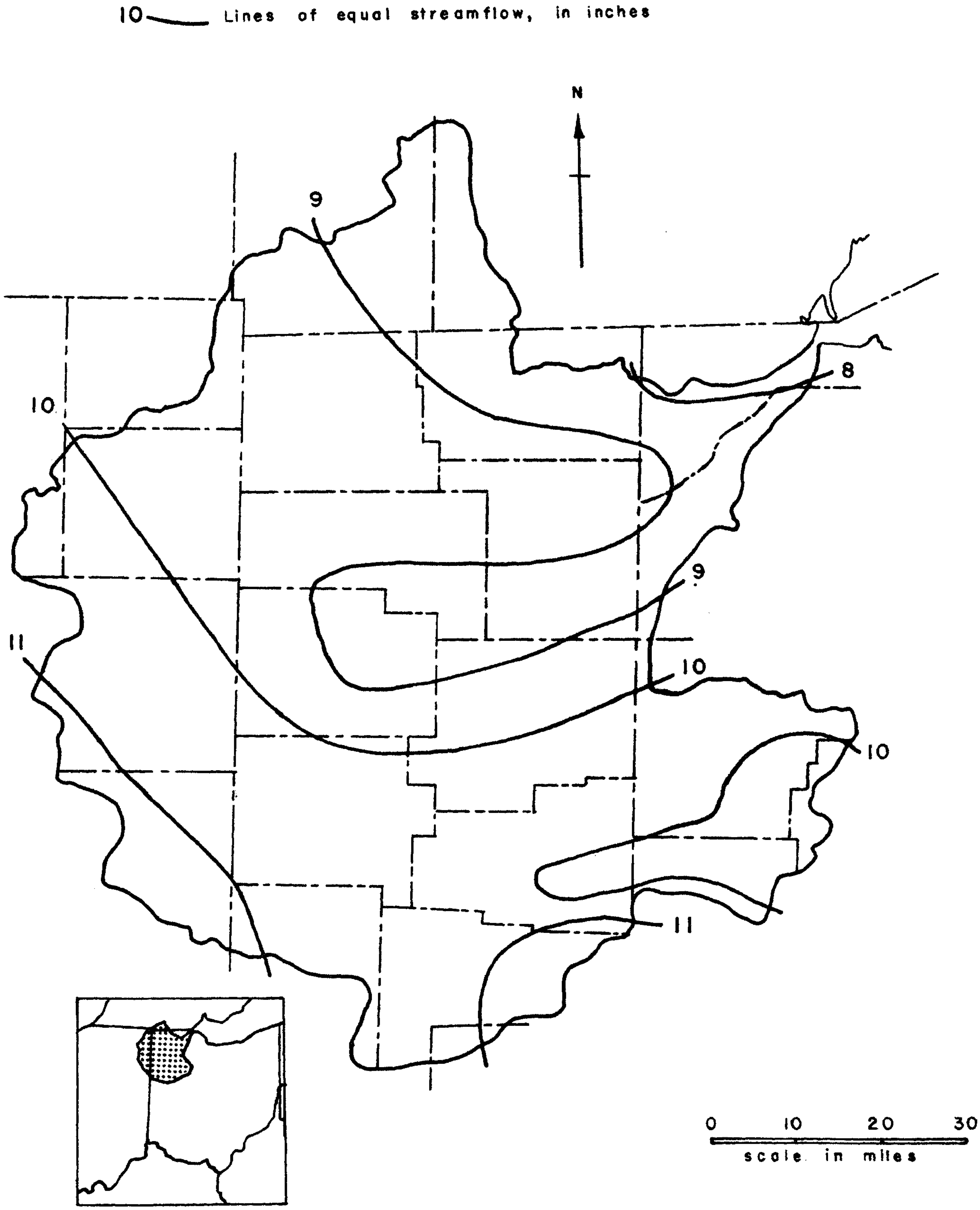

Figure 4. Surface water runoff in the Maumee River basin.

Gaging Station			Stream Discharge, cfs			
Number	Location	Drainage Area, Sq. Mi.	Min.	Max.	Mean	Total
041780	St. Joseph River near Newville, Ind.	609	33	2,090	391	142,672
041815	St. Marys River at Decatur, Ind	621	14	3,570	460	167,999
041830	Maumee River at New Haven, Ind.	1,966	98	10,200	1,491	544,078
041845	Bean Creek at Powers, Ohio	206	19	1,200	143	52,110
041850	Tiffin River at Stryker, Ohio	410	13	1,820	284	103,320
041875	Ottawa River at Allentown, Ohio	160	15	2,190	131	47,926
041890	Blanchard River near Findlay, Ohio	346	8.5	3,930	268	97,683
041915	Auglaize River near Defiance, Ohio	2,318	36	18,000	1,949	711,541
041935	Maumee River at Waterville, Ohio	6,330	114	33,300	4,894	1,786,468

Table 7. Surface water records of selected streams in the Maumee River Basin, October 1969 to September 1970. Adapted from 1970 Water Resources Data for Ohio (1971).

The Auglaize River, with a peak to average flow ratio of 9.3, drains lacustrine deposits and limestone-dolomite bedrock and also reflects significant recharge from ground-water sources. The Blanchard River, with a peak to average flow ratios of 15, shows almost no recharge from ground-water sources during the low flow months of August and September. The Ottawa River reflects a fairly constant, low rate of recharge from ground-water sources as well as a somewhat flashy appearance. This river has a peak to average flow ratio of 16, which may indicate that, for the most part, this river flows over relatively impermeable material. Indeed, although its headwaters are located along the edges of the Fort Wayne Moraine, the Ottawa River flows mainly over glacial till of low permeability.

Since long reaches of many of the major water courses in the Maumee River basin owe their relatively high sustained flow to ground-water discharge, the quality of water in the streams will reflect the quality of the ground-water.

Ground Water

Prior to 1880, water wells in the Maumee Basin were limited in depth by the surface of the bedrock. These shallow wells, which are drilled or dug in the glacial drift or alluvium, were adequate to meet limited domestic requirements. However, in order to meet the larger demands of industry and municipalities, it became necessary to tap the carbonate rocks. Water obtained from the carbonate aquifers was commonly extremely hard and locally contained objectionable amounts of hydrogen sulfide. Today, aquifers in the Maumee Basin are a major source of water for many small municipalities, some industries, and domestic water users.

Glacial Aquifers. Glacial deposits cover most of the Maumee River Basin and in many cases are important sources of ground water. The yield from glacial deposits is usually low with the exception of a fairly narrow, well defined belt along the fronts of the Fort Wayne and Wabash Moraines (Figure 5). In some areas of the basin, such as the Maumee Lake Plain, the yield from the glacial drift is only 20 gpm (gallons per minute) or less.

Bedrock Aquifers. Other important sources of ground water in the Maumee Basin are the limestone and dolomite bedrock formations (Figure 6). Norris and

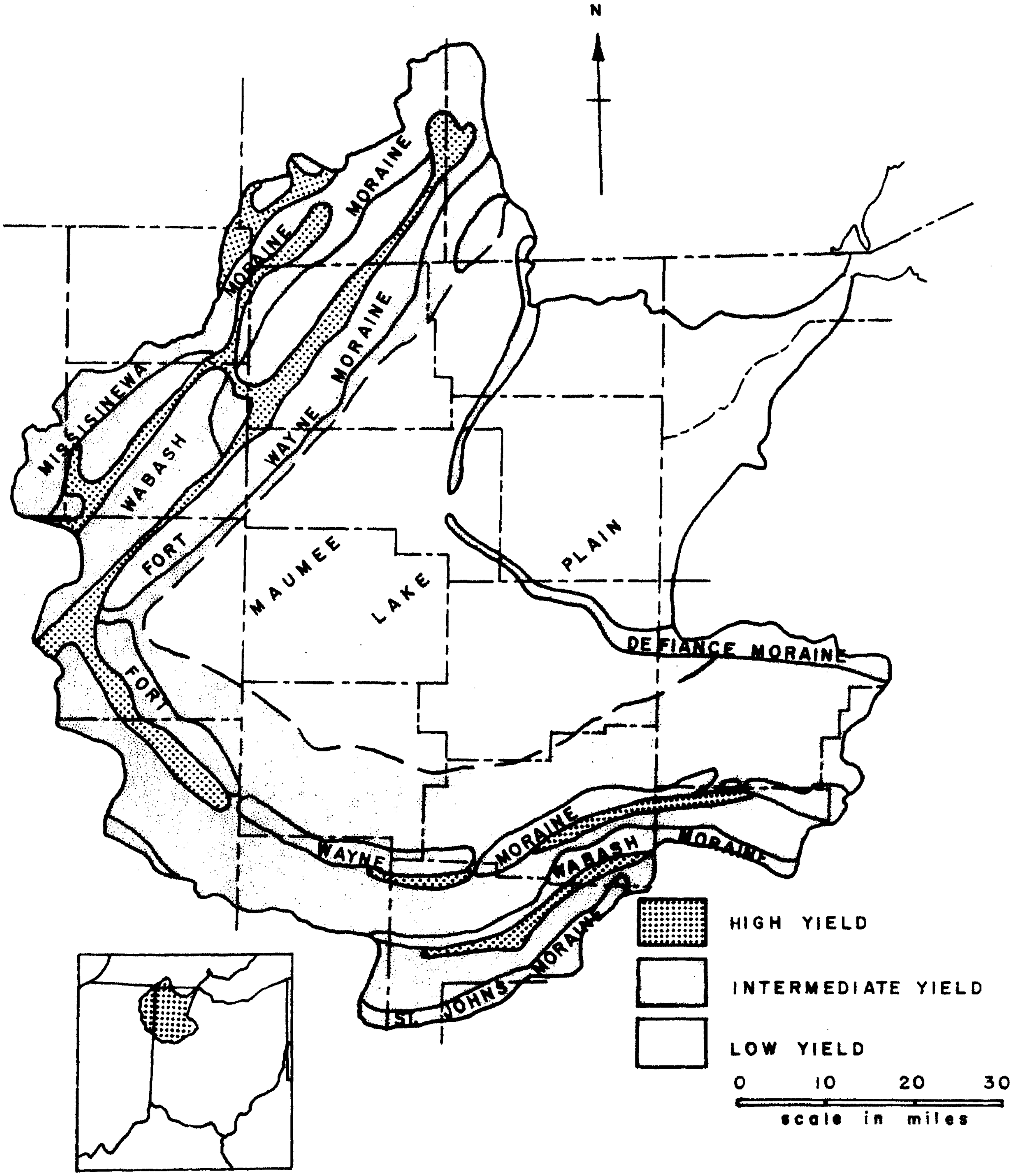

Figure 5. Relative potential yield of glacial deposits in the Maumee River basin.

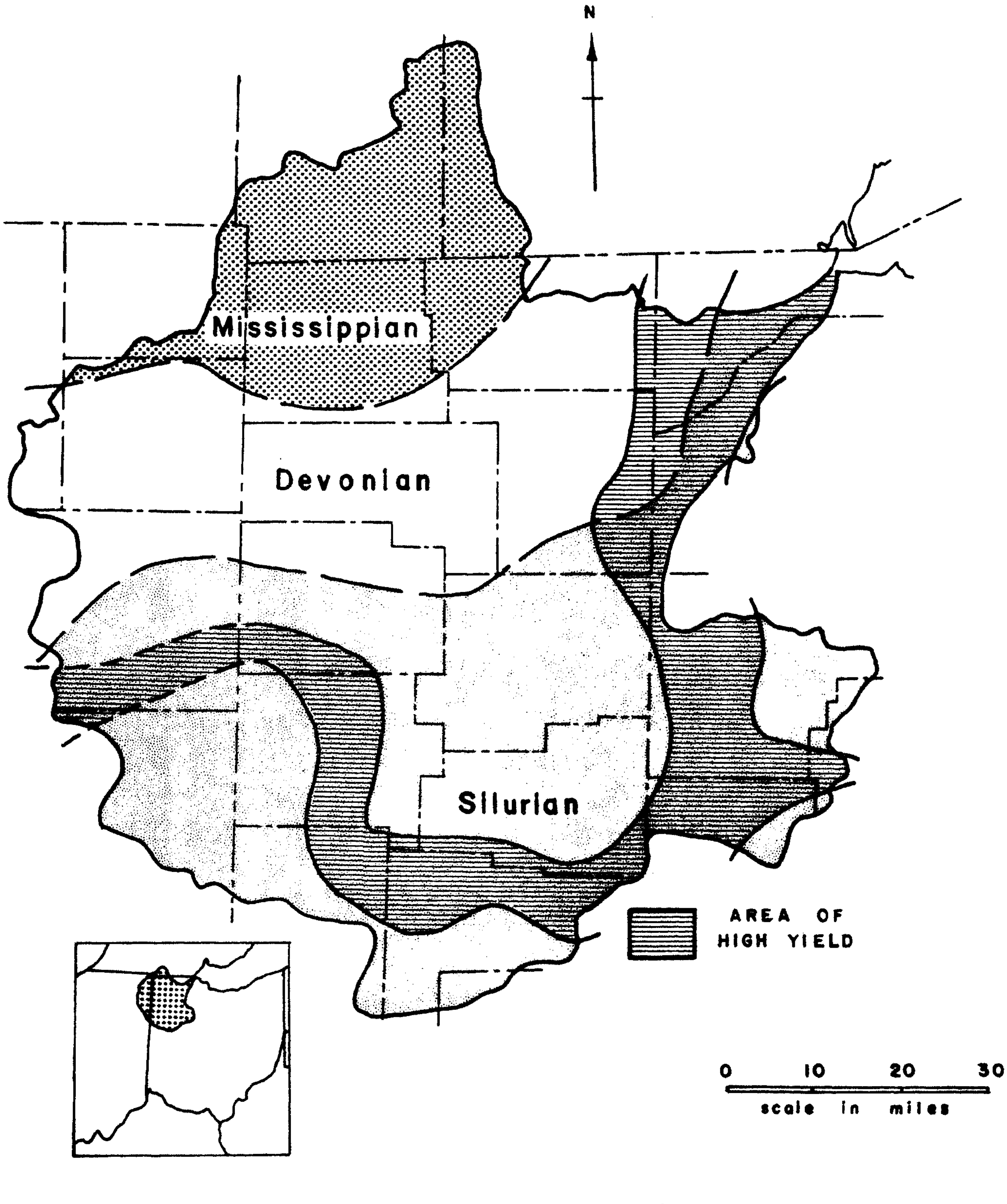

Figure 6. Generalized bedrock map and area of high yield in the Maumee River basin.

Fidler (1971) suggest that wells that produce the greatest yield are associated with structurally high areas. They mapped a long, strip-like area, 7 to 18 miles wide, that winds for many miles along the flanks of the north-plunging Cincinnati arch (Figure 6). It is their contention that this high-yield area is "the result of ground-water solution acting over long intervals in the geologic past on a structurally controlled, and periodically emergent, peninsula-like landmass." In another paper, Norris and Fidler (1971) show that this high-yield area coincides closely with areas in which the ground water is undersaturated with respect to calcium carbonate. Supported by a study by Back (1963), which showed that in Florida, water in a recharge area was typically undersaturated with respect to calcite, Norris and Fidler suggest that the Ohio high-yield area is the principal zone of recharge to the limestone and dolomite aquifers. Generally, the carbonate formations south of the Maumee River are capable of high yields, while to the north bedrock formations consist largely of shale or thin layers of limestone and yield but little water to wells.

Ground-water flow system. Movement of water in the glacial sediment is predominately controlled by the distribution and hydraulic characteristics of the deposits. Outwash deposits are usually quite permeable. Since outwash is associated with morainal fronts and the principal tributaries to the Maumee rise along these fronts, outwash deposits serve as the major source of recharge to streams. Till deposits are of low permeability and usually considered of little importance for providing stream flow. The glacial lake sediments are the least permeable and least productive galcial sediments.

Mississippian rocks in the northern part, Devonian strata in the central part, and Silurian formations in the southern part of the basin, all of which subcrop beneath the drift, are hydraulically connected. According to Norris and Fidler (1971), the regional flow of ground water in the basin is controlled by a generally uniform potentiometric surface (Figure 7) that slopes, as does the land surface, north and northeast toward Lake Erie. They consider the Lake Erie lowland as the chief area of natural ground-water discharge.

From an analysis of stream-flow data, Deutsch (unpublished) suggested that water enters the bedrock aquifers in the upper reaches of the Maumee River between Fort Wayne and Defiance and discharges into the lower reach between Defiance and Waterville. He also suggested that the St. Marys River

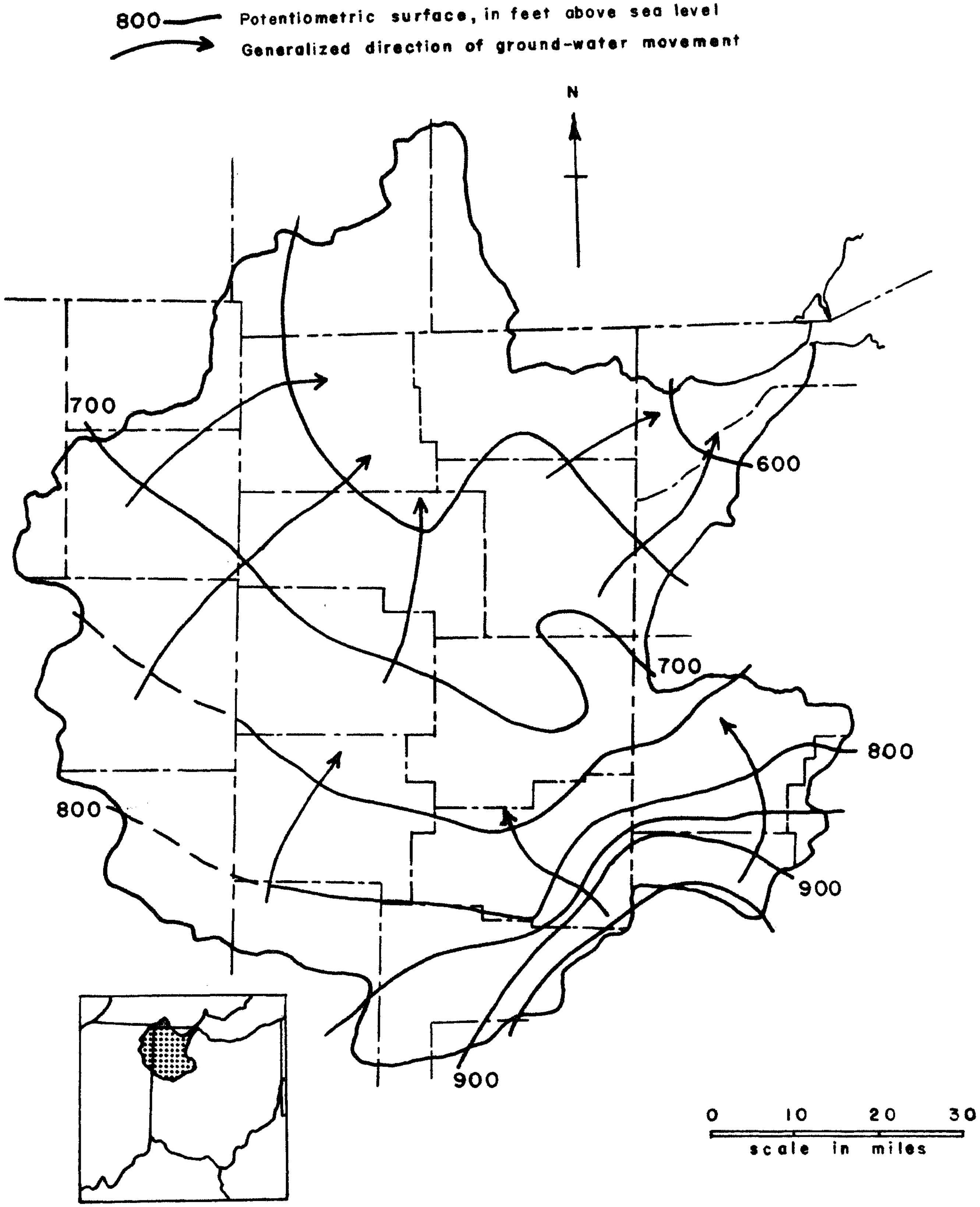

Figure 7. Potentiometric surface in bedrock aquifers in the Maumee River basin.

recharges the bedrock aquifers in the upper part of its basin, and that water discharges from these aquifers into the lower St. Marys River and to the upper reaches of the Maumee River. In addition, he believes that the Auglaize and Blanchard Rivers are limited sources of recharge to the carbonate aquifers. Reaches of significant losses and gains of stream discharge may indicate not only the presence of permeable bedrock but also changes in water quality.

SAMPLE COLLECTION, PREPARATION AND ANALYTICAL TECHNIQUES

General Description

Water and sediment samples were collected from various streams and rivers throughout the Maumee River Basin and numbered consecutively (plates 1-13). Each water and sediment sample from a particular site has the same identification number. No sediment samples were collected from sites 114-140, 148, 168, and 204. Samples 1 through 140 were collected and analyzed by Hayes (1973) during the period September, 1972 - April, 1973. Samples 141-225 were collected and analyzed by Schultz (1972) during the period August, 1971 - March, 1972. Three stream parameters were measured for each site: pH, temperature, and specific conductance. The pH was measured using a Photovolt 126A portable pH meter; stream temperature was measured with a laboratory calibrated mercury bulb thermometer; and specific conductance was measured with a portable Beckman RB3 Solu Bridge conductivity meter.

Water Samples

Water samples were taken, where possible, from the flowing portion of the stream. The water samples were collected in 125 ml polyethylene bottles, which had been washed with 1:1 reagent grade nitric acid and rinsed in double-distilled demineralized water. Immediately prior to taking the sample, the bottle was rinsed with river water. Upon return to the laboratory, the samples were stored at 5 degrees C. until analyzed. All water samples were analyzed directly from the collection bottle.

Sediment Samples

Sediment samples were collected in 250 ml wide mouth polyethylene bottles that had been washed with 1:1 reagent grade nitric acid and rinsed in double-distilled demineralized water. Where possible, grab samples were taken directly at the water sampling site from the upper few inches or less of sediment. Sometimes, however, the depth of water necessitated taking sediment samples from a slightly different location. The sediment samples were also stored at 5 degrees C. A modification of the extraction techniques described in Perkin-Elmer

Analytical Methods (1971) was used to displace adsorbed metal ions from the sediment and place them in solution. Exchangeable and extractable cations were displaced from each sample.

Prior to extraction the sediment sample was thoroughly mixed in the collection bottle using a variable speed laboratory stirrer with a polypropylene stirring blade. Approximately 10 grams of homogenized sample slurry were quickly poured into each of two polypropylene acid-washed 100 ml centrifuge tubes. Thirty ml of 1 N ammonium acetate (X-extractant) was added to one of the tubes and 30 ml of a 0.05 N hydrochloric acid and 0.025 N sulfuric acid solution (Y-extractant) to the other tube. The tubes were then agitated in a two-directional shaker at a rate of 180 excursions per minute for 30 minutes. The slurry was centrifuged for 15 minutes at 2000 RPM (revolutions per minute), after which the liquid portion was decanted into a 100 ml acid-washed volumetric flask. This entire procedure was repeated twice and then the flask was brought to 100 ml with the appropriate extractant. The solutions were then transferred to 125 ml acid-washed polyethylene bottles and stored at 5 degrees C. until they were analyzed using the methods described under analytical techniques (Perkin-Elmer, 1971). After the tubes containing the wet sediment were put in an oven and dried for 48 hours at a temperature of 90 degrees C., the dry weight of the sediment used in the extraction was determined and recorded.

Analytical Techniques

Standard Methods

All samples were analyzed using a Perkin-Elmer Model 303 atomic absorption spectrophotometer equipped with a recorder readout accessary and a Model 165 strip chart recorder. All light sources were Perkin-Elmer Intensitron Lamps, which were operated at the recommended amperage. Double distilled demineralized filtered water was aspirated as a blank for analysis of the water samples and the appropriate extractant was aspirated as a blank for the analysis of the sediment extractions.

The recorder readout, which is in percent absorption (peak height), must be converted to absorbance. The relationship is described by Beer's Law as:

$$Ab = 2 - \log (100 - At)$$

where Ab is the absorbance and At is the absorption. The relationship between concentration and absorbance is linear for small concentrations and can be expressed graphically (Perkin-Elmer, 1971). For sediment samples it was necessary to convert mg/l to mg/kg. This is done by multiplying the concentration, expressed in mg/l, by the volume of the extractant, expressed in ml, and dividing by the dry weight of the sample, expressed in kg. The graphical method is very time consuming when there are large numbers of samples involved, consequently a computer program was written to calculate the Beer's Law relationship, the proportional relationship between absorbance and concentration, and to provide a suitable format for printing the results. The program is written in Fortran IV with Watfiv and was processed on an IBM 370-165 computer (Table 8).

Adaptation for Computer Analysis

With two exceptions, the computer program follows the procedure outlined above. A mathematical equation, however, is needed to replace the straight-line graph. The general equation for a straight line is:

$$Y = mX + b \tag{1}$$

where X and Y are coordinate values for points on the line, m is the slope of the line, and b is the Y intercept. If Y is replaced by Qo, the concentration in mg/l, and X by Qi, the absorbance, then

$$Qo = mQi + b \tag{2}$$

If the location of two or more points are known, a least squares best-fit line can be set to these points using the equations:

$$m = \frac{N \Sigma Qi \;\; X \;\; Qo \; (\Sigma\, Qi) \; (\Sigma\, Qo)}{N\Sigma Qi^2 - (\Sigma\, Qi)^2} \tag{3}$$

$$b = \frac{(\Sigma\, Qo) \; (\Sigma Qi) \; - \; (\Sigma Qi \; X \; Qo) \; (\Sigma Qi)}{N\Sigma Qi^2 - (\Sigma Qi)^2} \tag{4}$$

where N is the total number of points or standards used in a given set of analyses. It is possible to solve for m and b by reading in values of N, Qo, and Qi for the standards. A second mathematical equation is implemented to replace the graphical method for determination of concentration from absorbance. When the percent of absorption is zero (concentration less than the detection limit), the program prints out N.D. (not detectable).

Presentation of Data

Analytical results for 140 water and 113 sediment X and Y extractant analyses representing samples 1-140 are provided in the report by Hayes (1973). The analytical results for 85 water, and 82 X and Y sediment extractants representing samples 141-225 are shown in Schultz (1972) and Hayes (1973). Concentrations of metals in water samples are expressed in mg/l (milligram of metal per liter of water) and concentrations of metals in sediment samples are expressed in mg/kg (milligram of metal per kilogram of sediment).

Table 9 lists the statistical results of the water analyses. The number of positive occurrences and percent frequency of detection include all those samples whose values were not printed out as zero or N.D. (not detectable). The minimum value, in most cases, represents the lowest concentration that could be detected for a particular element using the Perkin-Elmer 303 atomic absorption spectrophotometer and the analytical methods previously described.

For each element, an arithmatic mean value is given, and, in addition, for aluminum, cobalt, mercury, nickel, tin, strontium, and zinc, a graphical mean value is presented. The arithmatic mean value was determined as follows:

$$\frac{\sum_{1}^{n} \frac{S_1 + S_2 + S_3 + \dots + S_n}{n} \Sigma \sum_{1}^{k} \frac{s_1 + s_2 + s_3 + \dots + s_k}{k}}{2} \tag{5}$$

where:

if samples whose concentrations are printed as N.D. are considered to have a value of zero and

n = total number of samples

S_1 = concentration of sample 1

S_2 = concentration of sample 2

S_3 = concentration of sample 3

S_n = concentration of n^{th} sample

and

if samples having concentrations of zero or N.D. are not considered and

k = total number of samples

s_1 = concentration of sample 1

s_2 = concentration of sample 2

Element	Number of Positive Occurrences	Frequency of Detection, %	Positive Observed Values, mg/l				No. of Samples above P.H.S. Limit
					Mean		
			Min.	Max.	Arith	Graphical	
Ag	24	1.07	0.001	0.069	0.029	*	11
Al	70	31.1	0.012	5.320	0.158	.010	28**
As	6	7.06	1.54	2.300	1.031	*	6
Cd	41	18.2	0.001	0.070	0.016	*	17
Co	37	26.5	0.013	0.049	0.016	.008	30**
Cr	84	37.1	0.001	0.121	0.004	*	1
Cu	47	20.9	0.001	0.082	0.004	*	0
Hg	83	36.9	0.207	1.787	0.778	0.015	83
Ni	97	43.1	0.001	0.531	0.164	0.006	0
Pb	34	15.1	0.006	0.161	0.034	*	19
Sn	10	11.8	0.109	1.200	0.258	0.055	10**
Sr	140	100	0.102	3.072	0.688	0.400	35**
Zn	129	92.2	0.001	0.028	0.016	0.020	0

* Not enough data to determine a graphical mean.

** Samples having concentrations greater than 1 probable deviation above the graphical mean.

Table 9. Results of water analyses from the Maumee River Basin (from Hayes, 1973).

s_3 = concentration of sample 3
s_k = concentration of k^{th} sample

Eliminating samples with zero or N.D. concentrations would give a mean value biased towards the higher concentrations and equating all samples whose concentrations were not detectable equal to zero would result in a mean value biased towards the lower concentrations. The difference between the two values can vary by a factor of ten or more. For example, the mean value of arsenic as determined by the first method (elimination of all samples with a zero or N.D. concentration) is 1.92 mg/l, while the second method gives 0.136 mg/l. Equation 5 gives a value of 1.03, which is an average of the high and low values. Although this intermediate value may still be in error, it is probably more accurate than either of the other two.

The graphical mean concentration of an element was determined by plotting on probability paper a curve of concentration verses percent of time that a concentration is equalled or exceeded for that particular element. The concentration at which the 50 percent value is equalled is considered the mean concentration, that is, 50 percent of the concentrations are less than this value and 50 percent are greater. If more than 50 percent of the samples show detectable concentrations, this method will give a more accurate mean or average value than any of the other three previous techniques. Curves used to determine the graphical mean concentration of aluminum, cobalt, mercury, nickel, tin, strontium, and zinc in water are presented in the Appendix. The mean concentration as determined by this method is, in essence, the most probable concentration.

Probability analysis can also be used to determine the spread or dispension of individual values about the mean. For example, the concentration values include a few exceptionally large ones, a few small ones, and a preponderance of concentrations centered around some central value. The distribution of these values can be illustrated graphically by a curve that shows the number of times a particular concentration was equalled or exceeded. A characteristic of a normal distribution curve is that a spread of values may be defined within which 50 percent of the individual values fall (Statistical Methods in Geology, 1972). Such a spread is defined as one probable deviation on each side of the mean. Also, given percentages will fall within the limits defined by two probable deviations and three probable deviations on either side of the mean. It is a characteristic of normally distributed populations that 82 percent of the total number of cases will lie within 2 p.d. (probable deviations) on either side of the mean, and that 96 percent of the cases will lie within the limits of 3 p.d. on either side of the mean.

The last column in Table 9 indicates the number of samples with concentrations that exceed the U. S. Public Health Service recommended limits for drinking water (Table 10), or, in the case of aluminum, cobalt, tin, and strontium, which have no limit, those concentrations that are more than 1 p.d. above the graphical mean. The U.S.S.R. limits are used for mercury and nickel since limits have not as yet been defined in the United States.

A listing of the results, respectively, of the X and Y sediment extractions are shown in Tables 11 and 12. The same explanation applies to these two tables as to Table 9, with two exceptions. All mean values are graphical means and the number of samples exceeding a particular value is not included. Any concentrations falling above the 1 p.d. range were considered to be anomalously high.

The statistical methods employed in determining the p.d. range imply that approximately 25 percent of the samples will have concentrations above the 1 p.d. range and around 2 percent will have concentrations above the 3 p.d. range. Curves used to determine the graphical mean, the 1 p.d., and the 3 p.d. values for the X and Y extractions are shown in the Appendix.

Element	Permissible[2] Criteria, mg/l	Desirable[2] Criteria	Detection Limit
Ag	0.05	Absent	0.001
Al[3]	--	--	0.01
As	0.05	Absent	1.5
Cd	0.01	"	0.001
Co	--	--	0.01
Cr (VI)	0.05	Absent	0.001
Cu	1.0	Virtually Absent	0.001
Hg	0.005[1]	--	0.2
Ni	1.0	--	0.002
Pb	0.05	Absent	0.006
Sn[3]	--	--	0.01
Sr	--	--	0.005
Zn	5.00	Virtually Absent	0.001

[1] Permissible criteria in USSR (Kirkor, 1951)

[2] (Federal Water Pollution Control Administration, 1968)

[3] No criteria presently established.

Table 10. Comparison of drinking water standards and detection limits.

Element	No. of Positive Occurrences	Frequency of Detection, %	Positive Observed Values, mg/l		
			Min.	Max.	Mean
Ag	136	69.8	0.008	221	0.095
Al	115	59.0	0.314	750	1.5
As	5	6.1	7.81	110	0.70
Cd	126	64.6	0.007	16.3	0.15
Co	110	97.4	0.111	50.4	1.5
Cr	75	38.5	0.019	1.02	0.006
Cu	143	73.4	0.002	2030	0.085
Hg	161	82.7	0.759	661	20
Ni	176	90.3	0.033	41.7	0.80
Pb	137	70.4	0.026	117	0.85
Sn	10	12.2	2.38	35.0	0.45
Sr	113	100	1.56	439	40
Zn	113	100	0.20	506	3.0

Table 11. Results of sediment extraction analyses (exchangeable ions) from the Maumee River Basin.

Element	No. of Positive Occurrences	Frequency of Detection, %	Positive Observed Values, mg/l		
			Min.	Max.	Mean
Ag	152	77.9	0.026	331	0.095
Al	176	90.3	0.306	290	4.0
As	14	17.1	3.51	180	0.40
Cd	93	47.6	0.007	16.2	0.03
Co	112	99.1	0.006	83.3	0.90
Cr	121	62.1	0.001	160	0.02
Cu	144	73.9	0.052	3530	0.40
Hg	182	93.4	2.55	361	25
Ni	178	91.3	0.029	43	0.95
Pb	150	77.0	0.114	456	0.80
Sn	17	20.7	1.79	84.4	0.40
Sr	113	100	1.12	302	20
Zn	109	96.4	0.201	897	4.0

Table 12. Results of sediment extraction analyses (extractable ions) from the Maumee River Basin.

CONCENTRATION AND DISTRIBUTION OF SELECTED TRACE ELEMENTS IN THE MAUMEE RIVER BASIN

Introduction

The data gathered during the course of this two-year study are compared statistically and by areal distribution. It is the intention that a concentration-distribution map of each element can be used to (1) locate areas of possible contamination, and (2) derive relationships, if any exist, between areas of relatively high trace-metal concentrations and physical features of the basin such as bedrock, glacial deposits, high-yield aquifers, direction of ground-water flow, sources of highly mineralized water, and land use. The areal distribution and concentrations of Al, Ag, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sn, Sr, and Zn in water and sediment samples within the Maumee River Basin are illustrated, respectively, in Plates 1 through 13. Locations of the 225 sample sites are listed in the Appendix.

It must be understood, however, that a water sample represents a single instant in time. Water samples taken a few days, a few hours, or possibly even a few minutes apart, might give very different results. In order to derive any meaningful long term relationships on the basis of water samples alone, continuous monitoring would be necessary. Continuous monitoring was neither feasible or practical for this study. It is assumed, however, that analyses of sediment samples serve to indicate long-term effects of trace metals present in the streams and to delineate areas of anomalously high concentrations and possible sources.

The forms in which trace elements may be held in the soil or sediment are (Mitchell, 1972):

1. In solution in ionic or combined form in which case they can be removed from the soil by water extraction;
2. As readily exchangeable ions in inorganic or organic exchangeable complexes, extractable by neutral salts such as ammonium acetate;
3. As more firmly bound ions in the exchange complexes, extractable by dilute acetic acid or a chelating agent such as EDTA;
4. In insoluble organic or organo-mineral complexes, extractable by EDTA;
5. Incorporated in precipitated oxides or other insoluble salts, extractable by vigorous extractants such as acid ammonium oxalate;

6. In secondary minerals in a fixed form.

The exchangeable ion (X-extractant) and extractable ion (Y-extractant) used in this study correspond, respectively, to forms 2 and 3. The X-extractant reflects that amount of a metal that may be readily removed from the sediment by plants, while the Y-extractant represents, at least theoretically, the total amount present.

These extractants also indicate the enrichment factor of the trace metals in sediment in comparison to water. The ratio of the mean concentration of 13 selected trace metals in sediment to the mean concentration in water are shown in Table 13. These ratios, however, are only relative. Complete digestion of the sediment, which is necessary to determine the total concentration of metal ions available, was not done. Preliminary results of a study by Mustapha Ukayli, a geology graduate student at The Ohio State University, indicate that the extraction method used in the Maumee study removes only about 40 to 60 percent of the metal ions from the sediment (oral communication). Another study in progress by Christine Burbek, a senior geology major at The Ohio State University, seems to indicate that the efficiency of the extraction method and the concentrations of trace metals in any one sediment sample is highly dependent upon grain size (oral communication). Preliminary results indicate that although the extraction process is more efficient with sand-sized particles, higher concentrations are found in clay because of the much larger surface area of each clay particle.

Aluminum

Range in Concentration

Aluminum was looked for in 225 water samples (plate 1). Detected concentrations ranged from less than 0.012 to a maximum of 5.320 mg/l, with a mean concentration of 0.010 mg/l. Exchangeable and extractable aluminum ions were looked for in 195 sediment samples. Concentrations of exchangeable aluminum ions ranged from 0.314 to as high as 750 mg/kg, with a mean concentration of 1.5 mg/kg. Extractable concentrations ranged from 0.306 to 290 mg/kg, with a mean concentration of 4 mg/kg.

Element	Mean Concentration Ratio X/W	Mean Concentration Ratio Y/W
Ag*	3.37	3.28
Al	150	400
As*	5.15	2.94
Cd*	9.38	1.88
Co	188	113
Cr*	1.50	4.99
Cu*	21.2	100
Hg	1330	1660
Ni	133	158
Pb*	25.0	23.5
Sn	8.18	7.28
Sr	100	50
Zn	150	200

W = water

X = exchangeable ion

Y = extractable ion

* Arithmetic water mean used to determine ratio

Table 13. Sediment to water ratio of the concentration of selected trace elements.

Water Samples

Eleven water samples had concentrations greater than 3 p.d. above the mean (greater than 0.80 mg/l) and 34 contained concentrations ranging between 1 and 3 p.d. (0.080 to 0.80 mg/l). Of those samples with concentrations exceeding 3 p.d., one (sample 222) was from the St. Marys River at Fort Wayne, three (samples 84, 218, 219) were from the Maumee River downstream from Fort Wayne, two (samples 224 and 225) were from the St. Marys River at Decatur, Indiana, one (sample 113) was from the Maumee River at Maumee, Ohio, and four (samples 178, 220, 221, and 223) were from rural areas. Thirty two of the water samples with concentrations ranging from 1 to 3 p.d. above the mean were from rural areas (plate 1), one (sample 113) was from the Maumee River at Maumee, Ohio, and one (sample 193) was from the Ottawa River upstream from Lima.

Sediment Samples-Exchangeable

Forty-two sediment samples had exchangeable ion concentrations ranging from 1 to 3 p.d. above the mean (8.5 to 200 mg/kg), and one (sample 95) had an exchangeable concentration greater than 3 p.d. (greater than 200 mg/kg). Sample 95, with a concentration of 750.387 mg/kg, was from a rural area as were 39 of the other samples with concentrations in the 1 to 3 p.d. range. Two of these samples (149 and 151) were from the Blanchard River near Findlay, Ohio.

Sediment Samples-Extractable

Analyses of sediment for extractable ions revealed 41 samples with concentrations ranging from 1 to 3 p.d. above the mean (200 to 2,500 mg/kg) and two samples (samples 95 and 101) having concentrations greater than 3 p.d. (greater than 2,500 mg/kg). Samples 95 and 100 were from Lick Creek and the Tiffin River, respectively. Thirty-seven of the samples with concentrations in the 1 to 3 p.d. range were from rural areas. Of the remaining four samples in this range, sample 36 was from the Big Run at Butler, Indiana, samples 149 and 150 from The Outlet upstream from Findlay, and sample 200 was collected in Powell Creek at Defiance.

Discussion

In general, it seems that samples with aluminum concentrations greater than 3 p.d. above the mean are from or near municipalities, whereas samples with aluminum concentrations ranging from 1 p.d. to 3 p.d. above the mean are from rural areas. There does not appear to be any significant relationship between aluminum concentrations, glacial deposits, or bedrock. On the other hand, there does appear to be a higher detection rate for aluminum in the Maumee Lake Plain than elsewhere. This may be due to the preponderance of clay, the most common sedimentary aluminum-bearing rock, in this region.

Since water treatment plants use large amounts of alum (aluminum hydroxide), they are likely sources of high concentrations of aluminum in both water and sediment samples from urban localities. Industry may also be a source since aluminum compounds are widely used in many of the manufacturing and related processes centered around urban areas. On the other hand, the sediment-treatment processes and, in particular, the Y-extractant, may be breaking down clay particles and thus releasing more aluminum.

Arsenic

Range in Concentration

Arsenic (plate 2) was looked for in 85 water samples and detectable concentrations ranged from 1.544 to 2.296 mg/l, with a mean of 1.031 mg/l. Exchangeable and extractable arsenic ions were looked for in 82 sediment samples. Concentrations of exchangeable arsenic ions ranged from less than 7.81 to 110 mg/kg, with a mean of 0.70 mg/kg. Concentrations of extractable arsenic ions ranged from less than 3.51 to 180 mg/kg, with a mean of 0.40 mg/kg.

Water Samples

Water samples 162, 166, 168, 169, 177, and 217, all from small streams in rural areas, were found to contain concentrations of arsenic exceeding the Public Health Service limit of 0.05 mg/l. The concentrations of these samples were, respectively, 1.680, 2.091, 2.296, 1.544, 1.749, and 2.201 mg/l.

Sedmiment Samples-Exchangeable

Three sediment samples (159, 161, and 172) had concentrations of exchangeable arsenic ions ranging from 1 to 3 p.d. above the mean (2 to 24 mg/kg) and two (samples 163 and 173) had concentrations greater than 3 p.d. (greater than 25 mg/kg). Samples 159, 161, 163, 172, and 173 had concentrations of 22.200, 19.098, 25.046, 7.805, and 36,212 mg/kg. All of these samples were from streams in rural areas.

Sediment Samples-Extractable

Twelve sediment samples (142, 143, 152, 159, 160-162, 164, 167, 169, 170, and 175) had extractable arsenic ion concentrations ranging from 1 to 3 p.d. above the mean (0.70 to 100 mg/kg) and two samples (141 and 155) had concentrations greater than 3 p.d. (greater than 100 mg/kg). Samples 141-143, 152, 155, 159-162, 164, 167, 169, 170, and 175, all from rural areas, had concentrations of 148.504, 19.450, 12.537, 54.667, 179.824, 30.150, 22.744, 20.952, 8.016, 36.814, 14.541, 37.522, 35.117, and 7.914 mg/kg.

Discussion

Not enough arsenic samples were analyzed throughout the basin to determine relationships between glacial deposits, bedrock, and areas of high ground-water yield. However, with one exception, all water and sediment samples containing high concentrations of arsenic were from the southeastern corner of the basin in Hancock County, Ohio. In addition, these samples were collected within the area of high-yield wells tapping bedrock formations consisting of the Detroit River and Bass Islands Group of Devonian and Silurian age. Although containing varying amounts of sulfur, water from these rocks is the primary source of public water supply in this area. Since arsenic commonly occurs combined with sulfur, water from this bedrock aquifer may be a natural source of arsenic. Another possible source of arsenic in water and sediment in streams in agricultural areas is insecticides. On the other hand, atomic absorption methods used for the detection of arsenic are far from adequate. In fact, so much difficulty was encountered during this study that, during the second year of the project, samples were no longer analyzed for arsenic. Although the areas that appear to contain high concentrations of arsenic should be reevaluated, the values as reported herein may represent only instrument error.

Cadmium

Range in Concentration

Cadmium was looked for in 225 water samples (plate 3). Concentrations detected ranged from 0.001 to 0.070 mg/l, with a mean of 0.016 mg/l. Concentrations of exchangeable and extractable cadmium ions, looked for in 195 sediment samples, ranged from 0.007 to 16.3 mg/kg, with a mean concentration of 0.15 mg/kg. Detectable concentrations of extractable cadmium ions ranged from 0.007 to 16.2 mg/kg, with a mean concentration of 0.03 mg/kg.

Water Samples

Seventeen water samples had concentrations of cadmium exceeding the Public Health Service limit of 0.01 mg/l. Sample 112 (0.067 mg/l) was from the Maumee River at Waterville, sample 113 (0.062 mg/l) was from the Maumee River at Maumee, and sample 224 (0.011 mg/l) was from the St. Marys River downstream from Decatur. Samples 78-85, 111, 188, 197, 198, 204, and 210, with respective concentrations of 0.062, 0.054, 0.067, 0.056, 0.052, 0.056, 0.060, 0.054, 0.070, 0.035, 0.035, 0.025, 0.029, and 0.017 mg/l, were from rural areas.

Sediment Samples-Exchangeable

Two sediment samples (21 and 22) had exchangeable cadmium ion concentrations in excess of 3 p.d. above the mean (greater than 4.5 mg/kg), and 22 sediment samples had exchangeable cadmium ion concentrations ranging from 1 to 3 p.d. (0.55 to 4.5 mg/kg).

Both samples 21 (16.312 mg/kg) and 22 (11.989 mg/kg) were collected from Bean Creek at Hudson, and about five miles south of Hudson. Sample 36 (3.578 mg/kg) was from the Big Run at Butler, sample 113 (0.954 mg/kg) from the Maumee River at Maumee, sample 218 (1.192 mg/kg) from the Maumee River at New Haven, sample 219 (1.613 mg/kg) from the Maumee River downstream from New Haven, and samples, 16, 18, 23, 27, 28, 33, 64, 65, 72, 78, 82-84, 87, 93, 99, 103, and 104 with concentrations, respectively, of 0.630, 0.740, 1.265, 2.212, 2.933, 0.064, 0.573, 0.543, 0.628, 0.862, 1.965, 0.562, 0.790, 0.806, 1.496, 0.554, 0.640, and 0.969 mg/kg, were from rural areas.

Sediment Samples-Exchangeable

Two sediment samples (21 and 22) had extractable cadmium ion concentrations greater than 3 p.d. above the mean (greater than 2.5 mg/kg) and 42 sediment samples (3, 18, 19, 27, 36, 44, 52, 55-57, 60-65, 67, 72, 75, 77, 78, 96, 102, 103, 111, 113, 141, 144, 147, 151, 155, 164, 165, 169-171, 173, 176, 188, 208, 217, and 219) had extractable cadmium ion concentrations ranging from 1 to 3 p.d. (0.08 to 2.5 mg/kg).

Sample 21 from Bean Creek at Hudson had an extractable cadmium ion concentration of 16.247 mg/kg and sample 22 from Bean Creek about five miles south of Hudson had an extractable cadmium ion concentration of 3.227 mg/kg. Sediment sample 36 (2.186 mg/kg) was from the Big Run at Butler, while sample 113 (0.609 mg/kg) was from the Maumee River at Maumee. The remaining 40 sediment samples, with extractable cadmium ion concentrations ranging from 0.08 to 2.5 mg/kg, were from rural areas (plate 4).

Discussion

In general, higher cadmium concentrations in water occurred around Findlay, Decatur, and along the Maumee River downstream from Fort Wayne, Defiance, and Waterville. There was no discernable relationship between cadmium concentrations in water or sediment and glacial deposits, bedrock, or areas of high ground-water yield. Possible sources of cadmium in these areas are electroplating, paint, and chemicals industries, and plants burning high sulfur fuels. Oil refineries around Findlay, also, are likely sources. Thus, it seems probable that high concentrations of cadmium in the basin are a result of man's activities and are not due to natural causes.

Cobalt

Range in Concentration

Cobalt was looked for in 140 water and 113 sediment samples (plate 4). Concentrations of cobalt detected in water ranged from 0.013 to 0.049 mg/l, with a mean of 0.016 mg/l. Concentrations of detected exchangeable cobalt ions ranged from 0.111 to 50.4 mg/kg, with a mean of 1.5 mg/kg. Detected concentrations of extractable cobalt ions ranged from 0.006 to 83.3 mg/kg, with a mean of 0.90 mg/kg.

Water Samples

Water sample 131 from the Ottawa River at Lima and sample 139 from the John Diehl Ditch upstream from Auburn, Indiana, with cobalt concentrations, respectively, of 0.45 and 0.049 mg/l, had cobalt concentrations exceeding 3 p.d. above the mean (0.045 mg/l or greater). Water samples 24, 45, 53, 54, 69, 78, 79, 114, 115, 117-124, 126, 127, 130, 132, 133, 136-138, and 140 had cobalt concentrations ranging from 1 to 3 p.d. (0.015 to 0.045 mg/l). Anamalous concentrations were encountered in the following sites: sample 114, (0.029 mg/l) from the Auglaize River at Wapakoneta, sample 119, (0.037 mg/l) from the St. Marys River upstream from Fort Wayne, sample 120 (0.017 mg/l) from the Maumee River at Fort Wayne, sample 121 (0.033 mg/l) from the St. Joseph River at Fort Wayne, sample 122 (0.025 mg/l) from the Maumee River downstream from New Haven, sample 124 (0.017 mg/l) from Flatrock Creek at Paulding, Ohio, sample 132 (0.033 mg/l) from the Ottawa River downstream from Lima, sample 135 (0.021 mg/l) from the Blanchard River at Findlay, and sample 136 (0.033 mg/l) was from Town Creek at Van Wert. The remaining 19 water samples having cobalt concentrations ranging from 0.015 to 0.045 mg/l were from rural areas.

Sediment Samples-Exchangeable

Two sediment samples (21 and 22) had exchangeable cobalt ion concentrations greater than 3 p.d. above the mean (greater than 25 mg/kg) and 14 sediment samples (18, 23, 27, 28, 36, 64, 65, 78, 90, 91, 93, 106, and 107) had excnangeable cobalt concentrations ranging from 1 to 3 p.d. (5.0 to 25 mg/kg). Samples 21 and 22 from Bean Creek had exchangeable cobalt concentrations of

50.395 and 50.059 mg/kg. Sediment sample 36, from Big Run at Butler, had a concentration of 18.667 mg/kg. Samples 18, 23, 27, 28, 64, 65, 78, 90, 91, 93, 99, 106, and 107, having concentrations, respectively, of 9.020, 6.453, 11.476, 13.211, 5.515, 5.272, 6.337, 7.182, 12.75, 5.379, 5.873, 7.999, and 6.808 mg/kg. were from rural areas.

Sediment Samples-Extractable

Eight sediment samples (16, 18, 22, 27, 36, 95, 101, and 102) had extractable cobalt ion concentrations greater than 3 p.d. above the mean (greater than 9.0 mg/kg), and 15 sediment samples (3, 23, 28, 44, 65, 68, 71, 78, 91, 93, 94, 96, 97, 107, and 108) had extractable cobalt concentrations ranging from 1 to 3 p.d. (4.0 to 9.0 mg/kg). Sample 36, from Big Run at Butler, had an extractable cobalt ion concentration of 13.821 mg/l. Sample 16 (15.409 mg/kg) was from the East Fort, sample 18 (10.129 mg/kg) was from Bird Creek, samples 22 (83.333 mg/kg) and 27 (9.663 mg/kg) were from Bean Creek, sample 95 (9.796 mg/kg) was from Lick Creek, sample 101 (10.142 mg/kg) was from the Tiffin River, and sample 102 (17.810 mg/kg) was from Garret Creek. Samples 3, 23, 28, 44, 65, 68, 71, 78, 90, 91, 93, 94, 96, 97, 107, and 108 had concentrations, respectively, of 4.206, 5.000, 5.050, 4.304, 6.447, 4.504, 5.262, 7.612, 6.544, 8.918, 4.633, 4.799, 4.133, 4.311, 5.727, and 7.752 mg/kg, and were from rural areas.

Discussion

Cobalt concentrations in the water appear to be somewhat higher around the industrial areas of Findlay, Fort Wayne, Lima, Van Wert, and Wapakoneta than in rural areas. In all of these municipalities, cobalt alloys are used in the manufacture of machinery and electronic parts. Paint and varnish industries may be another source of cobalt. In general, there is an indication that higher concentrations of cobalt occur in the water and sediment in the vicinity of the Niagaran bedrock and in areas where relatively highly mineralized water is obtained from bedrock and glacial aquifers. Water passing through these aquifers may be taking into solution trace amounts of cobalt from the limestone and dolomite and from minerals within the glacial deposits. Any conclusion concerning the distribution pattern of cobalt concentrations is very speculative because an insufficient number of samples were taken throughout the basin to obtain a reasonably complete regional picture.

Chromium

Range in Concentration

Chromium was looked for in 225 water and 195 sediment samples (plate 5). Detectable values of chromium in water ranged from 0.001 to 0.121 mg/l, with a mean value of 0.004 mg/l. Exchangeable concentrations of chromium ions in the sediment samples ranged from less than 0.019 to 1.02 mg/kg, with a mean concentration of 0.006 mg/kg. Extractable concentrations of chromium ions ranged from less than 0.001 to 169 mg/kg, with a mean concentration of 0.02 mg/kg.

Water Samples

Only one water sample had a chromium concentration exceeding the Public Health Service limit of 0.05 mg/l. It (sample 179) was from the Blanchard River and had a chromium concentration of 0.121 mg/l.

Sediment Samples-Exchangeable

Three sediment samples had exchangeable chromium ion concentrations greater than 3 p.d. above the mean (greater than 0.80 mg/kg), and two samples (71 and 93) had exchangeable chromium concentrations ranging from 1 to 3 p.d. (0.065 to 0.80 mg/kg). Sediment sample 87 (0.914 mg/kg) was from the St. Joseph River, sample 101 (1.017 mg/kg) was from the Tiffin River, and sample 187 (2.058 mg/kg) was from Grass Creek. Sediment sample 71 (0.774 mg/kg) was from a tributary of the Auglaize River at Delphos, Ohio, while sample 93 (0.846 mg/kg) was collected from Brush Creek.

Sediment Samples-Extractable

Six sediment samples had extractable chromium concentrations greater than 3 p.d. above the mean (greater than 8.5 mg/kg), and 71 sediment samples had extractable chromium concentrations ranging from 1 to 3 p.d. (0.08 to 8.5 mg/kg). Sample 21 (8.610 mg/kg) was from Bean Creek, sample 36 (159.883 mg/kg) was from the Big Run, sample 87 (9.371 mg/kg) was from Cedar Creek, sample 98 (8.711 mg/kg) was from Lick Creek, sample 173 (9.397 mg/kg) was from Potato Run, and sample 187 (18.061 mg/kg) was from Grass Creek.

Sediment samples with extractable chromium concentrations ranging from 0.08 to 8.5 mg/kg including the following: sample 112 (0.115 mg/kg) from the Maumee River at Waterville, sample 113 (0.386 mg/kg) from the Maumee River at Maumee, sample 149 (4.167 mg/kg) from The Outlet at Findlay, sample 200 (0.170 mg/kg) from Powell Creek at Defiance, sample 218 (0.080 mg/kg) from the Maumee River at New Haven, sample 222 (0.184 mg/kg) from the St. Marys River at Fort Wayne, sample 224 (0.134 mg/kg) from the St. Marys River downstream from Decatur, sample 225 (0.160 mg/kg) from the St. Marys River at Decatur, and the remaining 63 were from rural areas.

Discussion

In general, surface water in the basin contains very little chromium and the sediment has only small amounts available as exchangeable ions. In view of the low number of water samples with high concentrations of chromium, no pattern between concentration and geology could be distinguished. This was also true for exchangeable chromium in sediment samples.

Although a large number of samples contained high concentrations of extractable chromium ions, no significant relationship could be determined between these occurrences and geology. However, there is the suggestion that higher chromium concentrations tend to occur more frequently in the vicinity of the higher yielding glacial moraines. Also, relatively speaking, chromium concentrations in the sediment around the larger municipalities in the southern half of the basin appear to be somewhat high. Refineries and electroplating industries in these areas may be discharging minute quantities of chromium into the water, which is then incorporated into the sediment. Chromate compounds used as water additives to prevent corrosion of piping and associated equipment may be a source of chromium in water leading to high concentrations in sediment.

It appears that while the sediment may contain relatively high concentrations of chromium, water usually does not. This may reflect the low solubility of chromium in water (0.5 ug/l) and suggests that chromium is quickly incorporated into the sediment. Since chromium is a relatively abundant trace element in the earth's crust, the higher concentrations in sediment may be of natural origin and not a result of industrial pollution.

Copper

Range in Concentration

Copper was looked for in 225 water samples and 195 sediment samples (plate 6). Detectable values of copper in water ranged from 0.001 to 0.082 mg/l, with a mean concentration of 0.004 mg/l. No water sample had a copper concentration exceeding the Public Health Service limit of 1 mg/l. Concentrations of exchangeable copper ions ranged from less than 0.002 to as high as 2030 mg/kg, with a mean value of 0.085 mg/kg. Extractable copper ranged from less than 0.052 to as much as 3530 mg/kg, with an average value of 0.40 mg/kg.

Sediment Samples-Exchangeable

Two sediment samples contained exchangeable copper ion concentrations greater than 3 p.d. above the mean (greater than 40 mg/kg) while 60 contained exchangeable copper ion concentrations ranging from 1 to 3 p.d. (0.55 to 40 mg/kg). Samples 21 (2034.821 mg/kg) and 22 (788.042 mg/kg) were collected from Bean Creek. Of those samples having exchangeable copper ion concentrations ranging from 0.55 to 40 mg/kg, sample 36 (2.362 mg/kg) was from the Big Run, sample 113 (1.362 mg/kg) was from the Maumee River at Maumee, sample 203 (0.698 mg/kg) was from Preston Run downstream from Defiance, sample 224 (0.614

mg/kg) was from the St. Marys River downstream from Decatur, sample 225 (0.712 mg/kg) was from the St. Marys River at Decatur, and the remaining 55 were from rural areas.

Sediment Samples-Extractable

Three samples had extractable copper ion concentrations greater than 3 p.d. above the mean (greater than 250 mg/kg) and 26 (samples 3, 16, 23, 28, 36, 44, 65, 78, 86, 87, 89-95, 97, 101-103, 105, 108, 109, 147, 208, and 216) had extractable copper ion concentrations ranging from 1 to 3 p.d. (2.0 to 250 mg/kg). Samples 21 (3527.911 mg/kg), 22 (1432.528 mg/kg), and 27 (282.677 mg/kg) were collected from Bean Creek. Of those samples containing extractable copper concentrations ranging from 2.0 to 250 mg/kg, sample 36 (26,387 mg/kg) was from the Big Run and the remaining 25 were from rural areas.

Discussion

There was no evidence of higher than normal concentrations of copper in water and sediment samples from the major industrial centers of the basin. In fact, the average values of copper in the water and sediment of the basin are, in general, less than the average values given by Durum and Haffty (1963) and Vinogradov (1959) for copper in the river waters and soils of the United States.

There appears to be a relationship between frequency of occurrence of higher values of copper in the water and sediment and areas where water obtained from glacial and bedrock sources contain relatively high quantities of dissolved minerals. Also there is a suggestion of higher copper values where the bedrock formations are composed of shale, limestone, and dolomite of Devonian age. Copper is generally associated with sulfide minerals and water from these glacial and bedrock aquifers contain sulfides in varying amounts. Consequently, these aquifers may be a natural source of copper.

Mercury

Range in Concentration

Mercury was looked for in 225 water samples and 195 sediment samples (plate 7). Concentrations of mercury detected in water samples ranged from less than 0.207 to as much as 1.787 mg/l, with a mean value of 0.778 mg/l. Concentrations of exchangeable mercury ions ranged from less than 0.207 to as much as 1.787 mg/l, with a mean value of 0.778 mg/l. Concentrations of exchangeable mercury ions ranged from less than 0.759 to as high as 661 mg/kg, with a mean value of 20 mg/kg. Concentrations of extractable mercury ions ranged from less than 2.55 to as high as 361 mg/kg, with a mean value of 25 mg/kg.

Water Samples

Eighty-three water samples contained mercury in excess of the limit set by the U.S.S.R. (0.005 mg/l). Six of these water samples were from municipalities and 77 were from rural areas. Sample 21 (0.488 mg/l) was from Bean Creek at Hudson, sample 36 (1.350 mg/l) was from the Big Run at Butler, sample 40 (0.776 mg/l) was from the Maumee River at Napoleon, sample 114 (0.252 mg/l) was from the Auglaize River at Wapakoneta, sample 129 (0.751 mg/l) was from the Maumee River at Toledo, and sample 222 (0.730 mg/l) was from the St. Marys River at Fort Wayne.

Sediment Samples-Exchangeable

Two sediment samples had exchangeable mercury concentrations greater than 3 p.d. above the mean (greater than 450 mg/kg), and 17 (samples 16, 18, 27, 28, 33, 36, 65, 78, 82, 88, 90, 91, 93, 95, 102, 108, and 109) had exchangeable mercury ion concentrations ranging from 1 to 3 p.d. (55 to 450 mg/kg). Samples 21 (661.375 mg/kg) and 22 (554.163 mg/kg) were from Bean Creek. Of those sediment samples containing concentrations of mercury ions ranging from 55 to 450 mg/kg, sample 36 (168.091 mg/kg) was from the Big Run at Butler, while the remaining 16 were from rural areas.

Sediment Samples-Extractable

Sample 21 from Bean Crrek had an extractable mercury ion concentration of 360.906 mg/kg, which was greater than 3 p.d. above the mean (greater than 350 mg/kg). Thirty samples (16, 18, 23, 27, 28, 36, 44, 64, 78, 86-88, 90, 91, 93, 97, 101, 107, 108, 113, 144, 151, 155, 156, 182, 187, 200, 208, 213, and 217) had extractable mercury ranging from 1 to 3 p.d. (50 to 350 mg/kg).

Of these 30 sediment samples, sample 36 (213.263 mg/kg) was from the Maumee River at Maumee, sample 200 (93.418 mg/kg) was from Powell Creek at Defiance, and the remaining 27 samples were from rural areas.

Discussion

There were no significant occurrences of high concentrations of mercury in the water and sediment samples from the majority of municipalities within the basin. The high value of mercury in the water at Fort Wayne, which was not reflected in the sediment, could be a result of pollution from paint, photographic, and chemical industries located in and near this city. Since only one water sample and no sediment samples at Fort Wayne had high mercury concentrations, the source of pollution may be of local origin, intermittent in duration, and quickly dissipated downstream. The high mercury concentration in the water sample from Toledo may be due to pollution from oil refineries or industries burning large amounts of low grade coal.

By far the highest rate of occurrence of high levels of mercury in water and sediment samples occurred in rural areas. With the exception of Fort Wayne, Toledo, Defiance, and Maumee, mercury was not detected in the water or sediment of any highly industrialized center. Since the early 1900's, mercury compounds have been widely used throughout the basin as insecticides and fungicides. High concentrations of mercury in sediment samples from agricultural regions may be reflecting this long-term and widespread use of mercury compounds.

Higher concentrations of mercury are commonly found in areas of high-yield glacial outwash. There is a positive correlation between mercury concentrations in water and sediment and the Niagaran strata. Highly mineralized water from this bedrock aquifer may be a natural source of mercury.

On the other hand, the analytical techniques used to detect mercury are far from absolute. Consequently, abnormally high values may reflect only instrument error.

Nickel

Range in Concentration

Nickel was looked for in 225 water samples and 195 sediment samples (plate 8). Concentrations in water ranged from less than 0.001 to as much as 0.531 mg/l, with a mean value of 0.006 mg/l. No water sample had a nickel concentration exceeding the limit set by the U.S.S.R. (1.0 mg/l). Concentrations of exchangeable nickel ions ranged from less than 0.033 to as high as 41.7 mg/kg, with a mean concentration of 0.80 mg/kg. Detected concentrations of extractable nickel ions ranged from 0.029 to 43 mg/kg, with a mean value of 0.95 mg/kg.

Sediment Samples-Exchangeable

Two sediment samples contained concentrations of exchangeable nickel greater than 3 p.d. above the mean (greater than 25 mg/kg), and 34 (samples 3, 16, 22, 27, 28, 33, 36, 79, 80, 82-84, 86-89, 91-93, 100, 101, 103, 104, 107-109, 113, 151, 182, 186, 187, 213, and 217) had exchangeable nickel ion concentrations ranging from 1 to 3 p.d. (2.5 to 25 mg/kg). Sample 21 (4.1683 mg/kg) was from Bean Creek and sample 102 (30.026 mg/kg) was from Garrett Creek, about four miles northwest of Napoleon. Of those sediment samples containing exchangeable nickel ion concentrations ranging from 2.5 to 25 mg/kg, sample 36 (2.726 mg/kg) was from the Big Run at Butler, sample 113 (3.184 mg/kg) was from the Maumee River at Maumee, and the remaining 32 samples were from rural

Sediment Samples-Extractable

One sediment sample had an extractable nickel ion concentration greater than 3 p.d. above the mean (greater than 36 mg/kg), while 35 (samples 3, 13, 16, 23, 27, 28, 44, 68, 71, 79, 88-92, 95, 97, 101, 108, 109, 141, 147, 149-151, 155, 160, 194, 200, 202, 206, 208, and 217) had extractable nickel ion concentrations ranging from 1 to 3 p.d. (4.5 to 35 mg/kg). Sample 21 from Bean Creek had an extractable concentration of 43.016 mg/kg. Of those sediment samples having extractable nickel ranging from 4.5 to 35 mg/kg, sample 150 (5.200 mg/kg) was from Lye Creek at Findlay, sample 200 (21,911 mg/kg) was from Powell Creek at Defiance, and the remaining 33 samples were from rural areas.

Discussion

In general, nickel concentrations in water and sediment samples throughout the basin are quite low. The majority of sediment samples containing higher concentrations of nickel are in rural areas. Neither water nor sediment from the larger industrial municipalities contained high concentrations. The locality high concentrations of nickel are probably of natural origin, but no relationships to bedrock formations or glacial deposits are apparent.

Lead

Range in Concentration

Lead was analyzed in 225 water samples and 195 sediment samples (plate 9). Concentrations of lead detected in water samples ranged from 0.006 to 0.161 mg/l, with a mean value of 0.034 mg/l. Values of exchangeable lead in sediment ranged from less than 0.026 to as much as 117 mg/kg, with a mean concentration of 0.85 mg/kg. Concentrations of extractable lead ions detected in sediment samples ranged from 0.114 to 456 mg/kg, with a mean value of 0.80 mg/kg.

Water Samples

Nineteen water samples had lead concentrations greater than the Public Health Service limit at 0.05 mg/l. Sample 150 (0.100 mg/l) was from Lye Creek at Findlay and sample 201 (0.086 mg/l) was from the Maumee River at Defiance. Water samples 91-93, 98, 100, 105, 153, 154, 158, 159, 164, 172, 176, 177, 209, 210, and 212, all from rural areas, had respectively, lead concentrations of 0.161, 0.155, 0.161, 0.155, 0.161, 0.155, 0.081, 0.090, 0.134, 0.199, 0.093, 0.069, 0.091, 0.069, 0.065, 0.070, and 0.057 mg/l.

Sediment Samples-Exchangeable

Two sediment samples had exchangeable lead ion concentrations greater than 3 p.d. above the mean (greater than 55 mg/kg), while 18 (samples 16, 18, 22, 27, 28, 36, 75, 76, 93, 95-97, 102, 104, 106-108, and 217) had exchangeable lead ion concentrations ranging from 1 to 3 p.d. (5 to 55 mg/kg). Sample 21 (114.275 mg/kg) was from Bean Creek at Hudson and sample 113 (116.945 mg/kg) was from the Maumee River at Maumee. Of the 18 sediment samples with exchangeable concentrations ranging from 5 to 55 mg/kg, sample 36 (15.874 mg/kg) was from the Big Run at Butler and the remaining 17 samples were from rural areas.

Sediment Samples-Extractable

Two sediment samples had extractable lead ion concentrations greater than 3 p.d. above the mean (greater than 60 mg/kg), and 32 sediment samples (4, 18, 36, 37, 44, 78, 86-89, 91-97, 101-109, 113, 153, 163, 185, 187, and 206) had extractable lead ion concentrations ranging from 1 to 3 p.d. (3.5 to 60 mg/kg). Samples 21 (456.104 mg/kg) and 22 (211.522 mg/kg) were collected from Bean Creek. Of the 32 sediment samples having extractable lead ion concentrations ranging from 3.5 to 60 mg/kg, sample 36 (10.551 mg/kg) was from the Big Run at Butler, sample 113 (3.289 mg/kg) was from the Maumee River at Maumee, and the remaining 30 samples were from rural areas.

Discussion

With the exception of Findlay and Defiance, high concentrations of lead in surface water are limited to rural areas. Oil and gas refineries are a likely source of lead pollution at Findlay. Industries in Defiance, which manufacture metal products and communications equipment, and electroplating industries are possible sources of lead waste. Industrial plants in Defiance and Findlay that burn quantities of coal and diesel fuel may, also, be sources of lead pollution.

In general, concentrations of lead in water and sediment are higher in the Maumee Lake Plain than in other areas of the basin. Artificial drainage of this relatively low, flat area has led to extensive agricultural practices. Fertilizers containing relatively large concentrations of lead and lead-based insecticides may act as sources of high lead concentrations in the water and sediment of these agricultural areas. Galena and other lead sulfides, which occur in limestone and dolomite throughout the region may be natural sources of lead.

Silver

Range in Concentration

Silver was looked for in 225 water samples (plate 10). Detected concentrations ranged from 0.001 to 0.069 mg/l, with a mean of 0.029 mg/l. Concentrations of exchangeable and extractable silver ions were looked for in 195 sediment samples. Concentrations of the exchangeable component ranged from 0.008 to 221 mg/kg, with a mean of 0.095 mg/kg. Concentrations of extractable silver ions ranged from 0.026 to 331 mg/kg, with a mean of 0.095 mg/kg.

Water Samples

Eleven water samples were found to contain silver concentrations exceeding the Public Health Service limit of 0.05 mg/l. Six of these (samples 115, 117, 126, 128, 137, and 139) were from rural areas and one was found at each of the following locations: the St. Joseph River at Fort Wayne (sample 121), the Maumee River downstream from Fort Wayne (sample 122), the Auglaize River at Wapakoneta (sample 114), the Blanchard River downstream from Findlay (sample 134), and the Blanchard River at Findlay (sample 135).

Sediment Samples-Exchangeable

Three sediment samples contained exchangeable silver ion concentrations greater than 3 p.d. above the mean (greater than 5.5 mg/kg). Of these, samples 21 and 22 were from Bean Creek at Hudson, Michigan, and about five miles south of Hudson, while sample 23 was from Lime Creek. Their respective concentrations were 220.899, 47.358, and 11.422 mg/kg. Twenty-nine samples had exchangeable silver concentrations ranging from 1 to 3 p.d. (0.35 to 5.5 mg/kg). The samples were collected from the Maumee River at Maumee (sample 113), from Powell Creek at Defiance (sample 200), the St. Marys River at Decatur (samples 224 and 225), and had respective concentrations of 0.599, 0.446, 1.772, 0.993, and 1.961 mg/kg. The remaining 24 samples with concentrations ranging from 0.35 to 5.5 mg/kg were from rural areas.

Sediment Samples-Extractable

Twenty-six sediment samples had extractable silver ion concentrations ranging from 1 to 3 p.d. above the mean (0.40 to 25.0 mg/kg). Of these, one each was from the St. Marys River at Fort Wayne (sample 222), the St. Joseph River at Butler (sample 36), the Maumee River at New Haven, Indiana (sample 218), the Van Hyrring Creek upstream from Napoleon, Ohio (sample 50), two from the St. Marys River at Decatur (samples 224 and 225), and the remaining 20 were from rural areas. Samples 21 and 22 from Bean Creek had concentrations of 330.542 and 150.461 mg/kg, respectively.

Discussion

An apparent weak relationship between high-yield glacial outwash and higher silver concentrations in sediment seems to exist. This relationship is most evident in the northern part of the basin around Morenci and Hudson, Michigan. Water samples containing high concentrations of silver were near, downstream from, or else in the vicinity of high-yield glacial outwash. There is, however, no noticeable connection between bedrock and silver concentration in sediment or water.

Electronic parts are manufactured in Fort Wayne, Findlay, and Defiance and, in the process, generate silver waste that eventually may end up in the nearby streams. Electroplating industries in these areas may also be a source. Finely divided silver used as a disinfectant in water supplies is another possible factor responsible for higher silver concentrations in water from urban areas. Bean Creek in the Morenci-Hudson, Michigan, area may be grossly contaminated with industrial wastes since several trace elements appear in abnormally high concentrations.

Tin

Range in Concentration

Tin was looked for in 85 water samples and 82 sediment samples (plate 11). Concentrations of tin in water ranged from less than 0.109 to 1.200 mg/l, with a mean of 0.055 mg/l. Concentrations of exchangeable tin in sediment ranged from less than 2.38 to as much as 35.0 mg/kg, with a mean value of 0.45 mg/kg. Concentrations of extractable tin ions in sediment ranged from less than 2.38 to as much as 35.0 mg/kg, with a mean value of 0.45 mg/kg.

Water Samples

One water sample had a tin concentration greater than 3 p.d. above the mean (greater than 0.80 mg/l), and nine water samples (samples 143, 149, 152, 163, 164, 173, 176, 198, and 210) had tin concentrations ranging from 1 to 3 p.d. (0.08 to 0.80 mg/l). Water sample 173, from Potato Run, had a tin concentration of 0.758 mg/l. Water samples 143, 149, 152, 163, 164, 173, 176, and 198 had tin concentrations of 0.250, 0.333, 0.333, 0.597, 0.109, 0.597, 0.405, and 0.164 mg/l and all were collected in rural areas.

Sediment Samples-Exchangeable

One sediment sample had an exchangeable tin ion concentration that was greater than 3 p.d. above the mean (greater than 25 mg/kg), while nine (samples 145, 165, 166, 169, 175, 176, 177, 210, and 216) had exchangeable tin ion concentrations ranging from 1 to 3 p.d. (0.70 to 26 mg/kg). Sample 217, from Little Blue Creek, had a tin concentration of 35.046 mg/kg. Sediment samples 145, 165, 166, 169, 175, 176, 177, 210, and 216 had tin concentrations of 2.384, 4.995, 7.410, 4.216, 3.305, 5.464, 4.087, 21.816, and 12.639 mg/kg and were from rural areas.

Sediment Samples-Extractable

Three sediment samples had extractable tin concentrations greater than 3 p.d. above the mean (greater than 30 mg/kg), and 14 samples (145, 154, 163, 165, 166, 169, 171-174, 177, 200, 207, and 210) had extractable tin ion concentrations ranging from 1 to 3 p.d. (0.70 to 30 mg/kg). Sample 147 (84.433 mg/kg) was from the Blanchard River, sample 208 (56.158 mg/kg) was from Hoffman Creek, and sample 213 (62.779 mg/kg) was from the St. Marys River. Samples 145, 154, 163, 165, 166, 169, 171-174, 177, 200, 207, and 210 had, respectively, extractable tin concentrations of 2.728, 8.910, 7.143, 4.412, 15.085, 7.671, 9.375, 6.383, 23.195, 1.792, 4.833, 8.381, 2.467, and 22.463 mg/kg and all were from rural areas.

Discussion

With the exception of Defiance, there is no evidence of high concentrations of tin in any water or sediment samples from urban areas within the Maumee Basin. Communications equipment and metal industries may be the main source of tin in the surface water at Defiance. Tin is a relatively abundant metal in the earth's crust, and the higher concentrations in the sediment samples from rural areas may reflect a high background influence. Not enough samples were examined to accurately determine a background value, and what appears high in this study may, in fact, be within normal limits. The paucity of samples made it impossible to determine any relationship between concentration and geology. As with arsenic and mercury, the analytical methods used to detect tin are subject to doubt.

Strontium

Range in Concentration

Strontium was looked for in 140 water samples and 113 sediment samples (plate 12). Concentrations of strontium in water ranged from 0.102 to 3.072 mg/l, with a mean of 0.40 mg/l. Concentrations of exchangeable strontium ions ranged from 1.56 to 4.39 mg/kg, with a mean of 40 mg/kg. Concentrations of extractable strontium ions ranged from 1.12 to 302 mg/kg, with a mean of 20 mg/kg. The frequency of detection for strontium was 100 percent for both water and sediment samples.

Water Samples

Two water samples had strontium concentrations greater than 3 p.d. above the mean (greater than 3.0 mg/l), while 33 samples (36, 37, 69, 70, 72, 74, 76, 77, 79, 80, 85, 87-91, 94-98, 100, 103, 104, 114-120, 130, and 131) had strontium concentrations ranging from 1 to 3 p.d. (0.75 to 3.0 mg/l). Sample 133 (3.037 mg/l) was from Lye Creek and sample 135 (3.072 mg/l) was from the Blanchard River at Findlay. Of those water samples with strontium concentrations ranging from 0.75 to 3.0 mg/l, sample 36 (1.255 mg/l) was from the Big Run at Butler, sample 114 (2.032 mg/l) was from the Auglaize River at Wapakoneta, sample 120 (1.048 mg/l) was from the Maumee River at Fort Wayne, sample 131 (1.358 mg/l) was from the Ottawa River at Lima, and the remaining 29 samples were from rural areas.

Sediment Samples-Exchangeable

No sediment samples had exchangeable strontium ion concentrations greater than 3 p.d. above the mean (greater than 350 mg/kg), although 29 (samples 18, 21-23, 27, 28, 36, 77-80, 87, 89-91, 93-98, 100-104, 106, 108, and 113) had exchangeable strontium ion concentrations ranging from 1 to 3 p.d. (70 to 350 mg/kg). Sample 36 (188.867 mg/kg) was from the Big Run at Butler, sample 113 (166.200 mg/kg) was from the Maumee River at Toledo, and the remaining 27 sediment samples were from rural areas.

Sediment Samples-Extractable

Two sediment samples had extractable strontium ion concentrations greater than 3 p.d. above the mean (greater than 220 mg/kg). Samples 21 (281.715 mg/kg) and 22 (254.889 mg/kg) were collected from Bean Creek. Twenty-three sediment samples (18, 23, 27, 28, 36, 44, 67, 77, 87, 90, 91, 93-97, 100-104, 108, and 113) had extractable strontium ion concentrations ranging from 1 to 3 p.d. (45 to 220 mg/kg). Sample 36 (152.919 mg/kg) was from the Big Run at Butler, sample 113 (108.900 mg/kg) was from the Maumee River at Toledo, and the remaining 21 samples were from rural areas.

Discussion

The highest concentration of strontium in surface water occurred at Findlay. An important industry in Findlay is the processing of beet sugar, which requires large amounts of strontium hydroxide. Thus, the processing of beet sugar may generate wastes that are responsible for high strontium concentrations. Glass, enamel, and fireworks industries may also be sources of strontium.

Strontium is common in limestone and clay in northern Ohio. The higher rural concentrations may be due to strontium from these sources. Not enough samples were analyzed to determine any regional trends, but a small area in the Maumee Lake Plain between Defiance and Bryan contains a relatively large number of sediment and water samples with higher strontium concentrations. In general, the ground-water flow is from the southwest towards this location. Streams in this area may be receiving relatively highly mineralized water from groundwater sources.

Zinc

Range in Concentration

Zinc was looked for in 140 water samples and 113 sediment samples (plate 13). Concentrations of zinc in water ranged from less than 0.001 to 0.028 mg/l, with a mean of 0.020 mg/l. No water samples had zinc concentrations aobve the Public Health Service limit of 5.00 mg/l. Concentrations of exchangeable zinc in sediment ranged from less than 0.20 to as much as 506 mg/kg, with a mean of 3.0 mg/kg. Concentrations of extractable zinc ions in sediment ranged from 0.201 to as high as 897 mg/kg, with a mean of 4.0 mg/kg.

Sediment Samples-Exchangeable

Two sediment samples had exchangeable zinc ion concentrations greater than 3 p.d. above the mean (greater than 90 mg/kg), and 25 (samples 3, 16, 18, 23, 27, 36, 69, 71, 72, 78, 87, 89-93, 95, 96, 98, 101, 102, 104, 106, 108, and 113) had exchangeable zinc ion concentrations ranging from 1 to 3 p.d. (8.0 to 90 mg/kg). Sample 21 (505.521 mg/kg) and 22 (268.883 mg/kg) were collected from Bean Creek. Sample 36 (73.358 mg/kg) was from the Big Run at Butler, sample 113 (35.306 mg/kg) was from the Maumee River at Toledo, and the remaining 23, with exchangeable zinc ion concentrations ranging from 8.0 to 90 mg/kg, were from rural areas.

Sediment Samples-Extractable

Three sediment samples had extractable zinc ion concentrations greater than 3 p.d. above the mean (greater than 300 mg/kg), while 34 (samples 3, 6, 15, 16, 18, 19, 23, 27, 28, 44, 64, 65, 69, 71, 78, 87-93, 95-98, 101-105, 108, 109, and 113) had extractable zinc ion concentrations ranging from 1 to 3 p.d. (10 to 300 mg/kg). Samples 21 (897.181 mg/kg) and 22 (488.833 mg/kg) were from Bean Creek, and sample 36 (334.718 mg/kg) was from the Big Run. Of those sediment samples with extractable zinc ion concentrations ranging from 10 to 300 mg/kg, sample 113 (24.470 mg/kg) was from the Maumee River at Toldeo and the remaining 33 samples were from rural areas.

Discussion

Although galvanizing, paint, electroplating, automotive, electrical, metal, textile, and other industries in the basin use large amounts of zinc, there is no evidence of high concentrations of zinc in any of the surface waters within the basin. Many of the sediment samples contained relatively high concentrations of zinc. However, since all of these samples, with the exception of one from Maumee, were from rural areas or small municipalities, it is unlikely that wastes from industry are responsible for the high concentrations. More likely, sphalerite associated with galena, chalcopyrite, pyrite, and other sulfide minerals in the carbonate bedrock are natural sources of zinc. No relationship appeared to exist between concentrations of zinc in the water and sediment and geology.

TRACE ELEMENTS AND HEALTH

Man has always lived in close relationship with trace elements, those elements that normally occur in water at concentrations less than 1 mg/l (milligram per liter). All organisms have evolved in their presence, and consequently all living things are composed of a complex mixture of elemental substances. The average composition of several rock types, relative to the 13 elements investigated during this study, are presented in Table 14. A crude relationship between occurrence in the lithosphere, soil, sea water, surface water, vegetables, man, and man's intake is suggested in Table 15 for seven of these metals.

The danger of certain metals to an individual depends on the concentration, chemical form, and association or combination with other elements as well as the general health, age, and other physiological conditions of the individual. In general, world-wide research has been confined to the more acute effects of the heavy metals and the present state of knowledge is inadequate concerning chronic long-term effects. Many serious effects, including those resulting from cancer (carcinogenicity), genetic mutations that cause permanent and transmissible change in the genes of offspring from those of the parent (mutagenicity), and production of physical or biochemical defects in the offspring (teratogenicity), can occur from the ingestion of these metals or their compounds.

The problems associated with the toxic effects of trace metals can be further complicated by chemical changes that may occur when these substances enter the environment. They may become more toxic through modification in the

Element	Igneous	Sandstone	Shale	Carbonate
Al	79,500	32,100	80,000	8,970
Sr	368	28	290	617
Cr	198	120	423	7.1
Cu	97	15	45	4.4
Ni	94	2.6	29	13
Zn	80	16	130	16
Co	23	.33	8.1	.12
Pb	16	14	80	16
Sn	2.5	.12	4.1	.17
As	1.8	1.0	9.0	1.8
Hg	.33	.057	.27	.046
Cd	.19	.020	.18	.048
Ag	.15	.12	.27	.19

Table 14 Average composition, in mg/kg, of igneous and some sedimentary rocks. Adapted from Horn and Adams (1966).

Element	Litho-sphere	Soil	Sea Water	Vege-tables	Man	Man's Intake
Ni	1	2	4	4	4	3
Zn	2	1	1	1	1	1
Cu	3	3	2	2	2	2
Co	4	5	5	5	5	5
Pb	5	4	3	3	3	4
Cd	6	6	?	6	6	6'
Hg	?	?	6	?	7	?

Table 15 Order of abundance of some elements in various media. Modified from Warren (1972).

ecosystem or as a result of synergistic actions with other substances. For example, inorganic mercury, which was thought to settle safely into the bottom sediments of streams and lakes, may be converted into a very toxic soluble mercury compound by anaerobic bacteria. In addition, the toxic effect of mercuric salts may be accentuated by the presence of trace amounts of copper, while cadmium acts as a synergist with zinc and cyanide in an aquatic environment to increase toxicity.

The beneficial effects of some of the trace metals are just as complicated and poorly understood. Copper, cobalt, and zinc are considered necessary to health and it is believed that chromium and aluminum, as well as several other metals, may be beneficial in the proper concentrations, but ingestion above a set of ill-defined values can result in serious toxic effects. Often the difference between toxic and beneficial effect is slight.

Man has adapted to many trace elements anomalies in his supplies of air, water, and food. The industrial and population explosions, coupled with the desires for higher standards of living and more consumer products, has led to a greater use of metals and fossil fuels, which is subjecting more individuals to higher concentrations and more kinds of trace metals than ever before. It is unreasonable to suppose that the uses of metal will decrease in the future.

In order to intelligently and successfully cope with the increasing problems of trace metals pollution and the associated health problems, it will be necessary to define "pollution limits" verses normal or acceptable limits; to determine their natural and man-made sources; to devise methods of eliminating or reducing to acceptable limits these sources; and to become aware of the ecological, toxicological, pharmacological, and clinical aspects related to ingestion of trace metals in excess or deficient amounts.

Significance of Selected Trace Elements

Aluminum

Aluminum is the most abundant metallic element present on the earth's surface. Although the third most abundant element, it is rarely found in natural waters in concentrations greater than a few tenths of a milligram per liter. It occurs in silicate rocks and gibsite, which in an aluminum hydroxide, is fairly common. Clays are the most common sedimentary aluminum-bearing rocks. The most important ore of aluminum is bauxite.

The development of aluminum dates back to 1825 when Orsted succeeded in obtaining aluminum by heating aluminum chloride and potassium amalgam. Today, because of its variety of uses, aluminum is produced in greater quantities than any other of the nonferrous metals. Aluminum acetate, is used in large quantities as a catalyst for the manufacture of many organic chemicals, as a dye fixitive, and also as an ingredient of waterproofing compositions. Aluminum chloride, is used in one of the gasoline cracking processes and in the preparation of organic compounds. Aluminum hydroxide is used to purify water by precipitating suspended organic matter. Aluminum nitrate is used largely as a catalyst in the petroleum industry. Aluminum stearate is a waterproofing agent and is also used as a plasticizer and an antisticking agent in industrial processes. Sodium aluminate is used in sizing paper. Sodium hexafluoluminate is used as the electrolyte in the Hall-Heroult process of extracting aluminum from alumina and as an insecticide.

According to Browning (1961), man ingests from 10 to 100 mg (milligrams) of aluminum per day, most of which is excreted. Aluminum does not seem to be essential to health, nor is there any evidence that it is harmful. The possibility does exist, however, that it may be a carcinogen.

Arsenic

Arsenic is a semimetallic element, widely distributed in nature, and virtually any sample of the environment will be found to contain a small quantity of it. In contrast to most of its compounts, pure arsenic, like mercury, is not poisonous. Arsenic may occur in rocks in a reduced form, in mineral veins, and as an oxide. Some metallic ores may contain arsenate, which can replace phosphate in apatite. Arsenic, however, usually occurs combined with sulfur or with sulfur and some metal such as silver, nickel, anitmony, lead, cobalt, or iron. Most of the arsenic produced in the United States is obtained from the sublimate formed during the roasting of sulfide ores, such as copper.

Arsenic forms two commercially important oxides: arsenic trioxide and arsenic pentoxide. Arsenic trioxide, is widely used in weed killers, insecticides, enamels, and textile mordants. Taxidermists and museum curators use it to preserve hides. Arsenic pentoxide was used as a pigment for tinting wallpaper, but this use has been discontinued because it was responsible for many cases of arsenical poisoning. It is now used in the manufacture of fireworks, as a pigment in paints, and in insecticides. Psoriosis and leukemia were at one time treated with inorganic compounds of arsenic, while syphilis and other protozoan infections were treated with organic arsenicals.

The poisonous effects of arsenic have been known since the Middle Ages, but only recently has the public become aware of the pervasiveness of arsenic in the environment. The average concentration of arsenic in the air in urban areas is 0.02 ug/m^3 (micrograms per cubic meter) and in non-urban areas less than 0.005 ug/m^3. The higher concentrations in the urban areas are probably a result of the burning of coal or emitted by industrial plants engaged in the smelting of ores (Hemphill, 1970).

The Federal Water Pollution Control Administration (1968) has recommended a permissable limit of 0.05 mg/l of arsenic in public drinking water supplies. Most water treatment processes do not remove this substance. In most potable water supplies, the concentration is usually less than 0.01 mg/l (milligram per liter). McKee and Wolf (1963) reported concentrations of as much as 1.0 mg/l in drinking water but no ill effects were produced over a short period of time. However, a concentration of 0.21 mg/l consumed over a long-term period was shown to be poisonous. The Kansas River contains concentrations of arsenic that closely approaches the recommended limit as set by the Public Health Service. This may be related to arsenic concentrations of 10 to 70 mg/l in presoaks and household detergents from this area (Angina and others, 1970). Thermal springs commonly have relatively high concentrations of arsenic--in some cases as high as 4 mg/l. Ground water in Lane County, Oregon contains as much as 1.3 mg/l (unpub. data, U.S. Geological Survey files). In New Zealand, sickness and death among cattle were attributed to high concentrations of arsenic of natural origin in their drinking water (Grimmett and McIntock, 1939). Similar cases have been reported in the western United States. About 20 milligrams of arsenic per pound of animal is considered a lethal dose (Hem, 1970).

Although sea water contains only a few parts per billion of arsenic, sea food concentrations may exceed several hundred milligrams per liter. According to Shrink and Schreibeis (1958), oysters may contain 3 to 10 mg/l, lobsters 70 mg/l, mussels 120 mg/l, and prawns as much as 170 mg/l. They demonstrated that a seafood dinner resulted in elevated urinary arsenic levels.

Most soils will average several milligrams per kilogram of arsenic. However, as in the case of water, local areas may contain considerably more through abnormal natural or man-made causes. Haywood (1970) reported that several animals died after grazing near a smelting plant due to the ingestion of arsenic-rich forage. Injuries to humans have occurred in at least one area in western United States (Birmingham, 1965) and in Chile (Oyanguren and Perez, 1966) as a result of natural, local high levels of arsenic in the soil, plants, and air.

In sufficient concentrations, most compounds of arsenic will cause death in man, animals, and plants. The lethal dosage for rats is 138 mg/kg (milligram per kilogram), and severe poisoning in man can occur from as little as 100 mg. Dinman (1960) described the early symptoms of arsenical poisoning as weakness, malaise, abdominal complaints, and pains in the arms and legs. Chronic poisoning is characterized by palsies, apathy, and death. Occupational ailments associated with arsenic are dermatitus, perforation of the nasal septum, and ulceration of the skin. Heryer (1963) considers arsenic as a possible cause of lung, skin, and liver cancer.

Arsenic is not known to provide any necessary function in the body. It is present almost everywhere, is not easily degraded, and is a cummulative poison. The burning of coal, smelting of ores, and use of arsenic-based insecticides are the largest sources of man-made arsenic contamination of the environment.

Cadmium

Cadmium averages only a half gram per ton in the earth's crust. It is chemically very active and is never found free in nature. Small quantities of greenockite, a cadmium sulfide, have been found, but cadmium is usually associated with zinc ores in the proportion of about one part cadmium to 200 parts zinc. Most of the commercial cadmium is obtained as a by-product in the smelting of zinc ores.

In 1910, the world production of cadmium was about 50 tons/year, but presently it exceeds 15,500 tons/year, with the United States producing almost 40 percent of the world output. The primary uses of cadmium include electroplating (auto industry), pigments and chemicals, plastic stabilizers, alloys and solders (silver solder and bearings), Ni-Cd batteries, semiconductors, and pesticides. Iron and steel are coated with cadmium to combat corrosion and it is alloyed with copper telegraph and power transmission lines to increase their strength and durability. Jewelers use cadmium in making watch and clock springs and in gold and silver fabrication. Metallic cadmium control rods are used in atomic energy piles.

The concentration of cadmium in fresh waters in the United States appears to be very low. Kopp and Kroner (1968) analyzed 1,500 raw and 380 finished waters in the United States and found cadmium to have a mean concentration of only 9.5 ug/l in raw water and 12 ug/l in the finished water. A study by the Bureau of Water Hygiene (1970) on 2,595 water samples showed that over 99.8 percent of the samples had cadmium concentrations less than 0.01 ug/l. The Federal Water Pollution Control Administration (1968) has recommended a maximum cadmium concentration of 0.01 mg/l in drinking water.

Cadmium is released to the air by industrial processes, the burning of coal, paper, trash, and fuel oil. Specht and others (1965) found concentrations of 1 to 2 mg/kg in eight samples of bituminous coal from Pennsylvania and Kentucky. They also determined that the cadmium content of various types of paper range between 0.08 and 0.55 mg/kg. Diesel oil was found to contain 0.07 to 0.11 mg/l and heating oil 0.42 to 0.53 mg/l (Korkisch and Hazan, 1965). Elevated values of cadmium have been found in the soil and vegetation along highways (Lagerwerff and Specht, 1970). These high values are attributed to the burning of motor oils and diesel fuels, and to particulate matter from car tires. Auto tires have been found to contain 20 to 90 mg/kg of cadmium, and it is estimated that the daily deposition of tire tread in the United States is approximately 830 tons (Marchesani and others, 1970).

The highest background concentration of cadmium appears to be in plants and animals. For these, Bowen (1966) gives a mean value of 0.64 mg/kg. Trace amounts of cadmium have been found in almost all of man's foods and beverages (Schroeder and others, 1967). Vegetables and cereals show the lowest values (0.03 to 0.19 mg/kg), followed by dairy products (0.27 mg/kg), oils and fats (0.83 mg/kg), meats (0.88 mg/kg), and sea foods (0.33 to 5 mg/kg). The average daily intake of cadmium was estimated to be 0.02 mg by Duggan and Lipscomb (1969) and 0.25 mg by Schroeder (1967).

The overt toxic effects of cadmium are well known. As little as 15 mg ingested orally can cause immediate nausea and vomiting. The use of cadmium plated food containers has led to a number of epidemics of acute nausea (Fairhall, 1957, California State Water Pollution Control Board, 1957). Inhalation of cadmium at levels of 3 to 100 mg/m^3 can be fatal. Non-fatal acute pneumonititus may be caused by intermittent exposure to cadmium fume concentrations of 0.5 to 2.5 mg/m^3 over a three day period (Hygienic Guides Committee, 1962).

Cadmium competes with zinc for various biological ligands and may impair processes dependent on the zinc-ligand interaction. Cadmium does not degrade in the environment.

There is much controversy over some of the possible toxic effects of cadmium. Schroeder (1965) concluded that it is responsible for hypertension. Studies by Morgan (1969), however, failed to show any significant relationship between cadmium concentration and hypertension. Gunn and others (1967) believe that cadmium may be a carcinogen, but Potts (1965) and Shubik (1951) doubt that cadmium is responsible for cancer in humans.

In Japan, Kobayoshi (1970) reported on a syndrome called "Itai-Itai". He attributed this condition to the consumption of rice grown in water and soil that contained high concentrations of cadmium. Characteristics of "Itai-Itai" are pains in the bones and joints, waddling gait, glycosuria, severe osteomalacia, and multiple pathological fractures (Lee, 1972). Tuscheya and Takeuchi (Fassett, 1972) disagreed with Kobayoshi and believe that the disease is a result of war-time malnutrition coupled with the ingestion of cadmium. From the foregoing, it should be obvious that total environmental interaction between man and cadmium is poorly understood.

Cobalt

Cobalt is a relatively abundant trace element but except in meteorites, it is not found free in nature. It is commonly associated with the ores skutterudite and cobalite. Although the United States produces very little cobalt, it is the largest user.

The uses of pure cobalt are limited, but its alloys and compounds are important economically. Alnico, an alloy of aluminum, nickel, and cobalt, is used in the manufacture of powerful permanent magnets. Cutting edges for high-speed machine tools and surgical instruments are made from some of the stellite alloys. These alloys contain cobalt, iron, chromium, molybdenum, and tungsten. Cobalt oxide, is used to impart a blue color to glass and acetate and oleate salts of cobalt are used as driers in paints and varnishes. The radioactive isotope, Co^{60}, is used in the treatment of cancer.

The concentration of cobalt in natural waters is very low. In the waters studied by Durham and Haffty (1961) and Durfor and Becker (1964), cobalt was usually too small to be detected. Durham, Hem, and Heidel (1971) examined more than 720 samples and found cobalt in the range of 1 to 5 ug/l in 37 percent of the samples. The concentration of cobalt in grass has been reported by Beeson and others (1947) to range tetween 0.05 and 0.14 mg/kg.

Trace amounts of cobalt are necessary for the health of animals and humans. A deficiency of cobalt in the soil and forage of a western section of Australia was responsible for a serious "wasting disease" in cattle and sheep (Lee, 1972). In humans, cobalt is an essential component of vitamin B_{12} and may speed blood regeneration in radiation anemia and in anemia of infection. However, in more than trace amounts it can have a toxic effect. In Canada consumption of large quantities of beer containing only 1.2 to 1.5 mg/l was associated with cardiac failure and death (Anon, 1968). Also, ingestion of cobalt may be a factor in polycythemia.

Chromium

Chromium, a bluish-white metallic element that does not occur free in nature, is present in the ores chromite and crocoite. Chromium makes up about 0.04 percent of the earth's crust.

Chromium is used extensively in industry as a protective cover for many metals since it resists rusting and is very durable. It is also used in a decorative capacity. Chromium is an important alloying element in the manufacture of stainless steel.

Chromate compounds are used in pigments and refractory materials. Sodium dichromate is utilized in tanning processes and is valued in medicine as an astringent and cauterizing agent. The widespread use of chromate compounds as water additives to prevent corrosion can be a mojor source of water pollution.

Latimer (1952) showed that the stable species of chromium in water are Cr^{+3} and Cr^{+6}, which have a maximum solubility in water of 0.5 ug/l. Although chromium is a relatively abundant trace element in the earth's crust, Durfor and Becker (1964) found a mean value of only 0.43 ug/l in the 100 public water supplies that they tested and Durum and Haffty (1963) give a mean value of 5.8 ug/l for North American rivers. The Federal Water Pollution Control Administration (1965) has recommended a maximum hexavalent chromium content in drinking water of 0.05 mg/l. Plants may contain from 0.1 to 0.5 mg/kg chromium. The tissues of persons who have not been occupationally exposed to chromium will generally contain 0.1 to 1.0 mg/kg.

It is most likely that all compounds of chromium are toxic in large concentrations, but some are more toxic than others. Hexavalent chromium compounds are generally considered the most toxic (Shearer, 1972), but divalent chromium is not generally considered to be toxic in the amounts normally encountered. Trivalent chromium may be a cause of lung damage to workers in the chromate industry. A high incidence of cancer of the lung has been associated with exposure to hexavalent chromium (Baetjer, 1950).

The present amounts of chromium that are likely to be encountered in the natural environment do not seem to pose a threat to health. Indeed, Mertz and others (1959) have shown that trace amounts of trivalent chromium may increase an individual's glucose tolerance.

Copper

Copper, a metallic element known from ancient times, occurs free in nature, but most of the world's supply is extracted from sulfide ores.

The largest user of copper is the electrical industry. Copper is used in the manufacture of ships, munitions, railroads, clocks and watches, tools and machinery. The building and automotive industries consume large amounts of copper and copper alloys. It is used widely in heat exchangers, heating and cooling devices, water pipes, cooking utensils, water heaters, and dairy machinery because of its resistance to corrosion and its ability to conduct heat.

Cuprous oxide is used in coloring porcelain and in making ruby glass, while cupric oxide is used for producing a light-green color in glass. Hydrated cupric sulfate is used in calico printing, dyeing, electroplating, preparation of pigments, preservation of timber, and in making Bordeaux mixture--a fungicide for grapevines, shrubs, and trees. Cupric carbonate, is used in making pigments, and cupric hydroxide for dissolving cellulose in the synthesis of rayon. These soluble compounds of copper impart a disagreeable metallic taste to water and are poisonous.

Durum and Haffty (1963) found concentrations of copper in river waters to average about 6.4 ug/l. Durfor and Becker (1964) reported a maximum concentration of 250 ug/l, a mean of 8.3, and a minimum of less than 0.61 ug/l in public drinking supplies. They attributed the higher values to contamination from copper sulfate, which had been added to the water to inhibit algal growth, and to contamination from pipes, valves, and pumping equipment in the treatment plants. The recommended limit of copper in drinking water is 1.0 mg/l since it imparts an undesirable taste at higher concentrations. Water draining from mines, ore dumps, and mill tailings may show high concentrations of copper. An average concentration of 200 mg/l of copper was found in water from a mineralized region in the southern Urals of the U.S.S.R. (Malinga, 1950).

Vinogradov (1959) reported that the average concentration of copper in the soils of the United States is 18 mg/kg, of the western soils is 21, and of the eastern soils is 14 mg/kg. Studies undertaken by Warren and others (Warren,

1969) on five sets of samples from widely different types of soils, gave a mean value of 7 mg/kg and a range of 7 to 128 mg/kg of copper. They concluded that concentrations of copper in the soil may vary by a factor that ranges from one to twenty or more, depending on the location and type of soil.

Copper, in small amounts, is necessary to the health of humans. Man contains 1.4 mg/kg of copper in his tissues and ingests about 2 mg daily (Warren, 1972). It is a component of red blood cells and participates in the actions of a number of enzyme systems. Laboratory animals have been found to need copper to utilize iron and it is believed that humans do also. A copper enzyme is involved in the formation of myelin and multiple sclerosis is characterized by the breakdown of this substance. Thus, it is possible that a deficiency of copper could prevent myelin formation and consequently be responsible for multiple sclerosis. A deficiency of copper may also result in an anemia and defects in vascular integrity (Carnes, 1968).

Usually, if an individual ingests too much copper, it is quickly expelled and is harmless. However, in cases where the organism is unable to expell the excess, it may produce a toxic effect. Ingestion of more than 60 ug/24 hr can result in Wilson's disease and nephrotic syndrome. In Wilson's disease, the liver, kidney, and brain may contain 15 times the normal concentrations of copper. Penicillamine, a chelating agent, has been used to remove excess copper and is a fairly successful means of coping with Wilson's disease (McCall, 1967).

Lead

Lead is second only to mercury as the heaviest common metal. Galena is the principal source, whereas anglesite and cerussite are minor sources. The United States is the largest producer of lead, the richest deposits being in

Missouri, Kansas, Oklahoma, and the Idaho-Montana and Utah-Colorado regions. Cadmium, antimony, arsenic, bismuth, and small amounts of copper, silver, and gold are commonly associated with lead ores. The mined ores have an average lead content of 3 to 8 percent. In 1969 the United States used approximately 1.5 million tons of lead.

Lead and its compounds have numerous uses, but the manufacture of storage batteries account for 40 percent of the lead consumption in the United States and gasoline additives account for another 20 percent (Leitz, 1970). Other uses are in plumbing, as cable covering, as a protective material in storage and reagent vessels, and as shielding in atomic reactors. Lead may be alloyed with antimony to produce antimonal lead, which is stronger and harder than ordinary lead. The low melting point of lead makes it useful in tin-lead solder, Wood's metal, and other alloys used in fire alarm systems.

The most important inorganic compound of lead, lead monoxide or litharge, is used in the manufacture of storage batteries, in some types of glass, in the ceramics industries, and in oil refining. Lead dioxide is the positive electrode of storage batteries. Minimum or red lead is used as a pigment for coating structural steel. White lead is used extensively as an exterior paint in areas where the air does not contain sulfur compounds. Other inorganic compounds such as lead arsenate, lead sulfide, and lead acetate have been used, respectively, in insecticides, semiconductors, and as a paint drier.

The most important organic compound of lead is tetraethyl lead, which is added to gasoline to prevent engine knocking. Organic compounds of lead are also used widely in paint driers, oil additives, and lubricating greases.

As a consequence of the low solubility of lead in water over the normal pH range, concentrations of lead in natural waters should be limited to no more than about 2 ug/l. The recommended limit for lead in drinking water is

0.05 mg/l. Durfor and Becker (1964) reported a mean value of 3.7 ug/l of lead in public water supplies. The mean value of lead in North American rivers is given by Durum and Haffty (1963) as 4.0 ug/l. Concentrations of 0.8 mg/l have been reported in areas where limestone and galena ores are found (Kopp and Kroner, 1968). Evidence given by Murozumi and others (1969) seems to indicate that the mean concentration of lead in the hydrologic cycle may be on the rise. Snow samples from the artic show an increase from less than .02 ug/kg (micrograms of lead per kilogram of snow) in 1750 to greater than 0.20 mg/kg in 1969. A striking fact in this study is that more than 70 percent of the increase has taken place in the last 20 years. In Columbus, Ohio, snow samples collected over a 20-square mile area were found to contain concentrations of lead exceeding the recommended limit for drinking water (Pettyjohn, 1972). These concentrations ranged between 0.05 and 1.09 mg/l of lead.

The mean concentration of lead in the air is from 1 ug/m^3 to 3 ug/m^3. The range of concentrations an individual might be exposed to varies greatly. Concentrations of lead in the air around industrial plants may be as high as 50 mg/m^3 (Working Group on Lead Contamination, 1970). The air and surrounding soil, water, and plants may be grossly contaminated by effluents from smelters and refining processes.

Another major source of lead pollution is the automobile exhaust. Some 70 to 80 percent of the lead in gasolines is discharged into the atmosphere. As a result, the mean concentrations of lead in heavy traffic areas may be as high as 40 ug/m^3. It has been estimated (Symposium on Environmental Lead Contamination, 1966) that the body retains 24 to 40 percent of the lead that is inhaled. These high concentrations of lead in the atmosphere combined with the ingestion of lead concentrations of as high as 300 ug/day (Kehoe, 1961) from food and beverages, could result in serious and widespread consequences. A prevalent source of lead poisoning among adults as well as unborn or nursing infants is moonshine whiskey (Pettyjohn, 1972), which may contain as much as 1 mg/l of lead.

The toxic effects of lead are varied and complex, usually involving either the nervous system, the hemotopoietic system, or the kidney. The levels of lead in the blood may range between 60 and 130 ug/100g (micrograms of lead per 100 grams of blood). The red blood cells show the characteristic features encountered in iron deficiency anemia because the lead interfers with the utilization of iron in the formation of hemoglobin (Griggs, 1964). Mild anemia is characterized by pallor, easy fatigability, irritability, and mild headaches. In cases where the level of lead in the blood exceeds 80 ug/100g, severe anemia or acute abdominal colic is encountered. The symptoms are headaches and muscle aches followed by constipation and abdominal pains. As the condition becomes more severe, the patient begins to vomit, experience a loss of appetite and weight, and complains about a "bad taste" in the mouth.

The most severe clinical form of lead poisoning is acute encephalopathy. Blood-lead levels greater than 120 ug/100g are associated with this condition. Acute encephalopathy syndromes are intractable convulsions, coma, cardiorespiratory arrest and death. One month is estimated to be the minimum period of ingestion of excessive lead required to produce acute encephalopathy (Klein, 1970). Chronic encephalopathy has been diagnosed as being responsible for a progressive mental deterioration in children. Blood-lead levels that are in excess of 60 ug/100g and x-rays of the long bones show evidence of continued absorption of excessive amounts of lead (Peristein and Attala, 1966).

Excessive ingestion of lead may effect the endocrine, reproductive, and pulmonary systems. Ingestion of lead-contaminated moonshine whiskey has been shown to have diminished secretions of pituitary gonadotropins (Sandstead, 1969). Sterility, still births, abortion, and neonatal deaths in man have been attributed to severe lead intoxication (Nishimuri, 1964). Renal cancer has been produced in rats by their ingestion of toxic amounts of lead (Van Esch and Kroes, 1970). However, there is no evidence that lead may cause cancer in humans. Warren (1967) found that in areas where garden and farm produce contained anomalous concentrations of lead, multiple sclerosis is especially prevalent.

Lead is not known to fulfill any useful function in human health. But its ubiquity in rocks, soils, the oceans, fresh waters, plant and animal tissues may indicate that it does have a place in human nutrition.

Mercury

Small amounts of free mercury are found as little globules or in association with gold or silver. The only economical source of mercury is cinnabar and since 1500, 75 to 80 percent of the world's mercury has come from five mines: the Almaden in Spain, the Idria in Yugoslavia, the Huancavelica in Peru, the New Almaden in California, and the Monte Amiata in Italy. It is estimated that about 5,000 tons of mercury circulate through the global environment each year as a result of natural processes such as erosion. This is considered to be approximately as much as man introduces through his uses of mercury.

The largest use of mercury is in the pure metal form. The metal is used in dental alloys, thermometers, barometers, electric switches, and control apparatus. It is also used as electrode material in the production of caustic soda and chlorine. Mercurous salts, most of which are prepared from mercurous nitrate are used in medicine, in paints, in dry cell batteries, and in the manufacture of mercury compounds.

Mercury compounds are widely used in agriculture. Since the early 1920's, organic compounds of mercury have been used in the United States in treating seeds to prevent fungal diseases prior to germination and to prevent fungal diseases in growing plants, fruits, and vegetables. Organic and inorganic forms of mercury are used as pesticides (Kirk, 1960). Mercuric and mercurous chloride are used to protect vegetable crops and to prevent and treat fungus diseases of turf grasses. Corrosive sublimate is used to control diseases of tubers and bulbs, and as a seed disinfectant.

Mercury, as with arsenic and lead, is found almost everywhere in the environment, but its concentration in natural waters is usually very small. Mercury was detected in seawater in 1799 (Proust, 1799) and found in some French mineral waters during the late 1800's and early 1900's. Stock (1934) determined the average concentrations of mercury in the North Sea, in fresh water, and in rain water, respectively, as 0.03 ug/l, 0.01 to 0.10 ug/l, and 0.05 to 0.48 ug/l. Scientists in the Soviet Union (Aydin'yam, 1962) looked for mercury in some of the major rivers of Eastern Europe, in the Black Sea, the Sea of Azov, parts of the Mediterranean Sea, and the Atlantic and Indian Oceans. The concentrations encountered ranged from 0.09 to 2.8 ug/l. They did not detect much difference in concentrations between the rivers and seas. Fujimura (1964) determined that the concentrations of mercury in Japan's rainwater was around 0.6 ug/l, and that water in some ditches contained mercury concentrations ranging from 4 to 100 ug/l.

Prior to 1970 in the United States, very little attention was paid to mercury. Kopp and Kroner (1968) in their five year summary of trace metals in waters of the United States did not even mention it. Similarly, Durfor and Becker (1964) neglected mercury in their study of public water supplies. Research conducted by the U. S. Geological Survey (Hem, 1970) indicates that the natural waters in the United States, generally, have a mercury concentration that ranges from 0.1 to 6.0 ug/l. Concentrations of as high as 10 ug/l have been reported in waters associated with hot springs and cinnabar deposits.

Very little is known about the content of mercury in the atmosphere. Mercury has a very high vapor pressure at ordinary temperatures, and consequently should be present everywhere. Since all compounds of mercury can be converted to aerosols, mercury may be present as an aerosol or vapor. Values determined for mercury in the atmosphere as a vapor, range from 1 to 50 ng/m^3 (namograms per cubic meter) in the air in the vicinity of Palo Alto, California and from 0.6 to 0.7 ng/m^3 at an elevation of 10,000 feet and 20 miles west of the California coast (Williston, 1968). Studies of aerosol concentrations of mercury are limited, but values ranging from 1 to 40 ng/m^3 have been determined for the air above New York City. A possible source of air pollution by mercury is the burning of coal mined in the eastern and midwestern states. It is estimated that this coal may contain as much as 100 mg/kg of mercury.

A common belief is that the ingestion of mercury in its metallic form can cause sickness and death. However, mercury in its liquid form is not considered to be harmful to health and at one time may have been used as a laxative. Research has indicated that amounts up to a pound or more can be ingested without adverse effects. Nevertheless, mercury vapors and compounds of mercury may have a very serious toxic effect.

Since mercury will vaporize at room temperatures, poisoning by inhalation of mercury vapor is not uncommon. Symptoms of acute poisoning as a result of inhaling mercury vapors are chills, fever, cough, and a tight feeling in the chest (Lee, 1972). Acute poisoning may result in pulmonary edema, necrosis of pulmonary tissue, and death. Inhalation of mercury vapors more commonly result in chronic poisoning, which is characterized by tremor, erethism, gingivitis, and numerous non-specific subjective complaints.

Mercuric chloride has been used in homicides and suicides since as early as 1000 A.D. Ingested orally it will corrode the intestinal tract and damage the kidneys. Mercurous chloride, which is less dangerous than mercuric chloride, can be responsible for acrodynia in children.

The alkyl mercurials have caused many deaths and nearly all cases of alkyl mercurial poisoning exhibit similar symptoms. The most pronounced being permanent organic injury to the brain resulting in weakness, paralysis, loss of vision, disturbed cerebral function, coma, and death (Swensson, 1952). Alkyl mercurial poisoning has been responsible for congenital defects taking the form of cerebral palsy (Matsumoto, Koya, and Takeuchi, 1965) and mental retardation (Englesson and Herner, 1952). It may also be responsible for chromosomal abnormalities (Ramel, 1967). The tragedy suffered by the Huckleby family in New Mexico after eating pork, which had been fed corn treated with a mercurial fungicide (Pettyjohn, 1972), and the numerous deaths in Iran, which resulted from the consumption of bread made from grain treated with an organic mercurial fungicide and meat from livestock fed the treated grain (Jalili and Abbasi, 1961), exemplify only too well the serious consequences resulting from the toxic effects of the alkyl mercurials.

Although natural waters may contain only small amounts of mercury, the effects may still be dangerous. Metallic mercury in the water may be changed into methyl mercury by anaerobic microorganisms that thrive in sludge or on the bottoms of lakes and rivers where oxygen is limited or absent. This methyl mercury is released into the water where it enters the food chain. As it is taken up by successively larger and more complex organisms, it becomes more concentrated. Studies in Japan, Sweden, and the United States have shown that the concentration factor in fish could be 3,000 or more to 1

(Johnels and Westermark, 1970).

Nickel

Nickel is similar to cobalt in its geochemical behavior and sulfide and silicate ores are its principal sources. Nickel is a relatively abundant metal, occurring in the earth's crust in amounts equal to one part in 10,000.

The metal is used extensively in the electroplating industry because it is hard, malleable, ductile, and corrosion-resistant and capable of taking a high polish. It has the ability to impart these properties to its alloys. Nickel-chromium alloys are widely used in the manufacture of stainless steel. Monel metal, a nickel-base alloy, is used in the manufacture of kitchen utensils, food processing equipment, marine and chemical laboratory equipment, and small denomination coins. Nickel has a low coefficient of linear expansion, which makes it useful in the manufacture of measuring devices such as surveyors' tapes, pendulums, and bimetallic thermostats.

Nickel monoxide is used as a coloring agent in the manufacture of glass and ceramic glazes and in the production of ferrites, and ferrous and nonferrous alloys. Nickel hydroxide is used in electroplating and as a constituent of the positive plates in storage batteries. Nickel sulfate is widely employed as an ingredient of nickel plating baths, as an enameling dip, and as a catalyst. Nickel acetate is used as a sealing agent for anodized aluminum, as a reagent in the preparation of metallized dyes, and as a catalyst. Nickel carbonate, which occurs in nature as the mineral zaratite, is also used as a catalyst.

Durum and Haffty (1963) give the medium concentration of nickel in North American rivers as 10 ug/l. Durfor and Becker (1964) give a mean concentration of 2.7 ug/l for the public water supplies of the 100 largest cities in the United States. Kopp and Kroner (1968) report a mean of 19 ug/l of nickel in the United States waters. The solubility of nickel in natural waters is about the same as cobalt. The higher mean values for nickel probably reflect its greater abundance in rocks. Nickel has been found to occur in concentrations considerably above these mean values. An average of 40 ug/l was reported by Maligua (1950) in water from a mineralized region in the southern Urals of the Soviet Union. A concentration of 130 ug/l of nickel was encountered in the Cuyahoga River at Cleveland, Ohio (Kopp and Kroner, 1968).

The mean concentration of nickel in the air of 30 cities of the United States has been reported by McMullan (1969) as 0.45 ug/m^3 for the four year period ending in 1960, and 0.35 ug/m^3 for the next four years. Coal ash has been shown to contain concentrations of nickel ranging from 3 to 10,000 mg/kg, depending upon the origin of the coal and Given (1966) reported a concentration of 100 mg/l in crude oil. Thus, the combustion of coal and oil may be the source of a large percentage of nickel in the atmosphere.

Trace concentrations of nickel have been reported in plants, food, and animal tissues (Schroeder, Balassa, and Tipton, 1962). The small concentrations of nickel encountered in the environment do not seem to pose a threat to the vegetation, domestic animals, or wild life. However, because of the possible carcinogenic threat to man (Frust, 1971), the atmospheric levels of nickel are of concern. No environmental air quality standard has been set for nickel or its compounds, but the American Conference of Governmental Industrial Hygienists have set a threefold limit value (TLV) of 1 mg/m^3 (Threshold Limit Values of Airborn Contaminants, 1970).

Although poisoning by nickel is rare, the salts are toxic if introduced directly into the blood. Occupational long-term exposure to nickel has been responsible for "nickel itch", a dermatitis, which may indicate an allergic response. Sunderman and others (1957) have shown conclusively that nickel carbonyl, the most toxic of the nickel compounds, can cause pulmonary cancer in animals and humans. However, the exposure to other metals at the time of exposure to nickel tends to cause controversy as to the true carcinogenicity of nickel compounds.

Nickel ions have been shown to simulate the action of insulin (Divit and Lazarow, 1965) and increase glucose incorporation into clycogen. Raben and Antonev (1966) have found evidence to indicate nickel may play a role in skin metabolism. Thus, there are indications that nickel may be a necessary trace element from the viewpoint of physiological health.

Silver

Silver, known to the Romans as "argentum", occurs in its native state, usually alloyed with gold, copper, and mercury, or in ores such as argentite and horn silver. Most of the silver produced in recent years has been obtained as a by-product of gold refining or of lead and zinc mining.

Sterling silver, which contains 925 parts of silver and 75 parts of some other metal, is used to make jewelry, table cutlery, candlesticks, vessels and bowls, and trophy cups. An alloy of silver and copper is used in the manufacture of coins. It is used extensively in photography and electroplating in dental alloys, stainless steel alloys, and in solder and brazing alloys. Silver paints are used for making printed circuits and mirrors. Finely divided silver has germicidal effects and is used in swimming pools and some water supplies as a disinfectant. Silver fulminate is a powerful explosive and silver iodide is used in seeding clouds to produce rain. Silver chloride is a cement for glass and silver nitrate, the most important silver compound, is widely used in photography. Solutions of silver nitrate are placed in the eyes of newborn infants to guard against infection and are used to cauterize wounds and treat warts.

Since many silver salts such as the chloride, sulfide, phosphate, and arsenate are insoluble, the concentration of silver ions in natural water should be low. Durfor and Becker (1964) show a mean concentration of 0.23 ug/l and a maximum of 7.0 ug/l in the public water supplies that they tested. Durum and Haffty (1963) report a mean of 0.09 mg/l, while Kopp and Kroner (1968) report a mean of 2.6 ug/l, a low of 0.1 ug/l, and a maximum of 38 ug/l for the river waters of the United States. The recommended limit of silver in public drinking water supplies is 0.05 mg/l.

Silver is not generally considered to be a toxic metal. However, concentrations in the range of 0.4 to 1 mg/l have caused pathological changes in the kidneys, liver, and spleen of rats. Also, high concentrations of silver can cause argyria, a permanent, blue-gray discoloration of the skin and eyes. The current mandatory limit of 0.05 mg/l for silver in water was set not because of the danger of silver in natural waters, but to limit the amount of silver added to water as a disinfectant.

Strontium

Strontium is similar in chemical properties to calcium. The chief ores of strontium are celestite and strontianite. Strontianite, the preferred ore is commonly associated with barite, celestite, and calcite in veins in limestone. It is also found as concretionary masses in limestone and in clay.

When strontium compounds are ignited they burn with a brilliant crimson color. This property makes them useful in the manufacture of flares, signal lights and fireworks. Strontium hydroxide is used to extract the sugar from uncrystallizable syrups. Strontium carbonate is used in the manufacture of iridescent glass and of glazes and enamels. Some strontium compounds are used in welding fluxes, in the treatment of steel, for coating fluorescent lamps, and for limited medicinal purposes. Strontium is not used to a large extent in industry because for most purposes calcium, which is much cheaper, can be used in its place.

Durham and Haffty (1963) reported a median strontium value in North American rivers as 0.06 mg/l, while Skougstad and Horr (1963) reported a median value of 0.11 mg/l, which included both surface water and ground water. Sea water contains 8.5 to 10 mg/l and brines commonly exceed 1000 mg/l of strontium. Durfor and Becker (1964) found strontium in all of the water supplies that they analyzed, the concentrations ranging from 2.2 to 1,200 ug/l, with a mean of 110. Kopp and Kroner (1968) detected strontium in 99 percent of the rivers and lakes of the United States that they sampled and found the concentrations to range from 3 to as much as 5,000 ug/l, with a mean concentration of 217. Streams in parts of northern and western Texas and southern New Mexico may contain more than 1,500 ug/l, while streams in the Pacific Northwest, northeastern United States, and the Central Lowlands usually contain less than 500 ug/l of strontium (Skougstad and Horr, 1960). It appears that the strontium concentration is higher in water draining calcarious soils.

The stable isotopes of strontium do not seem to pose any threat to health. However, strontium-90, a radioactive isotope with a half-life of 28 years, is a well-recognized hazard. Strontium tends to accumulate in the bones since it is chemically similar to calcium. Thus, long-term ingestion of small amounts of strontium-90 could result in radiation poisoning. Also, the possibility exists that cows grazing on grass grown in areas contaminated by radioactive fallout may transmit significant amounts of strontium-90 to the milk supply. This is an argument in favor of underground nuclear tests.

The Public Health Service Drinking Water Standards limit the concentration of strontium-90 in water to 10 pC/l (picocuries per liter). A picocurie is 0.037 disintegrations per minutes.

Tin

Cassiterite is the chief ore of tin and the alluvial deposits of the Kinta Valley in Malaya are its prime source. Bolivia, China, and Indonesia are also important sources, but the United States is the largest consumer.

The major use of tin in the United States is in the manufacture of tin plate, which is used to make tin cans. This accounts for 73 to 75 percent of the tin used in this country. Large amounts are used to make bronze, solder, babbitt, and other alloys. These alloys are used in the manufacture of bearings, printers' type, bullets, pewters, foil, terneplate, bar tin, pipe and tubing, and tinning.

Stannic oxide is used in the production of opaque glass, ceramic manufacturing, and enamels and porcelain, which are used to cover bathtubs and sinks. Stannic chloride is employed as a mordant in the dyeing of silk and for weighting of silk. Stannous chloride is used as a mordant in dyeing and for tinning small objects. Stannous sulfate and stannous oxalate are used in the dyeing and textile industries.

In their study of public water supplies, Durfor and Becker (1964) were unable to detect tin. Although a relatively abundant metal in the earth's crust, its concentration in water appears to be very low. It is not known to have any toxic or beneficial effects on human health.

Zinc

Zinc is not found free in nature, but its ores are widely distributed over the earth's surface. Sphalerite is the principal ore while smithsonite, willemite, and zincite are lesser ores. Sphalerite is found in association with galena in most of the important deposits. Large quantities of zinc have been produced from sphalerite deposits in Missouri, Kansas, and Oklahoma. The world-wide average annual production of zinc has been around 4 million tons, and the United States is the largest producer.

Galvanizing, the coating of steel or iron with a thin layer of zinc, is its most important use. Additionally, large amounts of zinc are used to make alloys, such as brass, typewriter metal, bronze, spring brass, German silver, soft solder, and aluminum solder. The automobile, electrical, and hardware industries make extensive use of zinc die castings. Zinc oxides are widely used in the manufacture of paints, rubber products, cosmetics, pharmaceuticals, floor coverings, plastics, printing inks, soap, storage batteries, textiles, electrical equipment, and other products. Lithopane, a mixture of zinc sulfide and barium sulfate, is an important pigment. Zinc sulfate is used in making luminous dials, x-ray and TV screens, and fluorescent lights.

Since in the weathering process soluble compounds of zinc are formed, its presence in trace amounts in surface waters is common. Usually these concentrations do not exceed 5.0 mg/l because the zinc ions are absorbed in hydrolyzate sediments. Kopp and Kroner (1968) give the mean concentration of zinc in the surface waters of the United States as 64 ug/l with a minimum of 2 ug/l and a maximum of 1,183 ug/l. The recommended maximum limit in drinking water is 5 mg/l. Mine waters with a low pH may contain as much as 345 mg/l (Hem, 1970) and some springs near ore deposits may exceed 1,500 mg/l. The concentrations of zinc in surface waters seems to reflect the availability of the zinc in the water and soil through which the water has passed.

Zinc occurs in many tissues and enzymes and is indispensable to growth and to the function of blood cells, liver, kidneys, and other organs (Spectrum, 1967). It has been shown that injections of zinc will accelerate early bone healing in guinea pigs and that chicks, which are fed on zinc deficient diets, show retarded growth, hyperkeratosis, shortened and thickened bones, enlarged joints, and frizzled feathering. Poor growth and skin lesions have been reported in swine raised in concrete-floored feedlots and Tucker and Salmon (1955) related these conditions to zinc deficiency.

Prasod and others (1963) eliminated symptoms of retarded growth and hypogonadism in Egyptian boys whose diet consisted largely of bread and beans by feeding them zinc supplements. Zinc may be present, in what would appear to be a sufficient quantity, in the diet and yet symptoms of zinc deficiency may appear. This is caused by agents binding the zinc and reducing its intestinal absorption. Phytic acid, present in unleavened whole wheat bread, and calcium can reduce the absorbtion of zinc significantly. It is possible that birth defects, particularly in those women who eat clay (geophagia) while pregnant, may be linked to a zinc deficiency. Henzel and others (1969) believe that large supplements of zinc may be useful in circulatory problems associated with atherosclerosis. Studies indicate that many factors, as yet unknown, effect zinc requirements.

Zinc is not considered to be toxic to humans, but inhalation of zinc oxide can produce a syndrome known as oxide shakes or zinc chills, and high concentrations may be highly toxic to fish. Concentrations of above 15 mg/m^3 of zinc oxide should be avoided. Zinc in concentrations above 5 mg/l can cause a bitter taste in drinking waters. Also, there is evidence that too much zinc may aggravate dental caries (Spectrum 1967).

Summary and Conclusions

Water-quality characteristics of the Maumee River basin are created by the natural environment and by man's use of the water and land resources. Pollution, rendering the water unfit for any beneficial use, can arise as a result of municipal, agricultural, industrial, and natural activities within the basin. Contaminants that may enter into the aquatic environment include a wide range of organic and inorganic chemicals, such as pesticides, fertilizers, petrochemicals, biochemicals, radioactive elements, pathogenic and nonpathogenic organisms, and trace metals among many others.

The purpose of this project was to determine the relative concentration and distribution of aluminum, arsenic, cadmium, cobalt, copper, chromium, lead, mercury, nickel, silver, strontium, tin, and zinc in the water and sediment in the Maumee River basin. Some of these elements can be very toxic to man in extremely small amounts, while others may be toxic if taken internally in larger quantities over long periods of time. Most, however, are, in small concentrations, necessary and beneficial to health.

This investigation was based on the premise that existing and probably short term pollution might be indicated in water samples, while sediment would tend to accumulate a record of past activities. Water was analyzed to determine if concentrations of selected trace elements exceeding the Public Health Service limits were present in the basin. Sediment was analyzed to determine what concentrations of metals might be readily available (X-extractant) to organisms and also to establish a some what arbitrary maximum limit on what might be available (Y-extractant) to organisms. Atomic absorption spectrophotometry was chosen as the method of analysis.

There are seven municipalities within the basin from which a relatively large number of water and sediment samples were found to contain abnormally high concentrations of some trace elements (Table 16). Samples from the Fort Wayne area contained high concentrations of aluminum, silver, cadmium, cobalt, chromium, and mercury. For example, water samples 218 , 222, and 223 contained concentrations of aluminum greater than 0.80 mg/l (mean concentrations of Al in water was 0.01 mg/l). In the same general area water sample 121 contained 0.056 mg/l (PHS limit 0.05 mg/l) of silver and sediment sample 222 showed exchangeable and extractable silver in concentrations, respectively, of 1.772 and 1.320 mg/kg (mean of 0.095 mg/kg for exchangeable and extractable silver ion concentrations). Sample 218 downstream from Fort Wayne on the Maumee River showed exchangeable and extractable cadmium ion concentrations, respectively, of 1.217 and 0.806 mg/kg (mean concentration of exchangeable and extractable cadmium ions 0.15 and 0.03 mg/kg). Water samples 119, 121, and 122 contained cobalt concentrations of 0.037, 0.033, and 0.025 mg/l (mean concentration of cobalt in water 0.008 mg/l). Sediment samples 218 and 222 had, respectively, extractable chromium ion concentrations of 0.080 and 0.184 mg/kg (mean chromium extractable ion concentrations 0.02 mg/kg). Water sample 222 showed a mercury concentration of 0.730 (U.S.S.R. limit .005).

Big Run at Butler, Indiana, (sample 36) contained high concentrations of aluminum, silver, cadmium, cobalt, copper, mercury, nickel, and lead. Concentrations of mercury in the water were 1.350 mg/l, one of the highest encountered during this study. Cadmium, copper, mercury, nickel, and lead exchangeable ion concentrations were, respectively, 3.578, 2.362 (mean value 0.085 mg/kg), 168.091 (mean value 20 mg/kg), 2.726 (mean value 0.80 mg/kg), and 15.874 mg/kg (mean value 0.85 mg/kg). Aluminum, silver, cadmium, cobalt, copper, mercury, and lead extractable ion concentrations were, respectively, 1351.753 (mean value 4.0 mg/kg), 5.295, 2.186 (mean value 0.03 mg/kg), 13.821

	Trace Elements Appearing in Anomalous Concentrations	
Municipality	Sediment	Water
Fort Wayne, Ind.	Ag, Cd, Cr	Al, Ag, Co, Hg
Butler, Ind.	Al, Ag, Co, Cd, Cu, Hg, Ni, Pb	Hg
Maumee, Ohio	Hg, Zn, Ag, Cd, Cu, Ni, Pb, Cr	Al, Cd
Findlay, Ohio	Ni	Ag, Co, Sr, Pb
Defiance, Ohio	Al, Ag, Cr, Hg, Ni, Pb, Sn	Pb, Sn
Decatur, Ohio	Ag, Cu, Cr	Al, Cd
Hudson, Mich.	Ag, Cd, Co, Cu, Hg, Ni, Pb, Sr, Zn, Al, Cr	Cu, Hg

Table 16. Trace elements that appear in anomalous concentrations in water and sediment in the vicinity of seven municipalities.

(mean value 0.90 mg/kg), 26.387 (mean value 0.40 mg/kg) 213. 263 (mean value 25 mg/kg), and 10,551 mg/kg (mean value 0.80 mg/kg). These high concentrations probably reflect contamination by industrial wastes.

Sample 113 from the Maumee River at Maumee, Ohio showed anomalously high concentrations of aluminum, silver, cadmium, chromium, copper, mercury, nickel, lead, and zinc. Concentrations of aluminun and cadmium in the water were, respectively, 0.750 and 0.062 mg/l (PHS limit 0.01 mg/l). Concentrations of exchangeable silver, cadmium, copper, nickel, and lead ions were, respectively, 0.599, 0.954, 10398, and 116.945 mg/kg. Extractable ion concentrations of cadmium, chromium, mercury, lead and zinc were respectively, 0.609, 0.396, 63.444, 3.289, and 24.470 mg/kg (mean value 4 mg/kg).

Four samples (samples 134, 135, 149, and 150) from the vicinity of Findlay, Ohio showed abnormally high values of silver, aluminum, cobalt, chromium, nickel, lead, and strontium. Water sample 134 from the Blanchard River slightly downstream from Findlay and water sample 135 from the Blanchard River at Findlay showed respective silver concentrations of 0.059 and 0.054 mg/l. Sample 135 also showed cobalt and strontium concentrations of 0.021 and 3.072 mg/l (mean strontium concentrations in water 0.40 mg/l). Sample 150 from Lye Creek at the south end of Findlay showed a lead concentration of 0.100 mg/l (PHS limits 0.05) and an extractable nickel ion concentration of 5.2 mg/kg (mean extractable nickel ion concentration 0.95 mg/kg). Sample 149 from the Outlet upstream from Findlay had an exchangeagle aluminum ion concentration of 35.251 mg/kg (mean exchangeable aluminum ion concentration 1.5 mg/kg). Sample 149, also, showed extractable aluminum, chromium, and nickel ion concentrations of 780.787, 4.167, and 7.286 mg/kg.

Two samples from Defiance (samples 200 and 201) contained high aluminum, silver, chromium, mercury, nickel, lead, tin, and strontium concentrations.

Exchangeable and extractable aluminum ion concentrations of 44.952 and 999.157 mg/kg were found in sediment sample 200, which was collected from Powell Creek upstream from Defiance. It also had extractable silver, chromium, mercury, nickel, lead, and tin concentrations of 0.446, 0.170, 93. 418, 21.911, 5.118, 8.381 mg/kg (mean extractable tin ion concentration 0.40 mg/kg). Water sample 201 (Maumee River at Defiance) had lead and tin concentrations of 0.086 and 0.758 mg/l (mean concentration of tin in water 0.055 mg/l).

Sample 224, from the St. Marys River slightly downstream from Decatur, showed high concentrations of aluminum, silver, cadmium, chromium, and copper. Aluminum concentrations of 1.928 and 2.722 mg/l were detected, respectively, in water samples 224 and 225, and cacmium concentrations of 0.011 and 0.01 (PHS limit 0.01 mg/l) were detected respectively, in water samples 224 and 225. Sediment sample 224 showed exchangeable silver and copper ion concentrations of 0.993 and 0.614 mg/kg, respectively, and extractable silver, chromium, and copper ion concentrationf of 0.683, 0.134, and 0.858 mg/kg, respectively. Sediment sample 225 had exchangeable silver and copper ion concentrations of 1.961 and 0.172 mg/kg, respectively, and extractable silver and chromium ion concentrations of 1.392 and 0.160 mg/kg, respectively.

Water sample 21, from Bean Creek at Hudson, Michigan, has anomalously high copper and mercury concentrations of 0.002 and 0.488 mg/l, respectively. Sediment from this site contained abnormally high concentrations of exchangeable silver, cadmium, cobalt, copper, mercury, nickel, lead, strontium, and zinc, respectively, of 220.799, 16.312, 50.395, 2034. 821, 661.375, 41.683, 114.275, 319.352, and 505.521 mg/kg. Extractable silver, aluminum, cadmium, chromium, copper, mercury, nickel, lead, strontium, and zinc ion concentrations of 330.542, 2010.470, 16.247, 8.610, 3527.91, 360.906, 43.016, 456.104, 281.715, and 897.181 mg/kg were detected at sample site 21.

It is probable that the high concentrations of various trace metals in the water and sediment in the vicinity of these seven municipalities are a result of industrial pollution. The high aluminum values may result from the practice of using alum in water treatment plants. Electroplating, electronics, and metal industries in these municipalities are likely sources of silver, cadmium, chromium, copper, nickel, lead, tin, and zinc. Oil refineries and plants burning large quantities of low grade coal containing relatively large amounts of sulfur are possible sources of cadmium, chromium, and lead pollution. The high concentrations of strontium at Findlay is most likely from the nearby sugar beet industry.

Not all anomalous concentrations are restricted to industrial centers. A large number of water and sediment samples (141-143, 152, 159-164, 166-170, 172, 173, 177, and 217) all from small streams in rural areas contained high concentrations of arsenic. It appears that higher concentrations of arsenic are found in areas where the ground water is highly mineralized and sulfur water from underlying bedrock aquifers may be a natural source. Arsenic from pesticides is another possible source of pollution. However, as only 85 arsenic samples were evaluated and much of the basin was not covered, more complete sampling of the basin needs to be done before any accurate regional distribution of arsenic can be determined. In addition, the analytical techinques used to detece arsenic are commonly unreliable and open to serious error. In fact arsenic determinations were discontinued early in this study due to significant analytical problems.

Concentrations of silver, copper, and mercury appear to be higher near or in high-yield glacial and bedrock aquifers. These high yield-areas may be discharging relatively highly mineralized water containing trace metals.

Lead, nickel, and zinc concentrations were usually higher in the rural areas than in urban regions. Lead and zinc are commonly used in agricultural practices and may be sources of pollution. Natural sources of nickel, lead, and zinc are sulfide minerals occurring in the glacial deposits and bedrock formations of the basin. Sulfur water from these formations may also contain relatively high concentrations.

Concentrations of strontium throughout the basin were relatively high (a mean concentration in water of 0.4 mg/l). The high background of strontium is probably a result of ground water taking into solution strontium derived from relatively soluble celestite in the limestone and dolomite bedrock formations.

Pollution in the Maumee River Basin appears to be from industrial wastes, agricultural practices, and natural sources. Electroplating, metal industries, and gas and oil refineries are probably the chief industrial sources, highly mineralized ground water containing ralatively large amounts of sulfur in the chief natural source of pollution, and the widespread and common use of insecticides and fungicides containing lead, arsenic, and mercury is probably responsible for trace metal pollution in agricultural areas.

Hudson, Michigan and Butler, Indiana require further investigation. Although industry is very limited in these two small municipalities, samples consistantly showed high concentrations of trace metals.

The areal distribution of several trace elements indicates that they are rapidly removed from water as they react with the stream's sediment load. Were this not the case, concenerations would tend to increase downstream. In view of the locally high concentrations in alluvium and the ability of plants to remove these substances, additional investigations along these lines should be initiated.

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APPENDIX I

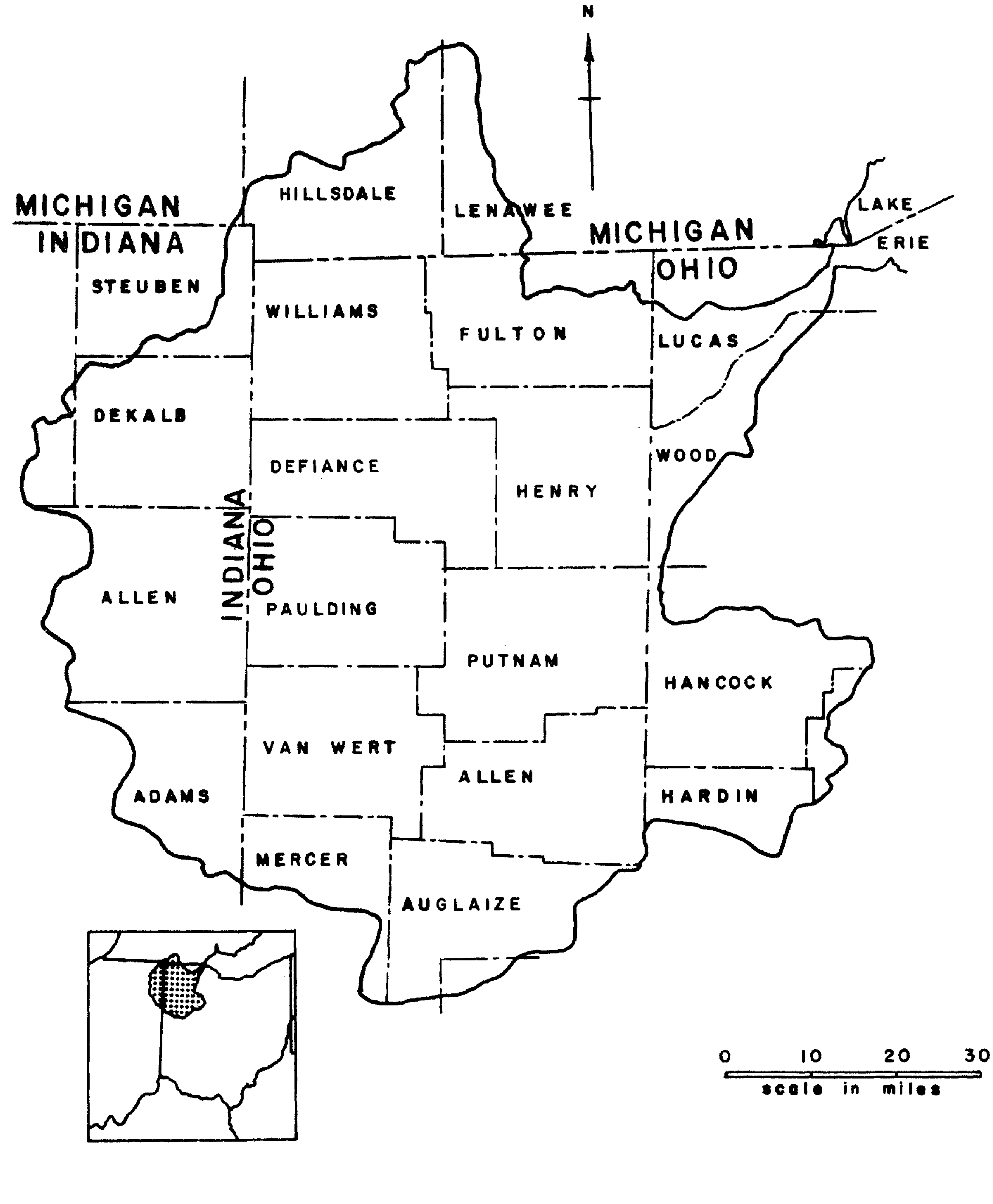


Figure 8. Index of map counties in the Maumee River basin.

SAMPLE LOCATIONS

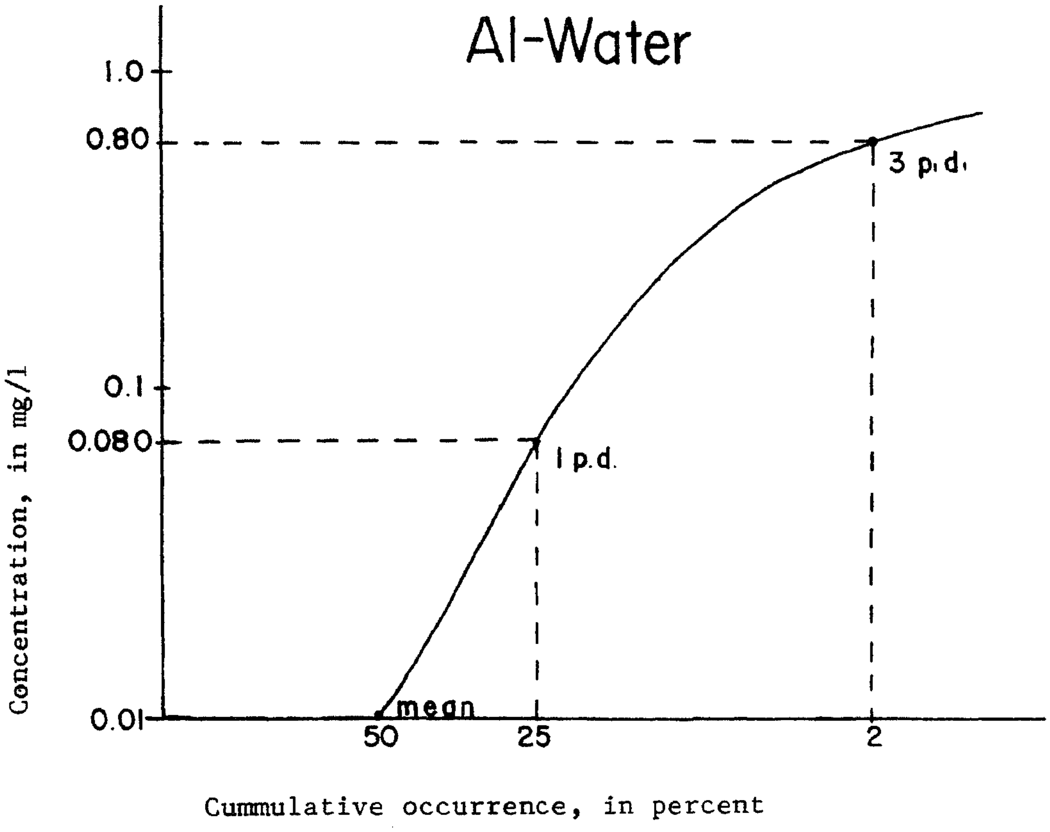
Sample No.	Stream	County	State
1	Fitts Creek	Hillsdale	Michigan
2	Posey Creek	Hillsdale	Michigan
3	Posey Creek	Lenawee	Michigan
4	Posey Creek	Lenawee	Mighigan
5	Fitts Creek	Lenawee	Michigan
6	Fitts Creek	Hillsdale	Michigan
7	St. Joseph River	Williams	Ohio
8	Nettle Creek	Hillsdale	Michigan
9	Posey Creek	Hillsdale	Michigan
10	Branch Creek	Hillsdale	Michigan
11	Fitts Creek	Hillsdale	Michigan
12	West Fork	Hillsdale	Michigan
13	East Fork	Hillsdale	Michigan
14	West Fork	Hillsdale	Michigan
15	West Fork	Hillsdale	Michigan
16	East Fork	Hillsdale	Michigan
17	Silver Creek	Hillsdale	Michigan
18	Bird Creek	Hillsdale	Michigan
19	Goose Creek	Hillsdale	Michigan
20	Lime Creek	Hillsdale	Michigan
21	Bean Creek	Hillsdale	Michigan
22	Bean Creek	Lenawee	Michigan
23	Lime Creek	Lenawee	Michigan
24	Lime Creek	Lenawee	Michigan
25	Lime Creek	Lenawee	Michigan
26	Iron Creek	Lenawee	Michigan
27	Bean Creek	Lenawee	Michigan
28	Bean Creek	Lenawee	Michigan
29	Bean Creek	Fulton	Ohio
30	Old Bean Creek	Fulton	Ohio
31	Brush Creek	Fulton	Ohio
32	Tiffin River	Fulton	Ohio
33	Beaver Creek	Williams	Ohio
34	Eagle Creek	Williams	Ohio
35	Fish Creek	Stuben	Ohio
36	Big Run	Dekalb	Indiana
37	St. Joseph River	Williams	Ohio
38	Lick Creek	Williams	Ohio
39	Tiffin River	Williams	Ohio
40	Maumee River	Henry	Ohio
41	Cedar Creek	Dekalb	Indiana
42	Cairl Creek	Lucas	Ohio
43	West Fork Creek	Lucas	Ohio
44	West Fork Creek	Fulton	Ohio
45	Turkeyfoot Creek	Fulton	Ohio
46	Turkeyfoot Creek	Fulton	Ohio
47	Konzen Ditch	Fulton	Ohio
48	Kozen Ditch	Henry	Ohio

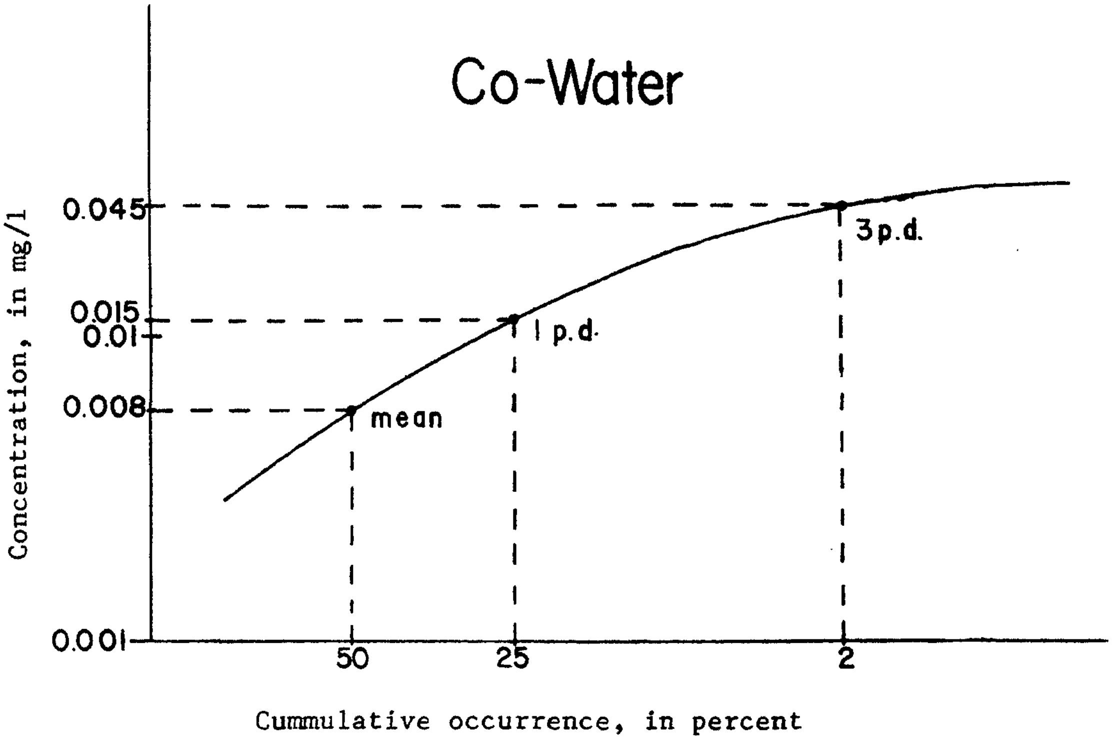
Sample No.	Stream	County	State
49	Konzen Ditch	Henry	Ohio
50	Van Hyrring	Henry	Ohio
51	Brinkman Ditch	Henry	Ohio
52	Bean Creek	Putman	Ohio
53	Yellow Creek	Putman	Ohio
54	Pusleta Creek	Auglaize	Ohio
55	Carter Creek	Auglaize	Ohio
56	Chickasaw Creek	Mercer	Ohio
57	Eightmile Creek	Mercer	Ohio
58	Twelvemile Creek	Mercer	Ohio
59	Twelvemile Creek	Mercer	Ohio
60	Twelvemile Creek	Mercer	Ohio
61	Tributary	Mercer	Ohio
62	Tributary	Mercer	Ohio
63	Little Blue Creek	Adams	Indiana
64	Blue Creek	Adams	Indiana
65	Tributary	Adams	Indiana
66	Town Creek	Van Wert	Ohio
67	Little Auglaize	Ven Wert	Ohio
68	Miami and Erie Canal	Allen	Ohio
69	Ottawa River	Allen	Ohio
70	Auglaize River	Allen	Ohio
71	Auglaize River	Allen	Ohio
72	Little Auglaize Creek	Van Wert	Ohio
73	Maddox Creek	Van Wert	Ohio
74	Hagerman Creek	Van Wert	Ohio
75	Praire Creek	Paulding	Ohio
76	Auglaize River	Paulding	Ohio
77	Auglaize River	Putnam	Ohio
78	Plum Creek	Putnam	Ohio
79	Cranberry Creek	Putnam	Ohio
80	Pike Run	Putnam	Ohio
81	East Beaver Creek	Henry	Ohio
82	Maumee River	Defiance	Ohio
83	Marte De Larme Creek	Paulding	Ohio
84	Maumee River	Allen	Indiana
85	Lost Creek	Defiance	Ohio
86		Allen	Indiana
87	Cedar Creek	Allen	Indiana
88	St. Joseph River	Allen	Indiana
89	St. Joseph River	Allen	Indiana
90	St. Joseph River	Dekalb	Indiana
91	Beaver Creek	Williams	Ohio
92	Beaver Creek	Williams	Ohio
93	Brush Creek	Williams	Ohio
94	Mud Creek	Defiance	Ohio
95	Lick Creek	Defiance	Ohio
96	Little Lick Creek	Defiance	Ohio
97	Little Lick Creek	Defiance	Ohio
98	Lick Creek	Williams	Ohio
99	Beaver Creek	Williams	Ohio
100	Leatherwood Creek	Williams	Ohio

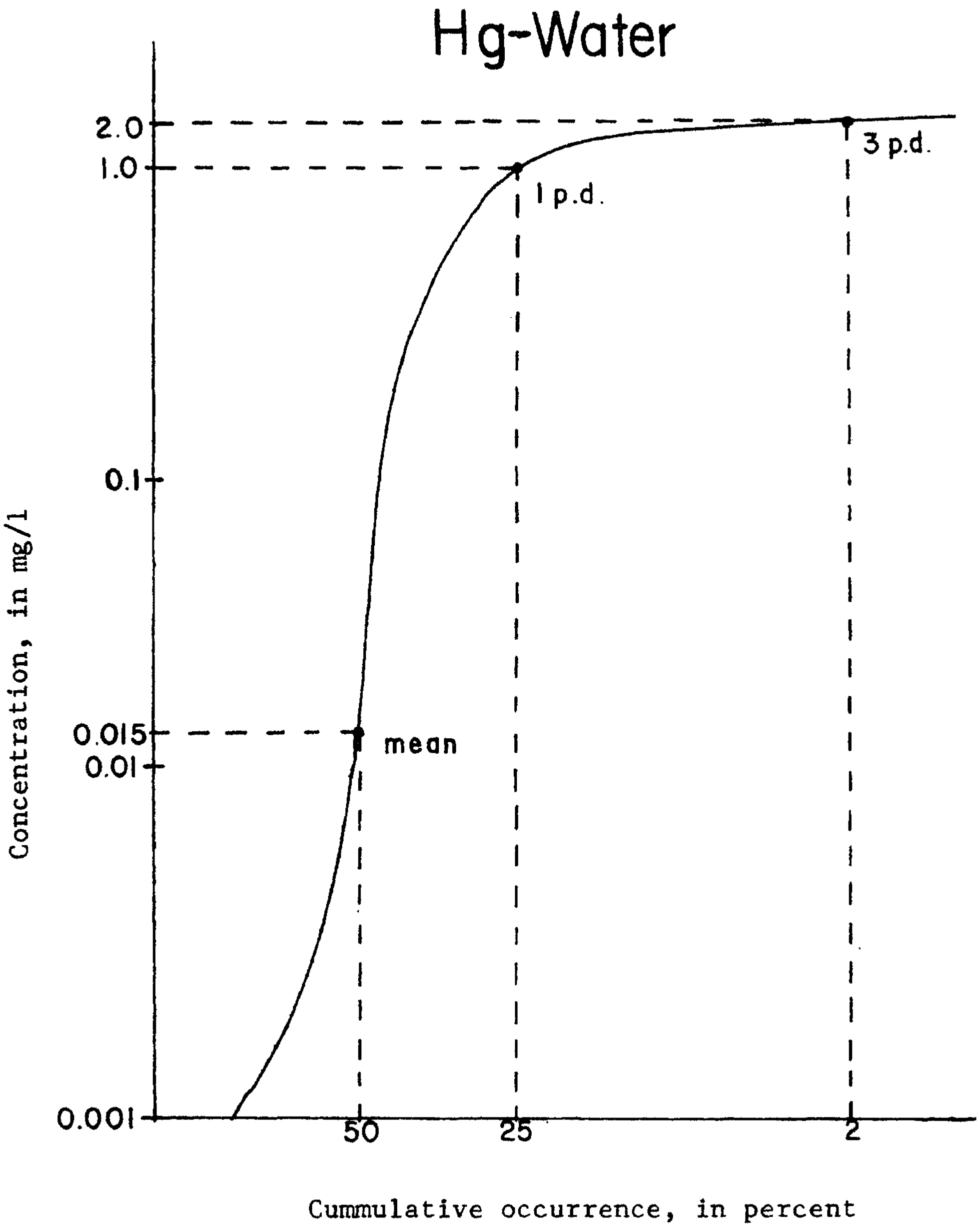
Sample No.	Stream	County	State
101	Tiffin River	Williams	Ohio
102	Garrett Creek	Henry	Ohio
103	Maumee River	Henry	Ohio
104	Maumee River	Lucas	Ohio
105	South Turkeyfoot Creek	Henry	Ohio
106	South Turkeyfoot Creek	Henry	Ohio
107	West Creek	Henry	Ohio
108	South Turkeyfoot Creek	Henry	Ohio
109	East Beaver Creek	Henry	Ohio
110	Little Cedar Creek	Dekalb	Indiana
111	Beaver Creek	Lucas	Ohio
112	Maumee River	Lucas	Ohio
113	Maumee River	Lucas	Ohio
114	Auglaize River	Auglaize	Ohio
115	Auglaize River	Auglaize	Ohio
116	St. Marys River	Auglaize	Ohio
117	St. Marys River	Mercer	Ohio
118	St. Marys River	Adams	Indiana
119	St. Marys River	Allen	Indiana
120	Maumee River	Allen	Indiana
121	St. Joseph River	Allen	Indiana
122	Maumee River	Allen	Indiana
123	Flatrock Creek	Paulding	Ohio
124	Flatrock Creek	Paulding	Ohio
125	Maumee River	Defiance	Ohio
126	Maumee River	Henry	Ohio
127	Turkeyfoot Creek	Henry	Ohio
128	South Swan Creek	Lucas	Ohio
129	Maumee River	Lucas	Ohio
130	Ottawa River	Allen	Ohio
131	Ottawa River	Allen	Ohio
132	Ottawa River	Allen	Ohio
133	Lye Creek	Hancock	Ohio
134	Blanchard River	Hancock	Ohio
135	Blanchard River	Hancock	Ohio
136	Town Creek	Van Wert	Ohio
137		Allen	Indiana
138	John Diehl Ditch	Dekalb	Indiana
139	Fish Creek	Dekalb	Indiana
140	St. Joseph River	Williams	Ohio
141	The Outlet	Hancock	Ohio
142	The Outlet	Hancock	Ohio
143	The Outlet	Hancock	Ohio
144	The Outlet	Hancock	Ohio
145	Blanchard River	Hancock	Ohio
146	Blanchard River	Hancock	Ohio
147	Blanchard River	Hancock	Ohio
148	Blanchard River	Hancock	Ohio
149	Blanchard River	Hancock	Ohio
150	Eagle Creek	Hancock	Ohio
151	Blanchard River	Hancock	Ohio
152	Blanchard River	Hancock	Ohio

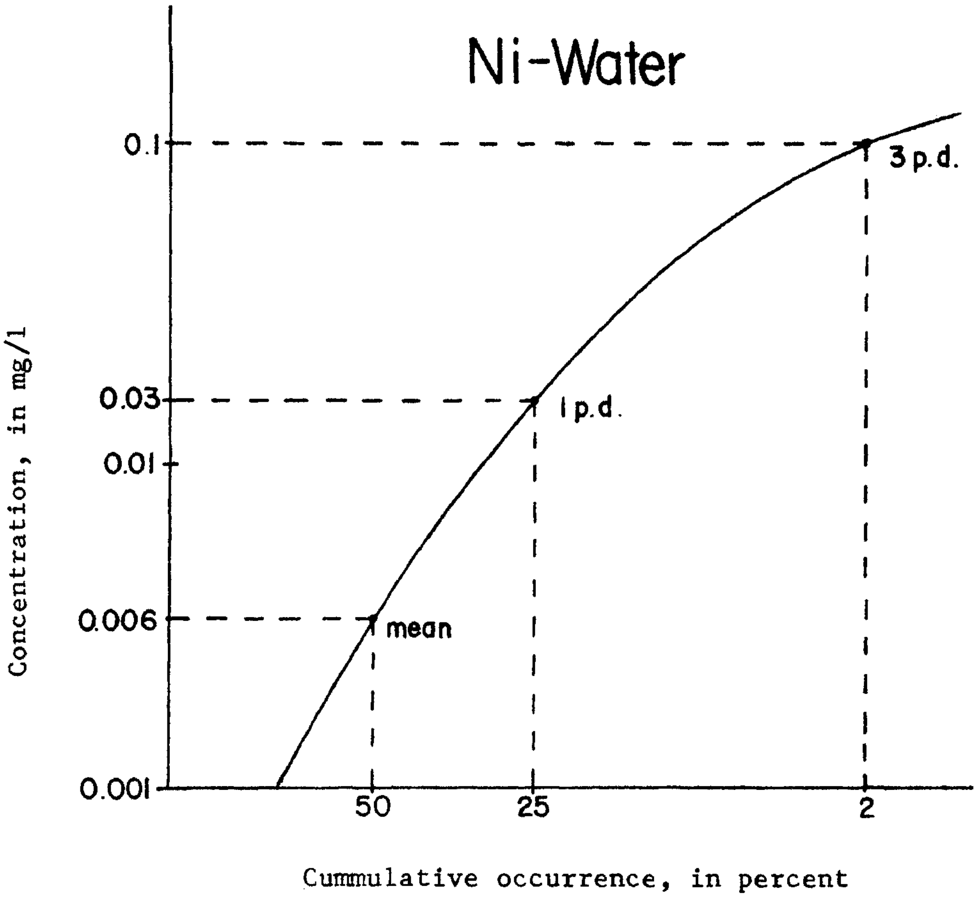
Sample No.	Stream	County	State
153	Oil Ditch	Hancock	Ohio
154	Avrand Run	Hancock	Ohio
155	Ottawa Creek	Hancock	Ohio
156	Blanchard River	Hancock	Ohio
157	Moffit Ditch	Hancock	Ohio
158	Ottawa Creek	Hancock	Ohio
159	Marsh Run	Hancock	Ohio
160		Hancock	Ohio
161	Ottawa Creek	Hancock	Ohio
162	Ottawa Creek	Hancock	Ohio
163	Eagle Creek	Hancock	Ohio
164	Eagle Creek	Hancock	Ohio
165	Buck Run	Hancock	Ohio
166	Jenera Creek	Hancock	Ohio
167	Blanchard River	Hancock	Ohio
168	Blanchard River	Hancock	Ohio
169	Blanchard River	Hancock	Ohio
170	Blanchard River	Hancock	Ohio
171	Stall Ditch	Hancock	Ohio
172	Stall Ditch	Hancock	Ohio
173	Potato Run	Hancock	Ohio
174	The Outlet	Hardin	Ohio
175	Blanchard River	Hardin	Ohio
176	Blanchard Tributary	Hancock	Ohio
177	Blanchard River	Hancock	Ohio
178	Blanchard Tributary	Hardin	Ohio
179	Blanchard River	Hardin	Ohio
180	Blanchard River	Hardin	Ohio
181	Blanchard River	Hardin	Ohio
182	Hog Creek Ditch	Hardin	Ohio
183	Eagle Creek	Hancock	Ohio
184	Flatbranch	Hancock	Ohio
185	Rily Creek	Hancock	Ohio
186	Hog Creek	Hardin	Ohio
187	Grass Creek	Hardin	Ohio
188	Cessna Creek	Hardin	Ohio
189	Tributary	Hardin	Ohio
190	Auglaize River	Allen	Ohio
191	The Tributary	Allen	Ohio
192	Lost Creek	Allen	Ohio
193	Lost Creek	Allen	Ohio
194	Auglaize River	Allen	Ohio
195	Ottawa River	Allen	Ohio
196	Little Cranberry	Allen	Ohio
197	Rattlesnake Creek	Allen	Ohio
198	Sugar Creek	Allen	Ohio
199	Auglaize River	Paulding	Ohio
200	Auglaize River	Defiance	Ohio
201	Tiffin River	Defiance	Ohio
202	Maumee River	Defiance	Ohio
203	Maumee River	Defiance	Ohio
204	Maumee River	Degiance	Ohio

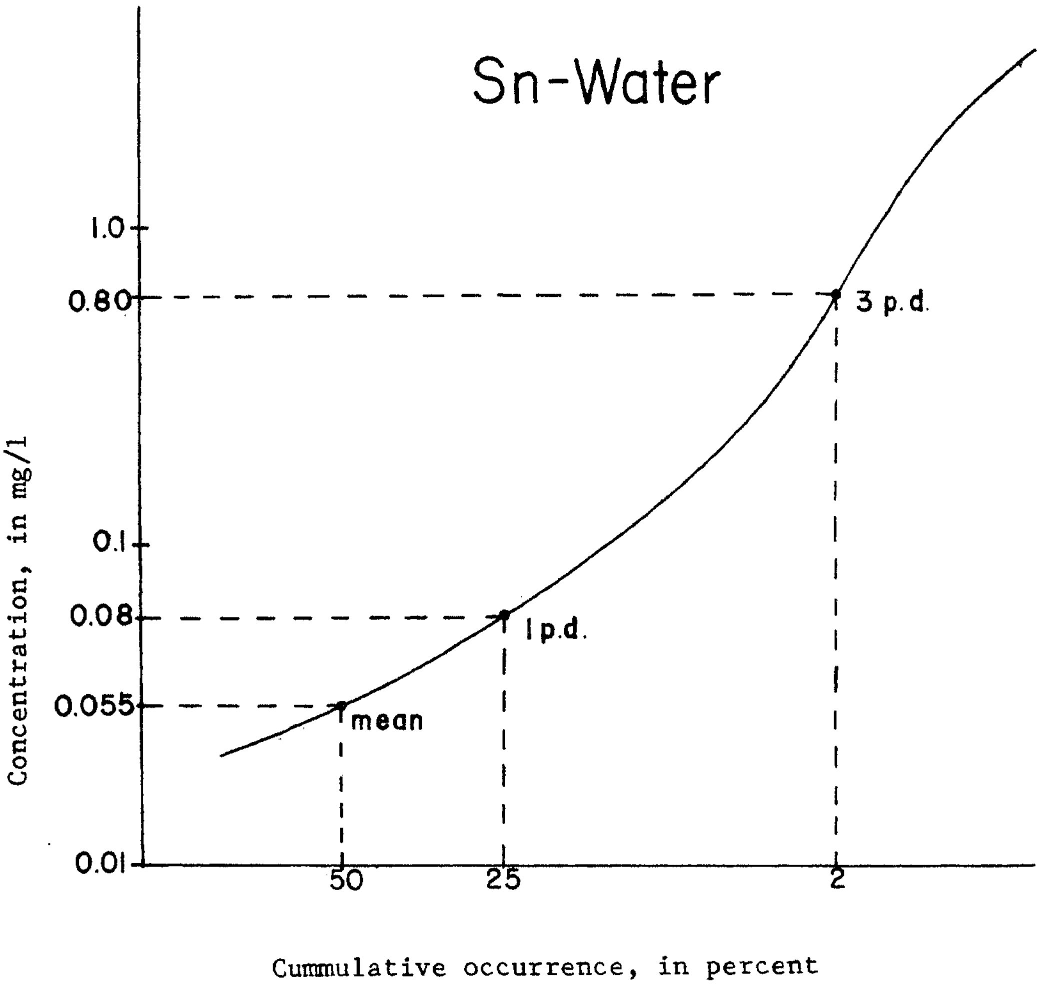
205	Mud Creek	Defiance	Ohio
206	Powell Creek	Defiance	Ohio
207	Flat Rock Creek	Paulding	Ohio
208	Flat Rock Creek	Allen	Indiana
209	Flat Rock Creek	Paulding	Ohio
210	Flat Rock Creek	Allen	Indiana
211	Flat Rock Creek	Allen	Indiana
212	Flat Rock Creek	Van Wert	Ohio
213	St. Marys River	Adams	Indiana
214	Blue Creek	Adams	Indiana
215	St. Marys River	Van Wert	Ohio
216	Duck Creek	Mercer	Ohio
217	Blue Creek	Adams	Indiana
218	Maumee River	Allen	Indiana
219	Maumee River	Allen	Indiana
220	St. Joseph River	Allen	Indiana
221	St. Joseph River	Allen	Indiana
222	St. Marys River	Allen	Indiana
223	St. Marys River	Allen	Indiana
224	St. Marys River	Adams	Ohio
225	St. Marys River	Adams	Ohio

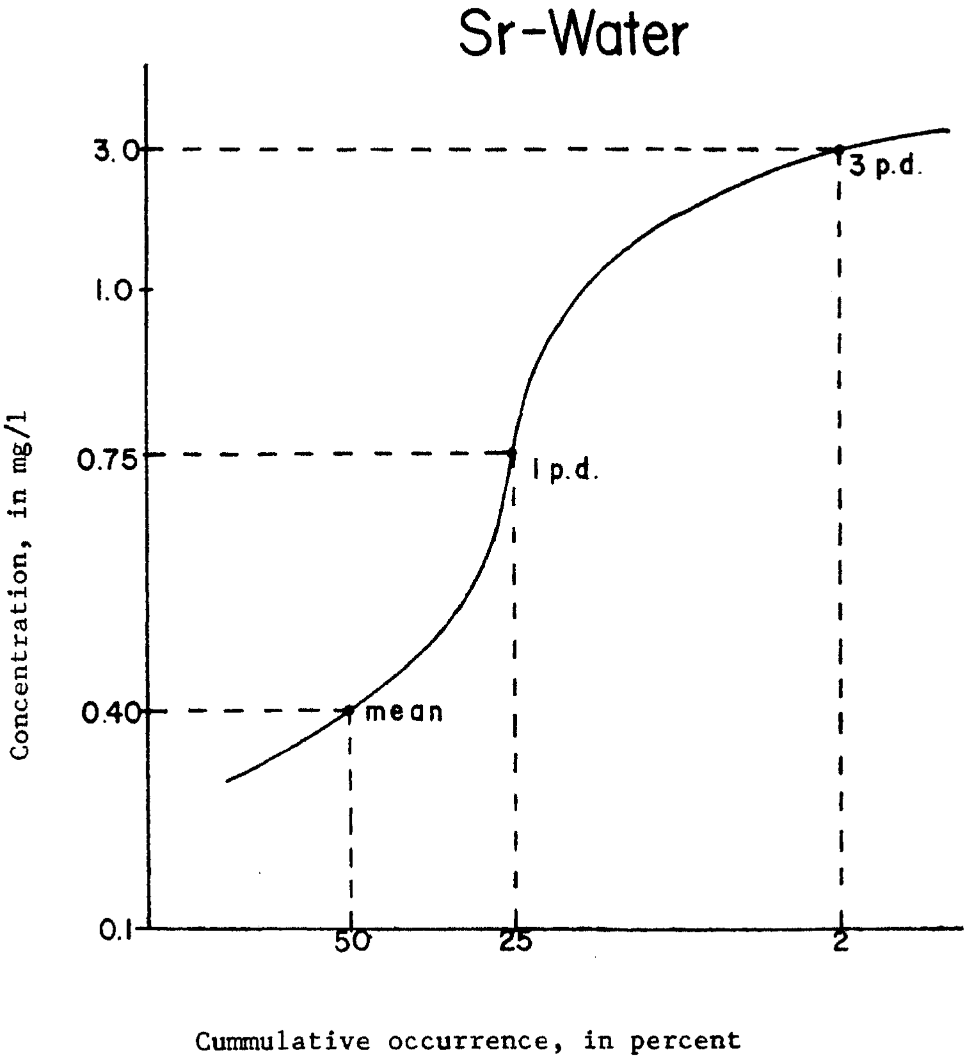

Al-Water
1.0
0.80
0.1
0.080
0.01
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/1
Cummulative occurrence, in percent


Co-Water
Concentration, in mg/l
0.045
0.015
0.01
0.008
0.001
3 p.d.
1 p.d.
mean
50
25
2
Cummulative occurrence, in percent

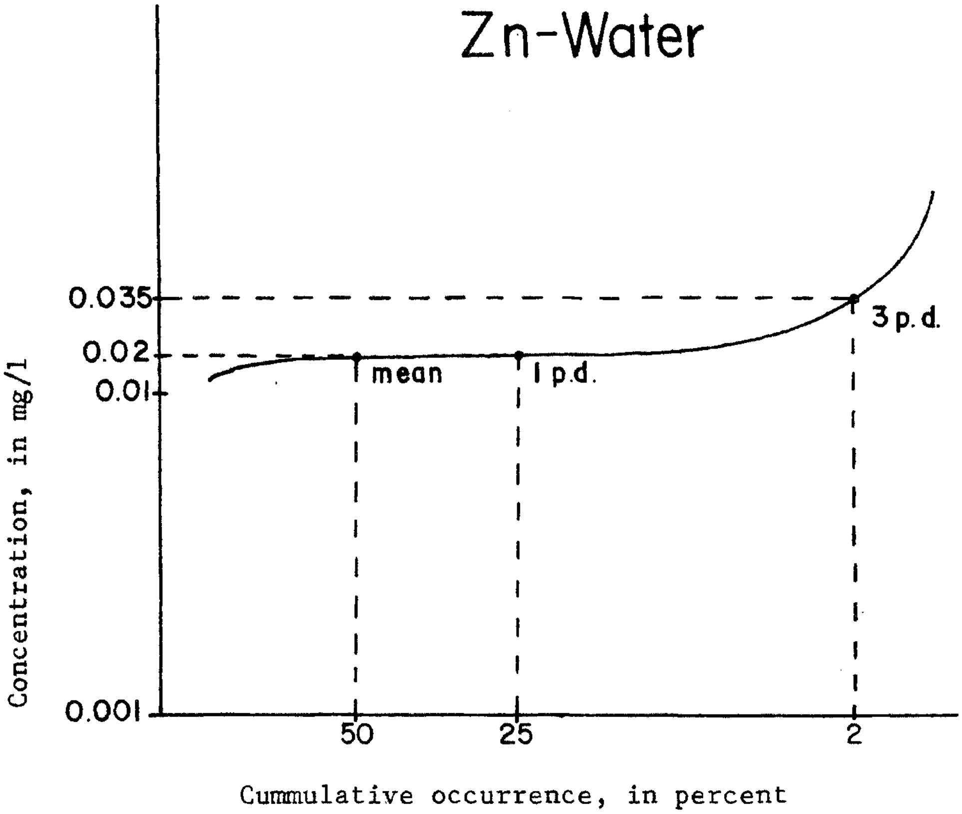

Hg-Water
2.0
1.0
0.1
0.015
0.01
0.001
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/l
Cummulative occurrence, in percent

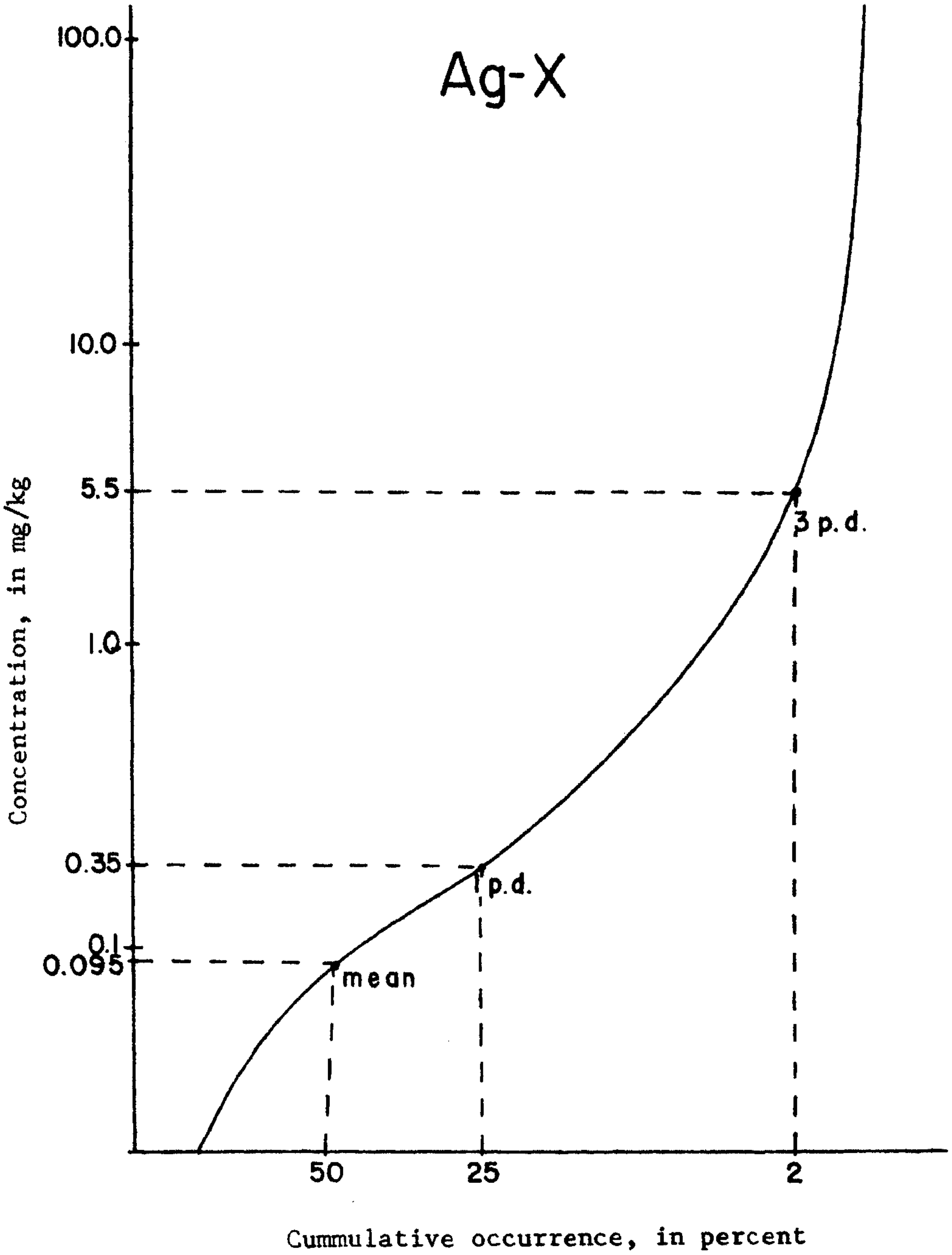

Ni-Water
0.1
0.03
0.01
0.006
0.001
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/1
Cummulative occurrence, in percent

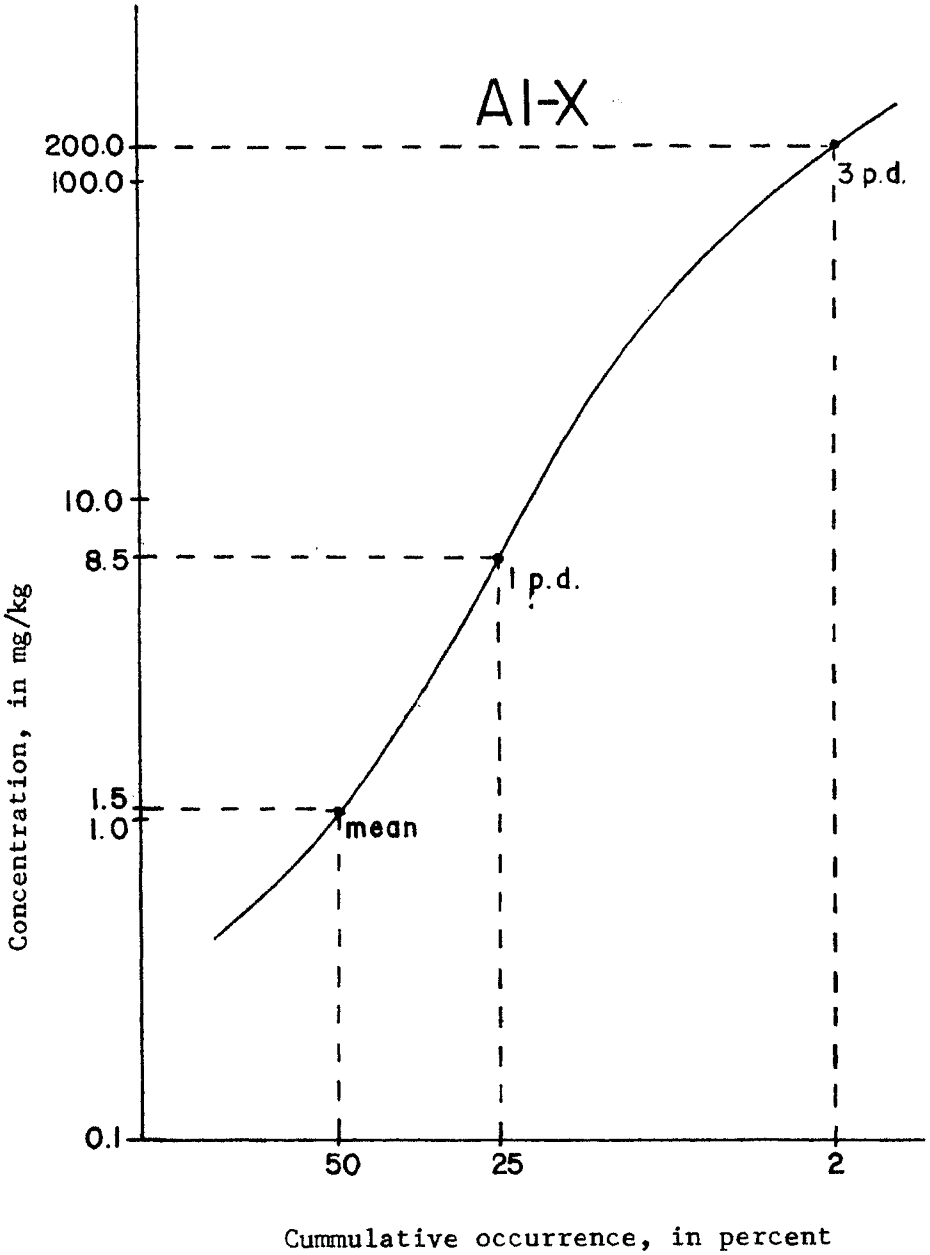
Sn-Water
1.0
0.80
0.1
0.08
0.055
0.01
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/l
Cummulative occurrence, in percent

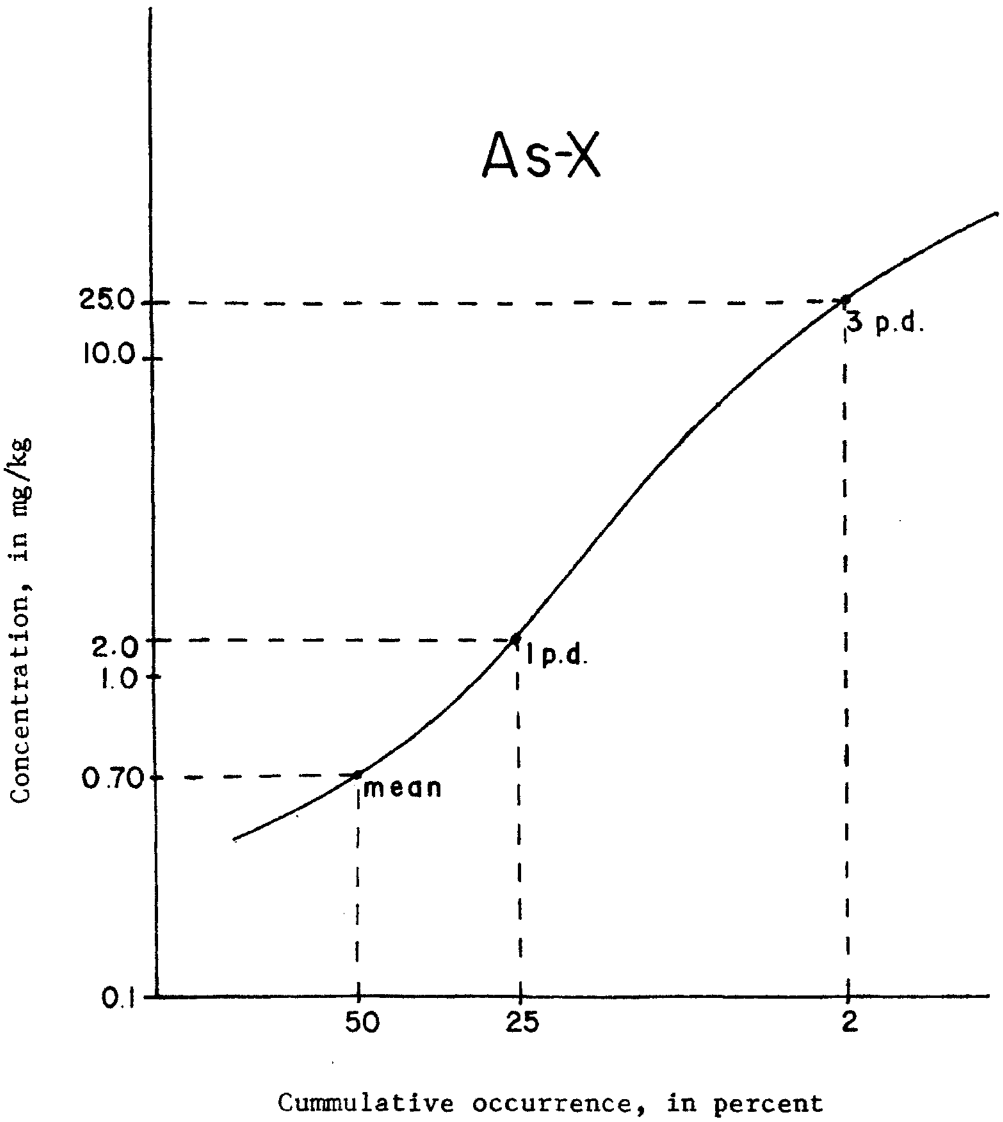


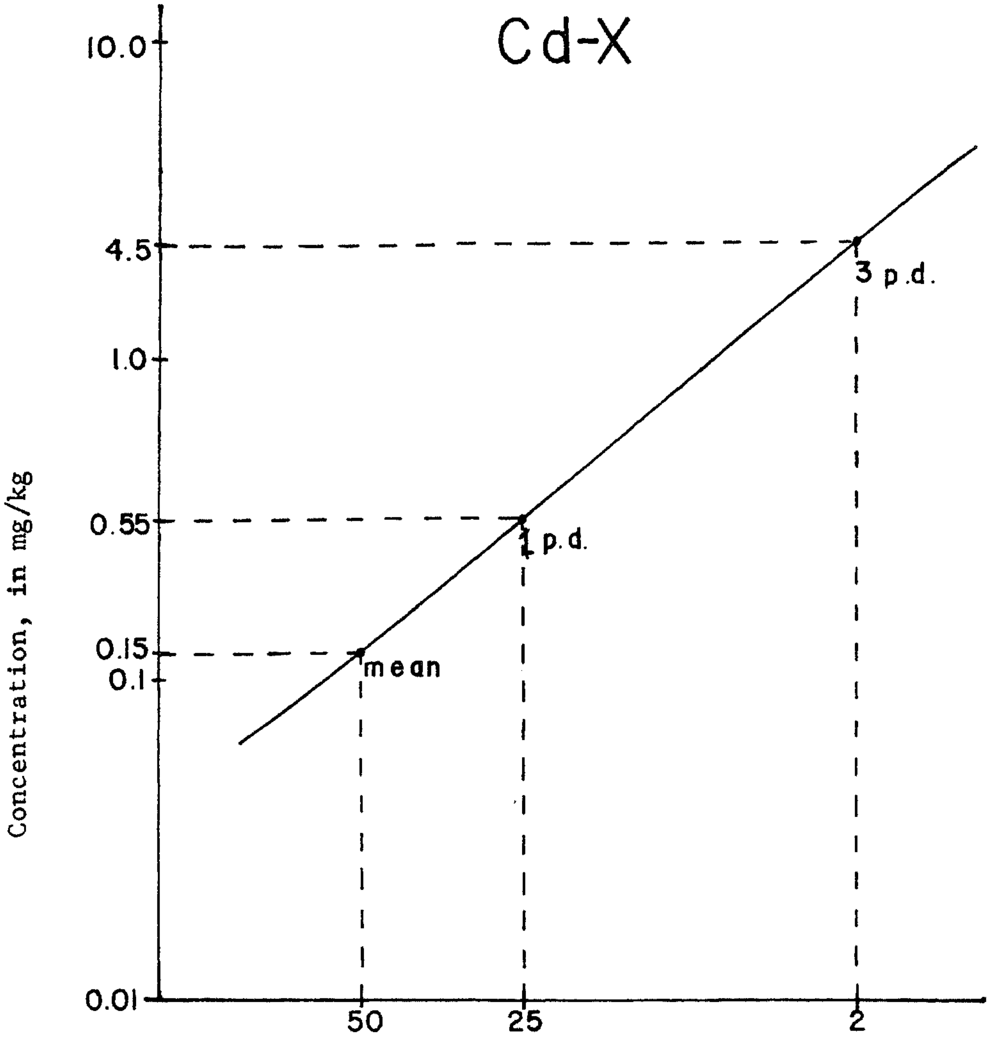
Sr-Water
3.0
1.0
0.75
0.40
0.1
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/l
Cummulative occurrence, in percent


Zn-Water
0.035
0.02
0.01
0.001
mean
1 p.d.
3 p.d.
50
25
2
Concentration, in mg/l
Cummulative occurrence, in percent

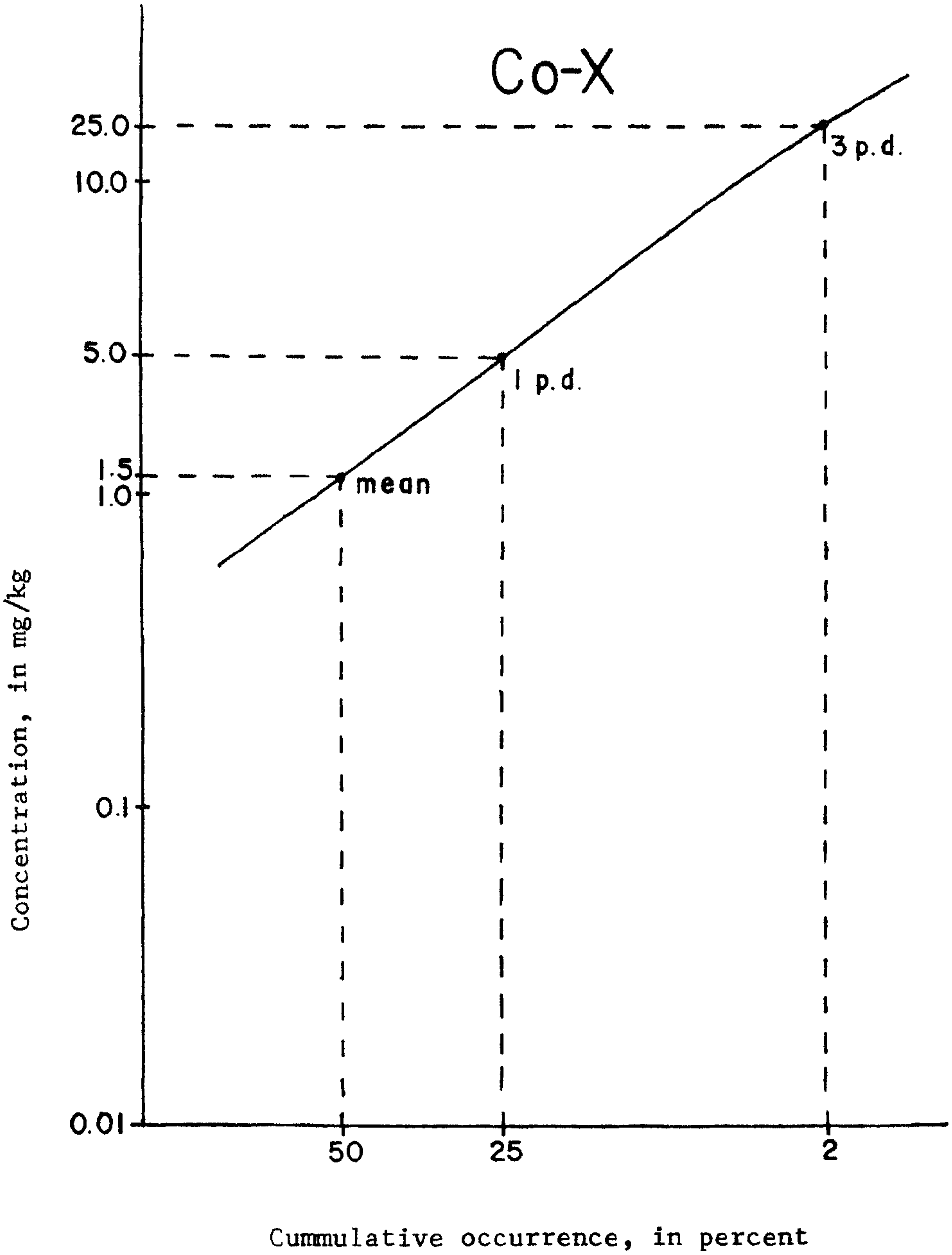

Ag-X
100.0
10.0
5.5
1.0
0.35
0.1
0.095
mean
p.d.
3 p.d.
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

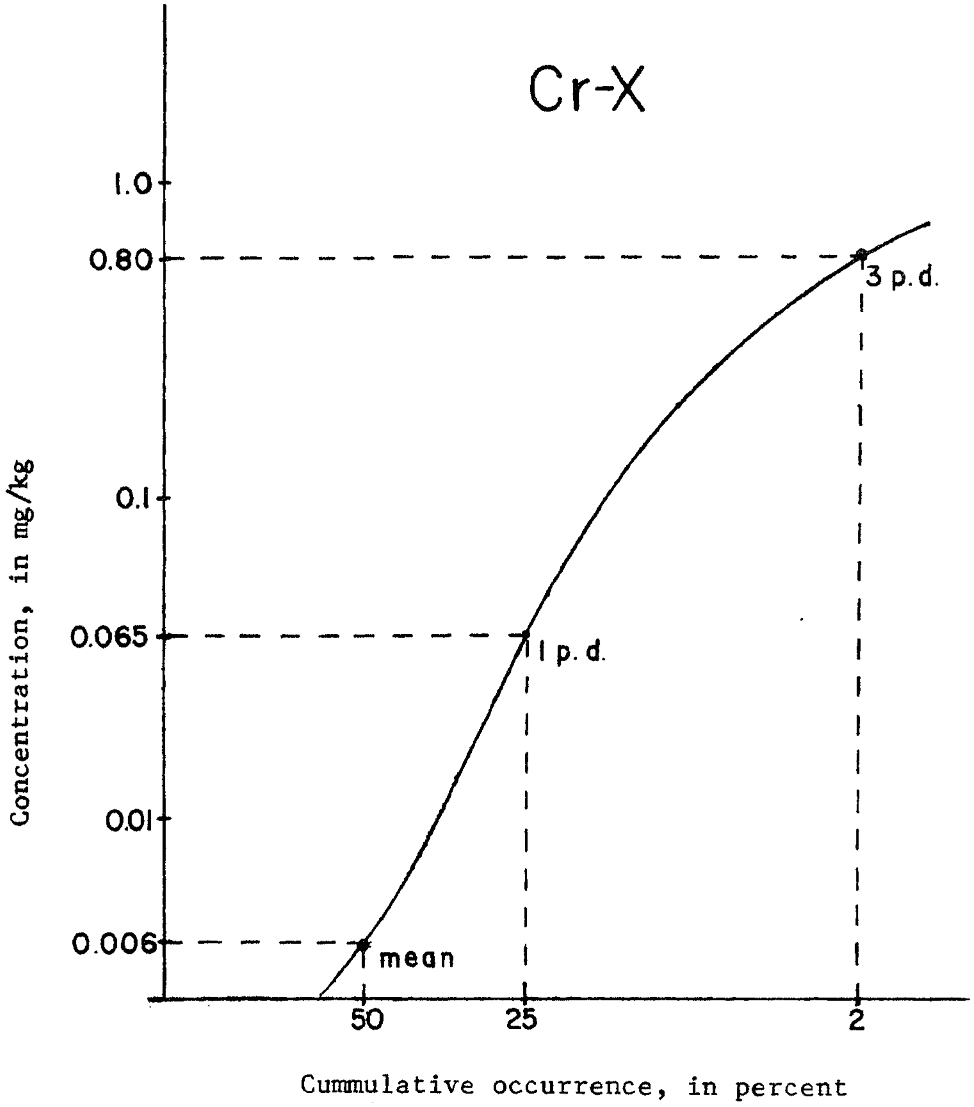

Al-X
200.0
100.0
10.0
8.5
1.5
1.0
0.1
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

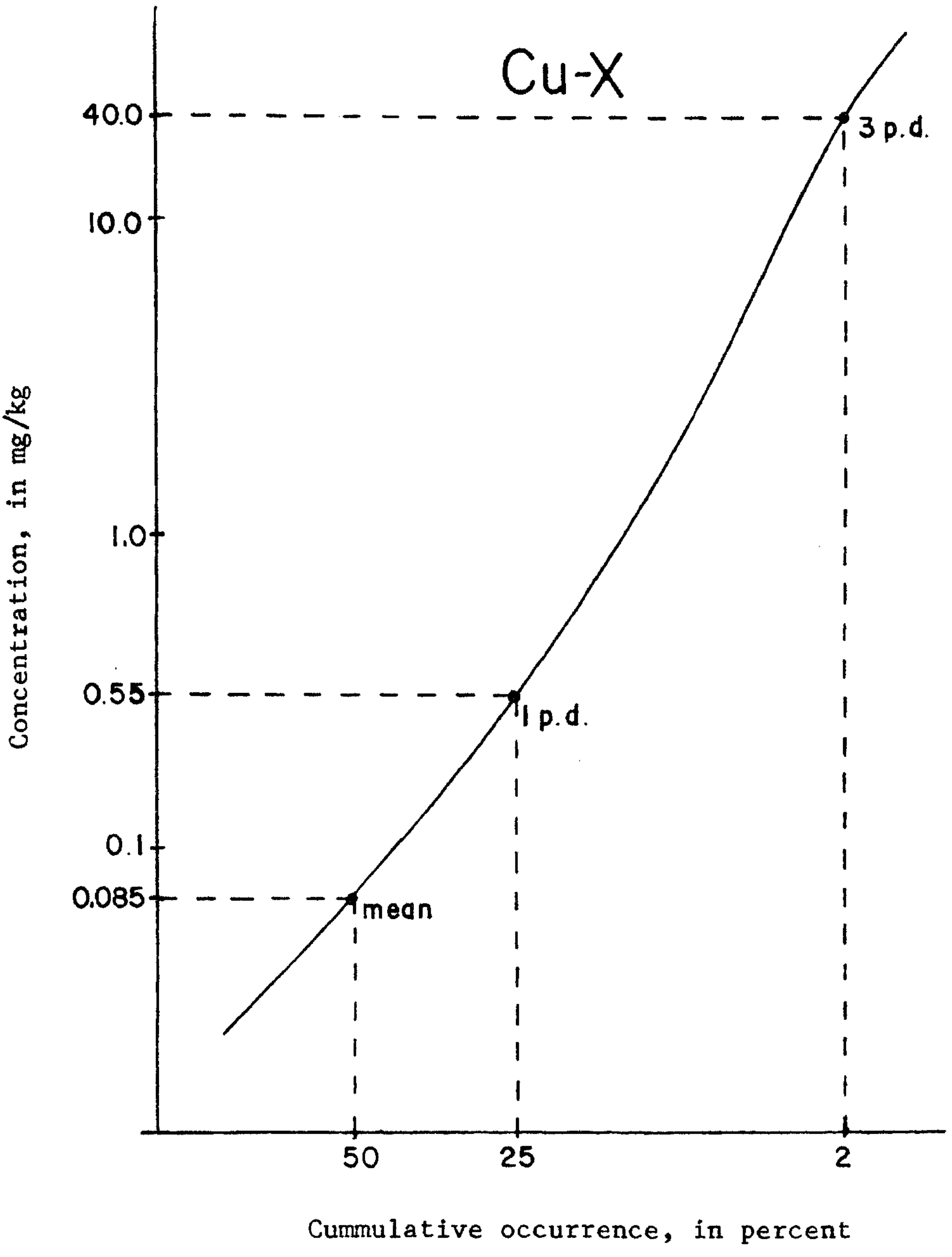

As-X
25.0
10.0
2.0
1.0
0.70
0.1
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

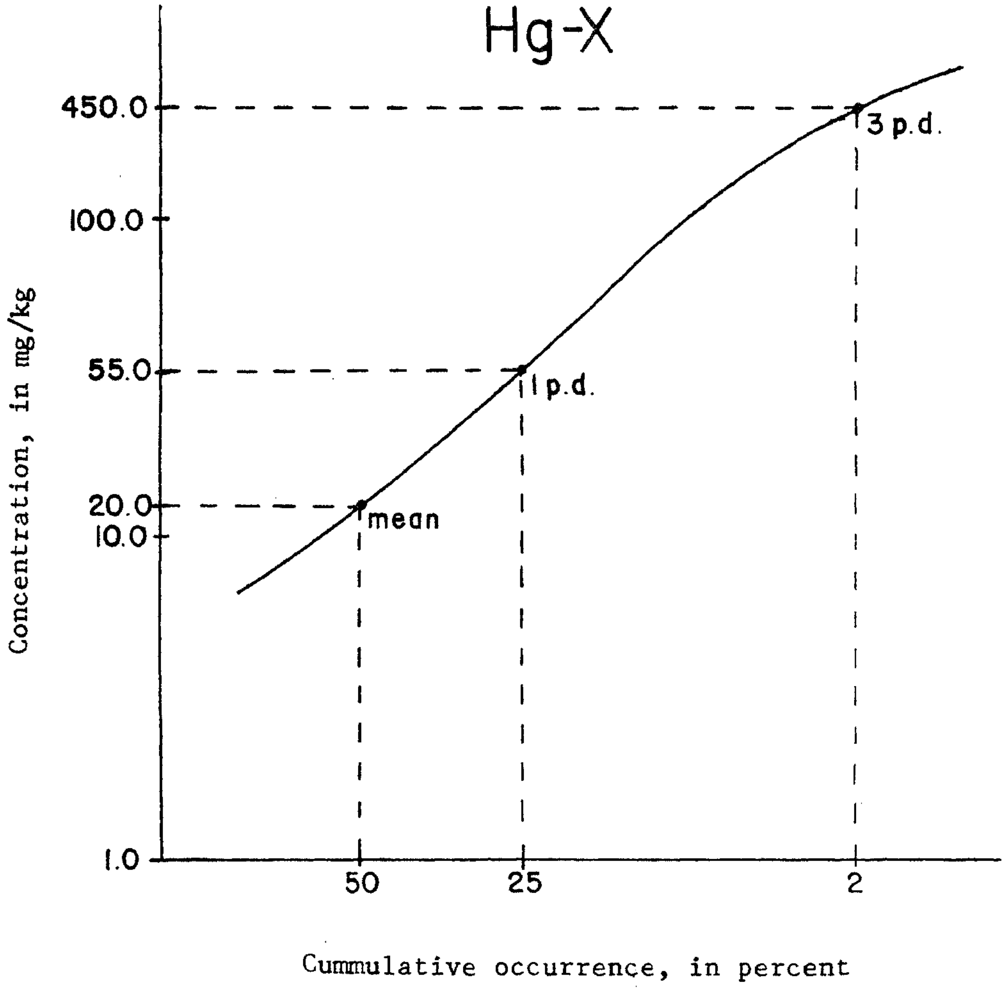


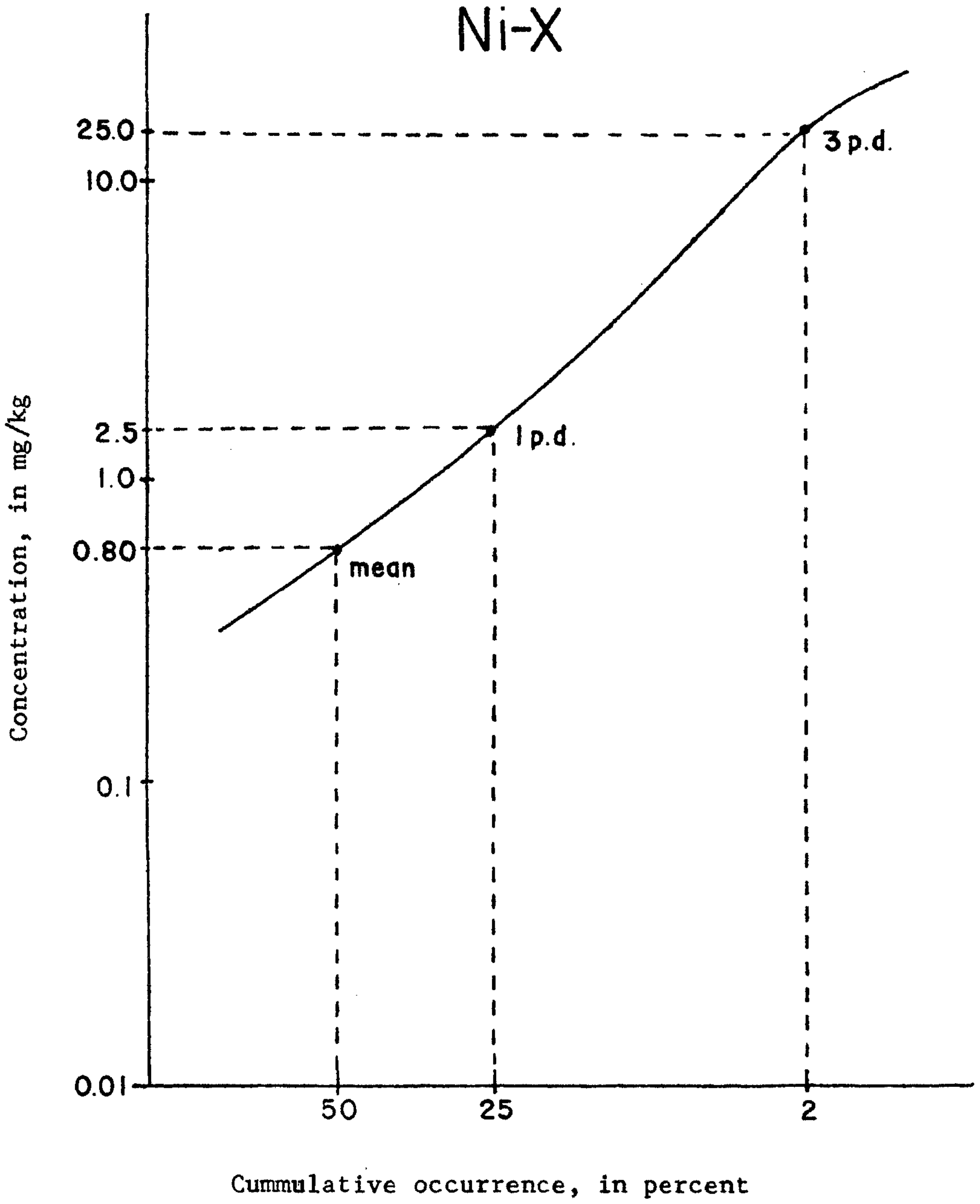
Cummulative occurrence, in percent

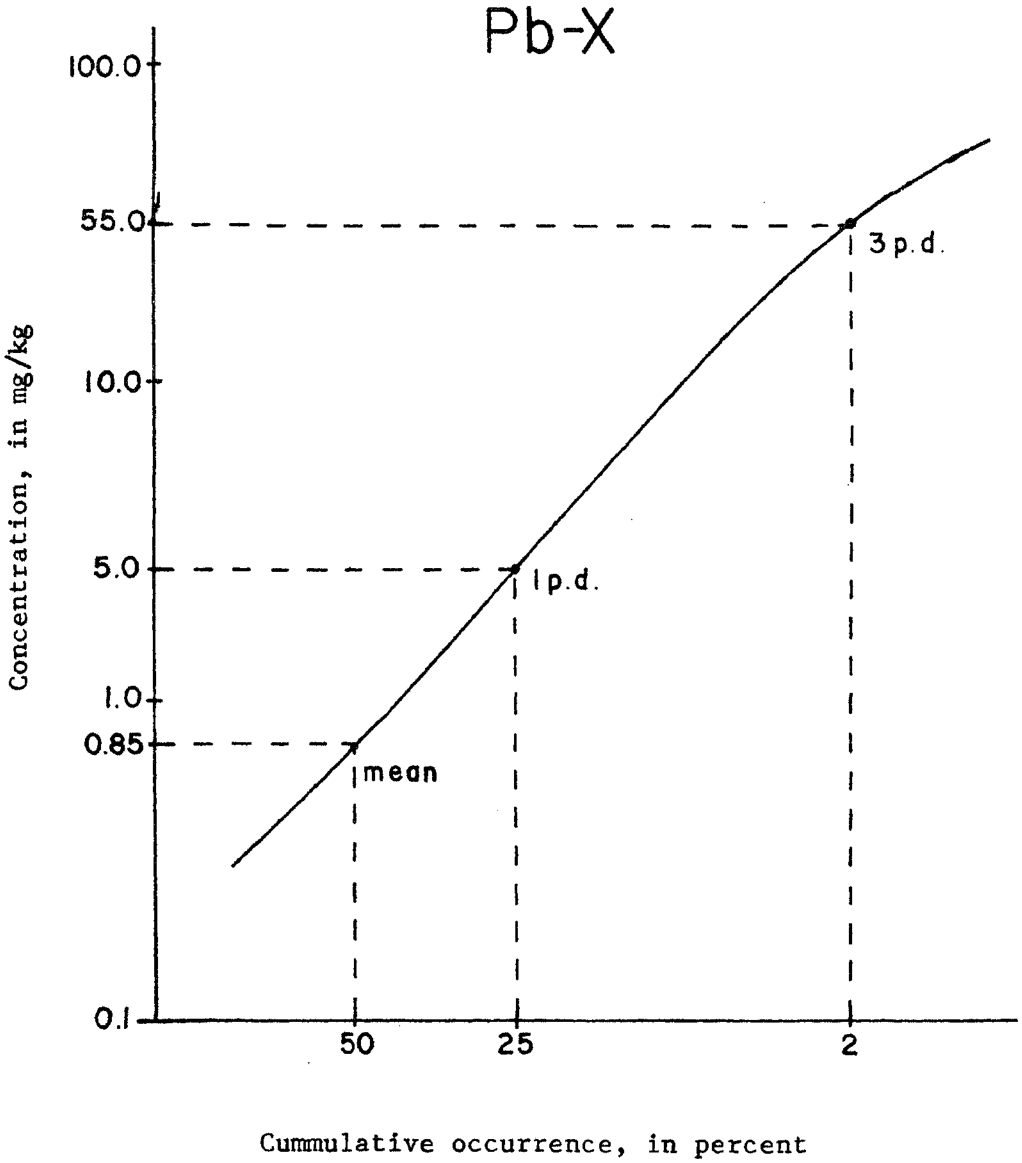

Co-X
25.0
10.0
5.0
1.5
1.0
0.1
0.01
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

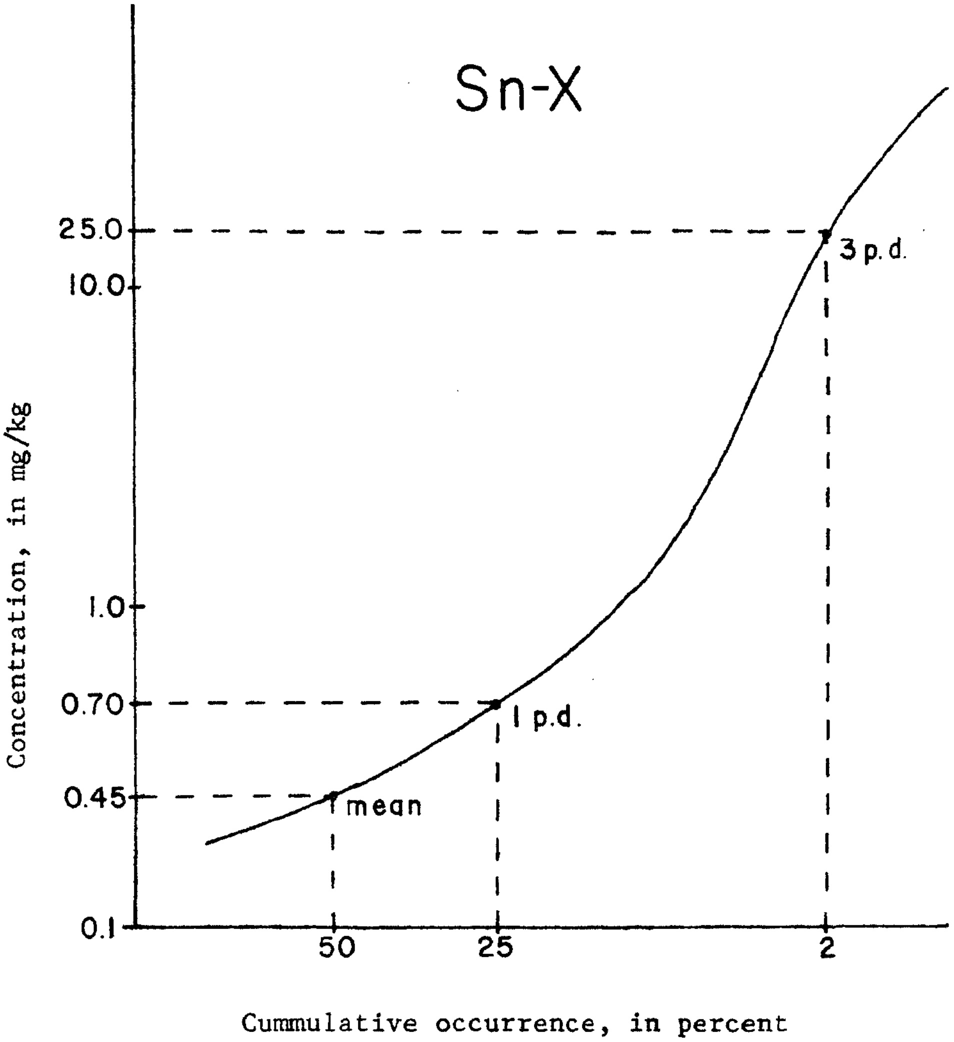

Cr-X
1.0
0.80
0.1
0.065
0.01
0.006
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

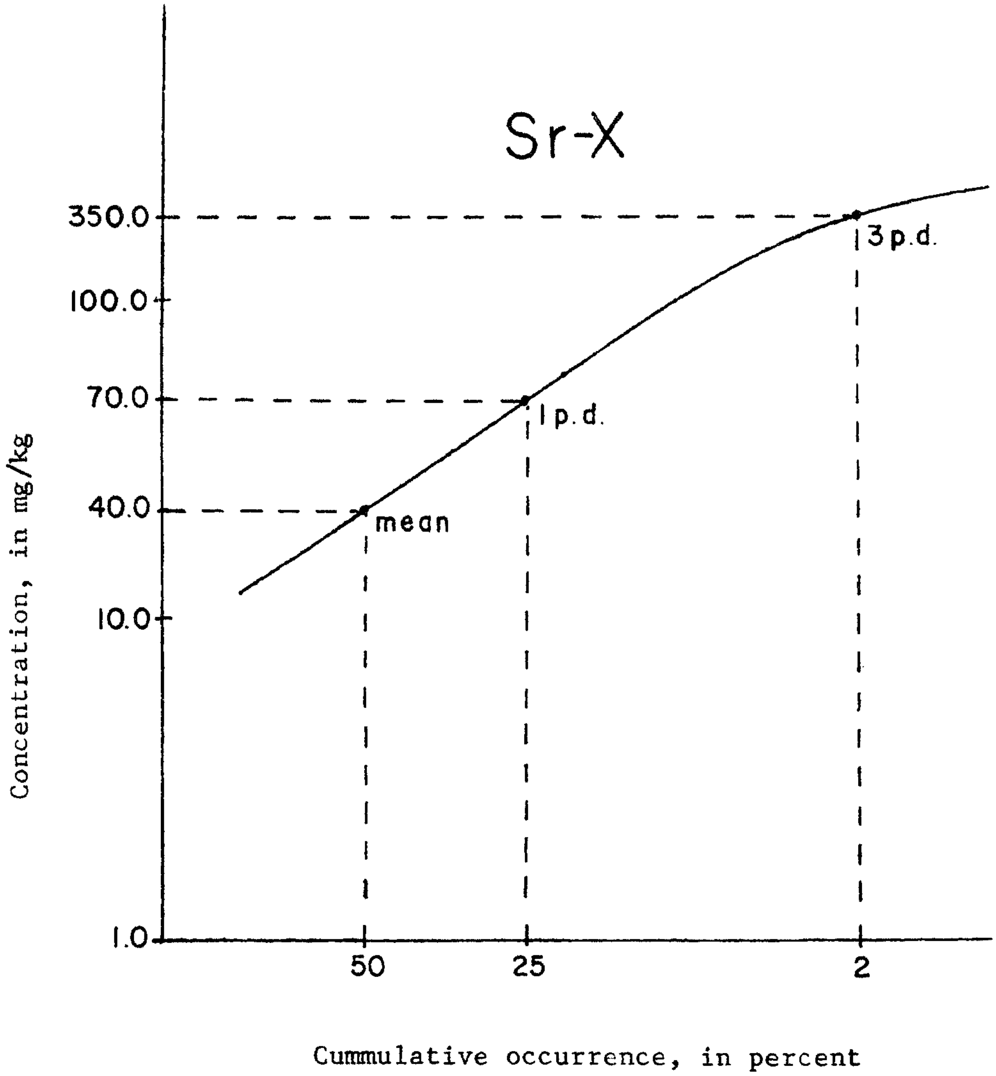

Cu-X
40.0
10.0
1.0
0.55
0.1
0.085
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

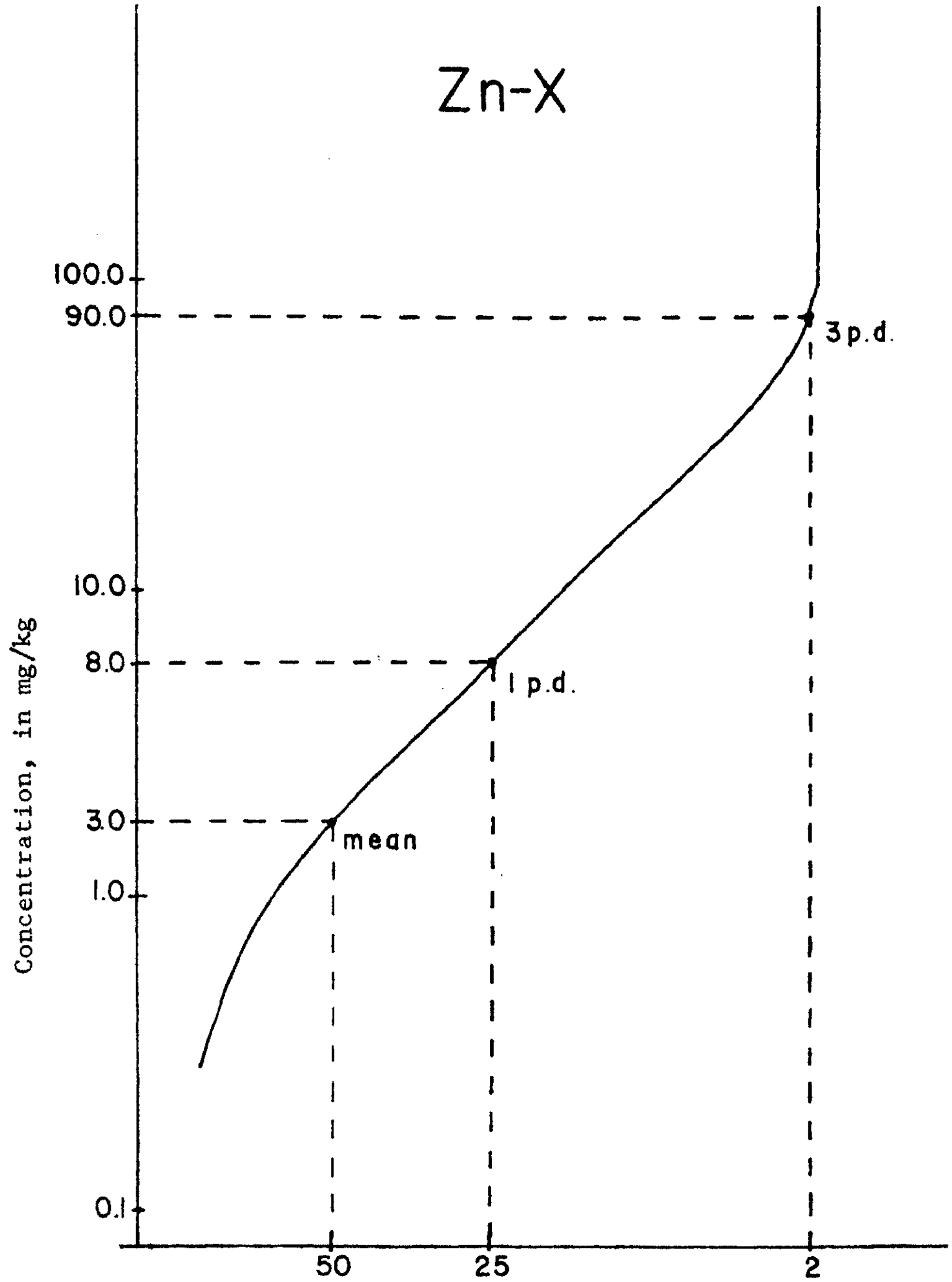

Hg-X
450.0
100.0
55.0
20.0
10.0
1.0
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent


Ni-X
25.0
10.0
2.5
1.0
0.80
0.1
0.01
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

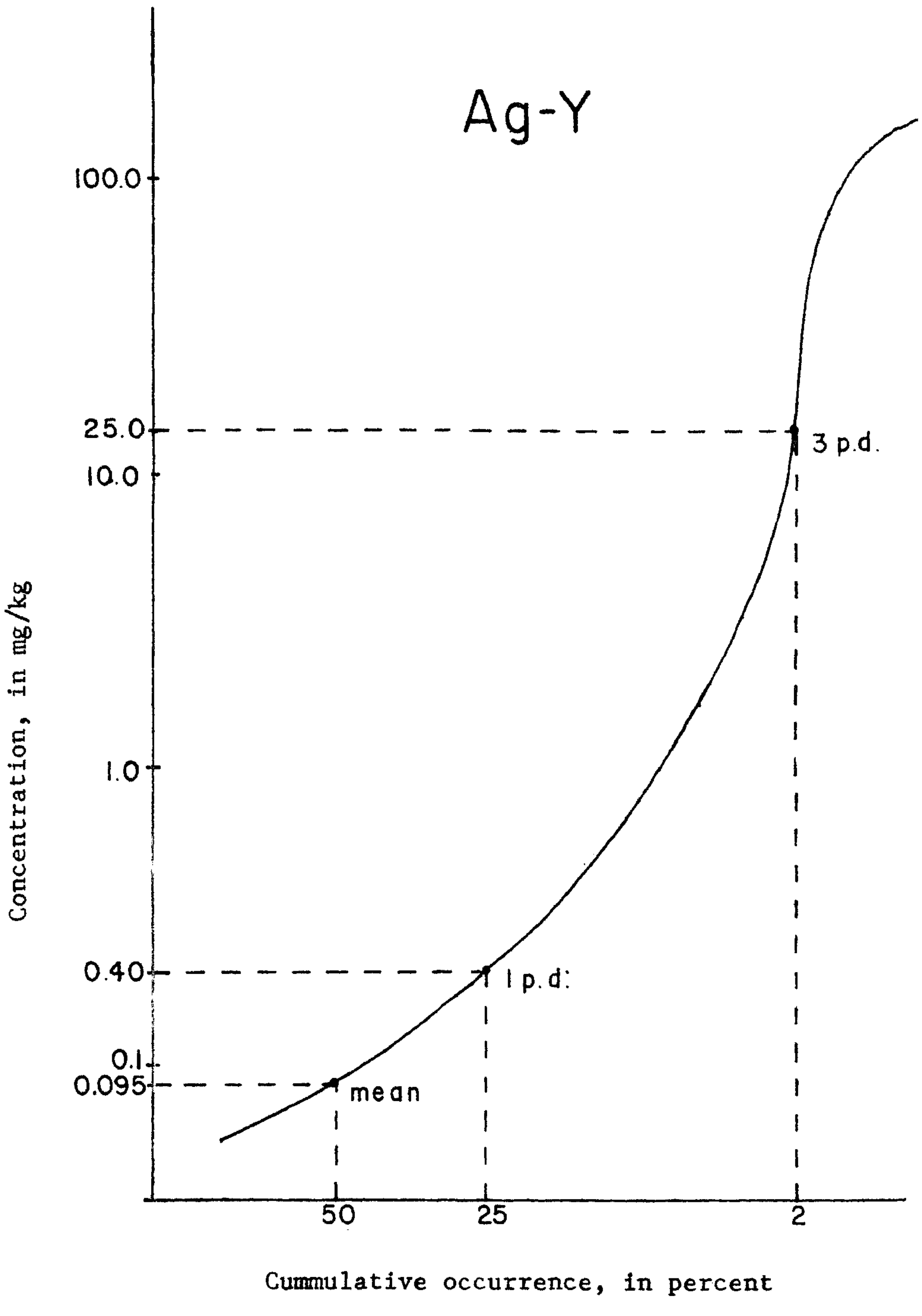

Pb-X
100.0
55.0
10.0
5.0
1.0
0.85
0.1
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent


Sn-X
25.0
10.0
1.0
0.70
0.45
0.1
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

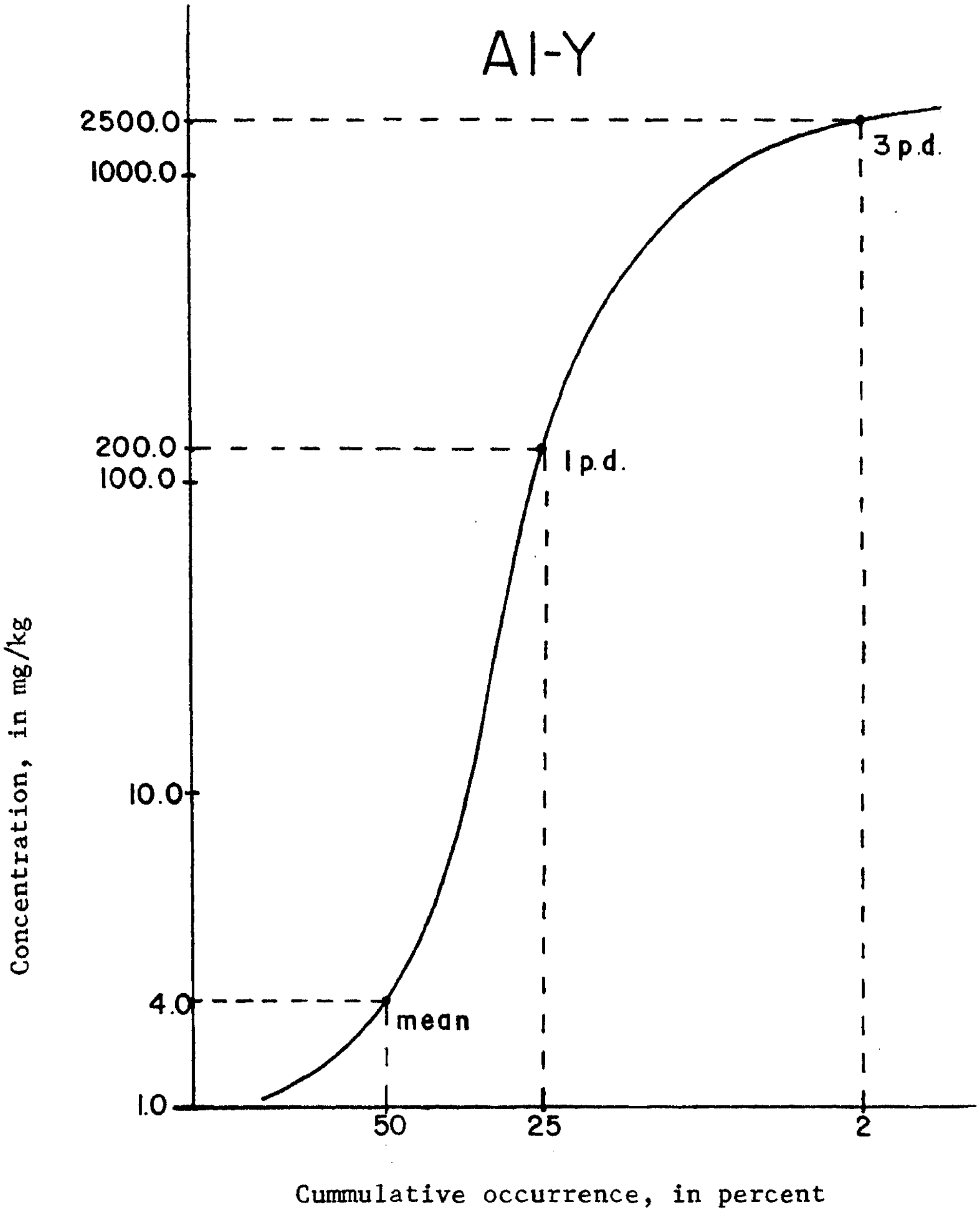

Sr-X
350.0
100.0
70.0
40.0
10.0
1.0
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

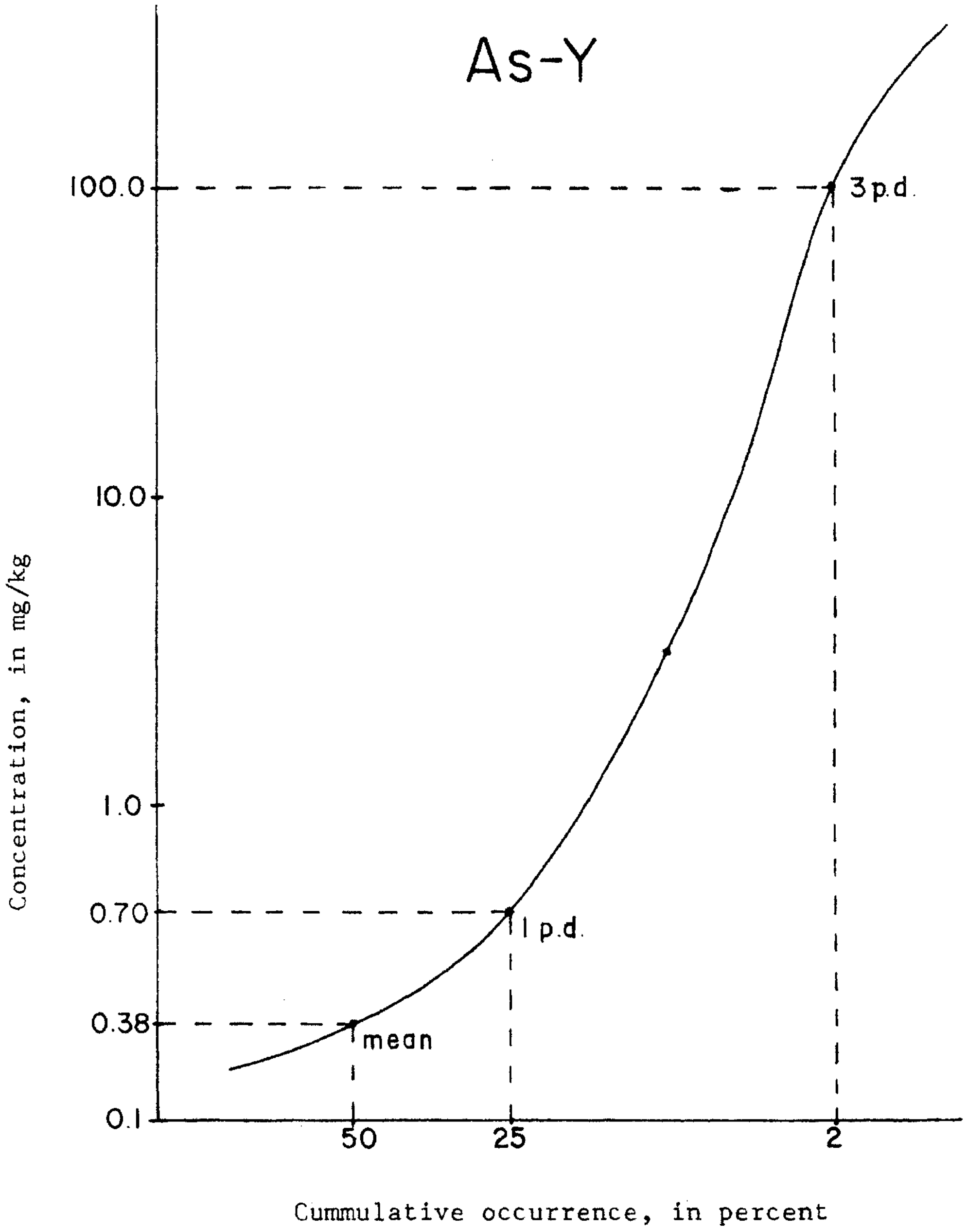


Cummulative occurrence, in percent

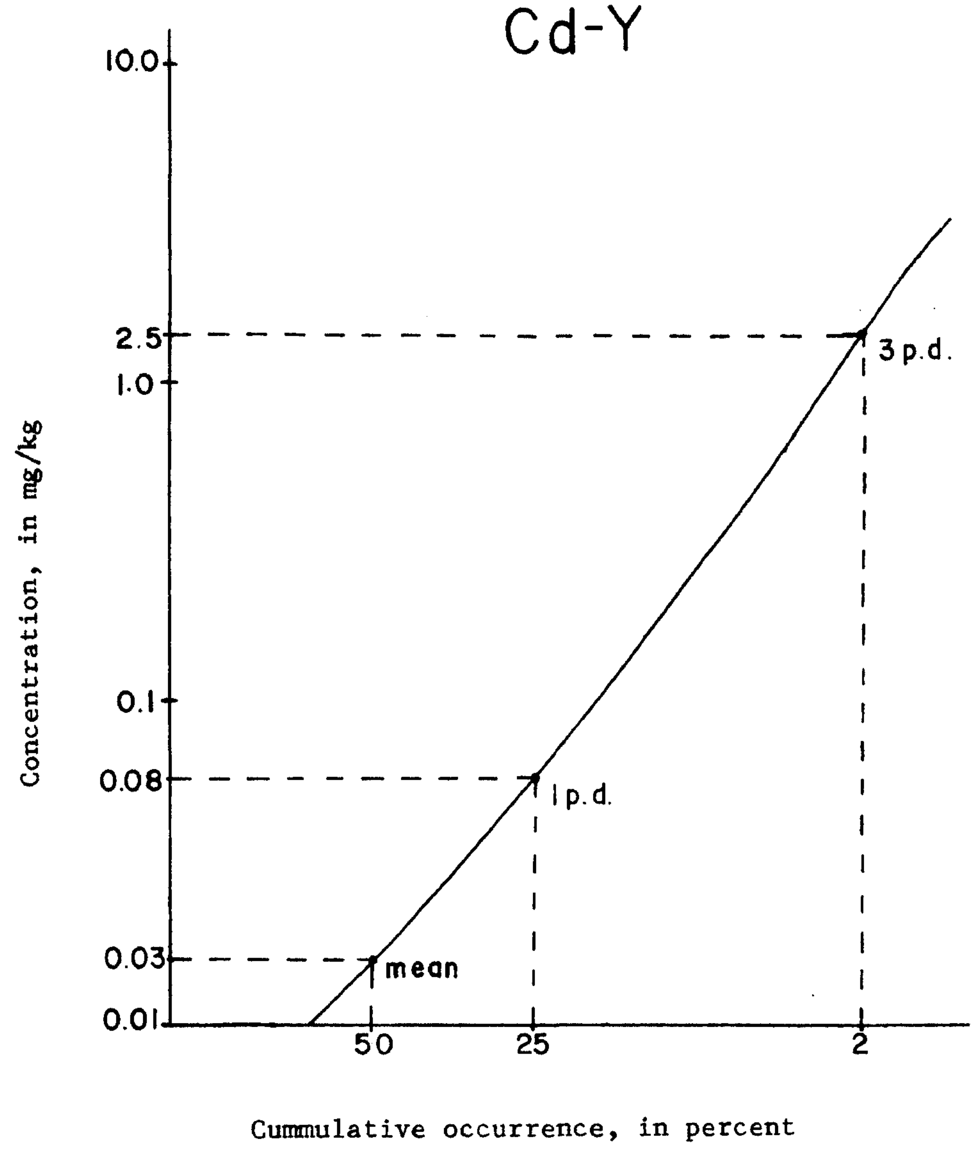


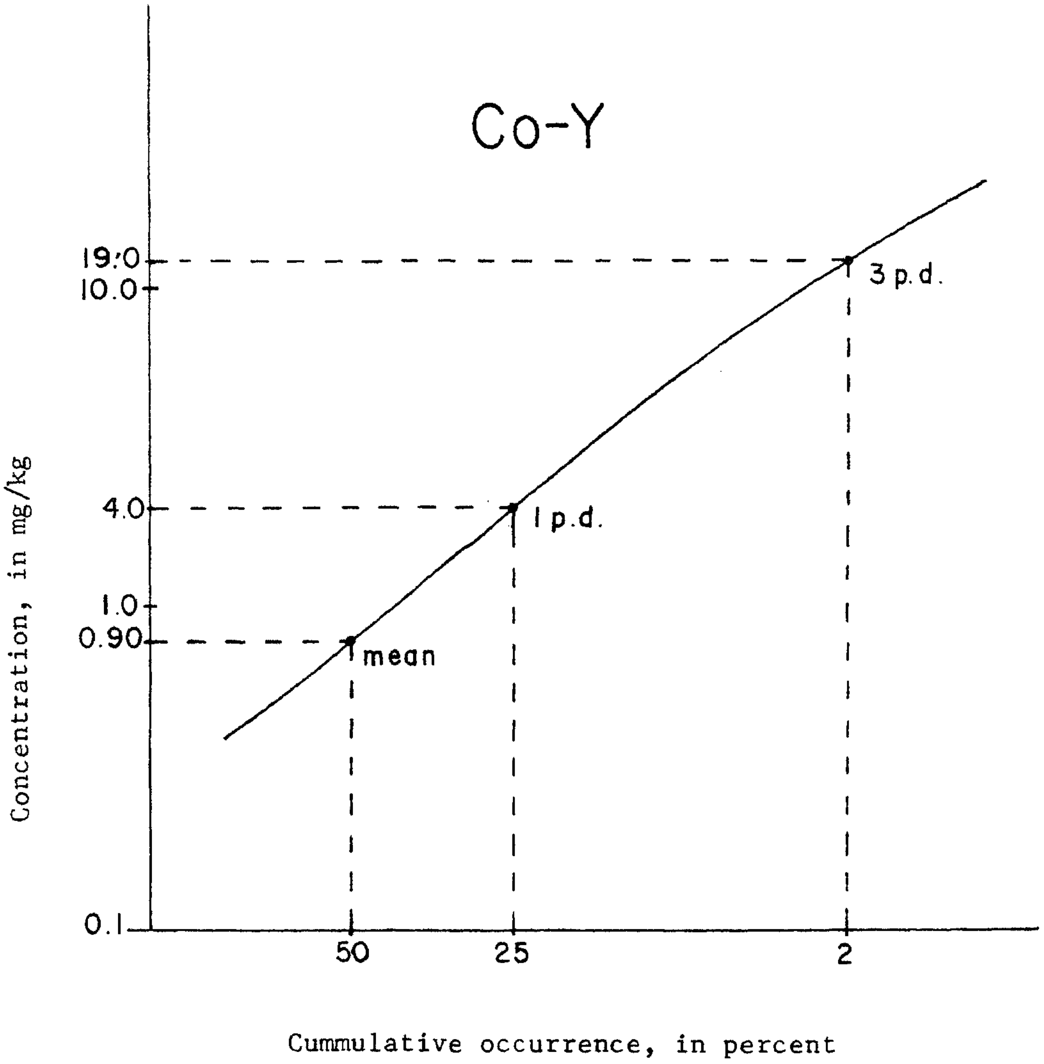
Ag-Y
100.0
25.0
10.0
1.0
0.40
0.1
0.095
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

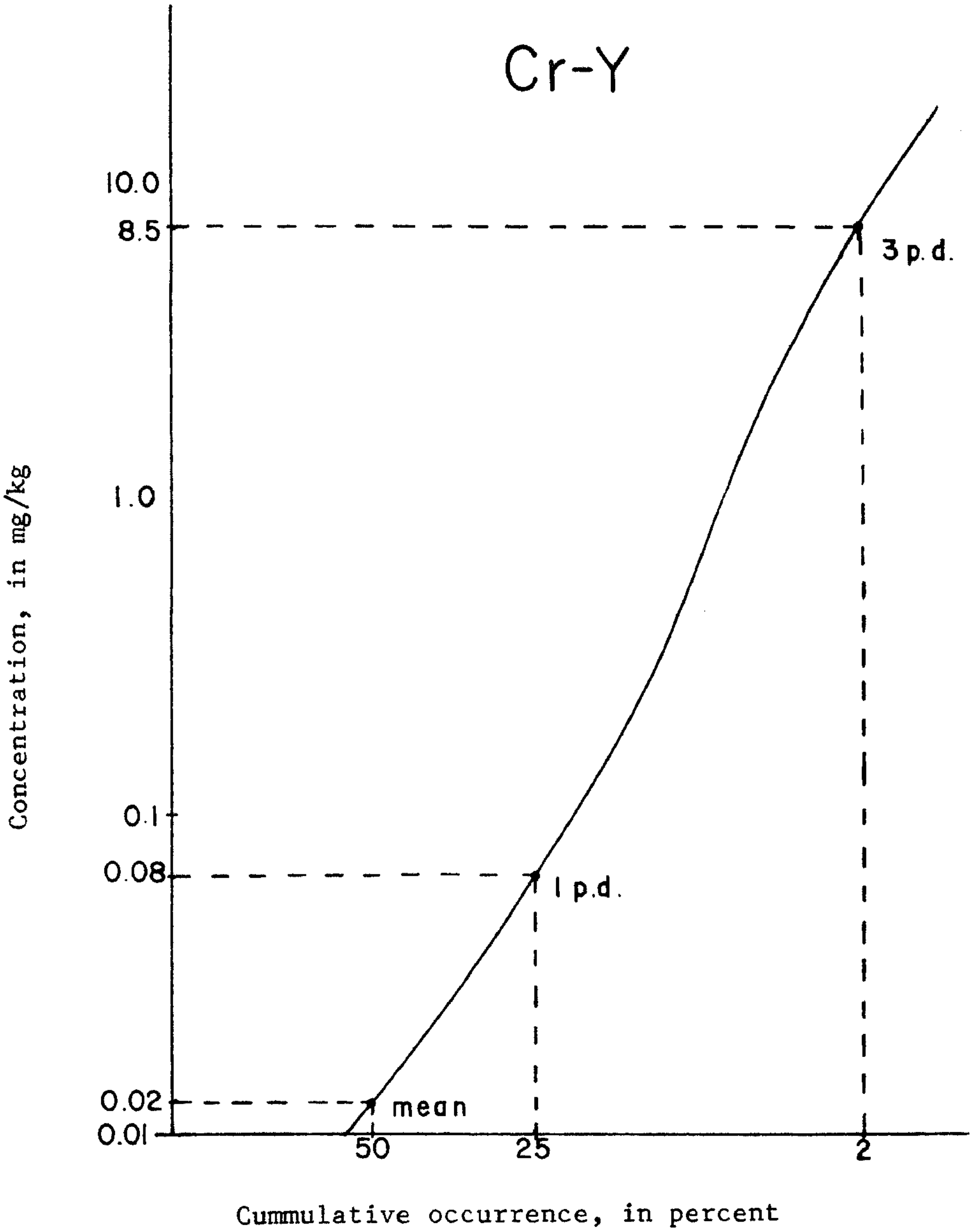

Al-Y
2500.0
1000.0
200.0
100.0
10.0
4.0
1.0
mean
1 p.d.
3 p.d.
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

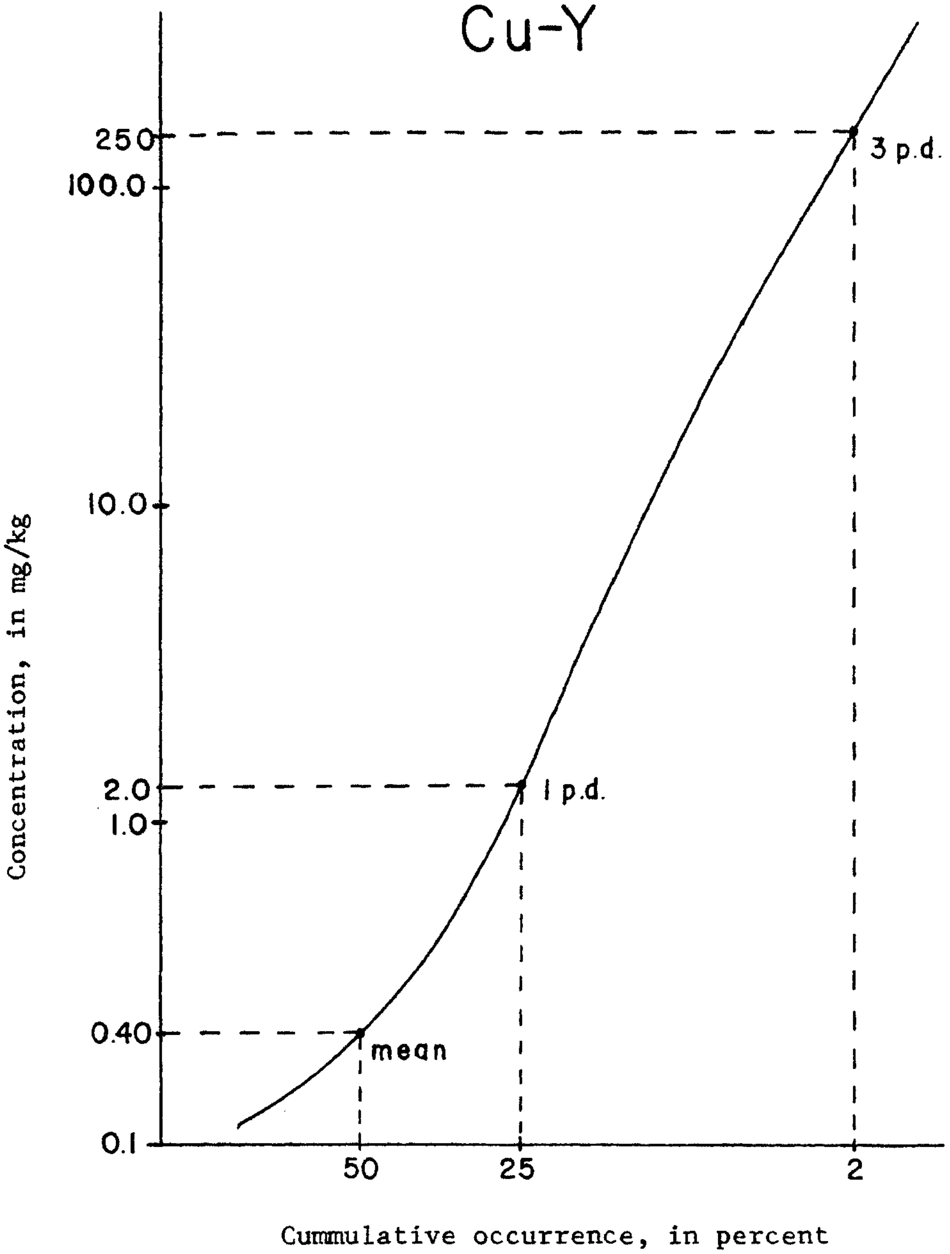


As-Y
100.0
10.0
1.0
0.70
0.38
0.1
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

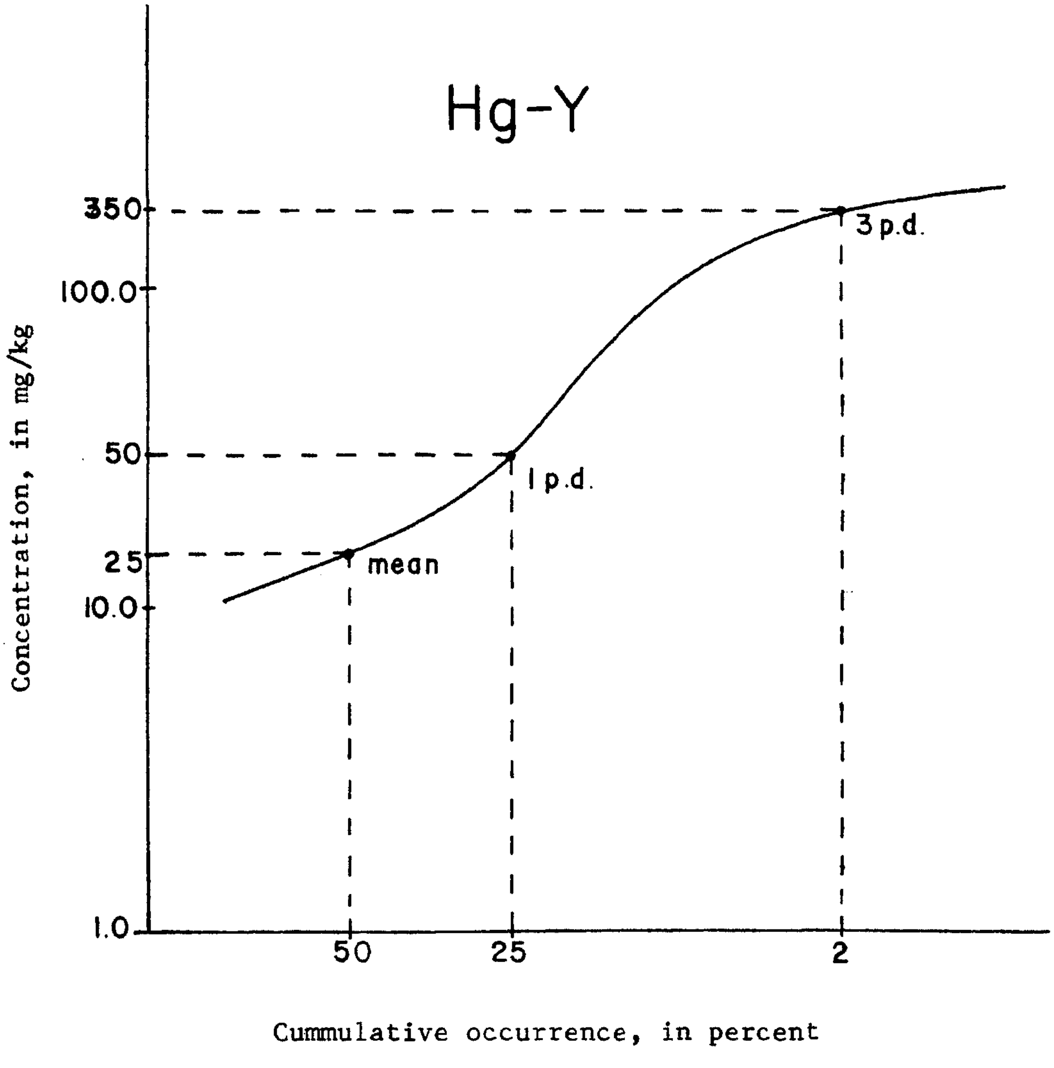

Cd-Y
10.0
2.5
1.0
0.1
0.08
0.03
0.01
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

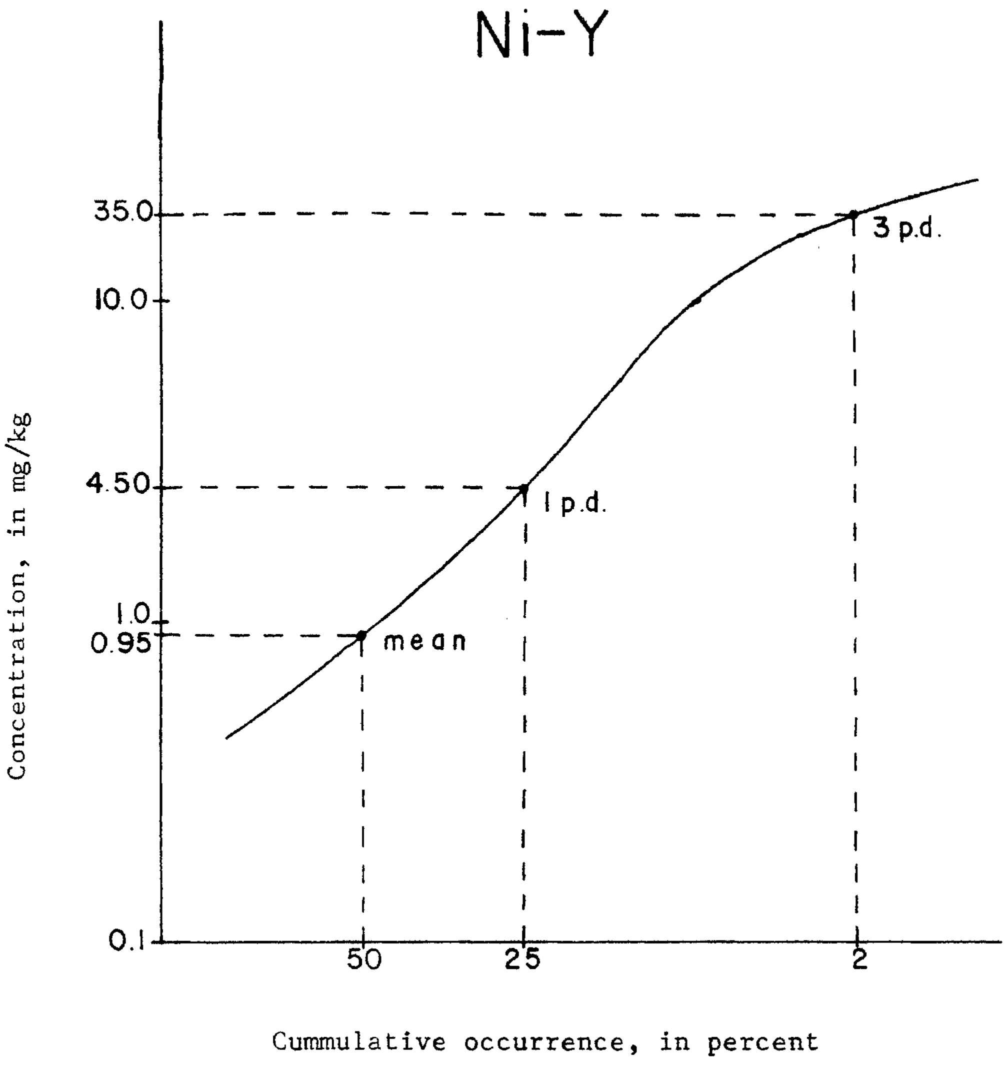

Co-Y
19.0
10.0
4.0
1.0
0.90
0.1
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

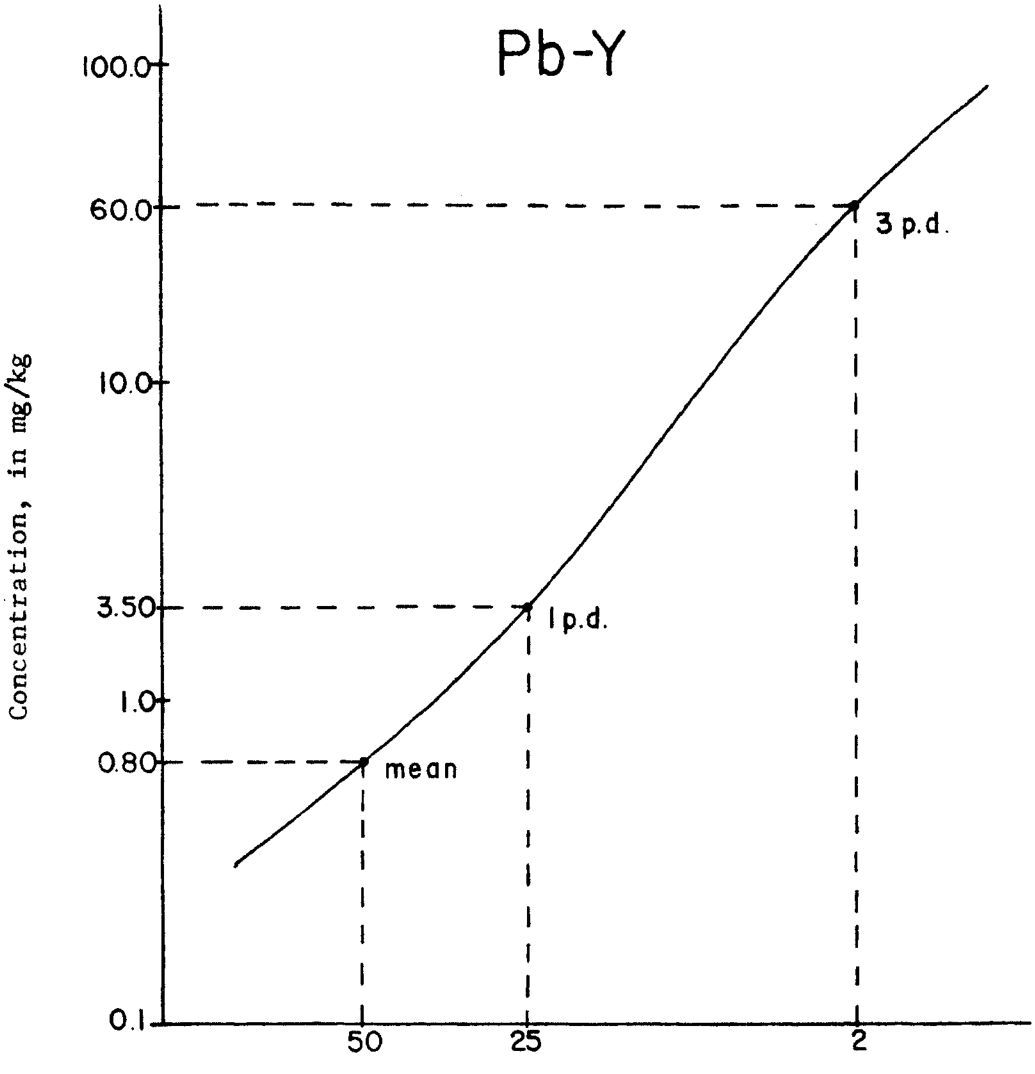

Cr-Y
10.0
8.5
1.0
0.1
0.08
0.02
0.01
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

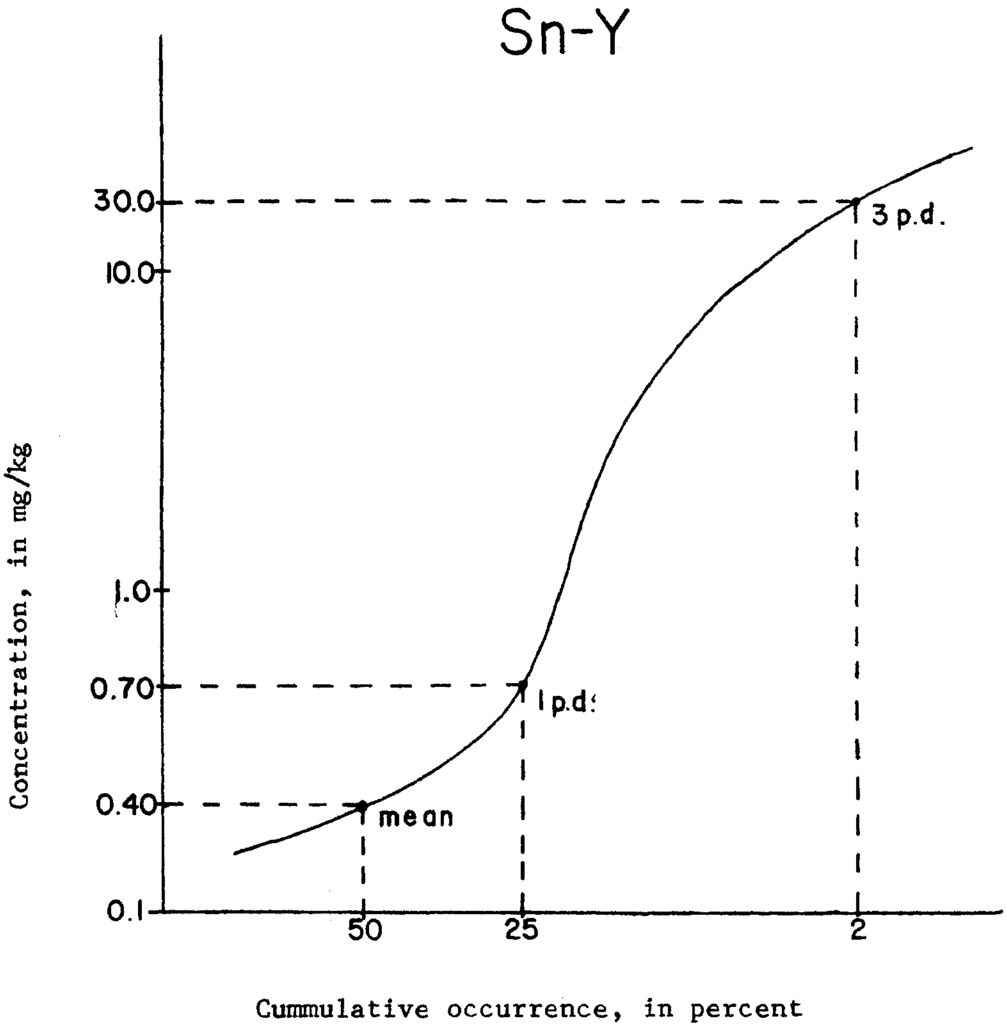


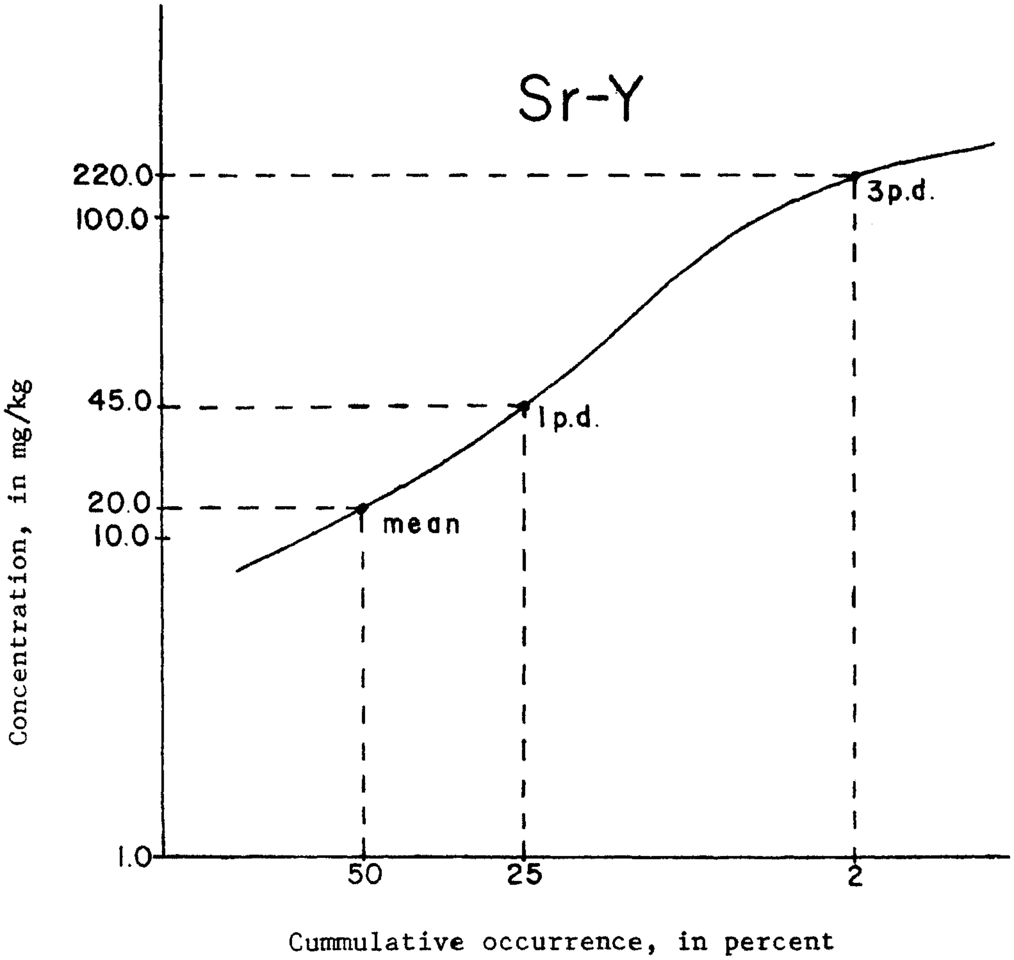
Cu-Y
250
100.0
10.0
2.0
1.0
0.40
0.1
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

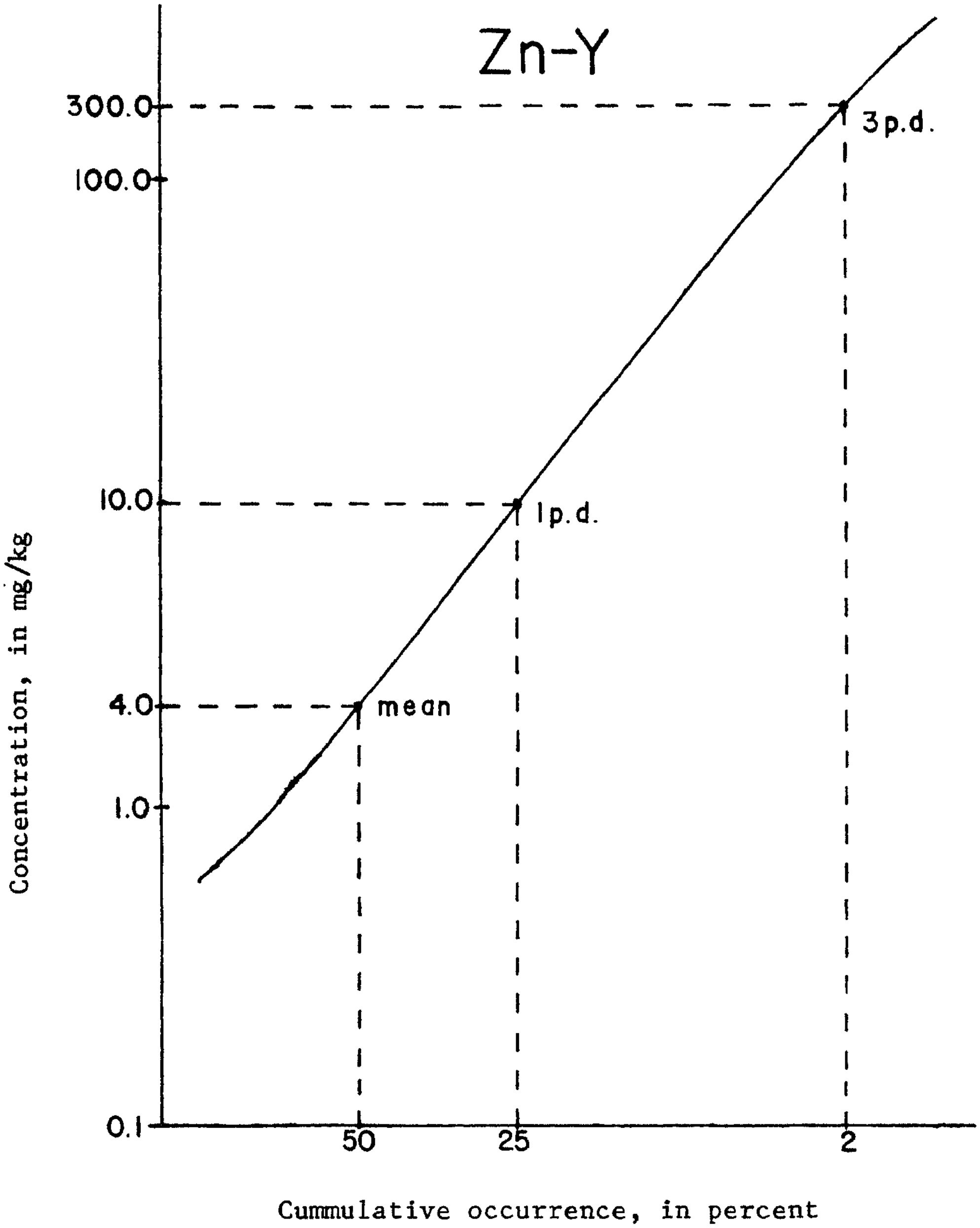

Hg-Y
350
100.0
50
25
10.0
1.0
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent


Ni-Y
35.0
10.0
4.50
1.0
0.95
0.1
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent


Pb-Y
100.0
60.0
10.0
3.50
1.0
0.80
0.1
3 p.d.
1 p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent


Sn-Y
30.0
10.0
1.0
0.70
0.40
0.1
50
25
2
mean
1 p.d.
3 p.d.
Concentration, in mg/kg
Cummulative occurrence, in percent

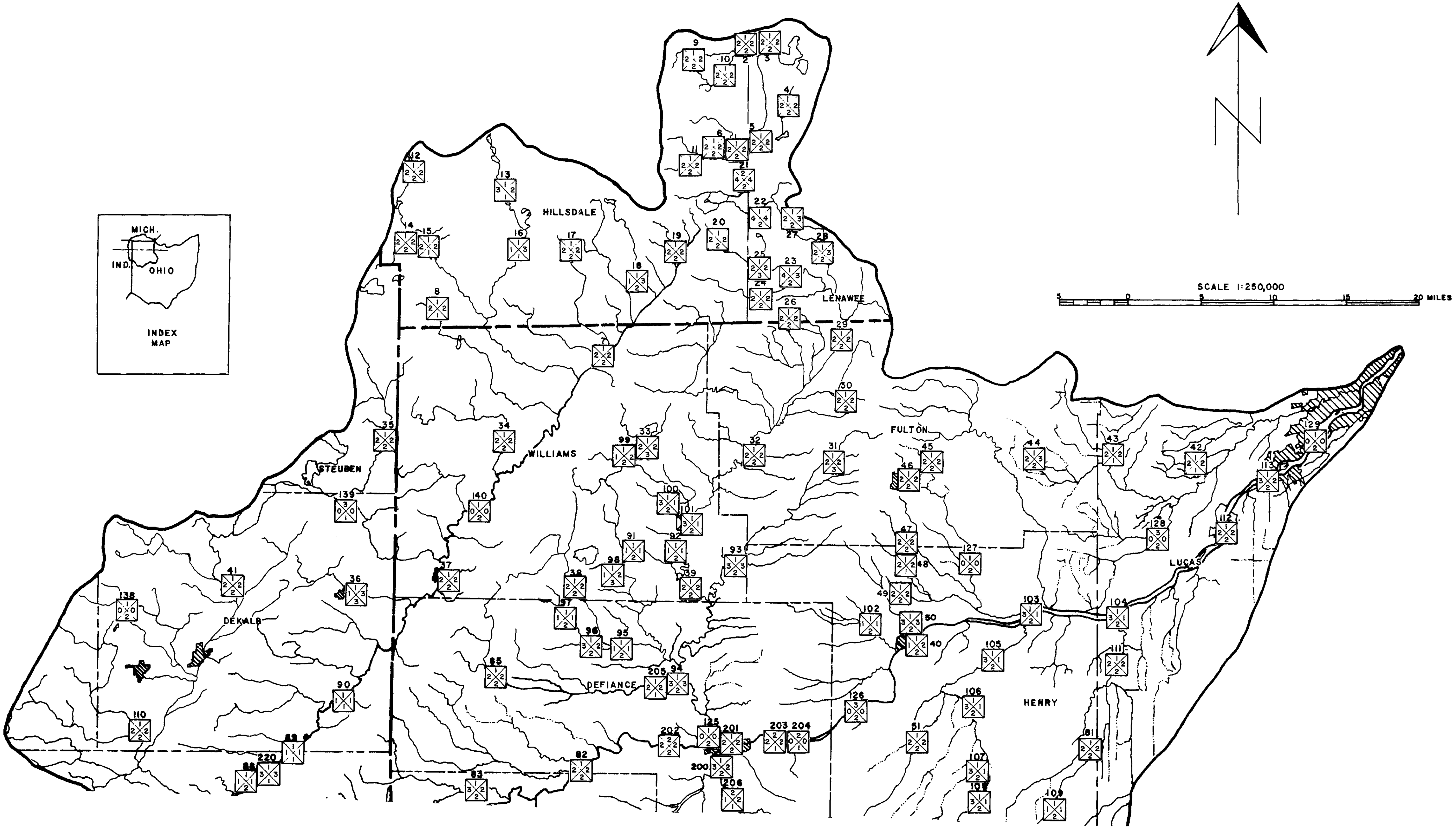

Sr-Y
220.0
100.0
45.0
20.0
10.0
1.0
3p.d.
1p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent



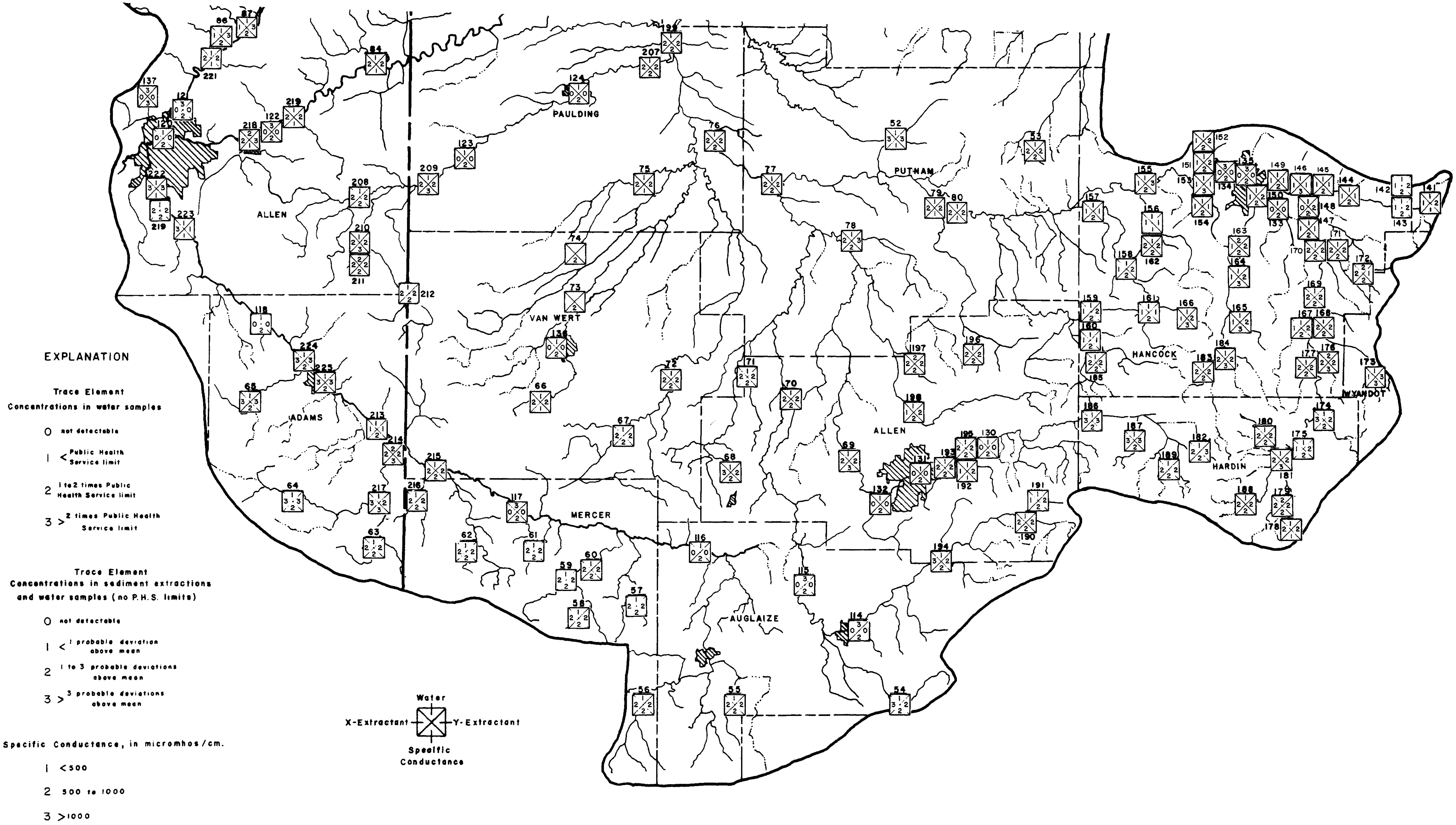
Zn-Y
300.0
100.0
10.0
4.0
1.0
0.1
3p.d.
1p.d.
mean
50
25
2
Concentration, in mg/kg
Cummulative occurrence, in percent

APPENDIX II

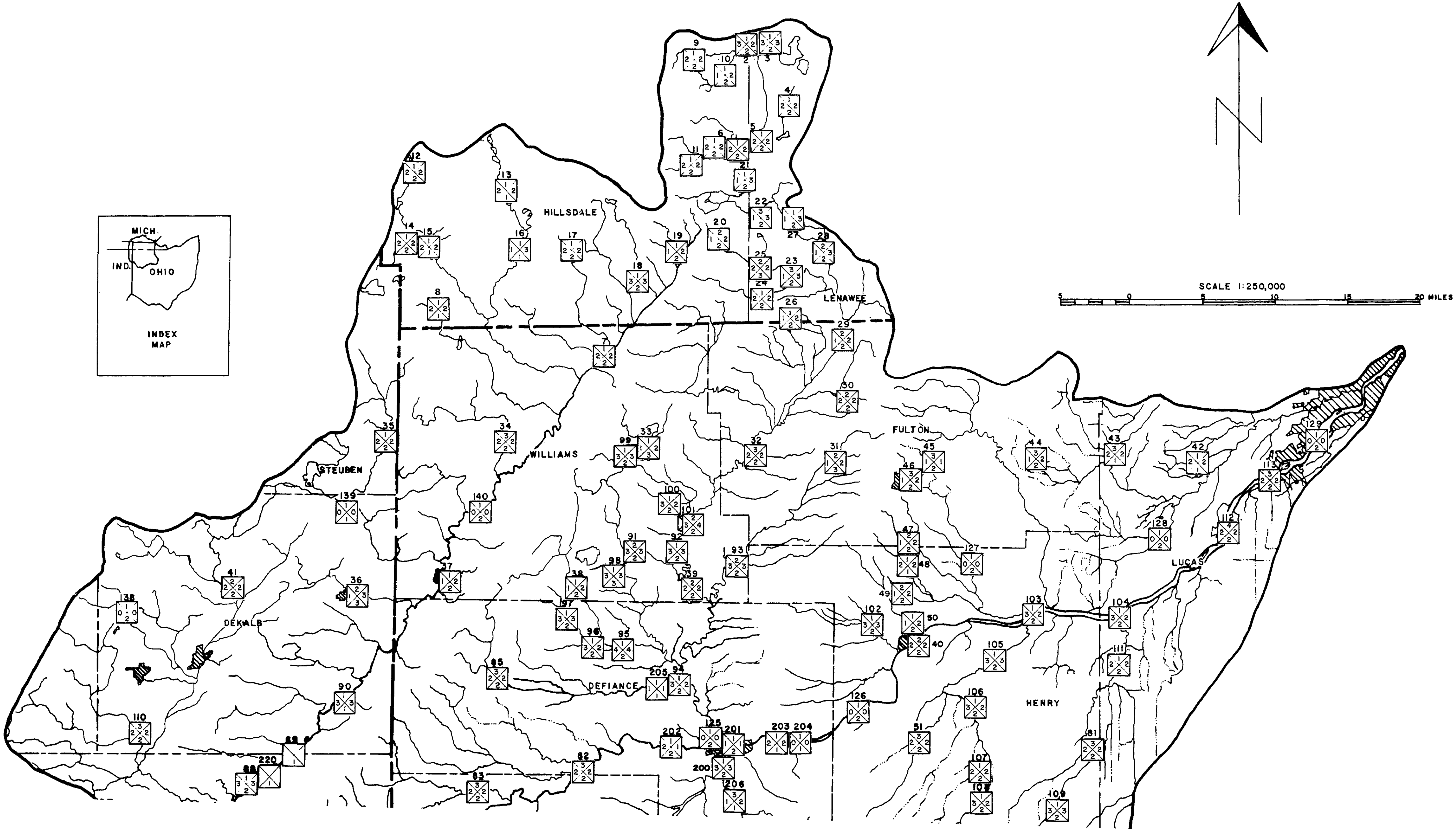
Maps showing concentration of selected parameters in the Maumee River Basin



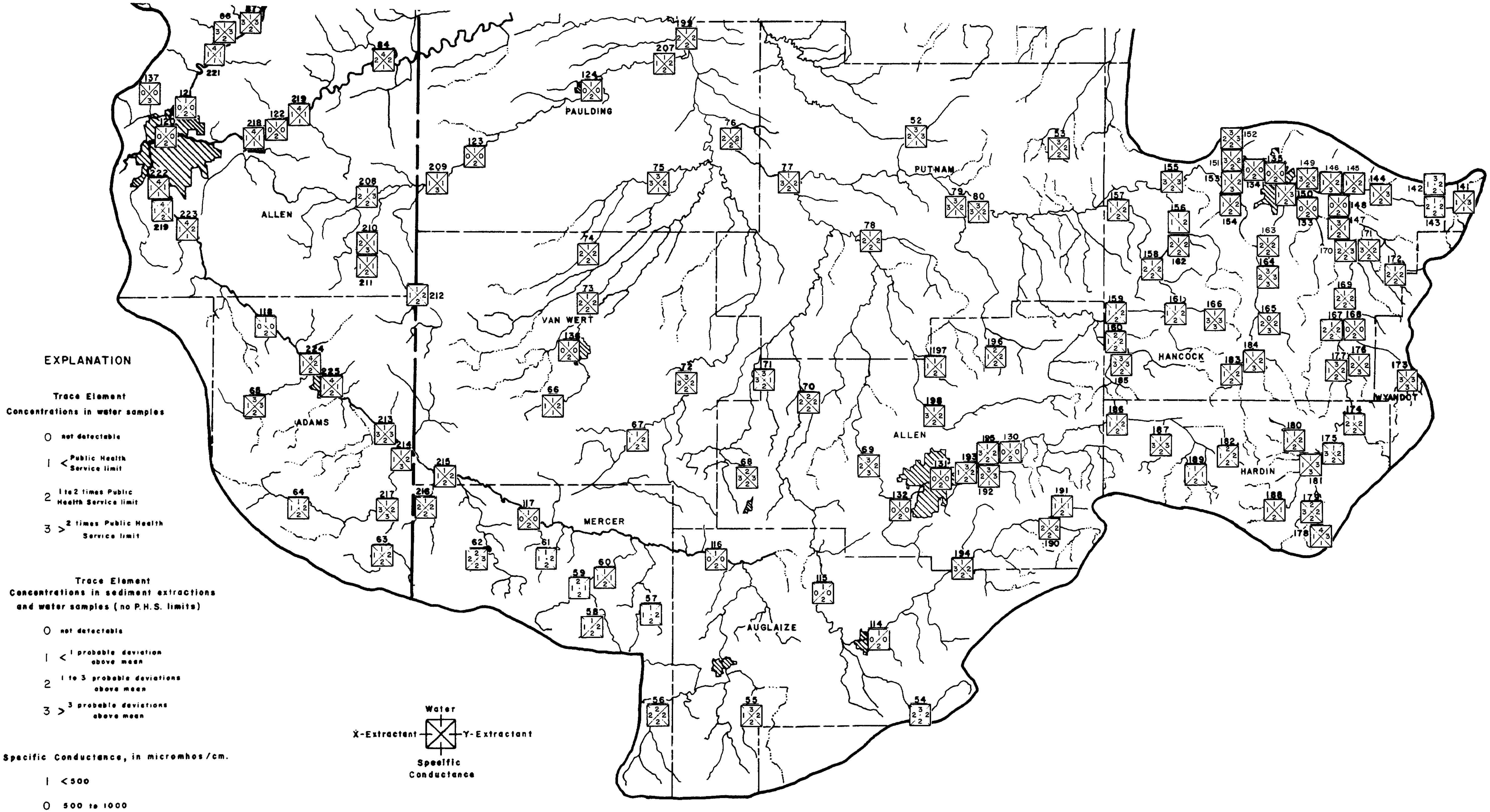
Ag Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



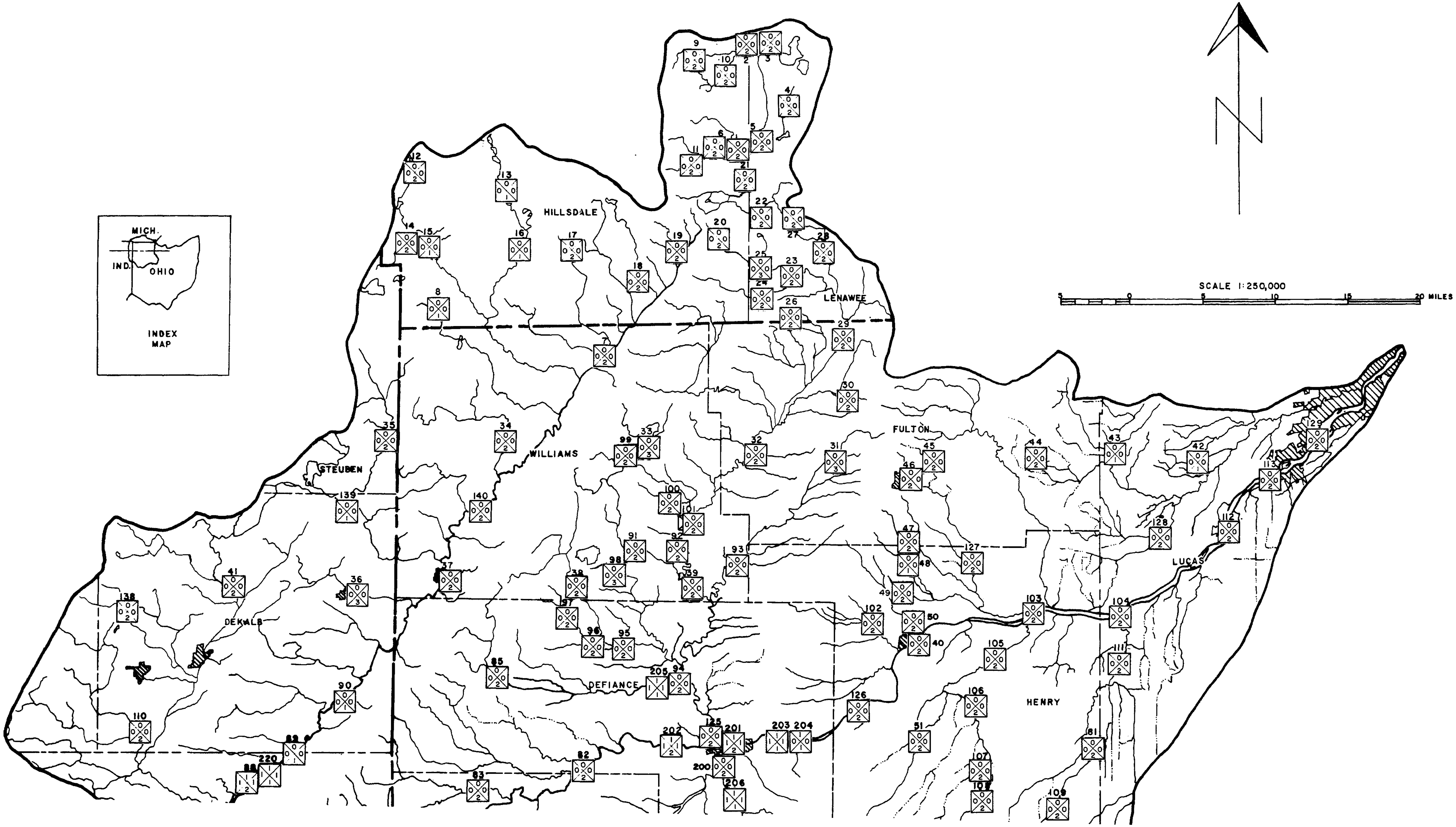
Ag Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



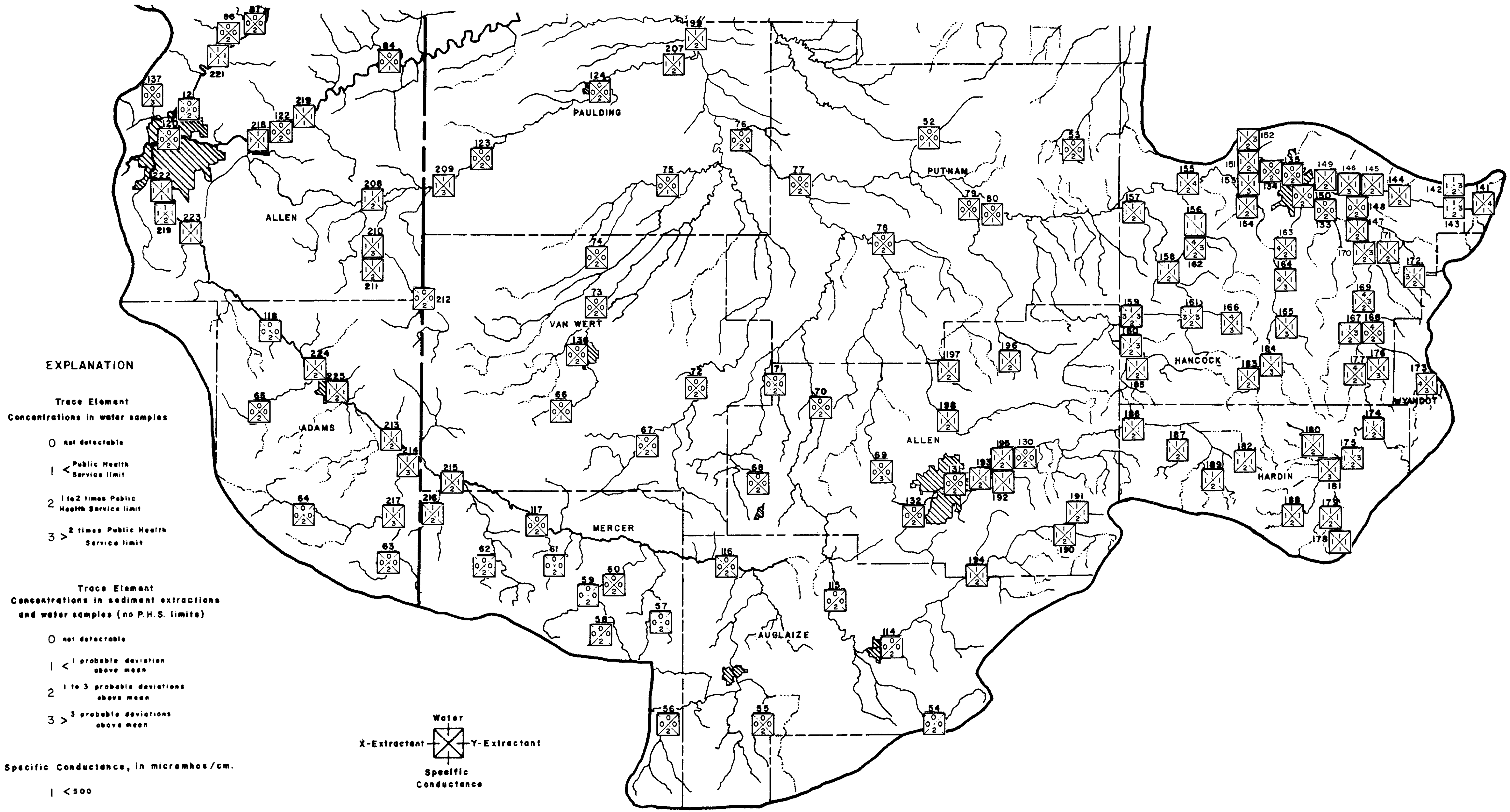
Al Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



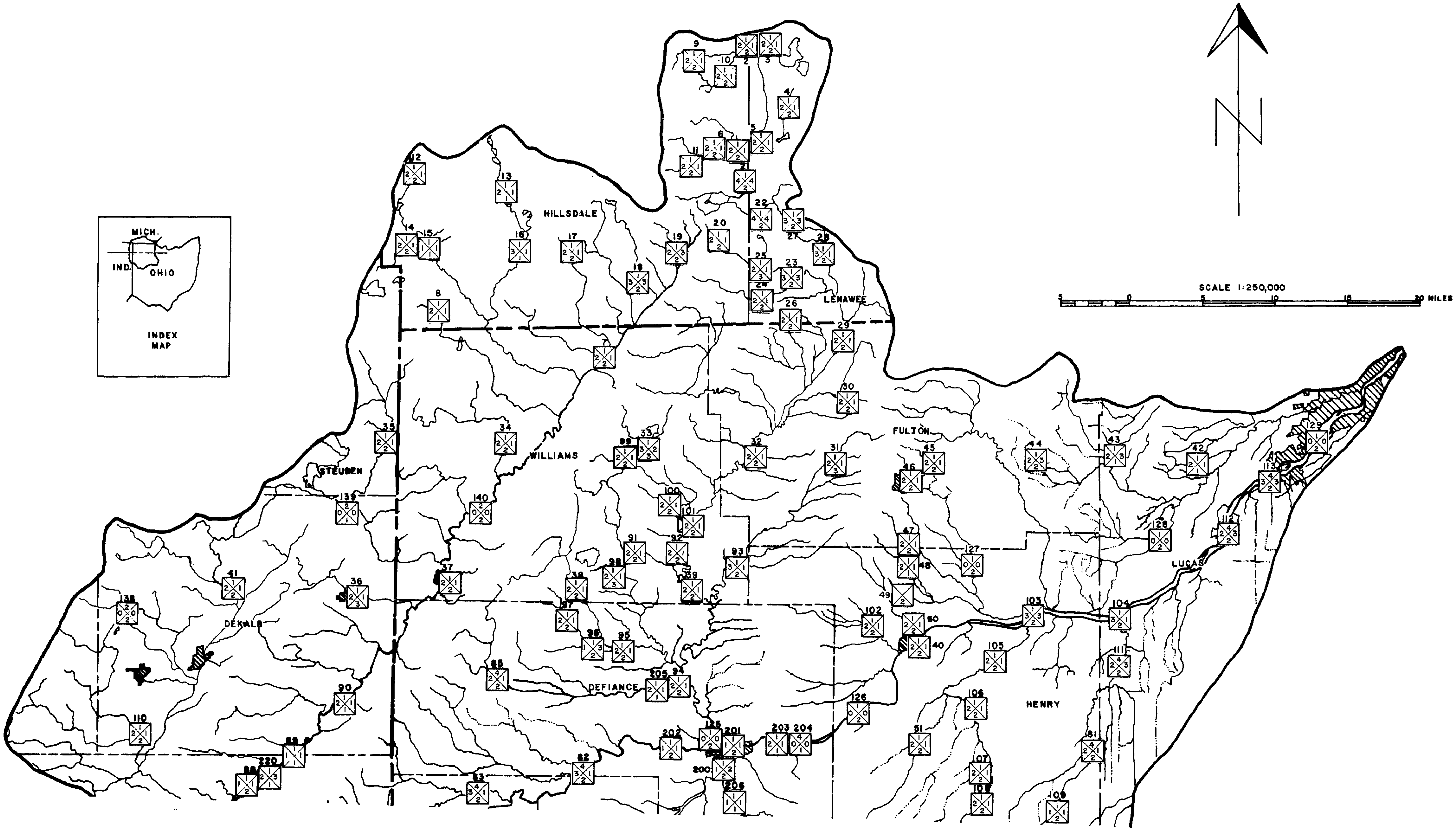
Al Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



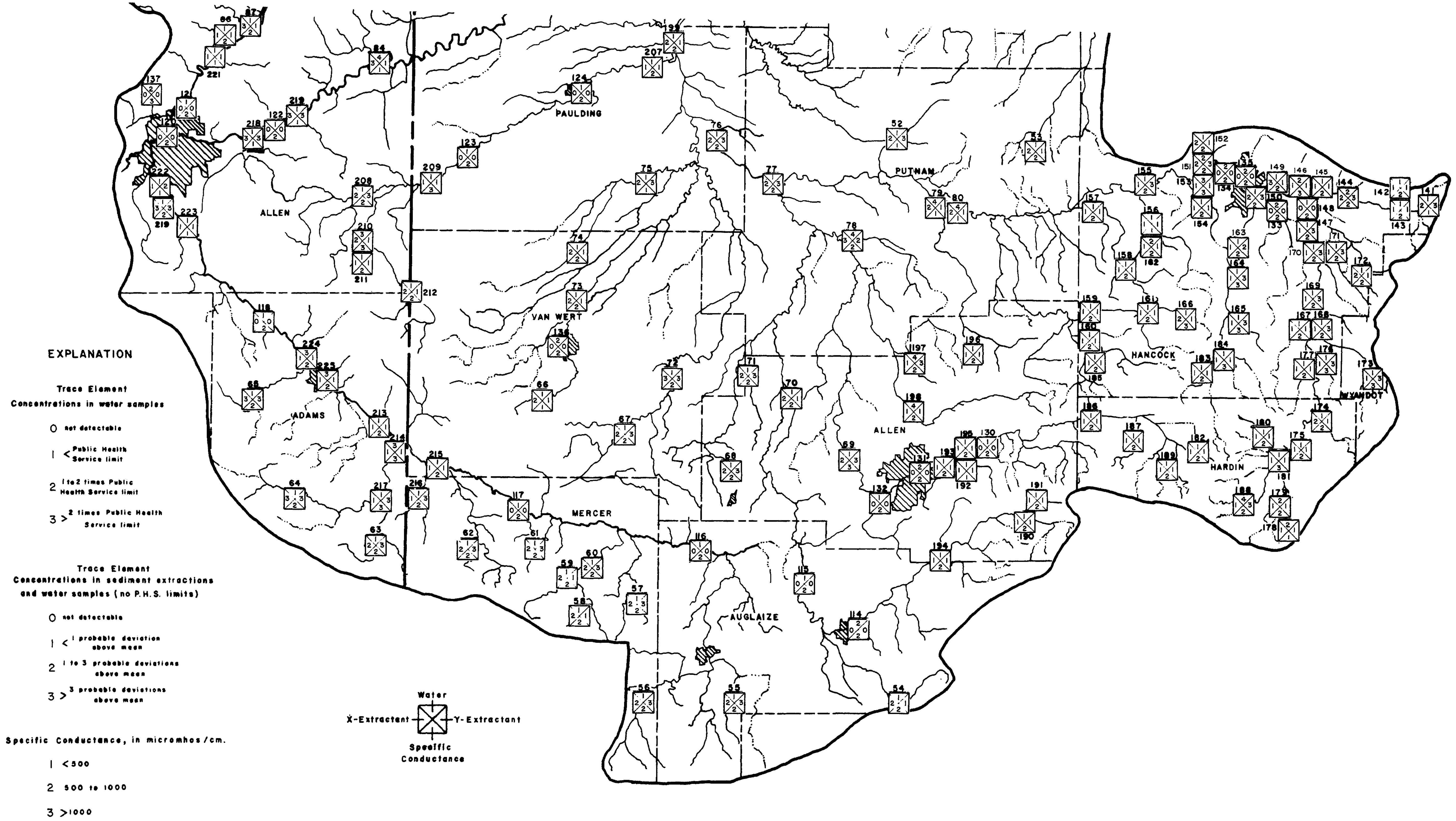
As Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



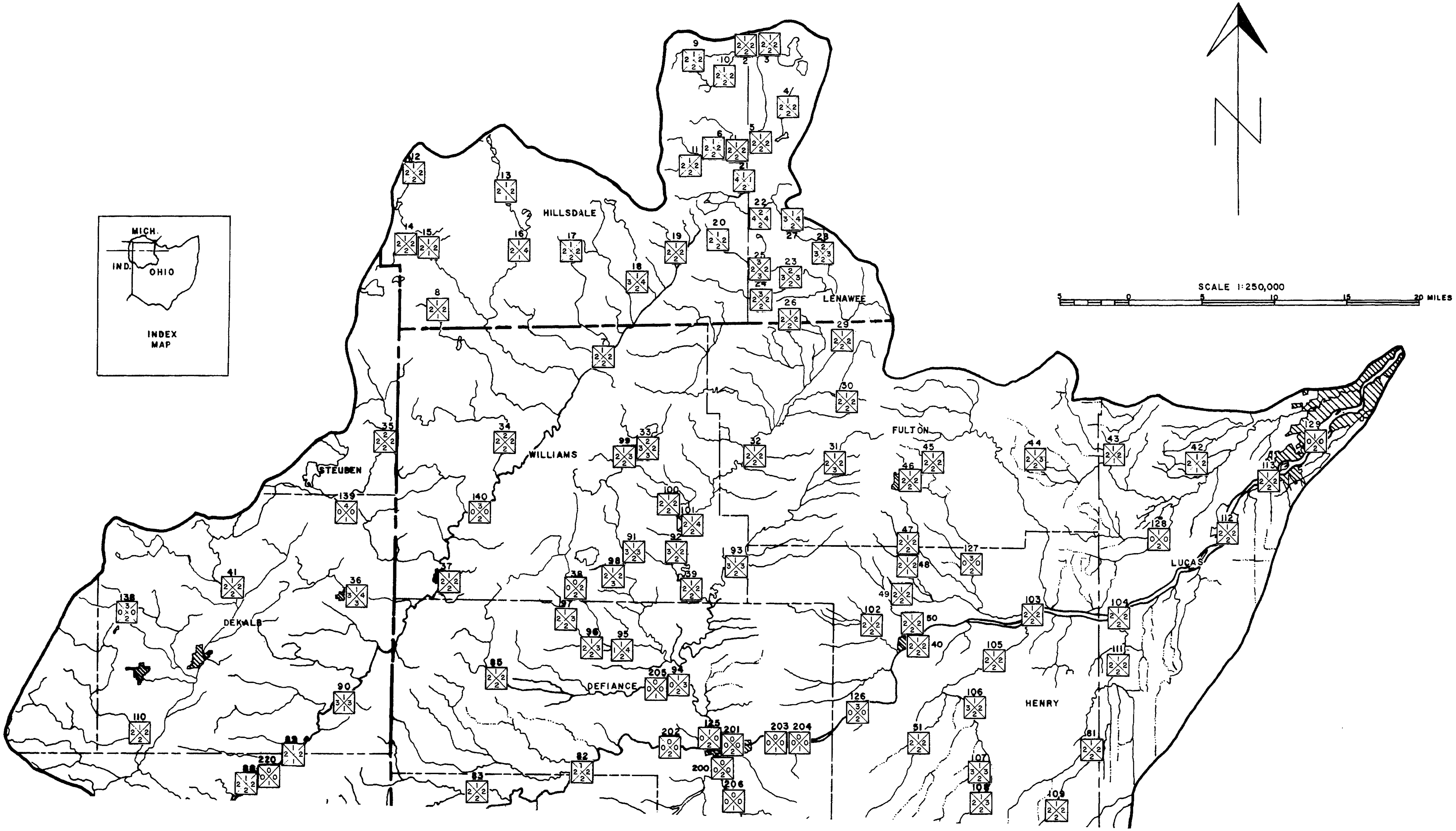
As Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



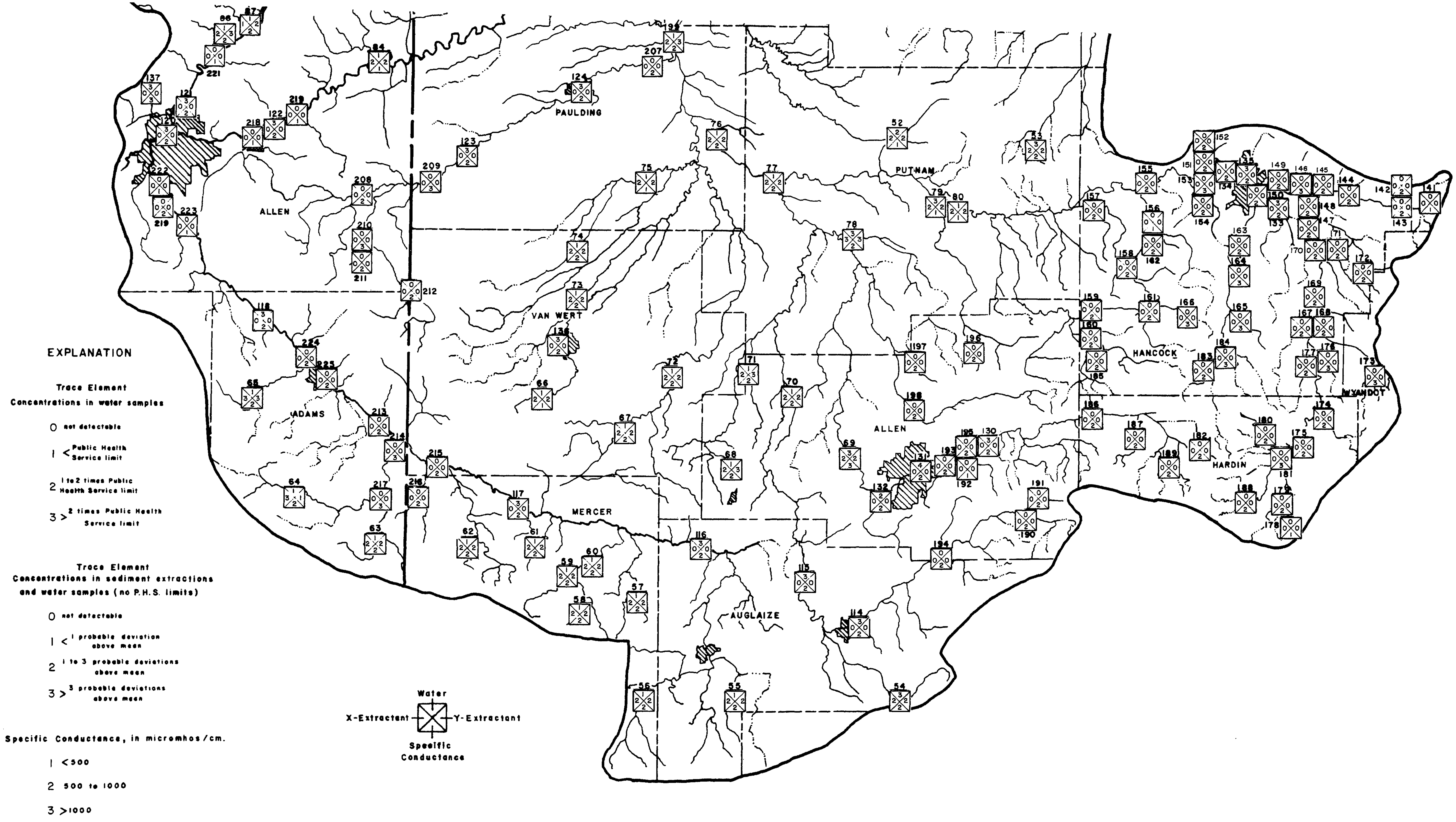
Cd Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



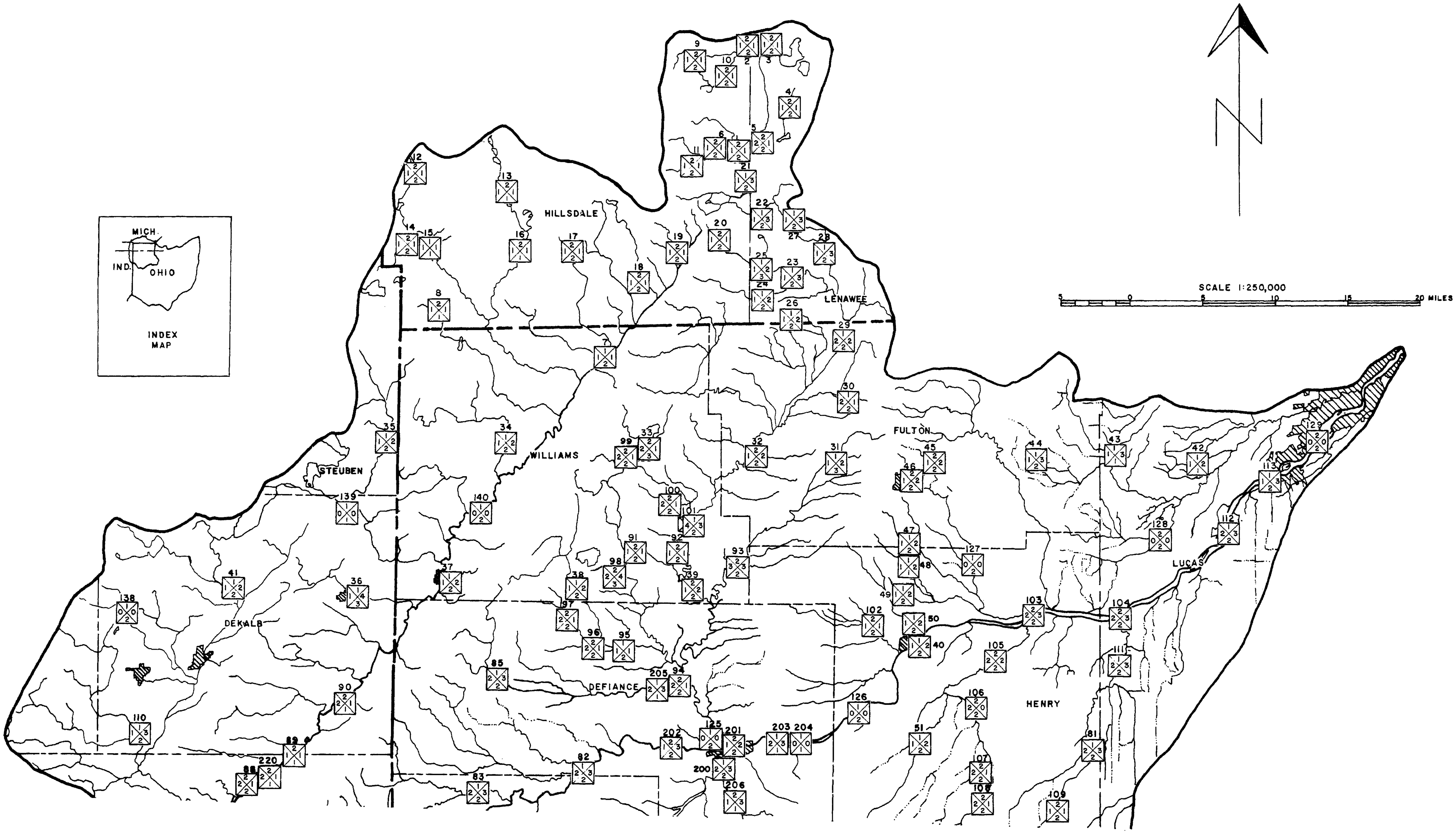
Cd Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



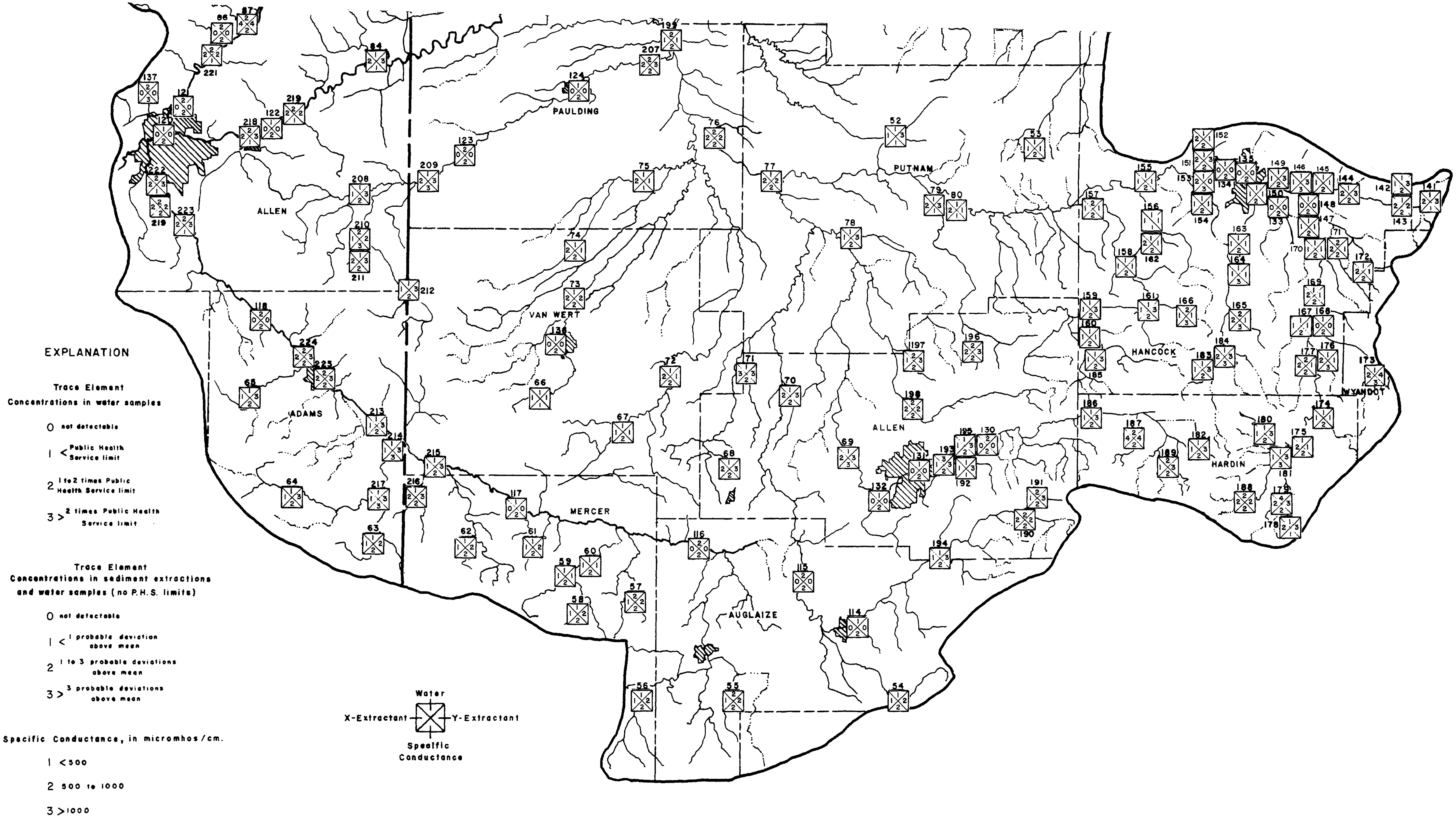
Co Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



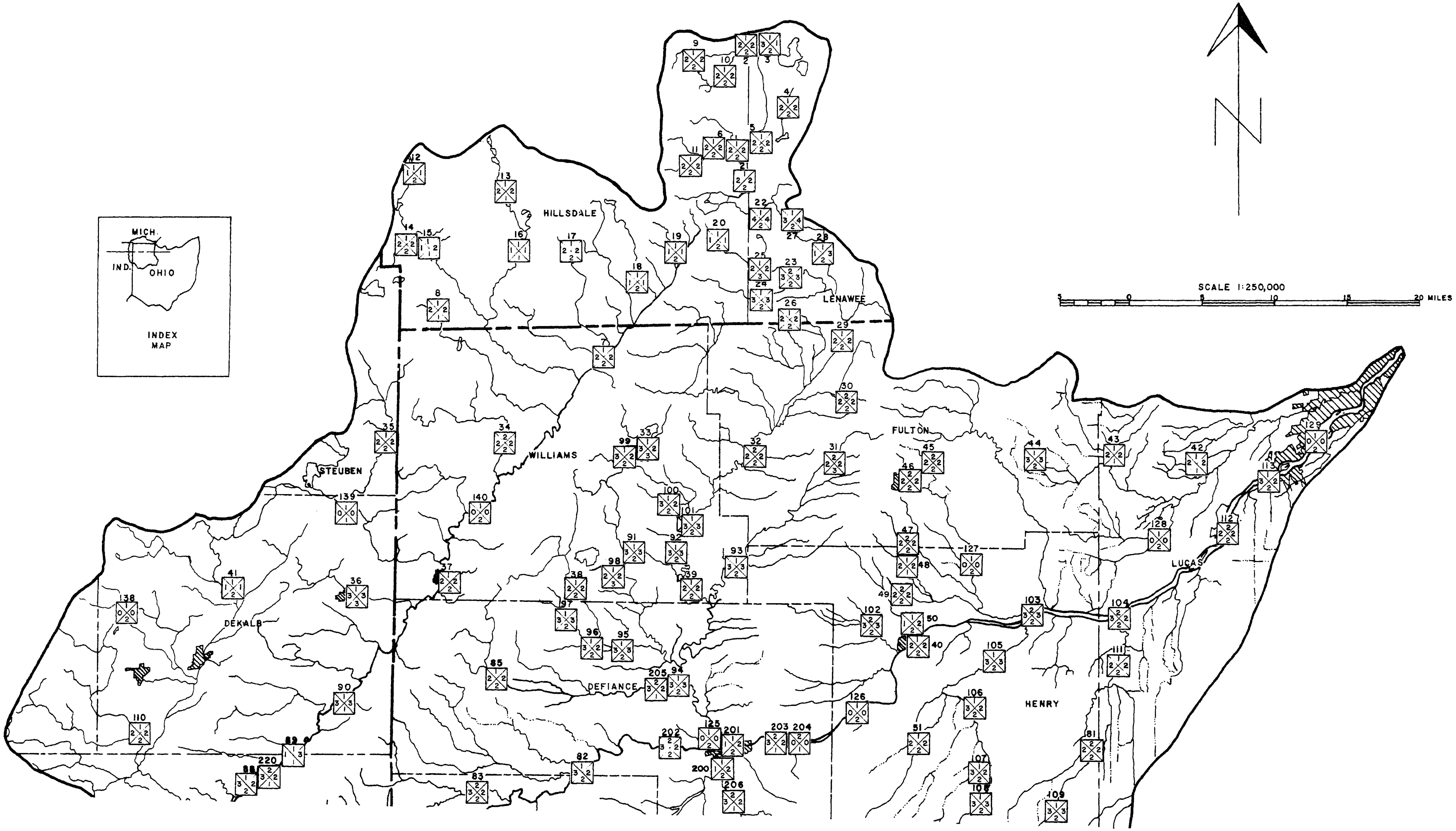
Co Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



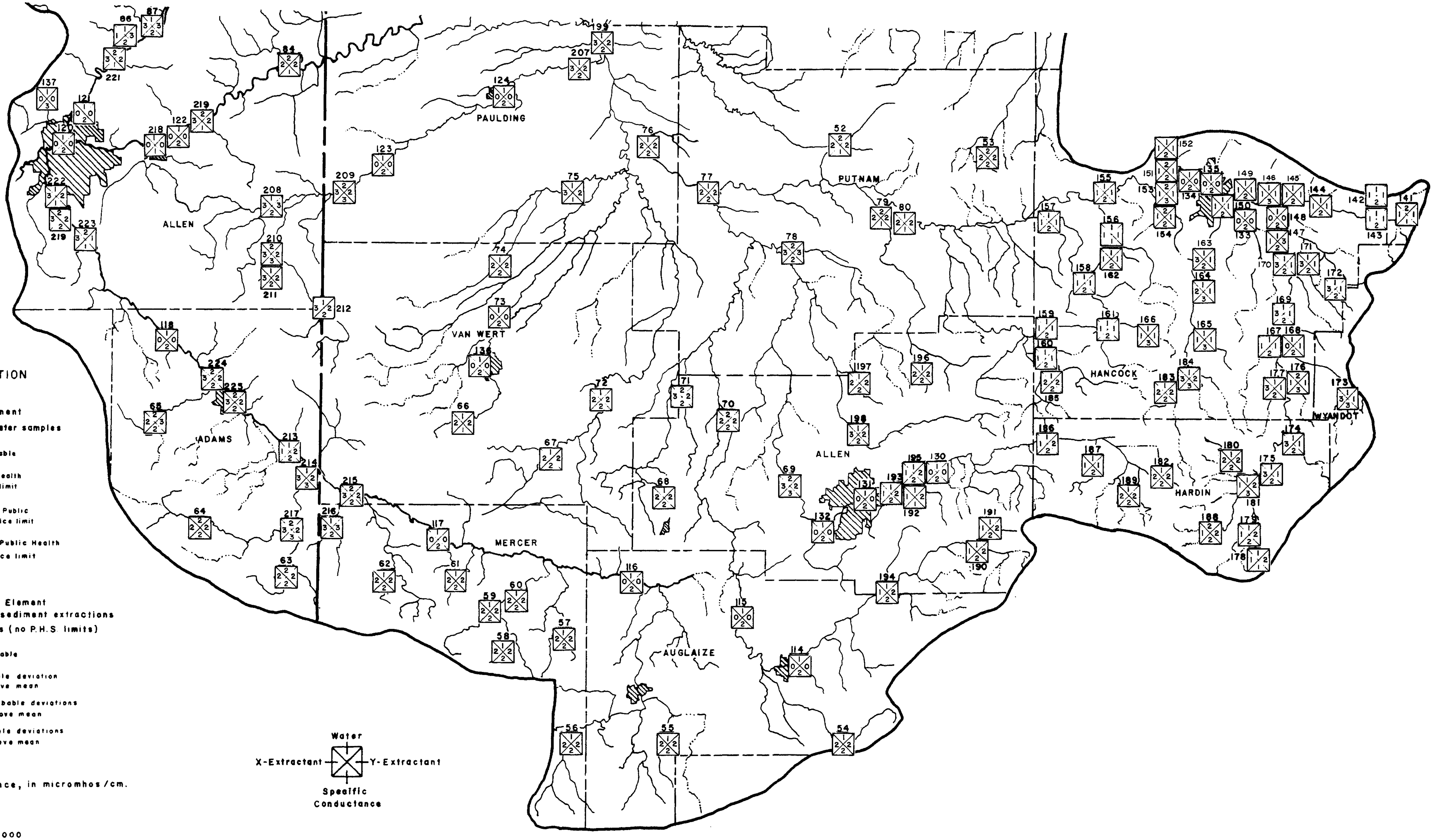
Cr Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



Cr Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



Cu Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



EXPLANATION

Trace Element Concentrations in water samples

0 not detectable

1 < Public Health Service limit

2 1 to 2 times Public Health Service limit

3 > 2 times Public Health Service limit

Trace Element Concentrations in sediment extractions and water samples (no P.H.S. limits)

0 not detectable

1 < 1 probable deviation above mean

2 1 to 3 probable deviations above mean

3 > 3 probable deviations above mean

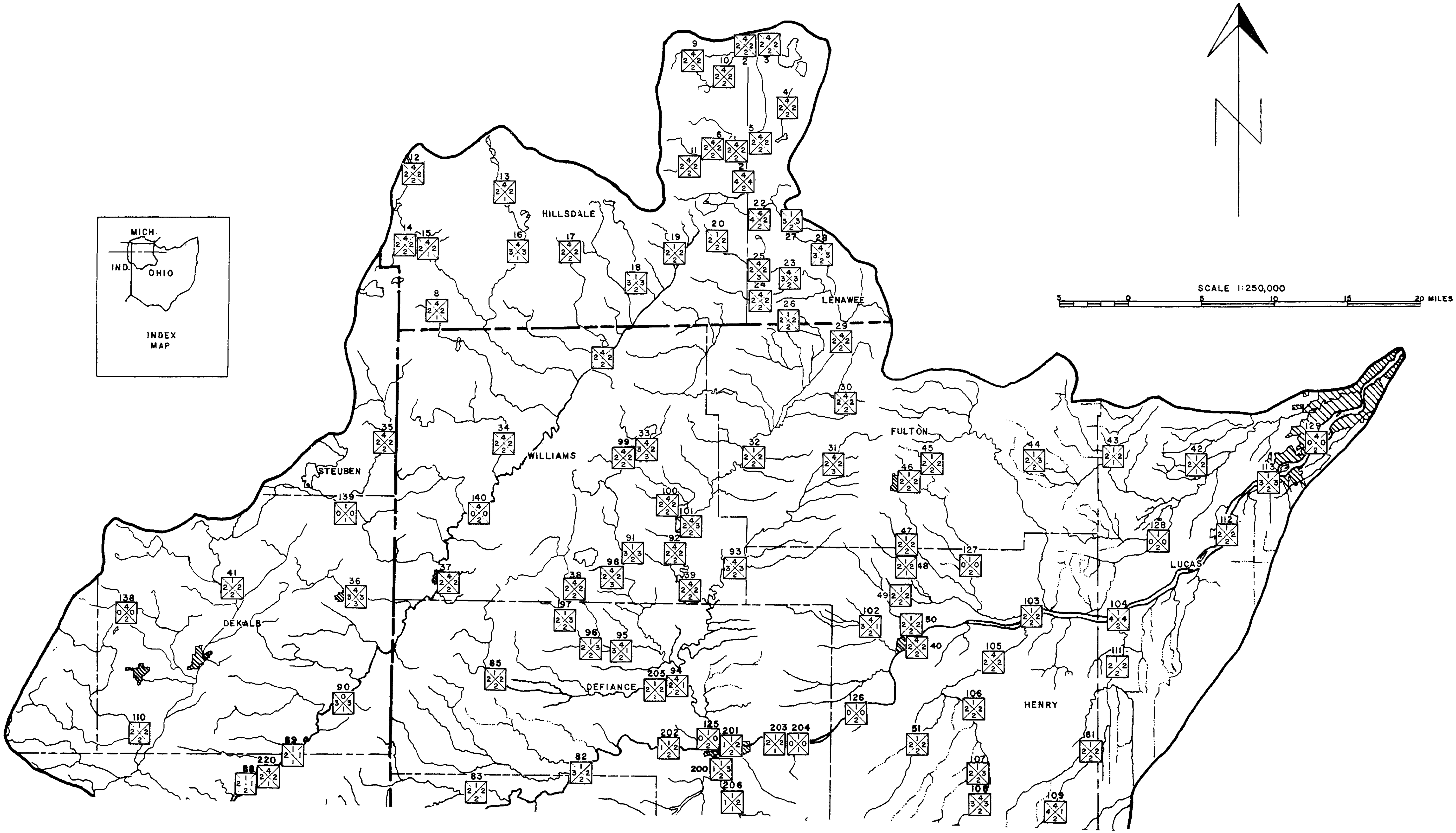
Specific Conductance, in micromhos/cm.

1 <500

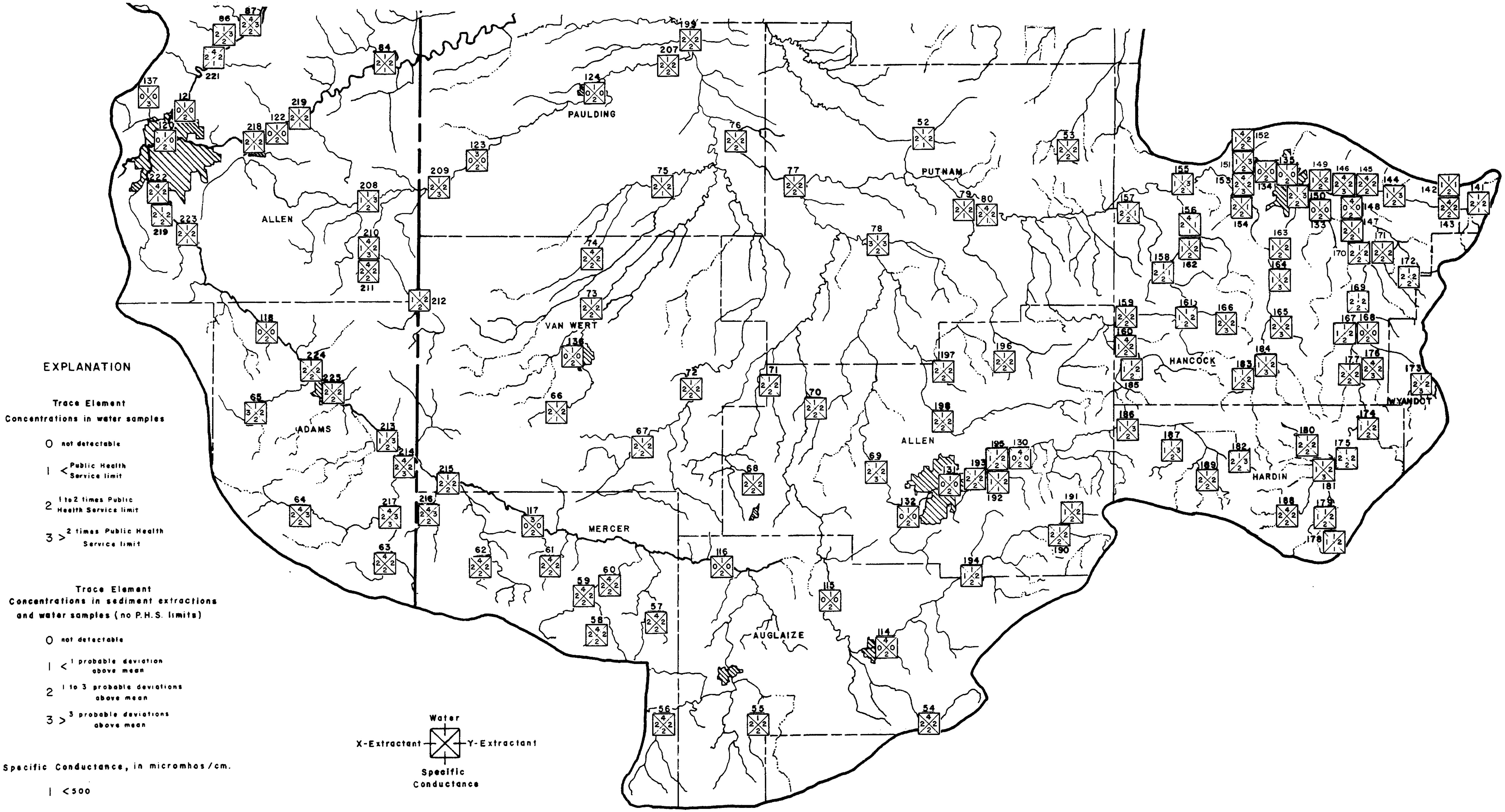
2 500 to 1000

3 >1000

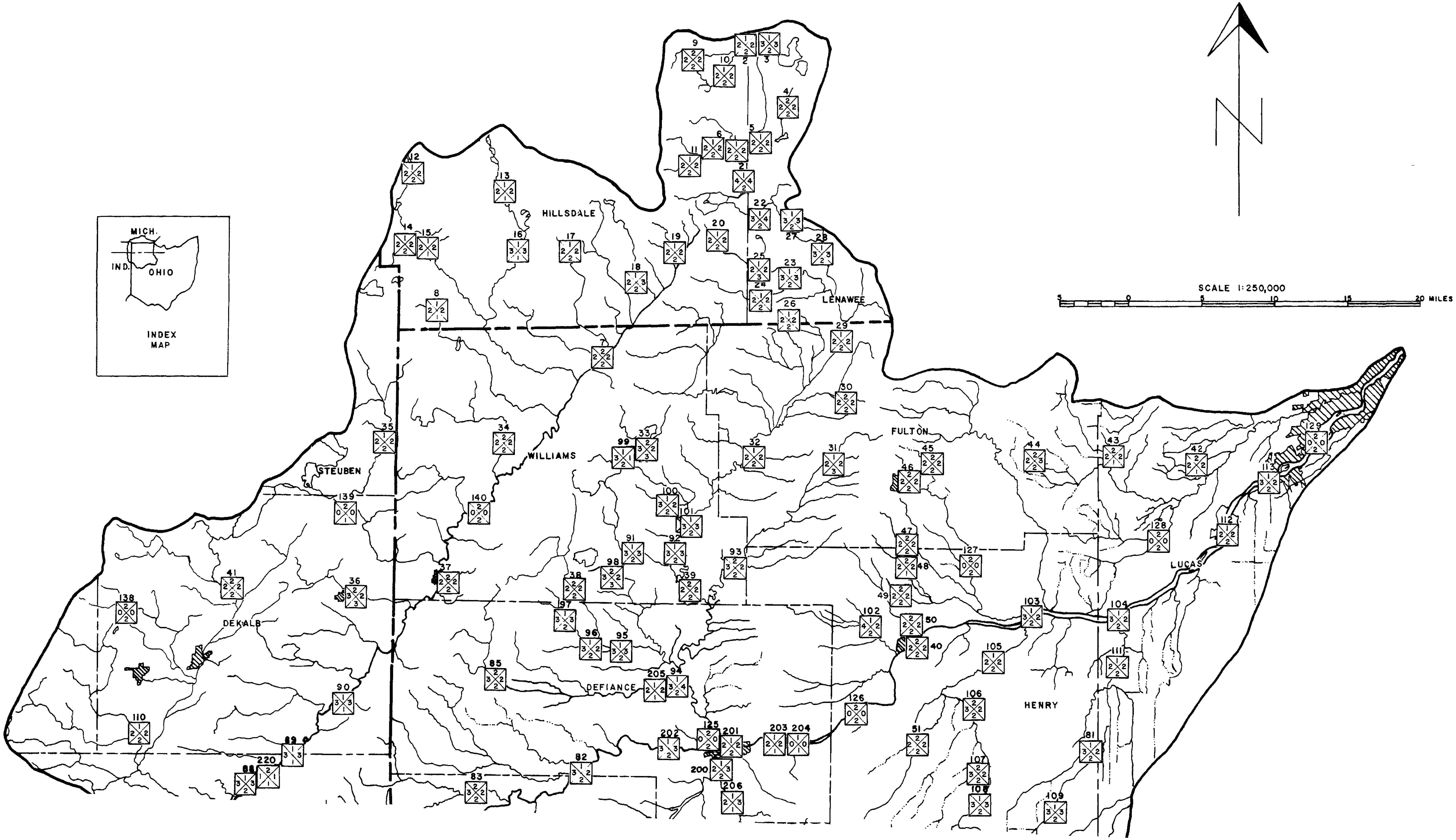
Cu Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



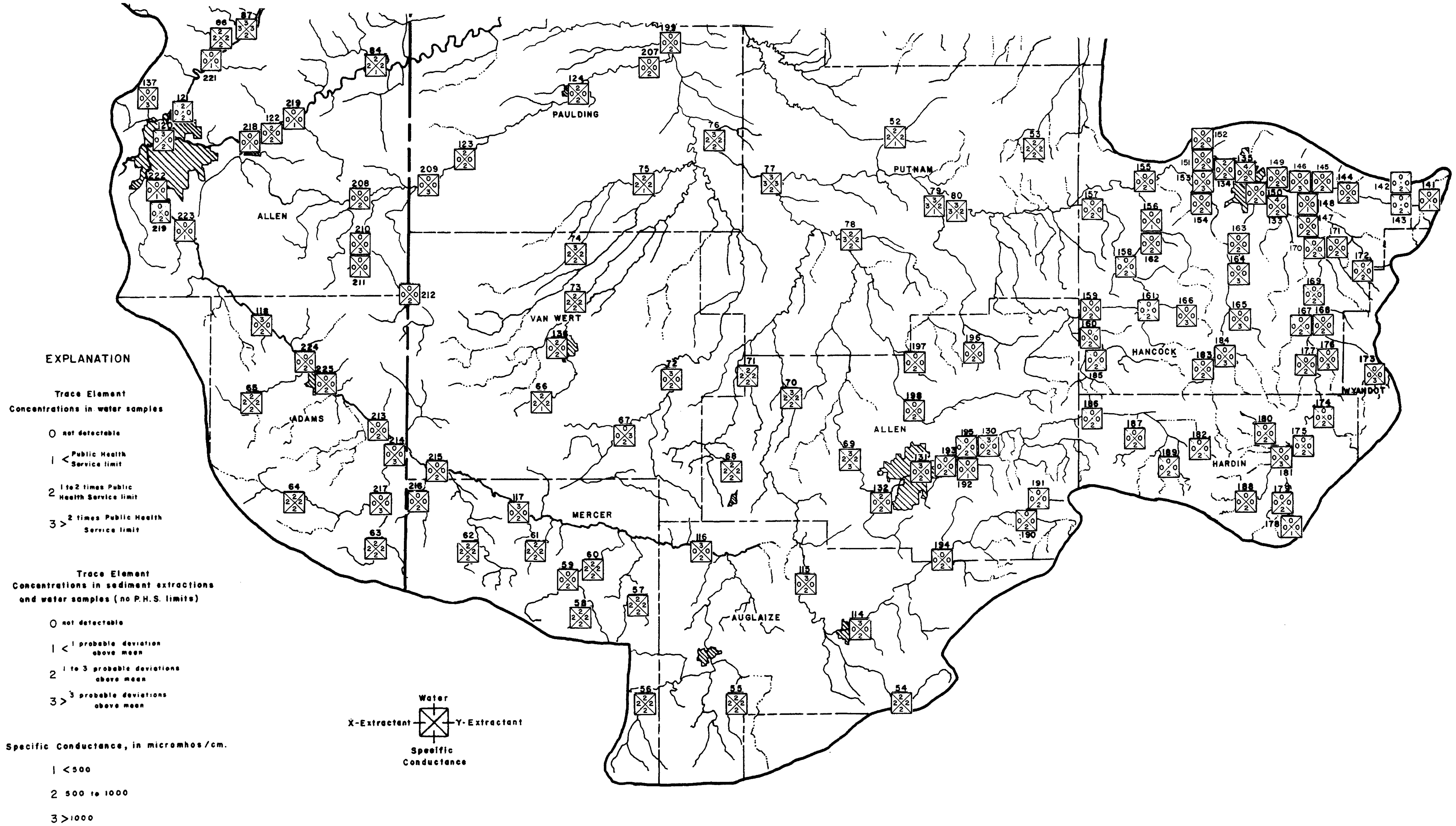
Hg Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



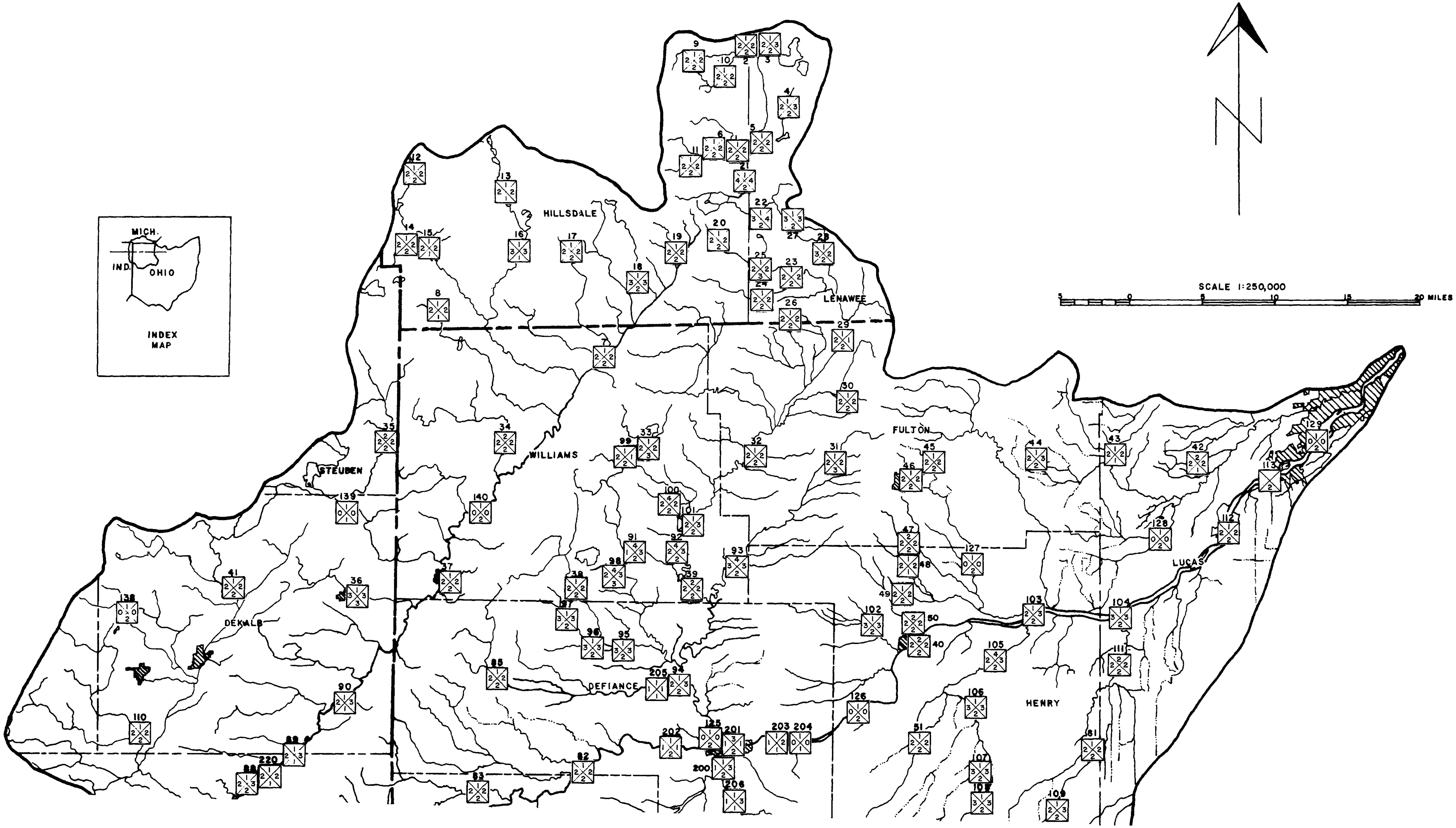
Hg Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



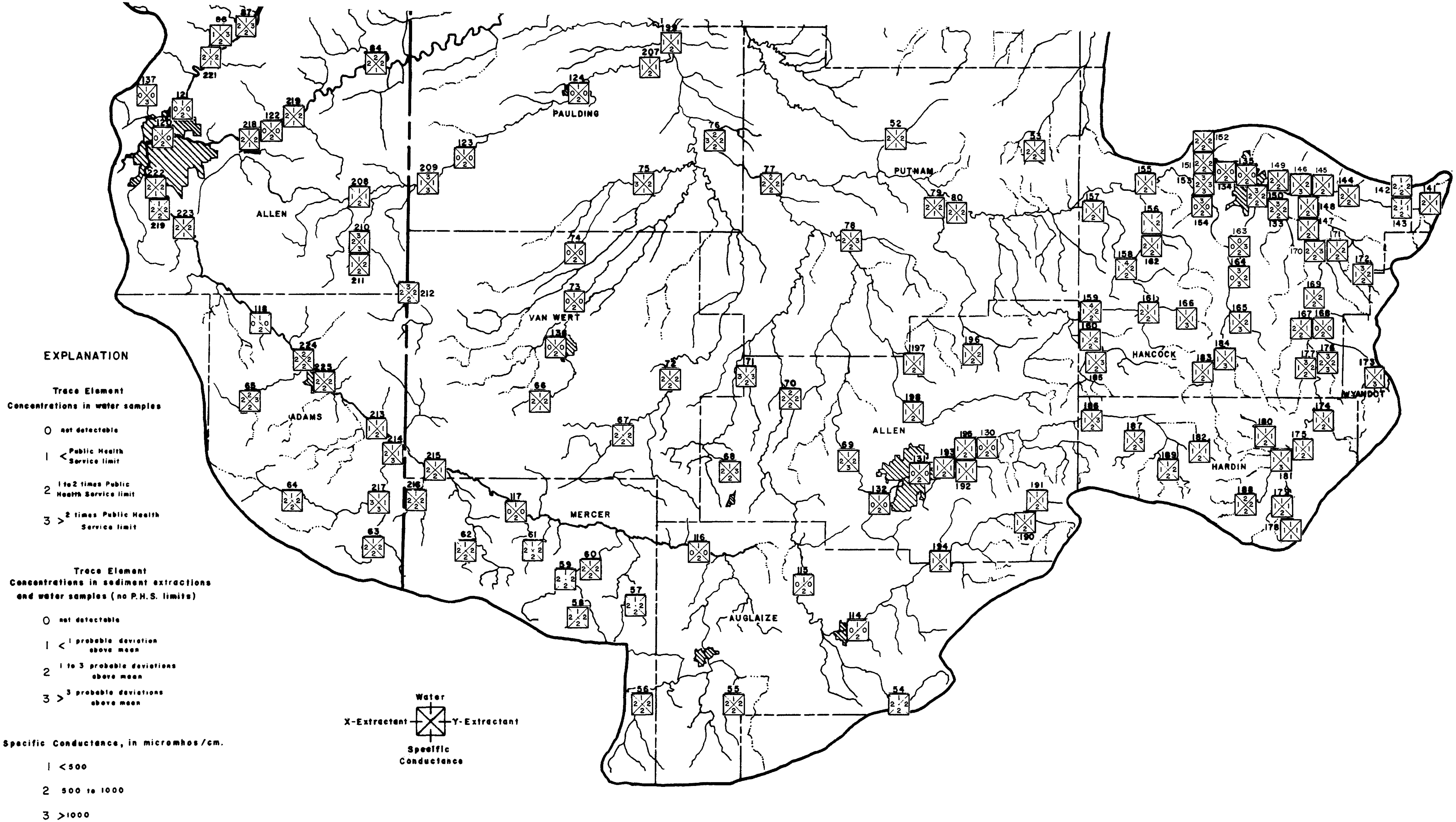
Ni Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



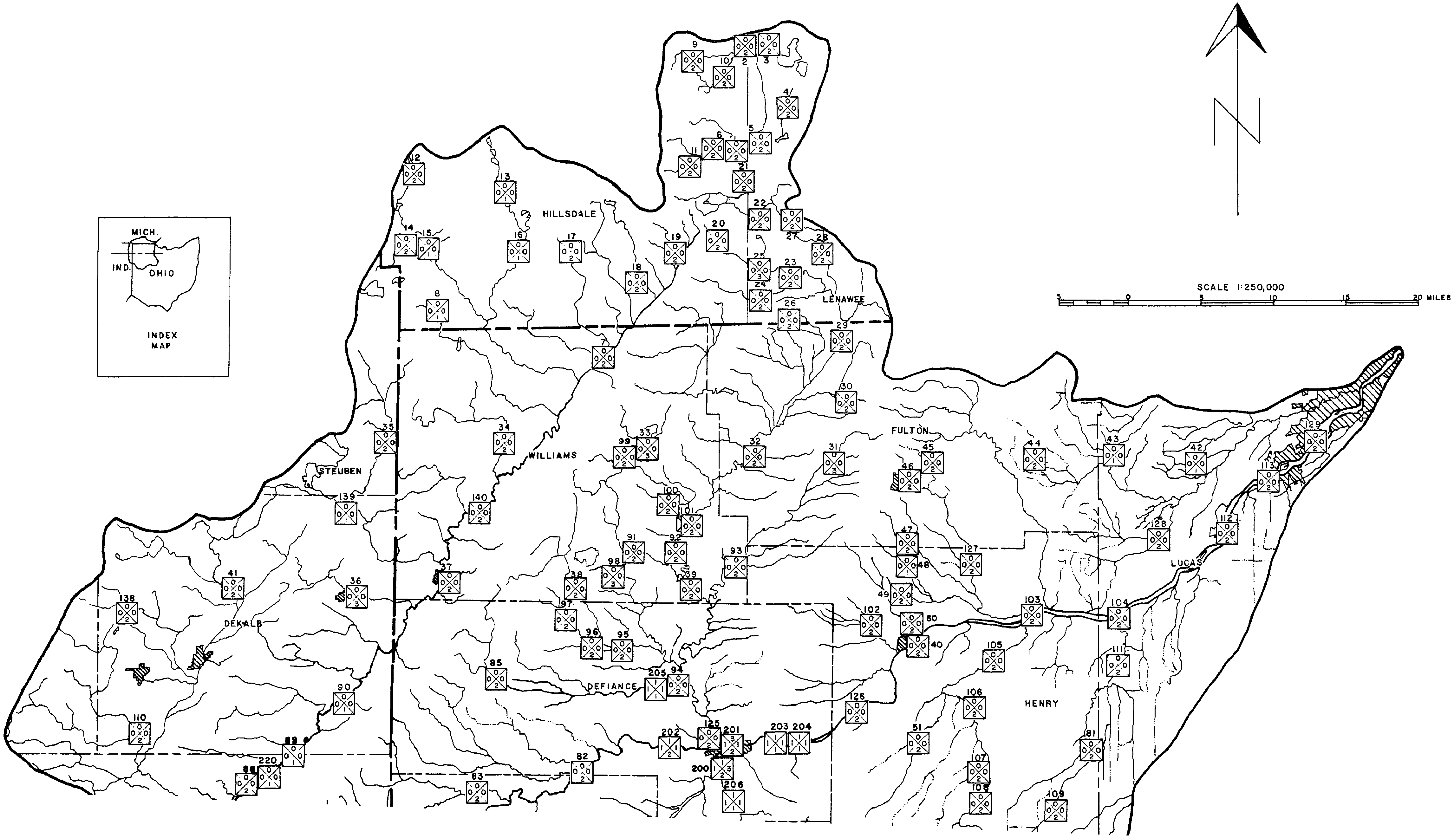
Ni Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



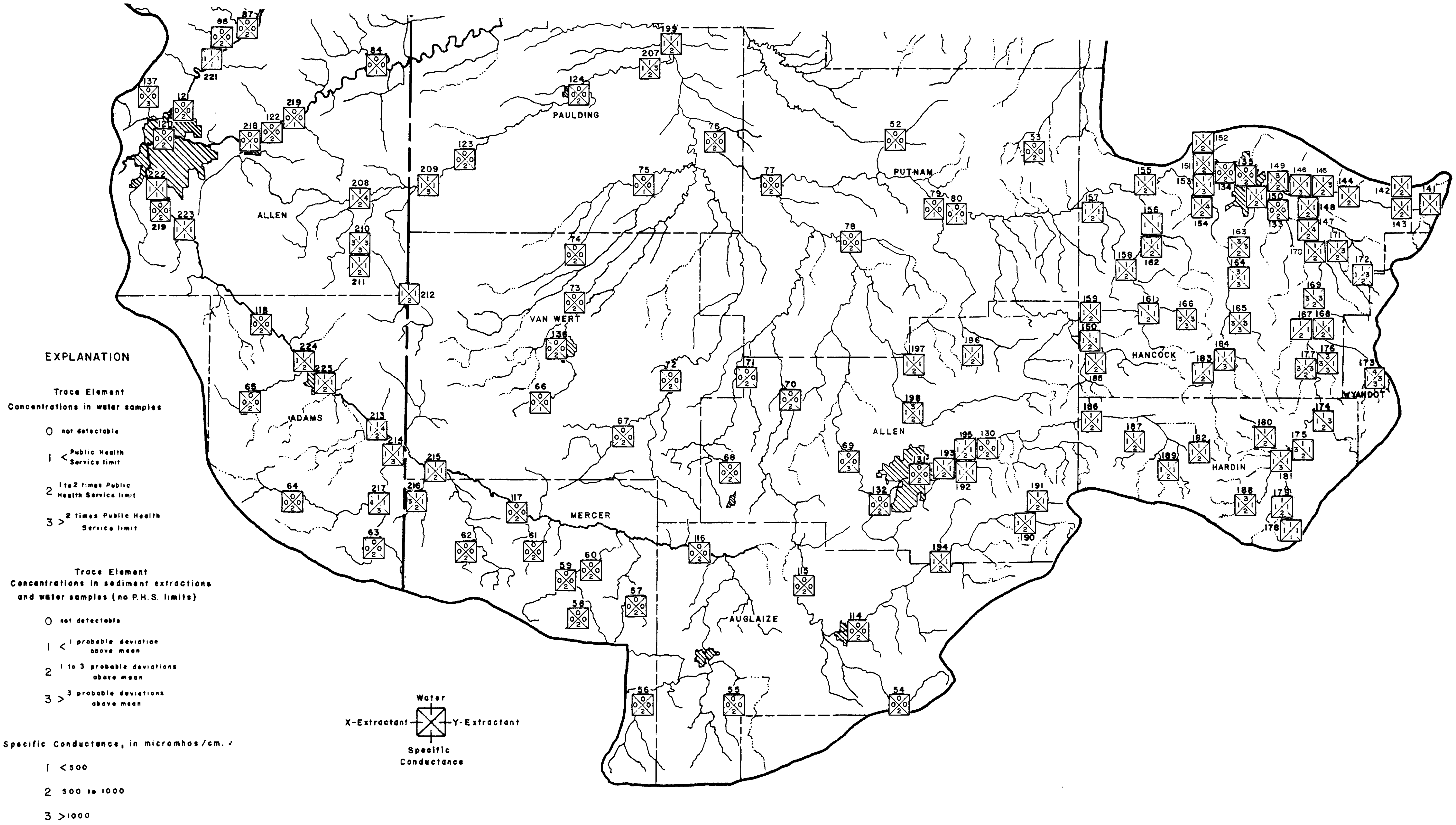
Pb Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



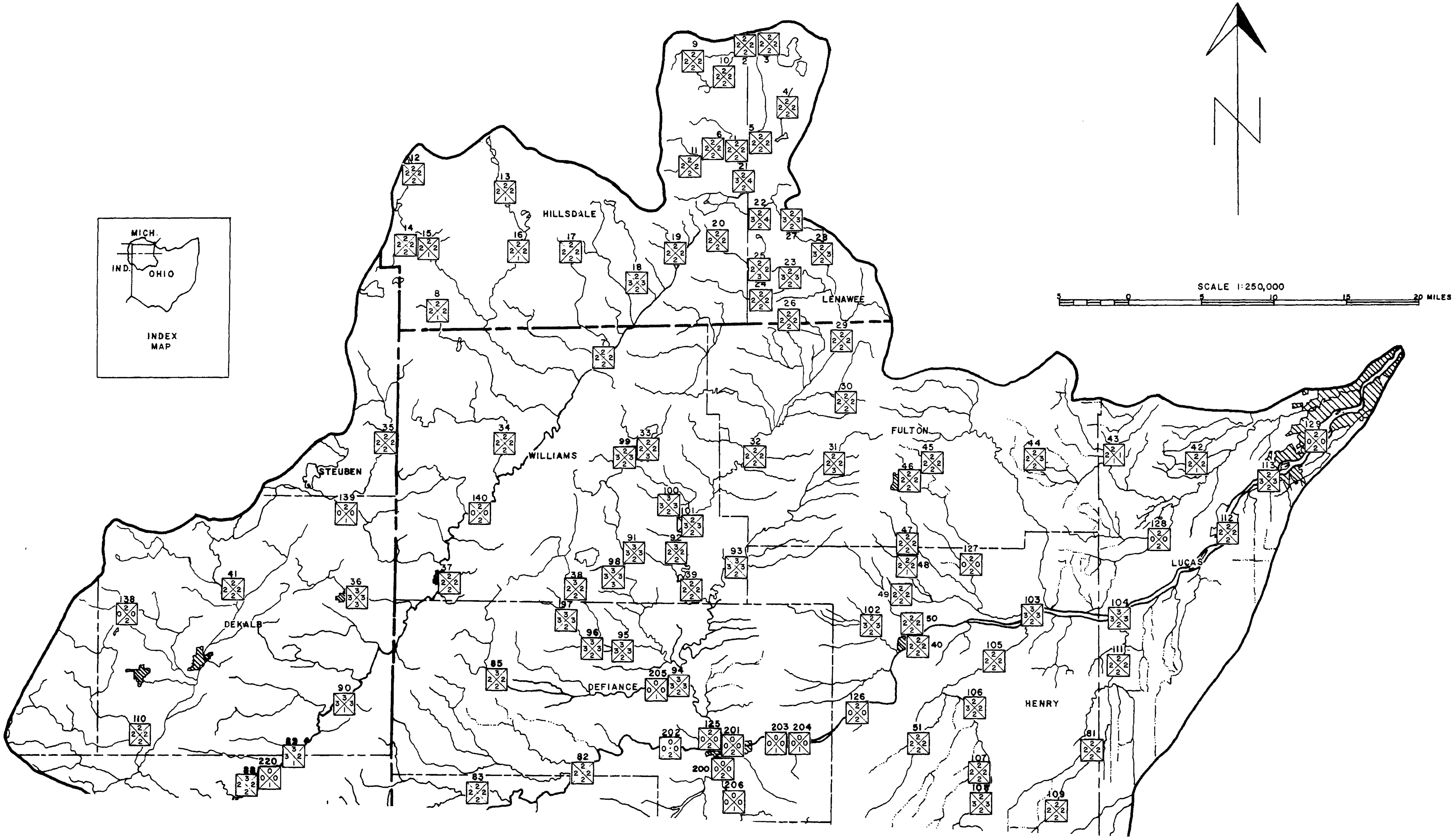
Pb Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



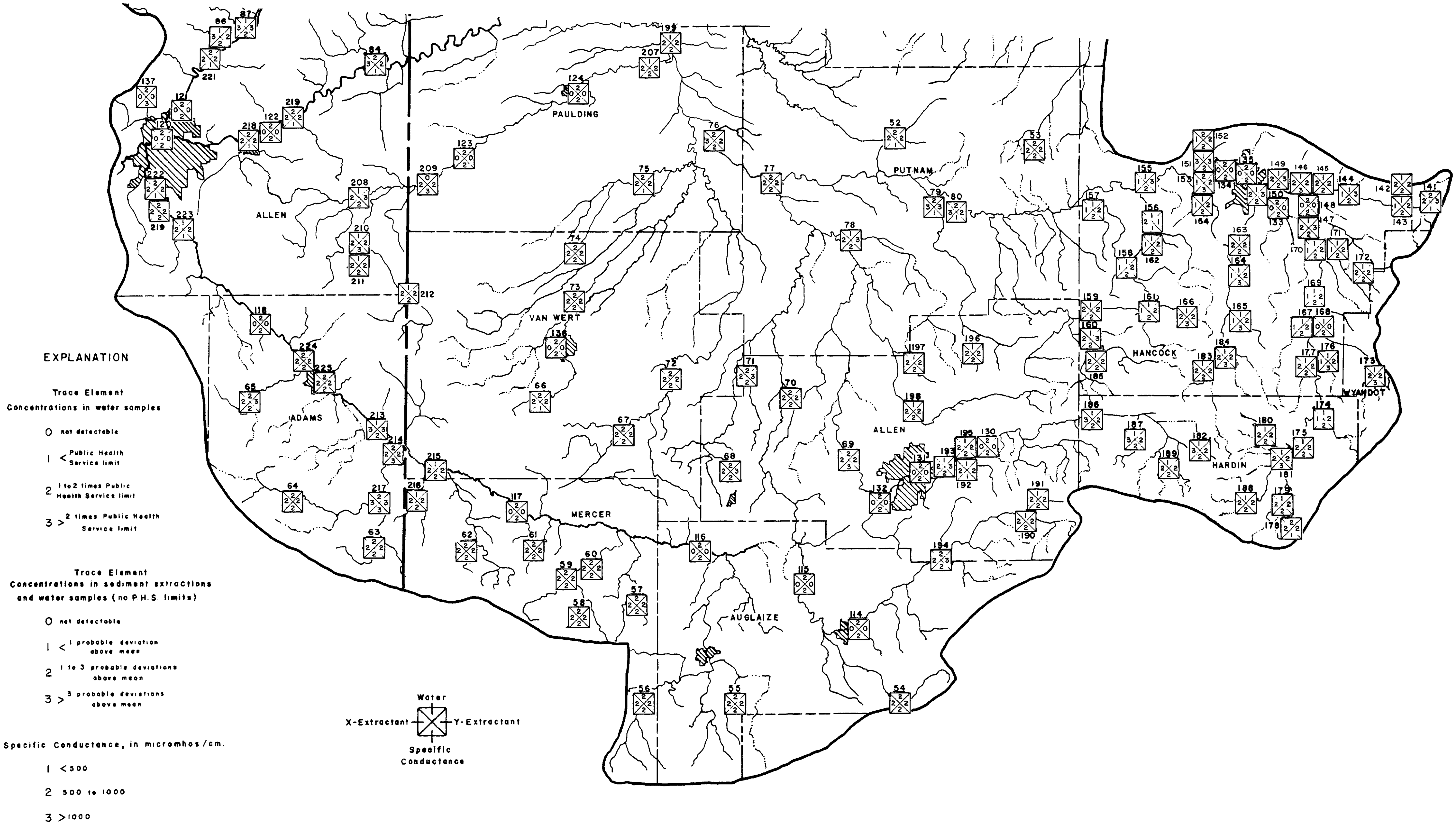
Sn Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



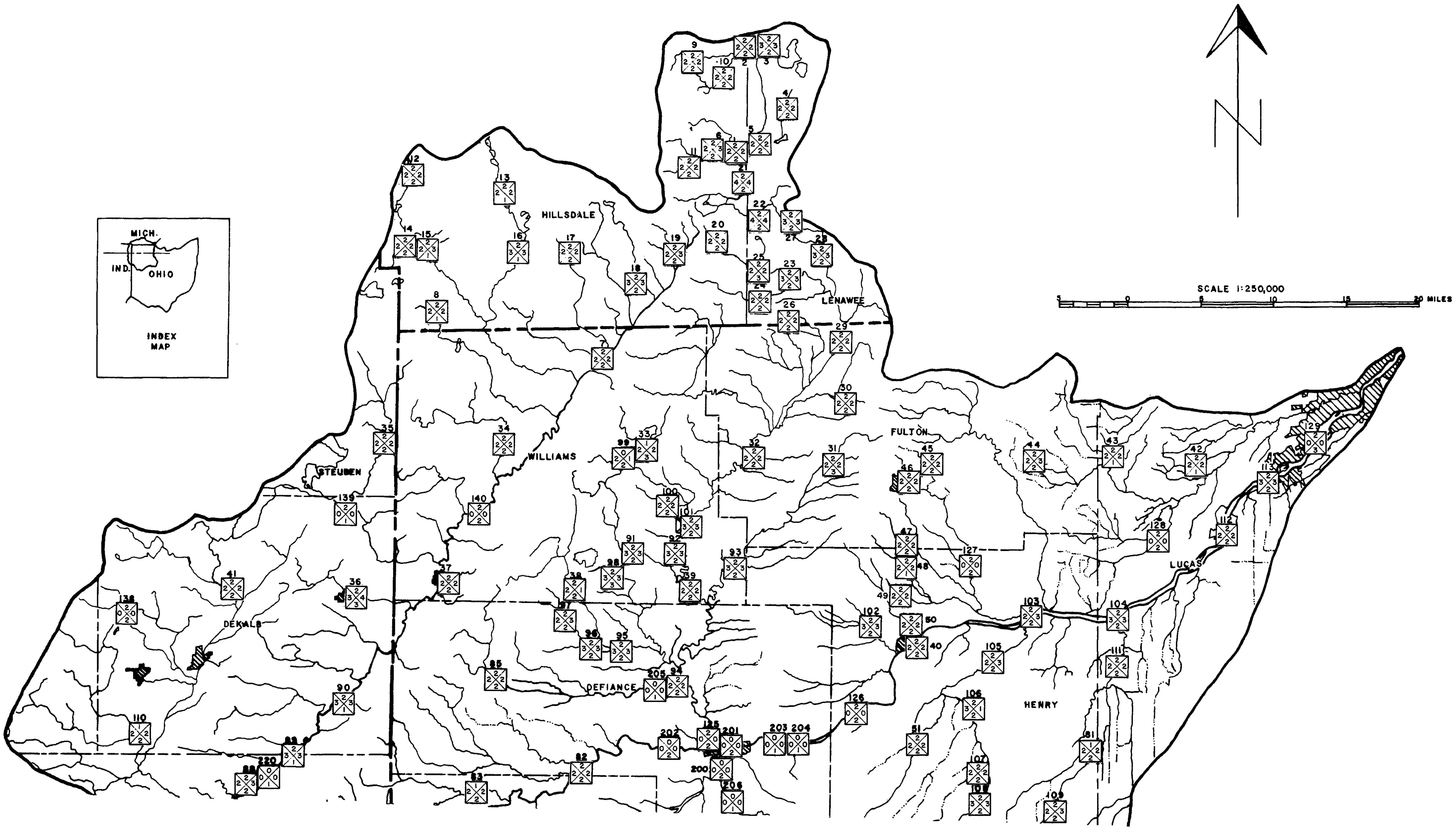
Sn Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



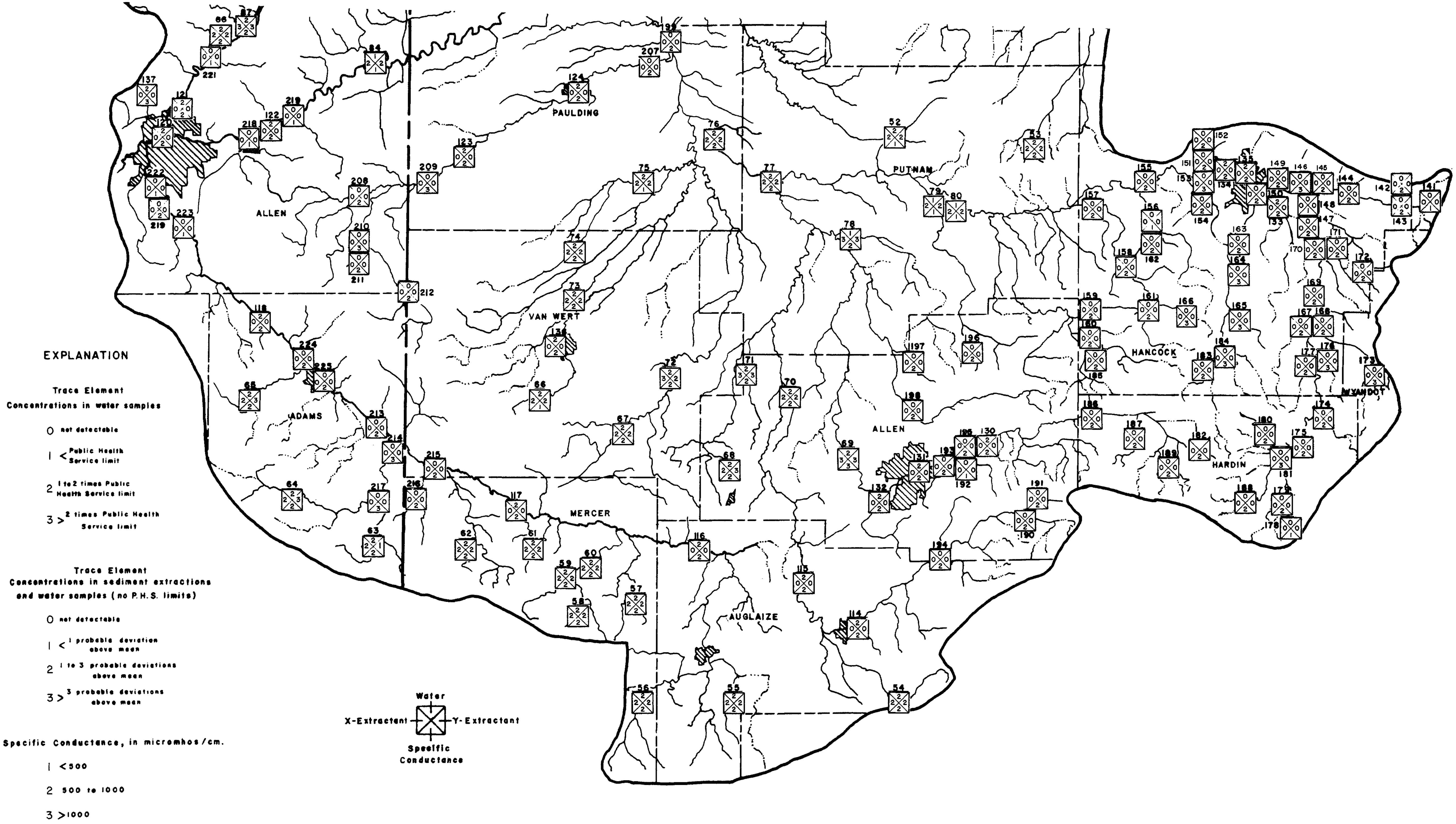
Sr Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



Sr Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)



Zn Trace Element Concentration and Distribution in the Maumee River Basin. (upper section)



Zn Trace Element Concentration and Distribution in the Maumee River Basin. (lower section)