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COLLEGE OF ENGINEERING
Department of Meteorology and Oceanography

Technical Report

AREA-WIDE DISTRIBUTION OF LEAD, COPPER, CADMIUM, AND BISMUTH IN ATMOSPHERIC PARTICLES IN CHICAGO AND NORTHWEST INDIANA: A MULTI-SAMPLE APPLICATION AND ANODIC STRIPPING VOLTAMMETRY

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ABSTRACT

AREA-WIDE DISTRIBUTION OF LEAD, COPPER, CADMIUM, AND BISMUTH IN ATMOSPHERIC PARTICLES IN CHICAGO AND NORTHWEST INDIANA: A MULTI-SAMPLE APPLICATION OF ANODIC STRIPPING VOLTAMMETRY

by

Paul Roger Harrison

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Standard air pollutant measurements such as dust fall, SO_2, and total suspended particulate for certain regions in the United States have been well documented for several years, but few measurements of elemental composition of airborne particulates have been reported. This study attempts to extend the list of basic monitoring parameters into the realm of elemental composition of aerosols on an area-wide, simultaneous basis in the southern Lake Michigan region in order to exhibit the feasibility and usefulness of such studies. In addition, more sensitive analysis techniques are further developed.

As a first attempt to exhibit the usefulness of area-wide surveys of elemental composition in aerosols in the Chicago and Northwest Indiana region, lead, copper, cadmium, and bismuth were analyzed from standard fiber glass filters obtained from the local high volume sampling networks. The sampling periods consisted of six weekdays selected from the summer months (May - August) of 1968 at nearly 50 stations which were well dispersed throughout the region.

During the analysis of these samples the highly sensitive techniques of anodic stripping voltammetry (ASV) were documented, and the physical characteristics of the cell design and hardware were further improved for routine use with multiple analysis.

Small variations in the distributions of these elements were found throughout the area except for an anomalous concentrated source of copper in East Chicago, Indiana, which reached values of greater than 10 μg/m^3. The total average concentrations were 19, 1900 and 1000 ng/m^3 for Cd, Pb and Cu respectively. The average copper concentration in the Chicago area was 230 ng/m^3 and represents the non-anomalous average. The source of the anomalous copper is not yet conclusively known. Comparisons with diffusion models where possible resulted in satisfactory results and an estimated source strength of 13 metric tons per year was proposed.

When comparisons with estimations of source strengths and distributions were tried the results suggested that lead aerosols were emanating almost completely from automobiles; whereas most of the cadmium and non-anomalous copper aerosols can be explained by fuel-burning sources. However, comparisons of the sulfur dioxide with the estimated inventories predict that the concentrations of these trace elements are higher than expected, or that the sulfur dioxide values reported by the local agencies are too low by a factor of 10, which is unlikely. This problem is not satisfactorily explained as yet although plausible arguments can be given.

Further studies in this area can be suggested and facilitated by the data and supporting information presented in this work.

1.0 STATEMENT OF THE PROBLEM

1.1 INTRODUCTION

From the academic point of view, we sometimes justify our research by the faith that something useful will result from our initial endeavors. There are some areas in which the importance and immediate need for investigation, and application of those results, are clearly in evidence. One such area is that of environmental management in general, and trace metals in particular. The importance of trace metals in the metabolic process of all living organisms is obvious, in a broad sense, but not always well documented as to cause and effect relationships, especially at low levels of chronic exposure.

It is not my purpose to review the literature of trace metals and their effect on organisms; indeed, to do so would be to review thousands of articles concerning lead alone. The purpose of this study is to investigate the concentrations and sources of three trace metals as found in atmospheric aerosols in a heavily industrialized region, their transport to some of the adjacent rural areas, and their possible effect on the trace metal content of southern Lake Michigan waters. In additinn, very sensitive analytical devices and techniques are further developed and used. Finally, some suggestions concerning the usefulness of some of the present day methods of monitoring trace metals in aerosols can be drawn from the data and remedial action is suggested.

1.2 IMPORTANCE OF TRACE METALS IN METABOLISM AND ECOLOGY

An interesting observation is that man is now passing through the metal age and is already entering a new age--the age of organics. The "plastic age" is a probable pseudonym with plastic money and other plastic substitutes being in abundance. This digression is useful only to point out how little we know about the effects of present pollutants as compared to the future problems from a, potentially, vastly larger variety of organic compounds and their possible combinations with trace elements.

Many trace metals are highly toxic to the organism, but others are necessary for life functions and without them we could not continue to exist. Simply looking at the table on a vitamin bottle will show many of the more necessary trace elements needed in man's metabolism. Phosphorus, iron, magnesium, zinc, calcium, iodine, and copper are found in the more expensive vitamin pills. What these metals contribute to the more efficient metabolic process is not completely known. In fact, larger amounts of these same elements are debilitating if not toxic.

A few examples of toxic elements being emitted directly into the environment are lead in automobile gasoline, thallium in some rat poisons, lanthanum as a defoliant, and copper as an algicide. Most are used in combination with other elements or as organic complexes.

The three metals we studied, lead, copper and cadmium, are classified in a broader unit called heavy metals, or those with a density greater than five. There are 40 elements so classified, and they are biologically important due to their inability to combine with a wide variety of organic molecules. In the organisms they can be thought of as "enzyme inhibitors," because they often combine more firmly with biologically important molecules than do the lighter metals. In fact, all the enzyme systems can be shown to be inactivated by heavy metals. In many cases the necessary amount of heavy metal needed to inhibit the system is very low (Passow *et al.*, 1961). The three trace metals studied can be classified as toxic in sufficient amounts (Threshold Limit Values for 1966). Their specific effects are still open to question and the reader is referred to the literally thousands of references (Flury *et al.*, 1934) found on the subject. More recently cadmium is under new investigations.

It is an important fact to keep in mind that the ecological effects of heavy metals found in the environment depend very much on their chemical forms. For example, if the element is tightly bound to another element or molecule it is less accessible to interactions with other chemical systems. If the element is in a neutral state and not ionized, it is more likely to react because of the diffusion barrier of the cell membrane to ionized molecules. Mercury is a good example. Valence and solubility are similarly important. Thus it is not sufficient to comment on toxicity of pollutants alone, but we must know their form in order to ascertain the transport mechanism, the likely location of deposition, and their final effect on the particular part or system of the organism (receptor) involved. This problem will become more evident as we further understand the toxicity of various forms of trace metals. An excellent introduction to the subject of heavy metals and biological processes has been written by Passow _et al_. (1961).

1.3 PREVIOUS RECENT SURVEYS OF TRACE METALS IN ATMOSPHERIC AEROSOLS FROM AVAILABLE LITERATURE

1.3.1 Junge

The literature prior to 1960 is thoroughly reviewed in the classical work of Junge (1963). In this text are studies of many areas concerning aerosols including both chemical and physical properties, such as formation and size distribution. Two sections are of primary interest concerning trace metals. In section 2.3, "Chemical Composition of Tropospheric Aerosols," there are references to Chambers _et al_. (1955). These data were taken from a United States Public Health Service study of 30 cities using glass fiber filters for a period of more than one year. These filters were analyzed for several trace metals. The study was broken into two parts. The first is concerned with urban areas of populations between 5,000,000 and 2,000,000, including seven major cities. In the second classification are five nonurban areas (nonurban defines as suburban as opposed to rural). Data are presented for sulfate, nitrate and ten metals: iron, lead, fluorine, manganese, copper, vanadium, titanium, tin, arsenic, and beryllium; see Junge's tables 33 and 34 in Tables 1.1 and 1.2. In section 5.2 of the Junge text, "Composition of Polluted Atmospheres," calcium, aluminum, iron, magnesium, lead, manganese, copper, zinc, and titanium were studied for 30 metropolitan areas in the United States and Alaska. Averages were calculated for each of these elements. From this 1956 study, the average copper value measured was 0.1 microgram per cubic meter (0.1 $\mu g/m^3$), and the lead value was 2.0 $\mu g/m^3$. There are no data for cadmium and we can probably assume that it was present only in very low quantities.

It is important to note that all of these data came from single point sampling in each area or, at very best, the averaged values of just a few stations. The state of are-wide sampling of trace metals in aerosols is best seen by noting the length of the discussion, "On the Area of Influence Around the Centers of Pollution." This discussion is less than two pages long and cites only sulfur dioxide data. As far as Junge is concerned, there had been little area-wide trace metal study prior to 1960. Two significant exceptions are Tabor and Warmer (1958, Section 1.9) in Toronto and the International Joint Commission in Detroit-Windsor (1960).

Of the three metals presented in this paper the most extensively investigated was lead. In the last decade there have been numerous articles concerning lead content of atmospheric aerosols. It was found in these studies that the

Table 1.1 Junge (1963)

TABLE 33

PARTICULATE ANALYSES IN $\mu g/m^3$ FROM CITIES HAVING POPULATIONS BETWEEN 500,000 AND 2,000,000 [a]

	Cincinnati	Kansas City	Portland (Oregon)	Atlanta	Houston	San Francisco	Minneapolis
Total load	176	146	143	137	129	104	120
Acetone soluble	31.4	18.4	32.1	24.2	18.5	19.4	15.8
Fe	4.5	4.1	5.1	3.3	4.0	2.4	4.4
Pb	1.6	1.0	1.2	1.8	1.0	2.4	0.5
F^-	0.21	0.01	Nil	0.05	Nil	0.37	0.06
Mn	0.24	0.08	0.23	0.12	0.23	0.11	0.08
Cu	0.18	0.04	0.05	0.01	0.02	0.07	0.60
V	0.09	0.002	0.009	0.024	0.001	0.002	0.002
Ti	0.06	0.21	0.24	0.12	0.29	0.04	0.11
Sn	0.03	0.03	0.01	0.03	0.02	0.02	0.01
As	0.02	0.02	0.02	<0.01	0.01	0.01	0.01
Be	0.0002	0.0003	0.0003	0.0002	0.0002	0.0001	0.0002
$So_4^=$	5.6	1.5	0.8	1.0	2.4	1.8	0.8
NO_3^-	1.0	0.6	0.2	0.8	1.0	3.4	1.3

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[a] Chambers *et al.* (1955).

Table 1.2 Junge (1963)

TABLE 34

PARTICULATE ANALYSES IN $\mu g/m^3$ FROM NONURBAN AREAS[a]

	Boonsboro	Salt Lake City	Atlanta	Cincinnati	Portland (Oregon)
Total load	68	55	71	45	86
Acetone soluble	8.7	6.2	9.3	9.0	12.6
Fe	3.7	4.1	2.7	2.4	3.6
Pb	0.1	0.1	0.9	0.4	0.3
F^-	—	—	Nil	0.26	—
Mn	0.00	0.04	0.11	0.07	0.04
Cu	Nil	0.28	0.01	0.19	<0.01
V	0.003	Nil	0.004	<0.001	0.002
Ti	0.26	Nil	0.13	0.01	Nil
Sn	<0.01	<0.01	<0.01	0.01	<0.01
As	0.01	0.03	0.01	<0.01	0.04
Be	0.0001	<0.0001	0.0002	0.0001	0.0001
$SO_4^{=}$	0.3	<0.01	0.5	1.9	0.4
NO_3^-	—	—	—	0.7	—

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[a] Chambers *et al* (1955).

probable source of lead in the atmosphere is due to emission of lead halide particles from motor exhaust. Each gallon of gasoline contains two grams of lead as tetraethyl lead which is carried out of the exhaust system by halogens, also added to gasoline as ethylene dichloride and dibromide in the ethyl fluid mixture. Almost all of the studies cited were taken from a single point sampling or were not simultaneous. Recently there have been a few papers concerning more than one simultaneous sample.

1.3.2 Nashville Study

In 1960 and 1961 there were several articles presented concerning a study in the Nashville, Tennessee, area (Nashville, 1960-61). This study is probably one of the most thorough attempts at discerning the density of sampling stations and the sampling gate that is optimum for a compromise between number of stations and sample period. The concept is that the larger the number of stations the shorter the sampling time needed to realize a representative description of the area. One hundred and nineteen stations were well distributed within Nashville and surrounding districts. Several subsets of stations were selected for the use of various criteria. Virtually no trace metals were analyzed in this study, however, and the information is applicable to our work in that if one is designing such experiments he could do well to read these articles and design his experiment according to the results of this study, as opposed to using sampling stations already in existence.

1.3.3 Atkins

Atkins (1970) used a three point sampling network in the San Francisco Bay region, of which one point was very close to traffic, the second was two and one half miles from a freeway, and the third was five miles from a freeway. At each station, high volume sampling of suspended particulate, dry fallout, and rainfall were measured, and lead was extracted by the dithizone technique. Atkins stated that he was able to measure as little as five minute samplings close to the highway, that is, ten cubic meters of air. However, his data were presented only as 30 minute averages. This work is timely but has some severe limitations. First the sampling was not done over a 24 hour period. Most of the data were taken during waking hours of 5 a.m. to approximately 6 p.m. As most meteorologists know, and have shown quite explicitly, this is probably insufficient to show the diurnal variations as well as the dependence upon climatological factors. In addition, it is obvious that insufficient meteorological data were taken. A topographical map of the region was not presented nor was wind direction.

The study did show that less lead was found when farther from the source of lead aerosols, both in rainfall and fallout, and in suspended particulate. Also, a dependence on traffic flow and atmospheric mixing was shown; however, proper parameters were not measured and these data cannot be sorted out easily. It is interesting to note that the solubility of lead particulate increased as one got further from the source, that is, the traffic. Since rainfall intensities were not taken, any conclusions concerning condensation nuclei by lead particulate or of the scavenging process is highly suspect.

An additional and potentially serious problem found in many other papers presenting lead values is that a chloroform method of extraction was used with subsequent use of a dithizone indicator. (The lower limit of sensitivity in this study is said to be 0.5 μg.) In some cases, this method seems to be in error and may underestimate the amount of lead present (NASN, 1966; Kneip, 1970). We will discuss this matter more extensively later in the paper.

1.3.4 Lundgren

An additional, pertinent reference to lead monitoring is by Lundgren (1969). In this study samples were taken for four hour sampling periods during a 15 day period at a station located 50 miles from Los Angeles, California. This would imply that the aerosol would be aged somewhat if one neglects any local sources. The samples were taken on glass fiber filters, and total particulate, particulate sulfate, nitrate, and lead concentrations were measured. In addition, size distributions were measured for a 16 hour period between 4 p.m. and 8 a.m. The lead was analyzed by atomic absorption spectroscopy. A 24 hour total suspended particulate and total sample was run for control with some losses found. In addition, a four stage impactor followed by a filter was used for lead and the other measurements listed above. The average suspended particulate value was 100 $\mu g/m^3$, and the average lead concentration was 0.6 $\mu g/m^3$. One significant factor to observe is a variation in the lead concentration between the four hour time gates, and the mass-median diameter also seems larger than the average values observed near the sources. This is explained by the author to be the coagulation effects due to the aging of aerosols. The average mean diameter is 0.5 microns for this study. Several days were observed having a particulate lead mass mean diameter of 1.0 microns and disagrees somewhat with recent data in our sample area (Gillette, 1970). This larger than average mean diameter occurred mostly during the summer days of high smog. Again, this was single point sampling.

1.3.5 McMullen, Faoro, and Morgan

One cannot discuss trace metals in atmospheric aerosols without mentioning the National Air Sampling Network (NASN) analysis (USPHS, 1968). These data provide averages and frequency distributions for about 30 pollutants including 17 trace metals as well as gases and solids. There is little information available from these studies concerning the seasonal effects of trace elements and the effects of the station location within the urban areas.

A more recent supplement to this work is presented by McMullen, Faoro and Morgan (1969) of the United States Department of Health, Education, and Welfare. Their approach was to average a three month period, consisting of 30 nonurban stations and 117 urban stations. Analyses of ammonium, nitrate and sulfate ions, and metals were completed. A significant change in procedure was that a low temperature ashing process was used with the metals. Previous analysis used a high temperature procedure to free the metal ions. The authors state that the loss was decreased by a factor of five for some metals, especially for volatile materials such as lead, zinc, and cadmium. Thus they indicate that there is a possibility of lack of sensitivity, if not accuracy, in previous studies. Copper, lead, titanium, and vanadium are outstanding insofar as both the urban and nonurban stations seem to have two overlapping but distinct groups of concentrations. The distinct vanadium concentrations are said to be geographical, probably because of the variability of domestic fuels used in heating. That is, imported fuels often contain a higher percentage of vanadium than do those of local or domestic origins.

Aside from monitoring seasonal variations, the classification of stations was broken down into two large areas named "urban and nonurban." The nonurban stations were further broken down into three areas: "remote, intermediate, and proximate." Proximate stations are technically nonurban but are obviously influenced by their closeness to large urban centers, intermediate stations are relatively close to populated areas but are also located in agricultural communities, and remote stations are furthest from large population and industrial centers. Their significant conclusions concerning trace metals are that nickel, iron, manganese, ammonium ions, and nitrate ions are present at constant percentages in the remote and intermediate categories, the implication being that these materials are probably present in the background. Copper and sulfate ions seem to be in constant amounts in the proximate and urban categories, and indicate that these substances are probably from urban areas and are advected to the proximate areas. In their final remarks McMullen _et_ _al_. point out that the nonurban stations have ranges of materials in airborne aerosols from one half to one tenth those found in urban stations. However, the proximate stations nearest the cities range from two to ten times the concentrations of those of the remote stations. This is the same ratio given for urban versus nonurban. From these values we can gain insight into the rate decrease in values of pollution materials from urban areas as they advect to the nonurban areas. For two of the metals studied we can see that this is probably true. See Table 1.3.

The copper values are the same in the urban and proximate stations, decreasing markedly to the intermediate and remote. Lead decreases fairly rapidly at an increasing rate from the urban to the nonurban areas. Although the filter pads were analyzed for quarterly values or averages, they were not presented as seasonal values. The value of this paper to our study is that one can gain additional perspective into the drop off values of various pollutants, in this case trace metals, as one progresses from urban to nonurban to rural locations, as well as giving us real numbers to compare.

Table 1.3 SELECTED PARTICULATE CONSTITUENTS AS PERCENTAGES OF GROSS SUSPENDED PARTICULATES (1966 - 1967).[1]

	URBAN		NONURBAN					
	(217 Stations)		Proximate (5)		Intermediate (15)		Remote (10)	
	$\mu g/m^3$	%	$\mu g/m^3$	%	$\mu g/m^3$	%	$\mu g/m^3$	%
Suspended Particulates	102.0		45.0		40.0		21.0	
Benzene Soluble Org.	6.7	6.6	2.5	5.6	2.2	5.4	1.1	5.1
Ammonium ion	0.9	0.9	1.22	2.7	0.28	0.7	0.15	0.7
Nitrate ion	2.4	2.4	1.40	3.1	0.85	2.1	0.46	2.2
Sulfate ion	10.1	9.9	10.0	22.2	5.29	13.1	2.51	11.8
Copper	**0.16**	0.15	**0.16**	0.36	**0.078**	0.19	**0.060**	0.28
Iron	1.43	1.38	0.56	1.24	0.27	0.67	0.15	0.71
Manganese	0.073	0.07	0.026	0.06	0.012	0.03	0.005	0.02
Nickel	0.017	0.02	0.008	0.02	0.004	0.01	0.002	0.01
Lead	**1.11**	1.07	**0.21**	0.47	**0.096**	0.24	**0.022**	0.10

[1] After McMullen et al. (1969).

1.3.6 Kneip, Eisenbud, Strehlo, and Freudenthal

A recent study, and probably one of the more complete works, is by Kneip, Eisenbud, Strehlo, and Freudenthal of the New York Medical Center (1969). The researchers took weekly samples for a full year using 20 x 25 cm (8 x 10 inch) glass fiber filters (Hi-Vol) at three and sometimes four stations located on Manhattan Island, New York. Again, an ash method was used for the trace metals and the analysis was by atomic absorption. The trace metals involved were lead, vanadium, cadmium, chromium, copper, manganese, nickel and zinc. Lead-210, total particulate, and benzene and acetone soluble organic materials were also determined. A fair amount of meteorological data was also used and seasonal, and source influences were examined. Significant inverse correlations of temperature with suspended particulate, vanadium, and nickel; and of average wind speed with lead, copper and cadmium; and direct correlation of temperature with lead, copper, and cadmium; point out the great necessity of properly measuring and presenting meteorological data with any of these urban studies. Urban areas are so complicated with respect to meteorological conditions and the profusion of source strengths and locations as to make it difficult to readily determine the source of trace metal pollutants by simply measuring trace metals alone. In this study, meteorological variables may not be quite as important because of the time gate of one week. However, observations that lead, copper, and cadmium seem to be higher in the summer than in the winter can be explained by the higher ventilation of the city in the winter than in the summer. In fact, their data bear out this conclusion. A variable not presented in any of these papers is ratios. That is, even though the ventilation rates may be different, if the sources are the same and are unique, such as coal or oil, the ratios should remain constant for all seasons. This would be true even if the rates of consumption of the materials at the pollution source were different. In fact, taking the cadmium to copper ratio we find a value of 0.1. This is within the error limits of the ratio of cadmium to copper present in fossil coal fuel. This average is represented within 75% at all three stations and is within the error limits of the determination of the metals themselves. The average concentrations of lead, copper, and cadmium are 3.1, 0.2, and 0.02 $\mu g/m^3$, respectively, for the three Manhattan Island stations.

A significant development in this work is that the lead concentrations seem to be 2 to 2.6 times higher than those of the NASN studies. This is an observation that we have made especially for low level rural areas. In a few hundred values, both in urban and nonurban areas, and in an intrusion of polar air we have found no less than 0.1 $\mu g/m^3$ of air taken over as little as a two hour average. This may be due to the extraction and ashing methods mentioned previously by McMullen _et_ _al_. (1969). From this study some conclusions can be made, but isopleths of concentrations cannot be drawn nor can a realistic comparison with rural or "non-polluted" areas be made. In other words, to this date there have been very few simultaneous studies of adjacent areas containing industrial, urban and rural areas.

1.3.7 Lee and Jervis

In 1968, Lee and Jervis published results for 13 elements in 30 samples in Toronto measured by neutron activation analysis using a NaI crystal. These metals are calcium, iron, sodium, zinc, bromine, arsenic, copper, silver, antimony, cobalt, scandium, mercury, and lanthanum, ranked in order of decreasing average concentration.

1.3.8 Tabor and Warner

An earlier study by Tabor and Warner (1958) is a study of 28 cities for 17 metals: antimony, barium, beryllium, bismuth, cadmium, chromium, nickel, tin, titanium, vanadium, and zinc. Iron, zinc, copper, lead, and manganese as presented represent an order of decreasing concentrations; that is, iron is the most abundant in the city study. The technique of analysis used was emission spectrometry. The criticism, again, is that the samples were not simultaneous and adjacent. In this study cadmium ranged from 2 to 100 ng/m^3, lead from 0.33 to 17.0 µg/m^3, and copper from 0.05 to 30 µg/m^3.

1.3.9 Brar, Nelson *et al.*

Brar, Nelson *et al.* (1969,1970) published the results of a study involving over 20 stations in the city of Chicago in which several trace elements were measured by neutron activation analysis. By virtue of using neutron activation analysis two presentations were secured, one for short-lived isotopes of trace metals and the other for longer-lived isotopes of trace metals. Twenty-one metals in all were presented. The samples were taken in one simultaneous 24 hour period in April, 1968. All stations, except that at Argonne National Laboratory, were in the urban or industrial regions of Chicago. Although isopleths were not drawn, the data could lend themselves to the drawing of a few. No meteorological data are presented with the papers.

The significant points made in the Brar _et_ _al_. paper are that (1) area-wide samples need to be made to show the variations and true concentration within an urban and industrial region, and (2) that simultaneous measurements are also necessary. Since no highly localized sources were found, and since only one day was presented, there could not be much meteorological analysis. Despite this limitation, this paper is an excellent presentation of a pioneering work to attempt simultaneous area-wide surveys throughout a metropolitan area.

It should be pointed out that a severe limitation for this type of study is the inability to find suitable, clean filter paper to be used on standard 20 x 25 cm high volume samplers that are commonly used throughout the United States. If suitable filter paper was available we could easily find many trace elements from pollution and natural sources by distributing these filter papers to local control officials for exposures, and thus minimize the sampling program for the researcher.

Since the institution of our program in May of 1968, contacts between the University of Michigan and Argonne National Laboratory have been made, and this and other problems concerning simultaneous area-wide sampling have been explored (Harrison *et al*., 1970).

1.3.10 Research Suggested by Literature Surveyed

The previous paragraphs discussing work presented in papers and journals to this date point out three major needs. One is for sampling grids or networks as opposed to the relatively few National Air Sampling Network and CAMP stations in each metropolitan area. Second is the need for more sensitive methods of analysis, and third is the careful monitoring of meteorological parameters pertinent to the transport and removal process.

1.4 NECESSITY AND DESIRABILITY FOR SAMPLING GRID NETWORKS

It is clear from the discussions by Kneip, McMullen and others that there is a great desirability by researchers and control personnel to gain a more detailed knowledge of the areas under study. For example, Jutze and Foster (1967), in their article concerning the recommended standard method for atmospheric sampling of particulate matter by high volume filters, recommended a compromise between urban areas and industrial areas; the placement should be as representative as possible for the total area, and so forth. In other words, most National Air Sampling Network stations, but not all, are placed to procure the most representative rather than the most severe concentrations of atmospheric pollutants in atmospheric aerosols. This attempt probably satisfies some receptor criteria, and due to the practical considerations of economics, is most likely the best compromise from all points of view. However, as analytical methods become more sensitive and more available to the control officers and local air pollution officials, there should be a re-examination of this concept as a national monitoring network. In this following work it will be shown that the National Air Sampling Network is not detecting some important pollution sources in an urban-industrial area, and that, in some cases, even the data obtained may be suspect due to the lack of sensitivity of the analytical procedure, e.g., lead. It is suggested that when a method becomes available studies should be instituted using a reasonably sensitive grid over a reasonable number of days under various meteorological conditions and should be done periodically and in great detail. The impetuses for this type of study are (1) it will find sources deleterious to the health of adjacent urban areas, or rural areas for that matter, (2) it will provide detailed information with which to model air pollution incident contingency plans, and (3) it will also be available for both industrial and scientific analysis and for reference for legal liability or lack thereof. A severe drawback is the chance that certain industries will change their process during the sampling periods, or that the processes may not be continuous in the first place and would be missed.

However, most industries of any size cannot, and probably will not, change their methods of production even for a pollution study unless the study shows that there is pollution in sufficient amounts to suspect their emission of some unpleasant or undesirable trace metal or other pollutant. If this is the case, I am sure, perhaps naively so, that industry and government and the general public would like to know as soon as possible. Some National Air Sampling Network stations can be relocated as a result of these studies in order to monitor any changes, especially increases, in certain types of trace metals. In other words, the stations should be located according to this type of survey in order to sample the desired parameters or pollutants, rather than based upon some good but subjective criteria. One of the major problems with the National Air Sampling Network and CAMP stations for that matter, is that the method of analysis used is usually not very sensitive and requires long periods of preparation. The presentation of the following results will probably illuminate and support this argument.

1.5 THE NEED FOR MORE SENSITIVE ANALYTICAL METHODS FOR ANALYZING TRACE METALS

We have mentioned previously the prevalent use of neutron activation analysis for trace metals. We have also discussed the problem of the lack of clean filter papers for routine use, as the glass fiber filters are used in the high volume sampling networks. What is desired is a clean filter paper for neutron activation analysis (or any other type of analysis), and a method of great sensitivity that can be used with the present glass fiber filters. Neutron activation analysis is more sensitive for some trace metals than for others, but, again, is not generally available because of the necessity for special filter papers and a nuclear reactor. Since atomic absorption and wet chemistry were not used in our study, we will not discuss them except to say that these methods are usually more time consuming and less sensitive.

Three to six trace metals can be measured by a relatively new development in anodic stripping voltammetry (ASV). This method (instrument) using a composite mercury graphite electrode can measure bismuth, indium, lead, copper, cadmium, and zinc (plus a few others with special reagents) to sensitivities of less than one nanogram *in situ* (Matson, 1968). Routinely we have analyzed less than one half a cubic meter of air for urban areas with adequate sensitivity. We have the capability of measuring only a few trace metals, but with minimum preparation and great sensitivity. It is, however, a great step forward for these three to five trace metals.

In addition, we have discovered, and are reinforced by Kneip *et al*. (1969), that the chloroform extraction and dithizone technique for lead is, in all probability, in error and is giving lead values that are too low. The probable cause for this error is that a great deal of sample preparation is required prior to using the indicator. This is not to criticize the analyst but to criticize the method of analysis. We will discuss both method and sensitivity and sample preparation of anodic stripping later in the text and Appendix V.

Thus one of the most severe restrictions in the study of airborne trace elements is the unavailability of sufficiently sensitive analytical techniques, and problems with high blanks in the sampling materials. We propose, therefore, to offer ASV as a solution for at least four trace elements using regular glass fiber filters and many more elements by neutron activation analysis if a suitable filter paper is found (Brar and Nelson, 1969; Dams _et_ _al_., 1970).

Finally, the question arises as to whether urban pollutants really do influence the adjacent areas and to what extent. The answer can lie within some studies involving ragweed pollens exhibiting evidence of their advection over large distances.

1.6 EVIDENCE OF LONG RANGE ADVECTION BY RAGWEED POLLEN STUDIES

If advection of pollen does indeed occur over substantial distances, with west winds the effect of Lake Michigan should be discernible to the east. On days with high pollen emission the morning peak of emission will occur over Wisconsin and over lower Michigan, but not over Lake Michigan. As these concentrations are advected eastward, the effect of the lake should appear at Ann Arbor as an afternoon minimum (no pollen from Lake Michigan) followed by a rise in the early evening as the morning peak of Wisconsin pollen arrives. A series of airplane soundings taken at Ann Arbor during the period of August 27-31, 1962, were analyzed for evidence of this lake effect. The measured pollen concentrations at 2000 ft. for August 27, 28 and 30 are shown in Figure 1.1; unfortunately no flight was made at about 20 h on August 29 so the earlier observations for that are not shown. The advection distances are as follows:

Milwaukee to Ann Arbor - 330 km ,

Muskegon or Holland, Michigan, to Ann Arbor - 210 km .

The wind speeds and directions given are an average of the 850 mb values for Green Bay, Wisconsin, and Flint, Michigan. The results of the analysis are given in Table 1.4 Figure 1.1 shows that an afternoon minimum did indeed occur on each of the three days for which appropriate concentration measurements were available. The wind data and other information in Table 1.4 are entirely consistent with the thesis that the afternoon minima are due to the absence of pollen emission over Lake Michigan. It should be emphasized that the time of maximum concentrations in Figure 1.1, being for 2000 ft., need not and do not agree with the times of surface high values given in Table 1.4.

The table thus indicates that for this period of W to WSW winds an afternoon maximum in pollen concentrations attributed to Lake Michigan did indeed occur. No such maximum should occur, on this basis, with S or SE winds, but unfortunately no airplane observations were made with such winds.

Table 1.4 Analysis of Wind Transport of Pollen from Wisconsin, over Lake Michigan and southern Michigan, to Ann Arbor as Observed by Airplane Concentration Measurements at Ann Arbor, August 27-30, 1962

Date	Wind		Advection Time to Ann Arbor (hrs)	Time of morning High Conc. at surface	Time of Advection High Conc.	
	Speed (km hr^{-1})	Dir. (deg.)			Calc.	Obs.
1962						
Aug.27	29	280	11	0930	2030	20
Aug.28	29	280	11	0930	2030	20
Aug.29	32	273	10	1000	2000	no data
Aug.30	32	241	10	1030	2030	20

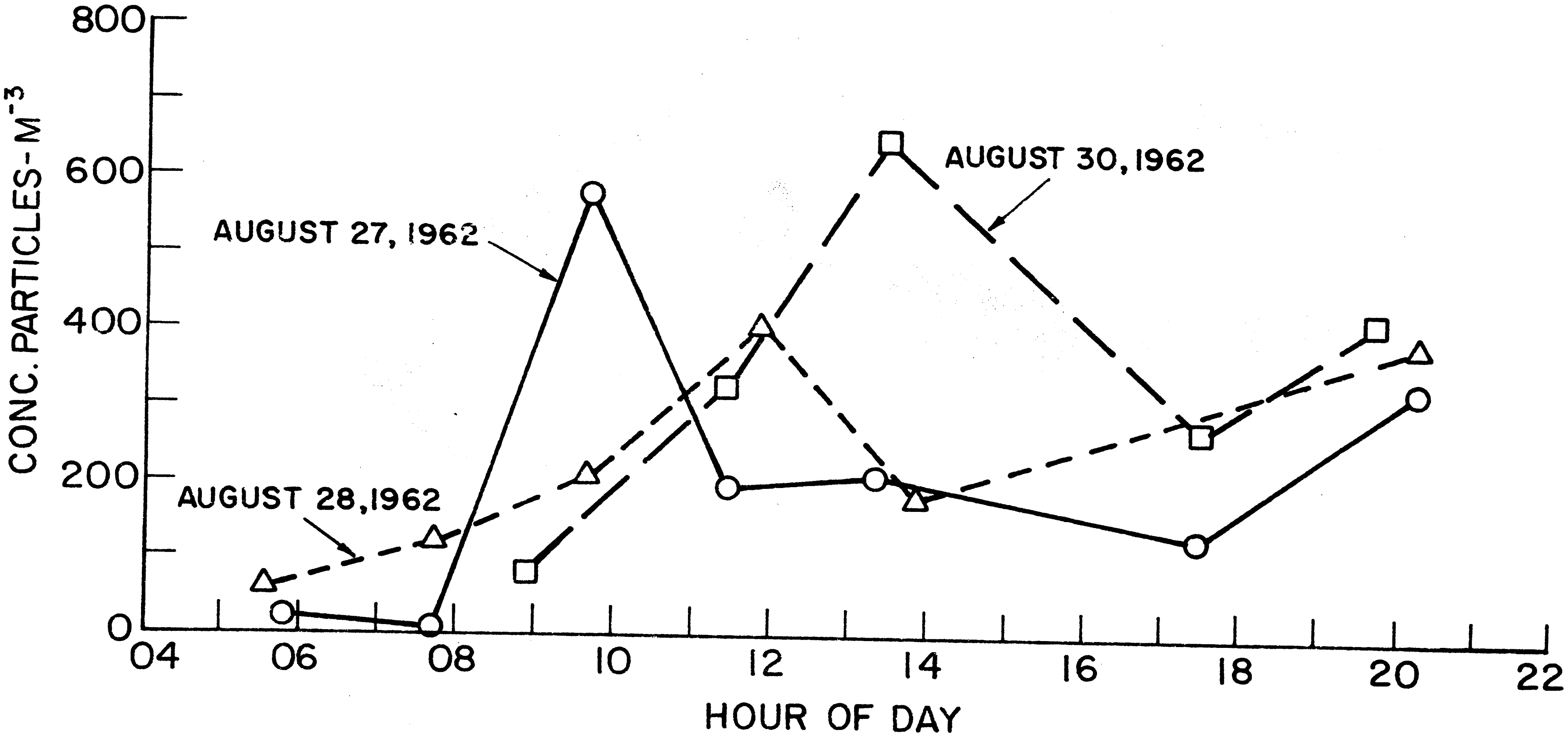


Figure 1.1: A time series of pollen concentrations at 2000 ft. over Willow Run Airport (1962).

2.0 THE EXPERIMENT

2.1 THE EXPERIMENTAL STUDY OF LEAD, COPPER, AND CADMIUM AND RELATED INFORMATION IN THE SOUTHERN LAKE MICHIGAN BASIN (CHICAGO AND NORTHWEST INDIANA)

Figure 2.1 shows the area under study and Figure 2.2 presents a greater detail of this area plus the sampling locations and the station key.

The most important differentiating factor for the Chicago--Northwest Indiana area as compared to other metropolitan areas is that it is adjacent to one of the major fresh water sources in the United States. Because of their proximity to Lake Michigan, Chicago and Northwest Indiana are subject to unique meteorological and, thereby, pollution conditions. In the Chicago area alone there are approximately 6.25 million persons, and in Northwest Indiana about 0.75 million, relative to the 1960 census. This represents about 7 million persons in an area of about 200 square miles, supporting about 5,000 major industries as listed in the _Metropolitan Chicago Industrial Development Guide_ (1968), many of which are shown in the foldout in Appendix VI. Noting the industrial areas and the station key (Figures 2.1 and 2.2), we can see that the sampling network covers the area quite well. One criticism of the network is that most of the outlying stations are found in small cities and towns. This would prejudice the lead data, especially, and would make us say that the outlying

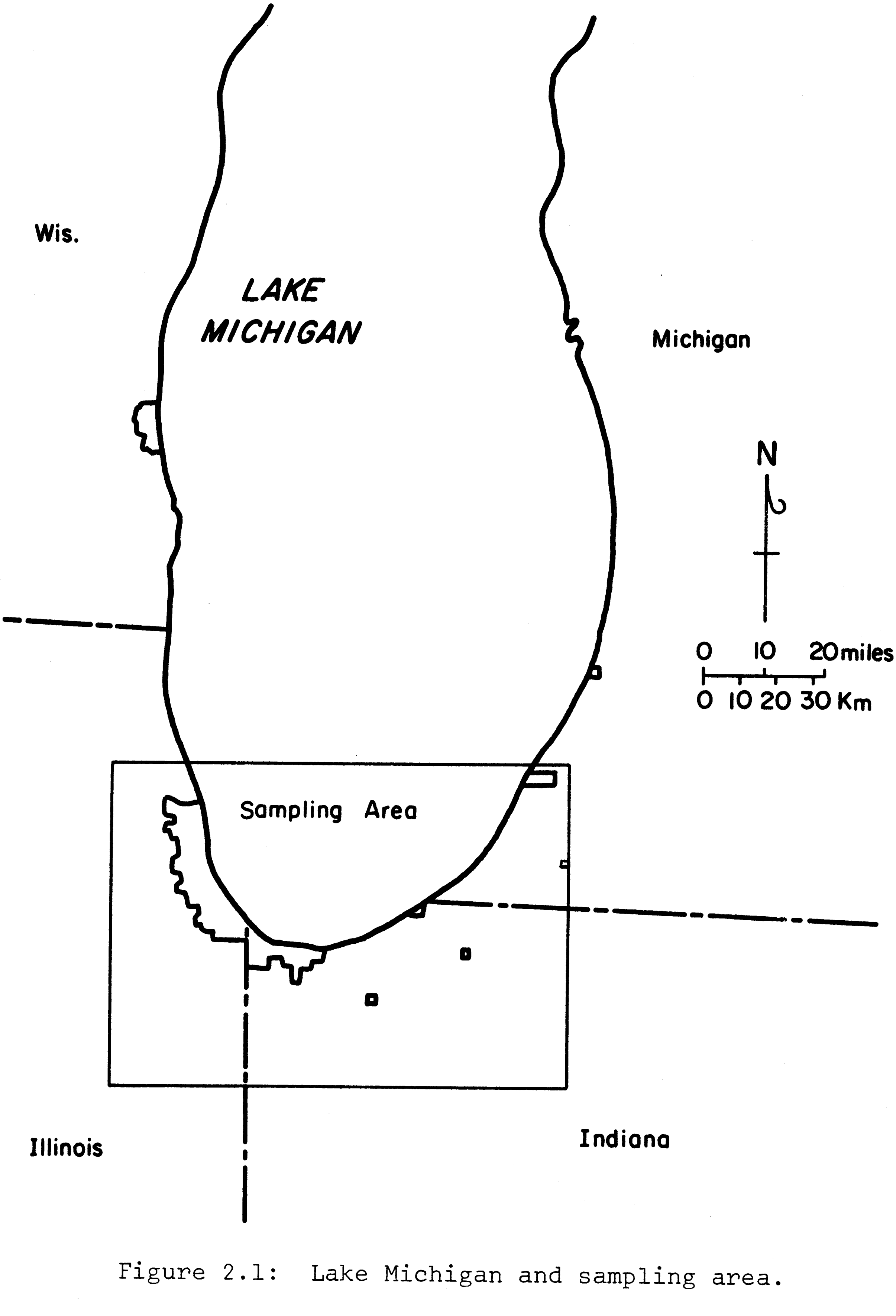


Figure 2.1: Lake Michigan and sampling area.

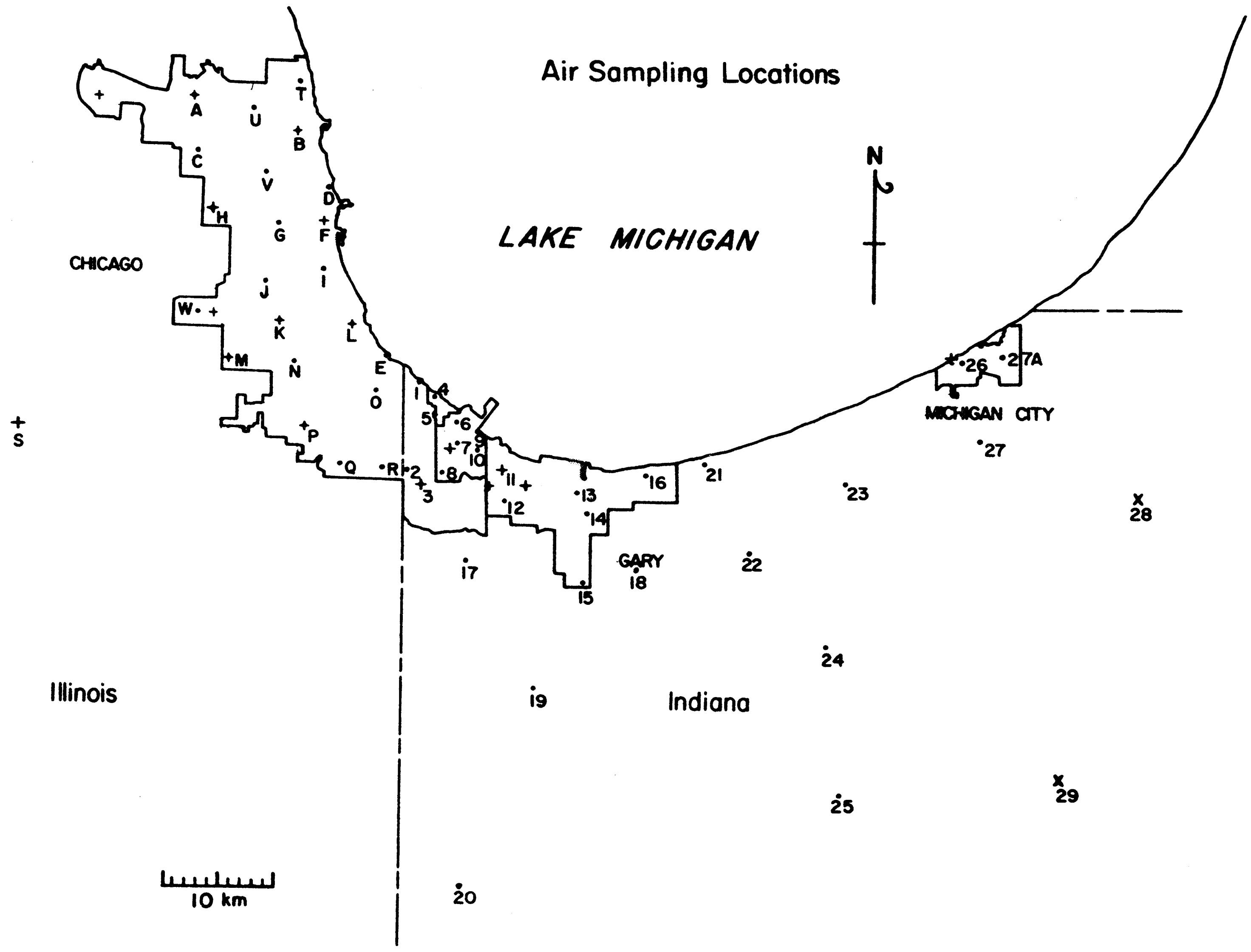


Figure 2.2: Key to high volume air sampling locations.

areas are probably not rural, but then again not urban or industrial; we would then probably call them proximate stations as per McMullen et al. (1969) (a crude estimate of the traffic density is presented in Appendix I.6 in order to roughly predict the areas of maximum lead emission). This type of information for Chicago is not available at this time and must be approximated. All stations are located two to three stories (10-15 meters) above ground level, and are usually located on top of schools and public buildings. (The addresses of the stations are presented in Appendix VI.)

Chicago has three major airports, two of which provide detailed meteorological data, and the air pollution officials for the city of Chicago maintain up to 13 stations that have telemetered meteorological data. However, during this period it was found that the Chicago data were somewhat inconsistent and very little information was used. In Northwest Indiana there are no full time meteorological stations. However, there are a few stations that take gross measurements of wind speed and wind direction. There are but one or two stations that give more detailed chart tracings. The locations of the meteorological stations are presented in Figure 2.3 and are listed in Appendix VI. Having personally inspected almost all of the sampling stations, especially in the Northwest Indiana area, the author would conclude that most are well-placed in order to gain the most accurate and descriptive results.

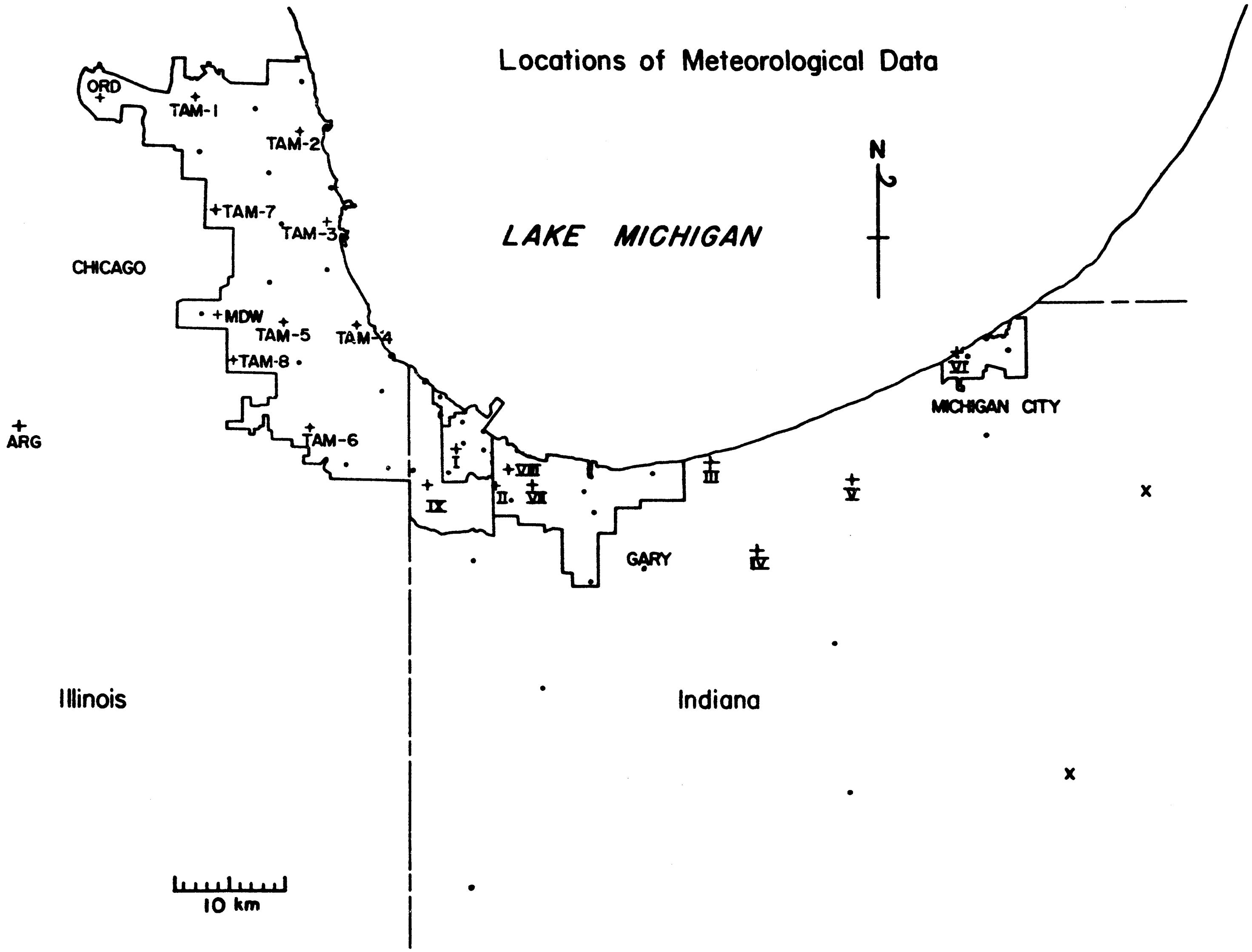


Figure 2.3: Key to locations of sources of meteorological data.

2.2 PURPOSE OF THE INVESTIGATION

The problem was approached at different levels. The first experiment was started with Professor Winchester and his students on Lake Michigan on the vessel operated by the Great Lakes Research Division of the University of Michigan, the Inland Seas. The Inland Seas sailed from Grand Haven, Michigan, on 21 May 1968 to Calumet Harbor, returned to Grand Haven, and again returned to the approximate center of the southern Lake Michigan basin, completing the cruise on 26 May 1968. At the time it was desirable to develop a way to determine the source strength of pollution going into the lake (see Appendix I). After many contacts, additional land-based samples taken on 21 May and 22 May were obtained from the local air pollution groups and were analyzed as a pilot study for lead, copper, cadmium, and bismuth. The method of collection was with standard 20 x 25 cm (8 x 10 inch) high volume filters taken by the local pollution officials for their routine suspended particulate analysis. There were no special preparation instructions given prior to the sampling; in fact, most of our samples were obtained after their sampling, which was for the sole purpose of obtaining suspended particulate data. After analyzing the May samples it appeared that the research was feasible and the analysis technique was sensitive enough, and it also became obvious that the data could be of extreme interest. After inspecting the scheduled sampling of Chicago, the Northwest Indiana Air Resource Management Group, and the Porter County network (under the supervision of Dr. El-Naggar of Valparaiso University), only five days of simultaneous sampling during the summer of 1968 were available for analysis. The city of Chicago collects samples three days a week on Tuesday, Thursday, and Saturday; Northwest Indiana has a somewhat random schedule; and Valparaiso (or Porter County) has a different random schedule. (The 1968-69 Northwest Indiana schedule is presented in Appendix VI.) Because of the analysis technique, lead, copper, and cadmium were simultaneously analyzed, but bismuth was too scarce and was analyzed only for the pilot study. Sulfur dioxide data and suspended particulate values were obtained from the local control agencies and are presented as additional data for information and comparison.

2.3 ANALYSIS PROCEDURES

2.3.1 Sample Preparation and Handling

All of the Northwest Indiana and Porter County districts offered the full 20 x 25 cm (8 x 10 inch) glass fiber filter paper which was already exposed, while Chicago samples consisted of a 2.5 cm (1 inch) strip from the center of the 20 x 25 cm filter paper. A 12 cm^2 (2 $in.^2$) section of each filter paper was cut into small strips and inserted into a 25 milliliter volumetric flask. Four milliliters of perchloric acid were added and then heated to 300°C. The carbon-containing material was dissolved and volatilized to carbon dioxide, leaving the free ions and glass fiber filter. Any vaporized ions were re-vaporized on the cool top of the flask.

The vials were equilibrated to the 25 milliliters and allowed to sit for a few days. No further sample preparations were necessary. (Several samples were prepared at once, but it is suggested that no too many samples be heated at one time due to the possibility of explosion from large amounts of perchloric acid. A hood was used.) At no time were metal objects allowed to come close to the fiber filters, but since the filters were originally used on a metal holder, there is no guarantee that some contamination was not present. However, the blanks were very low for the metals studied and little systematic contamination effect was observed in the final results.

2.3.2 Method of Analysis

Lead, copper, cadmium, and bismuth were chosen because of their electrochemical properties and the availability of an electrochemical technique called Anodic Stripping Voltammetry (ASV). Because of a unique cell design we were able to gain a much greater sensitivity than was previously available (Matson, 1968, 1970). Further design modification had made this instrument available for semi-routine use. The process is similar to the hanging drop electrode used extensively in electrochemistry, but has the advantage of stripping metal ions quickly as compared to the hanging drop. This is achieved by use of a composite carbon electrode to which the mercury is plated. For the non-electrochemist, it should be pointed out that all of the metals studied in this work are soluble in mercury; that is, during plating they form an amalgam with the mercury and then deplate easily. The limiting factor in the stripping or deplating is the distance the ions must travel through the mercury to get back into the solution. With a hanging drop electrode the mercury layer is quite thick. In the composite carbon electrode the thickness of the droplets or layer of mercury is quite small, and the metals strip quickly, forming a separate and discrete peak for each metal. The physical characteristics of the unit are shown in Figures 2.4 and 2.5, with a sample resultant stripping curve presented in Figure 2.6. From this latter trace we can see that the order of elements are zinc, cadmium, indium, lead, copper, bismuth, and mercury. Of these, zinc, cadmium, lead, and copper are found in large enough quantities to be far above that of indium and bismuth as found in nature. Thus only four peaks are usually observed before that of mercury. The location of each peak relative to the voltage is variable according to the reagent used and the acidity and the characteristics of the cell. An additional advantage of this equipment is that several samples can be run simultaneously. In this case, four units were used with one minute plating time separation being the rule. Several analyses were conducted in order to ascertain the cell characteristics, the repeatability, the deterioration and the overall sensitivity for each metal. It may be simply stated that the sensitivity can be as low as one nanogram in situ; and the deterioration is from less than 1% to typically 3-4%

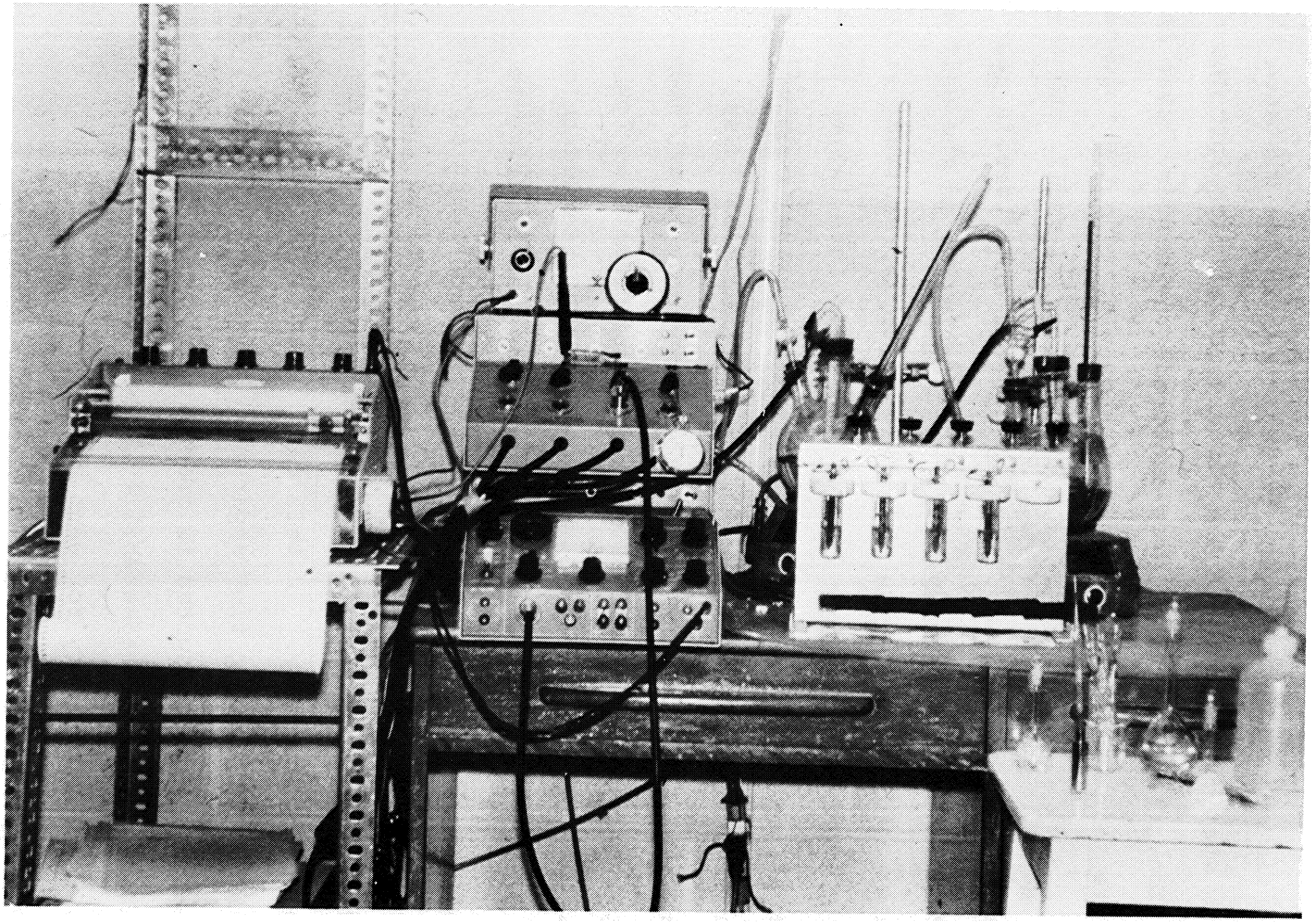


Figure 2.4: Complete ASV system, including a five module unit, plating amplifiers, stripping unit, and recorder. The cleaning units are in the background.

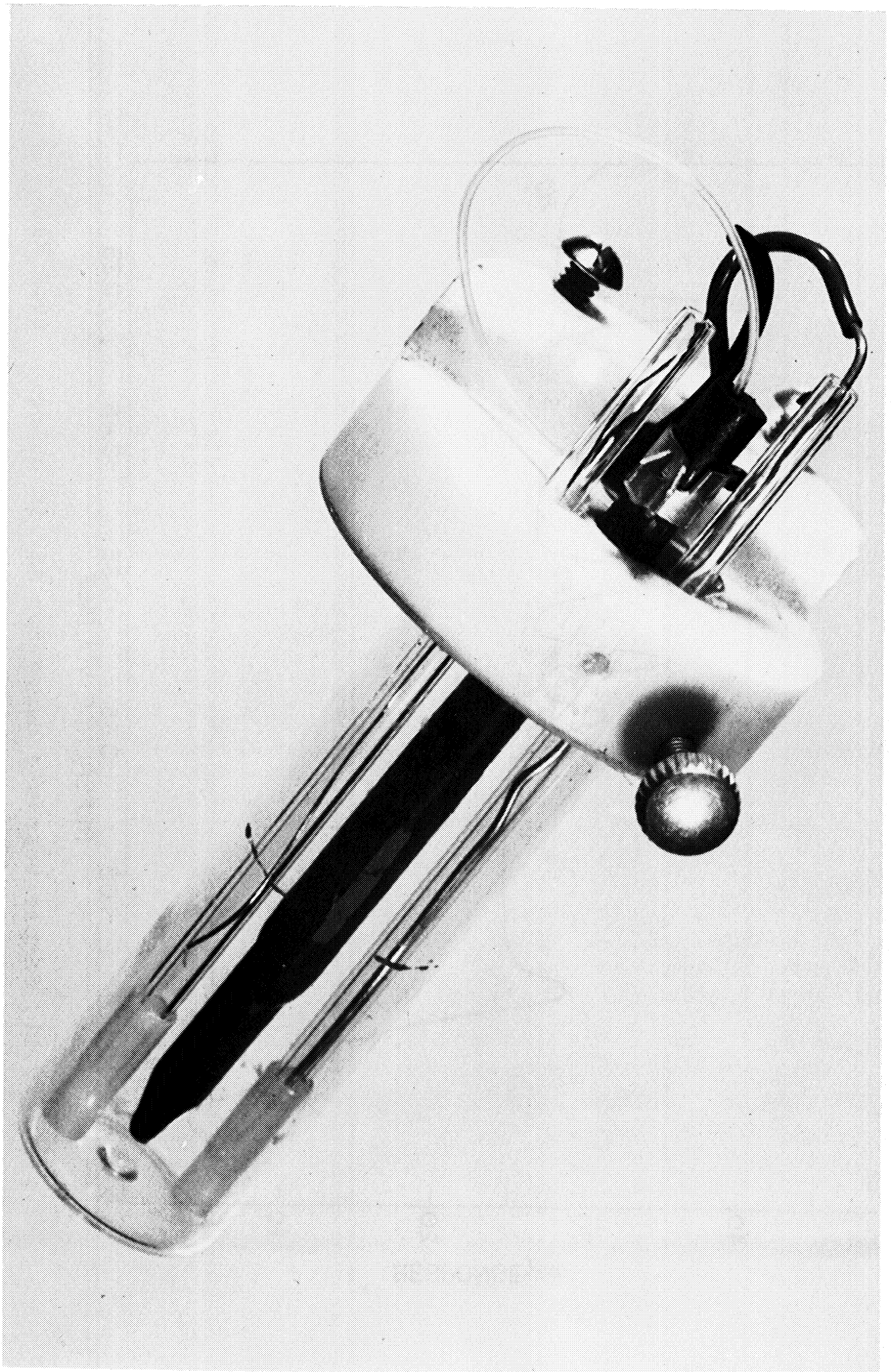


Figure 2.5: ASV cell, with pointed tip electrode.

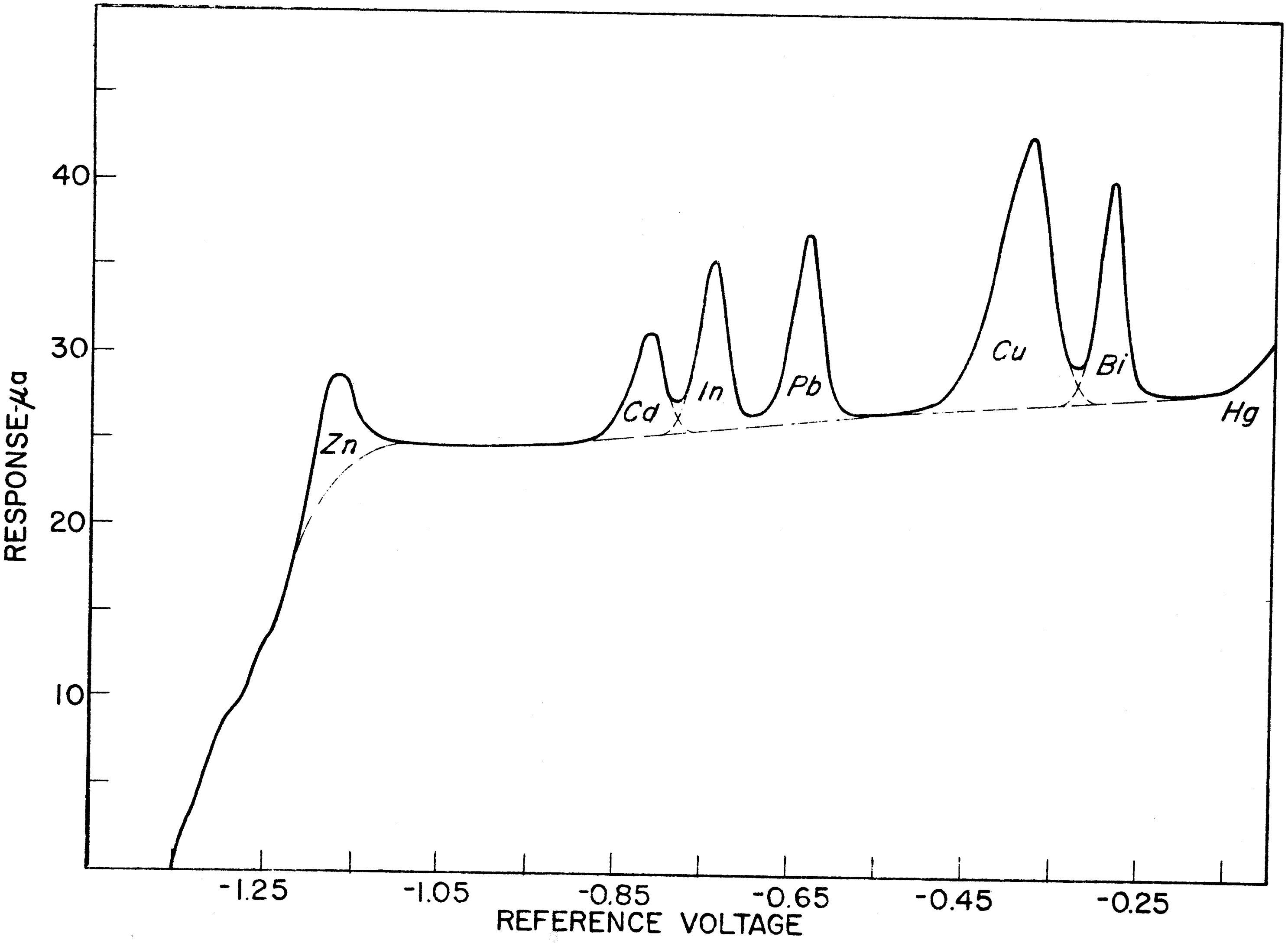


Figure 2.6: Sample response curve for ASV in chloride (0.2 M).

per run between washings (Appendix IV). All of this can be monitored and corrections can be made. The overall accuracy can be better than 20% (Matson, 1970). However, monitoring runs should be implemented in case of cell or reagent contamination or electrical charges. This was done routinely in all of this work. A lengthy discussion of these matters can be seen in Appendix V. Due to problems with standards, this study does not claim more than factors of 2 accuracy in all values although many points are much better.

2.3.3 Data Reduction

The standard procedure for each session of analysis was to run several spike runs with blank in order to ascertain the calibration values for each metal. The spike was typically 20 nanograms of cadmium, 100 nanograms of lead, and 100 nanograms of copper. After three to four uniform spike runs larger spikes were added to find the calibration curves over a large range of concentrations. These data are presented in Appendix IV.3. The cell was then washed and a new blank plus spike run was made. To this run was added, without washing, an aliquot of the sample. After this analysis the cell was washed and the blank plus spike run repeated, and so forth throughout the session. For the three elements, both peak heights and peak area under the curve were measured in order to compare and to find out which data reduction method was the most accurate. The area under the curve is the most physically significant, but the peak height is the easiest to measure and because of cell characteristics can be used over a large part of the concentration spectrum for analysis and calibration (Appendix V). The concentration versus response curves were not always run, but enough were done to solidify the calibration curves. A sample curve is presented in Figure 2.7.

The results of each session and each cell were separated and typed on computer tape. The original data tables are listed in Appendix IV.3. A computer program automatically sensed the code and determined whether the run was a spike run, a calibration run, or a sample run. The spike run was subtracted from the sample run or the repeat run and the volume was calculated as well as the value of the aliquot. The calibrations, also presented in Appendix IV.3, were fed into the computer separately and the concentrations were then calculated. The final output of the computer was in the format of run number, and the value of each of the three elements repeated for peak height calibration and the area under the curve calibrations as well as the averages of the two. When the two methods of calibration differed markedly we went back to the original curves and re-analyzed.

It was found that most of the errors were due to problems in reading the planimeter that was used to measure peak areas. With a little additional observation and experimentation it was found that drawing the base line could also be expedited by using a horizontal line rather than trying to follow the charging curve. For each session a plot of the

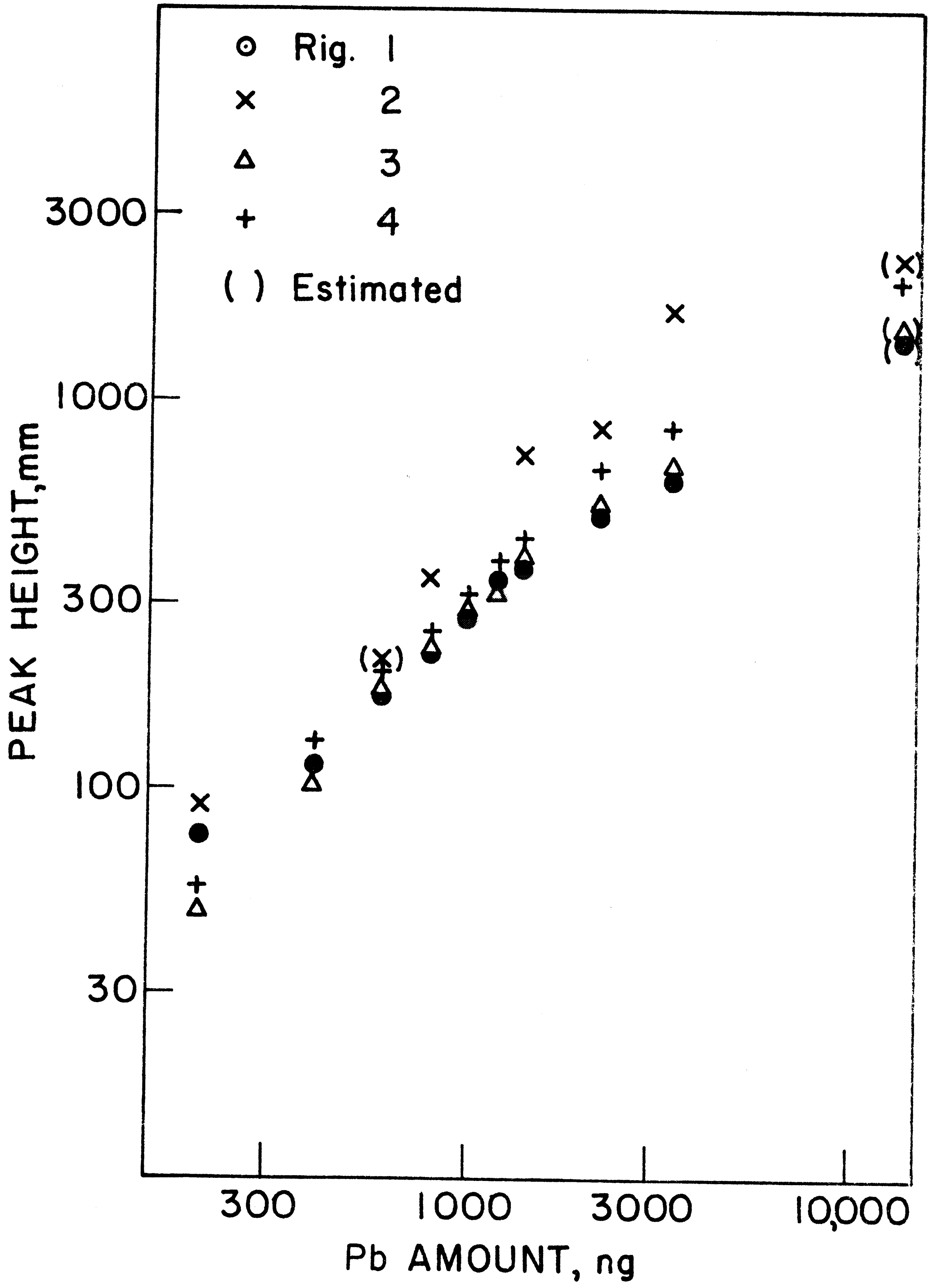


Figure 2.7: Sample concentration vs. response curves, cells 1 to 4.

spike plus blank curves was made and the percentage of deterioration was noted. Then the results were corrected for this deterioration and written in an additional table. All data were rounded to two significant figures and retyped on computer cards for listing and calculation of ratios. These data are presented in Appendix IV, and the ratios are also presented in Appendix IV. Additional discussions of cell design, cell characteristics, carry-over and reproducibility are found in Appendix V.

3.0 RESULTS

3.1 REPRESENTATION OF DATA

Tables 3.1 to 3.6 are tabulations of the concentrations of each element for the six days studied. Detailed meteorological data are in Appendix IV.1.

For each of the six days there are 11 figures depicting:

1. wind speed and direction;
2. suspended particulate isopleths;
3. suspended particulate values at their respective stations;

4.-11. sulfur dioxide, cadmium, lead and copper presented as for suspended particulate.

A brief description of each representation should be made before summarizing the results.

Wind, as presented in Figure 3.2.1, represents the wind speed and direction by hour, with the wind direction being represented opposite to the usual meteorological convention. That is, the line represents the direction towards which the wind is blowing, as the arrows indicate. The reason for this choice is that we would like to clearly represent the direction in which a pollution source would be advected if one were present at the meteorological station. The length of the line is the sum total of all the wind speeds along that 10° vector over the 24 hour period from midnight to midnight. The number at the end of the vector is the total number of

Table 3.1 Atmospheric Concentrations of Cadmium, ng/m^3

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	50	5	30	10	**	10
2	--	**	20	20	10	20
3	10	**	**	50	**	30
4	30	**	**	5	10	8
5	40	10	10	50	**	7
6	10	8	20	10	10	10
7	--	--	8	60	10	10
8	15	**	5	10	8	**
9	30	7	10	20	**	**
10	20	**	3	6	**	**
11	10	40	6	--	--	--
12	70	10	**	--	--	--
13	30	30	**	--	--	--
14	--	--	--	--	--	--
15	15	**	**	--	--	--
16	7	9	--	--	--	--
17	10	**	**	**	**	**
18	**	20	**	10	**	20
19	9	**	**	--	**	40
20	10	6	80	20	5	20
21	--	--	30	40	**	--
22	--	--	30	10	**	--
23	--	--	30	30	**	**
24	--	--	20	7	20	10
25	--	--	30	**	**	--
26	5	--	**	7	10	**
27	--	--	--	**	10	20
A	**	**	20	20	10	30
B	30	30	**	10	30	30
C	30	6	10	**	20	**
D	M	20	**	20	**	20
E	60	--	--	--	15	40
F	20	10	10	--	10	5
G	50	10	**	10	--	15
H	**	**	20	8	30	40
I	--	--	--	--	--	**
J	80	**	10	--	8	--
K	20	**	8	10	10	10
L	30	15	**	**	20	30
M	40	6	9	**	20	**
N	10	8	20	9	10	**
O	50	10	10	**	10	7
P	5	20	9	20	**	30
Q	30	10	6	15	--	6
R	20	--	7	**	10	--
T	10	10	9	**	**	--
U	9	**	10	**	20	--
V	40	7	40	6	30	30
W	40	9	10	--	**	**
SHIP	--	--	--	20	--	--

Individual Data Points are Reliable to a Factor of 2. **= $\leqslant 5$

Table 3.2 Atmospheric Concentration of Lead, ng/m^3

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	2000	800	1000	100	1000	1000
2	----	2000	3000	2000	3000	2000
3	3000	1000	3000	2000	2000	2000
4	3000	1000	2000	800	2000	2000
5	1000	900	2000	400	1000	1000
6	2000	900	4000	600	4000	2000
7	----	----	3000	700	3000	2000
8	1000	700	2000	1000	1000	1000
9	2000	500	600	2000	2000	500
10	2000	300	800	1000	700	600
11	2000	1000	2000	----	----	----
12	4000	700	2000	----	----	----
13	6000	2000	3000	----	----	----
14	----	----	----	----	----	----
15	1000	500	2000	----	----	----
16	3000	800	----	----	----	----
17	1000	500	2000	900	2000	700
18	400	300	800	500	100	2000
19	300	400	400	----	100	3000
20	900	700	1000	1000	600	1000
21	----	----	1000	500	600	----
22	----	----	1500	400	1000	----
23	----	----	700	100	500	700
24	----	----	1500	500	300	500
25	----	----	500	300	200	----
26	1000	----	1000	700	800	500
27	----	----	----	300	400	800
A	7000	1000	5000	2000	3000	4000
B	4000	2000	2000	800	4000	4000
C	5000	300	2000	600	2000	3000
D	3000	2000	300	2000	4000	3000
E	4000	----	----	----	1500	5000
F	6000	2000	3000	----	3000	4000
G	4000	2000	4000	1500	----	3000
H	2000	1000	3000	700	3000	4000
I	----	----	----	----	----	2000
J	6000	900	2000	----	2000	----
K	5000	1000	2000	500	2000	2000
L	3000	1500	2000	200	4000	2000
M	6000	1000	2000	400	2000	4000
N	5000	1000	3000	600	2000	2000
θ	6000	1000	2000	500	2000	1000
P	5000	1000	4000	600	2000	3000
Q	4000	700	2000	700	----	2000
R	4000	----	2000	300	2000	----
T	3000	1000	2000	800	----	----
U	4000	1500	3000	1000	3000	----
V	4000	1000	4000	1000	3000	2000
W	4000	800	2000	----	2000	3000
SHIP	----	----	----	700	----	----

Individual Data Points are Reliable to a Factor of 2.

Table 3.3 Atmospheric Concentrations of Copper, ng/m^3

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	70	300	400	150	150	300
2	---	100	1000	150	200	150
3	300	200	2000	200	80	600
4	900	2000	200	80	600	400
5	1000	3000	600	60	500	200
6	2000	7000	(7000)	2000	2000	4000
7	---	---	1000	300	1000	600
8	5000	9000	5000	2000	3000	9000
9	7000	5000	9000	7000	10000	10000
10	4000	5000	1500	2000	(9000)	10000
11	300	700	400	---	---	---
12	***	300	500	---	---	---
13	80	700	200	---	---	---
14	---	---	---	---	---	---
15	200	200	150	---	---	---
16	100	200	---	---	---	---
17	150	200	150	200	30	70
18	300	200	300	200	***	100
19	400	700	400	---	70	100
20	150	200	100	200	40	100
21	---	---	100	70	70	---
22	---	---	300	70	70	---
23	---	---	90	***	100	100
24	---	---	500	60	100	70
25	---	---	200	60	90	---
26	80	---	300	200	400	200
27	---	---	***	300	300	200
A	70	***	600	100	100	300
B	300	200	70	200	300	150
C	100	100	100	20	**	100
D	150	70	30	100	200	200
E	400	---	---	---	500	1000
F	200	***	80	---	100	100
G	400	100	70	200	---	200
H	500	20	80	20	100	***
I	---	---	---	---	---	200
J	200	100	***	---	200	---
K	200	***	***	200	100	100
L	200	100	70	***	800	200
M	80	***	60	***	600	90
N	100	80	300	60	300	100
O	300	200	200	100	200	200
P	300	100	200	200	200	200
Q	900	30	100	200	---	200
R	500	***	200	---	200	---
T	200	200	200	30	***	---
U	200	200	200	20	300	---
V	600	100	400	80	200	200
W	200	40	100	---	200	200
SHIP	---	---	---	100	---	---

Individual Data Points are Reliable to a Factor of 2. ***= ⩽20

Table 3.4 Atmospheric Concentrations of Bismuth, ng/m^3

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	**					
2	--					
3	3.					
4	1.					
5	2.					
6	3.					
7	--					
8	0.7					
9	2.					
10	1.5					
11	0.4					
12	0.6					
13	0.4					
14	--					
15	0.3					
16	**					
17	--					
18	--					
19	--					
20	--					
21	--					
22	--					
23	--					
24	--					
25	--					
26	**					
27	--					
A	M					
B	**					
C	**					
D	M					
E	0.8					
F	1.					
G	0.1					
H	M					
I	--					
J	**					
K	0.6					
L	**					
M	M					
N	**					
O	**					
P	0.3					
Q	0.4					
R	0.4					
T	0.2					
U	**					
V	**					
W	0.8					
SHIP	--					

Individual Data Points are Reliable to a Factor of 2. **= ≤ 0.05

Table 3.5 Atmospheric Concentrations of Total Suspended Particulate, $\mu g/m^3$

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	115	170	117	32	198	148
2	--	218	344	64	161	92
3	81	131	256	139	148	167
4	126	143	128	54	152	145
5	140	169	278	66	156	242
6	142	201	382	125	256	233
7	--	--	332	193	191	174
8	62	108	210	105	91	122
9	83	115	134	148	122	109
10	78	109	198	--	100	96
11	76	153	228	--	--	--
12	128	179	249	--	--	--
13	120	187	255	--	--	--
14	--	--	--	--	--	--
15	46	136	100	--	--	--
16	80	154	85	--	--	--
17	66	109	117	142	--	--
18	98	86	107	64	17	--
19	55	98	70	--	46	--
20	78	96	88	126	62	--
21	--	--	77	44	40	65
22	--	--	104	55	49	65
23	--	--	66	27	39	57
24	--	--	--	32	38	81
25	--	--	81	--	43	185
26	68	--	64	63	72	45
27	--	--	--	49	84	69
A	88	174	141	71	138	107
B	113	212	116	105	239	214
C	114	55	150	49	132	139
D	125	261	19	60	243	188
E	144	--	--	--	305	952
F	153	206	169	--	185	218
G	134	181	172	152	--	143
H	50	176	236	86	182	186
I	--	--	--	--	--	181
J	166	205	259	--	166	--
K	154	139	245	103	158	134
L	180	229	180	43	225	218
M	139	130	183	98	170	195
N	142	115	211	86	154	136
θ	163	205	263	108	174	178
P	141	153	286	51	177	214
Q	195	161	408	109	--	235
R	143	--	241	110	130	--
T	92	152	81	67	132	--
U	75	172	121	74	146	--
V	114	186	190	100	196	148
W	131	155	216	--	161	185

All Data Furnished by the Local Agencies

Table 3.6 Atmospheric Concentrations of SO_2, ppb

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 20
1						
2						
3	17	21	62	69	3	--
4						
5	13	24	--	48	4	--
6						
7	--	--	2	--	1	--
8	--	**	--	--	9	--
9						
10						
11	2	--	15	--	--	--
12						
13	**	--	**	--	--	--
15						
16						
17						
18						
19	--	--	1	--	**	--
20						
21	--	9	2	1	1	14
22	--	--	1	**	3	**
23	--	8	4	1	4	11
24	--	--	--	1	2	--
25						
26						
27						
A	75	5	10	8	3	4
B	14	1	27	35	3	26
C	54	17	10	1	4	6
D	22	67	12	30	13	11
E						
F	10	39	9	13	9	34
G	32	45	**	6	3	16
H	27	94	31	9	35	3
I						
J	7	1	7	1	6	7
K	80	12	14	12	24	--
L	23	15	29	1	27	--
M	1	--	6	1	15	32
N	1	--	25	12	4	39
θ	1	--	20	4	3	20
P	1	--	**	1	2	5
Q	24	8	51	7	2	44
R	17	7	51	4	2	--
T	1	2	12	12	28	16
U						
V						
W	4	9	13	24	22	20

$** = \leq 0.5$

All Data Furnished by the Local Agencies

hours that the wind came through that vector; for example, a 3 would mean that the wind was blowing in the direction of the arrow for 3 out of the 24 hours. (These hours need not be consecutive.) Non-labeled vectors are one hour occurrences, and calm (C) is defined as under 3 mph. This compromise seems to be the most reasonable method for a graphical representation of general medium-range advection of pollution in this area.

For reasons of clarity in the drafting of the data values at each sampling station, each element's data was uniformly scaled. Suspended particulate is given in $\mu g/m^3$ (parts per billion), SO_2 in pp billion, cadmium in ng/m^3 (pp trillion), lead in $\mu g/m^3$ multiplied by 10 (pp hundred trillion), and copper by ng/m^3 divided by 10 (pp tens of trillion). For each parameter both isopleths and data points are presented in separate figures.

In the following sections we will attempt to point out pertinent features of each day and each parameter in order. In addition to calling attention to the obvious facts we will comment on particular areas for later discussion under Section 4, "Interpretation."

3.2 21, 22 MAY 1968

Tuesday, 21 May, is represented generally by a northwest wind; that is, a wind coming from the northwest blowing to the southeast. We would then expect pollution from the Chicago area to be advected from the northwest to the southeast.

On Wednesday, 22 May, in the Northwest India a region, the general advection would be from the southwest to the northeast. The same wind directions occurred at East Chicago and Gary with slight differences at Michigan City, providing a good representation of a wind shift due to lake effects, and these effects can be observed throughout the six days studied. With these general wind directions in mind we can now inspect a transport of particulates.

3.2.1 21 May 1968, Chicago

Suspended particulate analyzed by each local air pollution facility shows a broad maximum in the southeast and central areas, Figures 3.2.2 and 3.2.3, with a minimum in the west. The sulfur dioxide in the Chicago region, also taken by the local control agency, shows a large maximum in the northwest region slowly diminishing towards the southeast. There is a single point maximum in the south central region, suggesting an advection to the east-southeast. Cadmium, Figures 3.2.5 and 3.2.6, is represented by two maxima, one in central Chicago and the other in southeast Chicago. Lead, interestingly enough, shows the northwest maximum, as in the SO_2, slowly diminishing to the southeast. There is also a maximum in the central and east central regions with a definite minimum in the west central region. Copper has not been isoplethed in as great detail as the other elements, but shows a maximum in the north central Chicago area with a slight bulge to the southeast and a maximum in the southeastern section.

Bismuth was analyzed for these two days only since it was found to be in such low levels, it is not usually thought of as a toxic material, and it requires a four fold increase in analytical time. There is a slight maximum in the central downtown ("Loop") area, but the value is only about 1 ng/m^3.

It seems that there could be a case presented for general advection of specific trace metal pollutants from the northwest to the southwest. It is especially interesting to note the large source region northwest of Chicago advecting into Chicago for sulfur dioxide and lead. The cadmium maximum in central Chicago is very close to a maximum of sulfur dioxide. Copper and sulfur dioxide coincide in south Chicago, copper and cadmium in the north central area, lead and suspended particulate in central and north Chicago, and lead and sulfur dioxide in the northwest regions.

3.2.2 22 May 1968, Northwest Indiana

For the 22nd of May in the Northwest Indiana area the suspended particulate is characterized by a heavier loading in the metropolitan Gary area, as well as in Whiting and north Hammond. It is to be remembered that the general wind direction for this day was from the southwest. There seems to be a relatively moderate amount of sulfur dioxide in the Hammond-Whiting area, and a small amount for the rest of the region. Cadmium presents an interesting pattern with a maximum in East Gary with isopleths to the east, and a slight maximum in northwest Hammond, but with a broad minimum in the east Chicago area. Lead seems to show a maximum in the central business districts of Gary and Hammond.

Probably the most significant occurrence is the large amounts of copper found in Northwest Indiana, with a copper maximum found at station 9 in East Chicago extending southwest to station 8. The maximum value at station 9 is 7 $\mu g/m^3$ and at station 8 is 5 $\mu g/m^3$, as shown in Figure 3.2.11. Bismuth seems to be more abundant in the Northwest Indiana area than in the Chicago area, but, again, the wind directions are different and a plume of bismuth seems to be present from southwest Hammond to northeast East Chicago and Whiting.

This data seems to show that suspended particulate is present in the metropolitan areas and seems to be advected from south Chicago into Whiting and north Hammond and East Chicago. In summary, for these days sulfur dioxide data is scarce and inconclusive, cadmium seems to be present in the northwest Hammond area (possibly from south Chicago and a source in east Gary), copper may have a source in southwest East Chicago and northeast East Chicago advecting with the southwest wind, and bismuth seems to be advected from southwest Hammond to the northeast. Additional shipboard data are available for 20 May through 23 May and are presented in Appendix I.1.

3.3 6 JUNE 1968

Thursday, 6 June 1968, is characterized by south to southeast winds. At the O'Hare station the wind direction is definitely southwest, while at Midway it is from the southwest to southeast, and at the East Chicago station there is a definite southwest wind. In Michigan City the wind is mostly out of the south with little variation because the meteorology station is located within 20 m of the lake, and the greater frictional retardation of the ground roughness is probably not seen as well as at the more inland stations. We can thus characterize this day by a southwest to south wind.

The suspended particulate data bears out this wind direction by showing a maximum in east downtown Chicago and minima in the west. In the Northwest Indiana--Chicago area there is a plume of particulate extending from central Hammond through northeast East Chicago, with a broad maximum in Gary exhibiting an effect of the combination of an urban and industrial region. The sulfur dioxide value is very high in the north central Chicago region, with a maximum in the west of the plume and another maximum occurring in the east side of the corridor. The wind direction from O'Hare and Midway is more northwest than west and the sulfur dioxide seems to be advecting from the west-southwest to the east-northeast. This could be explained by the lack of information at station V which may show a bulge or a northwest advection which we could not draw without this information. The Northwest Indiana region shows a corridor of sulfur dioxide at a much lower value extending through Hammond to Whiting. Cadmium, again, is present in low values with a broad plume from southern Chicago, extending along the shoreline in East Chicago, with a slight maximum in northeastern Chicago. A broad maximum seems to exist in northern Gary, in the industrial regions. Lead seems to follow the automobile traffic intensities with a shift to the northeast from central Chicago. In the Northwest Indiana area the maximum lead concentrations are somewhat concurrent with the urban traffic densities with advections to the north. Copper has not been contoured for Chicago due to the overpowering contrast in the Northwest Indiana area; however the data are accurate enough to warrant some contouring, if so desired. Copper is obviously available in very large amounts in Northwest Indiana. Station 8 with 9 $\mu g/m^3$ of copper exhibits maximum values, and station 6 shows 7 $\mu g/m^3$. The isopleth patterns tend to bear out the wind directions and seem to indicate that a source is present in southwest East Chicago, or somewhere close to Hammond.

Concurrent patterns occur, with suspended particulate showing a secondary maximum north of downtown Chicago, as well as with SO_2, cadmium and lead. An additional overlapping exists in Gary with cadmium and lead, and the maxima also overlap well with lead in most areas.

3.4 20 JUNE 1968

After presenting two days of northwest wind in northwestern Indiana and one day of northwest wind in Chicago, Thursday, 20 June, represents a southeasternly wind that should show some differences. It should be pointed out, however, that the winds are relatively light and that there are several periods of calm where aerosols might go just about anywhere, over a short distance. The suspended particulate loading seems to increase slightly because of the low wind speeds, especially in the south Chicago region. Most of the area is represented by broad maxima, with minima close to the lake due to the incursion of the cleaner lake air from the east and southeast. This is especially true at location D in Chicago which is close to the lake, and generally throughout the lake stations. The corridor from north East Chicago is a result of heavy concentrations of steel industries located close to the lake. (A point to be remembered is that the turbulence characteristics of the mixing layer are not the same over the lake as they are over land, and these effects can influence the ability of the mixing to bring a suspended particulate down from a high source region advecting over the land with a possibility of lifting occurring over the lake.) A maximum extending inland from downtown and a strong maximum in north Chicago are also present. Sulfur dioxide is similar to the suspended particulate in the southern Chicago and western Northwest Indiana regions, with an additional maximum occurring in the western edge of central Chicago and extending from the northeast. There does seem to be an unexplained large sulfur dioxide source either in Hammond or southern Chicago. Cadmium is slightly uniuue for this day in the Porter County area. We are not sure that these samples were nor uniformly contaminated, but this is not to say that they were. This was the only day that shows large amounts of cadmium present. One would not expect that all samples would be high due to the analytical procedures since they were run in different cells. The only possibilities are that the data is real or that the samples for that day were brought close to some cadmium-emitting device or material. In Figure 3.4.7 the bracketed data represent real measurements, and the second number is an estimation based on uniform contamination. There are two cadmium maxima for this day, one in north central Chicago and the other in northern Hammond. The isopleths show a somewhat northwest advection. Lead also displays a maximum in the northwestern Chicago area emanating from the downtown area in the east central region. A broad maximum exists in the southwest region as well as maxima in the business areas of Hammond, Gary and in northern East Chicago. The copper picture becomes somewhat clearer in the Northwest Indiana region. Stations 6, 8 and 9 show a double maximum, with a minimum at station 7. This would imply a double source. The advection to the east or northeast is of only a moderate extent, and there seems to be some advection or sources in the west Gary area. Again, there seems to be a source of copper particulate in the northwest Chicago region, but details north of this area are not available. Suspended particulate heavily correlates with sulfur dioxide in south Chicago as well as with lead in Hammond--East Chicago plume. Cadmium does not seem to correlate well and copper only in East Chicago. In northwest Chicago, cadmium and sulfur dioxide have overlapping maxima, and lead and copper also have a strong overlapping maximum but further north (Station A). This is the second time the lead has occurred in such large quantities but the first time that the copper was overlapping. The minimum at station D in east central Chicago is present in all parameters and at station 11 in East Chicago except for copper.

3.5 9 JULY 1968

Tuesday, 9 July 1968, was characterized by a strong south to southwesterly flow with a frontal passage approximately half way through the sample period. A strong north to northeasterly wind occurred in the second half of the sample day. Additional data were taken in the southern basin of Lake Michigan by the research ship Inland Seas (operated by the Great Lakes Research Division of the University of Michigan) by Dale Gillette (1970). These winds were strong and would imply a lower particulate loading and a greater amount of mechanical mixing and diffusion than previously seen. The deviation of the prefrontal passage wind direction at the Michigan City station is probably a lake effect, if one precludes instrument error. All the data show a decrease in concentrations. Suspended particulate loadings are low and present maxima in central Chicago and East Chicago. For this and the following two days there are no data available for the city of Gary. There were some administrative changes during the latter part of the summer of 1968, and no suspended particulate or Hi-Vol samples were taken. The sulfur dioxide data show a maximum in northern Chicago along the lake and one in the western section of Chicago. An additional maximum source occurs in Hammond, but due to lack of data in East Chicago and Gary, it is difficult to say much about wind direction or sources. Cadmium is present in south Chicago along the lake, somewhat coincidentally with the sulfur dioxide data. Northern Porter County again shows a relatively high amount of cadmium, leading us to believe that there is a possibility that the previous data set might be real for cadmium. Lead is low and shows a plume between northern Chicago and the central downtown area on the lake. This isopleth does not coincide with wind direction, but it does coincide somewhat with traffic patterns, but again the levels are low. An additional maximum occurs in Hammond in the business area. Copper shows a double maximum, one at station 9, as on 20 June. These isopleths seem to coincide with the wind directions.

To restate the overlapping of maxima and minima, we notice that all parameters have high values north of downtown Chicago, cadmium and copper in southwest Chicago, sulfur dioxide and cadmium in Hammond, and suspended particulate and cadmium in East Chicago, Indiana.

3.6 8 AUGUST 1968

Thursday, 8 August 1968, is a different day meteorologically as the winds are variable and light throughout. Only at Michigan City, Indiana, are the directions and velocities more pronounced. There is a lake breeze situation operating, and it is evident by comparing the close lake stations with the more inland stations such as O'Hare and Midway. One would be hard pressed to predict the general directions of advections for this day. We could say that this day could be representative of a random wind direction situation. This conclusion may be incorrect as industrial emissions as well as local wind can change from day to day. The suspended particulate data seem to bear out this random distribution fairly well, as all areas have above average values, but there are no real sources except in the southern Chicago area. This source is probably a steel mill located at the point of maximum (E), also the maximum in East Chicago is located close to a heavily polluted region.

For sulfur dioxide one could guess that there is a source in northeast Chicago, one at station H in west central Chicago, and one, possibly, at stations W and L. Cadmium is present in northern Chicago at moderate levels but does not seem to have any maximum for this day at other locations. Lead is high, but generally distributed, as expected, with a maximum northeast in Chicago and in northern East Chicago, with the isopleth extending through to the residential and business areas of Whiting and Hammond. Copper is present at two locations in Chicago but now in extremely large quantities. Again, station 7 is low and stations 6 and 8 are persistently moderately high.

The coincidences, or lack thereof, become very informative for this day. Sulfur dioxide does not correlate at all with suspended particulate, but lead, copper and cadmium coincide well in Chicago, except for station E in south Chicago at the steel industry. Lead is reasonably synonymous with suspended particulate in all areas. Cadmium and sulfur dioxide relate well in Chicago except for the northeast station.

3.7 29 AUGUST 1968

The last day, 29 August 1968, is similar to 20 June, but exhibits some lake effects but not to the extent of the 8 August situation. The wind direction is generally from the east with a moderate amount of meandering through the western half of the direction, but mainly to the northwest. Suspended particulate is moderately heavy with a maximum at station E on the south shore of Chicago, close to a steel-making facility (station E is usually run only when winds advect from this area), extending to a maximum in northeastern Chicago, and with a broad maximum in southwest Chicago. Similarly, in the East Chicago--Whiting area there is a maximum coinciding with the heaviest particulate sources. Sulfur dioxide shows maxima in the business district of Chicago and in the southwest, with a minimum intervening between another maximum occurring in the south. No sulfur dioxide data are available from any of the major cities in Northwest Indiana. Cadmium is present in a broad maximum seeming to advect from the east section of Chicago, and again in the heavy suspended particulate region in south Chicago. A slight maximum occurs in mid Lake County, south of Gary, and it is not at all clear as to its origin. Lead is quite high in northern Chicago with some minor maxima occurring in and to the west of the business area, forming a small corridor. In the business and industrial areas of Northwest Indiana, lead is slightly higher than at other locations. It is not clear how far copper advects, but we do see an increase at station 3 in Hammond, showing the extent of the eastern advection of copper aerosols due to the east-northeast wind. Again, station 7 is lower than the adjacent stations. Whiting also seems to show a little larger copper value than for the other winds, but the eastern advection is not as clear cut as would be desired. Thus it does seem that two sources are probably present. The unfortunate emission of data from Gary does not allow us to make more definite conclusions for this situation. The small maximum in southeast Chicago is due to the heavy dust loading at station E.

Isopleths of suspended particulate and sulfur dioxide are not overlapping at all, except in the downtown Chicago district, but cadmium and lead correspond well in most of Chicago. Copper and cadmium are not well matched with sulfur dioxide on this day.

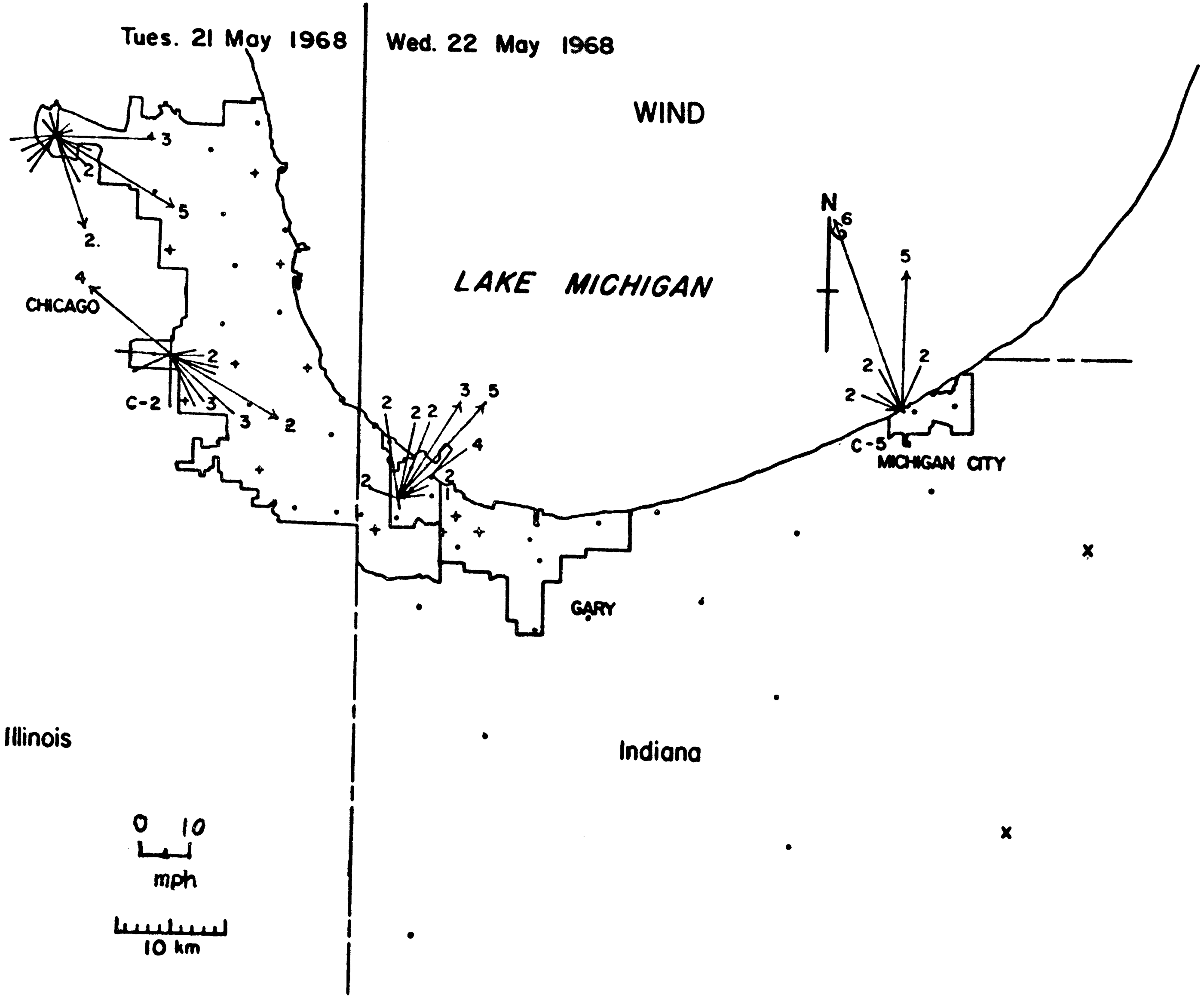


Figure 3.2.1: Wind rose for 21 and 22 May 1968.

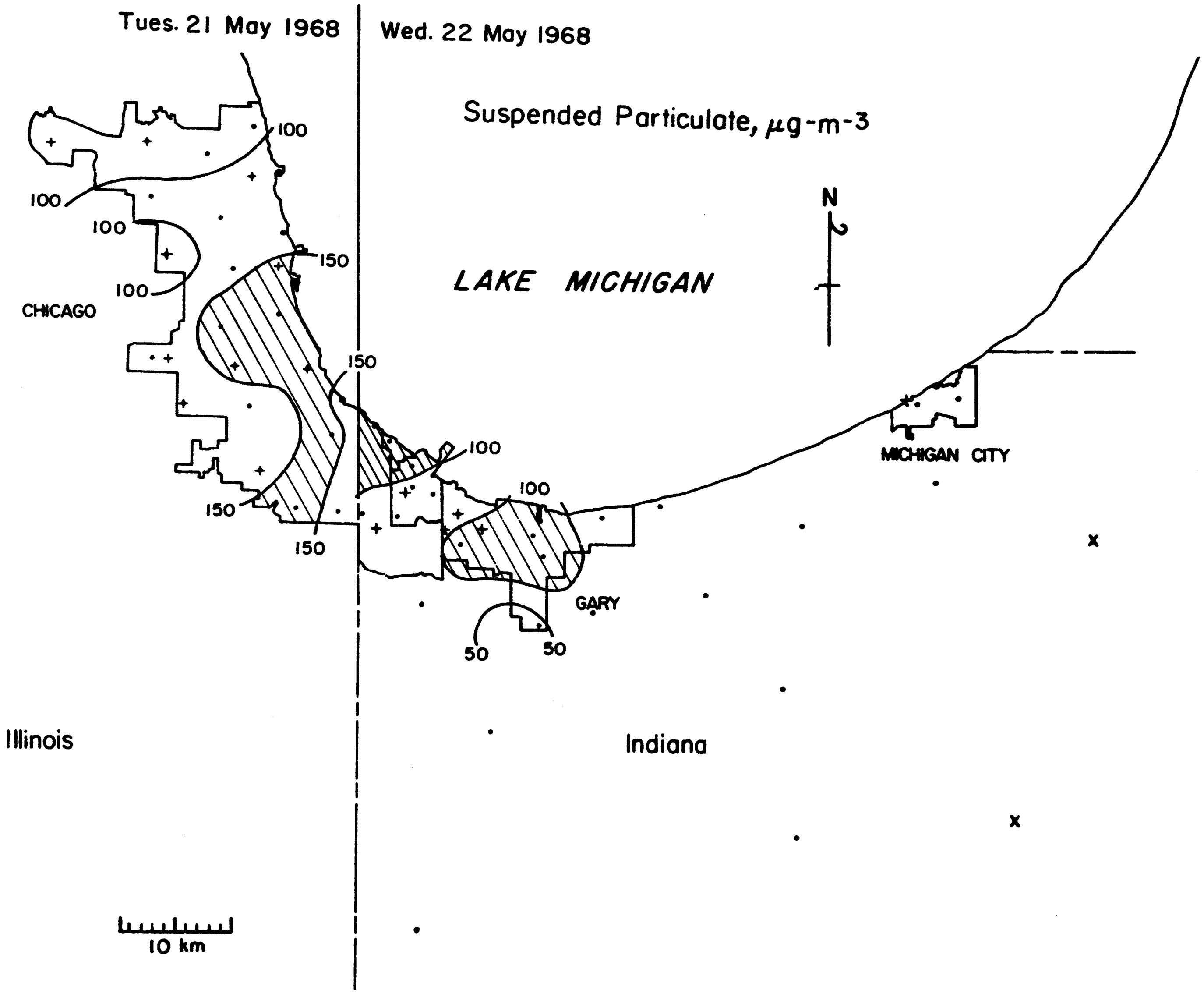


Figure 3.2.2: Suspended particulate isopleths for 21 and 22 May 1968.

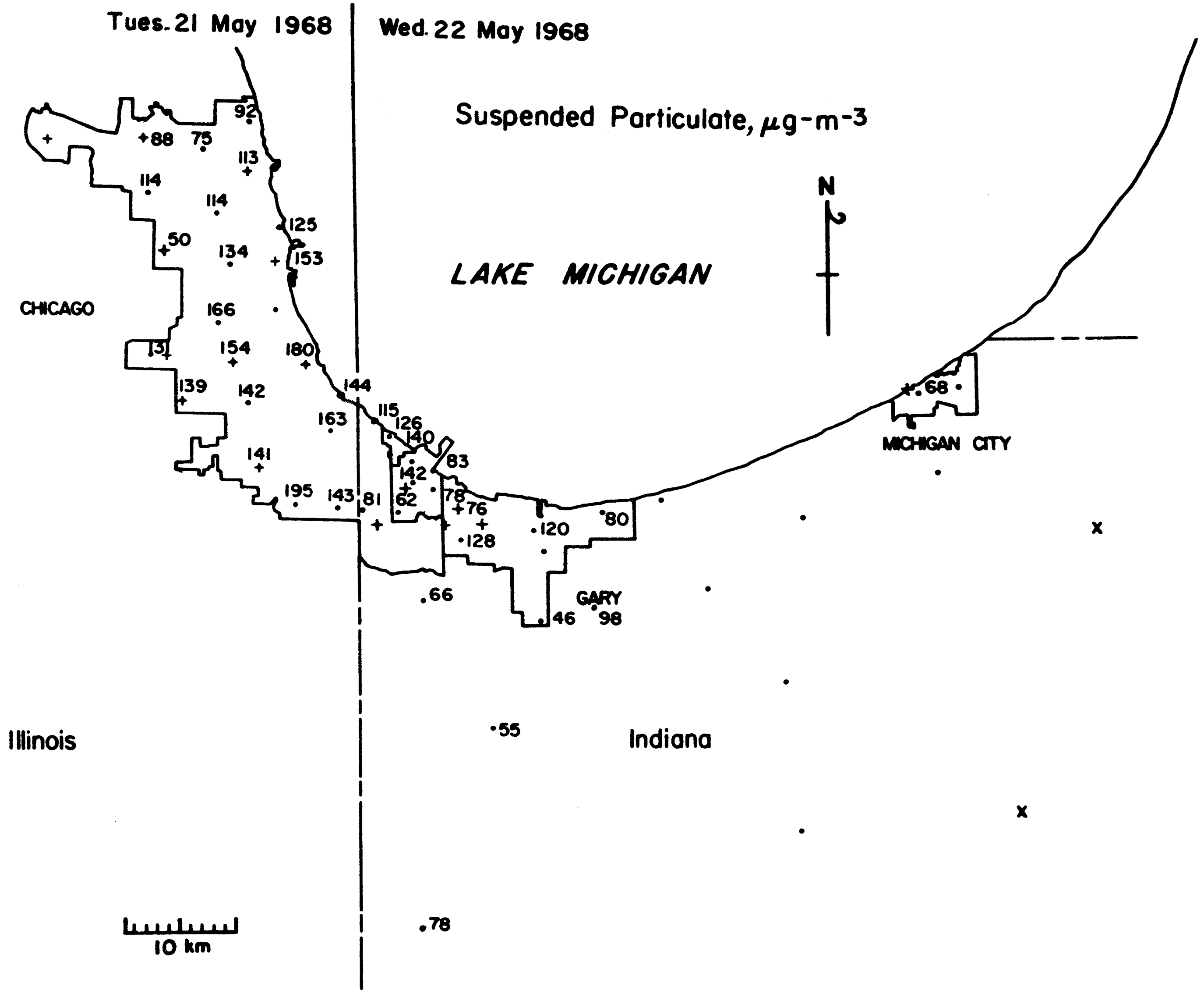


Figure 3.2.3: Suspended particulate data points for 21 and 22 May 1968.

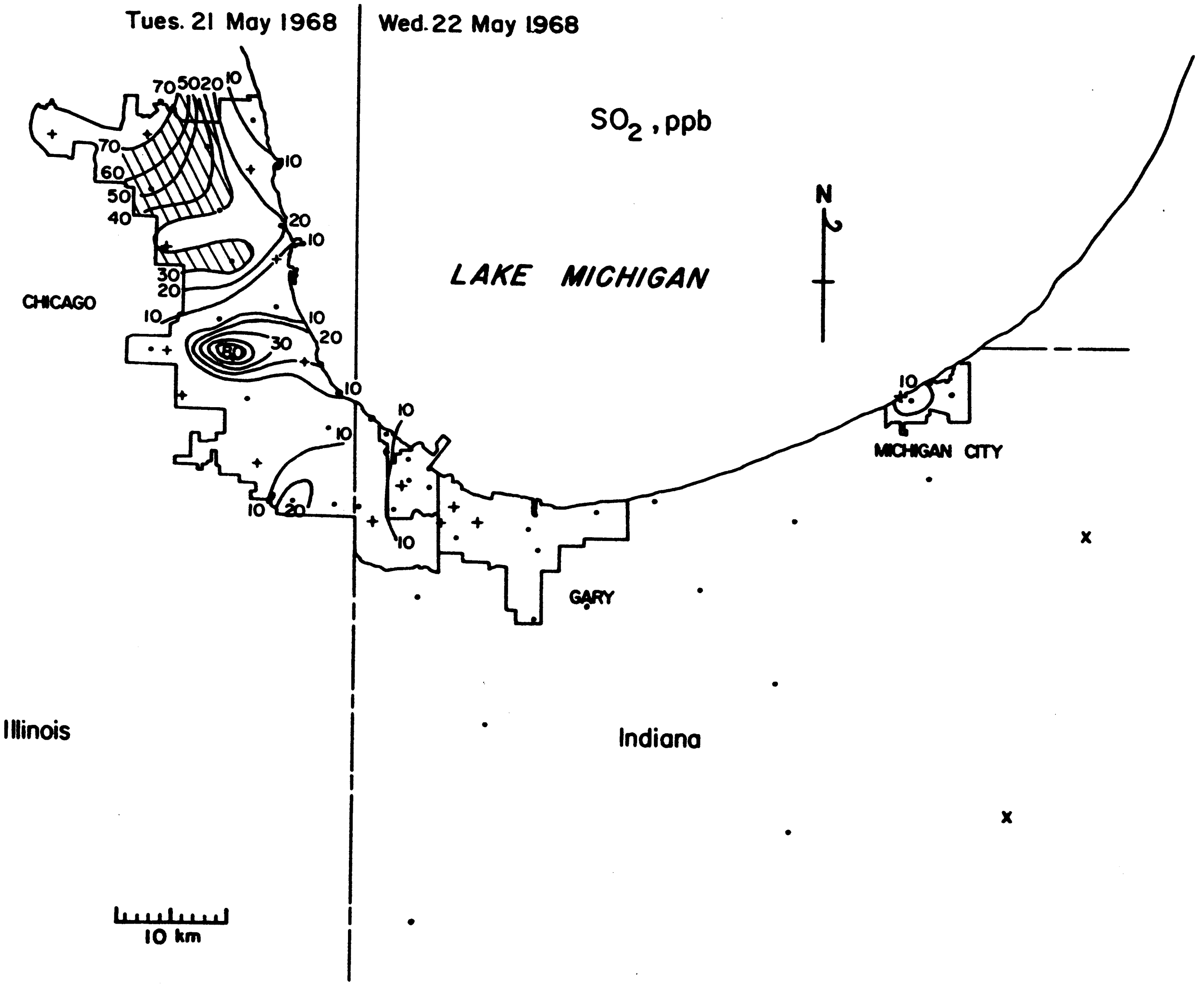


Figure 3.2.4: SO_2 isopleths for 21 and 22 May 1968.

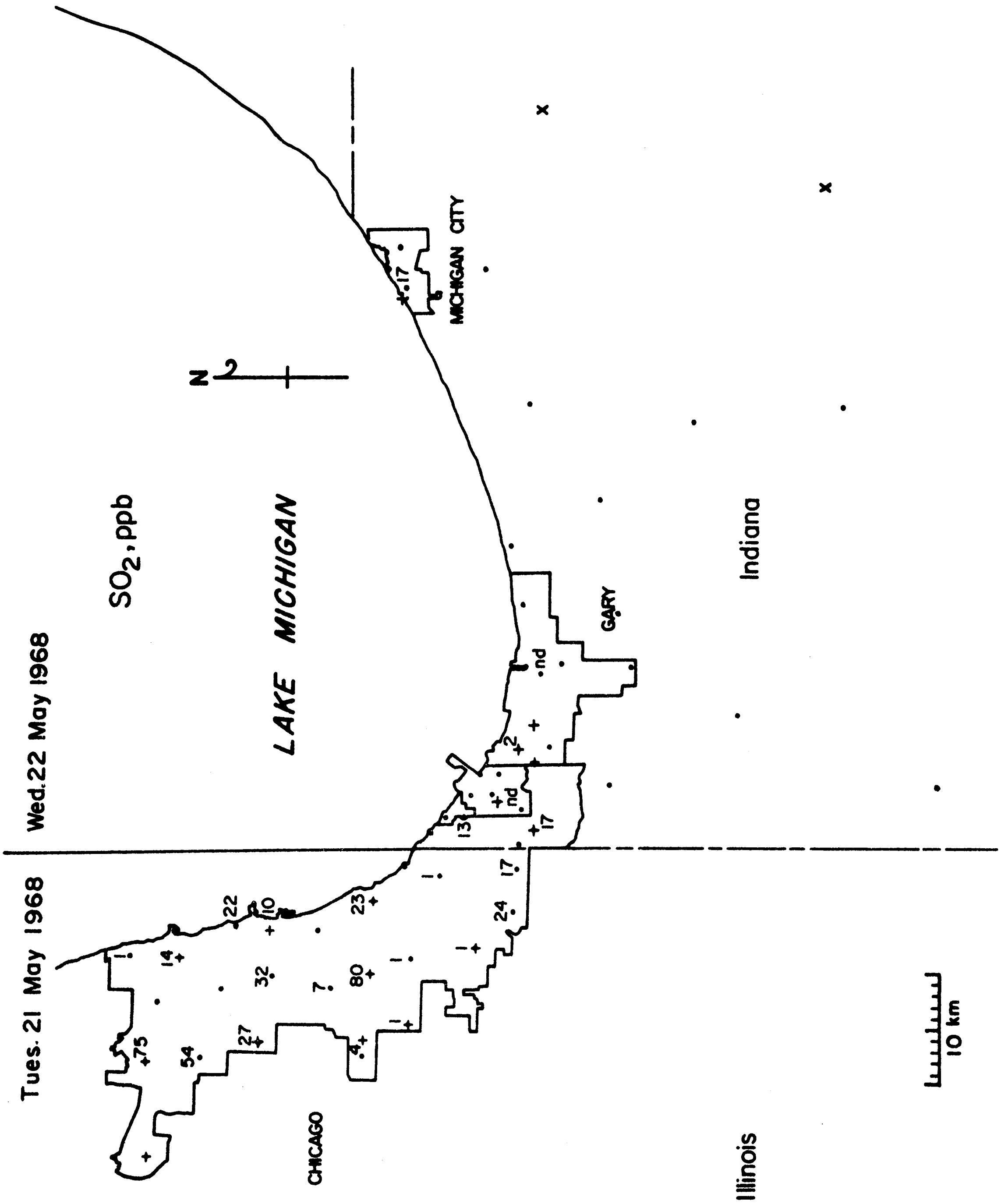


Figure 3.2.5: SO_2 data points for 21 and 22 May 1968.

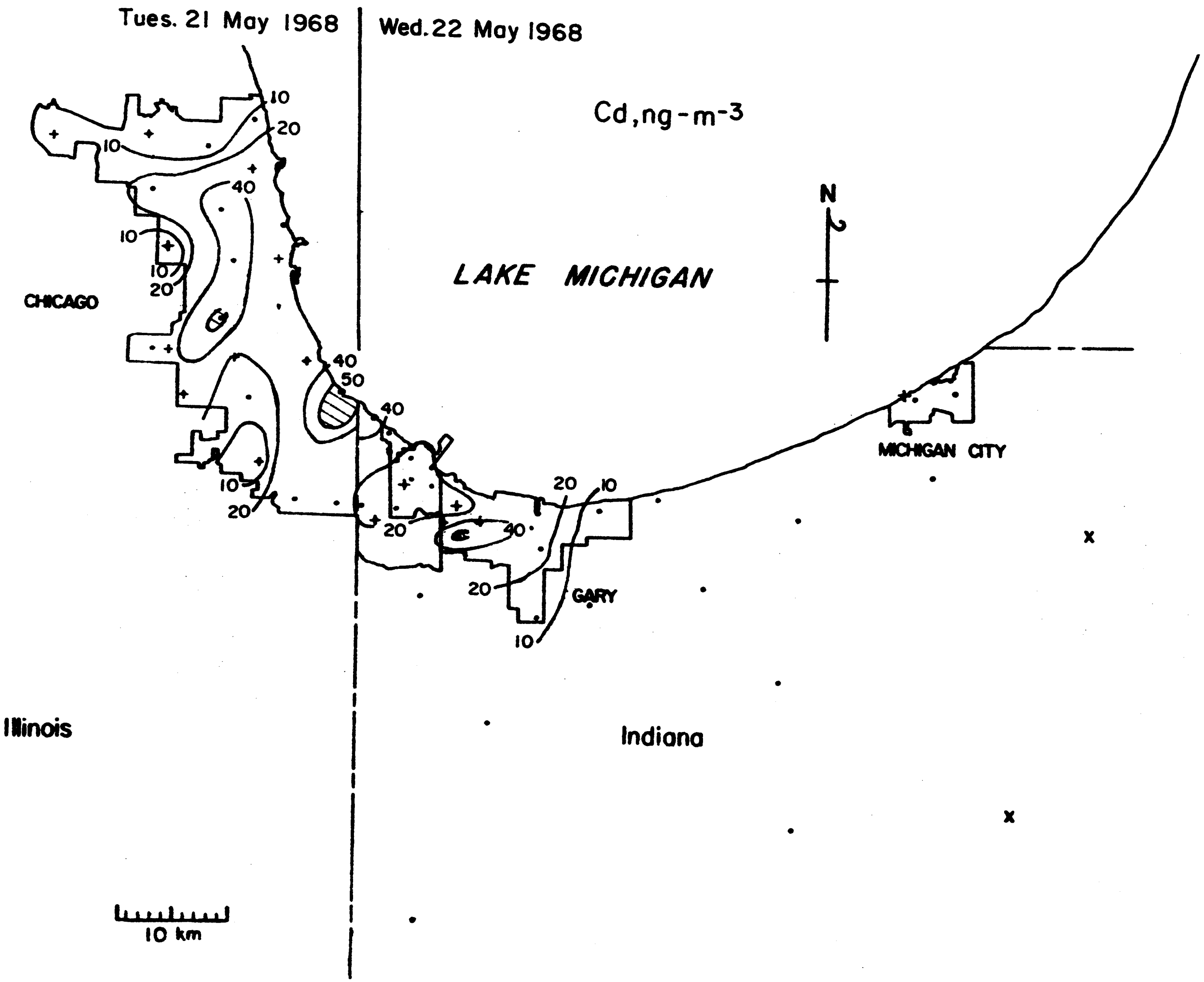


Figure 3.2.6: Cd isopleths for 21 and 22 May 1968.

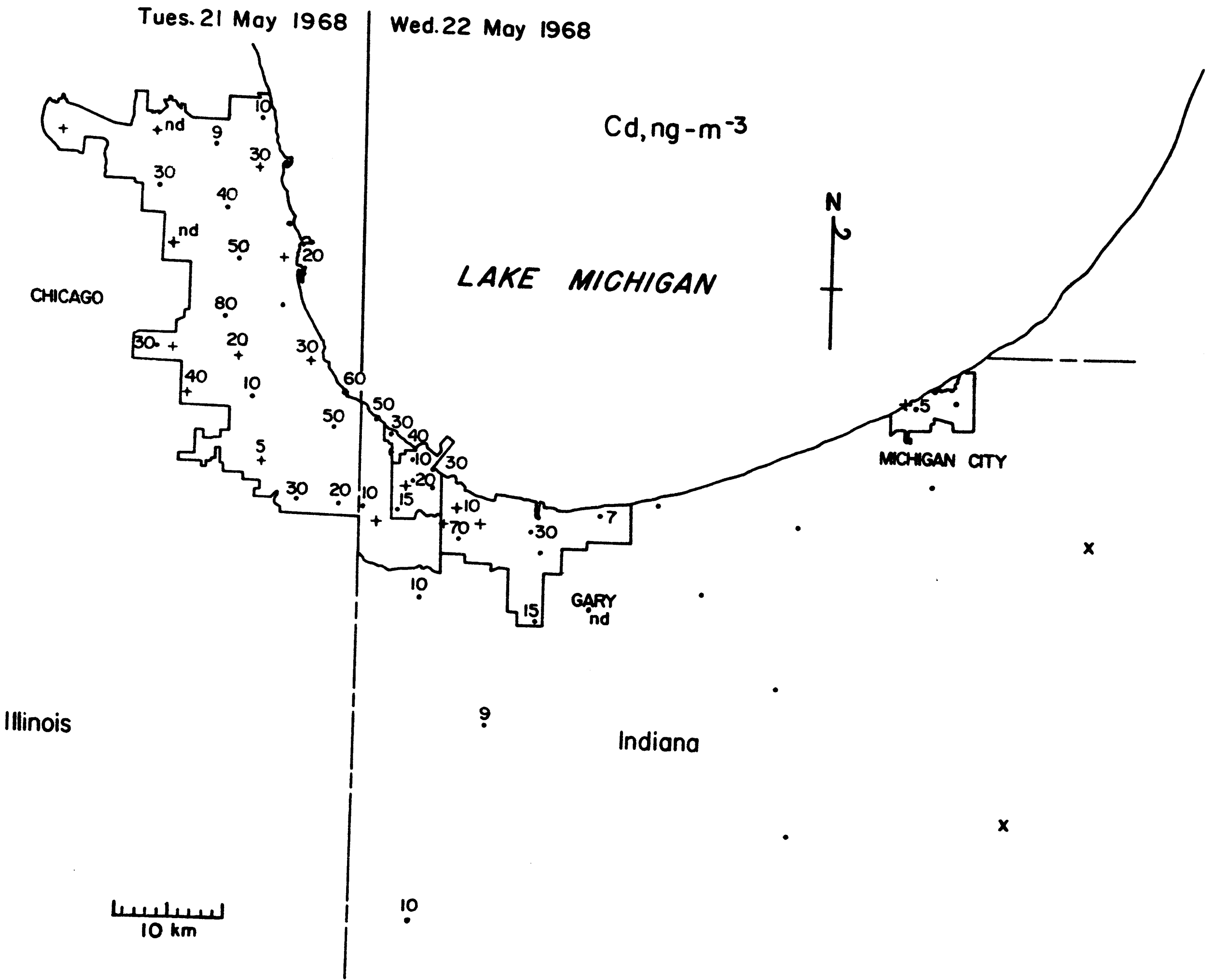


Figure 3.2.7: Cd data points for 21 and 22 May 1968.

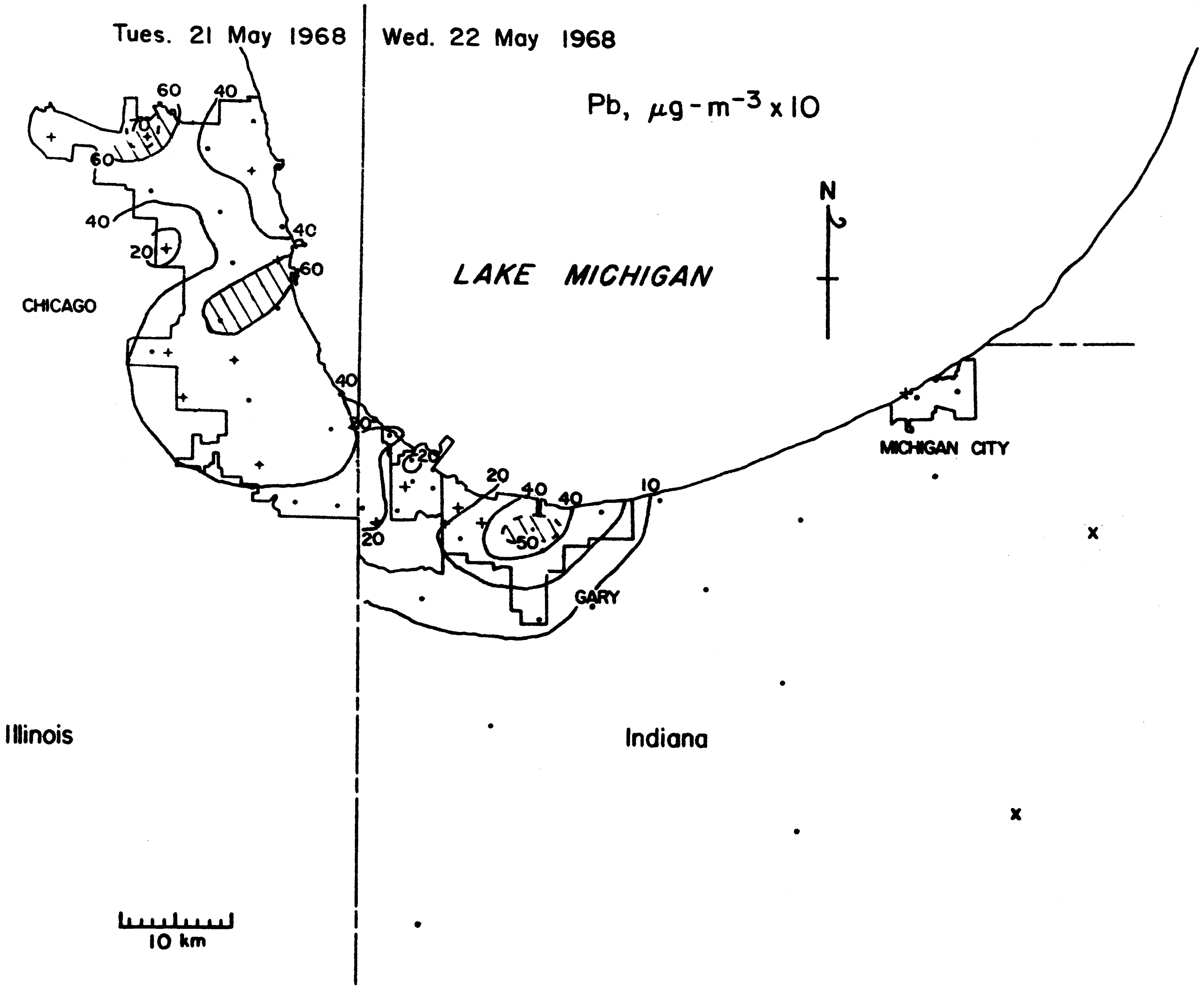


Figure 3.2.8: Pb isopleths for 21 and 22 May 1968.

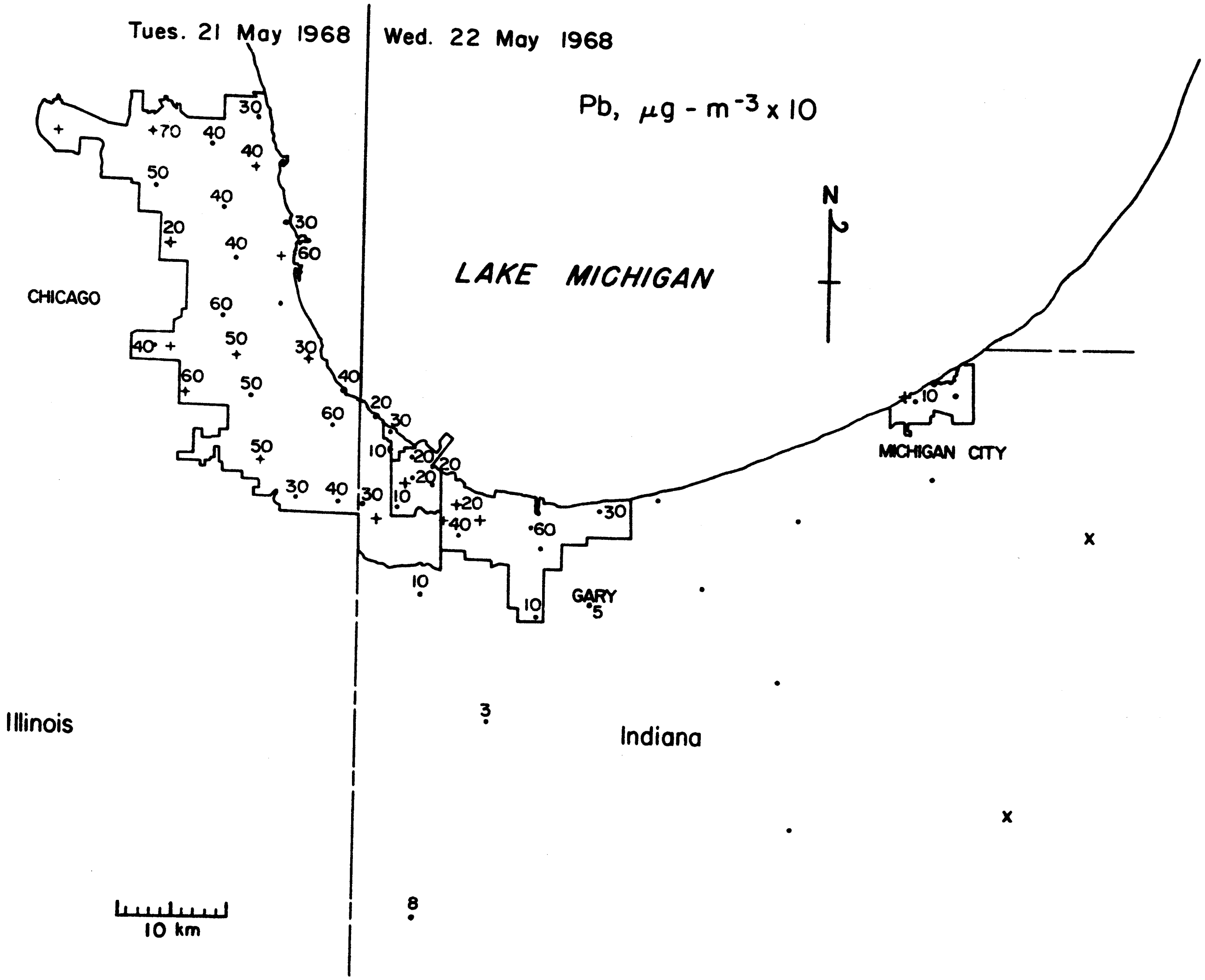


Figure 3.2.9: Pb data points for 21 and 22 May 1968.

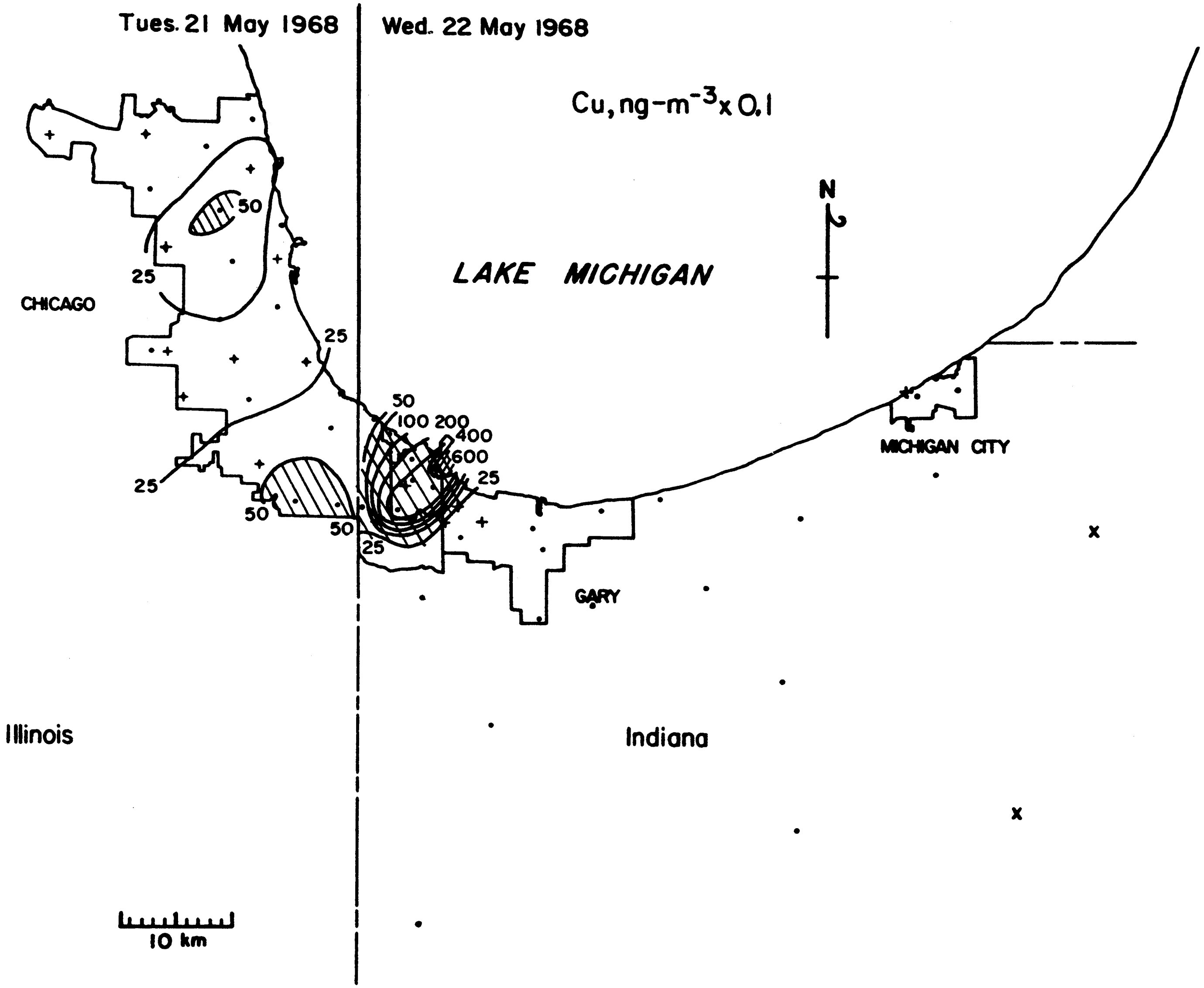


Figure 3.2.10: Cu isopleths for 21 and 22 May 1968.

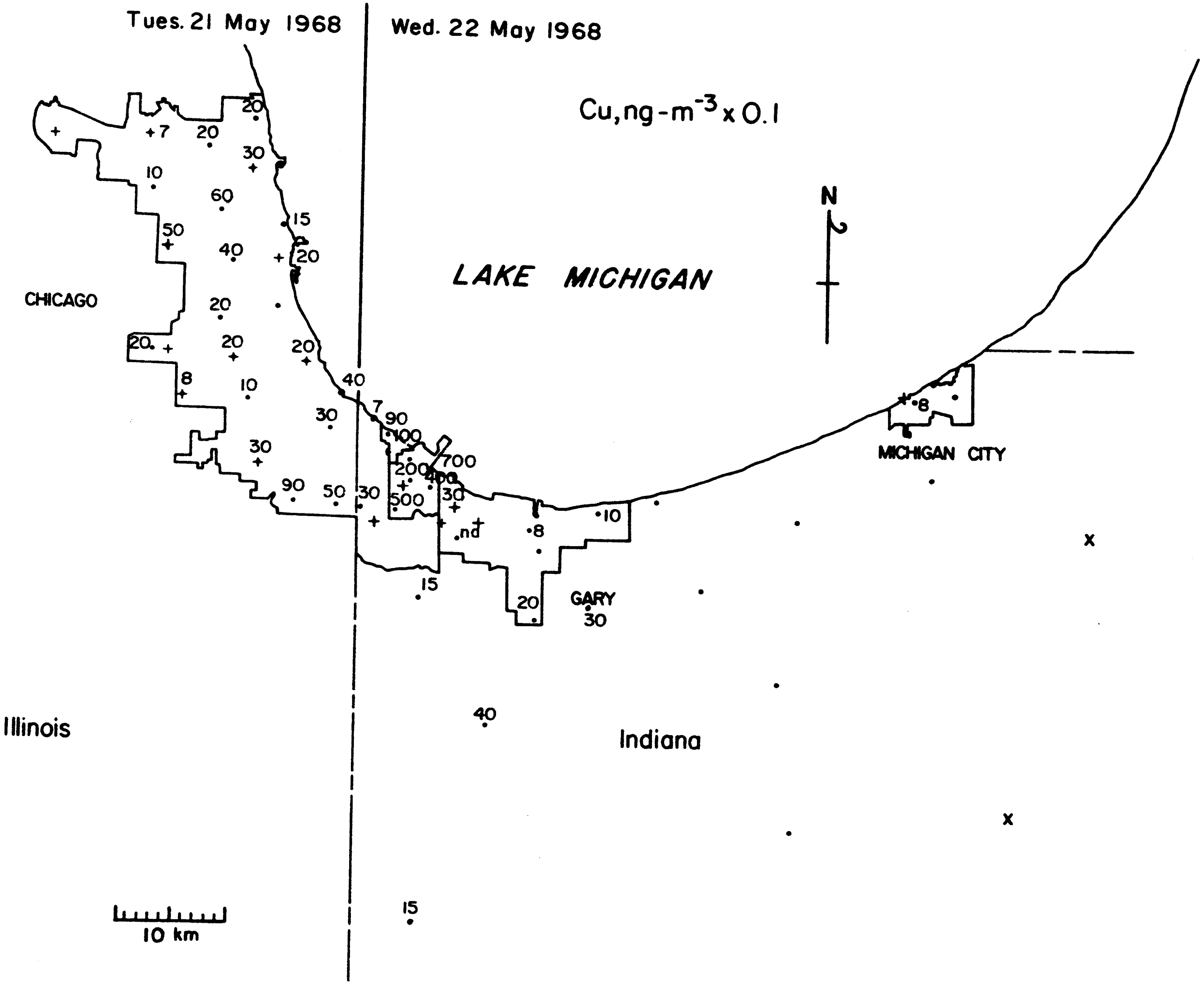


Figure 3.2.11: Cu data points for 21 and 22 May 1968.

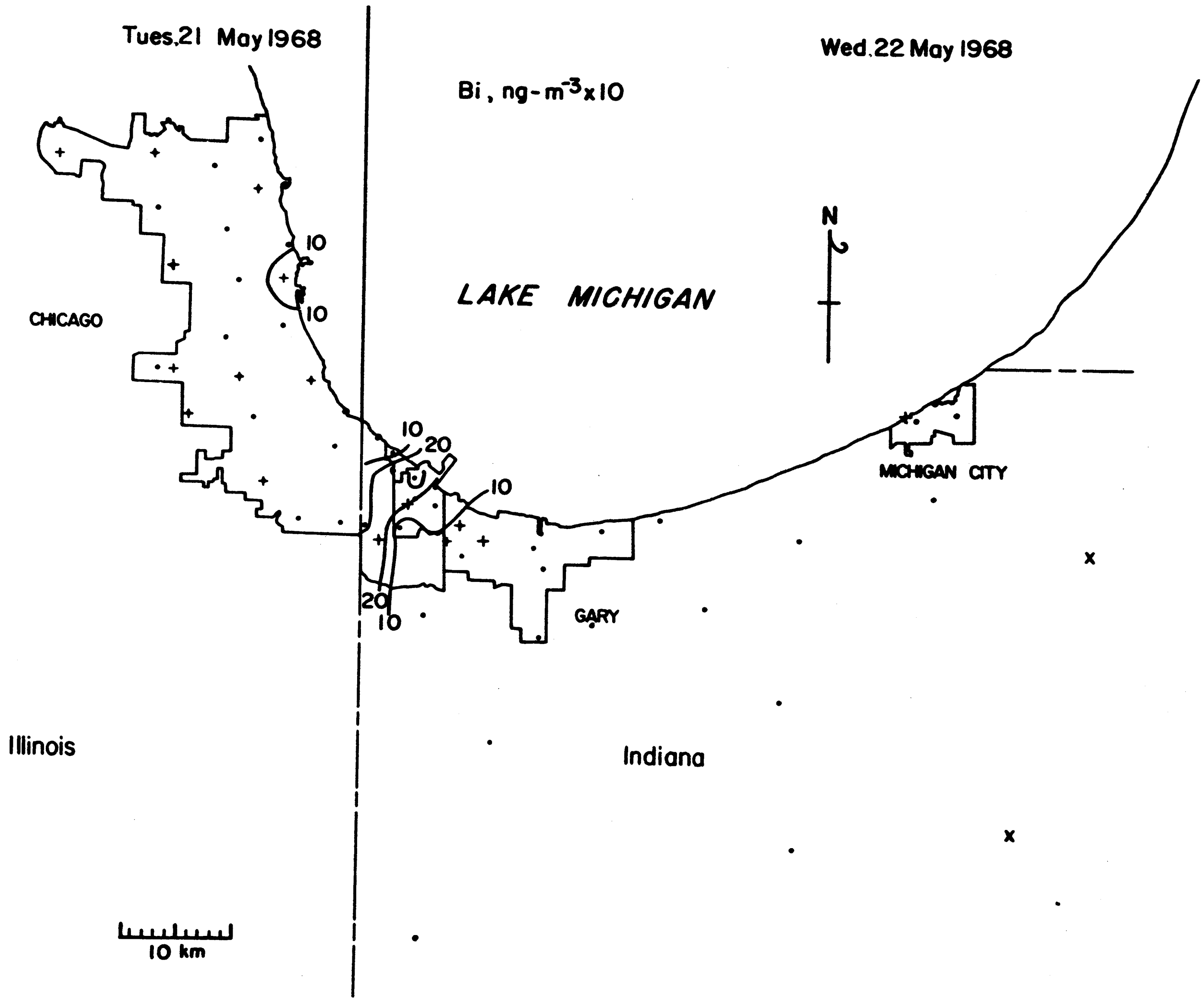


Figure 3.2.12: Bi isopleths for 21 and 22 May 1968.

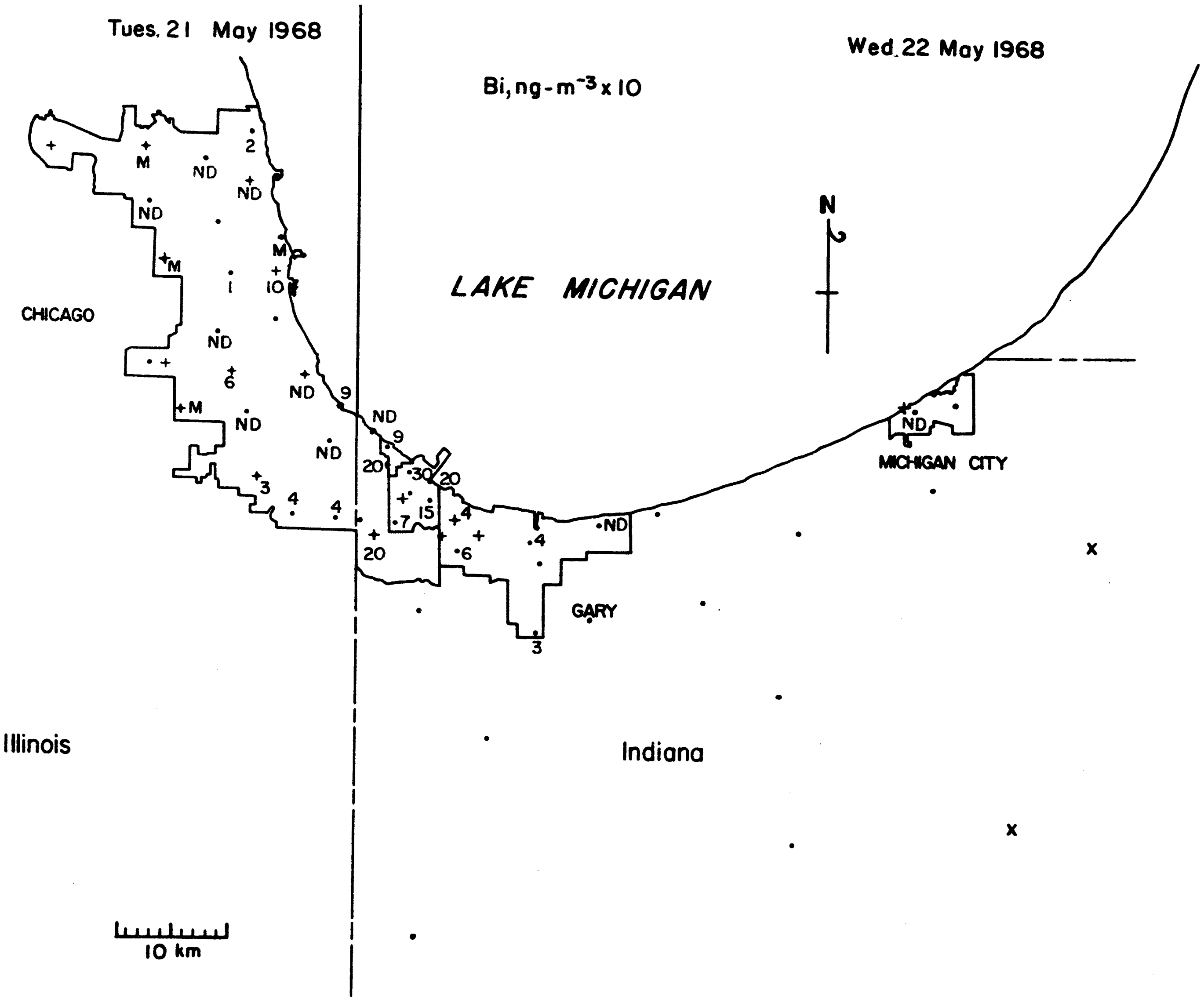


Figure 3.2.13: Bi data points for 21 and 22 May 1968.

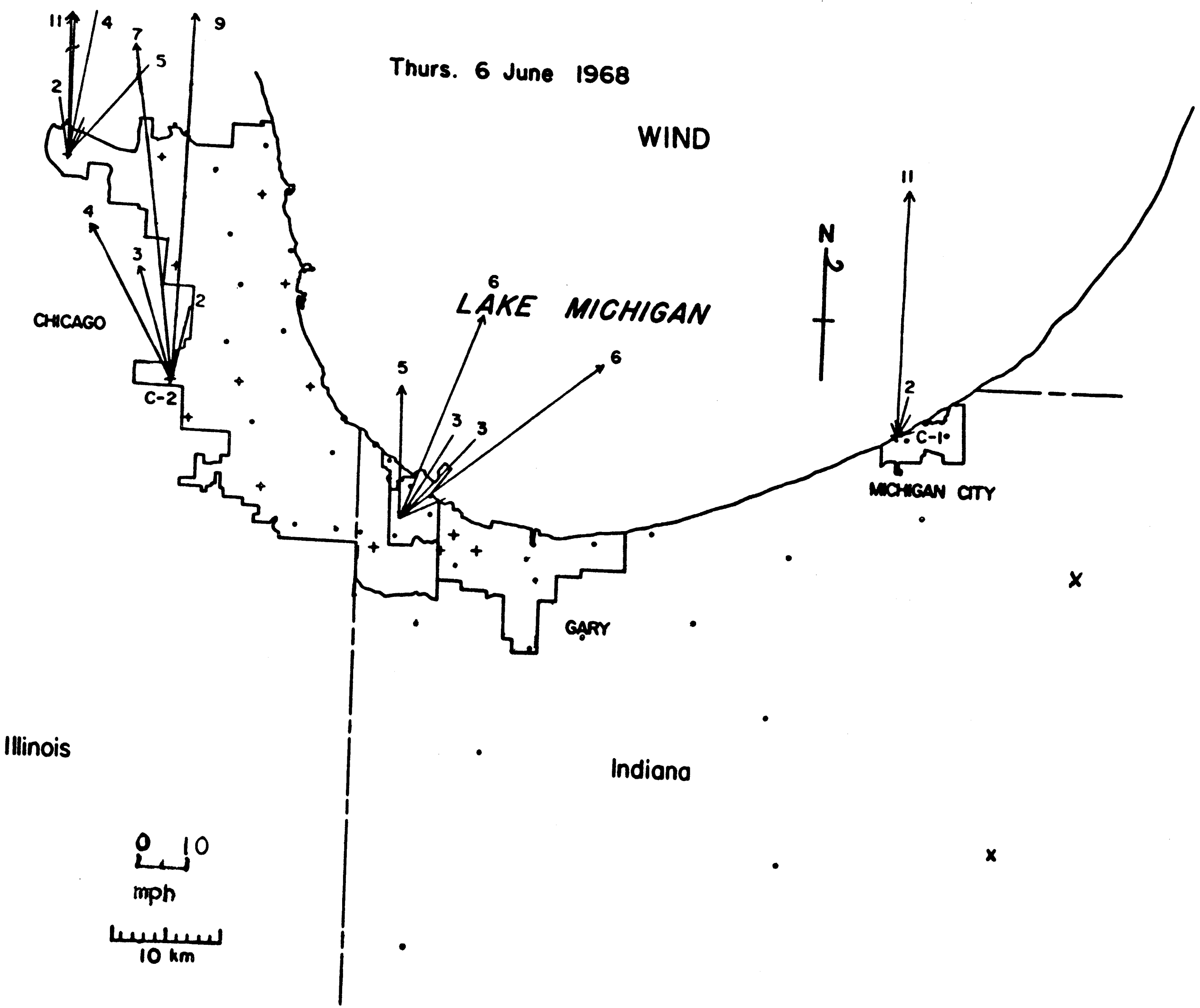


Figure 3.3.1: Wind rose for 6 June 1968.

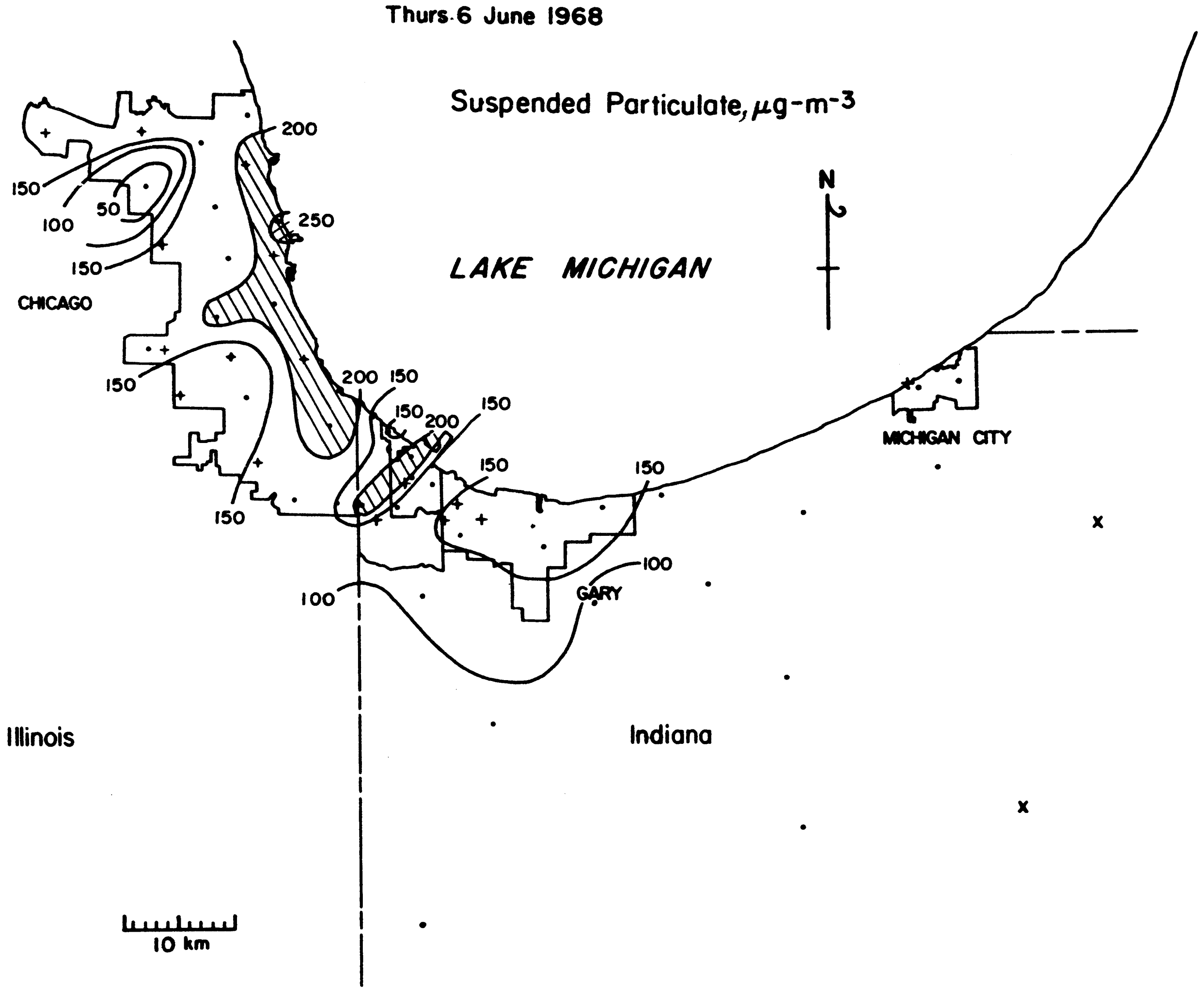


Figure 3.3.2: Suspended particulate isopleths for 6 June 1968.

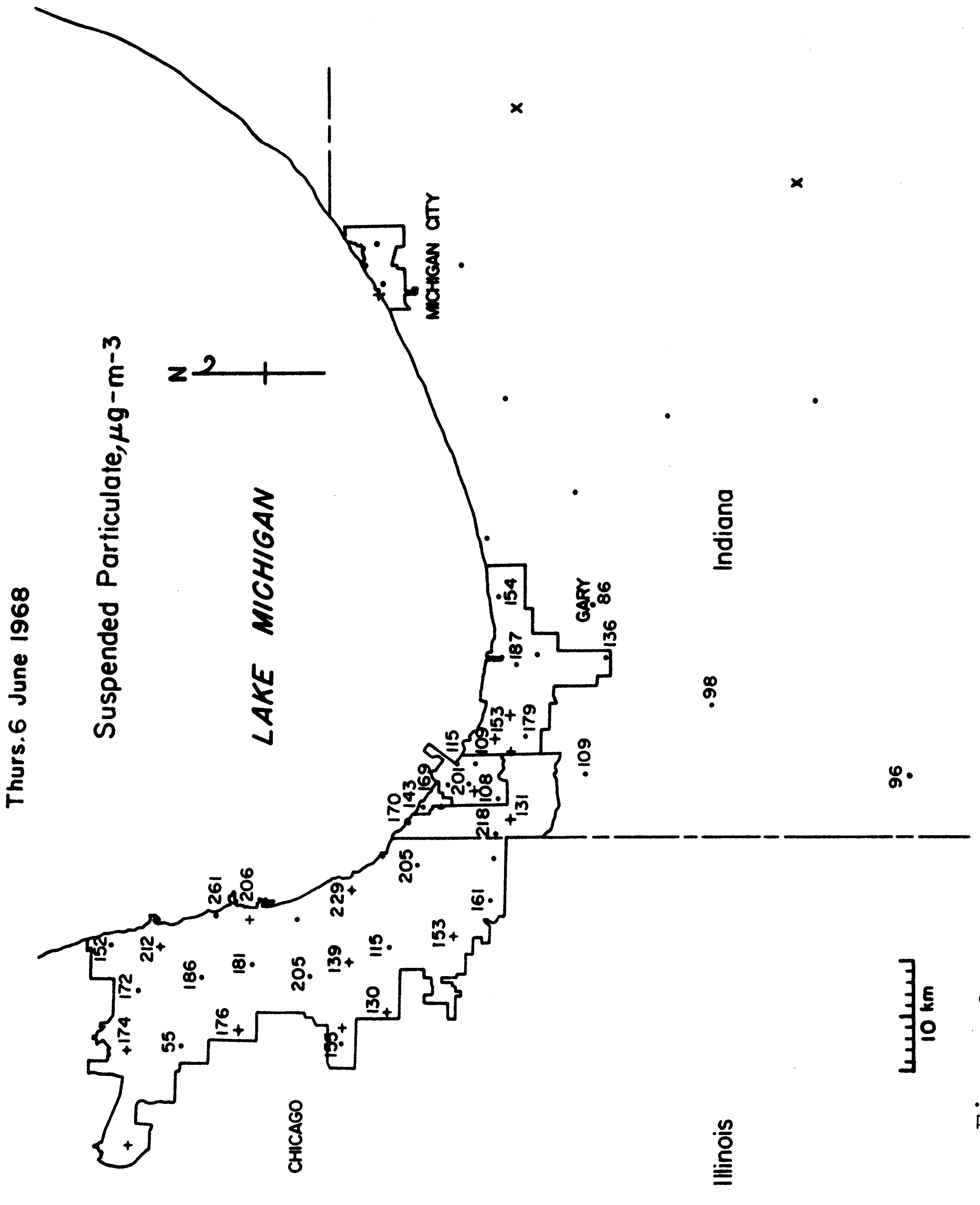


Figure 3.3.3: Suspended particulate data points for 6 June 1968.

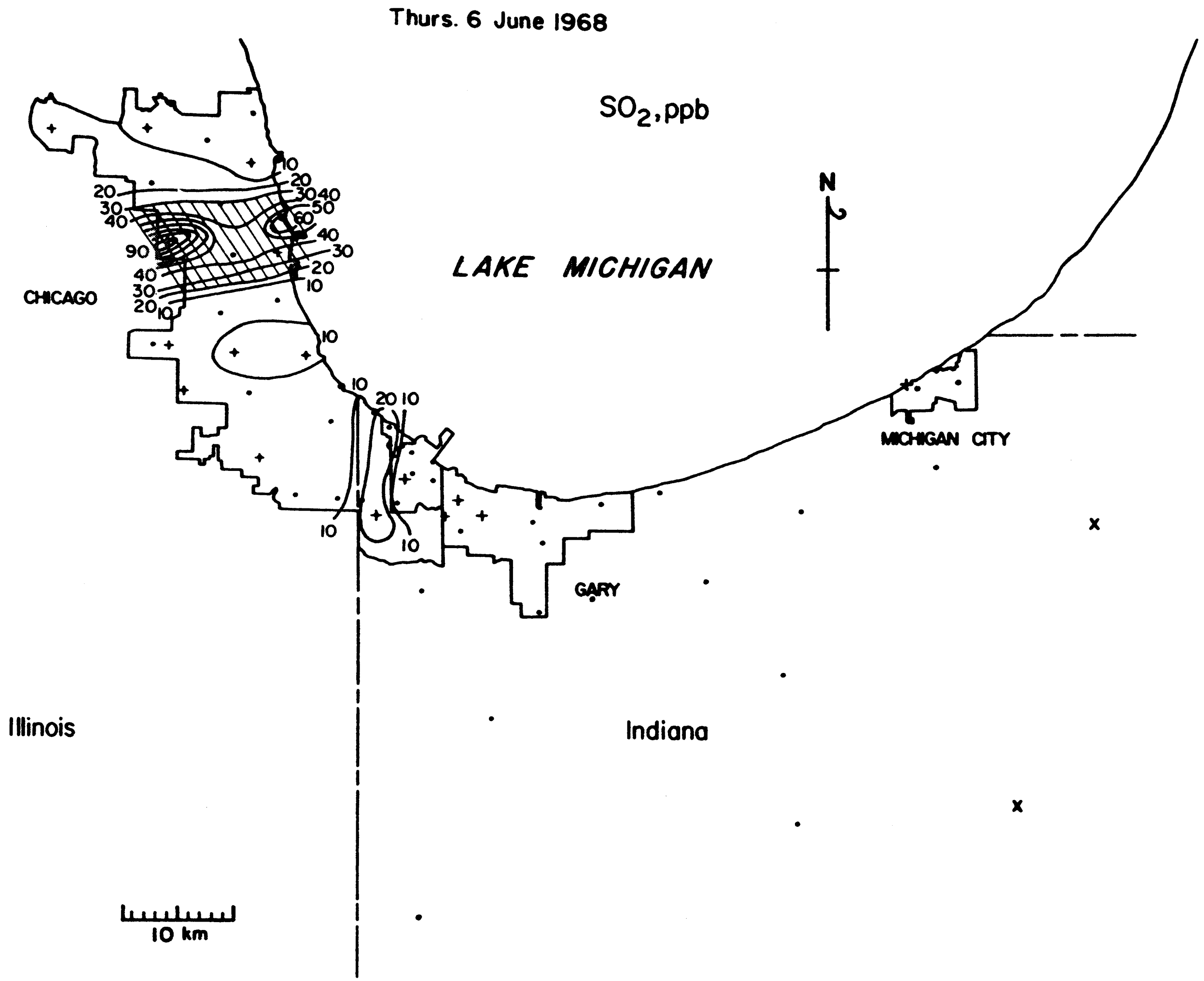


Figure 3.3.4: SO_2 isopleths for 6 June 1968.

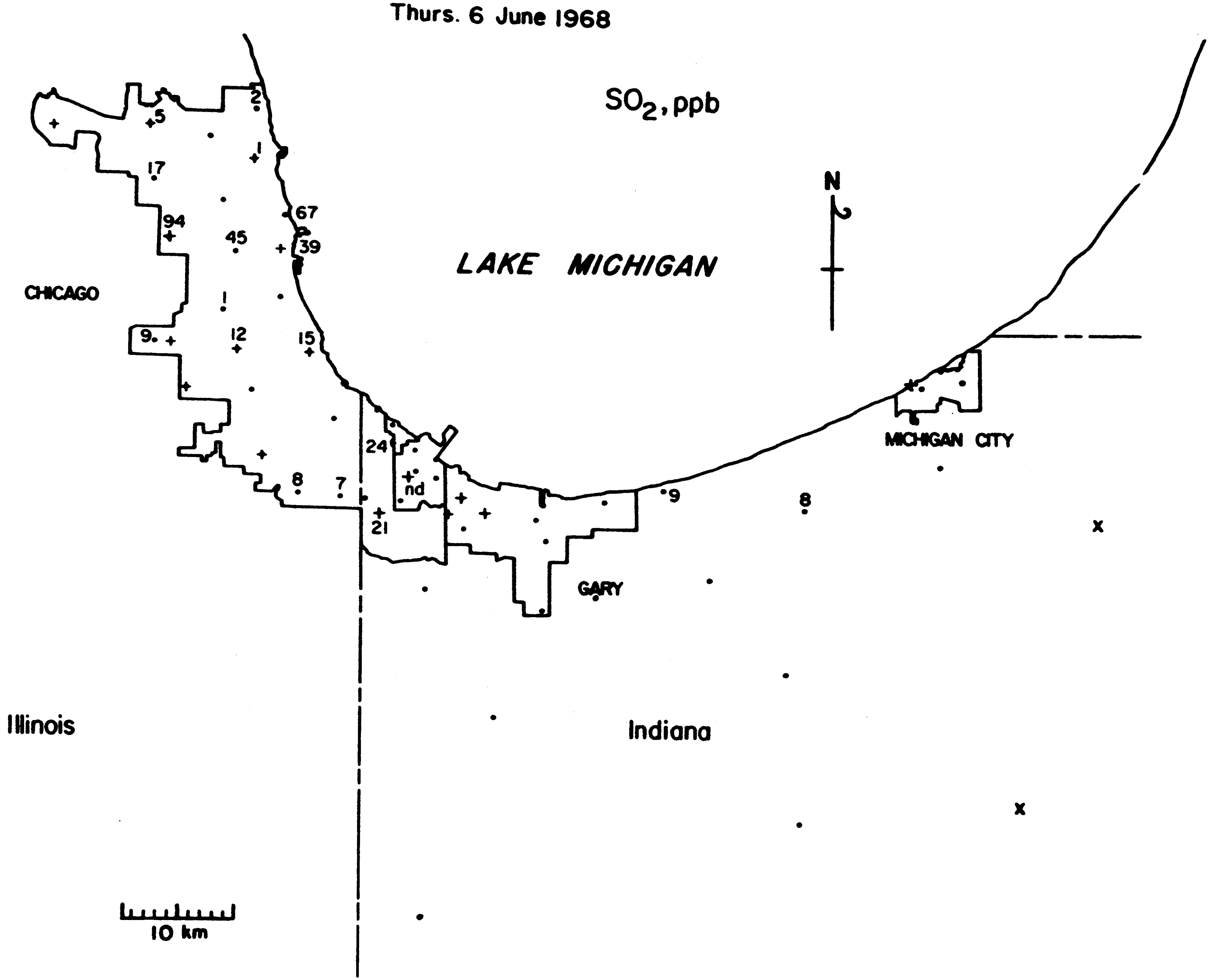


Figure 3.3.5: SO_2 data points for 6 June 1968.

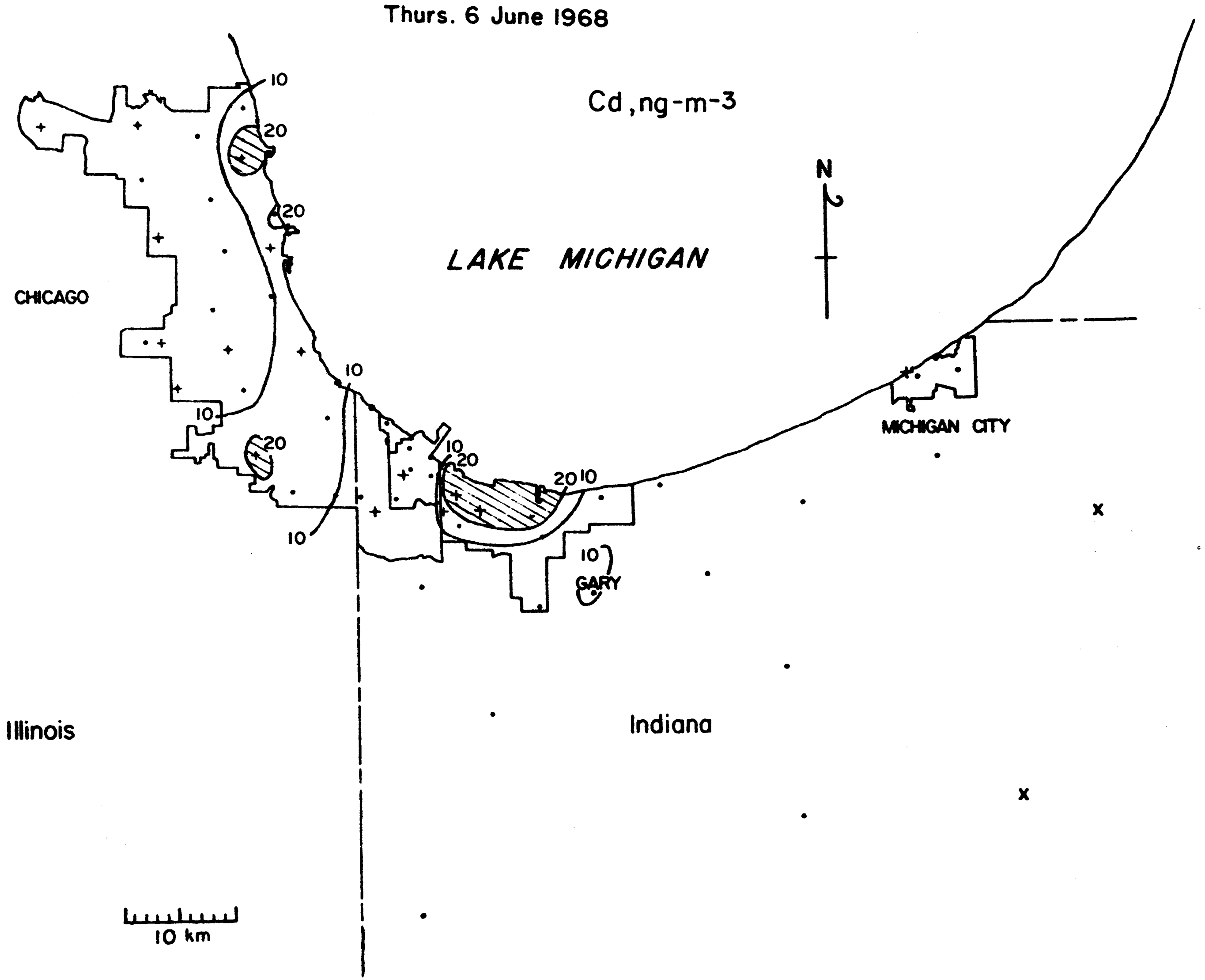


Figure 3.3.6: Cd isopleths for 6 June 1968.

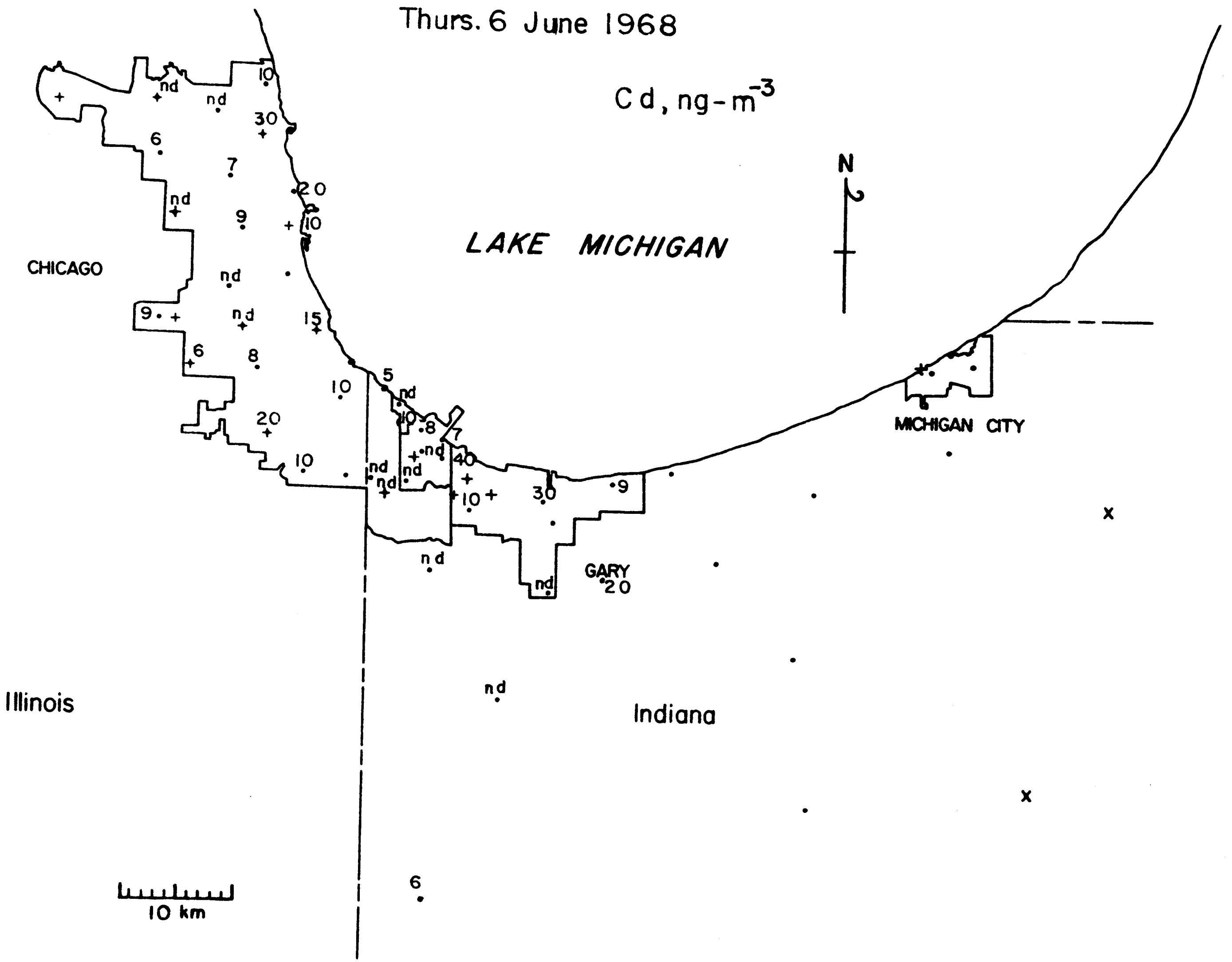


Figure 3.3.7: Cd data points for 6 June 1968.

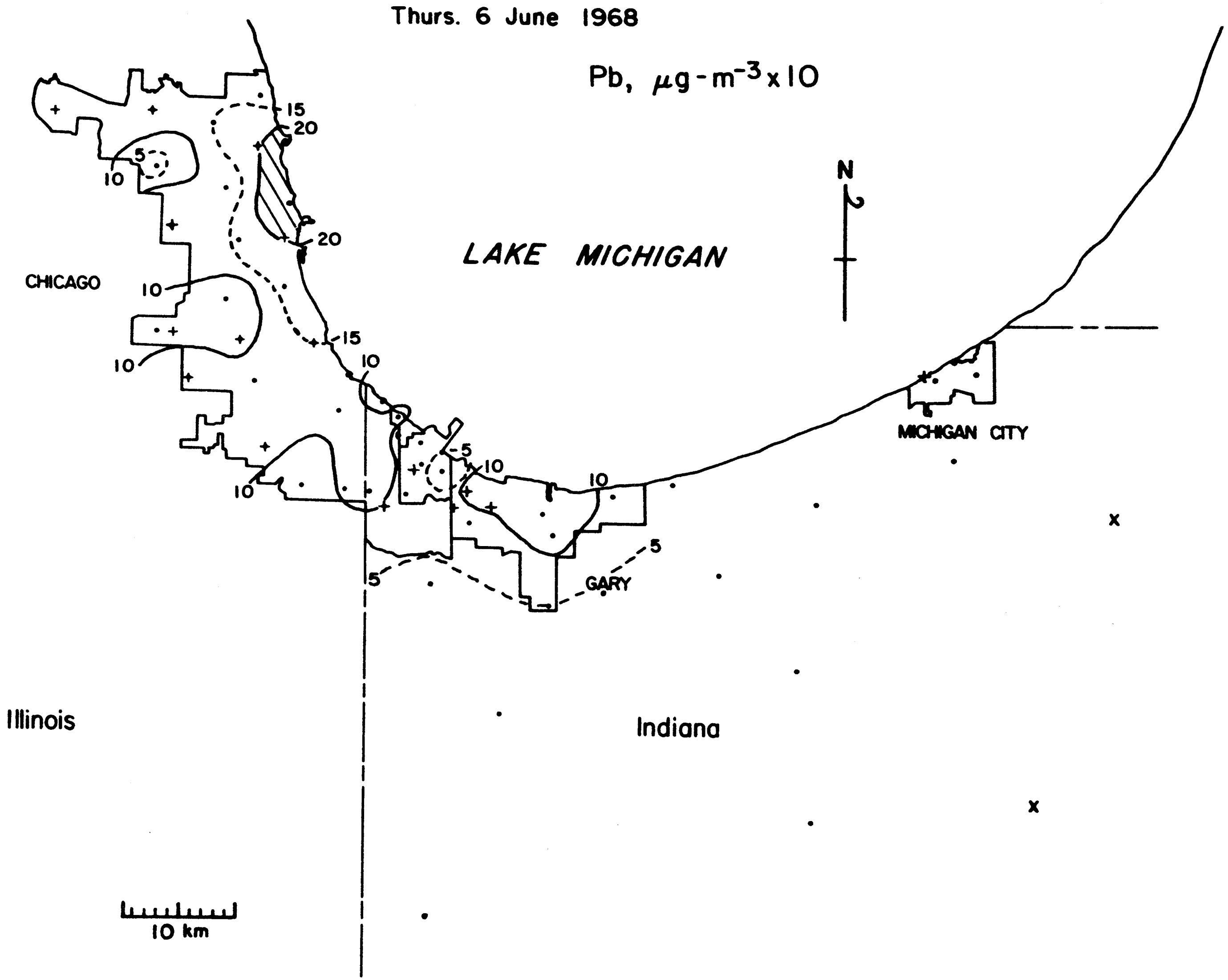


Figure 3.3.8: Pb isopleths for 6 June 1968.

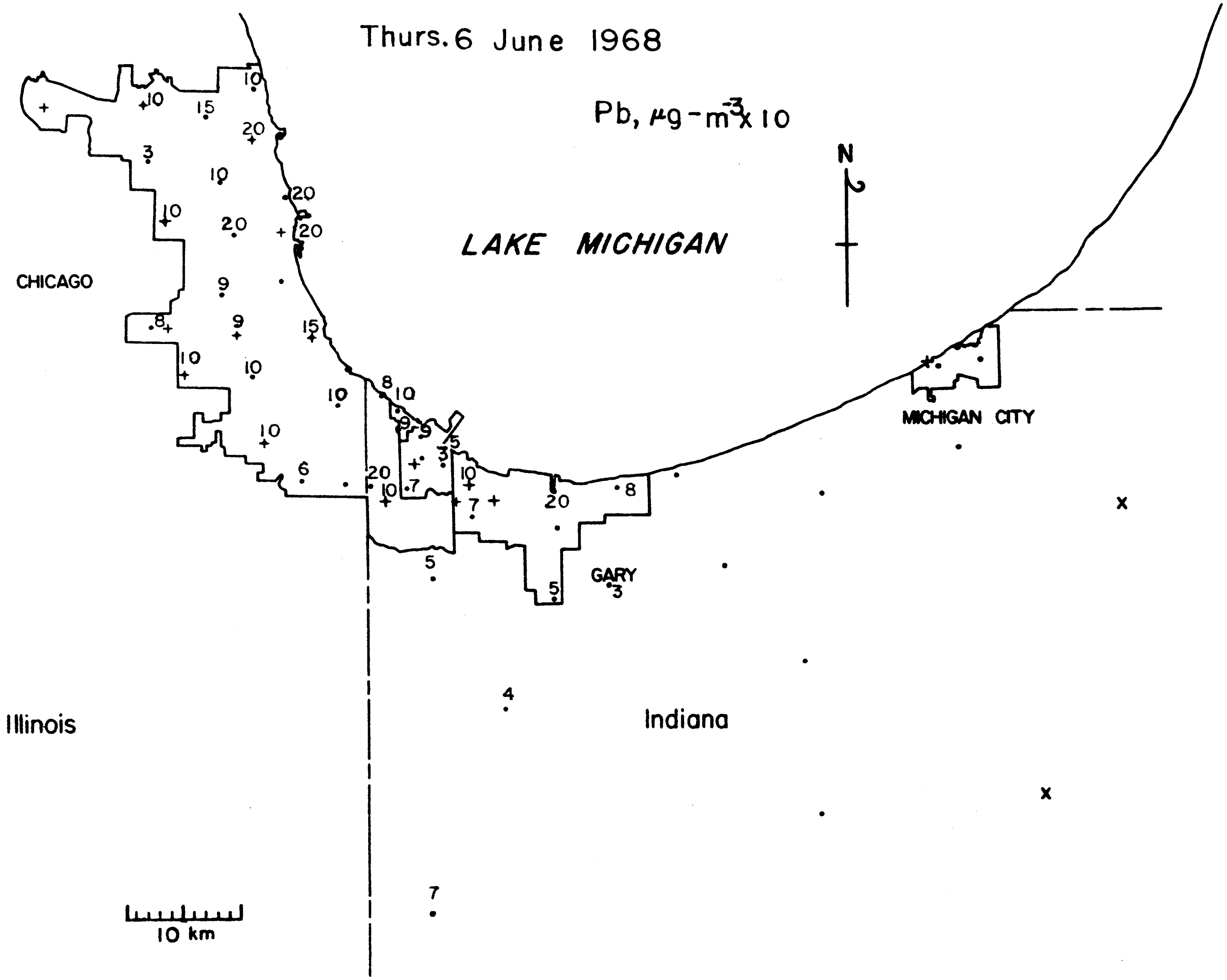


Figure 3.3.9: Pb data points for 6 June 1968.

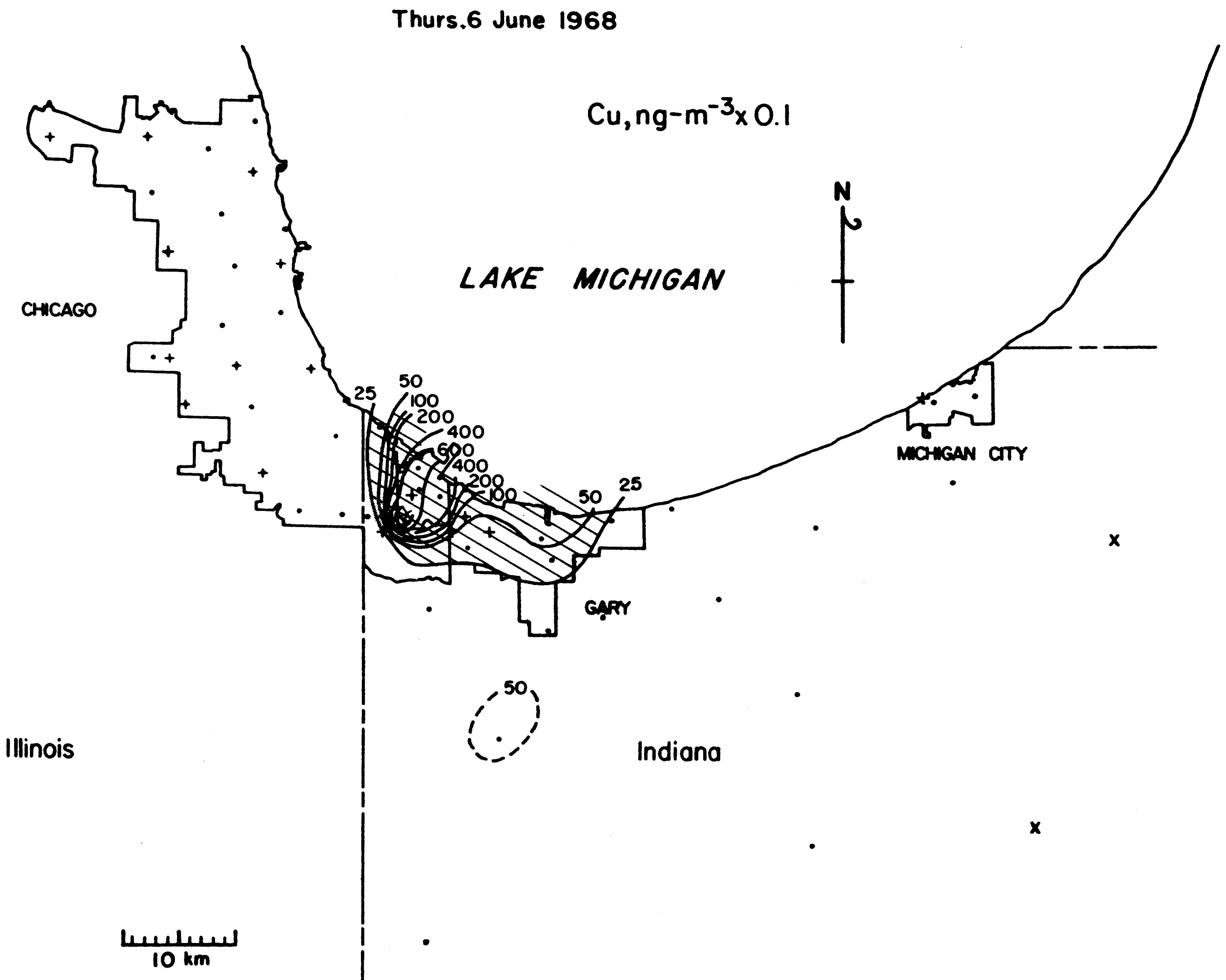


Figure 3.3.10: Cu isopleths for 6 June 1968.

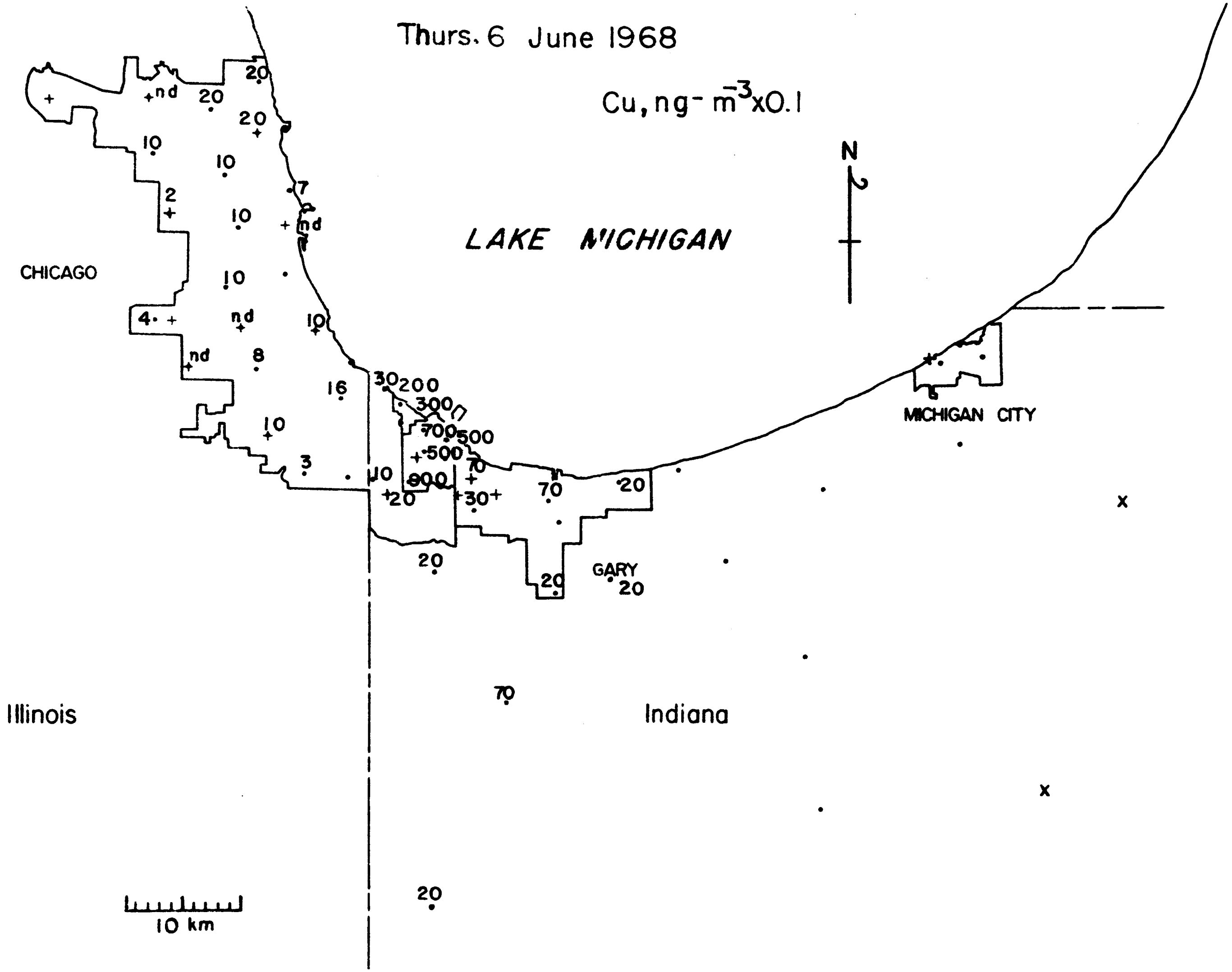


Figure 3.3.11: Cu data points for 6 June 1968.

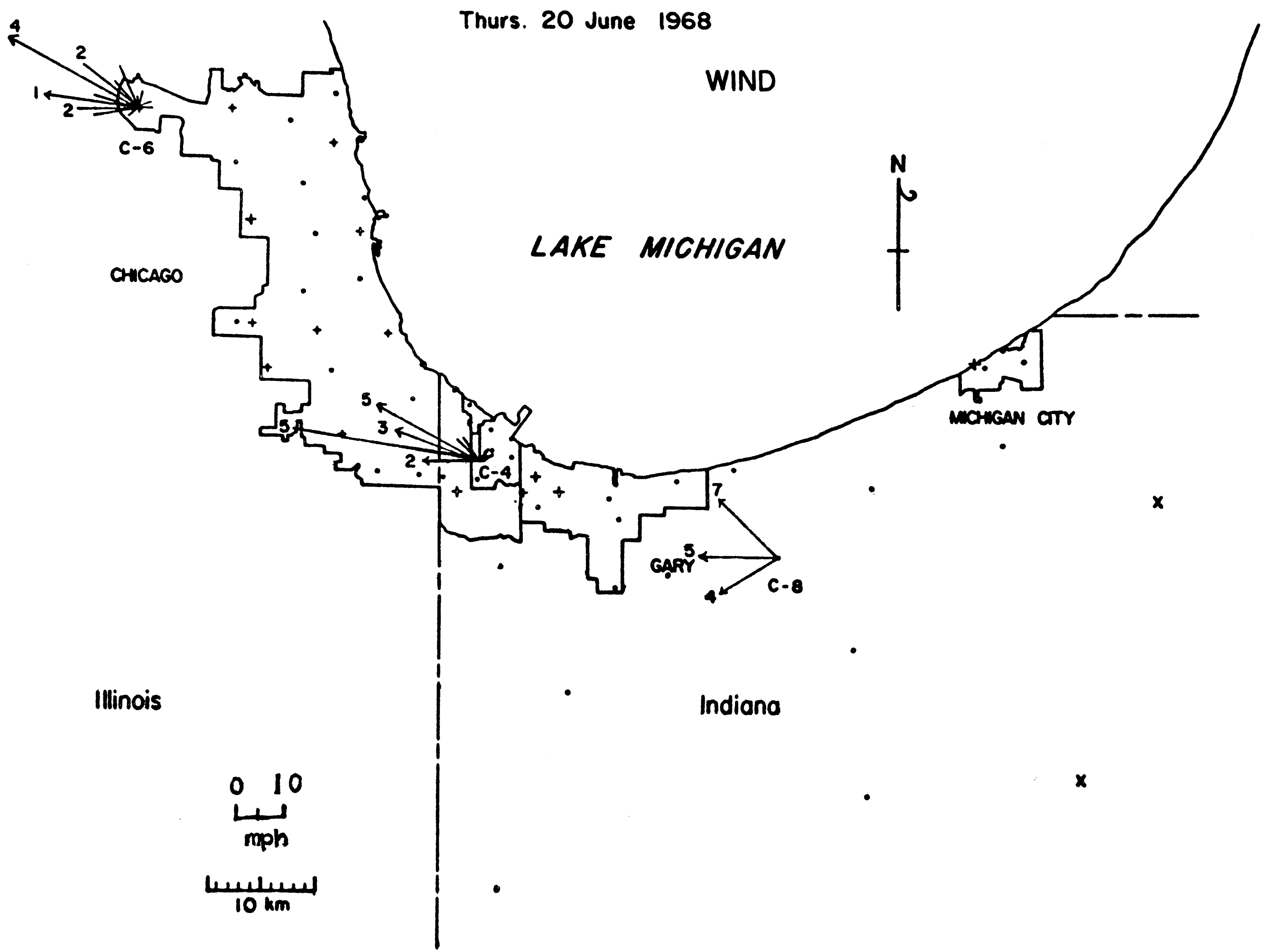


Figure 3.4.1: Wind rose for 20 June 1968.

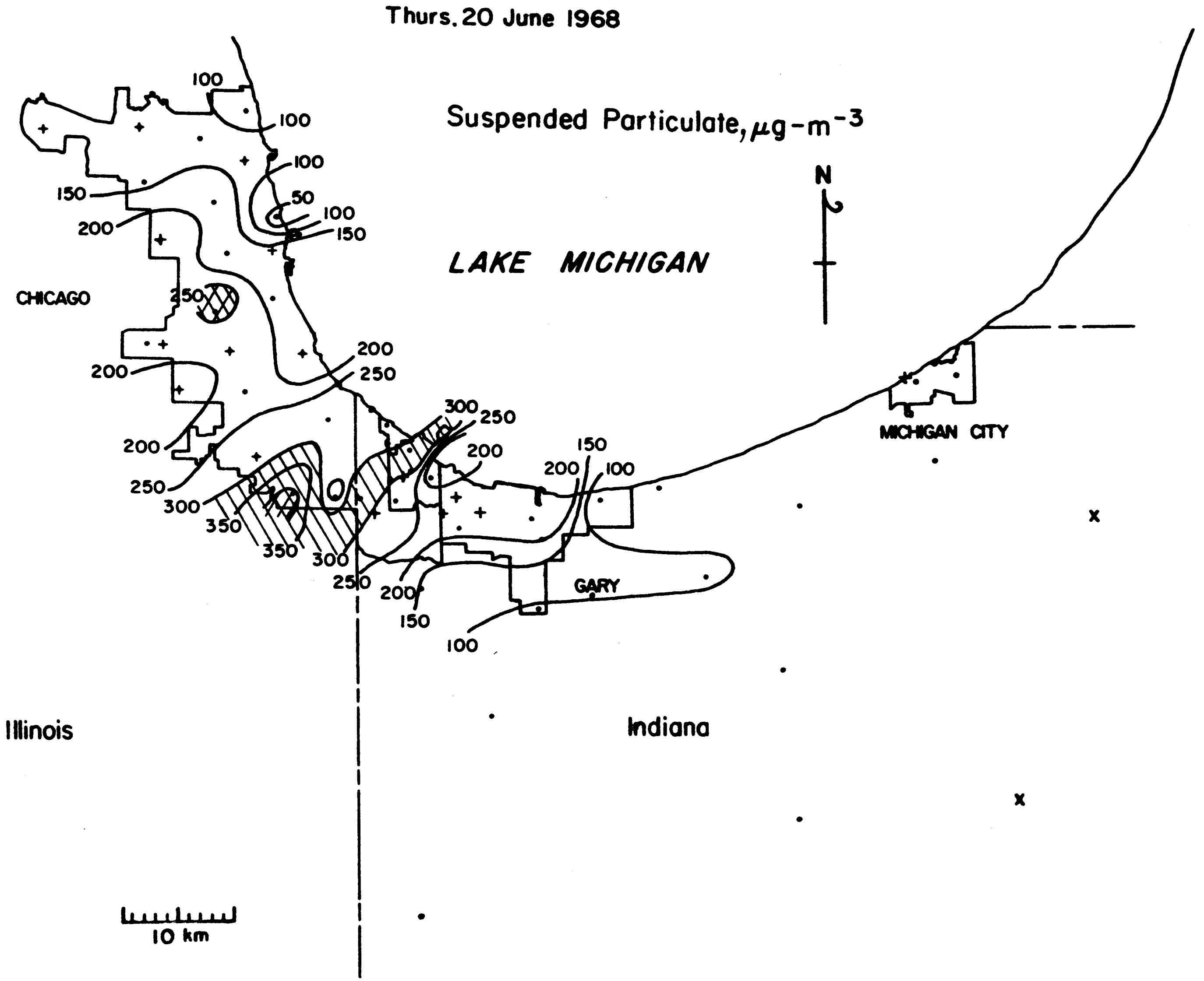


Figure 3.4.2: Suspended particulate isopleths for 20 June 1968.

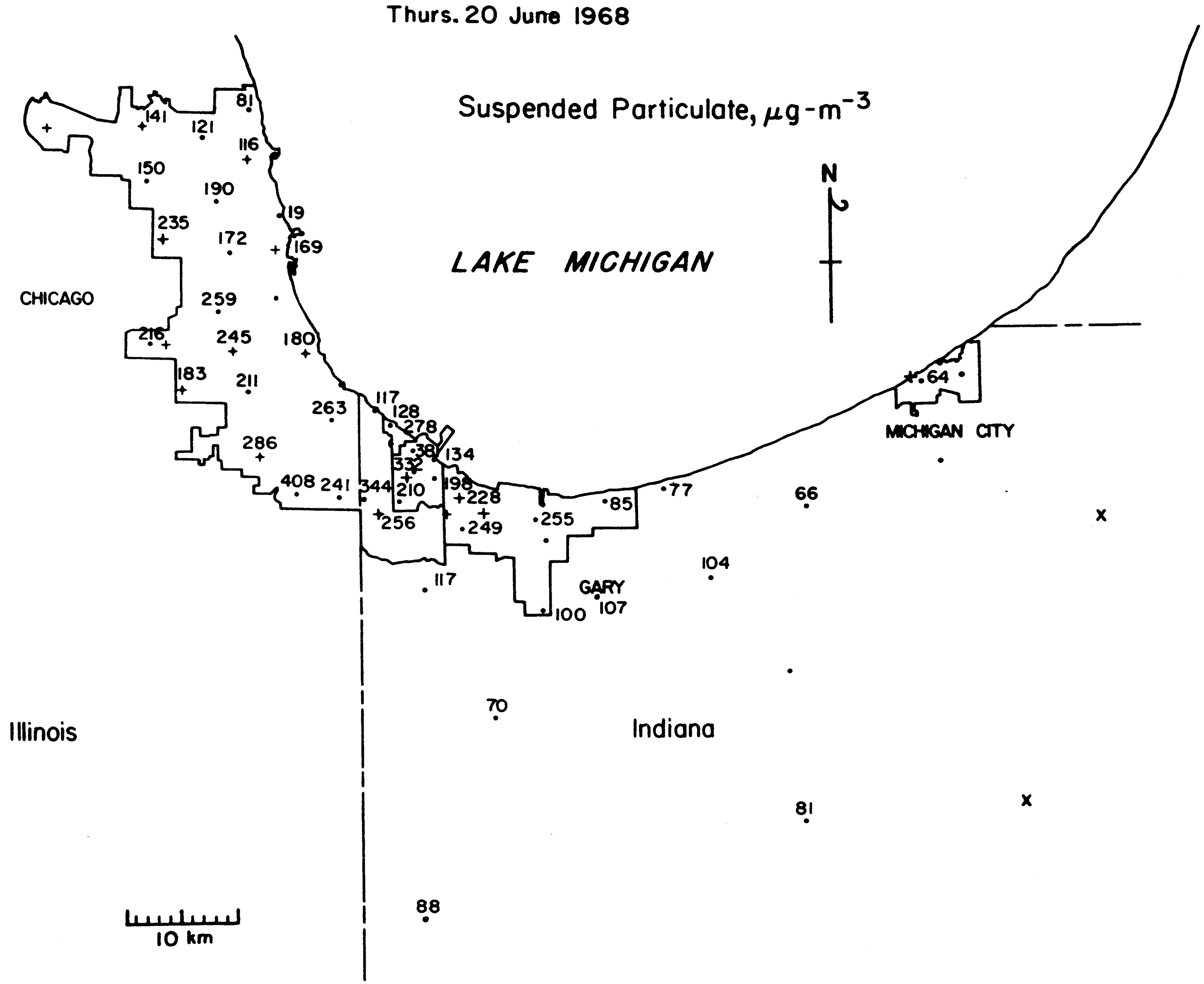


Figure 3.4.3: Suspended particulate data points for 20 June 1968.

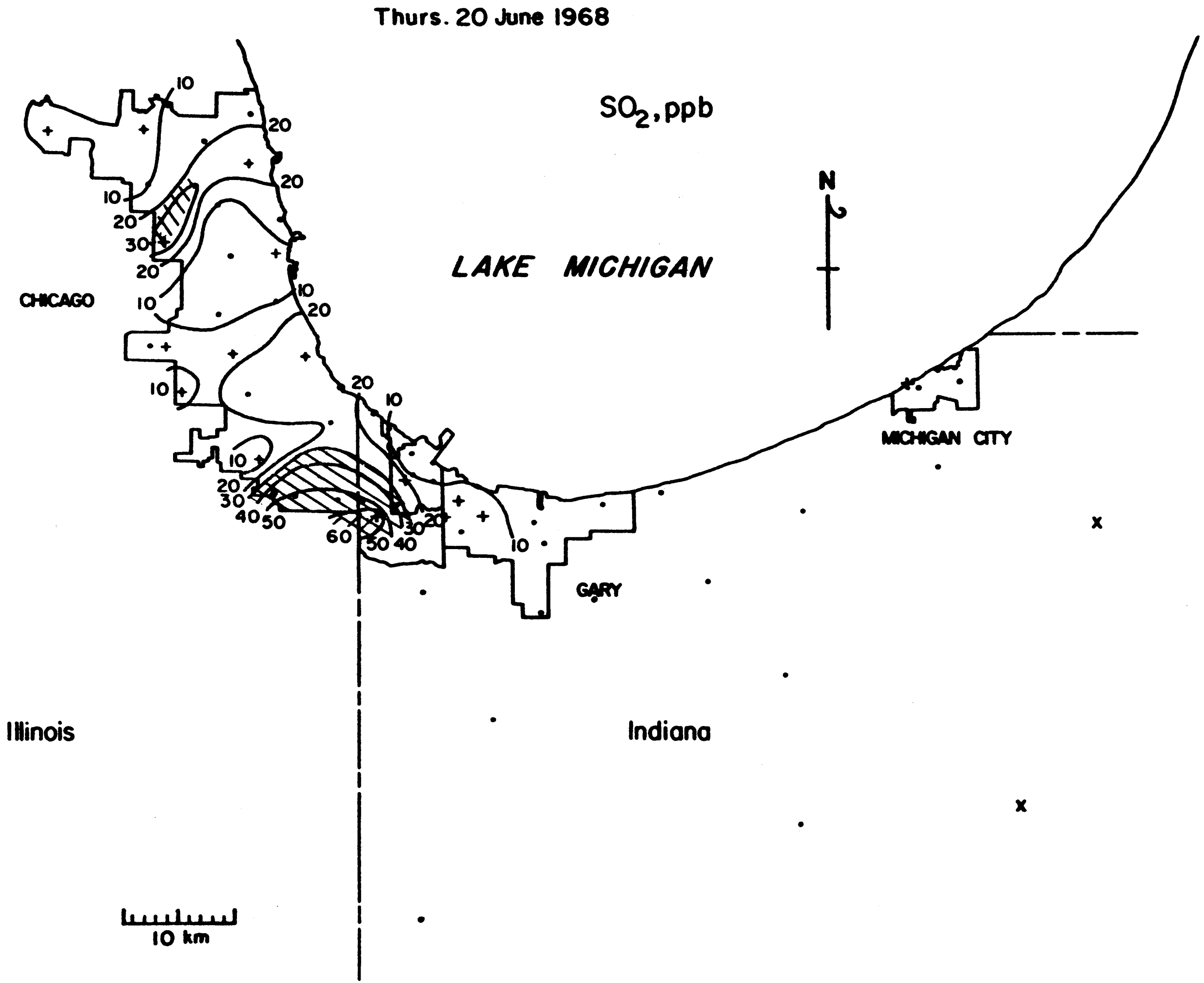


Figure 3.4.4: SO_2 isopleths for 20 June 1968.

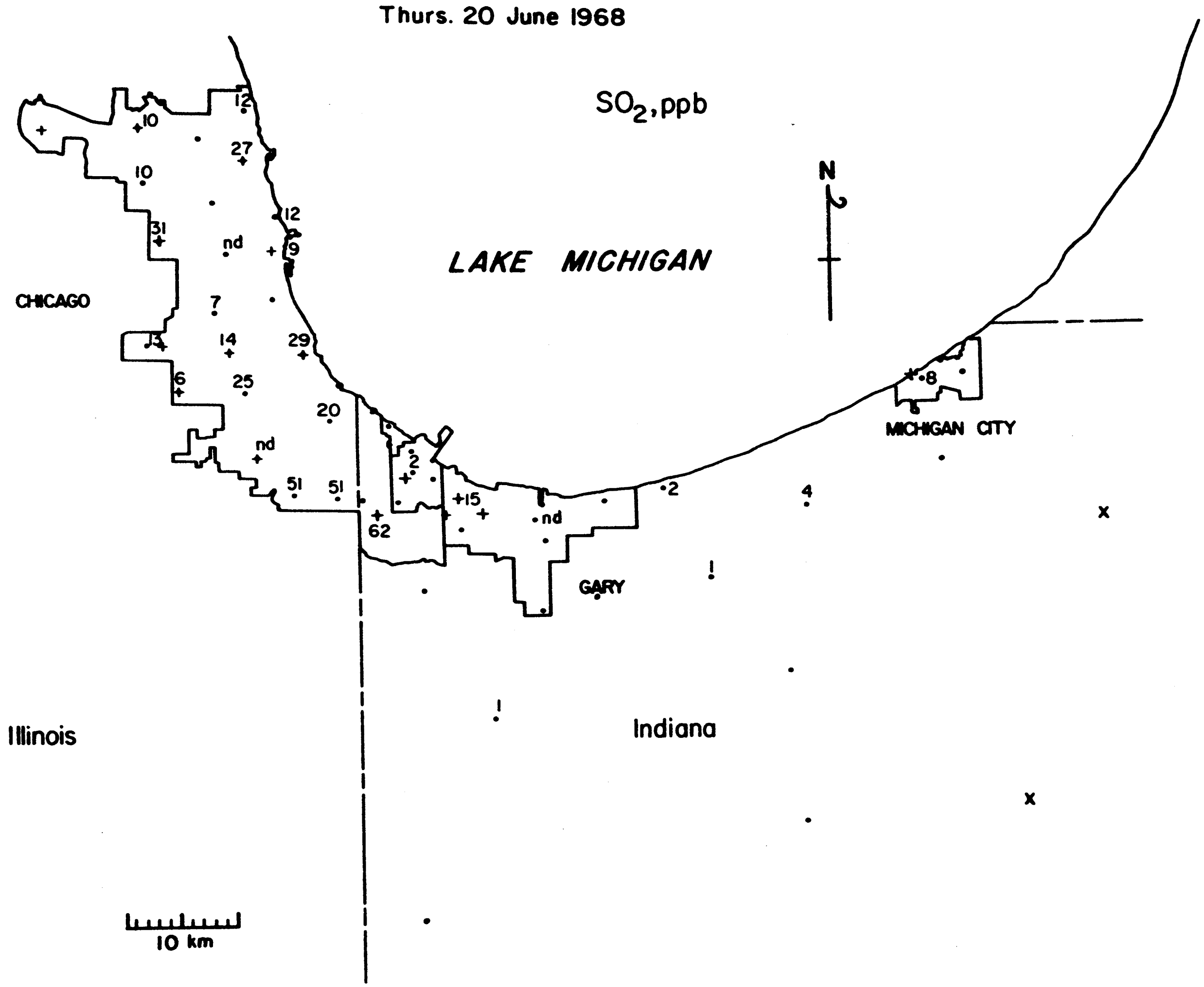


Figure 3.4.5: SO_2 data points for 20 June 1968.

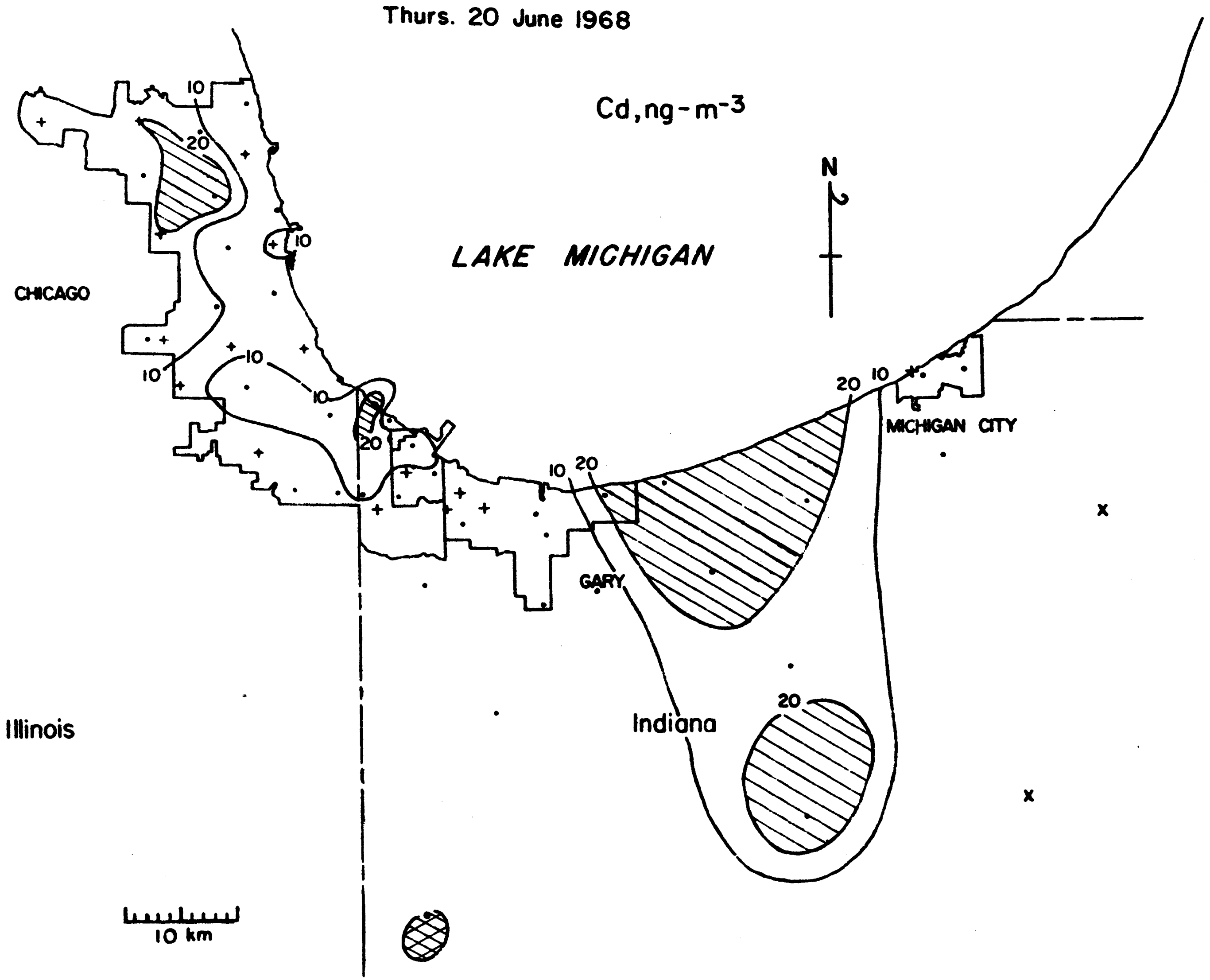


Figure 3.4.6: Cd isopleths for 20 June 1968.

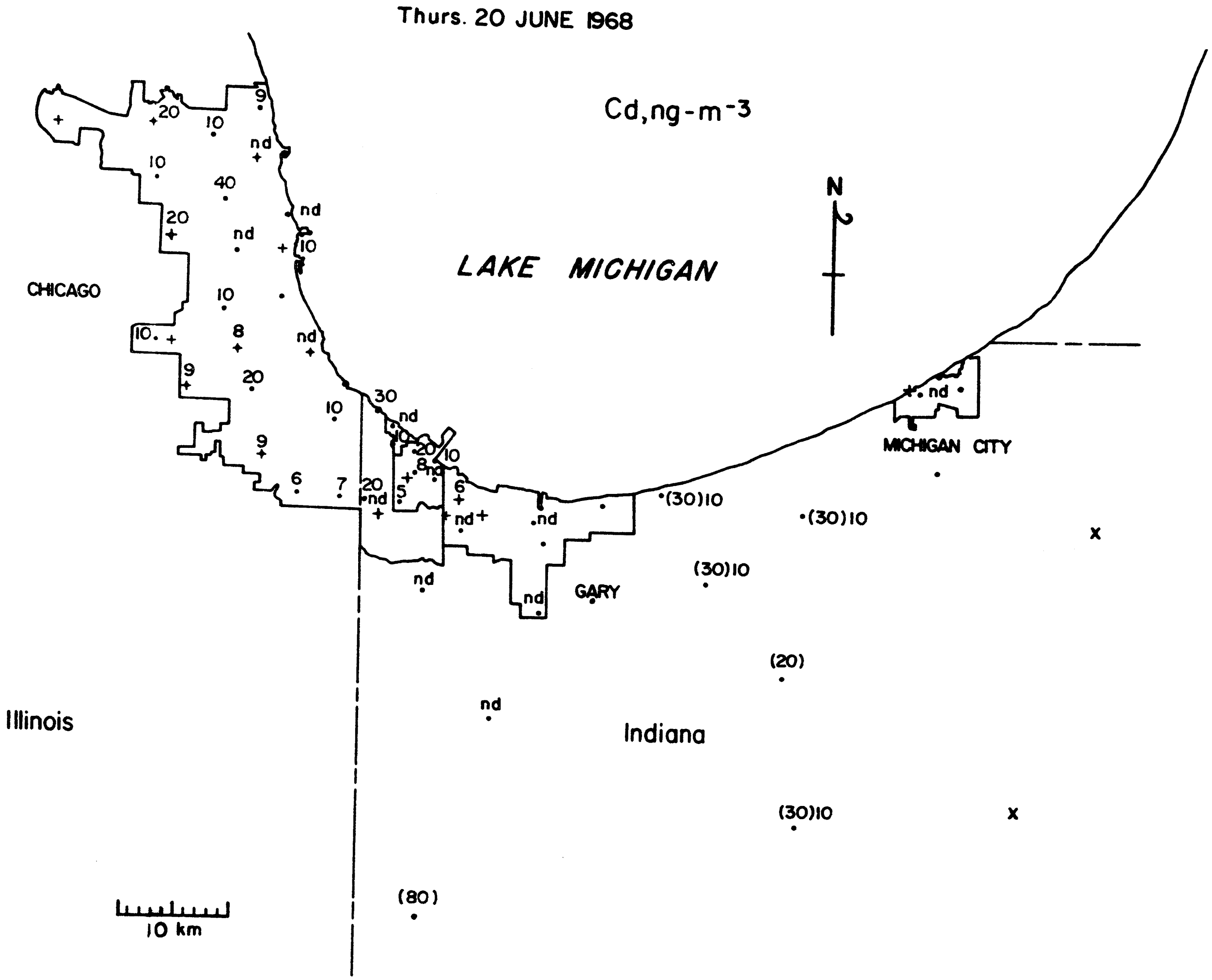


Figure 3.4.7: Cd data points for 20 June 1968.

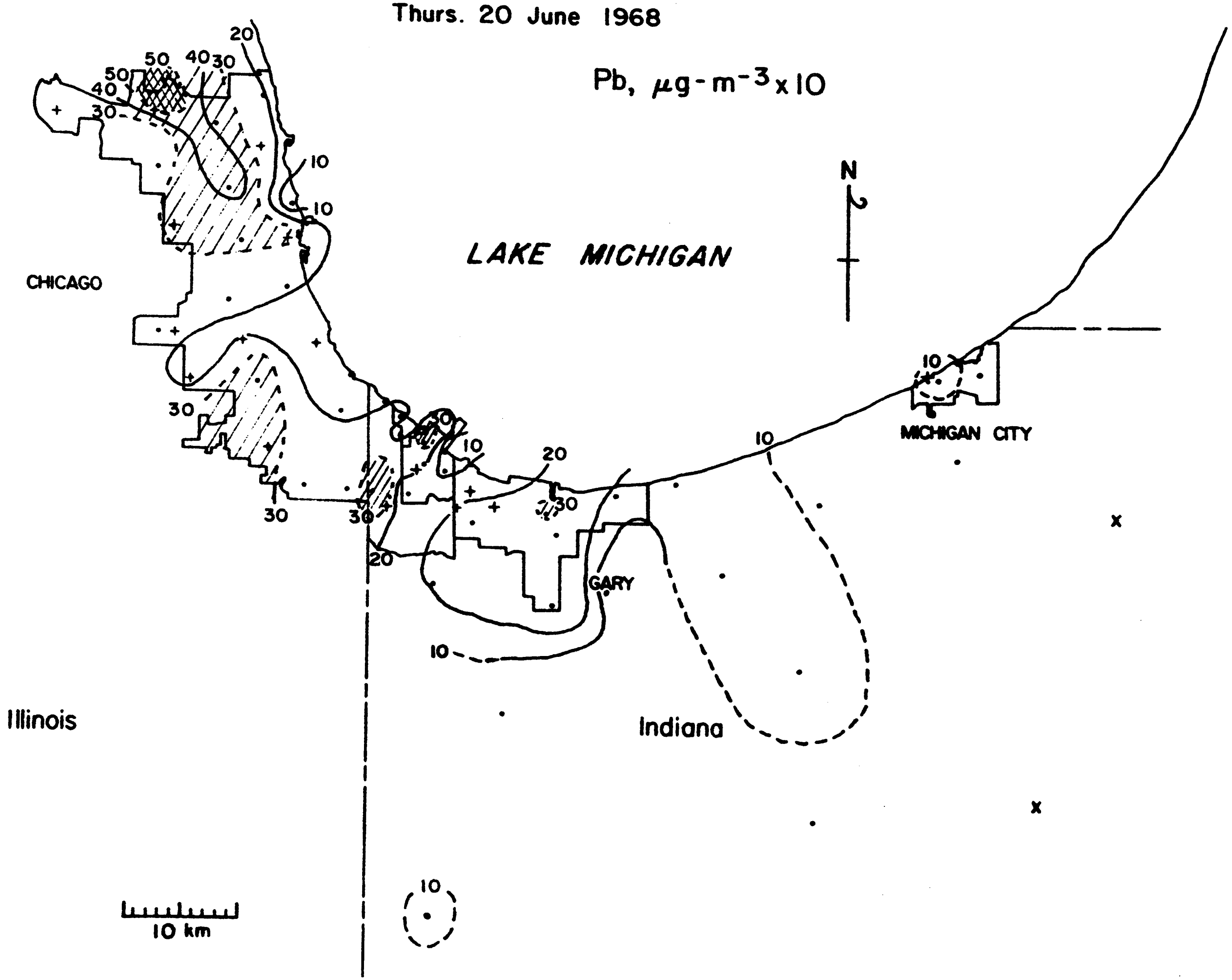
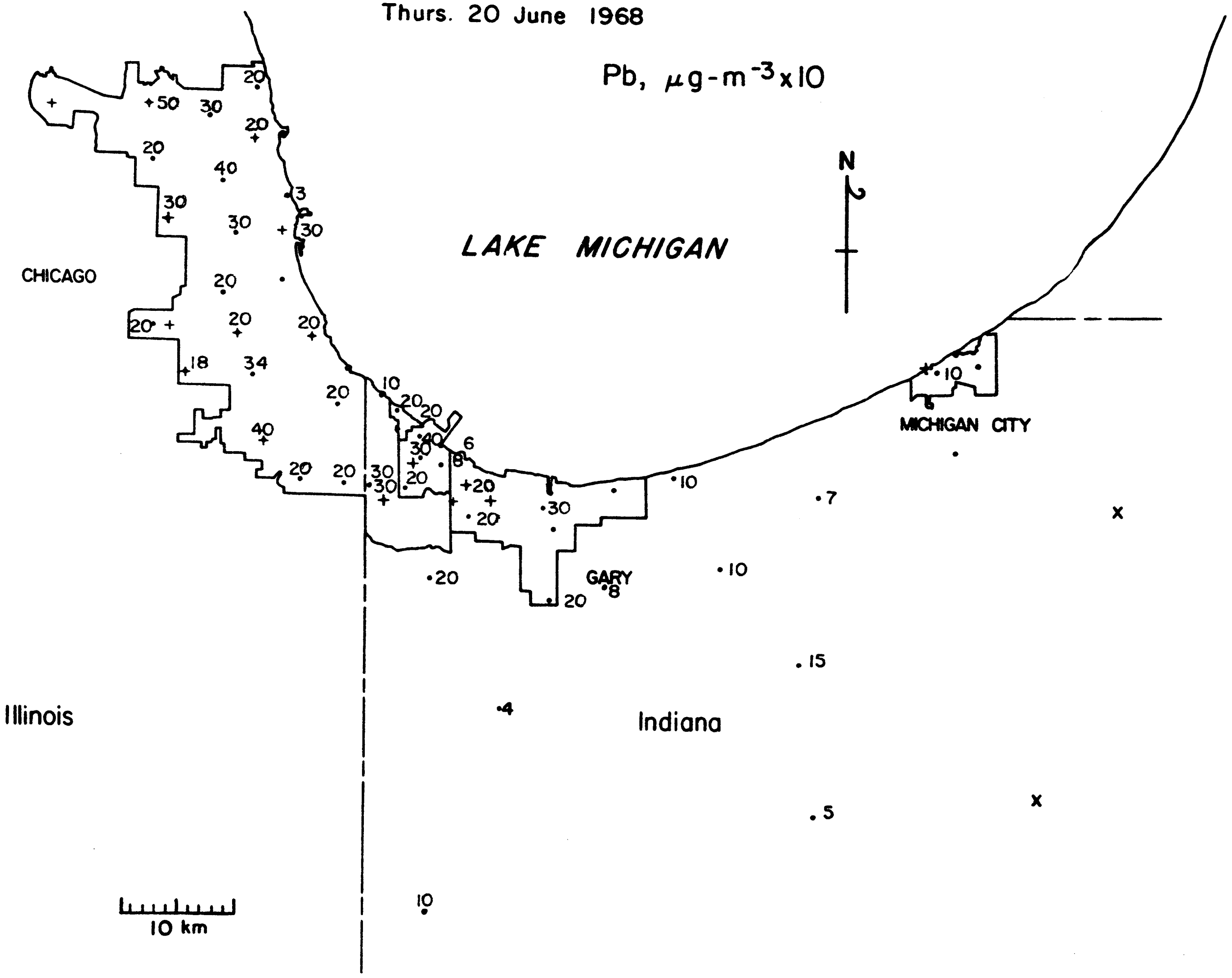


Figure 3.4.8: Pb isopleths for 20 June 1968.



Thurs. 20 June 1968

Pb, $\mu g\text{-}m^{-3} \times 10$

Figure 3.4.9: Pb data points for 20 June 1968.

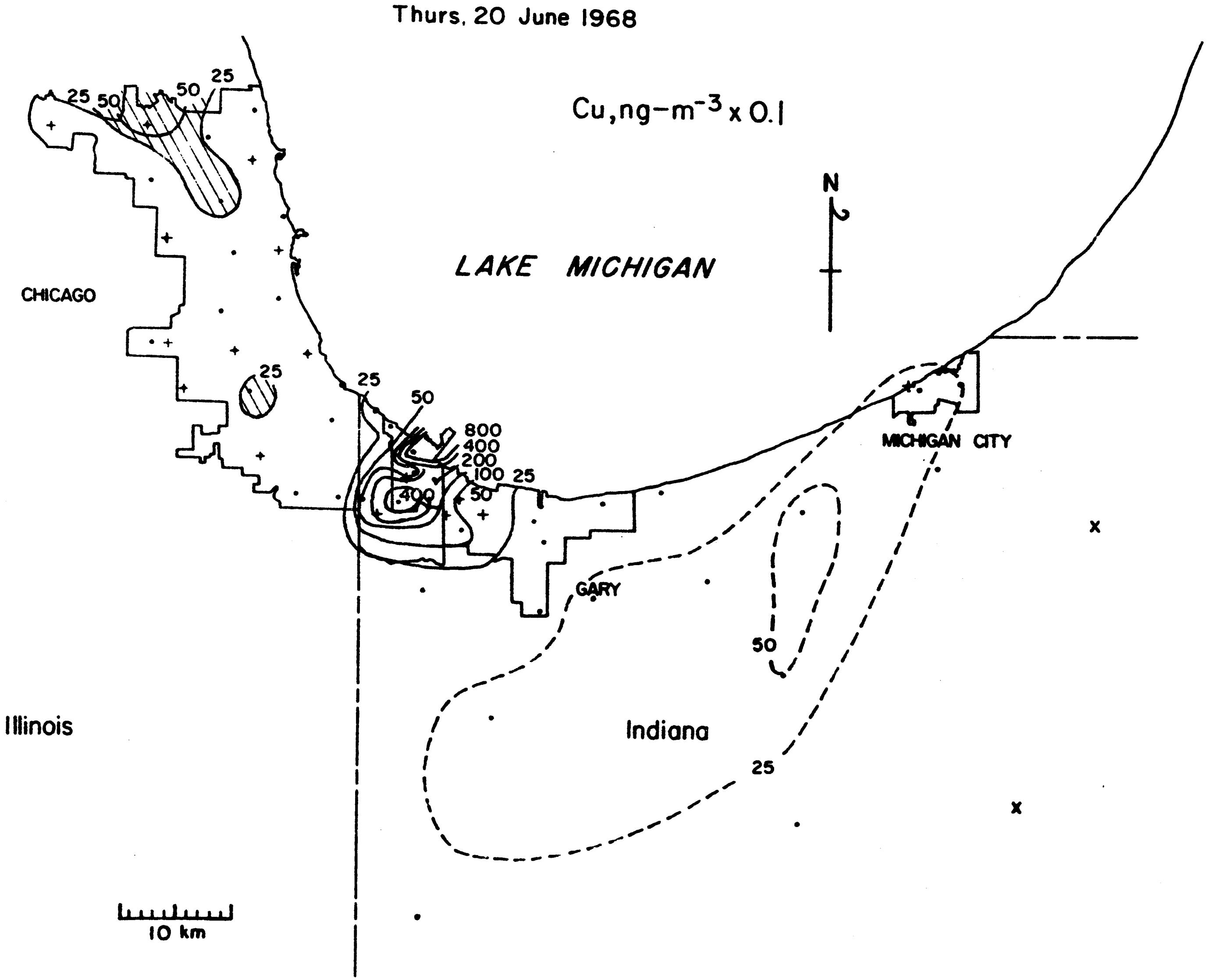


Figure 3.4.10: Cu isopleths for 20 June 1968.

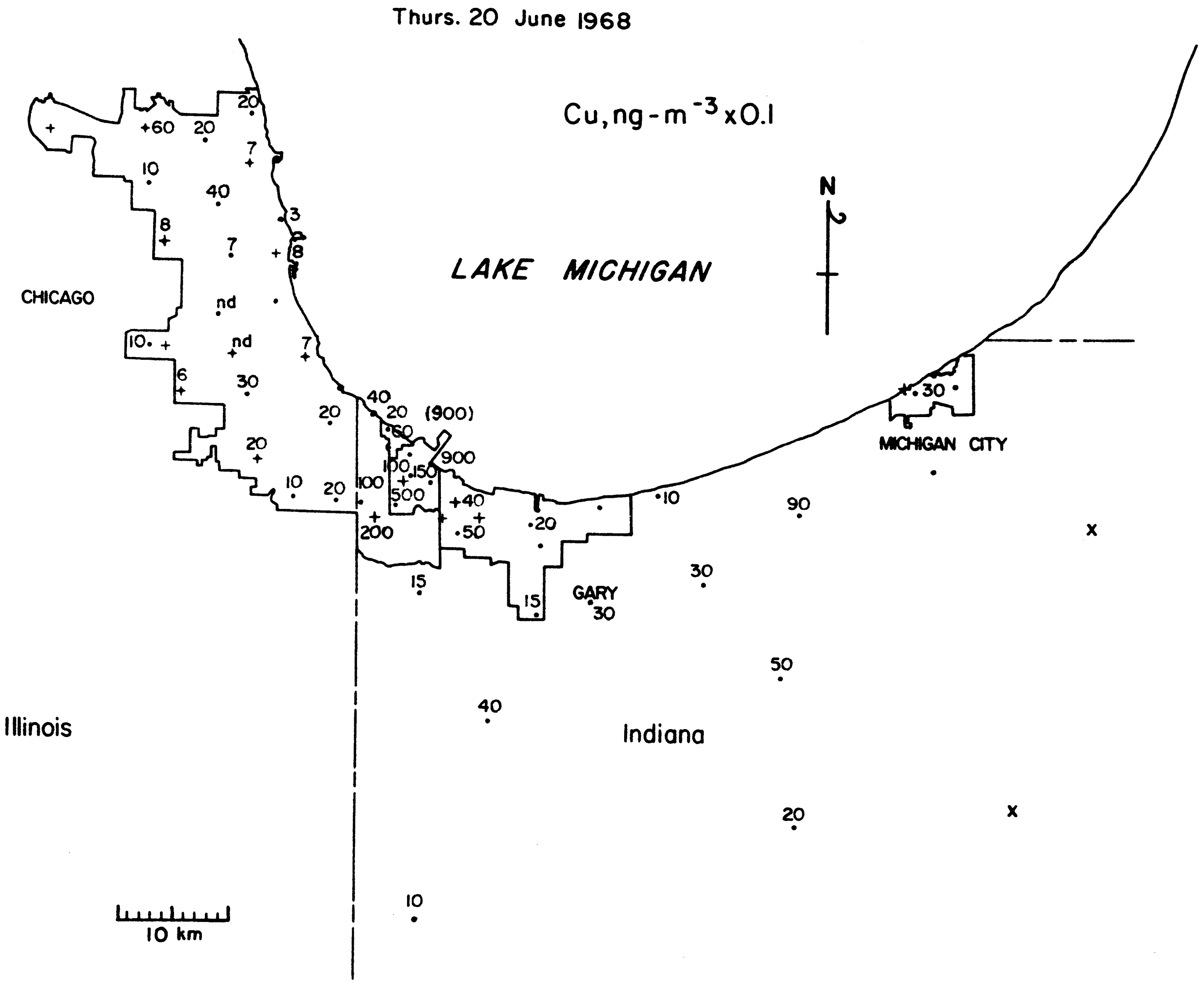


Figure 3.4.11: Cu data points for 20 June 1968.

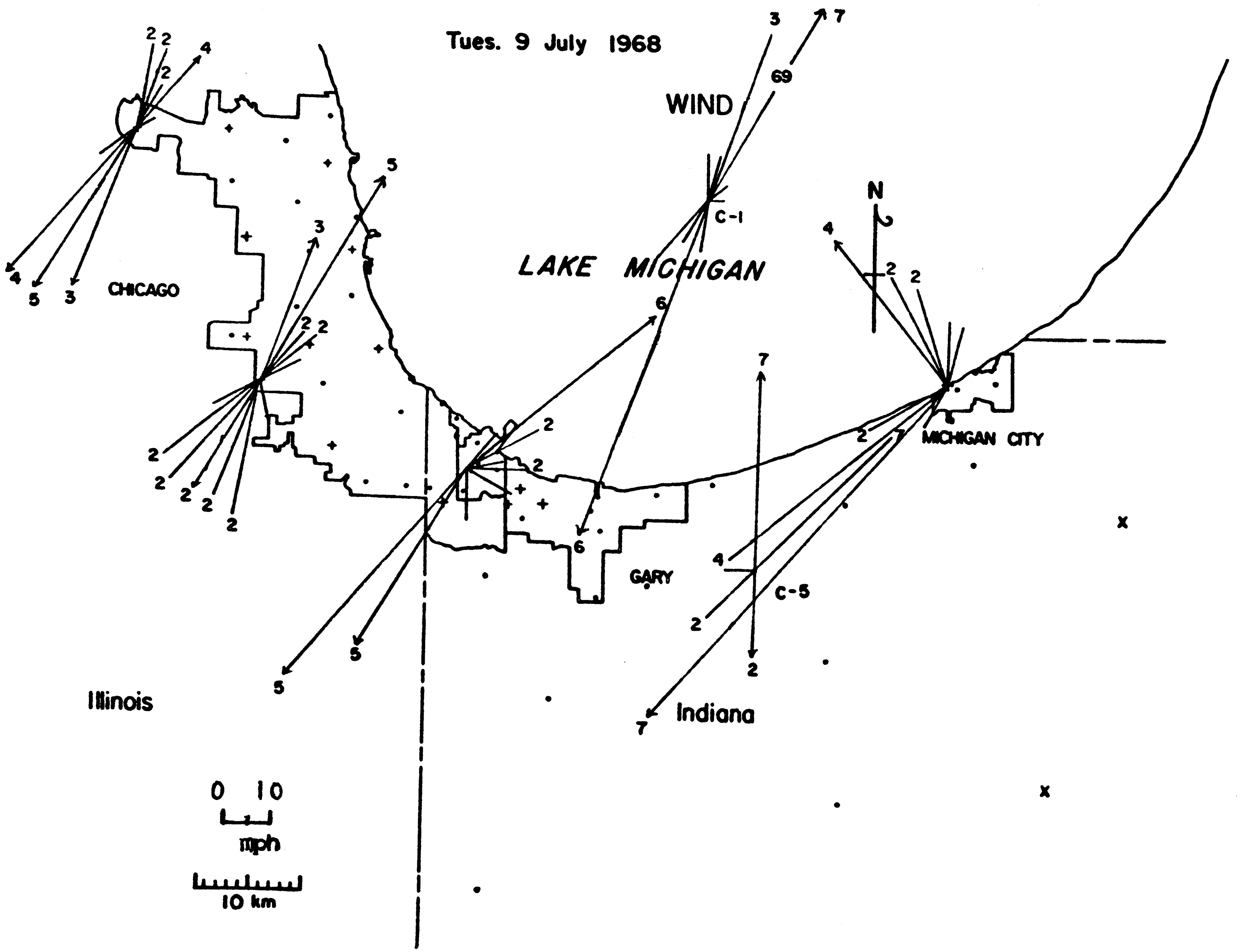


Figure 3.5.1: Wind rose for 9 July 1968.

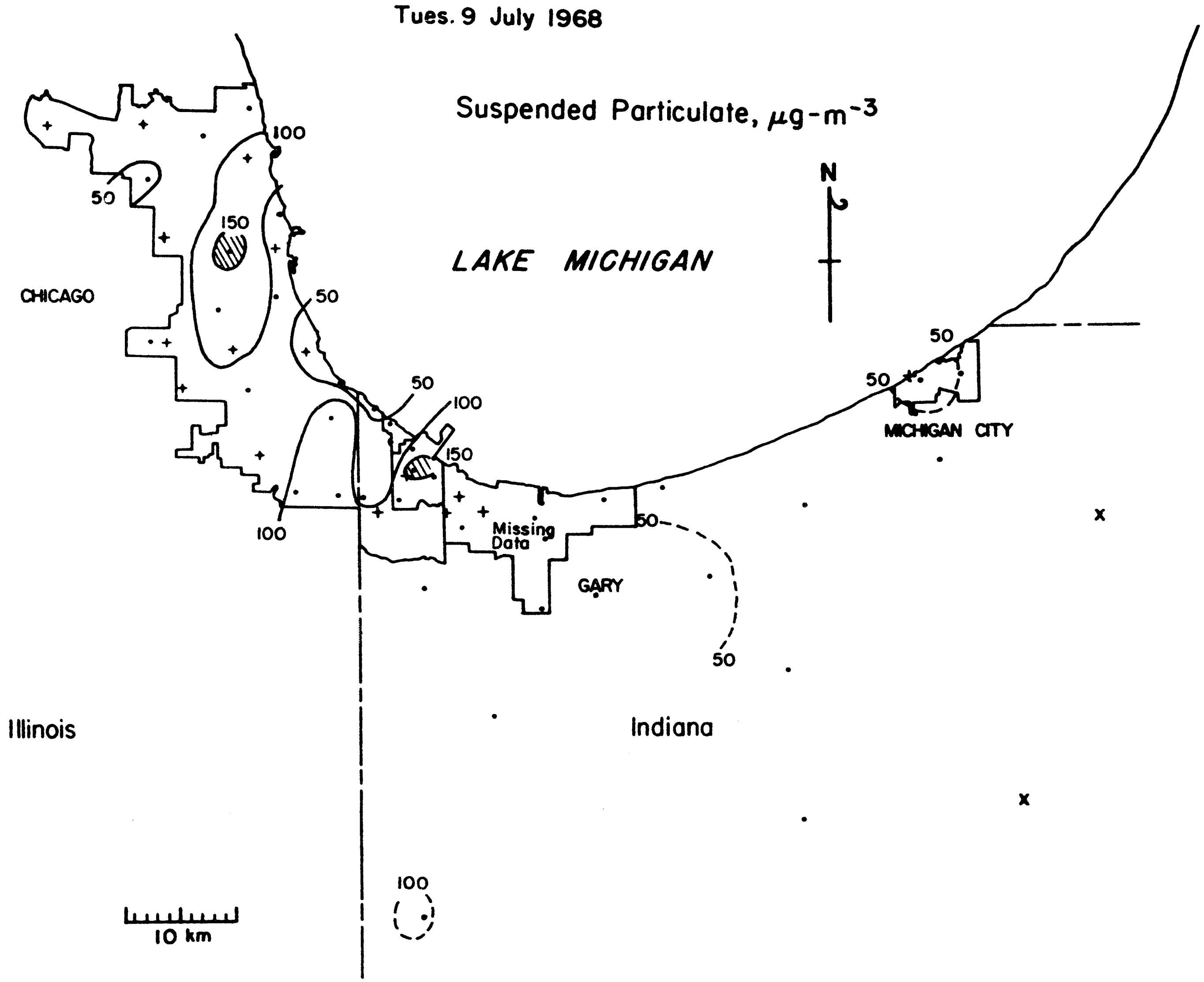


Figure 3.5.2: Suspended particulate isopleths for 9 July 1968.

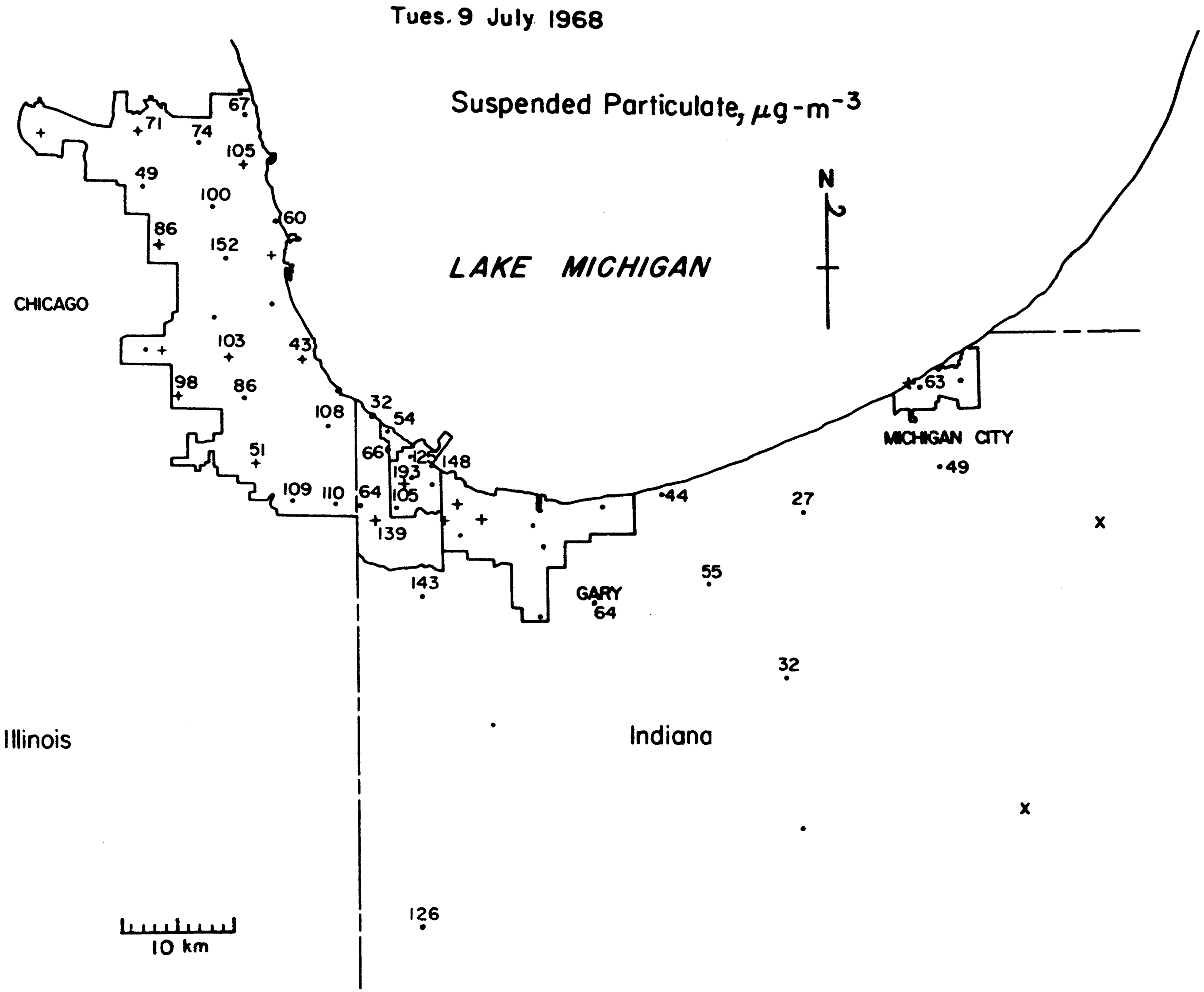


Figure 3.5.3: Suspended particulate data points for 9 July 1968.

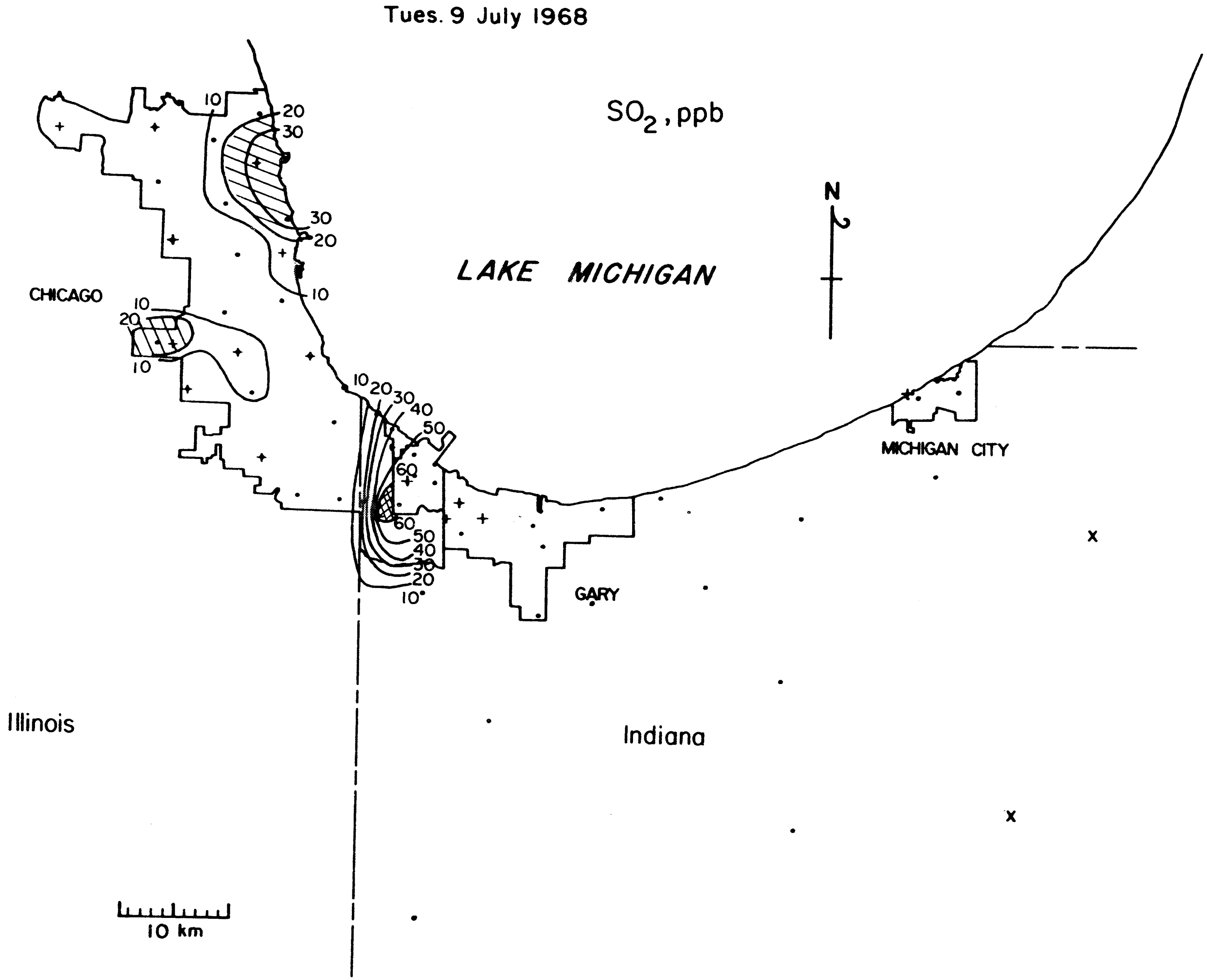


Figure 3.5.4: SO$_2$ isopleths for 9 July 1968.

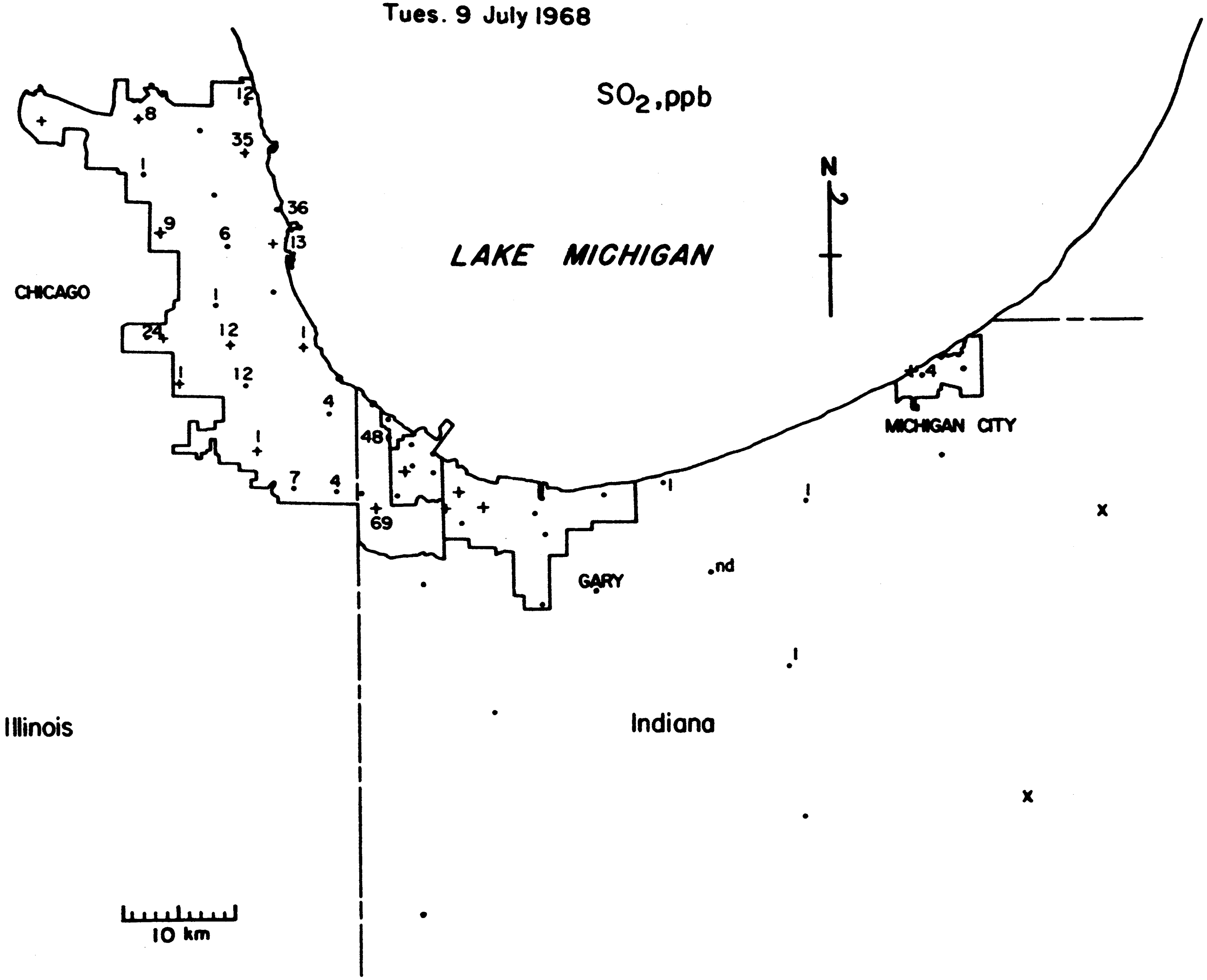


Figure 3.5.5: SO_2 data points for 9 July 1968.

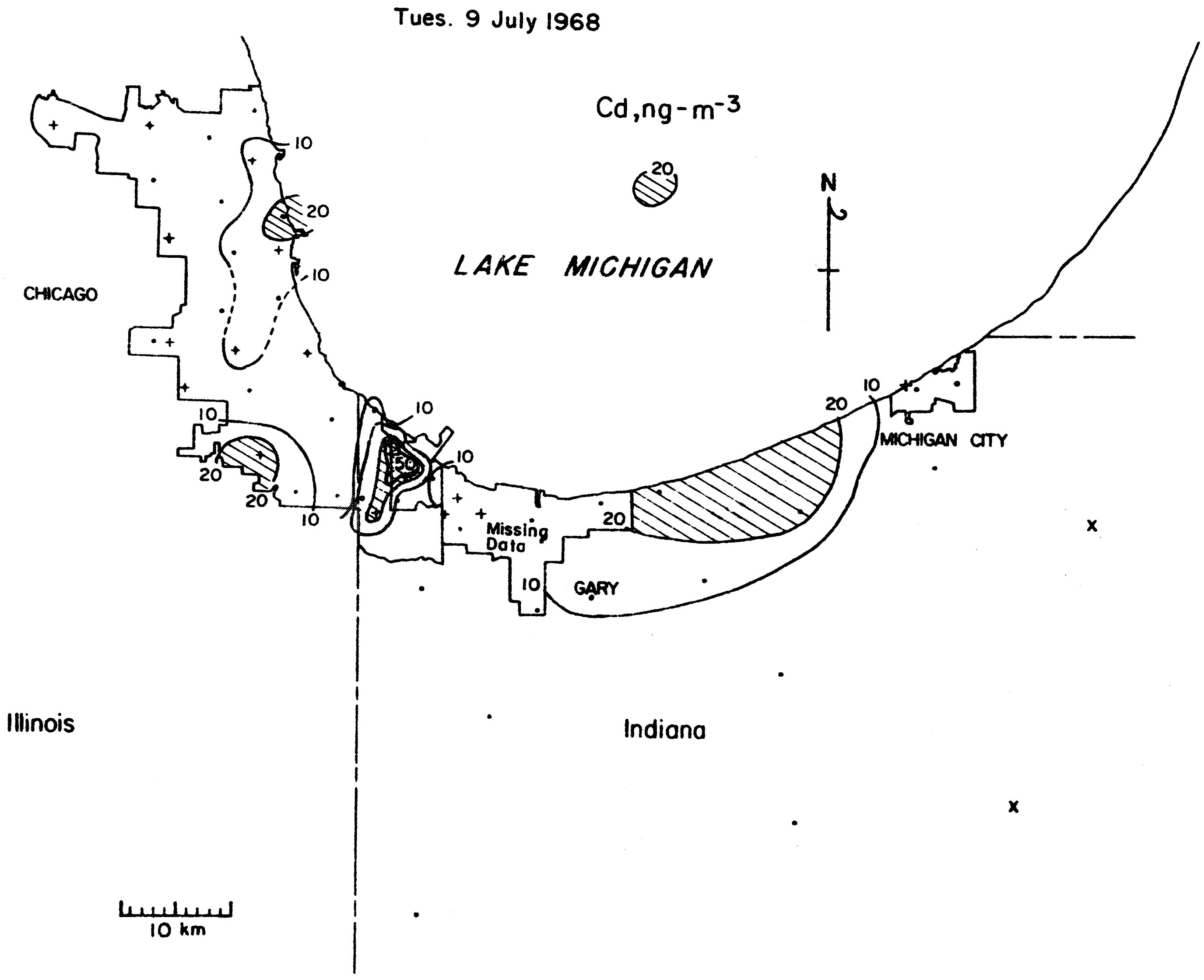


Figure 3.5.6: Cd isopleths for 9 July 1968.

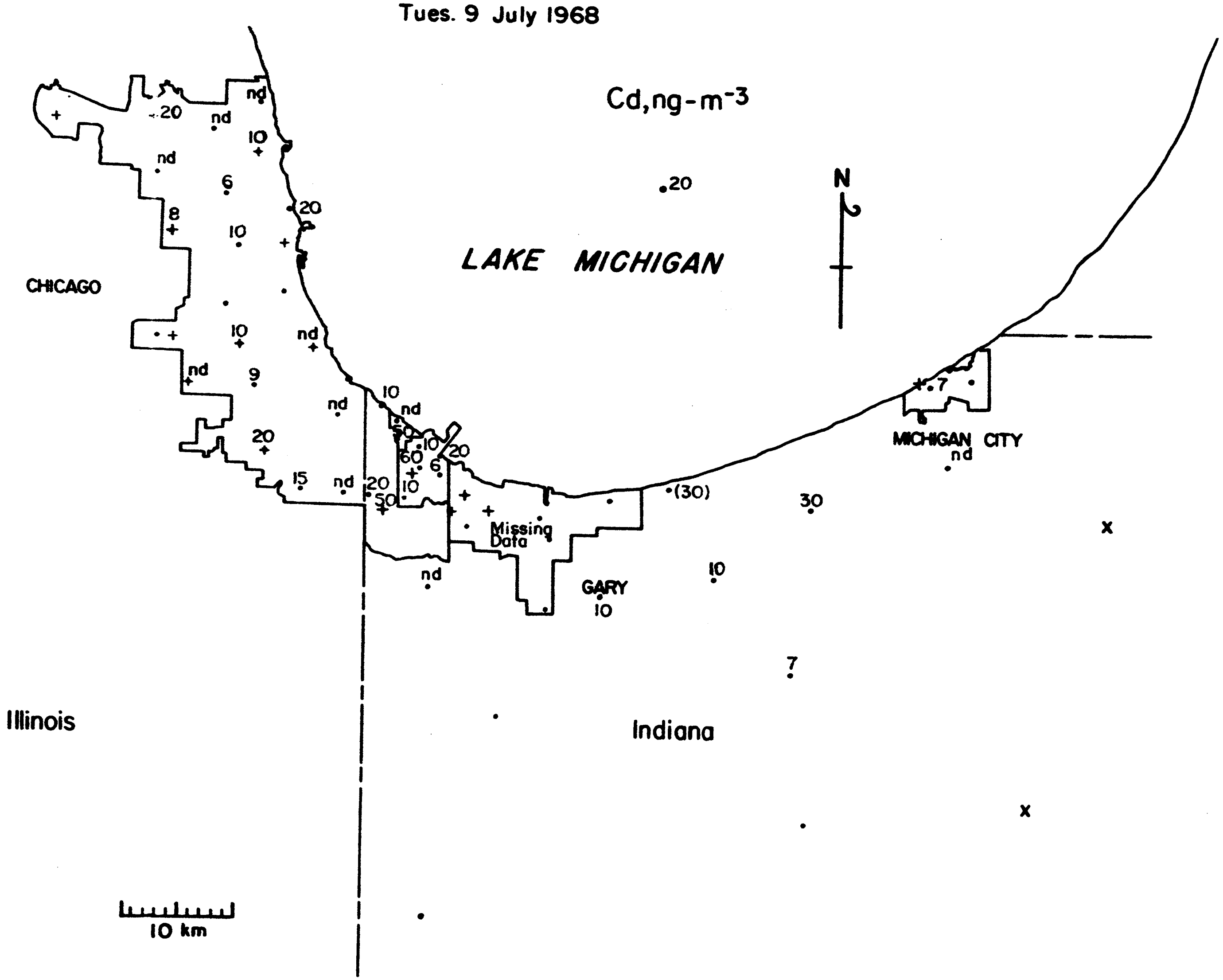


Figure 3.5.7: Cd data points for 9 July 1968.

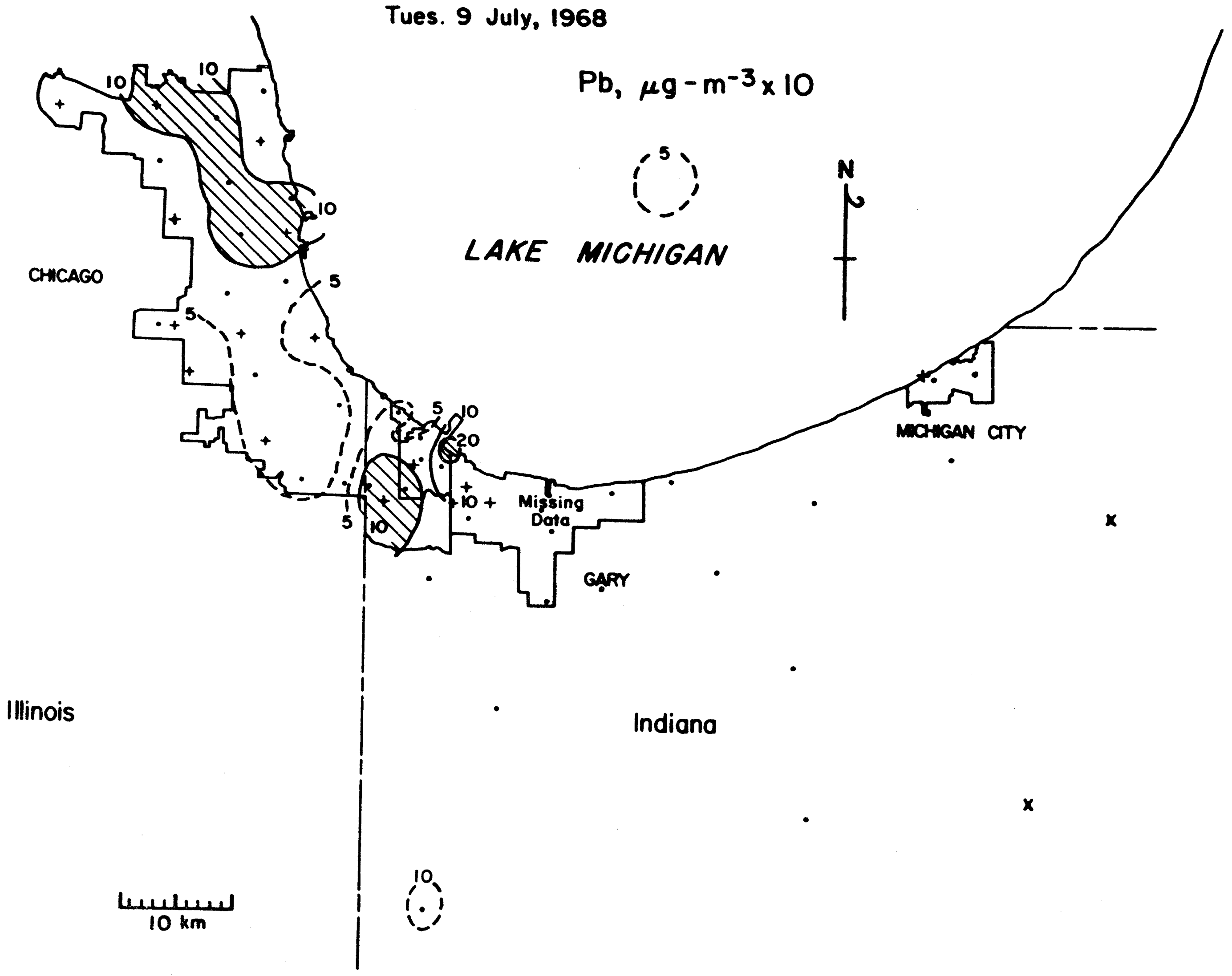


Figure 3.5.8: Pb isopleths for 9 July 1968.

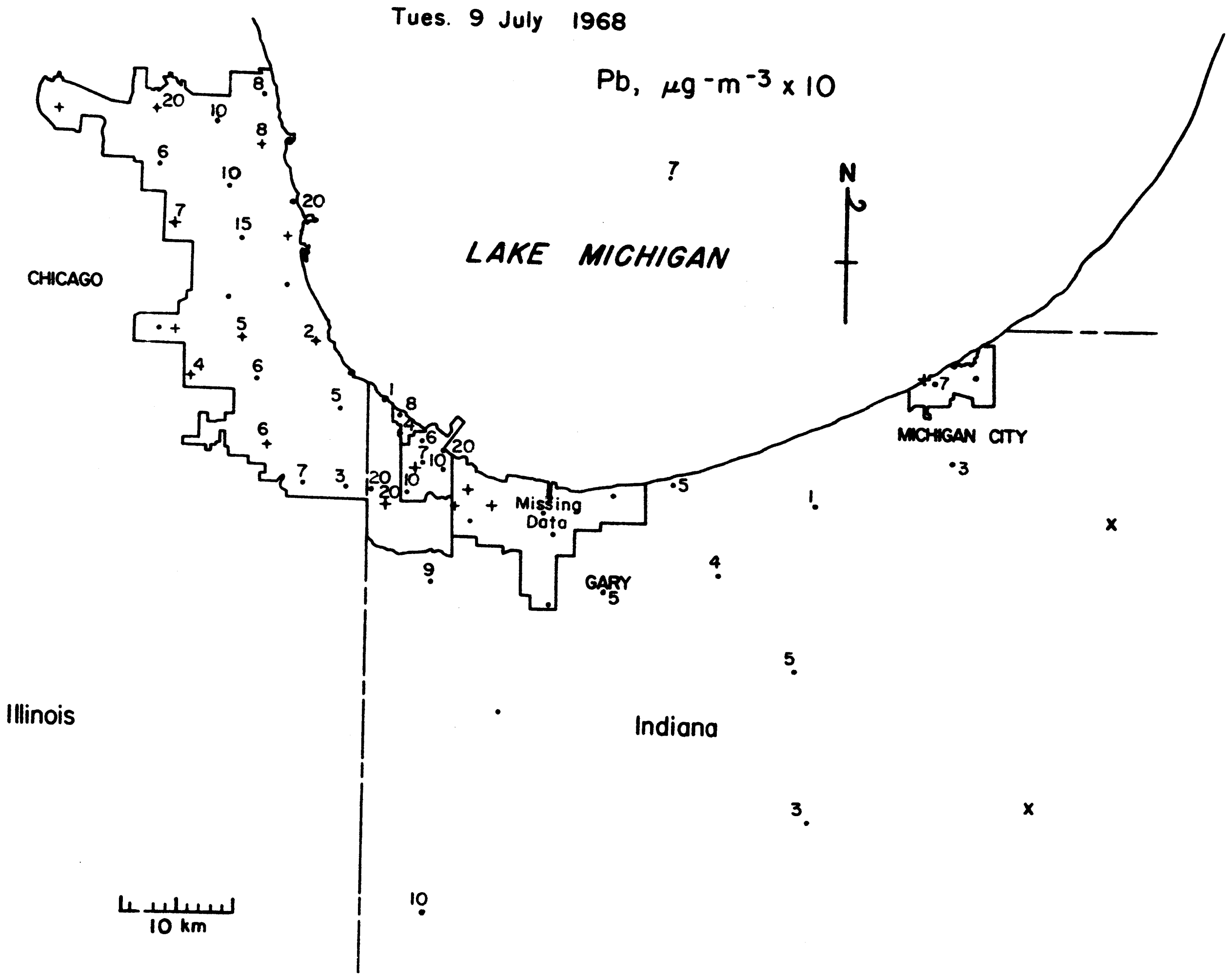


Figure 3.5.9: Pb data points for 9 July 1968.

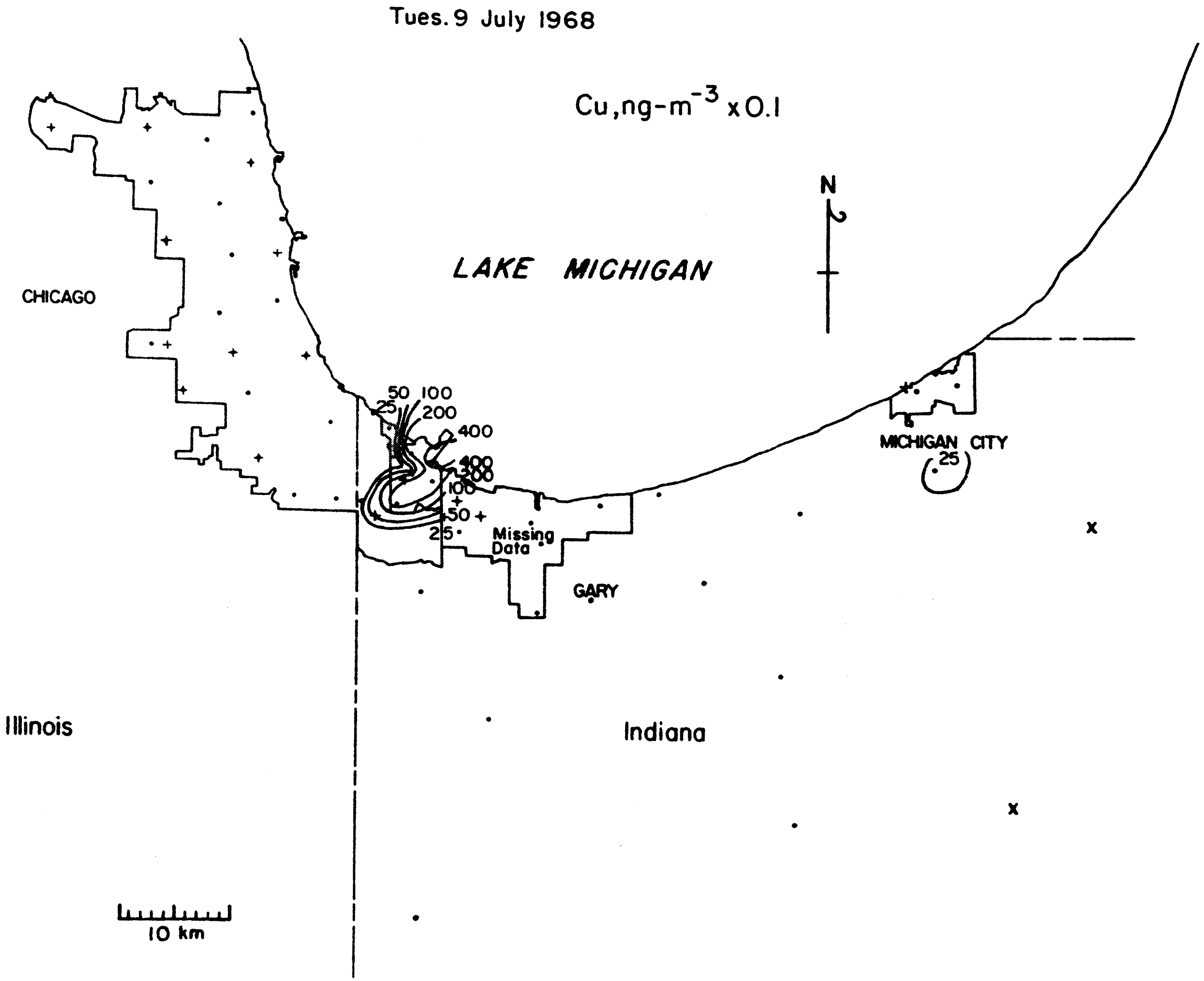


Figure 3.5.10: Cu isopleths for 9 July 1968.

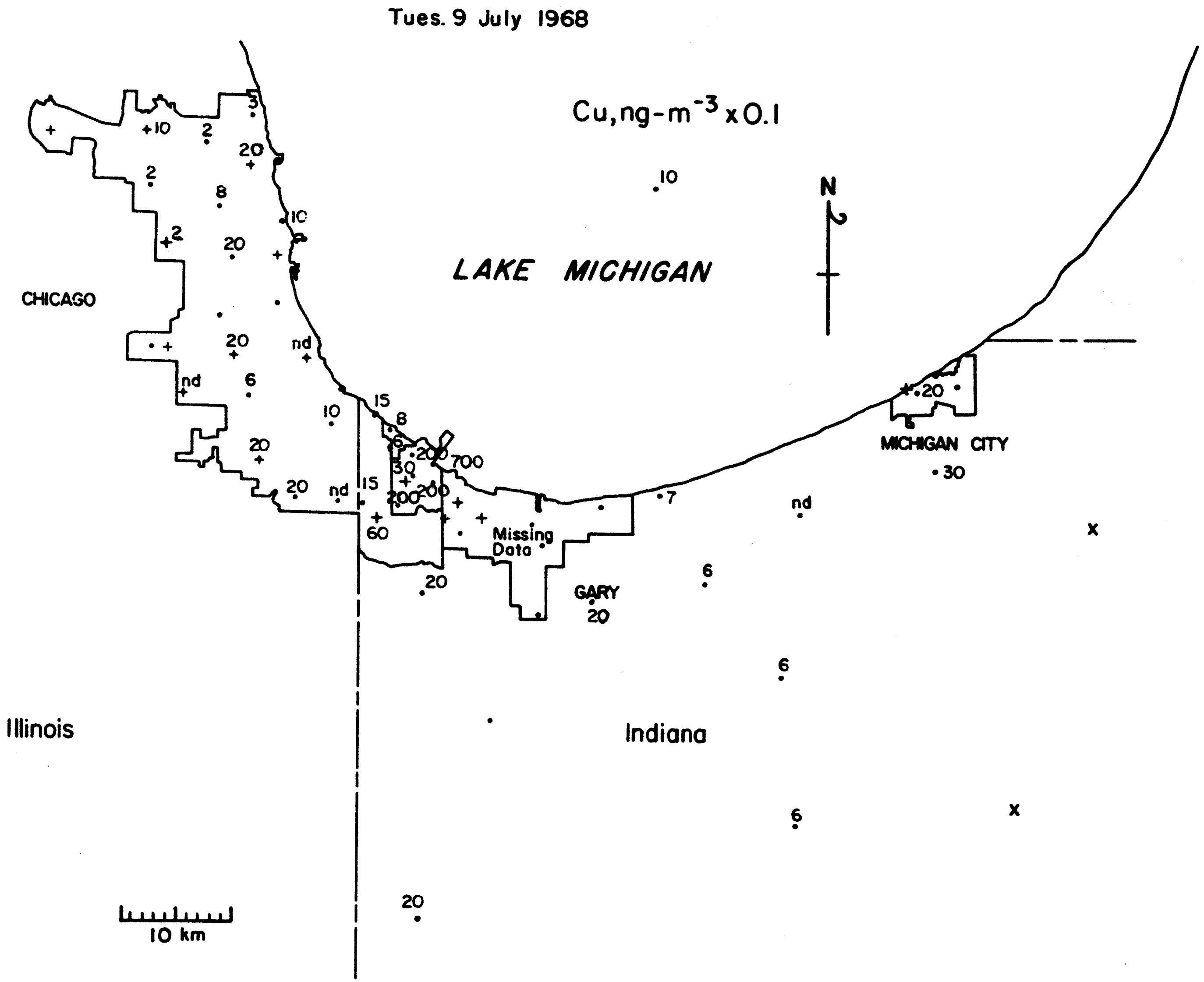


Figure 3.5.11: Cu data points for 9 July 1968.

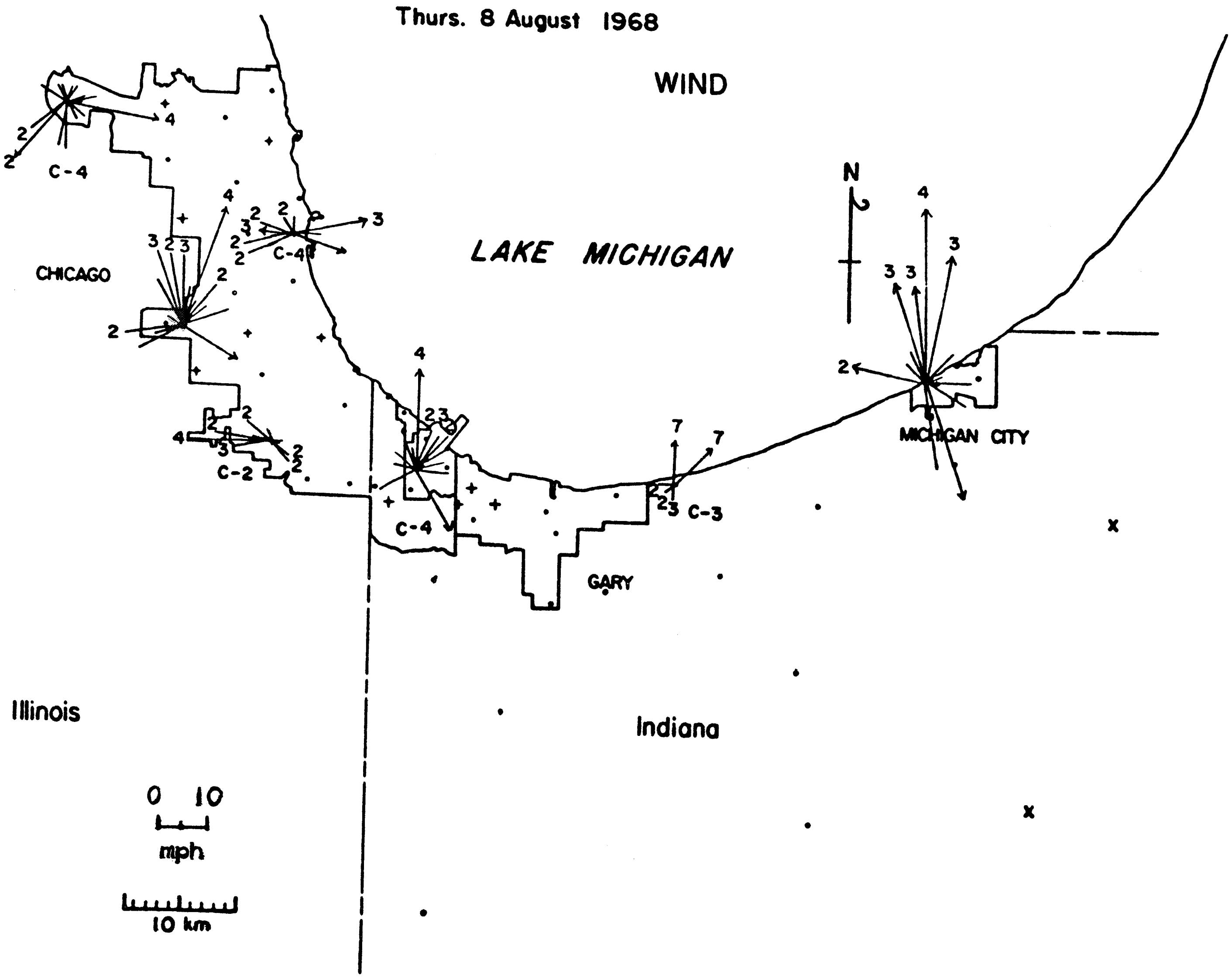


Figure 3.6.1: Wind rose for 8 August 1968.

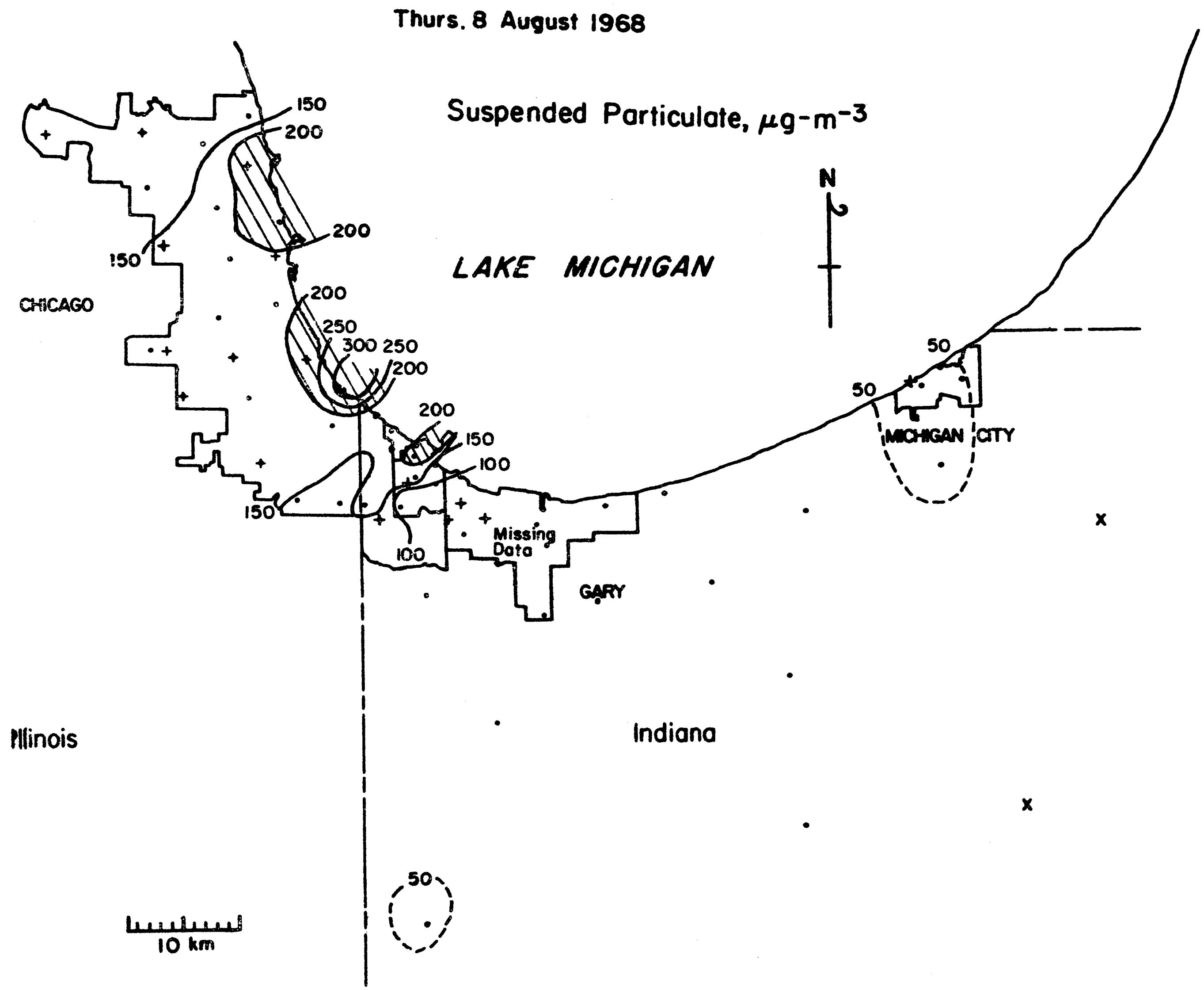


Figure 3.6.2: Suspended particulate isopleths for 8 August 1968.

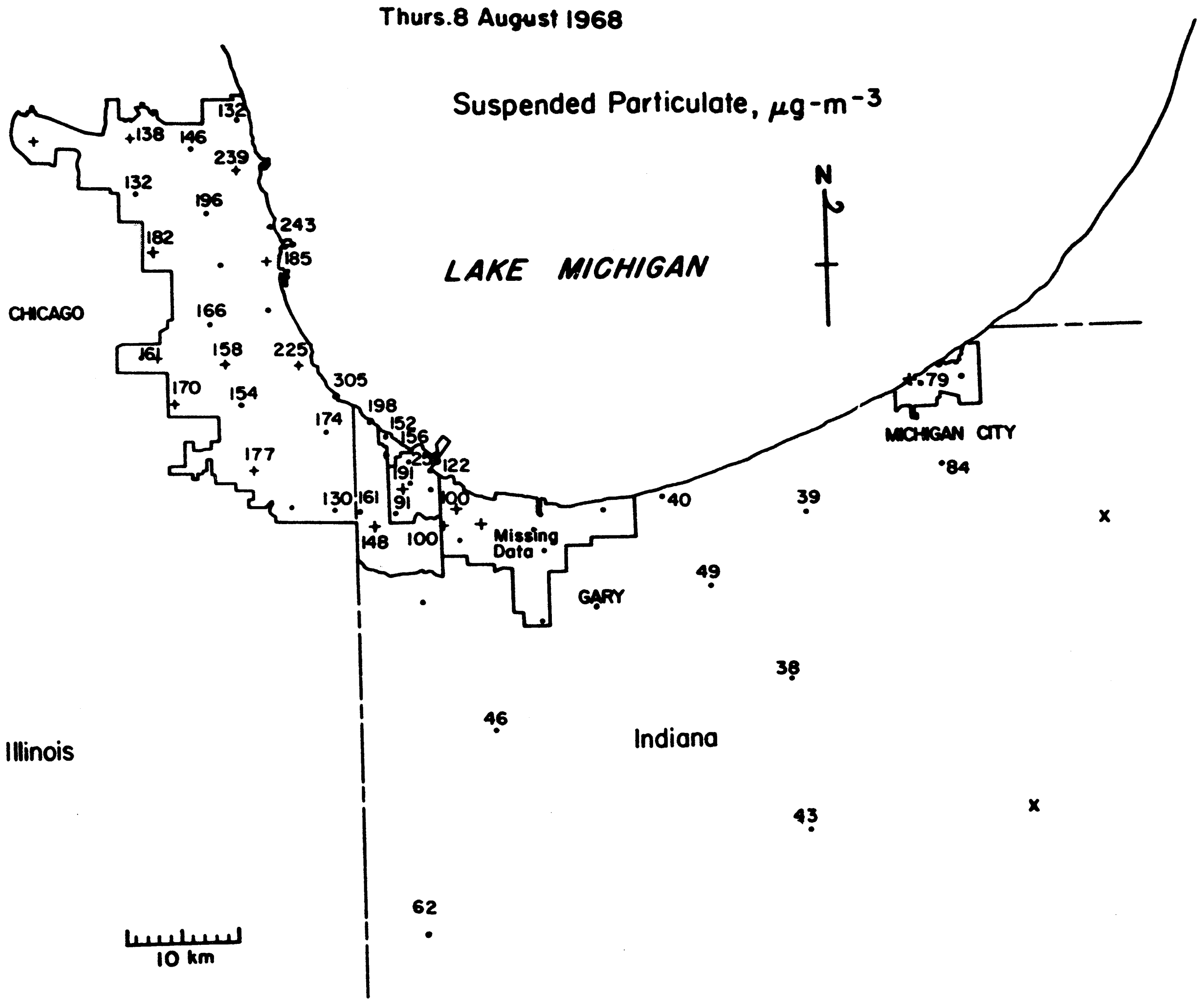


Figure 3.6.3: Suspended particulate data points for 8 August 1968.

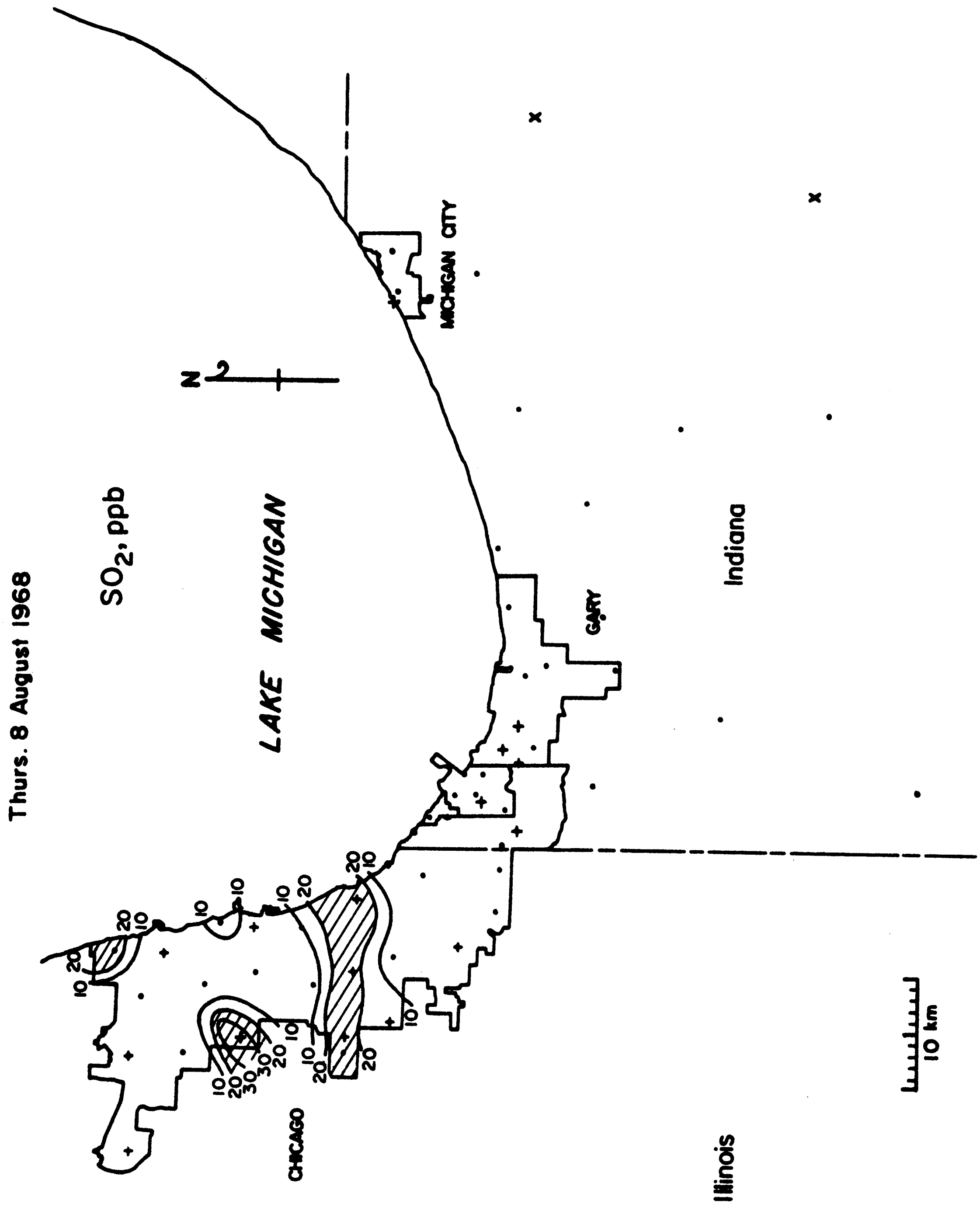


Figure 3.6.4: SO_2 isopleths for 8 August 1968.

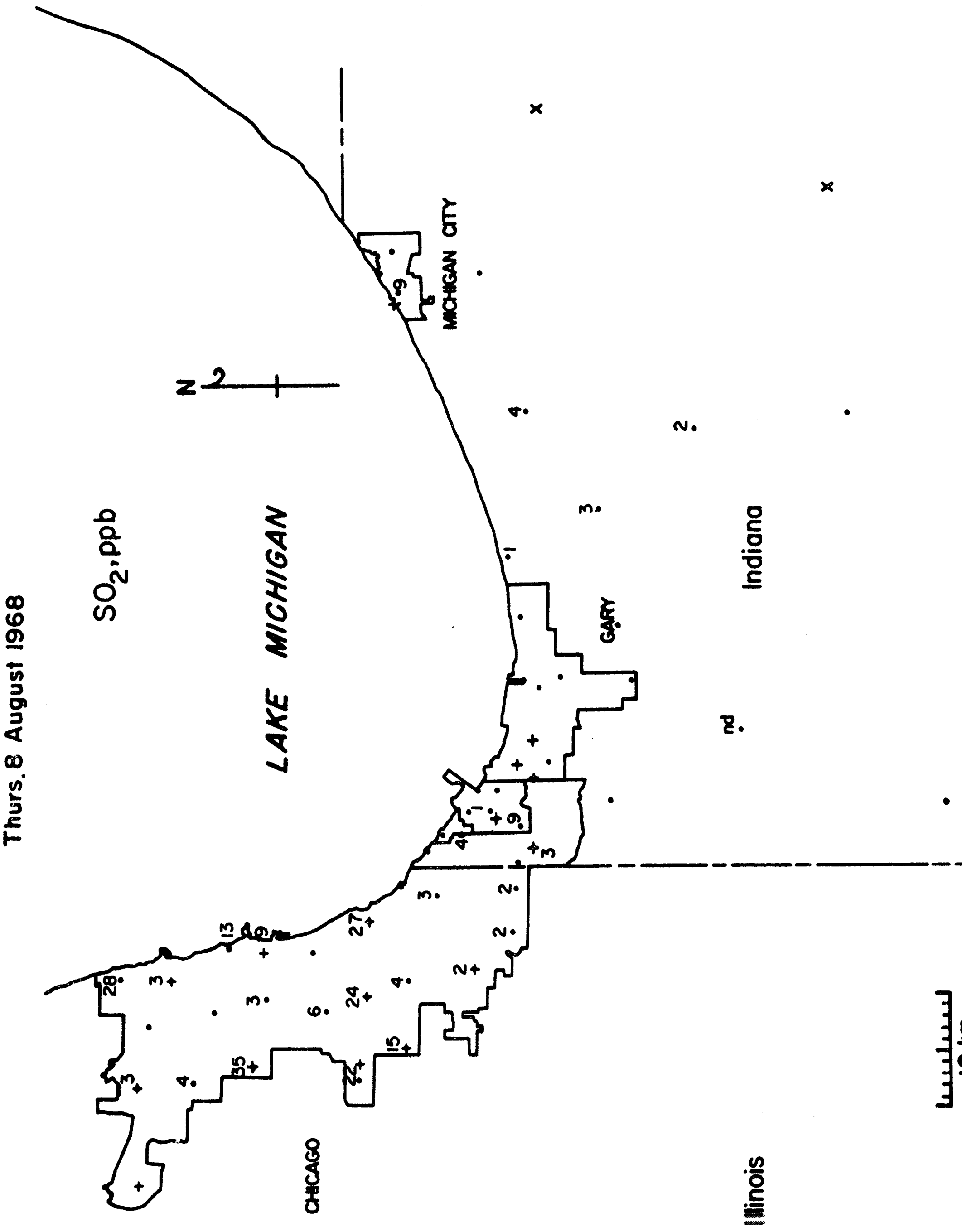


Figure 3.6.5: SO$_2$ data points for 8 August 1968.

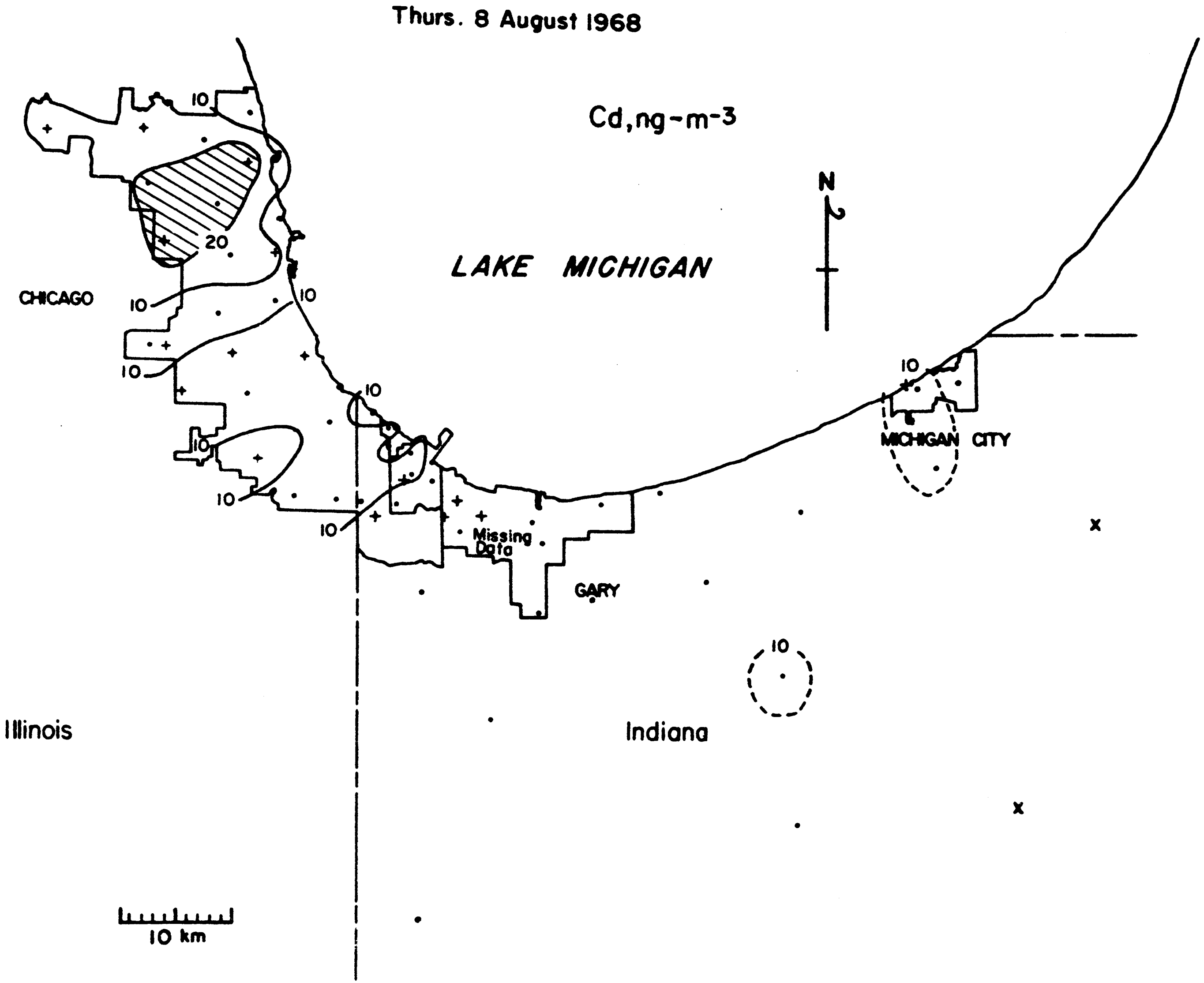


Figure 3.6.6: Cd isopleths for 8 August 1968.

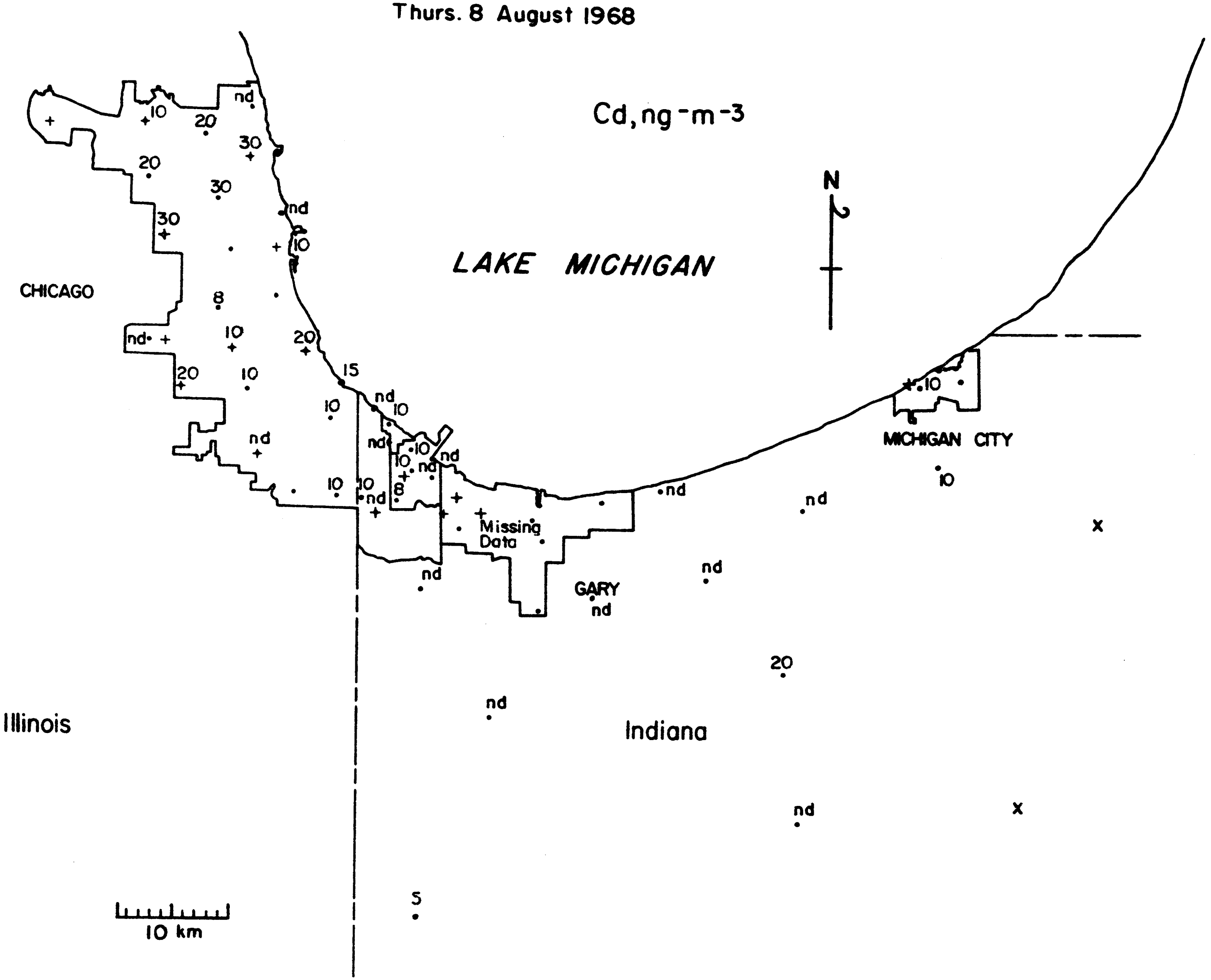


Figure 3.6.7: Cd data points for 8 August 1968.

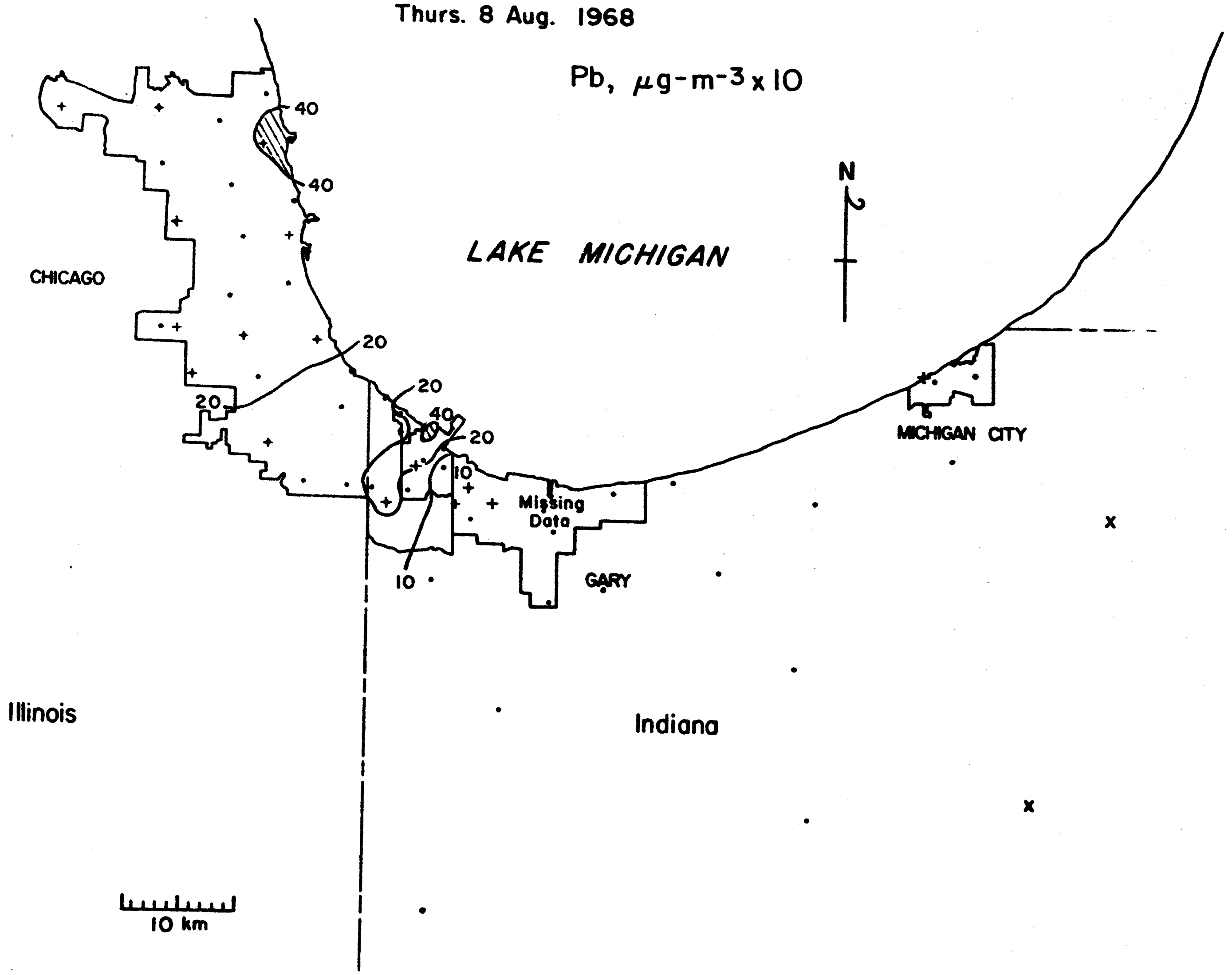


Figure 3.6.8: Pb isopleths for 8 August 1968.

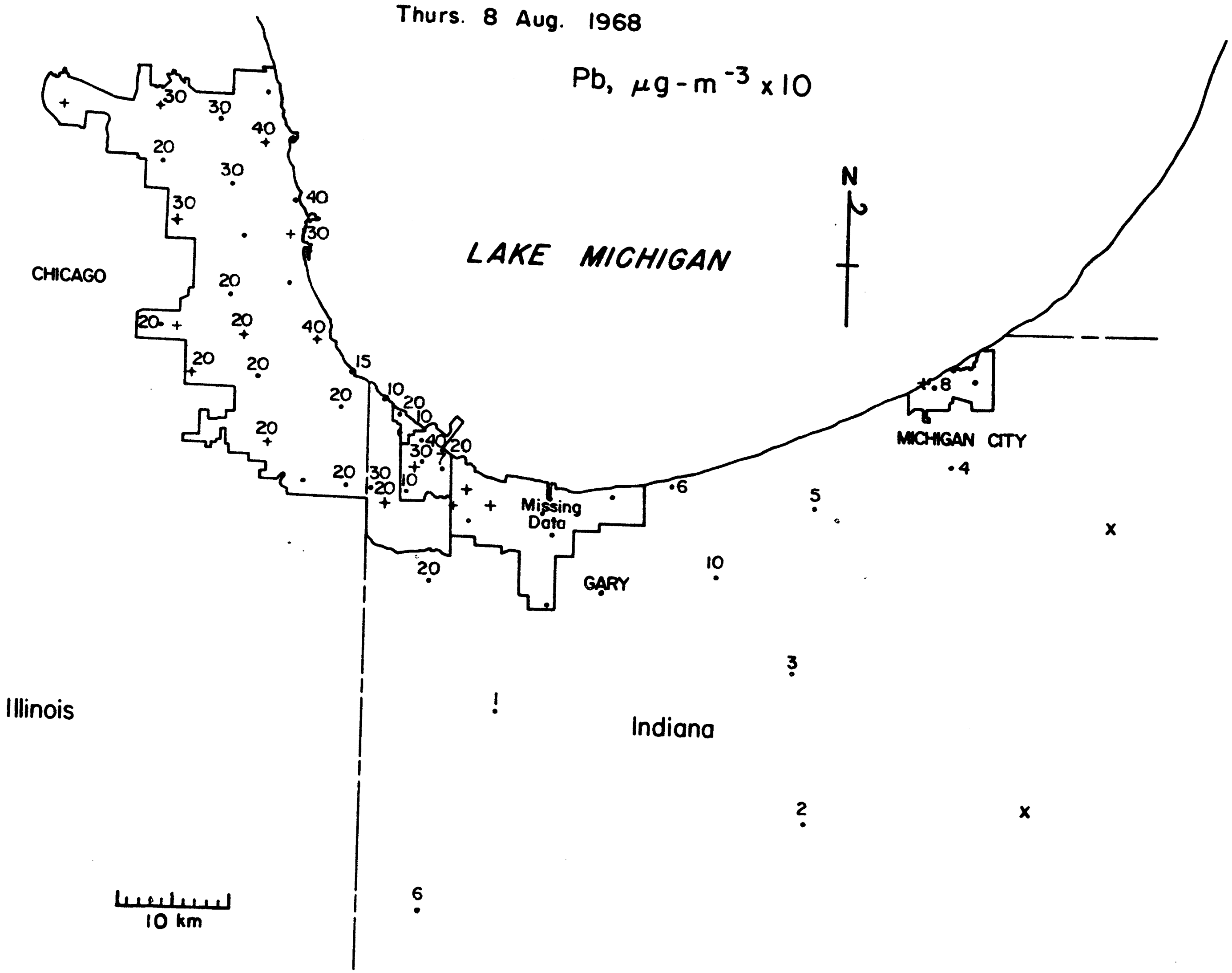


Figure 3.6.9: Pb data points for 8 August 1968.

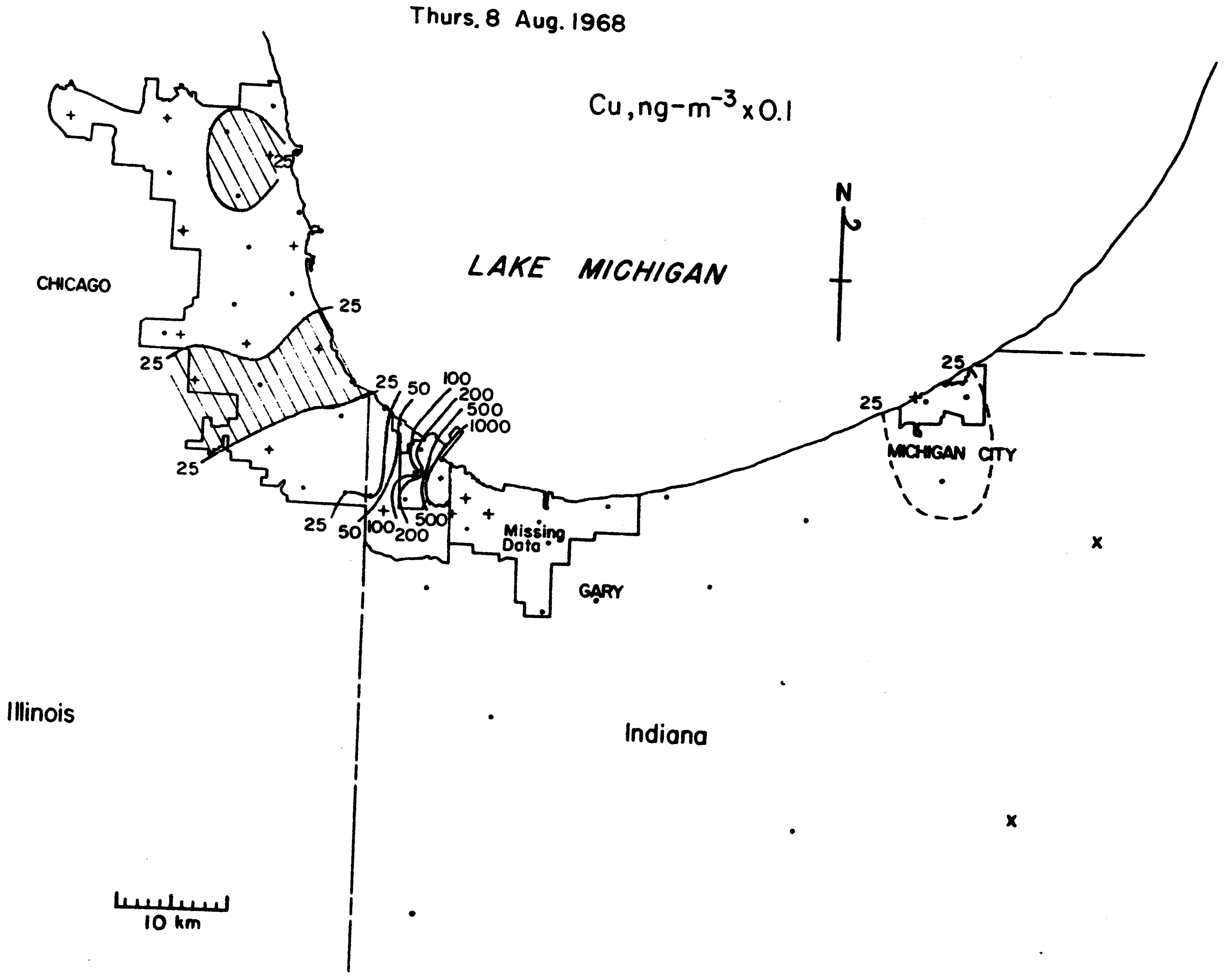


Figure 3.6.10: Cu isopleths for 8 August 1968.

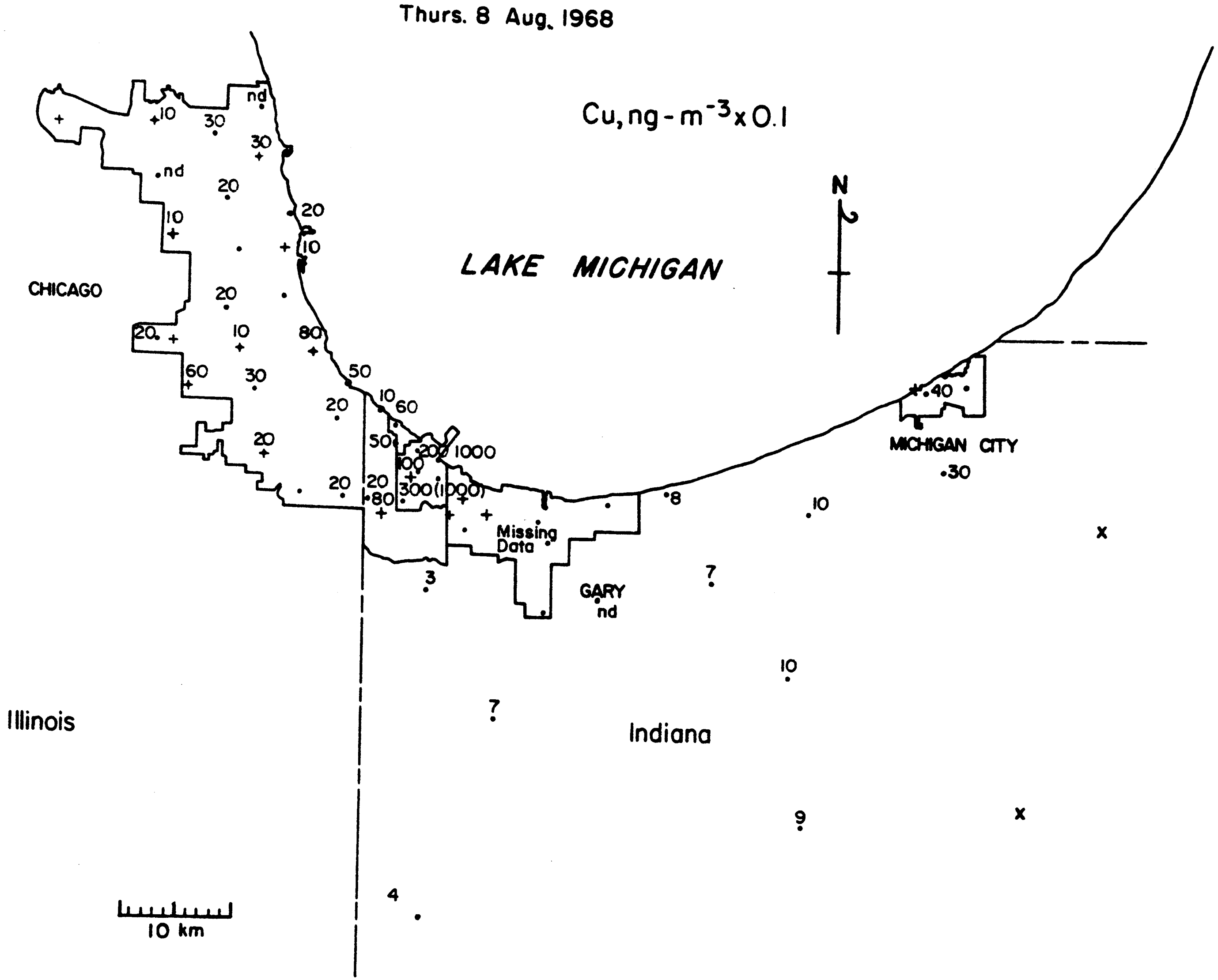


Figure 3.6.11: Cu data points for 8 August 1968.

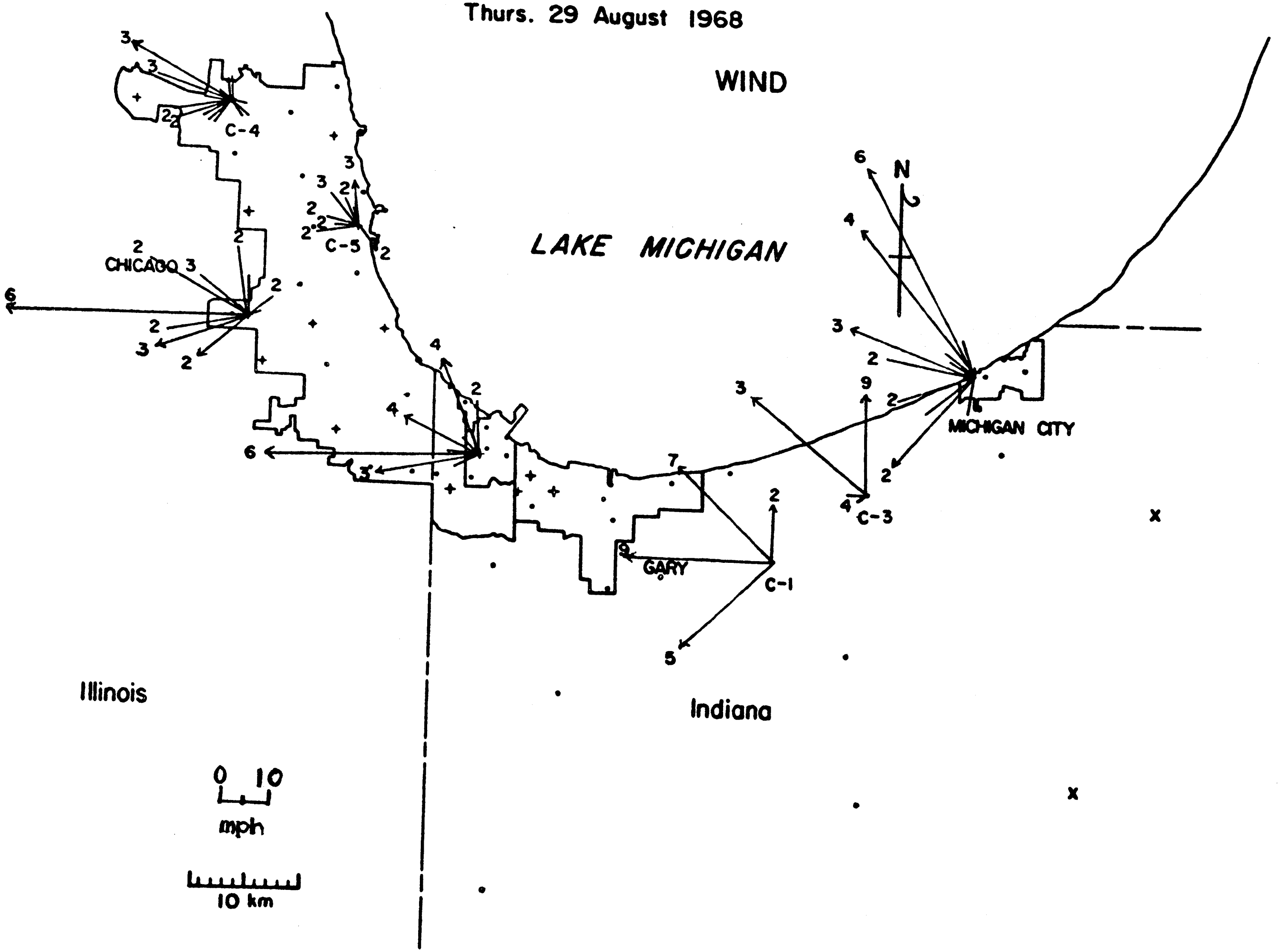


Figure 3.7.1: Wind rose for 29 August 1968.

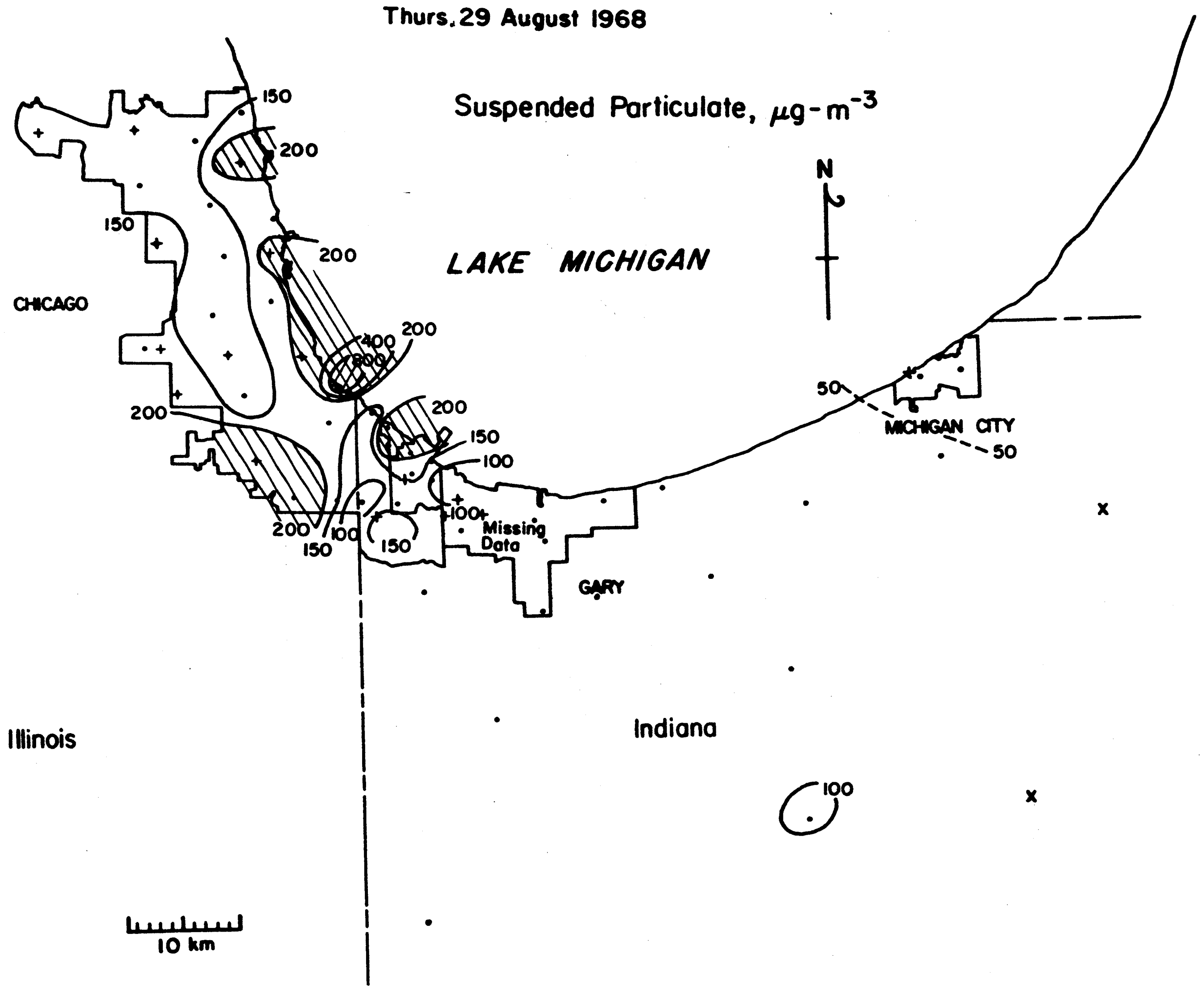


Figure 3.7.2: Suspended particulate isopleths for 29 August 1968.

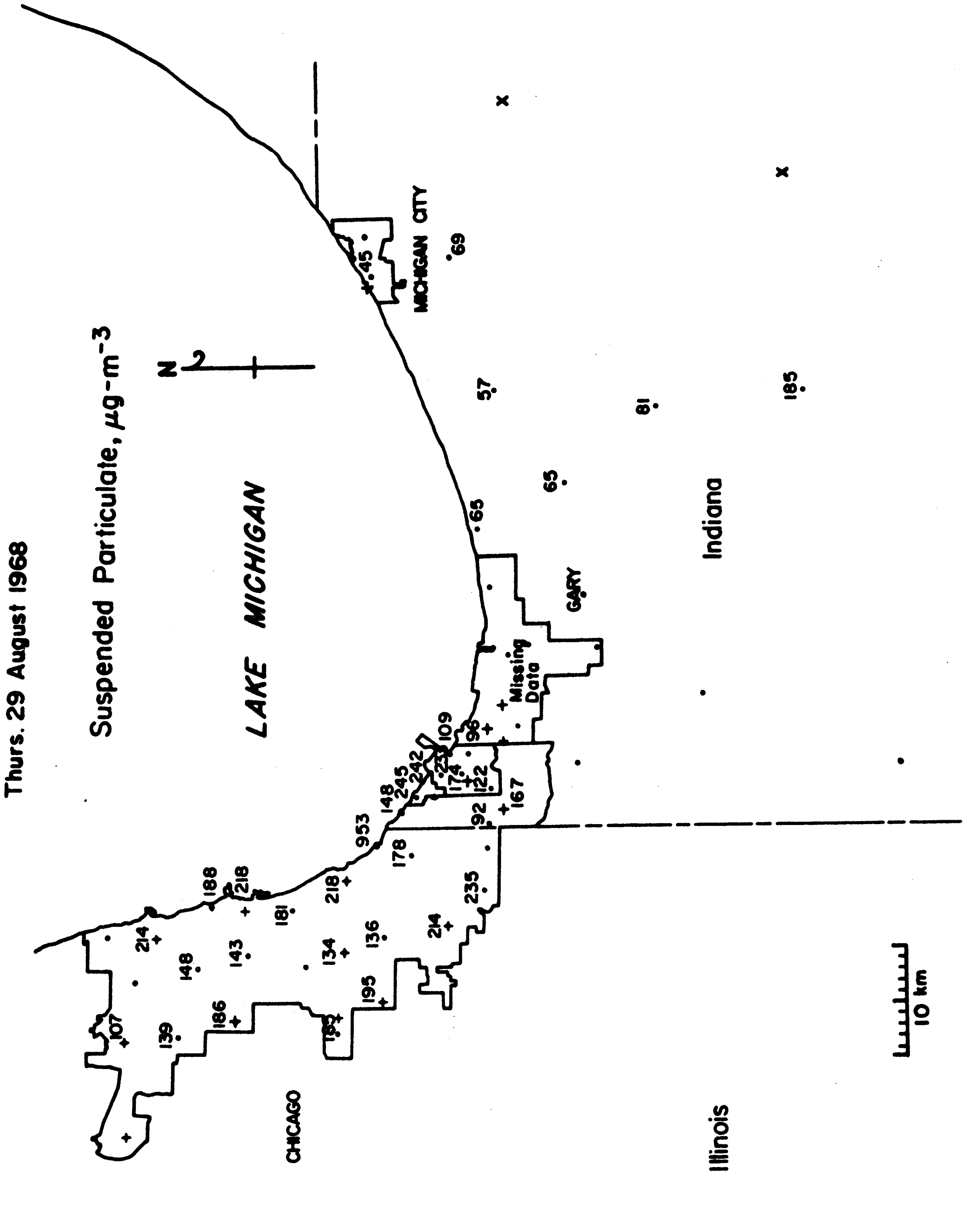


Figure 3.7.3: Suspended particulate data points for 29 August 1968.

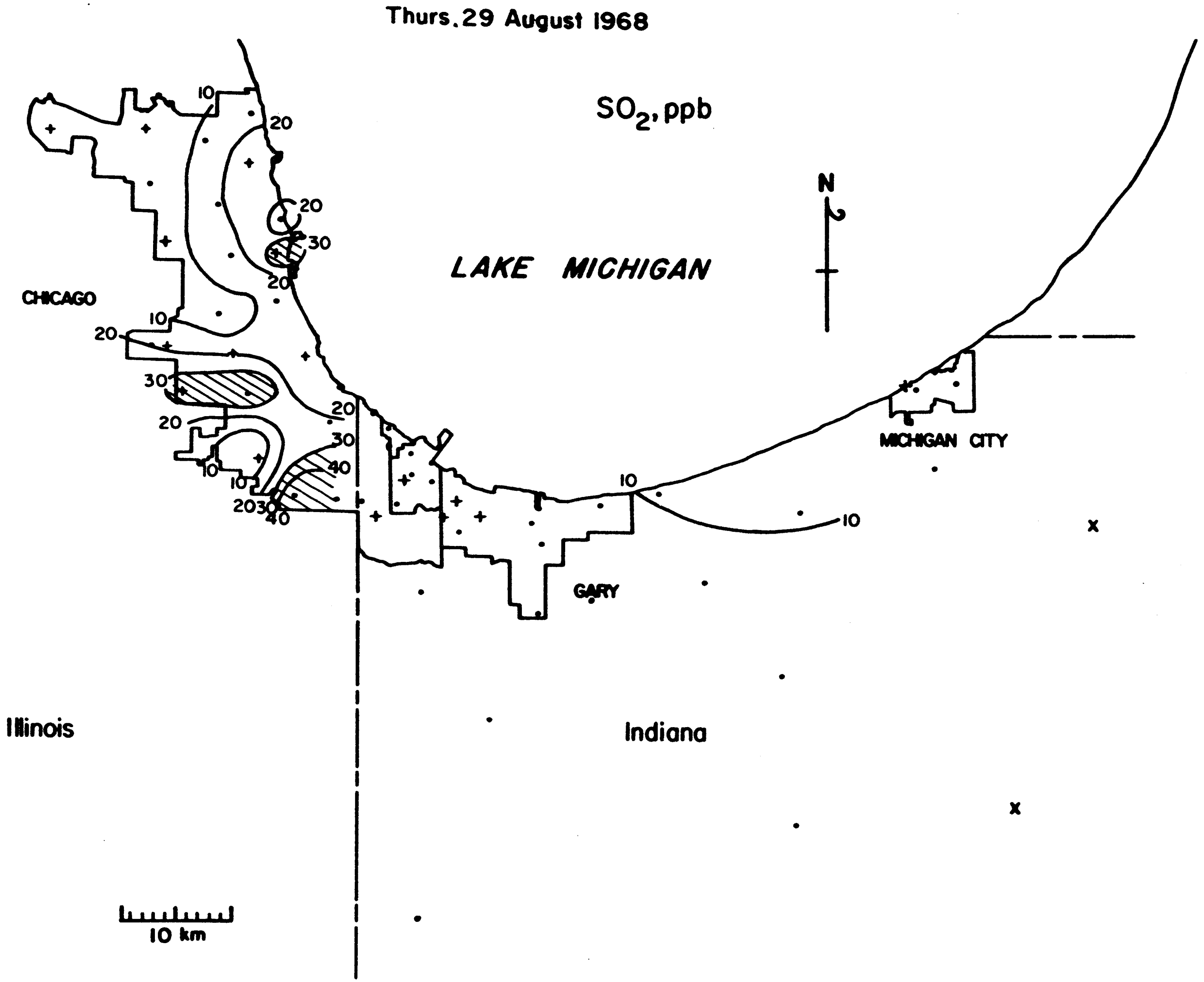


Figure 3.7.4: SO_2 isopleths for 29 August 1968.

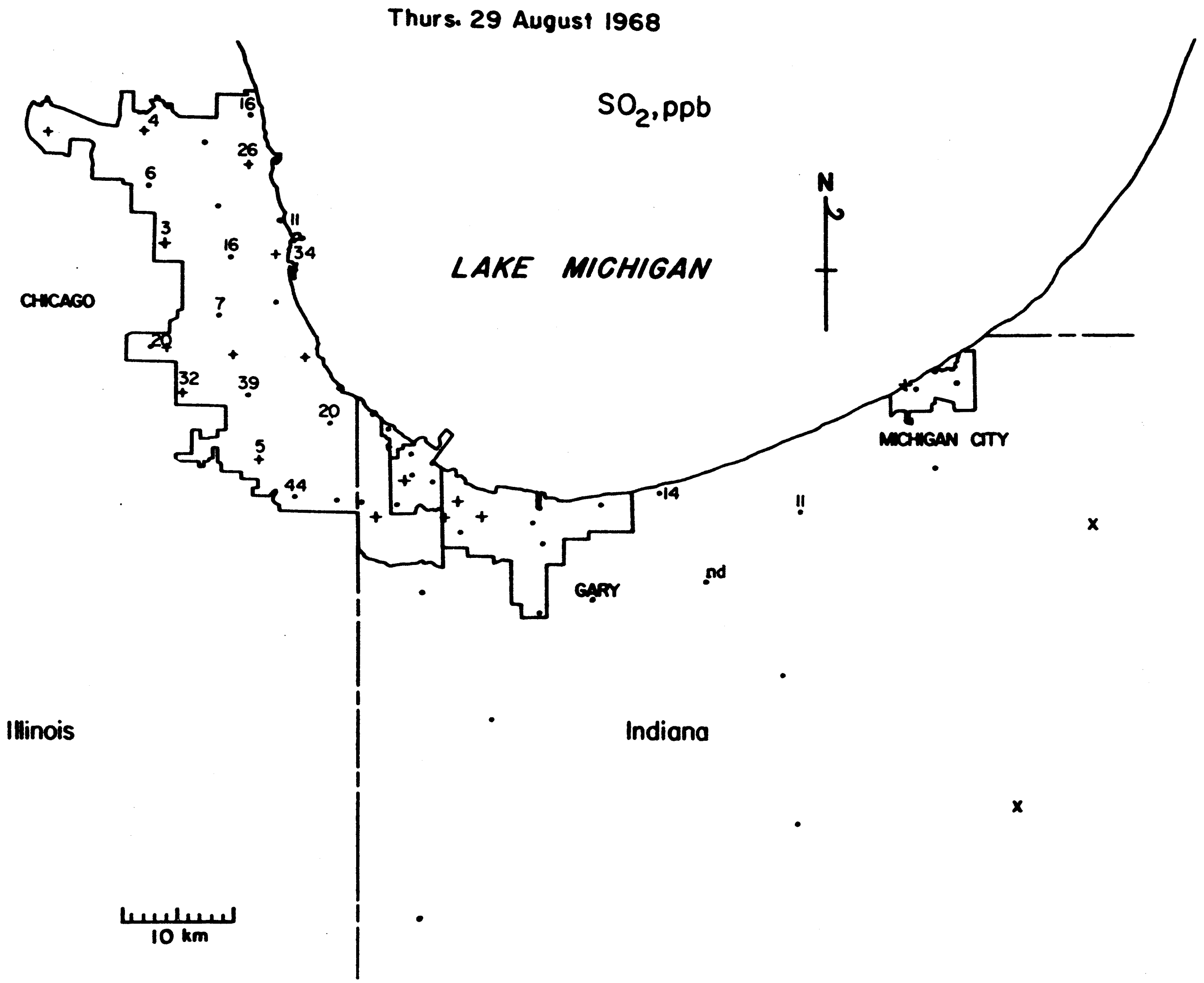


Figure 3.7.5: SO_2 data points for 29 August 1968.

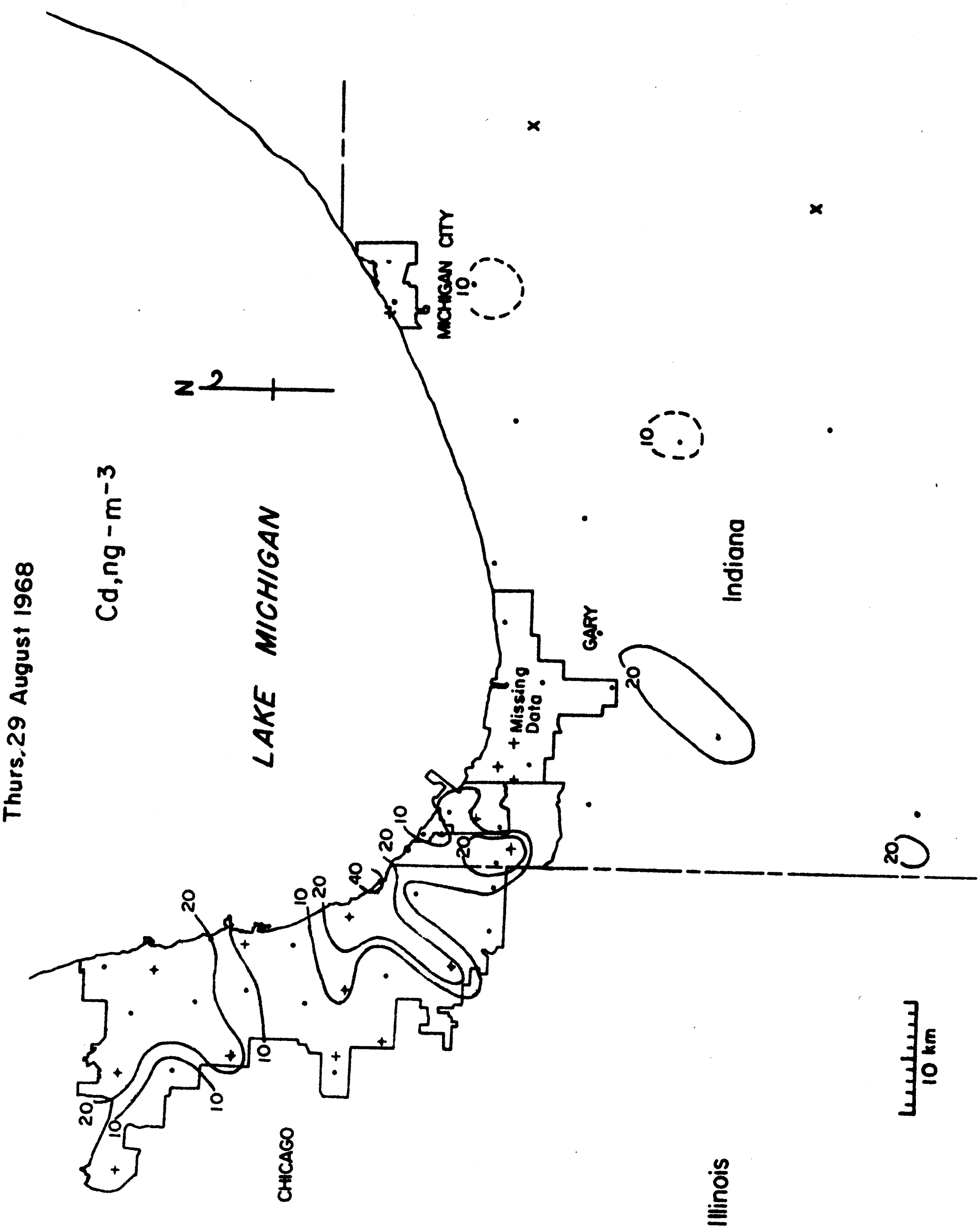


Figure 3.7.6: Cd isopleths for 29 August 1968.

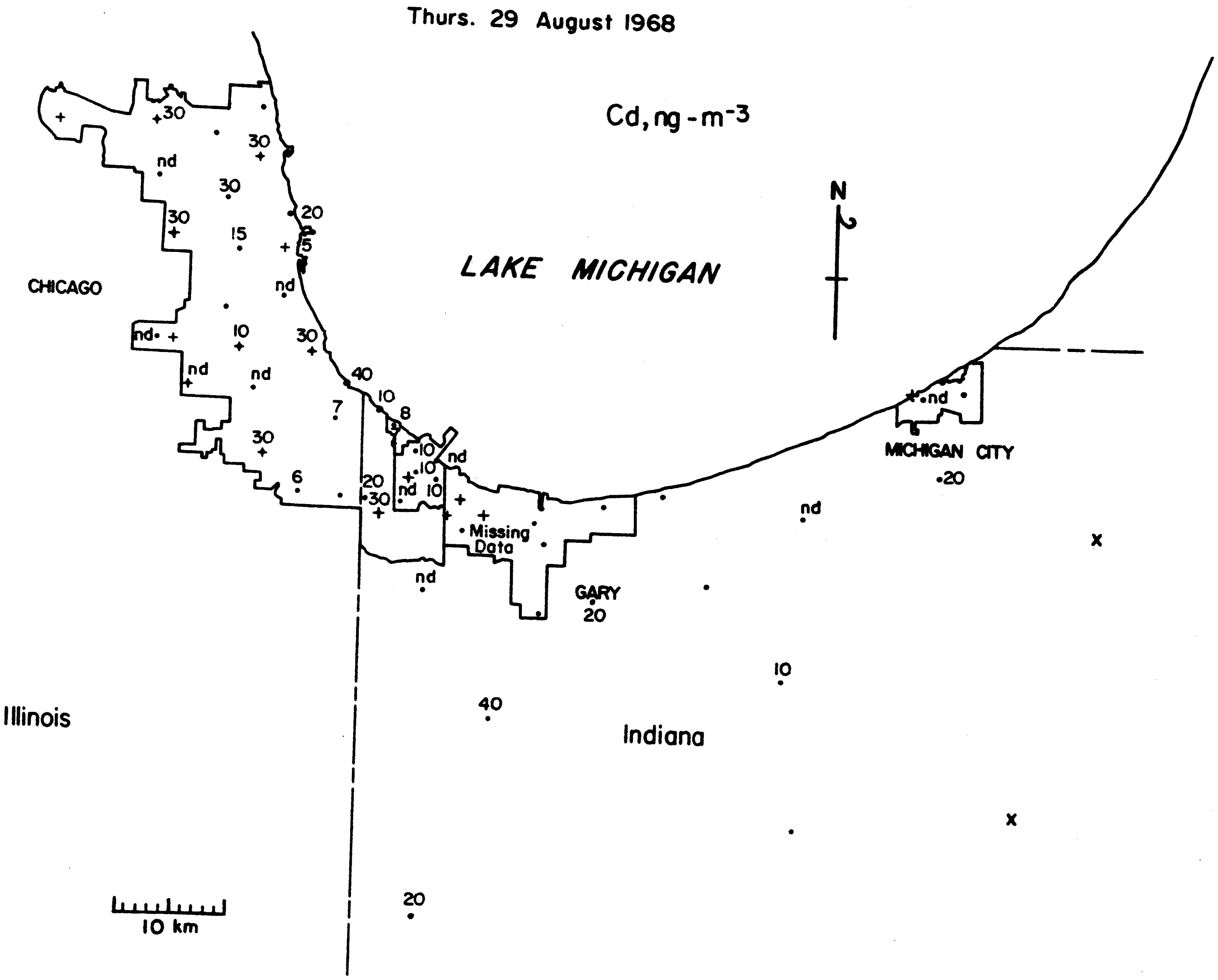


Figure 3.7.7: Cd data points for 29 August 1968.

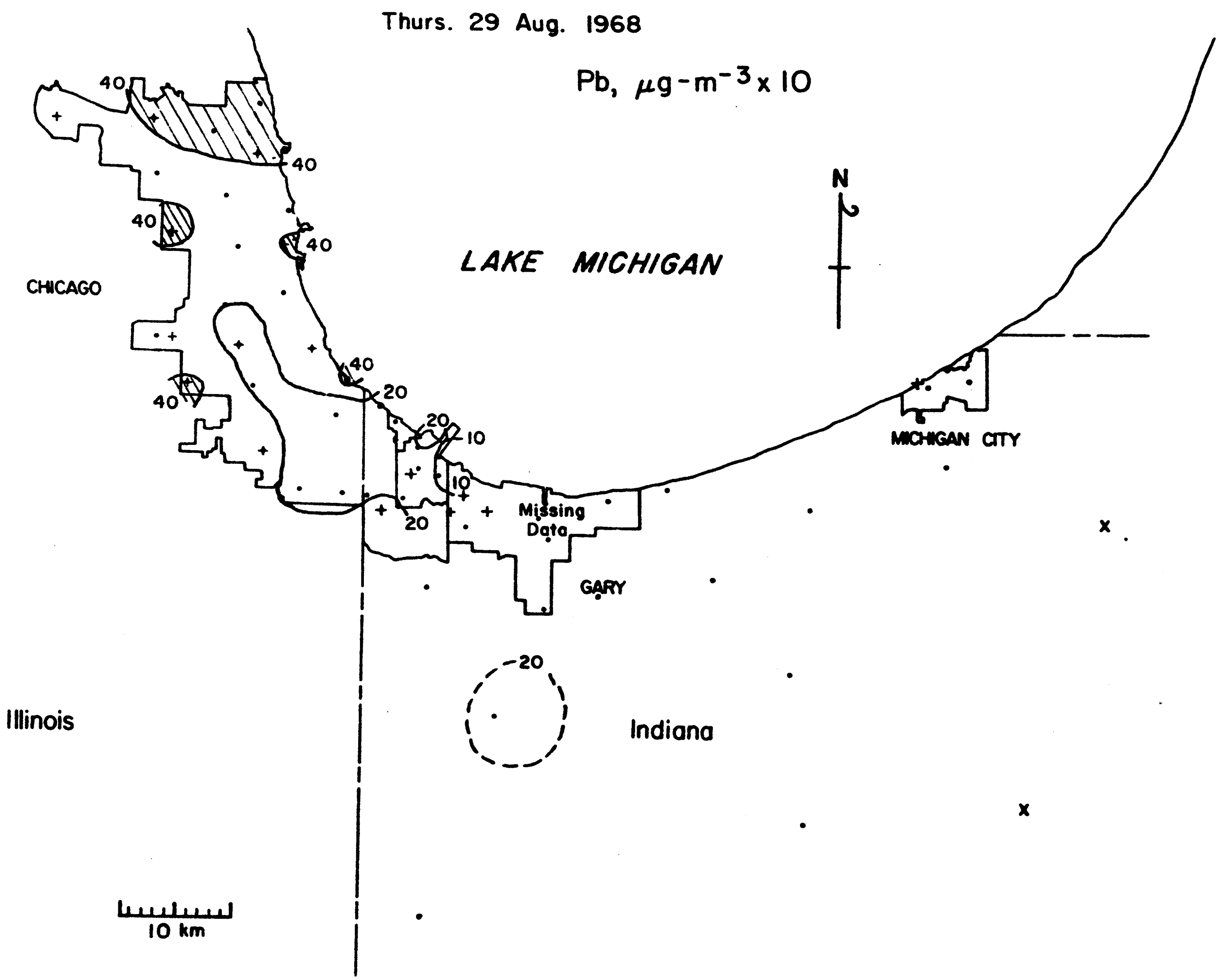


Figure 3.7.8: Pb isopleths for 29 August 1968.

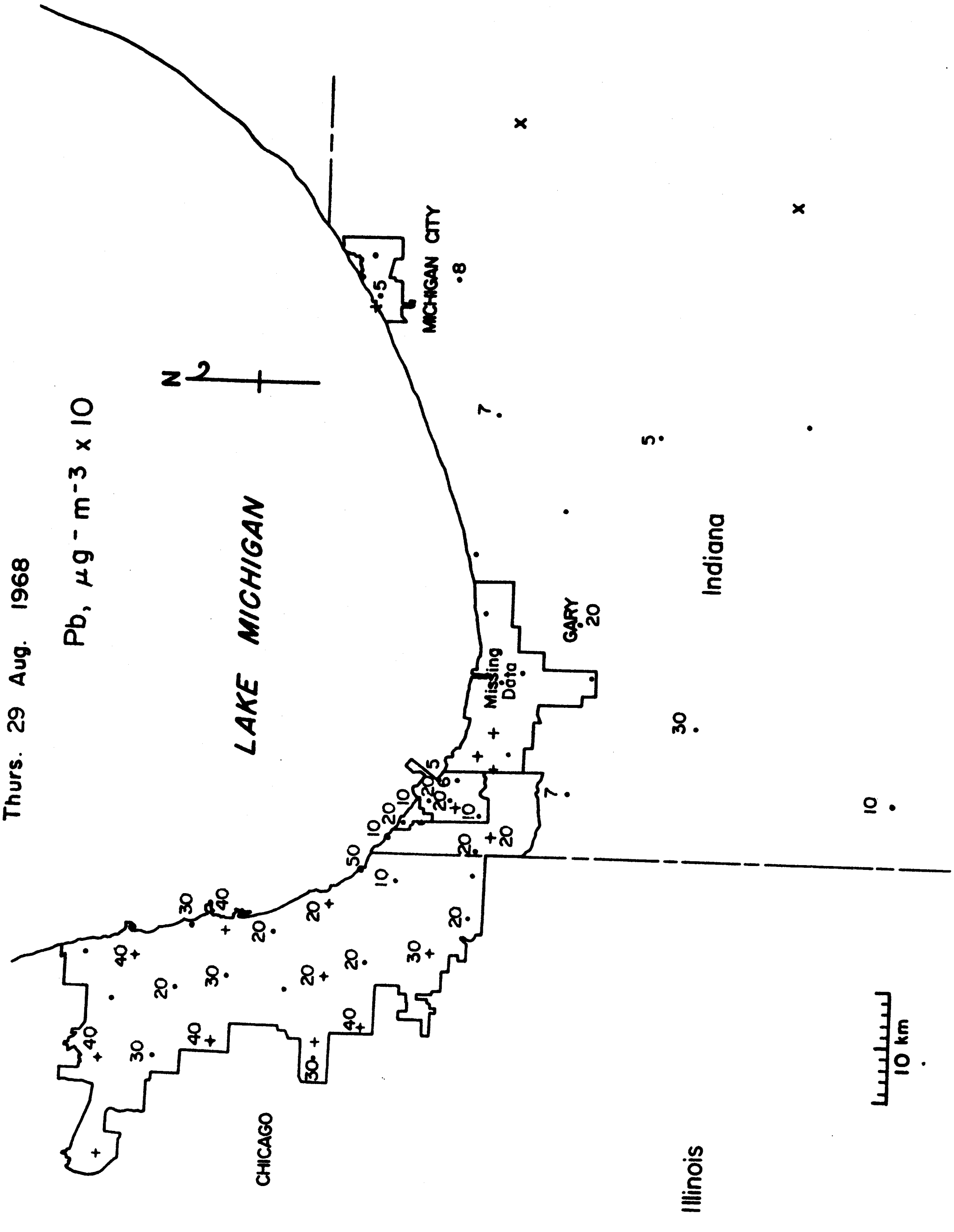


Figure 3.7.9: Pb data points for 29 August 1968.

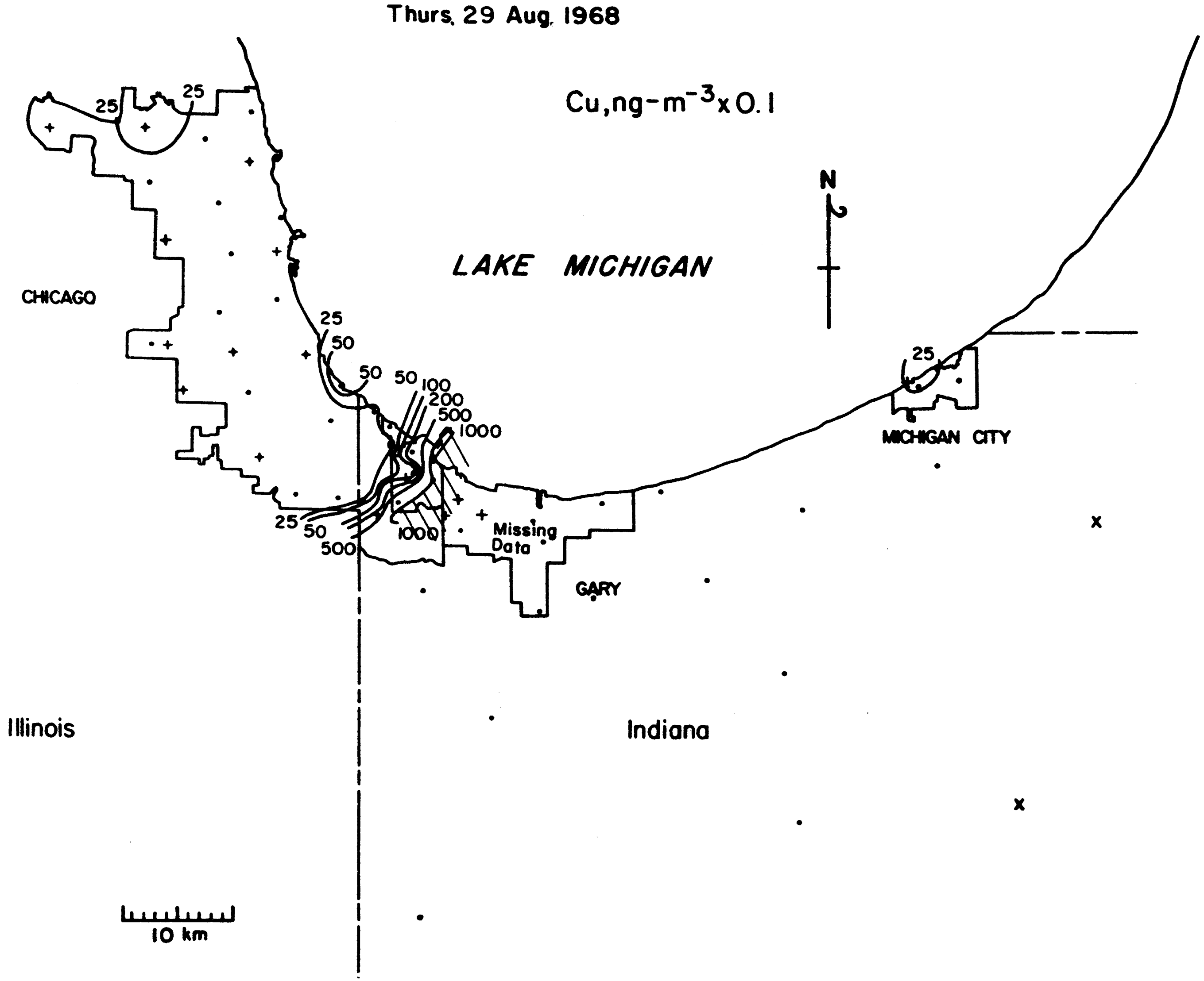


Figure 3.7.10: Cu isopleths for 29 August 1968.

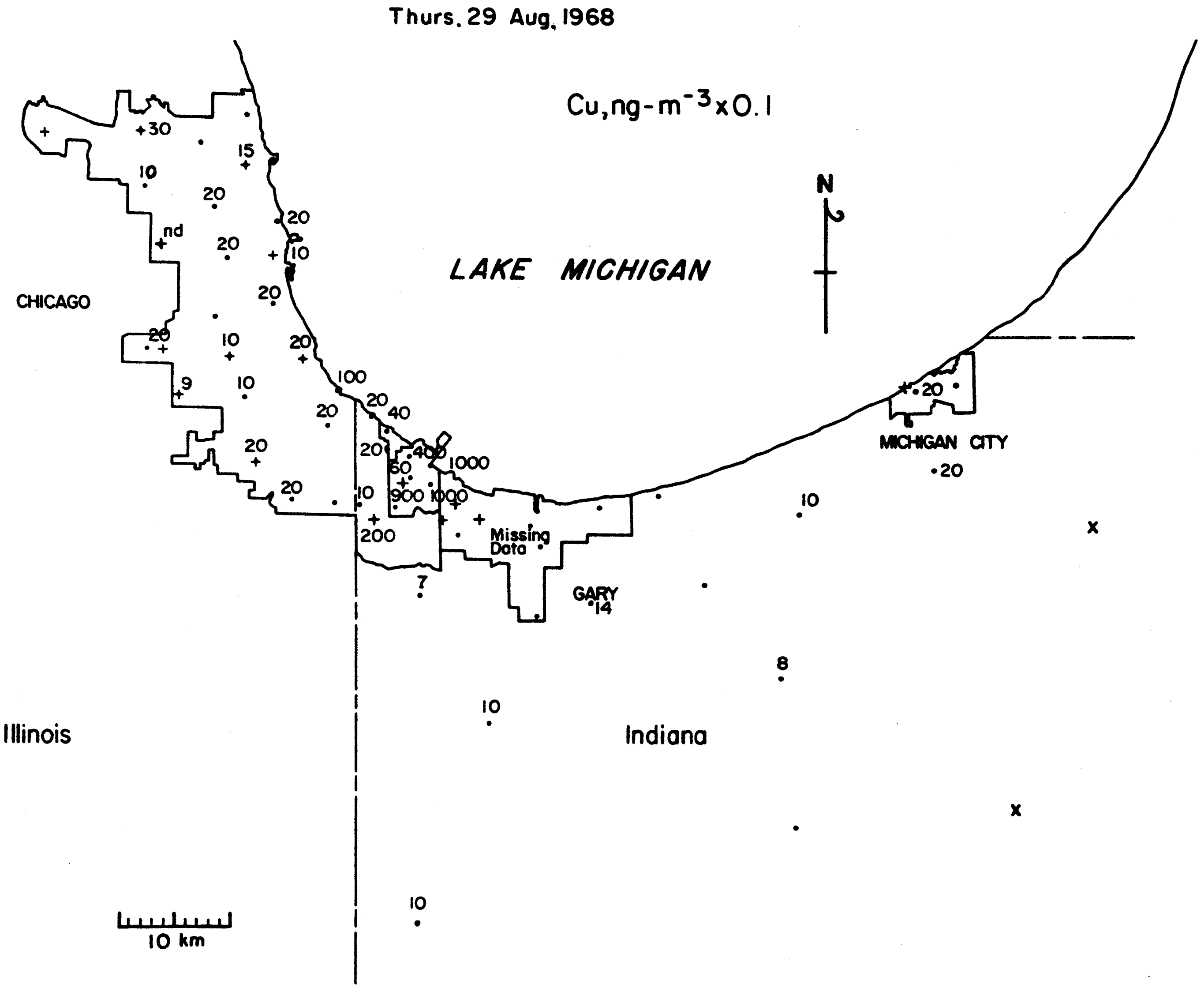


Figure 3. 11: Cu data points for 29 August 1968.

4.0 INTERPRETATION

4.1 SUMMATIONS AND AVERAGES OF THE DATA

Due to the large number of data points and the diversity of emission sources and conditions, many potential conclusions are not obvious. In order to attempt a further interpretation of such a large amount of data, Tables 4.1 to 4.4 have been constructed. Table 4.1 represents a compilation of pertinent meteorological data from Midway Airport in Chicago, Illinois. The average concentrations and their respective average ratios are presented in Tables 4.2 and 4.3. An attempt is made to separate the regions by tabulating Chicago and Northwest Indiana separately, and then a summation is given for both areas. Concentrations of copper for East Chicago, Indiana, (stations 6-10) are presented separately in order to eliminate an over bias in the rest of the Indiana region. This is not necessary for the ratios since the copper values in the numerator result in a very low number in the ratio. Table 4.4 presents correlation coefficients of each pair of elements. Additional representations in the form of histograms and of ratios of the element pairs are in Appendix IV.

4.2 TRANSPORT AND DIFFUSION

The meteorological data in Table 4.1 show that the sample days were similar. Wind direction was markedly different for 21 May and 29 August, but the range on those days tends

Table 4.1 Average Meteorological Characteristics

	Wind Direction degrees	Range degrees	Speed m/s	Range m/s	Temperature Max. °C	Min. °C	Ave. °C	Precip. mm	Relative Humidity %.
May 21	290	360	3.3	C-7	13.9	8.3	11.1	Trace	--
May 22	180	280	3.5	C-8	16.7	6.1	11.7	2	--
June 6	180	40	5.3	2-8	33.9	20.0	27.2	None	55
June 20	150	150	3.8	3-8	25.6	13.3	19.4	Trace	61
July 9	210	170	6.8	4-10	29.4	16.1	22.8	Trace	60
Aug. 8	200	360	3.9	2-16	31.1	22.2	26.7	0.5	77
Aug. 29	090	150	4.2	3-6	24.4	15.0	20.0	None	58

Table 4.2 Average Concentrations for Each Day in Chicago and Northwest Indiana

Day, 1968	Cd ng/m^3	Pb ng/m^3	Cu* ng/m^3	SP μgm/m^3	SO2 ppb	Bi ng/m^3
21/22 May			2000			
Ind.	21	2000	180	92		1.1
Ill.	29	4300	300	130		0.25
Both	25	3300	750	110	19	0.63
6 June			3500			
Ind.	8	830	390	140		
Ill.	9	1300	830	170		
Both	9	1100	970	160	20	
20 June			3900			
Ind.	13	1700	260	170		
Ill.	10	2700	230	200		
Both	12	2200	1000	180	16	
9 July			1600			
Ind.	19	810	130	84		
Ill.	9	810	99	83		
Both	14	810	510	84	12	
8 Aug.			4800			
Ind.	5	1300	120	100		
Ill.	13	2600	250	180		
Both	9	1900	1300	146	9	
29 Aug.			4000			
Ind.	12	1300	140	120		
Ill.	16	3100	220	180x		
Both	14	2200	1200	156x	17	
Totals: all data						
Mean	19	1900	1000	150	18	0.63
Max.	80	7000	10000	950	80	3.
Min.	≤5	100	≤20	30	≤0.5	≤.05

(*, stations 1-10 and 11-22 listed separately;
x, station E excluded)

Table 4.3 Average Values of Selected Ratios for Each Day in Chicago and Northwest Indiana

Day, 1968	Cd/Pb	Cd/Cu	Cd/SP*	Pb/SP*	Cu/SP*	Cu/Pb	Cd/S02 x0.5x10^{3}
21/22 May							
Ind.	0.012	0.099	0.023	2.2	1.7	0.89	
Ill.	0.007	0.14	0.023	3.5	0.25	0.080	
Both	(0.010)	(0.12)	(0.023)	(2.9)	(0.92)	(0.44)	(9.0)
6 June							
Ind.	0.018	0.031	0.0098	0.57	1.49	3.4	
Ill.	0.011	0.16	0.0078	0.76	0.071	0.13	
Both	0.014	0.10	0.0086	0.67	0.85	1.9	4.2
20 June							
Ind.	0.021	0.11	0.022	1.1	0.87	1.3	
Ill.	0.0044	0.087	0.0071	1.6	0.11	0.060	
Both	0.012	0.10	0.014	1.4	0.54	.78	3.8
9 July							
Ind.	0.047	0.15	0.034	0.97	0.73	0.88	
Ill.	0.018	0.15	0.019	1.0	0.13	0.15	
Both	0.036	0.15	0.029	1.0	0.48	0.56	7.3
8 August							
Ind.	0.014	0.053	0.013	1.1	2.4	2.6	
Ill.	0.007	0.083	0.010	1.5	0.15	0.12	
Both	0.009	0.070	0.011	1.3	1.3	1.5	3.8
29 August							
Ind.	0.012	0.095	0.012	1.0	2.5	5.4	
Ill.	0.007	0.096	0.013	1.7	0.11	0.082	
Both	0.009	0.095	0.013	1.4	1.2	1.6	3.2
Totals: all data							
Mean	0.015	0.11	0.016	1.4	0.87	1.11	5.5

(*, %)

Table 4.4 Correlation Coefficients

All Data

	Cd	Pb	Cu	SP	S02
Cd	--				
Pb	0.36	--			
Cu	-0.09	-0.10	--		
SP	0.02	0.40	0.05	--	
S02	0.05	0.21	0.04	0.29	--
	21/22 May				
Cd	--				
Pb	0.46	--			
Cu	-0.10	-0.32	--		
SP	0.54	0.60	-0.20	--	
S02	-0.04	0.21	-0.11	-0.09	--
	6 June				
Cd	--				
Pb	0.38	--			
Cu	-0.18	-0.28	--		
SP	0.29	0.75	-0.18	--	
S02	-0.10	0.35	-0.05	0.26	--
	20 June				
Cd	--				
Pb	-0.16	--			
Cu	-0.11	0.09	--		
Sp	-0.48	0.50	0.33	--	
S02	-0.42	0.29	0.37	0.52	--
	9 July				
Cd	--				
Pb	0.10	--			
Cu	-0.07	0.48	--		
SP	0.30	0.43	0.37	--	
S02	-0.64	0.49	0.06	0.37	--
	8 August				
Cd	--				
Pb	0.43	--			
Cu	-0.23	-0.16	--		
SP	0.35	0.79	-0.10	--	
S02	0.35	0.39	0.00	0.32	--

Table 4.4 (continued)

29 August

	Cd	Pb	Cu	SP	S02
Cd	--				
Pb	0.60				
Cu	0.03	-0.33	--		
SP	0.40	0.47	-0.10	--	
S02	-0.70	-0.18	-0.32	0.41	--

to negate their usefulness in diffusion calculations. June 6 is the only day with a reasonably small variation over the 24 hour samples, but its usefulness is also limited as far as a diffusion model in so far as the East Chicago plume is advected over the lake and much of the surface plume profile is lost. However, assuming that the source is close to station 8 and directly upwind and that station 6 and/or 9 is downwind on the plume axis we can estimate the source strength by the following arguments.

If we assume that the stations are located along the center line of the plume (y = 0) then Turner (1969) gives us the following equation.

$$\chi(x,0,0;H) = \frac{Q}{\pi\sigma_y\sigma_z\bar{u}} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] ,$$

where

Q (g/sec) = source strength;

χ (g/m^3) = concentration at sample point;

H (m) = effective stack height;

$\bar{u}$ (m/sec) = average wind speed;

σ_y, σ_z (m) = deviation of wind in the y, z directions.

At station 8 let $H = 20$ m, $x = 0.1$ km, $\chi = 9 \times 10^{-6}$ g/m^3, and from Turner (1969), $\sigma_y = 12$ m and $\sigma_z = 7.5$ m. At station 6 let $H = 20$ m, $x = 0.6$ km, $\chi = 7 \times 10^{-6}$ g/m^3, and from Turner (1969), $\sigma_y = 62$ m and $\sigma_z = 38$ m. Solving for Q at both locations:

$$Q_8 = 0.45 \text{ g/sec} ,$$

$$Q_6 = 0.27 \text{ g/sec} .$$

The agreement is satisfactory considering that no refinements of the estimation of H on σ_y,σ_z were made. Then, if we accept the value of Q = 0.4 g/sec, the output of the source would be 35 kg/day (13 tons/year) of copper-containing aerosols (at \$2/pound the dollar cost would be \$77/day or \$28,000/year!). This calculation points out the necessity for forecasting the wind conditions for optimum information in order to estimate the source strength of point sources.

The other source strengths are not so easily calculated by virtue of the area source nature. From the point of view of bulk transport of pollutants it is evident that a case can be made for a general transport by the gradient winds. The isopleths show concentrations along lines parallel to the wind direction and, in some cases, some semblances of a plume. Due to the complexity of the sources and the mesoscale wind effects it is difficult to completely convince oneself of this fact for every element for every day, but a general pattern usually becomes evident after close examination. An example of the complexity of this situation occurs 8 August with low wind speeds, variable direction, and a lake breeze effect during the late morning and early afternoon. A lake breeze can be shown to form a convergence zone that seems to concentrate pollutants in a very narrow band, and if this band passed slowly over a station, it would give a disproportionately high amount of suspended particulate and thus pollution elements. The lake stations would have lesser amounts of aerosols and the stations further inland beyond the lake breeze front would have a normal proportion of the suspended particulate.

One could probably argue that an attempt should be made to further model the concentration characteristics of the region for these particular days, but considering that only one station was available (East Chicago, Indiana) with any detailed wind information, it would be difficult to try to provide more detailed calculations.

Thus, in order to further interpret these data,greater meteorological detail must be obtained with more first order meteorological stations and a greater density of samplers. The present station is adequate for gross measurements but does not provide sufficient data to do a complete diffusion analysis.

4.3 REMOVAL PROCESSES

The primary removal processes are mixing and advection out of the source area, chemical reactions, fallout, and washout or rainout.

Mixing and advection are not usually thought of as removal processes but are used here as mechanisms for decreasing concentrations in the sample areas. From Table 4.1 the average wind speed is about 5 m/sec or 18 km per hour; thus, most aerosols emitted into the air have an average residence time of less than one-half hour over the cities, precluding fallout. Mixing is faster due to solar insolation during the day and is primarily mechanical at night. If we assume that airborne particles have an average fall rate of 1 m/min, then the particles would fall 30 meters in one-half hour, which is small compared to the horizontal advection and vertical mixing under normal conditions. We then would assume that a large part of the aerosols emitted in the metropolitan area are advected out of the immediate environment. Due to the proximity of Lake Michigan and the prevailing winds we should concern ourselves briefly with the possibilities of contamination of the lake and surrounding regions downwind from these sources.

Winchester and Nifong (1969) have calculated from available data various estimates of trace metal transport both by rivers and by fallout of air pollution. The positive argument presented is that almost half of the prevailing winds are from the southwest sector which would advect most of the industrial effluents over the lake. Looking closely at the total picture of isopleths for each metal, we can give an educated guess as to the various size distributions and thereby the fallout rates of these materials. First of all, lead is known to be of the order of less than one micron mean diameter and usually is stated to be about 0.25 microns mean diameter (see Appendix II). Therefore, lead, once airborne and thoroughly mixed into the mixing layer, will not settle out very quickly, although initial fallout should occur very close to expressways and emission sources. The copper component, especially in East Chicago, Indiana, shows a definite fallout close to the source with closely packed isopleths decreasing rapidly. Also, cadmium aerosol isopleths close, but not as quickly as the copper and not as slowly as the lead. It can be assumed that the cadmium fallout would lie somewhere between the lead and the copper.

In the Ann Arbor area the aged Cd and Cu aerosols have a similar size distribution with a maximum at 1.0 μ diameter. If we are allowed to make an inference from that data to this study area, we can predict that the Cd and Cu aerosols will behave similarly except in the anomalous regions in East Chicago, Indiana. Therefore, fallout would be slow except close to the sources where coagulation and agglomeration usually occur within the process system. Please see Appendix I.5 for a recent dust fall measurement.

Probably the most efficient method of removing these mixed aerosols from the atmosphere is convective rain and snow storms. Gunn (1960) has shown that electrified storms are extremely efficient at removing aerosols quickly. Thus, we predict that all of these trace elements are not falling into the lake by dry fallout in as large quantities as that due to precipitation once they are advected from their points of emission. Copper, close to East Chicago, Indiana, under southwest wind conditions, is falling into the lake but close to the shore. The primary area affected is probably no larger than twice the size of East Chicago itself, approximately 30 kilometers. Appendix I.4 presents a few rain samples from the area and indeed removal seems to be taking place.

4.4 SUGGESTED SOURCES--COMPARISON WITH EXISTING DATA

In Table 4.4 the correlation coefficients do not show the results expected. Only lead and suspended particulate are at all consistently positively correlated; the remaining parameters have varying coefficients from day to day. One would not necessarily expect lead and sulfur dioxide to correlate well, but copper and cadmium and possibly sulfur dioxide were expected to have resulted in some dependence due to their similar natures and possible sources. Frequency tables were generated by a multiple pass program eliminating data that contributed to less than 6% of the total on either side of the maximum category resulting in smoother distributions. Passes 1 and 5 are listed in Appendix IV. Some micro structure is apparent but the significance is questionable.

Also in Appendix IV we have listed all possible ratios of element pairs. Table 4.3 is a selected summary of that data. The usefulness of these ratios is apparent by considering that even though the total values vary and other elements are randomly contributing to the total suspended particulate, the ratios would remain the same if no other sources were present. These ratios are also useful in predicting the sources and the compositions of the aerosols.

As far as finding the sources of the elements, the persistent copper maxima in East Chicago, Indiana, are the only convincing small area (or point) sources. All other data seem to imply more area-wide sources except for a few occasions of suspended particulate at station E in south Chicago and Gary. The lead seems to be persistent in following the traffic densities, as far as we know them, with broad maxima and little fine structure. Also, cadmium and Chicago copper have only broad distributions with many other small sources implied. Sulfur dioxide is higher in the Chicago region, probably due to the larger amounts of coal being used there as compared with Northwest Indiana. Figure 4.1 is a representation of the fossil fuel burning facilities in the Chicago area. Comparison with the isopleths shows a good agreement in location of sources (e.g., 21 May), but insufficient information is available for comparison to source strengths.

A logical next step to be taken is to try to match the atmospheric data given here with known inventories. Source inventories of trace metals are very scarce for the Chicago and Northwest Indiana regions. Winchester and Nifong (1969) have compiled a conservative estimate of trace metal emissions in the study area. Table 4.5 is an excerpt of that inventory.

Table 4.6 presents a comparison of ratios obtained from independent sources for comparison to the data presented in this work. In addition to the Winchester and Nifong estimates of source emissions, Kneip _et al_. (1970) have presented data for four stations in New York City for cadmium, copper, and lead (section 1.3.5), and McMullen _et al_. (1969) have compiled averages for 147 stations throughout the United States for copper and lead, and sulfate particulates (section 1.3.4).

From the table it appears that the non-anomalous copper and the cadmium can be explained by the burning of fossil

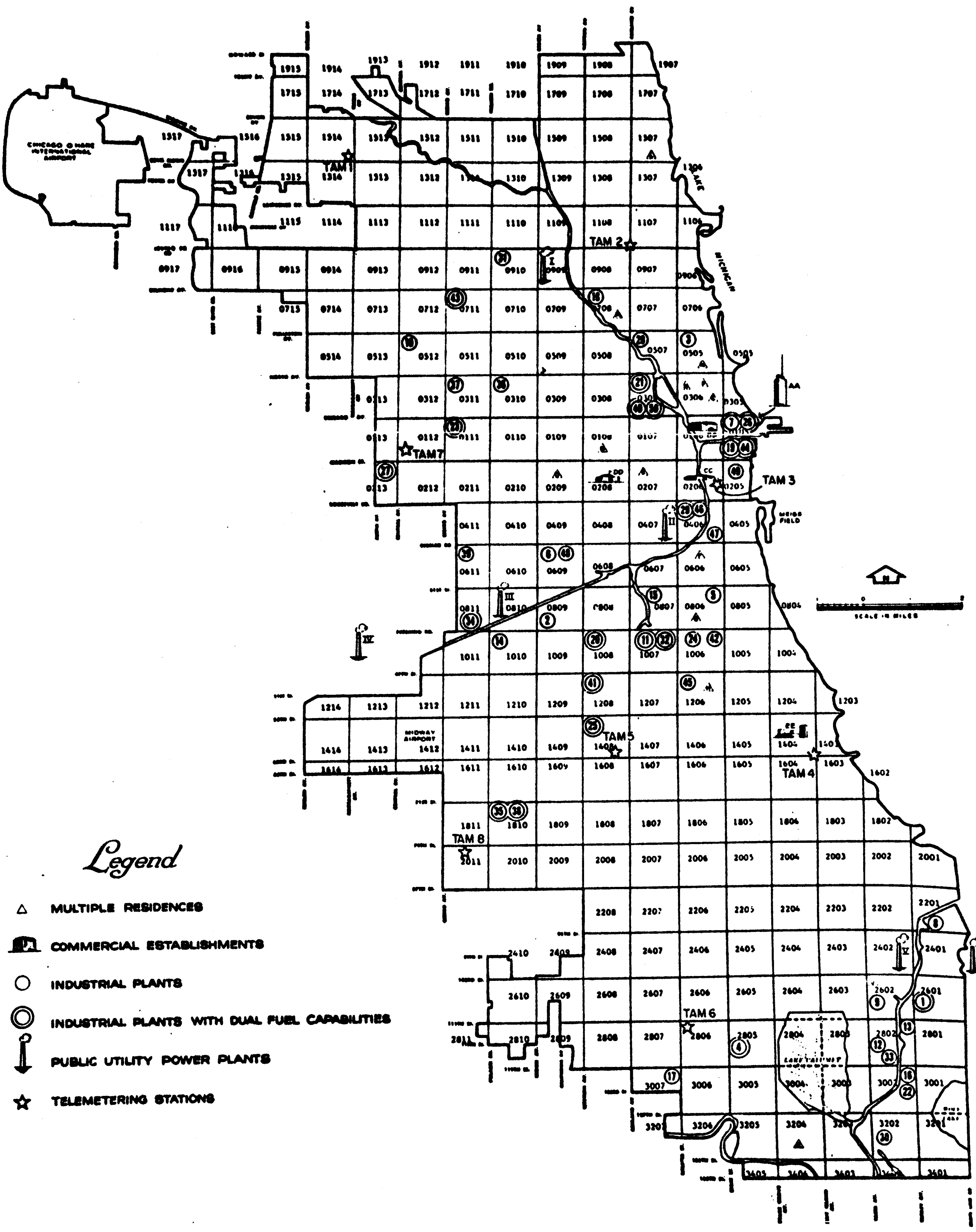


Figure 4.1: Locations of fossil fuel burning industries.

Table 4.5 Contributions of Fuels to Lead, Cadmium, and Copper to Chicago Area Suspended Particulate[a]

	Coal	Coke	Fuel Oil	Gasoline
Combustion estimate, megatons/yr	20	15	7	8
Particulate emission estimate, kilotons/yr	220	18	14	b
Pb emission estimate, tons/yr	300	22	30	1,800
Cd emission estimate, tons/yr	11	1	--	--
Cu emission estimate, tons/yr	100	7	26	--

[a] After Winchester and Nifong (1969). All units are metric.

[b] Assumed 2 g Pb/gallon and 25% of emissions airborne.

Table 4.6 Comparisons of Average Ratios from This Study to Independent Data

	Cu/Cd	Pb/Cu	Cd/SO_2	Cd/S	Cu/SO_2	Cu/SO_4^{--}	Cu/S	Pb/SO_2	Pb/S
This Study									
Chicago :	8	10	--	--	0.036	--	(0.018)	0.28	(0.14)
All Stations:	9	0.9	0.0055	(0.0027)	0.1	--	(0.05)	0.2	(0.1)
Winchester and Nifong (1969)									
Fuels Only :	11	18	--	0.000017	--	--	0.0002	--	0.0034
All Sources :	270	0.7	--	0.000017	--	--	0.005	--	0.0032
Kneip *et al.* (1970)									
New York :	10	15	--	--	--	--	--	--	--
McMullen *et al.* (1969)									
U.S. Average:	--	4.1[a]	--	--	--	0.016[a]	(0.005)	--	(0.022)

[a] Urban and "proximate" values only.

( ) Estimated from SO_2 or SO_4^{--} values.

fuels and that the data is consistent with that found in New York City by Kneip _et al_. (1970) and predicted by Winchester and Nifong (1969). There is a discrepancy between the predicted ratio in the Winchester and Nifong data from all sources including metallurgical for the Cu/Cd ratio. This difference may be partially due to the fact that our value is averaged over a fairly uniform grid over a large area, consisting of many low source regions, which may not have been representative of all metallurgical sources near the lake shore.

Similarly, the Pb/Cu ratios agree within reason considering the non-anomalous sources. The values for this work are close to the values of McMullen _et al_. for the U.S. and lie between those of Winchester and Nifong's estimations for all sources and those of fuel sources. The agreement is close for both categories.

If copper and cadmium are indeed emanating from coal ash or fuels, then there should be some agreement with the estimation of ratios from these elements and sulfur dioxide measurements. Since sulfur dioxide oxidizes into sulfates, the ratios should be taken with total sulfur, but as usual this data is not available but can be estimated.

Sulfur usually exists in the atmosphere as SO_2 gas or as sulfate particulate (and some H_2SO_4). The summation of each component should equal the total emission inventory of sulfur. By inspection of the Winchester and Nifong inventory values and those calculated from this study we can see that the element to sulfur ratios fall below the estimated by a factor of 10 to 100 for all three elements. The interpolated Cd/S values are larger by a factor of 100, the Cu/S by a factor of 10, and Pb/S by a factor of 100 as compared to the Winchester and Nifong data. Comparison to the McMullen <u>et al</u>. interpolated results show a similar discrepancy of 10 for Cu/S and five times higher for Pb/S. Since most values of the ratios of SO_2/SO_4^{--} are unity we probably could not make up the difference by adding the missing components as it would not be factors of ten.

Taking into account all the information in Table 4.6 we must invoke the possibility that the trace metal inputs estimated by Winchester and Nifong (1969) are too conservative or that our values are too high by a factor of around ten. (It seems unlikely that Winchester and Nifong have over-estimated the sulfur output in this area by ten-fold.) Four possible explanations for the discrepancy can be offered.

1. Since the emission inventory is a conservative one, and due to the small average size distributions of the elements (Appendix II), there exists the possibility that the Cd and Cu in the fly ash are differentially emitted in greater amounts than hitherto expected (Caffee and Gerstle, 1967). Since most collections are size dependent, this reasoning is a plausible explanation that leads us to be concerned about our projected emission and exposure rates.

2. There is a probability of a differential settling rate between the particulates Cd, Cu and Pb, and the SO_2 gas;

warm gases rise but most aerosols fall except under mixing conditions. When observing a plume one can sometimes see the fallout of aerosols from the plume with the steam and gases continuing in a normal diffusion manner, which leads us also to be reminded that the samples were all taken in the summer months with most of the sulfur emitted from power and manufacturing industries, which in all probability have high stacks. Thus the argument given previously about comparing the high volume emitters and their inventories with a wide-spread sampling grid, especially with the emitters high above the samplers, leads to difficulty.

3. The latter argument leans heavily on the notion that other sources of the trace elements exist but with low-sulfate contents. For example, most of the stations are located in populated areas where much home incineration and some trash burning is present. All of these emissions would contain trace materials but an unknown quantity of sulfur. The coincidence of maintaining the Cu/Cd ratios is not surprizing due to the fact that most of the material burned in these areas is of organic and, most probably, wood origins.

4. Finally there is a reasonable amount of reflotation of cinders, etc., in these areas, whereas the SO_2 is converted to sulfate and does not return to SO_2 to be refloated. Thus, a comparison of trace metals to SO_2 is difficult due to the many unknown behavioral characteristics of the SO_2 life cycle as compared to those of the aerosols.

In conclusion, the anomalous copper in East Chicago, Indiana, is due to a point source suspected but as yet unknown. Other copper particulates and those of cadmium are best explained by the burning of fossil fuels and incineration as pointed out by the close agreement in the ratios and their distribution characteristics. Lead is obviously emitted almost entirely by automobiles, and no other source is expected.

A final comparison should be made. The National Air Sampling Network (NASN) runs more than 100 Hi-Vol stations in communities all over the United States. Approximately 17 trace elements are analyzed and reported. Since a NASN station was in operation at location 2 in Hammond, an opportunity exists for a comparison. Table 4.7 represents three classifications of NASN stations in the state of Indiana: Hammond, an industrial-urban site; Beverly Shores, a proximate station; and Parke County, a rural location. These results are compared with the results of the six day study and point out some inadequacies of using the NASN station in Hammond to represent the whole southern Lake Michigan region. Only cadmium, and possibly bismuth, are representative, and then probably because of their low values. In addition, the station is not placed according to population exposures since the most populated area in the Northwest Indiana region is around station 9 (U.S., HEW, 1966), where the prevailing winds carry the copper, with a large amount of lead already being emitted in that area.

Table 4.7 Comparison with NASN 1963 Data, ng/m^3

	Pb	Cd	Cu	Bi
NASN, Parke Co., rural	24-57	1.8-5.2	17-80	≤0.5
NASN, Beverly Shores, proximate	100-200	ND-10	30-50	≤0.5
NASN, Hammond, urban	100-1,200	ND-55	30-180	≤0.5
This study, all stations[a]	100-7,000	<5-80	<20-10,000	<0.05-3.0
This study, station 2, Hammond[a]	1,000-3,000	<5-20	100-1,000	---

[a] Individual values reliable to a factor of 2.

4.5 ECOLOGICAL EFFECTS--TOXICOLOGY

Before presenting a discussion of toxicological levels of these pollutants we should point out once more that there is little known about the synergistic effects of these various pollutants for 24 hour exposures over several years. The arguments presented are based on eight-hour industrial exposures for healthy males, as listed in Table 4.8. In order to estimate a 24 hour exposure limit we can point out that a 40 hour work week is one-fifth of the total week and that, as in radiation limits, an additional factor of one-tenth is invoked to account for continuous exposure. Thus the eight-hour limits have been reduced by 50 for totally exposed receptors. No element is equal to or greater than the threshold limit values available, but lead and copper are approaching prohibitive quantities in some areas. This is especially evident considering the cumulative effects of lead and that these are not the highest values possible under extreme conditions that frequently do occur in this area.

Although the observed concentrations are below the human receptor levels, there is another parameter that must be considered--plant ecology and transport to clean waters in streams and lakes. Since the streams in the area are contaminated by industrial discharges, we will neglect this discussion except to note that some clean streams may exist in the out county areas and could be influenced by pollution aerosols.

Table 4.8 Comparison to Toxic Levels

Element	TLV*		Highest Level Observed 24 hrs.
	8 hr.[b]	30 days	
Cd	100 $\mu g/m^3$	5 $\mu g/m^3$[a]	0.08 $\mu g/m^3$
Pb	200 $\mu g/m^3$	10 $\mu g/m^3$[b]	7 $\mu g/m^3$
Cu	1,000 $\mu g/m^3$	50 $\mu g/m^3$[a]	$\geq$ 10 $\mu g/m^3$
Bi	None	--	3 ng/m^3

[a] Estimated, see text.

[b] American Industrial Hygiene Association (1969).

* Threshold limit values for healthy males of working age.

The only evidence of possible plant damage available to us at this time is indicated by a large copper maximum in East Chicago,* Indiana, and the more frequent occurrence of reported plant damage. If we accept the addition of copper by fallout to the soils to be over 30 micrograms per square meter ($\simeq$ 3 ppm) per year, we can predict that in a decade the topsoil will have approached the toxic limits found by Reuther and Smith (1955) of 160-180 ppm. This amount has already been achieved at station 9 by the results of measurements cited in Appendix I. Since the copper concentrates primarily in the tree roots, the toxic value can be allowed to go slightly higher since a large amount, but not all, of the roots are below the topsoil.

We must also ask whether the copper is in a soluble or organic form quickly available to the plants. Table I.6 shows that less than 10% of the copper fallout is water soluble. The question then arises of how long the copper has been deposited. Less than a century is sufficient to allow copper to enter into the larger percentage of the root systems, considering especially that the water supply usually comes from the topsoil. For example, a copper poisoned tree will exhibit blackened root tips and concentrations of up to 5000 ppm, but the leaves would contain a lower concentration of 32 ppm with young trees being especially susceptible to

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*Mr. Dennis Karas, Director of the East Chicago Air Quality Control Division, has found moderate damage hitherto blamed on SO_2.

copper poisoning. The problem, then, is not as straightforward as we would like, and lends itself immediately to the suggestion that the copper content of soils in this entire area should be measured with respect to solubility and insolubility fractions,and the real causes of already reported plant damage should be investigated. A partial bibliography has been prepared by Jerry Klein at Argonne National Laboratory, Illinois.

4.6 CONCLUSIONS AND SUGGESTIONS FOR FURTHER INVESTIGATIONS

An obvious situation in need of immediate further investigation is the large copper maximum in the East Chicago area. Since there are several industries capable of producing copper in large amounts, we cannot say as yet which specific industry or corporation is responsible. From the data presented in this work we can design experiments with which to discover the exact location and the industry causing the copper aerosols, and thus hopefully lead to its abatement.

This study has strongly shown the need for more areawide studies of this type not only in the southern Lake Michigan region but in all large metropolitan and industrial areas. Finding a large and potentially dangerous source such as the East Chicago copper plume is sufficient justification in itself. Additional information such as levels of receptor exposures and matching with source inventories are extremely useful. Anodic stripping voltammetry (ASV) is capable of sensing a few more elements, but recent developments in neutron activation analysis (NAA) and acquisition of new equipment has made an additional 30 or so elements available for analysis at the University of Michigan. Experiments have been and are being continued along the same concepts. Other agencies should also seek to enter into area-wide sampling and research using these more sensitive methods.

A simple way to investigate the problem of both dry fallout and precipitation is to analyze the dust fall taken at almost every station in this area, which is reported in the soluble fractions and the insoluble fractions that are available for analyses giving the input fraction. With a soil analysis we can obtain a good estimation of the amount of trace metals that are being washed from the topsoil into the streams and then into the lakes. A direct measurement of the streams could also be used and may be done more easily. More on site measurements should be taken before additional speculation is proposed.

A final parameter that has been examined at the University of Michigan is size distribution of various trace elements. Our inability to satisfactorily calculate the percentage of fallout of these various trace elements by classical diffusion equations points out the need for more information on the size distribution with respect to each trace metal, as well as simple dust fall measurements. In addition, a great amount of information is gained by examining the ratios and distribution of various trace elements in order to attain their probable form. For example, if a ratio is constant over a distribution, and the distribution shape is similar, it can probably be deduced that both, or all, such elements are from the same sources and are probably coagulated on the same aerosols.

A 42 hour continuous sampling study was conducted at the University of Michigan and was presented at the annual American Meteorological Society meeting in 1969. This paper is presented in Appendix II. In this paper we suggest that airborne particulates can be shown to be advected over moderately large distances from urban industrial regions to more nonurban areas if sufficient accuracy and meteorological data are present.

From the former discussions we can make several final observations pertinent to the criticisms of this type of area-wide survey.

The first, and perhaps the more important observation, is that from Table 4.2 one can now state clearly the general exposures of receptors in this area to the six parameters studied. The levels are high in some regions, but not yet to the toxic levels. We would hasten to add that these levels in conjunction with additional element stress could make these concentrations prohibitive, especially considering the long term exposures incurred.

A second important conclusion is that relative to copper the NASN station satisfies neither the maximum (source) concentrations nor the maximum population (receptor) exposure, and that the NASN lead values seem low for rural stations. From this conclusion we can immediately suggest that this type of area-wide survey be periodically undertaken to best suggest the proper location of the NASN stations for observing the criteria desired. This study, in conjunction with Harrison et al. (1970), suggests that station 9 is probably the best receptor location and also is nearly the maximum industrial exposure according to prevailing winds.

Due to the fact that this study was an initial attempt at a trace metal survey, with only 3-4 metals analyzed (Cd, Pb, Cu and Bi), and that the sampling days were predetermined, the maximum information was not obtained. Six days, weekdays at that, are more than sufficient to describe such an area. In the future, three forecast days will probably be sufficient: one with wind from X° with little variation, the second with wind from $X \pm \approx 90°$ (for source location), and a low wind day for maximum concentrations. This information, in conjunction with dust fall data, would greatly increase our knowledge of the source locations and fallout information. From the information presented here there is only one partial day with a rapid incursion of a "clean," new air mass, notably 9 July. Most of the other periods were similar; low ventilation and "old" air masses. Thus, forecasting is necessary if the cooperation of the local agencies is forthcoming.

The attempts at calculations of source strengths were tenuous at best. At least a lower limit can be found from the dust fall data by multiplying the area of measurable fallout by the average non-background concentrations. Probably the better procedure is an inventory and stack sampling study in conjunction with aerosol measurements, suggested by such area-wide surveys as presented in section 4.4.

Concerning sources for each element, only copper shows a definite and persistent source with concentrations of more than 100 times greater than those of rural areas. Subsequent studies by Harrison _et al_. (1970) have shown sources of other elements in the Northwest Indiana region obtained by neutron activation analysis. Lead shows the expected traffic dependency but cadmium and copper in other areas show no single source but have persistent non-stationary broad maxima in Chicago.

Another important observation is that suspended particulate measurements are extremely deceptive. Suspended particulate is a broadly distributed parameter not showing, at all, the large concentration gradient seen in this work. Suspended particulate is relatively stable except during rapid incursions of clean Canadian air and possibly during heavy precipitation. Thus, the fine structure of specific pollutants cannot be implied in any way from total suspended particulate data.

Boundaries of states, cities and counties are meaningless in pollution studies, and additional inter-agency cooperation is immediately necessary. The duplication of manpower and the scarcity of needed talent amoung these agencies, which seems necessary as long as boundaries and limits are set, seems to be a real waste of this manpower and talent.

An unexpected observation is that plumes of elements are lost very quickly into the background. This phenomenon was unexpected to the great degree in which it was observed. The pollen studies mentioned previously implied an advection by 850 mb winds of 20 micron particles of density one for a distance of over 300 km (section 1.6). This expectation of observing plumes into the proximate areas by ground-based stations was not at all realized due to high background levels and non-steady state meteorology. Proximate stations are affected by urban emission but cannot as yet be fully quantified.

We are then led to the question, what are the background levels? The data shown here can put an upper limit of < 20 ng/m^3 on copper, of < 5 ng/m^3 on cadmium, and < 0.05 ng/m^3 on bismuth, but lead is more elusive since it is more widely distributed and is measurable at all stations under all conditions. The lowest value of lead observed was 100 ng/m^3. Since the rural levels are so high, one is not able to trace the cities' contributions much further than the city limits. And, there are other trace metals equally as well distributed.

Sensitivity is a limitation in the NASN studies. A once-a-month sample in questionable locations leads to a questionable result, considering that one station represents several hundred kilometers and some of the values reported above are barely above the sensitivity of the instruments used. But, the data in the urban areas do seem to show a real persistence over the six days studied. Thus it seems that the random sampling is possibly sufficient if the sampler is properly placed. We would recommend more long-term, low-volume sampling with more sensitive techniques for receptor-oriented monitoring.

Finally, it would seem that a study of this type should be made in all suspected pollution regions at least once every decade as industrial activities may change significantly in even shorter times. The information is valuable to future interim studies both for abatement and scientific purposes. These initial results have been of use to other researchers in location and selection of sampler sites, as well as to the local abatement agencies in their abatement activities.

APPENDIX I

SUPPLEMENTAL TRACE METAL DATA

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SUPPLEMENTAL TRACE METAL DATA

I.1 RESEARCH SHIP INLAND SEAS--MAY 20-23, 1968

During the week of 20 May to 23 May 1968, the Great Lakes Research Division research ship, Inland Seas, made a voyage from Grand Haven, Michigan, to Calumet Harbor at the Indiana-Illinois border at Chicago, returning the following day (21 May) to Grand Haven, and then voyaging from Grand Haven to the central part of the southern Lake Michigan basin for a 24 hour on-station examination of trace metals in aerosols and size distribution. Table I.1 represents the time intervals, coordinates, meteorological parameters and the concentrations of lead, cadmium, and copper during each of the intervals cited. The first coordinates given are the beginning coordinates, and the following coordinates in the column are the beginning coordinates of the next sample interval, and so forth. Intervals are adjacent within 30 minutes of each other except for the night samples in the port of Grand Haven.

The interesting results of this study are that lead seems very high in the Calumet Harbor but is an average of 1.5 $\mu g/m^3$ in the center lake station (the 24 hour station) for a surface wind sector of 270°. Cadmium seems to be higher than expected and may be due to contamination from the ship itself. The data does seem fairly consistent throughout all stations except in the Calumet region where the cadmium increases markedly. The

Table I.1 Inland Seas Data for 20-23 May 1968

Date	Time Start CST	Interval Min.	Termination Coordinates	Wind Direction °	Wind Speed Knots	Temp. °C	Weather	Cd ng/m^3	Pb ng/m^3	Cu ng/m^3	Starting Number
20	0726	114	43.1x86.4	300	8	5.4	low	350	2,700	790	1
	1006	333	42.9x86.6	300	6	6.9	cloud	132	407	132	2
	1558	74	41.9x87.3	070	3	9.7	cloud	52	8,100	190	3
	1726	393	Calumet	090	-	---	-----	214	4,600	2500	4
21	0003	135	Calumet	270	-	---	-----	157	16,600	560	5
	0223	217	Calumet	280	C	---	-----	28	10,600	610	6
	0631	241	Calumet	230	5	9.3	-----	66	660	180	7
	1044	238	42.3x87.0	230	6	9.2	-----	48	4,200	350	8
	1516	255	43.0x86.5	27	9	7.1	-----	39	850	440	9
22	0645	235	Gr. Haven	170	6	8.3	-----	102	1,240	320	10
	1046	250	42.5x87.0	180	7	10.0	Fog	41	2,900	120	11
	1508	908	42.5x87.0	140-090	6.7	8.5	L. rain	18	1,100	160	12
23	0655	202	42.5x87.0	090	8.8	9.5	-----	20	1,200	230	13

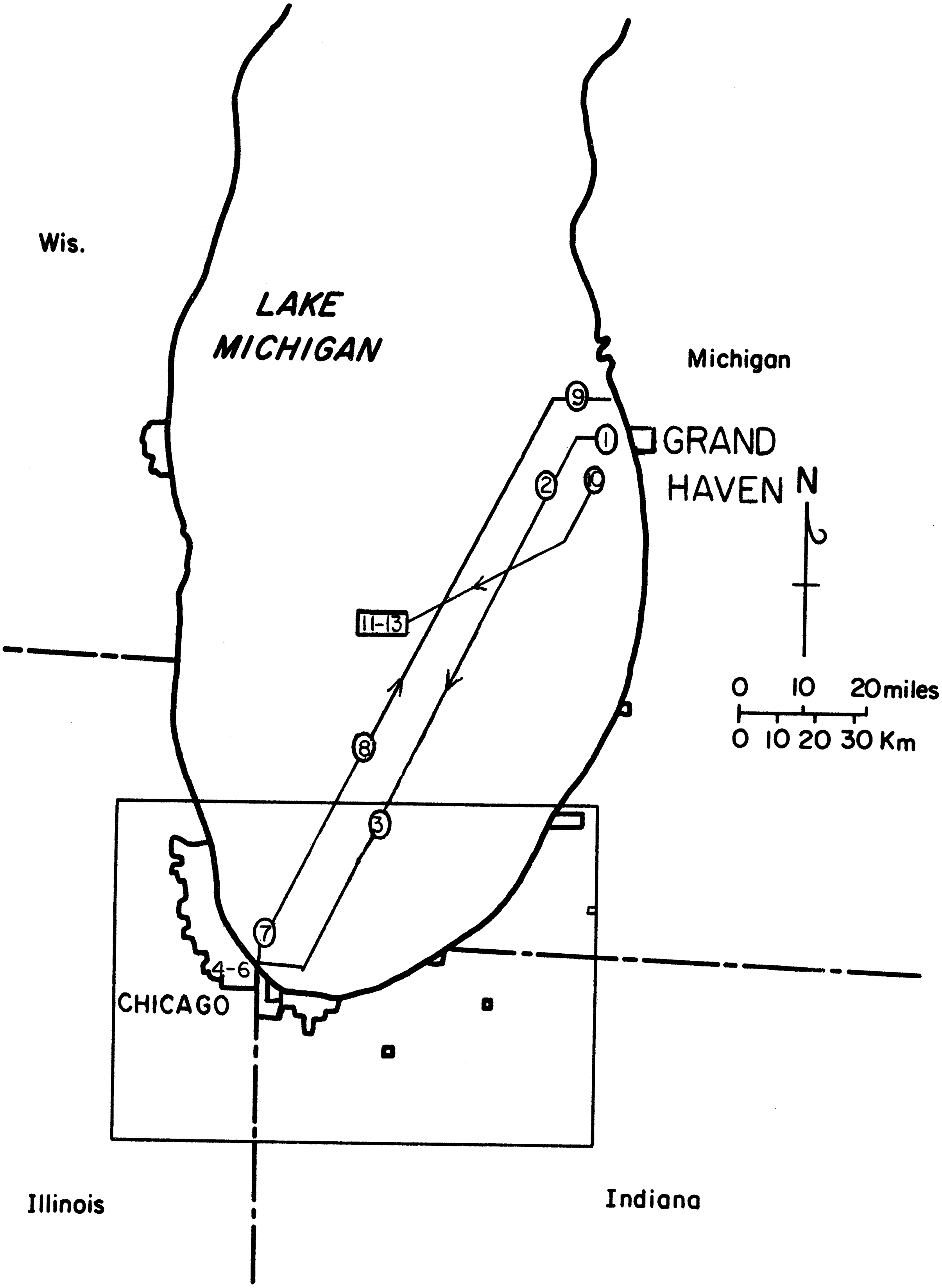

Figure I.1: Trajectory of research vessel Inland Seas, 20-23 May 1968.

levels of cadmium on the lake other than run 2 are below 0.1 μgm/m^3 as would be expected from the six day study, but Calumet and Grand Haven seemed to be above this value. The on-station values for cadmium are 20-40 ng/m^3. Copper also seems consistent except for the initial period in the Calumet Harbor when the wind shifted from the east, that is over East Chicago, Indiana, to Calumet, giving a single point anomalous high of 2.5 μgm/m^3. Another anomaly that exists shows up in run 8 where the low value for lead is 4.2 μgm/m^3 following a low value of 0.7 μgm/m^3. Either run 7 is in error for lead or the research ship went through a plume of lead aerosols at stations 8 to 9.

We would not say much more about this data in so much as this was a very preliminary attempt at grasping the values on a non-emission source area. All of these aerosols must have been advected from emission sources, be they either natural or human, or the vessel; thus, one can gain some idea of the background levels for the particulate air mass during the study days. It is interesting to note that the light rain did suppress the cadmium slightly, but not the other parameters. This decrease for cadmium is probably not significant due to the low signal. It also should be mentioned that the high volume samplers were not in shelters and sampled fallout as well as suspended aerosols, and the possibility of local contamination is always present. In conclusion, we can observe that the copper source in East Chicago is again validated by sample no. 4 and that lead values are increased for a sampling station located close to the ground, that is to say that the Inland Seas sampling station in Calumet Harbor was probably not more than 5 meters above water level and the Calumet Harbor is below the average street level and close to expressways. Thus the samples for lead should be higher than the above street level samples from the Hi-Vol stations in the six day study. The final suggestion is that more studies of this kind, with additional controls, be made to ascertain the fallout into the lake. Hi-Vols in conjunction with dust falls would give a great amount of additional information that our research group is now seeking.

I.2 MARIETTA, OHIO, 1969

Table I.2 presents the tabulation of a preliminary study in the mid Ohio Valley region of the Marietta, Ohio, region. There are large pollution sources in the area that are suspected for their rain suppression characteristics.

It was desired to gain some insight into the trace metals in the aerosols. The three metals were analyzed by Anodic Stripping Voltammetry and showed no significant anomalies except that an additional background level is gained by observing the average values of each trace element presented. Lead is usually less than 1.0 $\mu gm/m^3$ and cadmium is less than 0.07 $\mu gm/m^3$ except at one point which is probably a result of contamination.

Table I.2 Hi-Vols Taken of Marietta, Ohio, Region, 1969

Interval	Date	Weather	Wind mph	Cd ng/m^3	Pb ng/m^3	Cu ng/m^3	Station
	Jan.						
08-08	18/19	L.rain		7	870	460	3
"	20	L.rain		31	830	150	"
"	23	-----		(330)	1100	190	"
"	26	Clear		66	2700	590	"
"	29	-----		14	500	230	"
"	31	-----		69	860	240	"
	Feb.						
08-20	2	-----		19	660	250	"
20-08	2/3	-----		14	760	110	"
12-12	16	-----		38	600	180	2
	March						
"	5	-----		21	810	90	"
"	14	-----		43	500	120	"
"	21	-----		6	760	70	"
"	28	-----		8	540	70	"
	April						
"	5	-----		128	460	130	"
Average				36	850	220	

I.3 MEXICO CITY

During a brief vacation in Mexico City, Mexico, in 1968, two samples were taken using a low volume sampler and a 1964 high volume sample was obtained from local authorities. These data are presented without reference to location as the exact location of the 1964 study is not yet known, and in the 1968 sample there was a building under construction close by and might have led to contamination of the sample. The night sample is probably the most representative (S2M8) and the 1964 sample is also very representative but of a different area within the city. If these values are correct, Mexico City should quickly institute a trace metal study to determine the source and the true levels of some of the toxic elements. We cannot validate this information so we will not comment much further except by corresponding with the local authorities and urging them to look into this matter more completely.

I.4 RAINFALL

During the logistics of the 1968 study three rain samples were taken. On the south side of Chicago near the lake, the second at the Gary-East Interchange on the Indiana Tollway approximately 200 yards from the expressway, and the third in a park adjacent to LaPorte, Indiana. Table I.4 is a listing of the concentrations of the three trace metals with respect to the concentration per 10 ml sample and the concentration in the total rain collected. Cadmium exhibits a high concentration in south Chicago diminishing through LaPorte. The outstanding result for lead is that the total amount per rain

Table I.3 Mexico City Hi-Vol, 1964, and Low Vol, 1968

Date	Sample	Cd ng/m^3	Pb ng/m^3	Cu ng/m^3	Code
-- 1964	Hi-Vol 24 hrs.	23	6800	1030	S1M4
Aug 1968	LowVol Intermittent	2400 2400	30,400 21,800 28,000	11500 7700	S1M8
Aug 1968	Night LowVol	2700	4,000	M	S2M8

Table I.4 Rainfall, June 26, 1968

	ng/10 ml			ng/total rain		
	Cd	Pb	Cu	Cd	Pb	Cu
south Chicago	1932	453	437	77300	18200	17500
Gary-East	430	245	387	30100	17200	27100
LaPorte	246	209	109	20900	17800	9300

is the same for each occurrence within 5%. Copper, however, shows a high concentration at the Gary-East Interchange. These results are as expected, except for lead. The copper high in Gary-East is probably due to the advection of copper into a storm in East Chicago, Indiana, washing out by impaction and uptake by raindrops. The consistency of lead per storm is extremely interesting and is being further investigated by myself and A. N. Dingle of the Department of Meteorology at the University of Michigan.

I.5 FALLOUT

It is not the purpose of this work to investigate the complete cycle of aerosols in this area but to examine the concept of area-wide sampling and to test the reliability of the NASN stations for trace metals. In order to try to give some idea of the fallout, a suite of five samples of dust fall was analyzed for stations 6-10 in East Chicago, Indiana. These data are tabulated in Table I.5 and plotted in Figures I.3 and I.4. In addition, soil samples and grass roots were analyzed close to station 9. The local abatement personnel have related that the month of August, 1969, presented here was an exceptionally low dust fall month and can be assumed to be close to the lower limit. The data were obtained by perchloric acid digestion and analyzed by anodic stripping voltammetry (ASV).

Using this data we can calculate deposition rates of 50 ng/m^2-min and 30 ng/m^2-min for copper and lead respectively. If we use our average concentrations we can approximate

Table I.5 Dust Fall for August 1969, mg/m^2-month

	STATION						
	6	7	8	9	10	soil(9)	grass roots(9)
Pb							
Insoluble	5.2	29.	14.	16.	5.6		
Soluble	0.94	0.36	0.34	0.26	0.68		
Total	6.1	29.	14.	16.	6.3	0.7mg/gm	0.4mg/gm
%	2.6	7.2	7.6	6.8	3.5		
Cu							
Insoluble	0.76	4.1	3.7	2.0	0.31		
Soluble	0.24	0.20	0.21	0.10	0.16		
Total	1.0	4.3	3.9	2.1	0.47	0.16mg/gm	0.58mg/gm
%	0.43	1.1	2.1	0.89	0.26		

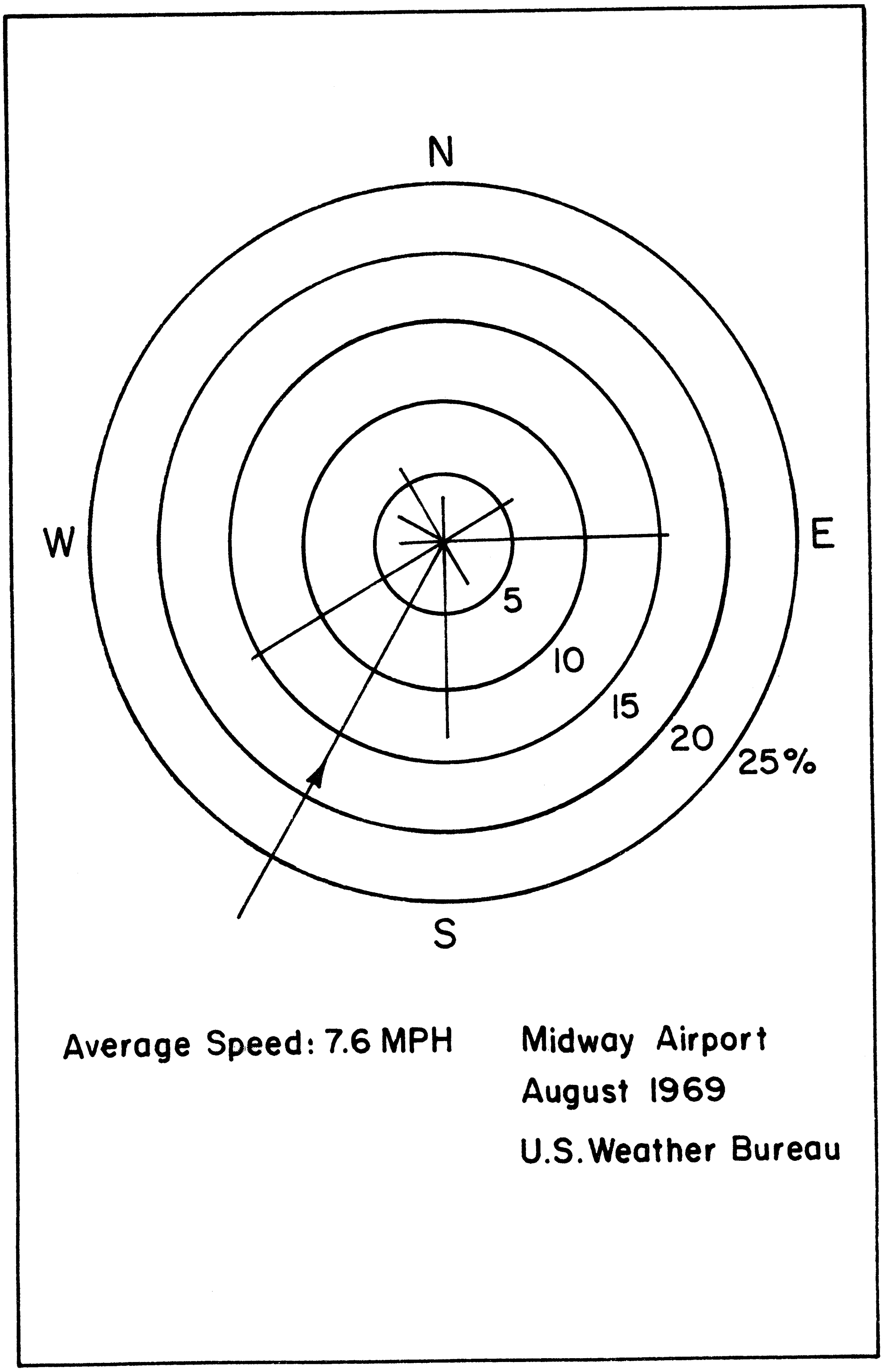

Figure I.2: Wind rose for August 1969.

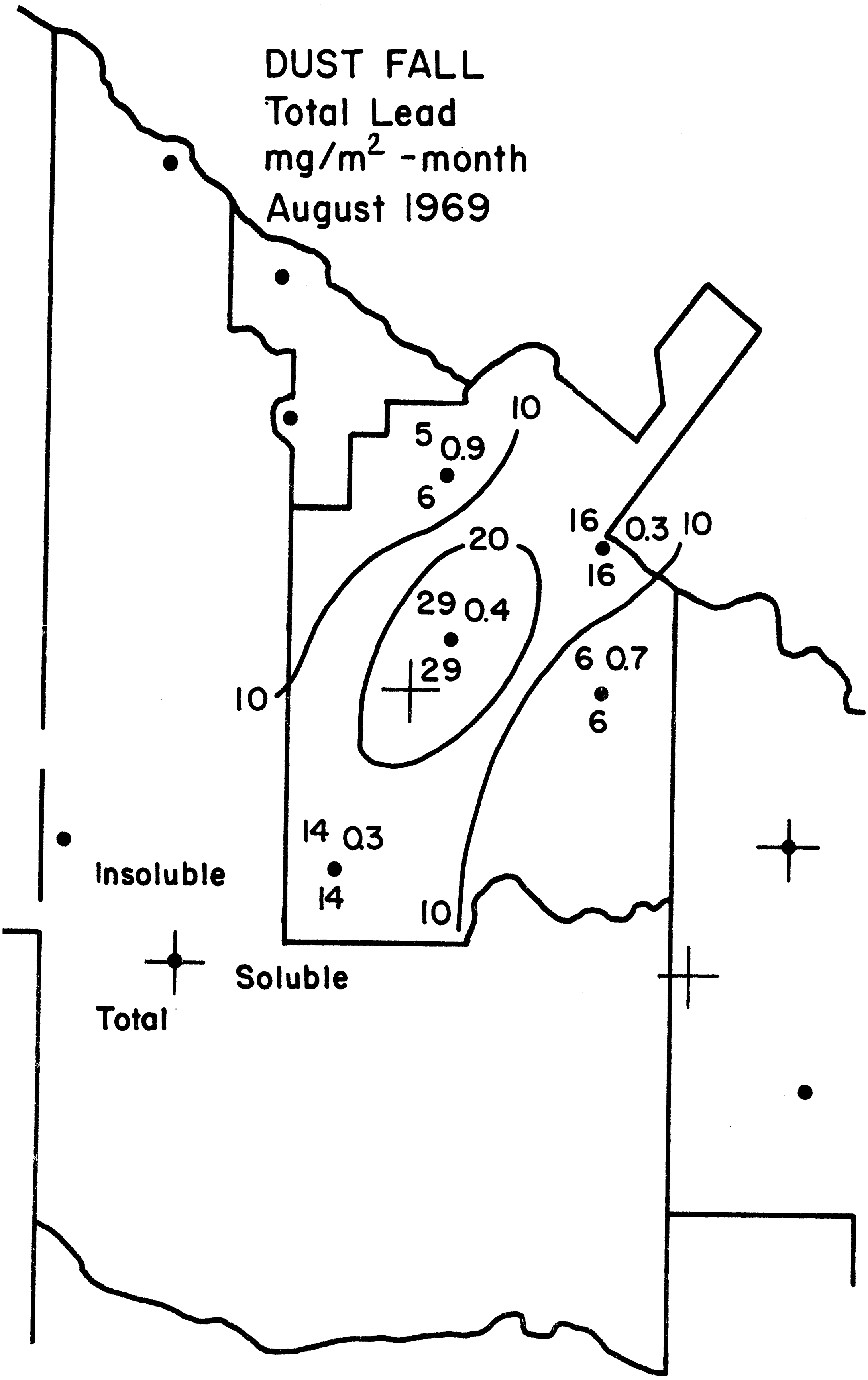

Figure I.3: Lead fraction of total dust fall.

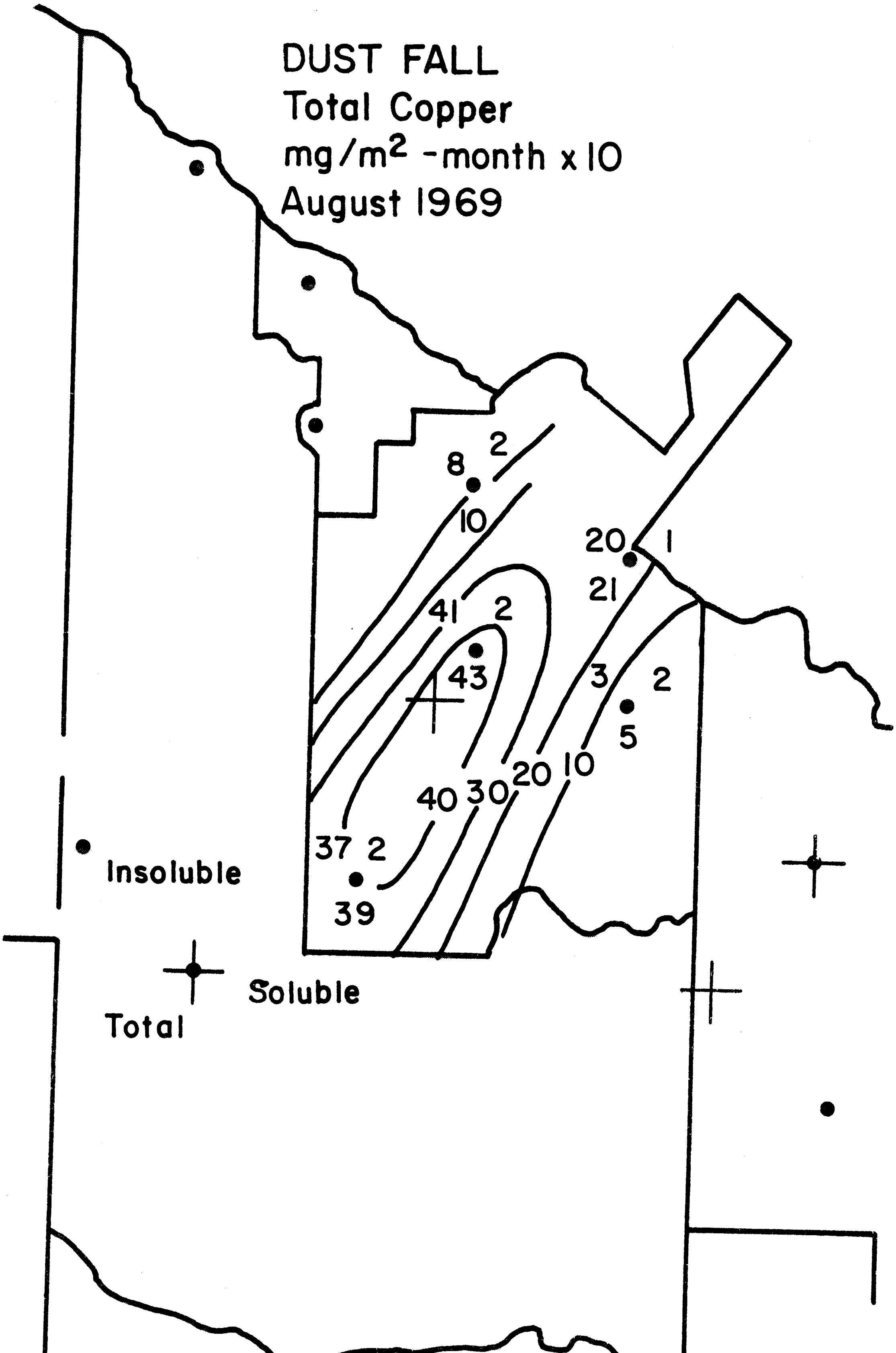

Figure I.4: Copper fraction of total dust fall.

a lower limit value of the fall velocity of 0.2 m/min and 0.3 m/min for copper and lead. Since the dust fall was said to be low for this period the results are not too far from the generally accepted average of 1.0 m/min. Thus the particles seem to be in the submicron to micron range. Future work by Nifong (1970) will further elucidate the size distributions in this area.

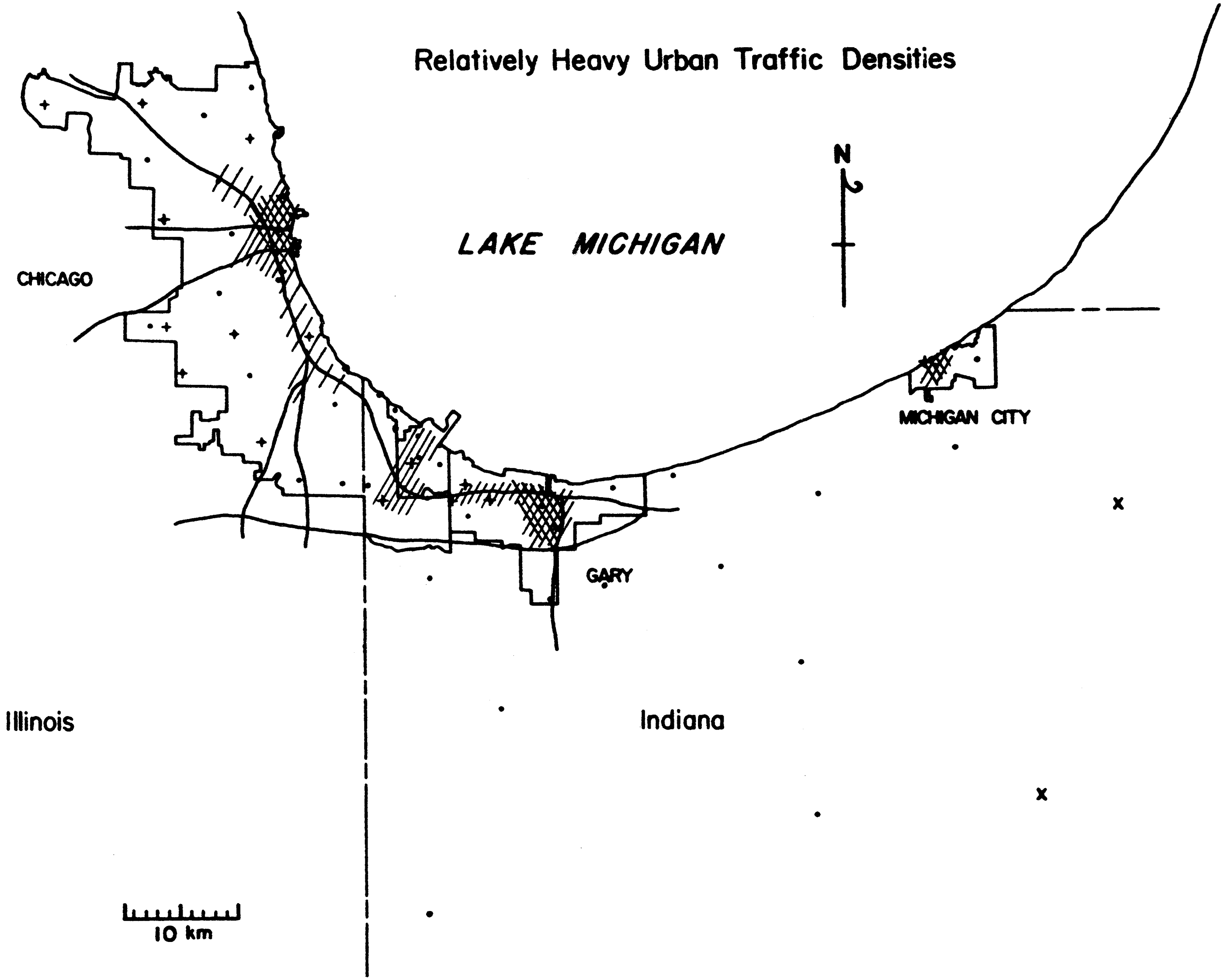

Figure I.5: Estimation of traffic densities.

APPENDIX II

TIME VARIATIONS OF LEAD, COPPER, AND CADMIUM CONCENTRATIONS IN AEROSOLS IN ANN ARBOR, MICHIGAN

American Meteorological Society
49th Annual Convention, January 20-23, 1969

APPENDIX II

TIME VARIATIONS OF LEAD, COPPER, AND CADMIUM CONCENTRATIONS IN AEROSOLS IN ANN ARBOR, MICHIGAN*

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II.1 ABSTRACT

The atmosphere in Ann Arbor (50 km west of Detroit) was sampled for aerosols for two-hour periods over a 42-hour interval Friday to Sunday, April 26-28, 1968, using a modified seven-stage Andersen cascade impactor and a glass backup filter. The eight particle size fractions from each sampling were analyzed separately for lead, copper, and cadmium by means of anodic stripping voltammetry (ASV) with the composite mercury graphite electrode. Average particle size distributions were similar for the three elements over $0.1 \leq r \leq 10\ \mu$, the radius range covered by the impactor stages which sort particles into factor of 2 radius intervals. Pb, however, showed a significantly greater proportion of its total concentration in particles caught by the filter ($r \leq 0.1\ \mu$) than did Cu or Cd. Detailed differences in size distribution from sample to sample for Cu and Cd were similar and differed from those for

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Pb. Substantial parallel time variations in total concentrations were seen in the ranges $6000 > Pb > 600$ ng/m^3, $1000 > Cu > 100$ ng/m^3, and $300 > Cd > 100$ ng/m^3. Two prominent maxima were observed at 0200-2400 EST, April 27, and suggested a wind shift from north to east. The results imply that some of the Cu and Cd, and much of the Pb at the maximum times came from the Detroit sector by easterly winds and that a two-hour sampling period is adequate for correlating changes in the environment with mesoscale meteorological parameters.

II.2 INTRODUCTION

The analysis of urban atmospheres for lead and other trace metals has been carried out for many years, but because of the small quantities involved the majority of the work has been done on total concentrations of the elements studied. Ludwig and Robinson (1968), Lee, Patterson and Wagman (1967), and Wagman, Lee and Axt (1967) have obtained information on the size distribution of a few trace elements and sulfates. All of these samples, however, were obtained for periods of at least six hours, and most often for 24 hours or more. A short sampling time is important in order to correlate the time variation of aerosol concentrations and size distribution with mesoscale meteorological phenomena. Also, definition of the extent of variation of the quantity of an element is of interest from the standpoint of problems involving nonlinear effects with concentration, such as the exposure and uptake in an urban population, removal and chemical reactions of aerosol particles, or changes in the size distribution.

II.3 SAMPLE COLLECTION AND ANALYSIS

On Friday afternoon, April 26, 1968, a modified seven-stage Andersen cascade impactor with an inline backup glass filter was attached to a Gelman Air Sampling Kit placed on a platform on the roof of the East Engineering Building at the University of Michigan in Ann Arbor. The area is characterized by gently rolling terrain with little local manufacturing or power generating industry. Located 50 km east of Ann Arbor, the metropolitan area of Detroit shown in Figure II.1 covers an area of approximately 200 km^2. It has a population of 2,000,000 persons, is heavily industrialized, and has a large amount of automotive traffic.

The sampling was carried out at two-hour intervals and terminated on Sunday afternoon, April 28. Ambient meteorological data were obtained from instruments located in the immediate proximity of the sampler.

The samples were obtained on 4 mil thick polyethylene discs which had been precleaned by ultrasonic agitation in double distilled water, dried, and placed over the stainless steel Andersen impactor plates. One half of each polyethylene disc was placed in a quartz cell with 10 ml of 0.1 M NaCl which had been pre-purified over a mercury pool electrode and the sample removed from the disc by ultrasonic agitation. The sample was then analyzed on a multiple plating anodic stripping apparatus using a composite mercury graphite electrode. The cell, electrode, and apparatus have been previously described by Matson *et al*. (1965) and Matson and Roe (1967).

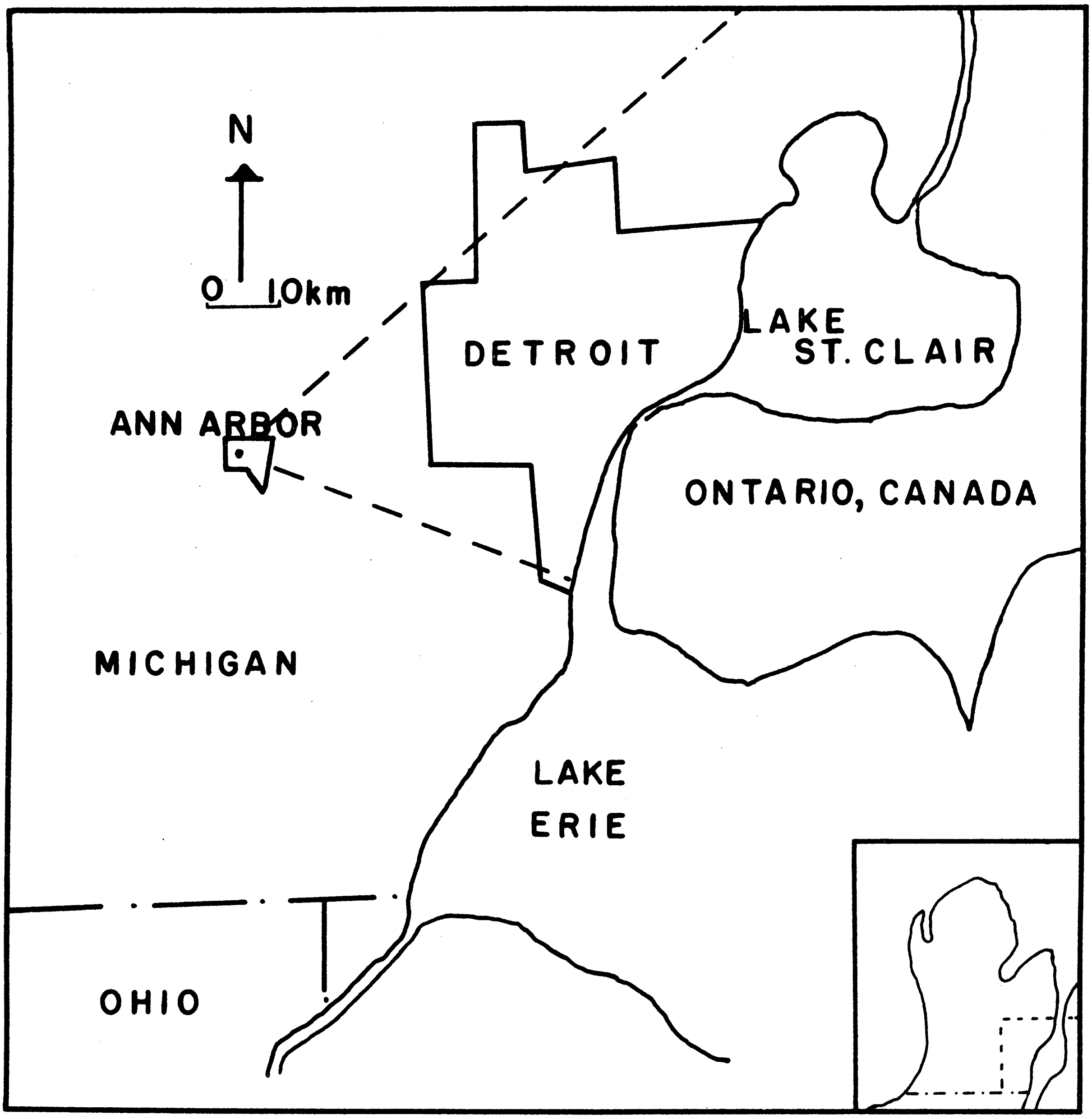

Figure II.1: Location of sampling area in relation to Detroit.

Successive ultrasonic agitations of the polyethylene disc with fresh solutions showed a removal efficiency of 90-97%. Runs on both halves of a polyethylene disc were within ±5% of their average at the sample size of 200 ng. The major errors in the data come at high concentrations from the measurement of volume passed through the impactor with the Gelman Air Sampling Kit (±10%) and at low values from the subtraction of the variable and system carry-over blanks from the procedure (e.g., Pb 144, Cd 38, Cu 42 ng/stage).

II.4 METEOROLOGY

The 24 hours preceding the beginning of the sampling period was under the influence of a low pressure system passing to the southeast through southern Ohio and Pennsylvania, west of the Appalachians. Light rain and high humidities with fog prevailed until the afternoon of Friday, April 26. At the beginning of the sampling period, the rain and fog had moved to the east and only light cirrostratus clouds remained. By morning of Saturday, April 27, a mesoscale high pressure area had moved into western Michigan and remained over the Michigan area throughout the sampling period. The tropospheric winds similarly decreased and remained moderate and out of the northwest. The air mass was of Continental Polar source region, and most of the residual aerosols would have been swept out of the air by the rain and fog leaving mostly recent and local material. The meteorological data and time intervals are listed in Table II.1 As seen in Figure II.2 the temperature reflects the absence of clouds and has a smooth diurnal trace.

Table II.1 Meteorological Data

Sample Number	Time EST	T Min.	Solar Ins.Ly.	Cloud Cover	Temp. T, °C	Dew Pt. Td, °C	Rel. Hum. %	Wind Speed m/s	Δ_v	Wind Dir.	Δ_θ
1	1900	111	25	2	6.7	+0.6	65	2	1	246	36
2	2206	107	0	0	6.1	+0.6	61	3	2	330	30
3	2405	104	0	0	5.0	-0.6	69	3	1	75	15
4	0159	110	0	0	4.4	-0.6	69	1	0	3	0
5	0400	110	10	0	2.8	-1.1	74	2	1	330	0
6	0602	118	160	0	3.9	+0.6	79	1	1	300	60
7	0825	85	430	0	8.3	+1.1	61	2	1	280	60
8	1002	108	515	1	11.7	-3.3	33	5	3	290	30
9	1201	110	625	1	13.3	-3.9	30	5	4	310	30
10	1400	109	550	2	14.4	-3.9	27	4	5	360	30
11	1600	109	280	1	14.4	-3.3	29	4	3	360	30
12	1759	117	60	0	13.3	-3.3	32	5	4	80	50
13	1959	110	0	0	7.8	-3.3	44	3	2	90	90
14	2157	113	0	0	6.1	-3.3	50	2	1	85	20
15	2357	113	0	0	5.6	-3.3	51	3	1	70	15
16	0156	112	0	0	5.0	-3.9	52	3	1	90	25
17	0355	115	0	0	4.4	-3.9	52	4	2	112	72
18	0600	110	110	0	6.7	-1.1	56	3	1	134	60
19	0759	113	400	0	10.6	-3.3	38	4	3	134	120
20	1001	136	550	0	13.3	-3.3	31	4	3	134	120
21	1223	121	570	0	14.4	-2.2	31	4	3	150	180

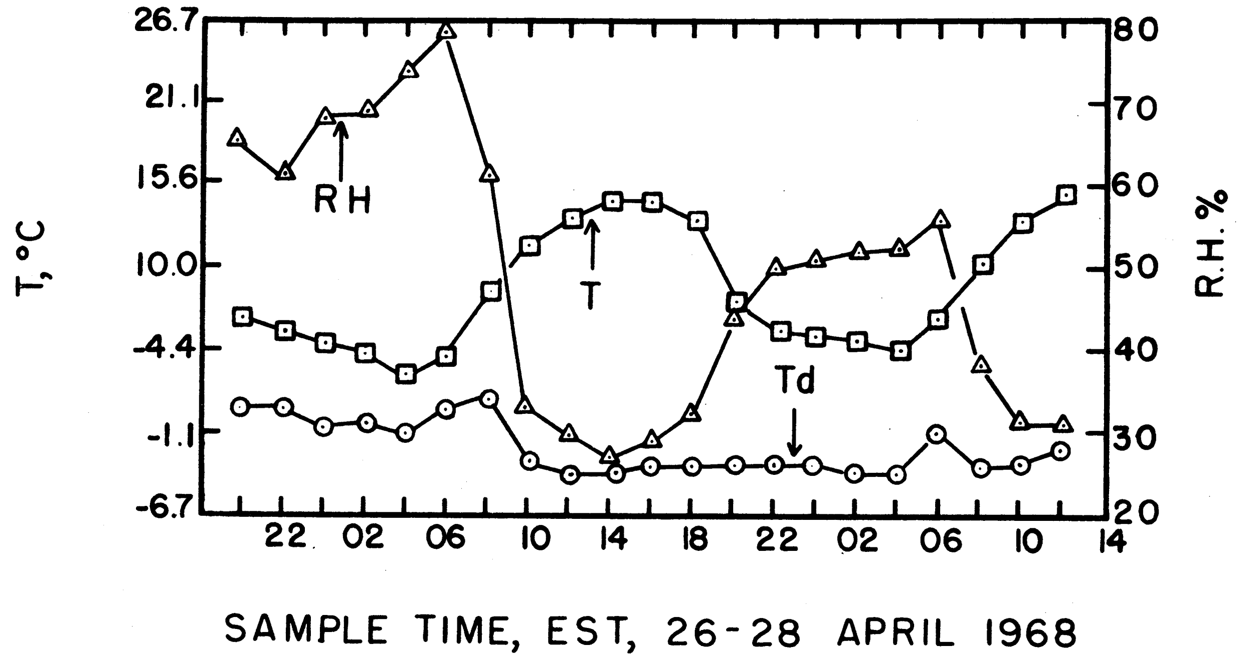

Figure II.2: T, RH, Td versus sample time.

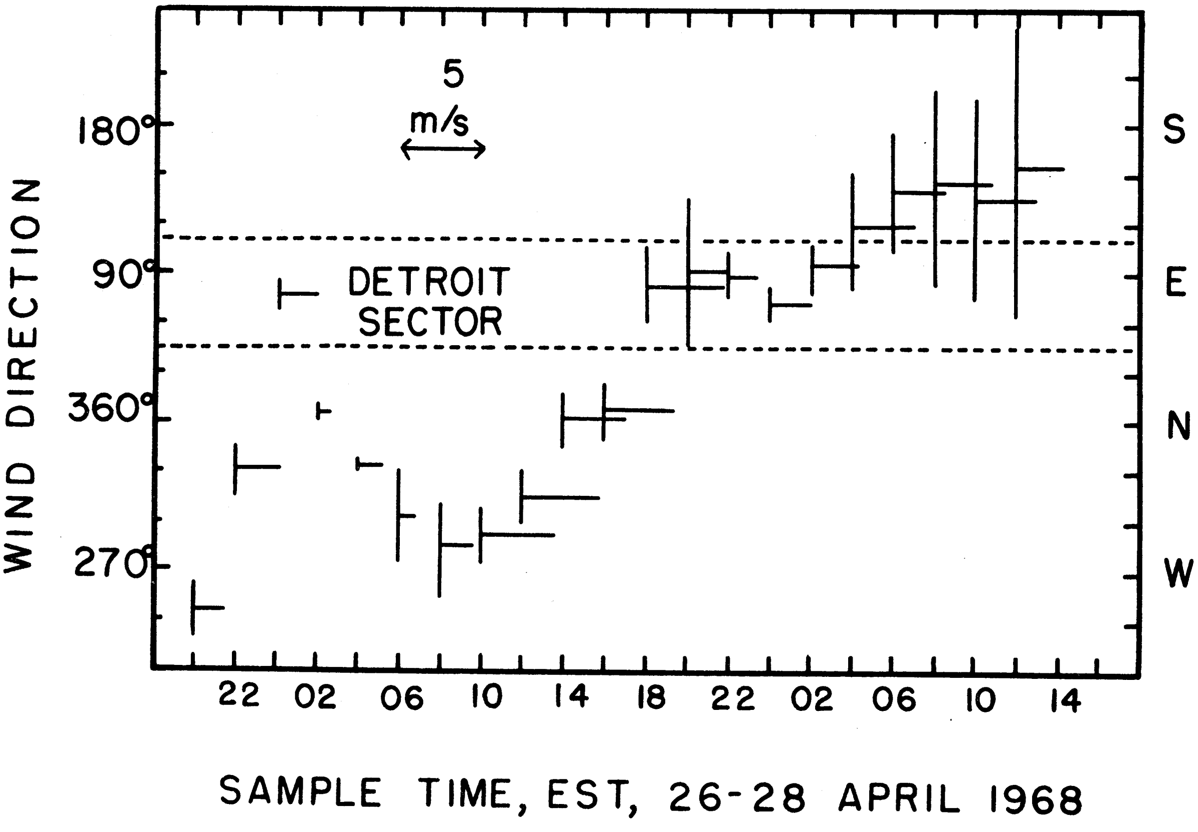

Figure II.3: Wind speed and direction versus sample time.

The dew point decreased slowly during the first day and remained constant during the second except for the slight perturbation each morning after the sunrise as the ground moisture was mixed to higher elevations by heating. This phenomenon is typical in areas dominated by an anticyclone. Since relative humidity is a function of the temperature and dew point, it also follows a diurnal variation inversely proportional to the temperature.

The winds were light and varied slowly through the two days. In Figure II.3 the average direction is depicted by the horizontal lines whose length represents the average wind speed in meters per second. The vertical line represents the beginning of the sample time and the variation in the direction of the wind. Again, the situation is typified by low velocities and variations in the nocturnal hours and higher velocities and variability during the hours of solar insolation. The combination of the direction and the degree of variability determine the direction of our source region, and the speed determines the distance.

Under these conditions we would expect no contribution due to large scale advection into the area. All variations should be due to diurnal meteorological changes and/or local changes in the source regions.

II.5 RESULTS AND DISCUSSION

Figures II.4 and II.5 and Tables II.2, II.3 and II.4 show the results for the variation of lead, copper, and cadmium during the period of sampling. Figure II.4 and

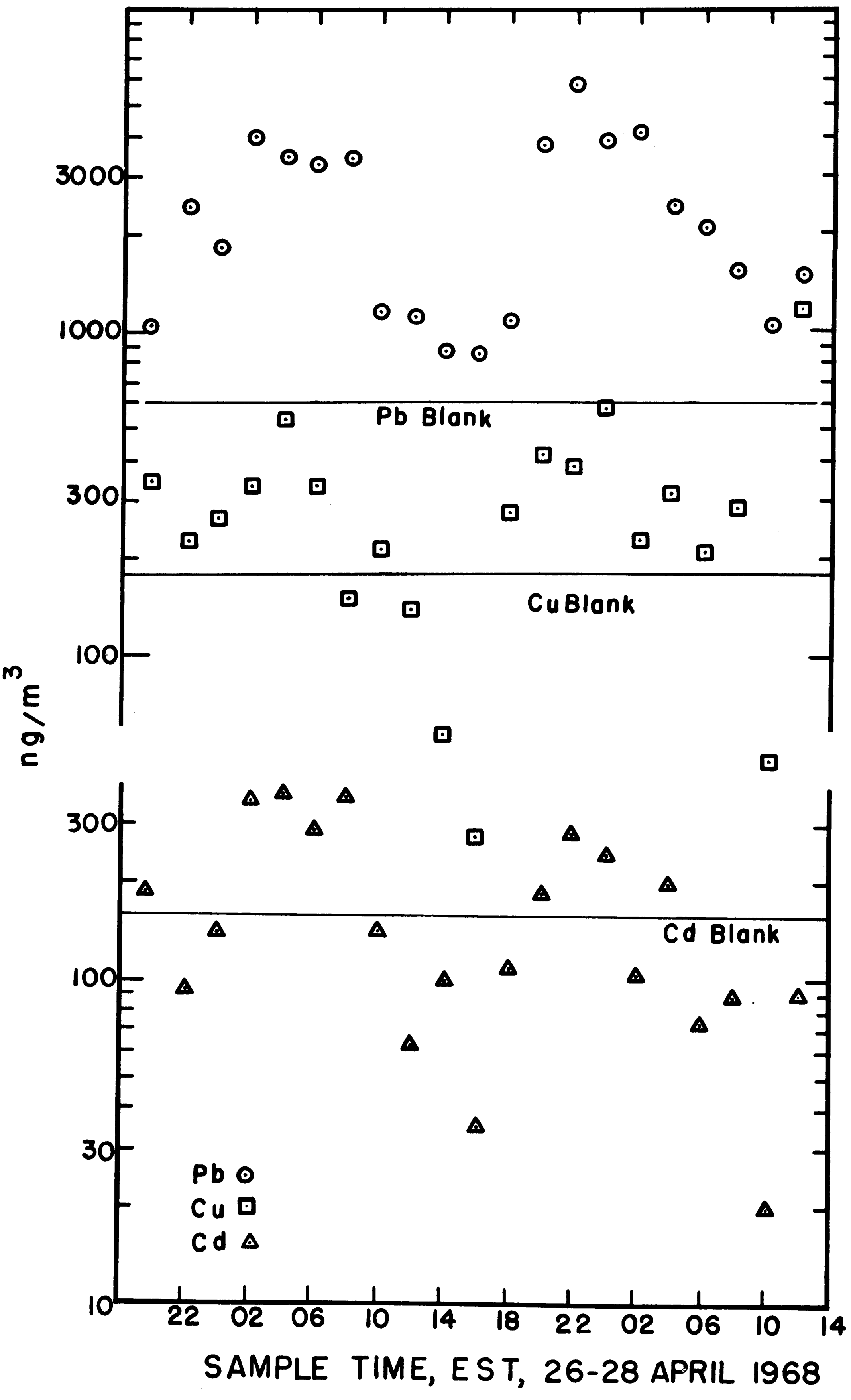

Figure II.4: Total concentrations of Pb, Cd and Cu vs. time.

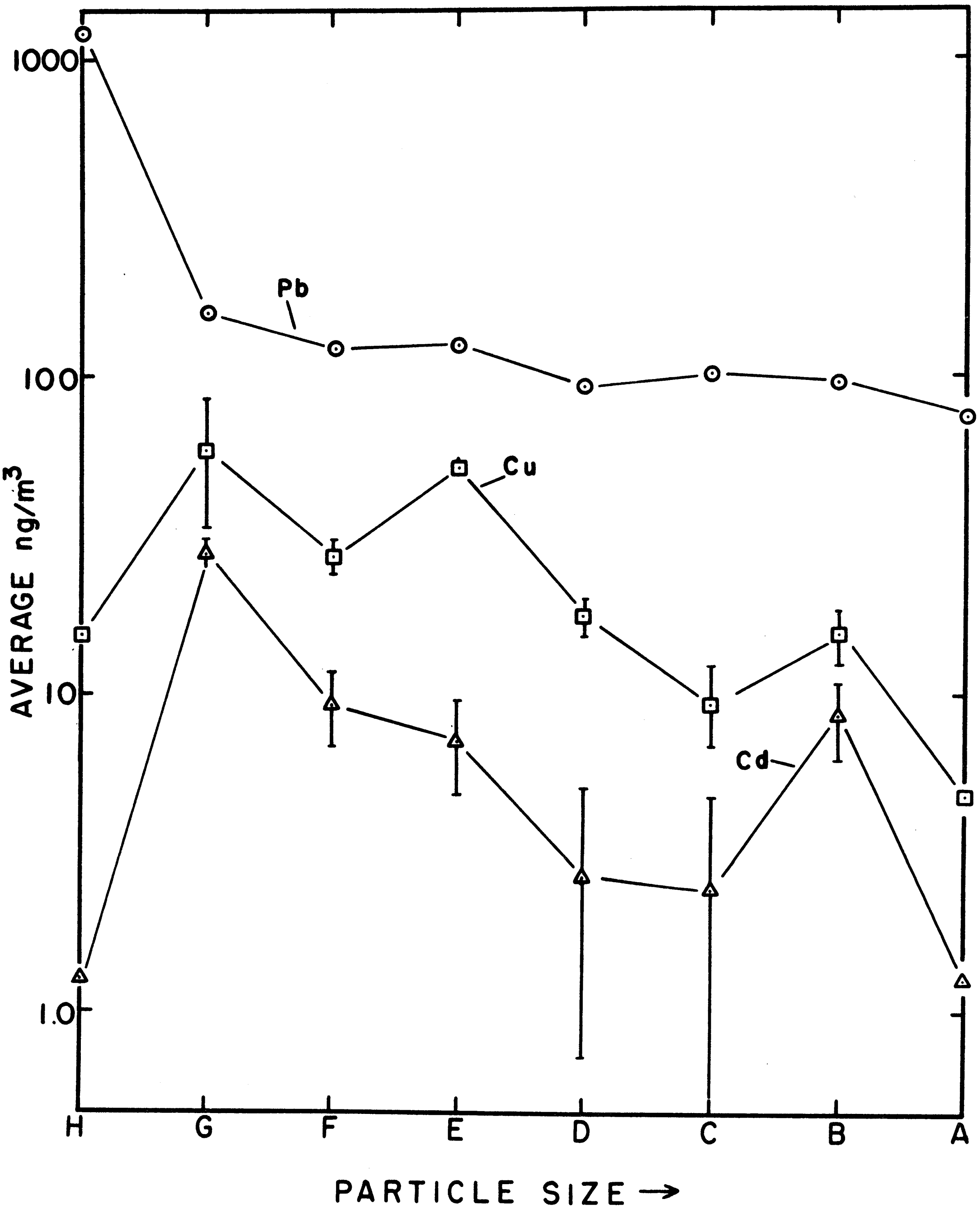

Figure II.5: Average particle size distributions of Pb, Cd, and Cu.

Table II.2: Average of 21 Runs Minus Blank Stages

ng/m^3

Stage	Cd	Pb	Cu
H	1.3	1230	15
G	28	159	59
F	9.1	122	27
E	7.0	126	52
D	2.7	92	18
C	2.4	100	9.3
B	8.6	95	15
A	1.3	74	4.8

Table II.3 Gross Sum of All Stages for Each Run

ng/m^3

Run	Cd	Pb	Cu
1	189	1030	347
2	93	2440	226
3	141	1830	270
4	358	4070	368
5	374	3410	539
6	292	3320	332
7	371	3400	152
8	142	1150	214
9	64	1120	140
10	100	864	57
11	35	850	28
12	110	1090	276
13	183	3760	418
14	281	5770	385
15	246	3920	575
16	101	4070	227
17	197	2410	312
18	73	2030	207
19	89	1530	288
20	20	1010	47
21	92	1480	1160

Table II.4 Lead on Individual Stages

ng/m^3

Run	Stage							
	A	B	C	D	E	F	G	H
1	108	50	67	141	100	50	25	154
2	78	139	104	50	173	160	82	1260
3	<50	80	<50	62	62	<50	76	1040
4	93	198	214	173	299	223	236	2240
5	105	109	168	143	168	219	227	1880
6	98	122	204	153	(145)	141	243	1850
7	180	218	174	109	104	71	180	1860
8	<50	<50	<50	<50	<50	<50	<50	618
9	<50	<50	<50	<50	<50	<50	<50	598
10	<50	<50	<50	<50	<50	<50	<50	690
11	<50	<50	<50	<50	<50	<50	<50	578
12	<50	<50	<50	<50	(<50)	<50	146	602
13	160	135	160	177	139	164	160	2280
14	181	164	284	189	460	310	566	3250
15	86	131	172	115	394	205	420	2020
16	157	220	240	228	256	261	290	2030
17	73	133	121	(125)	133	254	314	888
18	76	126	80	172	84	84	105	940
19	86	201	57	86	<50	57	82	542
20	65	<50	<50	<50	<50	<50	<50	449
21	<50	<50	<50	<50	103	80	103	734

Table II.3 represent the gross total concentrations without subtraction of blank for all stages of the individual samples. Figure II.5 and Table II.2 show the average concentration on each stage for the 21 runs with the blanks subtracted. Table II.4 shows the individual impactor stage values for lead. Because of the high blank to signal ratio of many of the runs for copper and cadmium, the tables for their individual stage values have not been included. The data indicate that there are wide variations within a 24 hour sample period. The variation of each of the elements studied is over a factor of ten within any 24 hour time period one chooses from the 42 hours represented. When initiating this experiment we expected to see some variations due to diurnal meteorological changes, but the large concentration differences in Figure II.4 seem to be best explained by non-diurnal wind variations. Maxima occurred near 0400 and again near 2200 on Saturday, April 27. The minima are approximately at 1600 Saturday and 1000 Sunday. Since the variations seem to result in maxima and minima that are not diurnal in their occurrence and since the diurnal meteorological parameters were classic and almost identical for the two days, it could be possible that the major factor in these variations is wind speed and direction. By inspection of the wind direction plotted in Figure II.3 and the total concentrations plotted in Figure II.4 one can see a definite coincidence with the occurrence of the wind direction coming from the Detroit sector as shown by the dashed lines. There is an expected phase lag of two to four hours.

One might also argue correctly that the concentration variations are caused by changes in the mixing depth and diffusion characteristics. It has been shown by Moses (1969) that under certain mixing conditions the variation in concentration can be over a factor of 1000. However, the conditions present at the time were not so extreme as to suggest that the large concentration differences found for each metal observed could be explained by simple changes in the mixing and diffusion regimes since lead must come from high concentrations of automobiles, i.e., the east sector. A much more extensive study would have been required to ascertain to what extent the changes in diffusion factor would control the concentration variations. As this experiment was a feasibility study the additional data was not gathered.

The total concentrations seem to follow each other closely except in the later runs where cadmium departs toward lower values. Another interesting departure comes at the first minimum at 1200 on Saturday where copper and cadmium continue to decline below the average blank while lead levels off to the value of about 500 ng/m^3. This implies that the lead is now coming from local sources or from the natural background during this minimum. One can argue that the variations are of local origin, but since lead is primarily from automobiles, and copper and cadmium are from other sources, either dependent or independent, it follows that the lead maximum comes from an area of large concentrations of autos, and there is no reason to suspect that the other elements do not advect from the same region.

It is also interesting to note from Table II.4 that in the samples taken during the minimum concentration, from 1000-1800 April 27 (samples 8 and 12), there is a much greater percentage of material in the smaller G and H stages than in samples 13-16 taken during the maximum concentration.

This could be interpreted as a result of the aerosols from the northwest sector being older or more like continental background than those from the east.

The average size distribution data is summarized in Figure II.5 and Table II.2. No attempt was made in this study to calibrate the Andersen impactor for the exact size of lead, copper or cadmium particles captured by the plates.

About 60% of the lead particles is below a 50% cutoff diameter of about 0.2 μ. This is in reasonable agreement with Robinson and Ludwig (1967) and substantiates the hypothesis that the lead is a product from a high temperature combustion source such as tetraethyl lead from automobile engines. The copper and cadmium tend to follow each other and show a slight preference for the middle range of particle size.

II.6 CONCLUSIONS

From an examination of the structure of the curves in Figures II.3 and II.4 it appears that a two hour sampling period is needed but adequate for experiments concerned with the diurnal and mesoscale meteorological effects on the concentration and size distribution of aerosols. From the wide variation in concentrations over a relatively short period of time it is apparent also that a great deal of caution must be used in interpreting the concentration of a trace element from a long period sample.

II.7 ACKNOWLEDGMENTS

The help of D. A. Gillette, R. H. Loucks, and K. Johnson on this project is gratefully acknowledged. The work was performed under Public Health Service Grant AP 00585 and NIH Air Pollution Traineeships.

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APPENDIX III

AREA-WIDE DISTRIBUTION OF LEAD, COPPER, AND CADMIUM IN AIR PARTICULATES FROM CHICAGO AND NORTHWEST INDIANA

APCA Paper No. 70-118, June 1970

AREA-WIDE DISTRIBUTION OF LEAD, COPPER, AND CADMIUM IN AIR PARTICULATES FROM CHICAGO AND NORTHWEST INDIANA

by
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To be presented at the Annual Meeting of the Air Pollution Control Association, St. Louis, Missouri, June 15-19, 1970.

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ABSTRACT

Published air pollution emissions inventories for the urbanized and industrialized area along the southwestern shore of Lake Michigan include few chemical analyses of particulates, and estimates of the elemental composition of airborne solids may be made only indirectly and compared with NASN analyses from a few locations. As a first attempt to examine the area-wide distribution of specific chemical elements in this region, lead, copper, cadmium, and bismuth were determined in 24-hour average samples collected on glass fiber filters at 50 stations throughout the region. Samples from most of the 50 stations were obtained from local air pollution control organizations for 6 different days from May to August 1968 and were analyzed electrochemically by highly sensitive anodic stripping voltammetry (ASV). Throughout the area the small variation of lead, generally a few micrograms per cubic meter of air, did not exceed that expected from the distribution of automobiles, the major source. Cadmium was generally 200 times lower without marked local variations and was close to the expected concentration if coal combustion is the major source. Copper was generally 20 times lower than lead throughout Chicago as expected if coal combustion is the major source of copper. However, certain stations in the northwest Indiana area showed reproducible anomalies where copper was 100 times greater than in Chicago and several times greater than lead at the same stations. The source of this anomalous copper has not been determined.

I. Introduction

Until recently area-wide air pollution surveys of suspended particulate have commonly been made without determination of elemental composition, primarily because of increased cost of chemical analysis over that of simply measuring weight of total particulate collected on a filter. However, as the present work has found, geographic variability in the atmospheric concentrations of certain elements composing the particulate may exceed that of total suspended particulate in an urban or industrial area, and detailed chemical data may be necessary to evaluate public health hazards or to locate sources and estimate their source strengths. We have carried out chemical analyses by anodic stripping voltammetry (ASV) of particulate sampled on glass fiber filters by several local control agencies in the Chicago-Northwest Indiana region for 6 24-hour periods during 1968: May 21-22, June 6 and 20, July 9, August 8 and 29. Data for Pb, Cd, and Cu are presented as well as data for Bi on the first day (May 21 for Chicago and May 22 for Indiana).

One of the most extensive area-wide surveys was carried out in Nashville, Tennessee, (Zeidberg et al., 1961) utilizing 119 sampling stations distributed in and around the city. The parameters measured included spot tapes, total particulate, and sulfur dioxide, but no trace element analyses were reported. One of the first trace metal studies was by Tabor and Warner (1958) where 17 metals in 28 cities were determined, although none of the sampling sites were adjacent to each other and few were simultaneous. More recently Lee and Jervis (1968) and Brar, Nelson et al. (1970) have determined by neutron activation analysis several trace metals in atmospheric particulate from Toronto, Canada, and Chicago, Illinois, respectively. The latter study reported concentrations of 21 metals in 22 samples taken simultaneously over a 24-hour period in April, 1968. Significant variations in concentrations were found, presumably reflecting variability in the distribution of industrial sources over the city. No data for Northwest Indiana were reported, and the relevance of meteorological conditions to the concentration patterns could not be determined from this one-day study. Kneip et al. (1970) have just published a trace metal study of New York with results consistent with ours in the present investigation.

II. Experimental

In the present work we present data for Pb, Cd, Cu, and Bi in aerosol particles from the Chicago and Northwest Indiana regions. This was a cooperative effort mainly with the City of Chicago and the Northwest Indiana Air Resource Management Group, consisting of Hammond, East Chicago, Whiting, Gary, Michigan City, and Lake County, with Porter County and Valparaiso University also participating. From these groups we obtained data for SO_2 and suspended particulate which we quote here as well as the samples which we analyzed in our laboratory for trace metals. Figure 1 shows the station designations in the area under study.

The six sampling days selected, all Tuesdays or Thursdays, give the greatest degree of simultaneity possible over the several jurisdictions involved. All samples were collected on standard 20 x 25 cm (8 x 10 in) glass fiber filter paper, used routinely for suspended particulate analysis. After each filter paper was weighed it was folded and placed in envelopes by the local agencies and stored in a filing cabinet until taken to our laboratory at the University of Michigan.

Our procedure consisted of the following steps: A 13 cm^2 (2 in^2) sample was cut as 2 equal-sized squares from the folded filter paper, and then slightly shredded and inserted into a standard 25 ml narrow neck volumetric flask. The organics were dissolved by digesting in 4 ml of perchloric acid heated to 300°C for approximately 1/2 hour. The samples were then diluted to 25 ml with water and allowed to sit for one to two days before analysis. Equivalent portions of blank filters obtained with the samples were treated in the same manner, although we found no evidence of significant contamination by the glass fiber for the elements measured.

The ASV technique, an electrochemical method akin to polarography, consists of electrodeposition of the trace elements from solution onto an electrode and then stripping by reversing the potential in a gradual sweep. The current caused by each element in turn re-entering the solution is recorded by a moving chart recorder, and the total charge collected, a measure of the element, is calculated by measurement of height or area of the current-voltage peaks characteristic for each element. Matson (1968) has given a description of the electrode used consisting of a thin Hg film coating a paraffin-impregnated graphite rod, and the construction of the electrochemical cell and associated electronics. In general, the technique is sensitive to nanogram amounts of metals which form amalgams and is well suited to air pollution investigations.

An aliquot of each 25 ml sample solution, representing about $0.3m^3$ of air, was added to a vial of 10 ml pre-treated solution and subjected to ASV analysis. In order to facilitate mass production of analyses a routine for handling samples, blanks, and standards in a cumulative fashion was devised and is described in detail by Harrison (1970). To alleviate carryover from one sample to another each electrode system and vial were washed thoroughly and then an aliquot of blank plus a standard spike was added and run. The subsequent stripping was the sample itself with the former response subtracted from the sample run, thus eliminating contamination in the vial and by carryover from the previous analysis. Analytical control was achieved by running different cells at different times for the same filter paper and by using aliquots from various regions in the filter paper in replicate determinations. Due to the response characteristics of the apparatus the errors are variable according to the response to blank ratio. Since the ASV technique is being given its first large scale test in an air pollution survey application by this work, we regard the relative concentration variations over the network to be of greater significance, and absolute concentrations for individual samples may be in error by as much as a factor of 2.

III. Results

Tables I through VI represent the results for the six days of lead, cadmium, copper, and bismuth by our work and of sulfur dioxide and suspended particulate data supplied to us by the local control agencies.

Concentrations are given as ng/m^3 of air sampled, the dashed lines (--) signify no sample was taken, the asterisks (*) signifiy weak signals near blank level, and M indicates data missing for various reasons.

All data have been plotted on maps and are given by Harrison (1970). Since a great deal of similarity is found among the six days of the study, in spite of differences in winds, we have selected only one of the days for plotting here. Thursday, June 6 is the day with the least variable wind direction, and Figure 2 shows the wind roses for four meteorological stations as lines in the direction toward which the wind was blowing for the number of hours indicated with lengths proportional to wind speed. C (calm) implies <1.5 m/sec winds. Lead in Figure 3 shows a mean concentration of 1-2 μg/m^3 and follows the average traffic density with no obvious strong local sources. Cadmium in Figure 4 has a mean value near 10 ng/m^3 and does not vary markedly with location although the variability is somewhat greater than for lead. Copper, in Figure 5 shows a mean value near 100 ng/m^3 over Chicago but has an anomalous "hot spot" in East Chicago, Indiana, where concentrations approach 100 times greater values. In Figure 6 isopleths of the region show the systematic decrease in concentration with increasing distance from an apparently localized source region. Total suspended particulate, Figure 7, does not reveal a maximum in this region but, like lead, seems to have a broad distribution with no obvious localized source. Figure 8 presents SO_2 concentrations with a pattern apparently unrelated to the particulate data. All six days investigated show essentially the same location of a pronounced copper maximum and qualitatively similar behavior for the other variables illustrated in Figures 3-7. Bismuth data, obtained only for May 21-22, show a low mean value near 1 ng/m^3.

IV. Discussion

It is seen from the data that a large amount of scatter is present even in the broadly distributed suspended particulate and lead values. Table VII summarizes the weighted average wind direction, the total range of wind direction variability, mean speed and variability, temperature, rainfall, and relative humidity for the six sampling days. Table VIII gives the averages of the parameters broken into two groups of Chicago and Northwest Indiana, with Indiana copper values for stations 1-11 and 12-27 listed separately because of the large anomaly in East Chicago. Meteorological effects do not appear to be important in this study in affecting the observed patterns of concentration variation. However, except for July 9, all days were influenced by old air masses and variable wind directions. A lake breeze was observed on August 29 but the 24 hour time gate does not permit an examination of this effect on trace metals. Thus, meteorology is still an unknown effect except for a bulk transport mechanism of pollutants.

The complexity of the study area is further seen in Table IX giving the average values of ratios for each day separately for the Chicago and Indiana areas. The values of the ratios do not show large differences between the Indiana and the Illinois regions except for the large copper anomalies in Indiana. The mean Cu/Pb ratio and mean % Cu/S.P. are weighted strongly to Cu anomaly stations and show the large difference between Indiana and Chicago. Cd/Pb, % Cd/S.P., and % Pb/S.P. do not show this difference as no large anomalies of Cd, Pb, or S.P. are found. The mean of the Cd/Cu ratios is weighted strongly to the low Cu stations in Indiana and shows a similarity to the Chicago mean as expected. Thus, the mean Cd/Cu ratio for all data is 0.11 and for the Chicago region is 0.12 for all 6 days. Correlation coefficients for all pairs and data points have been calculated (Harrison, 1970) but owing to relatively large random errors for individual analyses are not as informative as the averages.

Elemental abundance patterns in an area-wide survey are useful in locating sources and may aid in making estimates of source strengths. We suggest from this study that Pb, Cd, and Cu over most of the Chicago and Northwest Indiana region come from area sources, but, in addition, Cu has a strong source or sources near stations 8 or 9 in Indiana. The source is persistent since the anomaly is seen on all six days of the survey, and tightness of the isopleths in Figure 6 and other days implies a rather short atmospheric residence time and travel distance, seemingly unaffected by meteorological differences among the six days. Which urban or industrial activity is the actual source of this copper component may be determined by further investigation. We may ask whether conventional area sources of air pollution are adequate to account for Pb, Cd, and Cu outside the anomalous region. Winchester and Nifong (1969) attempted to inventory some 30 individual trace elements of the Chicago-Northwest Indiana region from published information about fuel combustion and the steel and cement industries. Although only approximate, these estimates may provide a basis for comparison of our results. Table X shows a summary of the data used to make these estimates, considering fuels to be the only important area for Pb, Cd, and Cu sources. These data lead us to expect ratios of elements coming from area fuel sources to be Cd/Cu$\sim$0.1, Cd/Pb $\sim$0.006, Cu/Pb$\sim$0.06. Comparison of Table IX shows approximate agreement of the observed means with these ratios, and it appears to be unnecessary at this time to invoke any other sources to account for these elements outside the Cu anomaly region. However, we consider it highly desirable to refine this comparison by use of improved data on the composition of particulate emissions when they should become available.

Finally table XI is a comparison of our 6 day study with the National Air Sampling Network (NASN, 1966) stations in the area for 1963. Since our station 2 at or near the NASN station was available 5 of the 6 sampling days, we single this out especially for comparison. Cadmium falls within the variability presented by the NASN data, as does bismuth. Lead and copper are both higher than the NASN data, a disagreement which we cannot explain adequately at this time. Kneip et al. (1970) also find lead values in New York higher than NASN values and suggest that NASN determinations are erroneously low. We should point out that the NASN station is not located in the region of the anomalous copper and therefore leads to lower concentrations of Cu than we have found on the average in Northwest Indiana. In this study we have seen that area-wide studies can reveal (1) the general level of exposure of various pollutants, (2) previously unknown contaminants and sources, and (3) better locations for the placement of routine monitoring stations. Further studies of this type should be conducted under forecast meteorological conditions to gain knowledge of the mesoscale effects. The preliminary data suggest that the plumes diffuse rapidly from such areas and are lost in the proximate or non urban background levels.

ACKNOWLEDGEMENTS. Cooperation of air pollution control agencies in Chicago and Northwest Indiana in providing samples for analysis and the Thesis Parts Program at Argonne National Laboratory are gratefully acknowledged. This work was supported in part by the U.S. Public Health Service through grant AP-00585 and through an Air Pollution Traineeship award to one of us (P.R.H.).

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Figure 1

Air Sampling Locations

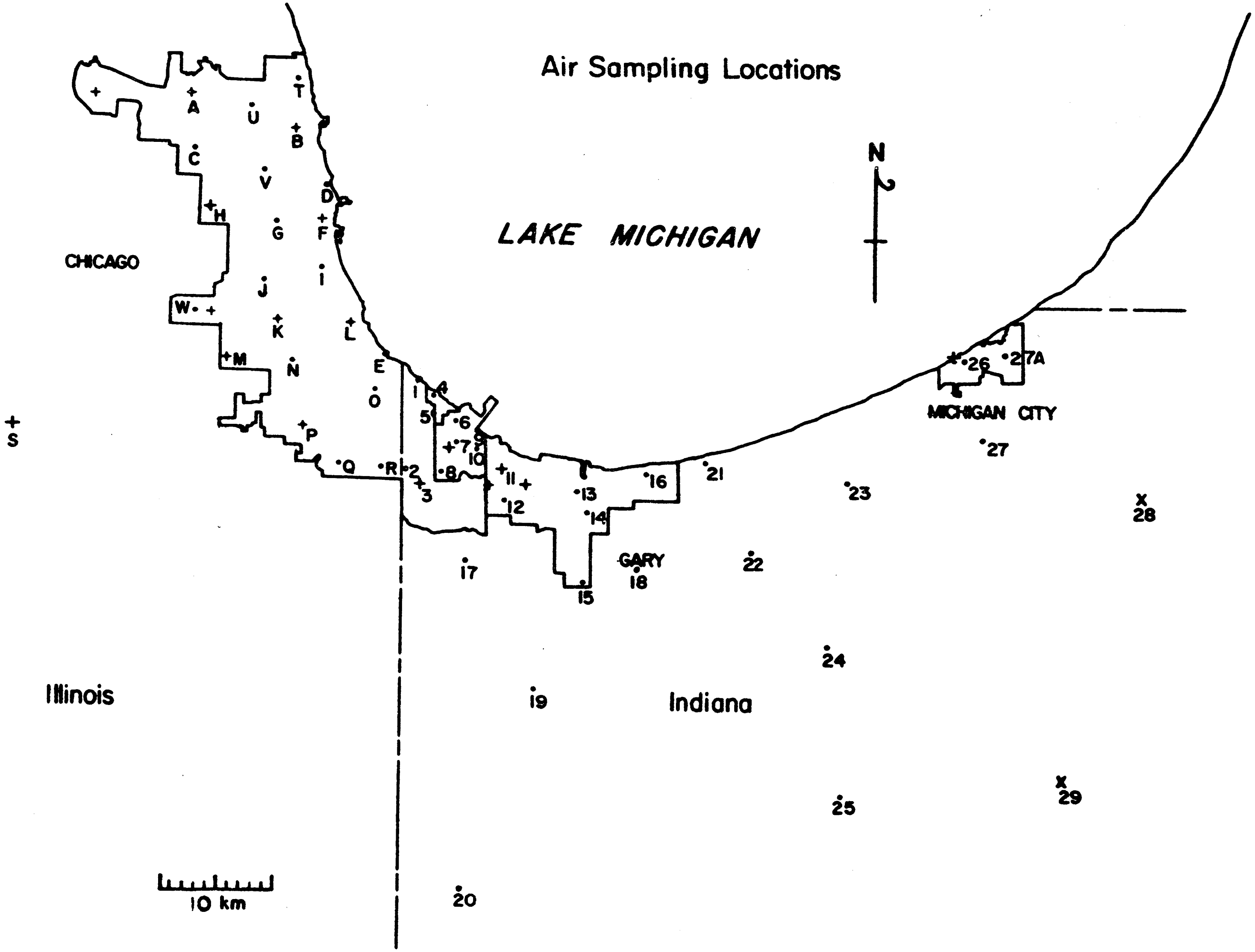
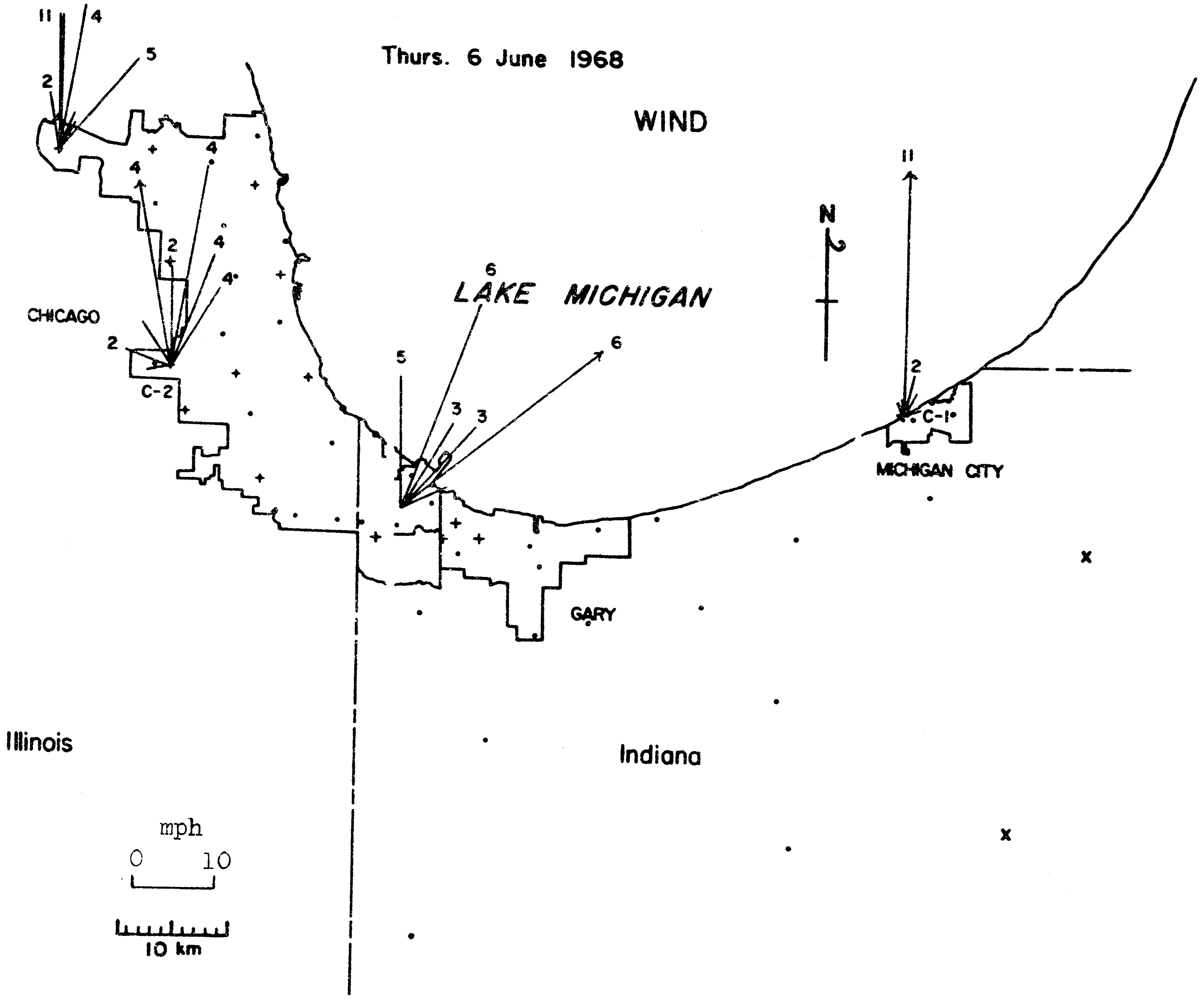
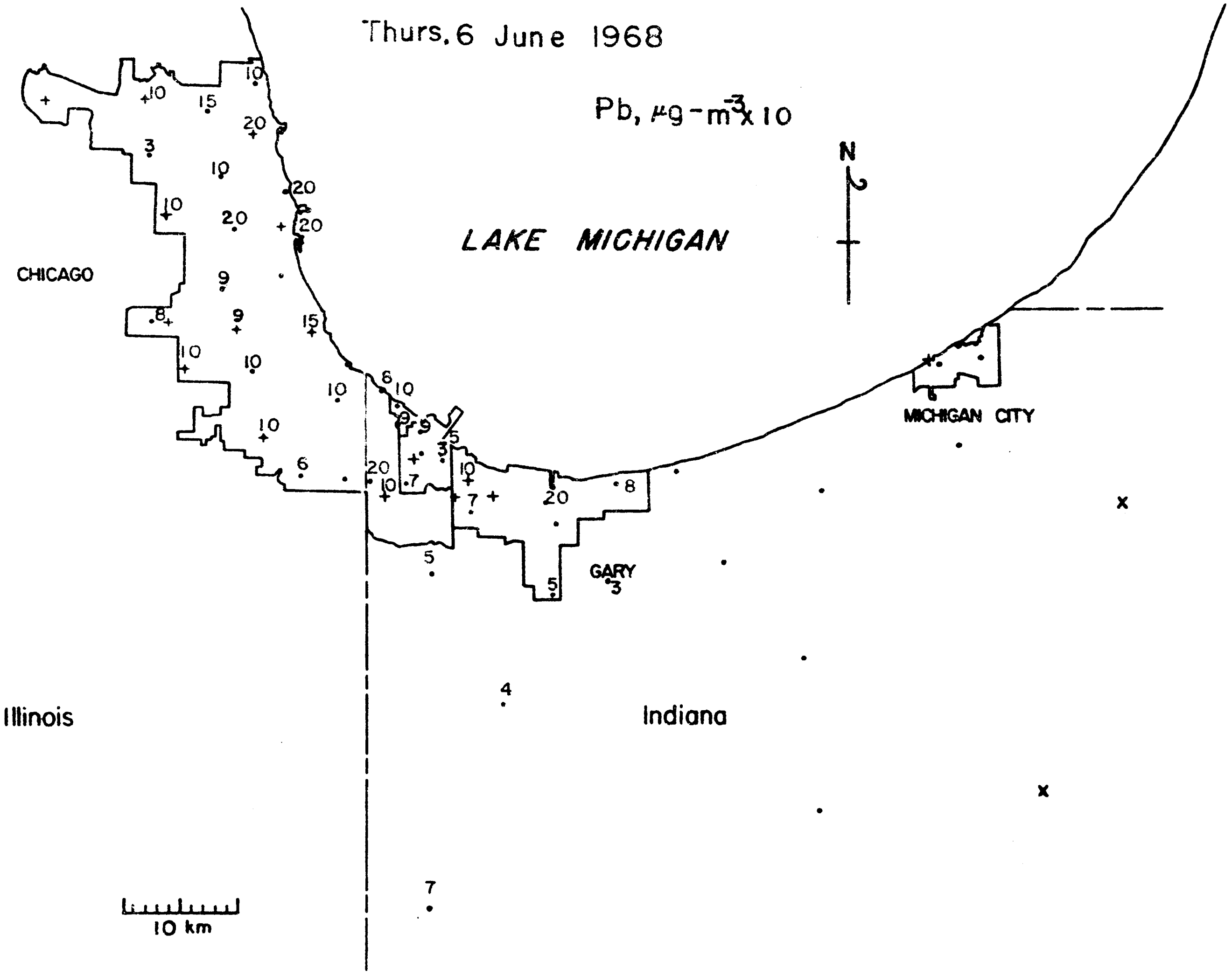


Figure 2


Thurs. 6 June 1968

WIND

Figure 3



Thurs. 6 June 1968

Pb, $\mu g\text{-}m^{-3} \times 10$

Figure 4

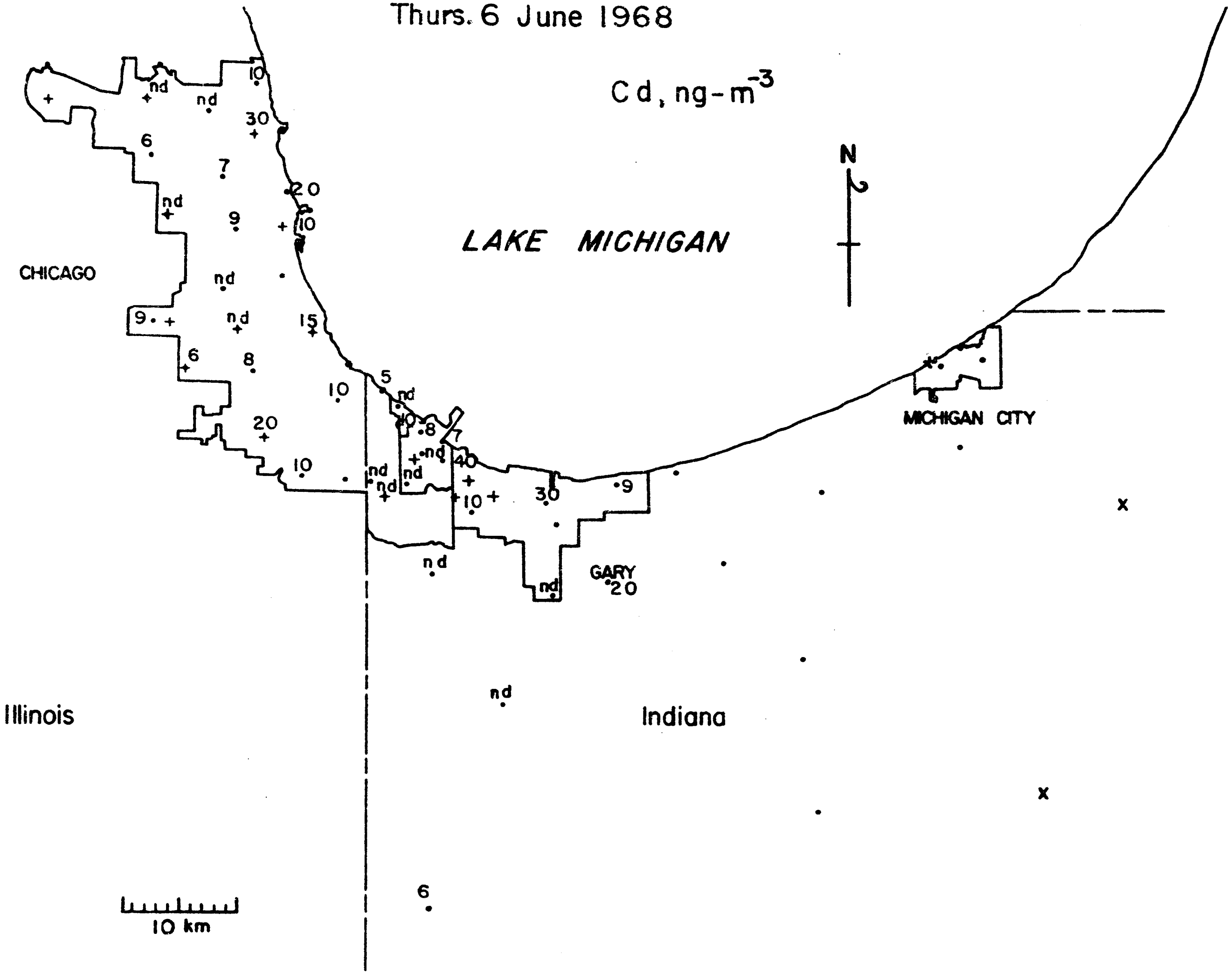
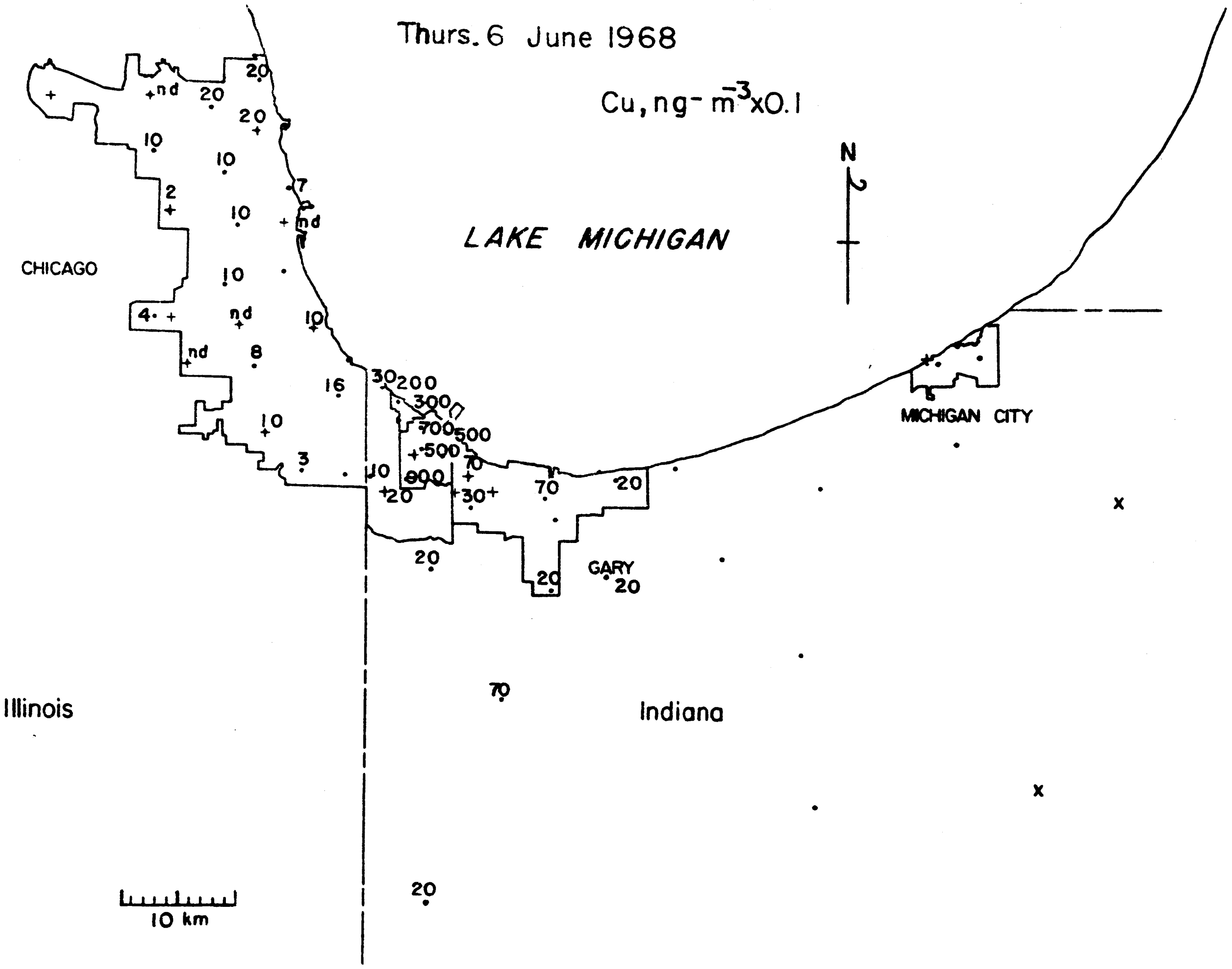

Thurs. 6 June 1968
Cd, ng-m^{-3}
LAKE MICHIGAN
N
CHICAGO
MICHIGAN CITY
GARY
Illinois
Indiana
10 km
10
nd
nd
30
6
7
20
nd
9
10
nd
9
nd
15
6
8
5
10
nd
20
10
8
7
10
nd
nd
40
nd
nd
10
30
9
nd
nd
20
nd
6
x
x

Figure 5



Thurs. 6 June 1968

Cu, ng-m^{-3} x0.1

Figure 6

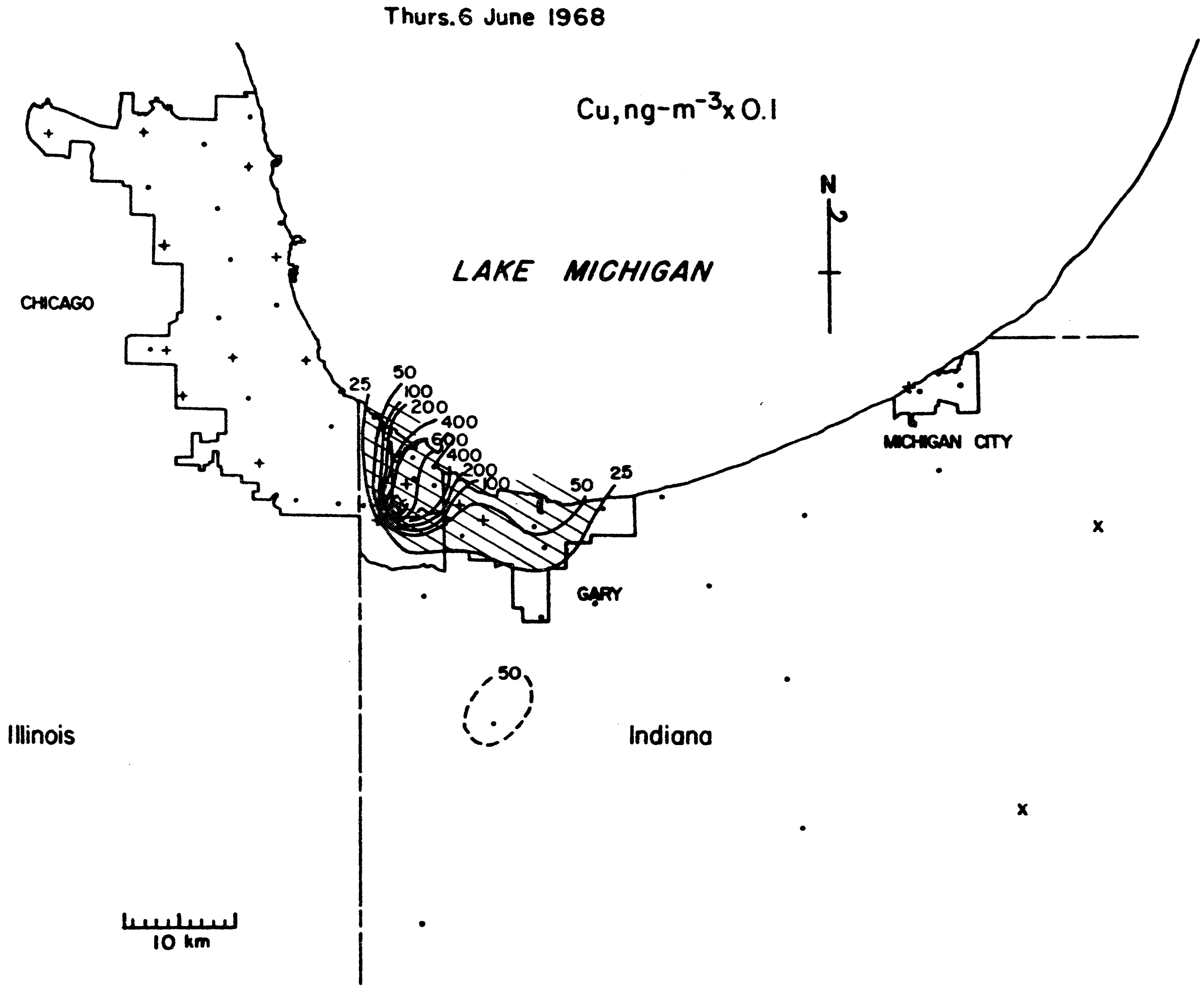
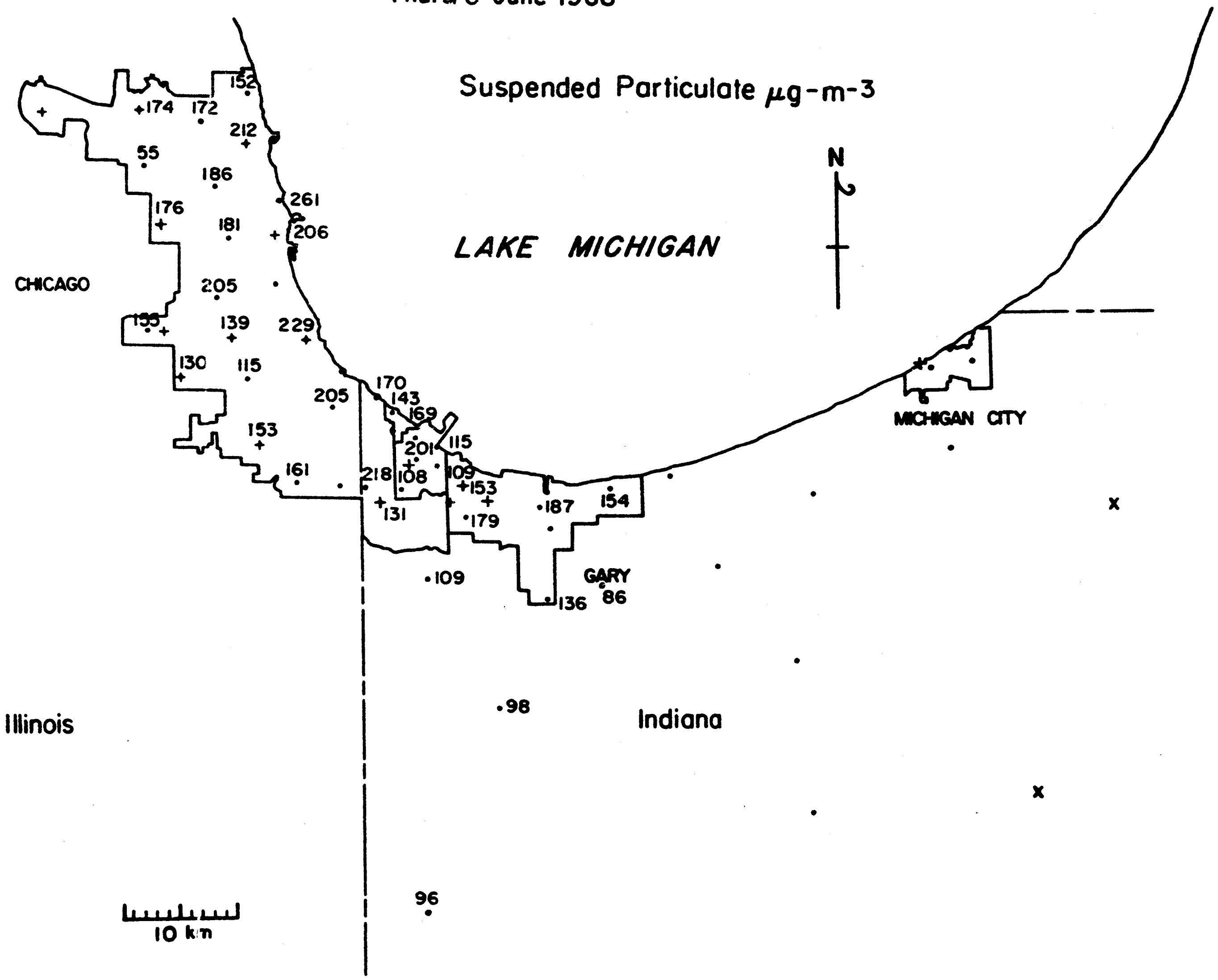

Thurs.6 June 1968
Cu, ng-m^{-3} x 0.1
LAKE MICHIGAN
N
CHICAGO
MICHIGAN CITY
GARY
Illinois
Indiana
25
50
100
200
400
600
400
200
100
50
25
50
10 km

Figure 7

Thurs. 6 June 1968



Suspended Particulate $\mu g\text{-}m^{-3}$

Figure 8

Thurs. 6 June 1968

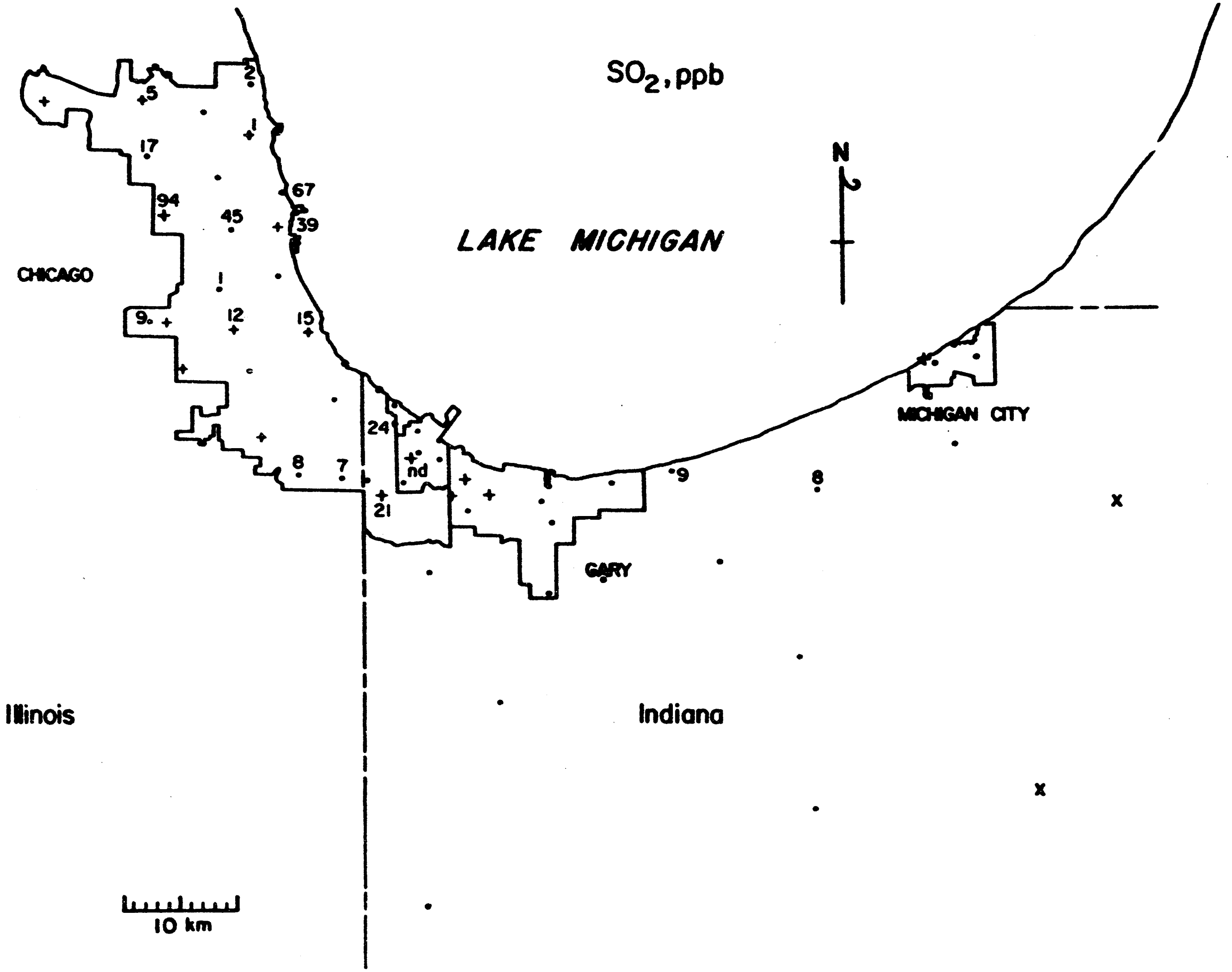


Table I . Atmospheric Concentration of Lead, ng/m^3

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	2000	800	1000	100	1000	1000
2	----	2000	3000	2000	3000	2000
3	3000	1000	3000	2000	2000	2000
4	3000	1000	2000	800	2000	2000
5	1000	900	2000	400	1000	1000
6	2000	900	4000	600	4000	2000
7	----	----	3000	700	3000	2000
8	1000	700	2000	1000	1000	1000
9	2000	500	600	2000	2000	500
10	2000	300	800	1000	700	600
11	2000	1000	2000	----	----	----
12	4000	700	2000	----	----	----
13	6000	2000	3000	----	----	----
14	----	----	----	----	----	----
15	1000	500	2000	----	----	----
16	3000	800	----	----	----	----
17	1000	500	2000	900	2000	700
18	400	300	800	500	100	2000
19	300	400	400	----	100	3000
20	900	700	1000	1000	600	1000
21	----	----	1000	500	600	----
22	----	----	1500	400	1000	----
23	----	----	700	100	500	700
24	----	----	1500	500	300	500
25	----	----	500	300	200	----
26	1000	----	1000	700	800	500
27	----	----	----	300	400	800
A	7000	1000	5000	2000	3000	4000
B	4000	2000	2000	800	4000	4000
C	5000	300	2000	600	2000	3000
D	3000	2000	300	2000	4000	3000
E	4000	----	----	----	1500	5000
F	6000	2000	3000	----	3000	4000
G	4000	2000	4000	1500	----	3000
H	2000	1000	3000	700	3000	4000
I	----	----	----	----	----	2000
J	6000	900	2000	----	2000	----
K	5000	1000	2000	500	2000	2000
L	3000	1500	2000	200	4000	2000
M	6000	1000	2000	400	2000	4000
N	5000	1000	3000	600	2000	2000
θ	6000	1000	2000	500	2000	1000
P	5000	1000	4000	600	2000	3000
Q	4000	700	2000	700	----	2000
R	4000	----	2000	300	2000	----
T	3000	1000	2000	800	----	----
U	4000	1500	3000	1000	3000	----
V	4000	1000	4000	1000	3000	2000
W	4000	800	2000	----	2000	3000
SHIP	----	----	----	700	----	----

Individual Data Points are Reliable to a Factor of 2.

Table II . Atmospheric Concentrations of Cadmium, ng/m^3

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	50	5	30	10	**	10
2	--	**	20	20	10	20
3	10	**	**	50	**	30
4	30	**	**	5	10	8
5	40	10	10	50	**	7
6	10	8	20	10	10	10
7	--	--	8	60	10	10
8	15	**	5	10	8	**
9	30	7	10	20	**	**
10	20	**	3	6	**	**
11	10	40	6	--	--	--
12	70	10	**	--	--	--
13	30	30	**	--	--	--
14	--	--	--	--	--	--
15	15	**	**	--	--	--
16	7	9	--	--	--	--
17	10	**	**	**	**	**
18	**	20	**	10	**	20
19	9	**	**	--	**	40
20	10	6	80	20	5	20
21	--	--	30	40	**	--
22	--	--	30	10	**	--
23	--	--	30	30	**	**
24	--	--	20	7	20	10
25	--	--	30	**	**	--
26	5	--	**	7	10	**
27	--	--	--	**	10	20
A	**	**	20	20	10	30
B	30	30	**	10	30	30
C	30	6	10	**	20	**
D	M	20	**	20	**	20
E	60	--	--	--	15	40
F	20	10	10	--	10	5
G	50	10	**	10	--	15
H	**	**	20	8	30	40
I	--	--	--	--	--	**
J	80	**	10	--	8	--
K	20	**	8	10	10	10
L	30	15	**	**	20	30
M	40	6	9	**	20	**
N	10	8	20	9	10	**
O	50	10	10	**	10	7
P	5	20	9	20	**	30
Q	30	10	6	15	--	6
R	20	--	7	**	10	--
T	10	10	9	**	**	--
U	9	**	10	**	20	--
V	40	7	40	6	30	30
W	40	9	10	--	**	**
SHIP	--	--	--	20	--	--

Individual Data Points are Reliable to a Factor of 2. **= $\leqslant 5$

Table III . Atmospheric Concentrations of Copper, ng/m^3

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	70	300	400	150	150	300
2	---	100	1000	150	200	150
3	300	200	2000	200	80	600
4	900	2000	200	80	600	400
5	1000	3000	600	60	500	200
6	2000	7000	(7000)	2000	2000	4000
7	---	---	1000	300	1000	600
8	5000	9000	5000	2000	3000	9000
9	7000	5000	9000	7000	10000	10000
10	4000	5000	1500	2000	(9000)	10000
11	300	700	400	---	---	---
12	***	300	500	---	---	---
13	80	700	200	---	---	---
14	---	---	---	---	---	---
15	200	200	150	---	---	---
16	100	200	---	---	---	---
17	150	200	150	200	30	70
18	300	200	300	200	***	100
19	400	700	400	---	70	100
20	150	200	100	200	40	100
21	---	---	100	70	70	---
22	---	---	300	70	70	---
23	---	---	90	***	100	100
24	---	---	500	60	100	70
25	---	---	200	60	90	---
26	80	---	300	200	400	200
27	---	---	***	300	300	200
A	70	***	600	100	100	300
B	300	200	70	200	300	150
C	100	100	100	20	**	100
D	150	70	30	100	200	200
E	400	---	---	---	500	1000
F	200	***	80	---	100	100
G	400	100	70	200	---	200
H	500	20	80	20	100	***
I	---	---	---	---	---	200
J	200	100	***	---	200	---
K	200	***	***	200	100	100
L	200	100	70	***	800	200
M	80	***	60	***	600	90
N	100	80	300	60	300	100
O	300	200	200	100	200	200
P	300	100	200	200	200	200
Q	900	30	100	200	---	200
R	500	***	200	---	200	---
T	200	200	200	30	***	---
U	200	200	200	20	300	---
V	600	100	400	80	200	200
W	200	40	100	---	200	200
SHIP	---	---	---	100	---	---

Individual Data Points are Reliable to a Factor of 2. ***= ⩽20

Table IV . Atmospheric Concentrations of Bismuth, ng/m^3

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	**					
2	--					
3	3.					
4	1.					
5	2.					
6	3.					
7	--					
8	0.7					
9	2.					
10	1.5					
11	0.4					
12	0.6					
13	0.4					
14	--					
15	0.3					
16	**					
17	--					
18	--					
19	--					
20	--					
21	--					
22	--					
23	--					
24	--					
25	--					
26	**					
27	--					
A	M					
B	**					
C	**					
D	M					
E	0.8					
F	1.					
G	0.1					
H	M					
I	--					
J	**					
K	0.6					
L	**					
M	M					
N	**					
O	**					
P	0.3					
Q	0.4					
R	0.4					
T	0.2					
U	**					
V	**					
W	0.8					
SHIP	--					

Individual Data Points are Reliable to a Factor of 2. **= $\leq$0.05

Table V . Atmospheric Concentrations of Total Suspended Particulate, $\mu g/m^3$

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	115	170	117	32	198	148
2	--	218	344	64	161	92
3	81	131	256	139	148	167
4	126	143	128	54	152	145
5	140	169	278	66	156	242
6	142	201	382	125	256	233
7	--	--	332	193	191	174
8	62	108	210	105	91	122
9	83	115	134	148	122	109
10	78	109	198	--	100	96
11	76	153	228	--	--	--
12	128	179	249	--	--	--
13	120	187	255	--	--	--
14	--	--	--	--	--	--
15	46	136	100	--	--	--
16	80	154	85	--	--	--
17	66	109	117	142	--	--
18	98	86	107	64	17	--
19	55	98	70	--	46	--
20	78	96	88	126	62	--
21	--	--	77	44	40	65
22	--	--	104	55	49	65
23	--	--	66	27	39	57
24	--	--	--	32	38	81
25	--	--	81	--	43	185
26	68	--	64	63	79	45
27	--	--	--	49	84	69
A	88	174	141	71	138	107
B	113	212	116	105	239	214
C	114	55	150	49	132	139
D	125	261	19	60	243	188
E	144	--	--	--	305	952
F	153	206	169	--	185	218
G	134	181	172	152	--	143
H	50	176	236	86	182	186
I	--	--	--	--	--	181
J	166	205	259	--	166	--
K	154	139	245	103	158	134
L	180	229	180	43	225	218
M	139	130	183	98	170	195
N	142	115	211	86	154	136
O	163	205	263	108	174	178
P	141	153	286	51	177	214
Q	195	161	408	109	--	235
R	143	--	241	110	130	--
T	92	152	81	67	132	--
U	75	172	121	74	146	--
V	114	186	190	100	196	148
W	131	155	216	--	161	185

All Data Furnished by the Local Agencies

Table VI . Atmospheric Concentrations of SO_2, ppb

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 20
1						
2						
3	17	21	62	69	3	--
4						
5	13	24	--	48	4	--
6						
7	--	--	2	--	1	--
8	--	**	--	--	9	--
9						
10						
11	2	--	15	--	--	--
12						
13	**	--	**	--	--	--
15						
16						
17						
18						
19	--	--	1	--	**	--
20						
21	--	9	2	1	1	14
22	--	--	1	**	3	**
23	--	8	4	1	4	11
24	--	--	--	1	2	--
25						
26						
27						
A	75	5	10	8	3	4
B	14	1	27	35	3	26
C	54	17	10	1	4	6
D	22	67	12	30	13	11
E						
F	10	39	9	13	9	34
G	32	45	**	6	3	16
H	27	94	31	9	35	3
I						
J	7	1	7	1	6	7
K	80	12	14	12	24	--
L	23	15	29	1	27	--
M	1	--	6	1	15	32
N	1	--	25	12	4	39
Θ	1	--	20	4	3	20
P	1	--	**	1	2	5
Q	24	8	51	7	2	44
R	17	7	51	4	2	--
T	1	2	12	12	28	16
U						
V						
W	4	9	13	24	22	20

**= ≤ 0.5

All Data Furnished by the Local Agencies

Table VII

AVERAGE METEOROLOGICAL CHARACTERISTICS.

	Wind Direction degrees	Range degrees	Speed m/s	Range m/s	Temperature Max. °C	Min. °C	Ave. °C	Precip. mm	Relative Humidity %
May 21	290	360	3.3	C-7	13.9	8.3	11.1	Trace	--
May 22	180	280	3.5	C-8	16.7	6.1	11.7	2	--
June 6	180	40	5.3	2-8	33.9	20.0	27.2	None	55
June 20	150	150	3.8	3-8	25.6	13.3	19.4	Trace	61
July 9	210	170	6.8	4-10	29.4	16.1	22.8	Trace	60
Aug. 8	200	360	3.9	2-16	31.1	22.2	26.7	0.5	77
Aug. 29	090	150	4.2	3-6	24.4	15.0	20.0	None	58

Table VIII

AVERAGE CONCENTRATIONS FOR EACH DAY IN CHICAGO AND N.W. INDIANA.

Day, 1968	Cd ng/m^3	Pb ng/m^3	Cu* ng/m^3	SP μgm/m^3	SO2 ppb	Bi ng/m^3
21/22 May			2000			
Ind.	21	2000	180	92		1.1
Ill.	29	4300	300	130		0.25
Both	25	3300	750	110	19	0.63
6 June			3500			
Ind.	8	830	390	140		
Ill.	9	1300	830	170		
Both	9	1100	970	160	20	
20 June			3900			
Ind.	13	1700	260	170		
Ill.	10	2700	230	200		
Both	12	2200	1000	180	16	
9 July			1600			
Ind.	19	810	130	84		
Ill.	9	810	99	83		
Both	14	810	510	84	12	
8 Aug.			4800			
Ind.	5	1300	120	100		
Ill.	13	2600	250	180		
Both	9	1900	1300	146	9	
29 Aug.			4000			
Ind.	12	1300	140	120		
Ill.	16	3100	220	180x		
Both	14	2200	1200	156x	17	
Totals: all data						
Mean	19	1900	1000	150	18	0.63
Max.	80	7000	10000	950	80	3.
Min.	≤5	100	≤20	30	≤0.5	≤.05

(*, stations 1-10 and 11-22 listed separately;
x, station E excluded)

Table IX

AVERAGE VALUES OF SELECTED RATIOS FOR EACH DAY IN CHICAGO AND NORTHWEST INDIANA.

Day, 1968	Cd/Pb	Cd/Cu	Cd/SP*	Pb/SP*	Cu/SP*	Cu/Pb	Cd/SO2
21/22 May							
Ind.	0.012	0.099	0.023	2.2	1.7	0.89	
Ill.	0.007	0.14	0.023	3.5	0.25	0.080	
Both	(0.010)	(0.12)	(0.023)	(2.9)	(0.92)	(0.44)	(9.0)
6 June							
Ind.	0.018	0.031	0.0098	0.57	1.49	3.4	
Ill.	0.011	0.16	0.0078	0.76	0.071	0.13	
Both	0.014	0.10	0.0086	0.67	0.85	1.9	4.2
20 June							
Ind.	0.021	0.11	0.022	1.1	0.87	1.3	
Ill.	0.0044	0.087	0.0071	1.6	0.11	0.060	
Both	0.012	0.10	0.014	1.4	0.54	.78	3.8
9 July							
Ind.	0.047	0.15	0.034	0.97	0.73	0.88	
Ill.	0.018	0.15	0.019	1.0	0.13	0.15	
Both	0.036	0.15	0.029	1.0	0.48	0.56	7.3
8 August							
Ind.	0.014	0.053	0.013	1.1	2.4	2.6	
Ill.	0.007	0.083	0.010	1.5	0.15	0.12	
Both	0.009	0.070	0.011	1.3	1.3	1.5	3.8
29 August							
Ind.	0.012	0.095	0.012	1.0	2.5	5.4	
Ill.	0.007	0.096	0.013	1.7	0.11	0.082	
Both	0.009	0.095	0.013	1.4	1.2	1.6	3.2
Totals: all data							
Mean	0.015	0.11	0.016	1.4	0.87	1.11	5.5

(*, %)

Table X

CONTRIBUTIONS OF FUELS TO LEAD, CADMIUM, AND COPPER TO CHICAGO AREA SUSPENDED PARTICULATE[a]

	Coal	Coke	Fuel Oil	Gasoline
Combustion estimate, megatons/yr	20	15	7	8
Particulate emission estimate, kilotons/yr	220	18	14	b
Pb emission estimate, tons/yr	300	22	30	1,800
Cd emission estimate, tons/yr	11	1	--	--
Cu emission estimate, tons/yr	100	7	26	--

[a] After Winchester and Nifong (1969). All units are metric.

[b] Assumed 2 g Pb/gallon and 25% of emissions airborne.

Table XI

COMPARISON WITH NASN 1963 DATA, ng/m^3

	Pb	Cd	Cu	Bi
NASN, Parke Co., rural	24-57	1.8-5.2	17-80	≤0.5
NASN, Beverly Shores, proximate	100-200	ND-10	30-50	≤0.5
NASN, Hammond, urban	100-1,200	ND-55	30-180	≤0.5
This study, all stations[a]	100-7,000	<5-80	<20-10,000	<0.05-3.0
This study, station 2, Hammond[a]	1,000-3,000	<5-20	100-1,000	---

[a] Individual values reliable to a factor of 2.

APPENDIX IV

DATA TABULATIONS AND RATIOS

IV.1 METEOROLOGICAL DATA

IV.1.1 East Chicago, Indiana

Table IV.1.1 Meteorological Data for East Chicago, Indiana, 1968

* xxyy; xx=tens of °, yy=mph

CST	21 May		22 May		6 June		20 June		9 July		8 Aug		29 Aug		
	xxyy*	Δ°		Δ°		Δ°		Δ°		Δ°		Δ°		Δ°	
1	30--	20	2304	20	1806	30	1203	30	2210	60	9002	90	1204	60	
2	30--	--	2303	20	1806	30	2002	120	2311	60	1202	90	1204	30	
3	29--	--	2204	20	1806	30	2203	30	2310	60	1403	60	1304	30	
4	29--	20	2204	60	1805	30	2200	--	2308	60	2103	120	1505	60	
5	30--	50	2204	40	1806	30	2200	--	2307	60	2103	90	1606	30	
6	30--	60	2304	30	2007	30	2404	30	2408	60	2103	60	1605	30	
7	2900	50	2404	30	2107	60	2400	120	2307	60	2004	60	1606	30	
8	28--	30	2505	90	2107	60	1203	90	2310	60	2005	60	1707	60	
9	30--	50	2105	70	2308	60	1206	60	2409	90	2205	60	1806	60	
10	30--	180	2206	60	2308	90	1105	90	2507	90	2206	60	1805	90	
11	2909	90	2209	60	2309	90	1206	90	2706	90	2307	90	1605	120	Lake
12	3111	60	2109	90	2409	120	1106	90	2708	90	2507	90	0907	90	Breeze
13	0407	60	1909	120	2309	120	0906	90	3010	90 FP	2707	90	0908	90	
14	0506	90	2110	90	2310	120	0907	60	3612	60	3314	90	0807	90	
15	0603	120	1910	60	2310	120	1008	60	0315	60	0608	90	0807	90	
16	0705	120	2010	60	2208	90	1007	60	0310	60	1307	60	0807	90	
17	0605	90	1907	60	2009	90	1008	60	0310	60	1206	90	0706	90	
18	----	--	1711	60	2011	60	1009	60	0409	60	1806	90	0908	60	
19	----	--	2008	120	2010	60	1008	60	0409	60	1804	90	0908	60	
20	----	--	2307	30	2009	30	1109	60	0409	90	1806	60	0907	60	
21	----	--	2403	60	2009	30	1207	60	0412	90	1607	60	0906	60	
22	----	--	3602	120	2107	30	1407	60	0412	60	1805	30	1006	60	
23	----	--	4703	30	2208	60	1507	60	0311	60	1704	30	1204	30	
24	----	--	4704	30	2207	30	1808	60	3410	60	1504	30	1205	30	

IV.1.2 Midway Airport, Chicago

Table IV.1.2 Wind Data - Midway Airport, Chicago, Illinois, 1968

CST	21 May xxyy*	22 May	6 June	20 June	9 July	8 Aug	29 Aug
0	3103		1708	1810	2110	0806	0805
1	3104	2104	1708	1912	2110	0806	1403
2	3205	2105	1808	2010	2012	0706	2304
3	3204	2003	1808	2010	2010	1204	2403
4	3203	0000	1805	2010	2110	1605	2303
5	0000	2004	1808	1914	2110	1803	1304
6	2703	2006	1807	2012	2111	1805	1304
7	2704	2105	1910	2014	2011	2007	1707
8	2606	2105	2009	2117	2309	2206	1708
9	2810	1911	1811	2415	2207	2007	1809
10	2910	1911	2112	1906	2307	1908	1306
11	3014	1910	2108	1809	2207	2007	0907
12	3312	2012	2008	2212	2409	2510	0911
13	3111	1812	1915	1716	3512	3013	1211
14	3013	1911	1910	1918	0416	0610	1212
15	3611	1810	2112	2014	0114	1608	0812
16	0608	1715	1912	1813	0313	1511	0710
17	0911	1511	1810	1716	0513	1708	0910
18	1307	1712	1910	1814	0514	2306	0910
19	1305	1708	1812	1614	0612	2205	0911
20	1305	1705	1810	1713	0414	1208	0908
21	1003	0000	1908	1812	0215	2105	0508
22	1305	0805	1906	1914	0117	2005	0705
23	1804	1005	2008	2012	0315	1806	0705
24	1904	1005	2106	2012	0213	1603	0505

* Key: xxyy; xx=tens of °, yy=mph

IV.1.3 O'Hare Airport, Chicago

Table IV.1.3 Wind Data - O'Hare Airport, Chicago, Illinois, 1968

CST	21 May	22 May	6 June	20 June	9 July	8 Aug	29 Aug
	xxyy*						
0	3005			2103	1806		
1	3104	2403	1705	2503	1910	0000	3304
2	3105	2103	1804	0000	2008	2104	0000
3	2906	2103	1805	2004	2010	2504	0000
4	3005	2303	1805	2703	1908	0000	0000
5	3003	1803	1805	0000	2205	0000	0000
6	2704	2204	1905	0000	2106	2804	2903
7	3005	2308	1908	0503	2105	0000	1304
8	2706	2005	2107	0000	2206	2003	1705
9	2908	2008	1808	1204	2205	2805	1205
10	2710	2109	2009	0903	2204	2606	1605
11	3011	1809	2205	1803	2405	2806	1006
12	3411	1809	1909	0000	0208	3105	1109
13	3311	1712	1811	0910	0414	2804	1209
14	3410	2012	2208	0809	0212	3304	1210
15	0810	1609	1810	1010	0412	2703	0707
16	0309	1809	1909	1211	0218	0506	0507
17	0608	1408	1707	1110	0410	1206	0807
18	0204	1611	1808	1010	0408	1504	0405
19	1405	1710	1805	1208	0410	1603	0805
20	0408	2105	1804	1208	0510	5004	0607
21	1705	1503	1807	1308	0409	0407	1103
22	1905	1105	2104	1307	0311	0409	1104
23	2504	0707	2205	1408	0307	3610	0704
24	2304	2351	2207	1610	0203	0109	3104

* Key: xxyy; xx=tens of °, yy=mph

IV.1.4 Michigan City, Indiana

TABLE IV.1.4

METEOROLOGICAL DATA-MICHIGAN CITY, INDIANA, 1968

*xxyy; xx=tens of °, yy=mph

CST	21 May xxyy*	Δ°	22 May	Δ°	6 June	Δ°	20 June	Δ°	9 July	Δ°	8 Aug	Δ°	29 Aug	Δ°
1	0410	20	1605	30	1604	30	17--	75	1914	60	1006	75	1206	30
2	0481	20	1605	15	1704	30	16--	30	1815	60	1306	75	1410	30
3	0308	20	1806	15	1806	15	15--	30	1612	60	1607	45	1508	30
4	0207	30	1806	30	1806	30	15--	30	1513	60	1709	45	1508	30
5	3608	30	1806	30	1806	30	15--	30	1514	60	1909	45	1508	30
6	3605	30	1807	30	1806	30	08--	75	1611	60	1809	45	1508	30
7	3402	20	1804	45	1806	45	05--	60	1411	60	1810	45	1508	30
8	3601	60	2103	45	1906	45	05--	45	1410	60	1809	60	1509	45
9	3600	60	2102	45	2006	45	03--	30	1410	60	1809	60	1410	60
10	3300	20	2801	60	2404	60	36--	30	1410	60	1909	75	1411	60
11	3600	60	2802	60	2902	60	3608	30	0609	30	1909	75	1110	(150)
12	3600	60	2107	75	2901	75	3608	30	0610	15	2709	75	1109	120
13	3601	60	2008	60	2802	75	3610	30	0507	30	3009	45	1408	120
14	3400	45	2007	60	3302	60	0308	45	0310	45	3425	45	1608	75
15	3502	45	2006	60	3401	45	0411	45	0410	45	3520	45	0110	45
16	3606	45	2008	45	3400	45	0412	60	0412	45	1009	45	0412	45
17	3603	45	2008	45	2201	60	0510	60	0411	45	1508	45	0413	45
18	0102	60	2006	45	1903	45	0609	60	0412	60	1607	45	0513	45
19	3400	60	2505	15	1803	45	0706	60	0513	60	1607	45	0711	60
20	3400		2504	15	1803	45	0805	75	04015	45	1707	60	0706	75
21	3600	30	2406	30	1804	45	1210	60	0414	45	1704	60	1009	45
22	1703	30	2704	15	1804	45	1412	45	0418	45	2306	45	1010	45
23	1703	30	0000		1804	45	1411	30	0520	60	2404	30	1109	30
24	1502	30	2500	30	1804	45	1510	30	0520	60	2208	45	1308	15

TABLE IV.1.4 continued

OD	8-8	5	S02=.0011	0	0	0.0	3	13	1.0	2	8	.7
			H.V.=39.5	0	0	0.0	3	19	.4	2	1	1.5
			SPOT=.1180	7	9	1.6	7	21	1.5	0	0	0.0
SH	8-29	5	S02=.0032	0	0	0.0	2	1	6.2	5	21	3.1
			H.V.=65.0	0	0	0.0	0	0	0.0	9	22	3.6
			SPOT=.3269	0	0	0.0	1	0	2.0	7	7	4.0
CH	8-29	5	S02=.0038	0	0	0.0	9	18	2.4	4	20	.6
			H.V.=57.0	0	0	0.0	3	23	0.0	1	0	4.0
			SPOT=.1831	0	0	0.0	0	0	0.0	7	6	4.5

IV.1.5 Porter County, Indiana

TABLE IV.1,5

PORTER COUNTY WIND DATA , 1968

*Key: x,y,z; x=No. of hrs in quadrant, y=sum of hrs between occurrences, z=av.wind speed
Groups I, II, III; I=NW, II=N, III=NE
W Variable E
SW S SE

Station	Date	Week Day	Contaminants	Wind Data I			Wind Data II			Wind Data III		
				x	y	z	x	y	z	x	y	z
SH	6-20	5	S02=-	0	0	0.0	0	0	0.0	4	9	3.6
			H.V.=103.8	0	0	0.0	6	8	3.0	5	16	3.2
			SPOT=.1680	1	0	.2	1	0	.2	7	21	2.5
OD	6-20	5	S02=.0088	1	0	.2	13	19	1.7	2	1	.8
			H.V.=76.8	2	1	0.0	1	0	1.0	2	13	1.0
			SPOT=.5298	0	0	0.0	1	0	0.0	0	0	0.0
SH	7-9	3	S02=.0009	0	0	0.0	2	2	9.5	2	2	6.7
			H.V.=54.6	0	0	0.0	5	6	5.7	1	0	6.0
			SPOT=.0893	7	9	6.3	7	15	6.1	0	0	0.0
OD	7-9	3	S02=.0023	0	0	0.0	9	11	2.1	1	0	2.5
			H.V.=43.9	9	8	3.2	1	0	1.0	1	0	2.0
			SPOT=.1301	3	2	2.6	0	0	0.0	0	0	0.0

IV.1.6 Surface Synoptic Weather Maps

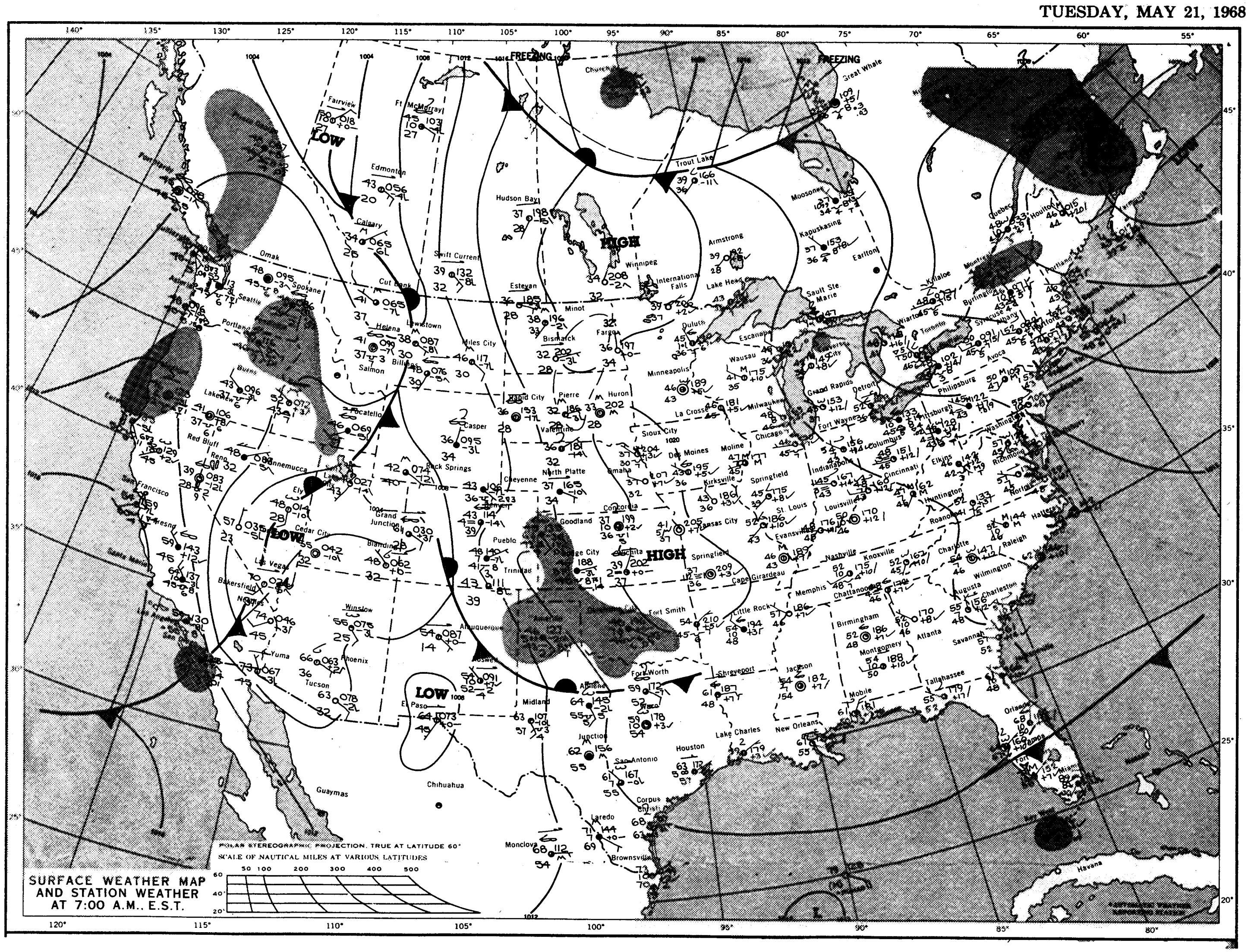


Figure IV.1.6.1:Synoptic analysis for May 21,1968 (ESSA).

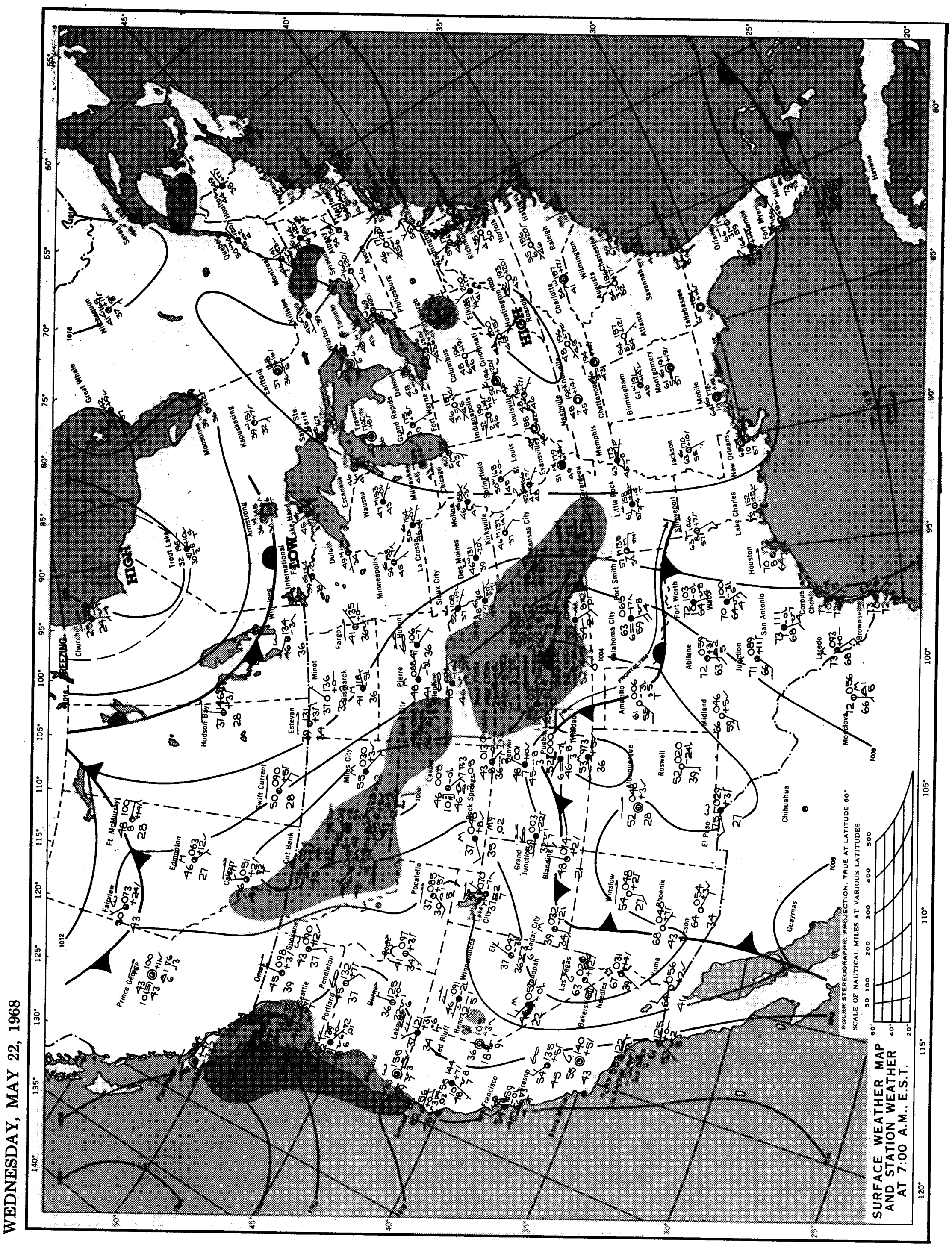


Figure IV.1.6.2:Synoptic Analysis for May 22, 1968 (ESSA).

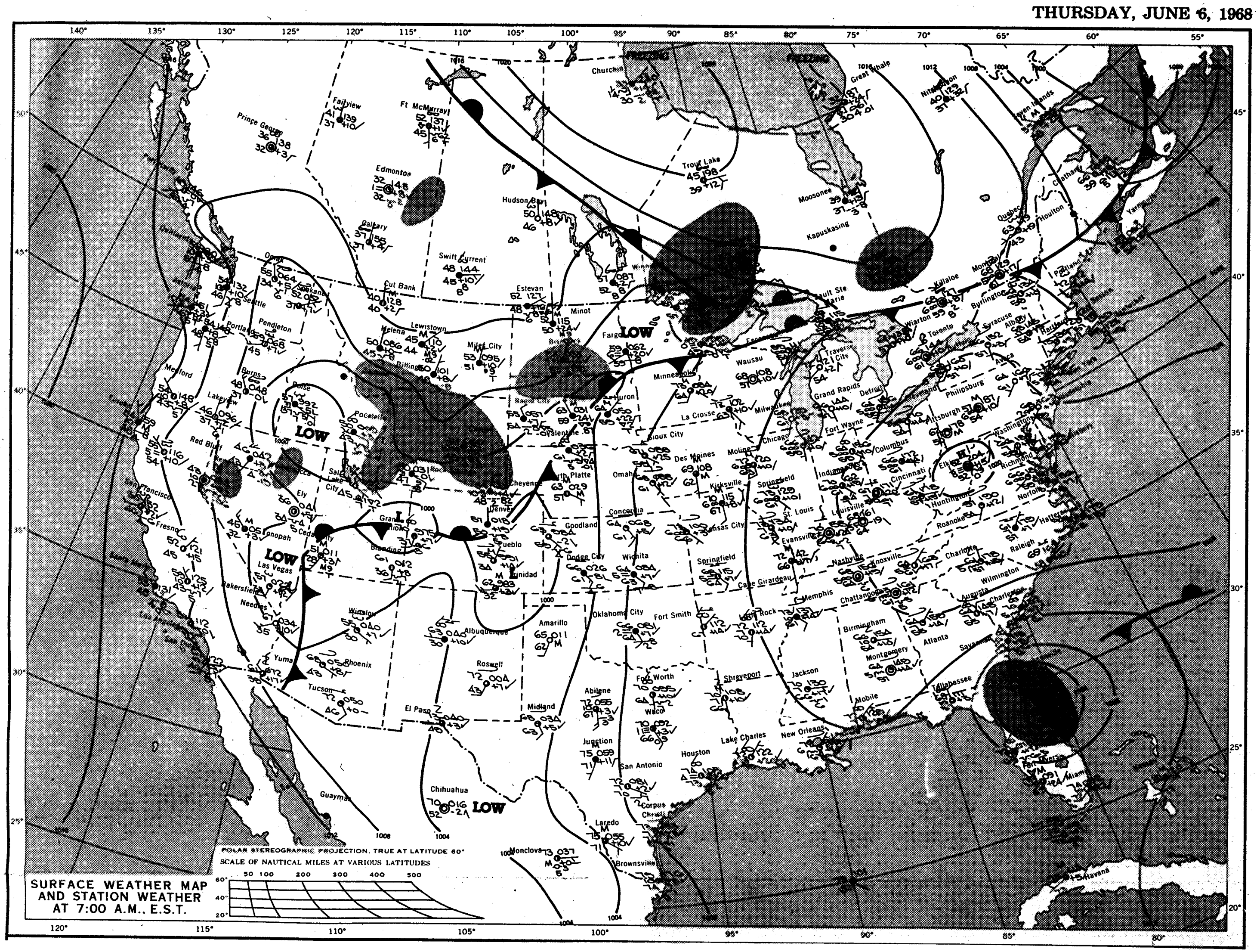


Figure IV.1.6.3: Synoptic analysis for June 6, 1968 (ESSA).

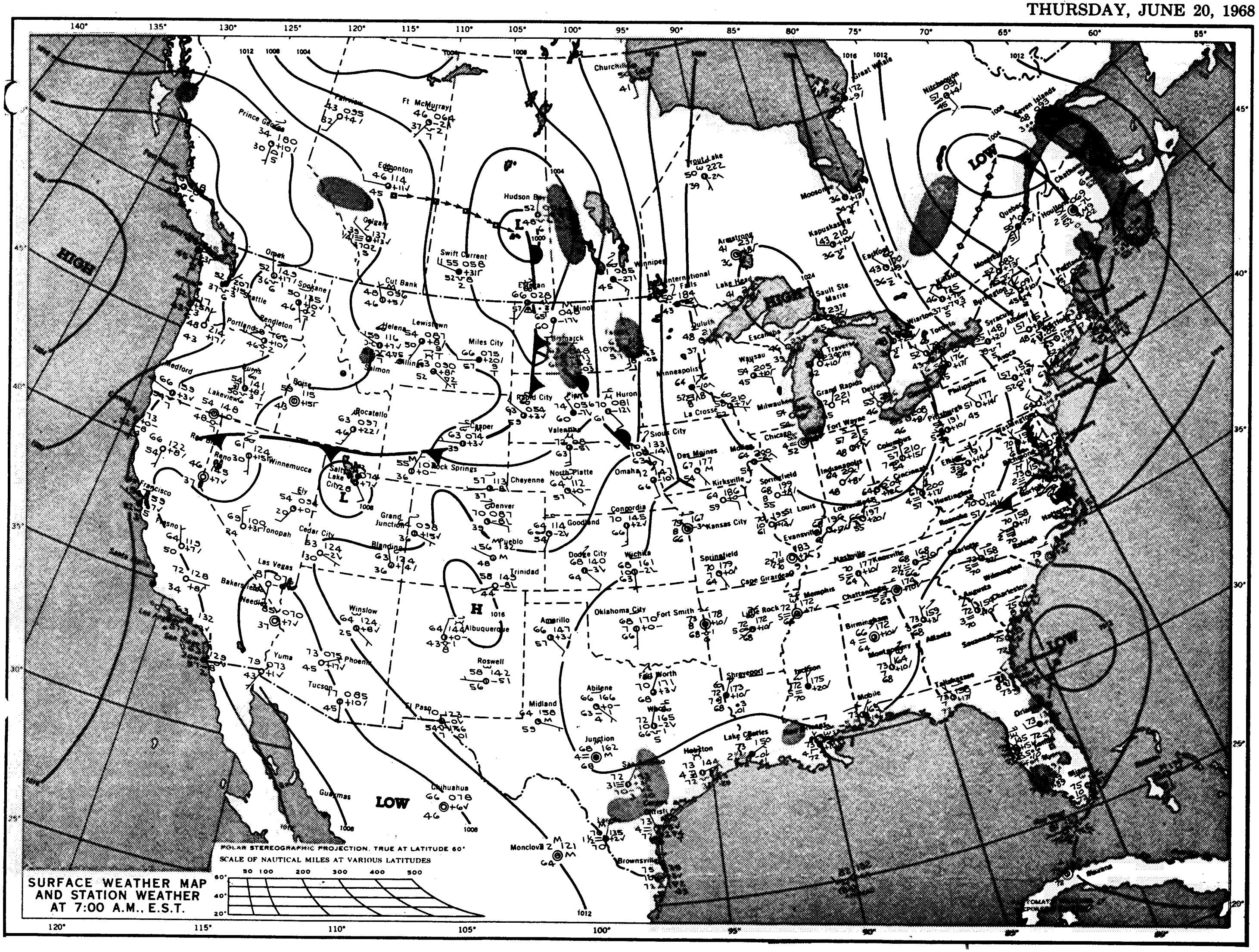


Figure IV.1.6.4: Synoptic analysis for June 20,1968 (ESSA).

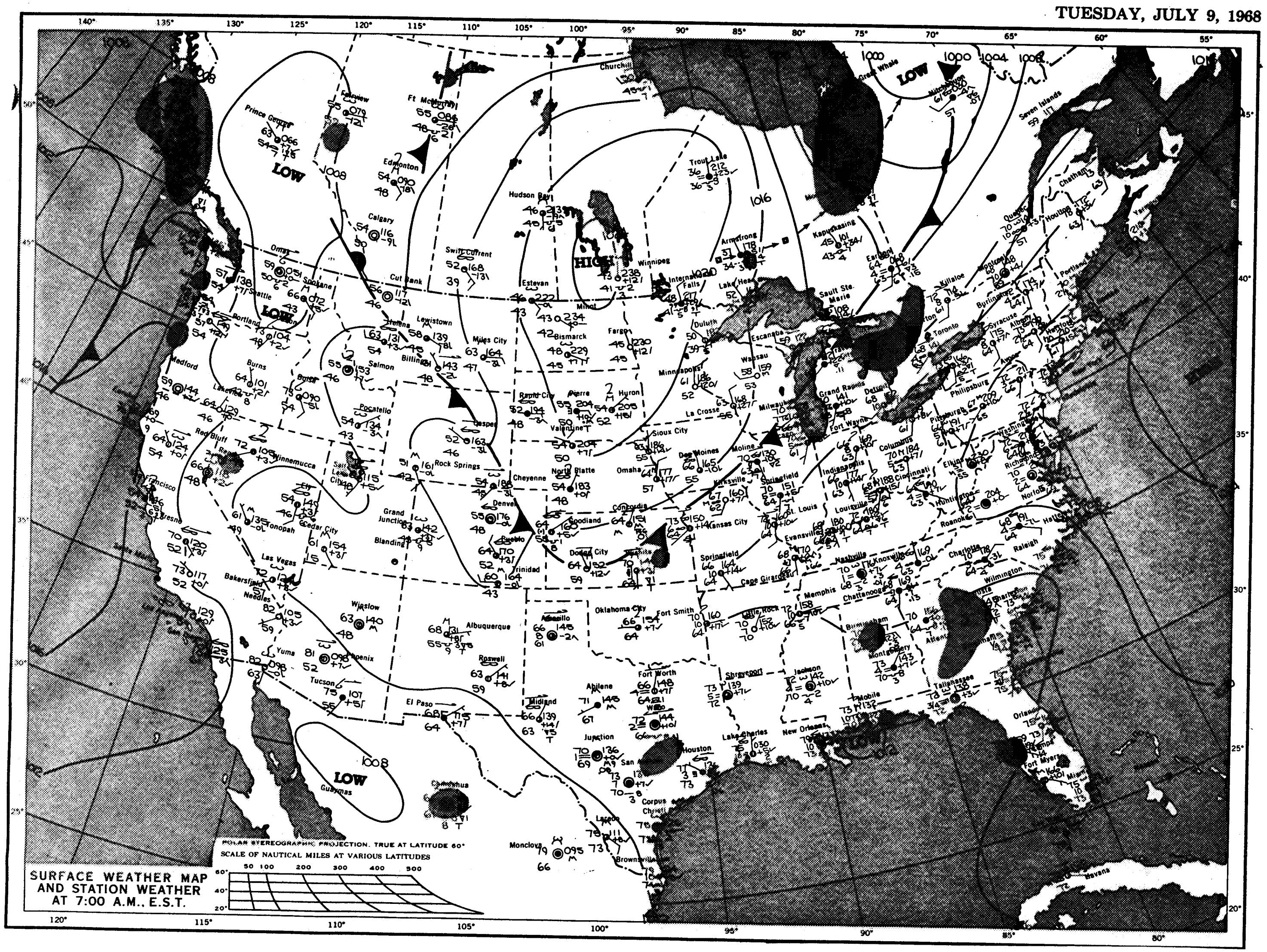


Figure IV.1.6.5: Synoptic analysis for July 9, 1968 (ESSA).

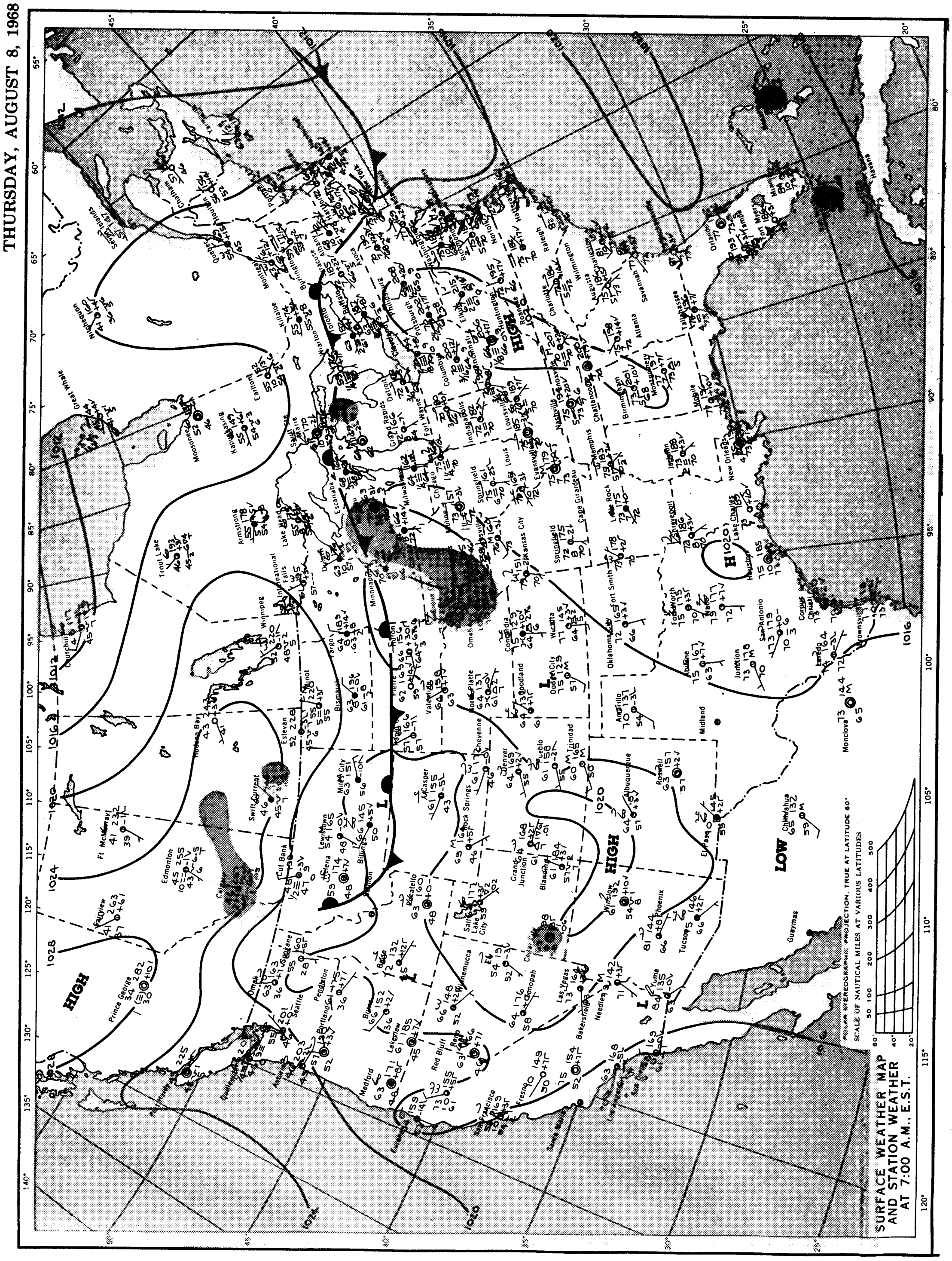


Figure IV.1.6.6: Synoptic analysis for August 8, 1968 (ESSA).

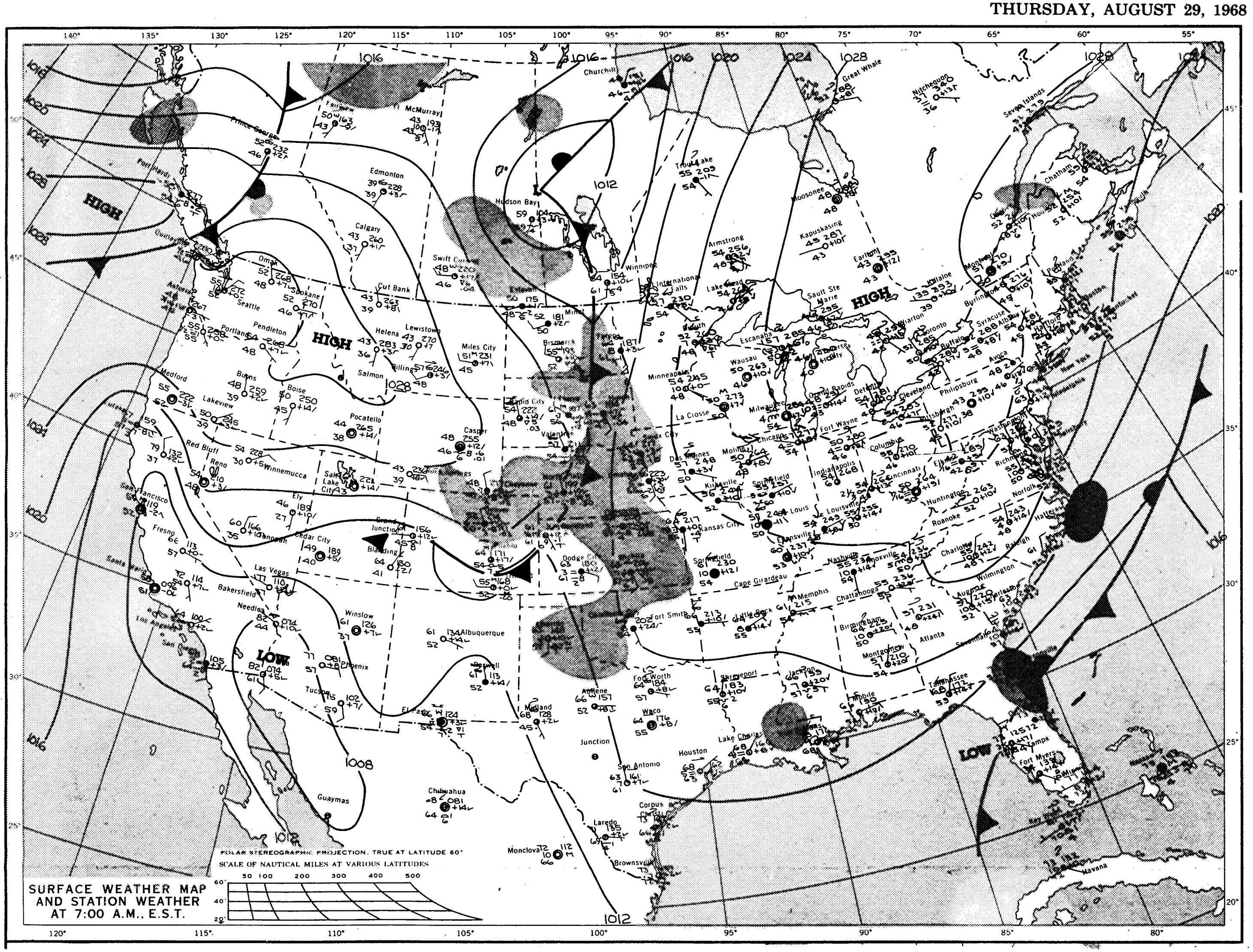


Figure IV.1.6.7: Synoptic analysis for August 29, 1968 (ESSA).

IV.2 RATIOS OF ELEMENT PAIRS, SUPPORTING COMPUTER PROGRAMS, AND DATA LOCATION TABLE

IV.2.1 Ratios of Element Pairs

Cd/Pb-Cu-SP-SO_2

Pb/Cd-Cu-SP-SO_2

Cu/Cd-Pb-SP-SO_2

SP/Cd-Pb-Cu-SO_2

SO_2/Cd-Pb-Cu-SP

RATIOS Cd/Pb 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	0.0253	0.0062	0.0273	0.1200	**********	0.0109
2	0.0041	**********	0.0057	0.0150	0.0048	0.0132
3	**********	**********	**********	0.0274	**********	0.0121
4	0.0104	**********	**********	0.0060	0.0050	0.0047
5	0.0279	0.0108	0.0056	0.1351	**********	0.0058
6	0.0065	0.0087	0.0043	0.0214	0.0027	0.0065
7	**********	**********	0.0030	0.0879	0.0044	0.0056
8	0.0107	**********	0.0028	0.0118	0.0062	**********
9	0.0150	0.0135	0.0207	0.0086	**********	**********
10	0.0089	**********	0.0038	0.0046	**********	**********
11	0.0063	0.0355	0.0035	**********	**********	**********
12	0.0179	0.0162	**********	**********	**********	**********
13	0.0054	0.0176	**********	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	0.0115	**********	**********	**********	**********	**********
16	0.0025	0.0110	**********	**********	**********	**********
17	0.0100	**********	**********	**********	**********	**********
18	**********	0.0515	**********	0.0283	**********	0.0119
19	0.0281	**********	**********	**********	**********	0.0130
20	0.0155	0.0083	0.0709	0.0162	0.0077	0.0208
21	**********	**********	0.0273	0.0750	**********	**********
22	**********	**********	0.0193	0.0262	**********	**********
23	**********	**********	0.0414	0.2000	**********	**********
24	**********	**********	0.0113	0.0149	0.0500	0.0192
25	**********	**********	0.0674	**********	**********	**********
26	0.0038	**********	**********	0.0097	0.0184	**********
27	**********	**********	**********	**********	0.0250	0.0212
A	**********	**********	0.0037	0.0117	0.0032	0.0066
B	0.0082	0.0148	**********	0.0158	0.0067	0.0081
C	0.0060	0.0214	0.0054	**********	0.0096	**********
D	**********	0.0083	**********	0.0137	**********	0.0074
E	0.0140	**********	**********	**********	0.0100	0.0091
F	0.0034	0.0048	0.0037	**********	0.0035	0.0012
G	0.0104	0.0047	**********	0.0093	**********	0.0047
H	**********	**********	0.0061	0.0108	0.0081	0.0080
I	**********	**********	**********	**********	**********	**********
J	0.0122	**********	0.0046	**********	0.0035	**********
K	0.0039	**********	0.0040	0.0240	0.0061	0.0058
L	0.0097	0.0100	**********	**********	0.0050	0.0112
M	0.0066	0.0043	0.0050	**********	0.0077	**********
N	0.0030	0.0067	0.0047	0.0148	0.0064	**********
O	0.0087	0.0092	0.0048	**********	0.0065	0.0054
P	0.0010	0.0175	0.0024	0.0417	**********	0.0107
Q	0.0077	0.0215	0.0026	0.0214	**********	0.0037
R	0.0067	**********	0.0032	**********	0.0076	**********
T	0.0045	0.0086	0.0045	**********	**********	**********
U	0.0024	**********	0.0031	**********	0.0066	**********
V	0.0112	0.0058	0.0084	0.0060	0.0100	0.0140
W	0.0078	0.0111	0.0052	**********	**********	**********
SHIP	**********	**********	**********	0.0338	**********	**********

RATIOS Cd/Cu 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	0.6575	0.0172	0.0789	0.0800	**********	0.0480
2	0.0433	**********	0.0155	0.1600	0.0684	0.1786
3	**********	**********	**********	0.0800	**********	0.0116
4	0.0319	**********	**********	0.0617	0.0190	0.0200
5	0.0325	0.0034	0.0175	0.8065	**********	0.0368
6	0.0059	0.0011	0.0009	0.0050	0.0057	0.0031
7	**********	**********	0.0083	0.2231	0.0124	0.0156
8	0.0029	**********	0.0009	0.0062	0.0024	**********
9	0.0040	0.0015	0.0013	0.0026	**********	**********
10	0.0036	**********	0.0020	0.0024	**********	**********
11	0.0414	0.0534	0.0154	**********	**********	**********
12	**********	0.0423	**********	**********	**********	**********
13	0.3846	0.0417	**********	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	0.0682	**********	**********	**********	**********	**********
16	0.0636	0.0500	**********	**********	**********	**********
17	0.0800	**********	**********	**********	**********	**********
18	**********	0.0708	**********	0.0812	**********	0.1357
19	0.0209	**********	**********	**********	**********	0.2917
20	0.0867	0.0273	0.5571	0.1235	0.1429	0.1923
21	**********	**********	0.3000	0.5217	**********	**********
22	**********	**********	0.1000	0.1692	**********	**********
23	**********	**********	0.3085	**********	**********	**********
24	**********	**********	0.0347	0.1167	0.1600	0.1333
25	**********	**********	0.1722	**********	**********	**********
26	0.0625	**********	**********	0.0389	0.0326	**********
27	**********	**********	**********	**********	0.0303	0.0773
A	**********	**********	0.0317	0.1615	0.1100	0.1000
B	0.0969	0.1824	**********	0.0480	0.1037	0.2267
C	0.2000	0.0500	0.0929	**********	**********	**********
D	**********	0.2817	**********	0.2000	**********	0.0952
E	0.1436	**********	**********	**********	0.0278	0.0429
F	0.1235	**********	0.1463	**********	0.1000	0.0357
G	0.1270	0.0750	**********	0.0875	**********	0.0833
H	**********	**********	0.2597	0.3810	0.2600	**********
I	**********	**********	**********	**********	**********	**********
J	0.3040	**********	**********	**********	0.0421	**********
K	0.1000	**********	**********	0.0500	0.1400	0.0786
L	0.1391	0.1071	**********	**********	0.0220	0.1125
M	0.4750	**********	0.1452	**********	0.0293	**********
N	0.1000	0.1067	0.0615	0.1385	0.0424	**********
O	0.1625	0.0687	0.0625	**********	0.0687	0.0389
P	0.0152	0.2188	0.0562	0.1389	**********	0.1304
Q	0.0290	0.4828	0.0545	0.0938	**********	0.0261
R	0.0462	**********	0.0368	**********	0.0520	**********
T	0.0684	0.0545	0.0529	**********	**********	**********
U	0.0500	**********	0.0417	**********	0.0559	**********
V	0.0750	0.0714	0.0900	0.0800	0.1080	0.1750
W	0.1750	0.2195	0.0857	**********	**********	**********
SHIP	**********	**********	**********	0.2500	**********	**********

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        RATIOS       Cd/S.P., %      1968

STATION    MAY 21/22   JUNE 6    JUNE 20     JULY 9    AUG. 8    AUG. 29

   1        0.0417    0.0029    0.0256    C.C375**********    0.0081
   2        0.0160**********    0.0049    0.0375    0.0081    0.0272
   3    ******************************    C.0374**********    0.0174
   4        0.0230********************    0.0093    0.0072    0.0055
   5        0.0279    0.0059    0.0036    0.0758**********    0.0029
   6        0.0092    0.0C40    0.0042    C.0096    0.0047    0.0056
   7    ********************    0.0024    C.C3C1    0.0063    C.0C57
   8        0.0242**********    0.0024    0.0124    0.0088**********
   9        0.0325    0.0C61    0.C09C    C.0128********************
  10        0.0205**********    0.0015******************************
  11        0.0158    0.0255    0.C026******************************
  12        0.0547    0.0061****************************************
  13        0.0250    0.0160****************************************
  14    ************************************************************
  15        0.0326**************************************************
  16        0.0087    0.0058****************************************
  17        0.0182**************************************************
  18    **********    0.0198**********    C.0203********************
  19        0.0164**************************************************
  20        0.0167    0.0062    C.C886    C.C167    0.0081**********
  21    ********************    0.C390    0.C818********************
  22    ********************    0.0279    C.0200********************
  23    ********************    0.0439    C.1C37********************
  24    ******************************    0.0219    0.0421    C.0123
  25    ********************    0.C383******************************
  26        0.0074********************    0.0111    0.C177**********
  27    ****************************************    0.0119    C.0246
   A    ********************    0.0142    0.0296    0.0080    0.0271
   B        0.0274    0.0146**********    C.0114    0.0117    C.0159
   C        0.0246    0.0109    0.0087**********    0.0174**********
   D    **********    0.0077**********    C.0367**********    0.0106
   E        0.0389******************************    0.0049    C.0044
   F        0.0137    0.0C49    0.0071**********    0.0059    C.0023
   G        0.0351    C.0050**********    C.CC92**********    C.0105
   H    ********************    0.0085    0.CC93    0.0143    C.0188
   I    ************************************************************
   J        0.0458**********    0.0042**********    0.0048**********
   K        0.0130**********    0.0033    C.0117    0.0089    C.0C82
   L        0.0178    0.0066********************    0.0080    0.0124
   M        0.0273    0.0C46    0.0C49**********    0.0100**********
   N        C.CC99    0.0070    0.0076    0.0105    0.0091**********
   O        0.0319    0.0C54    C.C038**********    0.0063    C.0C39
   P        0.0035    0.0137    0.0031    C.C490**********    0.0140
   Q        0.0138    0.0C87    0.0015    0.0138**********    C.0026
   R        0.0168**********    0.0029**********    0.C100**********
   T        0.0141    C.0079    0.0111******************************
   U        0.0120**********    0.0083**********    0.0130**********
   V        0.0395    0.0038    0.0189    C.0060    C.0138    0.0236
   W        0.0267    0.0058    0.0056******************************
  SHIP  ************************************************************
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RATIOS Ca/SO_2' 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	**********	**********	**********	**********	**********	**********
2	**********	**********	**********	**********	**********	**********
3	**********	**********	**********	C.7536	**********	**********
4	**********	**********	**********	**********	**********	**********
5	3.0000	0.4167	**********	1.0417	**********	**********
6	**********	**********	**********	**********	**********	**********
7	**********	**********	4.0000	**********	12.0000	**********
8	**********	**********	**********	**********	0.8889	**********
9	**********	**********	**********	**********	**********	**********
10	**********	**********	**********	**********	**********	**********
11	6.0000	**********	0.4000	**********	**********	**********
12	**********	**********	**********	**********	**********	**********
13	**********	**********	**********	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	**********	**********	**********	**********	**********	**********
16	**********	**********	**********	**********	**********	**********
17	**********	**********	**********	**********	**********	**********
18	**********	**********	**********	**********	**********	**********
19	**********	**********	**********	**********	**********	**********
20	**********	**********	**********	**********	**********	**********
21	**********	**********	15.0000	36.COCC	**********	**********
22	**********	**********	29.0000	**********	**********	**********
23	**********	**********	7.2500	28.CCCO	**********	**********
24	**********	**********	**********	7.0000	8.0CCC	**********
25	**********	**********	**********	**********	**********	**********
26	0.2941	**********	**********	1.7500	1.5556	**********
27	**********	**********	**********	**********	**********	**********
A	**********	**********	2.0000	2.6250	3.6667	7.2500
B	2.2143	31.0000	**********	C.3429	9.3333	1.3C77
C	0.5185	0.3529	1.3000	**********	5.7500	**********
D	**********	C.2985	**********	C.7333	**********	1.8182
E	**********	**********	**********	**********	**********	**********
F	2.1CC0	0.2564	1.3333	**********	1.2222	0.1471
G	1.4687	0.2000	**********	2.3333	**********	C.9375
H	**********	**********	0.6452	0.8889	0.7429	11.6667
I	**********	**********	**********	**********	**********	**********
J	10.8571	**********	1.5714	**********	1.3333	**********
K	0.2500	**********	0.5714	1.0000	0.5833	**********
L	1.3913	1.0000	**********	**********	C.6667	**********
M	38.0000	**********	1.5000	**********	1.1333	**********
N	14.0000	**********	0.6400	C.7500	3.5000	**********
O	52.0000	**********	0.5000	**********	3.6667	C.3500
P	5.0000	**********	**********	25.CCCO	**********	6.000C
Q	1.1250	1.7500	0.1176	2.1429	**********	0.1364
R	1.4118	**********	0.1373	**********	6.5000	**********
T	13.0000	6.0000	0.7500	**********	**********	**********
U	**********	**********	**********	**********	**********	**********
V	**********	**********	**********	**********	**********	**********
W	8.7500	1.0000	C.9231	**********	**********	**********
SHIP	**********	**********	**********	**********	**********	**********

RATIOS Pb/Cd 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	39.5833	160.0000	36.6667	8.3333	**********	91.6667
2	246.1538	**********	176.4706	66.6667	207.6923	76.0000
3	**********	**********	**********	36.5385	**********	82.7586
4	96.5517	**********	**********	166.0000	200.0000	212.5000
5	35.8974	93.0000	180.0000	7.4000	**********	171.4286
6	153.8461	115.0000	231.2500	46.6667	366.6665	153.8461
7	**********	**********	337.5000	11.3793	225.0000	180.0000
8	93.3333	**********	360.0000	84.6154	162.5000	**********
9	66.6667	74.2857	48.3333	115.7895	**********	**********
10	112.5000	**********	260.0000	216.6667	**********	**********
11	158.3333	28.2051	283.3333	**********	**********	**********
12	55.7143	61.8182	**********	**********	**********	**********
13	186.6667	56.6667	**********	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	86.6667	**********	**********	**********	**********	**********
16	400.0000	91.1111	**********	**********	**********	**********
17	100.0000	**********	**********	**********	**********	**********
18	**********	19.4118	**********	35.3846	**********	84.2105
19	35.5555	**********	**********	**********	**********	77.1429
20	64.6154	120.0000	14.1026	61.9048	130.0000	48.0000
21	**********	**********	36.6667	13.3333	**********	**********
22	**********	**********	51.7241	38.1818	**********	**********
23	**********	**********	24.1379	5.0000	**********	**********
24	**********	**********	88.2353	67.1429	20.0000	52.0000
25	**********	**********	14.8387	**********	**********	**********
26	260.0000	**********	**********	102.8571	54.2857	**********
27	**********	**********	**********	**********	40.0000	47.0588
A	**********	**********	270.0000	85.7143	309.0908	151.7241
B	122.5806	67.7419	**********	63.3333	150.0000	123.5294
C	167.8571	46.6667	184.6154	**********	104.3478	**********
D	**********	120.0000	**********	72.7273	**********	135.0000
E	71.4286	**********	**********	**********	100.0000	109.5238
F	295.2380	210.0000	266.6665	**********	281.8181	800.0000
G	95.7447	211.1111	**********	107.1429	**********	213.3333
H	**********	**********	165.0000	92.5000	123.0769	125.7143
I	**********	**********	**********	**********	**********	**********
J	81.5789	**********	218.1818	**********	287.5000	**********
K	255.0000	**********	250.0000	41.6667	164.2857	172.7273
L	103.1250	100.0000	**********	**********	200.0000	88.8889
M	152.6316	233.3333	200.0000	**********	129.4118	**********
N	335.7141	150.0000	212.5000	67.7778	157.1429	**********
O	115.3846	109.0909	210.0000	**********	154.5454	185.7143
P	1000.0000	57.1429	411.1111	24.0000	**********	93.3333
Q	129.6296	46.4286	383.3333	46.6667	**********	266.6665
R	150.0000	**********	314.2856	**********	130.7692	**********
T	223.0769	116.6667	222.2222	**********	**********	**********
U	411.1111	**********	320.0000	**********	152.6316	**********
V	88.8889	171.4286	119.4444	166.6667	100.0000	71.4286
W	128.5714	90.0000	191.6667	**********	**********	**********
SHIP	**********	**********	**********	29.6000	**********	**********

RATIOS Pb/Cu 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	26.0274	2.7586	2.8947	0.6667	9.2857	4.4000
2	10.6667	16.3636	2.7273	10.6667	14.2105	13.5714
3	**********	4.1667	1.4286	2.9231	2.8049	0.9600
4	3.0769	0.6667	8.8000	10.2469	3.7931	4.2500
5	1.1667	0.3207	3.1579	5.9677	2.4074	6.3158
6	0.9091	0.1243	0.2056	0.2333	2.0952	0.4762
7	**********	**********	2.8125	2.5385	2.7835	2.8125
8	0.2692	0.0759	0.3333	0.5238	0.3824	0.1196
9	0.2647	0.1106	0.0630	0.2973	0.1333	0.0473
10	0.4000	0.0491	0.5200	0.5200	0.0259	0.0500
11	6.5517	1.5068	4.3590	**********	**********	**********
12	**********	2.6154	4.4444	**********	**********	**********
13	71.7949	2.3611	17.0588	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	5.9091	2.0000	14.6667	**********	**********	**********
16	25.4545	4.5556	**********	**********	**********	**********
17	8.0000	2.1818	14.6667	4.8421	65.5172	9.4366
18	1.6667	1.3750	2.3437	2.8750	**********	11.4286
19	0.7442	0.6212	0.9474	**********	1.9718	22.5000
20	5.6000	3.2727	7.8571	7.6471	18.5714	9.2308
21	**********	**********	11.0000	6.9565	8.5333	**********
22	**********	**********	5.1724	6.4615	15.1515	**********
23	**********	**********	7.4468	**********	4.9000	5.8333
24	**********	**********	3.0612	7.8333	3.2000	6.9333
25	**********	**********	2.5556	5.3125	2.0930	**********
26	16.2500	**********	3.5556	4.0000	1.7674	2.0000
27	**********	**********	**********	0.8182	1.2121	3.6364
A	101.4493	**********	8.5714	13.8462	34.0000	15.1724
B	11.8750	12.3529	33.3333	3.0400	15.5556	28.0000
C	33.5714	2.3333	17.1429	26.2500	**********	28.3333
D	22.6667	33.8028	10.0000	14.5455	18.5000	12.8571
E	10.2564	**********	**********	**********	2.7778	4.6939
F	36.4706	**********	39.0244	**********	28.1818	28.5714
G	12.1622	15.8333	52.1739	9.3750	**********	17.7778
H	3.6170	50.0000	42.8571	35.2381	32.0000	**********
I	**********	**********	**********	**********	**********	10.9091
J	24.8000	7.2500	**********	**********	12.1053	**********
K	25.5000	**********	**********	2.0833	23.0000	13.5714
L	14.3478	10.7143	28.7879	**********	4.3902	10.0000
M	72.5000	**********	29.0323	**********	3.7931	50.5618
N	33.5714	16.0000	13.0769	9.3846	6.6667	15.3846
O	18.7500	7.5000	13.1250	3.9231	10.6250	7.2222
P	15.1515	12.5000	23.1250	3.3333	7.3913	12.1739
Q	3.7634	22.4138	20.9091	4.3750	**********	6.9565
R	6.9231	**********	11.5789	**********	6.8000	**********
T	15.2632	6.3636	11.7647	30.7692	**********	**********
U	20.5555	8.3333	13.3333	44.0000	8.5294	**********
V	6.6667	12.2449	10.7500	13.3333	10.8000	12.5000
W	22.5000	19.7561	16.4286	**********	11.0000	13.3333
SHIP	**********	**********	**********	7.4000	**********	**********

RATIOS Pb/S.P., % 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	1.6522	0.4706	0.9402	0.3125	0.6566	0.7432
2	3.9506	0.8257	0.8721	2.5000	1.6770	2.0652
3	**********	0.7634	1.1719	1.3669	1.5541	1.4371
4	2.2222	0.9790	1.7187	1.5370	1.4474	1.1724
5	1.0000	0.5503	0.6475	0.5606	0.8333	0.4959
6	1.4085	0.4577	0.9686	0.4480	1.7187	0.8584
7	**********	**********	0.8133	0.3420	1.4136	1.0345
8	2.2581	0.6111	0.8571	1.0476	1.4286	0.9016
9	2.1687	0.4522	0.4328	1.4865	1.3115	0.4862
10	2.3077	0.2385	0.3939	**********	0.7000	0.5729
11	2.5000	0.7190	0.7456	**********	**********	**********
12	3.0469	0.3799	0.9639	**********	**********	**********
13	4.6667	0.9091	1.1373	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	2.8261	0.3529	2.2000	**********	**********	**********
16	3.5000	0.5325	**********	**********	**********	**********
17	1.8182	0.4404	1.8803	0.6479	**********	**********
18	0.4592	0.3837	0.7009	0.7188	0.5882	**********
19	0.5818	0.4184	0.5143	**********	0.3043	**********
20	1.0769	0.7500	1.2500	1.0317	1.0484	**********
21	**********	**********	1.4286	1.0909	1.6000	**********
22	**********	**********	1.4423	0.7636	2.0408	**********
23	**********	**********	1.0606	0.5185	1.2564	1.2281
24	**********	**********	**********	1.4687	0.8421	0.6420
25	**********	**********	0.5679	**********	0.4186	**********
26	1.9118	**********	1.5000	1.1429	0.9620	1.0222
27	**********	**********	**********	0.5510	0.4762	1.1594
A	7.9545	0.8046	3.8298	2.5352	2.4638	4.1121
B	3.3628	0.9906	1.9828	0.7238	1.7573	1.9626
C	4.1228	0.5091	1.6000	1.2857	1.8182	2.4460
D	2.7200	0.9195	1.3684	2.6667	1.5226	1.4362
E	2.7778	**********	**********	**********	0.4918	0.4832
F	4.0523	1.0194	1.8935	**********	1.6757	1.8349
G	3.3582	1.0497	2.0930	0.9868	**********	2.2378
H	3.4000	0.6818	1.4043	0.8605	1.7582	2.3656
I	**********	**********	**********	**********	**********	1.3260
J	3.7349	0.4244	0.9266	**********	1.3855	**********
K	3.3117	0.6835	0.8163	0.4854	1.4557	1.4179
L	1.8333	0.6550	1.0556	0.5116	1.6000	1.1009
M	4.1727	1.0769	0.9836	0.3878	1.2941	2.3077
N	3.3099	1.0435	1.6114	0.7093	1.4286	1.4706
O	3.6810	0.5854	0.7985	0.4722	0.9770	0.7303
P	3.5461	0.7843	1.2937	1.1765	0.9605	1.3084
Q	1.7949	0.4037	0.5637	0.6422	**********	0.6809
R	2.5175	**********	0.9129	0.2818	1.3077	**********
T	3.1522	0.9211	2.4691	1.1940	**********	**********
U	4.9333	0.8721	2.6446	1.4865	1.9863	**********
V	3.5088	0.6452	2.2632	1.0000	1.3776	1.6892
W	3.4351	0.5226	1.0648	**********	1.3665	1.5135
SHIP	**********	**********	**********	**********	**********	**********

RATIOS Pb/SO_2 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	**********	**********	**********	**********	**********	**********
2	**********	**********	**********	**********	**********	**********
3	**********	47.6190	48.3871	27.5362	766.6665	**********
4	**********	**********	**********	**********	**********	**********
5	107.6923	38.7500	**********	7.7083	325.0000	**********
6	**********	**********	**********	**********	**********	**********
7	**********	**********	1350.0000	**********	2700.0000	**********
8	**********	**********	**********	**********	144.4444	**********
9	**********	**********	**********	**********	**********	**********
10	**********	**********	**********	**********	**********	**********
11	950.0000	**********	113.3333	**********	**********	**********
12	**********	**********	**********	**********	**********	**********
13	**********	**********	**********	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	**********	**********	**********	**********	**********	**********
16	**********	**********	**********	**********	**********	**********
17	**********	**********	**********	**********	**********	**********
18	**********	**********	**********	**********	**********	**********
19	**********	**********	360.0000	**********	**********	**********
20	**********	**********	**********	**********	**********	**********
21	**********	**********	550.0000	480.0000	640.0000	**********
22	**********	**********	1500.0000	**********	333.3333	**********
23	**********	**********	175.0000	140.0000	122.5000	63.6364
24	**********	**********	**********	470.0000	160.0000	**********
25	**********	**********	**********	**********	**********	**********
26	76.4706	**********	120.0000	180.0000	84.4444	**********
27	**********	**********	**********	**********	**********	**********
A	93.3333	280.0000	540.0000	225.0000	1133.3333	1100.0000
B	271.4285	2100.0000	85.1852	21.7143	1400.0000	161.5385
C	87.0370	16.4706	240.0000	630.0000	600.0000	566.6665
D	154.5454	35.8209	21.6667	53.3333	284.6152	245.4545
E	**********	**********	**********	**********	**********	**********
F	620.0000	53.8461	355.5554	**********	344.4443	117.6470
G	140.6250	42.2222	**********	250.0000	**********	200.0000
H	62.9630	12.7660	106.4516	82.2222	91.4286	1466.6665
I	**********	**********	**********	**********	**********	**********
J	885.7141	870.0000	342.8569	**********	383.3333	**********
K	63.7500	79.1667	142.8571	41.6667	95.8333	**********
L	143.4783	100.0000	65.5172	220.0000	133.3333	**********
M	5800.0000	**********	300.0000	380.0000	146.6667	140.6250
N	4700.0000	**********	136.0000	50.8333	550.0000	51.2820
O	6000.0000	**********	105.0000	127.5000	566.6665	65.0000
P	5000.0000	**********	**********	600.0000	850.0000	560.0000
Q	145.8333	81.2500	45.0980	100.0000	**********	36.3636
R	211.7647	**********	43.1373	77.5000	850.0000	**********
T	2900.0000	700.0000	166.6667	66.6667	**********	**********
U	**********	**********	**********	**********	**********	**********
V	**********	**********	**********	**********	**********	**********
W	1125.0000	90.0000	176.9231	**********	100.0000	140.0000
SHIP	**********	**********	**********	**********	**********	**********

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          RATIOS           Cu/Cd        1968

STATION  MAY 21/22    JUNE 6   JUNE 20    JULY 9    AUG. 8   AUG. 29

   1        1.5208   58.0000   12.6667   12.5000**********   20.8333
   2       23.0769**********   64.7059    6.2500   14.6154    5.6000
   3    ******************************   12.5000**********   86.2069
   4       31.3793********************   16.2000   52.7273   50.0000
   5       30.7692  290.0000   57.0000    1.2400**********   27.1429
   6      169.2308  925.0000 1125.0000  200.0000  175.0000  323.0769
   7    ********************  120.0000    4.4828   80.8333   64.0000
   8      346.6665********** 1080.0000  161.5385  425.0000**********
   9      251.8518  671.4285  766.6665  389.4736********************
  10      281.2500**********  500.0000  416.6665********************
  11       24.1667   18.7179   65.0000******************************
  12    **********   23.6364****************************************
  13        2.6000   24.0000****************************************
  14    ************************************************************
  15       14.6667**************************************************
  16       15.7143   20.0000****************************************
  17       12.5000**************************************************
  18    **********   14.1176**********   12.3077**********    7.3684
  19       47.7778****************************************    3.4286
  20       11.5385   36.6667    1.7949    8.0952    7.0000    5.2000
  21    ********************    3.3333    1.9167********************
  22    ********************   10.0000    5.9091********************
  23    ********************    3.2414******************************
  24    ********************   28.8235    8.5714    6.2500    7.5000
  25    ********************    5.8065******************************
  26       16.0000********************   25.7143   30.7143**********
  27    ****************************************   33.0000   12.9412
  A     ********************   31.5000    6.1905    9.0909   10.0000
  B        10.3226    5.4839**********   20.8333    9.6429    4.4118
  C         5.0000   20.0000   10.7692******************************
  D     **********    3.5500**********    5.0000**********   10.5000
  E         6.9643******************************   36.0000   23.3333
  F         8.0952**********    6.8333**********   10.0000   28.0000
  G         7.8723   13.3333**********   11.4286**********   12.0000
  H     ********************    3.8500    2.6250    3.8462**********
  I     ************************************************************
  J         3.2895******************************   23.7500**********
  K        10.0000********************   20.0000    7.1429   12.7273
  L         7.1875    9.3333********************   45.5555    8.8889
  M         2.1 53**********    6.8889**********   34.1176**********
  N        10.0000    9.3750   16.2500    7.2222   23.5714**********
  O         6.1538   14.5455   16.0000**********   14.5455   25.7143
  P        66.0000    4.5714   17.7778    7.2000**********    7.6667
  Q        34.4444    2.0714   18.3333   10.6667**********   38.3333
  R        21.6667**********   27.1429**********   19.2308**********
  T        14.6154   18.3333   18.8889******************************
  U        20.0000**********   24.0000**********   17.8947**********
  V        13.3333   14.0000   11.1111   12.5000    9.2593    5.7143
  W         5.7143    4.5556   11.6667******************************
  SHIP  ******************************    4.0000********************
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RATIOS Cu/Pb 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	0.0384	0.3625	0.3455	1.5000	0.1077	0.2273
2	0.0938	0.0611	0.3667	0.0938	0.0704	0.0737
3	**********	0.2400	0.7000	0.3421	0.3565	1.0417
4	0.3250	1.5000	0.1136	0.0976	0.2636	0.2353
5	0.8571	3.1183	0.3167	0.1676	0.4154	0.1583
6	1.1000	8.0435	4.8649	4.2857	0.4773	2.1000
7	**********	**********	0.3556	0.3939	0.3593	0.3556
8	3.7143	13.1818	3.0000	1.9091	2.6154	8.3636
9	3.7778	9.0385	15.8621	3.3636	7.5000	21.1321
10	2.5000	20.3846	1.9231	1.9231	38.5714	20.0000
11	0.1526	0.6636	0.2294	**********	**********	**********
12	**********	0.3824	0.2250	**********	**********	**********
13	0.0139	0.4235	0.0586	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	0.1692	0.5000	0.0682	**********	**********	**********
16	0.0393	0.2195	**********	**********	**********	**********
17	0.1250	0.4583	0.0682	0.2065	0.0153	0.1060
18	0.6000	0.7273	0.4267	0.3478	**********	0.0875
19	1.3437	1.6098	1.0556	**********	0.5071	0.0444
20	0.1786	0.3056	0.1273	0.1308	0.0538	0.1083
21	**********	**********	0.0909	0.1437	0.1172	**********
22	**********	**********	0.1933	0.1548	0.0660	**********
23	**********	**********	0.1343	**********	0.2041	0.1714
24	**********	**********	0.3267	0.1277	0.3125	0.1442
25	**********	**********	0.3913	0.1882	0.4778	**********
26	0.0615	**********	0.2813	0.2500	0.5658	0.5000
27	**********	**********	**********	1.2222	0.8250	0.2750
A	0.0099	**********	0.1167	0.0722	0.0294	0.0659
B	0.0842	0.0810	0.0300	0.3289	0.0643	0.0357
C	0.0298	0.4286	0.0583	0.0381	**********	0.0353
D	0.0441	0.0296	0.1000	0.0687	0.0541	0.0778
E	0.0975	**********	**********	**********	0.3600	0.2130
F	0.0274	**********	0.0256	**********	0.0355	0.0350
G	0.0822	0.0632	0.0192	0.1067	**********	0.0562
H	0.2765	0.0200	0.0233	0.0284	0.0312	**********
I	**********	**********	**********	**********	**********	0.0917
J	0.0403	0.1379	**********	**********	0.0826	**********
K	0.0392	**********	**********	0.4800	0.0435	0.0737
L	0.0697	0.0933	0.0347	**********	0.2278	0.1000
M	0.0138	**********	0.0344	**********	0.2636	0.0198
N	0.0298	0.0625	0.0765	0.1066	0.1500	0.0450
O	0.0533	0.1333	0.0762	0.2549	0.0941	0.1385
P	0.0660	0.0800	0.0432	0.3000	0.1353	0.0821
Q	0.2657	0.0446	0.0478	0.2286	**********	0.1437
R	0.1444	**********	0.0864	**********	0.1471	**********
T	0.0655	0.1571	0.0850	0.0325	**********	**********
U	0.0486	0.1200	0.0750	0.0227	0.1172	**********
V	0.1500	0.0817	0.0930	0.0750	0.0926	0.0800
W	0.0444	0.0506	0.0609	**********	0.0909	0.0750
SHIP	**********	**********	**********	0.1351	**********	**********

RATIOS Cu/S.P., % 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	0.0635	0.1706	0.3248	0.4688	0.0707	0.1689
2	0.3704	0.0505	0.3198	0.2344	0.1180	0.1522
3	**********	0.1832	0.8203	0.4676	0.5541	1.4970
4	0.7222	1.4685	0.1953	0.1500	0.3816	0.2759
5	0.8571	1.7160	0.2050	0.0939	0.3462	0.0785
6	1.5493	3.6816	4.7120	1.9200	0.8203	1.8026
7	**********	**********	0.2892	0.1347	0.5079	0.3678
8	8.3871	8.0556	2.5714	2.0000	3.7363	7.5410
9	8.1928	4.0870	6.8657	5.0000	9.8361	10.2752
10	5.7692	4.8624	0.7576	**********	27.0000	11.4583
11	0.3816	0.4771	0.1711	**********	**********	**********
12	**********	0.1453	0.2169	**********	**********	**********
13	0.0650	0.3850	0.0667	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	0.4783	0.1765	0.1500	**********	**********	**********
16	0.1375	0.1169	**********	**********	**********	**********
17	0.2273	0.2018	0.1282	0.1338	**********	**********
18	0.2755	0.2791	0.2991	0.2500	**********	**********
19	0.7818	0.6735	0.5429	**********	0.1543	**********
20	0.1923	0.2292	0.1591	0.1349	0.0565	**********
21	**********	**********	0.1299	0.1568	0.1875	**********
22	**********	**********	0.2788	0.1182	0.1347	**********
23	**********	**********	0.1424	**********	0.2564	0.2105
24	**********	**********	**********	0.1875	0.2632	0.0926
25	**********	**********	0.2222	**********	0.2000	**********
26	0.1176	**********	0.4219	0.2857	0.5443	0.5111
27	**********	**********	**********	0.6735	0.3929	0.3188
A	0.0784	**********	0.4468	0.1831	0.0725	0.2710
B	0.2832	0.0802	0.0595	0.2381	0.1130	0.0701
C	0.1228	0.2182	0.0933	0.0490	**********	0.0863
D	0.1200	0.0272	0.1368	0.1833	0.0823	0.1117
E	0.2708	**********	**********	**********	0.1770	0.1029
F	0.1111	**********	0.0485	**********	0.0595	0.0642
G	0.2761	0.0663	0.0401	0.1053	**********	0.1259
H	0.9400	0.0136	0.0328	0.0244	0.0549	**********
I	**********	**********	**********	**********	**********	0.1215
J	0.1506	0.0585	**********	**********	0.1145	**********
K	0.1299	**********	**********	0.2330	0.0633	0.1045
L	0.1278	0.0611	0.0367	**********	0.3644	0.1101
M	0.0576	**********	0.0339	**********	0.3412	0.0456
N	0.0986	0.0652	0.1232	0.0756	0.2143	0.0956
O	0.1963	0.0780	0.0608	0.1204	0.0920	0.1011
P	0.2340	0.0627	0.0559	0.3529	0.1299	0.1075
Q	0.4769	0.0180	0.0270	0.1468	**********	0.0979
R	0.3636	**********	0.0788	**********	0.1923	**********
T	0.2065	0.1447	0.2099	0.0388	**********	**********
U	0.2400	0.1047	0.1983	0.0338	0.2329	**********
V	0.5263	0.0527	0.2105	0.0750	0.1276	0.1351
W	0.1527	0.0265	0.0648	**********	0.1242	0.1135
SHIP	**********	**********	**********	**********	**********	**********

RATIOS Cu/SO_2 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	**********	**********	**********	**********	**********	**********
2	**********	**********	**********	**********	**********	**********
3	**********	11.4286	33.8710	9.4203	273.3333	**********
4	**********	**********	**********	**********	**********	**********
5	92.3077	120.8333	**********	1.2917	135.0000	**********
6	**********	**********	**********	**********	**********	**********
7	**********	**********	480.0000	**********	970.0000	**********
8	**********	**********	**********	**********	377.7776	**********
9	**********	**********	**********	**********	**********	**********
10	**********	**********	**********	**********	**********	**********
11	145.0000	**********	26.0000	**********	**********	**********
12	**********	**********	**********	**********	**********	**********
13	**********	**********	**********	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	**********	**********	**********	**********	**********	**********
16	**********	**********	**********	**********	**********	**********
17	**********	**********	**********	**********	**********	**********
18	**********	**********	**********	**********	**********	**********
19	**********	**********	380.0000	**********	**********	**********
20	**********	**********	**********	**********	**********	**********
21	**********	**********	50.0000	69.0000	75.0000	**********
22	**********	**********	290.0000	**********	22.0000	**********
23	**********	**********	23.5000	**********	25.0000	10.9091
24	**********	**********	**********	60.0000	50.0000	**********
25	**********	**********	**********	**********	**********	**********
26	4.7059	**********	33.7500	45.0000	47.7778	**********
27	**********	**********	**********	**********	**********	**********
A	0.9200	**********	63.0000	16.2500	33.3333	72.5000
B	22.8571	170.0000	2.5556	7.1429	90.0000	5.7692
C	2.5926	7.0588	14.0000	24.0000	**********	20.0000
D	6.8182	1.0597	2.1667	3.6667	15.3846	19.0909
E	**********	**********	**********	**********	**********	**********
F	17.0000	**********	9.1111	**********	12.2222	4.1176
G	11.5625	2.6667	**********	26.6667	**********	11.2500
H	17.4074	0.2553	2.4839	2.3333	2.8571	**********
I	**********	**********	**********	**********	**********	**********
J	35.7143	120.0000	**********	**********	31.6667	**********
K	2.5000	**********	**********	20.0000	4.1667	**********
L	10.0000	9.3333	2.2759	**********	30.3704	**********
M	80.0000	**********	10.3333	**********	38.6667	2.7812
N	140.0000	**********	10.4000	5.4167	82.5000	3.3333
O	320.0000	**********	8.0000	32.5000	53.3333	9.0000
P	330.0000	**********	**********	180.0000	115.0000	46.0000
Q	38.7500	3.6250	2.1569	22.8571	**********	5.2273
R	30.5882	**********	3.7255	**********	125.0000	**********
T	190.0000	110.0000	14.1667	2.1667	**********	**********
U	**********	**********	**********	**********	**********	**********
V	**********	**********	**********	**********	**********	**********
W	50.0000	4.5556	10.7692	**********	9.0909	10.5000
SHIP	**********	**********	**********	**********	**********	**********

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         RATIOS    S.P./Cd X 0.01    1968

STATION  MAY 21/22    JUNE 6   JUNE 20    JULY 9    AUG. 8   AUG. 29

   1       23.9583  340.0000   39.0000   26.6667**********  123.3333
   2       62.3077**********  202.3529   26.6667  123.8461   36.8000
   3    ******************************   26.7308**********   57.5862
   4       43.4483********************  108.0000  138.1818  181.2500
   5       35.8974  169.0000  278.0000   13.2000**********  345.7141
   6      109.2308  251.2500  238.7500  104.1667  213.3333  179.2308
   7    ********************  415.0000   33.2758  159.1667  174.0000
   8       41.3333**********  420.0000   80.7692  113.7500**********
   9       30.7407  164.2857  111.6667   77.8947********************
  10       48.7500**********  660.0000******************************
  11       63.3333   39.2308  380.0000******************************
  12       18.2857  162.7273****************************************
  13       40.0000   62.3333****************************************
  14     ************************************************************
  15       30.6667**************************************************
  16      114.2857  171.1111****************************************
  17       55.0000**************************************************
  18    **********   50.5882**********   49.2308********************
  19       61.1111**************************************************
  20       60.0000  160.0000   11.2821   60.0000  124.0000**********
  21    ********************   25.6667   12.2222********************
  22    ********************   35.8621   50.0000********************
  23    ********************   22.7586    9.6429********************
  24    ******************************   45.7143   23.7500   81.0000
  25    ********************   26.1290******************************
  26      136.0000********************   90.0000   56.4286**********
  27    ****************************************   84.0000   40.5882
   A    ********************   70.5000   33.8095  125.4545   36.8965
   B       36.4516   68.3871**********   87.5000   85.3571   62.9412
   C       40.7143   91.6667  115.3846**********   57.3913**********
   D    **********  130.5000**********   27.2727**********   94.0000
   E       25.7143******************************  203.3333  226.6667
   F       72.8571  206.0000  140.8333**********  168.1818  436.0000
   G       28.5106  201.1111**********  108.5714**********   95.3333
   H    ********************  117.5000  107.5000   70.0000   53.1429
   I    ************************************************************
   J       21.8421**********  235.4545**********  207.5000**********
   K       77.0000**********  306.2500   85.8333  112.8571  121.8182
   L       56.2500  152.6667********************  125.0000   80.7407
   M       36.5789  216.6667  203.3333**********  100.0000**********
   N      101.4286  143.7500  131.8750   95.5555  110.0000**********
   O       31.3461  186.3636  263.0000**********  158.1818  254.2857
   P      282.0000   72.8571  317.7776   20.4000**********   71.3333
   Q       72.2222  115.0000  680.0000   72.6667**********  391.6665
   R       59.5833**********  344.2856**********  100.0000**********
   T       70.7692  126.6667   90.0000******************************
   U       83.3333**********  121.0000**********   76.8421**********
   V       25.3333  265.7141   52.7778  166.6667   72.5926   42.2857
   W       37.4286  172.2222  180.0000******************************
SHIP    ************************************************************
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RATIOS S.P./Pb X 0.01 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	0.6053	2.1250	1.0636	3.2000	1.5231	1.3455
2	0.2531	1.2111	1.1467	0.4000	0.5963	0.4842
3	**********	1.3100	0.8533	0.7316	0.6435	0.6958
4	0.4500	1.0214	0.5818	0.6506	0.6909	0.8529
5	1.0000	1.8172	1.5444	1.7838	1.2000	2.0167
6	0.7100	2.1848	1.0324	2.2321	0.5818	1.1650
7	**********	**********	1.2296	2.9242	0.7074	0.9667
8	0.4429	1.6364	1.1667	0.9545	0.7000	1.1091
9	0.4611	2.2115	2.3103	0.6727	0.7625	2.0566
10	0.4333	4.1923	2.5385	**********	1.4286	1.7455
11	0.4000	1.3909	1.3412	**********	**********	**********
12	0.3282	2.6324	1.0375	**********	**********	**********
13	0.2143	1.1000	0.8793	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	0.3538	2.8333	0.4545	**********	**********	**********
16	0.2857	1.8780	**********	**********	**********	**********
17	0.5500	2.2708	0.5318	1.5435	**********	**********
18	2.1778	2.6061	1.4267	1.3913	1.7000	**********
19	1.7187	2.3902	1.9444	**********	3.2857	**********
20	0.9286	1.3333	0.8000	0.9692	0.9538	**********
21	**********	**********	0.7000	0.9167	0.6250	**********
22	**********	**********	0.6933	1.3095	0.4900	**********
23	**********	**********	0.9429	1.9286	0.7959	0.8143
24	**********	**********	**********	0.6809	1.1875	1.5577
25	**********	**********	1.7609	**********	2.3889	**********
26	0.5231	**********	0.6667	0.8750	1.0395	0.9783
27	**********	**********	**********	1.8148	2.1000	0.8625
A	0.1257	1.2429	0.2611	0.3944	0.4059	0.2432
B	0.2974	1.0095	0.5043	1.3816	0.5690	0.5095
C	0.2426	1.9643	0.6250	0.7778	0.5500	0.4088
D	0.3676	1.0875	0.7308	0.3750	0.6568	0.6963
E	0.3600	**********	**********	**********	2.0333	2.0696
F	0.2468	0.9810	0.5281	**********	0.5968	0.5450
G	0.2978	0.9526	0.4778	1.0133	**********	0.4469
H	0.2941	1.4667	0.7121	1.1622	0.5687	0.4227
I	**********	**********	**********	**********	**********	0.7542
J	0.2677	2.3563	1.0792	**********	0.7217	**********
K	0.3020	1.4632	1.2250	2.0600	0.6870	0.7053
L	0.5455	1.5267	0.9474	1.9545	0.6250	0.9083
M	0.2397	0.9286	1.0167	2.5789	0.7727	0.4333
N	0.3021	0.9583	0.6206	1.4098	0.7000	0.6800
O	0.2717	1.7083	1.2524	2.1176	1.0235	1.3692
P	0.2820	1.2750	0.7730	0.8500	1.0412	0.7643
Q	0.5571	2.4769	1.7739	1.5571	**********	1.4687
R	0.3972	**********	1.0955	3.5484	0.7647	**********
T	0.3172	1.0857	0.4050	0.8375	**********	**********
U	0.2027	1.1467	0.3781	0.6727	0.5034	**********
V	0.2850	1.5500	0.4419	1.0000	0.7259	0.5920
W	0.2911	1.9136	0.9391	**********	0.7318	0.6607
SHIP	**********	**********	**********	**********	**********	**********

RATIOS S.P./Cu X 0.01 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	15.7534	5.8621	3.0789	2.1333	14.1429	5.9200
2	2.7000	19.8182	3.1273	4.2667	8.4737	6.5714
3	**********	5.4583	1.2190	2.1385	1.8049	0.6680
4	1.3846	0.6810	5.1200	6.6667	2.6207	3.6250
5	1.1667	0.5828	4.8772	10.6452	2.8889	12.7368
6	0.6455	0.2716	0.2122	0.5208	1.2190	0.5548
7	**********	**********	3.4583	7.4231	1.9691	2.7187
8	0.1192	0.1241	0.3889	0.5000	0.2676	0.1326
9	0.1221	0.2447	0.1457	0.2000	0.1017	0.0973
10	0.1733	0.2057	1.3200	**********	0.0370	0.0873
11	2.6207	2.0959	5.8462	**********	**********	**********
12	**********	6.8846	4.6111	**********	**********	**********
13	15.3846	2.5972	15.0000	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	2.0909	5.6667	6.6667	**********	**********	**********
16	7.2727	8.5556	**********	**********	**********	**********
17	4.4000	4.9545	7.8000	7.4737	**********	**********
18	3.6296	3.5833	3.3437	4.0000	**********	**********
19	1.2791	1.4848	1.8421	**********	6.4789	**********
20	5.2000	4.3636	6.2857	7.4118	17.7143	**********
21	**********	**********	7.7000	6.3768	5.3333	**********
22	**********	**********	3.5862	8.4615	7.4242	**********
23	**********	**********	7.0213	**********	3.9000	4.7500
24	**********	**********	**********	5.3333	3.8000	10.8000
25	**********	**********	4.5000	**********	5.0000	**********
26	8.5000	**********	2.3704	3.5000	1.8372	1.9565
27	**********	**********	**********	1.4848	2.5455	3.1364
A	12.7536	**********	2.2381	5.4615	13.8000	3.6897
B	3.5312	12.4706	16.8116	4.2000	8.8519	14.2667
C	8.1429	4.5833	10.7143	20.4167	**********	11.5833
D	8.3333	36.7606	7.3077	5.4545	12.1500	8.9524
E	3.6923	**********	**********	**********	5.6481	9.7143
F	9.0000	**********	20.6097	**********	16.8182	15.5714
G	3.6216	15.0833	24.9275	9.5000	**********	7.9444
H	1.0638	73.3333	30.5195	40.9524	18.2000	**********
I	**********	**********	**********	**********	**********	8.2273
J	6.6400	17.0833	**********	**********	8.7368	**********
K	7.7000	**********	**********	4.2917	15.8000	9.5714
L	7.8261	16.3571	27.2727	**********	2.7439	9.0833
M	17.3750	**********	29.5161	**********	2.9310	21.9101
N	10.1429	15.3333	8.1154	13.2308	4.6667	10.4615
O	5.0937	12.8125	16.4375	8.3077	10.8750	9.8889
P	4.2727	15.9375	17.8750	2.8333	7.6957	9.3043
Q	2.0968	55.5172	37.0909	6.8125	**********	10.2174
R	2.7500	**********	12.6842	**********	5.2000	**********
T	4.8421	6.9091	4.7647	25.7692	**********	**********
U	4.1667	9.5556	5.0417	29.6000	4.2941	**********
V	1.9000	18.9796	4.7500	13.3333	7.8400	7.4000
W	6.5500	37.8049	15.4286	**********	8.0500	8.8095
•SHIP	**********	**********	**********	**********	**********	**********

RATIOS S.P./SO_2 X 0.01 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	**********	**********	**********	**********	**********	**********
2	**********	**********	**********	**********	**********	**********
3	**********	62.3810	41.2903	20.1449	493.3333	**********
4	**********	**********	**********	**********	**********	**********
5	107.6923	70.4167	**********	13.7500	390.0000	**********
6	**********	**********	**********	**********	**********	**********
7	**********	**********	1660.0000	**********	1910.0000	**********
8	**********	**********	**********	**********	101.1111	**********
9	**********	**********	**********	**********	**********	**********
10	**********	**********	**********	**********	**********	**********
11	380.0000	**********	152.0000	**********	**********	**********
12	**********	**********	**********	**********	**********	**********
13	**********	**********	**********	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	**********	**********	**********	**********	**********	**********
16	**********	**********	**********	**********	**********	**********
17	**********	**********	**********	**********	**********	**********
18	**********	**********	**********	**********	**********	**********
19	**********	**********	700.0000	**********	**********	**********
20	**********	**********	**********	**********	**********	**********
21	**********	**********	385.0000	440.0000	400.0000	46.4286
22	**********	**********	1040.0000	**********	163.3333	**********
23	**********	**********	165.0000	270.0000	97.5000	51.8182
24	**********	**********	**********	320.0000	190.0000	**********
25	**********	**********	**********	**********	**********	**********
26	40.0000	**********	80.0000	157.5000	87.7778	**********
27	**********	**********	**********	**********	**********	**********
A	11.7333	348.0000	141.0000	88.7500	460.0000	267.5000
B	80.7143	2120.0000	42.9630	30.0000	796.6665	82.3077
C	21.1111	32.3529	150.0000	490.0000	330.0000	231.6667
D	56.8182	38.9552	15.8333	20.0000	186.9231	170.9091
E	**********	**********	**********	**********	**********	**********
F	153.0000	52.8205	187.7778	**********	205.5555	64.1176
G	41.8750	40.2222	**********	253.3333	**********	89.3750
H	18.5185	18.7234	75.8064	95.5555	52.0000	620.0000
I	**********	**********	**********	**********	**********	**********
J	237.1429	2050.0000	370.0000	**********	276.6665	**********
K	19.2500	115.8333	175.0000	85.8333	65.8333	**********
L	78.2609	152.6667	62.0690	430.0000	83.3333	**********
M	1390.0000	**********	305.0000	980.0000	113.3333	60.9375
N	1420.0000	**********	84.4000	71.6667	385.0000	34.8718
O	1630.0000	**********	131.5000	270.0000	580.0000	89.0000
P	1410.0000	**********	**********	510.0000	885.0000	428.0000
Q	81.2500	201.2500	80.0000	155.7143	**********	53.4091
R	84.1176	**********	47.2549	275.0000	650.0000	**********
T	920.0000	760.0000	67.5000	55.8333	47.1429	**********
U	**********	**********	**********	**********	**********	**********
V	**********	**********	**********	**********	**********	**********
W	327.5000	172.2222	166.1538	**********	73.1818	92.5000
SHIP	**********	**********	**********	**********	**********	**********

RATIOS SO_2/Ca 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	**********	**********	**********	**********	**********	**********
2	**********	**********	**********	**********	**********	**********
3	**********	**********	**********	1.3269	**********	**********
4	**********	**********	**********	**********	**********	**********
5	0.3333	2.4000	**********	0.9600	**********	**********
6	**********	**********	**********	**********	**********	**********
7	**********	**********	0.2500	**********	0.0833	**********
8	**********	**********	**********	**********	1.1250	**********
9	**********	**********	**********	**********	**********	**********
10	**********	**********	**********	**********	**********	**********
11	0.1667	**********	2.5000	**********	**********	**********
12	**********	**********	**********	**********	**********	**********
13	**********	**********	**********	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	**********	**********	**********	**********	**********	**********
16	**********	**********	**********	**********	**********	**********
17	**********	**********	**********	**********	**********	**********
18	**********	**********	**********	**********	**********	**********
19	**********	**********	**********	**********	**********	**********
20	**********	**********	**********	**********	**********	**********
21	**********	**********	0.0667	0.0278	**********	**********
22	**********	**********	0.0345	**********	**********	**********
23	**********	**********	0.1379	0.0357	**********	**********
24	**********	**********	**********	0.1429	0.1250	**********
25	**********	**********	**********	**********	**********	**********
26	3.4000	**********	**********	0.5714	0.6429	**********
27	**********	**********	**********	**********	**********	**********
A	**********	**********	0.5000	0.3810	0.2727	0.1379
B	0.4516	0.0323	**********	2.9167	0.1071	0.7647
C	1.9286	2.8333	0.7692	**********	0.1739	**********
D	**********	3.3500	**********	1.3636	**********	0.5500
E	**********	**********	**********	**********	**********	**********
F	0.4762	3.9000	0.7500	**********	0.8182	6.8000
G	0.6809	5.0000	**********	0.4286	**********	1.0667
H	**********	**********	1.5500	1.1250	1.3462	0.0857
I	**********	**********	**********	**********	**********	**********
J	0.0921	**********	0.6364	**********	0.7500	**********
K	4.0000	**********	1.7500	1.0000	1.7143	**********
L	0.7188	1.0000	**********	**********	1.5000	**********
M	0.0263	**********	0.6667	**********	0.8824	**********
N	0.0714	**********	1.5625	1.3333	0.2857	**********
O	0.0192	**********	2.0000	**********	0.2727	2.8571
P	0.2000	**********	**********	0.0400	**********	0.1667
Q	0.8889	0.5714	8.5000	0.4667	**********	7.3333
R	0.7083	**********	7.2857	**********	0.1538	**********
T	0.0769	0.1667	1.3333	**********	**********	**********
U	**********	**********	**********	**********	**********	**********
V	**********	**********	**********	**********	**********	**********
W	0.1143	1.0000	1.0833	**********	**********	**********
SHIP	**********	**********	**********	**********	**********	**********

RATIOS SO_2/Pb 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	**********	**********	**********	**********	**********	**********
2	**********	**********	**********	**********	**********	**********
3	**********	0.0210	0.0207	0.0363	0.0013	**********
4	**********	**********	**********	**********	**********	**********
5	0.0093	0.0258	**********	0.1297	0.0031	**********
6	**********	**********	**********	**********	**********	**********
7	**********	**********	0.0007	**********	0.0004	**********
8	**********	**********	**********	**********	0.0069	**********
9	**********	**********	**********	**********	**********	**********
10	**********	**********	**********	**********	**********	**********
11	0.0011	**********	0.0088	**********	**********	**********
12	**********	**********	**********	**********	**********	**********
13	**********	**********	**********	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	**********	**********	**********	**********	**********	**********
16	**********	**********	**********	**********	**********	**********
17	**********	**********	**********	**********	**********	**********
18	**********	**********	**********	**********	**********	**********
19	**********	**********	0.0028	**********	**********	**********
20	**********	**********	**********	**********	**********	**********
21	**********	**********	0.0018	0.0021	0.0016	**********
22	**********	**********	0.0007	**********	0.0030	**********
23	**********	**********	0.0057	0.0071	0.0082	0.0157
24	**********	**********	**********	0.0021	0.0062	**********
25	**********	**********	**********	**********	**********	**********
26	0.0131	**********	0.0083	0.0056	0.0118	**********
27	**********	**********	**********	**********	**********	**********
A	0.0107	0.0036	0.0019	0.0044	0.0009	0.0009
B	0.0037	0.0005	0.0117	0.0461	0.0007	0.0062
C	0.0115	0.0607	0.0042	0.0016	0.0017	0.0018
D	0.0065	0.0279	0.0462	0.0187	0.0035	0.0041
E	**********	**********	**********	**********	**********	**********
F	0.0016	0.0186	0.0028	**********	0.0029	0.0085
G	0.0071	0.0237	**********	0.0040	**********	0.0050
H	0.0159	0.0783	0.0094	0.0122	0.0109	0.0007
I	**********	**********	**********	**********	**********	**********
J	0.0011	0.0011	0.0029	**********	0.0026	**********
K	0.0157	0.0126	0.0070	0.0240	0.0104	**********
L	0.0070	0.0100	0.0153	0.0045	0.0075	**********
M	0.0002	**********	0.0033	0.0026	0.0068	0.0071
N	0.0002	**********	0.0074	0.0197	0.0018	0.0195
O	0.0002	**********	0.0095	0.0078	0.0018	0.0154
P	0.0002	**********	**********	0.0017	0.0012	0.0018
Q	0.0069	0.0123	0.0222	0.0100	**********	0.0275
R	0.0047	**********	0.0232	0.0129	0.0012	**********
T	0.0003	0.0014	0.0060	0.0150	**********	**********
U	**********	**********	**********	**********	**********	**********
V	**********	**********	**********	**********	**********	**********
W	0.0009	0.0111	0.0057	**********	0.0100	0.0071
SHIP	**********	**********	**********	**********	**********	**********

RATIOS SO_2/Cu 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	**********	**********	**********	**********	**********	**********
2	**********	**********	**********	**********	**********	**********
3	**********	0.0875	0.0295	0.1062	0.0037	**********
4	**********	**********	**********	**********	**********	**********
5	0.0108	0.0083	**********	0.7742	0.0074	**********
6	**********	**********	**********	**********	**********	**********
7	**********	**********	0.0021	**********	0.0010	**********
8	**********	**********	**********	**********	0.0026	**********
9	**********	**********	**********	**********	**********	**********
10	**********	**********	**********	**********	**********	**********
11	0.0069	**********	0.0385	**********	**********	**********
12	**********	**********	**********	**********	**********	**********
13	**********	**********	**********	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	**********	**********	**********	**********	**********	**********
16	**********	**********	**********	**********	**********	**********
17	**********	**********	**********	**********	**********	**********
18	**********	**********	**********	**********	**********	**********
19	**********	**********	0.0026	**********	**********	**********
20	**********	**********	**********	**********	**********	**********
21	**********	**********	0.0200	0.0145	0.0133	**********
22	**********	**********	0.0034	**********	0.0455	**********
23	**********	**********	0.0426	**********	0.0400	0.0917
24	**********	**********	**********	0.0167	0.0200	**********
25	**********	**********	**********	**********	**********	**********
26	0.2125	**********	0.0296	0.0222	0.0209	**********
27	**********	**********	**********	**********	**********	**********
A	1.0870	**********	0.0159	0.0615	0.0300	0.0138
B	0.0437	0.0059	0.3913	0.1400	0.0111	0.1733
C	0.3857	0.1417	0.0714	0.0417	**********	0.0500
D	0.1467	0.9437	0.4615	0.2727	0.0650	0.0524
E	**********	**********	**********	**********	**********	**********
F	0.0588	**********	0.1098	**********	0.0818	0.2429
G	0.0865	0.3750	**********	0.0375	**********	0.0889
H	0.0574	3.9167	0.4026	0.4286	0.3500	**********
I	**********	**********	**********	**********	**********	**********
J	0.0280	0.0083	**********	**********	0.0316	**********
K	0.4000	**********	**********	0.0500	0.2400	**********
L	0.1000	0.1071	0.4394	**********	0.0329	**********
M	0.0125	**********	0.0968	**********	0.0259	0.3596
N	0.0071	**********	0.0962	0.1846	0.0121	0.3000
O	0.0031	**********	0.1250	0.0308	0.0187	0.1111
P	0.0030	**********	**********	0.0056	0.0087	0.0217
Q	0.0258	0.2759	0.4636	0.0437	**********	0.1913
R	0.0327	**********	0.2684	**********	0.0080	**********
T	0.0053	0.0091	0.0706	0.4615	**********	**********
U	**********	**********	**********	**********	**********	**********
V	**********	**********	**********	**********	**********	**********
W	0.0200	0.2195	0.0929	**********	0.1100	0.0952
SHIP	**********	**********	**********	**********	**********	**********

RATIOS SO_2/S.P. , % 1968

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUG. 8	AUG. 29
1	**********	**********	**********	**********	**********	**********
2	**********	**********	**********	**********	**********	**********
3	**********	0.0160	0.0242	0.0496	0.0020	**********
4	**********	**********	**********	**********	**********	**********
5	0.0093	0.0142	**********	0.0727	0.0026	**********
6	**********	**********	**********	**********	**********	**********
7	**********	**********	0.0006	**********	0.0005	**********
8	**********	**********	**********	**********	0.0099	**********
9	**********	**********	**********	**********	**********	**********
10	**********	**********	**********	**********	**********	**********
11	0.0026	**********	0.0066	**********	**********	**********
12	**********	**********	**********	**********	**********	**********
13	**********	**********	**********	**********	**********	**********
14	**********	**********	**********	**********	**********	**********
15	**********	**********	**********	**********	**********	**********
16	**********	**********	**********	**********	**********	**********
17	**********	**********	**********	**********	**********	**********
18	**********	**********	**********	**********	**********	**********
19	**********	**********	0.0014	**********	**********	**********
20	**********	**********	**********	**********	**********	**********
21	**********	**********	0.0026	0.0023	0.0025	0.0215
22	**********	**********	0.0010	**********	0.0061	**********
23	**********	**********	0.0061	0.0037	0.0103	0.0193
24	**********	**********	**********	0.0031	0.0053	**********
25	**********	**********	**********	**********	**********	**********
26	0.0250	**********	0.0125	0.0063	0.0114	**********
27	**********	**********	**********	**********	**********	**********
A	0.0852	0.0029	0.0071	0.0113	0.0022	0.0037
B	0.0124	0.0005	0.0233	0.0333	0.0013	0.0121
C	0.0474	0.0309	0.0067	0.0020	0.0030	0.0043
D	0.0176	0.0257	0.0632	0.0500	0.0053	0.0059
E	**********	**********	**********	**********	**********	**********
F	0.0065	0.0189	0.0053	**********	0.0049	0.0156
G	0.0239	0.0249	**********	0.0039	**********	0.0112
H	0.0540	0.0534	0.0132	0.0105	0.0192	0.0016
I	**********	**********	**********	**********	**********	**********
J	0.0042	0.0005	0.0027	**********	0.0036	**********
K	0.0519	0.0086	0.0057	0.0117	0.0152	**********
L	0.0128	0.0066	0.0161	0.0023	0.0120	**********
M	0.0007	**********	0.0033	0.0010	0.0088	0.0164
N	0.0007	**********	0.0118	0.0140	0.0026	0.0287
O	0.0006	**********	0.0076	0.0037	0.0017	0.0112
P	0.0007	**********	**********	0.0020	0.0011	0.0023
Q	0.0123	0.0050	0.0125	0.0064	**********	0.0187
R	0.0119	**********	0.0212	0.0036	0.0015	**********
T	0.0011	0.0013	0.0148	0.0179	0.0212	**********
U	**********	**********	**********	**********	**********	**********
V	**********	**********	**********	**********	**********	**********
W	0.0031	0.0058	0.0060	**********	0.0137	0.0108
SHIP	**********	**********	**********	**********	**********	**********

IV.2.2 Fortran Program for Computing Ratios and Histograms

```
$SIGNON SN87 7=1M   P=100

$RUN *FORTRAN
           DIMENSION DAT(6,50,5),DUM(6,50,20),IDAT(6,50,5),D(300,5)
           DIMENSION R(300,20),X(10) ,STUT (2,20),BID(20)
          DIMENSION FREQ(20),PCT(20),STATS(5),REAL(300),UBO(3),S(300)
           READ(5,100)(((DAT(I,J,K),I=1,6),J=1,50),K=1,5)
100        FORMAT(6F10.0)
           DO82 K=1,5
           SUM=0.
           DO 10 I=1,6
           DO 10 J=1,50
           SUM=SUM +DAT(I,J,K)
           IF(DAT(I,J,K))85,11,85
11         DAT(I,J,K)= 0.0000001
85         IF(K-4)10,86,10
86         DAT(I,J,K)=10.*DAT(I,J,K)
10         IDAT(I,J,K)=DAT(I,J,K )
82         CONTINUE
           DO12 K=1,5
           WRITE(6,101)
           WRITE(6,102 )
101        FORMAT(//40H1    ELEMENT:         1968    NG-M-3        )
102        FORMAT(/70H STATION   MAY 21/22    JUNE 6   JUNE 20     JULY
     19   AUG. 8   AUG. 29     /)
103        FORMAT( I6,2X,6I10)
12         WRITE(6,103)(J,(IDAT(I,J,K),I=1,6),J=1,50)
           JO=1
           DO 14 I=1,6
           DO 14 J=1,50
           DO 13 K=1,5
13         D(JO,K)=DAT(I,J,K)
14         JO=JO+1
          NN=JO-1
           CALL RATIO(D,R,NN)
           DO 17 K=1,20
           JIM=1
           DO 16 I=1,50
           JILL=JIM
           DO 15 JO=1,6
           DUM(JO,I,K)=R(JILL,K)
15         JILL=JILL+50
16         JIM=JIM+1
           WRITE(6,104)
           WRITE(6,102)
104        FORMAT(//41H1          RATIOS           /          1968
           WRITE(6,105)(I,(DUM(JO,I,K),JO=1,6),I=1,50)
105        FORMAT(I6 ,3X,6F10.4)
17         CONTINUE
           HAB=0
           DO 44 J=1,20
           DO 44 I=1,2
44         STUT(I,J)=10.
45         CONTINUE
           WRITE (6,312)
312        FORMAT(1H1)
           DO 41 J=1,20
           KOT=1
           DO 40 I=1,300
           IF(HAB)71,72,71
```

```
71            IF(R(I,J)-STUT(1,J))40,74,74
74            IF(R(I,J)-STUT(2,J))42,42,40
72            CONTINUE
              IF(R(I,J)-10000.)42,40,40
42            REAL(KOT)=R(I,J)
              KOT=KOT+1
40            S(KOT)=1.0
              KOT=KOT-1
             POT=KOT
              NOVAR=1
              UBO(1)=10.
              UBO(3)=10.
              IF(HAB)65,66,65
65            POT=BID(J)
66            TEMP=5.*(ALOG(POT)/2.30) +2.
77            UBO(2)=TEMP
222           FORMAT(1X,F10.2)
              IBO=UBO(2)
              UBO(2)=IBO
              CALL TAB1(REAL,S,1,UBO,FREQ,PCT,STATS,KOT,1)
              WRITE(6,204)
204           FORMAT(//31H2      HISTOGRAM OF RATIOS     /        /)
              WRITE(6,201)
              WRITE(6,200)(STATS(I),I=1,5)
              B=0.
              C=0.
              DIT=(STATS(5)-STATS(4))/(IBO-2)
              WRITE(6,207)DIT
207           FORMAT( 27H              INTERVAL VALUES=     ,F10.4)
              WRITE(6,203)
              LO=0
              DO 43 I=1,IBO
              WRITE(6,202)I,FREQ(I),PCT(I)
              IF(PCT(I)-6.)61,61,62
62            B=B+FREQ(I)
              BID(J)=B
              IF(LO)63,64,63
64            STUT(1,J)=STATS(4)+(I-2)*DIT
63            LO=LO+1
              STUT (2,J)=STATS(4)+(I-1)*DIT
61            C=PCT(I)+C
43            CONTINUE
              IB=B
              WRITE(6,205)
              WRITE(6,206)KOT,C
205           FORMAT( 35H    TOTAL         ------           ------      )
206           FORMAT(10X, I10 ,5X,F10.1)
              WRITE(6,222) B
41            CONTINUE
              HAB=HAB + 1
              IF(HAB-4)45,45,46
46            CONTINUE
201           FORMAT( 50H     TOTAL      MEAN     STAN DEV      MIN         MAX
     1     /)
200           FORMAT(1X,5F10.4//)
202           FORMAT( I7, 3X,F10.0,5X,F10.1)
203           FORMAT( /38H INTERVAL     FREQUENCY       PERCENT      )
              END
```

```
      SUBROUTINE RATIO (D,R,NN)
      DIMENSION R(300,20), D(300,5)   ,X(10)
C     NN= NUMBER OF STATIONS...DETERMINS SIZE, NO OF ROWS, OF IN
C     PUT ARRAY DAND OUTPUT ARRAY R
33    DO30 I=1,300
      DO 30 J=1,20
30    R(I,J)=7777777777.7
       DO 20 I=1,NN
      DO10 J=2,5
      J1=J-1
      IF(D(I,1)-0.5) 11,10,10
10    R(I,J1)=D(I,1)/D(I,J)
11    X(1)=D(I,1)
      X(2)=D(I,3)
      X(3)=D(I,4)
      X(4)=D(I,5)
      DO 12 J=1,4
      J4=J+4
      IF(D(I,2)-0.5) 13,12,12
12    R(I,J4)=D(I,2)/X(J)
13    X(2)=D(I,2)
      DO 14 J=1,4
      J8=J+8
      IF(D(I,3)-0.5) 15,14,14
14    R(I,J8)=D(I,3)/X(J)
15    X(3)=D(I,3)
      DO 16 J=1,4
      J12=J+12
      IF(D(I,4)-0.5) 17,16,16
16    R(I,J12)=D(I,4)/X(J)
17    X(4)=D(I,4)
      DO 18 J=1,4
      J16=J+16
      IF(D(I,5)-0.5) 19,18,18
18    R(I,J16)=D(I,5)/X(J)
19    CONTINUE
20    CONTINUE
      RETURN
      END
$ENDFILE
```

IV.2.3 Raw Data Sets--Computer Input (CDC 160-A)

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
952	-1	100	0	0	100	19	39	100	5	10	0	0
956	-3	200	6	8	200	34	43	200	30	42	0	100
960	-3	100	10	16	100	70	79	100	61	103	0	100
964	-3	100	20	30	100	119	139	100	134	190	0	200
968	-3	200	18	23	200	111	127	200	135	173	0	400
972	-3	500	15	23	500	91	108	500	117	154	0	900
976	-3	1000	15	16	1000	87	100	1000	113	145	0	1900
980	-1	100	5	7	100	10	14	100	8	25	0	0
984	-2	100	10	6	100	55	63	100	55	93	0	100
988	0	50	14	17	500	37	39	500	20	32	670	0
992	-2	100	8	8	100	73	95	100	58	95	0	100
996	0	100	11	16	500	38	50	500	104	136	660	0
1000	1	100	11	15	500	37	41	500	112	158	660	0
1004	-2	100	10	17	100	56	64	100	56	95	0	100
1008	0	100	9	3	500	18	20	500	156	207	605	0
1013	-2	50	18	21	100	50	58	100	52	86	0	100
1017	0	50			200	47	50	200	38	63	525	0
1021	1	50	16	19	100	102	109	100	79	120	525	0
1025	-2	50	16	24	100	59	60	100	48	77	0	100
1029	0	50	18	25	100	102	109	100	121	188	575	0
1033	3	50	20	19	100	45	50	100	42	74	0	100
-111	2	0	0	0	0	0	0	0	0	0	0	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
953	-1	100	4	5	100	24	30	100	6	11	0	0
957	-2	100	12	14	100	66	61	100	45	89	0	100
961	-2	100	12	18	100	65	66	100	46	85	0	100
965	-3	100	21	22	100	122	116	100	97	163	0	200
969	-3	200	18	20	200	126	97	200	101	155	0	400
973	-3	500	15	18	500	87	87	500	98	131	0	900
977	-3	1000	16	17	1000	93	92	1000	112	157	0	1900
981	-1	100	0	1	100	8	12	100	4	6	0	0
985	-2	100	1	16	100	55	63	100	55	93	0	100
989	0	50	3	14	500	64	63	500	14	25	595	0
993	-2	100	0	16	100	52	66	100	42	81	0	100
997	0	100	0	7	500	37	50	500			605	0
1001	1	100	2	20	500	35	42	1000	151	202	605	0
1005	-2	50	2	17	50	97	99	50	84	143	0	200
1009	0	50	20	43	500	33	37	200	67	106	520	0
1014	-2	50	2	28	100	51	50	100	43	76	0	100
1018	0	50	3	28	200	68	61	200	27	48	545	0
1022	1	50	5	22	100	147	145	100	64	114	545	0
1026	-2	50	1	22	100	49	52	100	39	70	0	100
1030	0	50	3	22	100	135	134	100	67	112	570	0
1034	3	50	2	26	100	43	55	100	35	72	0	100
-111	2	0	0	0	0	0	0	0	0	0	0	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
954	-1	100		3	100	22	25	100	6	12	0	0
958	-2	100	8	19	100	90	88	100	81	124	0	100
962	-2	100	8	20	100	91	84	100	85	137	0	100
966	-3	100	20	34	100	162	153	100	182	250	0	200
970	-3	200	21	41	200	156	155	200	189	264	0	400
974	-3	500	19	23	500	132	124	500	165	211	0	900
978	-3	1000	18	18	1000	123	127	1000	160	214	0	1900
982	-1	100	0	5	100	10	11	100	7	17	0	0
986	-2	100	8	17	100	85	87	100	78	97	0	100
990	0	50	10	17	500	70	68	500	24	35	685	0
994	-2	100	5	14	100	73	69	100	73	116	0	100
998	0	100	6	17	500	39	37	1000	164		620	0
1002	1	100	6	19	500	40	48	1000	181	228	620	0
1006	-2	100	5	18	100	70	63	100	77	109	0	100
1010	0	50	16	30	500	40	37	200	52	91	535	0
1015	-2	50	18	32	100	76	68	100	70	105	0	100
1023	1	50	16	32	100	171	158	100	99	160	575	0
1027	-2	50	1	25	100	80	81	100	68	109	0	100
1031	0	50	20	28	500	67	63	500	28	41	670	0
1035	3	50	14	18	100	69	54	100	57	94	0	100
-111	2	0	0	0	0	0	0	0	0	0	0	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
955	-1	100		1	100	21	25	100	3	11	0	0
959	-2	100	3	18	100	85	83	100	62	97	0	100
963	-2	100	3	17	100	95	89	100	63	109	0	100
967	-3	100	16	32	100	156	149	100	137	224	0	200
971	-3	200	18	35	200	147	131	200	154	215	0	400
975	-3	500	15	22	500	118	125	500	133	173	0	900
979	-3	1000	17	34	1000	124	130	1000	148	216	0	1900
983	-1	100	0	7	100	13	18	100	10	16	0	0
987	-2	100	8	23	100	92	82	100	69	123	0	100
991	0	50	13	23	500	96	79	500	107	171	700	0
995	-2	100	2	13	100	81	83	100	57	94	0	100
999	0	100	4	18	500	38	37	1000	103	138	620	0
1003	1	100	4	18	500	38	41	1000	106	125	620	0
1007	-2	100	4	15	100	79	82	100	68	124	0	100
1011	0	50	20	39	100			1000	17	33	575	0
1012	1	50	28	48	1000	42	39	500	39	67	575	0
1016	-2	50	0	16	100	65	64	100	56	96	0	100
1024	1	50	9	27	100	130	124	100	94	165	575	0
1028	-2	50	33	53	100	75	73	100	63	104	0	100
1032	0	50	42	63	500	135	122	500	47	82	600	0
1036	3	50	4	32	100	64	53	100	53	72	0	100

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1066	-2	100	4	37	100	66	140	100	78	218	0	100
1070	-2	100	4	35	100	62	128	100	82	250	0	100
1074	-2	100	11	51	100	123	253	100	169	493	0	200
1078	-3	200	14	45	200	121	246	200	172	498	0	400
1082	-3	200	37	38	200	210	565	500	149	478	0	900
1086	-3	1000	11	34	1000	101	210	1000	148	402	0	1900
1090	-1	100	0	9	100	6	18	100	5	18	0	0
1094	-2	50	14	65	100	66	119	100	74	218	0	100
1098	0	50	6	32	500	128	258	500	107	322	670	0
1102	1	50	7	37	500	125	259	500	115	350	670	0
1106	-2	50	53	133	100	64	131	100	77	241	0	100
1110	0	50	47	125	500	33	65	500			625	0
1117	-2	50	13	54	100	59	116	100	58	201	0	100
121	0	50	12	48	500	96	194	200	43	147	555	0
125	-1	50	0	3	100	9	31	100	3	11	0	0
129	-2	50	11	45	100	55	104	100	51	162	0	100
132	0	50	11	45	200	53	105	200	59	173	575	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1067	-2	100	3	41	100	73	151	100	62	214	0	100
1071	-2	100	3	40	100	72	139	100	64	221	0	100
1075	-3	100	15	53	100	129	243	100	158	560	0	200
1079	-3	200	14	52	200	132	255	200	200	654	0	400
1083	-3	500	13	41	500	106	196	500	173	491	0	900
1087	-3	1000	11	46	1000	97	189	1000	121	429	0	1900
1091	-1	100	0	6	100	7	19	100	3	5	0	0
1095	-2	50	13	67	100	60	110	100	63	218	0	100
1099	0	50	22	76	500	124	229	500			605	0
1103	1	50	23	76	500	124	229	1000			605	0
11052	1	50	12	48	500	67	108	1000	165	461	605	0
1107	-2	50	11	41	100	61	124	100	50	189	0	100
1111	0	50	12	45	500	36	66	500	141	398	610	0
1114	1	50	13	30	500	36	63	1000	68	169	610	0
1118	-2	50	11	55	100	60	108	100	45	171	0	100
1122	0	50	12	49	500			500	8	26	530	0
1126	1	50	11	50	500	75	131	200	32	130	530	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1068	-2	100	10	40	100	76	141	100	75	232	0	100
1072	-2	100	10	41	100	76	137	100	84	203	0	100
1076	-3	100	21	57	100	143	269	100	190	546	0	200
1080	-3	200	20	52	200	144	271	200	174	556	0	400
1084	-3	500	15	46	500	123	229	500	163	432	0	900
1088	-3	1000	15	47	1000	123	234	1000	167	422	0	1900
1092	-1	100	0	12	100	10	28	100	4	14	0	0
1096	-2	50	31	79	100	87	152	100	79	251	0	100
1100	0	50	37	78	500	122	225	1000	29	82	620	0
1104	1	50	35	80	500	116	209	500	76	231	620	0
1108	-2	50	20	58	100	78	148	100	55	155	0	100
1112	0	50	24	57	500	77	135	500	25	83	530	0
1115	0	50	21	55	500	144	264	500	55	171	530	0
1119	-2	50	18	54	100	66	116	100	44	160	0	100
1123	0	50	19	53	200	205	384	200	33	122	565	0
1127	-1	50	0	17	100	15	39	100	2	2	0	0
1130	-2	50	12	51	100	71	126	100	43	161	0	100

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1069	-2	100	4	34	100	65	121	100	50	161	0	100
1073	-2	100	4	33	100	64	119	100	53	174	0	100
1077	-3	100	13	48	100	121	221	100	104	370	0	200
1081	-3	200	13	35	200	115	186	200	119	366	0	400
1085	-3	500	11	39	500	97	186	500	111	310	0	900
1089	-3	1000	11	27	1000	100	184	1000	122	318	0	1900
1093	-1	100	0	1	100	7	25	100	3	11	0	0
1097	-2	50	15	56	100	67	123	100	56	200	0	100
1101	0	50	17	47	500			1000	87	249	600	0
1 11050	1	50	17	50	500	76	138	500	193	576	600	0
1109	-2	50	13	52	100	61	113	100	47	175	0	100
1113	0	50	11	44	500	60	153	500	26	78	540	0
1116	0	50	10	52	500	127	235	500	59	186	540	0
1120	-2	50	13	50	100	59	149	100	37	123	0	100
1124	0	50	14	46	200	87	165	200	39	137	575	0
1128	-1	50	0	8	100	10	36	100	1	1	0	0
1131	-2	50	15	48	100	60	113	100	36	148	0	100

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1150	-1	100	1	7	100	7	31	100	9	45	0	0
1154	-2	100	9	29	100	47	138	100	82	264	0	100
1158	-3	100	13	20	100	84	234	100	171	508	0	200
1162	-3	200	18	45	500	48	152	500	110	300	0	700
1166	-2	50	16	48	100	46	123	100	71	254	0	100
1170	-2	100	14	26	100	64	107	100	111	236	0	100
1174	-2	50	9	100	100	59	129	100	87	344	0	100
1178	0	50	28	199	100	168	345	100	125	410	585	0
1182	-2	50	5	69	100	52	109	100	42	194	0	100
1186	0	50	7	66	100	127	268	100	99	380	300	0
1190	-2	50	7	60	100	49	101	100	56	295	0	100
1194	0	50	12	69	100	72	146	100	77	345	85	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1151	-1	100	3	7	100	7	30	100	6	33	0	0
1155	-2	100	9	28	100	54	156	100	109	315	0	100
1159	-3	100	15	38	100	99	268	100	190	497	0	200
1163	-3	200	17	45	200	145	366	500	113	287	0	700
1167	-2	50	15	48	100	48	110	100	60	230	0	100
1171	-2	100	3	42	100	61	97	100	105	212	0	100
1175	-2	50	10	74	100	59	123	100	106	313	0	100
1179	0	50	17	88	100	186	373	100	58	284	570	0
1183	-2	50	3	53	100	50	107	100	47	214	0	100
1187	0	50	9	65	100	94	196	100	71	290	505	0
1191	-2	50	3	52	100	42	80	100	44	198	0	100
1195	0	50	5	74	500	7	14	500	9	39	640	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1152	-1	100	0	2	100	5	24	100	4	17	0	0
1156	-2	100	1	25	100	43	102	100	72	221	0	100
1160	-3	100	6	32	100	80	176	100	145	412	0	200
1164	-3	200	11	42	200	122	307	500	83	235	0	700
1168	-2	50	5	41	100	38	82	100	56	198	0	100
1172	-2	100	9	40	100	47	139	100	61	310	0	100
1176	-2	50	22	72	100	47	97	100	56	193	0	100
1180	0	50	28	82	100	151	312	100	93	316	515	0
1184	-2	50	7	45	100	33	67	100	41	148	0	100
1188	0	50	8	46	100	114	240	100	85	278	675	0
1192	-2	50	6	41	100	36	73	100	44	159	0	100
1196	0	50	12	51	500	31	62	500	16	61	590	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1153	-1	100	2	4	100	19	80	100	4	13	0	0
1157	-2	100	8	29	100	51	149	100	73	212	0	100
1161	-3	100	14	43	100	83	227	100	153	444	0	200
1165	-3	200	18	57	200	114	254	500	82	204	0	700
1169	-2	50	13	41	100	34	79	100	47	169	0	100
1173	-2	100	1	51	100	47	134	100	76	234	0	100
1177	-2	50	7	44	100	44	95	100	78	235	0	100
1181	0	50	14	67	100	105	220	100	84	270	540	0
1185	-2	50	3	41	100	31	68	100	36	143	0	100
1189	0	50	6	44	200	167	355	200	68	238	302	0
1193	-2	50	7	29	200	15	35	200	19	72	0	100
1197	0	50	31	82	500	44	95	500	46	166	685	0

RUN NC.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1200	-1	100			100	14	30	100	2	6	0	0
1204	-2	100	1	13	100	42	88	100	24	94	0	100
1208	-3	100	7	27	100	84	180	100	74	259	0	200
1212	0	100	108	246	100	96	203	100	104	342	640	0
1216	-2	100	6	20	100	42	83	100	35	140	0	100
1220	0	100	7	23	500	31	73	500	8	30	725	0
1224	1	100	7	24	100	158	332	100	47	177	725	0
1228	-2	50	9	39	100	42	91	100	33	138	0	100
1232	0	50	13	41	500	33	73	200	153	456	640	0
1240	1	50	14	41	200	85	177	200			640	0
1244	-2	50	7	27	100	47	101	100	30	129	0	100
1248	0	50	7	34	100	92	200	100	47	180	575	0
1252	-2	20	21	83	50	74	148	50	53	235	0	100
1256	0	20	101	264	100	67	140	100	29	123	440	0
1260	-2	20	17	64	50	79	166	50	57	252	0	100
1264	0	20	22	91	100	115	238	100	50	181	670	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1201	-1	100			100	7	22	100	2	5	0	0
1205	-2	100	2	20	100	44	102	100	37	147	0	100
1209	-3	100	7	27	100	79	169	100	95	302	0	200
1213	0	100	10	37	100	187	413	100	102	325	590	0
1217	-2	100	3	13	100	38	84	100	36	134	0	100
1221	0	100			100	76	165	100	45	165	635	0
1225	1	100	11	31	100	77	169	100	48	171	635	0
1229	-2	50	8	31	100	27	32	100	34	127	0	100
1233	0	50	14	38	200	129	288	500			645	0
1237	1	50	14	41	200	129	295	500			645	0
1241	1	50	13	43	200	130	286	1000	142	367	645	0
1245	-2	50	7	34	100	37	85	100	34	137	0	100
1249	0	50	6	31	100	156	348	100	63	210	585	0
1253	-2	20	20	74	50	83	186	50	69	272	0	100
12571	0	20	41	120	100	56	122	100	36	144	630	0
1261	-2	20	17	53	50	74	165	50	68	255	0	100
1265	0	20	19	69	100	61	134	100	82	259	555	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1198	-1	100	0	2	100	12	24	100	4	16	0	0
1202	-2	100	2	28	100	61	127	100	46	196	0	100
1206	-3	100	9	46	100	110	218	100	122	435	0	200
1210	0	100	12	54	100	132	271	100	134	496	85	0
1214	-2	100	2	28	100	53	119	100	37	172	0	100
1218	0	100	5	33	100	73	152	100	62	262	640	0
1222	1	100	5	32	100	72	147	100	62	260	640	0
1226	-2	50	9	55	100	48	103	100	37	157	0	100
1230	0	50	14	57	200	67	151	200			715	0
1234	1	50	15	53	200	69	152	500	141	383	715	0
1238	1	50	14	46	100	136	288	500	158	412	715	0
1242	-2	50	8	45	100	48	101	100	36	167	0	100
1246	0	50	10	52	200	41	88	500	120	335	600	0
1250	-2	20	6	88	100	48	101	100	34	156	0	100
1254	0	20	23	120	100	104	216	100	41	202	580	0
1258	-2	20	14	74	50	97	208	50	68	310	0	100
1262	0	20	17	66	100	78	168	100	37	183	300	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1199	-1	100	2	1	100	5	15	100	3	12	0	0
1203	-2	100	8	18	100	45	100	100	43	161	0	100
1207	-3	100	14	39	100	90	189	100	112	360	0	200
1211	0	100	19	49	100	116	224	100	107	351	85	0
1215	-2	100	8	21	100	47	100	100	47	171	0	100
1219	0	100	15	53	500	60	131	500	33	103	685	0
1223	1	100	17	54	200	145	259	200	81	269	685	0
1227	-2	50	4	34	100	43	39	100	42	157	0	100
1231	0	50	25	64	200			500			680	0
1235	1	50	27	74	50			200	42	154	680	0
1239	1	50	24	66	500	172	362	200	50	147	680	0
1243	-2	50	2	26	50	83	180	100	28	113	0	100
1247	0	50	2	34	200	66	141	200	27	99	575	0
1251	-2	20	7	60	50	83	172	50	66	268	0	100
1255	0	20			100	90	189	100	43	166	580	0
12572	1	50	12	96	100	89	187	100	44	175	580	0
1259	-2	20	11	57	50	87	176	50	66	289	0	100
1263	0	20	8	34	100	70	149	100	41	166	530	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1266	-2	50	30	74	100	112	219	100	85	272	0	100
1270	-3	50	54	125	200	94	190	200	98	283	0	200
1274	-3	50	51	130	200	90	178	200	89	274	0	200
1278	0	50	78	160	500			500	114	295	710	0
1282	1	50	73	168	1000	95	199	500	102	238	710	0
1283	-2	50	15	51	100	68	132	100	42	169	0	100
1287	0	50	19	56	500	79	158	200	46	156	650	0
1292	-2	50	14	57	100	14	41	100	5	19	0	100
1296	-3	50	15	54	100	85	168	100	68	233	0	100
1299	0	50	20	66	500	76	164	500	15	48	620	0
1301	-2	50	18	50	50	160	306	50	109	394	0	100
1305	0	50	24	64	500	79	165	200			685	0
1309	1	50	21	66	500	74	156	1000	130	328	685	0
1315	-2	50	11	55	50	157	304	50	106	371	0	100
1319	0	50	13	58	200	78	156	100	62	240	580	0
1324	-2	50	10	53	50	147	145	50	96	346	0	100
1328	0	50	18	63	200	151	314	100	121	406	650	0
1332	1	50	18	60	200	149	288	200	61	195	650	0
1336	1	50	19	75	200	160	302	200	86	245	650	0
-11	2	0	0	0	0	0	0	0	0	0	0	0
1338	-2	50	11	29	50	108	207	50	96	322	0	100
1342	0	50	14	42	500	46	91	500	16	43	640	0
1347	-2	50	9	32	50	101	195	50	65	255	0	100
1351	0	50	8	37	200	60	132	500			555	0
1355	1	50	9	38	200	59	128	1000	167	471	555	0
-11	2	0	0	0	0	0	0	0	0	0	0	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1267	-2	50	17	63	100	100	211	100	49	178	0	100
1271	-3	50	38	120	200	76	148	200	63	196	0	200
1275	-3	50	40	126	200	75	150	200	66	194	0	200
1279	0	50	47	150	500	84	166	500	127	347	610	0
1284	-2	50	11	57	100	73	154	100	51	185	0	100
1288	0	50	19	99	500	98	178	200	42	170	580	0
1293	-2	50	12	93	100	71	136	100	48	174	0	100
1297	0	50	22	102	500	155	313	500	105	270	625	0
1302	-2	50	17	46	50	161	303	50	111	372	0	100
1306	0	50	16	70	200	161	327	500			660	0
1310	1	50	14	63	200	156	310	1000			660	0
1313	1	50	2	47	200	67	195	1000	157	384	660	0
1316	-2	50	9	70	50	144	283	50	97	358	0	100
1320	0	50	11	95	100	124	244	100	102	324	570	0
1325	-2	50	9	60	50	143	283	50	97	352	0	100
1329	0	50	14	83	200	167	323	200	36	132	555	0
1333	1	50	23	64	200	163	310	200	41	131	555	0
1337	1	50	21		200			200	47	154	555	0
-11	2	0	0	0	0	0	0	0	0	0	0	0
1339	-2	50	9	34	50	87	168	50	71	244	0	100
1343	0	50	15	42	500	61	105	500	98	252	630	0
1348	-2	50	8	36	50	84	162	50	56	196	0	100
1352	0	50	9	49	200	55	116	1000	120	340	690	0
-11	2	0	0	0	0	0	0	0	0	0	0	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1268	-2	50	12	36	100	70	170	100	38	131	0	100
1272	-2	50	78	75	50			100	101	386	0	200
1276	-3	50	32	78	100	114	254	100	100	372	0	200
1280	0	50	30	78	500	86	207	500	30	84	710	0
1285	-2	50	12	39	100	58	127	100	34	127	0	100
1289	0	50	14	42	500	77	176	200	71	214	710	0
1294	-2	50	8	39	100	52	118	100	32	116	0	100
1298	0	50	13	40	500	107	258	500	61	171	625	0
1303	-2	50	14	40	50	116	237	50	75	274	0	100
1307	0	50	10	40	200	72	168	500			680	0
1311	1	50	9	43	500	23	53	1000			680	0
1314	1	50	2	27	200	42	112	1000	133	395	680	0
1317	-2	50	6	36	50	105	224	50	71	268	0	100
1321	0	50	7	56	100	131	267	100	40	137	520	0
1326	-2	50	6	41	50	107	223	50	62	238	0	100
1330	0	50	9	43	200	168	380	200	123	361	720	0
1334	1	50	24	36	200	180	429	200	163	492	720	0
-11	2	0	0	0	0	0	0	0	0	0	0	0
1340	-2	50	8	26	50	69	142	50	50	186	0	100
1344	0	50	11	30	500	46	84	500	12	39	690	0
1346	1	50	11	24	200	117	255	200	40	117	690	0
1349	-2	50	7	30	50	80	166	50	47	172	0	100
1353	0	50	7	31	200	35	71	100	42	152	640	0
-11	2	0	0	0	0	0	0	0	0	0	0	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1269	-2	50	19	46	100	69	139	100	47	160	0	100
1273	-2	50	36	84	100	122	241	100	127	363	0	200
1277	-3	50	37	91	100	124	246	100	127	376	0	200
1281	0	50	43	110	500	85	179	500	46	109	635	0
1286	-2	50	14	45	100	61	126	100	34	136	0	100
1291	0	50	21	55	500	94	197	200	66	189	700	0
1295	-2	50	18	52	100	64	130	100	42	156	0	100
1300	0	50	25	70	500	106	222	500	40	101	640	0
1304	-2	50	16	43	50	125	238	50	83	287	0	100
1308	0	50	18	52	200	80	174	500	6	34	570	0
1312	1	50	16	55	100	155	295	100	51	175	570	0
1318	-2	50	10	43	50	125	237	50	73	279	0	100
1322	0	50	18	54	100			100	97	304	610	0
1323	1	50	13	48	200	93	193	100	76	216	610	0
1327	2	50	14	54	50	128	247	50	83	307	0	100
1331	0	50	19	57	200			200	45	133	740	0
1335	1	50	11	60	500	80	170	200	59	154	740	0
-11	2	0	0	0	0	0	0	0	0	0	0	0
1341	-2	50	9	32	50	76	151	50	52	180	0	100
1345	0	50	11	32	500	39	75	1000	92	245	715	0
1350	-2	50	9	30	50	78	151	50	52	186	0	100
1354	0	50	10	29	50	204	413	100			640	0
-11	2	0	0	0	0	0	0	0	0	0	0	0

RUN NO.-	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1376	-2	50	11	95	200			200			0	100
1380	-3	50	41	214	500	63	169	500	103	252	0	200
1384	-3	50	98	320	500	98	257	500	174	446	0	400
1388	-2	50	37	180	200	127	308	200	149	383	0	100
1392	0	50	20	108	500	68	174	1000			555	0
1396	1	50	4	75	500	35	91	1000			555	0
1398	1	50	0	55	200	62	174	1000	180	466	555	0
1399	-2	50	11	102	200	68	178	200	95	308	0	100
1403	0	50	17	116	500	152	400	500			610	0
1407	1	50	20	105	500	151	400	1000	188	506	610	0
1408	-2	50	12	93	100	135	330	200	95	308	0	100
1412	0	50	22	103	500	207	554	500	55	162	540	0
1416	-2	50	14	92	100	173	377	200	75	238	0	100
1420	0	50	16	103	500	46	107	200	98	327	490	0
1424	-2	50	14	101	100	130	317	200	76	223	0	100
1428	0	50	12	88	200	194	488	200	81	242	530	0
1432	-2	50	12	82	100			100	172	545	0	100
1436	0	50	14	89	200	137	338	200	85	256	470	0
1440	-2	50	9	93	100	115	262	100	137	393	0	100
1444	0	50	13	91	200	129	305	200	69	225	450	0
1448	-2	50	8	64	100	108	249	100	127	414	0	100
1452	0	50	11	93	200	142	346	200	74	233	540	0
1457	-2	50	9	67	100	112	255	100	127	404	0	100
1461	0	50	8	59	200	85	196	200	75	207	550	0
1466	-2	50	3	63	100	94	216	100	103	332	0	100
1470	0	50	6	67	500	99	238	200	44	183	440	0
1474	-2	50	8	60	100	125	291	100	140	434	0	100
1478	0	50	12	70	200			200	105	351	425	0
1481	1	50	17	100	500	132	323	200	118	332	425	0
1483	-2	50	17	98	100	128	297	100	153	463	0	100
1487	0	50	19	84	500	101	249	200	108	343	470	0
1492	-2	50	15	77	100	143	336	100	142	469	0	100
1496	-3	50	40	144	200	111	232	200	139	404	0	200
-11	2	0	0	0	0	0	0	0	0	0	0	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1377	-2	50	27	113	200	131	262	200	158	462	0	100
1381	-3	50	60	236	500	71	142	500	84	238	0	200
1385	-3	50	118	353	500	100	206	500	127	347	0	400
1389	-2	50	25	147	200	110	223	200	94	313	0	100
1393	0	50	22	137	500	71	149	1000			690	0
1397	1	50	4	99	500	36	86	1000	180	515	690	0
1400	-2	50	15	96	100	138	290	100	140	439	0	100
1404	0	50	15	135	200	72	161	200	61	201	115	0
1409	-2	50	12	106	100	140	274	100	142	466	0	100
1413	0	50	25	129	500	210	439	200	93	272	420	0
1417	-2	50	14	97	100	124	265	100	121	402	0	100
1421	0	50	32	167	500	144	296	500	28	91	540	0
1425	-2	50	19	124	100	163	340	100	145	473	0	100
1429	0	50	19	127	200	174	367	200	87	272	480	0
1433	-2	50	10	71	100	129	258	100	137	441	0	100
1437	0	50	15	97	500	69	139	200	74	246	410	0
1441	-2	50	12	94	100	125	261	100	132	418	0	100
1445	0	50	22	86	500	93	182	200	90	293	535	0
1449	-2	50	9	65	100	126	261	100	124	391	0	100
1453	0	50	23	95	500	228	487	200	177	254	445	0
1458	-2	50	6	82	50			100	108	349	0	100
1462	0	50	19	68	200			200	65	199	515	0
1465	1	50	20	90	500	140	296	200	75	257	515	0
1467	-2	50	5	73	100	112	244	100	104	349	0	100
1471	0	50	10	54	500	93	193	200	44	179	425	0
1475	-2	50	7	65	100	122	265	100	120	379	0	100
1479	0	50	14	87	500	108	220	200	72	251	450	0
1484	-2	50	20	100	100			100	134	435	0	100
1488	0	50	27	117	500	84	170	200	84	277	515	0
1493	-2	50	17	86	100	128	271	100	132	422	0	100
1497	-3	50	47	152	200	107	224	200	115	344	0	200

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1378	-2	50	13	80	200	74	191	200	105	284	0	100
1382	-3	50	35	142	500	36	84	500	62	156	0	200
1386	-3	50	78	229	500	61	157	500	104	279	0	400
1390	-2	50	10	79	200	49	120	200	60	171	0	100
1394	0	50	7	72	500	55	140	200	79	223	530	0
1401	-2	50	6	59	100			100	102	276	0	100
1405	0	50	7	60	200	213	611	200	72	185	540	0
1410	-2	50	4	64	100	162	400	200	112	309	0	100
1414	0	50	4	56	500	70	175	200	54	143	455	0
1418	-2	50	9	77	100	63	190	100	104	283	0	100
1422	0	50	14	70	500	82	205	500	18	40	550	0
1426	-2	50	8	60	100	85	202	100	110	309	0	100
1430	0	50	5	60	200	101	246	200	57	147	435	0
1434	-2	50	1	45	100	77	180	100	119	320	0	100
1438	0	50	6	55	500	44	104	200	74	205	425	0
1442	-2	50	4	49	100	70	165	100	82	222	0	100
1446	0	50	5	46	500	58	129	200	64	156	495	0
1450	-2	50	7	55	50	172	404	100	88	211	0	100
1454	0	50	7	49	200	186	505	200	50	128	485	0
1459	-2	50	4	49	100	58	120	100	80	224	0	100
1463	0	50	2	31	500	96	270	200	47	131	480	0
1468	-2	50	3	47	100	73	173	100	80	217	0	100
1472	0	50	2	33	500	54	147	100	86	264	435	0
1476	-2	50	6	49	100	88	209	100	118	302	0	100
1480	0	50	11	39	500	121	319	200	79	159	560	0
1485	-2	50	4	27	100	81	168	100	86	248	0	100
1489	0	50	9	47				200	73	174	480	0
1491	1	50	9	49	500	89	239	500	23	48	480	0
1495	-2	50	9	52	100	91	213	100	113	284	0	100
1499	-3	50	25	85	200	67	155	200	97	247	0	200

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1379	-2	50	25	102	200	96	215	200	132	353	0	100
1383	-3	50	51	175	500	48	101	500	69	173	0	200
1387	-3	50	105	268	500	82	178	500	119	308	0	400
1391	-2	50	25	86	200	64	126	200	79	207	0	100
1395	0	50	25	100	200	120	260	200	120	319	640	0
1402	-2	50	19	79	100	113	247	100	128	363	0	100
1406	0	50	24	101	1000	47	99	200	75	230	420	0
1411	-2	50	13	72	100	112	240	100	125	347	0	100
1415	0	50	33	115	500	110	246	200	87	250	495	0
1419	-2	50	30	105	100	113	240	100	152	429	0	100
1423	0	50	36	109	500	112	240	200	96	266	540	0
1427	-2	50	19	80	100	113	231	100	143	393	0	100
1431	0	50	29	94	500	88	180	200	80	240	480	0
1435	-2	50	11	65	100	107	229	100	124	346	0	100
1439	0	50	26	98	200	186	406	200	81	210	555	0
1443	-2	50	15	64	100	103	206	100	126	345	0	100
1447	0	50	20	90	500	76	161	200	80	215	555	0
1451	-2	50	15	61	100	108	224	100	125	335	0	100
1455	0	50	23	75	200			200	84	217	490	0
1456	1	50	27	73	500	113	266	200	102	283	490	0
1460	-2	50	14	59	100	99	216	100	121	336	0	100
1464	0	50	25	80	500	142	320	200	70	199	465	0
1469	-2	50	5	43	100	75	164	100	65	208	0	100
1473	0	50	10	48	500	84	179	200	41	128	480	0
1477	-2	50	14	61	100			100	112	318	0	100
1481	0	50	17	67	500	80	173	200	68	203	445	0
1486	-2	50	26	97	100	95	196	100	102	288	0	100
1490	0	50	33	95	500	106	228	200	67	211	495	0
1494	-2	50	17	68	100	98	213	100	113	321	0	100
1498	-3	50	41	116	200	84	184	200	107	267	0	200

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1500	-1	50	0	53	100	37	108	100	15	70	0	0
1504	-2	50	22	123	100	130	327	100	148	447	0	100
1508	-3	50	53	194	200	110	271	200	152	407	0	200
1512	0	50	81	269	500	233	588	200	211	641	485	0
1516	-2	50	14	100	100	132	324	100	141	432	0	100
1520	0	50	16	109	500	55	137	200	67	247	500	0
1524	-2	50	11	88	100	121	321	100	122	400	0	100
1528	0	50	17	105	200	147	360	100	120	444	490	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1501	-1	50	0	21	50	43	111	50	18	78	0	0
1505	-2	50	9	80	100	102	222	100	92	308	0	100
1509	-3	50	33	136	200	97	234	200	105	297	0	200
1517	-2	50	5	72	100	104	222	100	97	314	0	100
1525	-2	50	15	54	100	129	289	100	124	376	0	100
1529	0	50	22	117	200	126	282	100			465	0
1532	1	50	25	116	200	126	275	200	94	276	465	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1502	-1	50	0	51	50	49	118	50	30	110	0	0
1506	-2	50	19	78	100	109	238	100	111	302	0	100
1510	-3	50	46	136	200	88	190	200	106	272	0	200
1514	0	50	60	171	500	95	200	200	116	325	480	0
1518	-2	50	15	97	100	96	202	100	105	274	0	100
1522	0	50	31	145	500	77	163	200	59	195	520	0
1526	-2	50	20	83	100	124	266	100	124	324	0	100
1530	0	50	20	87	200	80	171	200	58	157	460	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1503	-1	50	0	43	50	33	87	50	15	66	0	0
1507	-2	50	19	86	100	88	191	100	90	269	0	100
1511	-3	50	40	132	200	72	161	200	87	229	0	200
1515	0	50	53	156	500	52	111	200	105	309	490	0
1519	-2	50	12	80	100	89	189	100	90	266	0	100
1523	0	50	28	104	500	65	142	200	60	184	525	0
1527	-2	50	12	69	100	92	202	100	93	268	0	100
1531	0	50	15	67	200	72	164	200	46	140	480	0

RUN NO.	CODE	SCALE	PEAK HITF	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1533	-1	50	0	0	50	50	114	50	21	190	0	0
1537	-2	50	21	45	100	102	223	100	120	365	0	100
1541	-3	50	56	114	200	106	236	200	133	360	0	200
1545	0	50	65	127	500	-0	-0	200	181	460	450	0
1549	1	50	64	120	500	137	305	200	188	506	450	0
1553	-2	50	17	33	100	-0	-0	100	121	345	0	100
1557	-2	50	18	37	100	101	217	100	126	365	0	100
1558	0	50	23	43	500	46	97	200	69	209	425	0
1562	-2	50	26	47	100	118	242	100	125	374	0	100
1566	0	50	30	55	500	75	151	200	71	220	485	0
1570	-2	50	20	35	100	92	191	100	103	306	0	100
1574	0	50	23	36	500	210	443	200	81	237	515	0
1578	-2	50	23	40	100	111	234	100	115	336	0	100
1582	0	50	28	48	500	141	281	200	86	242	510	0
1586	-2	50	13	27	100	96	190	100	111	324	0	100
1590	0	50	15	24	500	103	209	200	86	249	480	0
1594	-2	50	16	24	100	106	232	100	114	327	0	100
1598	0	50	15	28	500	-0	-0	200	84	246	490	0
1602	1	50	17	22	500	122	270	200	96	271	490	0
1606	-2	50	15	31	100	114	237	100	124	370	0	100
1610	0	50	19	33	500	197	425	200	80	235	465	0
1611	-2	50	24	44	100	115	242	100	107	348	0	100
1615	0	50	18	43	500	229	490	200	174	559	510	0
1621	-2	50	12	23	100	106	237	100	95	310	0	100
1625	0	50	13	23	500	125	267	200	77	234	455	0
1629	-2	50	15	29	100	109	232	100	97	309	0	100
1633	0	50	14	26	500	101	210	100	126	396	420	0
1637	-2	50	16	32	100	115	236	100	98	312	0	100
1641	0	50	13	18	500	154	335	100	161	476	500	0
1645	-2	50	9	17	100	93	204	100	86	275	0	100
1649	-3	50	16	50	200	90	188	200	94	255	0	200
1653	-3	50	5	28	200	140	309	200	159	427	0	300
1657	0	50	40	72	500	93	226	1000	-0	-0	660	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKENG
1534	-1	50	-0	-0	50	-0	-0	100	38	142	0	0
1538	-2	50	16	17	100	125	249	100	116	400	0	100
1542	-3	50	49	76	200	108	209	200	120	345	0	200
1546	0	50	-0	-0	500	74	132	200	133	398	450	0
1550	1	50	49	76	500	74	138	200	132	403	450	0
1554	-2	50	17	21	100	130	249	100	128	405	0	100
1559	0	50	20	27	200	110	212	200	67	202	470	0
1563	-2	50	18	24	100	129	248	100	114	368	0	100
1567	0	50	25	33	500	204	386	200	65	227	420	0
1571	-2	50	20	25	100	133	258	100	109	365	0	100
1575	0	50	32	40	500	129	236	200	130	423	540	0
1579	-2	50	28	37	100	132	260	100	111	374	0	100
1583	0	50	38	50	500	161	302	200	61	245	455	0
1587	-2	50	18	23	100	138	275	100	110	370	0	100
1591	0	50	26	31	500	173	162	200	69	258	470	0
1595	-2	50	14	18	100	133	266	100	102	350	0	100
1599	0	50	34	43	500	187	357	200	79	278	480	0
1603	-2	50	16	20	100	140	282	100	106	367	0	100
1607	0	50	18	36	500	232	466	200	66	238	455	0
1612	-2	50	19	22	100	131	259	100	100	350	0	100
1616	0	50	30	40	500	232	447	200	71	252	515	0
1618	1	50	29	37	500	111	206	200	72	256	515	0
1622	-2	50	18	24	100	148	292	100	107	360	0	100
1626	0	50	26	36	500	145	276	200	66	247	480	0
1630	-2	50	13	16	100	132	271	100	88	323	0	100
1634	0	50	18	22	500	100	193	200	69	219	460	0
1638	-2	50	11	13	100	134	260	100	102	352	0	100
1642	0	50	37	50	500	175	338	200	74	258	490	0
1646	-2	50	6	9	100	113	226	100	77	298	0	100
1650	-3	50	34	51	200	112	216	200	82	274	0	200
1654	-3	50	65	94	200	176	347	200	148	438	0	300
1658	0	50	72	107	500	80	159	200	159	490	440	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1535	-1	100	-0	-0	50	39	80	50	50	176	0	0
1539	-2	50	25	41	100	118	217	100	106	339	0	100
1543	-3	50	56	90	200	102	184	200	101	293	0	200
1547	0	50	70	117	500	65	114	200	124	362	460	0
1551	1	50	71	122	200	178	338	200	132	334	460	0
1555	-2	50	24	38	100	107	200	100	100	320	0	100
1560	0	50	26	42	200	147	272	100	106	344	515	0
1564	-2	50	24	38	100	113	201	100	87	284	0	100
1568	0	50	38	61	500	179	327	200	72	229	405	0
1572	-2	50	23	39	100	101	181	100	85	278	0	100
1576	0	50	29	22	500	153	281	200	52	191	465	0
1580	-2	50	23	37	100	108	184	100	93	286	0	100
1584	0	50	32	48	500	157	286	200	131	420	415	0
1588	-2	50	23	37	100	118	234	100	97	305	0	100
1592	0	50	31	47	500	101	183	100	167	484	500	0
1596	-2	50	22	35	100	116	213	100	91	292	0	100
1600	0	50	38	59	500	200	386	200	81	247	450	0
1604	-2	50	20	34	100	117	219	100	91	301	0	100
1608	0	50	33	51	500	155	284	200	73	241	530	0
1613	-2	50	24	42	100	107	195	100	86	278	0	100
1617	0	50	50	81	1000	-0	-0	200	112	292	485	0
1619	1	50	46	73	1000	149	277	200	118	341	485	0
1623	-2	50	24	34	100	136	248	100	97	304	0	100
1627	0	50	37	53	500	113	209	200	70	233	400	0
1631	-2	50	14	38	100	122	232	100	94	307	0	100
1635	0	50	32	51	500	147	273	100	161	459	490	0
1639	-2	50	22	42	100	132	243	100	101	322	0	100
1643	0	50	20	31	500	18	34	100	86	292	515	0
16442	1	50	22	33	100	125	238	100	90	297	515	0
1657	-2	50	18	30	100	106	199	100	81	263	0	100
1651	-3	50	40	66	200	95	178	200	80	237	0	200
1655	-3	50	69	120	200	142	259	200	154	403	0	300
1659	0	50	71	121	500	98	185	1000	236	608	605	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1536	-1	50	-0	-0	50	41	95	50	43	158	0	0
1540	-2	50	23	39	100	102	200	100	96	315	0	100
1544	-3	50	53	92	200	93	174	200	96	282	0	200
1548	0	50	61	108	500	61	120	200	109	338	440	0
1552	1	50	61	108	200	168	334	200	108	310	440	0
1556	-2	50	20	35	100	100	200	100	103	326	0	100
1561	0	50	22	39	200	162	319	100	103	354	500	0
1565	-2	50	21	34	100	103	204	100	96	308	0	100
1569	0	50	34	53	500	113	222	200	28	156	490	0
1573	-2	50	19	31	100	93	178	100	69	262	0	100
1577	0	50	34	30	500	142	279	200	38	183	490	0
1581	-2	50	24	40	100	111	220	100	78	285	0	100
1585	0	50	32	56	500	91	178	200	77	323	410	0
1589	-2	50	31	53	100	119	116	100	68	256	0	100
1593	0	50	40	70	500	112	218	100	124	448	425	0
1597	-2	50	17	29	100	97	194	100	66	251	0	100
1601	0	50	32	54	500	144	290	200	39	180	395	0
1605	-2	50	24	42	100	103	205	100	64	249	0	100
1609	0	50	48	81	500	216	457	200	145	453	510	0
1614	-2	50	33	59	100	96	190	100	57	240	0	100
1620	0	50	51	88	500	167	346	100	63	239	470	0
1624	-2	50	20	33	100	106	217	100	61	250	0	100
1628	0	50	21	35	500	142	285	100	72	296	370	0
1632	-2	50	16	25	100	102	196	100	63	253	0	100
1636	0	50	19	29	500	72	146	100	109	368	450	0
1640	-2	50	18	33	100	109	222	100	67	258	0	100
16441	0	50	15	24	100	204	-0	100	90	324	540	0
16443	1	50	20	33	200	110	219	100	105	366	540	0
1648	-2	50	15	23	100	105	210	100	61	243	0	100
1652	-3	50	37	63	200	89	174	200	67	217	0	200
1656	-3	50	61	106	200	129	265	200	125	358	0	300
1660	0	50	68	116	1000	51	97	200	142	416	480	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1661	-2	50	17	35	100	88	183	100	124	371	0	100
1665	-3	50	32	62	200	73	163	200	114	302	0	200
[illegible]	0	50	42	[illegible]	1000	[illegible]	123	200	[illegible]	[illegible]	670	0
1674	-2	50	8	15	100	77	171	100	79	254	0	100
1678	0	50	14	26	200	213	509	1000	237	576	635	0
1681	1	50	13	24	500	80	186	1000	-0	-0	635	0
1684	-2	50	8	16	100	81	180	100	124	362	0	100
1688	0	50	19	35	500	136	327	200	45	183	515	0
1692	-2	50	5	13	100	71	154	100	75	229	0	100
1696	0	50	6	10	500	60	142	200	47	151	600	0
1700	-2	50	5	10	100	83	173	100	79	250	0	100
1704	0	50	12	21	500	114	270	200	75	240	415	0
1708	-2	50	5	10	100	83	182	100	76	241	0	100
1712	0	50	16	26	500	191	463	500	27	79	485	0
1716	-2	50	5	9	100	78	172	100	73	231	0	100
1720	0	50	12	25	1000	87	206	100	117	474	455	0
1728	-2	50	4	8	100	76	165	100	77	243	0	100
1732	0	50	6	10	500	105	234	100	106	408	525	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1662	-2	50	25	48	100	94	178	100	130	353	0	100
1666	-3	50	38	75	200	78	159	200	116	281	0	200
1670	0	50	43	86	500	179	387	200	160	424	710	0
1675	-2	50	12	27	50	175	362	100	119	315	0	100
1679	0	50	17	33	200	-0	-0	1000	139	335	615	0
1682	1	50	14	29	500	90	189	1000	131	317	615	0
1685	-2	50	11	24	100	81	167	100	119	314	0	100
1689	0	50	19	15	500	200	448	100	126	386	535	0
1693	-2	50	10	22	100	88	174	100	106	278	0	100
1697	0	50	9	19	500	204	465	200	56	164	450	0
1701	-2	50	7	16	100	66	145	100	95	254	0	100
1705	0	50	12	23	500	197	453	200	63	180	510	0
1709	-2	50	6	14	100	67	146	100	99	252	0	100
1713	0	50	10	21	500	140	319	200	70	167	440	0
1717	-2	50	6	14	100	62	133	100	91	244	0	100
1721	0	50	7	14	1000	69	164	100	150	417	470	0
1729	-2	50	3	9	100	66	151	100	111	298	0	100
1733	0	50	5	8	500	109	258	200	69	200	490	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1663	-2	50	35	60	100	131	223	100	123	355	0	100
1667	-3.	50	59	99	200	115	202	200	102	286	0	200
1671	0	50	84	146	500	138	249	200	-0	-0	635	0
1673	1	50	78	129	500	134	245	500	115	248	635	0
1686	-2	50	17	28	100	105	176	100	86	266	0	100
1690	0	50	24	37	200	224	431	100	130	415	535	0
1694	-2	50	22	39	100	119	202	100	84	263	0	100
1698	0	50	35	55	500	203	382	200	73	217	470	0
1702	-2	50	22	36	100	134	231	100	101	302	0	100
1706	0	50	42	67	500	238	476	200	87	256	485	0
1710	-2	50	26	40	100	124	210	100	92	295	0	100
1714	0	50	39	63	1000	236	470	200	66	213	460	0
1718	-2	50	22	36	100	125	214	100	99	300	0	100
1722	0	50	35	55	1000	92	169	100	-0	-0	440	0
1726	1	50	30	48	500	184	342	200	143	360	440	0
1735	-2	50	20	32	100	132	235	100	117	359	0	100
1736	0	50	42	65	500	239	502	200	118	312	540	0
1737	1	50	41	63	1000	121	225	200	145	370	540	0

RUN NO.	CODE	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	SCALE	PEAK HITE	AREA	VOL	SPIKE NG
1664	-2	50	32	53	100	107	193	100	68	211	0	100
1668	-3	50	52	92	200	96	167	200	73	208	0	200
1672	0	50	61	105	500	107	207	1000	167	415	625	0
1676	-2	50	58	104	100	107	196	100	67	212	0	100
1680	0	50	64	113	200	-0	-0	1000	7	22	540	0
1683	1	50	64	112	500	102	199	200	73	212	540	0
1687	-2	50	18	32	100	97	173	100	64	207	0	100
1690	0	50	21	39	500	130	258	200	42	137	510	0
1695	-2	50	13	22	100	93	169	100	55	183	0	100
1699	0	50	25	40	500	190	382	200	38	134	485	0
1703	-2	50	16	27	100	-0	-0	100	60	193	0	100
1707	0	50	17	28	500	59	111	500	27	91	460	0
1711	-2	50	14	24	100	101	185	100	58	183	0	100
1715	0	50	30	52	500	218	473	200	37	113	495	0
1719	-2	50	13	24	100	97	182	100	57	184	0	100
1723	0	50	23	40	1000	75	152	100	-0	-0	510	0
1731	-2	50	14	24	100	116	216	100	99	310	0	100
1734	0	50	29	52	500	183	388	200	70	214	530	0

IV.2.4 Key to Data Location

Table IV.2.4: Locations of raw data points

Station	21/22 May	6 June	20 June	9 July	8 August	29 August
1	1669	988	1031	1195,1212 1218,1222	1287	1328,1332 1336
2	1670	989	1032	1196 1213	1288	1329,1333 1337
3		990	1098 1102	1197,1219 1223	1289	1330 1334-12min.
4	1278 1282	991	1280	1220 1224	1291	1331 1335
5	1671 1673	996 1000	1281	1221 1225	1299	1342
6	1403,1407 1279	997,1001 1659	1099,1103 11052-5m	1230,1234 1238	1297 1298	1343
7			1100 1104	1231,1235 1239	1300	1344 1346
8	1672	998 1002	1101 11051	1232 1240	1305 1309	1345
9	1678 1681	999 1003	1110	1233,1237 1241	1306,1310 1313*,1657	1351,1355 1392,1396*,1398-3m
10	1679 1682	1008	1111 1114	1246	1307,1311 1314-5m	1352,1393 1397-5m
11	1680 1683	1009	1112 1115x2			
12	1688	1010	1113 1116x2			
13	1689	1011 1012	1121			
14						
15	1690	1017,1021 1394	1122 1126,1394			
16	1691	1018 1022				
17		1019 1023	1123	1247	(1308) (1312)	
18		1020 1024	1124	1248	(1319)	
19		1029	1132		1320	
20		1030	1178	1249	1321	
21			1179	1254,1255 12572,1658		
22			1180	1256		

*: 5 minute plates ( ) : 1967 data

Table IV.2.4: Location of raw data points, continued

Station	21/22 May	6 June	20 June	9 July	8 August	29 August
23			1181,16443 16441	12571		
24			1186	1262		
25			1187	1262		
26	1696		1188	1264	1322 1323	1353,1354 1395
27				1265		
A	1697	1414	1453	1514	1567	1600
B	1698	1415	1454	1515	1568	1601
C	1699	1420	1455 1456	1520	1569	1607
D	1405 1412	1421	1461	1522	1574	1608
E	1704				1575	1609 1615
F	1705	1422	1462 1465		1576	1610
G	1706	1423	1463	1523		1616 1618
H	1707	1428	1464	1528	1577	1617,1619 1620
I						1617,1619 1625
J	1712	1429	1470		1582	
K	1713	1430 1660-9min	1471	1529 1532	1583	1626
L	1714	1431	1472	1530	1584	1627
M	1715	1436	1473	1531	1585	1628
N	1406 1413	1437	1478 1482	1558	1545 1549	1633
θ	1720	1438	1479	1546 1550	1591	1634
P	1721	1439	1480	1547 1551	1590	1635
Q	1722 1726	1444	1481	1548 1552		1636

Table IV.2.4 Location of raw data points, continued

Station	21/22 May	6 June	20 June	9 July	8 August	29 August
R	1723		1487	1559	1592	
T	1732	1445	1488	1560	1643 16442	
U	1733	1446	1489 1491	1561	1593	
V	1736 1737	1447	1512	1566	1599	1642
W	1734	1452	1490		1598 1602	1641

S1M4: 1189

S1M8: 1194,1210,1211

S2M8: 1404

IV.2.5 Flow Rates

Table IV.2.5

AVERAGE FLOW RATES , cfm x10

STATION	MAY 21/22	JUNE 6	JUNE 20	JULY 9	AUGUST 8	AUGUST 29	SPECIAL
1	670	670	670	640	650	650	
2	710	595	600	590	580	555	
3	-	685	670	685	710	720	
4	710	700	710	725	700	740	
5	635	660	635	635	620	640	
6	610	605	605	715	625	630	
7	-	-	620	680	640	690	
8	625	620	600	640	685	715	
9	635	620	625	645	660	555	
10	615	605	610	600	680	690	
11	540	520	530	-	-	-	
12	515	535	540	-	-	-	
13	535	575	555	-	-	-	
14	-	-	-	-	-	-	
15	535	525	530	-	-	-	
16	510	545	545	-	-	-	
17	570	575	565	575	580	575	570
18	575	575	575	575	580	585	580
19	580	575	575	-	580	590	570
20	570	570	585	585	570	590	520
21	-	-	570	580	580	625	555
22	-	-	515	440	400	600	520
23	-	-	540	630	485	535	485
24	-	-	-	300	390	570	485
25	-	-	505	-	560	650	525
26	600	-	675	670	610	640	
27	-	-	-	555	535	595	
A	450	455	445	480	420	450	
B	470	495	485	490	405	395	
C	485	490	490	500	490	495	
D	540	540	550	520	515	530	
E	415	-	-	-	540	510	
F	510	550	515	-	465	465	
G	485	540	480	525	-	515	
H	460	530	465	490	490	470	
I	-	-	-	-	-	455	
J	485	480	440	-	510	-	
K	440	435	425	465	455	480	
L	460	480	435	460	415	400	
M	495	470	480	480	410	370	
N	420	410	425	425	450	420	
Ø	455	425	450	450	470	460	
P	570	555	560	460	480	490	
Q	440	450	445	440	-	450	
R	510	-	470	470	500	-	
T	525	535	515	515	515	-	
U	490	495	480	500	425	-	
V	540	555	485	485	480	490	
W	530	540	495	-	490	500	

S1M8:0.847,8/24-8/30 ; S2M8: 1.15,8/30 ; S1M4: 302,6/--/64

IV.3 DATA ANALYSIS

IV.3.1 Data Reduction Program (160-A)
IV.3.2 Calibration Factors
IV.3.3 Program for Editing Cd Peak Heights
IV.3.4 Corrected Values for Cd Peak Heights

IV.3.1 C D C 160-A Raw Data Reduction Program.

```
      dimension ida(14,42),cap(7),dat(7),ave(4,22),ratio(4,22)
103   pause 2
      k=xfilef(2,1)
10    pause 1
2201  continue
141   continue
      jock=0
      endfile 3
2001  format(/)
145   write output tape 3,2001
124   format(50h1  all data are scaled to 10 microamps full scale    /)
1006  format(13i6)
221   format(59h                     cd                   pb
     1 cu      )
122   format(78h  run  code  scale peak  area  scale peak  area  scale
     1peak  area   vol spike  )
123   format(78h  no.              hite                 hite
     1hite             ng   /)
2211  read flex 1901,(cap(i),i=1,6),al,nut
1901  format(6f6.1,f10.7,i2)
      if(nut)141,141,143
143   do 146 j=1,40
      read input tape 2,1006,(ida(i,j),i=1,13)
      if(xeof(v))142,146,142
146   continue
142   nut=j-1
      jo=1
      do 24 j=1,nut
      if(ida(1,j))333,334,333
334   jo=jo+1
333   do 24,i=4,10,3
      ida(i,j)=(ida(i,j))*(ida(i-1,j)/10)
24    ida(i+1,j)=(ida(i+1,j))*(ida(i-1,j))/10
      if (sense switch 2) 43,42
42    write out put tape 3, 124
      write output tape 3,221
      write output tape 3,122
      write output tape 3,123
      write output tape 3,1010,((ida(i,j),i=1,13),j=jo,nut)
1010  format(13i6)
43    write output tape 3, 1067
      write output tape 3, 1066
1067  format(// 39h  data are in nanograms per cubic meter      )
1066  format(//  72h  run                    cd                        pb
     1                 cu               /)
      jim=0
28    j=jo
27    if(ida(2,j))21,22,23
cc    test node, if-, data is a blank, if 0 data, and if + rerun or spike.
21    jim=j
```

IV.3.1 Data Reduction, continued.

```
        j=j+1
        if(j-nut) 27,27,1666
23      if(ida(2,j)-2)22,212,31
212     read flex 1901,(cap(i),i=1,6),al,mut
        j=j+1
        if(mut)27,1666,27
c       if + code, if 1 rerun, if 2 return to start, if 3 spike.
31      do 32 i=1,6,2
        ka=4
        cap(i)=((ida(ka,j))*(ida(13,j)))/100
        ka=ka+1
        cap(i+1)=((ida(ka,j))*(ida(13,j)))/100
32      ka=ka+2
        jim=j
        j=j+1
        if(j-nut) 27,27,1666
22      ka=4
        k=1
36      if(ida(12,j))34,34,30
34      dat(k)=ida(ka,j)-ida(ka,jim)/10
        ka=ka+1
                                      k=k+1
        dat(k)=ida(ka,j)-ida(ka,jim)/10
        ka=ka+2
        k=k+1
        if(k-6)36,36,133
30      bob=((al)*(ida(12,j))*14.4)/35.3
        m=1
        kill=1
        jock= jock+1
33      dat(k)=(ida(ka,j)-ida(ka,jim))/(cap(m)*bob)
        ka=ka+1
        m=m+1
        k=k+1
        dat(k)=(ida(ka,j)-ida(ka,jim))/(cap(m)*bob)
        ave(kill,jock)=(dat(k-1)+dat(k))/2.0
        kill=kill+1
        m=m+1
35      k=k+1
        ka=ka+2
        if(k-6)33,33,133
133     write output tape 3,1011, ida(1,j),(dat(k),k=1,6)
        if(jock) 988,988,989
989     ave(1,jock)=dat(1)
        ratio(1,jock)=ave(1,jock)/ave(2,jock)
        ratio(2,jock)=ave(1,jock)/ave(3,jock)
        ratio(3,jock)=ave(3,jock)/ave(2,jock)
1011    format(i6,3h   ,6f12.1)
988     j=j+1
        if(j-nut) 27,27,1666
1666    if(jock)6611,10,6611
6611    write output tape 3, 2468
        write output tape 3,4268
```

IV.3.1 Data Reduction, continued.

```
      write output tape 3, 8642,((ave(kill,j),kill=1,3),j=1,jock)
      write output tape 3, 8462
      write output tape 3, 8888,((ratio(i,j),i=1,3),j=1,jock)
8888  format(3(6h      ,f12.4,6h      ))
      go to 10
4268  format(65h                cd                          pb
    1       cu       )
2468  format(48h1   average values in nanograms per cubic meter       )
8642  format(3(6h      ,f12.1,6h      ))
8462  format(//10h    ratios /66h            cd/pb                       cd
    1/cu             cu/pb      /)
      end
```

IV.3.2 Calibrations for Raw Data Program (Cd, Pb, and Cu).

```
Starting Run Number

      952   90./100./45./49./48./68./0.000127/23
            0./0./0./
      953   70./150./47./51./51./87./0.000127/23
            0./0./0./
      954   110./120./75./76./71./80./0.000127/23
            0./0./0./
      955   100./160./79./64./59./107./0.000127/23

     1066   90./230./60./111./69./200./0.000127/17
     1067   100./270./53./91./60./209./0.000127/17
     1068   135./275./77./124./75./237./0.000127/17
     1069   70./270./60./98./53./183./0.000127/17

     1150   50./90./37./96./89./244./0.000127/12
     1151   50./100./45./112./81./180./0.000127/12
     1152   50./70./37./74./73./191./0.000127/12
     1153   50./140./32./78./80./232./0.000127/12

     1198   60./180./49./91./76./222./0.000127/18
     1199   60./190./45./89./69./177./0.000127/18
     1200   60./140./42./92./50./126./0.000127/18
     1201   50./130./35./67./58./155./0.000127/18

     1266   115./255./76./161./111./294./0.000127/20
            75./145./55./100./45./150./0.000127/20
            0./0./0./
     1267   105./285./52./90./77./214./0.000127/20
            75./175./40./60./30./110./0.000127/20
            0./0./0./
     1268   95./185./44./84./35./110./0.000127/20
            50./150./35./80./25./85./0.000127/6
            0./0./0./
     1269   90./190./53./107./40./140./0.000127/20
            60./170./30./75./26./90./0.000127/6
            0./0./0./
```

IV.3.2 Calibrations, continued.

Starting Run Number	
1376	70./265./83./243./217./494./0.000127/32 0./0./0./
1377	165./500./93./186./104./266./0.000127/32
1378	110./310./62./138./100./240./0.000127/32
1379	130./360./85./192./125./345./0.000127/32
1500	155./355./90./215./156./367./0.000127/9/
1501	145./280./92./246./118./286./0.000127/9/
1502	135./290./67./142./101./242./0.000127/9/
1503	205./230./56./131./84./189./0.000127/9/
1557	125./177./94./207./116./289./0.000127/20
1558	148./212./120./234./110./294./0.000127/20
1559	118./175./89./160./114./271./0.000127/20
1560	115./208./76./157./94./236./0.000127/20
1661	30./75./58./143./110./233./0.000127/20
1662	50./130./62./140./102./209./0.000127/20
1663	85./140./99./181./81./217./0.000127/20
1664	90./160./85./141./78./205./0.000127/20

IV.3.3

160-A Computer Program for Inserting Peak Height Cd Values Obtained by the Horrizontal Line Method into Raw Data Program.

```
             dimension ida(13,40)
             pause 1
             k=xfilef (2,1)
9            pause 2
             endfile 3
             read input tape 2, 999
             do 11j=1,40
             read input tape 2,1000,(ida(i,j),i=1,13)
1000         format(13i6)
999          format(//)
             if(xeof(v))10,11,10
11           continue
10           nut=j-1
             write output tape 3, 1001
             write output tape 3,1002
1001         format(78h  run  code  scale peak  area  scale peak  area  scale
     1peak   area   vol spike  )
1002         format(78h  no.                 hite              hite
     1hite              ng    /)
1003         format(40i6)
             read flex 1003,(ida(4,j),j=1,nut)
             write output tape 3, 1000,((ida(i,j),i=1,13),j=1,nut)
             go to 9
             end
```

IV.3.4 Raw Cd Peak Height Values Obtained by Horizontal Method.

0/6/10/20/18/15/15/5/10/14/8/11/11/10/9/18/-0/16/16/18/20/
4/12/12/21/18/15/16/0/1/3/0/0/2/7/20/2/3/5/1/3/2/
-0/8/8/20/21/19/18/0/8/10/5/6/6/5/16/18/16/1/20/14/
-0/3/3/16/18/15/17/0/8/13/2/4/4/4/20/28/0/9/33/42/4/
4/4/11/14/37/11/0/14/6/7/53/47/13/12/0/11/11/
3/3/15/16/13/11/0/13/22/23/12/11/12/13/11/12/11/
10/10/21/20/15/15/0/31/37/35/20/24/21/18/19/0/12/
4/4/13/13/11/11/0/15/17/17/13/11/10/13/14/0/15/
1/9/13/18/16/14/9/28/5/7/7/12/
3/9/15/17/15/3/10/17/3/9/3/5/
0/1/6/11/5/9/22/28/7/8/6/12/
2/8/14/18/13/1/7/14/3/6/7/31/
0/2/9/12/2/5/5/9/14/15/14/8/10/6/23/14/17/
2/8/14/19/8/15/17/4/25/27/24/2/2/7/-0/12/11/8/
-0/1/7/108/6/7/7/9/13/14/7/7/21/101/17/22/
-0/2/7/10/3/-0/11/8/14/14/13/7/6/20/41/17/19/
30/54/51/78/73/15/19/14/15/20/18/24/21/11/13/10/18/18/19/0/11/14/9/8/9/
17/38/40/47/11/19/12/22/17/16/14/2/9/11/9/14/23/21/0/9/15/8/9/
12/78/32/30/12/14/8/13/14/10/9/2/6/7/6/9/24/0/8/11/11/7/7/
19/36/37/43/14/21/18/25/16/18/16/10/18/13/14/19/11/0/9/11/9/10/
11/41/98/37/20/4/0/11/17/20/12/22/14/16/14/12/12/14/9/13/8/11/9/8/3/6/8
/12/17/17/19/15/40/
27/60/118/25/22/4/15/15/12/25/14/32/19/19/10/15/12/22/9/23/8/18/20/5/10
/7/14/20/27/17/47/
13/35/78/10/7/6/7/4/4/8/14/8/5/1/6/4/5/7/7/4/2/3/2/6/11/4/9/9/9/25/
25/51/105/25/25/18/24/13/33/30/36/19/29/11/26/15/20/15/23/27/14/25/5/10
/14/17/26/33/17/41/
0/22/53/81/14/16/11/17/
0/9/38/45/5/22/15/22/25/
0/19/46/60/15/31/20/20/
0/19/40/53/12/28/12/15/

IV.3.5 Program for Calculating Correlation Coefficients

```
      DIMENSION A(6), B(6), C(6)
      DIMENSION DS(300), WS(300)
      DIMENSION X(300), Y(300), W(300), U(300),XS(300), YS(300)
      DIMENSION TEMP(6)
      DIMENSION AV(6), N(6),VAR(6),VAL(6)
      DIMENSION D(5,6,50)
      DIMENSION NS(5)
      DATA NS/' CO  PE  CL  SP SO2'/
      DO 1 I=1.5
      DO 1 K=1, 50
    1 READ(5,100) (D(I,J,K),J=1,6)
  100 FORMAT(8F10.4)
      DO 2 I=1,5
      DO 3 J=1,6
      AV(J)=0.0
      N(J)=0
      VAR(J)=0.0
      VAL(J)=0.0
      DO 4 K=1, 50
      IF(D(I,J,K))4,4,5
    5 N(J)=N(J)+1
      AV(J)=AV(J)+D(I,J,K)
    4 CONTINUE
      AN=N(J)
      AV(J)=AV(J)/AN
      DO 6 K=1,50
      TRM=(D(I,J,K)-AV(J))/AV(J)
      VAR(J)=VAR(J)+TRM*TRM
    6 CONTINUE
      VAR(J)=SQRT(VAR(J)/AN)
    3 CONTINUE
      WRITE(6,200) (N(J), J=1,6)
  200 FORMAT(1H1, 15X,6(I3,7X))
       WRITE(6,201) (AV(J), J=1,6)
      WRITE(6,201) (VAR(J), J=1,6)
  201 FORMAT(12X,6(F8.3,2X))
      WRITE(6,203)
  203 FORMAT(//)
      DO 18 K=1, 50
      DO 8 J=1, 6
      TEMP(J)=(D(I,J,K)-AV(J))/AV(J)
      IF(D(I,J,K))123,123,124
  123 TEMP(J)=-0.0
  124 CONTINUE
    8 CONTINUE
      WRITE(6,201) (TEMP(J), J=1, 6)
   18 CONTI NUE
    2 CONTINUE
      WRITE(6,204)
  204 FORMAT(1H1 )
      DO 9 I=1, 5
      DO 9 II=1, 5
      WRITE(6,401) NS(I), NS(II)
  401 FORMAT(///,32X,A4,'  -',A4,/)
      JJ=0
```

```
      DO 10 J=1, 6
      KK=0
      DO 20 K=1, 50
      IF(D(I,J,K))20,20,21
   21 IF(D(II,J,K))20,20,22
   22 KK=KK+1
      JJ=JJ+1
      X(KK)=D(II,J,K)
      Y(KK)=D(I,J,K)
      XS(JJ)=X(KK)
      YS(JJ)=Y(KK)
      U(KK)=0.0
      W(KK)=0.0
      US(JJ)=U(KK)
       WS(JJ)=0.0
   20 CONTINUE
      CALL CORR(R,DR,SL,CP,X,Y,W,U,KK)
      A(J)=R
      B(J)=SL
      C(J)=CP
   10 CONTINUE
      WRITE(6,201) (A(J), J=1,6)
      WRITE(6,201) (B(J), J=1,6)
      WRITE(6,201) (C(J), J=1,6)
      CALL CORR(R,DR,SL,CP,XS,YS,WS,US,JJ)
      WRITE(6,501) R,SL,CP
  501 FORMAT(/,22X,3(F8.3,2X))
    5 CONTINUE
      STOP
      END
```

```
      SUBROUTINE CORR(R,CR,SL,CF,X,Y,V,W,N)
      DIMENSION X(300), Y(300), W(300),V(300
      AN=N
      SX=0.0
      SXX=0.0
      SXY=0.0
      SYY=0.0
      SY=0.0
      DO 1 J=1, N
      SX=SX+X(J)
      SXX=SXX+X(J)*X(J)
      SXY=SXY+X(J)*Y(J)
      SYY=SYY+Y(J)*Y(J)
      SY=SY+Y(J)
    1 CONTINUE
      TCP=AN*SXY-SX*SY
      BXX=AN*SXX-SX*SX
      BYY=AN*SYY-SY*SY
      BCT=SQRT(BXX*BYY)
      R=TCP/BCT
      CF=(SY*SXX-SXY*SX)/BXX
      SL=TCP/BXX
      SCR=0.0
      DO 2 J=1, N
      YT=AN*Y(J)-SY
      XT=AN*X(J)-SX
      TX=YT-TCP*XT/BXX
      TY=XT-TCP*YT/BYY
      SCR=SCR+(TX*V(J))**2+(TY*W(J))**2
    2 CONTINUE
      CR=SQRT(SCR)/BCT
      RETURN
```

IV.4 HISTOGRAMS OF DATA

IV.4.1 Pass Number 1

PASS NUMBER 1

```
HISTCGRAM CF RATIOS  Cd/Cu

TCTAL      MEAN     STAN CEV     MIN       MAX
17.11C8   0.1C76    0.1251     0.0009    C.8C65

      INTERVAL VALUES=     0.0732

INTERVAL    FRECUENCY      PERCENT
    1           1.            0.6
    2          8C.           50.3
    3          45.           28.3
    4          15.            9.4
    5           7.            4.4
    6           3.            1.9
    7           2.            1.3
    8           2.            1.3
    9           2.            1.3
   1C           1.            0.6
   11           0.            C.C
   12           C.            C.C
   13           1.            0.6
  TCTAL       ------        ------
               159          103.0
  14C.00
```

```
HISTCGRAM CF RATIOS  Cd/SO2

TOTAL       MEAN     STAN CEV      MIN       MAX
471.8081   5.4E61    9.5710     0.1176    52.CC00

      INTERVAL VALUES=     5.7647

INTERVAL    FRECUENCY      PERCENT
    1           1.            1.2
    2          62.           72.1
    3          11.           12.8
    4           5.            5.8
    5           0.            C.C
    6           2.            2.3
    7           2.            2.3
    8           2.            2.3
    9           0.            0.0
   1C           0.            0.0
   11           1.            1.2
  TCTAL       ------        ------
                86          100.0
  73.CC
```

```
HISTCGRAM CF RATICS  Cd/SP,%

TCTAL      MEAN     STAN CEV     MIN       MAX
2.6644    C.0165    0.0161     0.0C15    C.1C37

      INTERVAL VALUES=     0.CC93

INTFFVAL    FRECUENCY      PERCENT
    1           0.            0.0
    2          78.           48.4
    3          41.           25.5
    4          18.           11.2
    5          11.            6.8
    6           7.            4.3
    7           2.            1.2
    8           C.            C.0
    9           1.            C.6
   10           1.            C.6
   11           1.            0.6
   12           0.            0.0
   13           1.            0.6
  TCTAL       ------        ------
               161          1C0.C
  148.0C
```

```
HISTCGRAM CF RATICS  Pb/Cd

TOTAL         MEAN      STAN CEV      MIN       MAX
24397.4727  146.C926   124.6722    5.CCCC  1CCC.C000

      INTERVAL VALLES=     9C.4545

INTERVAL    FRECUENCY      PERCENT
    1           C.            0.0
    2          67.           4C.1
    3          56.           33.5
    4          27.           16.2
    5          11.            6.6
    6           4.            2.4
    7           C.            0.0
    8           0.            C.C
    9           C.            0.0
   10           1.            C.6
   11           C.            0.0
   12           0.            0.0
   13           1.            0.6
  TCTAL       ------        ------
               167          100.0
  161.00
```

```
   HISTOGRAM OF RATIOS  Pb/Cu

   TOTAL      MEAN     STAN DEV      MIN        MAX

 2587.9133  11.8170   14.0742     0.0255  101.4493

           INTERVAL VALUES=     9.2203

INTERVAL    FREQUENCY        PERCENT
    1            1.             0.5
    2          120.            54.8
    3           56.            25.6
    4           17.             7.8
    5           15.             6.8
    6            3.             1.4
    7            3.             1.4
    8            0.             0.0
    9            3.             1.4
   10            0.             0.0
   11            0.             0.0
   12            0.             0.0
   13            1.             0.5
  TOTAL       ------         ------
                219           100.0
  206.00
```

```
   HISTOGRAM OF RATIOS  Pb/SO2

   TOTAL       MEAN     STAN DEV        MIN        MAX

 63129.6875  530.5015 1036.8523     7.7083 6000.0000

           INTERVAL VALUES=   599.2288

INTERVAL    FREQUENCY        PERCENT
    1            1.             0.8
    2           94.            79.0
    3    [illegible]     [illegible]
    4            4.             3.4
    5            1.             0.8
    6            2.             1.7
    7            0.             0.0
    8            0.             0.0
    9            1.             0.8
   10            1.             0.8
   11            1.             0.8
   12            1.             0.8
  TOTAL       ------         ------
                119           100.0
  107.00
```

```
   HISTOGRAM OF RATIOS  Pb/SP, %

   TOTAL      MEAN     STAN DEV      MIN        MAX

  322.7275   1.4407    1.0573     0.2385     7.9545

           INTERVAL VALUES=     0.7015

INTERVAL    FREQUENCY        PERCENT
    1            0.             0.0
    2           85.            37.9
    3           74.            33.0
    4           30.            13.4
    5           13.             5.8
    6           13.             5.8
    7            6.             2.7
    8            2.             0.9
    9            0.             0.0
   10            0.             0.0
   11            0.             0.0
   12            0.             0.0
   13            1.             0.4
  TOTAL       ------         ------
                224           100.0
  189.00
```

```
   HISTOGRAM OF RATIOS  Cu/Cd

   TOTAL      MEAN     STAN DEV       MIN        MAX

 11079.5117  69.6824  177.5665     1.2400 1125.0000

           INTERVAL VALUES=   102.1600

INTERVAL    FREQUENCY        PERCENT
    1            1.             0.6
    2          139.            87.4
    3            5.             3.1
    4            3.             1.9
    5            3.             1.9
    6            3.             1.9
    7            0.             0.0
    8            1.             0.6
    9            1.             0.6
   10            0.             0.0
   11            1.             0.6
   12            1.             0.6
   13            1.             0.6
  TOTAL       ------         ------
                159           100.0
  139.00
```

```
   HISTOGRAM OF RATICS Cu/Pb

   TOTAL      MEAN    STAN CEV      MIN        MAX

 243.7263    1.1129    3.9CE1     C.CC99    38.5714

          INTERVAL VALUES=      3.5C56

INTERVAL     FRECUENCY       PERCENT
    1            1.             0.5
    2          2C4.            93.2
    3            4.             1.8
    4            4.             1.8
    5            1.             C.5
    6            1.             C.5
    7            2.             0.9
    8            1.             0.5
    9            0.             0.0
   10            C.             C.0
   11            C.             C.C
   12            C.             C.0
   13            1.             0.5
  TOTAL       ------         ------
                219           100.C
   2C4.CO
```

```
   HISTOGRAM OF RATIOS Cu/SO2

   TOTAL       MEAN     STAN DEV      MIN        MAX

 6949.4336   64.3466   125.9873     C.2553   97C.0000

          INTERVAL VALUES=      96.9745

INTERVAL     FREQUENCY       PERCENT
    1            1.             0.9
    2           88.            81.5
    3           11.            10.2
    4            2.       [illegible]
    5            4.             3.7
    6            1.             C.9
    7            0.             0.0
    8            C.             0.0
    9            C.             0.C
   10            C.             0.C
   11            0.             0.0
   12            1.             0.9
  TCTAL       ------         ------
                108            1CC.C
   99.00
```

```
   HISTOGRAM OF RATICS Cu/SP,%

   TOTAL      MEAN    STAN DEV      MIN        MAX

 182.7165    C.87C1    2.5879     0.0136    27.CCCC

          INTERVAL VALUES=      2.4533

INTERVAL     FRECUENCY       PERCENT
    1            1.             0.5
    2          192.            91.4
    3            6.             2.9
    4            3.             1.4
    5            4.             1.9
    6            3.             1.4
    7            0.             0.0
    8            C.             0.0
    9            0.             C.C
   10            C.             0.C
   11            0.             0.C
   12            C.             0.0
   13            1.             C.5
  TCTAL       ------         ------
                21C            1CC.C
   192.00
```

```
   HISTOGRAM OF RATICS SP/Cd X0.01

   TCTAL       MEAN     STAN DEV      MIN        MAX

 19705.8320  122.3965  110.8150     9.6429   68C.C000

          INTERVAL VALUES=      60.9415

INTERVAL     FRECUENCY       PERCENT
    1            1.             0.6
    2           61.            37.9
    3           49.            30.4
    4           21.            13.0
    5           12.             7.5
    6            6.             3.7
    7            4.             2.5
    8            5.             3.1
    9            0.             0.0
   10            0.             0.0
   11            0.             0.0
   12            1.             0.6
   13            1.             0.6
  TCTAL       ------         ------
                161            100.0
   143.0C
```

```
   HISTCGRAM CF RATIOS SP/Pb X0.01               HISTCGRAM CF RATIOS SP/SO2 X0.01

  TCTAL       MEAN    STAN CEV     MIN      MAX        TOTAL       MEAN     STAN CEV      MIN       MAX

 240.0764    1.C718   C.7094    0.1257   4.1523   37509.9062  309.9950  436.5027   11.7333 212C.CCOC

        INTERVAL VALUES=     0.3697                          INTERVAL VALUES=   210.8267

INTFRVAL   FRECLENCY        PERCENT                   INTFRVAL   FRECLENCY       PERCENT
    1          C.              0.0                        1          1.             0.8
    2         46.             20.5                        2         76.            62.8
    3         64.             28.6                        3         21.            17.4
    4         45.             20.1                        4          7.             5.8
    5         25.             11.2                        5          4.             3.3
    6         16.              7.1                        6          4.             3.3
    7         14.              6.2                        7          C.             0.0
    8          8.              3.6                        8          3.             2.5
    9          2.              C.9                        9          2.             1.7
   1C          2.              C.9                       1C          0.             0.C
   11          1.              0.4                       11          2.             1.7
   12          C.              C.C                       12          1.             C.8
   13          1.              0.4                     TCTAL       ------         ------
  TCTAL      ------          ------                                121            100.C
              224            100.C                        97.CC
  21C.00

   HISTCGRAM CF RATICS SP/Cu X 0.01               HISTCGRAM CF RATIOS SO2/Cd

  TCTAL       MEAN     STAN CEV     MIN      MAX       TCTAL       MEAN      STAN LEV      MIN       MAX

 1758.4136   8.3734   9.3452    C.C37C   73.3333   108.1180    1.2572    1.7282     0.C152    8.5CCC

        INTERVAL VALUES=     6.6633                          INTERVAL VALLES=     C.9423

INTERVAL   FRECUENCY        PERCENT                   INTFRVAL   FRECLENCY       PERCENT
    1          1.              0.5                        1          1.             1.2
    2        115.             54.8                        2         52.            60.5
    3         56.             26.7                        3         17.            19.8
    4         23.             11.0                        4          5.             5.8
    5          5.              2.4                        5          4.             4.7
    6          4.              1.9                        6          2.             2.3
    7          3.              1.4                        7          1.             1.2
    8          1.              C.5                        8          0.             0.C
    9          0.              0.0                        9          3.             3.5
   10          1.              0.5                       1C          0.             C.C
   11          0.              0.0                       11          1.             1.2
   12          0.              0.0                     TCTAL       ------         ------
   13          1.              0.5                                  86            100.0
  TCTAL      ------          ------                       69.00
              21C            100.0
  194.00
```

```
HISTOGRAM CF RATIOS SO2/Pb
TCTAL      MEAN     STAN DEV    MIN      MAX
1.2503    C.C1C5    0.C162    C.CC02   C.1257

        INTERVAL VALUES=    0.0130

INTERVAL    FRECUENCY      PERCENT
   1           1.            0.8
   2          93.           78.2
   3          17.           14.3
   4           3.            2.5
   5           2.            1.7
   6           1.            0.8
   7           0.            0.0
   8           1.            0.8
   9           C.            C.C
  10           0.            0.0
  11           0.            0.0
  12           1.            C.8
  TCTAL
              119          100.0
  110.00
```

```
HISTOGRAM OF RATIOS SO2/SP  %
TCTAL      MEAN     STAN DEV    MIN      MAX
1.5373    C.C127    0.C154    C.0C05   0.C852

        INTERVAL VALUES=    C.C085

INTERVAL    FREQUENCY      PERCENT
   1           1.            0.8
   2          64.           52.9
   3          29.           24.C
   4          15.           12.4
   5           3.            2.5
   6           0.            C.0
   7           3.            2.5
   8           3.            2.5
   9           1.            0.8
  10           1.            0.8
  11           0.            0.0
  12           1.            0.8
  TCTAL
              121          1CC.0
  1C8.00
```

```
HISTCGRAM CF RATICS SO2/Cu
TCTAL      MEAN     STAN CEV    MIN      MAX
17.7699   C.1645    C.4104    C.CC1C   3.9167

        INTERVAL VALUES=    C.3516

INTERVAL    FRECUENCY      PERCENT
   1           1.            C.9
   2          96.           88.9
   3           8.            7.4
   4           2.            1.9
   5           0.            C.C
   6           C.            0.0
   7           C.            C.C
   8           C.            0.C
   9           0.            0.0
  10           C.            0.0
  11           C.            0.C
  12           1.            0.9
  TCTAL
              1C8          100.C
  1C4.00
```

```
HISTCGRAM CF RATICS  Cu/Pb
TCTAL      MEAN     STAN CEV    MIN      MAX
2.5275    C.0151    0.0233    C.CC1C   C.200C

        INTERVAL VALUES=    C.0181

INTERVAL    FRECUENCY      PERCENT
   1           1.            0.6
   2         134.           8C.2
   3          21.           12.6
   4           4.            2.4
   5           2.            1.2
   6           2.            1.2
   7           C.            0.0
   8           1.            C.6
   9           1.            C.6
  10           C.            C.0
  11           0.            0.0
  12           C.            C.C
  13           1.            0.6
  TCTAL
              167          100.C
  155.0C
```

IV.4.2 Pass Number 5, 6% Significance Limits

PASS NUMBER 5

```
HISTOGRAM OF RATIOS Cd/Cu

 TOTAL      MEAN     STAN DEV     MIN       MAX
 7.1209    0.0574    0.0407     0.0009    0.1436

        INTERVAL VALLES=     0.0143

INTERVAL     FRECUENCY       PERCENT
    1            1.             0.8
    2           21.            16.9
    3           14.            11.3
    4           19.            15.3
    5           14.            11.3
    6           12.             9.7
    7           12.             9.7
    8           12.             9.7
    9            6.             4.8
   10            4.             3.2
   11            8.             6.5
   12            1.             0.8
  TOTAL       -----          -----
                124  78%       100.0
  112.00
```

```
HISTOGRAM OF RATIOS Cd/SO4

 TOTAL       MEAN     STAN DEV     MIN       MAX
 52.9969    0.9636    0.6038     0.1176    2.3333

        INTERVAL VALLES=     0.2770

INTERVAL     FRECUENCY       PERCENT
    1            0.             0.0
    2           12.            21.8
    3            9.            16.4
    4            9.            16.4
    5            7.            12.7
    6            8.            14.5
    7            4.             7.3
    8            2.             3.6
    9            3.             5.5
   10            1.             1.8
  TOTAL       -----          -----
                 55  64%       100.0
   49.00
```

```
HISTOGRAM OF RATIOS Cd/SP %

 TOTAL      MEAN     STAN DEV     MIN       MAX
 0.9076    0.0083    0.0040     0.0015    0.0167

        INTERVAL VALLES=     0.0015

INTERVAL     FRECUENCY       PERCENT
    1            0.             0.0
    2           10.             9.2
    3           11.            10.1
    4           18.            16.5
    5           10.             9.2
    6           17.            15.6
    7           11.            10.1
    8            9.             8.3
    9            6.             5.5
   10           10.             9.2
   11            5.             4.6
   12            2.             1.8
  TOTAL       -----          -----
                109  68%       100.0
   96.00
```

```
HISTOGRAM OF RATIOS Pb/Cd

  TOTAL        MEAN     STAN DEV     MIN        MAX
 15192.9922  107.7517   60.5136    5.0000   231.2500

        INTERVAL VALLES=     22.6250

INTERVAL     FRECUENCY       PERCENT
    1            0.             0.0
    2           11.             7.8
    3           19.            13.5
    4           18.            12.8
    5           19.            13.5
    6           17.            12.1
    7           13.             9.2
    8           13.             9.2
    9           13.             9.2
   10            6.             4.3
   11           11.             7.8
   12            1.             0.7
  TOTAL       -----          -----
                141  84%       100.0
  134.00
```

```
    HISTOGRAM OF RATIOS  Pb/Cu

  TOTAL      MEAN     STAN DEV      MIN        MAX

 765.1423   5.0338    3.9483     0.0259    13.1250

          INTERVAL VALUES=      1.3099

INTERVAL     FRECUENCY          PERCENT
    1           1.                0.7
    2          32.               21.1
    3          19.               12.5
    4          24.               15.8
    5          13.                8.6
    6           9.                5.9
    7          16.               10.5
    8           6.                3.9
    9           9.                5.9
   10          12.                7.9
   11          10.                6.6
   12           1.                0.7
  TOTAL       ------            ------
               152   69%         100.0
   126.00
```

```
    HISTOGRAM OF RATIOS  Pb/SO2

  TOTAL      MEAN     STAN DEV      MIN        MAX

 5524.3359  87.6879   43.4449     7.7083   166.6667

          INTERVAL VALUES=      15.8958

INTERVAL     FRECUENCY          PERCENT
    1           0.                0.0
    2           6.                9.5
    3           7.               11.1
    4          12.               19.0
    5           8.               12.7
    6           9.               14.3
    7           5.                7.9
    8          12.               19.0
    9           3.                4.8
   10           1.                1.6
  TOTAL       ------            ------
                63   53%         100.0
   59.00
```

```
    HISTOGRAM OF RATIOS  Pb/SP %

  TOTAL      MEAN     STAN DEV      MIN        MAX

 133.2960   0.9068    0.2405     0.3799     1.5226

          INTERVAL VALUES=      0.1143

INTERVAL     FRECUENCY          PERCENT
    1           0.                0.0
    2          21.               14.3
    3          16.               10.9
    4          16.               10.9
    5          14.                9.5
    6          13.                8.8
    7          22.               15.0
    8          10.                6.8
    9           6.                4.1
   10          11.                7.5
   11          17.               11.6
   12           1.                0.7
  TOTAL       ------            ------
               147   66%         100.0
   140.00
```

```
    HISTOGRAM OF RATIOS  Cu/Cd

  TOTAL      MEAN     STAN DEV      MIN        MAX

 1200.3591  10.8140   6.1971     1.2400    24.0000

          INTERVAL VALUES=      2.2760

INTERVAL     FRECUENCY          PERCENT
    1           0.                0.0
    2          12.               10.8
    3          15.               13.5
    4          18.               16.2
    5          15.               13.5
    6          13.               11.7
    7          12.               10.8
    8           5.                4.5
    9           7.                6.3
   10           7.                6.3
   11           5.                4.5
   12           2.                1.8
  TOTAL       ------            ------
               111   70%         100.0
   99.00
```

```
HISTOGRAM OF RATIOS  Cu/Pb
TOTAL      MEAN     STAN DEV     MIN       MAX
9.5585    C.C765    0.C394     C.CC99    C.1583

     INTERVAL VALUES=     0.C148
INTERVAL   FREQUENCY     PERCENT
   1          C.           0.0
   2          9.           7.2
   3         20.          16.0
   4         13.          10.4
   5         17.          13.6
   6         18.          14.4
   7         15.          12.0
   8          8.           6.4
   9          7.           5.6
  1C          7.           5.6
  11         10.           8.C
  12          1.           0.8
 TOTAL      ------       ------
             125   57%    100.0
 110.00
```

```
HISTOGRAM OF RATIOS  Cu/SO3
TOTAL       MEAN     STAN DEV     MIN       MAX
8C4.1C74   11.6537    9.5867    0.2953   33.75CC

     INTERVAL VALUES=     4.1868
INTERVAL   FREQUENCY     PERCENT
   1          1.           1.4
   2         21.          30.4
   3          9.          13.0
   4         15.          21.7
   5          5.           7.2
   6          4.           5.8
   7          6.           8.7
   8          2.           2.9
   9          5.           7.2
  10          1.           1.4
 TOTAL      ------       ------
              69   64%    100.0
 61.00
```

```
HISTOGRAM OF RATIOS  Cu/SP %
TOTAL      MEAN     STAN DEV     MIN       MAX
19.9524   C.1235    0.C719     C.0136    C.2892

     INTERVAL VALUES=     0.0276
INTERVAL   FREQUENCY     PERCENT
   1          0.           0.C
   2         12.           8.1
   3         23.          15.4
   4         17.          11.4
   5         23.          15.4
   6         22.          14.8
   7         10.           6.7
   8         13.           8.7
   9         13.           8.7
  10          5.           3.4
  11         10.           6.7
  12          1.           0.7
 TOTAL      ------       ------
             149   71%    100.0
 143.CC
```

```
HISTOGRAM OF RATIOS  SP / Cd  X0.01
TOTAL       MEAN     STAN DEV     MIN       MAX
9647.3633  76.5664   43.1629    9.6429   171.1111

     INTERVAL VALUES=     16.1466
INTERVAL   FREQUENCY     PERCENT
   1          0.           0.0
   2         13.          10.3
   3         24.          19.0
   4         14.          11.1
   5         18.          14.3
   6         13.          10.3
   7          8.           6.3
   8         14.          11.1
   9         10.           7.9
  10          3.           2.4
  11          8.           6.3
  12          1.           0.8
 TOTAL      ------       ------
             126   78%    100.0
 122.CC
```

```
HISTCGRAM CF RATICS SP/Pb X0.01                        HISTCGRAM CF RATICS SN/SO4 X0.01
TOTAL      MEAN     STAN CEV    MIN      MAX      TOTAL      MEAN     STAN DEV    MIN       MAX
90.1424   C.6628    C.2399    C.2531   1.C555   5225.5195  75.7322   42.7283   11.7333  166.1536

        INTERVAL VALLES=    0.0842                          INTERVAL VALLES=    17.1578

INTERVAL    FRECUENCY     PERCENT                 INTERVAL    FRECUENCY     PERCENT
    1           0.          0.0                       1           0.          0.C
    2          15.         11.0                       2           9.         13.0
    3          12.          8.8                       3           9.         13.0
    4          14.         10.3                       4          12.         17.4
    5          13.          9.6                       5          10.         14.5
    6          15.         11.0                       6          14.         20.3
    7          20.         14.7                       7           3.          4.3
    8          1C.          7.4                       8           2.          2.9
    9           8.          5.9                       9           1.          1.4
   1C          16.         11.8                      10           8.         11.6
   11          12.          8.8                      11           1.          1.4
   12           1.          0.7                     TCTAL
  TCTAL                                                         -----   57%   -----
               136  61%    100.0                                   69         1C0.0
  127.00                                              62.00


HISTCGRAM CF RATICS SP/Cu X0.01                        HISTCGRAM CF RATICS SO2/Ca
TCTAL      MEAN     STAN CEV    MIN      MAX      TCTAL      MEAN     STAN CEV    MIN       MAX
5P1.6072  4.0111    2.6146    0.C370   8.7368    26.3332    C.4389    0.3541    C.C192    1.1250

        INTERVAL VALLFS=    0.87CC                          INTERVAL VALLES=    C.1382

INTERVAL    FRFCUENCY     PERCENT                 INTERVAL    FRECUENCY     PERCENT
    1           1.          0.7                       1           1.          1.7
    2          23.         15.9                       2          19.         31.7
    3           9.          6.2                       3           9.         15.C
    4          17.         11.7                       4           3.          5.C
    5          13.          9.0                       5           7.         11.7
    6          18.         12.4                       6           5.          8.3
    7          17.         11.7                       7           6.         10.0
    8          10.          6.9                       8           3.          5.0
    9          11.          7.6                       9           5.          8.3
   10          14.          9.7                      1C           2.          3.3
   11          11.          7.6                     TCTAL
   12           1.          0.7                                  6C    70%    100.0
  TCTAL                                               51.CC
               145  69%    100.0
  143.0C
```

HISTCGRAM CF RATICS SO_2/Pb

TOTAL	MEAN	STAN CEV	MIN	MAX
C.3696	C.0043	C.CC33	C.CC02	0.0111

INTERVAL VALUES= 0.0012

INTERVAL	FRECUENCY		PERCENT
1	1.		1.2
2	19.		22.1
3	14.		16.3
4	12.		14.0
5	7.		8.1
6	5.		5.8
7	12.		14.0
8	5.		5.8
9	4.		4.7
10	6.		7.C
11	1.		1.2
TCTAL	86	72%	100.0

70.00

HISTCGRAM OF RATIOS SO_2/SP %

TCTAL	MEAN	STAN CEV	MIN	MAX
0.4075	C.0050	0.0037	C.CCC5	C.C124

INTERVAL VALUES= C.CC13

INTERVAL	FRECUENCY		PERCENT
1	0.		0.0
2	18.		22.2
3	16.		19.8
4	10.		12.3
5	6.		7.4
6	12.		14.8
7	1.		1.2
8	3.		3.7
9	4.		4.9
10	10.		12.3
11	1.		1.2
TCTAL	81	67%	1CC.C

72.00

HISTCGRAM CF RATICS SO_2/Cu

TCTAL	MEAN	STAN DEV	MIN	MAX
2.5952	C.0365	C.C34C	C.CC1C	C.1111

INTERVAL VALLES= 0.0122

INTFRVAL	FRECUENCY		PERCENT
1	1.		1.3
2	22.		28.6
3	12.		15.6
4	11.		14.3
5	7.		9.1
6	6.		7.8
7	3.		3.9
8	2.		2.6
9	7.		9.1
1C	5.		6.5
11	1.		1.3
TOTAL	77	71%	1C0.C

7C.0C

HISTCGRAM CF RATIOS Cd/Pb

TOTAL	MEAN	STAN CEV	MIN	MAX
C.7582	C.CC67	0.CC27	C.CC24	C.C121

INTERVAL VALLES= C.001C

INTFRVAL	FRECUENCY		PERCENT
1	0.		C.C
2	12.		10.6
3	13.		11.5
4	16.		14.2
5	16.		14.2
6	11.		9.7
7	10.		8.8
8	1C.		8.8
9	8.		7.1
10	9.		8.C
11	7.		6.2
12	1.		0.9
TCTAL	113	77%	100.0

112.00

IV.5 CALIBRATIONS AND RESPONSES

IV.5.1 Finding Calibrations and Correction Factors

The calibration factors used in the computer program are obtained by either (1) running a reagent plus blank sample then adding a spike and subtracting the former from the second run, or (2) by adding two successive spikes (100 ng) and subtracting as before. This is done because the first spike run must contain the proper amount of acid and therefore the blank aliquot is the best source of a near sample run. The additional signal from the second run is due only to the spike and not to carry-over, cell contamination or blank. This is usually called standard addition calibration.

This procedure is instituted prior to running the sample sequence of blank + spike + reagent, and then running a subsequent sample as mentioned before. An initial accurate calibration is provided as a starting basis for data reduction and scaling for the computer.

As we have seen, the cells can deteriorate at a nearly constant rate over reasonable time spans (see section IV.5.3). The method employed to correct for the decrease in response is to take the first calibration numbers and use them as standards and add a correction to each subsequent run. The details of the procedure are as follows:

Draw a graph for each spiked run in sequence. Draw a best-fit straight line, neglecting large deviations as these are usually caused by contamination and/or carry-over and are not usually due to cell deterioration. Find the average decrease in the standard units per subsequent run from the straight line graph to obtain a percentage decrease per subsequent sample runs. This midpoint should be calculated from the initial calibration value as used above in the first calibration. (One can do this for all elements and methods and arrive at an average percent.) Take this percentage and multiply it by the number of runs the data point is removed from the initial calibration point, and increase the value of the data point by that percent. A typical value would be 5% per data run. These results are shown in Table IV.5.1.

This procedure improves the data points so that the accuracy of the data point is more dependent on the original calibration values and less on carry-over and cell deterioration.

TABLE IV.5.1

% DECREASE PER SAMPLE RUN

Starting Run No.	Cd Pk.Ht.	Cd Area	Pb Pk.Ht.	Pb Area	Cu Pk.Ht.	Cu Area	%
952	4	-	4.7	6.7	5.1	5	5
953	3.1	7.1	5.1	3.6	4.9	5.1	4.8
954	-	10	3.9	3.9	5.8	3.1	4.2
955	-	13	3.6	3.2	3.3	2.9	7.3
1066	-	6.1	4.7	5.7	2.8	4.3	4.6
1067	-	5.9	7.9	3.3	9.5	3.5	6.0
1068	-	13.5	6.1	2.5	8.3	4.1	8.3
1069	-	4.8	4.9	1.9	(19.3)	6.9	4.6
1150	-	12.5	5.9	6.1	10.9	2.6	7.5
1151	-	12.5	9.0	9.6	9.0	3.8	8.7
1152	-	5.9	15.0	17.1	10.4	11.4	12.2
1153							5
1198	-	15.9	1.0	2.9	2.2	1.4	1.9/4.7
1199	-	16.7	4.2	3.9	7.4	7.3	7.9
1200	-	5.5	5.2	4.2	14.8	4.6	7.0
1201	-	2.1	0.8	1.2	1.5	3.8	1.9
1266	-	4.2	2.2	3.6	4.2	2.8	3.4
1267	-	1.2	1.9	1.4	1.7	0.6	1.4
1268	-	2.7	2.7	3.0	2.9	3.0	2.9
1269	-	0.8	.3	1.8	4.2	1.3	1.0
1376	-	1.7	2.7	2.2	2.8	1.3	2.1
1377	-	2.0	1.4	0.8	1.4	1.1	1.3
1378	-	2.7	1.8	1.4	1.7	1.4	1.8
1379	-	2.3	1.0	1.0	1.7	0.7	1.4
1500	-	(8)	1.6	.6	3.2	1.2	1.6
1501	-	-	-	-	-	-	0
1502	-	-	-	-	-	-	<1
1503	-	-	-	-	-	-	<1
1533	-	-	1.1	0.1	0.5	0.7	0.5
1534	-	-	0	0	1.1	0.5	0.4
1535	-	-	-	-	0.4	-	<.5
1536	-	3	0	0	2.2	0.6	1.1
1661	-	0.1	.3	2.3	.3	.2	.9
1662	15	(15.6)	2.8	2.3	3.3	2.2	2.6
1663	-	-	-	-	-	-	<.5
1664	-	-	1	1.3	2.6	1.2	2.0

IV.5.2 Sample Calculation

IV.5.2 Sample Calculation

$$\text{al} = \left(\frac{\text{Area Used}}{\text{Total Exposed Area}}\right)\left(\frac{\text{Aliquot}}{\text{Total Amount of Solution}}\right)$$

$$\begin{aligned}\text{Equivalent Volume} &= (\text{al})(\text{Flow Rate})(\text{Time})\\ &= (\text{m}^3/\text{min})(\text{min})\\ &= \text{m}^3\end{aligned}$$

Calculation for Run No. 1008; Variable, Pb:

$$\text{aliquot} = \left(\frac{2\ \text{in}^2}{9 \times 7\ \text{in}^2}\ \text{of filter paper}\right)\left(\frac{100\ \lambda}{25\ \text{ml}}\ \text{of solution}\right)$$

$$= 0.000127\ \text{parts}$$

$$\text{volume} = \frac{(0.000127\ \text{parts})(59.0\ \text{ft}^3/\text{min})(24 \times 60\ \text{min})}{35.3\ \text{ft}^3/\text{m}^3}$$

$$= 0.306\ \text{m}^3$$

From peak height:

$$\text{concentration} = \frac{32\ \text{units on a } 100\ \mu\text{a scale}}{(0.306\ \text{m}^3)(45\ \text{units}/100\ \text{ng on a } 100\ \mu\text{a scale})}$$

$$= 236\ \text{ng/m}^3\ .$$

From peak area:

$$\text{concentration} = \frac{81}{(0.306)(49)}$$

$$= 541\ \text{ng/m}^3\ .$$

IV.5.3 Sample Plots of Spike Runs 1-4

The following plots are curves similar to those from which the percentage decrease in sensitivity in Table IV.5.1 were calculated (runs No. 1835-1912).

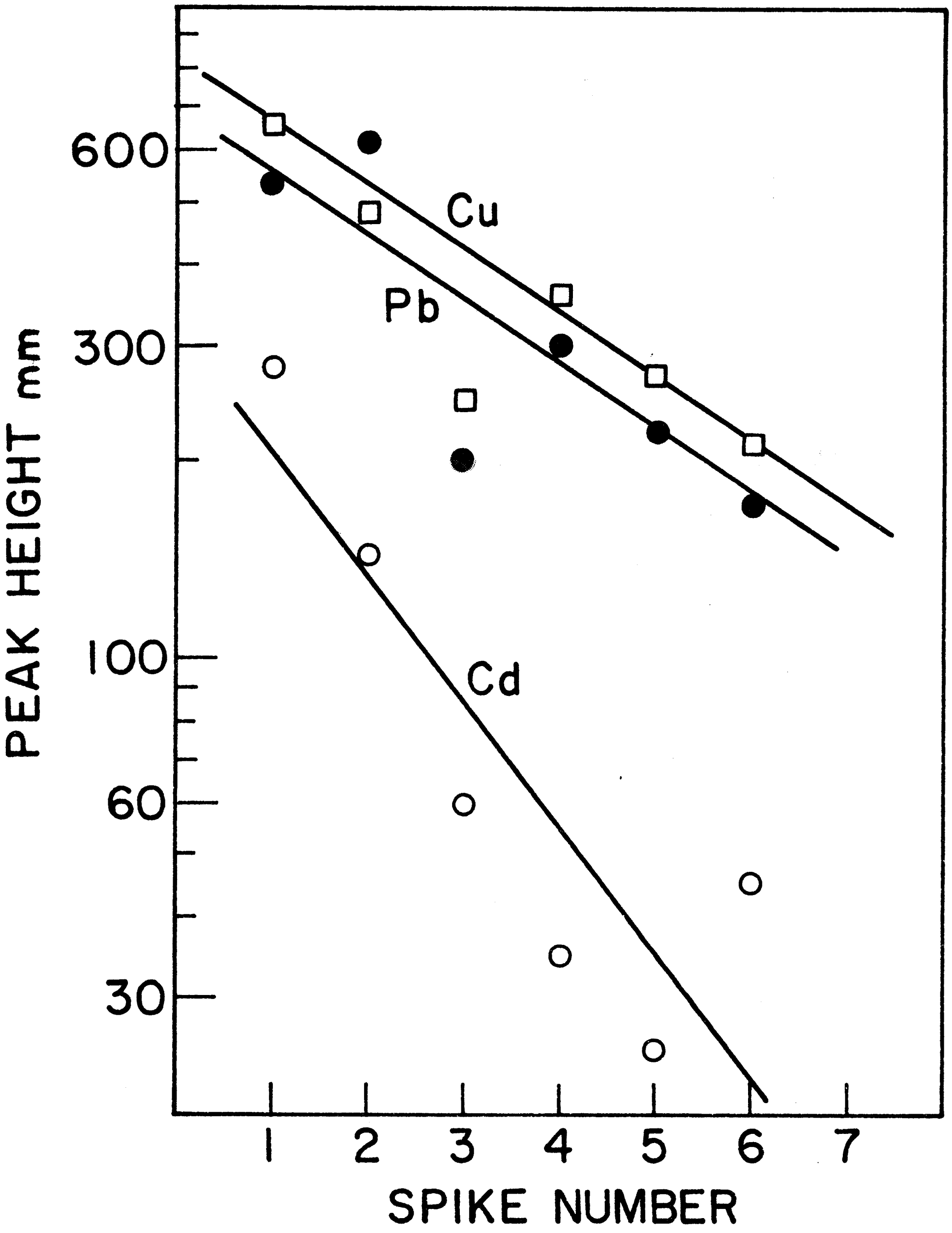

Figure IV.5.3.1 : Spike runs, 1835-1912,Cell 1.

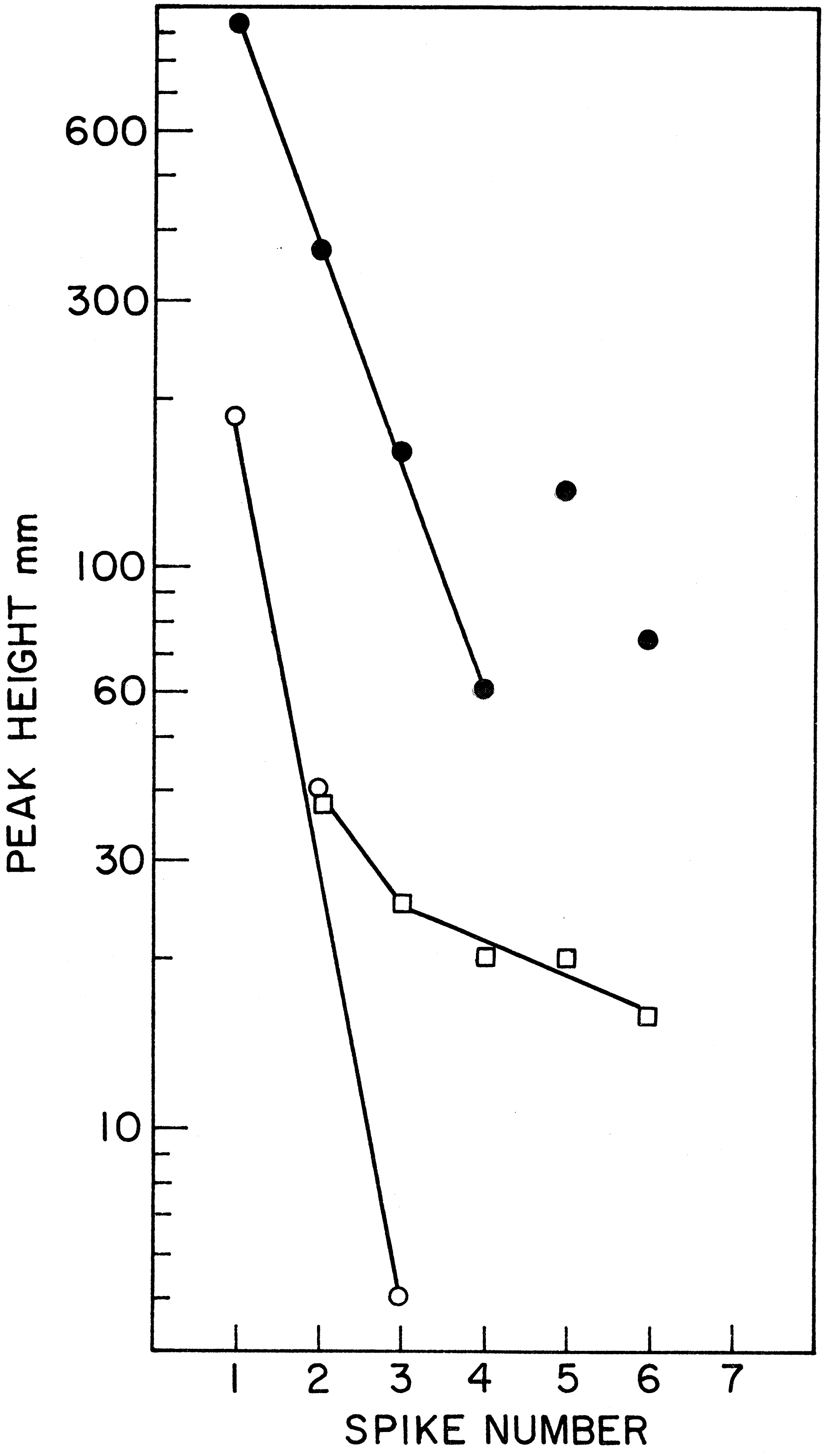

Figure IV.5.3.2 : Spike runs, 1835-1912,Cell 2.

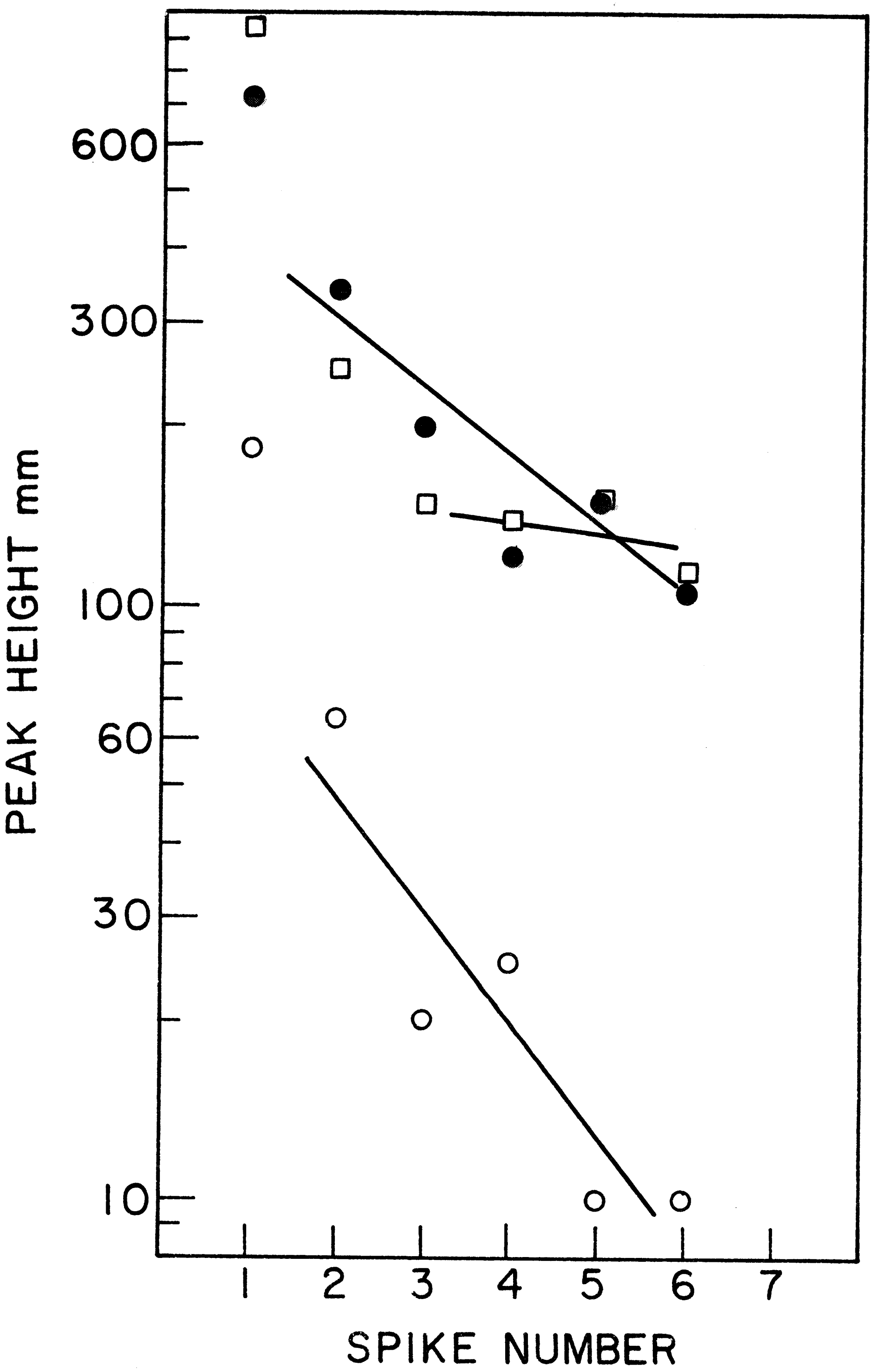

Figure IV.5.3.3 : Spike runs, 1835-1912, Cell 3.

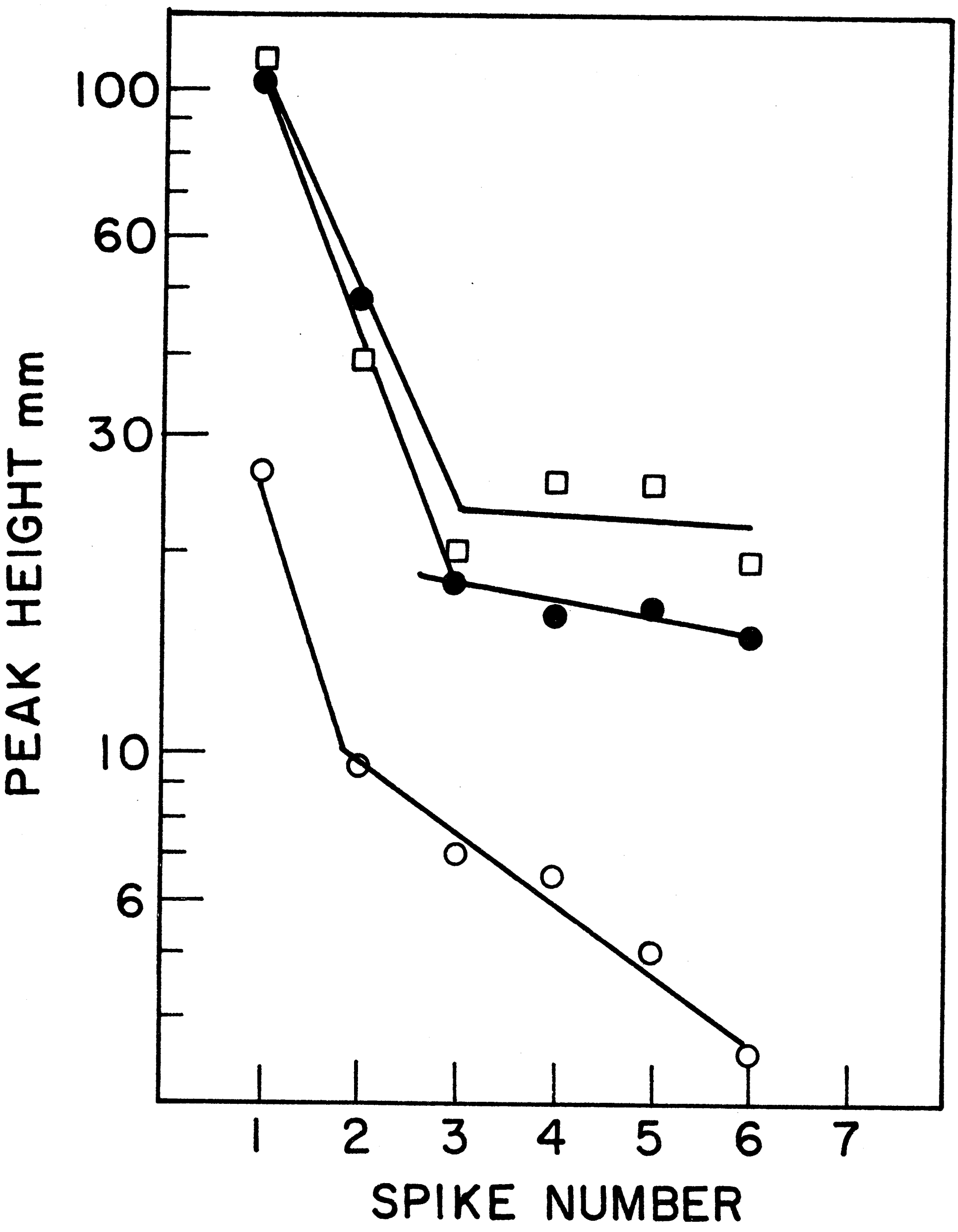

Figure IV.5.3.4 : Spike runs, 1835-1912, Cell 4.

IV.5.4 Sample Calibration Runs

The following six tables are samples of 10 minute calibration runs using four cells abstracted by both the peak height and area methods. It is obvious that the area method is noisier and thereby less accurate for the lower values (say less than 3 μgm/10 ml of solution).

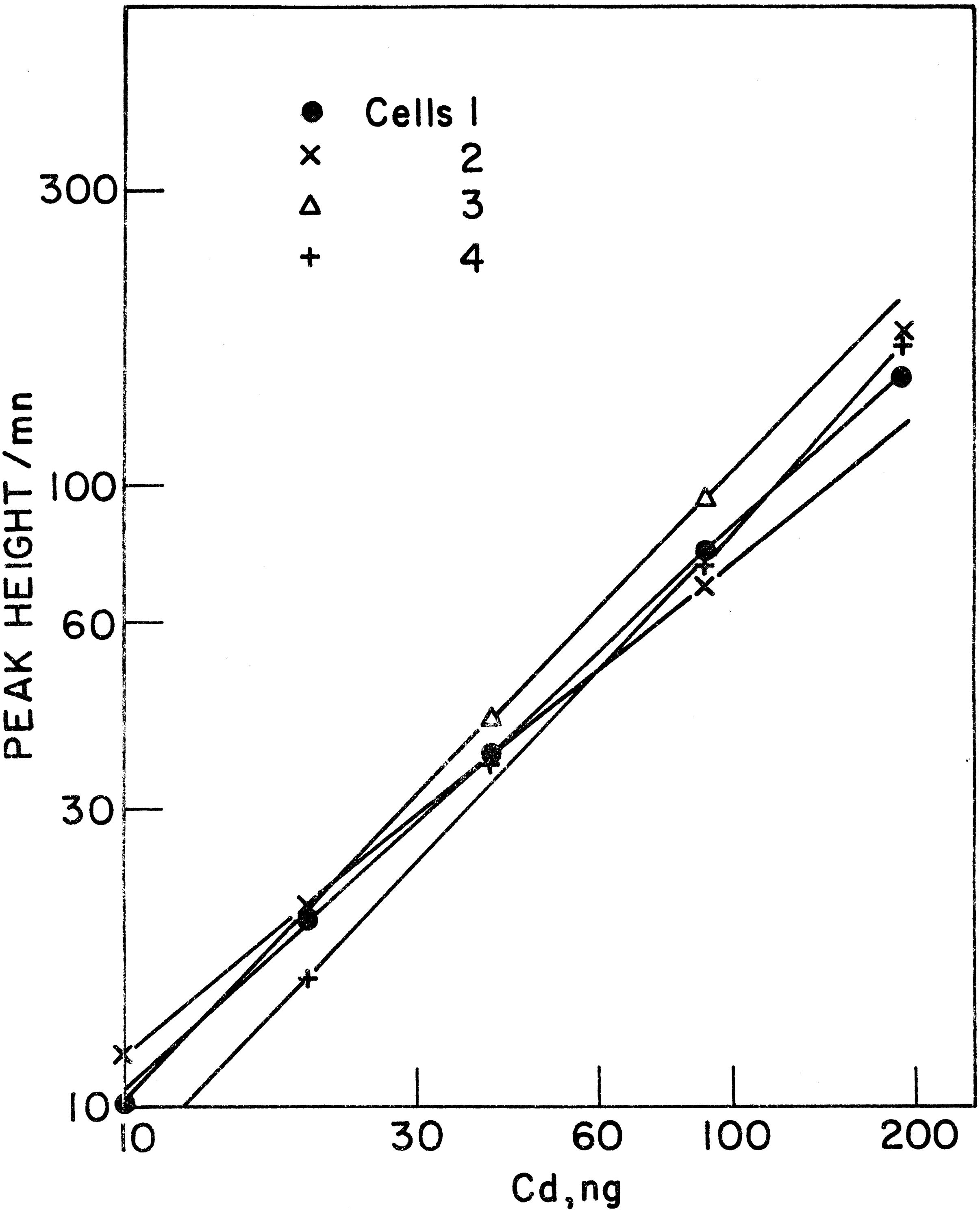

Figure IV.5.4.1: Sample calibration runs, Cells 1-4, Run No. 952-, Peak Height, Cd.

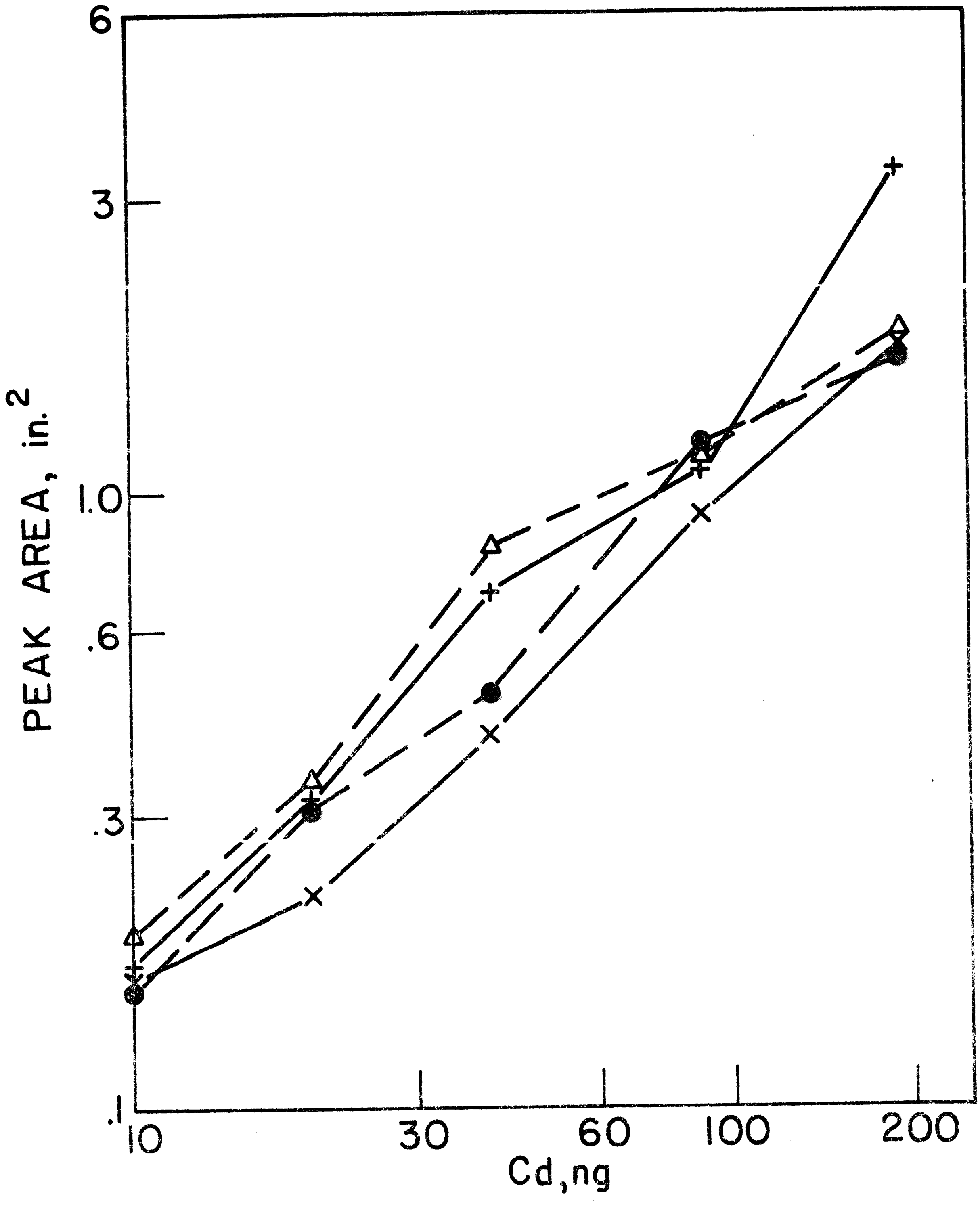

Figure IV.5.4.2: Sample calibration runs, Cells 1-4, Run No. 952-, Peak Area, Cd.

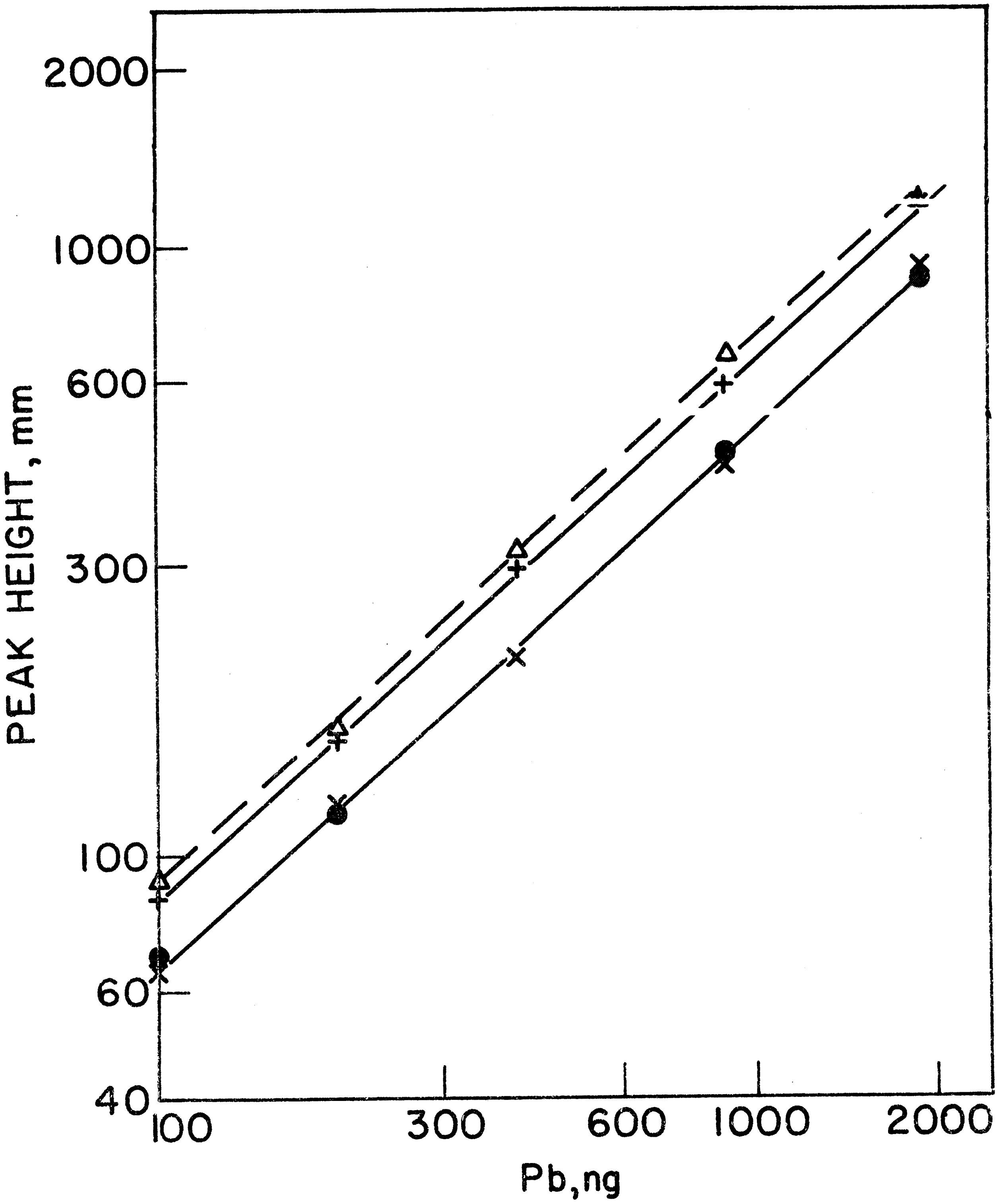

Figure IV.5.4.3 : Sample calibration runs, Cells 1-4, Run No. 952-, Peak Height, Pb.

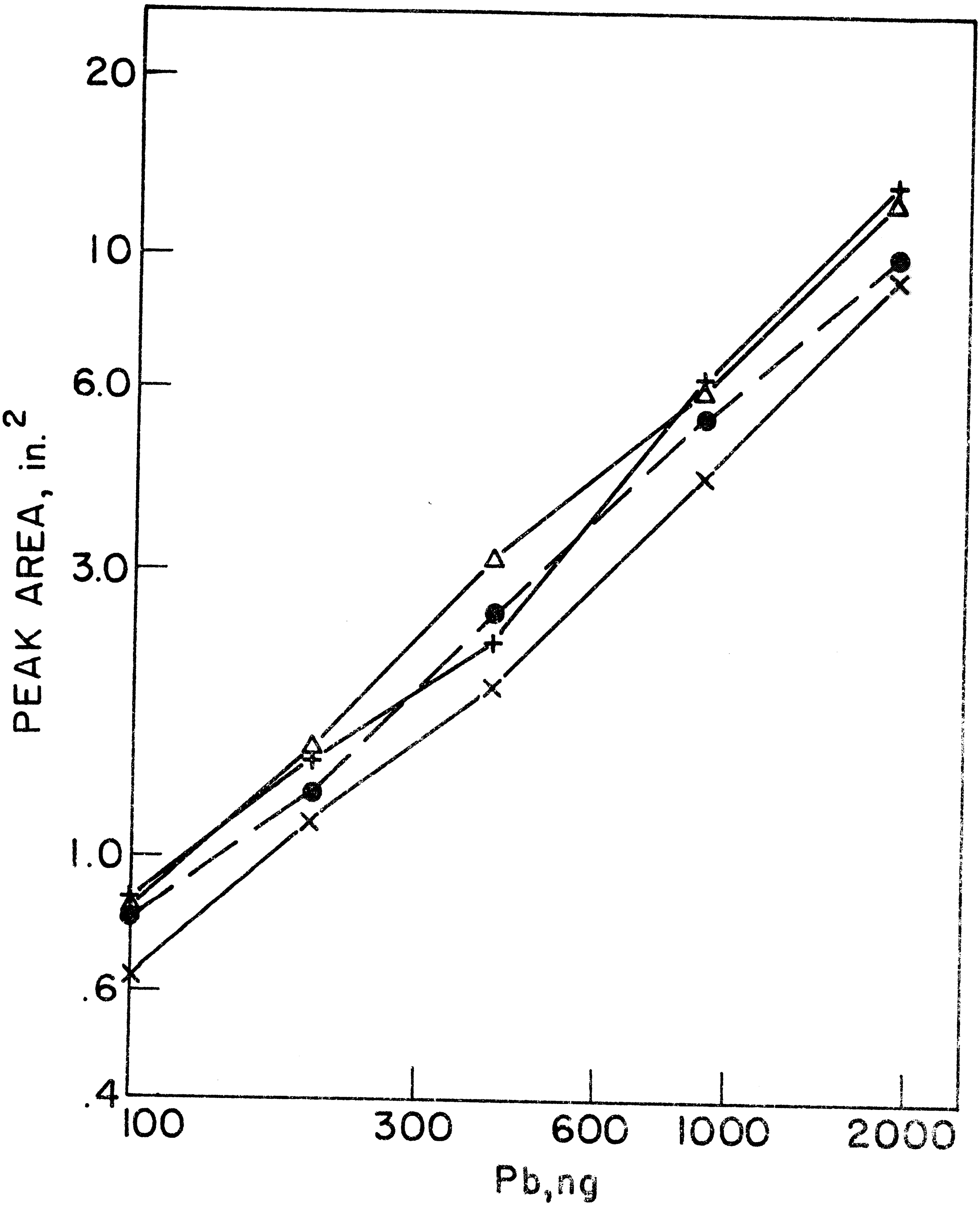

Figure IV.5.4.4: Sample calibration runs, Cells 1-4, Run No. 952-, Peak Area, Pb.

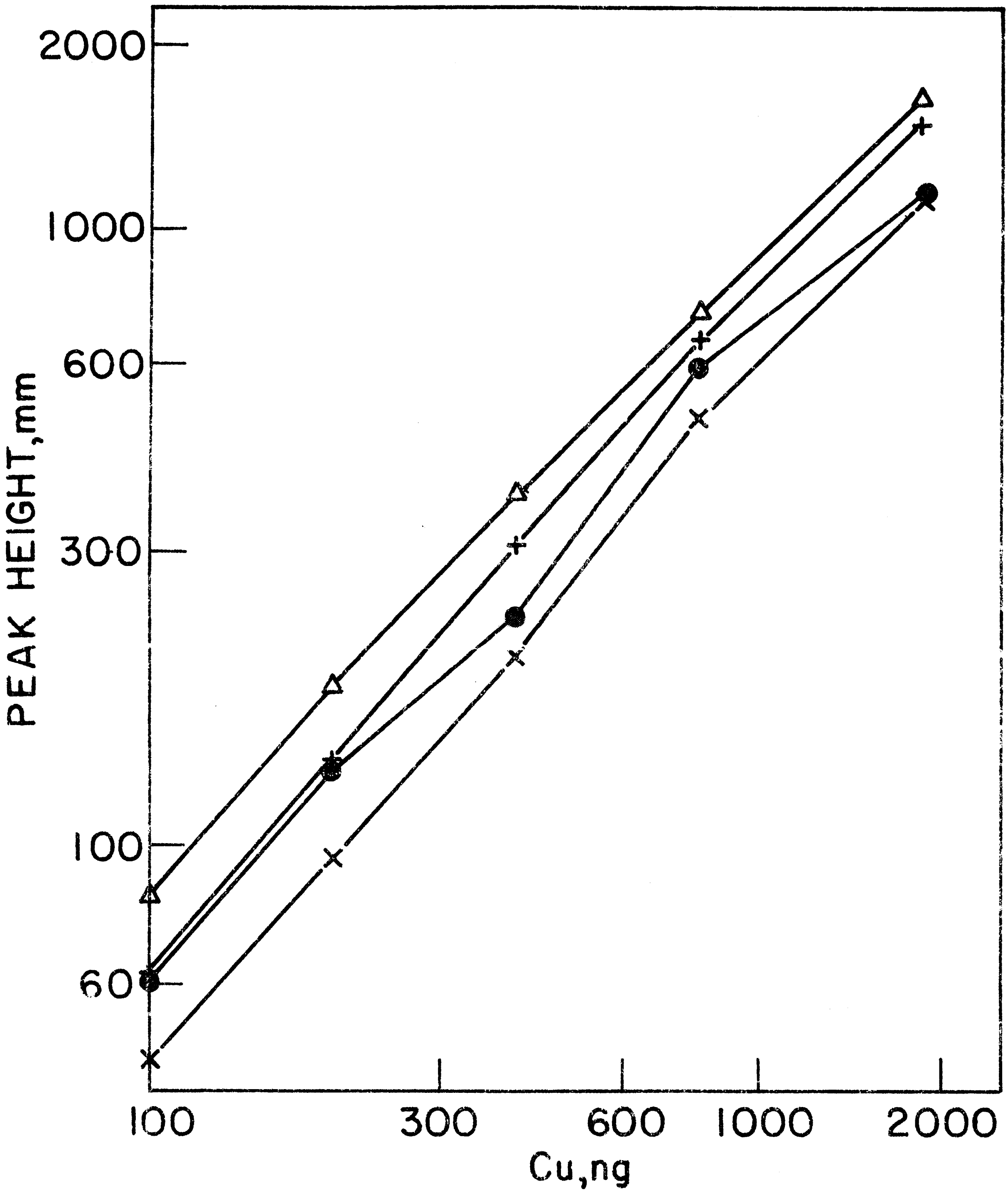

Figure IV.5.4.5 : Sample calibration runs, Cells 1-4, Run No. 952-, Peak Height, Cu.

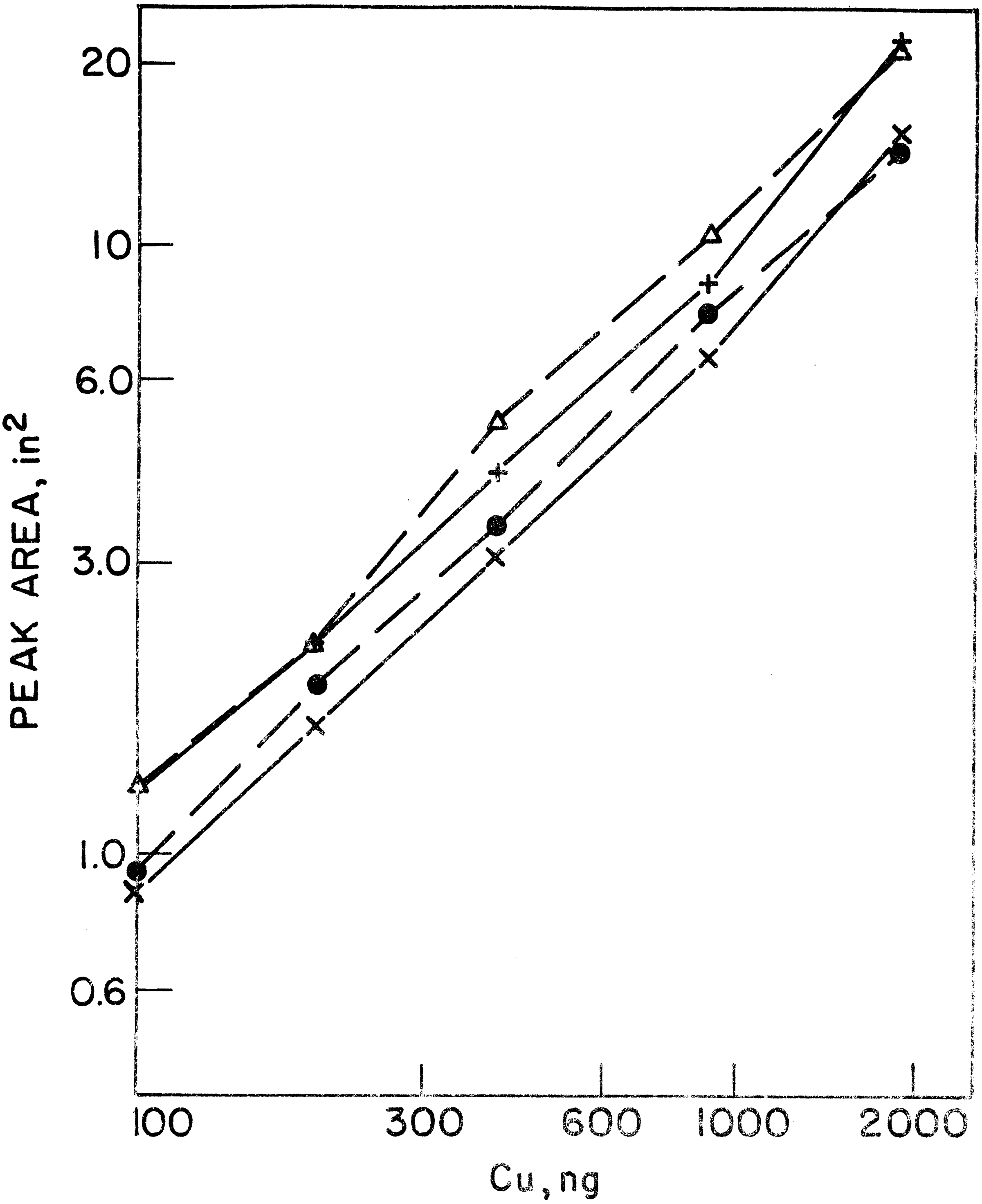

Figure IV.5.4.6 : Sample calibration runs, Cells 1-4, Run No. 952-. Peak Area, Cu.

APPENDIX V

ANODIC STRIPPING VOLTAMMETRY--THEORY AND OPERATIONS

APPENDIX V

ANODIC STRIPPING VOLTAMMETRY--THEORY AND OPERATIONS

V.1 DESCRIPTION OF ASV AND BASIC THEORY

V.1.1 Description of ASV

Anodic Stripping Voltammetry is not a new technique of analysis for trace metals. However, certain modifications were made by Matson (1968) which allowed an increase in sensitivity of about 100 times for metals forming amalgams with mercury. The basic theory is that the ions when plated into mercury diffuse uniformly into the mercury medium. However, if the mercury medium is too large when one strips or reverses the polarity slowly, the diffusion time is so large that the response is quite slow and the resulting peaks are broad. With mercury plated on the composite graphite electrode in very small droplets, the diffusion time is increased markedly with the metal ions being able to diffuse out of the mercury droplets quickly, forming sharp peaks and quick responses. Figure 2.6 of the text is a sample stripping response curve for some of the mercury soluble trace metals.

Figure V.1 is a schematic representation of the external electronic circuit. Most of the circuitry used in this study was from the Heathkit Company, Benton Harbor, Michigan, with an additional modification in the switching arrangement to allow four modules to be operated in sequence.

V.1.2 Theory of ASV Operation

The purpose of the following section is to present a brief description of the steps and a description of a simplified theory of a plating-stripping operation. No attempt will be made to give a complete description of electrochemistry as used in this study; it is suggested that the reader refer to basic texts such as Nicholson (1964).

Figure V.1 represents a description of the ASV cell and circuitry and the plating and stripping steps are explained as follows:

1. The Plating Step:

In stripping voltammetry the plating out is hastened by the stirring which brings the ions into close proximity to the test electrode. A large fraction of the total amount of a trace metal in the sample is concentrated on the test electrode. This amount plated produces a measurable faradaic current when it is stripped off rapidly.

We should be aware that the systematics of the electrochemical series often do not carry over directly to stripping voltammetry. For example, stable complexes require more energy than simple ions for cation reduction. Also slow kinetics of electron transfer leads to a requirement for overvoltage.

2. The Stripping Step:

The sharp rise of a stripping peak is, to a rough approximation, explained by examination of the Nernst equation. The Nernst equation governs the shape of the peak's leading edge.

Figure V.1 Simplified plating circuitry.

Key to Schematic Diagram:

1. Operational amplifier with infinite impedance and input terminals actively brought to ground.

2. Ag-AgCl reference electrode.

3. Test electrode (mercury on graphite). The potential at this electrode is $-E_{Bias}$ with respect to $E_{Ag-AgCl}$ which is +0.222 volts on the electrochemical scale. Therefore a plating potential, $E = E_{Ag-AgCl} - E_{Bias}$, is established. Electron transfer reactions occur at this potential. (For example, the trace metals are reduced and plated, e.g., $Cu^{2+} + 2e^- \rightarrow Cu$.) These electron transfer reactions cause a current which flows from the counter electrode (see 4) to the test electrode. The current (base current) thus depends on the concentration of the reducible materials (e.g., trace metals, residual oxygen, and H^+ ion).

4. Counter electrode (platinum wire). This is the site of the oxidation reaction (e.g., $2Cl^- \rightarrow Cl_2 + 2e^-$). The potential of the counter electrode floats and is determined by the current which it supplies in balancing reduction with oxidation.

The reference and counter electrodes are isolated to a degree by Vycor* plugs with holes of diameter forty angstroms. These are penetrated only by diffusing ions. Therefore these electrodes are not affected rapidly by differing sample composition.

As the mercury film of the test electrode becomes channeled and depleted, the associated double-layer shorting capacitance increases. This results in a higher base current.

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*Trade name by Owens Corning.

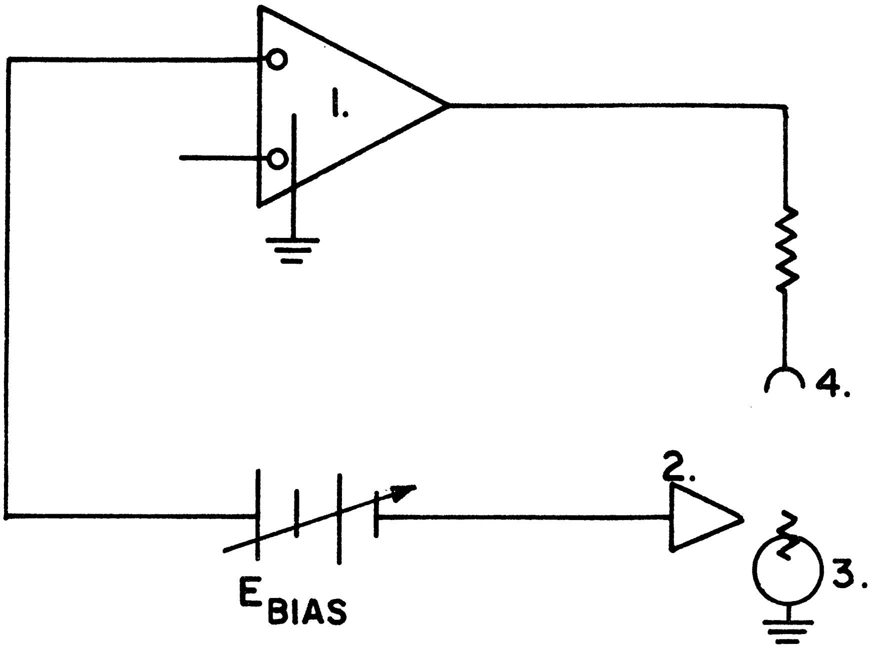

Figure V.1 : Simplified plating circuitry.

For example,

$$E = E_o - 2.3 \frac{RT}{nF} \ln \frac{Pb}{Pb^{++}} ,$$

where:

E_o is the standard potential, the electromotive force for the cell in which the activities of reactants and products of the cell reaction are each equal to unity;

n is the number of electrons transferred per molecule;

F is the Faraday.

Now $2.3 \frac{RT}{nF} \simeq 30$ mV. Suppose, at the start of the stripping step, $E - E_o = -90$ mV. Then $\ln \frac{Pb}{Pb^{++}} = 3$. As stripping progresses, the concentration of Pb^{++} increases rapidly. That is to say, for

$$E - E_o = -30 \text{ mV}, \ \ln \frac{Pb}{Pb^{++}} = 1 ,$$

$$E - E_o = 0, \ \ln \frac{Pb}{Pb^{++}} = 0 ,$$

$$E - E_o = +30 \text{ mV}, \ \ln \frac{Pb}{Pb^{++}} = -1 .$$

The trailing edge falls because the quantity of trace metal is finite. This edge is also influenced by diffusion of trace metal out of and away from the test electrode.

V.1.3 Description of Physical Cell Design and Modifications

Matson (1968) in 1968 brought to the University of Michigan Department of Meteorology and Oceanography his design of the mercury graphite composite electrode. Since this was a laboratory version consisting of several pipe stands and many wires and tubes strung about, and since there was always the danger of dropping the vials from the test tube clamps mounted on the ring stands, it was desirable to redesign the cells into a smaller, more compact and modular configuration. From this initial laboratory design the cell has been further modified and reduced as was presented in Figures 2.4 and 2.5 in section 2 of the text. The cell modification consisted primarily of drilling a hole through the electrode to allow a small piece of plastic tubing to be passed into the electrode. The tip of the graphite electrode was pointed in order to improve the stirring configuration of the electrode and to facilitate the more uniform and repeatable dissemination of the nitrogen bubbles which are used as an oxygen purging agent and as a stirring agent. An improvement patent has been applied for. Figure V.2 is a cut-away drawing of the cell with both a holed and solid electrode and, in addition, a schematic of the equivalent electronic circuit of the cell itself. Holed electrodes were used throughout this experiment.

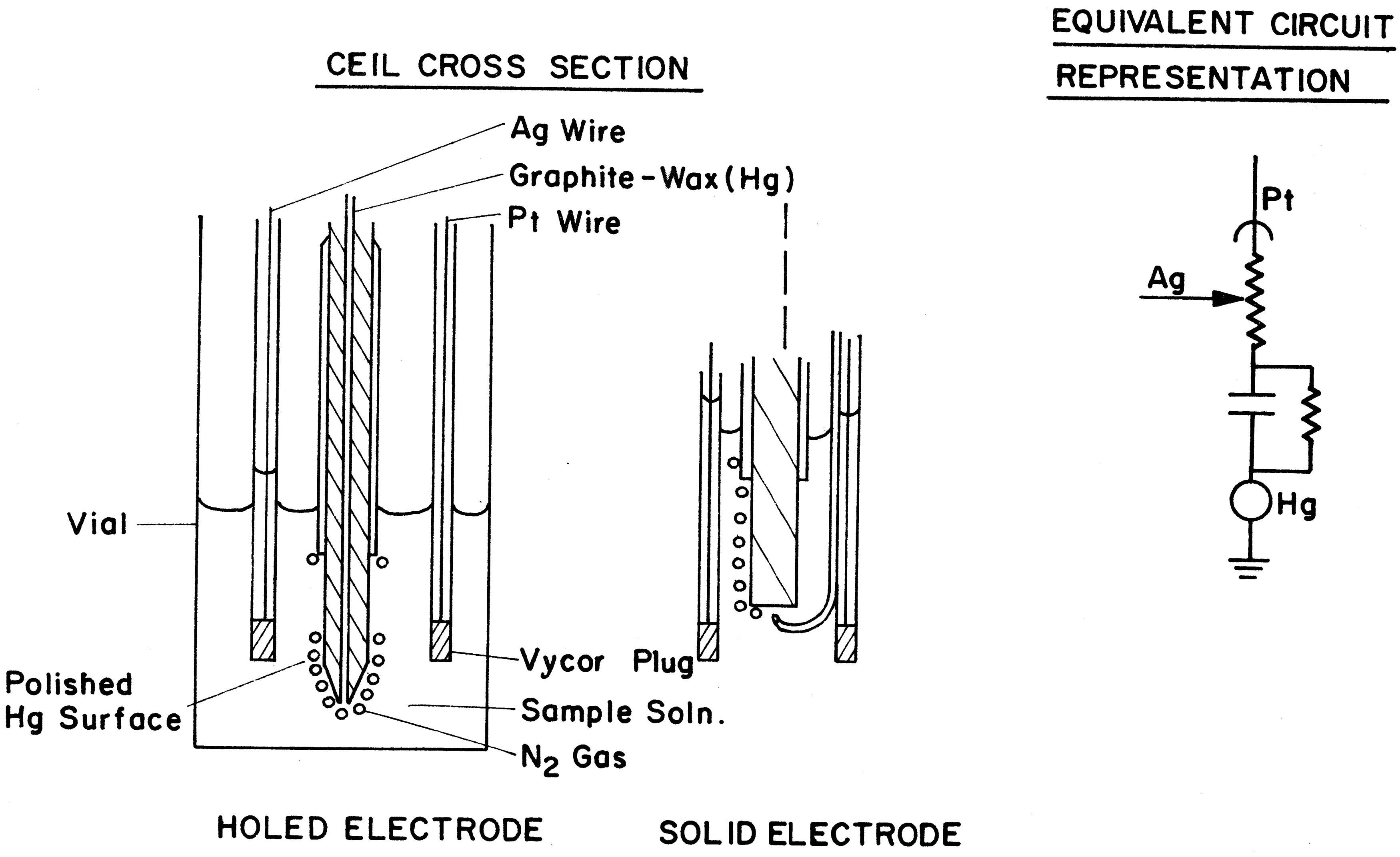

Figure V.2:Cell cross section and equivalent electronic circuitry.

V.1.4 Comparison of Holed and Solid Electrodes

Three solid electrodes were prepared for comparison. One was 1-1/8", one was 1", and one was 1" and pointed. The fourth one was of a modified design (holed) as shown in Figure V.2, and was 1" and pointed. Gas was provided to the first three electrodes by tubing in the solution as before.

From Figure V.3 we see that there is little variation among the electrodes and that the charging is comparable. The advantage of the holed electrode is that the stirring configuration remained the same from sample to sample with less danger of contamination and of bumping the gas tube. The disadvantage is that they are more difficult to make.

Sensitivity was checked by adding a lead standard and repeating the runs several times. The repeatability is good for both the charging and the spikes. The same spike was used in the repeat runs without changing the sample.

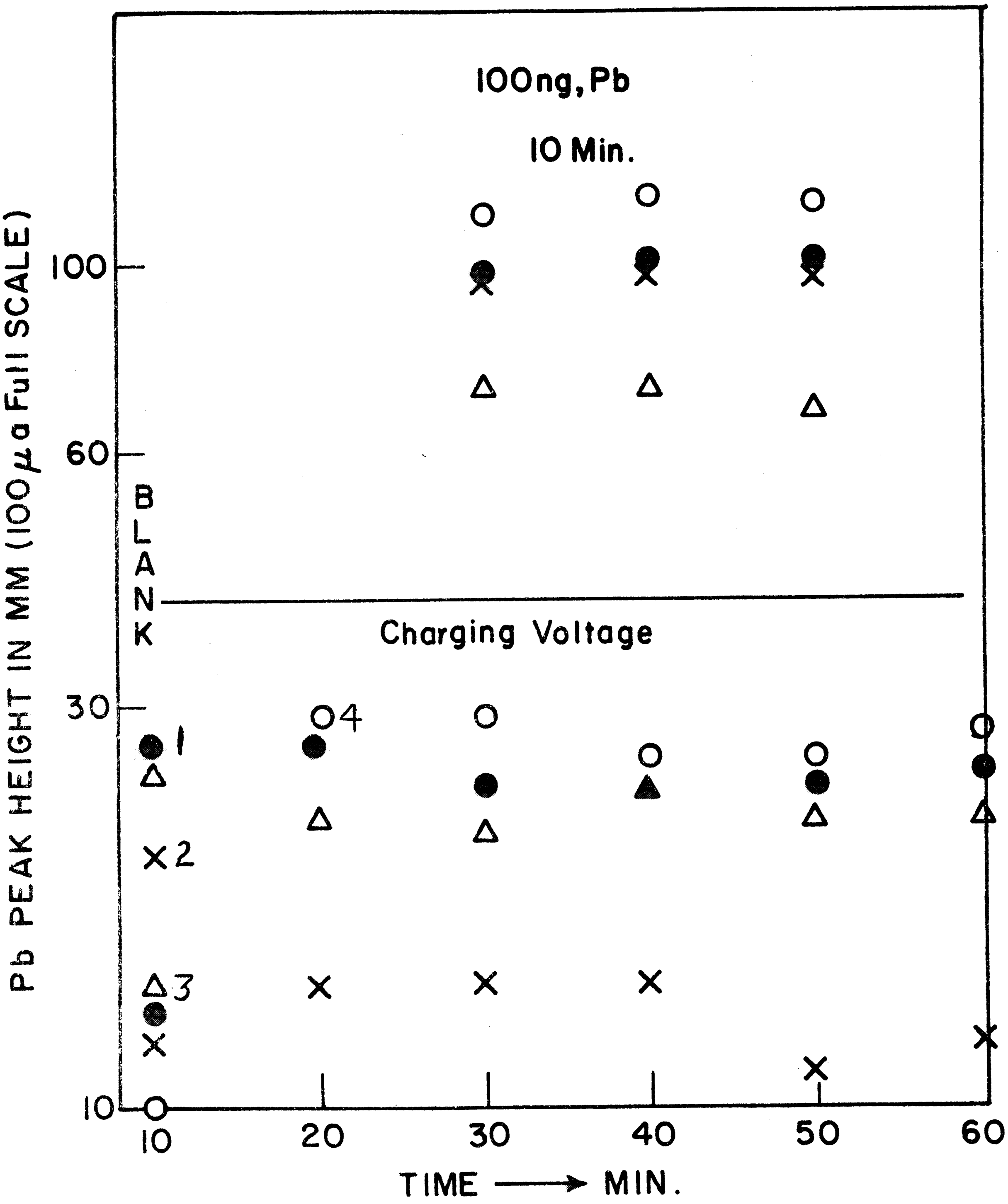

Figure V.3 : Comparison of holed versus solid electrode response.

V.2 OPERATION OF ASV APPARATUS

V.2.1 Stripping Potentials

The elements are stripped in the following order, beginning with the highest plating voltages; hydrogen, zinc, cadmium, indium, lead, copper, bismuth, and mercury. (In chloride, see Figure 2.6.) Of these zinc, cadmium, lead and copper are found in large enough quantities to be far above that of indium and bismuth. Thus, four peaks are usually observed before the mercury strips. (The location of each peak relative to the voltage is variable according to the reagent used, the acidity, and the characteristics of the cell.) Usually for the chlorides, a stripping voltage of 1.1 volts is almost into the zinc plating potential. If the acidity is high this voltage may be too large and hydrogen evolution is started. See diagnostics 6.

It is suggested that one try a few quick plates of a few minutes to find the plating potentials of the metals starting at about 0.8 volts and increasing to the zinc peak. Do this with 100 nanogram spikes for best results.

V.2.2 Preparation of Hg

Use 0.4 g of reagent grade Hg. Measure into a 100 ml volumetric flask, and add 5 ml nitric acid. Heat in a hood and dissolve the Hg. Equilibrate to 100 ml. This results in 2×10^{-3} molar Hg^{++}. 200 λ of this solution will result in a coating of 0.5×10^{-6} M/-cm^2 on a 4 cm^2 surface if entirely plated onto the electrode surface.

V.2.3 Preparation of Spikes

Spikes made from reagent grade materials are probably the easiest and least likely to be contaminated. The metal is weighed out in a reasonably precise manner, such as on a micro-balance, dissolved in a few milliliters of nitric acid and equilibrated in a volumetric flask with twice distilled water.

For my experiments the following procedure was used: One gram to the nearest hundredth of a gram was weighed on a micro-balance. For the powdered metal the job was easy, but for the solid and pellets a file was used to subtract a little from the larger piece to get the right amount. The metal was dissolved in nitric acid and equilibrated to 100 ml in a volumetric flask. This was to be the standard. One milliliter was pipetted from the standard flask and equilibrated to 100 ml in a second flask, again with double distilled water. One milliliter of the second standard was taken and equilibrated in a third 100 ml volumetric flask. This was the final standard and contained one microgram per milliliter.

Standards for all the metals were prepared in this way. The secondary standards were prepared from the first standards every two to four weeks. The third dilution was always prepared within 24 hours of the runs in which it was to be used.

For this work, a combination standard was prepared containing 100 ng of lead and copper, and 10 ng of cadmium. The cadmium standard was less, due to the low signal to spike ratio of cadmium in the samples. See running procedure.

V.2.4 New Cells

New cells are usually heavily contaminated and need to be cleaned. A good rinsing with distilled water and a little nitric acid is desirable for the cell electrodes. Be careful not to damage the silver wire and the solder on top of the cell head. Be sure to fill the glass electrode compartments 1/4 full with reagent before attempting to plate, and clear the gas from the bottom of the compartments frequently by gently flipping with fingernail with the wires partially removed. (See section V.2.9, diagnostic 6.) A syringe is probably the best way of getting the reagent into the glass, but the reagent may need to be jarred to the bottom. In some cases, the Vycor must be activated by blowing into the reagent charged tube and forcing the reagent through the Vycor plug.

The cells should be almost filled with reagent and plated for a few hours, stripped, washed, and the reagent changed. One to two days is usually enough for most applications, but more time may be needed for extremely sensitive analysis.

V.2.5 Plating of Mercury

For optimum performance the concentration of mercury on the graphite electrode should be 10^{-6} M per square centimeter of exposed graphite surface (Matson, 1968). Theoretically, one should add enough mercury solution to the reagent and wait for an hour or so to get the desired concentration. However, it has been found that the mercury does not always plate on to the graphite surface as quickly as desired, especially if the stirring rate is slow. For this reason, a visual means of inspection is desired for, at least, a good cell performance, if not an optimum performance.

Irrespective of the plating times and concentration added to the reagent, the electrode should not have any shiny places on the exposed portion. The mercury should cause an obvious dull grey or "dirty" surface to appear, but not a much heavier whitish grey appearance. In most cases the latter problem of too much mercury is easily controlled by never adding more than two to three times the optimum amount to the reagent solution. The amount of mercury added initially is dependent on the original condition of the electrode surface and the time allowed for the plating to take place. If the cells have been plated before and have Hg on them, then only a little is needed. If they are new or have been refurbished or well wiped, the near optimum amount is needed. Also, the shorter the plating time the more Hg one should add to get the minimum coating.

It should also be pointed out that the slower the Hg plate, the better the stability of the electrode surface. In addition, the bubbling can also cause some streaking on the electrode surface, and some bubbles tend to stick to the exposed graphite areas. For this reason, it is suggested that the following procedure be used.

Aliquot the optimum amount of Hg solution into the reagent. Let the stirring continue for about 15 minutes. Turn off the gas and jar the bubbles from the electrode surface. Allow to set over night at about 0.4 V, or just below the stripping potential for lead. Turn on the gas in the morning and allow the solution to equilibrate and mix for a few minutes. At the same time, turn the plating voltage to about 0.9 V and plate out contaminants for several minutes, then strip. You should be ready to run. The solution is usually contaminated and should be thrown away and the electrode washed with distilled water.

If, upon inspection, you see a mottled surface (black and grey), or the surface is still shiny, more mercury is needed. A drop or two from a pipette plated for about an hour at 0.9 V with the bubbler on, is usually enough to coat the surface properly. You will find some electrodes, especially the older ones, do not seem to coat as well as the others. The solution to this problem is to keep adding Hg until the desired surface is obtained, or to change the electrode.

V.2.6 Electrode Charging

V.2.6.1 Rate of Change

In order to determine the rate of change of the electrode charging, a series of runs with very short plating times was implemented. The results are shown in Figure V.4. It is obvious that the final current at the final potential (0.2 V--reference electrode) decreased with use. The plating times were 10 seconds in direct succession.

A second study used a longer plating time and the results are also plotted in Figure V.4. The plating times in minutes are shown above the points in minutes. Again, the maximum

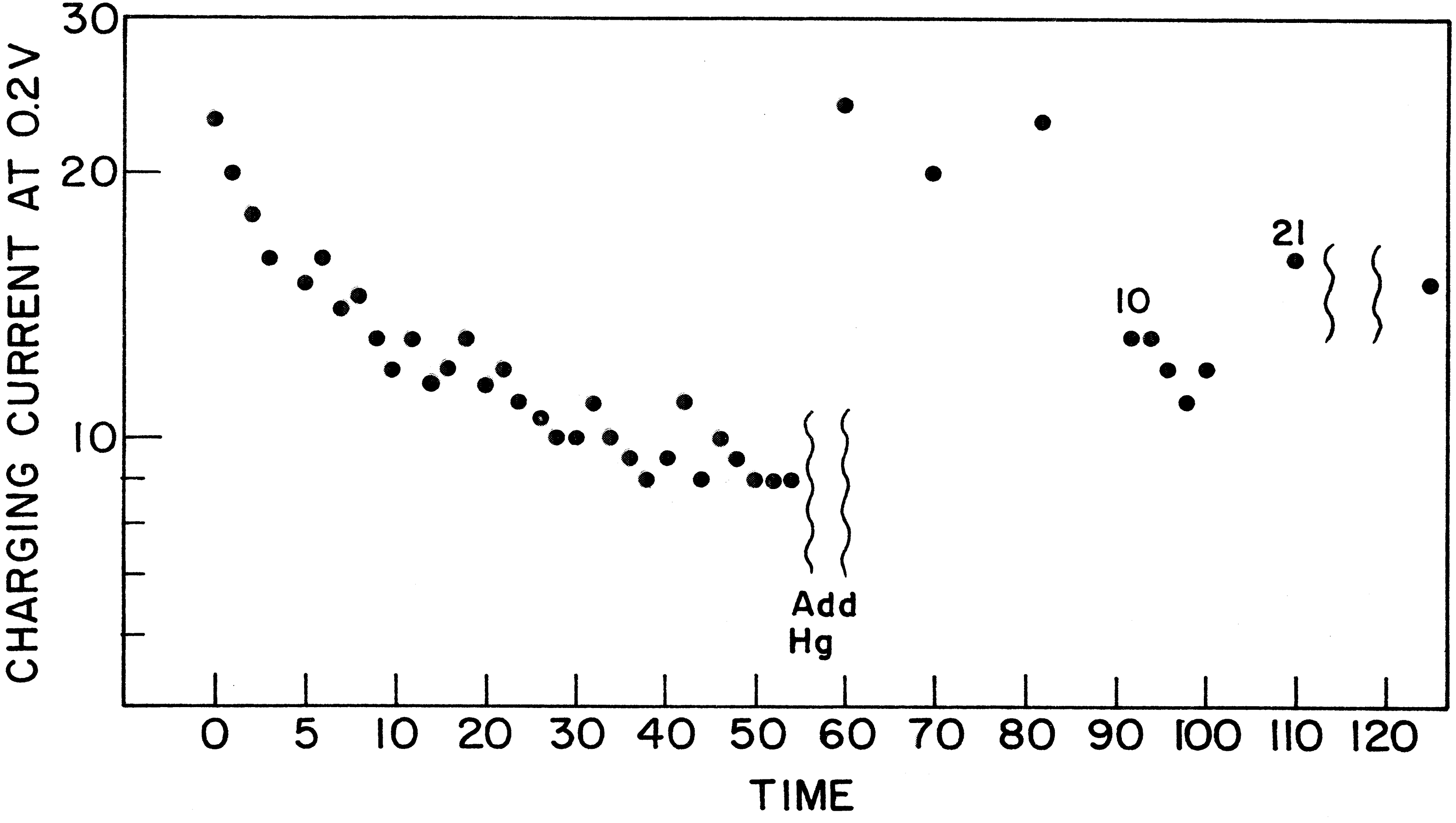

Figure V.4 : The change of charging current at 0.2 volts with time.

charging current at the terminal voltage decreases with usage, and in a similar manner, irrespective of plating time.

In both of the above cases it should be pointed out that the mercury layer was about ten times too little for optimum performance, and the decreasing tendency is observed consistently but at a slightly slower rate for a well coated electrode.

V.2.6.2 Exposure

To determine if the modified electrode was of the same characteristics as the solid electrode, a comparison study was tried. The exposed surfaces of the next four electrodes were 1-1/8 inches, 1 inch, 1/2 inch, and 1 inch, respectively. The surface preparations were to simply polish the exposed surface with crocus cloth and to plate with a weak solution of Hg for a few hours.

The results, presented in Tables V.1 and V.2, show that the additional exposed surface increases the charging. In addition, exposure to the air of some of the exposed surfaces increases the charging rate markedly. Also, the gas flow rate effects the charging but not substantially if the solution is allowed to equilibrate for a few minutes after turning on the gas. Finally, newer electrodes have a lower charging rate as seen in the decrease in the maximum value upon replacing the old electrode in rig No. 4 with a new electrode.

We should note two things at this point. One is that each electrode will usually not have the same charging characteristics even if the surfaces are the same area. This is

Table V.1

Charging current as a function of various conditions.

All electrodes are 1" exposure and holed, except No. 1 which is 1 1/8".

Peak heights of charging currents in mm.

Cell Number	1	2	3	4
Electrode Conditions				
Short Plate (sec.)	57	45	24	18
Long Plate (hrs.)	58	45	28	22
Short Plates:				
1/2 electrode exposed to air, no gas			85	
All covered, no gas			49	
All covered, with gas			64	
All covered, with gas			64	
All covered, with gas			64	
1/2 covered, with gas			83	
All covered, with gas			66	
3 Min. plate			48	25
gas off			33	
gas on			33	
gas on			32	
New Hg	46	42	27	22

TABLE V.2

FINAL CHARGING CURRENT AT 0.2V, mm

Cell No.	1	2	3	4
Exposed Length	1 1/8"	1"	1/2"	2 cm
Conditions:				
10 min.	44	29	18	26
24 hrs.	61	75	45	43
	55	25	22	55
Wash	68	23	18	55

probably due to the difference in preparation and polishing. They should not, however, be too different if the preparation was the same. Secondly, in the short run the decrease in charging also manifests itself by a decrease in sensitivity. The opposite is true for the long run of several weeks.

An optimum compromise was not determined by experimentation as there is a compromise that will best determine the exposed area. If you desire a certain plating time, determine the sensitivity needed from estimation of the sample level and by spikes. The charging should not exceed one half the total scale. If the charging is high and the sensitivity is low, use less surface and longer plating times, assuming good electrodes. For 10 minute plates at a sensitivity level of 50 μ a full scale, a surface length of 2 cm from the tip of the pointed electrode was satisfactory (≈ 3.5 cm^2).

V.2.7 Drawing of Base Lines

For very small quantities of the metals the traces are usually not peaks but a hump with a base line. Sometimes this humped trace will have a flat top with no maximum. Until enough material is present, a maximum will not occur for a given scale setting. Even with the existence of a maximum for cadmium (and zinc), there is a transition from a fast initial charging to a region of less charging and a flatter base line curve. Figure V.5 depicts a classical example. Because of this change in charging rate, it is sometimes difficult to establish just when the inflection occurs and stripping is started. For a calculation of the amount stripped based on

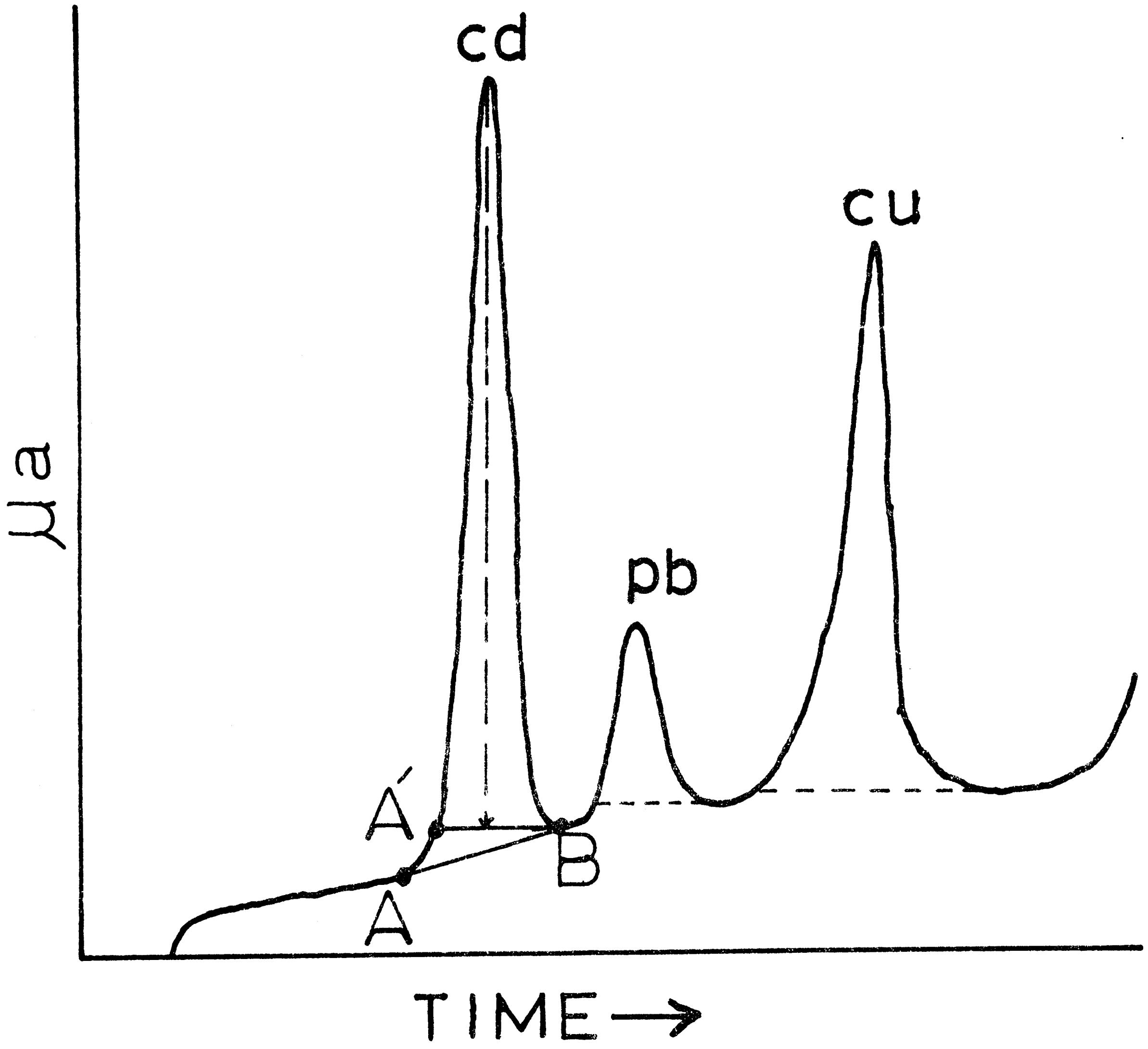

Figure V.5 : Drawing of base lines. A-B represents the slant line method and A'-B the horizontal method.

theoretical considerations, see Nicholson (1964), we would have to find the area or peak height from the beginning of the stripping to the end (line A-B). However, due to the linearity of the calibrations between peak heights and areas, and due to the fact that we are interested in differences and not absolute values of parameters, we can draw a base line horizontally from the left flat portion of the curve very accurately without estimating the initial inflection point (line A'-B), if a real maximum has already been established.

Table V.3 displays a real data sequence using both methods. The high base line on rig No. 2 best describes the advantage of the horizontal line method. The horizontal line method does not show a significant negative value, whereas the slant base line often does for small amounts of cadmium. A word of caution is in order; a maximum must be present for subtraction as a blank before a horizontal line can be used. Notice the increase from line 1 to line 2 and from line 2 to line 3. On line 1 there were no maxima present and part of the material went into the establishing of the initial maxima. This is another reason for the initial blank plus spike run with the sample added in the subsequent run. For large samples, as occurred with lead and copper, the horizontal line method was not used because of original advice, not because this method would not have worked. In subsequent work of this type, we plan to use the horizontal base line method.

TABLE V.3 :

SLANT VS. HORIZONTAL BASE LINE - Cd.

	Rig 1				Rig 2			
Sample	Horizontal		Slant		Horizontal		Slant	
	PH	Δ	PH	Δ	PH	Δ	PH	Δ
Blank	0		11		-		22	
+10ng	16	16	45	34	17	17	109	87
+10ng	49	33	81	36	m	m	151	42
Sample	59	10	79	-2	66	m	274	123
Blank	17		44		21		109	
Sample	20	3	48	4	27	6	108	-1
Blank	18		47		24		106	
Sample	25	7	50	3	33	9	103	-3
	Rig 3				Rig 4			
Blank	0		7		-		22	
+10ng	23	23	36	29	39	39	90	68
+10ng	53	30	67	31	92	53	152	62
Sample	61	8	76	9	108	16	167	15
Repeat	61	0	75	-1	108	0	163	-4
Blank	20		34		35		93	
Sample	22	2	35	1	39	4	80	-13
Blank	21		33		34		82	
Sample	34	13	48	15	53	19	113	29

V.2.8 Flat Peaks

On systems using the Heathkit recorder one will sometimes encounter a flat peak. This is sometimes due to an improper "Hum" adjustment. To correct, turn the damping off, adjust the hum to the minimum light on the indicator, and then restore the proper damping. If the phenomenon persists, check the reference battery, recorder sensitivity, and current amplifiers.

V.2.9 Diagnostics from the Traces

The following is a list of recurring problems and some suggested solutions.

1. Too little mercury: this situation leads to fast deterioration of the cell response and sometimes to double peaks. A semi-glossy surface is usually observed on the graphite electrode.
2. Uneven coating of mercury: this situation is similar to too little mercury, but the primary result is double peaks. The observed electrode surface is mottled and patchy.
3. Too much mercury: the result of too much mercury is broader peaks and slower response. This is due to the thickness of the mercury layer and the slower diffusion of the ions through the layer.
4. Large oscillations in the trace recorder: this is not to be confused with noise in the cell electronics. Usually this is caused by one of the electrodes not

being immersed in the reagent in the glass cell interior. Push the electrode down or add more reagent to the cell compartment.

5. Noisy signal: this problem is many faceted. For very sensitive work, turn the bubbler off just before stripping. Otherwise, you can position the bubbles so that they do not strike the glass and Vycor electrodes by turning the graphite electrode. Adjust the damping and hum adjustments, if present, on the recorder. Check wiring.
6. Lack of signal or sluggish response not associated with Hg coat: usually this is caused by bubbles forming in the counter or reference electrode. This is the first place to check for most troubles. Because of charging during the plating, some gas is evolved at the platinum electrode tip. Many times a gas bubble is formed at the porous Vycor and the current is diminished, thus the response is less. The reference electrode does not evolve gas but may have residual air in the porous Vycor that percolates slowly to the top of the Vycor, especially on new electrodes. These are common problems and cells should be inspected frequently for cell bubbles. Remove by flipping the glass gently but frequently with the fingernail with the wire partially removed from the cell. Check soldering and connections.

7. Fast deterioration of response: this is usually caused by two problems, lack of mercury and overvoltage on plating. See diagnostic 1. If numerous small bubbles form on the graphite electrode, hydrogen is being formed due to a plating voltage that is too high. For zinc, some of this is unavoidable but can be kept to a minimum by carefully calibrating the stripping potential for zinc and not exceeding it by more than 0.1 V. For the other metals, refurbish the electrodes by wiping and/or adding more mercury. The reason for this deterioration is that hydrogen forms at the electrode surface and alters the Hg coating to larger droplets and exposes graphite surfaces. This is not to be confused with larger bubbles from the stirring bubbler that stick to the electrode but cause little concern.
8. Reagent dries up: the stirring gas is usually very dry and will evaporate water from the cell over a prolonged plating. Pre-moisten by bubbling gas through distilled water and follow by a water trap. This is more than enough to moisturize the gas. To limit evaporation and to save nitrogen, turn the gas supply off overnight and for long periods of non-plating. Be sure to let the gas run for a few minutes before restarting the plating or stripping.

V.3 RUNNING PROCEDURES

V.3.1 Procedure for Cutting Filters

The Hi-Vol filter pads are usually folded along the longer axis and put into folders. This causes some settling into the fold from the rest of the filter surface if the folders are agitated too much. To attempt to gain a representative aliquot, a one inch square was cut through both sides of the filter close to the fold but not including the fold. Thus, a two inch^2 portion of the filter pad was obtained from different areas in the pad but near the center. A stainless steel scalpel was used to cut around a one square inch plastic template. The resulting sample was cut into small strips and put into the 25 ml volumetric flask using a plastic tweezers and a glass rod. All instruments were wiped after each use to minimize cross contamination.

V.3.2 Procedure for Cleaning Flasks

Several 25 ml volumetric flasks were washed in laboratory soap and tap water. They were rinsed twice in tap water and then in distilled water. They were then filled with tap water and HCl and allowed to stand for a few hours. After one more rinse with distilled water, the stoppers were inserted until the filter pads were cut and the flasks labeled.

V.3.3 Procedure for Digesting Samples

Four milliliters of 70% perchloric acid were pipetted into the volumetric flask and the material was shaken to position the filter material in the acid and not on the sides of the flask. A group of four to nine flasks were heated on a hot plate to 260°C for about one hour, or until all the black color disappeared from the filter strips. The flasks were removed from the heat, allowed to cool, and equilibrated to 25 ml with double quartz distilled water. Stoppers were inserted and the samples were allowed to set for at least 24 hours. With the acidity of the samples being so high, there was little absorption onto the glass sides of the flasks. However, there was a possibility of desorption from the glass. This is especially true for lead.

V.3.4 Codes for Flasks

The following code was used on the 25 ml sample flasks:

S/sample no./month/day/year.

For example, S806068 = sample 8, 6 June 1968. The blanks are designated by G B 1...N for the Gary area blanks, and C B 1...N for Chicago. The Gary blanks were processed and weighed while the Chicago blanks were new filter pads.

V.3.5 Procedure for Transferring Samples to the ASV Rig

Four 100 micropipettes were used to transfer the sample from the volumetric flask to the four quartz vials for ASV analysis. Each sample was drawn into the pipette and dumped into a waste beaker. A second sample was drawn and put into the quartz vial. The pipette was laid aside and a new pipette was used for the next sample. During the plating the pipettes were washed with distilled water, both inside and out, by squirting a generous supply of water from a squeeze bottle onto and through the pipettes. The carry-over was measured and found to be minimal, if this procedure was properly followed.

The quartz vials were cleaned by two rinsings with distilled water and subsequent shakings. A third rinse was left standing in the vials until they were needed in the next round of samples. Between the runs the vials were stored dry and inverted to minimize contamination.

Due to the amount of material we were sampling, and to the relative predictability of this study, most incidents of contamination were easily observed and usually predictable. Any unusual values were rerun to verify that the signal was not that of procedural contamination.

V.3.6 Running Procedure

After the cells were properly conditioned with mercury, they were cleaned with double distilled water and a 10 minute reagent plate was tried. If the signal was high, the cells were cleaned again to check for carry-over of high reagent blanks. If the reagent was plating for more than three days and the reference electrode read above 1.1 volts on the reagent jug, the problem was usually carry-over. When a low reagent blank was read, no more attempts were made to clean the cell. (For more sensitive work, this would have to be monitored more carefully.) A filter blank aliquot was then added and run for 10 minutes. A combination spike of 100 ng lead and copper and 10 ng cadmium was added and plated for

10 minutes as before. A second spike was added to obtain a better peak and a more accurate standard. (See section V.2.7, Drawing of Base Lines.) During some runs additional spikes were made by doubling the previous spike to obtain a concentration versus peak height and/or area curve for subsequent calibrations of large quantities of the metals. (See section IV.4.1, Calibration.)

After a standard run was completed, the process was repeated but a sample was added on top of the spike after it had been stripped and recorded. This sample was plated for 10 minutes, also, and then stripped. The reasoning behind this procedure was to eliminate the variable carry-over and to monitor the deterioration of the cell, if it existed. The carry-over was usually about 2-3%, but since the subsequent samples varied widely, the blanks would also vary even if the carry-over rate remained constant, which it probably did not. (See section V.3.7, Carry-over.) By subtracting the reagent blank, plus the filter blank, plus a spike, plus carry-over from the previous sample, a nearly true value of the sample is obtained, and the cell response is monitored in the long run. The filter blank spike was added to each spike run to ensure that the acid in the sample did not change the cell response between the spike and sample plus spike run. This was observed to happen on the pilot runs. The addition of more acid from the sample did not seem to change the calibration significantly as was expected.

V.3.7 Procedure for Minimizing Carry-over and Cross Contamination: Cleaning the Cells of the ASV Rig

Ten milliliters of pre-purified reagent was pipetted into the clean quartz vials. 100 λ of the blank solution and 100 λ (100 ng - Pb, 100 ng - Cu, 10 ng - Cd) of spike solution was also pipetted into the vial, in that order. After completion of the last round of samples, the other set of vials was removed, one at a time. The electrodes were squirted with a generous supply of distilled water immediately after the removal of the original vial to prevent the mercury film from drying, cracking, and oxidizing, and thus deteriorating the sensitivity of the cell. When the water jet is removed, the excess is blown off and the newly prepared vials inserted as soon as possible. This process was completed one cell at a time. The mercury surface was never under a direct stream of water in order to minimize mechanical deformation and change of the cell response.

V.4 REPRODUCIBILITY

V.4.1 Static Reproducibility

One probably would expect that cell deterioration would take place with the radical treatment of exposure to air and washing with a stream of distilled water; but, does the cell change significantly by simple repetition of the plating-stripping procedure? The answer is not a simple one as there are several parameters to consider. Some of these are: slow contamination from the electrode compartment through the Vycor plugs, change in the valence due to reagent changes, plating

Table V.4 :

Carry-over using wash-bottle stream.

Rig Number	100 ng spike	after washing	ratio
	Areas under curves, (in.^{2}).		
1	9.6	0.23	42
2	10.7	0.30	36
3	6.0	0.12	50
4	7.9	0.24	33

∴ The average carry-over is ≃ 2.5%, using area.

Rig Number	100 ng spike	after washing	ratio
	Peak Heights (mm).		
1	780	25	31
2	690	34	20
3	440	8	55
4	540	23	24

∴ The average carry-over is ≃ 3.0%, using peak heights.

potential, pH, and others. If we assume that the cells are properly cleaned and the mercury has been plated properly, a repeatability test can be conducted, (see Table V.5). The reagent is 2.0 N NaCl + 1 N NaAc. The repeatability is good, and variations are probably due to timing (and measurement).

Since we cannot always be assured that conditions are as good as those above, we should present a more realistic study, remembering that optimum performance can be achieved with enough patience and skill. Table V.6 and Figures V.6 - V.8 represent a sequence of eleven 10 minute plates of cell blanks. A significant deterioration does occur, but it is a fairly steady change.

When using acetate buffer solutions, you must be careful that the lead does not precipitate out as acetate. This is accomplished by using acid solution of sufficient strength, and is another reason for adding the filter blank to the spike sample before getting the background and carry-over values in an initial run.

An interesting phenomenon observed was that a dark spot appeared on the graphite electrode directly across from the charging electrode (current electrode). This spot grows with use and is usually about 2-3 mm in diameter, black at the center and diffusing gradually to the grey of the Hg coating. This is probably due to the electric or current field gradient in the vicinity of the current electrode. There does not seem to be any observable correlative effect, but it does show that the field is not uniform throughout the cell.

TABLE V.5 :

STATIC REPEATABILITY

Run	Cell 1 Peak ht. (mm)			Cell 2 Peak ht. (mm)			Cell 3 Peak ht. (mm)		
	Cd	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu
1	11	44	8	23	42	9	13	37	7
2	11	40	7	25	45	14	17	36	9
3	11	38	6	23	41	12	20	38	11
σ	0	2.5	.8	1	1.7	2.1	2.9	.8	1.6

Average of σ	Cd	Pb	Cu	All
	1.3	1.7	1.5	1.5

TABLE V.6 :

STATIC REPEATABILITY - 10 minute plating

Run No.	Rig 1			Rig 2			Rig 3			Rig 4		
	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd
1	20	70	45	17	55	35	7	32	21	6	32	10
2	18*	53*	46*	13	45	30	6	36	20	5	28	10
3	16	41	43	13	43	30	6	33	18	4	21	10
4	15	44	41	12	43	29	6	30	18	4	22	9
5	13	42	41	11	40	28	6	27	18	5	23	9
6	14.5	40	42	12	39	27.5	5.5	24.5	18	4	17	8
7	13.5	37	42	10.5	33	24	5.5	22.5	18.5	4.5	16	7.5
8	14	33.5	41.5	10	28.5	22.5	5.5	17	17.5	4.5	11	7
9	13.5	30.5	40	10	25	22	5.5	14.5	17.5	5	10	6.5
10	13	29	40	9	22.5	19	5	11.5	16.5	4	9.5	7.5
11	(75)	29	42	(54.5)	31	18.5	(85.5)	16	16	(60)	9	5

* =11 min; scale = 100μg; ( ) Spike $2x10^{-7}$ M,Pb

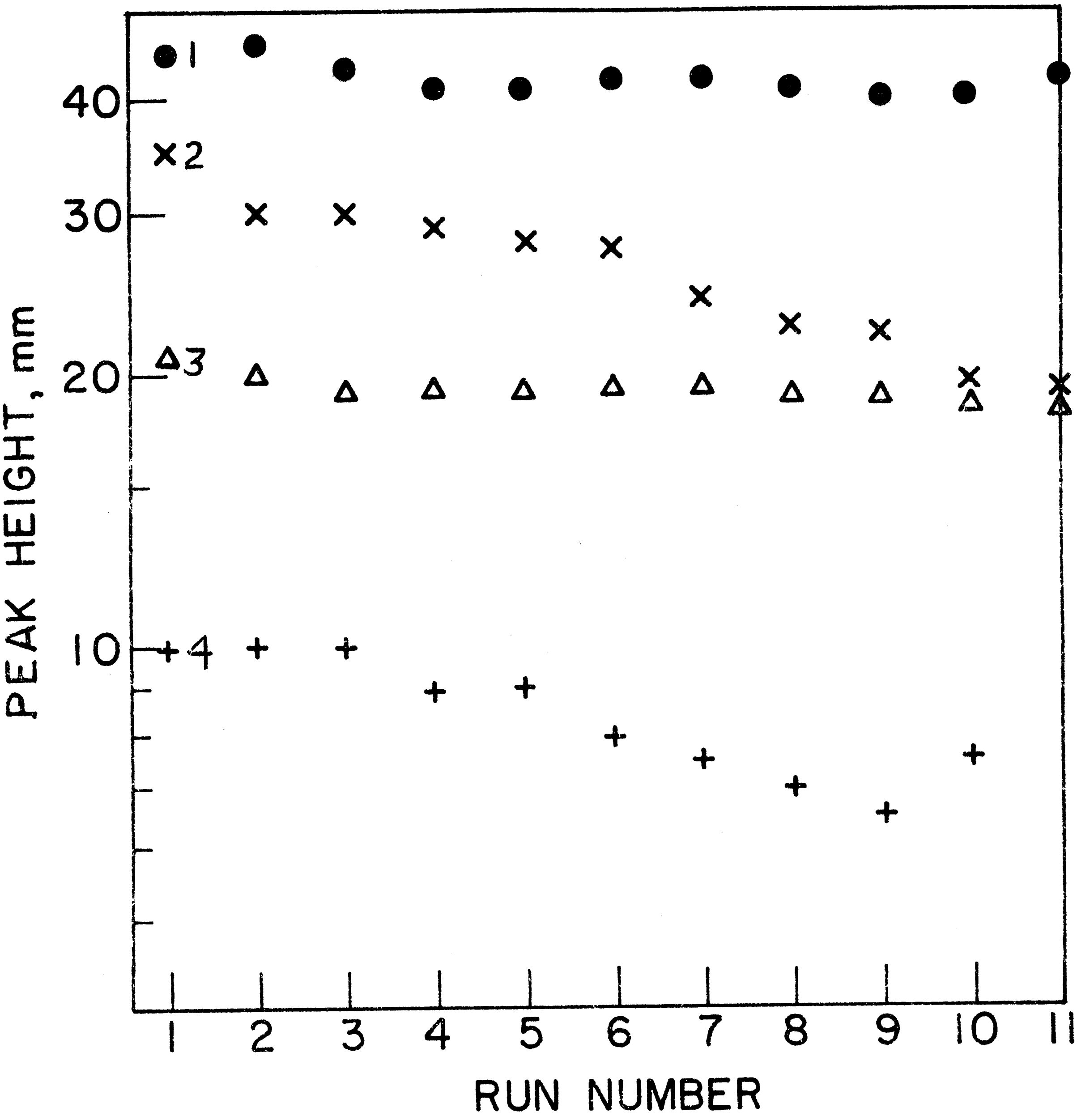

Figure V.6 : Static reproducibility, Cd.

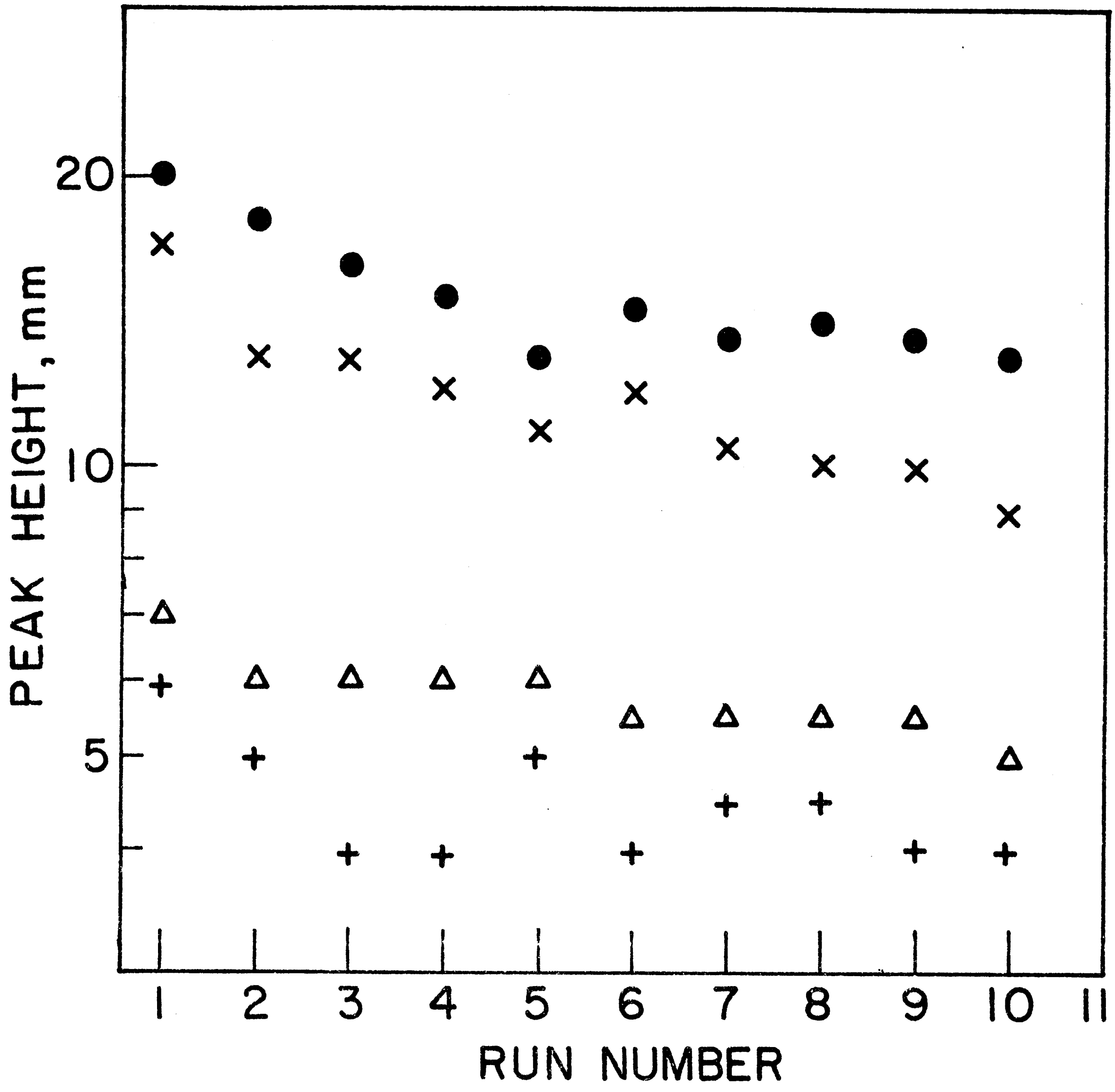

Figure V.7: Static reproducibility, Pb.

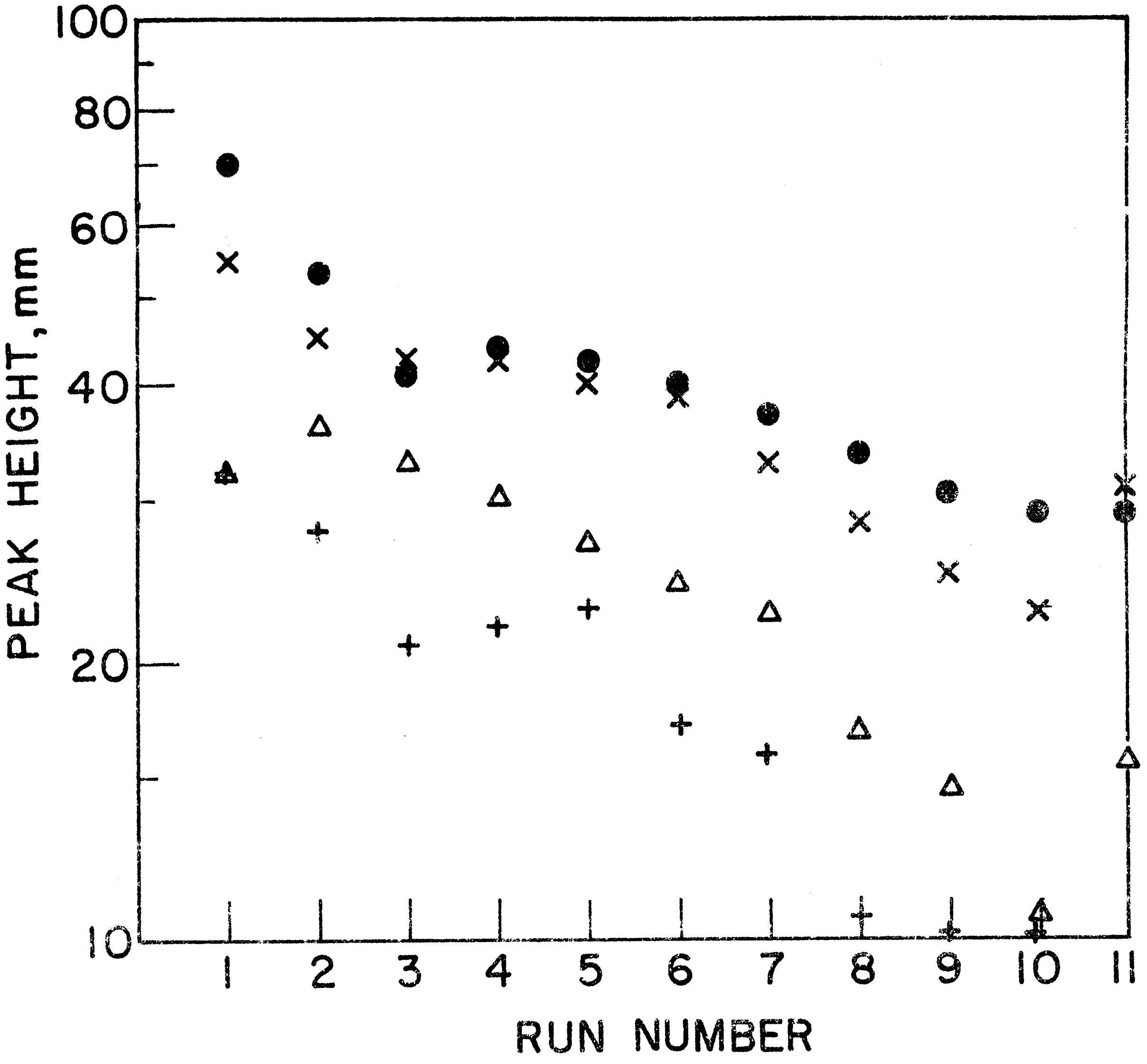

Figure V.8 : Static reproducibility, Cu.

Perhaps a future design improving the field characteristics would improve the cell performance. We should investigate further.

V.4.2 Repeatability Within the Same Filter Pad

Sample S106208 was sampled in three additional areas on a separate run. Each vial was treated as a regular run with the sample procedure as before. The standard deviation was 33% for Cd, 17% for Pb, and 3% for Cu within the four samples, resulting in an average of 18% reproducibility. The results are shown in Table V.7.

V.5 CALIBRATIONS: CONCENTRATION CURVES, CONCENTRATION VS. PEAK AREA AND HEIGHT

Preliminary investigations prior to the actual sample runs were made in order to determine representative relationships between concentrations and peak heights and areas. The results are tabulated in Table V.8 and plotted in Figures V.9 and V.10. As stated by Matson (1968), the area dependence is linear throughout the possible ranges. However, the peak heights start to roll off at about 2 micrograms absolute. That is to say, 2 micrograms within the sample vial for a 10 minute plating time. The standard amount of reagent was 10 ml in all of these studies. The following rule of thumb was observed: the peak height method is linear to 1-2 micrograms with a 30 to 40% error in the 10 to 20 microgram region.

These graphs, or similar graphs, can be used to quickly estimate the concentrations of large samples with reasonable

Table V.7 : Reproducibility within the same filter pad.

Run Number	Cd ng/m^3	Pb ng/m^3	Cu ng/m^3
1	3	780	1500
2	4	900	1400
3	6	840	1400
4	8	1200	--
Average :	5.2	930	1430
σ :	1.8	162	47
Percent σ:	33%	17%	3%

Table V.8 :

Concentration vs. **peak area and peak height.**

10 minute plates (in.^{2} x 100 and mm scaled to 100 μa)

Rig	1		2		3		4	
	Area	Peak	Area	Peak	Area	Peak	Area	Peak
Spike								
200 ng	57	76	51	92	35	49	41	56
400	88	114	-	-	80	101	93	135
600	140	177	-	218*	136	186	136	205
800	186	226	212	352	186	238	170	250
1000	244	278	-	-	218	282	234	320
1200	284	334	-	-	290	330	272	390
1400	356	376	470	720	328	390	312	442
2400	500	515	570	855	460	535	525	685
3400	655	615	800	1070	685	695	695	845
13,400	2230^{x}	1450	-	2370*	3190^{x}	1540	2960^{x}	2020

* : estimated by 2 x 1/2 width method.
x : non-linear peaks

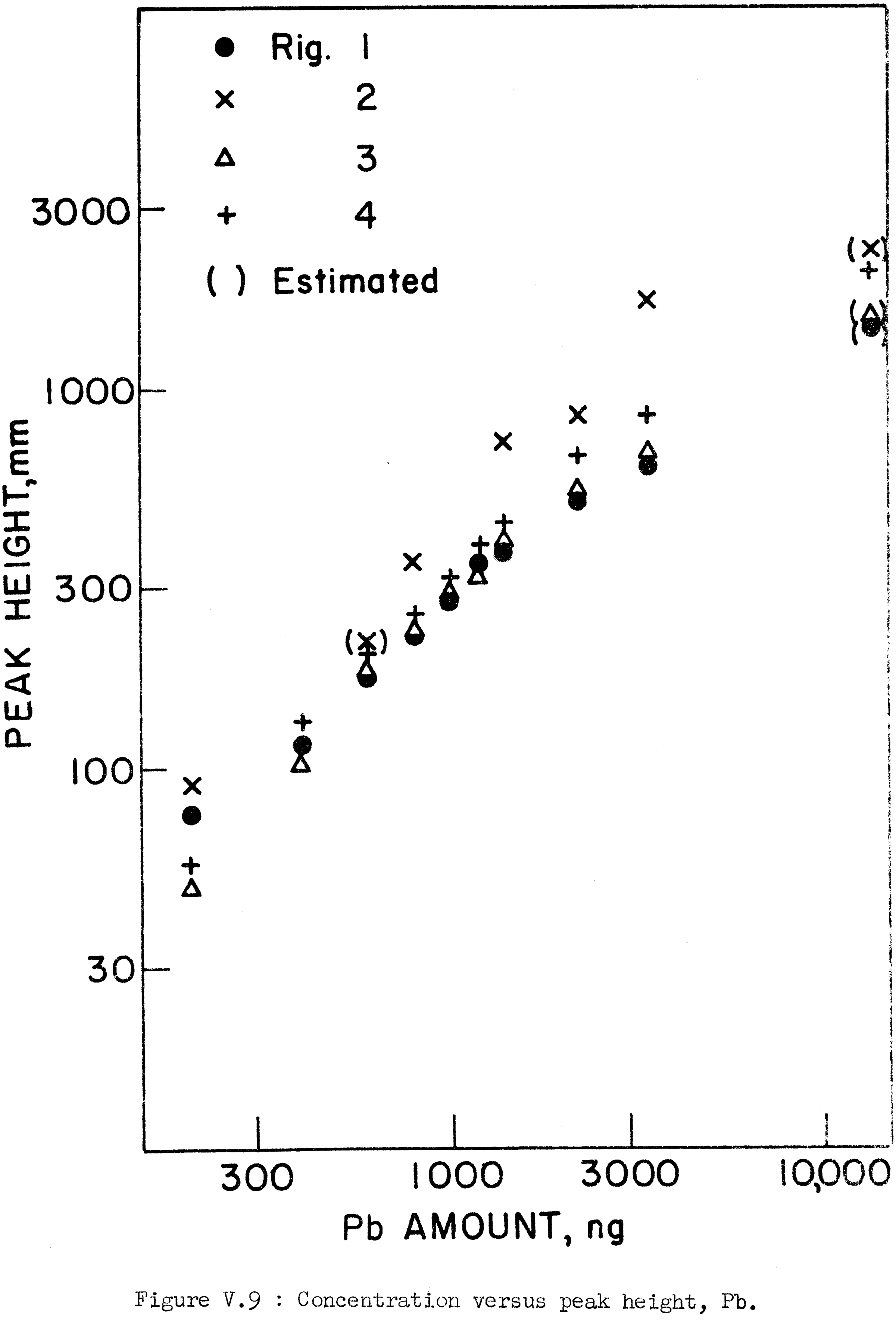

Figure V.9 : Concentration versus peak height, Pb.

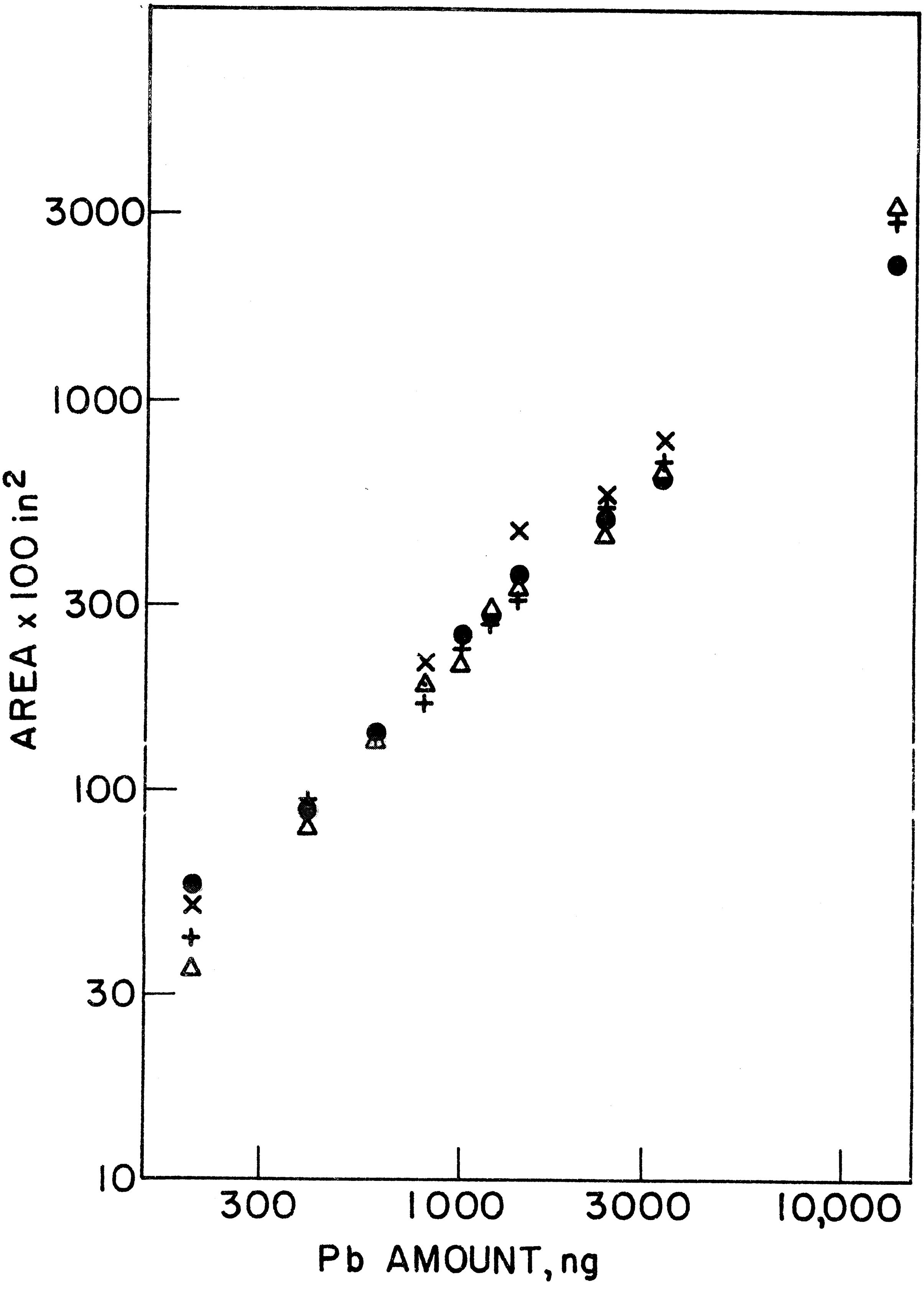

Figure V.10 : Concentration versus peak area, Pb.

accuracy. It is suggested that the aliquot be taken so that the concentrations are less than one microgram absolute, so that peak heights can be used. See the discussion concerning peak heights versus areas in section IV.5.4. Other graphs of this nature can be drawn from the runs of the area-wide samples.

It should be noted that the roll off in peak height may be due more to the electronics and less to the cell characteristics. It is, therefore, necessary to calibrate for each change in the electronic components. I would suggest that more efficient current amplifiers would help to alleviate this nonlinearity, but it is not necessary for proper selection of aliquots when such is possible.

In order to confirm the logarithmic dependence of the cell response on the plating time, a 200 ng spike was added to 10 ml of the reagent and the response recorded for several sequential plating intervals. Each interval was separated by 15 sec of stripping potential (0.2 V). This particular data set is presented in Table V.9 and graphically in Figure V.11. One cell was unique in that a fresh shot of mercury was added just prior to the study, while the other cells were several hours since their mercury plates and several plating periods had passed. It is interesting to note that the fresh mercury greatly improves the cell sensitivity.

The half times of the cells (that time to plate half the material) is of the order of 10 minutes in general with more time needed for older cells and less for freshly prepared ones.

TABLE V.9 :

PLATING TIME CONSTANTS: 200 ng Pb spike

Plating time*	Cell 1 Height (mm)	Cell 2 Height	Cell 3 Height
5	72	(Hg)	55
10	85	121	72
15	96	139	86
20	104	151	92
30	114	173	107
60	134	207	138
120	146	238	170
15	97	133	73

* 15 seconds between runs

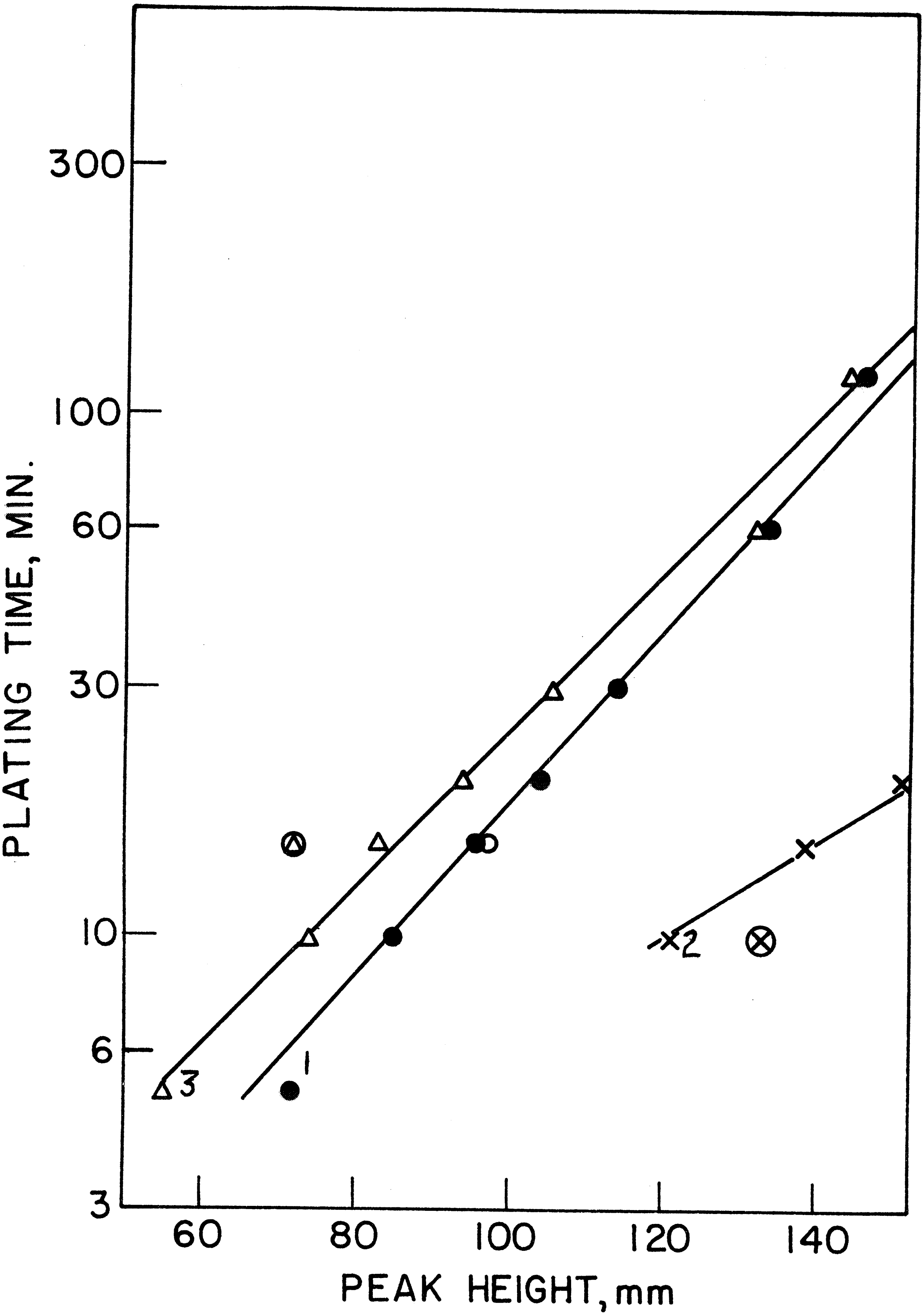

Figure V.11 : Plating time constants versus response.

At the termination of the 120 minute run a repeat of the 15 minute interval was implemented to check on the repeatability or deterioration of the cell. From this data the reliability is better than 15% in all cases presented here. Other studies were processed and showed similar results.

APPENDIX VI

DETAILS OF SAMPLING SITES

Figure VI.1 :

SUSPENDED PARTICULATE MONITORING NETWORK,

Chicago, Ill.

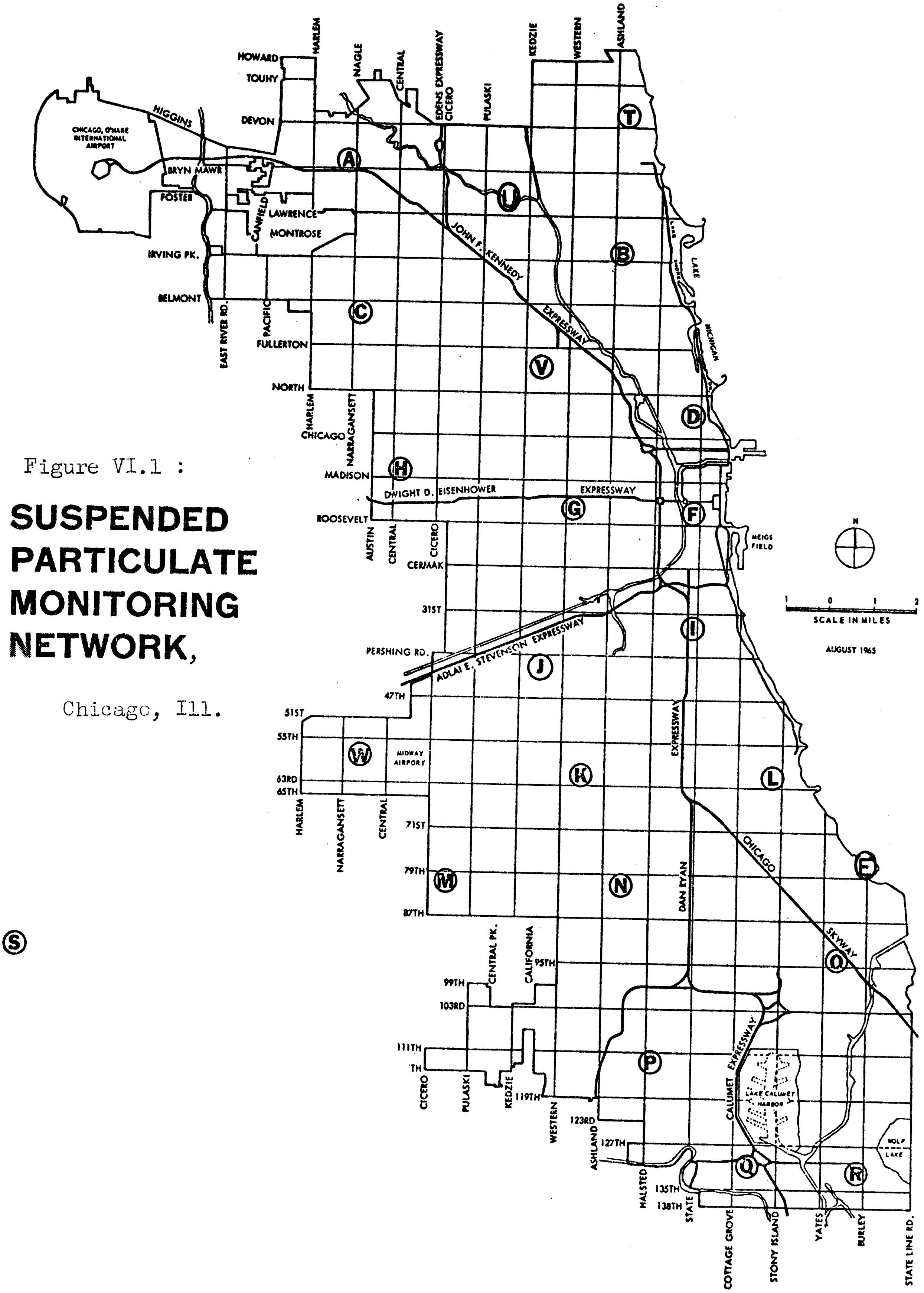

TABLE VI.1

STATION KEY FOR NORTHWEST INDIANA AIR SAMPLING NETWORK

	Area	Name	Address and Location
1	Hammond	Water Works	110th and Lake Avenue
2	" "	Goldblatt(NASN)	Hohman and Sibley
3	" "	City Hall	Highland and Calumet
4	Whiting	Fire Station	119th and Schrage Avenue
5	" "	South Side School	127th and Birch
6	East Chicago	Marktown	Brode and Pine
7	" "	Central Fire Station	450 E. Columbia Drive
8	" "	Roxana	Roxana Drive and S. Walsh Avenue
9	" "	Field School	Block and James Place
10	" "	Franklin School	142nd and Alden
11	Gary	Airport	U.S. 12,West Gary
12	" "	Ivanhoe	13th Avenue and Gerry
13	" "	Fire Station	5th and Connecticut
13A	" "	" "	(Directional)
14	" "	Williams School	19th and Indiana
15	" "	Kuny School	51st and Kentucky
16	" "	Wirt School	Birch and Gand
17	Lake County	Highland	9135 Erie Street, Highland
18	" "	Hobart	Forman School-S. Ind. Rt. 51, **Hobart**
19	" "	Crown Point	Taft School, S. Main Street,Crown Point
20	" "	Schneider	Standard Oil Station, R.R. 51, Schneider
21	Porter County	Ogden Dunes, Ind.	
22	" "	South Haven, Ind.	
23	" "	Chesterton, Ind.	
24	" "	Flint Lake	N. Valparaiso, Ind.

TABLE VI.1,continued :

25	Porter County	Kouts, Ind.	
26	Michigan City	Central School	9th and Spring
27	" "	Coolspring School	Niemer Road
27A	" "	Nieman School	Tryon and Cook Rd.
28	LaPorte County	LaPorte	(proposed)
29	" "	Hanna	(proposed)

TABLE VI.2 :

CITY OF CHICAGO, DEPARTMENT OF AIR POLLUTION CONTROL - TECHNICAL SERVICES DIVISION, SUSPENDED PARTICULATE, SULFUR DIOXIDE AND DUSTFALL MONITORING NETWORK, SAMPLING STATIONS

A	Taft High School	5625 N. Natoma Avenue
B	Lake View High School	4015 N. Ashland Avenue
C	Steinmetz High School	3030 N. Mobile Avenue
D	Cooley Voc. High School	1225 N. Sedgwick Street
E	South District Filtration Plant	3300 E. Cheltenham Place
F	G.S.A. Building	538 S. Clark Street
G	Crane High School	2245 W. Jackson Blvd.
H	Austin High School	231 N. Pine Street
I	Farr Dormitory	3300 S. Michigan Avenue
J	Kelly High School	4136 S. California Avenue
K	Lindbloom High School	6130 S. Wolcott Avenue
L	Hyde Park High School	6220 S. Stony Island Avenue
M	Stevenson Elementary	8010 S. Kostner Avenue
N	Calumet High School	8131 S. May Street
O	Chicago Voc. High School	2100 E. 87th Street
P	Fenger High School	11220 S. Wallace Street
Q	Carver High School	801 E. 133rd Place
R	Clay Elementary School	13231 S. Bursley Avenue
S	Argonne National Laboratory	Argonne, Illinois
T	Sullivan High School	6631 N. Bosworth Avenue
U	Von Steuben High School	5039 N. Kimball Avenue
V	Logan Square	Fullerton and Kedzie Avenues
W	Hale Elementary School	6140 S. Melvina Avenue

TABLE VI.3 :

METEOROLOGICAL STATIONS, NORTHWEST INDIANA

I	E. Chicago City Hall	4600 Indianapolis Blvd.
II	Kieser Corp., Gary	7501 W. 5th Ave.
III	Ogden Dunes, Ind.	(Station 21)
IV	South Haven, Ind.	(Station 22)
V	Chesterton, Ind.	(Station 23)
VI	NIPSCO., Michigan City	1st and Wabash
VII	Gary Air Pollution Dept.	6300 W. 3rd Ave.
VIII	Gary Airport	U.S. 12, West Gary
IX	Hammond City Hall	Calumet Ave. and Highland

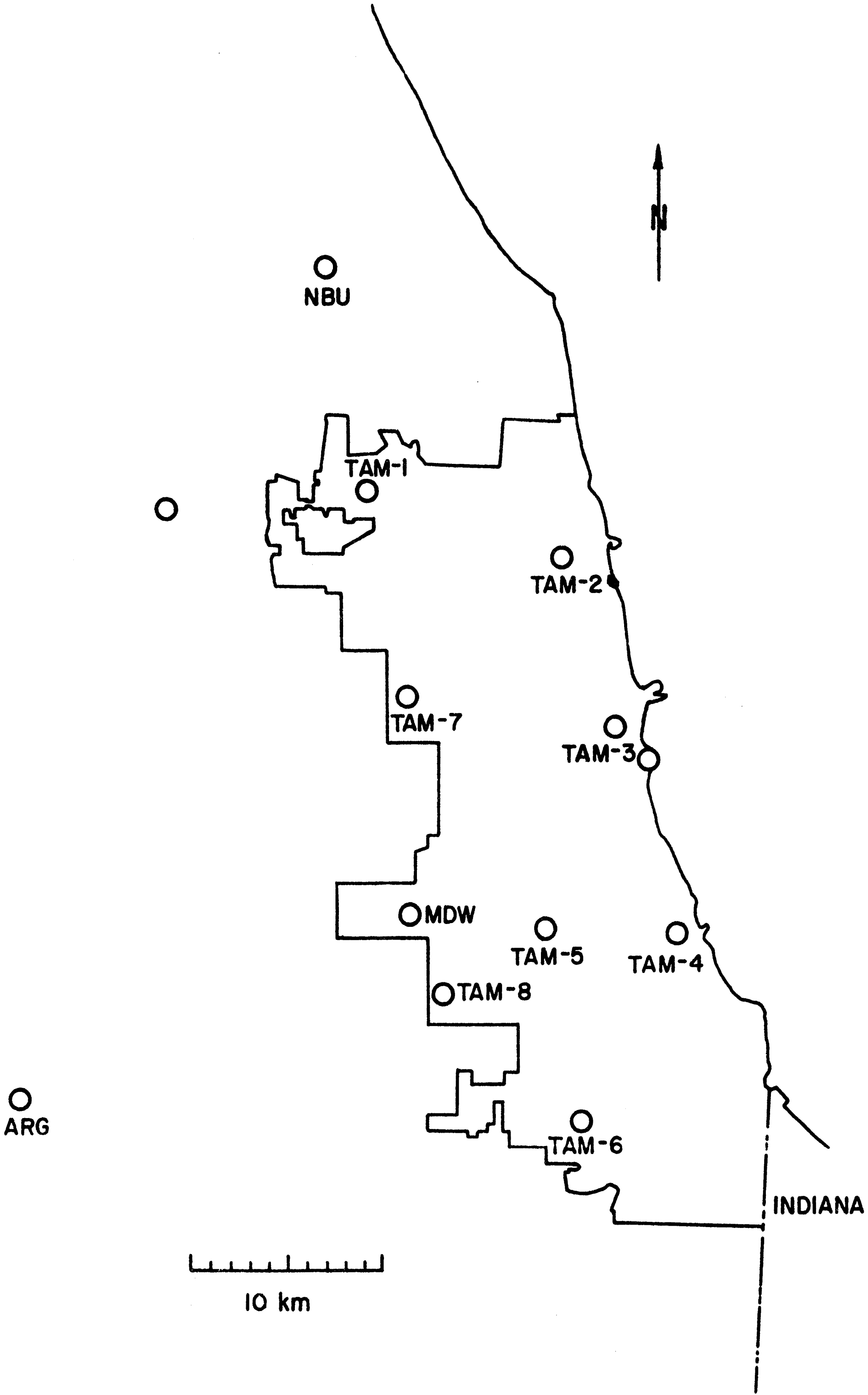

Figure VI.2:Telemetered data stations, Chicago, Ill.

TABLE VI.4

NORTHWEST INDIANA SAMPLING NETWORK RANDOM SAMPLING SCHEDULE, 1968
SAMPLING PERIOD (WEEK)

	Sampling day
1.	Wed. Jan. 3*
2.	Tues. Jan. 9
3.	Sat. Jan. 20*
4.	Thurs. Jan. 25
5.	Mon. Jan. 29*
6.	Tues. Feb. 6
7.	Fri. Feb. 16*
8.	Wed. Feb. 21
9.	Tues. Feb. 27*
10.	Thurs. March 7
11.	Tues. March 12
12.	Sun. March 17*
13.	Wed. March 27
14.	Thurs. April 4
15.	Fri. April 12*
16.	Wed. April 17
17.	Thurs. April 25*
18.	Tues. April 30
19.	Sat. May 11*
20.	Thurs. May 16
21.	Wed. May 22*
22.	Mon. May 27
23.	Thurs. June 6*^{x}
24.	Mon. June10
25.	Thurs. June 20^{x}
26.	Sun. June 23*
27.	Mon. July 1*
28.	Tue. July 9^{x}
29.	Tues. July 16*
30.	Wed. July 24
31.	Wed. July 31*
32.	Thurs. Aug. 8^{x}
33.	Sat. Aug. 17*
34.	Tues. Aug 20
35.	Thurs. Aug. 29*x
36.	Wed. Sept. 4
37.	Fri. Sept. 13*
38.	Thurs. Sept. 19
39.	Wed. Sept. 23*
40.	Thurs. Oct. 3
41.	Tues. Oct. 8
42.	Sun. Oct. 13*
43.	Thurs. Oct. 24*
44.	Thur. Oct. 31
45.	Sat. Nov. 9*
46.	Wed. Nov. 13
47.	Tues. Nov. 19*
48.	Tues. Nov. 26
49.	Fri. Dec. 6*
50.	Thurs. Dec. 12
51.	Mon. Dec. 16*
52.	Sat. Dec. 28

VALPARAISO° SAMPLING DAYS

June	6	August	4
	14		10
	20		19
	27		21
July	2		27
	9		
	11	Sept.	1
	19		14
	27		17
			25

* NAS days
x University of Michigan trace metal studies (ASV)
° Only Summer months are listed

TABLE VI.5

NORTHWEST INDIANA SAMPLING NETWORK RANDOM SAMPLING SCHEDULE, 1969
SAMPLING PERIOD (WEEK)

	Sampling Day
1.	Sat. Jan. 4*
2.	Tues. Jan. 7
3.	Wed. Jan. 15*
4.	Thurs. Jan. 23
5.	Tues. Jan. 28*
6.	Sun. Feb. 2
7.	Thurs. Feb. 13*
8.	Wed. Feb. 19
9.	Fri. Feb. 28*
10.	Thurs. March 6
11.	Mon. March 10*
12.	Mon. March 17
13.	Sun. March 23*
14.	Wed. April 2
15.	Mon. April 7*
16.	Sat. April 19
17.	Fri. April 25*
18.	Wed. April 30
19.	Sun. May 4*
20.	Fri. May 16
21.	Tues. May 20*
22.	Sat. May 31
23.	Sat. June 7*
23A.	Wed. June 11x
24.	Fri. June 13
25.	Wed. June 18*
26.	Thurs. June 26
27.	Wed. July 2*
28.	Tues. July 8
29.	Fri. July 18*
30.	Thurs. July 24
31.	Tues.July 29*
32.	Mon. Aug. 4
33.	Sat. Aug. 16*
34.	Sat. Aug. 23
35.	Thurs. Aug. 28*
36.	Tues. Sept.2
37.	Sun. Sept. 7*
38.	Sun. Sept. 14
39.	Mon. Sept. 22*
40.	Mon. Sept. 29
41.	Mon. Oct. 6*
42.	Sun. Oct. 12
43.	Thurs. Oct. 23*
44.	Fri. Oct. 31
45.	Fri. Nov.7*
46.	Sat. Nov. 15
47.	Wed. Nov. 19*
48.	Mon. Nov. 24
49.	Tues. Dec. 2*
50.	Wed. Dec. 10
51.	Sun. Dec. 14*
52.	Sun. Dec. 21

* NAS days
x University of Michigan
trace metal studies (NAA)

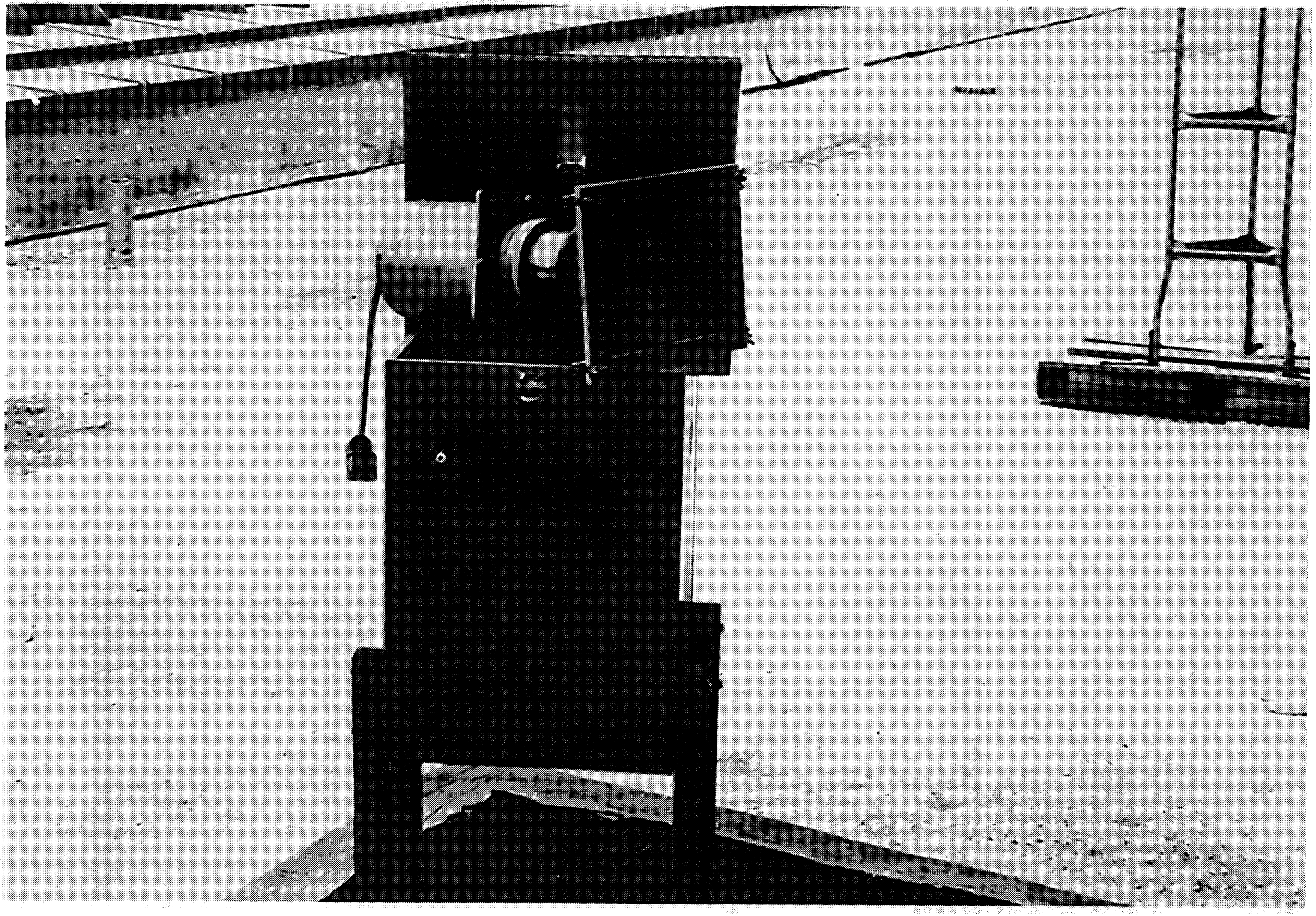

Figure VI.3 : Typical High Volume air sampler with wooden shelter.

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