

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

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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-h 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.

1. 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 six 24-h periods during 1968: 21–22 May, 6 and 20 June, 9 July, 8 and 29 August. Data for Pb, Cd, and Cu are presented as well as data for Bi on the first day (21 May for Chicago and 22 May 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

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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 *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-h 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.

2. 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

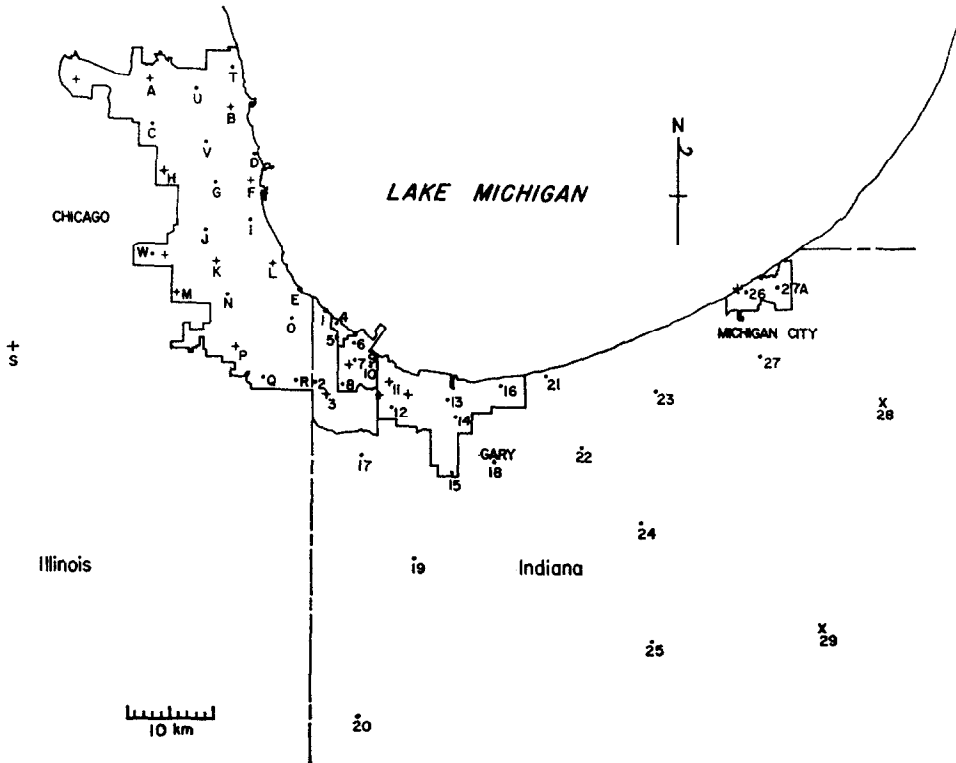


FIG. 1. Air sampling locations.

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 SO₂ 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 × 25 cm (8 × 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 cm² (2 in²) 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 and heated to 300°C for approximately 1/2 h. The samples were then diluted to 25 ml with water and allowed to sit for 1–2 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 0.3 m³ 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.

TABLE 1. ATMOSPHERIC CONCENTRATIONS OF LEAD (ng m^{-3})

Station	21/22 May	6 June	20 June	9 July	8 Aug.	29 Aug.
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
Ø	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 2. ATMOSPHERIC CONCENTRATIONS OF CADMIUM (ng m^{-3})

Station	21/22 May	6 June	20 June	9 July	8 Aug.	29 Aug.
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	**
Ø	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.

** = ≤ 5 .

TABLE 3. ATMOSPHERIC CONCENTRATIONS OF COPPER (ng m^{-3})

Station	21/22 May	6 June	20 June	9 July	8 Aug.	29 Aug.
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
Ø	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 4. ATMOSPHERIC CONCENTRATIONS OF BISMUTH (ng m^{-3})

Station	21/22 May	6 June	20 June	9 July	8 Aug.	29 Aug.
	Determinations made only for 21/22 May					
1	**					
2	—					
3	3.0					
4	1.0					
5	2.0					
6	3.0					
7	—					
8	0.7					
9	2.0					
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	1.0					
G	0.1					
H	M					
I	—					
J	**					
K	0.6					
L	**					
M	M					
N	**					
Ø	**					
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 5. ATMOSPHERIC CONCENTRATIONS OF TOTAL SUSPENDED PARTICULATE ($\mu\text{g m}^{-3}$)

Station	21/22 May	6 June	20 June	9 July	8 Aug.	29 Aug.
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
Ø	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 6. ATMOSPHERIC CONCENTRATIONS OF SO₂ (ppb)

Station	21/22 May	6 June	20 June	9 July	8 Aug.	20 Aug.
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
Ø	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.

3. RESULTS

TABLES 1-6 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 lines (—) signify no sample was taken, the asterisks (*) signify 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 6 days of the study, in spite of differences in winds, we have selected only one of the days for plotting here. Thursday, 6 June is the day with the least variable wind direction, and FIG. 2 shows the wind roses for four

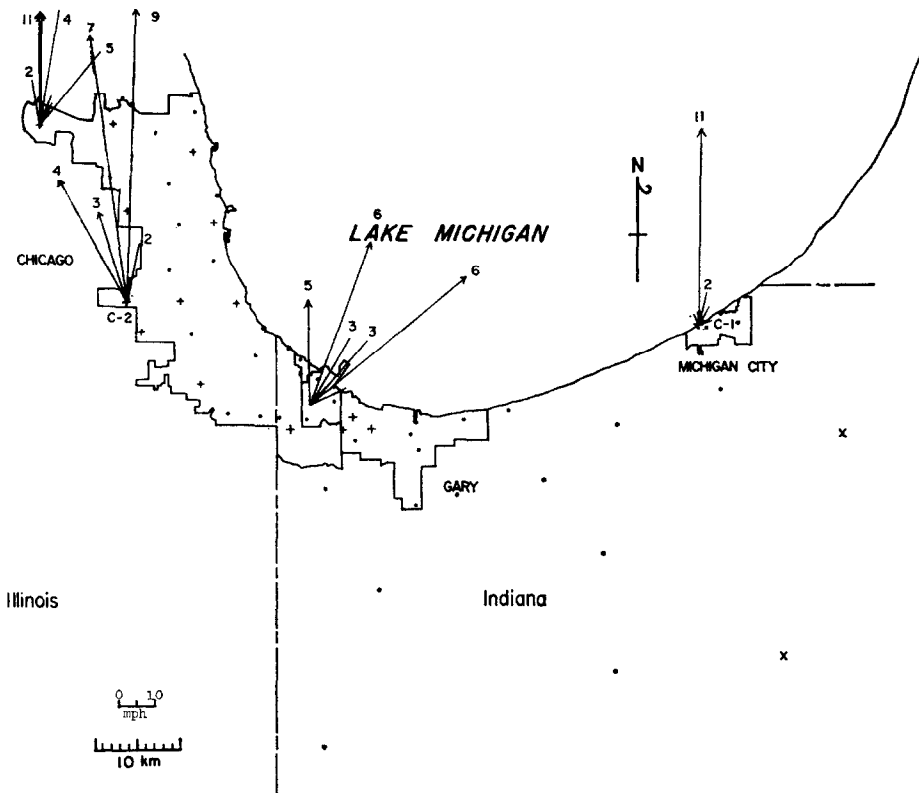


FIG. 2. Wind, Thursday, 6 June, 1968.

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 $< 1.5 \text{ m s}^{-1}$ winds. Lead in FIG. 3 shows a mean concentration of $1-2 \mu\text{g m}^{-3}$ and follows the average traffic density with no obvious strong local sources. Cadmium in FIG. 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 FIG. 5 shows a mean value near 100 ng m^{-3} over Chicago but has an anomalous "hot spot" in East

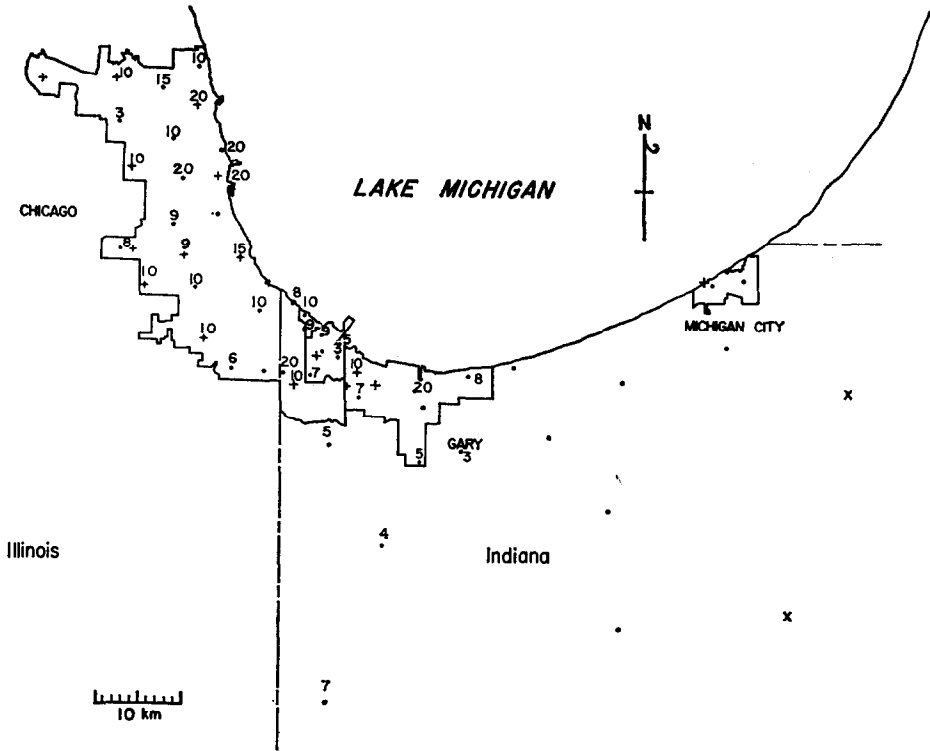


FIG. 3. Concentration of lead ($\mu\text{g m}^{-3} \times 10$), Thursday, 6 June, 1968.

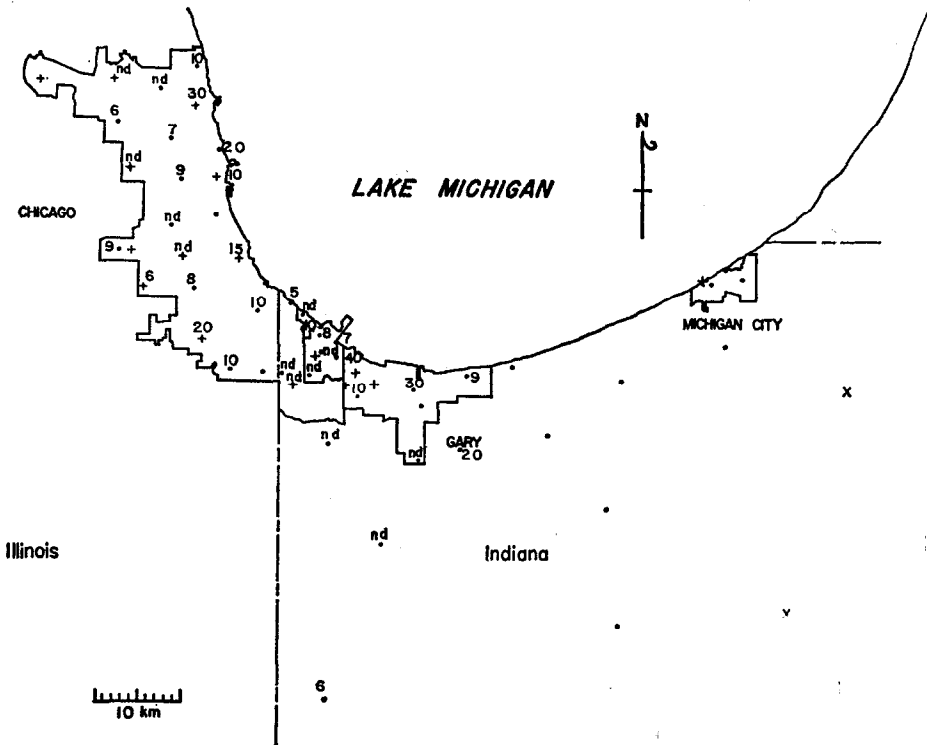


FIG. 4. Concentration of cadmium (ng m^{-3}), Thursday, 6 June, 1968.

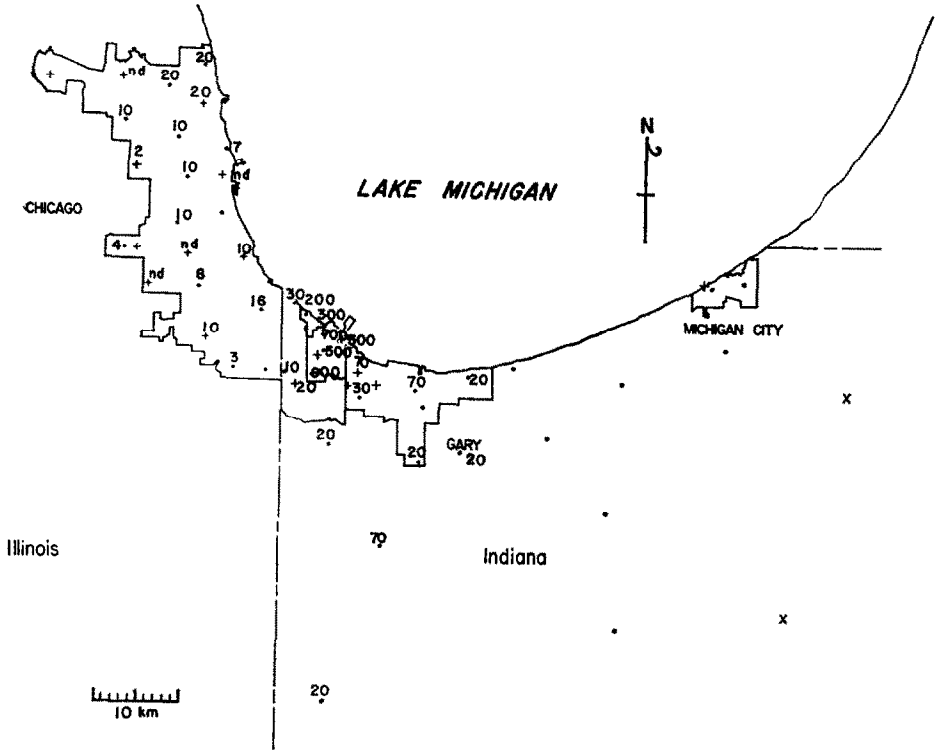


FIG. 5. Concentration of copper ($\text{ng m}^{-3} \times 0.1$), Thursday, 6 June, 1968.

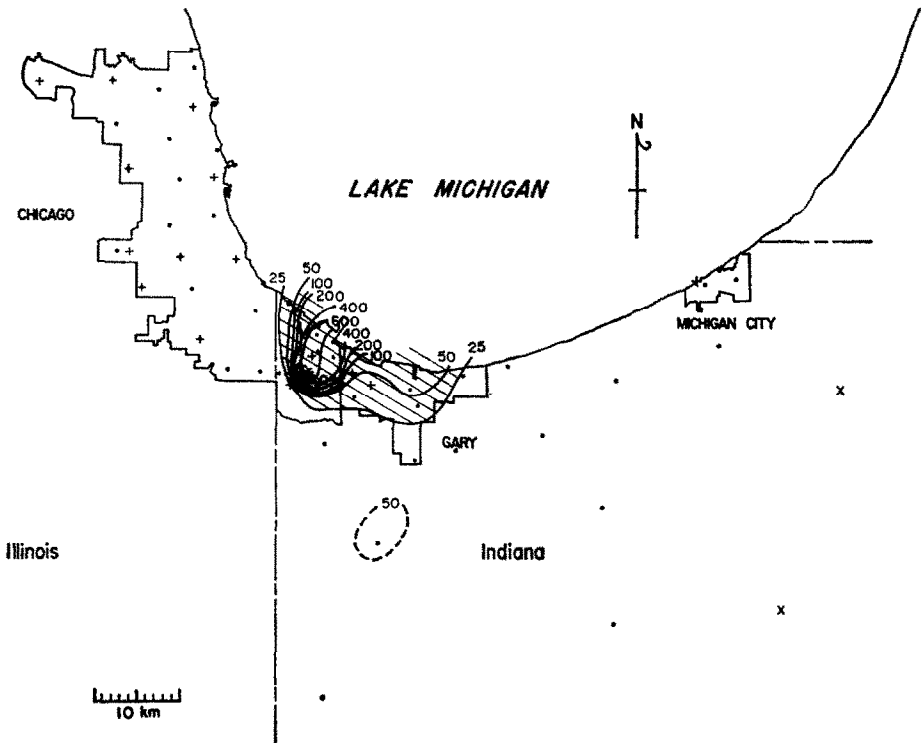


FIG. 6. Concentration of copper ($\text{ng m}^{-3} \times 0.1$), Thursday, 6 June, 1968.

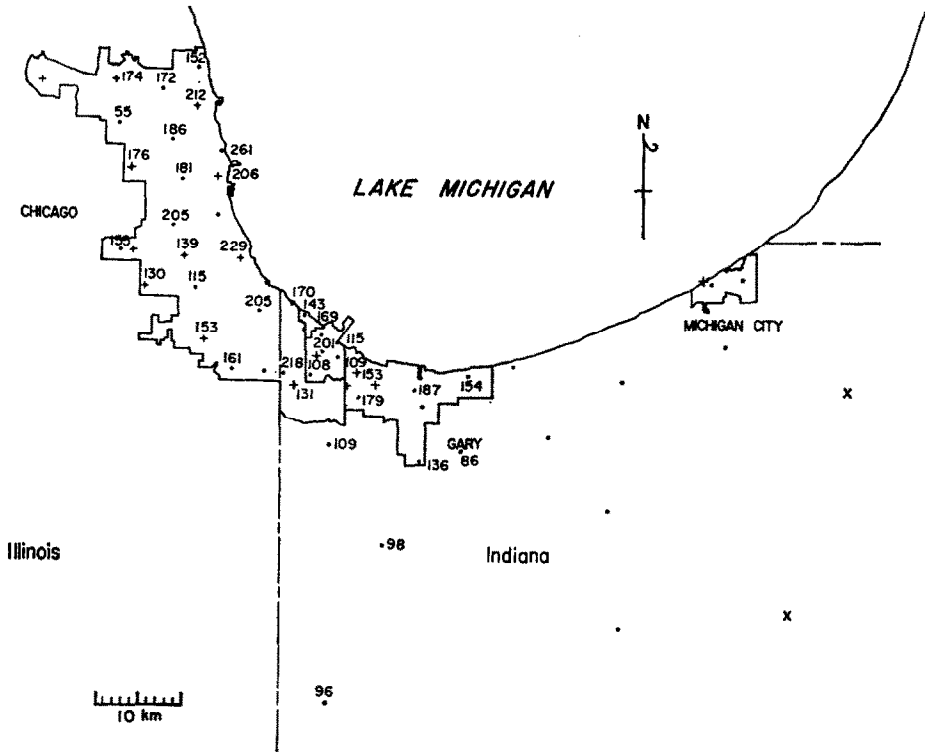


FIG. 7. Suspended particulate ($\mu\text{g m}^{-3}$), Thursday, 6 June, 1968.

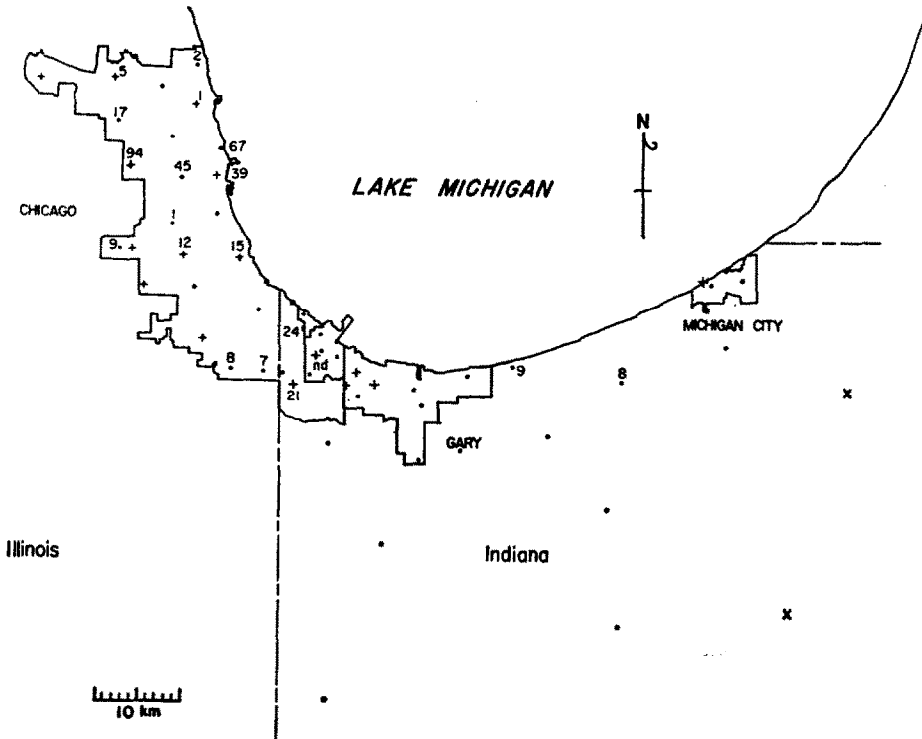


FIG. 8. Concentration of sulphur dioxide (ppb), Thursday, 6 June, 1968.

Chicago, Indiana, where concentrations approach 100 times greater values. In FIG. 6 isopleths of the region show the systematic decrease in concentration with increasing distance from an apparently localized source region. Total suspended particulate, FIG. 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 FIGS. 3–7. Bismuth data, obtained only for 21–22 May, show a low mean value near 1 ng m^{-3} .

4. 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 7 summarizes the weighted

TABLE 7. AVERAGE METEOROLOGICAL CHARACTERISTICS

	Wind direction (degrees)	Range (degrees)	Speed (m s^{-1})	Range (m s^{-1})	Temperature			Precip. (mm)	Relative humidity (%)
					Max. ($^{\circ}\text{C}$)	Min. ($^{\circ}\text{C}$)	Ave. ($^{\circ}\text{C}$)		
21 May	—	360	3.3	C-7	13.9	8.3	11.1	Trace	—
22 May	—	280	3.5	C-8	16.7	6.1	11.7	2	—
6 June	180	40	5.3	2-8	33.9	20.0	27.2	None	55
20 June	150	150	3.8	3-8	25.6	13.3	19.4	Trace	61
9 July	210	170	6.8	4-10	29.4	16.1	22.8	Trace	60
8 Aug.	200	260	3.9	2-16	31.1	22.2	26.7	0.5	77
29 Aug.	090	150	4.2	3-6	24.4	15.0	20.0		58

average wind direction, the total range of wind direction variability, mean speed and variability, temperature, rainfall, and relative humidity for the 6 sampling days. TABLE 8 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 9 July, all days were influenced by cold air masses and variable wind directions. A lake breeze was observed on 29 August but the 24-h 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 9 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

TABLE 8. 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 (μg m ⁻³)	SO ₂ (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	180†		
Both	14	2200	1200	156†	17	
Totals: all data						
Mean	19	1900	1000	150	18	0.63
Max.	80	7000	10000	950	80	3.0
Min.	≤5	100	≤20	30	≤0.5	≤.05

* Stations 1-10 and 11-22 listed separately.

† Station E excluded.

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 6 days of the survey, and tightness of the isopleths in FIG. 6 and other days implies a rather short atmospheric residence time and travel distance, seemingly unaffected by meteorological differences among the 6 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

TABLE 9. 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/SO ₂
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	0.78	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

* Per cent.

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 10 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 9 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 emission when they should become available.

Finally TABLE 11 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

TABLE 10. CONTRIBUTIONS OF FUELS TO LEAD, CADMIUM, AND COPPER TO CHICAGO AREA SUSPENDED PARTICULATE*

	Coal	Coke	Fuel oil	Gasoline
Combustion estimate (Mtons yr ⁻¹)	20	15	7	8
Particulate emission estimate (ktons yr ⁻¹)	220	18	14	†
Pb emission estimate (tons yr ⁻¹)	300	22	30	1800
Cd emission estimate (tons yr ⁻¹)	11	1	—	—
Cu emission estimate (tons yr ⁻¹)	100	7	26	—

* After WINCHESTER and NIFONG (1969). All units are metric.

† Assumed 2 g Pb gal⁻¹ and 25 per cent of emissions airborne.

TABLE 11. 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	100-1200	ND-55	30-180	≤0.5
This study, all stations*	100-7000	< 5-80	< 20-10,000	< 0.05-3.0
This study, station 2, Hammond*	1000-3000	< 5-20	100-1000	—

* Individual values reliable to a factor of 2.

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.

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