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Illinois State Water Survey
at the
University of Illinois
Urbana, Illinois

STUDY OF AIR POLLUTION SCAVENGING

Fifteenth Progress Report
Contract Number EY-76 S-02-1199

July 1977

by

Richard G. Semonin
Bernice Ackerman
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Steven D. Hilberg
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Randall K. Stahlhut
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Sponsored by

United States Energy Research and Development Administration
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STUDY OF AIR POLLUTION SCAVENGING

ABSTRACT

Selected analyses of air and rainwater chemistry and meteorological data are presented as part of the final efforts on the 5-year METROMEX study. The size characterization, air concentration, and source identification of aerosols over and near St. Louis are related to the urban-industrial activities of the metropolitan area. The precipitation studies are comprised of a comparison of chemical analyses of simulated rain samples between several laboratories, including the Survey. The results showed that the analytical technique used by the Survey for the chemical analysis of the METROMEX samples is excellent increasing confidence in the published data. Other precipitation analyses are directed toward the acid rain problem as demonstrated by historical and current measurements in Illinois. The meteorological investigations consist of analysis of diurnal temperature and moisture cycles at urban and rural sites which relates to the development of the planetary boundary layer (PBL) as perturbed by the city. The three-dimensional character of the PBL is also presented as determined by the radiosonde operations during METROMEX. Finally, the technique to calculate three-dimensional trajectories of air motion using the numerous pilot balloon observations acquired during the project is presented. These data are essential for the full interpretation of the air and rain chemistry observations, and the development of empirical models of pollutant scavenging.

STUDY OF AIR POLLUTION SCAVENGING

Fifteenth Progress Report

Contract No. AE(11-1)-1199

INTRODUCTION

The primary effort on this contract during the past 15 months has been focused on the analyses of field data on scavenging acquired during the METROMEX field project in St. Louis, Missouri. This major field effort directed toward quantification of urban effects on clouds and precipitation and their impact on the surrounding region has been adequately described in previous reports and published material under this contract. The ERDA support for the Survey activities during this nationally important project has been a vital part of the overall efforts.

The major thrust of this contract work in the field was related to 1) upper-air observation operations, 2) aircraft tracer chemical releases, 3) aircraft measurements of condensation nuclei and cloud parameters and 4) the air and precipitation chemistry distribution within the METROMEX study area. Each of these topics or subjects have been reported either in the scientific literature or as presentations at a variety of scientific meetings. In addition to these accomplishments under ERDA sponsorship during the past 6 years, an extensive analysis of the entire Survey METROMEX effort will culminate in a publication during the latter part of 1977. This report will summarize all of the efforts undertaken and will synthesize the findings for use by those concerned with inadvertent weather modification, atmospheric chemistry, and their impacts. In addition, two research reports specifically addressing certain of the topics mentioned above will be forthcoming during the next fiscal year. These reports are entitled "Atmospheric Chemistry and Tracers in Project METROMEX" and "A Numerical Study of the Microphysical Processes of Condensation, Collection, and Breakup." The first research report will reflect the analysis of many data on precipitation chemistry and the laboratory techniques employed for the chemical analyses of the samples, and the second report will exemplofy the direction of cloud modeling undertaken with partial support from ERDA. The model is being developed to aid interpretation of the scavenging by convective storms in the Midwest.

The following sections of this Progress Report present some of the topics subjected to intensive, interpretive analysis. These analyses will be more completely summarized in the two-part Survey final report on project METROMEX. This report consists of three sections individually dealing with aerosol chemistry, precipitation chemistry, and meteorology. The connective links between the sections are rapidly being identified which will allow a more synergistic interpretation of pollutant scavenging in an urban area.

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Particle Size Distribution Measurements
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Chapter 2

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Donald F. Gatz

CHAPTER 1

Particle Size Distribution Measurements

Mark E. Peden

Although the importance of particle size considerations in determining the potential adverse effects of aerosols is well documented (Davison et al., 1974), information on the chemical composition and related size distributions of specific components is still sparse and inconclusive. In addition to the detrimental health effects caused by direct inhalation of submicrometer toxic aerosol particulates, particle size factors are important in assessing residence times and subsequent transport distances. Residence times of airborne contaminants become the major factor in determining the extent of possible deleterious effects including: 1) reduction of visibility through haze formation, 2) cosmetic damage to surrounding structures, and 3) opportunities for reactions between gaseous and aerosol pollutants. Coupled with the fact that existing industrial particle capture devices are least effective in removing what are often times the most toxic of particles, those found in abundance in the submicrometer range, it is important that both the low-level concentrations and particle size distributions of aerosol components be accurately documented.

Andersen eight-stage cascade impactor samples, collected during METROMEX at seven locations both upwind and downwind from regions of concentrated industrial activity during the summers of 1972, 1973, and 1975 were returned to the laboratory, dissolved in a combination of hydrofluoric, sulfuric, and nitric acids, and analyzed for the potentially hazardous metals Cd, Pb, and Mn by direct flameless atomic absorption. Cadmium and lead were chosen for investigation due to their high toxicity and abundance in the respirable size range near one micrometer where particles deposit in the pulmonary region of the respiratory tract (Davison et al., 1974). Although toxic levels of airborne manganese are rarely found, even in heavily industrialized areas, it has been shown to act as a catalyst in the oxidation of SO_2 (Johnstone and Coughanaur, 1953) and warrants close monitoring as the interest in increased coal consumption continues. Additionally, recent studies (Campbell, 1976) indicate that incineration of municipal solid wastes may become the predominant source of lead emissions in some areas, as leaded gasoline is phased out, and also provide a major fraction of regional cadmium emissions. As more consideration is given to the implementation of solid wastes as a possible energy source, accurate detailed emission data for toxic metals from incineration facilities must also be available.

RESULTS

Results of the three metal determinations at various sites were plotted as concentration in air (ng m^{-3}) versus particle size (μm). The map of the St. Louis metropolitan area shown in Figure 1 includes the locations of sampling sites and industrial facilities known to be potential emission sources of Cd and Mn compounds. Airborne Pb is assumed to be entirely due to motor vehicle activity since no major lead processing plants are present within the sampling area. Particle size distribution spectra with associated mass median diameters (MMD) are shown in Figure 2 for two of the seven locations, Pere Marquette and Centreville. The illustrated mean spectra were obtained from two to three sampling periods during the summer months.

CADMIUM: Cadmium is known to be a naturally occurring constitutent of all zinc ores and to remain with the zinc ore throughout refining and separation processes (U. S. Environmental Protection Agency, 1975a). For this reason it is assumed that installations involved in the refining of zinc or any material containing appreciable amounts of zinc will also be a source of cadmium. Estimates of cadmium emissions on a nationwide basis attribute 76 percent to metallurgical processing involving cadmium or zinc, 12 percent to the consumption of coal in power plants and coke ovens, and 11 percent to the incineration and disposal of metal wastes (U. S. Environmental Protection Agency, 1975a).

The largest average concentration occurred at Centreville downwind of a zinc smelter located in Sauget, which is a likely source of high cadmium concentrations. The distribution illustrated for Pere Marquette State Park, the highest elevation in the area, is characteristic of a non-affected upwind site. The average MMD for cadmium lies between 1-2 μm. The bimodal histogram shown for Pere Marquette also appeared at Alton and the KMOX radio transmitter and is indicative of a dual or multiple mechanism for cadmium aerosol formation. Similar results were found in the 1972 National Air Surveillance Network (NASN) study at St. Louis (Lee et al., 1972).

LEAD: Lead distributions reveal a narrow range of MMD's between 0.55-0.66 micrometers. This characteristic is consistent with a common emission source for lead aerosols, in this case motor vehicle exhaust. The spectrum shown for Pere Marquette is again characteristic of an upwind non-affected site yielding the lowest total concentration, approximately six times less than the other stations. The Centreville histogram displays a typical spectrum obtained downwind of urban areas where motor vehicle lead is the dominant contributor.

MANGANESE: Manganese distributions exhibit markedly different particle spectra from either cadmium or lead, being much broader with less prominent highs and lows. These broadened spectra are consistent with the findings of the NASN study.

Manganese is used widely in the steel manufacturing industry as an agent in nullifying the harmful effects of sulfur and accounts for 80 percent of the nationwide anthropogenic emissions (U. S. Environmental Protection

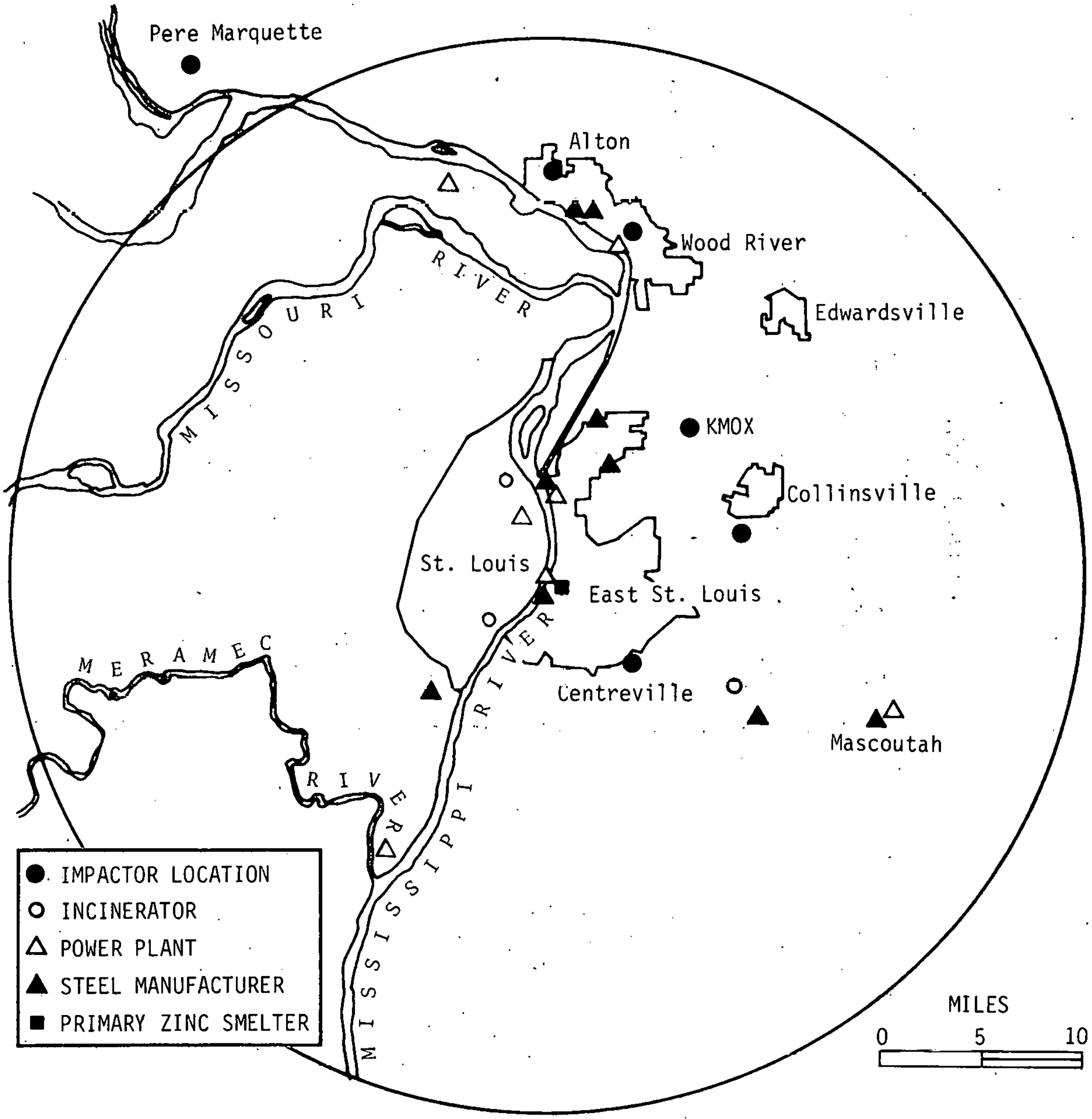

Figure 1. Map of St. Louis metropolitan area with major industrial installations

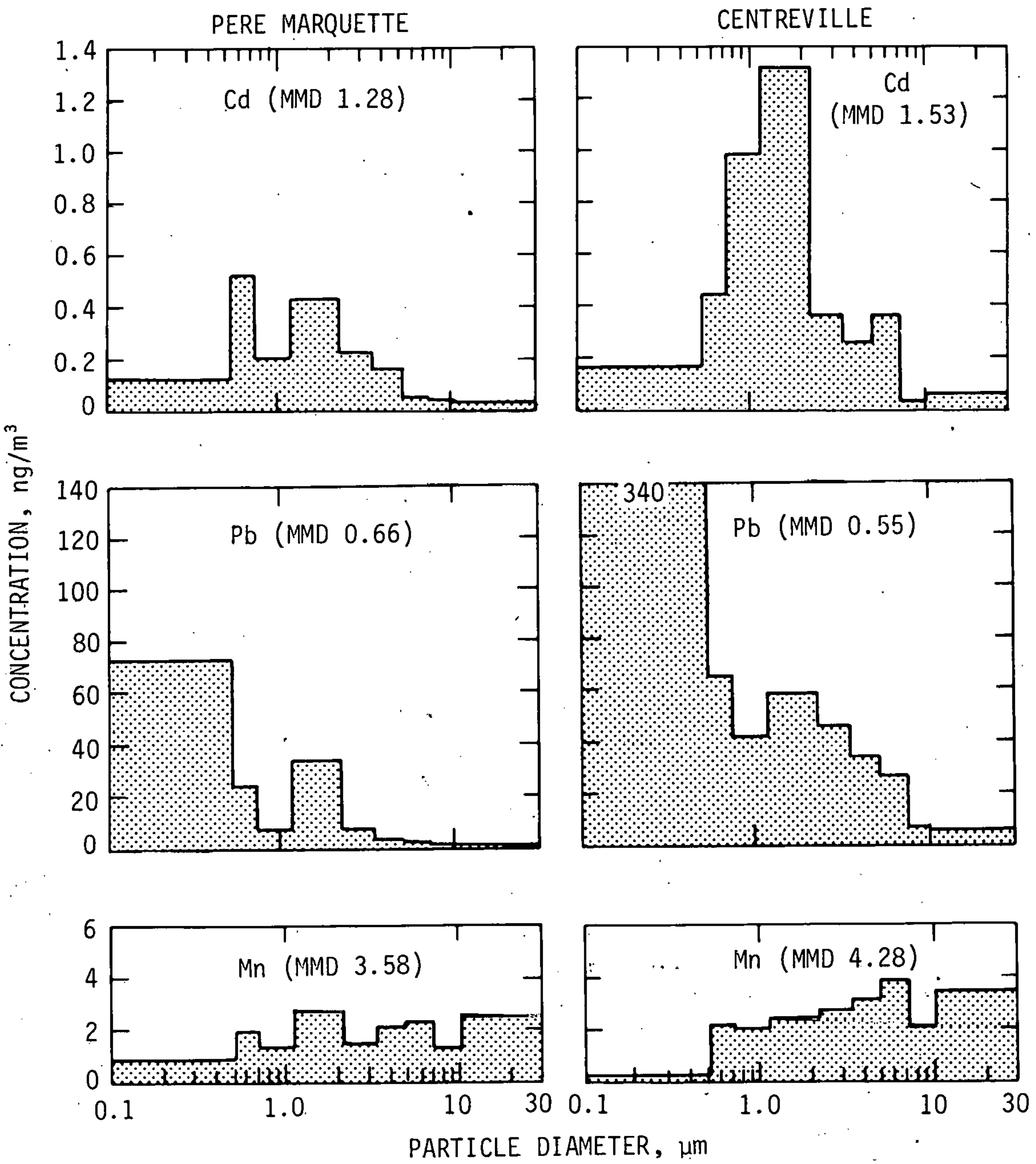

Figure 2. Cd, Pb, and Mn histograms at selected sites with associated mass median diameters (MMD)

Agency, 1975b). Other sources of lesser importance include cement manufacturing industries and facilities engaged in the manufacturing of dry cell batteries. The major anthropogenic source of manganese compounds in the research area is the steel industry, concentrated in the Alton-Wood River and East St. Louis areas.

The fairly uniform distributions shown are representative of all the sampling stations with the exception of Alton where a prominent peak between 1-2 μm occurred. The Alton sampler was in close proximity to the second largest blast furnace in the area which is the suspected source of that maximum. The average MMD for manganese at all stations is 3-4 μm. Once again Pere Marquette is a reference site for an upwind location.

The combined histograms for the three metals Cd, Pb, and Mn illustrate that a wide range in both concentrations and shapes of particle size distributions is obtained for metals which naturally occur at low levels but through localized emission sources show pronounced changes. These variations in particle size spectra emphasize the importance of not only total mass deposition of a particular element but also the distribution of small and large particles within that spectra. It is these differences in size distributions that yield useful information in source identification, human pathological studies, and delineation of atmospheric chemical transformations.

REFERENCES

Campbell, W. J., 1976: Metals in the wastes we burn? Envir. Sci., and Technol., 10(5), 436-439.

Davison, R. L., D. F. S. Natusch, J. R. Wallace, and C. A. Evans, Jr., 1974: Trace elements in fly ash. Dependence of concentration on particle size. Envir. Sci., and Technol., 8(13), 1107-1113.

Johnstone, H. F., and D. R. Coughanaur, 1953: Absorption of sulfur dioxide from air. Industrial and Engineering Chemistry, 50(8), 1169-1172.

Lee, R. E., S. S. Goranson, R. E. Enrione, and G. B. Morgan, 1972: National air surveillance cascade impactor network. II. Size distribution measurements of trace metal components. Envir. Sci., and Technol., 6(12), 1025-1030.

U. S. Environmental Protection Agency, 1975a: Scientific and technical assessment report on cadmium. Office of Research and Development, Washington, D.C.

U. S. Environmental Protection Agency, 1975b: Scientific and technical assessment report on manganese. Office of Research and Development, Washington, D.C.

CHAPTER 2

Aerosol Source Identification and Reconciliation in METROMEX

Donald F. Gatz

INTRODUCTION

Investigations of urban aerosols generally seek among their goals to answer one or more of the following questions:

1) What elements or molecules are present?
2) What are the sources of the aerosols?
3) How much does each source contribute to the total aerosol?

Analytical techniques have advanced to the point where it is possible to detect 20 to 30 elements in urban filter samples of reasonable durations (one day or less). Similarly, statistical techniques are available whereby multielement analytical data can be used to identify kinds of sources and to estimate their relative contribution to total aerosol concentrations.* Moreover, these estimates are made from observed aerosol concentrations, measured near ground level, so they identify sources of aerosols in the air that people breathe. Usually, both natural and man-made sources can be identified, so the relative contributions of these two important classes can be assessed.

EXPERIMENTAL METHODS

Methods to be described include those used in the field to collect samples, in the laboratory to analyze samples, and on the computer to analyze the data.

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* The process of assigning relative contributions to various aerosol sources is known as <u>source reconciliation</u>.

Field Methods

Elemental concentrations in air were measured during the METROMEX summer field seasons of 1973, 1974, and 1975 using Nuclepore filters. Figure 1 shows the sampling sites, along with their years of operation and sampler heights (near ground level, or on a roof).

Aerosol samples were collected on pre-weighed 37 mm or 47 mm diameter Nuclepore polycarbonate membranes with 0.8 μm diameter pores. Each filter was exposed face down under an inverted polyethylene funnel rain shield at 1 m above grass or a flat roof.

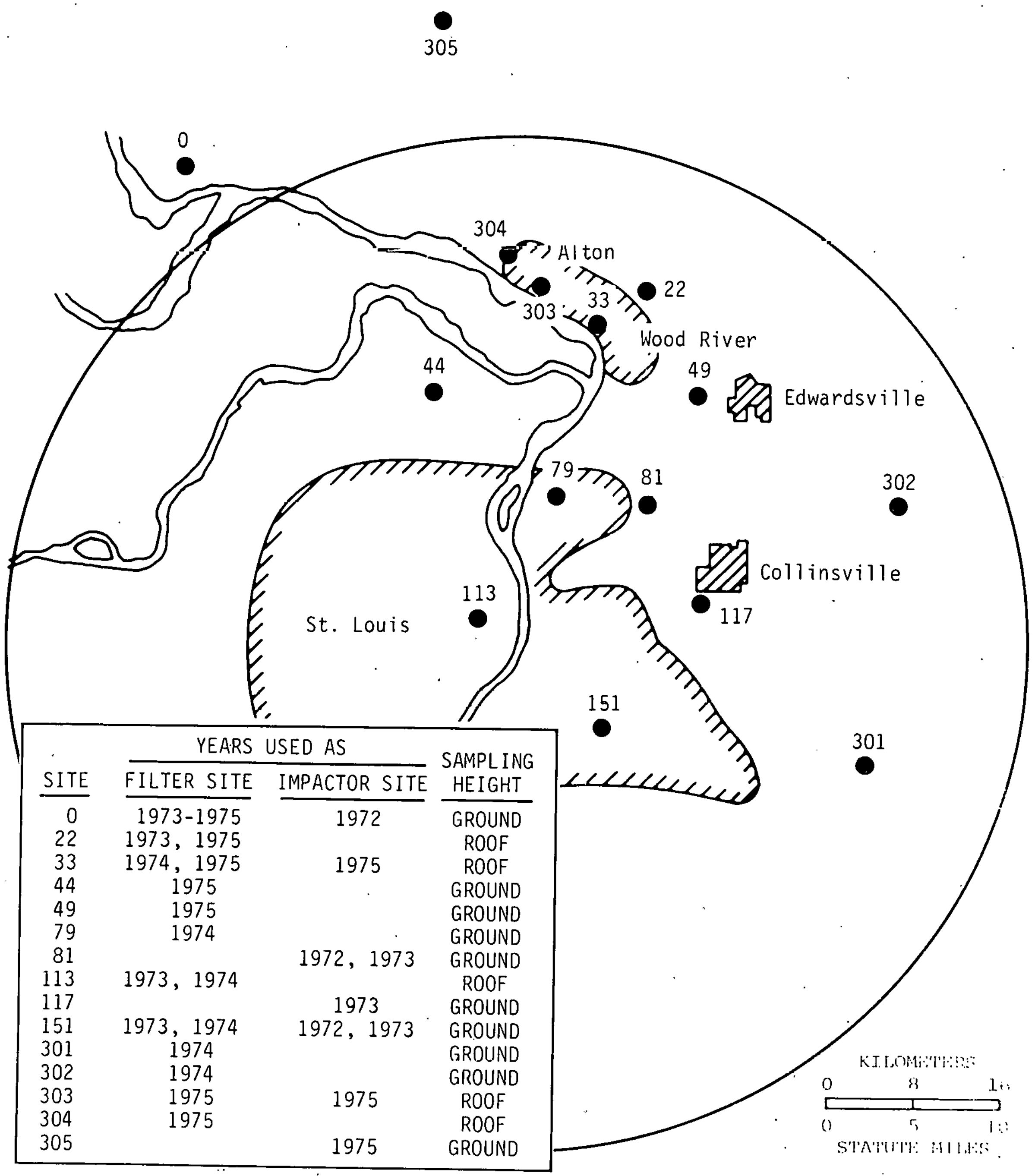
The filters collect at 100% efficiency for all particles larger than 0.8 μm, up to the size where particle inertia causes imperfect sampling, perhaps 20 μm. Below 0.8 μm, theoretical efficiencies drop to a minimum of about 20% at a particle diameter of 0.04 μm for our sampling conditions (Spurny and Lodge, 1972). Flocchini et al. (1976) obtained an experimental collection efficiency of 54% with the same filters on aerosols with diameters between 0.10 and 0.65 μm, compared to the theoretical value of 48% calculated from the collection efficiencies of Spurny and Lodge and the mass distribution of Whitby et al. (1972). For the results given here, 100% collection was assumed for all elements except S, Pb, and Br, which are known to be predominantly on particles smaller than 1 μm (Gladney et al., 1974; Hardy et al., 1976; Paciga et al., 1975; Johansson et al., 1976). An efficiency of 54% was assumed for these three elements, and their measured concentrations were increased accordingly.

Airflow through the filters was provided by 1/6 hp vacuum pumps. Sample volumes were estimated from sample durations and the mean of flow rates measured at the beginning and end of each sample. Rates were measured using a rotameter and vacuum gauge, calibrated against a dry gas meter known to be accurate to 0.5%. Concentrations are expressed in units of mass per standard (21°C, 76 mm Hg) cubic meter. Sample duration was measured by recording times when samples were started or ended manually, or by automatic timer verified with an electric clock.

Laboratory Methods

Filters were weighed to the nearest hundredth of a milligram on a microbalance, under a radioactive source to dissipate static charge. No humidity conditioning was necessary during pre-weighing since the polycarbonate membranes do not absorb moisture. After sample collection, the filters were conditioned for at least 24 hours at 47% relative humidity to allow moisture absorbed on the collected particulate matter to come to equilibrium. Filters were then reweighed under the radioactive source.

Elemental analysis on the filters was carried out at the Crocker Nuclear Laboratory, University of California-Davis, Davis, California, by ion-excited X-ray fluorescence (Flocchini et al., 1972; Flocchini et al., 1976). These authors quote absolute error limits of ±10% in most cases to as high as ±30% near detection limits. The analyses reported in this paper were only rarely



	YEARS USED AS		
SITE	FILTER SITE	IMPACTOR SITE	SAMPLING HEIGHT
0	1973-1975	1972	GROUND
22	1973, 1975		ROOF
33	1974, 1975	1975	ROOF
44	1975		GROUND
49	1975		GROUND
79	1974		GROUND
81		1972, 1973	GROUND
113	1973, 1974		ROOF
117		1973	GROUND
151	1973, 1974	1972, 1973	GROUND
301	1974		GROUND
302	1974		GROUND
303	1975	1975	ROOF
304	1975		ROOF
305		1975	GROUND

Figure 1. Sampling network for nuclepore filter and Andersen impactor measurements, 1973-1975

near detection limits. When not detected, elemental concentrations were assumed to have been half the detection limit. The following elements were detected regularly and make up most of the data set considered in this paper: Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Br, and Pb.

Statistical Methods

Separate statistical methods were used to 1) identify aerosol sources from the multielement analyses of filter samples, and 2) estimate the relative contributions of each source to the total aerosol.

A multivariate statistical technique known as factor analysis (Harman, 1967) was used for source identification. Factor analysis is a tool for explaining observed relationships between numerous variables in terms of fewer variables, where the fewer variables are linear combinations of the original ones. The input data are in the form of a matrix with each column being a measured variable and each row a separate entity. In this case the variables are element concentrations in air and the entities are separate filter samples.

The technique was described in detail and applied to source identification in the Boston area by Hopke et al. (1976). The analysis performed on the present data was very similar to that described by Hopke et al. except that a principal components model was used instead of the factor model described by Hopke et al. This means that the original variables are described completely in terms of common factors. Unique factors are not included. Comparison of both methods on the same data showed only minor differences in results for selected sets of our data.

Computations were carried out using the factor analysis program from the BMDP Biomedical Computer Programs (Dixon, 1975). After standardizing the data, a matrix of correlation coefficients between all variables is computed. Initial factors are then extracted. The first factor is that linear combination of original variables that explains more of the variance in the data than any other possible combination. The second factor explains more of the remaining variance than any other possible combination, and is independent of the first factor; that is, the correlation coefficient between factors is zero. Factor extraction continues until the number of factors equals the number of variables, but since the first few factors usually explain nearly all of the variance, only a few factors are kept for rotation to a final solution.

Rotation of the initial factors to final factors is possible because the factor structure is not unique. One solution can be rotated to another without violating the basic assumptions. One may choose a rotational method to yield a final solution that best meets the practical needs of the research problem.

In the present case, several methods of rotation were compared; only minor differences in the results were found for the several rotational methods, but all differed significantly from the unrotated solution. Furthermore the rotated factors always appear to be interpretable in terms of known sources of aerosols.

For this work, a matrix of correlation coefficients between variables was calculated from standardized data. Initial factors were extracted by a principal components solution. Factors having eigenvalues ≥ 0.6 were kept and rotated to a final solution using a Varimax rotation. The final factors have been interpreted in terms of aerosol sources.

Source reconciliation, or estimation of the relative contributions of several sources to the total observed aerosol, was accomplished by a separate mathematical-statistical method. The fundamentals of the method were given by Miller et al. (1972) and applied by them on an aerosol sample from Pasadena, California. Gatz (1975) applied the method to data from the Chicago area.

This method requires data on the chemical composition of source emissions as well as the chemical composition of the ambient aerosol. A series of equations may then be written such that the observed atmospheric abundance* of each element is set equal to the sum of the unknown contributions from all sources considered. If the number of elements (equations) equals the number of sources, the set of equations may be solved for the unknowns. In practice, however, the solution will vary depending on the elements chosen, and negative contributions may be calculated.

Mayrsohn and Crabtree (1976) have suggested a procedure for optimizing the source configuration for each ambient sample, using multivariate regression techniques. Their method was used in this report to estimate relative contributions of sources in the St. Louis area, using the emission compositions given in Table 1 and average aerosol compositions at each sampling site.

At this point the source reconciliation results must be considered preliminary and approximate. This is because the sources considered match only approximately those identified by factor analysis and because the emission compositions were mostly average values taken from the literature (Gatz, 1975) rather than being measured locally. A final calculation will be done later specifically for sources identified by factor analysis, and will use more representative emission compositions, if available.

RESULTS AND DISCUSSION

Several exploratory analyses were carried out using as variables the elements listed earlier plus a number of meteorological and miscellaneous parameters. These non-chemical parameters included in the exploratory analyses were:

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* An element's abundance is the ratio of its concentration in air to that of the total aerosol.

Day of the week
Mean wind speed
Maximum wind speed
Percent of time with wind from NE, SE, SW, or NW quadrants, or variable
Ventilation rate
Rain amount
Rain duration

Table 1. Source emissions composition data used in source reconciliation.

	Soil[a]	Cement & limestone[b]	Auto exhaust[c]	Coal flyash[d]	Steel-making[e]
Al	4.9	2.4		14	3.5
Si	22.6	10.7		20	
K	1.5	0.53			
Ca	0.45	46		4	9.0
Ti	0.32	0.14		0.9	
Mn	0.071			0.024	3.5
Fe	1.8	1.1	0.4	7.0	22
Zn	0.0053		0.14	0.09	3.5
Br	0.00025		7.9		
Pb	0.0029		40	0.12	

[a] Mean values from 41 samples from Illinois and Missouri (Shacklette et al., 1971) analytical results for individual samples provided by Shacklette (1976, personal communication). Br value is the crustal average from Taylor (1964). The Si value was calculated from the Al value using a ratio of Si/Al=4.64. Vinogradov (1959) gave 4.63 and Bowen (1966) gave 4.65 for this ratio in average soil.

[b] Friedlander (1973), quoting Wood and Rockwood (1963).

[c] Miller et al. (1972).

[d] Winchester and Nifong (1971).

[e] Winchester and Nifong (1971), quoting Sebesta (1968). St. Louis area emissions assumed to be entirely from blast furnaces and sinter plants.

These analyses showed that only the wind direction parameters (including variable) showed significant correlations with element concentrations. Therefore, all other parameters were omitted from subsequent analyses.

Single Site

Factor analyses were performed separately for each filter site shown in Figure 1. The factor loadings (or correlation coefficients between variables and factors) for a typical analysis are shown in Table 2. Values less than 0.50 explain less than 25% of the variance of an element and are generally not included. Some values have been included (in parentheses) for Pb and Br, however, because they aid interpretation. Site 79 is the sampling location closest to the extensive industrial area of Granite City, Illinois.

Table 2. Factor analysis for site 79, 1974; 21 samples.

	Factor				
	1	2	3	4	5
Variance explained	31%	20%	12%	10%	7%
Al	0.97				
Ti	0.96				
Si	0.94				
K	0.83				
Br		0.84	(0.44)		
S		-0.82			
Zn			0.92		
Pb		(0.43)	0.69		
Ca				0.66	
Mn					0.84
Fe					0.76
Varbl					
NE					
SE		-0.68		-0.56	
SW		0.76			
NW				0.94	

The five factors shown in the table account for 80% of the total variance. Two other factors had eigenvalues of 0.6 or more and were included in the rotation to a final solution. They are not shown in the figure, however, because their high loadings occurred only on a single meteorological variable, adding little information for identification of sources.

Interpretation of factors as sources is based on the particular combination of elements and wind directions that have high loadings on the same factor. Variables that are highly correlated with the same factor are, of course, also highly correlated with each other. Factor 1, explaining 31% of the total variance, has high loadings for Al, Ti, Si, and K. These elements are very abundant in soil, but also in coal flyash. Since it is difficult to separate these two sources based on the composition of their emissions, this factor, which was found at all sites, is referred to as the soil/flyash factor. However, the lack of a high loading for S and the lack of association with a particular wind direction suggest that no large point sources of coal flyash were involved.

The second factor, which accounts for 20% of the total variance, shows moderately high positive loadings for Br and SW winds and similar negative loadings for S and SE winds. This means that Br concentrations are high and S low with SW winds, and S is high and Br low with SE winds. A positive loading of 0.43 for Pb indicates that the Br is associated to some degree with Pb, suggesting an auto exhaust source from St. Louis. At other filter sites, the auto exhaust factor typically has a high Br loading and a high to low Pb loading, depending on the influence of non-auto sources of Pb. Sulfur from the SE is reasonable because the St. Louis Air Quality Control Region's largest SO_2 source is a steel mill in Granite City.

Factor 3, at 12% of total variance, has moderate to high loadings for Zn and Pb and a Br loading of 0.44, but is not associated with any particular wind direction. The lack of a directional association is somewhat puzzling because, with factor 2 representing auto exhaust, the main Pb source in factor 3 is almost certainly a secondary Pb smelter in Granite City. The Br loading, although low, shows that a portion of the Pb is still automotive, and indeed, air from the direction of the smelter also crosses a 4-lane expressway shortly before arriving at site 79. The high Zn loading also indicates Zn sources in the same direction, and several are known to be located in the area indicated. The Zn may even have come from the secondary Pb source, although measurements of others (Winchester, 1977) suggest not.

Factor 4 shows a Ca source NW of site 79. This matches the location of a Portland cement plant in the northern portion of St. Louis.

Factor 5 has moderately high loadings for Mn and Fe. Although there is no associated wind direction, this source would appear to be the large steel mill in Granite City, since iron, steel, and ferroalloy production accounts for about 80% of Mn emissions in the U.S. (U.S. Environmental Protection Agency, 1975).

Element concentration data from each of the filter sites shown in Figure 1 was analyzed by factor analysis in the same way as site 79. Further discussion of results from individual sites is not presented here. Rather, those factors found to be common to all sites will be discussed, and unique sources will be mentioned.

Common Factors

Most factors found at any given site were quite similar to others found at sites throughout the research area. For example, Table 3 compares soil/flyash factor loadings at all 12 locations. In each case, this was the first factor extracted, with the variance explained ranging from 31% to 49%.

Al, Si, and K had moderate or high loadings at all sites, with mean loadings of 0.89, 0.90, and 0.86, respectively. Fe had similar loadings at all but one site, with a lower mean loading, 0.77. Ti and Ca fell below the moderate range at two and three sites, respectively, with respective mean loadings of 0.70 and 0.62. The only other element with any moderate loadings was Mn, appearing at two sites. Only very weak wind direction loadings were observed.

It is apparent from comparing loadings of the various elements that these factors were the same or very similar at all sites. In fact, they are so similar that the occurrence of a low loading for one of the usual elements of this factor is a signal of a significant non-soil source of that element. For example, the absence of moderate loadings for Ti at site 151 reflects the presence of a nearby Ti pigment plant. Similarly, the low Ca loading at site 151 probably reflects several nearby limestone quarries.

These are exceptions, however, overall there is marked visual similarity. The coefficient of congruence (Rummel, 1970) is a quantitative measure of the similarity of two factors. The coefficient of congruence, δ, varies between -1.00 and +1.00, and is defined by

$$\delta_{\ell q} = \frac{\sum_{j=1}^{m} \alpha_{j\ell}\, \alpha_{jq}}{\left[\left(\sum_{j=1}^{m} \alpha_{j\ell}^{2}\right)\left(\sum_{j=1}^{m} \alpha_{jq}^{2}\right)\right]^{1/2}}$$

where $\alpha_{j\ell}$ = loading of variable X_j on factor S_ℓ at one site,
α_{jq} = loading of variable X_j on factor S_q at another site, and
m = the number of variables common to both sites.

This provides a comparison of factor ℓ at one site with factor q at another. The coefficient of congruence provides a quantitative measure of the similarity of visually similar factors at different locations. For example, the matrix of congruence coefficients for the soil/flyash factor is shown in Table 4. It

Table 3. Summary of the "soil and flyash" factor.

Site no.	*No. of samples*	*Factor no.*	*Variance explained, %*	*Loadings*											
				Al	*Si*	*S*	*K*	*Ca*	*Ti*	*Mn*	*Fe*	*Zn*	*Br*	*Pb*	*Wind direction*[b]
0	61	1	46	**0.94**	**0.91**		**0.90**	*0.67*	**0.90**		**0.90**				
22	48	1	37	**0.88**	*0.86*		*0.71*	*0.52*							
33	48	1	32	**0.96**	**0.88**		*0.62*		**0.94**	*0.57*	**0.94**				
44	29	1	49	**0.92**	**0.87**		**0.95**	**0.92**	*0.76*		**0.90**				NW: −0.32
49	29	1	43	**0.89**	*0.86*		*0.78*	**0.95**	*0.67*		*0.78*				SW: 0.28
79	21	1	31	**0.97**	**0.94**		*0.83*		**0.96**		*0.53*				
113	39	1	33	*0.84*	**0.89**		**0.94**	*0.79*	*0.55*		*0.85*				
151	29	1	29	*0.80*	**0.88**		**0.87**				*0.64*				SW: 0.34
301	20	1	36	**0.94**	**0.93**		**0.96**	*0.65*	*0.64*	*0.62*	**0.92**				
302	15	[a]	41[a]	*0.76*	**0.92**		**0.93**	*0.62*	**0.94**		*0.68*				
303	29	1	46	**0.89**	**0.96**		**0.90**	**0.95**	*0.80*		*0.77*				SE: 0.30
304	30	1	47	**0.90**	**0.94**		**0.96**	**0.92**	*0.79*		**0.88**				

[a] Variance explained and loadings for site 302 are median values of six separate factor analyses using different (arbitrarily chosen) combinations of elements. This unusual procedure was used because of the small number of samples at this site. It is impossible to perform the usual R-mode factor analysis on data having more variables than observations. A Q-mode factor analysis was performed on a transposed data matrix, but the results cannot be compared directly to the other sites. These loadings are very similar (except for K and Ca) to those obtained for this factor by performing a factor analysis omitting the K and Ca data so that observations exceeded variables.

[b] All loadings having absolute values ⩾ 0.25 are shown, except if positive loading (direct correlation) is present, negative loadings (inverse correlation) are omitted.

shows uniformly high values, indicating that this source is the same or very similar over the whole area.

Table 4. Matrix of congruence coefficients for soil/flyash factor.

Site No.	0	22	33	44	49	79	113	151	301	302	303	304
22	0.93											
33	0.94	0.84										
44	0.98	0.94	0.89									
49	0.98	0.91	0.87	0.97								
79	0.95	0.89	0.92	0.91	0.91							
113	0.96	0.93	0.89	0.98	0.95	0.90						
151	0.92	0.98	0.86	0.94	0.91	0.88	0.96					
301	0.96	0.93	0.92	0.98	0.94	0.90	0.98	0.95				
302	0.98	0.88	0.92	0.96	0.97	0.94	0.94	0.90	0.95			
303	0.98	0.93	0.88	0.99	0.98	0.92	0.97	0.93	0.97	0.98		
304	0.98	0.93	0.87	0.97	0.98	0.90	0.94	0.91	0.95	0.97	0.98	
Mean	.96	.92	.89	.96	.94	.91	.95	.92	.95	.95	.96	.94
Std.dev	.02	.04	.03	.03	.04	.02	.03	.04	.03	.03	.04	.04
Std.err	.01	.01	.01	.01	.01	.01	.01	.01	.01	.01	.01	.01

Other visually similar factors are compared in Table 5, which gives mean values and standard deviations of the coefficient of congruence for each site. The soil/flyash factor, as mentioned earlier, has quite uniformly high values, with an overall mean of 0.94. The factor interpreted as auto exhaust is somewhat lower at an overall mean of 0.77, but still indicates considerable similarity among sites. The "sulfur and metals" factor has the next highest overall mean congruence coefficient at 0.65, still suggesting substantial overall similarity among sites. Standard deviations for this factor are generally larger than the first two mentioned, which indicates greater variation in congruence between individual sites.

This is also revealed in the differences between maximum and minimum individual values, and the ratio of these two. The ratio is 1.2 for the soil/flyash factor and 2.2 for the auto exhaust factor, but 4.2 for the sulfur and metals factor. The ratio is still larger, at 9.5, for the "metals without sulfur" factor, which also has the smallest overall congruence coefficient, 0.63. This is still high enough to indicate considerable area-wide similarity between sites, but the greater variability is apparent.

To summarize, the coefficient of congruence is relatively high for all four factors shown in Table 5. The coefficient decreases from an overall mean of 0.94 to 0.63 in the order: soil/flyash, auto exhaust, sulfur and metals, metals without sulfur. The variability of values for individual pairs increases in the same order.

In addition to the factors found in common at most or all sites, a number of factors were found that were unique to one or a few sites. The most apparent ones have already been mentioned: The cement plant as a Ca source at site 79, the secondary Pb smelter as a Pb source at sites 79 and 49, and the Ti pigment plant as a Ti source at site 151 and others.

Table 5. Summary of mean coefficients of congruence for four visually similar factors.

	Factor			
	Soil/flyash	Sulfur and metals	Metals without sulfur	Auto exhaust
0	0.96(0.02)	0.72(0.13)	0.74(0.09)	0.80(0.06)
22	0.92(0.04)	0.53(0.19)	0.46(0.22)	0.79(0.09)
33	0.89(0.03)	0.62(0.13)	0.60(0.23)	0.80(0.08)
44	0.96(0.03)	0.73(0.14)	0.68(0.18)	0.73(0.14)
49	0.94(0.04)	0.68(0.14)	0.67(0.12)	0.73(0.11)
79	0.91(0.02)	0.50(0.16)	0.69(0.18)	0.61(0.11)
113	0.95(0.03)	0.57(0.15)	0.64(0.16)	0.79(0.12)
151	0.92(0.04)	0.74(0.11)	0.61(0.21)	0.74(0.09)
301	0.95(0.03)	0.62(0.16)	0.61(0.22)	0.77(0.10)
302	0.95(0.03)	0.69(0.13)	0.47(0.22)	0.84(0.07)
303	0.96(0.04)	0.74(0.12)	0.64(0.11)	0.82(0.09)
304	0.94(0.04)	0.63(0.17)	0.71(0.10)	0.80(0.08)
Overall mean	0.94	0.65	0.63	0.77
Single site maximum	0.99	0.93	0.95	0.94
Single site minimum	0.84	0.22	0.10	0.42
Ratio	1.2	4.2	9.5	2.2

The logical next question following the identification of sources is "How much does each source contribute to the total observed aerosol?" We present here a preliminary answer to that question, based on the calculation method described earlier. This method requires that the sources to be considered be selected in advance. Those selected were the ones identified by Winchester and Nifong (1971) as important sources of particulate matter in Chicago. They match approximately the sources identified for St. Louis by factor analysis, but another source reconciliation must be performed for strict consistency.

Separate reconciliations were performed for each filter sampling site, and results are given in Table 6. Results can be plotted and contoured for any of the various sources. For example, Figure 2 shows the percent contribution of iron and steel manufacturing to the total ambient aerosol concentration at the 12 sampling sites. The number of sites is adequate only for showing an approximate spatial pattern, but Figure 2 shows maximum values near locations of area steel mills. Spatial patterns were also drawn for other sources, but because of the preliminary nature of these results, they are not shown.

In addition to the primary sources included in the source reconciliation calculation, Table 6 shows the contribution of sulfate to the observed total aerosol concentrations at each site. All measured particulate sulfur was assumed to be secondary sulfate. The table shows sulfate relative contributions between 20 and 50%, soil contributions between 10 and 40%, cement dust contributions between 4 and 18%, auto exhaust between 2 and 7%, very minimal coal flyash contributions, and steel-making contributions between 6 and 14%. Total contributions of these sources range from 50 to over 100%.

Totals over 100% are, of course, physically impossible, and such large contributors as hydrocarbons and water are not even included. Thus, it appears that contributions of some sources are overestimated.

Sulfur could be overestimated if the collection efficiency were better than the 54% assumed. This is a definite possibility since sulfate particles increase in size in high relative humidity, such as that of St. Louis in the summer. Some preliminary comparisons of sulfate on simultaneous Nuclepore and Whatman filters exposed in central Illinois also suggest that the sulfate correction should be smaller. These comparisons, when completed, will be used to estimate the true collection efficiency of our Nuclepore filters for sulfate in St. Louis in summer.

Recall that the source reconciliation calculation attempts to distinguish soil from coal flyash. The results indicate that the soil contribution is much larger than that of coal flyash, which in most cases is negligible. This agrees with indications from the factor analysis results that the "soil/flyash" factor is indeed almost all soil, but again because these calculations are preliminary, it is wise to be cautious about such a conclusion. For example, large values of the soil contribution appear in a cluster in the northern half of the sampling network (sites 0,22,33,44,49,303, and 304). The reason for high values at both urban and rural sites in this particular area, in contrast to other urban and rural sites farther south is not clear, but several large power plants are located in the region of high values. Thus, there is still uncertainty about the relative contributions of soil and flyash.

Another uncertainty relates to the cement and limestone dust source. Only two sites (79 and 151) were found to have identifiable source factors for Ca that involved cement manufacturing or limestone quarrying. Yet Ca

STEEL SOURCE COEFFICIENT, %

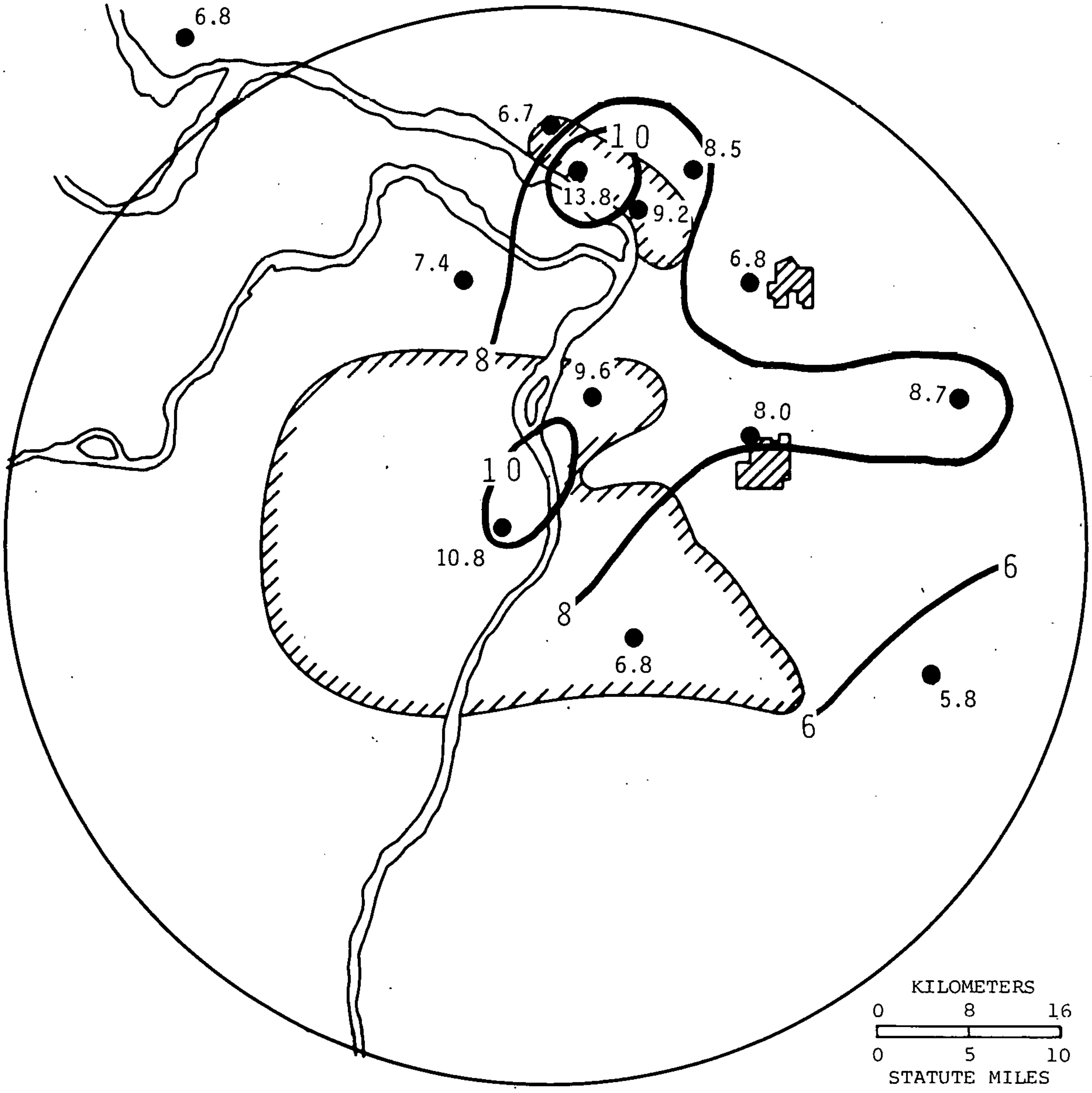


Figure 2. Percent contribution of steel making to the ambient ground level aerosol in the St. Louis aerosol (preliminary)

loadings on the soil/flyash factor are often in the moderate range, indicating significant non-soil sources. Further, enrichments (Rahn, 1971) of Ca in St. Louis area aerosols (relative to soil) also indicate non-soil sources for Ca. Perhaps limestone gravel or cement roads, or limed agricultural fields are other important sources.

Table 6. Preliminary source reconciliation for St. Louis area aerosols.

	Sources						
Site	Soil	Cement and limestone dust	Auto exhaust	Coal flyash	Steel	Secondary sulfate	Total
0	29	8.5	2.3	0.8	6.8	41.3	89
22	32	13	6.0	0	8.5	41.8	101
33	22	18	3.4	0.3	9.2	31.6	84
44	32	12	4.8	0.01	7.4	45.4	102
49	33	9.6	3.3	0	6.8	53.2	106
79	6.6	8.0	2.0	2.0	9.6	21.2	49
113	15	8.5	7.4	2.4	10.8	22.8	67
151	15	13	7.1	0.6	6.8	21.8	64
301	11	4.8	2.1	2.8	5.8	26.6	53
302	14	3.9	2.7	0	8.7	27.0	56
303	38	14	6.1	0	13.8	34.9	107
304	34	16	3.3	0	6.7	39.1	99

SUMMARY

Samples of aerosols from near ground level in the St. Louis area have been collected on Nuclepore filters and analyzed for 11 elements. The data were analyzed separately at each site using factor analysis to identify aerosol sources. A separate statistical-mathematical technique was used to estimate the relative contributions of various sources to the total aerosol. Although the sources assumed in the reconciliation were not precisely those identified by the factor analysis, some preliminary results were obtained.

Four general factors were found at all or almost all sampling sites. These, and their general range of relative contributions to the ambient aerosol are:

Soil/flyash:	10-40%
Secondary sulfate:	20-50%
Metals:	6-14%
Auto exhaust:	2- 7%

There are indications that the contribution of the sulfates has been over estimated.

In addition to these widespread sources, a number of specific sources were also identified, including a cement plant, a secondary Pb smelter, and a Ti pigment plant.

REFERENCES

Bowen, H. J. M., 1966: *Trace Elements in Biochemistry*. Academic Press, New York.

Dixon, W. J., Editor, 1975: BMDP Biomedical Computer Programs, University of California Press, Berkeley, 792 pp.

Flocchini, R. G., T. A. Cahill, D. J. Shadoan, S. J. Lange, R. A. Eldred, P. J. Feeney, and G. W. Wolfe, 1976: Monitoring California's aerosols by size and elemental composition. *Environ. Sci. & Technol.*, *10*, 76-82.

Friedlander, S. K., 1973: Chemical element balances and identification of air pollution sources. *Environ. Sci. & Technol.*, *1*(3), 235-240.

Gatz, D. F., 1975: Relative contributions of different sources of urban aerosols: application of a new estimation method to multiple sites in Chicago. *Atmos. Environ.*, *9*, 1-18.

Gladney, E. S., W. H. Zoller, A. G. Jones, and G. E. Gordon, 1974: Composition and size distributions of atmospheric particulate matter in Boston area. *Environ. Sci. & Technol.*, *8*, 551-557.

Hardy, K. A., R. Akselsson, J. W. Nelson, and J. W. Winchester, 1976: Elemental constituents of Miami aerosol as a function of particle size. *Environ. Sci. & Technol.*, *10*, 176-182.

Harman, H. H., 1967: *Modern Factor Analysis*, 2nd Ed. University of Chicago Press. Chicago.

Hopke, P. K., E. S. Gladney, G. E. Gordon, W. H. Zoller, and A. G. Jones, 1976: The use of multivariate analysis to identify sources of selected elements in the Boston urban aerosol. *Atmos. Environ.*, *10*, 1015-1025.

Johansson, T. B., R. E. VanGrieken, and J. W. Winchester, 1976: Elemental abundance variation with particle size in North Florida aerosols. *J. Geophys. Res.*, *81*, 1039-1046.

Mayrsohn, H., and J. H. Crabtree, 1976: Source reconciliation of atmospheric hydrocarbons. Atmos. Environ., 10, 137-143.

Miller, M. S., S. K. Friedlander, and G. M. Hidy, 1972: A chemical element balance for the Pasadena aerosol. J. Colloid Interface Science., 39, 165-176.

Paciga, J. J., T. M. Roberts, and R. E. Jervis, 1975: Particle size distributions of lead, bromine, and chlorine in urban-industrial aerosols. Environ. Sci. & Technol., 9, 1141-1144.

Rahn, K., 1971: Sources of trace elements in aerosols--an approach to clean air. Doctor Dissertation, University of Michigan Dept. of Meteorology and Oceanography.

Rummel, R. J., 1970: Applied Factor Analysis. Northwestern Univ. Press, Evanston, Ill., 617 pp.

Schacklette, H. T., 1976: Personal communication.

Schacklette, H. T., J. C. Hamilton, J. G. Boerngen, and J. M. Bowles, 1971: Elemental composition of surficial materials in the conterminous United States. U. S. Geological Survey Professional Paper 574-D, U. S. Government Printing Office, Washington, D.C.

Sebesta, W., 1968: "Ferrous Metallurgical Processes," In: Stern, A. C., Ed., Air Pollution, Vol. III, p. 143.

Spurny, K. R., and J. P. Lodge, 1972: Collection efficiency tables for membrane filters used in sampling and analysis of aerosols and hydrosols. NCAR Tech. Note, NCAR-TN/STR-77, National Center for Atmospheric Research, Boulder, CO.

Taylor, S. R., 1964: Abundance of chemical elements in the continental crust: a new table. Geochimica et Cosmochimica Acta, 28, 1273-1285.

U. S. Environmental Protection Agency, 1975: Scientific and technical assessment report on manganese. National Environmental Research Center, Research Triangle Park, N.C., USEPA Office of Research and Development. Washington, DC, EPA-600/6-74-002.

Vinogradov, A. P., 1959: The Geochemistry of Rare and Dispersed Chemical Elements in Soils, 2nd Edition, Consultants Bureau, Inc., NY, 209 pp.

Whitby, K. T., R. B. Husar, and B. Y. H. Liu, 1972: The aerosol size distribution of Los Angeles smog. J. Colloid Interface Sci., 39(1), 177-204.

Winchester, J. W., 1977: Personal communication.

Winchester, J. W., and G. D. Nifong, 1971: Water pollution in Lake Michigan by trace elements from pollution aerosol fallout. Water, Air, and Soil Pollution, 1, 50-64.

Wood, W. H., and N. C. Rockwood, 1962: "Cement," Encycl. Britan., 5, 108-115.

CHAPTER 3

Airborne Elements: Their Concentration Distributions at St. Louis

Donald F. Gatz

INTRODUCTION

Because of the possibility that pollutant aerosols might be at least a partial cause of urban precipitation anomalies (Changnon, 1968), METROMEX was planned to include studies to characterize St. Louis aerosols. These studies included measurement of such physical parameters as particle size distributions and cloud and ice nuclei concentrations, and such chemical measurements as atmospheric concentrations and size distributions of various airborne elements. This section reports measurements of atmospheric concentrations of about 10 elements in the St. Louis area.

The objectives of this work were:

1. To measure concentrations of a number of airborne elements near ground level in the St. Louis area, and
2. To map the mean horizontal distributions of concentrations in the research circle, so as to show differences between urban and rural areas.

Results of this work should allow a general qualitative comparison of the locations of high atmospheric elemental concentrations with mean locations of anomalously high precipitation. However, more quantitative applications of the data appear in other sections of this report. These include identification of major sources of specific elements.

Surveys of elemental concentrations in and around urban areas have been made before. A partial list of recent work of this kind appears in Table 1. The papers listed in the table all include measurements at 3 or more sites in an urban area, over periods varying from one day to one year. All measured concentrations consisted of at least 12 chemical constituents (sometimes including total mass). The most extensive set of data is that of King *et al*. (1976) at Cleveland, where 60 constituents were measured at 23 sites over 1 year. The studies in Table 1 used various sampling and analysis procedures. The procedures used in METROMEX at St. Louis are presented in the next section.

Table 1. Summary of urban aerosol elemental measurement programs using multiple sites

Authors	Location	No. of sites	No. components* measured	Sampling period
Dams _et al_. (1971)	Northwest Indiana	25	30	1 day
John _et al_. (1973)	San Francisco Bay Area	9	29	1 day
Brar _et al_. (1970)	Chicago	22	20	1 day
Hardy _et al_. (1976)	Miami	3	14	10 days
Gladney _et al_. (1974)	Boston	3	18	2 months
Kowalczyk _et al_. (1977)	Washington D.C.	4	27	3 months
Hopke _et al_. (1976)	Boston	5	18	5 months
Kneip _et al_. (1970)	New York	3	12	1 year
King _et al_. (1976)	Cleveland	23	60	1 year
Perone _et al_. (1976)	Tuscon	11	23	1 year

* Including elements, ions, and total mass.

EXPERIMENTAL METHODS

Methods to be described include those for both field sampling and laboratory analysis, which contains a discussion of analytical uncertainties.

Field Sampling

Concentration measurements were made using two different filter media, Whatman-41 cellulose filters and Nuclepore polycarbonate membranes. Analysis methods for the two types of filters also differed. Whatman-41 measurements were carried out from 1971 to 1973 and Nuclepore measurements from 1973 to 1975.

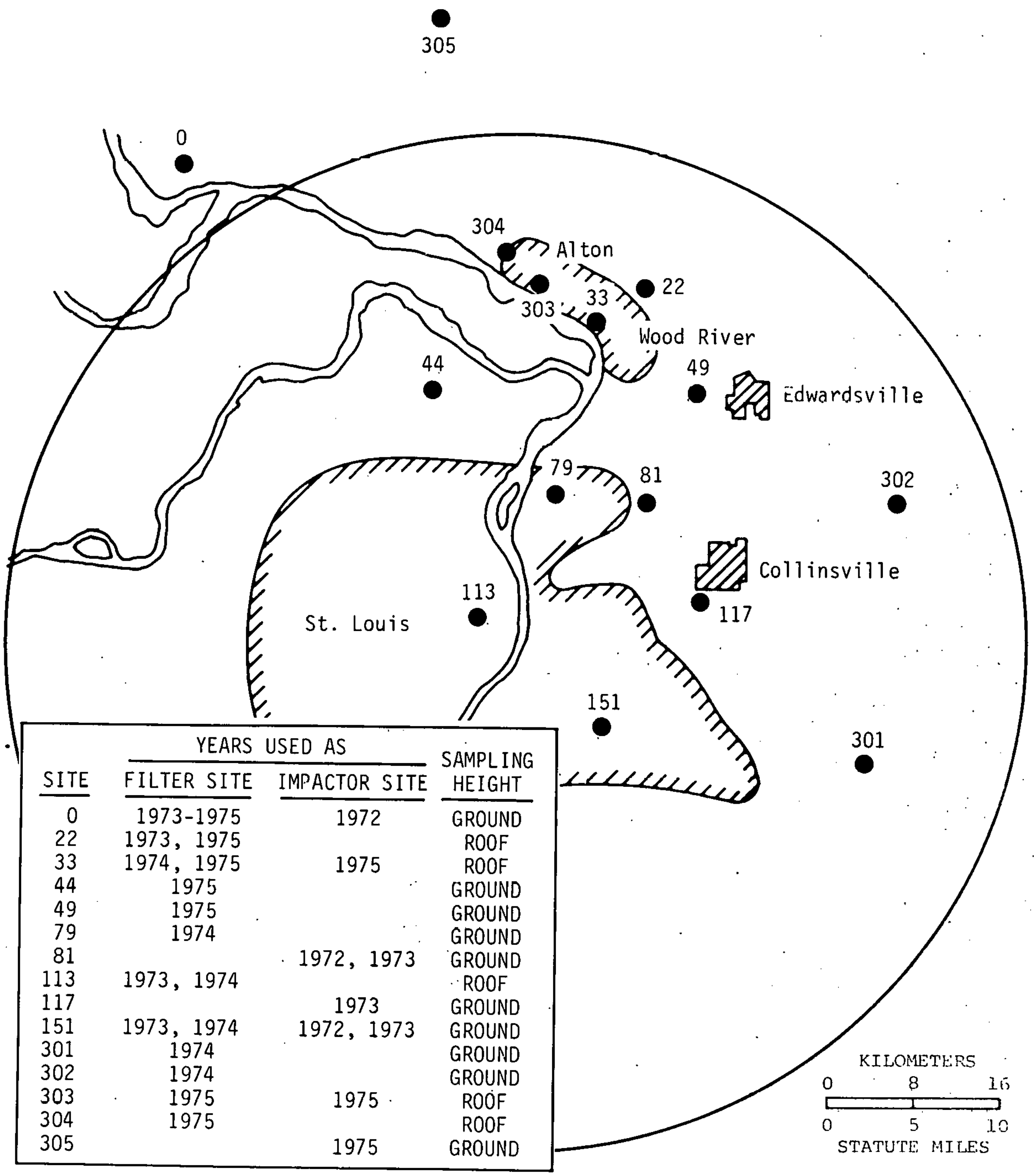
Nuclepore Measurements. Aerosol samples were collected on pre-weighed 37mm or 47mm diameter Nuclepore filters with 0.8μm pore diameters. Each filter was exposed face down under an inverted polyethylene funnel rain shield at 1m above grass or a flat roof.

The filters collect at 100% efficiency for all particles larger than 0.8μm, up to the size where particle inertia causes imperfect sampling, perhaps 20μm. Below 0.8μm, theoretical efficiencies (Spurny and Lodge, 1972) drop to a minimum of about 20% at a particle diameter of 0.04μm for our sampling conditions. Flocchini et al. (1976) obtained an experimental collection efficiency of 54% for the same filters on aerosols with diameters between 0.1 and 0.65μm, compared with a value of 48% calculated from the collection efficiencies of Spurny and Lodge and the mass distribution of Whitby et al. (1972). For the results given here 100% collection was assumed for all elements except S, Pb, and Br, which are known to be predominantly on particles smaller than 1μm. (Gladney et al., 1974; Hardy et al., 1976; Paciga et al., 1975; Johansson et al., 1976). An efficiency of 54% was assumed for these 3 elements, and their measured concentrations were corrected accordingly.

Airflow through the filters was provided by 1/6 hp vacuum pumps. Each sample's volume was estimated from its duration and the mean of flow rates measured at the beginning and end of the sample. Flow rates were measured using a rotameter and vacuum gage system, calibrated against a dry gas meter known to be accurate to 0.5%. Concentrations are expressed in units of mass per standard (21^{o}C, 76m Hg) cubic meter. Sampling duration was measured by manually recording the times, to the nearest minute, when samples were started or ended, or by automatic timer verified with an electric clock.

Measurements were made at filter sites shown in Figure 1.

Whatman-41 Measurements. Samples were collected for 24-hr periods on 15cm diameter filters, using high volume (about 40 m^3/hr) positive displacement pumps. Filters were exposed face up under rain shields at 1.5m above grass; they were handled only with clean Teflon-covered forceps. Exposed filters



	YEARS USED AS		
SITE	FILTER SITE	IMPACTOR SITE	SAMPLING HEIGHT
0	1973-1975	1972	GROUND
22	1973, 1975		ROOF
33	1974, 1975	1975	ROOF
44	1975		GROUND
49	1975		GROUND
79	1974		GROUND
81		1972, 1973	GROUND
113	1973, 1974		ROOF
117		1973	GROUND
151	1973, 1974	1972, 1973	GROUND
301	1974		GROUND
302	1974		GROUND
303	1975	1975	ROOF
304	1975		ROOF
305		1975	GROUND

Figure 1. Sampling network for nuclepore filter and Andersen impactor measurements, 1973-1975

were folded in half with sample inside and stored in polyethylene bags until analysis. Sample volume was estimated from pressure drop measurements, calibrated against a precision rotameter-type flow meter. Sample volumes obtained this way are accurate to ± 5%. Samples were collected at the 4 sites shown in Figure 2.

Laboratory Methods

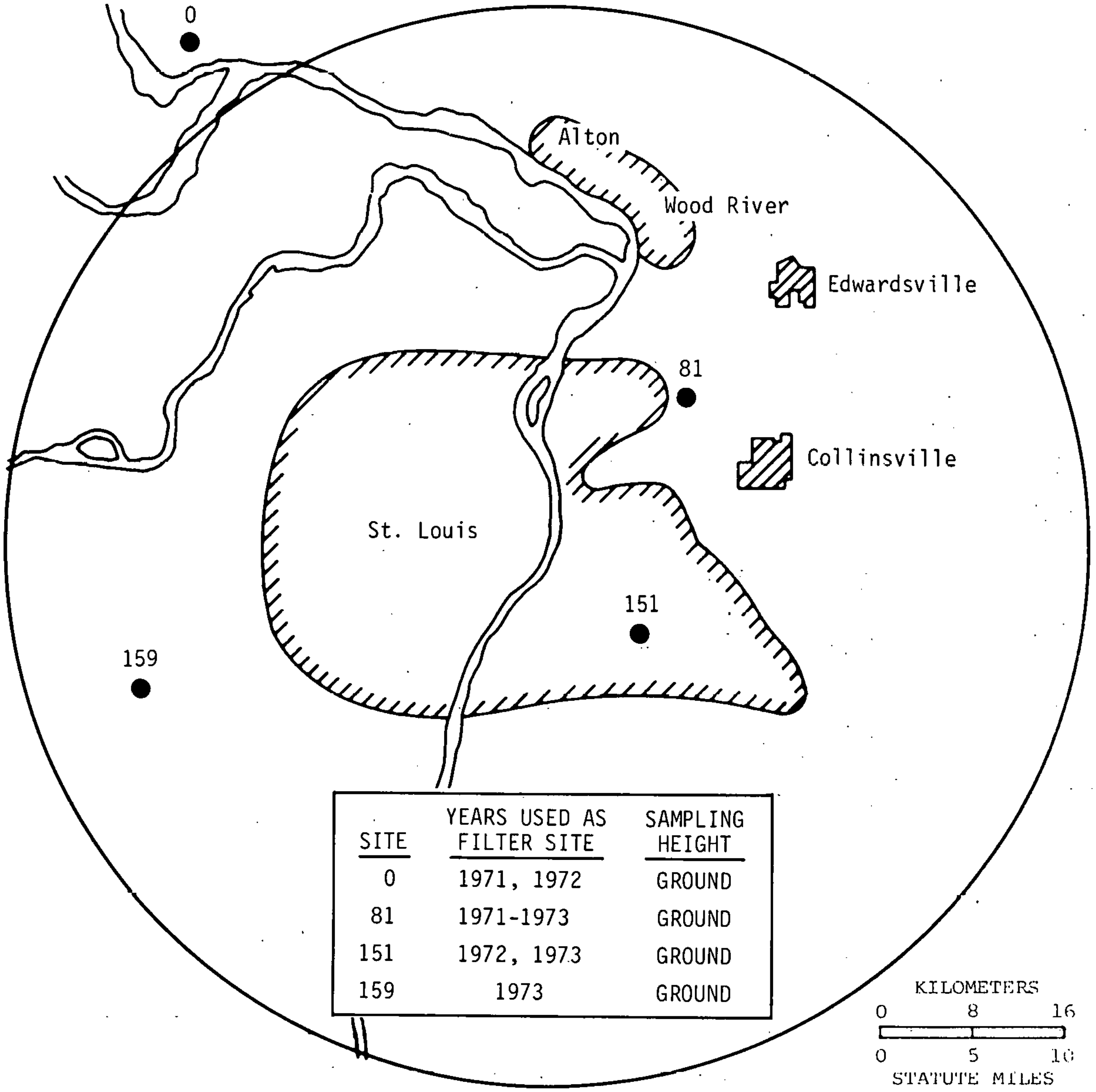
Nuclepore filters were weighed to the nearest hundredth of a milligram on a microbalance, under a radioactive source to dissipate static charge. No humidity conditioning was necessary during pre-weighing since the polycarbonate membrane does not absorb moisture. After sample collection the filters were conditioned for at least 24 hours at 47% relative humidity to allow moisture absorbed on the collected particulate matter to come to equilibrium. Filters were then reweighed under the radioactive source to measure the total mass collected.

Elemental analysis of the filters was carried out at the Crocker Nuclear Laboratory, University of California-Davis, Davis, California by ion-excited X-ray fluorescence (Flocchini et al., 1972; Flocchini et al., 1976). These authors quote absolute error limits of ± 10% in most cases to as high as ± 30% near detection limits. The analyses reported in this paper were only rarely near detection limits. When not detected, elemental concentrations were assumed to have been half the detection limit. The following elements were detected regularly and make up most the data set considered in this paper: Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Br, and Pb.

Whatman-41 filters were digested in a mixture of strong acids. Digestions were carried out in 100 ml Teflon beakers in a laminar flow hood to minimize contamination. Analyses were performed by atomic absorption spectrophotometry, using both flame and flameless methods. Absolute analytical errors are estimated at ± 5% at normal concentrations. Complete details of the analytical procedure were given by Peden (1976).

RESULTS

Since results of both Whatman and Nuclepore filter measurements are presented in this section, it is helpful to compare results obtained from the respective filters operated on the same days at the same sites. The filters compared are not duplicate samples, since the Whatmans collected aerosol for about 24 hr and the Nuclepores 6 to 12 hr, generally beginning about 1000 to 1200 CDT. Thus, the Whatman samples represent a complete 24-hr cycle, whereas the Nuclepore samples represent primarily daylight hours with a well-mixed boundary layer. It is thus possible that any observed differences could be caused by systematic differences in atmospheric concentration between daylight and nighttime hours, or by differences in filter sampling characteristics. Rain fell somewhere in



SITE	YEARS USED AS FILTER SITE	SAMPLING HEIGHT
0	1971, 1972	GROUND
81	1971-1973	GROUND
151	1972, 1973	GROUND
159	1973	GROUND

Figure 2. Whatman-41 filter sampling network, 1971-1973

the St. Louis area on each day of these filter samples, although not necessarily at every sampling site.

Comparisons of 14 pairs of filters are shown in Figure 3 for the elements K, Ca, Mn, Fe, Zn, and Pb. Three different sampling sites were used, as shown in the figure. Correlations coefficients, R, are also shown for each element.

Results for K, Fe, and Zn, while showing considerable scatter about the line of perfect agreement, show no particular bias toward higher concentrations on either filter. Ca, Mn, and Pb, on the other hand, had systematically higher concentrations on Nuclepore filters. For Ca and Pb, the samples where the Nuclepore filter measured significantly higher concentrations were collected predominantly at site 151. This site is within 50m east of a rather heavily-traveled 2-lane road, which probably accounts for the higher Pb concentrations on the Nuclepore, collected during hours of heaviest traffic. Limestone dust raised from the road shoulder by traffic could also account for the higher daytime Ca, but the site is also east and northeast of several limestone quarries, which could also emit Ca-containing dust preferentially during working hours.

In the case of Mn, the Nuclepore concentration was an upper limit for over half the pairs. Still, on the remaining pairs the Nuclepore concentration was substantially higher than the Whatman concentration. Further, all three sites are represented among these remaining data. The explanation is not readily apparent in this case, but it cannot be due to an erroneous correction of the Nuclepore data for collection efficiency, since no such correction was made for Mn.

In summary, comparing elemental concentrations measured on 24-hr Whatman-41 filters and 6 to 12-hr daytime Nuclepore filters generally shows either no systematic differences, or differences caused by diurnal variations in source strength. No reason is apparent for higher concentrations of Mn on Nuclepore filters.

Nuclepore Measurements

Table 2 presents an overall summary of Nuclepore measurements in METROMEX. Arithmetic means (designated AM in the table) standard deviations (SD), geometric means (GM), and standard geometric deviations (SGD) are given for each element and for each year of measurements, and all years combained, at each site.

A visual summary of the data is presented in Figure 4, showing statistical distributions for each element. Concentration is plotted against the probability of observing a concentration equal to or less than the given value. The log-normal distribution produces a straight line on these graphs. Clearly, elemental concentrations very frequently approximate log-normal distributions.

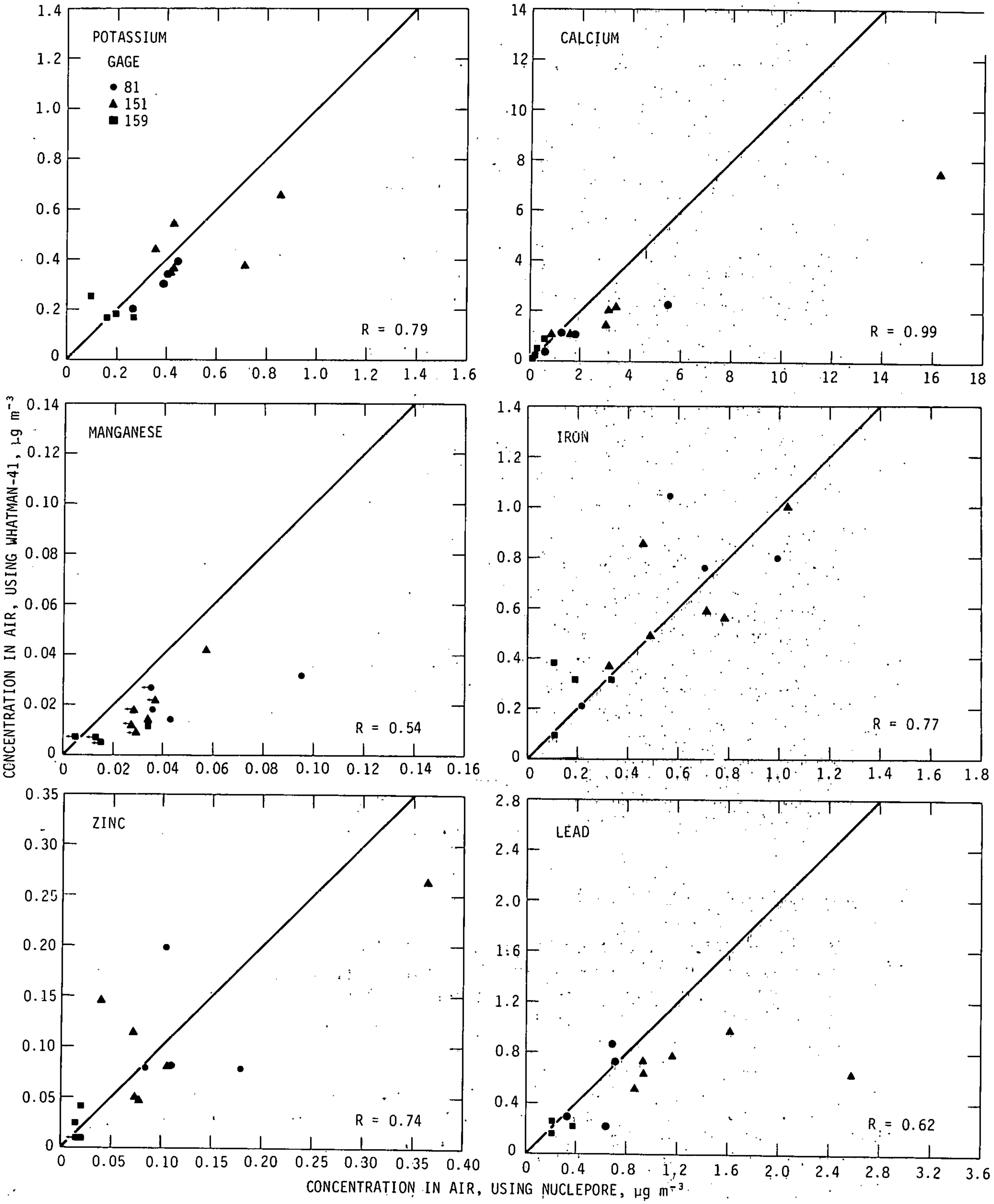


Figure 3. Comparison of concentrations measured by 24-hr Whatman-41 and 12-hr Nuclepore filters at three locations. R is the correlation coefficient.

Table 2. Summary of Nuclepore Filter Measurements in METROMEX, 1973-1975

Gage No.	Year	No. of Samples	Al				Si				S				K				Ca				Ti			
			AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SDG	AM	SD	GM	SGD
0	1973	18	418	378	256	3.05	1790	1270	1430	2.02	3780	3450	2870	2.12	321	205	275	1.72	1210	1000	914	2.12	90.6	72.6	65.5	2.43
	1974	18	981	1170	424	5.00	2470	2460	1170	5.36	4900	4380	2490	4.79	411	303	311	2.26	1530	1070	1060	2.82	122	112	84.3	2.47
	1975	25	426	440	268	2.92	1600	1250	1230	2.13	3040	2870	2120	2.40	187	118	160	1.76	993	918	767	2.03	44.0	35.5	32.0	2.39
	Σ	61	588	758	303	3.53	1910	1710	1270	2.96	3810	3560	2430	2.96	292	229	228	2.01	1220	1000	889	2.28	80.7	81.4	52.6	2.64
22	1973	20	753	866	407	3.24	3200	2120	2220	3.02	5820	4620	3970	3.07	496	212	423	2.09	2580	1970	1780	3.00	166	118	114	2.80
	1975	28	980	646	740	2.39	4080	2780	3240	2.04	7090	7740	4790	2.40	448	236	394	1.69	3010	1440	2650	1.70	106	98.2	78.0	2.20
	Σ	48	886	746	575	2.83	3720	2540	2770	2.48	6560	6590	4430	2.66	468	225	406	1.85	2830	1670	2250	2.30	130	110	91.4	2.48
33	1974	18	1580	1160	1240	2.07	3890	3280	2880	2.28	7270	6090	3400	5.55	670	362	541	2.21	6350	5190	4010	3.50	171	111	144	1.79
	1975	30	1100	569	946	1.84	4570	2260	4010	1.72	6860	5120	5560	1.91	521	248	449	1.94	5460	2730	4710	1.83	105	78.5	82.0	2.06
	Σ	48	1280	860	1050	1.94	4310	2670	3540	1.96	7010	5440	4620	3.24	578	301	482	2.04	5800	3810	4440	2.45	130	96.3	101	2.06
44	1975	29	677	532	470	2.74	2580	1680	2070	2.04	4820	3330	3760	2.11	354	187	307	1.76	1860	1150	1493	2.07	85.8	77.8	59.7	2.42
49	1975	29	689	400	507	2.65	2810	1270	2530	1.62	5950	3270	5150	1.74	376	118	349	1.39	1710	961	1450	1.84	82.3	66.0	56.4	2.67
79	1974	21	1090	906	774	2.52	2460	2230	1250	4.60	5910	4910	3120	4.58	682	315	603	1.73	3860	2310	3140	2.01	139	84.5	117	1.82
113	1973	19	1060	1020	659	2.99	2920	2160	1810	3.64	3980	2640	2900	2.64	530	273	425	2.37	2920	1580	2090	3.15	384	357	218	3.53
	1974	20	891	885	534	3.34	2160	2400	931	5.21	4740	4970	1780	6.50	512	356	382	2.56	2620	1300	2200	2.06	170	145	118	2.55
	Σ	39	974	947	593	3.14	2530	2280	1290	4.51	4370	3980	2250	4.50	520	314	403	2.44	2770	1430	2140	2.56	274	288	159	3.11
151	1974	23	832	470	703	1.90	2490	1490	1840	2.94	4460	3740	2750	3.51	504	162	476	1.43	3320	1340	3020	1.62	122	76.7	104	1.77
	Σ*	28	780	466	622	2.19	2610	1510	2000	2.73	4270	3490	2770	3.18	510	168	482	1.42	3610	2760	3020	1.81	115	72.4	96.4	1.84
301	1974	20	584	442	426	2.58	1610	1270	836	5.08	4330	3210	2690	3.78	340	150	311	1.53	1200	612	1050	1.73	82.6	54.7	74.6	1.75
302	1974	15	470	278	363	2.43	1800	1740	897	4.56	4610	3520	2520	4.85	348	158	318	1.55	1290	808	1070	1.94	77.2	41.3	68.2	1.67
303	1975	29	1160	742	857	2.57	4610	2460	3960	1.80	5770	4930	4360	2.13	503	268	436	1.74	3460	1680	3100	1.62	114	82.4	91.8	1.95
304	1975	30	957	503	802	2.00	4040	2010	3510	1.77	6100	4720	4670	2.15	452	191	412	1.57	3450	1870	2890	1.91	89.6	44.8	75.7	1.95

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* Includes 6 samples from 1973

Table 2, continued

Gage no.	Year	No. of samples	Mn				Fe				Zn				Br				Pb			
			AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD
0	1973	18	23.6	20.6	17.9	2.09	612	479	434	2.67	73.0	70.0	44.3	2.99	53.1	55.5	38.6	2.04	226	307	120	3.09
	1974	18	28.2	20.4	20.6	2.40	1070	980	608	3.74	80.6	78.5	46.3	3.30	22.0	9.5	20.6	1.42	289	279	168	3.24
	1975	25	25.8	42.8	15.6	2.39	426	501	301	2.19	46.8	79.6	25.6	2.71	32.9	20.9	28.0	1.75	183	187	135	2.12
	Σ	61	25.9	31.2	17.7	2.30	670	715	413	2.85	64.5	76.8	35.8	3.03	35.6	35.0	28.1	1.83	227	254	139	2.72
22	1973	20	64.9	43.8	54.6	1.82	1350	833	966	3.16	240	199	145	3.26	82.4	51.3	71.4	1.65	668	435	489	2.55
	1975	28	52.3	56.8	36.0	2.28	1050	666	869	1.89	114	141	69.2	2.68	131	109	94.4	2.31	1010	444	885	1.77
	Σ	48	57.5	51.7	42.8	2.14	1180	747	908	2.40	166	177	94.2	3.08	110	92.2	84.1	2.05	866	467	692	2.21
33	1974	18	61.3	34.2	51.6	1.92	2180	1130	1870	1.88	188	141	137	2.40	72.8	62.8	60.0	1.99	528	304	401	2.45
	1975	30	49.3	21.2	44.6	1.61	1430	584	1320	1.51	223	266	133	2.85	108	75.4	84.5	2.05	886	587	714	1.99
	Σ	48	53.8	27.1	47.1	1.73	1710	898	1510	1.69	209	226	134	2.65	94.5	72.2	74.6	2.05	752	526	575	2.26
44	1975	29	39.7	33.8	28.4	2.36	727	467	589	1.99	80.7	102	46.0	2.98	138	404	56.9	2.67	582	819	368	2.55
49	1975	29	34.9	27.6	28.3	1.91	759	398	661	1.74	91.9	85.7	59.2	2.71	72.9	107	49.9	2.09	438	303	343	2.14
79	1974	21	75.7	40.5	65.3	1.80	2210	1210	1880	1.87	188	108	148	2.28	96.4	80.8	69.7	2.26	677	370	590	1.73
113	1973	19	54.6	34.0	44.6	1.98	1670	851	1130	3.89	288	391	159	3.26	284	171	219	2.32	1230	1060	635	4.04
	1974	20	44.0	26.7	36.2	1.95	1630	1120	1290	2.08	279	338	158	3.11	257	127	214	2.08	1380	726	1220	1.67
	Σ	39	49.2	30.6	40.1	1.96	1650	982	1210	2.92	284	360	158	3.14	270	149	216	2.13	1310	895	887	2.94
151	1974	23	39.2	21.2	32.7	1.94	1240	495	1130	1.62	117	91.1	88.1	2.20	370	287	258	2.79	1420	724	1250	1.71
	Σ*	29	36.3	21.0	30.0	1.94	1120	518	989	1.71	118	95.5	88.9	2.16	329	272	226	2.74	1400	700	1240	1.67
301	1974	20	25.4	14.2	21.9	1.77	752	425	650	1.74	57.0	41.3	41.8	2.47	47.0	43.6	32.4	2.34	317	250	222	2.61
302	1974	15	33.1	16.1	29.8	1.60	1010	283	979	1.32	74.7	55.2	54.7	2.43	130	126	74.3	3.30	462	378	251	4.32
303	1975	29	66.0	42.8	51.4	2.21	1710	843	1480	1.81	147	85.4	112	2.47	129	86.6	101	2.09	919	365	849	1.52
304	1975	30	40.5	21.9	34.6	1.82	1024	603	851	1.91	90.5	88.4	56.4	2.80	66.0	52.7	52.6	1.92	554	337	460	1.89

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*Includes 6 samples from 1973

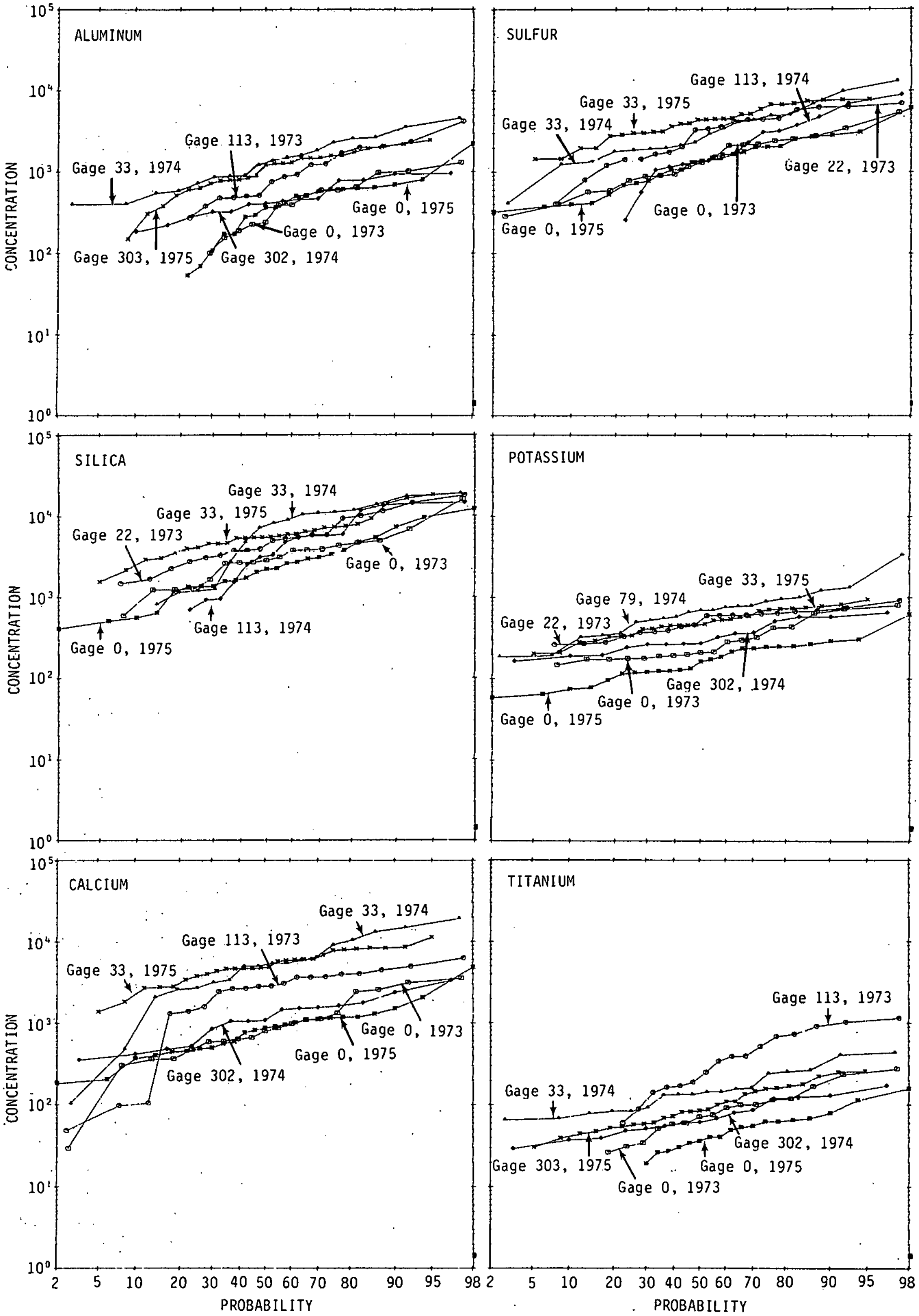


Figure 4. Cumulative probability distributions of airborne element concentrations, ng/m^3

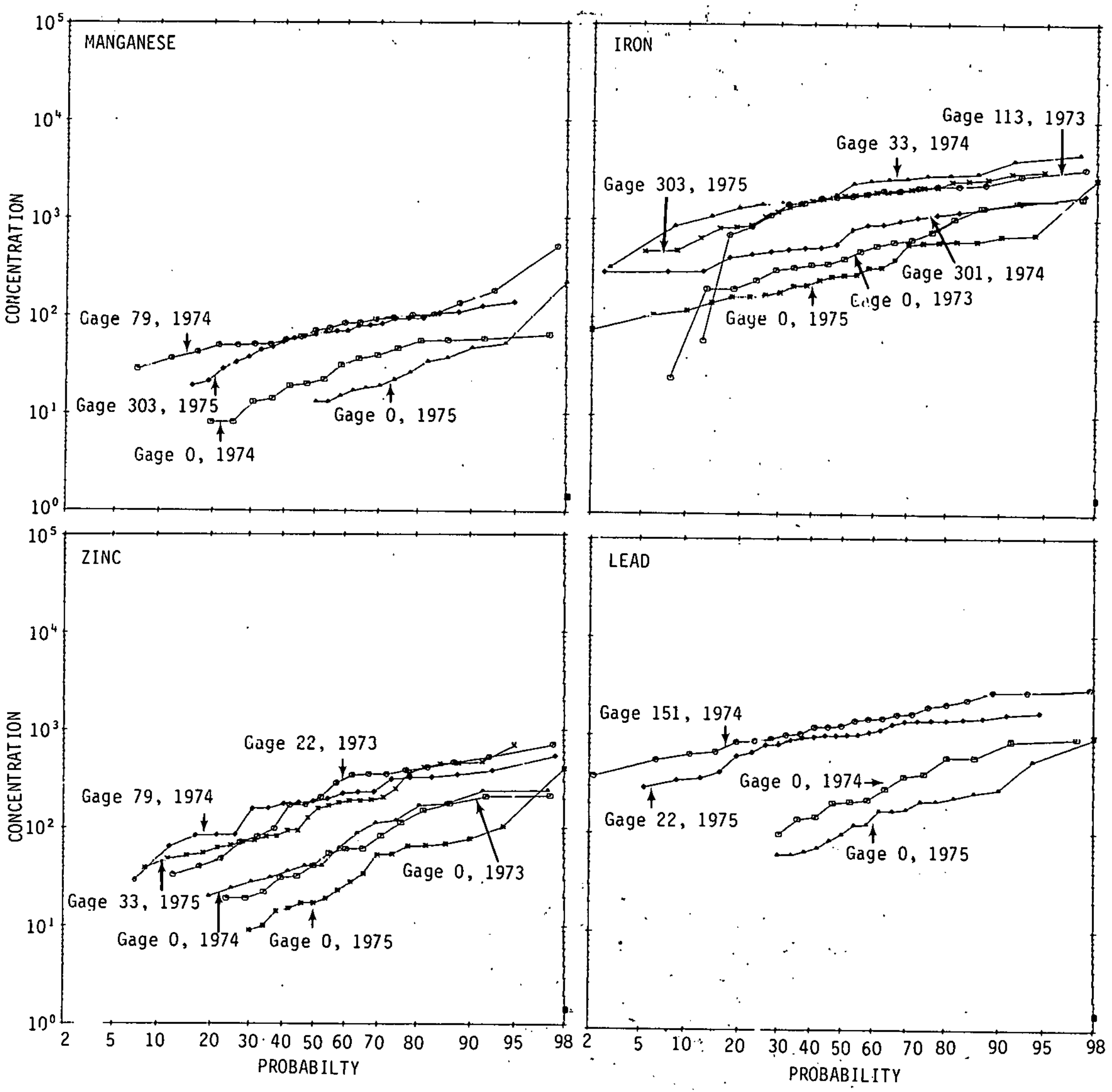


Figure 4. Concluded

For each element, distributions are plotted for those sites having the highest and lowest GM for each year of operation when enough values were obtained for a valid distribution. For example, the graph for Pb shows that in 1974 the highest GM was measured at site 151 and the lowest at site 0. Similarly in 1974 the maximum GM occurred at site 22 and the minimum at site 0. The variation in the locations of maxima and minima from year to year is caused, at least in part, by the fact that the network of sampling sites varied from year to year. Nevertheless, site 0 very often observed the lowest concentrations, and sites 33 and 113 the highest.

Maps showing the spatial distribution of overall GM values for each element are given in Figure 5. Keep in mind that for some sites these values represent only one summer, while at others they represent two or three. At most sites the number of filters exceeds 25, and this appears to be sufficient to give rather smooth and reasonable patterns in Figure 5.

Figure 5 shows seven elements with either primary or secondary maxima in the Alton-Wood River area. These elements include the major soil-derived elements, Al, Si, Ca, and Fe, as well as the auto exhaust elements, Br and Pb, and an industrial element, Zn.

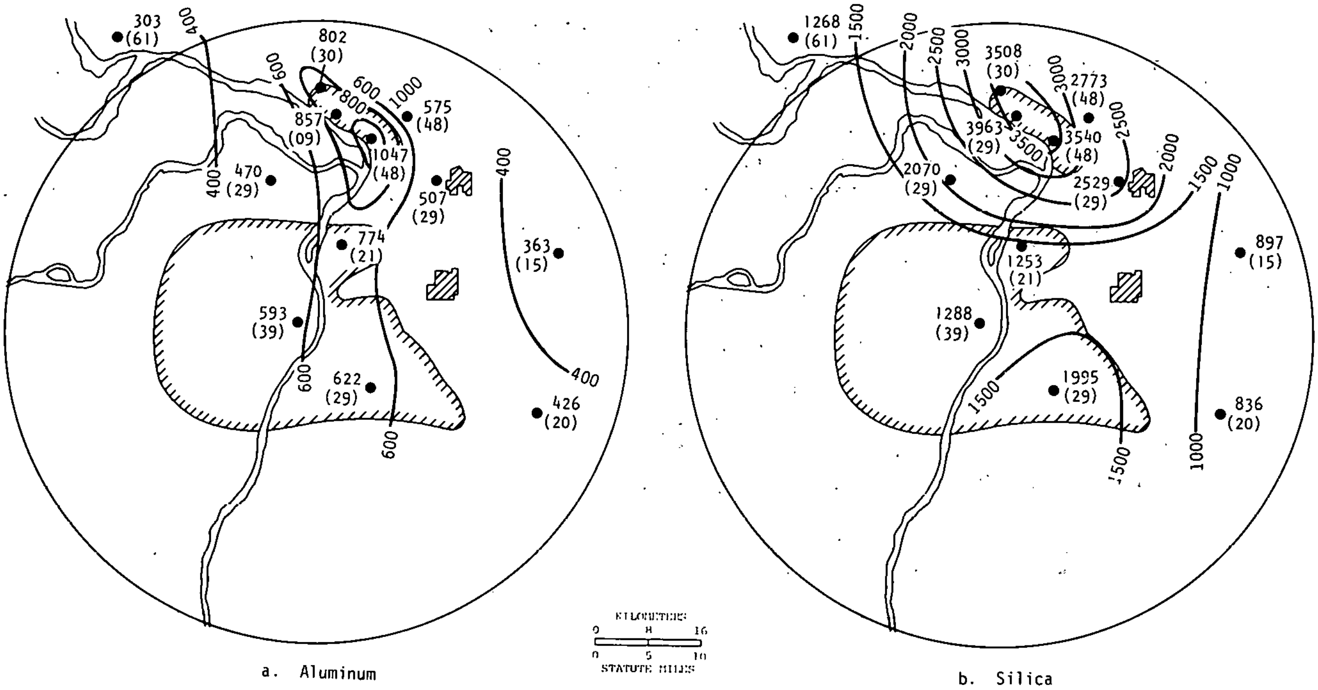
The maximum particulate S is generally downwind of the urban-industrial area, stretching from Alton to Edwardsville. The Granite City area is the location of the maximum Mn and Fe values, and for K as well. Mn and Fe are expected from the local steel plant, but the reason for the K peak is not apparent. The sampler in St. Louis recorded high GM values for Ti, Zn, Br, and Pb. The latter two would be expected from the high traffic densities of the urban area. Ti and Zn peaks reflect the single known Ti source to the south and multiple sources of Zn east of the sampler.

Whatman-41 Measurements

An overall summary of the data is provided in Table 3, which gives, as before, AM, SD, GM, and SGD for each element at each site in each year of operation. Data for all years combined are also listed.

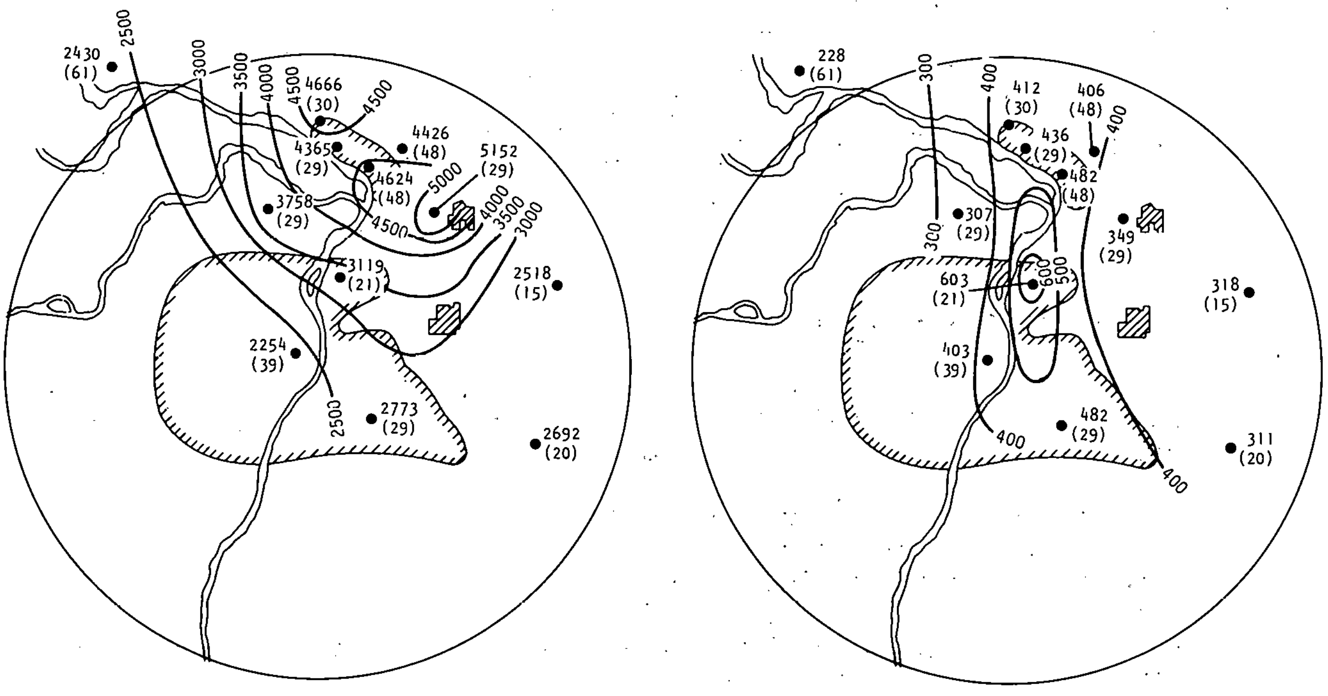
Statistical distributions of all data at each site are presented for each separate element in Figures 6, 7, and 8. Note that Li, Na, and Mg are included here but not in the Nuclepore data. Again the concentration distributions are good approximations to log-normal in most cases. The more distant and generally upwind sites (0 and 159) invariably show the lowest concentrations and the closer, downwind sites (81 and 151) the higher concentrations.

Ratios of maximum to minimum overall GM vary from element to element. In general, the soil-derived elements (Li, Na, Mg, K, Fe) have ratios of 2 to 3. Pb had a ratio of 2.5, quite modest in view of site 151 begin located near a rather heavily-traveled road. Perhaps the 24-hr sampling period smooths out the high values during peak traffic hours. Mn, with a ratio of 3.0, probably reflects both soil and industrial sources, while Zn at 4.2 and Ca at 5.1 indicate stronger local sources near sampling sites than any of the other elements.



a. Aluminum

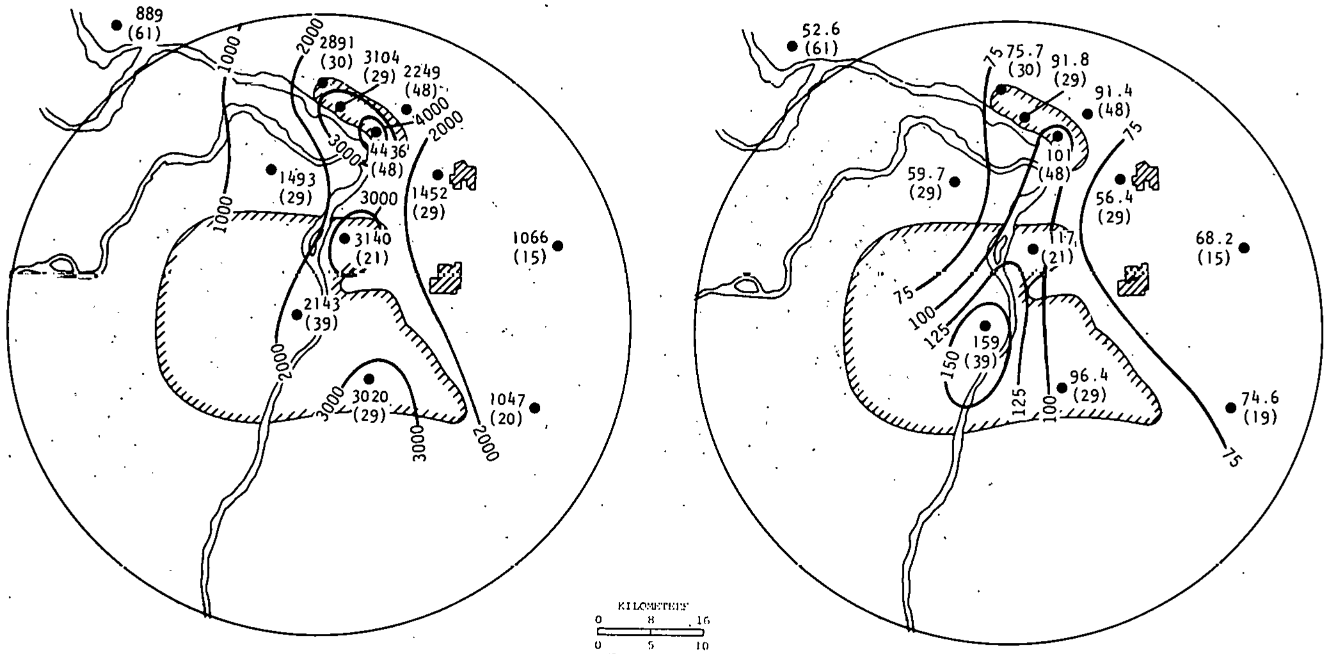
b. Silica



c. Sulfur

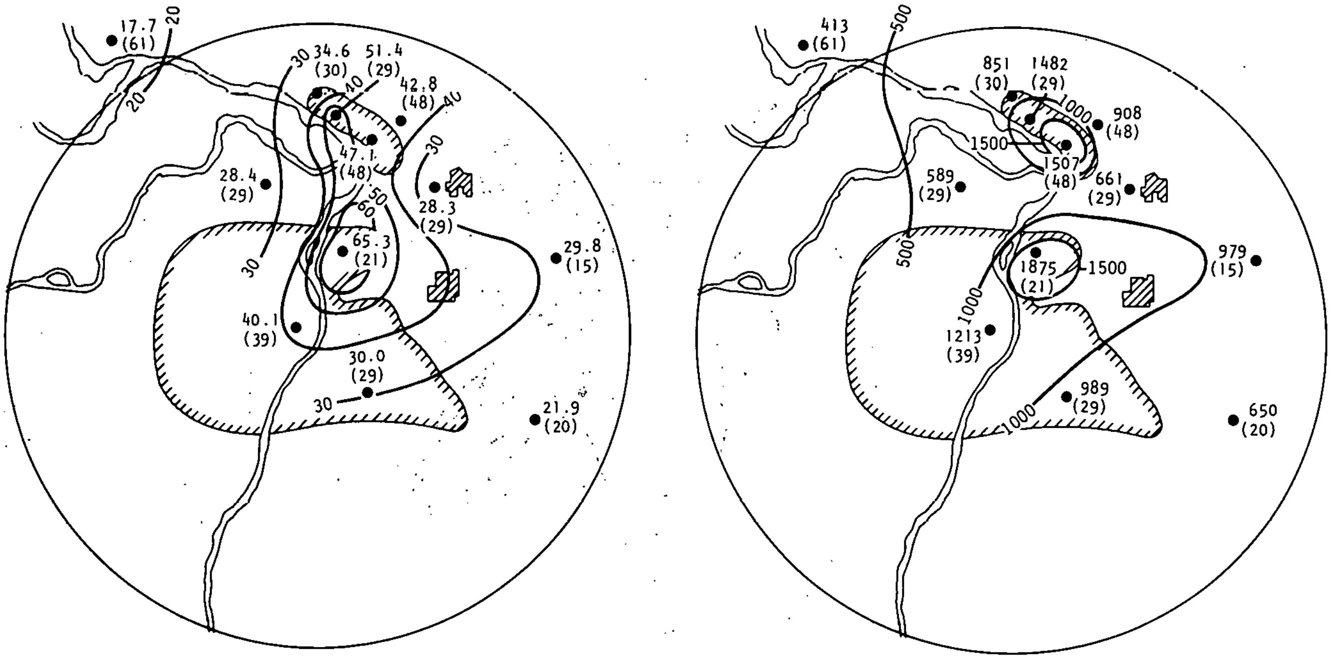
d. Potassium

Figure 5. Distribution of geometric mean concentrations of airborne elements, ng/m³. Values in parentheses are the number of samples at each site



e. Calcium

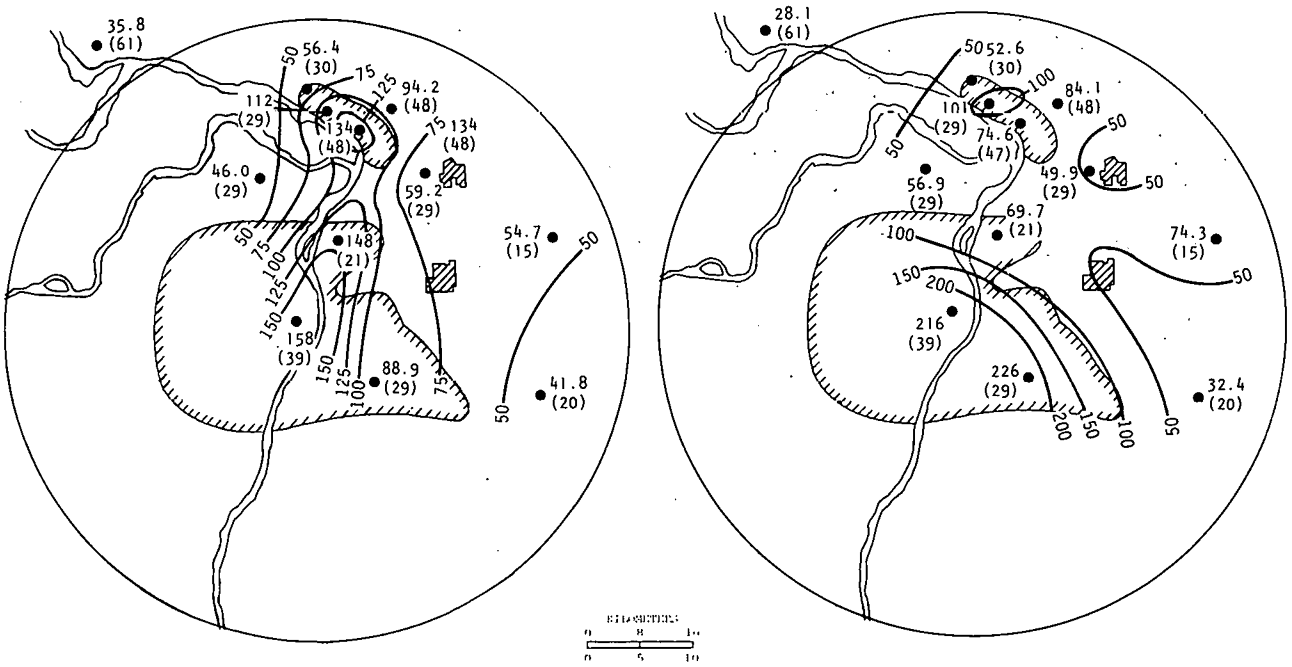
f. Titanium



g. Magnesium

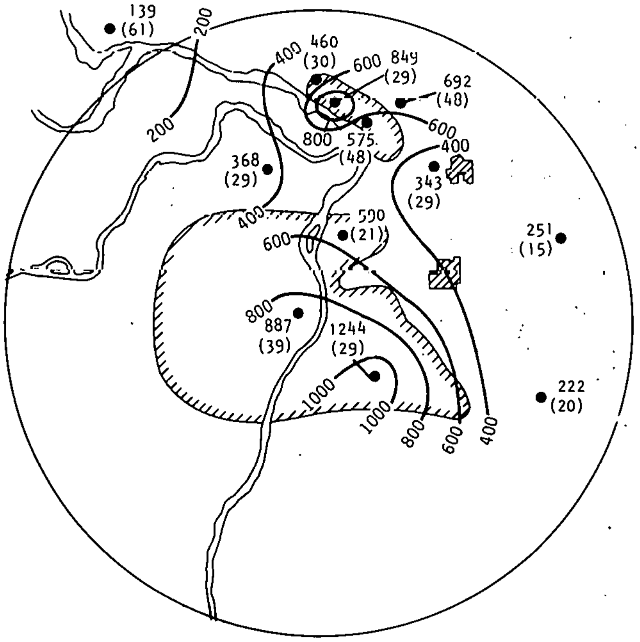
h. Iron

Figure 5. Continued



i. Zinc

j. Bromine



k. Lead

Figure 5. Concluded

Table 3. Summary of Whatman-41 Filter Measurements in METROMEX, 1971-1973

Gage no.	Year	No. of samples	Li				Na				Mg				K				Ca			
			AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD
0	1971	13									129	78	110	1.83								
	1972	28									185	105	154	1.90	360	194	334	1.62	1070	591	893	1.92
	Σ	41									167	100	139	1.90								
81	1971	12									491	265	434	1.67								
	1972	20									469	739	291	2.37	466	189	424	1.62	3610	4660	2390	2.39
	1973	25	1.07	0.87	0.88	1.84	429	211	380	1.69	270	154	226	1.91	419	186	385	1.51	1500	898	1260	1.85
	Σ	57									386	469	284	2.09								
151	1972	22									351	173	315	1.61	815	752	632	1.91	3490	1950	2960	1.86
	1973	25	1.06	0.66	0.89	1.82	475	283	399	1.91	472	353	363	2.16	572	293	516	1.57	2940	2630	2160	2.23
	Σ	47									415	290	340	1.91	686	564	568	1.79	3200	2350	2500	2.08
159	1973		0.73	0.66	0.50	2.47	165	62	154	1.47	108	85	87	1.90	254	95	240	1.40	508	345	399	2.17

Gage no.	Year	No. of samples	Mn				Fe				Cu				Zn				Cd				Pb			
			AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD	AM	SD	GM	SGD
0	1971	13	12	5	12	1.44	264	206	194	2.42					47	50	28	3.05					153	113	118	2.15
	1972	28	16	10	16	1.67	924	596	745	2.00					75	77	44	3.53	3.35	3 48	2.41	3.26	254	144	228	1.76
	Σ	41	15	9	14	1.62	715	591	486	2.67					66	70	38	3.38					222	142	184	2.02
81	1971	12	175	182	105	2.77	1220	355	1160	1.39	29	18	25	1.84	261	142	226	1.76					513	146	494	1.34
	1972	20	22	12	18	2.04	1050	479	953	1.60					241	468	126	2.67	3.36	3.85	3.13	3.03	294	164	249	1.87
	1973	25	51	68	33	2.32	901	399	804	1.69	16	15	14	2.26	162	128	122	2.20					412	229	356	1.77
	Σ		67	109	34	2.85	1020	431	922	1.62					210	295	141	2.33					392	206	336	1.81
151	1972	22	21	16	18	1.84	1450	846	1280	1.62					155	193	97	2.56	5.44	7.30	3.83	3.91	401	287	352	1.87
	1973	25	26	15	22	1.78	821	360	728	1.74	11	18	5	3.40	124	176	74	2.58					644	352	568	1.69
	Σ	47	23	16	20	1.82	1120	703	948	1.80					139	183	84	2.58					530	342	456	1.85
159	1973		12	9	9	1.90	355	272	312	2.01					34	34	25	2.07					324	151	298	1.52

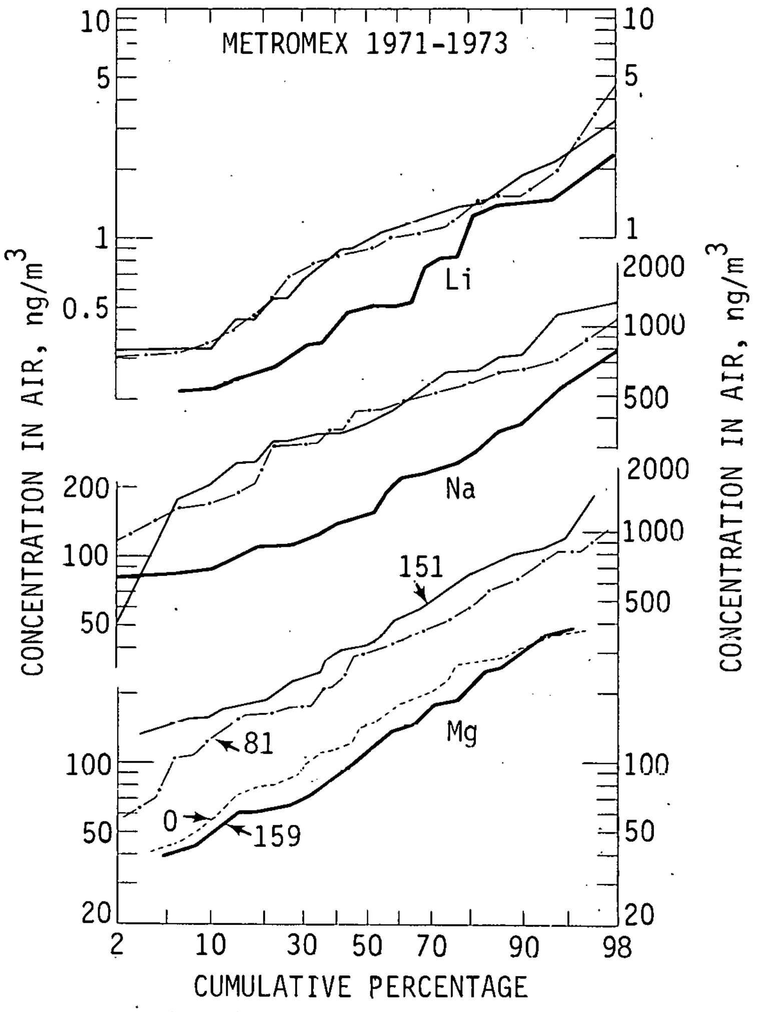


Figure 6. Cumulative probability distributions of Li, Na, and Mg from Whatman-41 filter samples

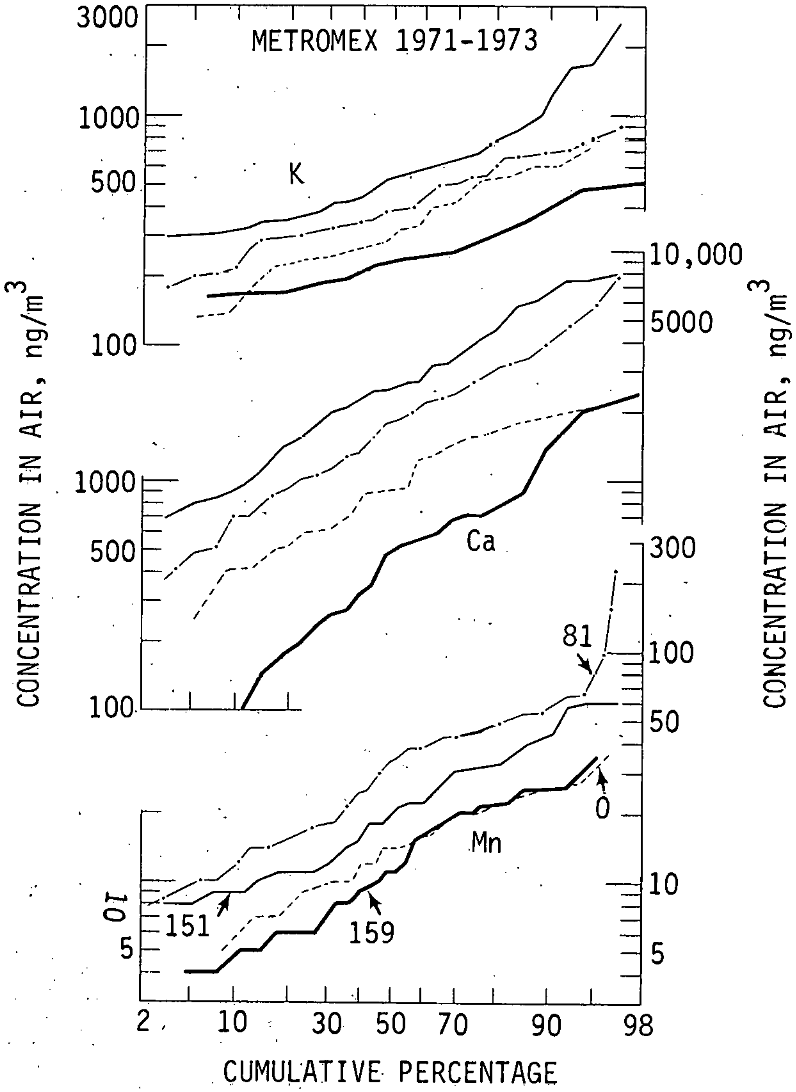


Figure 7. Cumulative probability distributions of K, Ca, and Mn from Whatman-41 filter samples

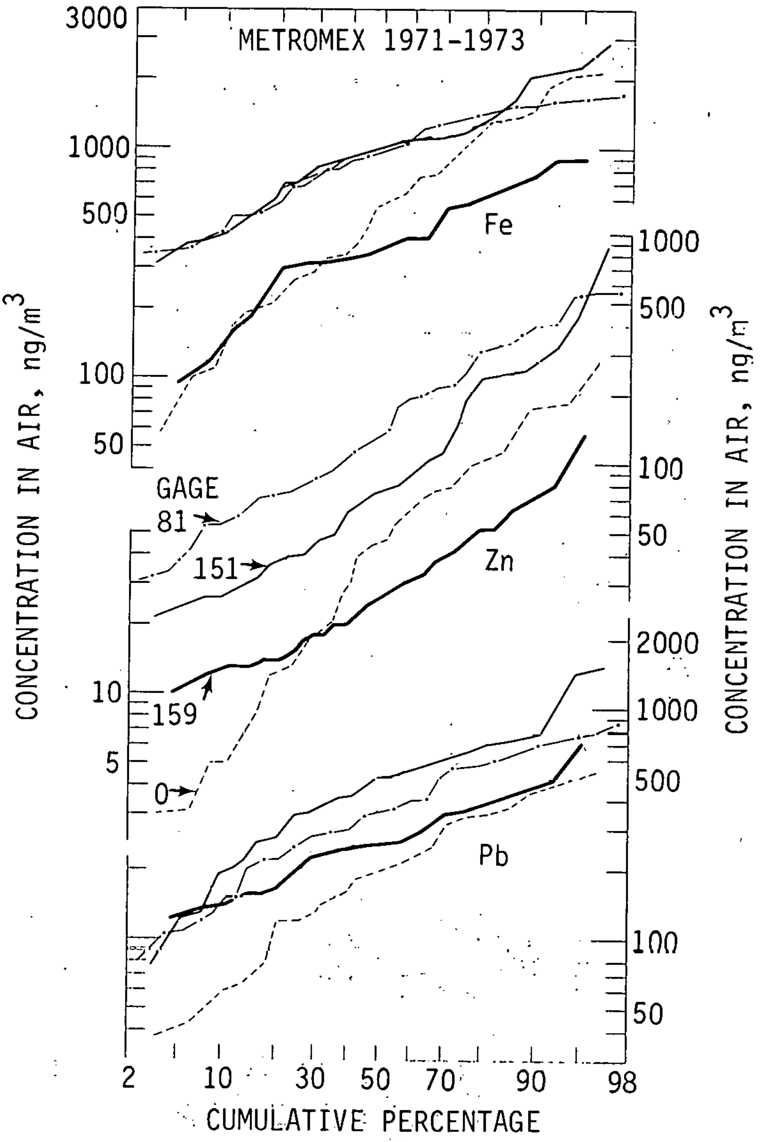


Figure 8. Cumulative probability distributions of Fe, Zn, and Pb from Whatman-41 filter samples

In summary, the Nuclepore measurements show that maxima in the fields of GM concentration almost always occurred in highly populated industrialized areas. The more limited Whitman-41 data are consistent with these findings. This was expected for elements having industrial or auto exhaust sources, and indeed the locations of the maxima are consistent with locations of known sources of these elements. Somewhat unexpected, at least at first sight, is the finding that elements strongly associated with soil dust also have their highest concentrations in urban areas.

DISCUSSION

Many studies of the chemical composition of urban aerosols have identified soil-derived aerosols as an important component (Dams *et al.*, 1971; John *et al.*, 1973; Hammerle and Pierson, 1975; Neustadter *et al.*, 1976; Hopke *et al.*, 1976; Perone *et al.*, 1976; Hardy *et al.*, 1976; Johansson *et al.*, 1976). This component typically includes Al, Si, K, Ca, Sc, Ti, Mn, Fe, and some rare earths (La, Ce, Sm, Eu, Th). However, in some areas, Ca, Mn, and Fe also have strong industrial sources.

A number of these studies compared urban concentrations with those in suburban or rural areas. Often urban concentrations are higher by factors of 4 or more for elements from local industry exhaust. For soil derived elements; *concentrations are also higher in the cities*, but by a small factor.

For example, at Cleveland, Neustadter *et al.* computed ratios of concentrations for 45 to 55 mean values at 16 *urban* stations to 5 to 8 mean values at 7 suburban stations and found values of 1.7 or 1.8 for the soil source elements Al, Si, V, and Sn. Industrial source elements had higher ratios: Be, 6.1; Cl, 6.5; Cr, 5.6; Sb, 6.9.

In Florida the ratios of mean large particle (>2μm) concentrations in downtown Miami to those in North Florida (Hardy *et al.*, 1976) were:

Fe: 2.3   K: 4.7

Ti: 2.8   Ca: 26.2

S: 4.6

Hardy *et al.* point out that Fe, Ti, and K, although much higher in concentration in Miami, have similar ratios to each other and to crustal dust both there and in North Florida, and interpret the Miami source to be soil dust raised by man's activities in the city. The high Ca value was explained by Hardy *et al.* as arising from a high limestone/clay ratio in Miami soils compared to those in North Florida. S was interpreted as having both natural and anthropogenic sources.

Our results for St. Louis agree with those for Cleveland and Miami in that all elements, including those derived mainly from the soil, were observed in higher concentrations in the city. Table 4 shows ratios of maximum to minimum goemetric mean concentrations calculated from both Whatman-41 and Nuclepore measurements. For each element except S, the maximum was at an urban site and the minimum at a rural site. Here again, the elements with strong local sources (Br, Pb, Zn, Ca) have the higher ratios, but soil derived elements (Li, Na, Al, Si, K) are also higher at urban sites, by factors of about 2 to 5.

Table 4. Ratios of maximum to minimum geometric means for both types of filters.

	Filter	
	Whatman-41	Nuclepore
Li	1.8	
Na	2.6	
Mg	3.9	
Al		3.5
Si		4.7
S		2.3
K	2.4	3.7
Ca	6.2	5.0
Ti		3.0
Mn	3.8	3.7
Fe	3.0	4.6
Zn	5.6	4.4
Br		8.0
Pb		8.9

REFERENCES

Brar, S. S., D. M. Nelson, J. R. Kline, P. R. Gustafson, E. L. Kanabrocki, C. E. Moore, and D. Hattori, 1970. Instrumental analysis for trace elements present in Chicago area surface air. J. Geophys. Res., 75, 2939-2945.

Changnon, S. A., 1968. The LaPorte anomaly-fact or fiction? Bull. Amer. Meteor. Soc., 49, 4-11.

Dams, R., J. A. Robbins, K. A. Rahn, and J. W. Winchester, 1971. Quantitative relationships among trace elements over industrialized N. W. Indiana. In: Nuclear Techniques in Environmental Pollution, International Atomic Energy Agency, Vienna, IAEA-SM-142a/5, pp. 139-157.

Flocchini, R. G., T. A. Cahill, D. J. Shadoan, S. J. Lang, R. A. Eldred, P. J. Feeney, G. W. Wolfe, D. C. Simmeroth, and J. K. Suder, 1976. Monitoring California's aerosols by size and elemental composition. Envir. Sci. & Technol., 10 (1), 76-82.

Gladney, E. S., W. H. Zoller, A. G. Jones, and G. E. Gordon, 1974. Composition and size distributions of atmospheric particulate matter in Boston area. Envir. Sci. & Technol., 8 (6), 551-557.

Hammerle, R. H., and W. R. Pierson, 1975. Sources and elemental composition of aerosol in Pasadena, Calif., by energy-dispersive X-ray fluorescence. Envor. Sci. & Technol., 9 (12), 1058-1068.

Hardy, K. A., R. Akselsson, J. W. Nelson, and J. W. Winchester, 1976. Elemental constituents of Miami aerosol as function of particle size. Envir. Sci. & Technol., 10 (2), 176-182.

Hopke, P., E. S. Gladney, G. E. Gordon, W. H. Zoller, and A. G. Jones, 1976. Use of multivariate analysis to identify sources of selected elements in the Boston urban aerosol. Atmos. Environ., 10, 1015-1025.

Johansson, T. B., R. E. Van Grieken, and J. W. Winchester, 1976. Elemental abundance variation with particle size in North Florida aerosols. J. Geophys. Res., 81 (6), 1039-1046.

John, W., R. Kaifer, K. Rahn, and J. J. Wesolowski, 1973. Trace element concentrations in aerosols from the San Fransisco Bay area. Atmos. Environ., 7, 107-118.

King, R. B., J. S. Fordyce, A. C. Antoine, H. F. Leibecki, H. E. Neustadter, and S. M. Sidik, 1976. Elemental composition of airborne particulates and source identification: An extensive one year survey. J. Air Pollut. Control Assoc., 26, 1073-1078.

Kneip, T. J., M. Eisenbud, C. D. Strehlow, and P. C. Freudenthal, 1970. Airborne particulates in New York City. J. Air Poll. Cont. Assoc., 20, 144-149.

Kowalczyk, G. S., C. E. Choquette, and G. E. Gordon, 1977. Chemical element balances and identification of air pollution sources in Washington, D. C. (Submitted for publication).

Neustadter, H. E., J. S. Fordyce, and R. B. King, 1976. Elemental composition of airborne particulates and source identification; data analysis techniques. J. Air Poll. Control Assoc., 26 (11), 1079-1084.

Paciga, J. J., T. M. Roberts, and R. E. Jervis, 1975. Particle size distributions of lead, bromine, and chlorine in urban-industrial aerosols. Environ. Sci. & Technol., 9, 1141-1144.

Peden, M. E., 1976. Flameless atomic absorption determinations of Cd, Pb, and Mn in particle size fractionated aerosols. Paper presented at National Bureau of Standards Symposium on Accuracy in Trace Analysis. Gaithersburg, Md., August, 1976.

Perone, S. P., M. Pichler, P. Gaarenstroom, and J. L. Moyers, 1976. The application of pattern recognition techniques to the characterization of atmospheric aerosols. Proceedings, International Conf. on Environ. Sensing and Assessment, 14-19 September 1975, Las Vegas, Nevada, Institute of Electrical and Electronic Engineers, 345 E. 4th St., New York City 10017, paper no. 5-4.

Spurny, K. R., and J. P. Lodge, 1972. Collection efficiency tables for membrane filters used in the sampling and analysis of aerosols and hydrosols. NCAR Technical Note NCAR-TN/STR-77, Laboratory of Atmospheric Sciences, National Center for Atmospheric Research, Boulder, CO.

Whitby, K. T., R. B. Husar, and B. Y. H. Liu, 1972. The aerosol size distribution of Los Angeles smog. J. Colloid Interface Science, 39, 177-204.

CHAPTER 4

The Weekly Aerosol Sampling Program

Donald F. Gatz

INTRODUCTION

A program of weekly aerosol sampling, using Nuclepore filters, has been in progress since June, 1975. Until May, 1977, samples were collected on the roof of the Water Survey Offices in Champaign. Beginning in June, 1977, the sampling site was moved about 10 km south to the University of Illinois Willard Airport, near Savoy, Illinois.

Two additional weekly filter sites have been established recently. These are at Charlottesville, Virginia and Whiteface Mountain, New York. The Charlottesville site was established through the cooperation of Dr. James Galloway of the University of Virginia, and the Whiteface site through the cooperation of Mr. Raymond Falconer of the Atmospheric Sciences Research Center, State University of New York at Albany.

METHODS

All three sampling sites use 37 mm diameter Nuclepore membrane filters with 0.8 μm pore diameters. The vacuum pumps are controlled by timers to draw air through each filter for 5 minutes out of every hour, over a period of one week. Filters run from Wednesday to Wednesday at all three sites. All other aspects of sample collection are similar to those used in METROMEX and explained in detail elsewhere in this report. One deviation from earlier practice is that the filter samples collected on the Water Survey roof were exposed in a standard weather shelter instead of an inverted funnel rain shield.

Sample analysis was carried out at the University of California-Davis using ion-excited X-ray fluorescence. Details of the analyses are given elsewhere in this report.

Data analysis has been carried out using factor analysis, which is also explained elsewhere.

RESULTS AND DISCUSSION

Mean concentrations and standard deviations are given in Table 1 for the 11 elements routinely detected on the filters. These are the results of 66 samples collected between June, 1975 and January, 1977. An additional group of samples was lost in shipment to California for analysis. These results must be considered preliminary at present because of uncertainties concerning Al and S. The samples were analyzed in two batches, and rather large differences were observed between the respective results. These differences were especially large for Al, which was not detected on many samples in the second batch. This caused the standard deviation of the Al concentration to be larger than the mean, and a Si/Al ratio for all 66 samples of 6.8, a very high value compared to other values in the literature (Rahn, 1976) and to our results at St. Louis (see Table on page in this report).

The S result is uncertain because of a possible error in correcting for filter penetration. As explained earlier, S, Br, and Pb concentrations were corrected assuming a collection efficiency of 54%, which from a number of indications may be too low a value for the central U. S. in summer. Further evaluations of the collection efficiency of 0.8 μm Nuclepores for particulate S in our area are in progress.

Table 1. Summary of results for 66 weekly filter samples in Champaign, Illinois from June, 1975 to January, 1977.

	Mean Concentration ng/m^3	Standard Deviation ng/m^3
Al	431	454
Si	2930	1300
S	4260	2450
K	458	176
Ca	3690	1770
Ti	75.3	38.8
Mn	31.3	15.3
Fe	924	325
Zn	90.0	33.0
Br	206	104
Pb	1100	412

Despite these uncertainties, the data were subjected to factor analysis. The suspected error in the S results is very likely to be systematic, rather than random. If this is the case, it will not affect the factor analysis, since the data are normalized to the mean before computation begins. The nature of the possible difficulty with Al is not at all clear, however, and it could affect the factor analysis results, which are given in Table 2.

Loadings less than 0.50 have been omitted from Table 2 for clarity, except as discussed below. Notice that these 5 factors account for 94% of the sample variance. Factor 1 has high loadings for elements abundant in soil and coal flyash, as discussed in an earlier section of this report. Factor 2 is high in Br and Pb and obviously represents the auto exhaust source. Factor 3 has high loadings for Ti and Zn, a combination not seen at any of our St. Louis sites. The preliminary interpretation is that its source is white paint weathering from the instrument shelter in which the filters were exposed.

Factor 4 has a high loading only for particulate S, but also has a low to moderate loading for Mn. In St. Louis also, Mn was occasionally found on the S factor. Mn and certain other metals are known from laboratory experiments to be catalysts for liquid-phase oxidation of SO_2 to SO_4. This factor offers evidence that Mn-catalyzed liquid-phase oxidation may be an important process in producing the sulfate observed in central Illinois.

The fifth factor is high-only Al. Such a factor was never observed at St. Louis, where Al was always associated with the soil/flyash factor. This is further evidence that the Al data are faulty. They will be thoroughly investigated before any further analyses are performed.

Table 2. Factor analyses for weekly samples in Champaign, Illinois, June, 1975 to January, 1977 (preliminary)

	1	2	3	4	5
Percent variance explained	51	16	13	9	6
K	0.96				
Si	0.92				
Fe	0.90				
Ca	0.86				
Mn	0.78			(0.42)	
Br		0.92			
Pb		0.91			
Ti			0.86		
Zn			0.80		
S				0.93	
Al					0.91

SUMMARY

Weekly filter sampling is now in progress at 3 sites: Champaign, Illinois; Charlottesville, Virginia; and Whiteface Mountain, New York. Preliminary analyses of 18 months of data from Champaign have shown possible difficulties with the Al values and sample contamination from thc weather shelter used to expose the samples. Despite these difficulties, soil dust appears to be a major source of aerosols in central Illinois, as might be expected. Auto exhaust was also identified as a source, and an association was found between airborne sulfate and Mn, a known catalyst for SO_2 conversion.

REFERENCE

Rahn, K. A., 1976: "Silicon and aluminum in atmospheric aerosols: Crust-air fractionation?" Atmos. Environ., 10, 597-601.

SECTION II.

Precipitation Chemistry

Chapter 1

An Interlaboratory Comparison of Simulated Rain Sample Analyses

Mark E. Peden

Chapter 2

Precipitation pH Decrease Since 1954 at Champaign-Urbana, Illinois

Gary J. Stensland

Chapter 3

Precipitation Acidity in Illinois

Donald F. Gatz

CHAPTER 1

An Interlaboratory Comparison of Simulated Rain Sample Analyses

Mark E. Peden

In an effort to accurately assess the state-of-the-art of inorganic chemical analysis of precipitation samples, the National Bureau of Standards (NBS) in conjunction with the U. S. Environmental Protection Agency Office of Research and Development developed a series of synthetic rainwater standards in four concentration ranges that approximate the values normally encountered in environmental samples. Standards were dispensed into borosilicate glass ampoules after synthesis and shipped to 25 participating World Meteorological Organization (WMO) laboratories for analysis of approximately 15 constituents. Nineteen reported their results (Table 1). The Illinois State Water Survey (ISWS) received replicate samples from NBS in April, 1977 in part to evaluate the effect of 18 months of ampoule storage on the analytical values. The Water Survey results are also presented in Table 1. The values for only eight constituents are reproduced since data on the remaining parameters are incomplete.

The most striking departure from the recommended concentrations exists with the pH determinations for both the ISWS results and the WMO determinations. The suspected cause of this difference is the use of glass ampoules as storage containers. Glass has been shown to be an active surface for the exchange of hydrogen ions and consequently an unsuitable vessel for accurate pH measurements. Agreement for the remaining constituents increases at the higher concentrations found in samples C and D. Assuming an arbitrary cutoff of ±20 percent error for an acceptable value, the means of the WMO laboratories yield unacceptable accuracy for sulfate, chloride, potassium, and magnesium determinations at and below the 1 mg^{-1} level.

In view of the fact that legislation to relax the current restraints on the burning of high sulfur coal is pending, it is important that the present state of atmospheric quality with respect to sulfate be accurately documented prior to the institution of legal guidelines. Results from this set of collaborative tests indicate that in many instances more work needs to be done to achieve reliable data, especially at trace levels. Although errors in the chloride, potassium, and magnesium determinations may have a less severe legislative impact, for purposes of atmospheric numerical modeling the use of any inaccurate input data can only result in errors compounding in the final output. Additionally, erroneous data at below mg l^{-1} concentrations for highly toxic, cumulative body poisons such as cadmium, lead, and nickel can have serious ramifications regarding emission standards set for metal processing and automobile industries, the primary sources of these compounds.

The Water Survey results for the eight constituents listed, with the exception of pH as mentioned earlier, show excellent agreement with the NBS recommended values at all concentration levels. This indicates that neglible changes have taken place in the ionic composition since ampouling. These results have also given added confidence to the measurements made throughout the course of the METROMEX study and have provided firm justification for extrapolation of the chemistry results to determine mass budgets for the St. Louis area.

A second set of reference samples have recently been completed and forwarded to the EPA Office of Research and Development in Research Triangle Park for compilation with the WMO results. It is hoped that the overall agreement in values will improve in the second exercise due to the more explicit handling and analytical procedures that were provided. Only by continued participation in collaborative testing efforts of this type, combined with a strong internal quality assurance program, can a uniformly reliable data base on atmospheric quality be attained.

TABLE 1. RESULTS OF THE NATIONAL BUREAU OF STANDARDS (NBS) PRECIPITATION REFERENCE SAMPLES

CONSTITUENT	RECOMMENDED VALUES - NATIONAL BUREAU OF STANDARDS (NBS)				ILLINOIS STATE WATER SURVEY (ISWS)			
	A	B	C	D	A	B	C	D
pH[1]	6.2	6.1	6.2	6.1	5.2	5.3	5.2	5.3
Conductivity[2]	5.8	18.3	59.8	117.0	6.0	18.0	57.0	112.0
$SO_4^=$(S)	0.36	1.19	1.67	3.33	0.3	1.3	1.7	3.4
Cl^-	0.11	1.26	7.63	17.79	0.1	1.0	7.5	17.7
Na^+	0.15	0.52	2.46	5.44	0.16	0.53	2.51	5.49
K^+	0.06	0.10	1.01	3.06	0.06	0.10	0.99	3.01
Ca^{++}	0.10	0.44	1.23	2.84	0.10	0.44	1.20	2.82
Mg^{++}	0.09	0.46	0.73	0.92	0.09	0.46	0.73	0.94

CONSTITUENT	MEAN - WORLD METEOROLOGICAL ORGANIZATION (WMO)[3]				RANGE - WORLD METEOROLOGICAL ORGANIZATION LABORATORIES (WMO)[3]			
	A	B	C	D	A	B	C	D
pH[1]	5.4	5.5	5.5	5.6	3.7 - 6.4	3.8 - 7.2	4.1 - 6.2	4.2 - 6.1
Conductivity[2]	6.9	17.3	56.3	109.3	3.9 - 22.0	20.0 - 28.0	44.0 - 62.0	84.0 - 119.0
$SO_4^=$(S)	1.35	2.02	2.52	3.87	0.16 - >9.99	0.79 - >9.99	0.97 - >9.99	2.40 - >9.99
Cl^-	1.60	2.42	8.98	17.75	0.09 - 9.57	1.00 - 11.52	5.40 - 16.66	10.30 - 26.10
Na^+	0.19	0.54	2.56	5.35	0.07 - 0.43	0.37 - 1.27	2.10 - 4.65	1.98 - 9.64
K^+	0.17	0.17	1.08	3.02	0.03 - 1.16	0.06 - 0.56	0.96 - 1.51	1.33 - 3.80
Ca^{++}	0.13	0.50	1.27	2.73	0.05 - 0.35	0.20 - 1.10	0.30 - 2.10	1.66 - 3.69
Mg^{++}	0.76	0.79	1.03	1.19	0.08 - >9.99	0.25 - 5.40	0.45 - 5.64	0.72 - 5.34

1 = pH units
2 = μS cm^{-1}
3 = n=19

All other units: mg l^{-1}

CHAPTER 2

Precipitation pH Decrease Since 1954 at Champaign-Urbana, Illinois

Gary J. Stensland

INTRODUCTION

Precipitation has been analyzed by many investigators for a great variety of chemical impurities (Junge, 1963). In the last thirty years the precipitation removal of radioactive species which resulted from the above ground detonations of atomic bombs has been the focus of many studies. In more recent years the precipitation scavenging of gases and aerosols from urban and industrial air pollution sources has received greater emphasis. The environmental regulatory agencies now recognize that the quality of the precipitation can be adversely affected by these anthropogenic sources.

Since the early 1950's a precipitation chemistry network has been in operation in northern Europe. An analysis of these data for the years 1956-1966 demonstrated that the pH of the precipitation had been decreasing (becoming more acidic) while the sulfate levels had increased (Oden, 1968). The explanation for this acid precipitation phenomena is not yet well understood but probably involves the increased SO_x emissions from industrial areas, which are subsequently oxidized to the sulfuric acid which lowers the precipitation pH.

Similar long term synoptic measurements of precipitation chemistry are not available for the United States. However, using the limited data that are available it has been suggested that the NE United States is also experiencing the acid precipitation phenomenon observed in Europe (Cogbill and Likens, 1974).

The purpose of this paper is to compare the pH for precipitation collected in 1954 in east central Illinois to data from a nearby location for 1975-76. The 1954 data (Larson and Hettick, 1956) are unique and especially valuable because of the very careful chemical analyses that were carried out on the samples and because the samples were wet only, dry deposition of extraneous materials between rains being completely eliminated. The 1975-76 data set, gathered by staff at the Water Survey, included pH and conductivity, but only some of the major ions. Therefore, to make the comparison between the data sets, the pH for the 1954 data had to be calculated since it was not measured.

THEORY

Granat (1972), Cogbill and Likens (1974) and Ruess (1975) have demonstrated that precipitation pH can be caluclated if the major ion concentrations are known. The procedure described below in analogous to that used by previous workers but is formulated in a somewhat different fashion.

Gases (e.g. SO_2 and CO_2) and aerosols (e.g. NaCl and $[NH_4]_2\ SO_4$) scavenged by precipitation can remain as electrically neutral entities in the water solution or can participate in a variety of chemical transformations, including simple dissociation, to form ions (charged entities). The basic premise that the solution must remain electrically neutral (i.e. charge is conserved) allows one to develop an expression to calculate pH.

As a simple example, consider a solution of only water and sulfuric acid (H_2SO_4). The solution contains H^+, OH^-, and $SO_4^=$ ions. At equilibrium,

$$(H^+)(OH^-) = 10^{-14}$$

if the ion concentrations are expressed in moles/liter (m/l). If we assume the pH = 4, then the defining relation pH = -log (H^+) allows us to state that

$$(H^+) = 10^{-4} m/l.$$

Therefore $(OH^-) = 10^{-10}$m/l and thus is so small that it can be ignored for further calculations. Since the dissociation of the acid in the water gives us one sulfate ion for each pair of hydrogen ions, it is concluded that

$$(SO_4^=) = 1/2(H^+) = 0.5 \times 10^{-4} m/l.$$

Now let us convert from moles/liter (which counts particles) to equivalents/liter (eq/l) as this allows us to count electrical charges. This is accomplished by multiplying the concentration in m/l by the valance (or charge) associated with each ion. Thus our example solution contains

$$(0.5 \times 10^{-4}\ m/l) \times (2) = 10^{-4}\ eq/l = 100\ \mu eq/l$$

of sulfate and

$$(1 \times 10^{-4}\ m/l) \times (1) = 10^{-4}\ eq/l = 100\ \mu eq/l$$

of hydrogen ion. Thus the total amount of positive charge (due to H^+ in this example) is equal to the amount of negative charge (due to $SO_4^=$) when the concentrations are expressed in eq/l (or µeq/l).

For almost all precipitation samples, the major ions are those listed in equation 1.

$$(H^+)+(Ca^{++})+(Mg^{++})+(NH_4^+)+(Na^+)+(K^+)=(SO_4^=)+(NO_3^-)+(Cl^-)+(OH^-)+(HCO_3^-) \quad \text{(Eq. 1)}$$

With each ion concentration expressed in µeq/l, the right hand side of (1) should exactly equal the left hand side. In practice, agreement within 10% for any one sample is probably acceptable. Greater deviations indicate that one or more ions were measured inaccurately or that an important ion has not been measured. For example, in some samples Al^{+++} contributes a significant amount and therefore needs to be included in (1). It should be noted that assumptions concerning the parent compounds of the ions are not necessary. However, if one did know, for example, that all Na^+ and all Cl^- resulted from the dissolution of NaCl, then these two ions would not be necessary in (1) since they cancel out on the two sides of the equation.

There are actually two checks as to whether or not all the major ions have been measured. First, one can compare to see if the sum of the negative charges does equal the sum of the positive charges. If all Na^+ and Cl^- did come entirely from NaCl, then this first check would produce an equality, even if these major ions were not measured. The second check is whether the measured ions account for the measured conductivity and in this check all the major ions must be included. The constants listed in Table 1 are multiplied by the respective ion concentrations and the sum of these terms should equal the measured conductivity if all the major ions for the sample have been included.

Table 1. Conductance factors used in the Calculations*.

Ion	Conductance factor at 25°C (micromhos/cm per eq/l)
H^+	.3500
HCO_3^-	.0436
Ca^{++}	.0520
Cl^-	.0759
Mg^{++}	.0466
NO_3^-	.0710
K^+	.0720
Na^+	.0489
SO_4^{++}	.0739
NH_4^+	.0725

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[*] From Standard Methods for the Examination of Water and Wastewater, 13th Edition.

In (1) everything is quite readily measured except (OH^-) and (HCO_3^-); (HCO_3^-) can be measured for the precipitation samples but it is more time consuming and difficult than the other ions and thus is often not measured. To calculate (OH^-) and (HCO_3^-) the following equilibrium relationships are used for the dissociation of water, and the solubility and first and second dissociations of carbon dioxide in water:

Chemical Reaction		Equilibrium Relationship	
$H_2O \rightleftarrows OH^- + H^+$	;	$K_w = (OH^-)(H^+)$	(2)
$P_{co_2} \rightleftarrows H_2O.CO_2$	;	$K_H = \frac{(H_2O.CO_2)}{P_{co_2}}$	(3)
$H_2O.CO_2 \rightleftarrows H^+ + HCO_3^-$	;	$K_1 = \frac{(H^+)(HCO_3^-)}{(H_2O.CO_2)}$	(4)
$HCO_3^- \rightleftarrows H^+ + CO_3^=$	;	$K_2 = \frac{(H^+)(CO_3^=)}{(HCO_3^-)}$	(5)

With the ion concentrations in the equilibrium relationships (2) - (5) expressed in m/l and P_{co_2} in atm, values for the equilibrium constants are tabulated in Table 2 for three temperatures.

From (5)

$$\frac{(HCO_3^-)}{(CO_3^=)} = \frac{(H^+)}{K_2} \qquad (5a)$$

For T = 25°C and pH = 8, $(H^+) = 10^{-8}$ m/l and

$$\frac{(HCO_3^-)}{(CO_3^=)} = \frac{10^{-8}}{4.7 \times 10^{-11}} = 213 \qquad (5b)$$

Thus the concentration of HCO_3^- is much greater than $CO_3^=$. For lower pH values, HCO_3^- dominates $CO_3^=$ even more and so $CO_3^=$ is not included in applications related to precipitation samples (i.e. equation 1). Actually, since the model (equation 1) requires concentrations to be expressed in μeq/l, one can see from (5) that K_2 is a factor of 2 larger when the ion concentrations are in μeq/l. Therefore from 5(a) and 5(b), at pH = 8 there is about 1 μeq/l of $CO_3^=$ for each 100 μeq/l of HCO_3^-.

From (3) and (4)

$$(HCO_3^-)(H^+) = K_H K_1 \; P_{co_2} \qquad (6)$$

From (2) and (6)

$$\frac{(HCO_3^-)}{(OH^-)} = \frac{K_H K_1 P_{co_2}}{K_w} \qquad (7)$$

where it is convenient to define

$$K \equiv \frac{K_H K_1 P_{co_2}}{K_w} \qquad (8)$$

with P_{co2} = 320 x 10^{-6} atm and with the values for the equilibrium constants in Table 2, K is calculated with equation (8) and tabulated in the last row in Table 2. The calculated values of K imply that the concentration of HCO_3^- is much greater than the concentration of OH^-.

Table 2. Equilibrium constants*.

	5^oC	20^oC	25^oC
K_H	0.064	0.039	0.034
K_1	3.0×10^{-7}	4.2×10^{-7}	4.5×10^{-7}
K_2	2.7×10^{-11}	4.2×10^{-11}	4.7×10^{-11}
K_w	0.2×10^{-14}	0.7×10^{-14}	1.0×10^{-14}
K**	3072	749	490

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* same values as used by Granat (1972).

** with P_{co_2} = 320 x 10^{-6} atm.

Equation (1) is now rearranged to give

$$(H^+ - OH^- - HCO_3^-) = (SO_4^= + NO_3^- + Cl^-) - (Ca^{++} + Mg^{++} + Na^+ + K^+ + NH_4^+) \tag{9}$$

with the definition

$$\text{Net Ions} \equiv (SO_4^= + NO_3^- + Cl^-) - (Ca^{++} + Mg^{++} + Na^+ + K^+ + NH_4^+) \tag{9a}$$

then (9) becomes

$$(H^+ -OH^- -HCO_3^-) = (\text{Net Ions}) \tag{10}$$

Because the model (i.e. equation (1)) requires concentrations to be expressed in charge units (μeq/l) it will be necessary to note that K from (7) and (8) is dimensionless. However, K_w in Table 2 has units of $(m/l)^2$ and therefore a new symbol K'_w will be used when the units are $(\mu eq/l)^2$. From (2) it follows that conversion of (OH^-) and (H^+) from m/l to μeq/l gives

$$K'_w = 10^{12} K_w \tag{11}$$

By using (2), (7), (8), and (11), then (10) becomes

$$(H^+) - \frac{K'_w}{(H^+)} - \frac{K K'_w}{(H^+)} = (\text{Net Ions})$$

Upon rearranging terms the resulting quadratic equation is

$$(H^+)^2 - (\text{Net Ions})\ (H^+) - K'_w\ (K + 1) = 0$$

Solving for the concentration of H^+ gives

$$2(H^+) = (\text{Net Ions}) \pm [(\text{Net Ions})^2 + 4\ K'_w\ (K + 1)]^{1/2} \qquad (12)$$

The quantity in brackets in (12) is always positive and greater than (Net Ions) and therefore only the plus sign is front of the bracketed term provides non-negative and therefore physically realistic solutions for (H^+).

The measurement of alkalinity provides another way to calculate the pH. Alkalinity (Alk) is defined as

$$\text{Alk} \equiv (HCO_3^-) + (CO_3^=) + (OH^-) - (H^+) \qquad (13)$$

where the ion concentrations are again in μeq/l. Since all precipitation samples are < pH = 8, the previous discussion allows us to neglect $(CO_3^=)$ compared to (HCO_3^-). Therefore (13) reduces to exactly the same form as (10) and thus by inspection alkalinity = -(Net Ions). Equation (12) can thus be rewritten as

$$2(H^+) = -(\text{Alk}) + [(-\text{Alk})^2 + 4\ K'_w\ (K + 1)]^{1/2} \qquad (14)$$

Therefore pH (via (H^+)) can be calculated when either (Net Ions) or (Alk) is known.

Equation (12) is plotted in Figure 1. If one has measured the major ions in a precipitation sample such that (Net Ions) is determined, then line B on the graph allows one to read the calculated pH. Any additional ions measured, besides those listed on the right side of (9), are simply added to (9) to make the determination of (Net Ions) just that much more accurate. If the water sample being considered was pure water in equilibrium with ambient carbon dioxide, then (Net Ions) = 0.0 and curve B indicates that the pH = 5.65.

The precipitation sample levels of HCO_3^-, OH^-, and H^+ are shown in Figure 1, where the absolute value of the ordinate is used to read off the concentrations ($pH = -\log(H^+)$, $(OH^-) = 0.01/(H^+)$ and $(HCO_3^-) = 490(OH^-)$ being used). It is seen that HCO_3^-) and H^+ approach curve B asymtotically. That is, at low pH, (Net Ions) → (H^+) and at high pH, (Net Ions) → (HCO_3^-).

If $P_{co_2} = 0$ (as it would be if one bubbled as inert gas such as nitrogen through the precipitation sample as the pH was being measured), then K = 0 (from (7)) and (12) is modified and provides the curves marked accordingly in Figure 1. In this case, with no HCO_3^- present (cf. (8)) the asymtotic limit at high pH is provided by the OH^- curve.

The sensitivity of the pH prediction via (12) to the assumed equilibrium conditions of temperature and P_{co_2} is displayed in Figure 1 by curves A - D (and of course the $P_{co_2} = 0$ curve as the extreme case). Values of the ratio (HCO_3^-) to (OH^-), K, were tabulated in Table 2. At T = 25°C and $P_{co_2} = 320 \times 10^{-6}$ atm, K = 490. Therefore at pH = 8, where $(OH^-) = 1$ μeq/l), and $(HCO_3^-) = 490$ μeq/l,

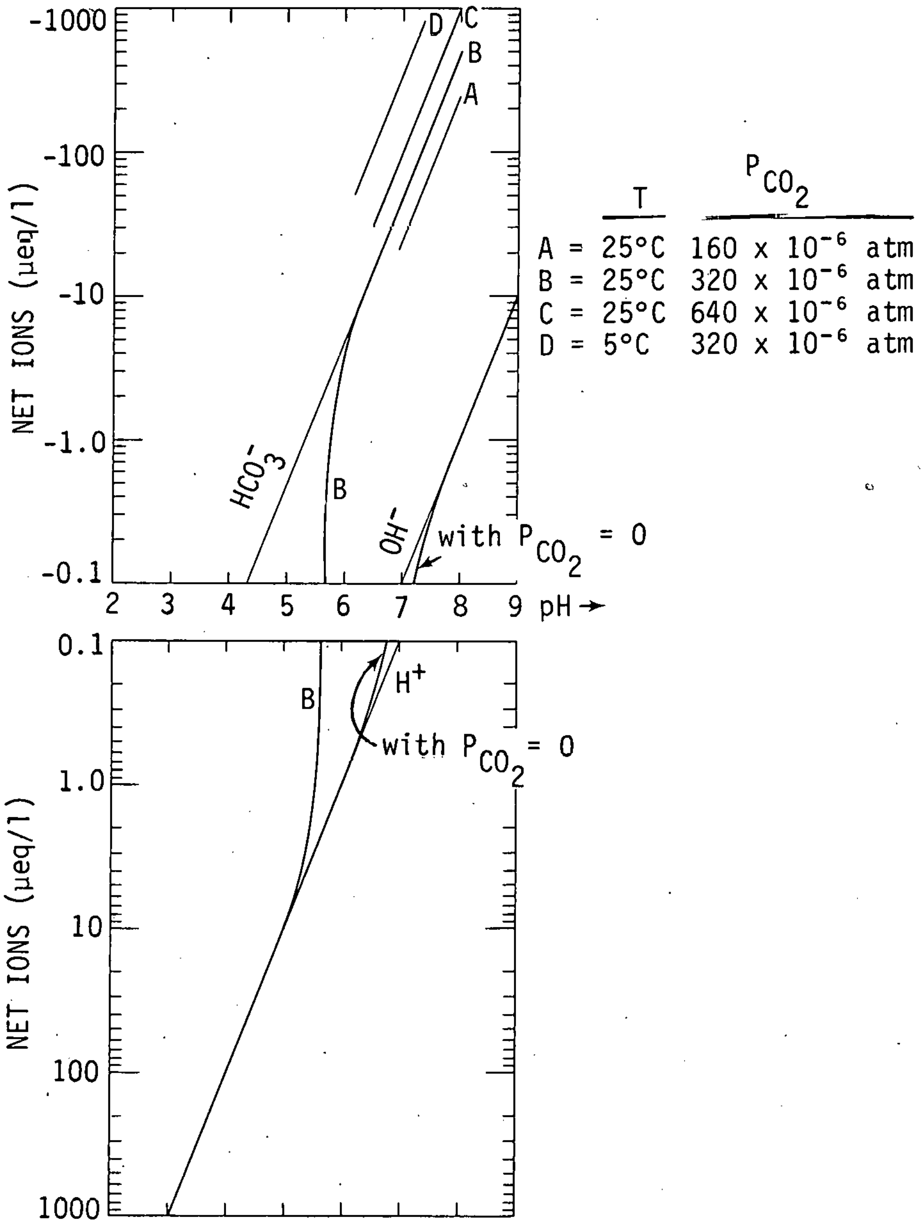

Figure 1. Curves to determine the pH if Net Ions are known, assuming various temperatures and P_{CO_2} values

and this procedure explains the spacing between the curves A - D and the OH^- curve in Figure 1. If the temperature is kept constant, K is proportional to P_{CO_2}. So if we double the CO_2 level (e.g. move from curve B to C), the pH = 8 intercept for HCO_3^- jumps up to (2)(490) = 980. Curves A, B, C, D (which are plots of (12) at only high (Net Ion) values) thus graphically demonstrate the sensitivity of pH to temperature and P_{CO_2}. As a specific example consider that (curve B) and (Net Ions) = -49, the pH = 7; when P_{CO_2} is doubled (curve C), the same (Net Ion) value gives pH = 6.69; if the temperature is lower (curve D), then the pH = 6.15.

Figure 1 also demonstrates why a bimodal pH distribution could be expected if both high and low pH values are present in a particular data set. Assume all (Net Ion) values between +45 and -45 are equally likely. From (Net Ion) = 45 to 15, ΔpH = 0.48; from (Net Ion) = 15 to -15, ΔpH = 1.65; and from (Net Ion) = -15 to -45, ΔpH = 0.48. Therefore the pH will most frequently be either very large or very small, giving the bimodal distributions. This may explain the bimodal pH distribution that has been reported by Semonin (1977).

RESULTS

The collection sites for the 1954 and the 1975-76 data are shown in Figure 2. The 1975-76 data included only pH and conductivity measurements from weekly samples from a shomewhat modified HASL wet/dry collector. This device was located on the roof of a two story building in the center of Champaign-Urbana, a college dominated community of about 100,000 people without any major industrial pollutors. The 1954 site was at the Willard Airport, near Savoy. This site was basically rural, the airport being quite small in 1954. In a later figure one month's data from 1960 will be presented and these data were also from the same airport site. Collection and chemical procedures, data interpretation, and a summary of the snyoptic weather conditions for the 1954 data are presented in detail in Larson and Hettick (1956).

The 1954 data did not include every rain event that occurred. Rain events with rainfall less than about 0.04" did not provide enough sample for a complete chemical analysis and thus were not useful for the present pH calculations. In several events, sequential samples were taken during the events, each sample corresponding to about 0.04" of rainfall. Overall, approximately 20% of the rainfall from January, 1954 to August, 1954 was sampled. The 35 event samples used in the pH calculations to follow, resulted from rains on 26 separate days.

The pH was calculated from the (Net Ions) and from the aklalinity. These data are presented in Figure 3. The dashed lines connecting

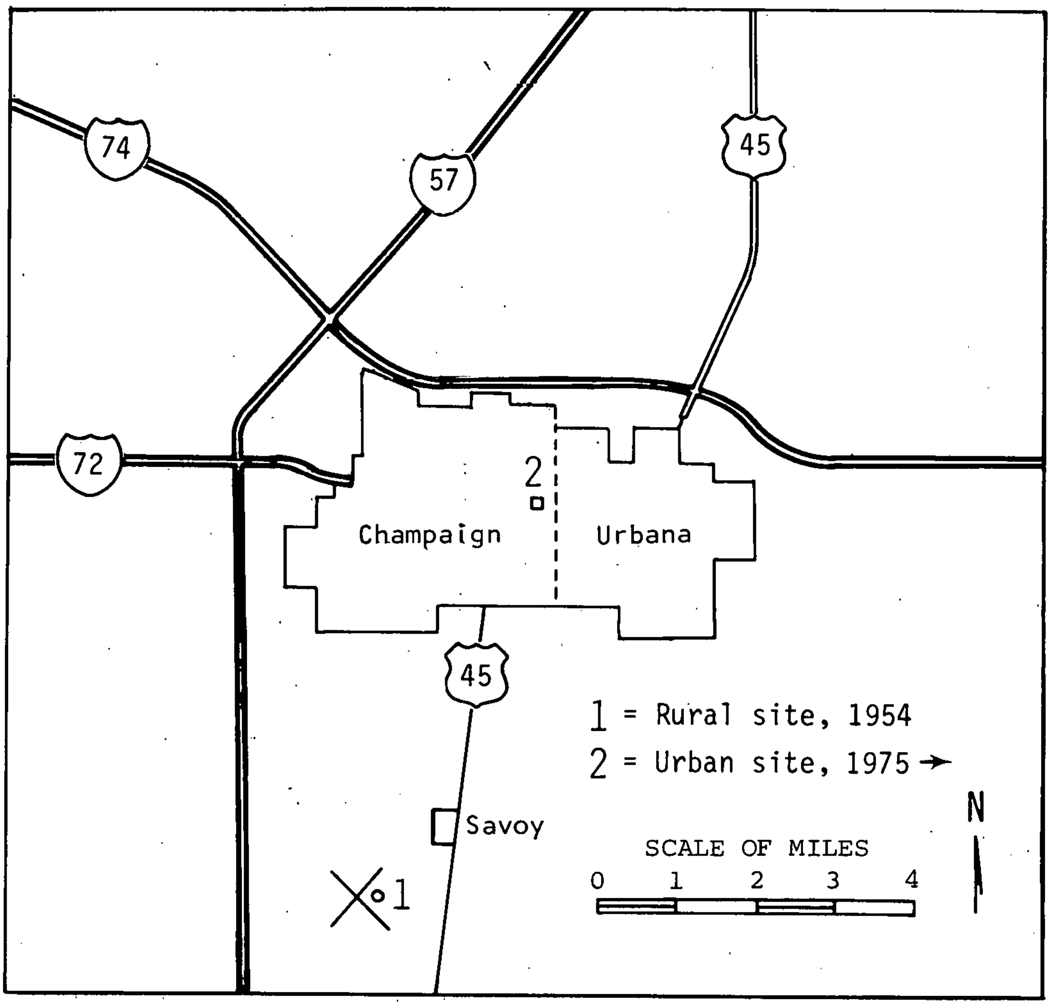

Figure 2. Precipitation collection sites

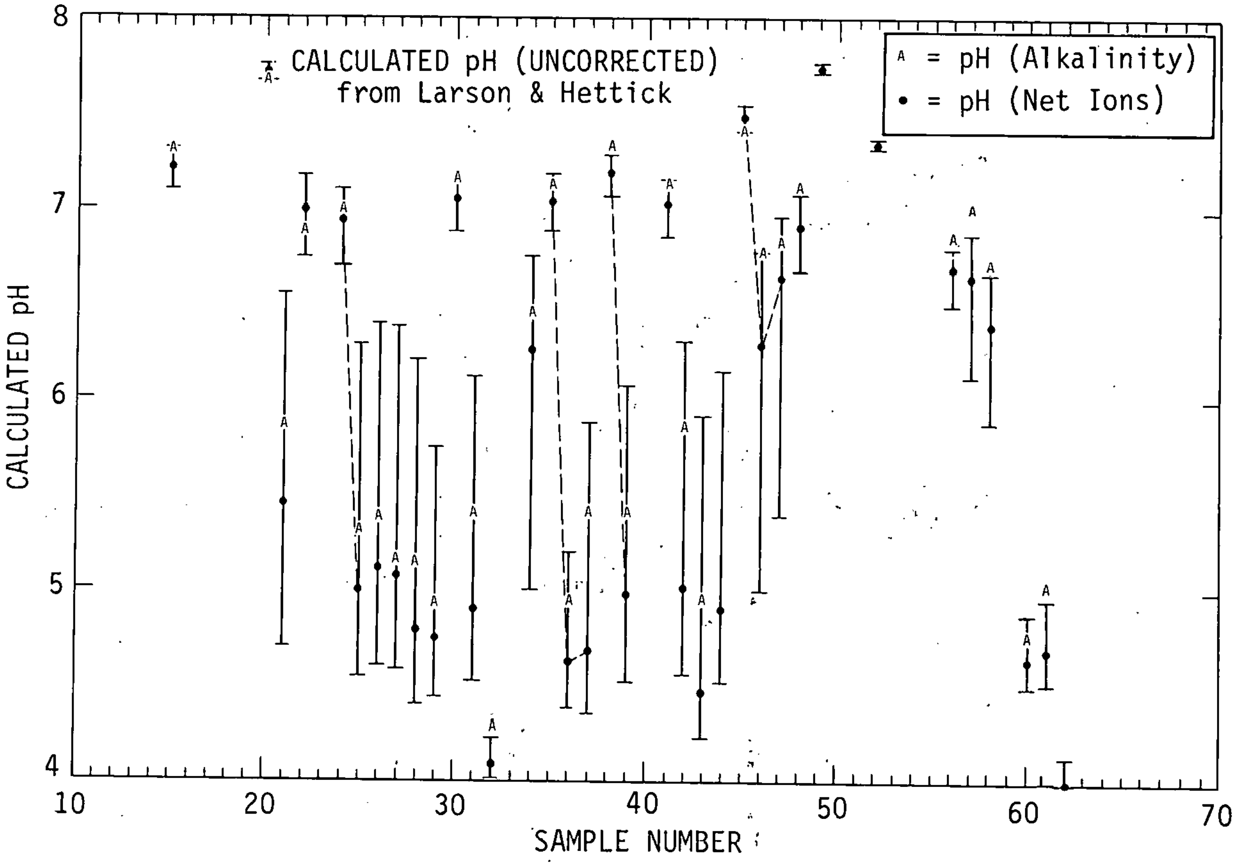

Figure 3. Calculated pH for 35 samples collected in 1954

some of the data points identify the sequential samples. The error bars were calculated by using the chemical precision estimates associated with the separate ion concentration determinations. For example, the upper limit error bars resulted from subtracting the respective precision estimate from each of the anions contributing to (Net Ions) [cf. (9)] and adding the respective precision estimate to each of the cations. The error bars thus suggest that the model is likely to produce the most accurate results for high and low pH values (i.e. $|\text{Net Ions}|$ or $|\text{Alkalinity}| >> 1$). This is reasonable since, as was shown in the last section, a small variation in (Net Ions) when the calculated pH is near 5.65 produced large differences in the values of pH.

In Figure 4 the pH calculated from the measured Ions is plotted versus the pH calculated from the alkalinity measurements. The 35 values from the 1954 data as well as 12 values from data collected by Mr. R. G. Semonin in May and June of 1960 are depicted. The two calculational procedures should provide the same predicted pH value, that is, fall on the straight line in Figure 4. The slight deviation may be due to the fact that A^{+++} was not determined for the samples. Larson and Hettick (1956) suggested this explanation for a related effect. The inclusion of Al^{+++} would result in a decrease in the value of (Net Ions) and therefore from Figure 1 an increase in pH. Overall the data in Figure 4 provide strong evidence that the pH values calculated for the 1954 and 1960 data are accurate.

Granat (1972) analyzed the data from approximately 2000 monthly precipitation samples from the European chemistry network and noted significant deviations between calculated and measured pH values. Stensland (1977) analyzed monthly data for about 1200 precipitation samples collected in the continental U. S. by the U. S. Public Health Service and found a very similar trend. From these data the following empirical correction is suggested:

$$\text{pH (Corrected)} = \text{pH (Calculated)} - C \qquad (15)$$

where $C = 0.70$ for pH (Calculated) ≥ 6.0
and $C = 0.15$ for pH (Calculated) ≤ 4.8.

$$\text{pH (Corrected)} = 0.54 \text{ pH (Calculated)} + 2.06 \qquad (16)$$

for $4.8 <$ ph (Calculated) < 6.0.

Using (15) and (16) the 1954, 1960, and 1975-1976 precipitation pH data are compared in Figure 5. The arithmetic average pH for the 1954 samples is 5.4 compared to 4.3 for the 1975-1976 weekly samples. Another indication of the decreasing pH trend at Champaign-Urbana is that of the 35 samples for 1954, 51% have calculated pH values greater than or equal to 5.6; for 1975-1976 only one such sample was observed. If the empirical corrections in (15) and (16) were not applied to the 1954 and 1960 data, the differences would be even greater.

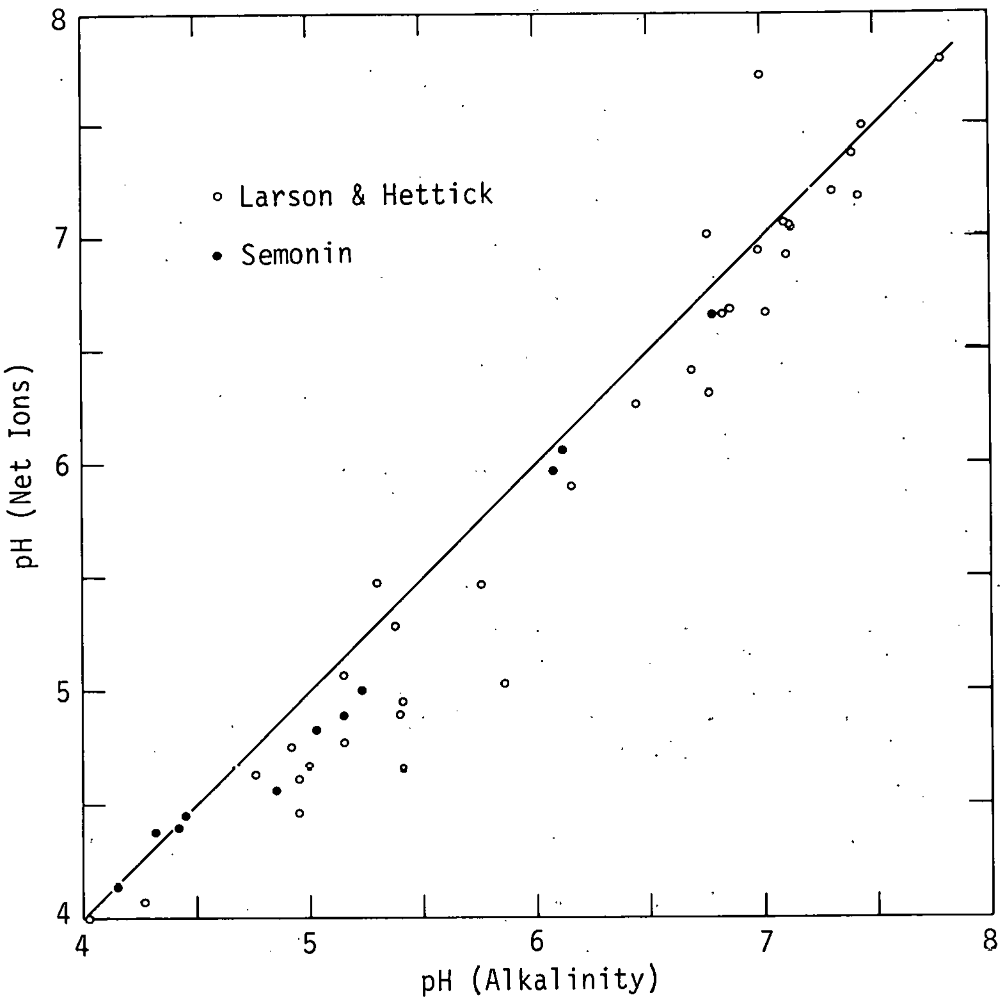

Figure 4. Comparison of calculating pH for each sample from two different chemical measurements

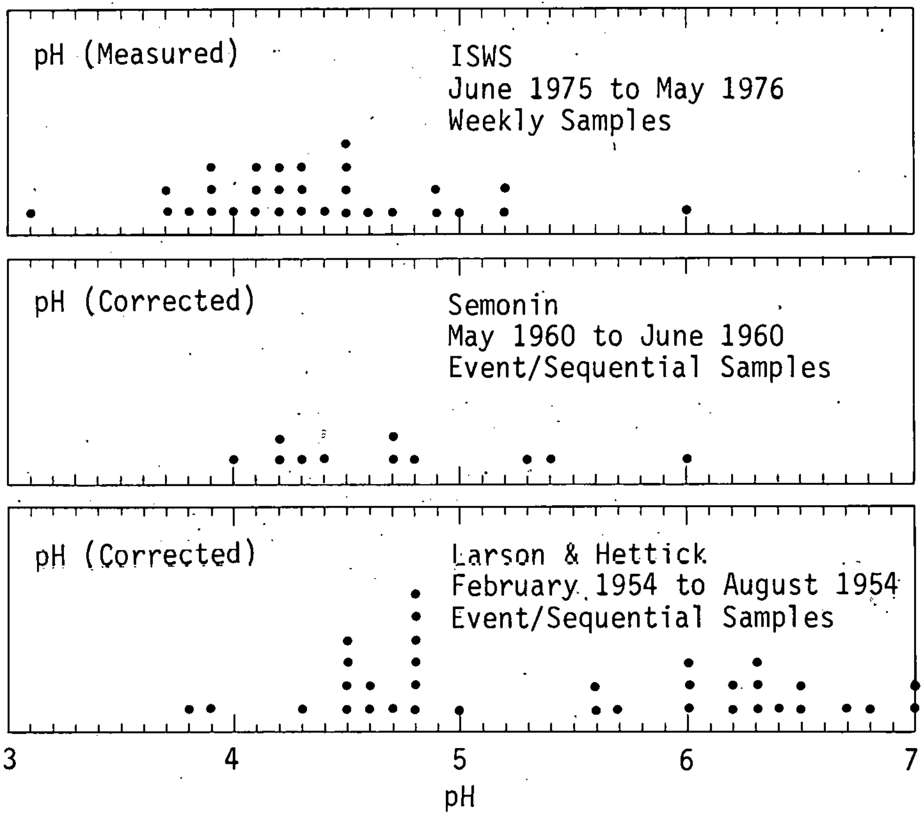

Figure 5. Time trend of precipitation pH at Champaign-Urbana, Illinois

To better understand why the pH was high in the 1954 samples the arithmetic average ion concentrations for the 35 samples from 1954 are compared in Table 3 with corresponding averages for the 12 highest pH samples. Hardness, Hd in Table 3, refers to a chemical determination which includes calcium and magnesium. The feature of note in the Table is that the ions with a strong soil source (Ca^{++}, Mg^{++}, Na^{+}) have elevated levels in the high pH samples while the likely acid components ($SO_4^{=}$ and $NO_3^{=}$) are similar in both data sets. This implies that certain precipitation samples acquired the high pH values due to extra inputs of such things as soil derived aerosols, not from the decreases in the acid components. This is further supported by Table 4 which examines the pH as a function time since the last rainfall. By using the pH as calculated from the alkalinity (and then corrected via (15) and (16)), a few extra samples were made available for this comparison. From Table 4 it is observed that when no rain had fallen for at least 48 hours, and thus the soil surface would be likely to be dry and susceptible to blowing dust conditions, the pH was very high for 8 out of 9 cases. The comparisons for $t = 0$ and $1h \leq t \leq 24h$ indicate more variable pH conditions but always less than pH = 6.28 (the lower limit for $t \geq 48h$ cases).

Since the 1975-76 data did not include measurements for all the major ions, the 1954 data have been compared with some other recent data in Table 5. The 1954 levels of $SO_4^{=} + NO_3^{-}$ are less than the New York values and similar to the Tennessee data; the major basic components (Ca^{++} + Mg^{++}) are much greater in the 1954 data than either the New York or Tennessee stations. These greater (Ca^{++} + Mg^{++}) levels explain why the Illinois site was more basic than the Tennessee site (i.e. compare the pH (Net Ions) values via Figure 1 for the (Net Ions) at the bottom of Table 5). The South Dakota site has a similar (Net Ion) value as the 1954 site but heavier loadings of both the cations and the anions in Table 5.

FINAL REMARKS

The agreement between pH (alkalinity) and pH (Net Ions) suggests that the calculated pH values for the 1954 data are quite accurate. The correction to the calculated pH via (15) and (16) awaits a comprehensive chemical explanation but the amount and diversity of the data used to formulate the expressions suggests that the empirical correction is necessary. Therefore, from Figure 5 it has to be concluded that a large downward shift in the pH (more than 1 pH unit) has occurred from 1954 to 1976 at the Illinois site. This trend could have resulted from both a decrease in the basic components (Ca^{++} and Mg^{++}) and an increase in the acidic components ($SO_4^{=} + NO_3^{-}$).

Table 3. Examination Of The High pH Samples

(12 Samples with corrected pH (Net Ions) ≥ 5.95)

Ion Concentrations (μeq/ℓ)

	$SO_4^=$	NO_3^-	Cl^-	Hd	Na^+	K^+	NH_4^+
Average of highest (12)	68	20	9	170	10	2	17
Average of all (35)	64	19	18	90	7	2	20
Percent Deviation	6%	5%	-50%	89%	43%	0%	-15%

Table 4. Relation of the Corrected pH (Alkalinity) to Time (t) Since Previous Rainfall

Time Since Last Rain (h)	Number of Cases	pH Distribution
$t = 0$*	16	$4.74 \le pH \le 6.15$
$1 \le t \le 24$	14	6 with $pH \le 4.84$ 8 with $pH \ge 6.18$
$t \ge 48$	9	8 with $pH \ge 6.28$ 1 with $pH = 5.22$

*This includes sequential samples or those samples where collection began sometime after the onset of the rain, except for one sample where there had been no rain for a 10 minute interval before sample collection began.

Table 5. Comparison of Precipitation Chemistry Data
(precipitation weighted average - μeq/ℓ)

	Ithaca, NY 9-72 to 8-73*	Aurora, NY 9-72 to 8-73*	Geneva, NY 9-72 to 8-73*	Gatlinburg, Tenn. 6-73 to 9-73*	Savoy, IL 1954	Huron, S. Dak. 1972-73**
$SO_4^=$	103	94	95	66	60	82
NO_3^-	46	44	53	20	18	40
Cl^-	13	13	10	4	8	34
Sum	162	151	158	90	86	156
Na^+	7	3	4	2	6	40
NH_4^+	18	22	23	11	19	38
K^+	2	2	2	2	2	7
Ca^{++}	41	22	36	10	88	69
Mg^{++}	7	6	11	2		22
Sum	75	55	76	27	115	176
Net Ions	87	96	82	63	-29	-20

* From Cogbill and Likens (1974).

**From Miller (1975).

To accept the hypothesis of the pH shift at this site, one must believe that both the 1954 data and the 1975 data were representative and comparable. It is this author's opinion that the fact that the 1954 data were rural, event samples while the 1975-76 samples were urban, weekly will not account for the observed trend. Since the immediate locality of the 1954 site has not changed very much to the present time, the detailed air and precipitation chemistry measurements recently reinitiated at the site will be most interesting.

Current farming practices would appear to be as "dusty" as they were in 1954. Also there does not appear to have been any significant change in the road surfaces since 1954 which might reduce the local atmospheric dust loading. However, the first eight months of 1954 (the precipitation sampling period) were warmer and dryer than usual (3.25^{o}F above average temperature and the precipitation was about 10% below average). Perhaps these conditions and the particular timing of the rains resulted in increased atmospheric dust loadings and therefore rains with high pH values. The current measurements at the 1954 site will provide for a comparison of the ion levels, especially for Ca^{++}, Mg^{++}, $SO_4^{=}$, and NO_3^{-}. By continuing the sampling over a relatively long period, which will include both abnormally wet and dry seasons, the influence of the relatively warm and dry sampling period in 1954 will be clarified.

Using a very few data points for the midwest, Cogbill (1975) has presented pH isopleth maps which suggest that a major pH shift did occur between 1955 and 1973 in a region including Illinois. The analysis in this paper agrees with this trend.

REFERENCES

Cogbill, C.V., and G.E. Likens, 1974. Acid precipitation in the northeastern United States. Water Resources Research, 10(6), 1133-1137.

Cobgill, C.V., 1975. The history and character of acid precipitation in Eastern North America. Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, Columbus, Ohio, p. 363-370.

Granat, L., 1972. On the relationship between pH and the chemical composition in atmospheric precipitation. Tellus, 24, 550-560.

Junge, C.E., 1973: Air Chemistry and Radioactivity. Acadmic Press, New York, 382 pp.

Larson, T.E., and I. Hettick, 1956. Mineral composition of rainwater. Tellus, 8, 191-201.

Miller, J., 1974: A statistical evaluation of the United States precipitation chemistry network. To be published in the Proceedings of the Symposium - Precipitation Scavenging, 1974, held at Champaign-Urbana, Illinois.

Oden, S., 1968: The acidification of air and precipitation and its consequences in the natural environment. Ecology Committee Bulletin No. 1. The State National Science Research Council, Stockholm. Translation Consultants, Ltd. Arlington, Virginia, 117 pp.

Ruess, J.O., 1975: Chemical/Biological Relationships Relevant to Ecological Effects of Acid Rainfall. U.S. E.P.A. Report EPA - 660/3-75-032, 46 pp.

Semonin, R.G., 1976. The variability of pH in convective storms. Water, Air, and Soil Pollution, 6, 395-406.

Stensland, G.J., 1977, journal note in preparation.

CHAPTER 3

Precipitation Acidity in Illinois

Donald F. Gatz

INTRODUCTION

The major source of precipitation acidity in the northeastern United States is sulfuric acid (Likens and Bormann, 1974; Gatz, 1976). This is supported by the observation of high airborne sulfate concentrations in the region of greatest precipitation acidity. National Air Sampling Network (NASN) data (Figure 1) and Water Survey observations of airborne sulfate in Champaign-Urbana suggest that rural sulfate concentrations in Illinois are almost as high as those observed in the rural northeast. Thus, one might suspect that unusually acidic precipitation may also be falling in Illinois. The same NASN data (Figure 1) indicate much lower sulfate concentrations immediately west of the Mississippi River, and published data on precipitation acidity for the same area show correspondingly greater precipitation pH values (corresponding to less acidity). Thus it appears that Illinois is located in a region of relatively high average concentrations of airborne sulfate, but very close to areas with much lower average values. The maximum airborne sulfate concentrations are found generally downwind of the Ohio River Valley, the region of maximum anthropogenic sulfur dioxide emissions, suggesting that man-made sources are a large, if not major, contribution to airborne sulfate concentrations.

The measurements summarized here have been derived from a variety of published and unpublished sources. It should be understood that the validity of measuring the pH of a very dilute unbuffered system such as precipitation has been questioned by some. Furthermore, the validity of measurements made on samples accumulated over periods as long as 1 month is uncertain, because of the possibility that chemical changes may have occurred in portions of the samples collected early in the period. Results will also be strongly dependent on whether the collector used was open continuously, or only during precipitation.

It is also important to keep in mind that local sources of acid or alkaline materials in the immediate vicinity of a sampling site can have a large influence on the measurements. Thus, trends are best inferred from stations having a long period of data with little or no change in local sources. No sites with a long period of pH measurements are known to exist in Illinois; however, we will discuss later possible trends based on a comparison of current measurements at Champaign-Urbana with some 1954 measurements at nearby Savoy, Illinois.

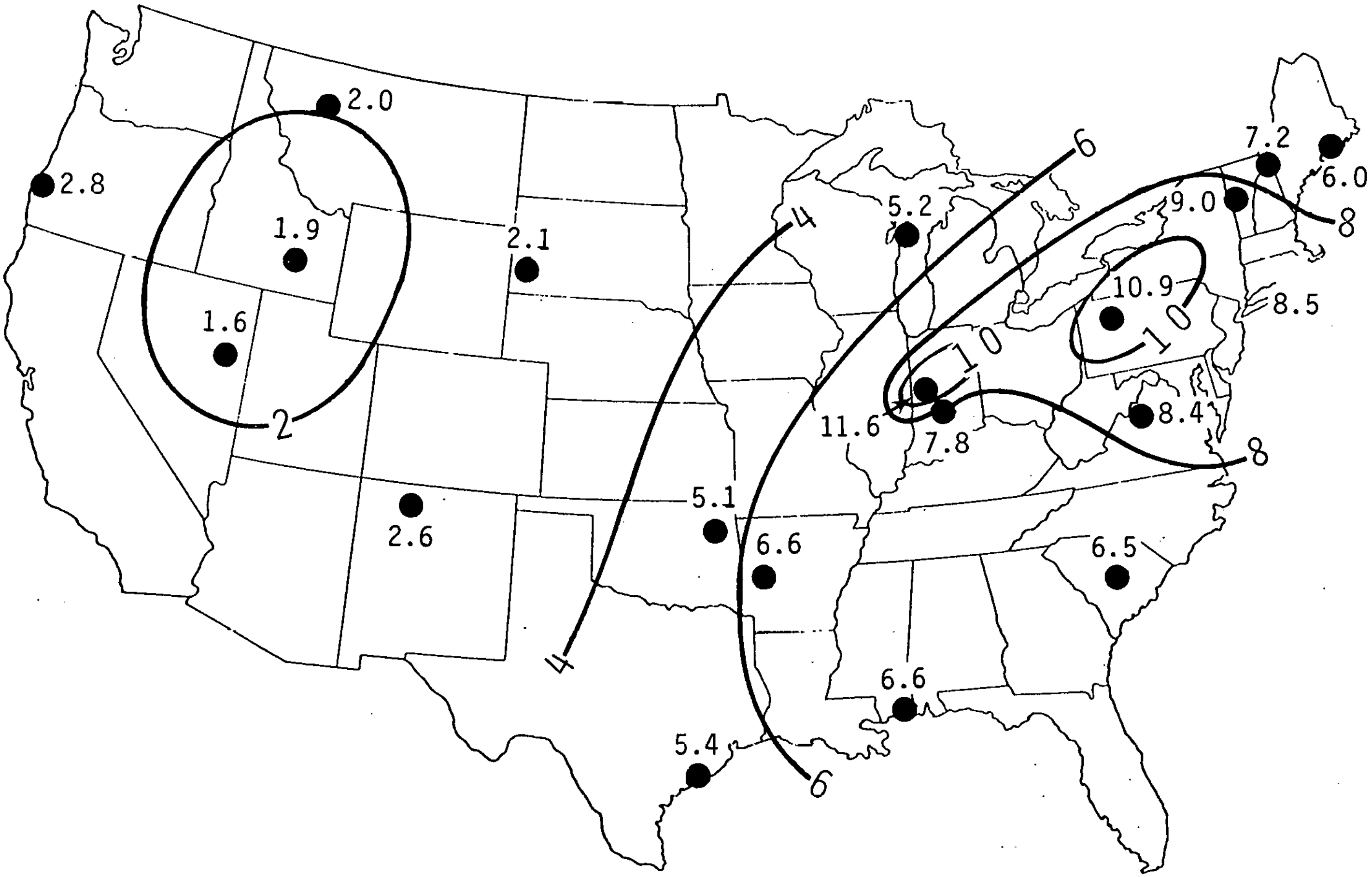

Figure 1. Geometric mean sulfate concentrations (μg/m³) at remote sites of the National Air Surveillance Network (EPA, 1977)

AVERAGE VALUES

With these caveats in mind, we examine reported measurements in Illinois, given in Table 1. The pH data are summarized using two different expressions of the central tendency. One of these is the usual "average," or "arithmetic mean." Since the arithmetic mean pH corresponds to the geometric mean hydrogen ion concentration, it is preferred for expressing the central tendency of a group of samples. The other parameter used to summarize data is the pH corresponding to the precipitation-weighted mean hydrogen ion concentration over the averaging period. From now on, this is referred to as the "weighted mean." This value is the proper one to use in calculating hydrogen ion deposition on the ground during the averaging period.

The oldest data in Table 1 are for Midway and O'Hare airports in Chicago, where monthly samples were collected between 1960 and 1964. Annual averages ranged from 5.5 to 6.4 at Midway and 5.8 to 6.5 at O'Hare. Data for the Chicago Loop between 1963 and 1966 show considerably more acid in the precipitation; annual averages range from 5.0 to 5.5.

No data are available anywhere in the state between 1966 and 1972. However, in the spring of 1972 nineteen samples of individual precipitation events were measured at Argonne National Laboratory, giving an average pH of 4.3. This agrees quite closely with the weighted mean value of 4.4 for 24 monthly samples from Salem, in southern Illinois, in 1972-1973.

The Argonne and Salem results also agree quite closely with a recent series of measurements on weekly samples from Champaign-Urbana, which show average values between 4.0 and 4.8.

VARIABILITY OF pH MEASUREMENTS

The average values presented above must be understood in terms of the kinds of variability that can occur between sites and even within a single rain event at one site.

Semonin (1975, 1976) has presented data on spatial and temporal variability of pH in rain near St. Louis. Data were summarized for samples collected from 25 summer rain events in 1972 and 1974 in an 80-sampler network covering 1800 km^2. The frequency distribution of values measured in all 853 samples from these events (Semonin, 1976 -- Figure 3) exhibits a major peak at pH 7 and a secondary peak at pH 4. The weighted mean of all samples in all 25 events was 4.9.

Table 1. Summary of precipitation pH measurements in Illinois.

Sampling location and period	Sample type	No. of samples	Mean pH	
			Arithmetic	Weighted-H^+
Chicago, Midway Airport(1)				
January-December, 1960	monthly	12	5.6	
January-December, 1961	monthly	12	6.0	
January-December, 1962	monthly	12	6.4	
January-December, 1963	monthly	12	6.0	
January-May, 1964	monthly	5	5.5	
Chicago, O'Hare Airport(1)				
January-December, 1960	monthly	12	5.8	
January-December, 1961	monthly	12	6.3	
January-November, 1962	monthly	11	6.4	
January-December, 1963	monthly	12	6.5	
February-May, 1964	monthly	4	6.0	
Chicago, Loop(1)				
June-December, 1963	monthly	7	5.5	
January-December, 1964	monthly	12	5.4	
January-December, 1965	monthly	12	5.4	
January-May, 1966	monthly	5	5.0	
Argonne National Laboratory(2)				
March-May, 1972	event	19	4.3	
Salem(3)				
January, 1972-December, 1973	monthly	24		4.4
East St. Louis Area(4)				
June-August, 1972, 1974	event	853		4.9
Champaign-Urbana(5)				
June-December, 1975	weekly	21	4.3	4.3
January-December, 1976	weekly	26	4.6	4.0
January-May, 1977	weekly	11	4.8	4.1

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(1) National Precipitation Sampling Network data, collected in samplers open only during precipitation.

(2) Gatz, D. F., unpublished data, collected in funnels open continuously.

(3) Data reported by Miller (1974); collected in samplers open only during precipitation.

(4) Semonin (1975), collected in bottles open continuously for ≤ 24 hr.

(5) Collected by Illinois State Water Survey in collectors open only during precipitation.

The weighted mean pH of all 25 events at individual collectors varied from a maximum of 6.8 to a minimum of 4.3 within the network. This shows the variability that can occur over distances of a few 10's of km, and illustrates the important role of local sources.

Semonin (1975) also showed an example of the degree of temporal variation in pH that can occur within a single rain at one location. On August 3, 1972, the pH varied between 7.1 and 3.7 during a rain sampled 15 km northeast of St. Louis. Other rains showed similar variations.

TRENDS

It is tempting to interpret Table 1 as showing a decrease in pH from a value of about 6 in the early 1960's to a present-day value of about 4.5. However, this interpretation disregards the warnings above concerning comparison between stations, since the earlier samples were from an industrialized urban area, whereas the recent samples are generally from less polluted areas. Of course, the urban pollutants can vary from alkaline to acidic materials, so their effect cannot be predicted. However, as seen in the data from St. Louis, stations relatively close to each other can exhibit variations similar to those in Table 1 during the same precipitation events. Thus, trends should not be inferred from Table 1.

Stensland (1977) has compared recent pH data from Champaign-Urbana with pH values calculated for a series of rain samples collected in 1954 and 1960 at Savoy, Illinois (Larson and Hettick, 1956; Semonin, 1960). For these samples pH was not measured, but the extensive chemical analyses performed on them made it possible to compute their pH with good accuracy. In 35 samples from 1954, the arithmetic mean was 5.4, whereas average values for 1975-1977 in Champaign-Urbana (Table 1) range from 4.3 to 4.8. Further, 51% of the 1954 samples had pH values greater than 5.6, while such values are very infrequent in 1975-1977.

Again, the apparent trend is toward more acidic precipitation, but the comparison is still between data from different sites, so the conclusion is uncertain. The two sites are only 8 km apart, but one is rural while the other is semi-urban. The Water Survey is currently beginning a program of parallel sample collections at the Savoy and Champaign-Urbana sites to try to resolve this question. However, some months of sampling will be necessary before a reliable comparison can be made.

It appears likely that wind blown soil dust may be an important local source of airborne alkaline materials in areas of extensive farming. The Water Survey recently submitted a proposal to the National Science Foundation to evaluate the role of soil dust in precipitation acidity.

PRECIPITATION pH MEASUREMENT NETWORKS

The only regular collection of precipitation samples for pH measurement now going on in Illinois, to our knowledge, is in and near Champaign-Urbana. The Water Survey is now negotiating for a permanent site for precipitation sampling about 10 km southwest of Champaign-Urbana. This site is one of three that would be used if the proposal mentioned earlier is funded. In addition, sample collections on the roof of the Water Resources Building will continue for the present, so as to provide a comparison of samples collected in Champaign-Urbana with those collected at the rural site 10 km southwest.

The Water Survey, under its ERDA contract, will begin a program of precipitation sampling in the Chicago area during 1978. Measurements will include pH, conductivity, and the major contributing ions.

Plans are also underway in the U. S. Department of Agriculture for a 100 station national network of precipitation samplers. This plan has been tentatively approved by the USDA North Central Region (including Illinois), but sampling will probably not start until 1978. Illinois will probably have between 1 and 3 sampling sites in this network, and the Water Survey will operate at least one of them, probably at the permanent sampling site now being acquired.

REFERENCES

Gatz, D. F., 1976: Comment on 'Acid precipitation in the northeastern United States,' by Charles V. Cogbill and G. E. Likens, Water Resources Research, 12(3), 569-570.

Larson, T. E., and I. Hettick, 1956: Mineral composition of rainwater. Tellus, 8, 191-201.

Likens, G. E., and F. H. Bormann, 1974: Acid rain: a serious regional environmental problem. Science, 184, 1176-1179.

Miller, J. M., 1974: A statistical evaluation of the United States Precipitation Chemistry Network. Paper presented at Precip. Scavenging Symposium -- 1974, Champaign, IL, Oct. 14-18, 1974.

Semonin, R. G., 1975: Temporal and spatial variability of rainwater pH. Paper presented at Conf. on Metropolitan Physical Environment, 25-29 August, 1975, Syracuse, NY.

Semonin, R. G., 1976: The variability of pH in convective storms. Water, Air, Soil Pollut., 6, 395-406.

Stensland, G. J., 1977: Precipitation pH decrease since 1954 at Champaign-Urbana, Illinois. Paper prepared for presentation at American Geophysical Union Annual Meeting, May 30 - June 2, 1977, Washington, DC.

SECTION III.

Meteorology

Chapter 1

Diurnal Temperature and Moisture Cycles
Steven D. Hilberg

Chapter 2

Upper Air Program
Bernice Ackerman

Chapter 3

Air Trajectory Data
Randall K. Stahlhut and Steven D. Hilberg

CHAPTER 1

Diurnal Temperature and Moisture Cycles

Steven D. Hilberg

INTRODUCTION

An investigation of the behavior of diurnal temperature and moisture cycles in the METROMEX area is continuing. Data collected from the hygrothermograph network is being used to provide hourly values of temperature and mixing ratio at approximately 30 locations in the research circle. It is hoped the analyses of the diurnal temperature and mixing ratio cycles will help provide more information about the formation and general characteristics of the urban heat island and the urban "dry island".

Data was available for the summer periods 1972-1975. However, there were some gaps in the data. Some sites in 1972 were not put into service until late in the summer, and in 1974 data were available for July and August only. A map of the hygrothermograph site locations appear in Figure 1. Because of the large number of sites and the large amount of data, two sites were selected for a concentrated study of the urban and rural characteristics. The stations selected were at the Arch (station 6, ARC) and at the SIU-Belleville Experimental Farms (station 20, FRM). ARC is the representative urban station and FRM the representative rural station.

DATA ANALYSIS

For the purposes of this study, a diurnal cycle is defined as the 24-hour period beginning at 0600 CDT. A computer program was written to average the data for all sites. The procedure averages a specified number of diurnal cycles, and then normalizes the average curve to the mean temperature. If more than three hourly values are missing in any one 24-hour diurnal period, that cycle is not included in the averaging. This is done to eliminate biasing when only a small number of cycles are being averaged. An average temperature curve and mixing ratio curve for the 92 day summer period (62 days in 1974) was calculated for each station in the network. These curves were then differentiated to yield the average rate of change of temperature and moisture.

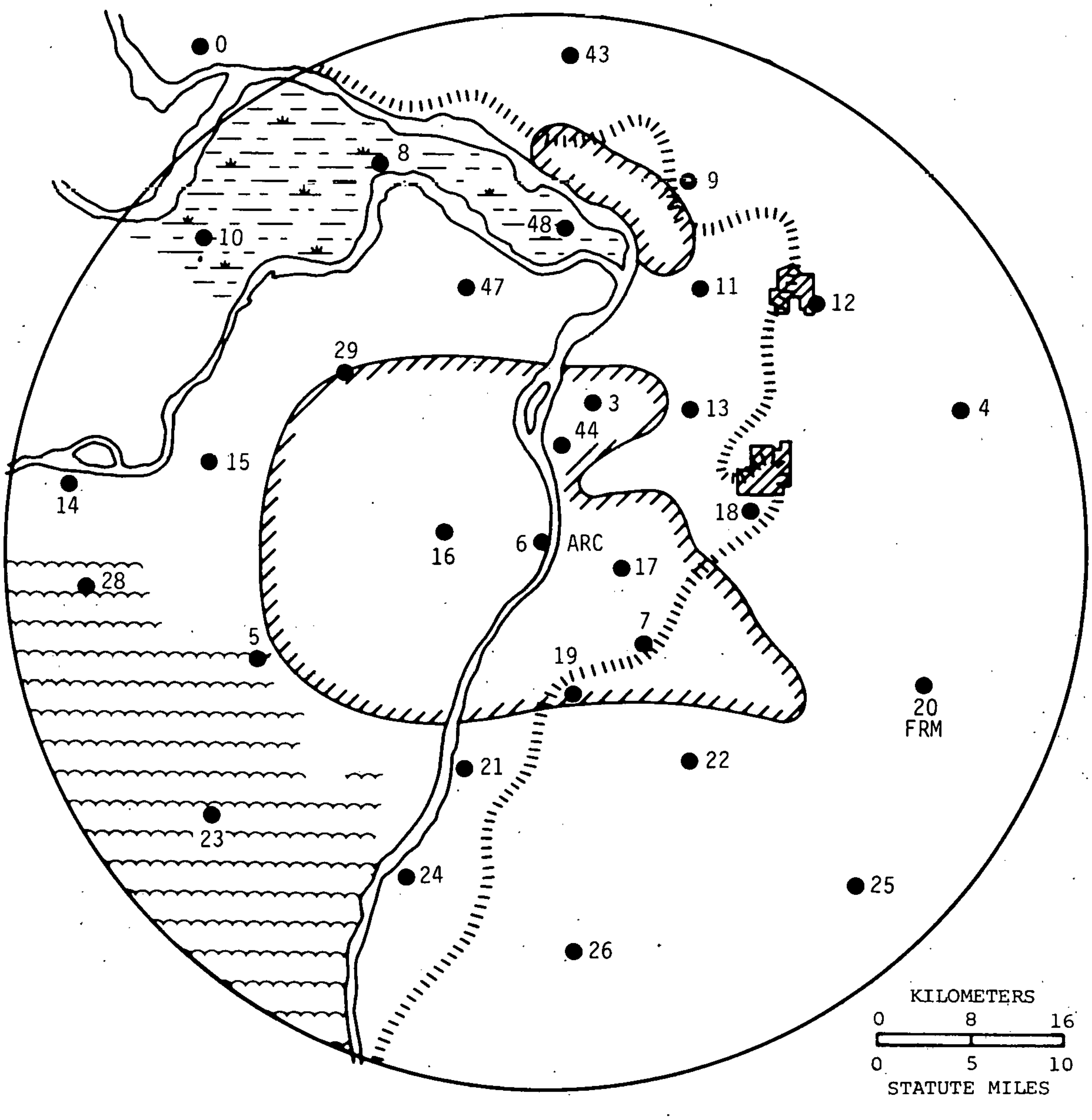

Figure 1. Locations of hygrothermographs in METROMEX research circle

The data were further stratified by sky condition. Fair (0.0-0.3 coverage), partly cloudy (0.4-0.7 coverage), and cloudy (0.8-1.0 coverage) days were tabulated for each summer using the observations taken at Lambert Field in St. Louis and Scott Air Force Base near Belleville. To insure that a sky condition persisted throughout a diurnal cycle, only periods in which a certain sky condition prevailed at least two consecutive days were used in the calculation of an average diurnal cycle.

COMPARISON OF THE DIURNAL TEMPERATURE CYCLES

The four year normalized diurnal temperature curves for ARC and FRM are shown in Figure 2. The FRM rural curve is markedly different from the urban curve (ARC) in several respects. It has greater amplitude, and larger rates of heating in the morning and larger rates of cooling after 1930 CDT. Both stations reach their maximum temperatures about 1500 CDT, approximately 9 hours after local sunrise. Even though the urban site normalized maximum temperature value is 1.4^{o}C less than the rural curve, the actual temperature is slightly greater than the rural area at the time of maximum temperature.

The urban heat island becomes established beginning with the period 1900-2000 CDT. At this time the rural area is cooling approximately 1^{o}C hr^{-1} faster than the urban area, (Figure 3) and continues to do so until 2100-2200 CDT, when it decreases to approximately the same rate of cooling as the urban area. Similar results were noted by Oke and Maxwell (1975) for days with light winds and clear skies. A majority of the stations in the METROMEX research circle recorded their maximum cooling rate between 2000 and 2100 CDT. Approximately one third of the stations attained the maximum rate of cooling between 1900 and 2000 CDT, with a slight decrease or no change between 2000 and 2100. Only one station, ARC, attained a maximum rate of cooling (1^{o}C hr^{-1}) between 1800 and 1900. However, the next two hours, before beginning a slow decrease. The time of occurrence of the maximum rate of cooling appears to be unrelated to the location of a site.

VARIATIONS IN DIURNAL HEATING AND COOLING RATES WITH SKY CONDITION

As expected, heating and cooling rates during days with cloudy skies were less than those days with fair or partly cloudy skies for both the rural and urban areas. However, the differences were less pronounced in the urban area. In the urban curve, there is very little difference between the diurnal curves for fair and partly cloudy skies. The obvious

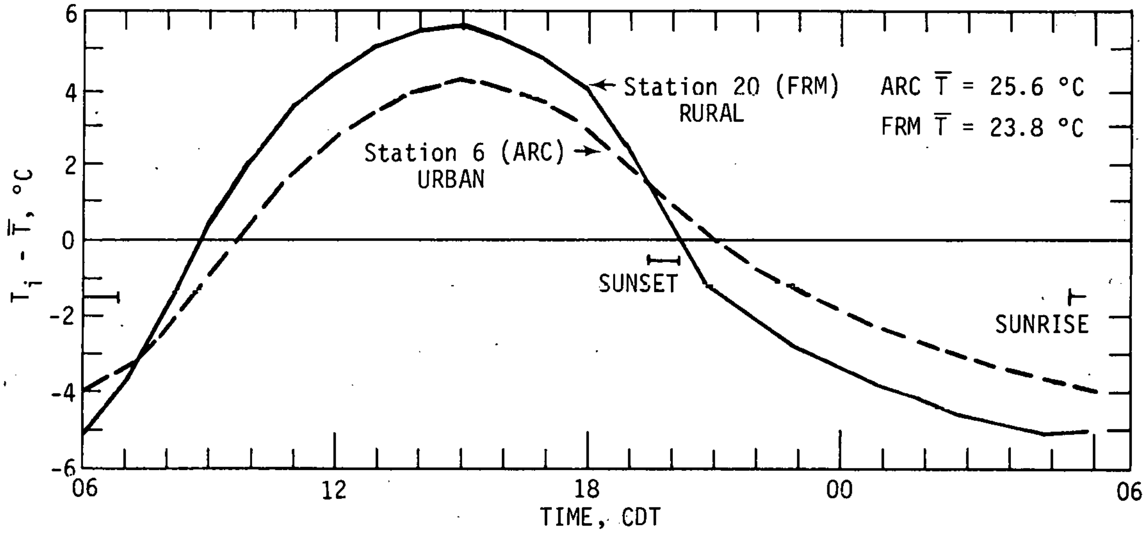

Figure 2. Four year average normalized diurnal temperature curves for a rural (FRM) and urban (ARC) station

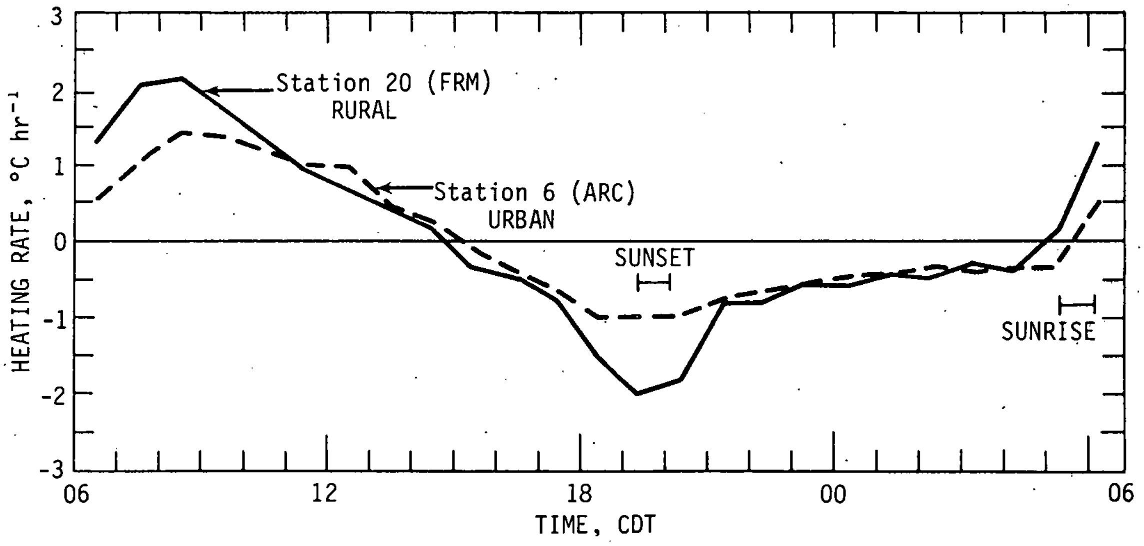

Figure 3. Four year average diurnal temperature rate curves for a rural (FRM) and urban (ARC) station

differences occur in the afternoon when clouds might be forming. At this time, heating rates are somewhat less with partly cloudy skies. Figures 4 and 5 contain the three sky condition curves for the rural and urban areas.

COMPARISON OF DIURNAL MIXING RATIO CYCLES

Like the diurnal temperature cycles, there were distinct differences between the urban and rural mixing ratio cycles. However, there were more variations between rural stations and between urban stations than with the temperature, and thus, it is much more difficult to determine whether or not a mixing ratio cycle is rural or urban from the shape or configuration of the curve.

The mixing ratio diurnal cycles for FRM and ARC are shown in Figure 6. As with the temperature, the variation about the mean of mixing ratio throughout the day is less in the urban area than in the rural area. The four year mean values for FRM and ARC are 14.5 g kg^{-1} and 14.0 g kg^{-1}, respectively.

Hage (1975) found the diurnal trace of absolute humidity at a rural airport to exhibit a distinct double wave, with the peaks occurring before sunset near the time of maximum cooling and the other following the maximum heating in the morning. The FRM curve did not exhibit a strong maximum after early morning heating, but did exhibit a maximum near sunset. Most of the other stations, urban and rural, did not exhibit a "double wave" pattern in their diurnal cycles, and the characteristics of the curves varied. However, the curves were classified into three general categories. Curves representative of the three types appear in Figure 7.

VARIATIONS OF DIURNAL MIXING RATIO WITH CLOUD COVER

The diurnal mixing ratio curves for ARC and FRM for three sky conditions described previously appear in Figures 8 and 9. As can be seen in the figures, there is decreasing amplitude of the curves with increasing cloud cover. However, while the mixing ratio varied less about the mean, the mean mixing ratio value increased with increasing cloud cover. This trend was noticed for both the urban and rural areas.

The formation and strength of the urban "dry island" also varies with cloud cover. The urban area is drier than the rural area during the late morning and afternoon, and generally does not become more moist until two to three hours after sunset. In Figure 10, the strength of the urban "dry island" can be seen to decrease with increasing cloud cover. This

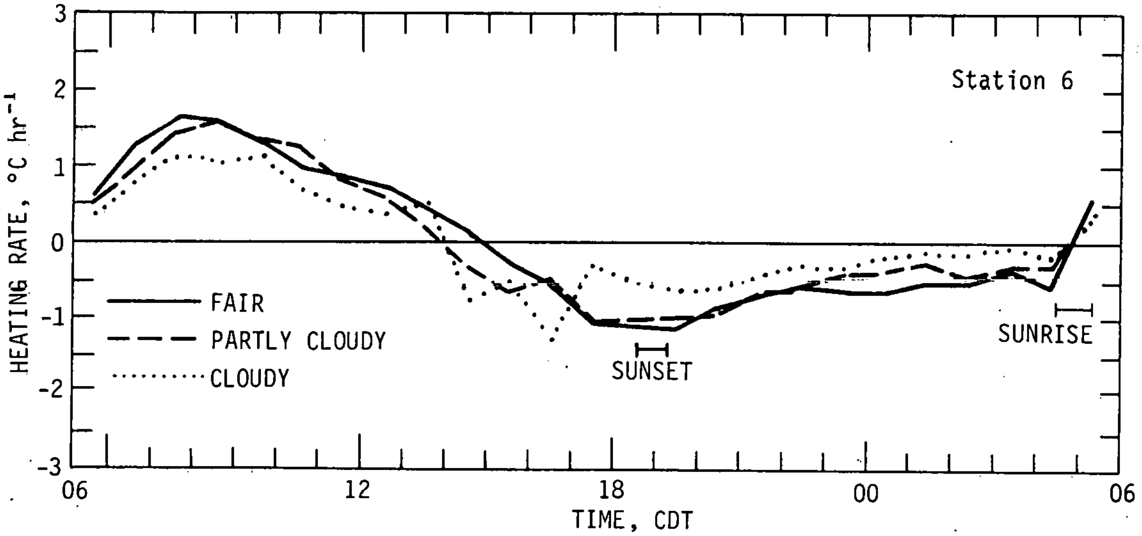

Figure 4. ARC (urban) temperature rate curves for three sky conditions, 4 year average

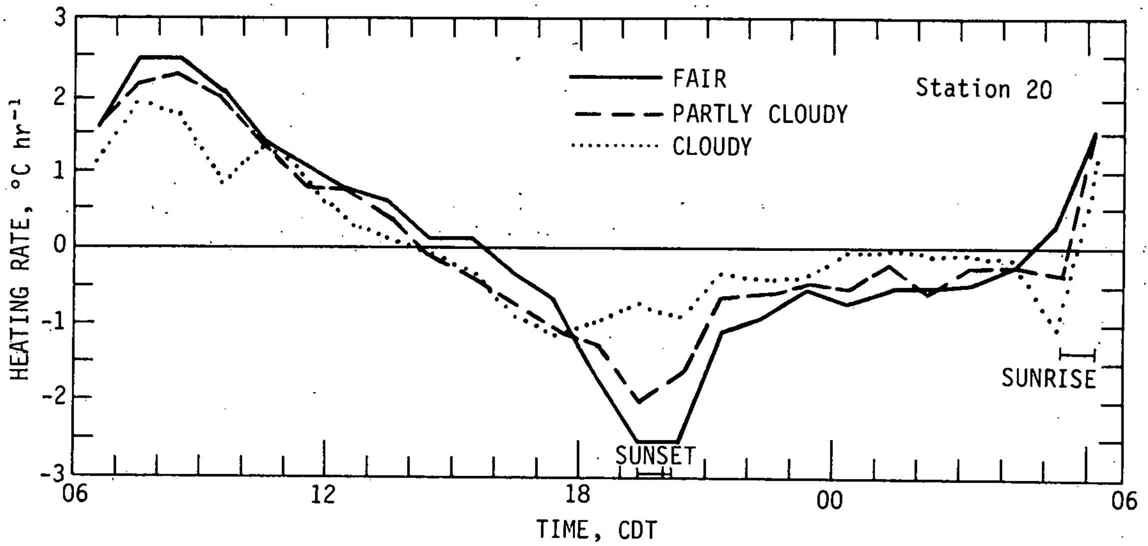

Figure 5. FRM (rural) temperature rate curves for three sky conditions, 4 year average

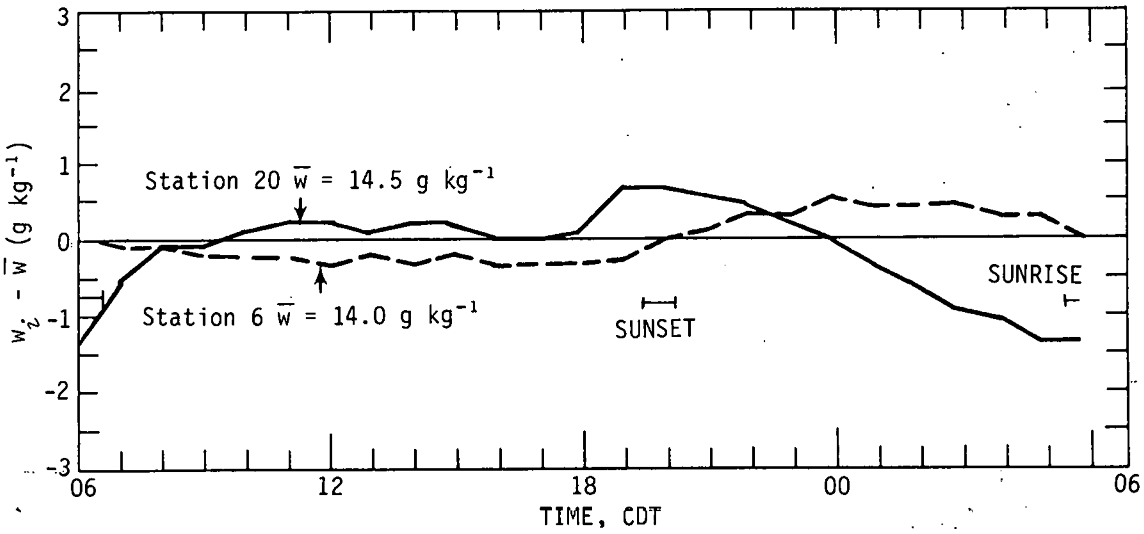

Figure 6. Four year average normalized diurnal mixing ratio curves for a rural (FRM) and urban (ARC) station

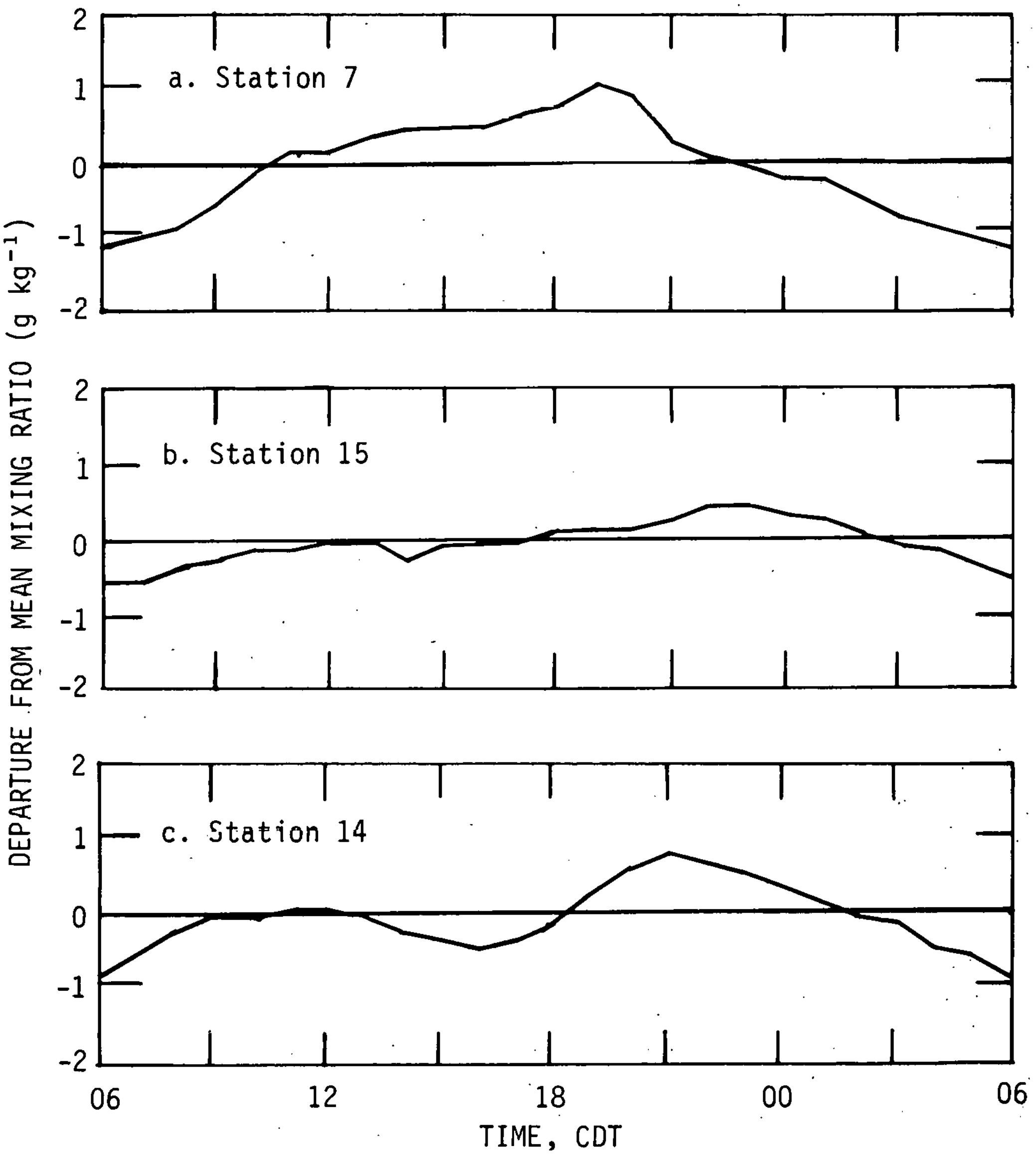

Figure 7. Mixing ratio curves representative of three types of diurnal distributions: a) type 1, single wave with maximum departure ≥ 1.0 g kg^{-1}, b) type 2, single wave with maximum departure <1.0 g kg^{-1}, c) type 3, double wave, difference between each maximum and minimum ≥ 0.4 g kg^{-1}

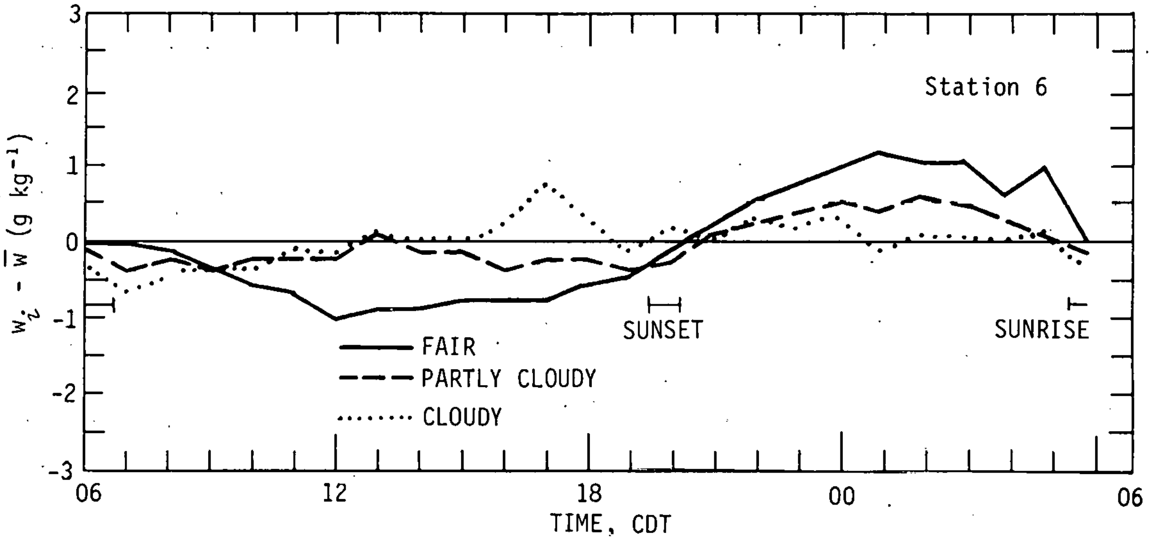

Figure 8. ARC (urban) normalized diurnal mixing ratio curves for three sky conditions, 4 year average

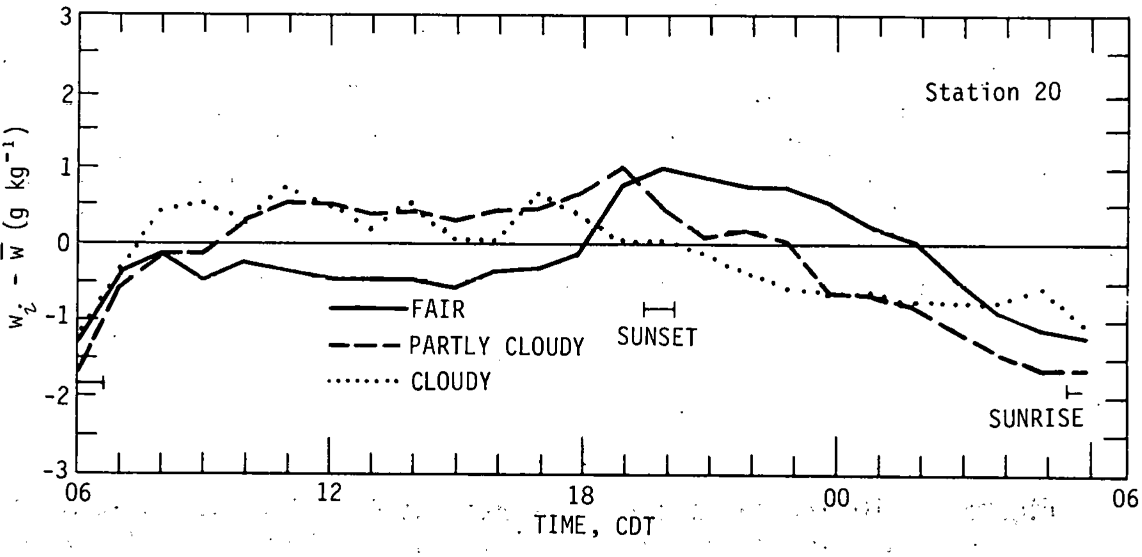

Figure 9. FRM (rural) normalized diurnal mixing ratio curves for three sky conditions, 4 year average

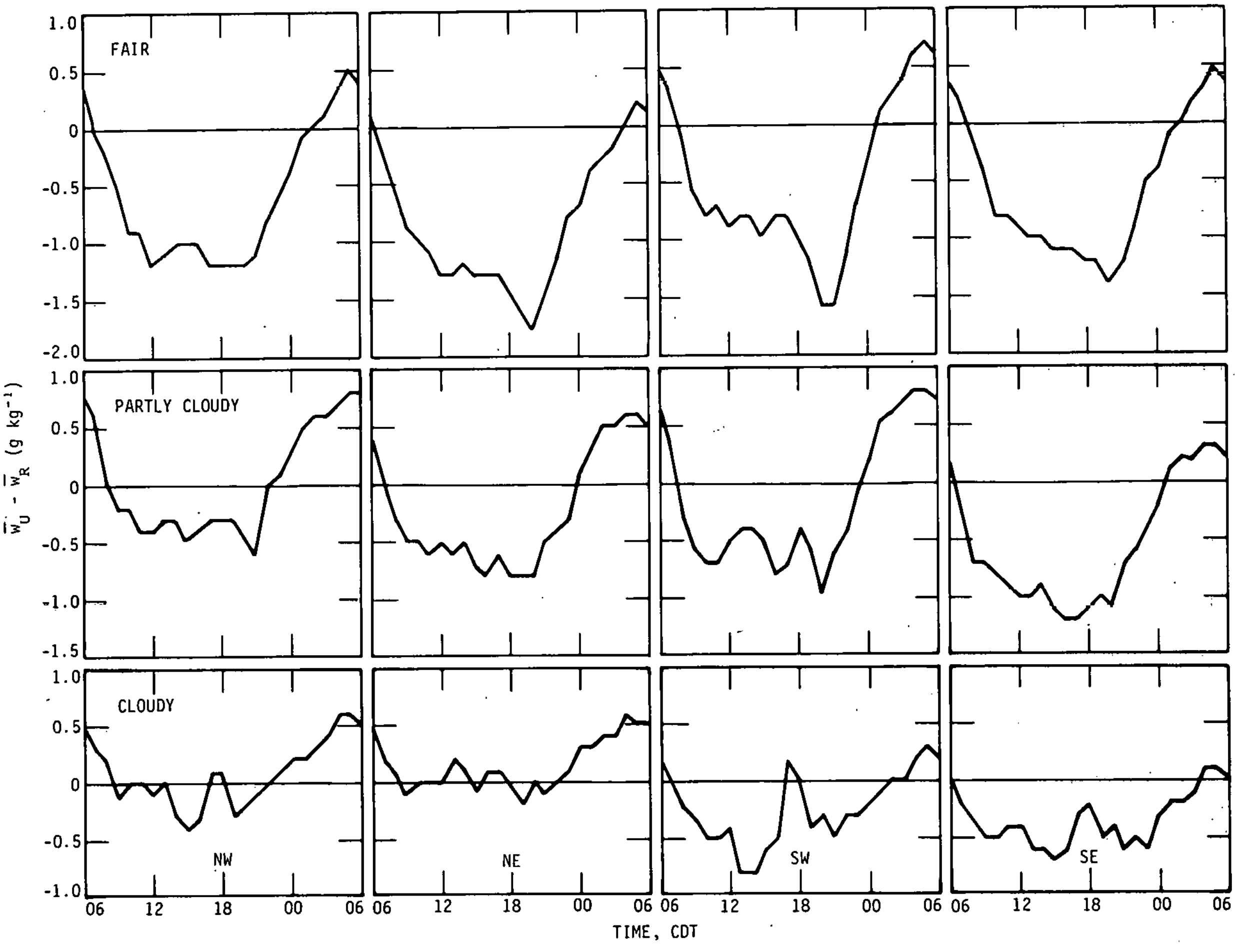

Figure 10. Strength of urban "dry island" with respect to four rural quadrants as a function of time and sky condition

data consists of areal means computed for four rural quadrants and one urban area in the METROMEX research circle. Negative values indicate the urban area is drier.

SUMMARY

This study of the diurnal variations of temperature and moisture will continue. As a basic understanding of these daily variation is acquired, an investigation into the possible correlation of cycle parameters to land use can be made. This may be especially useful in siting considerations for air sampling and meteorological instrumentation, where the ambient temperature and moisture fluctuations are of importance to the type and quality of data collected.

REFERENCES

Hage, K. D., 1975: "Urban-Rural Humidity Differences", Journal of Applied Meteorology, Vol. 14, 1277-1283.

Oke, T. R., and G. B. Maxwell, 1975: "Urban Heat Island Dynamics in Montreal and Vancouver", Atmospheric Environment, Vol. 9, 191-200.

CHAPTER 2

Upper Air Program

Bernice Ackerman

INTRODUCTION

The upper air wind and thermodynamic program in METROMEX has addressed a number of problems over the 5-year duration of the project. As a consequence, the field effort changed significantly between summers, as it was modified to meet different objectives. In 1971* the observations were made during special field experiments designed to investigate specific hypotheses concerning the modification of the planetary boundary layer (PBL) by the metropolitan area of St. Louis. In 1972, also, this general approach was used with part of the effort going to a continuation of the 1971 objectives and part to supporting the tracer experiments. In the last three years (1973-76), the measurements were made on a more routine basis, with scheduling appropriate to the weather conditions and the operations of the other research components in METROMEX.

OPERATIONS

Wind measurements were obtained by double-theodolite tracking of pilot balloons in 1971 and 1972.** In succeeding years wind measurements were based on single theodolite tracking of pilot balloons.

The field experiments in 1972 were carried out between 12 July and 10 August. Their objectives were (a) to support the tracer experiments during periods when the weather forecast indicated suitable convective storms would be moving through the METROMEX circle, (b) to test the hypothesis that a local circulation was induced by the nocturnal urban heat island, and (c) in support

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* In 1971 the field effort was carried out by Argonne National Laboratory; in 1972 through 1975 it was a part of the ISWS field program.

** Personnel and equipment for both pibal and radiosonde measurements were provided by the Air Weather Service of the U. S. Air Force. Supplies, per-diem and travel costs were supported by the AEC under this contract.

of scheduled "Metrodata" collection periods when all participants in METROMEX coordinated their operations in an effort to trace the urban plume.

The general operations were similar in all three types of experiments with wind observations made at 7-9 locations over periods of 3 to 4 hours. In addition, two to three radiosonde releases were made from 3 additional sites, located on a WNW - ESE line cutting across the center of the city. Pilot balloons were tracked to about 2 km, with 50 to 60 m vertical resolution in the measurements. Station array and balloon-release interval depended on the objectives of the experiment. In general, 8 pibal launches and 1 to 3 radiosonde launches were made during the 3 to 4 hour experimental period. A total of seventeen operations were carried out during which 1000 pilot balloon and 112 radiosonde profiles were obtained.

The 1973* program, which covered the period from 11 July to 23 August, stressed routine daily observations from a fixed network of stations, more-or-less uniformly distributed over the METROMEX research circle. The objectives were (a) to depict the summertime kinematic fields in the planetary boundary layer (PBL) over and around St. Louis, (b) to investigate the thermodynamic structure in the lower and mid-troposphere over and around St. Louis, and (c) to provide supporting wind and thermodynamic data during periods of specialized studies, particularly those involving tracer releases.

To meet these objectives, pilot balloon observations were made at 11 sites in and around the metropolitan area, and radiosonde measurements were taken at three of the pibal stations lying on a roughly NW-SE line across the METROMEX area. Wind measurements were made to 3 km with approximately 90-100 m vertical resolution using single theodolite tracking of pilot balloons. Pilot balloons were launched routinely 6-times daily between 1130 and 1600 CDT and radiosondes were launched routinely at 0700 and 1300 CDT. The operation was carried out daily, Monday through Saturday. During most periods of convective weather the launch intervals were increased to hourly for radiosondes and to half-hourly for pibals and the period of observation was extended to the time that the rain ended or night fell. Twenty-five hundred wind profiles and 275 thermodynamic soundings were obtained during the 6-week observational period.

During the last two summers (1974 and 1975) the objective of the upper air program was to define the meso-scale circulation patterns over the ISWS chemistry network. In 1974 the network was located over the city of St. Louis, extending eastward, and in 1975 it was located over and around the Alton-Wood River industrial complex. During both summers, single theodolite pilot balloon measurements, similar to those collected in 1973, were made from 11 sites more-or-less uniformly distributed around the chemistry network.

In 1974, observations were initiated on the basis of forecasted weather conditions. On working days, pilot balloons were launched every half hour from 1130 to 1630 CDT, with the observation period extended to 1800 CDT when

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* The field measurement program was partially supported by NSF-RANN under Grant NSF GI-39213.

convective storms were predicted. Radiosonde measurements which were scheduled for three of the wind stations lying on an approximately NW-SE line were very irregular because of equipment malfunction. A total of 2100 wind profiles and 150 thermodynamic profiles were obtained on 18 days between July 13 and August 18.

In 1975 operations were routinely scheduled for 5-consecutive working days, followed by one day off. Pibals were launched on the same schedule as that used in 1974. In addition, radiosonde releases were made every two hours, 1200-1600 CDT on non-storm days, and hourly, 1130-1730 CDT on storm days. In 33 operational days between 7 July and 15 August, about 4000 wind and 375 thermodynamic profiles were measured.

DATA ANALYSIS

Data collected in the boundary layer and upper air program have been used in a number of studies* focused on the urban precipitation anomaly and its causes (e.g., Grosh and Semonin, 1973; Changnon and Semonin, 1975). In addition, they have been, and are being, used in studies** investigating the alterations in the kinematic fields of the PBL by the urban-industrial area. These have addressed the temporal and spatial variability of the winds in the PBL (Ackerman, 1974c, d) the midday thermodynamic and kinematic structure of the PBL (Ackerman, 1973a, b, 1974a, b, 1975a, b, 1977a; Ackerman and Appleman, 1974) and the nocturnal heat island (Ackerman, 1972, 1974a, 1977b). These studies are ongoing but results to date indicate, without exception, that significant perturbations frequently exist over the area and there are strong indications that they are urban-induced.

Kinematic Fields

In Figure 1 are shown the average taken over 21 undisturbed afternoons, of the divergence pattern for the transport*** wind of the mixed sub-cloud layer and a few of the streamlines of the perturbation component**** of the transport wind. The perturbation streamlines indicate relative inflow into

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* Supported by the National Science Foundation under Grant GI-38317 and AEN73-07796 as well as by ERDA (formerly AEC) under Contract ERDA-1199.

** Supported by the National Science Foundation under Grants GI-38317, AEN73-07796, and DES74-13931.

*** The transport wind is the vector average of the wind in the layer from the surface to any specified height, in this case the cloud base.

**** The perturbation component (perturbation wind) is the deviation of the wind at any point from the vector mean wind over the network.

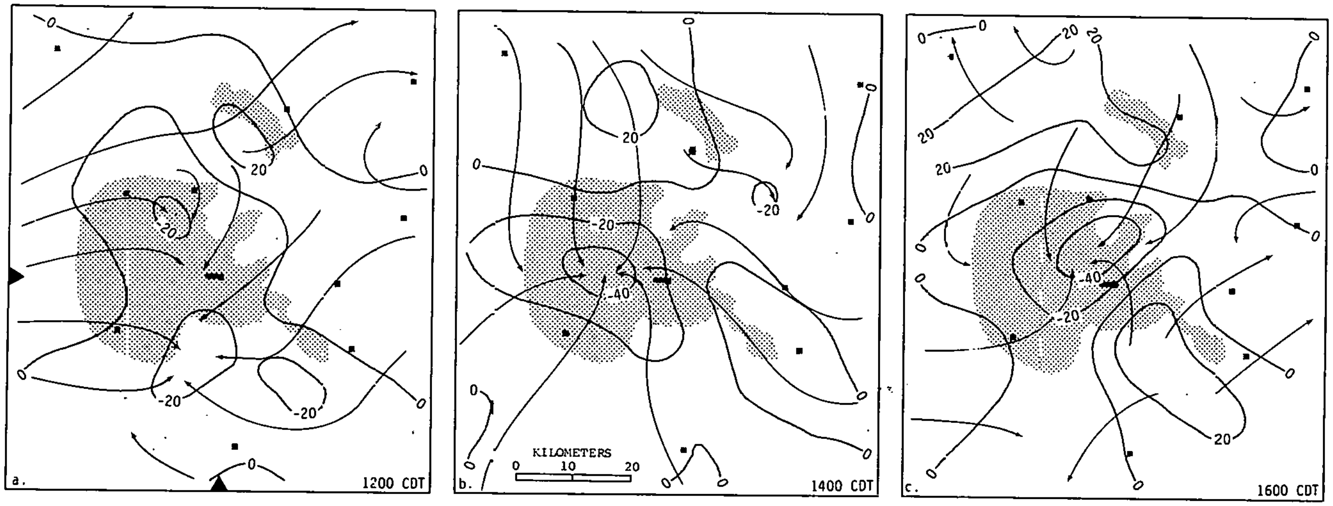


Figure 1. Mean divergence fields and streamlines of the mean "perturbation" velocity for the transport wind in the sub-cloud layer, at 1200, 1400, and 1600 CDT. The average was taken over 21 days with fair weather. Divergence is in units of 10^{-6} sec^{-1}. Coordinates of the St. Louis Arch are indicated by heavy arrows along the border of the chart for 1200 CDT.

the metropolitan area, and as might then be expected, convergence over the metropolis was found on the average throughout the afternoon. The convergence was greater and more closely associated to the urban-industrial region in the mid- and late-afternoon than at noon. At 1400 CDT a small but significant center of convergence was located in the vicinity of Edwardsville, where precipitation patterns indicate an anomalously high value. Although the values of the convergence in the average fields are rather small, it should be recognized that they are averages through depth as well as over days. In individual cases convergence in excess of 10^{-4} sec^{-1} was not uncommon.

In Figure 2 are shown the average divergence and vertical motion for 1600 CDT in height cross-sections cutting W to E and N to S across the city. The convergence over the Missouri metropolitan area extended throughout the sub-cloud layer, but with a maximum value at about 500 m. Since the center of convergence was displaced to the north of the city at 1600 (Figure 1c), the convergence zone in the W to E cross-section is somewhat shallower than in the N to S cross-section. Vertical velocities (calculated from the divergence fields) at the top of the layer above the center of low level convergence averaged about +7 cm sec^{-1}. However in individual cases, positive vertical velocities of 20-30 cm sec^{-1} were frequent near the top of the sub-cloud layer.

The kinematic fields over the area in pre-rain situations were very similar. The divergence field of the transport wind shortly before rain started in the network on July 14th is shown in Figure 3a. The storm of interest entered the network in the extreme west edge about 1600 CDT and rapidly propogated eastward (Figure 3b). The coincidence between the rain band and the pre-existing convergence zone is striking. The rate at which the rain propogated eastward increased significantly when the leading edge of the storm reached the convergence zone over the Missouri metropolitan area. In fact, the rains on the eastern edge of the 1630-1700 CDT rain area (Figure 3b), actually started some 15 minutes before any surface rain occurred immediately to the west. Moreover the rain accumulations were greater from the rain clouds in the convergence area downwind from the city, with the largest accumulation just downwind of the center of the pre-existing convergence zone in the southeast quadrant. The largest vertical velocities calculated at the top of the sub-cloud layer were +35 cm sec^{-1} in the southeast quadrant, and +30 cm sec^{-1} over the city.

Thermodynamic Structure

The effect of the urban area on the therodynamic structure of the PBL, if there is any, is difficult to discern in the radiosonde data, possibly because it is of the same order as the noise in the physical system or as the error in the measurements. The average midday (1330 CDT) pre-rain (1-4 hours) temperature and moisture profiles for the 1973 urban and rural stations are shown in Figure 4. The pre-rain profiles calculated from soundings at the rural stations have been averaged only for cases in which the upwind fetch was not over the metropolitan area; the average profile for the urban site was based on all pre-rain cases. The average temperature and moisture

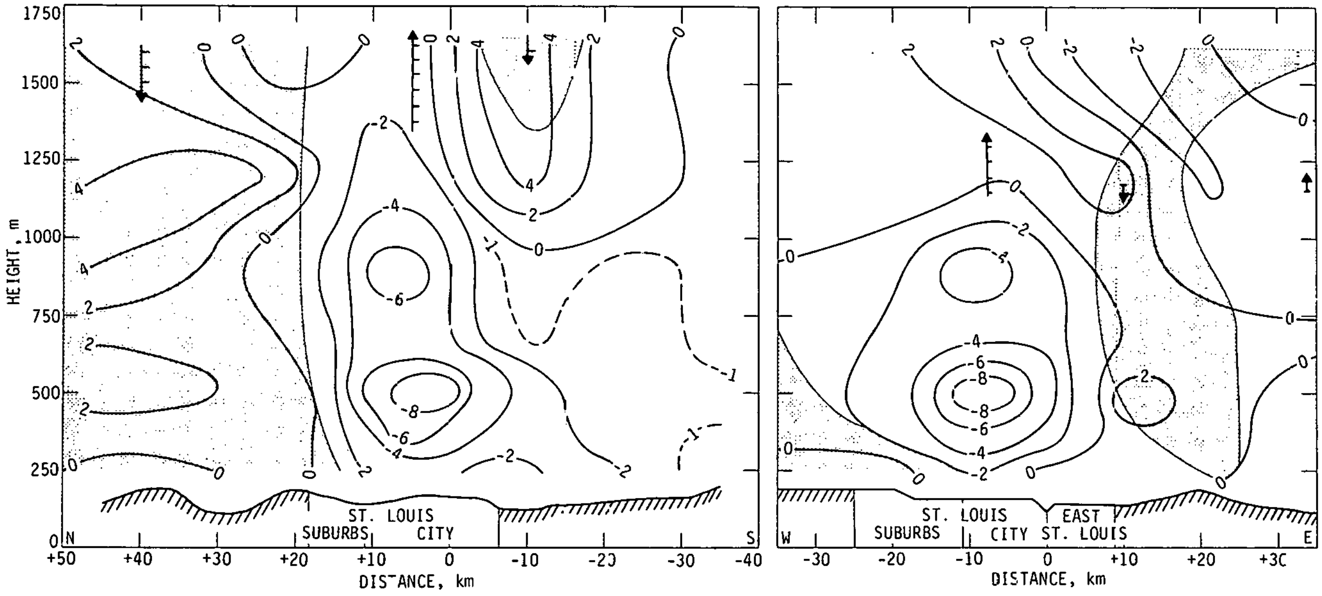


Figure 2. Mean vertical cross-sections showing contours of divergence (10^{-5} sec^{-1}), regions of downward (shaded) and upward (unshaded) motion calculated from the divergence fields, and arrows indicating locations and magnitudes of highest mean vertical velocities (1 tic = 1 cm sec^{-1}). Cross-section on the left is on a N to S line 5 km W of the Arch; 0 coordinate is due W of the Arch. Cross-section on the right is on a W to E line, with 0 coordinate indicating the river at the St. Louis Arch.

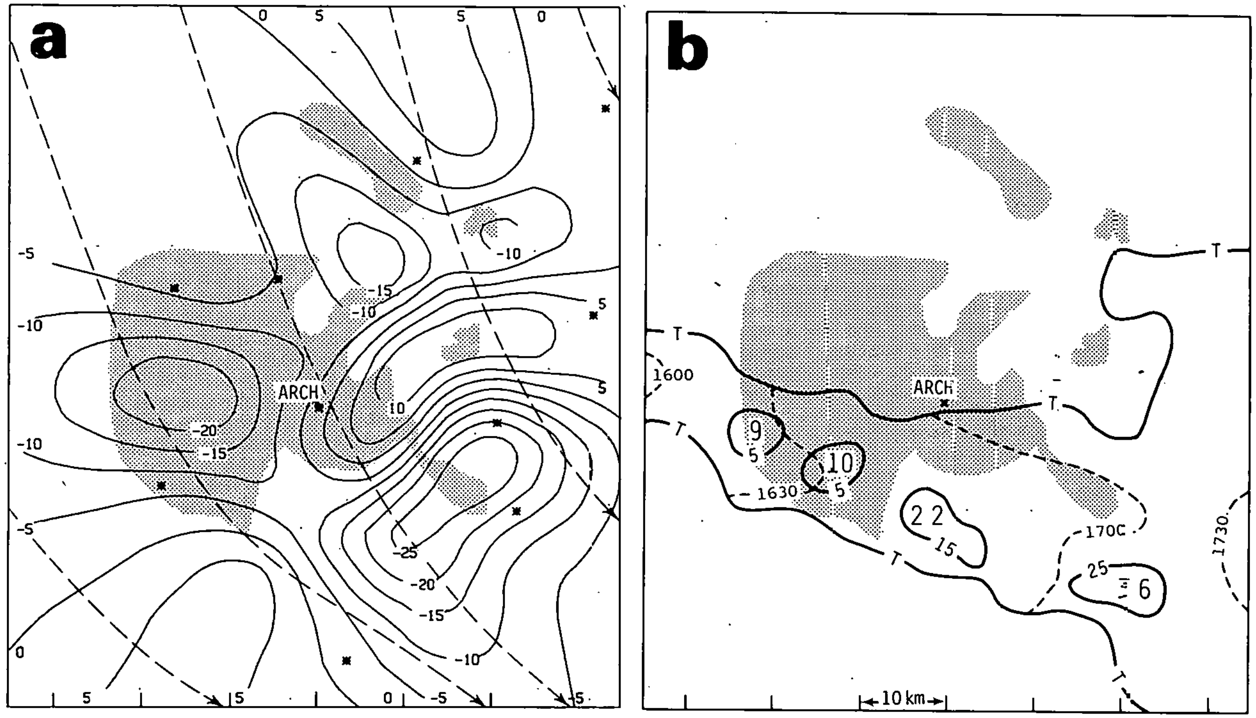


Figure 3. (a) Streamlines and divergence (10^{-5} sec^{-1}) at 1600 CDT on July 14. (b) The rain accumulations from a rainstorm on the late afternoon of July 14, with heavy lines enclosing the heaviest rain cores (amounts in mm) and the dashed lines giving the isochromes (times in CDT) of the leading edge of the rain area. Shading indicates urban area. In (a) stars show location of wind measurements; in (b) the large numbers give maximum point rainfall in mm.

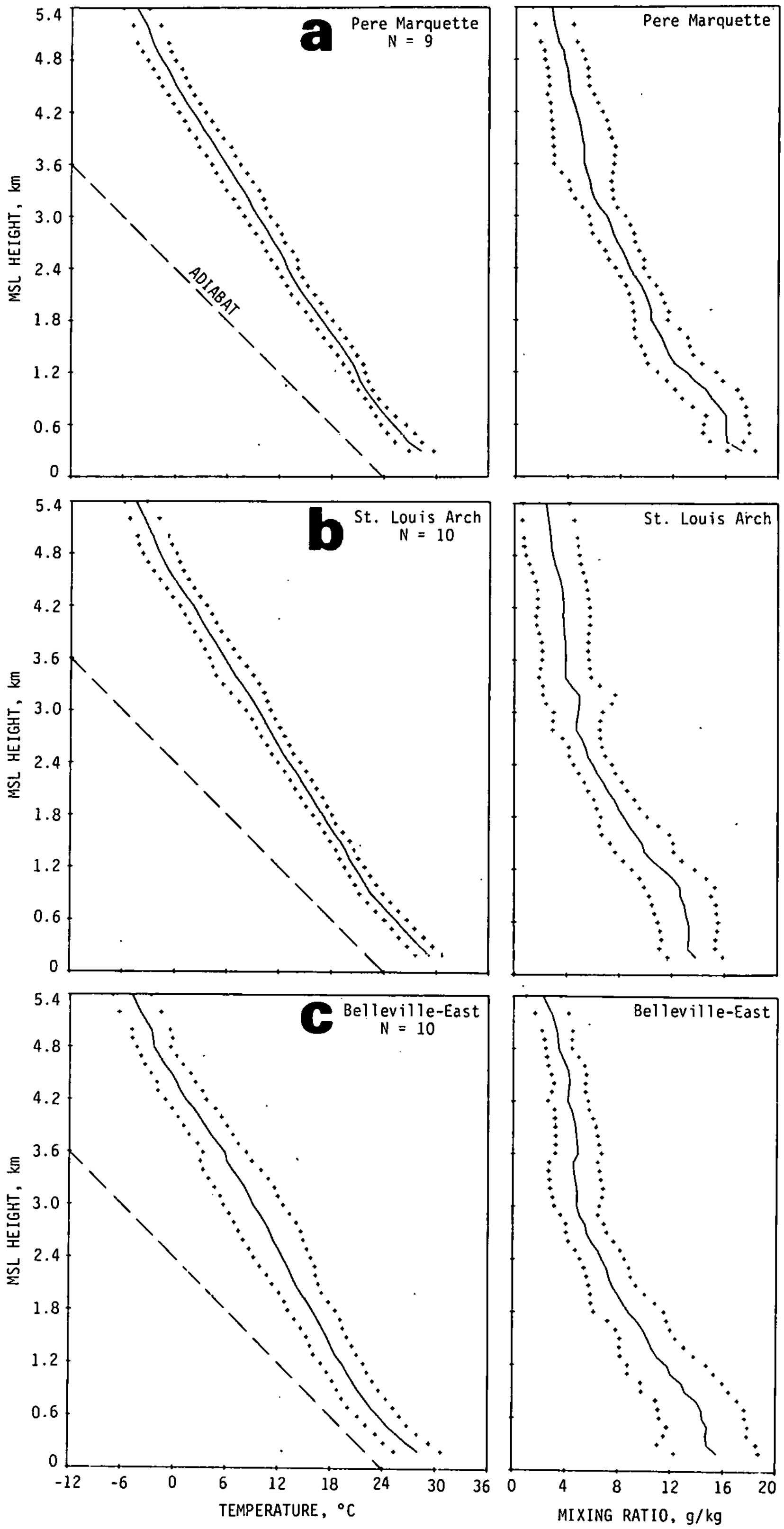


Figure 4. Average temperature and moisture profiles at 1330 CDT, and less than 4 hours before the start of the rain in the METROMEX area, at (a) rural site 50 km NW of downtown St. Louis, (b) downtown St. Louis, and (c) rural site 30 km ESE of downtown St. Louis. The ±1 standard deviation is indicated by the small plus signs; N gives the number of cases in the average.

profiles at the three stations are very similar, although there appears to be less interdiurnal variability in temperature at the city station than at the rural stations. The temperature at the Arch (ARC) was, on the average, about 1°C higher than at Belleville (BCC) east to about 2 km and the moisture about 1 g/kg lower to about 1 km. However, there is negligible difference in temperature between the Arch and Pere Marquette (PMQ) and the moisture in the air is significantly higher at PMQ than at either BCC or ARC.

Of the days in the average, 7 are common between PMQ and ARC (all are common between ARC and BCC), but averages taken only over the 7 common days also show negligible difference in temperature between ARC and PMQ and higher moisture content at PMQ. Since the moisture difference extends throughout the troposphere to 500 mb, some instrument error is suggested although the source of the error has not been identified despite extensive checking.

The most consistent difference between the urban and rural profiles is in the low-level lapse rates (Figure 5). The average potential temperature was essentially constant below 900 m MSL (about 760 m AGL) at the city station. On the other hand, the potential temperature started to increase with height at about 750 m MSL (600 m AGL) at BCC and just above the unstable surface layer at PMQ, indicating that the well mixed layer was significantly deeper in the city than in the country. This is also indicated by the more nearly constant moisture below 1 km at the Arch in Figure 1. The super-adiabatic lapses in temperature found at the two country stations just off the surface did not occur on the average in the city, most likely a consequence of the greater low-level mechanical mixing generated by the urban roughness.

SUMMARY

Over the years 1972-1975, the upper air program of the ISWS has collected an extensive data set consisting of about 9600 wind profiles and 900 thermodynamic soundings. This data bank has been tapped for supporting data for studies addressing a variety of METROMEX objectives. In addition, it has been used in a number of studies investigating the alteration of the kinematic and thermodynamic structure of the PBL. These strongly indicate significant perturbation in the airflow associated with the metropolitan area which result in sizeable convergence and significant upward motions of the air near the top of the sub-cloud layer. The thermodynamic perturbation, if any, is much smaller than that found in the wind field, although there is indication of significantly deeper mixed layer in the city than in the country.

REFERENCES

Ackerman, B., 1972: Winds in the Ekman Layer over St. Louis. Preprints, Conf. on Urban Meteor., Philadelphia, Oct. 31-Nov. 2, 1972, Amer. Meteor. Soc., 22-27.

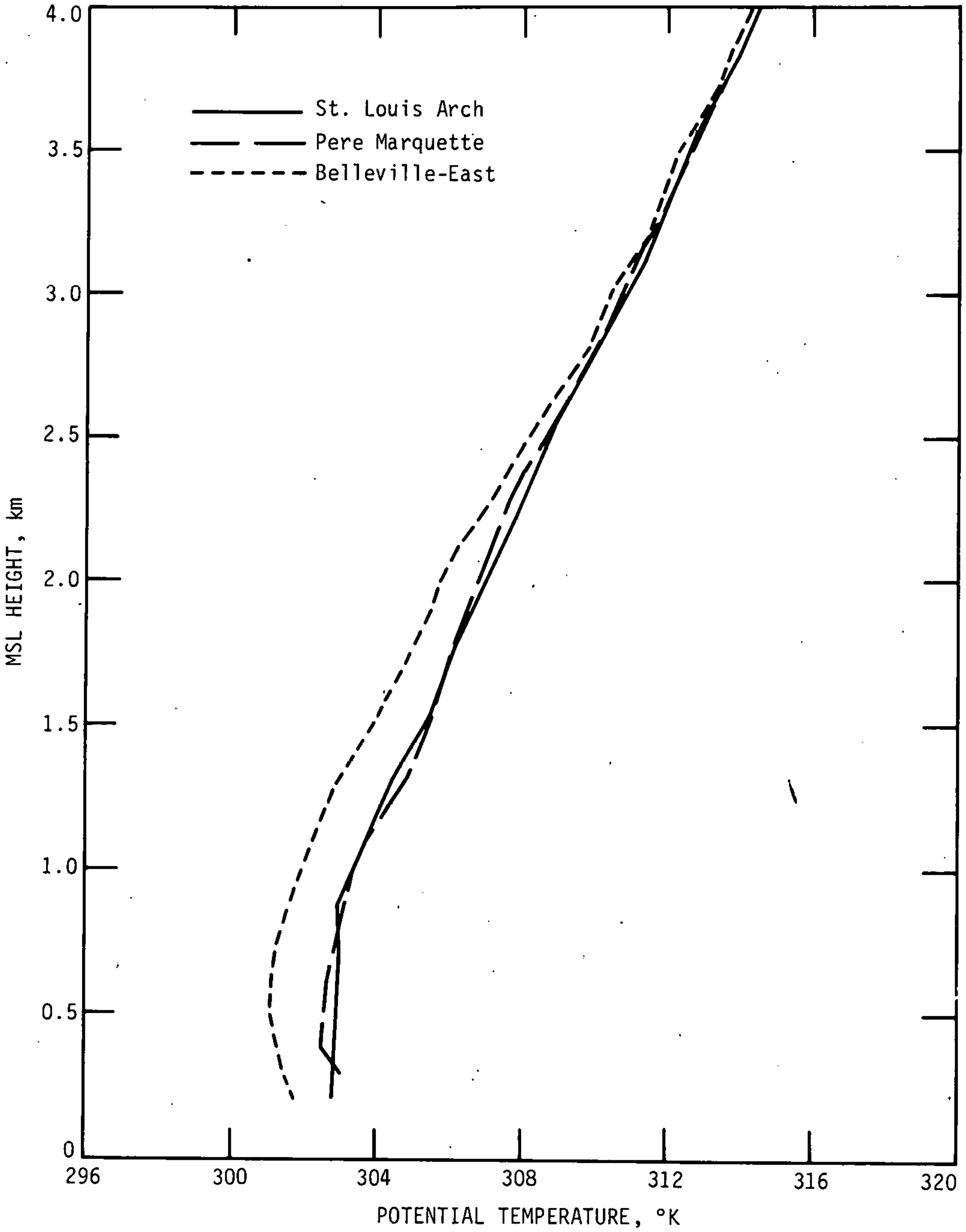


Figure 5. Average profiles of potential temperature at 1330 CDT, and 1 to 4 hours prior to the start of rain in the METROMEX network at the city station (solid line) and the two country stations.

Ackerman, B., 1973a: The airflow program in METROMEX. Summary Rept. of METROMEX Studies, F. A. Huff, Ed., Ill. State Water Survey, Rept. of Inv. 74, ISWS-73 RI-74. Urbana, 113-125.

Ackerman, B., 1973b: Airflow over the metropolitan area of St. Louis. Reprint #73-26, 66th Annual Meeting of the Air Poll. Control Assn., June 24-28, 31 pp.

Ackerman, B., 1974a: METROMEX: Wind fields over St. Louis in undistrubed weather. Bull. Amer. Meteor. Soc., 55, 93-94.

Ackerman, B., 1974b: Wind fields over the St. Louis metropolitan area. J. of Air Poll. Control Assoc., 24, No. 3, 232-236.

Ackerman, B., 1974c: Wind profiles and their variability in the planetary boundary layer. Preprint, Symposium on Atmos. Diff. and Air Pollution. Santa Barbara, September 9-13, Amer. Meteor. Soc., 19-22.

Ackerman, B., 1974d: Spatial Variability of the Wind Velocity in the Lowest 500 Meters. Preprints, Conf. on Aerosp. and Aeronaut. Meteorology, El Paso, November 12-15, Amer. Meteor. Soc., 325-328.

Ackerman, B., 1975a: Thermodynamic structure across a city on days with convective rains. 55th Annual Meeting of the Amer. Meteor. Soc., Denver, Jan. 20-23.

Ackerman, B., 1975b: Observational studies of the mesoscale wind field over an urbanized region. First Conf. on Regional and Mesoscale Modeling, Analysis, and Prediction. Las Vegas, May 6-9, Amer. Meteor. Soc.

Ackerman, B., 1977a: Mesoscale wind fields over St. Louis. Preprint, Sixth Conf. on Weather Modif., Champaign, Oct. 10-13, Amer. Meteor. Soc.

Ackerman, B., 1977b: Selected case studies of the wind field over the nocturnal urban heat island. Final Report to the National Sci. Found. under Grant DES74-13931.

Ackerman, B., and H. Appleman, 1974: Boundary layer program. Section J, Int. Rept. of METROMEX Studies 1971-73, NSF Grant GI-38317, F. A. Huff, Ed., 121-146. Ill. State Water Survey.

Changnon, S. A., and R. G. Semonin, Editors, 1975: Studies of Selected Precipitation Cases from METROMEX. Rept. of Invest. 81, ISWS/RI-81/75, 329 pp. Ill. State Water Survey, Urbana.

Grosh, R. C., and R. G. Semonin, 1973: Moisture budgets and wind fields of thunderstorms passing over an urban area in the Midwest. Preprint, Eighth Conf. on Severe Local Storms, Denver, Amer. Meteor. Soc., 130-137.

CHAPTER 3

Air Trajectory Data

Randall K. Stahlhut and Steven D. Hilberg

INTRODUCTION

The air trajectory data consisting of pibal and radiosonde data releases made in 1974 and 1975 were still in the process of reduction at the time of the last progress report. Since then, the reduction of the pibal and radiosonde data collected has been completed. The reduction process included transcribing the pibal observations for card punching, computer processing of the data, editing of the data, and final interpolation of the corrected data at specified levels above ground. Over 4000 individual pibal runs were involved in this phase of the data reduction, and the interpolated data for each run is now stored on disk, available for various analyses.

The radiosonde data also underwent a similar reduction routine. After the data were punched on cards, they were processed on the computer. Computer listings were made of all measured and derived thermodynamic parameters, and plots of temperature and dewpoint versus height were generated. These plots were used to check the data for possible errors. If errors were found, they were corrected, plots were generated and the data simultaneously stored on disk. This reduction process was carred out on 148 radiosondes released in 1974 and 369 radiosondes released in 1975.

In processing the radiosonde data, it was noted that there were sometimes large variations (6 to 20 m) in the heights of pressure surfaces over very small distances, which is unlikely in the absence of a large temperature difference. To find out why the computed heights behaved contrary to expected trends, a small study was initiated. The results of this study proved valuable to the understanding and interpretation of the data generated. It was found that the computed height of a pressure surface is very sensitive to the surface pressure. A small error in the surface pressure setting of the baroswitch of the radiosonde could induce errors in the height data. If two sites a small distance apart had errors of the opposite sign, then the apparent error could be quite large. This study indicated that care should be used in the interpretation of data collected on the microscale by instrumentation designed for the mesoscale, such as the GMD-1 rawinsonde system.

AIR TRAJECTORY ANALYSIS

The air trajectory data analyzed is being used for various case studies of the airflow and thermodynamic structure of the atmosphere in the research area. These studies will be useful in the determination of the scavenging efficiency of convective storms. One parameter of interest generated from the radiosonde data was the mixing height. The mixing height is important in the determination of how deep pollutants in the lower atmosphere will mix. Mixing heights were determined for the radiosonde runs made in 1974 and 1975, and will hopefully provide further insight into the scavenging process.

The pibal data generated in the past year are being used in a three dimensional parcel trajectory program that was under development at the time of the last progress report. The program is discussed in greater detail in the following section.

THREE-DIMENSIONAL TRAJECTORIES

A three-dimensional kinematic parcel trajectory program was developed to help understand the complex motions of convective storm activity. The trajectory model was designed to calculate a large number of trajectories over the METROMEX upper air network. At the present time, parcels may be started from any point within the upper air network and followed either forward or backward in time.

Input to the model consists of objectively analyzed wind speeds and vertical velocities calculated from pilot balloon data collected during METROMEX. Objectively analyzed data is available at 250m, 350m, 500m, 700m, 900m, 1200m, and 1600m msl. By integrating the continuity equation over successive heights, the following formula for vertical velocities was derived:

$$W_T = W_B - 0.5(DIV_T + DIV_B)\Delta Z$$

where: W_T = vertical velocity at the top of the layer,

W_B = vertical velocity at the bottom of the layer,

DIV_T = divergence at the top of the layer,

DIV_B = divergence at the bottom of the layer, and

ΔZ = height difference between the layers in meters.

Divergence values used in the vertical velocity calculations were found using the objectively analyzed u and v components of the wind and the following equation:

$$DIV = \{u(i+1,j) - u(i-1,j) + v(i,j+1) - v(i,j-1)\}/DX$$

where: $DX = GS/500$ and GS = grid spacing = 5km. (Figure 1).

This method of generating divergence values was used because of its simplicity in our application, although the Bellamy method could also have been used.

A fixed, three-dimensional grid of u, v, and w wind components result from these calculations. By applying the divergence and vertical velocity equations to all successive data sets (data are available every thirty minutes), additional wind speed grids at different times are obtained. This effectively gives a four-dimensional grid of u, v, w, and t from which trajectories can be generated.

Trajectories are calculated by following the procedure below.

1. Pick an initial parcel position (x,y,z) at a time t. The initial time t should be a multiple of the time step used (five minutes). For example, a parcel might be started from a position (10km., 10km., 1km.) at a time of 1310.

2. Interpolate at (x,y,z) at the closest grid in time before time t to get the values of u,v, and w at these points. The time at this grid is noted as t_n. Repeat these calculations for the grid at time t_{n+1}.

3. Calculate the values of u,v, and w at (x,y,z) and time t by interpolating between the values at times t_n and t_{n+1}. (Figure 2).

4. Using the values of u,v, and w from step 3, move the parcel for five minutes to find a new parcel position.

5. Continue interpolating and moving the parcel through all time grids t_n, t_{n+1},...t_m or until the parcel moves out of the network.

Equations for the trajectory model were derived in a Lagrangian reference frame to exclude advection terms. At any parcel position, values of u, v, and w can be determined by interpolation of the existing wind fields. Interpolations are carried out in both space and time to ensure continuity of the data between successive grids. Values of the wind components at a given point at time t_n is given by:

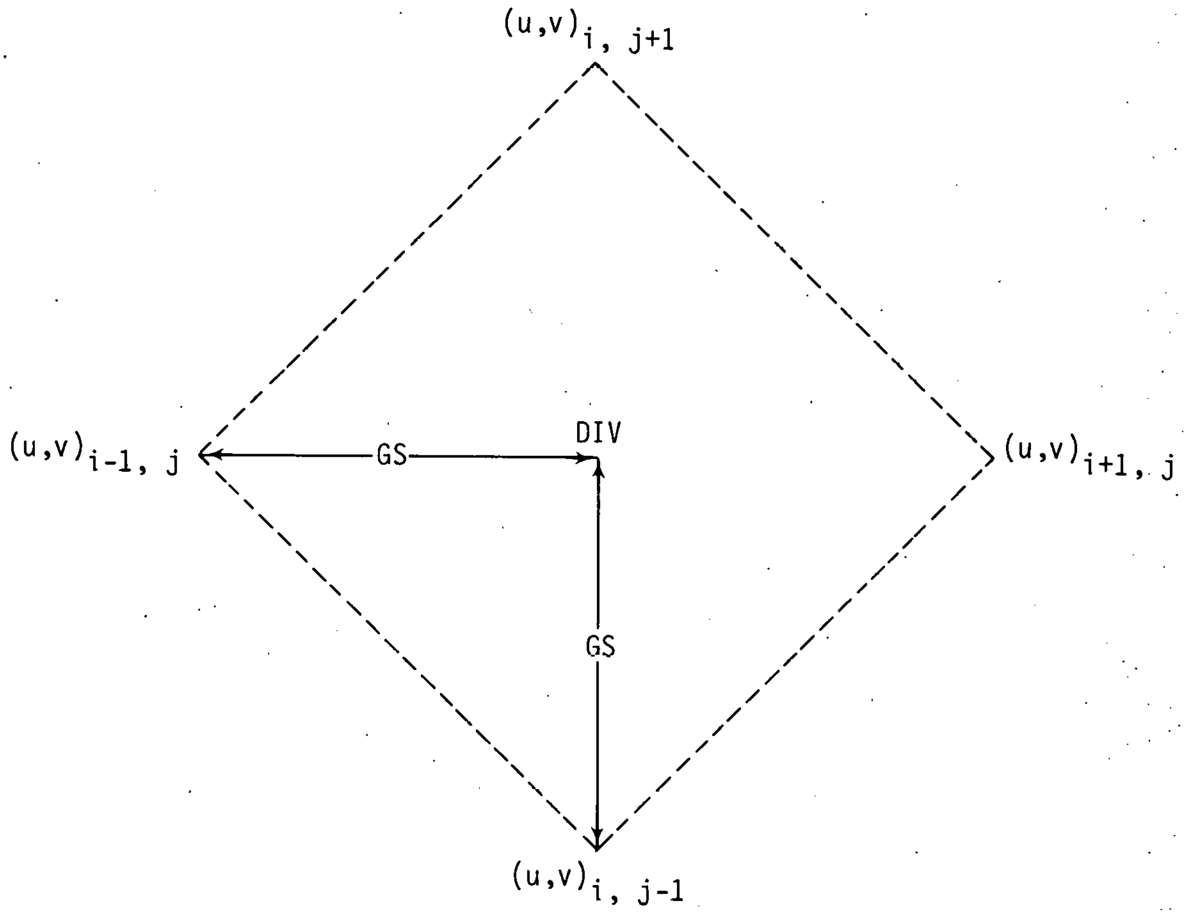
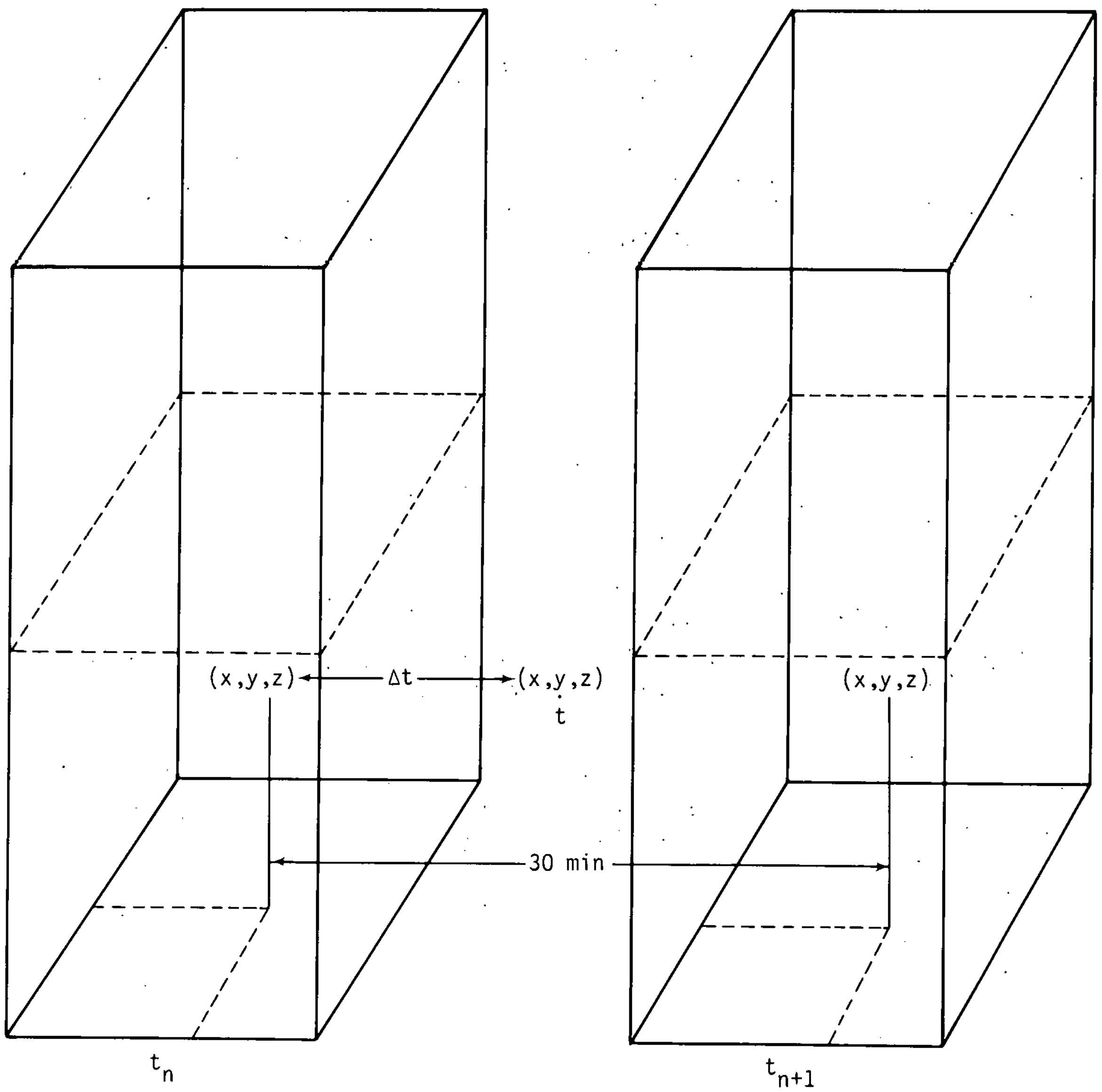


Figure 1. Grid used in the calculation of divergences



$$u(x,y,z,t) = u(x,y,z,t_n) + \frac{\Delta t}{30}[u(x,y,z,t_{n+1}) - u(x,y,z,t_n)]$$

Figure 2. Method of interpolation of values in space and time

$$V = (VT-VB)(Y/L) + VB$$

where:

$$VB = (V2-V1)(X/L) + V1$$

$$VT = (V4-V3)(X/L) + V3$$

L is the grid spacing, V1, V2 V3, and V4 are the wind components u,v, or w at the corners of the grid, and X and Y are the distances from the corner to the parcel. (Figure 3). After interpolating in x and y, these values of u,v, and w are interpolated in height to get the wind components in three-space at time t_n. Identical calculations are carried out at time t_{n+1} and an interpolation is done between these two times to get the wind speeds at the point (x,y,z,t). New values of x,y, and z are now calculated using the u,v, and w values and the following equations:

$$x' = x + u\,t$$

$$y' = y + v\,t$$

$$z' = z + w\,t$$

where: $t = 300$ sec = 5 minutes

As each trajectory segment is generated, its coordinates are printed along with the corresponding values of u,v, and w. The x,y, and z coordinates may optionally be punched on cards for use with a three-dimensional plotting routine. A sample trajectory plot is show in Figure 4.

The three-dimensional trajectory calculations are being used for the case study of several cases to interpret the rain concentration of selected species. Utilizing the air concentration and the trajectory data, a simple model is being sought to correspond to the observed precipitation deposition patterns.

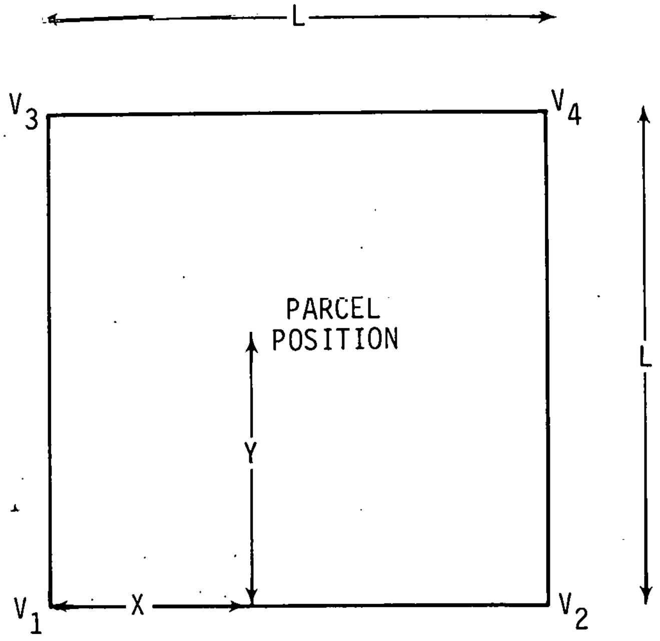


Figure 3. Grid used to interpolate in X and Y dimensions

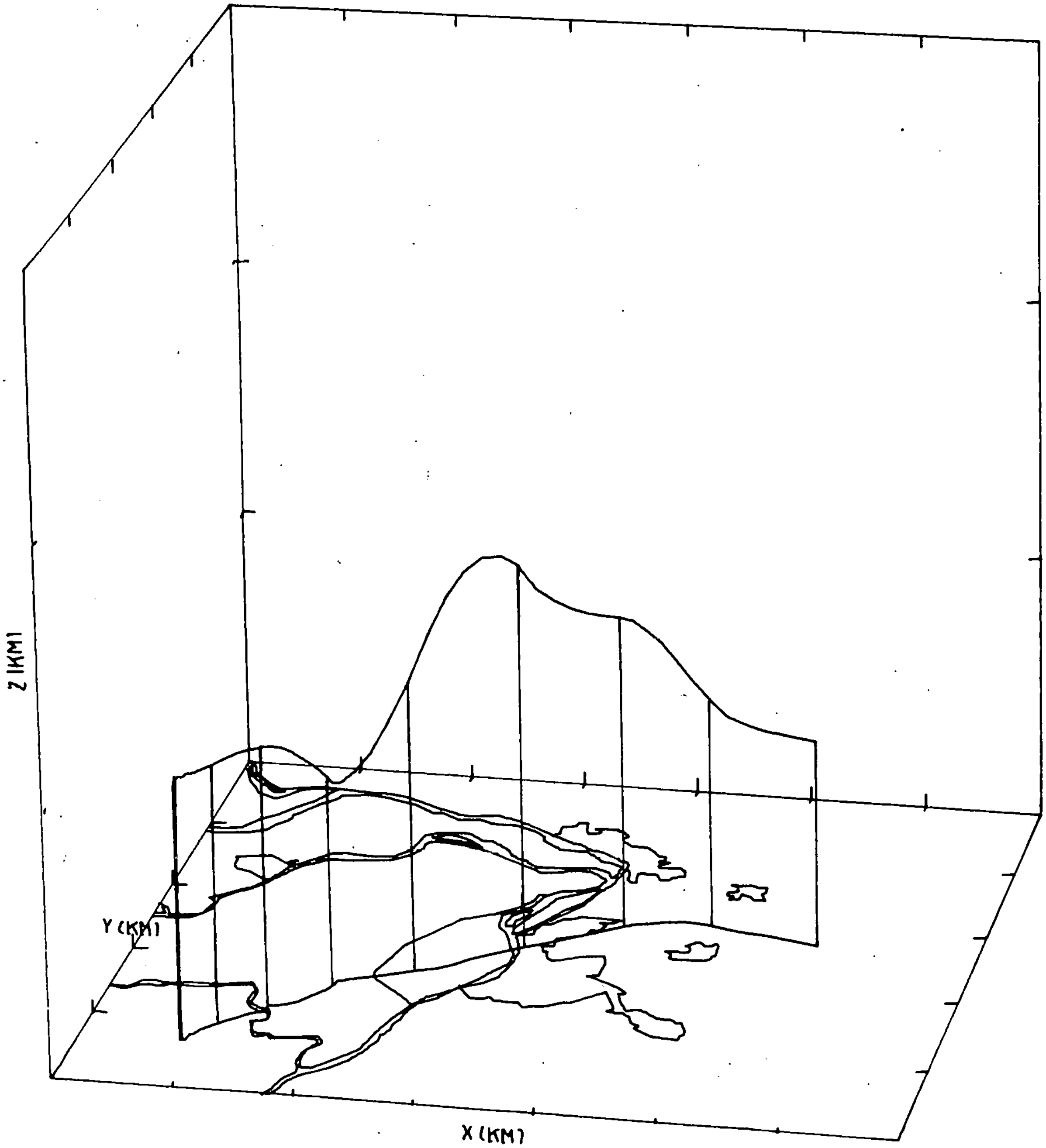


Figure 4. Sample trajectory generated on August 2, 1974, starting at 1200 CDT

APPENDIX A

Publications, July 1976 Through September 1977

Changnon, S.A., R.G. Semonin, and F.A. Huff, 1976: "A hypothesis for urban rainfall anomalies." J. Appl. Meterol., 15, 544-560.

Ochs, H.T. III and R.G. Semonin, 1976: "Microphysical computation in urban and rural clouds." Proceedings Intern. Conf. Cloud Physics, AMS, Boston, 22-26.

Semonin, R.G., 1976: "The variability of pH in convective storms." J.Water, Air, Soil Pollution, 6, 395-406.

Gatz, D.F., 1977: "A review of chemical tracer experiments on precipitation systems." Atmos. Environ. (accepted for publication).

Talks and Presentations

Semonin, R.G., 1976: "METROMEX to CORMEX: The need for regional programs." Paper presented at the Symposium of Man's Impact on Atmospheric Composition and Processes, Northeast Regional Meeting, American Chemical Society, Albany, N.Y., August.

Gatz, D.F., 1976. The chemical composition of precipitation and aerosols at St. Louis. Paper presented at the Symposium of Man's Impact on Atmospheric Composition and Processes, Northeast Regional Meeting, American Chemical Society, Albany, N.Y., August.

Peden, M.E., 1976: "Flameless atomic absorption determinations of Cd, Pb, and Mn in particle size fractionated aerosols." Paper presented at the 8th Materials Research Symposium, National Bureau of Standards, Gaithersburg, Md., September.

Semonin, R.G., 1976: "A raindrop size spectrometer." Paper presented at American Geophysical Union meeting, San Francisco, Calif., December.

Peden, M.E., F.F. McGurk, and L.M. Skowron, 1976: "Distribution of cadmium and zinc depositions in the St. Louis metropolitan area." Paper presented at American Geophysical Union meeting, San Francisco, Calif., December.

Gatz, D.F., 1977. Atmospheric aerosol sources in the St. Louis area. Seminar presented at the Illinois Institute for Environmental Studies Environmental Toxicology Seminar, Urbana, 10 March, and at the Illinois Environmental Protection Agency, Springfield, 15 March.

Stensland, G.J., 1977: Precipitation pH decrease since 1954 at Champaign-Urbana, Illinois. Presented at the Symposium on Quality of Precipitation, Spring Meeting of the American Geophysical Union, Washington, D.C., April.

APPENDIX B
ERDA-1199
Reports, Reprints, and Preprints

COO-1199-1	Huff, F. A., 1963: Study of rainout of radioactivity in Illinois. First Progress Report to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 58 p.
COO-1199-2	Huff, F. A., 1964: Study of rainout of radioactivity in Illinois. Second Progress Report to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 61 p.
COO-1199-3	Huff, F. A., 1965: Radioactive rainout relations on densely gaged sampling networks. Water Resources Res., 1(1), 97-108.
COO-1199-4	Huff, F. A. and G. E. Stout, 1965: Distribution of radioactive rainout in convective rainfall. J. Appl. Meteorol., 3(6), 707-717.
COO-1199-5	Huff, F. A., 1965: Study of rainout of radioactivity in Illinois. Third Progress Report to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 66p.
COO-1199-6	Huff, F. A., 1965: Radioactive rainout relations in convective rainstorms. Res. Report No. 1 to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 131 p.
COO-1199-7	Feteris, P. J., 1965: 1964 Project Springfield studies. Res. Report No. 2 to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 20 p.
COO-1199-8	Huff, F. A. and W. E. Bradley, 1965: Study of rainout of radioactivity in Illinois. Fourth Progress Report to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 20 p.
COO-1199-9	Stout, G. E. and F. A. Huff, 1967: Rainout characteristics for hydrological studies. Symposium on Isotopes in Hydrology. Vienna, 61-72.
COO-1199-10	Bradley, W. E. and P. J. Feteris, 1966: Study of rainout of radioactivity in Illinois. Fifth Progress Report to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 26 p.
COO-1199-11	Bradley, W. E. and G. E. Martin, 1967: An airborne precipitation collector. J. Appl. Meteorol., 6(4), 717-723.
COO-1199-12	Huff, F. A. and G. E. Stout, 1968: Relation between Ce^{144} and Sr^{90} rainout in convective rainstorms. Tellus, 20(1), 82-87.
COO-1199-13	Huff, F. A. and G. E. Stout, 1967: Time distributions of radioactivity and chemical constituents in rainfall. Proc. USAEC Meteorol. Info. Meeting, Chalk River, Canada, 503-513.

COO-1199-14 Huff, F. A., W. E. Bradley, and P. J. Feteris, 1967: Study of rainout of radioactivity in Illinois. *Sixth Progress Report* to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 19 p.

COO-1199-15 Wilson, J. W. and P. T. Jones III, 1968: Tracing tropospheric radioactive debris by isentropic trajectories. *Res. Report No. 3* to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 33 p.

COO-1199-16 Lyons, W. A. and J. W. Wilson, 1968: The control of summertime cumuli and thunderstorms by Lake Michigan during non-lake breeze conditions. *Satellite and Mesometeorol. Res. Paper No. 74* to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 32 p.

COO-1199-17 Wilson, J. W. and W. E. Bradley, 1968: Study of rainout of radioactivity in Illinois. Seventh Progress Report to U.S. Atomic Energy Commission. Contract AT(11-1)-1199, 64 p.

COO-1199-18 Stout, G. E., 1969: Study of rainout of radioactivity in Illinois. *Eighth Progress Report* to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 49 p.

COO-1199-19 Semonin, R. G., 1970: Study of rainout of radioactivity in Illinois. *Ninth Progress Report* to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 55 p.

COO-1199-20 Semonin, R. G., 1971: Study of rainout of radioactivity in Illinois. *Tenth Progress Report* to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 56 p.

COO-1199-21 Adam, J. R. and R. G. Semonin, 1970: Collection efficiencies of raindrops for submicron particulates. *Proc. Symposium on Precip. Scavenging*, Richland, Wash., 151-159.

COO-1199-22 Adam, J. R. and R. G. Semonin, 1970: A technique for the experimental measurement of collection efficiency. *Proc. Conf. Cld. Phys.*, Ft. Collins, Colo., 139-140.

COO-1199-23 Semonin, R. G. and J. R. Adam, 1971: The washout of atmospheric particulates by rain. *Proc. Conf. Air Pollution Meteorol.*, Raleigh, N. Car., 65-68.

COO-1199-24 Changnon, S. A., Jr., F. A. Huff, and R. G. Semonin, 1971: METROMEX: an investigation of inadvertent weather modification. *Bull. Am. Meteorol. Soc.*, *52*(10), 958-967.

COO-1199-25 Cataneo, R., J. R. Adam, and R. G. Semonin, 1971: Interaction between equal-sized droplets due to the wake effect. *J. Atmos. Sci.*, *28*(3), 416-418.

COO-1199-26	Cataneo, R. and D. L. Vercellion, 1972: Estimating rainfall rate-radar reflectivity relationships for individual storms. J. Appl. Meteorol., 11(1), 211-213.
COO-1199-27	Semonin, R. G., 1972: Tracer chemical experiments in Midwest convective clouds. Proc. Third Conf. Weather Mod., Rapid City, S. Dak., 83-87.
COO-1199-28	Semonin, R. G., 1972: The use of chemical and biological tracers in cloud physics. Intern. Conf. Cld. Phys., London.
COO-1199-29	Semonin, R. G., 1972: Study of rainout of radioactivity in Illinois. Interim Eleventh Progress Report to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 12 p.
COO-1199-30	Adam, J. R., R. Cataneo, D. F. Gatz, and R. G. Semonin, 1973: Study of rainout of radioactivity in Illinois. Eleventh Progress Report to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 157 p.
COO-1199-31	Henderson, T. J. and D. W. Duckering, 1973: Final Report METROMEX 1973: A summary of operations conducted by Atmospherics Incorporated during the period 7 July through 19 August 1973, 51 pp.
COO-1199-32	Changnon, S. A., Jr., R. G. Semonin, and W. P. Lowry, 1972: Results from METROMEX. Preprint Vol. Conf. on Urban Environ. and Second Conf. on Biometeor., Philadelphia, Amer. Meteor. Soc., 191-197.
COO-1199-33	Grosh, R. C. and R. G. Semonin, 1973: Moisture budgets and wind fields of thunderstorms passing over an urban area in the Midwest. Preprint Vol. Eighth Conf. on Severe Local Storms, Denver, Amer. Meteor. Soc., 130-137.
COO-1199-34	Huff, F. A., Editor, 1973: Summary Report of METROMEX Studies, 1971-1972. Illinois State Water Survey Rept. of Invest. No. 74, Urbana, 169 pp.
COO-1199-35	Gatz, D. F., 1972: Washout ratios in urban and non-urban areas. Preprint Vol. Conf. on Urban Environ. and Second Conf. on Biometeor., Philadelphia, Amer. Meteor. Soc., 124-128.
COO-1199-36	Lowry, W. P., 1973: 1973 Operational Report for METROMEX. Illinois State Water Survey, Urbana, 63 pp.
COO-1199-37	A collection of papers, 1974: Staff: METROMEX: An overview of Illinois State Water Survey Projects. Huff, F. A. and P. T. Schickedanz: METROMEX: Rainfall analysis. Gatz, D. F.: METROMEX: Air and rain chemistry analysis.

Ackerman, B.: METROMEX: Wind fields over St. Louis in undisturbed weather.

Semonin, R. G. and S. A. Changnon, Jr.: METROMEX: Summary of 1971-1972 results.

Bull. Amer. Meteor. Soc., 55(2), 89-100.

COO-1199-38 R. G. Semonin and D. F. Gatz, 1974: Study of Rainout of Radioactivity in Illinois. Twelth Progress Report to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 21 pp.

COO-1199-39 Henderson, T. J. and D. W. Duckering, 1972: Final Report METROMEX 1973: A summary of operations conducted by Atmospherics Incorporated during the period 5 July through 15 August 1972, 34 pp.

COO-1199-40 Ackerman, B., 1974: Wind fields over the St. Louis metropolitan area. J. Air Poll. Cont. Assoc., 24, 232-236.

COO-1199-41 Rattonetti, A., 1974: Determination of soluble Cadmium, Lead, Silver, and Indium in rainwater and stream water with the use of flameless atomic absorption. Anal. Chem., 46, 739-742.

COO-1199-42 Ackerman, B., 1974: Wind profiles and their variability in the planetary boundary layer. Prep. Vol. Symp. on Atmos. Diffusion and Air Poll., Santa Barbara, Amer. Meteor. Soc., 19-22.

COO-1199-43 Gatz, D. F., 1974: St. Louis air pollution: Estimates of aerosol source coefficients and elemental emission rates. Prep. Vol. Symp. on Atmos. Diffusion and Air Poll., Santa Barbara, Amer. Meteor. Soc., 109-114.

COO-1199-44 Ackerman, B., 1974: Spatial variability of the wind velocity in the lowest 500 meters. Prep. Vol. Sixth Conf. on Aerospace and Aeronautical Meteorol., El Paso, Amer. Meteor. Soc., 325-328.

COO-1199-45 Cataneo, R., 1974: Operational aspects of Project METROMEX - an inadvertent weather modification study. Prep. Vol. Fourth Conf. on Wea. Mod., Ft. Lauderdale, Amer. Meteor. Soc., 379-381.

COO-1199-46 Semonin, R. G. and S. A. Changnon, Jr., 1974: METROMEX: Lessons for precipitation enhancement in the Midwest. Prep. Vol. Fourth Conf. on Wea. Mod., Ft. Lauderdale, Amer. Meteor. Soc., 353-357.

COO-1199-47 Braham, R. R., Jr., 1974: 1974 Operational Report for METROMEX. Univ. of Chicago, 39 pp.

COO-1199-48 Gatz, D. F., 1975: Relative contributions of different sources of urban aerosols: Application of a new estimation method to multiple sites in Chicago. Atmos. Environ., 9, 1-18.

C00-1199-49	Henderson, T. J. and D. W. Duckering, 1975: Final Report METROMEX 1974: A summary of operations conducted by Atmospherics, Incorporated during the period 7 July through 17 August 1974, 48 pp.
C00-1199-50	Semonin, R. G., 1975: Study of rainout of radioactivity in Illinois. Thirteenth Progress Report to U. S. Atomic Energy Commission. Contract AT(11-1)-1199, 24 pp.
C00-1199-51	Henderson, Thomas, Jr., and Donald W. Duckering, 1976: METROMEX 1975: A summary report, 53 pp.
C00-1199-52	Hall, N. D., and K. V. Beard, 1975: Electrostatic force between a conducting sphere and dialectic sphere. Pure and Applied Geophysics, 113, 515-524.
C00-1199-53	Grover, S. N., and K. V. Beard, 1975: A numerical determination of the efficiency with which electrically charged cloud drops and small raindrops collide with electrically charged spherical particles of various densities. Journal of Atmos. Sciences, 32, 2156-2165.
C00-1199-54	Vogel, J. L., 1975: Surface effects from thunderstorms. Prep. Vol. Ninth Severe Local Storms Conf., Norman, Amer. Meteor. Soc., 113-119.
C00-1199-55	Auer, August H., Jr., 1975: 1975 Operational Report for METROMEX, University of Wyoming, 47 pp.
C00-1199-56	Changnon, S. A., Jr., and R. G. Semonin, editors, 1975: Studies of selected precipitation cases from METROMEX. Illinois State Water Survey Rep. of Invest. No. 81, Urbana, 329 pp.
C00-1199-57	Semonin, R. G., 1976: Study of air pollution scavenging. Fourteenth Progress Report to the Energy Research and Development Admin. Contract AE (11-1)-1199, 23 pp.
C00-1199-58	Semonin, R.G., B. Ackerman, D. F. Gatz, S. D. Hilberg, M.E. Peden, R. K. Stahlhut and G. J. Stensland, 1977: Study of air pollution scavenging. Fifteenth Progress Report to the Energy Research and Development Admin., Contract AE (11-1)-1199,