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

STUDY OF ATMOSPHERIC POLLUTION SCAVENGING

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

July 1978

by

Richard G. Semonin
Donald F. Gatz
Mark E. Peden
Gary J. Stensland

MASTER

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United States Department of Energy
Environmental Programs
Division of Biomedical and Environmental Research
Washington, D. C.

Richard G. Semonin
Principal Investigator

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STUDY OF ATMOSPHERIC POLLUTION SCAVENGING

ABSTRACT

The relative spatial variability of atmospheric deposition was studied for sampling networks of various areas in the U.S., Sweden, and the U.S.S.R. The data were derived from event, monthly, and yearly sample collection periods. The results indicate the relative variability for precipitation, chemical concentration of constituents, and the deposition increase in that order.

A factor analysis approach to interpretation of the role of aerosol in altering rainfall is presented. The results indicate that either aerosol does not influence rainfall amount, or a critical chemical component of the aerosol was not included in the analysis.

Careful analyses were carried out, comparing historical and current precipitation chemistry at Champaign-Urbana. The results show that the apparent high pH values of rainfall in 1954 were due to high values of calcium and magnesium and not due to low concentrations of sulfate and nitrogen species.

New field efforts were initiated in 1978 in east-central Illinois to measure rain chemistry with improved precision over previous effort. The preliminary results from the first light rainshower show some puzzling relationships between the amount of rain and various chemical concentrations. The pH appears to be inversely related to rain volume, but other ionic species are not so easily identified with rain amount. The summer field experiment has, thus far, produced approximately 12 additional events which are in various stages of analysis.

The study of the stability of ions in precipitation was continued and is the subject of additional proposed work. The results are very firm at this time, that either wet-only sampling must be carried out, or the sample must be preserved at 4°C to retain the chemical integrity of the sample. It is recommended, however, that filtration of the sample be accomplished within 12 hours of the cessation of precipitation to ensure stability of the ionic composition.

The METROMEX effort has been summarized in a two-volume report by the Survey. A synopsis of the Volume 2, "Causes of Precipitation Anomalies," is given.

CHAPTER 1

Spatial Variability of Atmospheric Deposition

Donald F. Gatz

INTRODUCTION

Three typical purposes for measuring atmospheric deposition in precipitation with a network of collectors have been listed by Granat (1976). These are:

- 1) measurements of the input of elements or ions to ecosystems over time periods such as daily, monthly, or yearly,
- 2) evaluation of sources of chemical species in rain, and
- 3) measurement of long-term trends in deposition or concentration in precipitation.

To these might be added (Gatz, 1974):

- 4) measurement of deposition of tracer materials released in known amounts into precipitation systems.

To achieve most of these objectives, it is necessary to understand the accuracy with which a network of stations can measure deposition over various time and space scales. For example, for the METROMEX network, how accurately were 80 samplers able to measure event deposition over an area of 1900 km²? This information is crucial to assessing the accuracy of scavenging efficiency measurements, where the estimated tracer deposition is expressed as a fraction of that released. On a larger scale, to look for differences in annual or seasonal deposition between geographic regions, we must know how accurately deposition can be measured on these time and space scales.

In all these situations, we use a sum of measurements at a discrete number of sampling points to estimate the integral of a continuous function (deposition) over an area. The accuracy of this approximation depends on the variability of the deposition field over the time period and area of interest. The greater the spatial variability, the less accurate the estimate of deposition over an area for any time period.

Two types of variability may be identified here. One has obvious causes, such as known sources. For example, high Zn deposition occurs near a Zn smelter, and sea salt deposition decreases with distance from a sea coast. The other type of variability is random and results from the stochastic processes of precipitation formation, scavenging, and deposition, and their interactions. Most observations

include both types of variability. In some cases the situation is such that local sources are small or absent. Then observed variability is all random. In other cases local sources add some systematic variability to that attributable to random processes.

Estimation of total rainfall over an area from a discrete number of raingages is completely analogous to estimation of deposition of materials in rain. The problem of estimating rainfall over an area from a network of gages has received considerable attention in hydrological literature (see, for example Bras and Rodriguez-Iturbe, 1976 a,b), and the statistical treatments developed for deposition of rainwater apply equally well to deposition of chemical species in rain. Unfortunately, the few investigations that have reported spatial variability of rainwater constituents have so far not taken full advantage of the mathematical formulations developed for the analogous problem of rainfall.

The purpose of this chapter is:

- 1) to review critically the information currently available in the literature on spatial variability of precipitation constituents, and
- 2) to present new results from the METROMEX precipitation chemistry network.

DEFINITION OF TERMS

At this point we define some terms that will be used throughout this report. The first group of terms refers to materials reaching the earth's surface in precipitation, or to the falling water itself.

Precipitation may be either rain or snow. It has units of length (cm), which is equivalent to volume/area (cm^3/cm^2). If snow, the melted water depth is referred to.

Concentration is the mass of a rainwater constituent per unit volume of rainwater. The units are mass/volume ($\mu\text{g}/\text{cm}^3$).

Deposition is the mass of a rainwater constituent deposited on a unit area of land surface. It has units of mass/area ($\mu\text{g}/\text{cm}^2$) and is the product of precipitation (cm^3/cm^2) and concentration ($\mu\text{g}/\text{cm}^3$).

The next group of terms refers to the variability of precipitation, concentration, or deposition over an area. The average deviation, AD, is given by

$$AD = \frac{1}{N} \sum_{i=1}^N |x_i - \bar{x}|$$

where x_i is a measurement at one of a total of N sampling sites, and $\bar{x}$ is the mean of the N measurements. In words, one first calculates the mean of all measurements in the network. Then a deviation from the mean (absolute value) is calculated for each site. These deviations are summed and divided by the number of measurements, to get the average deviation.

The standard deviation, SD, is given by

$$SD = \left[\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2 \right]^{\frac{1}{2}}$$

The procedure here is to square the deviations from the mean before summing; then dividing, in this case by $N-1$, and then taking the square root of the result.

The root mean square deviation (RMSD) is defined by some (Bevington, 1969) identically to the standard deviation, but it is frequently applied to situations where deviations are computed separately for a number of different groups, always with reference to the means of the respective groups, before squaring, summing, and averaging. Thus, the RMSD is given by

$$RMSD = \left[\frac{\sum_{i=1}^{N_1} (x_{i1} - \bar{x}_1)^2}{N_1 - 1} + \frac{\sum_{i=1}^{N_2} (x_{i2} - \bar{x}_2)^2}{N_2 - 1} + \dots + \frac{\sum_{i=1}^{N_p} (x_{ip} - \bar{x}_p)^2}{N_p - 1} \right]^{\frac{1}{2}}$$

where p is the number of separate groups.

The term relative variability refers to any of the deviations just defined divided by the mean value and multiplied by 100 to convert to units of percent.

In a normal distribution, the interval from $\bar{x} - SD$ to $\bar{x} + SD$ is the 68% confidence interval. Similarly, for a normally distributed variable, 90% confidence corresponds to the interval $\bar{x} \pm 1.64 SD$ and 95% confidence corresponds to the interval $\bar{x} \pm 1.96 SD$.

Rainfall, concentrations, and depositions are not usually normally distributed, so that these confidence intervals are only approximations for such data. Further, these confidence intervals are not exact for RMSD's, even for normally-distributed variables, since the deviations are with respect to group means rather than the overall mean.

LITERATURE REVIEW

Available data on the variability of deposition of materials in precipitation are limited to those in four published papers and a set of unpublished data. The data may be stratified according to the various space and time scales investigated, as shown in figure 1.

	Event	Monthly	Yearly
Small <10 ⁴ km ²	Stout and Huff, 1967 Granat, 1976 Gatz, 1978 (this paper)	Stout and Huff, 1967 Granat, 1976 Gatz, 1978 (this paper)	Granat, 1976
Medium 10 ⁴ -10 ⁶ km ²		Granat, 1976	
Large >10 ⁶ km ²		Karol and Myatch, 1972	

Figure 1. Summary of available data on variability of chemical species in precipitation, stratified by space and time scales.

Small Scale

Most of the information available has been collected over small scales, on individual events or in monthly samples. The data include radioactive materials, naturally occurring substances, and materials available to precipitation from man's activities.

Results from Illinois. Stout and Huff (1967) presented daily values of relative variability, V (average deviation/mean value), for both concentration and deposition of gross beta radioactivity, and rainfall, over 1000 km². Rain was collected in open collectors from 100 storms during the convective precipitation seasons (spring and summer) of 1962 to 1965. Results are shown in Table 1.

Table 1. Relative variability of gross beta radioactivity and rainfall in 1964 storms over a 1000 km² network (from Stout and Huff, 1967).

<u>Date</u>	<u>Number of stations</u>	<u>Mean rain, mm</u>	<u>Relative variability (%)</u>		
			<u>Rainfall</u>	<u>Concentration</u>	<u>Deposition</u>
24 March	15	37.1	19	19	20
18 April	25	48.5	15	26	31
19 April	26	66.3	17	19	20
20 April	31	30.0	23	27	31
23 April	27	9.4	22	18	24
11 May	13	7.9	38	49	45
5 June	25	4.1	11	51	53
12 June	21	9.4	48	25	61

Mean			24	29	36
Median			20	26	30

The daily values of V in eight rains ranged from 11 to 48% for rainfall, from 18 to 51% for concentration, and from 20 to 61% for deposition. Median values were 20% for rainfall, 26% for concentration, and 30% for deposition. In two of the eight cases, continuous rain fall, while the others were convective showers or storms. One of the continuous rain cases had the lowest V , at 11%. This was expected, but the same case had unexpectedly high values of V for concentration (51%) and deposition (53%). Thus, continuous rains do not necessarily provide element concentrations or depositions of low relative variability, even if precipitation variability is low.

Stout and Huff (1967) presented median values of V for 5 to 15 rain events (a time scale approximating a month) for gross beta and Sr^{90} radioactivity over areas of 25, 1000, and 7800 to 15,500 km^2 . These results are shown in Table 2.

Table 2. Median values of network relative variability in 1962-1964 storms (from Stout and Huff, 1967).

Network area, km ²	Year	Number of storms	Number of sampling stations	Relative variability (%)		
				Rainfall	Concentration	Deposition
<i>Gross beta radioactivity</i>						
25	1962	15	5- 6	14	25	25
1000	1963	9	9-15	24	26	33
1000	1964	8	13-31	21	26	31
<i>Sr⁹⁰ radioactivity</i>						
25	1962	5	5- 6	12	14	21
1000	1962	5	5-10	13	20	20
7800- 15500	1963	10	6-15	57	57	37

Again, relative variability was found to increase in the order rainfall, concentration, deposition. Table 2 also shows that V increased as the area of the network increased and collector density decreased.

Stout and Huff (1967) also estimated the sampling error of single stations in the center of their 25 and 1000 km^2 networks, by comparing their values with network means. Median V values for 15 storms on the 25 km^2 network and 17 storms on the 1000 km^2 network were in the range of 20 to 25% for both concentration and deposition, both considerably higher than the corresponding values for rainfall, which were 5 to 15%. Sampling errors were only slightly greater over 1000 km^2 than over 25 km^2 ; 13 vs. 6% for rainfall, 25 vs. 23% for concentration, and 23 vs. 18% for deposition.

Results from Sweden. Granat (1976, 1977) expressed areal variability in terms of the standard deviation divided by the mean. This parameter is also known as the coefficient of variation. Rain samples were collected in open funnel-and-bottle collectors, and snow in polyethylene buckets. The samples were obtained

from frontal precipitation systems. Variability of concentrations in several individual events sampled near the coast of Sweden are given in Table 3.

Table 3. Variability of precipitation and ion concentrations for several precipitation events over 800 km² near the coast of Sweden (Granat, 1976).

Event no.	No. of collectors	Standard deviation/mean (%)					
		Precipitation	SO ₄ ⁼	NO ₃ ⁻	NH ₄ ⁺	Na	Ca
1	62	26	33	--	--	68	--
2	57	67	51	30	--	56	--
3	46	54	37	31	114	77	--
4	66	10	40	--	--	62	--
5	68	119	13	36	87	44	148
6	70	16	12	--	--	60	--
7	66	40	20	31	61	57	59
Mean		47	29	32	87	61	104
Median		40	33	31	87	60	104

Part of the measured variability of Na concentration is caused by the well-known depletion of Na aerosol with distance from the coast.

The median value for precipitation variability in Table 3 is 40%. The variability of both sulfate and nitrate concentrations was less -- about 30% -- while that for Na was greater, at 60%, partly due to reasons already mentioned. Large median values were also observed for NH₄⁺ and Ca, but only two or three events were analyzed.

Granat (1976, 1977) also discussed areal variability of monthly samples collected during seven months over five areas, each about 2500 km². Variabilities of both concentrations and depositions are summarized in Table 4. Variability is expressed here as root mean square deviation. In each area, differences between individual monthly values and the monthly area mean were squared and averaged over all sites and months; then a square root was taken. The error was then expressed relative to the 7-month mean in each area.

Comparison between event and monthly variability is not possible for Granat's data (Tables 3 and 4) because the respective data sets were collected at different locations, over areas of different size. For the monthly data, however, we can compare the relative magnitudes of the rainfall, concentration, and deposition variabilities and compare the Swedish and United States (Stout and Huff, 1967) results.

Table 4. Variability of monthly concentration and deposition over five areas of approximately 2500 km² in Sweden (Granat, 1976).

Area	RMSD/7-month mean (%)								
	Precipitation	SO ₄ ⁼	Cl ⁻	NO ₃ ⁻	NH ₄ ⁺	NA	K	Mg	Ca
<i>Concentration</i>									
Forshult		15	23	17	24	25	37	18	21
Sjöängen		18	27	16	19	30	47	26	34
Plönninge		14	21	12	28	21	75	33	28
Smedby		12	34	14	23	31	75	25	59
Arup		16	24	19	35	33	60	31	34
Mean		15	26	16	26	28	59	27	35
Median		15	24	16	24	30	60	26	34
=====									
<i>Deposition</i>									
Forshult	21	18	22	20	23	24	32	18	17
Sjöängen	31	27	28	25	35	25	38	21	26
Plönninge	26	24	34	21	36	35	86	33	26
Smedby	14	13	22	14	30	18	77	19	50
Arup	19	24	30	23	30	29	49	22	31
Mean	22	21	27	21	31	26	56	23	30
Median	21	24	28	21	30	25	49	21	26

Deposition median minus concentration median		9	4	5	6	5	-11	-5	-8

In Sweden, as in the United States, variability in general increased from precipitation to concentration to deposition. Notable exceptions were that sulfate and nitrate concentrations showed values about 5% less than precipitation, and deposition values for K, Mg, and Ca were 5 to 11% higher than concentration, although both deposition and concentration variability were greater than precipitation.

Granat (1977) also reported results for areal variability on an annual basis for both concentration and deposition for the five areas listed in Table 4. The results are given in Table 5. For each area, yearly average concentrations and

total depositions were computed at each site and the ratios of the standard deviations to the respective means were calculated for each area. The values given in Table 5 are the means of these results over the 5 areas.

Table 5. Yearly variability for five areas listed in Table 4.

		Five-area mean value of (standard deviation/area mean)							
	Precipitation	SO ₄ ⁼	Cl ⁻	NO ₃ ⁻	NH ₄ ⁺	Na	K	Mg	Ca
Concentration		4	8	5	8	8	17	8	10
Deposition	5	6	8	6	9	8	16	7	9

Table 5 shows that yearly variability over areas of 2500 km² is approximately the same for concentration and deposition. Variabilities of yearly concentrations or depositions are approximately one-third to one-fourth of the respective variabilities of monthly samples. The yearly variability of precipitation over the same areas is 5%, just at the lower end of the range of the observed variabilities of the ions.

Results from METROMEX. Results are presented here for the first time on variability of rainfall and deposition over 1900 km² near St. Louis measured as part of the METROMEX study (Changnon et al., 1971; Gatz, 1974). Samples were taken in 80 open collectors, changed daily during summer seasons from 1972 to 1975. The samples were predominantly from convective rainfall. Results are summarized in Table 6, where variability is expressed in terms of the standard deviation divided by the mean, the same parameter used by Granat for his event results (Table 3). Table 6 shows minimum, mean, median, and maximum values of standard deviation/mean, calculated for individual days. Also shown are analogous values calculated from the standard deviation and the mean of the mean depositions over all days at each of the 80 sampling sites. These latter values approximate the variability of the summer season precipitation and deposition.

Summary of Small Scale. The small scale event results from Sweden and St. Louis cannot be compared in detail, since the St. Louis results are for deposition over 2500 km² and the Swedish results for concentration over 8000 km². However, a general comparison may be made using the results from Stout and Huff (1967) and Granat (1976) that relative variability increases in the order rainfall, concentration, deposition.

Table 6. Summary of variabilities (standard deviation/mean value, %) for precipitation and element deposition over event and seasonal time scales.

	<u>Rainfall</u>	<u>Li</u>	<u>Na</u>	<u>Mg</u>	<u>K</u>	<u>Ca</u>	<u>Zn</u>
Number of Days	41	27	20	20	26	20	26
<i>Individual Days</i>							
Minimum	17	37	56	58	54	50	105
Mean	112	112	98	100	147	92	195
Median	100	101	84	92	126	86	176
Maximum	316	224	193	222	281	160	494
<i>All Days</i>	35	38	32	44	45	35	125

First, we note that rainfall variability for the St. Louis network was about 2.5 times that of the Swedish network, based on medians. This would be expected when comparing United States convective rainfall with frontal rainfall in Sweden. The remaining results may be compared with reference to the differences in rainfall variability, using median values in all cases. A direct comparison is possible only for Na, which was the only element measured in common, except for Ca, which Granat measured on only two days. Variability of Na deposition at St. Louis was higher than that of Na concentration in Sweden, but only by a factor of 1.5, which is less than the difference found for rainfall. The variabilities of the other elements measured at St. Louis generally exceeded those of sulfate and nitrate measured in Sweden by factors of about 3. Thus, we can say that the differences between the St. Louis and the Swedish event results are generally consistent with the differences in network area, sampling, density, and with rainfall type for the two sets of data.

Comparison of seasonal variability at St. Louis and monthly variability in Sweden may also be made with reference to the differences in rainfall variability. The seasonal rainfall variability for convective rain over 1900 km² at St. Louis exceeds that for monthly frontal rainfall over 8000 km² in Sweden by a factor of 1.7. The comparable ratio for Na is 1.3, and for the means of the other analyses at the two locations, about 1.4. Thus, the monthly/seasonal differences between the St. Louis and Swedish results are again approximately as expected from differences in rainfall variability.

One exception to this general agreement in event and monthly/seasonal results is Zn deposition at St. Louis. There are known Zn sources, including a

Zn smelter, within the sampling network at St. Louis, and this is reflected in the consistently higher variability values for Zn on both time scales. Some systematic variability is probably also present in the results for the other elements measured at St. Louis, since airborne element concentrations are known to be higher in urban areas relative to surrounding rural areas by factors of 2 to 3 even for soil elements such as Na, Mg, K, and Ca (Gatz, 1978).

For small scale studies, results in the literature have generally been expressed as some form of relative variability -- average deviation or root mean square deviation divided by a mean. The few results available on medium and large scale variability have used an alternate approach -- that of calculating correlation coefficients between pairs of collectors and plotting the results as a function of distance between collectors.

Medium Scale

The correlation vs. distance approach has been used by Granat (1976) to express variability of monthly concentrations of $\text{SO}_4^{=}$, Cl^- , NO_3^- , NH_4^+ , Na, K, Mg, and Ca in samples from open collectors over 144,000 km^2 in Sweden. Correlation coefficients were very near 1.0 for collectors within 300 m of each other. They dropped to 0.5 to 0.8 for the various constituents within 100 km. Between 100 and 350 km the range of correlation coefficients remained approximately constant at 0.4 to 0.7. Between 350 and 550 km the range dropped to about 0.15 to 0.5.

Large Scale

The only paper to discuss the variability of precipitation composition over large areas in quantitative terms is by Karol and Myatch (1972). They discuss the statistical structure of the fields of mean monthly concentrations and depositions of several chemical constituents measured over large areas in the USSR from 1958 to 1965. Only data from samples collected between April and September were used.

Karol and Myatch also showed a graph of correlation coefficient vs. distance for precipitation, concentration, and deposition. All the curves dropped rapidly from 1.0, reaching correlation coefficients of 0.35 to 0.50 at 200 km, and 0.20 to 0.30 at 400 km. Beyond 400 km, the curves dropped very slowly, reaching values of 0.15 to 0.20 at 2000 km.

Random observational errors were determined by extrapolating correlation functions to the zero point. A root mean square relative random error of 35 to 45% was found. These values agree reasonably well with corresponding values for much smaller areas in Sweden and near St. Louis.

The results of this literature review are summarized and synthesized in the following section, in which the current status of knowledge is assessed.

SUMMARY AND CONCLUSIONS

With only a handful of studies available in the literature, the current status of knowledge on spatial variability of atmospheric deposition can only be called "fragmentary." The various studies were carried out under widely varying conditions of network area, collector density, elements or ions analyzed, and precipitation type. Furthermore, several different methods of expressing spatial variability have been used.

Nevertheless, in an attempt to show some of the major relationships that appear in the available data, Table 7 has been prepared. Each author's results have been reduced to a single relative variability value for each of the three categories (rainfall, concentration, and deposition), in each separate network area investigated. Thus, for concentration and deposition, the numbers that appear may be averages over all elements or ions measured in a given network and time period.

Table 7. Summary of information in the literature on variability of atmospheric deposition over various sampling times.

References	Area km ²	No. of samplers	Relative variability (%)		
			Rainfall	Concentration	Deposition
<i>Event</i>					
Stout and Huff (1967)	1000	13-31	20	26	30
Gatz (this report)	1900	80	100	--	111
Granat (1976, 1977)	8000	80	40	30	--
<i>Monthly</i>					
Stout and Huff (1967)	25	5-6	13	19	23
Stout and Huff (1967)	1000	5-31	19	24	28
Gatz (this report)	1900	80	35	--	40
Granat (1976, 1977)	2500	7-12 ^a	21	29	28
Stout and Huff (1967)	7800-15500	6-15	57	57	37
Karol and Myatch (1972)	4x10 ⁶	28-45	--	35-45	35-45
<i>Yearly</i>					
Granat (1976, 1977)	2500	7-12 ^a	5	8	9

^aIn each of 5 different areas.

For monthly samples, Table 7 suggests that relative variability generally increases from small areas to large areas. For rainfall, the relative variability increases from less than 15% for 25 km² to over 50% for areas of 7800 to 15500 km². For concentration, the values increase from about 20% at 25 km² to 35 to 60% in the largest areas. Similar values occurred for deposition. This is contrary to the results of Huff and Neill (1957) for rainfall over areas up to 2500 km² where sampler density was constant with varying network size. Thus, the increase in variability with size noted here may actually reflect a decrease in sampler density with increasing network area.

For all time periods, the relative variabilities of concentration and deposition were quite similar, but both generally exceeded those for rainfall over the same size area.

Finally, for areas of 1000 to 2500 km², relative variabilities were in the 20 to 30% range for event and monthly samples, but dropped to less than 10% for yearly samples.

Exceptions to these values occur when significant non-random variability occurs, as for example at St. Louis. The large urban area causes a systematic variability in both rainfall and element deposition.

The U. S. Atmospheric Deposition Network currently plans about 50 stations in states with areas totaling about 4 million km². Thus each sampling station represents about 80,000 km². This is a much larger network and a much lower density than all except one of the networks for which variability has been discussed in the literature. The area of the United States network is about the same, and the density slightly greater, than the USSR network (Karol and Myatch, 1972).

Thus, the only information available in the literature would suggest that we should expect root mean square random relative variability of 35 to 45% for both concentration and deposition, for monthly samples. It can reasonably be expected that annual deposition and mean concentration would have considerably less variability, perhaps 10 to 15%.

For a normal distribution, this is equivalent to an accuracy of ± 10 to 15% with 68% confidence. Other confidence intervals could of course be calculated for a normally-distributed parameter, as explained earlier.

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CHAPTER 2

A Test of the "Pollution Causes Rain" Hypothesis at St. Louis

Donald F. Gatz

INTRODUCTION

The rapid increase in annual precipitation at LaPorte, Indiana during the 1940's was accompanied by a similar jump in the number of smoke and haze days at Chicago (Changnon, 1968). This caused speculation that airborne pollutants might be somehow involved in increasing the precipitation at LaPorte. Since then a number of papers have examined relations between aerosols and rainfall.

Both increases and decreases in rainfall have been attributed to increased concentrations of aerosols or some component of aerosols such as condensation nuclei. Warner (1968) found a decrease in rainfall coinciding with an increase in sugar cane production in areas affected by smoke from cane fires in Australia. Conversely, increased concentrations of condensation nuclei in pulp and paper mill plumes were associated with increased rainfall in Washington State (Hobbs et al., 1970).

Braham (1974) found that increases in the numbers of small cloud droplets near an area of increased summer rainfall east of St. Louis could be attributed to enhanced condensation nuclei concentrations. Other studies (Vogel and Huff, 1977) have shown that the distribution of summer rainfall in the St. Louis area varies with surface wind direction before the rain and with the direction of cell motion within the rain systems. The locations of the rainfall maxima under various combinations of surface wind direction and storm cell motion suggest a tendency for cell rainfall to maximize shortly after ingestion of the "urban plume" of heat, moisture, and aerosols. Also at St. Louis, Gatz (1978) identified four area-wide sources (including a natural one) and three prominent local sources of airborne trace elements using factor analysis. This method also produced factor scores (indices of source strength) for each of the sources identified at 12 separate filter sampling locations.

It appears that daily indices of various pollutant source strengths could be combined with rainfall data from METROMEX in various subnetworks (Huff and Vogel, 1978) to test whether it is the pollutant aerosol component of the urban plume that causes excess summer rainfall near St. Louis. If pollutants cause the excess urban-related rainfall, then the indices of pollutant source strength downwind of the sources should be highly correlated with rainfall at locations determined by the surface winds and storm motion.

This paper investigates correlations between 1) daily factor scores (indices of source strength) and 2) storm rainfall in 22 selected areas (Huff and Vogel,

1978) near St. Louis. The purpose of this paper is to test the hypothesis that the aerosol component of the urban plume causes the excess summer rainfall observed near St. Louis.

METHODS

Rainfall was measured in the 250-gage METROMEX network of recording raingages. Average storm amounts were tabulated for the 22 areas shown in figure 1.

The factor scores used in the correlation analysis with rainfall data were calculated as part of the factor analyses performed for an earlier paper (Gatz, 1978). A principal components model was used in the analysis. For any observation, variables are related to the factors by the expression

$$z_j = a_{j1}F_1 + a_{j2}F_2 + \dots a_{jm}F_m$$

where

z_j is the j th standardized variable,

$$z_j = \frac{x_j - \bar{x}}{\sigma_j}$$

x_j is the observed value of variable j ,

$\bar{x}$ is the mean value of variable j over all observations,

σ_j is the standard deviation of variable j ,

m is the number of factors common to all the variables, and

a_{ji} are the factor loadings.

One of the attractive features of factor analysis is that the original variables (in this case element concentrations in air) can be replaced by the factors without losing much of the original information. For each case (in this situation, a case is a filter sample) a score may be computed for each factor i from the equation

$$F_i = b_{i1}z_1 + b_{i2}z_2 + \dots b_{ip}z_p$$

where p is the number of variables and the b_{ij} are the factor score coefficients. The factor scores may be used to replace the original variables in further

Figure 1. Map of rainfall areas (Fig. B-25, METROMEX Vol. 1, p. 54). Huff, F.A., and J.L. Vogel, 1977: Comparison of urban and topographic effects in selected network areas, In: Changnon, S.A., F.A. Huff, P.T. Schickedanz, and J.L. Vogel, Summary of METROMEX, Weather Anomalies and Impacts, Bull. 62, Ill. State Water Survey, Urbana.

analyses. In this paper the factor scores are used as indices of the daily "source strength" of the various pollution sources identified, at each of several sampling sites. The scores have mean zero and standard deviation one.

Further discussion of factor analysis may be found in Harman (1967) or Rummel (1970).

RESULTS

Correlation coefficients between mean storm rainfall and aerosol source factor scores were calculated for every combination of the 22 areas shown in figure 1, and 48 separate factors identified at the 12 filter sampling sites shown in figure 2. Key results are summarized in Table 1. The number of pairs of data used in each correlation analysis varies from 25 to 52, reflecting the number of valid filter samples collected at each site during the summers of 1973, 1974, and 1975.

Table 1. Selected results of correlation analysis.

	Site Number				
	33	49	79	113	303
Factor number	3	2	5	3	1
Number of data pairs	52	31	25	49	32
Number of correlations	22	22	22	22	22

Correlation expected to be exceeded in 5% of the cases by chance	0.27	0.36	0.40	0.28	0.35
Percent of cases in which this correlation actually was exceeded	18	14	23	45	45

Correlation expected to be exceeded in 1% of the cases by chance	0.36	0.45	0.50	0.36	0.45
Percent of cases in which this correlation actually was exceeded	4	4	9	4	4

Figure 2. Map of filter sites (from earlier factor analysis paper).

In any procedure where samples are selected repeatedly from two populations, and their correlation coefficients calculated, a certain number of high coefficients will occur by chance. To exclude factors having high correlations only by chance, the factors selected for listing in Table 1 include only those for which more than 1% of the 22 correlations were higher than the value expected 1% of the time. For example, for factor 3 at site 33, a correlation coefficient of 0.36 should be exceeded only 1% of the time by chance (Bevington, 1969). It was actually exceeded 4% of the time. The coefficients expected to be exceeded in 5% of the cases, and the actual percent of cases exceeding that value, are also shown.

Thus, the factors listed in Table 1 had more high correlation coefficients than would be expected by chance, and must be examined for their possible causal relationships with rainfall in the various St. Louis area subnetworks. Note that for 22 correlations, even one correlation above the 1% value means that 4% of the observations exceed the criterion, qualifying the factor for listing in Table 1. With this in mind, it is clear that the factors listed in Table 1 had either one or two correlations above the 1% criterion value. Considerably more than 5% exceeded the 5% criterion value, however.

We will now examine each of the five selected factors, for spatial relationships between filter site location and the location of rain areas where correlation coefficients exceeded the value expected 5% of the time. The results are given in figures 3-7, each figure corresponding to a separate factor for which high correlations with rain were found.

There are several general things to notice about the results. The five factors having the highest correlations with rainfall occurred at five different filter sampling locations. The five factors were all different in the sense that a different set of elements was associated with each. Four of the five factors could be classified as being "pollutants." These include auto exhaust (site 33, figure 3), secondary sulfate (site 113, figure 6), and industrial metals (sites 49 and 79, figures 4 and 5, respectively). All these had positive correlations, indicating that rainfall increased with enhanced element concentrations. The last factor (Fig. 7) had a soil dust source, and negative correlations with rainfall. The following paragraphs give further details on each of the five factors.

Figure 3 shows the areas most highly correlated with factor 3 at site 33, and their correlation coefficients. This is an auto exhaust factor, with high loadings on Br and Pb, as shown in the figure, and accounting for 12% of the total variance of element concentrations at site 33. None of the 5 wind direction categories (four quadrants plus variable) was associated with this factor. That is, all wind direction loadings were less than 0.25. Still, it should be pointed out that a four-lane divided highway runs north and south about 0.5 km west of the filter sampling site.

The one area (refineries) exceeding the 1% criterion and two of the three areas exceeding the 5% criterion are clustered near the filter sampling site. The third area that exceeded the 5% criterion was in west suburban St. Louis, far from the filter site.

Figure 3.. Rain areas having highest correlations with factor 3 at filter site 33.

Figure 4 shows the three rain areas most highly correlated with factor 2 at filter site 49, and their respective correlation coefficients. This is an industrial metals factor, accounting for 13% of the variance at site 49. It is strongly associated with southwest winds, which bring the highly-loaded metals (Ti, Fe, Zn, and Pb) from industrial areas in St. Louis, East St. Louis, Granite City, and nearby municipalities. See Gatz (1978) for further discussion of these sources.

Again in this case the refineries area had the highest correlation coefficient, and was the only one to exceed the 1% criterion. Filter site 49 was located within the refineries rain area. One of the remaining two areas exceeding the 5% criterion was also located relatively close to the filter site, while the third rain area was once again the suburban west area.

Figure 5 shows the five rain areas most highly correlated with factor 5 at site 79. This again is an industrial metals factor, almost certainly the large steel mill in Granite City, located just a few kilometers southeast of the filter site. It accounts for 7% of the variance in the element concentrations at site 79.

Two rain areas exceeded the 1% criterion. They are overlapping and located generally east and southeast of the filter site. Two of the remaining three areas exceeding the 5% criterion overlap the first two mentioned and are located somewhat more to the east. The last area includes all rainages east of the Mississippi River, and includes all four of the areas mentioned previously in connection with this factor.

Figure 6 shows the 10 rain areas most highly correlated with factor 3 at filter site 113. This factor represents secondary sulfate and has a weak association with southeast winds. It accounts for 10% of the total variance at the filter site.

Only the Edwardsville rain area had a correlation coefficient in excess of the 1% criterion, but it and nine others exceeded the 5% criterion. The 10 areas overlap heavily and are located primarily in the northeastern quadrant of the research circle. Most of the area of these 10 regions lies more than 20 km from the filter site.

Figure 7 shows 10 rain areas most highly correlated with factor 1 at site 303. This factor represents a soil dust source and accounts for 46% of the variance in element concentrations at the filter site.

In contrast to the first 4 factors, where highly correlated areas were generally clustered together, these 10 areas are scattered over the research circle. Their correlations are all negative, indicating an inverse correlation between rainfall and airborne soil dust concentrations at site 303.

Figure 4. Rain areas having highest correlations with factor 2 at filter site 49.

Figure 5. Rain areas having highest correlations with factor 5 at filter site 79.

Figure 6. Rain areas having highest correlations with factor 3 at filter site 113.

Figure 7. Rain areas having highest correlations with factor 1 at filter site 303.

DISCUSSION

Two major results have been observed. The first is that pollutant factors (auto exhaust, secondary sulfates, and metals) were found to be correlated positively with rainfall, while a soil aerosol factor was found to be correlated negatively.

The second major result is that the rainfall areas that were highly correlated with pollution factors are generally (with a few exceptions) clustered together in locations where one might feasibly expect rain to fall from storm systems that intercepted and ingested the urban plume.

Since earlier studies (Vogel and Huff, 1977) showed differing surface rainfall patterns near St. Louis to be associated with different combinations of surface wind direction and direction of storm motion, it is of interest to compare their results with the present ones. Two factors had moderate or high loadings for wind direction. Factor 2 at filter site 49 (Fig. 4) had a loading of 0.87 for SW winds, while factor 3 at filter site 113 (Fig. 6) had a loading of 0.41 for SE winds.

The rainfall distributions found by Vogel and Huff (1977) for SE and SW surface winds are shown in figures 8 and 9, respectively. For each surface wind, the patterns associated with SW and NW storm motions are shown. For SE surface winds and SW storm motion (Fig. 8a), the broad rainfall maximum across the northern part of the research circle coincides with many of the rain areas highly correlated with factor 3 at site 113 (Fig. 6). The pattern for NW storm motion (Fig 8b) does not match figure 6 at all, however.

For SW surface winds and NW storm motion (Fig 9b) an area of maximum rainfall near Alton-Wood River coincides with an area where rainfall was highly correlated with factor 2 at filter site 49 (Fig. 4). For SW storm motion, however, the patterns do not coincide at any point.

Thus, there is separate evidence for

- 1) rainfall distribution near St. Louis being affected markedly by surface wind direction and direction of storm cell motion (Vogel and Huff, 1977), and
- 2) correlations in excess of those expected by chance (at 5% and 1% levels) between rainfall in certain areas and pollutant factor scores, some of which are associated with specific wind directions.

The locations of areas where rainfall correlates most highly with pollutant source strength indices match moderately well with those areas where the heaviest rains tend to fall following surface winds from the same direction. There may be valid reasons not to expect perfect agreement because of differences in the averaging periods of the winds in the two cases.

Figure 8. Rainfall patterns for SE surface winds and storms from the WSW and NW (from Vogel and Huff, 1977).

Figure 9. Rainfall patterns for SW surface winds and storms from the WSW and NW (from Vogel and Huff, 1977).

The question remains whether the observed correlations between source strength indices and rainfall in given areas should be regarded as evidence for aerosol involvement in the mechanisms of urban rain enhancement, or whether both the enhanced pollutant concentrations and the rainfall distribution are caused by some third unanalyzed aerosol factor, which is manifested by surface wind direction.

The fact that the four pollutant factors found to be significantly correlated with rainfall all represent *different* pollutant sources appears to be a crucial observation. If rain was being enhanced by some component of the urban aerosol, and if that aerosol component was represented by an analyzed pollutant identified by factor analysis, then one could reasonably expect that the same type of source (e.g., auto exhaust) would exhibit high correlations with some, but perhaps different, rainfall areas at all filter sampling sites.

What we have observed, instead, is that, while four different sites had positively correlated pollutant factors, those factors represented four different sources.

It would appear far more likely that both rainfall distribution and pollutant concentrations are caused by a third factor which may involve an unanalyzed aerosol component. This third factor may include the wind direction *per se*, or a physical phenomenon manifested by the wind direction.

Thus, while evidence remains strong that urban rainfall distributions are strongly determined by the trajectory of the urban plume and cell motion after ingesting it, it is likely that some factor other than the urban aerosol components analyzed herein is the cause of urban rainfall enhancement.

SUMMARY AND CONCLUSIONS

Indices of pollutant source strength (factor scores for pollutant sources identified by factor analysis in an earlier study) were correlated against rainfall in 22 separate subareas near St. Louis. This was done as a test of the hypothesis that urban pollutants are responsible for an observed urban summer rainfall anomaly.

Five pollutant sources were found to have more than 1% of their correlations exceeding the value expected 1% of the time by chance. The same sources also had considerably more than 5% of their correlation coefficients above the value expected 5% of the time just by chance. Examination of the spatial relationships between the filter site where the pollutant source was detected, and the rain areas, showed that the most highly correlated rain areas were frequently clustered near the filter site or in a position where rain from cells that intercepted the urban plume might fall.

However, the fact that the four pollution sources having the highest correlations with rainfall all represented *different* kinds of sources suggested that

the high correlations may result from both pollutant concentrations and rainfall being causally related to a third factor not included in this analysis.

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CHAPTER 3

A Comparison of Precipitation Chemistry Data at Champaign, Illinois in 1954 and in 1977

Gary J. Stensland

INTRODUCTION

The purpose of this chapter is to investigate the difference in the precipitation chemistry for a rural, east-central Illinois site for 1954 compared to 1977. The major question being addressed is whether or not the precipitation has become more acidic at this midwestern site and if so, why? An examination of the atmospheric sulfate data from the U.S. Environmental Protection Agency NASN stations shows that Illinois is in a transition region between the high sulfate areas of the East and the low sulfate areas of the Plains states. Therefore one should not necessarily expect to find the same precipitation chemistry trends as observed in the East. The 1954 data set has been described in some detail in the 15th Progress Report, including a comprehensive discussion of the procedure used to calculate the pH from the measured ion concentrations (Stensland, 1977). The 1954 data set is unique for its time because the sampling technique carefully eliminated any dry deposition and because individual precipitation events were sampled.

The data sets to be compared were collected from May 15, 1977 to February 6, 1978, and from October 26, 1953 to August 12, 1954. For convenience the two sets are being referred to as the 1977 data and the 1954 data.

The sampling site in 1977 and in 1954 was at the Champaign-Urbana airport (referred to as CMI in this chapter). CMI is located four miles south of Champaign and is surrounded by cultivated fields except for a golf course to the east.

1977 DATA SAMPLE

For the 1977 study an automatic wet/dry collector, of the HASL design, was used. Only the results from the wet-side bucket are considered in this chapter. The polyethylene bucket was changed within 24 hours of the end of the precipitation event and then brought immediately to the laboratory where pH and conductivity were measured followed by sample filtration with a 0.45 micrometer membrane filter. Since the filtration procedure has been shown to satisfactorily stabilize the precipitation chemistry, the samples were stored at room temperature (Peden and Skowron, 1978). The ions SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ ,

Ca^{++} , Mg^{++} , K^+ , and Na^+ were determined by standard methods on AutoAnalyzer and atomic absorption units.

RESULTS

The frequency distributions of the calculated pH for events for 1954 and for the measured pH for 1977 are presented in figure 1. The 1977 data are divided into *green* period data and *brown* period data. In east central Illinois, in general, and in particular around the CMI site, the land is used almost exclusively for secondary roads, residential/urban areas, and farming, and almost all the farm acreage is utilized for growing corn and soybeans. Thus from about May 15 to September 30 the landscape is *green* due to the fields of corn and soybeans. In the fall, the farmland is plowed leaving a *brown* landscape until spring, except for periods of snow cover. Thus, dustier air due to wind erosion of bare soil surfaces should be more common in the *brown* period, and this may be reflected in the seasonal rain and snow chemistry. In fact, for the October 1, 1977 to February 6, 1978 *brown* period on figure 1, the ground surface was either generally moist due to frequent rains or it was snow covered. Due to the relatively small number of data points for 1954, these events were not divided into *brown* and *green* periods.

The experimental procedures used in 1977 allowed small precipitation events to be sampled and analyzed. These small samples ($0.35 \text{ mm} \leq \text{precipitation} < 0.70 \text{ mm}$ and precipitation $< 0.35 \text{ mm}$) are indicated with special symbols on figure 1. The 1954 data on figure 1 does not include any small precipitation events (i.e., $< 0.70 \text{ mm}$). From figure 1 it can be seen that the 1977 event median pH does not change significantly when the small samples are included. The numbers in parentheses on figures 1-4 indicate the number of events considered in determining the median values. The small precipitation events are always heavily loaded with all the ions. However, it is interesting that in figure 1 the small rains in the *green* period in 1977 generally had lower than average pH, while those for the *brown* period generally had higher than average pH.

For 1954 events there were eight cases where from two to five samples were collected consecutively during the event (sequential samples). Using the approximate volume indicated for each sequential sample, a volume weighted average was computed for the event for each ion. These average ion values were then used to calculate the pH for the event, denoted as a composite sample on figure 1.

There were some 1954 samples which were collected after the precipitation had begun to fall. These samples would be expected to be relatively clean since they missed the higher ion concentrations generally found at the beginning of precipitation events, and therefore have been explicitly identified on figures 1-4 as "precipitation at beginning" samples.

From the event data in figure 1, it is observed that the *brown* period of 1977 had a somewhat greater median pH than the *green* period, although when the

Figure 1. Frequency distribution of measured pH for 1977 precipitation events and calculated pH for 1954 precipitation events.

small samples are excluded, the two medians differ by only 0.2 pH unit. The 1977 median pH for the *brown* and *green* periods combined, for events ≥ 0.70 mm, is 4.1. This is to be compared with a calculated median pH for 1954 of 5.9. If those 1954 samples with precipitation at the beginning are excluded, the 1954 median pH = 6.05.

The more basic precipitation in 1954 could have resulted from low levels of acidic ions (e.g., sulfate and nitrate) or from high levels of basic ions (e.g., calcium and magnesium). This issue is addressed with figures 2-4. For these figures the small rainfall samples (<0.70 mm) have not been included.

The sulfate data are presented in figure 2. For 1977, the median for the *green* period was 80 $\mu\text{eq/l}$; for the *brown* period the median was 65 $\mu\text{eq/l}$. The median for 1954 was 50 $\mu\text{eq/l}$; when samples with precipitation at the beginning are excluded the 1954 median is 60 $\mu\text{eq/l}$. For later calculations, the median value of 60 $\mu\text{eq/l}$ will be assumed for 1954 while for 1977 a value for the combined *green* and *brown* periods of 70 $\mu\text{eq/l}$ will be assumed.

The nitrate data are presented in figure 3. As with sulfate for 1977, nitrate had a larger median for the *brown* period. The median nitrate value for 1977 for the combined *brown* and *green* periods is 30 $\mu\text{eq/l}$; for the *brown* period alone it is 38 $\mu\text{eq/l}$ and for the *green* period alone it is 28 $\mu\text{eq/l}$. For 1954, the median nitrate value is 18 $\mu\text{eq/l}$; when samples with rain at the beginning are excluded the median for nitrate is 20 $\mu\text{eq/l}$.

For the 1954 data, the hardness was actually reported but this is equal to $(\text{Ca}^{++} + \text{Mg}^{++})$. In figure 4 the data for $(\text{Ca}^{++} + \text{Mg}^{++})$ is presented. The median $(\text{Ca}^{++} + \text{Mg}^{++})$ value for the combined *green* and *brown* period is 10 $\mu\text{eq/l}$. For 1954, the median $(\text{Ca}^{++} + \text{Mg}^{++})$ value is 65 $\mu\text{eq/l}$. When samples with rain at the beginning are excluded the 1954 median is 82 $\mu\text{eq/l}$. For the nine 1954 events with $(\text{Ca}^{++} + \text{Mg}^{++})$ greater than 100 $\mu\text{eq/l}$, two were in the *green* period and seven in the *brown* period.

DISCUSSION

With the data in figures 1-4 there can be little question that the samples in 1954 were much more basic than the 1977 samples. Although both $\text{SO}_4^{=}$ and NO_3^{-} were apparently lower in the 1954 samples, it was the high levels of soil related species, $\text{Ca}^{++} + \text{Mg}^{++}$, which produced the high pH in 1954. If the $\text{Ca}^{++} + \text{Mg}^{++}$ levels in 1954 had been 10 $\mu\text{eq/l}$ (the 1977 level), then the pH would have been 4.18 instead of 5.9. The median pH = 5.9 for 1954 includes the empirical correction discussed in the 15th Progress Report (Stensland, 1977). Without this correction the 1954 median pH value would have been about 6.6. If once again it is assumed that the 1954 level of $\text{Ca}^{++} + \text{Mg}^{++}$ was 10 $\mu\text{eq/l}$, then the pH would have been reduced from 6.6 to 4.28.

CMI PRECIPITATION

Figure 2. Frequency distribution of sulfate for 1954 and 1977 precipitation events.

Figure 3. Frequency distribution of nitrate for 1954 and 1977 precipitation events.

Figure 4. Frequency distribution of calcium plus magnesium for 1954 and 1977 precipitation events.

With respect to the CMI data, several reasons for the higher $\text{Ca}^{++} + \text{Mg}^{++}$ levels in 1954 compared to 1977 can be suggested. First, recent work has shown that for bulk rain samples which are not filtered soon after collection, the levels of $\text{Ca}^{++} + \text{Mg}^{++}$ can rise by an order of magnitude over several days, presumably due to the slow dissolution of particles in the samples (Peden and Skowron, 1978). This research is being continued in order to assess the importance of the phenomenon for precipitation samples where dry deposition effects are carefully excluded but where filtering is not carried out, analogous to the 1954 samples. The $\text{Ca}^{++} + \text{Mg}^{++}$ levels for the 16 filtered samples from 1954 were compared with the 48 unfiltered samples and no significant difference was observed. However, it is not known by this author if the 16 samples were filtered immediately after collection or later when the samples were being analyzed.

In the 1954 data set there were eight cases where consecutive samples were collected during a rain event. In one case the values of $\text{Ca}^{++} + \text{Mg}^{++}$, in the order of occurrence, were 214, 86, 36, and 4 $\mu\text{eq}/\ell$. Since four samples were obtained, they should have been analyzed immediately according to the analysis schedule that was being used, and thus the dissolution effect should have been minimized. From figure 4 it can be seen that the value of 214 $\mu\text{eq}/\ell$ is greater than any observed in 1977.

Assuming now that the reported $\text{Ca}^{++} + \text{Mg}^{++}$ values accurately represented the precipitation falling in 1954, one must then conclude that more calcium and magnesium were present in the atmospheric aerosols in 1954 than in 1977. A possible source could have been the dust from rural gravel roads. However, a scientist living in the area since 1954 has expressed to this author the feeling that most of the rural roads in the area had an asphalt type surface in 1954, just as they do today, such that the roads would not have been a greater dust source in 1954.

The types of crops grown and the size of the machinery used to cultivate the fields has changed in the CMI area since 1954. This could have modified the local dust levels to some extent, but no quantitative assessment is available.

The final suggestion offered for the elevated $\text{Ca}^{++} + \text{Mg}^{++}$ levels in the atmospheric aerosols is that the years 1953-1954 were very dry in many states of the Midwest and the Plains, and thus more susceptible to soil erosion by the wind as compared to 1977. For instance, in 1954 the precipitation was -33% (below normal) in Oklahoma, -25% for Kansas, -14% for Nebraska, -13% for Missouri, +9% for Iowa, and -6% for Illinois. Actually 6% below normal precipitation for Illinois probably indicates that crop yields will be below normal but there would still be sufficient rain to keep the ground well covered with green crop canopies in the summer. On the contrary, below normal precipitation in the more arid Plains states can more easily lead to the lack of green vegetative ground cover and therefore much dustier conditions. The weather records do indicate that dust storms were present in Oklahoma on February 19 and June 7 of 1954.

CONCLUSIONS

A comparison of the precipitation chemistry data for wet-only event samples for 1954 and 1977 has been made for an east central Illinois site. The precipitation samples from 1954 were much more basic than those of 1977, due to the higher levels of calcium and magnesium as opposed to lower levels of sulfate and nitrate. There is some concern that the elevated levels of calcium and magnesium could have, in part, resulted from a lack of filtering of the 1954 samples soon after they were collected. To compensate for this possibility an empirical correction was applied to the calculated pH values for 1954. This resulted in a median pH for 1954 of 5.9. Without this empirical correction the median pH for 1954 was 6.6. These values are both much more basic than the 1977 median measured pH value of 4.1.

Greater amounts of calcium and magnesium in the precipitation imply greater amounts in the air. Several suggestions for the cause of elevated levels of calcium and magnesium in the air are made. The one most favored by this author is that the droughts occurring in the 1952-1954 time period resulted in the transport of elevated levels of soil dust to Illinois from upwind states. If the trends of precipitation acidity are to be understood, this regional transport of basic aerosols should be evaluated just as the regional transport and transformation of anthropogenic acidic gases and aerosols is currently being evaluated.

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CHAPTER 4

SCORE-78 Case Study

Gary J. Stensland

DESCRIPTION OF THE EXPERIMENT

Our Summer Chemistry Of Rain Experiment for 1978 (SCORE-78) began on 1 June 1978. The objective of the study is to assess the variability of convective rainfall chemistry on very small time and space scales, and to relate this variability to meteorological parameters, air quality parameters, and the chemical sources. To accomplish this objective, precipitation chemistry sampler sites, which are separated by about 1.5 kilometers and serviced after individual rain showers, are in operation until about 1 August 1978. The rapid servicing of the sites protects against ion concentration increases due to evaporation. The rain samples are filtered or refrigerated within a few hours of collection, in order to minimize sample changes due to such things as the slow dissolution of particulate matter.

The 23 sites in the SCORE-78 network are shown on figure 1. Basically there are two sampling lines, oriented north-south, with a site separation of about 1.5 kilometer. At the airport site (AT) and at sites 1-12 are located the weighing type of recording raingages, with 6-hour rotation of the chart allowing excellent time resolution of rain accumulation rate. Similar raingages are located at sites 13-21 except that 24-hour chart rotation gears are used. At each site a hailpad is located. Bulk rain chemistry samplers are located at sites 4, 9, and 13-21. Wet/dry samplers of the HASL type are located at sites 1-9, BT, and AT. BT refers to the sampling platform 35 meters off the ground, on the top of a wooden tower.

Ten air filtration devices are in operation at sites 4, BT, and AT. The sampling interval for these devices ranges from 2 to 24 hours. These filters will be analyzed for all the major ions being measured in the rain samples, plus many other trace metals. Sulfur dioxide and nitrogen oxides are measured at site 4. Wind, temperature, and dewpoint temperature are measured at sites 4 and BT. A sequential rain sampler and two raindrop spectrometers are operated at site 4. A daily soil sample is collected at site 4 to measure the soil moisture content, and thus provide a measure of the potential of this local source to provide aerosols which are captured on the air filters or by the raindrops.

Figure 1. Rainfall (millimeters) for light rainshower event of 12 June 1978.

JUNE 12 CASE STUDY PRELIMINARY RESULTS

To obtain rain chemistry samples from individual showers, the network is being serviced by one to three field people during the daylight hours in June and July. After a rain shower has passed over the network, the east line, consisting of sites 1-12 and thus including the wet/dry samplers, is serviced first and if there is time before the next rain shower, the west line is serviced.

On June 12, 1978, a single small rain shower passed over the network between 0708 CDT and 0717 CDT. Figure 1 shows the rainfalls greater than 0.25 mm produced by the shower which had a lateral dimension of about 5 kilometers. The rain samples from the east line have been analyzed for some of the chemical parameters and these data are shown in figure 2. The sample volumes from the wet/dry samplers are shown in figure 2(a), with about seven ml sample being collected for each 0.25 mm of rainfall. It was fortunate indeed that this shower passed over the dense subnetwork composed of sites 4-8 and BT. The sample pH values are shown in figure 2(b). Sites 2 and 7, with the smallest sample volume, and thus smallest rainfalls, have the highest pH values. The variation of the pH values across the short distance is impressive. Figures 2(d), 2(e), and 2(f) present the concentrations of $\text{SO}_4^{=}$, Ca^{++} , and Mg^{++} , respectively. The patterns for the three are impressively similar. Sites 2 and 7, with the lowest rainfalls, have the lowest ion concentrations. Site BT values appear to be somewhat anomalous but this might be due to the fact that the collector is 33.5 m above the ground. The greater winds at this level may lead to a different collector efficiency as compared to a collector located on the ground. Also the raindrops captured by the BT collector have not scavenged in the 33.5 m air layer adjacent to the earth's surface.

The higher sulfate values in 2(d) do coincide with the lower pH values in 2(b). But the higher sulfate values are paralleled by higher calcium values. Therefore the details of the pH pattern cannot really be explained until all the major ions have been measured for each of the samples.

The frequently noted pattern of higher ion concentrations with smaller rainfalls is not consistent with the single rain shower data shown in figures 1 and 2. Hopefully many more single shower cases will be obtained during SCORE-78, in order that some generalizations about the rain chemistry patterns resulting from individual rain showers can be made.

Figure 2. Sample volume, pH, conductivity, and chemical analysis for $\text{SO}_4^{=}$, Ca^{++} , and Mg^{++} for the 12 June 1978 shower event.

CHAPTER 5

Ionic Stability of Precipitation Samples

Mark E. Peden and Loretta M. Skowron

INTRODUCTION

The chemical analysis of rainwater is a relatively new tool used by atmospheric scientists interested in man's impact on his environment, specifically to study the aerosol composition of the troposphere. Precipitation, because of its unique scavenging or cleansing properties, is a useful indicator of ambient pollution levels, and its chemical analysis yields valuable data concerning inputs of both nutrients and toxic compounds to terrestrial and aquatic biota. Interest in the increased acidity of precipitation has been heightened from cases of decreased forest productivity (Bolin, 1971) and incidences of fish kills in lakes exhibiting lowered pH values (Beamish, 1976).

Presently available instrumental techniques used for inorganic analysis are sufficiently refined to provide accurate determinations down to $\mu\text{g l}^{-1}$ levels in most cases. Because of the low ionic concentrations ($\sim 20 \text{ mg l}^{-1}$) routinely encountered in precipitation samples, biases introduced in sampling, handling, and storage procedures can become the determining factors affecting reliable data acquisition and interpretation.

One source of error particularly important in precipitation chemistry and a subject of controversy among water chemists is ionic instability. Significant changes in ionic concentrations have generally been attributed to precipitation, adsorption, or leaching phenomena occurring between collection and analysis. Investigations into the proper choice of sampler material and subsequent handling procedures have been carried out by numerous researchers with sometimes conflicting recommendations.

The most extensive investigation to date, comparing sampler types specifically related to precipitation chemistry, was carried out by Galloway and Likens (1976) who concluded that polyethylene is the best collection vessel for inorganic determinations, with glass or stainless steel recommended for organic analysis. In addition, they encouraged the use of wet-only collectors to eliminate the positive biases introduced by dry deposition components. An ion stability study performed in conjunction with the sampler comparisons revealed no significant concentration changes in the major inorganic components after six months of storage at 4°C . The authors attributed this to the stabilizing effect of a large amount of hydrogen ions present (pH 3.5-4.5).

The many investigators interested in the ionic stability of aqueous systems have gone to great pains to select the proper sampling vessel to avoid leaching or adsorption reactions and in doing so have often utilized a synthetic solution in a deionized water matrix to approximate natural water conditions. The danger in using artificial solutions lies in the fact that natural waters, whether surface, or precipitation, are dynamic systems composed of a heterogeneous mixture of particulates which have been shown by Morrison and Pierce (1974) and Rattonetti (1976) to have a significant influence on ionic stability. Particle-solute reactions taking place after sample collection can seriously bias interpretation of water chemistry data if all constituents are not somehow preserved through chemical or mechanical means.

In designing a scheme to analyze the nine major inorganic constituents found in rainwater, H^+ , Ca^{++} , Mg^{++} , Na^+ , K^+ , NH_4^+ , NO_3^- , $SO_4^{=}$, and Cl^- , caution must be exercised to insure that all aspects of collection, handling, and analysis are mutually compatible to guarantee that measurements of individual ions accurately document a particular rain event. In order to arrive at such a scheme, a systematic comparison was initiated between three sampler designs, various sampling durations, and six storage procedures to ascertain optimal handling methods for obtaining accurate, representative precipitation chemistry data.

EXPERIMENTAL

Samples were collected on the roof of the Illinois State Water Survey (ISWS) in Champaign, Illinois. Measurements obtained were representative of a relatively small, minimally industrialized midwestern city, centered in a highly agriculturalized area. Bulk collectors consisting of 2 liter, 8.6 cm diameter wide-mouth bottles with removable polyethylene liners, and 1 liter polyethylene bottles mounted with 20 cm diameter funnels were exposed using stands which held four bottles each within a horizontal surface area of $0.25\ m^2$. Wet-only samples were acquired utilizing a wet-dry collector of the design published by the Energy Research and Development Administration Health and Safety Laboratory (HASL) (Volchok and Graveson, 1975). Collection containers were cylindrical 5 liter buckets with 19.5 cm diameter openings. All three types of samplers were used concurrently. One snow and six rain events were collected from 17 March 1977 through 6 May 1977. In order to evaluate dry deposition and evaporation effects, exposure lengths ranged from 16 hours to 7 days.

The effects of six types of storage conditions were compared. Precipitation was collected, allowed to reach room temperature, weighed and then stored as follows:

- (A) Unfiltered sample left in collection vessel, $25^\circ C$;
- (B) Unfiltered, refrigerated at $4^\circ C$;

- (C) Filtered, acidified to pH 2 with HNO_3 , 25°C ;
- (D) Filtered, 25°C ;
- (E) Filtered, refrigerated at 4°C .

Samples under treatments C, D, and E were filtered within twelve hours of collection.

All samples under all conditions were analyzed for inorganic ions four times. Conductivity was also measured. The time intervals were:

- (0) As soon as practically possible after sample collection (0 to 3 days);
- (1) About 1 week after the original determination (7 to 11 days after sample collection);
- (3) About 3 weeks after the original determinations (21 to 25 days after sample collection);
- (6) About 6 weeks after the original determinations (42 to 46 days after sample collection).

RESULTS AND DISCUSSION

Wide-Mouth, Bulk Collectors

Of the sampler types investigated, the wide-mouth bottles proved to be the least suitable collection device. Three events were sampled with exposure lengths varying from 22 hours to 7 days. In all cases, bottles were exposed as close to the beginning of a rain event as possible to minimize any dry deposition prior to collection. Samples were returned to the laboratory for analysis from one hour after a shower to 7 days later to facilitate investigation of dry deposition and evaporation effects. Only one set of four identical samples from a single event had sufficient volume to allow for an extensive analysis of all constituents, as originally envisioned in the experimental design. The mean concentrations for that event are illustrated in figure 1, a 24-hour sample of rain mixed with snow exposed on 21 March 1977. Conductivity and pH values immediately after collection were 30 microSiemens (μS) and 4.3 units, respectively. Samples stored by method A underwent dramatic increases in the concentrations of Ca^{++} , K^+ , Na^+ , Cl^- , and Mg^{++} over a 9-day period, accompanied by a significant increase in pH to a value of 4.9 units. Conductivity values remained stable throughout this same period for treatment A, indicative of an ion exchange phenomenon resulting in no change in net dissolved solids.

Efforts to stabilize ions at their original concentrations by filtration and refrigeration were successful as shown for treatments B-E.

Figure 1. Concentrations versus time for wide-mouth bottle collectors exposed 21 March 1977, 1630 to 22 March 1977, 1655 CST (duration of 24 hours, 25 minutes). The mean sample volume was 164.0 ml. Winds, SE at 9 mph. All data represent the means of four separate samples. Error bars indicate analytical precision at a 99% confidence level. A--original collection vessel, 25°C; B--unfiltered, 4°C; C--filtered, acidified to pH 2, 25°C; D--filtered, 25°C; E--filtered, 4°C.

No significant differences are seen in this case between filtration and refrigeration as a preservation mechanism.

Although only limited measurements of NH_4^+ and SO_4^{2-} were made, the good agreement in data points for all treatments at different times suggests that they are relatively stable. Sulfate appears to be a conservative parameter based on all the events examined, but the stability of NH_4^+ in this instance can be explained by both the low pH and the low temperature at which the samples were collected (0 to 10°C).

A closer examination of the unfiltered treatment A reveals concentrations identical to those found in B-E if the curves are extrapolated back to a point 12 hours after collection. The resultant linear plots obtained suggest an exponential relationship for changes in Ca^{++} , K^+ , Na^+ , Cl^- , Mg^{++} , and H^+ over a 9-day period. The relative slopes are then indicative of reaction rates for individual ions.

A second event, shown in figure 2 illustrates the effect of a large particulate loading when coupled with a light rain (0.9 cm). Average wind speed during the collection period was 15 mph with gusts to 50 mph. A heavy dust loading was visible upon collection and was further substantiated by the high concentrations of calcium discovered. Airborne soil particles are the apparent dominant source.

Because sample volume in this case was limited to 48 ml, an abbreviated analysis was performed using unfiltered treatment A only. Figure 2 depicts the results for Ca^{++} , Mg^{++} , K^+ , H^+ , and conductivity, all of which exhibit unacceptable concentration changes over the 10-day period investigated. Hydrogen ion decreased more than an order of magnitude after 9 days accompanied by an average increase of 50% in the remaining parameters. The relative rates of change are in good agreement with those in figure 1. Based on the conductivity and pH measurements 23 days after collection, equilibrium values are reached after 8 to 10 days revealing a markedly different ionic composition from that of 3 days after collection. A pH of 6.0 increased to 7.5 units and a conductivity of 34 μS increased to 66 μS in this case, supporting the hypothesis that 1) soil (clay) particles not yet in equilibrium with the aqueous phase were slowly dissolving, and 2) an ion exchange mechanism is probably involved with the clay particles acting as a cation exchange medium. These effects will obviously be most pronounced when the particulate to sample volume ratio is highest.

Examination of figures 1 and 2 points out that ion stability is attainable if samples are filtered to remove particulates or kept at 4°C to retard chemical activity. If no attempt is made, however, to address the presence of particulate matter, any analyses not completed immediately after sample collection are subject to gross error. Consequently, the use of bulk collectors are suitable only on an event basis or for total deposition.

Figure 2. Concentrations versus time for wide-mouth bottle collectors exposed 1 April 1977, 1615 to 2 April 1977, 1430 CST (duration of 22 hours, 15 minutes). All data represent the means of two separate samples. Sample volume was 48 ml. Winds, SW at 15 mph. A--original collection vessel, 25°C.

Funnel and Bottle, Bulk Collectors

Twenty-three samples representing seven events were obtained with the funnel and bottle bulk collectors. When the ionic concentrations of different storage methods were compared, a complex situation involving particulates, sampling duration, and temperature was revealed.

Comparisons between filtered and unfiltered samples illustrate the significant role played by particulate matter, and that particle interference effects can be minimized or eliminated. The concentrations in filtered portions (C, D, and E), with the exception of NH_4^+ in one case, were identical for all ions under investigation for replicate samples of an event, as well as within each sample. Results indicate that once particulates are removed, the ionic integrity is not affected by either temperature (D at 25°C versus E at 4°C) or acidity (C at pH versus D and E at original pH, range = 4.1 to 7.1).

Two exposure intervals of approximately 1 and 7 days were used, and figures 3 and 4 illustrate the data obtained during these periods. The mean concentrations of C, D, and E, the filtered aliquots, are assumed to represent the true ionic composition at the time of sampling for the following comparisons with A and B, the unfiltered portions. Data plots indicate that as exposure times increase, with concurrent increases in the particulate load, the concentrations of several ionic species become more susceptible to pronounced alterations.

Figure 3 represents the ionic concentrations in a sample of rain mixed with snow from 21 March 1977 and collected after an exposure of 39 hours. Analysis of A resulted in Na^+ , K^+ , NH_4^+ , H^+ , $\text{SO}_4^{=}$, and NO_3^- concentrations that were in agreement with the values of C, D, and E, both initially and throughout the storage period, without displaying any significant changes. Ca^{++} and Mg^{++} concentrations in A were also stable during storage, but their mean values were 7% and 15% larger, respectively, than those of the filtered portions. The Cl^- concentrations in A were the same as in C, D, and E throughout, with an average increase of 57% over 6 weeks. The concentrations of all ions in B paralleled those in A with the exception of Cl^- . Initial values were comparable, but rather than increasing, the amount of Cl^- in B decreased 58%.

Figure 4 represents the mean concentrations of samples collected 1 April 1977 through 8 April 1977, a period characterized by high winds and a visible particulate load. During the exposure time of 6 days and 22 hours there were 3 rainshowers, the last mixed with snow. Only two constituents in A, $\text{SO}_4^{=}$ and H^+ , remained stable throughout the storage interval with the same concentrations as C, D, and E. After 6 weeks, the concentrations of all other ions in A had changed markedly. NO_3^- and NH_4^+ decreased by 63% and 96%, respectively, in relation to the filtered concentrations. In fact, if it is assumed that the filtered sample represents the original concentration more faithfully, the NH_4^+

Figure 3. Concentrations versus time for funnel and bottle collectors exposed 21 March 1977, 1700, to 23 March 1977, 0825, CST (duration of 39 hours, 25 minutes). Winds, SE at 9 mph. All data represent the means of four separate samples. Sample volume was 621 mL. Treatment codes same as in figure 1.

Figure 4. Concentrations versus time for funnel and bottle collectors exposed 1 April 1977, 1600, to 8 April 1977, 1400, CST (duration of 6 days, 22 hours). Winds, SW at 12 mph. All data represent the means of two samples. Sample volume was 415 mL. Treatment codes same as in figure 1.

decreased about 2500% as compared with C-E. Increases of 90% for Ca^{++} , 504% for Mg^{++} , 33% for Na^+ , 179% for K^+ , and 56% for Cl^- took place, the greatest changes occurring during the first 10 days of storage and then reaching a quasi-equilibrium.

In portion B, $\text{SO}_4^{=}$, NO_3^- , and Cl^- were stable, while the H^+ concentration decreased by 23%. The remaining constituents increased as follows: Ca^{++} by 23%, Mg^{++} by 110%, K^+ by 35%, and NH_4^+ by 32%. Refrigeration apparently slowed the rates of change but was inadequate as a means of completely retaining the true ionic concentrations.

HASL, Wet-Only Collector

The composition of a wet-only sample collected 5 May 1977 after three days exposure is illustrated in figure 5. Initial pH and conductivity measurements were 4.1 units and 23.4 μS , respectively. As expected, the elimination of dustfall during the dry periods of the sampling interval resulted in increased ionic stability for the unfiltered aliquots. After 6 weeks of storage, only two constituents in A displayed a significant concentration increase over the mean values of C, D, and E. Ca^{++} and Mg^{++} showed increases of 14% and 19%, respectively. All other ions except NH_4^+ were stable both with respect to time and in comparison to unfiltered samples. NH_4^+ concentrations in the refrigerated portion, B, were equivalent to those in C, D, and E. This sample was typical of the seven events collected.

Although overall improvement in ionic stability is striking when a wet-only sampler is used rather than bulk collectors, filtration is still deemed necessary as a preservation technique when terrestrial components are to be quantitatively assayed. Contamination due to airborne soils and dustfall can be effectively eliminated with the use of tight fitting lids and appropriately calibrated sensor mechanisms, but particulate matter from other unavoidable sources can still be an interfering factor. These sources include cloud condensation nuclei, particulates removed by diffusion and phoretic forces within the cloud, and particle scavenging by impaction on drops falling in and beneath the cloud.

Summary and Recommendations

The data presented have emphasized the important role played by extraneous particulate matter in affecting the ionic integrity of precipitation samples. The particles of terrestrial origin are of the greatest importance and are intimately related to meteorological, geographical, and cultural factors.

Wind speed, relative humidity, temperature, and convective activity all have a direct effect on the amount of airborne particulates present at a given time. Areas with a protective snow cover are likely to have lower concentrations of soil components.

Figure 5. Concentrations versus time for a wet-only collector exposed 2 May 1977, 0825, to 5 May 1977, 0825, CST (duration of 3 days). Winds, SW at 6 mph. Sample volume was 1037 mL. Treatment codes same as in figure 1.

Geographical considerations were examined by Winkler (1976) who stressed the importance of natural dusts in neutralization of potentially acidic precipitation. The occurrence of soluble airborne soil materials can be partially predicted based on: 1) the geologic history of a region (soil composition, topography, etc.); and 2) the associated ground cover (forest, plains, etc.).

Cultural practices relating to farming and logging operations can leave vast expanses of previously protected soil exposed to the wind, suddenly increasing the particulate loading of an area. Unpaved roads nearby a sampler location can add to the problem.

The unpredictable nature of aerosol particulates necessitates sampling criteria that yield accurate data for all conceivable cases. It would be naive to assume that any sampling location would be free from interfering soil components under all conditions.

The severe limitations of the wide-mouth bulk collectors caused by dry deposition effects, precludes their use except in cases where true event sampling is envisioned. Immediate filtration, or refrigeration as a second alternative, is recommended to minimize alterations in chemical constituency.

In situations where power supplies and funds for automated wet-only samplers are limited, bulk sampling is often the only means by which to obtain precipitation chemistry measurements. Under these circumstances, a funnel and bottle configuration has proven to be more effective at eliminating dry deposition, presumably due to the scouring action of the wind on the funnel, and preventing evaporation. Ionic instability is still a problem in many cases and requires filtration within 12 hours to maintain sample integrity.

The wet-only sampler consistently provided precipitation of superior ionic integrity based solely on its ability to reduce the effects of particulates. However, the presence of scavenged particles in collected precipitation can be significant during periods of either light rainfall or heavy aerosol dust loadings. As illustrated in figure 5, calcium and magnesium increased an average of 16% for a 3-day exposure characterized by a 2.8 cm rainfall and light winds (5 mph). In this case, refrigeration adequately preserved the sample, but under conditions of stronger winds, longer sampling duration, or less rainfall, filtration provides the greatest assurance of retaining ionic integrity after collection.

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CHAPTER 6

MAP3S Laboratory Intercomparison Study

Mark E. Peden

Eight samples prepared by the Department of Energy, Environmental Measurements Laboratory (EML) were sent to 23 participating laboratories under the auspices of the Multistate Atmospheric Power Production Pollution Study (MAP3S). Six samples (A-F) were actual precipitation and two (G, H) consisted of spiked deionized water. All aliquots were filtered through 0.45 μm membranes prior to shipment to each laboratory. Analysis was requested for a list of 30 ions including electrical conductance.

Results are tabulated in Table 1 for those parameters analyzed by ten or more laboratories. Computed with the Water Survey results are the means and standard deviations after outliers have been excluded using Chauvenet's criterion (Jarrett, 1946). The constituents listed account for over 95% of the ionic loading in rainwater samples and therefore the accuracy of these parameters is crucial to the characterization of precipitation.

The Water Survey results are within the acceptable limits for all constituents listed in Table 1 with the exception of NH_4 . The poor results shown for NH_4 were traced to a malfunction in the heating bath unit of the automated wet chemical analyzer. Replacement of this unit alleviated errors associated with the ammonium determinations.

The Water Survey participation in this exercise was carried out to ensure compatibility between precipitation samples collected and analyzed locally and those analyzed by PNL for the MAP3S network. This represents the third exercise this laboratory has been involved in and the results continue to be quite favorable. The procedures carried out in this laboratory give analytical results which enhance confidence in the measured concentrations observed in precipitation.

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Table 1. Illinois State Water Survey Results of MAP3S Interlaboratory Comparison.

Constituent	Units	N*	A	B	C
pH					
Mean	µeq/l	19	9.8 15.9 $\pm$ 7.0	0.9 0.9 $\pm$ 0.6	0.3 0.4 $\pm$ 0.3
Conductivity					
Mean	µS/cm	17	42.3 38.7 $\pm$ 2.2	36.0 35.2 $\pm$ 1.7	40.8 40.9 $\pm$ 2.2
Na					
Mean	mg/l	16	0.227 0.234 $\pm$ 0.042	0.713 0.728 $\pm$ 0.060	3.260 3.223 $\pm$ 0.377
K					
Mean	mg/l	17	0.774 0.809 $\pm$ 0.034	0.583 0.593 $\pm$ 0.056	0.558 0.579 $\pm$ 0.056
Mg					
Mean	mg/l	17	0.171 0.171 $\pm$ 0.016	0.149 0.149 $\pm$ 0.013	0.146 0.145 $\pm$ 0.014
Ca					
Mean	mg/l	18	0.74 0.74 $\pm$ 0.06	0.44 0.45 $\pm$ 0.03	0.45 0.45 $\pm$ 0.03
NH ₄					
Mean	mg/l	16	1.63 2.75 $\pm$ 0.32	1.97 2.81 $\pm$ 1.26	1.62 2.88 $\pm$ 0.22
Cl					
Mean	mg/l	18	0.45 0.43 $\pm$ 0.04	0.73 0.70 $\pm$ 0.16	0.65 0.62 $\pm$ 0.12
NO ₃					
Mean	mg/l	18	0.20 0.23 $\pm$ 0.03	0.09 0.09 $\pm$ 0.06	0.10 0.07 $\pm$ 0.04
SO ₄					
Mean	mg/l	19	11.9 11.4 $\pm$ 1.1	8.1 7.6 $\pm$ 0.5	7.7 7.4 $\pm$ 0.5
PO ₄					
Mean	mg/l	15	0.41 0.44 $\pm$ 0.04	0.35 0.40 $\pm$ 0.08	0.45 0.48 $\pm$ 0.07

A minus sign (-) indicates less than values.

*N = number of laboratories included in tabulations of means and standard deviations.

Table 1. (Continued)

D	E	F	G	H
1.0	26.3	38.5	1380.8	758.6
30.4 $\pm$ 20.0	27.1 $\pm$ 7.8	38.9 $\pm$ 6.2	1374.2 $\pm$ 142.8	708.0 $\pm$ 92.6
43.5	41.0	41.5	589.5	303.0
44.8 $\pm$ 4.7	39.5 $\pm$ 2.7	41.7 $\pm$ 2.0	560.4 $\pm$ 30.7	284.9 $\pm$ 12.4
3.830	0.595	0.363	0.066	0.014
3.828 $\pm$ 0.332	0.592 $\pm$ 0.052	0.368 $\pm$ 0.044	0.087 $\pm$ 0.041	0.019 $\pm$ 0.011
0.621	0.172	0.131	0.006	0.293
0.620 $\pm$ 0.033	0.150 $\pm$ 0.071	0.108 $\pm$ 0.048	0.033 $\pm$ 0.028	0.250 $\pm$ 0.109
0.286	0.480	0.420	0.011	-0.002
0.285 $\pm$ 0.028	0.464 $\pm$ 0.029	0.414 $\pm$ 0.043	0.019 $\pm$ 0.007	0.009 $\pm$ 0.006
1.06	2.03	1.64	-0.02	-0.02
1.05 $\pm$ 0.07	2.07 $\pm$ 0.27	1.74 $\pm$ 0.13	0.06 $\pm$ 0.05	0.04 $\pm$ 0.02
0.94	0.41	0.39	-0.03	-0.03
0.35 $\pm$ 0.09	0.69 $\pm$ 0.07	0.64 $\pm$ 0.07	0.02 $\pm$ 0.01	0.02 $\pm$ 0.02
0.65	2.74	1.30	20.31	18.27
0.66 $\pm$ 0.11	2.01 $\pm$ 1.23	1.07 $\pm$ 0.33	19.99 $\pm$ 0.80	18.96 $\pm$ 0.89
5.57	3.28	3.35	49.57	13.75
4.60 $\pm$ 3.33	3.10 $\pm$ 0.43	3.32 $\pm$ 0.34	54.59 $\pm$ 2.97	13.20 $\pm$ 0.40
9.3	6.5	8.1	-0.2	0.3
9.0 $\pm$ 0.7	6.3 $\pm$ 0.4	8.0 $\pm$ 0.8	0.03 $\pm$ 0.04	0.2 $\pm$ 0.2
0.33	0.41	0.12	-0.01	-0.01
0.46 $\pm$ 0.09	0.46 $\pm$ 0.05	0.13 $\pm$ 0.05	0.01 $\pm$ 0.01	0.03 $\pm$ 0.02

CHAPTER 7

Summary of METROMEX, Volume 2: Causes of Precipitation Anomalies

Richard G. Semonin

INTRODUCTION

The 5-year St. Louis METROMEX project which ended in August 1975 resulted in the acquisition of extensive data on aerosol and precipitation chemistry, and measurements of the planetary boundary layer airflow. The unique nature of these data and the supporting aircraft, and other surface measurements continue to inspire new interpretation of the inadvertent effects on the weather related to urbanization and industrialization.

The Water Survey completed analyses of the identification of anomalous weather and their impacts and published the findings in a report entitled "Summary of METROMEX, Volume 1: Weather Anomalies and Impacts" (Changnon et al., 1977). This report focused on the final interpretations and conclusions obtained primarily through climatological-statistical analyses of spatial and temporal distributions of surface precipitation and severe storms.

The key climatic effects delineated in the Volume 1 report are increased cloudiness (+10%), increased total summer rainfall (+30%), and increased severe storm activity (+100%). These increases occur over the city and 15 to 50 kilometers beyond the urban-industrial areas.

The urban-induced anomalies occur most often with squall lines and cold fronts, and they maximize in the afternoon and again at night. Furthermore, the anomalies appear in dry periods as in wet periods.

The impacts include more runoff, but also more local flooding, soil erosion, silting, and water pollution. The effect of altered weather leads to a 3 to 4% average increase in local crop yields. Overall, the urban-induced anomalies are generally disbeneficial in the floodplain area, and have mixed impacts in the rural uplands.

The findings summarized above are complemented by the second publication entitled "Summary of METROMEX, Volume 2: Causes of Precipitation Anomalies." The key results from this report (attached as Appendix A) are briefly described in the following section.

CAUSES OF PRECIPITATION ANOMALIES

The findings presented in Volume 2 begin with the urban-perturbed surface measurements and extend upward eventually leading to clouds and precipitation. Hypotheses based on the observed perturbed weather are developed in an attempt to explain the initiation of small clouds and the observed precipitation patterns by using the measured physical parameters in a consistent chain of reasoning.

There are three stages of development of precipitation to be considered when examining the potential effects of an urban-industrial complex on the atmosphere. The first of these is the development of small convective clouds without the ensuing development of precipitation. The study of this cloud development can provide information on preferred areas for the cloud initiation or enhancement. Admittedly, the conditions under which the large scale atmosphere produces scattered convective clouds may also provide unique circumstances and emphasize cloud development over a particular area that may not be representative during synoptic scale pre-storm situations.

The second stage of cloud development to be considered is that of convective clouds that extend beyond the planetary boundary layer, but do not produce organized precipitation, that is, cumulus congestus. More frequently than not, these clouds are observed as precursors to the development of precipitation or precede migratory precipitation systems as the atmosphere destabilizes. The observations required to ascertain urban effects on such clouds would include cloud base height and cloud top height, as well as microphysical parameters such as the droplet size spectrum.

Finally, the urban area is suspected of influencing those clouds which either are about to precipitate or are already producing rainfall across or in proximity to the urban center. The direct influence of the metropolitan area on such clouds is difficult to ascertain, because the increased rainfall arises from initiation of new showers or the enhancement of an existing, moving system. To quantitatively separate and study the contribution from these two possible mechanisms requires more sophisticated analyses than straight-forward rainfall observation.

Synoptic Situation Characterization. The summer synoptic conditions that precede these three stages are those conducive to scattered cumulus activity. They generally include the presence of a high pressure system centered to the east of southeast of Illinois, providing southerly component flow across the state. On the west side of such a high, a capping inversion is frequently observed inhibiting vertical development of convective clouds. With time, the high pressure migrates eastward and is replaced by a more disturbed atmosphere usually associated with a migratory frontal system approaching from the west. The capping inversion is gradually dissipated and the lower troposphere becomes less stable throughout, with continuous influx of moisture at low levels preparing the atmosphere for more active convection. The atmosphere is now suitable for the development of scattered convective showers which are free to develop to great heights. Unless this condition is associated with a surface disturbance or a passing upper air trough, the showers will remain scattered and disorganized.

With the approach of a synoptic scale disturbance (front, upper trough) the convective activity becomes more organized, resulting in either frontally associated precipitation or a squall line (or both).

Boundary Layer Characterization. Under any of these synoptic situations, there are three ways in which an urbanized area may affect clouds and precipitation: 1) through the point and area sources of effluents as a consequence of man's activities, that is, aerosols (CCN, IN), water vapor, and heat; 2) increased upward flux of heat, moisture, and effluents on the turbulence or thermal scales; and 3) mesoscale mechanical deformation of airflow resulting in converging flow in the lower layers.

There is evidence that all three exist, at least in part, in St. Louis. Direct measurements of the aerosols and of the droplet spectra near cloud base indicate that the city tends to increase the number concentration of cloud condensation nuclei, thus increasing the continental character of the clouds originating or passing over the urban area. Evidence concerning ice nuclei is much less definite. Although there is evidence of low-level sources, measurements in the troposphere indicate there may not be increased activity of this kind.

Although water vapor is produced in many of man's urban-industrial activities, this source is much smaller during the summer than that due to evapotranspiration from rural vegetation. Consequently, the urban surface represents a reduced rather than an enhanced source of moisture, and the vapor content of the surface boundary layer is generally lower than that in the country.

The very complicated group of processes involved in the heat balance at the urban surface does not necessarily predict uniformly warmer temperatures in the city during midday. However, there is evidence that in the lower boundary layer, a midday positive temperature differential does exist, particularly in cloudy weather. The urban-rural temperature difference has been found to exist throughout much of the depth of the planetary boundary layer.

First Cloud Initiation Hypothesis. The nocturnal inversion is observed to be stronger in rural areas than in the urban center where the heat island maximizes at night. In the early morning, the solar radiation on a relatively clear city (as evidenced from satellite cloud studies) begins to dissipate the inversion at the surface. The inversion is weakest in the urban center, and the morning heating allows surface air to reach the lifting condensation level earlier than in a rural area, where a much stronger inversion must be overcome. The urban surface, by virtue of its roughness characteristics and its slightly warmer temperature, produces an increased flux of heat and water vapor through mechanical mixing or through enhanced thermal transport. Further, the boundary layer airflow is perturbed by the urban structure inducing convergence over the city throughout much of the PBL. The depth of the convergence increases during the day as the PBL increases in depth.

These features of the evolving boundary layer prepare the atmosphere for the appearance of the first clouds. The dissipation of the nocturnal inversion

by solar heating, in conjunction with the city-related mesoscale convergence, allows mixing of near-surface properties throughout the lower levels of the boundary layer. This process results in the formation of the first clouds of the day over the urban areas with bases coinciding with LCL. Continued mixing of the lowest atmospheric layers produces cloud bases more nearly at the convective condensation level by early and mid-afternoon. The observed convective level is higher over the urban center because the city is warmer and somewhat drier than the surrounding rural countryside resulting in higher cloud bases.

Isolated Shower Initiation Hypothesis. The development of air mass showers may follow the cloud initiation hypothesis for fair weather cumulus, but in a general atmospheric environment conducive to deeper convection. These clouds are commonly quasi-stationary and consequently are more responsive to localized perturbations in their immediate environment. For example, the qualitative relationship between condensation nuclei observations at a level in the mid-planetary boundary layer and the air mass precipitation suggests that there may be a physical relationship between them.

In addition, neutral stratification extends through a much deeper layer over the city than over the rural area. The country exhibits a superadiabatic lapse rate in the surface boundary layer and lower PBL, and a conditional instability in the upper half of the PBL. Both of these are destroyed in the city stratification, possibly indicating either thorough mixing, or possibly mesoscale dynamic effects. Regardless, this rural-urban difference means that mechanical and thermal eddies rise through greater depth in proximity to the city. Because these clouds are either stationary or very slowly moving, a source of condensation nuclei will be available for transport by the subcloud base kinematic flow, leading to ingestion by the cloud and possible modification of the microphysics. Equally accessible to the cloud is the sensible heat released from the urban area if the clouds are situated in proximity to the heat island.

Since cloud bases are higher in city-affected regions, and since the temperatures in the middle troposphere are observed to be very similar over city and country surfaces, initial lower parcel buoyancy is expected, possibly resulting in lower urban vertical velocities. This expectation, however, is partially offset by the urban-produced mesoscale convergence which provides a more continuous and extensive source of low-level moisture and sensible heat.

These features of the altered urban atmosphere suggest that cloud modification should occur in simple, unorganized air mass shower situations. In other words, isolated shower activity (often including the defined squall zone classification) should be more readily related to the disturbed boundary layer and the urban effects more easily identified than they should be with migratory, organized precipitation systems. However, the five-year precipitation sample does not indicate that the major inadvertent influence on the precipitation pattern occurs in air mass conditions, although the urban influence on air mass showers is apparent in summer dry periods.

Organized Storm Enhancement Hypothesis. The next resulting question is, do these urban influences exist in organized convective systems? The organized synoptic scale precipitation systems, squall lines and fronts, represent another aspect of atmospheric instability. The atmospheric baroclinicity, or degree of atmospheric stratification, is altered significantly in proximity to fronts and

upper-level troughs. The horizontal boundary between air masses is a region where the atmosphere is very unstable since it is striving to achieve equilibrium. These boundaries provide a mechanism for cloud and precipitation development which would produce precipitation in a reasonably organized fashion over the METROMEX area, irrespective of the presence of the St. Louis metropolitan region.

We are then faced with one or two choices (or both) as contributing causes of the observed anomalous precipitation pattern. The first of these follows from the previous discussion of air mass showers, whereby the showers develop in response to urban effects, and are rooted in the urban area. These showers are then in existence and available to merge with an approaching migratory system. In this sequence of events, no enhancement in precipitation would occur until the migratory cells join with the urban-related cells, somewhere in proximity to the Mississippi River, to be followed by increased precipitation somewhere to the east.

The second possibility is that in the absence of urban-developed air mass showers, the urban area in some way directly modifies either the dynamics or cloud microphysics of the clouds composing the storm.

Since other evidence from all over the Midwest shows that such migratory storms are not a steady-state system, but rather undergo continuous growth and decay of the individual cells, it seems more logical to consider in greater detail the first of these alternatives as the connecting link between urban effects and precipitation from moving systems.

It is known that any deep convection tends to deform the airflow around it, and that new cloud cells, or newly developing cloud areas, occur preferentially in one or two quadrants around the cloud. The quadrant in which the new cloud formation occurs is more closely related to the direction of the wind shear in the cloud layer than to the direction of the wind. Thus in some cases the storm may be continually generated on the upwind side (so called back feeder cells) and in other cases on the downwind side of the storm (front feeder cells). The urban effect will depend on the location and character of these feeder clouds in the migratory system.

The major precipitation anomaly has been found to the east and most particularly to the northeast of St. Louis. The winds above the PBL in the summer are most commonly from the WSW through the NW. Thus, this particular area is downwind (east) from the main St. Louis metropolitan area, from the heavily industrialized Granite City, and from the Alton-Wood River refinery and industrial area. In addition, the anomaly also extends downwind from a major moisture source over the Missouri-Mississippi River bottoms. Since the effect that is seen over Edwardsville is apparently due to a relatively few major rainstorms, and those primarily classified as squall lines, it is obvious that the pattern is due to an enhancement of previously existing, migratory systems.

In summary, there is a great deal of evidence available from previous studies of squall lines and lines of thunderstorms, to show that these lines frequently propagate new lines ahead of it. The metropolitan area, with its observed urban to downwind convergence zone and other features conducive to

cloud and precipitation development, is a preferred region for either development of a new line or intensification of an existing line. Thus, the modification of a line attributed to the urban area might not result from direct effects on the original migratory system, but possibly is due to either the greater likelihood of additional rain through pre-line initiations, or through strengthening the existing line by mergers with urban-affected cells.

Unresolved Questions and Recommendations

The hypotheses set forth in the above section follow from the key findings presented in the summary, and the following questions arise from the hypotheses.

- 1) Can the initial cloud development be related to various land use patterns?
- 2) What is the evolution behavior of the PBL with increasing atmospheric instability and passage of a synoptic scale system?
- 3) What is the role of the PBL in cloud and precipitation development?
- 4) What is the effect of antecedent conditions in urban and rural areas on cloud and precipitation morphology?
- 5) Where are the cloud initiations corresponding to individual first echoes?
- 6) Where are the first echo initiations corresponding to individual raincells?
- 7) Does the urban area act to enhance the strength and/or duration of convection in existing and developing cells?
- 8) Do urban-generated CN, CCN, and IN measurably modify the precipitation process?
- 9) Is there an increased urban-related dynamic effect leading to enhancement of feeder cells around pre-existing large storms in organized systems?
- 10) What is the urban effect apt to be during and between a series of rain events (separation of less than three hours), i.e., does the city 'look' more rural or uniquely different with a wetted surface?
- 11) What is the recovery time for the city to return to the pre-rain atmospheric state following a rain event?
- 12) Why are precipitation cell mergers further east in wet months than in relatively dry or near-normal periods?
- 13) What is the mechanism for increased rainfall after merger?

This list of significant unresolved questions is not meant to be all encompassing, but is representative of the more important problems remaining after our five-year field research. Certain of these questions can be answered from the

available data, whereas some will require limited additional field measurements. The major recommendations, then, are simply to

- Undertake a series of detailed case studies, being careful to select from the data bank those cases with the most comprehensive sets of measurements;
- Initiate appropriate modeling efforts for transferability of results to other cities;
- Carefully design a future field measurement program to address specific remaining questions.

The fulfillment of the first recommendation may require considerable effort since much of the focus to date has, of necessity, been on the climatological approach. Other findings, developed in great detail, have not yet been adequately interrelated to other detailed results. The case studies will require a careful blending of the measurements to answer questions concerning mesoscale cloud events as opposed to focused data subsets. The enormity of such efforts, elapsed time, and support have limited the attention that could be given to case study investigations.

The outcome from such studies will direct attention to gaps in the data bank requiring additional field experimentation and will provide initialization and verification data for future modeling efforts. Hopefully, the variables to be measured will be limited and the synoptic conditions to be sampled carefully specified.

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