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AN URBAN INFLUENCE ON DEPOSITION OF SULFATE AND SOLUBLE METALS IN SUMMER RAINS

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ABSTRACT

Recent observations of abnormally acidic precipitation have raised questions regarding the distribution of acidic precipitation, its time trend, its sources of acidity, and the relevant physical and chemical processes involved in its formation. This paper attempts to answer some of these questions based on the content of sulfate and other materials in the atmosphere and in samples of summer convective rainfall from mesoscale sampling networks near St. Louis.

These and other observations in the literature agree that rainfall deposits locally emitted sulfur at short distances downwind of cities. This causes enhanced deposition and concentration of sulfur in local rainfall and increases the local variability of these parameters relative to that of rain and crustally-derived materials, on both daily and seasonal scales.

Airborne sulfate concentrations vary by a factor of at least 2-4 from urban to rural areas on individual days. This is similar to the observed variation of sulfate deposition or concentrations in rain. Thus, there may be no need to invoke extensive SO_2 scavenging in rain systems to explain the observed enhancements; nucleation scavenging of atmospheric sulfate appears adequate.

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INTRODUCTION

Observations of abnormally acidic precipitation in northern Europe and the northeastern United States have raised questions regarding:

1. The geographical distribution of acid precipitation,
2. Its trend with time,
3. The sources of its acidic materials, and
4. The physical and chemical processes involved in its formation.

The purpose of this paper is to attempt at least partial answers to some of these questions for the St. Louis area. Specifically, this paper describes the urban influence on sulfate deposition in rain at St. Louis and interprets the deposition data in terms of possible sources and scavenging mechanisms of sulfur in precipitation.

Hales and Dana (1979) measured sulfate, nitrate, and ammonium ion concentrations in rain near St. Louis during the summers of 1972 and 1973 as part of Project METROMEX. They concluded:

1. That there was sufficient airborne particulate sulfate to

account for the sulfate in rain, but

2. That, for several reasons, the elevated sulfate concentrations found in the rain downwind of the city could only be explained by a mechanism in which locally-emitted sulfur dioxide was scavenged in the cloud.

Also as part of METROMEX the Illinois State Water Survey measured the areal deposition of both soluble and insoluble fractions of a number of elements or ions in rain during the summers of 1972 to 1975 (Gatz et al. ,1978). The measurements included Li, Na, Mg, K, Ca, Fe, Zn, Pb, and Cd. These elements represent both natural and man-made sources. Soluble sulfate deposition was measured in four of the events sampled in 1974 and 1975. Further, the data set includes measurements of sulfate and metal concentrations in ground level air, which allows the testing of a key feature in the reasoning of Hales and Dana (1979) that led to their conclusion that sulfur dioxide scavenging was significant.

These data are analyzed to show the urban effect on sulfate deposition and its variability. In addition, the data are analyzed to test whether they are consistent with the conclusions of Hales and Dana (1979) regarding the importance of local sources and sulfur dioxide scavenging.

EXPERIMENTAL METHODS

The methods used to collect and analyze both precipitation samples (Gatz et al. ,1978) and aerosol samples (Gatz, 1978) have been given in detail previously. They are outlined here only briefly.

Precipitation Samples

In METROMEX, rain samples were collected in the two different sampling networks shown in Figures 1 and 2. The 1900 sq km, 80-collector, rectangular network extending eastward from St. Louis was used between 1972 and 1974, and the 2200 sq km, 85-collector network covering Alton and Wood River, Illinois, was used in 1975. Rain was collected in pre-cleaned open wide-mouth polyethylene bottles mounted atop metal fence posts. Samples were ordinarily changed daily.

In the laboratory, sample bottles were weighed with and without the water sample to determine sample mass and volume. The samples were measured for pH and conductivity, and then filtered through leached 0.45 micrometer pore diameter Millipore type HA filters to remove insoluble particulate matter. The filtrate was acidified to pH 2 and stored in polyethylene bottles. Filters were dried, folded, and stored in plastic vials.

Filtrates were analyzed for cations directly using standard flame or flameless atomic absorption spectrophotometry. Sulfate was determined by an automated colorimetric barium-methylthymol blue method on a Technicon Autoanalyzer II system (Peden et al. ,1979) after neutralizing the samples with ammonium hydroxide. Filters were dissolved in strong acids and analyzed using the same methods.

The raw analytical data were computer-corrected for blanks, dilutions, and dry deposition, and the data were edited to remove obvious outliers caused by contamination.

Aerosol Samples

Airborne particulate matter was collected on pre-weighed 37 mm Nuclepore 0.8 micrometer pore diameter filters, exposed face down under 25 cm diameter polyethylene funnel rain shields, about 1 m above grass or a flat roof. The locations of the sampling sites in 1974 and 1975 are shown in Figure 5. Sample durations varied from 6 to 12 hr, but most collections were 12 hr.

In the laboratory, loaded filters were reweighed to determine sample mass, after conditioning at 47% relative humidity for 24 hr to allow the moisture absorbed on the particulate matter to come to equilibrium.

Elemental analysis of the filters was performed at Crocker Nuclear Laboratory, University of California--Davis, using ion-excited X-ray fluorescence (Flocchini *et al.* ,1972;1976).

RESULTS

Deposition Patterns

Consider first some previous results which show which of the various soluble and insoluble constituents of rain have similar deposition patterns. Tables 1 to 4 are loadings tables from factor analyses performed separately on four rain events in which sulfate was measured (Gatz, 1979). The loadings are correlation coefficients between the variables and the factors. They show which variables have similar deposition patterns (those with high loadings on the same factors). In addition, they show how similar a variable's deposition pattern is to that of the factor. High loadings (0.86 or higher) indicate very similar patterns; moderate loadings (0.71 to 0.85) show that the patterns are moderately similar. Loadings less than 0.50 are usually not shown; they explain little of the variance, and the tables are easier to read without them.

In each rain event, factor analysis grouped the sulfate deposition pattern with that of soluble pollutant metals and with rainfall, while soluble soil elements, insoluble soil elements, and insoluble pollutants grouped on different factors. Only in the 1 August 1975 case did one of the soluble pollutant elements occur on a different factor from sulfate. Note, however, that loadings were often in the moderate range for at least some of the variables in the "soluble pollutants" factor.

With this indication from factor analysis that the soluble pollutants and rainfall have similar deposition patterns, it is of interest to compare the actual deposition patterns. This is done for the four events in Figures 1 to 4. Figure 1 shows results for the rain of 2 August 1974, which deposited an average of 11.3 mm of rain in the network. The figure shows good agreement between the deposition patterns of soluble sulfate soluble Zn, and rainfall. (After this, mention of sulfate or any of the metals means the soluble portion, unless specified otherwise.) This agrees with the loadings shown in Table 1. Ordinary product-moment correlation coefficients for sulfate with the other variables were: sulfate--rainfall, 0.94; sulfate--Zn, 0.53.

Figure 2 shows results for the storm of 13 July 1975, which deposited an average of 10.2 mm of rain. As a group the loadings were smaller in this case than the previous one (0.55 to 0.77), and this is reflected in the comparison of deposition patterns. Generally high element and ion deposition occurred over or near the industrial areas of Alton--Wood River and Granite City, Illinois, and this was accompanied by a similar rainfall pattern. However, some individual differences between patterns may be seen. For example, a maximum in Zn deposition occurred near

Granite City, while a corresponding Cd maximum was displaced somewhat to the east. Product-moment correlations for this event were: sulfate--rainfall, 0.41; sulfate--Zn, 0.59; and sulfate--Cd, 0.41.

Similar results were found for the event of 19 July 1975, which gave an average of 2.0 mm of rain over the network. Figure 3 shows that there was general agreement between the main features of the various deposition patterns, but differences in some details. The product-moment correlations were: sulfate--rainfall, 0.76; sulfate--Zn, 0.56; and sulfate--Pb, 0.52.

The event of 1 August 1975 gave an average of 7.3 mm of rain over the network and was the only one in which the soluble Zn depositon did not occur on the same factor as sulfate and rainfall. Nevertheless, its deposition pattern is included along with the others in Figure 4, where it clearly shows itself to be different. As in the other cases, sulfate, Cd, and rainfall display general similarity in the area of maximum deposition in the southwestern portion of the network, but differ elsewhere in minor ways. The product-moment correlations were: sulfate--rainfall, 0.43; sulfate--Cd, 0.41; and sulfate--Zn, 0.19.

The general agreement between sulfate deposition and soluble Zn deposition for the four events discussed above suggests that the long-term average deposition pattern (i.e., over many events) for soluble Zn is similar to that of sulfate, which was measured in only four events. The average soluble Zn deposition (ng per sq cm per event) patterns for the 1972-1974 and 1975 networks are shown in Figure 5, along with average rainfall patterns for the same respective events. Both Zn and rainfall depositions have been normalized (i.e., divided by) their respective network mean values. This facilitates comparisons, because both Zn and rainfall depositions appear in the same non-dimensional units. The figure shows maximum soluble Zn deposition very close to the suspected sources , and not related to the rainfall pattern. Since sulfate deposition was similar to soluble Zn deposition in three of the four events presented earlier, it is reasonable to expect a similar, but not identical urban influence for sulfate deposition.

Spatial Variability of Deposition

The urban influence on the spatial variability of Zn deposition, and by analogy, on sulfate deposition, is shown in Table 5 in terms of the relative standard deviation. Data for rainfall and the soluble portion of elements for which the earth's crust is a major source are shown for comparison. Spatial variabilities are presented for daily deposition , as well as for integrated deposition over all days in which the various elements were measured. The table shows median relative standard deviations near 100% for rainfall and the earth's crust elements on a daily time scale, while that for Zn is over 175%. On the seasonal time scale, rain and the crustal elements had spatial variabilities of 30-45%, while that for Zn was 125%. Thus, as expected, the influence of the city on Zn deposition, and probably sulfate deposition, is to increase the spatial variability on both daily and seasonal time scales.

Patterns of Concentrations in Air

Since deposition of materials in rain is influenced by their concentrations in air, it is of interest to examine the distribution of sulfate and pollutant elements in the St. Louis area. Figure 6 shows median values at 12 locations where measurements were taken during the summers of 1973 to 1975. Not all sites were sampled each summer, however. Please note that the concentrations shown in Figure 6 represent total concentrations, not just the soluble portion. Sulfate concentrations were calculated from measurements of elemental sulfur, assuming that particulate sulfur was 100% sulfate. Sulfur in rain is virtually 100% soluble, but that is not true for the pollutant metals.

Sulfate, Zn and Pb all show the highest median concentrations in urban areas and lowest concentrations in rural areas. Ratios of highest to lowest medians for sulfate, Zn, and Pb were 2.3, 5.8, and 8.0, respectively. The value of 2.3 for sulfate agrees quite closely with the urban/rural sulfate ratios in the eastern United States reported by Altshuller (1976).

Examination of spatial patterns of airborne concentrations on many individual days from the summers of 1973-1975 (not shown) confirm that the same patterns as seen in Figure 6 also occurred on individual days.

The maximum in the Pb distribution east of St. Louis is an anomaly in the data caused by two sites near heavily-traveled roads. The true maximum was probably over the St. Louis urban area, where the greatest traffic density occurs.

DISCUSSION

The two matters of most concern in this paper are:

1. The urban influence on deposition and its variability, and
2. The implications of the data regarding sources and scavenging mechanisms for sulfur in rain near St. Louis.

We shall discuss them in this order.

The four rain events in which sulfate was measured show sulfate deposition peaks associated with both 1) heavy rain areas, and 2) urban-industrial source areas, independent of rainfall. The results over many events, using soluble Zn as an analog of sulfate, suggest that on seasonal time scales the deposition maxima associated with rainfall maxima in single events tend to "average out", away from the city, just as rainfall itself does, while the local maxima near the sources persist.

This is confirmed and expressed quantitatively by the calculated variability results (Table 5). Over single events, rain and crustal element deposition had relative standard deviations near 100%, while that of Zn was greater by a factor of 1.75. On the seasonal scale, the spottiness in the rainfall and its contribution to the crustal element variability was considerably smoothed , so that their relative standard deviations decreased to 30-45 %. The local Zn anomaly persisted, however, so that overall the Zn relative standard deviation was still 125%, a factor of 3 to 4 higher than rain and the crustal elements.

Sources and Scavenging Mechanisms

Now we examine the implications of the data regarding sources and scavenging mechanisms of the locally-deposited sulfur. Hales and Dana (1979) found that there was more than enough sulfate aerosol present in the St. Louis atmosphere to account for all the sulfate in the rain solely by scavenging of sulfate particles. Yet, because of the locally-enhanced sulfate concentrations in rain downwind of the city, and the perceived "highly uniform" atmospheric sulfate concentrations , local sulfur dioxide was presumed to have been converted to sulfate by a gas-phase oxidation in the precipitation system. We will examine this argument in the light of data presented earlier.

Two aspects of the data appear to be the most pertinent. First, we will compare the observed variabilities of sulfate concentrations in air to those in rain, and secondly we will consider the association between the deposition patterns of sulfate and the other soluble pollutants, such as Zn, Pb, and Cd.

Airborne Sulfate Distributions

Hales and Dana (1979) did not give a quantitative definition of "highly uniform" airborne sulfate concentrations, but there is evidence in the literature that sulfate concentrations differ by a factor of at least 2 between urban and rural areas. For example, Altshuller (1976) reported ratios of mean urban and rural sulfate concentrations near 2 for much of the eastern United States. Further, it should be noted that these urban concentrations were probably conservative, since they were measured near the center of an urban or industrial area. On individual days, larger concentrations would be expected some distance downwind after conversion of some of the sulfur dioxide to sulfate.

The distribution of median airborne sulfate concentrations measured in METROMEX (Figure 6) illustrates the variability of sulfate concentrations in the St. Louis area. This distribution exhibits a maximum / minimum ratio of 2.3.

For individual days, the ratios were greater. Plotted distributions of airborne sulfate for the four rain events (Figures 1-4) are not shown because of space limitations, but their respective maximum / minimum sulfate ratios , based on our data, were 7.9, 4.2, 3.0, and 3.5, respectively. Similar ratios were obtained for the EPA Regional Air Pollution Study (RAPS) total sulfate concentrations on the last three of these days, based on particulate sulfur measurements by 10 dichotomous virtual impactors in the St. Louis area (Dzubay, 1979).

These urban/rural ratios <u>are</u> more uniform than those of some of the other pollutants, such as Zn or Pb, for which distant sources are relatively less important than for sulfate. This may be seen in Figure 6. The maximum / minimum ratios for the median Zn and Pb concentrations in Figure 6 are 5.8 and 8.0, respectively, and ratios on individual days would ordinarily be greater. Nevertheless, the urban/rural sulfate ratios are clearly greater than about 2 or 3 on individual days.

The next question is, "How will such urban/rural differences in sulfate aerosol be reflected in the sulfate in rain?" The answer to this is, unfortunately, not at all clear.

One may examine either concentrations in rain (micrograms of sulfate per ml) or deposition to the surface (micrograms of sulfate per sq cm), but both are strongly affected by rainfall amount. Hales and Dana (1979) have made a step in the right direction in their attempt to normalize sulfate concentrations to 1 cm of rain. The distribution of such values should show clearly any urban influence on sulfate concentrations in rain, apart from effects caused by rainfall amount. The variability of these normalized concentrations, then, is the proper one to compare against the variability of airborne sulfate. Hales and Dana , however, listed only non-normalized data at individual collection sites. The non-normalized maximum / minimum concentration ratio for their storm of 23 July 1973 was 4.5. Since the highest concentrations usually occur in small samples, and the lowest in large samples, a normalization to unit rainfall should reduce the maximum / minimum ratio. Thus the maximum / minimum ratio in the normalized data should be no more than 4.5. This ratio is the same order as those found for sulfate in air in the St. Louis area. Since there is a well-known process, namely nucleation, by which sulfate aerosol is efficiently scavenged, there appears to be no compelling reason in the 23 July 1973 storm for concluding that sulfur dioxide scavenging must have occurred.

The sulfate depositions in the four events presented earlier have not been normalized to unit rainfall, but again, ratios of such data should be "worst cases" , since normalization of <u>depositions</u> to unit rainfall should decrease the high values, which occur with the heaviest rainfall (Figures 1-4), and increase the low values, which occur with the lightest rainfall. Maximum/ minimum ratios of sulfate deposition for the events shown in Figures 1-4 were, respectively, 22.7, 3.4, 32.4, and 5.0. Thus, even for such "worst cases" , two of the four events had ratios of the same order as those of airborne sulfate. Again, there appears to be no strong reason to require sulfur dioxide scavenging in the cloud if, as has been shown previously by Hales and Dana (1979), there is sufficient airborne sulfate to account for the sulfate in rain.

These data are similar to those of Hales and Dana (1979) in that they show local enhancement of sulfur in rain near the city. Nothing in these data disagrees with the conclusion of Hales and Dana that this observed enhancement was caused by deposition of sulfur emitted from local sources.

Associations Between Deposition Patterns

Factor analyses showed that sulfate deposition patterns group consistently with those of other soluble pollutants and rainfall. The loading values from the factor analyses suggested, and a comparison of actual deposition patterns showed, that soluble pollutants and rainfall depositions were generally similar in their major features, but differed in some details.

It appears very significant that sulfate deposition patterns are similar to soluble pollutant metals and rainfall, but not to insoluble metals or soluble soil elements. These relationships should be determined by the distribution of sources and by the processes of scavenging and/or precipitation formation. Source distribution can probably explain why pollutant distributions are different from those of soil elements, but the reason why soluble and insoluble materials have different deposition patterns would appear related to scavenging and/or precipitation formation processes.

Any further statements at this time are speculative. One could speculate that the association between the deposition patterns of sulfate and soluble metals implies that the sulfur is scavenged in the same way as the metals, namely by particulate (sulfate) scavenging. Other explanations, however, involving sulfur dioxide scavenging by cloud droplets with high catalyst concentrations, can also be envisioned. Whatever mechanisms are eventually proposed, however, they must now be consistent with the observations reported here.

CONCLUSIONS

Observations reported here and others in the literature agree that rainfall deposits at least some locally-emitted sulfur at short distances downwind of the sources. This causes enhanced deposition and variability in the affected areas.

Airborne sulfate concentrations near St. Louis vary by a factor of 2-4 from urban to rural locations on individual days. This variation is roughly the same as that observed in either concentration or deposition of sulfate in rain. Thus, there is no need to invoke in-cloud scavenging of sulfur dioxide to explain enhanced sulfur in rain near the city, since there is ample aerosol sulfate and an available scavenging mechanism (nucleation) to account for it.

The observation of consistently similar deposition patterns for sulfate and soluble pollutant metals places some interesting constraints on possible scavenging mechanisms and suggests that more detailed study of this group of materials would be fruitful for understanding the processes involved.

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FIGURES

Figure 1. Distribution of rainfall and constituent deposition for rain of 2 August 1974.

Figure 2. Distribution of rainfall and constituent deposition for rain of 13 July 1975.

Figure 3. Distribution of rainfall and constituent deposition for rain of 19 July 1975.

Figure 4. Distribution of rainfall and constituent deposition for rain of 1 August 1975.

Figure 5. Distribution of median deposition per event, for Zn and rainfall in multiple storms. Values are normalized to their respective network means.

Figure 6. Distribution of median airborne pollutant concentrations, for measurements made during summers, 1973-1975.

REFERENCES

Altshuller, A. P. 1976. Regional transport and transformations of sulfur dioxide to sulfates in the U. S., J. Air Poll. Control Assoc., 26(4):318-324.

Dzubay, T. 1979. Personal communication.

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

Flocchini, R. G., P. J. Feeney, R. J. Sommerville, and T. A Cahill. 1972. Sensitivity versus target backings for elemental analysis by alpha-excited X-ray emission. Nuclear Instruments and Methods, 100:379-402.

Gatz, D. F. 1978. Identification of aerosol sources in the St. Louis area using factor analysis. J. Appl. Meteor. 17(5):600-608.

Gatz, D. F. 1979. Associations and spatial relationships among rainwater constituents deposited in mesoscale sampling networks by individual storms near St. Louis. Paper presented at the Commission on Atmospheric Chemistry and Global Pollution Symposium on the Budgets and Cycles of Trace Gases and Aerosols in the Atmosphere, Boulder, CO, August, 1979.

Gatz, D. F., R. G. Semonin, and M. E. Peden, 1978. Deposition of Aerosols. IN Ackerman, B.,et al., 1978. Summary of METROMEX, Vol 2. Causes of Precipitation Anomalies. Bulletin 63, Illinois State Water Survey, Urbana, pp.345-381.

Hales, J. M., and M. T. Dana. 1979. Precipitation scavenging of urban pollutants by convective storm systems. J. Appl. Meteor., 36:294-316.

Peden, M. E., L. M. Skowron, and F. M. McGurk. 1979. Precipitation sample handling, analysis, and storage procedures. Research Report 4, Contract No. EY-76-S-02-1199, U. S. Department of Energy, Illinois State Water Survey, Urbana, COO-1199-57.

Table 1. Loadings table from factor analysis on deposition data from storm of 2 August 1974

	Factor	
	1	2
Soluble K	0.90	
Soluble Ca	0.81	
Soluble Li	0.78	
Soluble Mg	0.71	
Soluble $SO_4^=$		0.85
Soluble Zn		0.83
Rainfall		0.79
Soluble Na	(0.49)	(0.48)
Variance explained, %	56	15

Table 2. Loadings table from factor analysis on deposition data from storm of 13 July 1975[a]

	Factor			
	1	2	3	4
Insoluble Fe	0.91			
Insoluble K	0.86			
Insoluble Li	0.64			
Soluble $SO_4^=$		0.77		
Soluble Zn		0.72		
Soluble Cd		0.62		
Rainfall		0.55		
Soluble Ca			0.92	
Soluble K			0.88	
Soluble Mg			0.61	
Soluble Li				0.76
Insoluble Zn				-0.65
Variance explained, %	32	15	13	9

[a] Source: Gatz, D. F., 1979. Associations and spatial relationships among rainwater constituents deposited in mesoscale sampling networks by individual storms near St. Louis. Paper presented at Commission on Atmospheric Chemistry and Global Pollution Symposium on the Budgets and Cycles of Trace Gases and Elements in the Atmosphere, Boulder, CO, August, 1979.

Table 3. Loadings table from factor analysis on deposition data from storm of 19 July 1975

	Factor				
	1	2	3	4	5
Soluble $SO_4^=$	0.91				
Rainfall	0.86				
Soluble Zn	0.72				
Soluble Pb	0.66				
Soluble Mg		0.86			
Soluble Ca		0.84			
Soluble K		0.70			
Soluble Li		0.64			
Insoluble Fe			0.91		
Insoluble K			0.86		
Insoluble Li			0.72		
Insoluble Mg				0.95	
Insoluble Ca				0.94	
Insoluble Zn					0.75
Insoluble Pb					0.74
Variance Explained, %	21	17	13	12	9

Table 4. Loadings table from factor analysis on deposition data from storm of 1 August 1975[a]

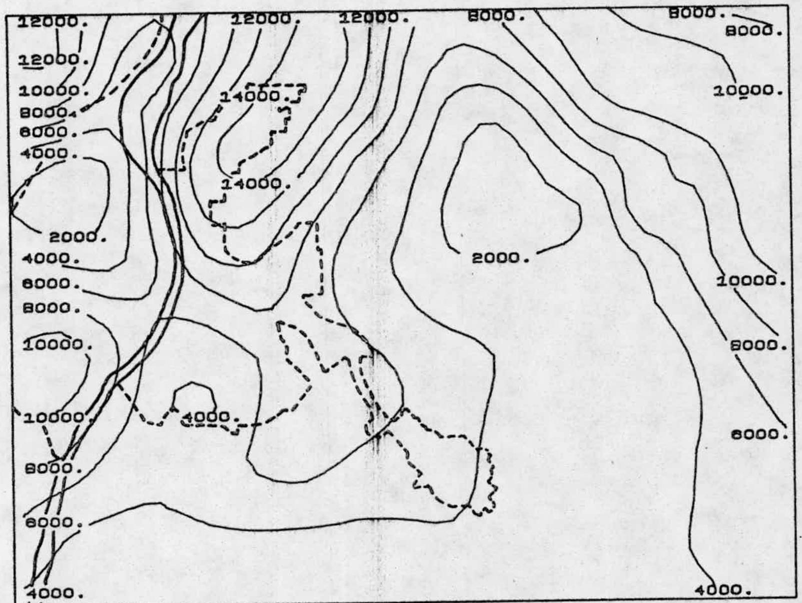
	Factor			
	1	2	3	4
Insoluble Fe	0.96			
Insoluble Li	0.96			
Insoluble K	0.96			
Insoluble Zn	0.50	(0.49)		
Soluble K		0.92		
Soluble Mg		0.84		
Soluble Ca		0.59		
Soluble $SO_4^=$			0.78	
Soluble Cd			0.73	
Rainfall			0.73	
Soluble Zn				0.80
Soluble Li				0.77
Variance explained, %	33	17	15	10

[a] Source: Gatz, D. F., 1979. Associations and spatial relationships among rainwater constituents deposited in mesoscale sampling networks by individual storms near St. Louis. Paper presented at Commission on Atmospheric Chemistry and Global Pollution Symposium on the Budgets and Cycles of Trace Gases and Elements in the Atmosphere, Boulder, CO, August, 1979.

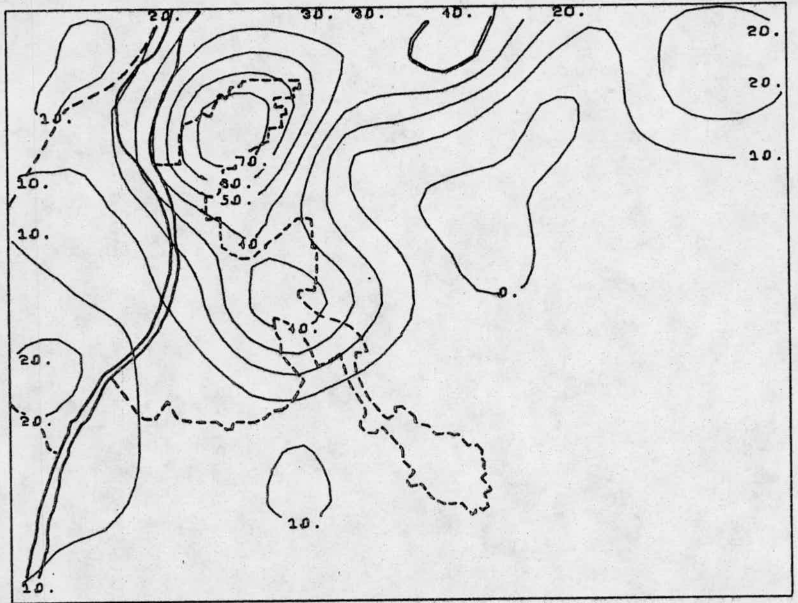
Table 5. Summary of spatial variabilities (standard deviation/mean value, %) for precipitation and soluble wet element deposition over daily and seasonal time scales

	Rainfall	Li	Na	Mg	K	Ca	Zn
Number of days	41	27	20	20	26	20	26
Individual Days							
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
All Days	35	38	32	44	45	35	125

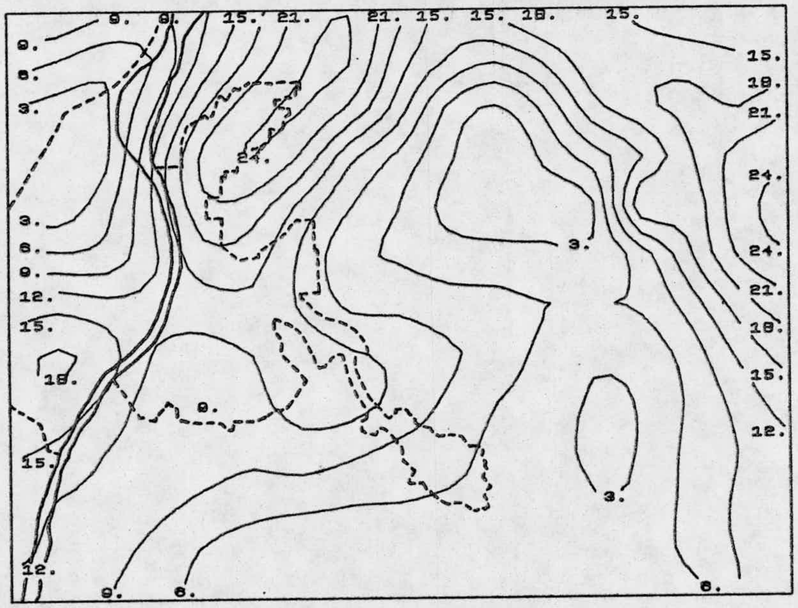
2 August 1974



SOLUBLE $SO_4^{=}$ DEPOSITION IN RAIN, ng cm^{-2}

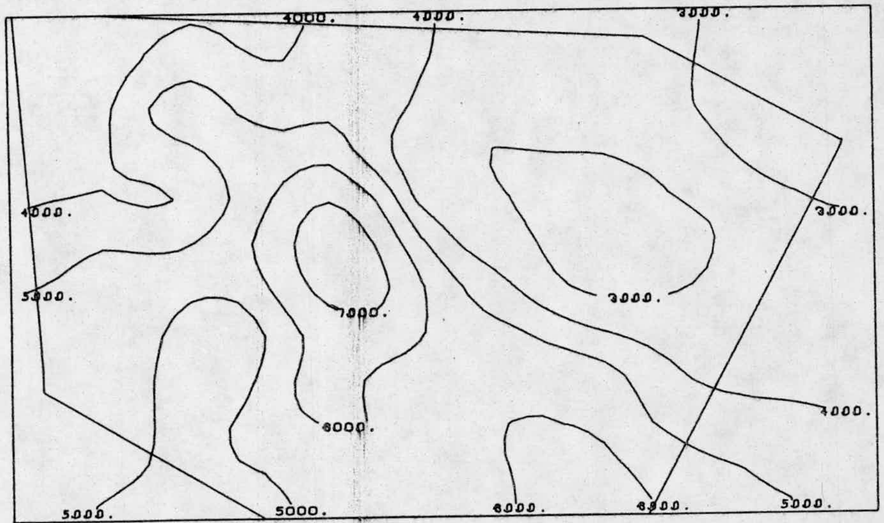


SOLUBLE Zn DEPOSITION IN RAIN, ng cm^{-2}

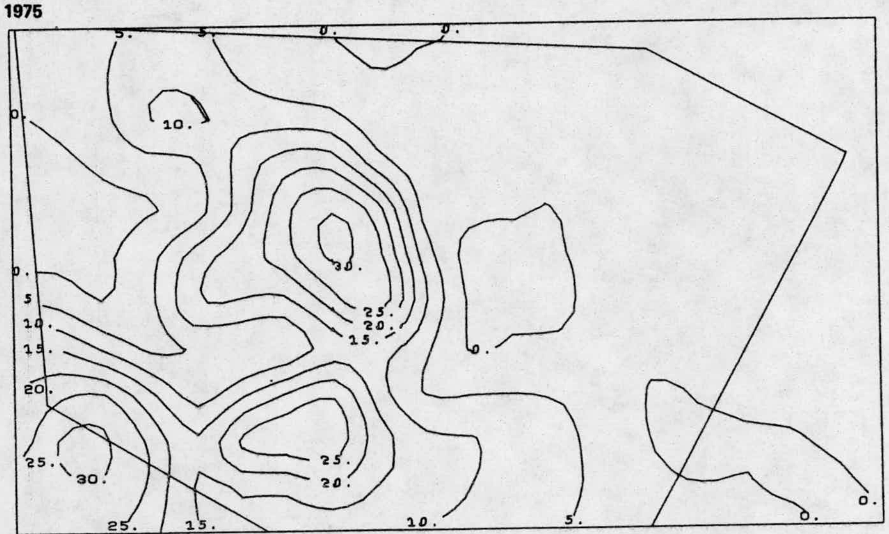


RAINFALL, mm

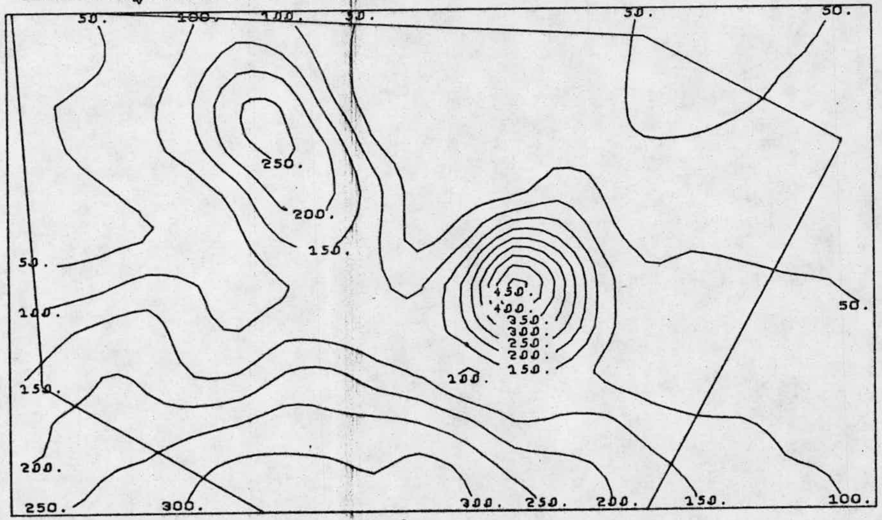
13 July 1975



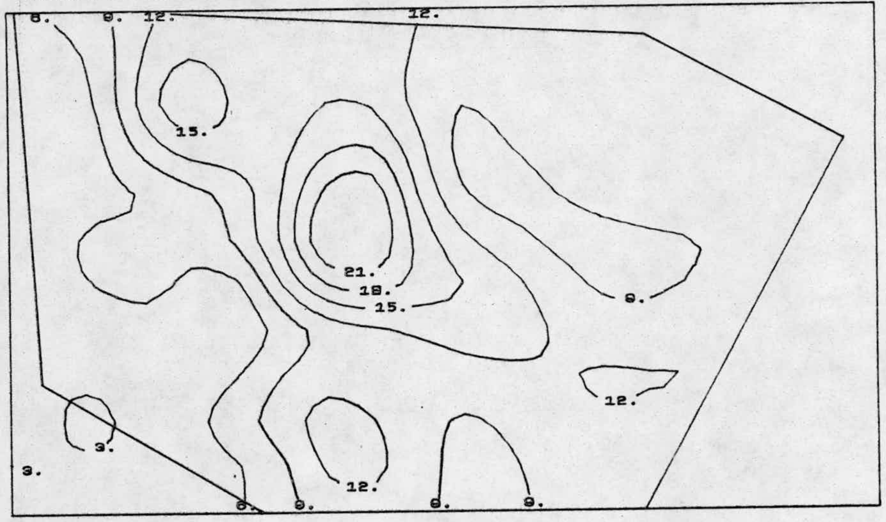
SOLUBLE $SO_4^=$ DEPOSITION IN RAIN, ng cm^{-2}



SOLUBLE Zn DEPOSITION IN RAIN, ng cm^{-2}

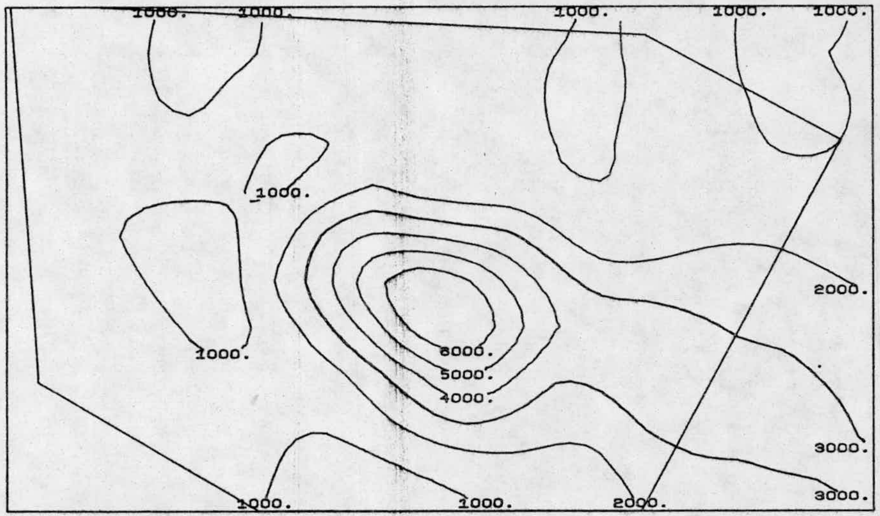


SOLUBLE Cd DEPOSITION IN RAIN, pg cm^{-2}

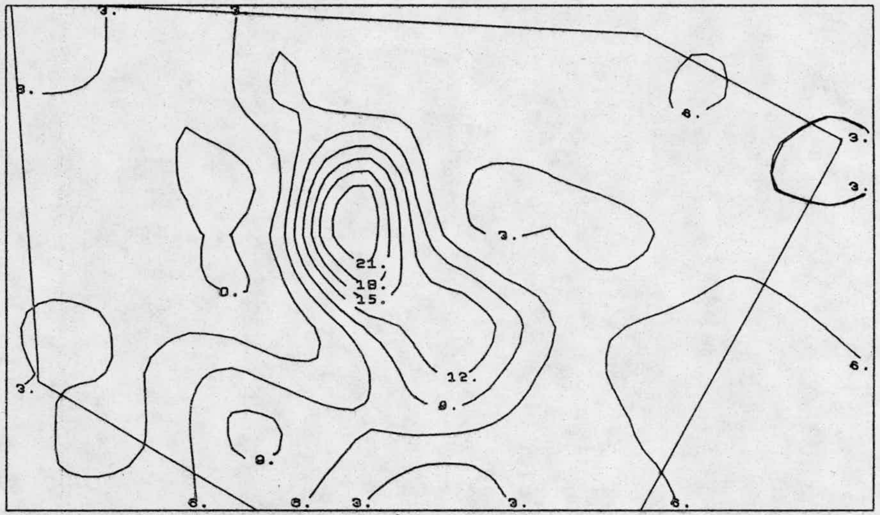


RAINFALL, mm

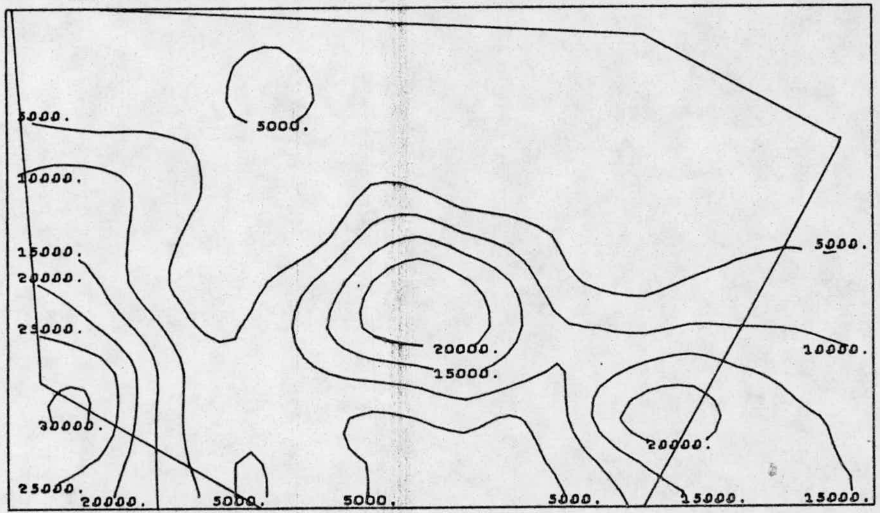
19 July 1975



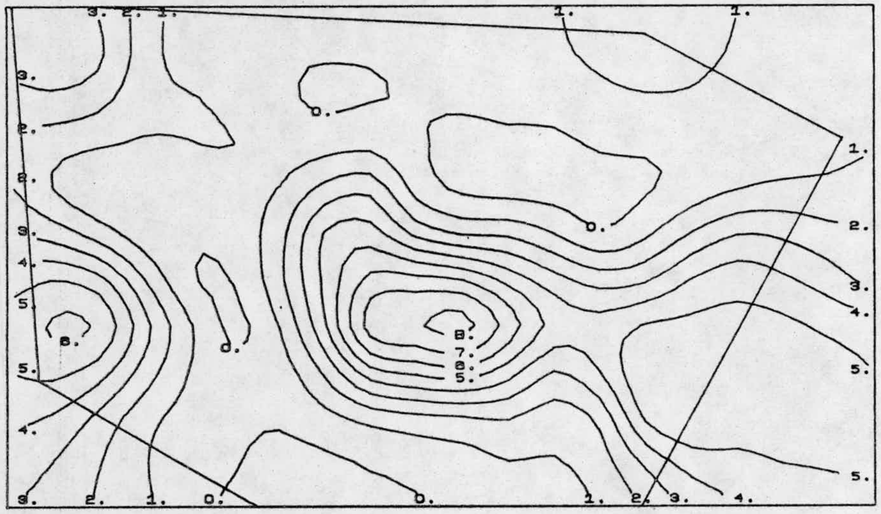
SOLUBLE SO$_4^=$ DEPOSITION IN RAIN, ng cm^{-2}



SOLUBLE Zn DEPOSITION IN RAIN, ng cm^{-2}

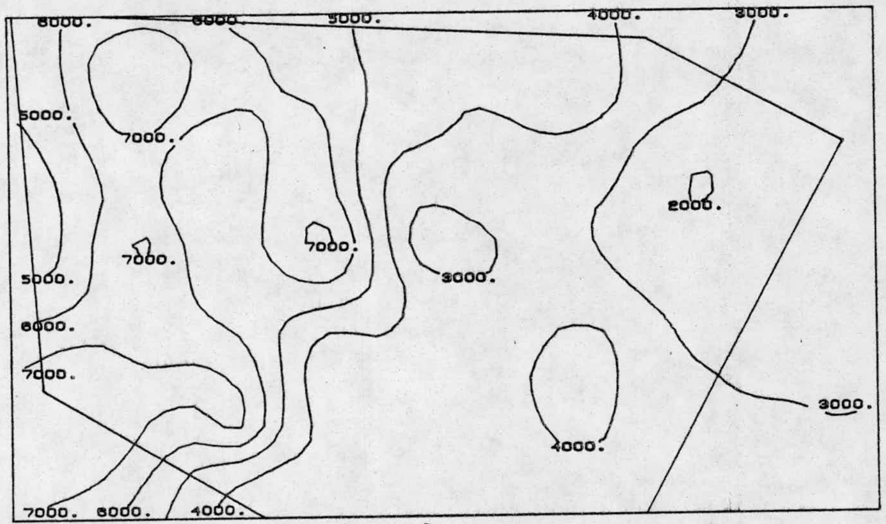


SOLUBLE Pb DEPOSITION IN RAIN, pg cm^{-2}

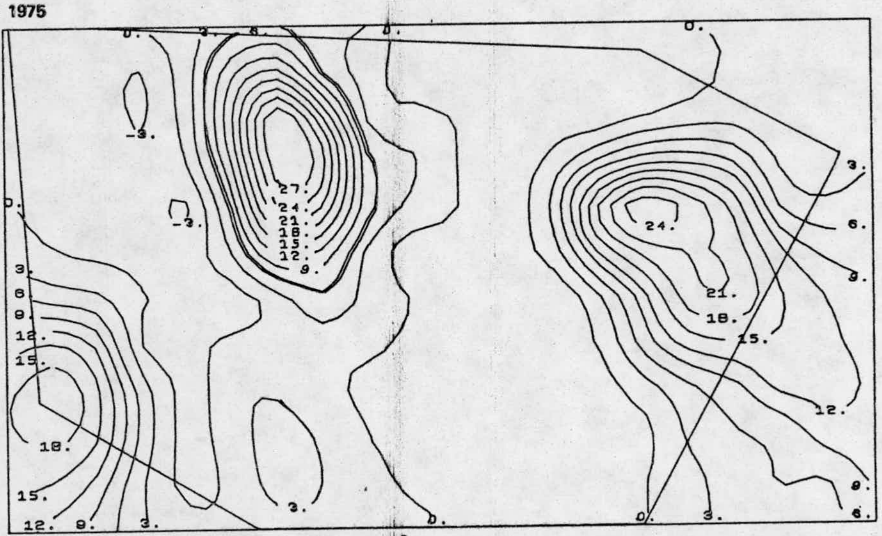


RAINFALL, mm

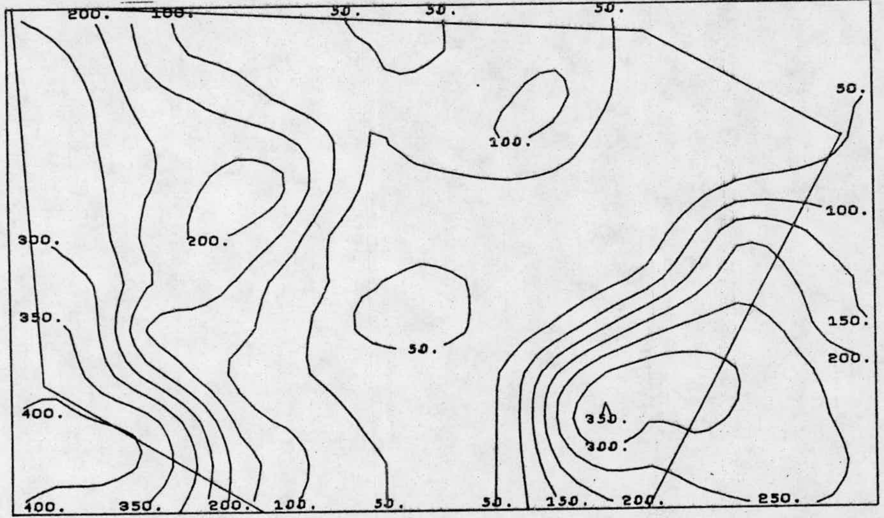
1 August 1975



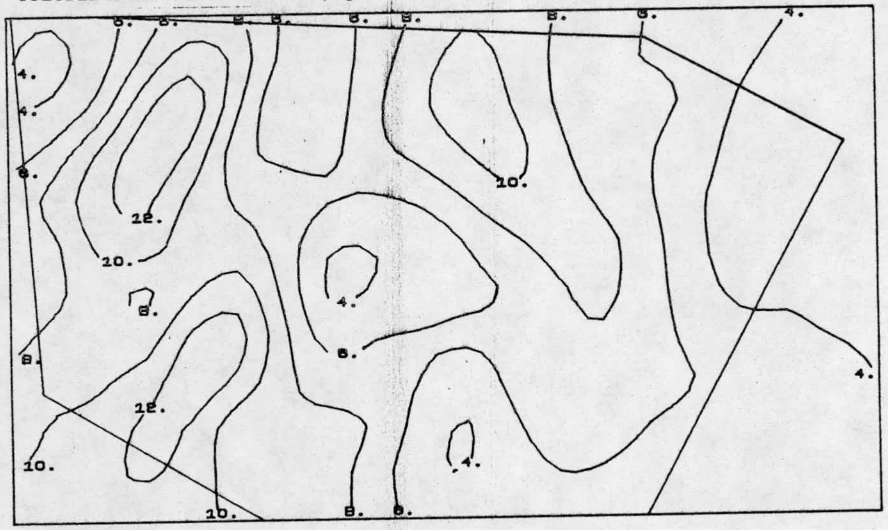
SOLUBLE $SO_4^=$ DEPOSITION IN RAIN, ng cm^{-2}



SOLUBLE Zn DEPOSITION IN RAIN, ng cm^{-2}

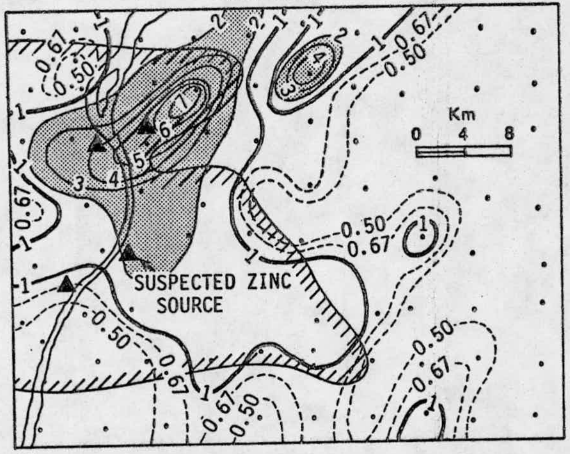


SOLUBLE Cd DEPOSITION IN RAIN, pg cm^{-2}



RAINFALL, mm

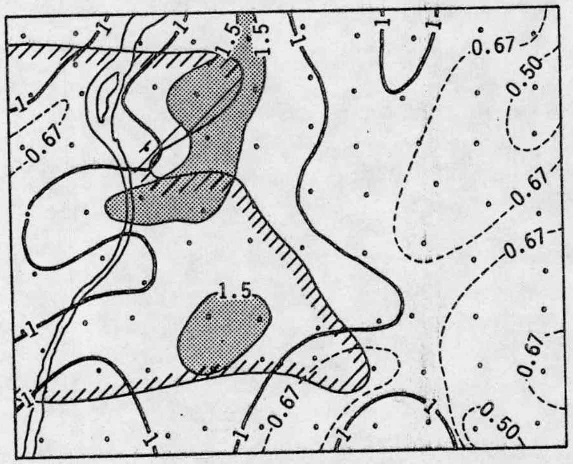
1972–1974



Zn:

Network mean: 8.90 ng cm^{-2} event^{-1}

Number of events: 26

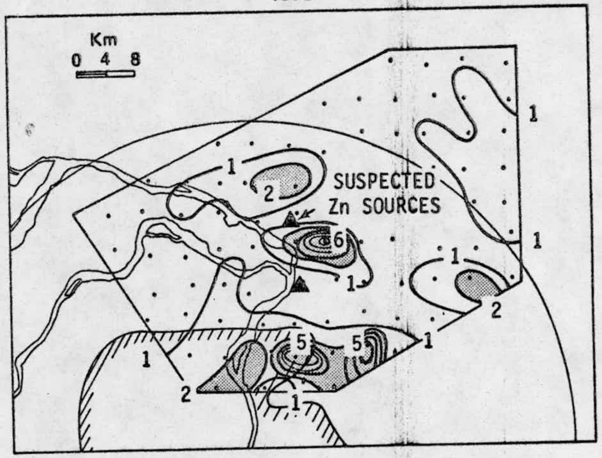


Rainfall:

Network mean: 8.02 mm event^{-1}

Number of events: 26

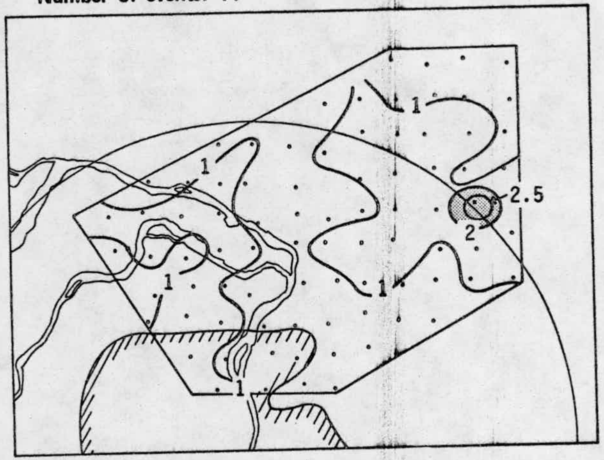
1975



Zn:

Network mean: 4.31 ng cm^{-2} event^{-1}

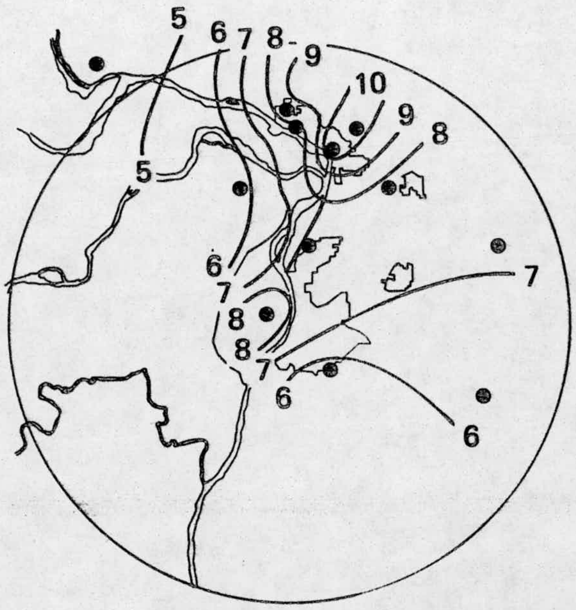
Number of events: 11



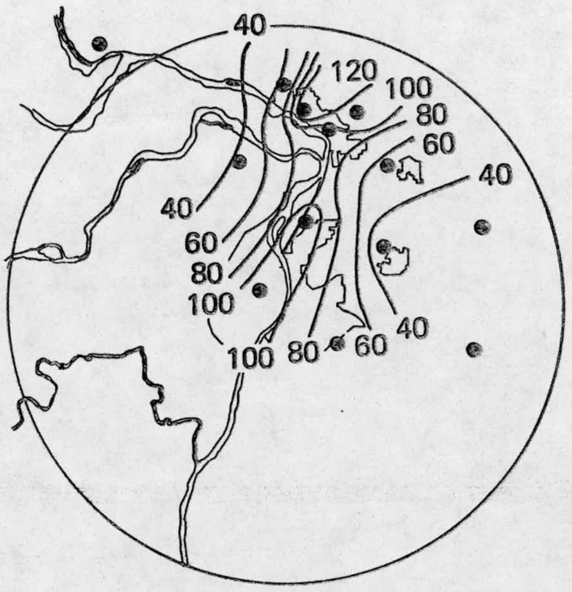
Rainfall:

Network mean: 3.85 mm event^{-1}

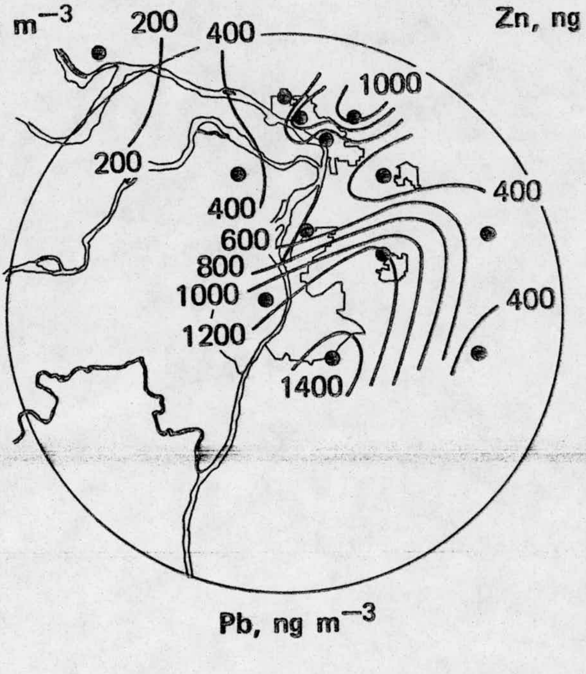
Number of events: 11



$SO_4^{=}$, $\mu g\ m^{-3}$



Zn, ng m^{-3}



Pb, ng m^{-3}