THE VARIABILITY OF pH IN CONVECTIVE STORMS

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ABSTRACT

The rainwater pH was measured in a total of 22 storms which occurred in 1972 and 1974 in the METROMEX (METROpolitan Meteorological EXperiment) rainwater sampling network. The network consists of 81 collectors in an area of 1800 km^2 over and east of St. Louis, Missouri.

The data set is composed of dry fallout samples as well as precipitation samples which have been analyzed independently. An analysis of the frequency distribution of these data show the rainfall samples form a bimodal distribution of pH with relative frequency maxima at pH 7.0 and 4.0 while the dry samples are unimodal with the maximum frequency at pH 7.0.

The areal distribution of precipitation weighted mean pH indicates a variability unrelated to total precipitation. However, the derived deposition of H^+ is more similar to the areal rainfall pattern than to the pH. The dH is defined which incorporates both the rainfall and pH which is useful for climatological trend studies of acid rainfall.

Examples of two individual storm events illustrate an inexplicable area-wide variation from nearly an all acid rain ($pH \leq 4.5$) to an all alkaline rain ($pH \geq 5.5$). These case studies indicate some of the meteorological as well as chemical problems which must be considered when attempting to characterize convective storm rainfall pH.

INTRODUCTION

A five-year research program on inadvertent weather modification was initiated in St. Louis, Missouri in the summer of 1971 under the acronym of METROMEX (METROpolitan Meteorological EXperiment) to examine the effects of human activity on local climate (Changnon et al., 1971). The research program represents the most comprehensive study of its

kind undertaken anywhere in the world incorporating diverse research groups possessing expertise in several areas of atmospheric science. A summary of the results after 3 years of field measurement efforts were published in the Bulletin of the American Meteorological Society (1974) with nearly all of the participants included as authors of various sections.

The major emphasis of METROMEX field effort is on the quantification, location, and causes of a summer season precipitation anomaly previously defined by climatological research (Huff and Changnon, 1972). In addition, the most important result anticipated from this large research effort is the identification of the *impacts* of the anomaly on various segments of society.

One of the obvious impacts involves the wet and dry deposition of atmospheric aerosol over both urban and rural areas in the downwind region of the St. Louis metropolitan area. The potential problem is analogous to the radioactive "hotspots" which periodically arose during the atmospheric testing of nuclear devices. In essence, the argument for concern with inadvertent precipitation modification rests upon the concept that convective storms result from the confluence of water substance in a localized atmospheric volume. Subsequent change-of-state initiates cloudiness with attendant microphysical processes forming precipitation.

All of these processes are active as transport and sink mechanisms for natural and anthropogenic aerosols. Consequently, either increased frequency of precipitation initiation or enhancement of precipitation processes can lead to localized enrichment of chemical deposition posing various topics for further research including impacts dealing with water quality, soil chemistry, agriculture, and structural damage.

Much of the air and precipitation chemistry research in METROMEX is directed toward assessing the magnitude of the alteration of rainwater quality in the region of the precipitation anomaly using a case study approach. As a part of this chemistry research effort, the pH of storm event wet and dry deposition samples is examined to assess its variation in proximity to an urban-industrial complex and to elucidate the sampling problem with regard to monitoring future trends.

SAMPLE ACQUISITION AND PROCESSING

The major goals (Changnon et al., 1971) of the METROMEX research program necessitated the installation and operation of the world's largest raingage network of 250 gages concentrated in an area of 8000 km^2. A subsection of this network shown in Figure 1 comprised a precipitation sampling network of 81 collectors in an area of 1800 km^2. The collectors were colocated with a recording raingage to aid interpretation of rainwater chemistry relationships to storm structure with regard to wet deposition of aerosols.

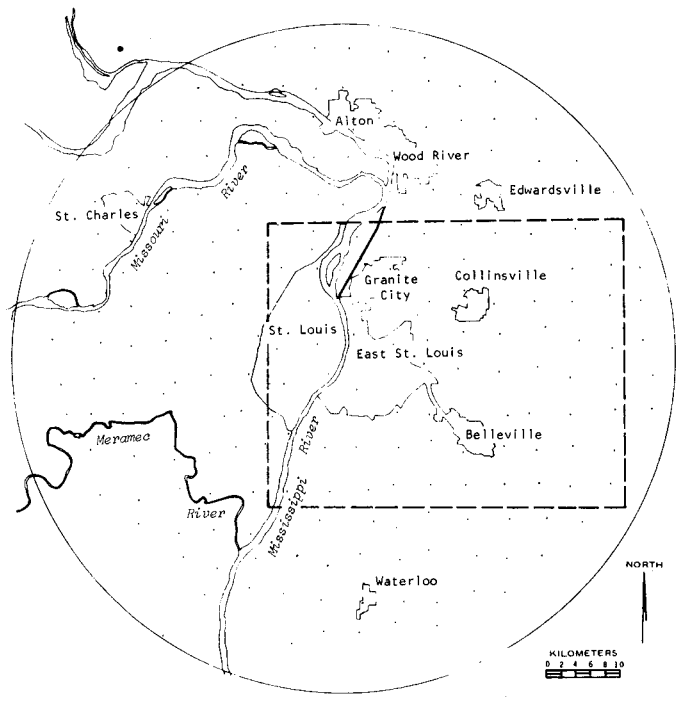

Figure 1. The research area encompassed by the St. Louis METROMEX field project. The recording raingage sites are indicated by the dots. The rectangle delineated east of the city is the precipitation chemistry network.

The collectors used in this program consisted of fence-post mounted polyethylene bottles installed approximately 1.5 m above ground level within clearly exposed areas. The bottle capacity was 2 liters with an opening of 60 cm^2. Typically the bottles were deployed in the field based on a weather forecast of precipitation during the immediate 24 hour period. During 1972 the samples were collected within one or two hours after the cessation of precipitation whereas those acquired in 1974 were collected on a 24 hour schedule.

Since the entire data collection was dependent upon the accuracy of the meteorological forecast of precipitation, it was inevitable that some data on completely dry samples occurred.

Each of the predicted precipitation events was assigned an experiment number to ease the later identification of samples for further processing and the chemical analyses for trace metals by flame emission and atomic absorption spectrophotometry. All of the collected samples were transferred from the field location to the analytical facility within 48 hours of the storm event. Within 24 hours of receipt of an experiment, the pH was determined and the rain sample was then

processed for subsequent elemental analysis. The samples obtained in the absence of precipitation were treated in exactly the same way after the addition of 50 ml of double-distilled, deionized water and allowed to equilibrate for 24 hours.

A commercial pH meter was used for the measurement. In a few instances, the meter was used in the field to determine the pH in near real time, at the field headquarters as samples were prepared for shipment to Champaign, and at the laboratory facility in Champaign. A comparison between these measurements did not indicate any significant variance in the values and all subsequent pH determinations were made in the laboratory.

pH FREQUENCY DISTRIBUTION

The field samples consisted of both wet and dry data since the area was sufficiently large that showers frequently did not cover the entire network and occasionally forecasted precipitation did not occur. A total of 941 determinations of pH were made with samples collected from 88 dry and 853 convective shower and thunderstorm events.

The frequency distribution of pH for the dry fallout samples is shown in Figure 2. This limited set of data shows a distinct trend

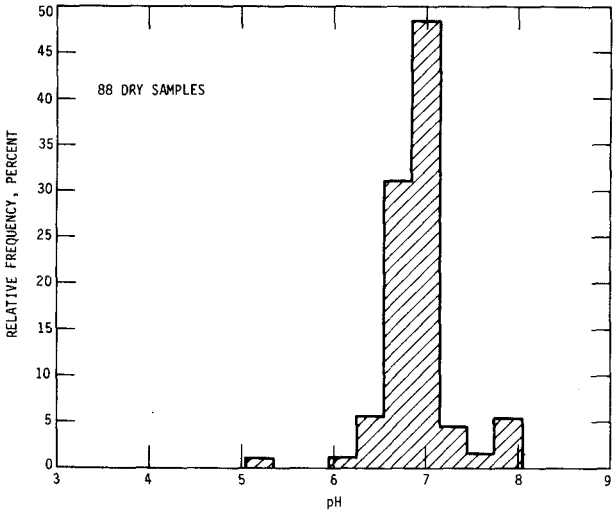

Figure 2. The relative frequency distribution of pH values derived by the addition of 50 ml of 6.5 pH laboratory water.

toward a normal distribution with a mean of pH 7. The deionized laboratory water has pH 6.5 and the observed distribution is not unexpected. However, it is worth noting that the dry deposition of potentially acid aerosol and the subsequent dissolution was not detected in these samples. In fact, it can be concluded that these observations indicate the presence of water soluble, alkaline materials in the dry samples.

The rainwater pH frequency data are shown in Figure 3. In contrast

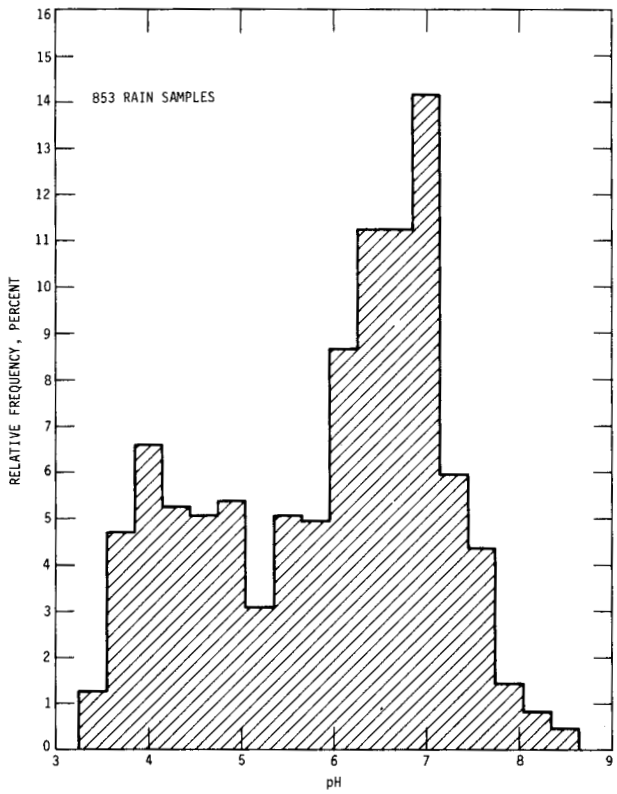

Figure 3. The rainwater pH relative frequency distribution obtained from 853 samples during 22 strom events in 1972 and 1974.

to the dry samples, the precipitation exhibits a bimodal distribution with only 12.6% of the data equal to or less than pH 4 and 27.2% equal to or greater than pH 7. It is interesting to note that the minimum between the two modes occurs at a value corresponding to equilibrium between air containing CO_2 and pure water of approximately 5.7.

The cumulative relative frequency distribution obtained from these data indicated that 50% of the values exceed pH 6.0 which is still more alkaline than CO_2 saturation. These data are not unlike those reported by Merva (1974) for various stations in Michigan. Merva showed separate distributions for maximum and minimum values with average values of 7.7 and 4.7 respectively. The overall average for the state of Michigan was reported as 6.17.

AREAL DISTRIBUTION OF pH

The precipitation weighted mean pH values at each of the sampling sites within the raingage network (Figure 1) are shown in Figure 4 for the 22 rain events. The weighted mean pH value for the entire 1800 km^2 area is 4.9. The corresponding mean rainfall is shown in Figure 5. It

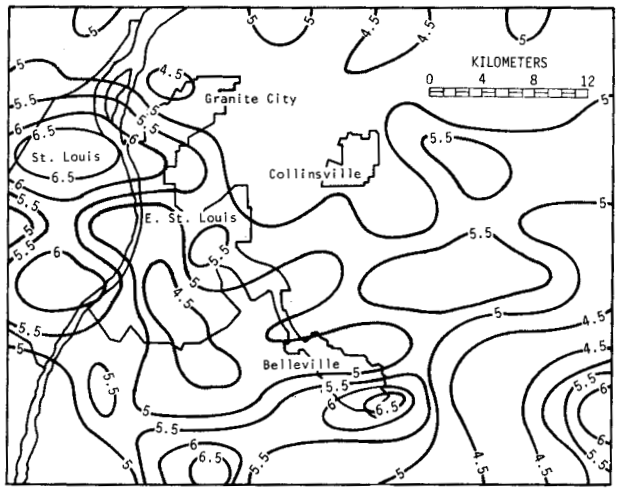

Figure 4. The rainfall-weighted mean pH pattern resulting from data acquired at 81 sites in the 1800 km^2 area. The areal mean of these data is pH 4.9 with a range of values from 4.3 to 6.8.

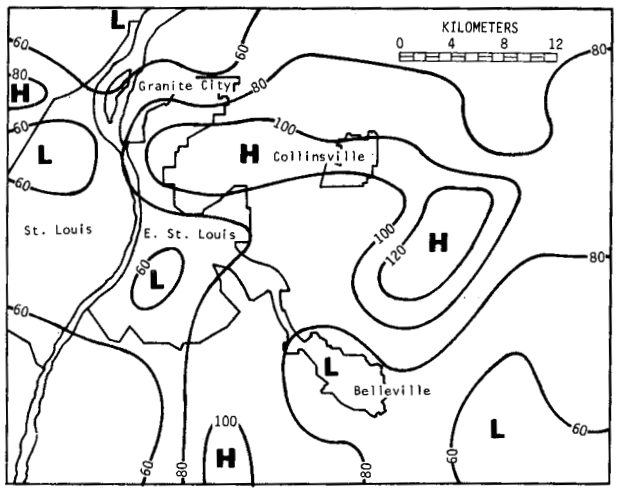

Figure 5. The mean rainfall in ml associated with the pH data in Figure 4 from 22 storms in 1972 and 1974.

is obvious that there is little correspondence between these data. The low pH values near E. St. Louis extending SE correspond to a gradient in rainfall from a low of < 60 ml to a high of > 100 ml. It should be noted that the maximum rainfall area in Figure 5 is in the same region as the climatically defined rainfall anomaly associated with St. Louis (Huff and Changnon, 1972). It is within this area that 20% to 30% increases in rainfall occur during the summer season amplifying the seriousness of understanding the local alteration of rainwater quality.

The relatively large areas of pH > 6 in the W-central, S-central and SE portions of the network appear perplexing in view of the distribution of SO_2 point sources shown in Figure 6. Equally difficult to relate to industrial activity is the area of pH < 4.5 in the SE part of the network which is an active agricultural area removed from any point SO_2 sources.

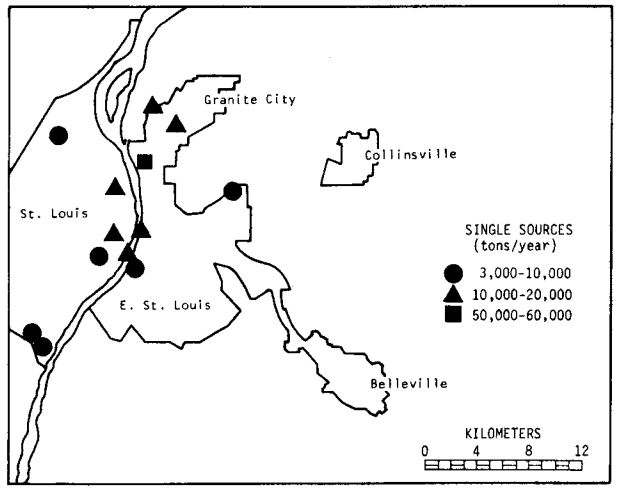

Figure 6. The location and extimated source strength of sulfur oxide in proximity to the chemistry network. These data were obtained from an emission inventory conducted during 1963-1964 as part of the St. Louis - East St. Louis Interstate Air Pollution Study and is contained in their report.

On the other hand, Kemmerer and Jackson (1973) demonstrated the balance between calcium aerosol and oxidized SO_2 as an explanation of neutral pH precipitation. Departures from this balance were shown to relate to acid or alkaline rains depending upon the proximity of the sample site to particulate sources. The pH data of Kemmerer and Jackson in Syracuse, New York relate quite well to these data for St. Louis. The absolute range of the data from the 4 Syracuse sites extended from 4.05 to 9.20 and the average values from 4.26 to 7.8. The range of the St. Louis data in Figure 4 extended from 4.3 to 6.8.

In addition to the SO_2 point sources shown in Figure 6, there are several point and areal sources in proximity to the chemistry network ascribed to the cement manufacturing industry. Several active quarries align the Mississippi and Missouri River valleys which are abundant sources of aerosol containing calcium carbonate and other basic anhydrides. In addition there are 2 cement processing plants providing additional sources of aerosol capable of neutralizing otherwise acidic rainfall. It has been shown by Semonin (1972) that surface released materials are transported by convective air motions to clouds and returned to the surface by precipitation relatively near the source. These experiments with unique chemical tracers suggest the possible rapid response of precipitation formation processes to scavenging of either water soluble alkaline or acid aerosol resulting in the observed pH.

In a review of rainwater as a chemical agent in geologic processes, Carroll (1962) indicated the potential importance of the H^+ to the weathering of soil minerals. As a first approximation, we may assume the pH as representative of the H^+ concentration and calculate the deposition by precipitation. The mean H^+ deposition in μg is shown in Figure 7. There is a reasonable correlation between the mean precipitation shown in Figure 5 and the deposition illustrating the dominating influence of rainfall on the spatial variability.

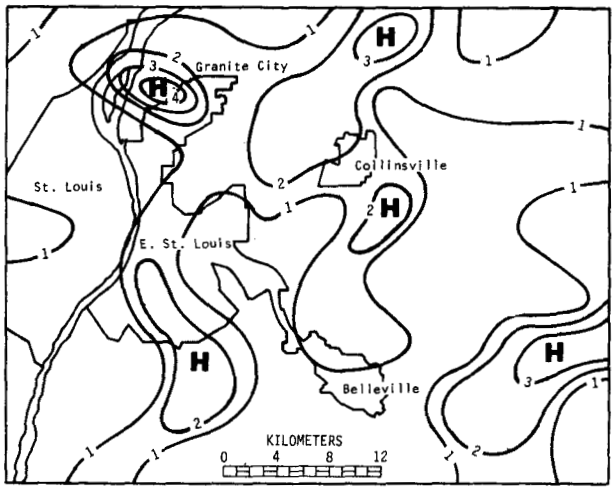

Figure 7. The mean H^+ deposition in μg calculated from the pH and rainfall of the 22 individual storm occurrences in 1972 and 1974.

For applications in the geophysical sciences, it seems apparent that rainfall pH alone is not sufficient to describe its potential impact. As with other chemical properties of rainfall, the quantity of material deposited at the surface is not specified by the concentration, but must be calculated from simultaneous measurement of the total rainfall. The environmental response may vary considerably between high concentrations with light rainfall and relatively low concentrations with heavy rainfall. A number can be defined, analogous to pH, which also includes the weighting factor of precipitation,

$$dH = -\log_{10} [P \cdot 10^{-(pH+3)}]$$

where P is the total sample precipitation.

The use of dH is an attempt to introduce a single number for investigations involving rainfall pH. The antilog of the negative dH is a direct indication of the H^+ deposition accounting for not only the acidity of the rainfall, but also the water volume involved. To illustrate the dH concept, the numbers were calculated for the mean pH and precipitation data discussed previously. The results are shown in Figure 8. The dH values range from 5.37 to 7.93 and these extremes are both found in the NW quadrant of the chemsitry network. The corresponding mean values of pH and precipitation at these sites were 4.3 and 6.6, and 78.4 and 45.5 ml, respectively. None of these individual site measurements were extreme values for either pH or rainfall.

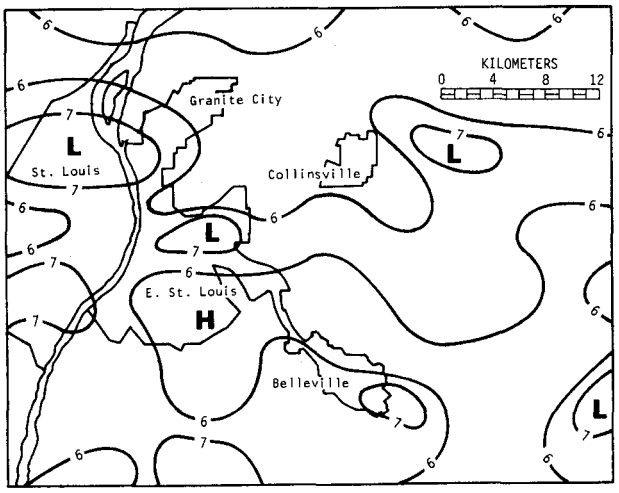

Figure 8. The pattern of the mean dH, a number incorporating both pH and rainfall.

CASE STUDIES OF INDIVIDUAL STORMS

28 July 1972

The St. Louis area was under the influence of circulation around a low pressure center in central Kentucky with a stationary front extending WSW through SE Missouri to W Texas. The winds throughout the lower 2 km were from the NE at 2 to 5 mps. The slow advection of the entire storm system to the E carried showers with it moving through the sampling network from the NW. Due to the complex relationship between the sub-cloud airflow, the movement of individual storms, and the advection of the cyclonic system, it is difficult to relate the measured pH to known industrial sources of gaseous and particulate materials.

The pH pattern observed from this storm system is shown in Figure 9. The corresponding rainfall (Figure 10) illustrates the variability of the convective shower activity. The high pH shown in the NW corner can be associated with cement plant operations in that area, but no comparable explanation is offered for the N - S band of high pH at the E edge of the network. The relatively low values S of E. St. Louis and extending SE can be related to the dense industry in the area, but, again, the low values in the N-central and NE are unrelated to known sources in the immediate area.

The weighted mean pH for this event was 4.8 with a standard deviation of 1.3. The range of values observed was from 3.4 to 8.2. This type of pattern is not unlike many others and would be classed as an acid rain for this area.

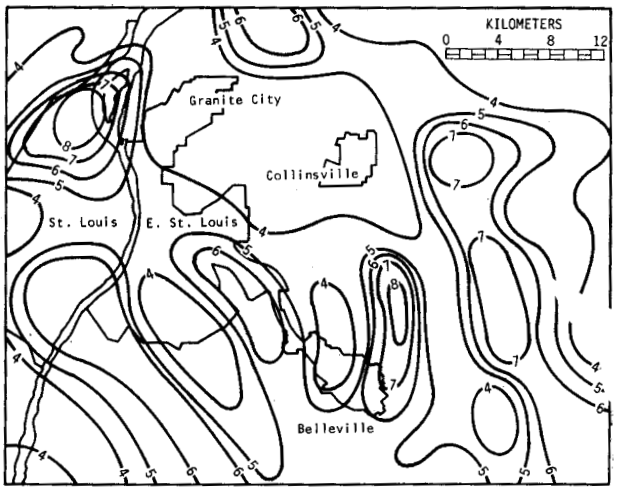

Figure 9. An example of the pH variability from a convective storm on 28 July 1972 with areal mean pH 4.8 and a range extending from 3.4 to 8.2.

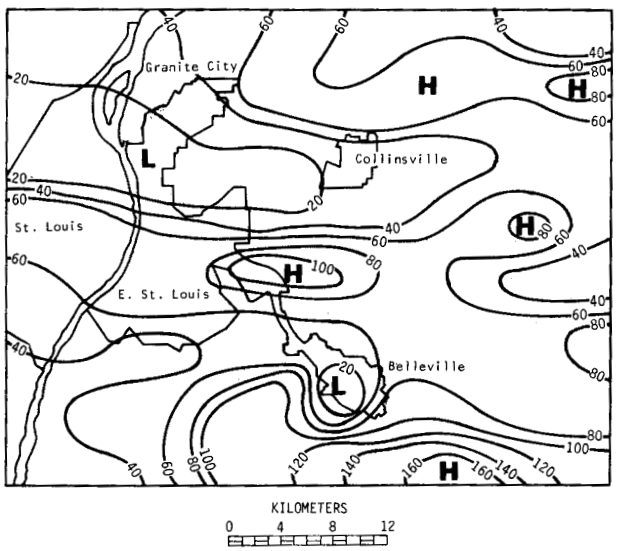

Figure 10. The precipitation in ml associated with pH shown in Figure 9.

6 August 1972

A cold front passed through the research area during the evening of 6 August with showers and thunderstorms preceding it during the day. The surface winds in advance of the approaching front were from the S at 3 mps becoming stronger from the NW after the frontal passage.

The pH distribution from this event is shown in Figure 11. The thunderstorm rainfall (Figure 12) was obviously more alkaline than the case of 28 July and with the low-level transport wind from the S, which is an agricultural flood-plain, the source of neutralizing aerosol remains a subject for future research.

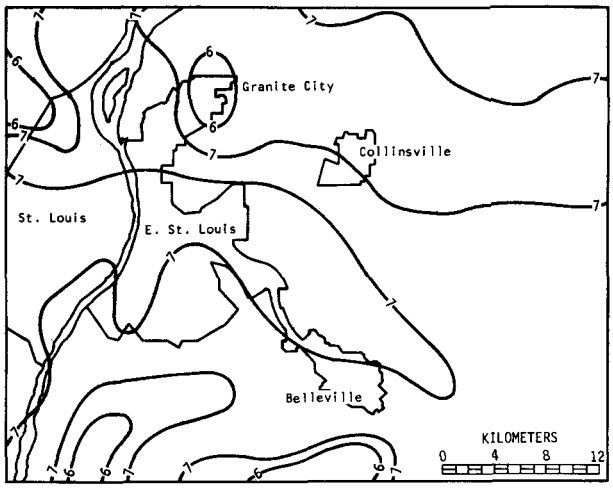

Figure 11. The pH pattern which occurred with a convective storm system prior to a cold frontal passage on 6 August 1972. The areal mean pH was 6.4 with values between 5.2 and 7.9. This case shows the alkalinity of many observed precipitation events.

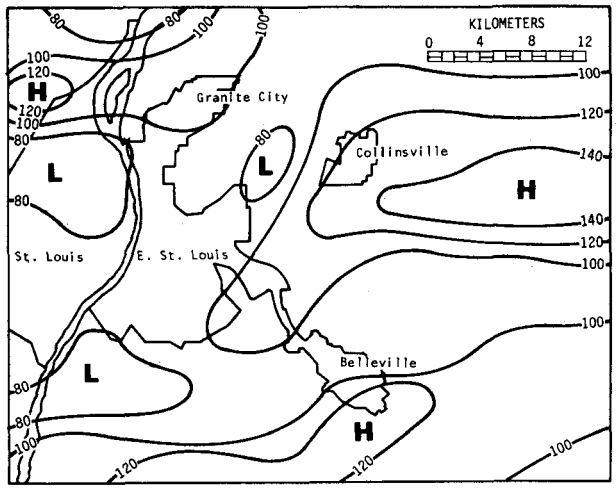

Figure 12. The rainfall in ml which produced the pH pattern shown in Figure 11.

The areal mean pH was 6.4 with a standard deviation of 0.7. The pH values ranged from 5.2 to 7.9. As in the case of the acid rain of 28 July, this pattern of pH occurs frequently, but is classed as an alkaline rain.

SUMMARY AND DISCUSSION

The two case study events illustrate the difficulties in sampling precipitation for chemical analyses. Even possessing knowledge of the locations and general character of industrial effluents, the causes of acid or alkaline rainfall will not be uniquely determined. The complex chemical matrix of rainfall in an urban area with numerous and diverse sources of gases and aerosols is certainly a contributing factor toward

the inability to clearly define the observed pH variability. In addition, many of the difficulties of interpretation arise from inadequate observational data with regard to meteorological measurements in conjunction with a poor understanding of the interaction between cloud and precipitation processes and the atmospheric aerosol.

These studies also indicate the difficulties encountered when siting sampling stations. The purpose of an individual study must be made clear to ensure adequate sampling. For the investigation of storm variability, identification of individual sources, and attempting to clarify mechanisms, a network *at least* as dense as the one used in METROMEX (1/22 km^2) is necessary.

The deposition of the H^+ is, of course, directly related to both the acidity and the quantity of precipitation. For climatological studies of long term trends of pH, a term, dH, is defined which is analogous to the pH, but also incorporates the precipitation. Since the impact of pH on much of the environment is related to both the acidity and the amount of rainfall, it is recommended that studies of dH be undertaken which will automatically include the climatic change of precipitation.

The METROMEX research has established the existence of an anomaly of 20% to 30% increase of precipitation downwind of the St. Louis area within 20 to 60 km. The increase of precipitation occurs in a locale favorable for the ingestion of the urban aerosol and, consequently, the quality of the water is subject to alteration. The impacts of such alterations in rainwater quality on the agricultural production, soil chemistry, and many other facets of economy in such a localized region have not been fully assessed. With the likely increase in fossil fuel usage in the coming years, it is time to seriously address these problems.

Finally, the frequency distribution presented indicate a distinct bimodality and together with the variations in the summer mean pH serve to further emphasize the caution which should be exercised in establishing and operating monitoring stations. Benchmark stations should be inaugurated in remote areas with several sites in and surrounding urban areas. While it would be economically beneficial to collect samples on a random, synoptic basis, the frequency data suggest that a biased selection of storm data might be acquired in a short duration project. The proposed network of stations should be operated continuously for many years to fully understand the incremental change in rainwater quality attributable to the increased rate of fossil fuel consumption in the United States.

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