Temporal and Spatial Variability of Rainfall pH

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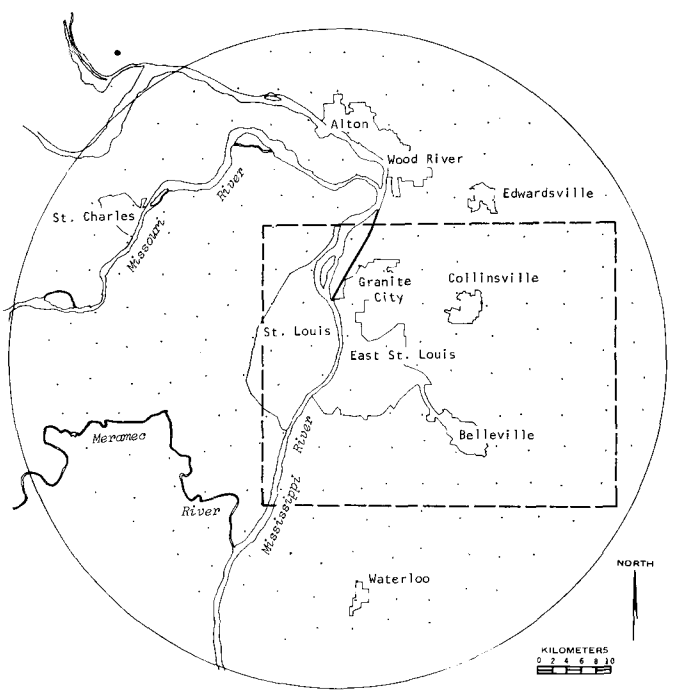
ABSTRACT.—The distribution of average rainwater pH over an area of 1,800 km^2 containing 81 collectors was determined from 25 storm events. The areal average of the data was pH 4.9, with a range of values from 4.3 to 6.8. A single storm event was studied to determine the change of pH as a function of time. The initial rain was pH 7.1, decreasing to 4.1. An excellent agreement was observed between the H^+ deposition rate and the rainfall rate.

THE STUDY OF PRECIPITATION chemistry is an essential component of the METROMEX (METROpolitan Meteorological EXperiment) research on inadvertent weather modification at St. Louis, Mo. Through the use of chemical tracers and analytical techniques, it has been established *(Semonin 1972)* that materials released from near the surface are processed, scavenged, and deposited by migratory storm systems in an area defined in climatological studies of Huff and Changnon *(1972)* as the St. Louis precipitation anomaly. The chemistry research is directed toward the estimation of convective cloud scavenging efficiency by the analysis of several elements found in rainwater, but also includes the occasional measurement of pH and conductivity.

Figure 1.—The St. Louis METROMEX field project research area. The dashed rectangle delineates the precipitation chemistry network.



Much of the land area within the METROMEX research circle (fig. 1) is in agriculture, and the deposition of the hydrogen ion in a localized high-rainfall area is a feature of inadvertent weather modification pertinent to crop production in proximity to urban centers. In addition, the effect of pH on the quality of storm runoff water and shallow groundwater supplies is a subject requiring serious attention as continued industrial development proceeds.

The data presented here begin to address these problem areas by illustrating the local variability of precipitation pH. An evaluation of the impact of such pH variability on regional planning, crop production, and local water supplies is treated. Though these impacts are extremely important, the nearly total lack of validation of rainwater pH effects on agriculture and water quality relegate this paper to presenting data with little interpretation of its meaning to longer-range problems of environmental quality.

DATA COLLECTION

Twenty-five convective storm days in the summers of 1972 and 1974 comprise the data set. The area studied covers 1,800 km^2 and contains a network of 81 rainwater collectors and 3 sequential rain samplers described by Gatz et al. *(1971)*.

The network samplers consist of a 1-liter polyethylene bottle fixed to a metal farm fencepost by an adjustable large-diameter hose clamp. The samples were collected within 2 hours after cessation of precipitation and transported to the laboratory facility for analysis within 36 hours. The pH was determined immediately upon arrival of the sample in the laboratory and before any preparations for subsequent elemental analysis by atomic absorption spectrophotometry.

The sequentially collected samples were treated in the same way as those from the network. However, these samples were acquired as a function of rainfall rate by a tipping-bucket arrangement in a housing containing 72 collector bottles. The bucket emptied into polyethylene bottles after sufficient volume of rain fell on the 1-m^2 collection surface (usually ½ liter), and the local time was recorded for each collection event. The recorded time interval for the sample collection was used to calculate the rates of deposition for the precipitation, various elements, and the hydrogen ion.

AREAL VARIABILITY

The pH determinations from each site for all 25 storm events were combined to provide an average distribution over the sampling network. The average pH values were calculated by first computing the total grams of hydrogen ion deposited by the 25 storms and dividing by the total water collected. The results (fig. 2) show that it is difficult to envision a direct relationship between known SO_2 sources (fig. 3) and the areal pattern of the pH.

The area of pH $\leqslant$ 4.5 can, of course, be qualitatively related to the concentration of point sources along the Mississippi River in St. Louis and E. St. Louis. Likewise, the small area of pH $\leqslant$ 4.5 near Granite City coincides with the indicated nearby sources. However, the large areas of pH $\geqslant$ 6.5 over the St. Louis urban center, and the low pH values in the southeastern corner of the network do not correlate well with known industrial operations. The overall average pH for the entire 1,800-km^2 area determined by combining the measurements for all storms from all sampling sites was 4.9

An examination of the frequency of pH $\leqslant$ 4.5 (fig. 4) was made to determine the persistance of low pH values at each site. The high frequency in the southeastern corner of the network remains an anomaly and requires verification by additional data. The remaining centers of frequent occurrence can be attributed to SO_2 sources in proximity.

Figure 2.—The rainfall-weighted average pH pattern derived from 25 storms. The areal mean is 4.9 with a range of values from 4.3 to 6.8.

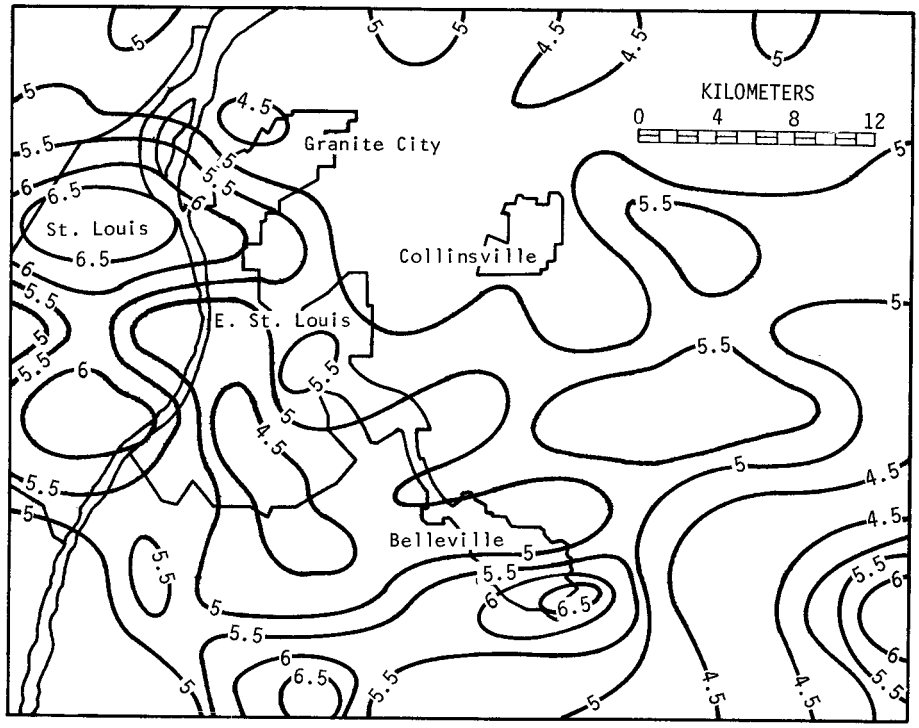


Figure 3.—The location and estimated sulfur oxide source strength in proximity to the chemistry network.

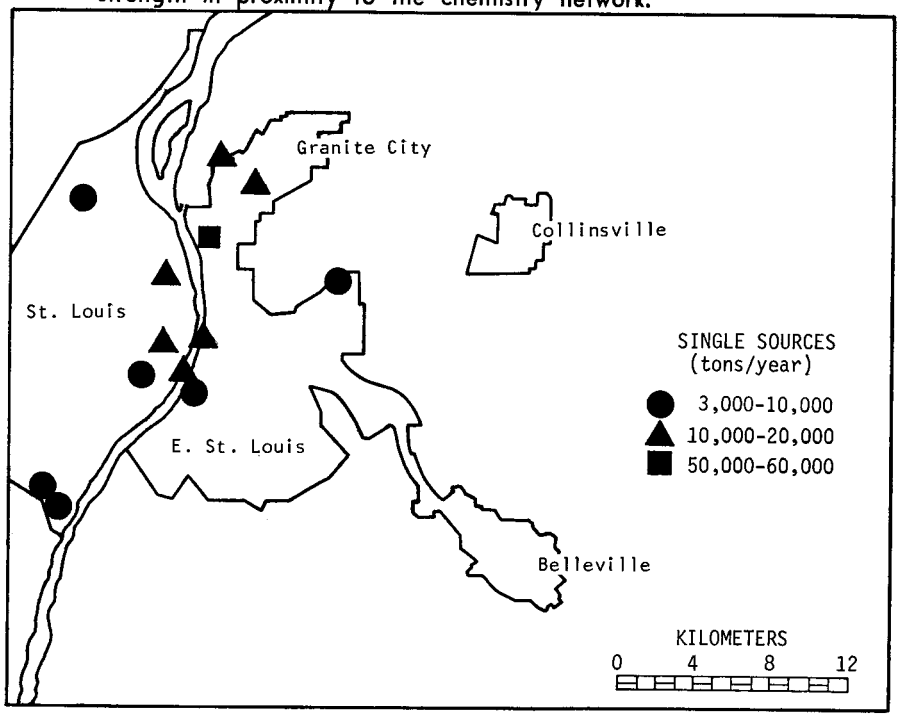
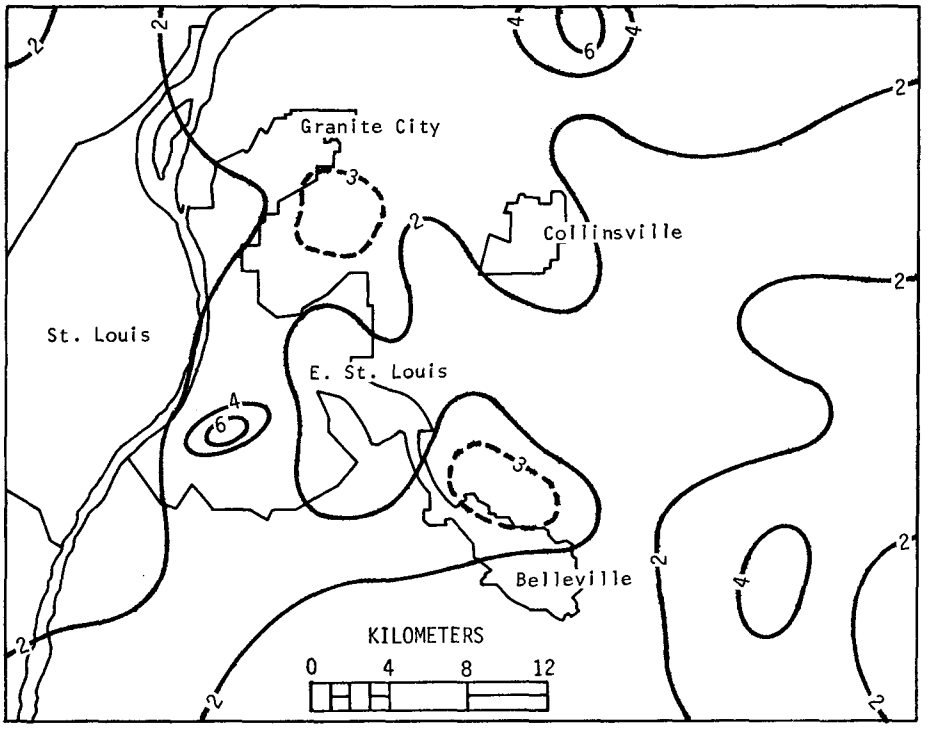


Figure 4.—The point frequency of pH $\leqslant$ 4.5 from the 25 storm data set.



The value near Edwardsville may be due to the Wood River refineries 10 km northwest of the network. It is interesting to note that only 15 to 25 percent of the rain samples in these areas produced the average pH values $\leqslant$ 4.5.

The average rainwater (fig. 5) associated with the 25 storm events is consistent with the concept of inadvertent precipitation modification by an urban complex. The historical records for the St. Louis region indicate a rainfall anomaly extending north to south approximately 15 to 25 km east of the Mississippi River. Even the small sample of storm events used for this study indicates an average high rainfall in the anomaly area, which points to the problems of selecting data-collection sites.

The hydrogen ion deposition (fig. 6) calculated from the pH and rain volume shows somewhat better spatial correlation with the SO_2 sources. However, the removal processes by convective storms are extremely complex and variable, resulting in a spatial averaging and smoothing of the observed rainfall and pH data. The results from METROMEX *(Huff 1973)* indicate two major areas of importance to inadvertent precipitation modification. The first of these is the city of St. Louis; the second is the Alton-Wood River industrial complex. The latter is not included within the network boundaries, and the contribution of Alton-Wood River to the pH variability can only be surmised at this time.

The deposition pattern can be envisioned as consisting of three bands of relatively high deposition oriented approximately north to south and separated by 15 to 20 km. Though this orientation is not unlike that of organized convective storm systems, there is no meteorological explanation for the apparent banded structure of deposition. A superficial comparison between the patterns of average rainfall (fig. 5)

Figure 5.—The average rainfall from the 25 convective storms used in this study, in milliliters.

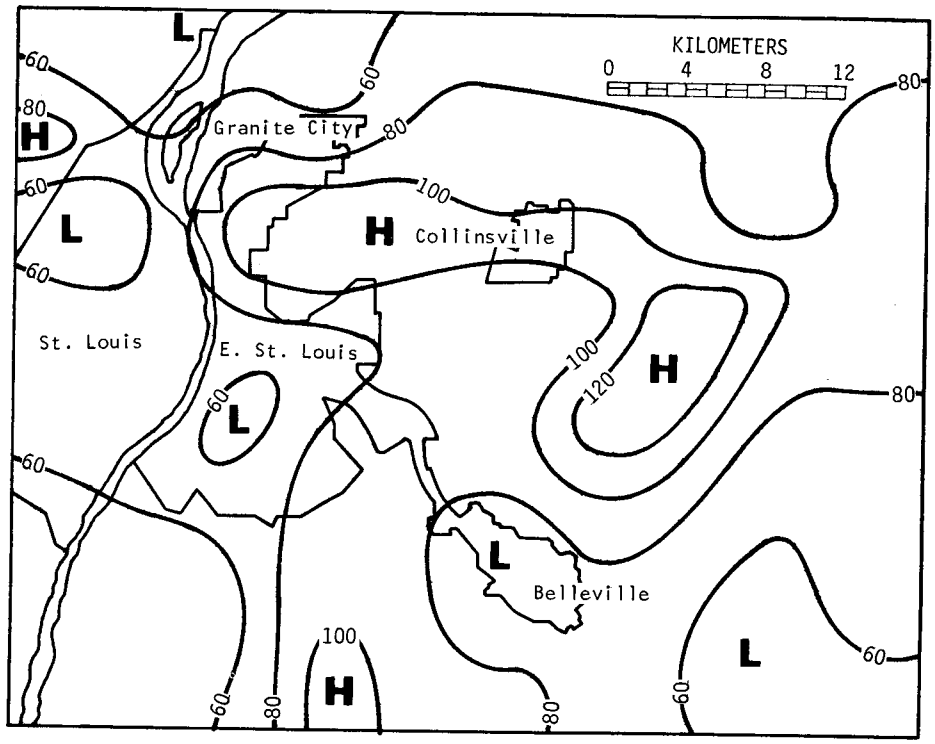


Figure 6.—The average H^+ deposition calculated from the rainfall and pH measurements, in micrograms.

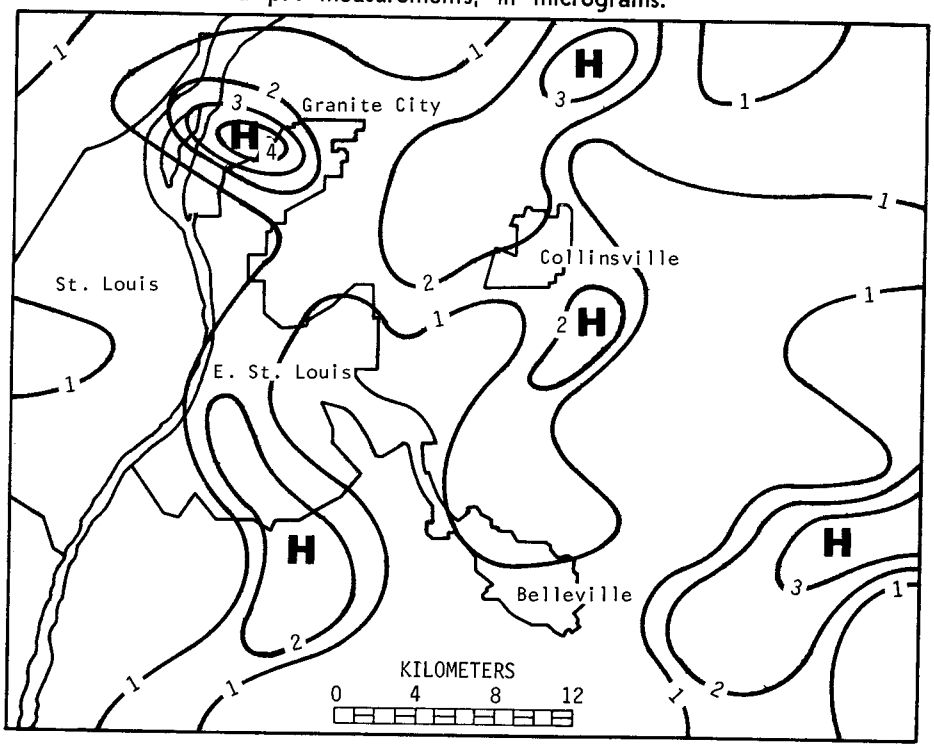
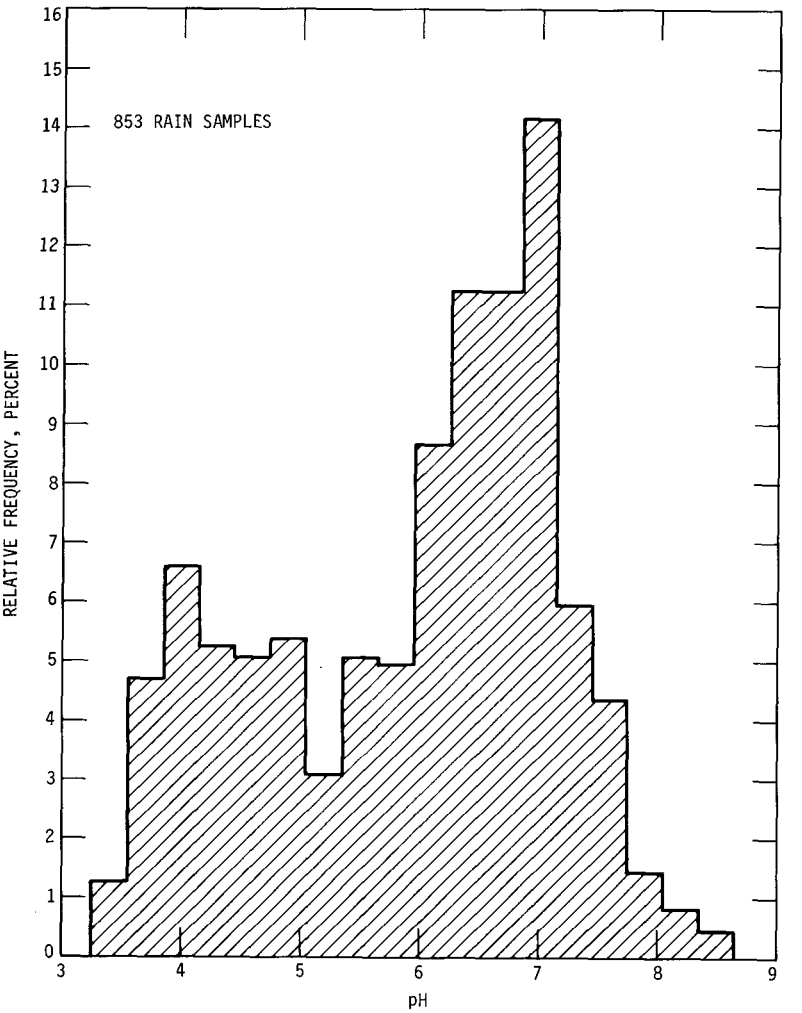


Figure 7.—The relative frequency distribution of rainwater pH from 25 storms in 1972 and 1974.



and average pH (fig. 2) suggests little correlation and emphasizes the independence of these two variables. Consequently, it is necessary to measure both the total rainfall and the pH to assess the potential environmental response to acid rainfall.

The relative frequency of pH (fig. 7) obtained by combining all 853 observations from the network is another way of illustrating the variability of acid rainfall. The most striking feature of this analysis is the high frequency of neutral rainfall and the secondary peak at 4.2 pH. This secondary peak is created by the relatively few sites that undergo frequent low pH precipitation as previously described. Further measurements are necessary, however, to determine the precipitaton pH frequency in other seasons of the year when urban and industrial emissions may be quite different from those during the summer months.

TEMPORAL VARIABILITY

The potental impact of pH on the environment cannot be fully determined by study of bulk rain samples as acquired from the network. For example, all the

pH-determining compounds could be deposited either at the beginning or at the end of a convective storm, with different implications as to the expected effects.

The data obtained on 3 August 1972 exemplify the temporal change of pH and the changes of rainfall rate (fig. 8). Throughout the first 45 minutes of rain the pH decreased dramatically from 7.1 to 4.1 while the rainfall rate remained relatively constant between 1 and 7mm hr^{-1}. The independent, nearby total rain sample had a pH of 3.9. Apparently the high pH of the initial light rain was insufficient to neutralize the later more intense and more acid precipitation.

The measurements from other storm events show opposite temporal change of pH; that is, increasing from low values to relatively constant values. This is an important feature of precipitation deposition of materials, making it possible to estimate the time rate of change of deposition. Since the concentration approaches a constant shortly after the initiation of a storm event at a point, the variation of the deposition rate is directly related to the preciptation rate (fig. 9). Therefore, as a first approximation for the depiction of the rate of hydrogen ion deposition, simple measurements of total storm rainfall pH and rainfall rate are all that is required.

SUMMARY AND DISCUSSION

The areal variability of average pH appears to be independent of the average rainfall variability and cannot be related easily to known SO_2 sources. With the exception of a few sites, the

Figure 8.—The variation of pH (closed circles) with time during the convective storm of 3 August 1972. The nearby total storm sample pH of 3.9 is indicated by the horizontal line. The rainfall rate (open circles) in millimeters per hour is shown for reference.

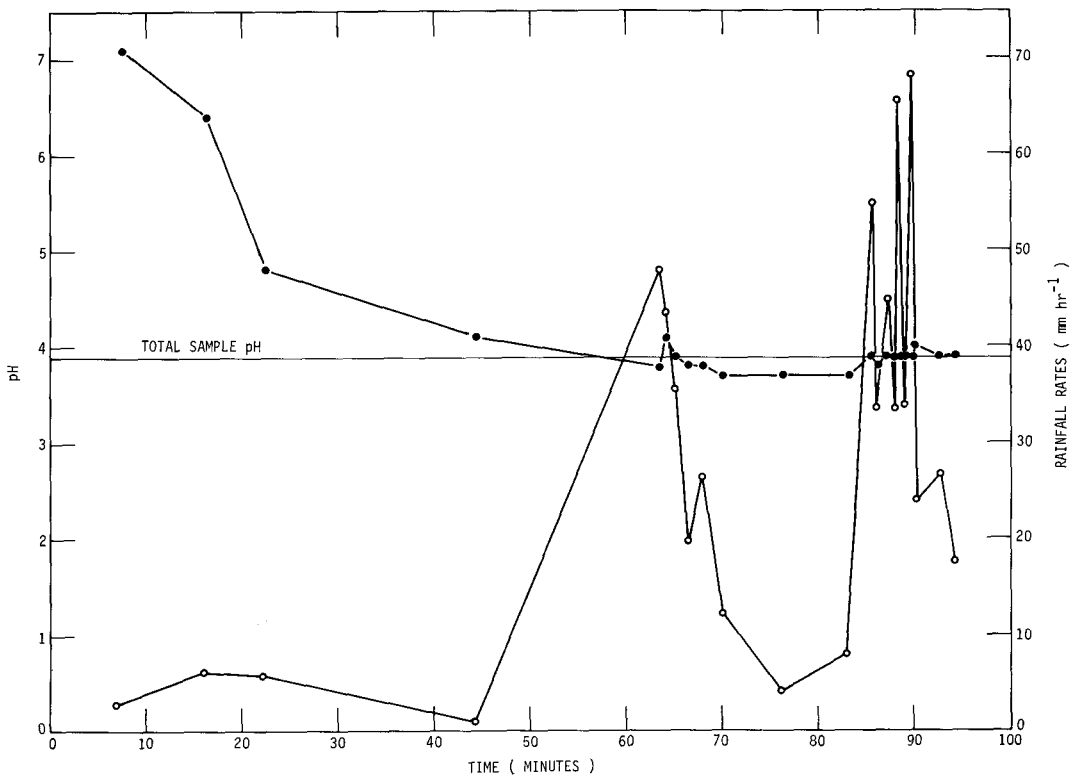
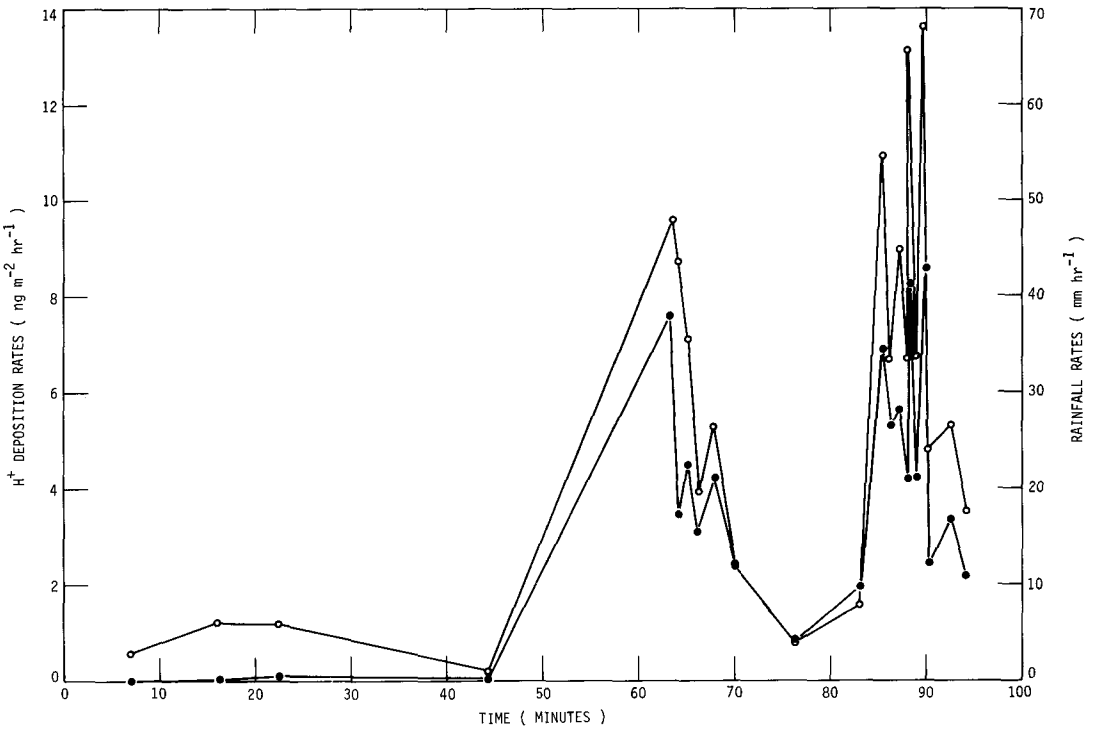


Figure 9.—The H^+ deposition rate (closed circles) and rainfall rate relationship for the storm of 3 August 1972.



most frequently observed pH was 7.0, indicating that acid rainfall is not an extremely serious problem in the 1,800-km^2 area immediately east of St. Louis. These data do point out the difficulties with regard to point measurements, and suggest that any conclusions regarding long-term trends must be viewed cautiously. The average pH may vary from an acid value ($\leqslant$ 4.0) to an alkaline value over a distance of a few kilometers.

The study of the temporal change of pH in convective precipitation further complicates the assessment of the variability. The case study presented showed a three-unit change of pH during the initial 45 minutes of a storm, with little subsequent change. During the period of nearly constant pH, the rainfall rate varied rapidly throughout the storm duration.

The observations reported here illustrate certain problems that must be treated in discussions on acid rainfall. The first is related to the desired use of the data. For the study of precipitation chemistry without regard to environmental impact, the long-term monitoring of pH from a single site may be acceptable. However, when the ultimate utility of pH data for the soil scientist, water quality expert, agriculturalist, and many other potential users is considered, these data show that single-site observations can lead to erroneous relationships between environmental degradation and precipitation.

The second problem area addressed in this paper is the relationship between the time-varying and total storm rainwater pH. The measurements show variations of pH during the storm to be as large as the spatial variations. Therefore, the study of the response of the environment to the acid content of precipitation must carefully consider such wide variations both in space and time.

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