# Illinois State Water Survey Division

### ATMOSPHERIC CHEMISTRY SECTION
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# STUDY OF ATMOSPHERIC POLLUTION SCAVENGING

*Twenty-Second Progress Report*
*Grant Number DE - FG02 - 88ER60635*

*August 1988*

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**ENR** Illinois Department of Energy and Natural Resources

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**A DESCRIPTION OF THE SEQUENTIAL CHEMISTRY OF RAIN EXPERIMENT-1988,
A COMPONENT OF 3CPO**

Van C. Bowersox

Introduction

A cooperative project to measure the chemistry and physics of convective storms was conducted during the period 1 May-30 June 1988 in an 80 km x 80 km area of east-central Illinois near Champaign-Urbana.  An organization named the Cloud Chemistry and Cloud Physics Organization, or 3CP0, coordinated the project, which was hosted by the Illinois State Water Survey.  Atmospheric chemists, physicists, and meteorologists comprised the scientific groups that formed this organization to plan, coordinate and conduct the project.  Project objectives (Daum, 1988) included:

(1)    to describe the air, water, and pollutant flow, and deposition fields in convective storms;

(2)    to identify and quantitatively describe the dominant chemical and microphysical processes that determine the fraction of water and pollutants deposited in precipitation during convective storms;

(3)    to examine the role of horizontal and vertical transport of moisture and pollutants in the evolution and maintenance of convective storms; and

(4)    to obtain data that will permit the development and evaluation of numerical models of convective storm dynamics, microphysics, and pollutant scavenging.

To achieve objectives 1, 2, and 4, it was necessary to measure the amount, rate of occurrence, spatial distribution, and chemical composition of precipitation.  Two components of the 3CP0 were funded to provide these measurements, PRECP-VI and SECORE-88.

PRECIP-VI, or Processing of Emissions by Clouds and Precipitation (PRECP, 1986), operated a network of more than 40 stations in an array covering the 3CP0 surface domain (Sisterson, 1987).  Each station was equipped with an automated wet-only sampler set to collect and separate rainfall increments of 0.1 cm depth. Chemical species measured by this network included the common anions and cations plus dissolved $SO_2$.

SECORE-88, or Sequential Chemistry of Rain Experiment-1988, operated a smaller network of four wet-only sequential samplers and 13 raingage sites. Sites were separated by about 1.1 kilometers and rainfall sequences were collected every .05 cm.  The common anions and cations were measured at three locations and at one of these locations, the Bondville site, samples from one sequential sampler were collected exclusively for aqueous $H_2O_2$ analyses.  SECORE-88 stations were nested within the larger PRECP-VI array and measurements were made on a higher time resolution than at PRECP-VI stations.

Together data from these two surface networks will be used to address the question of the temporal and spatial variability of wet deposition chemistry from convective cells, storms, and complexes within the area of one grid square of the Regional Acid Deposition Model (RADM). RADM is a predictive Eulerian model that has the capacity to predict wet and dry deposition fluxes given emissions and meteorological data. A primary objective of 3CP0 is to provide a data set that can be used for RADM verification purposes.

Objectives

The objectives of SECORE-88 were:

(1)     to measure the wetfall chemistry of convective raincells and to quantitatively describe the variability of ion concentrations in time and space for convective cells;

(2)     to examine the variations in chemistry both along and lateral to the motion of convective raincells and to relate these variations to the dominant scavenging processes;

(3)     to look for differences in the wet fluxes of species with gaseous precursors ($HNO_3$), gaseous and small particle precursors ($SO_2 +$ aerosol $SO_4^{2-}$), large particle precursors ($Ca^{2+}$ from soils and road dust), and others;

(4)     to apply statistical techniques of source identification; and

(5)     to provide data to the 3CP0 community for use in collaborative research with other investigators.

Experimental Design and Methods

Since the objectives of SECORE-88 focused on the chemistry of convective cells and not on storm complexes or larger features, it was necessary to limit the distance between sampling stations to a finer space scale than that used in the PRECP-VI surface network. In a previous study of non-severe midwestern thunderstorms, Westcott (1988) reported that the maximum area of detectable rain (defined as a radar reflectivity of >15 dBZ or a rain rate -0.2 mm/hr) averages about 57 $km^2$, which corresponds to a storm radius of 4.3 km. A core of heavier rain within this area of detectable rain is a typical feature of these storms. This storm core, or rain shaft (defined as a radar reflectivity of >35 dBZ or a rain rate -5.5 mm/hr.), averages about 24 $km^2$, which corresponds to a storm radius of 2.7 km. Within this rain shaft, rainfall rates can vary by a factor of 10 or more, depending on the depth and degree of organization of the convection. To examine the variations in chemistry across convective rain shafts of this type constrains the separation of the samplers to 2-3 km.

Figure 1 shows the location of the SECORE-88 network of 13 stations in operation from 20 May 1988 through 26 July 1988. Stations were located near the intersections of the 1-square-mile section lines, where there were asphalt or gravel roads, and near the centers of the sections, where there were public rights-of-way or where permission for access to private lands had been secured.
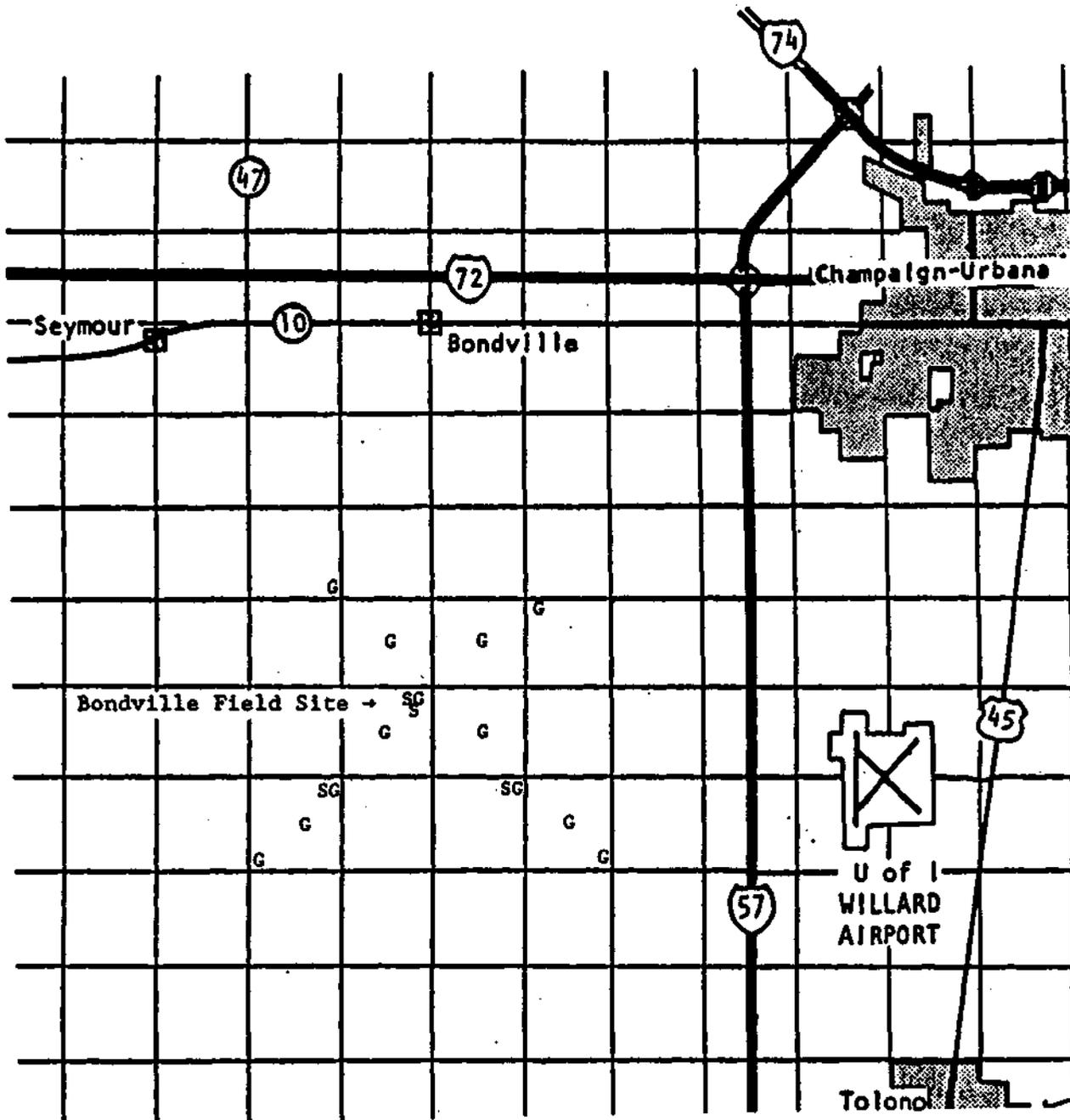
Figure 1.  SECORE-88 network of precipitation gages (G) and
           sequential chemistry collectors (S)

Spacing between stations was about 1.1 km (or 0.7 miles). Stations were located along two axes, a southwest to northeast axis, parallel to the typical direction of storm tracks, and a northwest to southeast axis, perpendicular to the first axis. Both axes shared a common station at their intersection at the Bondville field site (see Dossett, 1987, for a description of this site). Two automatic sequential samplers were operated at the Bondville site, along with a precipitation gage to measure the amount and rate of occurrence of rainfall. Elsewhere there was a sequential sampler 2.3 km SW of the Bondville site and another 2.3 km SE of the Bondville site. Every one of the 13 stations in the network was equipped with a precipitation gage.

The SECORE-88 network of gages and samplers was designed to define the ground path of convective cells as they crossed the network and to measure the chemistry of rainfall along and perpendicular to the rain shafts, or cores of these cells. From end to end the axes of the network were 6.8 km long, which is about 1.5 km longer than the cross-section of a typical non-severe thunderstorm in Illinois (Westcott, 1988).

To obtain a continuous rainfall record that could be used to accurately identify the onset and cessation of rain, a Belfort, weighing, recording gage was employed. In place of the (U.S. Weather Service) standard, 8-inch, collection orifice, a modified top with a diameter of -12.6 inches was installed, so that the response of the gage to rain increments was increased by a factor of 2-1/2 over the standard configuration. A modification was also made in the speed of the chart rotation, by replacing the 24-hr. rotation gears with 6-hr. rotation gears. In speeding the chart motion by a factor of 4, rainfall rates based on an averaging time of less than 5 minutes could be determined with accuracy.

Samples for chemical analysis were collected with wet-only samplers that were designed to automatically segregate a new sample for analysis after a pre-set amount of rain had occurred. As rain continued, a new sample was collected with each increment of this pre-set amount; that is, the samplers sequenced or stepped from one collection vessel to the next, and so on, until the rain stopped (hence the name sequential samplers). Sequential samplers of two different designs were used in the SECORE-88 network.

Because of the design of the samplers used, the pre-set amount of rain for the collection of individual storm sequences was set at .02 inches. This was a lower limit, because it assured that each sample would satisfy the minimum volume requirements for a complete set of analyses without the prior need for dilution. Nominally, 35 mL of sample are needed to complete the full suite of measurements:

$(H^+$, conductance, $SO_4^{2-}$, $NO_3^-$, $Cl^-$, $NH_4^+$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+)$.

This volume is needed because some samples are measured in duplicate and because extra volume is needed to dilute aliquots of the sample when the original concentration of an analyte exceeds the calibration range of the analytical technique. The need for dilution is greater in sequential samples than in whole-storm, or event, samples since the concentrations vary over a larger range of values.

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At the Bondville field site, two sequential samplers designed and built at the Oak Ridge National Laboratory (Lindberg, 1988), were installed within five meters of one another. This installation had four major components:

(1)    two wet-only collectors built after the Health and Safety Laboratory design of Volchok and Graveson (1975);

(2)    two sample collection and storage chambers, each with a carousel that could sequence from one collection vessel to the next, up to 48;

(3)    a tipping bucket precipitation gage, that served as an electrical switch to signal an accumulation of .01 inches of rain; and

(4)    a computer that controlled and integrated the function of the collectors and carrousels, taking signals from the collector sensors and the tipping bucket gage.

With the computer, the two carrousels were programmed to step with each two tips (i.e. .02 inches of rain) from the tipping bucket gage. In addition, the printer attached to the computer recorded the date and time when the collectors opened or closed and the date and time that the carrousels advanced to the next collection vessel. Since the carrousels sequenced in near synchronous fashion and since the collectors were opened together manually at the onset of rain, the collection vessels collected samples that were virtually duplicates in time and space. One set of samples was analyzed for the major inorganic ions and conductance and one set was analyzed for aqueous hydrogen peroxide ($H_2O_2$).

At the other two SECORE-88 sites where sequential chemistry collectors were located, collectors that were designed and built by Northrup Services, Inc., under contract to the U.S. Environmental Protection Agency, were installed. These were stand-alone units that could collect wet-only samples sequentially, measure solution conductance then pH on an aliquot of each sample in near real time, and store a second aliquot in a refrigerated compartment for later analysis. As with the Oak Ridge samplers, a carousel would step through the collection vessels with each .02 inches of rain, up to 1.00 inches (capacity was 50 vessels). A microprocessor essentially controlled the operation of the system and a printer recorded the date and time when the lid opened or closed and the date and time that the carousel advanced to the next sample. The signal to step to the next sample was sent when water in a temporary holding chamber had accumulated a volume resulting from .02 inches of rain. Since rainfall rates in excess of about 2 inches/hour would overload the capacity of the instrument to measure pH and conductance and since rates >2 inches/hour are not uncommon from convective cells, these near-real-time analytical measurements were preempted during SECORE-88. All samples from these collectors were analyzed for the same major inorganic ions as the one sampler at the Bondville site. A more detailed description of these "Acid Precipitation Monitors for Fractional Event Sampling with Real-time pH and Conductivity Measurement Capability" can be obtained from Bromberg (1988).

While the network of 13 recording raingages was operated continuously throughout the SECORE-88 field experiment, the sequential chemistry collectors were powered up and fully prepared for collection only when rain was anticipated.

Preparation of the collectors involved the cleaning of collection surfaces and connecting tubes with copious rinses of deionized $H_2O$. Then, collection vessels (60 mL high density polyethylene bottles for the Oak Ridge samplers and 50 mL polypropylene centrifuge tubes for the EPA samplers), which were pre-cleaned at the laboratory, were installed in the carrousels. Next, system blank samples were collected by rinsing de-ionized $H_2O$ through the collector plumbing and into the bottles or tubes for later chemical analysis. And finally, the collector electronic controls were set in a ready state for operation. When rain began, the two Oak Ridge samplers were set to open together, manually, and the EPA samplers were left to open automatically. When the EPA samplers failed to open as expected, they were manually set to open, as well.

Upon cessation of a rain event, the tubes and bottles were removed from the collectors, sealed and labelled, and transported to the laboratory. Field forms were completed to document the sample set from each collector by listing places, dates, times and sequence numbers. These completed forms were obligatory for laboratory processing and analysis to begin. Samples were stored overnight at 4°C, when necessary, or laboratory check-in and processing was begun at once. For the major inorganic anions and cations, the standard procedures described in Peden et al. (1986, 1979) were used, and for the peroxide analyses, the procedures described by Bachman and Peden (1988) were used.


## Summary of Network Operations

Below in tabular form is a synopsis of SECORE-88 field operations. Prior to the installation of equipment in the field, raingages and sequential chemistry collectors were assembled, prepared, and tested for proper operation and reliability of operation at ISWS facilities.

- 10 to 20 May 88: raingages installed at SECORE-88 field site locations (see Figure 1)

- 20 to 25 May 88: four sequential chemistry collectors installed at three SECORE-88 sites (see Figure 1)

- 1 June 88: began to capture and store hourly average meteorological data, surface ozone concentration data, and solar insolation data from National Dry Deposition Network station at the Bondville field site

- 2 June 88: some scattered rain reported from PRECP VI surface network but none at SECORE-88 sites

- 2 June 88: began to capture and store 5-minute average meteorological data, surface ozone concentration data, and solar insolation data from National Dry Deposition Network station at the Bondville field site (this was done for days when rain was reported from the PREC-VI/SECORE-88 surface networks)

- 2 June 88: took field blanks from sequential chemistry collectors to test systems

- 7 June 88: took field blanks from sequential chemistry collectors

- 8 June 88: rain occurred across SECORE-88 network; amounts ranged from .25 inches at northern sites to .38 inches at southern sites; 109 rain samples plus field blanks and QA samples were submitted to laboratory for analysis

- 9 June to 13 July 88: no rain across SECORE-88 network; several studies done to isolate sources of contamination (high system blank levels) in sequential chemistry collectors

- 14 July 88: scattered rain showers during night time hours, with amounts ranging from 0 to .15 inches at SECORE-88 stations; six rain samples plus field blanks were submitted to the laboratory for analysis

- 18 July 88: three rain events, one stratiform rain with some light embedded convection beginning at about 0730L and ending at about 1000L and two convective showers at 1540L -1630L and 1800L - 1845L; rainfall amounts ranged from .60 inches to .80 inches and 198 rain samples plus field blank and QA samples were submitted to the laboratory for analysis

- 20 July 88: two rain events, one stratiform rain beginning at about 0700L and ending at 1100L and one convective shower at 1630L to 1745L; rainfall amounts ranged from .37 inches to .91 inches and 158 rain samples plus field blanks and QA samples were submitted to the laboratory for analysis

- 26 July 88: SECORE-88 field operations were terminated

## Status of Laboratory Operations and Data Management

Chemical analysis of the 596 samples submitted to the laboratory is nearly completed. Solution conductance, pH, $SO_4^{2-}$, $NO_3^-$, $Cl^-$ and $NH_4^+$ measurements have been completed and are being verified and entered into computer files. Analysis of the alkali and alkaline earth metals ($Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$) will be completed by 30 September. Data will be verified and entered into computer files by 31 October. Precipitation data will also be entered into computer files by 31 October. Surface meteorological data, $O_3$ concentration measurements, and solar insolation data are now available for computer use.

## Acknowledgements

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PROCEDURES FOR THE ANALYSIS OF AQUEOUS HYDROGEN PEROXIDE
IN RAIN SAMPLES COLLECTED DURING SECORE-88

Susan R. Bachman and Mark E. Peden


During the Sequential Chemistry of Rain Experiment in the summer of 1988 (SECORE-88), some wet-only deposition samples were collected exclusively for hydrogen peroxide ($H_2O_2$) determinations at a rural sampling station near Bondville, IL.  In the months of May and June, SECORE-88 operations were a component of the Cloud Chemistry and Cloud Physics Organization (3CPO) field project.  Six separate collection events were recorded during SECORE-88, but only the 8 June event occurred during 3CPO activities.

One of the measurement objectives of SECORE-88 was to obtain data on the $H_2O_2$ content of rain samples from convective showers.  An efficient method, relatively free of interference, and with sufficient sensitivity to detect aqueous peroxide in rain samples, was sought.  Below is a description of the techniques employed.

Sample Collection and Handling

Samples were collected in 60 mL high density polyethylene bottles or 50 mL polypropylene centrifuge tubes, depending upon the type of automatic sequential sampler employed.  Both the bottles and tubes and the collection surfaces of the automatic sampler were cleaned with deionized water.  System blank samples, prepared by collecting water that had been poured over the collection surfaces and then allowed to accumulate in pre-cleaned bottles or tubes, were measured to assess the potential for contamination from the sample collection and handling procedures.

Upon cessation of a rain event, samples (rain and field blanks) were recovered from the field and transported to the lab and placed in a 4°C refrigerator.  Within 24 hours, the samples designated for $H_2O_2$ analysis were numbered, weighed, and prepared for analysis.  Samples were not filtered prior to analysis.  Sample preparation involved addition of a fixing reagent, whereby a 2 mL aliquot of sample was removed from the collection bottle and added to an equal amount of a freshly prepared derivatizing (fixative) solution (see reagents).  Analysis followed within one hour.  Details of the fluorescence procedure for the determination of $H_2O_2$ are included in Kelly et al. . (1985) and Lazrus et al.. (1985).

Apparatus

A Farrand Ratio-2 Fluorometer was used to detect the fluorescence reaction of peroxide in the samples.  The sample was introduced into a flowing stream of TRIS/EDTA buffer (via a pumping system at 0.80 mLs per minute) to which NaOH (0.16 mLs per minute) was added downstream.  The sample then passed through a flow cell at which time the fluorescence was measured at a wavelength of 400 nm. A phototube provided the light source and the fluorescence signal was read from a digital display, as well as from peak height measurements on the strip chart of an analog recorder (Lee, 1988).

1.   Stock TRIS/EDTA buffer          30.3  gm TRIS (Fisher Scientific)
     (kept at room temperature)       0.94 gm EDTA (Fisher Scientific)
                                        3 mL conc. HCl
     -dissolved in 500 mL DI water

2.   NaOH 0.1 M (500 mL, kept at room temperature)

3.   Fixing Reagent (p-hydroxyphenyl acetic acid - PHOPA)

                                    10.0 mL stock TRIS/EDTA
                                     0.23 gm PHOPA (Sigma Chemical Co.)
                                     3 mg peroxidase enzyme (Sigma
                                      Chemical Co.)
     -made fresh/per each event or analysis period
     -used in fixing samples and as the carrying solution for the
      fluorometer

## Standards

1.   A stock $H_2O_2$ standard was prepared at the beginning of the 3CP0
     experimental period.  A 30% hydrogen peroxide solution (Fisher
     Scientific) was first diluted to approximately 1%.  It was then
     titrated with $KMnO_4$ (potassium permanganate) to derive a calculated
     concentration. This solution is stable for over a month if kept
     refrigerated and preserved with $Na_2SnO_3$ (sodium stanate).

2.   Fresh calibration standards were prepared in glass volumetrics just
     prior to each event. The stock standard was diluted (500 µL/100 mL)
     to make a working stock from which the six calibration standards
     were made. Standard concentrations ranged from approximately 50 µg/L
     to 2.50 mg/L.  A zero standard was also analyzed.  All calibration
     standards were discarded after a batch of samples was analyzed.

## **Sample** Analysis Procedure

Once samples had been received and fixed, analysis occurred within 24
hours.  The fluorometer power was turned on and the proper setting for
sensitivity and filter slit width were adjusted.  The peristaltic pumping system,
which included PHOPA & NaOH, was initiated and monitored until a steady baseline
was achieved.  Once the system was equilibrated and zeroed, fresh calibration
standards were analyzed.  A 2.0 mL portion of the prefixed standard was
introduced into the analytical stream.  The maximum fluorescence signal was noted
by monitoring the digital display as well as being recorded on the strip chart.
Calibration data for one of the 3CP0 events are shown in Figure 1.  After the
calibration standards were analyzed, the same steps were followed with each fixed
sample. **Note:  The reagent used to fix the samples must be from the same batch
as that used in the pumping system.  Make sure that the volume prepared is
sufficient to fix all the samples and for use in the pumping system.**  The speed
of analysis was 2.5 min./sample once initial set-up and sampling began.  Standard
and reagent preparation usually took 45 mins. prior to sample analysis.

  System and sample blanks (reagent, bottle, DI) were analyzed throughout the experimental study. The method detection limit for this study was 0.020 mg/L with precision at the low μg/L level of 18% RSD, but improving to 5% RSD at 1.00 mg/L.
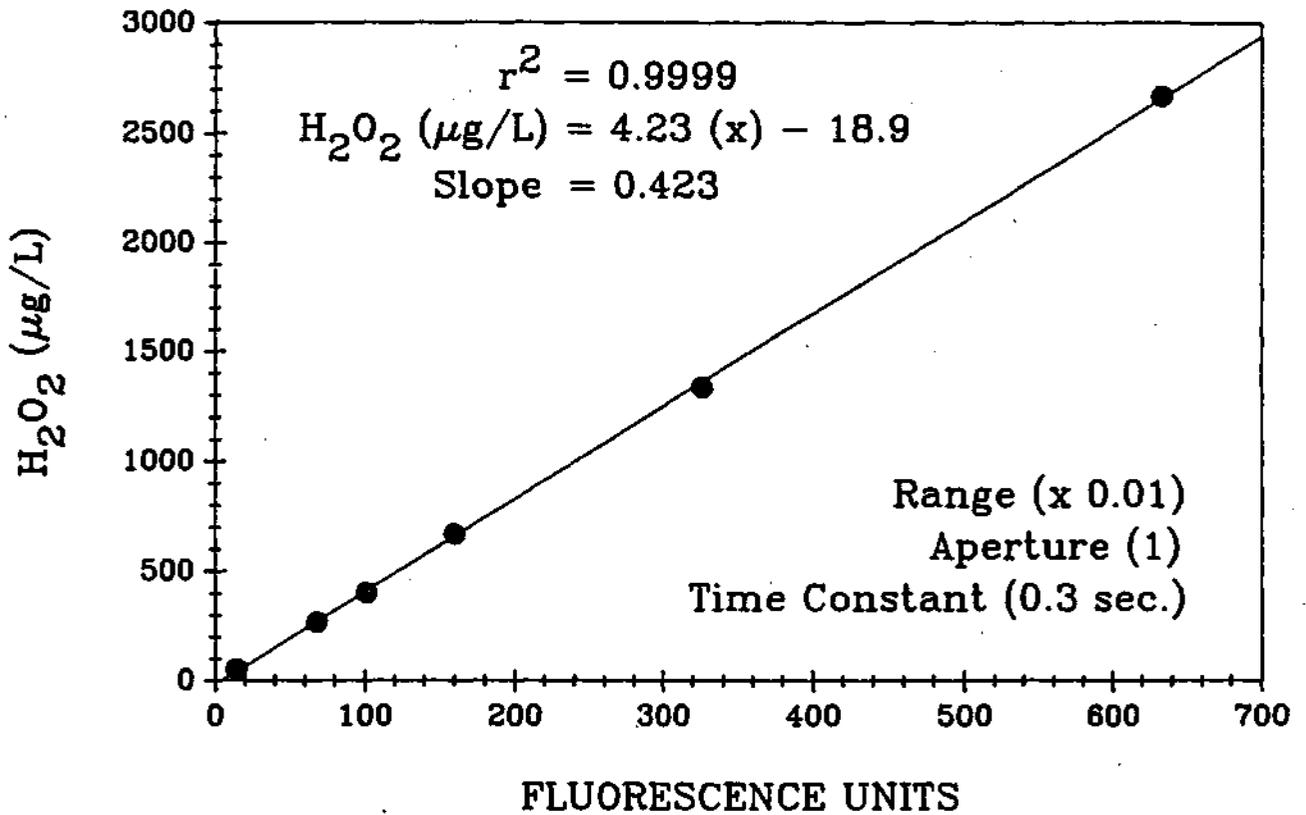


Figure 1. $H_2O_2$ Standard Calibration Curve

## References

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Lee, R. N., Personal Communication, Atmospheric Science Dept., Battelle Northwest Laboratory, Richland, Washington.

Van C. Bowersox and Mark E. Peden

On 8 June 1988 the 13 raingages and four sequential chemistry samplers in the SECORE-88 network all recorded the first precipitation event to occur after the network was activated on 20 May 88. Rain fell from a stratiform deck associated with the passage of a mesoscale low that tracked across southern Illinois.

Rainfall amounts were light and relatively uniform across the network, with an average amount of 0.32 ± 0.04 inches and a range of 0.25 inches to 0.38 inches. Rain began at about 1600L and continued without interruption for 3 hours and 10 minutes to 3 hours 20 minutes. Averaged over the entire event, the rainfall rates were about .09 - .11 inches/hour. During the first 45 minutes of the event, the rainfall rate was .16 - .20/hour, and for the duration of the event, the rates remained uniform and steady at .08 - .10 inches/hour.

At the outset of rain, the relative humidity at the surface measured 62% and it rose rapidly to 88% during the first 45 minutes. Thereafter as the rain rates decreased, the rise in surface relative humidity slowed until it reached 94%. Given the light rainfall rates and corresponding small drop sizes, the potential effects of evaporation on raindrop sizes and concentrations must be considered.

Another change which must be considered is the surface (10 meter) wind direction. For the first 30 minutes of the event, winds were out of 327°. At that point the wind direction began to back toward a more northerly direction until it reached 17° ±4°, where it remained until the end of the event. Figure 1 displays the aqueous peroxide concentrations in samples collected at the Bondville field site during the 8 June event. The drop in concentrations from about 1 mg/L (~56 µ equiv/L) to about 0.3 mg/L corresponds to the time period during which the wind direction shifted. One hypothesis, which must be tested, is that fresh $SO_2$ from Champaign may have accounted for the drop in $H_2O_2$. There is no apparent rise in $SO_4^{2"}$ concentrations to support this hypothesis, however (see Figure 2).

Figures 2, 3, and 4 show the ion concentrations for a set of six major anions and cations in the sample sequences from the three sequential chemistry stations in the SECORE-88 network. Since this rain event was associated with a relatively uniform stratiform cloud layer, resulting in a steady rainfall rate, the correlative behavior of these ion concentrations will be examined both in space and time to address the question of spatial and temporal variability over space scales of several kilometers and time scales of minutes. Clearly there is a strong correspondence between the concentrations of $Ca^{2+}$ and $Mg^{2+}$, reflecting their common source in rainfall (scavenged soil and road dust aerosols). For the N and S species, which have both gaseous and particulate sources, however, the correspondence is not so strong. Careful analyses of these data will be a first step in the interpretation of the data from two other stratiform cases, one on July 18 and one on July 20, and the three convective rain cases sampled during the month of July.
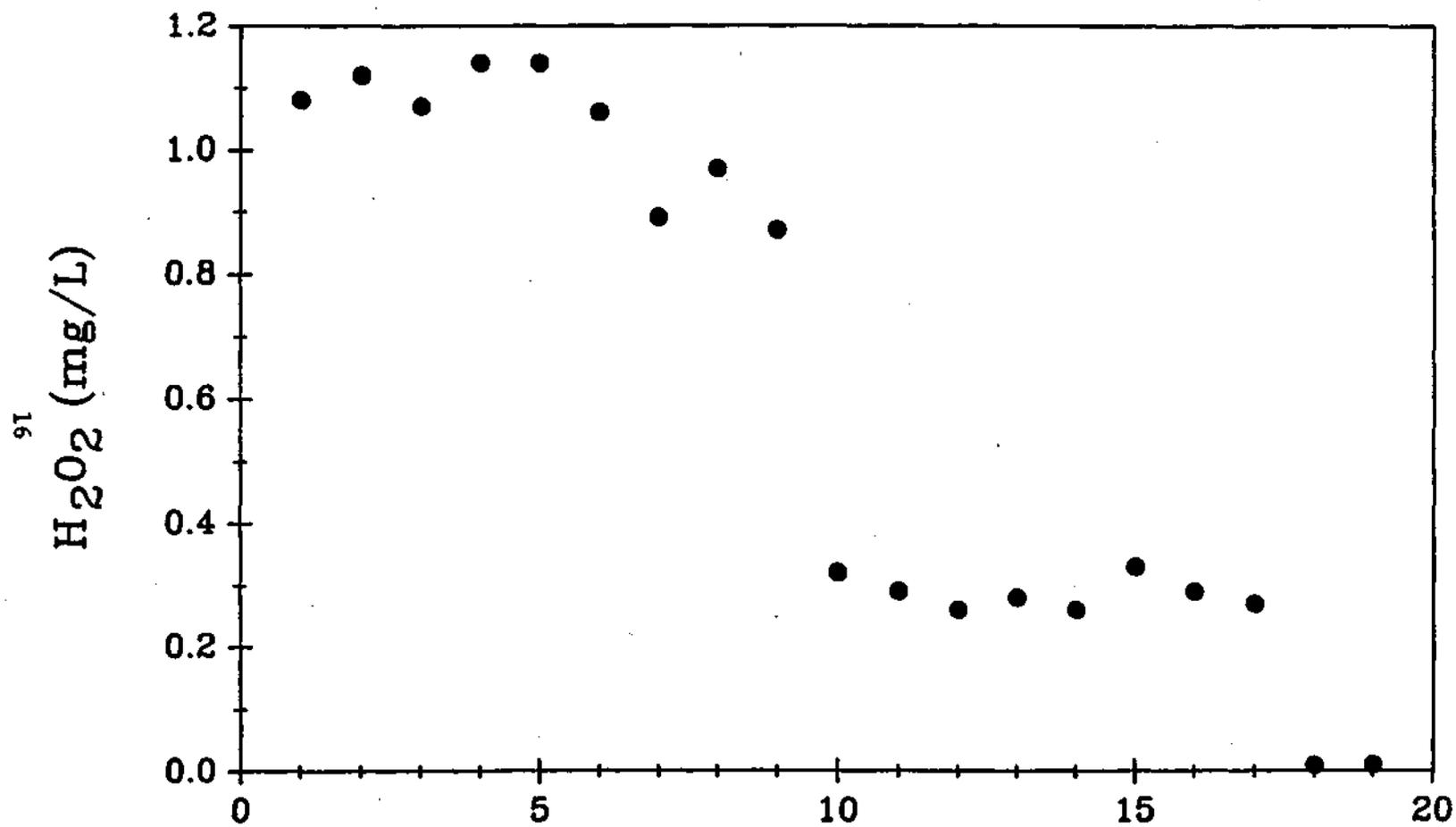
Figure 1.   Aqueous peroxide concentrations in rain samples from the 8 June 88
            event at the Bondville field site (SECORE-88).  The X-axis is sample
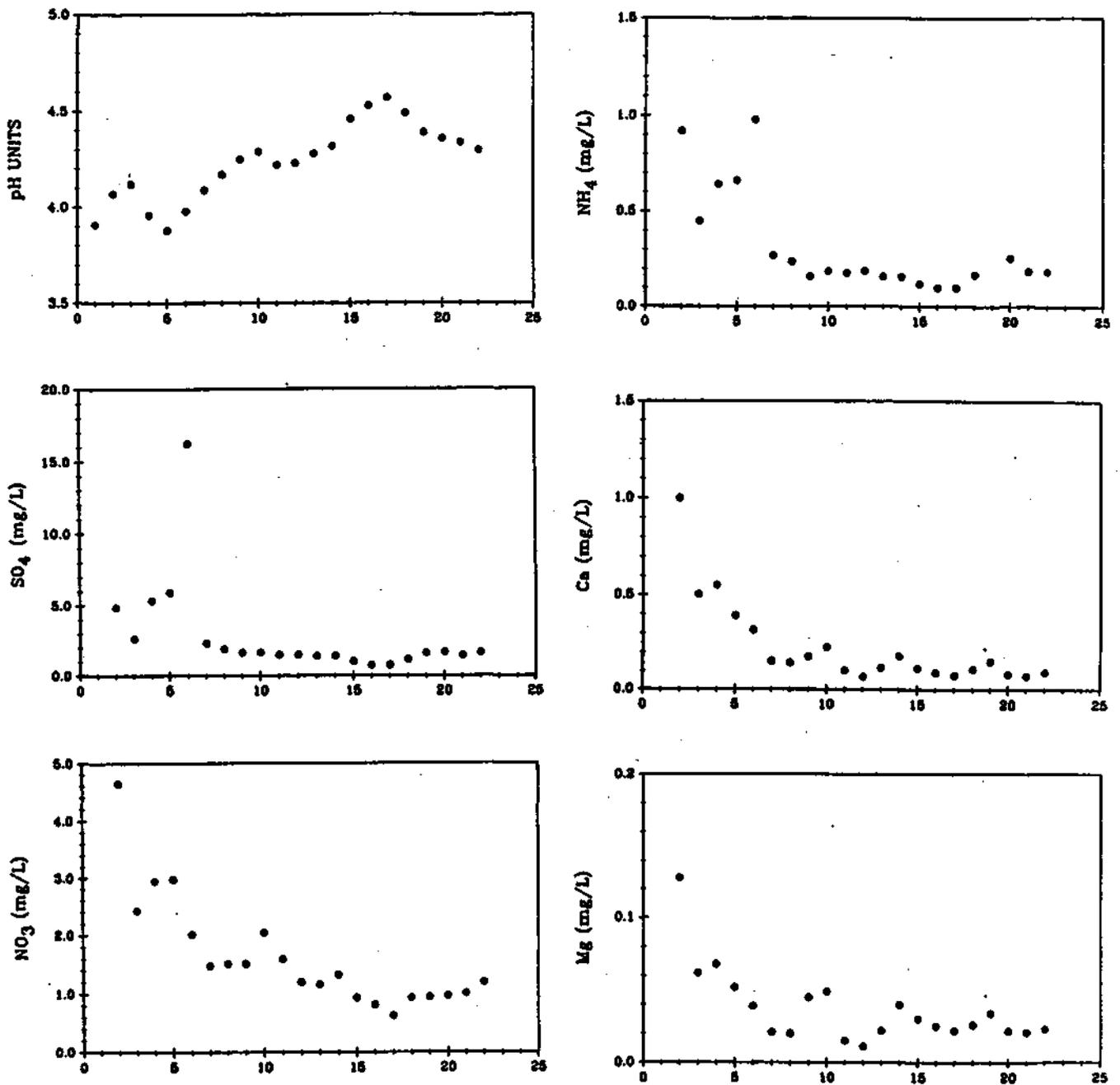            number from the beginning to the end of rain.

Figure 2.    Concentrations in SECORE-88 samples for the 8 June 88 event at the Bondville site.  The X-axis is the sample sequence number from the beginning to the end of rain.
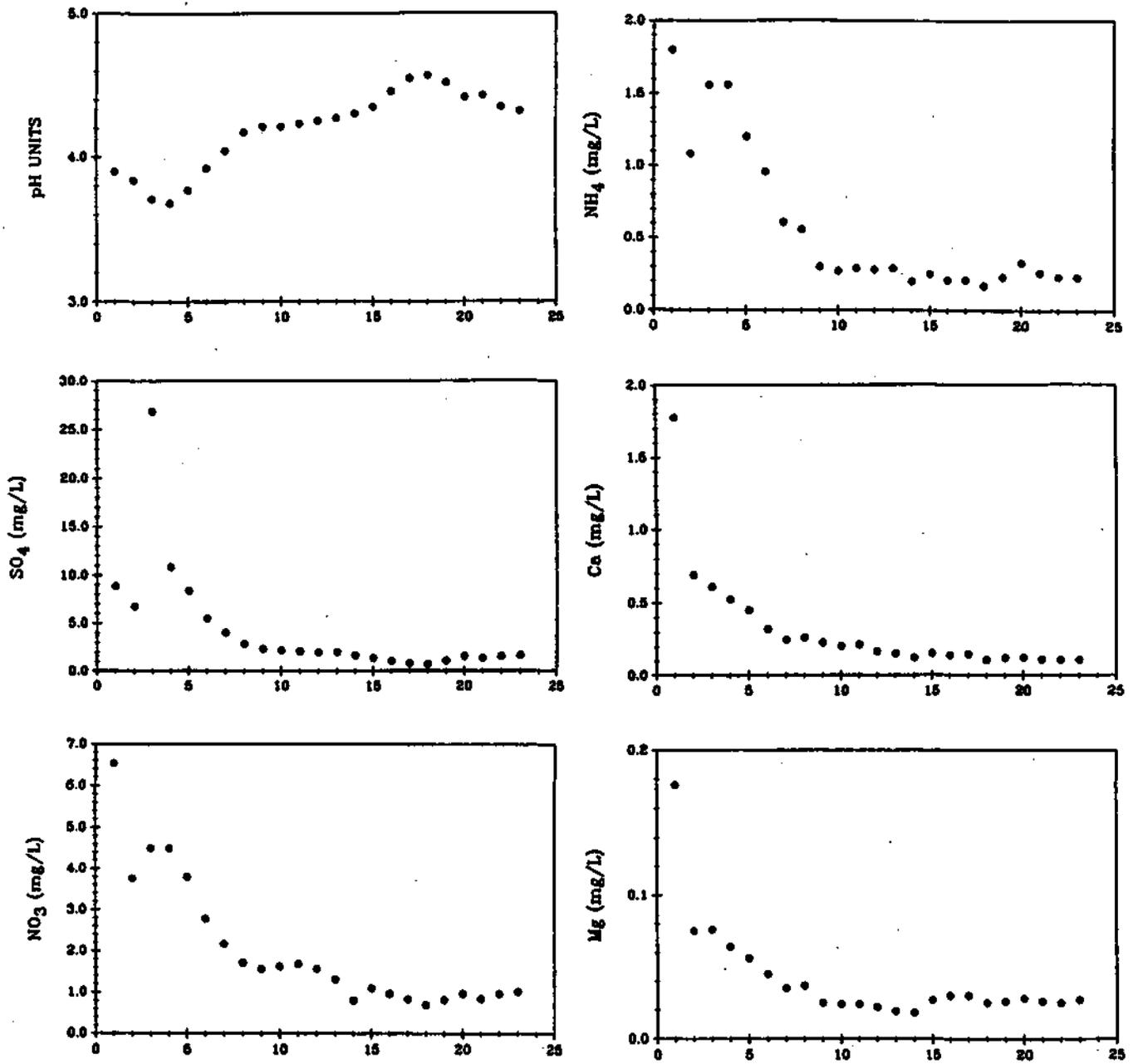
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Figure 3. Concentrations in SECORE-88 samples for the 8 June 88 event at a site 2.3 kilometers southwest of the Bondville field site. The X-axis is the sample sequence number from the beginning to the end of rain.

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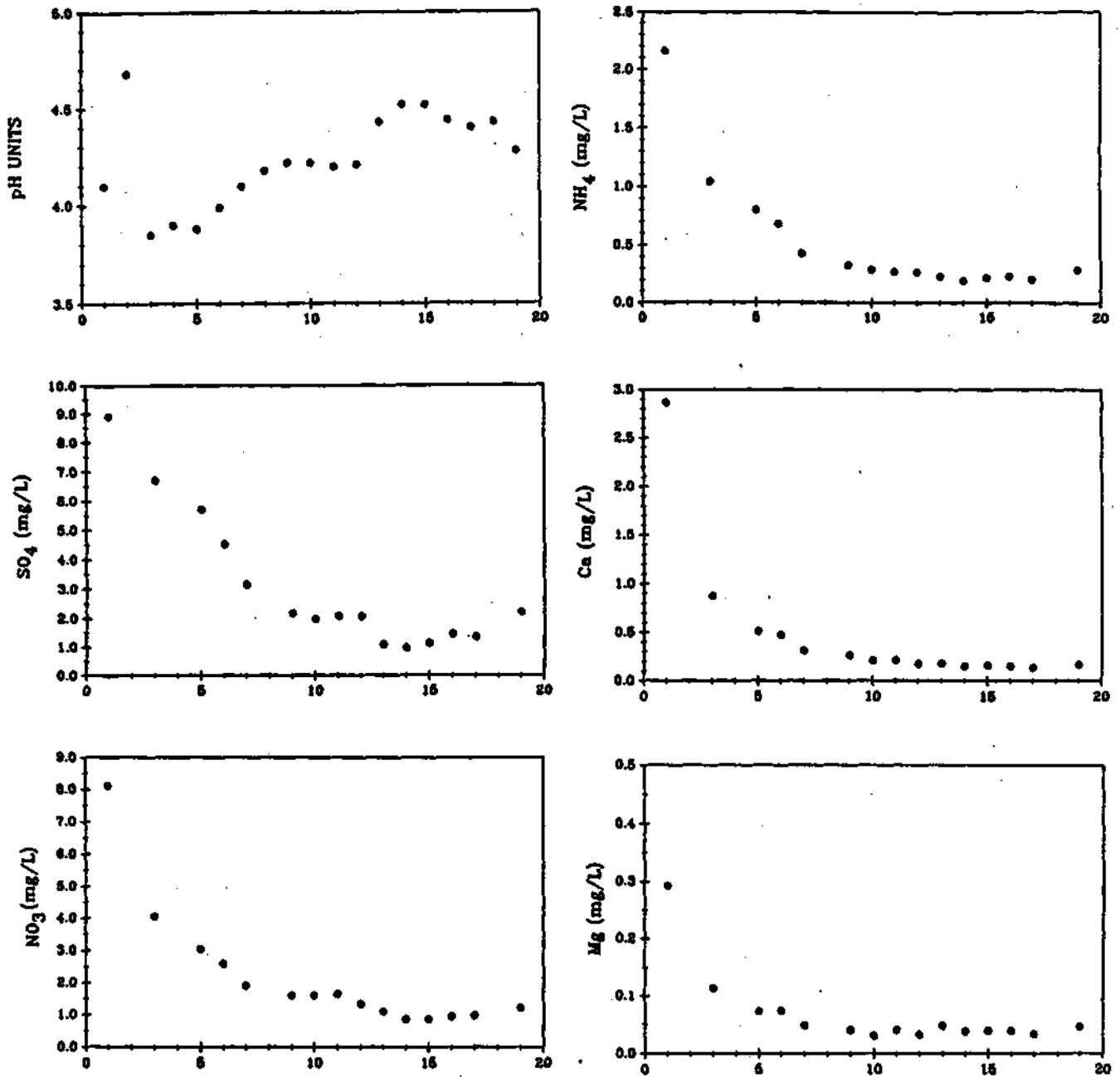
Figure 4.    Concentrations in SECORE-88 samples for the 8 June 88 event at a
site 2.3 kilometers southeast of the Bondville field site.   The X-
axis is the sample sequence number from the beginning to the end of

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**RESEARCH SUMMARY REPORT**
**TO THE NATIONAL ACID PRECIPITATION ASSESSMENT PROGRAM --**
**TASK GROUP III ACTIVITIES**

Van C. Bowersox and Richard G. Semonln

## Introduction

Studies of the scavenging of atmospheric pollutants that affect the acidity of precipitation have been done in pursuit of the goals of Task Group III: to investigate meteorological and chemical influences on acidic deposition. This effort has focused on the analysis of existing wet deposition data sets, such as NADP/NTN and MAP3S data, that have been collected in response to NAPAP needs to quantify spatial and temporal patterns and trends in wet deposition. These data sets have been used to identify the important chemical contributions to the ionic balance in precipitation samples, then to examine the influence of meteorological factors and source regions on concentrations of these constituents. Results of this work can provide insight into the important processes that modelers must consider to accurately estimate acidic deposition.

## Hypotheses

(1) A gradient in the free acidity of precipitation, from pH values less than 4.5 in the northeastern U.S. to values well above 5.5 in midwestern states, can be explained from the chemical balance of a set of 4 inorganic anions and cations ($SO_4^{2-}$, $NO_3^{-}$' $NH_4^{+}$, $Ca^{2+}$ derived primarily from combustion, agricultural practices, and natural processes.

(2) Soil aerosols from dust storms can be transported long distances (750-1500 km) and then deposited by precipitation, markedly affecting the concentrations of $Ca^{2+}$, $H^{+}$, and other ions (e.g. $Mg^{2+}$, $K^{+}$).

(3) Highest $SO_4^{2-}$ and $NO_3^{-}$ fluxes from precipitation occur in the spring and summer and are associated with convective showers (often thunderstorms) in air that, relative to low flux cases, has had more passes and/or longer residence times over high emissions areas.

(4) Near point and areas sources of urban pollution, chemical concentrations in precipitation are demonstrably increased, relative to concentrations at regional NADP/NTN sites.

(5) Sedimentation fluxes of soluble inorganic cations and anions can be estimated from screened dryfall bucket analyses from the NADP/NTN data set.

## Results and Discussion

From east-central Illinois to west-central Kansas the pH of precipitation (Figure 1) rises from 4.3 to nearly 6.3, using median values from the NADP/NTN. This is nearly a 100-fold decrease in free acidity over a distance of about 1000 km and is the sharpest synoptic-scale gradient in the NADP/NTN data set. This feature was evident in the calculated pH values from the Junge data of 1955-56, but it was 600 km further east. Though evident in the NADP data as early as 1980, the installation of several NTN sites in the Midwestern region in 1984 resulted in data that added spatial definition to the gradient and enabled a better study of its causes.

Across the mid-continental U.S. $SO_4^{2-}$ decreases by a factor of 3-4 from east to west, and this is insufficient to account for the change in pH. A two-fold increase in $Ca^{2+}$, too, is inadequate to explain the gradient. To identify the set of ions that explain the $H^+$ behavior, several empirical models that related the measured pH to the pH calculated from a chemical balance in an open system (i.e. a system exposed to ambient $CO_2$) were tested. NADP/NTN data from this mid-continental region were used. One group of models used the full set of ions measured in NADP/NTN samples to calculate the $H^+$. Another group used a reduced set of just 4 ions, $SO_4^{2-}$, $NO_3^-$, $NH_4^+$, and $Ca^{2+}$. Independently, it was determined that these 4 ions were the minimum needed to obtain the pH values above 5.6 observed in the western portion of the region. Should this reduced set be sufficient to predict the observed pH, then comprehensive models, that integrate source, transport, transformation, and wet deposition phenomena, could focus on the processes that govern the concentrations of these ions in precipitation.

Linear, second, and third order models of measured pH versus calculated pH were tried. Second order models did best and explained significantly more variance than either linear or third order models. This is consistent with the effect of monoprotic acids, such as formic and acetic acids, in precipitation. Although formate and acetate are not measured in NADP/NTN samples, second order models provide an empirical correction to account for them. Use of the full set of measured ions in the second order model resulted in a significantly higher $R^2$(0.88) than use of the reduced set ($R^2$=0.79); however, given the reduced computational demands of a comprehensive acidic precipitation model when $Cl^-$, $Mg^{2+}$, $Na^+$, $K^+$ and $PO_4^{3-}$ are neglected, the choice of the reduced set may be warranted. Figure 2 shows the results of the second order model, where the reduced set of four ions was used to determine the calculated pH.

To predict how the pH of precipitation in eastern North America will respond to future changes in emissions, acidic deposition models (at a minimum) should be able to estimate the concentrations of the four, major, conservative, inorganic ions in precipitation: $SO_4^{2-}$, $NO_3^-$, $NH_4^+$, and $Ca^{2+}$.
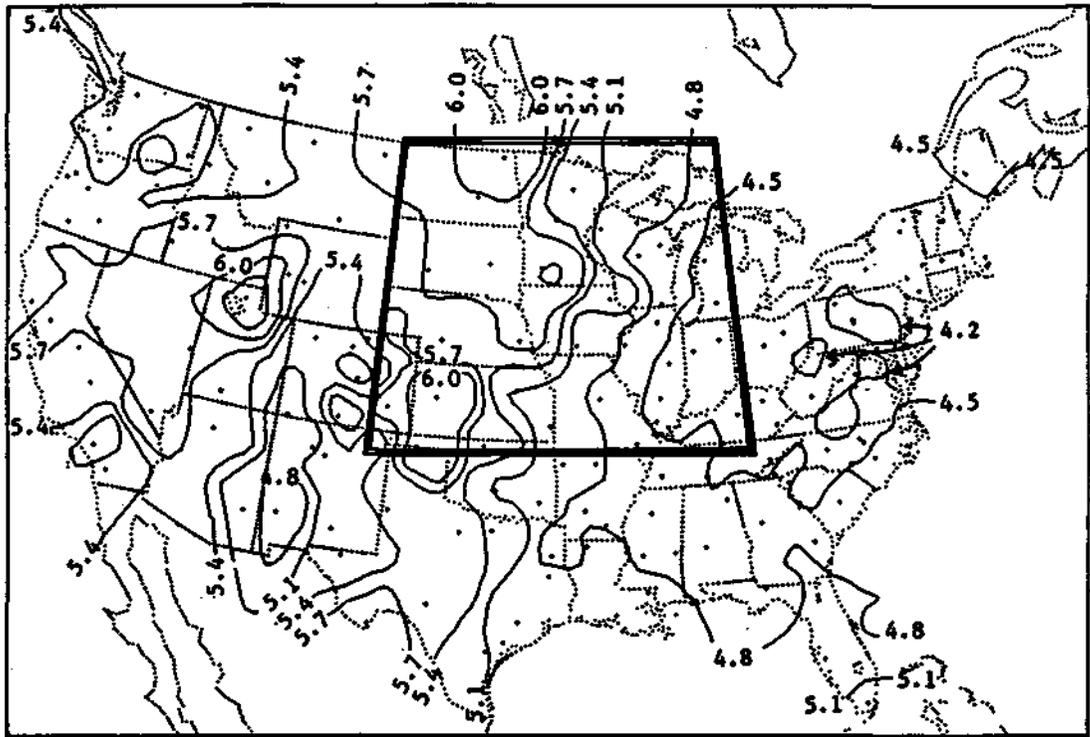
Figure 1. Median laboratory pH, NADP/NTN data (1978–1986).



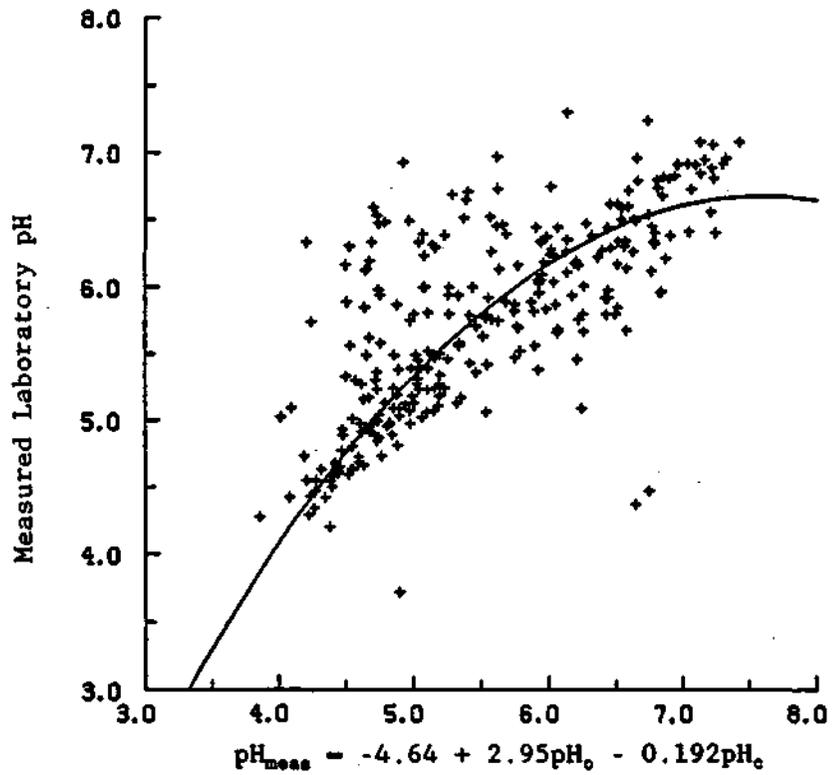$$pH_{meas} = -4.64 + 2.95pH_o - 0.192pH_c$$

Figure 2.    Results of a 2nd order model, using NADP/NTN data from a NE site, where $pH_c$ is the pH calculated assuming $SO_4$, $NO_3$, $NH_4$, Ca were in equilibrium with ambient $CO_2$.

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Given the importance of $Ca^{2+}$ to the issue of pH trends between the '50's and '70's and to the causes of the current gradient in pH across the mid-continental U.S., the role of dust storm aerosol as a source of $Ca^{2+}$ in precipitation was investigated. Two case studies of the long-range transport of aerosols from major dust events in the Texas/New Mexico/Oklahoma area were done. A quadrangular box was drawn enclosing the dust storm area. The NOAA ARL/ATAD model was used to track the horizontal movement of the dust plume (so derived) forward in time. (There was no provision for vertical motions in this model.) Finally, radar summaries were reviewed to determine where the advected plume intercepted precipitation, particularly over NADP/NTN sites. This occurred at four sites, two for each study. These sites were between 750 and 1500 km downwind (northwest AR, eastern NE, southern IL, west-central GA) of the dust storm area. Figure 3 shows the surface analysis and the forward movement of the dust plume into an area where precipitation was occurring at an NADP/NTN site in northwestern Arkansas.
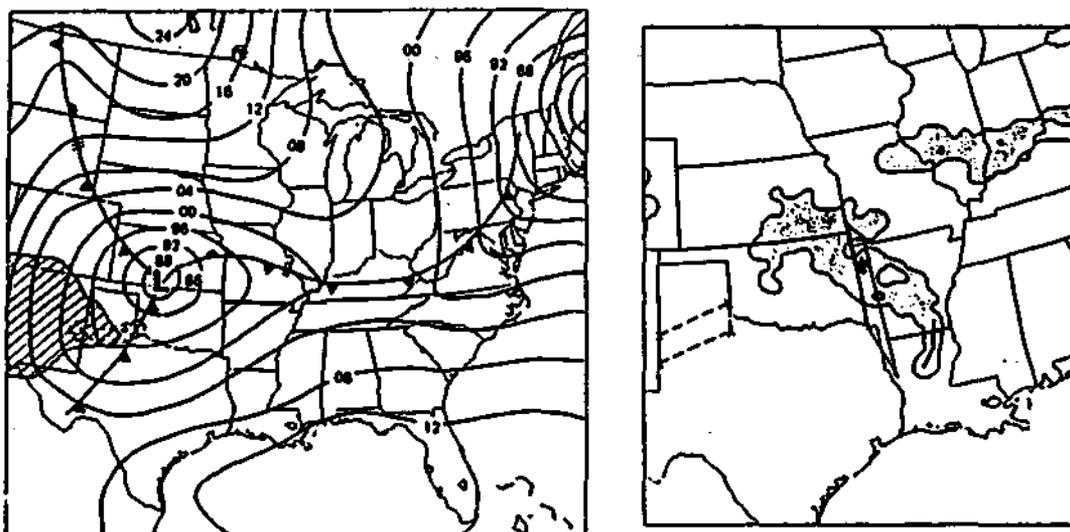
A. Surface isobaric analysis, 3/17/81. B. Forward movement of dust
Stippled area is TX dust storm. plume to precipitation area
Diagonal lines show $T_{DP} = -9C$. over collection site.

Figure 3. Transport of dust plume from TX to AR NADP/NTN site (asterisk in panel B), where observer reported "red dust" in sample (Doty and Semonin, 1987).

Both the physical description and the results of the chemical analyses of these samples were used to look for evidence that the dust plume had affected the chemistry of the rain. Unusual amounts of "red dust", which is typical of west Texas soils, were reported in 3 of the 4 samples. Red dust was not reported at NADP/NTN sites where the plume had not intercepted rain. Calcium in every one of the four samples was higher than any concentration previously observed for samples of the same volume class (sample volume ± 175 mL or sample depth ± 0.25 cm). Potassium and magnesium were also anomalously high in concentration and all three of these elements are abundant in west Texas soils and readily soluble in rainwater.

Results of these case studies demonstrate that the occasional transport of dust storm aerosols over long distances can have a marked impact on the chemistry of rain.   What is not evident is the importance to the average precipitation chemistry of long range transport of dust aerosols relative to dust derived from local sources.  Whether of local or distant origin, however, wind-eroded soils and road dust are most important sources of $Ca^{2+}$ in precipitation, and acidic precipitation models need to address their sources, transport, and deposition.

To examine the relationship between sources and deposition of $SO_x$ and $NO$^, trajectories were calculated backward from an east-central Illinois site, where "event/daily" precipitation samples were collected for analysis.   Data from January 1981 through December 1985 were used.   As for the dust storm studies, the ARL/ATAD model was used to calculate trajectories. Back trajectory loci were determined from 48 hours back in time forward to the precipitation event at the collection site.   The chemistry data were stratified by cold (Sep-Feb) and warm (Mar-Aug) seasons and within season by 3 flux categories, top 30% (actually the 65th - 95th percentile) bottom 30% and middle 30%.   Comparisons were then made between the pattern of clusters of back trajectory loci in each flux category against the two other flux categories in the same season.  These cluster patterns were examined relative to their distance from the collection site and relative to their location with respect to the $SO_x$ and $NO_x$ emissions in 1° latitude X 1° longitude boxes.   Changes in these patterns from 48 hours to 36 hours to 24 hours, etc., were used to draw inferences about transport speed and residence time of air parcels over source regions.

Both the highest $SO_4^{2-}$ and the highest $NO_3^-$ fluxes  from precipitation occurred during the warm season, i.e. the spring and summer, and both were associated with convective activity (often thunderstorms).  Mean $SO_4^{2-}$ fluxes in each of the warm season flux categories were about twice the mean $SO_4^{2-}$ fluxes in the respective cold season flux categories.  The same was true of mean $NO_3^-$ fluxes.  On a chemical equivalent basis, $SO_4^{2}$" fluxes were 2.0 - 2.4 times the $NO_3^-$ fluxes over all six categories of data. The highest fluxes for both ions were strongly dominated by southwesterly flow and low transport speeds, with long residence times and multiple passes over the high emissions areas of western and southwestern Illinois and eastern Missouri.   Neither the directional flow patterns nor the transport speeds were dominated by any one type for the low flux cases of either ion.  A thorough statistical analysis of these data is needed to quantify the extent to which the transport speed, transport direction, residence time over source areas of variable strengths, and other variables correlate with flux or with deposition.

Since roughly half of the deposition of $SO_4^{2-}$ occurs from just 20% of the precipitation events (Summers, Bowersox and Stensland, 1986) and since these events are primarily thunderstorms, which occur in the spring and summer months under conditions where air movement is low (this study), it is essential that acidic precipitation models be able to address these meteorological situations accurately.

In another project to look for influences of nearby sources on the chemistry of precipitation, data from the Great Lakes Atmospheric Deposition (GLAD) network were combined with NADP/NTN data in the Great Lakes region. Except for one site, GLAD network stations were located within several kilometers of the U.S. shores of each of the 5 Great Lakes. Many of these sites were located in cities (e.g. Chicago, IL and Erie, PA) or in or near (<15 km) towns of population 10,000 - 100,000, particularly sites near Lakes Erie, Ontario, and Michigan. In contrast, most NADP/NTN sites were selected for their "regional representativeness" and are more than 20 - 40 km from large area sources of $SO_x$ and $NO_x$ and from large point sources, such as fossil fuel burning power plants.

There were 35 GLAD and 29 NADP/NTN sites in the Great Lakes region in 1982 and 1983, the years analyzed. Objectively analyzed fields of the 2-year average concentrations, using GLAD+NADP and NADP-only data, were compared. For $SO_4^{2-}$ (Figure 4), derived mostly from gaseous $SO_2$ and submicron aerosol $SO_4^{2-}$, the urban GLAD sites on the shores of Lakes Erie and Ontario had concentrations 50-100% higher than nearby NADP sites. GLAD versus NADP differences in the Chicago and Duluth areas were smaller than this (17-33%, resp.), and elsewhere the differences were insignificant. For $Ca^{2+}$, derived mostly from supermicron aerosols from road dust, soils, and construction/demolition activities, it was only at the rural sites along Lakes Huron, Michigan and Superior that GLAD and NADP concentrations were similar. At virtually every other GLAD site, concentrations exceeded NADP values by up to 2 to 3 times. Except for pH, concentration differences at 12 pairs of GLAD and NADP sites (not co-located) could be attributed to local influences from siting differences, though data from co-located stations and from interlaboratory comparisons are needed to test for other sources of bias (e.g. sampling or analytical practices).

There are significant increases in chemical concentrations of ions in precipitation collected near point and area sources of urban pollution. More research is needed to determine the spatial extent of the influence of urban plumes and to quantify the urban effect on deposition and budget studies. Acidic deposition models should address this issue, as well.

To complement the analyses of the meterological and chemical influences on wet deposition, an exploratory investigation of the dryfall data from NADP sites has begun. For large particles, surrogate surfaces with suitable aerodynamic flow characteristics have been used to measure the sedimentation flux (Hicks, et al, 1986). Although buckets were not in the class of aerodynamically-designed collectors, the dryfall bucket data from NADP offers the only synoptic scale measure of sedimentation flux available, if valid. Thus it is prudent to establish whether these data are valid and representative or not.

Dry-bucket sampling at NADP sites began in 1978 and it continued at 46 sites, as of January 1987. The standard sampling period was 8 weeks. An important concern has been the high frequency of contamination in samples if left in the field for such a long period of time. Over the 8 years of sample collection, 53% of the samples contained some form of extraneous debris, such as pieces of leaves, seeds, bird feces, etc. An immediate question was: can the data be screened to remove the influences of contaminants so that other tests of validity can be performed?
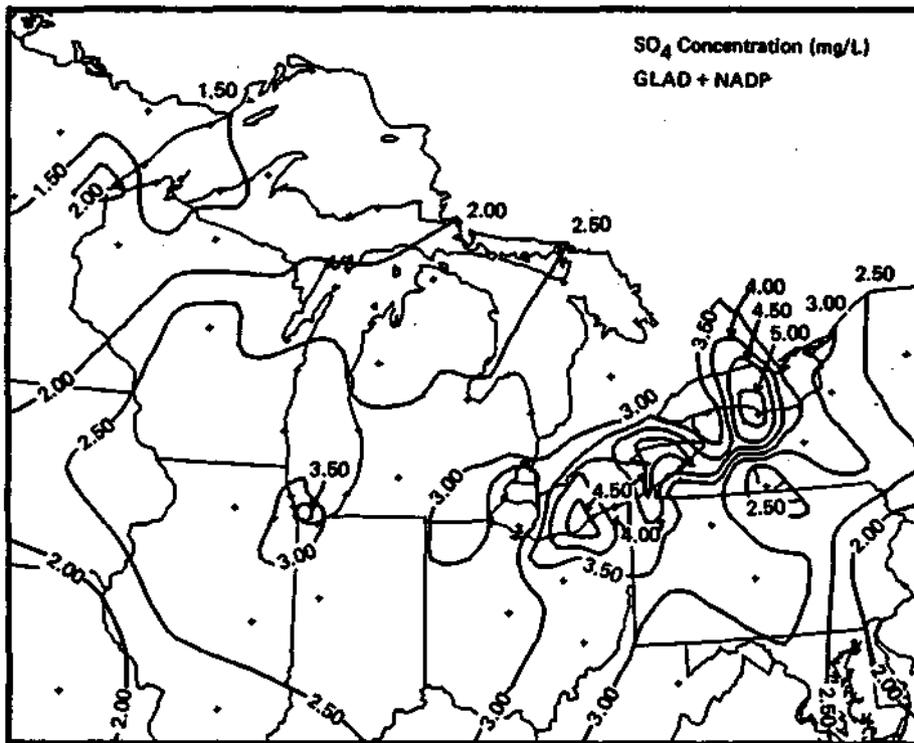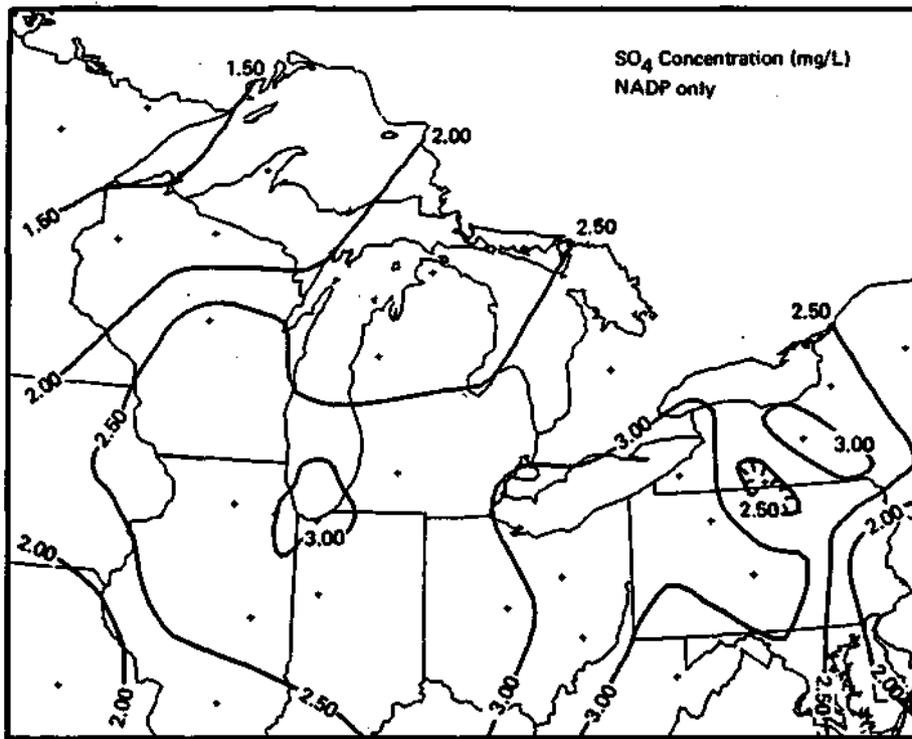
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Figure 4.    Spatial distribution of volume-weighted coverage $SO_4^{2-}$ concentrations in the Great Lakes region, using data for 1982-83.  Top panel is based on data only from the NADP. Bottom panel is based on the combined NADP and GLAD data sets. (Gatz et al., 1988).

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To address this question, the available data (1986 samples) were stratified into 6 successively more stringent screening categories. These categories of data were created for each of four regional-seasonal groups: E-winter, E-summer, W-winter, W-summer. The 6 categories were: (A) unscreened data, (B) removal of grossly mishandled samples from set A, (C) removal of samples containing precipitation from set B, (D) removal of samples with evidence of (evaporated) water from set C, (E) removal of samples with visible contaminants from set D, and (F) removal of samples that were only exposed part of the time during dry weather from set E. Nonparametric tests for significance of differences between sets were performed. Regional-seasonal differences were observed but were not tested for significance.

For $Mg^{2+}$ and $Na^+$, there were no significant differences as the data were screened. For $Ca^{2+}$, the mean flux rose from step A to step F, though this rise was only significant for $Ca^{2+}$ in the W-winter group. (The increase resulted from the removal of interfering substance with the removal of contaminated samples.) For $NH_4^+$, $K^+$, and $PO_4^{3-}$ removal of visible contaminants resulted in a large drop in the flux, consistent with the removal of organics. For $H^+$ and $NO_3^-$ removal of water resulted in a large drop in the flux, and this is consistent with the notion that these ions are principally from precipitation and are not present as salts. Finally, the mean flux results for $SO_4^{2-}$ did not show a consistent pattern as the samples were screened. This suggests that the sedimentation flux of $SO_4^{2-}$ is relatively unaffected by visible and other contaminants.

This research continues in an effort to better quantify the biases in unscreened dry bucket data and to compare the screened data to independent measurements of sedimentation flux. Ultimately, these comparisons will be used to assess the validity and representativeness of dry bucket measurements of dry sedimentation fluxes.


Conclusions

1.  Except for coastal areas where marine salts are an important influence on the chemistry of precipitation, the pH of precipitation in the 31 eastern states of the U.S. can be calculated from the chemical balance of 4 inorganic anions and cations ($SO_4^{2-}$, $NO_3^-$, $NH_4^+$, $Ca^{2+}$) in equilibrium with $H^+$ and $HCO_3^-$.

2.  A 2nd order empirical model of the measured pH versus the calculated pH can account for the weak inorganic acids, (formic and acetic) in precipitation in the eastern U.S.

3.  Soil aerosols from dust storms can be transported long distances (750-1500 km) and then deposited by precipitation, markedly affecting the concentrations of $Ca^{2+}$ and other ions.

4.  Highest $SO_4^{2-}$ and $NO_3^-$ fluxes from precipitation occur in the spring and summer and are associated with convective showers (often thunderstorms) in air that, relative to low flux cases, has had more passes and/or longer residence times over high emissions areas.

5.    Near point and areas sources of urban pollution, chemical concentrations in precipitation are demonstrably increased, relative to concentrations at regional NADP/NTN sites.

6.    Screening the dryfall bucket data from the NADP network results in physically consistent changes in the measured dry sedimentation fluxes, though independent studies are needed to test the validity and representativeness of these fluxes.

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# A MODIFIED SUCCESSIVE CORRECTIONS METHOD THAT MEETS STATISTICAL GOALS

Jack Su and Gary J. Stensland

The problem of determining the best placement of isopleth lines is of great importance for acid rain research. For a set of environmental data unevenly distributed in space and time, objective analysis is a method for estimating the regular grid point values from which isopleth lines can be drawn. There are many objective analysis schemes, including Thiessen polygons, polynomial fitting, variational method, smoothing splines, optimal interpolation, Kriging, and successive corrections.

Kriging and statistical methods in general are of great interest to acid rain research. Kriging calculates the interpolation weights by minimizing the standard error of interpolation and provides the uncertainty associated with the interpolated values. This is a powerful tool when comparing two sets of atmospheric chemistry data that vary in space and time. A major drawback of Kriging is the amount of computer resources that it requires. Utilizing the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) data set for 1986 on a VAX 11/750, Kriging took 8.6 times longer to run than a successive corrections method and required 3 times more core memory. As the size of the data set becomes larger, these differences grow. Successive corrections schemes, on the other hand, are widely used in numerical weather modeling precisely because they require more modest computer resources. Unfortunately, the available successive corrections methods do not incorporate the uncertainty associated with the data and cannot provide the analyst with a standard error of interpolation, nor can they calculate an optimal set of interpolation weights. It is our aim to implement error estimation for a successive corrections method and to formalize procedures for finding an optimal set of successive corrections parameters, thus maintaining the best of both Krieging and the successive corrections methods.

The successive corrections method (SC) we chose to alter is called BOBARY. It is a two-step procedure developed by Barnes (Barnes, 1964) and modified by Achtemeier (Achtemeier, et al., 1977). This scheme makes successive corrections to initial grid values using negative exponential weighting factors in the interpolation. Unlike Kriging, an analyst needs to choose the following three parameters specific to a given network of sites before applying BOBARY:

1. the number of sites nearest to the grid corner to be used in the interpolation,

2. the size of the interpolation grids, and

3. the relative importance of each site used in the interpolation as a function of its distance away from the grid corner.

This last parameter, called CHNG, changes the steepness of the negative exponential weighting function. The weighting factor for each site used in interpolating to a grid corner is defined as

$$(1) \quad WT(k) = (EXP(-DIST(k) / AVGDIST^2) * CHNG) + SCF(k)$$

where for site k, WT(k) is the weighting factor, DIST(k) is the distance from site k to the corner of the grid square, AVGDIST is the average distance to the corner of the grid square from all the sites used in the interpolation, CHNG is the parameter that changes the steepness of the function, and SCF(k) is the successive corrections factor. The corrections factor is defined as

$$(2) \quad SCF = 1 - (PRED(k) / VAL(k))$$

where PRED(k) is the predicted value at site k after the first pass and VAL(k) is the measured value at site k. The interpolated value at any given grid corner $Z_{x,y}$ is defined as

$$(3) \quad Z_{x,y} = \sum_{k=1}^{N} WT(k) * VAL(k) \quad .$$

where N is the number of sites used in the interpolation.

We developed two methods for determining the optimum set of successive corrections parameters for the NADP/NTN network. Specifically the network consists of sites in 1986 where there are valid sulfate data (see Figure 1). The first selection method is based on the mean error associated with the interpolation procedure. After running BOBARY, we calculated from the interpolated grid point values back to the original data sites. The difference between the two values is averaged over all sites and expressed as a percentage deviation. This is done a number of times varying the three parameters listed above. The second method is a pure validation procedure using completely independent samples. The data from a randomly selected site are omitted from the analysis, and the rest of the data are used by BOBARY to obtain grid point values. From the grid point values we then calculate the predicted value at the omitted site. A measure of how well the initial set of parameters fits the network design is the percentage difference between the predicted and actual value at that site.

The first selection method is computationally inexpensive. One BOBARY run over the data set will yield N number of comparisons, where N is the number of sites. Unfortunately, this method is not an independent validation procedure because the same data set is used both in the interpolation procedure and in the comparisons. The second method is an independent validation procedure, but to make N comparisons, we would have to make N number of BOBARY runs. This is economically prohibitive when we also need to vary the three parameters in question. Consequently, only 10 comparisons were made for each set of parameters using the second method.

# Figure 1.  1986 NADP/NTN Sites Where There Are Valid Sulfate Data
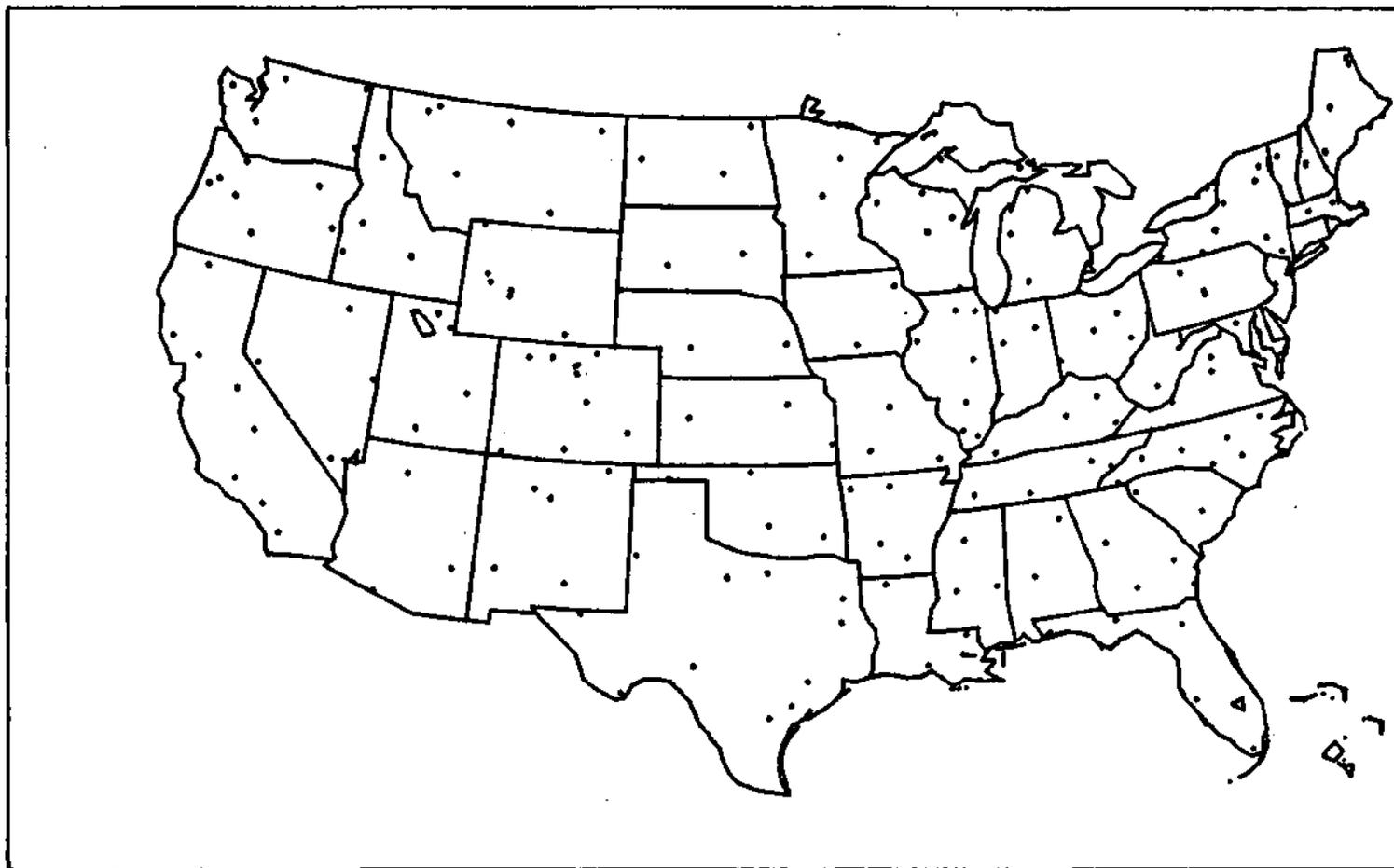
Figures 2, 3, and 4 summarize the results of the selection procedures and address the three parameters listed previously. Figure 2 is an example of the result from method one. It is a plot of the least square mean percentage differences as a function of the number of sites used in the interpolation. It clearly shows that for the NADP/NTN network, while holding the other parameters constant, the optimal number of sites to use in the interpolation can be 3, 4, or 5, but not 6 or 7. Figure 3 shows an example of the result using the second selection method. In this case for a CHNG of .4, one would clearly choose a grid size of less than 125 km and use either 3, 4, or 5, but not 6 or 7 sites. Figure 4 demonstrates the trade-off between changing the steepness parameter CHNG and grid size. Isolines of the predicted percentage differences are plotted as a function of CHNG and the grid size. It shows that for a grid size of 100 km and an average error of interpolation limited to less than five percent, the analyst needs to choose a CHNG value of between .5 and .77. Figure 4 is of particular interest from an economic standpoint. Changing the CHNG value will have no effect on computation time, but a linear decrease in grid size will square the number of computations.

Based on our preliminary analysis, we have found the optimal set of BOBARY parameters for the 1986 NADP/NTN network. Optimization is based on both the accuracy of interpolation and the amount of computer time required to run BOBARY. We found the best set of parameters to be a grid size of 100 km, using 5 sites in the interpolation and a CHNG value of .76.

It is important to note that another, more qualitative method of selecting a set of parameters exists. In many circumstances, one is interested in how well computer-generated isopleth lines agree with hand-plotted lines. In that case, the criteria for selecting a set of parameters are not based on how accurate the interpolation is in the global sense, but based on how well the interpolated grid point values, when contoured, will reflect the actual measured data. Thus, one would be more interested in the interpolation error at each site of the network rather than the mean error.

The second part of our research effort is to implement error estimation for BOBARY. The variance of the interpolated value (equation 3) is derived from basic statistical principles. It can be shown that the variance of $Z_{x,y}$ is

$$(4) \quad VAR(Z_{x,y}) = \sum_{k=1}^{N} (WT^2(k) * VAR(VAL(k))) + \sum_{l=1, l \neq k}^{N} (WT(k) * WT(l) * COV(VAL(k), VAL(l)))$$

where WT(k) is the weighting factor from equation 1, VAR(VAL(k)) is the variance of the measurement at site k, and COV(VAL(k),VAL(l)) is the covariance between site k and the other sites, l, used in the interpolation procedure. We are currently making the necessary modifications to the BOBARY program to output both the interpolated values and the standard errors of interpolation.

An extension of current research efforts in this area would be to perform a rigorous intercomparison between Kriging and the modified BOBARY procedure with error estimation. Such an intercomparison would be useful when evaluating isopleth maps generated by either method and may result in a significant saving of computer resources.

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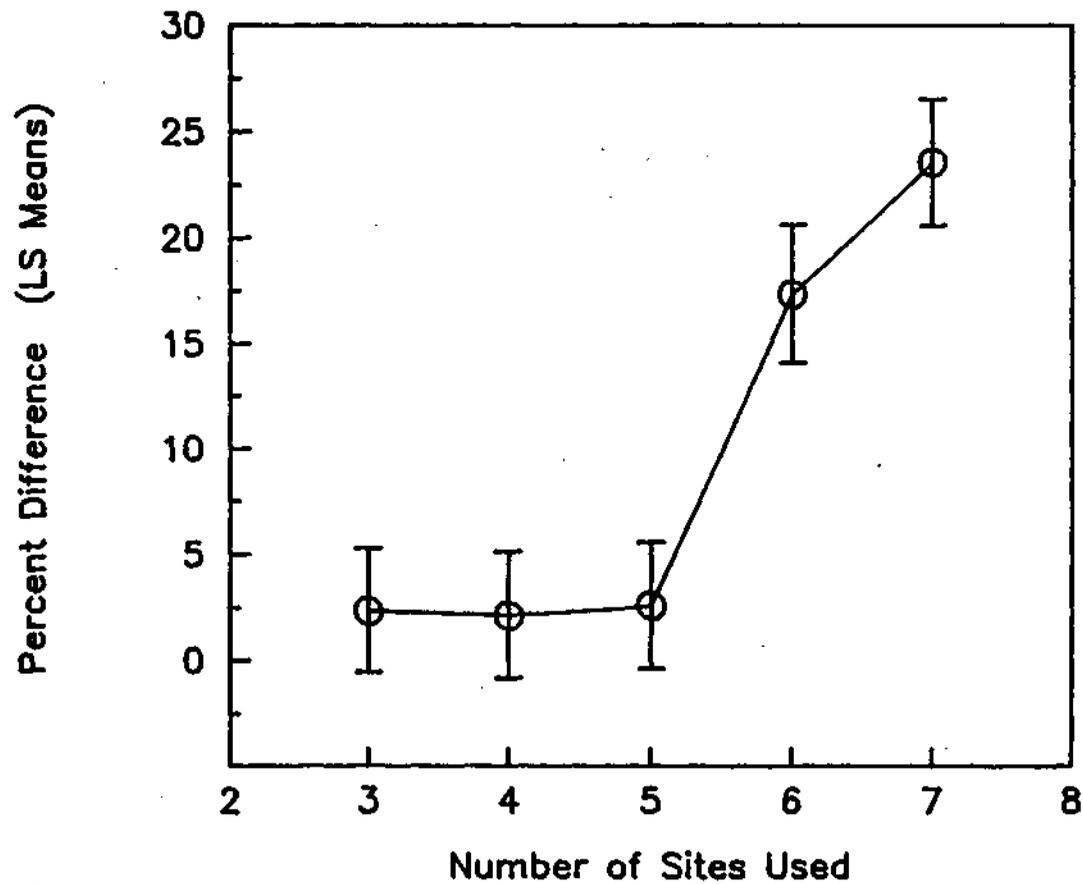Figure 2. Least Squares Mean Percentage Differences As a Function of the Number of Sites Used

Figure 3.  Median Percentage Difference as a Function of Grid Size and Number of Sites Used

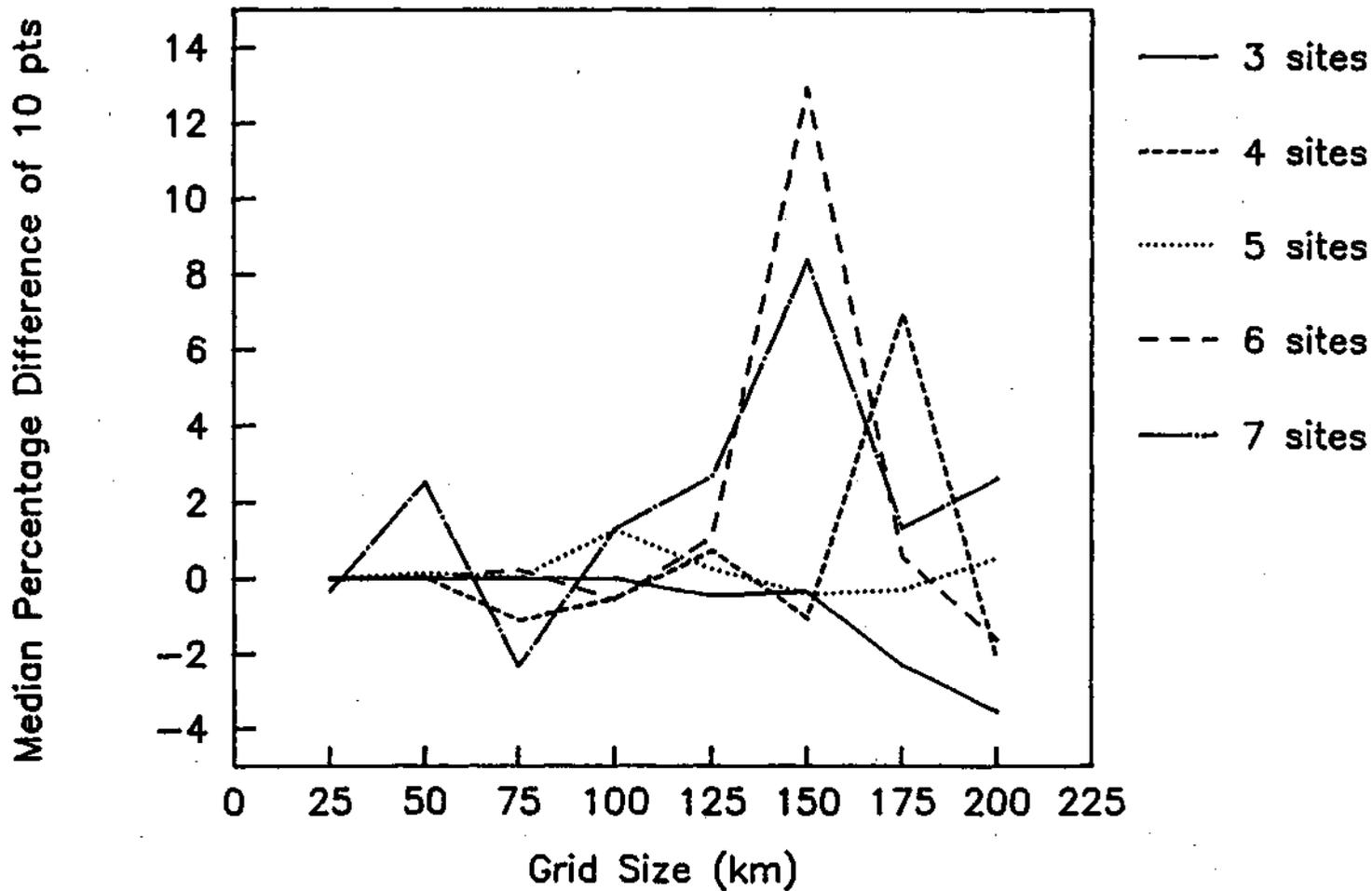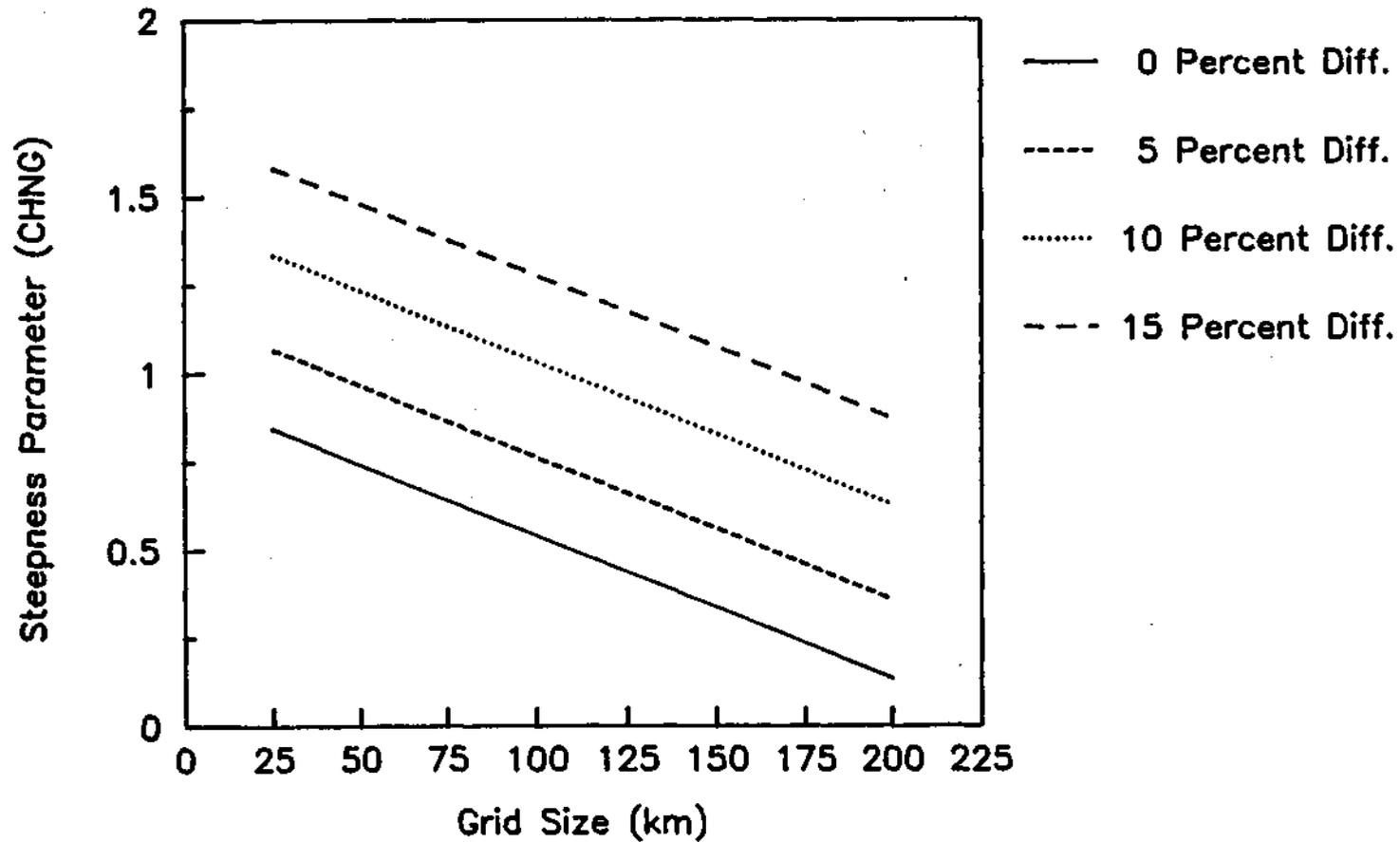steepness parameter (CHNG) = .4

Figure 4. Isolines of Percentage Difference as a Function of Grid Size of Steepness Parameter

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DRY DEPOSITION FLUX ESTIMATES FOR LARGE-PARTICLE ELEMENTS
FROM DRY-BUCKET MEASUREMENTS

Donald F. Gatz, Van C. Bowersox, and Jack Su

Introduction

There were two main purposes for this work. The first purpose was to explore methods for screening the data set, by:

1.  Comparing distributions of dry deposition rates in dry "uncontaminated" samples with those in samples containing various single "contaminants" (including water), and

2.  Determining the effects of various screening criteria on the statistical distributions of dry deposition rates measured by the NADP dry bucket samplers.

The second main purpose was to derive mean dry deposition fluxes for Ca, Mg, K, and Na for the eastern and western U.S., and for "dusty" and "clean" seasons.

This paper is based on analytical data for 2170 dry-bucket samples collected at original National Atmospheric Deposition Program (NADP) sites in what is now the combined National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Samples were collected between 1978 and 1987, but the period of record varies between sites. Data from a small subset of the samples were examined previously by Hicks (1985), who found high frequencies of contaminated samples at many of the sampling sites.

This points up one of the main objections to dry bucket measurements--the fact that many of the samples are contaminated or contain water from precipitation. The other, more fundamental, objection is that dry fluxes of small (primarily sub-micrometer) particles to buckets cannot readily be extrapolated to natural environmental surfaces.

One may then question whether detailed examination of the dry-bucket data set can be justified. We believe such efforts are useful, for at least four reasons. The main reason is that the dry bucket data set may indeed be scientifically valid (at least as a first approximation) for large-particle elements, especially terrestrially-derived cations, for which sedimentation from the atmosphere is a major dry deposition mechanism. This is the only extensive data set available for the dry deposition of particles. Another reason is that the data may be useful for investigating atmospheric gas-particle interactions, and perhaps other atmospheric chemistry issues, quite apart from their utility for estimating dry deposition fluxes.

The third reason relates to the very practical decision that must be made from time to time at individual collection sites--whether to continue or discontinue the measurements. Such decisions are best made in the light of comprehensive analyses of the existing data. Finally, since the data exist, some people will use them, and users should be aware of how various screening criteria will affect the distributions of dry fluxes for the various ions.

Methods

Samples were collected at many sites in the approximately 200-site NADP/NTN network in the United States, using the AeroChem Metrics wet/dry sampler. Collections were made in white linear polyethylene buckets cleaned at the Central Analytical Laboratory (CAL) at the Illinois State Water Survey. Sample durations were 2-month until December, 1980; since then they have been 8-week, beginning on Tuesdays. Collected samples were shipped to the CAL, where 250 mL of deionized water were added. The samples were then swirled to allow the water to contact the walls, and allowed to stand overnight to equilibrate. Samples were filtered through 0.45 um Millipore HA filters. The filtrates were then handled and analyzed in the same way as rain samples (Peden et al., 1986).

Samples were grouped into four regional-seasonal categories. Sites in the eastern 31 states were called the eastern group and those in the western 17 states the western group. Samples beginning between 1 March and 31 August, and ending on or before 30 September were included in the "dusty" season (spring and summer, for the most part), while all other samples were considered to have been collected in the "clean" season (primarily fall and winter).

Results and Discussion

Each sample in the database can have associated with it codes that indicate the presence of particular "contaminants," including water, water spots, bird droppings, insects, plant parts, and "other" materials. In addition, there are codes that signal multiple contaminants and incomplete (partial) samples. Tallies of the numbers of samples having various single contaminants revealed that water in the dry bucket was primarily a clean season phenomenon, while contaminants such as bird droppings, insects, and plant parts occurred primarily in the dusty season. In almost every contaminant group, there were more samples from the east than the west, sometimes by as much as a factor of 2.

The median water volume in samples containing precipitation was about 100 mL in both east and west regions in winter, but only about 10 mL in summer. We suggest that this is the result of the combined effects of poor sensitivity of the precipitation sensor to snow (especially when dry and windblown) in winter, and strong evaporation from the container when heated by the sun in summer.

Distributions of dry fluxes of Na, Mg, K, and Ca computed for samples in each contaminant group in each regional-seasonal category were compared with those for dry non-contaminated samples, using non-parametric methods (SAS Institute, Inc., 1982). Based on the finding of significant (5% level) differences in dry-flux distributions between the dry uncontaminated samples and some wet or contaminated sample groups, a different sequence of successive removal of particular sample groups was devised for each of the four ions. For each ion, the initial data set included all except grossly contaminated samples. The final data sets, which included only dry samples with no contaminants or water spots, represented between 21% and 41% of the initial data sets in the four regional-seasonal sample categories.

Dry flux medians, means, and standard errors were computed for each ion in all four regional-seasonal categories to show how the choice of screening criterion affected the dry flux distributions. Mean values typically exceeded medians by substantial margins, indicating that distributions were skewed toward a few large values.

Comparisons of median fluxes between the successive data sets within specific regional-seasonal categories showed only limited changes as wet or contaminated samples were removed. The biggest difference between data sets (as a percentage of the mean between the two extremes) in the median dry flux of Ca was 39% for the clean season in the west. The biggest difference for Mg was 10%, and occurred in the dusty season in the west. The biggest differences for K and Na were 42% and 24%, respectively, both in the clean season in the west.

For three of the four ions, median fluxes generally tended to decrease as wet and contaminated samples were removed from the data set. For Ca, however, an opposite trend was observed in all four regional-seasonal categories. Removal of bird droppings from the full data set caused small decreases in the median dry flux in all four categories, but subsequent removal of the remaining contaminants, wet samples, and water spotted samples generally resulted in increasing median dry fluxes. Specific reasons for this behavior are not known with certainty. However, we suggest that systematically smaller fluxes in samples containing precipitation could result from a bias of such samples toward wetter than normal sampling periods, when Ca emissions from terrestrial sources would be inhibited by wet surfaces. We also suggest that systematically smaller fluxes in contaminated samples could have resulted from interferences in the analysis of Ca by large amounts of other contaminants (e.g., phosphate) present in such samples.

Mean dry fluxes of Na, Mg, K, and Ca for each regional-seasonal category are shown in Table 1. These values are in good agreement with the few previous dry-bucket measurements available in the literature (Johannes, 1985; Cadle et al. , 1986, and Dasch and Cadle, 1984) as well as with dry fluxes measured by other techniques (Lindberg, 1986; Integrated Forest Study, 1988; Dasch, 1986; Dasch and Cadle, 1986; Cadle et al.. 1986; Davidson and Elias, 1982; Davidson et al. , 1985). For Mg, K, and Ca, mean dry fluxes were mostly higher in the east than the west, and higher in the dusty season than the clean season. For Na, however, both of these relationships were reversed. This may reflect a major contribution to Na dry deposition from non-terrestrial sources such as sea salt in coastal areas and road salt in densely populated areas.

Table 1. Mean dry fluxes computed for dry uncontaminated dry-bucket samples in four regional-seasonal categories.

Mean dry flux +/- standard error (mg/M$^{2-}$wk)

| | East | | West | |
|---|---|---|---|---|
| | Clean | Dusty | Clean | Dusty |
| Sodium | 1.49 ± 0.14 | 0.65 ± 0.06 | 2.29 ± 0.78 | 1.16 ± 0.18 |
| Magnesium | 0.66 ± 0.04 | 0.82 ± 0.05 | 0.49 ± 0.10 | 0.45 ± 0.04 |
| Potassium | 0.68 ± 0.11 | 1.39 ± 0.12 | 0.43 ± 0.04 | 1.04 ± 0.14 |
| Calcium | 4.76 ± 0.30 | 4.84 ± 0.30 | 3.36 ± 0.38 | 4.61 ± 0.41 |

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SPATIAL RELATIONSHIPS BETWEEN ACID RAIN,
AIR QUALITY, AND VISIBILITY DATA

Gary J. Stensland


Visibility and acid rain are two different phenomena which both have direct relationships to air quality.  The objective of this study (Stensland, 1987) was to explore the relationships between all three data sets, with emphasis on the situations for the eastern U.S.


Precipitation Sulfate Seasonality

Seasonal (3-month) and period (5-month) variations in the concentrations of the major anions and cations in the precipitation of the United States were examined by Bowersox and Stensland (1985) using data from the NADP/NTN for 1978 through 1983.  For most ions, concentrations during the warm (growing) period were higher than during the cold (dormant) period throughout much of the country.  Previous investigators had often focused their time variation studies on hydrogen, sulfate, and nitrate ion behavior for the eastern U.S.  Results of the Bowersox and Stensland study indicated that seasonal variations are neither confined to the East nor limited to the ions most frequently associated with acidic deposition.  Median Values by region of the warm/cold period ratio are shown in Table 1.

In a more recent analysis (Stensland, 1987) seasonal ratios for 1984-86 were determined.  The seasonality remained largest for the NE region, especially for the New England states.  For two coastal states, FL and TX, the winter season sulfate concentrations were equal to or exceeded the summer values.  For the east central IL site (known as the Bondville site) the warm/cold season ratio was about 1.5.


Aerosol Sulfate Seasonality

At the Bondville, IL site, daily medium volume aerosol samples were collected and summarized for February 1983 to June 1986.  Sulfate was determined by ion chromatography and calcium, magnesium, and potassium were measured by flame atomic absorption.

The seasonal concentrations for these constituents are shown in Table II. The summer concentrations exceed the winter concentrations for sulfate as well as the dust type constituents.  These results agree with the time variations for precipitation shown in Table I.  It was noted above that the seasonal precipitation ratio is 1.5 for Bondville; the aerosol ratio in Table II is 2.1. One possible explanation for the difference in these ratio values is that higher winter ambient $SO_2$ may provide the extra winter sulfate in precipitation to lower the ratio to 1.5.

Table I.  Summary of ratio values (warm period/cold period
precipitation concentration) for all sites in
four regions (from Bowersox and Stensland, 1985)

| Region[a] | N [b] | $SO_4^{2-}$ | $NO_3^-$ | $NH_4^+$ | $Ca^{2+}$ | $H^+$ |
|---------|-----|------|------|------|------|------|
| MW | 20 | 1.32 | .92 | 1.38 | 1.46 | 1.08 |
| SE | 15 | 1.56 | 1.72 | 2.00 | 1.58 | 1.48 |
| NE | 23 | 2.20 | 1.20 | 2.21 | 1.47 | 1.86 |
| RM | 16 | 2.10 | 2.33 | 2.54 | 2.40 | 2.53 |

| Region[a] | N [b] | $Mg^{2+}$ | $K^+$ | $Na^+$ | $Ca^-$ |
|---------|-----|------|------|------|------|
| MW | 20 | 1.34 | 1.48 | .68 | .78 |
| SE | 15 | 1.28 | 1.41 | .93 | .83 |
| NE | 23 | 1.14 | 1.50 | .70 | .67 |
| RM | 16 | 1.96 | 2.52 | 1.39 | 1.50 |

[a]MW is Midwest; SE is Southeast; NE is Northeast; and RM is Rocky Mountain.
[b]N is number of sites in each region.


Table II.  February 1983 - June 1986 aerosol median
concentrations ($\mu xg/m^3$) for Bondville, IL.

|  | W | Sp | Su | F | All Seasons |
|---|------|------|------|------|------|
| Sulfate | 2.91 | 3.22 | 5.98 | 3.29 | 3.56 |
| Calcium | .19 | .35 | .61 | .45 | .37 |
| Magnesium | .031 | .058 | .093 | .068 | .060 |
| Potassium | .058 | .056 | .078 | .090 | .068 |

Note: W = Dec, Jan., and Feb.;
Sp = Mar., Apr., and May;
Su - June, July, and Aug.;
F = Sept., Oct., and Nov.

Number of samples by season was 273 for W; 322 for Sp; 281
for Su; and 288 for F.

## Visibility Seasonality

Sloane (1983) reported the quarterly 60th percentile visibility for the 1947-78 period for 15 sites in the northeastern quadrant of the U.S. The summer and winter values listed in the upper portion of Table III are averages of the 1975 and 1977 quarterly values reported by Sloane. The Vinzani and Lamb (1985) data in Table III are similar, except that they reported data through 1980, considered only sites near or in Illinois, and used meteorological definitions of seasons (Dec.-Feb. for winter and June-Aug. for summer) instead of the quarterly intervals used by Sloane. In the ratio column in the upper portion of Table III we note that winter visibility exceeds summer visibility at almost all sites considered by Sloane. This is consistent with the higher summer sulfate in both the precipitation and air quality data discussed earlier. The exception is Chicago. The Moline, Peoria, and Springfield sites at the bottom of Table III indicate that the feature of summer visibility (Chicago) <u>equal to or exceeding</u> winter visibility is not due to one anomalous urban site but instead covers a larger region. The Evansville site with a ratio value exceeding 1.0 is on the east edge of the Vinzani and Lamb study area. The seasonal visibility pattern for Illinois is not consistent with the precipitation sulfate data nor the rather comprehensive aerosol sulfate record for Bondville, IL. The primary winter landscape in the general area near the Illinois sites is relatively bare tilled fields or snow cover. One might then suggest that airborne dust leads to decreased winter visibility. The precipitation quality calcium and magnesium data (Semonin, 1986) indicate that the concentrations of these dust type constituents increase steadily from the eastern states toward the plains states, with values of about 0.1 mg/L along the East Coast and 0.5 mg/L in the Plains. The Bondville, IL aerosol data for $Ca^{2+}$ and $Mg^{2+}$ indicate that the concentrations are very low compared to $SO_4^{2-}$ and are <u>lower</u> in the winter than in the summer. Therefore dust does not seem to explain why the visibility at the Illinois site is lower in the winter. Perhaps studies should be done to see if meteorological gradients combined with the exposed soil surfaces might produce relative humidity gradients that can explain the seasonal visibility patterns for Illinois.

Table III. The 60th percentile visibility (miles) and
winter/summer ratios.

| From Sloane (1983):[a] | Summer[a] | Winter[a] | Winter⁄Summer |
|---|---|---|---|
| Dayton, OH | 6.4 | 9.0 | 1.4 |
| Columbus, OH | 7.2 | 9.8 | 1.4 |
| Cleveland, OH | 7.8 | 9.7 | 1.2 |
| Louisville, KY | 8.0 | 10.7 | 1.3 |
| Lexington, KY | 7.2 | 11.6 | 1.6 |
| Williamsport, PA | 9.0 | 17.7 | 2.0 |
| Washington, DC | 10.2 | 11.9 | 1.2 |
| Richmond, VA | 6.2 | 10.9 | 1.8 |
| Roanoke, VA | 12.8 | 38.4 | 3.0 |
| Lynchburg, VA | 10.9 | 30.4 | 2.8 |
| Knoxville, TN | 7.8 | 9.1 | 1.2 |
| Greensboro, NC | 6.6 | 12.6 | 1.9 |
| Charlotte, NC | 6.8 | 15.4 | 2.3 |
| Columbia, SC | 8.6 | 10.4 | 1.2 |
| Chicago, IL | 9.6 | 9.9 | 1.0 |
| From Vinzani and Lamb (1985): | | | |
| Chicago, IL | 10.1[b] | 8.7[b] | .9 |
| Moline, IL | 10.6 | 7.9 | .7 |
| Peoria, IL | 12.5 | 10.0 | .8 |
| Springfield, IL | 8.9 | 8.7 | 1.0 |
| Evansville, IN | 7.2 | 7.7 | 1.1 |

[a]Average of 1975 and 1977 values.
[b]Average of 1976, 1977, 1978, 1979, and 1980 values.  For Springfield 1976 was
 missing and for Chicago 1979 and 1980 were missing.

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# SYNTHETIC PRECIPITATION REFERENCE SAMPLES

## Mark E. Peden

The need for stable precipitation reference samples was described in the Twenty-First Progress Report to the U.S. Department of Energy (Skowron and Peden, 1987). Although the National Bureau of Standards (NBS) has recently developed a Standard Reference Material (SRM) for precipitation chemistry studies, the NBS solutions (SRM 2694) do not include certified concentration values for nitrate, chloride, or ammonium. SRM's are also relatively expensive, so that their cost becomes prohibitive when they are used for several parameters by several chemists on a daily basis. Another drawback is that the certified concentrations of the parameters in SRM 2694 do not adequately reflect those actually found in wet-only deposition. NBS has also reported problems associated with the long-term stability of ammonium ion and pH in low ionic strength solutions (Koch, 1986).

Because of these limitations, our laboratory developed its own internal formulations with the following characteristics:

1.  NBS traceable bias and precision
2.  Long-term stability
3.  Low cost
4.  Analyze concentrations approximating the range found in natural precipitation

Preliminary data from the analysis of two different dilutions of the stock synthetic solution in 1987 indicated that, even at very low concentrations, these solutions were chemically stable for at least five months when stored at room temperature in high density polyethylene bottles.

These preliminary results, reported in the previous Progress Report, generated a great deal of interest in the use of these solutions by other researchers. Because a single concentrated stock solution that can be used for ten constituents is prepared as the original formulation, dilutions can easily be made to adjust concentrations for low or high level work. This flexibility has recently been used to adapt these reference solutions to cloud water sample analyses, which are generally characterized by concentrations 2-4 times higher than precipitation. The USEPA sponsored Mountain Cloud Chemistry Program (MCCP) is now using these solutions as quality control check samples for their six cooperating laboratories, including the Central Analytical Laboratory housed at the Illinois State Water Survey.

The U.S. Geological Survey is also using these solutions to supplement their existing external blind audit program which monitors bias and precision form the collection and analysis of precipitation from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Since early 1988, these solutions have been sent to the field observers responsible for site operation and sample collection. The field observers are instructed to pour these solutions into a clean collection bucket and forward them to the laboratory with a weekly field observer report form. The identity of these samples is unknown

to the laboratory staff so that a realistic estimate of bias and precision from field and laboratory handling and analysis can be made. In the past, the blind audit program has been hindered by a lack of stable, low level solutions that contained all of the analytes routinely determined at the laboratory. With the development of these synthetic solutions, the blind audit program can now more reliably assess bias and precision at concentrations characteristic of precipitation.

An additional use of these samples in the past year has been for interlaboratory testing for the American Society for Testing and Materials (ASTM). ASTM Committee D-22 is currently developing test procedures for precipitation chemistry analyses and has used these solutions to validate methods for pH, $SO_4^{2-}$, $NO_3^-$, $Cl^-$", $Ca^{2+}$, $Mg^{2+}$, $Na^+$, and $K^+$. For each ASTM test procedure, an interlaboratory study is required to establish single operator and interlaboratory precision and bias. The precision and bias data are then incorporated into the methods documentation and become part of the formalized methodology descriptions that appear in the Annual Book of ASTM Standards.

Ten laboratories participated in an interlaboratory study conducted during the past year. Based on the results obtained from these solutions, bias and precision data were incorporated into the test methods which are currently being balloted within ASTM. Future methods development within ASTM will also rely on these synthetic materials for additional parameters such as $NH_4^+$, acidity, and specific conductance.

The original objective at the beginning of this study was to develop internally formulated reference materials that could be used in conjunction with NBS Standard Reference Materials. The purpose of the NBS reference material program is to provide source materials that can be used to ensure NBS traceability. The high cost of certified standards provided through this program, however, precludes their use on a routine basis to monitor laboratory performance. A review of the certified analytes contained in the NBS SRM for rainwater indicated that many laboratories could benefit from using internally formulated solutions that more closely approximated the concentration levels characteristic of wet deposition. In addition, solutions that contained all of the major ions of interest in precipitation were needed.

The recent incorporation of these solutions into new and existing quality assurance programs has emphasized the need for low cost reference materials for precipitation chemistry studies. These solutions have been proven to be chemically stable when stored at room temperature and are formulated to provide the user with a choice of analyte concentrations depending on the dilution used when preparing samples from the concentrated stock solution. The reagents used in preparing the stock solution are currently available in most water chemistry laboratories or are readily available from chemical supply vendors.

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