STUDY OF ATMOSPHERIC POLLUTION
SCAVENGING

Twenty-Fourth Progress Report
Grant Number DE - FG02 - 88ER60635

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Author:

Allen L. Williams
Office of Precipitation Quality

Sponsored by:
United States Department of Energy
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Principal Investigator
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Apportionment of Multiple Aerosol Size Distributions Modes
Using Factor Analysis Techniques

by Allen Williams
Illinois State Water Survey
Champaign, IL

Presented at the Ninth Annual Meeting of the American Association

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Research of the United States Department of Energy
Introduction

This research in progress is concerned with developing the capability to objectively partition aerosol size distribution data into a small number of modes, that together explain most of the variation of the observed data. It is desired to determine from analysis in the field of the optical spectrometer data when a particular mode is present and to collect filter samples to determine the chemical composition of that mode. The results would relate aerosol size distributions to chemical composition.

Through the work of Whitby (1978) and others the notion that the atmospheric aerosol can be split into the sum of different modes has been recognized. The Whitby tri-modal distribution has appeal because the three modes are attributed to different physical aerosol formation processes, and the mathematical description identifying each mode as a lognormal distribution that is mathematically tractable. The present effort attempts to identify the different modes statistically rather than ascribing lognormal distributions that can be made to fit the data. Aside from the desirability of identifying the different modes objectively, a different prescription for mode identification is needed since the optical counter used sizes particles from only .1µm to 2µm. Over this limited size range there is too much uncertainty involved in identifying a size distribution as the sum of two or three lognormal distributions.

The underlying assumption that makes the dichotomous aerosol samplers so useful for chemical characterization of the ambient aerosol relates to the objective of the present effort. The dichot separates the aerosol into two size fractions; typically one fraction between 2.5µm and 10µm, and another less than 2.5µm. The chemical analysis of the fine fraction corresponds roughly to anthropogenic emissions, while the coarse fraction is considered to be of crustal origin. Typical analysis of such data by chemical mass balance techniques, including factor analysis, attempts to identify the different sources of aerosol from elemental analysis of the filter samples. The goal of the present effort is to identify different aerosol populations by monitoring their size distributions. A basic assumption is that different aerosol sources that produce distinctive chemical signatures also produce distinctive aerosol size distributions.

The method of analysis is through the use of the techniques of factor analysis (Joreskog et. al., 1976, Hopke, 1985), or more specifically, the method of principal component analysis (PCA). A data matrix, consisting of many observations of the aerosol size distribution, is factored into the product of two matrices. One, the loading matrix, represents a rotation of the data into a new coordinate system, and the other, the score matrix, represents the value of the data in the new coordinates. An important feature of
the factorization is that, usually, a few factors can be identified that explain most of the variance of the data. Further, the factors are independent and each explain successively the maximum amount of remaining variance. It is possible to develop the factors so that each represents a particle size distribution, and any of the individual size distribution measurements can be interpreted as some linear combination of the factors.

The specific application of the analysis for the present project is to use the knowledge that the ambient aerosol being monitored is composed predominately of one of the factors, or a particular combination of factors, to decide when the aerosol filter sampler should be operating. The filter loading should, therefore, correspond to a particular aerosol mode. By chemical analysis of the filters the unique chemical composition of the different modes can be determined. It is desired to identify the various modes from present data, supplemented with new data, and develop the capability to identify the presence of the various modes as the optical data is being collected. Monitoring of the aerosol size distribution over time shows radical changes to occur rather abruptly. In order to directly determine the chemical composition of different occurring aerosol size distribution modes, a computer controlled decision process is needed that runs a dichotomous sampler only while a particular aerosol mode is present.

The PCA problem posed has wider application than the aerosol size distribution problem described. A satisfactory formulation could be applied, for example, to the MAP3S precipitation data to investigate the question of what is gained by collecting event versus longer time sampling protocols. It could also be used to overcome some of the problems associated with using PCA techniques to identify the chemical source profiles from the chemical analysis of aerosol filters.

There are basically two problems about which the present analysis is concerned, and progress towards their resolution is discussed below. First, is the question of handling the small concentration values so they are justly reflected in the final factors. This is important for size distribution data since the feature of small particle concentrations at some particle sizes is an essential aspect of the size distribution specification. This problem is also of concern for the application of PCA to aerosol filter analysis (Alpert and Hopke, 1980) if the elemental source profiles are desired, since trace values of some elements are important as markers of the underlying source. Some trace elements can be detected at extremely low concentrations. The concentrations can be normalized in the analysis to accentuate the smaller values at the expense of loosing information about the relative magnitudes of the variables in the factors. It then becomes difficult to specify factors representing the aerosol size distribution or the aerosol source profiles.
The other problem relates to the question of negative loadings. For aerosol size distributions the factors representing particle concentrations in different size ranges should not be negative on physical grounds. The mathematical solution to this problem has received attention in the developing field of linear and non-linear programming. It appears that the non-negative condition can be enforced through the application to the Kuhn-Tucker theorem which is an essential result in non-linear programming theory.

This research-in-progress report presents a technique for handling the question of variables with small absolute values. An example of aerosol size distribution data is examined as part of the discussion. The results contain negative concentrations. The anticipated approach to solving the negativity problem is discussed. The less constrained result featuring negative factors, while not representing aerosol modes from different characteristic sources, are of some value as they can be interpreted in terms of the asymmetry and sharpness of the aerosol distribution shape.

### Theory and Discussion

Suppose aerosol size distribution data are presented in the form

\[
Y = \begin{bmatrix}
 n_{11} & n_{12} & \cdots & \cdots & \cdots \\
 n_{21} & n_{22} & \cdots & \cdots & \cdots \\
 \vdots & \vdots & \ddots & \ddots & \ddots \\
\end{bmatrix}
\]

The particular data set examined represents one-minute size distribution measurements collected into 658 five-minute averages using a PMS optical spectrometer (model ASASP). There are 31 size channels on the PMS optical probe ranging from .1 to 2 microns in diameter. Figures 1 shows the total concentrations as a function of time over the sampling period. Some of the mass distributions corresponding to the noted high or low number concentrations of figure 1 are shown in figure 2. It is desired to develop a technique for identifying a few characteristic modes that explain most of the variation of the data, and to be able to specify the composition of measured data in terms of the characteristic modes.

According to the common procedure of R-mode PCA (Joreskog, 1976) the data matrix is transformed by covariance or correlation
Figure 1
Hourly overages of the aerosol concentrations in the size range 0.09-0.101 microns for the week of 6/20-6/26, 1988

Figure 2
Aerosol mass distribution dm/dln(D) (micrograms/m^3).
Selected examples for peak values of total aerosol number concentration (see Figure 2) during the week of June 20—26, 1988
scaling. Correlation scaling about the origin is chosen here (Alpert and Hopke, 1980) yielding the matrix $Y$

$$XD = Y$$ (2)

The transformation matrix, $D$, is defined according to

$$D = \delta \Sigma, X^2 \times \mu$$ (3)

where $X_{ij}$ are the elements of $X$.

Performing a PCA on the $Y$ matrix yields

$$Y = fa'$$ (4)

where the factor loadings, $a$, are orthonormal

$$a' a = 1$$ (5)

and the factor scores, $f$, satisfy

$$f' f = \lambda$$ (6)

As usual $\lambda$ represents the eigenvalues of the covariance matrix $Y'Y$.

A listing of the first 5 factors of the loading matrix, $a$, is shown in Table I. The percent variance explained by each of the five factors is respectively 77.5, 7.58, 6.89, 3.63, and 2.71.

A PCA can also be performed on the original data matrix, $X$, and its relation to equation 4 can be seen through the underlying structure of a singular value decomposition of $X$ which gives

$$X = U \Lambda V'$$ (7)

where $U$ and $V$ are both orthonormal and $\Lambda$ represents the eigenvalues of $X'X$. Writing this in terms the factors $F$ and $A$ is identical to a PCA of $X$. 

6
**Table I**

Loadings for PCA after transformation to correlation about the origin

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</tr>
</tbody>
</table>
\[ X = FA' \quad (8) \]

where the loading matrix \( A \) becomes

\[ A = V \quad (9) \]

and the score matrix \( F \) is

\[ F = U A^{\Omega} \quad (10) \]

Table II shows the first five columns of the loading matrix, \( A \), which explains successively 92.2, 6.27, .93, .16, and .06 percent of the remaining variance.

Although \( X \) is related to \( Y \) through a linear transformation, the respective factors of each from a PCA are not necessarily related. It is this feature of PCA that makes it difficult to decide on the scaling, if any, to use since the resulting factors are not invariant under a linear transformation, while the different common scalings are represented as linear transformations. For example, the factors derived from correlation scaling and those from covariance scaling on the same data set can be quite different (Rozett and Petersen, 1975) which leaves considerable uncertainty in how to interpret the data. In the present situation drastically different amounts of the variance are explained depending on how the data is normalized.

The scheme advocated here is to require the factors of the transformed data set and the original data set to satisfy the same linear transformation as relates the two data sets. Since from equation 2 we have

\[ X = YD' \quad (11) \]

we can require

\[ FA' = fa'D'^{-1} \quad (12) \]

or
### Table II

Loadings for PCA on the original data matrix

<table>
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This is satisfied if

\[ F (T')^{-1} T' A' = f a' D^{-1} \] (13)

Thus the PCA of \( X \) and of \( Y \) are at least constrained to satisfy the linear transformation depicted by equation 2.

It turns out that the form of \( T \) is the same as a Procrustes transformation, since \( A \) and \( a \) are both orthogonal and \( D^{-1} \) is diagonal. According to the definition of a Procrustes transformation, the target \( D^{-1}a \) represents a least squares approximation to \( A \). We, therefore, have a transformation that forces the two factored expressions for \( X \) and \( Y \) to be related by the same linear transformation that relates \( X \) and \( Y \). Of the solutions for the factors of \( X \), expressions for \( F \) and \( A \) can now be found that not only satisfy a PCA of \( X \), but also are related in a least squares sense to a PCA of \( Y \) which represents a particular scaling of \( X \).

An Orthogonal Procrustes transformation matrix \( T \) can be found through the single value decomposition (Shoneman, 1966)

\[ A' D^{-1} a = u \gamma v' \] (15)

with

\[ T = u v' \] (16)

Table III shows the first five columns of the loading matrix, in the example considered, after the transformation described by equation 16. Table IV shows the results after a varimax rotation which is a common transformation that helps achieve simple structure. It is seen that despite the varimax rotation there are still some negative loadings present.

The size distribution represented by each of the various modes can be found through a Q-mode analysis. In a Q-mode analysis the transpose of the data matrix is analyzed according to PCA. From the singular value decomposition the relation of the Q-mode factors and loadings to those of an R-mode analysis can be seen. The SVD of \( X' \)
Table III

PCA loadings on the original data matrix after Orthogonal Procrustes target transformation with the target specified by PCA on correlation scaling.

\[
\begin{array}{cccccc}
[1,] & [2,] & [3,] & [4,] & [5,] \\
1.0 & 6.031261e-1 & -3.307816e-1 & -4.459368e-1 & -1.495181e-1 & 4.311985e-1 \\
2.0 & 2.442931e-1 & -6.072861e-2 & 1.601881e-1 & -6.371232e-1 & 3.883944e-2 \\
3.0 & -6.748154e-3 & -4.939033e-2 & 3.69007e-1 & -3.566046e-1 & 2.172942e-1 \\
4.0 & -1.147749e-1 & -1.404096e-1 & 4.241727e-1 & -1.639598e-1 & 1.967629e-1 \\
5.0 & -1.377478e-1 & -3.198716e-1 & 3.759331e-1 & 7.500123e-2 & 2.149543e-1 \\
7.0 & 1.849713e-1 & -4.475598e-1 & 1.192621e-1 & 2.539210e-1 & 2.428772e-1 \\
8.0 & 4.779648e-1 & -1.143432e-1 & 1.828683e-1 & 1.907963e-1 & -4.04834e-2 \\
9.0 & 3.390552e-1 & 1.831823e-1 & 2.017736e-1 & 5.146567e-2 & -1.799191e-1 \\
10. & 2.494104e-1 & 2.407215e-1 & 2.038649e-1 & 5.995774e-2 & -2.181197e-2 \\
12. & 2.348963e-1 & 3.770868e-1 & 2.887644e-1 & 2.009373e-1 & 2.055316e-1 \\
16. & 2.395842e-3 & 4.851321e-3 & 1.555812e-3 & 1.318038e-2 & 1.801902e-2 \\
17. & 4.500673e-3 & 2.153033e-3 & 4.559743e-4 & 7.190336e-3 & 6.256638e-3 \\
18. & 7.936646e-4 & 1.189936e-3 & 3.314575e-4 & 3.479135e-3 & 7.807211e-3 \\
19. & 5.602786e-4 & 2.065998e-4 & -1.391448e-4 & 1.232226e-3 & 1.349638e-3 \\
20. & 3.972591e-4 & 5.100635e-5 & 2.085227e-4 & 9.839709e-4 & 1.076897e-3 \\
22. & 1.815616e-4 & 4.638514e-6 & 1.274948e-4 & 5.118015e-4 & 5.829730e-4 \\
23. & 1.324289e-4 & 3.806207e-6 & -8.101353e-5 & 3.136173e-4 & 3.461615e-4 \\
27. & 5.404912e-5 & 3.124980e-6 & -4.367982e-5 & 2.040101e-4 & 2.465962e-4 \\
29. & 3.634420e-5 & 5.161598e-6 & -2.562469e-5 & 1.294605e-4 & 1.576519e-4 \\
30. & 2.912962e-5 & 3.707720e-6 & -2.482544e-5 & 1.187492e-4 & 1.464218e-4 \\
31. & 2.262356e-5 & 5.154373e-6 & -1.808683e-5 & 9.260103e-5 & 1.166267e-4 \\
\end{array}
\]
### Table IV

PCA loadings on the original data matrix after a Varimax rotation subsequent to the Procrustes target transformation.

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from equation 7 can be written

\[ X' = V \Lambda^{1/2} U' \]

\[ = F_q' A_q' \]

Here, \( F_q \) and \( A_q \) are the Q-mode score and loading matrices respectively.

By inspection

\[ A_q = F \Lambda^{-1/2} \]  \hspace{1cm} (19)

and

\[ F_q = A \Lambda^{1/2} \]  \hspace{1cm} (20)

For the size distribution example being considered, the columns of the Q-mode factor scores represent independent size distributions that successively account for the maximum remaining variance. It is
vital that the values with small magnitude be accurately represented, which has been assured by the target transformation relating $A$ and $F$ to $a$ and $f$. Table V shows the first five columns of the Q-mode score matrix.

The values from the first three columns are plotted versus the PMS size channel numbers in figures 3, 4, and 5 respectively. If a non-negativity constraint had been enforced, the Q-mode result would represent the desired aerosol size modes. As it is the result represents an empirical analysis. The first mode explains most of the variance of the data. The second two modes, while explaining successively more of the variance, seem to complement the first mode. Larger amounts of modes 2 and 3 have a tendency to level out the peaks and valleys of the mode 1 distribution.

Physically meaningful size distribution modes must avoid identifying a negative number of particles in a given size channel, so the search must be extended to exclude factors with negative values. The Kuhn-Tucker theorem (Menke, 1989, Lawson and Hanson, 1974) specifies conditions for enforcing such constraints on the transformed data. The constraint, that $F \geq 0$ for example, can be developed as defining a volume in the abstract space containing $F$ inside which the constraint is satisfied. The space of $F$ can be identified through the interpretation of the single value decomposition on the data that defines $F$. The Kuhn-Tucker theorem defines conditions associated with the normals to the abstract volume from which a procedure for extracting a solution satisfying the constraints can be found. Work is continuing to include the non-negativity constraint into the analysis.

Figure 5. Mode 3 Size Distribution
Table V

Q-mode score matrix. Each column represents independent size distributions that together explain most of the variance of the data.

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Summary of calculation scheme

1. Factor both $X$ and $XD=Y$.

2. Require that the factors satisfy the same linear transformation. This can be done by identifying a target matrix and performing a Procrustes target transformation.

3. Further rotate the factors of $X$ to obtain simple structure using, for example, a varimax rotation.

4. From the factors of $X$ calculate the Q-mode factors of $X'$ which are related because of the underlying properties of the single-value decomposition.

5. The Q-mode score matrix should yield independent size distributions that account for a large portion of the total variance of the data set.
References


Implications of the Formation of Cloud Condensation Nuclei from Gaseous Precursors

by Allen Williams
Illinois State Water Survey
Champaign, IL

Presented at the 83rd annual meeting of the Air and Waste Management Association in Pittsburgh, PA, June 24-29, 1990.

Research supported by the Office of Health and Environmental Research of the United States Department of Energy
ABSTRACT
The question of the derivation of the characteristic shape of the cloud condensation nucleus (CCN) spectrum from commonly used aerosol size distributions is examined. The shape of the CCN spectrum is important since it determines if the cloud droplets are controlled by the number of CCN or by cloud dynamics. It is found that both a Junge and a Whitby size distribution of soluble particles over-predict the exponent of the CCN spectrum, and the situation is made worse by considering the fraction of soluble material to be particle size dependant. Approximate agreement is obtained from a model that assumes the number of CCN to be proportional to the surface area of the ambient aerosol as might be the case if the particle surface catalyzes a chemical reaction to form the soluble material.

INTRODUCTION
Stratocumulus clouds, which cover over 34% of the oceans at any given time, are recognized as having an important affect on the global radiation balance, with an increase in the stratocumulus cloud cover tending toward climate cooling. One aspect of the cloud-climate question relates to changes in cloud condensation nuclei (CCN), the small particles in the air on which cloud droplets form. Continuing atmospheric pollution may increase the number of CCN and increase the amount of cloud cover, at least for stratocumulus clouds. Higher CCN concentrations over the Atlantic than over the Southern Oceans are attributed to anthropogenic emissions. Another postulated mechanism is through the increase in marine phytoplankton resulting from a sea surface temperature increase. The phytoplankton produce dymethylsulphide, which is assumed to be a source of CCN, and the increase in CCN would increase the marine stratocumulus cloud cover resulting in an increased albedo. Anthropogenic sulfur emissions should likewise be a source of CCN, and since the sulfur emissions in the northern hemisphere greatly exceed those of the southern hemisphere, the effect ought to be measurable. One notable general circulation modeling effort shows the observed temperature differences between hemispheres to be consistent with the cooling resulting from an increase in CCN due to anthropogenic sulfur emissions, and concludes that CCN forced cooling may be largely compensating the CO2 warming in the northern hemisphere. Although the parameterization of the cloud microphysics that would relate the increase in CCN to changes in radiation balance is an area of considerable uncertainty, a key question relating to global warming is the future trends in CCN concentrations.
THEORETICAL DISCUSSION

The nature of CCN, however, make them very difficult to study\textsuperscript{7}. Their only means of detection are by activating them under supersaturated conditions. Since they nucleate at only a few percent supersaturation, the temperature and pressure control that are necessary for their laboratory production are demanding. They often represent a small percent of the total atmospheric aerosol yet occur at nearly the peak of the atmospheric number distribution. Their mass is very small making direct chemical analysis difficult. The only evidence of the chemical composition of the CCN is through indirect methods, which points to (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} as the dominant CCN constituent\textsuperscript{8}. There is difficulty in identifying the natural sources of CCN\textsuperscript{8}, and correlating CCN concentrations with anthropogenic emissions\textsuperscript{9,10}. The questions of the chemical composition of CCN and their long term trends are significant among the many other problems in predicting the impact of clouds on climate warming.

In a typical description of non-freezing cloud formation\textsuperscript{11} a parcel of air is considered to be lifted adiabatically in the atmosphere under humid conditions. If the adiabatic lapse rate exceeds the actual lapse rate, the parcel at some point may become saturated with respect to water vapor, and further lifting would supersaturate the parcel. If no CCN were present, the supersaturation would rise to several hundred percent before spontaneous droplet formation would occur through homogeneous nucleation or nucleation on ions. Particles are always abundantly present in the atmosphere, however, and the supersaturation seldom exceeds several tenths of a percent before droplet formation occurs on a few of the particles. Although the latent heat released provides additional lifting of the parcel to help drive the process toward increasing supersaturation, the droplets that are first produced are very efficient at removing excess water vapor by their diffusional growth. Once enough droplets are formed, they quickly reduce the supersaturation and effectively preclude further droplet formation. The CCN are those particles that are able to aggressively respond to form droplets under supersaturated conditions.

The most common method for detecting CCN is to expose an air sample to cloud level supersaturations, produced in a thermal diffusion cloud chamber, for example, and to count the droplets formed. A convenient characterization of CCN is to plot the number concentration verses supersaturation on a log-log graph. In such a representation the curves usually follow a relatively straight line, and about the same slope but a different intercept is observed when the data is collected from different measurements. The observed spectrum, due to Twomey\textsuperscript{7}, relates the CCN concentration, $n$, to the supersaturation, $s$, according to:

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\[ n = c s^k \]  \hspace{1cm} (1)

where the value of \( k \) is in the neighborhood of \(.5\). The value of \( c \) varies over quite a range to yield, for \( n \), values of order \(100/cm^3\) over oceans, several hundreds over continents, and to fall off with height.

From the standpoint of modeling cloud formation the value of \( k \) has important consequences. From thermodynamic and hydrodynamic considerations of a rising air parcel in which condensation occurs, the droplet concentration is proportional to \( c^{(1-k)/(k+2)}v^{3k/2(k+2)} \), where \( V \) is the updraft speed. For the observed value of \( k = .5 \) this becomes \( c^{.8}v^{.3} \), so the cloud droplet concentration is predominantly determined by the CCN concentration. Accordingly, the question of the role of clouds on climate change must focus on the trends in the CCN concentration.

It is interesting to consider the derivation of \( k \) from observed aerosol distributions. If the aerosol particles are assumed to be soluble, then the well known Kohler curves (see for example Fletcher) and corresponding analysis, shows the square of the critical supersaturation, at which a particle of a given radius, \( r \), is activated to become a droplet, varies as \( r^{-3} \). The Junge aerosol distribution, relating the number of particles larger than radius \( r \), also varies as \( r^{-3} \). Therefore, a Junge particle distribution of soluble particles yields a CCN spectrum,

\[ n \propto s^2 \]  \hspace{1cm} (2)

with the value of \( k = 2 \). Such a relation would have important consequences, since the cloud droplet concentration would be proportional to \( c^{.5}v^{.75} \). The amount of cloud cover would be more influenced by cloud dynamics than the CCN concentration.

Since the observed CCN spectrum, with \( k = .5 \), falls off much faster with decreasing particle size than does the spectrum derived from an assumed Junge distribution of completely soluble particles \((k=2)\), agreement may be found by considering a cumulative aerosol size distribution that falls off more rapidly with small particle size. The validity of the Junge parameterization, admittedly, becomes less certain for particles of radii much below \(.1\mu m\). One approach to describing the size distribution over the smaller sizes is the approach of Whitby's trimodal distribution. In the size range of interest a description consisting of the nuclei mode, centered below \(.01\mu m\) radius, and the accumulation mode, centered above \(.01\mu m\) radius, was postulated by Whitby to provide a suitable parameterization based on numerous observations. The trimodal distribution is formed as a sum three lognormal particle distributions, where in addition to the nuclei and accumulation modes, the coarse mode consists of a lognormal distribution centered at several tenths of microns particle radius. In the Whitby's grand average continental size distribution, the
lognormal parameters for the nuclei mode are a geometrical mean radius of .065 µm, a geometric standard deviation of 1.7, and a total number of 7.7x10^4 cm^-3. The corresponding parameters for the accumulation mode are .035 µm, 2.03, and 1.3x10^4. The accumulation mode distribution falls off rapidly below .03 µm radius, and the nuclei mode contribution to particles in the size range just below .03µm is negligible, so the trends favor obtaining agreement between the observed aerosol distributions and the observed CCN spectrum. If the sum of the particles above a given size is found graphically on log-probability paper (the coarse particle mode hardly contributes to the particle number since the normalization constant is 4.2 cm^-3 compared to ≈ 10^5 cm^-3 particles in total), the cumulative distribution is found to vary approximately as r^{-3/2} between .1 µm and .01 µm. This, indeed, falls of faster than the r^{-3} Junge distribution for smaller sizes. Again assuming all the particles are soluble, and noting that the critical supersaturation varies as r^{-3/2} for soluble particles, the Whitby distribution predicts the CCN concentration, n, to vary as:

\[ n \propto s^1 \]  

(3)

This is considerable improvement, but not agreement, since the value of k≈.5 can be considered accurate to better than a factor of 2.

Easing the restriction of complete particle solubility would have an effect on the derivation of the CCN spectrum from the aerosol size distribution. The Kohler theory was altered to account for the activation of partially soluble particles by Junge and McLaren in terms of \( \epsilon \), the volume fraction of soluble material in the dry aerosol particle. Critical to the development is the assumption that, when wetted, the non-soluble part of the aerosol particle is completely submerged in the liquid. Numerically solving equation 1 in the Junge and McLaren paper, using the same representative values for the various constants describing the soluble material and environmental parameters, and setting the derivative with respect to droplet radius equal to zero, the critical supersaturation can be found. Repeating the calculation for dry particle radii ranging from .02 to .1 µm and for \( \epsilon \) ranging from .001 to 1, the critical supersaturation is seen to closely follow a regression formula:

\[ s = 0.2 \ r^{-3/2} \epsilon^{-0.43} \]  

(4)

As expected the supersaturation varies as r^{-3/2} if \( \epsilon=1 \)

If a dependance of \( \epsilon \) on r were determined, equation 4 could be solved for r and substituted variously into equations 2 and 3 to find the resulting CCN spectra. Consider a model in which the soluble material is present either as small aerosol particles (r<.01µm) or as a vapor which can diffuse to the otherwise non-soluble aerosol particles. Since we are interested in CCN particles
less than .1 μm, which corresponds to the molecular mean free path, the growth of the aerosol by attachment of the smaller soluble particles or the vapor can be described on kinetic grounds. The flux of the vapor depends on the pressure and temperature of the fluid, and the soluble particle flux on the corresponding Brownian diffusion coefficient. In either case, the flux multiplied by the aerosol particle surface area is proportional to the rate that soluble mass deposits on the aerosol, so the rate of mass increase is proportional to \( r^2 \), and the radial increase is independent of \( r \). All the aerosol would have a deposit of the same thickness, \( \delta \), which is either directly condensed soluble material or attached small soluble particles. Assuming \( \delta \) is small compared to the aerosol particle size, thus neglecting terms with higher powers than \( \delta/r \), the fraction of soluble material on the particles can be seen to vary as:

\[ \varepsilon \propto r^{-1} \]  

(5)

Substituting this into equation 4, the critical supersaturation becomes:

\[ s \propto r^{-1.07} \approx r^{-1} \]  

(6)

For the cumulative Junge aerosol distribution that varies as \( r^{-3} \), the resulting CCN spectrum is proportional to \( s^3 \). The cumulative Whitby distribution resulting from the grand average continental distribution, which varies as \( r^{-3/2} \) over the size range of interest as discussed above, yields a CCN spectrum varying as \( s^{3/2} \).

Under the assumption that the soluble material is present either as very small particles or as a vapor that attaches to the surface of existing aerosols, the smaller aerosol particles receive proportionately more soluble material (\( \varepsilon \propto r^{-1} \)). This accentuates the disagreement between the observed CCN spectra with \( k=\cdot5 \) and the spectra derived from the Junge distribution, \( k=3 \), or the Whitby distribution, \( k=3/2 \). A more rigorous analysis would include the larger Brownian diffusion coefficient between the smaller aerosol and the attaching soluble particles, which would further enhance the disagreement. The process that produces the accumulation mode aerosol, ie. the coagulation of nuclei mode aerosol with each other and with particles in the accumulation mode, is similar to the model described here, and apparently is not the mode of formation of CCN.

Consider another model, to account for the observed CCN spectrum, in which soluble material attaches to existing particles of a given size at a rate proportional to the total surface area of particles of that size. This type of process would follow if the particle surface acts as a catalyst for a chemical reaction, and certain photochemical reactions could occur in this way. Under these conditions it would further seem plausible that the amount of soluble material formed would also be proportional to areal distribution, in which case \( \varepsilon \propto r^{-1} \) and, following equations 4-6,
s \propto r^{-1}. For the Junge distribution, where the number per radius size interval varies as r^{-4}, the particle area greater than a given size varies as r^{-3}. Using graphical techniques to find the cumulative particle area for sizes from .01 to .1 \mu m for the Whitby grand average areal distribution, and fitting the results to a power distribution, the cumulative areal distribution varies as r^{-3.34}. The resulting value of k is 1, for the Junge distribution, and 1/3, for the Whitby distribution.

CONCLUSIONS

The value of the empirical exponent of the supersaturation, k, in Twomey's expression relating the number of cloud droplets to the supersaturation, is significant from the standpoint of global warming. The established value is in the range of .5, and a significantly larger value would imply that atmospheric dynamics, not cloud condensation nuclei number, would determine the global number of cloud droplets, and hence the cloud radiative effects. Attempts to derive the value of k based on common aerosol size distribution expressions and particle solubility characteristics.

Assuming a Junge aerosol size distribution of completely soluble particles the value of k becomes 2, whereas with a Whitby continental size distribution of soluble particles, k=1. However, if the aerosol is assumed initially non-soluble and subjected to either, a vapor that would condense into a soluble material on their surface, or smaller soluble particles that diffuse to the aerosol surface, the value of k becomes 3 for the Junge distribution and 3/2 for the Whitby distribution. It is hard to see how coagulating particles from the Whitby nuclei mode could form an accumulation mode aerosol that has the recognized CCN spectrum.

An interesting case is investigated in which the number of CCN is assumed proportional to the areal distribution of the aerosol as might occur if the aerosol material catalyzes a chemical reaction on its surface. The amount of soluble material is, likewise, assumed proportional to the particle surface area, resulting in a r^{-1} dependence of the fraction of soluble material in the particles. The value of k becomes 1 and 1/3 for the Junge and Whitby distributions respectively.

REFERENCES


Study of Atmospheric Pollution Scavenging
Ten Year Review (1980-1990) of DOE Research

by Allen Williams
Illinois State Water Survey
Champaign, IL

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I. Introduction

Atmospheric scavenging research conducted by the Illinois State Water Survey under contract with the Department of Energy has been a significant factor in the historical development of the field of precipitation scavenging. Emphasis of the work during the 1980's became focused on the problem of acid rain problem with the Survey being chosen as the Central Analytical Laboratory for sample analysis of the National Atmospheric Deposition Program National Trends Network (NADP/NTN). The DOE research was responsible for laying the groundwork from the standpoint of sampling and chemical analysis that has now become routine features of NADP/NTN. A significant aspect of the research has been the participation by the Water Survey in the MAP3S precipitation sampling network which is totally supported by DOE, is the longest continuous precipitation sampling network in existence, and maintains an event sampling protocol.

The following review consists of a short description of each of the papers appearing in the Study of Atmospheric Scavenging progress reports starting with the Eighteenth Progress Report in 1980 to the Twenty-Third Progress Report in 1989. In addition a listing of the significant publications and interviews associated with the program are given in the bibliography.


A. Ambient Aerosol Measurements at Champaign, IL, G. J. Stensland and J. D. Bartlett

The sampling and extraction procedures for all the aerosol filter samples is described and three types of data are presented. First, a comparison of Whatman versus Nuclepore filters for about 70 samples is presented. Second, a comparison of Nuclepore versus Fluoropore filters for six samples is presented. The final section presents the results for one year of daily aerosol sampling at the Willard Airport site.

B. Nitrate Measurements in Precipitation for the Study of Trends and Patterns, G. J. Stensland

Spatial patterns and the time trends of nitrate in precipitation are examined. The data are from studies carried out in the United States in the mid 1950's and the late 1970's. For the temporal trends, data from the northeastern United States are emphasized. An annual
cycle of the nitrate concentrations in precipitation for Champaign, Illinois is compared to ambient aerosol data for the same location.

C. SCORE-78 Case Study for July 2, 1978, G. J. Stensland

The concentrations of the various ion concentrations in a single precipitation event over an approximately 50 square mile area is examined. Contours of the ammonium, sulfate, nitrate, calcium, magnesium, sodium, potassium, chloride, pH, and conductivity are presented. Sequential data at one of the sites is also discussed.

D. Multielement Analyses of Selected Samples from SCORE-1979, D. F. Gatz and G. J. Stensland

This preliminary report describes a case study to determine if the SCORE-1979 rain chemistry data falls into the same factor analysis groupings of soluble and insoluble crustal elements, soluble metals and sulfate, and insoluble metals as was found in a METROMEX analysis. The rain sampling network and sample analysis procedures are describe.

E. An Urban Influence on Deposition of Sulfate and Soluble Metals in Summer Rains, D. F. Gatz

Observations suggest that rainfall deposits at least some locally-emitted sulfur at short distances downwind of the sources which causes enhanced deposition and variability in the affected areas. The variation in airborne sulfate concentrations is roughly the same as that observed in either concentration or deposition of sulfate in rain. Thus, there is no need to invoke in-cloud scavenging of sulfur dioxide to explain enhanced sulfur in rain near the city, since there is ample aerosol sulfate and an available scavenging mechanism (nucleation) to account for it. The observation of consistently similar deposition patterns for sulfate and soluble pollutant metals places some interesting constraints on possible scavenging mechanisms and suggests that more detailed study of this group of materials would be fruitful for understanding the processes involved.

F. Associations and Mesoscale Spatial Relationships Among Rainwater Constituents, D. F. Gatz

Factor analysis of multielement deposition of both soluble and insoluble materials in single storms over networks of approximately 2000 km² near St. Louis have revealed that four main groupings of deposition patterns occur.
1) Soluble soil-derived elements,
2) Insoluble soil-derived elements,
3) Soluble pollutants, and
4) Insoluble pollutants.

G. Spatial Variability of Rain Water Impurities in Mesoscale Events, D. Q. Naiman and D. F. Gatz

A summary of an investigation of the spatial variability of precipitation impurities in the METROMEX network of precipitation samplers is presented. Reasons why precipitation impurity variations are important are discussed and on some typical results presented. It is shown that taking account of spatial correlation improves the accuracy of estimating summer rainfall and deposition from single events using open collectors (corrected for dry deposition contributions) over 2000 km² in the St. Louis area.

H. A Precipitation Chemistry Data Management System - Summary, R. K. Stahlhut and V. C. Bowersox

An automated data management system for precipitation chemistry is described. The system has two principle features: (1) a computerized data base to store the information in an easily and selectively accessible form, and (2) a library of computer programs to process and check the data for consistency and errors and to organize and report the data in formats amenable to the data user and to the data analyst. Together these features combine to provide a simple and efficient means of managing large precipitation chemistry data sets.

I. Analytical Chemistry Laboratory, M. E. Peden

The expansion of the Analytical Chemistry Laboratory with the installation of an automated ion chromatograph and associated equipment is described. In addition, the Analytical Chemistry participation in the Fourth-Environmental Protection Agency Precipitation Reference Sample Interlaboratory Comparison is discussed.

J. Ambient Air Filter Extraction Procedures, J. Bartlett and G. J. Stensland

The development of an extraction technique for the analysis of aerosol filter samples is described. The
cation exchange capacity of the soil particles can influence the ionic concentrations of Ca, Mg, Na, and K in the extraction medium and complicate the determination of the amount of soluble ionic material. The extraction method developed accounts for the exchangeable ions to better simulate the soluble ions scavenged by precipitation.


A. Summary of Sulfate and pH for SCORE-79, G. J. Stensland

The Summer Chemistry Of Rain Experiment for 1979 (SCORE-79) had the objectives of assessing the surface rainfall chemistry variability. All available data from each site for the 1979 field experiment were included in the analysis. The sulfate values varied between 0.5 and 15 mg/L or by more than a factor of 30. The range of median values for the data set was 1.7 to 4.7 mg/L or a factor of 2.8. The range of pH values was 3.3 to 7.4 for all data, but for heavier rainfalls the range was 3.4 to 7.1. The median pH for all data was about 4.3.

B. Reproducibility of Aerosol Samples Collected on Nuclepore Filters Under Inverted Funnel Rain Shields, D. F. Gatz

An experiment is reported in which samples were collected simultaneously on identically exposed filters using inverted funnel rain shields. Good agreement was found for Si, S, K, Ca, Fe, and TSP and poorer agreement for Ti, Mn, Zn, Br, and Pb. However, statistical analyses reveals that the agreement is clearly less than desired. Some possible explanations for the discrepancies are offered, but additional experiments are needed to clarify the problem for addressing spatial variability problems.

C. Comparison of Two Sampling Methods for Medium-Volume Aerosol Sampling, D. F. Gatz

A comparison was carried out between an inverted funnel aerosol collection method and an isokinetic sampler free to move with the wind. The data shows that the isokinetic sampler collects more aerosol for the 11 elements analyzed and TSP than the inverted funnel. The isokinetic/funnel ratio ranged from 1.05 for S to 1.32 for Si and Ti. This finding must now be placed in the context of its impact on scavenging ratio calculations.
D. Comparison of Total Versus Soluble Data for Ambient Aerosol Filter Samples, G. J. Stensland and D. F. Gatz

An attempt was made to determine the soluble/insoluble ratio for Ca, K, and S of daily aerosol samples. The total concentration was found by ion-excited X-ray fluorescence while the soluble contribution was determined by flame atomic absorption and automated colorometric methods. The results are inconclusive and a number of possible problems need to be explored before quantitative values will be available.


Statistical methods to estimate background lithium in tracer experiments were used to help predict the deposition patterns. The principal components regression did not yield a result useful to estimate scavenging efficiency. The primary useful result is that the background concentration of any tracer must be carefully assessed in designing future experiments, and the methods development points the direction that such assessments must take.

F. Design of a Feasibility Study to Assess the Impact of Precipitation Quality on Soil Water Quality, V. C. Bowersox

To study the impact of precipitation soil water quality, the chemical composition of the rain would be compared to the ground water chemical composition. A field lysimeter device is discussed by which the soil water can be collected at different depths. The results would depend on the soil chemistry eg soil exchange capacity and pH, which would also be assayed at the sampling site.

G. A New Search for Old Evidence to Identify Trends in the Chemistry of Precipitation in the Continental United States, V. C. Bowersox

In order to more clearly identify the trends in precipitation chemistry it is desirable to have a records that pre-date the current high levels of SO\textsubscript{x} and NO\textsubscript{x}. Data is being collected for the early decades of this century and evaluated according to sample location, sampling protocol, laboratory and analytical techniques, and contamination sources.
H. Seasonal Precipitation concentrations and Depositions for North American from the CANSAP/NADP Networks, R. G. Semonin

Using combined data sets from the NADP and CANSAP networks, descriptive maps of calcium, ammonium, nitrate, sulfate and pH were prepared. Seasonal and annual distributions are shown for the data period July 1978 through September 1980.

I. A New Sequential Rainwater Sampler, G. J. Stensland

The evaluation of a newly designed sequential sampler for precipitation chemistry was carried out in a field experiment in 1980. The results are quite promising although some minor changes will be made as a result of the evaluation prior to construction of additional units.

IV. Review of Twentieth Progress Report, (Contract Number DE-AC02-76EV01199) Report Number C00-1199-64, SWS Contract Report 347, September 1984

A. Acid Rain Data Collection, Handling, Analysis and Interpretation, R. G. Semonin

Some recent data are shown for pH to illustrate its great spatial variability in the United States. These data show that the lowest values exist in the Northeast while the Great Plains show the highest pH values. The ratios of hydrogen, ammonium, and calcium ions to the sum of sulfate and nitrate reveal that maximum values occur in the Northeast, central Great Plains, and the intermountain basin, respectively. Finally, a brief account of reinterpreting the older data show that the previously perceived rapidly worsening precipitation acidity problem is not true. When account is taken of different sampling procedures, analytical methods, and, most importantly, meteorological sampling conditions, the early chemistry was proven to be inadequate as an initiating point to determine a trend in the United States.

B. A Comparison of Four Methods of Computing Precipitation pH Averages, G. J. Stensland and V. C. Bowersox

The question of the calculation and presentation of pH data is one of importance to the determination of acidic precipitation trends owing to the fact that different numbers can be obtained even from the same data set. Examples are shown for the calculation of various climatological values of pH. These range from the
precipitation-weighted average pH calculated from the weighted average conservative ion concentrations. Since all of these methods have appeared in one or more publications dealing with the spatial distribution and the trend of precipitation acidity across the U.S., it is important to consider which of these methods is most appropriate for an assessment of the acid rain issue. In summary, this study shows there is no "correct" answer to provide the best value of pH. However, a clearly stated purpose for which the average or central tendency value is needed will help to determine which method will give the most representative value.

C. Regional Characterization of Rain Acidity Utilizing Gran's Plot Titrations, M. E. Peden and J. M. Lockard

In addition to the major anions (sulfate and nitrate) contributing to the acidity of precipitation, it is now recognized that organic acids also contribute to the total acidity. Some preliminary work is reported on the regional characterization of rain acidity through the use of Gran's plot titrations. It was found that the ratio of strong to weak acids decreases from east to west as a result of both decreased strong acidities and increased ammonium concentrations. Due to sampling problems, no evidence of a significant contribution of organic acids was found in samples from any of the sites used in the study. Considerable additional work is needed in this area.

D. The Chemistry and Meteorology of Extreme pH Departures in Precipitation on the Regional Scale, K. G. Doty and R. G. Semonin

To explore this possibility that airborne surficial material may have biased the precipitation chemistry of the mid-1950's statistical methods were employed on NADP network data sets selected from recent years. A case was selected from 1981 with relatively high pH values over the Northeast, and an additional case was chosen with relatively low pH values in the same area. Using these data, a meteorological explanation was then sought related to suspended airborne material. Trajectory analyses in one case in the spring of 1981 provided evidence for the potential transport of crustal dust aerosol from the southern Great Plains and incorporated in precipitation at sites in the Midwest. The more acid case of July 1981 revealed high concentrations of most ions in comparison with adjacent weeks. These high concentrations appeared to be related to the smaller average sample volume across the Midwest and Northeast and the relatively long dry period that was observed.
prior to the main rainfall event. Additional case studies will be pursued to assist in understanding the natural variability of precipitation acidity.

E. Dry Bucket Analysis of the NADP Network, R. G. Semonin

The MAP3S and NADP networks both use a sampler with a collector for wet-only samples and a collector exposed to dry deposition during non-precipitating periods. The analysis of the dry bucket samples collected from the NADP are presented. Lack of agreement over a dry deposition measurement method has resulted in a lack of data for a full assessment of the impact of acidic deposition. The dry bucket data may be questioned by the "purist." This is a first attempt to describe the regional dry deposition using readily available data. While more work is needed, these results show between station consistency within large areas of the eastern half of the United States. The absolute magnitude of the dry deposition values may be questioned, but the data do give a first glimpse of the areal distribution that is expected with implementation of more sophisticated equipment in the future.

F. Metal Solubility in Atmospheric Deposition, D. F. Gatz and L. C. Chu

The assessment of the effects of acidic deposition can not be independently achieved without due consideration given to other coincident and potentially important precipitation chemistry. A set of atmospheric deposition samples in wet, dry, and bulk precipitation were analyzed for metal solubility. The samples were analyzed for zinc, aluminum, copper, iron, cadmium, and lead. The percent soluble metals show zinc is about equal to cadmium and both are greater than copper, which is greater than lead. In general, the wet-only samples showed more solubility than bulk and dry which were nearly equal. These results have important implications for precipitation sampling for metal analysis as well as for the understanding metal chemistry in precipitation, airborne metal scavenging processes, metals as tracers for sources of acidity, and the effects of acidic precipitation on ecosystems.

G. Source Apportionment of Rain Water Impurities in Central Illinois, D. F. Gatz

The identity and relative contributions of various sources of impurities in precipitation are needed to understand the acidic precipitation phenomenon. Factor analysis was used to identify, and chemical element balance calculations were performed to apportion,
possible sources of impurities in event precipitation samples from central Illinois collected over a two year period. Although factor analyses could group elements or ions that occurred together for chemical, meteorological, or microphysical reasons, as well as that of having a common source, the following likely sources were identified: crustal dust, sea and/or road salt, and possibly strong acids. In addition, a gaseous precursor factor was identified. The smallest contribution appears to be sea and/or road salt with the greatest contribution in the acids and the gaseous precursors. The contribution of crustal dust is sizable and certainly warrants further investigation. Extensions of this work should include plotting the factor scores against the date of the sample collection as a means to relate the source term to meteorological conditions.

H. A Few Preliminary Precipitation Chemistry Statistics, R. G. Semonin

The NADP network data were used to examine the correlation coefficients between the various ions that are commonly analyzed. The relationships between these various ions are described and maps are presented indicating areas of relatively high correlations between specific ions. These maps indicate that the Northeast United States experiences very high correlations between the acid-forming ions, and high correlations of acid neutralizing materials over the interior continent. The coastal regions show correlations which are equal or greater than either the acid or base ions between sea salt components.

I. Results of the World Meteorological Organization (WMO) Interlaboratory Comparison of Reference Precipitation Samples, M. E. Peden

The research results presented in this report are given with full confidence in the quality of the analytical values that form the basis for interpretation and subsequent conclusions concerning acidic deposition. To sustain high quality analytical methodology, the laboratory continues to participate in various interlaboratory comparisons for low concentration water samples. The most recent World Meteorological Organization comparison results are presented in chapter 10. Throughout the past four years, the laboratory results have consistently yielded mean percent deviations of 3 to 5% from the test sample input. These activities will be continued to insure the highest level of accuracy for reported numbers from precipitation samples to insure the user that the data are meaningful and can be
interpreted and reported with confidence.

J. Microcomputer Based Data Acquisition and Reduction System for Ion Chromatography, S. R. Bachman and R. K. Stahlhut

The dependability of analyses is only one essential part of the laboratory performance. The other part is the rapidity with which samples can be analyzed and made available to the research community. A microcomputer based data acquisition and reduction system for ion chromatography is described. A microcomputer is connected on-line to an ion chromatograph forming an analytical system of proven accuracy and efficiency for data acquisition and reduction of precipitation sample ion determinations. The most important aspect of this automation is that the analyst time devoted to data reduction tasks has been reduced by an estimated 25%. Another way of viewing this automation is that the through-put in the laboratory has been increased by a comparable percent.


Acidic precipitation samples are generally thought to be composed of a mixture of the strong acids sulfuric and nitric. The potential contribution of other components, such as weak acids that are only partially disassociated, can not be overlooked. Some preliminary work on the determination of organic acids to the chemistry of rainfall can be quite varied. The weak to strong acid ratio for Illinois precipitation is similar to that of sites in the northeastern United States. Based on the data accumulated thus far for central Illinois, the findings are in agreement with those reported for the Northeast U.S. that strong acids control the pH of rainfall, but weak acids are important to the total chemistry of precipitation. Since this preliminary data base is limited to samples collected during the spring months, however, additional work needs to be carried out to examine seasonal differences in weak acid concentrations, and weak to strong acid relationships.

L. Feasibility Study to Assess the Impact of Precipitation Quality on Soil Water Quality, V. C. Bowersox

The acidity of precipitation over the eastern half of the cash grain belt across Iowa, Illinois, Indiana, Ohio, and north and south of those states is of the same value as the much publicized Adirondack lake area of New York state. One of the early concerns in assessment of the
acidic deposition problem was the short or long-term damage to soil productivity. Because of this concern and the fact that Illinois represents much of the corn belt (from a climatological point of view), a small effort was devoted, to estimating the effects of precipitation quality on soil water quality. The results from this preliminary and limited effort are discussed. With the data available using lysimeters to sample soil water, a few results indicate that the precipitation pH is clearly less than the soil water pH for the soils of central Illinois and that neutralization of the precipitation occurs in the top most layer of the soil for even the most acidic rainfalls observed (pH of 3.82). These data also indicate that a weak relationship exists between soil water pH and free hydrogen ion deposition with the soil water pH slightly depressed with increased hydrogen ion input. However, much additional research effort is needed to clarify this relationship and to further estimate the impact of acidic deposition on the soils of the Midwest.

M. Precipitation, Chemical Depositions and Water Resource Issues, R. G. Semonin

Drawing upon the extensive literature on the various presumed effects of acidic deposition on water resources, some of the knowns and unknowns concerning this aspect of a total assessment are described. The material presented was collected together for presentation before an international conference, but the material bears repeating in this Progress Report as it addresses a topic of some national interest. The final conclusion of this is that little is known concerning the effects of acidic deposition on the chemical quality of surface and ground water supplies.

N. A Review of Particle Tracers of Atmospheric Process, D. F. Gatz

A review of particle tracers of atmospheric processes is presented in Chapter 15. This paper was presented at the Department of Energy Workshop on Atmospheric Tracers held in the spring of 1984, but is relevant to the entire subject of acidic deposition assessment since it reviews one of the possible research techniques available to investigators.

O. Tracer Applications for the Study of Precipitation Processes, R. G. Semonin

Application of tracers to the study of precipitation processes with specific application to the acidic
deposition question is discussed. The precipitation process is described as beginning with the availability of water vapor and condensation nuclei, and then moves through the requirement for motions in the atmosphere to produce clouds and precipitation. There is a clear need for tracers in the study of all of these atmospheric attributes leading to precipitation production. However, the presently available suite of gaseous and particle tracers each have inadequacies which inhibit their direct application to resolving acidic precipitation research problems. There is a need for the development of a new tracer which can be freely used in the atmosphere and will have a direct bearing on the conversion and scavenging of acidic deposition precursors.


A. Wet Deposition Chemistry, R. G. Semonin

Interest in precipitation chemistry dates back to the 18th century, but only since 1977 has the U.S. established a national network for monitoring at a level sufficient to describe the chemical climate. The siting criteria, quality assurance, and standardized equipment and analytical methodology are addressed to insure the highest quality data for interpretative research. The national distribution of concentration and deposition for calcium, ammonium, chloride, nitrate, sulfate, and pH are shown in a series of maps. The maps show high concentrations of calcium and ammonium in the Great Plains, high concentrations of nitrate, sulfate, and hydrogen ion in the eastern states, and high concentrations of chloride along the coastal states. The primary conclusions are 1) the greatest deposition is directly associated with the largest emission regions, and 2) dry deposits are largely unknown but clearly must be measured before the biochemical and geochemical cycles will be fully understood.

B. Intra-Annual Variations in the Concentrations of Major Inorganic Ions in the Precipitation of the United States, V. C. Bowersox and G. J. Stensland

This study examines the intra-annual variations of inorganic ion concentrations in precipitation across the U.S. These variations were summarized on contour maps showing the spatial distribution of ratios of warm period to cold period weighted average and median ion concentrations. The data suggests that precipitation
concentrations followed a rather well defined pattern of intra-annual variations with summer and winter extremes. For sodium and chloride, the Northern Plains and nearly all of the East had warm/cold period ratios <1.0. Some east coast sites even had ratios <0.5, probably owing to high wintertime airborne sea-salt concentrations. For ions other than sodium and chloride there were generally higher average warm (growing) season than cold (dormant) season concentrations over much of the country.

C. Estimation of Bias in the Average Wet Deposition of Calcium, Sulfate, and Sodium from National Atmospheric Deposition Program/National Trends Network (NADP/NTN) Data, G. J. Stensland

Estimates were made of the percent bias in the wet deposition loading of Ca, SO$_4^{2-}$, and Na from the NADP/NTN data set. These estimates were based on the data of record from mid-1978 through 1986 and are thus applicable to long-term averages. The calculations of an overall bias were based on data for the contamination from field handling of dry buckets, laboratory handling and analysis, and the buckets themselves. Sources of possible contamination that were not addressed included (a) field handling to remove a liquid aliquot of sample for field chemistry measurements and (b) chemical degradation of the liquid sample from time of collection to time of analysis. No attempt was made to address the bias due to samples undercatch or overcatch of precipitation. Infiltration of the lid to bucket seal by aerosol Ca, SO$_4^{2-}$, and Na occurred over large spatially contiguous areas, and contamination from the lid (gasket) was typically the largest single source of bias.

D. Spatial Relationships Between Acid Rain, Air Quality, and Visibility Data, G. J. Stensland

Visibility and acid rain are two different phenomena which both have direct relationships to air quality. The objective of this paper is to explore the relationships between all three data sets, with emphasis on the situations for the eastern U.S. This paper presents interpretation of the most current precipitation chemistry data from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN), which started in the eastern U.S. in 1978 with less than 20 sites and continues today with over 200 sites spread across the entire U.S. The high site density and relatively long data record make the precipitation sulfate data particularly important. Correspondence is found between precipitation sulfate and air quality sulfate for areas
to the east. In coastal areas the spatial pattern for visibility is not consistent with the precipitation sulfate pattern, presumably due to the effect of relative humidity.

E. Variations in Precipitation Composition and Deposition with Synoptic Weather Type, K. G. Doty and D. F. Gatz

As one portion of a broader analysis of five years of event precipitation chemistry data for central Illinois, we examined variations in ion composition and deposition with synoptic weather type. Variations of H, NO$_3^-$, and SO$_4^{2-}$ deposition and concentration with synoptic weather type were very consistent in all four seasons. Deposition frequencies were strongly a function of the sample volume distributions, which was in turn largely determined by the frequency of the various synoptic types, while concentrations were relatively constant over all synoptic types. The highest concentrations occurred in spring and summer, the lowest in fall and winter. The results suggest that historical depositions of certain ions in precipitation might be estimated from precipitation records, combined with appropriate annual mean concentrations of the major ions. The appropriate concentrations might be inferred from airborne concentration measurements, if available, or relevant emissions data.

F. Back Trajectory Climatologies for Sulfate and Nitrate Wet Deposition Fluxes at a Central Illinois Site, K. G. Doty and V. C. Bowersox

Precipitation samples have been routinely collected with automated wet-only collectors since September 1979 at a field site in rural east-central Illinois. Event record data were combined with the chemical concentration measurements of samples from the collectors to compute wet-only fluxes of sulfate and nitrate. Back trajectory calculations for these flux classes utilizing the ISWS trajectory model are presented. The analysis involves approximately 250 precipitation chemistry samples, and the calculation of about 1100 back trajectories each 72 hours in length.

G. Interlaboratory Comparisons of Reference Precipitation Samples, M. E. Peden and J. M. Lockard

The analytical chemistry laboratory has continued its participation in the interlaboratory comparisons of precipitation chemical analyses sponsored by the World Meteorological Organization (WMO). In the past three
years our involvement in international precipitation chemistry intercomparisons has expanded to include participation in studies conducted by the Canadian Long Range Transport of Atmospheric Pollutants (LRTAP) Program and the European Monitoring and Evaluation Program (EMEP) carried out by the Norwegian Institute for Air Research. These programs provide valuable data on the comparability of chemical determinations made at geographically disperse laboratories as well as documentation of the analytical procedures that are being utilized for precipitation chemistry measurements. This data base is an important source of information when comparing chemical results from different monitoring programs. Summaries of these programs and results from our laboratory are presented.

H. Quality Assurance of Precipitation Chemistry Analyses Using Ion Balance Calculations, J. M. Lockard

The National Atmospheric Deposition Program (NADP) was initiated in 1978 to assess spatial and temporal trends in precipitation chemistry within the United States. From the beginning of the program, the Illinois State Water Survey (ISWS) has been responsible for the chemical analyses of precipitation and dry deposition samples generated from the monitoring network. A rigorous internal quality assurance program has been developed to ensure that the laboratory measurements are of the highest quality. As a part of this program, each sample analysis is verified by the use of an ion balance calculation. The ion balance data have been used in part to develop objective criteria for the reanalysis of samples on a routine basis. A closer examination of these data has revealed patterns in the ion ratios that are a function of sample pH, site location, and collection season. These patterns are discussed in terms of how to most effectively utilize ion balance data to verify the accuracy of laboratory measurements.

I. A Comparison of Ion Chromatography and Automated Colorimetry for the Determination of Major Anions in Precipitation, S. R. Bachman

The two analytical methods of automated colorimetry and ion chromatography have been compared with respect to comparability of analytical results and physical features. Detection limits are somewhat improved with the ion chromatograph, although a bias for one method over the other was not detected with regard to sample concentrations. A wide range of analyte values was examined and correlations between the two methods are excellent.
J. Long-Term Ionic Stability of Precipitation Samples, M. E. Peden and L. M. Skowron

The long-term stability of precipitation samples has been investigated by measurement of samples stored in a refrigerator for six years. Of the eight constituents measured, Ca, Mg, Cl, SO$_4$ and NO$_3$ revealed reanalysis results within 10% of their original values. Evaporative losses during storage were not evident. Hydrogen ion concentrations increased by nearly 40%, on average, with a concomitant increase in solution conductivity. Ammonium results did not reveal a significant change in mean concentration, although the data were highly variable compared to the other analyte differences that were measured. No distinct patterns of long-term stability related to geographic regions or collection seasons were evident in the study.

K. Synthetic Rainwater Reference Samples, L. M. Skowron and M. E. Peden

The objective of this study was to develop internally formulated reference materials that could be used in conjunction with NBS Standard Reference Materials, which cannot be used on a routine basis to monitor laboratory performance because of their high cost. Results presented indicate that a concentrated stock solution containing all of the major constituents in wet deposition can be easily prepared using commonly available salts and mineral acids. Dilutions of this single stock solution to the concentration levels characteristic of wet deposition have resulted in stable formulations that can be used for routine quality control checks, as well as for internal blind audit samples. Five months of data indicate that sample integrity is maintained without the addition of any chemical preservatives or refrigerated storage. Ongoing studies are focusing on the long term stability of the stock concentrate as well as the dilutions to develop statistical guidelines for using data obtained from these solution analyses to ensure traceability to the NBS Standard Reference Material.

L. Preliminary Data for Daily Ambient Aerosol Measurements at the Bondville Research Site, G. J. Stensland

Results from the chemical analysis of daily aerosol filter samples are presented. It is found that:

- The teflon filters are significantly more efficient in collecting SO$_4$ and K particulate matter than are 0.8 µm polycarbonate filters.
• The Na blank levels are unacceptably large for the aerosol data.

• \( \text{SO}_4 \), Ca, and Mg are maximum in summer and minimum in winter; K is maximum in fall and minimum in winter and spring; and Na is maximum in winter.

M. Ratios of Ion Concentrations in Precipitation to Aerosols at the Bondville Site, G. J. Stensland and V. C. Bowersox

Gases and aerosols are incorporated into precipitation by scavenging processes which occur within and below clouds. In this chapter we present aerosol and precipitation chemistry data for \( \text{SO}_4 \), Ca, Mg, K, and Na. These data are summarized by season from measurements made at the Bondville Field Site, operated under this contract. Of the five species, only \( \text{SO}_4 \) has both particle and gaseous species to consider.

• From this preliminary report we conclude that scavenging ratios for Na and K may be affected by problems related to sampling, handling, and extraction methods, which make the values unrepresentative. Values cannot be directly compared to those for \( \text{SO}_4 \), Ca, and Mg.

• Further sensitivity and statistical analyses are required to see if differences in the scavenging ratios for \( \text{SO}_4 \) and Ca or for \( \text{SO}_4 \) and Mg can be used to predict the gaseous versus particulate contributions to the total \( \text{SO}_4 \) in precipitation. The present results indicate that particulate removal is more important than gaseous removal for sulfur, especially in the summer.

N. A Computer Program for Calculating State Averages from Point Values, J. Su and G. J. Stensland

We have developed a computer program to calculate a single representative statistic for each state, given a variable that is measured at a limited number of sites across the United States. Our program is called AREA for ARea Estimating Algorithm. The AREA program is a useful program that will calculate area-weighted statistics on a state-by-state basis for variables that change with geographical locations. The current implementation of AREA can be easily altered to suite the user's needs, being, for example, general enough that with only a few minor changes it can be incorporated as a subroutine of another program.
O. The Description and Comparison of a Prototype Trajectory Model with the ARL-ATAD Model, K. G. Doty

Concerns surrounding air and precipitation quality have led to frequent use of trajectory models in the past decade. An example of a relatively simple diagnostic model is the Air Resources Laboratories Atmospheric Transport and Dispersion Model (ATAD). The ATAD model was designed to calculate large numbers of boundary layer trajectories from several origins in an economical manner. The results of trajectory analyses for five years of event precipitation chemistry data for a site in Central Illinois are shown. The analyses led to the development of a new trajectory model (ISWS) which is described and compared to ATAD.

P. Screening Criteria for NADP Dry Bucket Data, D. F. Gatz, V. C. Bowersox, and J. Su

It is quite clear from the results presented that "dry" fluxes of H ion are substantially decreased if samples containing water are eliminated from the data set, and some evidence that the same may be true for nitrate. Similarly, the dry fluxes of K, NH₄, and PO₄, while relatively insensitive to elimination of samples containing water, are much reduced when samples having one or more types of visual contamination are eliminated. The dry flux of Ca actually increased as the screening level increased. The dry fluxes of the remaining ions examined--Na, Mg, Cl, and SO₄--showed no significant differences between screening levels. The present analyses suggest that additional future work on the current data set should include quantification of the individual effects of each potential difficulty (e.g., water in the sample, or visual contamination), and particularly, each different form of contamination. In addition, the samples might be grouped regionally (at least east vs west) to see whether there are regional differences in the way that potential contaminants affect the measurement of dry fluxes using buckets.

Q. An Annotated Description of the Atmospheric Chemistry Sampling Station at Bondville, Illinois, S. R. Dossett

The maps, figures and text included describe the area surrounding the Bondville Field station, detail the history of the research activities, and briefly describe the research currently supported at the site. DOE contract funds make up a considerable portion of the
budget upon which the Bondville site depends. Data collected at the Bondville site offer a mix of precipitation and air chemistry information with meteorological measurements. As such, the site offers a good opportunity for the research community to study in detail the interrelated nature of the climatology, wet deposition, dry deposition, and aerosol components of the atmosphere.


A. A Description of the Sequential Chemistry of Rain Experiment-1988, A Component of 3CP0, V. C. Bowersox

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$_2$O$_2$ 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.

The objectives of SECORE-88 were:

1. to measure the wet fall 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.
B. Procedures for the Analysis of Aqueous Hydrogen Peroxide in Rain Samples Collected During SECORE-88, S. R. Bachman and M. E. Peden

One of the measurement objectives of SECORE-88 was to obtain data on the $\text{H}_2\text{O}_2$ 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.

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 $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$ are included in Kelly et al., (1985) and Lazrus et al., (1985).

C. Preliminary Data for SECORE-88 Case 1: June 8, 1988, V. C. Bowersox and M. 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 1988. 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 10 minutes to 3 hours 20 minutes. Averaged over the entire event, the rainfall rates were about 0.09 - 0.11 inches/hour. During the first 5 minutes of the event, the rainfall rate was 0.16 - 0.20/hour, and for the duration of the event, the rates remained uniform and steady at 0.08 - 0.10 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 reach 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 SO₂ from Champaign may have accounted for the drop in H₂O₂. There is no apparent rise in SO₄²⁻ concentrations to support this hypothesis, however (see Figure 2).

D. Research Summary Report to the National Acid Precipitation Assessment Program -- Task Group III Activities, V. C. Bowersox and R. G. Semonin

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.

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 four inorganic anions and cations (SO₄²⁻, NO₃⁻, NH₄⁺, Ca²⁺) in equilibrium with H⁺ and HCO₃⁻.

2. A second 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 ares.

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.

E. A Modified Successive Corrections Method that Meets Statistical Goals, J. Su and G. 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, polynominal fitting, variational method, smoothing isopleth lines, 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 three 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 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 Kriging and the successive corrections methods.

F. Dry Deposition Flux Estimates for Large-Particle Elements, from Dry-Bucket Measurements, D. F. Gatz, V. C. Bowersox and J. Su

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.

G. Spatial Relationships Between Acid Rain, Air Quality, and Visibility Data, G. 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.

H. Synthetic Precipitation Reference Samples, M. 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 (SR) for precipitation chemistry studies, the NBS solutions (SR 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.

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.

VII. Review of Twenty-Third Progress Report, (Grant Number DE-FG02-88ER60635) Report Number C00-1199-67, SWS Contract Report 468, August 1989

A. The Removal of Atmospheric SO₂ by Dry Deposited Road Dust, A. L. Williams

B. Sensitivity Analyses of Area Weighted Average Algorithm, J. Su and G. J. Stensland
The computer program was developed on the VAX 11/750 using standard Fortran 77. An UNIX version and an IBM PC version of the program are also available. In this chapter we will discuss the algorithm as applied to calculating deposition to states. We digitized simplified state boundaries for all 48 contiguous states of the USA using the boundaries found in the graphics package distributed by the National Center for Atmospheric Research (NCAR, 1981). This step was necessary to minimize the computational time required by the algorithm so that it could be run on a PC. In this simplified scheme, each state is defined by an average of 30 points. A very small deviation in state area, less than one percent, was introduced by using the simplified boundaries.

The program itself consists of two parts. The first part reads in the data record for each site and calculate descriptive statistics for the variable of interest. This statistic along with the spatial coordinates of the data collection site are then piped into a spatial analysis routine. The spatial analysis subprogram interpolates the values of the environmental variable at the sites to the corners of each grid square. Any spatial analysis algorithm will suffice; some examples include Laplacian smoothing splines, potimum interpolation, and Kriging. We implemented an objective analysis scheme developed by Barnes (Barnes, 1964) and modified by Achtemeier (Achtemeier, et al., 1977). The second part of the algorithm reads in the digitized state boundaries and integrate the spatial field over each state to solve for the state area weighted average. The algorithm was described in detail in the last progress report.

C. A First Look at Data to Examine the Stability of Major Inorganic Ions in Rain Samples in Central Illinois, V. C. Bowersox and M. E. Peden

At the recent meeting of Multistate Atmospheric Power Production Pollution Study (MAP3S) scientists in Bethesda, MD, in April of this year, workshop sessions were held to highlight major accomplishments of MAP3S research over the last 10+ years, as well as important research needs of the future. Under research needs, one topic that received extensive discussion was the question of sample stability. Are event or daily samples chemically stable? Are the changes in concentrations of the major inorganic ions small over the daily (or event) sampling period used at MAP3S sites? Are chemical changes effectively arrested by refrigeration? Apart from the addition of TCM (a preservative for dissolved SO$_2$) to a sample aliquot used only for SIV) analyses, the only routine sample preservation procedure employed in the MAP3S network is refrigeration. What happens to the chemistry of a sample left in the sampler at ambient temperatures in the summer? The consensus of the group of researchers was that we do not know enough about the short term changes in the chemistry of samples held for 24-48 hours with no added preservative.
A study was designed to examine the stability of the chemistry of samples from a summer rain event. Major inorganic cations and anions were the focus of this study, since these all are reported by the networks presently in operation in North America. In a previous study, Peden and Skowron (1978) had found that bulk deposition samples exhibited large changes in Ca and Mg when left unfiltered at about 25°C. The present study, however, focused on wet-only deposition samples, which contain much less dry deposited soil than bulk samples, because exposure is limited to the occurrence of precipitation.

D. Lead and Cadmium Loadings to the Great Lakes from Precipitation, D. F. Gatz, V. C. Bowersox and J. Su

We present the first analysis of precipitation chemistry data from the Great Lakes Atmospheric Deposition (GLAD) network of wet-only precipitation samplers. Lake loadings were calculated from 1- or 2-yr (1982-1983) volume-weighted mean ion concentrations and 30-yr mean annual precipitation amounts, using an objective analysis method to interpolate measurements to a 40 x 40 km square grid over the Great Lakes region. The results show that atmospheric loadings of Cd, Pb, and other cations to the Great Lakes are in many cases considerably smaller than those estimated from the bulk precipitation measurements of the early 1970s. For Pb, some portion of the differences can be accounted for by the decrease in emissions that resulted from reductions in the Pb content of gasoline. Valid dry deposition in the bulk samplers also accounts for a portion of the differences. However, for the most extreme differences, contamination of the bulk collectors by resuspended local surface dust is likely to be a major cause. Good agreement was noted between the precipitation-only loadings derived from the GLAD data and those recently given by Strachan and Eisenreich (1987).

VIII. Bibliography of Papers, Reports, and Interviews associated with the Study of Atmospheric Pollution Scavenging research over the ten year period 1980-1989


Stensland, G.J. and A.L. Williams, 1989: Dry deposited road dust as a major sink of atmospheric sulfur dioxide. **EOS.**


Bowersox, V.C, 1989: "What we have learned about the differences in daily or event samples and weekly NADP/NTN samples," presented at NADP Technical Committee Meeting, Provincetown, MA, 25 October.


Bowersox, V.C., 1988: "Research at the Illinois MAP3S site," presented at MAP3S Review Meeting, Gaithersburg, MD, 26 January.

Bowersox, V.C., 1989: "Acid Rain, an Update of Recent Research Findings," radio interview, WILL, Champaign, IL, 12 January.


Bowersox, V.C., 1988: "SECORE-88 Field Project to Study Acid Rain," TV interview, WCIA, Champaign, IL, 7 July.

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