Illinois State Water Survey Division

ATMOSPHERIC CHEMISTRY SECTION
AND
ANALYTICAL CHEMISTRY UNIT

SWS Contract Report 476

CENTRAL ANALYTICAL LABORATORY FOR NADP/NTN:

SECOND PROGRESS REPORT

by

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Champaign, Illinois

November 1989

Illinois Department of Energy and Natural Resources

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November 1989

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by

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INTRODUCTION

Historical Background

That rains were not pure, but were a mixture of dissolved and undissolved impurities in water, intrigued scientists as early as the 18th century. First came the search to identify these impurities. Miller (1905) traced a report of "nitric acid, chlorine, and lime in rain water collected during the winter of 1749-50" to Marggraf. Detection of dissolved ammonia, organic matter, sulfur compounds and sea spray followed these first discoveries in the early and middle 1800's at several European laboratories (see Gorham, 1981). With the recognition of its nutrient value to plant growth, particular interest was directed in these early studies to the nitrogen content of precipitation. Systematic studies, such as the Rothamsted experiments to assess the long-term deposit of nitrates, ammonia, and other substances to the soils and agricultural crops of southern England, began as early as 1853 (Brimblecombe and Pitman, 1980). These studies continued regularly into the 20th century in Europe and in North America. Data collected today at stations in the United States and elsewhere are used to determine the flux of nutrients to agricultural, forested, and aquatic ecosystems.

Parallel to the interest in the nutrient value of chemicals deposited by precipitation, there emerged the concern that certain of these chemicals may also have noxious impacts. One phenomenon noted early on was "acid rain." In an extraordinary account of studies in and around the industrial city of Manchester, England, in the 1840's to the 1870's, Smith (1872) used his measurements of rain chemistry to describe acid rain as coming from air laden with sulfuric acid and acid sulfate. Thus local air pollution was recognized as a source of acidifying gases and particles over 100 years ago (see Cowling, 1982). Nineteenth and early twentieth century studies of precipitation chemistry focused largely on local effects, measurements made at a single location or around a town or over distances of only tens of kilometers from pollutant sources. These data were too limited to know of the geographic extent of acidic precipitation.

It was in Sweden in the late 1940's that a network of samplers was installed to study the chemistry of precipitation over an entire nation (Emmanuelsson, et al, 1954). In ten years this network spread over Scandinavia and much of industrial western Europe and the British Isles. It came to be known as the European Atmospheric Chemistry Network, which with its successors has the distinction of having the longest continuous record of regional-scale chemistry to be found in the literature. Data from this early network were used to define "acid rain" as rain with a pH below 5.6, the equilibrium pH of water in equilibrium with CO_2 at its average atmospheric concentration (Barrett and Brodin, 1955). Well-defined regions that persistently receive acidic precipitation were found even in rural areas (Gorham, 1955) far from local anthropogenic sources (Barrett and Brodin, 1955). Rossby and Egner (1955) suggested that acidic deposition was spread over whole regions in and downwind of the Eurasian continent by the transport and mixing of pollutants during air-mass circulation. The attention of the scientific community was heightened when, working with the European data set, Oden reported a trend from 1956-1966 toward lower mean pH values in central and western Europe and in Scandinavia (Reiquam, 1970). There was considerable speculation that the increased acidity resulted from (1) greater use of high sulfur fuels, and (2) construction of tall smoke stacks that release their exhaust at heights where wind could disperse the sulfur emissions over large downwind areas. Finally, by examining the stoichiometric relationships between hydrogen ion and the other ions in European precipitation, Granat (1972) found that though sulfate was the dominant anion, nitrate, too, was an important contributor to the acidification of precipitation.

In North America regional-scale studies of precipitation chemistry were first conducted in the 1950's. A 67-station network was operated at Weather Bureau facilities across the United States for a 1-year period in 1955-56 (Junge and Gustafson, 1956). Junge and Werby (1958) published maps of the major anions and cations in precipitation collected in this network, except for hydrogen ion concentrations, which were not measured. Under the auspices of the U.S. Public Health Service, another network was operated across the U.S. in the 1960's (Lodge et al., 1968). Also in the mid-1960's research on precipitation chemistry had begun at the Hubbard Brook Experimental Forest in New Hampshire. Measurements at Hubbard Brook established that hydrogen ion was the predominant cation in precipitation there and that acidic precipitation (pH below 5.6) occurred regularly in that watershed, remote from major industrial and utility sources (Fisher et al., 1968). As in Europe, the attention of the scientific community in the United States was piqued when Likens et al., (1972) identified "acid rain" as a serious regional environmental problem, primarily in the northeastern United States. With no long-term continuous record of hydrogen ion measurements over a whole region, it was necessary to compare data from the Junge network, 1955-1956, to the Public Health Service (PHS) network 1965-1966. The pH values for the Junge network were calculated from the measurements of major cations and anions reported, while these were compared to the pH measurements from the PHS network. In doing this, Cogbill and Likens (1974) concluded that over a 10-year period acidic precipitation had worsened (pH lower) and had spread southward and westward from New York and New England to much of the eastern U.S. Some 65% of the free acidity was attributed to sulfuric acid, 30% to nitric acid, and the remainder to hydrochloric acid. As in Europe, it was posited that changes in fuel use, taller smokestacks, and reduced emissions of the (alkaline) particles in smoke had resulted in the spread of "acid rain" and in its worsening.

To assess the cause for the drop in pH over a 10-15 year period, Stensland and Semonin (1982) looked for changes in major cation and anion concentrations to discover that the decreases in pH were nearly balanced stoichiometrically by large decreases in the alkaline cations, calcium and magnesium, apart from sulfate and nitrate changes. Indeed, at some locations hydrogen had increased while sulfate and nitrate had decreased. Extensive droughts and dust storms, resulting in anomalously high calcium concentrations in the mid-1950's, along with improvements that reduced the potential dust contamination of collected samples, were the hypothesized causes for the decrease in neutralizing constituents. Much subsequent research in North America and in Europe has focused on trends in cations and anions in precipitation, on sources of acidic and alkaline constituents (both natural and anthropogenic), and on atmospheric transport and transformation processes. For more details on the historical background of precipitation chemistry measurements, see Smith (1872), Miller (1905), Brimblecombe and Pitman (1980), Bowersox (1980), Gorham-(1981), Cowling (1982), Bowersox (1985), and Schwartz (1989).

National Atmospheric Deposition Program/National Trends Network (NADP/NTN)

Alerted to the possibility that "acid rain" had grown markedly worse over one to two decades and that there might be profound impacts on natural and managed systems, the scientific community sensed urgent needs to measure the chemistry of atmospheric deposition over broad regions of the country and to assess the effects of deposition on soils, crops, forests, aquatic systems, and building materials. To address these needs, the State Agricultural Experiment Stations (SAES) organized a Regional Project on Atmospheric Deposition (NC-141) in 1977, which became Interregional Project 7 (IR-7) in 1982, called the National Atmospheric Deposition Program (NADP). Through the SAES and federal, state, and private research organizations, NADP coordinated efforts:

> (1)   to measure and characterize the supply of beneficial and injurious chemical substances in atmospheric deposition,

> (2)   to determine spatial patterns and temporal trends in atmospheric chemical deposition, and

> (3)   to determine the effects of atmospheric deposition on forest and agricultural productivity, on soils, on the survival and productivity of animals, on the chemistry of surface and ground waters, and on the corrosion of materials (see NADP, 1987).

Measurements of wet deposition chemistry began at 21 locations in 1978 in the NADP. Figure 1 shows the number of active, inactive, and intercomparison sites at the end of each calendar year through 1988. From 1978 to 1982 the NADP sampling network grew to over 100 stations, with the greatest site density in the East, where acidic precipitation was worst. With the establishment of the National Acid Precipitation Assessment Program (NAPAP, under the aegis of the Acid Precipitation Act of 1980) precipitation sampling on a more representative basis by ecosystem area became an important part of network design (Robertson, 1985). To fulfill this objective, new sites were added in 1983 and later years, many in the West. These new sites, plus a substantial number of pre-existing NADP sites that satisfied NAPAP objectives, carried the label National Trends Network (NTN). The national network then came to be called the NADP/NTN. Most of the growth after 1983 was due to the addition of sites that met NAPAP requirements and the NADP/NTN sampling network doubled to about 200 sampling locations by 1988. Throughout its 11-year history, shown in Figure 1, are short periods of duplicate, or intercomparison sampling, which was done to quantify the precision of point estimates of wet deposition. Currently there are five intercomparison sites in the NADP/NTN. Continuation of the sampling network is expected at least through 1992.

METHODS

NADP/NTN Precipitation Chemistry Network Operations

Site selection, site and laboratory operations, and data validation were all done according to documented procedures that were developed for the NADP/NTN precipitation chemistry network. Using Bailey's Ecoregions of the U.S. (Bailey and Cushwa, 1982), NTN sites were chosen so that the number of sites in an ecoregion province was proportional to the area of the province (Robertson, 1985). To this basic design concept, sites were added east of the Rockies where, based on available data, there were large gradients in pH, sulfate, nitrate, or ammonium ions. Sites were added, too, in areas especially sensitive to acidic deposition effects and where special studies were being conducted (see Robertson, 1985, for NTN design criteria). Collection sites in the NADP were often located where research in nutrient cycling, watershed chemistry, agricultural or forest effects, or in other areas, was already underway. An overriding concern was to choose a site so that the data were typical of the area where the site was located; thus criteria for site selection and installation were specified so that the impact of local point and area sources would be minimized (Bigelow, 1984). These criteria included regional, local, and on-site requirements for finding and installing a suitable NADP site. Documentation of the site locations was required and sites were visited about once every third year to update this documentation and to check for continued compliance with the siting criteria (Eaton and Tew, 1985).

In addition to siting and installation criteria, participation in the NADP/NTN required that equipment and operating procedures be standardized. All sites were required to use an automatic wet/dry collector and a recording precipitation gage of specific design and manufacture. These instruments were linked in the field so that the open and close operation of the collector would be recorded on the same chart as the timing and amount of precipitation, thus allowing for their direct comparison. There were specifications for other equipment used at field sites to measure sample mass, pH, and conductance, as well. An instruction manual for site operation (Bigelow and Dossett, 1988) lists the step-by-step procedures for collecting, handling, and measuring samples. Samples were collected weekly, on Tuesday, and the sample buckets were all sent to a single Central Analytical Laboratory (CAL) at the Illinois State Water Survey. At the CAL, sample volume, pH, conductance, sulfate, nitrate, chloride, phosphate, calcium magnesium, sodium, potassium, and ammonium, were measured according to standard procedures (Peden, et al., 1986). Samples were neither decanted nor refrigerated in the field, but were filtered upon arrival at the CAL to remove insoluble materials and to arrest chemical degradation. Along with analytical services, the CAL provided clean sample buckets and other supplies required for site operations.

Data for each NADP/NTN sample were reviewed by CAL data management staff to identify and flag those samples that were contaminated or did not otherwise satisfy NADP/NTN objectives. First, the chart from the precipitation gage, along with information recorded by the station operator on the Field

Observer Report Form (FORM), were reviewed to assure that the collector was only open during precipitation. Any failure of the equipment that left the wet deposition sample exposed to more than six hours of dry weather would cause the data to be flagged as not being a wet-only deposition sample. Next, any sample that was grossly mishandled and compromised in the field or at the CAL was flagged. Examples of samples that were flagged because standard procedures were grossly violated include use of an unwashed collection bucket in the field or an uncleaned filter at the lab. Finally, samples with visible extrinsic contaminants, e.g. a leaf or insects, and unrepresentative chemical concentrations were flagged as contaminated. The 90th percentile concentrations were used as references for assessing representativeness. When four or more ion concentrations were at or above the 90th percentile for that site and the sample contained an extrinsic contaminant, it was flagged. For details of the validation procedures used at the CAL for NADP/NTN sample data, see Bowersox (1984).

Data Selection

Spatial Analysis: Spatial patterns of pH, sulfate, nitrate, ammonium, and calcium ions in valid NADP/NTN samples are presented in this paper. Isopleth maps of average ion concentrations in the continental U.S. are used to display these patterns. Included, too, is a sulfate deposition map. These maps are intended to show differences on a synoptic scale, not point-to-point differences but regional differences; and so these isopleths should not be treated as inviolate contours that bound areas with only concentrations above the contour value from areas with only concentrations below. There are many local inhomogeneities, highs and lows, in the concentration and deposition fields. Indeed the design of the network was to avoid the effect of local sources or precipitation anomalies, such as urban areas, power plants, unpaved roadways, deep valleys, etc. Nevertheless, each site in the network is affected to some extent by subregional sources and precipitation patterns.

To obtain spatial patterns that were robust, the data at each site were averaged over several years. The year-to-year variations in precipitation amounts suggest why this was done. In Pennsylvania, for example, there were 47 weather observer stations that reported complete annual precipitation depths for each year from 1982 through 1987. At these stations the interannual variability ranged from 9% to 64%, with a median value of 33%. For half of these stations the annual precipitation total from one year to another varied by 1/3 or more. At Pennsylvania sites in the NADP/NTN network over this same time period, annual weighted average calcium concentrations varied by 6% to 125% (median = 42%), while sulfate variations were 13% to 42% (median = 26%). In another study, Summers et al. (1986) reported coefficients of variation of 10-16% for annual wet sulfate deposition over three years (1981-1983) in eastern North America Large interannual variations are characteristic of both precipitation amounts and ion concentrations; thus to obtain a more stable spatial pattern requires averaging out as much year-to-year variability as possible. The assumption in this approach is that any underlying trends over the averaging period are small relative to the interannual variations. For this spatial analysis of NADP/NTN data, a five-year period from October 1983 through September 1988 was chosen. Though NADP operations began in 1978, the number of sites was small (see Figure 1.) and the geographic distribution of sites highly non-uniform. By late 1983 the number of active sites was well over 100 and the number of sites west and east of the Mississippi River was about the same. By 1988 there were about 200 sampling stations active in the network. Choosing 1983 for the start and 1988 for the end of the summary period allowed calculation of a full five-year average at 100 or more sites.

Data from all operating stations were screened to assure that a minimum level of sampling completeness had been attained between 10/83 and 9/88. Only valid data were used in this screening. Any week when the recorded precipitation was < 0.25 mm (i.e. a trace in National Weather Service records) was considered valid by default, because measurable precipitation had not occurred; that is, it was a "dry week." All other weeks were considered "wet weeks," or weeks when it could not be verified that precipitation had not occurred. "Wet weeks" were invalid when measurements were missing or unavailable or incomplete. To be valid, data from "wet weeks" also had to be free of screening flags assigned by the CAL. In other words, the collected sample had to be a wet-only deposition sample that was not compromised in the field or at the CAL due to mishandling and that was not grossly contaminated by debris extrinsic to precipitation. For the valid-only data from each site, four measures

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of sampling completeness were evaluated. First, measurements of precipitation depth had to be reported from the recording gage, or in its absence the sample collection bucket, for at least 2/3 of the summary period. Likewise, analytical chemistry measurements had to be reported for at least 2/3 of the summary period. These two criteria assured that both precipitation amount data and precipitation chemistry data representing a minimum of 3-1/2 years were available. Next, there had to be analytical chemistry measurements for 3/4 or more of the measured precipitation. Finally, the pooled sample volume from all valid "wet weeks" had to be 75% or more of the volume expected from the gage measurements. In other words, the catch efficiency of the collector relative to the gage had to average 75% or higher. All four of these criteria had to be met for the data from a site to be included in the five-year summary. These criteria were used in a six-year (1979-1984) summary of NADP data by Knapp et al. (1988), though those authors adhered to more restrictive percentages. Other authors also have applied similar completeness criteria in an effort to minimize the potential for bias from unrepresentative data (NADP, 1985; Olsen, 1989).

Every NADP/NTN site that met the four sampling completeness criteria for the 10/83 through 9/88 summary period was used in this analysis, though the spatial displays covered only the continental U.S. A sample volume-weighted-average concentration (C_v) was calculated for the summary period at each site. Formula (1) was used for these calculations:

$$C_v = \frac{\sum_{i=1}^{m} V_i C_i}{\sum V_i} \tag{1}$$

where V_i was the volume in liquid milliliters of a valid sample from a "wet week" and C_i was the concentration of element C in that sample; i was incremented from 1 to m, the number of valid "wet weeks" in the summary period. For sulfate, the annual wet deposition flux at each site was calculated also. The product of C_v for sulfate and the average annual precipitation amount was formed to calculate the sulfate deposition flux. Since the average annual precipitation amount (P_A) was not reported explicitly in the NADP/NTN data set, this quantity was obtained from formula (2):

$$P_A = (365) \times \frac{\sum_{i=1}^{n} P_j}{\sum T_j} \tag{2}$$

where P. was the recording gage depth reported for each sampling period, or in its absence the sample collection bucket depth, and Tj was the number of days in the sampling period; j was incremented from 1 to n, the number of actual sampling periods in the summary period.

Finally, to construct isopleth maps of concentrations and deposition fluxes, the data at the NADP/NTN sites were analyzed objectively, then computer-generated contours were drawn. Objective analysis of the irregularly spaced site data produced a field of values on a regular grid. Interpolation to the grid points was done through an algorithm based on a successive corrections scheme developed by Barnes (1964) and modified by Achtemeier (1986). The key element in this algorithm is a negative exponential weighting factor. A pre-set number of sites nearest the grid point are used in evaluating this weighting factor. This factor weights the site data value according to the distance between the site and grid point locations, giving the greatest weight to the nearest site. Initial grid point values are calculated in a first pass through the data. This initial grid point field of interpolated values is then used to estimate values at the site locations. Differences between these estimates and the actual site values are used in a second pass to correct the initial grid point values. Su and Stensland (1988) have examined this algorithm to optimize its use for analyzing NADP/NTN data, where optimization meant to minimize jointly the interpolation error and the computer time necessary to reach a final solution. For NADP/NTN sulfate concentrations, they found a grid size of 100 km, using the five nearest sites, to be the best settings. These parameters were used in this analysis. Isopleth lines were drawn from these regular grid point data fields.

Trend Estimates: In this paper trend estimates recently made by Olsen (1989) were summarized for hydrogen, sulfate, nitrate, ammonium, and calcium ions. Because of their requirements for consistent and well-documented field and laboratory procedures and because they sampled over whole regions or countries, precipitation chemistry networks were used in this analysis. Data from three U.S. networks were selected, the Multi-State Atmospheric Power Production Pollution Study (MAP3S), the Utility Acid Precipitation Study Program (UAPSP), and NADP/NTN. At the time of the data analysis, the longest unbroken record of observations from these networks was 1979-1986. As for the spatial analyses, only valid data from these networks were used and to be included, data completeness criteria had to be met. Two of the five data completeness criteria agreed upon by the Unified Deposition Database Committee (Sweeney and Olsen, 1987) were applied: (1) precipitation gage (or in its absence sample depth) measurements covering 90% of the annual period were required and (2) valid analytical chemistry measurements for 60% of the measured annual precipitation were required. If these two criteria were met at a site in six of the eight years in the 1979-1986 period, the site was included in the trend estimate set. For sites in this set, a Kendall seasonal tau test developed by Hirsch et al. (1982) for the detection of trends in the presence of seasonal effects, was used. Seasons were defined as a month. Monthly precipitation-weighted-average concentrations were calculated, using equation (1) but substituting precipitation, P_i, for sample volume, V_i. To estimate the trend, January values from 1979 at a site were compared to January values from 1980, etc. A Mann-Kendall test statistic was computed to evaluate the significance of the trend and an estimate of the magnitude of the trend was calculated using Sen's median slope (see Olsen, 1989 for details of these calculations).

RESULTS AND DISCUSSION

Spatial Analyses

Figure 2 shows the location of the sites that met all of the completeness criteria for the spatial analyses of NADP/NTN data for the 10/83 through 9/88 summary period. Data from 157 sites were accepted. Since the number of sites east and west of the Mississippi River was 79:78, respectively, the areal density of sites in the West was, in general, less than the East. Noticeably lacking in data points were parts of the Great Basin in Utah and Nevada, parts of the Great Plains in western Nebraska, parts of the Tennessee Valley in western Tennessee and northern Alabama, and northeastern Georgia and South Carolina. Similarly, some states were relatively over-represented, such as Oregon, Colorado, Illinois, New York, and North Carolina. Because the algorithm that effects the objective analysis takes data from the nearest five data points, these differences in station density would be manifest in the size of the average distance of the data points from the grid points. Where stations were sparse, the average distance, or area of influence, would be large, and where stations were dense, the average distance small. In general, the area of influence of stations in the western U.S. was much greater than in the eastern U.S. As a result, smaller scale features could be resolved by the spatial analyses in the East than in the West. Further sampling and analysis of data on a space scale smaller than the NADP/NTN is needed to determine the importance of these differences.

Another measure of the respresentativeness of the NADP/NTN data is the completeness of the record. Did the data from the summary period at each site adequately represent the temporal variations in the precipitation chemistry record? Did the data represent the variations that accrue from small and large storms or from rain and snow? Bowersox and Stensland (1985) published maps of the ratio of warm to cold period concentrations and found that, in general, concentrations of sulfate were higher in the warm than the cold period at almost every site in the network. Indeed the greatest excursions occurred in the New England and Rocky Mountain states. Warm period concentrations were more than a factor of two greater than cold period concentrations in those regions. This feature was not unique to sulfate, primarily from fossil fuel combustion, but was repeated in the ammonium and calcium data, pollutants that arise mostly from area sources, such as animal waste, soils, construction and demolition activities, and from line sources, such as travel on unpaved roads. These observations suggest the importance that seasonal variations in weather patterns, air mass stagnations, boundary layer depths, and transport speeds, have on air quality and thus precipitation quality. In comprehensive analyses of NADP/NTN data, Krupa et al. (1987) and Knapp et al. (1988) found significant seasonal variations both in the

correlative behavior of ions in precipitation and in the ion concentrations themselves. To represent these important seasonal variations requires that there be an equal proportion of data from all seasons. The objective of the four completeness criteria, previously described, was to impose adequate constraints on the data so that important sources of variations would be represented. Below is a table that shows the breakdown of the percentage completeness in each of the four categories for the 157 sites that met all four criteria. Perhaps the most important criterion for the calculation of weighted-average concentration and deposition fluxes is criterion three, because it is based on precipitation amount, which is directly related to the weighting factor in equation (1). At over 60% of the sites, 90% or more of the measured precipitation was represented. Clearly, criterion two was the most poorly met criterion. Closer examination of the sensitivity of the results to this criterion, and to the others, is needed.

	Percent of 157 Sites With		
Completeness Criteria	90% or above	75% to 89%	67% to 74%
1 -fraction of time with precipitation measurements	78	21	1
2-fraction of time with chemistry measurements	41	48	11
3-fraction of measured precipitation with chemistry measurements	62	38	-
4-fraction of catch in chemistry sample relative to gage	83	17	-

Figure 3 shows the spatial distribution of the five-year volume-weighted-average laboratory hydrogen ion concentrations, expressed as pH, for NADP/NTN data from the 10/83 through 9/88 summary period. The interval between solid isopleth lines on this map is 0.3 pH units, which represents an approximate factor of two change in the hydrogen ion concentration (e.g. pH 4.2 equals a hydrogen ion concentration of 63 μeq/L and pH 4.5 a concentration of 32 μeq/L). As in previous studies (see Knapp et al., 1988) the lowest pH values occurred in the eastern Ohio/western Pennsylvania area. Except for much of Maine, Wisconsin, and western Illinois, the average pH throughout the northeastern quadrant of the country was below 4.5. In the preparation of the state of science summary of wet deposition monitoring in the U.S., Sisterson (1989) has reviewed the literature for remote precipitation chemistry measurements; and he reports an average background pH of about 5.1, though remote values in the pH 4 range are not uncommon. From the pH map in Figure 3, it is apparent that virtually all of the eastern U.S. had an average pH below 5.1 for the 10/83-9/88 summary period. Where the pH was lowest, the hydrogen ion concentrations were more than eight times this background average value. In the West, the areas of highest average pH occurred in the Great Plains and in the Great Basin, while the lowest pH occurred in the Los Angeles basin, parts of central Washington, and in an area extending from Arizona and New Mexico into the central Rockies. Whereas in the East the average pH was rarely above 4.8, in the West it was rarely below that value.

Figures 4 and 5 show the five-year volume-weighted-average sulfate and nitrate concentrations, respectively. These ions have been implicated as the cause for high acidity and low pH, especially in the northeastern U.S. (e.g. Bowersox and de Pena, 1980). Both ions maximized, on average, in the Ohio/Pennsylvania/New York area, where the pH tended to be at a minimum. Sulfate concentrations were lowest along parts of the West Coast and values rose nearly ten-fold from west to east across the country. Nitrate concentrations also rose from west to east, although there was a local maximum in the southern California/southern Nevada area. As for sulfate, average nitrate concentrations varied by nearly a factor of ten. The spatial distributions of both ions was similar to the distribution of sulfur and nitrogen

oxide emissions from point and area sources (OTA, 1984). At 1.5 mg/L or above, concentrations of sulfate alone in the Northeast could result in a pH of 4.5 or below, if completely un-neutralized. Nitrate, too, was highest in this same region, though unneutralized it could effect a pH of only 4.7 or below. Together these two major acidic anions acting alone in precipitation would cause the pH in the Northeast to be everywhere 4.3 or below. Although this region receives the lowest pH, these low values are offset by alkaline cations such as ammonium and calcium.

Figures 6 and 7 show the five-year volume-weighted-average concentrations of ammonium and calcium ions, respectively. Unlike the spatial distributions of the acidic anions and hydrogen ion, these alkaline ions tend to maximize in the interior of the country, where the pH of precipitation is highest. While point and area combustion sources emit these elements, fossil fuels are not a major source of either one. Instead, ammonium results from denitrification in soils, from decomposing organic matter, and most importantly, from animal waste. Ammonium concentration maxima in the Great Plains reflect these source distributions. The maximum in northern Utah may be the result of a local source, however, and requires further investigation. Major sources of calcium are windblown soil particles, road and cultivation dust, and construction and demolition activities. Calcium maxima occurred in the Great Plains and Great Basin, coincident with the maxima in aerosol dust sources. Both ammonium and calcium concentrations minimize in the Pacific Northwest and in the Southeast.

Finally, Figure 8 shows the distribution of annual sulfate deposition fluxes. Except for the Pacific Northwest, where the maximum reflects a local precipitation maximum, the highest fluxes occurred in the Northeast, where the sulfate concentrations maximized. Fluxes in excess of 30 kg/ha/yr occurred over eastern Ohio, western Pennsylvania, and central New York.

Trend Estimates

Thirty stations (17 NADP/NTN, 8 MAP3S, and 5 UAPSP) met the completeness criteria set by Olsen (1984) for performing a trend analysis for the period 1979-1986. The table below summarizes the results of a test of the significance (at the 5% level) of the trends for the ions indicated. With the exception of calcium, the weight of evidence was for "no change" in ion concentrations at the 30 sites. Calcium concentrations tended to drop at over half of the thirty stations, with the median decrease being about -5%/yr or a 35% drop over the seven-year period. The weight of evidence aside, more sites had significant down trends than up trends. In fact, only one site had a significant increase and that was in hydrogen ion. Taking the median changes at the 30 sites as an indication of direction and magnitude of the trend, sulfate concentrations decreased by -1.8% per year, hydrogen by -0.7% per year, while ammonium and nitrate showed essentially no change.

**Trends: 1979 - 1986
at
30 NADP/NTN, MAP3S And UAPSP Sites
(Olsen, 1989)**

	Up	No Change	Down
H^+	1	25	4
SO_4^{2-}	0	22	8
NO_3^-	0	26	4
NH_4^+	0	28	2
Ca^{2+}	0	13	17

ACKNOWLEDGMENTS

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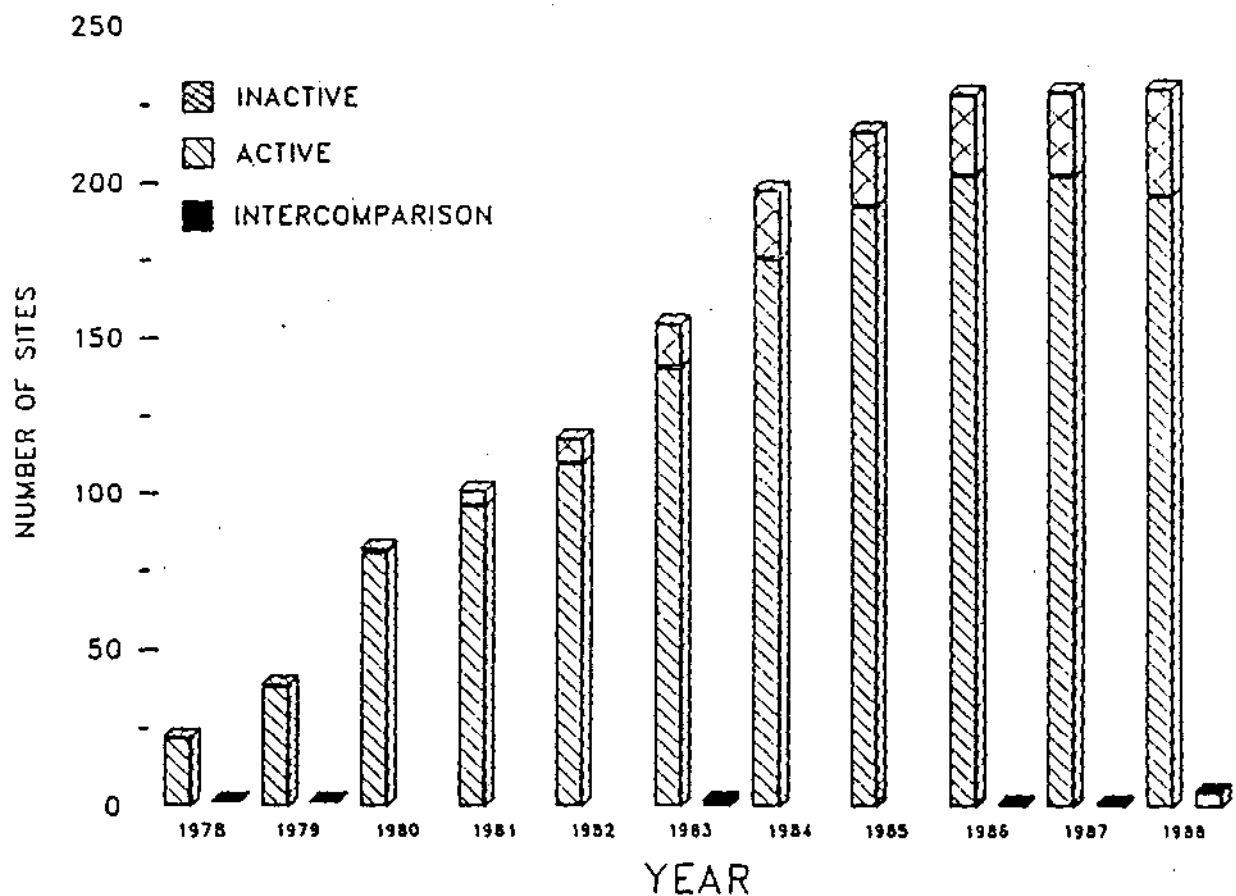
Figure 1. NADP/NTN precipitation chemistry network sites (active, inactive, inlercomparison) on 31 December of each year.
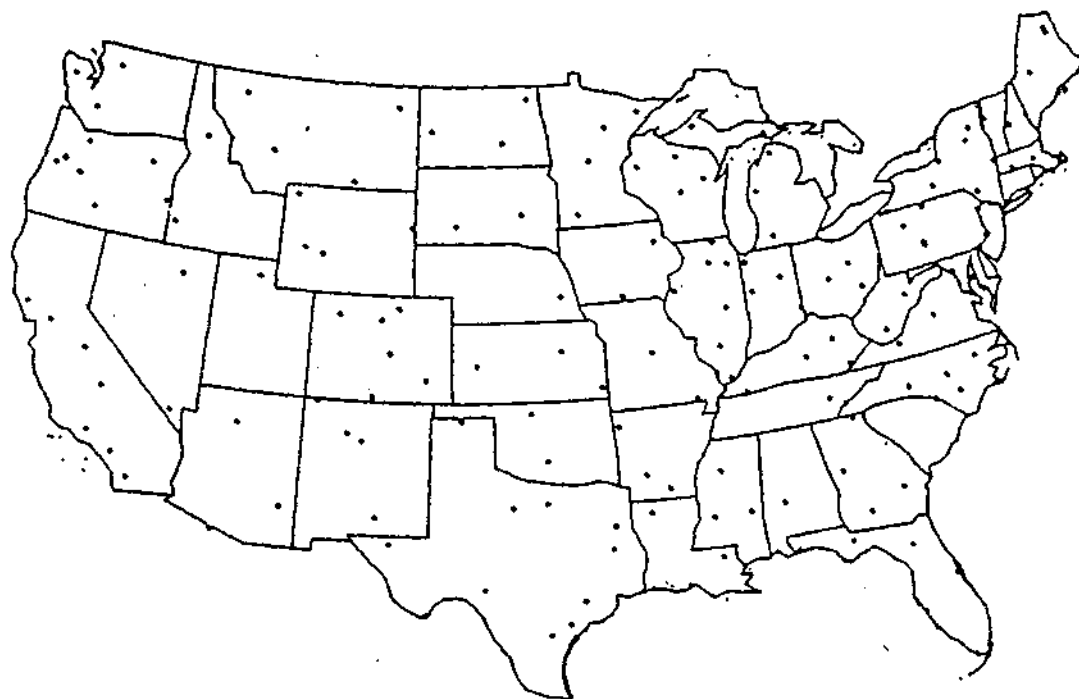

Figure 2. NADP/NTN sites that met all four completeness criteria for the spatial analysis of a five-year-average (10/83-9/88) data set
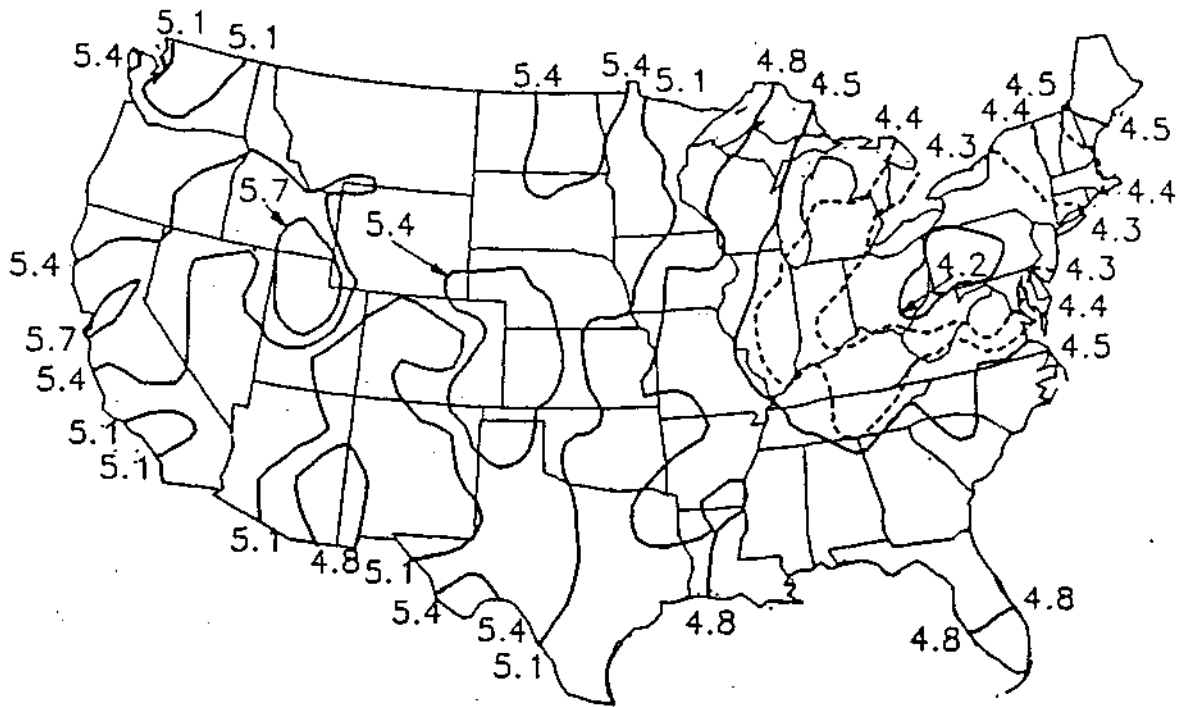
Figure 3:   Five-year-average (10/83-9/88) laboratory pH map from the volume-weighted-average hydrogen ion concentrations for NADP/NTN data

Figure 4.   Five-year-average (10/83-9/88) sulfate concentration (mg/L) map from the volume-weighted-average sulfate ion concentrations for NADP/NTN data

Figure 5.   Five-year-average (10/83-9/88) nitrate concentration (mg/L) map from the volume-weighted-average nitrate ion concentrations for NADP/NTN data

Figure 6.   Five-year-average (10/83-9/88) ammonium concentration (mg/L) map from the volume-weighted-average ammonium ion concentrations for NADP/NTN data
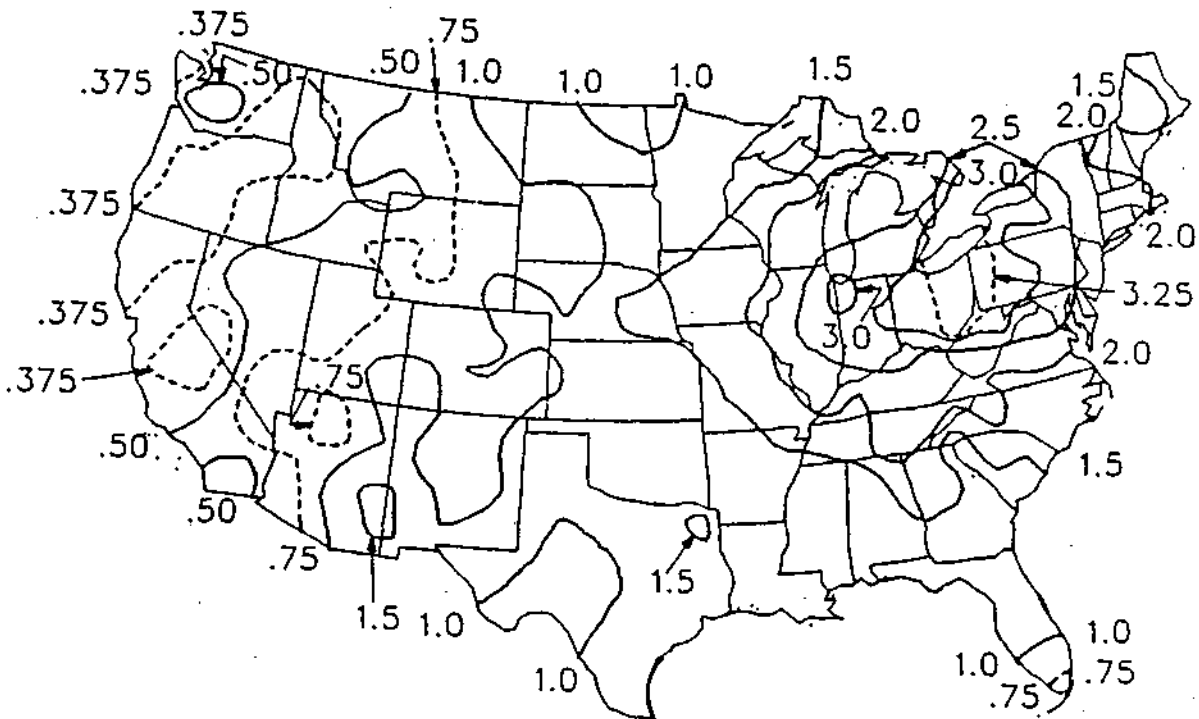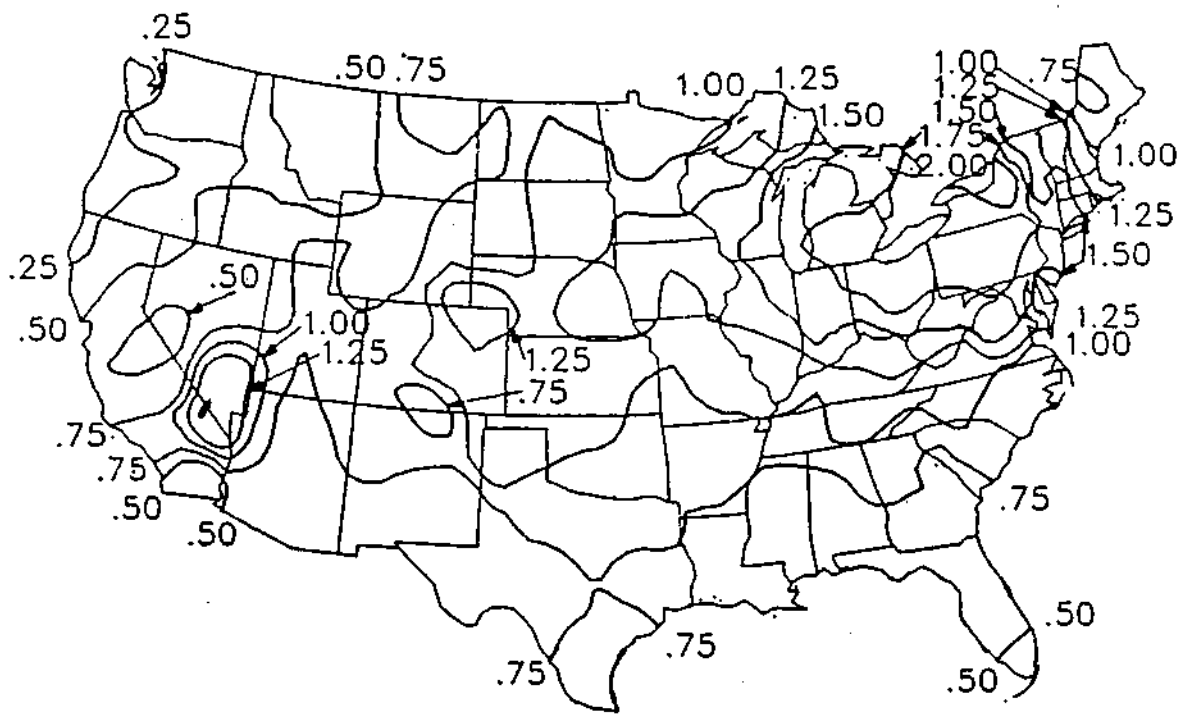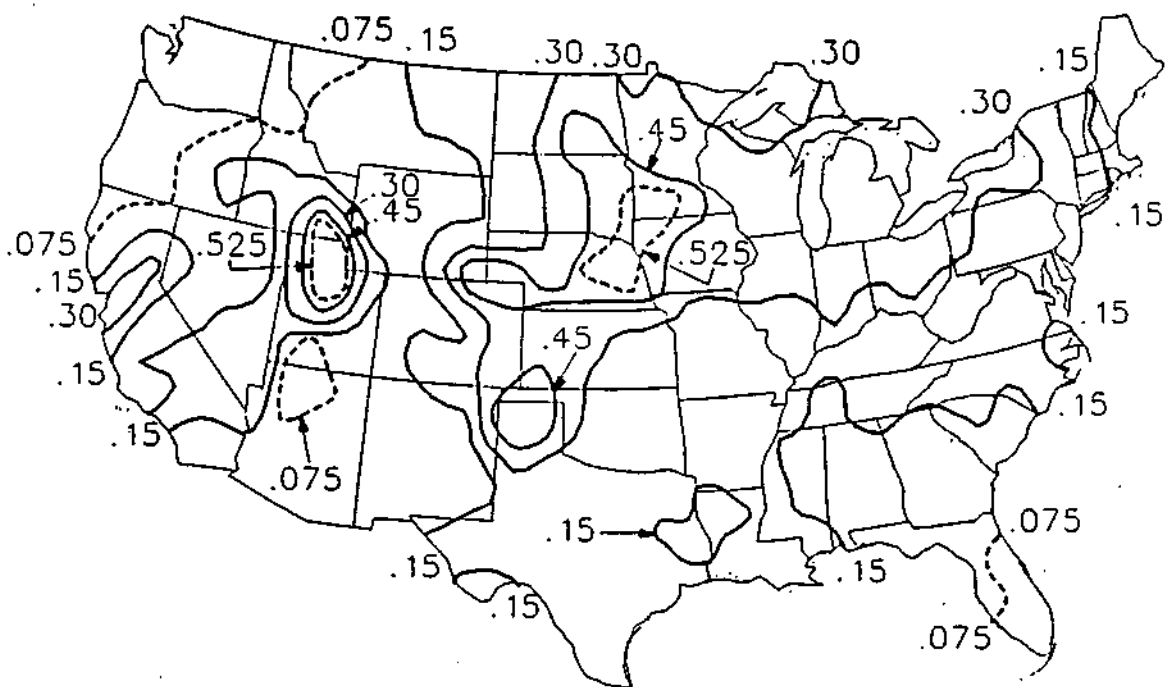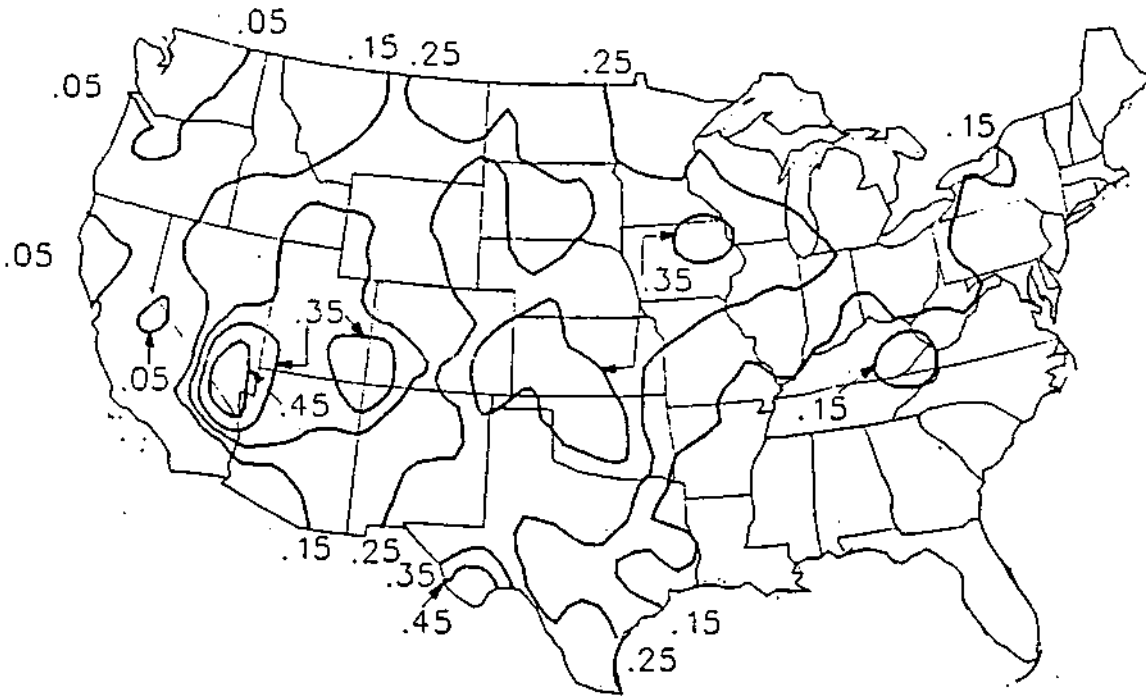
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Figure 7.   Five-year-average (10/83-9/88) calcium concentration (mg/L) map from the volume-weighted-average calcium ion concentrations (or NADP/NTN data
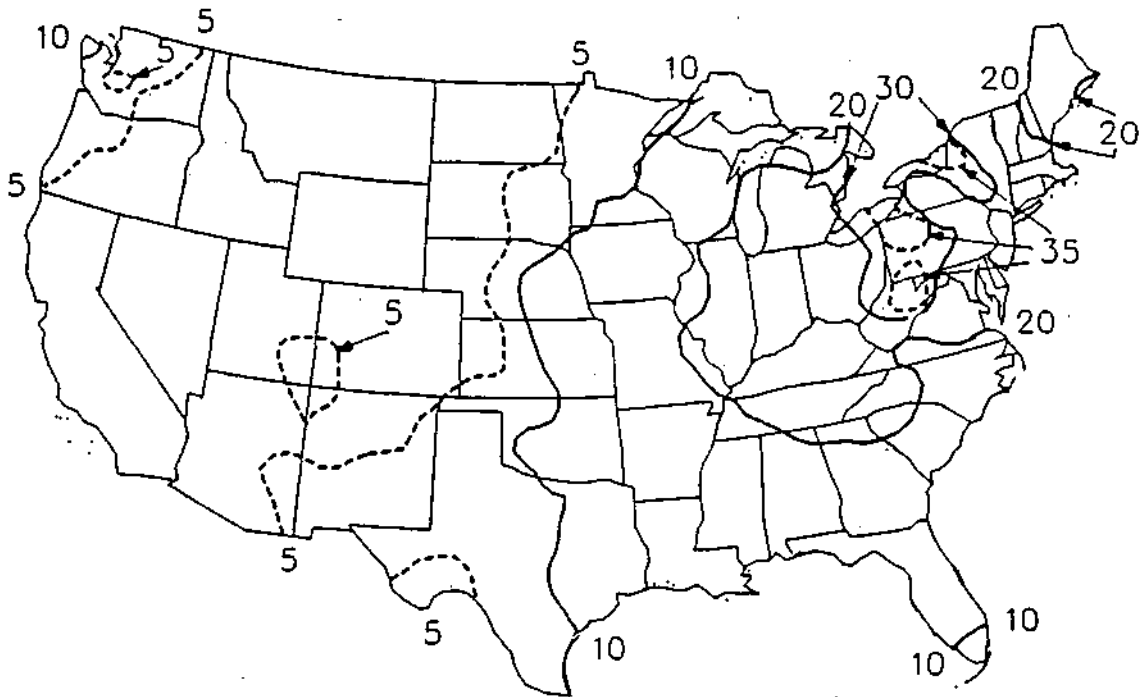

Figure 8.   Annual sulfate deposition flux (Kg/ha/yr) calculated from the five-year-average sulfate concentration and the annual average precipitation amount over a five-year period (10/83-9/88)

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FLOW INJECTION ANALYSIS METHOD VALIDATION STUDY

by

Leon Olszewski, Susan R. Bachman, and Mark E. Peden

INTRODUCTION

This study investigated the linear analytical range, detection limit, precision, bias, and sample carryover effects for the determination of ammonium concentrations by Flow Injection Analysis (FIA). It also compared Flow Injection Analysis results to Segmented Flow Analysis (SFA) results. SFA was the method for ammonium determination at the CAL prior to August 1989. This work is outlined in applied research task 1 (evaluation of new laboratory equipment and chemical analytical techniques) of the CAL Work Statement (Section A.3.3.).

To compare FIA with SFA, two sets of natural samples were analyzed using both methods. The first set was analyzed using SFA on March 1, 1989, and the second using SFA on June 6, 1989. The same analyst then repeated the analyses using FIA on the days following the SFA analyses.

Comparison of the SFA concentration percentiles to 1988 network precipitation percentiles shows that the samples selected for the comparison reflect the range of concentrations seen throughout the NADP/NTN network (1). The percentiles are listed in Table 1.

The full range of values (up to the maximum) was not used for two reasons. First, the samples used in the study were naturally occurring precipitation samples. For the two periods studied, extremely high values of NH_4^+ did not occur. The second reason is that the linear analytical range of the FIA method is up to 2.00 mg/L NH_4^+. Samples above this value would have to be diluted. The samples chosen covered the normal range, as shown in Table 2 and Figure 1.

There are several differences, listed in Table 3, between the two sets of instruments. Based on these differences, it was clear that FIA would improve laboratory efficiency. The larger concentration range for FIA meant that fewer samples would have to be diluted. The faster cycle time for FIA meant that more analyses could be done in one day. Finally, the data collection and reduction for FIA was more sophisticated. In addition, calibration curves were calculated automatically and the data was electronically, rather than manually, transcribed.

RESULTS

Linear Analytical Range

A set of six standards was used to calibrate the FIA instrument. The response was plotted against the known concentration and was assumed to be a linear function of concentration. A regression was calculated, based on the calibration. The calibration was accepted only if the correlation coefficient was greater than or equal to 0.999.

The six standards consisted of a blank (DI water) and solutions with concentrations of 0.07, 0.20, 0.50, 1.0, and 2.0 mg/L NH_4^+. On the dates that the paired samples were analyzed, the FIA calibration curve had correlation coefficients of 0.99970, 0.99979, and 0.99931.

Table 1. Comparison of SFA and 1988 Precipitation Percentile Ammonium Concentrations (mg/L)

Percentile	1988	SFA
Minimum	<0.02	<0.02
5th	<0.02	<0.02
10th	<0.02	<0.02
25th	<0.02	0.03
50th	0.10	0.15
75th	0.31	0.25
90th	0.59	0.54
95th	0.85	0.70
99th	1.72	1.67
Maximum	5.71	1.80
Number of samples	6386	211

Table 2. Frequency Distribution of NH_4^+ Concentration of SFA Samples

Conc. Range (mg/L)	n^a
< 0.02	42
0.02 - 0.05	21
0.06 - 0.10	26
0.11 -0.15	23
0.16 - 0.20	22
0.21 - 0.25	25
0.26 - 0.30	10
0.31 - 0.40	9
0.41 - 0.50	8
0.51 - 0.60	10
0.61 - 0.80	7
0.81 - 1.00	5
> 1.00	3

n^a = number of samples in Conc. Range

Figure 1. Frequency Distribution of SFA NH$_4^+$ Concentration
All samples, total number = 211
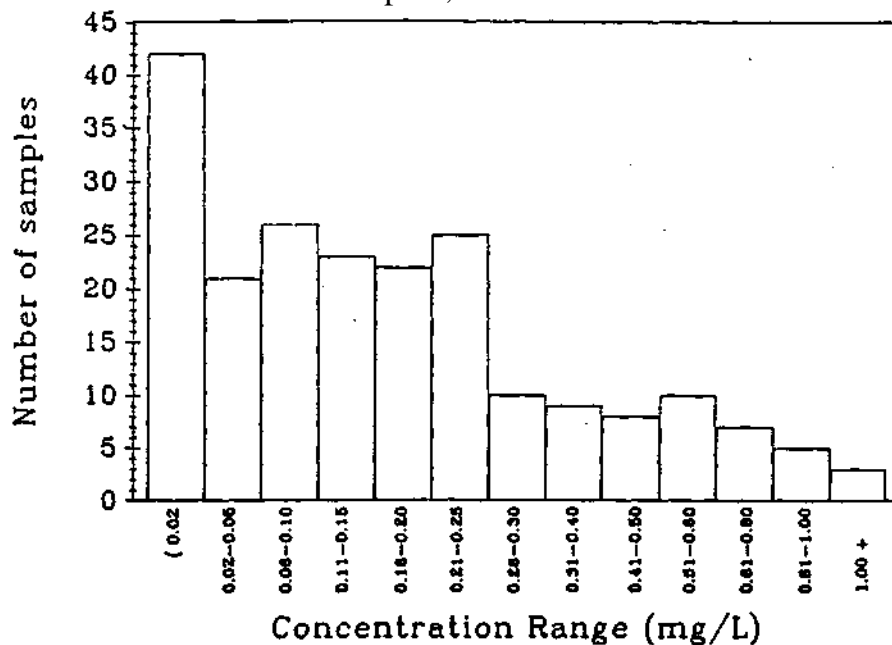
Table 3. Instrumentation Differences between SFA and FIA

	SFA	FIA (6)
Manufacturer	Technicon-Modified	Lachat Instruments
Concentration Range	0.02-1,00 mg/L	0.02-2.00 mg/L
Method Detection Limit	0.02 mg/L	0.02 mg/L
Sample Cycle Time	130 sec.	54 sec.
Sample Volume	0.21 mL	3.00 mL
Start-up Time (reagents, standards, equipment warm-up)	~1 hr.	~1 hr.
Data Collection/Reduction	Limited	Sophisticated
Total number of Analyses/Day	~150	~400

Precision

To compare the precision of SFA and FIA, U.S. EPA standards, used as CAL QC solutions, were run using both methods, at two concentration levels. The U.S. EPA standard "theoretical" values for mean and standard deviation were provided with the solution concentrates. Paul Britton of the U.S. EPA provided the number of analyses (n). Data from the FIA system were collected on nine dates from 2/15/89 to 6/6/89. The precision of the SFA was calculated from the year-to-date Quality Control samples for the NADP/NTN program. Both sets of results were compared to the results presented in Methods for Collection and Analysis of Precipitation (3). The results are presented in Table 4.

Table 4. Single Operator Bias and Precision for Ammonium Determined from Quality Control Check Samples

Concentration (mg/L)			Bias		Precision	
Theoretical	Measured[a]	n[b]	mg/L[a]	%	mg/L[a]	%
Methods for Collection and Analysis of Precipitation (3):						
0.19	0.18	215	-0.01	-5.3	0.02	11.1
0.36	0.36	82	0.00	0.0	0.02	5.6
0.98	0.92	224	-0.06	-6.1	0.05	5.4
1.22	1.24	81	0.02	1.6	0.03	2.4
Segmented Flow Analysis (1/5/89 to 5/31/89):						
0.1275	0.1297	115	0.0022	1.7	0.0113	8.7
0.6376	0.6417	99	0.0041	0.6	0.0203	3.2
Flow Injection Analysis (2/15/89 to 6/6/89):						
0.1275	0.1263	27	-0.0012	-0.9	0.0131	10.4
0.6376	0.6438	21	0.0062	1.0	0.0186	2.9

[a] Extra (non-significant) digits are included for calculations.
[b] Number of analyses

Before SFA was replaced by FIA, FIA had to meet several requirements. One of the requirements was that the precision of FIA be equal to or better than that of SFA. In other words, the variance of FIA had to be equal to or less than the variance of SFA. The one-tailed F test was used to test the variances. The null hypothesis was that the two variances were equal (2, pp. 54-59), and the alternative hypothesis was that the variance of FIA was greater than the variance of SFA.

Case 1. EPA Standard WP048601DF0020, Concentration = 0.1275 mg/L

$$n_{SFA} = 115 \qquad n_{FIA} = 27$$

$$F = \frac{\sigma_{FIA}^2}{\sigma_{SFA}^2} = \frac{(0.013052)^2}{(0.011274)^2} = 1.340$$

At the 95% confidence level, reject the null hypothesis if
F > 1.59 (interpolated from Table 2A, 2, pp. 290-291).

Conclusion: Do not reject the null hypothesis.

Case 2. EPA Standard WP048601DF0004, Concentration = 0.6376 mg/L.

$$n_{SFA} = 99 \qquad n_{FIA} = 21$$

$$F = \frac{\sigma_{FIA}^2}{\sigma_{SFA}^2} = \frac{(0.018567)^2}{(0.020303)^2} = 0.836$$

At the 95% confidence level, reject the null hypothesis if
F > 1.91 (interpolated from Table 2A, 2, p. 290-291).

Conclusion: Do not reject the null hypothesis.

In conclusion, the variance of FIA cannot be proven to be greater than the variance of SFA. Also, the precision for FIA is better than that reported for SFA in Methods for Collection and Analysis of Precipitation (3).

Bias

The previous results were also used to determine the bias for FIA. The bias can be tested using a t test (4, pp. 116-117).

$$t = \frac{|X_1 - X_2|}{s_p \sqrt{(1/n_1) + (1/n_2)}}$$

$$s_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}$$

X = Mean of values, subscript 1 refers to the expected value for EPA standard,
subscript 2 refers to the FIA measured values
s = Standard deviation
n = Number of samples

For EPA standard WP048601DF0020 (i. e. conc. = 0.1275 mg/L):

$$t = \frac{|\ 0.1275 - 0.1263\ |}{S_p\ \sqrt{(1/200) + (1/27)}}$$

$$S_p^2 = \frac{(200 - 1)(0.00644)^2 + (27 - 1)(0.01305)^2}{200 + 27 - 2} = 5.636 \times 10^{-5}$$

$t = 0.780$

At the 95% confidence level, for 225 degrees of freedom, reject if
$t > 1.971$.

Conclusion: Do not reject the null hypothesis that the two means are the same.

For EPA standard WP048601DF0004 (i. e. conc. = 0.6376 mg/L):

$$t = \frac{|\ 0.6376 - 0.6438\ |}{s_p\ \sqrt{(1/200) + (1/21)}}$$

$$s_p^2 = \frac{(200 - 1)(0.0322)^2 + (21 - 1)(0.018567)^2}{200 + 21 - 2} = 9.736 \times 0\text{-}4$$

$t = 0.866$

At the 95% confidence level, for 219 degrees of freedom, reject if
$t > 1.971$.

Conclusion: Do not reject the null hypothesis that the two means are the same.

In conclusion, FIA does not demonstrate a significant bias, at either the low or high concentration.

Method Detection Limit

A set of standard solutions was run, following the EPA guidelines for establishing a Method Detection Limit (MDL) (5). The results for Standard #A, concentration = 0.07 mg/L were:

Number of analyses = 48
Average concentration = 0.068854 mg/L
Standard Deviation = 0.009931 mg/L
RSD % = 14.42%

For 47 degrees of freedom, the t value at the 99% level is 2.41.

$MDL = t * s_D$

= 2.41 * 0.009931
= 0.02398   0.02 mg/L

The MDL for FIA is the same as the MDL calculated for SFA.

Carryover Effects

Carryover effects were studied by running a high concentration sample (>75th percentile) followed by a low concentration sample (<25th percentile). Twenty pairs of samples were run. SFA gave a detection limit value for each of the twenty; FIA gave a detection limit for all twenty also.

In conclusion, neither SFA nor FIA showed a significant carryover. The amount of carryover, if any, was less than the detection limit and less than the precision of the method.

Student's t test

The Student's t test was used to test whether the above two populations, the FIA and the SFA, had the same mean. There was an assumption that the variances of the two populations were equal (excluding detection limit values). Therefore, the first test was the F test, to compare these variances and test this hypothesis. Since we were testing that the two variances were equal, we used the two-tailed F test (2, pp. 55-56). The statistic was calculated as in Precision, above, and the null hypothesis was the same, but the alternative hypothesis was that the two variances were not the same.

$$n_{SFA} = 164 \qquad n_{FIA} = 164$$

$$F = \frac{\sigma_{FIA}^2}{\sigma_{SFA}^2} = \frac{(0.271)^2}{(0.267)^2} = 1.030$$

At the 95% confidence level, reject the null hypothesis if
F > 1.39 (interpolated from Table 2B, 2, pp. 292-293).

Conclusion: Do not reject the null hypothesis that the two variances are equal. Therefore, it was appropriate to use the t test to check for a difference in the two methods.

The equations for the t test are the same as for Bias (above):

$$t = \frac{|\ 0.270 - 0.266\ |}{s_p \sqrt{(1/164) + (1/164)}}$$

$$s_p^2 = \frac{(164 - 1)(0.267)^2 + (164 - 1)(0.271)^2}{164 + 164 - 2} = 0.072365$$

t = 0.1346

At the 95% confidence level, for 326 degrees of freedom, reject if
t > 1.970.

Conclusion: Do not reject the null hypothesis that the two means are the same.

Paired t test

One problem with using the Student's t test was that there was a large variance between samples, which was (probably) larger than the difference between methods. To study only the difference between methods, another test can be run, the paired t test (4, pp. 119-121).

The samples were paired; that is, the same sample was tested using both methods. Subtracting the result of one method from the result of the second method provided an estimate of the difference in methods. The difference was defined as the result for SFA minus the result for FIA. The null hypothesis was that there was no difference between methods.

$$t = \frac{|d|}{s_D/\sqrt{n}}$$

Where d = Average difference
       n = Number of pairs
       s_D = Standard deviation of the difference

Table 5. Comparison of SFA and FIA using the Paired t test

	n	Mean Difference (mg/L)	t	t_{crit}	Reject?
Above detection limit	164	0.00317	2.928	1.975	Yes
At or below detection	47	0.00055	1.891	2.010	No
All samples	211	0.00289	3.323	1.972	Yes

The paired t test indicated a statistically significant difference between the two methods at the 95% confidence level. However, the difference was quite small; in fact, it was smaller than the uncertainty in the measurements. Therefore, even though there was a statistically significant difference, there was not a physically significant difference.

Another concern of the study was the relationship between the concentration and the difference of the two methods. The difference between SFA and FIA is plotted against SFA concentration in Figure 2. There is no noticeable relationship.

Regression Analysis

A regression line was calculated to fit the relation between SFA and FIA. Since the relationship was assumed to be linear, the equation relating the two variables was:

FIA = slope*SFA + constant

The results of the regression are given in Table 6.

Table 6. Regression line coefficients for FIA plotted against SFA

	n^a	slope	constant	correlation coefficient
Samples above detection limit	164	1.01275	-0.00661	0.99877
All samples	211	1.00949	-0.00488	0.99888

n^a = number of samples

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Figure 2. Difference of Segmented Flow and Flow Injection Analyses
as a function of SFA Concentration
All samples included
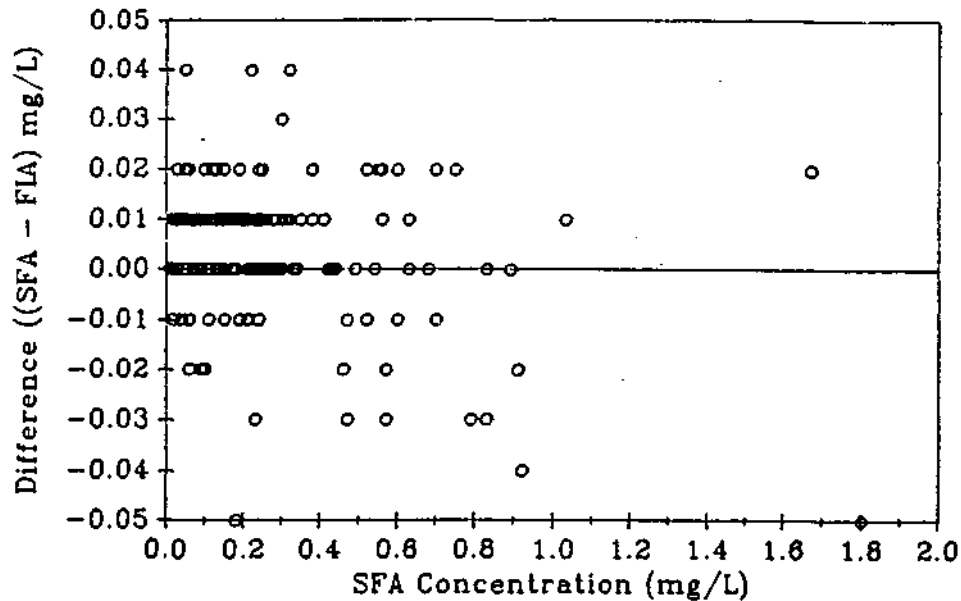
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THE CONTRIBUTION OF BUCKET LID RUBBER O-RINGS
TO SAMPLE CHEMISTRY

by

Kenni O. W. James

ABSTRACT

The contribution of the shipping container to the chemistry of NADP/NTN samples has been a subject of concern since the inception of the network. The results of the USGS blind-audit program consistently have implicated the effect of routine sample handling, processing, and shipping as the cause for significant increases in the concentrations of calcium, magnesium, sodium, and chloride ions and a decrease in hydrogen ion and specific conductance. A series of worst-case experiments was conducted in the laboratory in order to assess the contribution of the container. Results, using internally prepared simulated rain at the 75th percentile concentration values of network wet samples, show that the standard bucket, remaining in an upright position, has little or no effect on the sample chemistry. The same solution exhibits the changes in calcium, magnesium, hydrogen ion and conductance noted in the blind-audit program when it has contacted the butadiene rubber o-ring used to ensure a seal of the container lid. An O-ring in one liter of synthetic rain neutralizes, to (pH 6.99), the solution.

INTRODUCTION

At the CAL, investigations of the lid O-ring as a source of contamination of NADP/NTN wet deposition samples have continued. These studies have focused on quantification of the bias in ion concentrations due to the elements leached from the O-ring. Changes in free acidity have been examined, in particular because other investigators have reported significant differences in field and laboratory pH measurements. This report summarizes the progress made to characterize the effect of the rubber 0-ring on acidic synthetic rain samples. A poster describing this work was presented at the October 1989 NADP Technical Committee Meeting and this report contains the salient portions of that presentation. This research is described under applied research tasks 1 (evaluation of sample handling procedures), 6 (leaching tests on bucket lid O-rings), and 8 (evaluation of sample storage conditions) of the CAL Work Statement (Section A.3.3.).

RESULTS AND DISCUSSIONS

Bucket blanks have been part of the CAL QA/QC program from the beginning of the NADP. Bucket blank measurements were begun to assess the effectiveness of CAL bucket cleaning procedures and to evaluate possible changes in these procedures. A related use of bucket blank data was (and is) to quantify biases in CAL ion concentration measurements resulting from contact with and storage of the samples in the buckets. A regular schedule for taking bucket blanks included at least two blanks per week, usually more. In addition to these routine QC measurements, many special studies have been conducted over the past ten years. Random buckets and lids have been selected from each new shipment received at the CAL for evaluation as a contamination source.

Butadiene rubber gaskets are inserted in the groove of the sample bucket lid to insure a complete seal, when the lid is pounded onto the bucket. In past studies it was determined that these O-rings influence the chemistry of samples that they contact. The bucket and lid, without the O-ring, have little or no effect on sample chemistry.

The most recent study involved two different experiments. The first was a worst case scenario where O-rings were inserted into one-liter bottles and the bottles filled with synthetic rain. This synthetic rain was prepared with analyte concentrations at the seventy-fifth percentile levels of samples from the

NADP/NTN network. Three O-rings leached for 48 hours in deionized water, with the leachate discarded and renewed after 24 hours, were used in the experiment. One O-ring was placed in each of three one-liter bottles of the synthetic rain. Aliquots of the leachate from each bottle were removed and analyzed after 1, 3, 5, and 7 days. The second phase of the recent study was a comparison of the chemistry of 400 mL samples of the same synthetic rain formulation stored in upright and inverted buckets over a period of 1 to 7 days.

The results of the analyses of aliquots taken from the synthetic rain solutions containing O-rings are presented in Table 1. These average results show that the solutions were neutralized by O-ring contaminants. Over a seven-day period, the pH rose from 4.33 to 6.82, a loss of over 46 microequivalents of free acidity. In response to this loss of acidity, the conductance decreased the first day, but then began to rise. Analysis of the samples by inductively coupled plasma indicated a zinc concentration that started at less than 0.001 mg/L and rose to greater than 2.5 mg/L in the aliquot taken on the seventh day. The rise in conductance after day one was largely the result of the increase of zinc in the leachate solution. In addition, calcium and magnesium concentrations rose by ~7% and —21%, respectively, while the ~5% sodium increase may have resulted from handling or the O-ring or a combination of both.

Figures 1 through 6 depict the ion concentrations presented in Table 1. The large drops in free acidity (H^+) and solution conductance in the first 24-hour period are evident in Figures 1 and 2. Figure 2 further shows the slow increase in conductance, after day 1, that can be explained by the increase in zinc ion concentrations, depicted in Figure 6. Figures 3 and 4 show the parallel rise in alkaline earth elements, Ca^{2+} and Mg^{2+}, leached from the O-rings. And finally, Figure 5 presents the small changes in sodium ion in the leachate. Other elements, NH_4^+, SO_4^{2-}, NO_3^-, and Cl^-, remained virtually constant over the one-week period.

An experiment that may mimic more nearly the exposure of wet deposition samples to the bucket lid O-ring is the comparison of solutions of equal volumes left in upright and inverted buckets for 1, 2, 3, 5, and 7 days. This, too, might overestimate the potential for contamination due to the O-ring, because typically buckets are not left inverted for long periods of time. Four hundred milliliters (equivalent to ~0.23 inches) of synthetic rain were poured into each of 20 buckets. Ten of the buckets were capped with snap-on lids and left upright. The other ten were covered with the usual lid, which was pounded on as is necessary; and then the sealed bucket was inverted, allowing maximum contact of the sample with the lid and O-ring. As for the first experiment, the average results are presented in Table 2. Differences between the upright and inverted bucket results are an indication of the contamination potential resulting from the lid and O-ring. Changes in ion concentrations in the upright buckets over the seven-day period were less than 3%. In general, the concentrations did not change monotonically, as would be the case if the upright buckets were a significant source of sample contamination. Results for the inverted buckets, however, were consistent in direction, though not magnitude, with the first experiment. Hydrogen ion concentrations decreased by nearly 23% over seven days. Solution conductance dropped, then rose as it did in the first experiment. Calcium rose by almost 5%, magnesium and sodium by about 4%, while NH_4^+, NO_3^-, and Cl^- remained approximately constant. Zinc was not measured.

CONCLUSION

In conclusion, this most recent round of bucket and bucket-lid studies shows that the bucket contribution alone to sample chemistry is less than 3% and unimportant. Contact with the O-ring in the lid, however, lowers the hydrogen ion concentration of acidic (pH ~4.3) samples of 400 mL by 23%. Calcium, magnesium, and sodium rose by up to 5% in the same solution. Based on the results of the first experiment, zinc concentrations, though not measured in the second experiment, would be expected to become detectable and play a role in the loss of free acidity, as well. Finally, since the contaminant mass is finite and since the contact with the O-ring is limited, one would expect these effects to decrease, i.e. be diluted away, with larger samples. Smaller samples may show an even greater effect, though the inverted bucket experiment is a worst case test.

TABLE 1. ANALYSES OF ALIQUOTS OF SYNTHETIC RAIN SOLUTION USED TO LEACH BUTADIENE RUBBER GASKETS. THESE MEASUREMENTS ARE THE AVERAGE OF THREE ONE-LITER SOLUTIONS, EACH CONTAINING A SINGLE GASKET.

DAYS IN SOLUTION	pH	HYDROGEN[1] (μeq/L)	CONDUCTANCE[2] (μS/cm)	CALCIUM[3] (mg/L)
INITIAL (0)	4.33	46.8	27.6	0.289
1	5.41	3.89	14.8	0.306
3	6.67	0.214	16.0	0.305
5	6.70	0.200	17.3	0.305
7	6.82	0.151	18.2	0.310

DAYS IN SOLUTION	MAGNESIUM[3] (mg/L)	SODIUM[3] (mg/L)	POTASSIUM[3] (mg/L)	AMMONIUM[4] (mg/L)
INITIAL (0)	0.072	0.187	0.051	0.36
1	0.085	0.191	0.053	0.35
3	0.088	0.195	0.053	0.32
5	0.087	0.193	0.055	0.35
7	0.087	0.196	0.055	0.34

DAYS IN SOLUTION	SULFATE[5] (mg/L)	CHLORIDE[5] (mg/L)	NITRATE[5] (mg/L)	ZINC[6] (mg/L)
INITIAL (0)	2.75	0.52	1.99	.00(1)
1	2.70	0.52	1.99	1.20
3	2.68	0.52	2.00	1.87
5	2.68	0.52	2.00	2.21
7	2.70	0.53	2.01	2.56

[1] Combination glass electrode; hydrogen ion concentrations from 10^{-PH}
[2] Conductance cell (constant ~1)
[3] Atomic absorption spectrophotometry
[4] Automated wet chemistry
[5] Ion chromatography
[6] Inductively coupled plasma

TABLE 2. COMPARISON OF SOLUTIONS OF SYNTHETIC RAIN SOLUTIONS TAKEN FROM UPRIGHT AND INVERTED BUCKETS. THESE MEASUREMENTS ARE THE AVERAGE OF TEN REPETITIONS OF EACH TREATMENT.

DAYS IN BUCKET	pH		HYDROGEN (µeq/l)		CONDUCTANCE (µS/cm)	
	UPRIGHT	INVERTED	UPRIGHT	INVERTED	UPRIGHT	INVERTED
INITIAL	4.35	4.34	44.7	45.7	28.0	28.2
1	4.35	4.38	44.7	41.7	27.7	26.9
2	4.36	4.39	43.6	40.7	27.7	26.8
3	4.35	4.39	44.7	40.7	27.4	26.6
5	4.35	**4.40**	44.7	39.8	27.8	26.7
7	4.36	4.43	44.7	37.2	28.0	28.2

DAYS IN BUCKET	CALCIUM (mg/L)		MAGNESIUM (mg/L)		SODIUM (mg/L)	
INITIAL	0.281	0.285	0.070	0.070	0.185	0.188
1	0.284	0.288	0.070	0.070	0.183	0.190
2	0.284	0.291	0.070	0.070	0.184	0.194
3	0.280	0.296	0.070	0.072	0.183	0.194
5	0.284	0.296	0.070	0.072	0.184	0.192
7	0.284	0.298	0.070	0.073	0.188	0.195

DAYS IN BUCKET	POTASSIUM (mg/L)		AMMONIUM (mg/L)	
INITIAL	0.051	0.050	0.39	0.38
1	0.050	0.051	0.38	0.36
2	0.050	0.051	0.38	0.36
3	0.050	0.050	0.37	0.35
5	0.050	0.050	0.37	0.36
7	0.051	0.050	0.38	0.38

DAYS IN BUCKET	SULFATE (mg/L)		CHLORIDE (mg/L)		NITRATE (mg/L)	
INITIAL	2.63	2.58	0.51	0.51	1.97	1.96
1	2.60	2.57	0.51	0.50	1.94	1.88
2	2.62	2.58	0.51	0.50	1.96	1.90
3	2.62	2.58	0.50	0.50	1.96	1.92
5	2.62	2.60	0.52	0.52	1.96	1.92
7	2.64	2.63	0.52	0.52	1.97	1.94

H+

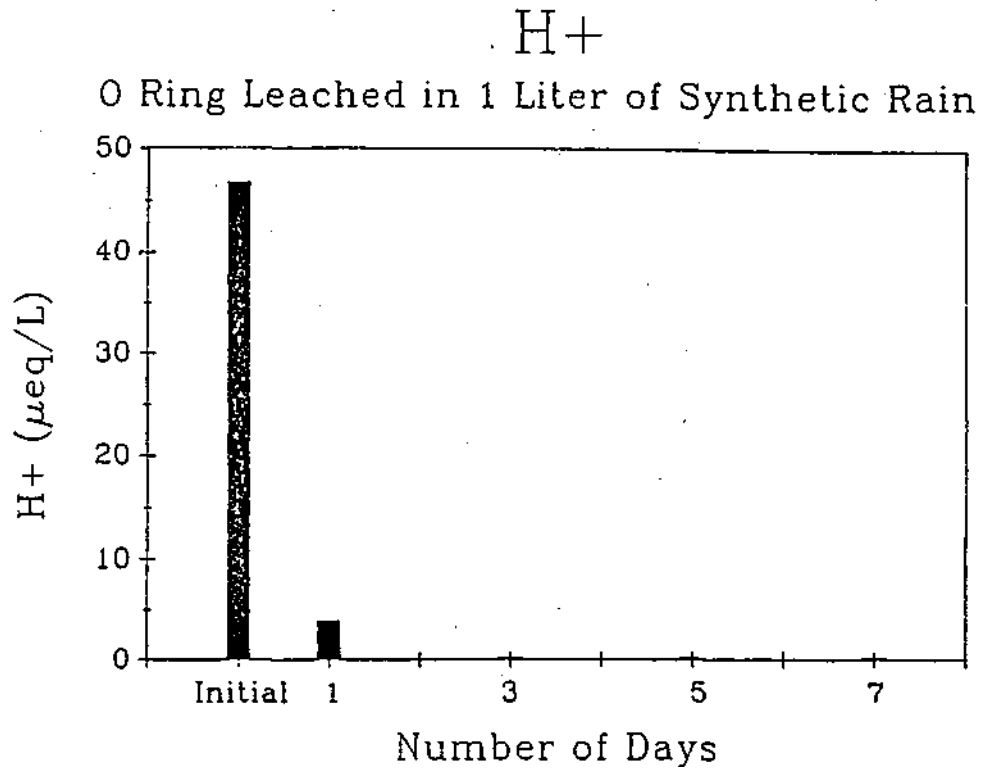## O Ring Leached in 1 Liter of Synthetic Rain

Figure 1.   Hydrogen ion concentrations in O-ring leachate solution over a one-week period.   Initial concentrations were measured prior to immersing the O-ring in the synthetic rain solution. Less than 1% of the free hydrogen remained by day 7.
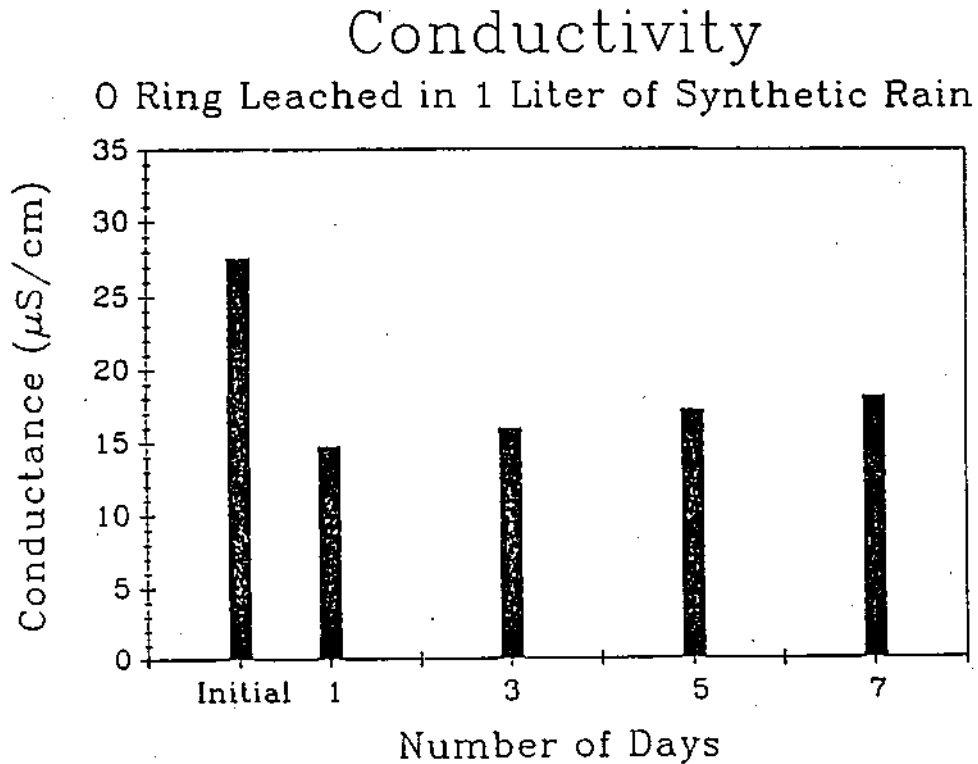
Conductivity

O Ring Leached in 1 Liter of Synthetic Rain

Figure 2.   Same as Figure 1, except for solution conductance (μS/cm).

Calcium
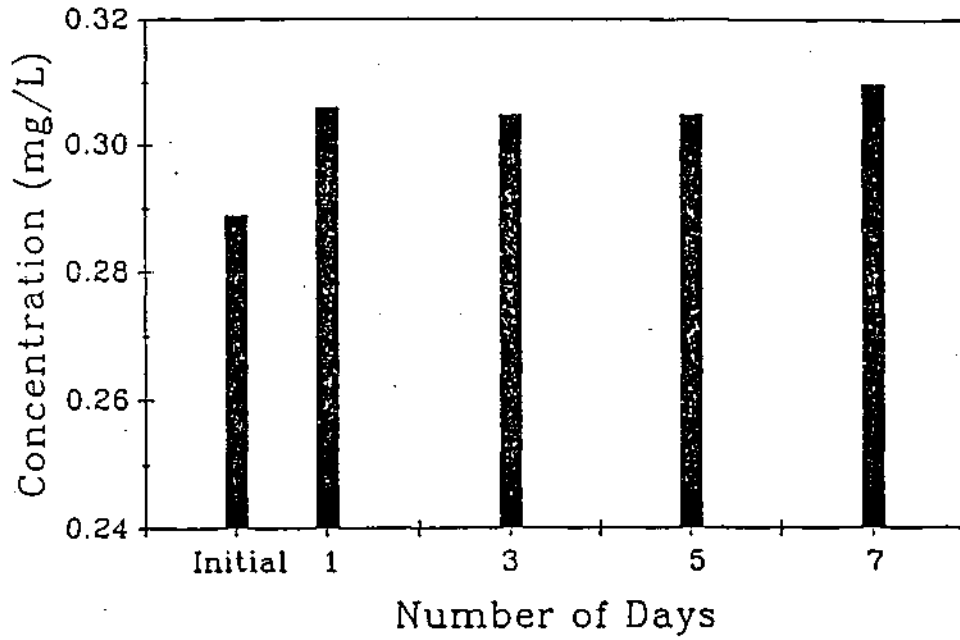## O Ring Leached in 1 Liter of Synthetic Rain

Figure 3.   Same as Figure 1, except for calcium concentrations. Calcium rose by about 7%.

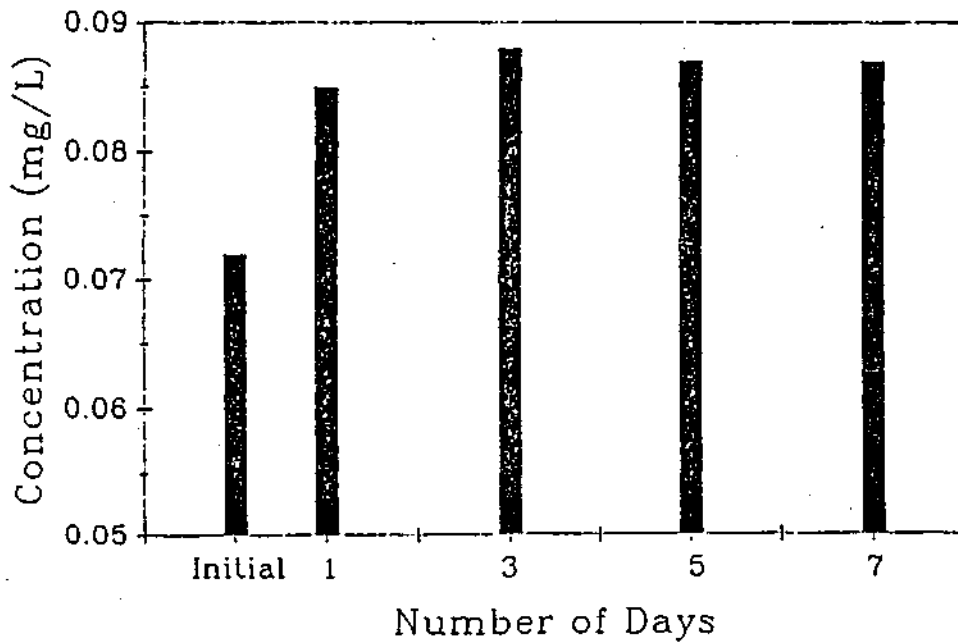# Magnesium
O Ring Leached in 1 Liter of Synthetic Rain

Figure 4.   Same as Figure 1, except for magnesium concentrations. Magnesium rose by about 21%.
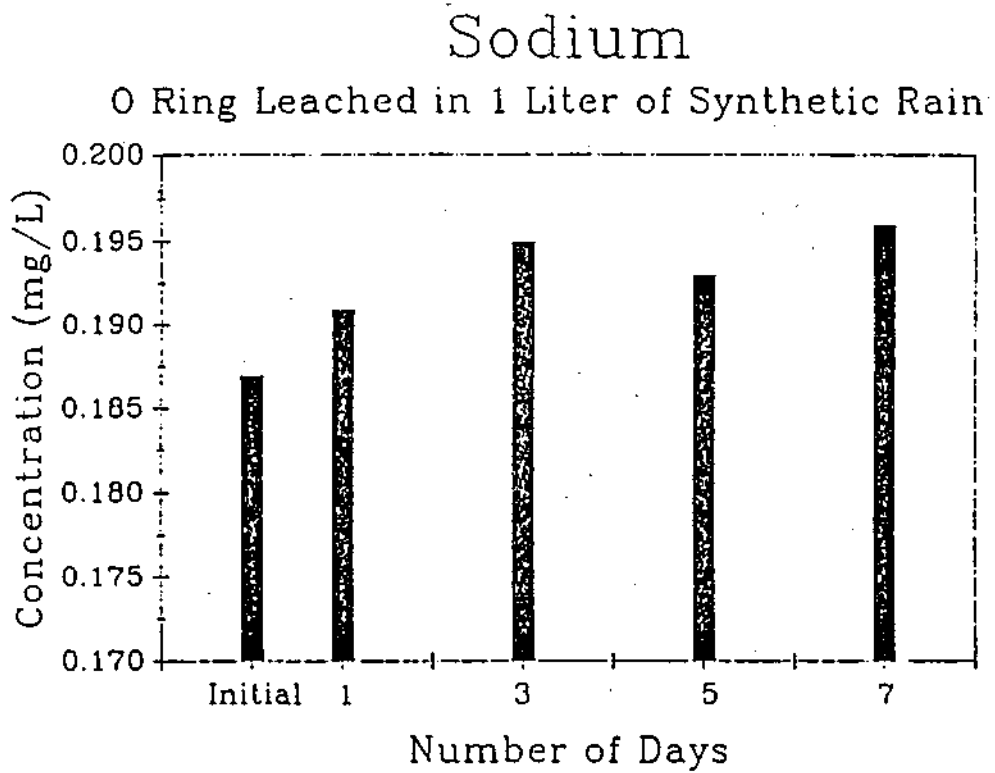
Sodium

O Ring Leached in 1 Liter of Synthetic Rain

Figure 5.   Same as Figure 1, except for sodium concentrations. Sodium rose by about 5%.

Zinc

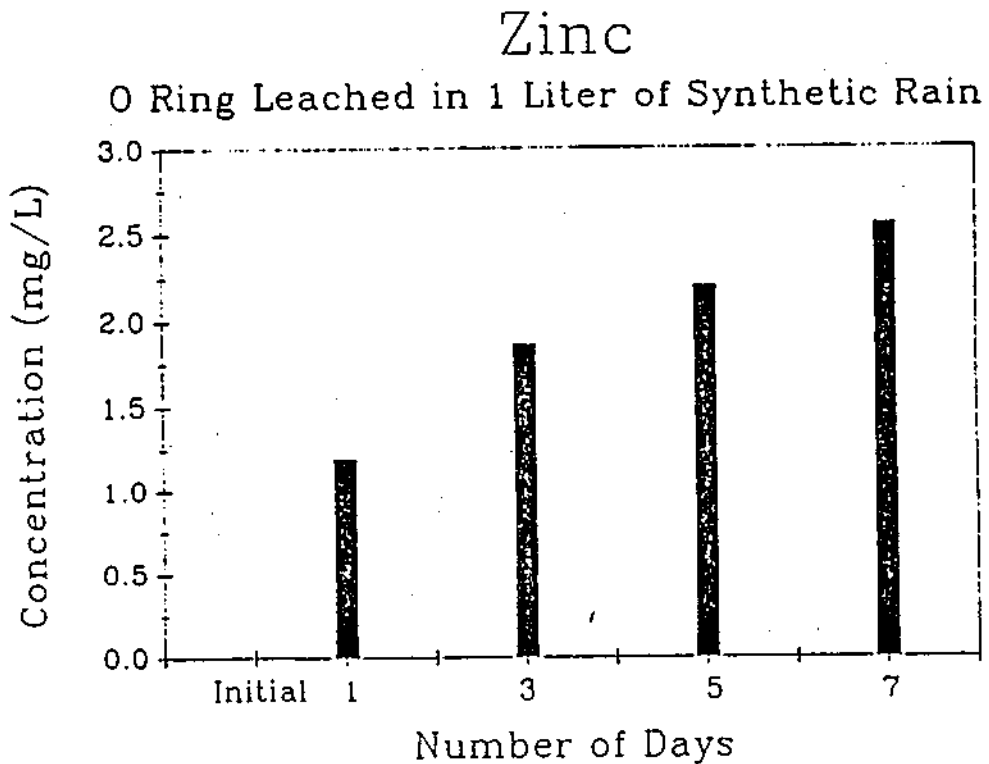## O Ring Leached in 1 Liter of Synthetic Rain

Figure 6.   Same as Figure 1, except for zinc concentrations. Zinc rose from less than .01 mg/L to over 2.5 mg/L, an increase of over 200%.

EVALUATION OF pH ELECTRODES FOR USE AT NADP/NTN FIELD SITES

by

Jackie Sauer

INTRODUCTION

This report outlines the procedures used at the Central Analytical Laboratory (CAL) to supply field sites in the NADP/NTN network with an operating pH electrode. Field site operators measure the pH of aliquots of wet deposition samples when the net sample weight is greater than 70 grams. Prerequisite to measuring the precipitation pH, the electrode response recorded on the meter is calibrated with pH 4 and 7 buffer solutions and the system response is checked with a QC solution, the "pH check sample." Should the electrode fail to respond properly to the buffer solutions or should its performance violate the QC limits for the pH check sample (4.3 ± 0.1), the operator is instructed to report the problem to the CAL. Where warranted, the CAL provides a replacement electrode to the site operator and the failed or malfunctioning electrode is returned to the CAL. Before the replacement electrodes are sent, each one is tested for minimum performance specifications. This report summarizes CAL activities related to electrode replacement and performance checks during the October 1988 - October 1989 period. It was first presented at the recent meeting of the Network Operations Subcommittee in October 1989. These activities are described in topics 1 (evaluation of new laboratory equipment) and 7 (evaluation of field site equipment) under the applied research task (Section A.3.3) of the CAL Work Statement.

SUPPLIES SENT TO EACH SITE FOR FIELD pH MEASUREMENTS

- Fisher brand pH 7.00 buffer solution
- Fisher brand pH 4.00 buffer solution
- Quality Control Check Solution, pH = 4.30 ± 0.1, prepared at the CAL from reagents
- 1 packet 4 mL polystyrene vials used for sample measurement

There are now several different types of electrodes, supplied by the CAL, that are in use at NADP/NTN field sites. Starting in July 1989, Orion electrodes were sent in place of the Beckman electrodes that had been used since 1984. The list below summarizes the electrodes and associated connectors and solutions now in use:

	Price
Beckman	
- 39835 semi-micro, refutable combination electrode	$ 77.00
- pH electrode filling solution, 4 M KCl	$ 8.00
- cable, either BNC or U.S. Standard connector	$ 25.00
Orion	
- 8172BN Sure-Flow Ross refillable combination electrode	$135.00
- 8175BN Sure-Flow Ross semi-micro refillable combination electrode, epoxy body	$195.00
- 8103 Ross refillable all glass combination electrode (25 on order)	$195.00
- Application pH Electrode Storage solution, #910001	$ 16.00
- Adapters, BNC to U.S. Standard (approximately 75% of the sites need adapters; the Sure-Flow electrodes come only with BNC connection)	$ 28.00

The Beckman electrode, plus cable and fill solution, that were sent to each site before July 1989 had a total cost of $110.00. The Orion Sure-Flow semi-micro electrode and 2 bottles of fill solution (included with the electrode), plus storage solution and adapter, sent to each site beginning in July 1989 costs $239.00.

SITE ELECTRODE REQUEST AND SUPPLY

The CAL supplied 165 replacement electrodes to sites between November 1988 and October 1989. Below is a breakdown of the types of electrodes sent:

- 72 were new or rejuvenated Beckman electrodes.
- 63 were Orion Sure-Flow 8172BN (regular size), beginning in July 1989
- 30 Orion Sure-Flow 8175BN semi-micro electrodes were sent during October 1989

Since there are 199 sampling locations in the NADP/NTN, at least 34 of these had their electrode a year or longer. Of the 63 Orion Sure-Flow electrodes sent to sites, 8 have been returned to the lab. Four of these electrodes were cracked when site operators attempted to place the electrode in a conventional electrode holder. This happened because of a slight manufacturing error in the diameter of the top of the electrode. The other four were returned because of complaints about excessive electrode drift.

Because of the continued difficulty in obtaining electrodes that meet the minimum NADP/NTN performance specifications, the lab was unable to supply electrodes to sites for approximately two months, mid-August to mid-September 1989. The semi-micro Sure-Flow (Orion B175BN) was a new electrode coming to market during the third quarter of 1989. Its size and geometry were better suited to the small volume constraints of field measurements in the network, and so other electrodes were not aggressively pursued at the CAL at that time. Site operators were instructed to use a working back-up electrode, if they had one, or to discontinue the pH measurements until they received a replacement. Thirty of these new electrodes were received, tested, and ready for use in October 1989, as soon as a packaging error with Orion was resolved.

ELECTRODE QUALITY CONTROL TESTING AT THE CAL

All electrodes must meet minimum performance specifications before being sent to site personnel. These specifications are the same as the calibration and QC checks performed by operators, before they report field pH measurements of wet deposition samples. Electrodes must perform well enough so that the meter with its electrode can be calibrated, and after calibration will read 7.00 ± 0.03 units in the pH 7 buffer solution. In addition, once calibrated, a reading of 4.3 ± 0.1 units must be attained in the pH 4.3 QC check solution, a dilute, unbuffered, mineral acid solution, prepared from nitric acid stock solution at the CAL. Rejected electrodes typically fall into the following categories:

1. Will not calibrate properly, usually due to a short, crack, etc.; less than 5% of the electrodes.

2. Will not read $7.00 \pm .03$ units during the pH 7 buffer solution re-check after calibration; up to 30% of the electrodes.

3. Will not read 4.30 ± 0.1 pH units in the Quality Control Check Solution; as high as 75% to 80% of the electrodes in some batches received.

4. Other - connection bad (less than 5%), faulty manufacturing (has been 100% in several cases), excessively leaky junction in the case of the Orion electrodes (up to 40% at times).

Electrodes are ordered in batches of 50. The percentage of satisfactorily operating electrodes seems to be related to lot numbers and batches received. Variations in the manufacturing process may account for how well electrodes perform. For example, since October 1988 the following batches of electrodes were ordered and tested:

- 50 Beckman S808A (received Oct 88) - 100% worked satisfactorily.
- 50 Beckman 39835's, lot #S808B (received Dec 88) - <u>100% failure</u> due to faulty manufacturing (electrodes were not shielded). <u>Returned entire batch.</u>
- 50 Beckman 39845's, lot.#S809A (received Jan 89) - AL, AM, BM (the 39845 is a new model number replacing the 39835's)-<u>88% failure</u> rate-did not read 4.30 ± 0.1 in the Quality Control Check Solution and had an excessively slow response time to reach stabilization (15-20 min.). <u>Returned entire batch.</u>
- 50 Orion 8172BN, lot #TW1 (received Apr 89) - <u>28% failure</u>-did not read 7.00 ± .03 units in the pH7 buffer re-check; did not read in the 4.30 ± 0.1 pH unit range for the QC Check Solution; faulty connections, excessively leaky junctions.
- 50 Orion 8172BN (received Jun 89) - lot #TW1 -<u>46% failure</u>-same reasons as above.
- 50 Orion 8175BN (received Oct 89) - lot #TS1-<u>30% failure</u>-same reasons as above.

The 8175BN electrodes are a newly developed device from Orion. The CAL received some of the first batches made available to customers. A serious problem was found with these electrodes, however. When attempting to remove the protective rubber cap from the bulb, several of the electrodes broke very easily in the middle of the body. The bottom portion of the glass electrode was literally pulled out of the epoxy body. Orion was notified and will most likely supply another type of cap. It was hoped that by switching to the new Orion Ross semimicro electrodes, better performance would result. So far, that has not been the case. The lab is currently working with Orion to supply an electrode that will more consistently meet the needs of the network.

PROCEDURAL CHANGES FOR ELECTRODE USE AT FIELD SITES

With the switch from Beckman electrodes to Orion electrodes, several important procedural changes are required:

1. The Beckman electrode typically had slower response times than the Orion Ross electrodes, eventually stabilizing permanently on a pH value. For this reason, site operators were instructed to wait anywhere from 3 to 10 minutes for a pH reading, and not to use the auto-function on their meter, even if it was available. The Orion electrodes have a much faster response time (generally within 30 seconds) and stabilize on the correct pH value for only a brief time (1 to 3 minutes), depending on the electrode. After stabilization is reached, fill solution starts to contaminate the sample, and the pH (of the 4.30 ± 0.1 QC Check Sample or precipitation sample) will continue to rise (drift), until it reaches the pH of the fill solution (~6.5). Therefore, site operators are instructed to follow carefully the guidelines carefully in the NADP/NTN Instruction Manual for Site Operation, which are to identify the stabilization point as occurring when the pH changes less than 0.01 units in 30 seconds. Additionally, it is advised to use the auto-function on the pH meter, if available.

2. The Beckman electrodes were stored dry; i.e., not in any solution. The Orion electrodes are stored in Orion Electrode Storage Solution.

3. Site operators were warned never to interchange the fill solutions between the Beckman and Orion electrodes. The 4 M KCl Beckman fill solution will damage the internal elements of the Orion electrodes; therefore, all site operators receiving Orion electrodes were requested to discard their Beckman fill solutions.

CORRESPONDENCE WITH MANUFACTURERS ABOUT ELECTRODE PROBLEMS

BECKMAN

Electrodes which did not meet NADP/NTN performance criteria were returned to Beckman with pH buffers, QC Check Solutions, vials, and detailed letters, charts, and graphs describing the problems, so that they could confirm or reject the findings. The following conclusions were reached by Beckman:

1. Beckman electrodes are guaranteed only to calibrate properly in buffer solutions and are not guaranteed to work consistently in any other solutions.
2. The CAL Quality Control Check Sample is in error and really should read 4.40 ± 0.1 to agree with Beckman electrode performance.

3. Beckman feels they cannot meet our specifications and therefore does not wish to supply us any longer. They do not wish to continually accept non-working electrodes from us and replace them with another batch for us to test.

The CAL has requested this denial of service in writing, but has received nothing to this date.

ORION

Electrodes which did not meet NADP/NTN performance criteria were returned to Orion with pH buffers, QC Check Solutions, vials, and a detailed letter describing the NADP/NTN and laboratory measurement requirements. Electrodes were tested by Orion staff and the following conclusions were reached:

1. The electrodes meet their specifications: using a 50 mL sample size and stirring will result in correct readings. They feel the problem is in the small sample size (2-4 mL vials) constraints. In response to that, the CAL tested 8 electrodes that initially did not meet NADP/NTN requirements, using a potentially realistic sample size of 15 mL. Four of the electrodes worked and four did not, even when a 50 mL sample size was used. No stirring was done.

2. Use of low ionic strength buffers and a fixing agent was suggested. Orion manufactures a high purity water kit, which has been ordered and received but not yet tested. The directions suggest using a 100 mL sample size and stirring all solutions measured. 1 mL of pHiX™ adjuster is to be added to 100 mL of sample; therefore 0.02 mL pHiX™ would be used for a 2 mL sample size, making it difficult for site operators to use. Additionally, the buffers supplied read 4.10 and 6.97, instead of 4.00 and 7.00, and many site operators (who don't own Orion equipment) cannot adjust their calibration points.

Active correspondence with Orion is ongoing as to the type of return procedure they will allow.

FUTURE ALTERNATIVE ELECTRODE SUPPLY

The CAL continues to test other brands of electrodes for potential site and lab use. However, only 1 or 2 electrodes at a time are ordered and tested. These may not be representative of how entire batches will work. The following brands of electrodes have been investigated in the last year or are in the process of being examined:

1. *Radiometer* semi-micro, all glass, combination, general purpose electrode.
   - This electrode worked well only a few times in the lab. Although at first it satisfied the 4.30 ± 0.1 Quality Control Check Sample requirement, it did not read well at higher pH's. The company will sometimes specially manufacture an electrode for a client, but their lab personnel suggested that this electrode would meet NADP/NTN specifications.

2. *Sensorex* general purpose, semi-micro, gel filled electrode.
   - Two electrodes were ordered. The company manufactured them especially for high purity water measurements. Neither one met the 4.30 ± 0.1 Quality Control Check Sample criteria.

3. *HNU Systems*
   - electrode on order. A company representative said that although this electrode is good for high purity waters, a fixing agent should be added.

4. *American Scientific Products* general purpose combination electrode
   -did not meet the 4.30 ± 0.1 Quality Control Check Sample criteria.

5. *Fisher Scientific* general purpose combination electrode
   -reads well in the 4.30 ± 0.1 QC Check Sample. Drifts at higher pH's, but works OK using the Auto function. The lab will test more of these.

6. *Corning* semi-micro combination electrode
   -did not meet the 4.30 ± 0.1 QC Check Sample criteria.

7. *Hach* electrode
   - a company representative said they don't make an electrode small enough to measure a 2-4 mL sample. The suggested minimum sample size is 100 mL

8. *Brinkman* general purpose, semi-micro, combination electrode
   - electrode on order.

9. *Broadly-James* double junction, semi-micro, combination electrode
   - an excellent electrode provided:

   1. The auto-function on the pH meter is used
   2. Personnel stay <u>away</u> from the pH meter, since the electrode is extremely sensitive and "noisy."

   Two specially made prototypes were manufactured for the CAL Both worked the same way. Like the Orion electrodes, after the correct pH value is reached, it will stabilize for only 1 - 3 minutes before rapidly drifting (pH decreases in this case). Electrode response is extremely "noisy" and in fact the Auto Function will not find a stable reading when movement occurs around the electrode, making it extremely annoying to use. This, plus the rapid drift, makes it difficult to determine the correct pH value. Although the company was notified of this, further discussion is needed.