

NADP QUALITY ASSURANCE REPORT  
CENTRAL ANALYTICAL LABORATORY

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## I. Introduction

The Atmospheric Chemistry Laboratory at the Illinois State Water Survey (ISWS) was selected in the summer of 1978 to be the Central Analytical Laboratory (CAL) for the National Atmospheric Deposition Program (NADP). CAL operations began on October 1, 1978, with 14 NADP sites sending samples.

The United States Geological Survey (USGS) was selected by NADP to monitor the quality assurance program of CAL. Draft copies of the CAL quality assurance reports are reviewed by the USGS, by the Methods Development and Quality Assurance Subcommittee of NADP, and by the NADP Project Coordinator.

## II. Description of The CAL Analytical Quality Assurance Program

The methods in use at CAL have been documented by Stensland et al.<sup>1</sup>. Appendix A described the analytical methods for those parameters currently being measured in NADP. No significant modifications in the analytical or data management procedures occurred at CAL in the six month period covered by this present quality assurance report.

## III. Quality Control Data

### A. Discussion of Results

This section presents the data for the various quality control samples. The glossary preceding the tables defines terms and lists mathematical formulas which were used for the calculations. Most of the tables are cumulative, i.e., contain data for the current reporting period as well as previous reporting periods.

Tables 1-11 report the CAL analytical accuracy. The unbuffered CAL quality control samples referred to in Tables 1 and 2 are sulfuric and nitric acid solutions which simulate unbuffered precipitation samples. The concentrations (activities) of these synthetic solutions, in pH units, are calculated from the normality of the reagent being diluted and are cross checked by measuring the sulfate and nitrate levels in the solutions. Corrections are made for incomplete acid dissociation if ion concentrations warrant such treatment (e.g., the  $pK_a$  of  $HSO_4^-$  is 1.92 at  $25^\circ C^2$  and thus has a small effect for a pH = 3 sulfuric acid solution). The specific conductances in the middle column of Table 2 are determined as the product of the equivalent concentration of the ions in the synthetic solutions and the tabulated equivalent conductance values (at infinite dilution). Empirical (Kohlrausch) corrections are made in these equivalent conductance values if the concentrations of ions are large enough to introduce a measurable error. The pH and conductivity precision for the 1/80 to 6/80 period is worse than for the earlier period. However, the number of analyses was too small and thus the precision values may not be very representative. As of 1/81 a total of three analyses per week are available, producing about 75 analyses for use in each future quality assurance report by CAL. The ion balance checks which are carried out for all precipitation samples did not suggest that any dramatic change in pH and conductivity precision had occurred from the 1979 period to the 1980 period. The  $\pm 21.1\%$  precision for the pH = 4.08 samples in Table 1 corresponds to a precision of  $\pm 0.09$  pH units (i.e., the  $\pm 21.1\%$  is applied to the hydrogen ion activity for the specified pH values).

Tables 3-11 present the precision and bias for the rest of the ions being measured for NADP precipitation samples. Chloride is the only ion showing a

consistently significant bias, although one could almost justify that calcium also shows the bias. In our previous report we noted that the bias for chloride was small and our calculations suggested it might be accounted for by interference from the fluoride levels in the EPA reference samples. For the 1/80 to 6/80 period, the bias is much larger for the low concentration samples than for the higher concentration samples. This observation is not consistent with the fluoride explanation.

The only other significant change with time is for nitrate in Table 9, where the precision value has increased. An orthophosphate precision value in Table 11 also appears to have increased but this is explained by the fact that the samples had a lower concentration value.

Tables 12-22 present the analysis of the replicate (split or duplicate) samples. Every 25th precipitation sample, or the first one thereafter having sufficient volume, is filtered into two LPE containers to provide the replicate set. The RMS percent deviation of these replicate analyses provides a measure of precision at CAL which can be compared to the precision column for the corresponding Tables 1-11. The RMS percent deviation values in Tables 12 and 13 do indicate that the precision values for pH and conductivity have not changed significantly with time (1980 data versus 1979 data in Table 12 or 13), as would be implied with the limited data in Tables 1 and 2.

A more straight-forward procedure to estimate precision is to do multiple measurements on a standard solution or even a precipitation sample. However, an advantage of using split samples for this quality control procedure is that all the various types of precipitation samples are randomly being included in the study and also data are accumulated on essentially every day of ion analysis instead of a few days a year.

Tables 23-28 present results for the analytical blanks for the two time periods. The water blanks, Tables 23-24, consist of 50 mL aliquots of the deionized water used at CAL. The water blank samples, stored at room temperature in LPE bottles, are not filtered but are otherwise handled as though they were a precipitation sample. The data in Tables 23 and 24 display the pattern we have come to expect, namely most of the values are at detection limit.

The filter blank data are presented in Tables 25-26. Filter blank solutions consist of aliquots collected on a weekly basis during a normal filtration procedure of NADP samples with 0.45  $\mu\text{m}$  membrane filters (Millipore HA). Since 3/80 the blanks have consisted of two sequential 50 mL aliquots of deionized water collected after the filter has been leached with 200 mL of deionized water. From 1/79 to 3/80 the procedure was to collect only a single 50 mL aliquot. The data in Tables 25-26 show that the ions likely to be associated with human contamination namely Na, K, and Cl, are detectable in some of the samples, usually at levels close to the detection limit. For completeness the maximum observed values are reported in the tables to indicate the potentially highest amount of contamination to a 50 mL precipitation sample being filtered at CAL.

The median volume of a NADP precipitation sample processed at CAL is about 1000 mL. Therefore it is useful to investigate how the ion levels for the analytical blanks change with blank sample volume. Data for the first and second 50 mL filter leachate blanks, done consecutively with the same filter, are summarized in Table 25B. For the 11 pairs of data, there were 3 pairs where Na was greater than the detection limit for at least one member of the pair. For Na, the first leachate blank had a higher concentration than the

second leachate blank for all 3 pairs. The limited data in Table 25B does suggest that the filter blank values decrease with volume.

The bucket blank leachate analyses are presented in Tables 27-28. At least every other week buckets for these tests are randomly selected from the inventory of buckets and lids which are clean and ready for shipment to the sites. The bucket blank procedure is: add 50, 150, or 500 mL aliquots of deionized water to each of three buckets; pound on a lid and shake the contents so the water touches all the inside surfaces; let contents stand for about 24 hours; and finally shake the contents again and then transfer to a 60 mL LPE bottle which is processed in the same manner as a precipitation sample except that it is not filtered. Until February 1980, only a 50 mL blank was collected. It should be noted that 50 mL of water would produce a 0.03 inch deep layer of water in the bucket if uniformly distributed. However, due to ridges in the bottom, only the 500 mL aliquot provides for a complete covering of the bucket bottom with water.

A comparison of the 50 mL bucket blank data for the two time periods, Tables 27A and 28, suggests that the blank levels have increased some with time, especially for magnesium. No explanation for this increase is available. The blank levels for the 150 mL and 500 mL aliquots, Table 27B and 27C, become progressively lower. The data do not suggest a 1:1 relationship with aliquot volume. All the 90 percentile concentrations for the 500 mL blanks are at or near detection limit except for Mg.

The NADP network average concentration data are presented for the two time periods in Tables 29 and 30. These data should be useful in assessing the rationale for choosing the various parameter ranges depicted in Tables 1-22.

Also the data are useful in assessing the importance of the analytical blank data in Tables 23-28. It is important to note that the median sample volume is 1008 and 1240 mL for the two periods. The 50-500 mL volumes were selected for the analytical blanks in order to avoid having all detection limit values. The water and filter blank levels are quite insignificant in magnitude when compared to the precipitation sample averages in Tables 29-30. A comparison of the 90th percentile column in Table 27C and the 50th percentile column in Table 29 indicates that the bucket blank levels are usually low compared to the network average concentrations, except for Mg. The more useful comparison would be Table 27 versus the equivalent of Table 29 for each site. At CAL we feel that the bucket blank values above detection limit are generally associated with "people" contamination during the bucket washing and bagging process. Thus, we feel strongly that the NADP procedure of centralizing this operation was indeed a wise decision. Bucket washing at each of the field sites would lead to very difficult quality assurance problems and, in general, would probably seriously lower the quality of the precipitation data for some or most of the ions.



B. Glossary of Terms for the Tables

Accuracy	Degree of conformity of measured values with true value; accuracy includes both bias (systematic error) and precision (random error) <sup>3</sup> .
Bias	<p>Persistent positive or negative deviation of measured value from true value, expressed as <math>\frac{(\text{mean value measured} - \text{certified value})}{\text{certified value}} \times 100\%</math></p> <p>The quantity in parentheses in the bias column of the tables is the limit-of-error<sup>4</sup> in the calculated bias. If the absolute value of the bias exceeds the absolute value of this quantity, the bias is taken to be significant; conversely, if the error exceeds the bias, the bias can be taken to be insignificant.</p> <p>Significant values of the bias can often be accounted for by chemical species which interfere with the analysis of the constituent under consideration. These interfering species may be part of the chemical matrix of the standard solution used for accuracy determinations but might not be present at interfering levels in precipitation samples. In this instance no bias would follow for precipitation measurements. On the contrary, analyses which suggest no bias with the standard solution may in fact exhibit bias for precipitation samples because of the presence of some interfering chemical not part of the standard matrix.</p>
Calculated Concentration	Table 1 only - hydrogen ion activity (pH units) calculated from strong mineral acid dilutions.
Calculated Conductance	Table 2 only - calculated specific conductance for strong mineral acid dilutions; empirical (Kohlrausch) corrections made where appropriate.

Concentration	Tables 3 thru 11 only - EPA certified concentrations or dilutions thereof
Detection Limit	Lowest concentration of an analyte that the analytical process can reliably detect. Operationally it is the $2\sigma$ value for 10 determinations of the concentration of a blank solution.
Number of Analyses	Number of individual measurements
Number of Days of Analyses	Number of separate days on which individual measurements were made
Period	Time period over which analyses were performed
Precision	Degree of agreement of repeated measurements <sup>3</sup> expressed as $\pm \frac{(2 \times \text{standard deviation}) \times 100\%}{(\text{mean value})}$ For cases in which the instrumental error exceeds two times the standard deviation this quantity is substituted for the numerator in the above formula and the resulting precision is reported in parentheses (instrumental error is governed by the practical limitations of the apparatus and its output and is equal to one half of the sensitivity)
Replicate Samples	Precipitation samples which are split to provide identical samples for analysis
Sensitivity (pH and conductance only)	Minimum reported difference between measurements
Unbuffered CAL Samples	Synthetic solutions which simulate pH and specific conductance levels typical of precipitation samples

Equations:

Percent Deviation	$= \pm [(\text{value2} - \text{value1}) / (\text{value2} + \text{value1}) / 2] 100\%$
Mean Percent Deviation	$= \pm \frac{\sum  \text{percent deviation} }{n}$
Root Mean Square (RMS) Percent Deviation	$= \pm \left( \frac{\sum (\text{percent deviation}_i^2)}{n} \right)^{\frac{1}{2}}$

C. Data Tables

1. Tables for Accuracy

Table 1. Hydrogen Ion Analysis - Analytical Accuracy Based on Unbuffered CAL Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Calculated Concentration (pH units)	Sensitivity (pH units)	Precision* (percent)	Bias* (percent)
1/79 - 12/79	14	14	3.06	±.01	± 3.0	+ 3.4(+4.1)
"	14	12	4.08	±.01	+10.1	+ 4.5(+8.6)
1/80 -	5	5	4.08	±.01	+21.1	+15.4(+15.8)
6/80	2	2	4.27	±.01	+ 6.5	+ 1.9(+ 6.6)
"	2	2	4.53	±.01	+32.4	+28.1(+24.8)

\*For hydrogen ion activities

Table 2. Conductance Analysis - Analytical Accuracy Based on Unbuffered CAL Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Calculated Conductance (µS/cm)	Sensitivity (µS/cm)	Precision (percent)	Bias (percent)
1/79 - 12/79	9	9	35.5	±.1	± 9.7	+1.0(+8.1)
"	14	14	401	± 1	± 2.3	+0.6(+1.3)
1/80 -	2	2	22.9	±.10	+20.1	+19.7(+15.8)
6/80	5	5	35.5	±.10	+28.2	+17.4(+20.3)
"	2	2	40.0	±.10	+ 5.9	+ 1.6(+ 4.8)

Table 3. Calcium Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	9	6	.35	.02	+4.0	+4.4(+3.8)
"	6	5	.53	.02	+5.3	+4.3(+4.5)
"	24	15	1.45	.02	+2.6	+3.1(+2.6)
1/80 -	60	23	.53	.02	+3.7	-1.0(+3.0)
6/80	60	23	.81	.02	+3.6	+0.9(+3.9)
"	13	5	1.45	.02	+2.1	+3.8(+2.3)

Table 4. Magnesium Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	9	6	.114	.002	+3.1	+2.0(+3.3)
"	6	5	.171	.002	+2.1	+1.3(+2.8)
"	24	15	.300	.002	+2.0	-0.2(+2.1)
1/80 -	60	23	.168	.002	+3.0	+3.6(+3.7)
6/80	59	23	.180	.002	+2.5	+3.6(+2.5)
"	13	5	.300	.002	+1.4	-0.3(+1.8)

Table 5. Sodium Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	5	2	.157	.004	+1.4	+0.4(+2.4)
"	6	5	.314	.004	+5.0	-0.2(+4.2)
"	5	4	.472	.004	+2.6	-0.2(+3.0)
"	25	14	.500	.004	+1.5	-0.1(+1.9)
1/80 -	12	5	.500	.004	+1.8	-0.6(+2.0)
6/80	60	25	.820	.004	+1.3	-0.2(+1.8)
"	60	25	.932	.004	+1.1	-0.5(+2.6)

Table 6. Potassium Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	5	2	.033	.004	+10.7	-7.4(+6.7)
"	6	5	.067	.004	+ 6.8	-1.1(+5.0)
"	3	3	.100	.004	+ 2.3	+0.9(+2.8)
"	29	15	.270	.004	+ 3.1	+0.5(+2.7)
1/80 -	59	25	.196	.004	+ 3.2	-3.0(+2.7)
6/80	59	25	.210	.004	+ 2.6	-0.2(+2.4)
"	11	5	.270	.004	+ 3.7	-0.7(+3.0)

Table 7. Ammonium Analysis - Analytical Accuracy Based on EPA Nutrient Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	24	18	.30	.02	$\pm 10.1$	+1.1(+6.2)
"	23	17	2.05	.02	$\pm 3.3$	+0.1(+2.7)
1/80 -	36	18	.30	.02	$\pm 12.9$	-1.0(+7.4)
6/80	38	19	2.05	.02	$\pm 2.9$	-0.4(+2.5)

Table 8. Sulfate Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	31	26	1.20	.10	$\pm (2.1)$	+0.1(+1.9)
"	24	22	5.12	.10	$\pm 1.7$	+0.3(+2.1)
"	18	16	10.24	.10	$\pm 1.2$	-0.2(+1.8)
1/80 -	57	32	.72	.10	$\pm 13.5$	-2.2(+7.8)
6/80	74	36	9.36	.10	$\pm 3.8$	+0.7(+3.1)

Table 9. Nitrate Analysis - Analytical Accuracy Based on EPA Nutrient Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	38	26	.49	.02	$\pm (5.1)$	+1.6(+3.6)
"	40	26	1.68	.02	$\pm 3.6$	-0.5(+2.8)
1/80 -	51	26	.49	.02	$\pm 15.1$	-3.2(+8.4)
6/80	53	26	1.68	.02	$\pm 10.6$	+2.2(+6.5)

Table 10. Chloride Analysis - Analytical Accuracy Based on EPA Mineral Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	3	3	1.41	.05	+ 1.4	+ 4.6(+2.0)
"	21	16	2.81	.05	+ 2.1	+ 4.4(+2.2)
"	19	16	4.32	.05	+ 1.2	+ 4.9(+1.9)
1/80 -	22	10	.35	.05	+11.6	+10.4(+0.1)
6/80	22	9	1.84	.05	+ 4.5	-02.4(+3.4)

Table 11. Orthophosphate Analysis - Analytical Accuracy Based on EPA Nutrient Quality Control Samples

Period	Number of Analyses	Number of Days of Analyses	Concentration (mg/L)	Typical Detection Limit (mg/L)	Precision (percent)	Bias (percent)
1/79 - 12/79	16	14	.058	.003	+ (3.4)	+0.6(+ 2.4)
"	17	14	.080	.003	+ 4.0	-1.4(+ 3.1)
1/80 -	24	11	.016	.003	+30.1	-8.8(+15.0)
6/80	21	12	.099	.003	+ 9.6	-3.7(+ 6.8)

2. Tables for Precision from Replicate Samples

Table 12. Hydrogen Ion Analysis - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (pH units)	Median Concentration (pH units)	Sensitivity (pH units)	RMS Percent Deviation*	Mean Percent Deviation*
1/79 - 12/79	34	3.63-4.99	4.29	$\pm .01$	$\pm 2.8$	$\pm 1.4$
"	11	5.00-6.56	5.71	$\pm .01$	$\pm 17.4$	$\pm 8.3$
1/80 -	40	3.88-4.99	4.42	$\pm .01$	$\pm 3.2$	$\pm 2.1$
6/80	13	5.00-7.11	5.57	$\pm .01$	$\pm 12.8$	$\pm 6.9$

\*For hydrogen ion activities

Table 13. Conductance Analysis - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range ( $\mu\text{S/cm}$ )	Median Concentration ( $\mu\text{S/cm}$ )	Sensitivity ( $\mu\text{S/cm}$ )	RMS Percent Deviation	Mean Percent Deviation
1/79 -	11	6.3-9.9	8.2	$\pm .01$	$\pm 2.9$	$\pm 1.2$
12/79	33	10.0-99.9	24.9	$\pm .1$	$\pm 4.0$	$\pm 1.6$
"	1	100-117	117	$\pm 1$	$\pm 0.0$	$\pm 0.0$
1/80 -	11	3.5- 9.9	6.8	$\pm .01$	$\pm 1.8$	$\pm 0.9$
6/80	42	10.0-62.6	24.2	$\pm .10$	$\pm 1.7$	$\pm 1.3$

Table 14. Calcium - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	27	<.20	.10	.02	$\pm 6.6$	$\pm 3.2$
"	18	.20-1.60	.41	.02	$\pm 0.5$	$\pm 0.1$
1/80 -	26	<.20	.08	.02	$\pm 13.7$	$\pm 6.3$
6/80	26	.20-2.55	.34	.02	$\pm 2.9$	$\pm 1.8$

Table 15. Magnesium - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	12	<.020	.015	.002	+4.6	+1.8
"	33	.020-.302	.045	.002	+2.2	+1.2
1/80 -	13	<.020	.015	.002	+6.5	+3.5
6/80	40	.020-.669	.051	.002	+1.7	+0.9

Table 16. Sodium - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	3	<.040	.038	.004	+3.8	+3.1
"	42	.040-1.89	.183	.004	+2.7	+1.3
1/80 -	4	<.040	.024	.004	+5.8	+4.3
6/80	49	.040-11.716	.238	.004	+1.4	+0.9

Table 17. Potassium - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	26	<.040	.020	.004	+6.5	+4.7
"	19	.040-.341	.083	.004	+4.3	+2.4
1/80 -	32	<.040	.021	.004	+8.3	+6.0
6/80	19	.040-.468	.057	.004	+3.0	+2.2



Table 18. Ammonium - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	15	<.20	.08	.02	+5.0	+1.7
"	29	.20-1.54	.38	.02	+5.6	+2.2
1/80 -	15	<.20	.12	.02	+2.2	+0.8
6/80	24	.20-1.69	.51	.02	+1.7	+1.0

Table 19. Sulfate - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	5	<1.00	.88	.10	+2.6	+1.1
"	40	1.00-14.60	2.75	.10	+2.5	+1.6
1/80 -	12	<1.00	.59	.10	+9.0	+5.4
6/80	41	1.00-9.60	2.65	.10	+2.3	+1.5

Table 20. Nitrate - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	1	<.20	.10	.02	0.0	0.0
"	44	.20-7.85	1.38	.02	+ 2.8	+ 1.3
1/80 -	4	<.20	.15	.02	+16.2	+11.4
6/80	46	.20-4.92	1.80	.02	+ 2.2	+ 1.4

Table 21. Chloride - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	37	<.50	.19	.05	<u>+14.8</u>	<u>+10.5</u>
"	6	.50-1.75	.92	.05	<u>+ 3.8</u>	<u>+ 2.3</u>
1/80 -	40	<.50	.24	.05	<u>+14.4</u>	<u>+10.5</u>
	10	.50-1.85	.92	.05	<u>+ 1.5</u>	<u>+ 0.8</u>

Table 22. Orthophosphate - Analytical Precision Based on Replicate Sample Analyses

Period	Number of Analyses	Concentration Range (mg/L)	Median Concentration (mg/L)	Typical Detection Limit (mg/L)	RMS Percent Deviation	Mean Percent Deviation
1/79 - 12/79	2	<.030	.006	.003	0.0	0.0
"	1	.030-.338	.338	.003	0.0	0.0
1/80 -	3	<.030	.010	.003	<u>+18.2</u>	<u>+10.5</u>
	1	.030-.055	.055	.003	<u>+ 1.8</u>	<u>+ 1.8</u>

3. Tables for Analytical Blanks

Table 23. Water Blank Analyses for the Period  
1/80 through 6/80

Ion	Number of Analyses	Number of Days of Analyses	Typical Detection Limit (mg/L)	Frequency of Detection Limit (percent)	Percentile (mg/L)		Maximum (mg/L)
					90th	95th	
Ca	6	6	.02	100	<.02	<.02	<.02
Mg	6	6	.002	100	<.002	<.002	<.002
Na	6	6	.004	100	<.004	<.004	<.004
K	6	6	.004	83	.005	.005	.005
NH <sub>4</sub>	6	6	.02	100	<.02	<.02	<.02
SO <sub>4</sub>	6	6	.10	83	.20	.20	.20
NO <sub>3</sub>	6	6	.02	100	<.02	<.02	<.02
Cl	6	6	.05	100	<.05	<.05	<.05
PO <sub>4</sub>	6	6	.003	100	<.003	<.003	<.003

Table 24. Water Blank Analyses for the Period  
1/79 through 12/79

Ion	Number of Analyses	Number of Days of Analyses	Typical Detection Limit (mg/L)	Frequency of Detection Limit (percent)	Percentile (mg/L)		Maximum (mg/L)
					90th	95th	
Ca	10	10	.02	100	<.02	<.02	<.02
Mg	10	10	.002	100	<.002	<.002	<.002
Na	10	10	.004	90	.012	.012	.012
K	10	10	.004	100	<.004	<.004	<.004
NH <sub>4</sub>	10	10	.02	100	<.02	<.02	<.02
SO <sub>4</sub>	10	10	.10	100	<.10	<.10	<.10
NO <sub>3</sub>	10	10	.02	100	<.02	<.02	<.02
Cl	10	10	.05	100	<.05	<.05	<.05
PO <sub>4</sub>	10	10	.003	100	<.003	<.003	<.003

Table 25. Filter Blank Leachate Analyses<sup>a</sup> for the Period 1/80 through 6/80

A. Initial 50 mL Leachate Blanks

Ion	Number of Analyses	Number of Days of Analyses	Typical Detection Limit (mg/L)	Frequency of Detection Limit (percent)	Percentile		Maximum (mg/L)
					90th (mg/L)	95th	
Ca	32	32	.02	100	<.02	<.02	<.02
Mg	32	32	.002	100	<.002	<.002	<.002
Na	32	32	.004	75	.012	.015	.037
K	32	32	.004	97	<.004	<.004	.006
NH <sub>4</sub>	32	32	.02	100	<.02	<.02	<.02
SO <sub>4</sub>	32	32	.10	81	.25	.30	.35
NO <sub>3</sub>	32	32	.02	88	.05	.07	.15
Cl <sup>-</sup>	32	32	.05	91	<.05	.10	.12
PO <sub>4</sub>	32	32	.003	100	<.003	<.003	<.003

<sup>a</sup>After filters are pre-leached with 200 mL of water.

B. Paired Consecutive 50 mL Leachate Blanks

Ion	Number of Paired Analyses	Number of Pairs with at least 1 Concentration > Detection Limit			
		First > Second	First = Second	First < Second	Total
Ca	11	-	-	-	0
Mg	11	-	-	-	0
Na	11	3	0	0	3
K	11	-	-	-	0
NH <sub>4</sub>	11	-	-	-	0
SO <sub>4</sub>	11	2	0	0	2
NO <sub>3</sub>	11	2	0	0	2
Cl <sup>-</sup>	11	1	1	1	3
PO <sub>4</sub>	11	-	-	-	0

Table 26. Filter Blank Leachate Analyses<sup>a</sup> for the Period 1/79 through 12/79

A. Initial 50 mL Leachate Blanks

Ion	Number of Analyses	Number of Days of Analyses	Typical Detection Limit (mg/L)	Frequency of Detection Limit (percent)	Percentile		Maximum (mg/L)
					90th (mg/L)	95th	
Ca	348	282	.02	96	<.02	<.02	.09
Mg	348	282	.002	96	<.002	<.002	.012
Na	348	282	.004	60	.016	.021	.283
K	348	282	.004	72	.006	.008	.194
NH <sub>4</sub>	348	282	.02	95	<.02	<.02	.13
SO <sub>4</sub>	348	282	.10	95	<.10	<.10	.30
NO <sub>3</sub>	348	282	.02	97	<.02	<.02	.15
Cl	348	282	.05	92	<.05	.07	.60
PO <sub>4</sub>	348	282	.003	100	<.003	<.003	<.003

<sup>a</sup>50 mL leachate blanks, collected after pre-leaching the filter with 200 mL of water.

Table 27. Bucket Blank Leachate Analyses for the Period 1/80 through 6/80

A. 50 mL Leachate Blanks

Ion	Number of Analyses	Number of Days of Analyses	Typical Detection Limit (mg/L)	Frequency of Detection Limit (percent)	Percentile (mg/L)		Maximum (mg/L)
					90th	95th	
Ca	17	17	.02	65	.12	.12	.12
Mg	17	17	.002	29	.061	.112	.112
Na	17	17	.004	59	.228	.780	.780
K	17	17	.004	76	.007	.018	.018
NH <sub>4</sub>	16	16	.02	75	.03	.04	.04
SO <sub>4</sub>	17	17	.10	82	.30	.40	.40
NO <sub>3</sub>	17	17	.02	76	.13	2.70	2.70
Cl	16	16	.05	63	.13	.17	.17
PO <sub>4</sub>	16	16	.003	100	<.003	<.003	<.003

B. 150 mL Leachate Blanks

Ion	Number of Analyses	Number of Days of Analyses	Typical Detection Limit (mg/L)	Frequency of Detection Limit (percent)	Percentile (mg/L)		Maximum (mg/L)
					90th	95th	
Ca	12	12	.02	75	.04	.05	.05
Mg	12	12	.002	33	.038	.055	.055
Na	12	12	.004	67	.018	.107	.107
K	12	12	.004	92	<.004	.032	.032
NH <sub>4</sub>	12	12	.02	92	<.02	.03	.03
SO <sub>4</sub>	12	12	.10	83	.15	.25	.25
NO <sub>3</sub>	12	12	.02	75	.11	.22	.22
Cl	12	12	.05	75	.06	.11	.11
PO <sub>4</sub>	12	12	.003	92	<.003	.012	.012

C. 500 mL Leachate Blanks

Ion	Number of Analyses	Number of Days of Analyses	Typical Detection Limit (mg/L)	Frequency of Detection Limit (percent)	Percentile (mg/L)		Maximum (mg/L)
					90th	95th	
Ca	12	12	.02	83	.03	.04	.04
Mg	12	12	.002	33	.017	.031	.031
Na	12	12	.004	83	.005	.065	.065
K	12	12	.004	100	<.004	<.004	<.004
NH <sub>4</sub>	12	12	.02	92	<.02	.03	.03
SO <sub>4</sub>	12	12	.10	83	.15	.15	.15
NO <sub>3</sub>	12	12	.02	92	<.02	.06	.06
Cl	12	12	.05	75	.06	.06	.06
PO <sub>4</sub>	12	12	.003	100	<.003	<.003	<.003

Table 28. Bucket Blank Leachate Analyses<sup>a</sup> for the Period 1/79 through 12/79

Ion	Number of Analyses	Number of Days of Analyses	Typical Detection Limit (mg/L)	Frequency of Detection Limit (percent)	Percentile		Maximum (mg/L)
					90th (mg/L)	95th	
Ca	12	12	.02	91	<.02	.03	.03
Mg	12	12	.002	75	.004	.007	.007
Na	12	12	.004	58	.019	.028	.028
K	12	12	.004	66	.010	.026	.026
NH <sub>4</sub>	12	12	.02	50	.23	.32	.32
SO <sub>4</sub>	12	12	.10	100	<.10	<.10	<.10
NO <sub>3</sub>	12	12	.02	66	.15	.25	.25
Cl	12	12	.05	100	<.05	<.05	<.05
PO <sub>4</sub>	12	12	.003	100	<.003	<.003	<.003

<sup>a</sup>50 mL leachate blanks.

4. Network Averages for the Chemical Parameters

Table 29. NADP Precipitation Chemistry Network Statistics for Wet-Deposition-Only Samples with Lab Type 'W' (i.e., Volume >35 mL) for Period: 1/80-6/80

Ion	Number of Analyses	Typical Detection Limit (mg/L)	Chemical Concentrations (mg/L)				
			Minimum	10th Percentile	50th Percentile	90th Percentile	Maximum
Ca	1055	.02	<.02	.05	.18	.75	11.93
Mg	1055	.002	<.002	.012	.037	.133	1.482
Na	1055	.004	<.004	.039	.216	1.418	29.290
K	1055	.004	<.004	.008	.028	.099	8.780
NH <sub>4</sub>	1055	.02	<.02	<.02	.20	.84	10.00
SO <sub>4</sub>	1055	.10	<.10	.70	2.40	5.73	28.30
NO <sub>3</sub>	1055	.02	<.02	.32	1.54	4.10	21.76
Cl	1054	.05	<.05	.10	.26	.82	8.02
PO <sub>4</sub>	1055	.003	<.003	<.003	<.003	<.003	4.709

  

Parameter and Units	Number of Analyses	Sensitivity	Minimum	Percentile			Maximum
				10th	50th	90th	
pH in pH Units	1055	+0.01	3.26	4.06	4.51	5.91	7.64
Conductance in $\mu$ S/cm	1055	+ .1	2.2	7.6	21.6	49.1	217
Volume in mL					1008		



Table 30. NADP Precipitation Chemistry Network Statistics for Wet-Deposition-Only Samples with Lab Type 'W' (i.e., Volume >35 mL) for Period: 1/79-12/79

Ion	Number of Analyses	Typical Detection Limit (mg/L)	Chemical Concentrations (mg/L)				Maximum
			Minimum	10th Percentile	50th Percentile	90th Percentile	
Ca	1147	.02	<.02	.05	.18	.87	6.84
Mg	1147	.002	<.002	.013	.041	.181	1.325
Na	1146	.004	.009	.050	.228	1.318	23.129
K	1147	.004	<.004	.009	.031	.131	4.570
NH <sub>4</sub>	1147	.02	<.02	<.02	.22	.92	25.00
SO <sub>4</sub>	1147	.10	<.10	.85	2.60	6.87	40.40
NO <sub>3</sub>	1147	.02	<.02	.39	1.35	3.60	16.30
Cl	1147	.05	<.05	.07	.20	.92	15.96
PO <sub>4</sub>	1147	.003	<.003	<.003	<.003	<.003	10.000

  

Parameter and Units	Number of Analyses	Sensitivity	Minimum	Percentile			Maximum
				10th	50th	90th	
pH in pH Units	1147	<u>+.01</u>	3.50	4.00	4.52	5.94	7.79
Conductance in $\mu$ S/cm	1147	<u>+.1</u>	2.1	8.2	20.6	53.1	193
Volume in mL					1240		

#### IV. Results of USGS/NADP Blind Audit Program<sup>a</sup>

The blind audit portion of the USGS/NADP Quality Assurance Program began with the distribution of samples to the field in October 1979. This part of the quality assurance program depends on the cooperation of NADP site operators for the submission of known reference material samples to the Central Analytical Laboratory (CAL). The quality assurance or blind audit samples are submitted during those one-week periods when no wet deposition occurs at a cooperating site. Since samples are only submitted during dry weeks, there is no way to precisely control the number of samples received by the laboratory in a given period. The goal of the program is to achieve a submission of one reference sample for each two-week period, thus insuring that each batch of analyses that go through CAL contains one audit sample. To date this level has not been achieved. The analytical values determined by CAL are compared to calculated or expected values for the given reference samples. The term calculated value is used since the reference materials currently employed by the program are quantitative dilutions of Standard Reference Water Samples employed by the Geological Survey in their methods development and quality assurance investigations.

Examination of the following tables indicates that the CAL analysis compared extremely well with the expected values from the reference samples. The sample submission scheme includes potential errors from contamination sources attributable to the field transfer of reference materials and CAL's

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<sup>a</sup>This section of the report was provided by L. J. Schroder of the USGS, Denver, CO.

cleaning of the sample container. The difference between the CAL analysis and the expected values are minimal.

Two National Bureau of Standards Reference Samples were analyzed by CAL. CAL analysis compared well with the NBS reported means except for acidity. The method used by CAL does not differ substantially from the method reportedly used by NBS. The probable reason for the difference between CAL acidity values and reported NBS values has not been determined at this time.

Table 1. Analytical Results of National Bureau of Standards Simulated Precipitation Sample 910000 by the Central Analytical Laboratory.

Constituent	NBS Reported <sup>1</sup> Mean mg/L	NBS Reported <sup>1</sup> Standard Deviation mg/L	CAL Reported mg/L
pH	5.03	0.24	5.06
Specific Conductance	13.20 $\mu$ S/cm	.08 $\mu$ S/cm	10.8 $\mu$ S/cm
Acidity <sup>2</sup>	17.38 $\mu$ eq/L	.45 $\mu$ eq/L	10.9 $\mu$ eq/L
SO <sub>4</sub> as S	.260	.003	.28
NH <sub>4</sub> as N	.166	.008	.17
NO <sub>3</sub> as N	.186	.0005	.19
Cl	.908	.008	.98
F <sup>2</sup>	.154	.002	.14
Ca	.248	.0014	.24
Mg	.056	.0006	.056
Na	.284	.0050	.282
K	.156	.001	.146

<sup>1</sup>Results reported are NBS internal determinations. (n=7)

<sup>2</sup>Constituent not routinely determined by CAL for the NADP.

Table 2. Analytical Results of National Bureau of Standards Simulated Precipitation Sample 920000, 930000, and 940000 by the Central Analytical Laboratory.

Constituent	NBS Reported <sup>1</sup> Mean mg/L	NBS Reported <sup>1</sup> Standard Deviation mg/L	CAL Reported mg/L
Sample 920000			
pH	4.35	.12	4.28
Specific Conductance	43.49 $\mu\text{S/cm}$	.08 $\mu\text{S/cm}$	39.1 $\mu\text{S/cm}$
Acidity <sup>2</sup>	66.02 $\mu\text{eq/L}$	.75 $\mu\text{eq/L}$	86.5 $\mu\text{eq/L}$
SO <sub>4</sub> as S	.776	.08	.91
NH <sub>4</sub> as N	.514	.010	.54
NO <sub>3</sub> as N	.485	.001	.49
Cl	3.274	.014	3.29
F <sup>2</sup>	.256	.003	.24
Ca	.654	.0048	.67
Mg	.226	.0026	.230
Na	.558	.0078	.542
K	.506	.0074	.488
Sample 930000			
pH	3.91	.025	3.94
Specific Conductance	69.12 $\mu\text{S/cm}$	.20 $\mu\text{S/cm}$	51.6 $\mu\text{S/cm}$ <sup>3</sup>
Acidity <sup>2</sup>	5.90 $\mu\text{eq/2amp}$	.24 $\mu\text{eq/2amp}$	4.8 $\mu\text{eq/2amp}$
Sample 940000			
pH	3.62	.015	3.71
Specific Conductance	121.44 $\mu\text{S/cm}$	.22 $\mu\text{S/cm}$	91.3 $\mu\text{S/cm}$ <sup>3</sup>
Acidity <sup>2</sup>	9.98 $\mu\text{eq/2amp}$	.40 $\mu\text{eq/2amp}$	8.8 $\mu\text{eq/2amp}$

<sup>1</sup>Results reported are NBS internal determinations. (n=7)

<sup>2</sup>Constituent not routinely determined by CAL for the NADP.

<sup>3</sup>USGS measured specific conductance was 50.5  $\mu\text{S/cm}$  for 930000 series and 89.0  $\mu\text{S/cm}$  for 940000 series.

Table 3. Analytical Results by the Central Analytical Laboratory of Field Submitted Samples prepared from U.S. Geological Survey Reference Samples.

Constituent	USGS Calculated Concentration mg/L	CAL Reported Concentration mg/L	USGS Calculated Concentration mg/L	CAL Reported Concentration mg/L
Ca	2.44	2.48	2.67	2.55
Mg	.56	.570	.67	.67
Na	1.45	1.393	2.20	2.10
K	.32	.376	.44	.47
NH <sub>4</sub>	<sup>1</sup> / <sub>---</sub>	<.02	<sup>1</sup> / <sub>---</sub>	<.02
NO <sub>3</sub>	.07	.25	.002	<.02
Cl	1.40	1.40	.88	.90
SO <sub>4</sub>	3.52	3.76	5.97	6.23
PO <sub>4</sub>	.11	.155	.10	.054
Specific Conductance (μS/cm)	23.7	26.3	30.	32.8
pH (units)	<sup>1</sup> / <sub>---</sub>	7.06	<sup>1</sup> / <sub>---</sub>	7.11
CAL ID Number	2366		1815	
Date Off	040880		010280	

<sup>1</sup>Not reported.

Table 3 Continued.

Constituent	USGS Calculated Concentration mg/L	CAL Reported Concentration mg/L	USGS Calculated Concentration mg/L	CAL Reported Concentration mg/L
Ca	2.67	2.68	1.16	1.16
Mg	.67	.682	.20	.199
Na	2.20	2.361	.32	.351
K	.44	.650	.10	.178
NH <sub>4</sub>	1 ---	<.02	1 ---	<.02
NO <sub>3</sub>	.002	<.02	1 ---	<.02
Cl	.88	.86	.17	.28
SO <sub>4</sub>	5.97	6.66	1.35	1.43
PO <sub>4</sub>	.10	.626	1 ---	<.003
Specific Conductance ( $\mu$ S/cm)	30.0	36.3	9.7	10.8
pH (units)	1 ---	7.28	1 ---	6.84
CAL ID Number	2545		2505	
Date Off	042980		042280	
-----				
Ca	2.32	2.35	4.80	4.88
Mg	.40	.396	1.03	1.016
Na	.64	.695	4.95	6.317
K	.18	.242	.34	.306
NH <sub>4</sub>	1 ---	<.02	1 ---	<.02
NO <sub>3</sub>	1 ---	<.02	<.10	<.02
Cl	.34	.39	3.87	4.01
SO <sub>4</sub>	2.70	2.94	9.6	10.97

Table 3 Continued.

Constituent	USGS Calculated Concentration mg/L	CAL Reported Concentration mg/L	USGS Calculated Concentration mg/L	CAL Reported Concentration mg/L
PO <sub>4</sub>	1 ---/	<.003	.10	<.003
Specific Conductance (μS/cm)	19.3	20.7	53.	67.9
pH (units)	1 ---/	7.12	1 ---/	7.46
CAL ID Number	2806		2748	
Date Off	060380		052780	
-----				
Ca	1.16	1.20		
Mg	.20	.200		
Na	.32	.355		
K	.10	.104		
NH <sub>4</sub>	1 ---/	<.02		
NO <sub>3</sub>	1 ---/	<.02		
Cl	.17	.27		
SO <sub>4</sub>	1.35	1.80		
PO <sub>4</sub>	1 ---/	<.003		
Specific Conductance (μS/cm)	9.7	10.5		
pH (units)	1 ---/	6.81		
CAL ID Number	2954			
Date Off	062480			



Table 4. Differences of CAL Reported Results and USGS Calculated Concentration for the Blind Audit Program<sup>1</sup>.

Constituent	Range of Differences mg/L	Average Absolute Difference mg/L	Maximum Absolute Difference mg/L	Average of USGS Recommended Values mg/L
Ca	-0.12 to 0.08	0.05	0.12	2.71
Mg	-0.01 to 0.01	0.01	0.01	0.60
Na	-0.10 to 1.37	0.30	1.37	2.07
K	-0.03 to 0.21	0.05	0.21	0.30
Cl	-0.16 to 0.14	0.08	0.16	1.39
SO <sub>4</sub>	+0.08 to 1.37	0.47	1.37	4.96

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<sup>1</sup>Insufficient data available for NH<sub>4</sub>, NO<sub>3</sub>, PO<sub>4</sub>, pH, and Specific Conductance.

V. CAL Staff

As of March, 1980, the following ISWS employees contributed a fraction of their time to the CAL project.

<u>Name</u>	<u>Activity</u>
Van Bowersox	Data Manager
Susan Engroff	Student Assistant
Florence F. McGurk	Chemical Analyst
Mark E. Peden	Laboratory Manager
Sara Reed	Student Assistant
Herminio Reyes	Student Assistant
Richard G. Semonin	Project Co-Principal Investigator
Loretta M. Skowron	Chemical Analyst
Michael Slater	Chemical Analyst
Randall K. Stahlhut	Computer Programmer
Gary J. Stensland	CAL Director and Project Co-Principal Investigator

Other ISWS support staff members contribute to the project, including those in graphic arts, keypunching, the machine shop, the electronics shop, and typing.

VI. References

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