QUALITY ASSURANCE REPORT
NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
1986

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

A Cooperative Research Program of the
State Agricultural Experiment Stations
and other Federal, State and Private
Research Organizations • IR-7

A contribution to the
Task Group on Deposition Monitoring
Lead Agency: U.S. Geological Survey

The National Atmospheric Deposition Program (NADP) was organized in 1978 by the North Central Region of the State Agricultural Experiment Stations as Project NC-141 to address the problem of atmospheric deposition and its effects on agriculture, forest, rangelands, and fresh water streams and lakes. In 1982 the program was endorsed by all four regions of the State Agricultural Experiment Stations and subsequently became Interregional Project IR-7.

The assessment of the linkage between environmental effects and atmospheric deposition requires a knowledge of geographical patterns of the chemical composition and flux of deposition on a national scale. To establish long term trends in composition and flux it is necessary that these measurements be carried out for a period of ten years or longer. In response to these needs, in 1978 the National Atmospheric Deposition Program established a regional atmospheric deposition monitoring network with national coverage. In 1982, the federally-supported National Acid Precipitation Assessment Program (NAPAP) was established to provide broadened support for research into the causes and effects of acid deposition. This program includes research, monitoring and assessment activities that emphasize the timely development of a firm scientific basis for decision making. As a result of its experience in designing, organizing and operating a national scale monitoring network, NADP was asked in 1982 to assume responsibility for coordinating the operation of the National Trends Network (NTN) of NAPAP. Since NADP and NTN had common siting criteria and operational procedures as well as sharing a common analytical laboratory, the networks were merged with the designation NADP/NTN. As a result of NAPAP support, approximately 50 additional sites administered by the U.S. Geological Survey were added to the network. In addition to the State Agricultural Experiment Stations, NADP research and monitoring is now supported as part of NAPAP by the Department of Agriculture, the Department of the Interior, the Environmental Protection Agency, the Department of Commerce and the Department of Energy. Additional support is provided by various state agencies, public utilities and industry.

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Laboratory Operations
Central Analytical Laboratory
January 1986 through December 1986

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I. INTRODUCTION

This Quality Assurance (QA) Report for the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) for 1986 is the fourth in a series of reports documenting the progress and results of the QA program.

The NADP/NTN Review Team from Subcommittees 2 and 3 audited the laboratory and data management groups in early January and made suggestions which were implemented as soon as conditions permitted.

This report follows the format established in the 1978-1983 report, and used again for the 1984-1985 report. Section II documents changes which took place as a result of the audit as well as improvements in laboratory operations. The laboratory blank data follow, with changes explained. The number of bucket blanks was reduced because upright and 500 milliliter inverted samples exhibited little or no contamination (Section III). Quality control check samples (QCS) continued to be analyzed so that a better assessment of bias and precision could be made. In 1986, a monthly schedule was established for the plotting of control charts. These charts are now on file with the analyst as well as in the quality assurance office (Section IV). The internal blind program was expanded and formalized with the introduction of National Bureau of Standards Simulated Rainwater samples submitted on a weekly basis. The data from the analyses of these samples augment the QCS bias and precision data. Replicate analysis of A and B samples was changed to a blind 0 and Q split system (Section IV). Section V discusses the reanalysis process and documents the changes that took place during 1986. A report of the CAL performance in external quality assurance audits and interlaboratory testing programs shows the validity of the quality assurance program (Section VI). Finally, an overall assessment of the performance of the CAL during 1986 is summarized in Section VII.

II. LABORATORY QUALITY ASSURANCE PROGRAM

A. GENERAL DESCRIPTION

The QA program changes which occurred in 1986 were minimal compared to those put into place in previous years. The new laboratory facility, with minor modifications, provided the needed space for sample processing and storage as well as analysis. In September of 1986, several members of the CAL staff moved their offices from the laboratory building to a new, shared 5,000-square-foot office building next door. The move created additional space for laboratory analysis. The analytical methods employed have remained the same as at the end of 1985 (Table II-1), and hence the sample processing flowchart for 1986 is the same as the May-December 1985 flowchart (Figure II-1) in the previous report (1). Several modifications to the existing laboratory quality assurance program were made in 1986. The number of bucket blank samples was reduced by deleting the upright weekly samples and analyzing only the 50 and 150 milliliter inverted leachates (Section III). The A-B replicates became blind 0-Q splits. The internal blind sample procedure was refined, National Bureau of Standards simulated precipitation samples were used, and a weekly submission schedule was established. The internal blind program is discussed at length in Section IV.

B. DATA AVAILABILITY

The data presented in this report, as in the previous report, have been verified by either a double entry procedure or a visual check. The data have been stored in the CAL data base and are available from the director upon request.

C. LABORATORY PERSONNEL

The laboratory staff, with one exception, remained the same as in late 1985. Sheri Uber was hired in April 1986 to assume the duties of sample processing, pH, and specific conductance from Jackie Sauer whose employment terminated on May 20, 1986. The staff continued to attend pertinent training courses and workshops. Table II-2 alphabeticaly lists the laboratory personnel who participated in the project in 1986.

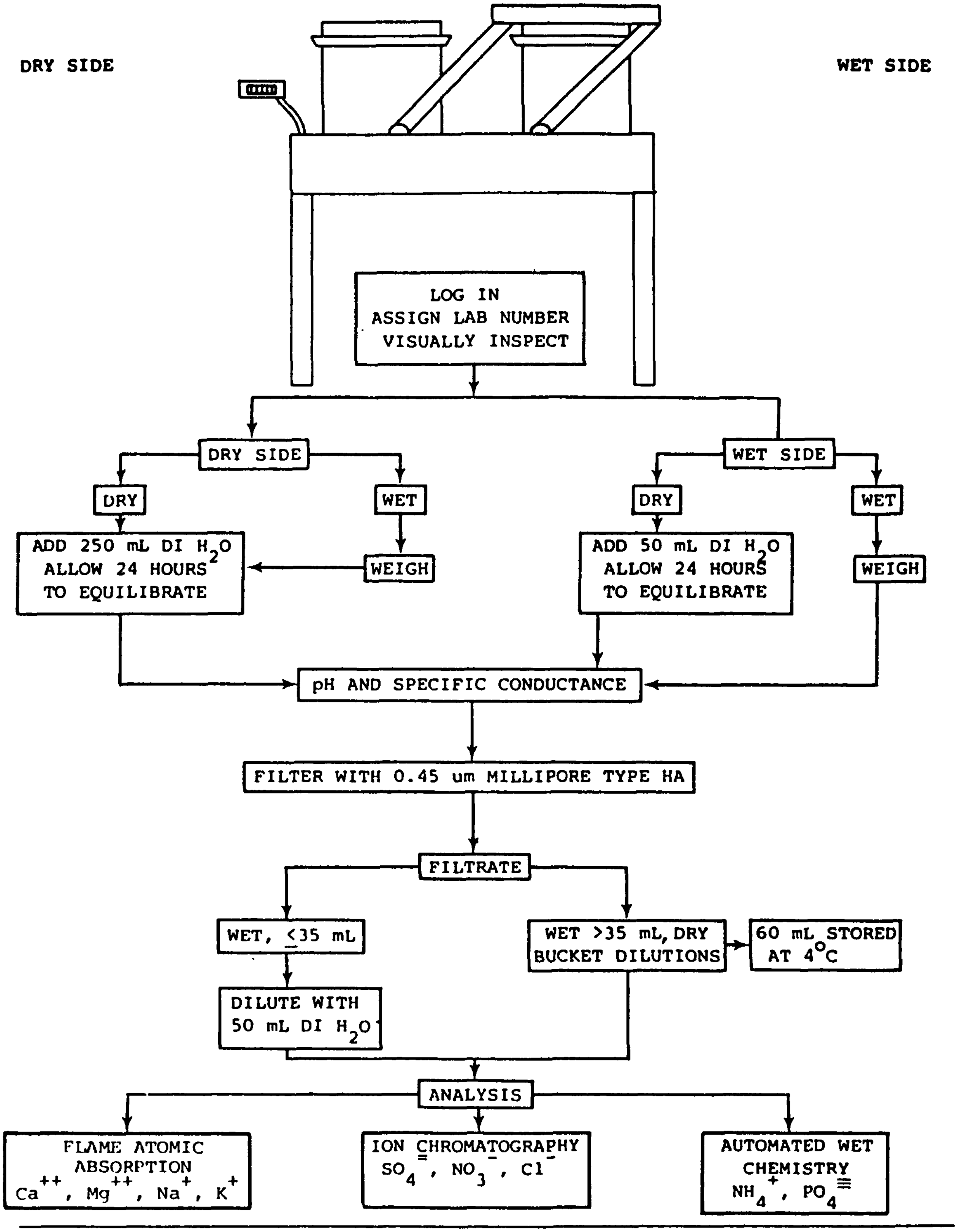

FIGURE II-1. Sample processing flowchart for January 1986 through December 1986.

TABLE II-1 Method Detection Limits For The Analysis Of Precipitation Samples For 1986.

Analyte	Method[a]	Method Detection Limit (MDL) mg/L	Dates
Calcium	Flame Atomic Absorption	0.009	1/86 - 12/86
Magnesium	Flame Atomic Absorption	0.003	1/86 - 12/86
Sodium	Flame Atomic Absorption	0.003	1/86 - 12/86
Potassium	Flame Atomic Absorption	0.003	1/86 - 12/86
Ammonium	Automated Phenate, Colorimetric	0.02	1/86 - 12/86
Sulfate	Ion Chromatography	0.03	1/86 - 12/86
Nitrate	Ion Chromatography	0.03	1/86 - 12/86
Chloride	Ion Chromatography	0.03	1/86 - 12/86
Ortho-phosphate	Automated Ascorbic Acid, Colorimetric	0.003 0.01	1/86 - 2/86 2/86 - 12/86

[a] For a complete method description, see Methods for Collection and Analysis of Precipitation, Peden et al.(2), March 1986.

TABLE II-2 Central Analytical Laboratory (CAL) Analytical Staff Personnel Summary - 1986

STAFF MEMBER/JOB FUNCTION (month, year)[a]	PERIOD OF SERVICE JFMAMJJASOND
Beth Allhands Sample Receipt and Processing (February, 1984)	————————————
Sue Bachman Ion Chromatography (August, 1980)	————————————
Brigita Demir SO_4, NO_3, Cl (September, 1981)	————————————
Pat Dodson Sample Processing (September, 1980)	————————————
Clarence Dunbar Sample Receipt and Processing (July, 1981)	————————————
Theresa Eckstein Sample Receipt (March, 1985)	————————————
Jacqueline Lockard Quality Assurance (October, 1982)	————————————
Mark Peden Laboratory Manager (July, 1978)	————————————
Jackie Sauer Sample Processing, pH, Specific Conductance (September,1983)	—————
Loretta Skowron Ca, Mg, Na, K (July, 1978)	————————————
Mike Slater NH4, PO_4 (September, 1979)	————————————
Sheri Uber Sample Processing, pH, Specific Conductance (April, 1986)	————————————

[a] Starting date with the CAL

III. LABORATORY BLANK DATA

The data presented in this section represent values from the analysis of deionized (DI) water used in the laboratory, deionized water left in an inverted sample collection bucket for 24 hours, and deionized water that had been filtered through a pre-leached 0.45 µm Millipore (HAWP) filter. The information obtained from these analyses is valuable in assessing the contribution of the collection/shipping container, the filter apparatus, and the sample processing procedure to the analyte concentrations measured in actual samples. The procedures used to obtain each blank sample type have been described in the NADP/NTN Quality Assurance Report for 1978-1983 (3) and elaborated upon in the report for 1984-1985 (1). The resulting data and modifications to procedures which occurred in 1986 will be presented in the following sections.

A. BUCKET LEACHATES

The high density polyethylene sampling buckets continued to be cleaned in a commercial dishwasher with deionized water used for all cycles. The lid washing procedure was revised to include a longer prewash leaching time. Since March of 1986 all new lids are soaked in deionized water for a minimum of 24 hours before being placed in the dishwasher for 1.25 hours. There they are rinsed repeatedly with deionized water. At the end of the cycle the lids are removed, excess water is shaken off, and they are placed in plastic bags and immediately sealed.

In late January the number of weekly bucket blanks was decreased from six to two. Past data clearly indicated that the samples from the upright buckets and the 500 mL sample from the inverted bucket consistently exhibited extremely low levels or no detectable amount of the analytes. Therefore these samples were eliminated from the weekly sample load. In the new procedure, two clean buckets and lids are randomly selected and used to determine container blanks. Either 50 mL or 150 mL of deionized water is poured into the test bucket, the lid is pounded on and the bucket inverted. After 24 hours these leachates are poured into DI water-washed 60 mL high density polyethylene (HDPE) bottles and the concentration of analytes determined. Figures B-1 - B-5 in Appendix B are plots of the analyte masses measured in the bucket blanks for 1986.

As in the 1984-1985 report, the plots of orthophosphate have not been included. The concentrations were below the method detection limit. This was still the case in 1986. As in previous reports, the concentrations of the measured analytes have been converted to micrograms per bucket in order to place the data for both volumes on the same plot. Mass per bucket is calculated by multiplying the analyte concentration in units of micrograms per milliliter by the sample volume in milliliters. A legend defining the symbols being used is presented with each series of analyte plots. The dashed line near the bottom of each plot represents the minimal detectable mass for that analyte.

This minimum value was determined by multiplying the MDL expressed as micrograms per milliliter by 50 mLs. For both volumes, values measured as less than the method detection limit were plotted on this line. Table B-1 in Appendix B lists the MDL mass for all of the parameters for which there are bucket blank plots.

Table III-1 summarizes the annual median masses for the 50 mL and 150 mL leachates analyzed in 1986.

TABLE III-1 1986 Median Analyte Concentrations Expressed as Mass (µg)/Bucket Found in Inverted Buckets

Analyte	**50** mL	**150** mL
Calcium	1.6	2.1
Magnesium	0.7	1.1
Sodium	1.4	2.0
Potassium	0.4	0.3
Ammonium	<1.0	<1.0
Sulfate	3.0	<1.5
Nitrate	<1.5	<1.5
Chloride	<1.5	<1.5
Ortho-phosphate	<0.5	<0.5
pH (units)[a]	6.12	5.86
µeq/bucket	0.04	0.21
Conductivity (µS/cm)	2.1	1.4

a. pH of DI water 5.66 (units) = 00218µeq/mL
50 mL x .00218/µequiv./mL = 0 .11 µeq
150mL x .00218/µequiv./mL = 0 .33 µeq

B. FILTER LEACHATES

Two weekly filter leachates continued to be collected in 1986. The leaching procedure that was in place in 1984 and 1985 continued to be used. Each filter was leached initially with 250 milliliters of deionized water. After this initial 250 milliliter leaching, a 50 mL portion of deionized water, leachate A, was poured through the filter and collected for analysis. A second 50 mL portion, leachate B, was poured through the same filter and collected. Table III-2 provides the median concentrations of the analytes found in these leachates for 1986. A more complete annual summary of the analysis of these leachates is found in Tables B-2, B-3 and B-4 in Appendix B.

As in previous reports, the data indicate that the filters are a negligible source of contamination. A few random high concentrations for several ions have caused the resulting standard deviation and precision values to be high. The median values are more representative of most of the data. This routine weekly procedure serves as an integral part of the CAL quality assurance program. A continuing effort is being made to reduce inadvertent high levels of sodium caused by human activities and the laboratory environment.

TABLE III-2 Median Analyte Concentrations Found in Filter Leachates A and B in 1986.

	Median Concentration (mg/L)		
Analyte	A	B	n[a]
Calcium	<0.009	<0.009	49
Magnesium	<0.003	<0.003	49
Sodium	0.007	<0.003	49
Potassium	<0.003	<0.003	49
Ammonium	<0.02	<0.02	47
Sulfate	<0.03	<0.03	47
Nitrate	<0.03	<0.03	47
Chloride	<0.03	<0.03	47
Orthophosphate	<0.01	<0.01	47
pH (units)	5.64	5.64	49
(µeq/L)	2.29	2.29	
Conductivity (µS/cm)	1.1	1.0	49

a. n - number of analyses

C. DEIONIZED WATER

The quality of the deionized water used throughout the laboratory area is monitored daily by checks of the specific conductance through the use of in-line conductivity meters. The complete analysis of a deionized water sample from two locations at the CAL is a vital part of the quality control program. During 1986, weekly DI samples were collected in the sample processing laboratory (Room Number 209) and the atomic absorption laboratory (Room Number 304). The deionization systems and laboratory facilities have been described in detail in the two previous Quality Assurance Reports (1,3).

Table III-3 lists the median analyte concentrations found in the deionized water used by the CAL in 1986. Tables B-5 and B-6 in Appendix B contain a more complete annual summary of the data obtained from the analysis of the laboratory deionized water.

TABLE III-3 **Median Analyte Concentration Values for Deionized Water Blanks in 1986**

Analyte	**Room 209**	**Room 304**
	Median Concentration (mg/L)	
Calcium	<0.009	<0.009
Magnesium	<0.003	<0.003
Sodium	<0.003	<0.003
Potassium	<0.003	<0.003
Ammonium	<0.02	<0.02
Sulfate	<0.03	<0.03
Nitrate	<0.03	<0.03
Chloride	<0.03	<0.03
Orthophosphate	<0.01	<0.01
pH (units)	5.64	5.68
(µieq/L)	2.29	2.09
Conductivity (µS/cm)	0.8	**1.1**
Number of analyses	45	48

D. COOPERATIVE BUCKET BLANK STUDY

In August of 1986, several members of NADP Subcommittee 2 met in Champaign to resolve an apparent bias in values reported by the CAL from the U.S. Geological Survey (USGS) blind audit program. The data used to assess this bias resulted from blind audit samples submitted by the site operators during the period from 1981-1983, 1983 being of particular interest. The positive bias calculated by the USGS for some ions was much larger than that reported by the CAL for internal quality control solutions (QCS), and the difference could not be accounted for by the analyte concentrations measured in the CAL inverted bucket blanks. One hypothesis discussed was that the Standard Reference Water Sample (SWRS) solutions used by the USGS during that time leached more from the bucket than the deionized water the CAL was using for blanks, particularly since most of the SWRS solutions were acidified with perchloric acid.

A laboratory test was designed to test this hypothesis. Three matrices were used which were similar to those used in the blind audit program in 1983. SRWS 62 was diluted 10-1 and 25-1 and sent to the Environmental Measurements Laboratory of the Department of Energy (EML). SRWS 70 was diluted 10-1 and 20-1 and sent to the CAL. SRWS 66 was diluted 20-1 and sent to both laboratories. All the dilutions were prepared by the USGS laboratory in Arvada, Colorado.

To test the hypothesis at the CAL, 21 bucket blanks were prepared using the samples provided by the USGS. The USGS formulated the three solutions in 2000 mL volumetric flasks. These dilutions were then split into two 1 liter aliquots. One of the liter aliquots was acidified to a pH of approximately 4.0 with perchloric acid. The other was left unacidified. These six bottles were shipped to the CAL. From each of the six bottles, 50, 150, and 500 mL samples were poured into three different sampling buckets, the lids were pounded on, and the buckets inverted and left to leach for 24 hours. At the same time, the CAL performed a similar leaching procedure using deionized water aliquots in three different inverted buckets. In order for the results to be comparable with data from 1983, the cleaning procedure for the buckets was modified to simulate the handwashing procedures in place at that time. At the end of the 24 hours, the samples were poured into laboratory rinsed 60 mL bottles. These bottles, as well as the original 1 liter containers, were then sent to the laboratory for routine analysis. A summary of the samples used and the CAL results are tabulated in Tables III-4 and III-5.

The raw data from both the EML and CAL laboratories were sent to the USGS, where they were analyzed using standard statistical tests. These tests indicated significant effects from matrix, volume, and acidification for some parameters. The level of sodium in the inverted bucket blanks was elevated and a corresponding anion was lacking. The sodium concentrations found in the CAL samples were much larger than those found in 1983 or ever. It was felt that this resulted from insufficient soaking of the container lids. EML found the same high Na bias and also noted a negative bias in Ca, a positive bias in Cl, and a neutralizing effect on

TABLE III-4 Sample Identification

Sample No.	Description
1	50 mL D.I. water
2	150 mL D.I. water
3	500 mL D.I. water
4	USGS SWRS # 66/20-1
5	USGS SWRS # 66/20-1 50 mL
6	USGS SWRS # 66/20-1 150 mL
7	USGS SWRS # 66/20-1 500 mL
8	USGS SWRS # 66/20-1 acidified
9	USGS SWRS # 66/20-1 acidified 50 mL
10	USGS SWRS # 66/20-1 acidified 150 mL
11	USGS SWRS # 66/20-1 acidified 500 mL
12	USGS SWRS # 70/10-1
13	USGS SWRS # 70/10-1 50 mL
14	USGS SWRS # 70/10-1 150 mL
15	USGS SWRS # 70/10-1 500 mL
16	USGS SWRS # 70/10-1 acidified
17	USGS SWRS # 70/10-1 acidified 50 mL
18	USGS SWRS # 70/10-1 acidified 150 mL
19	USGS SWRS # 70/10-1 acidified 500 mL
20	USGS SWRS # 70/20-1
21	USGS SWRS # 70/20-1 50 mL
22	USGS SWRS # 70/20-1 150 mL
23	USGS SWRS # 70/20-1 500 mL
24	USGS SWRS # 70/20-1 acidified
25	USGS SWRS # 70/20-1 acidified 50 mL
26	USGS SWRS # 70/20-1 acidified 150 mL
27	USGS SWRS # 70/20-1 acidified 500 mL

Note: Samples 4, 8, 12, 16, 20 and 24 were poured from the original bottle and did not contact the collection buckets or lids.

The remaining samples represent 50, 150, and 500 mL portions poured into sampling buckets which were inverted and leached for 24 hours. The solutions were then poured into 60 mL bottles and sent to the laboratory for analysis.

TABLE III-4 CAL. Sample.' Recovery Study Results[a]

Sample No.	Ca	Mg	Na	K	SO_4	NO_3	CL	NH_4	PO_4	pH	Conductivity
1	5 0.078	0.038	1.91	0.030	0.35	0.02	0.15	<0.02	<0.01	6.99	9.9
2	1.6 0.026	0.007	0.699	0.012	0.04	<0.03	0.04	<0.02	<0.01	6.65	3.8
3	1 0.016	0.004	0.348	0.010	0.04	<0.03	0.03	<0.02	<0.01	6.37	2.3
4	2.446	0.563	1.42	0.324	3.65	<0.03	1.48	<0.02	0.06	7.06	27.3
5	2.412	0.574	3.47	0.316	3.75	<0.03	1.53	**<0.02**	0.01	7.33	35.2
6	2.446	0.571	2.10	0.322	3.74	<0.03	1.50	0.05	0.04	7.22	30.0
7	2.438	0.570	1.63	0.316	3.63	<0.03	1.42	**<0.02**	0.07	7.14	27.9
8	2.440	0.561	1.44	0.311	3.82	0.33	1.47	**<0.02**	0.11	3.35	217.2
9	2.438	0.562	4.40	0.307	3.78	0.35	1.54	0.09	0.07	3.54	166.9
10	2.461	0.575	2.17	0.308	3.85	0.36	1.50	**<0.02**	0.08	3.42	195.4
11	2.488	0.576	1.89	0.312	3.90	0.34	1.47	**<0.02**	0.10	3.39	203.9
12	1.371	0.210	0.475	0.290	2.73	<0.03	0.27	<0.02	0.05	6.59	13.7
13	1.324	0.206	3.48	0.280	2.80	<0.03	0.39	**<0.02**	<0.01	7.19	25.9
14	1.380	0.211	1.30	0.285	3.11	<0.03	0.33	**<0.02**	<0.01	6.87	18.6
15	1.375	0.208	0.680	0.281	2.73	<0.03	0.28	**<0.02**	<0.01	6.72	14.7
16	1.369	0.208	0.481	0.290	2.73	<0.03	0.27	<0.02	0.06	4.12	46.8
17	1.444	0.245	2.15	0.297	3.26	<0.03	0.44	**<0.02**	<0.01	5.76	26.8
18	1.381	0.206	1.08	0.281	2.84	0.034	0.32	**<0.02**	<0.01	4.37	37.9
19	1.392	0.210	0.880	0.289	2.80	0.059	0.30	<0.02	<0.01	4.26	40.7
20	0.689	0.105	0.236	0.144	1.34	<0.03	0.13	<0.02	<0.01	6.33	6.9
21	0.704	0.106	1.20	0.140	1.35	<0.03	0.19	<0.02	<0.01	6.91	11.5
22	0.676	0.101	0.834	0.137	1.35	<0.03	0.19	**<0.02**	<0.01	6.83	9.6
23	0.698	0.103	0.600	0.139	1.40	<0.03	0.14	**<0.02**	<0.01	6.76	9.2
24	0.695	0.102	0.235	0.140	1.36	<0.03	0.13	**<0.02**	<0.01	3.98	51.5
25	0.753	0.105	2.29	0.145	1.40	<0.03	0.23	**<0.02**	<0.01	5.13	23.0
26	0.705	0.103	1.45	0.144	1.41	<0.03	0.17	**<0.02**	<0.01	4.33	34.9
27	0.700	0.102	0.247	0.139	1.38	<0.03	0.14	**<0.02**	<0.01	4.01	49.8

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a. Values for major ions are in mg/L, pH is **expressed in uni**ts, and conductivity is as; *µS/cm.*

pH from the bucket for low volume samples. None of these results, however, approximates the large biases observed in the blind audit data set. One possible explanation for this is a change in the bucket and/or lid manufacturing process from 1981-1983 **to** 1986. It was concluded that the apparent bias observed in the 1983 data set could not be duplicated from laboratory studies.

TABLE III-5 CAL Analyte Concentrations Expressed As Mass(µg)/Bucket Found in Deionized Water Samples Poured From Inverted Buckets Cooperative Bucket Blank Study

	Volume (mLs)		
Analyte	**50**	**150**	**500**
Calcium	3.9	3.9	8.0
Magnesium	1.9	1.0	2.0
Sodium	95.5	104.8	174.0
Potassium	1.5	1.8	5.0
Ammonium	**<1.0**	<1.0	**<1.0**
Sulfate	17.5	6.0	20.0
Nitrate	1.1	<1.0	<1.0
Chloride	7.5	6.0	15.0
pH (units)[a]	6.99	6.65	6.37
Conductivity (µS/cm)[b]	9.9	3.8	2.3

a. Median pH value for deionized water is 5.66.
b. Median conductivity for deionized water is 0.9µS/cm.

IV. LABORATORY BIAS AND PRECISION

The quantification of the bias and precision of measurements made in the laboratory is the most essential part of the quality assurance program. One of the primary procedures used at the CAL since its inception has been the use of Quality Control Check Samples (QCS) as an immediate verification of the analyst's calibration standards and validation of the samples being analyzed. Internal dilutions of mineral and nutrient concentrates provided by the United States Environmental Protection Agency, Envrionmental Monitoring and Support Laboratory (EMSL)-Cincinnati, Ohio, are used for the major cations and anions. Internally formulated and verified solutions are used for pH and conductivity. The analysis of replicate samples provides additional laboratory precision information. An internal blind sample program has evolved and become a regular part of the bias and precision assessment. Samples of known analyte concentrations are incorporated into the weekly sample routine, and are double blind to the analysts. Summary tables and plots of the analyses of the QCS, replicates, and blind samples are included in this section, as well as a brief discussion of their significance.

A. QUALITY CONTROL CHECK SAMPLE DATA

As in previous years, the QCS used for pH and specific conductance were internally formulated solutions. Dilutions of the USEPA mineral and nutrient concentrates to analyte concentrations near the twenty-fifth and the seventy-fifth percentile concentrations in precipitation serve as QCS for the cations and anions. These percentile concentration values for 1986 are displayed in Table IV-1. As in the previous summary, only the results for samples which had a volume greater than 35 milliliters have been included in the table.

A review of the percentile concentrations in this table shows these values to be similar to those in the corresponding compilation for 1985 (1). The number of samples used for the statistics is larger, and hence the number of quality control check samples was increased to ensure consistent and verifiable data.

Solutions Used by Analysts

A solution of the same formulation used since 1981, a dilute nitric acid (5.01×10^{-5} N HNO_3) prepared by the CAL, continued to be used to monitor pH and specific conductance. Each time the solutions are prepared they are verified by ion chromatographic measurements of the nitrate concentration as well as pH and specific conductance. The solution must have a calculated pH of 4.30 + 0.03 and a calculated specific conductance of 21.8 + 2 µS/cm to be considered suitable for use in both the laboratory and the field. These values are calculated from ion measurements and the ion balance program used by the CAL in the determination of reanalysis samples.

A second internally formulated solution, 5.0 x 10^{-4}N KCl, is used to calibrate the conductivity bridge and monitor pH measurements at a second level. The verification of this sample includes the measurement of pH and specific conductance, the ion chromatographic determination of the chloride concentration, and the flame atomic absorption analysis for the potassium concentration. The range of acceptable readings for this solution for pH is 5.63 +0.3 pH units, and for specific conductance, 74.8 +2 7µS/cm. The larger range of acceptability for this second solution results from the calculated pH being in a range of pH where the effects of atmospheric carbon dioxide fluctuations affect hydrogen ion concentrations. Both of these internally formulated solutions are shipped to the field sites to be used when calibrating pH meters and conductivity cells.

The mineral concentrate obtained from the United States Environmental Protection Agency, EMSL-Cincinnati is diluted to values near the twenty-fifth and seventy-fifth percentile concentrations for use as a QCS for the quantification of calcium, magnesium, sodium, and potassium by flame atomic absorption and sulfate and chloride by ion chromatography. The USEPA nutrient concentrate diluted in the same manner is used as the QCS when samples are analyzed for nitrate by ion chromatography and ammonium and phosphate by automated colorimetry.

TABLE IV-1 Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation - 1986.

	Percentile Concentration **Values (mg/L)**									
Parameter	**Min.**	**5th**	**10th**	**25th**	**50th**	**75th**	**90th**	**95th**	**99th**	**Max.**
Ca	<0.009	0.020	0.030	0.050	0.120	0.260	0.540	0.840	1.79	12.7
Mg	<0.003	0.005	0.008	0.014	0.028	0.057	0.109	0.169	0.342	1.75
K	<0.003	0.003	0.005	0.010	0.021	0.044	0.087	0.126	0.313	1.65
Na	<0.003	0.019	0.025	0.041	0.080	0.186	0.449	0.769	2.169	14.6
NH_4	<0.02	<0.02	<0.02	0.04	0.15	0.38	0.67	0.93	1.66	9.2
NO,	<0.03	0.08	0.21	0.51	1.05	1.86	3.02	4.06	6.34	15.86
Cl	<0.03	<0.03	0.04	0.08	0.14	0.30	0.69	1.26	3.93	26.72
SO_4	<0.03	0.23	0.35	0.68	1.36	2.57	4.20	5.50	8.83	28.92
PO_4	**<0.010**	<0.010	<0.010	<0.010	<0.010	<0.010	0.010	0.010	0.030	1.01
pH (units)	3.15	4.01	4.13	4.38	4.81	5.37	6.02	6.39	6.88	7.85
Conductivity (µS/cm)	1.3	3.6	4.6	7.6	13.8	25.5	41.7	54.3	84.1	309.7

Source: 1National Atmospheric Deposition Program (NAOP)
1986 - wet. side samples (w)
Number of **samples** (N) ~ 6136

TABLE IV-2 Analytical Bias and Precision for 1986 - Determined from Analysis of Quality Control Check Samples-

Parameter	Theoretical Concentration, mg/L	Heasured Concentration, mg/L	n[8]	Bias, mg/L	X	Precision, s mg/L	RSD X	Critical X	Statistically Significant Bias?[b]
Calciun	0.053	0.053	263	0.000	0.0	0.001	3.8	2.2	NO
	0.053	0.054	340	0.001	1.9	0.001	3.7	2.1	NO
	0.402	0.405	258	0.003	0.7	0.003	1.2	1.5	NO
	0.402	0.405	346	0.003	.7	0.003	0.7	1.5	NO
Magnesiun	0.018	0.018	269	0.000	0.0	0.001	5.6	3.2	NO
	0.018	0.018	349	0.000	0.0	0.001	5.6	3.1	NO
	0.083	0.083	257	0.000	0.0	0.001	1.2	2.0	NO
	0.083	0.085	345	0.002	2.4	0.001	1.2	2.0	YES
Sodium	0.083	0.082	251	-0.001	-1.2	0.001	1.2	1.7	NO
	0.083	0.083	343	0.000	0.0	0.001	1.2	1.7	NO
	0.459	0.472	252	0.013	2.8	0.005	1.1	1.3	YES
	0.459	0.464	352	0.005	1.1	0.003	0.6	1.3	NO
Potassium	0.021	0.021	246	0.000	0.0	0.001	4.8	2.7	NO
	0.021	0.022	348	0.001	4.8	0.001	4.5	2.7	YES
	0.100	0.095	256	-0.005	-5.0	0.002	2.1	2.2	YES
	0.100	0.101	339	0.001	1.0	0.005	5.0	2.0	NO
Ammonium	0.10	0.08	268	-0.02	-20.0	0.02	25.0	3.7	YES
	0.19	0.18	21	-0.01	-5.3	0.03	16.7	7.1	NO
	0.49	0.47	283	-0.02	-4.1	0.06	12.8	1.7	YES
	0.98	0.93	21	-0.05	-5.1	0.03	3.2	1.6	YES
Sulfate	0.92	0.94	235	0.02	2.2	0.02	2.1	1.4	YES
	0.93	0.94	390	0.01	1.1	0.02	2.1	1.4	NO
	3.43	3.66	204	0.23	6.7	0.08	2.2	4.4	YES
	3.43	3.62	351	0.19	5.5	0.09	2.5	4.4	YES
Nitrate	0.62	0.63	288	0.01	1.6	0.01	1.6	2.0	NO
	0.80	0.80	306	0.00	0.0	0.02	2.5	1.6	NO
	3.14	3.20	282	0.06	1.6	0.07	2.2	0.7	YES
	3.54	3.64	317	0.10	2.8	0.09	2.5	0.7	YES
Chloride	0.12	0.12	417	0.00	0.0	0.01	8.3	2.3	NO
	0.18	0.18	152	0.00	0.0	0.01	5.6	1.7	NO
	0.81	0'.80	395	-0.01	-1.2	0.01	1.2	1.0	YES
	0.86	0.86	234	0.00	0.0	0.03	3.5	1.0	NO
Ortho-phosphate	0.03	0.02	305	-0.01	-33.3	0.01	50.0	6.0	YES
	0.03	0.03	25	0.00	0.0	0.01	33.3	13.9	NO
	0.05	0.05	25	0.00	0.0	0.01	20.0	9.7	NO
	0.06	0.05	323	-0.01	-16.7	0.01	20.0	5.0	YES
pH units (µeq/L)	4.30(50.1)	4.32	1420	0.02	-5.0	4.35	5.1	12.8	NO
	5.50(3.16)	5.49	1421	-0.01	1.3	5.57	16.1	30.9	NO
Conductivity (µS/cm)	21.8	21.5	1087	-0.3	-1.4	0.7	3.3	5.7	NO

a. number of replicates
b. 95% confidence level

Analytical Bias and Precision Tables

Table IV-2 was prepared from the data obtained from the analysis of QCS solutions in 1986. Whenever the theoretical concentration is repeated more than once, a new dilution is indicated. A QCS solution is measured at least once every twelve samples for the major ions. For pH and specific conductance, at least one QCS measurement is made for every twenty precipitation samples. This summary of bias and precision employs the formulas for bias and precision found in the Glossary (Appendix A). As in the last report, all data presented for the measurement of pH required the conversion of the measurements from pH units to hydrogen ion concentration in microequivalents per liter in order to perform the calculations necessitated by these formulas. The theoretical concentrations used on the table for the USEPA QCS were supplied with the concentrates when they were sent. These values represent the mean recovery values obtained from referee laboratories' analyses and are used in the calculation of analytical bias. The column on the far right indicates whether the calculated bias is or is not statistically significant. To determine this, a t-test was used to compare the mean values measured at the CAL to those provided with the concentrates. This comparison resulted in the critical percent value listed on the table. Whenever the calculated percent bias for a measured parameter was greater than or equal to the critical percent, the bias was considered to be statistically significant. The formula for the calculation of critical percent is also listed in the Glossary.

Discussion of Results

The results shown in Table IV-2 indicate several paramaters for which the results are considered statistically biased. The actual percent bias is less than 5% for 74% of the 39 measured solutions comparing quite favorably with 76% of the 29 solutions measured in 1984 and 69% of the 32 measured in 1985. Those analytes exhibiting a greater than 5% bias are usually associated with very low ionic concentrations. Inspection and comparison of the measured and theoretical concentrations reveals minute differences in many of the "significantly biased" values. As in the past, the analytical bias and precision measurements for all the analytes measured at the CAL were within the acceptable limits specified in the Quality Assurance Plan (4).

B. REPLICATE SAMPLE DATA

Replicate samples have been analyzed since the beginning of the program and continue to be an integral part of the quality assurance program. In the past, three filtered 60 mL aliquot samples were collected from 4% of the precipitation samples received at the CAL. The samples were all given the same number. The first sample was designated as A, the second as B, and the third refrigerated for archival purposes. Samples A and B were placed next to each other on the trays which went to the laboratory for analysis. These were split samples that were analyzed consecutively and known to be splits by the analyst.

In July of 1984, changes in the replicate procedures were made and half of the samples split into the three aliquots were submitted as the A/B splits described above. The other 2% were treated differently. The first and refrigerated aliquots were given the usual sequential laboratory number and the first placed in sequence on the tray. The second aliquot, the former B sample, was returned to the sample receiving group, given a new number and submitted as a regular sample, blind to the analysts. The original number and new number were noted on the field observer report forms, kept as part of the permanent records, and noted in the quality assurance specialist's files. These splits are referred to as 0 (original)/Q (quality assurance) splits. After the analyses have been performed, but before the data are entered into the computer, the data management staff changes the sample number of the Q sample to the original number followed by a Q.

Since the audit by the NADP/NTN Review Team from Subcommittees 2 and 3 in early 1986, all of the replicate analyses have followed the 0/Q procedure.

Explanation of Replicate Sample Tables and Plots

The figures in Appendix C are plots of the concentration differences between replicate samples 0 and Q in mg/L versus the average concentration of 0 and Q in mg/L. The differences are calculated using the following formula: analyte concentration of 0 minus analyte concentration of Q. The average is analyte concentration of 0 plus analyte concentration of Q divided by two. The annual summaries for each ion have been split into two sections. The median concentration for the year was determined for each analyte. The first plot in each figure includes the range from 0 mg/L to the median value. The second plot begins with the median value and continues to the ninety-fifth percentile concentration of the analyte of interest found in the replicate samples in 1986. The median and ninety-fifth percentile concentrations used for the plots are shown in Table IV-3.

Table IV-3 Fiftieth and Ninety-fifth Percentile Concentration Values of Chemical and Physical Parameters Measured in Replicate (0/Q) Samples in 1986

Parameter	Percentile Concentration Values (mg/L) Fiftieth	Ninety-fifth
Calcium	0.100	1.000
Magnesium	0.035	0.225
Sodium	0.075	0.750
Potassium	0.025	0.125
Ammonium	0.15	1.50
Sulfate	1.20	6.00
Nitrate	1.00	5.00
Chloride	0.15	3.00
pH (µeq/L)	3.62	185.0
Conductivity (µS/cm)	15.0	75.0

Discussion of Results

The data presented in the figures and tables indicate that the concentration differences in the analyses of 0/Q pairs are similar to the differences between side-by-side A/B replicates(l). These differences and the resulting precision are as expected when the samples are blind and separated in time. Inspection of the figures and Table C-1 in Appendix C and comparison of these figures and table to the corresponding tables and figures for 1984 and 1985 yield similar results and acceptable precision. The differences are almost always within three times the MDL for each analyte, more often within two times the MDL. The standard deviation of the differences for each analyte, listed in Table C-1, gives an indication of precision and how it varies for each.

C. INTERNAL BLIND SAMPLE DATA

The internal blind sample program instituted in 1984 continued to be refined in following years in an effort to provide another means of assessing the quality of the CAL data. In 1986, several different samples of known analyte concentration were prepared by the Quality Assurance Specialist and submitted to the sample processing staff; samples were given NADP/NTN sample identification numbers and sent through laboratory for routine analysis.

The following section will describe the various solutions used as blind samples. In an effort to establish a regular schedule and a consistent rotation of samples, several different combinations and many solutions were evaluated in 1986. Tables of the analytical bias and precision are also provided, noting that in some cases the sample number is quite small but the information valuable in assesing the potential for the sample's use in a year-long or longer program.

Solutions Used

For the first six months of 1986, the same samples used throughout 1985 were submitted as the internal blind audit samples. The concentrates for these samples were obtained from the U.S. Environmental Protection Agency in Research Triangle Park, North Carolina. These were prepared originally as samples for the USEPA/World Meteorological Organization (WMO) laboratory intercomparison which took place in October of 1983. The CAL QA Specialist diluted these concentrates further than instructed by a factor of 10 in order that the concentration range fall within the range of the weekly precipitation samples. She also monitored the stability of the samples, noting that only one liter of solution should be prepared at a time due to the instability of the nitrate ion.

From mid-February to mid-March, bottles of 4.30 internal pH QCS sample were also submitted as blind samples. During the month of August, Research Material (RM) 8409 Samples I and II, supplied by the National Bureau of Standards (NBS), Gaithersburg, Maryland, were submitted, as received, to the laboratory. These simulated rainwater samples were not yet avialable as Standard Reference Materials even though the values supplied were based on proven NBS methods. The Standard Reference Material (SRM) 2694, I and II, Simulated Rainwater, issued in July 1985, replaced the earlier samples and contain NBS certified values for most of the determinations included in RM 8409. SRM 2694, I and II, were submitted to the laboratory as the blind samples from the middle of September until the end of 1986. They were continued into 1987 and used for the entire year so that bias and precision data for these samples will be tabulated in future reports as well as the end of 1986. Table IV-4 is a brief compilation of the samples used as blind audit samples in the beginning of 1986. Table IV-5 represents the results of the analysis of the SRM 2694 I and II for the last three and a half months of 1986.

TABLE IV-4 1986 ANALYTICAL BIAS AND PRECISION RESULTS FROM THE INTERNAL BLIND AUDIT PROGRAM

Parameter	n[a]	USEPA	CAL	Bias (mg/L)	Precision (% RSD)	Bias Significant?[b]
		(mg/L)				
		USEPA 2001A And USEPA 3014A				
Calcium	21	0.363	0.318	-0.045	2.8	Yes
	19	0.206	0.187	-0.019	3.2	Yes
Magnesium	21	0.037	0.039	0.002	7.7	Yes
	19	0.025	0.027	0.002	11.1	Yes
Potassium	21	0.147	0.150	0.003	2.7	Yes
	19	0.268	0.263	-0.005	19.0	No
Sodium	21	0.145	0.176	0.031	14.2	Yes
	19	0.026	0.067	0.041	74.6	Yes
Sulfate	21	1.11	1.14	0.03	3.5	Yes
	19	1.77	1.80	0.03	3.3	Yes
Nitrate	21	0.61	0.61	0.00	4.9	No
	19	0.45	0.34	-0.11	44.1	Yes
Chloride	21	1.03	1.04	0.01	4.8	No
	19	0.42	0.44	0.02	38.8	No
Ammonium	21	0.23	0.12	-0.11	66.7	Yes
	19	0.04	0. 02	-0.02	100.0	Yes
pH (units)	21	4.73	4.68	-0.05	14.7	Yes
	19	4.48	4.48	0.0	10.4	No
Conductivity	21	13.7	15.3	1.6	4.6	Yes
(µS/cm)	19	16.6	18.4	1.8	2.7	Yes
		4.30 Check Sample as SWS1 and SWS2				
Sodium	5	<0.003	0.026	0.026	30.8	Yes
	4	<0.003	0.024	0.024	33.3	Yes
Nitrate	5	3.12	3.20	0.08	4.1	No
	4	3.12	3.26	0.14	0.6	Yes
pH (units)	5	4.30	4.30	0.00	2.9	No
	4	4.30	4.29	-0.01	2.0	No
Conductivity	5	21.8	22.2	0.4	1.8	No
(µS/cm)	4	21.8	22.0	0.2	1.4	No

a. number of samples
b. 95% confidence level

TABLE IV-4 1986 ANALYTICAL BIAS AND PRECISION RESULTS FROM THE INTERNAL BLIND AUDIT PROGRAM (Continued)

Parameter	n[a]	NBS (mg/L)	CAL (mg/L)	Bias (mg/L)	Precision (%RSD)	Bias Significant?[b]
RH 8409 I and II (NBS)						
Calcium	5	0.027	0.025	-0.002	20.0	No
	4	0.050	0.048	-0.002	8.3	No
Magnesium	5	0.026	0.027	0.001	7.4	No
	4	0.050	0.052	0.002	3.8	No
Sodium	5	0.208	0.234	0.026	12.4	No
	4	0.410	0.454	0.044	13.0	No
Potassium	5	0.058	0.048	-0.010	6.2	Yes
	4	0.112	0.101	-0.011	1.0	Yes
Sulfate	5	2.62	2.67	0.05	3.8	No
	4	10.50	10.68	0.18	3.8	No
Nitrate	5	0.54	0.24	-0.30	75.0	Yes
	4	7.18	7.23	0.05	1.2	No
Chloride	5	0.23	0.28	0.05	14.3	Yes
	4	1.00	1.05	0.05	8.6	No
Ammonium	4	1.07	1.06	-0.01	21.7	No
pH (units)	5	4.32	4.24	-0.08	4.4	Yes
	4	3.61	3.58	-0.03	2.9	Yes
Conductivity	5	25.0	27.0	2.0	4.8	Yes
(µS/cm)	4	128	128	0.0	1.7	No

a. number of samples
b. 95% confidence level

TABLE IV-5 ANALYTICAL BIAS AND PRECISION RESULTS FROM THE INTERNAL BLIND AUDIT PROGRAM

Parameter	n[a]	NBS (mg/L)	CAL (mg/L)	Bias (mg/L)	Precision (%RSD)	Bias Significant?[b]
NBS SRM 2694 I and II						-
Calcium	21	0.014	0.029	0.015	44.8	Yes
	22	0.049	0.058	0.009	29.3	Yes
Magnesium	21	0.024	0.029	0.005	20.7	Yes
	22	0.051	0.053	0.002	13.2	No
Sodium	21	0.205	0.228	0.023	15.6	Yes
	22	0.419	0.415	-0.004	6.3	No
Potassium	21	0.052	0.044	-0.008	9.1	Yes
	22	0.106	0.099	-0.007	7.1	Yes
Sulfate	21	2.75	2.70	-0.05	4.8	No
	22	10.90	10.53	-0.37	5.3	Yes
Nitrate	22	7.06	6.80	-0.26	5.2	Yes
Chloride	21	(0.24)	0.28	0.04	25.0	N.A.
	22	(1.0)	1.01	0.01	5.9	N.A.
Ammonium	22	(1.0)	1.04	0.04	13.5	N.A.
pH (units)	21	4.27	4.26	-0.01	5.0	Yes
	22	3.59	3.57	-0.02	3.4	Yes
Conductivity (µS/cm)	21	26	27.0	1.0	4.1	Yes
	22	130	131.6	1.6	1.9	Yes

a. number of samples
b. 95% confidence interval
( ) Values in ( ) are not certified but are provided by NBS for information only

Explanation of Bias and Precision Tables

The data included in the previous tables are similar to those presented for the replicate analyses of the QCS. Outliers were not removed and their inclusion is obvious when the high %RSD values occur. The difference is in the procedure used to determine whether the calculated bias was or was not significant. The calculation for the critical percent used to determine the significance of the calculated bias is given in the Glossary, Appendix A. That formula was used with the QCS data because the standard deviation of the true value and the number of analyses used to determine the value and standard deviation were supplied by the USEPA. This information was not available for the USEPA/WMO samples used in the internal blind program. Instead, a confidence interval was calculated for the laboratory mean using the formula (5):

$$\text{Confidence Interval} = \bar{x} \pm (t_{.95}s)/\ n$$

where $\bar{x}$ = laboratory sample mean
$t_{.95}$ = the t value at the 95% confidence interval for n-1 degrees of freedom
s = sample standard deviation
n = number of analyses

When the recommended or true value lies within this confidence interval, the bias is not considered significant. When that value is outside of the interval, it is said to be significant. This is how the significance of the bias was determined for the bias calculated from the analyses of the 4.30 check solution, the RM 8409 I and II, and the SRM 2694 I and II solutions supplied by the NBS, as well as the USEPA/WMO used the previous year and continued into 1986.

Bias in these tables refers to the difference between the CAL measured concentration and the theoretical or recommended concentration.

Percent RSD is calculated from the equation (Standard Deviation/Mean Measured Concentration) x 100. Precision of pH measurements is expressed in terms of hydrogen ion concentration.

Discussion of Results

As in the 1984-1985 report, a comparison of the bias and precision data for the blind samples to those for the analyst-known QCS indicates that the blind analyses show a greater bias and a higher precision as calculated using the % RSD equation. These results are to be expected. Not only were the internal blind samples submitted as samples and therefore the concentrations completely unknown to the analysts, but they also have been filtered and handled by several analysts, not just the person analyzing a sample for a particular parameter. The additional handling procedures and bottle changes increase the potential for contamination, especially sodium contamination.

The analyte concentration for every ion in each sample is multiplied by its individual conversion factor, and these values are used in the following formula to establish the Ion Percent Difference.

$$\text{Ion \% Difference} = \frac{(\text{Anions} - \text{Cations})}{(\text{Anions} + \text{Cations})} \times 100$$

The anions include sulfate, nitrate, chloride, orthophosphate, and bicarbonate. The cations are calcium, magnesium, sodium, potassium, ammonium, and hydrogen. The bicarbonate and hydrogen are calculated from the measured pH of the sample.

The ion balance calculations continue to be a valuable component of the CAL quality assurance program. In many cases, a large imbalance is indicative of an error in analysis or in transcribing the numbers onto the data sheets. These errors can be reevaluated and quickly corrected. At other times, the imbalance is simply due to species which are not detected in the CAL sample profile. Under these circumstances, further analyses would be required to completely characterize the sample.

Using the equation at the beginning of this page, the ion percent difference for each sample is calculated, and the following criteria are used for flagging the sample for reanalysis. IS is the ion sum which equals the sum of the anions and the cations expressed in microequivalents per liter.

Samples are reanalyzed if:

IS < 50 µeq/L and IPD> ± 60%

50 < IS < 100 µeq/L and IPD> ± 30%

IS > 100 µeq/L and IPD> + 15%

B. SPECIFIC CONDUCTANCE CRITERIA

The other part of the reanalysis program is the comparison of the conductance measured in the laboratory to the calculated theoretical conductance using the measured analyte concentrations. The formula used is:

$$\text{Calculated Conductance} - [(H^{+})(350) + (HC0_{3}^{-)}(43.6) + (Ca^{+2})(52.0)$$

$$+ (Cl^{-)}(75.9) + (Mg^{+2})(46.6) + (K^{+})(72.0) + (Na^{+})(48.9)$$

$$+ (NO_{3}^{-)}(71.0) + (S0_{4}^{-2})(73.9) + (NH_{4}^{+})(72.5)] /1000$$

where ion concentrations are expressed as microequivalents per liter.

V. REANALYSIS PROCEDURES

When the laboratory analyses have all been completed on a tray of 108 samples, the numbers are entered into the CAL data base. The analyte concentrations are converted from milligrams per liter to microequivalents per liter in order to perform an ion balance for each sample. Another method of checking the analytical data is to compare the calculated theoretical conductance and the actual conductance measured in the laboratory. When approximately 450 to 500 samples have been entered into the data base, a computer program is run on the data, and those samples which fall outside of the reanalysis criteria for ion percent difference and conductivity percent difference are flagged. These samples, plus samples selected from a random sample list, are noted, and the list is sent back to the laboratory. The samples are then retrieved and analyzed a second time. The reanalysis results are compared to the original data, and reasons are evaluated for any differences found. For all samples reanalyzed, the original, the reanalysis, and the corrected final data are all maintained in the computerized data base. A short explanation of the ion balance and theoretical conductance calculations follows.

A. ION BALANCE CRITERIA

The original set of criteria established in the fall of 1981 to select samples for reanalysis due to a large ion imbalance was still in effect in 1986. The factors used to convert milligrams per liter to microequivalents per liter are listed below in Table V-1. These values were taken from Standard Methods for the Examination of Water and Wastewater (6).

TABLE V-1 Factors Used to Convert Milligrams per Liter to Microequivalents per Liter

Analyte	Conversion Factor
Calcium	49.90
Magnesium	82.26
Sodium	43.50
Potassium	25.57
Ammonium	55.44
Sulfate	20.83
Nitrate	16.13
Chloride	28.21
Orthophosphate	31.59

The analyte concentration for every ion in each sample is multiplied by its individual conversion factor, and these values are used in the following formula to establish the Ion Percent Difference.

$$\textbf{Ion \% Difference} = \frac{(\text{Anions} - \text{Cations})}{(\text{Anions} + \text{Cations})} \times 100$$

The anions include sulfate, nitrate, chloride, orthophosphate, and bicarbonate. The cations are calcium, magnesium, sodium, potassium, ammonium, and hydrogen. The bicarbonate and hydrogen are calculated from the measured pH of the sample.

The ion balance calculations continue to be a valuable component of the CAL quality assurance program. In many cases, a large imbalance is indicative of an error in analysis or in transcribing the numbers onto the data sheets. These errors can be reevaluated and quickly corrected. At other times, the imbalance is simply due to species which are not detected in the CAL sample profile. Under these circumstances, further analyses would be required to completely characterize the sample.

Using the equation at the beginning of this page, the ion percent difference for each sample is calculated, and the following criteria are used for flagging the sample for reanalysis. IS is the ion sum which equals the sum of the anions and the cations expressed in microequivalents per liter.

Samples are reanalyzed if:

$\text{IS} < 50$ µeq/L and IPD> ± 60%

$50 \leq \text{IS} < 100$ µeq/L and IPD> ± 30%

$\text{IS} \geq 100$ µeq/L and IPD> ± 15%

B. SPECIFIC CONDUCTANCE CRITERIA

The other part of the reanalysis program is the comparison of the conductance measured in the laboratory to the calculated theoretical conductance using the measured analyte concentrations. The formula used is:

$$\begin{aligned}\text{Calculated Conductance} - [&(H^{+})(350) + (HCO_3^{-})(43.6) + (Ca^{+2})(52.0)\\ &+ (Cl^{-})(75.9) + (Mg^{+2})(46.6) + (K^{+})(72.0) + (Na^{+})(48.9)\\ &+ (NO_3^{-})(71.0) + (SO_4^{-2})(73.9) + (NH_4^{+})(72.5)] /1000\end{aligned}$$

where ion concentrations are expressed as microequivalents per liter.

The conductance factors used in this calculation for hydrogen and ammonium are from the CRC Handbook of Chemistry and Physics (7). The other factors are from Standard Methods for the Examination of Water and Wastewater (6).

The calculated conductance is compared to the measured conductance and the conductance percent difference is found using the following equation:

Conductance Percent Difference - CPD -

$$\frac{\text{(Calculated Conductance - Measured Conductance)}}{\text{Measured Conductance}} \times 100$$

As with the ion percent difference calculation, the conductance percent difference is a valuable tool when used to indicate measurement errors or mistakes in data transcription. Often these samples have been flagged for ion percent difference as well. Sometimes when the ion percent difference is acceptable, the conductance percent difference will indicate that other sample errors have occurred or that the laboratory conductance measurements have been reported incorrectly. The conductance criteria were added to the ion balance program in October, 1981.

Samples are reanalyzed if:

Conductance measured $\leq$ 10 μS/cm and CPD > $\pm$ 65%

10 μS/cm < $\text{Conductance}_m \leq$ 30 μS/cm and CPD > $\pm$ 45%

30 μS/cm < $\text{Conductance}_m \leq$ 50 μS/cm and CPD > $\pm$ 30%

Conductance_m > 50 μS/cm and CPD > $\pm$ 20%

The percentage of samples that exceed these criteria is generally less than 2% but it has been proven to be a valuable means of detecting analytical and reporting errors.

C. HISTOGRAMS

Figures V-1 and V-2 are histograms of the ion percent difference values and the conductance percent difference values for the samples analyzed from the NADP/NTN network for 1986. With each histogram, a median, mean, and a standard deviation are noted.

The Ion Percent Difference histogram approximates a normally distributed curve centering around the 0% difference point. The mean of 4.3% indicates a slight positive skew which indicates a small anion excess. The mean percent as well as the median value have increased slightly and steadily since 1983, a fact that might be related to the changes in the composition of the network as more sites have been added in the western part of the United States.

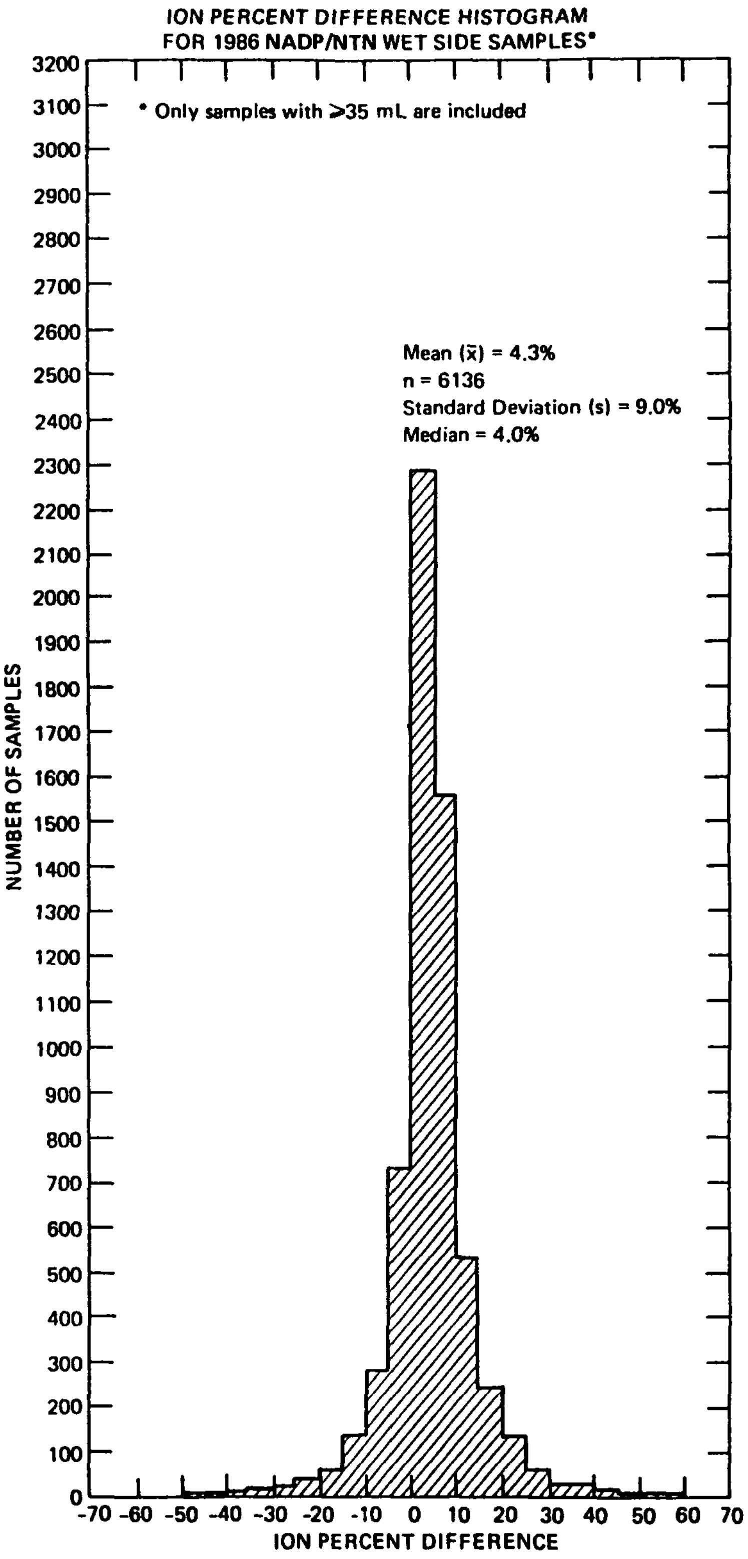


FIGURE V-1. Ion percent difference histogram for NADP/NTN wet side samples in 1986.

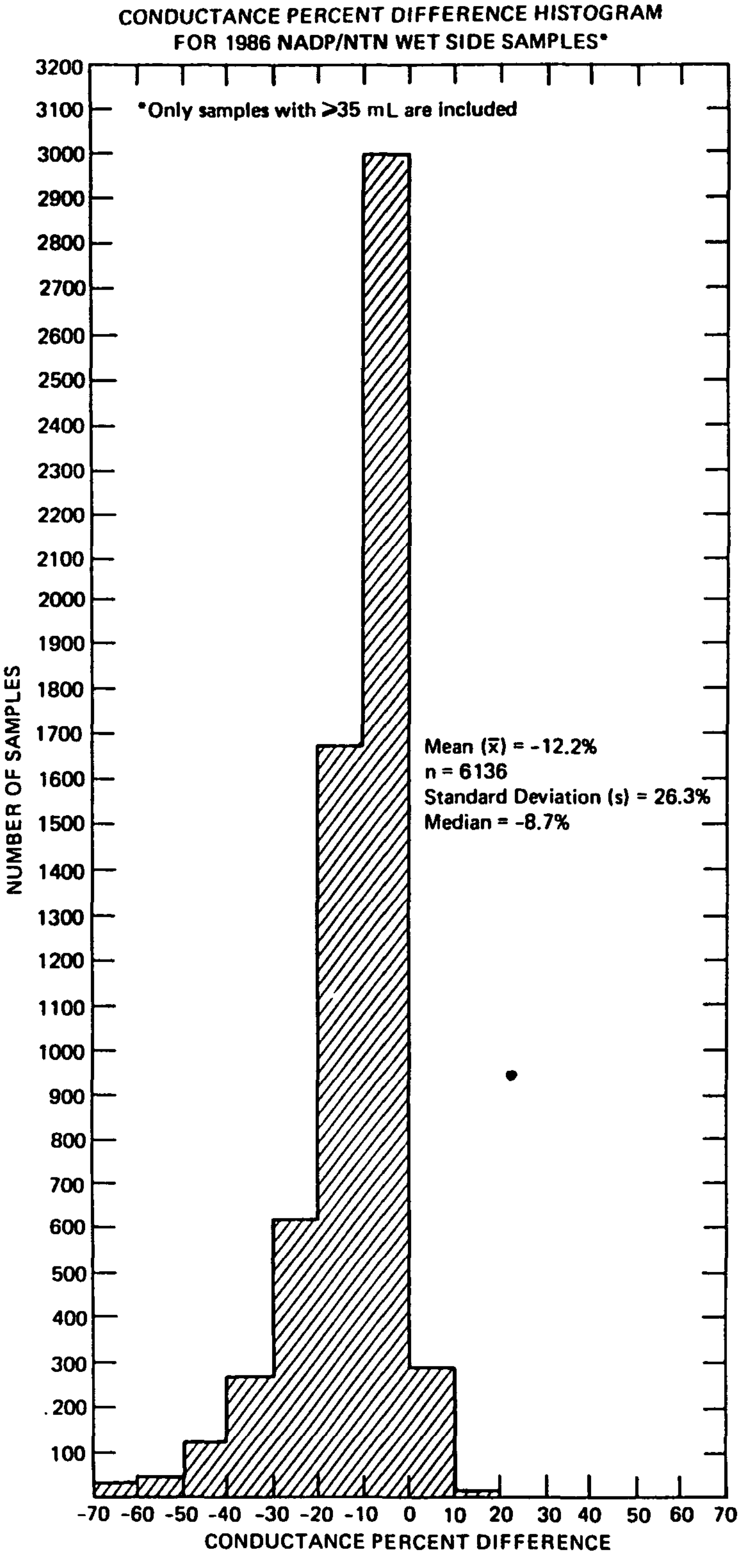


FIGURE V-2. Conductance percent difference histogram for NADP/NTN wet side samples for 1986.

The Conductance Percent Difference histogram has a negative skew as it has in the past. This skew indicates that the measured conductance is higher than the calculated conductance. The negative skew was addressed in the 1984-1985 Report (1), where it was noted that the conversion factors used might cause it to be more negative than if those from the CRC Handbook were used. These conversion factors are the ones used in other networks, and there is a complete set for both measured and calculated ions. It was felt that the mean of the resulting curve would shift from -10% to -5%, and the samples most affected would be those with small hydrogen ion concentrations.

The information from both of these histograms may indicate that trace amounts of other ions, which are measured in the conductivity determination but not quantified by individual ion analysis, are present.

D. DISCUSSION OF RESULTS

Not all of the samples identified for reanalysis by the Ion Percent Difference and Conductance Percent Difference programs are reanalyzed. Insufficient sample precludes reanalysis. If all data values from an 0/Q split are in agreement or very similar, reanalysis would be redundant. All others are located and returned to the laboratory for analysis.

When the reanalysis results differ from the original, the refrigerated aliquot, if available, is analyzed. Because refrigeration is a form of preservation, the chemistry of this sample should more closely agree with that of the original sample when first analyzed. When there are discrepancies among the original, reanalysis, and refrigerated values, it is necessary to have input from the analyst about the source of the error.

If an explanation cannot be found, the original data are reported, If the reason for the discrepancy is known and the reanalysis value is preferable, the data are changed and the new values are used. In 1986, 519 samples, representing 5.16% of the annual total, were reanalyzed as described. Of these 519, 89 samples required changes for one or more of the analytes. Transcription and dilution errors are the reasons most often cited for change and the changes are evenly distributed among the different analytes.

VI. EXTERNAL QUALITY ASSURANCE PROGRAM PARTICIPATION

The accuracy and validity of the results obtained at the CAL on a daily basis are verified by its performance in several different external evaluations. The U. S. Geological Survey is the official external auditing agency for the CAL. In addition to this program, the CAL participates annually in other national and international interlaboratory comparison studies. The following section provides a brief description of the programs participated in during 1986 and the performance of the CAL in each.

A. U. S. GEOLOGICAL SURVEY EXTERNAL AUDIT PROGRAM

The U. S. Geological Survey NADP/NTN external audit program is much the same as it has been since the beginning of the network. It consists of two components: a blind audit sample routine and an interlaboratory comparison study. The data are used not only to test for laboratory bias and precision, but also to study the effects of sample handling and shipping.

A brief summary of the Blind Audit Program was included in the 1984-1985 Report (1). The sample solutions were prepared from several sources for the 1986 blind-audit program. Seven of the solutions were diluted standards from the U.S. Environmental Protection Agency's performance audit solutions, and three of the solutions were prepared from standard reference water solutions available from the U.S. Geological Survey. Two solutions were used as blanks. Ultrapure, deionized water was prepared by the U.G. Geological Survey's National Water Quality Laboratory in Colorado, and dilute nitric acid quality control check solution was prepared by the CAL. During 1986, 100 samples were submitted from randomly selected NADP/NTN sites, distributed evenly among four geographic areas of the United States. The site operator poured two-thirds of the blind-audit sample into a clean network sampling container, which is the bucket sample. This sample is then treated as a routine precipitation sample and shipped to CAL with a fictitious field form. The remaining one-third of the blind-audit sample, in the original bottle, is mailed to CAL separately from the bucket sample and is also processed as a rain sample (8). The comparison of the two analyses is a valuable tool for assessing the effects of the bucket and shipping on the integrity of the sample.

The analysis of the data from 1986 is included in a report recently issued by the USGS, Denver, Colorado: External Quality-Assurance Results for the National Atmospheric Deposition Program and the National Trends Network During 1986. Water-Resources Investigations Report 88-4007, is available upon request (8).

The second phase of the external audit is the interlaboratory comparisons begun in late fall of 1982. This program is also explained in the 1984-1985 Report. Four types of samples were prepared for this program. Ultrapure, deionized water was prepared by the USGS, and dilute pH 4.3 nitric acid was prepared by the CAL for use as blanks. Natural wet-deposition samples that had a volume of 750 mL or greater were selected randomly by CAL for use in the program. These samples are split and sent to the USGS. Standard reference samples from the U.S. Environmental Protection Agency, the National Bureau of Standards, and the U.S. Geological Survey also were used as comparison samples.

The laboratories participating in the comparison are: Inland Waters Directorate, Ontario, Canada (IWD); Illinois State Water Survey, Champaign, Illinois (CAL); the Environmental Monitoring and Services laboratory (EMSI) of Combustion Engineering Inc.; and the U.S. Geological Survey, National Water Quality Laboratory (DEN). The audit samples are analyzed by the laboratories, and the data are sent to the USGS so that it can be analyzed to determine if the laboratories are producing comparable results. The results are also used to document analytical bias and estimate analytical precision for each lab. A summary of the comparisons are included in the aforementioned report.

B. **INTERLABORATORY COMPARISON** STUDIES

In 1986, the CAL participated in several national and international interlaboratory performance studies. The Analytical Chemistry Unit of the Illinois State Water Survey, of which the CAL is a component, was recertified by the Illinois Environmental Protection Agency (IEPA) for the chemical analysis of public water supplies. A brief discussion and summary of results are presented in the following paragraphs. A detailed presentation of the analytical results for the samples submitted are provided in the tables in Appendix D.

United States Environmental Protection Agency

Since December of 1978, the CAL has participated in the interlaboratory comparison study for precipitation samples, formerly overseen by the World Meteorological Organization, which is now conducted by the Environmental Monitoring Systems Laboratory of the United States Environmental Protection Agency, Research Triangle Park, North Carolina. In 1986, there were two studies, one in April and the second in October.

The results of these two performance surveys are found in Tables D-1 and 2. The CAL results and the EPA expected results are shown. As in the previous World Meteorological Organization/Environmental Protection Agency intercomparisons, the CAL mean percent difference from the expected values is considerably smaller than that of all of the laboratories participating, even when all outliers are removed.

Only the 10 major chemical and physical parameters routinely measured by the CAL are listed in the Appendix tables and summarized in Table VI-1, which follows.

TABLE VI-1 Summary **of Results from** U.S. Environmental Protection **Agency Comparison** of Reference **Precipitation Samples**

Intercomparison Date	**Number of Participating Laboratories**	**Mean** % Difference[a] from Expected **Value**	
		CAL	**All** Labs
April, 1986	33	3.16	25.93
December, 1986	28	2.32	25.93

a. **Mean % Difference**

$$= \frac{\sum \left[\frac{|\text{Expected Value} - \text{Reported Value}|}{\text{Expected Value}} \times 100 \right]}{n}$$

where n = the number of analytes determined

Illinois Environmental Protection Agency

The Analytical Chemistry Unit of the Illinois State Water Survey has been certified by the Illinois Environmental Protection Agency for the analysis of public water supply samples for specific inorganic parameters since the fall of 1981. Illinois state law now requires that certification be applied for and reissued every two years. The most recent certificate was issued in July of 1986 following an on site visit by two members of the IEPA certification staff.

The CAL is a major part of this unit and many of the analysts who routinely analyze NADP/NTN samples were included in the on site interviews and inspections. Many of the parameters which are certified are included in the CAL daily precipitation analysis schedule. Certification protocol also requires participation in at least one U.S. Environmental Protection Agency Performance Study per year. Several CAL analysts are part of these studies, as well as those in which they are the exclusive participants.

Canada Centre for Inland Vaters

The Canadian Long Range Transport of Atmospheric Pollutants (LRTAP) program begun in December of 1982 continues to be administered by the Canada Centre for Inland Waters and to include the CAL as a participating laboratory. In 1986, the CAL participated in LRTAP Studies L-12 and L-14. Both studies consisted of selected major ions, nutrients, and physical measurements in water. The specific conductances of 18 of the 20 samples were reported to be below 100 umhos/cm. The CAL analyzed eight of the 10 samples from L-12 and six of 10 from L-14. The concentrations of the samples not analyzed were considerably higher than the CAL working range and normally represent lake and stream waters and not precipitation.

Median concentrations for each parameter were determined using the data reported by the participating laboratories. The results of both L-12 and L-14 are reported in Tables D-3 and D-4 in Appendix D. The CAL data and the median values are reported. The CCIW uses these values to determine whether the results are biased high or low. If a bias exists, the samples are flagged, and the number of flagged results are used to rank the participating laboratories. Their relative performances are then ranked. The CAL was ranked sixth of the 45 participants in L-12 (9) and first of 46 in L-14 (10) indicating a very low percentage of flagged results.

Norwegian Institute for Air Research

The ninth intercomparison of analytical methods within the European Monitoring and Evaluation Programme began with the arrival of samples in March 1986. The four samples from the Norwegian Institute for Air Research consisted of distilled and deionized water containing known amounts of sulfate, nitrate, ammonium, strong acid, magnesium, sodium, chloride, calcium, and potassium. The CAL results compared to the theoretical concentrations are shown in Table D-5 in Appendix D. The final report, dated April 1987, presents graphical displays of the results using Youden plots (11). These plots show the CAL results to compare well to other participants from 24 European and three North American laboratories.

The continuing participation of the CAL in these external, independently refereed comparisons is a valuable component of the quality assurance program. Thse data, combined with results of the CAL's internal QA program, provide data users with a comprehensive assessment of laboratory performance on an ongoing basis.

VII. SUMMARY

The CAL laboratory, following the guidelines set forth in the NADP Quality Assurance Plan (4) , has produced data with bias and precision values which have been quantified in a systematic program. The minimum detection limits are defined and the limits for variance and accuracy established in relation to them. Complete documentation of all quality assurance procedures in use at the CAL was required, as well as annual reports detailing the modifications made in that year and the information derived from the data produced.

This report, continues the documentation begun with the previous QA Reports. Most of the suggestions of the January 1986 audit team were implemented immediately, and the continuing evolution of a comprehensive quality control system has resulted.

The 1986 data indicate that the CAL has been able to work within the QA Plan and meet its specifications. The analytical bias and precision results indicate that the limits for accuracy and variance continue to be achieved. The modification of the replicate analysis procedure has proven a valuable tool for evaluating precision in a more realistic manner. The streamlining and systematizing of the internal blind sample procedure has already proven to be a valid alternate method for calculating precision and bias statistics. The results of these program improvements are more appropriate for evaluating the analytical process for actual samples. Once again, the CAL performance in external interlaboratory comparisons verified the results obtained from the internal laboratory QA program.

TABLE VII-1 SUMMARY OF QUALITY ASSURANCE CHANGES AND INNOVATIONS - 1986

A. Analytical Methods

Phosphate detection limit change from 0.003 to 0.01 mg/L due to minor changes in instrumentation and the more recent method for calculating MDLs (2) (February).
Analysis of phosphate by ion chromatography approved by NADP Subcommittee 2(October).

B. New Facilities

Laboratory Manager and six other staff members moved out of the laboratory building and into a shared office building, creating additional analytical space (September).

C. Laboratory Blanks

A more rigorous lid soaking and washing procedure involving a 48 hour pre-leach in deionized water and longer dishwasher cycle (March).
Number of bucket blanks reduced from six to two. 50 and 150 mL inverted blanks analyzed weekly (January).
Cooperative bucket blank study (August, September).

D. Analytical Bias and Precision

All replicates following 0/Q procedure (February).
Control charts for all parameters due in quality asssurance specialist's office by the fifteenth of each month (January).
Introduction of NBS Simulated Rainwater samples for continued use in internal blind audit (October).

E. Interlaboratory Comparisons

Certification as an environmental laboratory renewed by Illinois EPA (July).

VIII. REFERENCES

1. Peden, Jacqueline M. L. : Quality Assurance Report. NADP/NTN Deposition Monitoring. Laboratory Operations. Central Analytical Laboratory. January 1984 through December 1985: NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; May 1988.

2. Peden, M. E., S. R. Bachman, C. J. Brennan, B. Demir, K. 0. W. James, B. W. Kaiser, J. M. Lockard, J. E. Rothert, J. Sauer, L. M. Skowron, and M. J. Slater: Development of Standard Methods for the Collection and Analysis of Precipitation: Illinois State Water Survey Contract Report 381; Analytical Chemistry Unit; 2204 Griffith Drive; Champaign, IL 61820; March 1986.

3. Lockard, Jacqueline M.: Quality Assurance Report. NADP/NTN Deposition Monitoring. Laboratory Operations. Central Analytical Laboratory. July 1978 through December 1983: NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; May 1987.

4. NADP Quality Assurance Plan: Deposition Monitoring; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80532; July 1984.

5. Taylor, John K., Quality Assurance of Chemical Measurements. Lewis Publishers, Inc.; Chelsea, Michigan; pp. 27 and 247; 1987.

6. Standard Methods for the Examination of Water and Wastewater: 14th Edition; American Public Health Association; Washington, D.C. ; 1976; p.35.

7. CRC Handbook of Chemistry and Physics: 49th Edition; 1968-1969; CRC Press, Inc.; Boca Raton, Florida; p. D-93.

8. See, Randolph B. and Leroy J. Schroder: External Quality-Assurance Results for the National Atmospheric Deposition Program and the National Trends Network During 1986: U.S. Geological Survey; Denver Federal Center, Arvada, CO 80002; 1988.

9. Lawrence, John, and S. Villard: LRTAP Interlaboratory Comparability Study #L-12 Selected Major Ions: Canada Center For Inland Waters; Burlington, Ontario; September 1986.

10. Lawrence, John, and S. Villard: LRTAP Interlaboratorv Comparability Study #L-14 Selected Major Ions. Nutrients and Physical Measurements in Water: Canada Centre for Inland Waters; Burlington, Ontario; April, 1987.

11. Hanssen, J. E., and N. E. Ladegard; The Ninth Intercomparison of Analytical Methods Within EMEP: EMEP/CCC Report 4/87; Norwegian Institute for Air Research; August 1987.

APPENDIX A

Glossary of Terms

GLOSSARY OF TERMS

Term	Abbreviation	Definition
Accuracy		The difference between the mean value and the true value, when the latter is known or assumed. The concept of accuracy includes both bias (systematic error) and precision (random error).
Bias		A persistent positive or negative deviation of the measured value from the true value due to the experimental method. In practice, it is expressed as the difference between the mean value obtained from repetitive analysis of a homogenous sample and the accepted true value. Bias = measured value - true value
Control Chart		A graphical plot of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control (5).
Critical Percent		A calculated percent used to determine if the measured bias is or is not statistically significant.

$$\text{Critical } \% = \frac{s_{sp} - t_{0.95,(n1 + n2) -2}}{\bar{x}_{true}} \text{ X } 100$$

where:

$$s_{sp} = \sqrt{\frac{s^2_{true}}{n_{true}} + \frac{s^2_{measured}}{n_{measured}}}$$

and:

s - standard deviation

n - number of values

$t_{0.95,(n1 + n2) - 2}$ = t statistic at the 95% confidence level and (n1 + n2)-2 degrees of freedom

External Blind Sample		A quality assurance sample of known analyte concentrations submitted to the laboratory by an external agency. At the CAL these samples arrive as normal weekly rain samples and undergo routine processing and analysis. The identity of the sample is unknown to the CAL until all analyses are complete. Data are used to assess contamination potential from handling and shipping.
Internal Blind Sample		A quality assurance sample of known analyte concentrations submitted to the laboratory by the Quality Assurance Specialist. The identity of the sample is known to the processing staff only. The analyte concentrations are unknown to all. These data are valuable in assessing bias and precision for real samples.
Mean	$\bar{x}$	**The average obtained by dividing a sum by the number of its addends.** $\bar{x} = \sum_{i=1}^{n} x_i/n$
Mean Bias		The sum of the bias for each sample divided by the total number of replicates (n).
Mean Percent Recovery		The sum of the percent recovery for each sample divided by the number of replicates (n).
Method Detection Limit	MDL	The minimum concentraion of an analyte that can be reported with 99% confidence that the value is greater than zero.

Percent Bias	The difference between the mean value obtained by repeated analysis of a homogenous sample and the accepted true value expressed as a percentage of the true value. $\%\mathrm{Bias} = 100 \text{ x } \left[(V_m - V_t)/V_t\right]$ where: V_m = measured value V_t = true value
Percent Recovery	An estimate of the bias of an analytical method determined from analyte spikes of natural samples. The percent recovery is calculated as: $\%\ \mathrm{Recovery} = 100 \text{ X } (a-b)/c$ where: a = measured concentration of a spiked sample b = measured concentration of sample before spiking c = calculated concentration spiked sample
Precision	The degree of agreement of repeated measurements of a homogenous sample by a specific procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation (s).
Quality Assessment	The system of procedures that ensures that quality control practices are achieving the desired goal in terms of data quality. Included is a continuous evaluation of analytical performance data.
Quality Assurance Program	A plan designed to reduce measurement error to tolerable limits and to provide the means of ensuring data validity. Included are both quality control and quality assessment activities.

Quality Control	**QC**	The system of procedures designed to eliminate analytical error. These procedures determine potential sources of sample contamination and monitor analytical procedures to produce data within prescribed tolerance limits.
Quality Control Sample	**QCS**	A sample containing known concentrations of analytes used by the analysts to verify calibration curves and validate sample data. The values obtained from the analysis of these samples are used for calculation of bias and precision and for the monthly control charts.
Relative Standard Deviation	**RSD**	The standard deviation expressed as a percentage: $\mathbf{RSD - 100\ X\ (s/\bar{x})}$ where: s - sample standard deviation $\bar{x}$ — mean value
Replicates (Splits)		Two aliquots of the same sample treated identically throughout the laboratory analytical procedure. Analyses of laboratory replicates are beneficial when assessing precision associated with laboratory procedures but not with collection and handling. Also referred to as splits.
Sensitivity		The method signal response per unit of analyte.
Spiked Sample		A sample of known analyte concentration to which a known volume and concentration of analyte is added. The difference in the final measured analyte concentration and the theoretical final concentration is used to calculate the percent recovery. These samples are valuable for providing an estimate of accuracy of a method of analysis.

Standard Deviation	s	The number representing the dispersion of values around their mean. $s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$ where: x_i = each individual value $\bar{x}$ = the mean of all the values n = number of values

APPENDIX B

Laboratory Blanks

Plots and Tables

1986

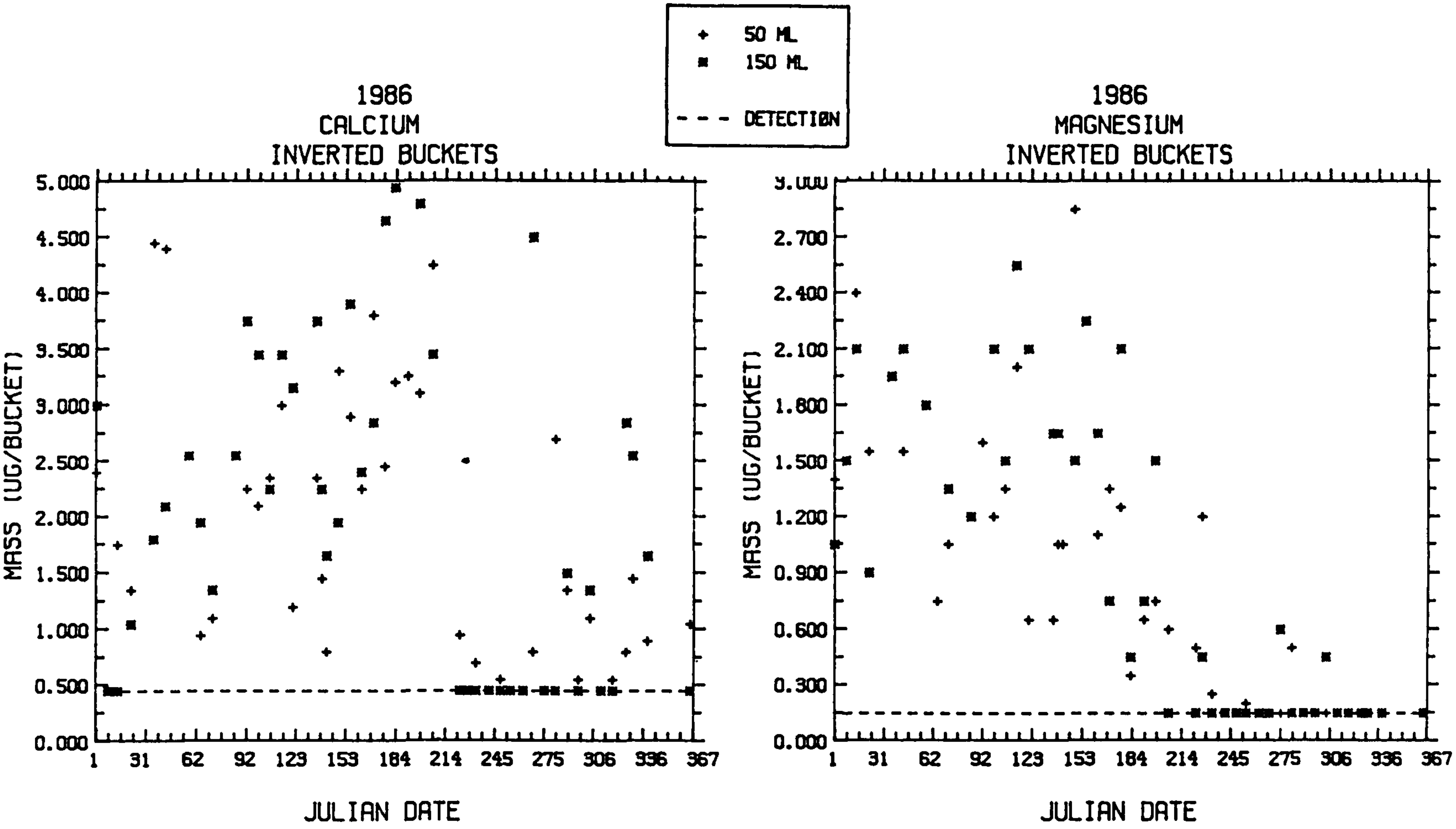
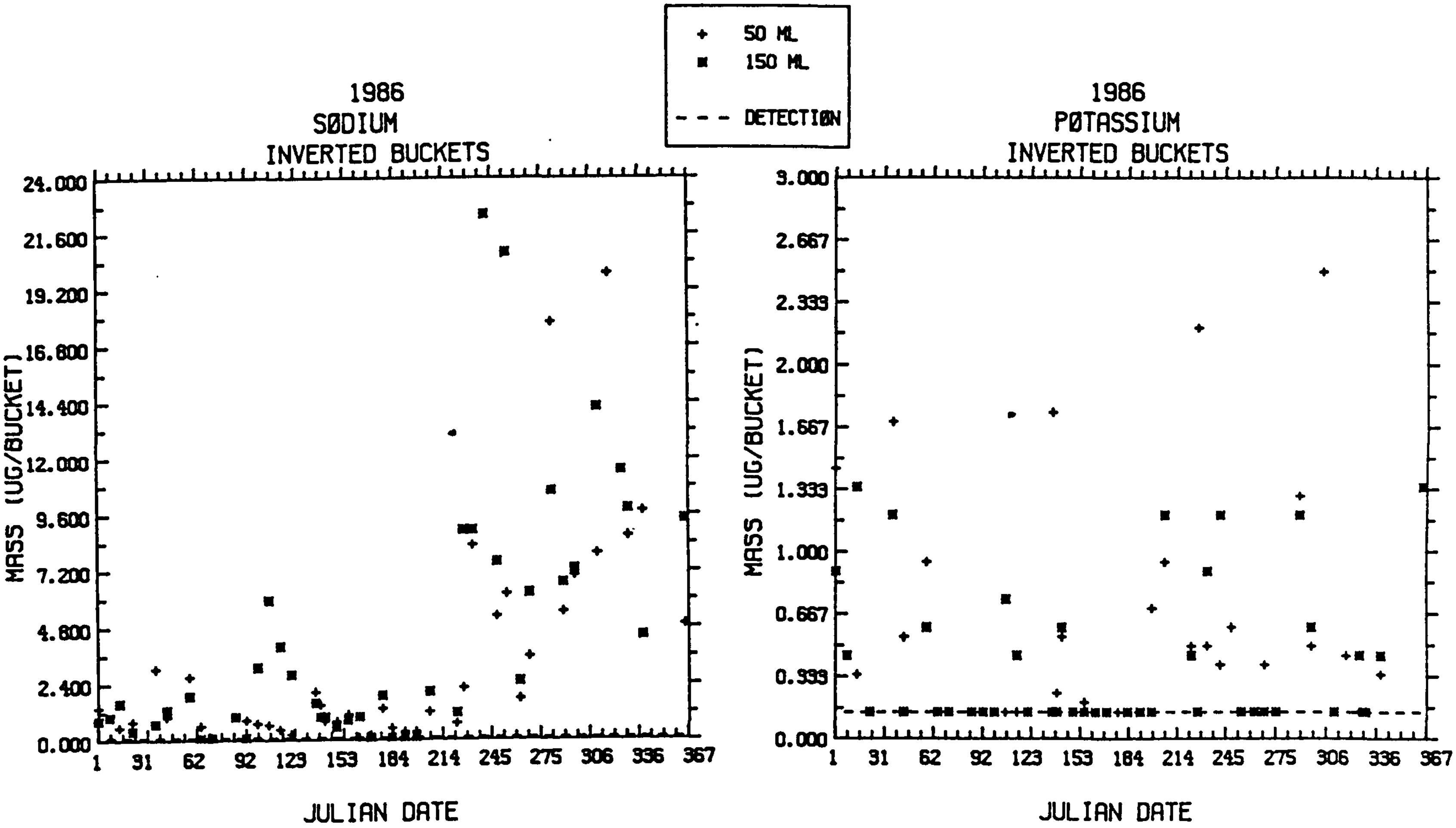


FIGURE B-1. Measured calcium and magnesium mass in inverted buckets for 1986.



PIGURE B-2. Measured sodium and potassium mass in inverted buckets for 1986

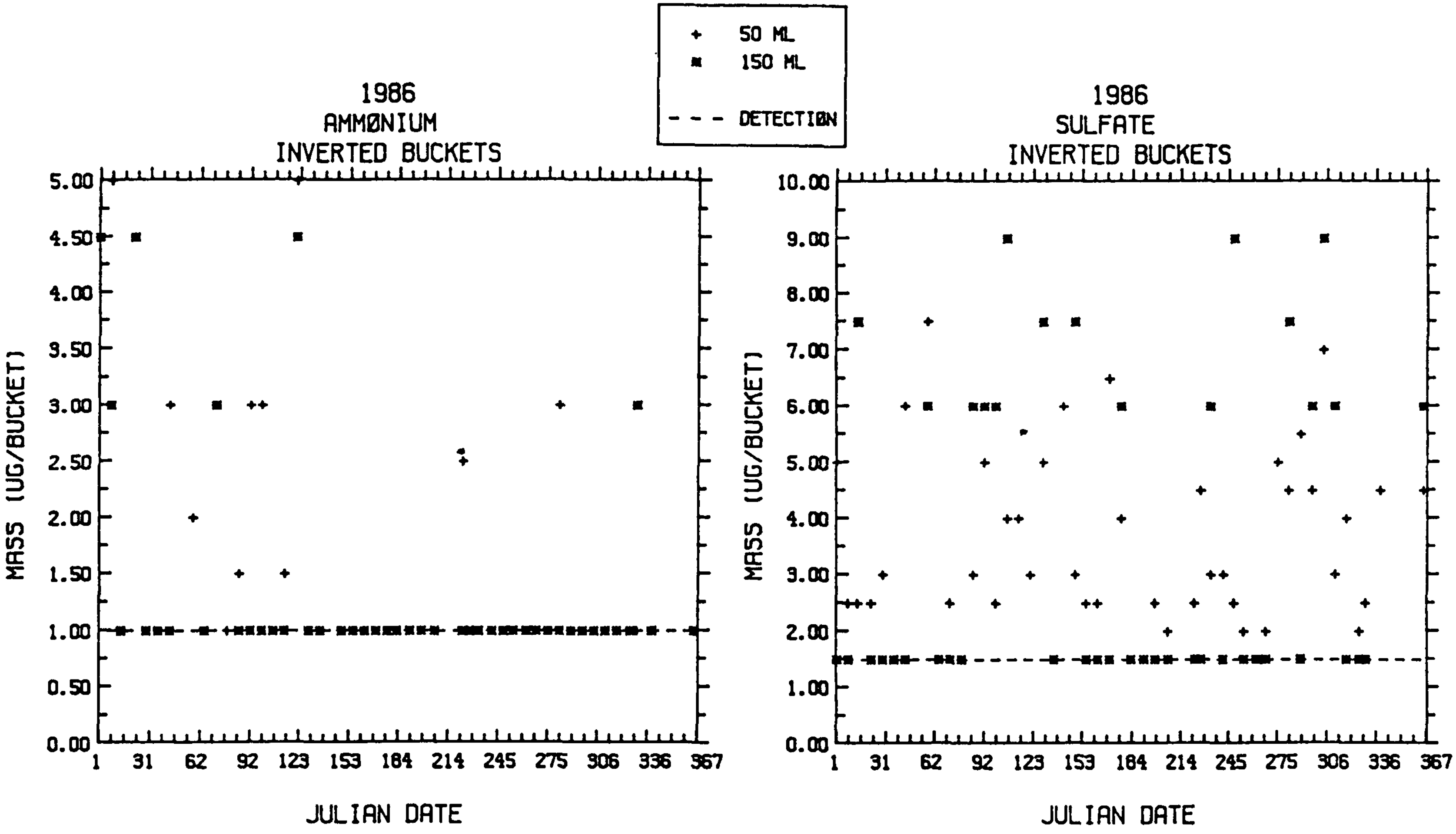


FIGURE B-3. Measured ammonium and sulfate mass in inverted buckets for 1986.,

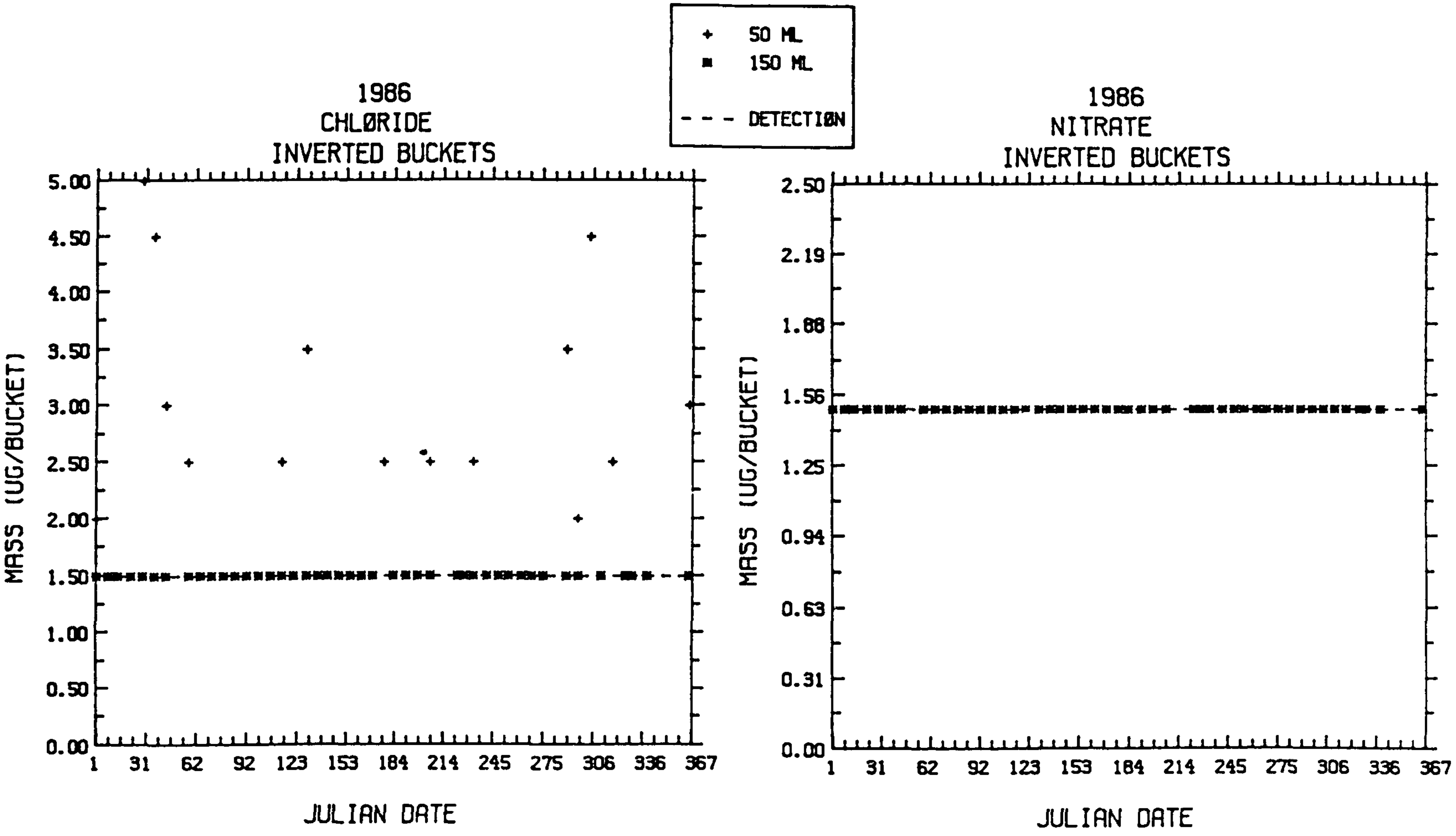


FIGURE B-4. Measured chloride and nitrate mass in inverted buckets for 1986.

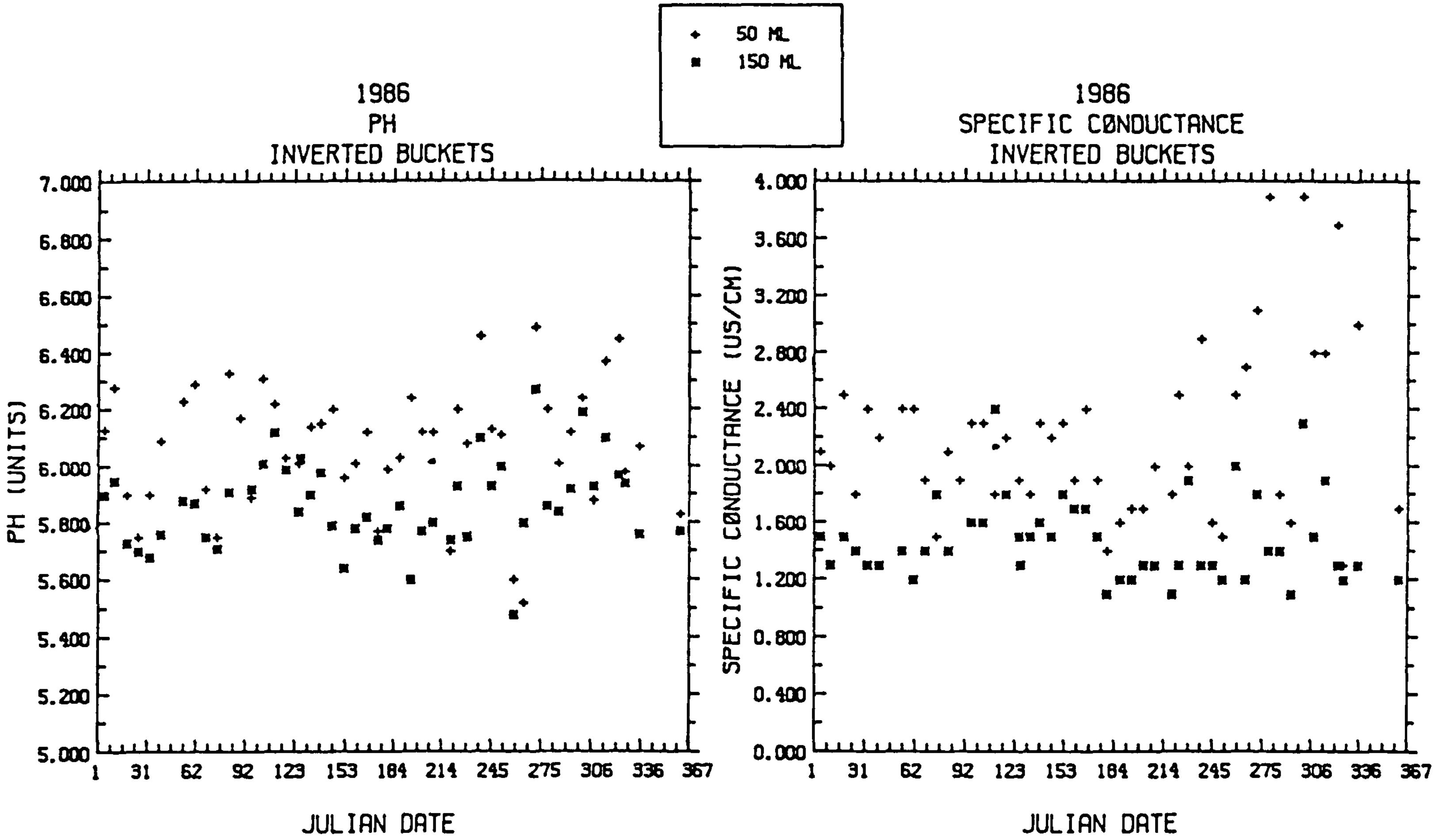


FIGURE B-5. Measured pH and specific conductance in inverted buckets for 1986.

TABLE B-1 Minimum Detectable Mass[a] Values for Bucket Blanks Analyzed in 1986

Analyte	Minimum Mass Value (ug/bucket)
Calcium	0.45
Magnesium	0.15
Sodium	0.15
Potassium	0.15
Ammonium	1.0
Sulfate	1.5
Nitrate	1.5
Chloride	1.5

a. Calculated by multiplying the MDL expressed as µg/mL by 50 mLs.

TABLE B-2 Analyte Concentration Summary for Filter Leachate A - 1986

Analyte	n[a]	Frequency of MDL (%)	Percentile Concentration (mg/L> 50%	95%
Calcium	49	87.8	<0.009	0.011
Magnesium	49	95.9	<0.003	<0.003
Sodium	49	38.8	0.007	0.028
Potassium	49	98.0	<0.003	<0.003
Ammonium	47	93.6	<0.02	<0.02
Sulfate	47	97.9	<0.03	<0.03
Nitrate	47	95.7	<0.03	<0.03
Chloride	47	89.4	<0.03	0.04
Ortho-phosphate	47	80.8	<0.01	0.02
pH (units)	49	0.0	5.64	5.78
Conductivity (µS/cm)	49	0.0	1.1	1.7

a. number of analyses

TABLE B-3 ,Analyte Concentration Summary for Filter Leachate B - 1986

Analyte	n[a]	Frequency of MDL (%)	Percentile Concentration (mg/L> 50%	95%
Calcium	49	89.8	<0.009	0.010
Magnesium	49	98.0	<0.003	<0.003
Sodium	49	61.2	<0.003	0.016
Potassium	49	95.9	<0.003	<0.003
Ammonium	47	97.9	<0.02	<0.02
Sulfate	47	97.9	<0.03	<0.03
Nitrate	47	100.0	<0.03	<0.03
Chloride	47	97.9	<0.03	0.04
Ortho-phosphate	47	95.7	<0.01	0.01
pH (units)	49	0.0	5.64	5.80
Conductivity (µS/cm)	49	0.0	1.1	1.7

a. number of analyses

TABLE B-4 Analyte Concentration Summary for Deionized Water Room 209* - 1986

Analyte	n^b	Frequency of MDL (%)	Concentration (ng/L) 50%	95%
Calcium	45	95.6	<0.009	<0.009
Magnesium	45	95.6	<0.003	<0.003
Sodium	45	77.8	<0.003	0.014
Potassium	45	97.8	<0.003	<0.003
Ammonium	45	100.0	<0.02	<0.02
Sulfate	45	100.0	<0.03	<0.03
Nitrate	45	100.0	0.03	<0.03
Chloride	45	100.0	<0.03	<0.03
Ortho- phosphate	45	97.8	<0.01	<0.01
pH (units)	45	N.A.	5.64	5.81
Conductivity (µS/cm)	45	N.A.	0.8	1.3

a. Sample processing laboratory
b. number of analyses

TABLE B-5 Analyte Concentration Summary for Deionized Water Room 304* - 1986

Analyte	n^b	Frequency of MDL (%)	Concentration (mg/L) 50%	95%
Calcium	48	87.5	<0.009	<0.009
Magnesium	48	97.9	<0.003	<0.003
Sodium	48	60.4	<0.003	0.043
Potassium	48	85.4	<0.003	0.007
Ammonium	47	100.0	<0.02	<0.02
Sulfate	47	100.0	<0.03	<0.03
Nitrate	47	100.0	<0.03	<0.03
Chloride	47	97.9	<0.03	<0.03
Ortho- phosphate	47	100.0	<0.01	<0.01
pH (units)	48	N.A.	5.68	6.04
Conductivity (µS/cm)	48	N.A.	1.1	1.6

a. Atomic absorption laboratory
b. number of analyses

APPENDIX C

Replicate (0/Q) Sample Analyses

Plots and Tables

1986

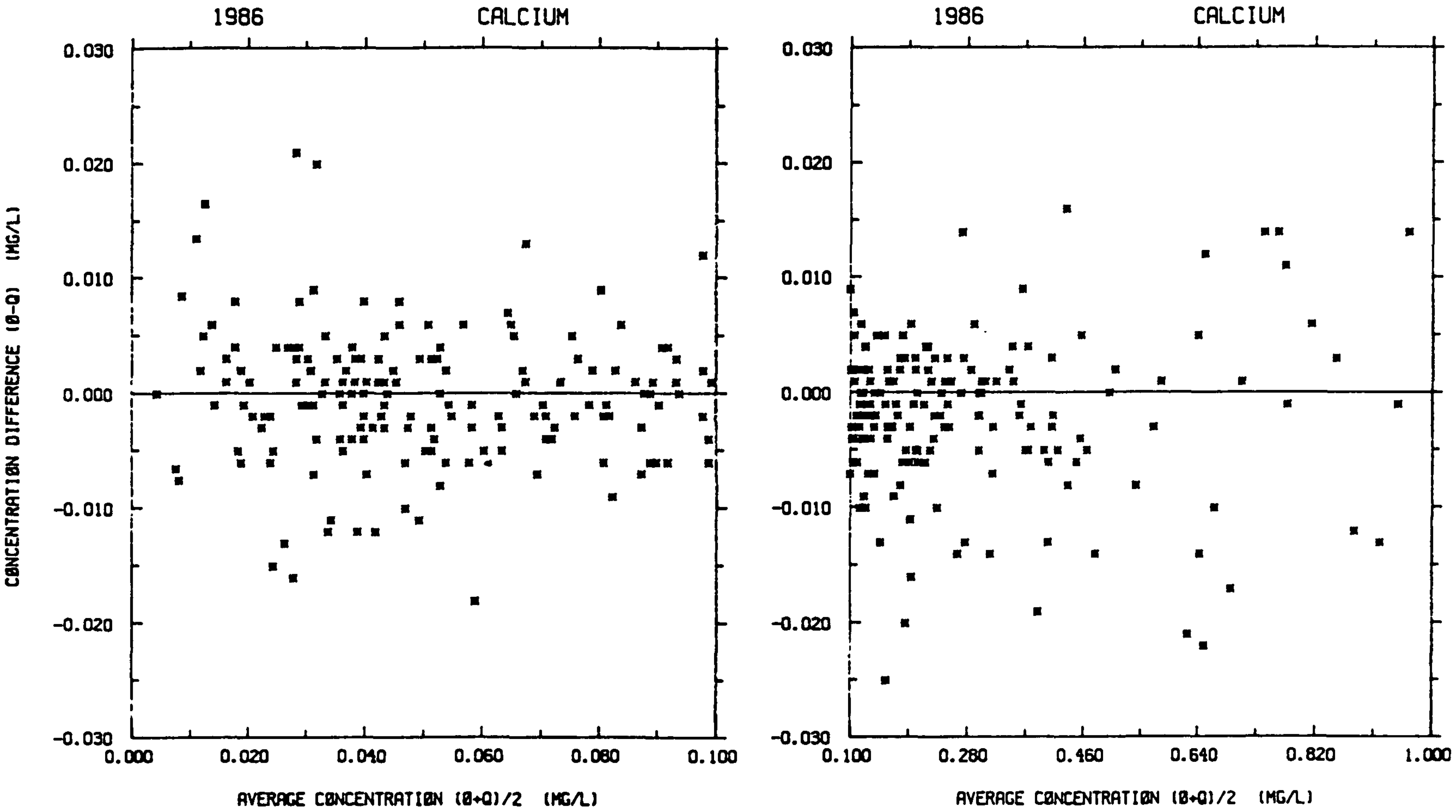


FIGURE C-1. 0/Q replicate plots for calcium for 1986.

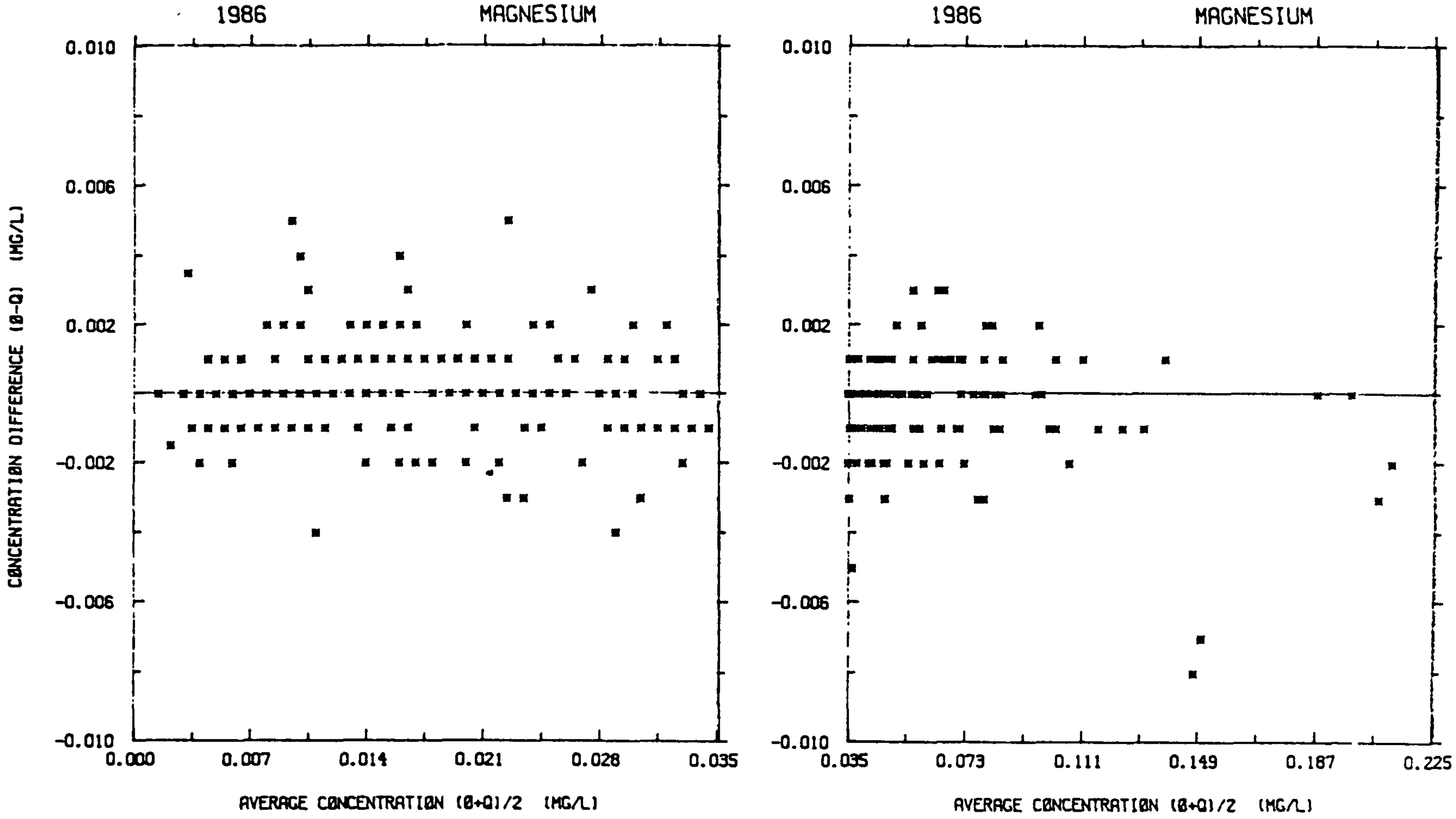


FIGURE C-2. 0/Q replicate plots for magnesium for 1986.

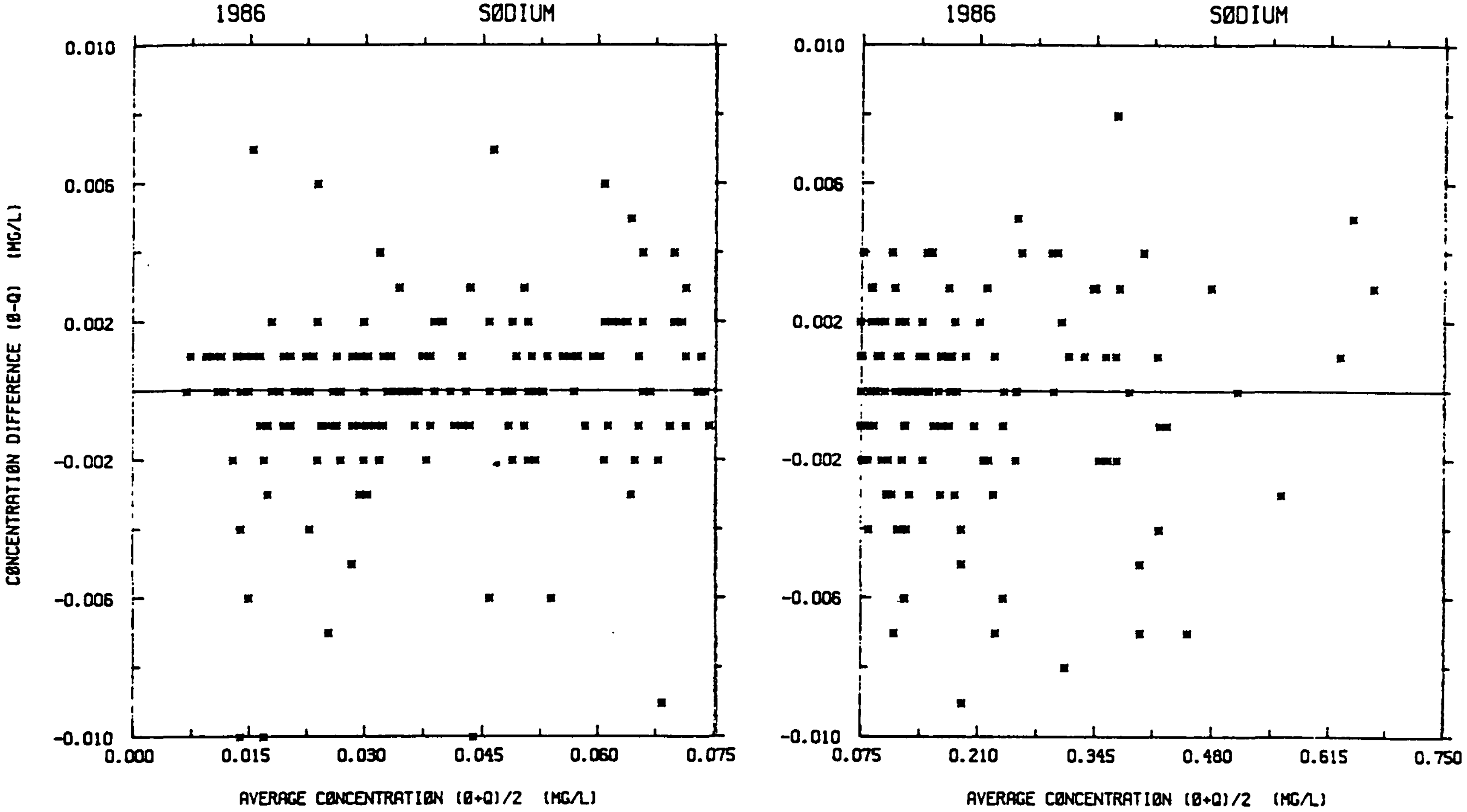


FIGURE C-3. 0/Q replicate plots for sodium for 1986.

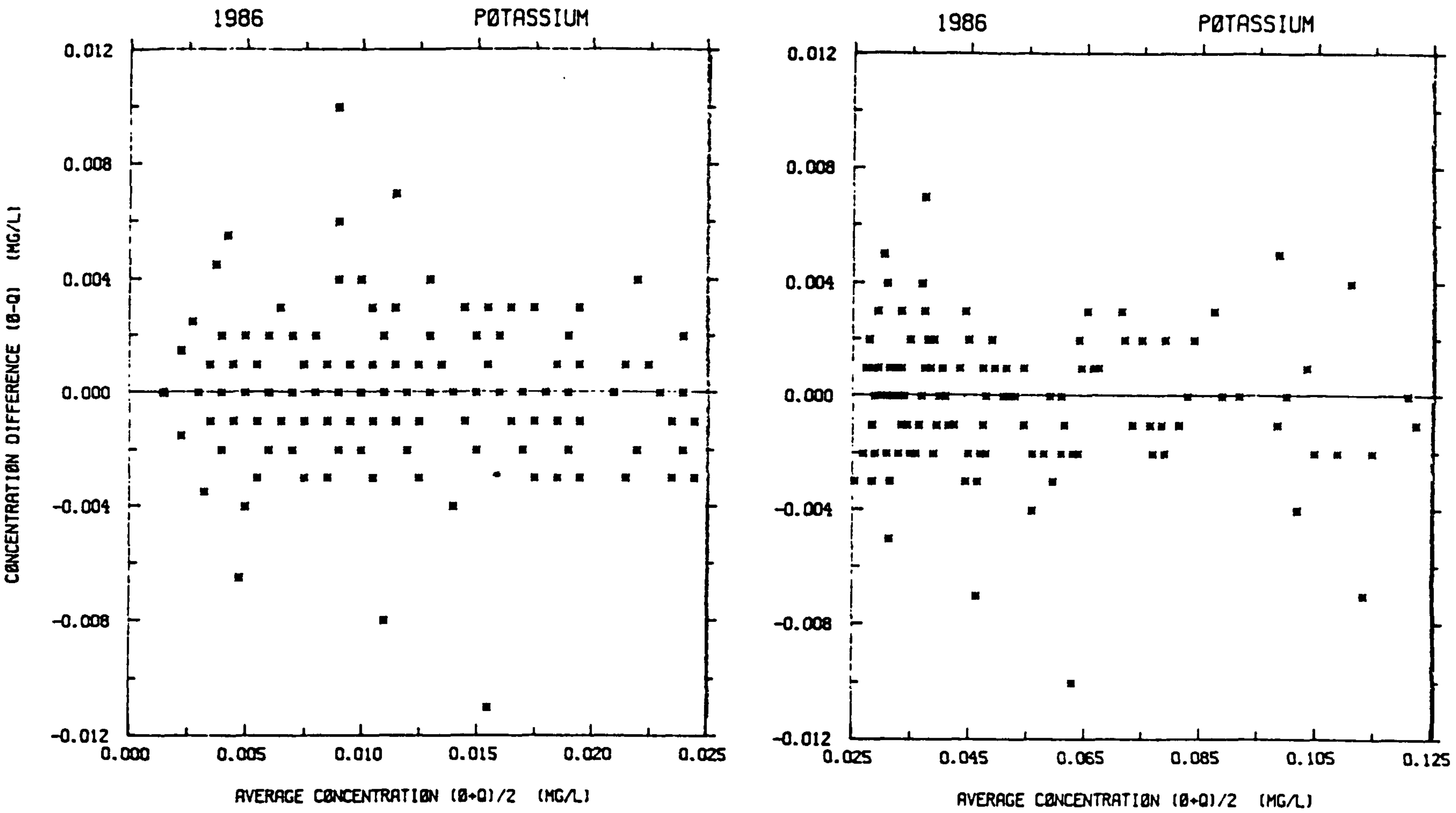


FIGURE C-4. 0/Q replicate plots for potassium for 1986.

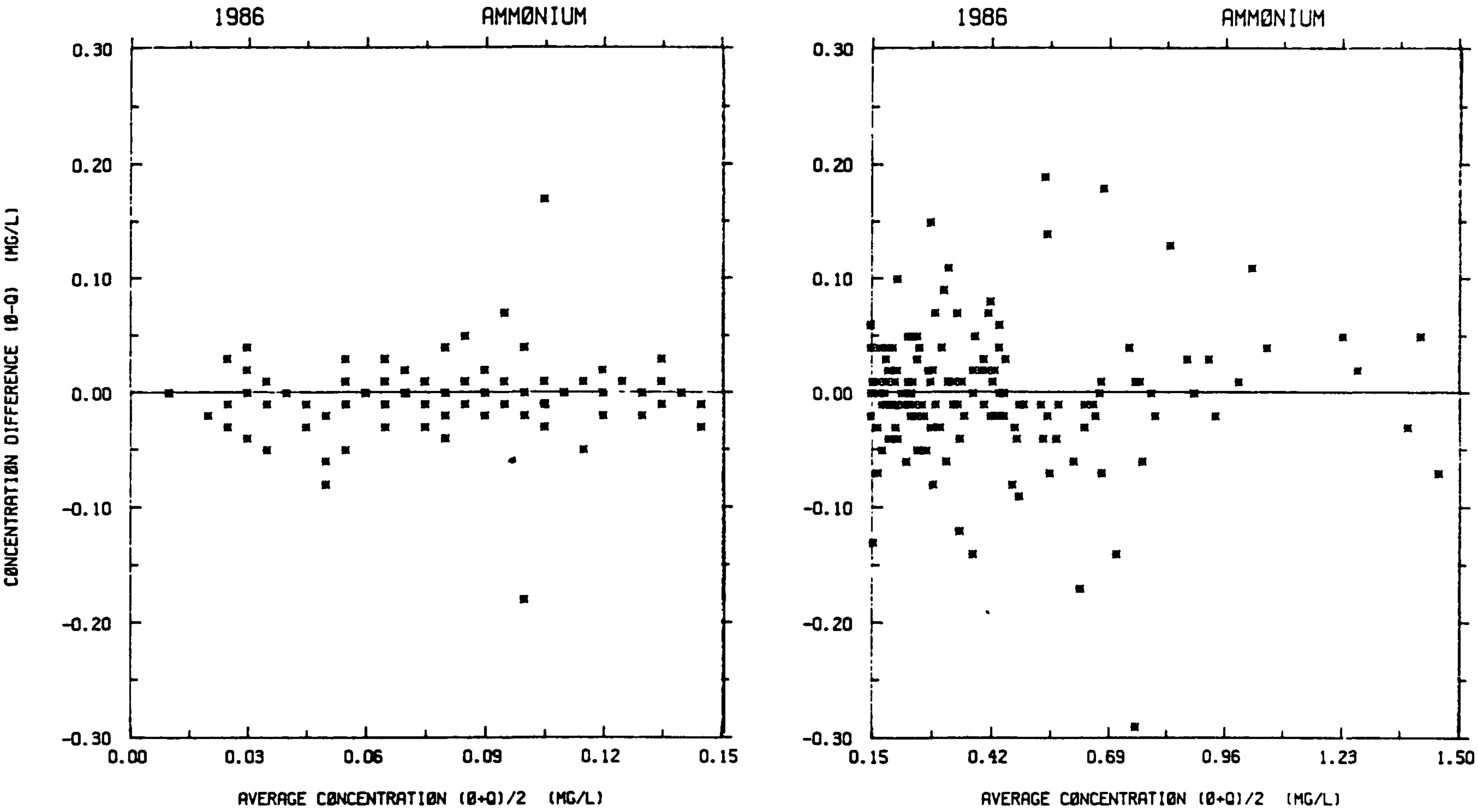


FIGURE C-5. 0/Q replicate plots for ammonium for 1986.

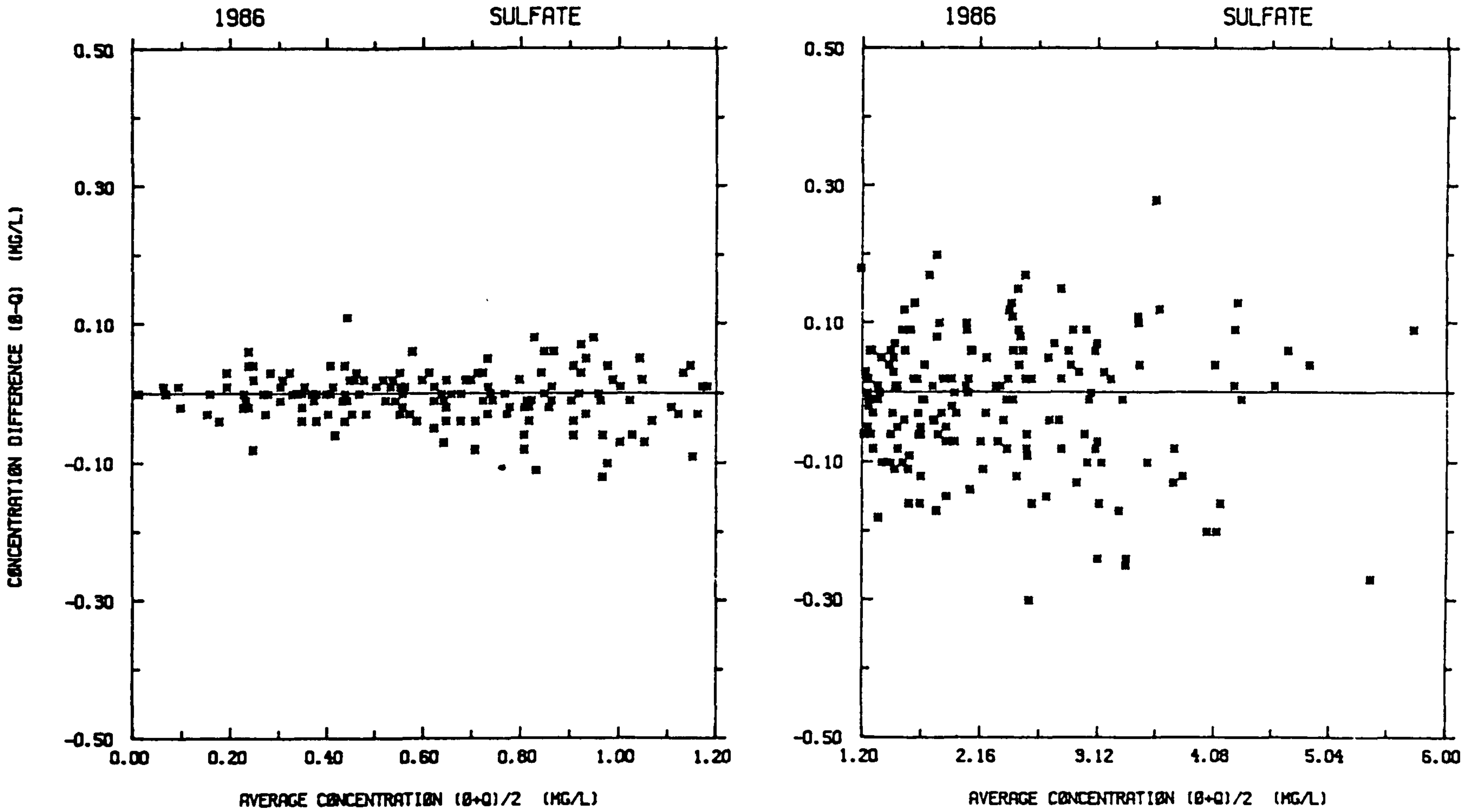


FIGURE C-6. 0/Q replicate plots for sulfate for 1986.

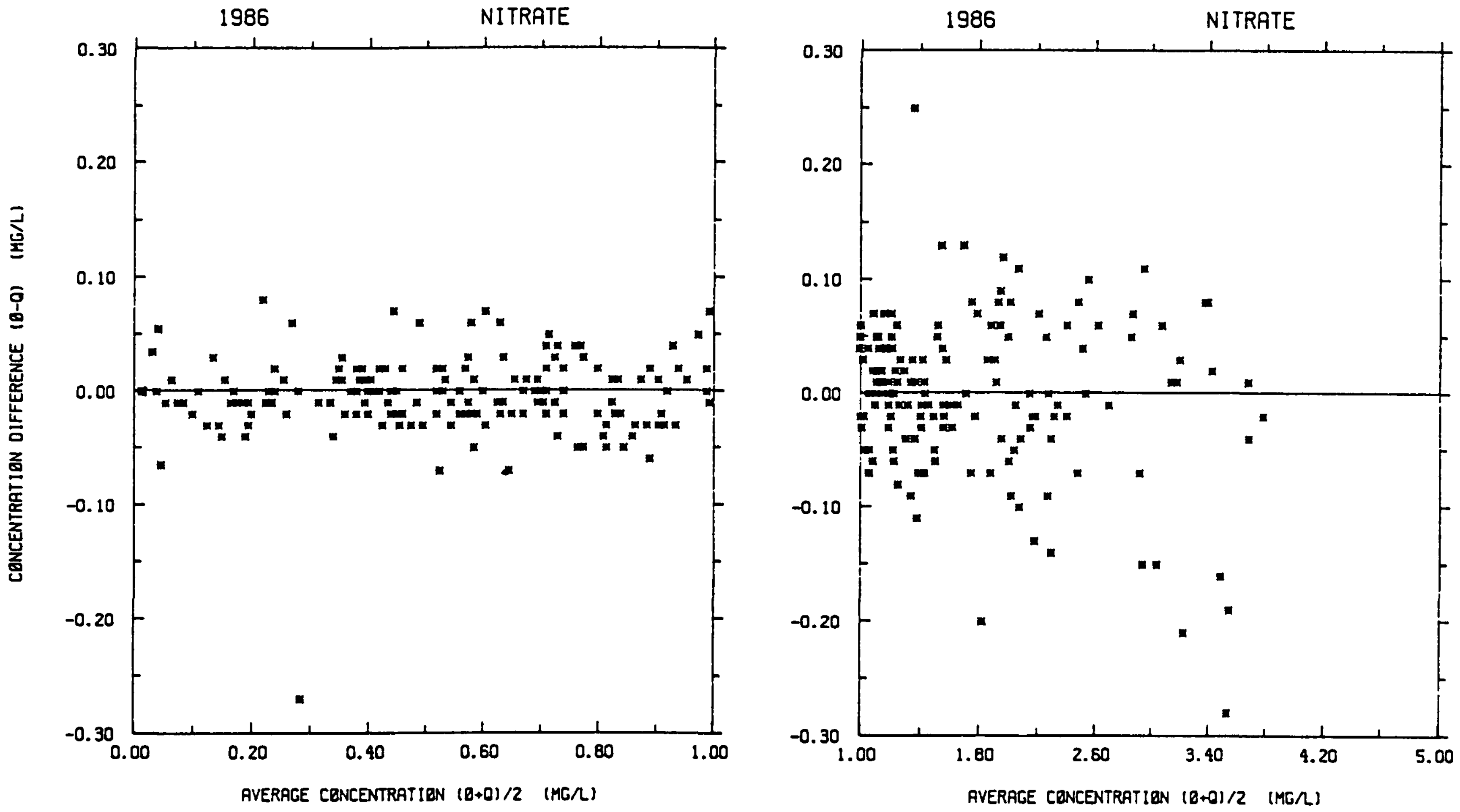


FIGURE C-7. O/Q replicate plots for nitrate for 1986.

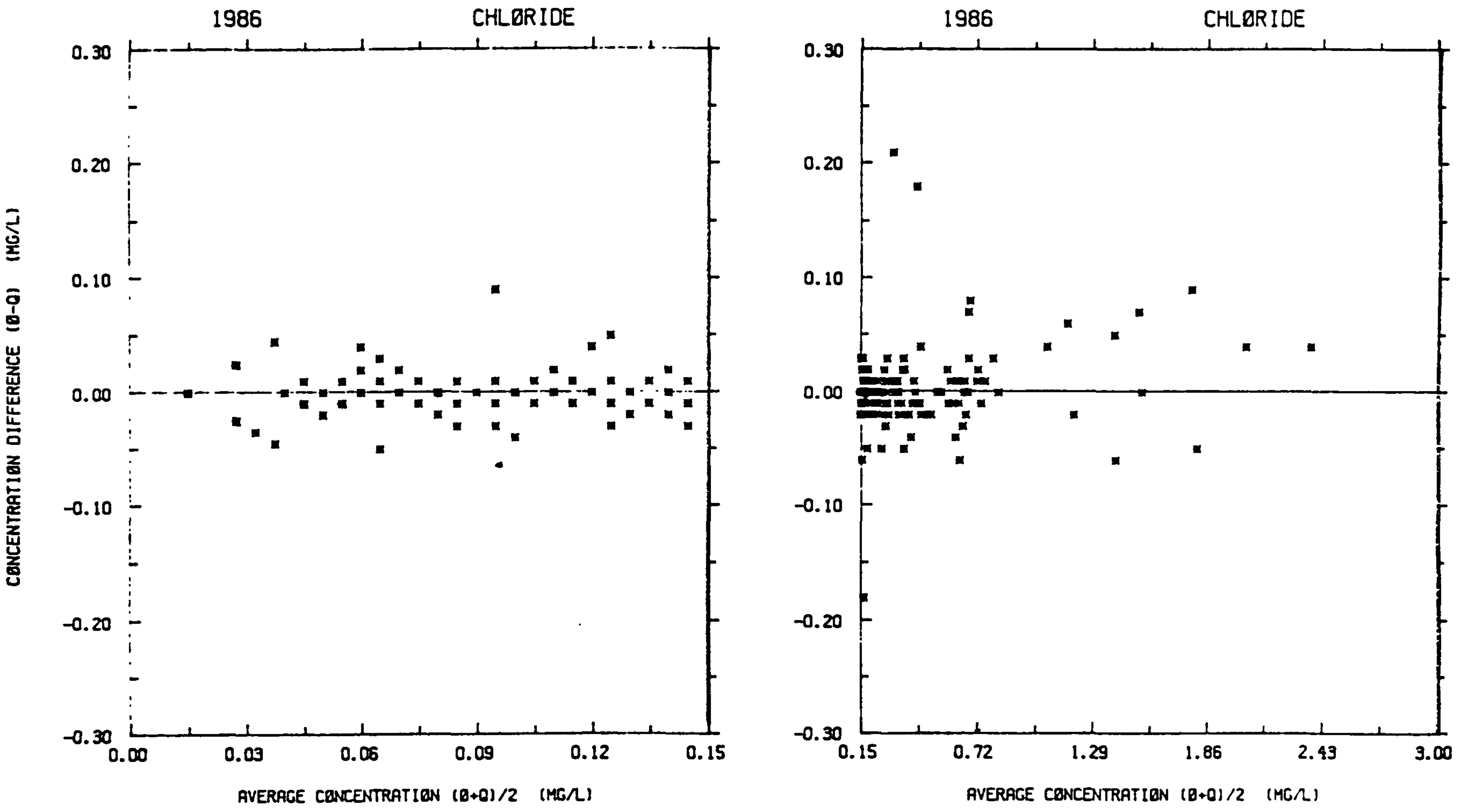


FIGURE C-8. 0/Q replicate plots for chloride for 1986.

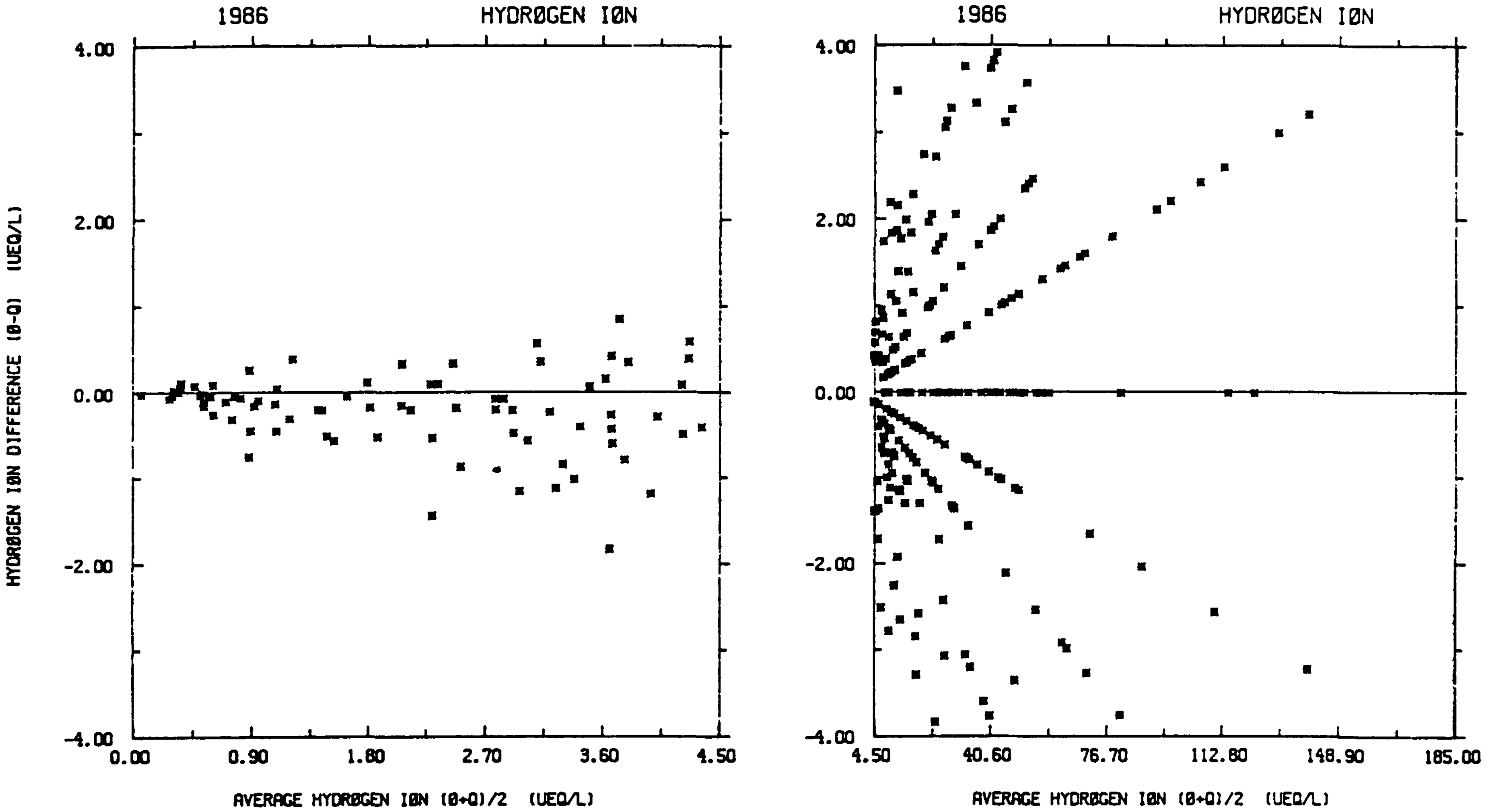


FIGURE C-9. 0/Q replicate plots for hydrogen ion for 1986.

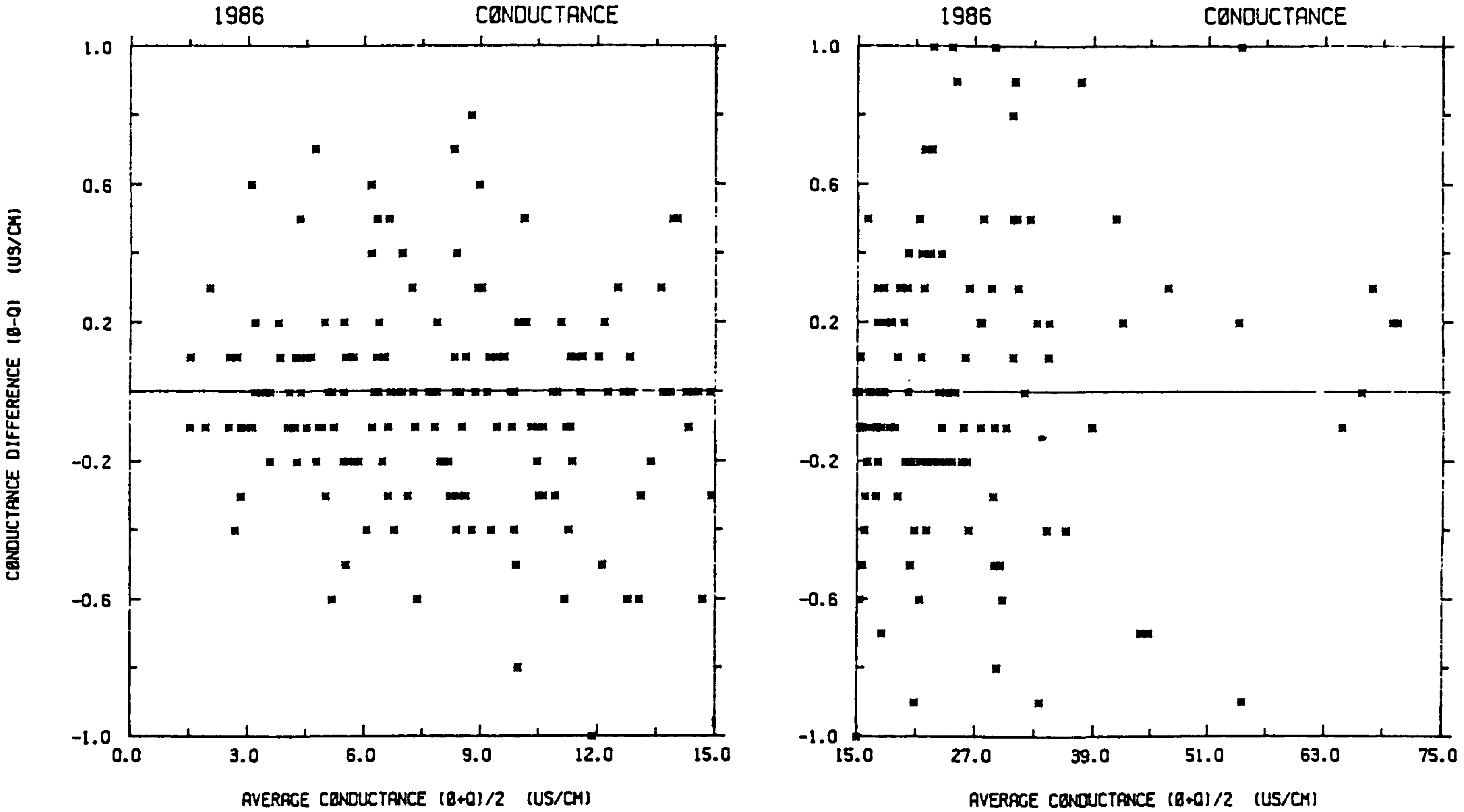


FIGURE C-10. O/Q replicate plots for conductance for 1986.

TABLE C-1 Data Summary for Replicate (0/Q) Analyses in 1986

Parameter	n[a]	Median Difference (mg/L	Mean Difference (mg/L)	Standard Deviation of Difference (mg/L)
Calcium	344	-0.001	0.000	0.018
Magnesium	344	0.000	0.000	0.004
Sodium	344	0.000	0.002	0.053
Potassium	344	0.000	0.000	0.003
Ammonium	344	0.00	0.00	0.06
Sulfate	344	0.00	0.01	0.25
Nitrate	344	0.00	-0.01	0.06
Chloride	344	0.00	0.00	0.04
pH (µeq/L)	344	0.00	6.90	5.56
Specific Conductance OS/cm)	344	0.0	0.2	3.7

a. number of replicate pairs

APPENDIX D

Interlaboratory Comparison Data

USEPA, LRTAP, and EMEP

1986

TABLE D-1 **EPA Interlaboratory Comparison of Reference Precipitation Samples - April 1986 -** CAL **Values Compared to Expected Values.**

Parameter	1055 CAL	1055 EPA	2067 CAL	2067 EPA	3230 CAL	3230 EPA
Calcium (mg/L)	0.058	0.061	6.17	6.25	0.150	0.155
Magnesium (mg/L)	0.014	0.012	0.530	0.522	0.056	0.053
Sodium (mg/L)	0.241	0.243	2.90	2.92	1.32	1.34
Potassium (mg/L)	0.078	0.082	2.99	2.97	0.556	0.535
Ammonium (mg/L)	0.14	0.134	4.57	4.651	0.46	0.438
Nitrate (mg/L)	0.66	0.660	12.66	12.173	3.94	3.780
Chloride (mg/L)	0.39	0.40	20.82	20.53	1.17	1.103
Sulfate (mg/L)	1.62	1.589	22.02	21.442	6.50	6.231
pH (units)	4.53	4.53	3.45	3.43	3.92	3.93
Specific Conductance (μS/cm)	16.7	15.9	265.6	265.8	66.4	65.3

Number of participating laboratories - 33

TABLE D-2 **EPA Interlaboratory Comparison of Reference Precipitation Samples - October 1986 -** CAL **Values Compared to Expected Values.**

Parameter	1043 **CAL**	1043 **EPA**	**2181 CAL**	**2181 EPA**	**3884 CAL**	**3884 EPA**
Calcium (mg/L)	0.065	0.070	0.162	0.166	0.009	0.009
Magnesium (mg/L)	0.037	0.036	0.019	0.019	0.074	0.075
Sodium (mg/L)	0.243	0.243	0.310	0.312	0.608	0.617
Potassium (mg/L)	0.108	0.106	0.108	0.107	0.124	0.124
Ammonium (mg/L)	0.13	0.133	1.08	1.015	1.39	1.293
Nitrate (mg/L)	0.62	0.606	0.66	0.646	8.01	7.862
Chloride (mg/L)	0.37	0.37	0.800	0.782	1.20	1.21
Sulfate (mg/L)	2.61	2.478	10.16	9.677	14.71	13.850
pH (units)	4.36	4.31	3.85	3.80	3.51	3.47
Specific Conductance (μS/cm)	24.4	24.1	78.5	77.1	161.9	162.4

Number of participating laboratories - 28

TABLE D-3 LRTAP Interlaboratory Comparability Study L12-
April 1986 - CAL Reported Values Coopered to
CCIW Median Values for all Participating Laboratories,[a]

Parameter	Sample Number 1		2		3		4	
	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	0.152	0.160	0.291	0.300	0.690	0.700	2.281	2.300
Magnesium (mg/L)	0.082	0.080	0.158	0.160	0.441	0.450	0.489	0.490
Sodium (mg/L)	0.456	0.445	1.29	1.30	3.14	3.165	0.979	0.985
Potassium (mg/L)	0.081	0.080	0.206	0.200	0.281	0.270	0.178	0.160
Ammonium(mg/L)	0.06	0.04	0.16	0.10				
Nitrate (mg/L)	0.26	0.29	0.49	0.46	0.22	0.24	0.35	0.35
Chloride (mg/L)	0.75	0.750	2.75	2.700	5.12	5.000	0.27	0.270
Sulfate (mg/L)	1.00	1.00	1.84	1.800	2.89	2.870	3.42	3.455
pH (units)	4.97	5.00	4.54	4.57	5.25	5.25	7.10	6.79
Specific Conductance (µS/cm)	10.2	9.60	25.2	24.05	29.4	29.95	21.9	22.15

Parameter	Sample Number 5		6		8		10	
	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	5.61	5.670	1.787	1.810	1.760	1.800	3.85	3.980
Magnesium (mg/L)	0.500	0.510	0.652	0.670	0.397	0.410	0.647	0.672
Sodium (mg/L)	0.618	0.619	4.03	4.025	0.531	0.531	0.915	0.940
Potassium (mg/L)	0.240	0.230	0.291	0.290	0.142	0.141	0.415	0.400
Ammonium (mg/L)			0.06	0.05				
Nitrate (mg/L)	0.97	0.96	0.09	0.12			0.62	0.62
Chloride (mg/L)	0.26	0.260	5.25	5.090	0.20	0.200	0.27	0.267
Sulfate (mg/L)	6.19	6.275	2.78	2.775	8.04	8.080	12.66	12.63
pH (units)	7.40	7.115	6.60	6.310	4.40	4.42	6.40	6.27
Specific Conductance (µS/cm)	39.2	39.6	36.5	36.85	35.9	35.3	38.3	39.00

a. number of participating laboratories; = 45

TABLE D-4 LRTAP Interlaboratory Comparability Study L14 - December 1986 - CAL Reported Values Compared to CCIW Median Values for All Participating Laboratories.[a]

Parameter	Sample Number							
	1		2		3		4	
	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	0.296	0..290	0.172	0.164	0.036	0..040	4.43	4.465
Magnesium (mg/L)	0.051	0..050	0.084	0.090	0.733	0,.780	0.725	0.730
Sodium (mg/L)	0.333	0..333	0.468	0.460	0.705	0..708	5.90	5.95
Potassium (mg/L)	0.158	0..160	0.089	0.080	1.08	1,.080	0.779	0.779
Ammonium (mg/L)	0.04	0..04	0.05	0.05	0.009	0..013	0.005	0.006
Nitrate (mg/L)	0.93	0.93	0.31	0.30	0.49	0..47	1.02	0.99
Chloride (mg/L)	0.48	0..495	0.75	0.765	0.89	0..865	11.34	10.90
Sulfate (mg/L)	0.37	0..360	1.04	1.005	3.15	3.,100	7.40	7.485
pH (units)	5.59	5..620	5.07	5.040	5.14	5.,140	6.50	6.430
Specific Conductance (μS/cm)	6.4	6..400	9.8	9.320	19.0	18.,4	68.3	67.00

Parameter	Sample Number			
	5		6	
	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	2.08	2.080	**2.36**	2.390
Magnesium (mg/L)	0.427	0.420	**0.691**	0.690
Sodium (mg/L)	0.738	0.750	0.578	0.580
Potassium (mg/L)	0.768	0.760	0.408	0.400
Ammonium (mg/L)	0.006	0.010	0.010	0.018
Nitrate (mg/L)	0.80	0.76	1.11	1.06
Chloride (mg/L)	0.53	0.543	0.41	0.438
Sulfate (mg/L)	4.91	4.874	8.38	8.362
pH (units)	5.68	5.650	5.63	5.557
Specific Conductance (MS/cm)	24.1	23.70	29.3	29.00

a. number of participating laboratories = 46

TABLE D-5 EMEP Study #9 Interlaboratory Comparison Study April 1986 - CAL Reported Values Compared to EMEP Expected Values

	Sample Number							
	G1		G2		G3		**G4**	
Parameter	**CAL**	**EMEP**	**CAL**	**EMEP**	**CAL**	**EMEP**	**CAL**	**EMEP**
Calcium (mg/L)	0.189	0.19	0.851	0.86	0.159	0.16	0.801	0.80
Magnesium (mg/L)	0.468	0.48	0.402	0.41	0.056	0.06	0.069	0.07
Sodium (mg/L)	1.99	2.02	2.98	3.02	2.14	2.18	3.34	3.37
Potassium (mg/L)	0.394	0.36	0.303	0.30	0.126	0.12	0.158	0.15
Ammonium (mg/L)	0.22	0.27	0.24	0.31	1.48	1.55	1.30	1.39
Nitrate (mg/L)	5.53	5.44	0.93	0.84	6.02	5.89	1.11	1.02
Chloride (mg/L)	2.26	2.27	2.08	2.09	3.24	3.32	3.10	3.08
Sulfate (mg/L)	4.94	4.76	8.93	8.78	4.73	4.52	9.65	9.44
pH (units)	4.04	4.05	4.52	4.66	4.05	4.07	4.45	4.59
Specific Conductance **(µS/cm)**	61.2	58.5	43.3	40.2	65.4	62.6	51.6	48.1