

QUALITY ASSURANCE REPORT NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
1987

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

Illinois State Water Survey
National Atmospheric Deposition Program
2204 Griffith Dr.
Champaign, IL

ROOM#

908

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.

For further information, Please write or call:

J.H. Gibson
NADP/NTN Coordinator
Natural Resource Ecology Laboratory
Colorado State University
Fort Collins, CO 80523
(303) 491-1978

1987 QUALITY ASSURANCE REPORT
NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
January 1987 through December 1987

prepared by Kenni O. W. James
Quality Assurance Specialist
Analytical Chemistry Unit
Illinois State Water Survey
2204 Griffith Drive
Champaign, Illinois 61820-7495
October 1989

ACKNOWLEDGEMENTS

This Quality Assurance Report was prepared with the help and direction of Mark E. Peden, Laboratory Manager for the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN). The analytical data summarized in this report were produced by the laboratory personnel listed in Section II. The figures were prepared by the Support Services Unit of the Illinois State Water Survey. The statistical analyses, computer-generated plots, and network percentile concentration data were prepared by Peg A. Folta and Leon Olszewski. Their efforts are greatly appreciated. I am indebted to Jacqueline Lockard Peden for her fine past examples, which I followed. At this time, I wish to thank Lacie Jeffers for her secretarial assistance. Also, I thank Gary Stensland and Van Bowersox for their comments and assistance with the past, present, and future quality assurance program at the CAL. I appreciate all comments and suggestions that were made by the external and in-house reviewers: Sue Bachman, Loretta Skowron, Leon Olszewski, Laurie McCarthy, Randy See, Cary Eaton, Berne Bennett, and David Bigelow.

CONTENTS

	Page
Acknowledgements	iii
Figures and Tables	vi
I. Introduction	1
II. Laboratory Quality Assurance Program	3
A. General Description of Changes	3
B. Data Availability	4
C. Laboratory Personnel	4
III. Laboratory Blank Data	9
A. Bucket Leachates	9
B. Filter Leachates	11
C. Deionized Water	14
IV. Laboratory Bias and Precision	15
A. Quality Control Check Sample Data	15
1. Solutions Used by the Analysts	15
2. Analytical Bias and Precision Tables....	15
3. Discussion of Results	16
B. Replicate Sample Data	19
1. Explanation of Replicate Sample Tables and Plots	19
2. Discussion of Results	19
C. Internal Blind Sample Data	21
1. Solutions Used	21
2. Explanation of Bias and Precision Tables	22
3. Discussion of Results	22
V. Reanalysis Procedures	37
A. Ion Percent Difference	38
B. Conductance Percent Difference	39
C. Histograms	40
D. Discussion of Results	40
VI. External Quality Assurance Program Participation	45
A. U.S. Geological Survey External Audit Program	45
B. Interlaboratory Comparison Studies	46
1. U. S. Environmental Protection Agency	46
2. Canada Centre for Inland Waters	47
VII. Summary	49
VIII. References	53
APPENDIX A: Glossary of Terms	55
APPENDIX B: Laboratory Blanks: Plots and Tables	61
APPENDIX C: Replicate (O/Q) Sample Analyses: Plots and Tables	73
APPENDIX D: Interlaboratory Comparison Data: USEPA and LRTAP	87

FIGURES AND TABLES

	Page
FIGURE II-1 Sample processing flowchart, January 1987 through June 1987.....	6
FIGURE II-2 Sample processing flowchart, July 1987 through December 1987.....	7
FIGURE III-1 Comparison of A and B filter blanks with filtered blind deionized water and 4.30 check solution.....	13
FIGURE IV-1 Comparison of filtered and unfiltered internal blind samples (calcium I). 1987...	28
FIGURE IV-2 Comparison of filtered and unfiltered internal blind samples (magnesium I), 1987.	28
FIGURE IV-3 Comparison of filtered and unfiltered internal blind samples (sodium I), 1987....	29
FIGURE IV-4 Comparison of filtered and unfiltered internal blind samples (potassium I), 1987.	29
FIGURE IV-5 Comparison of filtered and unfiltered internal blind samples (sulfate I), 1987...	30
FIGURE IV-6 Comparison of filtered and unfiltered internal blind samples (pH I), 1987.....	31
FIGURE IV-7 Comparison of filtered and unfiltered internal blind samples (specific conductance I), 1987.....	31
FIGURE IV-8 Comparison of filtered and unfiltered internal blind samples (calcium II), 1987..	32
FIGURE IV-9 Comparison of filtered and unfiltered internal blind samples (magnesium II), 1987	32
FIGURE IV-10 Comparison of filtered and unfiltered internal blind samples (sodium II), 1987...	33
FIGURE IV-11 Comparison of filtered and unfiltered internal blind samples (potassium II), 1987	33
FIGURE IV-12 Comparison of filtered and unfiltered internal blind samples (sulfate II), 1987..	34
FIGURE IV-13 Comparison of filtered and unfiltered internal blind samples (nitrate II), 1987..	34
FIGURE IV-14 Comparison of filtered and unfiltered internal blind samples (pH II),1987.....	35
FIGURE IV-15 Comparison of filtered and unfiltered internal blind samples (specific conductance),1987.....	35
FIGURE V-1 Ion percent difference histogram for NADP/NTN wet side samples, 1987.....	41
FIGURE V-2 Conductance percent difference histogram for NADP/NTN wet side samples, 1987.....	42
TABLE II-1 Method Detection Limits for the Analysis of Precipitation Samples, 1987.....	5
TABLE II-2 Central Analytical Laboratory (CAL) Analytical Staff Personnel Summary, 1987...	8
TABLE III-1 Median Analyte Concentrations Expressed as Mass/Bucket Found in Inverted Buckets, 1987	10

FIGURES AND TABLES (Concluded)

		Page
TABLE III-2	Median Analyte Concentrations Found in Filter Leachates A and B, 1987.....	12
TABLE III-3	Median pH and Conductivity for Deionized Water Blanks, 1987.....	14
TABLE IV-1	Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation, 1987.....	17
TABLE IV-2	Analytical Bias and Precision Determined from Analysis of Quality Control Check Samples, 1987.....	18
TABLE IV-3	Fiftieth and Ninety-fifth Percentile Concentration Values of Chemical and Physical Parameters Measured in Replicate (O/Q) Samples, 1987.....	20
TABLE IV-4	Analytical Bias and Precision Results from the Internal Blind Audit Program (SWS1), 1987.....	24
TABLE IV-5	Analytical Bias and Precision Results from the Internal Blind Audit Program (SWS2), 1987.....	25
TABLE IV-6	Analytical Bias and Precision Results from the Internal Blind Audit Program (SWS3-1), 1987.....	26
TABLE IV-7	Analytical Bias and Precision Results from the Internal Blind Audit Program (SWS3-2), 1987.....	27
TABLE V-1	Factors Used to Convert Milligrams per Liter to Microequivalents per Liter for Ion Percent Difference Calculations....	43
TABLE VII-1	Summary of Quality Assurance Changes and Innovations, 1987.....	50

I. INTRODUCTION

This 1987 Quality Assurance (QA) Report for the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) documents the progress and results of the laboratory QA program now in place and yet to evolve. For six months beginning on March 24, eighteen National Park Service sites sent their weekly samples to another laboratory. The effect of this absence on the quality assurance program can be noted in the smaller number of samples analyzed and used to identify the chemical characteristics of the network samples for the year (Table IV-1).

This report follows the format used in previous QA reports with changes and additions implemented where appropriate. Section II contains a brief review of changes that occurred in 1987 and an update of the CAL personnel. Modifications to the blank procedures and details of special studies to identify contamination sources are described in Section III. Laboratory bias and precision are being assessed in three distinct programs that provide valuable information and identify areas requiring remedial action as well as areas that require only continued monitoring (Section IV). Revision of the reanalysis procedure resulted in several changes in the computer program used to identify samples that require further study and analysis (Section V). Section VI briefly reviews the U.S. Geological Survey (USGS) Blind Audit Program and CAL participation in interlaboratory testing programs. The final section summarizes the changes that occurred in 1987 and gives an overall assessment of the performance of the CAL (Section VII). The appendices include a glossary of terms used in the report and tables and figures containing information in addition to that presented with the text in the individual sections.

II. LABORATORY QUALITY ASSURANCE PROGRAM

A. GENERAL DESCRIPTION OF CHANGES

The changes implemented in 1987 consisted of modifications and improvements on the QA program that had evolved in previous years. The laboratory facility remained unchanged from 1986. Orthophosphate analysis was changed from automated colorimetric analysis to ion chromatography in July. This change was approved at a meeting of the NADP Subcommittee on Methods Development and Quality Assurance in October 1986, where it was noted that the detection limit would change from 0.01 to 0.02 mg/L, and that the analysis would be used as a sample screening procedure.

The final motion was to measure the orthophosphate by ion chromatography and to make the data available only upon special request. The sample processing flowchart (Figures II-1 and II-2) changed accordingly in July 1987, as did the detection limit for phosphate (Table II-I).

The number of bucket blanks remained the same as in 1986, while additional deionized water samples were analyzed to verify the quality of the supply in various laboratories at the CAL. The prerinse water quantity was increased to 300 mL before collecting the filter leachates A and B (Section III).

The control limits for Quality Control Samples (QCS) were revised by using the statistics from 1986, and control charts were plotted with these values. The replicate samples continued to be the blind O-Q splits used the previous year, but the number was reduced from 4% to 2% of the total sample throughput.

National Bureau of Standards (NBS) simulated rainwater standard reference materials were submitted as internal blind samples each week, along with alternating samples of deionized water and pH 4.30 check solution. A third internal blind weekly sample was submitted to assess the effects of filtration on samples (Section IV).

The criteria for reanalysis were modified by including calculated hydrogen, bicarbonate, and hydroxide ion concentrations in the ion sum and changing the factors used for the calculated conductance (Section V).

The External Quality Assurance Program continued with the official Interlaboratory Comparison by the USGS and voluntary participation in other interlaboratory comparison studies.

B. DATA AVAILABILITY

The data presented in this report, as in the previous report, have been verified by either a double-entry procedure or by a visual check. The raw data have been stored in the Illinois State Water Survey CAL database and are available from the CAL director upon written request.

C. LABORATORY PERSONNEL

There were several changes in the analytical staff in 1987 (Table II-2). Clarence Dunbar left to resume his studies; his position in sample receipt and processing was filled by Theresa Eckstein Ingersoll. Jacqueline Peden resigned in July and Kenni James became the quality assurance specialist in October. Jeffrey Pribble replaced Theresa Ingersoll in sample receipt, and Michael Slater left at the end of June. His duties were assumed by Sue Bachman and Brigita Demir.

TABLE II-1 Method Detection Limits for the
Analysis of Precipitation Samples,
1987.

Analyte	Method*	Method Detection Limit (MDL) mg/L	Dates
Calcium	Flame Atomic Absorption	0.009	10/80 - 12/87
Magnesium	Flame Atomic Absorption	0.003	10/80 - 12/87
Sodium	Flame Atomic Absorption	0.003	10/80 - 12/87
Potassium	Flame Atomic Absorption	0.003	10/80 - 12/87
Ammonium	Automated Phenate, Colorimetric	0.02	1/79 - 12/87
Sulfate	Ion Chromatography	0.03	5/85 - 12/87
Nitrate	Ion Chromatography	0.03	5/85 - 12/87
Chloride	Ion Chromatography	0.03	5/85 - 12/87
Ortho- phosphate	Automated Ascorbic Acid, Colorimetric	0.01	2/86 - 7/87
	Ion Chromatography	0.02	7/87 - 12/87

* For a complete method description, see Methods for
Collection and Analysis of Precipitation (I)

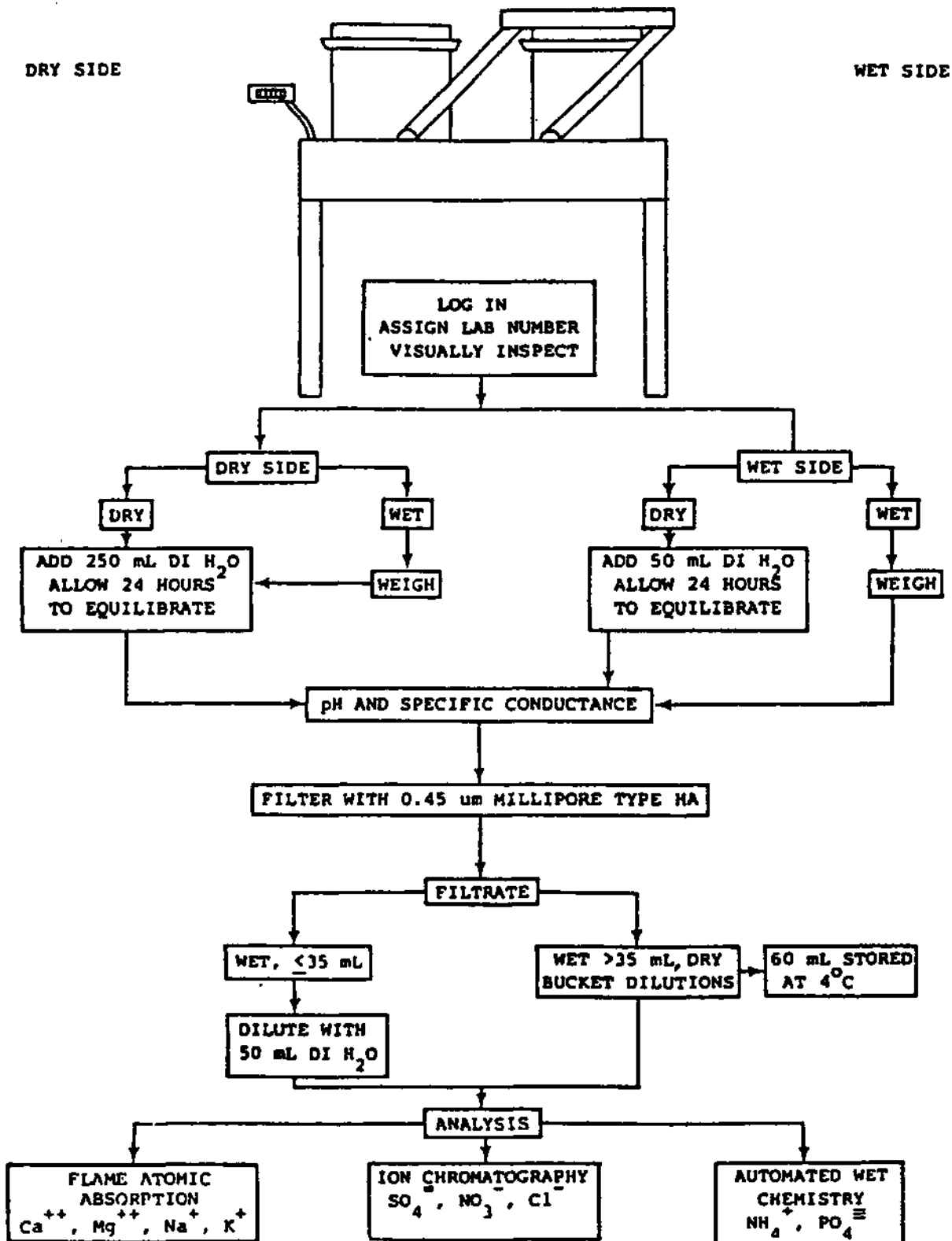


FIGURE II-1. Sample processing flowchart, January 1987 through June 1987.

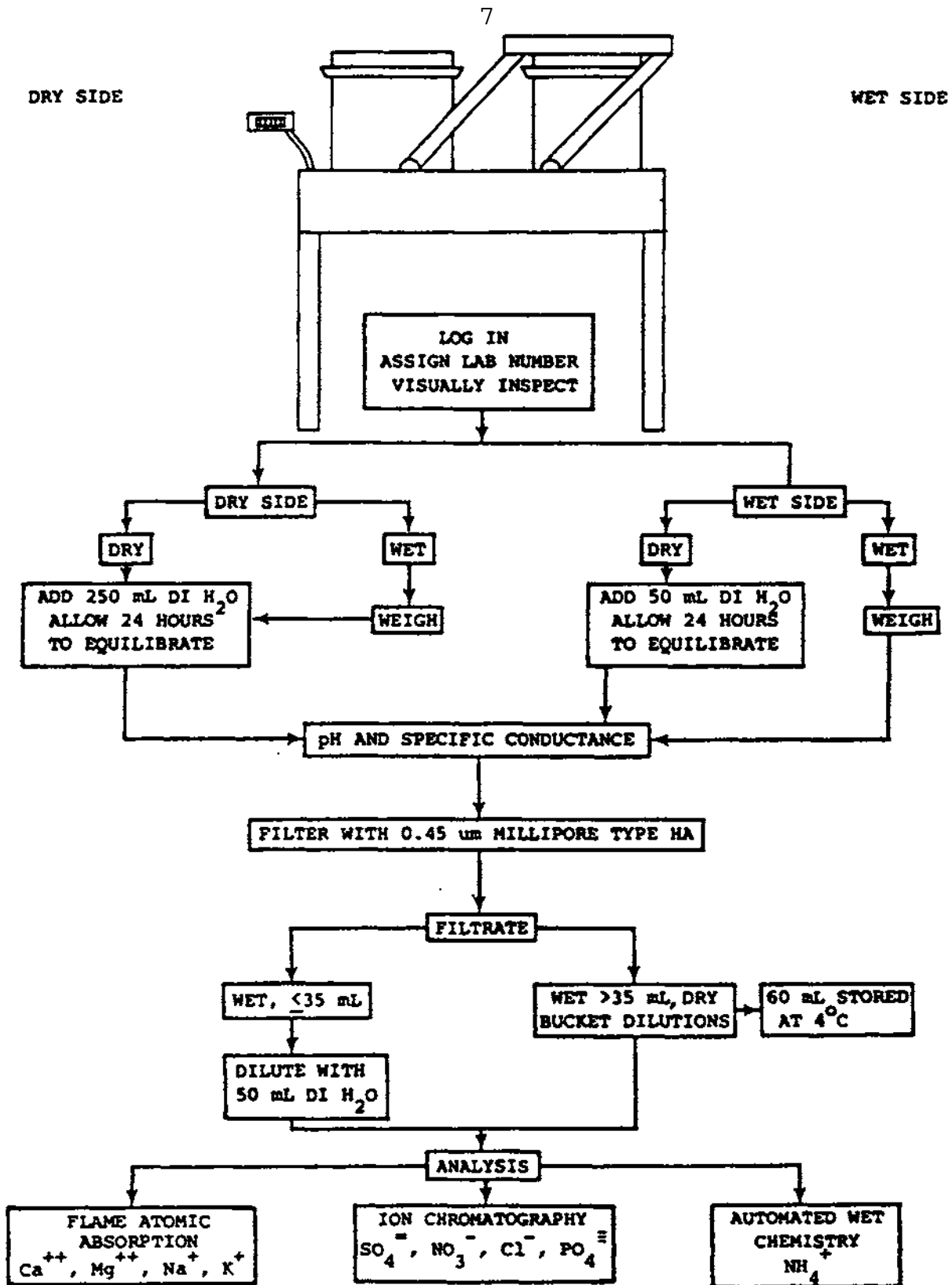


FIGURE II-2. Sample processing flowchart, July 1987 through December 1987.

TABLE II-2 central Analytical Laboratory (CAL)
Analytical Staff Only, 1987.

Staff Member/Job Function	Period of Employment
Beth Allhands/ Sample Receipt and Processing	February, 1984 - December, 1987
Sue Bachman / NH ₄ analysis	August, 1980 - December, 1987
Brigita Demir/ SO ₄ , NO ₃ , Cl, PO ₄ analysis	September, 1981 - December, 1987
Pat Dodson/ Sample Processing	September, 1980 - December, 1987
Clarence Dunbar/ Sample Receipt and Processing	July, 1981 - August, 1987
Theresa Eckstein Ingersoll/ Sample Receipt and Processing	March, 1985 - December, 1987
Kenni James/ Quality Assurance	October, 1987 - December, 1987
Jacqueline Lockard/ Quality Assurance	October, 1982 - July, 1987
Mark Peden/ Laboratory Manager	July, 1978 - December, 1987
Jeffrey Pribble/ Sample Receipt	July, 1987 - December, 1987
Loretta Skowron/ Ca, Mg, Na, K analysis	July, 1978 - December, 1987
Mike Slater/ NH ₄ , PO ₄ analysis	September, 1979 - June, 1987
Sheri Uber/ Sample Processing, pH, and Conductance	April, 1986 - December, 1987

III. LABORATORY BLANK DATA

This section presents the changes and modifications made to the set of blanks collected weekly. This set consists of bucket, filter, and deionized water blanks. The number of blanks per week depends on whether or not a contamination problem has been noticed. The routine set includes two leachates from inverted sample buckets with the lids pounded on, two leachates from a preleached filter, and two deionized water samples - one from the sample processing laboratory, the other from the analytical laboratories. In 1987 an additional deionized water blank was added from the laboratory area. The blanks are collected randomly at different times of the week and day. These blank samples are incorporated into the daily analysis routine, and the data sheets are submitted for data entry when a page that accommodates 25 samples is filled. The quality assurance specialist is notified as soon as a contamination problem has been detected and the source is sought immediately.

A. BUCKET LEACHATES

The bucket and lid washing procedure continued as modified in 1986(2), and the weekly leachates were collected in the same manner. Two buckets are selected from different wash loads, and lids are selected randomly from those that have been washed and bagged for shipment. Fifty mL of deionized water are added to the first bucket and 150 mL are added to the second. The lids are pounded on and the buckets inverted. After 24 hours the leachates are poured into 60 mL, high density polyethylene (HDPE) bottles and routed through the analytical process.

Appendix Figures B-1, 2, 3, and 4 display plots of the analyte masses measured in the bucket blank samples in 1987. 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 ($\mu\text{g}/\text{mL}$) by the sample volume in milliliters. The dashed line near the bottom of each plot represents the minimal detectable mass for that analyte. The dashed lines on the pH and conductivity plots (Appendix Figure B-5) represent the median value for the deionized water from the sample processing laboratory (Room 209), where these samples are prepared.

Table III-1 summarizes the annual median masses for the 50-mL and 150-mL leachates analyzed in 1987. Comparison of

these masses and conductivities to the summaries in previous reports (2,3) reveals that, with the exception of sodium and chloride, the analyte concentrations in the leachates from the bucket blanks have improved in 1987. The sodium contamination was detected and reported early in the year, and a continuing series of bucket blank analyses were run for sodium. The high concentrations appear to be random and unrelated to personnel or physical processes. Several variables were examined as sources for the sodium contamination, including the containers used to presoak the lids. The tests indicated that the sodium contamination seems to be caused by the o-ring in the outer groove of the sample bucket. Without this o-ring, however, considerable leakage would occur. Efforts to eliminate excess sodium have not proven entirely successful so far. Sources of contaminants are always being investigated as part of the ongoing quality assurance program, including the special lid experiments. The contribution from the buckets with the elevated sodium and often chloride concentrations would be of particular concern for low-volume samples with little or no dilution effect.

TABLE III-1 Median Analyte Concentrations
Expressed as Mass (μg) per Bucket
round in Inverted Buckets, 1987.

Analyte	50 mL	150 mL
Calcium	0.7	<0.45
Magnesium	<0.15	<0.15
Sodium	3.7	3.45
Potassium	<0.15	<0.15
Ammonium	<1.0	<1.0
Sulfate	2.5	<1.5
Nitrate	<1.5	<1.5
Chloride	2.0	<1.5
Ortho-phosphate	<1.0	<1.0
pH (units)*	5.94	5.81
$\mu\text{equiv}/\text{bucket}$	0.057	0.23
Conductivity ($\mu\text{S}/\text{cm}$)	1.9	1.3
Number of Samples	51	51

* pH of DI water 5.59 = 2.57 $\mu\text{equiv}/\text{L}$
 50 mL \times 0.00257 $\mu\text{equiv}/\text{mL}$ = 0.13 μequiv
 150 mL \times 0.00257 $\mu\text{equiv}/\text{mL}$ = 0.38 μequiv

B. FILTER LEACHATES

The weekly filter blank procedure used for several previous years was modified in April by increasing the initial rinse volume from 250 to 300 mL. After this initial leaching, a 50 mL portion of deionized water is filtered, collected, and labeled "A". A second 50 mL sample of deionized water is passed through the same filter and labeled "B". Table III-2 provides the median concentrations of the analytes found in the filter blanks in 1987. The tables in Appendix B present a complete annual summary of the analyses of these leachates.

In contrast to previous years, it is obvious that the only analyte greater than its detection limit is sodium. Traces of this ion have been measured continually in filtrate A. As in the past, the B leachate median values are below the method detection limit for all of the cations and anions. The conductivity and pH values of both the A and B leachates are not statistically different from the values for the deionized water from the same initial source (Table III-2).

In fall 1987 the laboratory quality assurance specialist and the data management quality assurance specialist examined the effect of filtration on the sodium concentrations measured in blind samples submitted both internally and from the USGS external blind audit program. Each person looked at the data graphically. The sodium concentration in milligrams per liter (mg/L) was plotted on the y axis, while the x axis represented the date of the analysis. The two sets of data appeared similar when graphed: the sodium concentrations, ranging from just above the method detection limit to as high as 0.05 mg/L, seemed to appear and disappear randomly.

The internal blind sample data were then plotted on a graph that also included the A and B filter leachates for the entire year. The occurrence of high sodium peaks for the A and B blanks and filtered blind samples is random but when there are measurable amounts in the A sample, there are trace amounts remaining in the B portion (Figure III-1). As in the past, it was concluded that human activities and the laboratory environment introduce several micrograms per liter of sodium into the filtered samples. As a result, modifications have been made on the filter apparatus, and more stringent rules have been enacted for the filtering area and personnel. Filter blank results indicate that these efforts have reduced sodium concentrations, however, the problem has not been eliminated. The effect of the filtration process will be discussed again in Chapter IV in connection with the section on the internal blind program.

TABLE III-2 Median. Analyte Concentrations
Found in Filter Leachates A and B,
1987.

Analyte	Median Concentration (mg/L)		Number of Analyses
	A	B	
Calcium	<0.009	<0.009	53
Magnesium	<0.003	<0.003	53
Sodium	0.011	<0.003	53
Potassium	<0.003	<0.003	53
Ammonium	<0.02	<0.02	53
Sulfate	<0.03	<0.03	53
Nitrate	<0.03	<0.03	53
Chloride	<0.03	<0.03	53
Orthophosphate	<0.02	<0.02	53
pH (units)	5.61	5.61	53
(μ eq/L)	2.45	2.45	
Conductivity	1.0	0.9	53
(μ S/cm)			

Filter Blanks for 1987 Sodium

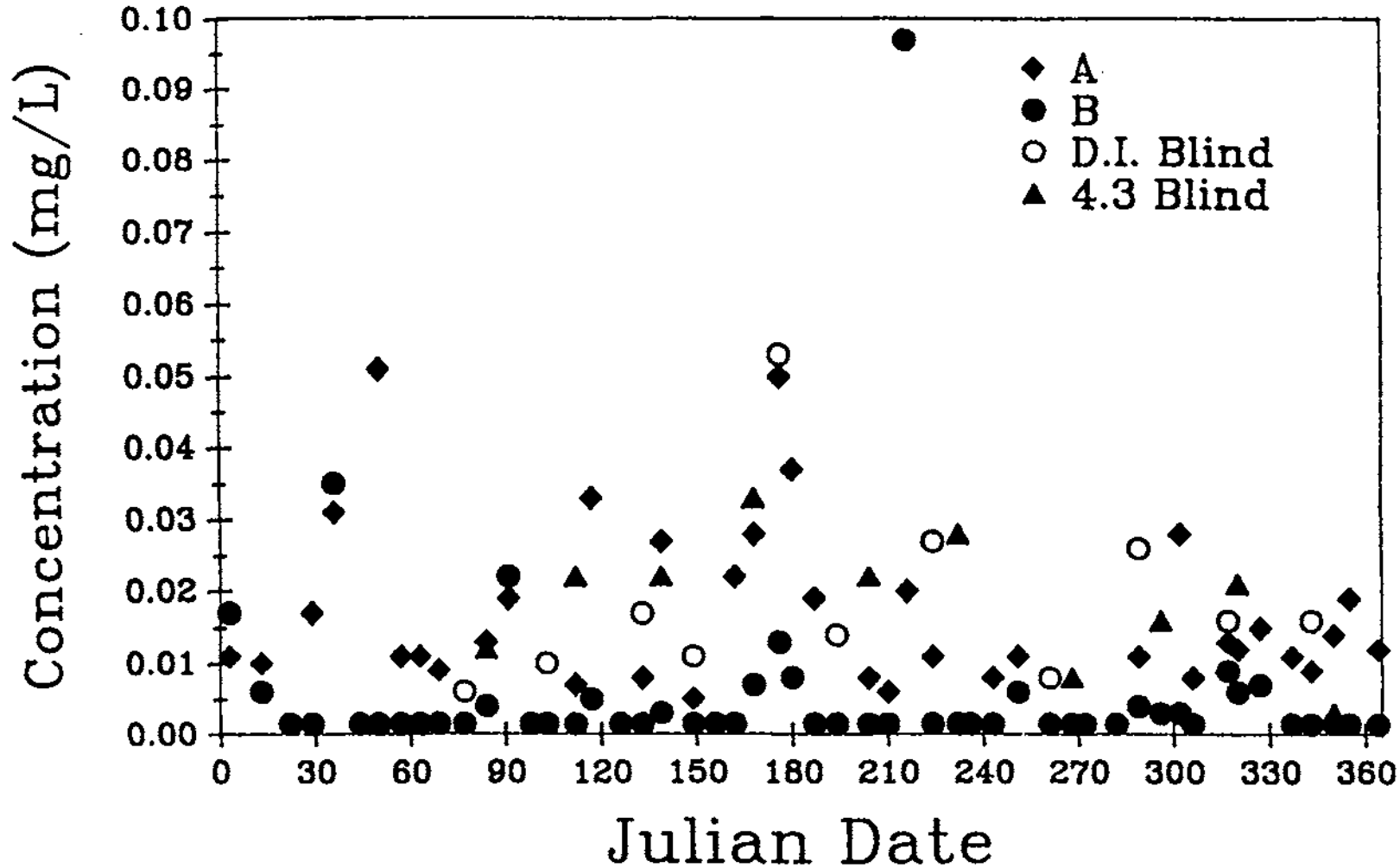


FIGURE III-1. Comparison of A and B filter blanks with filtered blind deionized water and 4.30 check solution.

C. DEIONIZED WATER

The quality of the deionized water used in the laboratories continues to be monitored daily. The point-of-use deionization cartridges in the laboratories contain in-line conductivity monitors. To ensure high quality water for all of the CAL measurements, weekly samples are collected on random days from both the sample processing laboratory, and the atomic absorption (AA) laboratory. In 1987 weekly analyses were performed on deionized water samples from the Inductively Coupled Argon Plasma (ICP) Laboratory and the bucket and lid washing laboratory. The ICP laboratory was monitored for twenty-seven weeks. Deionized water from the bucket and lid-washing laboratory continues to be analyzed so that it can be ruled out as a possible contamination source.

The median concentrations of the major ions determined in the routine precipitation analyses for samples collected at all four locations are all less than the laboratory's method detection limits. A tabular representation therefore seems redundant. Table III-3 is condensed to show only the pH and conductivity values determined this year. Appendix Tables B-4 through B-7 contain the more complete annual summaries from four sources.

TABLE III-3 Median pH and Conductivity for
Deionized Water Blanks, 1987.

Room Use	PH (units)	[H ⁺] (μ equiv/L)	Conductivity (μ S/cm)	Number of Analyses
Sample Processing	5.59	2.57	0.7	49
AA	5.68	2.09	0.9	51
ICP	5.58	2.63	1.0	29
Bucket Washing	5.65	2.24	0.7	27

IV. LABORATORY BIAS AND PRECISION

The use of quality control check samples (QCS) to verify instrument calibration and to validate sample analyses continues to be a valuable component of the quality assurance program. Repeated analysis of these samples provides the data used to generate monthly control charts and annual bias and precision statistics. Additional precision information is obtained by analyzing replicate samples. The third and final component of the bias and precision assessment is the internal blind sample program, which was further refined in 1987.

A. QUALITY CONTROL CHECK SAMPLE DATA

QCSs are internally diluted reference solutions that have expected concentrations at the 25th and 75th percentile values of precipitation samples analyzed the previous year.(2)

Solutions Used by the Analysts

The formulations for QCS solutions in 1987 were the same as those used in 1986. The pH and conductivity solutions are prepared internally and verified by additional analyses in the laboratory. A dilute nitric acid solution (5.01×10^{-5} N HNO_3) is used to monitor pH and conductivity, and a 5.0×10^{-4} N KCl solution is used to calibrate the conductivity bridge and monitor pH at a second level. Prior to use by the analysts, both of these solutions are tested in the laboratory for pH and conductivity and by ion chromatography. The potassium concentration of the KCl is determined by atomic absorption. The results of these analyses must be within predetermined control limits, and they must meet the criteria of the ion balance program used on all CAL precipitation samples. These solutions are identical to those provided by CAL to each of the monitoring sites.

Mineral and nutrient concentrates obtained from the U. S. Environmental Protection Agency (USEPA), Environmental Monitoring and Support Laboratory (EMSL)-Cincinnati are diluted to the 25th and 75th percentile concentrations (Table IV-1) of the ion of interest and used whenever that parameter is quantified. Two lower level concentrations for sodium and potassium were used this year to better coincide with the actual network concentrations.

Analytical Bias and Precision Tables

Table IV-2 was prepared from the data obtained from the analysis of QCS solutions in 1987. These solutions are measured as soon as the calibration curve is derived and run

at least once every 12 samples thereafter for the major ions. For pH and conductivity, at least one QCS measurement is made for every 20 precipitation samples. The statistics for the pH measurement required conversion of the pH value to hydrogen ion concentration in microequivalents per liter.

The theoretical concentrations for the USEPA QCS represent the mean recovery values obtained from referee laboratories' analyses and are supplied with the concentrates. A t-test (4) was used to compare the mean values measured at the CAL to those provided with the concentrates. The results of this comparison are then used to determine whether or not the results are significantly biased. The equations used for bias and precision and the calculation of the critical concentration are listed in the Glossary (Appendix A). The critical concentration calculation used this year differs from the previous critical percent calculation. It is the same as used previously for the NBS simulated rainwater submitted to the laboratory as internal blind samples. By using the same calculations, the comparison of bias evaluation of the known QCS and the unknown NBS simulated rainwater becomes valid.

Discussion of Results

The percentile concentrations for 1987 NADP/NTN samples are tabulated in Table IV-1. Samples included in this compilation consist of volumes of 35 mL or more each. The number is smaller in 1987 than in 1986 due to the six month absence of the eighteen National Park Service sites' samples. The concentrations are not significantly different, however, from those in the corresponding table in the 1986 report (2).

The data presented in Table IV-2 show several significantly biased results. Closer inspection of the actual bias reveals that the quantities are extremely small and that a bias of one $\mu\text{g/L}$ can lead to a statistically significant difference. Results are considered biased if the absolute difference between the theoretical value and the measured concentration is greater than or equal to the critical value. In comparing the results for 1985(3), 1986(2), and 1987, note that the sulfate samples of 3.43 mg/L have consistently exhibited a positive bias, although it seems to be decreasing. The percent biases for the two formulations are 5.0 and 6.1%, making them the only two examples where the larger percentage represents more than 0.01 mg/L. The precision, expressed as percent relative standard deviation (%RSD), has improved as well. Efforts to explain the bias continue. If the theoretical or "true" EPA value of 3.6 mg/L is used instead of the experimental mean, the bias is diminished considerably, although it is still positive. The problem is evident in the internal blind audit and interlaboratory comparison samples, so it is of concern as solutions are sought.

The actual percent bias for these samples compares quite favorably to previous years. Of the thirty solutions used, twenty five, or 83%, exhibit a bias of less than 5%. All of the results are within the maximum allowable bias defined in the NADP/NTN QA Plan. Monthly control charts, with warning and control limits set by the quality assurance specialist, are an immediate and ongoing means of detecting bias and monitoring the measurement process.

TABLE IV-1 Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation - 1987.

Parameter	Percentile Concentration Values (mg/L)									
	Kin.	5th	10th	25th	50th	75th	90th	95th	99th	Max.
Ca	<0.009	0.020	0.030	0.060	0.130	0.280	0.570	0.880	1.90	17.90
Hg	<0.003	0.007	0.010	0.016	0.028	0.057	0.103	0.159	0.373	6.40
K	<0.003	0.003	0.005	0.011	0.022	0.043	0.082	0.122	0.282	1.92
Na	<0.003	0.025	0.031	0.049	0.090	0.194	0.421	0.728	2.128	47.00
NH ₄	<0.02	<0.02	<0.02	0.07	0.20	0.43	0.73	1.01	1.84	6.50
NO ₃	<0.03	0.19	0.30	0.61	1.12	1.94	3.15	4.23	6.84	18.24
Cl ⁻	<0.03	0.05	0.06	0.09	0.15	0.28	0.62	1.12	3.84	87.50
SO ₄	<0.03	0.23	0.35	0.70	1.40	2.61	4.28	5.54	9.00	17.04
PO ₄	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.12	0.68
pH (units)	3.46	4.00	4.12	4.38	4.78	5.36	6.05	6.40	6.84	7.89
(μ equiv/L)	347	100.0	75.8	41.7	16.6	4.36	0.89	0.40	0.14	0.01
Conductivity	1.3	3.6	4.7	7.8	14.2	25.5	42.0	53.4	84.6	346.6
(μ S/cm)										

Source: National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) 1987 - wet side samples (w).
Number of samples = 5624.

TABLE IV-2 Analytical Bias and Precision Determined from
Analysis of Quality Control Check Samples, 1987.

Parameter	Theoretical	Measured	Number of Replicates	Size		Precision,		Critical ^a [] mg/L	Statistically Significant Bias? ^b
	Concentration (mg/L)	Concentration (mg/L)		mg/L	%	mg/L	ISO %		
Calcium	0.053	0.053	707	0.000	0.0	0.002	3.8	0.001	No
	0.402	0.405	703	0.003	0.7	0.003	0.7	0.002	Yes
Magnesium	0.018	0.018	707	0.000	0.0	0.001	5.6	0.000	No
	0.083	0.085	705	0.002	2.4	0.001	1.2	0.001	Yes
Sodium	0.041	0.041	466	0.000	0.0	0.001	2.4	0.000	No
	0.083	0.083	200	0.000	0.0	0.002	2.4	0.001	No
	0.230	0.233	469	0.003	1.3	0.001	0.4	0.001	Yes
	0.4S9	0.454	207	-0.005	-1.1	0.061	13.4	0.017	No
Potassium	0.011	0.010	465	-0.001	-9.1	0.001	10.0	0.000	Yes
	0.021	0.021	212	0.000	0.0	0.001	4.8	0.000	No
	0.050	0.050	469	0.000	0.0	0.001	2.0	0.000	No
	0.100	0.098	211	-0.002	-2.0	0.002	2.0	0.000	Yes
Ammonium	0.12	0.11	159	-0.01	-8.3	0.01	9.1	0.00	Yes
	0.13	0.13	184	0.00	0.0	0.01	7.7	0.00	No
	0.49	0.47	158	-0.02	-4.1	0.03	6.4	0.01	Yes
	0.64	0.64	184	0.00	0.0	0.02	3.1	0.01	No
Sulfate	0.93	0.94	568	0.01	1.1	0.02	2.1	0.01	Yes
	3.43	3.60	281	0.17	5.0	0.04	1.1	0.07	Yes
	3.43	3.64	232	0.21	6.1	0.08	2.2	0.08	Yes
Nitrate	0.44	0.45	257	0.01	2.3	0.01	2.2	0.00	Yes
	0.62	0.63	355	0.01	1.6	0.01	1.6	0.01	Yes
	2.19	2.26	279	0.07	3.2	0.03	1.3	0.01	Yes
	3.15	3.21	270	0.06	1.9	0.06	1.9	0.02	Yes
Chloride	0.12	0.12	508	0.00	0.0	0.01	8.3	0.00	No
	0.81	0.80	600	-0.01	-1.2	0.02	2.5	0.01	Yes
Ortho- phosphate	0.03	0.03	134	0.00	0.0	0.00	0.0	0.00	No
	0.05	0.05	135	0.00	0.0	0.01	20.0	0.00	No
pH (μ eq/L)	4.30(50.1)	4.31	1736	0.01	2.2	4.33	4.8	2.68	No
	5.50(3.2)	5.47	1736	-0.03	-7.2	5.53	13.9	0.33	No
Conductivity (μ S/cm)	21.8	21.7	1457	-0.1	-0.5	0.5	2.3	0.3	No

a. Critical = $t \times S_{\text{pooled}}$

b. At 95% confidence level

$$\sqrt{1/\sigma_{\text{EPA}} + 1/\sigma_{\text{CAL}}}$$

B. REPLICATE SAMPLE DATA

Replicate samples are analyzed every week as part of the regular sample routine. Since early 1986 these samples have been selected and analyzed by the same procedure. When a replicate sample is split, three 60 mL aliquots are taken. Two of the samples are given the same number, one of these goes to the laboratory for analysis, and the other is refrigerated for archival purposes. The third bottle returns to the sample receiving group where it is given another number and resubmitted blind to the analysts. These splits are referred to as "O/Q" (original/quality assurance) splits. After the analyses have been performed, but before the data are entered into the computer, the data management staff changes the number of the "Q" sample to the original number followed by a "Q". In September 1987 the number of replicate samples was reduced from 4% to 2% of the total samples analyzed. Table IV-3 briefly lists the distribution of samples selected for replication.

Explanation of Replicate Sample Tables and Plots

The figures in Appendix C plot the concentration differences between replicate samples O and Q in mg/L on the y-axis versus the average concentration of the two samples, which is plotted on the x-axis. There are two plots for each ion as well as pH and conductivity. Each pair of plots represents the concentrations from detection limit to the median value and the concentrations from the median value to the highest concentration for the analyte being measured. Appendix Table C-1 summarizes the information presented on the plots.

Discussion of Results

These samples prove valuable in assessing the repeatability of values obtained for samples that are treated alike in the laboratory, but analyzed from a different container on a different day. Repeatability has been defined as the precision of a method expressed as the agreement attainable between independent determinations performed by a single analyst using the same apparatus and techniques on more than one day (4). In the case of the CAL O/Q splits, the sample processing routine is involved as well as the chemical analysis procedure. The handling and resubmission of a second sample bottle is also a variable in this evaluation.

The tables and plots in this report appear basically as they have in past reports. Table IV-3, which characterizes the samples selected in 1987, indicates that these samples contained a wide range of concentrations of the different

analytes. The 50th percentile concentration of these samples falls within the 25th to 50th percentile values for the wet samples analyzed during this year. The 95th percentile values are all between the 90th and 99th percentile for the same set of samples.

Appendix Table C-1 includes the pertinent summary of the data. Because the purpose of this part of the program is to evaluate the precision of the CAL laboratory operation, the variability of the pairs is the most relevant information. The data for the median and mean values indicate no significant difference in the chemistry of the O/Q pairs. The standard deviations of the mean differences approximate the variability between paired analyses for each parameter.

Table IV-3 Fiftieth and Ninety-fifth Percentile Concentration Values of Chemical and Physical Parameters Measured in Replicate (O/Q) Samples, 1987.

Parameter	Percentile Concentration Values (mg/L)	
	50th	95th
Calcium	0.109	0.73
Magnesium	0.024	0.14
Sodium	0.075	2.00
Potassium	0.022	0.09
Ammonium	0.19	1.03
Sulfate	1.44	6.23
Nitrate	1.12	4.06
Chloride	0.13	1.10
pH ($\mu\text{eq/L}$)	18.4	101.4
(units)	4.74	3.99
Conductivity ($\mu\text{S/cm}$)	13.9	52.94

C. INTERNAL BLIND SAMPLE DATA

The internal blind program was begun in 1984. It has been expanded and refined during the intervening years to the form in place at the beginning of 1987.

The following section describes the solutions used as the blind samples. A final schedule was established using four different solutions. Four tables evaluating the results of the repeated analyses of these samples, are included in this section. They follow the same format used in Table IV-2. Study of these tables invites comparison between analyst-known QCS of concentrations in the range of the 25th to 75th percentile of the precipitation samples and samples submitted double-blind to the laboratory.

Solutions Used

The blind samples were given the NADP/NTN site designations of SWS1 and SWS2 and were submitted weekly beginning in January. Two different samples alternated weekly for each site designation. The SWS 1 samples were NBS Simulated Rainwater, Standard Reference Material (SRM)2694-I and 2694-II. They were submitted to the sample processing staff in their original bottles as SWS1. The samples were then transferred to the standard 60 mL sample bottles and given a sequential NADP/NTN number. These samples were not filtered and were placed in sequence on the laboratory trays for additional analyses after the pH and conductance were measured.

The SWS 2 samples alternated weekly between deionized water from Room 302 and the pH 4.30 QCS, used to validate pH measurements in the laboratory and at the sites. These samples were submitted to the sample processing staff in 60 mL sample bottles labeled "SWS2." They were then transferred to another sample bottle and numbered in the same manner as the SWS1 samples. Neither of these samples was filtered and the procedure followed that of the SWS1 samples.

In March it was decided to submit yet another weekly blind, which was designated "SWS3." This blind sample comprised the four samples mentioned above, all of which were submitted in rotation so that each one appeared once every four weeks. They were sent to the sample processing staff, as were the SWS1 and SWS2 samples. The procedure for the SWS3 blind differed in that after the pH and conductance were measured, the sample was filtered like network precipitation samples. They were then placed on the laboratory tray for cation and anion analyses.

The results in the tables were calculated using the same method used for the QCS; the NBS provides an estimate of uncertainty for each analyte present in the SRMs and certified values for each.

Explanation of Bias and Precision Tables

Tables IV-4, 5, 6, and 7 were prepared using the data obtained from the analyses of the internal blind solutions in 1987. The same t-test used for the QCS was used for these samples. Again, the formulas employed for bias, precision, and critical concentration difference are listed in the Glossary (Appendix A).

Discussion of Results

The most immediate comparison to be drawn from the annual summaries of the internal blind sample analyses is between the SWS1 and 2 and the SWS3. These data show the effect of filtration and the increased bias of the cations, most especially the calcium. The calcium concentrations in the filtered NBS samples are higher than those in the filter blanks. A near detection limit calcium concentration has also noted in the 4.30 check solution, which has been filtered. Both the calcium and magnesium biases have increased in the NBS filtered samples. The sodium difference has increased in the lower concentration and is more negative in the higher one. Potassium concentrations have decreased in both filtered samples. The decrease in the positive sulfate bias between the unfiltered SWS1 and the filtered SWS3 is noted with interest but the cause is not clear. Figures IV-1 through IV-15 are graphic representations for each certified ion from each NBS solution. The figures are cast in the same format as Figure III-1, and the key and information printed on each are self-explanatory.

The concentrations of the NBS samples differ greatly from those of the EPA QCS. Calcium and magnesium concentrations are low-- SRM 2694 I is just above the calcium detection limit-- and the concentration of SRM 2694 II is near the 15th percentile value for samples from the network. The other certified values are higher than 75% of the network samples.

When comparing the precision of the NBS samples, both filtered and unfiltered, to the EPA QCS, the percentages are higher. The %RSD values for 1987 do, however, compare favorably to those for the same samples in 1986(2).

The comparison of results from the SWS2s and the SWS3s where the same solutions were used is interesting in that the effects of the filtering process are evident. The deionized water, when filtered exhibits a slight sodium contamination

that is higher than the mean of the filter blanks. The 4.30 QCS results show calcium and magnesium as well as sodium, so that a bias is noted. The standard deviation for the filtered samples is also higher than unfiltered blind samples for most of the parameters, indicating that the physical process of filtering does contribute to the variability of some sample results.

Two SWS1 samples possessed obviously anomalous concentrations: an SRM-I with high calcium, magnesium, and sodium and an SRM-II with high sulfate and sodium concentrations. They appear contaminated, but were not selected for reanalysis and so must be considered outliers. They did affect both the bias and precision, however, especially for calcium in the SRM-I and sulfate in the SRM-II. The Grubbs test for outliers (6) was run on the SRM-I sample, and the concentrations for calcium and magnesium were rejected with a 0.1% risk of false rejection. The same test was run on the high concentration of sulfate. This value could be rejected with a 5% risk of false rejection.

At this time, it is important to point out that any bias observed in these analyses of the internal blind samples is specific to these samples. It cannot be assumed for any individual site chemistry or deducted from other analyses. These biases have been found to be pH- and, to some extent matrix-dependent, which would invalidate any attempt to correct for them in network-wide chemistry data. Most precipitation samples with a volume greater than 60 mL are filtered and, since the volume of samples vary, the effect of filtration on the concentration of specific analytes cannot be assumed.

An ongoing effort is being made to identify the contribution of the filtering process to the chemistry of samples. The internal blind audit has proved valuable and is continuing into the future with modifications as indicated and additional studies as required.

TABLE IV-4 Analytical Bias and Precision Results from
the Internal Blind Audit Program (SWS1). 1987,
NBS SRM 2694-I AND 2694-II.

Parameter	Number of Samples	Concentration (mg/L)		Bias (mg/L)		Precision (%RSD)	Bias Significant? ^a
		NBS	CAL				
Calcium	26 ^b	0.014	0.015	0.001	0.004	26.7	No
	21 ^c	0.049	0.046	-0.003	0.002	4.3	No
Magnesium	26	0.024	0.024	0.000	0.001	4.2	No
	21	0.051	0.050	-0.002	0.002	4.0	No
Sodium	26	0.205	0.205	0.000	0.002	1.0	No
	21	0.419	0.413	-0.006	0.010	2.4	No
Potassium	26	0.052	0.048	-0.004	0.002	4.2	Yes
	21	0.106	0.105	-0.001	0.002	1.9	No
Sulfate	26	2.75	2.87	0.12	0.09	3.0	Yes
	21	10.90	11.44	0.56	0.33	3.0	Yes
Nitrate	21	7.06	7.27	0.21	0.14	2.0	Yes
Chloride	26	(0.24) ^d	0.25	0.01	0.01	4.0	N.A. ^e
	21	(1.0)	1.04	0.04	0.03	3.0	N.A.
Ammonium	21	(1.0)	1.06	0.06	0.04	4.0	N.A.
pH(μeq/L)	26	53.70	55.27	1.57	2.78	5.0	No
	21	257.04	268.95	11.91	14.54	5.0	Yes
(units)	26	4.27	4.26	-0.01			
	21	3.59	3.57	-0.02			
Conductivity (μS/cm)	26	26	26.1	0.1	0.8	3.4	No
	21	130	130.5	0.5	2.5	2.1	No

a. At 95% confidence interval

b. The first set of values for each parameter is for NBS SRM 2694-I.

c. The second set of values for each parameter is for NBS SRM 2694-II.

d. Values in parentheses are not certified but are provided by NBS for information only.

e. N.A. - not applicable.

TABLE IV-5 Analytical Bias Results from the
Internal Blind Audit Program (SWS2), 1987,
D.I. Water and pH 4.30 QCS.

Parameter	Number of Samples	Concentration (mg/L)		Bias (mg/L)	s	Bias Significant? ^b
		True	GAL			
Calcium	23 ^c	<0.009	<0.009	0.000	0.002	No
	21 ^d	<0.009	<0.009	0.000	0.001	No
Magnesium	23	<0.003	<0.003	0.000	0.002	No
	21	<0.003	<0.003	0.000	0.002	No
Sodium	23	<0.003	0.004	0.001	0.007	No
	21	<0.003	<0.003	0.000	0.003	No
Potassium	23	<0.003	<0.003	0.000	0.000	No
	21	<0.003	<0.003	0.000	0.000	No
Sulfate	23	<0.03	<0.03	0.00	0.01	No
	21	<0.03	<0.03	0.00	0.02	No
Nitrate	23	<0.03	<0.03	0.00	0.01	No
	21	3.12	3.32	0.20	0.07	Yes
Chloride	23	<0.03	<0.03	0.00	0.01	No
	21	<0.03	<0.03	0.00	0.01	No
Ammonium	23	<0.02	<0.02	0.00	0.00	No
	21	<0.02	<0.02	0.00	0.00	No
pH(μ equiv/L)	23	2.24	2.52	0.28	0.36	Yes
	21	50.12	48.36	-1.76	1.44	No
(units)	23	5.65	5.60	-0.05		
	21	4.30	4.32	0.02		
Conductivity (μ S/cm)	23	1.0	1.0	0.0	0.1	No
	21	21.8	21.4	-0.4	0.5	No

a. At 95% confidence interval

b. The first set of values for each parameter is for deionized water.

c. The second set of values for each parameter is for pH 4.30 QCS.

TABLE IV-6 Analytical Bias and Precision Results from the Internal Blind Audit Program (SWS3), 1987, NBS SRM 2694-I and 2694-II (filtered).

Parameter	Number of Samples	Concentration (mg/L)		Bias s (mg/L)		Precision (%RSD)	Bias Significant? ^a
		NBS	CAL				
Calcium	11 ^b	0.014	0.027	0.013	0.006	22.2	Yes
	11 ^c	0.049	0.062	0.013	0.008	12.9	Yes
Magnesium	11	0.024	0.030	0.006	0.003	10.0	Yes
	11	0.051	0.055	0.004	0.005	9.1	Yes
Sodium	11	0.205	0.213	0.008	0.011	5.2	Yes
	11	0.419	0.407	0.012	0.011	2.7	Yes
Potassium	11	0.052	0.044	-0.008	0.003	6.8	Yes
	11	0.106	0.103	-0.003	0.004	3.9	Yes
Sulfate	11	2.75	2.72	-0.03	0.07	3.0	No
	11	10.90	10.78	-0.12	0.46	4.0	No
Nitrate	11	7.06	6.88	-0.18	0.22	3.0	Yes
Chloride	11	(0.24) ^d	0.26	0.02	0.01	4.0	N.A. ^e
	11	(1.0)	1.02	0.02	0.04	3.9	N.A.
Ammonium	11	(1.0)	0.99	-0.01	0.06	6.0	N.A.
pH(μ equiv/L) (units)	11	53.70	55.59	1.89	2.71	5.0	Yes
	11	257.04	269.91	12.87	10.59	4.0	Yes
	11	4.27	4.26	-0.01			
	11	3.59	3.57	-0.02			
Conductivity (μ S/cm)	11	26	26.0	0.0	0.5	1.9	No
	11	130	129.3	-0.7	1.6	1.2	No

a. At 95% confidence interval

b. The first set of values for each parameter is for NBS SRM 2694-I.

c. The second set of values for each parameter is for NBS SRM 2694-II.

d. Values in parentheses are not certified but are provided by NBS for information only.

TABLE IV-7 Analytical Bias from the
Internal Blind Audit Program (SWS3), 1987,
D.I. Water and pH 4.30 QCS (filtered).

Parameter	Number of Samples	Concentration (mg/L)		Bias (mg/L)	s	Bias Significant? ^a
		True	CAL			
Calcium	11 ^b	<0.009	<0.009	0.000	0.002	No
	10 ^c	<0.009	0.012	0.003	0.006	Yes
Magnesium	11	<0.003	0.003	0.001	0.003	No
	10	<0.003	0.006	0.004	0.004	No
Sodium	11	<0.003	0.020	0.018	0.010	Yes
	10	<0.003	0.020	0.018	0.008	Yes
Potassium	11	<0.003	<0.003	0.000	0.001	No
	10	<0.003	<0.003	0.000	0.001	No
Sulfate	11	<0.03	<0.03	0.00	0.01	No
	10	<0.03	0.03	0.01	0.03	No
Nitrate	11	<0.03	<0.03	0.00	0.01	No
	10	3.12	3.21	0.08	0.10	Yes
Chloride	11	<0.03	0.03	0.01	0.01	No
	10	<0.03	0.03	0.01	0.01	No
Ammonium	11	<0.02	<0.02	0.00	0.01	No
	10	<0.02	<0.02	0.00	0.01	No
pH(μ equiv/L) (units)	11	2.24	2.80	0.56	0.53	Yes
	10	50.12	49.02	-1.10	2.04	No
	11	5.65	5.55	-0.10		
	10	4.30	4.31	0.01		
Conductivity (μ S/cm)	11	1.0	1.1	0.1	0.1	No
	11	21.8	21.3	-0.5	0.7	No

a. At 95% confidence interval

b. The first set of values for each parameter is for deionized water.

c. The second set of values for each parameter is for pH 4.30 QCS.

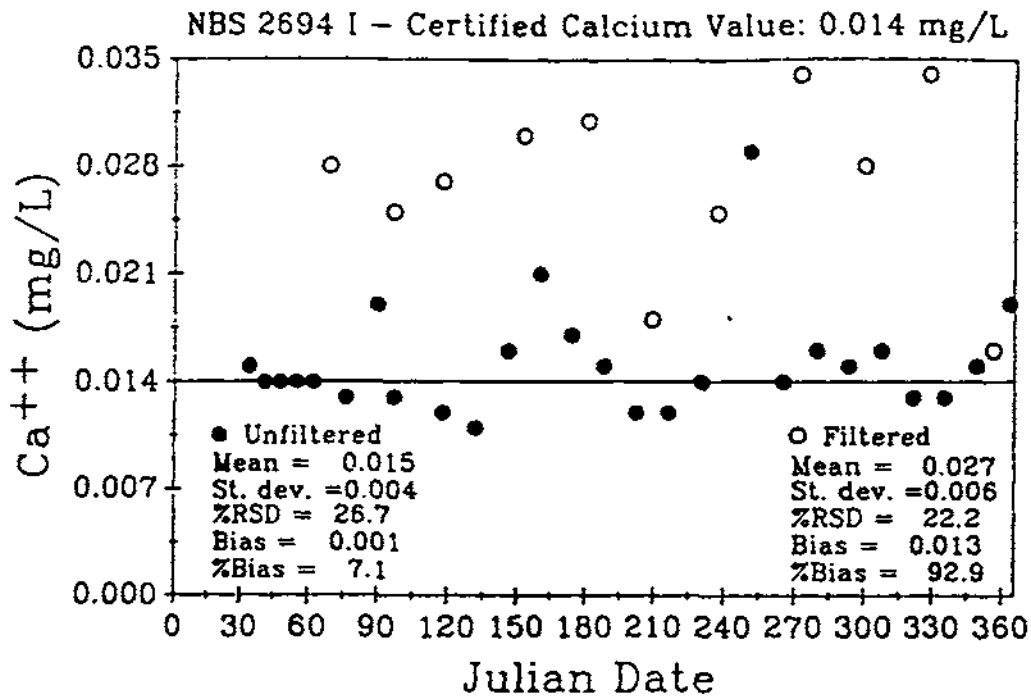


FIGURE IV-1. Comparison of filtered and unfiltered internal blind samples (calcium I), 1987.

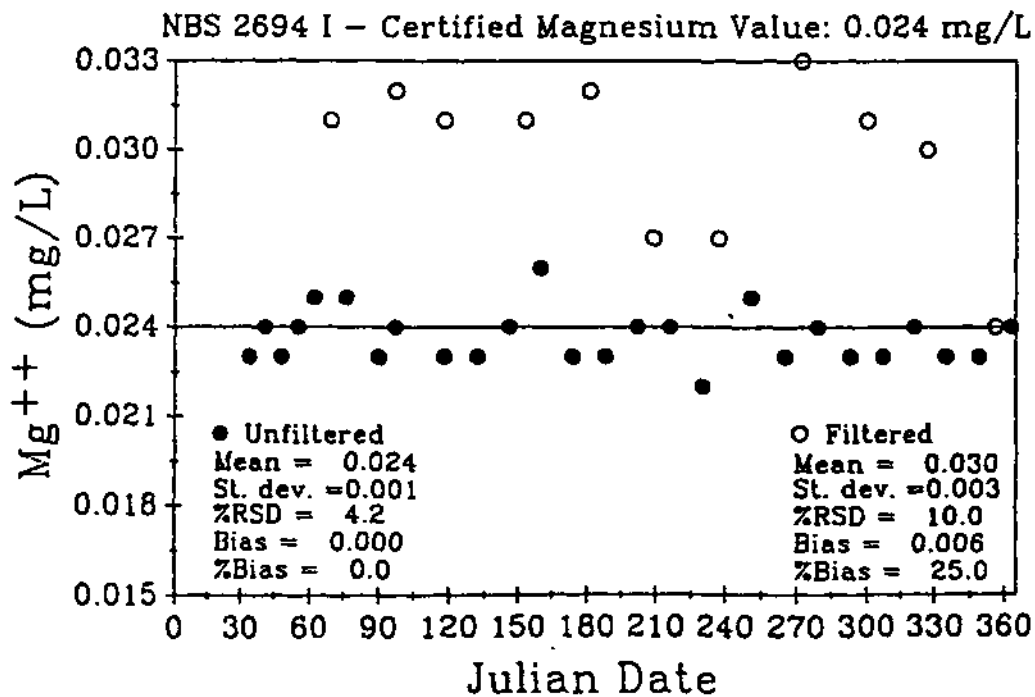


FIGURE IV-2. Comparison of filtered and unfiltered internal blind samples (magnesium I), 1987.

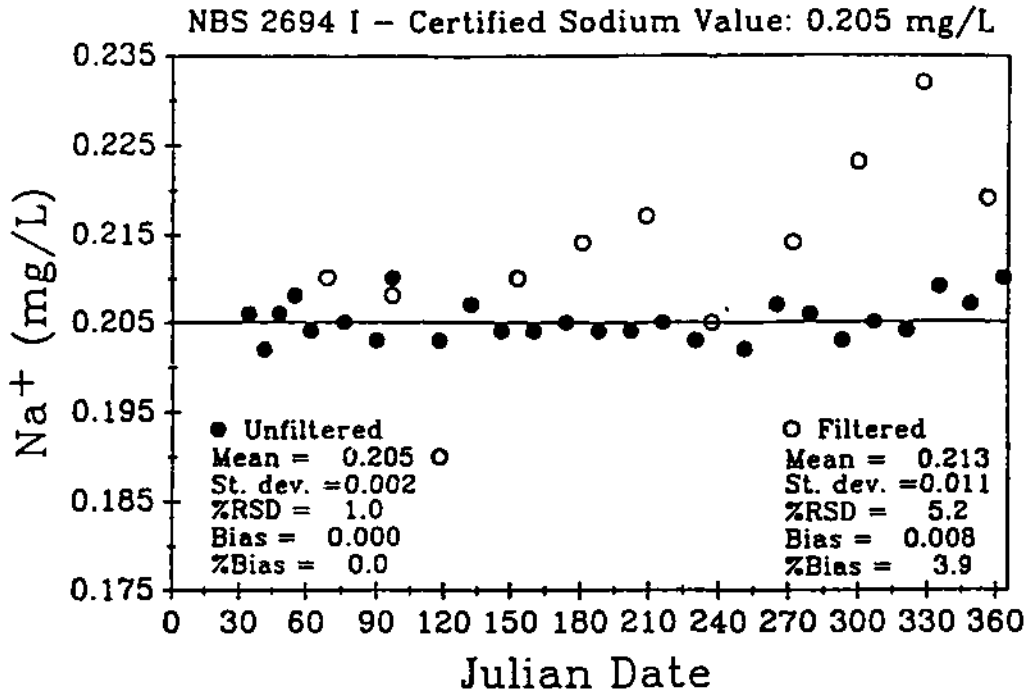


FIGURE IV-3. Comparison of filtered and unfiltered internal blind samples (sodium I), 1987.

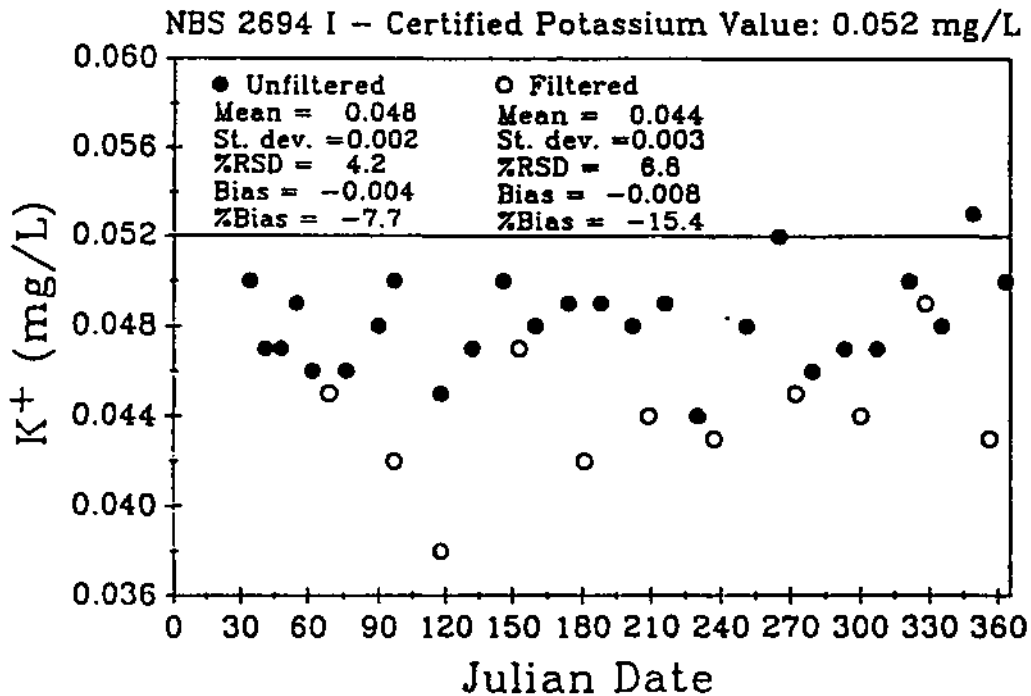


FIGURE IV-4. Comparison of filtered and unfiltered internal blind samples (potassium I), 1987.

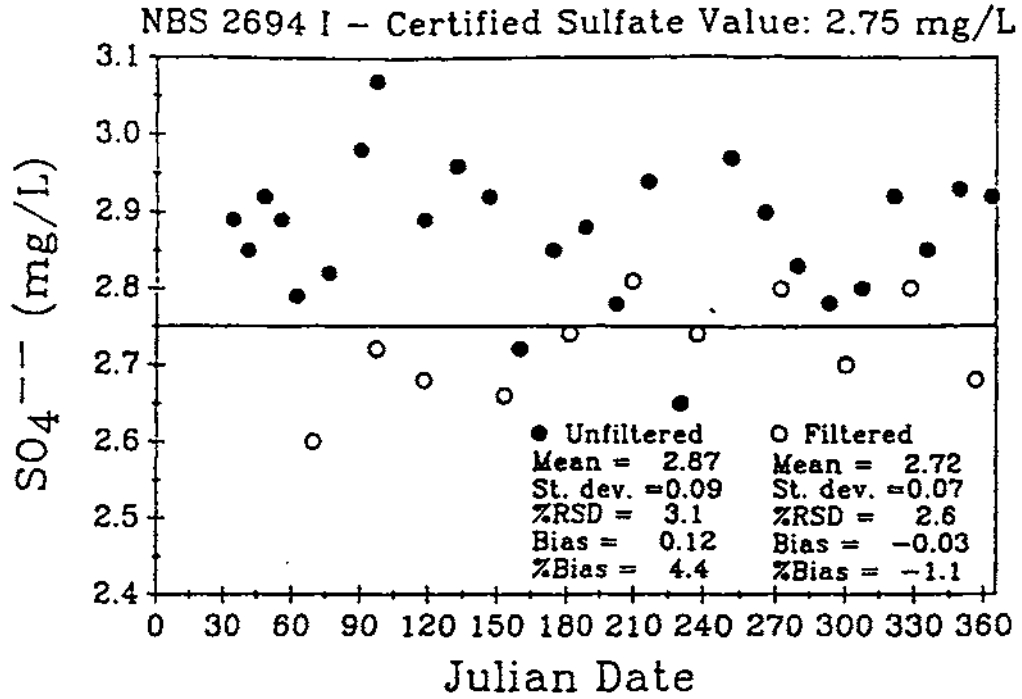


FIGURE IV-5. Comparison of filtered and unfiltered internal blind samples (sulfate I), 1987.

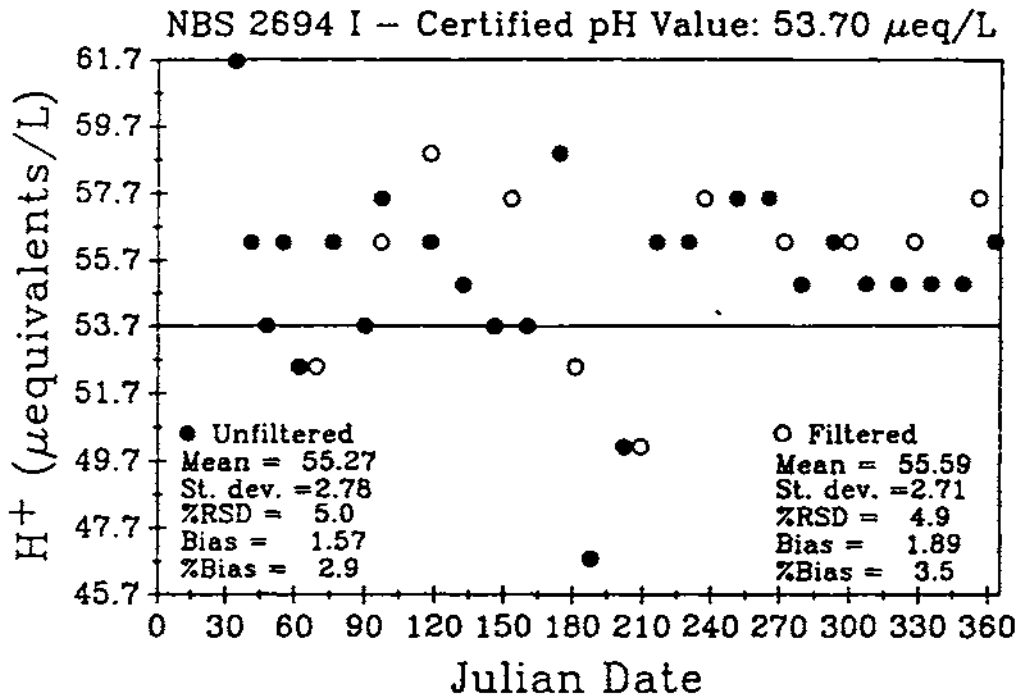


FIGURE IV-6. Comparison of filtered and unfiltered internal blind samples (pH I), 1987.

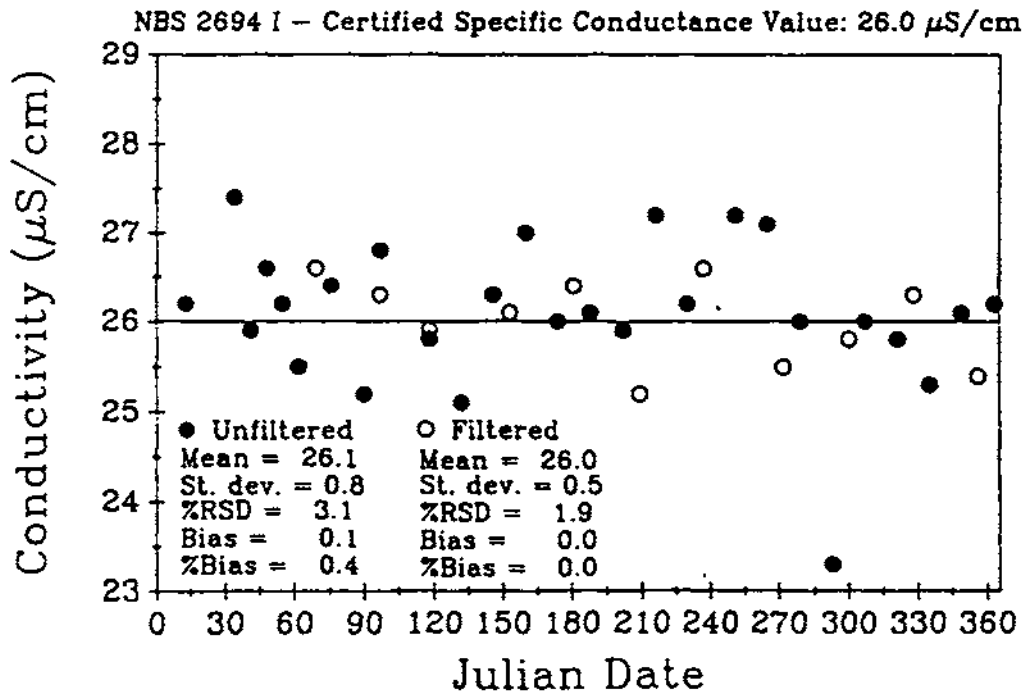


FIGURE IV-7. Comparison of filtered and unfiltered internal blind samples (conductance I), 1987.

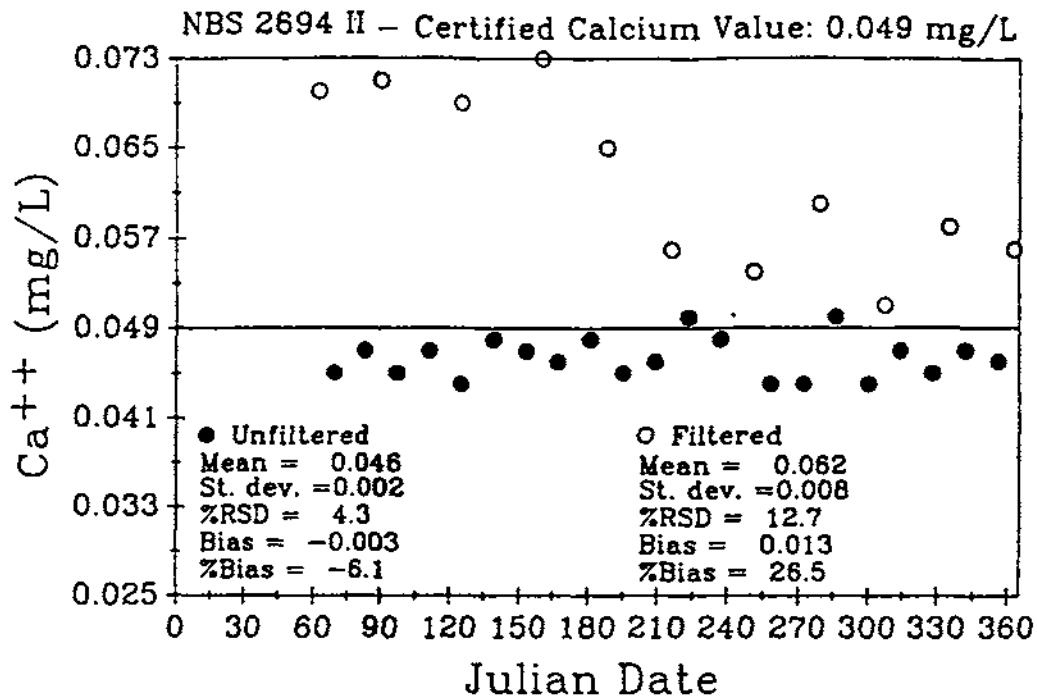


FIGURE IV-8. Comparison of filtered and unfiltered internal blind samples (calcium II), 1987.

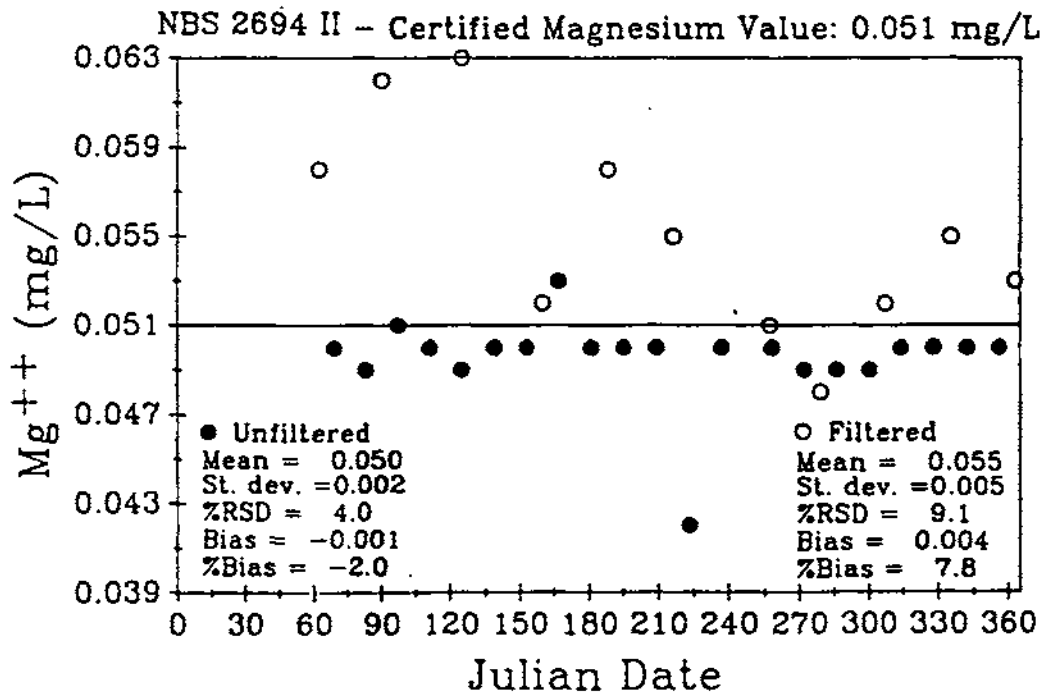


FIGURE IV-9. Comparison of filtered and unfiltered internal blind samples (magnesium II), 1987.

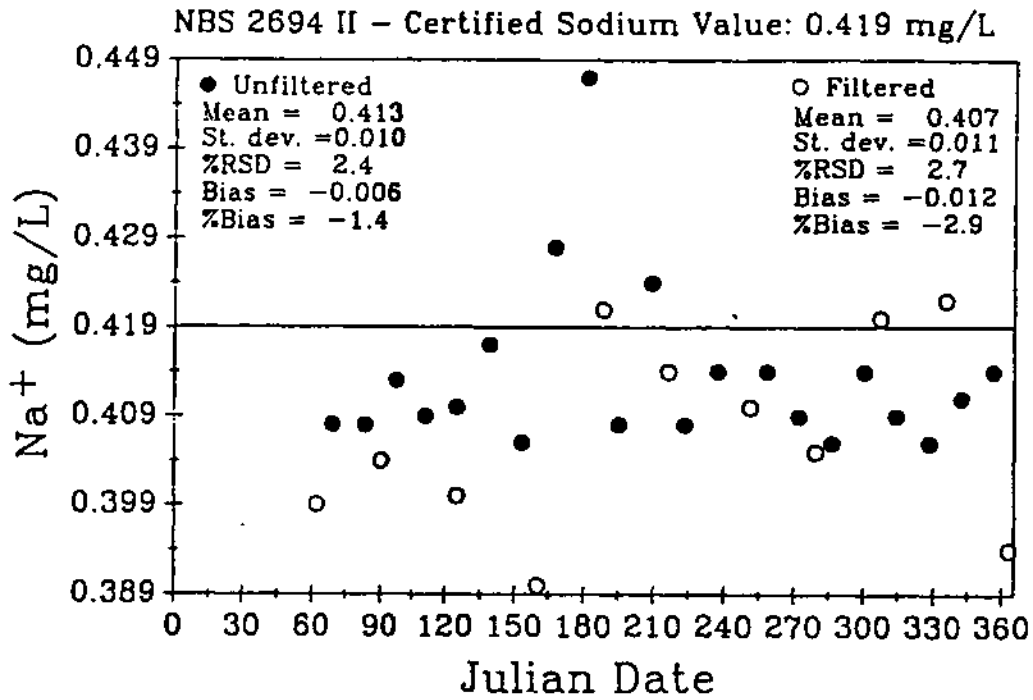


FIGURE IV-10. Comparison of filtered and unfiltered internal blind samples (sodium II)/ 1987.

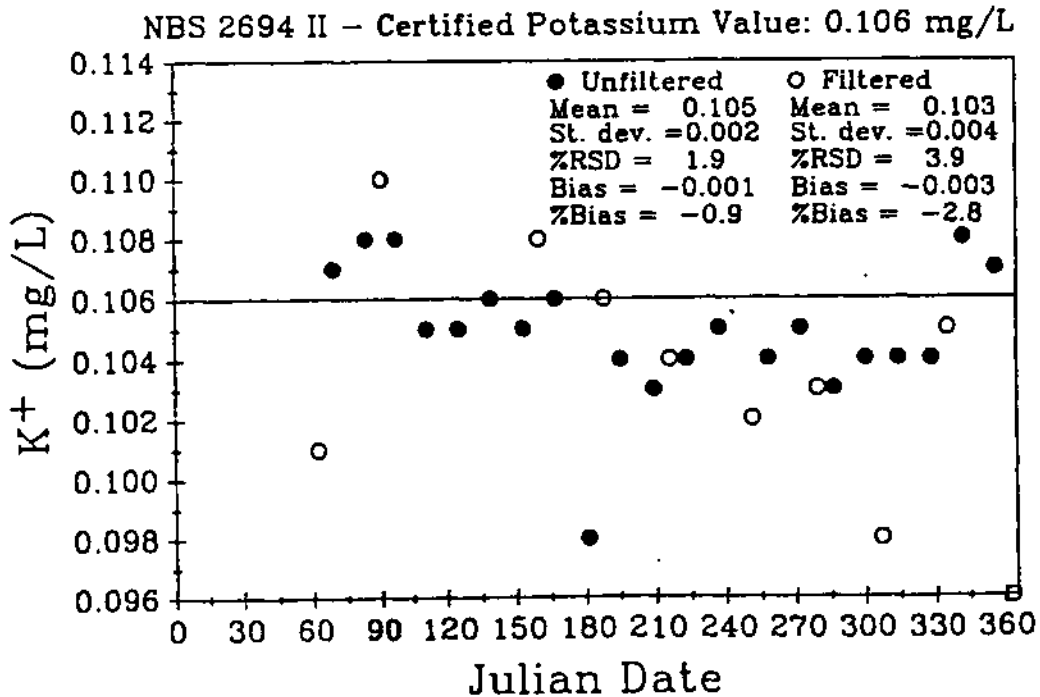


FIGURE IV-11. Comparison of filtered and unfiltered internal blind samples (potassium II), 1987.

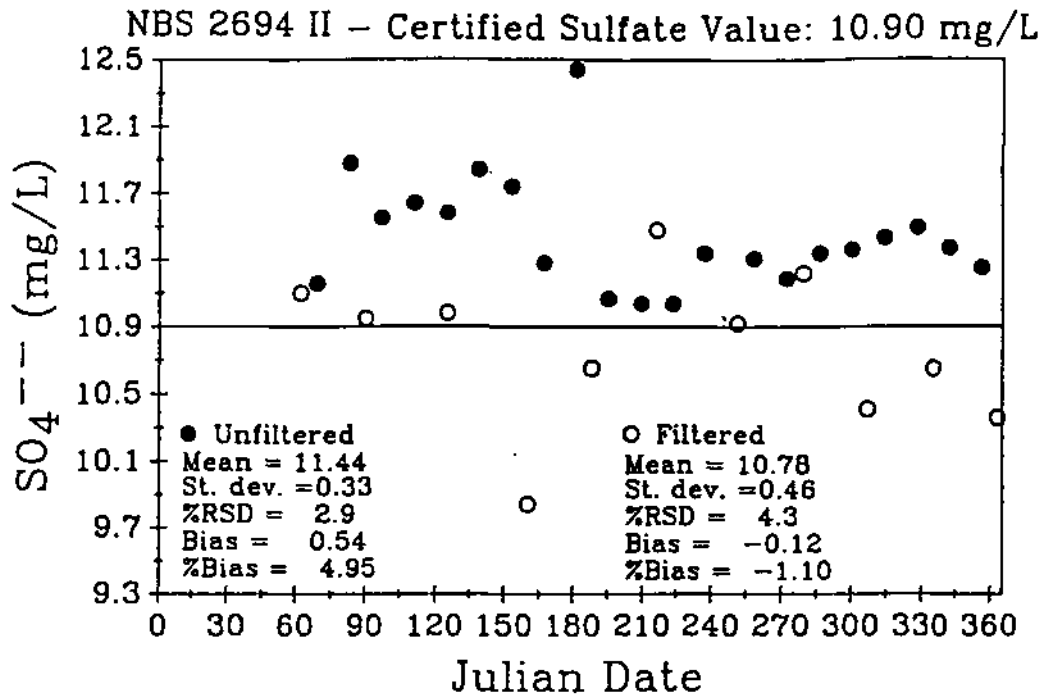


FIGURE IV-12. Comparison of filtered and unfiltered internal blind samples (sulfate II), 1987.

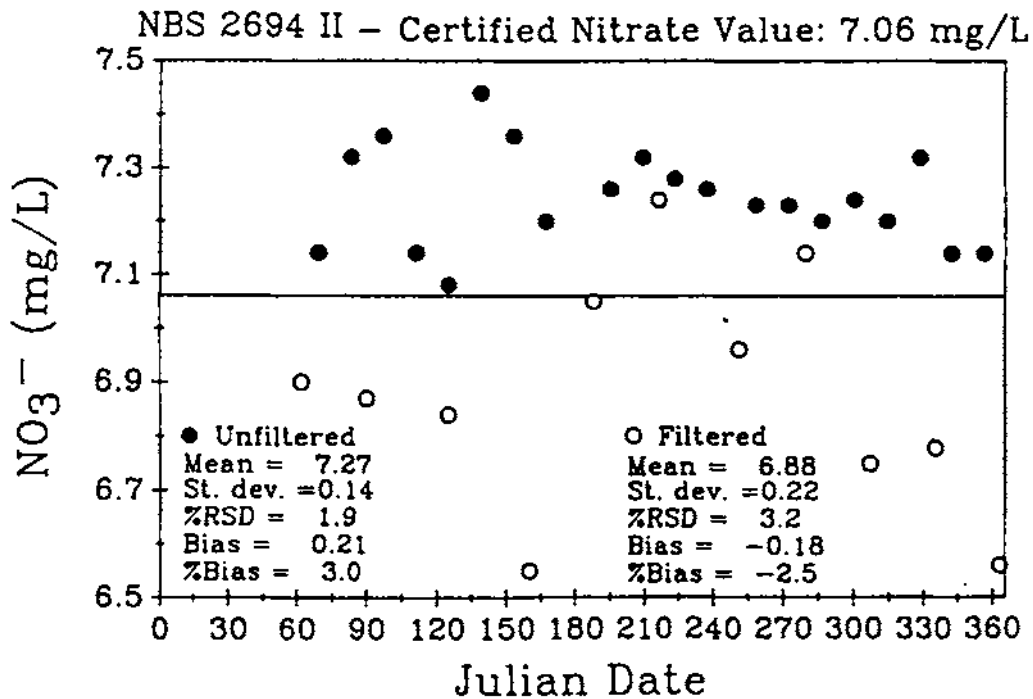


FIGURE IV-13. Comparison of filtered and unfiltered internal blind samples (nitrate II), 1987.

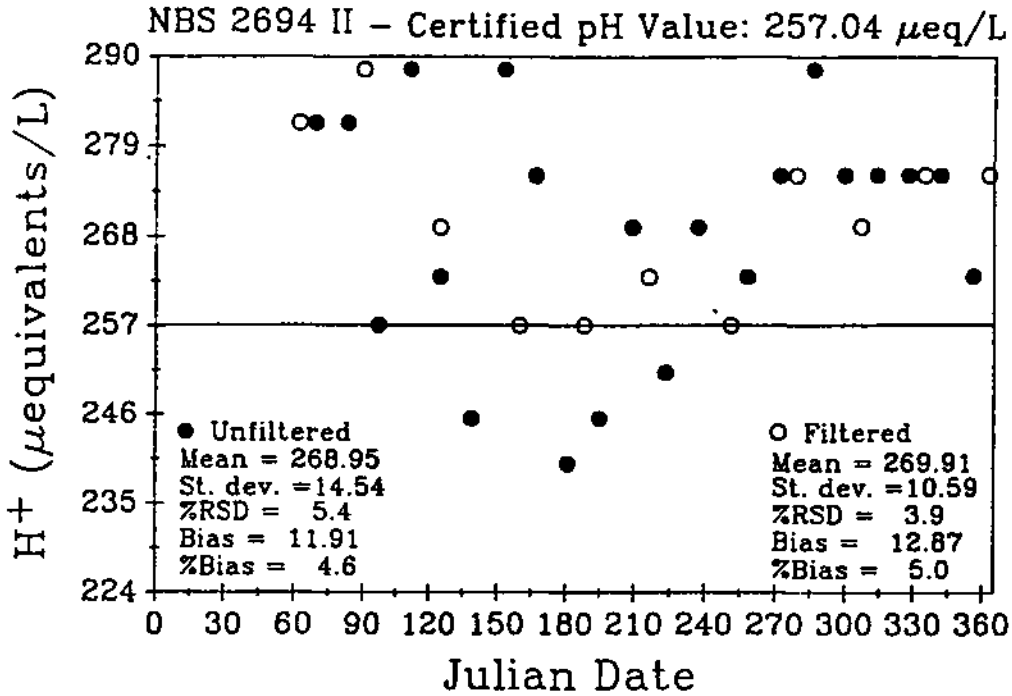


FIGURE IV-14. Comparison of filtered and unfiltered internal blind samples (pH II), 1987.

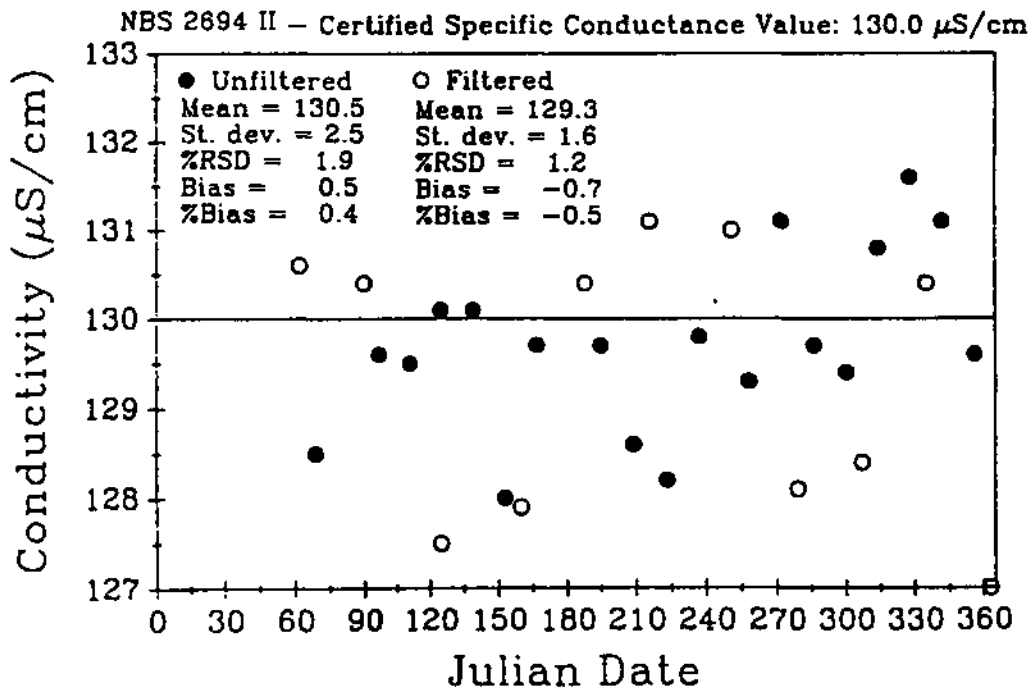


FIGURE IV-15. Comparison of filtered and unfiltered internal blind samples (conductance II), 1987.

V. REANALYSIS PROCEDURES

As soon as a tray of 108 samples has undergone complete processing and analysis, the data are presented to the data management section. In 1987 the initial log-in information, pH, and conductivity were entered on a floppy disk with personal computers in the sample receiving office and sample processing laboratory. The analysis data from the ion chromatographs and automated colorimetric equipment were submitted on handwritten data sheets, as were the cation determinations performed by atomic absorption spectrophotometry. These data for 400 or 500 samples were then merged, and the final results for each sample were processed by an ion balance program, which determines if the sample requires reanalysis. If the cation-anion balance is unacceptable, or if the difference between the measured and calculated conductivity is too great in either direction, reanalysis is indicated.

The "ionbal" printout is given to the laboratory quality assurance specialist, who notes the sample numbers selected by the program and reviews the chemistry of each selected sample. Samples with insufficient volume, obvious deionized water blinds, split samples that show agreement between all measured parameters, and grossly contaminated samples are deleted from the list. Random samples, selected from a list at the end of the program, are added to the list at a rate of 1% of the total number included in that printout. The list of reanalysis samples is sent to the analysts in the laboratory, and the samples are retrieved and analyzed. The new numbers, as well as the original values, are then submitted on handwritten sheets to the quality assurance officer. The results are compared and analysts' comments are noted. The samples with justification for correction are recorded and sent back to data management with the requested change as well as the reason. The original, the reanalysis, and the final corrected data are all maintained in the computerized database for these samples.

The reanalysis program was revised in March 1987 and the changes are described in the appropriate sections following.

A. ION PERCENT DIFFERENCE

The ion percent difference (IPD). is calculated by using the measured pH, cations, and anions plus the values calculated for bicarbonate and hydroxide. The ion sum (IS) is set equal to "+ ions meas extra" plus "- ions meas extra." The quantities are best defined by the following equations:

$$\begin{aligned} \text{+ions meas extra} &= [\text{H}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + \\ &\quad [\text{K}^+] + [\text{NH}_4^+] \\ \text{-ions meas extra} &= [\text{HCO}_3^-] + [\text{OH}^-] + [\text{SO}_4^{2-}] + [\text{NO}_3^-] \\ &\quad + [\text{Cl}^-] + [\text{PO}_4^{3-}]. \end{aligned}$$

The analyte concentration for each species in every sample is multiplied by the appropriate conversion factor (Table V-1) to change it to microequivalents per liter. These products are used in the following formula to establish the ion percent difference.

$$\text{IPD} = \frac{\text{-ions meas extra} - \text{+ions meas extra}}{\text{-ions meas extra} + \text{+ions meas extra}} \times 100$$

By using this equation, a computer program flags samples for reanalysis according to the following criteria which, have been in place since 1981. The ion sum is expressed in microequivalents per liter.

Samples are reanalyzed if:

IS < 50 μequiv/L	and IPD > \pm 60%
50 \leq IS < 100 μequiv/L	and IPD > \pm 30%
IS \geq 100 μequiv/L	and IPD > \pm 15%

The new IS differs from the previous one in that the hydrogen, bicarbonate, and hydroxide ion concentrations are actually calculated and included. The revision of the definition of the constituents of the ion sum theoretically should identify more very low and very high pH samples for reanalysis than in the past. The allowable IPD decreases as the IS increases. Every time the IS doubles from the lowest base of 50 μ equiv/L, the allowable IPD is cut in half.

B. CONDUCTANCE PERCENT DIFFERENCE

The second part of the reanalysis program determines the conductance percent difference (CPD) criteria. This operation involves equations similar to those described for ion percent difference but the ion concentrations included in the ion sum, expressed in microequivalents per liter, are then multiplied by the appropriate equivalent ionic conductance. In 1987 all of these conversion factors were taken from the CRC Handbook of Chemistry and Physics (7). The calculated conductance equals the sum of the aforementioned products divided by 1000 because these factors, are used with ions in units of milliequivalents per liter. The equation for calculated conductance follows:

$$\begin{aligned} \text{Calculated conductance} = & \left[[\text{H}^+] (349.65) + [\text{Ca}^{2+}] (59.47) + \right. \\ & [\text{Mg}^{2+}] (53.0) + [\text{Na}^+] (50.08) + [\text{K}^+] (73.48) + \\ & [\text{NH}_4^+] (73.5) + [\text{HCO}_3^-] (44.5) + [\text{OH}^-] (198) + \\ & [\text{SO}_4^{2-}] (80.0) + [\text{NO}_3^-] (71.42) + [\text{Cl}^-] (76.31) \\ & \left. + [\text{PO}_4^{3-}] (69.0) \right] / 1000 \end{aligned}$$

where ion concentrations are expressed as microequivalents per liter.

From this sum the conductance percent difference can be calculated by using the following equation:

$$\text{Conductance percent difference} = (\text{CPD}) =$$

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

The CPD calculation results are then used in the criteria for flagging samples that require reanalysis for this imbalance. In 1987 the multiple ranges for rejection were simplified: the CPD of the sample must now be greater than 10% or less than minus 40% to be identified for reanalysis on that basis.

The most significant change in the calculation of the conductance using the new equivalent conductivities is the increase in the sulfate factor from 73.9 to 80.0. Changing the factors could cause the mean of the CPD distribution to shift from minus 10% to minus 5%. The samples that would be most affected are those with low hydrogen ion concentrations where SO_4 contributes significantly to the solution conductivity. These would tend to be "clean," high-pH samples from the western states.

C. HISTOGRAMS

Figures V-1 and V-2 are histograms of the 1987 ion percent differences and the conductance percent differences, respectively, for all samples of more than 35 mL. The arithmetic mean, number of samples included, median, and standard deviation are included on the figure for easy reference.

The IPD histogram has a slight positive skew this year; the median and mean are 3.11% and 3.17%, respectively. These values indicate a slight decrease from the previous year (2) but a small anion excess remains.

The CPD histogram, predicted to have a smaller negative skew due to CRC Handbook (7) factors, shows a reduced negative mean and median compared to 1986 (2). The difference does not appear to be significant. The standard deviation did decrease compared to 1986 data.

D. DISCUSSION OF RESULTS

The introduction to this section noted that several categories of samples were designated for reanalysis and are subsequently deleted by the quality assurance specialist. If an obvious and confusing difference appears between the original and the reanalysis results, the refrigerated archival sample is analyzed, if it is available. From the three analyses and any notes the analyst may have recorded during the course of the analysis, the decision to change or retain the original data is made and sent to the data management staff.

In 1987, 392 samples were selected for reanalysis. This figure represents 4.7% of the total 8280 samples entered into the data file. Of these reanalyzed samples, 70 ion concentration changes were entered on the data, representing 17.9% of the samples reanalyzed and 0.8% of the total number of samples analyzed during the year. The most common reasons given for changes were calculated dilution or transcription errors.

The change of factors for the calculated conductance did not produce a significant change in the negative bias of the annual histogram. The mean value changed from minus 12.2% in 1986 to minus 9.5% in 1987; the corresponding changes for the median range were from minus 8.7% to minus 6.5%.

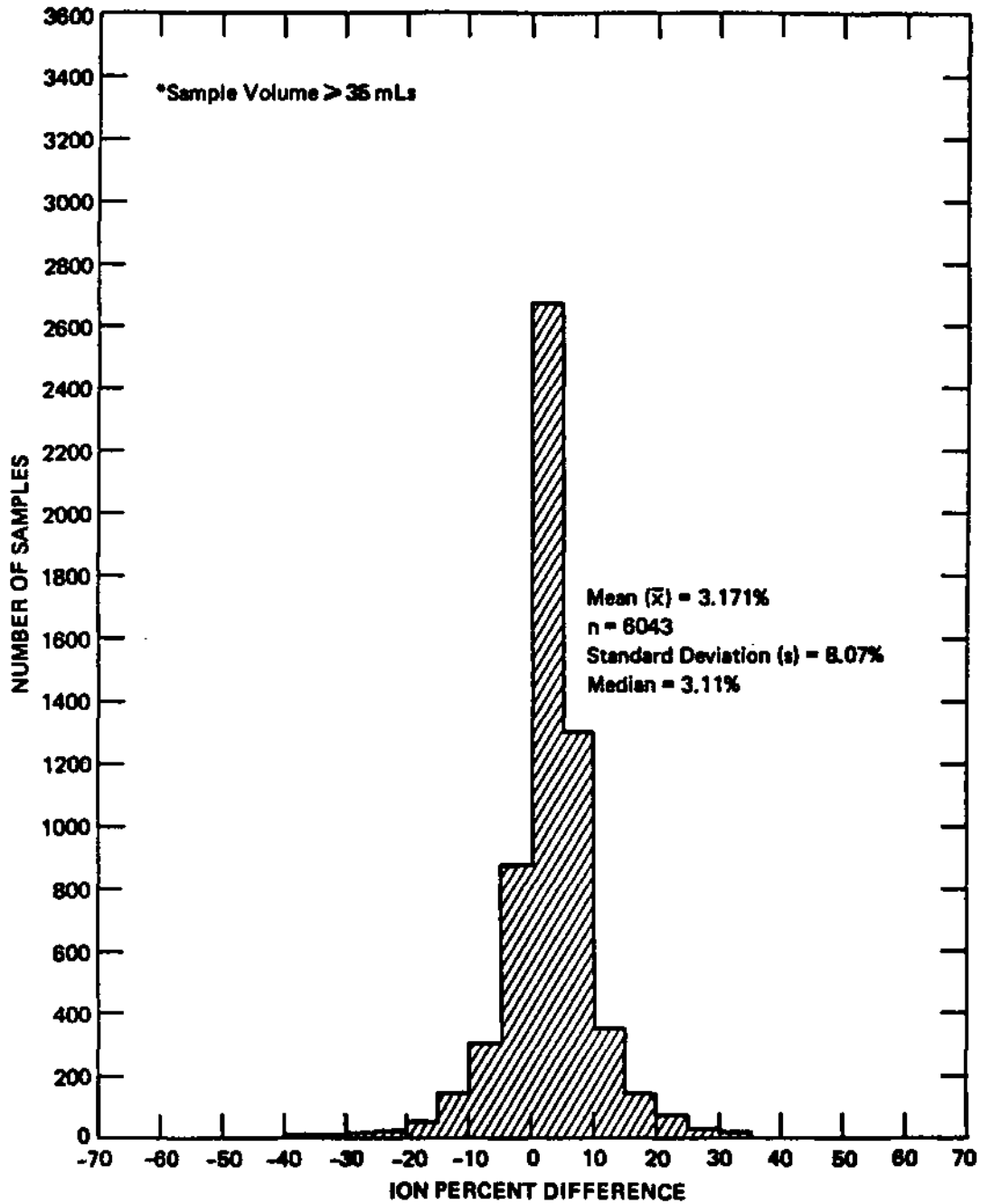


FIGURE V-1. Ion percent difference histogram for NADP/NTN vet-side samples, 1987.

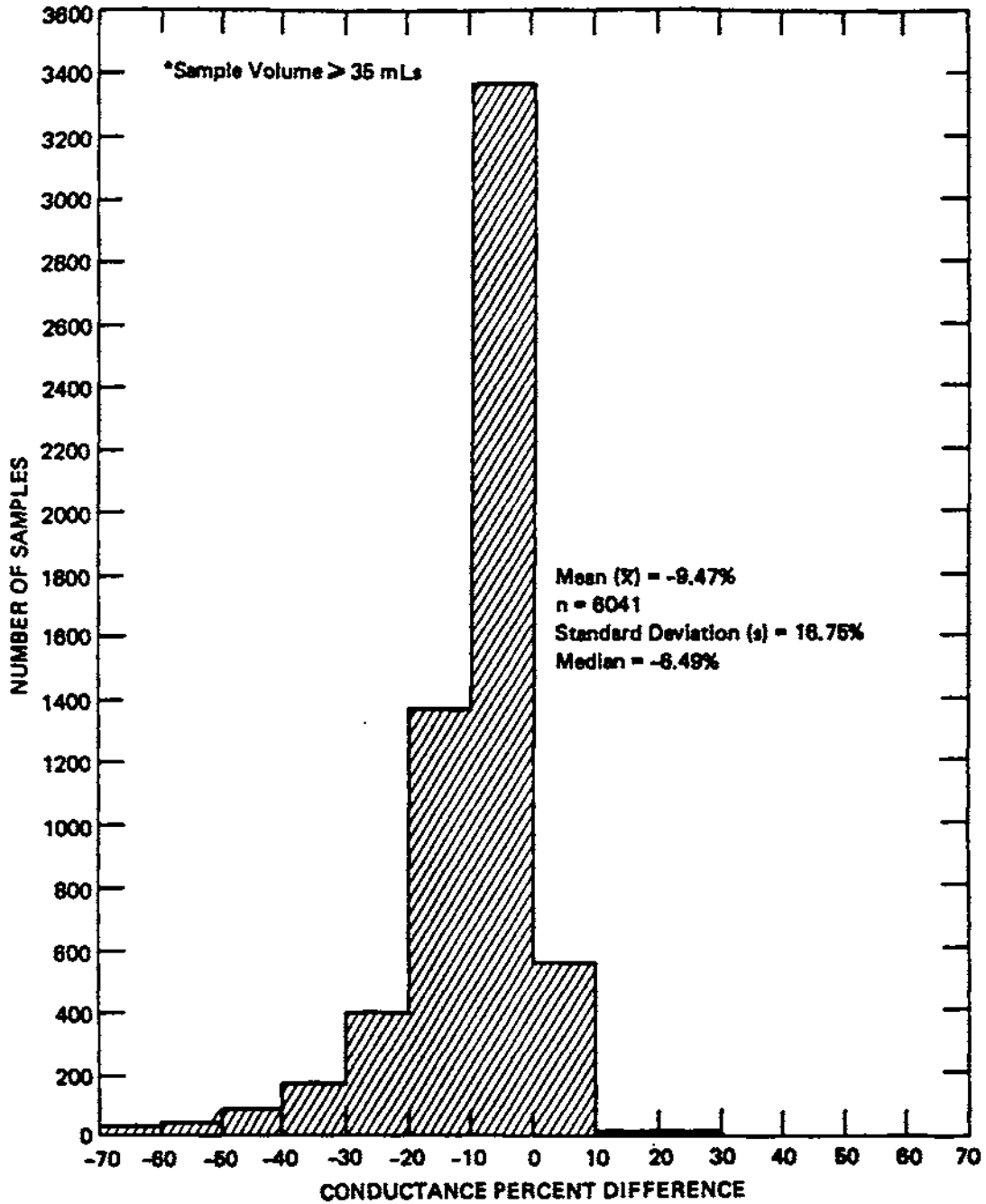


FIGURE V-2. Conductance percent difference histogram for NADP/NTN wet-side samples, 1987.

TABLE V-1 Factors Used to Convert Milligrams per Liter to Microequivalents per Liter for Ion Percent Difference Calculations.

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

VI. EXTERNAL QUALITY ASSURANCE PROGRAM PARTICIPATION

The external quality assurance program at the CAL has two major components: the official external audit performed by the USGS and voluntary participation in several other national and international laboratory intercomparison studies. The following sections address the programs in which the CAL participated during 1987 and the laboratory's performance in each.

A. U.S. GEOLOGICAL SURVEY EXTERNAL AUDIT PROGRAM

The USGS NADP/NTN external audit program for CAL consists of two parts: a blind audit sample routine and an interlaboratory comparison study. The data from the audit are used to evaluate the effects of sample handling as well as laboratory bias and precision. The interlaboratory comparison assesses the differences between analytical results and estimates the analytical precision of several laboratories.

The blind audit program was explained in the previous report (2). Briefly, reference samples are provided to site operators who disguise them as actual samples and submit them to CAL for routine analysis. No chemical information is provided to the site operators or CAL analysts. Eleven solutions were prepared for the 1987 blind audit program. These solutions, included two dilutions of solution 1085 prepared by the USEPA; four dilutions of standard reference water solutions, M-2 and M-4, prepared by the USGS; three dilutions of stock solutions of sodium nitrate and sulfuric acid and two blanks: ultrapure, deionized water prepared by the USGS and a diluted pH 4.30 nitric acid solution prepared by CAL.

The same laboratories participated in the interlaboratory comparison in 1986 and 1987. The samples were from five sources. Ultrapure deionized water and synthetic precipitation samples were prepared by the USGS; natural wet-deposition samples were prepared by CAL; and standard reference samples were supplied by the USEPA, NBS and USGS.

The results of the blind audit program indicated significant positive ($\alpha = 0.01$) bias for all analytes except nitrate and sulfate, obvious contamination occurring for some analytes, and reduced levels of H^+ . The lesser precision in the analysis of blind audit samples compared to interlaboratory studies indicated that most of the uncertainty in data resulted from field operations. According to the 1987 results from the interlaboratory program, the CAL had the fewest mean analyses results that differed significantly from the certified values(8).

B. INTERLABORATORY COMPARISON STUDIES

The CAL continued its participation in national and international interlaboratory performance studies in 1987. The CAL analysts also participated in several USEPA performance evaluation studies as part of the Analytical Chemistry Unit of the Illinois State Water Survey. The IEPA requires participation in these studies by laboratories that wish to retain certification as an environmental laboratory. In 1987 the CAL analysts participated in the EPA Inter laboratory Comparison of Reference Precipitation Samples and the Canada Centre for Inland Waters (CCIW) Long Range Transport of Atmospheric Pollutants (LRTAP) Interlaboratory Comparability Study. These two studies are discussed briefly in the following paragraphs. Tables detailing the results for the samples submitted are presented in the tables in Appendix D.

U. S. Environmental Protection Agency

The Environmental Monitoring Systems Laboratory of the USEPA, Research Triangle Park, North Carolina, regularly conducts an interlaboratory comparison study for laboratories analyzing precipitation samples. In 1987 the CAL participated in the November study.

The results for the individual parameters included in this performance survey are found in Appendix Table D-1. The CAL performed only those analyses which are part of the standard NADP/NTN routine. Thirty-five laboratories participated in this study. The CAL mean percentage difference from the expected value was 5.2% with a standard deviation of 5.8%; this may be compared to a mean percentage difference of 28.9% and a standard deviation of 37.9% for all of the laboratories with outliers removed. The mean percentage difference is calculated by using the following formula:

Mean % difference =

$$\frac{\sum \left[\frac{|\text{Expected value} - \text{Reported value}|}{\text{Expected value}} \times 100 \right]}{\text{Number of analytes determined}}$$

The CAL mean percentage difference is higher this year than for the two studies in 1986 (3.2% and 2.3% in April and December). A 2 or 3 $\mu\text{g/L}$ difference of a low level analyte causes a high percentage difference for these samples, just as it results in a bias when the check sample data are analyzed. Inspection of Appendix Table D-1 shows that potassium, magnesium, and ammonium demonstrated the highest percentage difference values from this study.

Canada Centre for Inland Waters

The LRTAP program, begun in December of 1982, is administered by the Canada Centre for Inland Waters (CCIW). In 1987 the CAL participated in Interlaboratory Comparability Study L-15, which consisted of measuring selected major ions, nutrients, and physical characteristics in water. Samples 7, 8, and 9 were not analyzed. The tabulated results for samples 1 through 6 and 10 are found in Appendix Table D-2.

The CCIW values reported in Appendix Table D-2 are median concentrations for each parameter. They are determined by using the data reported by the participating laboratories. From these results, the data for each parameter from each laboratory are evaluated and flags and bias are assessed. The CAL 2.9% sum of percent bias and percent flags represents a very good score.

An additional study, LRTAP Study L-15A, was titled "pH Measurements in Diluted Buffers. This part of the study was a pH round robin initiated by the Quality Assurance Office at the Ontario Ministry of the Environment, Laboratory Services Branch. The median values of the 44 participating laboratories and the values reported by the CAL are summarized in Appendix Table D-3.

VII. SUMMARY

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

This report follows the form of the previous Quality Assurance Reports and contains the information required by the QA Plan. The 1987 quality assurance data were evaluated and presented in tables and figures with accompanying text for explanation and interpretation. Many of the tables and figures are similar to those used in past reports. Additional figures have been incorporated to present as much information as possible in a concise and understandable format.

The 1987 information presented in Table VII-1 outlines modifications to the QA program at the CAL. The analytical bias and precision results presented in this report indicate that the specifications for precision and bias continue to be met. The ongoing modification of the laboratory blanks procedure is an effort to eliminate any sources of external contamination that might affect the chemistry of the samples. Revised limits for the quality control samples represent an effort to reduce analytical bias and improve precision. The internal blind program, using the same samples for an extended period of time, has proved useful in identifying biases that could exist in similar real samples. The modifications to the reanalysis computer program have been useful for identifying all questionable sample analyses. Finally, the performance of the CAL in external interlaboratory comparisons verifies the results obtained in the internal laboratory QA program.

TABLE VII- 1 (Continued)

D. Reanalysis Procedures

The computer programs used to identify samples for reanalysis were modified to include calculated values for hydrogen, bicarbonate and hydroxide ion concentrations. All conductance conversion factors are taken from the CRC Handbook of Chemistry and Physics(7) (March).

VIII. REFERENCES

1. Peden, M. E., S. R. Bachman, C. J. Brennan, B. Demir, K. O. 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 61820-7495; March 1986.
2. James, Kenni O. W.: Quality Assurance Report. NADP/NTN Deposition Monitoring. Laboratory Operations. Central Analytical Laboratory. January 1986 through December 1986; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Fort Collins, CO 80523; October 1988.
3. 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.
4. Anderson, Robert L.: Practical Statistics for Analytical Chemists, Van Nostrand Reinhold Company; New York, NY; pp. 74 and 75; 1987.
5. Standard Methods for the Examination of Water and Wastewater; 16th Edition; American Public Health Association; Washington D.C.; p. 18; 1985.
6. Taylor, John K.: Quality Assurance of Chemical Measurements, Lewis Publishers, Inc.; Chelsea, MI; pp. 36 and 247; 1987.
7. CRC Handbook of Chemistry and Physics; 67th Edition; 1986-1987; CRC Press, Inc.; Boca Raton, FL; pp. D-167 and D-168; 1987.
8. See, Randolph B., L. J. Schroder, and T. C. Willoughby: External Quality-Assurance Results for the National Atmospheric Deposition Program and the National Trends Network During 1987; U. S. Geological Survey; Denver Federal Center; Arvada, CO; 1989.

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 (6).
Critical Concentration		A calculated concentration used to determine whether or not the measured bias is statistically significant.

$$\text{Critical concentration} = t \times s_{sp} \sqrt{1/n_1 + 1/n_2}$$

where:

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

s = standard deviation

n = number of values

t = t statistic at the 95% confidence level and $(n_1 + n_2) - 2$ 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} <p>The average obtained by dividing a sum by the number of its addends.</p> $\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$
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 concentration 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. $\%Bias = 100 \times (V_m - V_t)/V_t$ 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:
	Percent recovery = $100 \times (a-b)/c$ 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 among 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	QA 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:

$$\text{RSD} = 100 \times (s/\bar{x})$$

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 estimating 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

1987

TABLE B-1 Minimum Detectable Mass Values for
Bucket Blanks Analyzed in 1987.

Analyte	Minimum Mass Value ($\mu\text{g}/\text{bucket}$)
Calcium	0.45
Magnesium	0.15
Sodium	0.15
Potassium	0.15
Ammonium	1.0
Sulfate	1.5
Nitrate	1.5
Chloride	1.5

NOTE: Minimum mass values were calculated by multiplying the MDL expressed as micrograms per milliliter by 50 mL.

TABLE B-2 Analyte Concentration Summary for
Filter Leachate A, 1987.

Analyte	Number of Analyses	Frequency of MDL (%)	Percentile Concentration (mg/L)	
			50%	95%
Calcium	53	81.1	<0.009	0.019
Magnesium	53	69.8	<0.003	0.006
Sodium	53	26.4	0.011	0.033
Potassium	53	92.4	<0.003	0.003
Ammonium	58	94.8	<0.02	<0.02
Sulfate	58	100	<0.03	<0.03
Nitrate	58	91.4	<0.03	0.04
Chloride	58	67.2	<0.03	0.07
Ortho- phosphate	58	94.8	0.01	0.01
pH (units)	65	N.A.	5.61	5.90
Conductivity (μ S/cm)	65	N.A.	1.0	1.7

TABLE B-3 Analyte Concentration Summary for
Filter Leachate B, 1987.

Analyte	Number of Analyses	Frequency of MDL (%)	Percentile Concentration (mg/L)	
			50%	95%
Calcium	53	88.7	<0.009	0.012
Magnesium	53	84.9	<0.003	0.005
Sodium	53	64.2	<0.003	0.017
Potassium	53	86.8	<0.02	<0.02
Ammonium	58	98.3	<0.02	<0.02
Sulfate	58	100	<0.03	<0.03
Nitrate	58	100	<0.03	<0.03
Chloride	58	91.5	<0.03	0.05
Ortho- phosphate	58	100	<0.01	0.01
pH (units)	65	N.A.	5.61	5.90
Conductivity (μ S/cm)	65	N.A.	0.9	1.5

NOTE: N.A. = not applicable.

TABLE B-4 Analyte Concentration Summary for
Deionized Water from the Sample
Processing Laboratory, 1987.

Analyte	Number of Analyses	frequency of MDL (%)	Percentile Concentration (mg/L)	
			50%	95%
Calcium	49	95.9	<0.009	<0.009
Magnesium	49	87.8	<0.003	0.004
Sodium	49	91.8	<0.003	0.005
Potassium	49	93.9	<0.003	<0.003
Ammonium	49	100.0	<0.02	<0.02
Sulfate	49	100.0	<0.03	<0.03
Nitrate	49	100.0	<0.03	<0.03
Chloride	49	100.0	<0.03	<0.03
Ortho- phosphate	49	100.0	<0.02	<0.02
pH (units)	54	N.A.	5.59	5.82
Conductivity (μ S/cm)	54	N.A.	0.7	1.0

TABLE B-5 Analyte concentration Summary for
Deionized Water from the Atomic
Absorption Laboratory, 1987.

Analyte	Number of Analyses	frequency of MDL (%)	Percentile Concentration (mg/L)	
			50%	95%
Calcium	52	96.2	<0.009	<0.009
Magnesium	52	88.4	<0.003	0.003
Sodium	52	76.9	<0.003	0.031
Potassium	52	90.4	<0.003	0.005
Ammonium	52	100.0	<0.02	<0.02
Sulfate	51	100.0	<0.03	<0.03
Nitrate	51	100.0	<0.03	<0.03
Chloride	51	100.0	<0.03	<0.03
Ortho- phosphate	51	100.0	<0.02	<0.02
pH (units)	54	N.A.	5.68	6.02
Conductivity (μ S/cm)	54	N.A.	0.9	1.2

NOTE: N.A. - not applicable.

TABLE B- 6 Analyte Concentration Summary for
Deionized Water from the ICP
Laboratory, 1987.

Analyte	Number of Analyses	Frequency of MDL (%)	Percentile Concentration (mg/L)	
			50%	95%
Calcium	27	100.0	<0.009	<0.009
Magnesium	27	100.0	<0.003	<0.003
Sodium	27	81.5	<0.003	0.008
Potassium	27	100.0	<0.003	<0.003
Ammonium	26	96.2	<0.02	<0.02
Sulfate	26	92.3	<0.03	<0.03
Nitrate	26	100.0	<0.03	<0.03
Chloride	26	100.0	<0.03	<0.03
Ortho- phosphate	26	100.0	<0.02	<0.02
pH (units)	29	N.A.	5.58	5.66
Conductivity' (μ S/cm)	29	N.A.	1.0	1.2

TABLE B-7 Analyte Concentration Summary for
Deionized Water Boom from the Bucket
Washing Laboratory, 1987.

Analyte	Number of Analyses	Frequency of MDL (%)	Percentile Concentration (mg/L)	
			50%	95%
Calcium	23	91.3	<0.009	<0.009
Magnesium	23	73.9	<0.003	0.004
Sodium	23	95.6	<0.003	<0.003
Potassium	23	95.6	<0.003	<0.003
Ammonium	26	100.0	<0.02	<0.02
Sulfate	26	100.0	<0.03	<0.03
Nitrate	26	100.0	<0.03	<0.03
Chloride	26	100.0	<0.03	<0.03
Ortho- phosphate	26	100.0	<0.02	<0.02
pH (units)	26	N.A.	5.65	5.74
Conductivity (μ S/cm)	27	N.A.	0.7	1.0

NOTE: N.A. = not applicable.

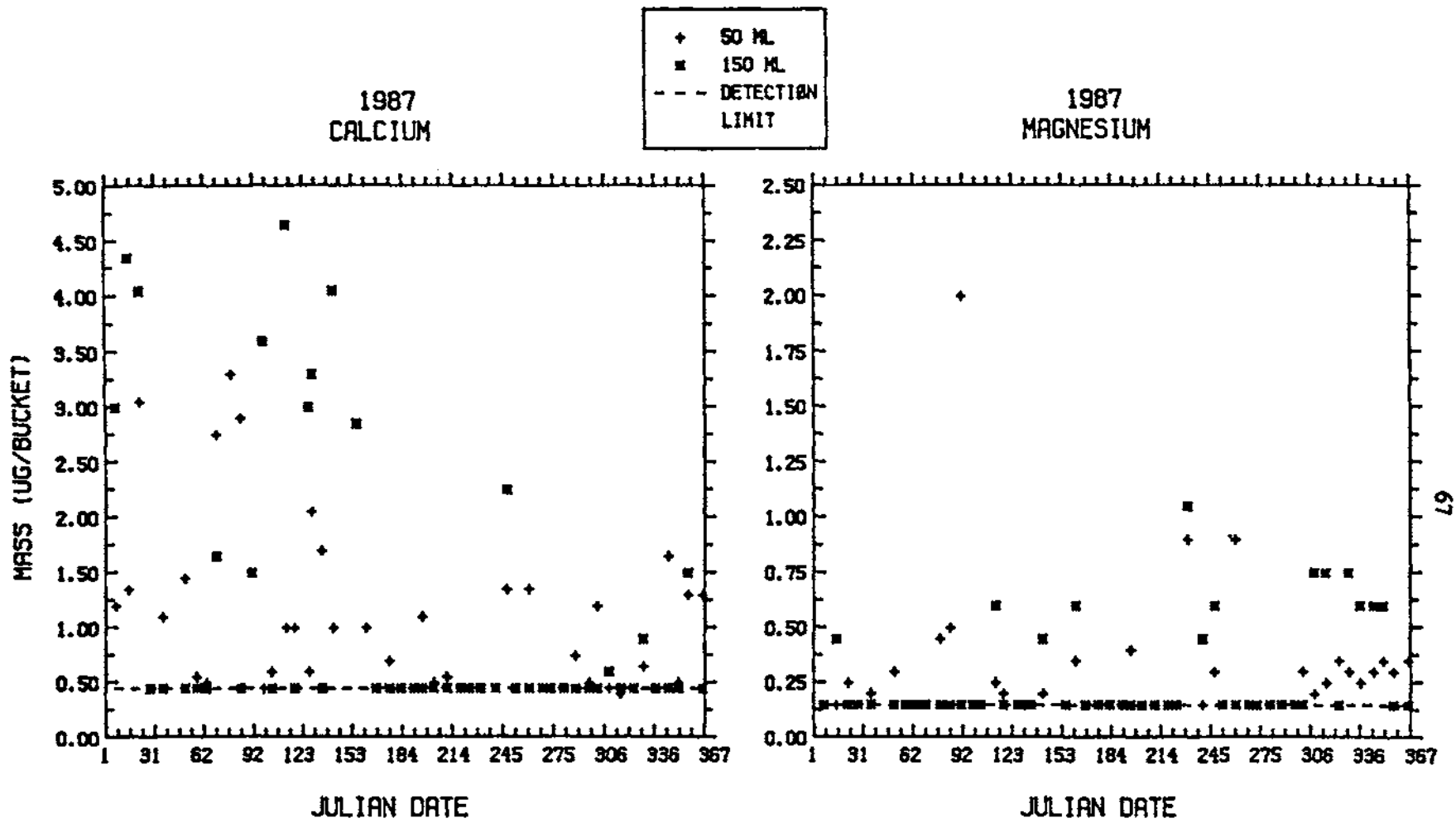


FIGURE B-1. Measured calcium and magnesium mass in inverted buckets, 1987.

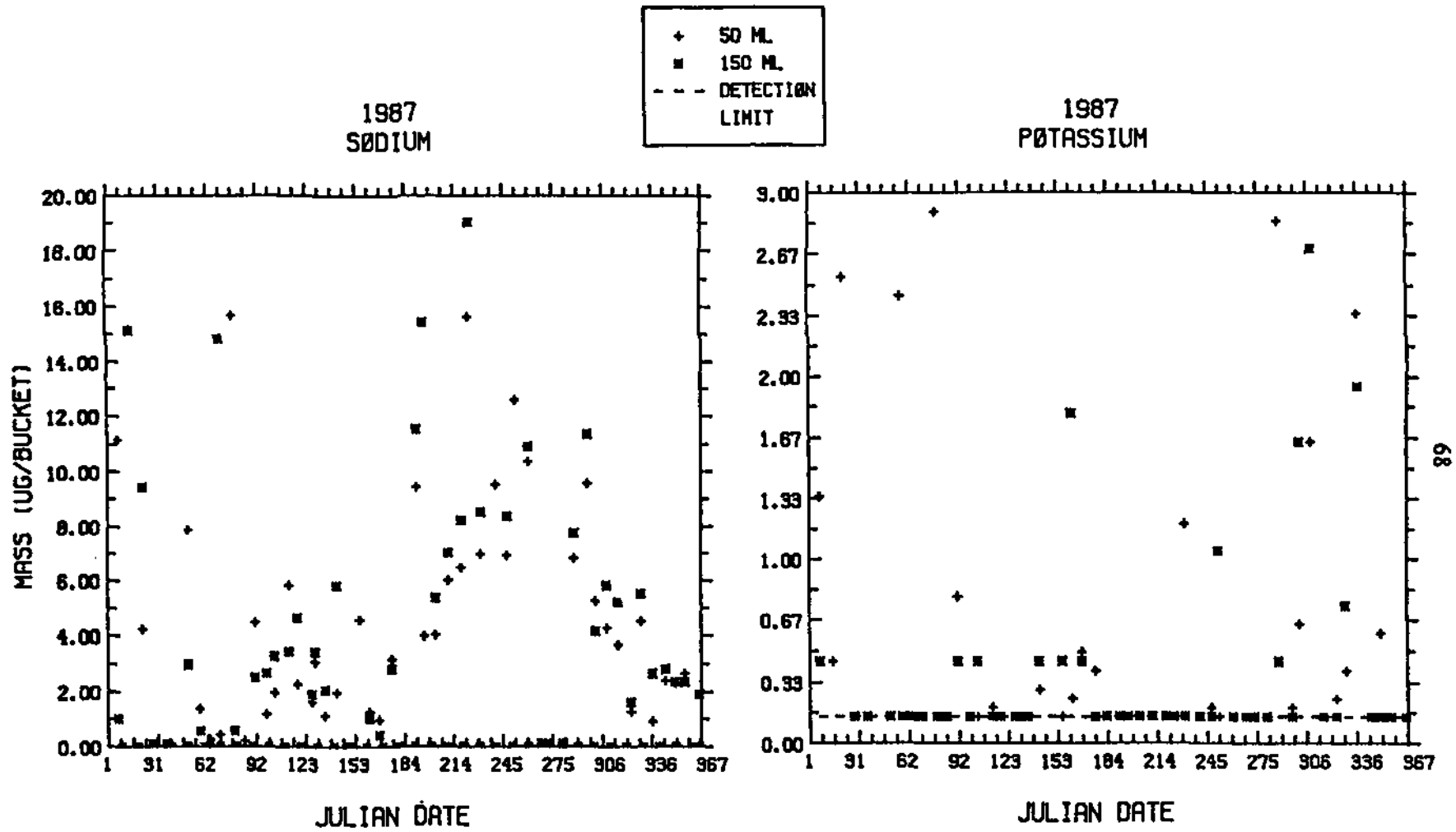


FIGURE B-2. Measured sodium and potassium mass in inverted buckets, 1987.

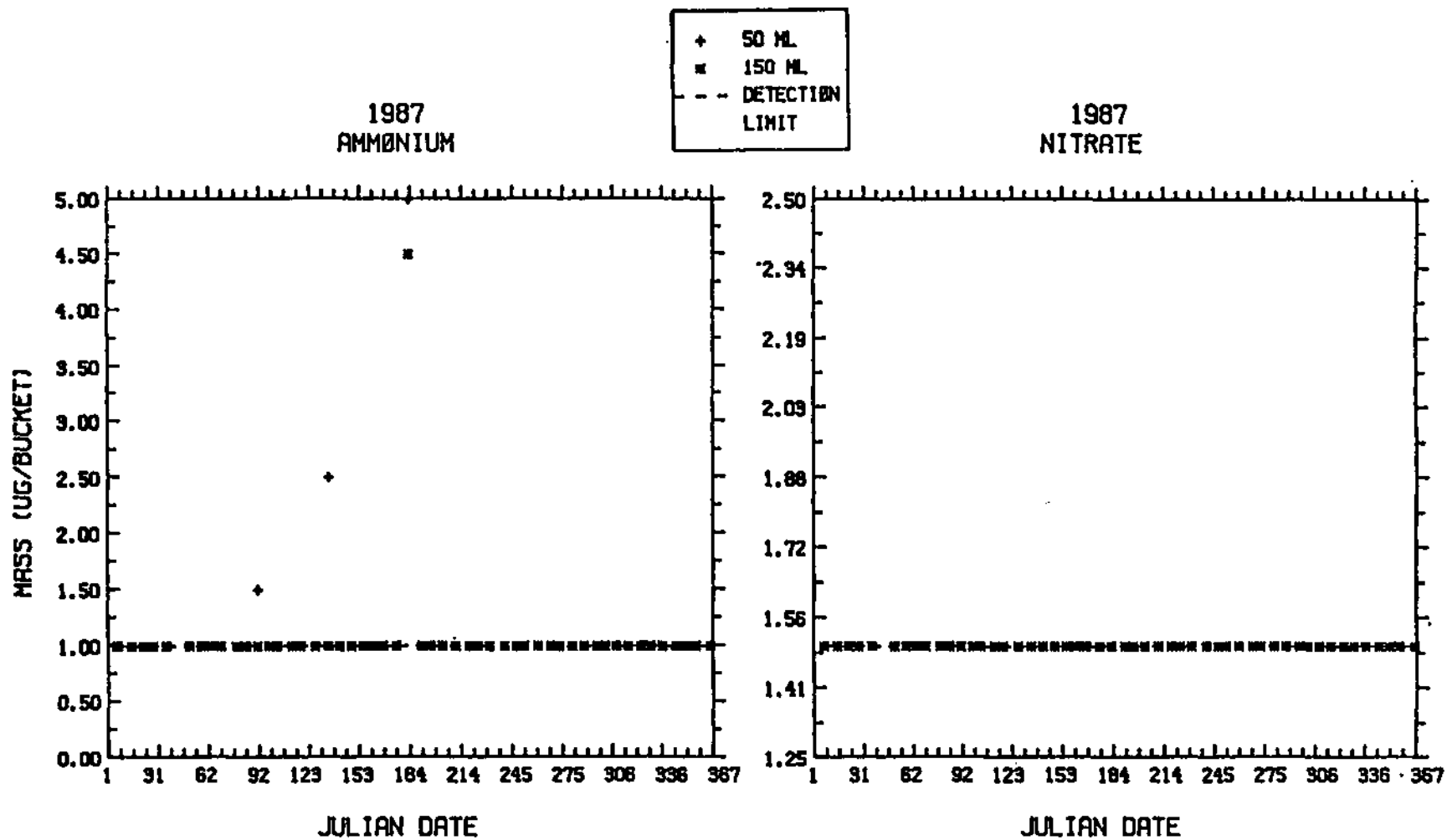


FIGURE B-3. Measured ammonium and nitrate mass in inverted buckets, 1987.

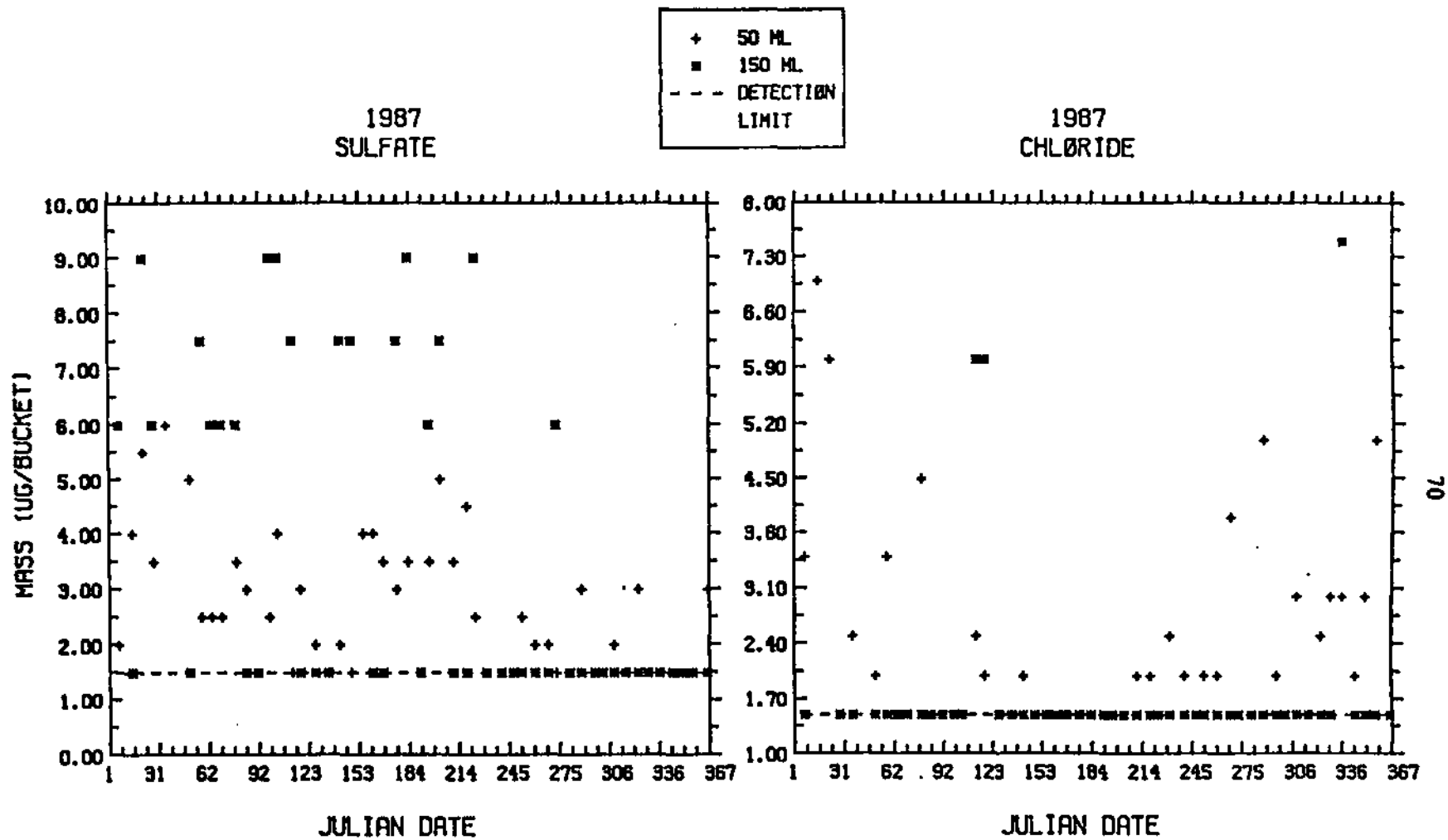


FIGURE B-4. Measured sulfate and chloride mass in inverted buckets, 1987.

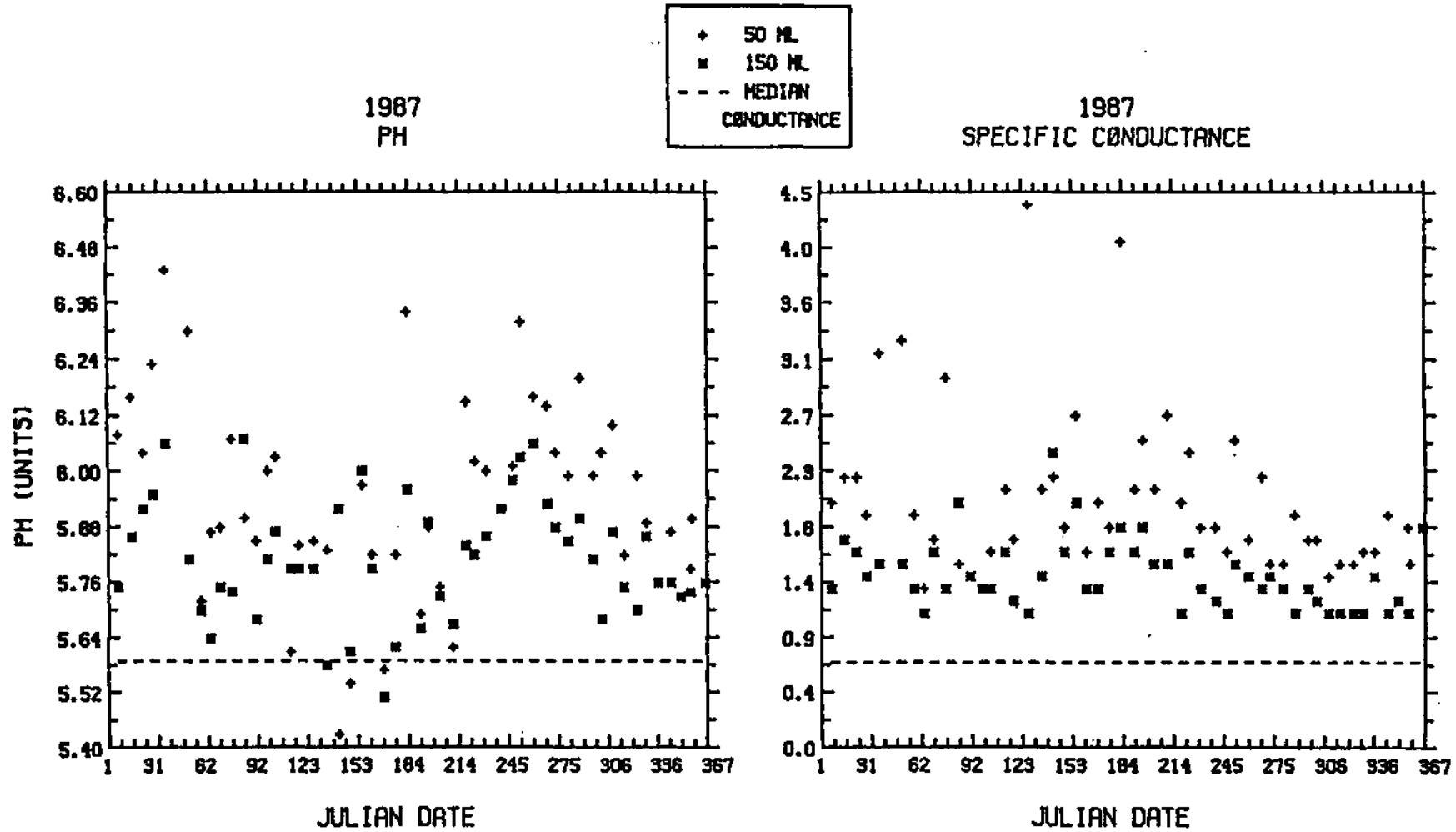


FIGURE B-5. Measured pH and conductance in inverted buckets, 1987.

APPENDIX C

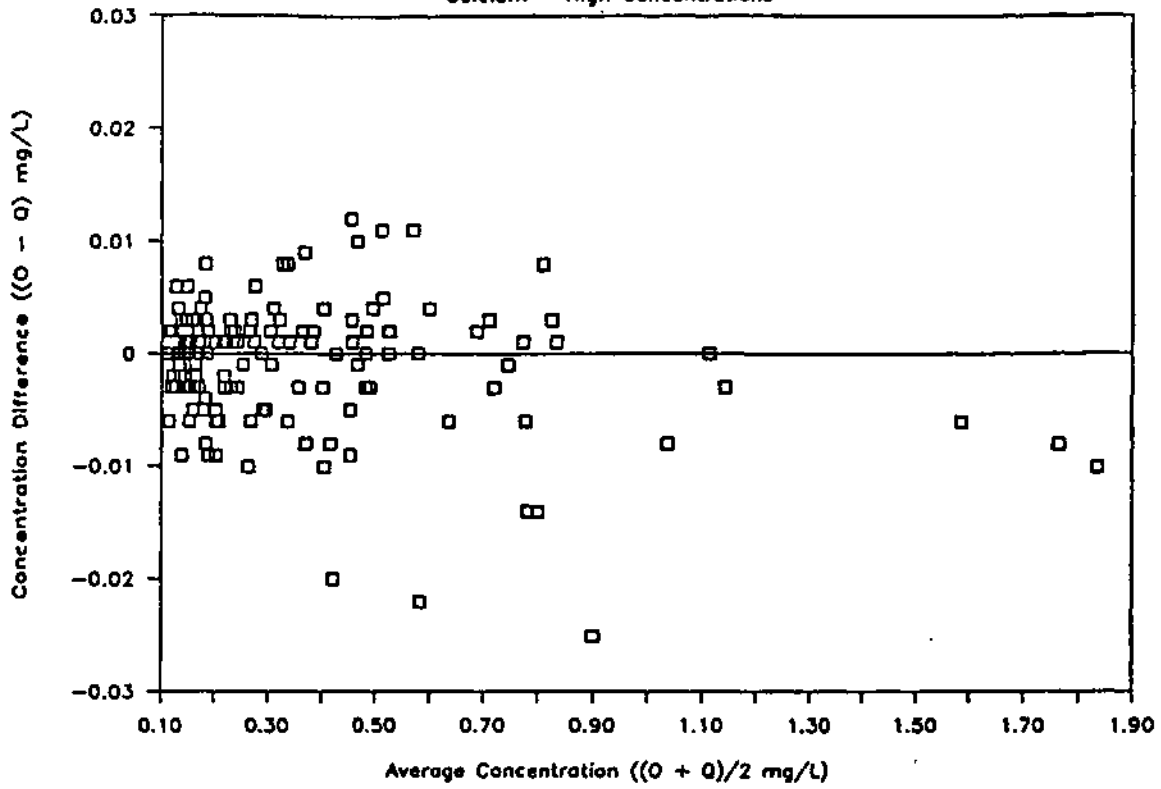
Replicate (O/Q) Sample Analyses:
Plots and Tables

1987

TABLE C-1 (O/Q) Data Summary for Replicate Analysis, 1987.

Parameter	Number of Replicate Pairs	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation Difference (mg/L)
Calcium	292	0.000	0.000	0.010
Magnesium	292	0.000	0.000	0.009
Sodium	292	0.000	0.002	0.006
Potassium	292	0.000	0.000	0.002
Ammonium	292	0.00	0.00	0.02
Sulfate	292	-0.01	-0.01	0.36
Nitrate	292	0.00	0.00	0.04
Chloride	292	0.00	0.00	0.19
pH (μ eq/L)	292	0.00	7.05	1.57
Conductivity (μ S/cm)	292	0.1	0.1	0.9

76
1987 O/Q SPLITS
Calcium - High Concentrations



1987 O/Q SPLITS
Calcium - Low Concentrations

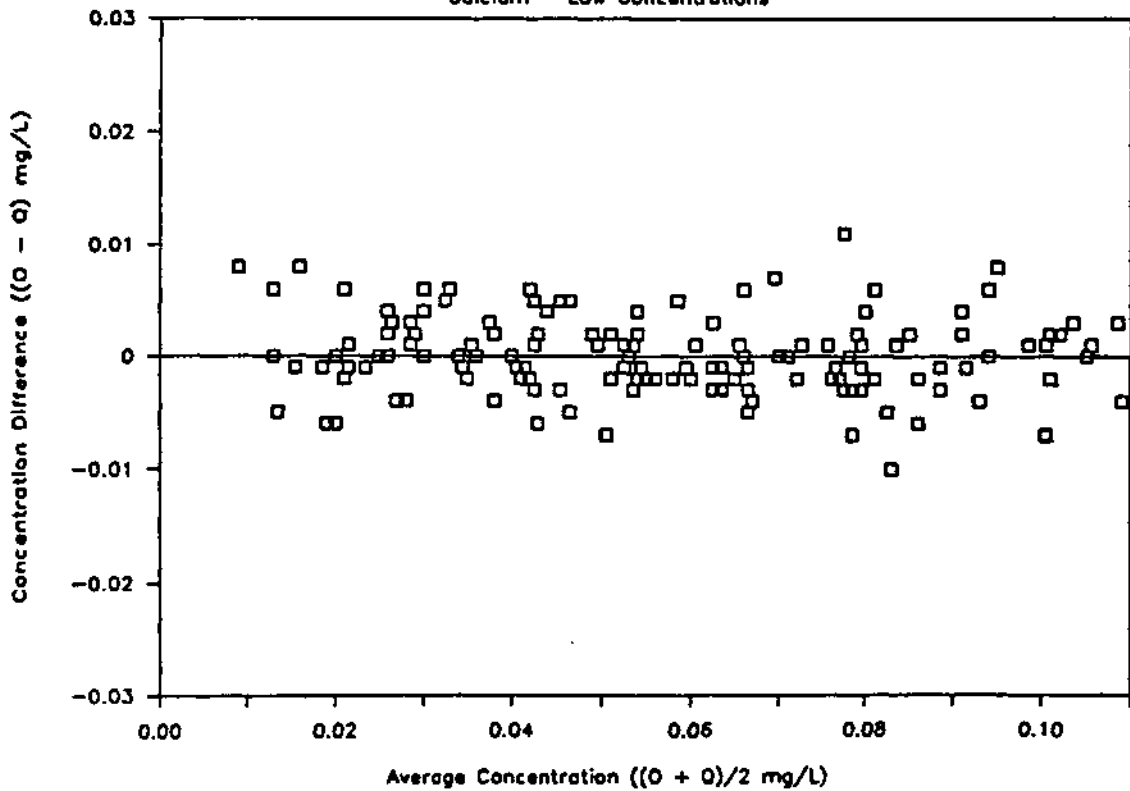
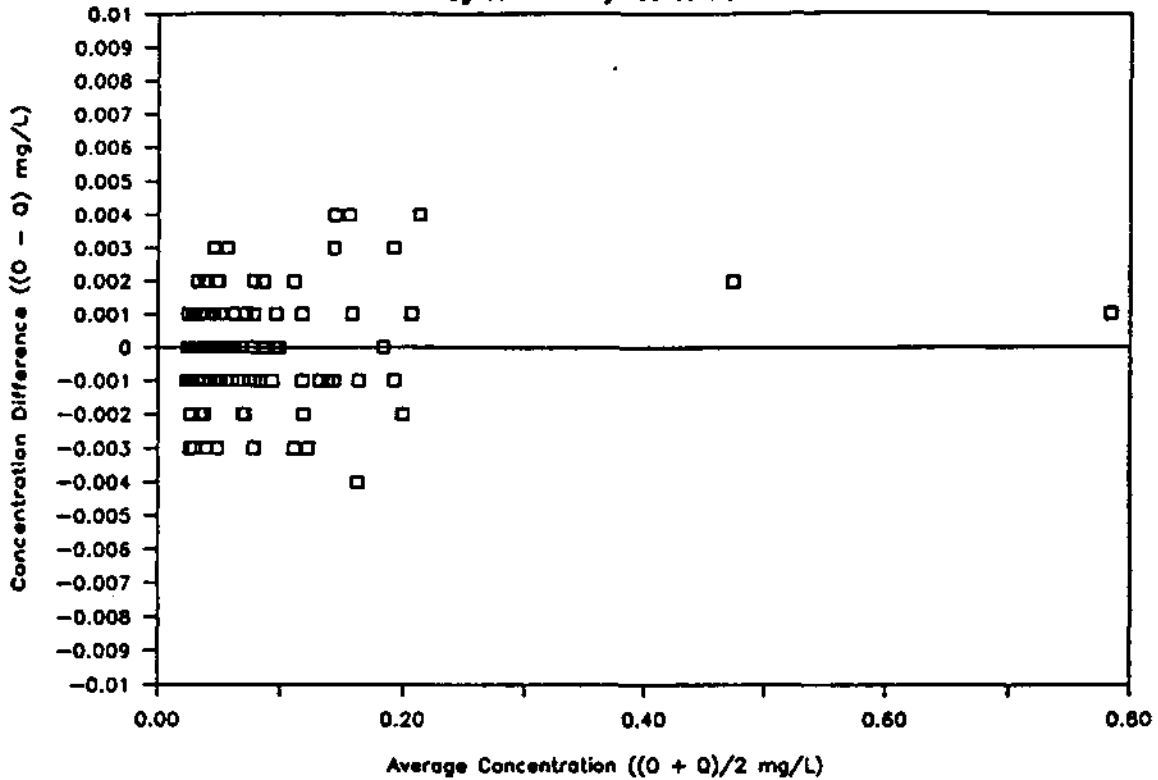


FIGURE C-1. O/Q replicate plots for calcium, 1987.

1987 O/Q SPLITS

Magnesium - High Concentrations



1987 O/Q SPLITS

Magnesium - Low Concentrations

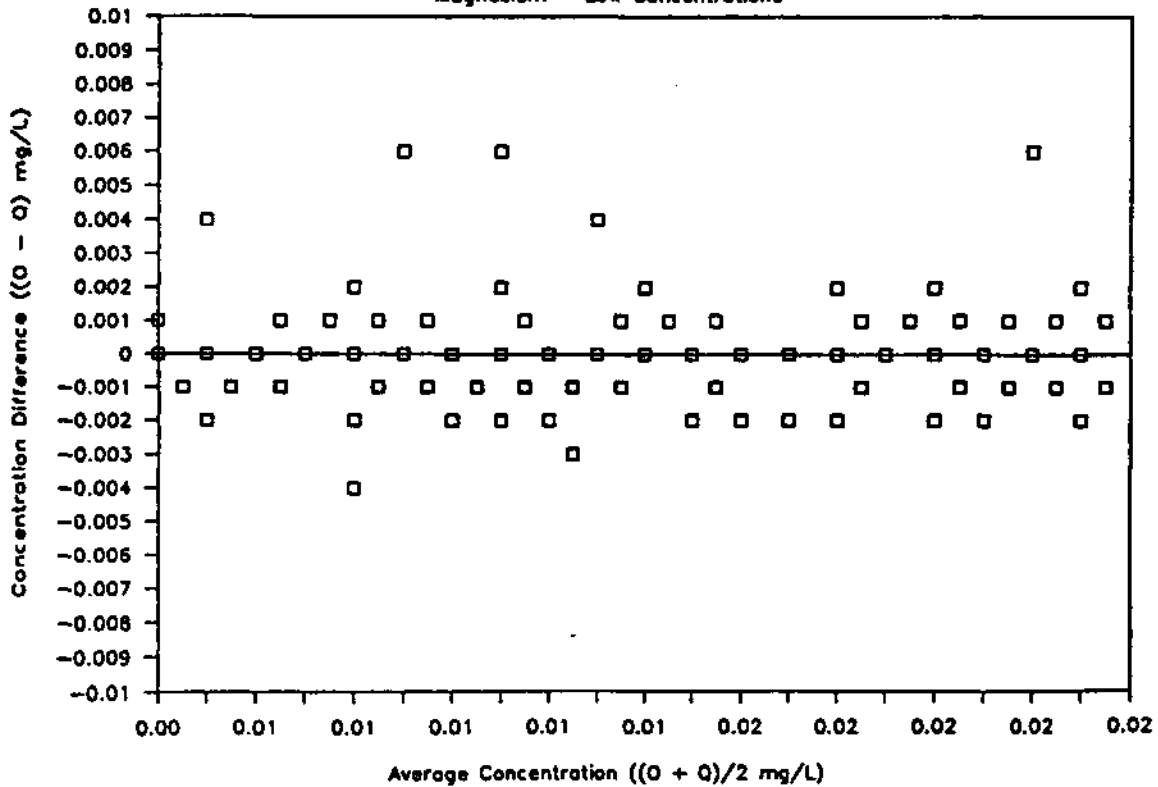
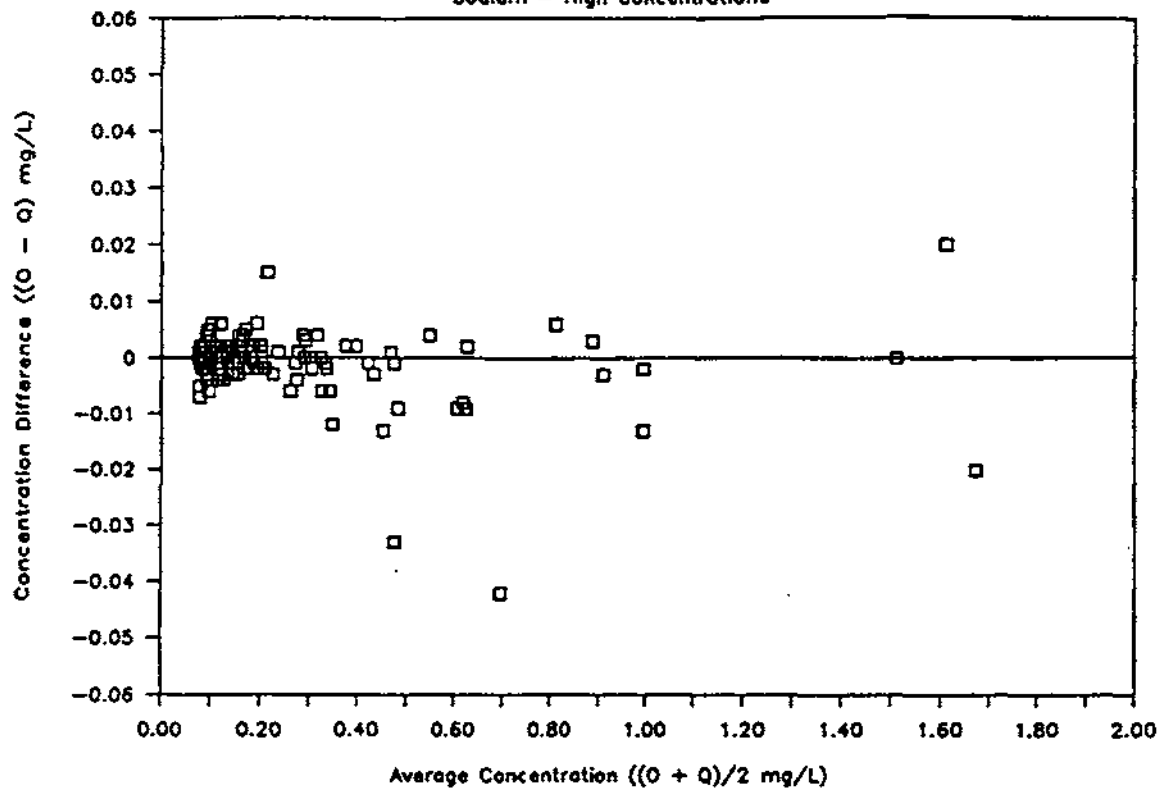


FIGURE C-2. O/Q replicate plots for magnesium, 1987.

1987 O/Q SPLITS

Sodium - High Concentrations



1987 O/Q SPLITS

Sodium - Low Concentrations

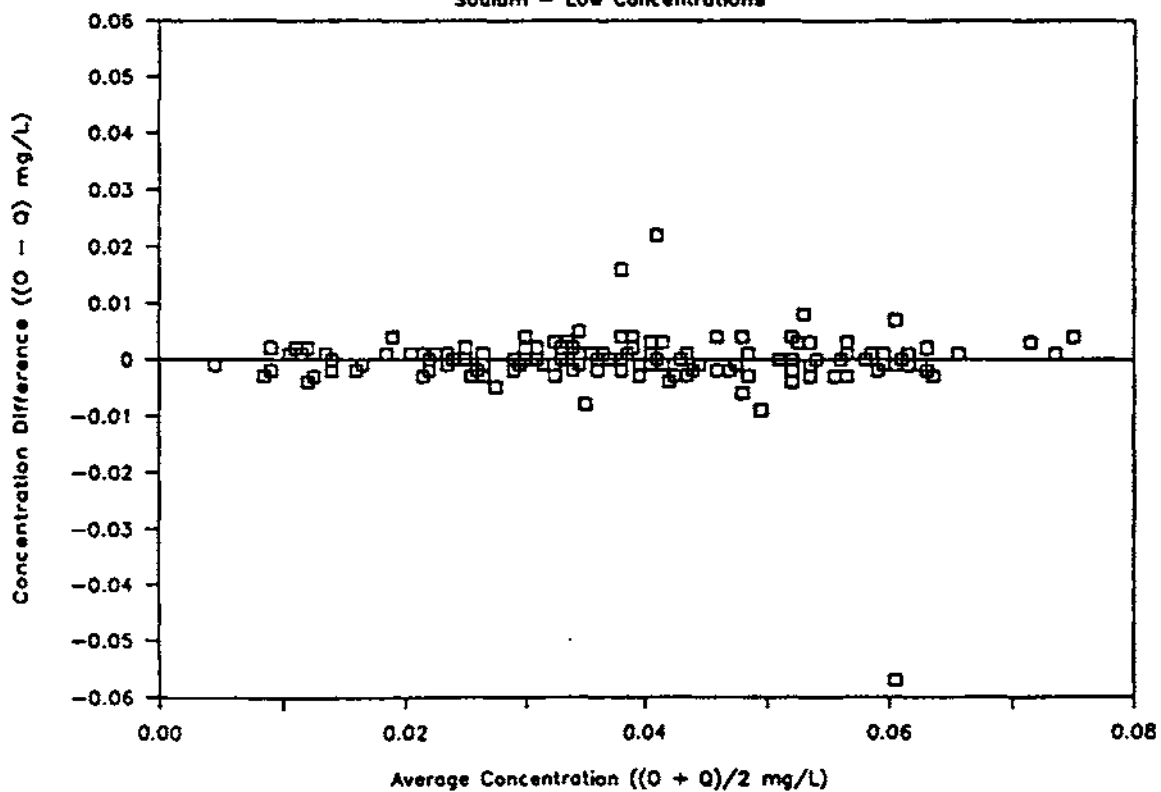
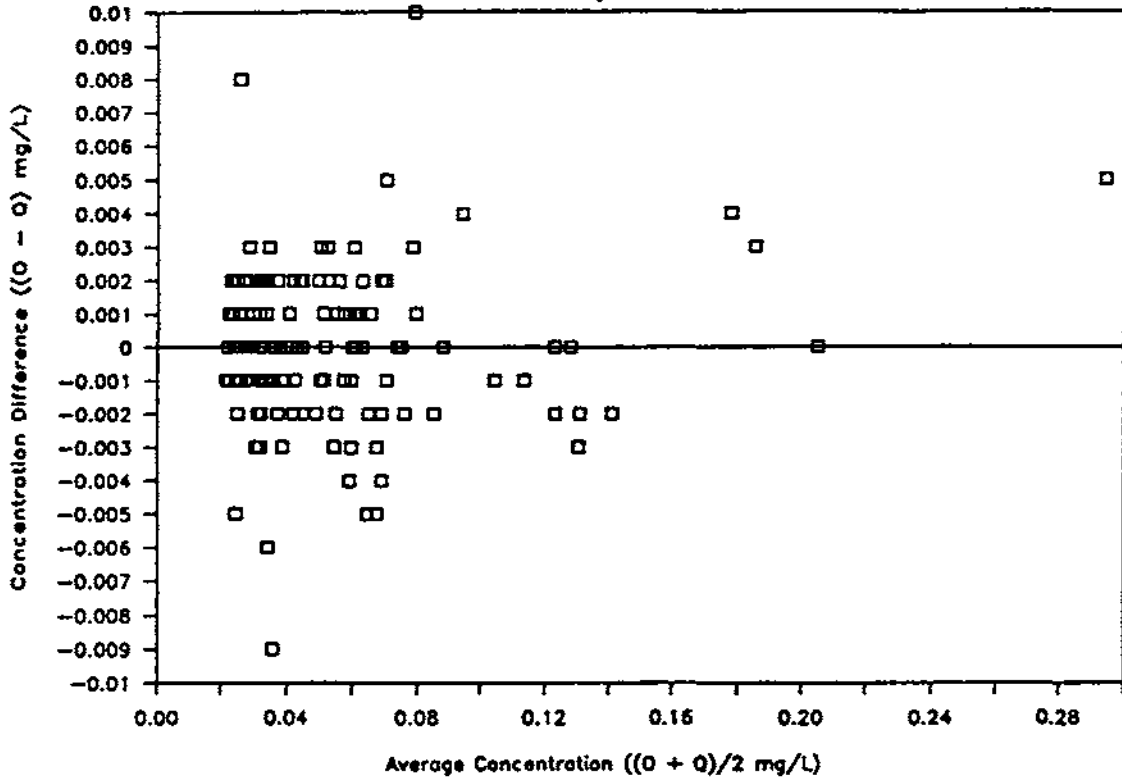


FIGURE C-3. O/Q replicate plots for sodium, 1987.

1987 O/Q SPLITS

Potassium - High Concentrations



1987 O/Q SPLITS

Potassium - Low Concentrations

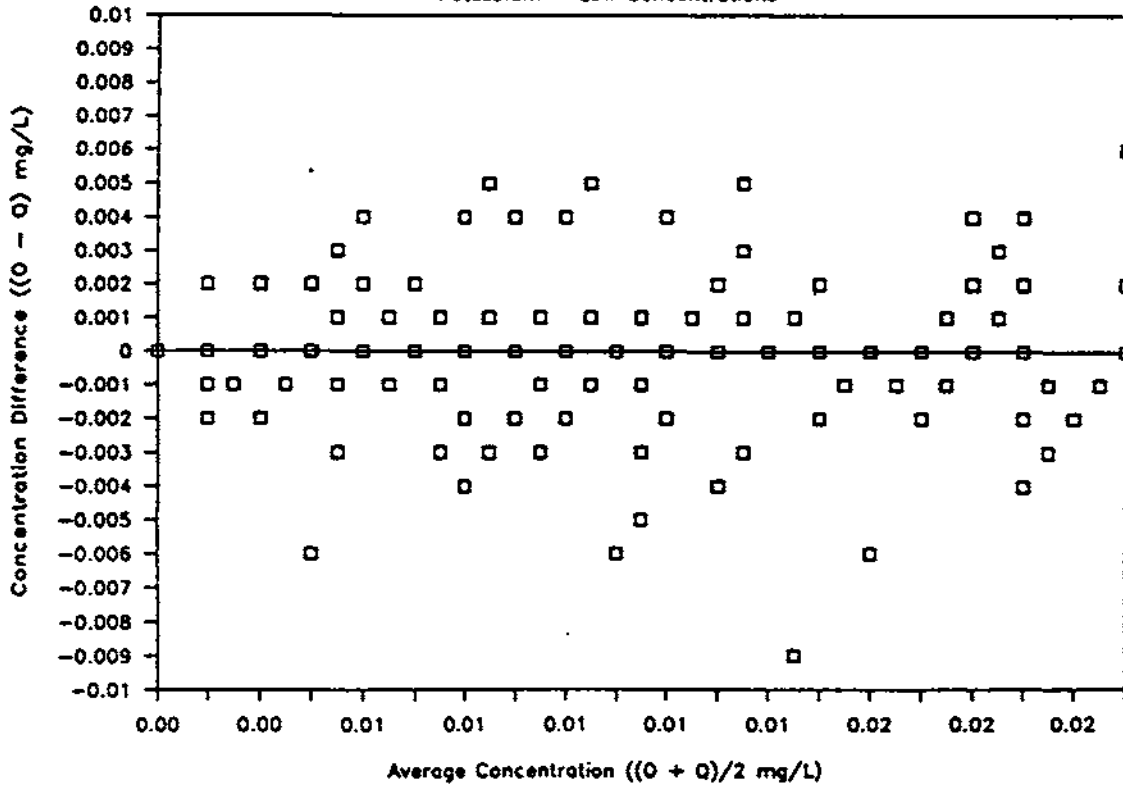
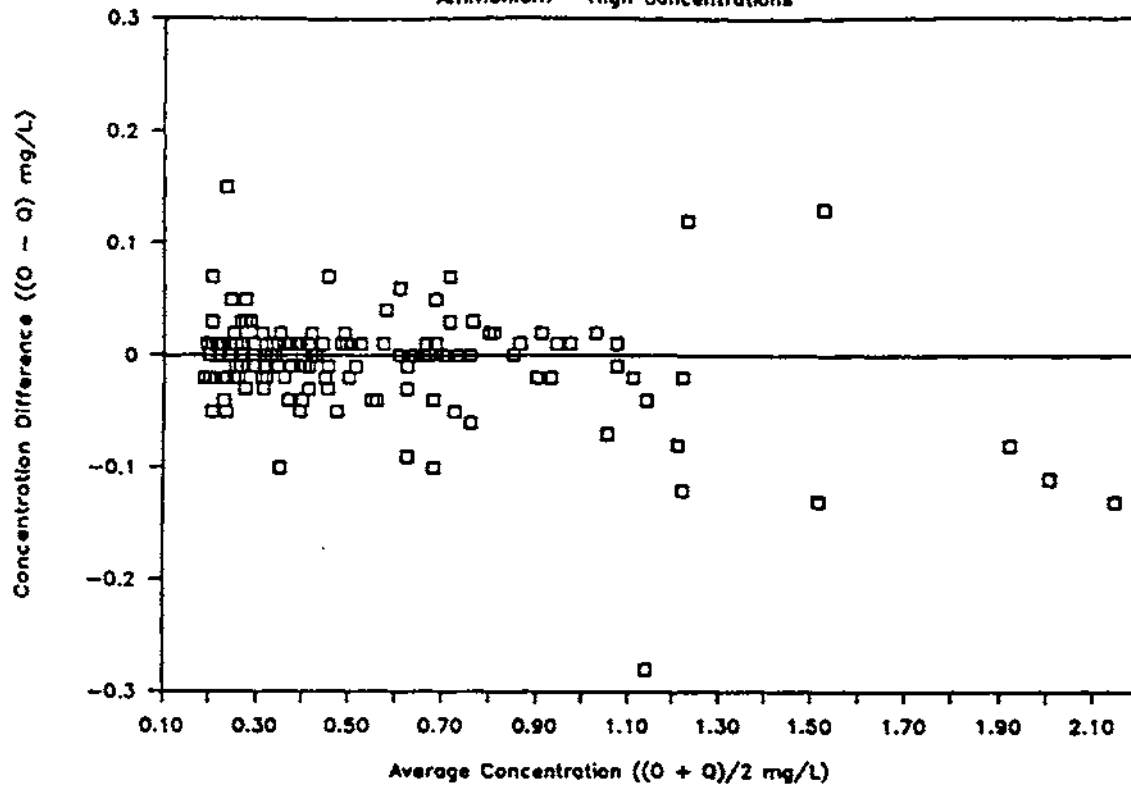


FIGURE C-4. O/Q replicate plots for potassium, 1987.

1987 O/Q SPLITS

Ammonium - High Concentrations



1987 O/Q SPLITS

Ammonium - Low Concentrations

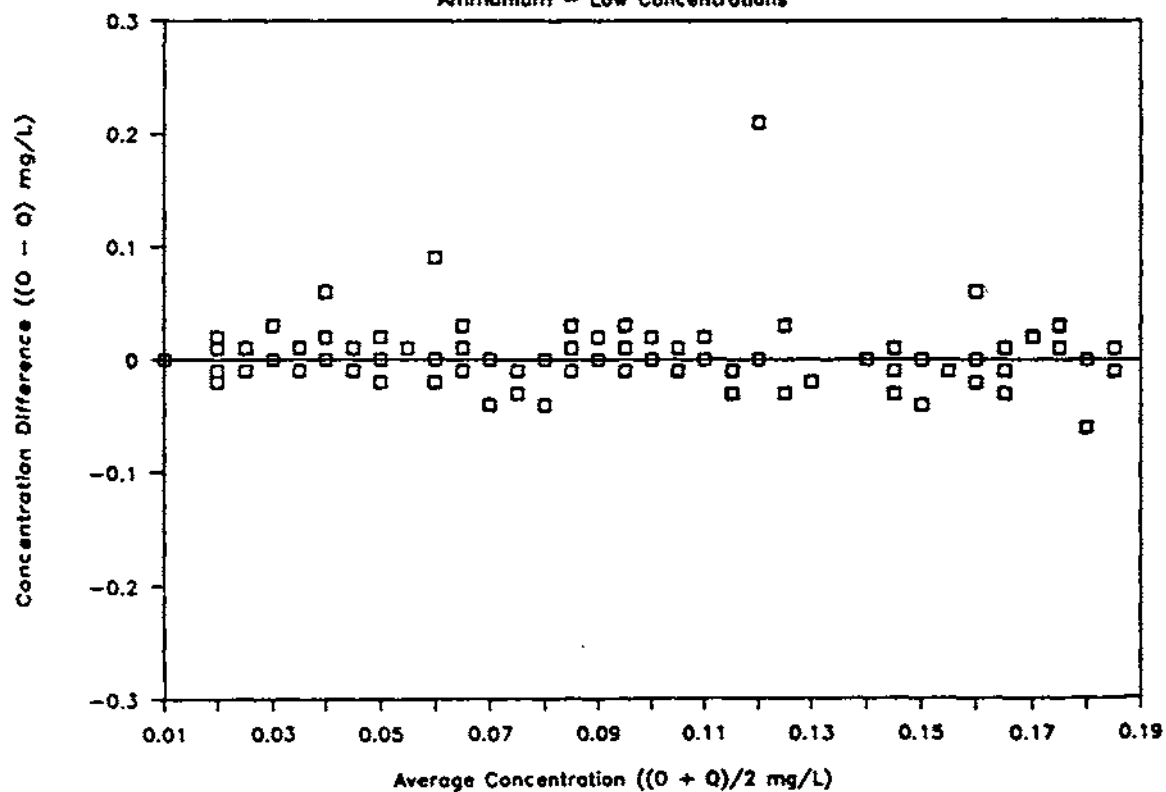
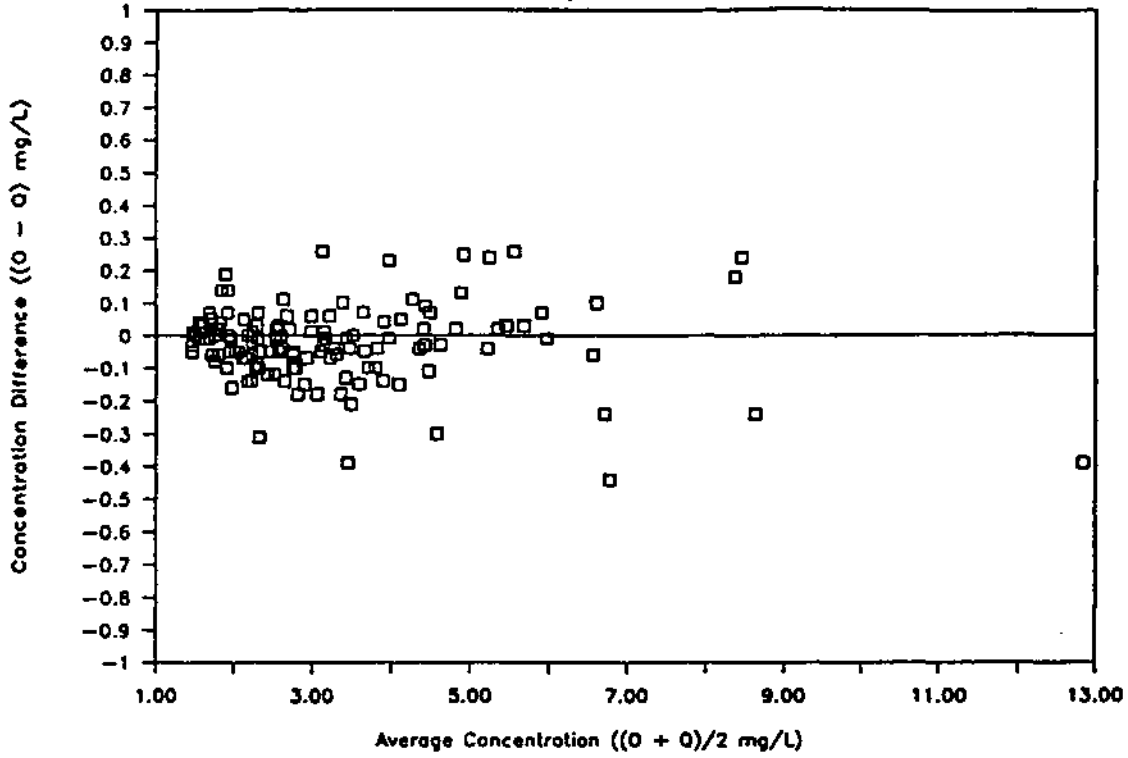


FIGURE C-5. O/Q replicate plots for ammonium, 1987.

1987 O/Q SPLITS

Sulfate - High Concentrations



1987 O/Q SPLITS

Sulfate - Low Concentrations

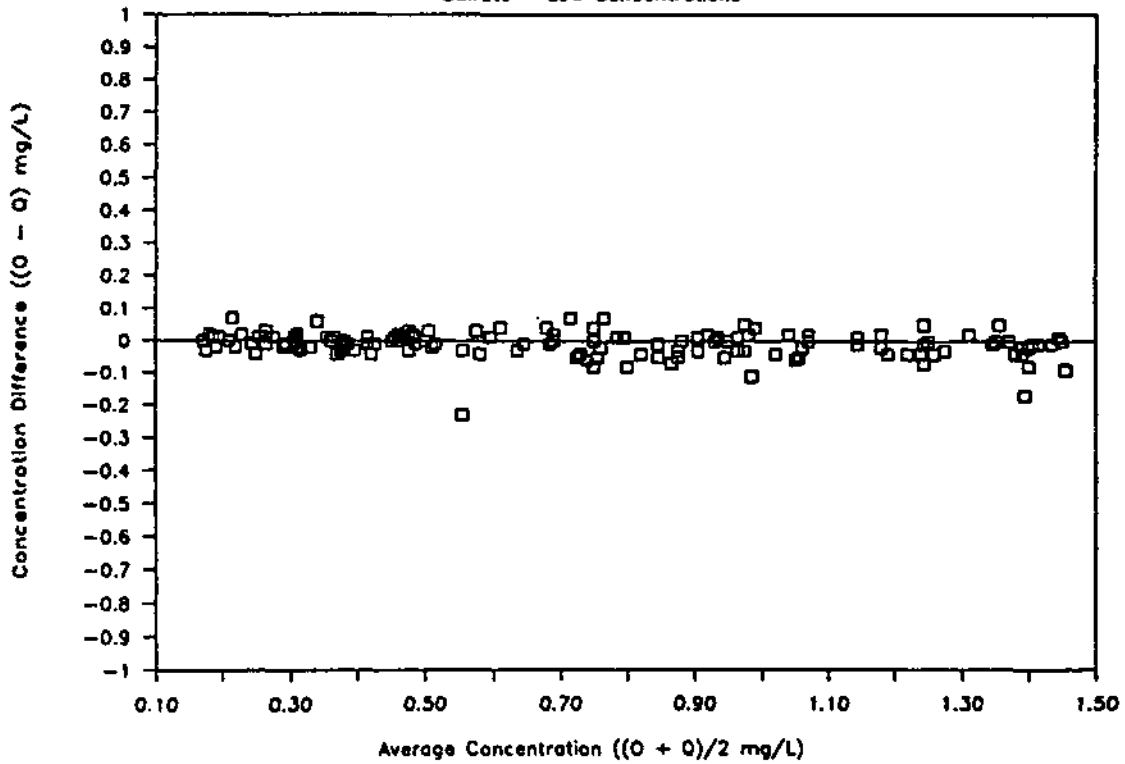
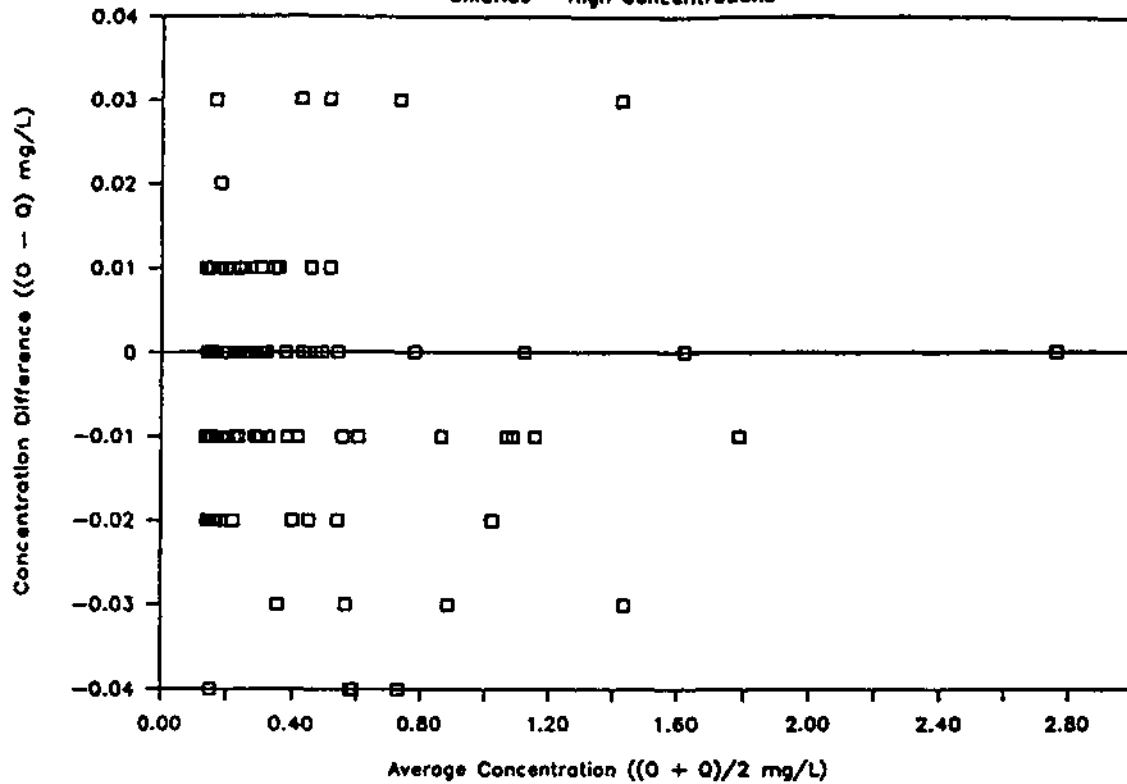


FIGURE C-6. O/Q replicate plots for sulfate, 1987.

1987 O/Q SPLITS

Chloride - High Concentrations



1987 O/Q SPLITS

Chloride - Low Concentrations

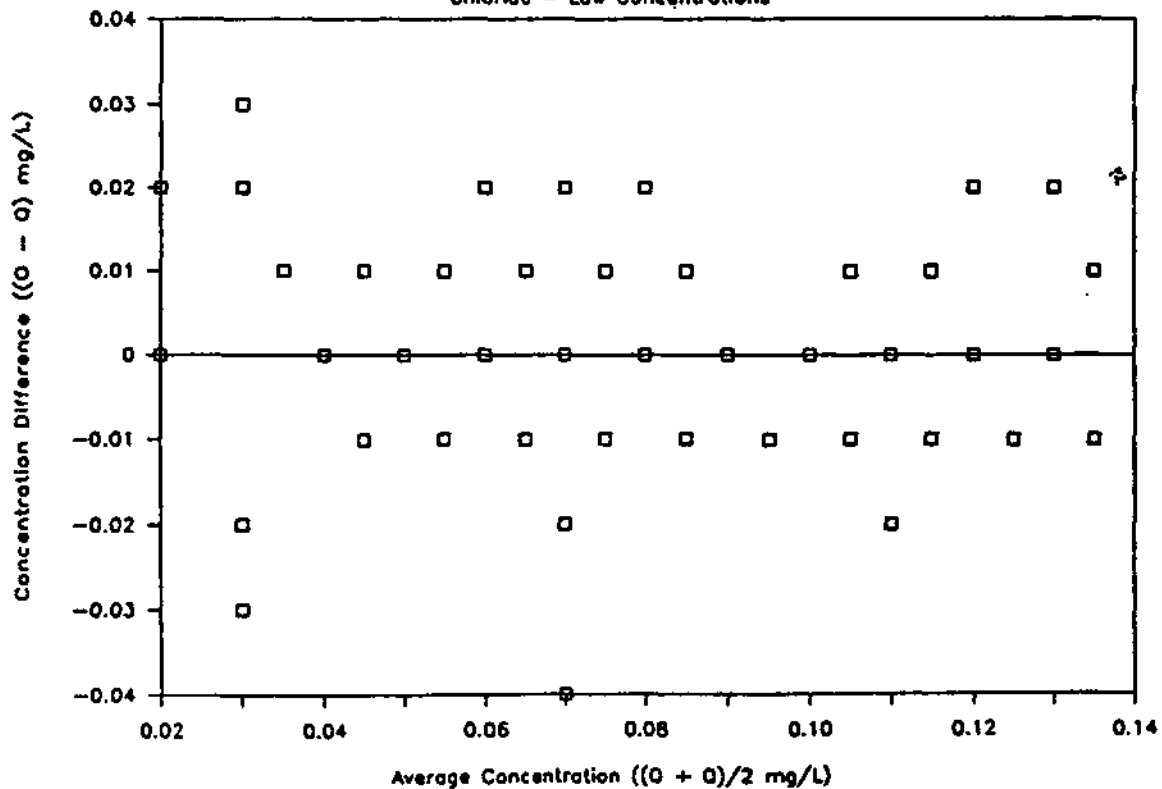


FIGURE C-7. O/Q replicate plots for chloride, 1987.

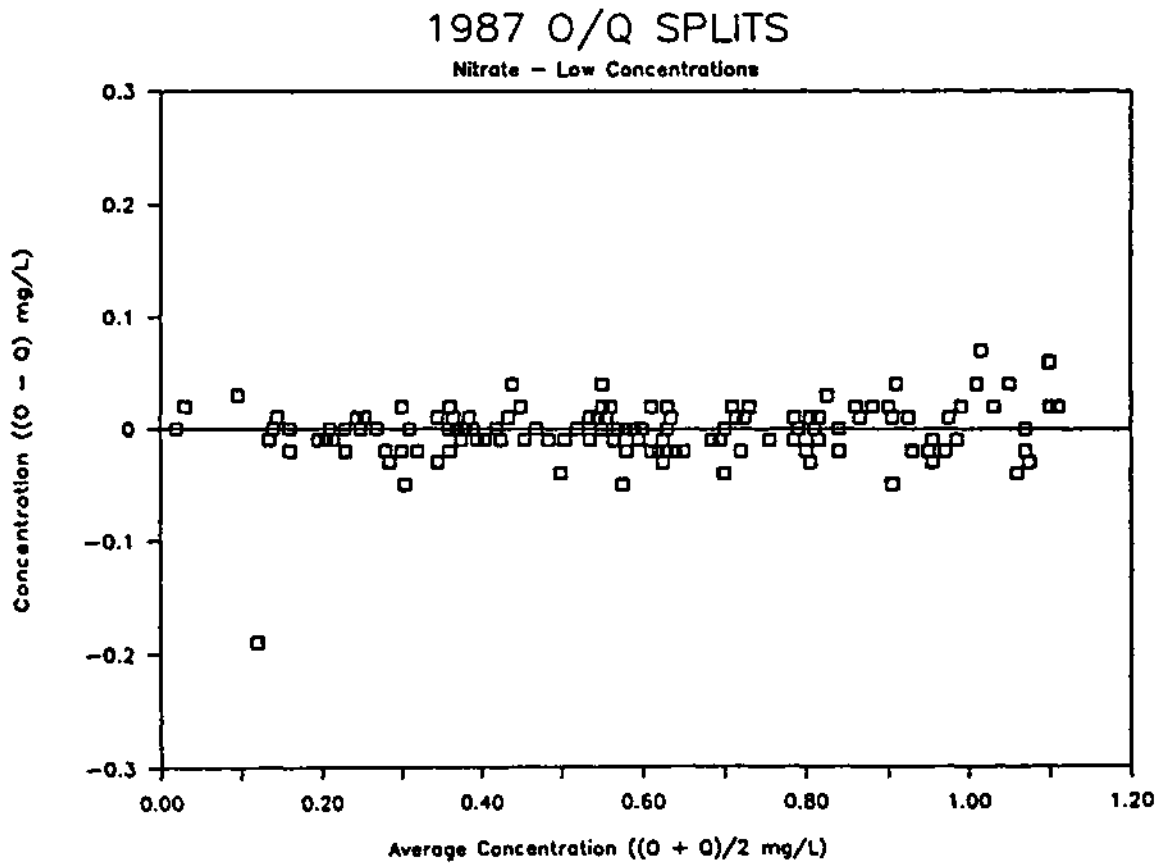
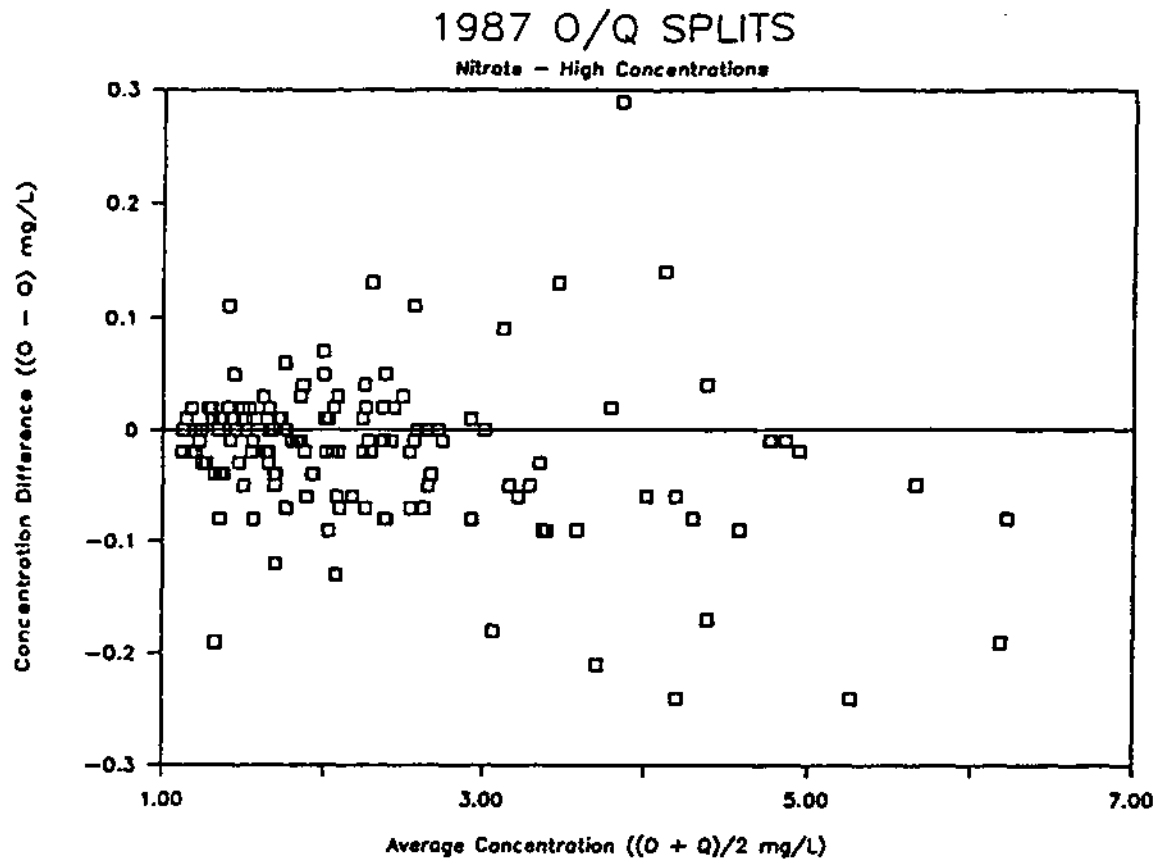
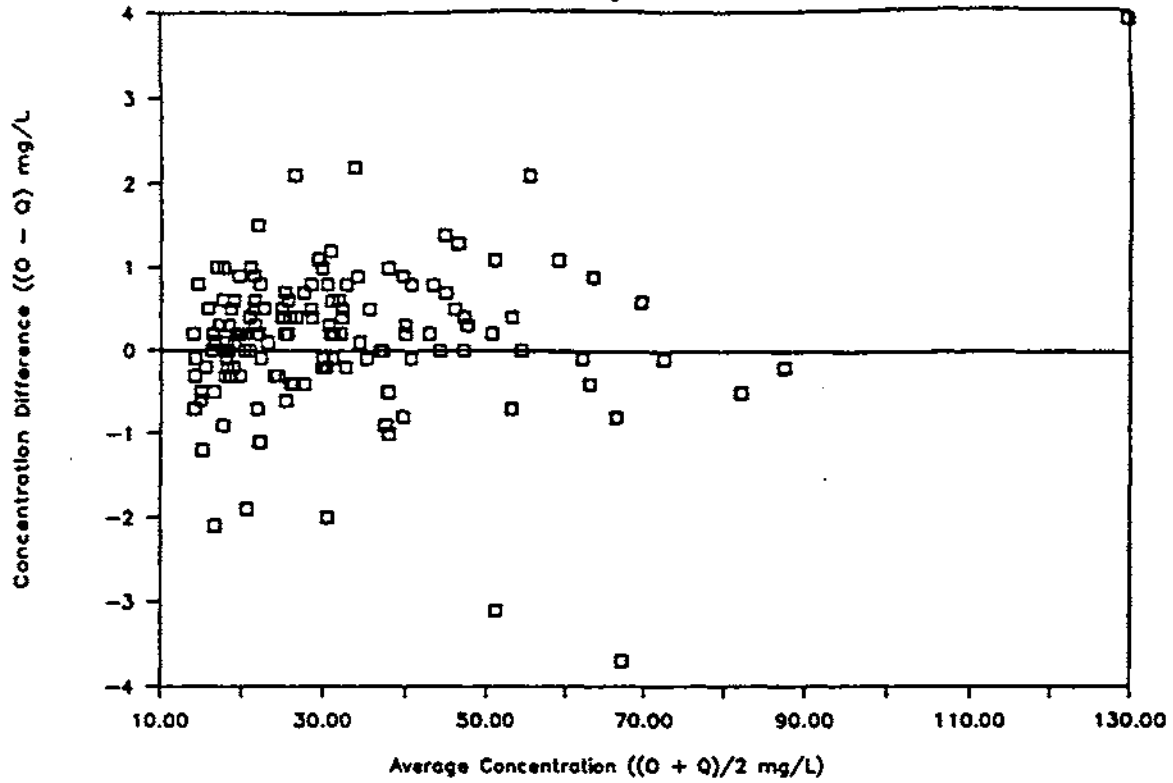


FIGURE C-8. O/Q replicate plots for nitrate, 1987.

1987 O/Q SPLITS

Conductance - High Concentrations



1987 O/Q SPLITS

Conductance - Low Concentrations

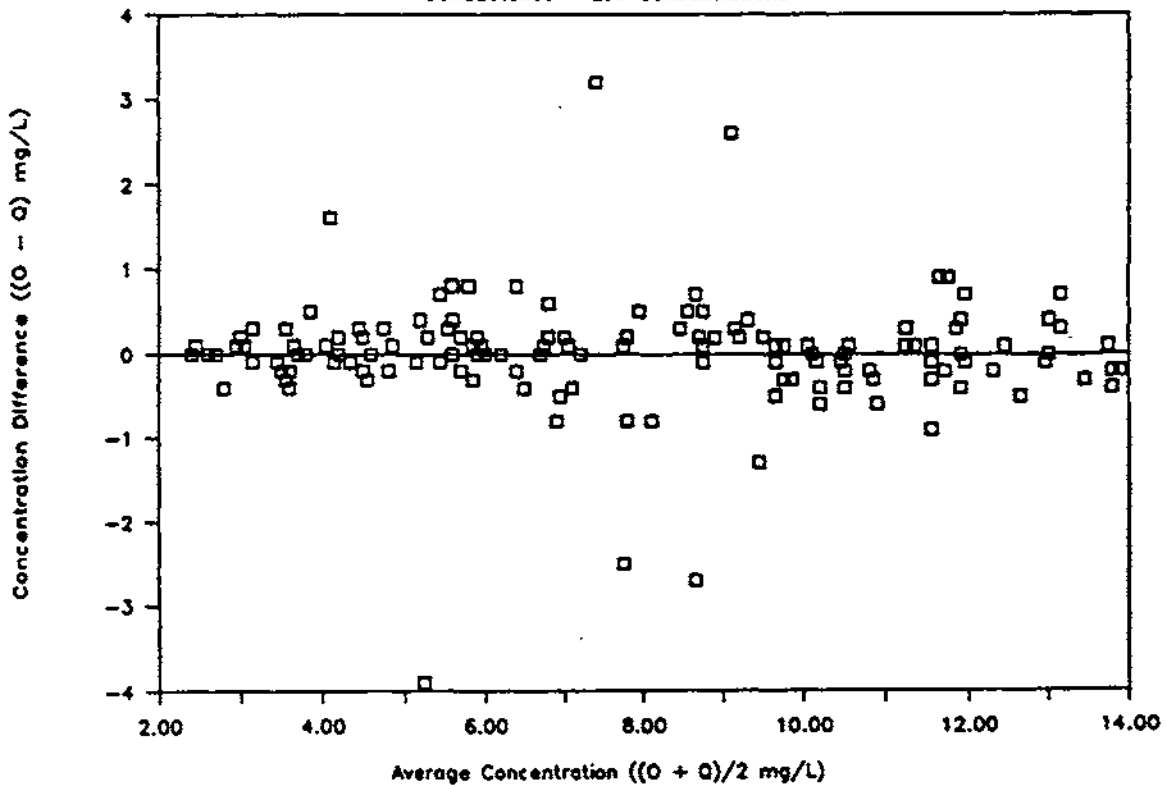
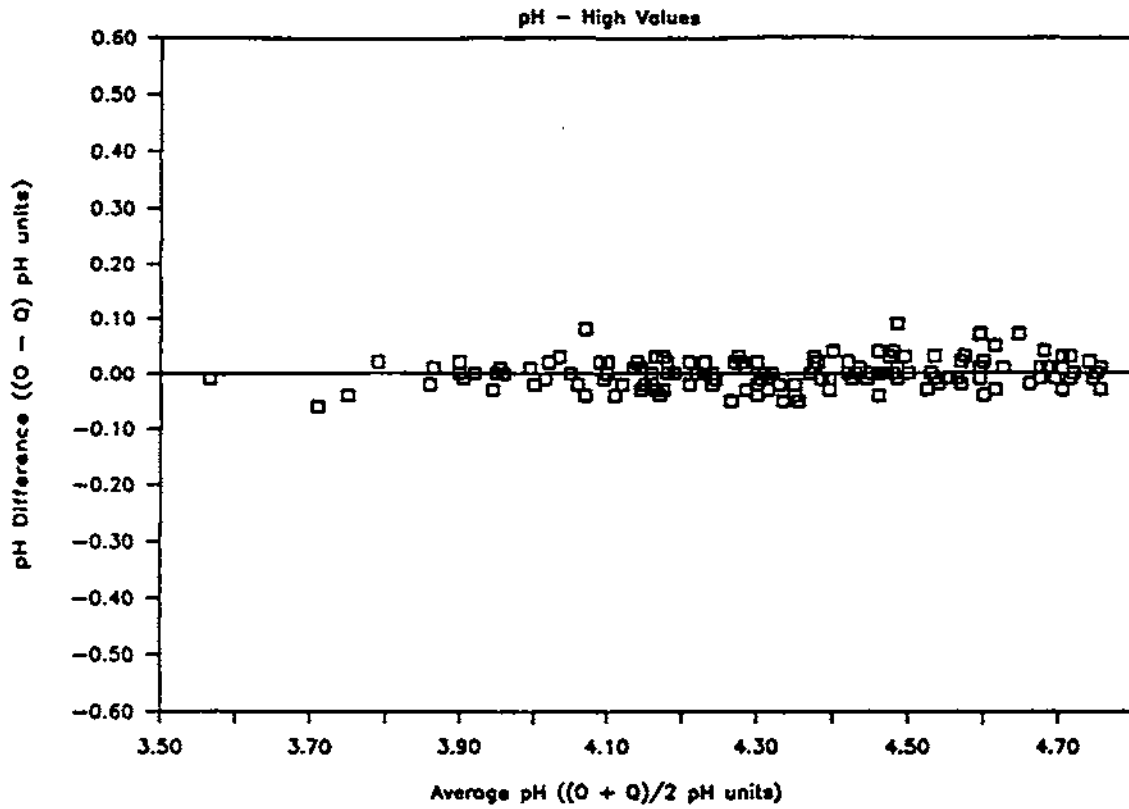


FIGURE C-9. O/Q replicate plots for conductance, 1987.

1987 O/Q SPLITS



1987 O/Q SPLITS

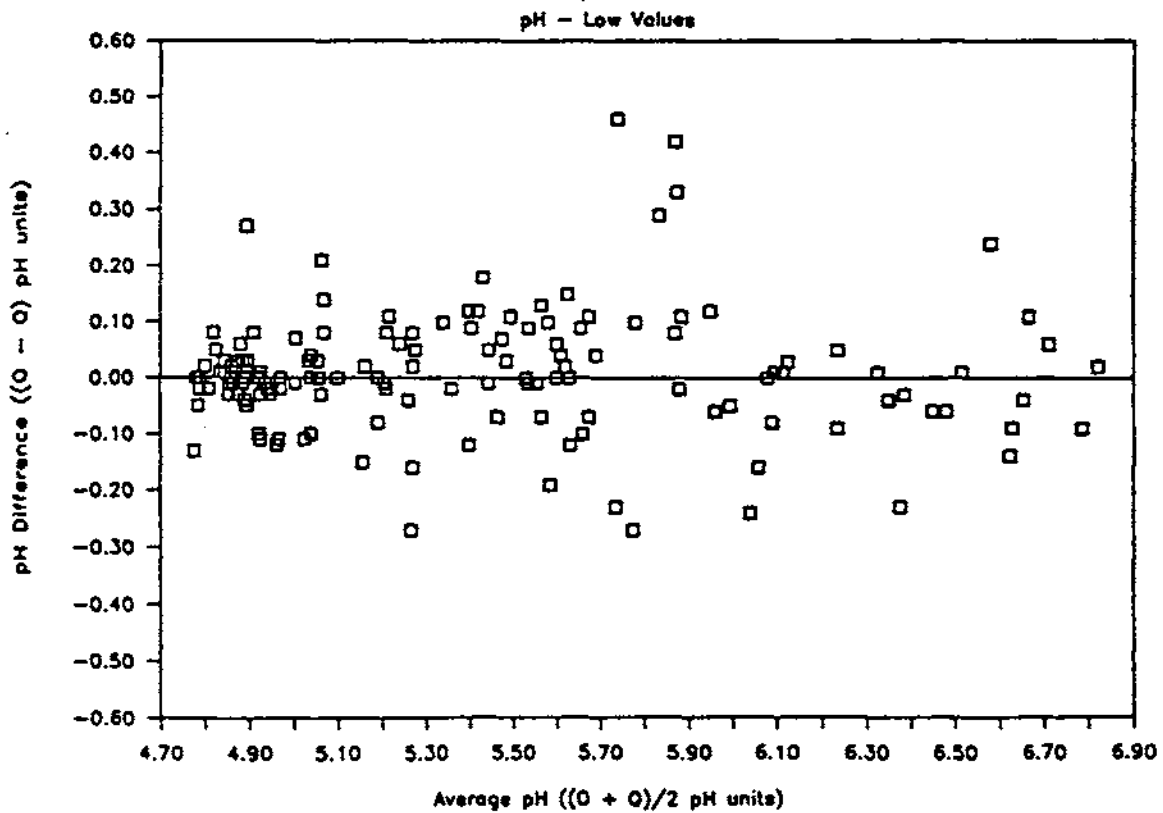
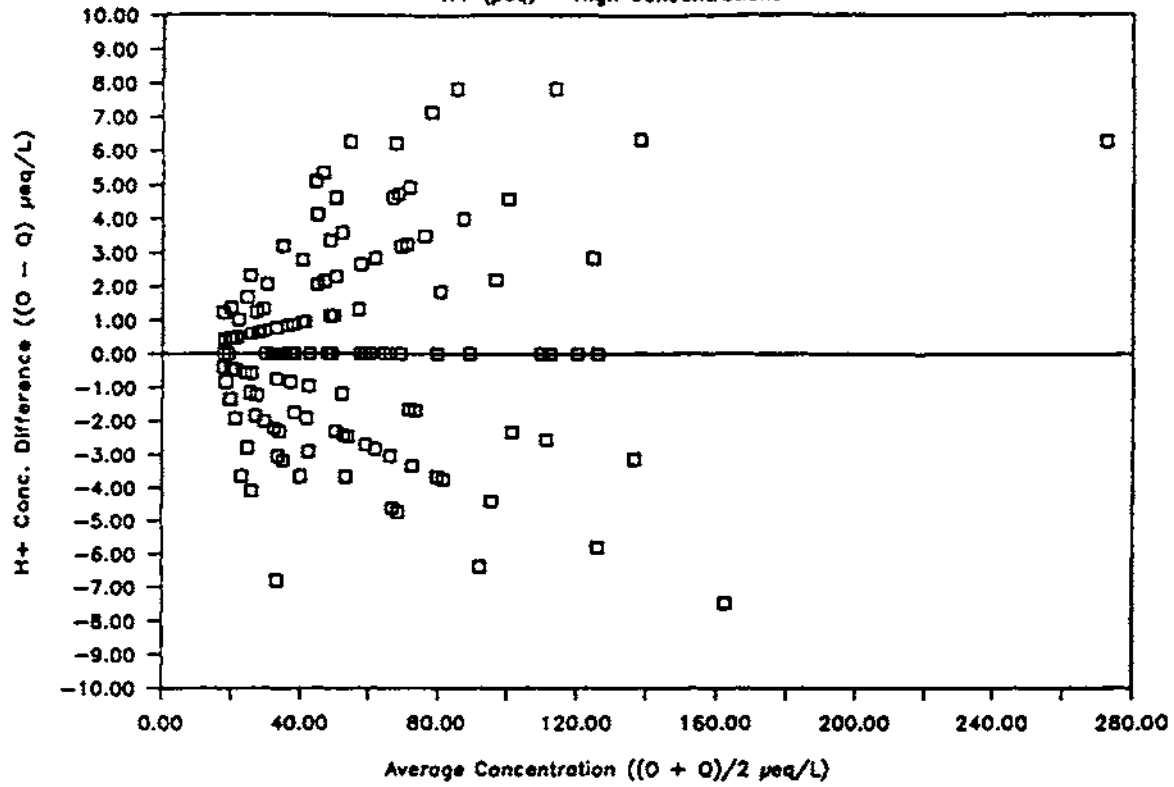


FIGURE C-10. O/Q replicate plots for pH, 1987.

1987 O/Q SPLITS

H+ (μeq) - High Concentrations

1987 O/Q SPLITS

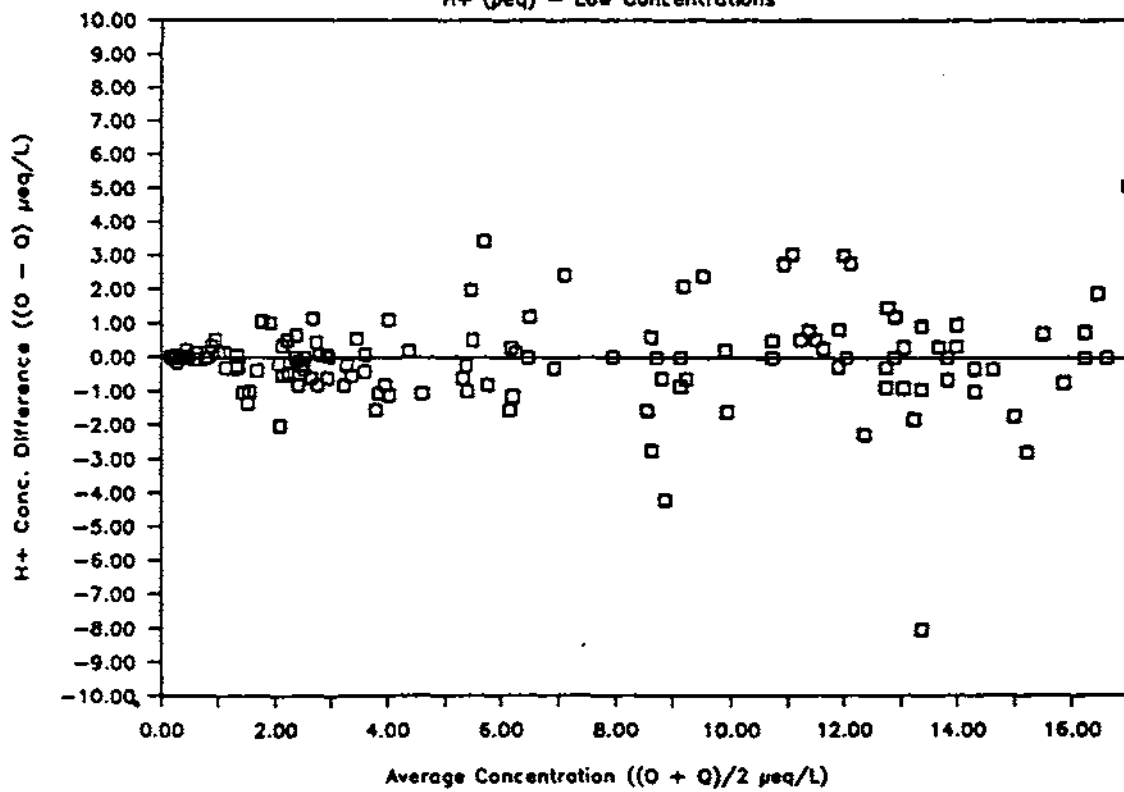
H+ (μeq) - Low Concentrations

FIGURE C-11. O/Q replicate plots for hydrogen ion, 1987.

APPENDIX D

Interlaboratory Comparison Data:

USEPA and LRTAP

1987

TABLE D-1 EPA Interlaboratory Comparison of Reference
Precipitation Samples (CAL Values Compared
to Expected Values), November 1987.

Parameter	1090		Sample Number 2267		3586	
	CAL	EPA	CAL	EPA	CAL	EPA
Calcium (mg/L)	0.056	0.055	0.135	0.130	-----	-----
Magnesium (mg/L)	0.016	0.014	0.014	0.011	0.053	0.050
Sodium (mg/L)	0.243	0.238	0.250	0.246	0.488	0.485
Potassium (mg/L)	0.080	0.072	0.088	0.080	0.101	0.095
Ammonium (mg/L)	0.14	0.139	0.88	0.788	1.13	1.001
Nitrate (mg/L)	0.62	0.602	0.53	0.500	6.46	6.25
Chloride (mg/L)	0.380	0.389	0.64	0.642	0.97	0.931
Sulfate (mg/L)	1.59	1.57	8.36	7.89	11.62	11.26
pH (units)	4.53	4.51	3.91	3.91	3.56	3.57
Specific Conductance (μ S/cm)	17.3	16.5	64.2	62.8	132.1	128.7

NOTE: Number of participating laboratories = 35.

TABLE D-2 LRTAP Interlaboratory Comparability study L15
 (CAL Reported Values Compared to CCIW Median Values
 for all Participating Laboratories), April 1987.

Parameter	Sample Number													
	1		2		3		4		5		6		10	
	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	0.726	0.750	3.77	3.810	2.15	2.190	2.32	2.37	1.77	1.805	3.86	3.880	12.9	13.2
Magnesium (mg/L)	0.246	0.250	0.461	0.465	0.546	0.550	0.729	0.740	0.669	0.670	0.660	0.670	2.72	2.73
Sodium (mg/L)	0.847	0.870	0.791	0.800	0.765	0.770	0.139	0.140	4.05	4.090	0.913	0.940	1.24	1.240
Potassium (mg/L)	0.440	0.440	0.504	0.502	0.197	0.190	0.088	0.090	0.292	0.290	0.410	0.410	0.496	0.493
Ammonium (mg/L)	0.32	0.310	0.02T*	0.008	0.03	0.011	0.12	0.129	0.03	0.037	0.02T*	0.009	0.02T*	0.012
Nitrate (mg/L)	1.15	1.16	0.80	0.800	0.22	0.182	5.71	5.71	0.13	0.128	0.66	0.620	1.37	1.328
Chloride (mg/L)	3.12	3.050	0.41	0.410	0.75	0.740	0.39	0.390	5.34	5.17	0.27	0.270	1.28	1.280
Sulfate (mg/L)	2.67	2.525	5.65	5.600	7.02	7.000	6.55	6.500	2.92	2.800	12.77	12.675	3.23	3.133
pH (units)	4.53	4.50	6.86	6.67	5.29	5.21	4.47	4.45	6.40	6.200	6.40	6.140	8.09	7.750
Specific Conductance (μ S/cm)	30.3	30.00	30.7	31.00	26.4	26.75	40.5	40.00	35.8	36.0	38.4	38.45	92.6	94.00

NOTE: Number of participating laboratories - 44.

* A "T" code indicates instrument response below the MDL.

TABLE D-3 LRTAP Interlaboratory Comparability study L15a
(CAL Reported pH Values Compared to CCIW Median
Values for All Participating Laboratories in a
pH Round Robin), April 1987.

Sample #	CAL	CCIW
1	5.42	5.40
2	5.94	5.88
3	6.60	6.59
4	6.91	6.98
5	5.20	5.19
6	5.77	5.77
7	6.41	6.54
8	6.96	6.96
9	5.08	5.07
10	5.65	5.65
11	6.44	6.46
12	6.84	6.86
13	5.01	5.00
14	5.58	5.58
15	6.35	6.37
16	6.76	6.79

NOTE: Number of participating laboratories = 44.

