QUALITY ASSURANCE REPORT
NADP/NTN DEPOSITION MONITORING

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

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.

QUALITY ASSURANCE REPORT
NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
January 1984 through December 1985

prepared by Jacqueline Lockard Peden
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May 1988

QUALITY ASSURANCE REPORT
ACID/RAIN DEPOSITION MONITORING

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I. INTRODUCTION

The Quality Assurance Report for the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) for the years 1978 through 1983 was published in May 1987 (1). That report detailed the early development of the laboratory quality assurance program. This report continues the documentation of that program as it was expanded and refined in 1984 and 1985.

This report follows the format established in the report for 1978-1983. Section II documents the changes that occurred in the analytical methodology being used, in the laboratory staff, and in the laboratory facilities from January 1984 through December 1985. This is followed by the laboratory blank data (Section III). These data again resulted from the analyses of bucket leachates, filter leachates, and deionized water, providing the information necessary for assessing the potential contribution of sample collection and processing to the analyte concentrations found in the network samples. Quality control check sample (QCS) analyses continued to be utilized to quantify analytical bias and precision (Section IV). An internal blind program (Section IV) was introduced to provide another means of determining analytical bias and precision. Additional estimates of precision are achieved through replicate sample analyses (Section IV). The validity of these bias and precision estimates continues to be supported by the performance of the CAL in external quality assurance audits and interlaboratory testing programs (Section VI). Section V again details the criteria used to select samples for reanalysis and presents a discussion of the changes to the data that may result from this reanalysis process. Finally, an assessment of the performance of the CAL during 1984 and 1985 in following the guidelines set forth in the 1984 QA Plan is presented in the summary (Section VII).

In both 1984 and 1985, the laboratory was visited by members of the NADP Quality Assurance Steering Committee. The members of this committee, in conjunction with NADP Subcommittee 2 on Methods Development and Quality Assurance, advised the CAL on quality assurance (QA) program changes they felt would enhance the still developing program. By the end of 1984, the QA Steering Committee had produced the NADP Quality Assurance Plan (2), which provided formal guidelines for the laboratory quality assurance program.

II. LABORATORY QUALITY ASSURANCE PROGRAM

A. GENERAL DESCRIPTION

During 1984 and 1985 there were several changes at the CAL which affected the laboratory quality assurance program. These included the development of a methods manual for the analysis of precipitation (3); a change in the method used for the analysis of sulfate, nitrate, and chloride in precipitation samples in May 1985; and a move to new laboratory facilities in November 1985. This section addresses those changes and their impacts on the QA program. During this period, an internal blind sample submission procedure was developed, and changes were made to the existing procedures for replicate analyses. These changes are discussed in Section IV.

1. Analytical Methods Manual

Development of the analytical methods manual was made possible through funding from the U.S. Environmental Protection Agency. The laboratory manager and his staff at the Illinois State Water Survey were solely responsible for the resultant volumes. The manual provides complete procedures to be used for the analysis of precipitation samples. Included within Volume 1 are the procedures used by the CAL to determine analyte concentrations for the 11 parameters routinely analyzed in precipitation samples collected at NADP/NTN sites. Each method includes recommended quality control procedures specific to that method.

During the development of this manual, the U.S. Environmental Protection Agency requested that the method detection limits (MDL) for each method described be calculated according to the formula derived by Glaser et al. (4). This formula, which can be found in the Glossary (Appendix A), uses the standard deviation of repeated measurements of a solution containing the analyte at a concentration near the expected MDL, rather than repeated analyses of a blank sample. The formula was first used to calculate the MDLs in 1985. The publication of this manual in March 1986 provided documented standard operating procedures (SOP) for the analytical methods in use at the CAL. With the addition of this and previously published quality assurance reports detailing the QA procedures in the laboratory, SOPs for the entire laboratory operation are now available.

2. Anion Analysis by Ion Chromatography

Until May 1985, the concentrations of sulfate, nitrate, and chloride in the network samples were measured by using automated wet chemical techniques. Before requesting approval from the NADP Technical Committee for the change to analysis of these three anions by ion chromatography (IC), the CAL undertook a methods comparison study to confirm the belief that the two methods produced comparable results. A detailed account of this methods comparison was prepared by Bachman (5) and the information presented to NADP Subcommittee 2 in November 1984.

The Subcommittee found that the differences between the data from the two methods was minimal and unimportant and recommended that the full Technical Committee approve the change as requested by the CAL. Approval by the full Technical Committee for the change in methods was also given in November 1984.

As part of the comparison, 200 randomly selected precipitation samples were analyzed by both methods and the resulting analytical values compared. The plots in Figures II-1, II-2, and II-3 present the concentration ranges for sulfate, nitrate, and chloride, respectively. These plots also indicate how well the two methods compared at the different concentrations. Additionally, ten randomly selected precipitation samples were spiked with specified amounts of solutions containing known concentrations of the three anions. These spiked samples were analyzed and the percent recovery of the spiking solution calculated. Figure II-4 is a bar graph of the results from this comparison. The solutions used to spike the precipitation samples were labeled A for a solution containing low levels of the three analytes and B for one containing high levels. Results from the analysis by automated wet chemical methods are shown by the bars shaded with dots, and those resulting from analysis by IC are shown by the bars with the diagonal lines.

The plots in Figures II-1 through II-4 indicate that the data produced by the two methods for the analysis of both spiked and natural precipitation samples were comparable. Analysis using a paired t-test indicated a neglible, but statistically significant, difference at the 95% confidence interval between the data produced by the two methods. The median concentration differences for all three anions were 0.05 mg/L or less.
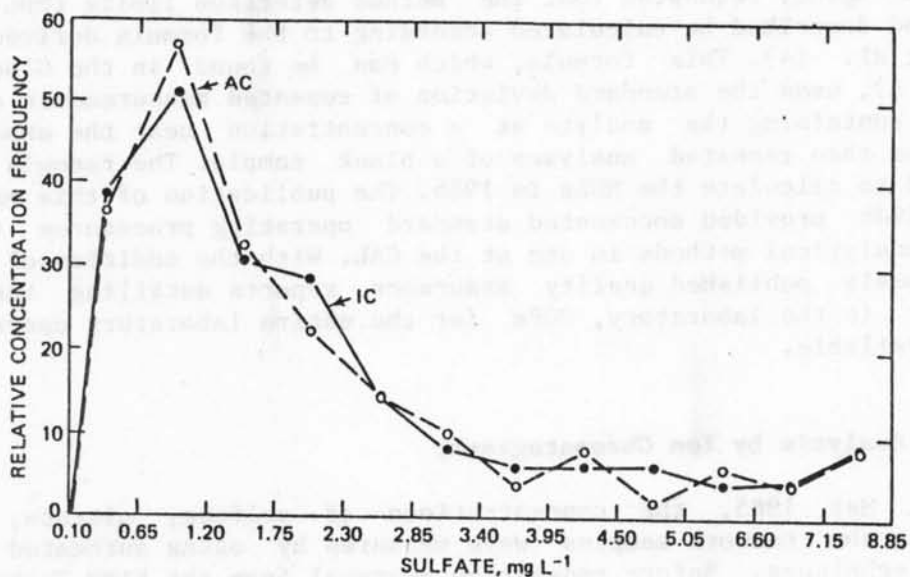
FIGURE II-1. Comparison of the data from the analysis of the same precipitation sample by automated wet chemical methods (AC) and ion chromatograpy (IC) for sulfate.
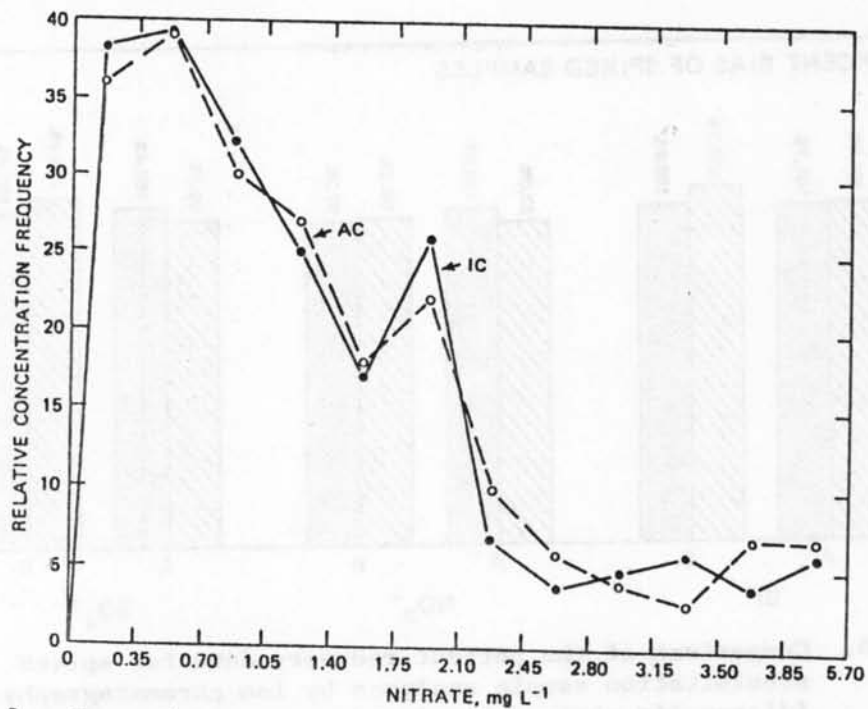
FIGURE II-2. Comparison of the data from the analysis of the same precipitation sample by automated wet chemical methods (AC) and ion chromatograpy (IC) for nitrate.
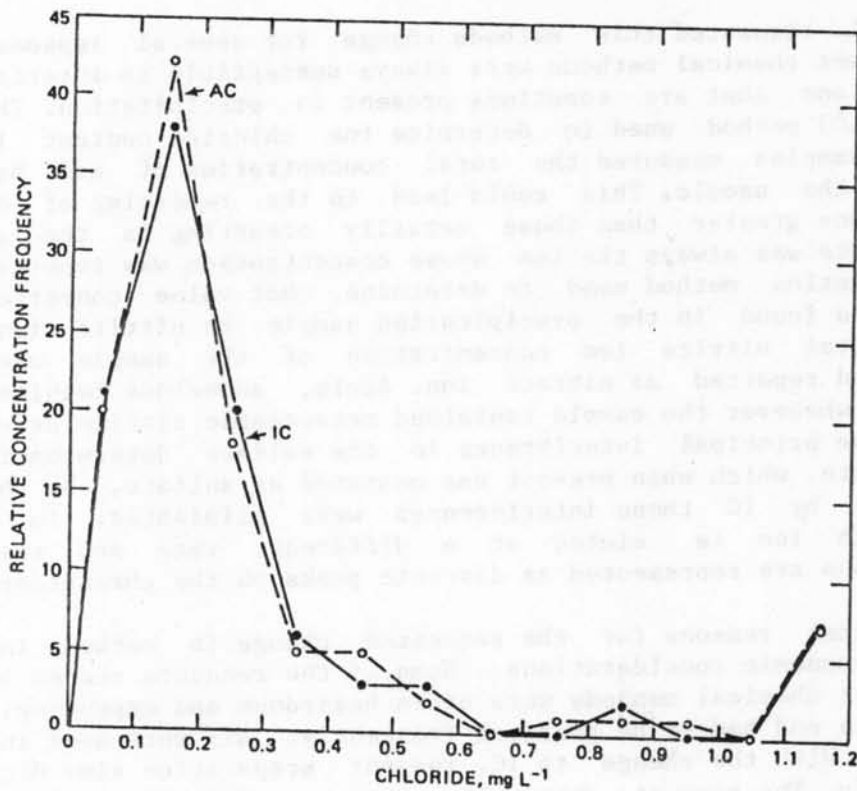
FIGURE II-3. Comparison of the data from the analysis of the same precipitation sample by automated wet chemical methods (AC) and ion chromatography (IC) for chloride.
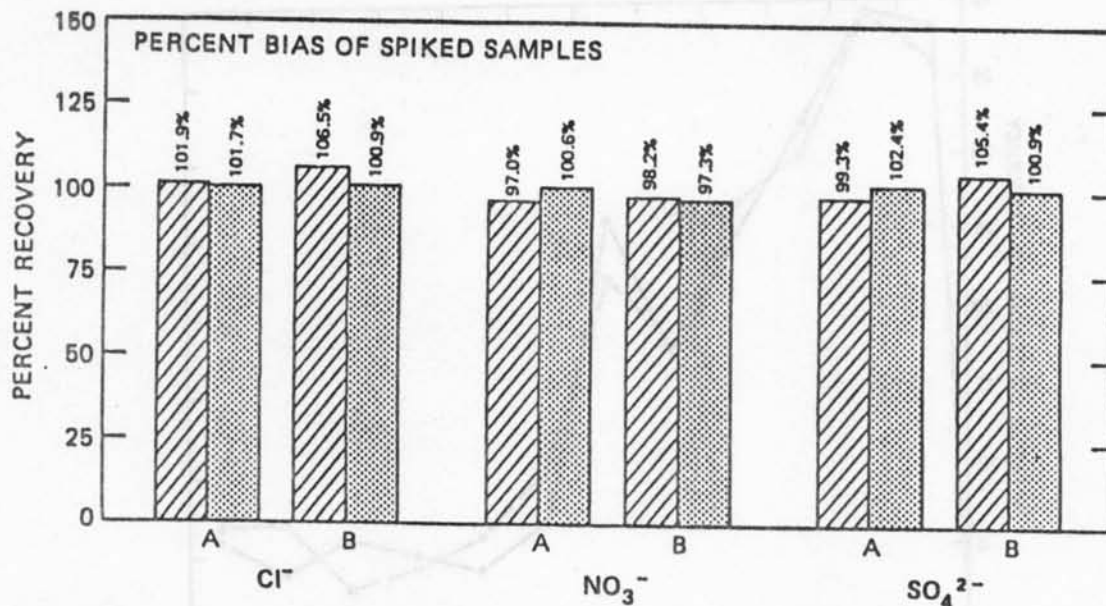
FIGURE II-4. Comparison of the percent recovery data for spiked precipitation sample analyses by ion chromatography (diagonally striped bars) and automated wet chemical methods (dotted bars). Spiking solutions approximated the 25th (A) and 75th (B) percentile concentration levels of each analyte.

The CAL requested this methods change for several reasons. The automated wet chemical methods were always susceptible to interferences from other ions that are sometimes present in precipitation. The wet chemical (AC) method used to determine the chloride content in precipitation samples measured the total concentration of all halogens present in the sample. This could lead to the reporting of chloride concentrations greater than those actually occurring in the sample. While nitrate was always the ion whose concentration was reported, the cadmium reduction method used to determine that value converted all nitrate ions found in the precipitation sample to nitrite ions. The resulting total nitrite ion concentration of the sample was then measured and reported as nitrate ion. Again, anomalous results would be reported whenever the sample contained measureable nitrite as well as nitrate. The principal interference in the sulfate determination was orthophosphate, which when present was measured as sulfate. By changing to analysis by IC these interferences were eliminated. In the IC method, each ion is eluted at a different rate and the ion concentrations are represented as discrete peaks on the chromatogram.

The other reasons for the requested change in methods included safety and economic considerations. Some of the reagents needed for the automated wet chemical methods were often hazardous and expensive. Some were unstable and had to be prepared frequently. All were used in large quantities. With the change to IC, reagent preparation time decreased significantly. The reagent chemicals needed are inexpensive and safe, and the quantities needed are smaller than those required by the wet chemical methods. These factors coupled with the increased sensitivity of the method made the change to analysis by IC very desirable and prompted the request.

The different instrumentation also resulted in different method detection limits (MDL). These increased slightly for the nitrate and chloride analyses, and decreased significantly for sulfate. Table II-1 lists the MDLs for 1984 and 1985 for all of the analytes routinely measured in precipitation samples. These new MDLs also reflect the new method of MDL calculation based on the formula used by Glaser et al. (4). The values listed in Table II-1 show that this new method for determining the MDL resulted in the same MDLs for all analytes in 1985 as in 1984. The differences seen in the MDLs for sulfate, nitrate, and chloride were due to the difference in instrument sensitivity. Finally, Figure II-5 is a sample processing flowchart for January 1981 through April 1985. With the change to analysis by IC in May, the flowchart became that depicted in Figure II-6.

TABLE II-1 Method Detection Limits for the Analysis of Precipitation Samples for 1984 and 1985.

Analyte	Method[a]	Method Detection Limit (MDL) (mg/L)	Dates
Calcium	Flame Atomic Absorption	0.009	1/84 – 12/85
Magnesium	Flame Atomic Absorption	0.003	1/84 – 12/85
Sodium	Flame Atomic Absorption	0.003	1/84 – 12/85
Potassium	Flame Atomic Absorption	0.003	1/84 – 12/85
Ammonium	Automated Phenate, Colorimetric	0.02	1/84 – 12/85
Sulfate	Automated Methyl Thymol Blue, Colorimetric	0.10	1/84 – 5/85
	Ion Chromatography	0.03	5/85 – 12/85
Nitrate-Nitrite	Automated Cadmium Reduction, Colorimetric	0.02	1/84 – 5/85
Nitrate	Ion Chromatography	0.03	5/85 – 12/85
Chloride	Automated Ferricyanide, Colorimetric	0.02	1/84 – 5/85
	Ion Chromatography	0.03	5/85 – 12/85
Ortho-phosphate	Automated Ascorbic Acid, Colorimetric	0.003	1/84 – 12/85

a. For a complete method description, see Development of Standard Methods for the Collection and Analysis of Precipitation (3).

DRY SIDE

WET SIDE

LOG IN
ASSIGN LAB NUMBER
VISUALLY INSPECT

DRY SIDE

WET SIDE

DRY

WET

DRY

WET

ADD 250 mL DI H$_2$O
ALLOW 24 HOURS
TO EQUILIBRATE

WEIGH

ADD 50 mL DI H$_2$O
ALLOW 24 HOURS
TO EQUILIBRATE

WEIGH

pH AND SPECIFIC CONDUCTANCE

FILTER WITH 0.45 um MILLIPORE TYPE HA

FILTRATE

WET, ≤35 mL

WET >35 mL, DRY
BUCKET DILUTIONS

60 mL STORED
AT 4°C

DILUTE WITH
50 mL DI H$_2$O

ANALYSIS

FLAME ATOMIC
ABSORPTION
Ca^{++}, Mg^{++}, Na^{+}, K^{+}

AUTOMATED WET
CHEMISTRY
SO$_4^=$, NO$_3^-$, Cl$^-$, PO$_4^\equiv$, NH$_4^+$

FIGURE II-5. Sample processing flowchart for January 1981 through April 1985.

DRY SIDE

WET SIDE

LOG IN
ASSIGN LAB NUMBER
VISUALLY INSPECT

DRY SIDE

WET SIDE

DRY

WET

DRY

WET

ADD 250 mL DI H_2O
ALLOW 24 HOURS
TO EQUILIBRATE

WEIGH

ADD 50 mL DI H_2O
ALLOW 24 HOURS
TO EQUILIBRATE

WEIGH

pH AND SPECIFIC CONDUCTANCE

FILTER WITH 0.45 um MILLIPORE TYPE HA

FILTRATE

WET, $\leq$35 mL

WET >35 mL, DRY
BUCKET DILUTIONS

60 mL STORED
AT $4^{o}C$

DILUTE WITH
50 mL DI H_2O

ANALYSIS

FLAME ATOMIC
ABSORPTION
Ca^{++}, Mg^{++}, Na^+, K^+

ION CHROMATOGRAPHY
$SO_4^=$, NO_3^-, Cl^-

AUTOMATED WET
CHEMISTRY
NH_4^+, $PO_4^{\equiv}$

FIGURE II-6. Sample processing flowchart for May 1985 through December 1985.

3. New Facilities

The move to newly renovated facilities in November 1985 provided larger laboratories, a designated area for storage of supplies, and walk-in coolers for sample storage. The laboratory space not only increased, but also improved. Each analyst was consulted as to the design of his/her laboratory, and their suggestions were used to create large work areas that provided easy access to the instrumentation for servicing.

Laminar flow clean air workstations were installed for use in sample processing and preparation to eliminate the possible introduction of airborne contaminants into the samples. Introduction of external sources of contaminant gases and particulates was further eliminated by the positive pressure environment maintained in each laboratory and an extensive laboratory air filtration system. Disposable tacky floor mats were placed at the entrance of each laboratory to help reduce particulate loading. Two large walk-in coolers provide ample space for refrigerated storage of archival samples as well as site and laboratory supplies such as pH buffers and standard solutions.

A new reverse osmosis (RO) deionizing water system, capable of producing 500 L of deionized water with a specific conductance of <1 uS/cm, daily was installed. Wall-mounted Barnstead Nanopure systems located in each laboratory continued to be used in conjunction with point of use 0.2 um filters. Finally, the laboratory and office areas were separated for most analysts.

B. DATA AVAILABILITY

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

C. LABORATORY PERSONNEL

All of the analysts who were on the CAL staff in December 1983 remained during 1984 and 1985. Additional personnel were hired to accommodate the increasing shipping and receiving demands created by the network expansion. The only job reassignments were the result of the change in methods that occurred in 1985. The staff continued their educational development by attending manufacturers' training courses and workshops whenever possible. Table II-2 alphabetically lists the laboratory personnel who participated in the project during 1984 and 1985. It also includes a brief description of each staff member's primary function within the program and shows the duration of his/her employment as part of the CAL.

TABLE II-2 Central Analytical Laboratory (CAL)
Personnel Summary (1984-1985) -
Analytical Staff Only.

Staff Member/ Job Function (month, year)[a]	Period of Service	
	1984	1985
	JFMAMJJASOND	JFMAMJJASOND
Beth Allhands Sample Receipt and Processing (Februaury, 1984)	————	————
Sue Bachman Ion Chromatography (August, 1980)	————	————
Brigita Demir NH_4, NO_3, Cl SO_4, NO_3, Cl (September, 1981)	————	—— ————
Pat Dodson Sample Processing (September, 1980)	————	————
Clarence Dunbar Sample Receipt and Processing (July, 1981)	————	————
Theresa Eckstein Sample Receipt (March, 1985)		————
Jacqueline Lockard Quality Assurance (October, 1982)	————	————
Mark Peden Laboratory Manager (July, 1978)	————	————
Jackie Sauer Sample Processing, pH, Specific Conductance (September, 1983)	————	————
Loretta Skowron Ca, Mg, Na, K (July, 1978)	————	————
Mike Slater SO_4, PO_4 NH_4, PO_4 (September, 1979)	————	—— ————

a. Date started with the CAL

III. LABORATORY BLANK DATA

The data presented in this section were generated from analyses of the deionized (DI) water used by the laboratory, DI water left in a clean sample collection bucket for 24 hours, and DI water that had been filtered through a preleached 0.45 um Millipore (HAWP) filter. All the data obtained were used to define the potential contributions of the collection vessel and the sample processing procedures to the measured analyte concentrations in precipitation. The procedures used to obtain each blank sample type are described in the NADP/NTN Quality Assurance Report for 1978-1983 (1). The resultant analytical data are presented as graphs or in tables.

A. BUCKET LEACHATES

Since May 1982, the high density polyethylene sampling buckets used in the program have been cleaned in a commercial dishwasher. The wash cycle originally used city tap water with three deionized water rinses. In November 1984 the system was changed to use only deionized water for all cycles, both wash and rinse. To determine the contribution the container might make to the analyte concentrations, clean buckets and lids were randomly selected and used to establish container blanks. Either a 50 mL, 150 mL, or 500 mL portion of deionized water was poured into the test bucket, the lid was pounded on, and the water was left to equilibrate in the bucket. Three test buckets, each containing a different volume of DI, were inverted during this period of equilibration, and another three were allowed to remain in an upright position. After 24 hours, these bucket leachates were poured into DI water-washed 60 mL polyethylene (LPE) bottles and the concentration of analytes was determined. Figures 1 through 20 in Appendix B are plots of the analyte masses measured in these bucket blanks for 1984 and 1985.

For all volumes of all types of bucket blanks, the measured orthophosphate concentrations were at or below the method detection limit; therefore, plots of orthophosphate masses are not included. The concentrations of the measured analytes have been converted to micrograms per bucket in order to place the data for all three volumes on the same plot. Mass per bucket is calculated by multiplying the analyte concentration in units of micrograms per milliliter by the sample volume in milliliters. A legend defining the symbols being used is presented with each series of analyte plots. The dashed line near the bottom of each plot represents the minimum detectable mass for that analyte. This minimum value was determined by multiplying the MDL, expressed as micrograms per milliliter, by 50 mLs. For all three volumes, values measured as less than the method detection limit were plotted on this line. Table 1 in Appendix B lists the MDL mass for all of the parameters for which there are bucket blank plots.

Table III-1 presents annual median masses again expressed as micrograms per bucket, for both inverted and upright bucket blanks analyzed in 1984 and 1985. The data document high concentrations of analytes for 1984 and very small concentrations of analytes for 1985.

The source of these differences in concentrations was traced to a clogged spray arm in the dishwasher. The city tap water used in the wash cycle, which contains high levels of calcium, magnesium, and sodium, was not being completely removed by the three DI water rinses. To correct the situation and prevent it from recurring, the entire wash cycle was converted in November 1984 to utilize deionized water only. The median values for 1985 indicate that the problem was corrected and the bucket leachates now contain very limited amounts of all of the analytes of interest.

TABLE III-1 Median Analyte Concentrations Expressed as Mass (ug)/Bucket Found in Upright and Inverted Bucket Blanks in 1984 and 1985.

Analyte	Upright		Inverted	
	1984	1985	1984	1985
Calcium	7.10	0.58	16.83	1.95
Magnesium	4.62	0.30	9.17	1.38
Sodium	9.58	0.47	20.57	1.45
Potassium	1.68	0.18	3.20	0.43
Ammonium	1.4	<1.0	1.3	<1.0
Sulfate	8.9	<1.5	24.2	3.2
Nitrate-Nitrite	<1.0	<1.5	1.5	<1.5
Chloride	4.3	<1.5	14.6	1.8
Ortho-phosphate	<0.15	<0.15	<0.15	<0.15
pH (units)	5.97	5.59	6.24	5.75
Specific Conductance (uS/cm)	2.2	1.4	3.6	1.6

In 1984, a decision was made to add the measurements of pH and specific conductance for these bucket leachates to the analysis for the other analytes. Figures 9 and 19 in Appendix B show that the pH of these samples is typically greater than pH 5.5. The expected pH for DI water in equilibrium with atmospheric CO_2 would be approximately pH 5.7. The deviation from that theoretical value is not very large and is accounted for by the presence of ions other than CO_2 in the samples. The larger the concentration of other ions, the greater the variability in the measured pH. This is clearly evident in the two plots for pH. Figures 10 and 20 in Appendix B are plots of the measured specific conductance values. The expected specific conductance would be between 1 and 2 uS/cm. For the majority of the blanks, this is the case; however, these data follow the same patterns as do the data for

pH. Again, the presence of other ions in the precipitation results in specific conductance values higher than anticipated. As with the pH measurements, the higher the concentration of ions, the more variability seen in the specific conductance measurements.

Concern about the collection bucket lid gasket as a potential source of contaminants continued and prompted two special studies to investigate the problem. In the first of these studies, the leaching effect of an acidic solution on the sample container was tested. Two dilute nitric acid solutions were substituted for the DI water that was routinely used for bucket leachate tests. One of the solutions had a pH of 4.30, and the other had a pH of 4.60. The standard three sample volumes were used and the acidic solutions were allowed to equilibrate in both inverted and upright clean buckets for the usual period of 24 hours. Table III-2 gives the median analyte concentrations expressed as micrograms/bucket for these acid blanks. The calculated nitrate is 160 ug for the pH 4.30 sample and 80 ug for the pH 4.60 sample. This leachate test was performed at two different times. The test using the pH 4.60 nitric acid solution took place in late 1983. During the testing period the dishwasher problems previously discussed had already begun. Elevated levels of analytes, particularly cations, that are evident in Table III-2 were most likely due to this problem. The test using the pH 4.30 solution was performed in 1985 when routine blanks indicated that the buckets were analyte free. Keeping the testing periods in mind, the analyte concentrations for these acid bucket leachates are similar to the concentrations found in the routine bucket blanks from the same period (Table III-1).

The second study compared the data obtained from the analysis of blanks that utilized either DI water or a pH 4.30 QCS nitric acid as the leaching solutions. Again three sample volumes were used and some buckets were inverted while others remained upright. The variable being examined in this study was prolonged exposure of the bucket to the acid or the DI water. It was determined that the maximum time of travel for samples from network sites to the CAL was one week. The samples collected for this experiment remained in the buckets for one week to simulate this maximum time of contact with the container surface. All samples and buckets used for this test were prepared and analyzed in 1985. Table III-3 presents the results of this experiment. These data indicate that prolonged exposure to the bucket surface (and particularly contact with the lid gasket that occurs when the bucket is inverted) may result in increased analyte concentrations in the sample. The upright blanks, however, show that the actual risk of sample contamination from the collection container, even when there is prolonged exposure to the bucket surface, does not increase significantly with increased sample acidity.

TABLE III-2 Median Analyte Concentrations Expressed as Mass (ug)/Bucket Found in Upright and Inverted Bucket Blanks Using Dilute Nitric Acid as the Leaching Solution - One Day Equilibration.

Analyte	Upright		Inverted	
	4.30	4.60	4.30	4.60
Calcium	0.65	3.85	1.95	8.90
Magnesium	1.45	2.10	2.90	4.20
Sodium	6.50	8.00	6.05	16.90
Potassium	<0.15	6.60	1.50	17.83
Ammonium	<1.0	<1.0	<1.0	<1.0
Sulfate	<1.5	<5.0	5.5	<5.0
Nitrate-Nitrite	161.0	80.0	162.0	80.0
Chloride	<1.5	9.0	<1.5	22.5
Ortho-phosphate	<0.5	<0.15	<0.5	<0.15
pH (units)	4.35	4.79	4.41	4.89
Specific Conductance (uS/cm)	20.0	9.1	18.9	7.1

TABLE III-3 Median Analyte Concentrations Expressed as Mass (ug) /Bucket Found in Upright and Inverted Bucket Blanks Using Dilute Nitric Acid and Deionized Water as the Leaching Solutions - One Week Equilibration.

Analyte	Upright		Inverted	
	DI	4.30	DI	4.30
Calcium	<0.45	<0.45	5.50	1.75
Magnesium	<0.15	0.90	5.01	1.40
Sodium	0.45	1.50	0.80	1.35
Potassium	<0.15	<0.15	<0.15	<0.15
Ammonium	<1.0	<1.0	<1.0	<1.0
Sulfate	7.5	<1.5	10.5	<1.5
Nitrate-Nitrite	<1.5	161.0	<1.5	160.5
Chloride	<1.5	<1.5	<1.5	<1.5
Ortho-phosphate	<0.5	<0.5	<0.5	<0.5
pH (units)	5.56	4.35	6.20	4.38
Specific Conductance (uS/cm)	1.6	20.3	1.8	18.5

B. FILTER LEACHATES

Two filter leachates were collected each week during 1984 and 1985. All filters are leached before use with a 250 mL aliquot of DI water. After this leaching procedure, a 50 mL portion of DI is poured through the same filter and this time the leachate collected for analysis. This is filter leachate A. A second 50 mL portion of DI is then poured through this same filter and the leachate again collected for analysis. This second sample is leachate B. Table III-4 provides the median concentrations of the analytes found in these leachates for 1984 and 1985. More complete annual summaries of the analyses of these filter leachates can be found in Tables 2 through 6 in Appendix B. The data presented in these tables show the filters to be a negligible source of contamination. If elevated levels of analytes occur in these blank samples, it is usually in those analytes associated with human activities, namely sodium and chloride. The data do not show these increased analyte concentrations to be a constant problem, but they do appear in some degree in 50% of the A type filter leachates. The data also show that these problems disappear in the B leachates. As a result of this observation, in 1986 the CAL increased the initial leaching volume from 250 to 300 mL to further reduce the occurrence of this type of contamination. The routine weekly monitoring of these leachates continues as an integral part of the CAL quality assurance program.

TABLE III-4 Median Analyte Concentration Found in Filter Leachates A and B for 1984 and 1985.

| Analyte | Median Concentration (mg/L) | | | |
| | Leachate A | | Leachate B | |
	1984	1985	1984	1985
Calcium	<0.009	<0.009	<0.009	<0.009
Magnesium	<0.003	<0.003	<0.003	<0.003
Sodium	0.004	0.010	<0.003	<0.003
Potassium	<0.003	<0.003	<0.003	<0.003
Ammonium	<0.02	<0.02	<0.02	<0.02
Sulfate	<0.10	<0.10 <0.03	<0.10	<0.10 <0.03
Nitrate-Nitrite	<0.02	<0.02 <0.03	<0.02	<0.02 <0.03
Chloride	<0.02	<0.02 <0.03	<0.02	<0.02 <0.03
Orthophosphate	<0.003	<0.003	<0.003	<0.003
n^a	50	47	50	47

a. number of analyses

C. DEIONIZED WATER

The final routine quality control check was on the quality of the deionized water used throughout the laboratory. Although the purity of the water was monitored by daily checks of specific conductance through use of an in-line conductivity meter, the complete analysis of DI water samples was begun in 1980 and continues to the present. During 1984 and 1985 weekly samples were routinely taken from both the sample processing laboratory and the atomic absorption laboratory for complete analysis. A description of the deionizing systems in use at the laboratory during 1984 and 1985 can be found in the QA Report for 1978-1983 (1) and in the discussion of the new laboratory facilities in Section II of this report.

Table III-5 lists the median analyte concentrations found in the deionized water used by the CAL in 1984 and 1985. Tables 7 through 11 in Appendix B contain more complete annual summaries of the data obtained from the analyses of this DI water. As with the filters, the laboratory deionized water has proven to be a negligible source of contamination. Analysis of deionized water used in the sample processing laboratory as well as of a DI water sample taken from one of the analytical labs at the CAL continues as part of the routine quality assessment program.

TABLE III-5 Median Analyte Concentration Values
for Deionized Water Blank for 1984-1985.

| | Median Concentration Value (mg/L) | | | |
| | Room 61[a] | | Room 129[a] | |
Analyte	1984	1985	1984	1985
Calcium	<0.009	<0.009	<0.009	<0.009
Magnesium	<0.003	<0.003	<0.003	<0.003
Sodium	<0.003	<0.003	<0.003	<0.003
Potassium	<0.003	<0.003	<0.003	<0.003
Ammonium	<0.02	<0.02	<0.02	<0.02
Sulfate	<0.10	<0.10 <0.03	<0.10	<0.10 <0.03
Nitrate-Nitrite	<0.02	<0.02 <0.03	<0.02	<0.02 <0.03
Chloride	<0.02	<0.02 <0.03	<0.02	<0.02 <0.03
Orthophosphate	<0.003	<0.003	<0.003	<0.003
n[b]	49	41	29	37

a. sample processing laboratory is room 61, and atomic absorption spectroscopy laboratory is room 129
b. number of analyses

IV. LABORATORY BIAS AND PRECISION

An essential part of every quality assurance program is the deter-mination of the accuracy of the measurements being made by the labora-tory. For the years 1984 and 1985, the CAL used data obtained from replicate analyses of Quality Control Check Samples (QCS) as one means of assessing analytical bias and precision. These QCS were either internally formulated solutions or dilutions of mineral and nutrient concentrates provided by the United States Environmental Protection Agency, EMSL-Cincinnati, Ohio. Additional information regarding laboratory precision was obtained through the analysis of replicate samples, i.e., the analysis of two aliquots of the same sample. The third means employed by the CAL for data assessment was the use of samples with known analyte concentrations that were submitted as blinds to the analysts. This section contains descriptions of the samples used by the CAL to assess laboratory performance. Summary tables and plots of the analyses of these samples are provided in this report accompanied by a discussion of what the data indicate about the performance of the Central Analytical Laboratory.

A. QUALITY CONTROL CHECK SAMPLE DATA

As was the case during the previous six-year period, the QCS used by the laboratory were internally formulated samples to monitor the pH and specific conductance measurements, and dilutions of the USEPA mineral and nutrient concentrates to monitor the remaining parameters. The laboratory diluted the EPA sample concentrates so the resulting concentration for the analyte being monitored fell near the 25th and 75th percentiles for the NADP/NTN network samples. The percentile concentration values for all the routinely analyzed precipitation parameters for the years 1984 and 1985 are given in Table IV-1 and Table IV-2.

A minimum volume of 35 mL of sample is necessary for a complete analysis of all eleven precipitation parameters. Samples containing less than 35 mL are diluted as indicated in Figures II-1 and II-2. Because of this processing procedure, only samples which were greater than 35 mL in volume have been included in the preparation of the percentile concentration tables.

During 1984 and 1985 the network continued to expand primarily westward. By the end of 1985 there were nearly 200 sites in operation throughout the country, including ones in Alaska, Hawaii, and Puerto Rico. An examination of the percentile concentration values indicates that differences in the ionic concentrations during this period occurred only for the major cations. The concentrations measured in 1984 are greater than those found in 1985. Some of these differences may have been the result of the bucket washing problem that occurred in 1984. This problem was explained in more detail in Section III of this report. The elimination of the problem is most obvious in the bucket blank plots for 1985 that are found in Appendix B.

TABLE IV-1 Percentile Concentration Values of Chemical and
Physical Parameters Measured in Precipitation — 1984.

Percentile Concentration Values (mg/L)

Parameter	Min.	5th	10th	25th	50th	75th	90th	95th	99th	Max.
Ca	<0.009	0.030	0.050	0.080	0.170	0.380	0.760	1.20	2.82	22.8
Mg	<0.003	0.013	0.016	0.026	0.047	0.094	0.201	0.296	0.603	2.3
K	<0.003	0.008	0.010	0.017	0.030	0.061	0.125	0.186	0.447	5.8
Na	<0.003	0.027	0.035	0.059	0.118	0.269	0.625	1.05	3.14	10.8
NH_4	<0.02	<0.02	<0.02	0.08	0.19	0.40	0.69	0.95	1.62	3.5
NO_3	<0.02	0.15	0.27	0.58	1.13	1.99	3.13	4.11	6.70	27.4
Cl	<0.02	0.06	0.08	0.11	0.19	0.39	0.93	1.63	6.13	37.8
SO_4	<0.10	0.39	0.50	0.83	1.49	2.65	4.27	5.68	9.51	45.7
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.006	0.009	0.013	12.6
pH (units)	2.98	4.01	4.15	4.38	4.80	5.46	6.08	6.34	6.80	7.85
Specific Conductance (uS/cm)	1.6	3.7	5.0	8.5	15.2	26.9	42.4	54.2	91.2	566.8

Source: National Atmospheric Deposition Program (NADP)
1984 - wet side samples
Number of samples = 5450

TABLE IV-2 Percentile Concentration Values of Chemical and
Physical Parameters Measured in Precipitation — 1985.

Percentile Concentration Values (mg/L)

Parameter	Min.	5th	10th	25th	50th	75th	90th	95th	99th	Max.
Ca	<0.009	0.030	0.040	0.060	0.140	0.290	0.610	0.930	2.09	14.9
Mg	<0.003	0.010	0.014	0.021	0.037	0.071	0.135	0.200	0.416	1.4
K	<0.003	0.004	0.006	0.012	0.025	0.049	0.100	0.153	0.383	2.9
Na	<0.003	0.015	0.020	0.036	0.075	0.185	0.480	0.881	2.59	10.80
NH_4	<0.02	<0.02	<0.02	<0.02	0.16	0.37	0.65	0.92	1.79	7.4
NO_3	<0.03	<0.03	0.12	0.48	1.05	1.84	3.05	4.09	7.23	25.4
Cl	<0.03	<0.03	0.05	0.09	0.17	0.36	0.86	1.53	4.70	20.9
SO_4	<0.10	0.24	0.35	0.71	1.41	2.55	4.01	5.32	8.73	30.5
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.009	0.012	0.028	2.2
pH (units)	3.38	4.03	4.14	4.37	4.76	5.30	5.89	6.25	6.73	7.7
Specific Conductance (uS/cm)	1.6	3.6	4.9	8.1	15.0	26.6	41.1	52.8	87.6	262.2

Source: National Atmospheric Deposition Program (NADP)
1985 - wet side samples
Number of samples = 6089

As the network expanded, the number of precipitation samples being collected and analyzed increased. This resulted in an increase in the number of analyses of quality control samples as well. The program grew in terms of the quantity of quality assessment data being produced but did not change in the types of samples being analyzed to produce these data. The following subsections describe the quality control solutions used by the laboratory, present summary tables of the data that resulted from their analysis, and provide an explanation of what these data imply about the performance of the CAL.

1. Solutions Used

Since 1981, a dilute nitric acid solution (5.01×10^{-5} N HNO_3) prepared by the CAL has been used to monitor pH and specific conductance measurements. The solution preparation is verified by measuring the pH and specific conductance and by analysis colorimetrically or chromatographically for NO_3 and titrimetrically for acidity. The information obtained from these determinations is used to derive the calculated pH and specific conductance values. The solution must have a calculated pH of 4.30 ± 0.03 and a calculated specific conductance of 21.8 ± 2 uS/cm to be considered suitable for use in both the laboratory and the field.

Also since 1981, a dilute potassium chloride solution (5.0×10^{-4} N KCl) formulated and prepared at the CAL has been used both to calibrate the conductivity bridge and cell and to monitor pH measurements at a second concentration level. The accuracy of this preparation is determined by measurement of pH and specific conductance, colorimetric or chromatographic determination of the chloride concentration, and analysis of the potassium concentration by flame atomic absorption spectroscopy. These analytical data are used to calculate the pH and specific conductance of the preparation. Although this is a stable solution, its calculated pH of 5.63 falls within the range of pH at which the effects of atmospheric carbon dioxide fluctuations can be significant. For that reason the range of acceptable readings for pH is 5.63 ± 0.3 pH units. The acceptable range for the calculated specific conductance is 74.8 ± 2 uS/cm.

The bias and precision of the remaining analytical parameters were monitored by performing replicate analyses of dilute QCS solutions prepared from USEPA mineral and nutrient concentrates. The mineral sample was used to prepare QCS solutions for calcium, magnesium, sodium, potassium, sulfate, and chloride. The QCS solutions for nitrate-nitrite, ammonium, and orthophosphate were made by diluting the USEPA nutrient concentrates. Two QCS solutions were prepared for each analyte. One solution approximated the 25th percentile concentration found for the specified analyte, and the other approximated the 75th.

2. Analytical Bias and Precision Tables

The formulas used to calculate the bias and precision data can be found in the Glossary (Appendix A). All data presented for the measurement of pH required the conversion of the measurements from pH units to hydrogen ion content as microequivalents per liter before these

formulas could be employed. Table IV-3 lists several pH values and their corresponding hydrogen ion content. The summaries of pH data present the mean and standard deviation values in both pH units and microequivalents per liter. The percent bias and percent relative standard deviation (RSD) values are calculated by using the hydrogen ion concentration only.

TABLE IV-3 Selected pH Values and the Corresponding Hydrogen Ion Content Expressed as Microequivalents per Liter.

pH (units)	Hydrogen Ion (ueq/L)
3.50	316.2
4.00	100.0
4.30	50.1
4.50	31.6
4.70	20.0
5.00	10.0
5.30	5.0
5.50	3.2
5.70	2.0

Tables IV-4 and IV-5 were prepared from the data obtained from replicate analysis of QCS solutions. For all parameters except pH and specific conductance, at least one QCS was analyzed with each group of twelve precipitation samples. For pH and specific conductance measurements, the frequency was approximately one QCS measured for every twenty precipitation samples. The annual summaries of bias and precision for each parameter were produced by using the results obtained from the statistical analysis of these QCS data. These tables provide one means of assessing the quality of the analytical data produced at the CAL by presenting summaries of the analyses of solutions whose analyte concentrations were known to each analyst.

As mentioned before, the primary source of the QCS being analyzed was the USEPA. With each of the mineral and nutrient concentrates that it supplies, the USEPA provides directions for sample preparation plus a data sheet which lists an expected analyte concentration, a mean analyte concentration with a standard deviation, and a confidence interval for the analyte concentrations that should result after dilution. These mean and standard deviation values were obtained from statistical analysis of the data received from USEPA-sponsored interlaboratory performance studies (6). Summaries of the data obtained from these performance

TABLE IV-4 Analytical Bias and Precision for
1984 - Determined from Analysis of
Quality Control Check Samples.

Parameter	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias		Precision			Statistically
				mg/L	%	s mg/L	RSD %	Critical %	Significant Bias?[b]
Calcium	0.053	0.050	473	-0.003	-5.7	0.003	6.0	2.2	YES
	0.067	0.065	37	-0.002	-3.0	0.002	3.1	2.7	YES
	0.317	0.322	36	0.005	1.6	0.003	0.9	1.4	YES
	0.402	0.414	478	0.012	3.0	0.004	1.0	1.5	YES
Magnesium	0.018	0.017	474	-0.001	-5.6	0.001	5.9	3.1	YES
	0.024	0.024	37	0.000	0.0	0.001	4.2	3.8	NO
	0.070	0.070	36	0.000	0.0	0.001	1.4	2.5	NO
.	0.083	0.084	473	0.001	1.2	0.001	1.2	2.0	NO
Sodium	0.071	0.071	32	0.000	0.0	0.001	1.4	1.7	NO
	0.083	0.084	467	0.001	1.2	0.002	2.4	1.7	NO
	0.395	0.403	32	0.008	2.0	0.003	0.7	1.3	YES
	0.459	0.477	468	0.018	3.9	0.004	0.8	1.3	YES
Potassium	0.017	0.017	32	0.000	0.0	0.001	5.9	3.9	NO
	0.021	0.020	466	-0.001	-4.8	0.001	5.0	2.7	YES
	0.074	0.072	33	-0.002	-2.7	0.001	1.4	2.3	YES
	0.100	0.094	465	-0.006	-6.0	0.002	2.1	2.2	YES
Ammonium	0.36	0.37	294	0.01	2.8	0.01	2.7	1.2	YES
	1.23	1.24	302	0.01	0.8	0.03	2.4	0.8	NO
Sulfate	0.92	0.91	475	-0.01	-1.1	0.08	8.8	1.6	NO
	6.86	7.30	476	0.44	6.4	0.30	4.1	4.4	YES
Nitrate	0.62	0.63	298	0.01	1.6	0.02	3.2	1.4	YES
	3.14	3.11	310	-0.03	1.0	0.07	2.3	1.3	NO
Chloride	0.86	0.87	292	0.01	1.2	0.02	2.3	0.9	YES
	1.80	1.85	291	0.05	2.8	0.03	1.6	1.4	YES
Ortho- phosphate	0.15	0.14	468	-0.01	-8.5	0.01	7.1	2.3	YES
	0.22	0.20	467	-0.02	-7.0	0.02	10.0	2.1	YES
pH units (ueq/L)	4.30 (50.1)	4.32 (48.0)	222	0.02 (-2.1)	-4.2	0.02 (2.4)	5.0	6.3	NO
	5.63 (2.3)	5.44 (3.5)	222	-0.19 (1.2)	52.2	0.05 (0.4)	11.4	88.4	NO
Specific Conductance (uS/cm)	21.8	21.0	222	-0.8	-3.7	0.6	2.9	6.3	NO

a. number of replicates
b. 95% confidence level

TABLE IV-5 Analytical Bias and Precision for
1985 - Determined from Analysis of
Quality Control Check Samples.

Parameter	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias mg/L	Bias %	Precision s mg/L	RSD %	Critical %	Statistically Significant Bias?[b]
Calcium	0.053	0.053	512	0.000	0.0	0.002	3.8	2.1	NO
	0.402	0.409	503	0.007	1.7	0.004	1.0	1.5	YES
Magnesium	0.018	0.018	537	0.000	0.0	0.001	5.6	3.1	NO
	0.083	0.083	538	0.000	0.0	0.001	1.2	2.0	NO
Sodium	0.083	0.083	485	0.000	0.0	0.001	1.2	1.7	NO
	0.459	0.475	507	0.016	3.5	0.004	0.8	1.3	YES
Potassium	0.021	0.022	489	0.002	4.8	0.002	9.1	2.8	YES
	0.100	0.094	485	-0.006	-6.0	0.002	2.1	2.2	YES
Ammonium	0.19	0.18	215	-0.01	-5.3	0.02	11.1	2.6	YES
	0.36	0.36	82	0.00	0.0	0.02	5.6	1.7	NO
	0.98	0.92	224	-0.06	-6.1	0.05	5.4	1.1	YES
	1.22	1.23	81	0.01	0.8	0.02	1.6	0.8	NO
Sulfate	0.69	0.72	340	0.03	4.4	0.03	4.2	4.4	NO
	0.92	0.92	655	0.00	0.0	0.04	4.4	1.4	NO
	3.43	3.69	122	0.26	7.6	0.11	3.0	4.4	YES
	6.86	7.13	172	0.27	3.9	0.11	1.5	4.4	NO
Nitrate	0.62	0.63	88	0.01	1.6	0.02	3.2	1.5	YES
	0.80	0.81	509	0.01	1.3	0.02	2.5	1.6	NO
	3.14	3.11	88	-0.03	1.0	0.07	2.3	1.4	NO
	3.54	3.63	438	0.09	2.5	0.13	3.6	0.8	YES
Chloride	0.18	0.18	132	0.00	0.0	0.02	11.1	2.4	NO
	0.86	0.87	584	0.01	1.2	0.03	3.5	0.9	YES
	1.80	1.87	360	0.07	3.9	0.04	2.1	1.4	YES
Ortho-phosphate	0.03	0.03	151	0.00	0.0	0.01	33.3	6.9	NO
	0.06	0.05	161	-0.01	-19.4	0.01	20.0	5.2	YES
	0.12	0.12	84	0.00	0.0	0.01	8.3	3.9	NO
	0.15	0.13	59	-0.02	-15.0	0.01	7.7	3.2	YES
	0.21	0.19	84	-0.02	-8.2	0.02	10.5	2.9	YES
	0.22	0.20	74	-0.02	-7.0	0.01	5.0	2.2	YES
pH units (ueq/L)	4.30 (50.1)	4.32 (47.3)	248	0.02 (-2.8)	-5.6	0.02 (3.2)	6.8	6.3	NO
	5.63 (2.3)	5.43 (3.7)	248	-0.20 (1.4)	60.9	0.06 (0.5)	13.5	88.4	NO
Specific Conductance (uS/cm)	21.8	21.5	248	-0.3	-1.4	0.6	2.8	6.3	NO

a. number of replicates
b. 95% confidence level

studies can be obtained from the USEPA, EMSL-Cincinnati, Ohio. In Tables IV-4 and IV-5, the USEPA mean is listed in the theoretical concentration column and is used to calculate the analytical bias values. The last column of the tables indicates whether the bias that has been calculated from the CAL data is or is not statistically significant. To determine this, a t-test was used to compare the mean values measured at the CAL to those provided by the USEPA on its data sheets. This comparison resulted in the critical percent value which is listed in Table IV-4 and Table IV-5. Whenever the calculated percent bias for a measured parameter was greater than or equal to the critical percent, that bias was considered to be statistically significant. The formula used for the calculation of the critical percent is listed in the Glossary (Appendix A).

3. Discussion of Results

A review of Tables IV-4 and IV-5 indicates few problems with analytical bias during 1984 and 1985. Although the results of the t-test show that the deviation of the CAL mean from the theoretical value (USEPA mean) was often statistically significant, the actual percent bias is <5% for 76% of the 29 measured parameters in 1984 and for 69% of the 32 measured parameters in 1985. For those parameters whose percent bias measures >5%, that greater percentage difference often represents a very small difference in the actual analyte concentration. This is particularly true when the analyte concentrations are very low, as are those that fall near the 25th percentile levels. As analyte concentrations decrease, the degree of difficulty in obtaining accurate dilutions increases. Increased variability of the analytical measurements (decreased precision) is also typically present for samples containing very small amounts of analyte.

The data presented in Table IV-4 for 1984 indicate that most of the measured parameters are statistically biased. A closer look at the actual concentrations show that the only areas where problems may really exist are with orthophosphate and pH measurements. The bias in the orthophosphate measurements is negative. This is most likely due to the instability of the orthophosphate ion. Both fresh dilutions of stock QCS and standards are prepared every three days to eliminate this problem. The data show that this procedure has been effective and that the percent bias and the percent relative standard deviation are <10%. The large bias in the pH 5.63 QCS is principally due to the allowable inaccuracy in the sample preparation. The deviation in pH units is within the desired limits (+ 0.03 pH units) for sample use. These limits were discussed earlier in this section. The bias and precision calculations, however, were performed by using the hydrogen ion concentration. The result is alarmingly large bias percentages and relative standard deviation. This pH (5.63) corresponds to only 2.3 ueq of hydrogen ion. Very small changes in the pH and the calculated hydrogen ion content will result in a very large percent bias.

In 1985, problems again occur in the orthophosphate and the pH measurements. The reasons for these deviations are the same as those to which the differences were attributed in 1984. In 1985 the concentration of the orthophosphate QCS was lowered to better simulate the analyte

the bias and precision. Finally, it should be noted that during both 1984 and 1985, the analytical bias and precision measurements for all analytes measured at the CAL were within the acceptable limits specified in the Quality Assurance Plan (2).

B. REPLICATE SAMPLE DATA

From the inception of the program, replicate samples were analyzed and the data used to evaluate laboratory precision. These splits were made in the sample processing section of the lab. Three filtered 60 mL aliquots were collected from 4% percent of the precipitation samples arriving at the CAL. The same laboratory sample number was given to each of the samples, with the first aliquot taken being designated A and the second, B. The third aliquot was refrigerated for storage in the sample archives. Samples A and B were subsequently placed side by side on a sample tray and submitted for analysis. Typically, the analysis of the B sample immediately followed analysis of the A sample. The fact that these were two aliquots of the same sample was known to all of the analysts.

In July 1984 a change was made in the replicate procedures. Four percent of the samples received by the CAL continued to be split into three 60 mL portions. Half of these splits were treated as described above and labeled with an NADP/NTN sample number followed by an A or a B. The other half were labeled and analyzed very differently. The first and third aliquots were labeled with the NADP/NTN sample number. The first aliquot was placed on the sample tray and sent to the laboratory for analysis. The third aliquot was put into refrigerated storage. The second aliquot was returned to the receiving area where it was given a new sample number. This step could require one or two days, after which the sample would be placed on the tray being sent for analyses. Careful records were maintained by the Quality Assurance Specialist and the data processing staff to assure that the original sample number and the new sample number were available for later use in interpreting the results of these replicate analyses; however, these samples remained blind to the analysts. After all analyses had been performed, but before the data were entered into the computer, the sample number was changed on the second aliquot to the original sample number followed by a Q. These blind splits will subsequently be referred to as O/Q pairs.

This section of the report discusses the plots of the data derived from both the A/B and the O/Q replicate analyses. The plots are presented as Figures 1 through 40 in Appendix C. They are arranged by parameter, with each figure representing one year's analyses. They are also grouped by split type with all of the A/B data presented first, and followed by those for the O/Q pairs. Interpretation of the data and a summary statement about laboratory precision for 1984 and 1985 are included.

1. Range Selection

The figures in Appendix C are plots of the concentration differences between replicate samples A and B (or O and Q) in mg/L versus the

average concentrations of A and B (or O and Q) in mg/L. The differences are always calculated by using the formula [analyte concentration of A (O) minus analyte concentration of B (Q)]. The average is [analyte concentration of A (O) plus analyte concentration of B (Q)] divided by 2. To facilitate the usefulness of the plots, the yearly assessments for each ion have been split into two sections. A median concentration for the two-year period was determined for each analyte. The first plot in each figure includes the range from 0 mg/L to the median concentration of the analyte of interest. The second plots of the figures begin with the 50th percentile concentration value and continue to the 95th percentile concentration of that analyte found in the replicate samples analyzed during the period. Table IV-6 lists the 50th percentile and the 95th percentile concentrations for each analyte for the replicate samples analyzed in 1984 and 1985.

TABLE IV-6   **Fiftieth and Ninety-fifth Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation Samples Selected for Replicate Analyses in 1984-1985.**

| Parameter | Percentile Concentration Values (mg/L) | |
	50th	95th
Calcium	0.100	1.00
Magnesium	0.035	0.225
Sodium	0.075	0.750
Potassium	0.025	0.125
Ammonium	0.15	1.50
Sulfate	1.20	6.00
Nitrate	1.00	5.00
Chloride	0.15	3.00
pH (units)	4.50	3.64
Specific Conductance (uS/cm)	15.0	75.0

2. Tables and Plots

Figures 1 through 40 in Appendix C are plots of the differences found at the CAL between two aliquots (A/B) of the same precipitation sample analyzed in succession, and two aliquots (O/Q) of the same precipitation sample analyzed at different times. The plots are grouped by analyte, and each figure contains both low and high concentration plots for a single year. Plots of the difference between A and B (or O and Q) are presented for all analytes except orthophosphate. The number

of precipitation samples containing orthophosphate is small, and the number of replicate samples containing differences greater than 0.000 mg/L in the orthophosphate concentrations is even smaller. For the A/B replicate pairs, 88.3% of the samples analyzed in 1984 and 85.4% of those analyzed in 1985 contained no measureable orthophosphate. Of the 11.7% of the samples analyzed in 1984 and the 14.6% analyzed in 1985 containing orthophosphate, the difference between the orthophosphate concentration measured in samples A and B was 0.000 mg/L for all but 2% of the samples. For the O/Q replicate pairs, 77.8% of the samples analyzed in 1984 and 77.3% of those analyzed in 1985, contained no measureable orthophosphate. Of the 22.% (1984) and 22.7% (1985) of the O/Q pairs that contained the analyte, all had differences of 0.000 mg/L. Plots of these differences were deemed unnecessary.

Table IV-7 lists the mean differences for each analyte for both A/B and O/Q sample pairs for the two years. Tables 1 through 4 in Appendix C present complete annual statistical summaries of the differences plotted in Figures 1 through 40.

TABLE IV-7 Mean Differences for Replicate Analyses of Precipitation Samples for 1984-1985.

Parameter	Mean Difference (mg/L)			
	1984		1985	
	(A/B)[a]	(O/Q)[b]	(A/B)[a]	(O/Q)[b]
Calcium	0.001	−0.003	0.000	−0.001
Magnesium	0.000	−0.001	0.000	0.000
Sodium	0.000	0.007	0.000	0.000
Potassium	0.000	−0.006	−0.001	0.000
Ammonium	0.00	0.00	0.00	0.00
Sulfate	0.01	0.01	−0.01	−0.01
Nitrate-Nitrite	0.00	0.01	−0.01	−0.01
Chloride	0.00	0.01	0.00	0.01
pH (units)	0.00	−0.01	0.00	−0.01
Specific Conductance (uS/cm)	−0.1	−0.2	0.0	−0.1
n[c]	231	108	177	176

a. (A/B) = aliquots of same precipitation sample analyzed in succession
b. (O/Q) = aliquots of same precipitation sample analyzed at different times
c. number of replicate pairs

3. Discussion of Results

The data presented in both the figures and the tables indicate that the precision at the CAL for splits analyzed in succession was always very good. The differences are almost always within three times the MDL

for each analyte and in most cases are within two times the MDL. Precision of this quality is what should be expected for these types of analyses where the analyses are performed in succession.

The O/Q pairs show larger differences between the two analyses or less precision in the measurements. This is what would be predicted of sample pairs analyzed as blinds and at different times. The time period between the analyses of the two samples may be sufficient for changes in the ionic composition of the sample to occur. Despite this possibility, a comparison of the differences found in both the A/B and the O/Q pairs for 1984 and 1985 indicates that the precision for these samples is satisfactory for all analytes.

C. INTERNAL BLIND SAMPLE DATA

In July 1984 an internal blind sample program was started to provide still another means of assessing the quality of the CAL data. Samples of known analyte concentrations were prepared by the Quality Assurance Specialist and submitted to the sample processing staff at a frequency of two samples per week. In the processing laboratory, the samples received an NADP/NTN sample identification number, and an aliquot of each was removed for later measurement of pH and specific conductance. The samples were filtered, placed on a sample tray, and sent to the analytical staff for routine analysis.

Although the sample processing staff were aware of the fact that these were not precipitation samples, they did not know the expected analyte concentrations of the samples. The remaining CAL analytical staff were not only unaware of the analyte concentrations of these samples, but were also unaware which samples on the trays were synthetic.

The following sections of this report provide more detail on the samples that were used in the internal blind program. Tables of the analytical bias and precision calculated from the data resulting from the analysis of these samples, as well as a discussion of what the data in these tables indicate about the performance of the CAL, are included.

1. Solutions Used

Samples of known analyte concentrations were obtained from the U.S. Environmental Protection Agency in Research Triangle Park, North Carolina. These samples were originally prepared for a USEPA/WMO laboratory intercomparison that took place in October 1983. The samples contain all of the routine parameters, except for orthophosphate, that are determined in the network samples. The analyte concentration levels are comparable to those found in the network samples. Both of these factors made these samples preferable to samples that were dilutions of the EPA drinking water reference samples used as QCS.

Three different samples, with directions for dilution and a table of analyte concentrations that should result from the dilution, were supplied to the CAL. These samples had been checked by the USEPA for

both accuracy and stability. The stability was also monitored by the CAL QA Specialist, and new dilutions were made whenever warranted. Only one liter of each sample was prepared because of the presence of unstable species such as nitrate and the possible need for frequent preparations of the samples to maintain these analytes at the expected levels.

In 1984, all three samples were diluted as directed by the USEPA and used in the program. Two of these samples, however, contained higher concentrations of most analytes than were normally found in the network. By diluting these two samples further, by a factor of 10, the resultant analyte levels were very similar to those in the network samples. These additionally diluted samples were used for the program throughout 1985. This second dilution increased the instability of both the nitrate and the ammonium ions and required more frequent sample preparation.

2. Analytical Bias and Precision Tables

The data that resulted from the analyses of these samples are contained in Tables IV-8 and IV-9. These tables contain similar information to that found in Tables IV-4 and IV-5 for replicate analyses of QCS. There is a difference, however, in the procedure used to determine whether the calculated bias was or was not significant.

The calculation for the critical percent used to determine the significance of the calculated bias is given in the Glossary (Appendix A). That formula was used with the QCS data because the standard deviation of the true value and the number of analyses used to determine the value and the standard deviation were supplied by the USEPA. This information was not available for the USEPA/WMO samples used in the internal blind program. Instead, a confidence interval was calculated for the laboratory mean using the following formula recommended by Taylor (7):

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

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

When the recommended or true value lies within this confidence interval, the bias is not considered significant. When that value is outside of the interval, it is said to be significant. This is how the significance of the bias was determined for the bias calculated from the analyses of the internal blind samples. The results appear in the last columns of Tables IV-8 and IV-9.

3. Discussion of Results

Comparison of the bias and precision calculated from replicate analysis of QCS (Tables IV-4 and IV-5) to those obtained from analysis of the internal blinds (Tables IV-8 and IV-9) indicate that bias and precision are better for known samples than for unknowns. What is

**TABLE IV-8 1984 Analytical Bias and Precision
from Internal Blind Audit Program.**

Parameter	Recommended Concentration (mg/L)	Number Samples (n)	Mean Concentration Measured (mg/L)	Bias[a] (mg/L)	Precision[b] (% RSD)	Bias[c] Significant ?
Ca^{+2}	0.110	19	0.111	0.001	6.2	No
	2.060	15	1.858	-0.202	1.9	Yes
	3.630	18	3.203	-0.427	1.9	Yes
Mg^{+2}	0.010	19	0.009	-0.001	17.3	Yes
	0.250	15	0.249	-0.001	2.4	No
	0.370	18	0.369	-0.001	1.9	No
K^+	0.050	19	0.054	0.004	4.5	Yes
	1.470	18	1.493	0.023	2.5	Yes
	2.680	15	2.684	0.004	1.8	No
Na^+	0.080	19	0.084	0.004	5.2	Yes
	0.260	15	0.261	0.001	2.4	No
	1.440	18	1.461	0.021	2.2	Yes
SO_4^{-2}	1.71	19	1.62	-0.09	4.3	Yes
	11.14	18	10.65	-0.49	5.2	Yes
	17.73	15	16.18	-1.55	9.8	Yes
NO_3^-	0.13	19	0.14	0.01	16.2	No
	4.52	15	4.25	-0.27	1.6	Yes
	6.11	18	5.84	-0.27	7.8	Yes
Cl^-	1.01	19	1.04	0.03	2.1	Yes
	4.17	15	4.21	0.04	2.2	No
	10.33	18	10.00	-0.33	4.8	Yes
NH_4^+	0.42	19	0.40	-0.02	10.4	No
	0.44	15	0.43	-0.01	3.4	Yes
	2.31	18	2.23	-0.08	3.9	Yes
pH (units)	3.49	15	3.50	0.01	5.6	No
	3.72	18	3.73	0.01	6.8	No
	4.45	19	4.48	0.03	8.5	Yes
Conductivity (uS/cm)	19.0	19	19.7	0.7	2.3	Yes
	135.0	18	135.6	0.6	1.7	No
	165.8	15	164.6	-1.2	1.8	No

a. Bias = (Measured Concentration - Recommended Concentration)
b. % RSD = (Standard Deviation/Mean Measured Concentration) X 100; precision of pH measurements
    expressed in terms of hydrogen ion concentration
c. Calculated from 95% confidence interval of measured mean concentration. If this interval
    includes the recommended concentration, reported bias is not significant.

TABLE IV-9   1985 Analytical Bias and Precision
from Internal Blind Audit Program

Parameter	Recommended Concentration (mg/L)	Number Samples (n)	Mean Concentration Measured (mg/L)	Bias[a] (mg/L)	Precision[b] (% RSD)	Bias[c] Significant ?
Ca^{+2}	0.206	45	0.197	-0.009	4.4	Yes
	0.363	46	0.327	-0.036	2.9	Yes
Mg^{+2}	0.025	45	0.033	0.008	14.5	Yes
	0.037	46	0.043	0.006	8.8	Yes
K^{+}	0.147	46	0.150	0.003	4.2	Yes
	0.268	45	0.274	0.006	2.8	Yes
Na^{+}	0.026	45	0.047	0.021	28.2	Yes
	0.145	46	0.166	0.021	8.9	Yes
SO_4^{-2}	1.11	46	1.07	-0.04	6.3	Yes
	1.77	45	1.70	-0.07	7.8	Yes
NO_3^{-}	0.45	45	0.37	-0.08	41.2	Yes
	0.61	46	0.62	0.01	9.2	No
Cl^{-}	0.42	45	0.45	0.03	5.5	Yes
	1.03	46	1.04	0.01	11.6	No
NH_4^{+}	0.04	45	0.01	-0.03	75.4	Yes
	0.23	46	0.14	-0.09	65.0	Yes
pH (units)	4.48	45	4.49	0.01	7.6	Yes
	4.73	46	4.71	-0.02	7.2	Yes
Conductivity (uS/cm)	13.7	46	14.7	1.0	3.1	Yes
	16.6	45	18.1	1.5	3.2	Yes

a. Bias = (Measured Concentration - Recommended Concentration)
b. % RSD = (Standard Deviation/Mean Measured Concentration) X 100; precision of pH measurements expressed in terms of hydrogen ion concentration
c. Calculated from 95% confidence interval of measured mean concentration. If this interval includes the recommended concentration, reported bias is not significant.

important to note is that while the blind sample data appear somewhat more biased and less precise, the accuracy is within the limits set in the QA Plan (2).

There are several additional points that should be raised about the data contained in Tables IV-8 and IV-9. First, the sodium for both years is biased high and those biases were generally considered significant. The QCS data show that the problem does not lie with the analytical method. The problem is believed to result from the handling procedures for the blind samples. These included the use of two or more sample containers and filtration. Such additional handling always increases the potential of sample contamination, with sodium being the most likely contaminant.

The possible disappearance of the unstable nitrate and ammonium ions has already been suggested in the discussion of QCS and replicate analysis results. Although all of the raw data for these unstable ions have not been supplied for review, they show steadily decreasing concentrations of the ions with each sample taken. Predictably, preparation of a new sample dilution results in nitrate and ammonium values at theoretical levels. This fact is most apparent in the precision for the two analytes. In an attempt to eliminate the problem, samples were prepared monthly. Even with this procedure, decomposition occurred at varying rates and the data obtained from the analysis of these samples are not a reliable indicator of laboratory bias or precision.

Finally, as with the QCS data, most of the data from the blind sample program show a statistically significant bias. Examination of the amount of the bias in milligrams per liter shows that the actual deviations from the true values are often extremely small and of no real concern to the data user. Because the samples analyzed as part of this program receive very similar handling to the network samples, the estimates of bias and precision derived for the stable ions in these samples provide better approximations of the accuracy of the network sample measurements than the data obtained from the analysis of the known QCS solutions.

V. REANALYSIS PROCEDURES

Once the analyte concentrations in a precipitation sample are determined, the information is entered into the CAL data base. The analyte concentrations are converted from milligrams per liter to micro-equivalents per liter, and an ion balance calculation is made for each sample. The information resulting from this calculation is used to select approximately 8% of the samples for reanalysis.

A detailed explanation of different ion balance calculations appeared in the Laboratory Quality Assurance Report for 1978-1983 (1) and will not be repeated here. It is important to know which method a laboratory employs, however, not only for purposes of data comparisons, but also for data interpretation, particularly when this information will be used to evaluate laboratory performance.

The calculation method used by the CAL is described in Figure V-1. The factors used to convert the measured analyte concentrations from milligrams per liter to microequivalents per liter are listed in Table V-1. These were taken from Standard Methods for the Examination of Water and Wastewater (8).

Ion balance calculations are a valuable component of the CAL quality assurance program. A large imbalance can be indicative of an error in the analyses. It may also be an indication that additional ionic species are present in the sample and further analyses are

NADP/NTN Ion Balance
Calculation Method

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

$$\text{Anion}^* = (SO_4^{-2}) + (NO_3^-) + (Cl^-) + (PO_4^{-3})$$
$$+ (OH^-) + (HCO_3^-)$$

$$\text{Cation}^* = (Ca^{+2}) + (Mg^{+2}) + (Na^+) + (K^+)$$
$$+ (NH_4^+) + (H^+)$$

* Concentrations are expressed in microequivalents/liter

**FIGURE V-1. Formula used by the CAL to calculate an
ion percent difference (IPD)**

TABLE V-1   The Factors Used to Convert Analyte
            Concentrations from Milligrams per
            Liter to Microequivalents per Liter.[a]

Analyte	ueq/L = mg/L x
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

a. Factors taken from Standard Methods for the Examination of
   Water and Wastewater (8).

necessary to completely characterize the sample. By selecting a maximum
allowable imbalance and reanalyzing all samples with an imbalance
greater than this maximum, an imbalance that resulted from analytical
error can be found and corrected.

In the following sections, the criteria used to select samples for
reanalysis are presented. Discussions of the information that can be
derived from these reanalysis procedures and how this information is
used to change the original analytical data are also included.

A. ION BALANCE CRITERIA

In October 1981, a set of criteria was developed to select samples
for reanalysis due to a large ion imbalance. These criteria were
selected after an examinaton of the data from the previous three years
of network operation. Regional differences in rainfall amounts and
analyte concentrations were compared, and the criteria that had been
used since 1979 (1) were altered to better select those samples which
were truly outliers. The goal was to select 5-6% of the samples analyzed
at the CAL for reanalysis. Time has proven this to be an adequate set of
criteria to reach the desired goal, and it has remained unchanged since
its formulation in 1981.

The computer program that calculates an ion balance for each sample
also determines the ion sum (IS) or total ionic strength of the sample.
The analyte concentrations have already been converted to
microequivalents per liter as part of the ion balance calculation. To
obtain the ion sum (IS), the total anion concentration expressed in
microequivalents is added to the total cation concentration, also in

microequivalents. Both the ion sum and the ion percent difference that result from the ion balance calculation are used to determine which samples should be reanalyzed. The ion balance criteria for reanalysis selection are:

When IS < 50 ueq/L, reanalyze if IPD > $\pm$ 60%;

when 50 $\leq$ IS < 100 ueq/L, reanalyze if IPD > $\pm$ 30%; and

when IS $\geq$ 100 ueq/L, reanalyze if IPD > $\pm$ 15%

where IS = Ion Sum = (Anion + Cation) ueq/L, and

$$IPD = \text{Ion Percent Difference} = \frac{(\text{Anion} - \text{Cation})}{(\text{Anion} + \text{Cation})} \times 100$$

B. SPECIFIC CONDUCTANCE CRITERIA

Another part of the ion balance program uses the measured concentration of analytes to calculate a theoretical conductance for the sample. The formula used is:

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

where ion concentrations are expressed as microequivalents per liter.

The conductance factors used in this calculation for hydrogen ion and ammonium can be obtained from the CRC Handbook of Chemistry and Physics (9). The remaining factors can be found in Standard Methods for the Examination of Water and Wastewater (8).

The calculated conductance is compared to the measured conductance, and a conductance percent difference is found. This comparison uses the following equation:

Conductance Percent Difference = CPD =

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

Once the CPD has been calculated, it can be used as another means of selecting samples for reanalysis. It was not until 1981 that suitable criteria were developed to utilize this CPD information. As with the ion percent difference, a large CPD may indicate a measurement error in one or more of the analytes. Percentile values for measured specific conductance from 1978-1981 were used to formulate a set of CPD criteria

that were added to the ion balance program in October 1981. The CPD criteria are:

When measured conductance $\leq$ 10 uS/cm,
reanalyze if CPD $> \pm$ 65%;

when 10 uS/cm < measured conductance $\leq$ 30 uS/cm,
reanalyze if CPD $> \pm$ 45%;

when 30 uS/cm < measured conductance $\leq$ 50 uS/cm,
reanalyze if CPD $> \pm$ 30%; and

when measured conductance > 50 uS/cm,
reanalyze if CPD $> \pm$ 20%.

The percentage of samples that meet these criteria is generally less than 2%, and most often they have already been flagged because of an ion imbalance. Nevertheless, this provides another means of detecting large analytical errors and is a useful calculation to perform.

C. HISTOGRAMS

Figures V-2 through V-5 are histograms of the ion percent difference values (IPD) and the conductance percent difference values (CPD) for the samples from the NADP/NTN network for the years 1984 and 1985. With each histogram, a median, a mean, and a standard deviation are noted.

The IPD histograms approximate a normally distributed curve centering around the 0% difference point. This is what one would expect if the sample analysis includes the measurement of all of the major anions and cations in precipitation. The eleven parameters selected for analysis at the CAL appear to adequately characterize the precipitation samples collected within the NADP/NTN network. Again, a normal distribution around the 0% difference point would be expected for the CPD histograms. However, it does not occur. These plots have a negative skew. The calculated conductance is typically less than the measured conductance. This suggests either a measurement or a calculation problem. Specific conductance values obtained for quality control samples with certified conductivity values are consistently within the acceptable limits. This suggests that the accuracy of the specific conductance measurements is good. A problem in the calculations was investigated as one source of the skewed curve. Using the constants found in the CRC Handbook (9) instead of those in Standard Methods (8) to determine the calculated specific conductance results in a population mean difference closer to 0%. The change to these constants was put into effect beginning in March 1987. This negative skew may also be the result of the presence of ions not being routinely measured by the CAL. The curve is centering near -10% in most years, which may result from the presence of low concentrations of ions whose presence goes undetected in the IPD calculations and resultant histograms. The presence of trace amounts of metal ions complexed with unmeasured

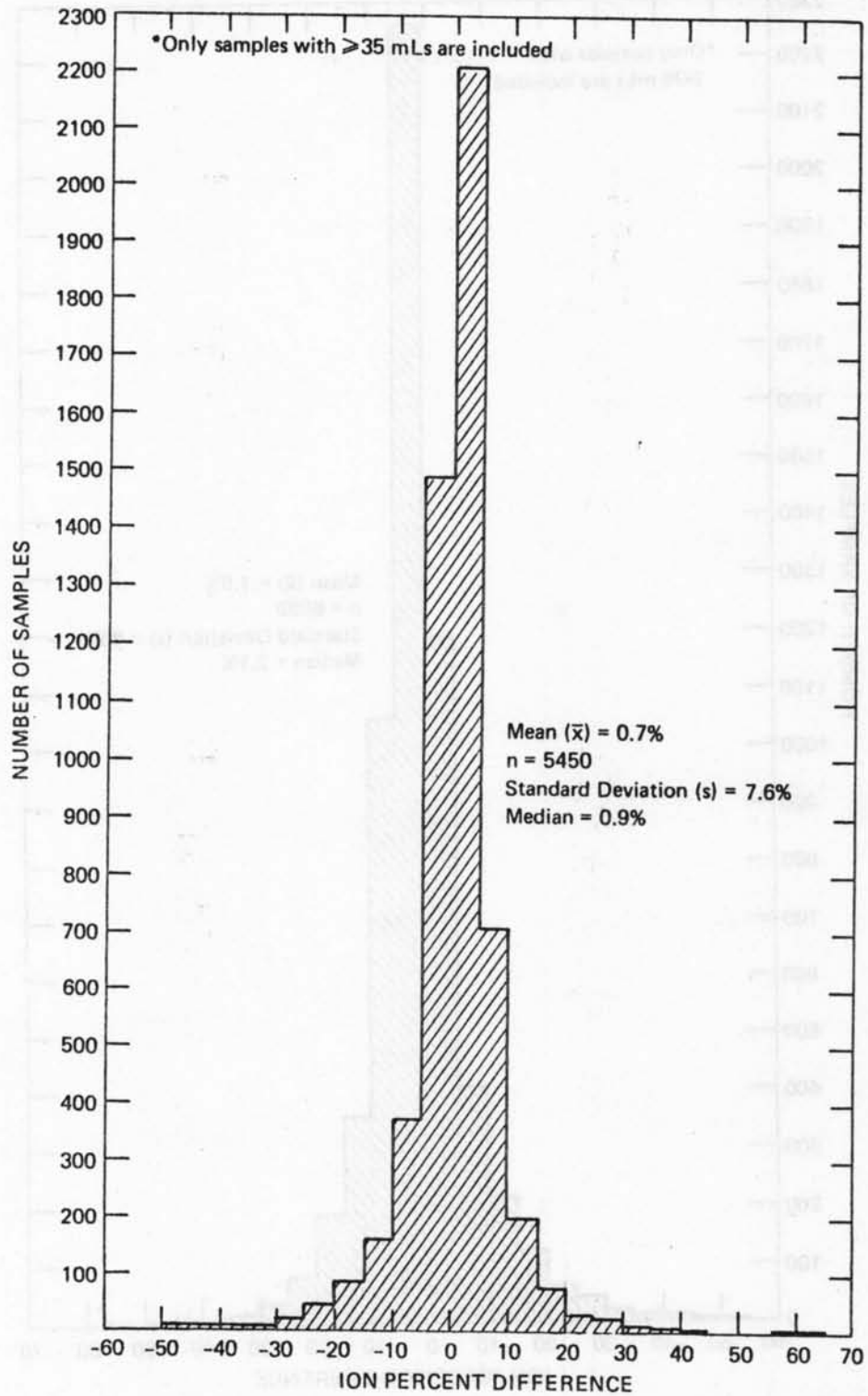ION PERCENT DIFFERENCE HISTOGRAM FOR 1984 NADP/NTN WET SIDE SAMPLES*

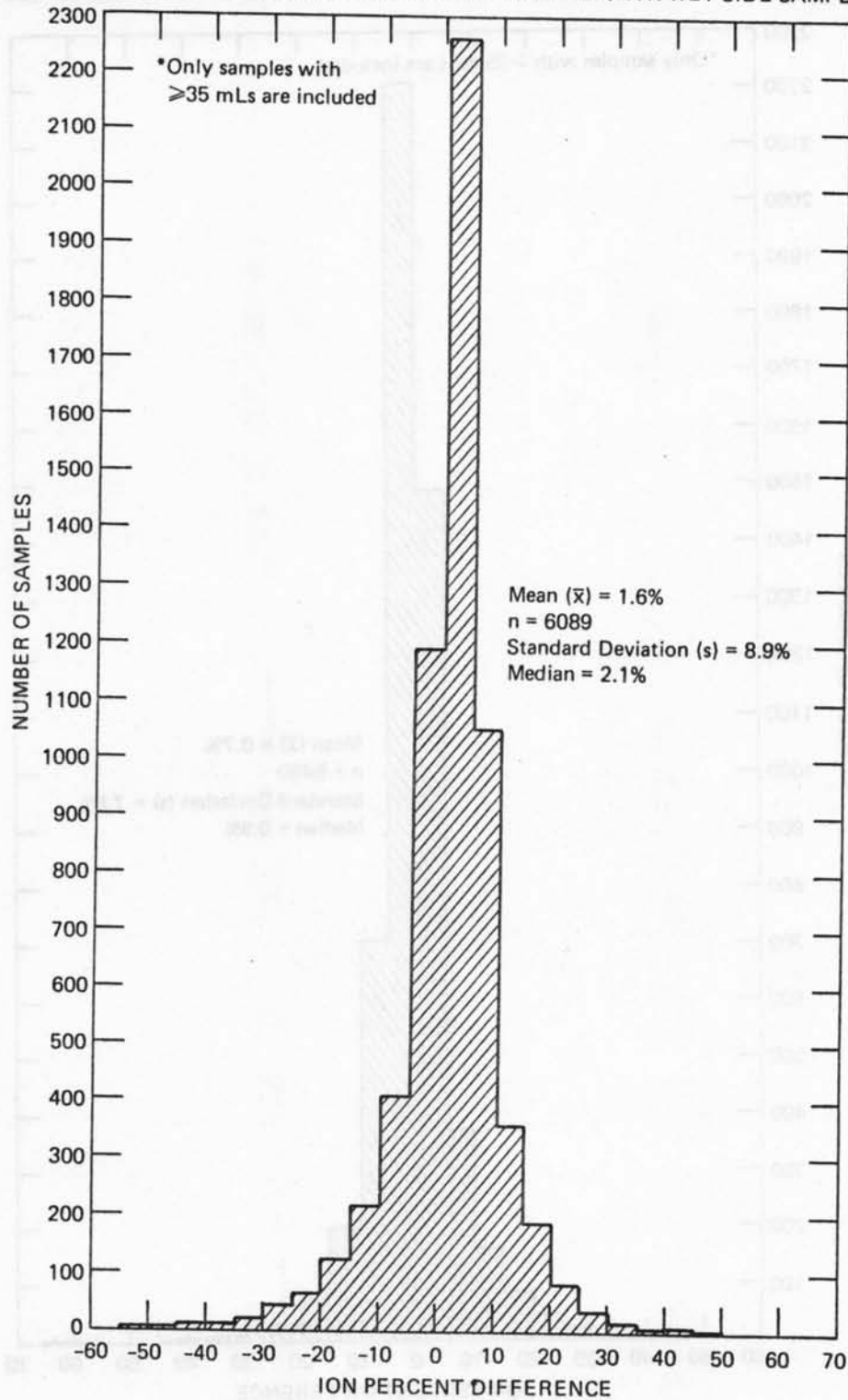FIGURE V-2. Ion percent difference histogram for NADP/NTN wet side samples in 1984.

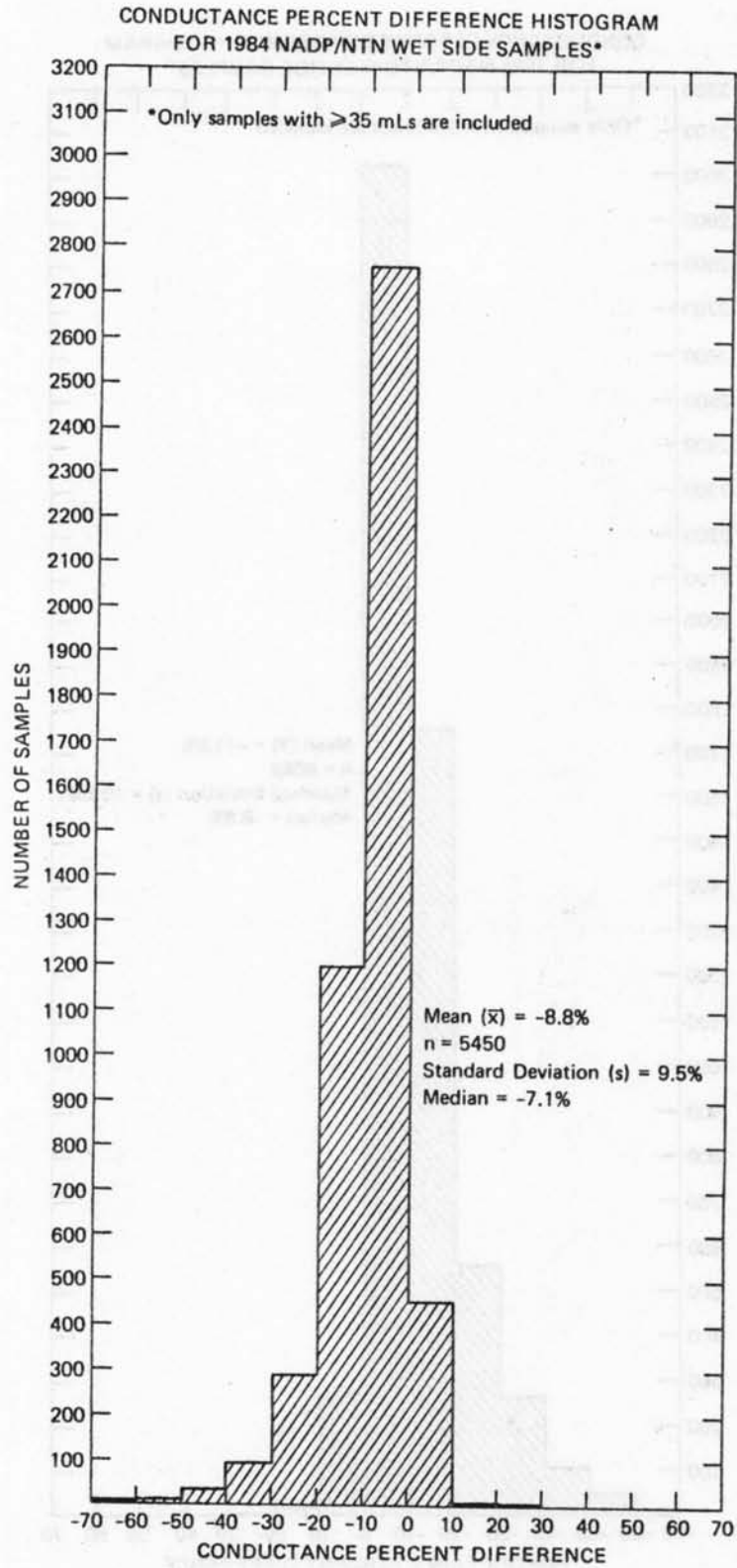FIGURE V-3. Ion percent difference histogram for NADP/NTN wet side samples in 1985.

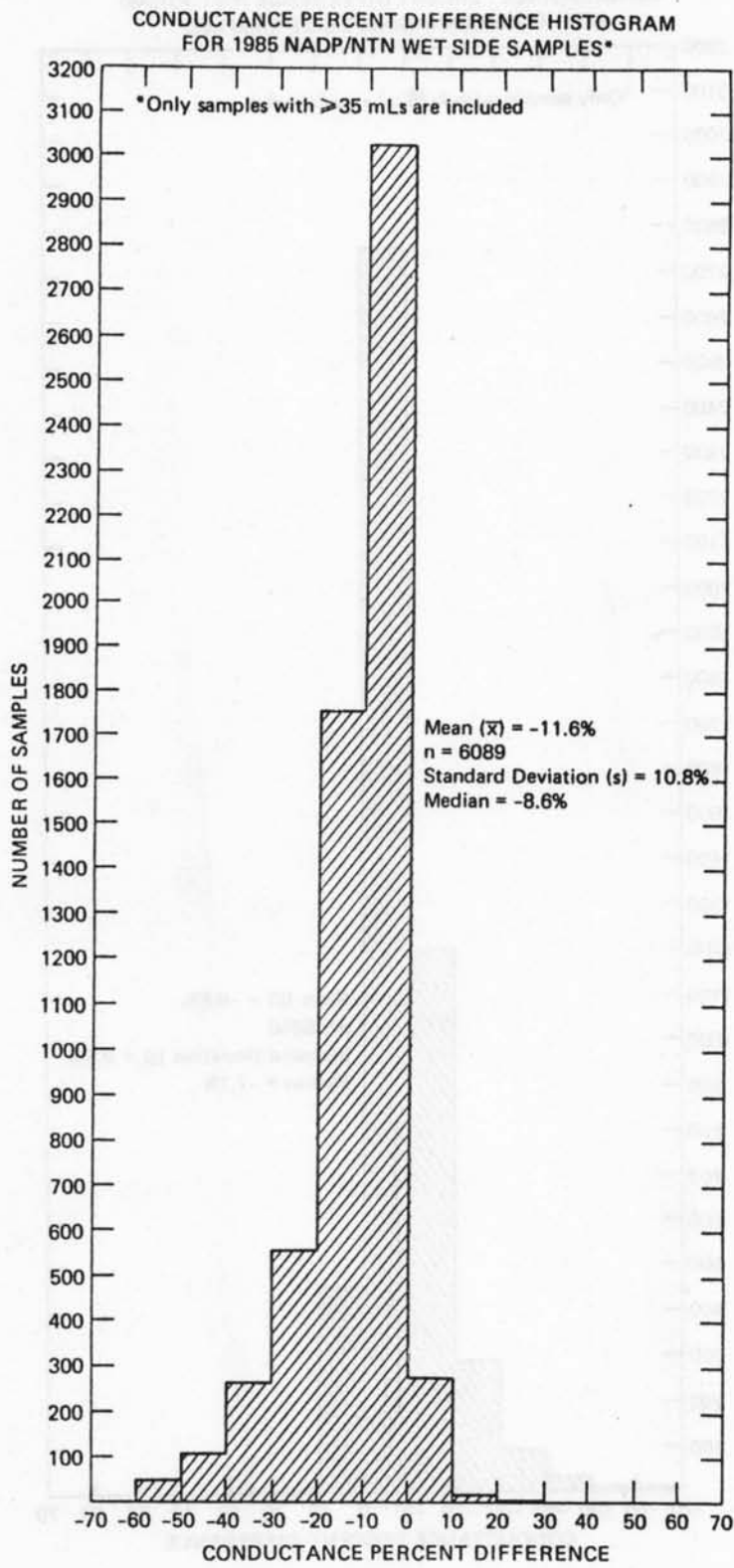FIGURE V-4. Conductance percent difference histogram for NADP/NTN wet side samples in 1984.

FIGURE V-5. Conductance percent difference histogram for NADP/NTN wet side samples in 1985.

anions, such as bromide, could go undetected by the ion balance calculation but result in a negative conductance percent difference.

D. DISCUSSION OF RESULTS

The fact that a sample does not satisfy the criteria previously described and is selected by the program for reanalysis does not necessarily mean it will be reanalyzed. Reanalysis may be impossible simply because all of the sample was used during the initial analyses. Also, A/B and O/Q splits are not reanalyzed if the original duplicate analyses were the same or very similar to each other. All other samples flagged by the ion balance program are retrieved and reanalyzed for all constituents.

Once the reanalysis has been completed, the new data are compared to the original data. When substantial differences are found between the two results, reasons for the difference are sought. The first step is to analyze the refrigerated aliquot when one is available. Since refrigeration is a means of sample preservation, the integrity of the refrigerated aliquot should have been maintained. If the difference was the result of decomposition of the sample stored at room temperature, this will be apparent. When the results from the analysis of the refrigerated aliquot are more like the reanalysis value, the source of the error in the original analysis is sought. Analysts' input as to the possible source of error is always utilized to explain discrepancies between original and reanalysis results.

When a difference in original and reanalysis values occurs and no explanation can be found, the original data are reported. If the difference is explained, the data will be changed and a new value reported. For all of the samples reanalyzed, less than 1% will require any change in the original data. The overall result is that approximately 0.1% of the final data is changed from the value that was initially reported.

VI. EXTERNAL QUALITY ASSURANCE PROGRAM PARTICIPATION

The analytical bias and precision data reported in Section IV are supported by the CAL's performance in several different external quality assurance programs. One program, operated by the U.S. Geological Survey (USGS), audits the CAL's performance for the NADP/NTN program. In addition to this external quality assurance program, the CAL voluntarily participates in other national and international performance studies. The performance of the CAL in each of these studies is addressed below.

A. U.S. GEOLOGICAL SURVEY EXTERNAL AUDIT PROGRAM

The U.S. Geological Survey's external audit program for the CAL has two components: a blind sample program and an interlaboratory comparison study. The data obtained from these programs provide information about not only the CAL's performance but also the effects of sample handling in the field.

The NADP/NTN Blind Audit Program that started in October 1979 (10) continued with only minor changes through 1985. During the years 1984 and 1985, the USGS reformulated some of the Standard Reference Water Samples (SRWS) being supplied to sites in the sampling network so the resultant analyte concentrations in these SRWS more closely resembled those found in network precipitation samples. During 1984 and 1985, Nanopure deionized water from the USGS National Water Quality Laboratory in Denver, Colorado, the dilute nitric acid quality control check solution prepared by the CAL, and National Bureau of Standard certified simulated rainwater samples were made available for possible use in the program.

The first week a site did not have rain, the site operator was directed to pour the sample he/she had previously received from the USGS into a clean bucket and submit it to the CAL as the rain sample for the week. The site operator was to notify the USGS and the Coordinator's Office of the date that the blind sample had been sent. The sample would subsequently be processed by the CAL as a routine precipitation sample. This program relies heavily on the cooperation of the site operators. The data from the analyses of these external blind samples reflect the effects of the sample handling from the time it is bottled at the USGS until it is analyzed at the CAL.

The audit program focuses on the analytical data obtained from the analysis of the samples for calcium, magnesium, sodium, potassium, sulfate, and chloride. Despite the reformulations of the sample composition by the USGS mentioned earlier, many of the SRWS used in the program through 1985 had analyte concentrations higher than those found in rainwater and often required dilution by the laboratory before analysis. Table VI-1 lists the maximum analyte concentration that can be present in a sample before a dilution is necessary. The fact that a dilution of the sample has been made adds another variable to be considered when interpreting the data. The USGS has issued three reports that analyze the data from the blind audit program from January 1980

through December 1985 (11, 12, 13). Inquiries about additional details of this program should be directed to the USGS, Denver Federal Center, Denver, Colorado.

TABLE VI-1 **Maximum Analyte Concentration Measured Before Sample Dilution Is Required.**

Analyte	Concentration (mg/L)	Dates
Calcium	3.00	1/79 - 12/83
Magnesium	1.00	1/79 - 12/83
Sodium	1.00	1/79 - 12/83
Potassium	1.00	1/79 - 12/83
Ammonium	2.00	1/79 - 12/83
Sulfate	10.00	1/79 - 1/83
	9.00	1/83 - 12/83
Nitrate-Nitrite	5.00	1/79 - 12/83
Chloride	5.00	1/79 - 4/81
	3.00	4/81 - 12/83
Orthophosphate	0.100	1/79 - 1/83
	0.250	1/83 - 12/83

The USGS interlaboratory comparisons were started in the late fall of 1982. Participants in the study were: Inland Waters Directorate, Ontario, Canada (IWD); Illinois State Water Survey, Champaign, Illinois (CAL); U.S. Geological Survey National Water Quality Laboratory, Atlanta, Georgia (ATL); and U.S. Geological Survey National Water Quality Laboratory, Denver, Colorado (DEN). In 1984, the Bituminous Coal Research Laboratory (BCR) was briefly added as a participant in the program. In November 1985, the USGS laboratories in Atlanta and Denver were consolidated; therefore, the USGS report for the 1985 intercomparison (13) includes data for only the first nine months of 1985 for all of the participating laboratories.

This intercomparison study was designed to determine whether the four participating laboratories were producing comparable results. At each laboratory, analytical bias was documented, and estimates of analytical precision were made. Precipitation samples from sites in the NADP/NTN network were split at the CAL and sent to the USGS National Water Quality Laboratory in Denver. The samples were renumbered at the USGS and distributed to each of the four participants for analysis. In addition to natural precipitation samples, synthetic samples of known analyte concentrations were also routinely submitted to the participating laboratories for analysis. Data obtained from the analysis of calcium, magnesium, sodium, potassium, ammonium, sulfate, nitrate, chloride, pH, and specific conductance were subsequently returned to the Denver facility. Water-Resources Investigations Reports 87-4067 (14) and 87-4219 (13) discuss the USGS analysis of the data received from October 1983 - December 1985.

B. INTERLABORATORY COMPARISON STUDIES

During 1984 and 1985, the CAL participated in several other interlaboratory performance studies in addition to the USGS-sponsored comparisons just discussed. These studies were sponsored by state and federal government agencies as well as international organizations. This section continues with a brief description of the studies in which the CAL participated. The CAL data for each study under discussion are presented in Tables 1 through 10 in Appendix D. These tables also include the expected or target concentrations of each analyte. Summary information on the CAL's performance in these studies is included in this section. More detailed explanations of the laboratory intercomparisons are contained in the agency summaries in the reference list at the end of this report.

1. World Meteorological Organization/
United States Environmental Protection Agency (WMO)

In an attempt to establish cooperation among international precipitation laboratories and to better evaluate its network data, the World Meteorological Organization (WMO) selected a Precipitation Reference Laboratory (PRL) in 1975. It designated the Environmental Monitoring Systems Laboratory (EMSL) of the U.S. Environmental Protection Agency, Research Triangle Park, N.C., to be this PRL and directed it to achieve the goals it had set by designing and conducting interlaboratory comparison studies (15).

Details of the CAL's participation in the WMO intercomparison program from 1980-1983 were presented in the laboratory Quality Assurance Report for 1978-1983 (1). The CAL's participation in this program continued in 1984 and 1985. During this period there were four intercomparison studies. Tables 1 through 4 in Appendix D compare the CAL data to the expected analyte concentrations for these four inter-comparison studies. The data in these tables indicate continued good performances by the CAL.

Table VI-2 summarizes the CAL performance for all WMO studies in which the laboratory had participated by the end of 1985. This table provides the mean percent deviation of the CAL reported values from the WMO expected values for the 10 principal constituents routinely analyzed in precipitation. Analysis for orthophosphate is not included in these intercomparison studies. Table VI-2 also includes the mean percent deviation values from the WMO expected values for all participating laboratories. The data presented in this table combine those which first appeared in the ISWS 20th (16) and 21st (17) Progress Reports to the U.S. Department of Energy.

In each of the WMO interlaboratory comparisons, the CAL also determined acidity and trace metal concentrations for the test samples. Information regarding these analyses can be found in the final reports for each study. Most of the participants in these studies do not routinely include trace metals in their analytical results. Trace metal analyses are also not performed for the network samples. For these reasons, only the 10 major chemical and physical parameters routinely

TABLE VI-2 Summary of Results from World
Meteorological Organization (WMO)
Interlaboratory Comparison of
Reference Precipitation Samples.[a]

Intercomparison Number	Date	Number of Participating Laboratories (n)	Mean % Difference[b] From Expected Value	
			CAL	All Labs
Four	7/80	27	4.38	17.67
Six	4/83	22	3.89	17.47
Seven	11/83	22	2.65	23.51
Eight	4/84	22	4.73	39.53
Nine	10/84	25	6.49	43.82
Ten	4/85	27	3.61	33.04
Eleven	10/85	23	3.57	19.19

a. Chemical parameters used in the calculation were Ca, Mg, Na, K, NH_4, NO_3, Cl, SO_4, pH, and Specific Conductance.

b. Mean % Difference $= \dfrac{|\text{Expected Value} - \text{Reported Value}|}{\text{Expected Value}} \times 100$
   $\phantom{\text{Mean % Difference} =}\overline{\phantom{\dfrac{|\text{Expected Value} - \text{Reported Value}|}{\text{Expected Value}}}}$ 10 (constituents)

measured by the CAL and a large number of participating laboratories are
included in this summary table. The data presented for each summary
represent pooled results for the analysis of the measured constituents
in three samples (17). The percent deviations were calculated for the
combined laboratory data set after outliers were removed. The method
used to classify which results were outliers is detailed in the WMO
study summary (15). Each participating laboratory received a listing of
the true values for the samples analyzed as part of the study and a
percentile listing of the percent deviations from the true values for
each parameter, both for all analyses and for those that remained once
the outliers were removed. Mean percent deviations for each parameter,
both with and without outliers, were also included in these study
summaries. The CAL did not receive published study reports for the
studies conducted in 1984 and 1985; however, information about these
studies can be obtained from the PRL.

An examination of the data in Table VI-2 indicates that the CAL
continued to produce high-quality analytical data during 1984-1985. The
percent deviation from the true values for the CAL ranged from
3.57%-6.49% for the two years, while that for all laboratories ranged
from 19.19%-43.82%. Had the outliers been included in the
all-participant data, the range would have been 28%-52%.

2. Illinois Environmental Protection Agency (IEPA)

In December 1981 the Analytical Chemistry Unit of the Illinois
State Water Survey, of which the CAL laboratory is a part, received
certification from the Illinois Environmental Protection Agency (IEPA).
As part of the certification procedure, a team of reviewers from the

IEPA inspected the facilities and interviewed the staff to determine if the regulations set by the IEPA (18) were being followed. The IEPA also requires the analysis of performance evaluation samples containing the parameters for which certification is requested. Each laboratory is rated satisfactory or unsatisfactory for every analytical value it reports. Information regarding the true or expected values for the analytes present in the test samples is not made available to the participants. The CAL received a satisfactory rating for all values reported.

This certification was for chemical analysis of public water supply samples; however, the parameters that were certified included those found in precipitation, and the analytical methods were those used by the CAL. The CAL laboratory staff were among those interviewed and were responsible for much of the analytical data reported.

The certification was valid for two years, and recertification was requested in 1983 and again in 1985. After an on-site review of the laboratory, its staff, and the analytical methods being used, new Certificates of Approval were issued to the laboratory in December 1983 and July 1986.

3. Long Range Transport of Atmospheric Pollutants (LRTAP)

The Canadian Long Range Transport of Atmospheric Pollutants (LRTAP) program began interlaboratory comparability studies in December 1982 under the direction of the Quality Assurance and Methods Division of the National Water Research Institute (19). The first study in which the CAL participated was Study L4, which took place in August 1983. The CAL and 35 Canadian laboratories were asked to analyze 11 water samples that included natural waters, precipitation, and synthetic internal reference waters. Those parameters which were routinely analyzed by the participating laboratories were determined. Median concentrations for each parameter were selected from the data reported by all of the participating laboratories. These medians became the target values used to judge laboratory performance. Participants received a rating of satisfactory, moderate, or poor based on the percentage of results from that laboratory that were flagged for being biased high or low. The CAL has consistently received a satisfactory rating.

In 1984-1985, the CAL participated in six LRTAP intercomparison studies. Each study typically requested the participating labs to analyze 10 samples for those parameters routinely determined by the laboratory. In some of the intercomparisons, the samples were primarily surface waters with high ionic strengths. These samples often created problems with the analytical instruments at the CAL because they were unfiltered and frequently contained large amounts of particulate matter. Because these samples were not comparable to the precipitation samples the CAL routinely analyzed a simple screening protocol was established for the selection of samples in each LRTAP study that would be analyzed by the CAL staff. Samples that had a measured specific conductance >100 uS/cm, were highly colored, and/or contained large amounts of particulates were not analyzed by the CAL. For some studies this eliminated all but three samples from those the CAL analyzed. Tables 5

through 10 in Appendix D contain the CAL data and the Canada Center for Inland Waters (CCIW) medians for all of the samples analyzed by the CAL for LRTAP intercomparison studies of "Major Ions, Nutrients and Physical Properties in Water" in 1984 and 1985.

For each study, the participants received study summaries (19, 20, 21, 22) providing the data for all participants and the medians or target values used to assess laboratory performance. Samples considered to be biased high or low, were flagged and the percentage of flagged results was used to rank the participants in each study. Table VI-3 contains these percentages for the CAL as well as a mean percent flagged for all participants. A more detailed explanation of this calculation and the criteria used to determine bias in each study can be found in the project summaries listed in the references. Portions of Table VI-3 appeared in the ISWS 21st Progress Report to the Department of Energy (17).

Although the last published report (22) for these studies was issued for study L-9, summaries of all succeeding studies are available from the CCIW. The study summary for L-11 included a ranking of the

TABLE VI-3 Summary of Results from the Long Range Transport of Atmospheric Pollutants (LRTAP) Program Laboratory Intercomparison Studies.

Laboratory Study #	Date	Number of Participating Labs (n)	Average Score (%) [a]	
			All Labs	ISWS Lab
L-5	01/84	44	31.40	6.00
L-6	04/84	39	31.68	0.00
L-8	11/84	44	33.14	0.00
L-9	04/85	33	27.44	0.00
L-10	08/85	42	26.98	0.00
L-11	12/85	51	31.92	10.00

a. Average score equals the combined percent of results that were either flagged or biased. If all results were flagged and determined to be biased, a maximum score of 200% is possible.

participating laboratories based on their performance in studies 6, 8, 9, 10, and 11. The summary ranked 51 laboratories according to the accuracy of the data submitted. Of these 51 laboratories, only 25 (including the CAL) had participated in all 5 studies. The percentage of biased results for the combined studies was the criterion used to determine the laboratory ranking. The CAL was ranked first with an average score of 2.0%. The mean score for all 51 laboratories was 34.6%. Examination of the CAL data in Table VI-3 shows that the CAL results are consistently characterized by a lack of bias for all of these LRTAP studies (22). As with the summary results from the WMO intercomparisons, the CAL scores on the LRTAP studies indicate that consistency and a lack of bias are typical for the CAL results.

4. European Monitoring and Evaluation Program (EMEP)

The third international program that the CAL participated in during this time period was sponsored by the Norwegian Institute for Air Research in Lillestrom, Norway. Designated the EMEP, this project is designed to assess the comparability of analytical methods in use by European laboratories conducting research in the area of acidic deposition. This program is a cooperative effort of the United Nations Economic Committee for Europe as a part of the monitoring and evaluation of the long range transport of air pollutants in that region (23).

Four synthetic precipitation samples containing known amounts of sulfate, nitrate, ammonium, strong acid, magnesium, sodium, chloride, calcium, and potassium were provided to each laboratory participating in this study, with the results forwarded to the Norwegian Institute for compilation and data reporting. Supporting methods documentation and quality assurance protocols in use at each facility were also provided. The CAL laboratory was first invited to participate in this program in 1984. A summary of the CAL measured results compared with the expected concentrations is presented in Table VI-4. No data on the performance of the CAL laboratory relative to the rest of the EMEP participants is available; however, the mean percent deviation of the CAL results was approximately 4%. This value is consistent with the mean percent deviations reported for the WMO and LRTAP intercomparisons.

Continued participation in interlaboratory comparisons such as this is an integral part of the CAL's quality assurance program. In addition to providing an independent assessment of the accuracy of our laboratory measurements, the methods documentation supplied with the analytical results forms a data base that can be used by all participants to compare their methodologies to those used by other laboratories.

TABLE VI-4   EMEP Study #8 Interlaboratory Comparison Study
April 1984 – CAL Reported Values
Compared to EMEP Expected Values.

Parameter	G1 EMEP	G1 CAL	G2 EMEP	G2 CAL	G3 EMEP	G3 CAL	G4 EMEP	G4 CAL
Calcium (mg/L)	0.97	0.962	0.58	0.577	0.46	0.461	0.89	0.884
Magnesium (mg/L)	0.46	0.444	0.40	0.386	0.10	0.097	0.08	0.077
Sodium (mg/L)	1.57	1.54	3.59	3.44	3.99	3.84	1.80	1.76
Potassium (mg/L)	0.43	0.429	0.52	0.505	0.22	0.213	0.17	0.172
Ammonium (mg/L)	0.31	0.27	0.26	0.22	1.12	1.11	1.40	1.37
Nitrate + Nitrite (mg/L)	4.25	4.24	2.43	2.44	2.08	2.07	4.82	4.82
Chloride (mg/L)	2.33	2.32	2.13	2.13	2.69	2.69	3.14	3.15
Sulfate (mg/L)	5.09	4.67	7.82	7.70	8.51	8.39	5.48	5.18
pH (units)	4.24	4.28	4.78	4.78	4.88	4.85	4.16	4.18
Specific Conductance (uS/cm)	44.0	46.6	35.6	38.3	38.3	41.0	52.7	56.1

VII. SUMMARY

When first organized, the NADP established as one of its primary goals the production of analytical data which were of the highest quality. To achieve this end, the NADP Quality Assurance Plan-Deposition Monitoring (2) was developed in 1984 to clearly define the guidelines for field, laboratory, and data management operations. This QA Plan also fully documents the requirements of the network for all three areas of operation.

The CAL was directed to produce data whose precision and bias were quantified. Minimum method detection limits were established for all analytical parameters, and limits for variance in accuracy were defined. Finally, complete documentation of all quality assurance procedures in use at the CAL was required as well as annual reports of the information derived from the quality assurance data.

The QA Report for 1978-1983 (1) described the early stages in the development of the CAL laboratory quality assurance program. The present report continues that documentation by detailing the refinements to the program that occurred during 1984 and 1985. Suggestions from members of NADP/NTN Subcommittee 2 on Quality Assurance were integral to this continued development, as were the guidelines set forth in the QA Plan.

The data presented in this report indicate that the CAL has been successful in meeting the network requirements as detailed in the QA Plan (2). The analytical bias and precision tables in Section IV show that the desired limits for variance in accuracy were achieved. The MDLs listed in Table II-1 meet or exceed those listed in the QA Plan. The initiation of an internal blind program, coupled with the changes to the replicate analysis procedures, provide the data user with additional information for assessing the quality of the CAL data. The data that result from these new procedures provide a truer indication of the quality of the network sample data than did the information obtained from the analysis of internal reference samples alone. Confirmation of the CAL data quality is provided by the CAL's performance in several interlaboratory performance studies. Table VII-1 highlights the changes that have occurred to the laboratory quality assurance program.

The analytical methods manual (3) that became available in 1986 documents all the laboratory procedures used to analyze the network samples. This report in conjunction with the one published in 1987 (1) provides documentation of the procedures and the data produced for the laboratory quality assurance program through 1985. The CAL, in conjunction with the NADP/NTN Quality Assurance Manager and the Coordinator's Office, is currently working to provide quality assurance data in a more timely manner, thus meeting all of the goals of the Quality Assurance Plan.

TABLE VII-1   Changes to the Laboratory Quality Assurance Program.

A. Documentation of Standard Operating Procedures
   1984-1985 – Development of analytical methods manual (includes new method for calculating MDL).
   1987 – Publication of Quality Assurance Report for 1978-1983 (March).

B. Change in Analytical Methods
   1985 – Analysis of sulfate, nitrate, and chloride ions changed from automated wet chemical methods to ion chromatography resulting in minor changes in the MDLs for the three ions (May).

C. New Facilities
   1985 – Move to new facilities results in improved laboratory, office, and storage areas; equipment to maintain a clean air environment installed in the laboratories; new deionizing system installed; walk-in coolers available for sample and supplies storage (November).

D. Laboratory Blanks
   1982 – Dishwasher installed to wash buckets; city tap water used for wash cycle with DI water rinse (May).
   1984 – Dishwasher replumbed to use only DI water for all cycles (November).
   1984 – pH and specific conductance measured for all blank samples (January).
   1984-1985 – Special bucket blank studies performed to investigate both prolonged and normal exposure of acidic solutions and prolonged exposure of DI water to the sample containers.

TABLE VII-1 (concluded) Changes to the Laboratory
Quality Assurance Program.

E. Analytical Bias and Precision
    1984 - O/Q replicate split analyses begun (July).
    1984 - Internal blind sample program begun (July).

F. Reanalysis
    1981 - Criteria for IPD and CPD established (October).
    1987 - Factors used to calculate conductivity changed
           (March).

G. Interlaboratory Comparisons
    1980 - First CAL participation in WMO intercomparisons.
    1981 - Certification as an environmental laboratory
           granted by IEPA; recertification obtained in
           1983 (December) and 1986 (July).
    1982 - USGS interlaboratory comparisons begun
    1983 - First CAL participation in LRTAP inter-
           laboratory comparability studies (August).
    1984 - First CAL participation in EMEP studies (April).

TABLE VII-I (concluded) Changes to the Laboratory
Quality Assurance Program.

B. Analytical Bias and Precision
1984 - ORP replicate split analyses begun (July).
1984 - Internal blind sample program begun (July).

C. Reanalysis
1981 - Criteria for TNC and CPD established (December).
1987 - Factors used to calculate conductivity changed
       (March).

D. Interlaboratory Comparisons
1980 - First CAL participation in CPD intercomparisons.
1981 - Certification as an environmental laboratory
       granted by IERA; recertification obtained in
       1983 (December) and 1985 (Italy).
1982 - USGS interlaboratory comparisons begun
1983 - First CAL participation in ERDAL inter-
       laboratory comparability studies (August).
1984 - First CAL participation in EMSP studies (April).

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APPENDIX A

Glossary of Terms

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

Term	Abbreviation	Definition
Critical Percent		A calculated percent used to determine if the measured bias is or is not statistically significant. It is calculated from the formula:

$$\text{critical } \% = \frac{s_{sp} - t_{0.95,(nl + n2)-2}}{\overline{x}_{true}} \times 100$$

where:

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

and:

s = standard deviation
n = number of values

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

External Blind Sample

A quality assurance sample of known analyte concentrations submitted to the CAL by an external agency. These samples arrive in normal sample containers and undergo routine processing and analysis. The fact that the sample was not a routine sample is not known by the CAL until all analyses are complete. Data from the analysis of these samples can be used to assess the potential for contamination of the network samples through routine field and laboratory handling procedures.

Internal Blind Sample

A quality assurance sample of known analyte concentrations submitted for sample processing and routine analysis by the Laboratory Quality Assurance Specialist. The fact that these samples are blinds is known only to the processing staff. The expected analyte concentrations are unknown to both the processing staff and the analysts. Data from the analysis of these samples provide another means of assessing laboratory bias and precision.

Laboratory Spike

A known volume of analyte added to one portion of a replicate or split sample. The concentration of the added analyte should approximate that found in the unspiked sample. The difference in analyte concentration between the spiked and unspiked samples is used to determine the percent recovery. These samples are used in methods development and comparisons and provide an estimate of the accuracy of the methods selected for analysis.

Mean

$$\bar{x} = \sum_{i=1}^{n} x_i/n$$

Mean Bias $\dfrac{\sum \text{bias for each sample}}{\text{total number of replicates (n)}}$

Mean Percent $\dfrac{\sum \text{percent recovery for each sample}}{\text{total number of replicates (n)}}$
Recovery

Method Detection   MDL   The minimum concentration of an
   Limit   analyte that can be reported with
99% confidence that the value is
above zero. The MDL is operation-
ally defined as:

$$MDL = (s)t_{n-1, 1-\alpha = 0.99}$$

where:

s = standard deviation of
repetitive measurements (≥ 7)
of a solution containing the
analyte at a concentration near
the estimated MDL.

$t_{n-1, 1-\alpha = 0.99}$ = student's t value for a one-
tailed test appropriate for a
99% confidence level and a
standard deviation estimate
with n-1 degrees of freedom.

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:

$$\% \text{ Bias} = 100 \times [(V_m - V_t)/V_t]$$

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:

$$\% \text{ Recovery} = 100 \times [(a-b)/c]$$

where:

        a = measured concentration
            of spiked sample

b = measured concentration
of unspiked sample

c = calculated spike
concentration

Precision

The degree of agreement of repeated measurements of a homogenous sample by a specific procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation (s).

Quality Assessment

The system of procedures that ensures that quality control practices are achieving the desired goal in terms of data quality. This includes continuous evaluation of analytical performance data.

Quality Assurance
Program

A program designed to reduce measurement error to tolerable limits and provide the means of ensuring data validity. This includes 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   QCS
Check Sample

A sample containing known concentrations of analytes . The laboratory uses this sample to routinely demonstrate that it can obtain acceptable results with procedures being used to analyze wet deposition samples. Analyte true values are known by the analyst.

Relative Standard
Deviation

RSD

The standard deviation expressed as a percentage.

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

where: s = sample standard
deviation
$\overline{x}$ = mean value

Replicates
(Splits)

Two aliquots of the same sample treated identically throughout a laboratory analytical procedure. Analyses of laboratory replicates indicate the precision associated with laboratory procedures but not with sample collection and field handling (processing). These samples may also be referred to as splits.

Sensitivity

The method signal response per unit of analyte.

Standard Deviation

s

A number that represents the dispersion of values around their mean, calculated as:

$$s = \sqrt{\frac{\sum (x_i - \overline{x})^2}{n - 1}}$$

where: x_i = each individual
value
$\overline{x}$ = average of all
values
n = number of values

Relative Standard
Deviation

RSD

The standard deviation expressed as a percentage.

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

where: s = sample standard deviation
$\bar{x}$ = mean value

Replicates

Two aliquots of the same sample treated identically throughout a laboratory analytical procedure. Analyses of laboratory replicates indicate the precision associated with laboratory procedures but not with sample collection and field handling (processing). These samples may also be referred to as splits.

Sensitivity

The method signal response per unit of analyte.

Standard Deviation

s

A number that represents the dispersion of values around their mean, calculated as:

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n - 1}}$$

where: x_i = each individual value
$\bar{x}$ = average of all values
n = number of values

APPENDIX B

Laboratory Blanks
Plots and Tables
1984–1985
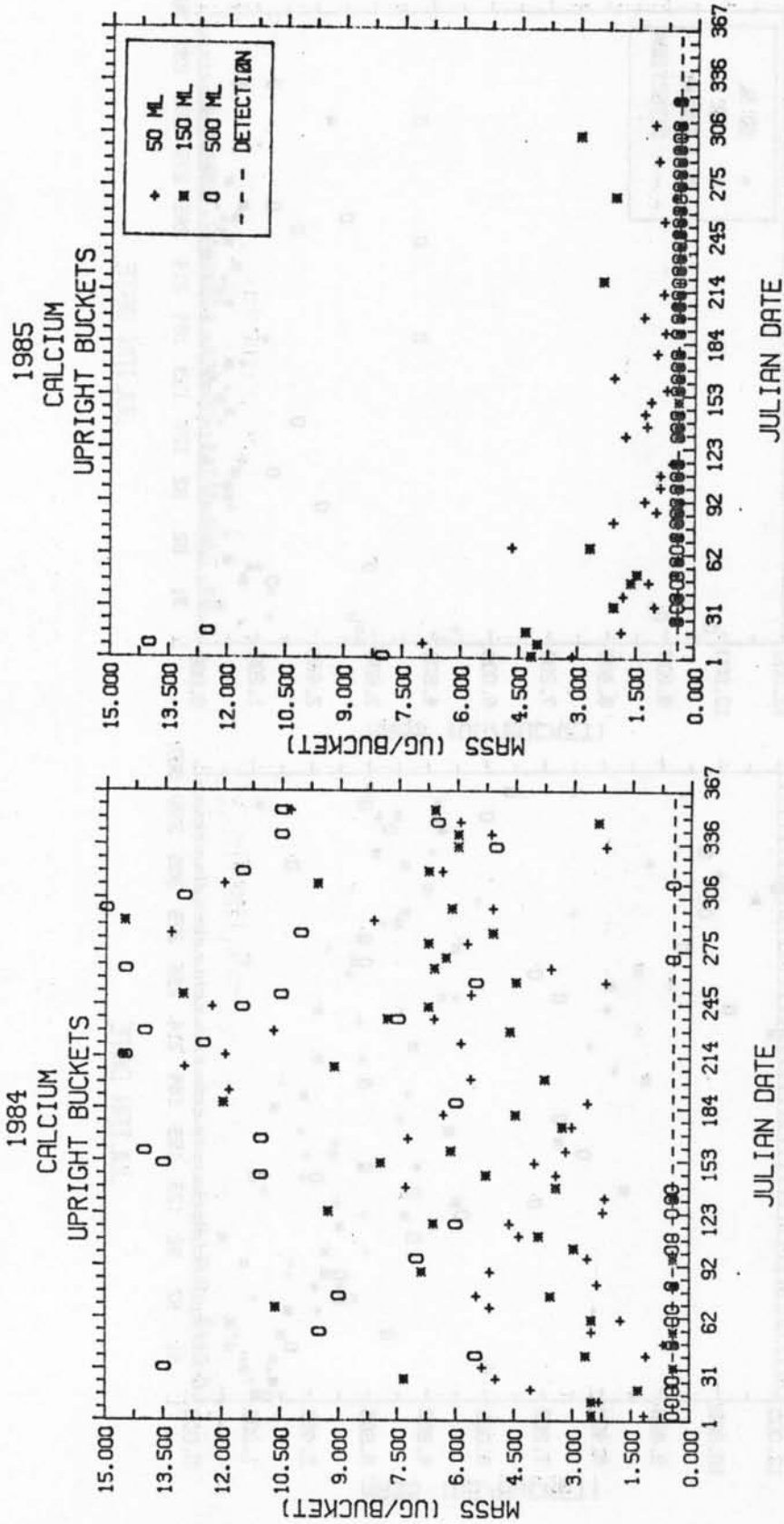
FIGURE 1. Measured calcium mass in upright bucket blanks for 1984 and 1985.
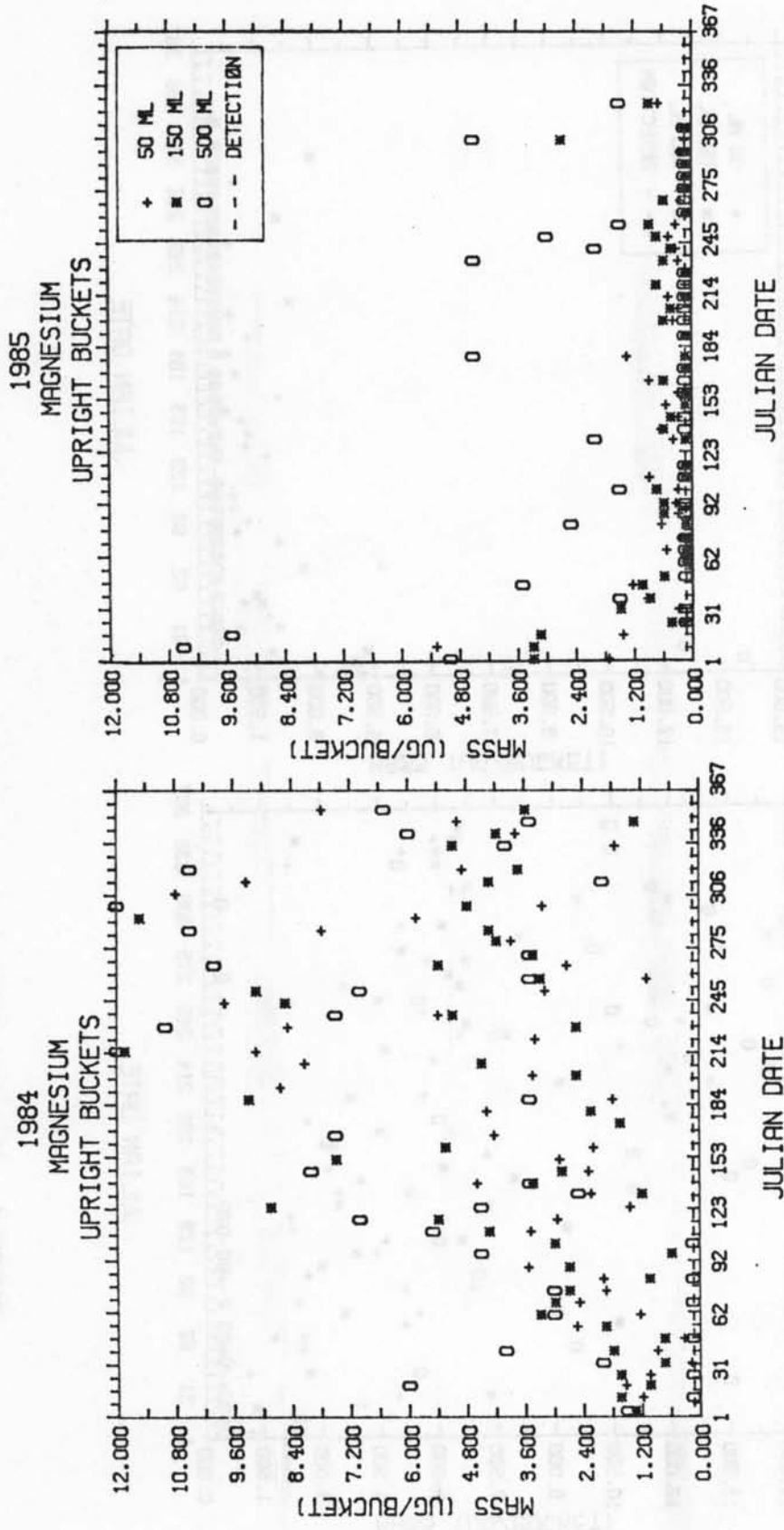
FIGURE 2. Measured magnesium mass in upright bucket blanks for 1984 and 1985.
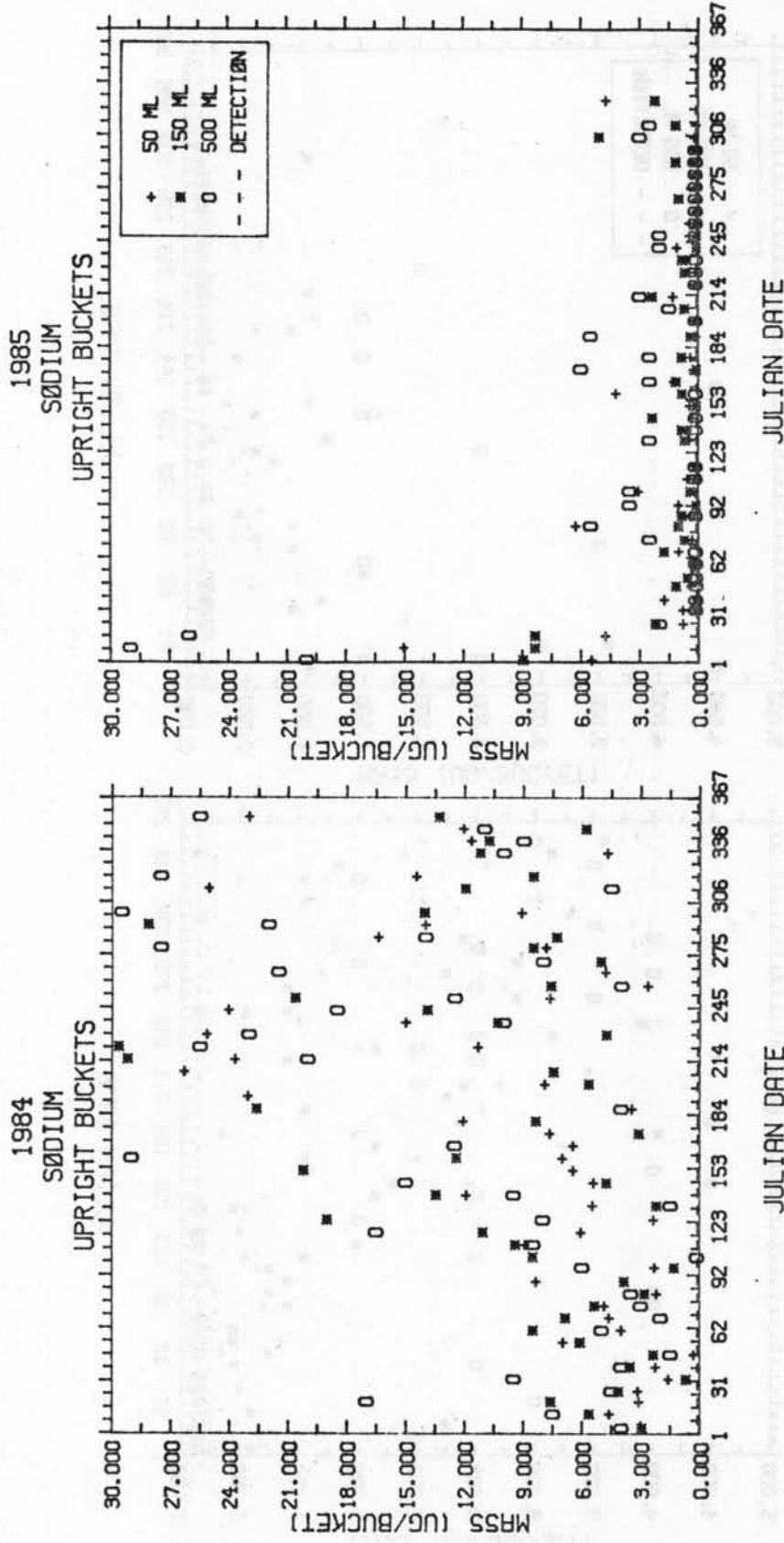
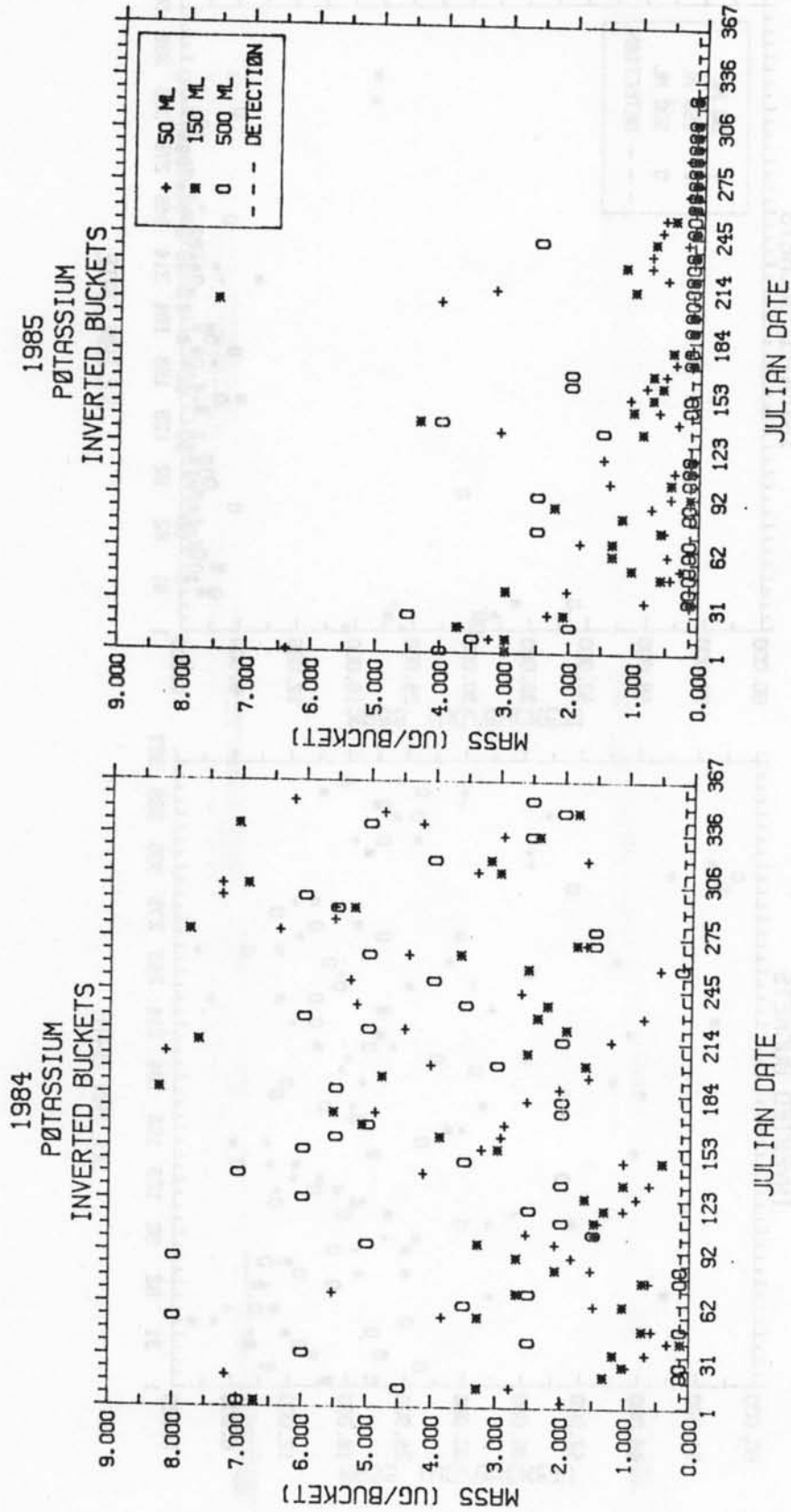FIGURE 3. Measured sodium mass in upright bucket blanks for 1984 and 1985.
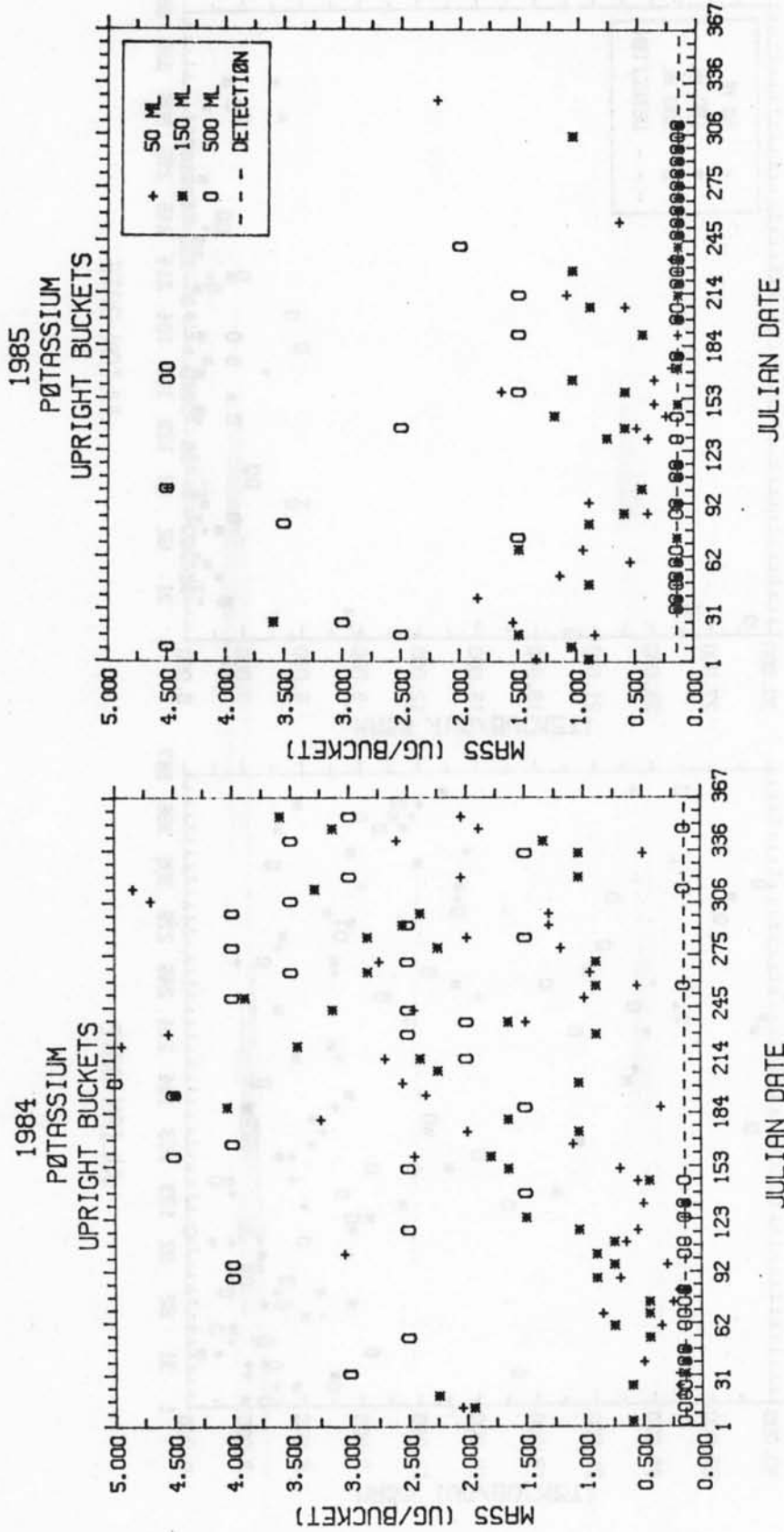
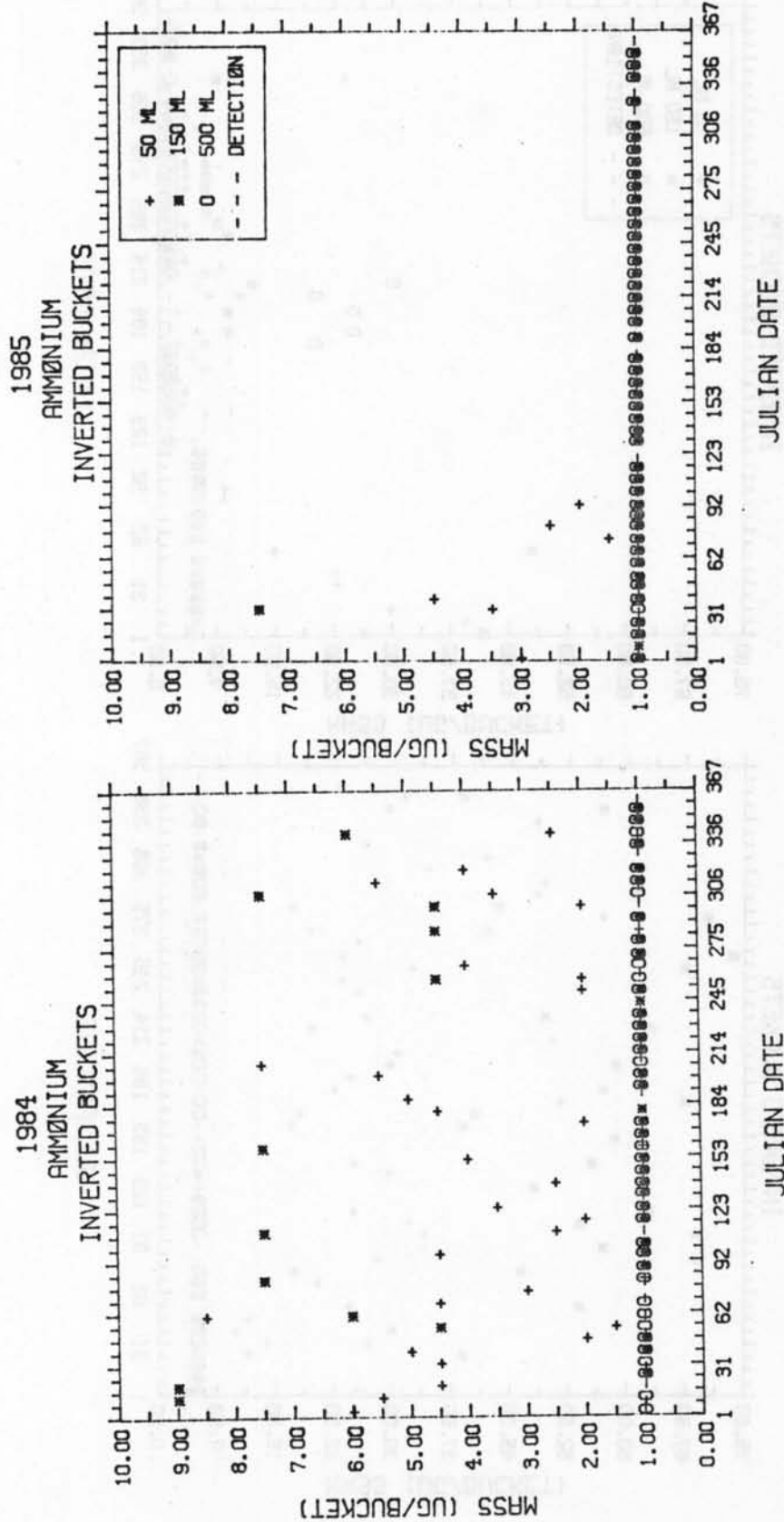FIGURE 4. Measured potassium mass in upright bucket blanks for 1984 and 1985.
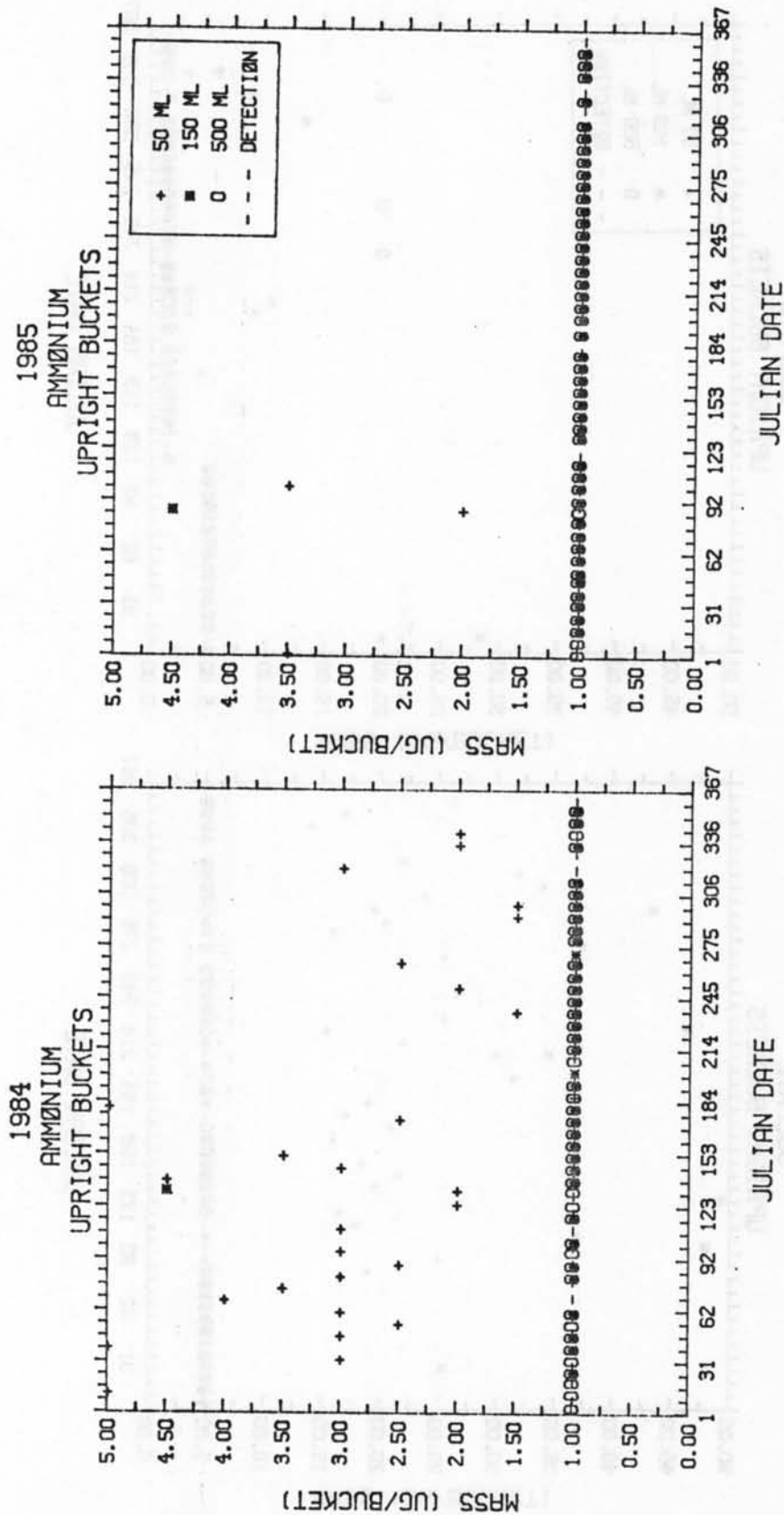
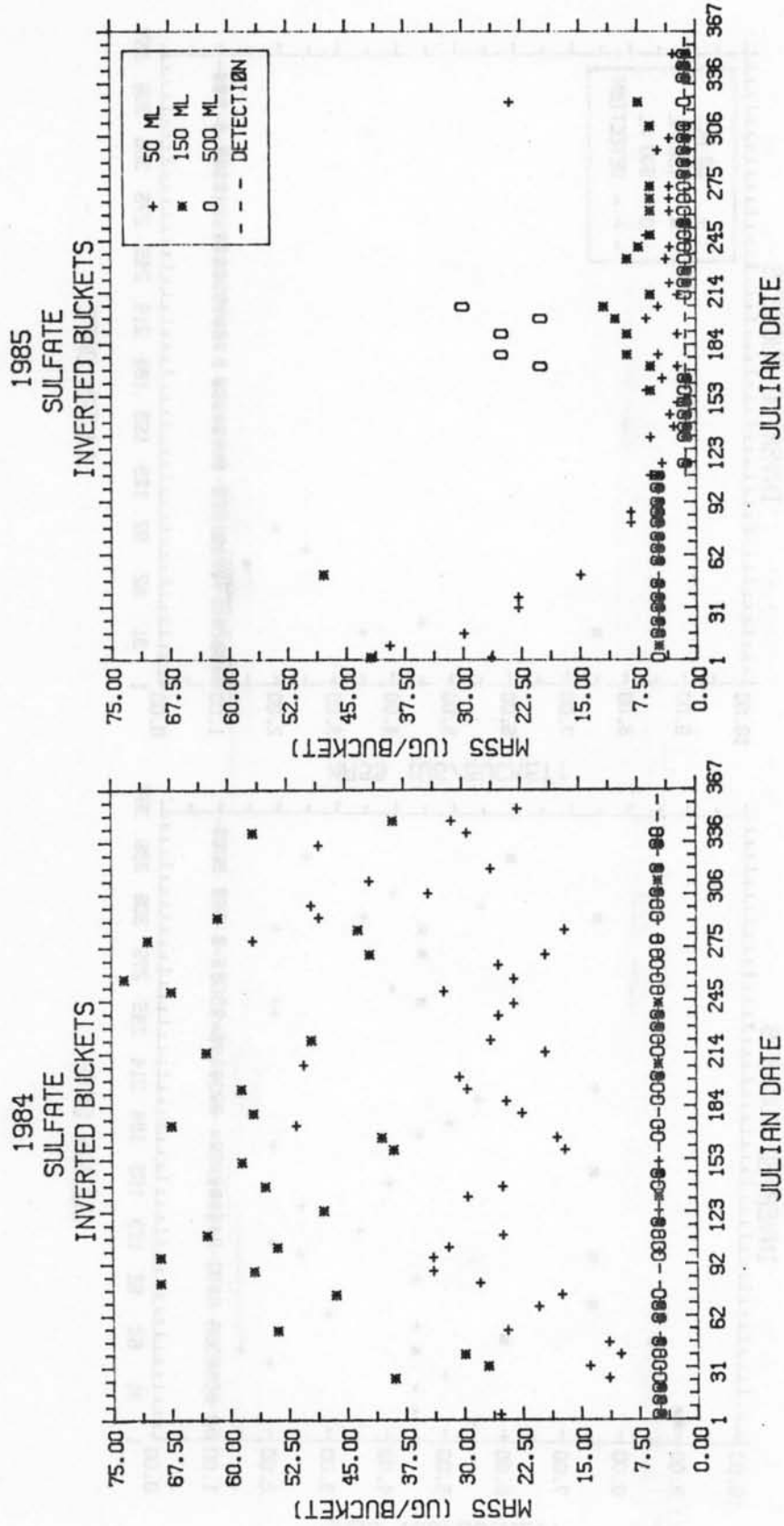FIGURE 5. Measured ammonium mass in upright bucket blanks for 1984 and 1985.
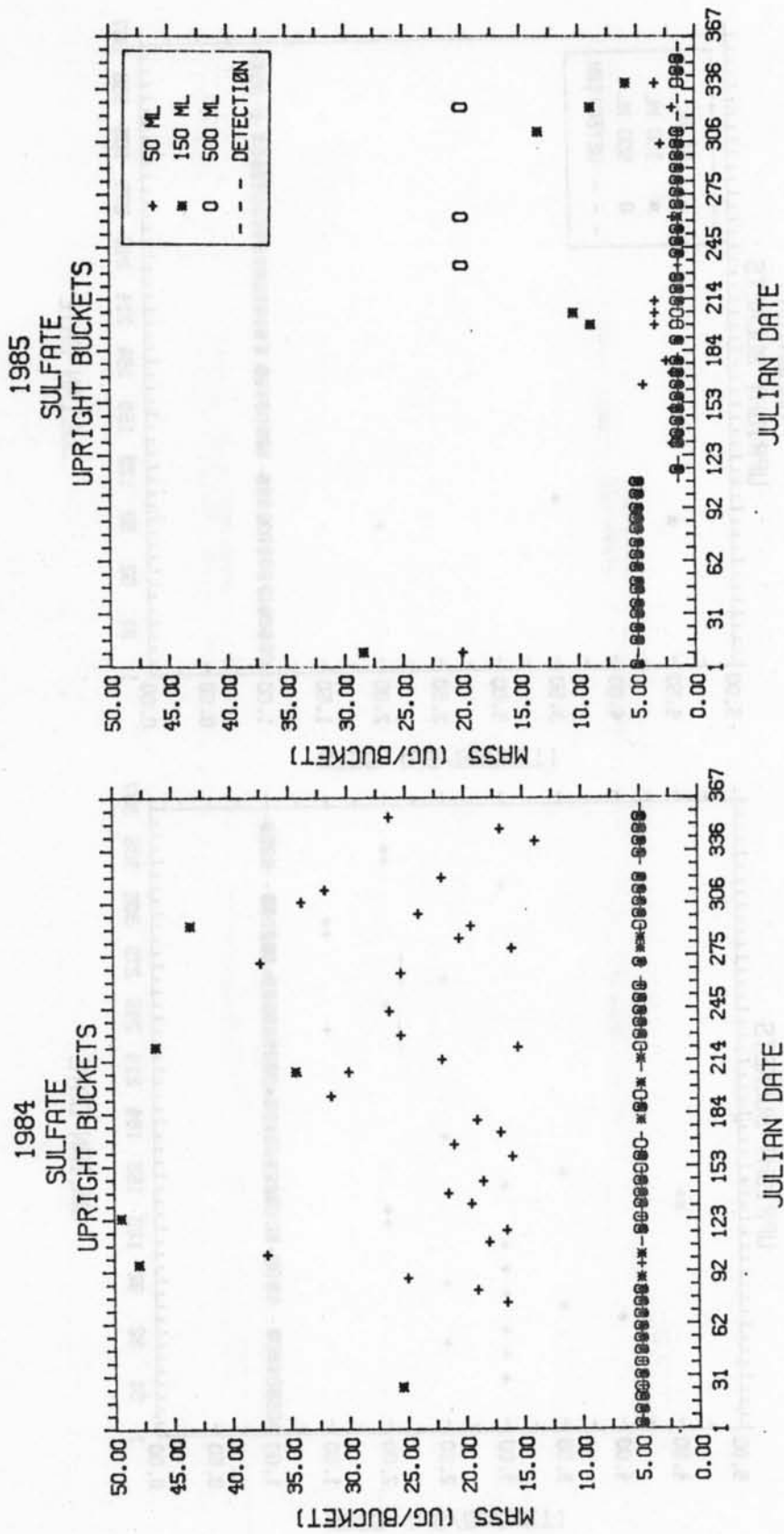
FIGURE 6. Measured sulfate mass in upright bucket blanks for 1984 and 1985.
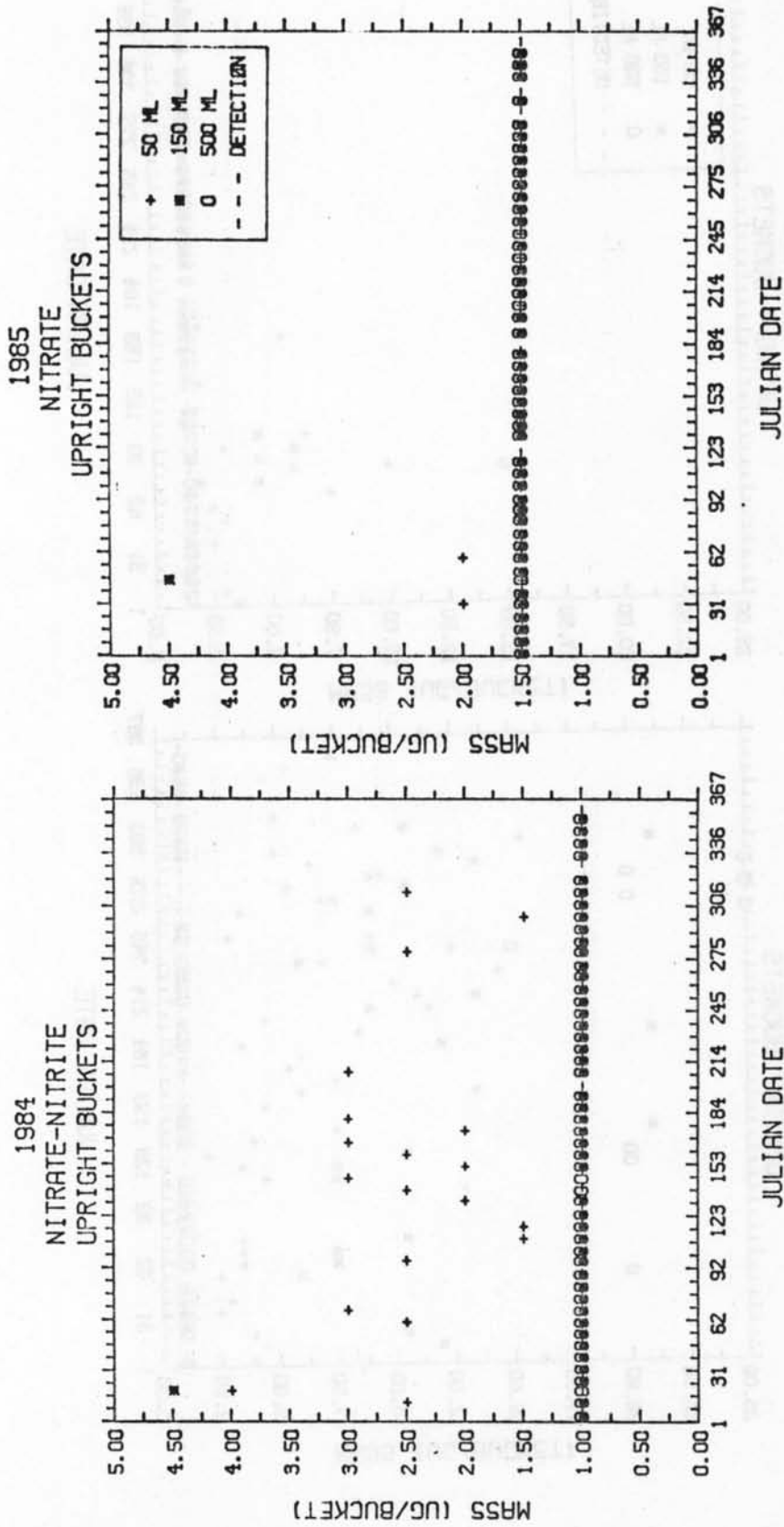
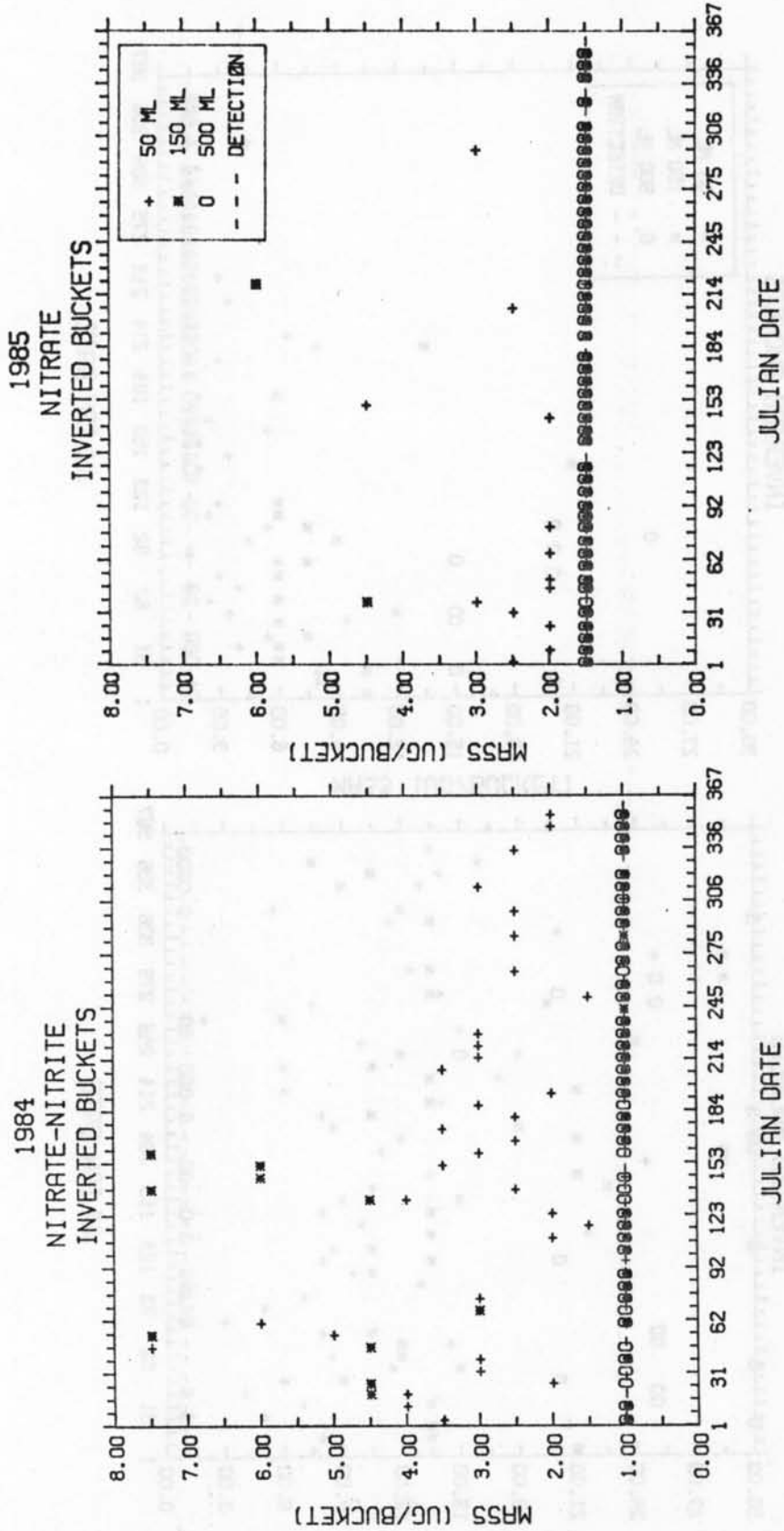FIGURE 7. Measured nitrate-nitrite mass in upright bucket blanks for 1984 and measured nitrate mass in upright bucket blanks for 1985.
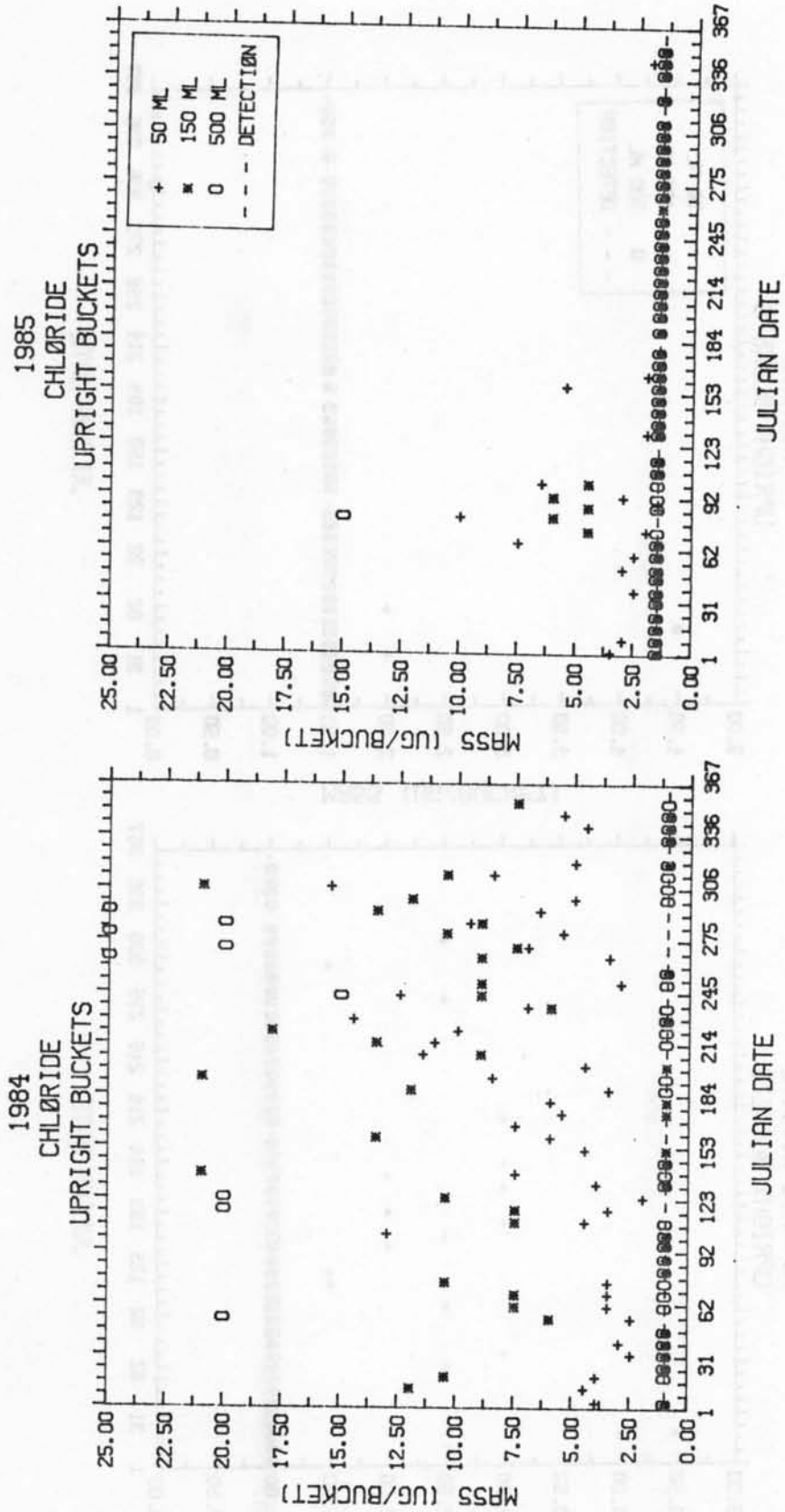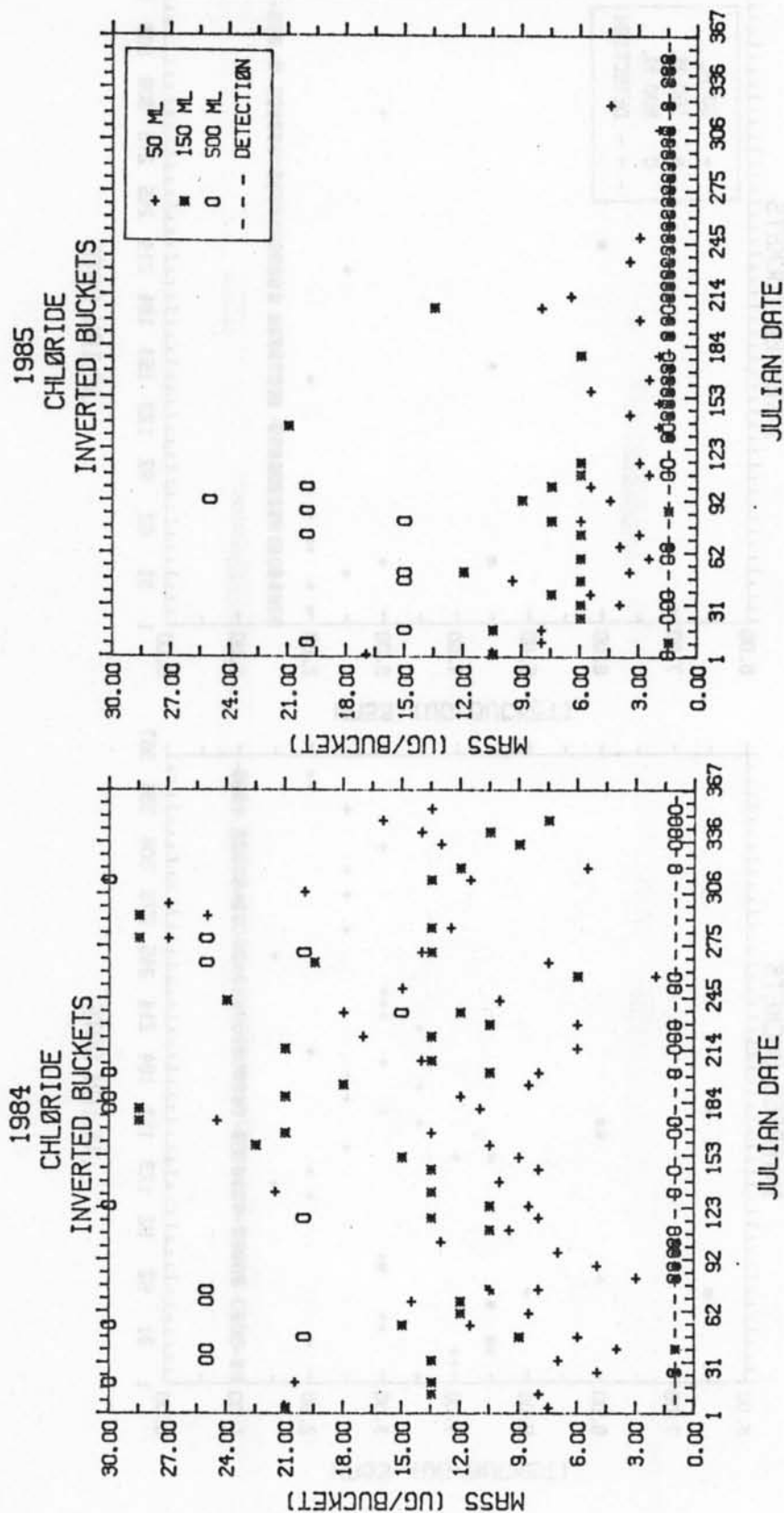
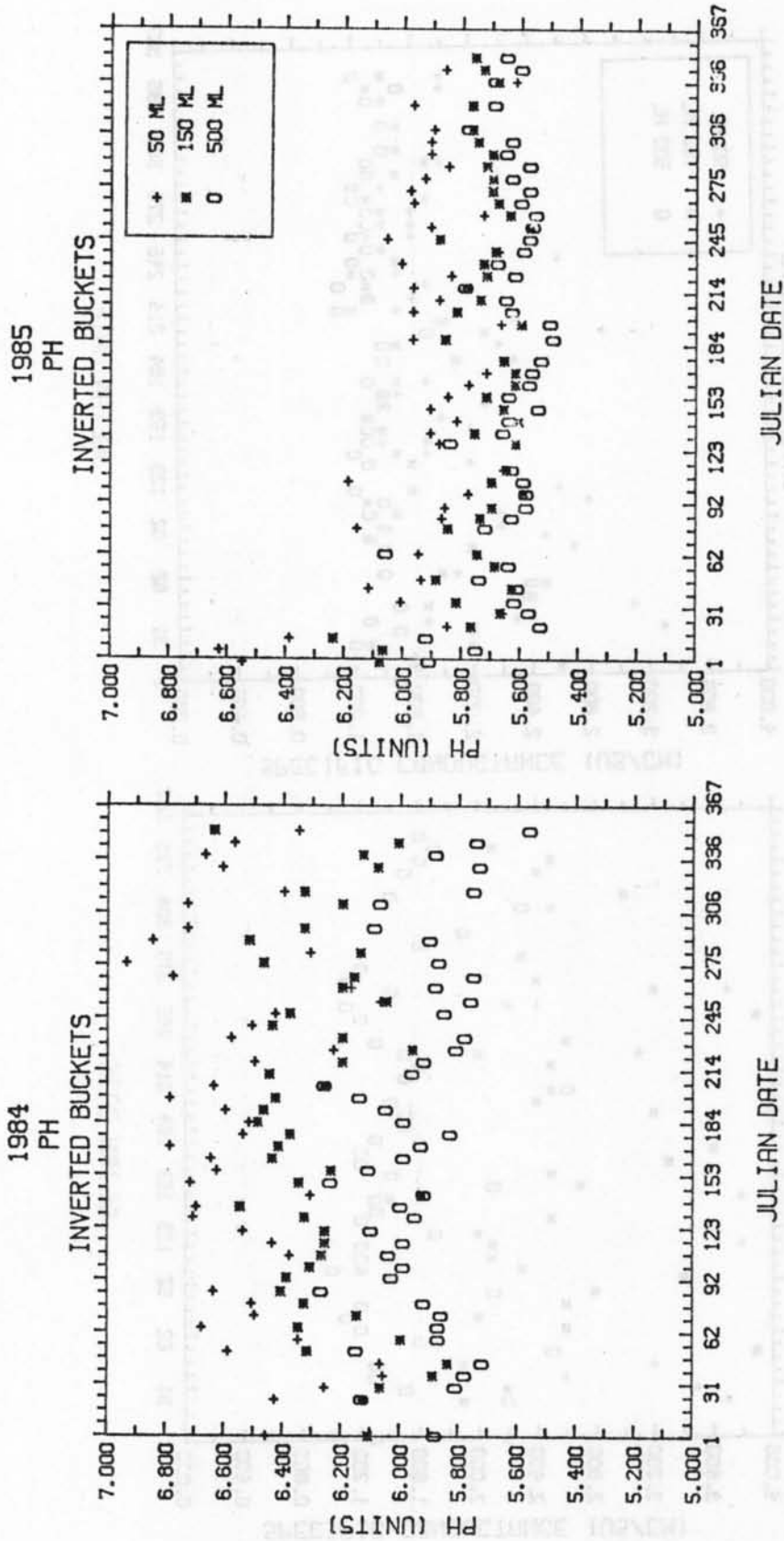FIGURE 8. Measured chloride mass in upright bucket blanks for 1984 and 1985.
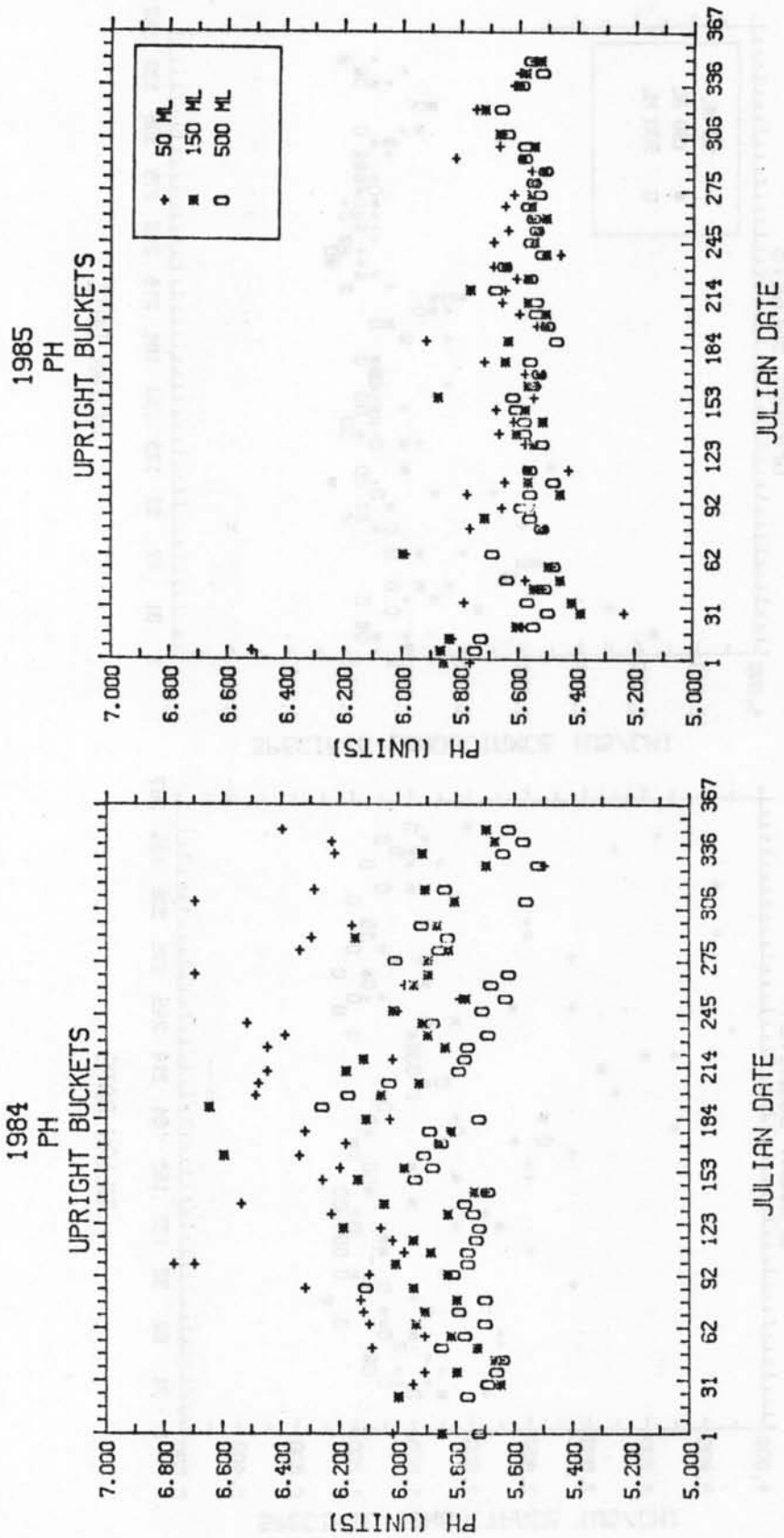
FIGURE 9. Measured pH in upright bucket blanks for 1984 and 1985.
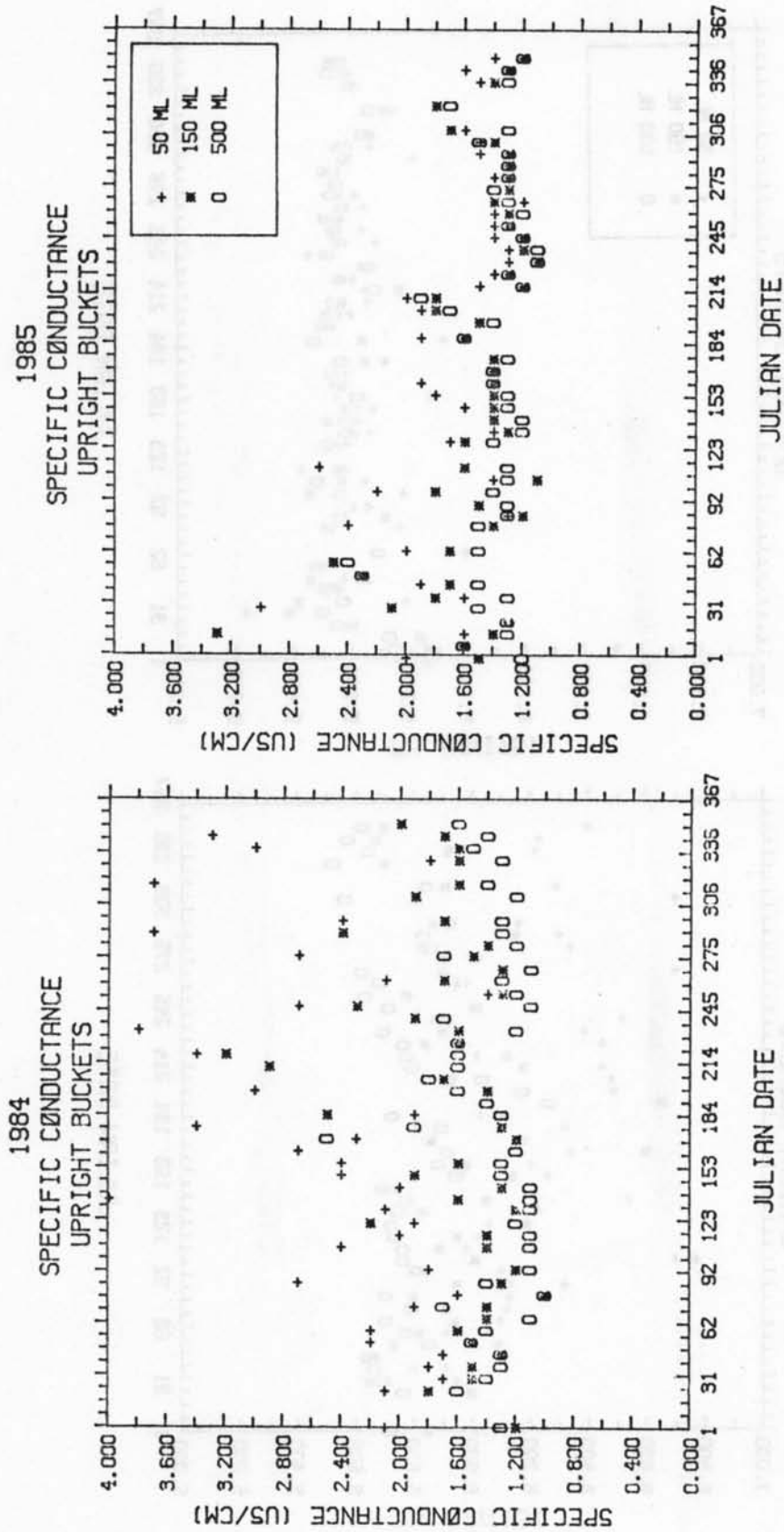
FIGURE 10. Measured specific conductance in upright bucket blanks for 1984 and 1985.
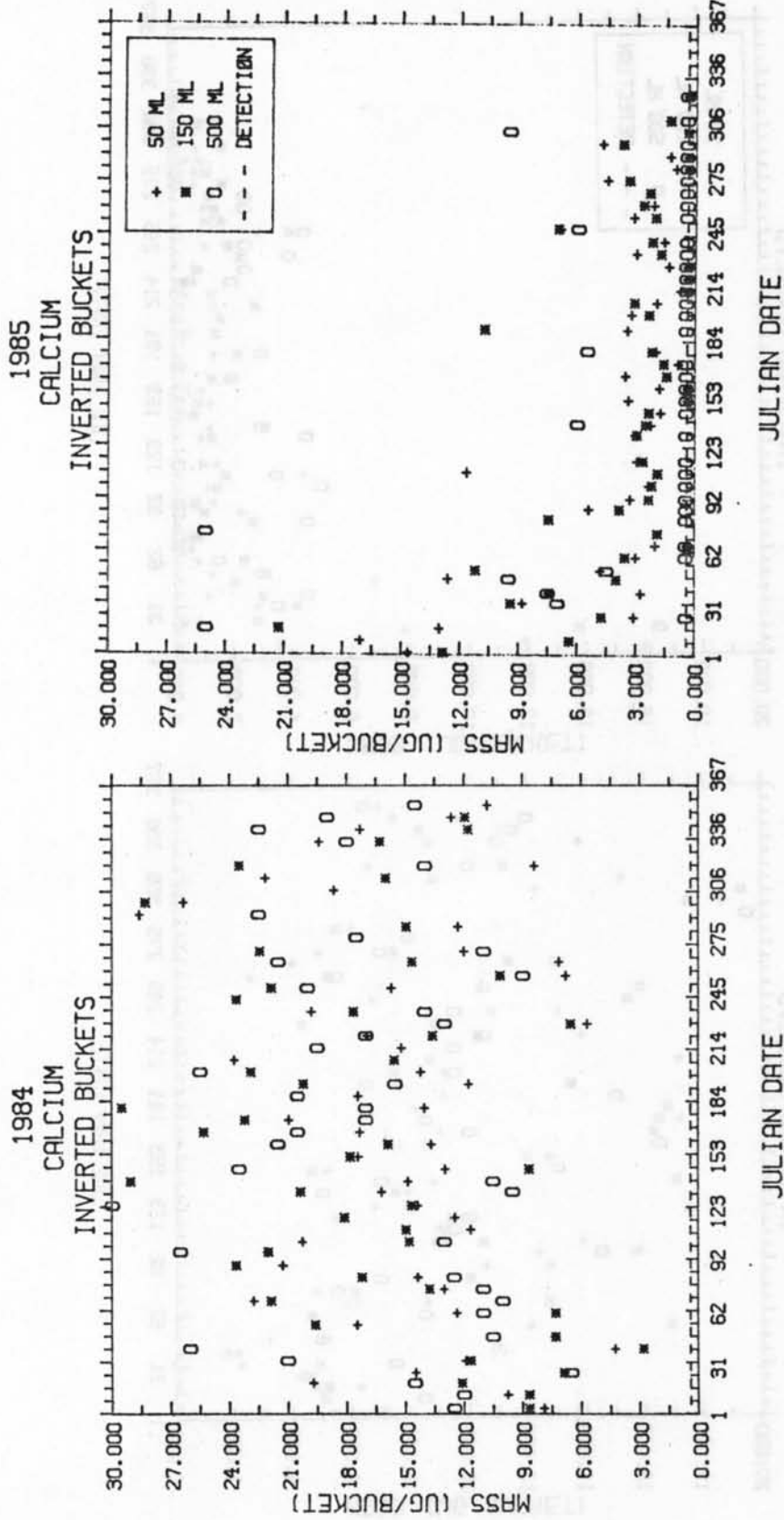
FIGURE 11. Measured calcium mass in inverted bucket blanks for 1984 and 1985.
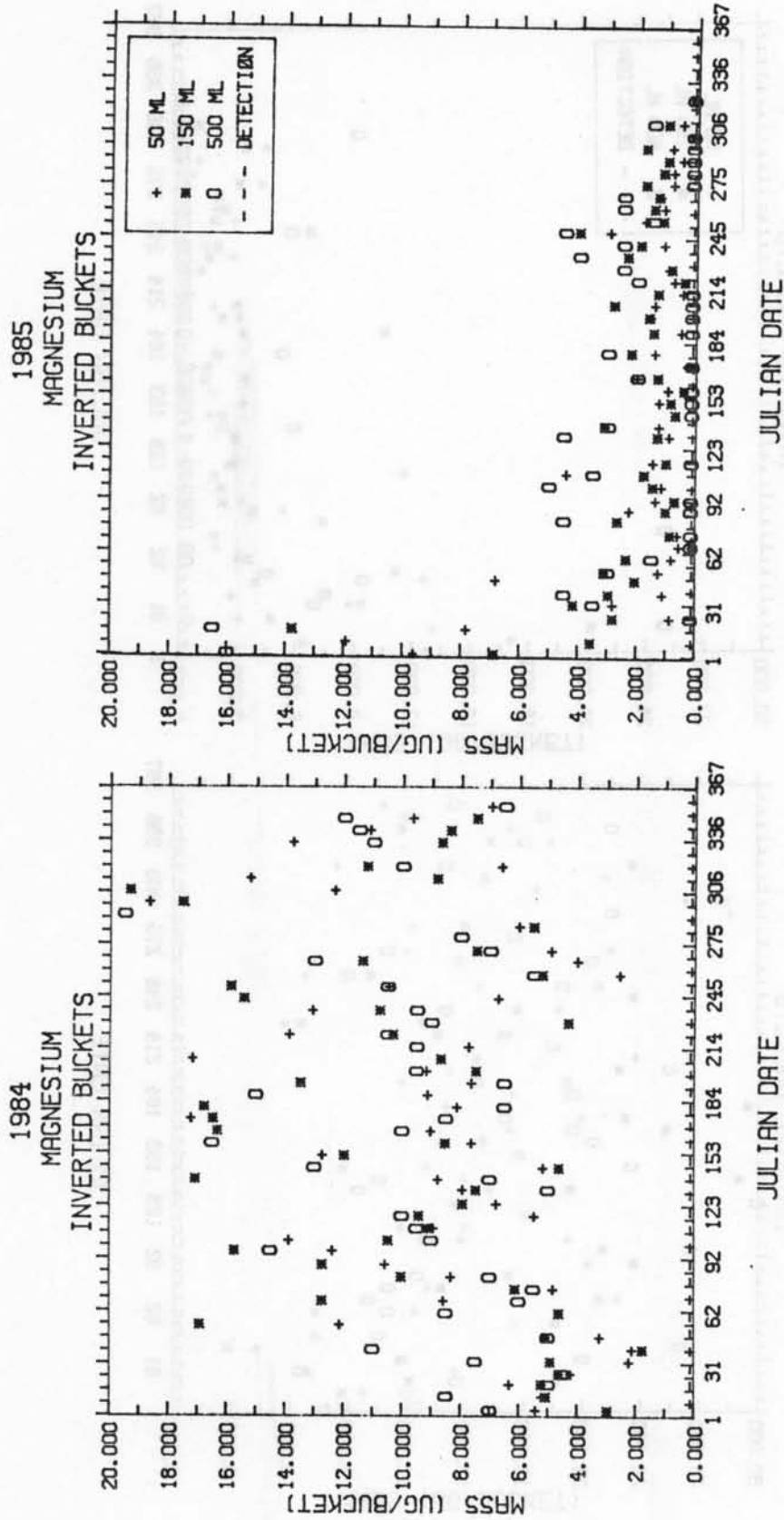
FIGURE 12. Measured magnesium mass in inverted bucket blanks for 1984 and 1985.
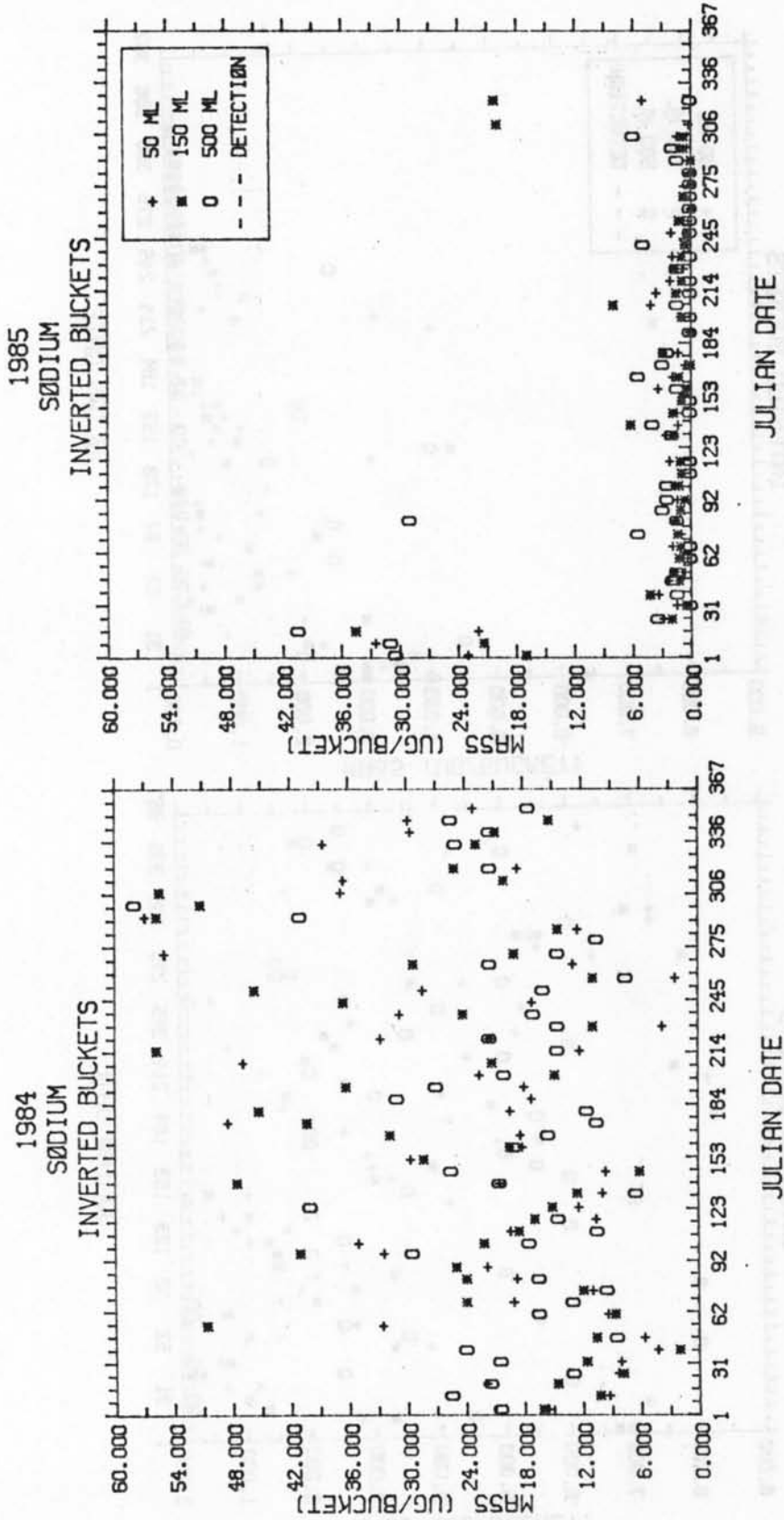
FIGURE 13. Measured sodium mass in inverted bucket blanks for 1984 and 1985.

FIGURE 14. Measured potassium mass in inverted bucket blanks for 1984 and 1985.

FIGURE 15. Measured ammonium mass in inverted bucket blanks for 1984 and 1985.

FIGURE 16. Measured sulfate mass in inverted bucket blanks for 1984 and 1985.

FIGURE 17. Measured nitrate-nitrite mass in inverted bucket blanks for 1984 and measured nitrate mass in inverted bucket blanks for 1985.

FIGURE 18. Measured chloride mass in inverted bucket blanks for 1984 and 1985.

FIGURE 19. Measured pH in inverted bucket blanks for 1984 and 1985.
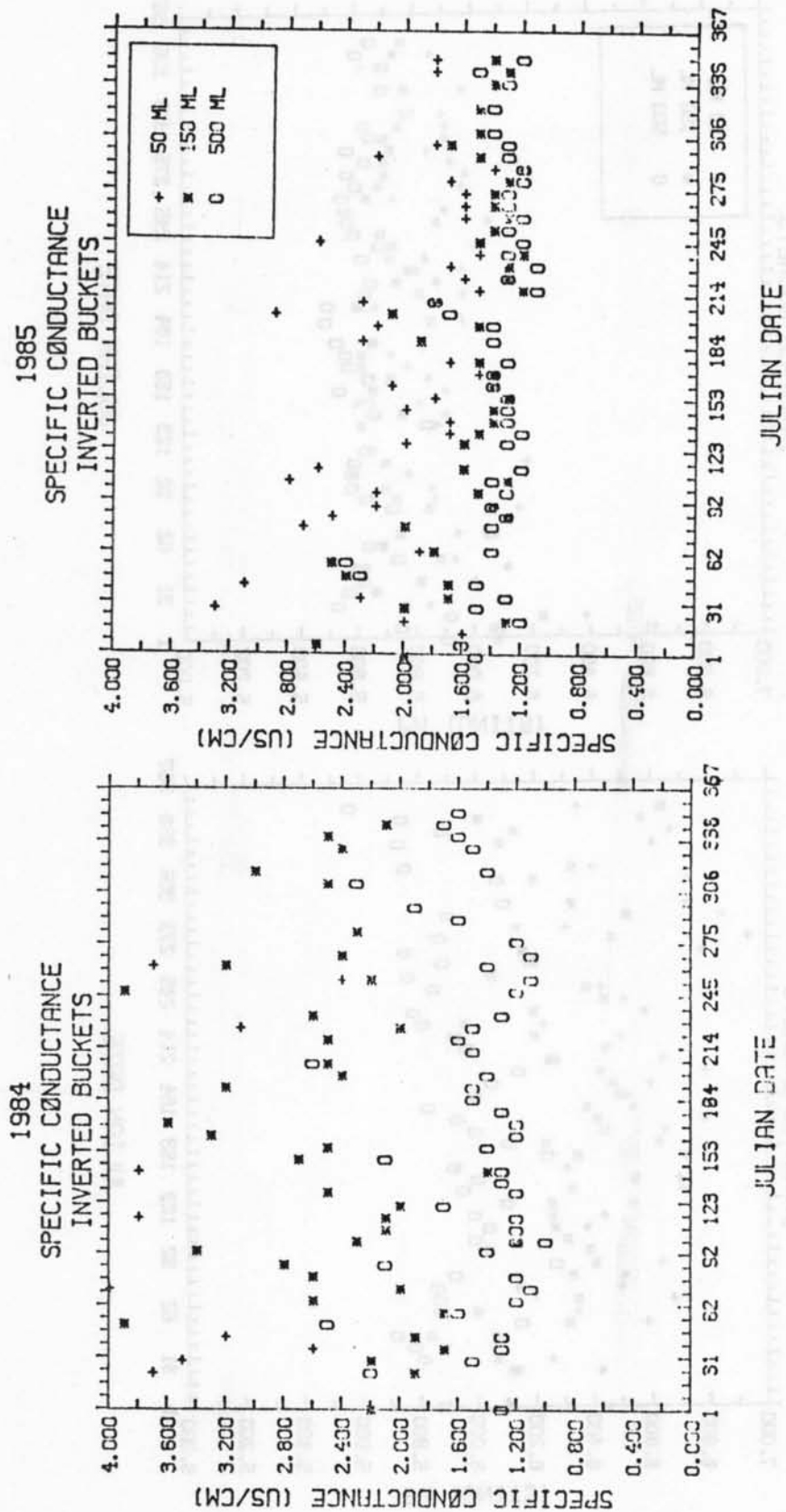
FIGURE 20. Measured specific conductance in inverted bucket blanks for 1984 and 1985.

**TABLE 1   Minimum Detectable Mass Values for Bucket
Blanks Analyzed in 1984 and 1985.**

Analyte	Minimum Mass Value (ug/bucket)	
	1984	1985
Calcium	0.45	0.45
Magnesium	0.15	0.15
Sodium	0.15	0.15
Potassium	0.15	0.15
Ammonium	1.0	1.0
Sulfate	5.0	1.5
Nitrate-Nitrite	1.0	1.5
Chloride	1.0	1.5
Orthophosphate	0.15	0.15

TABLE 2 Analyte Concentration Summary for Filter Leachate A for 1984.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	50	0.009	98.0	<0.009	<0.009
Magnesium	50	0.003	90.0	<0.003	0.004
Sodium	50	0.003	46.0	0.004	0.012
Potassium	50	0.003	84.0	<0.003	0.004
Ammonium	50	0.02	78.0	<0.02	0.05
Sulfate	50	0.10	74.0	<0.10	0.39
Nitrate-Nitrite	50	0.02	88.0	<0.02	0.02
Chloride	50	0.02	78.0	<0.02	0.05
Ortho-phosphate	50	0.003	90.0	<0.003	0.010

a. number of analyses

TABLE 3 Analyte Concentration Summary for Filter Leachate B for 1984.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	50	0.009	96.0	<0.009	<0.009
Magnesium	50	0.003	94.0	<0.003	<0.003
Sodium	50	0.003	80.0	<0.003	0.006
Potassium	50	0.003	90.0	<0.003	0.004
Ammonium	50	0.02	80.0	<0.02	0.05
Sulfate	50	0.10	80.0	<0.10	0.41
Nitrate-Nitrite	50	0.02	100.0	<0.02	<0.02
Chloride	50	0.02	88.0	<0.02	<0.02
Ortho-phosphate	50	0.003	80.0	<0.003	0.007

a. number of analyses

TABLE 4 Analyte Concentration Summary for Filter
Leachate A for 1985.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	47	0.009	87.0	<0.009	0.010
Magnesium	47	0.003	59.6	<0.003	0.006
Sodium	47	0.003	23.4	0.010	0.042
Potassium	47	0.003	95.7	<0.003	<0.003
Ammonium	45	0.02	97.8	<0.02	<0.02
Sulfate					
AC	15	0.10	100.0	<0.10	<0.10
IC	30	0.03	86.7	<0.03	0.04
Nitrate-					
Nitrite AC	15	0.02	93.3	<0.02	0.02
Nitrate IC	30	0.03	90.0	<0.03	0.05
Chloride					
AC	15	0.02	66.7	<0.02	0.04
IC	30	0.03	70.0	<0.03	0.06
Ortho-					
phosphate	45	0.003	64.4	<0.003	0.023

a. number of analyses

TABLE 5 Analyte Concentration Summary for Filter
Leachate B for 1985.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	47	0.009	95.7	<0.009	<0.009
Magnesium	47	0.003	91.5	<0.003	0.003
Sodium	47	0.003	72.3	<0.003	0.007
Potassium	47	0.003	97.9	<0.003	<0.003
Ammonium	45	0.02	100.0	<0.02	<0.02
Sulfate					
AC	15	0.10	80.0	<0.10	0.35
Nitrate-					
Nitrite AC	15	0.02	93.3	<0.02	0.02
Nitrate IC	30	0.03	96.7	<0.03	<0.03
Chloride					
AC	15	0.02	93.3	<0.02	0.02
IC	30	0.03	100.0	<0.03	<0.03
Ortho-					
phosphate	45	0.003	82.2	<0.003	0.010

a. number of analyses

TABLE 6 Median pH and Specific Conductance
Measurements Found in Filter Leachates
A and B for 1984 and 1985.

| Leachate | Median Value Measured | | | |
| Analyte | A | | B | |
	1984	1985	1984	1985
pH (units)	5.60	5.56	5.59	5.56
Specific Conductance (uS/cm)	1.2	1.3	1.2	1.5
n^a	50	47	50	47

a. number of analyses

TABLE 7 Median Analyte Concentration Values
for Deionized Water Blank for 1984-1985.

| | Median Concentration Value (mg/L) | | | |
| | Room 61^a | | Room 129^a | |
Analyte	1984	1985	1984	1985
pH (units)	5.59	5.57	5.60	5.61
Specific Conductance (uS/cm)	1.1	1.0	1.1	1.0
n^b	49	41	32	37

a. sample processing laboratory is room 61 and atomic absorption
   spectroscopy laboratory is room 129
b. number of analyses

TABLE 8   Analyte Concentration Summary for
the Sample Processing Laboratory
Deionized Water for 1984.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	48	0.009	100.0	<0.009	<0.009
Magnesium	48	0.003	97.9	<0.003	<0.003
Sodium	48	0.003	91.7	<0.003	0.003
Potassium	48	0.003	100.0	<0.003	<0.003
Ammonium	49	0.02	91.8	<0.02	0.03
Sulfate	49	0.10	73.5	<0.10	0.35
Nitrate- Nitrite	49	0.02	100.0	<0.02	<0.02
Chloride	49	0.02	100.0	<0.02	<0.02
Ortho- phosphate	49	0.003	95.9	<0.003	<0.003

a. number of analyses

TABLE 9   Analyte Concentration Summary for
the Sample Processing Laboratory
Deionized Water for 1985.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	41	0.009	100.0	<0.009	<0.009
Magnesium	41	0.003	100.0	<0.003	<0.003
Sodium	41	0.003	92.7	<0.003	0.003
Potassium	41	0.003	97.6	<0.003	<0.003
Ammonium	41	0.02	97.6	<0.02	<0.02
Sulfate AC	17	0.10	88.2	<0.10	0.12
IC	24	0.03	87.5	<0.03	0.03
Nitrate- Nitrite AC	17	0.02	94.1	<0.02	0.02
Nitrate IC	24	0.03	95.8	<0.03	<0.03
Chloride AC	17	0.02	100.0	<0.02	<0.02
IC	24	0.03	95.8	<0.03	<0.03
Ortho- phosphate	41	0.003	85.4	<0.003	0.006

a. number of analyses

96

TABLE 10   Analyte Concentration Summary for
the Atomic Absorption Spectroscopy
Laboratory Deionized Water for 1984.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	29	0.009	100.0	<0.009	<0.009
Magnesium	29	0.003	96.6	<0.003	<0.003
Sodium	29	0.003	100.0	<0.003	<0.003
Potassium	29	0.003	96.6	<0.003	<0.003
Ammonium	32	0.02	90.6	<0.02	0.04
Sulfate	32	0.10	84.4	<0.10	0.37
Nitrate-Nitrite	32	0.02	100.0	<0.02	<0.02
Chloride	32	0.02	96.9	<0.02	<0.02
Ortho-phosphate	32	0.003	96.9	<0.003	<0.003

a. number of analyses

TABLE 11   Analyte Concentration Summary for
the Atomic Absorption Spectroscopy
Laboratory Deionized Water for 1985.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	37	0.009	100.0	<0.009	<0.009
Magnesium	37	0.003	94.6	<0.003	0.003
Sodium	37	0.003	94.6	<0.003	0.003
Potassium	37	0.003	100.0	<0.003	<0.003
Ammonium	37	0.02	100.0	<0.02	<0.02
Sulfate AC	13	0.10	84.6	<0.10	0.10
IC	24	0.03	91.7	<0.03	0.03
Nitrate-Nitrite AC	13	0.02	100.0	<0.02	<0.02
Nitrate IC	24	0.03	100.0	<0.03	<0.03
Chloride AC	13	0.02	100.0	<0.02	<0.02
IC	24	0.03	100.0	<0.03	<0.03
Ortho-phosphate	37	0.003	83.8	<0.003	0.010

a. number of analyses

APPENDIX C

Replicate Sample Analyses
Plots and Tables
1984-1985
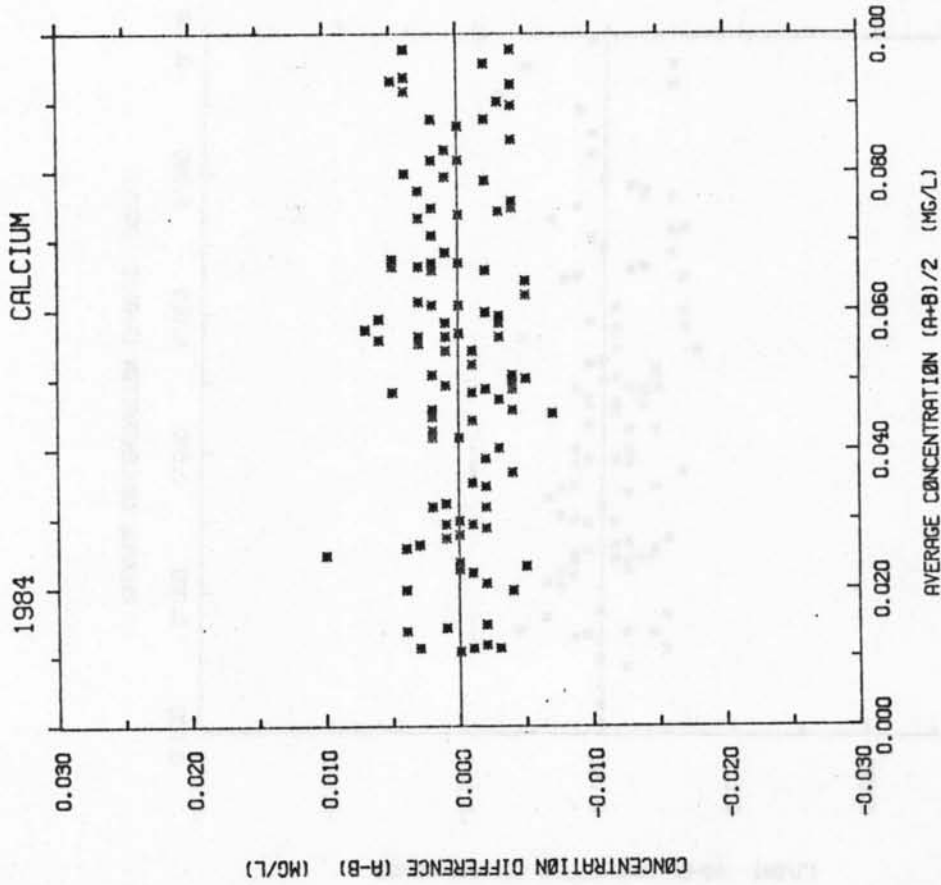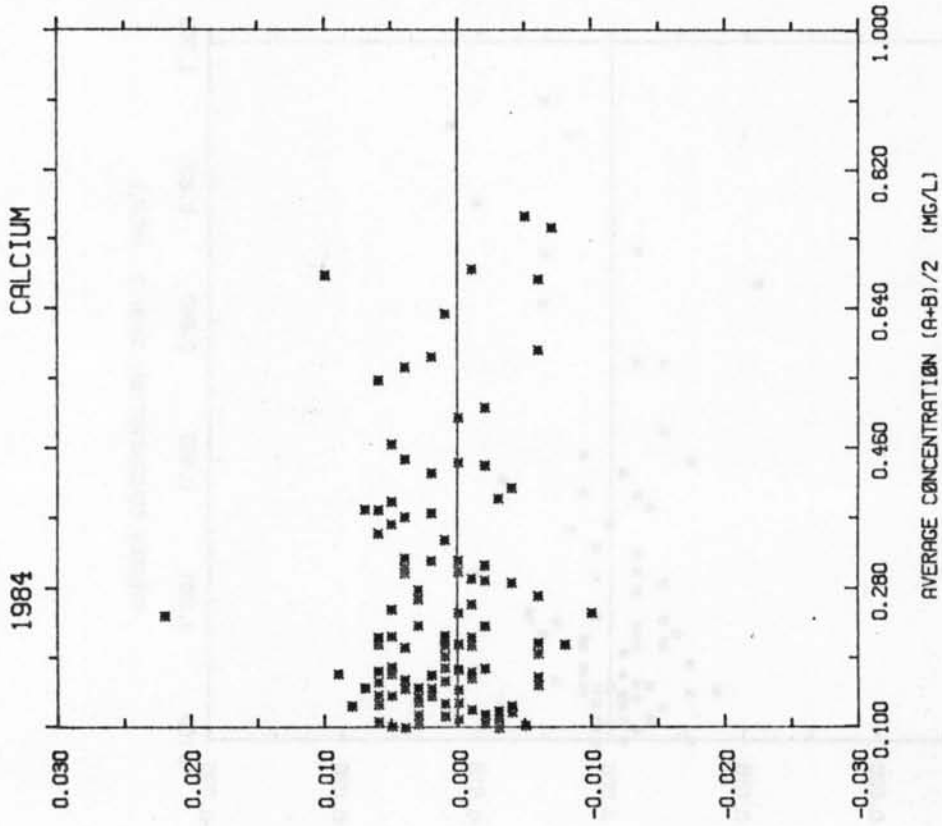
FIGURE 1. A/B replicate plots for calcium for 1984.
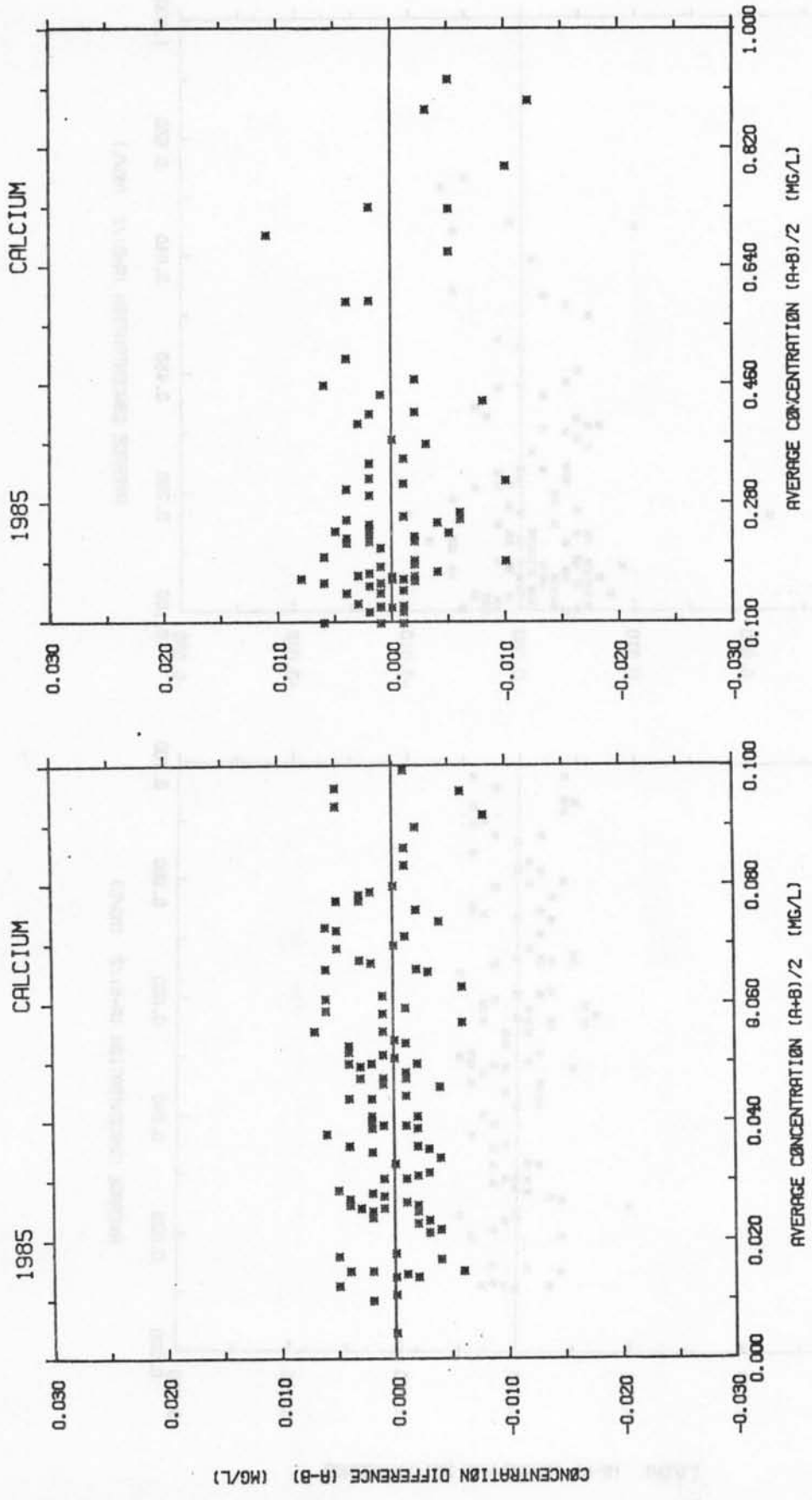
FIGURE 2. A/B replicate plots for calcium for 1985.
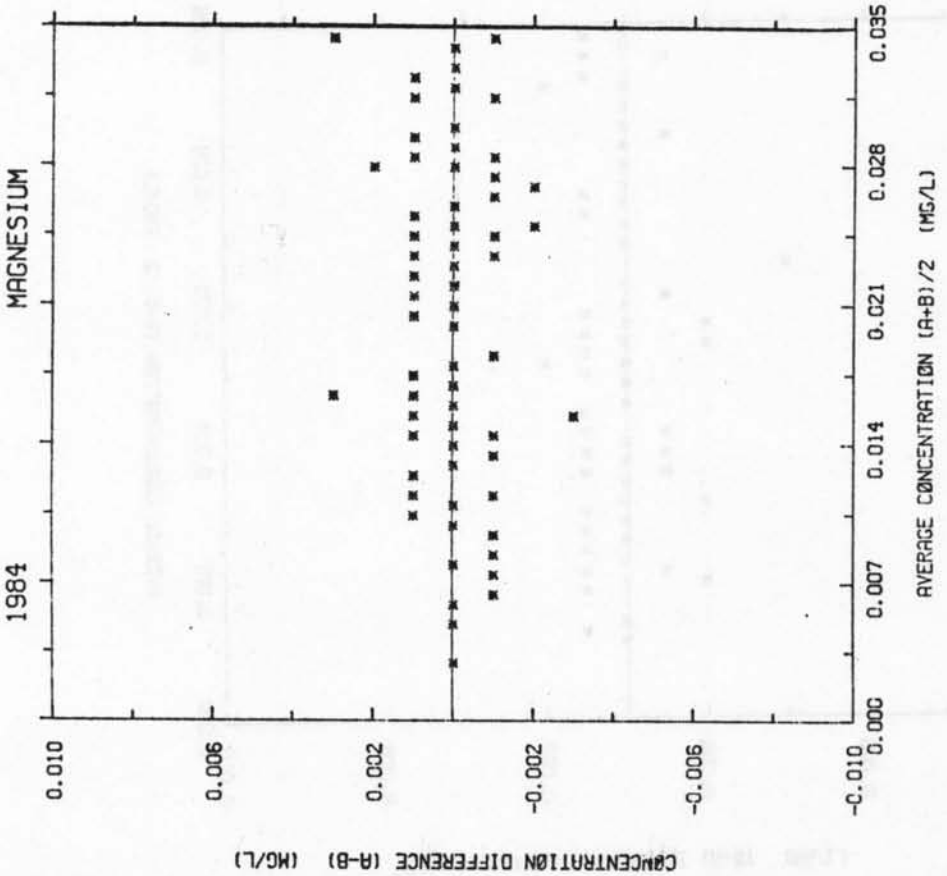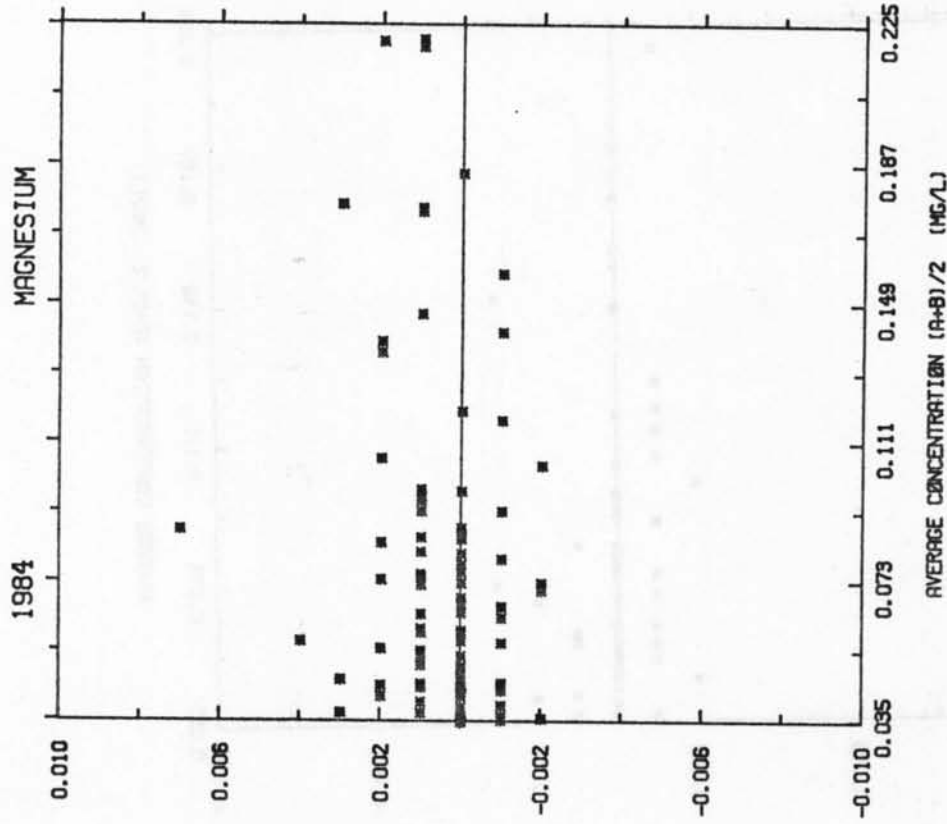
FIGURE 3. A/B replicate plots for magnesium for 1984.
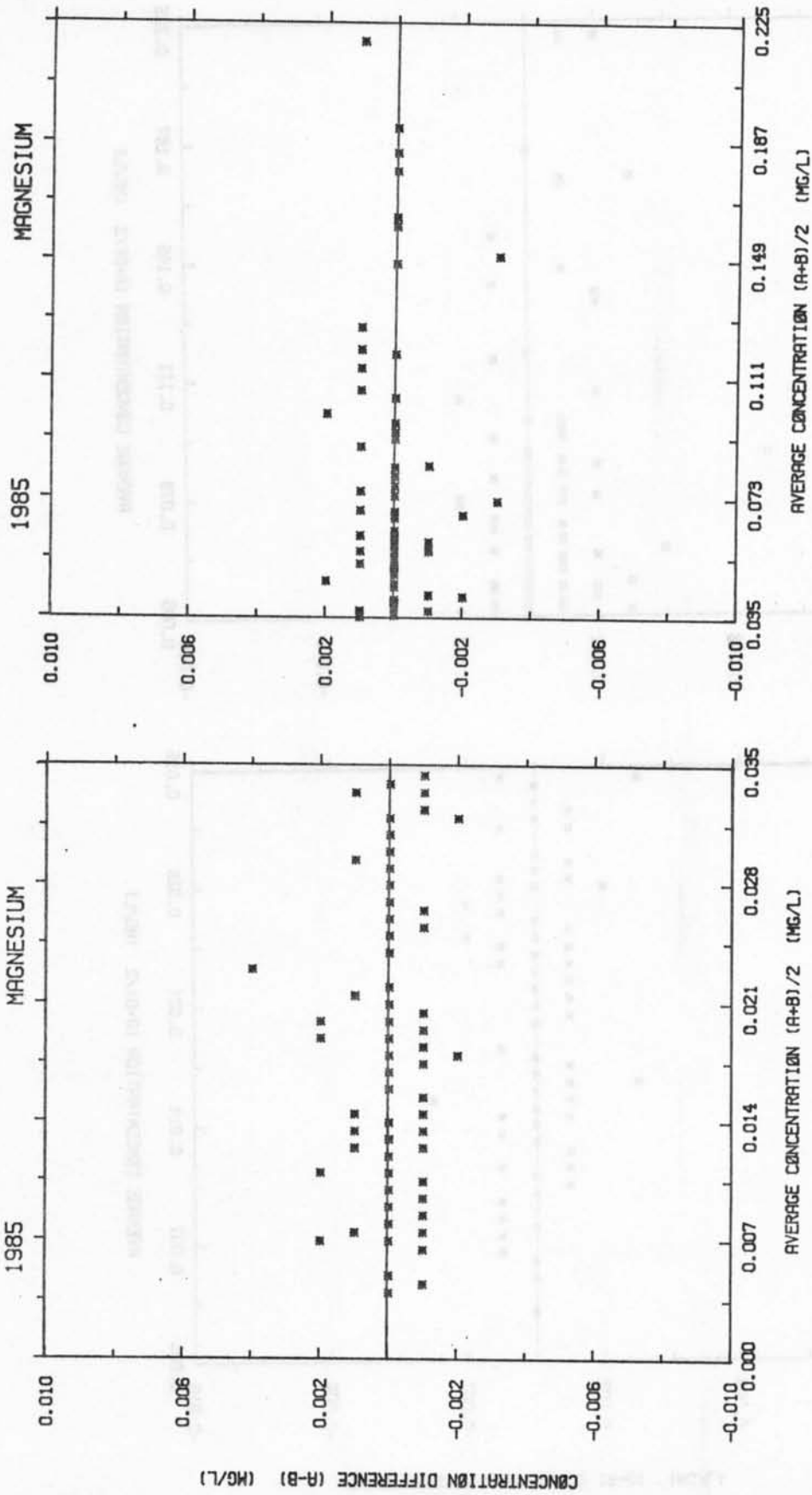
FIGURE 4. A/B replicate plots for magnesium for 1985.
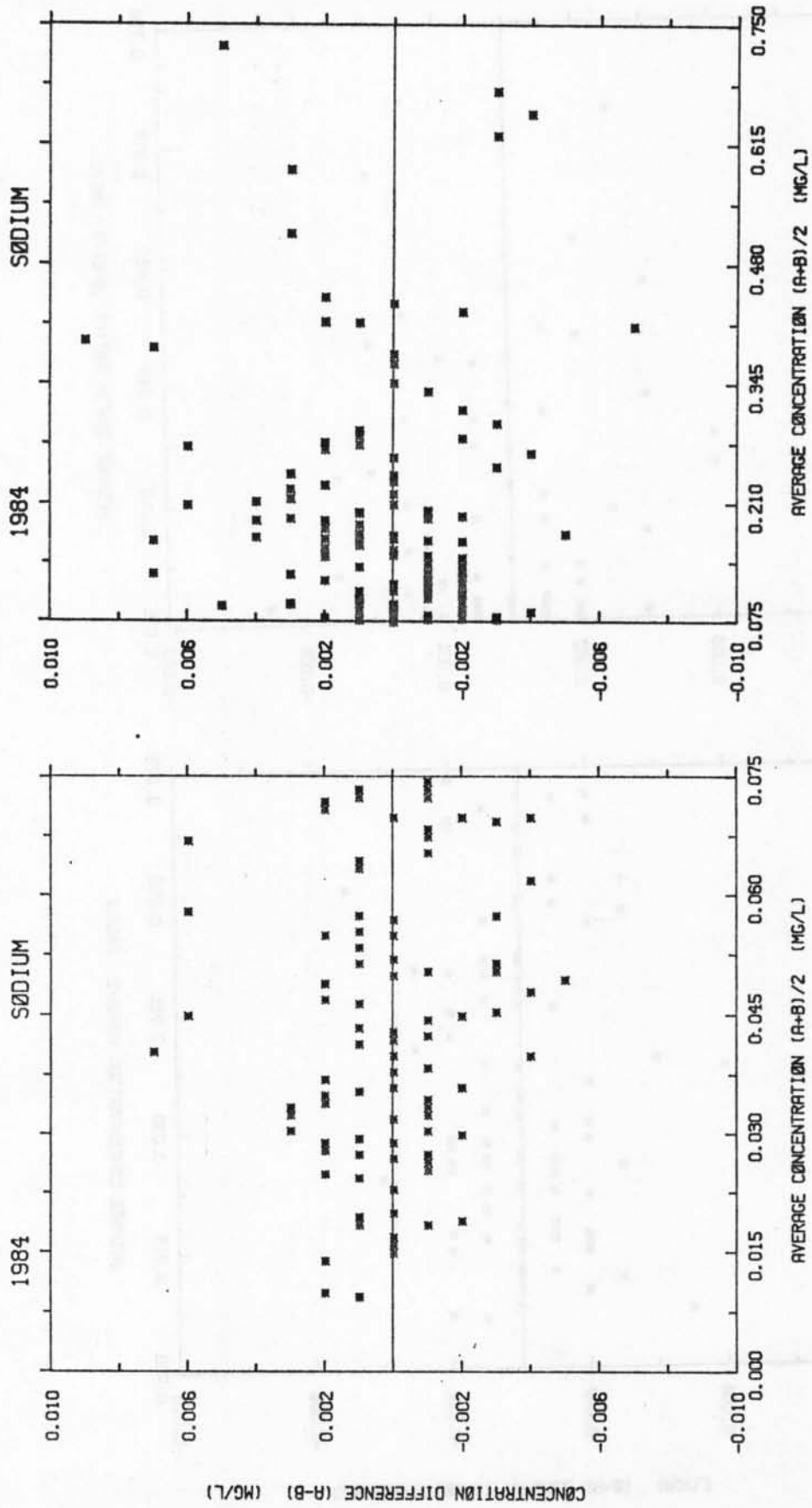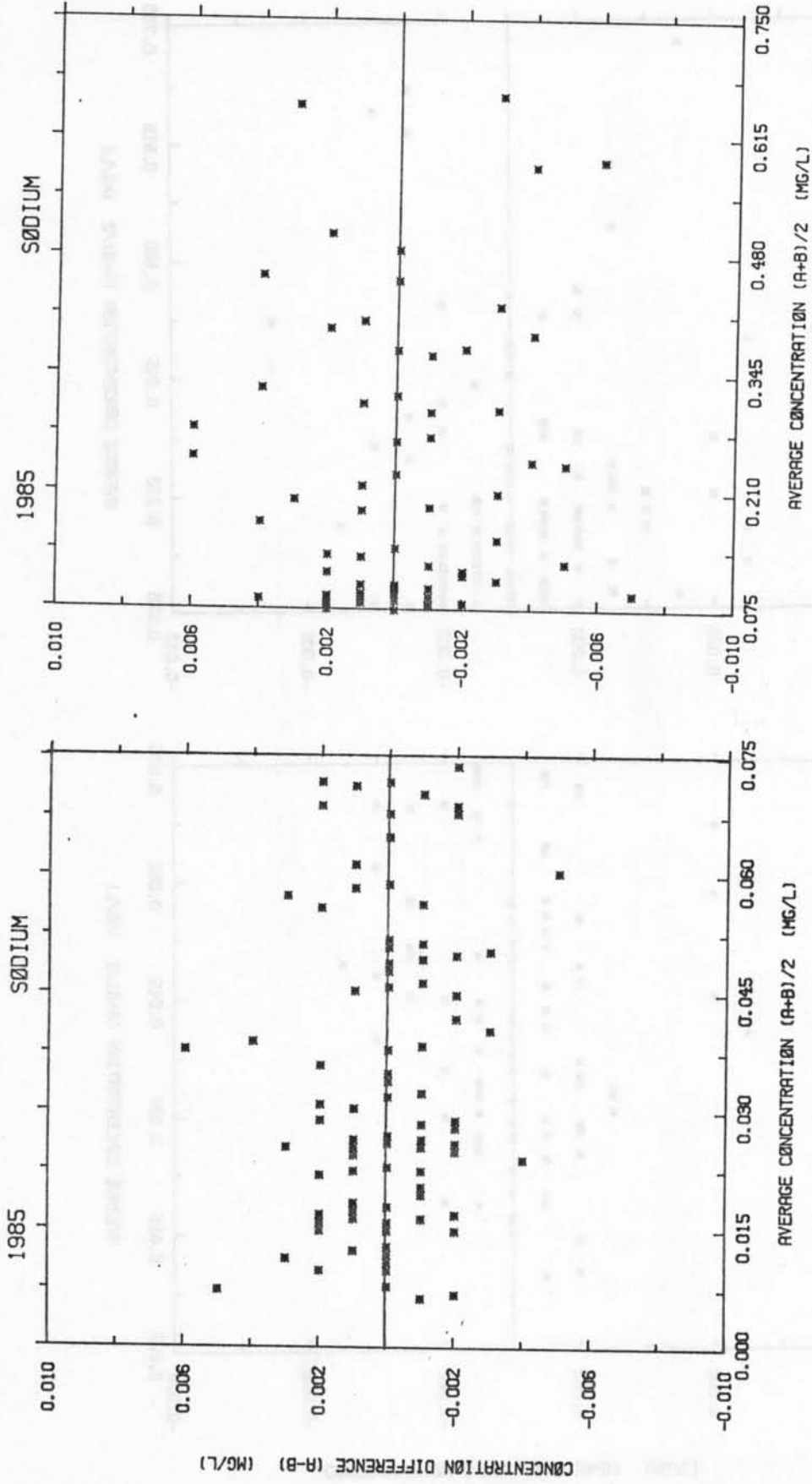
FIGURE 5. A/B replicate plots for sodium for 1984.

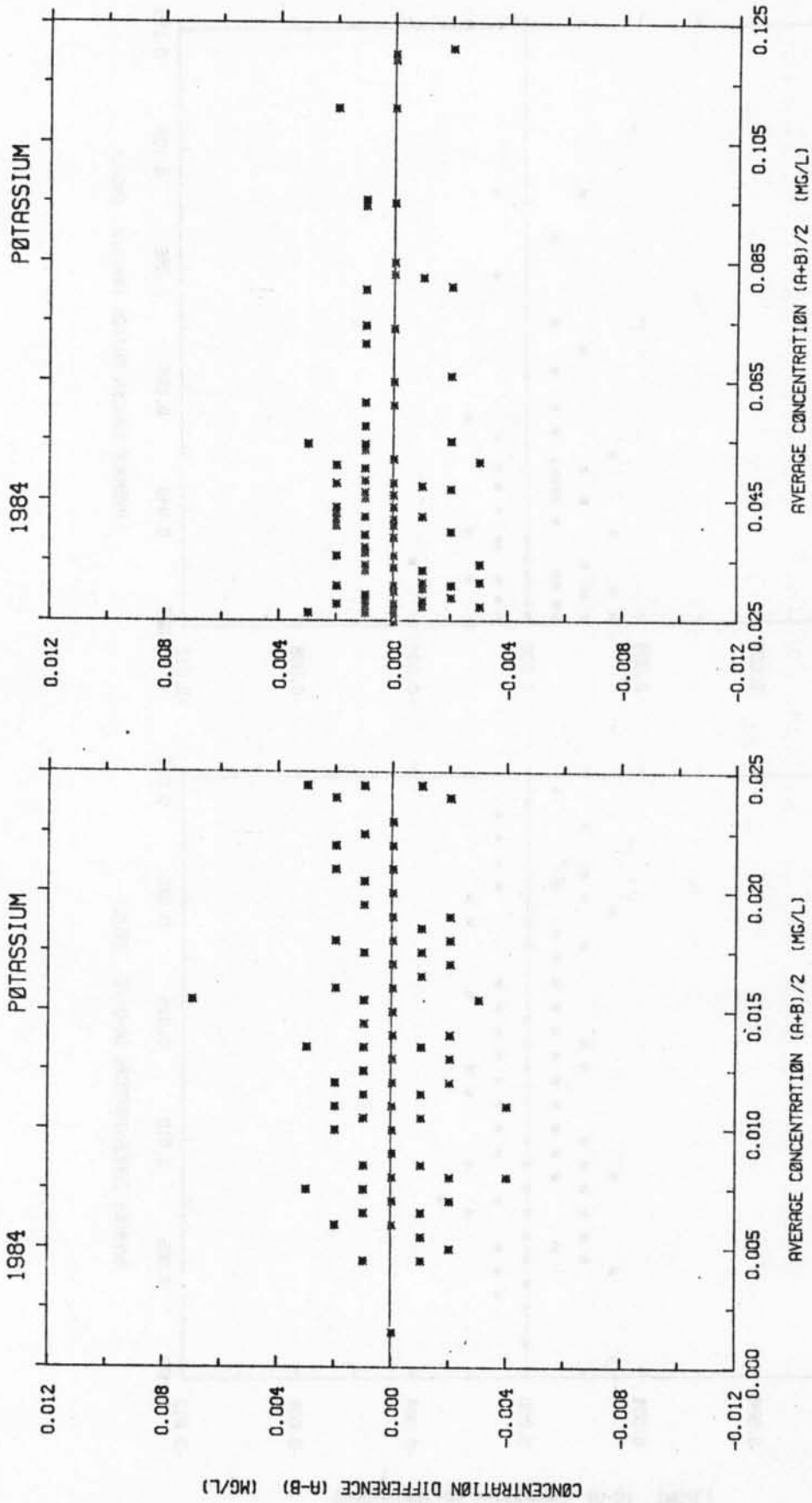FIGURE 6. A/B replicate plots for sodium for 1985.

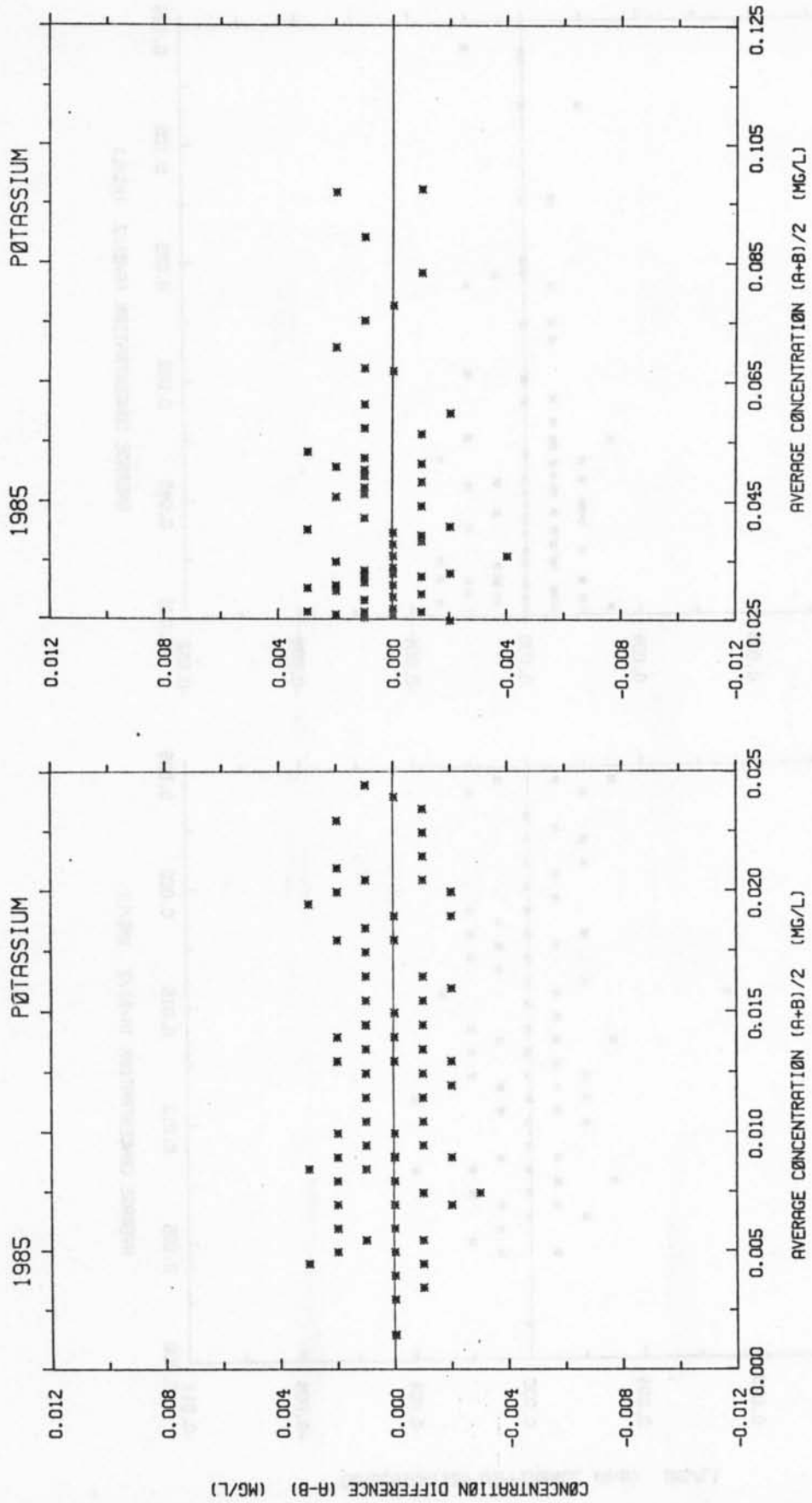FIGURE 7. A/B replicate plots for potassium for 1984.
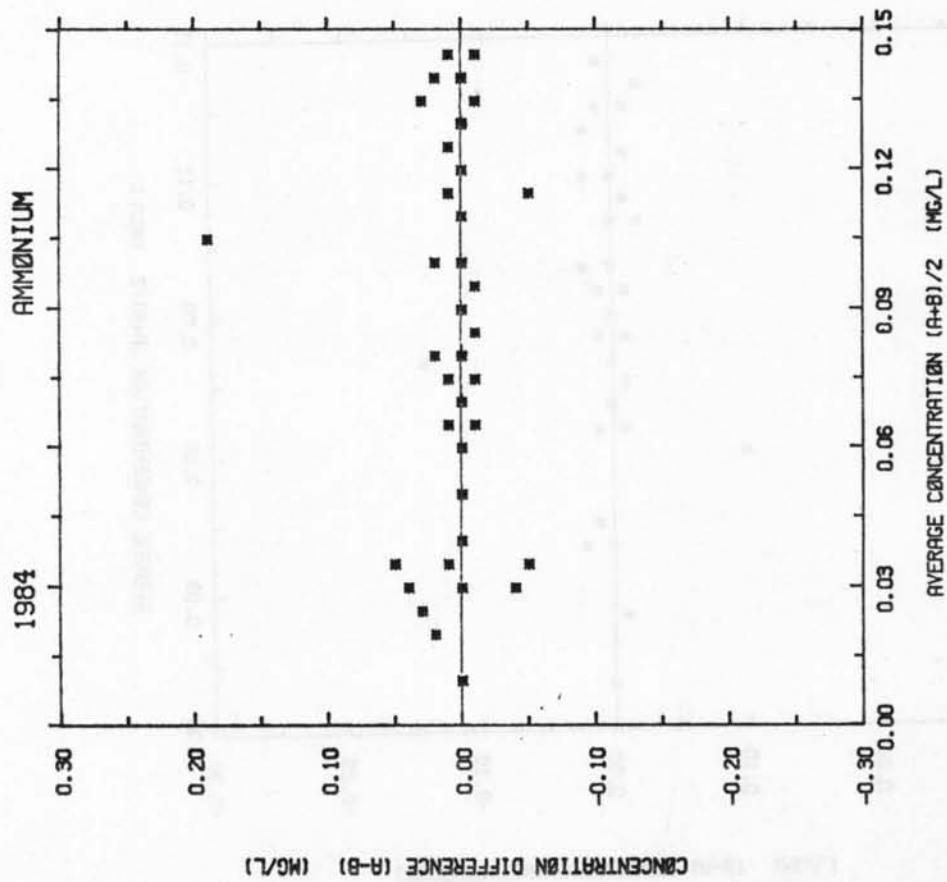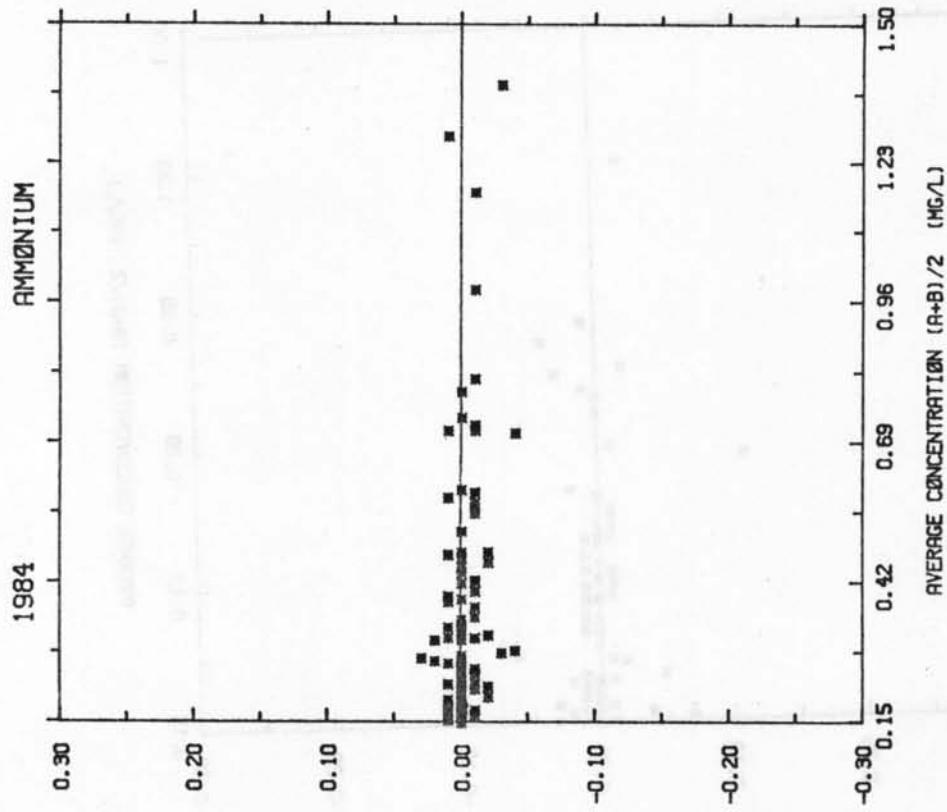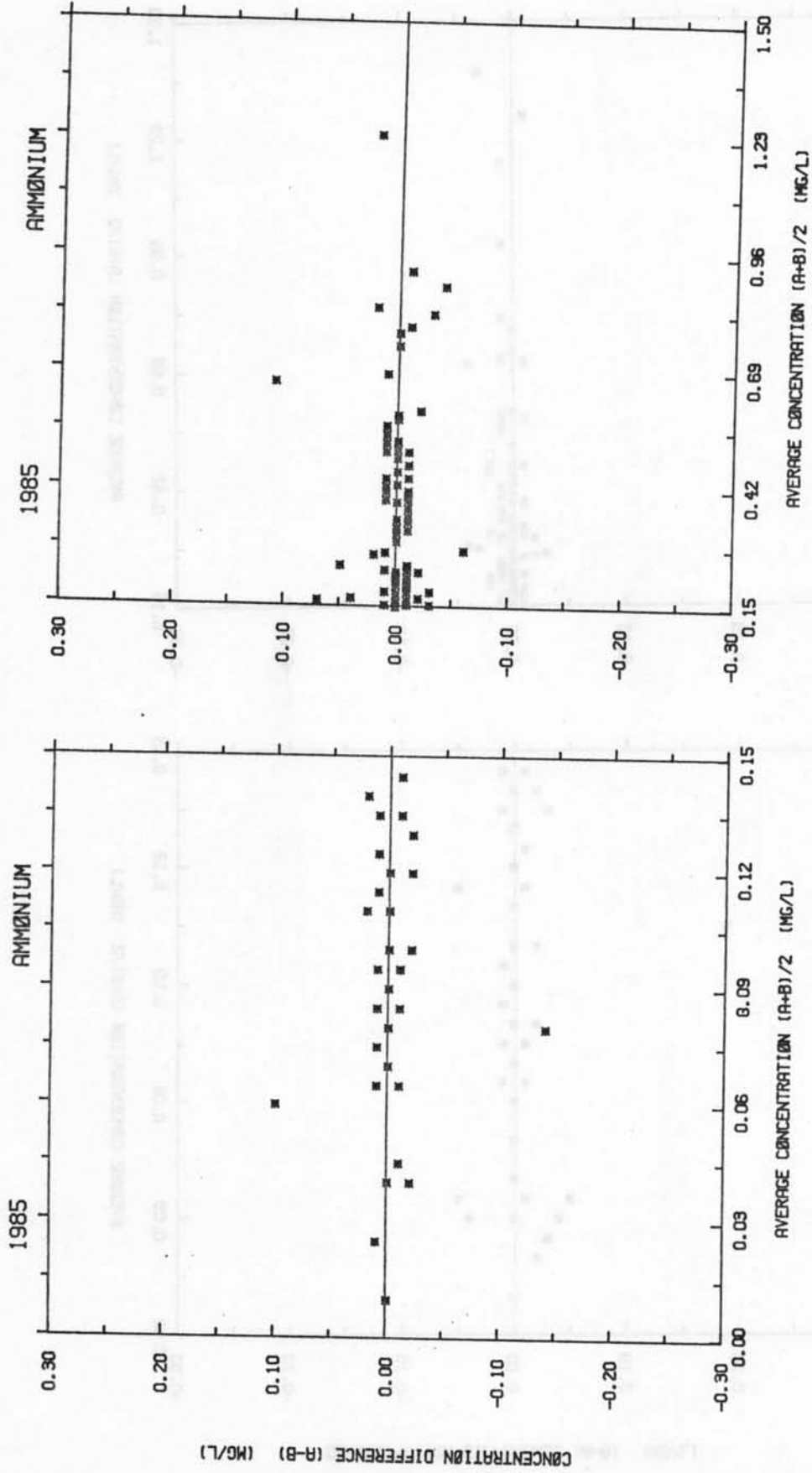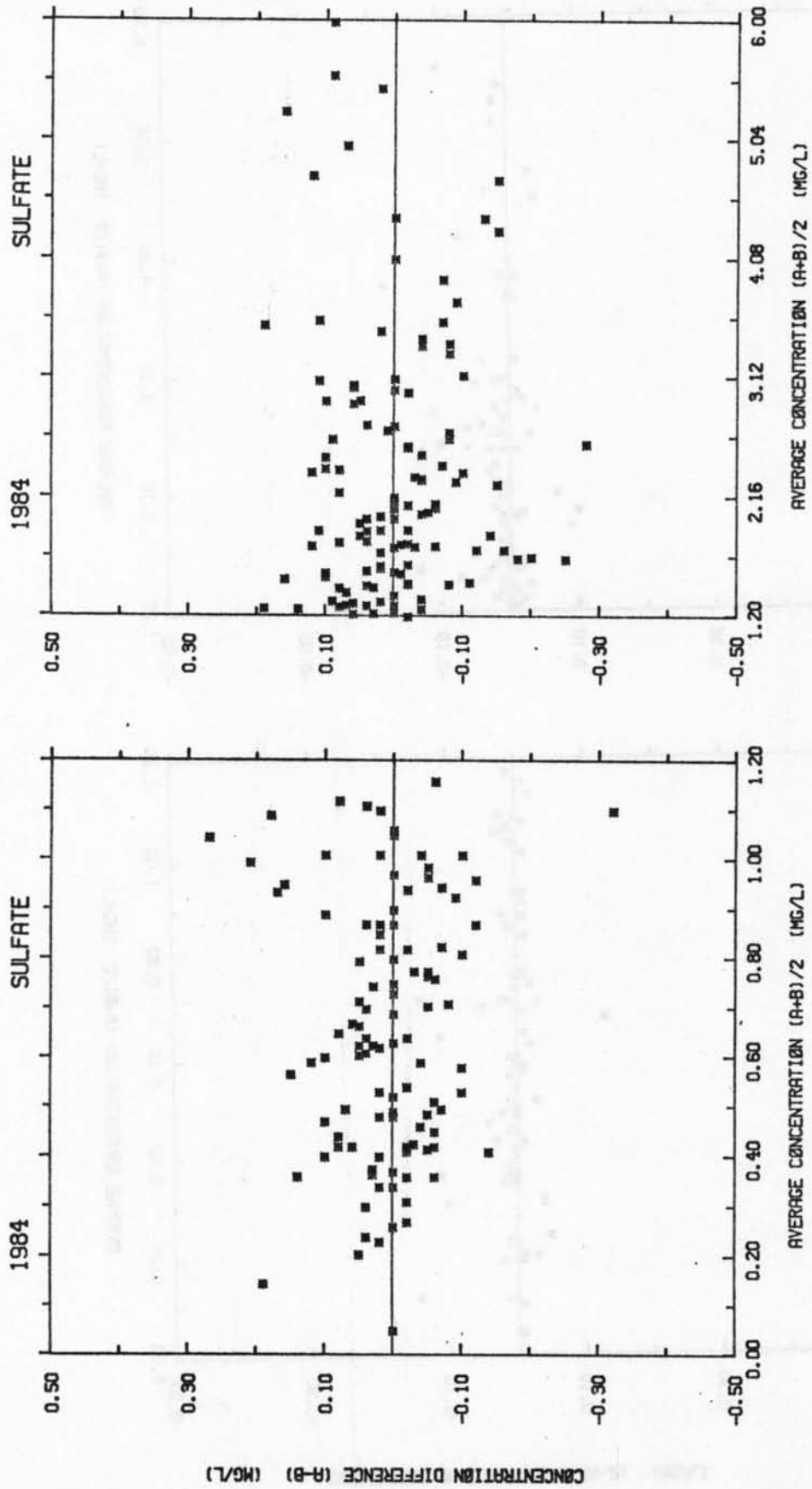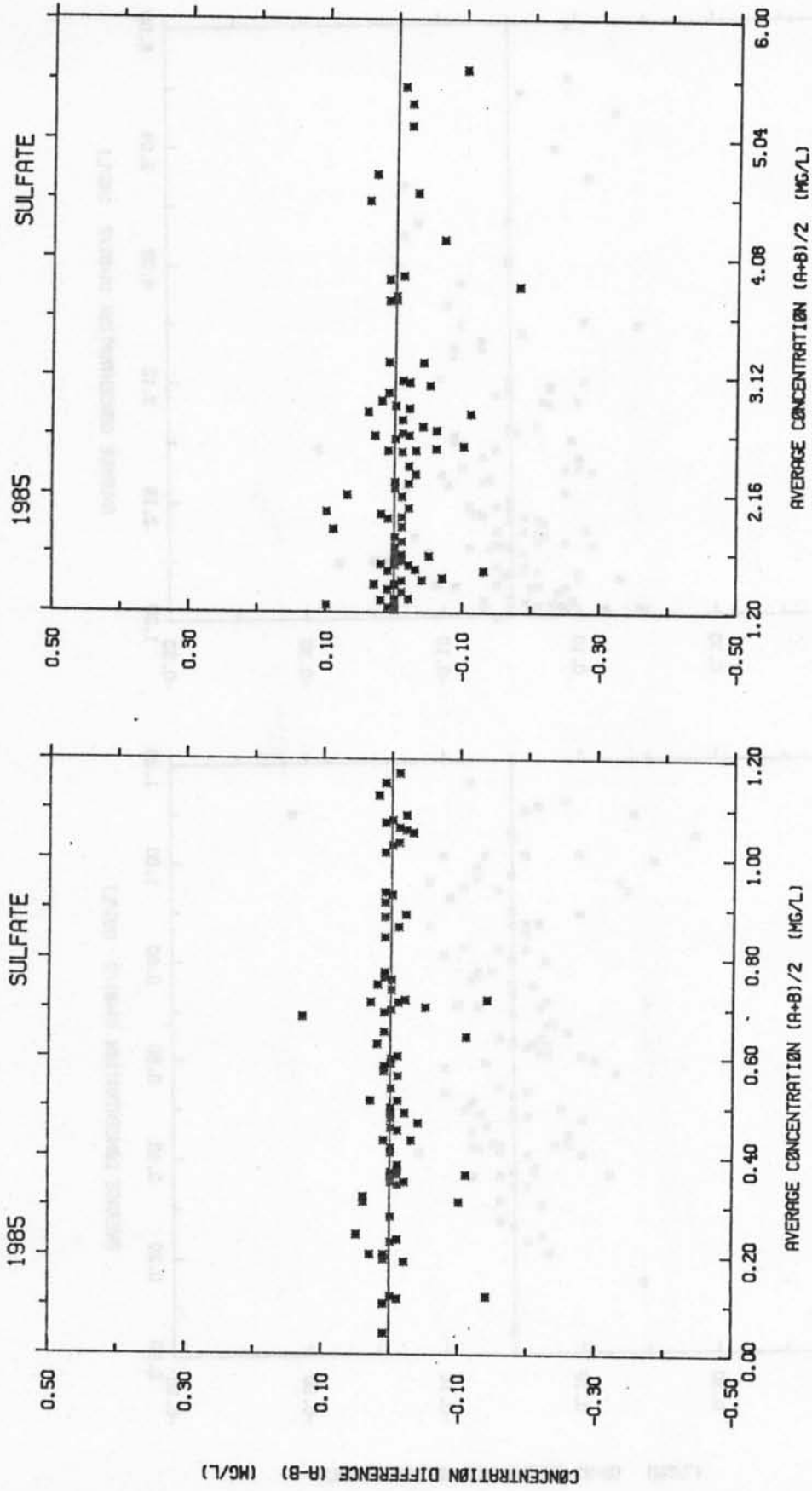
FIGURE 8. A/B replicate plots for potassium for 1985.

FIGURE 9. A/B replicate plots for ammonium for 1984.

FIGURE 10. A/B replicate plots for ammonium for 1985.

FIGURE 11. A/B replicate plots for sulfate for 1984.

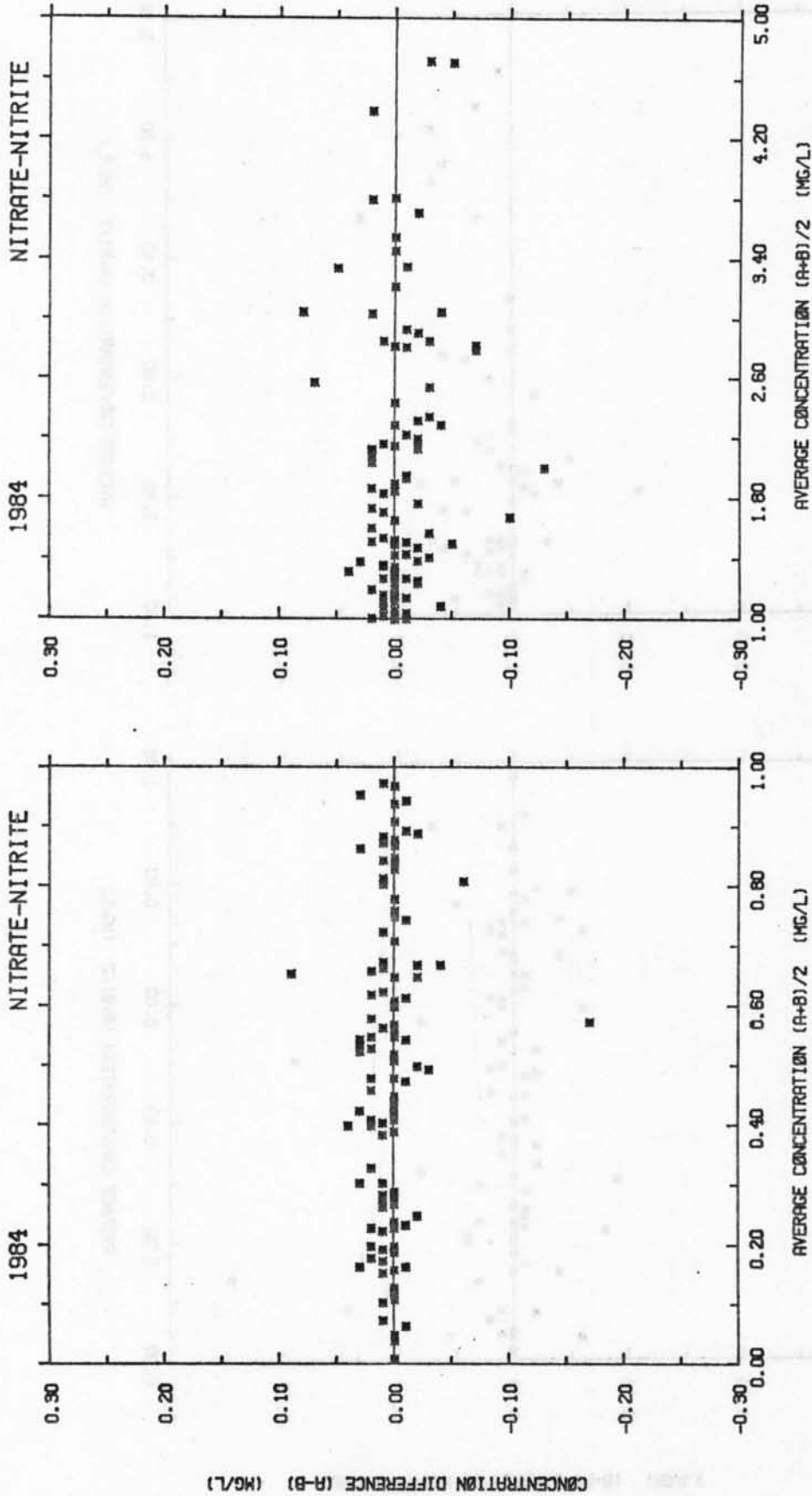FIGURE 12. A/B replicate plots for sulfate for 1985.

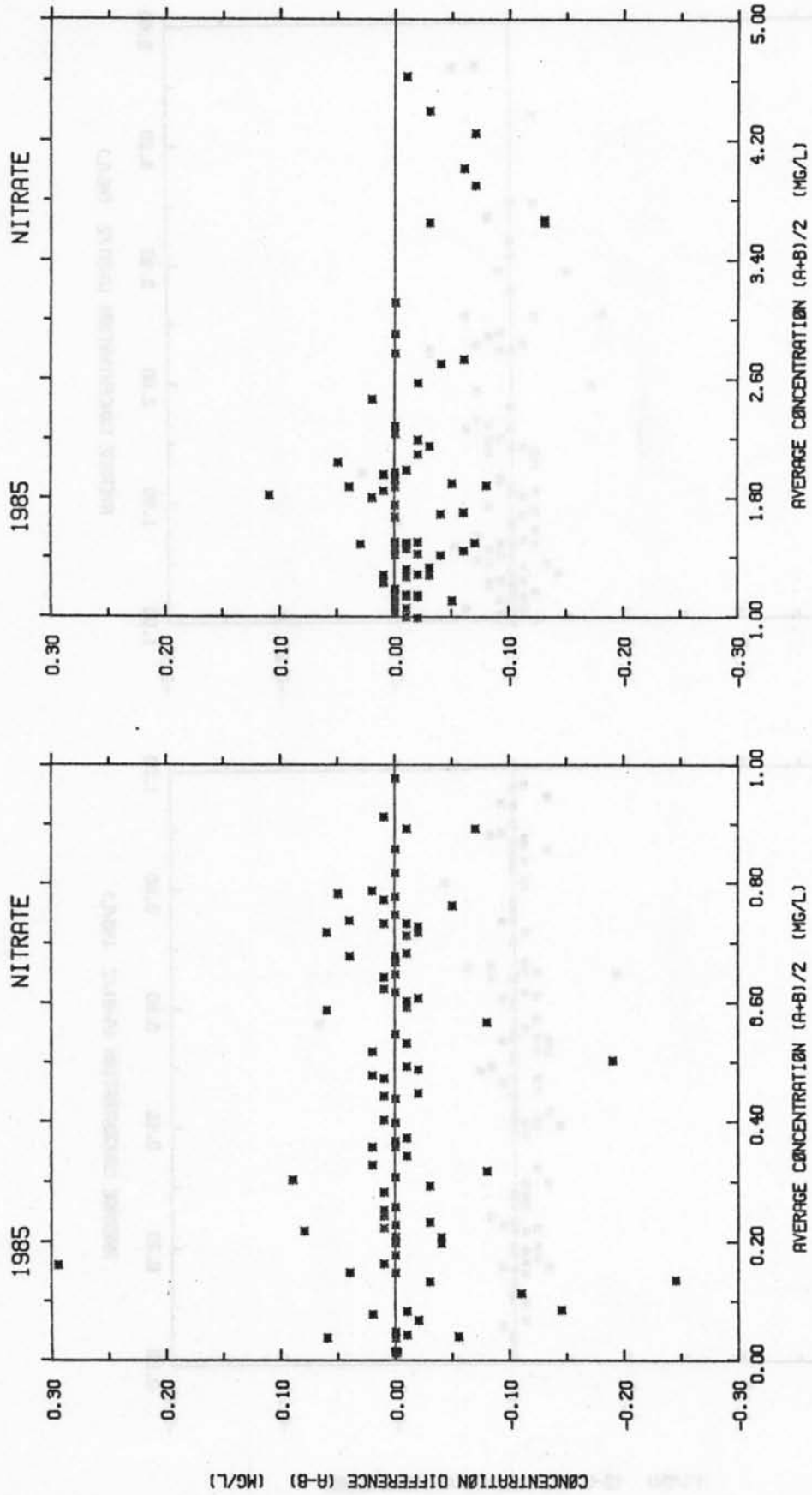FIGURE 13. A/B replicate plots for nitrate-nitrite for 1984.

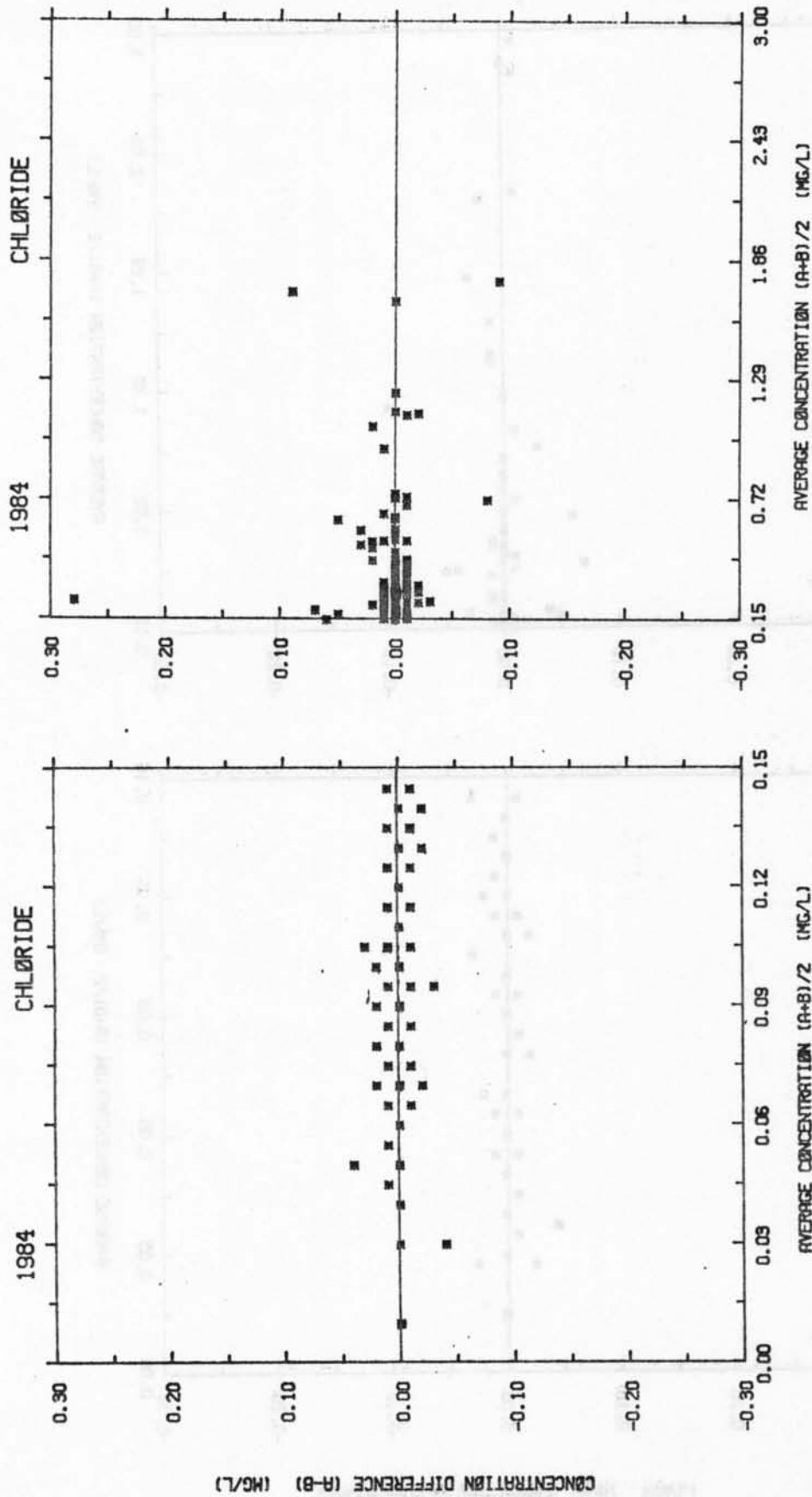FIGURE 14. A/B replicate plots for nitrate for 1985.

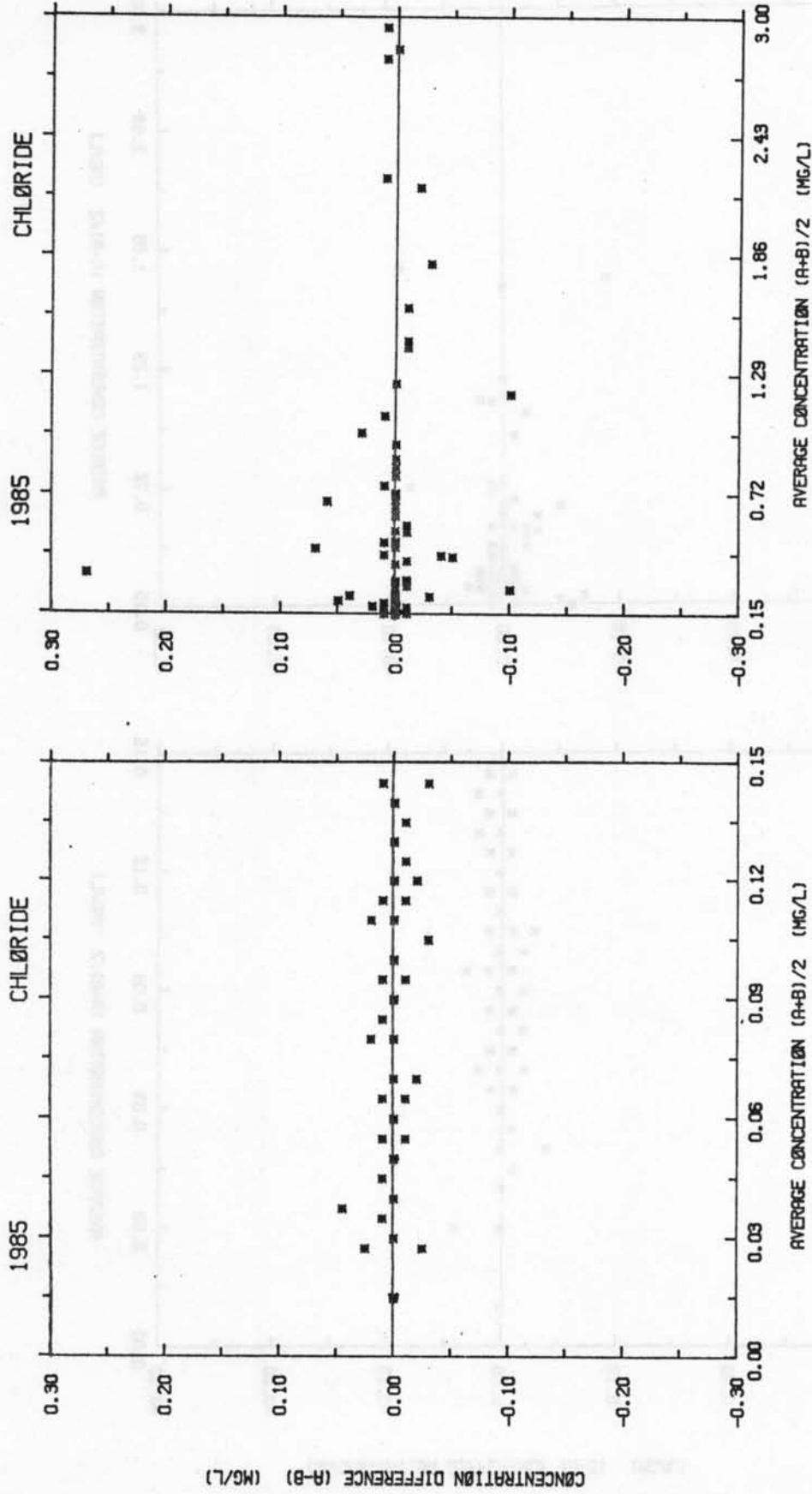FIGURE 15. A/B replicate plots for chloride for 1984.

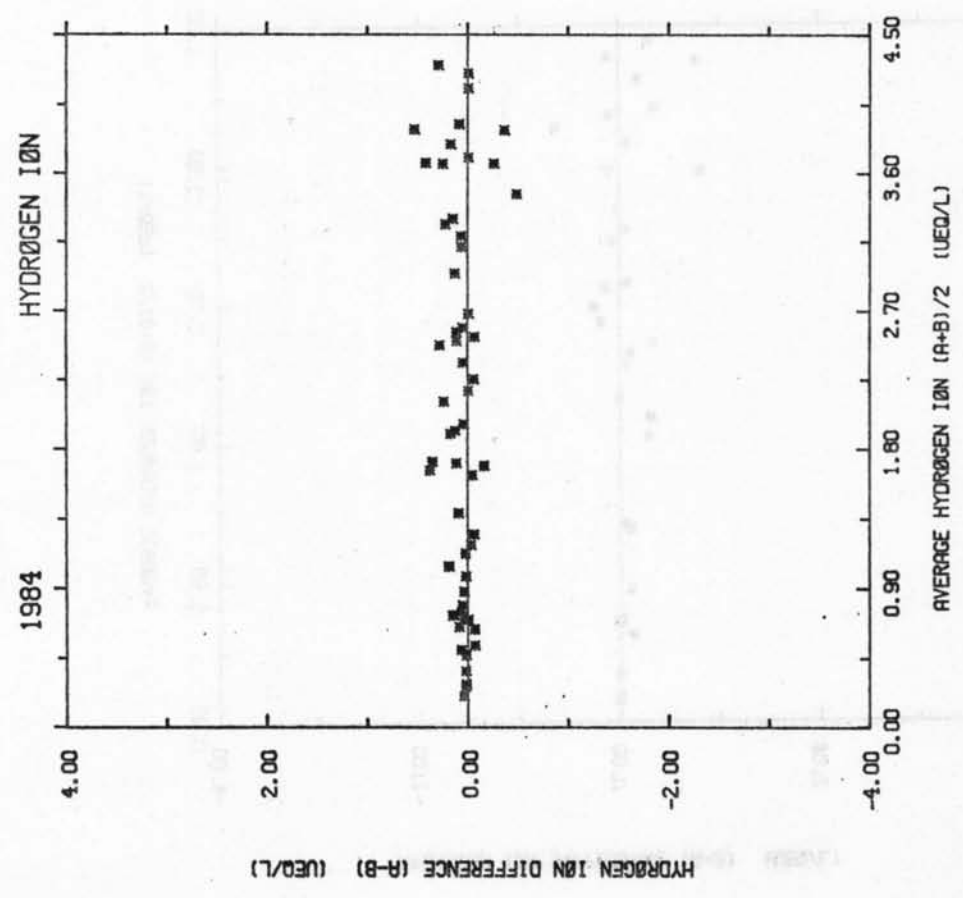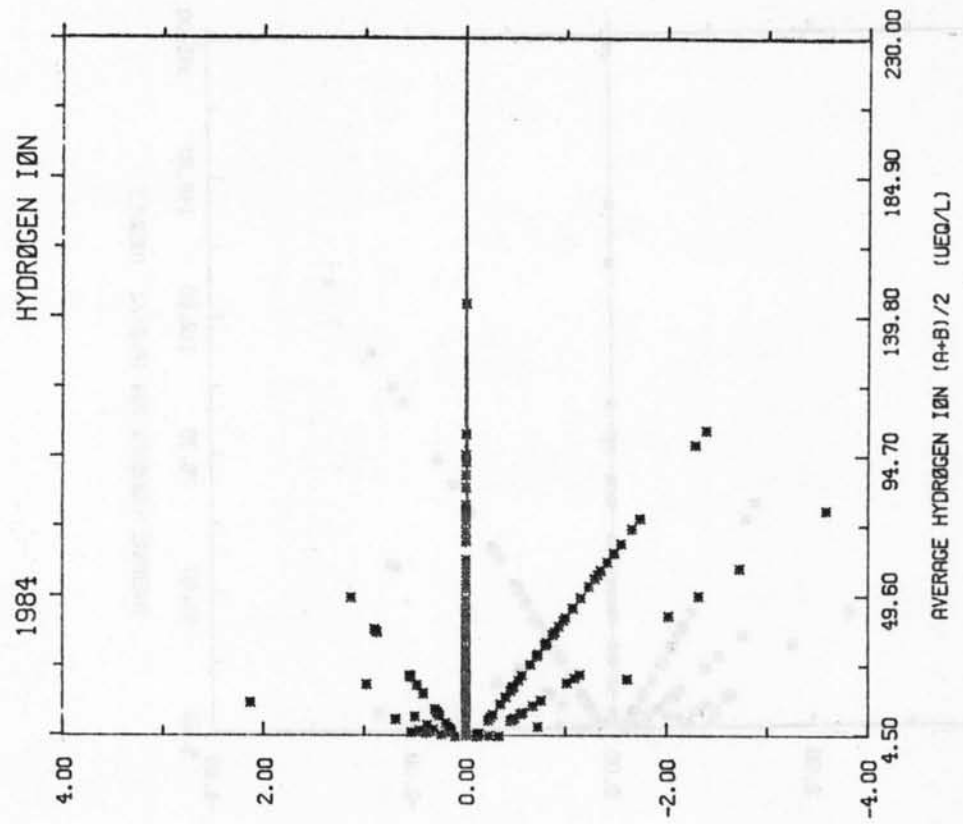FIGURE 16. A/B replicate plots for chloride for 1985.

FIGURE 17. A/B replicate plots for hydrogen ion for 1984.
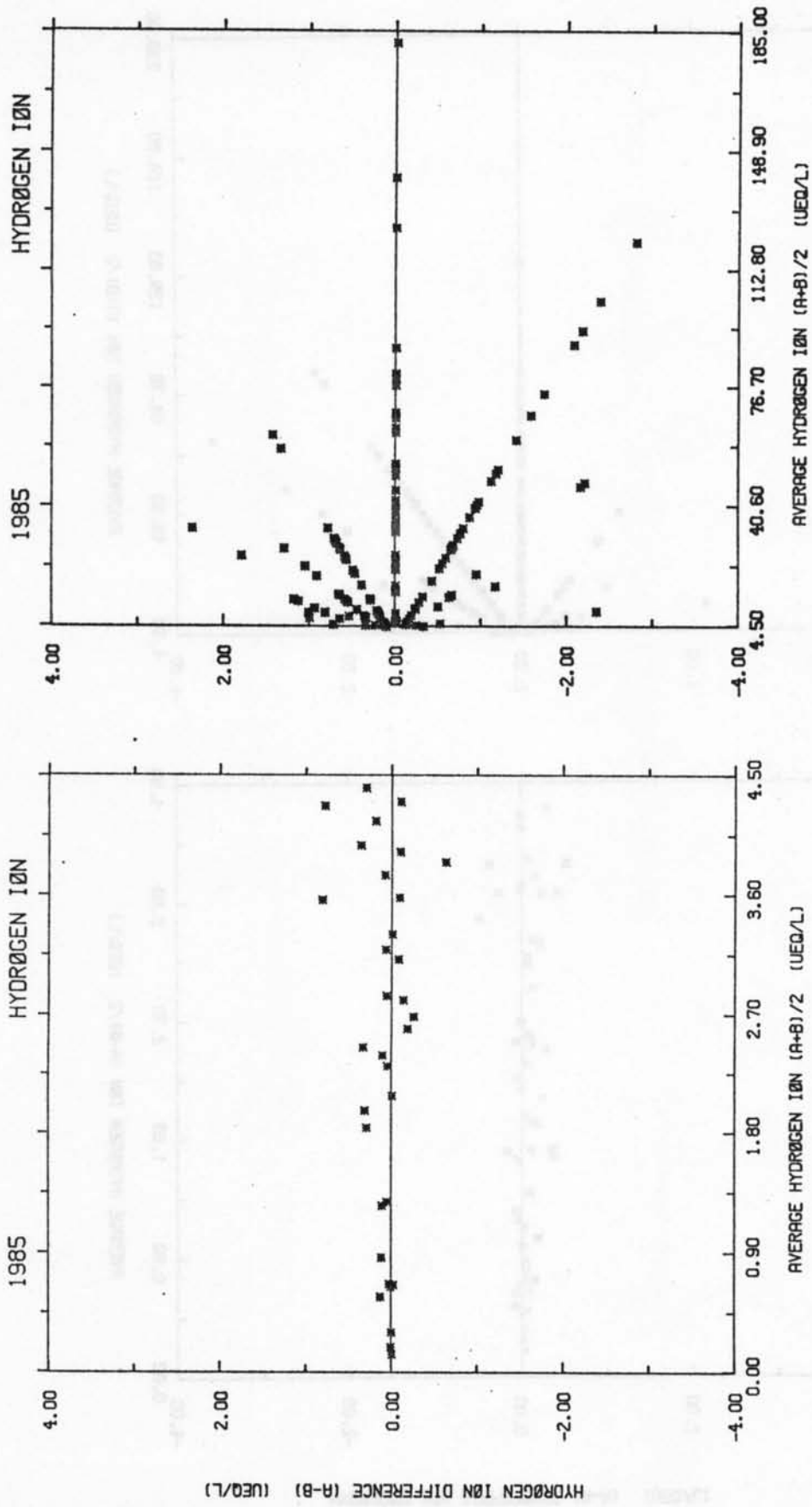
FIGURE 18. A/B replicate plots for hydrogen ion for 1985.
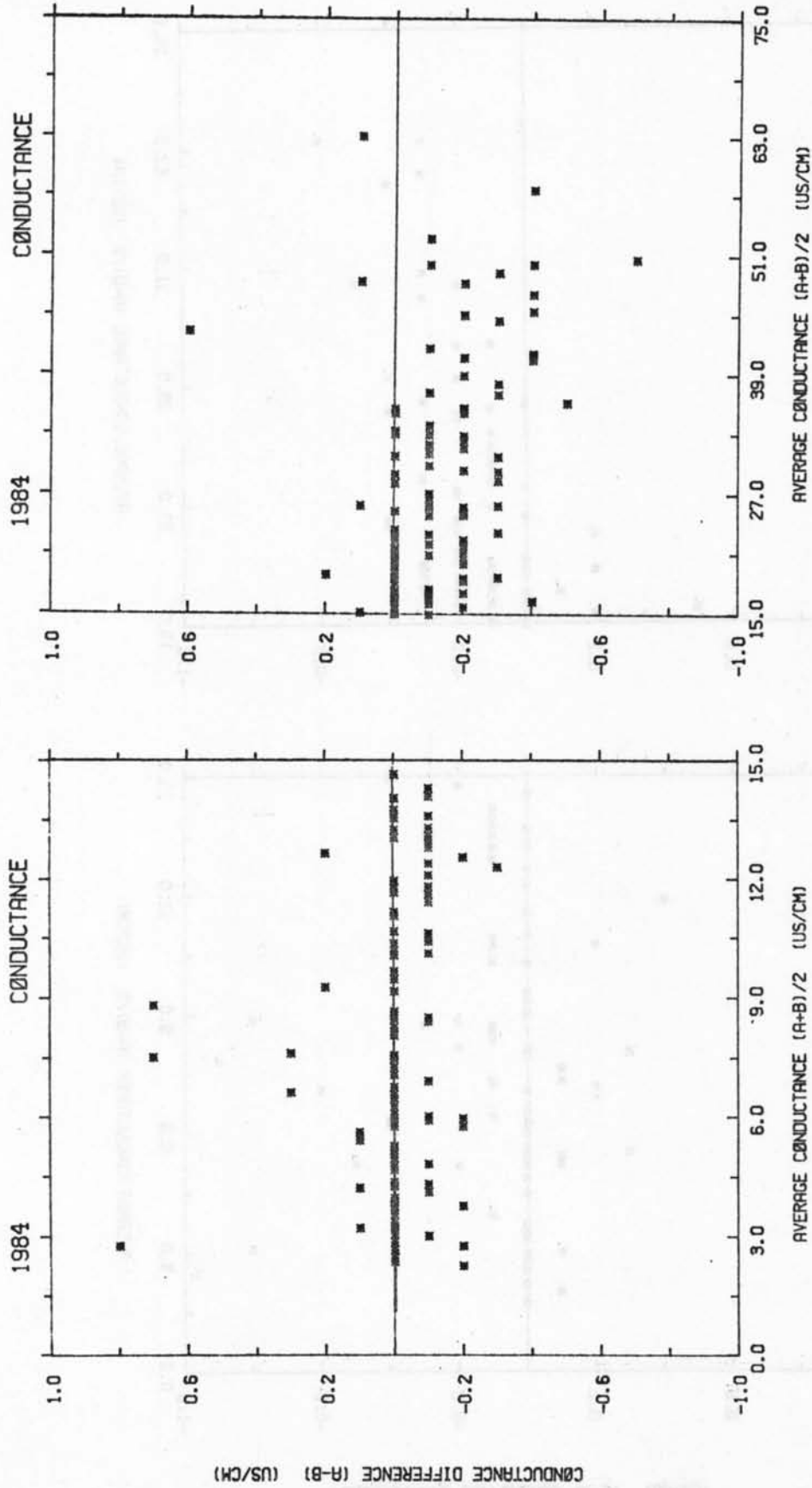
FIGURE 19. A/B replicate plots for specific conductance for 1984.

FIGURE 20. A/B replicate plots for specific conductance for 1985.
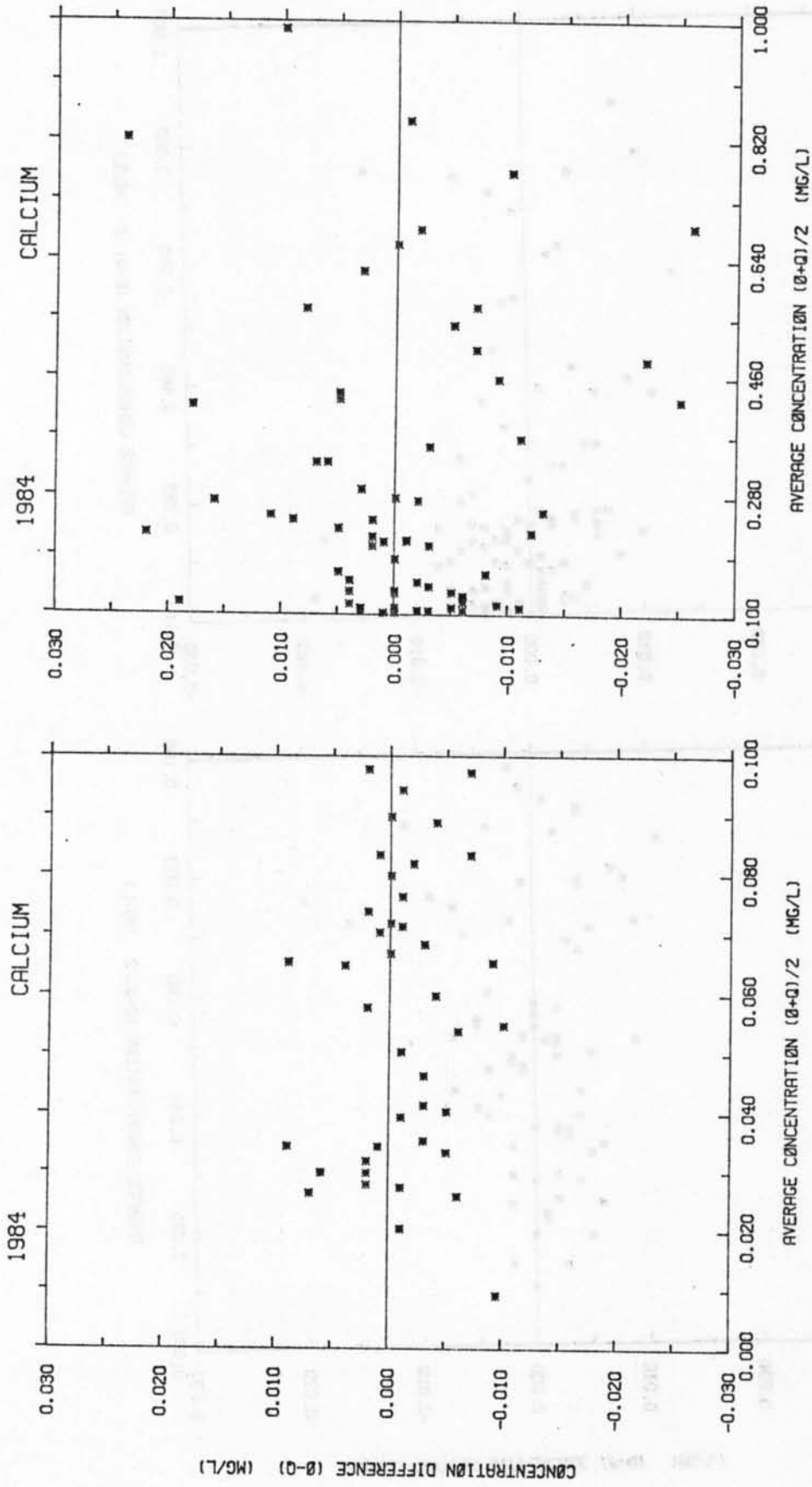
FIGURE 21. O/Q replicate plots for calcium for 1984.
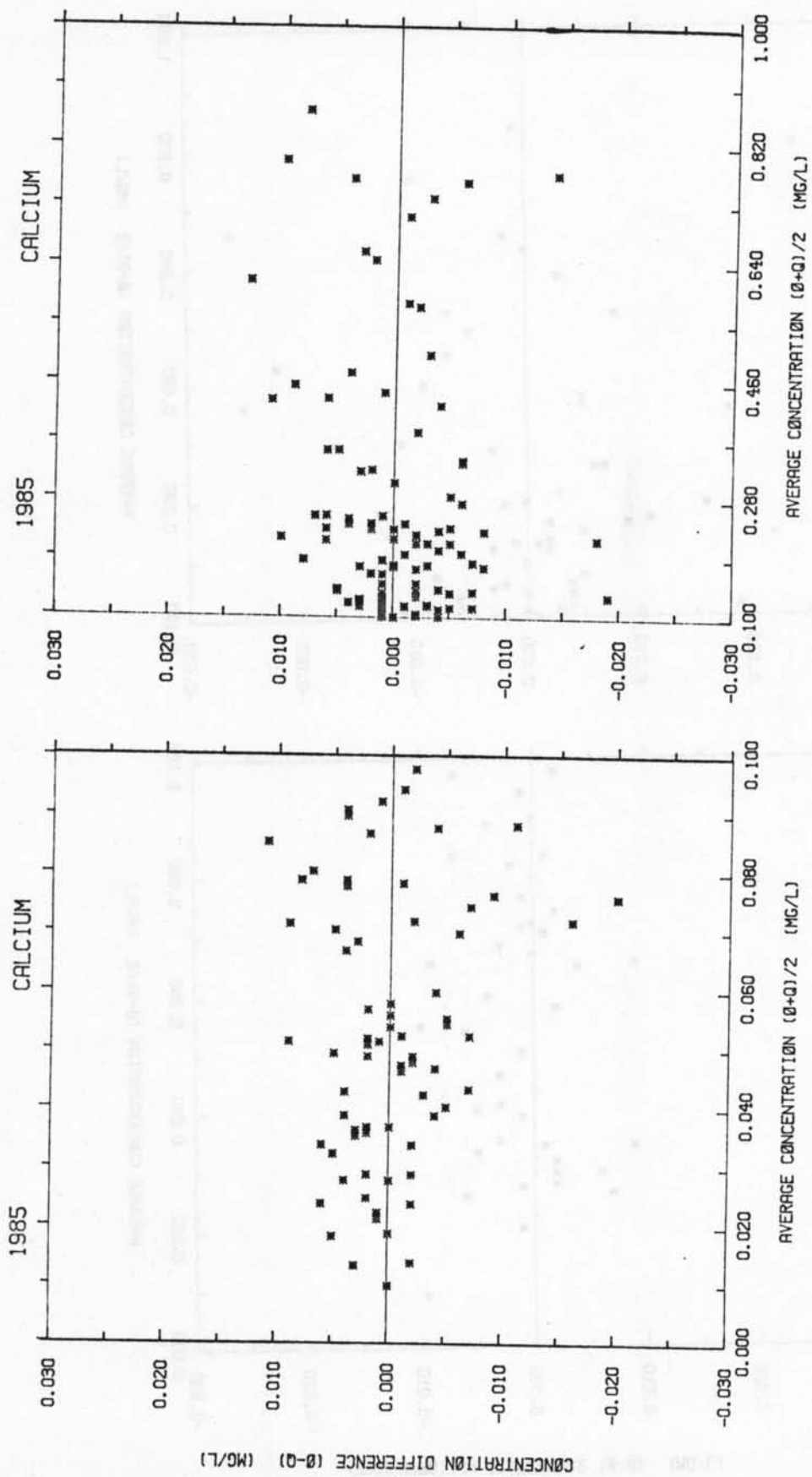
FIGURE 22. O/Q replicate plots for calcium for 1985.
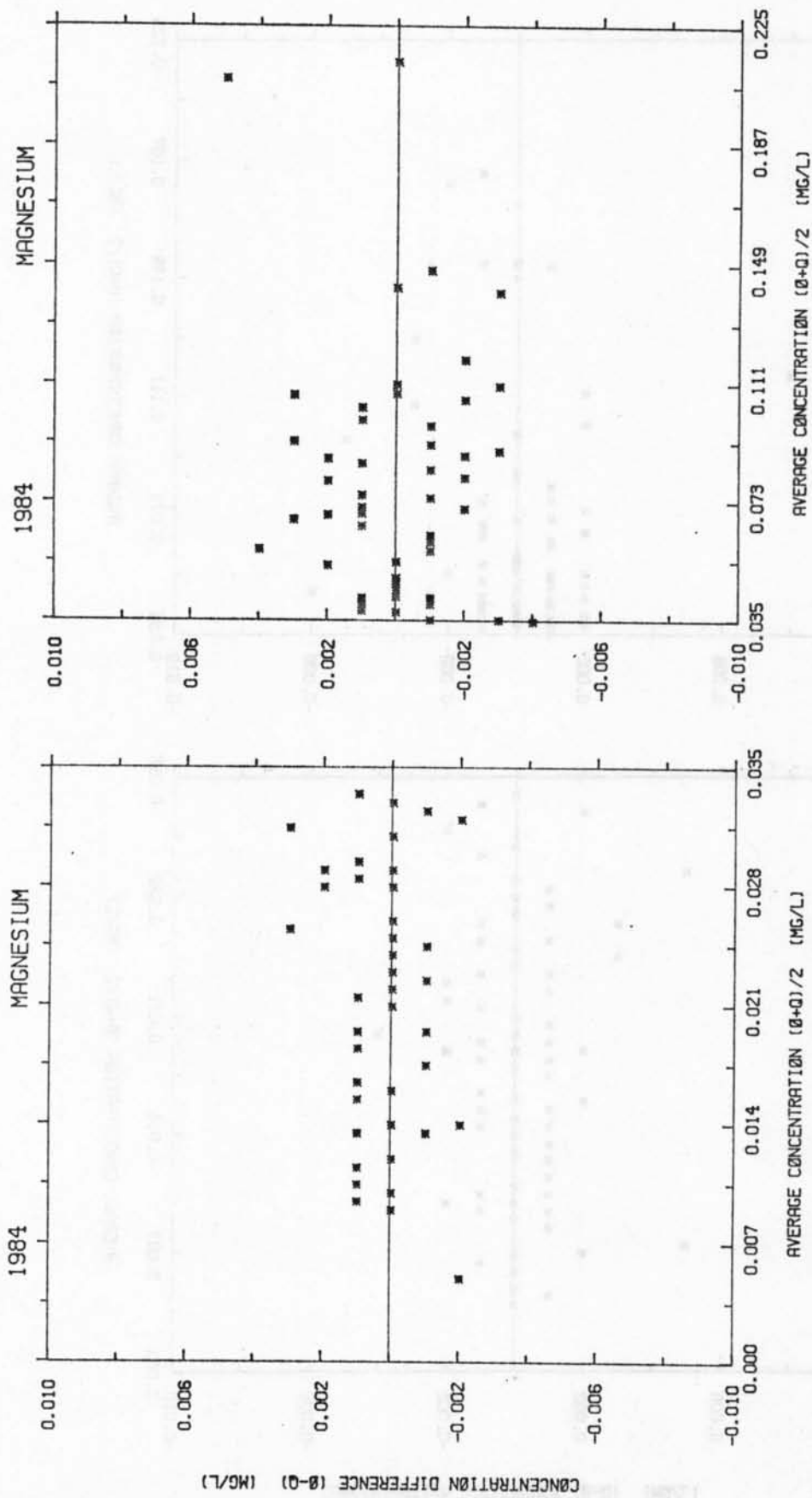
FIGURE 23. O/Q replicate plots for magnesium for 1984.
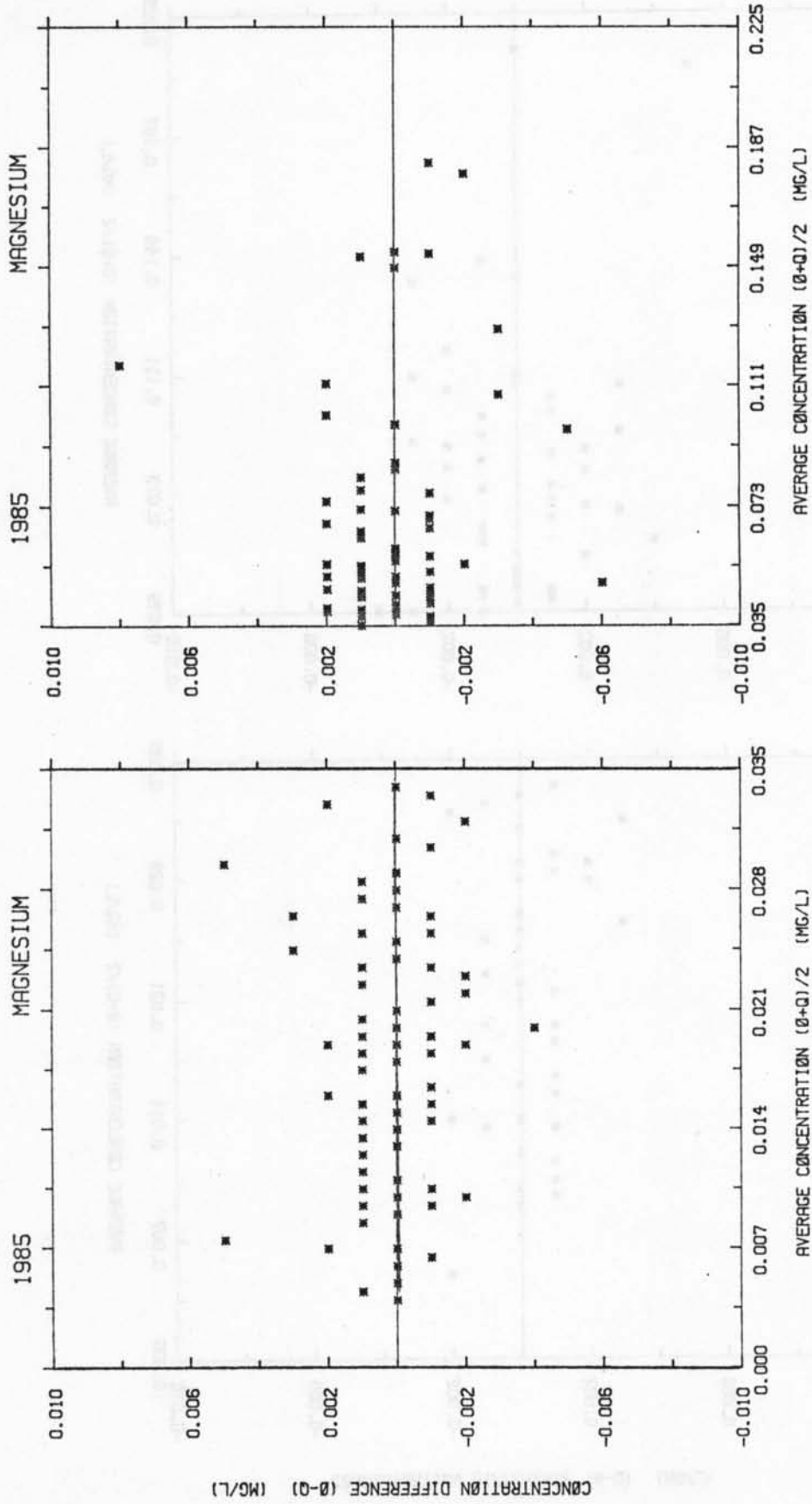
FIGURE 24. O/Q replicate plots for magnesium for 1985.
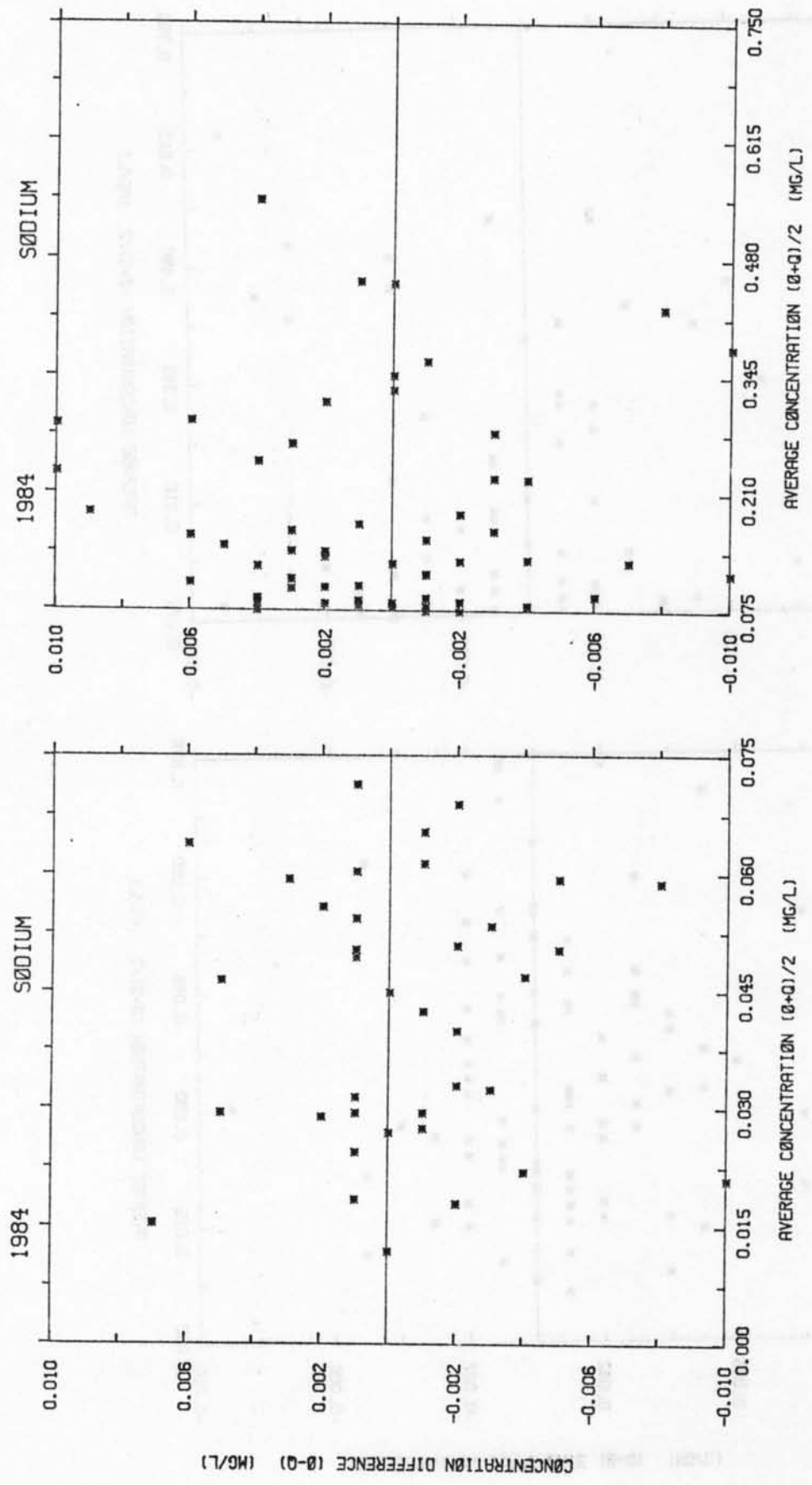
FIGURE 25. O/Q replicate plots for sodium for 1984.
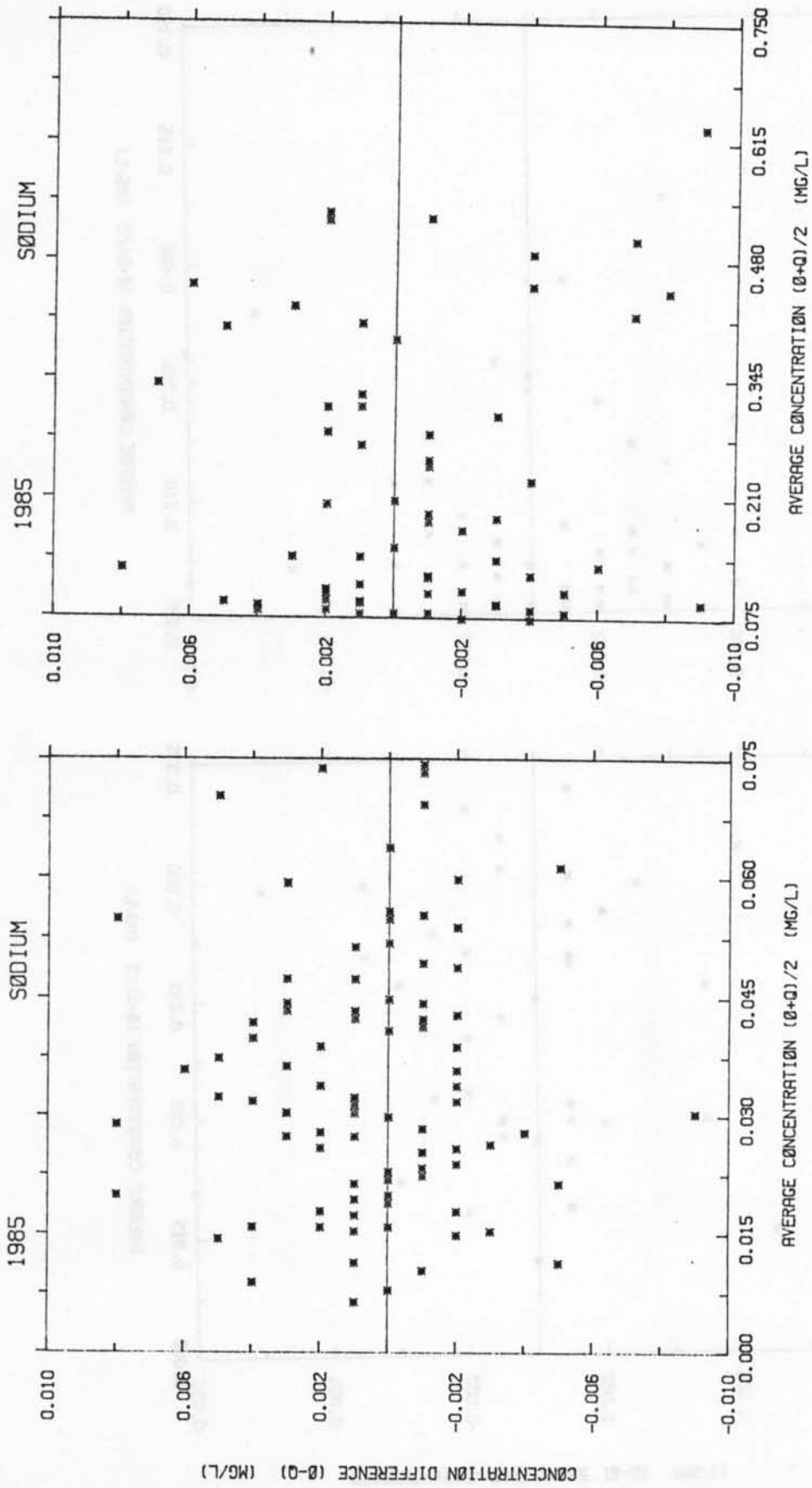
FIGURE 26. O/Q replicate plots for sodium for 1985.
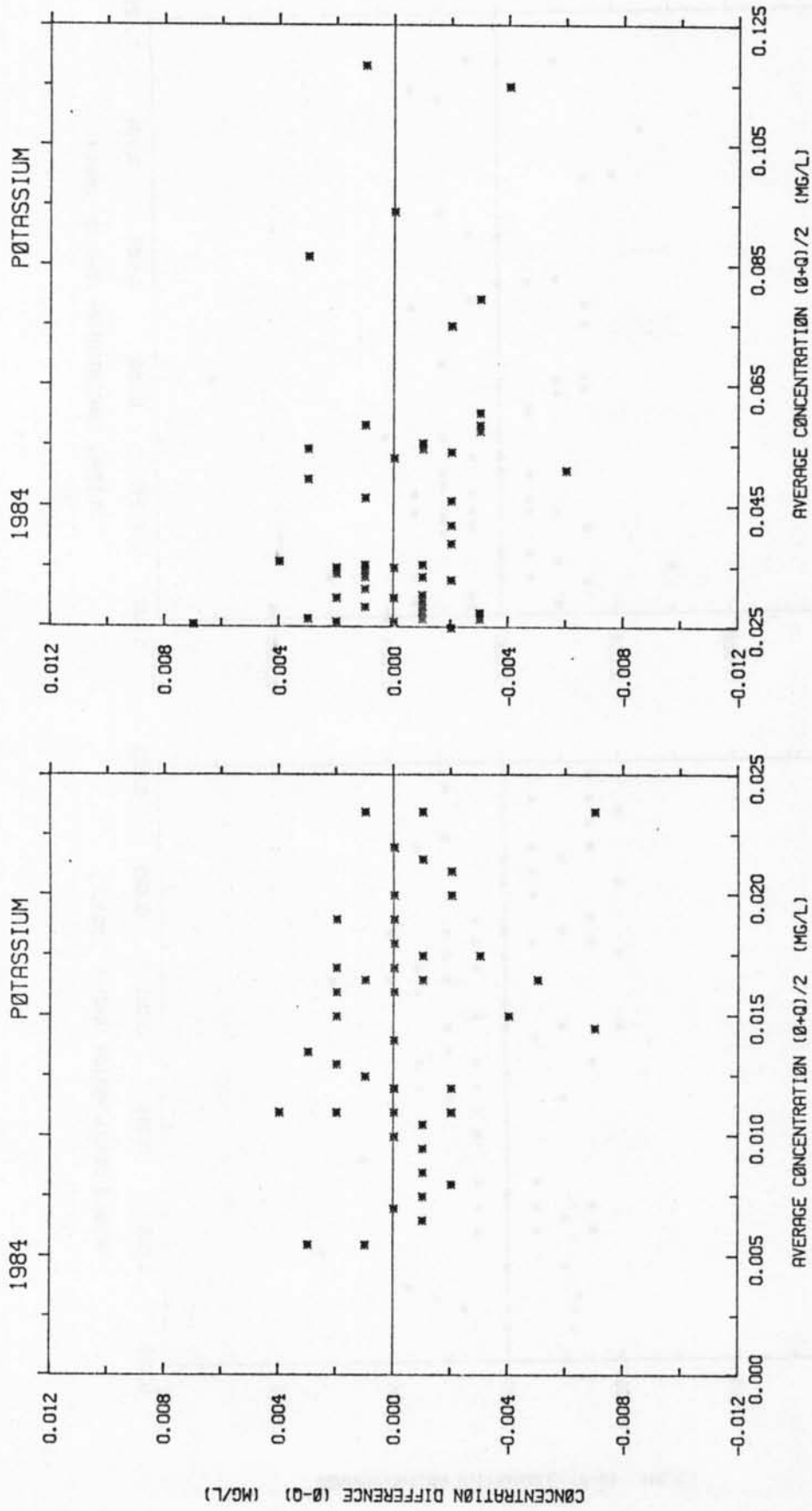
FIGURE 27. O/Q replicate plots for potassium for 1984.
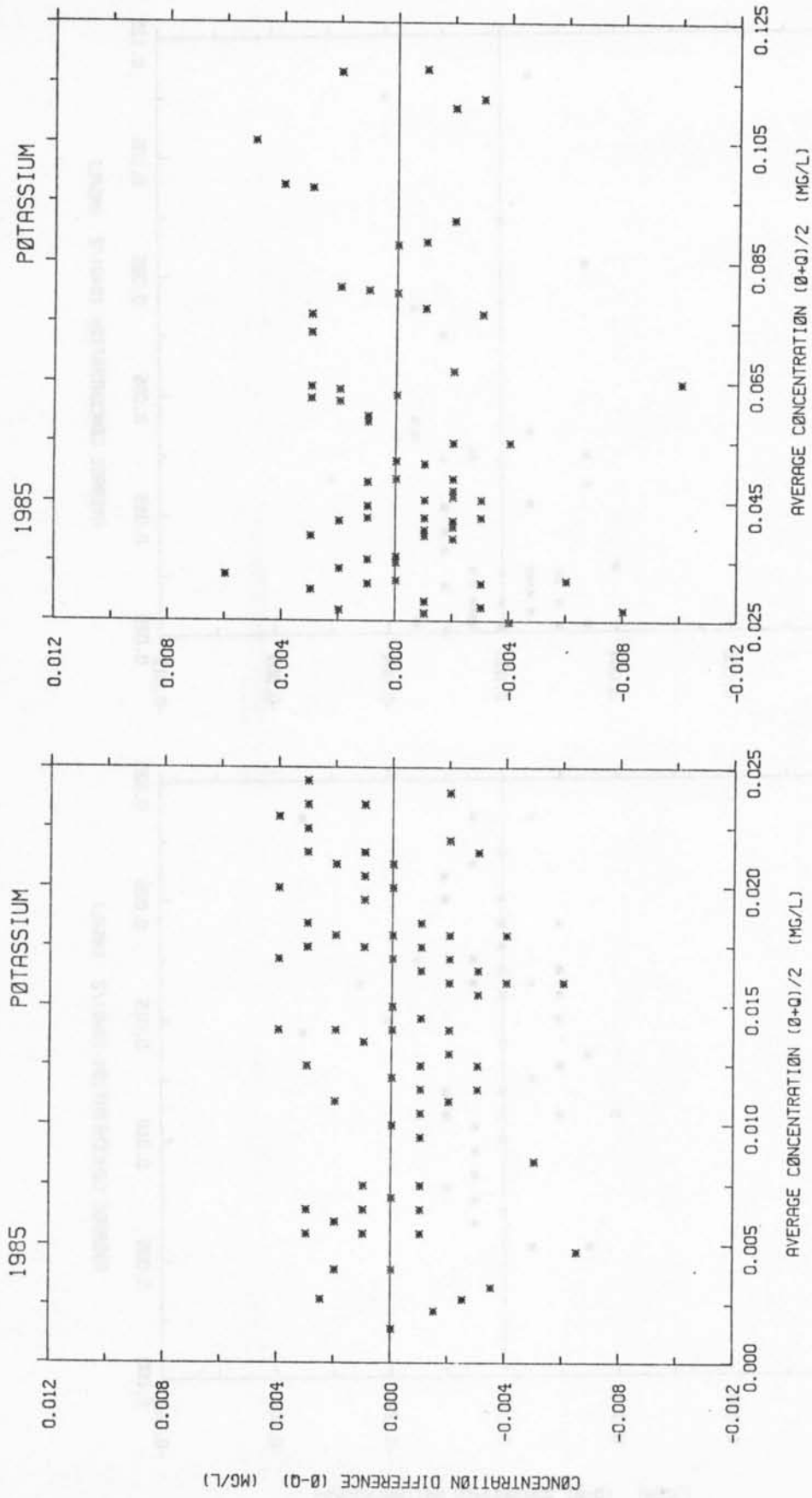
FIGURE 28. O/Q replicate plots for potassium for 1985.
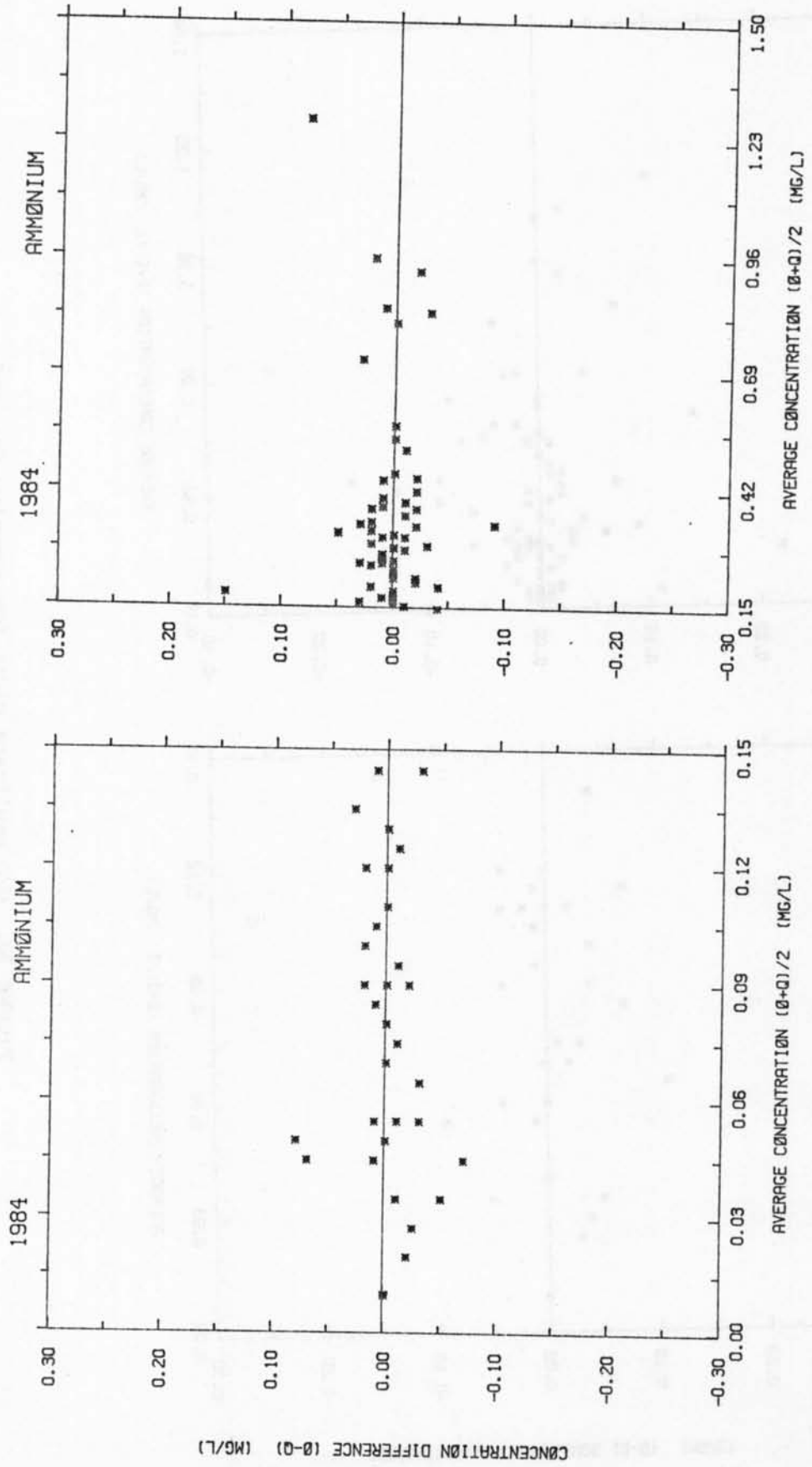
FIGURE 29. O/Q replicate plots for ammonium for 1984.
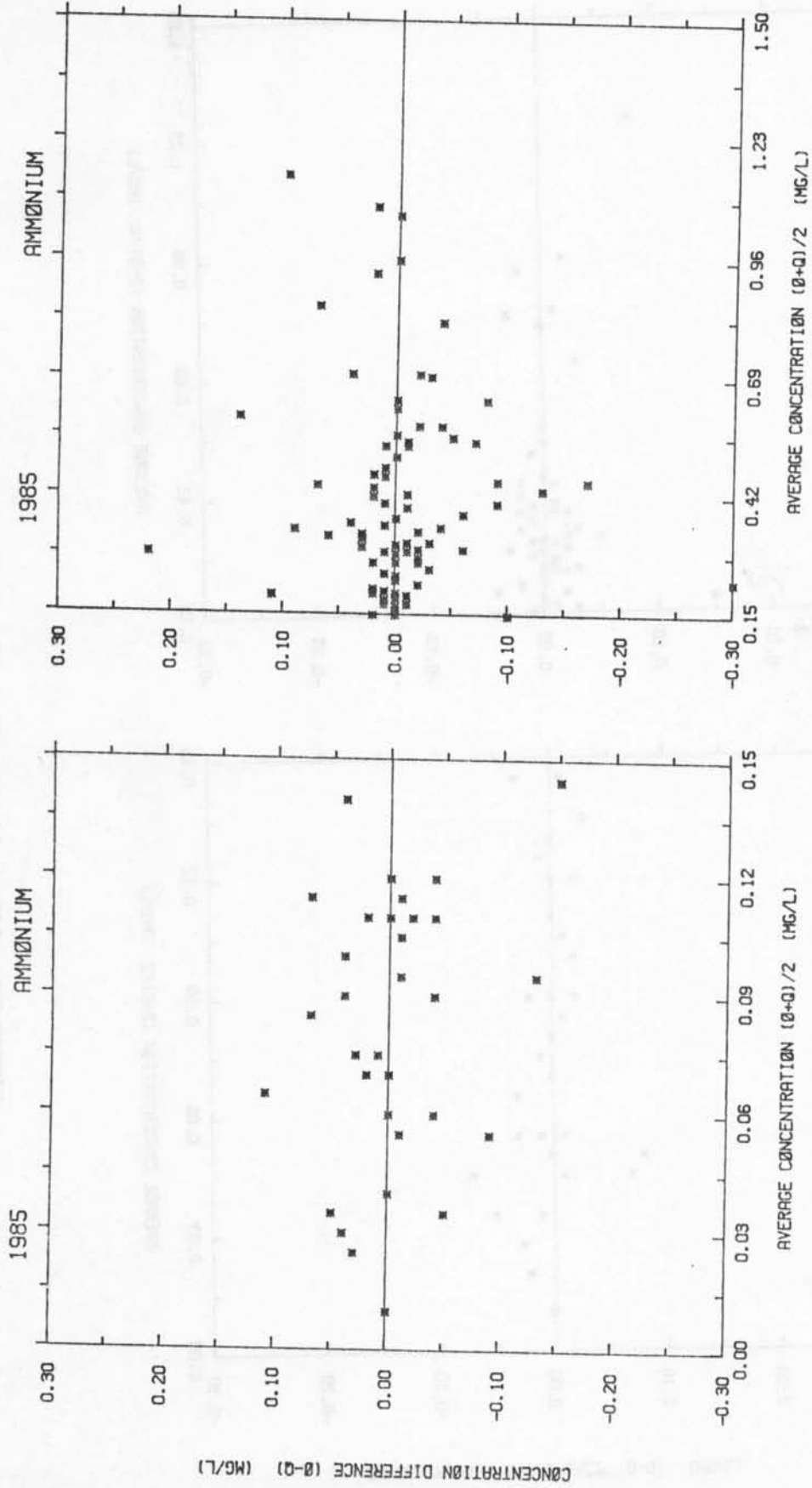
FIGURE 30. O/Q replicate plots for ammonium for 1985.
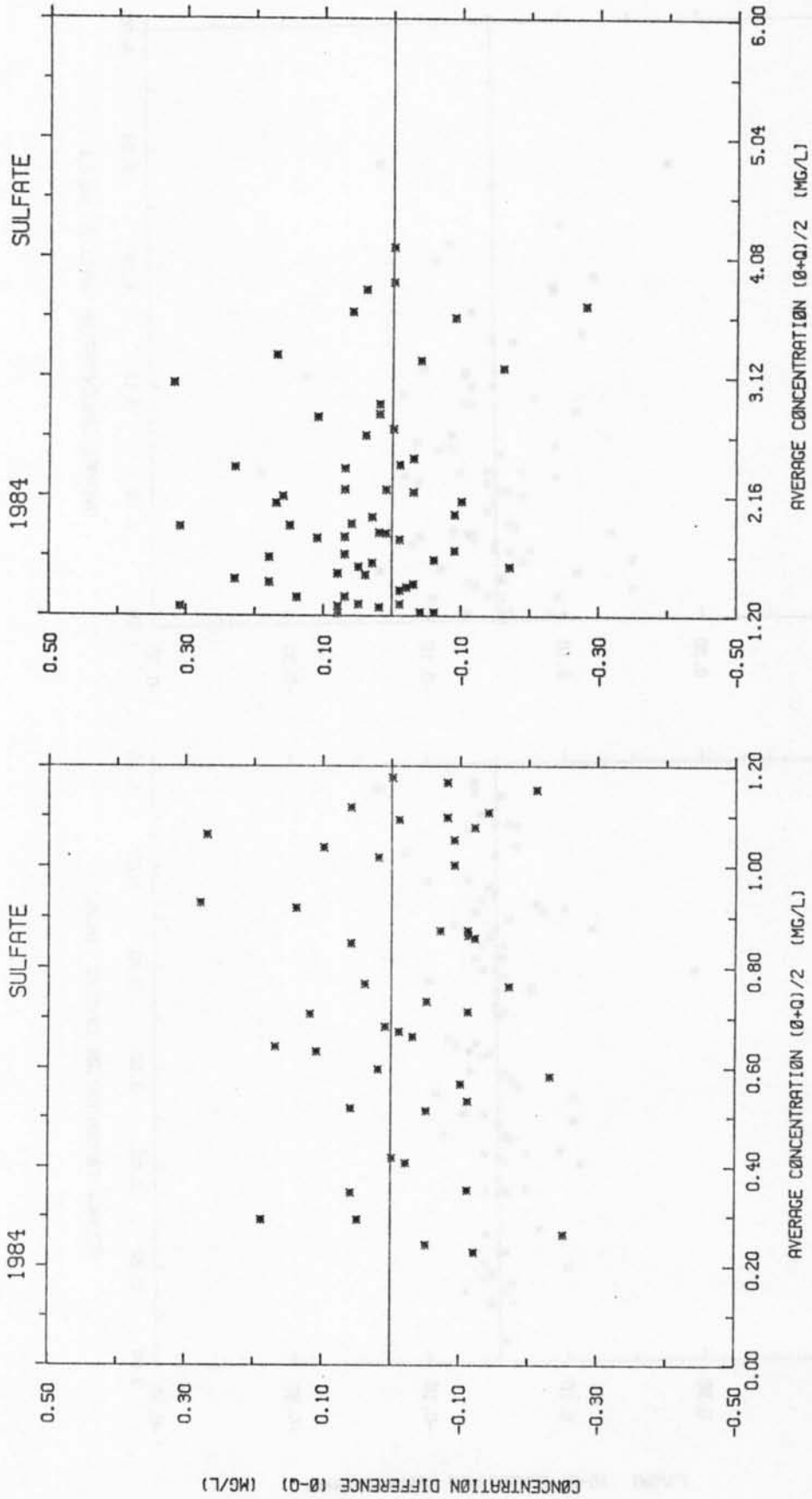
FIGURE 31. O/Q replicate plots for sulfate for 1984.
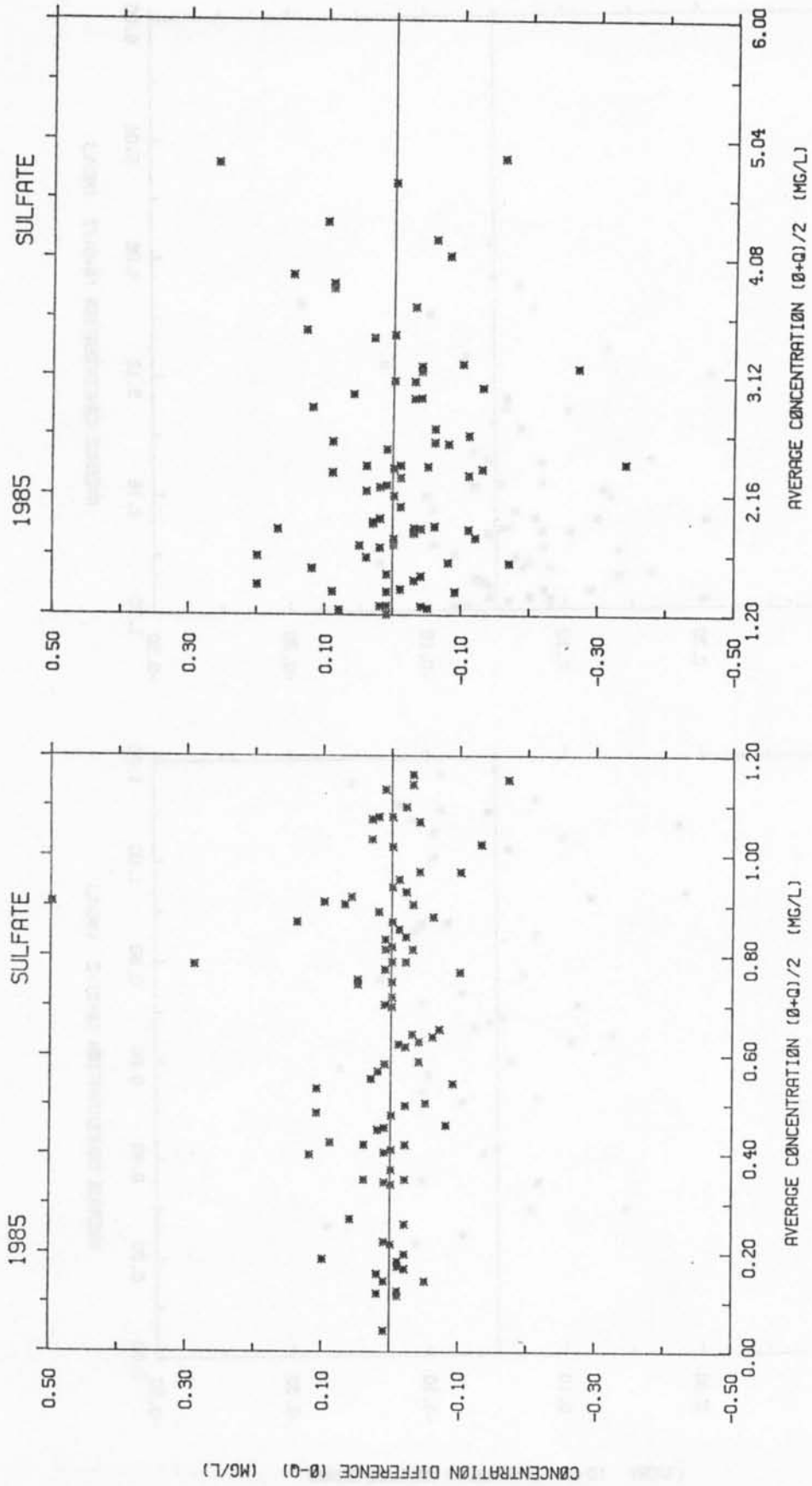
FIGURE 32. O/Q replicate plots for sulfate for 1985.
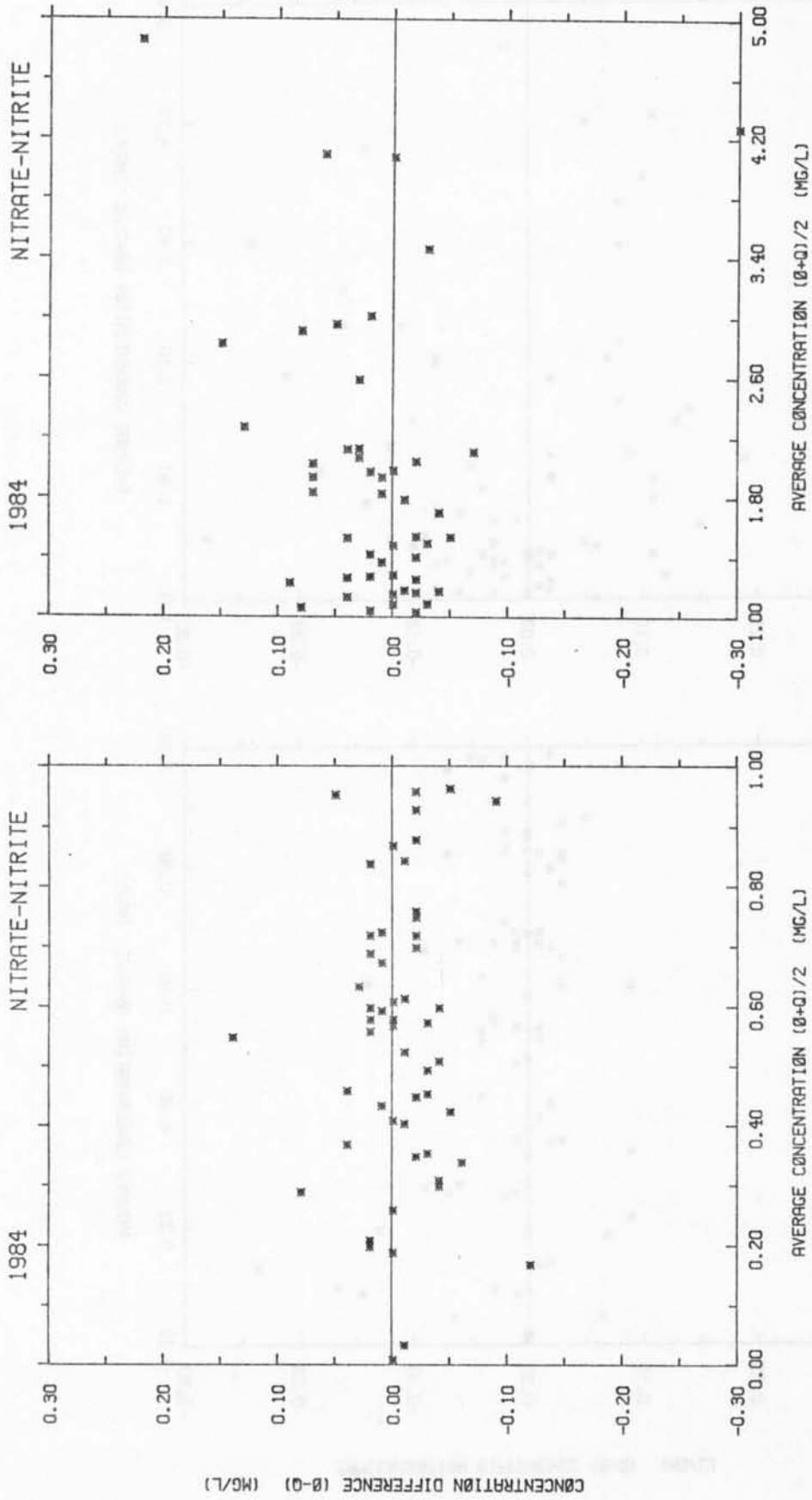
FIGURE 33. O/Q replicate plots for nitrate-nitrite for 1984.
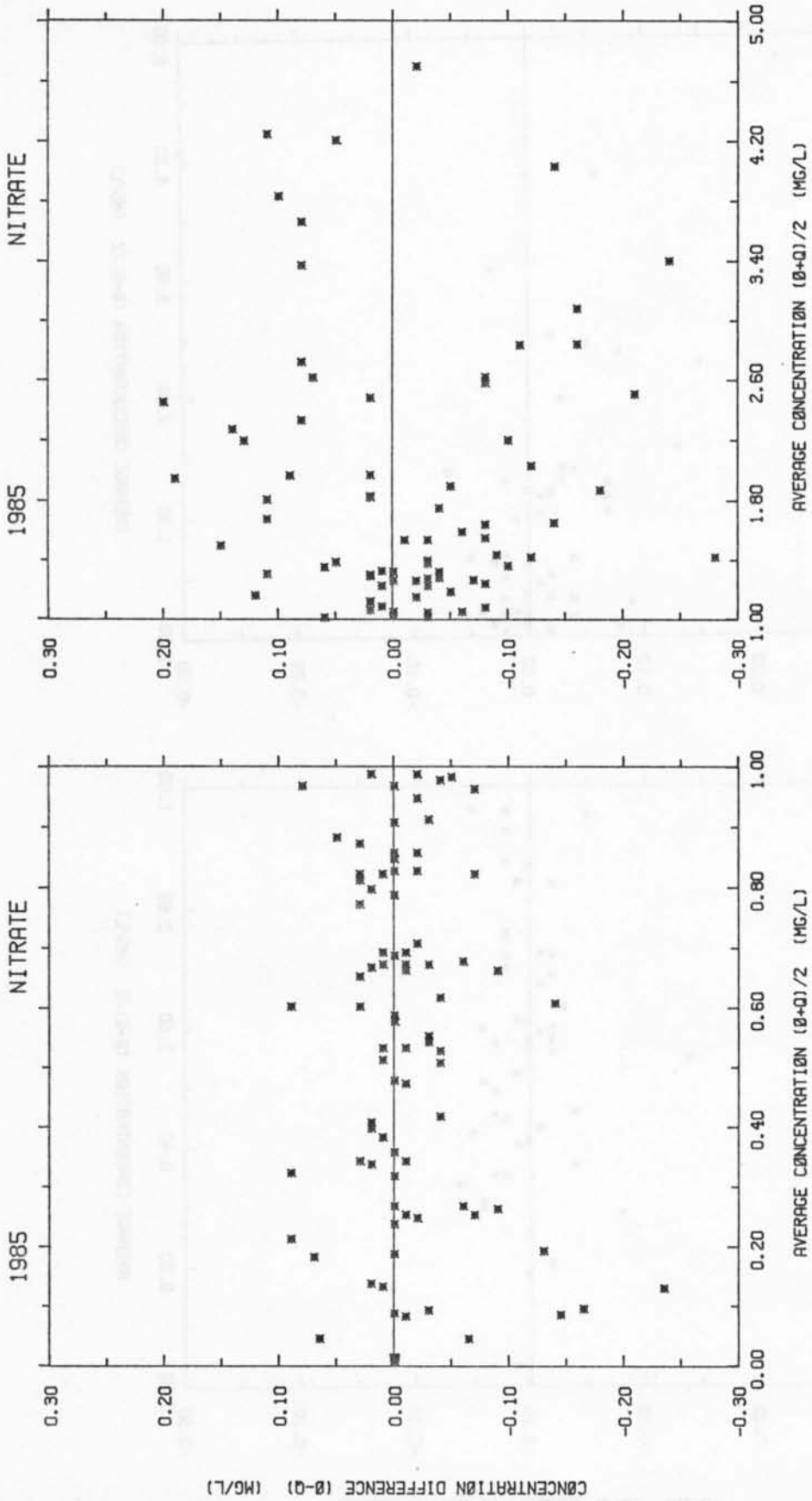
FIGURE 34. O/Q replicate plots for nitrate for 1985.
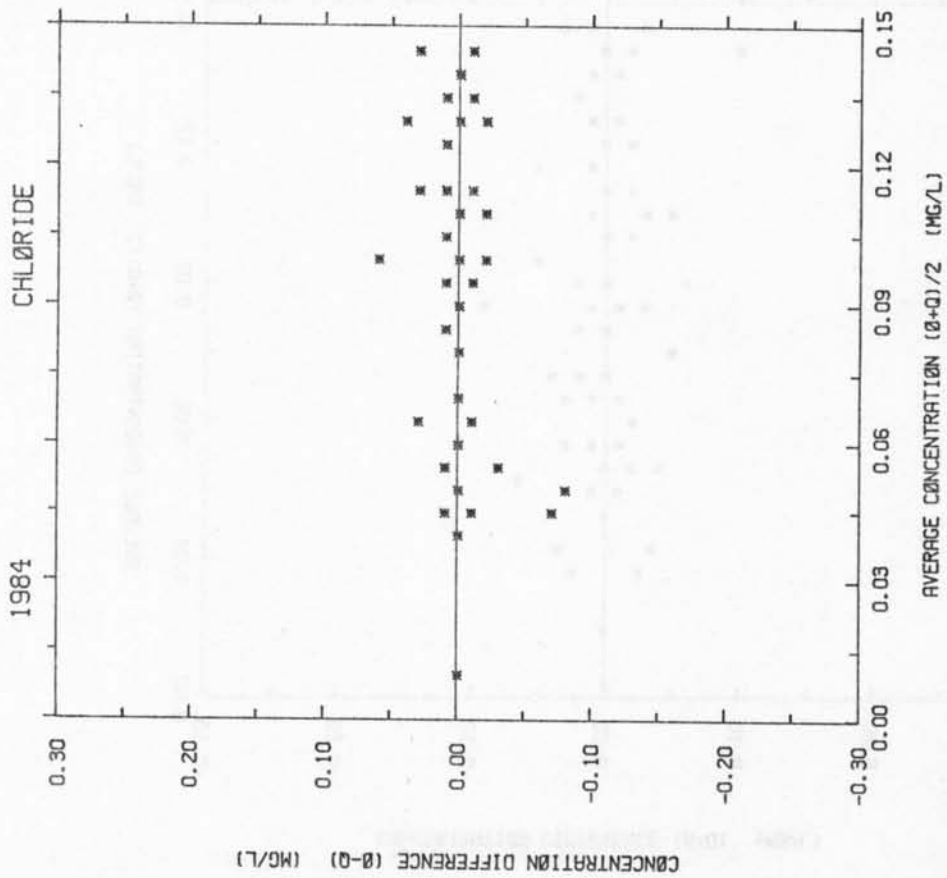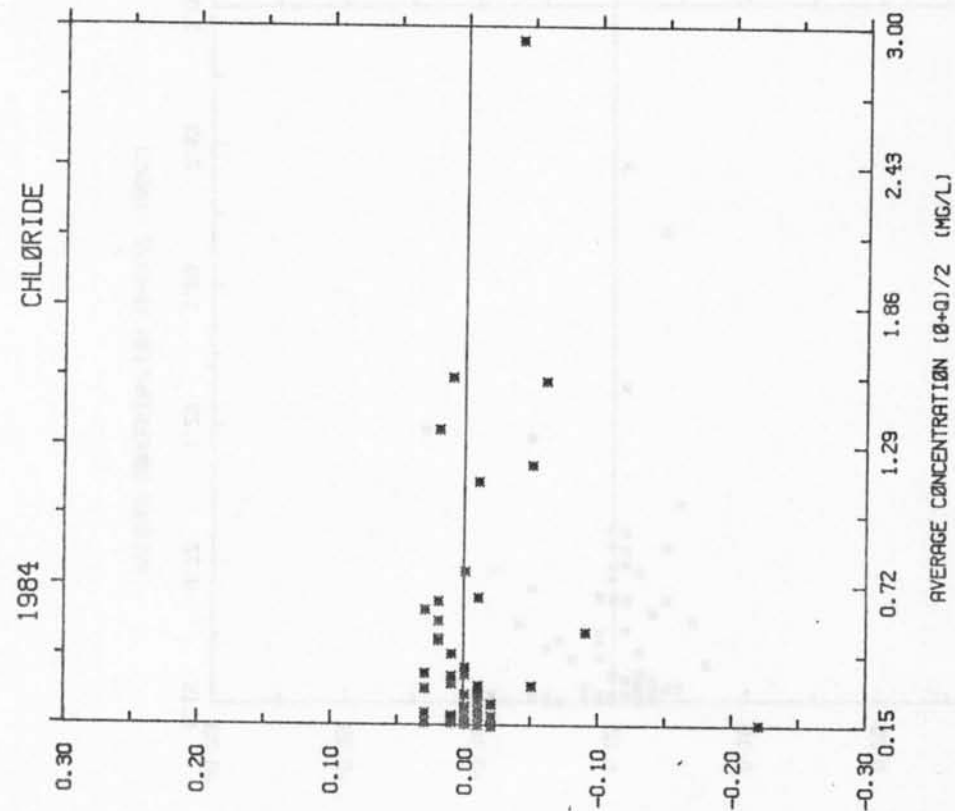
FIGURE 35. O/Q replicate plots for chloride for 1984.
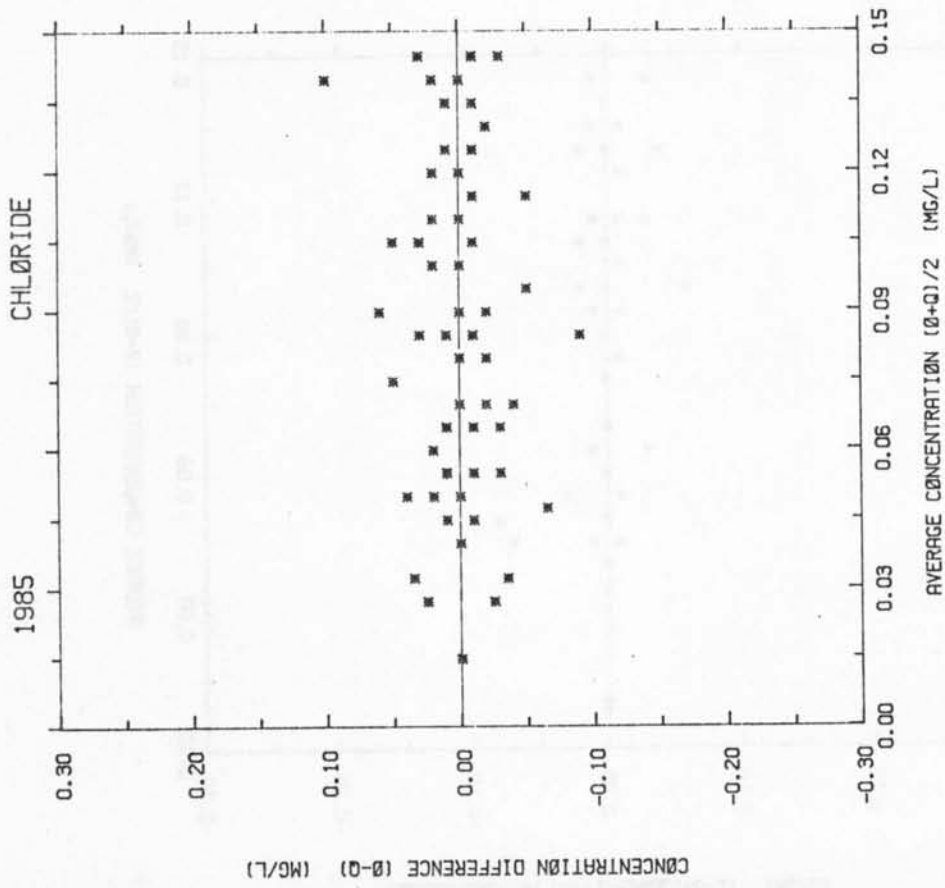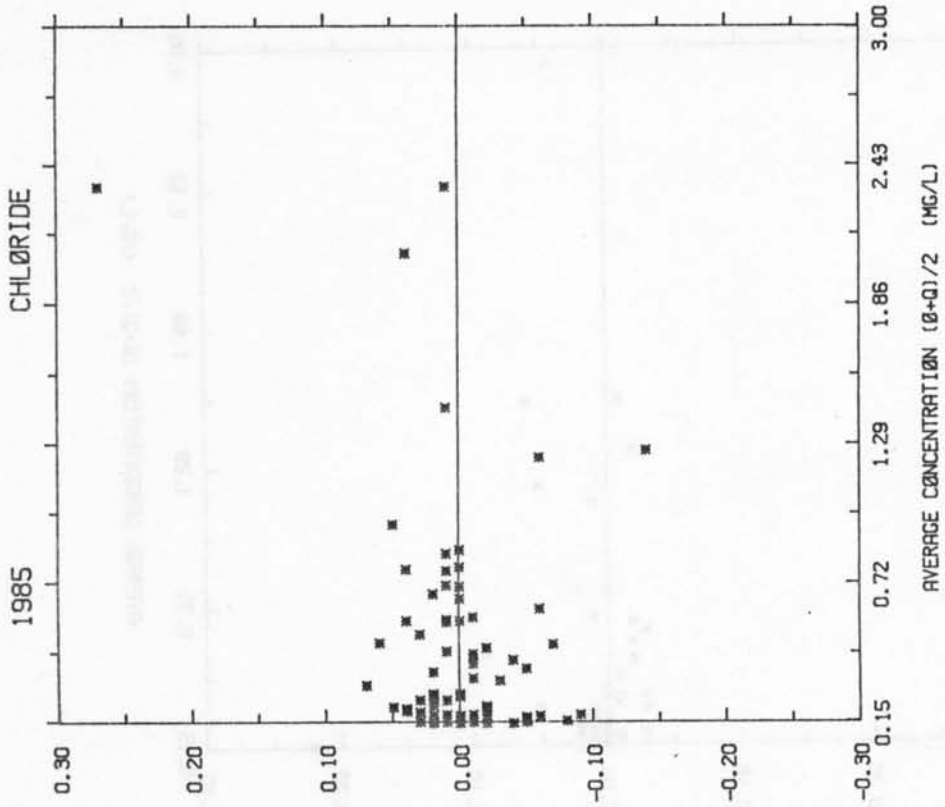
FIGURE 36. O/Q replicate plots for chloride for 1985.
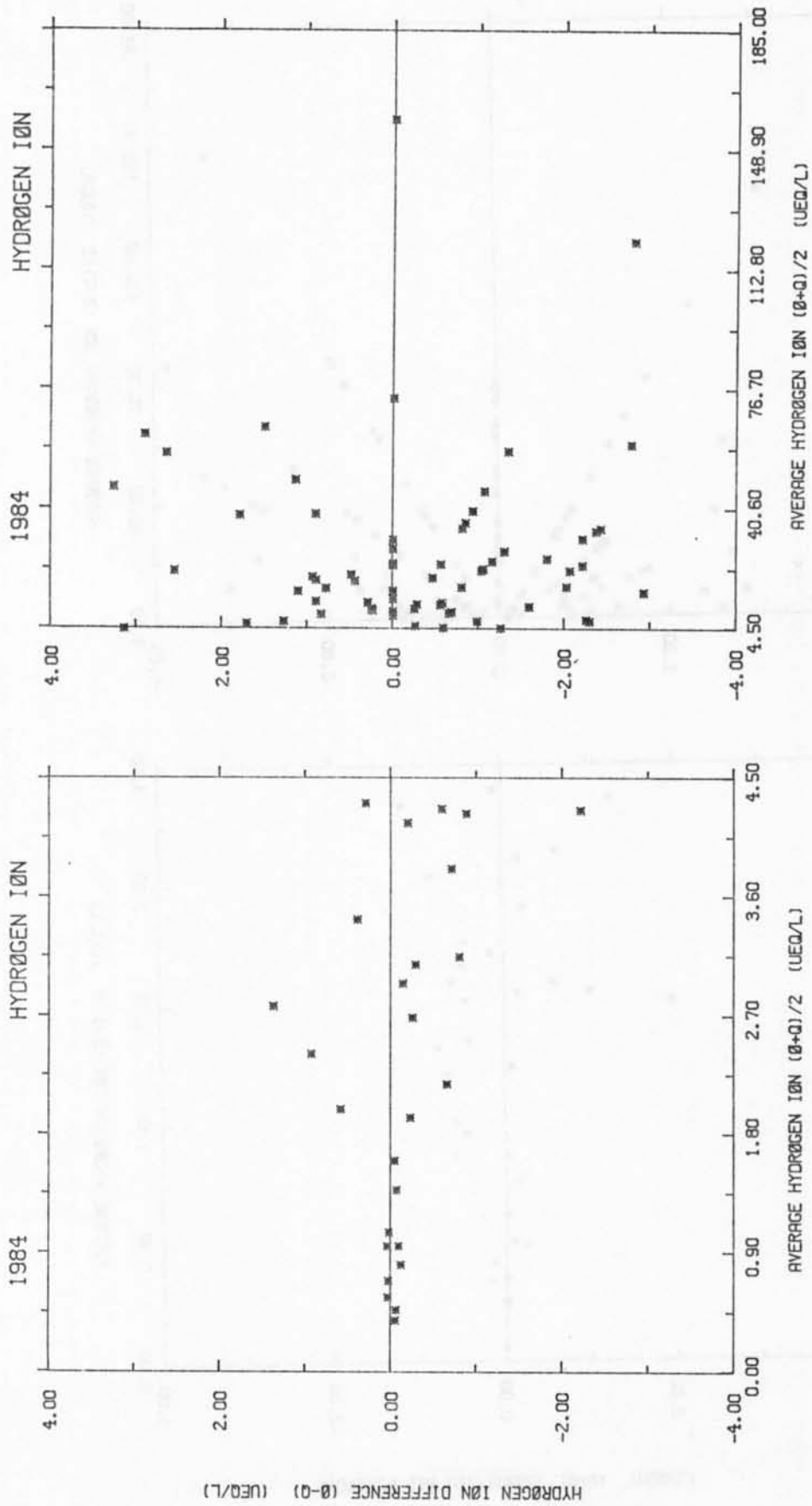
FIGURE 37. O/Q replicate plots for hydrogen ion for 1984.
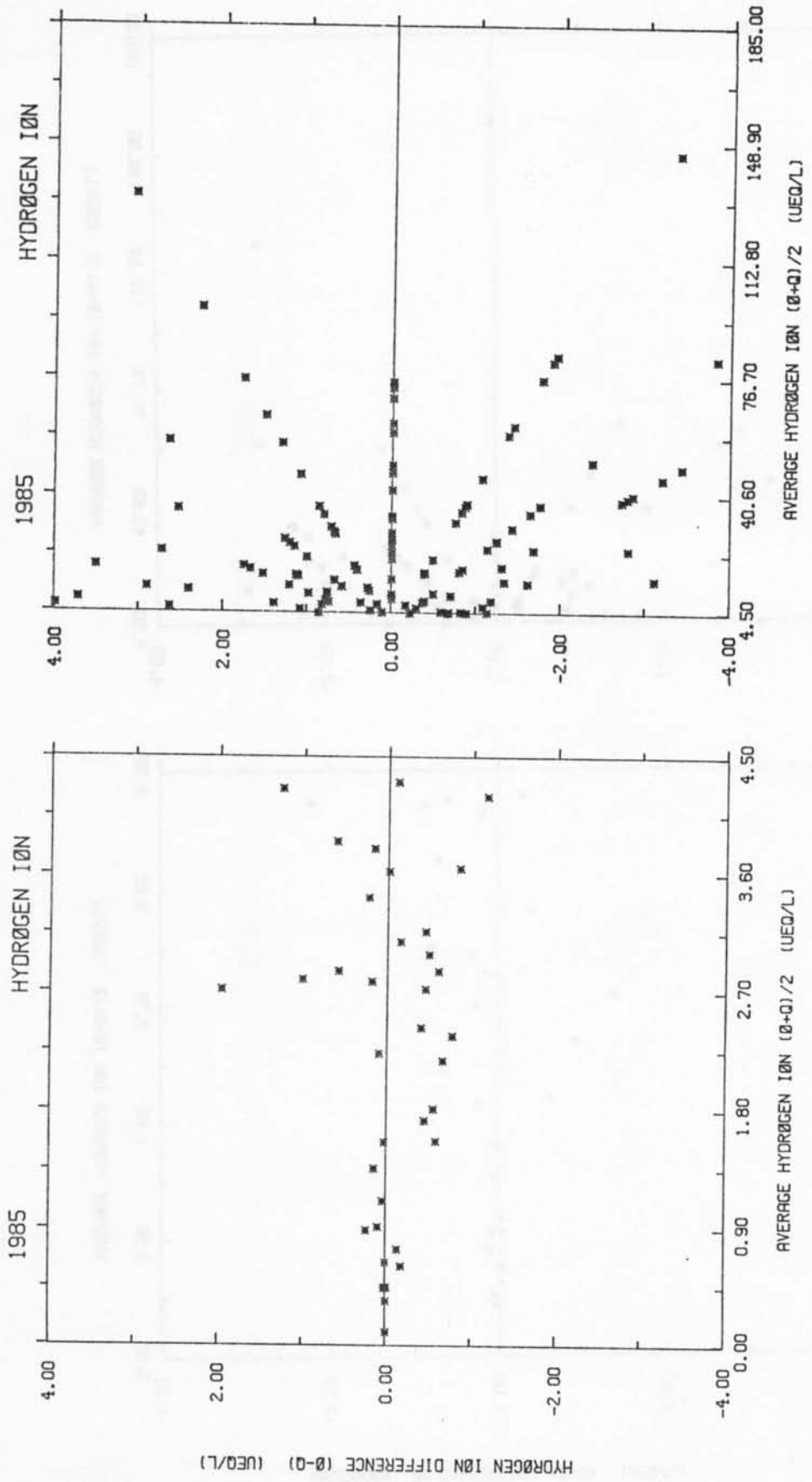
FIGURE 38. O/Q replicate plots for hydrogen ion for 1985.
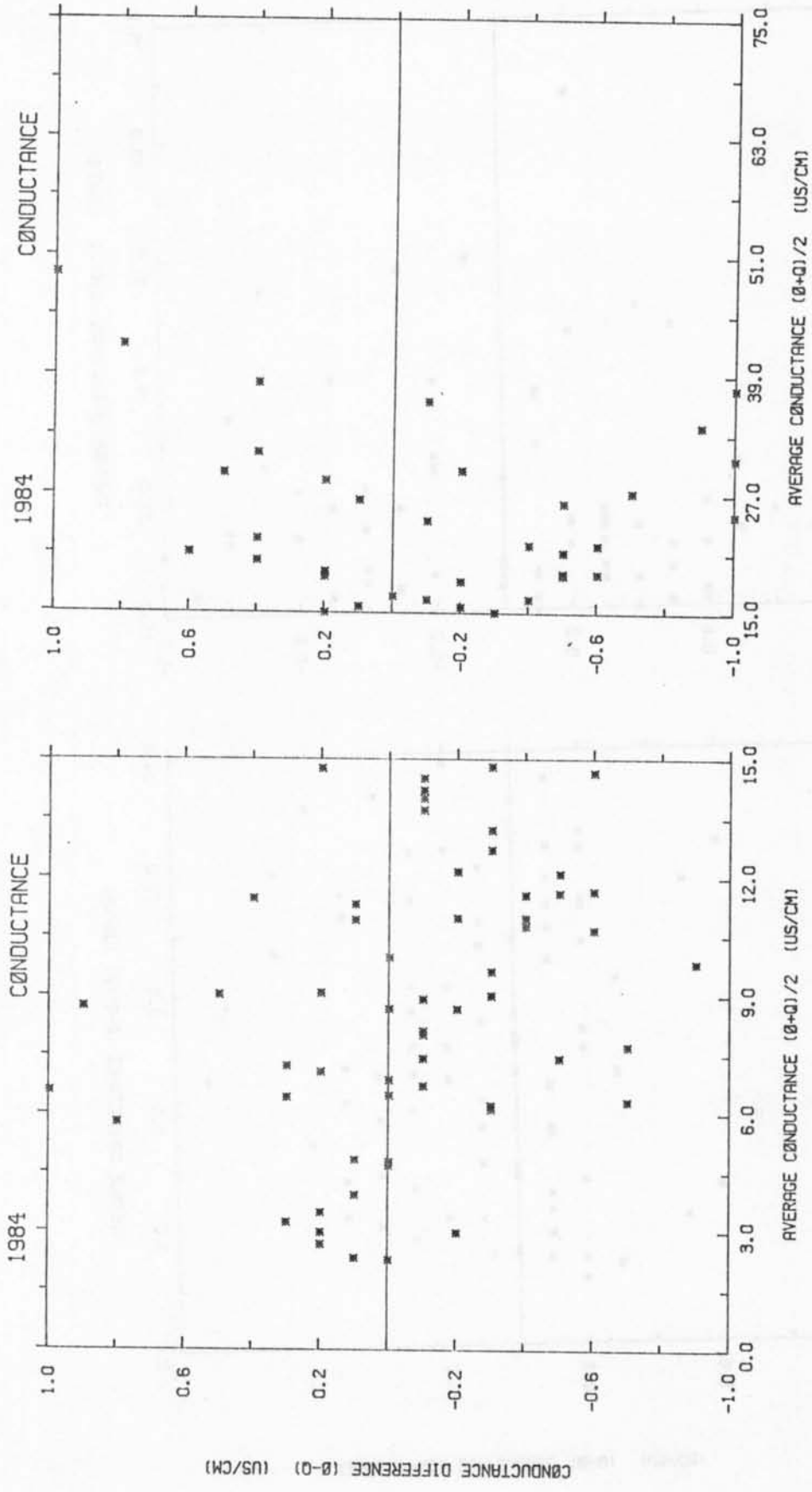
FIGURE 39. O/Q replicate plots for specific conductance for 1984.
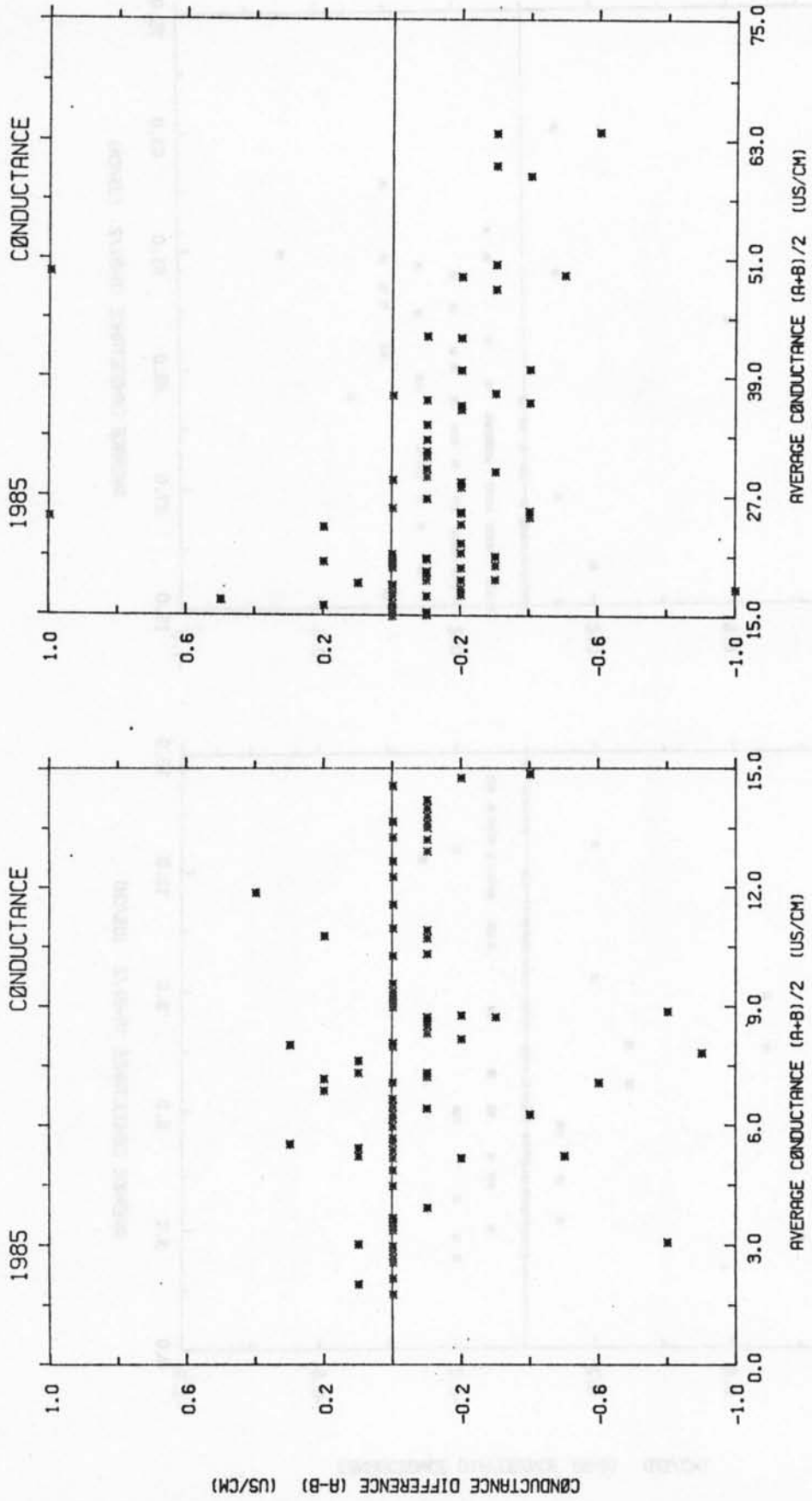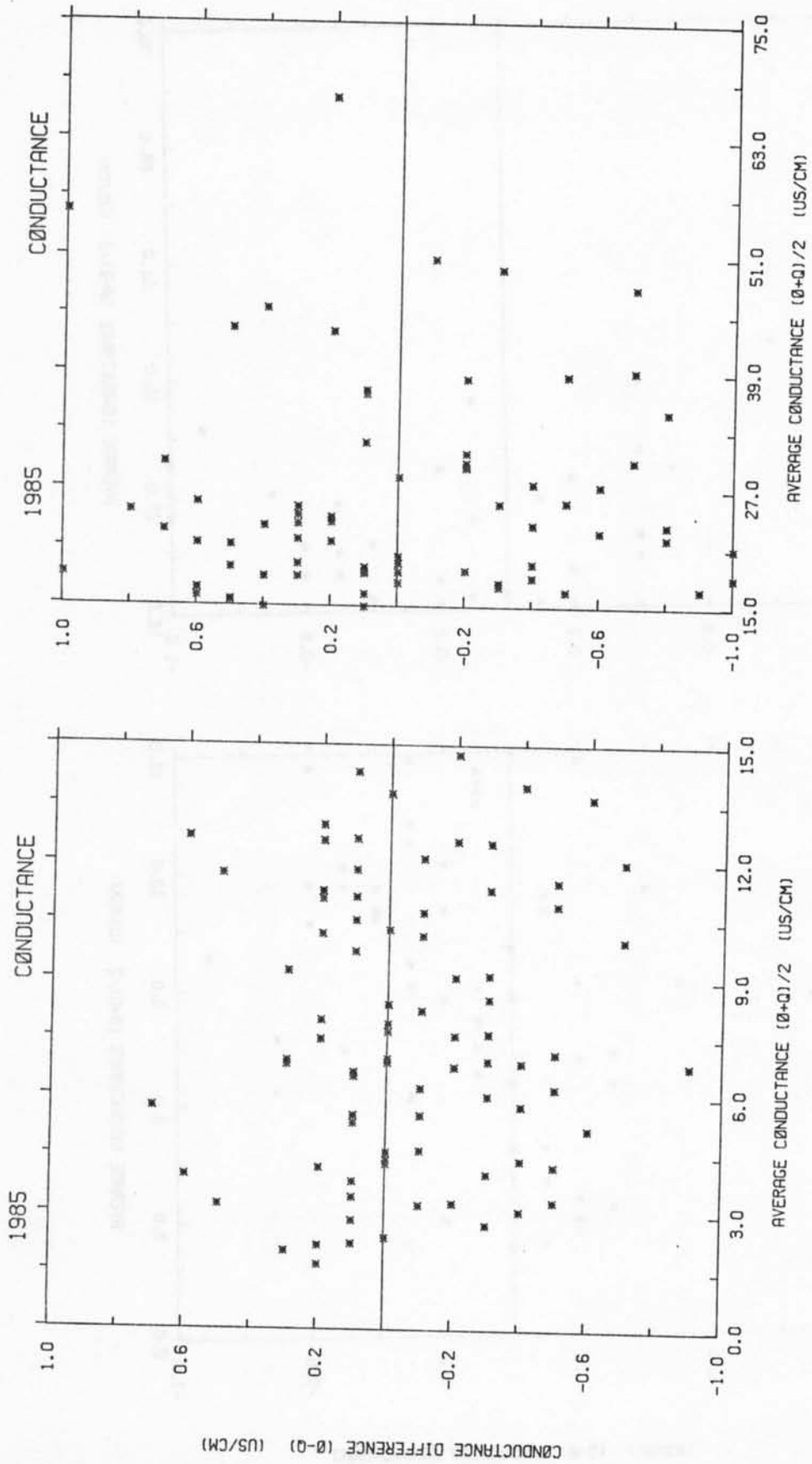
FIGURE 40. O/Q replicate plots for specific conductance for 1985.

TABLE 1 (A-B) Data Summary for Replicate
Analysis in 1984.

Parameter	n[a]	Median Difference (ug/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	231	0.001	0.001	0.006
Magnesium	231	0.000	0.000	0.001
Sodium	231	0.000	0.001	0.006
Potassium	231	0.000	0.000	0.001
Ammonium	231	0.00	0.00	0.02
Sulfate	231	0.00	0.01	0.08
Nitrate-Nitrite	231	0.00	0.00	0.03
Chloride	231	0.00	0.00	0.03
pH (units)	231	0.00	0.00	0.02
Specific Conductance (uS/cm)	231	0.0	-0.1	0.2

a. number of replicate pairs

TABLE 2 (O-Q) Data Summary for Replicate
Analysis in 1984.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	108	-0.001	-0.003	0.034
Magnesium	108	0.000	-0.001	0.009
Sodium	108	0.000	0.007	0.156
Potassium	108	0.000	-0.006	0.059
Ammonium	108	0.00	0.00	0.05
Sulfate	108	0.01	0.01	0.12
Nitrate-Nitrite	108	0.00	0.01	0.12
Chloride	108	0.00	0.01	0.15
pH (units)	108	-0.01	-0.01	0.02
Specific Conductance (uS/cm)	108	-0.1	-0.2	1.2

a. number of replicate pairs

TABLE 3 (A–B) Data Summary for Replicate Analysis in 1985.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	177	0.000	0.000	0.003
Magnesium	177	0.000	0.000	0.002
Sodium	177	0.000	0.000	0.005
Potassium	177	0.000	-0.001	0.014
Ammonium	177	0.00	0.00	0.01
Sulfate	177	0.00	-0.01	0.06
Nitrate	177	0.00	-0.01	0.05
Chloride	177	0.00	0.00	0.03
pH (units)	177	0.00	0.00	0.02
Specific Conductance (uS/cm)	177	0.0	0.0	0.4

a. number of replicate pairs

TABLE 4 (O–Q) Data Summary for Replicate Analysis in 1985.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	176	0.000	-0.001	0.007
Magnesium	176	0.000	0.000	0.002
Sodium	176	0.000	0.000	0.048
Potassium	176	0.000	0.000	0.012
Ammonium	176	0.00	0.00	0.05
Sulfate	176	0.00	-0.01	0.27
Nitrate	176	0.00	-0.01	0.11
Chloride	176	0.00	0.01	0.08
pH (units)	176	0.00	-0.01	0.02
Specific Conductance (uS/cm)	176	0.0	-0.1	0.7

a. number of replicate pairs

APPENDIX D

Interlaboratory Comparison Data
WMO and LRTAP
1984-1985

TABLE 1   Interlaboratory Comparison of Reference
Precipitation Samples — April 1984 —
Compares CAL Values to Expected Values.

Parameter	Samples					
	1XXX		2XXX		3XXX	
	CAL	Expected	CAL	Expected	CAL	Expected
Calcium (mg/L)	0.052	0.056	0.010	0.013	0.104	0.115
Magnesium (mg/L)	0.020	0.022	0.010	0.010	0.038	0.040
Sodium (mg/L)	0.185	0.185	0.243	0.241	0.483	0.490
Potassium (mg/L)	0.078	0.066	0.096	0.094	0.097	0.094
Ammonium (mg/L)	0.12	0.107	0.84	0.808	1.09	1.028
Nitrate (mg/L)	0.49	0.496	0.53	0.505	6.95	6.861
Chloride (mg/L)	0.27	0.28	0.40	0.41	1.23	1.26
Sulfate (mg/L)	2.52	2.427	6.14	6.318	10.31	11.028
pH (units)	4.31	4.28	4.03	4.01	3.58	3.55
Specific Conductance (uS/cm)	23.8	24.2	48.5	50.7	129.2	136.2

TABLE 2   Interlaboratory Comparison of Reference
Precipitation Samples — October 1984 —
Compares CAL Values to Expected Values.

Parameter	Samples					
	1XXX		2XXX		3XXX	
	CAL	Expected	CAL	Expected	CAL	Expected
Calcium (mg/L)	0.048	0.053	0.132	0.133	<0.009	0.005
Magnesium (mg/L)	0.019	0.019	0.010	0.010	0.039	0.038
Sodium (mg/L)	0.190	0.187	0.251	0.246	0.488	0.486
Potassium (mg/L)	0.069	0.067	0.088	0.082	0.101	0.099
Ammonium (mg/L)	0.10	0.097	0.85	0.788	1.11	1.020
Nitrate (mg/L)	0.49	0.509	0.53	0.522	0.58	0.611
Chloride (mg/L)	0.31	0.29	0.64	0.63	0.96	0.92
Sulfate (mg/L)	2.61	2.615	8.09	8.230	11.68	11.034
pH (units)	4.24	4.28	3.86	3.88	3.73	3.73
Specific Conductance (uS/cm)	25.0	24.4	64.1	66.0	90.2	92.7

TABLE 3 Interlaboratory Comparison of Reference
Precipitation Samples — April 1985 —
Compares CAL Values to Expected Values.

	Samples					
	1XXX		2XXX		3XXX	
Parameter	CAL	Expected	CAL	Expected	CAL	Expected
Calcium (mg/L)	0.049	0.054	0.050	0.057	0.052	0.053
Magnesium (mg/L)	0.019	0.019	0.010	0.010	0.039	0.039
Sodium (mg/L)	0.191	0.194	0.247	0.247	0.400	0.401
Potassium (mg/L)	0.087	0.086	0.080	0.079	0.079	0.080
Ammonium (mg/L)	0.09	0.100	0.82	0.788	1.20	1.153
Nitrate (mg/L)	0.49	0.486	0.49	0.513	7.92	7.959
Chloride (mg/L)	0.39	0.390	0.35	0.376	1.29	1.29
Sulfate (mg/L)	1.77	1.992	6.26	7.115	8.78	10.159
pH (units)	4.40	4.39	4.00	4.00	3.58	3.56
Specific Conductance (uS/cm)	21.2	20.2	54.6	53.1	136.4	134.3

TABLE 4 Interlaboratory Comparison of Reference
Precipitation Samples — October 1985 —
Compares CAL Values to Expected Values.

	Samples					
	1XXX		2XXX		3XXX	
Parameter	CAL	Expected	CAL	Expected	CAL	Expected
Calcium (mg/L)	0.052	0.050	0.134	0.140	3.68	3.603
Magnesium (mg/L)	0.021	0.020	0.012	0.012	0.362	0.352
Sodium (mg/L)	0.178	0.176	0.244	0.243	0.507	0.504
Potassium (mg/L)	0.071	0.074	0.087	0.090	5.389	5.430
Ammonium (mg/L)	0.12	0.103	0.80	0.808	0.91	0.846
Nitrate (mg/L)	0.62	0.638	0.53	0.520	9.03	8.919
Chloride (mg/L)	0.31	0.290	0.68	0.630	8.63	8.33
Sulfate (mg/L)	2.70	2.52	7.98	7.73	35.0	34.2
pH (units)	4.27	4.29	3.92	3.92	3.20	3.19
Specific Conductance (uS/cm)	26.8	24.7	64.6	51.6	333.5	322.2

TABLE 5   LRTAP Interlaboratory Comparability Study L5 –
January 1984 – CAL Reported Values
Compared to CCIW Median Values for All
Participating Laboratories.[a]

Parameter	Sample Number					
	5		6		8	
	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	1.00	0.99	1.54	1.5	0.315	0.31
Magnesium (mg/L)	0.212	0.21	0.337	0.33	0.067	0.07
Sodium (mg/L)	0.214	0.21	0.310	0.30	0.518	0.51
Potassium (mg/L)	0.125	0.12	0.148	0.15	0.335	0.32
Nitrate + Nitrite (mg/L)	0.57	0.56	0.78	0.76	0.01	0.009
Chloride (mg/L)	0.63	0.67	0.91	0.90	1.53	1.5
Sulfate (mg/L)	4.84	4.9	5.32	5.4	0.36	0.43
pH (units)	4.38	4.3	4.46	4.4	5.80	5.7
Specific Conductance (uS/cm)	33.3	35.6	35.2	36.5	7.4	8.1

a. number of participating laboratories = 44

TABLE 6   LRTAP Interlaboratory Comparability Study L6 –
May 1984 – CAL Reported Values Compared
to CCIW Median Values for All
Participating Laboratories.[a]

Parameter	Sample Number					
	1		2		3	
	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	1.51	1.50	2.44	2.42	0.343	0.310
Magnesium (mg/L)	0.336	0.34	0.719	0.73	0.068	0.06
Sodium (mg/L)	0.309	0.31	0.056	0.060	0.581	0.510
Potassium (mg/L)	0.144	0.144	0.091	0.09	0.342	0.33
Nitrate + Nitrite (mg/L)	3.41	3.41	5.00	5.13	0.04	0.04
Chloride (mg/L)	1.00	0.900	0.83	0.795	1.66	1.50
Sulfate (mg/L)	5.28	5.24	5.29	5.20	0.41	0.40
pH (units)	4.40	4.40	4.75	4.79	5.74	5.64
Specific Conductance (uS/cm)	36.9	36.8	33.1	32.5	8.6	8.0

a. number of participating laboratories = 39

TABLE 7 LRTAP Interlaboratory Comparability Study L8 –
December 1984 – CAL Reported Values
Compared to CCIW Median Values for All
Participating Laboratories.[a]

Parameter	Sample Number							
	2		4		7		8	
	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	0.038	0.075	3.11	3.00	1.217	1.22	0.325	0.300
Magnesium (mg/L)	0.716	0.720	0.874	0.900	0.334	0.340	0.069	0.070
Sodium (mg/L)	0.702	0.700	0.162	0.160	0.318	0.320	0.528	0.501
Potassium (mg/L)	1.08	1.075	0.082	0.082	0.691	0.700	0.347	0.330
Nitrate + Nitrite (mg/L)	0.49	0.487	4.51	4.515	1.15	1.107	0.09	0.044
Chloride (mg/L)	0.86	0.900	0.80	0.800	3.28	3.250	1.52	1.500
Sulfate (mg/L)	2.97	3.000	5.63	5.650	3.40	3.400	0.42	0.410
pH (units)	5.11	5.13	6.27	6.19	4.61	4.58	5.74	5.70
Specific Conductance (uS/cm)	18.0	18.20	29.0	30.80	31.1	31.20	8.0	8.00

a. number of participating laboratories = 44

TABLE 8 LRTAP Interlaboratory Comparability Study L9 –
May 1985 – CAL Reported Values Compared
to CCIW Median Values for All
Participating Laboratories.[a]

Parameter	Sample Number					
	3		4		5	
	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	3.06	3.03	1.21	1.23	0.973	0.98
Magnesium (mg/L)	0.865	0.89	0.335	0.34	0.207	0.21
Sodium (mg/L)	0.160	0.16	0.324	0.32	0.222	0.21
Potassium (mg/L)	0.081	0.08	0.700	0.70	0.133	0.13
Ammonium (mg/L)	<0.02	0.013	0.59	0.580	0.58	0.554
Nitrate + Nitrite (mg/L)	4.52	4.47	1.15	1.11	2.39	2.51
Chloride (mg/L)	0.78	0.78	3.24	3.24	0.64	0.62
Sulfate (mg/L)	5.45	5.50	3.30	3.30	4.53	4.80
pH (units)	6.21	6.10	4.61	4.60	4.36	4.33
Specific Conductance (uS/cm)	30.7	30.70	32.4	31.25	35.5	35.00

a. number of participating laboratories = 33

TABLE 9   LRTAP Interlaboratory Comparability Study L10 —
August 1985 — CAL Reported Values
Compared to CCIW Median Values for All
Participating Laboratories.[a]

| Parameter | Sample Number | | | | | | | |
| | 1 | | 2 | | 3 | | 4 | |
	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	13.0	13.00	8.49	8.61	1.497	1.50	7.44	7.35
Magnesium (mg/L)	2.63	2.74	1.83	1.90	0.328	0.332	1.53	1.58
Sodium (mg/L)	1.23	1.22	3.74	3.80	0.311	0.30	1.91	1.90
Potassium (mg/L)	0.491	0.50	0.174	0.17	0.148	0.14	0.617	0.63
Ammonium (mg/L)	<0.02	0.010	<0.02	0.013	0.49	0.477	<0.02	0.010
Nitrate + Nitrite (mg/L)	1.37	1.33	0.04	0.040	3.41	3.32	1.15	1.08
Chloride (mg/L)	1.26	1.24	20.98	21.00	0.94	0.930	2.14	1.94
Sulfate (mg/L)	3.23	3.10	7.62	7.50	5.35	5.29	9.04	8.89
pH (units)	7.78	7.79	5.54	5.60	4.44	4.42	7.43	7.26
Specific Conductance (uS/cm)	95.4	94.85	97.1	95.85	36.3	36.00	64.7	64.00

a. number of participating laboratories = 42

TABLE 9   (continued) LRTAP Study L10 — August 1985 —
CAL Reported Values Compared to CCIW Median
Values for All Participating Laboratories.[a]

| Parameter | Sample Number | | | | | | | |
| | 5 | | 6 | | 7 | | 8 | |
	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	3.92	3.92	1.30	1.30	2.38	2.36	0.292	0.289
Magnesium (mg/L)	0.650	0.670	0.274	0.281	0.720	0.730	0.048	0.050
Sodium (mg/L)	0.890	0.915	0.516	0.510	0.133	0.130	0.323	0.310
Potassium (mg/L)	0.402	0.411	0.270	0.270	0.082	0.086	0.155	0.150
Ammonium (mg/L)	<0.02	0.021	<0.02	0.012	0.12	0.124	0.14	0.122
Nitrate + Nitrite (mg/L)	0.58	0.56	0.44	0.41	5.67	5.62	0.62	0.620
Chloride (mg/L)	0.26	0.26	0.25	0.24	0.38	0.37	0.50	0.48
Sulfate (mg/L)	12.79	12.75	5.02	4.91	6.47	6.34	0.35	0.33
pH (units)	6.27	6.10	5.30	5.30	4.48	4.45	6.07	5.90
Specific Conductance (uS/cm)	38.8	39.00	18.1	18.00	40.9	40.00	6.2	6.20

a. number of participating laboratories = 42

TABLE 9 (concluded) LRTAP Study L10 – August 1985 –
CAL Reported Values Compared to CCIW Median
Values for All Participating Laboratories.[a]

| | Sample Number | | | | |
| | 9 | | | 10 | |
Parameter	CAL	CCIW		CAL	CCIW
Calcium (mg/L)	1.74	1.78		0.275	0.28
Magnesium (mg/L)	0.394	0.40		0.154	0.15
Sodium (mg/L)	0.515	0.50		1.30	1.29
Potassium (mg/L)	0.136	0.14		0.200	0.20
Ammonium (mg/L)	0.04	0.013		0.08	0.070
Nitrate + Nitrite (mg/L)	<0.03	0.031		0.44	0.443
Chloride (mg/L)	0.20	0.20		2.77	2.71
Sulfate (mg/L)	8.21	8.04		1.86	1.84
pH (units)	4.41	4.40		4.54	4.52
Specific Conductance (uS/cm)	36.4	35.60		24.4	24.70

a. number of participating laboratories = 42

TABLE 10 LRTAP Interlaboratory Comparability Study L11 –
December 1985 – CAL Reported Values
Compared to CCIW Median Values for All
Participating Laboratories.[a]

| | Sample Number | | | | | | | |
| | 1 | | 2 | | 3 | | 4 | |
Parameter	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	2.66	2.630	4.45	4.450	0.978	0.990	0.291	0.280
Magnesium (mg/L)	0.371	0.376	0.714	0.718	0.206	0.210	0.049	0.050
Sodium (mg/L)	0.656	0.653	5.88	5.925	0.219	0.210	0.332	0.320
Potassium (mg/L)	0.243	0.230	0.770	0.780	0.125	0.120	0.154	0.150
Ammonium (mg/L)	<0.02	0.010	<0.02	0.013	0.55	0.534	0.14	0.129
Nitrate + Nitrite (mg/L)	2.77	2.745	0.90	0.908	2.50	2.480	0.61	0.611
Chloride (mg/L)	0.66	0.710	11.04	11.000	0.58	0.622	0.44	0.472
Sulfate (mg/L)	3.42	3.360	7.56	7.475	5.01	4.900	0.36	0.360
pH (units)	6.00	6.00	6.54	6.30	4.33	4.33	6.05	5.92
Specific Conductance (uS/cm)	23.2	22.75	70.0	67.70	36.5	34.05	6.3	6.00

a. number of participating laboratories = 51

TABLE 10 (continued) LRTAP Interlaboratory Comparability
Study L11 — December 1985 — CAL Reported Values
Compared to CCIW Median Values for All
Participating Laboratories.[a]

| | Sample Number | | | | | | | |
| | 5 | | 6 | | 7 | | 8 | |
Parameter	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	2.53	2.510	1.21	1.230	2.39	2.385	5.68	5.670
Magnesium (mg/L)	0.866	0.870	0.336	0.340	0.675	0.680	0.501	0.510
Sodium (mg/L)	0.168	0.160	0.328	0.320	0.578	0.570	0.622	0.620
Potassium (mg/L)	0.080	0.080	0.704	0.700	0.406	0.400	0.236	0.230
Ammonium (mg/L)	<0.02	0.009	0.66	0.656	<0.02	0.023	<0.02	0.013
Nitrate + Nitrite (mg/L)	4.89	4.828	1.18	1.152	1.04	1.062	0.92	0.930
Chloride (mg/L)	0.73	0.783	3.15	3.260	0.35	0.405	0.20	0.240
Sulfate (mg/L)	5.98	5.890	3.48	3.355	8.58	8.510	6.50	6.345
pH (units)	5.03	5.05	4.65	4.67	5.47	5.50	7.17	7.10
Specific Conductance (uS/cm)	32.3	31.30	32.3	31.15	29.5	29.00	40.5	39.00

a. number of participating laboratories = 51

TABLE 10 (concluded) LRTAP Interlaboratory Comparability
Study L11 — December 1985 — CAL Reported Values
Compared to CCIW Median Values for All
Participating Laboratories.[a]

| | Sample Number | | | |
| | 9 | | 10 | |
Parameter	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	6.11	6.115	4.23	4.305
Magnesium (mg/L)	1.24	1.27	0.926	0.950
Sodium (mg/L)	0.581	0.580	1.91	1.910
Potassium (mg/L)	0.234	0.230	0.089	0.090
Ammonium (mg/L)	<0.02	0.010	<0.02	0.013
Nitrate + Nitrite (mg/L)	0.60	0.620	<0.03	0.044
Chloride (mg/L)	0.52	0.560	10.77	10.70
Sulfate (mg/L)	1.51	1.470	3.89	3.750
pH (units)	7.54	7.44	5.57	5.64
Specific Conductance (uS/cm)	45.7	44.45	50.2	49.65

a. number of participating laboratories = 51