QUALITY ASSURANCE REPORT NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
July 1978 through December 1983

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

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

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

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

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

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This Quality Assurance Report was prepared under the general direction of Mark E. Peden, Laboratory Manager for the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN). The analytical data summarized in this report were produced by the laboratory personnel listed in Section II. Most of the figures were prepared by the Communications Unit of the Illinois State Water Survey. The statistical analyses and computer generated plots were capably prepared by Peg A. Folta. Randall K. Stahlhut was responsible for most of the network history summaries. I wish to thank Lacie L. Jeffers for the secretarial support she provided during the preparation of this report. I also extend my appreciation to Van Bowersox and the Data Management staff of the CAL for their technical support. Recommendations made by NADP Subcommittee #2 have been influential in the development of the overall quality assessment program at the CAL and we gratefully acknowledge the continuing support of its members. The final note of thanks goes to David Bigelow, NADP/NTN Quality Assurance Manager; Douglas L. Sisterson, Chairman NADP Subcommittee #2; Richard G. Semonin, Chief of the Illinois State Water Survey; Gary J. Stensland, CAL Director; and the members of the NADP/NTN Quality Assurance Steering Committee, whose assistance as reviewers of this report resulted in the document you now read.

This report is the second in a series of Quality Assurance Reports documenting the quality assurance activities in the NADP/NTN monitoring network through 1983.

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I. INTRODUCTION

The first Quality Assurance Report for the Central Analytical Laboratory (CAL) (1) of the National Atmospheric Deposition Program (NADP) was published in 1980. It detailed the beginnings and the goals of the quality assessment program being developed for the laboratory. This report incorporates the data from that original report with quality assurance data from the years 1980 through 1983. Also included are discussions of changes to the program that have occurred as it has been refined throughout the six-year period.

The first set of data presented in this report resulted from the routine analysis of laboratory blanks (Section III). These blank samples include bucket leachates, filter leachates, and deionized water. The data provide information that can be used to assess the potential contribution of sample collection and processing to the analyte concentrations found in the network samples. The CAL quality assurance program utilizes quality control check (QCC) samples (Section IV) to quantify analytical bias and precision. An additional estimate of precision is achieved through replicate sample analyses (Section IV). The validity of these bias and precision estimates is supported by the performance of the CAL in external quality assurance audits and round robin testing programs (Section VI) sponsored by both state and federal government agencies in the United States, and the governments of Canada and several European countries. Finally, an assessment of how well the CAL succeeded during this six-year period in meeting its original goals is presented in the summary (Section VII).

II. LABORATORY QUALITY ASSURANCE PROGRAM

A. GENERAL DESCRIPTION

The published report of 1980 presented a complete description of the laboratory quality assurance program at the CAL. This program experienced relatively few changes between 1978 and 1983. The methods documented by Stensland, et al. (1) continued to be used throughout the six-year period. This section addresses the changes that have occurred since the 1980 report. These include changes in sample processing, quality control sample analyses, detection limits, and personnel.

The sample processing flowchart represented by Figure II-1 changed to that depicted in Figure II-2 in early 1981. Starting in 1981, the filters were no longer dried and stored and the wet bucket was no longer reweighed. A single 60 mL aliquot was taken after filtration for sample analysis. If sufficient sample remained, a second 60 mL aliquot was taken after filtration for archiving (refrigerated storage). The remainder of the sample, as well as the filter, was then discarded.

The number of quality control samples analyzed increased steadily over this six-year period. Internal formulations were developed for quality control check (QCC) samples to monitor pH and specific conductance measurements. These samples were analyzed at a frequency of two QCC samples for every 25-30 pH measurements and two different QCC samples for every 25-30 specific conductance measurements. Dilutions of mineral and nutrient series concentrates provided by the United States Environmental Protection Agency-EMSL, Cincinnati, Ohio, were used to monitor the accuracy of the analyses of the remaining parameters measured in the program. Early in the development of the quality assurance program the frequency of analysis of these quality control check samples was established. The result was a minimum of one quality control check sample analyzed with each group of twelve precipitation samples.

New instrumentation resulted in improvements in the method detection limits (MDLs). A further change in the MDLs occurred in 1981 when they were redefined from two to three times the baseline or instrument noise. The baseline or instrumentation noise was determined either by direct measurement of the noise through use of a strip chart recorder or by using the standard deviation that resulted from a minimum of ten analyses of deionized water blanks. This redefinition of the term made the CAL usage of MDL consistent with that recommended by the American Chemical Society (ACS). The MDLs for the years 1979 through 1983 are listed in Table II-1. The data published by the NADP/NTN network reflect the MDLs that existed during the time of the analysis.

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 Director.

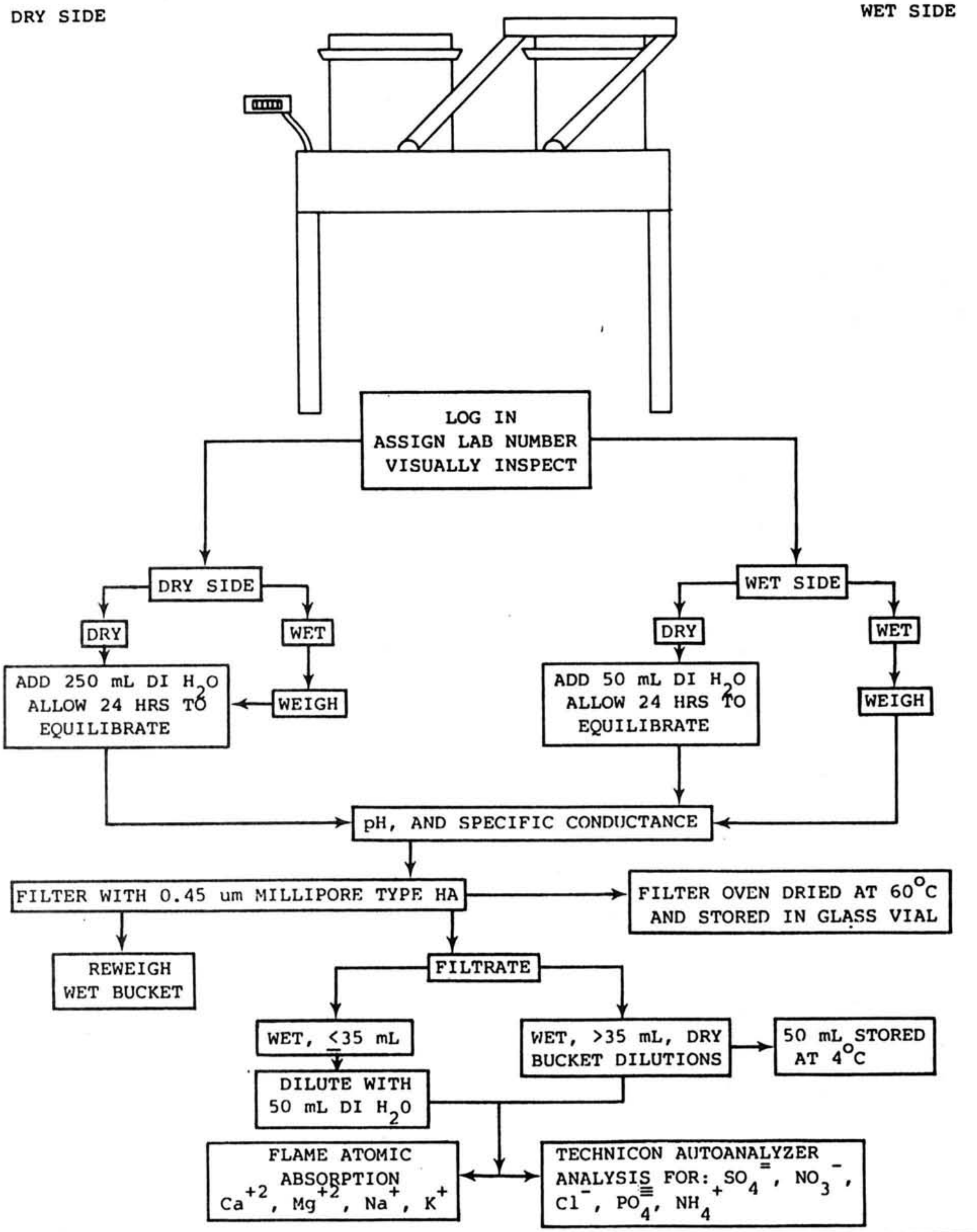

FIGURE II-1. Sample processing flowchart for 1978 through 1980.

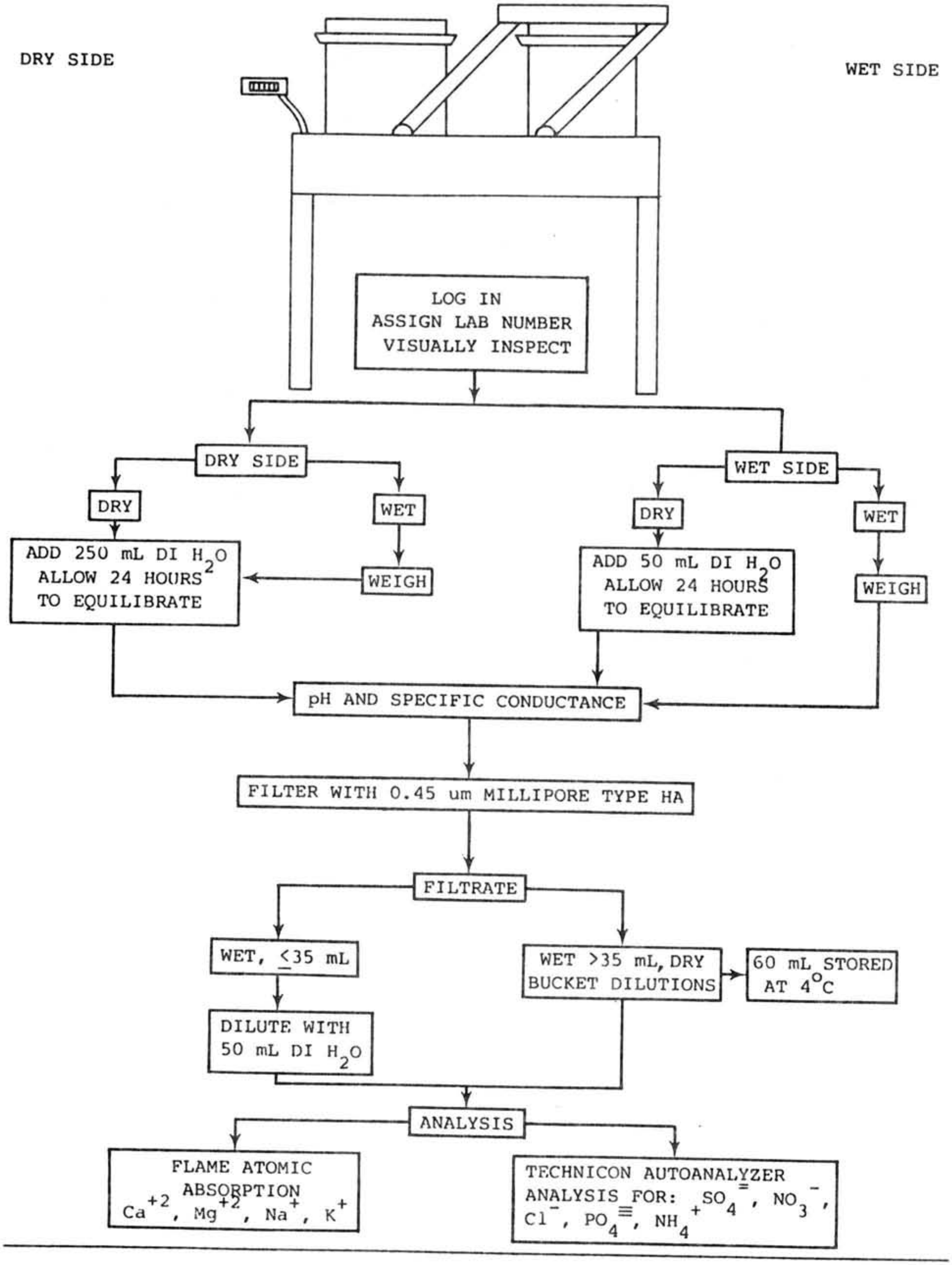

FIGURE II-2. Sample processing flowchart for 1981 through 1983.

TABLE II-1 Method Detection Limits for the Analysis of Precipitation Samples from 1979 through 1983.

Analyte	Method[a]	Method Detection Limit (MDL) mg/L	Dates
Calcium	Flame Atomic Absorption	0.02 0.009	1/79 - 10/80 10/80 - 12/83
Magnesium	Flame Atomic Absorption	0.002 0.003	1/79 - 10/80 10/80 - 12/83
Sodium	Flame Atomic Absorption	0.004 0.003	1/79 - 10/80 10/80 - 12/83
Potassium	Flame Atomic Absorption	0.004 0.003	1/79 - 10/80 10/80 - 12/83
Ammonium	Automated Phenate, Colorimetric	0.02	1/79 - 12/83
Sulfate	Automated Methyl Thymol Blue, Colorimetric	0.10	1/79 - 12/83
Nitrate-Nitrite	Automated Cadmium Reduction, Colorimetric	0.02	1/79 - 12/83
Chloride	Automated Ferricyanide, Colorimetric	0.05 0.02	1/79 - 3/81 3/81 - 12/83
Ortho-phosphate	Automated Ascorbic Acid, Colorimetric	0.003	1/79 - 12/83

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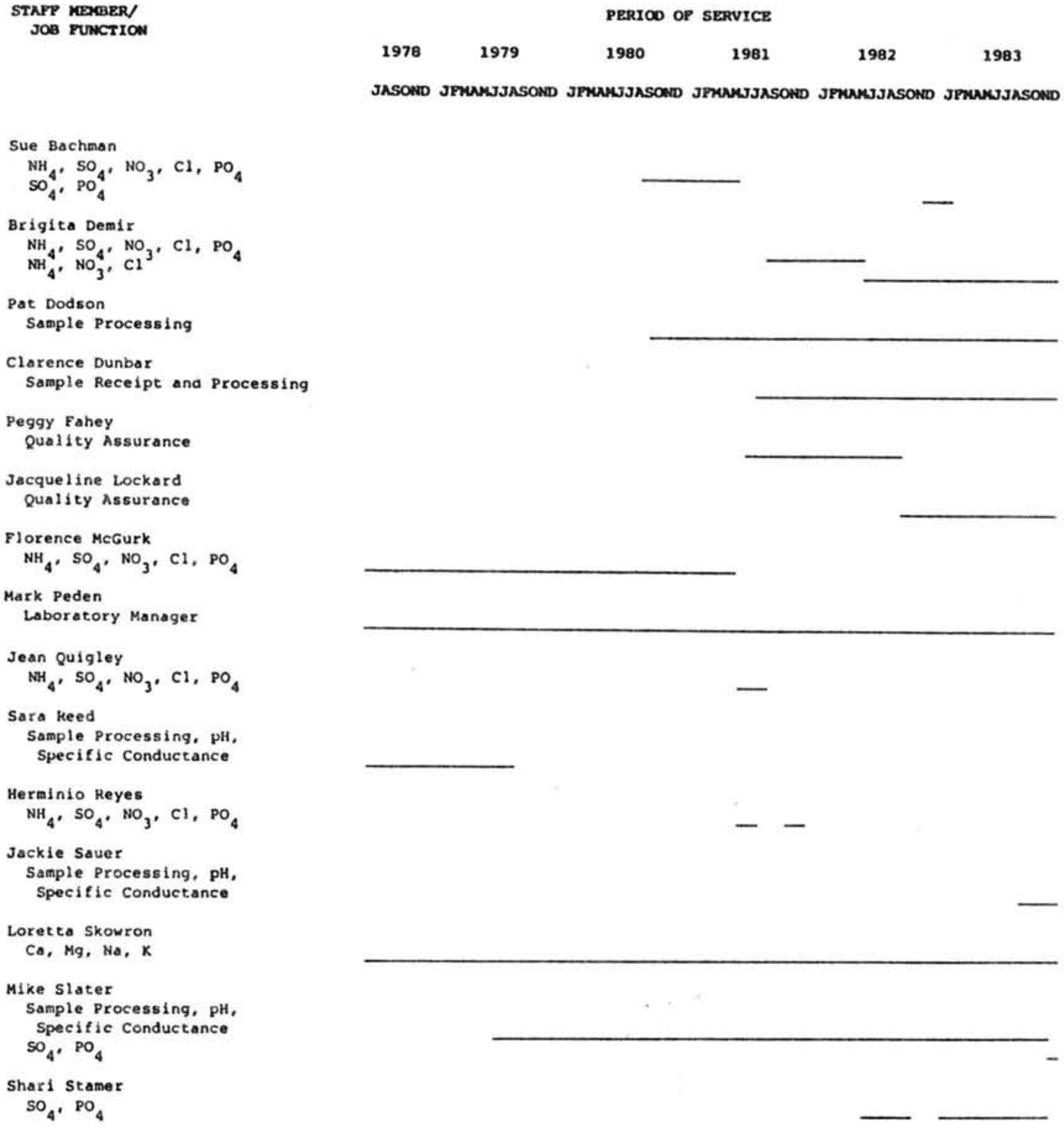
a. For a complete method description, see NADP Quality Assurance Report - Central Analytical Laboratory, Jan. 1979-Dec. 1979, Stensland, et al., 1980.

C. LABORATORY PERSONNEL

The educational and training requirements for the laboratory staff and the general laboratory procedures remain unchanged since the 1980 Quality Assurance Report. There were personnel changes during the first six years of the program including staff additions, replacements for departing analysts, and job reassignments. Until June 1981 the quality assurance program for the laboratory was directed by the laboratory manager. In June, the position of quality assurance specialist was created and the responsiblity for the laboratory QA program given to the person filling that position. Table II-2 alphabetically lists the laboratory personnel who participated in the project during this time period. It also includes a brief description of each staff member's primary function within the program and the duration of their employment as part of the CAL.

TABLE II-2 Central Analytical Laboratory (CAL) Personnel Summary (1978-1983)
Analytical Staff Only.



III. LABORATORY BLANK DATA

The data presented in this section were generated from the analysis 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 of 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 this section and the resultant analytical data are presented graphically or in tables.

A. BUCKET LEACHATES

At the start of the program the sample collection buckets were cleaned by hand. This cleaning included scrubbing of the bucket using a natural sponge to remove any particulates adhering to the plastic surface followed by repeated rinsings with DI until the specific conductance of the rinse water measured less than 2 uS/cm. In May 1982 the procedure was changed. Since that time, the buckets have been emptied of sample, wiped free of particulate matter, then washed in a commercial dishwasher. The wash cycle used city tap water and the three rinse cycles, deionized water. Once washed and rinsed, the buckets were shaken free of excess water and immediately placed in plastic bags and sealed. No detergent was ever utilized in any of the cleaning procedures.

The bucket lids contain a butadiene rubber gasket that assures a watertight seal of the bucket once the lid has been securely hammered in place. These gaskets may be either black or white, the only difference being the addition of carbon black to the molten rubber to produce the color. Although this rubber compound is relatively inert, the releasing agent used in the molds in which the gaskets are formed contains calcium, magnesium and zinc. Also as part of the extrusion process, the gasket may be placed in a salt bath of potassium nitrate and sodium nitrite. Residual amounts of both the releasing agent and the potassium and sodium salts may remain on the gasket and could result in contamination of the precipitation samples. In 1979 and 1980 concern about sample contamination from the leaching of calcium, magnesium and sodium from the gasket of the bucket lids was raised. Extensive testing was begun at the CAL to quantify and solve the problem. Begining in October 1981 the lids were pre-soaked for 24 hours in deionized water. This water was removed and a fresh supply used to soak the lids for an additional 24 hours. The lids were then washed (at first by hand and then in the dishwasher once it was available), shaken free of excess water, and placed in plastic bags and sealed. This routine soaking of the bucket lids for 48 hours was shown to effectively eliminate the problem. In an effort to further minimize the contact of precipitation samples with the gasket materials, in August 1982, the CAL affixed cautionary labels to all black shipping boxes requesting shipment and handling in an upright position.

To determine the contribution the container might make to the analyte concentrations, clean buckets and lids were randomly selected and used to determine container blanks. A predetermined volume of deionized water was poured into the test bucket, the lid pounded on, and the water left to equilibrate in the bucket. After 24 hours, this bucket leachate was poured into a DI water-washed 60 mL polyethylene (LPE) bottle and the concentration of analytes determined.

The first sets of blanks were obtained using 50 mL of DI water with the buckets remaining upright during the period of equilibration. For all of the bucket blanks, after the water was added and the lid securely hammered in place, the bucket was vigorously shaken to contact all surfaces of the bucket and lid before being left to equilibrate. In 1980, two additional blanks were added to explore the effect of larger volumes of DI water on the analyte concentrations. In addition to the bucket with a 50 mL portion of DI water, a second containing 150 mL and a third with 500 mL of DI water, were allowed to equilibrate overnight. One 60 mL aliquot was collected from each of these test buckets to provide the sample for analysis. Figures 1-24 in Appendix B are plots of the analyte masses found in these bucket blanks for 1979 through 1983.

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 minimal detectable mass for that analyte. This minimum value was determined by multiplying the MDL expressed as milligrams per liter 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.

It was hypothesized that the effect of increasing the volume of DI water used for the bucket leachates would be that of diluting the analyte concentrations. The figures for the data from 1980 and afterwards indicate that this was a correct assumption. It applies to both the upright and the inverted blanks.

The precipitation samples received and analyzed by the CAL arrive from all sections of the country. The time a sample spends in transit may vary from a few hours to several days. The upright bucket blanks did not adequately represent the container exposure a precipitation sample would have during transit since during transport the buckets would not always remain in an upright position. In an attempt to more truly mimic the actual conditions of 3 or 4 days of agitation while in transit from the field to the CAL, inverted bucket blanks were added in 1981. Figures 25 through 40 in Appendix B are plots of the analyte masses found in these inverted buckets for 1981 through 1983. These are again arranged chronologically and grouped by analyte. The same symbols for the three sample volume masses are used. The same three sample volumes were used, but the buckets were inverted for the period of equilibration. This provided maximum contact between the DI water and the rubber gasket, the suspected primary source of the contaminants. The figures of these inverted blanks indicate the potential for contamination that exists. They are, however, designed to demonstrate a worst case situation.

Table III-1 lists the number of bucket leachates analyzed for each year from 1978 to the present. Tables III-2 and III-3 present annual median masses again expressed as micrograms per bucket, from the start of the program to the present. The data document increased levels of analyte for 1983 and 1984. The source of this problem 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 the problem was corrected and the bucket leachates now contain very limited amounts of all of the analytes of interest.

TABLE III-1 The Number of Bucket Blanks Analyzed Each Year from 1978 through 1985.

Year	Number of Blanks					
	Upright			Inverted		
	50mL	150mL	500mL	50mL	150mL	500mL
1979	14	----	----	----	----	----
1980	34	30	30	----	----	----
1981	28	28	28	6	6	6
1982	10	9	9	52	52	52
1983	10	10	10	45	45	45
1984	50	50	50	50	50	50
1985	47	47	47	44	44	44

TABLE III-2 **Upright Bucket Blanks - Median Concentrations Expressed as Micrograms/Bucket.**

				Year			
Analyte	**1979**	**1980**	**1981**	**1982**	**1983**	**1984**	**1985**
Calcium	<1.00	<1.00	8.63	2.77	2.33	7.10	0.58
Magnesium	<0.10	0.27	2.12	1.23	1.70	4.62	0.30
Sodium	<0.20	<0.20	4.87	1.98	6.27	9.58	0.47
Potassium	<0.20	<0.20	1.27	1.58	2.88	1.68	0.18
Sulfate	<5.0	<5.0	23.3	<5.0	<5.0	8.9	<1.5
Chloride	<2.5	<2.5	1.9	<1.0	3.9	4.3	<1.5
Nitrate-Nitrite	<1.0	<1.0	<1.0	<1.0	1.2	<1.0	<1.5
Ammonium	<1.0	<1.0	<1.0	<1.0	1.5	1.4	<1.0
Ortho-phosphate	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15

TABLE III-3 **Inverted Bucket Blanks - Median Concentrations Expressed as Micrograms/Bucket.**

			Year		
Analyte	**1981**	**1982**	**1983**	**1984**	**1985**
Calcium	5.57	8.92	11.02	16.83	1.95
Magnesium	6.91	2.48	4.13	9.17	1.38
Sodium	5.12	4.95	11.18	20.57	1.45
Potassium	0.65	1.27	2.10	3.20	0.43
Sulfate	8.3	5.5	6.0	24.2	3.2
Chloride	14.8	3.3	4.8	14.6	1.8
Nitrate-Nitrite	<1.0	1.3	1.3	1.5	<1.5
Ammonium	<1.0	1.2	1.8	1.3	<1.0
Ortho-phosphate	<0.15	<0.15	<0.15	<0.15	<0.15

B. FILTER LEACHATES

Before being used to filter precipitation samples, the 0.45 um Millipore filters are leached with a 200 mL aliquot of deionized water. The routine procedure consists of taking a new filter for each sample, leaching that filter, filtering the sample, then discarding the used filter. To ensure that the leaching procedure removes all analytes that are routinely measured in precipitation samples, analyses of filter leachates have been performed since 1979. This quality control check is performed by pouring a 50 mL portion of DI water through a leached filter and collecting the sample for analysis. These filter leachates are labeled the "A" sample.

In 1979, these samples were collected and analyzed each day precipitation samples were processed at the CAL. Table III-4 summarizes the data obtained from the analysis of these daily filter leachates. The data indicate that neither the filters nor the filtration procedure represented a significant source of sample contamination in 1979. These findings resulted in a change in the procedure used to collect the filter leachates.

TABLE III-4 Analyte Concentration Summary for Filter Leachate A for 1979.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	Percentile (mg/L) 95th
Calcium	227	0.02	95.2	<0.02	<0.02
Magnesium	227	0.002	95.2	<0.002	<0.002
Sodium	227	0.004	58.6	<0.004	0.017
Potassium	227	0.004	76.2	<0.004	0.006
Ammonium	233	0.02	94.9	<0.02	<0.02
Sulfate	233	0.10	95.7	<0.10	<0.10
Nitrate-Nitrite	233	0.02	95.7	<0.02	<0.02
Chloride	233	0.05	93.1	<0.05	<0.05
Ortho-phosphate	233	0.003	65.7	<0.003	0.010

a. number of analyses

The frequency of filter leachate collection was reduced to once per week in 1980. By March of that year it was decided to make a further change in the procedure by collecting and analyzing a second 50 mL portion of DI water that had been poured through the same leached filter as had the "A" sample. This leachate is labeled the "B" sample. The new procedure provided additional information regarding the sample processing by indicating the possible contamination that may occur when more that one sample aliquot was collected. These data become important when reviewing the replicate sample analyses and analysis of those samples placed into archival storage. Tables III-5 and III-6 present the median concentration values found from the routine analyses of these A and B filter leachates for the period 1980-1983. More complete annual summaries of the analyses of the filter leachates can be found in Tables 2-9 in Appendix B. The data presented in these tables show the filters to be a negligible source of contamination. The routine weekly monitoring of these leachates continues as an intergral part of the CAL quality assurance program.

TABLE III-5 Median Analyte Concentration Found in Filter Leachate A for 1980 through 1983.

Analyte/Year	Median Concentration (mg/L) 1980	1981	1982	1983
Calcium	<0.02	<0.009	<0.009	<0.009
Magnesium	<0.002	<0.003	<0.003	<0.003
Sodium	<0.004	0.008	0.008	0.004
Potassium	<0.004	<0.003	<0.003	<0.003
Ammonium	<0.02	<0.02	<0.02	<0.02
Sulfate	<0.10	<0.10	<0.10	<0.10
Nitrate-Nitrite	<0.02	<0.02	<0.02	<0.02
Chloride	<0.05	<0.02	<0.02	<0.02
Orthophosphate	<0.003	<0.003	<0.003	<0.003
n[a]	65	35	41	49

a. number of analyses

TABLE III-6 Median Analyte Concentration Found in Filter Leachate B for 1980 through 1983.

	Median Concentration (mg/L)			
Analyte/Year	1980	1981	1982	1983
Calcium	<0.02	<0.009	<0.009	<0.009
Magnesium	<0.002	<0.003	<0.003	<0.003
Sodium	<0.004	<0.003	<0.003	<0.003
Potassium	<0.004	<0.003	<0.003	<0.003
Ammonium	<0.02	<0.02	<0.02	<0.02
Sulfate	<0.10	<0.10	<0.10	<0.10
Nitrate-Nitrite	<0.02	<0.02	<0.02	<0.02
Chloride	<0.05	<0.02	<0.02	<0.02
Orthophosphate	<0.003	<0.003	<0.003	<0.003
n[a]	34	34	41	49

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 always monitored by daily checks of specific conductance by an in-line conductivity meter, the complete analysis of a DI water sample did not begin until 1980, and was at first was done somewhat irregularly. By 1981 weekly samples were regularly being taken from the sample processing laboratory for a complete analysis.

During the six years under discussion three different types of deionizing systems were used by the CAL. The first system was utilized by the entire Water Survey and was supplied by the Illinois Water Treatment (IWT) Company. It consisted of a mixed bed ion exchange column with automatic shut down when the conductivity of the DI water being produced exceeded 0.5 uS/cm. The water produced by the IWT system was then passed through a two cartridge Barnstead Nanopure mixed bed ion exchange system before being used. In June of 1981 the sample processing lab moved to another section of the Water Survey and a separate deionizing system was installed. The sample processing laboratory is that part of the CAL where the network samples are filtered and collected for analysis. The pH and specific conductance measurements are made by the processing laboratory staff. The newly installed system employed reverse osmosis (RO) to convert the city tap water to DI water with a conductivity of <1 uS/cm. Because of the high pH of the tap water (pH 8.5) an acid feed line was needed to inject dilute sulfuric acid into the tap water before it was sent through the RO system. This was necessary because the high pH degraded the RO membrane. In April 1983 this early membrane was replaced by a thin film composite type which was unaffected by high pH and the need for the acid feed step was eliminated. This RO system produced 40 L of DI water per hour and remained in use in the processing laboratory until the CAL moved to new facilities in November 1985. The remaining analytical staff of the CAL continued to use DI water produced by the IWT system in conjunction with Barnstead wall-mounted Nanopure systems for sample dilutions and standards and reference sample preparations. The water system available for their use also changed with the move in November 1985.

Table III-7 lists the median analyte concentrations found in the deionized water used by the CAL. Tables 10-13 in Appendix B contain 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 a DI water samples taken from one of the analytical labs at the CAL continues as part of the routine quality assessment program.

TABLE III-7 Median Analyte Concentration Values for Deionized Water Blank for 1980-1983.

	Median Concentration Value (mg/L)			
Analyte/Year	1980	1981	1982	1983
Calcium	<0.02	<0.009	<0.009	<0.009
Magnesium	<0.002	<0.003	<0.003	<0.003
Sodium	<0.004	<0.003	<0.003	<0.003
Potassium	<0.004	<0.003	<0.003	<0.003
Ammonium	<0.02	<0.02	<0.02	<0.02
Sulfate	<0.10	<0.10	<0.10	<0.10
Nitrate-Nitrite	<0.02	<0.02	<0.02	<0.02
Chloride	<0.05	<0.02	<0.02	<0.02
Orthophosphate	<0.003	<0.003	<0.003	<0.003
n[a]	20	33	39	48

a. number of analyses

IV. LABORATORY BIAS AND PRECISION

An essential part of every quality assessment program is the determination of the accuracy of the measurements being made by the laboratory. One way of making this determination is to examine the bias and precision of data obtained from replicate analyses of Quality Control Check (QCC) samples. The QCC samples used by the CAL for these calculations are 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 can be obtained through the analysis of replicate samples, i.e. the analysis of two aliquots of the same sample. Section IV contains descriptions of both the QCC and replicate 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

The types of internal quality control samples have not changed for the period being discussed. However, the sample concentrations for the quality control check samples used to determine analytical bias and precision have changed for two reasons. The first is a reformulation of the concentrates by the USEPA. This typically occurs once every year. The second reason is an attempt by the laboratory to dilute the USEPA concentrates so the resulting analyte concentrations approximate the twenty-fifth and seventy-fifth percentile concentrations measured in the samples from the sites in the NADP/NTN network. These values vary some from year to year. Table IV-1 lists the twenty-fifth percentile concentration values for each parameter measured in the precipitation samples collected in the NADP/NTN network from 1978 through 1983. Table IV-2 presents the seventy-fifth percentile concentration values for the same period. More comprehensive annual percentile concentration summaries can be found in Tables 1 through 6 in Appendix C.

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.

A cursory examination of Tables IV-1 and IV-2 reveals changes in analyte percentile concentration values during the 1978-1983 period. These changes are primarily due to the geographical distribution of monitoring sites as the program grew in size. In the early stages of the program, most of the network sites were located in the northeastern and central regions of the country. Precipitation from these areas is generally characterized by lower pH values and higher sulfate and nitrate concentrations than the rain from sites in the west and the high plains. The network expansion from 1979 through 1981 added new

TABLE IV-1 Twenty-fifth Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation for 1978-1983.

Parameter/Year	Percentile Concentration Values (mg/L) 1978	1979	1980	1981	1982	1983
Ca	0.07	0.09	0.09	0.10	0.07	0.07
Mg	0.019	0.022	0.022	0.033	0.023	0.021
K	0.020	0.015	0.015	0.016	0.015	0.016
Na	0.090	0.100	0.054	0.058	0.043	0.048
NH_4	0.04	0.07	0.07	0.08	0.08	0.06
NO_3	0.60	0.76	0.72	0.60	0.58	0.51
Cl	0.13	0.10	0.18	0.10	0.09	0.10
SO_4	1.30	1.45	1.13	1.08	0.85	0.78
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
pH (units)	4.19	4.26	4.25	4.29	4.35	4.42
Specific Conductance (uS/cm)	11.7	12.2	12.4	11.9	9.3	8.3
n^a	239	1254	3030	3370	3590	4308

a. number of samples

TABLE IV-2 Seventy-fifth Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation for 1978-1983.

Parameter/Year	Percentile Concentration Values (mg/L) 1978	1979	1980	1981	1982	1983
Ca	0.32	0.42	0.43	0.48	0.35	0.36
Mg	0.081	0.086	0.093	0.137	0.091	0.082
K	0.060	0.060	0.065	0.066	0.052	0.060
Na	0.565	0.620	0.351	0.313	0.216	0.238
NH_4	0.38	0.50	0.50	0.44	0.39	0.40
NO_3	2.25	2.49	2.63	2.15	1.94	1.86
Cl	0.51	0.40	0.48	0.47	0.38	0.36
SO_4	3.96	4.30	3.74	3.82	2.99	2.59
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
pH (units)	4.93	5.07	5.36	5.46	5.33	5.37
Specific Conductance (uS/cm)	31.2	34.3	35.7	35.1	29.8	26.0
n^a	239	1254	3030	3370	3590	4308

a. number of samples

sites along both eastern and western coasts, as well as, in the south and midwest. The increased levels of both sodium and chloride in the network samples during this period was principally due to the inclusion of these new coastal sites. Similarly, midwestern rainfall is generally characterized by higher calcium, magnesium, and ammonium concentrations and increased levels of these ions is also seen during this period. By the end of 1981, the area east of the Mississippi River was well represented in the network and subsequent expansion has been predominated by the addition of sites from the western and great plains regions of the country. The addition of these western sites has resulted in the general decline in the analyte concentrations found in the network as a whole during 1982 and continuing into 1983.

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. One example of this increase is that in 1980 a total of 275 QCS analyses were performed for calcium. By 1983 that number had grown to 934. The program grew in quantity of quality assessment data being produced but did not change in the types of samples being analyzed to produce these data. This section continues with a description of the quality control solutions used by the laboratory, presents summary tables of the data that resulted from their analysis and provides an explanation of what these data imply about the performance of the CAL.

Solutions Used

In 1979 and 1980 in-house formulations of sulfuric acid and nitric acid were used to monitor the pH measurements. Similar solutions were utilized as quality control samples for the specific conductance. The frequency of measurement of these quality control samples was irregular until 1981. By 1981, samples with a pH and specific conductance more representative of the levels found in precipitation were formulated and a systematic program of measurements initiated.

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 analyzing it colorimetrically 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. The information available on Tables 1 through 6 in Appendix C indicates that the pH of this solution falls near the 25th percentile concentration level and the specific conductance near the 50th percentile for all of the years being discussed.

Again, since 1981, a dilute potassium chloride solution (5.0×10^{-4}N KCl) formulated and prepared at the CAL, has been used to both 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, the colorimetric determination of the chloride concentration and the 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 where the effects of atmospheric carbon dioxide fluctuations can be significant. For the aforementioned 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 QCC solutions prepared from USEPA mineral and nutrient concentrates. The mineral sample was used to prepare QCC solutions for calcium, magnesium, sodium, potassium, sulfate, and chloride. The QCC solutions for nitrate-nitrite, ammonium, and orthophosphate were made by diluting the USEPA nutrient concentrates. Two QCC solutions were prepared for each analyte. One solution approximated the 25th percentile concentration found for the specified analyte and the other, the 75th. These percentile concentration values were derived from the network history of the preceding year and can be found in Tables IV-1 and IV-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 1 in Appendix D lists several pH values and their corresponding hydrogen ion content. Table 2 summarizes the pH data and presents 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 using hydrogen ion concentration only.

Tables 2 through 12 in Appendix D were prepared from the data obtained from replicate analysis of QCC samples. For all parameters except pH and specific conductance, at least one QCC sample was analyzed with each group of twelve precipitation samples. For pH and specific conductance measurements, the frequency was approximately one QCC sample measured for every twenty precipitation samples. The annual summaries of bias and precision for each parameter (Tables 2-12) found in Appendix D were produced using the results obtained from the statistical analysis of this QCC sample 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 QCC samples 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 containing the expected concentrations that should result after dilution. Beginning with the USEPA reference samples the CAL was using in 1981, the data sheet that accompanied the sample concentrates listed an expected concentration, a mean concentration with a standard deviation, and a confidence interval for the concentrations that should result after dilution. These mean and standard deviation values were obtained from statistical analysis of the data received from USEPA sponsored round robin performance studies (2). Summaries of the data obtained from these performance studies can be obtained from the USEPA, EMSL-Cincinnati, Ohio. Beginning with the data from 1981, the USEPA mean is listed in the theoretical concentration column and is used to calculate the analytical bias values listed in Tables 4-12 in Appendix D.

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. For the years prior to 1981 when the mean and standard deviation values were not available from the USEPA, the theoretical value was used for the analytical bias calculations and an estimated standard deviation consistent with those found in the succeeding years was used to test for the statistical significance of that bias.

Discussion of Results

A review of the annual data summaries of bias and precision indicates few problems with analytical bias. It was not possible to calculate the significance of the bias for pH and specific conductance for 1979 and 1980 as the samples used were in-house formulations and the preparations were not verified through analyses of the ions in solution. During this period, the CAL staff was experimenting with what formulations might be appropriate for use in the sample processing lab and were not as concerned with the accuracy of the preparation as with the stability of the samples. The bias in the pH measurements reported in 1979 may in large part be due to this preparation inaccuracy. By 1980 the QCC samples for pH and specific conductance were carefully prepared and the bias reported more accurately reflects what might have existed at that time. Beginning in 1981, when sample preparation verification became routine, the uncertainty in the sample preparation was used to perform the same statistical analysis for the significance of the bias as was used for the other analytical parameters. For all pH and specific conductance measurements of the pH 4.30 QCC sample (specific conductance of 21.8 uS/cm) for 1981-1983, the bias found was not statistically significant. The allowable variation in the preparation of the dilute nitric acid solution (pH 4.30 QCC sample) was 0.10 pH units and that for the dilute potassium chloride conductivity standard (pH 5.63 QCC sample), 0.30 pH units. These large uncertainties allow for a considerable bias in sample measurements before that bias becomes statistically significant, particularly for the pH 5.63 sample. The bias in 1982 and 1983 for the pH 5.63 sample proved to be statistically significant. As noted earlier, at pH levels of greater then 5.0 the effect of atmospheric carbon dioxide on sample pH becomes important. Also at this pH level, the hydrogen ion concentration is very low and acceptable variations in pH values result in large percent bias. The bias listed in Table 2 of Appendix D for the pH 5.63 sample are at first startling, but the preceeding discussion should have shown that the variation allowable in the sample preparation was the primary reason for the large discrepancies. The standard deviation for this sample provides a better assessment of the laboratory peformance and that improved or remained consistent, particularly for the last three years under discussion.

Although the results of the t-test sometimes show the deviation of the CAL mean from the theoretical value or USEPA mean to be statistically significant, the actual amount of the difference in terms of analyte concentration is small. When the percent bias is large, as with the 13.4% negative bias for the lowest concentration reference sample used for calcium in 1980, it is primarily due to the small amount of analyte present in the solution. As analyte concentrations decrease, the degree of difficulty in obtaining accurate dilutions and analyses increases. This fact is emphasized by the increased variability in precision that accompanied this large bias. Of more importance, particularly when reviewing the data summaries for the metal cations, is the fact that with the increased experience of the analyst comes improvement in both the percent bias and the precision at even the lowest concentration levels.

When considering the data summaries for the analytes ammonium, nitrate-nitrite, and orthophosphate, the instability of these species must be remembered. The percent bias and RSD for nitrate-nitrite are quite acceptable at all levels. The ammonium data are also satisfactory. The orthophosphate data, however, reflect the effects of sample instability. Although not apparent from the data summaries presented in Table 12, the negative percent bias present in 1981, 1982, and 1983 was primarily due to QCC sample decomposition. Review of all of the data for each year showed a consistent downward trend in the orthophosphate concentration of the QCC sample over a relatively short time (3-4 days). This information led to a procedural change that required both the standards and the QCC samples to be prepared more frequently. The new procedure resulted in improved bias and precision data for orthophosphate in the subsequent years.

Finally, the data summaries for chloride exhibit the expected improvement in measurement accuracy as analyst's experience with both the method and instrumentation increased. The generally poor precision of the sulfate data from 1982 and 1983 reflects the importance of the analyst's skills to the accuracy of the measurements in yet another manner. The staff summary in Table II-2 shows that during this period there were three different analysts performing the sulfate determinations. The Methyl Thymol Blue method used for these determinations requires a rigorous routine maintenance program to ensure precise results. Analyst turnover during the 1982-1983 time period likely resulted in the degradation of precision due to inexperience.

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 60 mL aliquots were collected after filtration from four 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; the second, B; and the third 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.

The next section of this report discusses the plots of the data derived from these replicate analyses. The plots are presented as Figures 1-50 in Appendix E. They are arranged by parameter with each figure representing one year's analyses. Because of the limited data from 1978, the analytical values for the replicate analyses from that year have been combined with those from 1979. Interpretation of the data and a summary statement about laboratory precision from 1978 through 1983 are included.

Range Selection

The figures in Appendix E are plots of the concentration differences between replicate samples A and B in mg/L versus the average concentration of A and B in mg/L. The differences are always calculated using the formula [analyte concentration of A minus analyte concentration of B]. The average is [analyte concentration of A plus analyte con- centration of B] divided by two. To facilitate the usefulness of the plots, the yearly assessments for each ion have been split into two sections. A median concentration for the six-year period under discussion 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 median concentration value and continue to the ninety-fifth percentile concentration of that analyte found in the replicate samples analyzed during the entire period. Table IV-3 lists the median or fiftieth percentile and the ninety-fifth percentile concentrations for each analyte for the period 1978-1983.

Tables and Plots

Figures 1-50 in Appendix E are plots of the differences found at the CAL between two aliquots of the same precipitation sample analyzed in succession. 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 are presented for all analytes except orthophosphate. The number of precipitation samples containing orthophosphate is small and the number of replicate samples containing differences in the orthophosphate concentrations, still smaller. Table IV-4 lists the percentage of splits which contained no measurable orthophosphate from 1978 through 1983. The difference between the orthophosphate concentration measured in samples A and B of the four to eight percent of the splits that contained the analyte was 0.000 mg/L for all but 1% of the samples. Plots of these differences were deemed unnecessary.

TABLE IV-3 **Fiftieth and Ninety-fifth Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation Samples Selected for Replicate Analyses for 1978-1983.**

Parameter	**Percentile Concentration Values (mg/L)** **Fiftieth**	 **Ninety-fifth**
Calcium	0.100	0.500
Magnesium	0.025	0.125
Sodium	0.100	0.500
Potassium	0.025	0.125
Ammonium	0.20	1.00
Sulfate	1.50	7.50
Nitrate-Nitrite	1.00	5.00
Chloride	0.30	1.50
pH (units)	4.50	6.50
Specific Conductance (uS/cm)	15.0	75.0

TABLE IV-4 **Percentage of Replicates in which the Concentration of Orthophosphate Is Less Than the Method Detection Limit.**

Year	**Percent**
1978-1979	92.6
1980	96.0
1981	93.1
1982	94.8
1983	93.7

Table IV-5 lists the mean differences for each analyte for the period being discussed. Tables 1-5 in Appendix E present complete annual statistical summaries of the differences plotted in Figures 1-50. Again, because the number of splits taken in 1978 and 1979 was small, the data from these two years have been combined in both the plots and the statistical summaries.

Discussion of Results

The data presented in both the figures and the tables indicate that the precision at the CAL for splits analyzed in sucession was always very good. The plots in particular show a continuous improvement in analyst precision from the start of the program through 1983. 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 need for a different source of information to be used in the assessment of analytical precision was apparent. Splits that were blind to the analysts and analyzed at different times were added to the quality assurance program in 1984 to provide this additional imformation. The data that resulted from the analysis of these blind splits will appear in the Quality Assurance Report for the years 1984-1985.

TABLE IV-5 Mean Differences for Replicate Analyses of Precipitation Samples for 1978-1983.

	Mean Difference (mg/L)				
Parameter/Year	**1978-1979**	**1980**	**1981**	**1982**	**1983**
Calcium	0.001	0.000	0.000	-0.001	0.001
Magnesium	0.000	0.000	0.000	0.000	0.000
Sodium	-0.001	0.000	-0.001	0.000	0.001
Potassium	0.000	0.000	0.000	0.000	0.000
Ammonium	-0.01	0.00	0.00	0.00	0.01
Sulfate	0.00	0.00	0.00	-0.01	-0.01
Nitrate-Nitrite	0.00	0.00	0.00	0.01	0.00
Chloride	0.00	0.00	0.00	0.00	0.00
pH (units)	0.01	0.01	-0.01	0.00	-0.01
Specific Conductance (uS/cm)	-0.2	-0.1	0.0	0.0	0.0
n[a]	54	125	175	212	255

[a] number of replicate pairs

V. REANALYSIS PROCEDURES

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

An ion balance may be calculated using one of several different methods. Figure V-1 presents four commonly employed methods and demonstrates how the results obtained from each can be compared to those derived from the other methods. These methods may vary from a simple ion ratio as utilized by the NADP/NTN in the annual data summaries (3) to the more complex calculations recommended by the USEPA (4). Although similar to the calculation method employed at the CAL, the formula recommended by the American Society for Testing and Materials (ASTM) (5) is:

$$\text{Percentage Error} = \frac{\text{Cations} - \text{Anions}}{\text{Cations} + \text{Anions}} \times 100$$

It is important to know which method a laboratory employs, 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 more completely described in Figure V-2. 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 (6).

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 (6).

COMPARISON OF
ION BALANCE CALCULATION METHODS

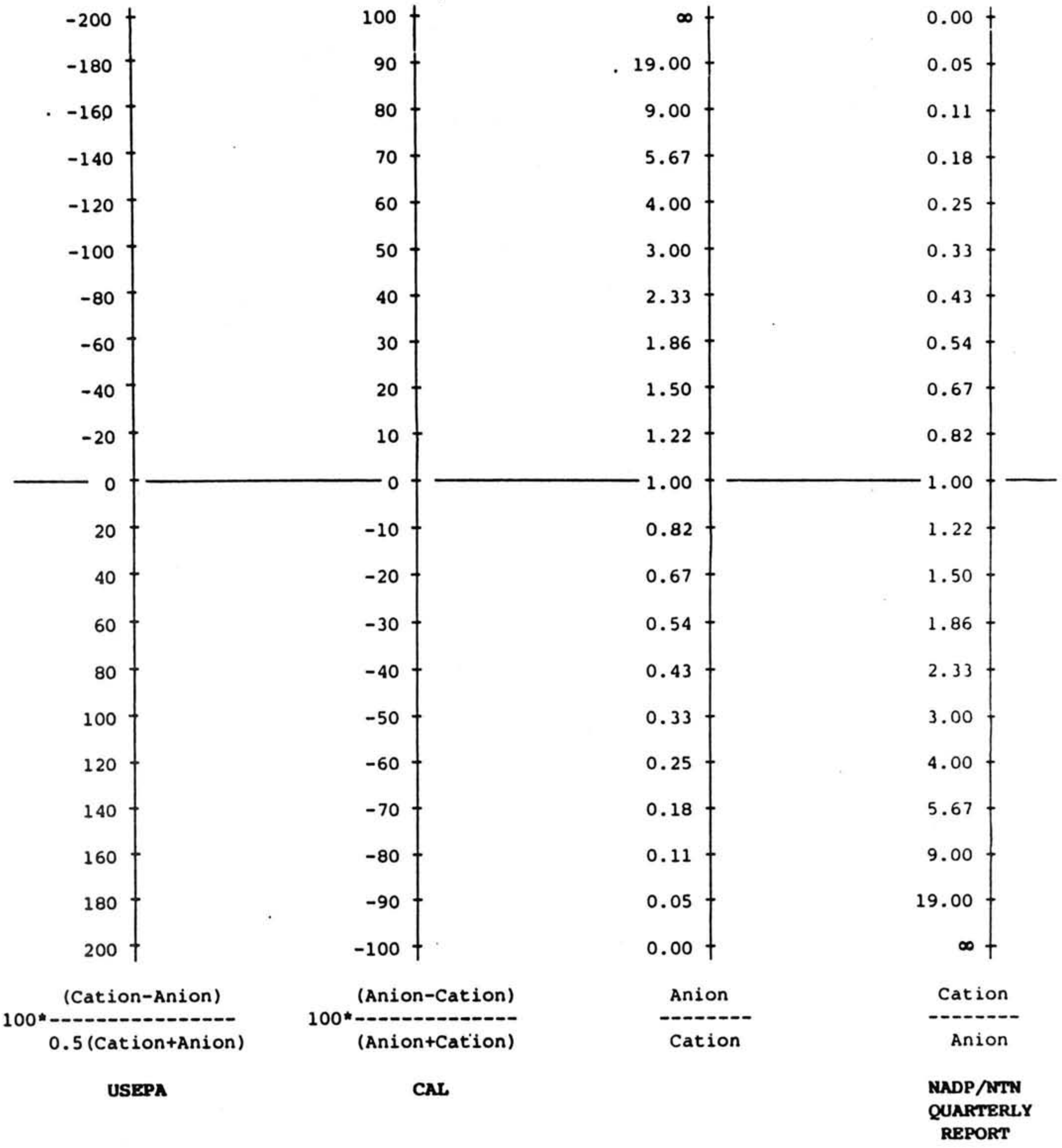


FIGURE V-1. A comparison of four methods that can be used to calculate an ion balance.

NADP/NTN Ion Balance
Calculation Method

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

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

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

* Concentrations are expressed as microequivalents/liter

FIGURE V-2. The formula used by the CAL to calculate an ion balance.

It should be noted that the CAL includes bicarbonate ion concentration when calculating the anion sum for each sample. This is a calculated value that is based on the assumption that the sample is in equilibrium with atmospheric carbon dioxide. The final formula used to derive this calculated HCO_3^- concentration is:

$$(HCO_3^-) = \frac{K_1 \; K_H \; P_{CO_2}}{10^{-pH}} = \frac{5.11 \times 10^{-12}}{10^{-pH}}$$

where, K_1 = 4.46×10^{-7} moles per liter
K_H = 0.0342 moles per liter - atmosphere
P_{CO_2} = 335×10^{-6} atmospheres.

The bicarbonate concentration that is found by using the above formula is expressed as moles per liter. It is converted to microequivalents per liter by multiplying the calculated concentration by 10^6. A calculated HCO_3^- concentration is not necessarily part of the ion balance calculations used by other laboratories. Therefore, I stress again the importance of knowing the exact procedures utilized by each laboratory in its calculation of an ion balance, before attempting to compare laboratory performance by using ion balance as the criteria.

Ion balance calculations are a valuable component of the CAL quality assurance program. A large imbalance can be indicative of an error in the analysis. It may also be an indication that additional ionic species are present in the sample and further analyses are 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 this section, the criteria used to select samples for reanalysis are presented. A discussion of the information that can be derived from these reanalysis procedures and their effect on the network data are also included.

A. Ion Balance Criteria

In 1978 and 1979, when the criteria for reanalysis were being formulated, very little information about the network was available. Initially, all samples with an ion imbalance of ± 15% or greater were selected for reanalysis. By early 1979, computer programs had been developed to generate plots that related measured pH values to the calculated ion percent difference (IPD) values generated by the ion balance calculation. Using the information provided by these plots and other information about analyte concentration changes that had resulted from the reanalyses of samples selected by the 15% criterion, the CAL director determined that more specific criteria based both on pH and IPD would be more appropriate. In October 1979, the criteria became:

when the CAL measured pH was ≤ 4.7,
reanalyze if the IPD was $> \pm 13\%$;

when the CAL measured pH was > 4.7,
reanalyze if the IPD was
a. greater than $[(-10.0 \times \text{pH}) + 61.0]$, or
b. less than $[(-10.0 \times \text{pH}) + 35.0]$.

These criteria were used throughout 1980 and most of 1981 to select approximately 8% of the total number of samples analyzed by the CAL to be reanalyzed.

During 1981, the nature of the network began to change as it expanded farther into the west. While the number of data changes that resulted after samples were reanalyzed remained the same, the number of samples being selected for reanalysis continued to increase with this network expansion. This occurred because many of the precipitation samples from the western sites met the second criterion for reanalysis selection. This also resulted in a progressively regionalized sample set being selected for reanalysis. The obvious need for different selection criteria prompted another analysis of the data changes made as the result of sample reanalysis. A closer look was taken at the types of samples that were collected and analyzed from the different regions within the network. In October 1981 a new set of criteria had been developed and the necessary changes made in the computer program.

The computer program that calculates an ion balance for each sample determines the ion sum 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 were used in the new criteria to determine which samples should be reanalyzed. The ion balance criteria for reanalysis selection then became:

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

when 50 $\leq$ IS $\leq$ 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,

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

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.

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 in 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(7). The remaining factors can be found in Standard Methods for the Examination of Water and Wastewater(6).

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

$$\text{Conductance Percent Difference} = \text{CPD} = \frac{(\text{Calculated Conductance} - \text{Measured Conductance})}{\text{Measured Conductance}} \times 100$$

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

when conductance measured ≤ 10 uS/cm,
reanalyze if CPD > ± 65%;

when 10 uS/cm < conductance measured ≤ 30 uS/cm,
reanalyze if CPD > ± 45%;

when 30 uS/cm < conductance measured ≤ 50 uS/cm,
reanalyze if CPD > ± 30%;

and when conductance measured > 50 uS/cm,
reanalyze if CPD > ± 20%.

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

C. Histograms

Figures V-3 and V-4 are histograms of the ion percent difference values and the conductance percent difference values for the samples from the NADP/NTN network for the year 1983. The histograms for 1978 through 1982 can be found in Appendix F. With each histogram, a median, a mean, and a standard deviation are noted.

Although only samples with volumes greater than 35 mL are included in these graphs, they are still representative of the overall increase in the number of network samples during the period 1978 through 1983. Sampling did not begin until July 1978 and the histograms for that year represent only samples collected in the fall and winter from sites in the eastern and central regions of the United States. The increases in the numbers of samples analyzed in the succeeding years are the result of network expansion from the original 14 eastern and midwestern sites to aproximately 130 sites throughout the country by the end of 1983.

The IPD histograms for all six years depict a very similar pattern, as do the six CPD histograms. 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 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. It does not, however, 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. The accuracy of the measurement has been checked

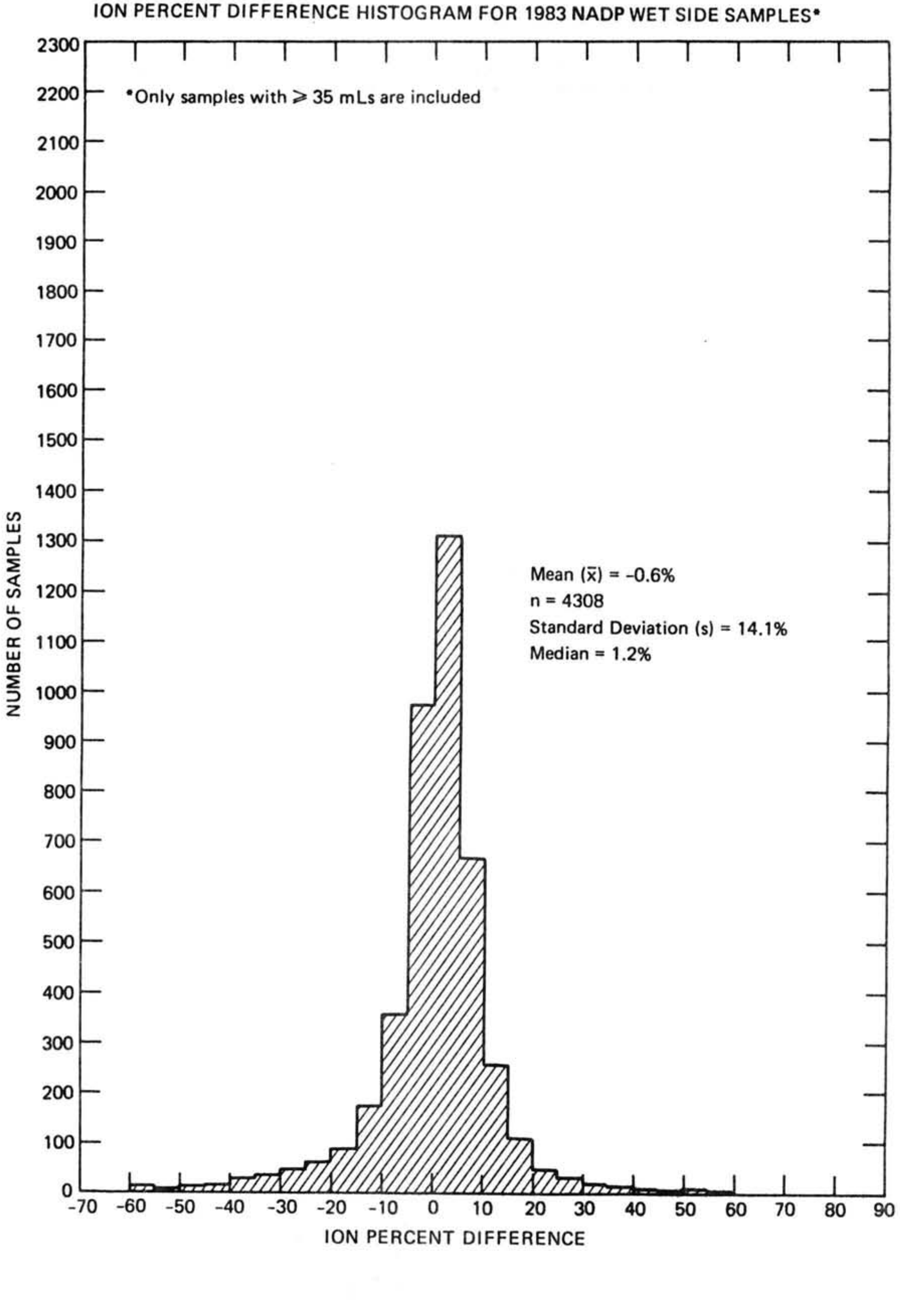


FIGURE V-3. Ion percent difference histogram for NADP/NTN wet side samples in 1983.

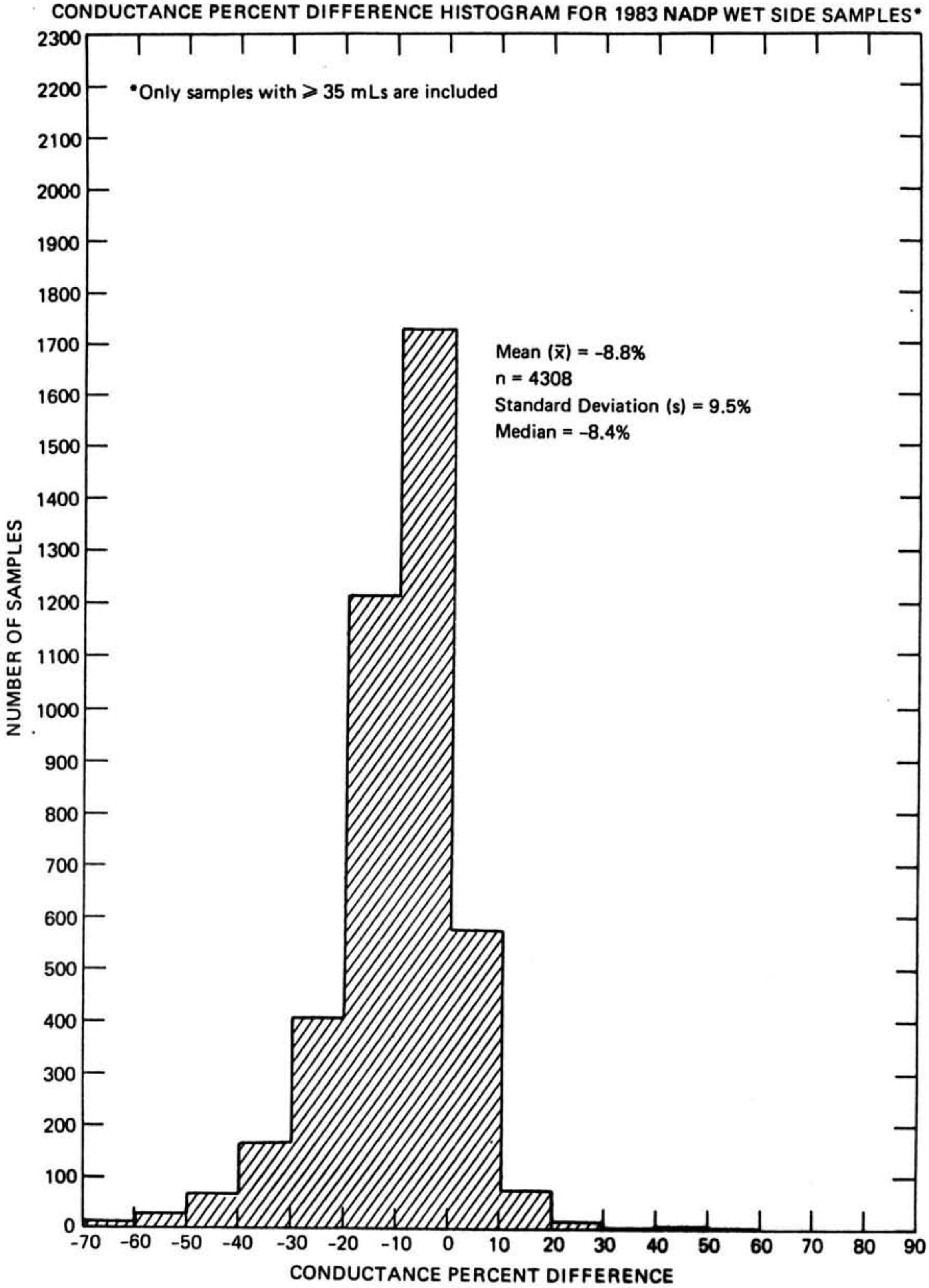


FIGURE V-4. Conductance percent difference histogram for NADP/NTN wet side samples in 1983.

and the specific conductance values obtained for quality control samples with certified conductivity values are consistently within the acceptable limits. This leaves a problem in the calculations as the source of the skewed curve. Using the constants found in the CRC Handbook instead of those in Standard Methods 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 at the CAL. The curve is centering near -10% in most years which may result from the presence of low concentrations of ions whose presence go undetected in the IPD calculations and resultant histograms. The presence of very trace amounts of metal ions complexed with unmeasured 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, 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, it 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. Analyst's input as to the possible source of error is always requested and 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 one percent will require any change in the original data. The overall result is approximately 0.1% of the final data changed from what was initially reported.

and the specific conductance values obtained for quality control samples with certified conductivity values are consistently within the acceptable limits. This leaves a problem in the calculations or the source of the skewed curve. Using the constants found in the <u>CRC Handbook</u> instead of those in <u>Standard Methods</u> 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 at the CAL. The curve is centering near -10% in most years which may result from the presence of low concentrations of ions whose presence go undetected in the ion calculations and resultant histograms. The presence of very trace amounts of metal ions complexed with unmeasured 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, 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, it 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. Analyst's input as to the possible source of error is always requested and 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 one percent will require any change in the original data. The overall result is approximately 0.1% of the final data changed from what was initially reported.

VI. EXTERNAL QUALITY ASSURANCE PROGRAM PARTICIPATION

The analytical bias and precision information reported in Section IV and Appendix D of this report are supported by the CAL's performance in several different external quality assurance programs. The U.S. Geological Survey has accepted the position as the external auditing agency of the CAL for the national monitoring network. In addition to this external quality assurance program, the CAL voluntarily participates in other national and international performance studies. In the following section of this report, the performance of the CAL in each of these studies is addressed.

A. U.S. Geological Survey External Audit Program

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

The NADP/NTN Blind Audit Program was started in October 1979 (1). At that time the USGS supplied Standard Reference Water Samples (SRWS) to the sites in the sampling network. The first week a site did not have rain, the site operator was directed to pour this known sample into a clean bucket and submit it to the CAL as the rain sample for the week. The site operator was to also notify the USGS and the Coordinator's Office that the SRWS had been sent and on what day. The sample would be processed by the CAL as a normal rain sample. This program relies on the cooperation of the site operators. It reflects 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 analysis of the samples for calcium, magnesium, sodium, potassium, sulfate and chloride. Many of the SRWS samples used in the program through 1983 have analyte concentrations higher than those found in rainwater and often must be diluted by the laboratory before analysis. Table VI-1 lists the maximum analyte concentration that can be present in a sample before a dilution prior to analysis is necessary. The fact that a dilution of the sample has been made adds another variable to be considered when interpreting the data. A report on the information obtained from the program has been prepared by Schroder, et al.(8).

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). The study was designed to determine if the four test laboratories were producing comparable results, document an analytical bias for each lab, and estimate analytical precision. Precipitation samples from sites in the NADP/NTN network were split at the CAL and sent to the USGS Central Laboratory in Denver. The samples were then distributed to each of the four participants 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 Report 85-4313 by Brooks, et al.(9) discusses the USGS analysis of the data received from November 1982 - August 1983.

TABLE VI-1 The 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 9.00	1/79 - 1/83 1/83 - 12/83
Nitrate-Nitrite	5.00	1/79 - 12/83
Chloride	5.00 3.00	1/79 - 4/81 4/81 - 12/83
Orthophosphate	0.100 0.250	1/79 - 1/83 1/83 - 12/83

B. Interlaboratory Comparison Studies

Between 1978 and 1983, the CAL participated in several other interlaboratory performance studies in addition to the USGS sponsored comparison just discussed. These studies were sponsored by state and federal government agencies and international organizations. This section continues with a brief description of the studies in which the CAL participated. The CAL data for each study are presented in tables which also include the expected analyte concentrations. More detailed explanations of the laboratory intercomparisons are contained in the agency summaries referenced at the end of this report.

World Meteorological Organization/ United States Environmental Protection Agency

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. The first WMO sponsored study in which the CAL participated was the Third Intercomparison. Table VI-2 lists the CAL data and the National Bureau of Standards (NBS) expected values. The CAL performance at that time was generally very good at the low analyte concentrations with some potential problem areas at very high analyte concentrations, e.g. a chloride value of 37.7 mg/L instead of the expected 42.4. Rating of each laboratory was not a part of this WMO intercomparison. Overall improvement by all of the participating laboratories since the second intercomparison was the only assessment of laboratory performance made (10).

With the report for the Fourth Interlaboratory Comparison, individual laboratory evaluations were included. Table V1-3 presents the CAL data and the NBS expected values for the two test samples. The analyte concentrations in these samples were closer to those found in precipitation, and the deviation of the CAL results from the expected values was quite small for all analytes.

The CAL data and NBS expected analyte concentrations for the samples in the Sixth and the Seventh Intercomparisons are found in Tables VI-4 and VI-5, respectively. These data indicate continued improvement in the accuracy of the CAL data. This improvement is more clearly evident in the summary presented in Table VI-6. The calculations used to prepare this summary are those used by the WMO in its analysis of individual laboratory performance and are taken from the final report for the Fourth Intercomparison (11) and the report for the intercomparisons performed in 1983 (12). Table VI-6 was first presented in Chapter 10 of Semonin, et al. (13) which discusses in more detail the CAL participation in the WMO studies.

TABLE VI-2 Third Interlaboratory Comparison of Reference Precipitation Samples - December 1978 - Compares CAL Values to NBS Expected Values.

Parameter	71XXXX CAL	71XXXX Expected	72XXXX CAL	72XXXX Expected	73XXXX CAL	73XXXX Expected
Calcium (mg/L)	0.09	0.08	0.88	0.77	7.2	6.0
Magnesium (mg/L)	0.117	0.110	1.20	1.12	<0.002	-----
Sodium (mg/L)	0.151	0.151	2.71	2.86	9.76	9.66
Potassium (mg/L)	0.193	0.199	0.957	0.994	4.90	4.94
Ammonium (mg/L)	0.13	0.11	1.07	1.07	10.1	10.2
Nitrate (mg/L)	0.44	0.50	3.14	3.02	15.5	14.5
Chloride (mg/L)	0.95	1.35	6.63	7.22	37.7	42.4
Sulfate (mg/L)	3.3	2.7	9.3	7.9	10.2	9.9
pH (units)	4.24	4.48	4.07	4.08	5.75	5.98
Specific Conductance (uS/cm)	27.9	28.8	76.5	77.9	199.1	190.5

TABLE VI-3 Fourth Interlaboratory Comparison of Reference Precipitation Samples - July 1980 - Compares CAL Values to NBS Expected Values.

Parameter	91XXX CAL	91XXX Expected	92XXX CAL	92XXX Expected
Calcium (mg/L)	0.24	0.25	0.67	0.65
Magnesium (mg/L)	0.056	0.056	0.230	0.226
Sodium (mg/L)	0.282	0.284	0.542	0.554
Potassium (mg/L)	0.146	0.156	0.488	0.506
Ammonium (mg/L)	0.22	0.21	0.70	0.66
Nitrate (mg/L)	0.84	0.82	2.17	2.15
Chloride (mg/L)	0.98	0.91	3.29	3.27
Sulfate (mg/L)	0.84	0.78	2.73	2.32
pH (units)	5.06	5.03	4.28	4.35
Specific Conductance (uS/cm)	10.8	9.9	39.1	38.5

TABLE VI-4 Sixth Interlaboratory Comparison of Reference Precipitation Samples - April 1983 - Compares CAL Values to NBS Expected Values.

Parameter	Samples					
	1XXX		2XXX		3XXX	
	CAL	Expected	CAL	Expected	CAL	Expected
Calcium (mg/L)	0.06	0.06	0.42	0.40	0.14	0.15
Magnesium (mg/L)	0.02	0.02	0.08	0.08	0.06	0.06
Sodium (mg/L)	0.24	0.25	1.75	1.83	1.23	1.36
Potassium (mg/L)	0.08	0.08	0.81	0.80	0.51	0.55
Ammonium (mg/L)	0.17	0.14	1.06	1.11	0.45	0.41
Nitrate (mg/L)	0.66	0.62	3.65	3.34	3.72	3.72
Chloride (mg/L)	0.39	0.40	2.84	2.82	1.06	1.15
Sulfate (mg/L)	1.74	1.80	13.4	12.79	6.23	6.32
pH (units)	4.48	4.51	3.48	3.51	3.93	3.92
Specific Conductance (uS/cm)	18.2	17.1	165.3	156.0	66.1	65.5

TABLE VI-5 Seventh Interlaboratory Comparison of Reference Precipitation Samples - November 1983 - Compares CAL Values to NBS Expected Values.

Parameter	Samples					
	1XXX		2XXX		3XXX	
	CAL	Expected	CAL	Expected	CAL	Expected
Calcium (mg/L)	0.11	0.11	3.35	3.63	1.92	2.06
Magnesium (mg/L)	0.01	0.01	0.38	0.37	0.25	0.25
Sodium (mg/L)	0.07	0.08	1.49	1.44	0.25	0.26
Potassium (mg/L)	0.05	0.05	1.53	1.47	2.71	2.68
Ammonium (mg/L)	0.44	0.43	2.31	2.31	0.45	0.44
Nitrate (mg/L)	0.13	0.13	6.20	6.11	4.52	4.52
Chloride (mg/L)	1.05	1.01	10.12	10.33	4.22	4.17
Sulfate (mg/L)	1.65	1.71	10.7	11.1	17.0	17.7
pH (units)	4.50	4.45	3.75	3.72	3.50	3.49
Specific Conductance (uS/cm)	19.2	19.0	135.9	135.0	153.4	165.8

TABLE VI-6 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
Fourth	7/80	27	4.38	17.67
Sixth	4/83	22	3.89	17.47
Seventh	11/83	22	2.65	23.51

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 =

$$\frac{\dfrac{|\text{Expected Value} - \text{Reported Value}|}{\text{Expected Value}}}{10\ (\text{constituents})} \times 100$$

In each of the 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.

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY

In December of 1981 the Analytical Chemistry Unit of the Illinois State Water Survey, of which the CAL laboratory is a part, received certification as an environmental laboratory 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 were being followed (14). Analysis of performance evaluation samples containing the parameters for which certification was requested, was also required. Each laboratory was rated satisfactory or unsatisfactory for every analytical value it reported. Information regarding the true or expected values for the analytes present in the test samples was 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 most of the analytical data reported.

The certification was valid for two years and recertification was requested in 1983. The on-site review of the laboratory, its staff, and the analytical methods being used, took place in September and the new Certificate of Approval was issued in December 1983.

CANADA CENTRE FOR INLAND WATERS (CCIW)

The Canadian Long Range Transport of Atmospheric Pollutants (LRTAP) program began interlaboratory comparability studies in December 1982 (15). 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, for all the parameters which were routinely analyzed by the individual labs. Median concentrations for each parameter were determined using the data reported by the 36 participating laboratories. This became the target value used to judge laboratory performance. Tables VI-7 though VI-9 list the median value and the value reported by the CAL for the 11 test samples.

The agreement between the CAL value and the CCIW median was generally very good. The noticeable exceptions were the nitrate-nitrite analyses. The samples were analyzed by Ion Chromatography and the difference between the CAL reported values and the median was consistently equal to the measured nitrite concentration. This was particularly apparent in sample 11 when the discrepancy between the two results and the nitrite levels were quite large.

All participants received a rating of satisfactory, moderate, or poor with the CAL receiving a satisfactory. The data from and evaluation for all participants can be found in the "LRTAP Intercomparison Study L4" by Aspila and Todd (16).

TABLE VI-7 LRTAP Interlaboratory Comparability Study #4 - August 1983 - CAL Reported Values Compared to CCIW Median Values for Calcium, Magnesium, Sodium, and Potassium.

Sample Number	Calcium (mg/L)		Magnesium (mg/L)		Sodium (mg/L)		Potassium (mg/L)	
	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
1	0.444	0.442	0.402	0.390	3.12	3.20	0.264	0.260
2	0.457	0.435	0.330	0.310	2.81	2.62	0.208	0.200
3	0.902	0.895	0.453	0.440	3.19	3.10	0.288	0.284
4	0.465	0.443	0.330	0.310	2.72	2.63	0.174	0.170
5	1.82	1.76	0.488	0.470	2.50	2.46	0.173	0.165
6	<0.009	0.040	0.741	0.700	0.722	0.711	1.09	1.09
7	0.304	0.300	0.068	0.070	0.533	0.519	0.347	0.325
8	2.22	2.13	0.626	0.605	0.050	0.060	0.085	0.088
9	1.00	0.970	0.213	0.210	0.216	0.200	0.118	0.120
10	13.3	13.0	2.76	2.70	1.24	1.24	0.508	0.500
11	42.4	42.0	9.3	9.10	18.9	18.95	0.894	0.897

TABLE VI-8 LRTAP Interlaboratory Comparability Study #4 - August 1983 - CAL Reported Values Compared to CCIW Median Values for Chloride, Sulfate, and Nitrate/Nitrite.

Sample Number	Chloride (mg/L)		Sulfate (mg/L)		Nitrate/Nitrite (mg/L)	
	CAL	CCIW	CAL	CCIW	CAL	CCIW
1	4.07	4.06	2.70	2.65	0.18	0.04
2	3.14	3.15	1.75	1.75	0.13	0.02
3	4.50	4.48	7.30	7.10	0.13	0.02
4	3.32	3.26	2.05	1.98	0.13	0.03
5	3.08	2.98	3.74	3.47	0.53	0.40
6	0.81	0.82	3.23	3.03	0.49	0.45
7	1.44	1.45	0.25	0.33	0.09	0.04
8	0.76	0.74	5.60	5.21	2.35	2.28
9	0.62	0.585	5.19	4.80	2.48	2.48
10	1.09	1.17	3.36	3.20	1.37	1.35
11	107.6	104.7	39.0	37.0	4.29	0.15

TABLE VI-9 LRTAP Interlaboratory Comparability Study #4 - August 1983 - CAL Reported Values Compared to CCIW Median Values for pH and Specific Conductance.

Sample Number	pH (units)		Specific Conductance (uS/cm)	
	CAL	CCIW	CAL	CCIW
1	4.62	4.60	31.9	32.2
2	4.49	4.50	30.5	30.8
3	4.11	4.10	55.9	59.0
4	4.61	4.64	28.0	28.9
5	6.07	6.24	26.7	27.6
6	5.08	5.02	18.5	18.6
7	5.60	5.60	7.5	7.97
8	5.98	6.30	25.4	26.8
9	4.31	4.31	33.2	33.9
10	7.36	7.70	88.5	93.2
11	5.91	5.51	418.6	434.0

VII. SUMMARY

When first organized, the NADP established as one of the primary goals of the project the production of analytical data which were of the highest quality. To achieve this end, guidelines and expectations were established for field, laboratory and data management operations. The original guidelines can be found in the NADP Plan of Research (17) that was published in 1982. The NADP Quality Assurance Plan for Deposition Monitoring (18) prepared in 1984 more clearly defines these guidelines and fully documents the requirements of the network regarding all three areas of operation.

The CAL laboratory was directed to produce data whose precision and bias were quantified. Minimum method detection limits were established for all analytical parameters and limits for the 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 data presented in this report indicate the CAL has achieved what was required. This report as a whole documents the quality assurance program practices as they have developed. The data tables in Appendix D provide annual assessments of the analytical bias and precision and indicate that the limits set for variance in accuracy were met. The MDLs listed in Table II-1 meet or exceed those required. With this report for 1978-1983, quality assurance data for the early years of the project become available to the data user. The CAL, in conjunction with the NADP/NTN Quality Assurance Manager and the Coordinator's Office, is currently attempting to provide the more recent quality assurance data in a more timely manner and thus meet all of the desired goals of the Quality Assurance Plan.

VIII. REFERENCES

1. Stensland, G.J., R.G. Semonin, M.E. Peden, V.C. Bowersox, F.F. McGurk, L.M. Skowron, M.J. Slater, and R.K. Stahlhut: NADP Quality Assurance Report - Central Analytical Laboratory, Jan. 1979 - Dec. 1979; 1980; Champaign, Illinois.

2. Britton, Paul W., Statistician - U. S. Environmental Protection Agency; EMSL - Cincinnati, Ohio; personal communication.

3. NADP/NTN Annual Data Summary. Precipitation Chemistry In The United States. 1983; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Ft. Collins, CO 80523; June 1985.

4. Topol, L.E., M. Lev-On, J. Flanagan, R.J. Schwall, A.E. Jackson: Quality Assurance Manual for Precipitation Measurement Systems; U. S. Environmental Protection Agency; Environmental Monitoring Systems Laboratory; Research Triangle Park, NC 27711; 1985.

5. American Society for Testing and Materials: "Standard Method of Reporting Results of Analysis of Water"; Method D596; 1983 Annual Book of ASTM Standards; p.43.

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

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

8. Schroder, L.J., A.W. Bricker, and T.W. Willoughby: Precision and Bias of Selected Analytes Reported by the National Atmospheric Deposition Program and National Trends Network - January 1980 Through September 1984; Water-Resources Investigations Report 85-4275; U.S. Geological Survey; Lakewood, Colorado; 1985.

9. Brooks, M.H., L.J. Schroder, and B.A. Malo: Interlaboratory Comparability Bias and Precision for Four Laboratories Measuring Constituents in Precipitation - November 1982 - August 1983; Water-Resources Investigations Report 85-4313; U.S. Geological Survey; Lakewood, Colorado; 1985.

10. Lampe, R.L., and J.C. Puzak: Third Analysis on Reference Precipitation Samples; World Meteorological Organization; 1980.

11. _____ and J.C. Puzak: Fourth Analysis on Reference Precipitation Samples by the Participating World Meteorological Organization Laboratories; December 1981.

12. Lampe, R.L., B.F. Parr, G. Pratt, O.L. Dowler, and W.J. Mitchell: National Performance Audit Program - Ambient Air Audits of Analytical Proficiency - 1983; Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency; Research Triangle Park, N.C. 27711.

13. Semonin, R.G., G.J. Stensland, V.C. Bowersox, M.E. Peden, J.M. Lockard, K.G. Doty, D.F. Gatz, L.C. Chu, S.R. Bachman, and R.K. Stahlhut: Study of Atmospheric Pollution Scavenging; Twentieth Progress Report to the U.S. Department of Energy; September 1984.

14. State of Illinois Rules and Regulations; Title 35: Environmental Protection; Subtitle A: General Provisions; Chapter II: Environmental Protection Agency; Part 183 - Joint Rules of the Illinois Environmental Protection Agency and the Illinois Department of Public Health: Certification and Operation of Environmental Laboratories; December 1, 1983.

15. Aspila, K.I., and S. Todd: LRTAP Intercomparison Study L1: Major Ions, Nutrients and Physical Parameters in Water; National Water Research Institute; Burlington, Ontario; July 1983.

16. ______, and S. Todd: LRTAP Intercomparison Study L4: Major Ions, Nutrients and Physical Parameters in Water; National Water Research Institute; Burlington, Ontario; February 1984.

17. Cowling, E.B., J. Fulkerson, K. Huston, and J.H. Gibson: 1977 Plan of Research for NC-141 North Central Regional Project on Atmospheric Deposition: Chemical Changes in Atmospheric Deposition and Effects on Agricultural and Forested Land and Surface Waters in the United States; Natural Resource Ecology Laboratory; Colorado State University; Ft. Collins, CO 80523; September 1982.

18. NADP Quality Assurance Plan: Deposition Monitoring; NADP/NTN Coordinator's Office; Natural Resource Ecology Laboratory; Colorado State University; Ft. Collins, CO 80523; July 1984.

APPENDIX A

Glossary of Terms

GLOSSARY OF TERMS

Item	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 testing of a homogenous sample and the accepted true value: Bias = measured value - true value
Mean	$\overline{x}$	$\overline{x} = \sum_{i=1}^{n} x_i/n$
Mean Bias		$\dfrac{\sum \text{bias for each sample}}{\text{total number of replicates (n)}}$
Method Detection Limit	MDL	The minimum concentration of an analyte that can be reported with 99% confidence that the value is above zero. The MDL is operationally defined as 3X the standard deviation of repetitive measurements at or near the blank level.

Percent Bias		The difference between the mean value obtained by repeated testing 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
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 Program		A program that utilizes quality control and quality assurance data to verify that the analytical system is operating within acceptable limits and to evaluate the quality of the sample data produced.
Quality Control Sample		Sample prepared and analyzed to determine the source and amount of potential contamination possible due to the sampling container, sample processing, and sample handling in the laboratory. This type of sample includes bucket leachates, filter leachates, and distilled or deionized water blanks.
Quality Control Check Sample	QCC	A sample containing known concentrations of analytes prepared by the analyst or a laboratory other than the laboratory performing the analysis. The performing 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		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

APPENDIX B

Laboratory Blanks
Plots and Tables
1978-1983

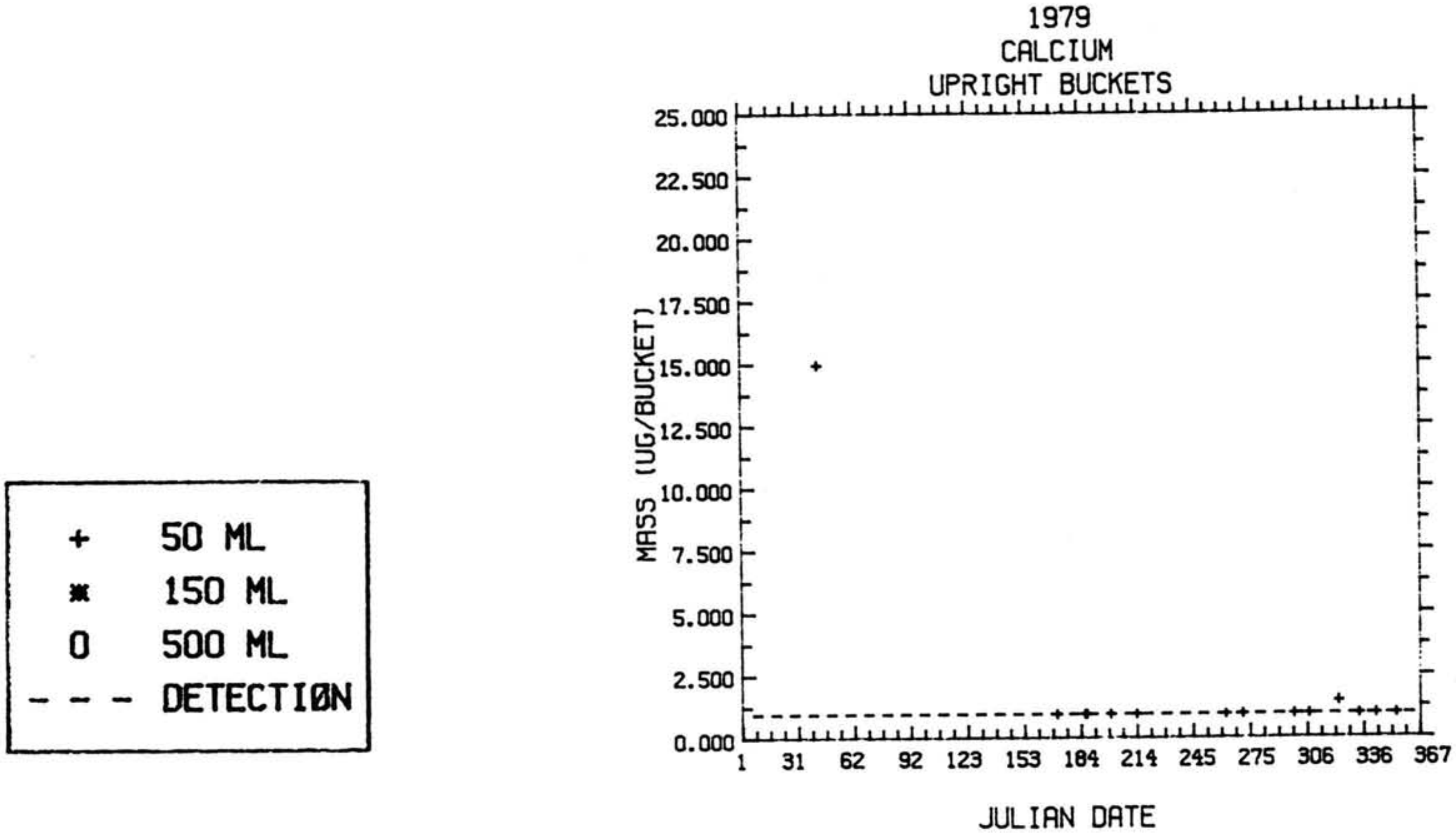


FIGURE 1. Measured calcium mass in upright bucket blanks for 1979.

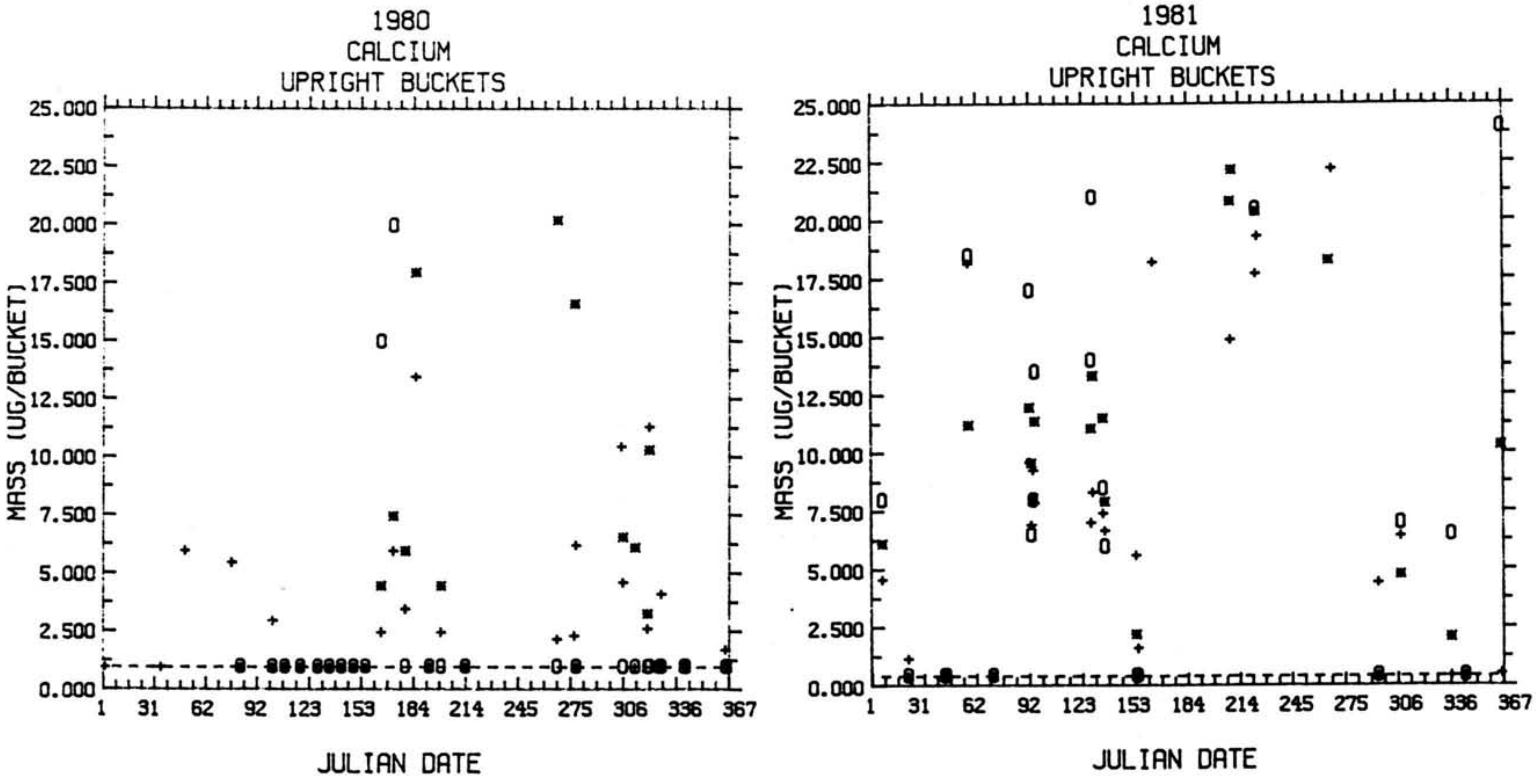


FIGURE 2. Measured calcium mass in upright bucket blanks for 1980 and 1981.

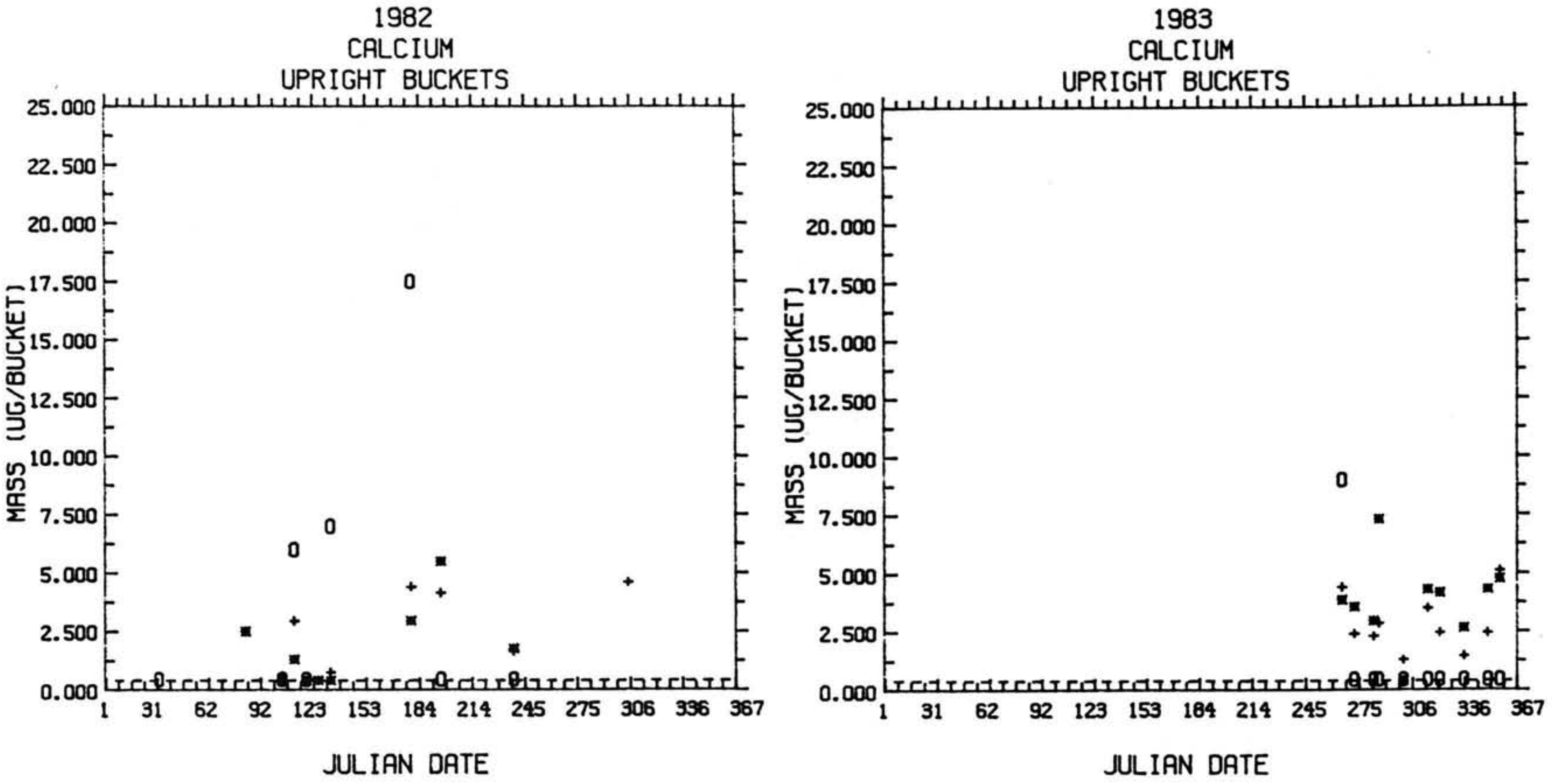


FIGURE 3. Measured calcium mass in upright bucket blanks for 1982 and 1983.

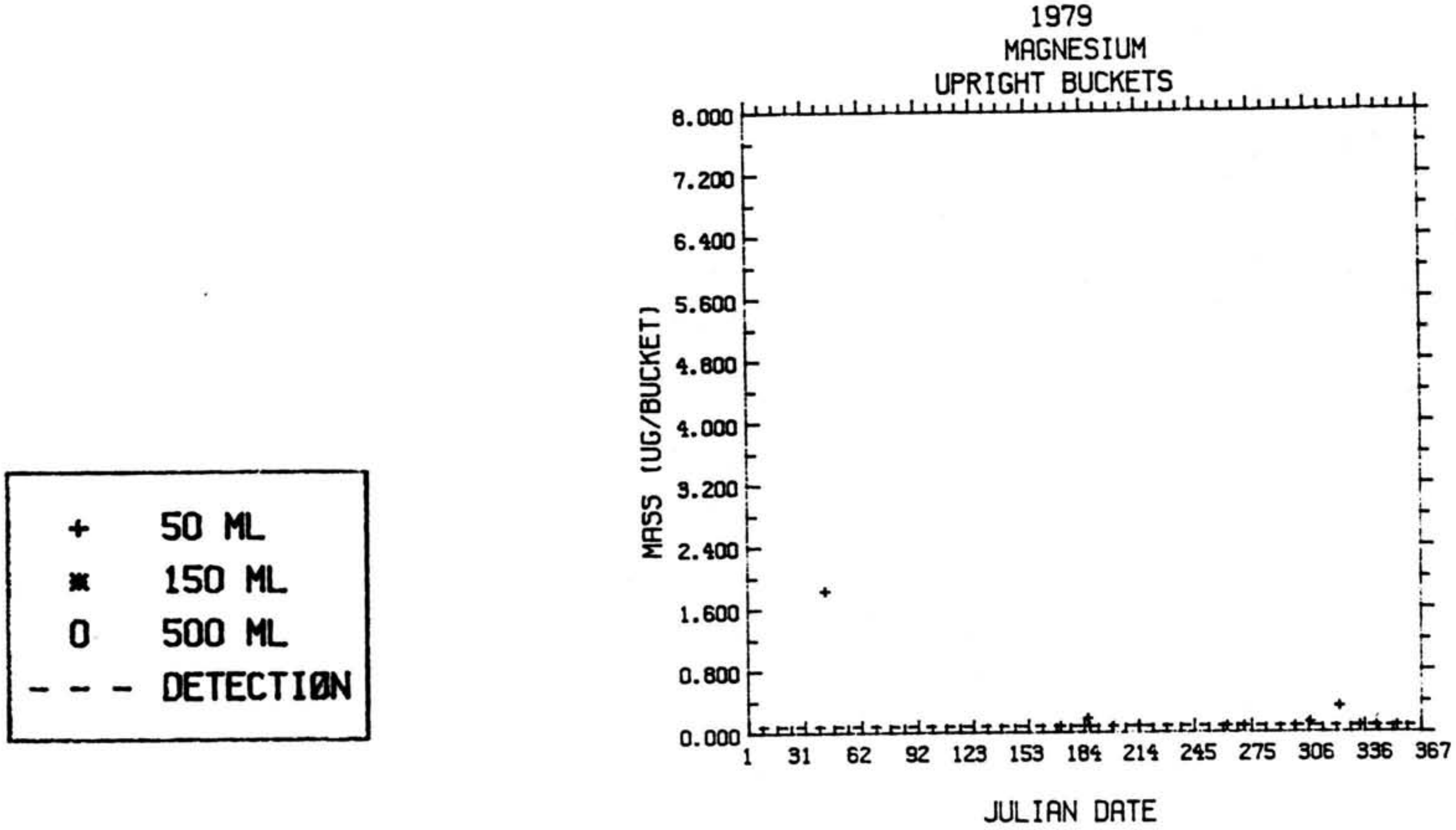


FIGURE 4. Measured magnesium mass in upright bucket blanks for 1979.

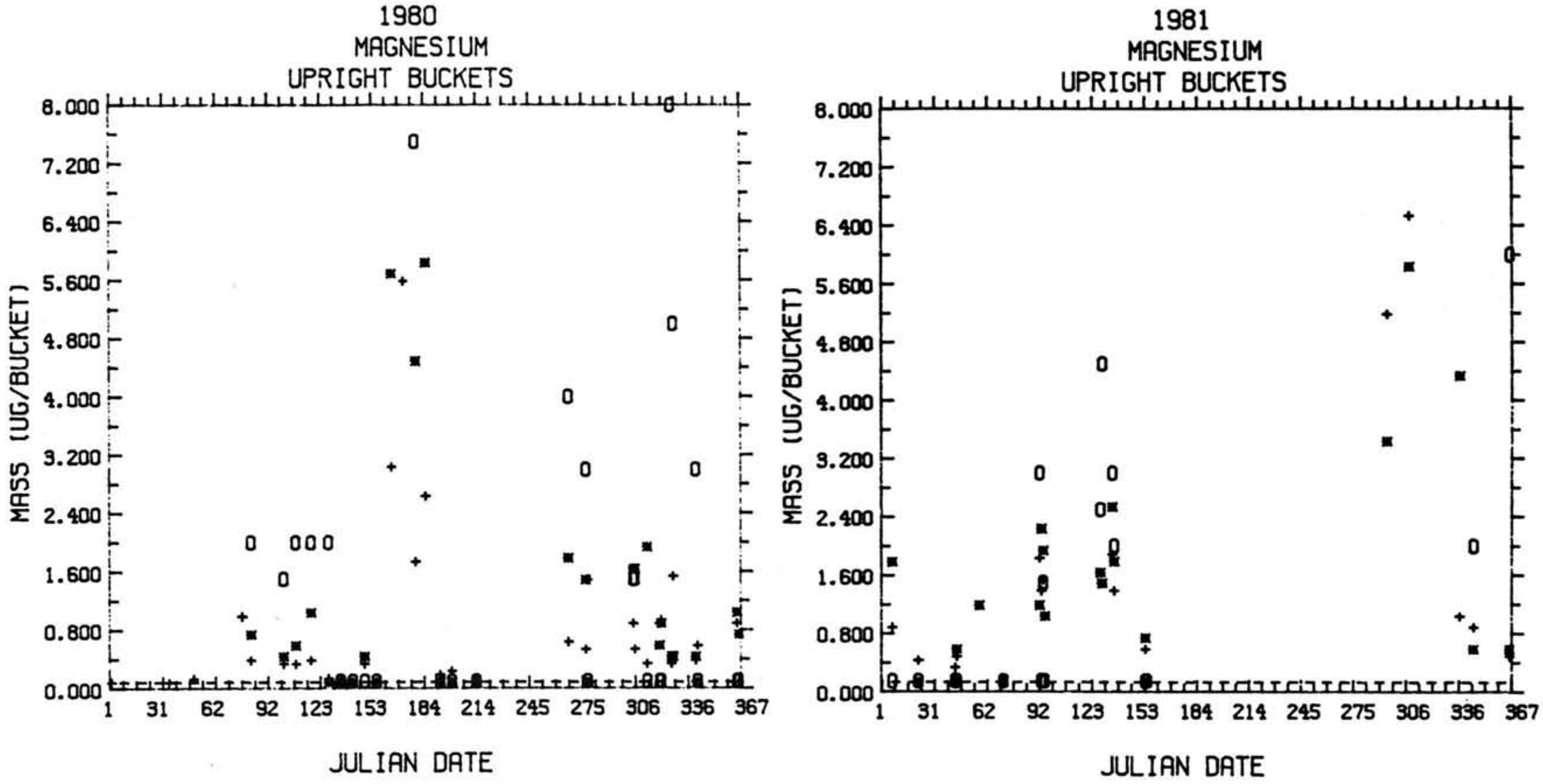


FIGURE 5. Measured magnesium mass in upright bucket blanks for 1980 and 1981.

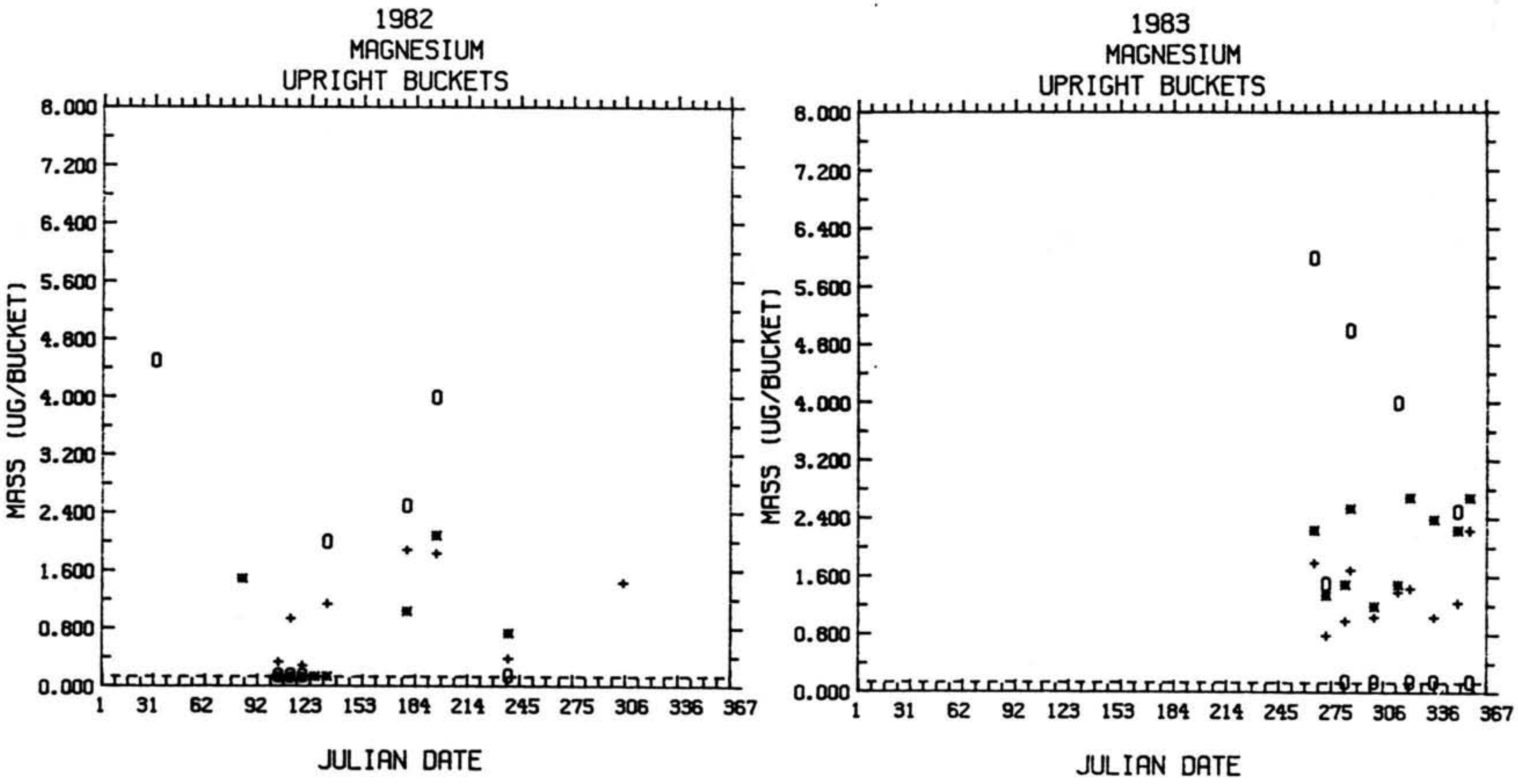


FIGURE 6. Measured magnesium mass in upright bucket blanks for 1982 and 1983.

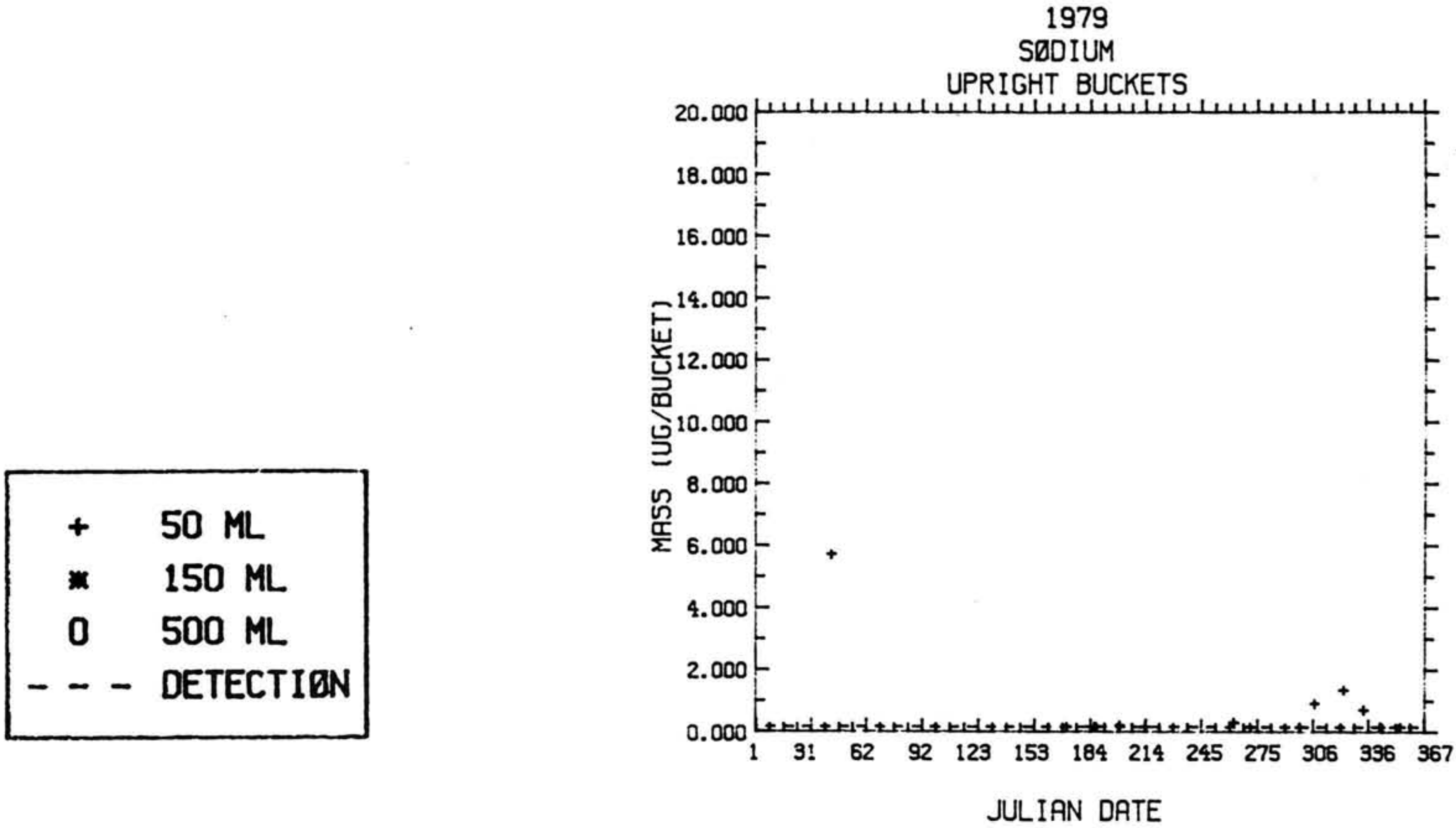


FIGURE 7. Measured sodium mass in upright bucket blanks for 1979.

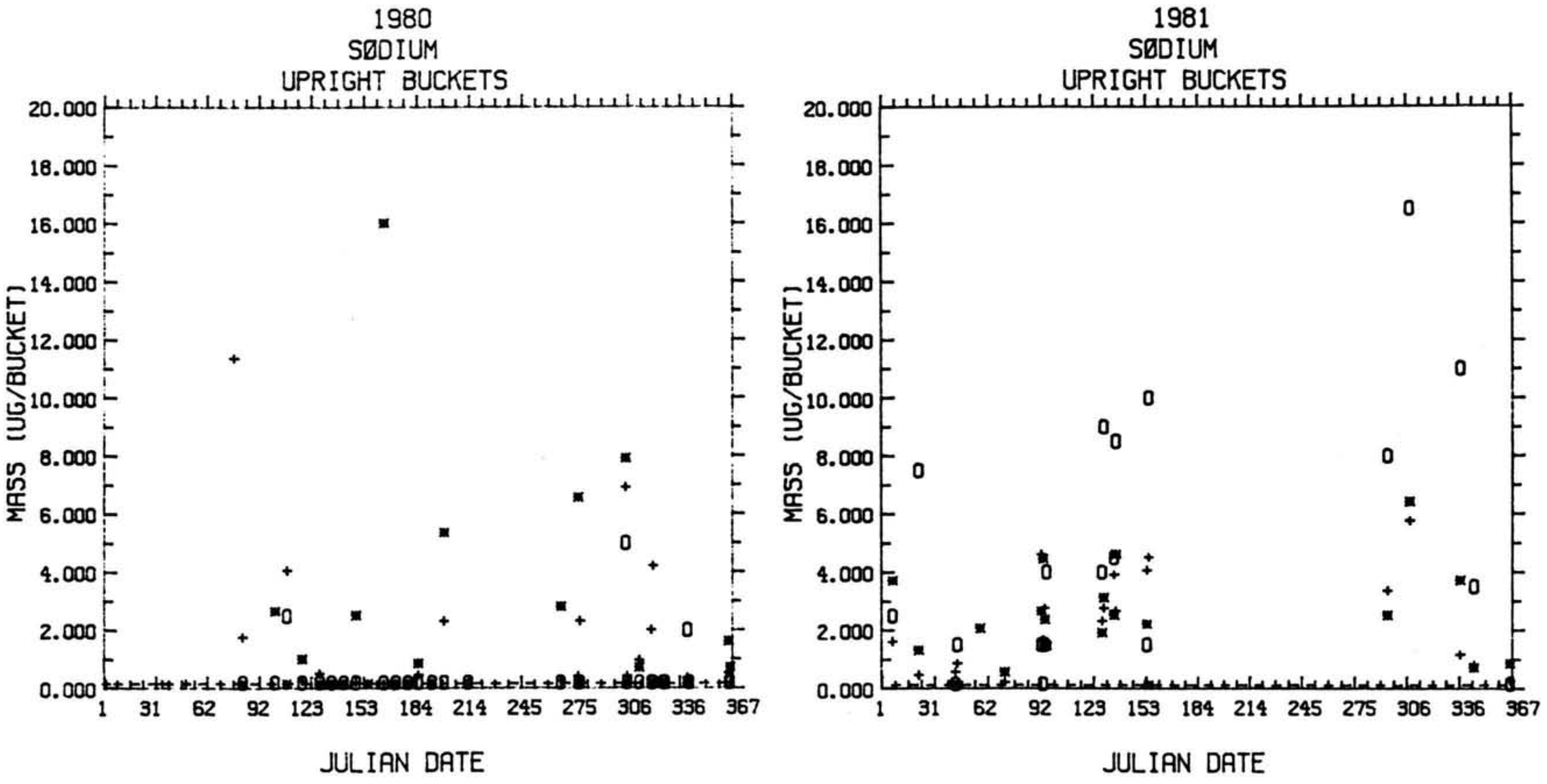


FIGURE 8. Measured sodium mass in upright bucket blanks for 1980 and 1981.

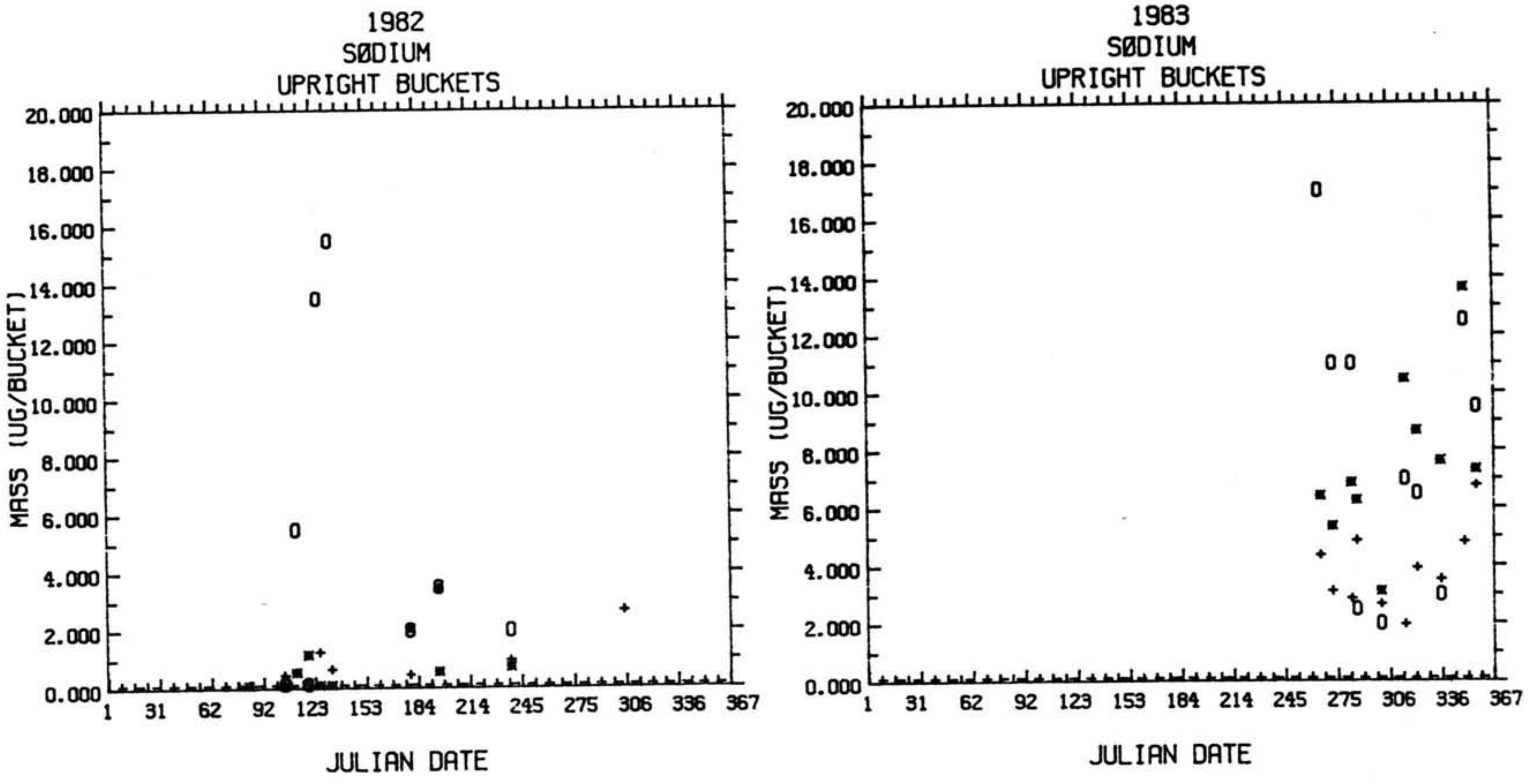


FIGURE 9. Measured sodium mass in upright bucket blanks for 1982 and 1983.

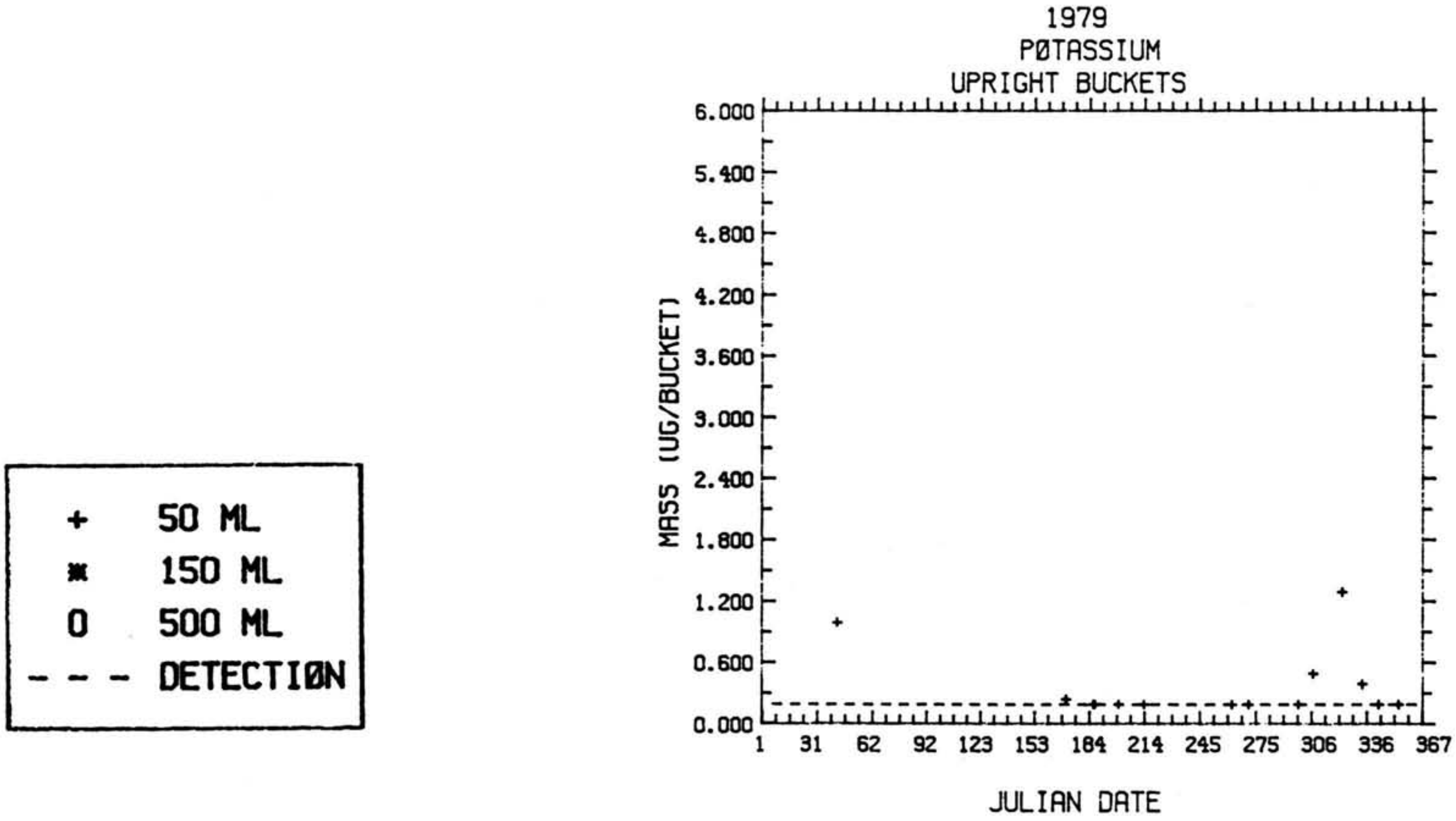


FIGURE 10. Measured potassium mass in upright bucket blanks for 1979.

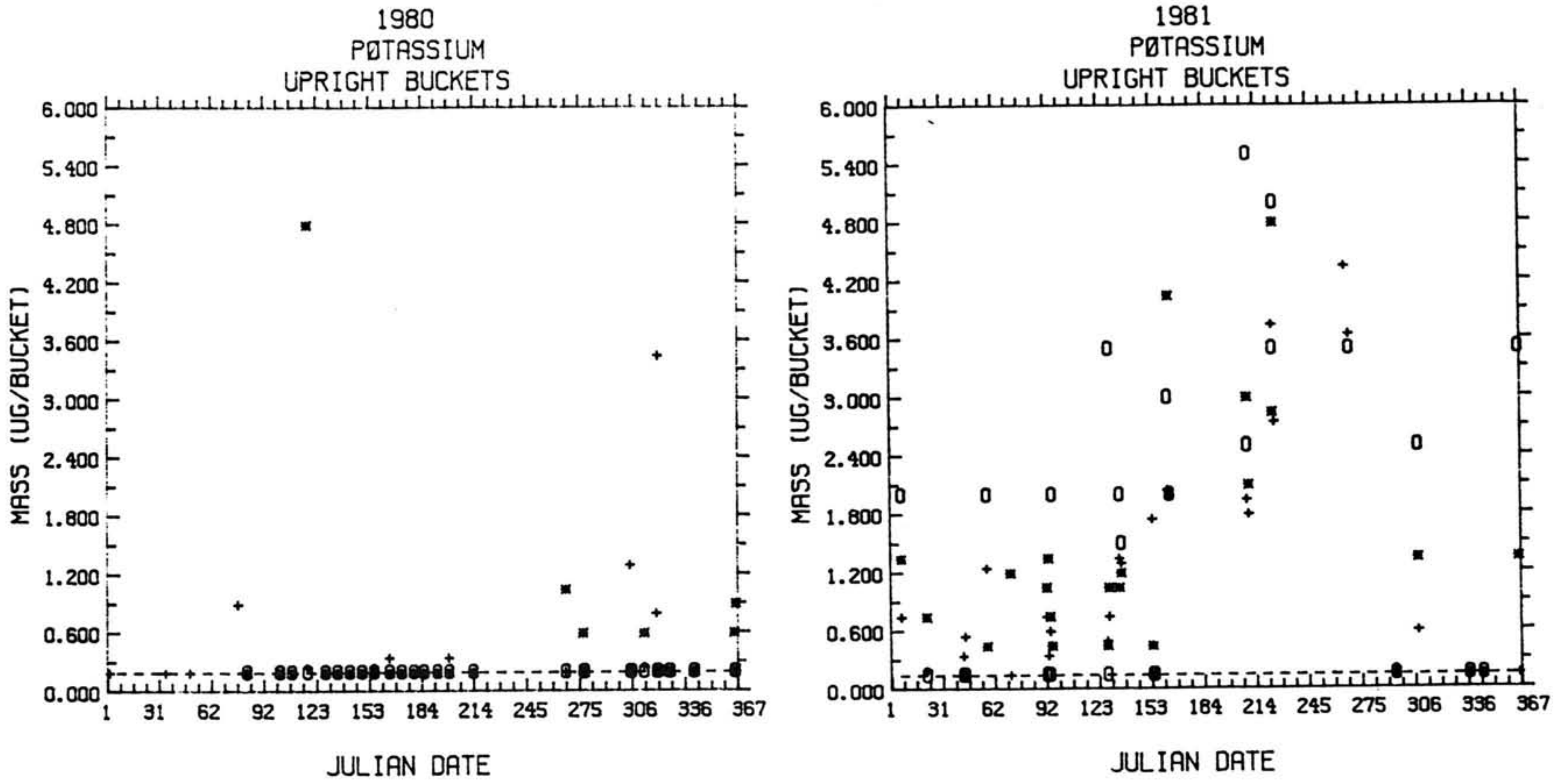


FIGURE 11. Measured potassium mass in upright bucket blanks for 1980 and 1981.

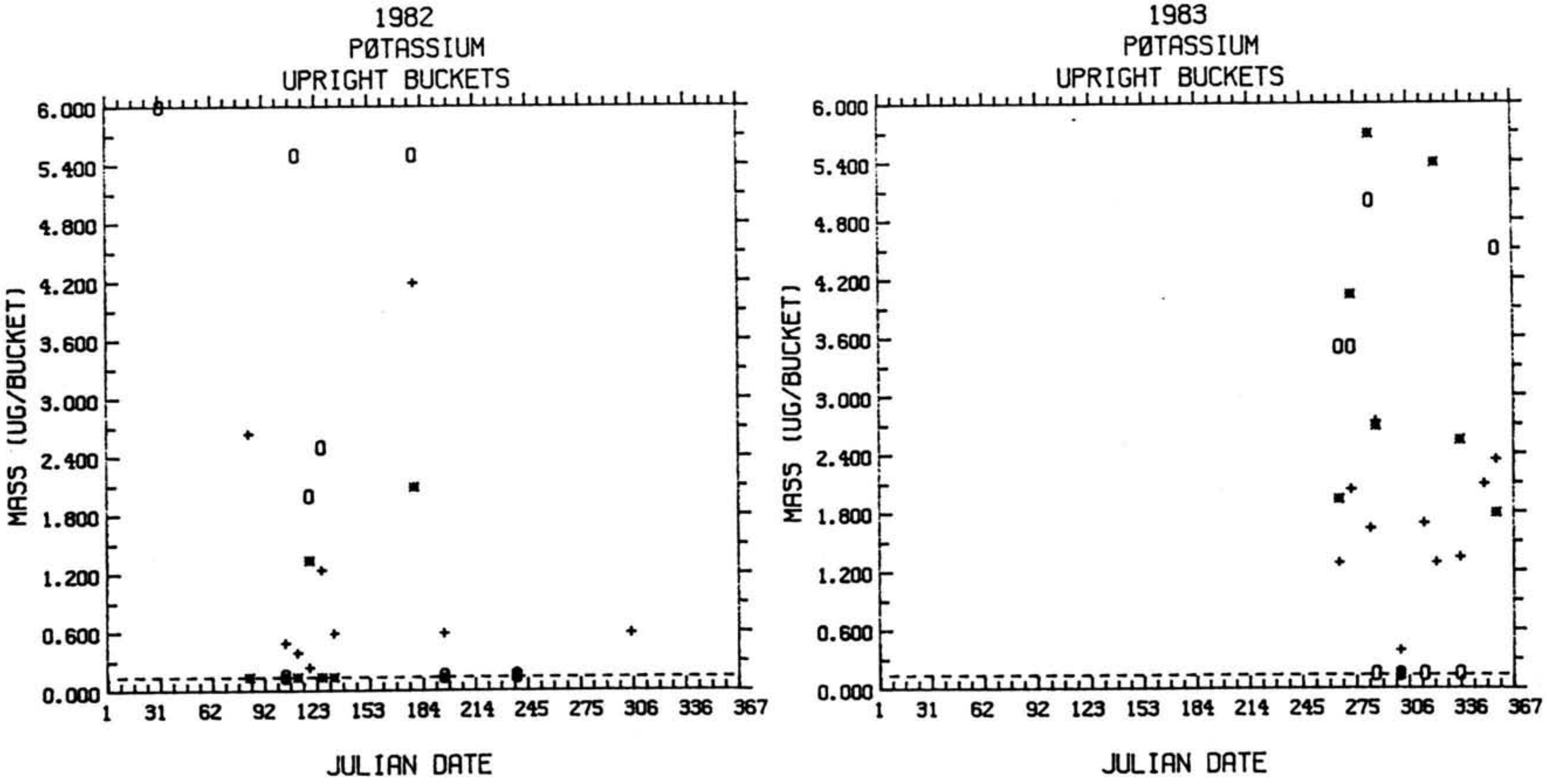


FIGURE 12. Measured potassium mass in upright bucket blanks for 1982 and 1983.

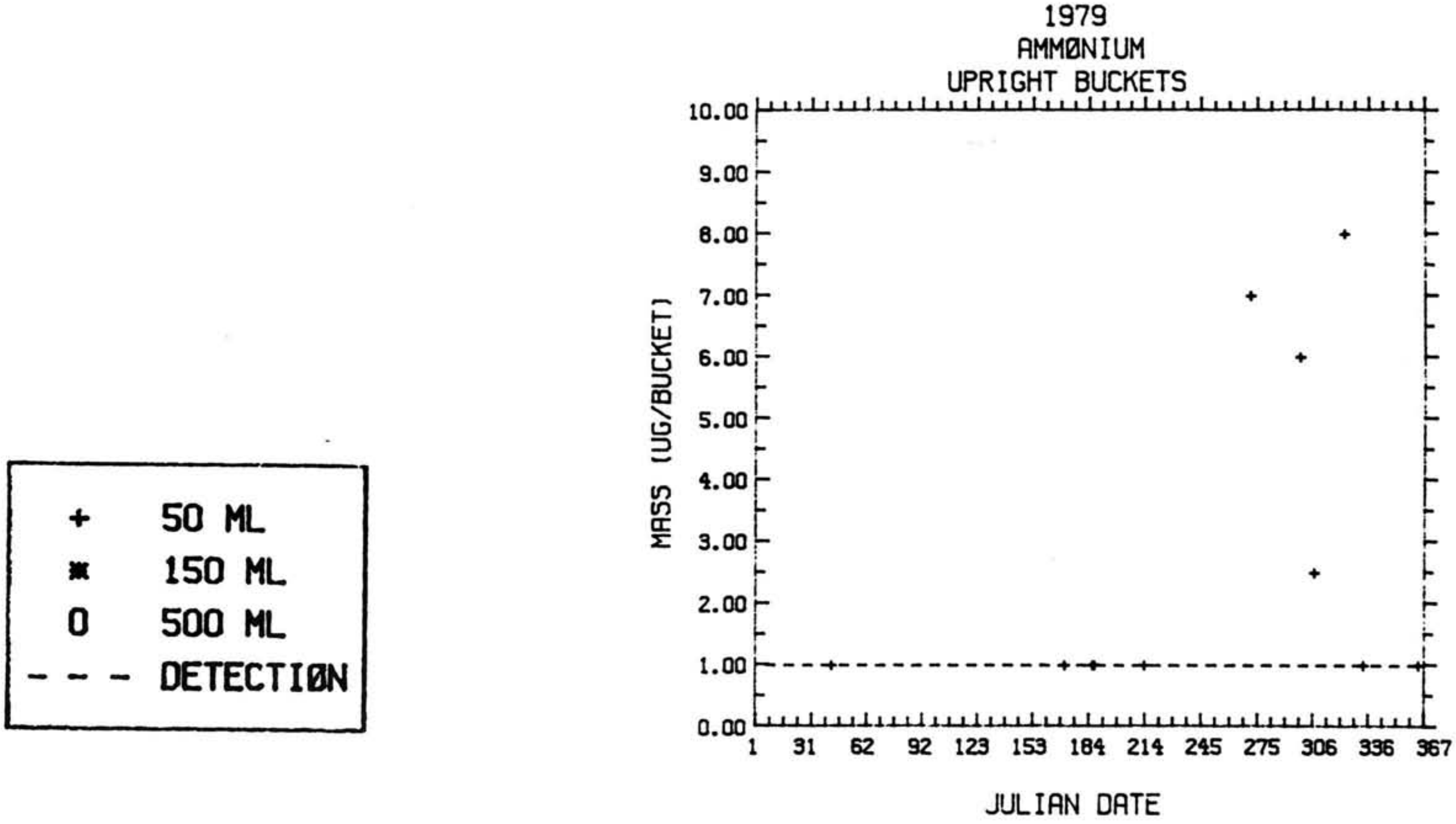


FIGURE 13. Measured ammonium mass in upright bucket blanks for 1979.

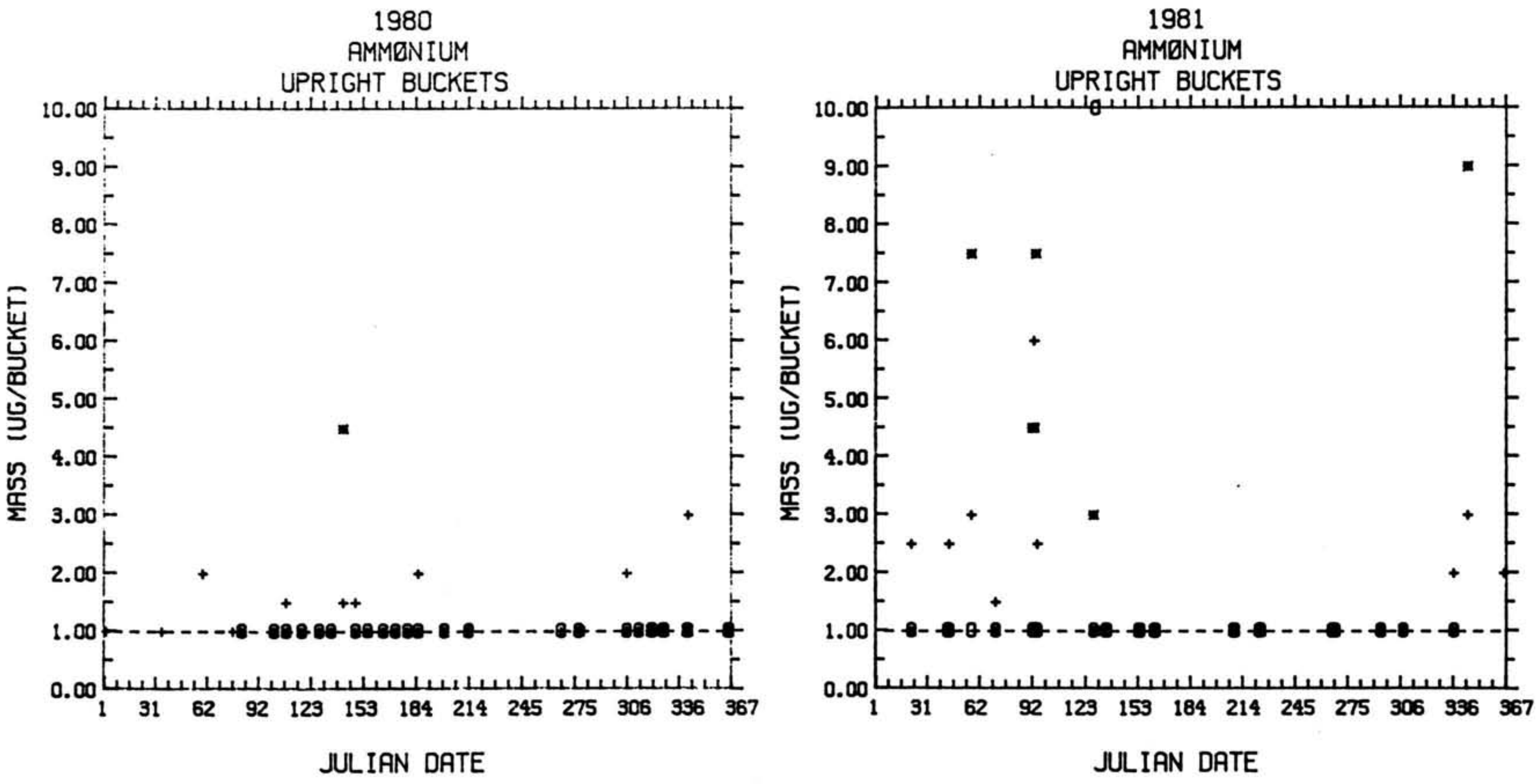


FIGURE 14. Measured ammonium mass in upright bucket blanks for 1980 and 1981.

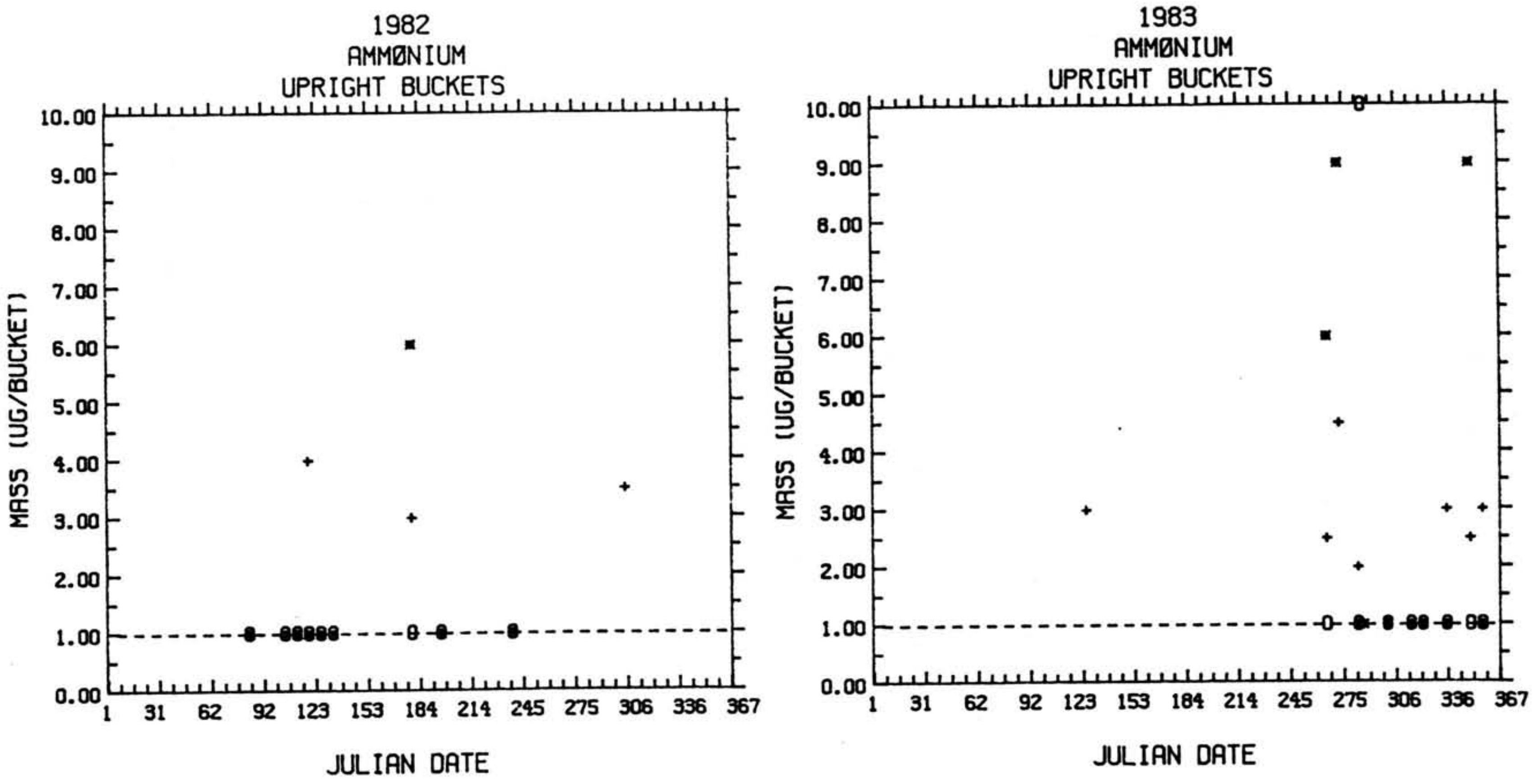


FIGURE 15. Measured ammonium mass in upright bucket blanks for 1982 and 1983.

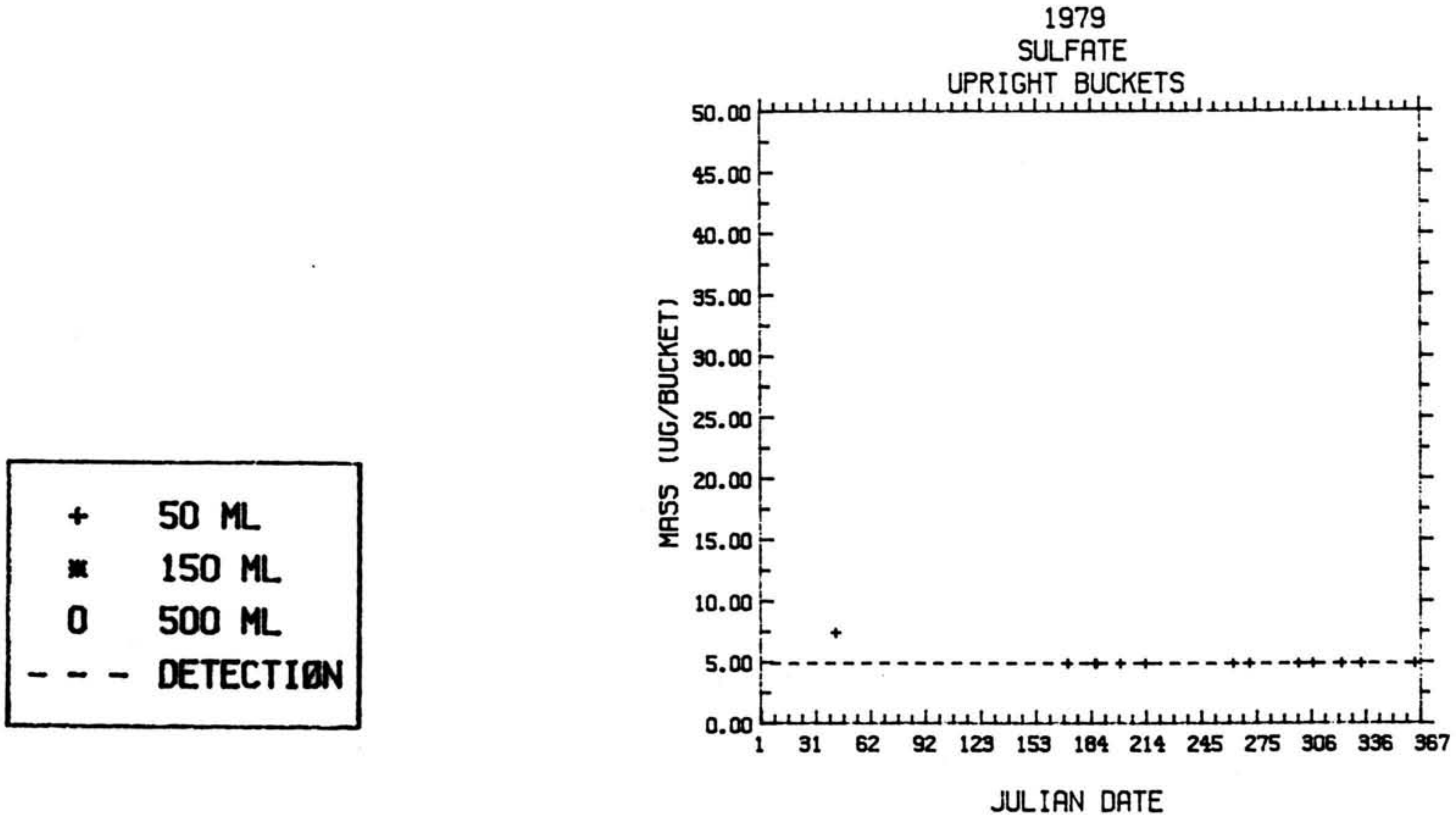


FIGURE 16. Measured sulfate mass in upright bucket blanks for 1979.

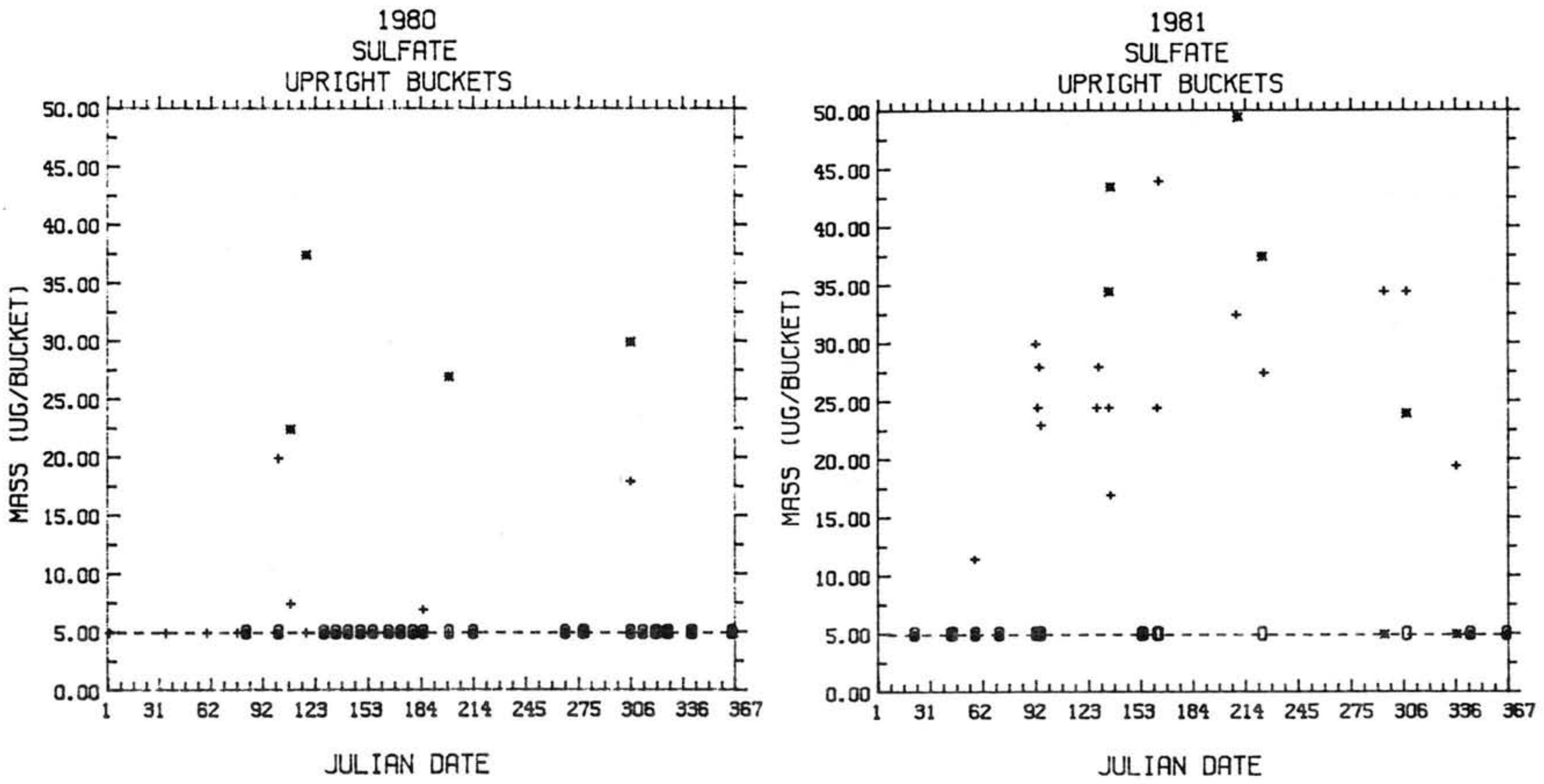


FIGURE 17. Measured sulfate mass in upright bucket blanks for 1980 and 1981.

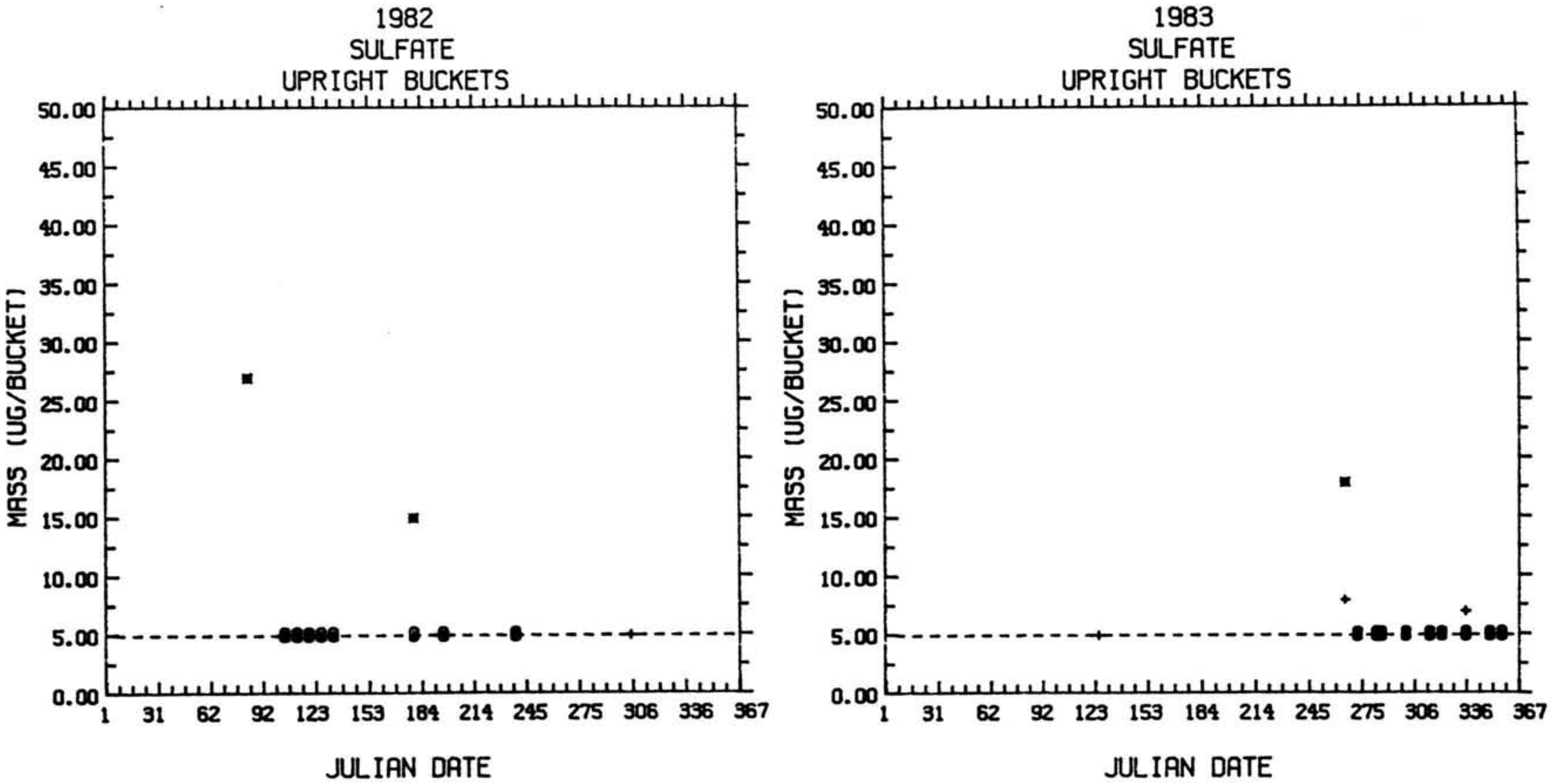


FIGURE 18. Measured sulfate mass in upright bucket blanks for 1982 and 1983.

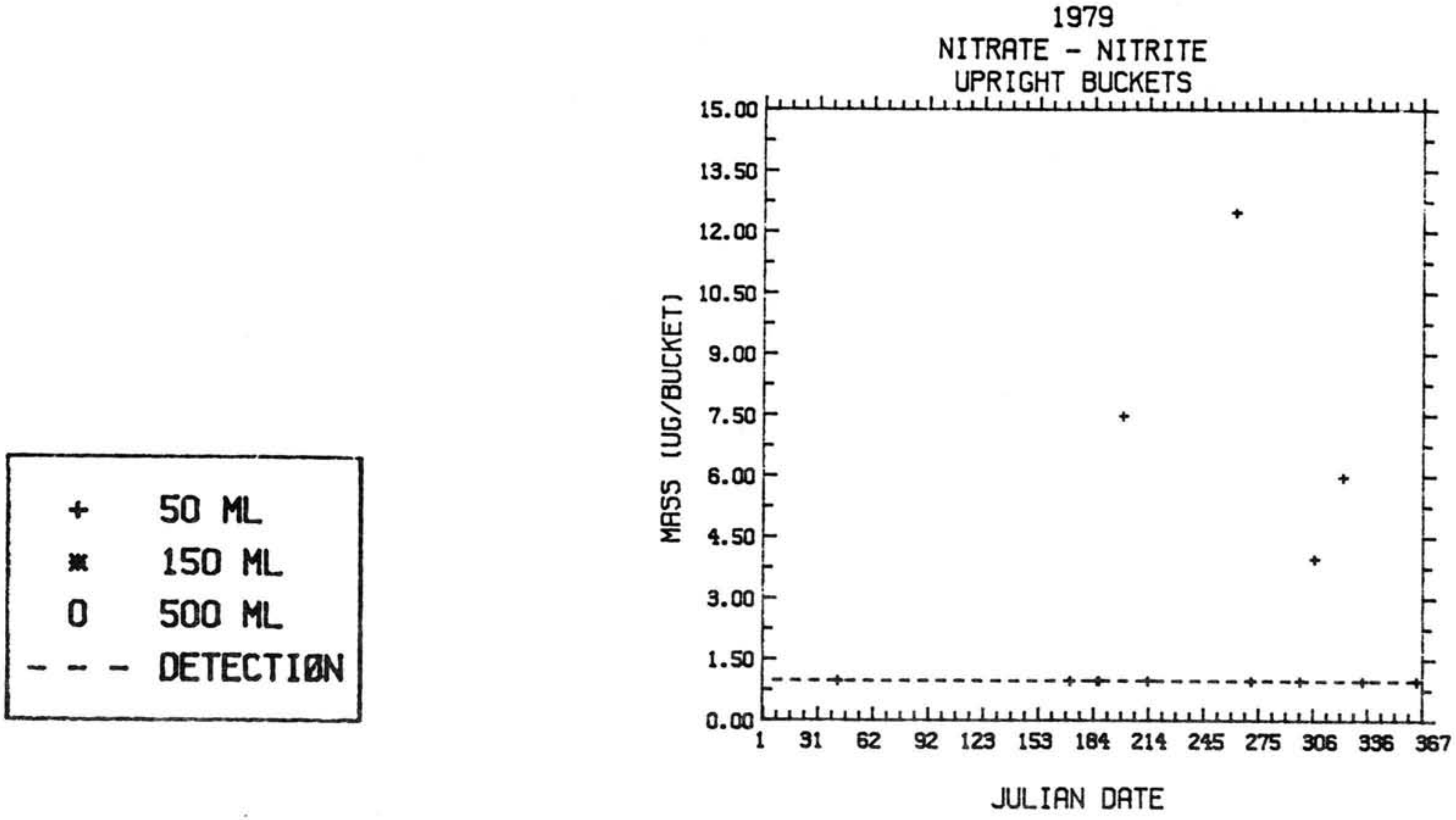


FIGURE 19. Measured nitrate-nitrite mass in upright bucket blanks for 1979.

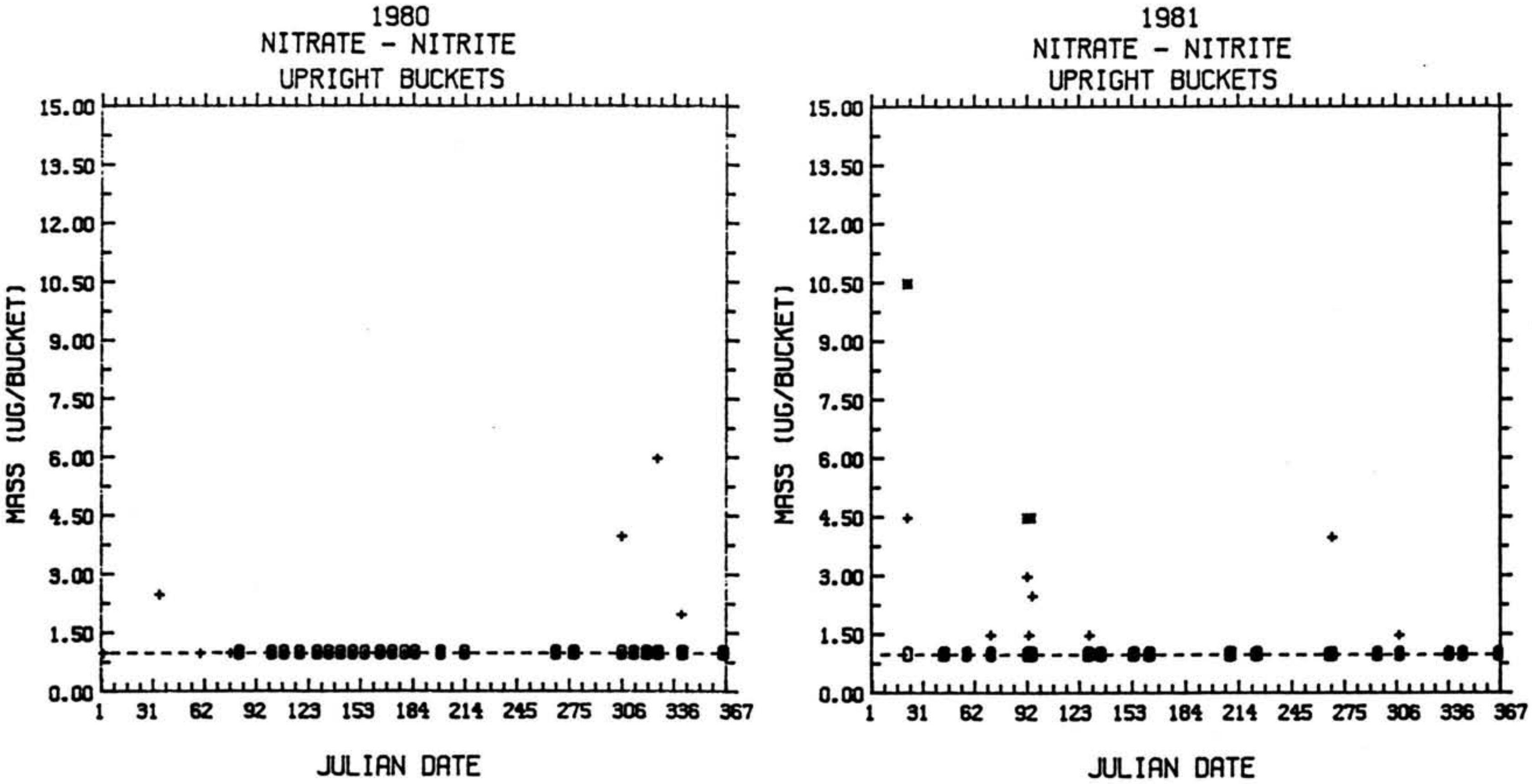


FIGURE 20. Measured nitrate-nitrite mass in upright bucket blanks for 1980 and 1981.

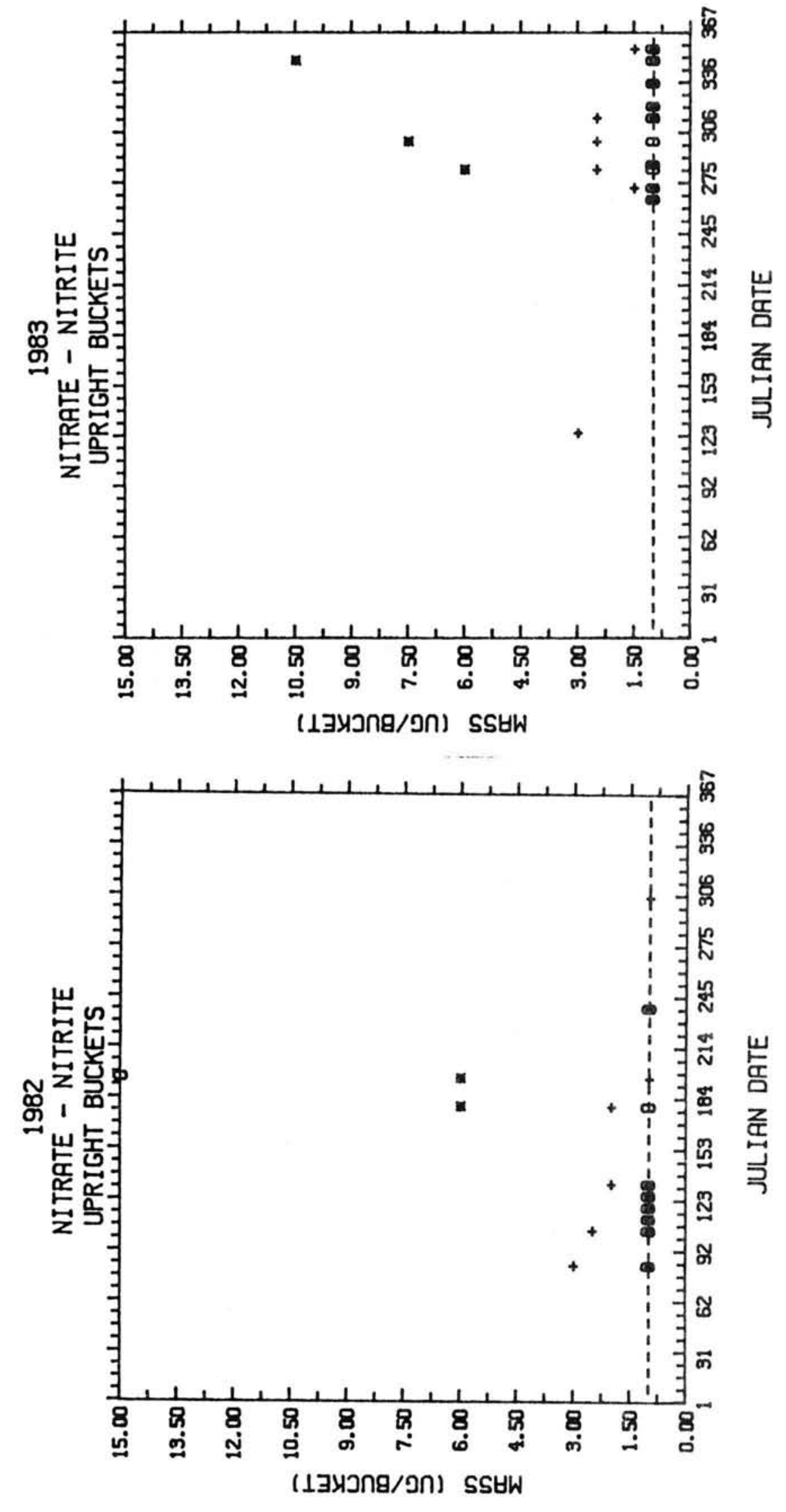


FIGURE 21. Measured nitrate-nitrite concentration in upright bucket blanks for 1982 and 1983.

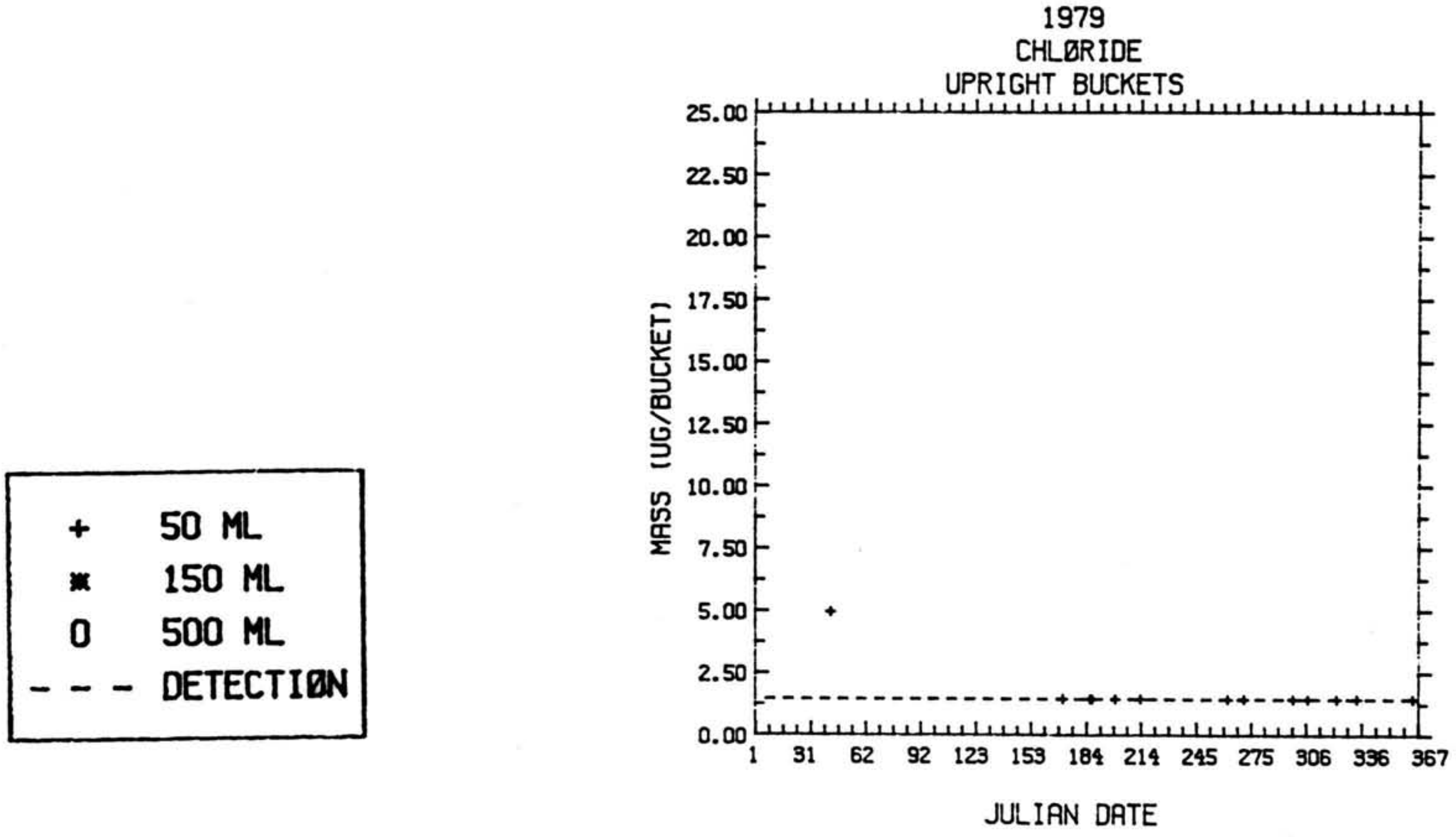


FIGURE 22. Measured chloride mass in upright bucket blanks for 1979.

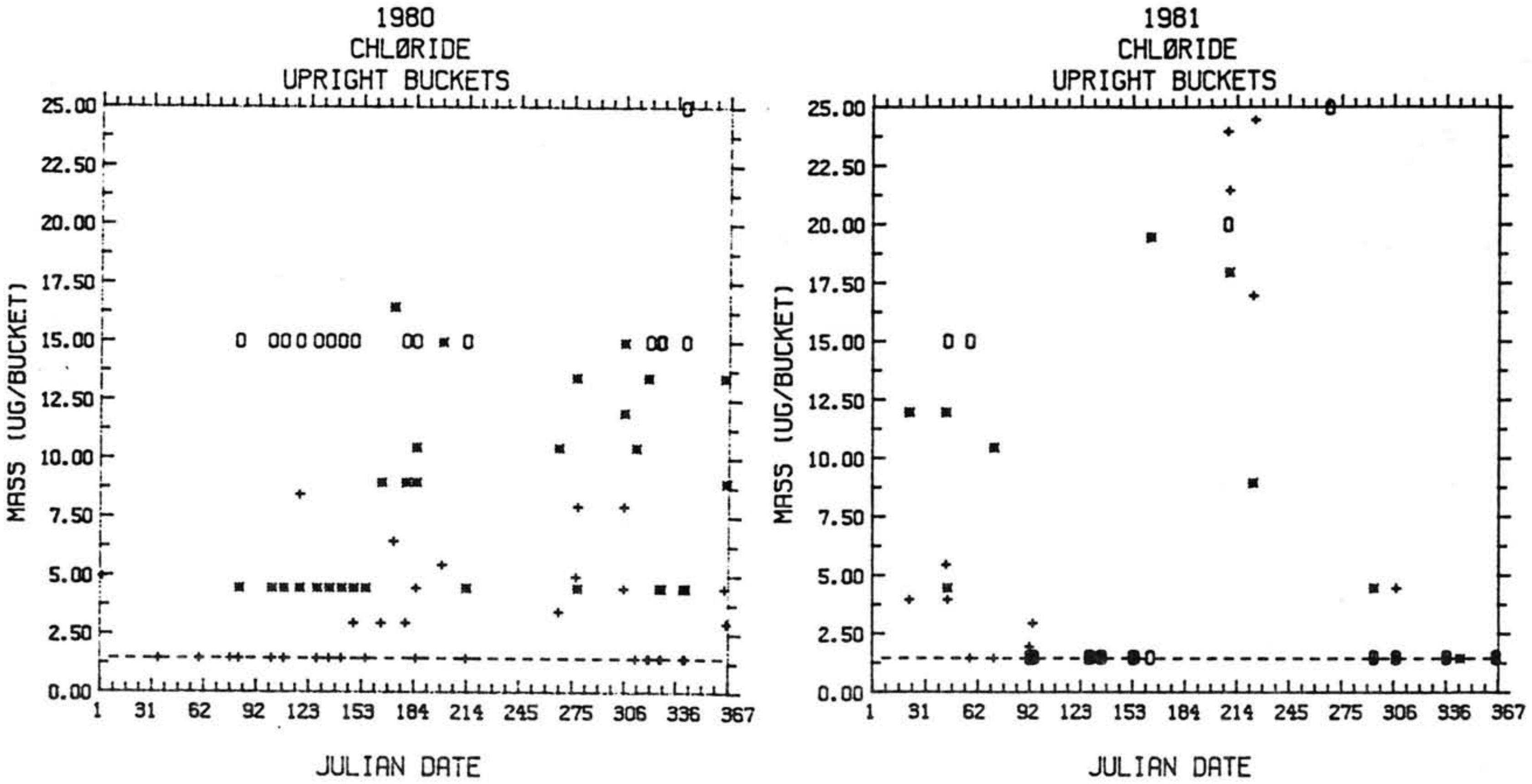


FIGURE 23. Measured chloride mass in upright bucket blanks for 1980 and 1981.

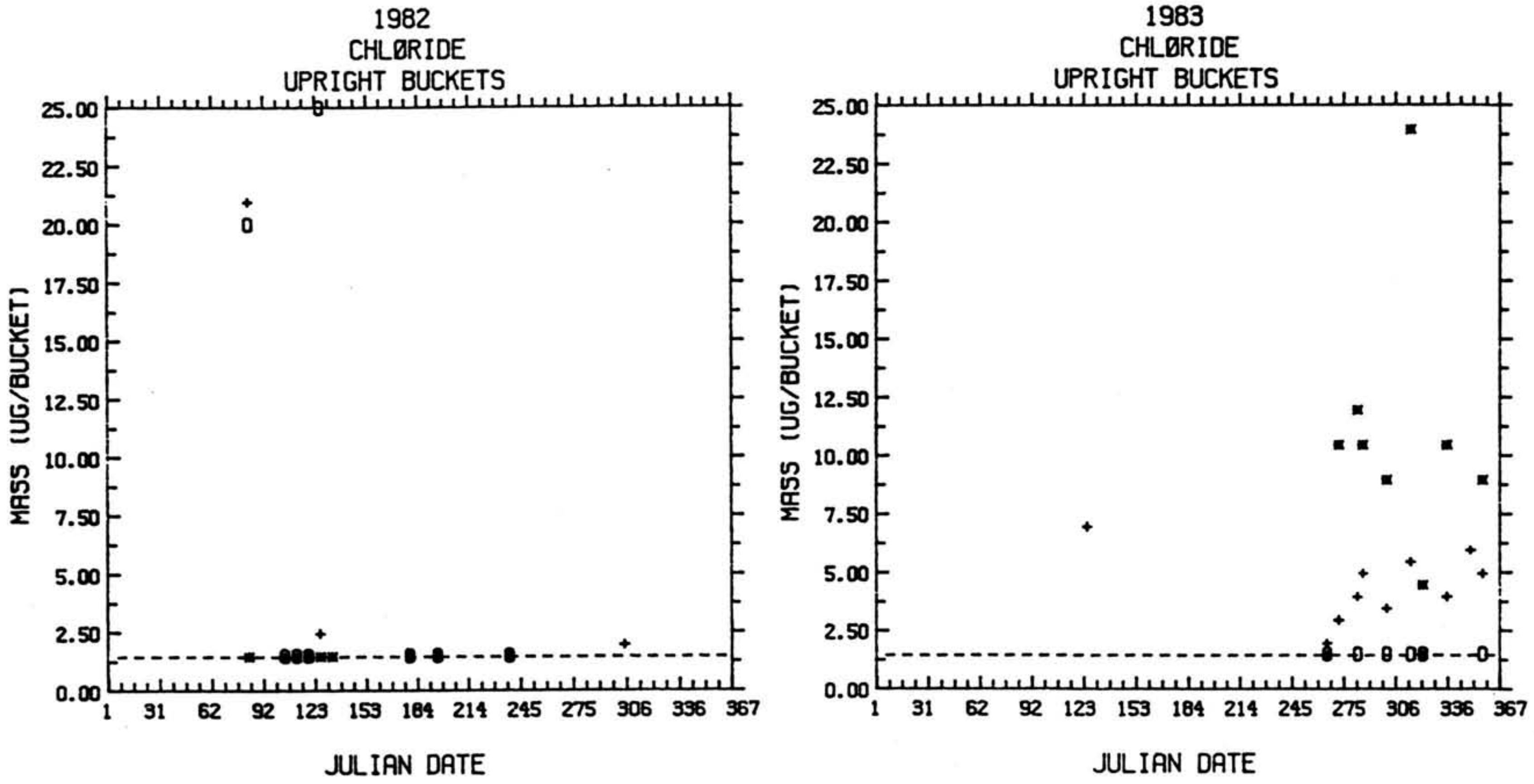


FIGURE 24. Measured chloride mass in upright bucket blanks for 1982 and 1983.

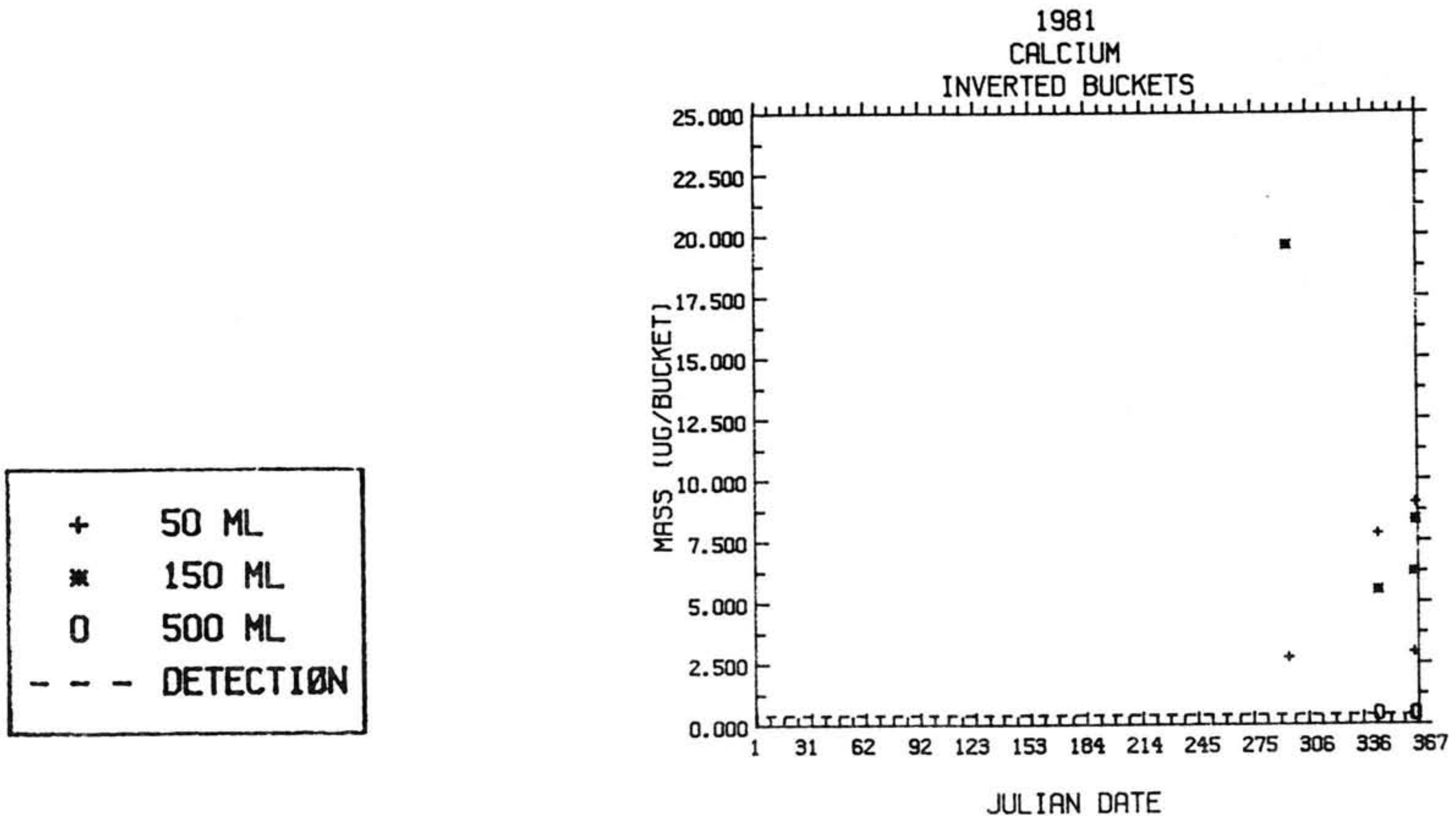


FIGURE 25. Measured calcium mass in inverted bucket blanks for 1981.

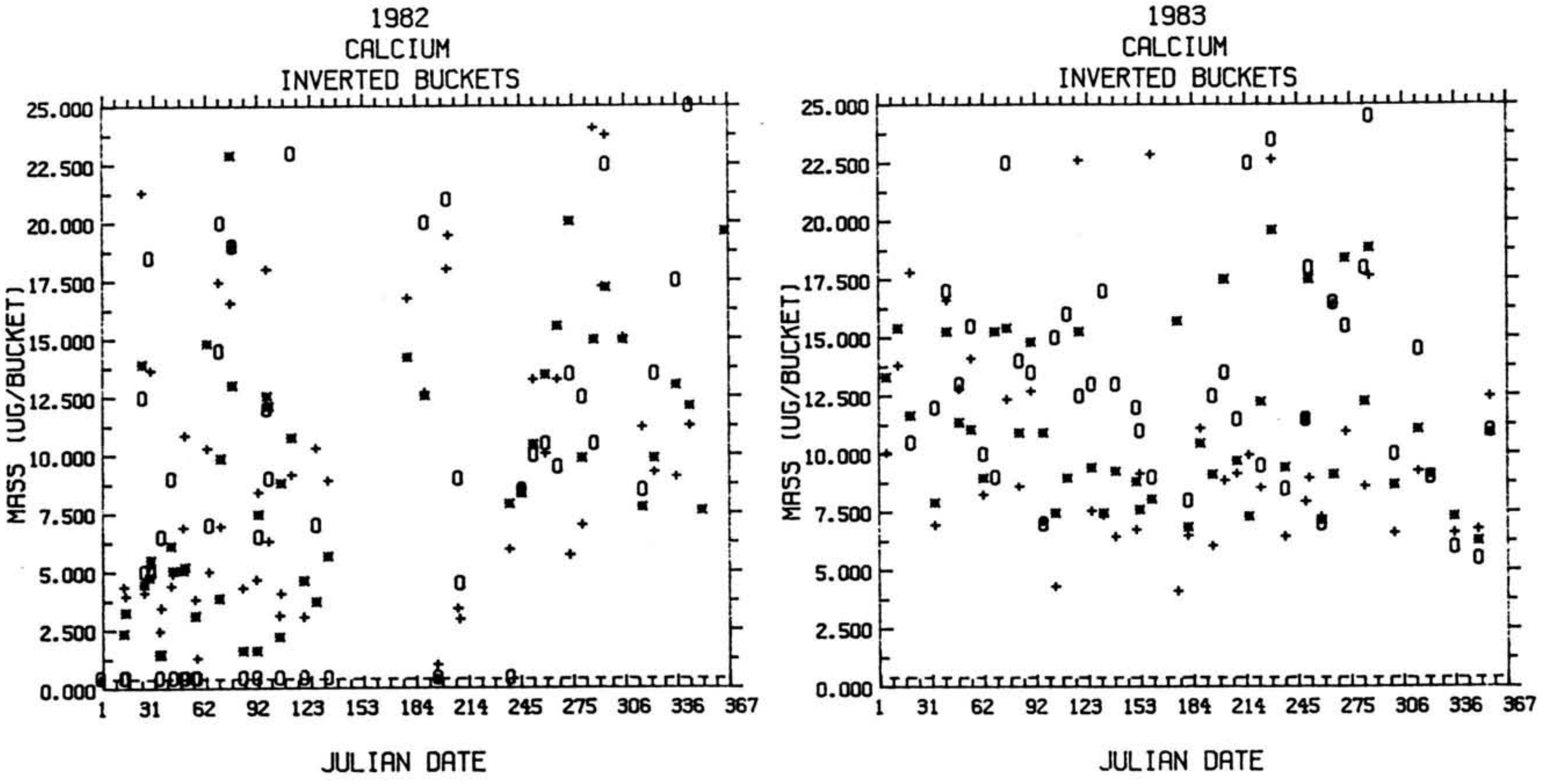


FIGURE 26. Measured calcium mass in inverted bucket blanks for 1982 and 1983.

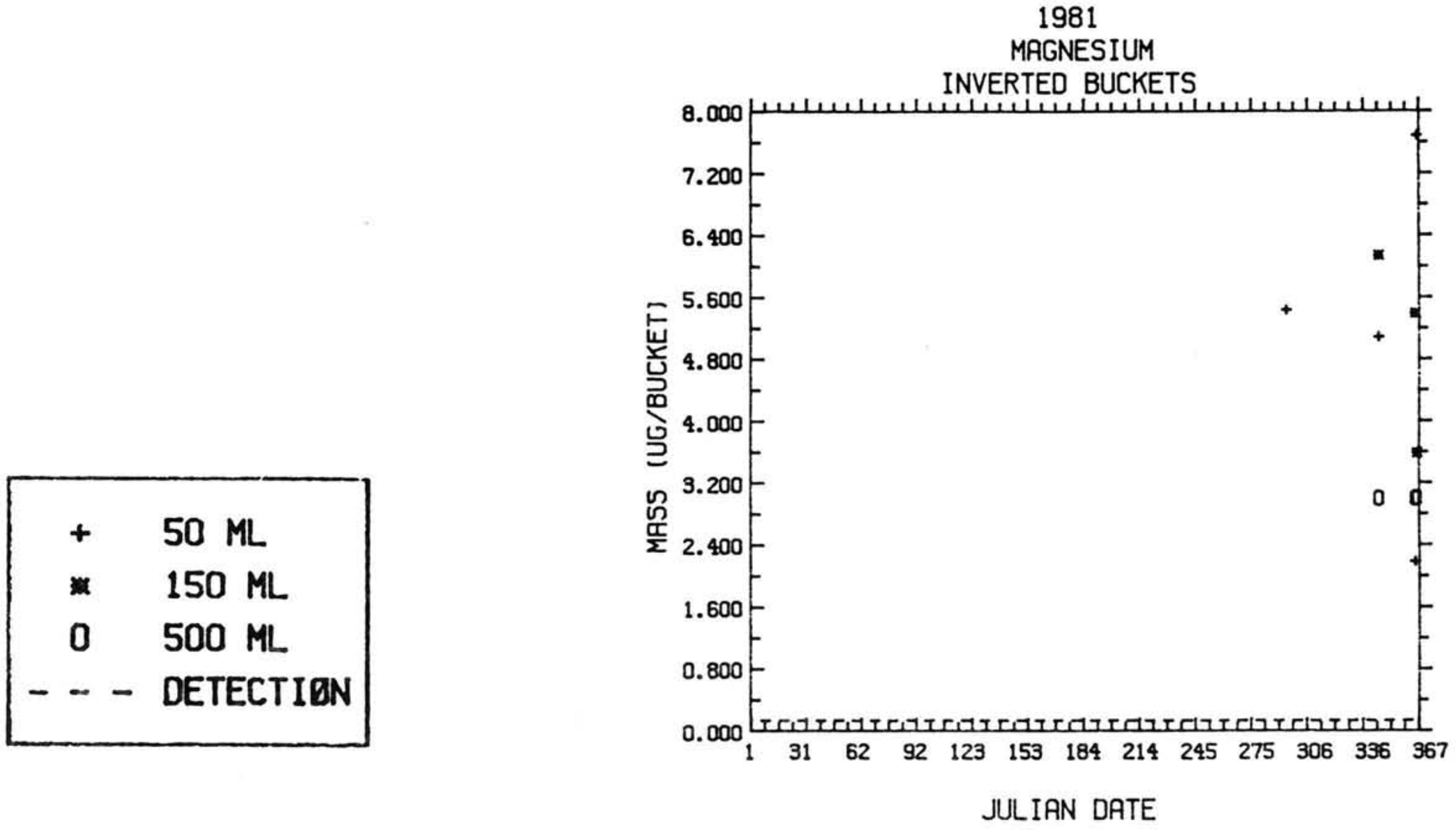


FIGURE 27. Measured magnesium mass in inverted bucket blanks for 1981.

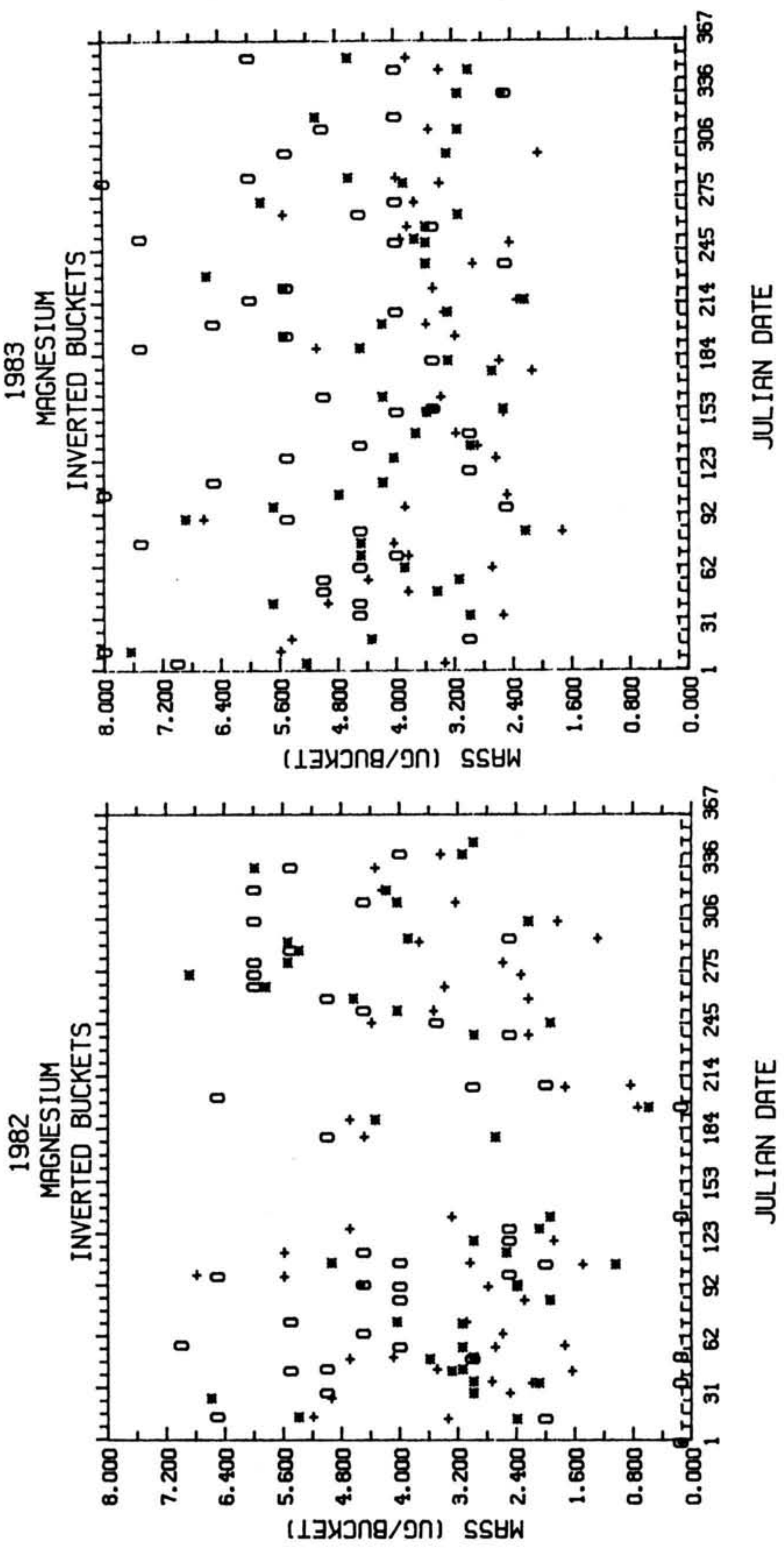


FIGURE 28. Measured magnesium mass in inverted bucket blanks for 1982 and 1983.

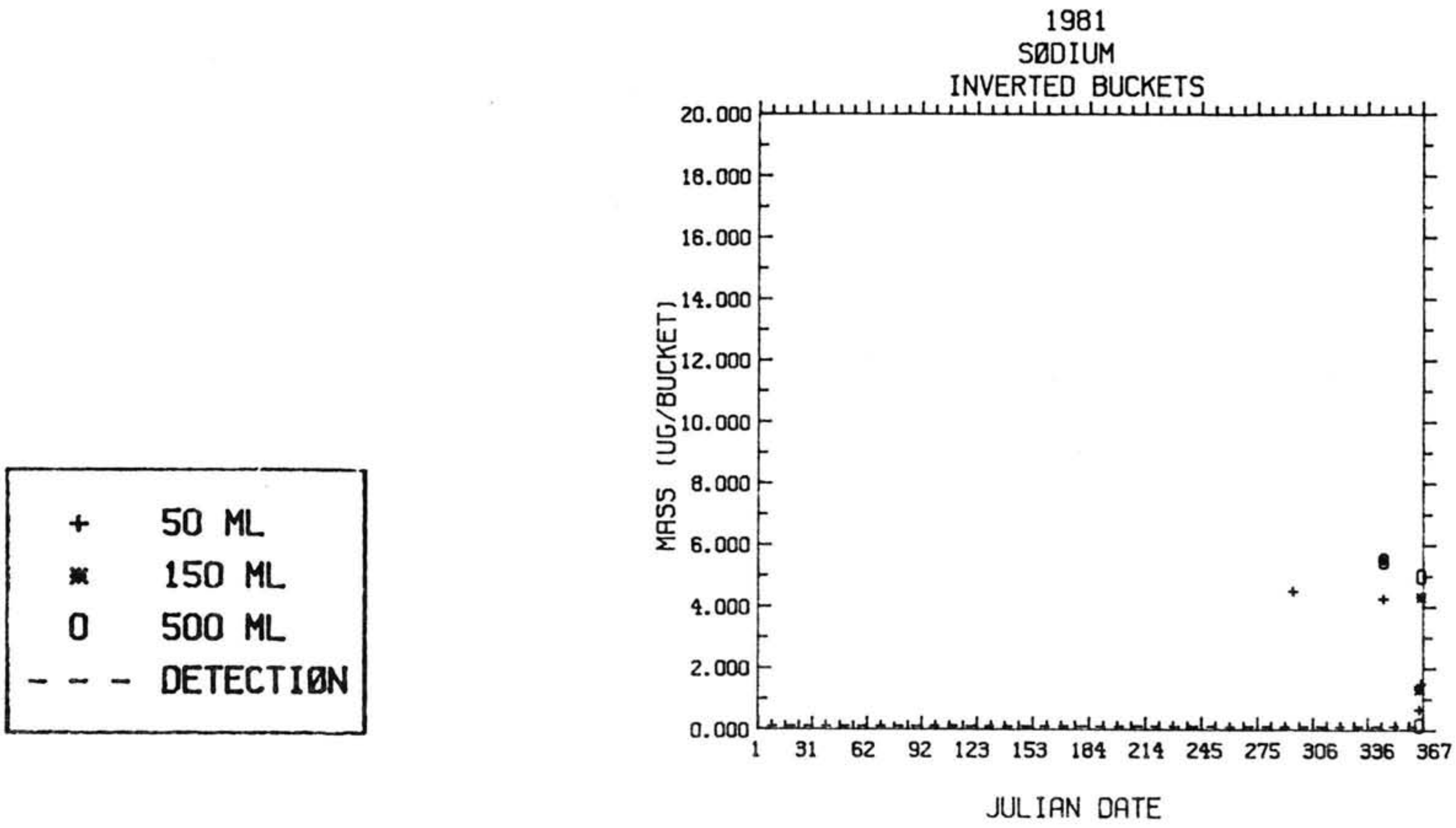


FIGURE 29. Measured sodium mass in inverted bucket blanks for 1981.

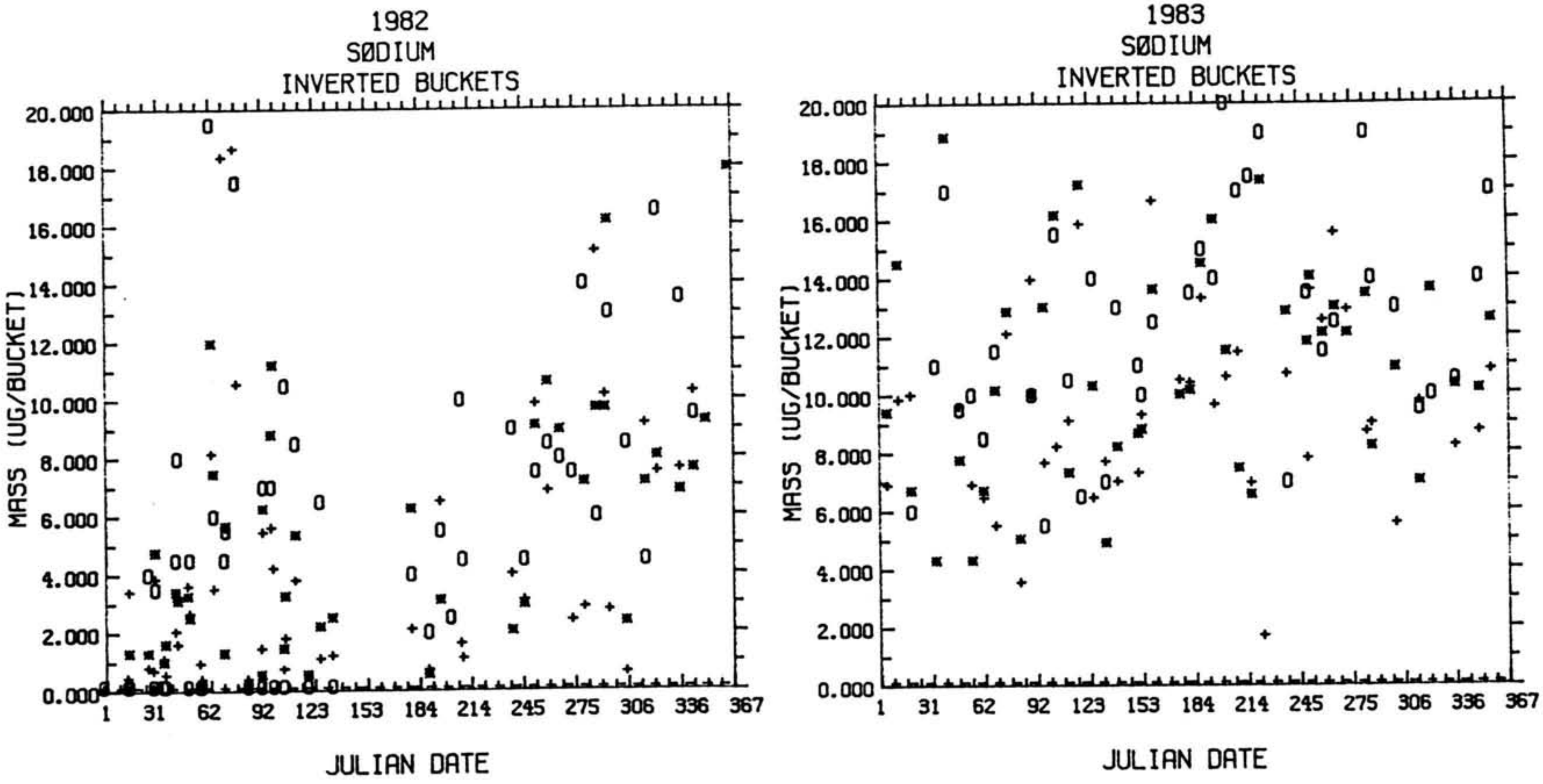


FIGURE 30. Measured sodium mass in inverted bucket blanks for 1982 and 1983.

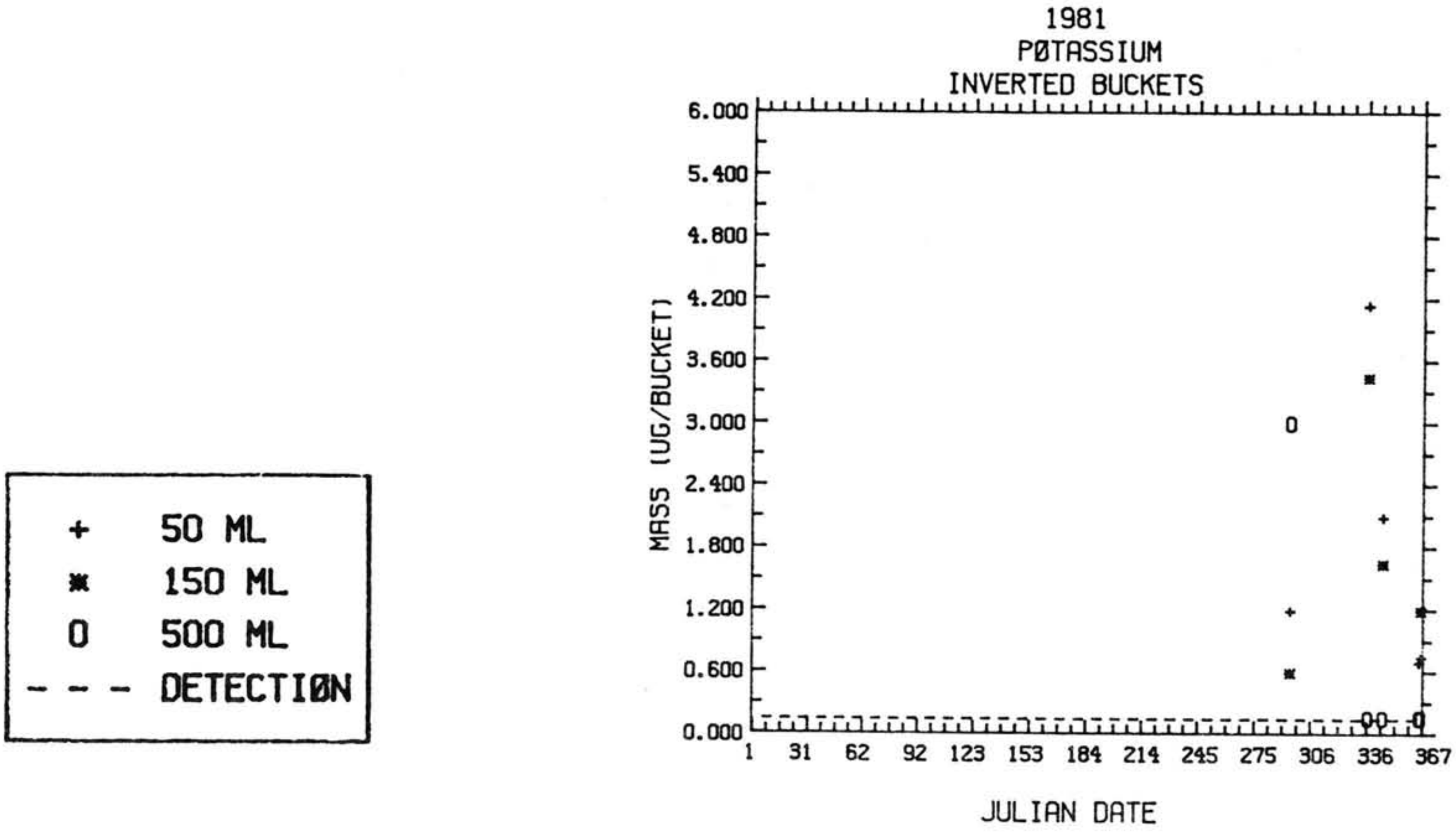


FIGURE 31. Measured potassium mass in inverted bucket blanks for 1981.

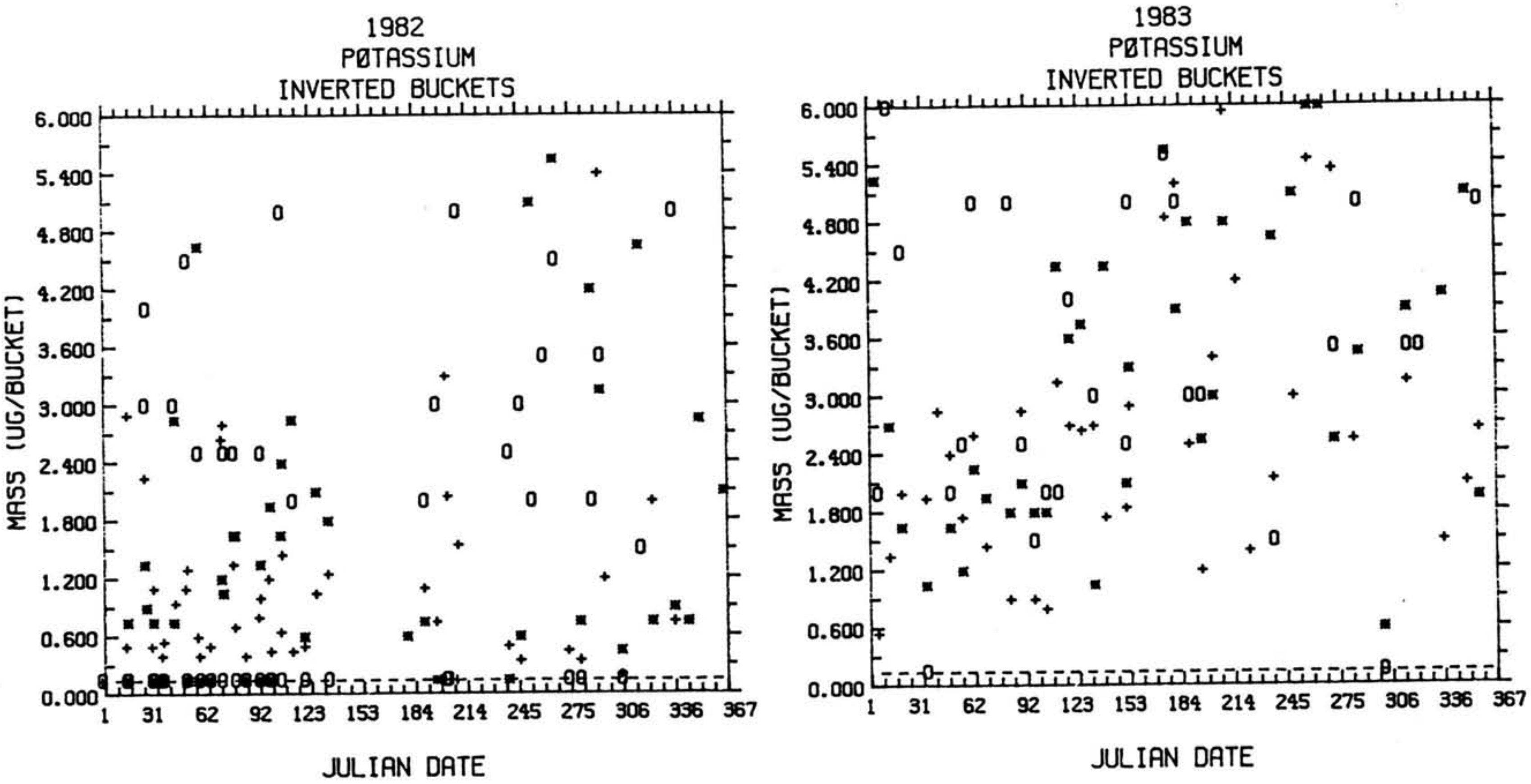


FIGURE 32. Measured potassium mass in inverted bucket blanks for 1982 and 1983.

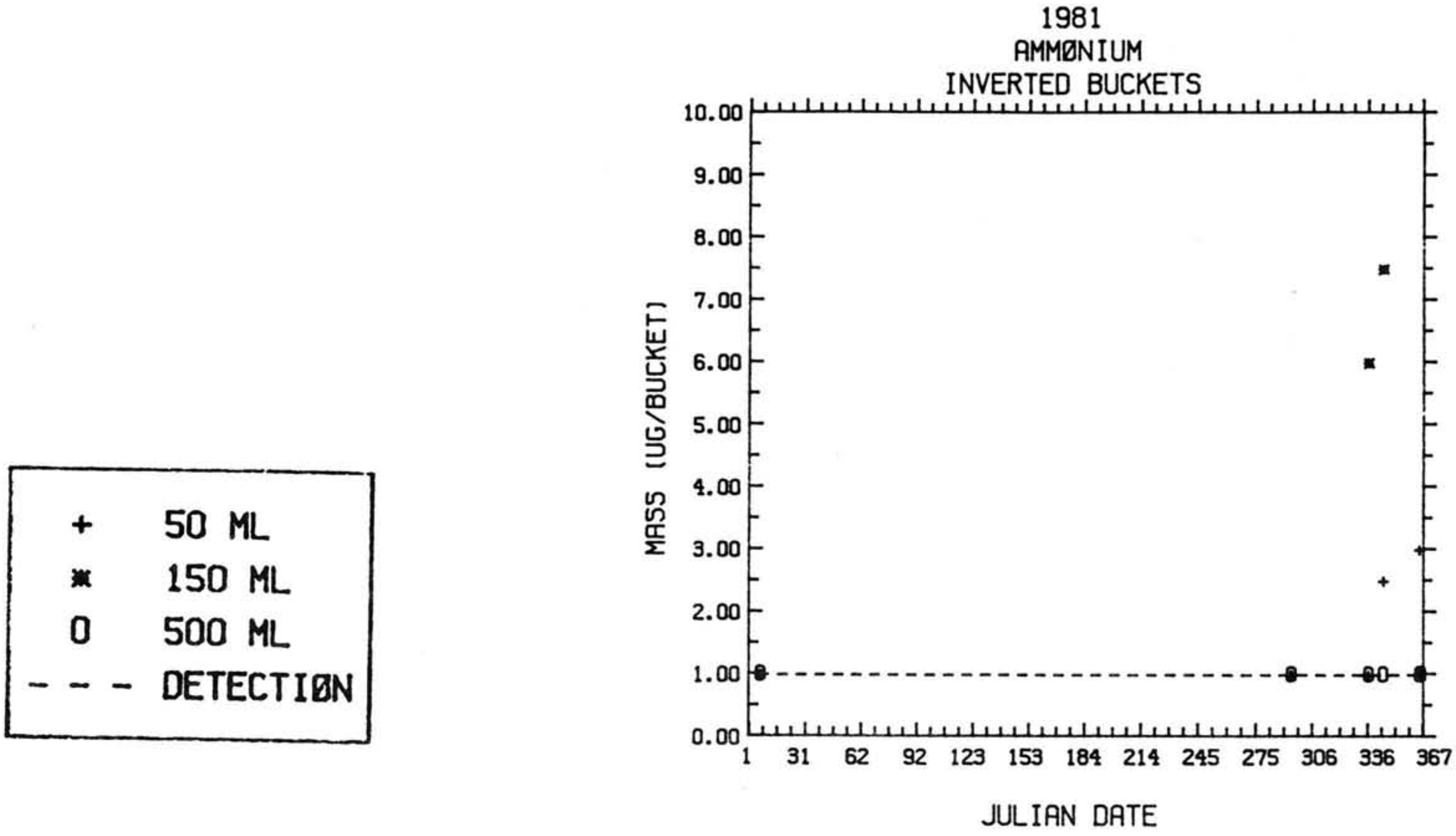


FIGURE 33. Measured ammonium mass in inverted bucket blanks for 1981.

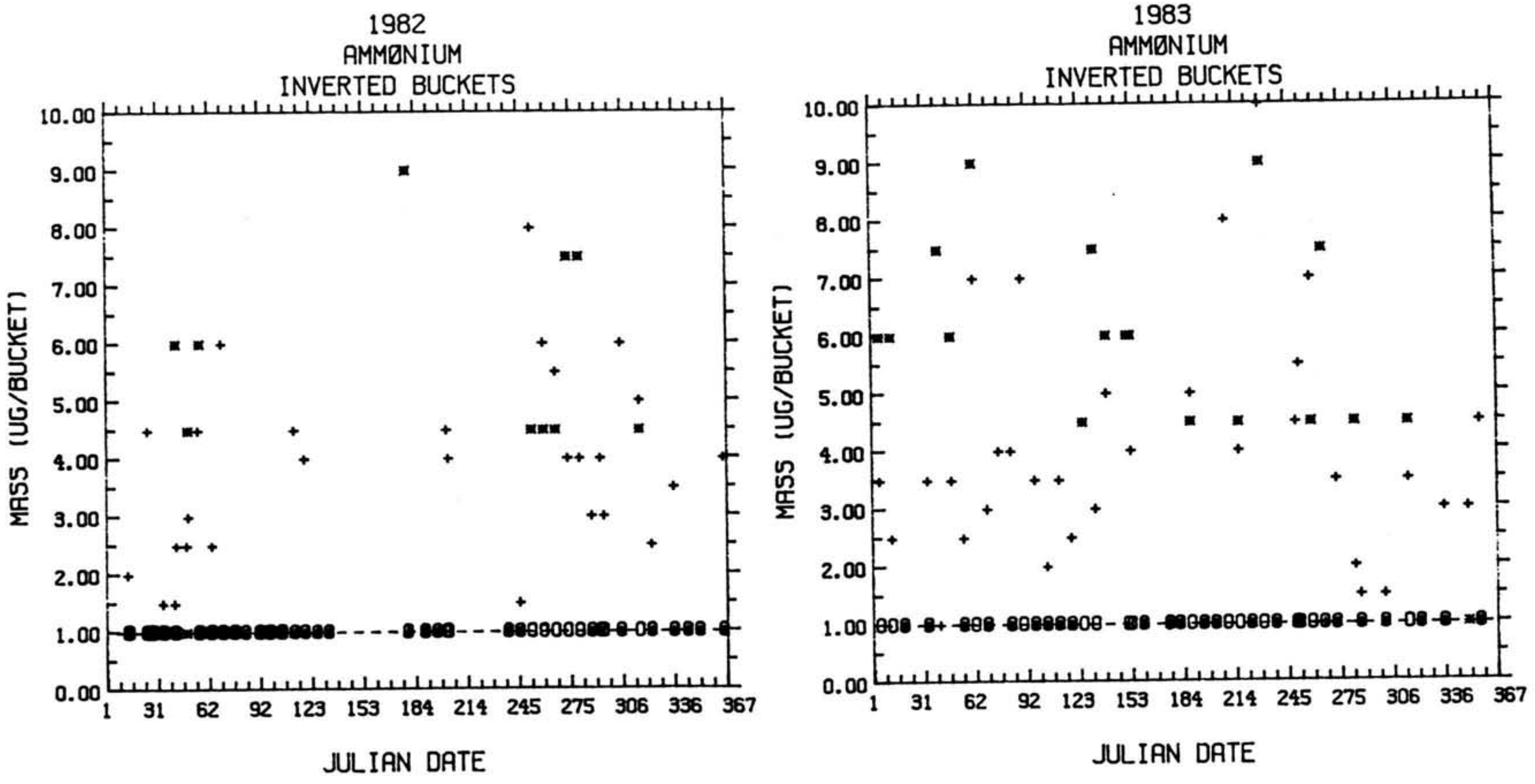


FIGURE 34. Measured ammonium mass in inverted bucket blanks for 1982 and 1983.

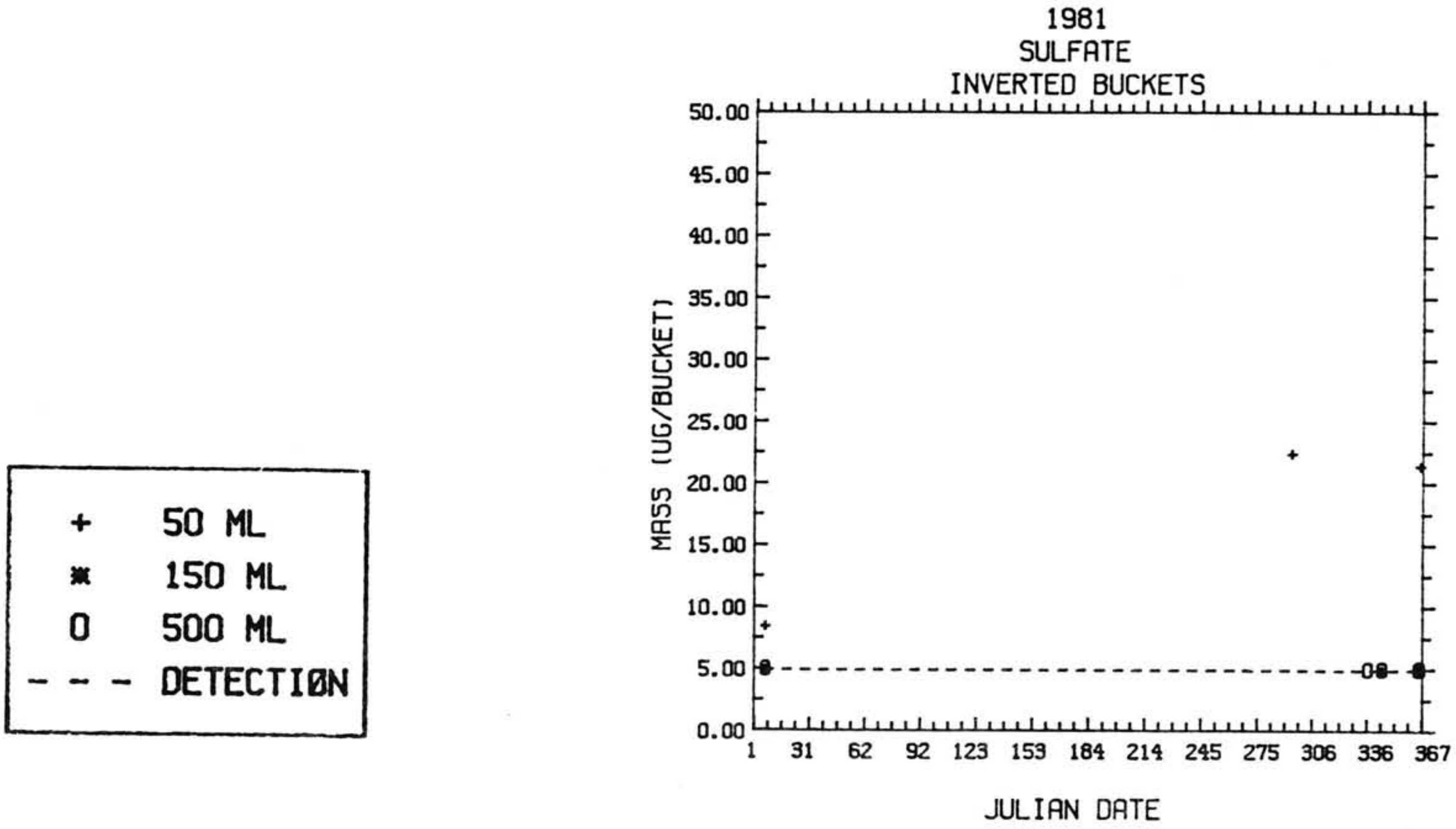


FIGURE 35. Measured sulfate mass in inverted bucket blanks for 1981.

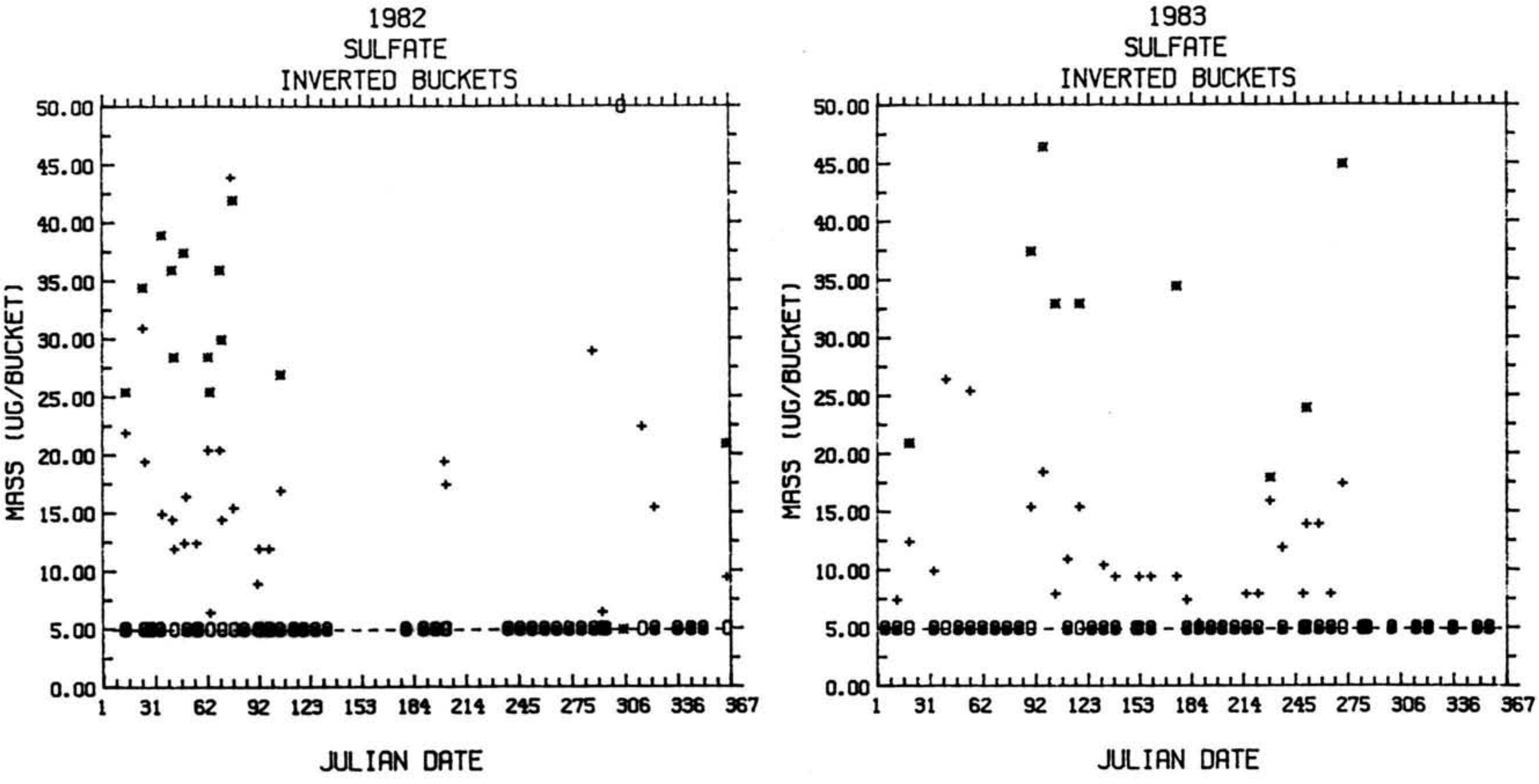


FIGURE 36. Measured sulfate mass in inverted bucket blanks for 1982 and 1983.

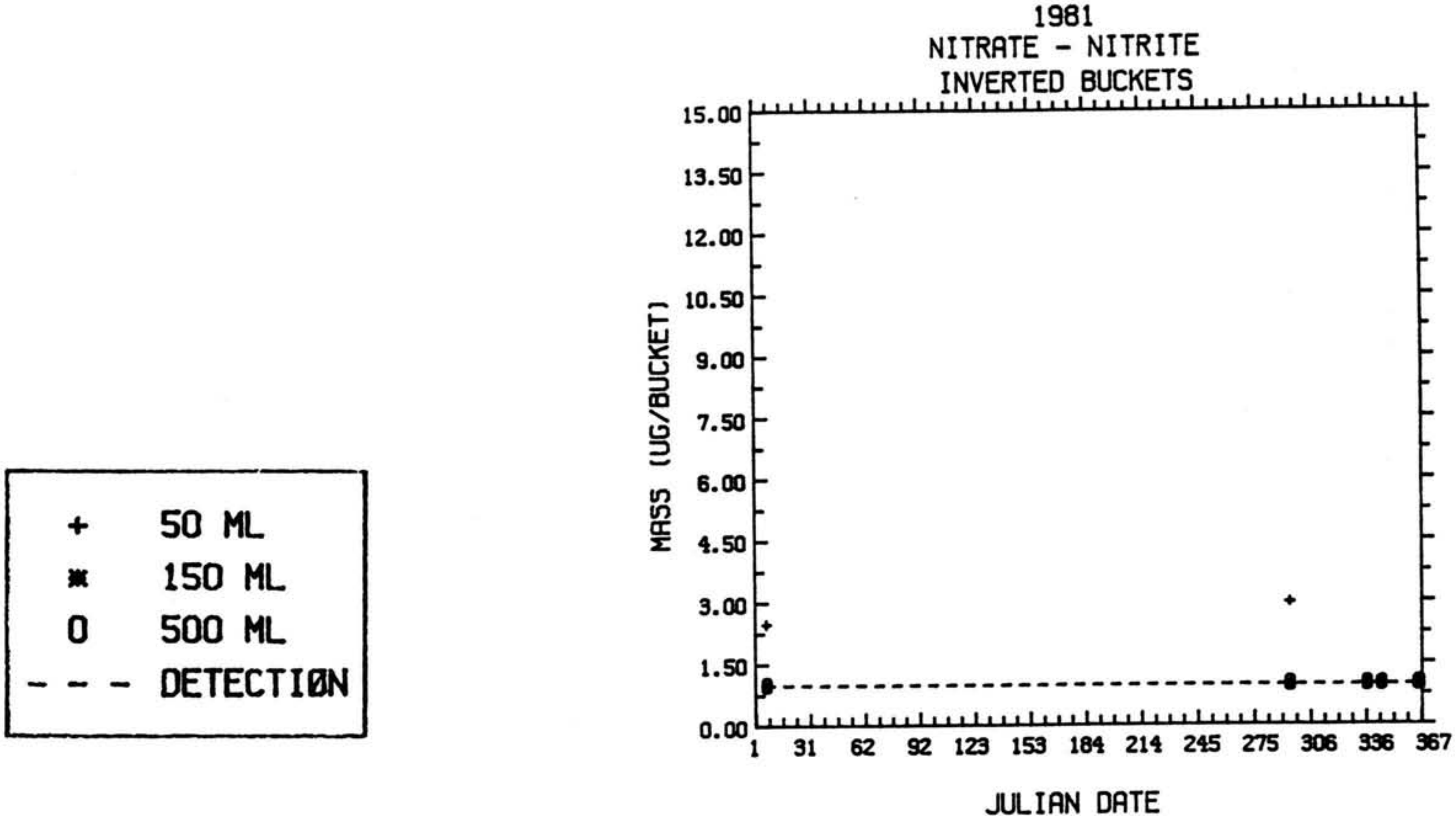


FIGURE 37. Measured nitrate-nitrite mass in inverted bucket blanks for 1981.

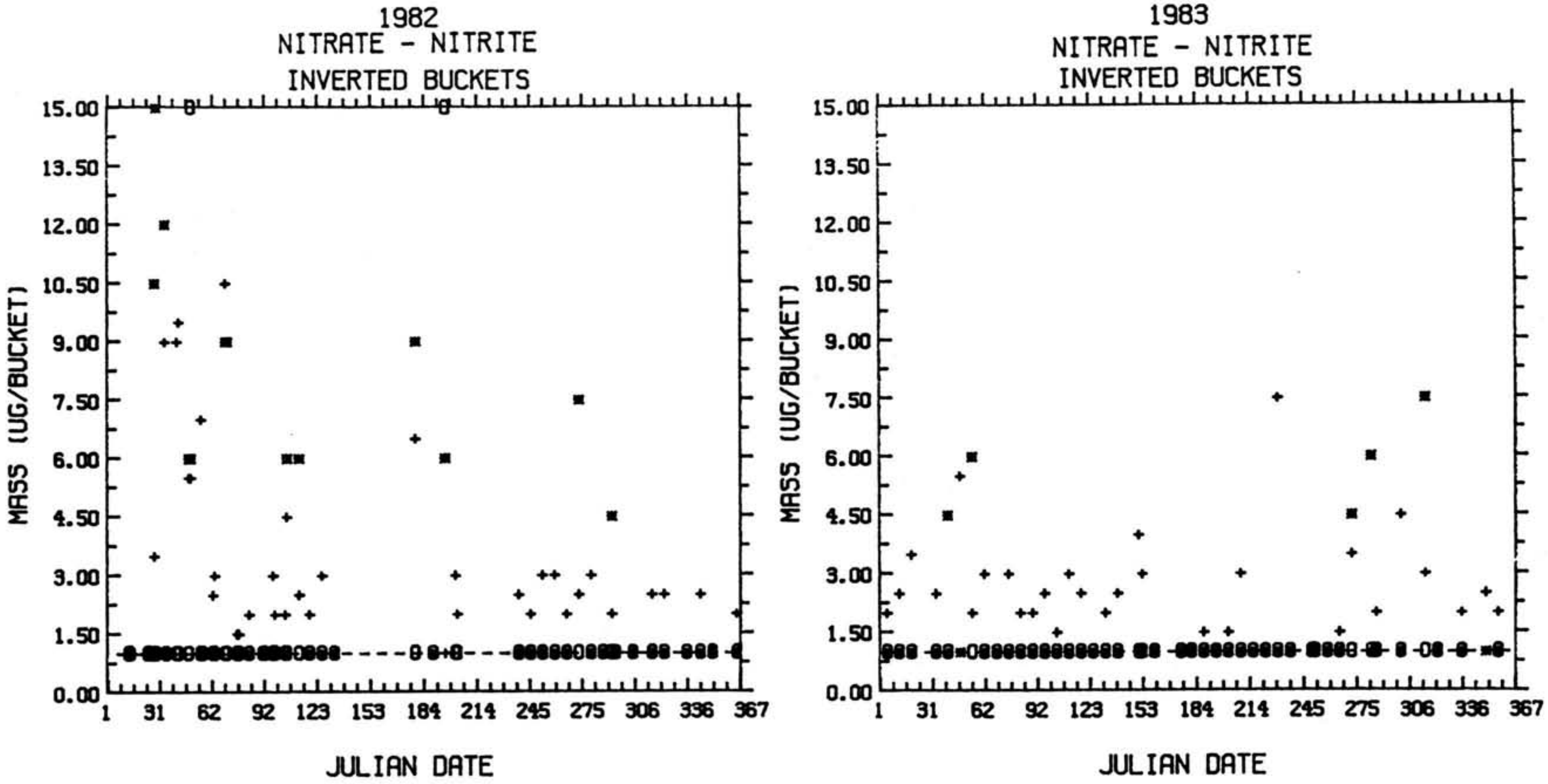


FIGURE 38. Measured nitrate-nitrite mass in inverted bucket blanks for 1982 and 1983.

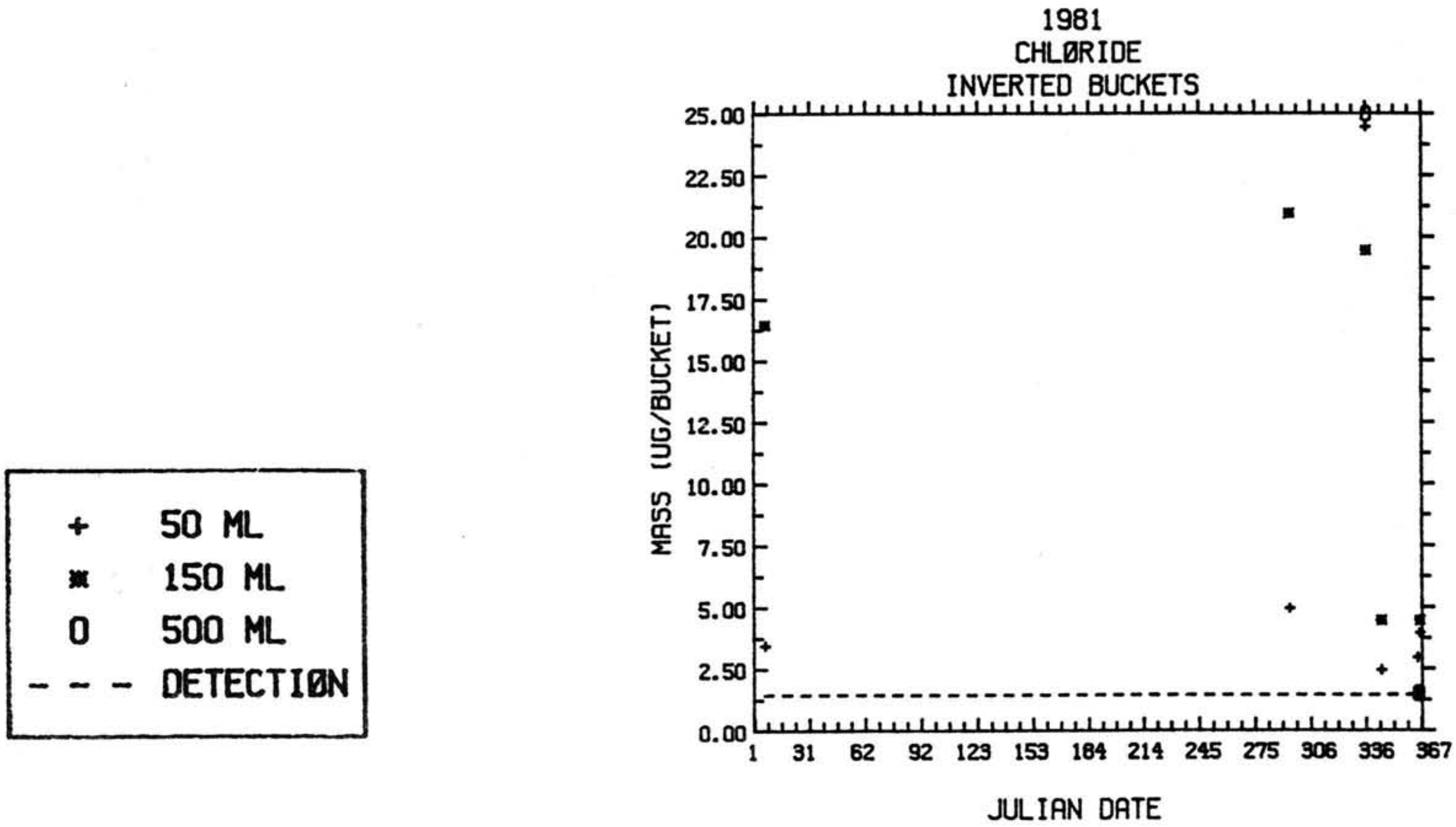


FIGURE 39. Measured chloride mass in inverted bucket blanks for 1981.

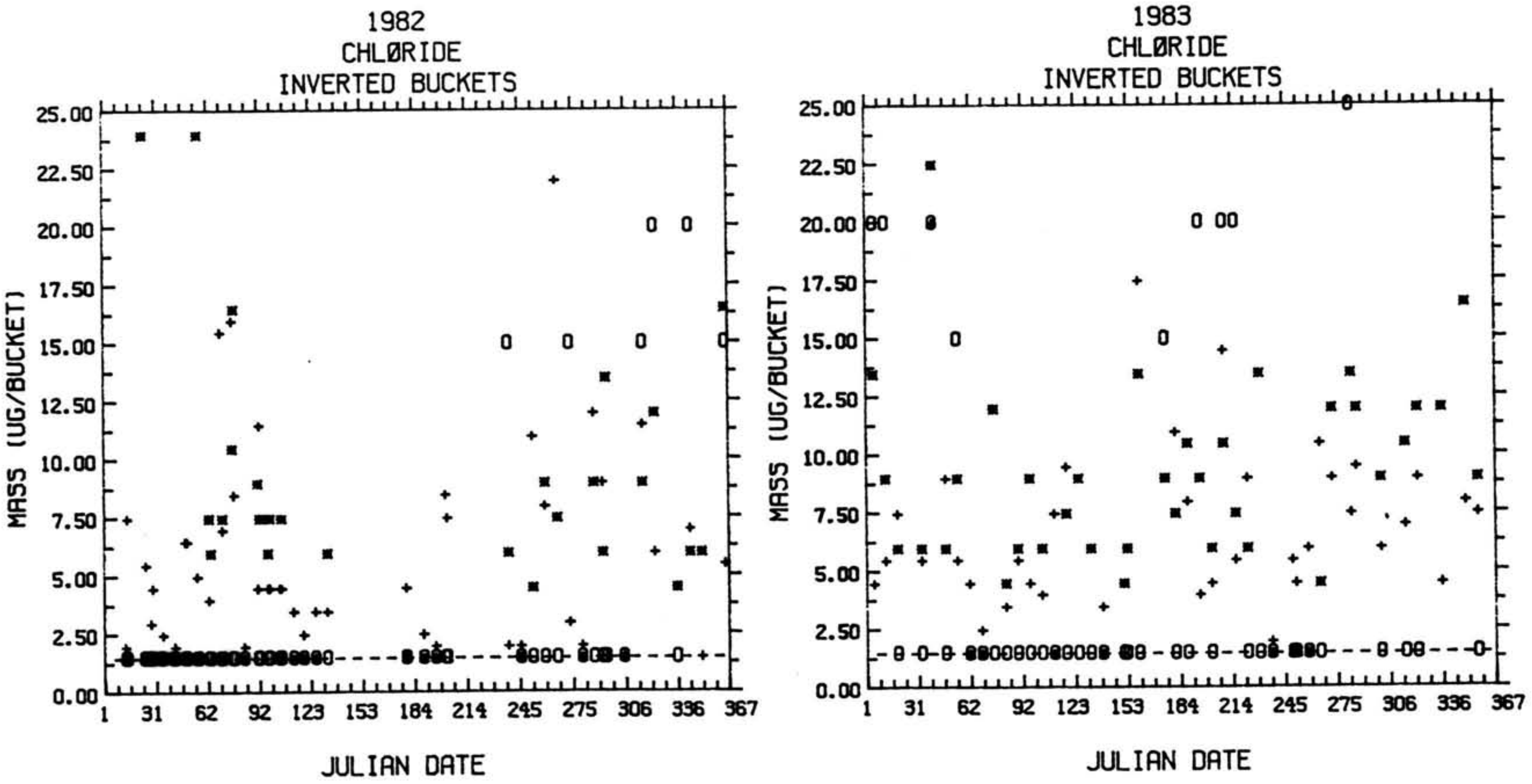


FIGURE 40. Measured chloride mass in inverted bucket blanks for 1982 and 1983.

TABLE 1 Minimum Detectable Mass Values for Bucket Blanks Analyzed from 1978 through 1983.

Analyte/Year	Minimum Mass Value (ug/bucket) 1978-1979	1980	1981	1982	1983
Calcium	1.00	1.00	0.45	0.45	0.45
Magnesium	0.10	0.10	0.15	0.15	0.15
Sodium	0.20	0.20	0.15	0.15	0.15
Potassium	0.20	0.20	0.15	0.15	0.15
Ammonium	1.0	1.0	1.0	1.0	1.0
Sulfate	5.0	5.0	5.0	5.0	5.0
Nitrate-Nitrite	1.0	1.0	1.0	1.0	1.0
Chloride	2.5	2.5	1.0	1.0	1.0
Orthophosphate	0.15	0.15	0.15	0.15	0.15

TABLE 2 Analyte Concentration Summary for Filter Leachate A for 1980.

Analyte	n^a	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	69	0.02	98.6	<0.02	<0.02
Magnesium	69	0.002	95.7	<0.002	<0.002
Sodium	69	0.004	69.6	<0.004	0.012
Potassium	69	0.004	94.2	<0.004	<0.004
Ammonium	65	0.02	100.0	<0.02	<0.02
Sulfate	64	0.10	89.1	<0.10	<0.10
Nitrate-Nitrite	65	0.02	83.1	<0.02	0.07
Chloride	65	0.05	70.8	<0.05	0.10
Ortho-phosphate	65	0.003	100.0	<0.003	<0.003

a. number of analyses

TABLE 3 Analyte Concentration Summary for Filter Leachate A for 1981.

Analyte	n^a	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	35	0.009	82.9	<0.009	0.019
Magnesium	35	0.003	65.7	<0.003	0.006
Sodium	35	0.003	8.6	0.008	0.030
Potassium	35	0.003	74.3	<0.003	0.005
Ammonium	35	0.02	97.1	<0.02	<0.02
Sulfate	35	0.10	95.1	<0.10	<0.10
Nitrate-Nitrite	35	0.02	82.9	<0.02	0.04
Chloride	35	0.02	65.9	<0.02	0.06
Ortho-phosphate	35	0.003	100.0	<0.003	<0.003

a. number of analyses

TABLE 4 Analyte Concentration Summary for Filter Leachate A for 1982.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	41	0.009	97.6	<0.009	<0.009
Magnesium	41	0.003	90.2	<0.003	<0.003
Sodium	41	0.003	17.1	0.008	0.024
Potassium	41	0.003	90.2	<0.003	<0.003
Ammonium	41	0.02	100.0	<0.02	<0.02
Sulfate	41	0.10	95.1	<0.10	<0.10
Nitrate-Nitrite	41	0.02	95.1	<0.02	<0.02
Chloride	41	0.02	65.9	<0.02	0.06
Ortho-phosphate	41	0.003	97.6	<0.003	<0.003

a. number of analyses

TABLE 5 Analyte Concentration Summary for Filter Leachate A for 1983.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	49	0.009	77.6	<0.009	0.017
Magnesium	49	0.003	83.7	<0.003	0.003
Sodium	49	0.003	38.8	0.004	0.016
Potassium	49	0.003	71.4	<0.003	0.008
Ammonium	49	0.02	100.0	<0.02	<0.02
Sulfate	49	0.10	93.9	<0.10	<0.10
Nitrate-Nitrite	49	0.02	100.0	<0.02	<0.02
Chloride	49	0.02	81.6	<0.02	0.06
Ortho-phosphate	49	0.003	98.0	<0.003	<0.003

a. number of analyses

TABLE 6 Analyte Concentration Summary for Filter Leachate B for 1980.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L)	
				50th	95th
Calcium	34	0.02	100.0	<0.02	<0.02
Magnesium	34	0.002	97.1	<0.002	<0.002
Sodium	34	0.004	97.1	<0.004	<0.004
Potassium	34	0.004	100.0	<0.004	<0.004
Ammonium	34	0.02	100.0	<0.02	<0.02
Sulfate	34	0.10	97.1	<0.10	<0.10
Nitrate-Nitrite	34	0.02	100.0	<0.02	<0.02
Chloride	34	0.05	73.5	<0.05	0.07
Ortho-phosphate	34	0.003	100.0	<0.003	<0.003

a. number of analyses

TABLE 7 Analyte Concentration Summary for Filter Leachate B for 1981.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L)	
				50th	95th
Calcium	34	0.009	94.1	<0.009	<0.009
Magnesium	34	0.003	88.2	<0.003	<0.003
Sodium	34	0.003	70.6	<0.003	0.014
Potassium	34	0.003	88.2	<0.003	<0.003
Ammonium	34	0.02	100.0	<0.02	<0.02
Sulfate	34	0.10	94.1	<0.10	<0.10
Nitrate-Nitrite	34	0.02	85.3	<0.02	0.03
Chloride	34	0.02	55.9	<0.02	0.04
Ortho-phosphate	34	0.003	100.0	<0.003	<0.003

a. number of analyses

TABLE 8 Analyte Concentration Summary for Filter Leachate B for 1982.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	41	0.009	97.6	<0.009	<0.009
Magnesium	41	0.003	97.6	<0.003	<0.003
Sodium	41	0.003	85.4	<0.003	0.004
Potassium	41	0.003	95.1	<0.003	<0.003
Ammonium	41	0.02	97.6	<0.02	<0.02
Sulfate	41	0.10	95.1	<0.10	<0.10
Nitrate-Nitrite	41	0.02	97.6	<0.02	<0.02
Chloride	41	0.02	95.1	<0.02	<0.02
Ortho-phosphate	41	0.003	100.0	<0.003	<0.003

a. number of analyses

TABLE 9 Analyte Concentration Summary for Filter Leachate B for 1983.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	49	0.009	79.6	<0.009	0.021
Magnesium	49	0.003	85.7	<0.003	0.004
Sodium	49	0.003	79.6	<0.003	0.007
Potassium	49	0.003	75.5	<0.003	0.006
Ammonium	49	0.02	100.0	<0.02	<0.02
Sulfate	49	0.10	93.9	<0.10	<0.10
Nitrate-Nitrite	49	0.02	100.0	<0.02	<0.02
Chloride	49	0.02	91.8	<0.02	<0.02
Ortho-phosphate	49	0.003	100.0	<0.003	<0.003

a. number of analyses

TABLE 10 Analyte Concentration Summary for Deionized Water Blank for 1980.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	20	0.02	100.0	<0.02	<0.02
Magnesium	20	0.002	95.0	<0.002	<0.002
Sodium	20	0.004	100.0	<0.004	<0.004
Potassium	20	0.004	100.0	<0.004	<0.004
Ammonium	24	0.02	100.0	<0.02	<0.02
Sulfate	24	0.10	95.8	<0.10	<0.10
Nitrate-Nitrite	24	0.02	91.2	<0.02	<0.02
Chloride	24	0.05	70.8	<0.05	0.12
Ortho-phosphate	24	0.003	100.0	<0.003	<0.003

a. number of analyses

TABLE 11 Analyte Concentration Summary for Deionized Water Blank for 1981.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	33	0.009	93.9	<0.009	<0.009
Magnesium	33	0.003	97.0	<0.003	<0.003
Sodium	33	0.003	90.9	<0.003	<0.003
Potassium	33	0.003	97.0	<0.003	<0.003
Ammonium	34	0.02	97.1	<0.02	<0.02
Sulfate	34	0.10	88.2	<0.10	<0.10
Nitrate-Nitrite	34	0.02	100.0	<0.02	<0.02
Chloride	34	0.02	61.8	<0.02	0.04
Ortho-phosphate	34	0.003	97.1	<0.003	<0.003

a. number of analyses

TABLE 12 Analyte Concentration Summary for Deionized Water Blank for 1982.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	40	0.009	100.0	<0.009	<0.009
Magnesium	40	0.003	97.5	<0.003	<0.003
Sodium	40	0.003	90.0	<0.003	<0.003
Potassium	40	0.003	97.5	<0.003	<0.003
Ammonium	39	0.02	100.0	<0.02	<0.02
Sulfate	39	0.10	94.9	<0.10	<0.10
Nitrate-Nitrite	39	0.02	97.4	<0.02	<0.02
Chloride	39	0.02	100.0	<0.02	<0.02
Ortho-phosphate	39	0.003	100.0	<0.003	<0.003

a. number of analyses

TABLE 13 Analyte Concentration Summary for Deionized Water Blank for 1983.

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	100.0	<0.003	<0.003
Sodium	48	0.003	93.8	<0.003	<0.003
Potassium	48	0.003	97.9	<0.003	<0.003
Ammonium	48	0.02	97.9	<0.02	<0.02
Sulfate	48	0.10	100.0	<0.10	<0.10
Nitrate-Nitrite	48	0.02	100.0	<0.02	<0.02
Chloride	48	0.02	95.8	<0.02	<0.02
Ortho-phosphate	48	0.003	95.8	<0.003	<0.003

a. number of analyses

APPENDIX C

Tables of Annual Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation 1978 - 1983

APPENDIX C

Tables of Annual Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation 1978 - 1981

TABLE 1 Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation - 1978.

Parameter	Percentile Concentration Values (mg/L) Min.	5th	10th	25th	50th	75th	90th	95th	99th	Max.
Ca	<0.02	0.02	0.04	0.07	0.14	0.32	0.67	1.13	2.15	3.3
Mg	<0.002	0.008	0.010	0.019	0.037	0.081	0.209	0.254	0.631	1.3
K	<0.004	0.005	0.010	0.020	0.033	0.060	0.130	0.196	0.334	3.8
Na	0.009	0.028	0.051	0.090	0.222	0.565	1.52	2.33	7.24	23.1
NH_4	<0.02	<0.02	<0.02	0.04	0.16	0.38	0.74	1.27	2.28	3.0
NO_3	<0.02	0.22	0.32	0.60	1.30	2.25	3.36	4.82	10.41	15.3
Cl	<0.05	0.07	0.10	0.13	0.23	0.51	1.55	2.78	6.75	16.0
SO_4	<0.10	0.57	0.78	1.30	2.30	3.96	6.61	10.32	15.71	22.8
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.006	0.013	0.048	0.3
pH (units)	3.50	3.75	3.97	4.19	4.43	4.93	5.48	6.12	6.58	7.0
Specific Conductance (uS/cm)	3.4	6.4	7.6	11.7	20.5	31.2	54.5	88.9	141.0	175.5

Source: National Atmospheric Deposition Program (NADP)
1978 - wet side samples (w)
Number of samples (N) = 239

TABLE 2 Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation - 1979.

Parameter	Percentile Concentration Values (mg/L) Min.	5th	10th	25th	50th	75th	90th	95th	99th	Max.
Ca	<0.02	0.03	0.05	0.09	0.19	0.42	0.93	1.45	2.35	6.8
Mg	<0.002	0.010	0.013	0.022	0.041	0.086	0.168	0.223	0.505	1.5
K	<0.004	0.005	0.008	0.015	0.030	0.060	0.124	0.223	0.569	35.2
Na	0.009	0.037	0.050	0.100	0.248	0.620	1.40	2.52	7.10	23.5
NH_4	<0.02	<0.02	<0.02	0.07	0.22	0.50	0.90	1.35	2.55	134.0
NO_3	<0.02	0.25	0.38	0.76	1.40	2.49	3.83	5.30	8.90	16.3
Cl	<0.05	<0.05	0.07	0.10	0.20	0.40	0.85	1.40	2.69	53.0
SO_4	<0.10	0.60	0.85	1.45	2.60	4.30	6.67	8.70	13.57	40.4
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.007	0.419	21.8
pH (units)	3.57	3.93	4.04	4.26	4.55	5.07	6.01	6.44	7.01	8.2
Specific Conductance (uS/cm)	2.1	6.1	8.1	12.2	21.1	34.3	51.0	65.7	101.9	644.0

Source: National Atmospheric Deposition Program (NADP)
1979 - wet side samples (w)
Number of samples (N) = 1254

TABLE 3 **Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation - 1980.**

	Percentile Concentration Values (mg/L)									
Parameter	**Min.**	**5th**	**10th**	**25th**	**50th**	**75th**	**90th**	**95th**	**99th**	**Max.**
Ca	<0.02	0.03	0.05	0.09	0.19	0.43	0.93	1.57	5.22	16.4
Mg	<0.002	0.008	0.012	0.022	0.042	0.093	0.200	0.338	0.966	4.9
K	<0.004	0.004	0.008	0.015	0.030	0.065	0.159	0.306	1.14	29.9
Na	<0.004	0.016	0.025	0.054	0.130	0.351	0.981	1.99	5.55	29.3
NH_4	<0.02	<0.02	<0.02	0.07	0.22	0.50	0.94	1.42	3.24	47.0
NO_3	<0.02	0.11	0.23	0.72	1.49	2.63	4.12	5.16	9.16	54.1
Cl	<0.05	0.10	0.12	0.18	0.27	0.48	1.02	1.96	6.75	23.1
SO_4	<0.10	0.36	0.57	1.13	2.20	3.74	5.92	7.75	15.56	56.2
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.008	0.903	15.9
pH (units)	3.16	3.89	4.02	4.25	4.56	5.36	6.07	6.49	7.16	7.9
Specific Conductance (uS/cm)	1.9	5.4	7.5	12.4	22.2	35.7	53.5	68.5	115.7	427.1

Source: National Atmospheric Deposition Program (NADP)
1980 - wet side samples (w)
Number of samples (N) = 3030

TABLE 4 **Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation - 1981.**

	Percentile Concentration Values (mg/L)									
Parameter	**Min.**	**5th**	**10th**	**25th**	**50th**	**75th**	**90th**	**95th**	**99th**	**Max.**
Ca	<0.02	0.04	0.05	0.10	0.22	0.48	1.08	1.82	4.40	16.7
Mg	0.009	0.013	0.019	0.033	0.062	0.137	0.325	0.557	1.120	8.5
K	<0.003	0.006	0.009	0.016	0.031	0.066	0.142	0.255	0.863	17.3
Na	<0.003	0.022	0.032	0.058	0.122	0.313	0.779	1.39	4.43	65.0
NH_4	<0.02	<0.02	<0.02	0.08	0.23	0.44	0.81	1.19	2.40	78.2
NO_3	<0.02	0.10	0.21	0.60	1.25	2.15	3.31	4.53	8.10	27.3
Cl	<0.02	0.04	0.05	0.10	0.21	0.47	1.12	1.94	6.88	121.9
SO_4	<0.10	0.39	0.54	1.08	2.19	3.82	5.78	7.57	14.65	31.8
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.013	0.248	16.8
pH (units)	3.34	3.96	4.06	4.29	4.67	5.46	6.11	6.44	6.92	8.5
Specific Conductance (uS/cm)	1.5	5.3	6.9	11.9	22.0	35.1	54.1	69.0	113.5	538.2

Source: National Atmospheric Deposition Program (NADP)
1981 - wet side samples (w)
Number of samples (N) = 3370

TABLE 5 **Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation - 1982.**

	Percentile Concentration Values (mg/L)									
Parameter	**Min.**	**5th**	**10th**	**25th**	**50th**	**75th**	**90th**	**95th**	**99th**	**Max.**
Ca	<0.01	0.02	0.04	0.07	0.16	0.35	0.71	1.08	2.51	27.3
Mg	<0.003	0.009	0.013	0.023	0.044	0.091	0.176	0.287	0.775	6.5
K	<0.003	0.006	0.008	0.015	0.027	0.052	0.105	0.170	0.475	3.3
Na	<0.003	0.018	0.023	0.043	0.092	0.216	0.546	1.08	3.29	46.7
NH_4	<0.02	<0.02	<0.02	0.08	0.19	0.39	0.68	0.95	1.93	6.6
NO_3	<0.02	0.12	0.24	0.58	1.11	1.94	3.23	4.32	7.90	43.2
Cl	<0.02	0.04	0.05	0.09	0.17	0.38	0.92	1.72	5.59	78.1
SO_4	<0.10	0.30	0.45	0.85	1.65	2.99	4.89	6.26	11.21	34.3
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.025	1.5
pH (units)	3.19	3.99	4.10	4.35	4.74	5.33	5.81	6.12	6.58	7.6
Specific Conductance (uS/cm)	1.8	4.1	5.7	9.3	17.2	29.8	47.8	62.8	101.0	402.5

Source: National Atmospheric Deposition Program (NADP)
1982 - wet side samples (w)
Number of samples (N) = 3590

TABLE 6 **Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation - 1983.**

	Percentile Concentration Values (mg/L)									
Parameter	**Min.**	**5th**	**10th**	**25th**	**50th**	**75th**	**90th**	**95th**	**99th**	**Max.**
Ca	<0.01	0.03	0.04	0.07	0.16	0.36	0.73	1.15	2.54	18.9
Mg	<0.003	0.010	0.013	0.021	0.040	0.082	0.165	0.259	0.599	4.4
K	<0.003	0.007	0.009	0.016	0.031	0.060	0.123	0.192	0.534	3.9
Na	0.007	0.022	0.029	0.048	0.102	0.238	0.592	1.09	3.25	36.0
NH_4	<0.02	<0.02	<0.02	0.06	0.17	0.40	0.71	1.04	1.93	7.7
NO_3	<0.02	0.12	0.23	0.51	1.02	1.86	3.09	4.21	7.26	28.4
Cl	<0.02	0.05	0.07	0.10	0.17	0.36	0.93	1.73	5.92	64.9
SO_4	<0.10	0.32	0.46	0.78	1.38	2.59	4.41	5.92	10.93	21.4
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.006	0.021	3.1
pH (units)	3.15	3.99	4.15	4.42	4.81	5.37	5.86	6.12	6.56	7.4
Specific Conductance (uS/cm)	1.5	3.6	4.8	8.3	14.8	26.0	43.0	58.6	110.4	431.4

Source: National Atmospheric Deposition Program (NADP)/
National Trends Network (NTN)
1983 - wet side samples (w)
Number of samples (N) = 4308

APPENDIX D

Tables of Analytical Bias and Precision Determined from Analysis of Quality Control Check Samples 1978-1983

TABLE 1 Selected pH Values and the Corresponding Hydrogen Ion Content Expressed as Microequivalents per Liter.

pH (units)	Hydrogen Ion (uequivalents/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

TABLE 2 pH Measurements - Bias and Precision Determined from Analysis of Quality Control Check Samples.

Year	Theoretical Concentration, pH units (uequivalents/L)	Measured Concentration, pH units (uequivalents/L)	n[a]	Bias[b] units	Bias[b] %	Precision[b] s units	Precision[b] RSD %
1979	3.06 (871.0)	3.16 (691.8)	14	0.10	-20.7	0.05	10.9
	4.08 (83.2)	4.26 (55.0)	12	0.18	-33.9	0.22	39.8
1980	4.06 (87.1)	4.01 (98.2)	14	-0.05	12.7	0.07	16.1
	4.25 (56.2)	4.27 (54.3)	11	0.02	- 3.4	0.03	7.0
1981	4.30 (50.1)	4.30 (50.1)	158	0.00	0.0	0.04	8.8
	5.63 (2.3)	5.60 (2.5)	57	-0.03	8.7	0.12	24.0
1982	4.30 (50.1)	4.32 (48.3)	467	0.02	-3.6	0.02	4.3
	5.63 (2.3)	5.45 (3.5)	452	-0.18	52.2	0.05	11.1
1983	4.30 (50.1)	4.31 (49.0)	444	0.01	-2.2	0.03	6.7
	5.63 (2.3)	5.43 (3.7)	444	-0.20	60.9	0.08	18.9

a. number of replicates

b. calculations of bias and precision were made using hydrogen ion concentration

TABLE 3 Specific Conductance Measurements - Bias and Precision Determined from Analysis of Quality Control Check Samples.

Year	Theoretical Concentration, uS/cm	Measured Concentration, uS/cm	n[a]	Bias		Precision	
				uS/cm	%	s uS/cm	RSD %
1979	35.5	35.9	9	0.4	1.1	1.7	4.7
	401	403.4	14	2.4	0.6	4.6	1.1
1980	25.0	23.7	4	-1.3	-5.2	1.3	5.5
	36.4	41.8	10	5.4	14.8	4.5	10.8
1981	21.8	22.7	105	0.9	4.1	2.9	12.8
1982	21.8	22.1	448	0.3	1.4	0.9	4.1
1983	21.8	21.5	443	-0.3	-1.4	0.7	3.3

a. number of replicates

TABLE 4 Calcium Measurements - Bias and Precision Determined from Analysis of Quality Control Check Samples.

Year	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias		Precision		Statistically Significant Bias?[b]
				mg/L	%	s mg/L	RSD %	
1979	0.35	0.37	9	0.02	5.7	0.01	2.7	YES
	0.53	0.55	6	0.02	3.8	0.01	1.8	YES
	1.45	1.49	24	0.04	2.8	0.02	1.3	YES
1980	0.53	0.53	131	0.00	0.0	0.02	3.8	NO
	0.81	0.82	131	0.01	1.2	0.01	1.2	NO
	1.45	1.51	13	0.06	4.1	0.02	1.3	YES
1981	0.067	0.058	59	-0.009	-13.4	0.004	6.9	YES
	0.317	0.314	59	-0.003	-1.0	0.005	1.6	NO
	0.530	0.530	138	0.000	0.0	0.008	1.5	NO
	0.812	0.811	138	-0.001	-0.1	0.010	1.2	NO
1982	0.067	0.062	302	-0.005	-7.5	0.004	6.5	YES
	0.317	0.315	302	-0.002	-0.6	0.005	1.6	NO
1983	0.053	0.052	35	-0.001	-1.9	0.003	5.8	NO
	0.067	0.066	434	-0.001	-1.5	0.003	4.6	NO
	0.317	0.323	429	0.006	1.9	0.004	1.2	YES
	0.402	0.412	35	0.010	2.5	0.003	0.7	YES

a. number of replicates
b. 95% confidence level

TABLE 5 Magnesium Measurements - Bias and Precision Determined from Analysis of Quality Control Check Samples.

Year	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias mg/L	Bias %	Precision s mg/L	Precision RSD %	Statistically Significant Bias?[b]
1979	0.114	0.116	9	0.002	1.8	0.002	1.7	NO
	0.171	0.173	6	0.002	1.2	0.002	1.2	NO
	0.300	0.299	24	-0.001	-0.3	0.003	1.0	NO
1980	0.168	0.174	129	0.006	3.6	0.002	1.2	YES
	0.180	0.186	141	0.006	3.3	0.002	1.1	YES
	0.300	0.299	14	-0.001	-0.3	0.002	0.7	NO
1981	0.024	0.021	59	-0.003	-12.5	0.001	4.8	YES
	0.070	0.069	59	-0.001	-1.4	0.001	1.4	NO
	0.168	0.171	138	0.003	1.8	0.002	1.2	YES
	0.180	0.184	138	0.004	2.2	0.003	1.6	YES
1982	0.024	0.022	302	-0.002	-8.3	0.001	4.5	YES
	0.070	0.070	302	0.000	0.0	0.001	1.4	NO
1983	0.018	0.018	35	0.000	0.0	0.001	5.6	NO
	0.024	0.023	444	-0.001	-4.2	0.001	4.3	YES
	0.070	0.070	435	0.000	0.0	0.001	1.4	NO
	0.083	0.083	35	0.000	0.0	0.001	1.2	NO

a. number of replicates
b. 95% confidence level

TABLE 6 Sodium Measurements - Bias and Precision Determined from Analysis of Quality Control Check Samples.

Year	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias mg/L	Bias %	Precision s mg/L	Precision RSD %	Statistically Significant Bias?[b]
1979	0.157	0.158	5	0.001	0.6	0.001	0.6	NO
	0.314	0.313	6	-0.001	-0.3	0.008	2.6	NO
	0.472	0.471	5	-0.001	-0.2	0.006	1.3	NO
	0.500	0.499	25	-0.001	-0.2	0.004	0.8	NO
1980	0.500	0.497	13	-0.003	-0.6	0.004	0.8	NO
	0.820	0.818	149	-0.002	-0.2	0.004	0.5	NO
	0.932	0.926	149	-0.006	-0.6	0.006	0.6	NO
1981	0.071	0.068	60	-0.003	-4.2	0.002	2.9	YES
	0.395	0.381	60	-0.014	-3.5	0.003	0.8	YES
	0.820	0.818	121	-0.002	-0.2	0.005	0.6	NO
	0.932	0.919	121	-0.013	-1.4	0.007	0.8	NO
1982	0.071	0.068	310	-0.003	-4.2	0.002	2.9	YES
	0.395	0.392	310	-0.003	-0.8	0.008	2.0	NO
1983	0.071	0.070	425	-0.001	-1.4	0.002	2.9	NO
	0.083	0.084	17	0.001	1.2	0.002	2.4	NO
	0.395	0.399	417	0.004	1.0	0.005	1.3	NO
	0.459	0.472	17	0.013	2.8	0.003	0.6	YES

a. number of replicates
b. 95% confidence level

TABLE 7 Potassium Measurements - Bias and Precision Determined from Analysis of Quality Control Check Samples.

Year	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias		Precision		Statistically Significant Bias?[b]
				mg/L	%	s mg/L	RSD %	
1979	0.033	0.031	5	-0.002	-6.1	0.002	6.5	YES
	0.067	0.066	6	-0.001	-1.5	0.002	3.0	NO
	0.100	0.101	3	0.001	1.0	0.001	1.0	NO
	0.270	0.271	29	0.001	0.4	0.004	1.5	NO
1980	0.196	0.190	149	-0.006	-3.1	0.003	1.6	YES
	0.210	0.210	146	0.000	0.0	0.002	1.0	NO
	0.270	0.268	13	-0.002	-0.7	0.005	1.9	NO
1981	0.014	0.014	60	0.000	0.0	0.002	14.3	NO
	0.056	0.058	60	0.002	3.6	0.004	6.9	YES
	0.196	0.188	121	-0.008	-4.1	0.003	1.6	YES
	0.210	0.210	121	0.000	0.0	0.002	1.0	NO
1982	0.014	0.014	156	0.000	0.0	0.001	7.1	NO
	0.017	0.017	154	0.000	0.0	0.001	5.9	NO
	0.056	0.057	156	0.001	1.8	0.002	3.5	NO
	0.074	0.071	154	-0.003	-4.1	0.002	2.8	YES
1983	0.017	0.017	425	0.000	0.0	0.001	5.9	NO
	0.021	0.020	17	-0.001	-4.8	0.001	5.0	YES
	0.074	0.071	427	-0.003	-4.1	0.001	1.4	YES
	0.100	0.092	17	-0.008	-8.0	0.002	2.2	YES

a. number of replicates
b. 95% confidence level

TABLE 8 Ammonium Measurements - Bias and Precision Determined from Analysis of Quality Control Check Samples.

Year	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias		Precision		Statistically Significant Bias?[b]
				mg/L	%	s mg/L	RSD %	
1979	0.30	0.30	24	0.00	0.0	0.02	6.7	NO
	2.05	2.05	23	0.00	0.0	0.03	1.5	NO
1980	0.24	0.24	23	0.00	0.0	0.01	4.2	NO
	0.30	0.29	76	-0.01	-3.3	0.02	6.9	YES
	1.67	1.67	26	0.00	0.0	0.05	3.0	NO
	2.05	2.03	84	-0.02	-1.0	0.05	2.5	YES
1981	0.24	0.23	178	-0.01	-4.2	0.02	8.7	YES
	0.84	0.83	90	-0.01	-1.2	0.03	3.6	YES
	1.67	1.66	90	-0.01	-0.6	0.04	2.4	NO
1982	0.19	0.21	116	0.02	10.5	0.02	9.5	YES
	0.24	0.24	133	0.00	0.0	0.02	8.3	NO
	0.84	0.80	149	-0.04	-4.8	0.03	3.8	YES
	0.98	0.96	121	-0.02	-2.0	0.11	11.5	NO
1983	0.19	0.21	231	0.02	10.5	0.02	9.5	YES
	0.36	0.37	116	0.01	2.8	0.02	5.4	YES
	0.98	1.01	200	0.03	3.1	0.04	4.0	YES
	1.22	1.23	116	0.01	0.8	0.03	2.4	NO

a. number of replicates
b. 95% confidence level

TABLE 9 Sulfate Measurements - Bias and Precision Determined from Analysis of Quality Control Check Samples.

Year	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias		Precision		Statistically Significant Bias?[b]
				mg/L	%	s mg/L	RSD %	
1979	1.20	1.20	31	0.00	0.0	0.02	1.6	NO
	5.12	5.14	24	0.02	0.4	0.04	0.8	NO
	10.24	10.22	18	-0.02	-0.2	0.06	0.6	NO
1980	0.72	0.72	116	0.00	0.0	0.05	6.9	NO
	9.36	9.33	182	-0.03	-0.3	0.25	2.7	NO
1981	0.36	0.36	74	0.00	0.0	0.02	5.6	NO
	1.17	1.19	61	0.02	1.7	0.06	5.0	NO
	1.87	1.90	92	0.03	1.6	0.08	4.2	YES
	7.35	7.33	172	-0.02	-0.3	0.21	2.9	NO
	9.36	9.42	140	0.06	0.6	0.21	2.2	NO
1982	1.17	1.15	216	-0.02	-1.7	0.11	9.6	NO
	7.35	7.31	262	-0.04	-0.5	0.27	3.7	NO
1983	0.92	0.86	285	-0.06	-6.5	0.12	14.0	YES
	1.17	1.10	76	-0.07	-6.0	0.11	10.0	YES
	6.86	7.05	261	0.19	2.8	0.39	5.5	NO
	7.35	7.29	69	-0.06	-0.8	0.27	3.7	NO

a. number of replicates
b. 95% confidence level

TABLE 10 Nitrate-Nitrite Measurements - Bias and Precision Determined from Analysis of Quality Control Check Samples.

Year	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias		Precision		Statistically Significant Bias?[b]
				mg/L	%	s mg/L	RSD %	
1979	0.49	0.50	38	0.01	2.0	0.01	2.0	YES
	1.68	1.67	40	-0.01	-0.6	0.03	1.8	NO
1980	0.49	0.48	111	-0.01	-2.0	0.03	6.3	YES
	1.37	1.41	24	0.04	2.9	0.03	2.2	YES
	1.68	1.72	111	0.04	2.4	0.07	4.2	YES
	3.52	3.60	17	0.08	2.3	0.08	2.2	NO
	7.04	7.12	8	0.08	1.1	0.20	2.8	NO
1981	1.37	1.38	201	0.01	0.7	0.07	5.1	NO
	3.52	3.51	205	-0.01	-0.3	0.12	3.4	NO
1982	0.80	0.77	121	-0.03	-3.8	0.01	1.3	YES
	1.37	1.31	142	-0.06	-4.4	0.05	3.8	YES
	3.54	3.38	226	-0.16	-4.5	0.14	4.1	YES
1983	0.62	0.63	117	0.01	1.6	0.02	3.2	NO
	0.80	0.80	119	0.00	0.0	0.03	3.8	NO
	3.14	3.15	118	0.01	0.3	0.05	1.6	NO
	3.54	3.57	191	0.03	0.9	0.06	1.7	YES

a. number of replicates
b. 95% confidence level

TABLE 11 Chloride Measurements - Bias and Precision Determined from Analysis of Quality Control Check Samples.

Year	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias mg/L	Bias %	Precision s mg/L	Precision RSD %	Statistically Significant Bias?[b]
1979	1.41	1.47	3	0.06	4.3	0.01	0.7	YES
	2.81	2.93	16	0.12	4.3	0.03	1.0	YES
	4.32	4.53	16	0.21	4.9	0.03	0.7	YES
1980	0.36	0.37	80	0.01	2.8	0.03	8.1	YES
	0.92	0.88	19	-0.04	-4.4	0.02	2.3	YES
	1.84	1.82	101	-0.02	-1.1	0.06	3.3	YES
	4.40	4.42	17	0.02	0.5	0.07	1.6	NO
	8.79	8.91	12	0.12	1.4	0.08	0.9	YES
1981	0.71	0.71	78	0.00	0.0	0.04	5.6	NO
	0.92	0.91	137	-0.01	-1.1	0.04	4.4	YES
	1.84	1.74	45	-0.10	-5.4	0.04	2.3	YES
	2.08	2.09	80	0.01	0.5	0.07	3.3	NO
1982	0.71	0.71	262	0.00	0.0	0.03	4.2	NO
	2.08	2.00	243	-0.08	-3.9	0.07	3.5	YES
1983	0.71	0.70	100	-0.01	-1.4	0.03	4.3	YES
	0.86	0.86	220	0.00	0.0	0.04	4.7	NO
	1.80	1.83	217	0.03	1.7	0.07	3.8	YES
	2.08	2.03	91	-0.05	-2.4	0.09	4.4	YES

a. number of replicates
b. 95% confidence level

TABLE 12 Orthophosphate Measurements - Bias and Precision Determined from Analysis of Quality Control Check Samples.

Year	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias mg/L	Bias %	Precision s mg/L	Precision RSD %	Statistically Significant Bias?[b]
1979	0.058	0.058	16	0.000	0.0	0.001	1.7	NO
	0.080	0.079	17	-0.001	-1.3	0.002	2.5	NO
1980	0.016	0.016	54	0.000	0.0	0.001	6.3	NO
	0.095	0.095	53	0.000	0.0	0.004	4.0	NO
	0.236	0.234	16	-0.002	-0.9	0.003	1.3	YES
	0.583	0.568	9	-0.015	-2.6	0.021	3.7	YES
1981	0.095	0.089	184	-0.006	-6.3	0.006	6.7	YES
	0.236	0.235	196	-0.001	-0.4	0.012	5.1	NO
1982	0.095	0.091	139	-0.004	-4.2	0.004	4.4	YES
	0.123	0.116	79	-0.007	-5.7	0.009	7.8	YES
	0.234	0.223	233	-0.011	-4.7	0.017	7.6	YES
1983	0.123	0.111	149	-0.012	-9.8	0.006	5.4	YES
	0.153	0.149	170	-0.004	-2.6	0.006	4.0	NO
	0.215	0.205	169	-0.010	-4.7	0.008	3.9	YES
	0.237	0.209	145	-0.028	-11.8	0.010	4.8	YES

a. number of replicates
b. 95% confidence level

APPENDIX E

Replicate Sample Analyses
Plots and Tables
1978-1983

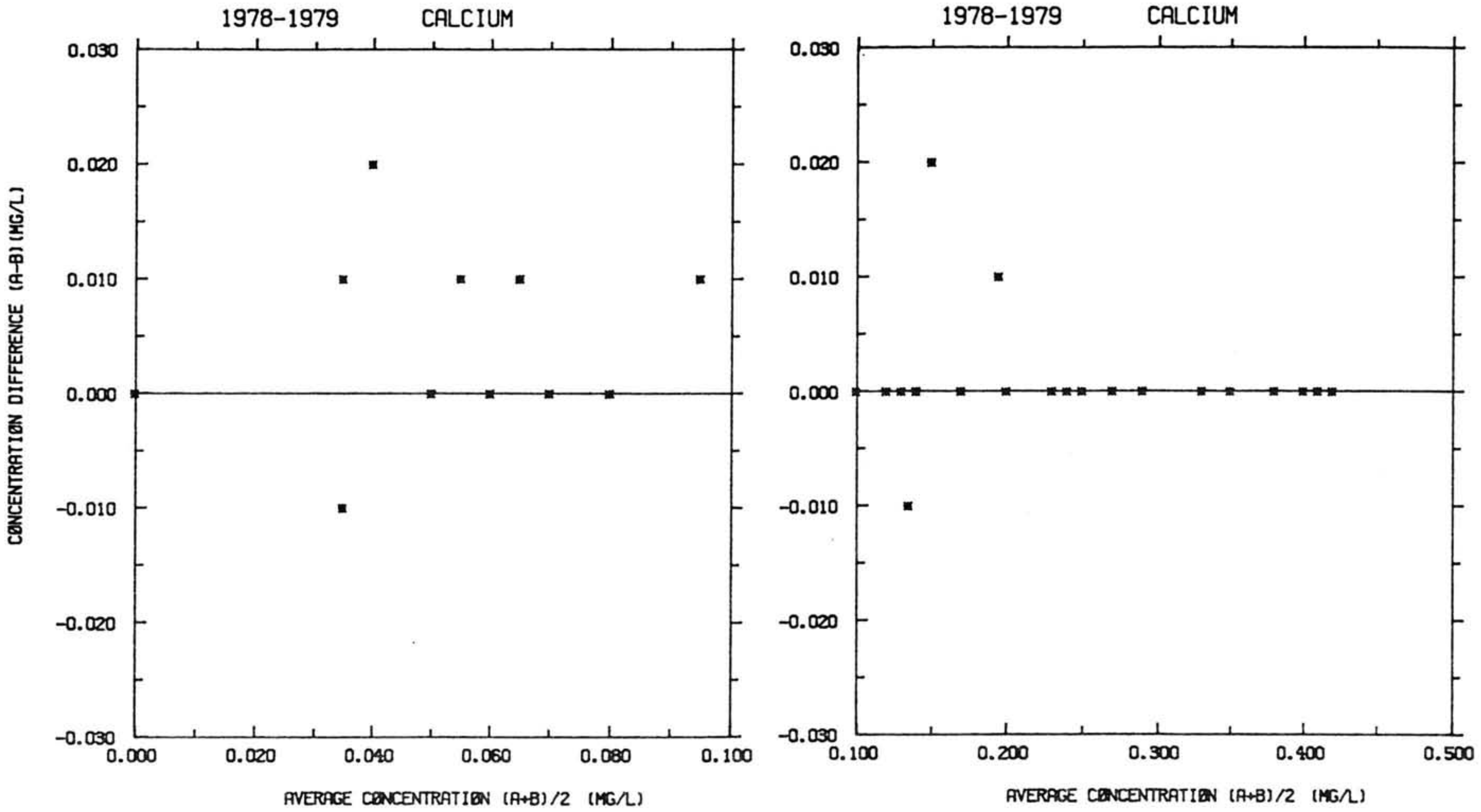


FIGURE 1. Replicate plots for calcium for 1978 and 1979.

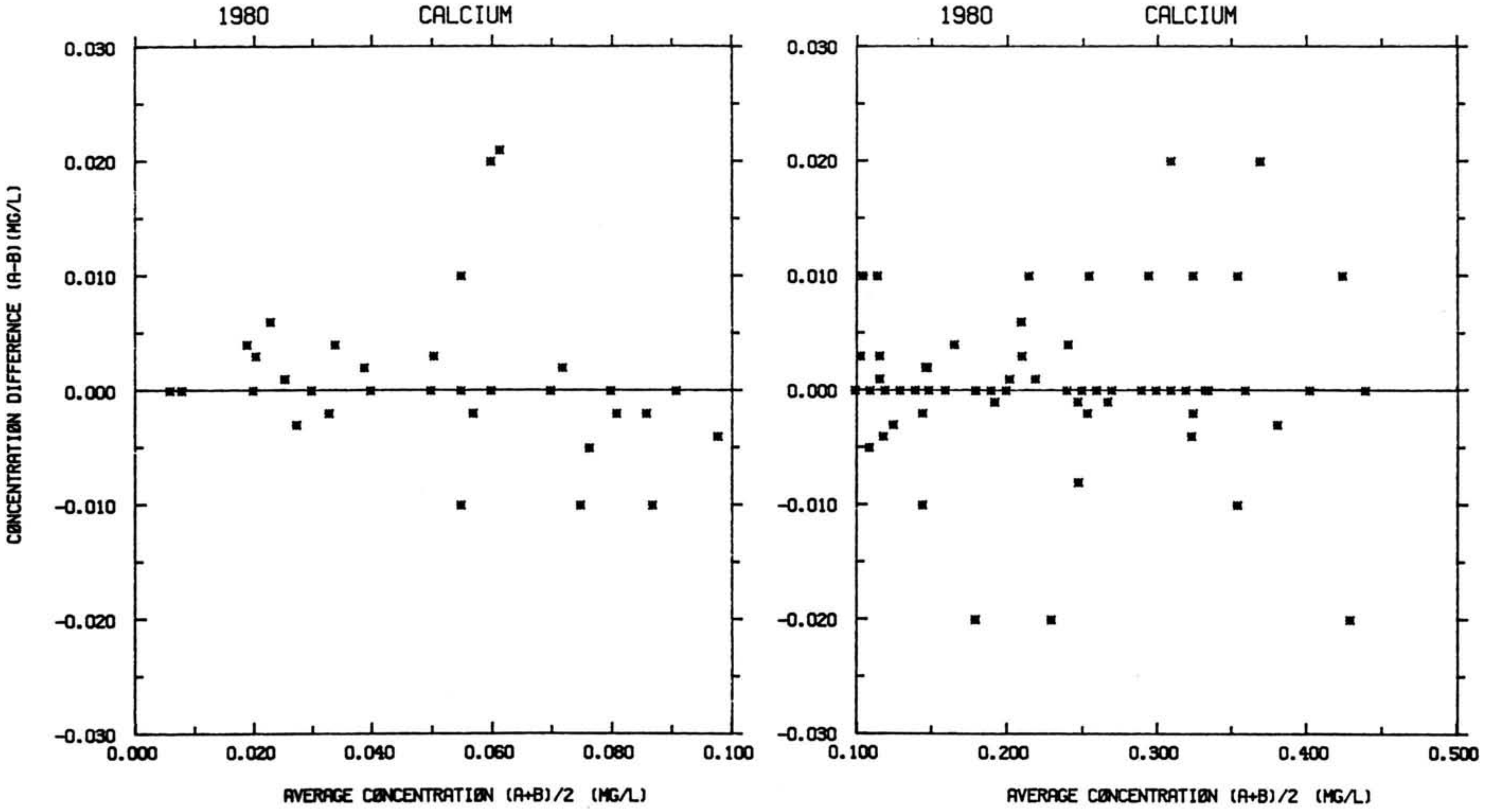


FIGURE 2. Replicate plots for calcium for 1980.

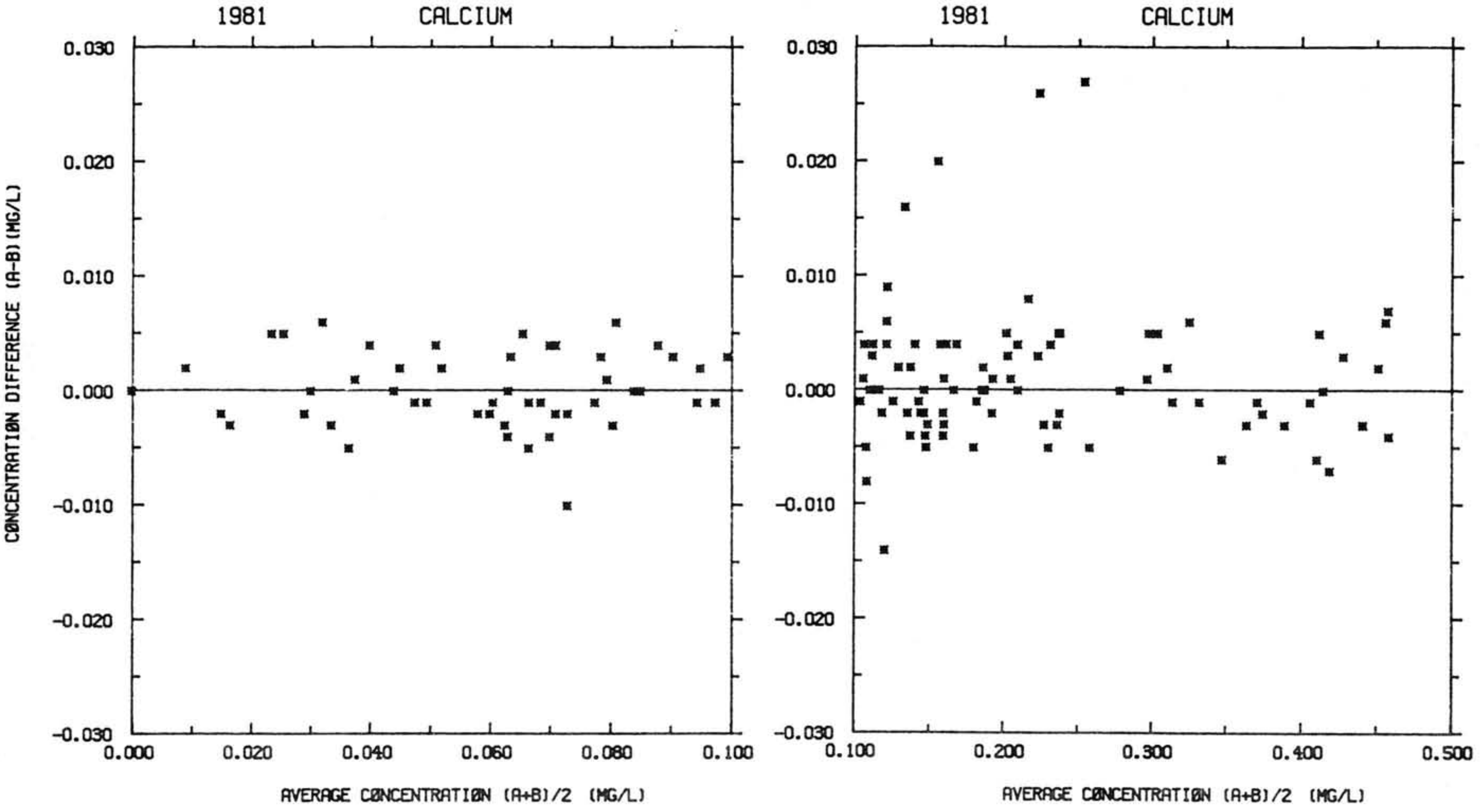


FIGURE 3. Replicate plots for calcium for 1981.

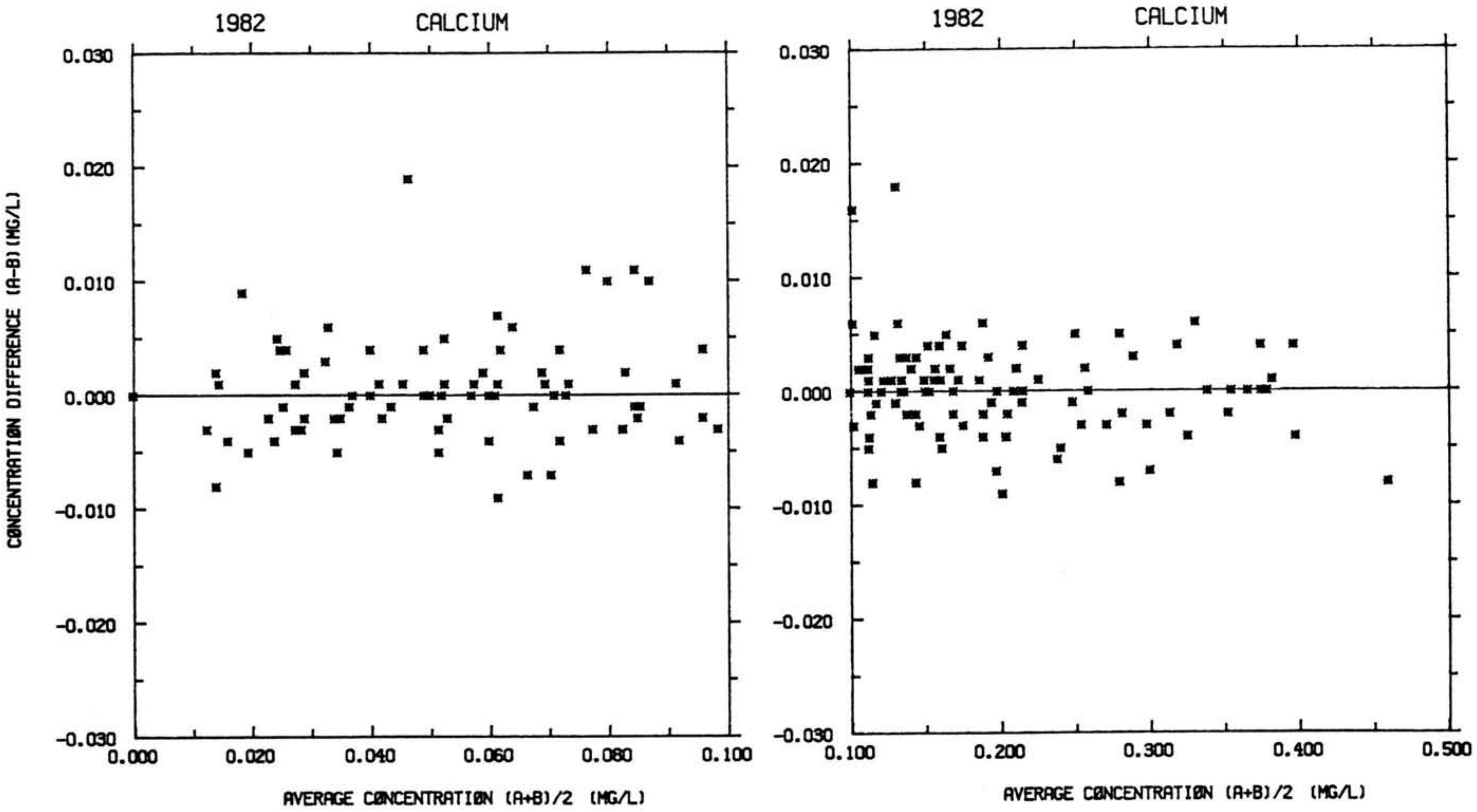


FIGURE 4. Replicate plots for calcium for 1982.

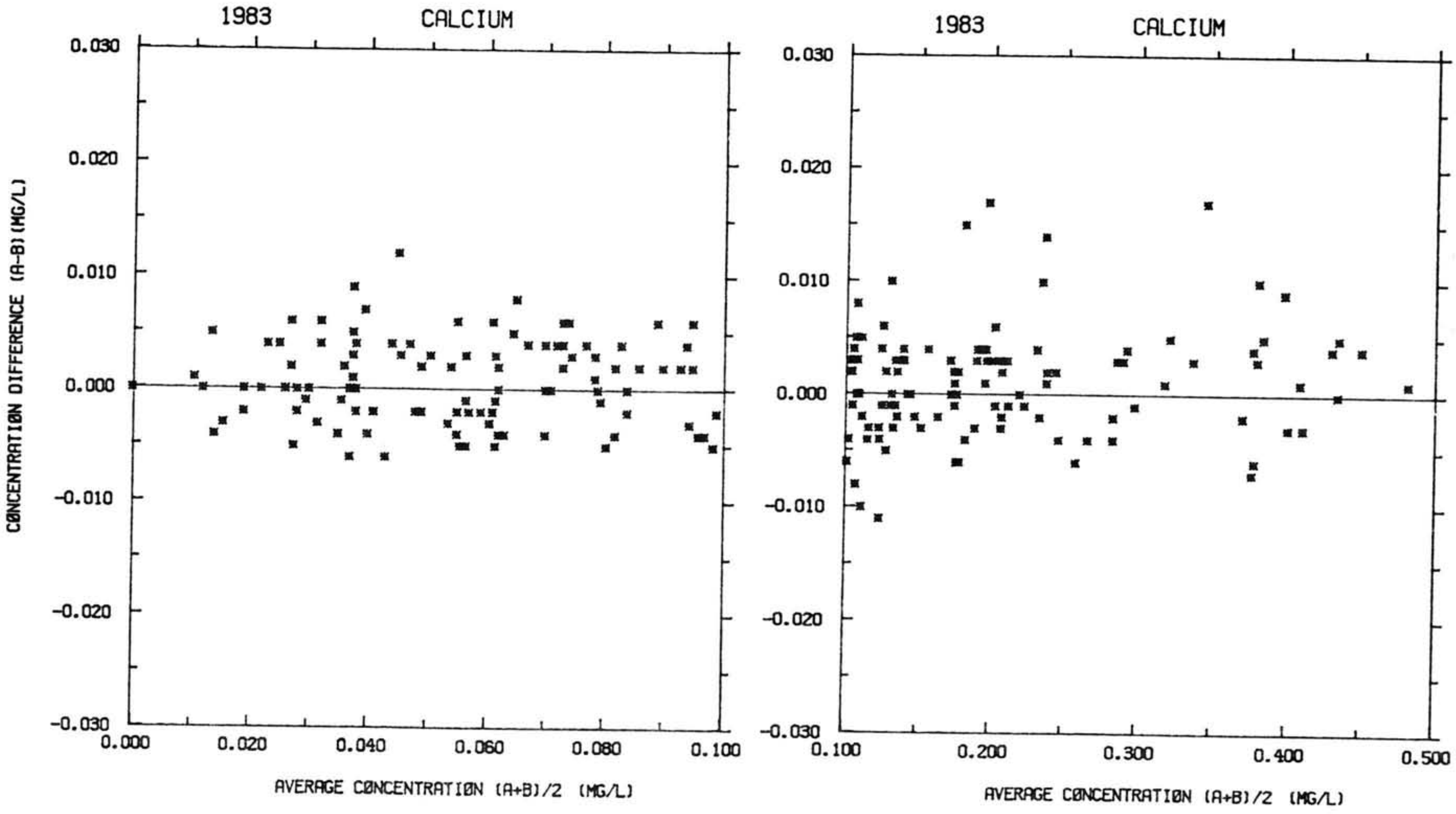


FIGURE 5. Replicate plots for calcium for 1983.

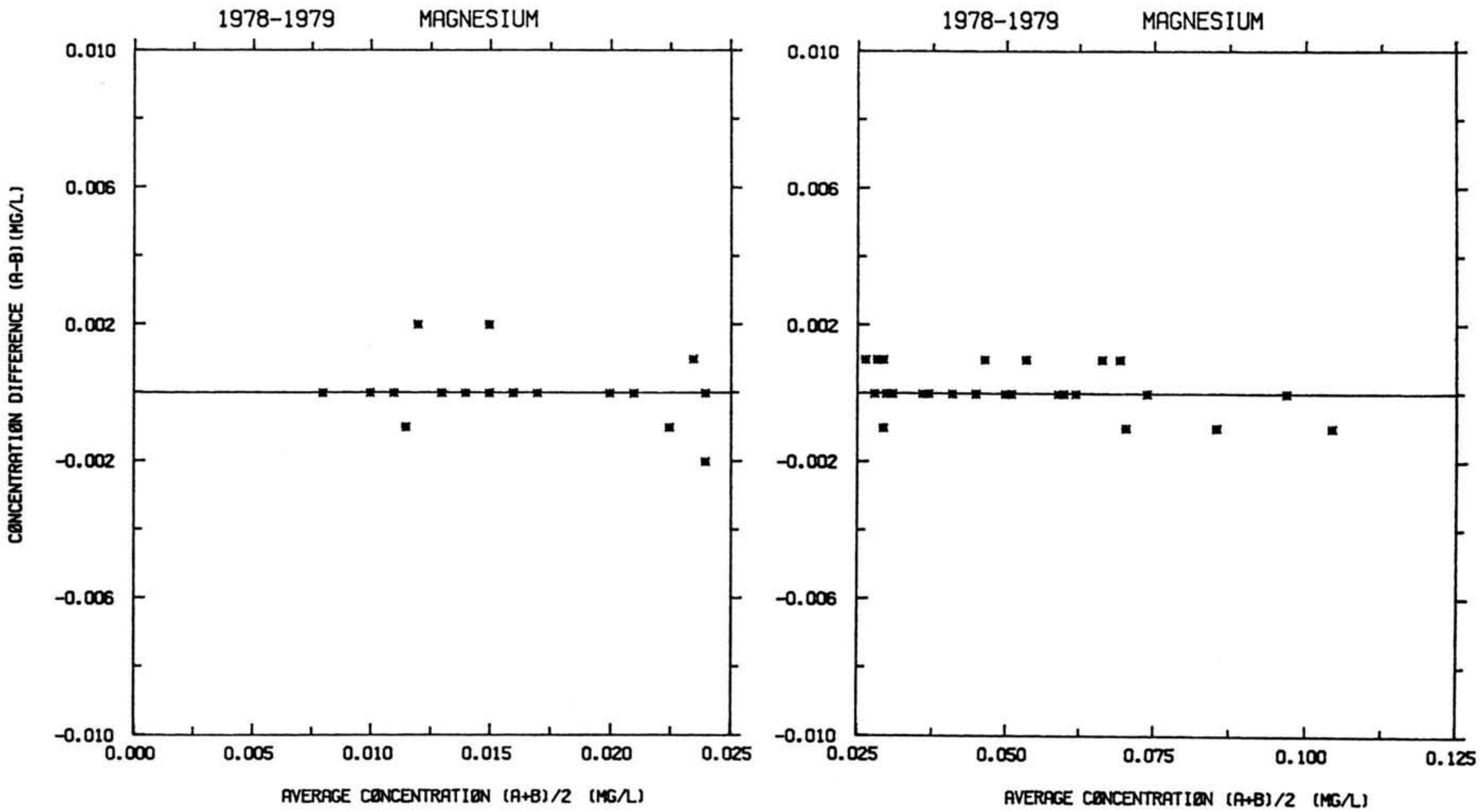


FIGURE 6. Replicate plots for magnesium for 1978 and 1979.

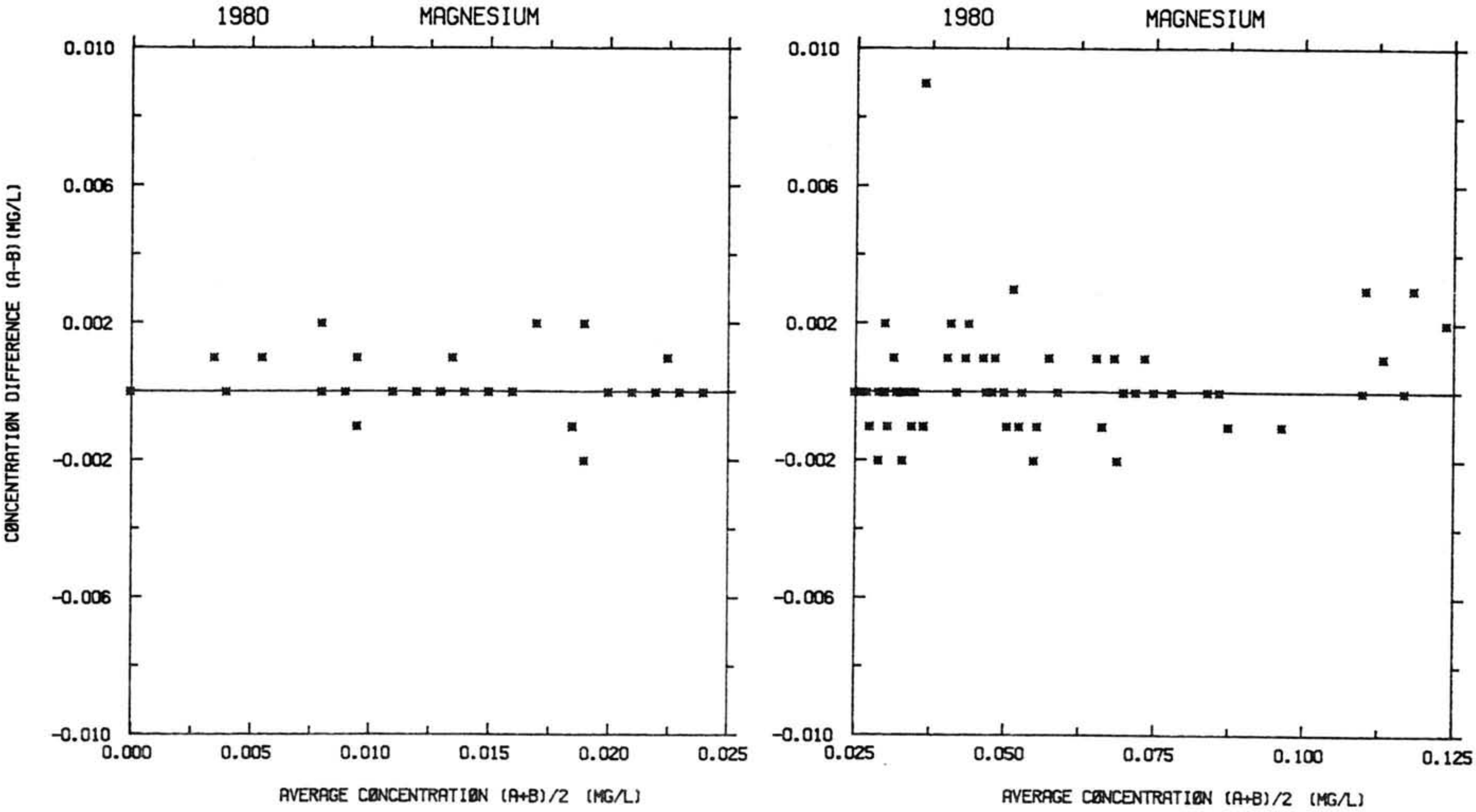


FIGURE 7. Replicate plots for magnesium for 1980.

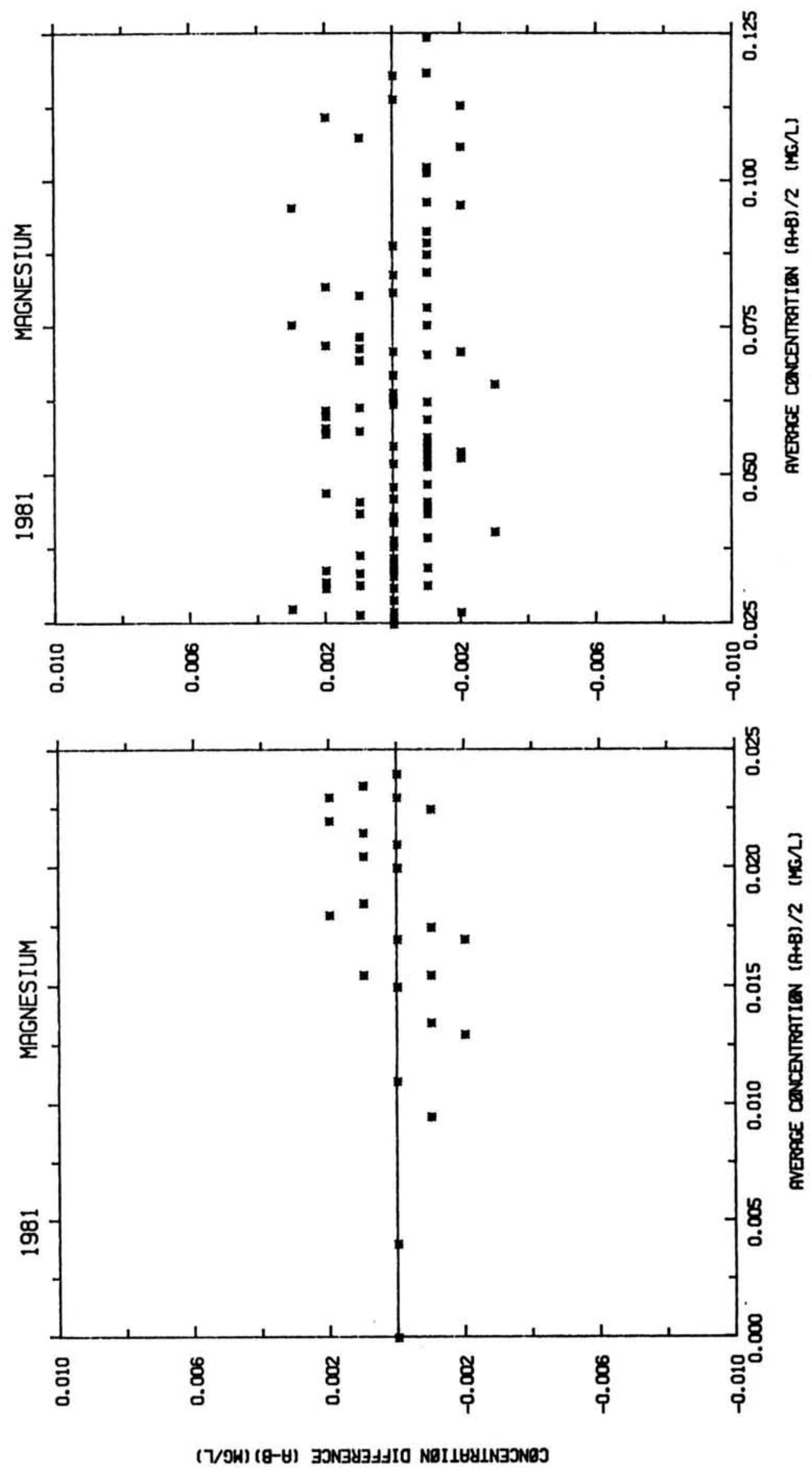


FIGURE 8. Replicate plots for magnesium for 1981.

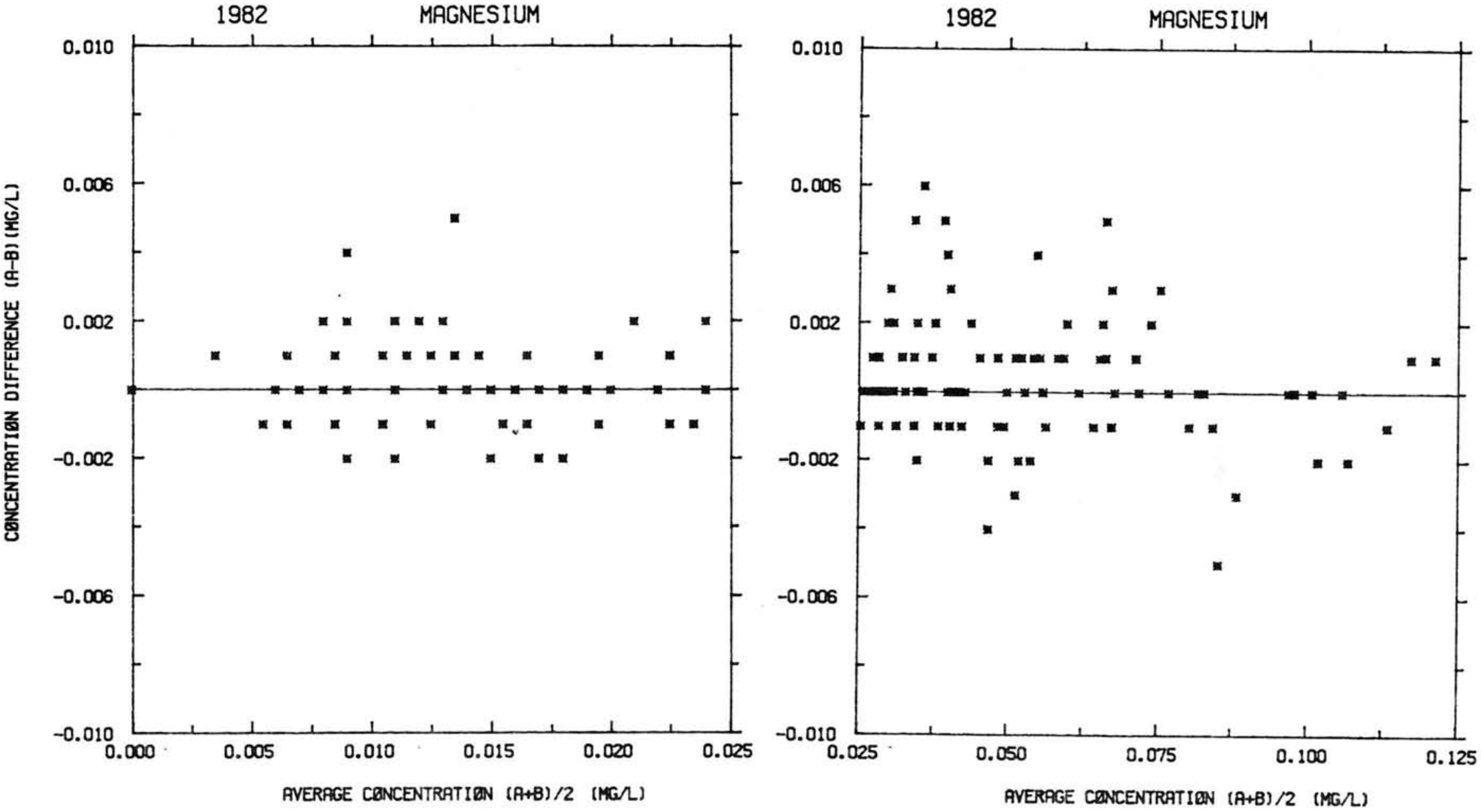


FIGURE 9. Replicate plots for magnesium for 1982.

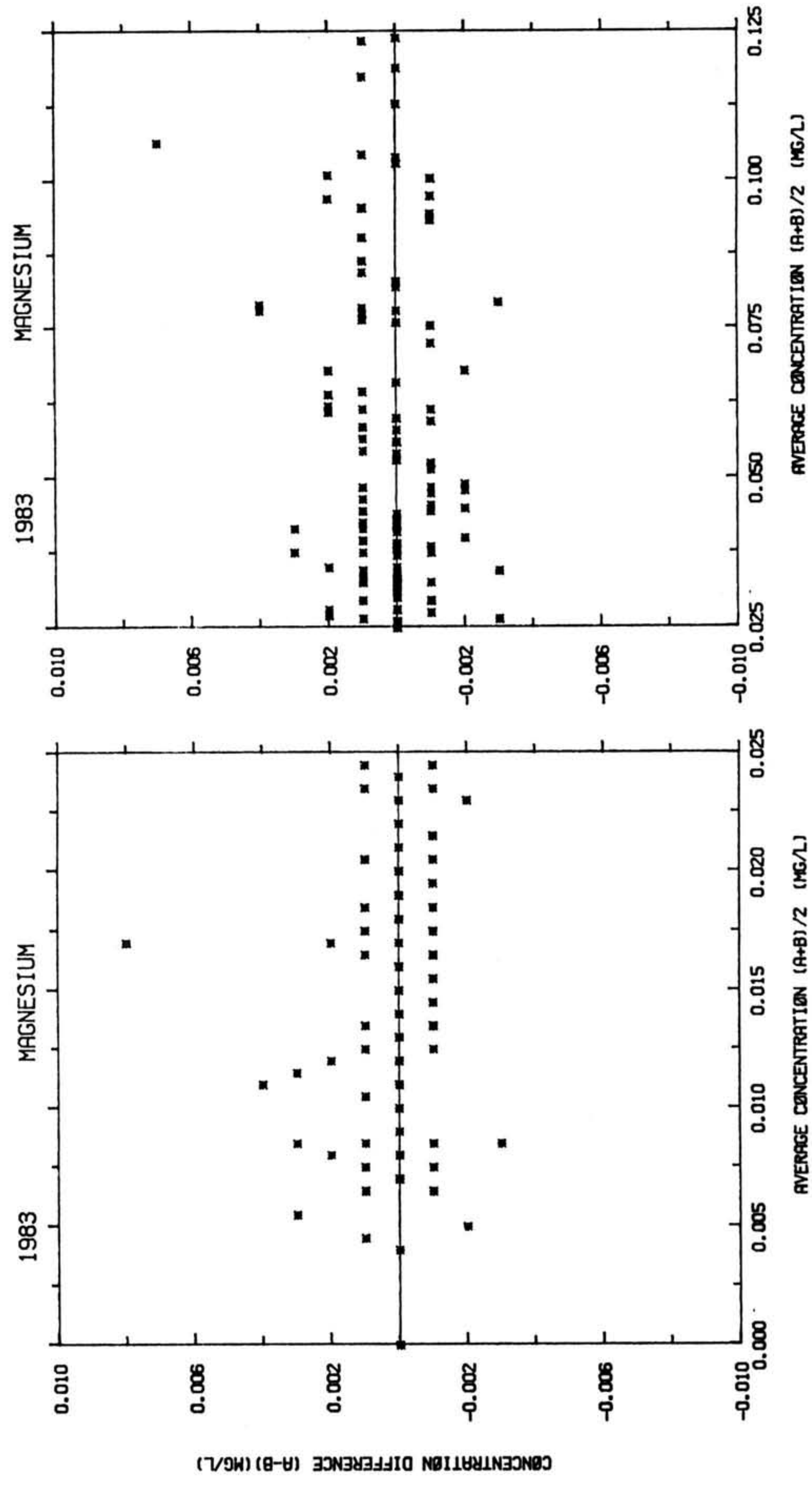


FIGURE 10. Replicate plots for magnesium for 1983.

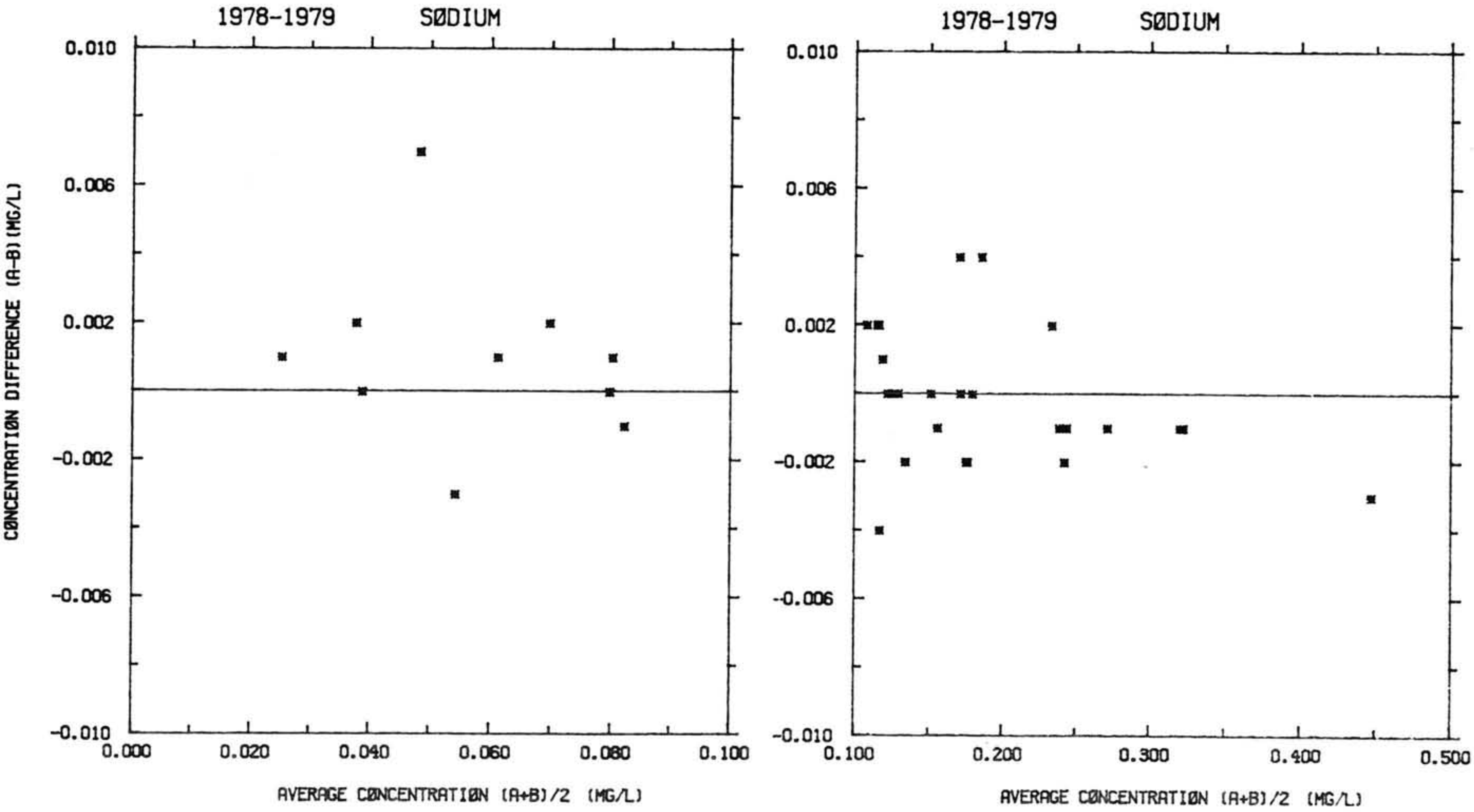


FIGURE 11. Replicate plots for sodium for 1978 and 1979.

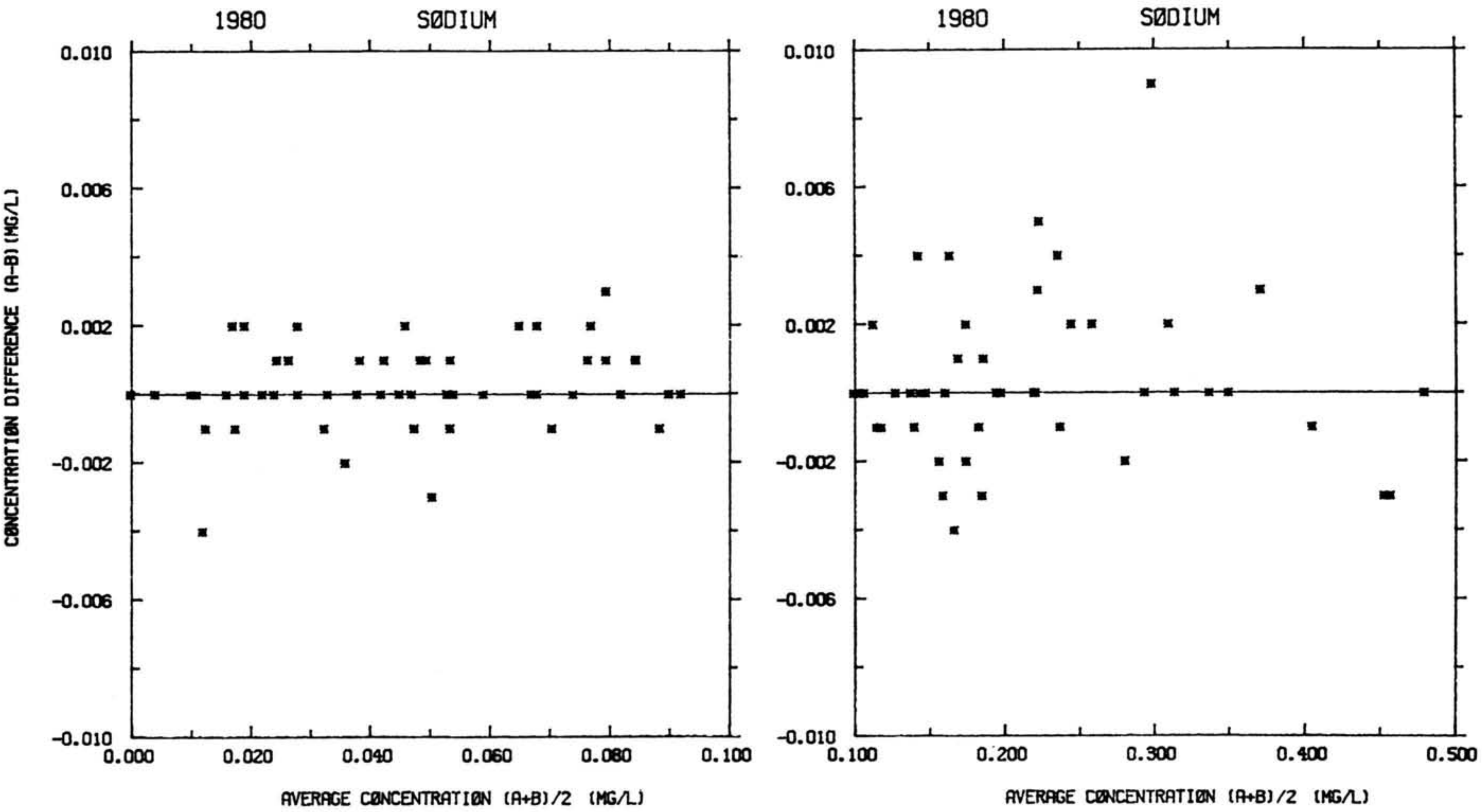


FIGURE 12. Replicate plots for sodium for 1980.

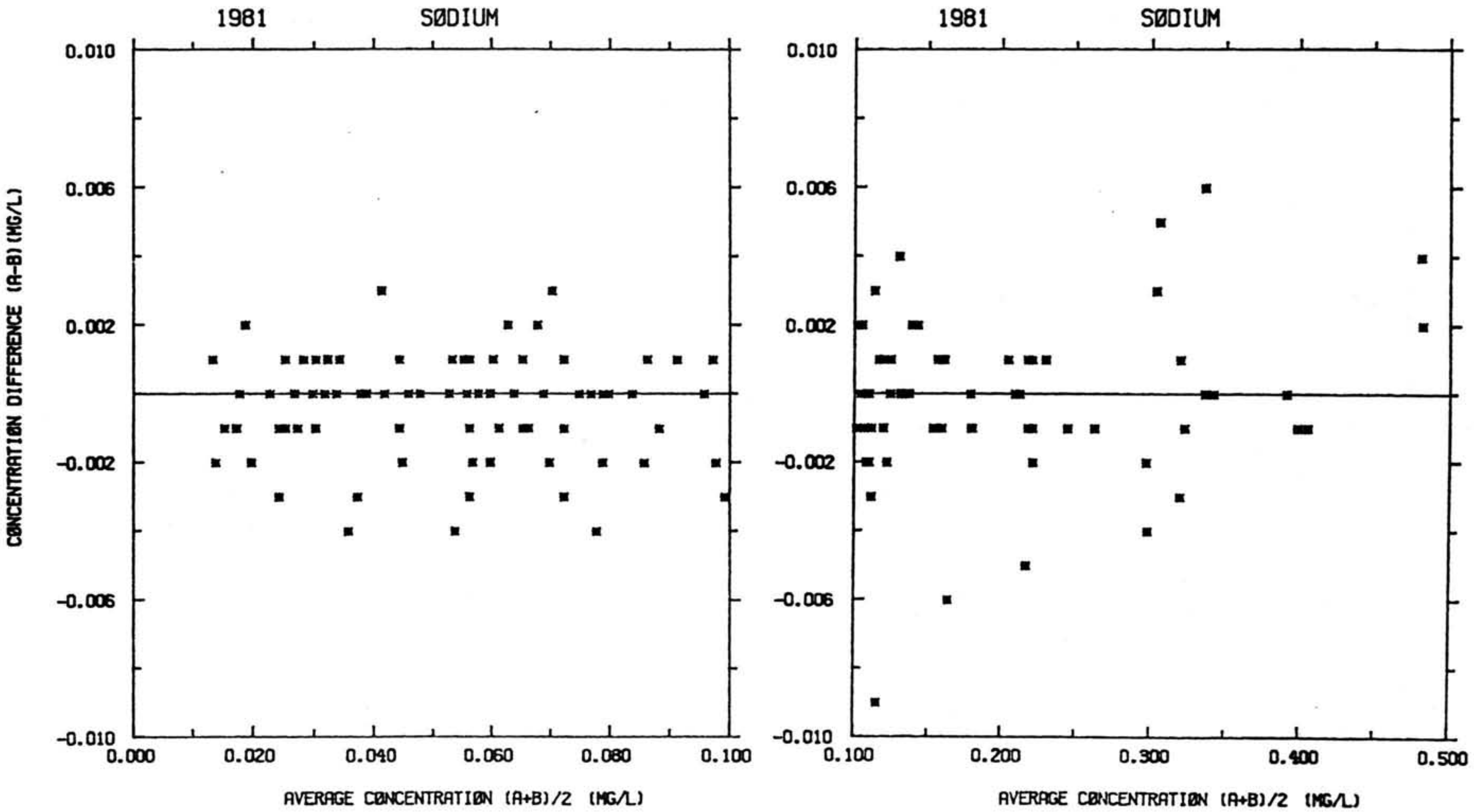


FIGURE 13. Replicate plots for sodium for 1981.

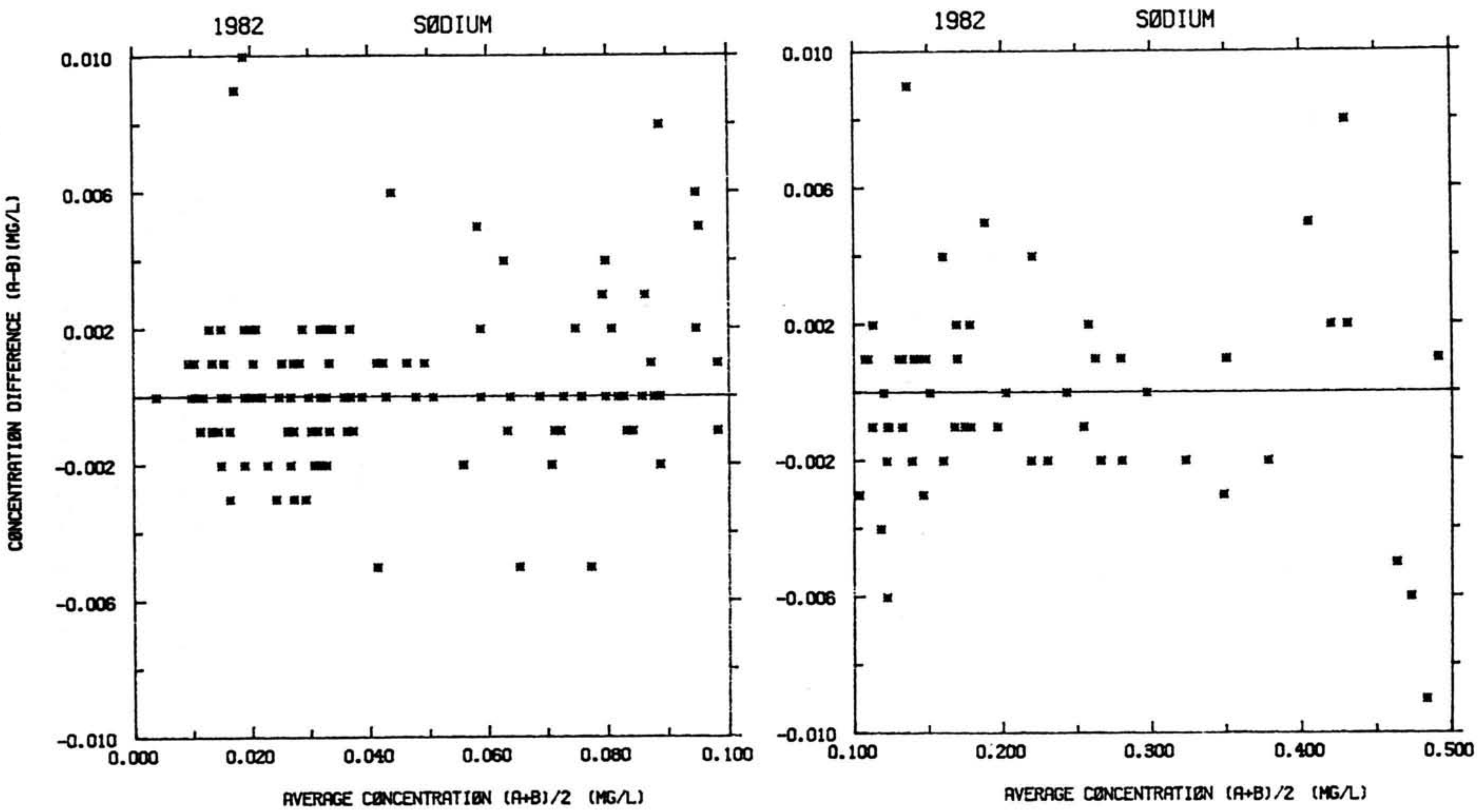


FIGURE 14. Replicate plots for sodium for 1982.

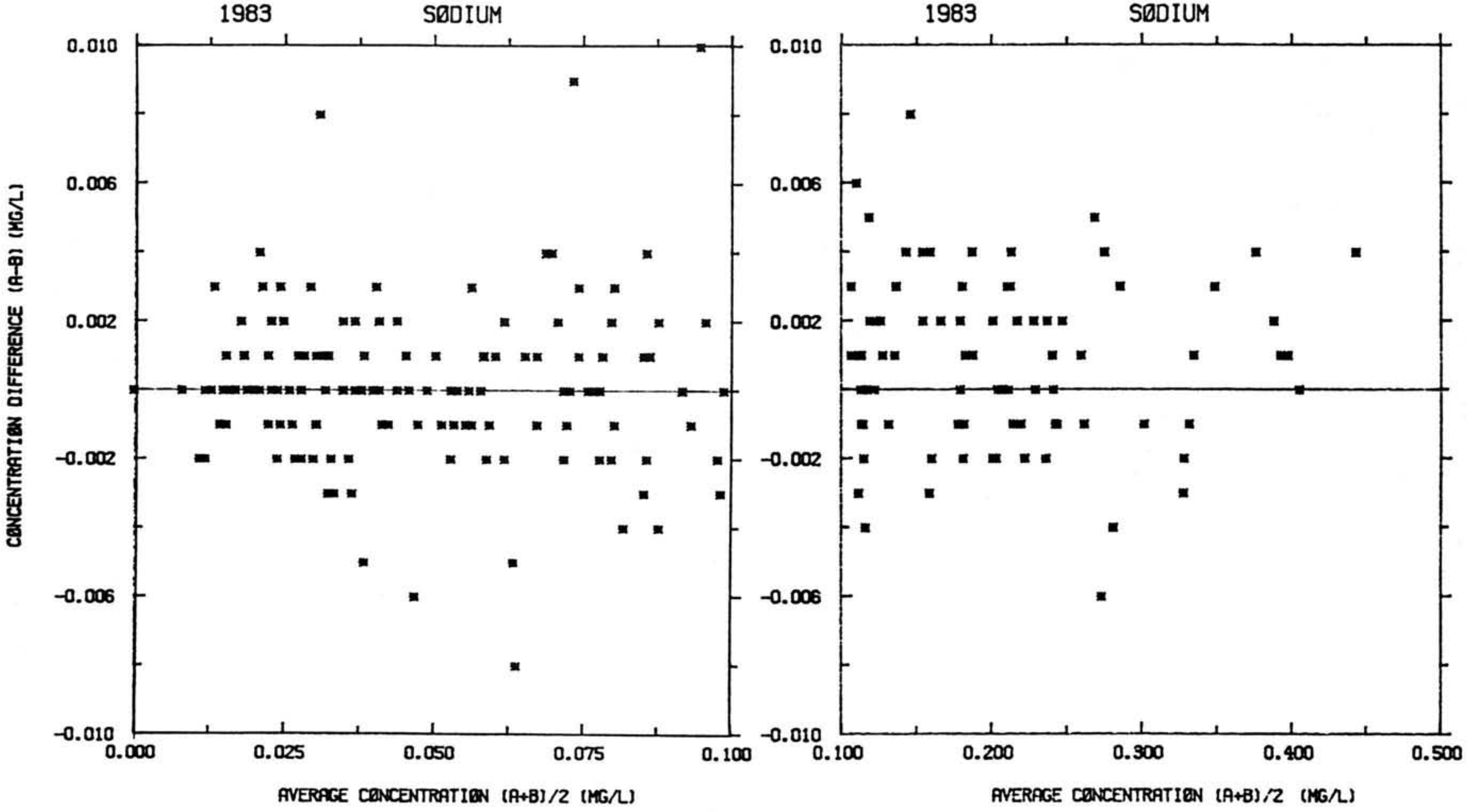


FIGURE 15. Replicate plots for sodium for 1983.

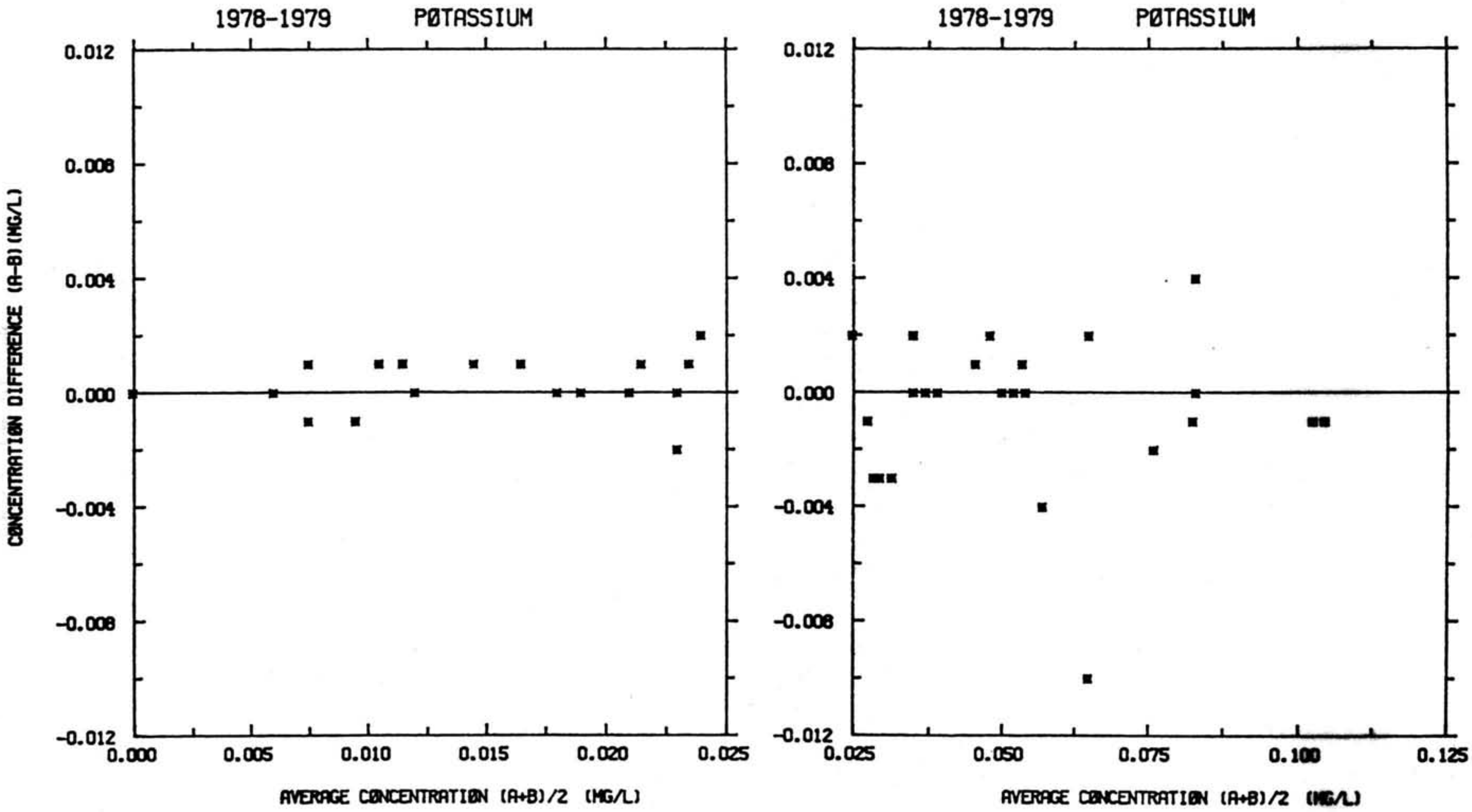


FIGURE 16. Replicate plots for potassium for 1978 and 1979.

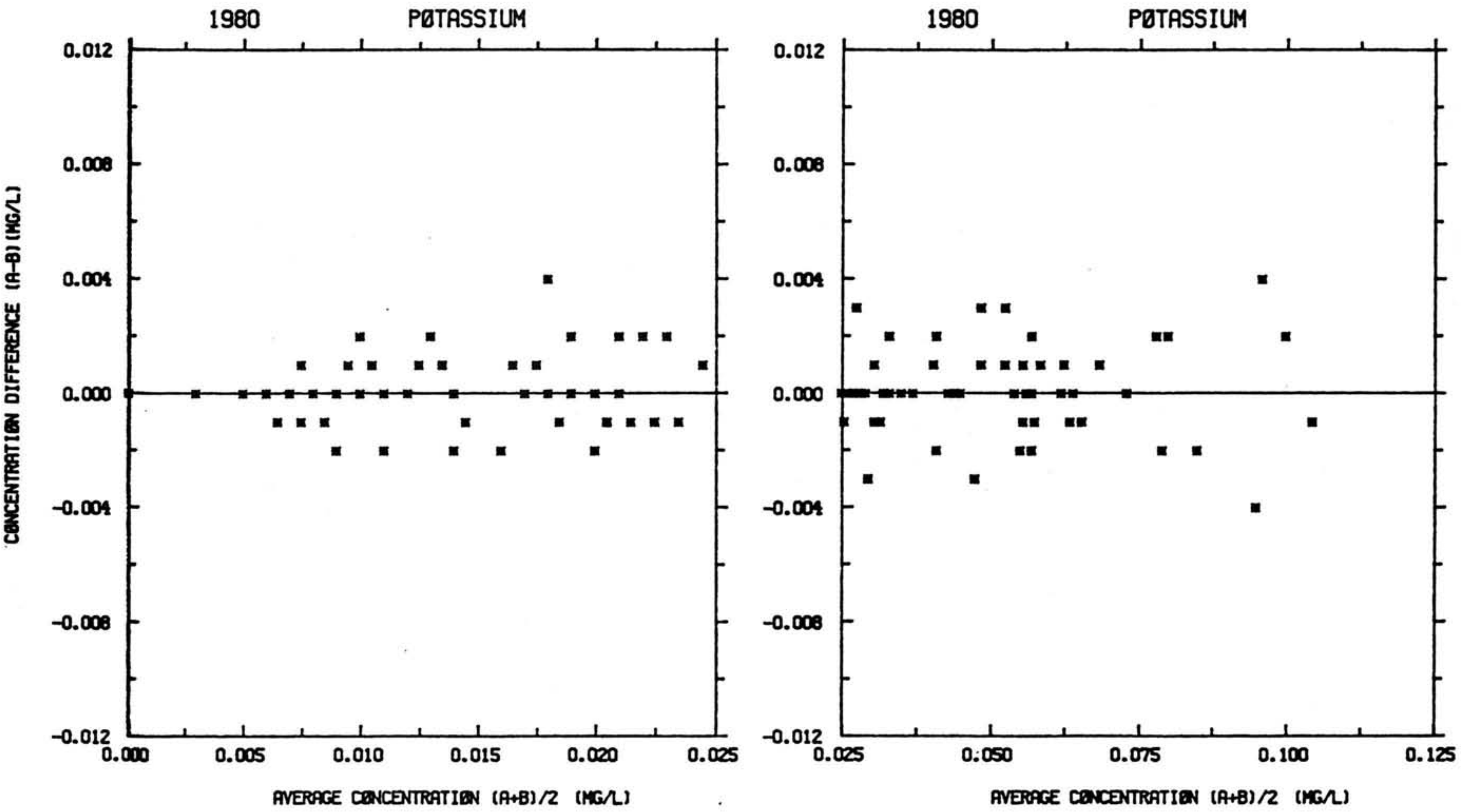


FIGURE 17. Replicate plots for potassium for 1980.

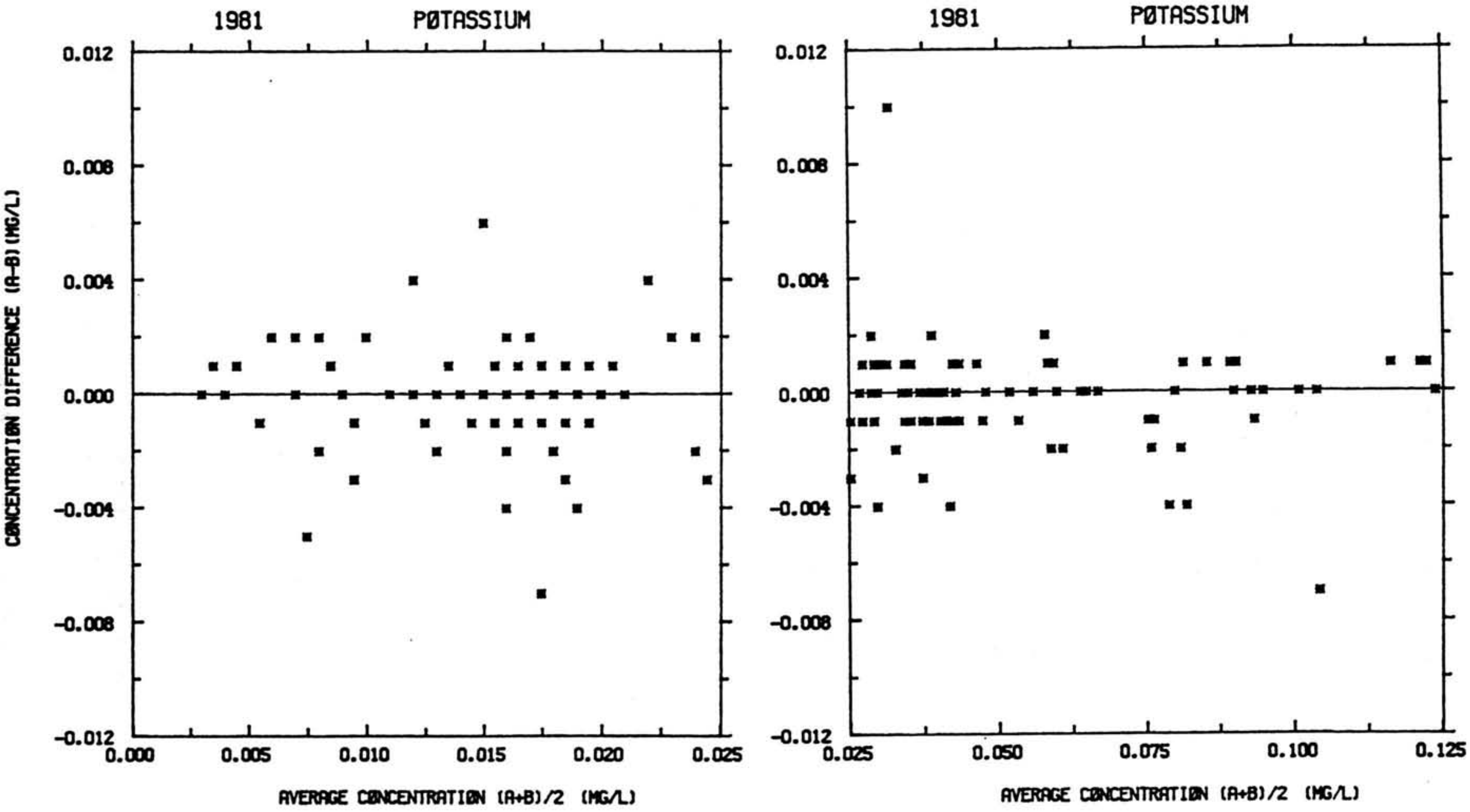


FIGURE 18. Replicate plots for potassium for 1981.

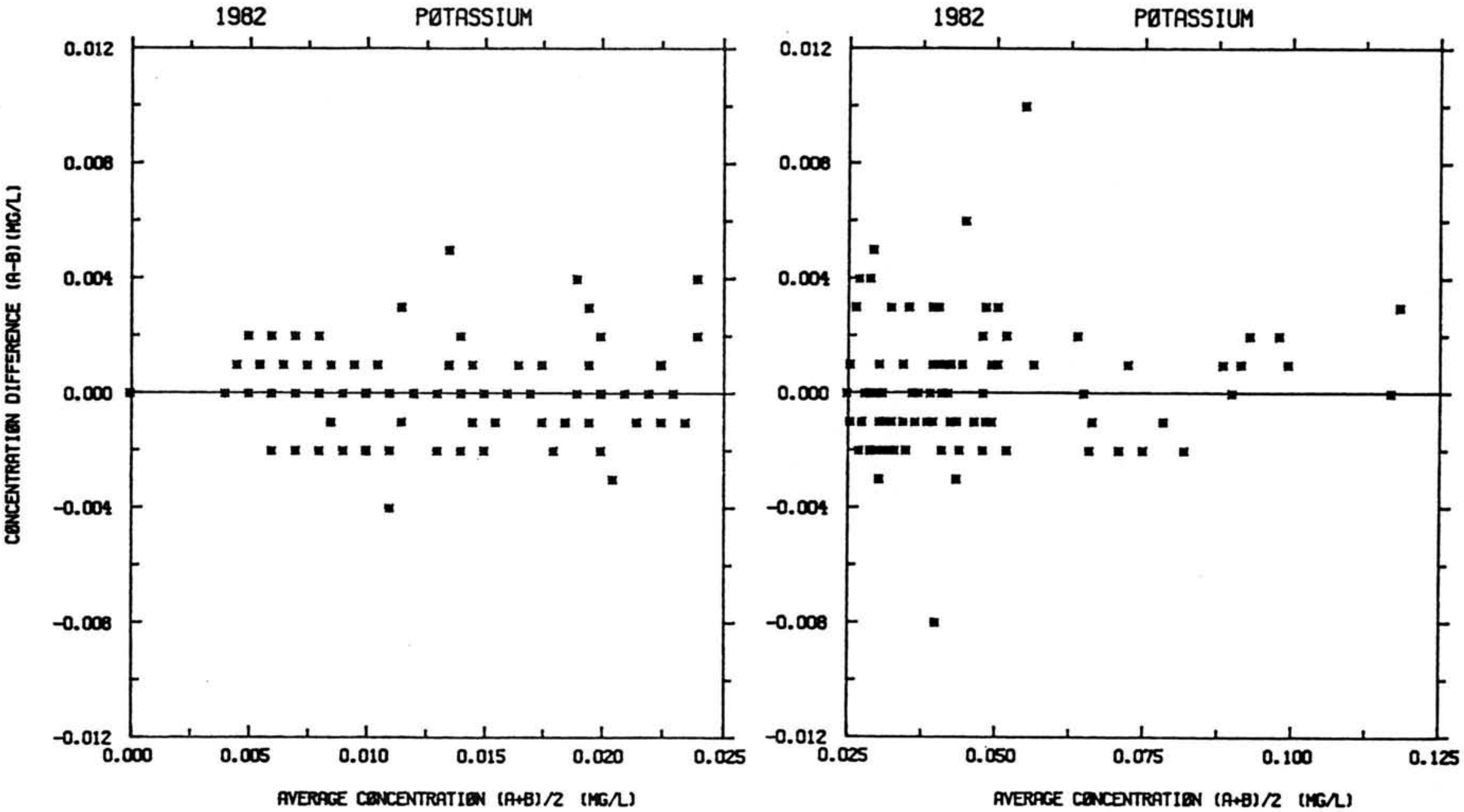


FIGURE 19. Replicate plots for potassium for 1982.

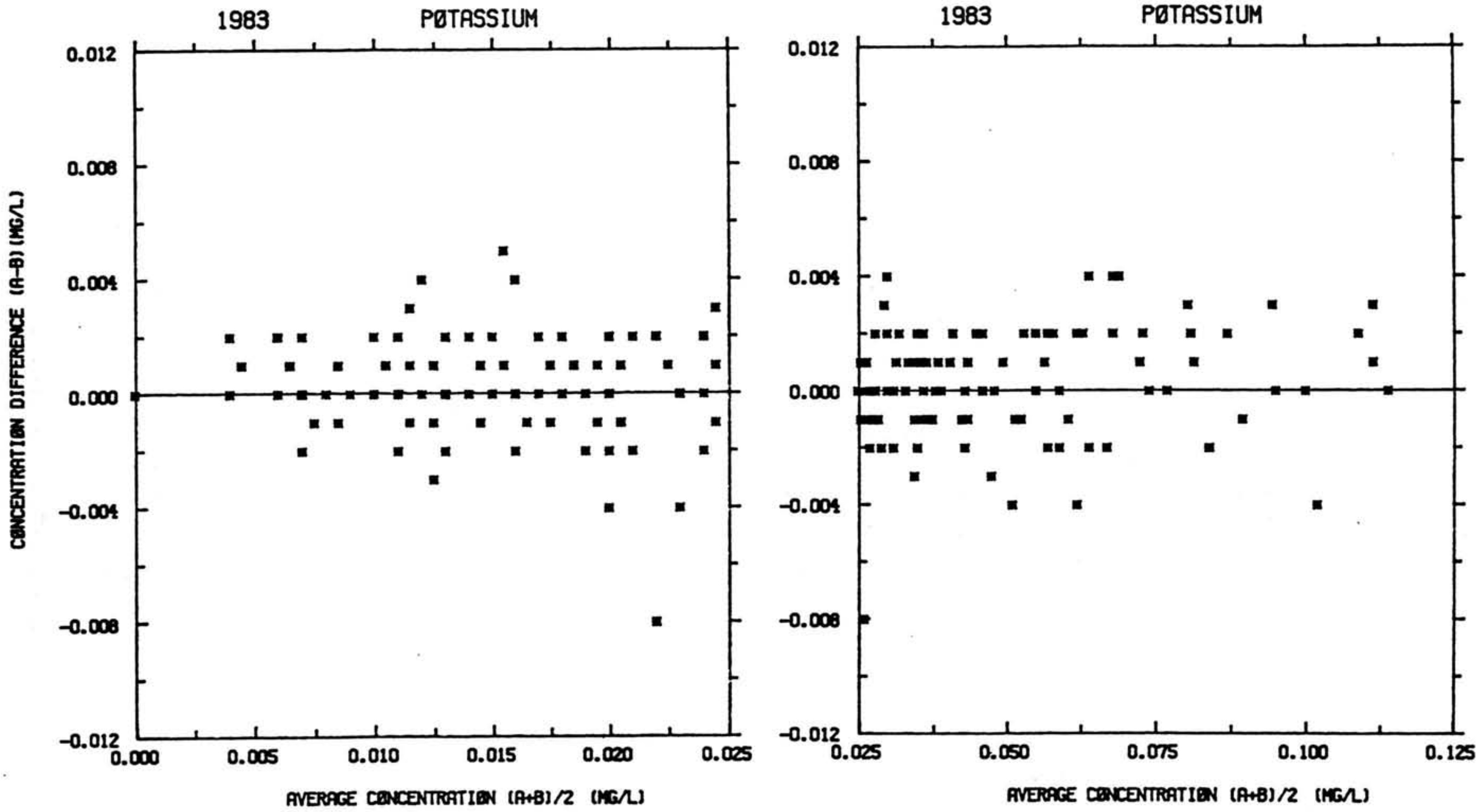


FIGURE 20. Replicate plots for potassium for 1983.

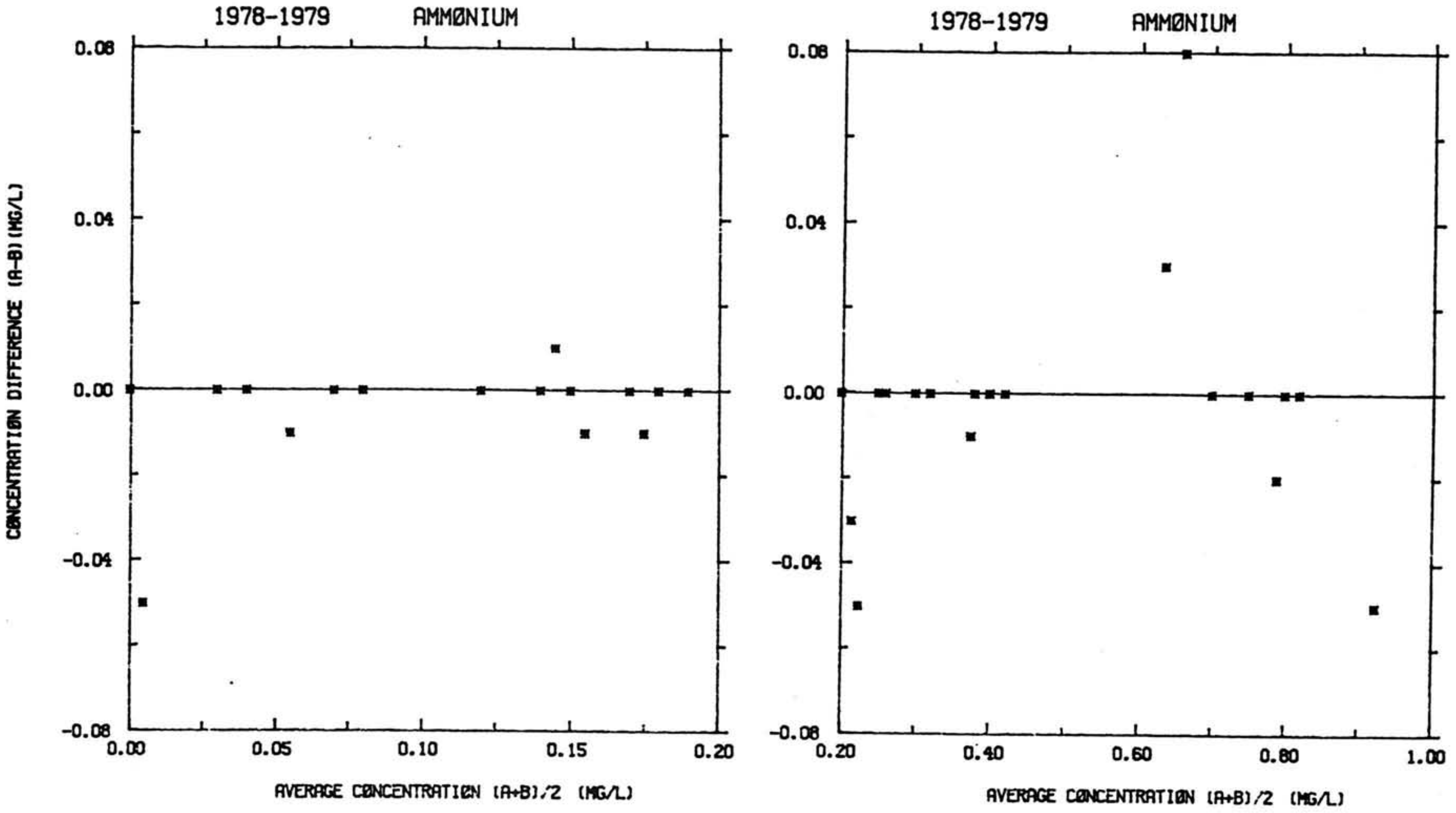


FIGURE 21. Replicate plots for ammonium for 1978 and 1979.

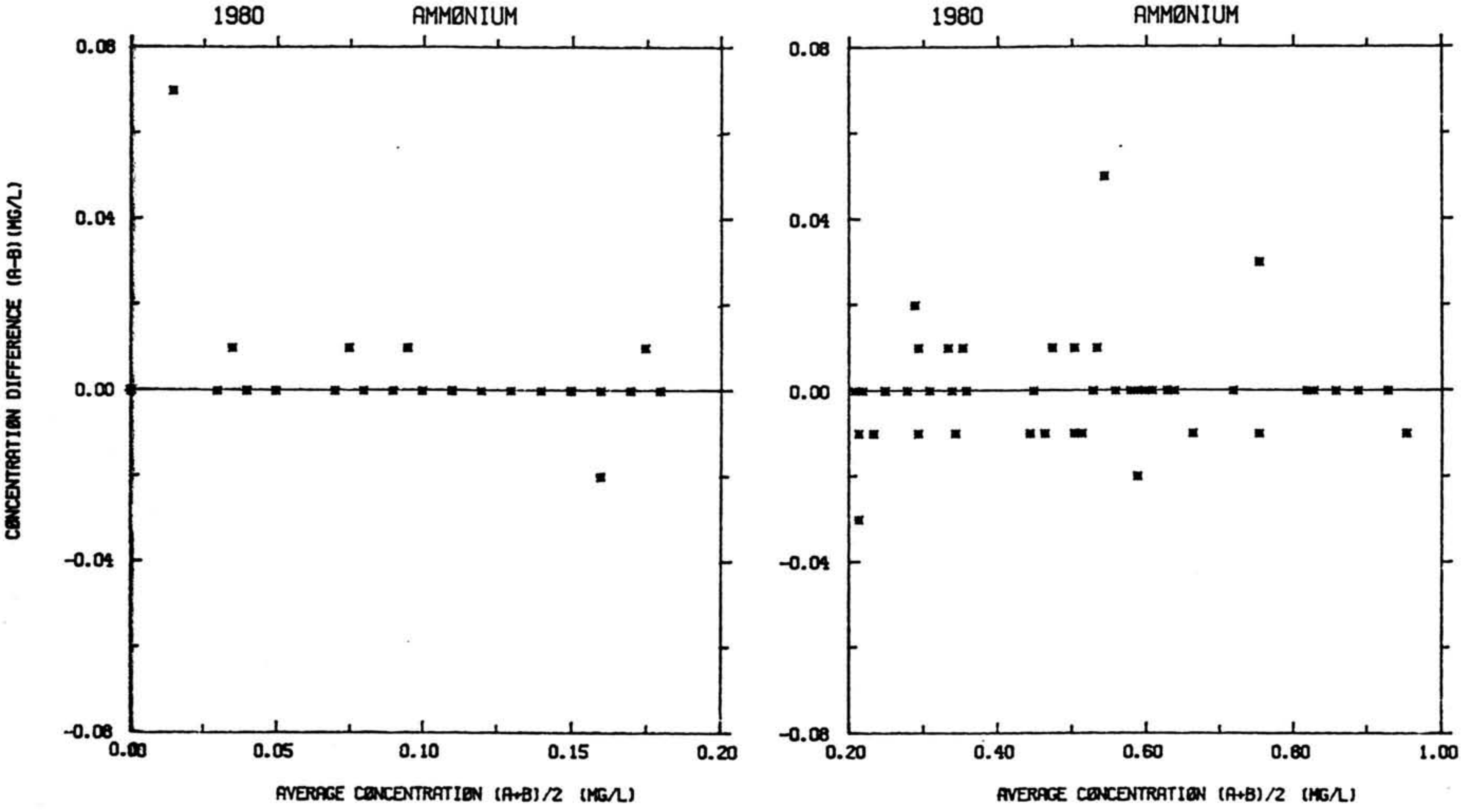


FIGURE 22. Replicate plots for ammonium for 1980.

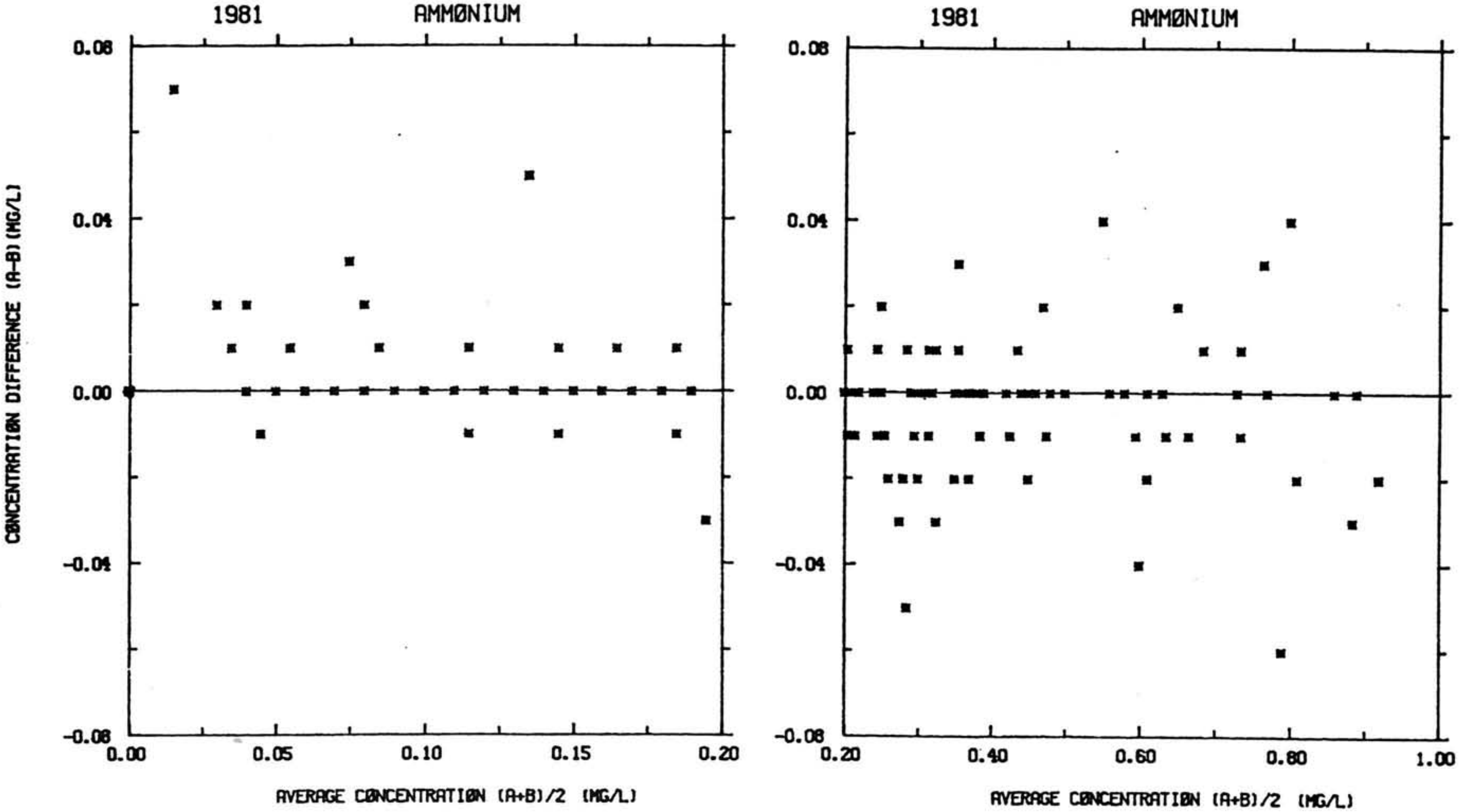


FIGURE 23. Replicate plots for ammonium for 1981.

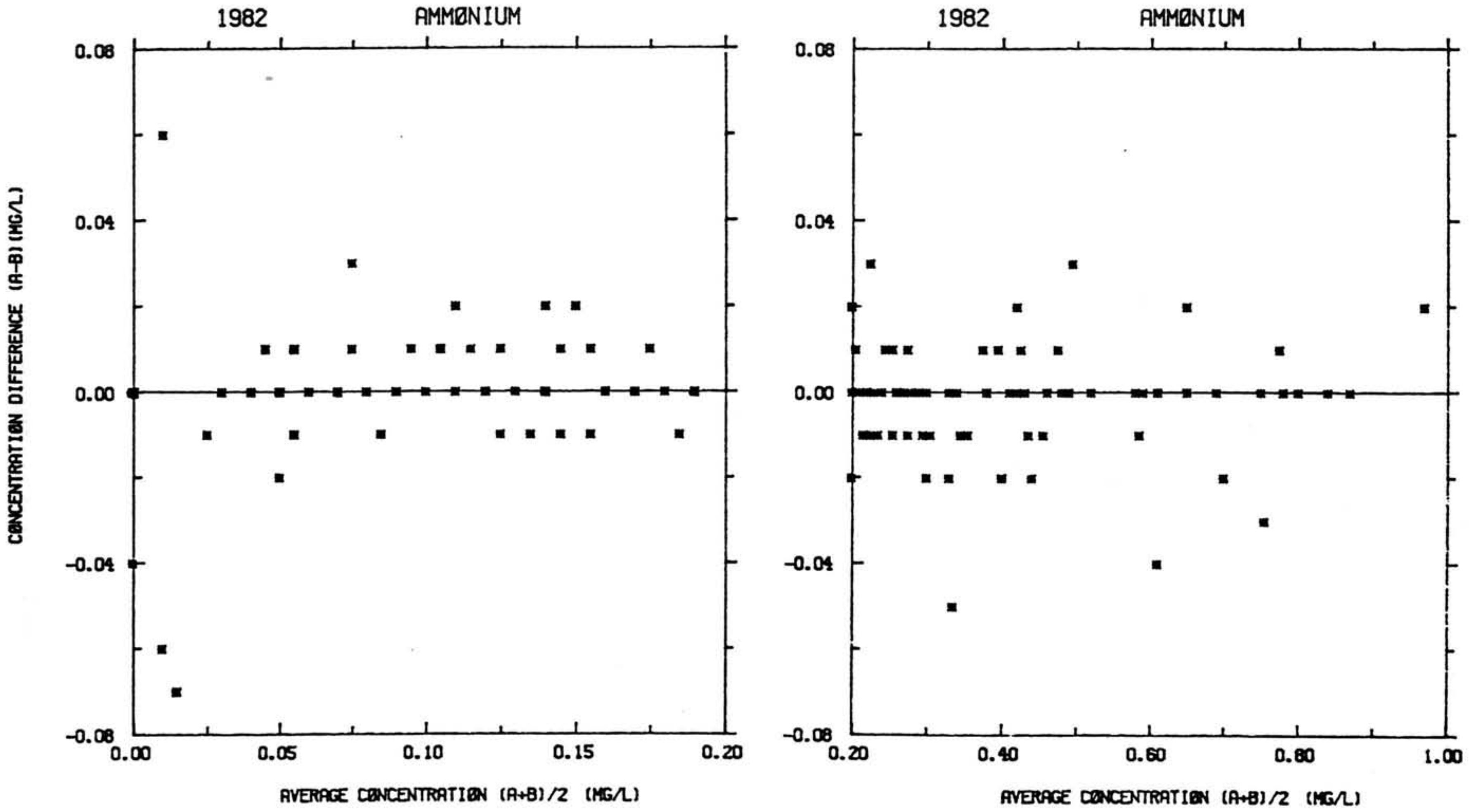


FIGURE 24. Replicate plots for ammonium for 1982.

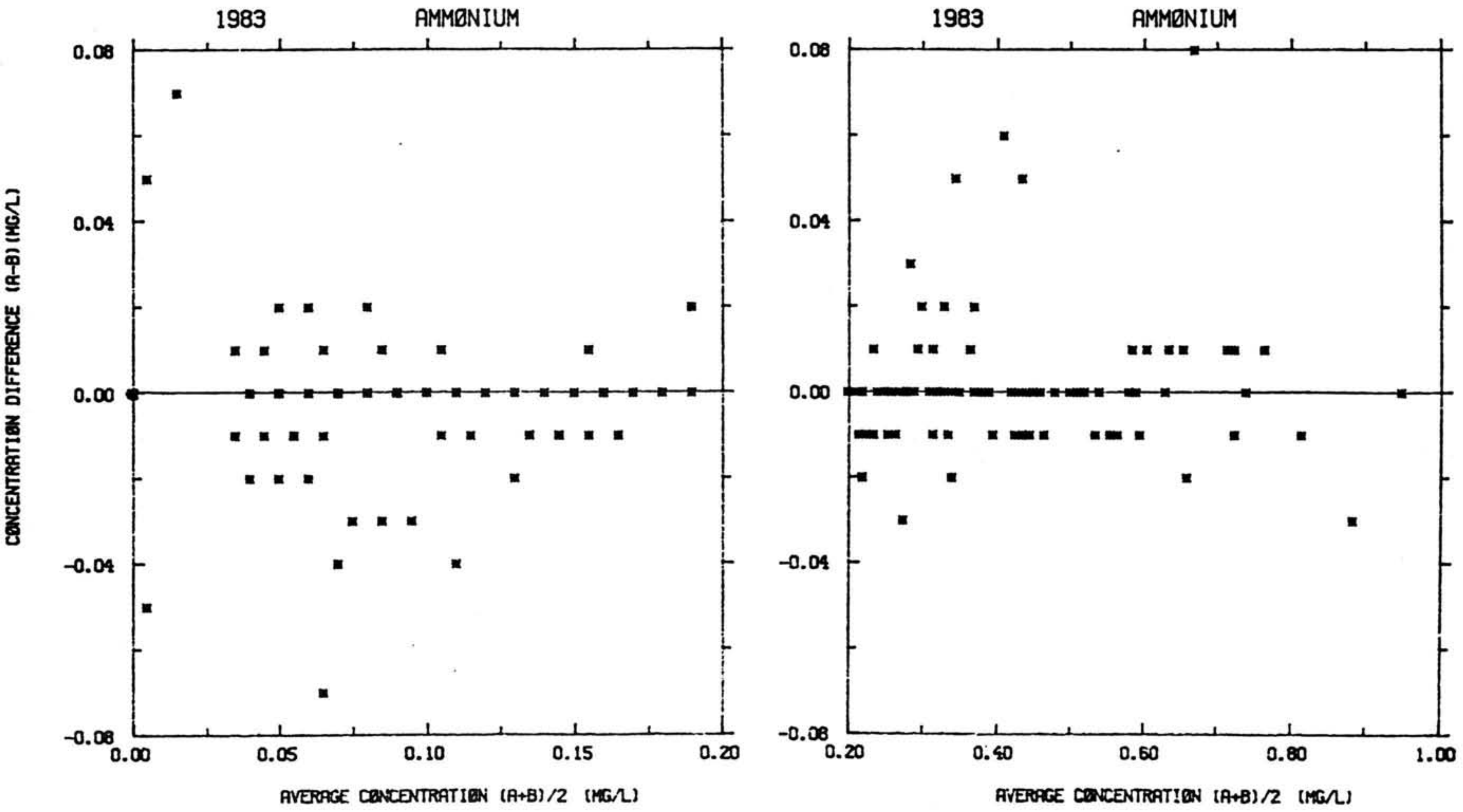


FIGURE 25. Replicate plots for ammonium for 1983.

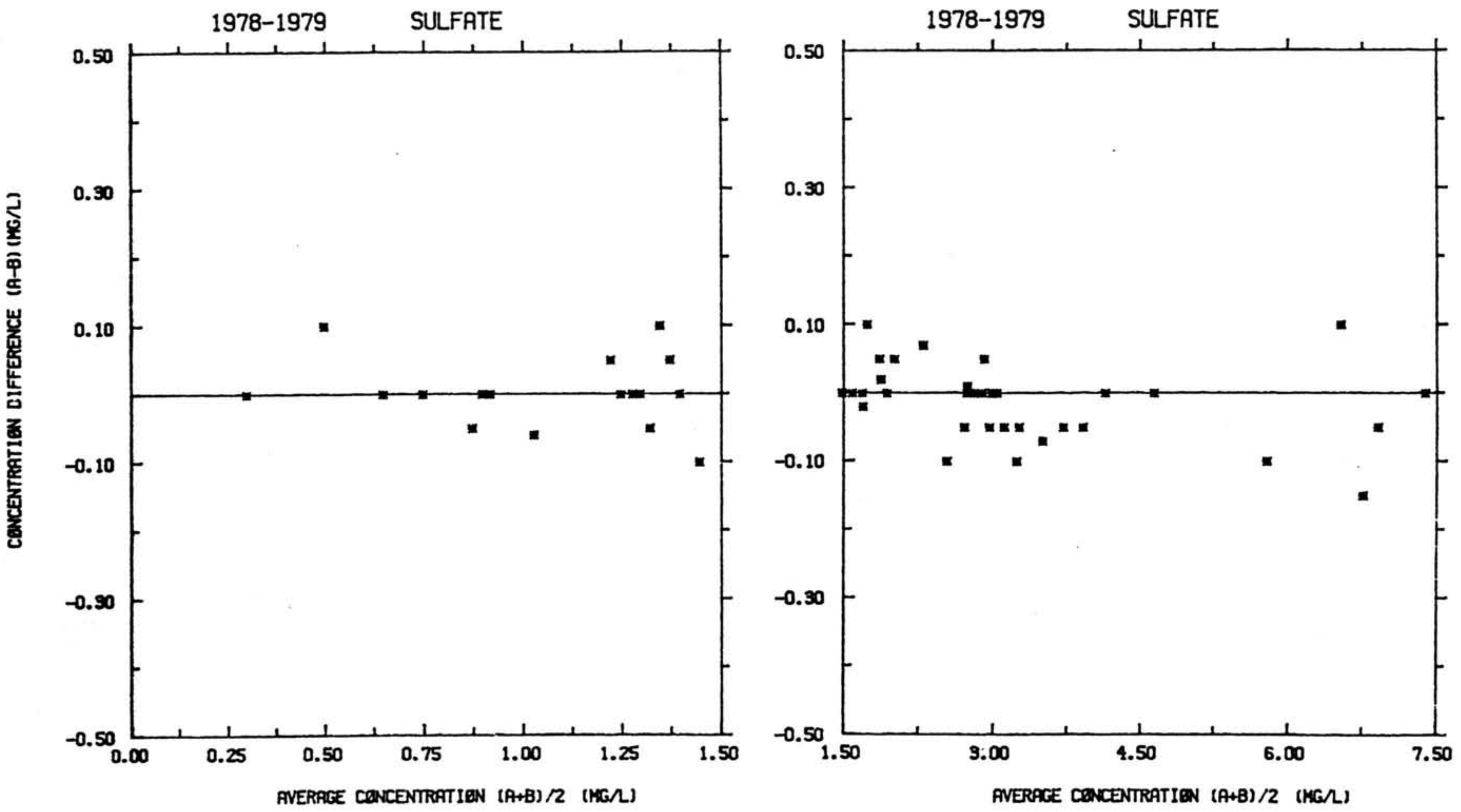


FIGURE 26. Replicate plots for sulfate for 1978 and 1979.

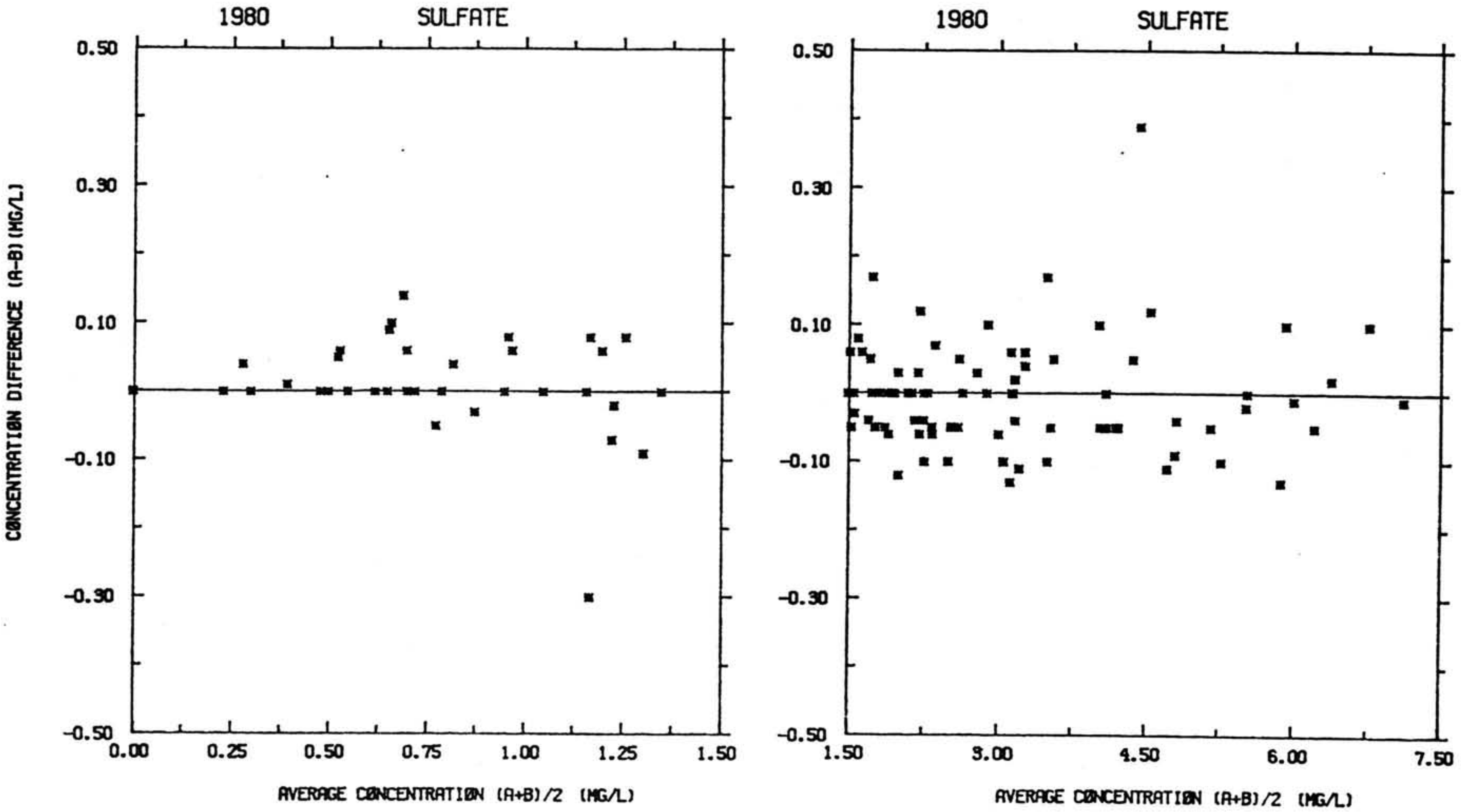


FIGURE 27. Replicate plots for sulfate for 1980.

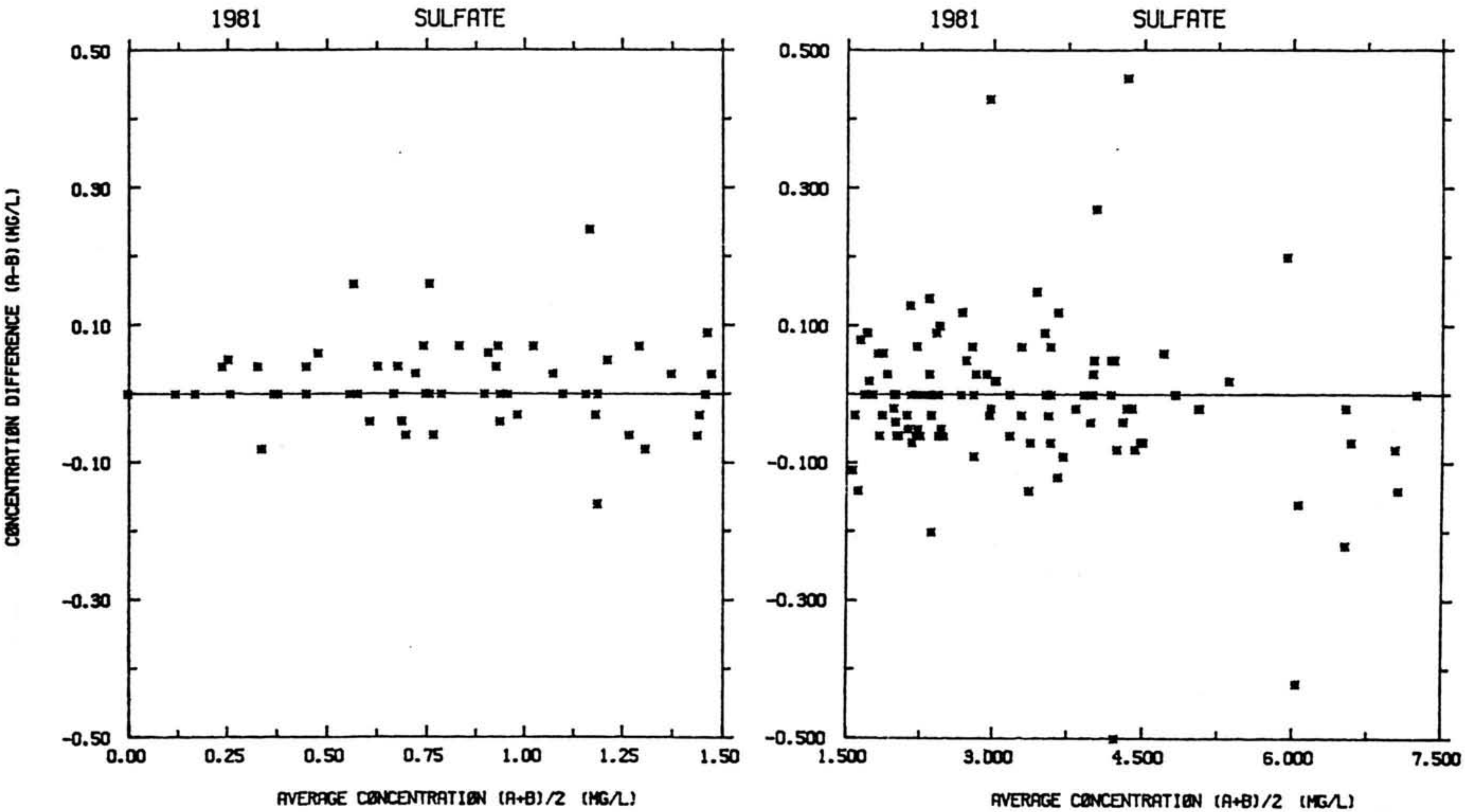


FIGURE 28. Replicate plots for sulfate for 1981.

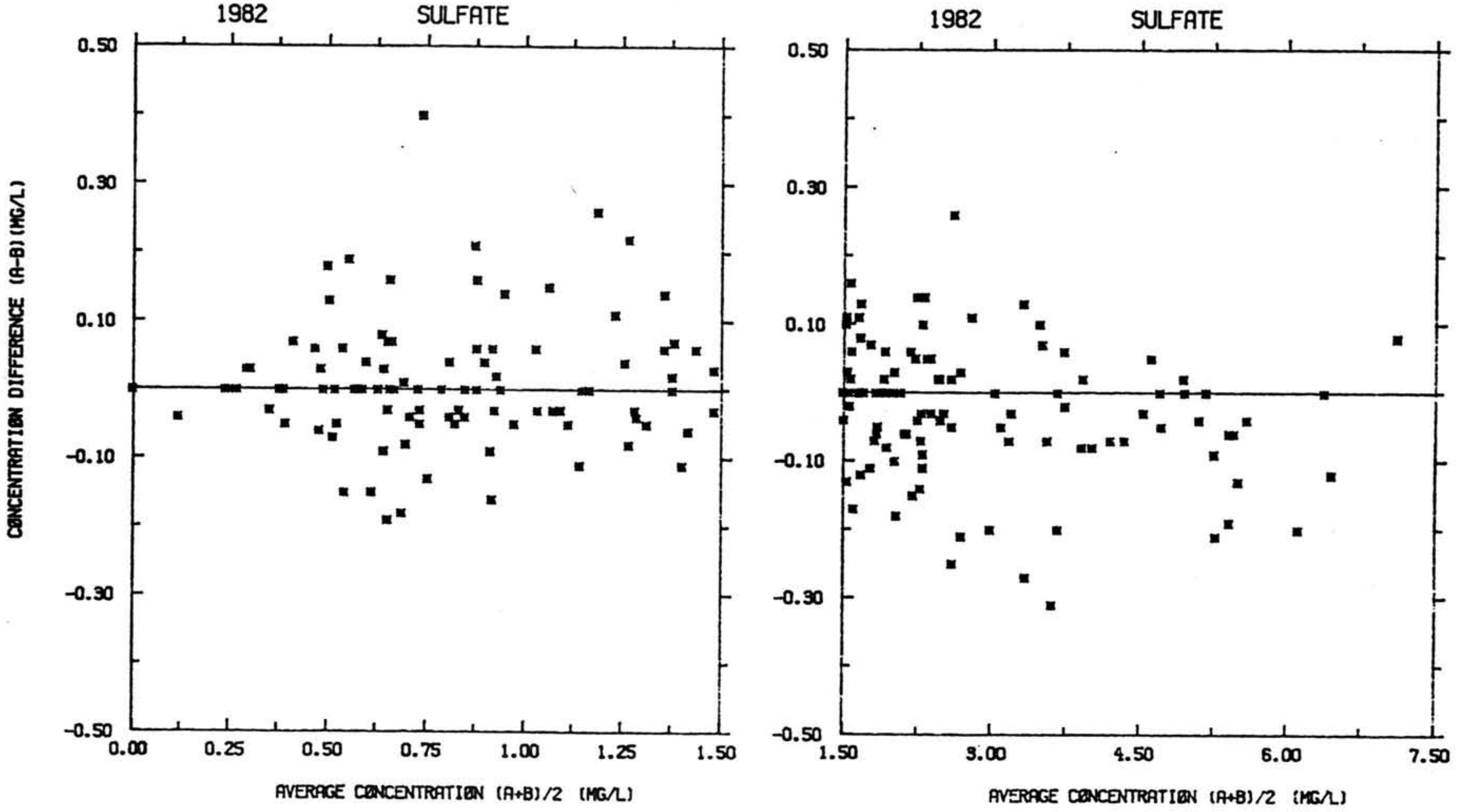


FIGURE 29. Replicate plots for sulfate for 1982.

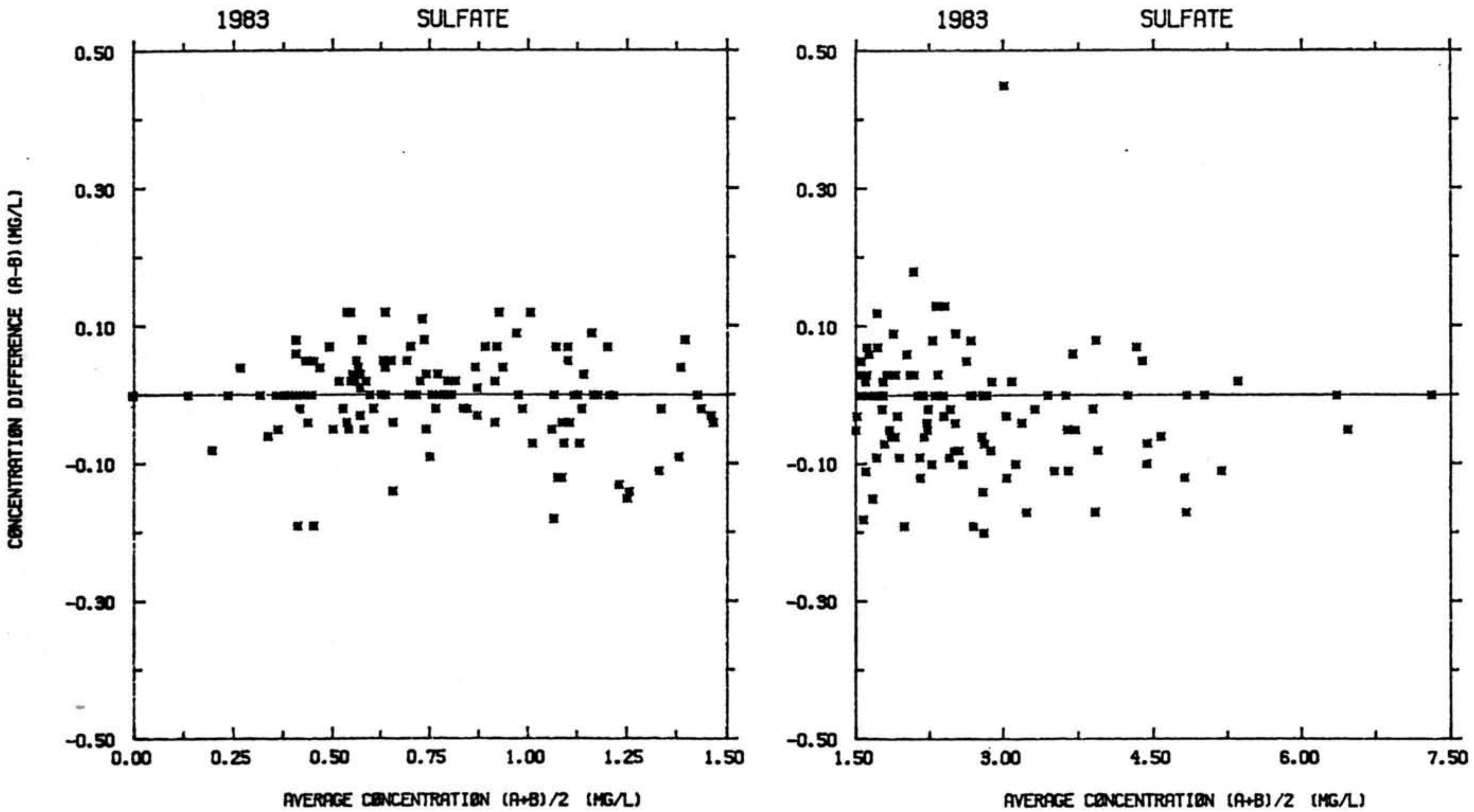


FIGURE 30. Replicate plots for sulfate for 1983.

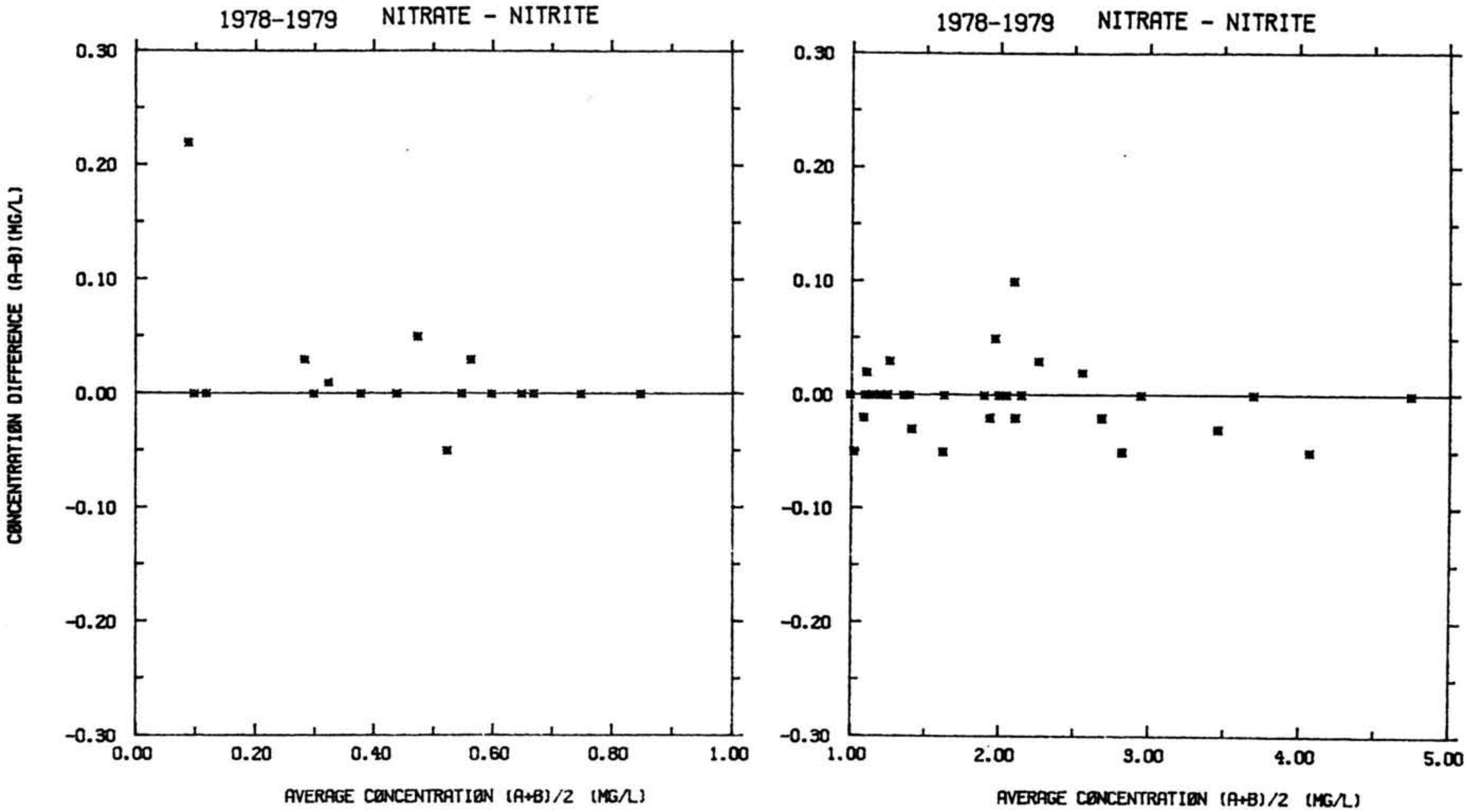


FIGURE 31. Replicate plots for nitrate-nitrite for 1978 and 1979.

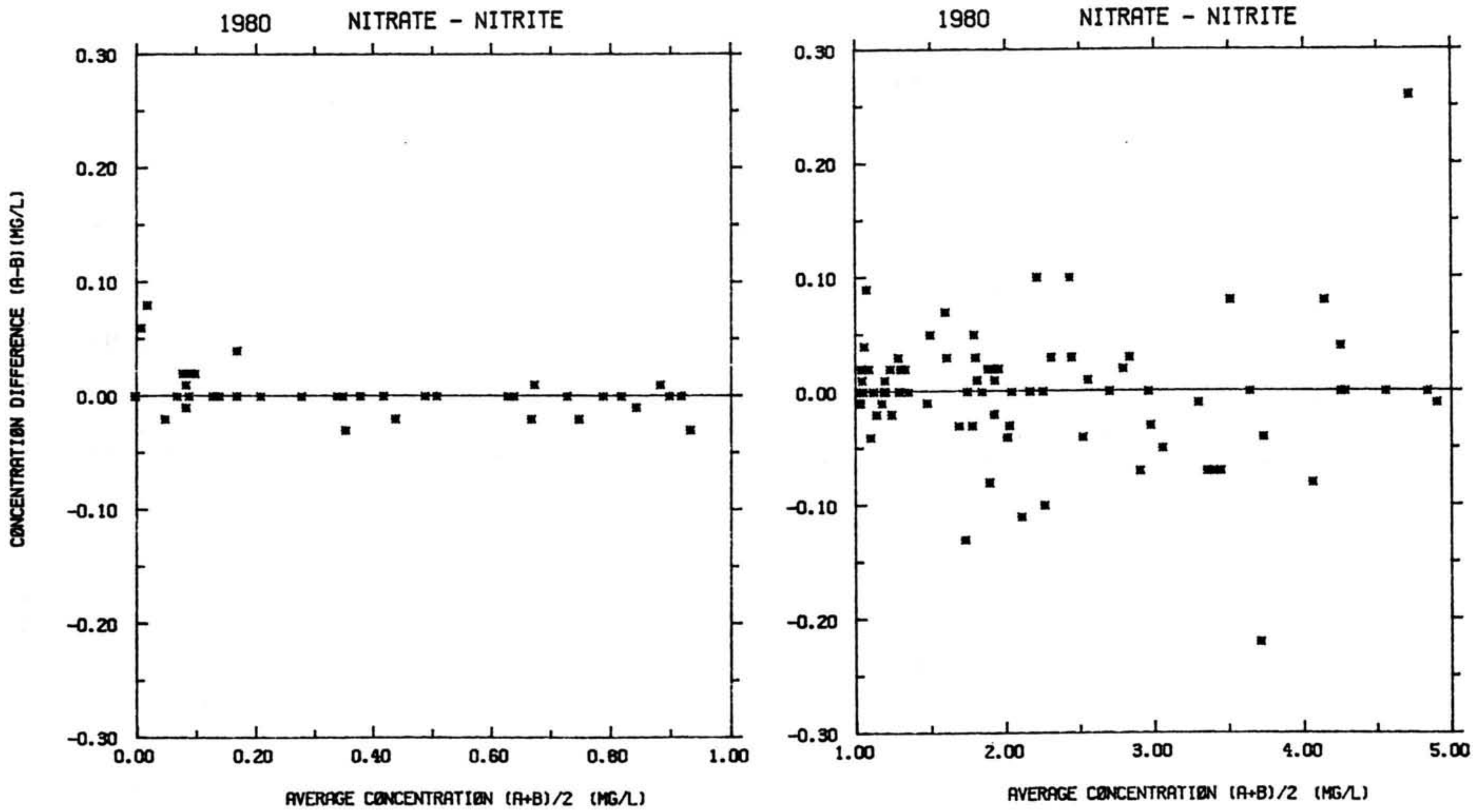


FIGURE 32. Replicate plots for nitrate-nitrite for 1980.

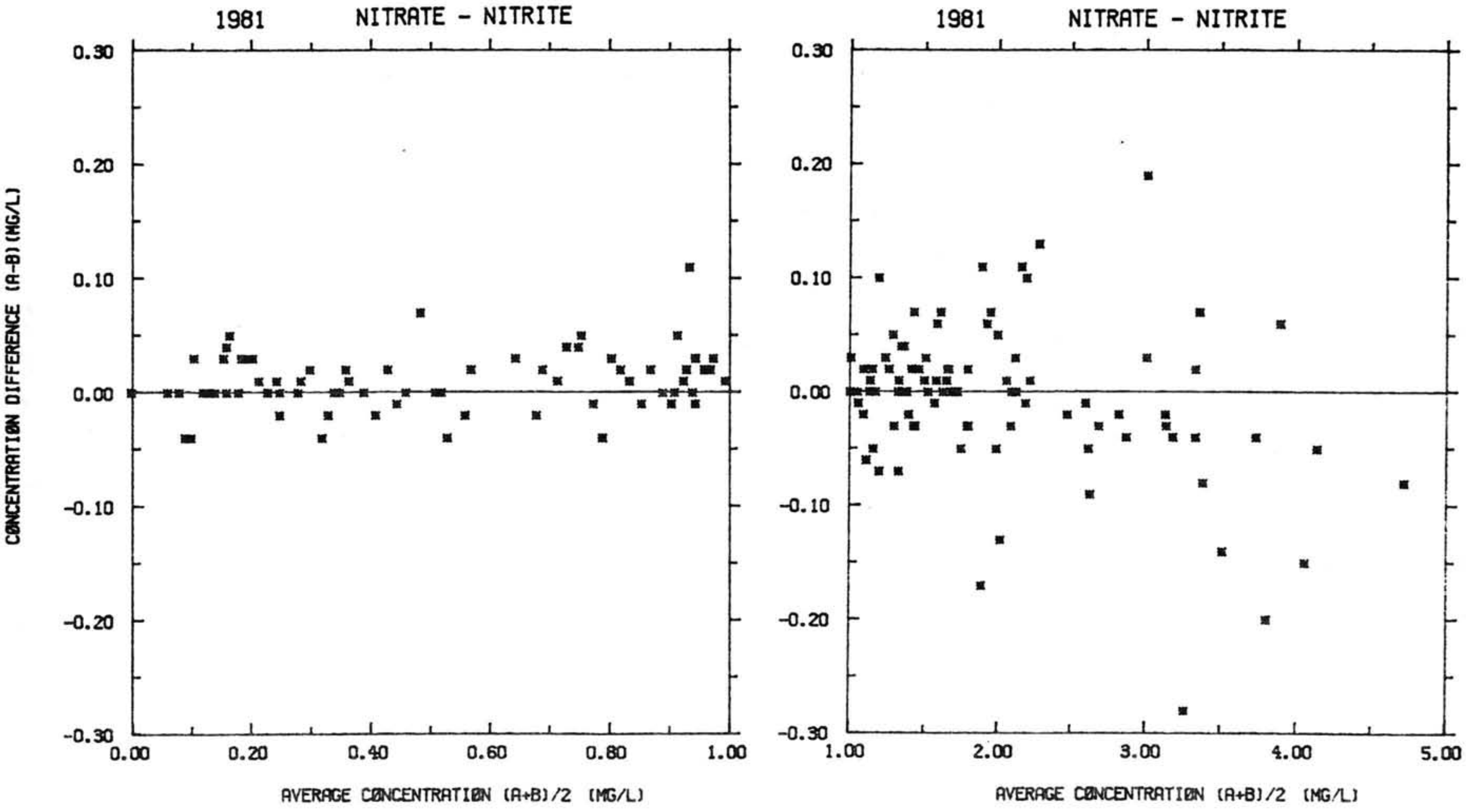


FIGURE 33. Replicate plots for nitrate-nitrite for 1981.

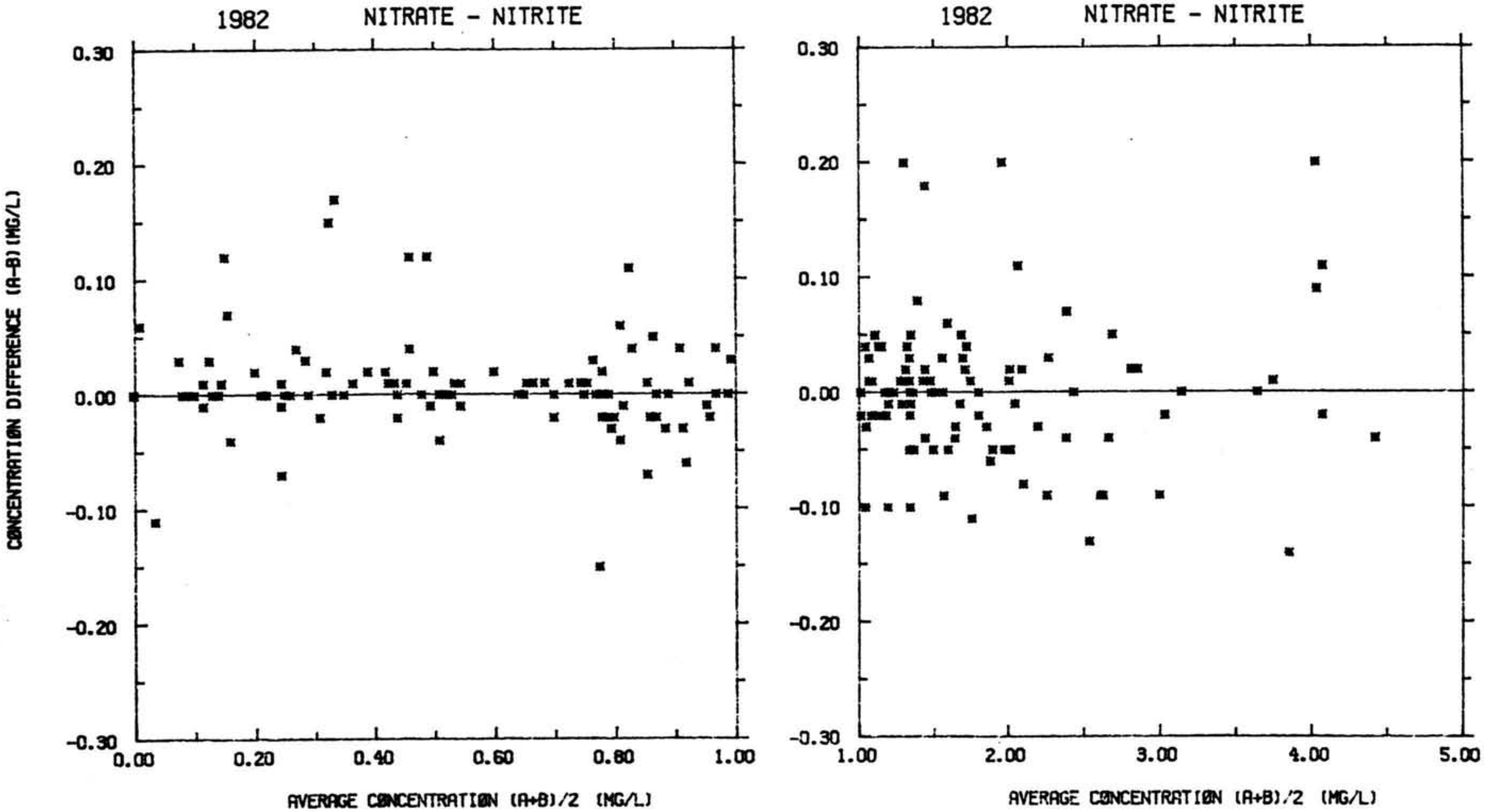


FIGURE 34. Replicate plots for nitrate-nitrite for 1982.

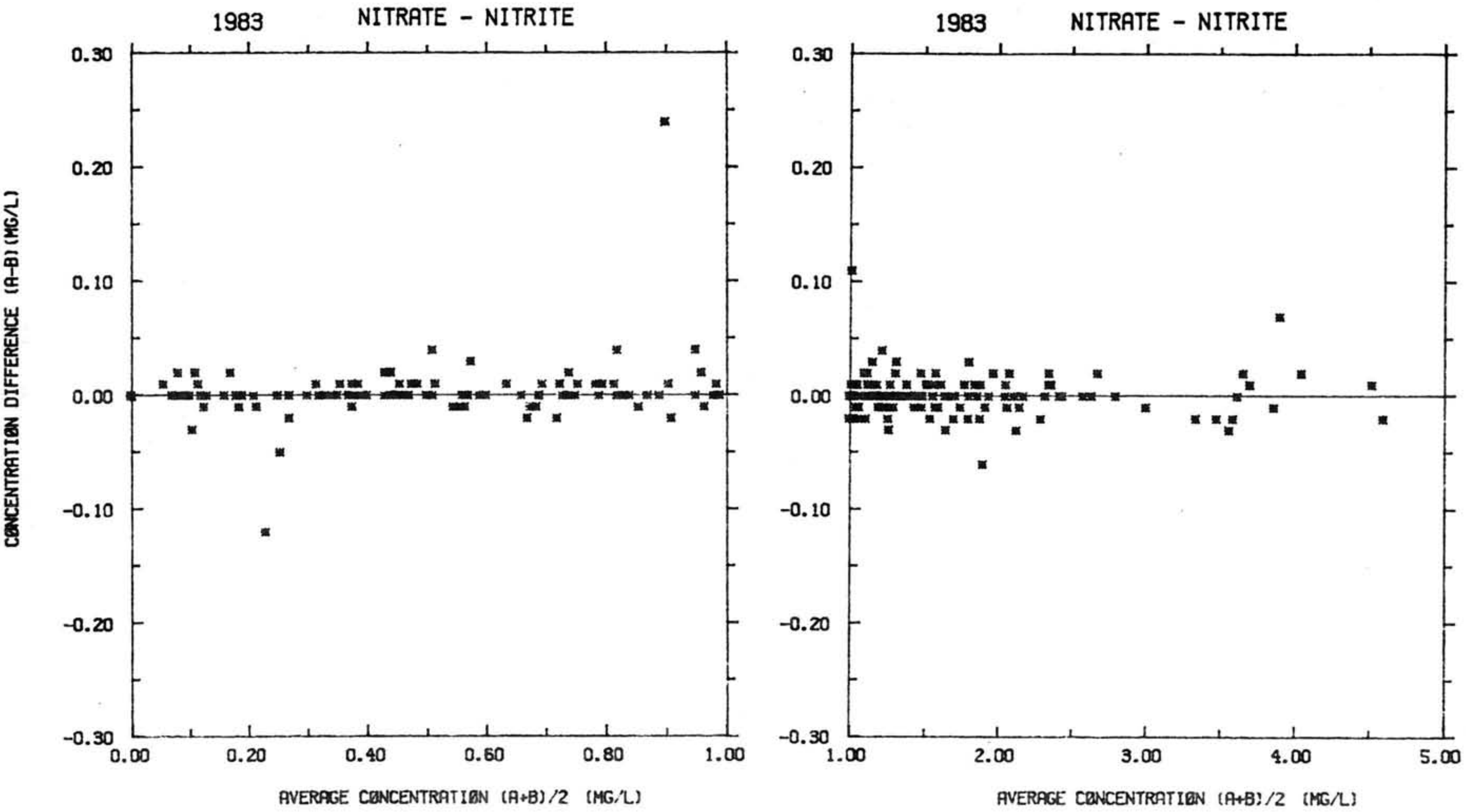


FIGURE 35. Replicate plots for nitrate-nitrite for 1983.

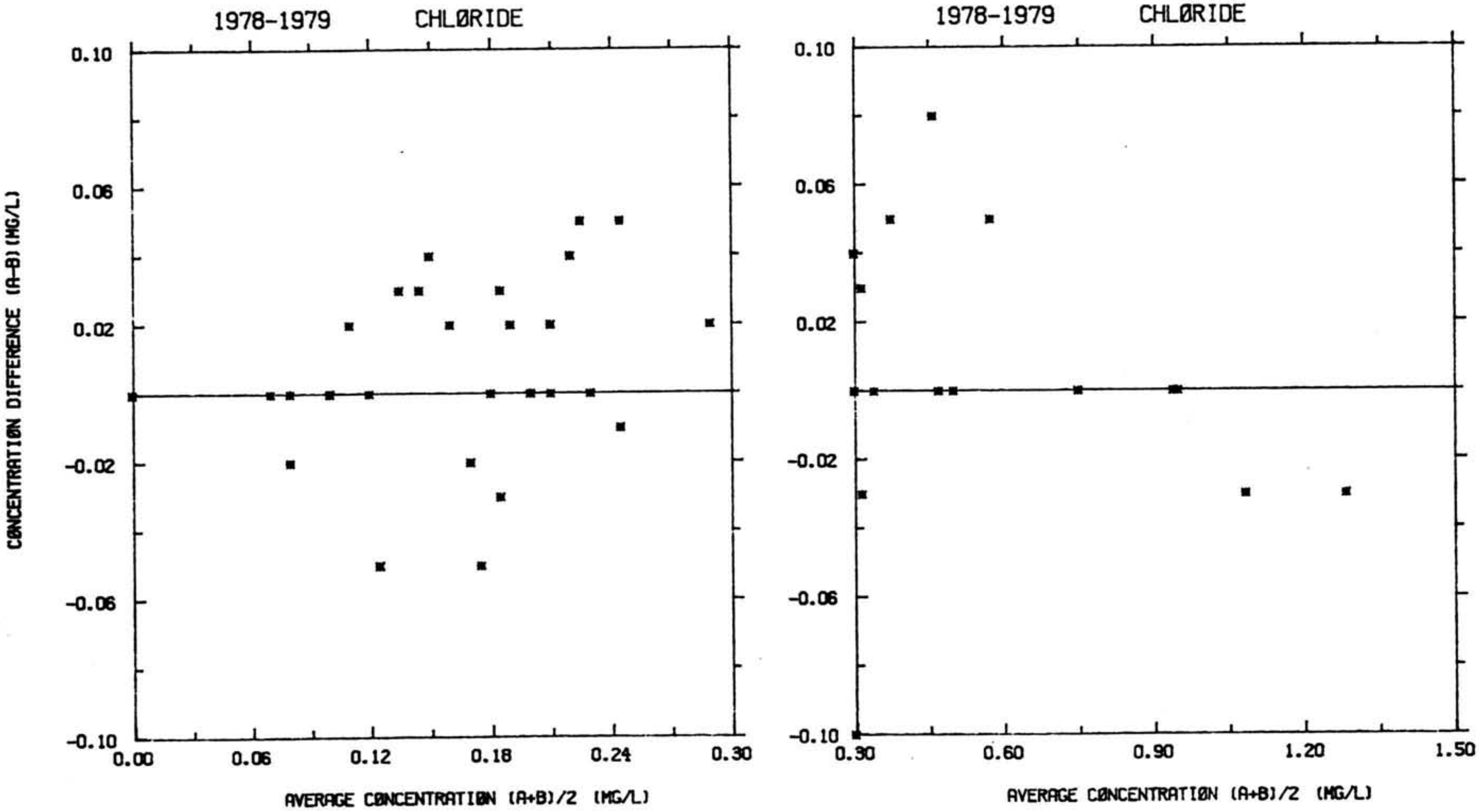


FIGURE 36. Replicate plots for chloride for 1978 and 1979.

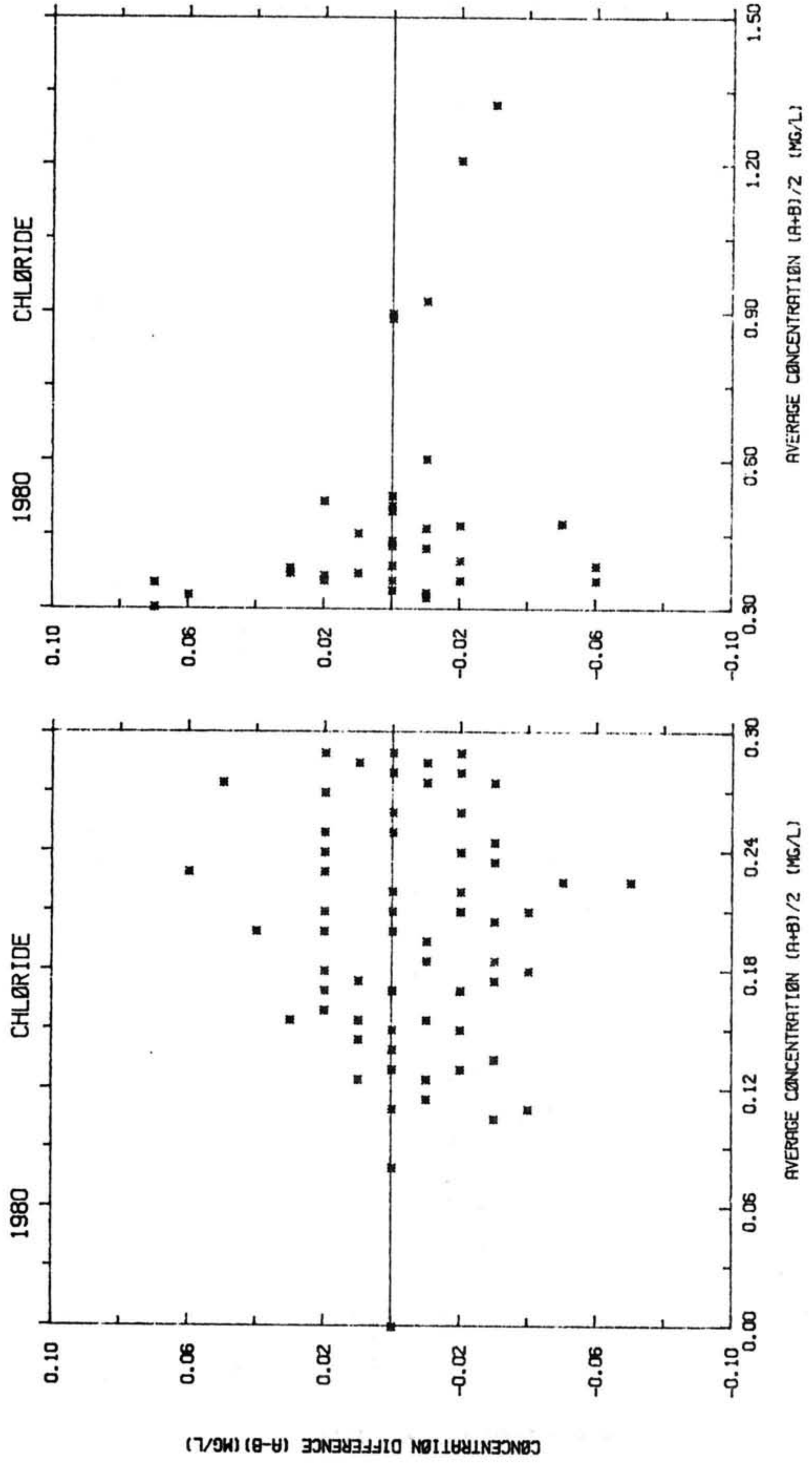


FIGURE 37. Replicate plots for chloride for 1980.

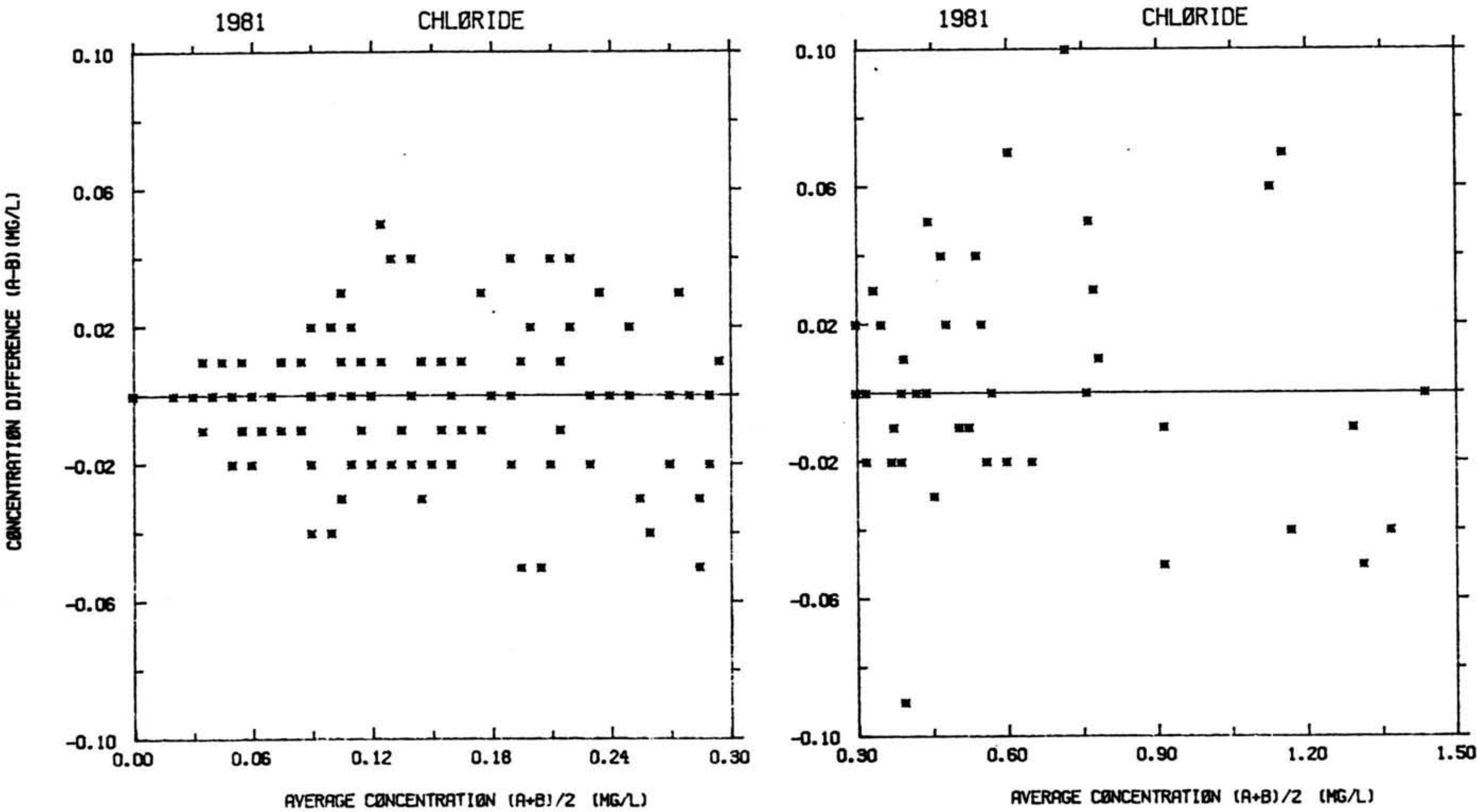


FIGURE 38. Replicate plots for chloride for 1981.

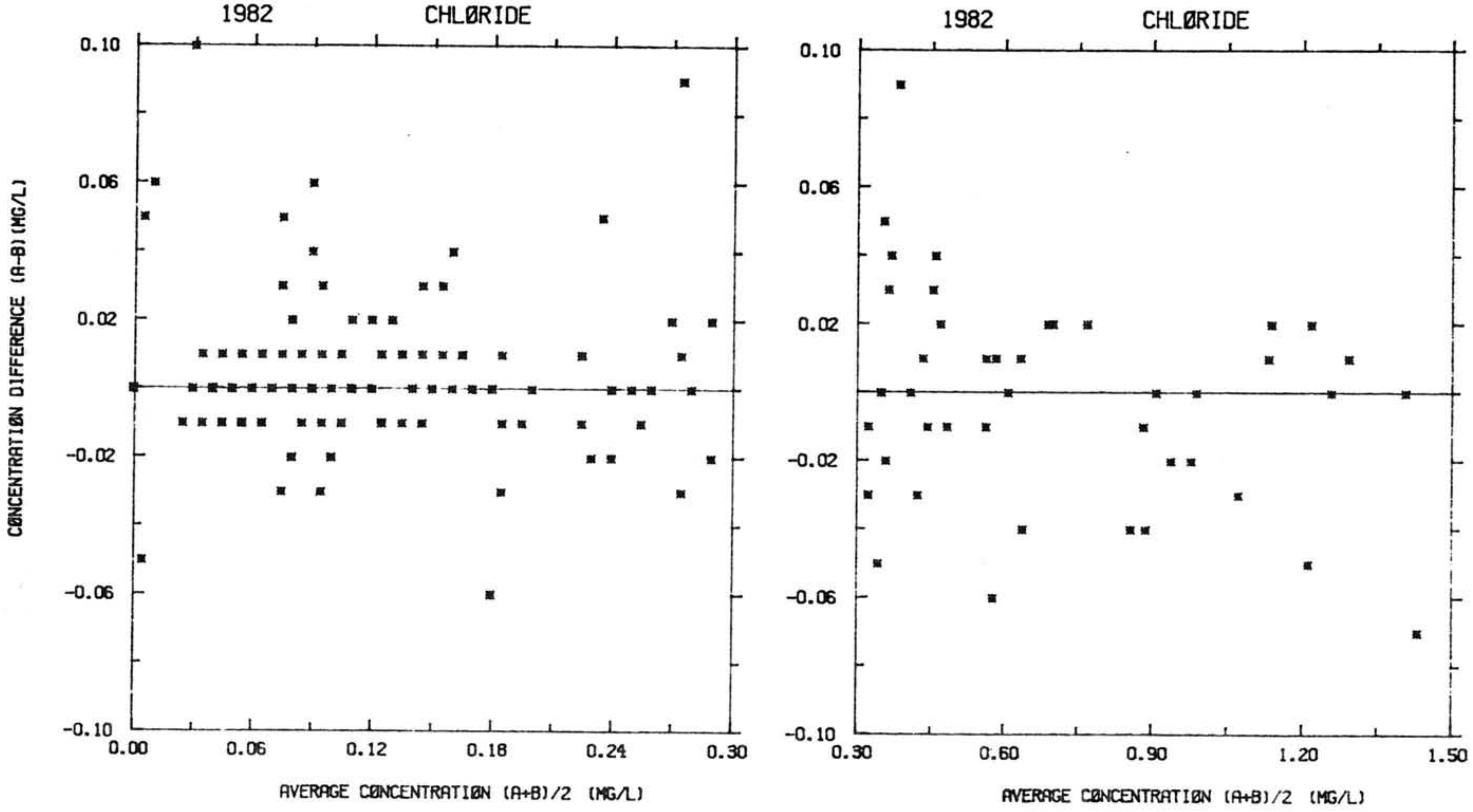


FIGURE 39. Replicate plots for chloride for 1982.

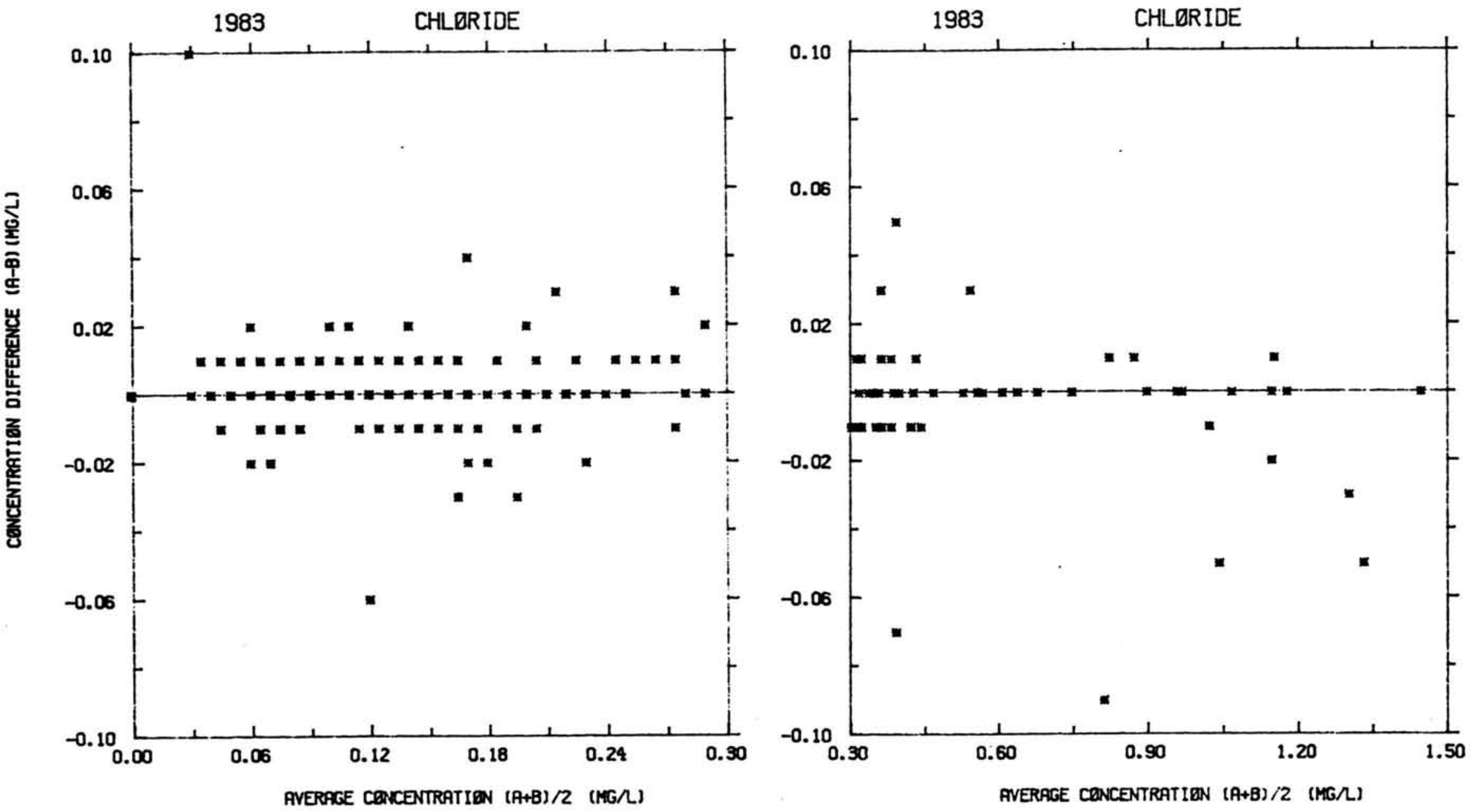


FIGURE 40. Replicate plots for chloride for 1983.

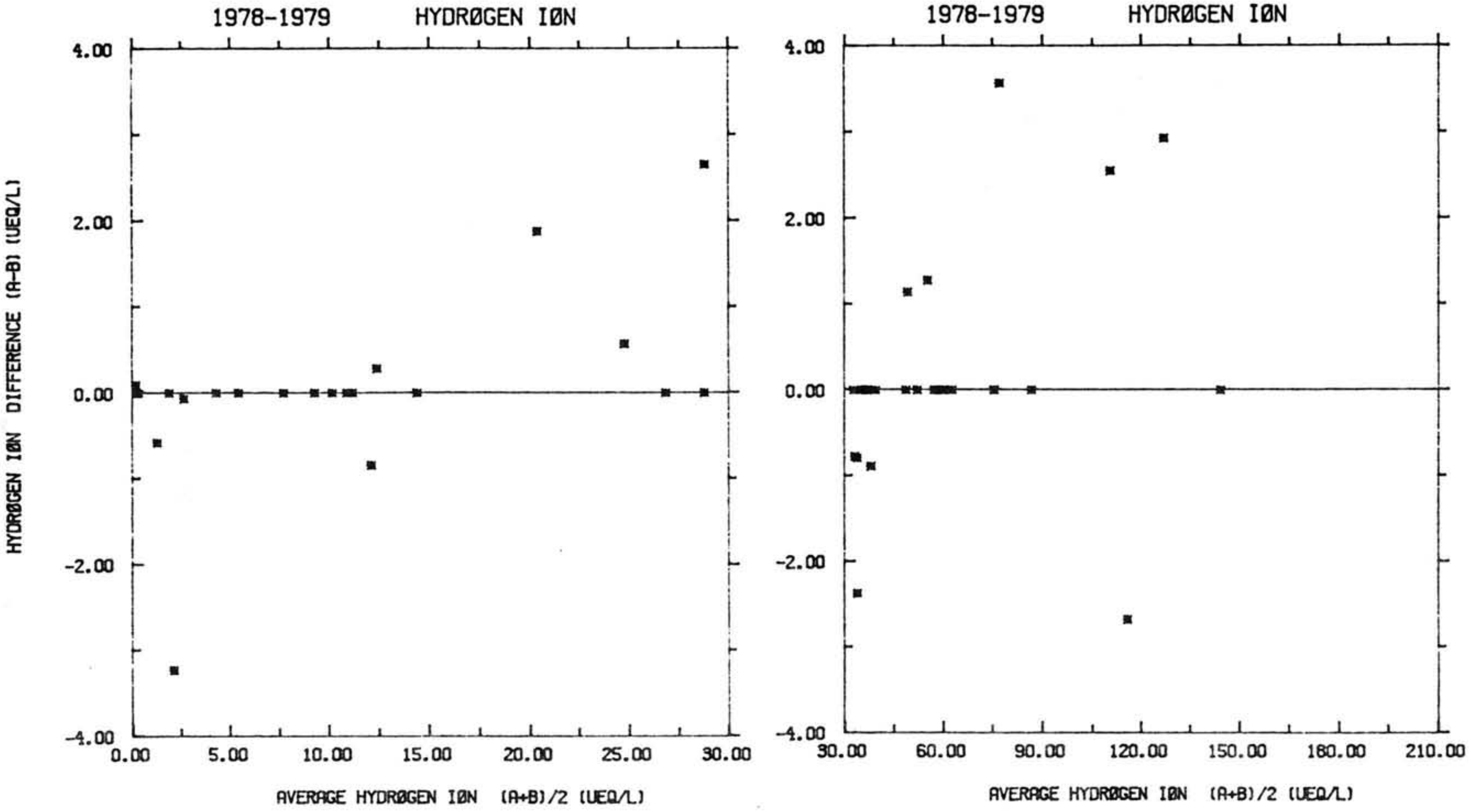


FIGURE 41. Replicate plots for hydrogen ion concentration for 1978 and 1979.

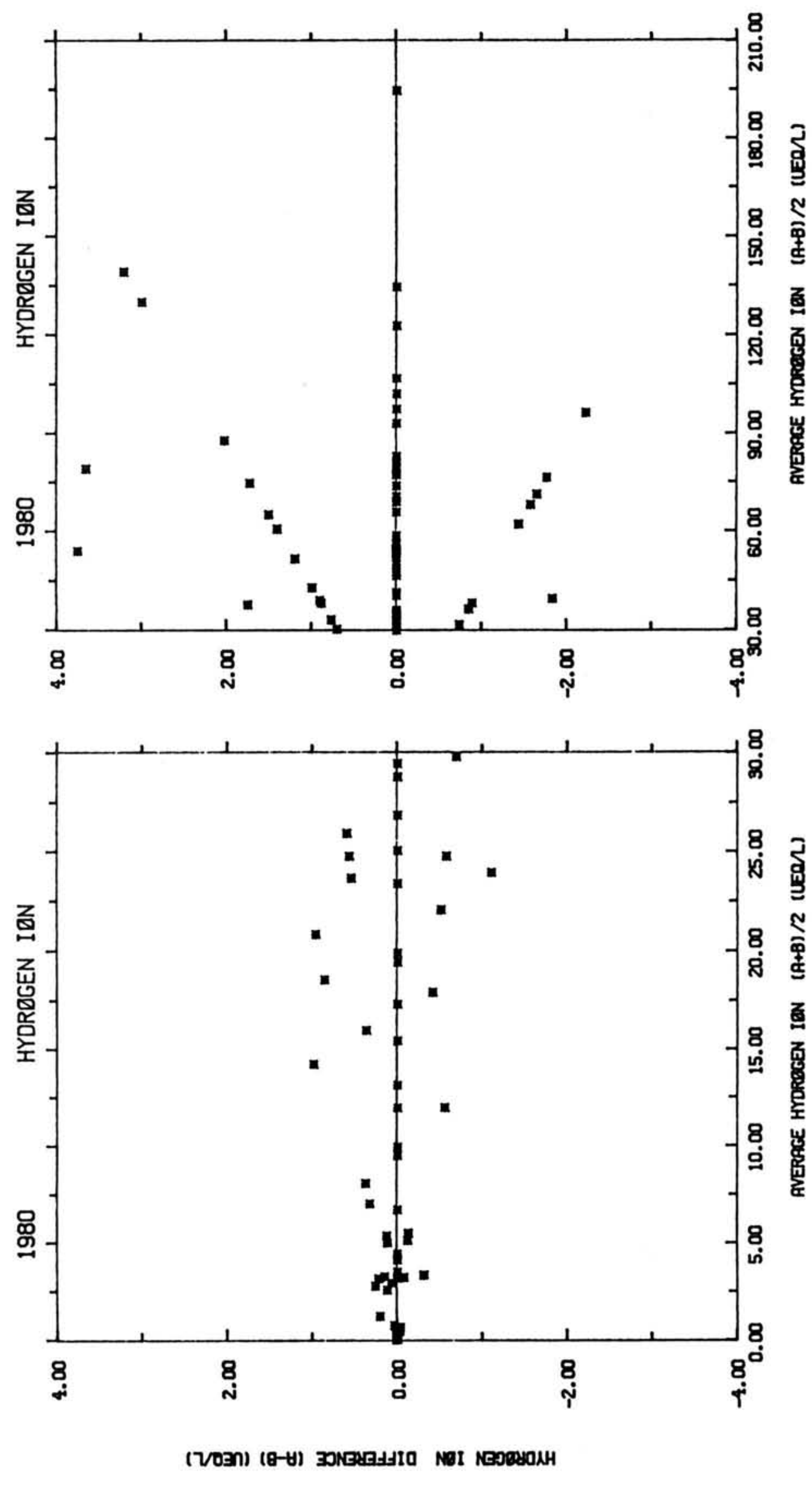


FIGURE 42. Replicate plots for hydrogen ion concentration for 1980.

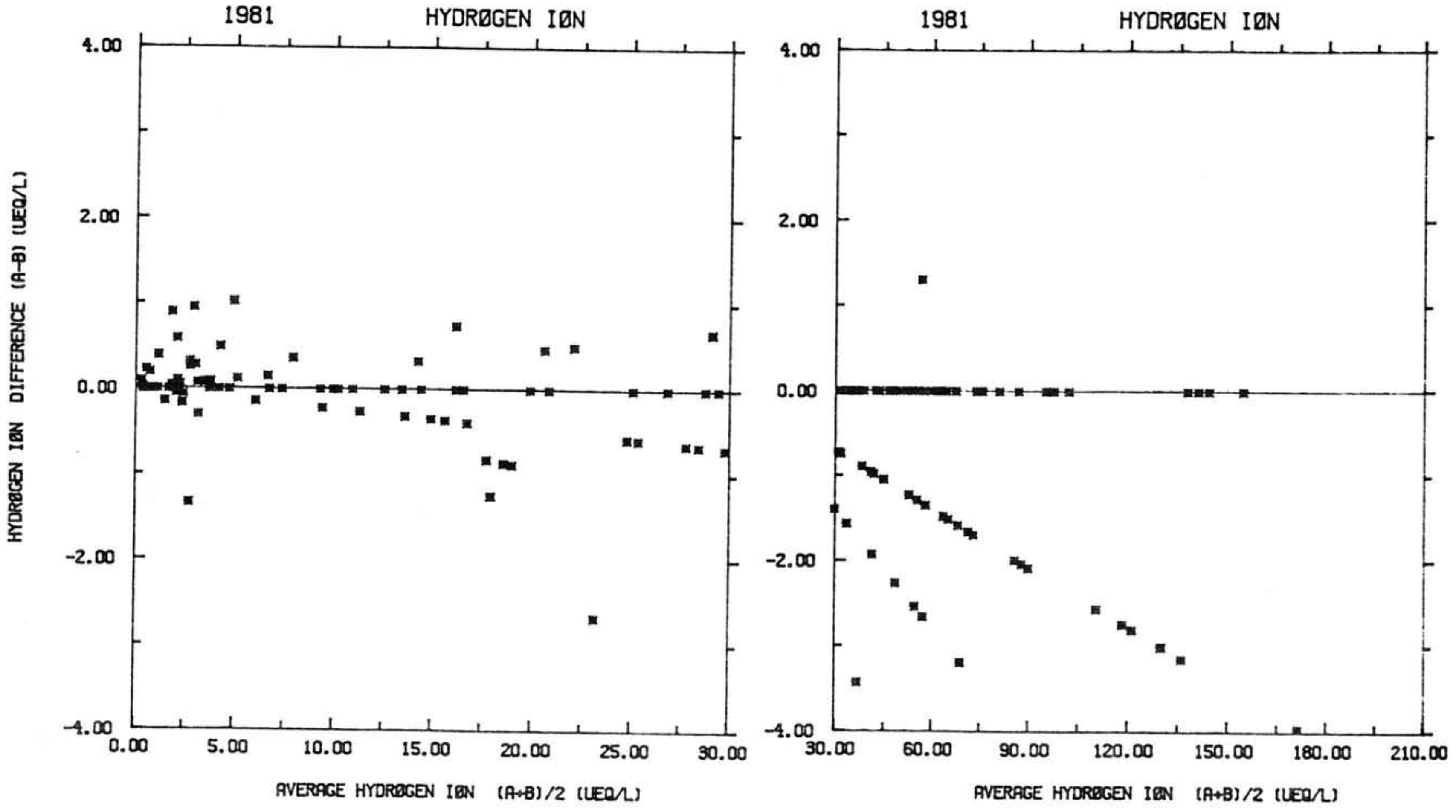


FIGURE 43. Replicate plots for hydrogen ion concentration for 1981.

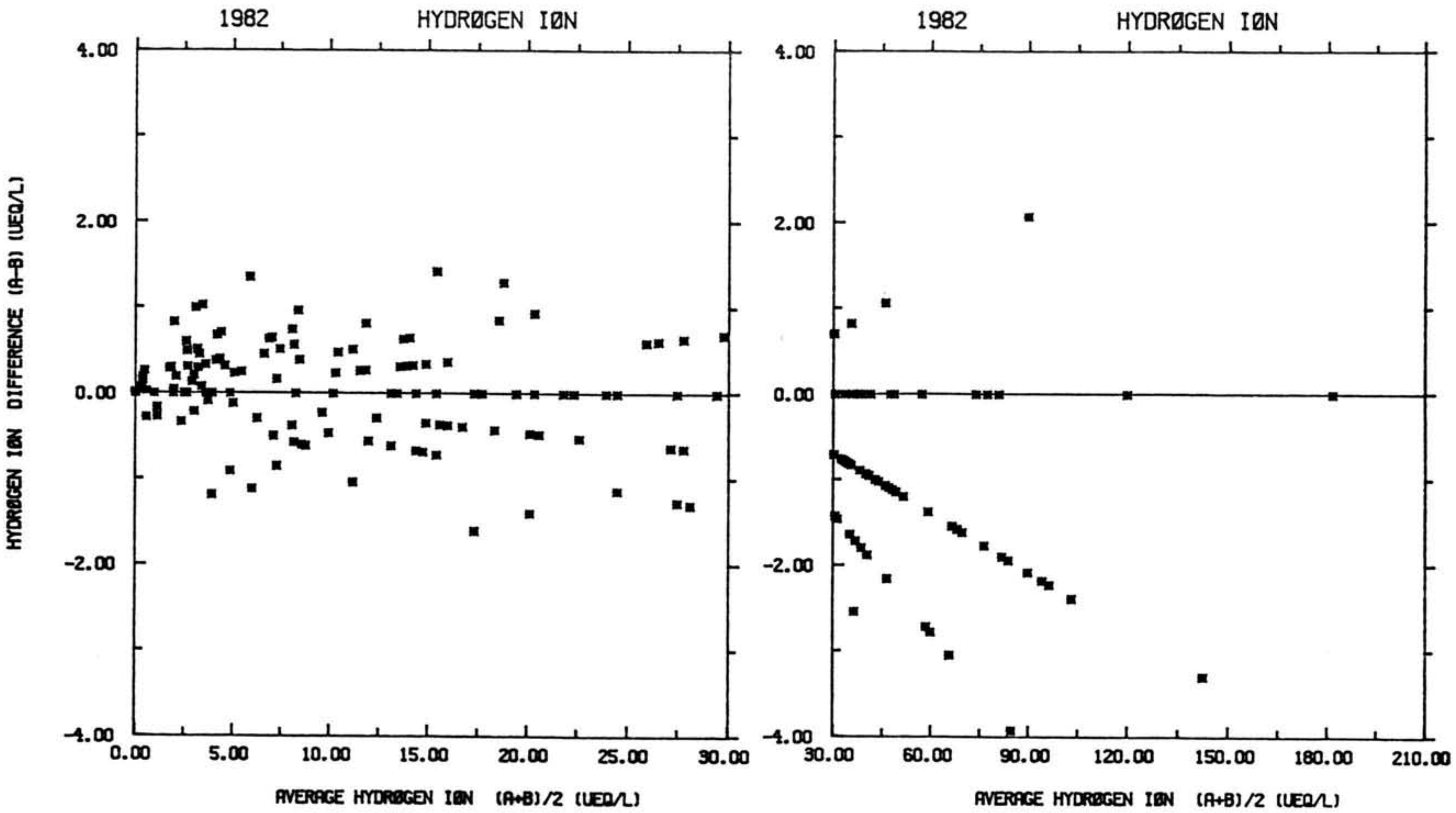


FIGURE 44. Replicate plots for hydrogen ion concentration for 1982.

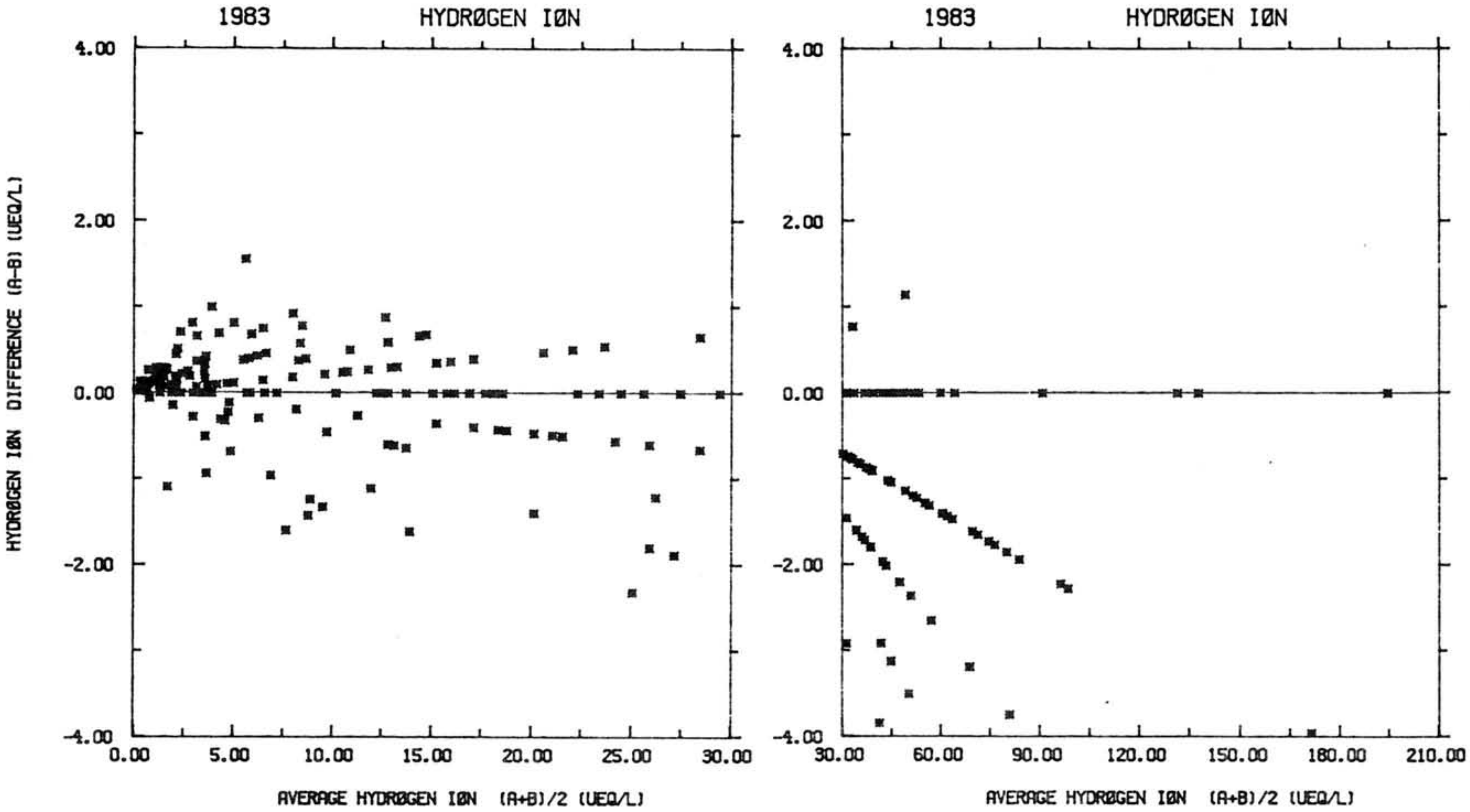


FIGURE 45. Replicate plots for hydrogen ion concentration for 1983.

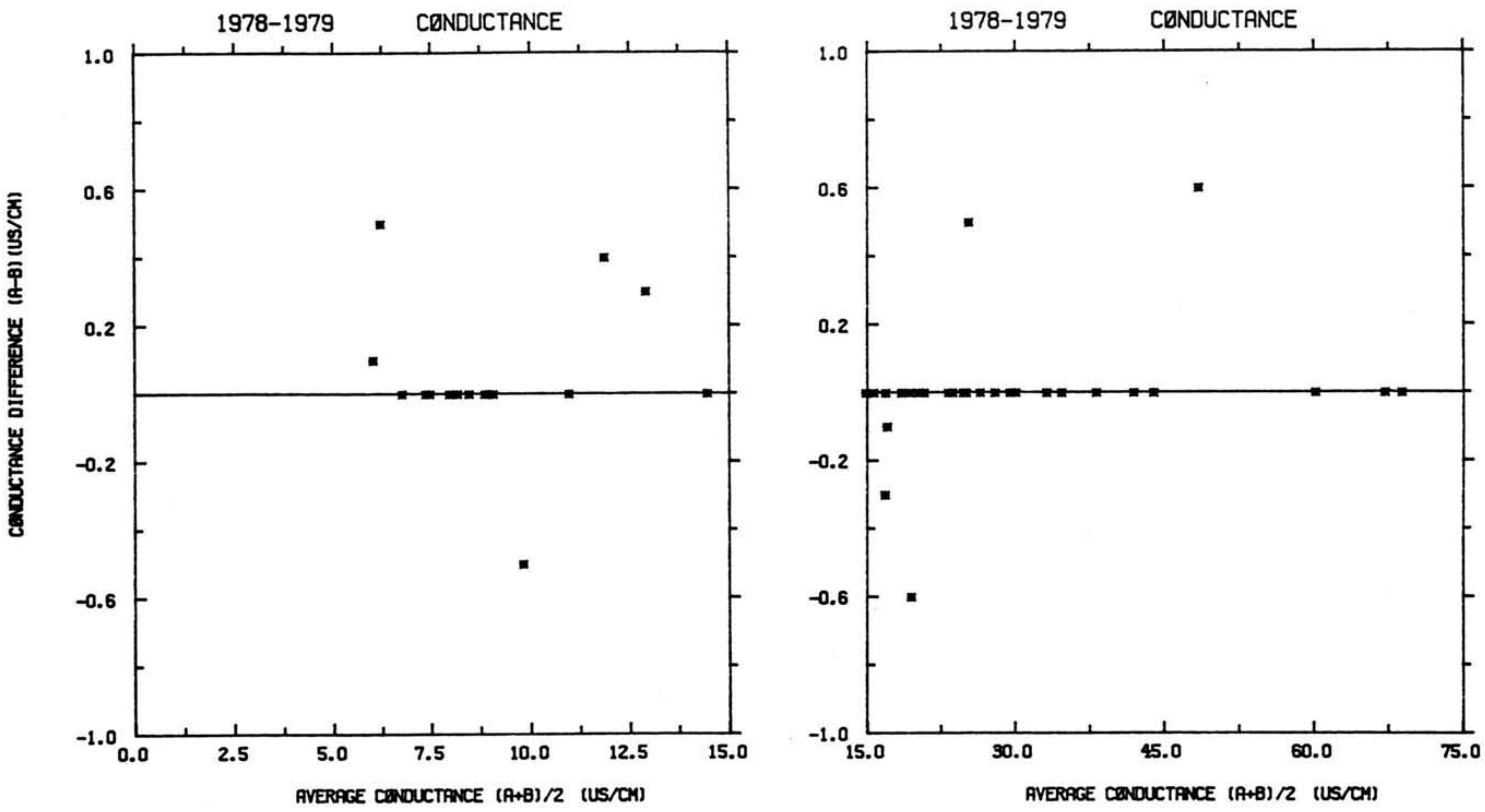


FIGURE 46. Replicate plots for specific conductance for 1978 and 1979.

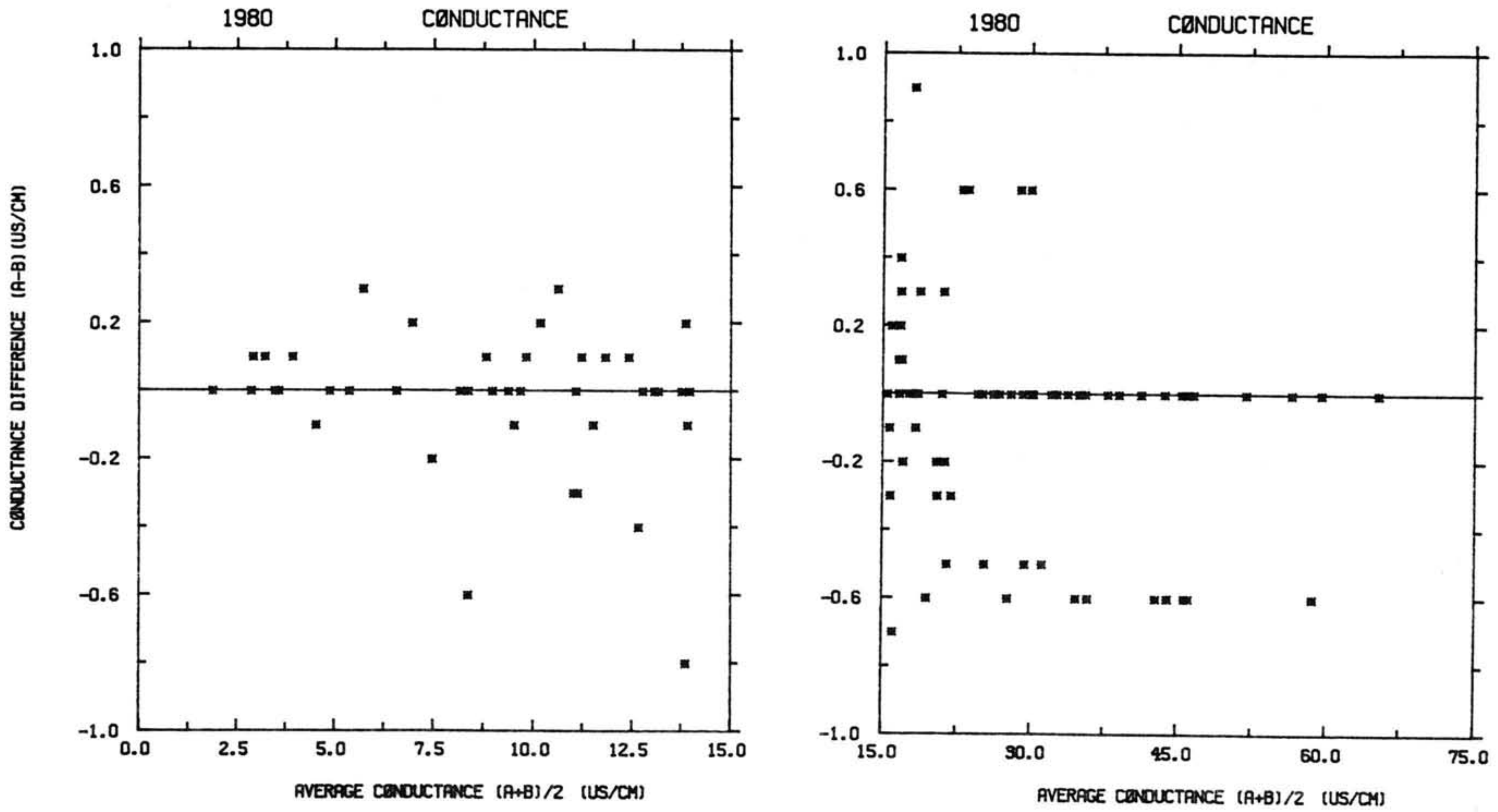


FIGURE 47. Replicate plots for specific conductance for 1980.

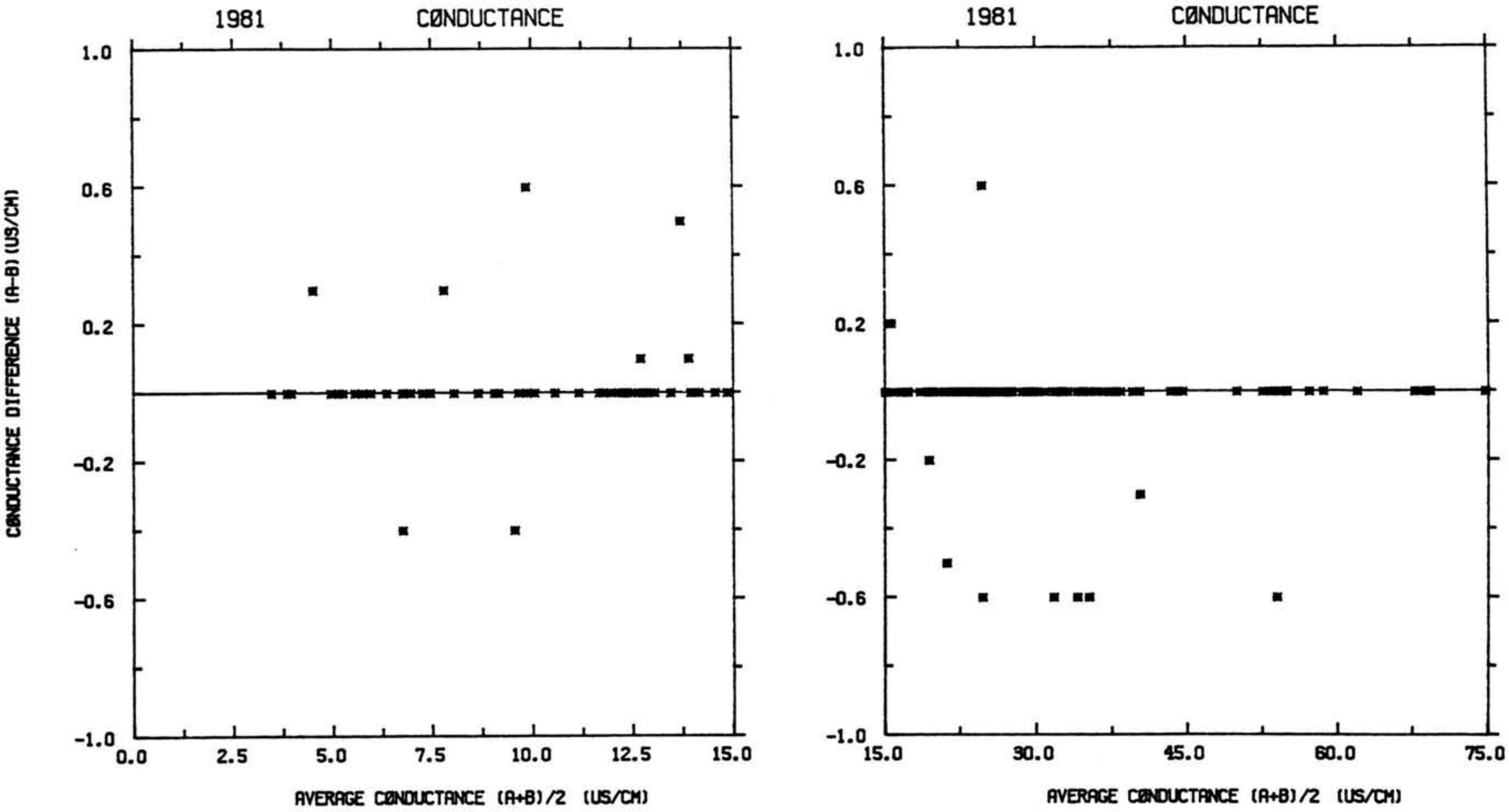


FIGURE 48. Replicate plots for specific conductance for 1981.

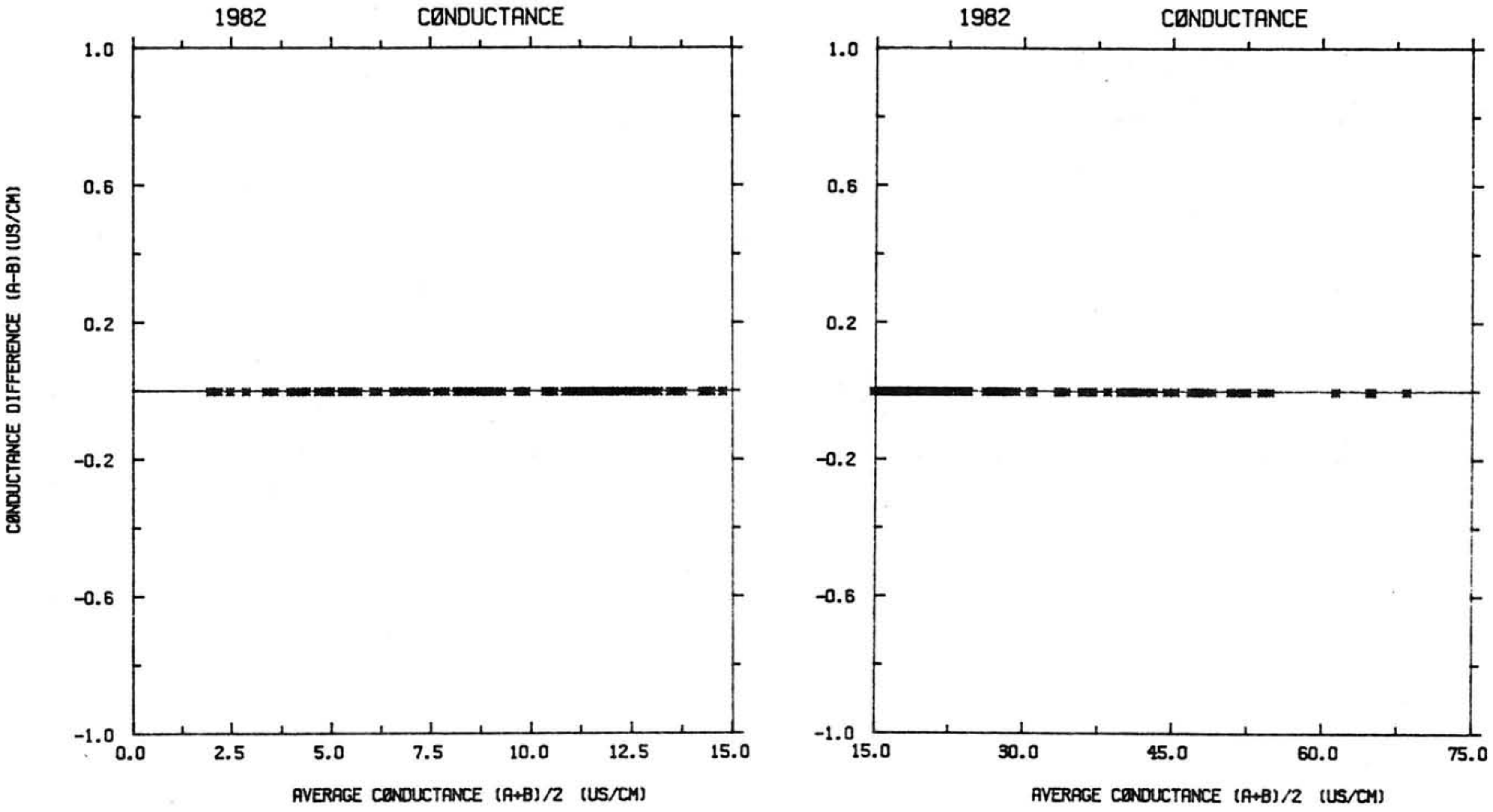


FIGURE 49. Replicate plots for specific conductance for 1982.

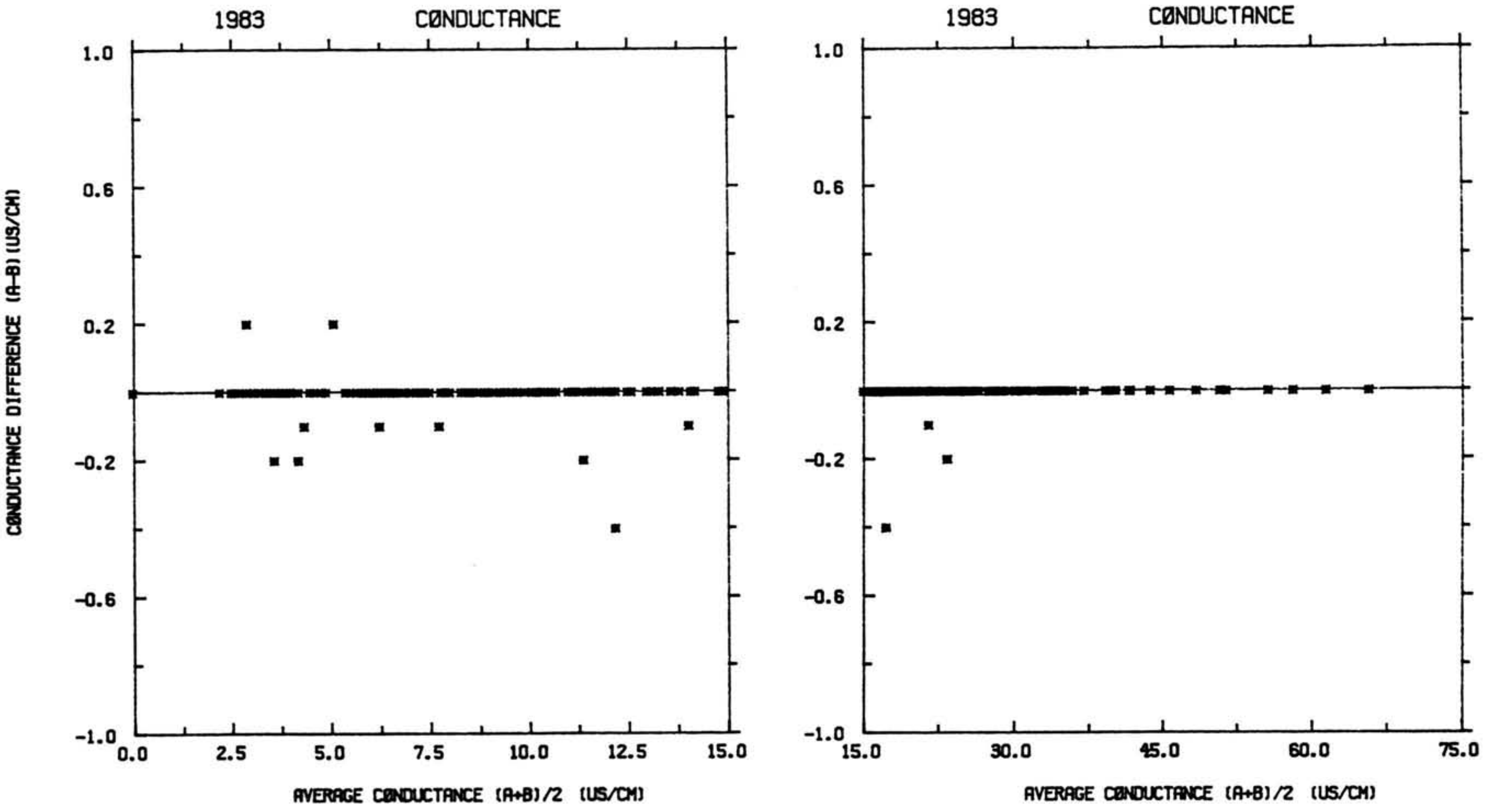


FIGURE 50. Replicate plots for specific conductance for 1983.

TABLE 1 (A-B) Data Summary for Replicate Analysis in 1978 and 1979.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	54	0.000	0.001	0.006
Magnesium	54	0.000	0.000	0.001
Sodium	54	0.000	-0.001	0.005
Potassium	54	0.000	0.000	0.002
Ammonium	54	0.00	-0.01	0.02
Sulfate	54	0.00	0.00	0.08
Nitrate-Nitrite	54	0.00	0.00	0.04
Chloride	54	0.00	0.00	0.04
pH (units)	54	0.00	0.01	0.12
Specific Conductance (uS/cm)	54	0.0	-0.2	0.9

a. number of replicate pairs

TABLE 2 (A-B) Data Summary for Replicate Analysis in 1980.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	125	0.000	0.000	0.008
Magnesium	125	0.000	0.000	0.001
Sodium	125	0.000	0.000	0.008
Potassium	125	0.000	0.000	0.002
Ammonium	125	0.00	0.00	0.01
Sulfate	125	0.00	0.00	0.08
Nitrate-Nitrite	125	0.00	0.00	0.06
Chloride	125	0.00	0.00	0.03
pH (units)	125	0.00	0.01	0.02
Specific Conductance (uS/cm)	125	0.0	-0.1	0.6

a. number of replicate pairs

TABLE 3 (A-B) Data Summary for Replicate Analysis in 1981.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	175	0.000	0.000	0.009
Magnesium	175	0.000	0.000	0.002
Sodium	175	0.000	-0.001	0.005
Potassium	175	0.000	0.000	0.003
Ammonium	175	0.00	0.00	0.02
Sulfate	175	0.00	0.00	0.10
Nitrate-Nitrite	175	0.00	0.00	0.06
Chloride	175	0.00	0.00	0.03
pH (units)	175	0.00	-0.01	0.05
Specific Conductance (uS/cm)	175	0.0	0.0	0.3

a. number of replicate pairs

TABLE 4 (A-B) Data Summary for Replicate Analysis in 1982.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	212	0.000	-0.001	0.007
Magnesium	212	0.000	0.000	0.002
Sodium	212	0.000	0.000	0.012
Potassium.	212	0.000	0.000	0.003
Ammonium	212	0.00	0.00	0.02
Sulfate	212	0.00	-0.01	0.14
Nitrate-Nitrite	212	0.00	0.01	0.06
Chloride	212	0.00	0.00	0.03
pH (units)	212	0.00	0.00	0.04
Specific Conductance (uS/cm)	212	0.0	0.0	0.0

a. number of replicate pairs

TABLE 5 (A-B) Data Summary for Replicate Analysis in 1983.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	255	0.001	0.001	0.008
Magnesium	255	0.000	0.000	0.002
Sodium	255	0.000	0.001	0.019
Potassium	255	0.000	0.000	0.002
Ammonium	255	0.00	0.01	0.05
Sulfate	255	0.00	-0.01	0.08
Nitrate-Nitrite	255	0.00	0.00	0.09
Chloride	255	0.00	0.00	0.07
pH (units)	255	0.00	-0.01	0.04
Specific Conductance (uS/cm)	255	0.0	0.0	0.1

[a] number of replicate pairs

APPENDIX F

Ion Percent Difference and Conductance Percent Difference Histograms for 1978-1982

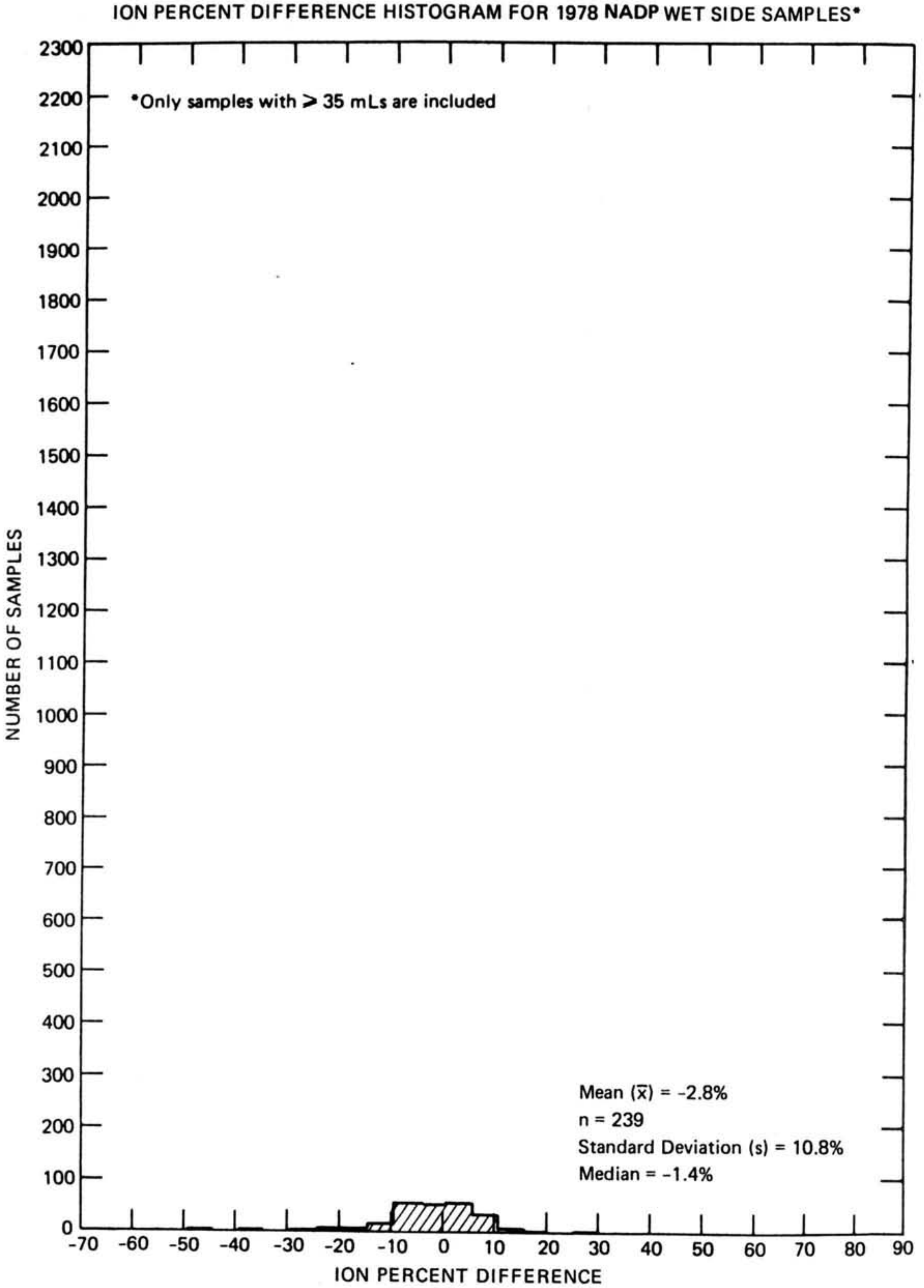


FIGURE 1. Ion percent difference histogram for NADP/NTN wet side samples in 1978.

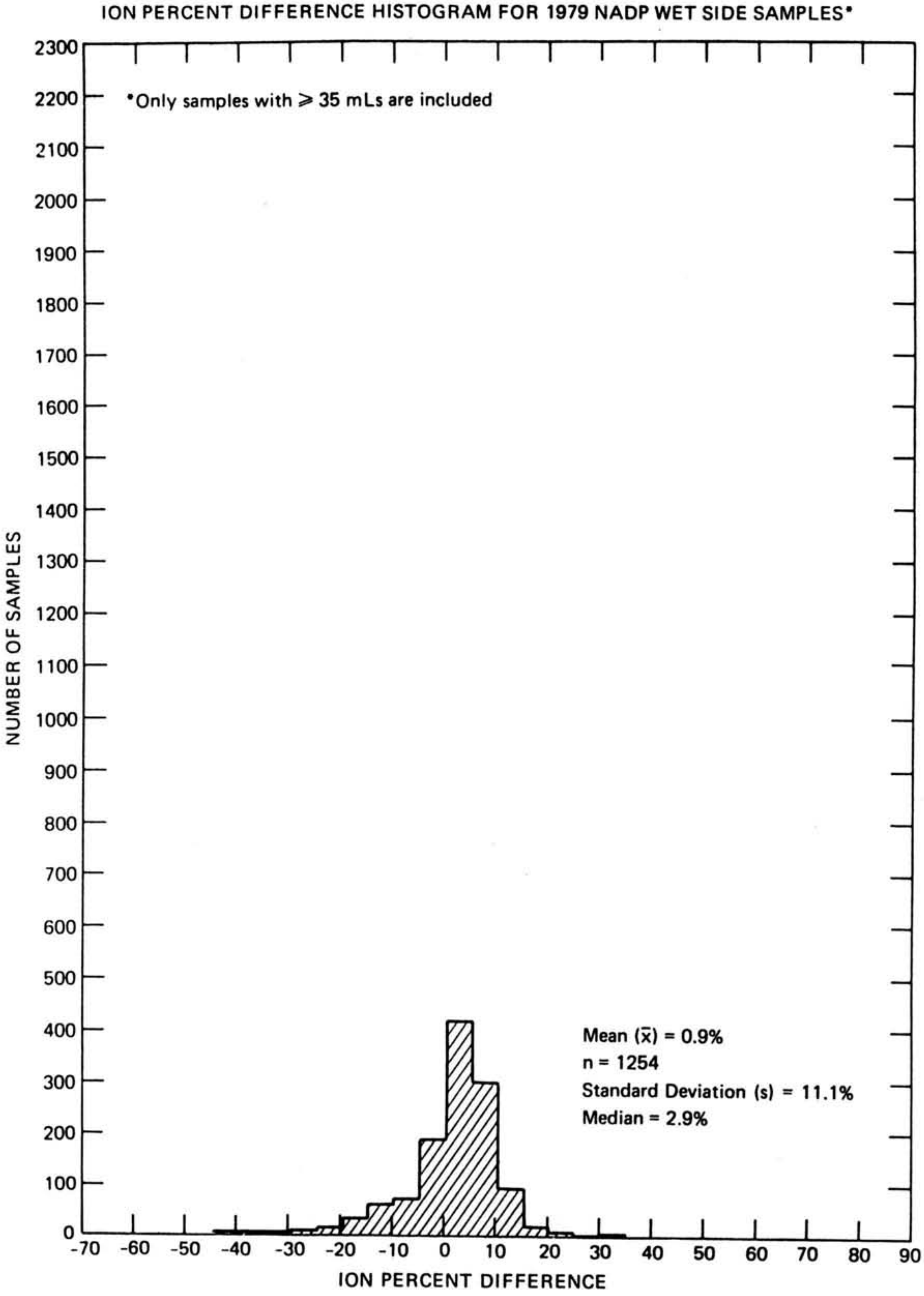


FIGURE 2. Ion percent difference histogram for NADP/NTN wet side samples in 1979.

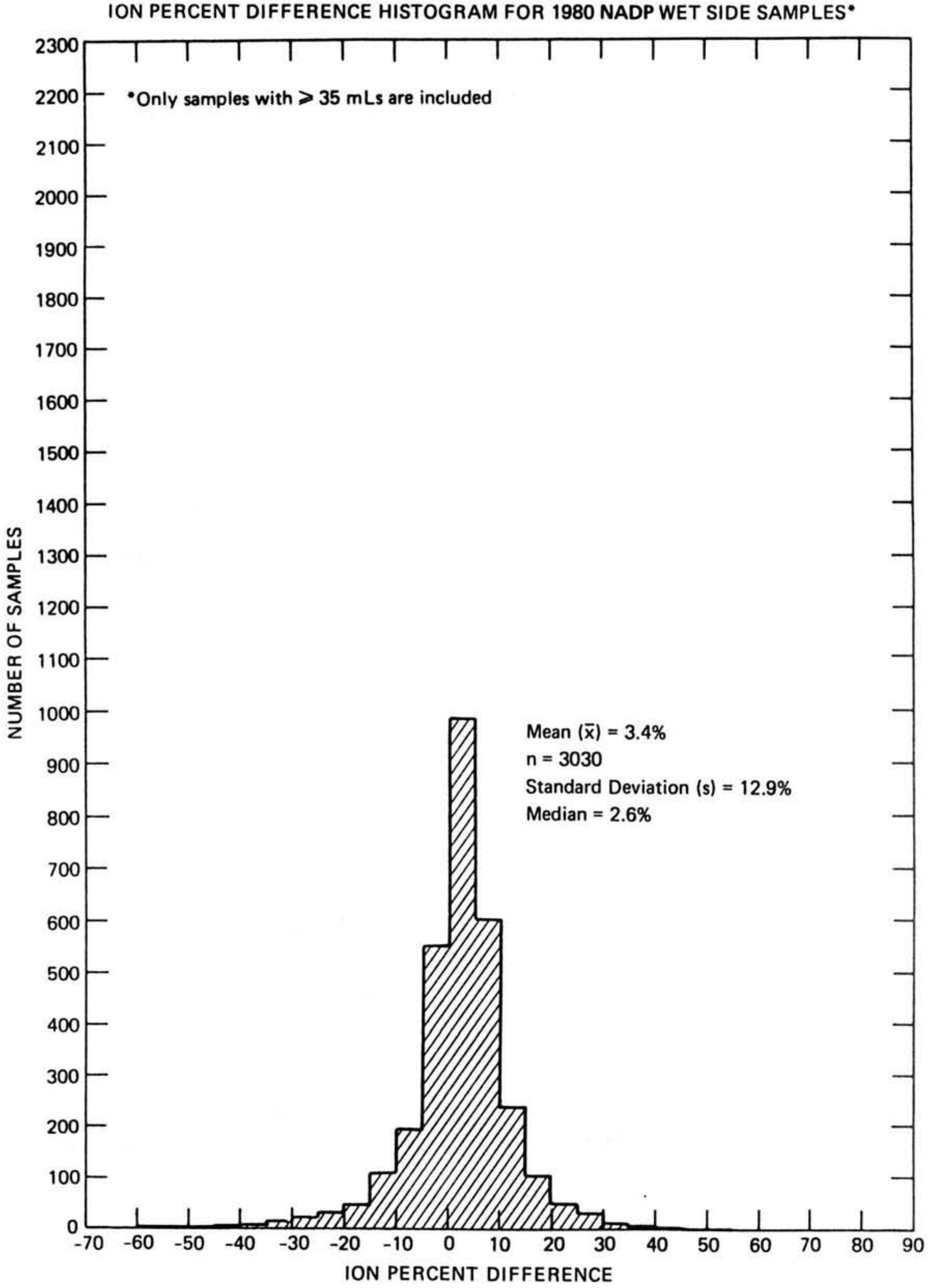


FIGURE 3. Ion percent difference histogram for NADP/NTN wet side samples in 1980.

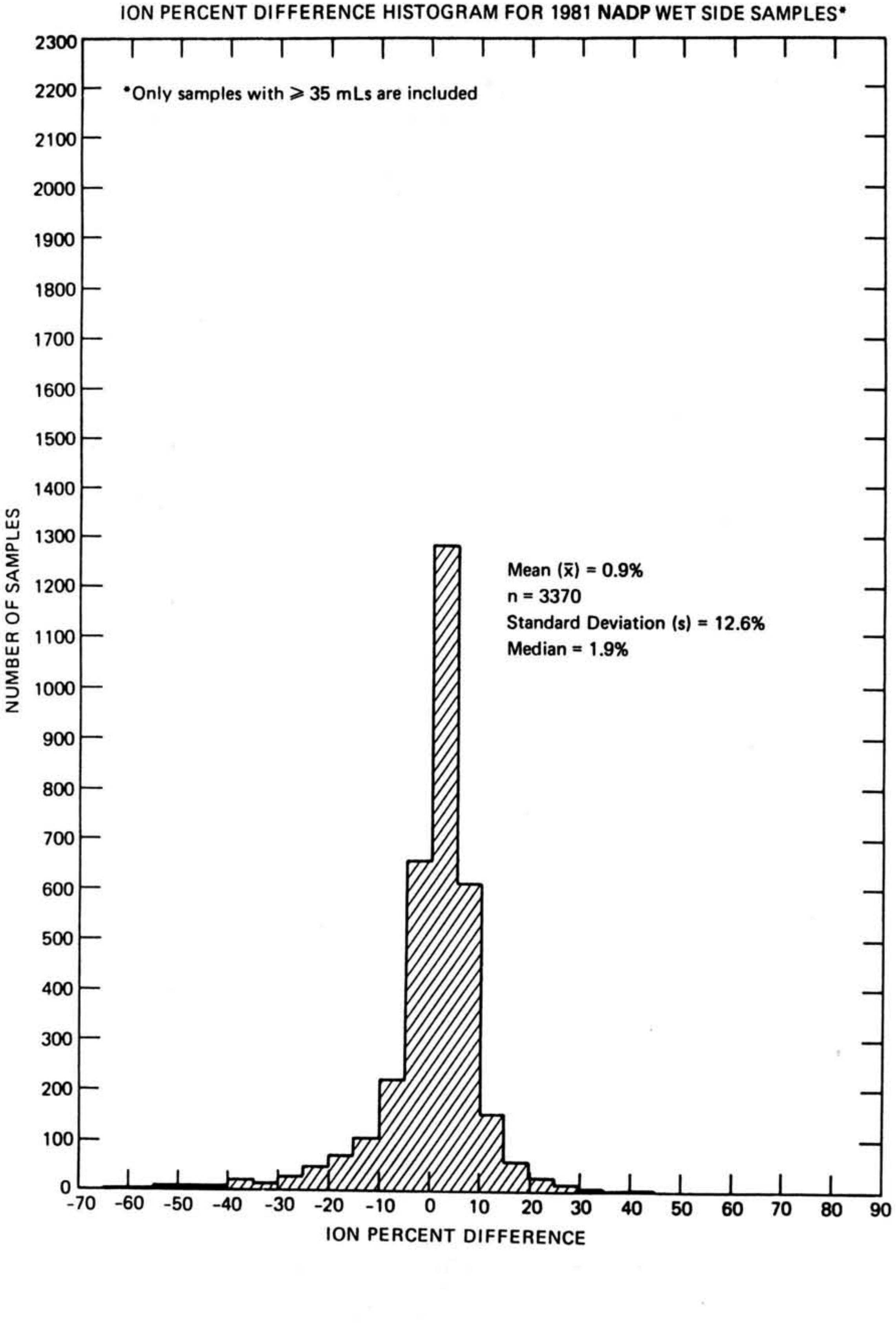


FIGURE 4. Ion percent difference histogram for NADP/NTN wet side samples in 1981.

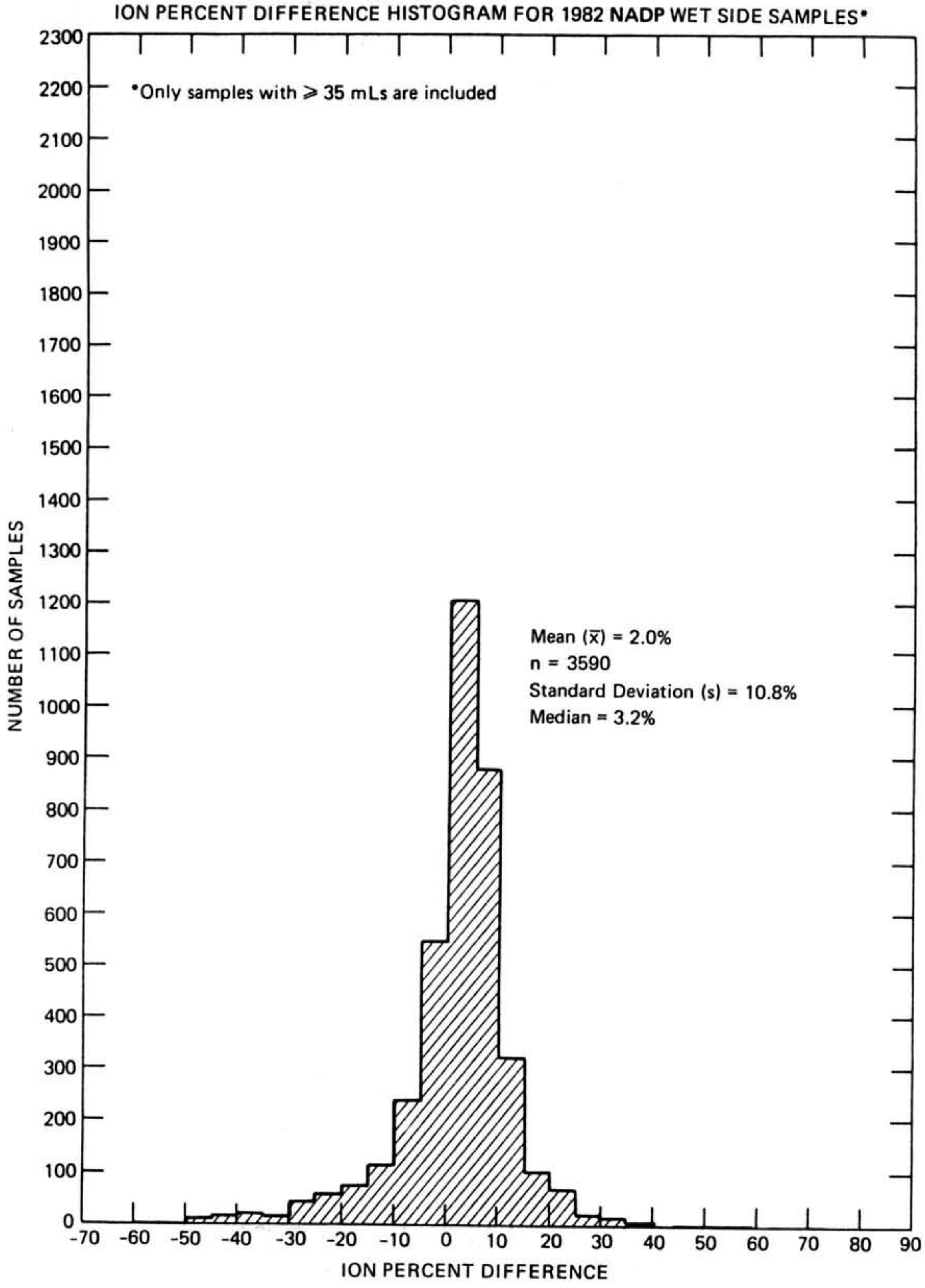


FIGURE 5. Ion percent difference histogram for NADP/NTN wet side samples in 1982.

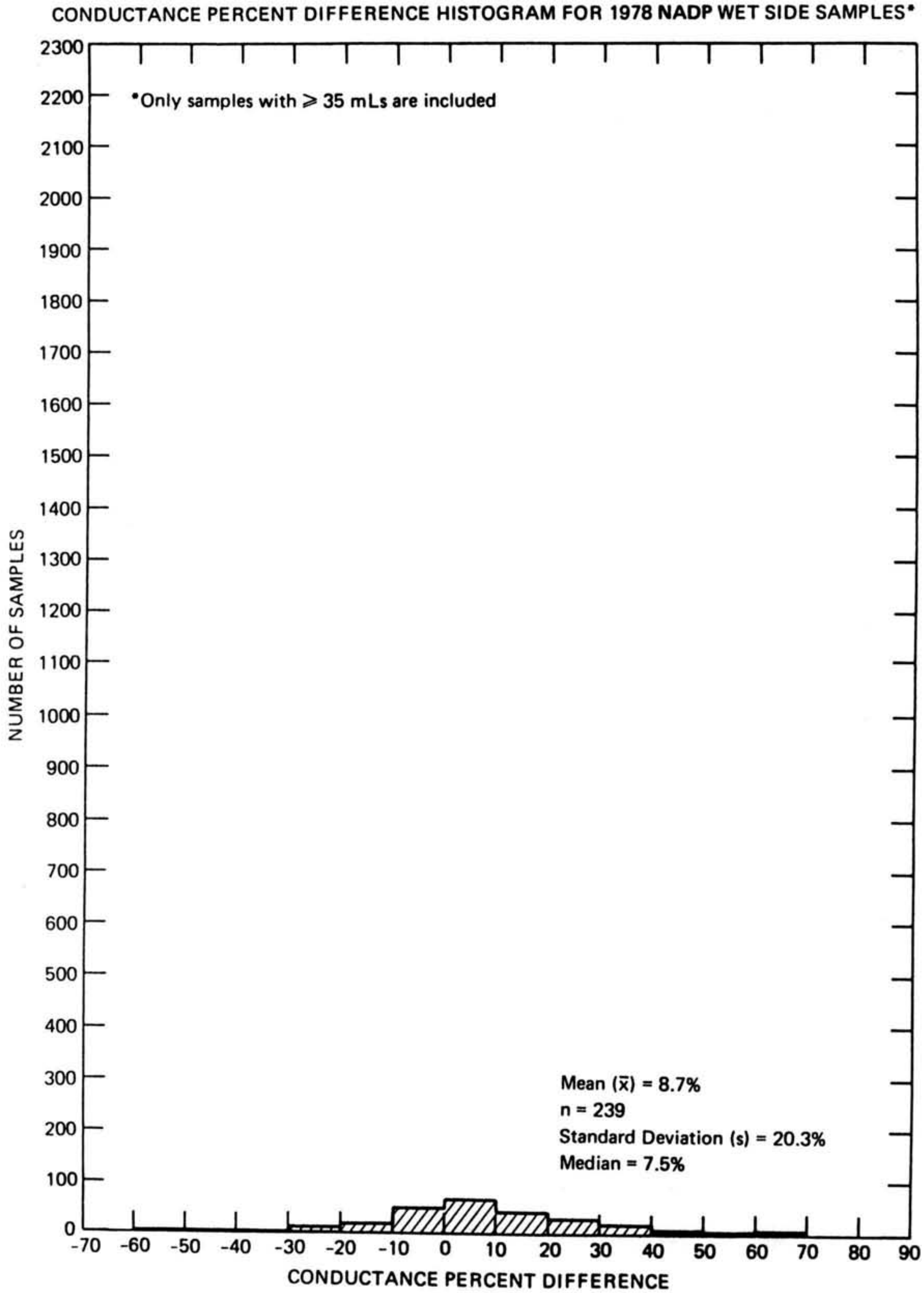


FIGURE 6. **Conductance percent difference histogram for NADP/NTN wet side samples in 1978.**

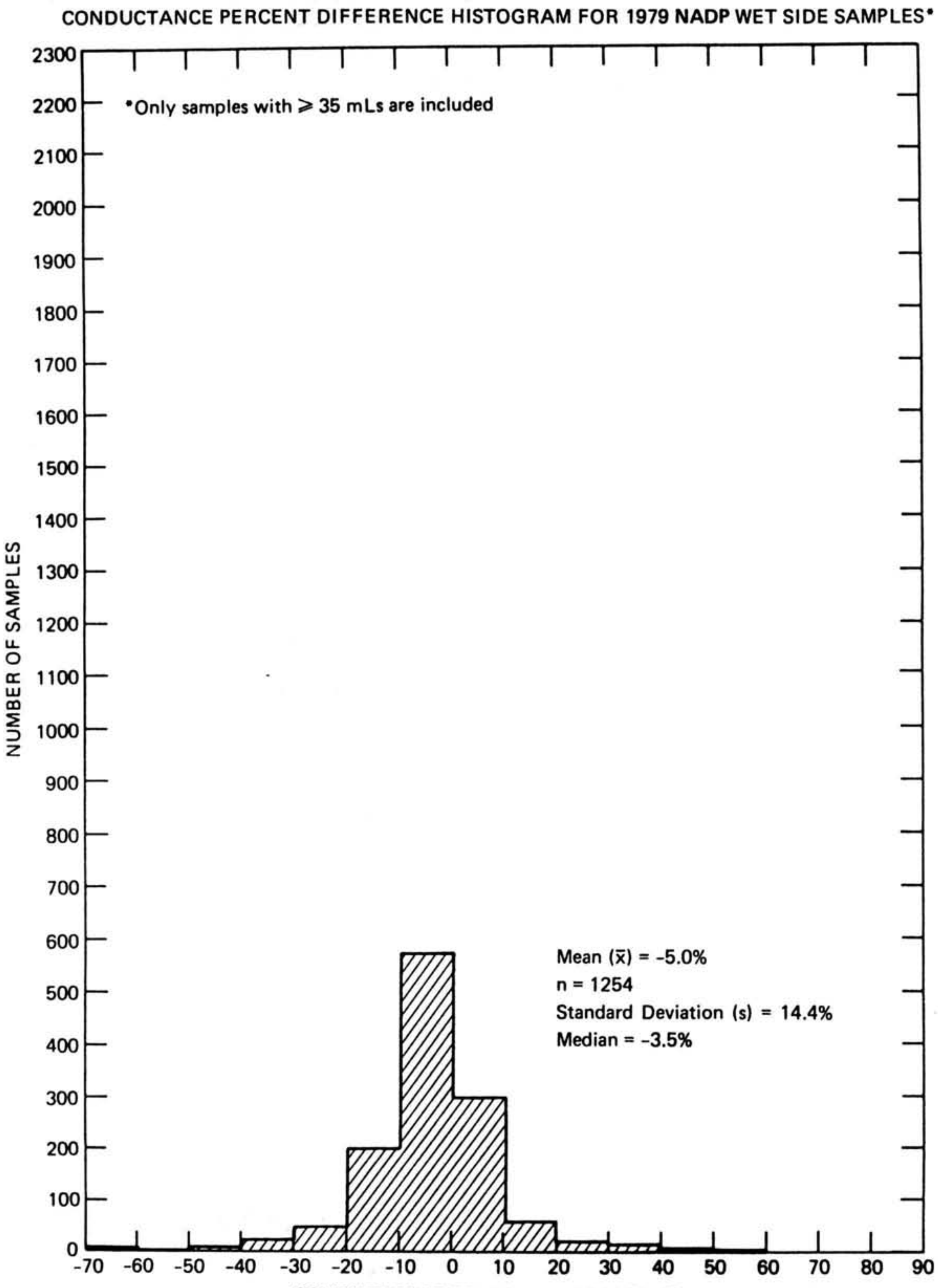


FIGURE 7. Conductance percent difference histogram for NADP/NTN wet side samples in 1979.

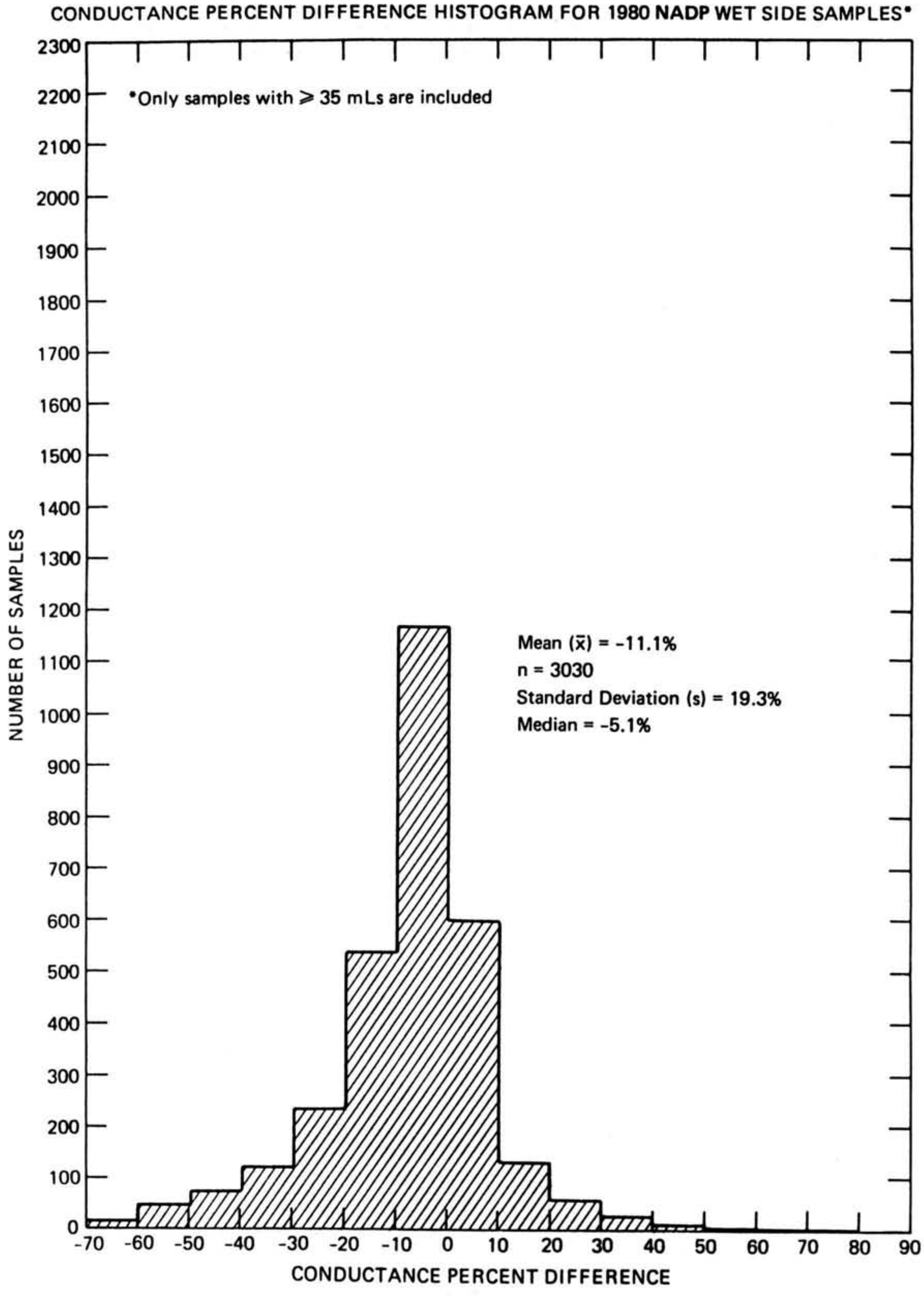


FIGURE 8. Conductance percent difference histogram for NADP/NTN wet side samples in 1980.

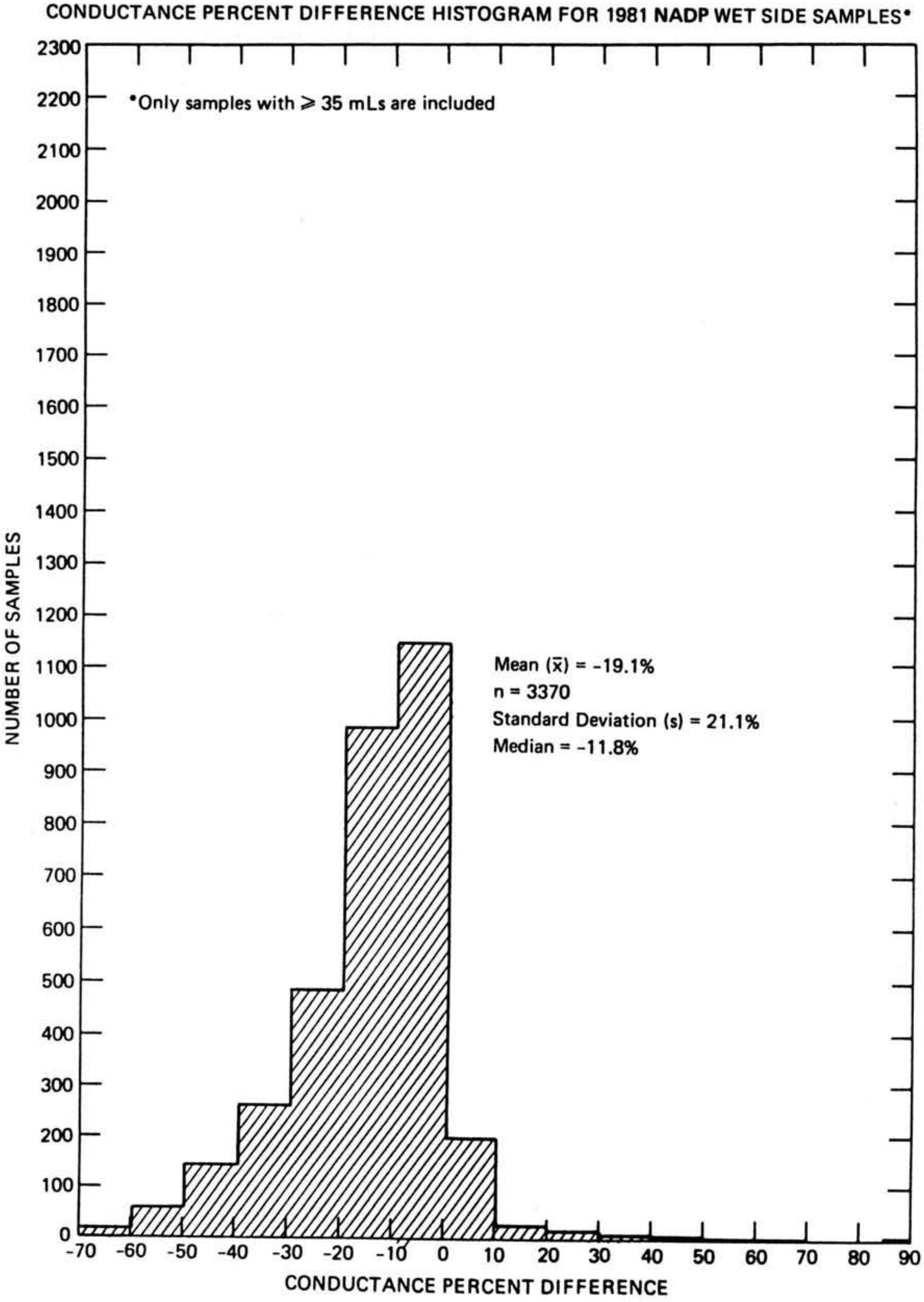


FIGURE 9. Conductance percent difference histogram for NADP/NTN wet side samples in 1981.

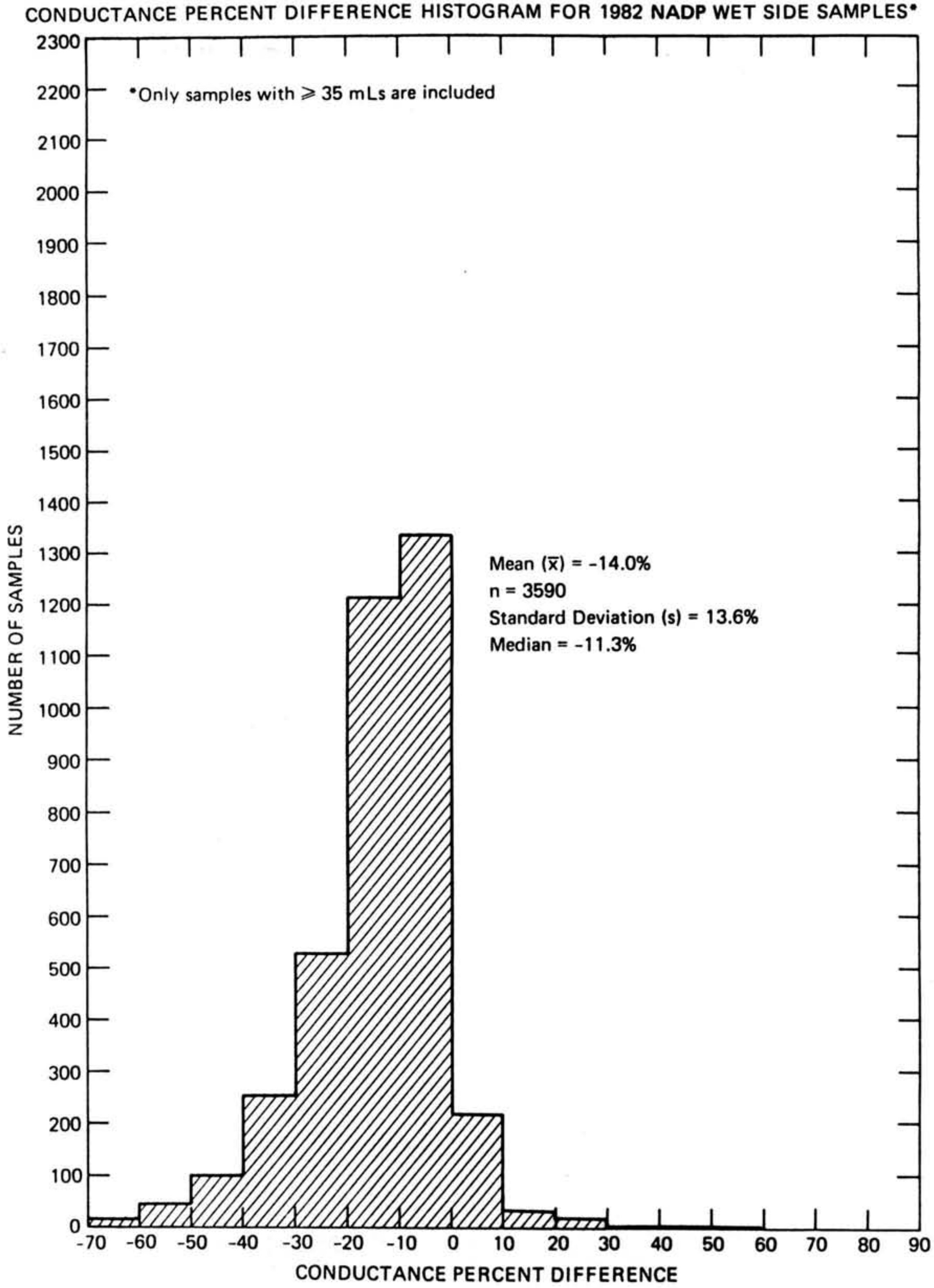


FIGURE 10. Conductance percent difference histogram for NADP/NTN wet side samples in 1982.