

Quality-Assurance Data for Routine Water Analyses by the U.S. Geological Survey Laboratory in Troy, New York

May 1991 through June 1993

By Tricia A. Lincoln, Debra A. Horan-Ross, Mark. L. Olson, and Gregory B. Lawrence

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U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Gordon P. Eaton, Director

For additional information
write to:

District Chief
U.S. Geological Survey
425 Jordan Road
Troy, N.Y., 12180

Copies of this report can be
purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Denver, CO 80225-0286

CONTENTS

Abstract 1

Introduction 1

 Participating Projects 2

 Purpose and Scope 2

Quality-Assurance/Quality-Control Program Description 2

 Quality-Control Samples 2

 Filter Blanks and Analytical Blanks 4

 Duplicate and Triplicate Environmental Samples 4

 U.S. Geological Survey's Standard Reference Sample Program 4

 Environment Canada's LRTAP Interlaboratory Study 4

Control-Chart Development and Evaluation 4

 Quality-Control Samples 6

 Filter Blanks and Analytical Blanks 7

 Duplicate and Triplicate Environmental Samples 7

 Environment Canada's LRTAP Interlaboratory Study 7

Summary of Results. 7

 Quality-Control Samples 7

 Filter Blanks and Analytical Blanks 9

 Duplicate and Triplicate Environmental Samples 10

 U.S. Geological Survey's Standard Reference Sample Program 10

 Environment Canada's LRTAP Interlaboratory Study 10

Selected References 11

FIGURES

1-4. Graphs showing results of quality-control data for water-sample analyses from May 1991 through June 1993.

1. High- and low-concentration quality-control samples

 A. Acid-neutralizing capacity 12

 B. Aluminum, total monomeric. 12

 C. Aluminum, total 12

 D. Ammonium. 12

 E. Calcium. 13

 F. Carbon, dissolved inorganic 13

 G. Carbon, dissolved organic 13

 H. Chloride 13

 I. Fluoride. 14

 J. Magnesium 14

 K. Nitrate (ion chromatography) 14

 L. Nitrate (colorimetric method). 14

 M. pH 15

 N. Potassium 15

 O. Silicon. 15

 P. Sodium 15

 Q. Sulfate. 16

FIGURES (continued)

2. Filter blank and analytical blank samples

A. Aluminum, total monomeric	17
B. Aluminum, organic monomeric	17
C. Aluminum, total	17
D. Ammonium	17
E. Calcium	17
F. Carbon, dissolved organic	17
G. Chloride	17
H. Fluoride	17
I. Magnesium	18
J. Nitrate (ion chromatography)	18
K. Potassium	18
L. Silicon	18
M. Sodium	18
N. Sulfate	18

3. Duplicate and triplicate environmental samples

A1. Acid-neutralizing capacity (for triplicate means not in the range of $\pm 20 \mu\text{eq/L}$)	19
A2. Acid-neutralizing capacity (for triplicate means in the range of $\pm 20 \mu\text{eq/L}$)	19
B. Aluminum, total monomeric	19
C. Aluminum, organic monomeric	19
D. Aluminum, total	19
E. Calcium	19
F. Carbon, dissolved organic	19
G. Chloride	19
H. Magnesium	20
I. Nitrate (ion chromatography)	20
J. pH	20
K. Potassium	20
L. Silicon	20
M. Sodium	20
N. Sulfate	20

4. Environment Canada's LRTAP Interlaboratory Study

A1. Acid-neutralizing capacity (for triplicate means not in the range of $\pm 20 \mu\text{eq/L}$)	21
A2. Acid-neutralizing capacity (for triplicate means in the range of $\pm 20 \mu\text{eq/L}$)	21
B. Ammonium	21
C. Calcium	21
D. Carbon, dissolved organic	21
E. Chloride	21
F. Magnesium	21
G. Nitrate (ion chromatography)	21
H. pH	22
I. Potassium	22
J. Silicon	22
K. Sodium	22
L. Sulfate	22

TABLES

1. Number of environmental samples and quality-control samples analyzed by USGS New York District Laboratory and summary of quality control (QC) data for each constituent from May 1991 through June 1993 3

2. Reporting limits and data-quality objectives for accuracy, precision, and blanks for solution analyses performed by the U.S. Geological Survey New York District Laboratory in Troy, N.Y., May 1991 through June 1993 5

3. Results obtained by Troy, N.Y. Laboratory for U.S. Geological Survey Standard Reference Sample (SRS) Program, May 1991 through June 1993 6

ABBREVIATED UNITS OF MEASUREMENT

mg/L	milligrams per liter
µeq/L	microequivalents per liter
µmol/L	micromoles per liter

Other Abbreviations

ANC	acid-neutralizing capacity
CV	coefficient of variation
DI	deionized water
DQO	data-quality objective
LRTAP	Long-Range Transport of Atmospheric Pollutants
MCV	median concentration value
MPV	most probable value
QA	quality assurance
QC	quality control
QC-high	high-concentration quality-control sample
QC-low	low-concentration quality-control sample
SRS	Standard Reference Sample
USGS	U.S. Geological Survey

Quality-Assurance Data for Routine Water Analyses by the U.S. Geological Survey Laboratory in Troy, New York, May 1991 through June 1993

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Abstract

A laboratory for analysis of low-ionic-strength water has been developed at the New York District office of the U.S. Geological Survey (USGS) in Troy, N.Y., to analyze samples collected by USGS projects in the Northeast. The laboratory's quality-assurance program is based on both internal and interlaboratory quality-assurance samples and quality-control procedures developed to ensure proper sample collection, processing, and analysis. The quality-assurance/quality-control data are stored in the laboratory's SAS¹ data-management system, which provides efficient review, compilation, and plotting of quality-assurance/quality-control data. This report presents and discusses data analyzed from May 1991 through June 1993.

Quality-control results for 18 analytical procedures were evaluated for bias and precision. Control charts show that four of the procedures have biases but were within control limits; they are: total aluminum (high in March and May 1993); calcium (low in 1991); chloride (low from January through June 1993); and nitrate (colorimetric method—low from June 1992 through June 1993). No quality-control sample has been developed for the organic monomeric aluminum procedure. Results from the filter-blank and analytical blank analyses indicate that, in 4 of the 14 procedures in which blanks were run, measurements approached or exceeded control limits. Organic and total monomeric aluminum concentrations showed upward trends in analytical-blanks in June 1992, but most of these values were within control limits. Total aluminum, calcium, and chloride concentrations periodically exceeded control limits. Blanks were not analyzed for pH,

acid-neutralizing capacity, dissolved inorganic carbon, or nitrate (colorimetric method).

Sampling and analysis precision are evaluated in terms of the coefficient of variation obtained for duplicate and triplicate samples in 14 of the 18 procedures. Data-quality objectives were met for at least 95 percent of duplicate and triplicate samples. Data quality objectives were not met in 32 percent of the total aluminum samples; 20 percent of the total monomeric aluminum samples; and 23 percent of the dissolved organic carbon samples. Duplicate and triplicate samples were not analyzed for ammonium, fluoride, dissolved inorganic carbon, or nitrate (colorimetric method).

Results of interlaboratory quality-assurance programs are presented. Laboratory ratings for the U.S. Geological Survey's Standard Reference Sample Program show satisfactory results overall. Environment Canada's LRTAP interlaboratory study results are plotted on control charts. Data quality objectives were met in 7 of the 12 procedures, for more than 80 percent of the LRTAP samples. Data quality objectives were not met for 25 percent of the ammonium and calcium samples; 35 percent of the dissolved organic carbon and silicon samples; and 45 percent of the sodium samples.

INTRODUCTION

The U.S. Geological Survey (USGS) maintains a laboratory at its Troy, N.Y. office to analyze low-ionic-strength water for USGS watershed-research projects that require major-ion analyses of precipitation, soil-water, shallow ground-water, stream-water, and lake-water samples. The methods used in this laboratory are described in detail in Lawrence and others (1995).

¹ Use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Analyses done during the 2-year period (May 1991-June 1993) represented by this report were: acid-neutralizing capacity (ANC), total monomeric aluminum, organic monomeric aluminum, total aluminum, ammonium, calcium, chloride, fluoride, dissolved inorganic carbon (DIC), magnesium, nitrate (ion chromatograph and colorimetric method), dissolved organic carbon (DOC), pH, potassium, silicon, sodium, and sulfate.

Participating Projects

The numbers and types of samples analyzed by the laboratory during the 2-year period are summarized below, by project for which they are associated; numbers in parentheses are USGS project numbers.

Project: Neversink Watershed Study (NY91-200)

Cooperator: New York City Department of Environmental Protection

Analyses: 3,095 stream, shallow ground water, and snow samples.

Project: Biogeochemical Processes that Control Nitrogen Cycling and Associated Hydrogen and Aluminum Leaching in an Undeveloped Headwater Basin (NY91-204)

Cooperator: New York City Department of Environmental Protection

Analyses: 1,147 stream, shallow ground-water, soil-solution, soil-extraction, and snow samples.

Project: Long-Term Monitoring of Five Streams in the Catskill Mountains (NY85-152)

Cooperator: U.S. Environmental Protection Agency

Analyses: 726 stream samples.

Project: Forest-Floor Aluminum and Calcium Chemistry—Relations with Acid Deposition, Root Vitality, Stand Dynamics, and Red Spruce (NY91-208)

Cooperator: U.S. Forest Service

Analyses: 868 stream, soil-solution, and soil-extraction samples.

Project: Variable Source-Area Control of Episodic Stream Chemistry (NY91-209)

Cooperator: U.S. Forest Service

Analyses: 229 stream samples.

Project: Hydrologic Budget and Changes in Aquatic Chemistry of Woods Lake Outlet After Watershed Liming (NY 88-173)

Cooperator: Cornell University Department of Natural Resources

Analyses: 56 stream samples.

Project: Relations Among Geochemical Processes that Control Pond-Water Chemistry in Hodge Pond Watershed in the Catskill Mountains (NY90-193)

Cooperator: Town of Rockland, N.Y.

Analyses: 245 stream and shallow ground-water samples.

Additional information on projects of the New York District is given in Marshall (1992) and Lee (1996).

Purpose and Scope

This report is the first in a planned series to document the quality-assurance practices of this laboratory and is intended for use by current and prospective cooperating agencies. It (1) describes quality-control and quality-assurance procedures of the laboratory, (2) presents graphs showing the results from analyses of quality-control samples, filter blanks and analytical blanks, and duplicate and triplicate environmental samples, and (3) explains analytical biases and outliers and the corrective actions taken.

QUALITY-ASSURANCE/QUALITY-CONTROL (QA/QC) PROGRAM DESCRIPTION

The quality of the data produced at this laboratory is maintained by adherence to the standard operating procedures described in Lawrence and others (1995) and by participation in externally administered quality-assurance (QA) programs. Results of QA data are evaluated by the laboratory supervisor and primary analysts, and appropriate corrective action is taken when needed.

Quality-Control Samples

Quality-control (QC) samples are used to determine the accuracy of an instrument's calibration and to detect variations in instrument response within an analytical run. Source material for all QC samples is

obtained from a manufacturer other than the producer of the source material used to make calibration standards, or is obtained from a different lot.

The concentrations of QC samples are chosen to bracket the expected range of the environmental-sample concentrations. A high-concentration QC sample and a low-concentration QC sample (referred to herein as QC-high and QC-low) are prepared for most constituents; exceptions are inorganic monomeric aluminum, for which column efficiency is used to determine the acceptability of the data, and fluoride, for which only one QC sample is prepared because of the narrow range of environmental concentrations measured by the laboratory.

Quality-control samples are analyzed immediately after calibration, after every 10 analyses of environmental samples, and at the end of each run. Exceptions to the frequency of QC sample analyses are ANC (QC sample after every 17 environmental samples), and pH (QC sample after every 10 to 13

environmental samples). The allowable differences—both greater than and less than the theoretical value of each QC sample—set the control limits for acceptance or rejection of environmental-sample data. QC samples that do not meet data-quality objectives (DQO's) for accuracy are rerun, and if the value is acceptable, the run is continued. If the rerun-QC-sample value is unacceptable, the environmental-sample data preceding it are rejected, and the instrument is recalibrated. Only accepted QC-sample and environmental-sample data are entered into the database. An exception to this practice occurs when the volume of an environmental sample is insufficient for a rerun. In this case, the environmental-sample and QC data are entered into the database and flagged, and the project chief then decides whether to accept or reject these data. The number of samples analyzed, and a summary of the quality-assurance data, are given in table 1.

Table 1. Number of environmental and quality-control samples analyzed by USGS New York District Laboratory and summary of quality-control (QC) data for each constituent, May 1991 through June 1993

Constituent	Summary of QC data						
	Number of samples analyzed			Number of QC samples exceeding control limits		Number of QC samples exceeding control limits by more than 5 percent	
	Environmental samples	QC samples		QC-high	QC-low	QC-high	QC-low
Acid-neutralizing capacity	5318	220	240	5	20	0	2
Aluminum, total monomeric	5665	587	587	1	0	0	0
Aluminum, organic monomeric	5665	0	0	0	0	0	0
Aluminum, total	3250	343	343	9	3	7	1
Ammonium	5544	546	546	3	4	1	0
Calcium	5148	371	371	0	4	0	1
Carbon, dissolved inorganic	411	31	31	1	0	1	0
Carbon, dissolved organic	5705	417	415	9	52	0	19
Chloride	5795	449	436	8	13	1	2
Fluoride	381	43	0	0	0	0	0
Magnesium	5144	361	361	2	0	0	0
Nitrate	6279	472	473	2	15	2	2
pH	5691	208	345	4	19	2	4
Potassium	5759	357	357	8	7	0	0
Silicon	5605	368	368	19	11	5	5
Sodium	5746	347	347	1	2	0	0
Sulfate	5803	449	449	4	10	3	1

Filter Blanks and Analytical Blanks

A filter blank and an analytical blank are included in each group of 50 environmental samples.

Filter blanks are aliquots of deionized (DI) water that are processed and analyzed in the same manner as environmental samples. Filter blanks are analyzed only for those constituents that require filtration. Filter-blank analysis indicates whether contamination has occurred during bottle-washing procedures, sample processing, or laboratory analysis.

Analytical blanks are aliquots of DI water that are processed and analyzed as environmental samples, except that the filtration step is omitted. Contamination found in analytical blanks may be attributed to bottle washing, sample preservation, or laboratory analysis, but not to filtration.

Duplicate and Triplicate Environmental Samples

One set of field duplicate or triplicate environmental samples is included in each group of 50 samples. The purpose of environmental duplicate or triplicate samples is to determine long-term analytical precision. Precision can be affected by bottle washing and by sample-collection and processing procedures. Environmental samples are selected for triplicate analysis on a rotating basis to ensure a wide range of sample concentrations.

Duplicate and triplicate environmental samples were collected until November 1991, after which all samples used to estimate precision were collected in triplicate.

U.S. Geological Survey's Standard Reference Sample Program

The USGS Standard Reference Sample Program (SRS) conducts a national interlaboratory analytical evaluation program semiannually. The Troy, N.Y. laboratory participates in the low-ionic-strength component of this program. Reference samples are prefixed by a P and are analyzed for calcium, chloride, magnesium, pH, potassium, sodium, and sulfate. Typically, the low-ionic-strength sample consists of snow that is collected, melted, filtered, and possibly diluted or concentrated, to meet the goals of the SRS program. Laboratory personnel are

aware of the presence of the SRS sample at the time of analysis but do not know the constituent concentrations until a published report is received from the USGS. The most probable value (MPV) for each constituent is determined through nonparametric statistics. Individual laboratory performances are rated numerically; the highest score is 4.0, and the lowest is 0.0.

Environment Canada's LRTAP Interlaboratory Study

The Troy laboratory participates in the LRTAP interlaboratory quality-assurance program, in which a set of 10 samples is analyzed three times per year. The samples are obtained from predominantly low-ionic-strength waters from various sources, such as precipitation, snow, lakes, and streams throughout North America and western Europe. The concentrations of the constituents in the LRTAP samples are similar to those of the environmental samples analyzed at the Troy laboratory. Laboratory results are compared with a median concentration value (MCV) determined from results from all participants in the LRTAP program. Laboratory personnel are aware of the presence of LRTAP samples at the time of analysis but do not know the MCV of the constituents until Environment Canada publishes a report after each study.

CONTROL-CHART DEVELOPMENT AND EVALUATION

Control charts (figs. 1-4) are plots of QC data in relation to time; in this report, they are used to (1) confirm that laboratory DQO's are met for individual QC samples, (2) detect long-term biases within the control limits, and (3) provide comparisons with results from other laboratories. All control charts, except those for the blanks, are edited by deleting each point that has a value below the laboratory's established reporting limits (table 2).

Quality-Control Samples

Results of QC sample analyses are plotted on control charts in which the central line is equal to the theoretical value of the control sample. Each analyte

Table 2. Reporting limits and data-quality objectives for accuracy, precision, and blanks for solution analyses performed by the U.S. Geological Survey New York District Laboratory in Troy, N.Y., May 1991 through June 1993.

[DQO, data-quality objective. $\mu\text{mol/L}$, micromoles per liter. CV, coefficient of variation. ANC, acid-neutralizing capacity. Numbers in "dividing value" column are concentrations that divide high range from low range of precision DQO's. pH and ANC values (in parentheses) are in pH units and microequivalents per liter, respectively.]

Constituent or property	Reporting limit ($\mu\text{mol/L}$)	Accuracy				Precision	
		Low-concentration quality-control sample		High-concentration quality-control sample		DQO (CV)	Filter and analytical blanks DQO ($\mu\text{mol/L}$)
		DQO (percent error)	Concen- tration ($\mu\text{mol/L}$)	DQO (percent error)	Concen- tration ($\mu\text{mol/L}$)		
Acid-neutralizing capacity ¹	none	10	(-39.9)	10	(125)	10	none
Aluminum, total monomeric	1.5	10	7.4	10	18.5	10	0.75
Aluminum, organic monomeric ²	1.5	none	none	none	none	10	0.75
Aluminum, total	1.0	15	1.8	10	28	10	0.5
Ammonium	2.0	15	7.1	10	17.5	10	1.0
Calcium	2.0	10	25	10	100	10	1.0
Chloride	2.0	10	8.5	10	85	10	0.5
Carbon, dissolved inorganic ³	41.0	15	83	10	415	10	18
Carbon, dissolved organic ³	41.0	15	83	10	415	10	18
Fluoride ⁴	0.5	15	1.6	none	none	10	none
Magnesium	1.0	10	8.2	10	33	10	0.5
Nitrate (ion chromatography)	2.0	10	5	10	50	10	0.3
Nitrate (colorimetric method)	5.0	12	42.9	10	100	10	none
pH ⁵	none	10	(4.41)	20	(6.88)	20	none
Potassium	1.0	10	5.1	10	20	10	0.5
Silicon	6.0	15	35.6	10	107	10	3
Sodium	1.0	10	8.7	10	35	10	1.0
Sulfate	2.0	10	8.3	10	83	10	0.3

¹ ANC: Values in parentheses are in microequivalents per liter. For values within ± 20 microequivalents per liter, an absolute data-quality objective of ± 6 microequivalents per liter is used for precision. Blanks are not run for ANC.

² Quality-control samples for organic monomeric aluminum are unavailable.

³ Concentrations are expressed as $\mu\text{mol C/L}$ (carbon per liter).

⁴ Fluoride: No data are yet available for precision. Blanks are not run for fluoride.

⁵ pH: Percent error and coefficient of variation determined from $[\text{H}^+]$. Blanks are not run for pH.

has prescribed control limits that have been established to meet project DQO's (table 2). The limits are represented by the upper and lower control-limit lines on each chart. QC-high and QC-low samples are plotted on separate graphs by constituent and date of analysis, and the control charts are evaluated for trends and/or bias. All data are reported in micro-moles per liter ($\mu\text{mol/L}$) except pH (pH units) and ANC (microequivalents per liter, $\mu\text{eq/L}$).

During the period represented by this report, several theoretical values for quality-control samples were changed to reflect more accurately than before environmental-sample concentrations (for example, fig. 1B). Control limits were also changed in response to the improvement and refinement of certain analyses (for example, figure 1C). The dates on which the changes were made are identified on the graphs.

Table 3. Results obtained by Troy, N.Y. Laboratory for U.S. Geological Survey Standard Reference Sample (SRS) Program, May 1991 through June 1993

(MPV, most probable value; TV, Troy laboratory value; mg/L, milligrams per liter; dash indicates no results reported)

Analyte	MPV, TV, and rating ^a	SRS sample number			
		P-17 6/91 ^b	P-18 10/91 ^c	P-19 12/92 ^d	P-20 6/93 ^e
Calcium	MPV, mg/L	0.30	—	0.24	0.160
	TV, mg/L	0.37	—	0.224	0.160
	Rating	0	—	3	4
Chloride	MPV, mg/L	0.416	0.94	1.14	0.140
	TV, mg/L	0.372	0.85	1.03	0.275
	Rating	4	3	3	4
Potassium	MPV, mg/L	0.057	—	0.17	0.100
	TV, mg/L	0.080	—	0.11	0.080
	Rating	1	—	1	3
Magnesium	MPV, mg/L	0.045	—	0.045	0.020
	TV, mg/L	0.080	—	0.05	0.020
	Rating	0	—	4	4
Sodium	MPV, mg/L	0.283	—	0.06	0.168
	TV, mg/L	0.270	—	0.018	0.130
	Rating	4	—	4	0
pH	MPV	5.55	6.60	4.72	5.53
	TV	5.55	6.74	4.83	5.40
	Rating	4	4	3	3
Sulfate	MPV, mg/L	0.500	1.60	0.45	0.831
	TV, mg/L	0.55	1.59	0.335	0.809
	Rating	4	4	4	4

a Laboratory rating system: 4 is highest score; 0 is lowest

b Date submitted

c Date analyzed

d Sample described in Long and Ferrar (1993a)

e Sample described in Long and Ferrar (1993b)

Filter Blanks and Analytical Blanks

Results from blank analyses (fig. 2) are plotted on control charts, by constituent. The control limit was established to meet project DQO's (table 2) and is represented by a horizontal line on the control charts. Data are plotted as concentration in relation to date of collection. The control charts are evaluated to identify possible contamination or positive interferences. All negative numbers, except ANC values, for samples analyzed before May 8, 1992, were entered as zero in the data base; this explains the lack of scatter on several of the control charts for blanks analyzed before this date.

Duplicate and Triplicate Environmental Samples

The coefficient of variation (CV) for each triplicate sample is plotted by constituent and date of collection in figure 3. Data with mean concentrations less than the defined reporting limit (table 2) are excluded. For this report, the DQO for all constituents is a CV of less than 10 percent. Each circle within the control charts represents the CV of a duplicate or triplicate environmental sample. CV values that plotted off the scale are represented by a circle accompanied by a number that gives the CV for that group of samples:

$$CV = \frac{s}{\bar{x}}(100)$$

where: s = standard deviation, and

\bar{x} = arithmetic mean of triplicate samples

ANC duplicate and triplicate sample means were plotted on two graphs. The first graph shows the CV for duplicate and triplicate sample means outside the range of -20 to +20 $\mu\text{eq/L}$ (fig. 3A1); the second graph shows values that fall between -20 and +20 $\mu\text{eq/L}$ (fig. 3A2). Each symbol on the graph represents the difference between the duplicate or triplicate sample mean and the individual values of that duplicate or triplicate sample.

Environment Canada's LRTAP Interlaboratory Study

Interlaboratory comparison graphs (fig. 4) are based on results from LRTAP samples and represent LRTAP studies from August 1991 through

May 1993. Samples with MCV's less than the reporting limits were excluded from the graphs. The MCV and the control limits of ± 10 percent are represented by lines on the graphs; the percent difference (D) is calculated as:

$$D = [(AV - MCV)/MCV] \times 100$$

where: AV = analyzed value, and

MCV = mean concentration value

A separate graph is shown for ANC values in the +20 to -20 $\mu\text{eq/L}$ range; results for these samples are plotted as the difference between the laboratory value and the MCV (fig. 4A2). The LRTAP pH results consist of two sets of data—pH values less than 6.00, and pH values equal to or greater than 6.00. The two sets of data have different DQO's, which are represented by a solid line and a dashed line on the pH graph (fig. 4H).

SUMMARY OF RESULTS

The following sections summarize the results for (A) quality-control samples (fig. 1, p.12-16), (B) filter blanks and analytical blanks (fig 2, p. 17-18), (C) duplicate and triplicate environmental samples (fig. 3, p.19-20), (D) SRS samples (table 3, p. 6), and (E) LRTAP samples (fig. 4, p.21-22).

A. Quality-Control Samples

Acid-Neutralizing Capacity (fig. 1A).—DQO's were met for more than 95 percent of the samples. No apparent trends or biases were evident among the QC-high and QC-low samples.

Aluminum, Total Monomeric (fig. 1B).—DQO's were met for 100 percent of the samples. No apparent trends or biases were evident among the QC-high and QC-low samples. The total monomeric aluminum QC-high concentration was decreased from 27.8 to 18.5 $\mu\text{mol/L}$ in April 1992 to reflect environmental-sample concentrations from the projects more accurately than before.

Aluminum, Organic Monomeric.—A QC sample has not been developed for this analysis.

Aluminum, Total (fig. 1C).—DQO's were met for more than 95 percent of the samples. The control limit for the QC-low was decreased from 37 percent to 20 percent in March 1993 as a result of refinements of the analytical procedure. No apparent trends or biases were evident, except for the QC-high in March and May 1993. The bias did not appear in June 1993.

Ammonium (fig. 1D).—DQO's were met for more than 95 percent of the samples. No apparent trends or biases were evident. The ammonium QC-high concentration was changed from 21.4 to 17.8 $\mu\text{mol/L}$ in April 1992; the QC-low concentration was changed from 10.7 to 7.1 $\mu\text{mol/L}$ in March 1992. These lower concentrations reflect environmental-sample concentrations from the projects more accurately than before.

Calcium (fig. 1E).—DQO's were met for more than 95 percent of the samples. A slight low bias was observed for analyses performed in 1991.

Carbon, Dissolved Inorganic (fig. 1F).—DQO's were met for more than 95 percent of the samples. No apparent trends or biases were evident for the QC-high and QC-low samples.

Carbon, Dissolved Organic (fig. 1G).—DQO's were met for more than 90 percent of the samples. Dissolved organic carbon analysis was performed by the New York City Department of Environmental Protection Laboratory in Gramsville, N. Y., from May 1991 until January 1992, after which analyses were performed in the Troy laboratory. A high bias was observed for the QC-low sample from May 1991 through December 1991.

Chloride (fig. 1H).—DQO's were met for more than 95 percent of the samples. The QC-high graph illustrates a low bias after January 1993; this was due to an error in preparation of QC stock solution and has been corrected. No bias or trend was evident for the QC-low sample.

Fluoride (fig. 1I).—DQO's were met for more than 95 percent of the samples. No trends or biases were evident for the quality-control sample.

Magnesium (fig. 1J).—DQO's were met for more than 95 percent of the samples. No trends or biases were evident for the QC-high and QC-low samples.

Nitrate (ion chromatography) (fig. 1K).—DQO's were met for more than 95 percent of the samples. No trends or biases were evident for the QC-high and QC-low samples.

Nitrate (colorimetric method) (fig. 1L).—DQO's were met for more than 95 percent of the samples. The QC-high and QC-low samples appear to be biased low; this is attributed to incomplete conversion of nitrate to nitrite by the cadmium-reduction column. The column was operating at 90-percent efficiency during this period. Multiplying the environmental- and QC-sample concentrations by 1.1 would correct the bias. The project chief determines whether to apply this correction factor.

pH (fig. 1M).—DQO's were met for more than 95 percent of the samples. No apparent trends or biases were evident for the QC-high and QC-low samples.

Potassium (fig. 1N).—DQO's were met for more than 95 percent of the samples. No trends or biases were evident for the QC-high and QC-low samples. The potassium QC-high concentration was increased from 12.8 to 25.6 $\mu\text{mol/L}$ in 1993 to reflect environmental-sample concentrations from the projects more accurately than before..

Silicon (fig. 1O).—DQO's were met for more than 90 percent of the samples. No trends or biases were evident for the QC-high and QC-low samples. In December 1991, the QC-high concentration was increased from 35.6 to 106.8 $\mu\text{mol/L}$ and the QC-low concentration from 18.3 to 35.6 $\mu\text{mol/L}$ to reflect environmental-sample concentrations of the projects more accurately than before. In May 1992, the silicon method was changed from segmented-flow analysis to flow-injection analysis.

Sodium (fig. 1P).—DQO's were met for more than 95 percent of the samples. No trends or biases were evident for the QC-high and QC-low samples. The sodium QC-high concentration was increased from a theoretical value of 34.8 to

43.5 µmol/L in 1993 to reflect environmental-sample concentrations of the projects more accurately than before.

Sulfate (fig. 1Q).—DQO's were met for more than 95 percent of the samples. The slight high bias for the QC-low was corrected by upgrading components of the ion chromatograph in January 1993. A slight low bias was evident for the QC-high sample.

B. Filter Blanks and Analytical Blanks

Aluminum, Total Monomeric (fig. 2A).—The DQO was met for more than 85 percent of the samples. An upward trend in analytical blanks began in June 1992. The software, which calculates sample-analysis results, was upgraded, and an incorrect default setting was discovered that subtracted the absorbance of the leading baseline from the sample peak absorbance. This has been corrected; the software now calculates an average absorbance from the leading and trailing baselines and subtracts this value from the sample peak.

Aluminum, Organic Monomeric (fig. 2B).—The DQO was met for more than 95 percent of the samples. An upward trend in analytical blanks began in June 1992. The software, which calculates sample-analysis results, was upgraded, and an incorrect default setting was discovered that subtracted the absorbance of the leading baseline from the sample peak absorbance. This has been corrected; the software now calculates an average absorbance from the leading and trailing baselines and subtracts this value from the sample peak.

Aluminum, Total (fig. 2C).—The DQO was met for more than 75 percent of the samples. Periodic blank contamination was attributed to inconsistent bottle-washing procedures; this conclusion was based on a study of washing procedures used for total aluminum aliquot bottles. As a result, a new aliquot container-preparation procedure was implemented in March 1993 and is being tested.

Ammonium (fig. 2D).—The DQO was met for more than 90 percent of the samples. No systematic trends were evident for this analysis.

Calcium (fig. 2E).—The DQO was met for more than 70 percent of the samples. The large number of samples that did not meet the DQO in 1992 was corrected through installation of a new hollow-cathode lamp.

Carbon, Dissolved Organic (fig. 2F).—The DQO was met for more than 75 percent of the samples. The DQO is being reevaluated to determine whether it should be increased.

Chloride (fig. 2G).—The DQO was met for more than 80 percent of the samples. A higher frequency of blank contamination in 1993 than for previous results was caused by the use of a dilute hydrochloric acid solution to wash sample bottles. Chloride aliquot bottles are now washed with deionized water only.

Fluoride (fig. 2H).—The DQO was met for all of the samples. No systematic trends were evident for this analysis.

Magnesium (fig. 2I).—The DQO was met for more than 95 percent of the samples. No systematic trends were evident for this analysis.

Nitrate (ion chromatography) (fig. 2J).—The DQO was met for more than 95 percent of the samples. No systematic trends were evident for this analysis.

Potassium (fig. 2K).—The DQO was met for more than 90 percent of the samples. No systematic trends were evident for this analysis.

Silicon (fig. 2L).—The DQO was met for more than 95 percent of the samples. No systematic trends were evident for this analysis. In March 1992, the silicon analysis was upgraded from a segmented-flow instrument with a strip-chart recorder to a flow-injection analyzer with a computer for data capture. The greater resolution of electronic data capture than was possible with the strip chart recorder was indicated by the greater variability of measurements after March 1992.

Sodium (fig. 2M).—The DQO was met for more than 80 percent of the samples. The atomic absorption spectrophotometer was upgraded in the fall of 1992. The graph of blank data shows the effect of improved software.

Sulfate (fig. 2N).—The DQO was met for all of the samples. No systematic trends were evident for this analysis.

C. Duplicate and Triplicate Environmental Samples

Acid-neutralizing Capacity (figs. 3A1 and 3A2).—More than 95 percent of the duplicate and triplicate samples met the DQO.

Aluminum, Total Monomeric (fig. 3B).—Twenty percent of the duplicate and triplicate sample CV values were above the DQO of 10 percent. Nine percent of the duplicate and triplicate CV values were above DQO of 15 percent.

Aluminum, Organic Monomeric (fig. 3C).—The DQO was met for more than 95 percent of the duplicate and triplicate samples.

Aluminum, Total (fig. 3D).—Thirty-two percent of the samples exceeded the established precision DQO. The change in aliquot bottle-washing procedures discussed above is expected to significantly reduce this number.

Ammonium.—All duplicate and triplicate sample data fell below the reporting limits for this constituent.

Calcium (fig. 3E).—More than 95 percent of the duplicate and triplicate samples met the DQO.

Carbon, dissolved organic (fig. 3F).—Thirty-five percent of samples exceeded the established DQO. This was attributed to a reporting limit that was too low (18 $\mu\text{mol/L}$). The reporting limit has since been increased to 41 $\mu\text{mol/L}$.

Chloride (fig. 3G).—More than 95 percent of the duplicate and triplicate samples met the DQO.

Magnesium (fig. 3H).—More than 95 percent of the duplicate and triplicate samples met the DQO.

Nitrate (ion chromatography) (fig. 3I).—More than 95 percent of the duplicate and triplicate samples met the DQO.

pH (fig. 3J).—All duplicate and triplicate samples met the DQO.

Potassium (fig. 3K).—More than 95 percent of the duplicate and triplicate samples met the DQO.

Silicon (fig. 3L).—More than 95 percent of the duplicate and triplicate samples met the DQO.

Sodium (fig. 3M).—More than 95 percent of the duplicate and triplicate samples met the DQO.

Sulfate (fig. 3N).—More than 95 percent of the duplicate and triplicate samples met the DQO.

D. U.S. Geological Survey's Standard Reference Sample (SRS) Program

Overall laboratory results for all SRS samples were satisfactory. Average ratings for each SRS sample were:

P-17 2.4

P-18 3.7

P-19 3.1

P-20 3.1

Chloride, pH, and sulfate were rated 3 or 4 for each SRS sample. Calcium and magnesium were rated zero for sample P-17, but were satisfactory in samples P-19 and P-20. Potassium rated 1 for samples P-17 and P-19, and improved to a rating of 3 by sample P-20. Sodium was rated zero for sample P-20. This was corrected through installation of a new hollow cathode lamp.

E. Environment Canada's LRTAP Interlaboratory Study

Acid-neutralizing capacity (figs. 4A1 and 4A2).—The DQO was met for more than 95 percent of the LRTAP samples. No trend or bias was evident.

Ammonium (fig. 4B).—The DQO was met for 75 percent of the LRTAP samples. A low bias for ammonium which was corrected by use of a new standard stock.

Calcium (fig. 4C).—The DQO was met for 75 percent of the LRTAP samples. A high bias for calcium in studies 31 and 32 was corrected by use of a new hollow cathode lamp.

Carbon, dissolved organic (fig. 4D).—The DQO was met for 65 percent of the LRTAP samples. A low bias for studies 28 through 30 was corrected by use of a new standard stock.

Chloride (fig. 4E).—The DQO was met for 80 percent of the LRTAP samples. No trend or bias was evident.

Magnesium (fig. 4F).—The DQO was met for more than 90 percent of the LRTAP samples. No trend or bias was evident.

Nitrate (ion chromatography).—The DQO was met for more than 85 percent of the LRTAP samples. The outliers were most often biased low.

pH (fig. 4H).—The DQO was met for more than 95 percent of the LRTAP samples with a pH less than 6.00. In study 27, the pH values above 6.00 were biased low. This was corrected by use of a new pH probe. The DQO was met for more than 80 percent of the LRTAP samples with a pH greater than 6.00 for studies 28 through 32.

Potassium (fig. 4I).—The DQO was met for more than 85 percent of the LRTAP samples. The outliers were most often biased low.

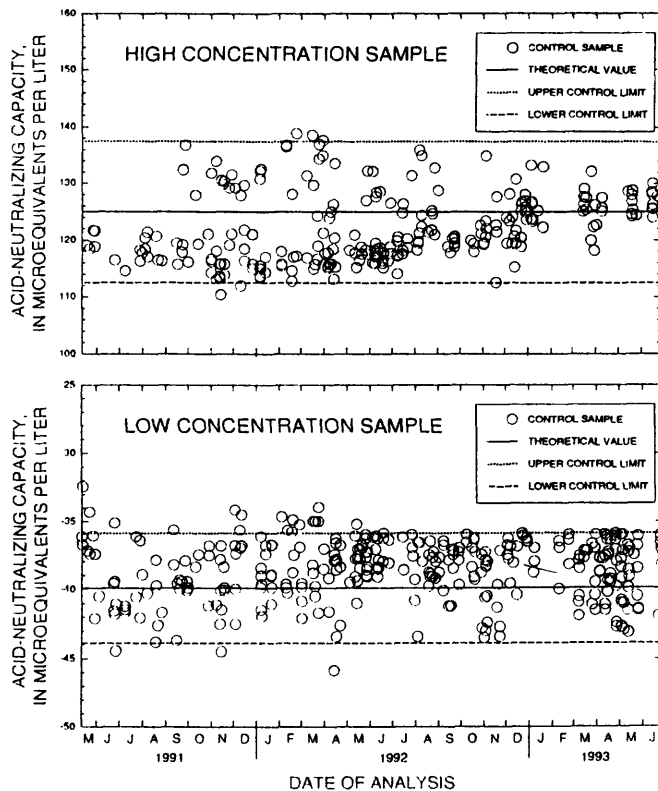
Silicon (fig. 4J).—The DQO was met for 65 percent of the LRTAP samples. A high bias for silicon was solved by use of a different type of standard stock.

Sodium (fig. 4K).—The DQO was met for 55 percent of the LRTAP samples. A low bias in studies 31 and 32 was corrected through the installation of a new hollow-cathode lamp.

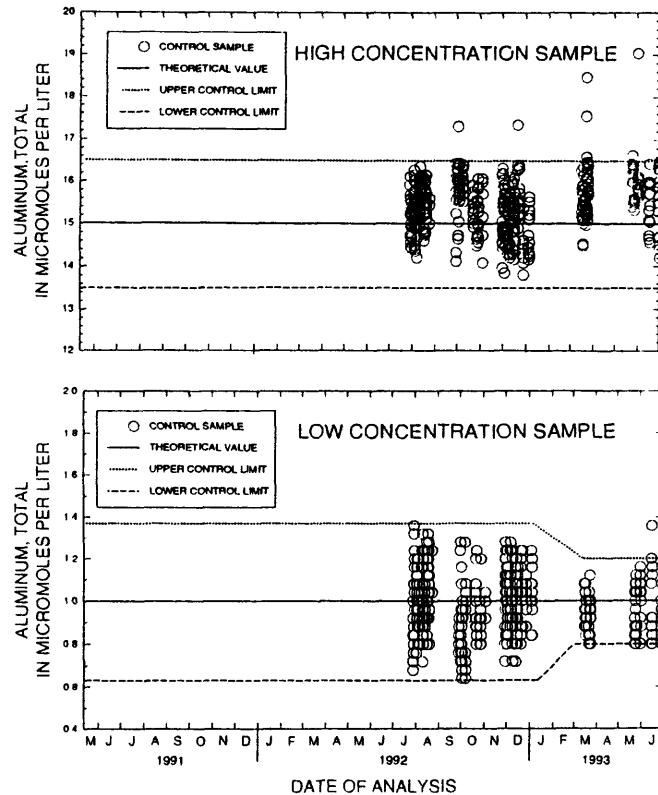
Sulfate (fig. 4L).—The DQO was met for more than 95 percent of the samples. No trend or bias was evident.

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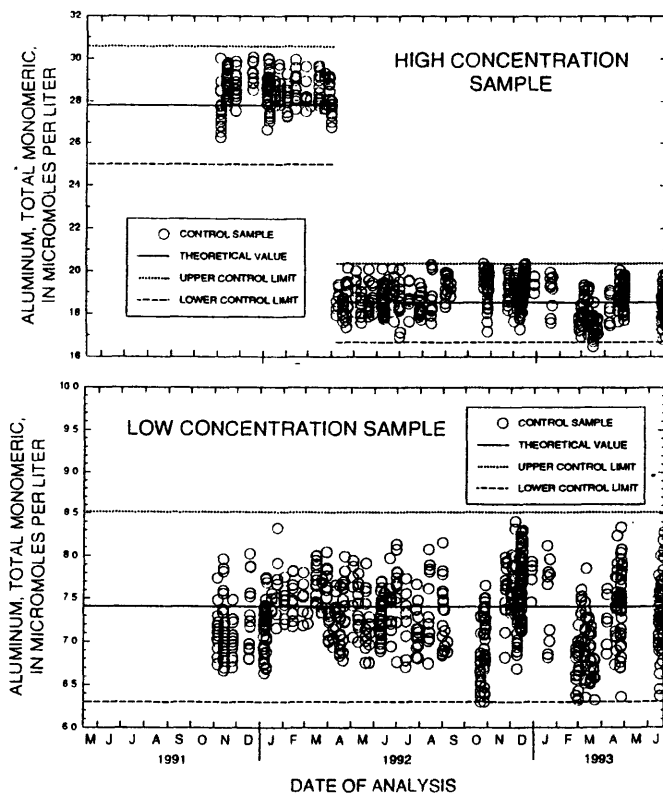
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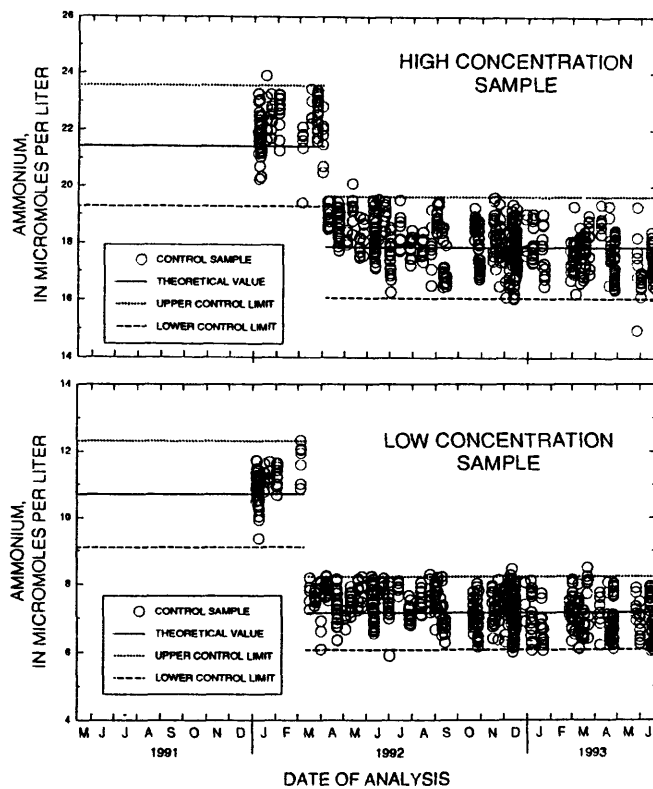
A. ACID-NEUTRALIZING CAPACITY



C. ALUMINUM, TOTAL



B. ALUMINUM, TOTAL MONOMERIC



D. AMMONIUM

Figure 1. High- and low-concentration quality-control samples: A. Acid-neutralizing capacity. B. Aluminum, total monomeric. C. Aluminum, total. D. Ammonium.

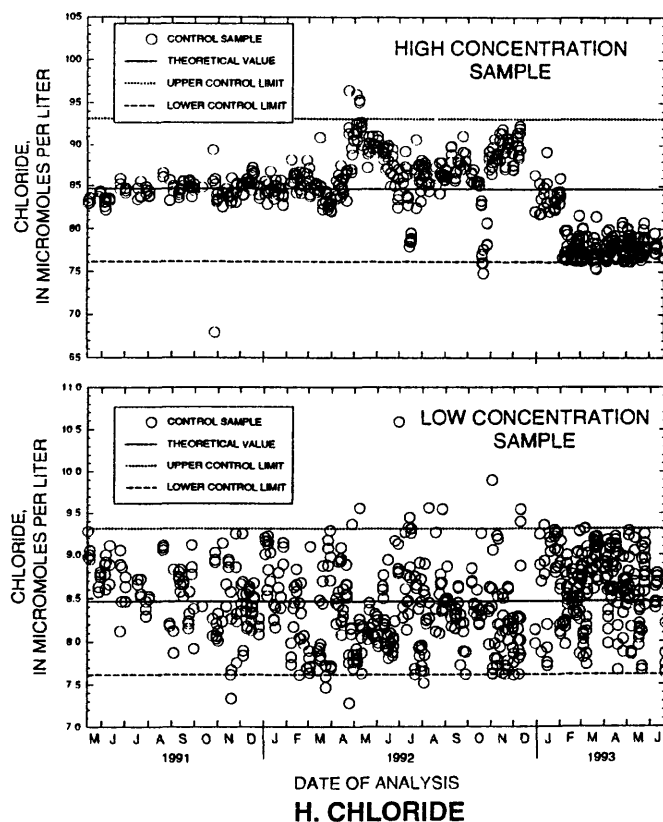
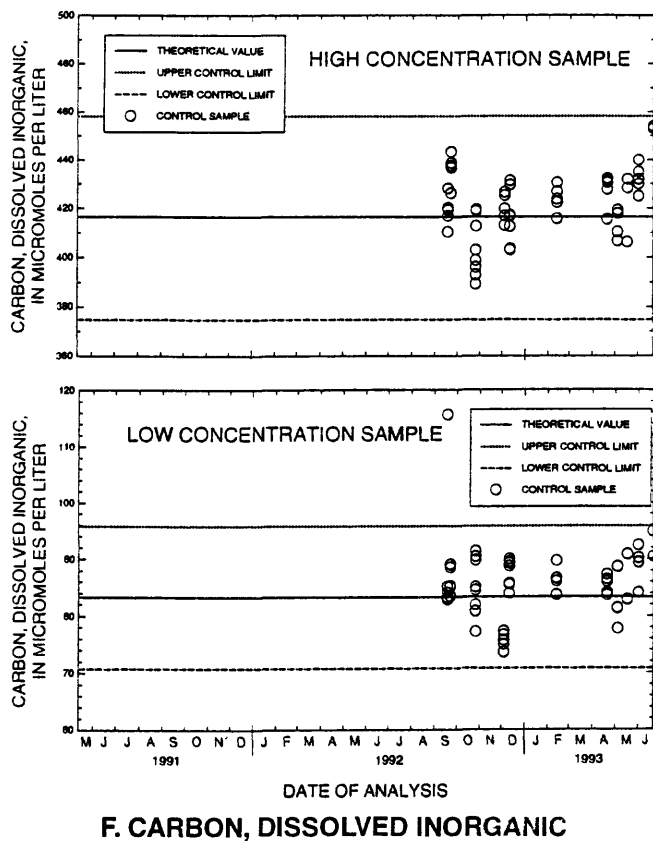
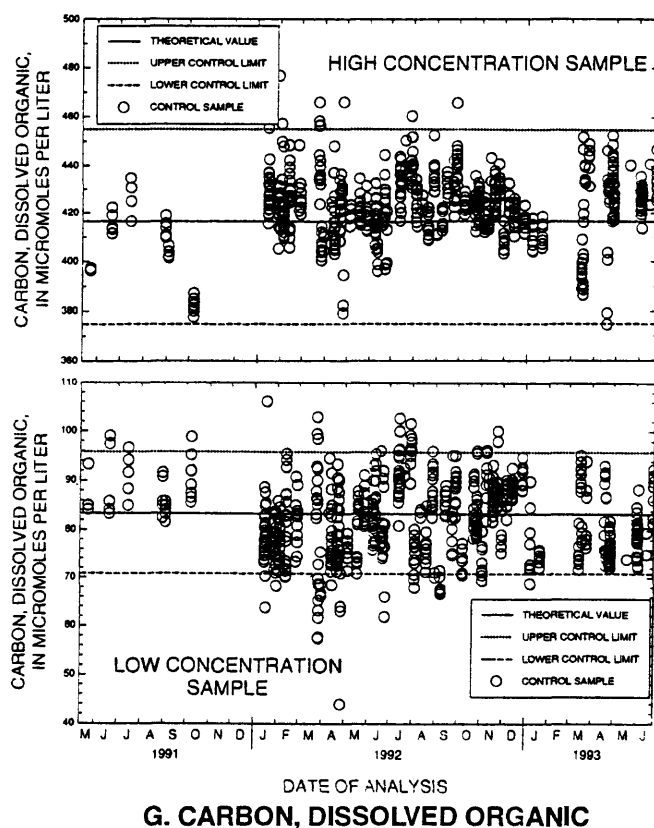
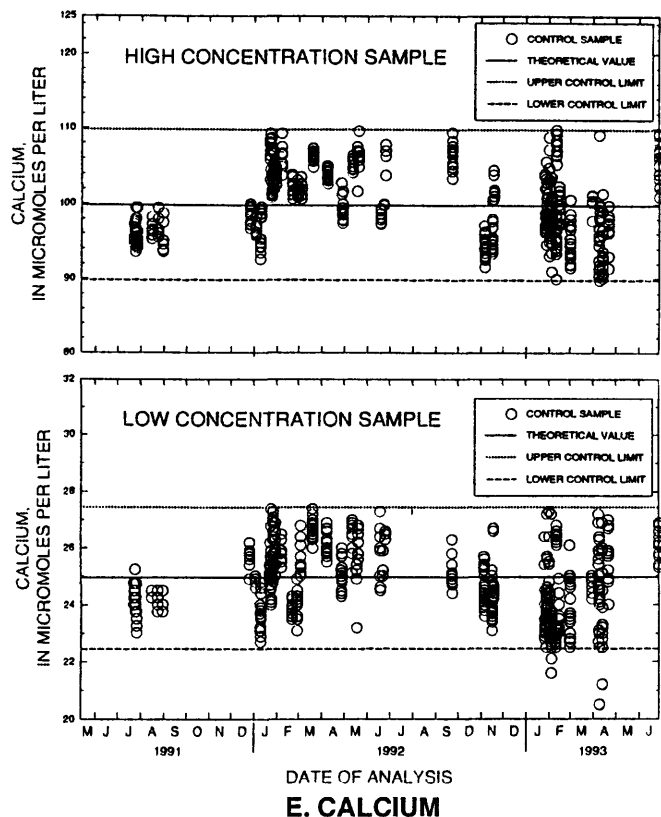
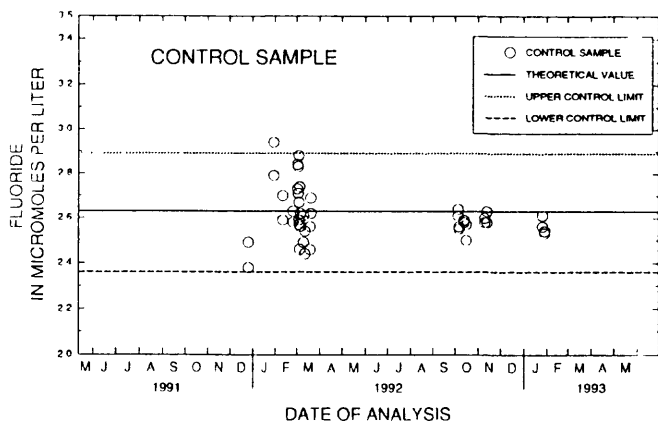
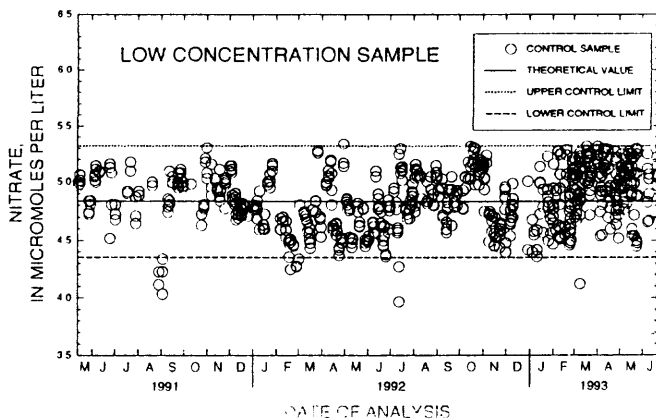
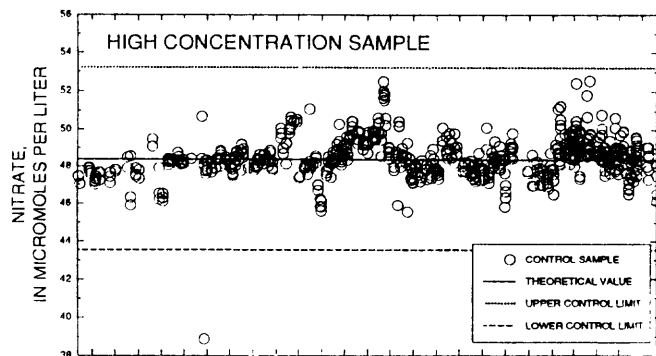


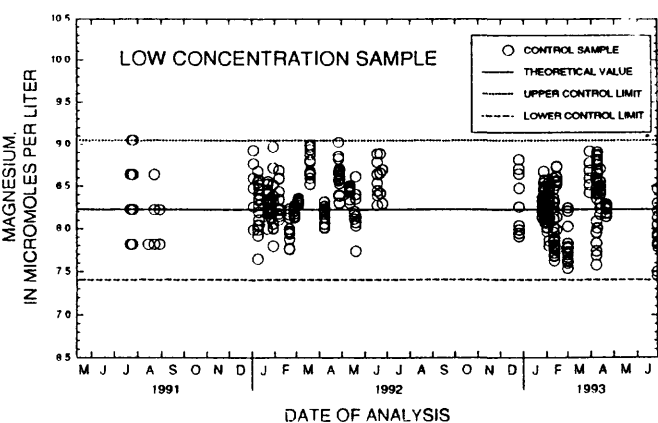
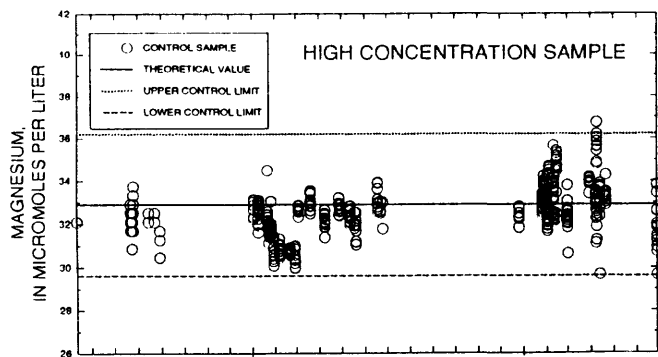
Figure 1. High- and low-concentration quality-control samples (continued): E. Calcium. F. Carbon, dissolved inorganic. G. Carbon, dissolved organic. H. Chloride.



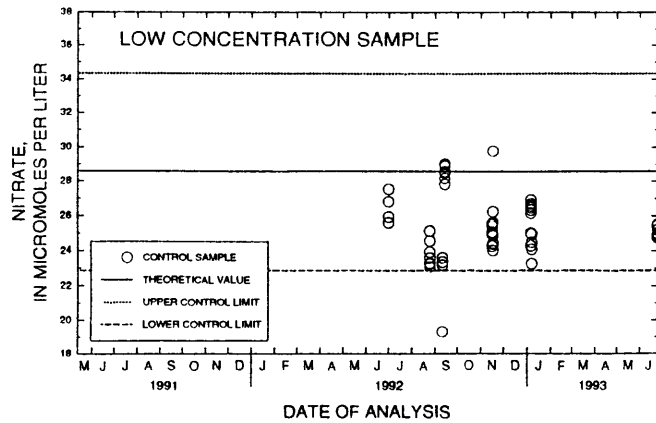
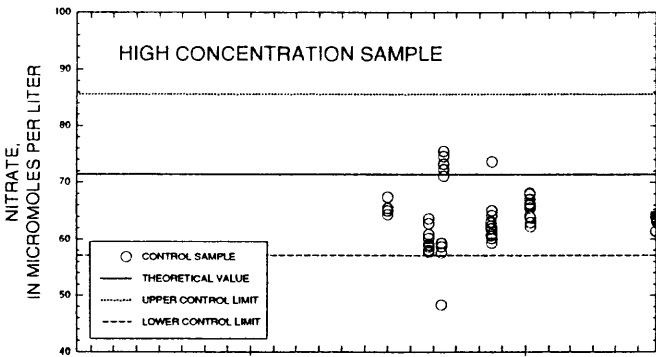
I. FLUORIDE



K. NITRATE (ION CHROMATOGRAPHY)



J. MAGNESIUM



L. NITRATE (COLORIMETRIC METHOD)

Figure 1. High- and low-concentration quality-control samples (continued): I. Fluoride. J. Magnesium K. Nitrate (ion chromatography). L. Nitrate (colorimetric method).

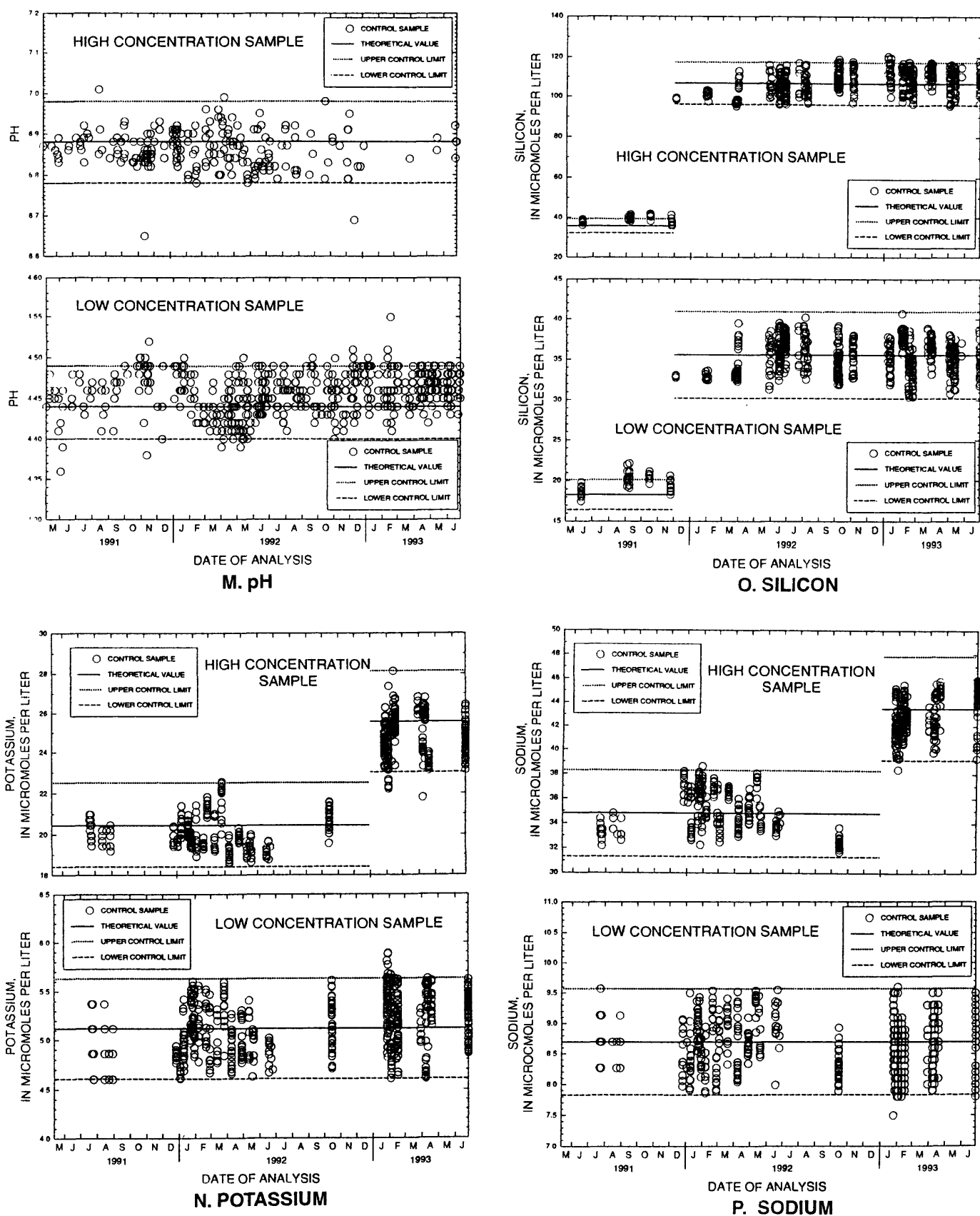


Figure 1. High- and low-concentration quality-control samples (continued): M. pH N. Potassium. O. Silicon. P. Sodium.

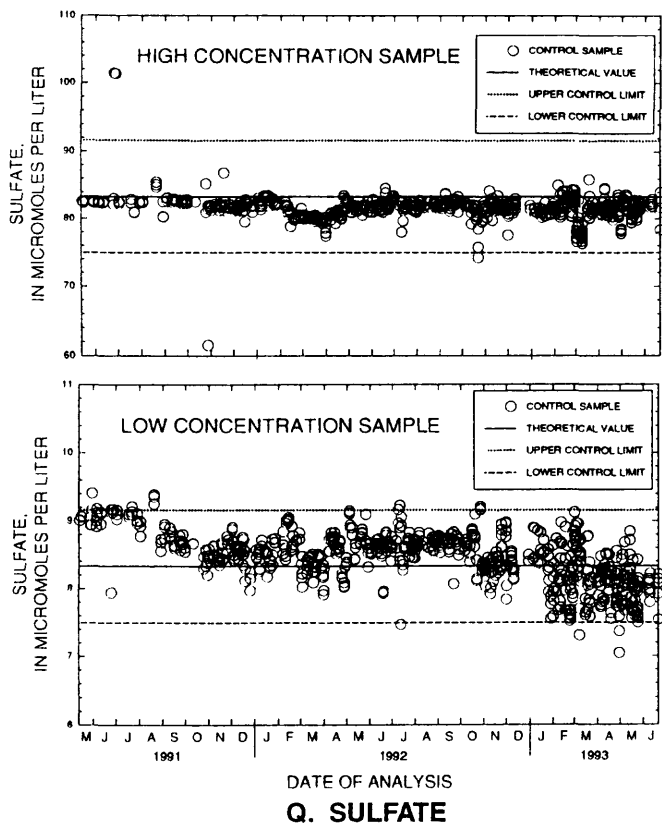


Figure 1. High- and low-concentration quality-control samples: Q. Sulfate.

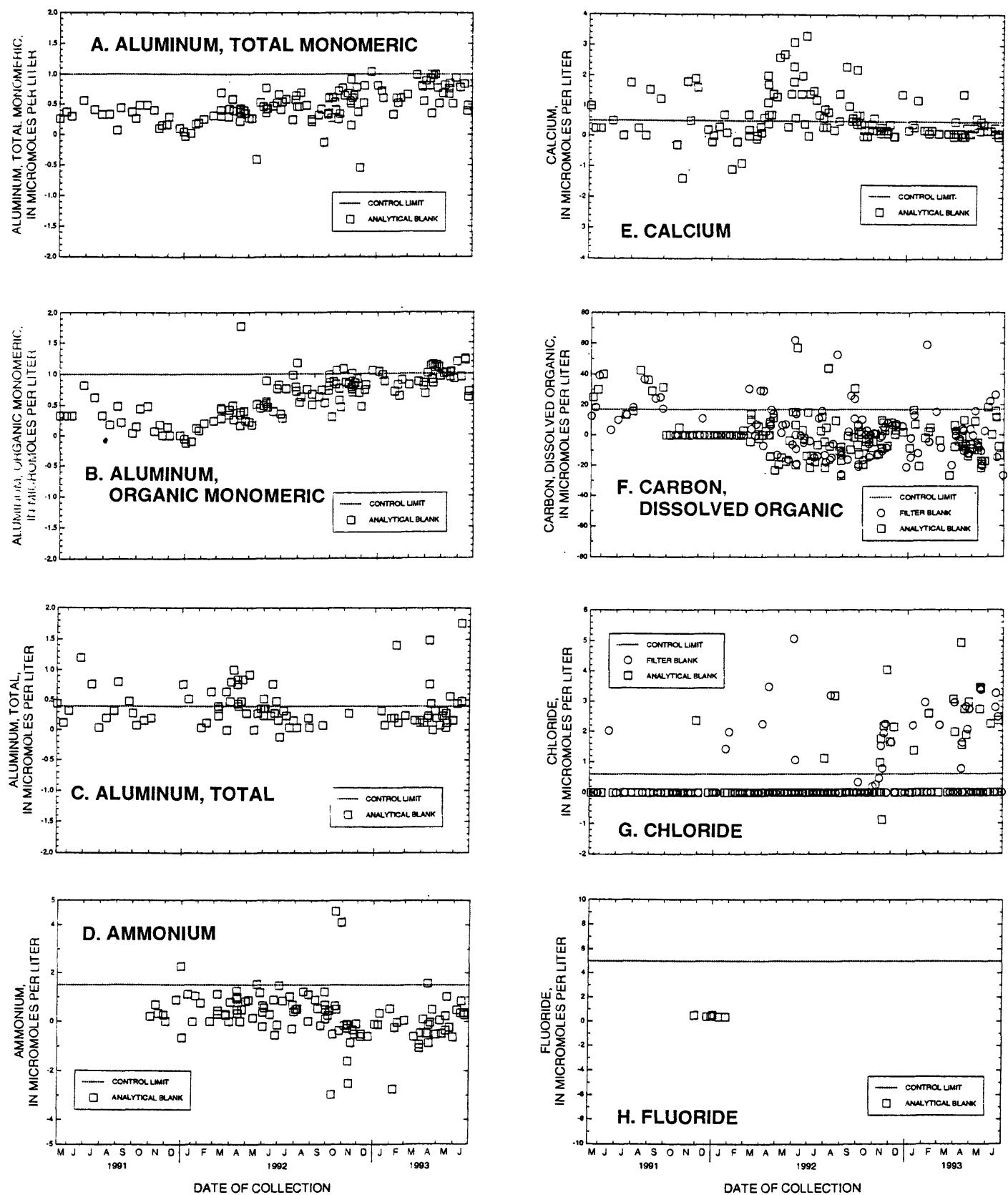


Figure 2. Filter-blank and analytical-blank samples: A. Aluminum, total monomeric B. Aluminum, organic monomeric. C. Aluminum, total. D. Ammonium. E. Calcium. F. Carbon, dissolved organic. G. Chloride. H. Fluoride.

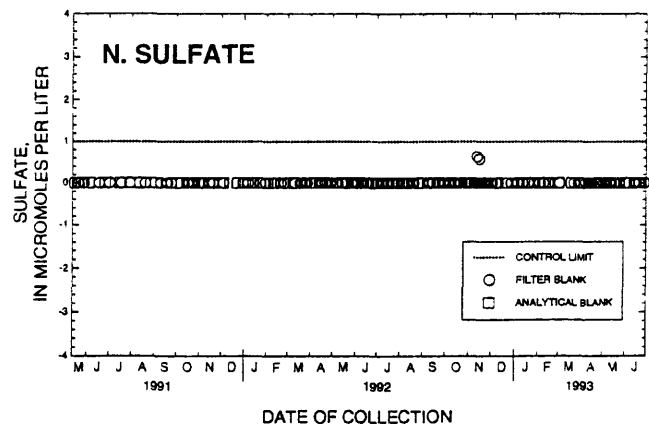
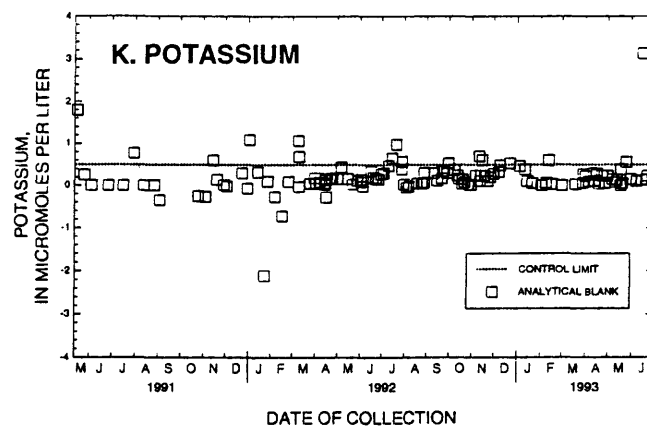
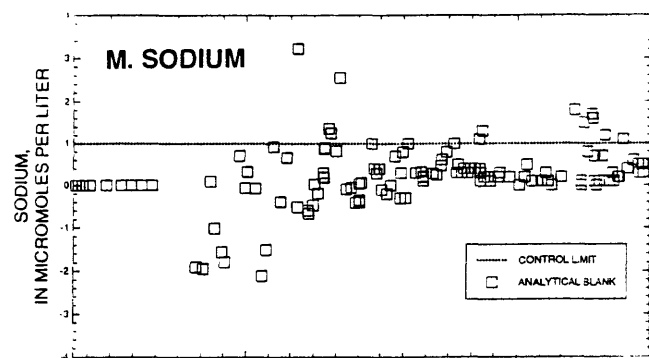
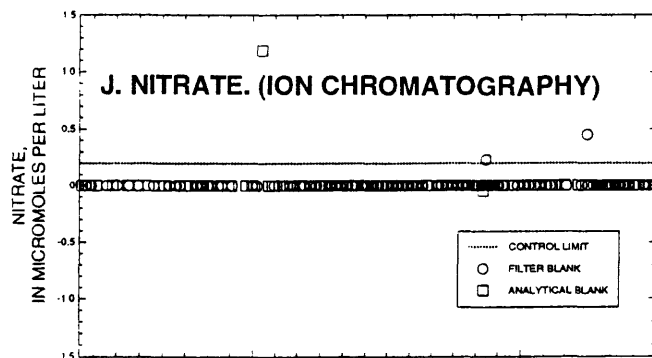
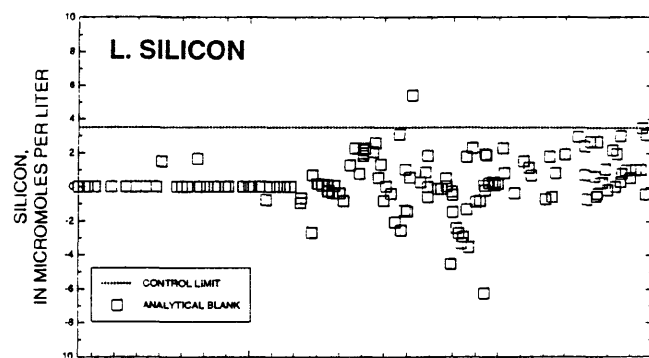
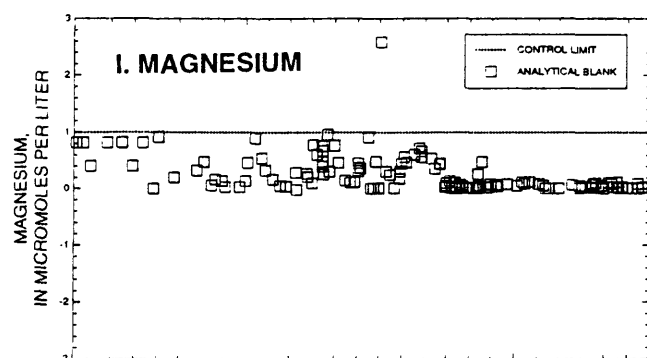


Figure 2. Filter-blank and analytical-blank samples (continued): I. Magnesium. J. Nitrate. (ion chromatography). K. Potassium. L. Silicon. M. Sodium. N. Sulfate.

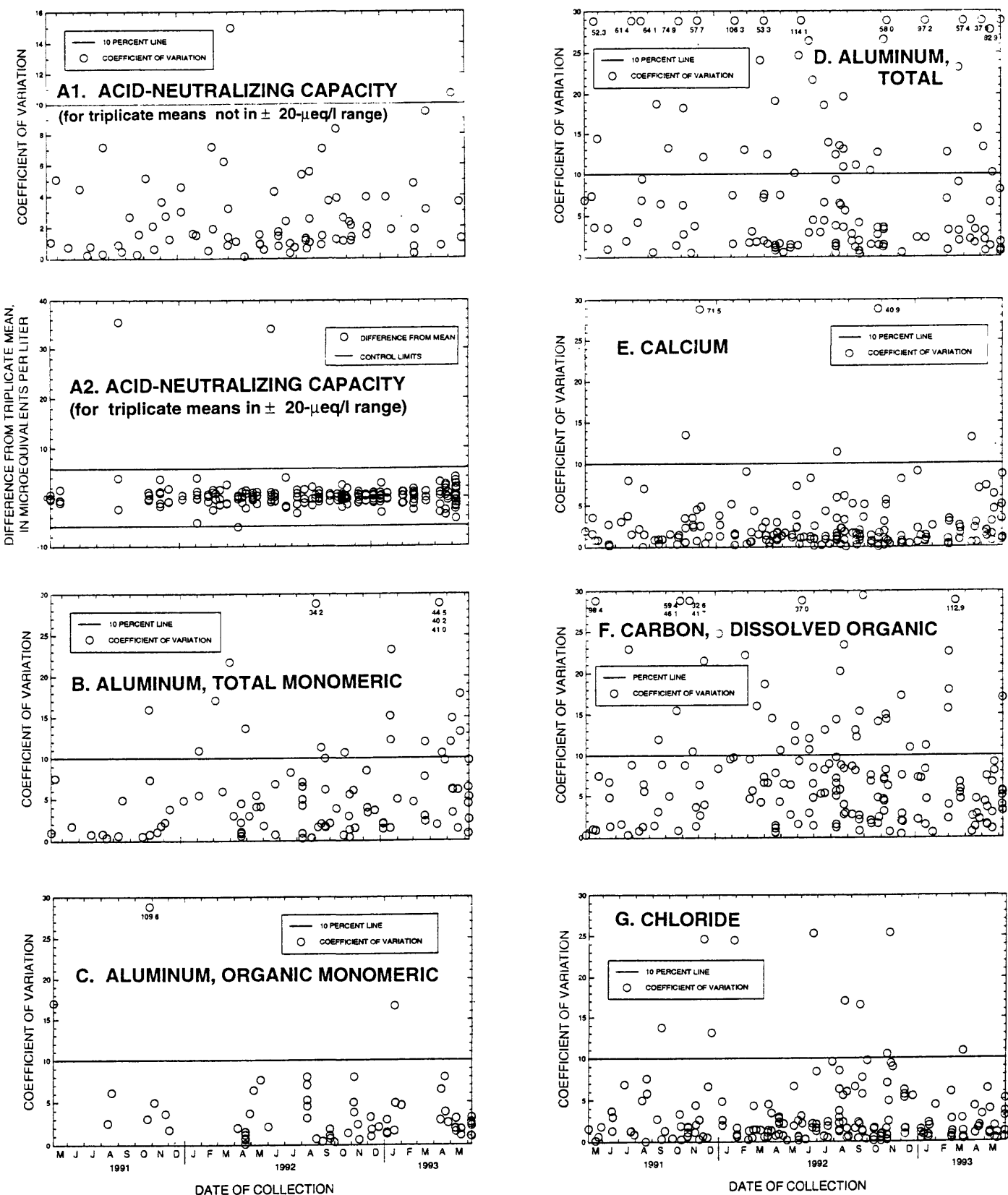


Figure 3. Duplicate and triplicate environmental samples: A1. Acid-neutralizing capacity (for triplicate means not in $\pm 20\text{-}\mu\text{eq/L}$ range). A2. Acid-neutralizing capacity (for triplicate means in $\pm 20\text{-}\mu\text{eq/L}$ range). B. Aluminum, total monomeric. C. Aluminum, organic monomeric. D. Aluminum, total. E. Calcium. F. Carbon, dissolved organic. G. Chloride.

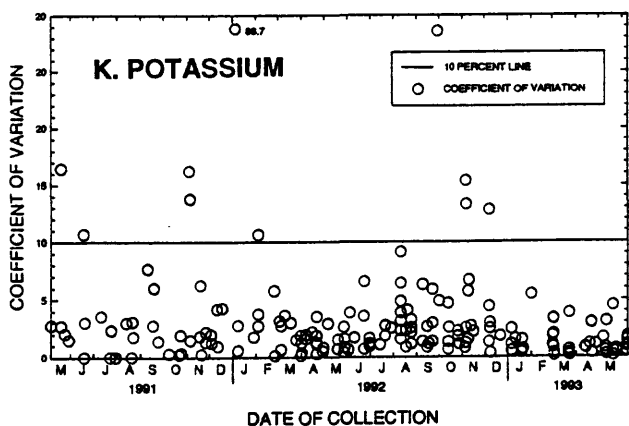
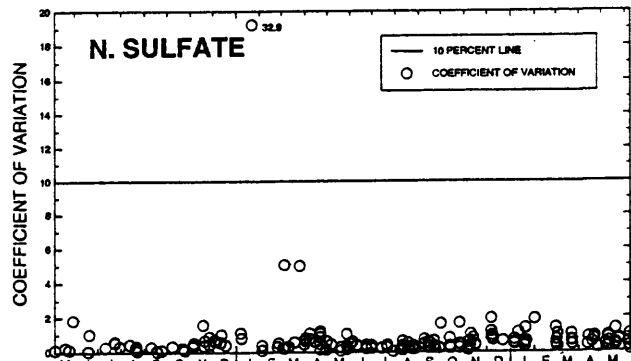
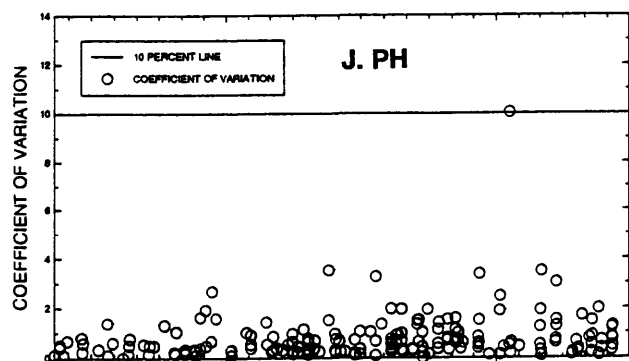
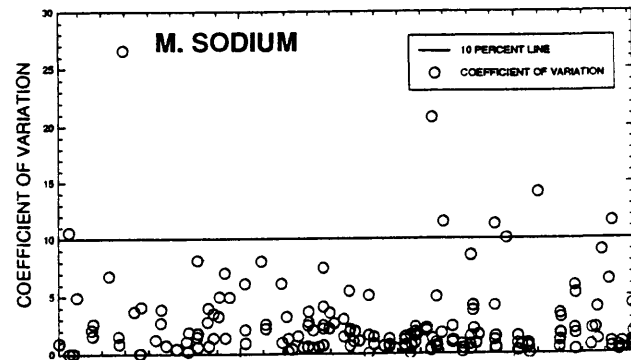
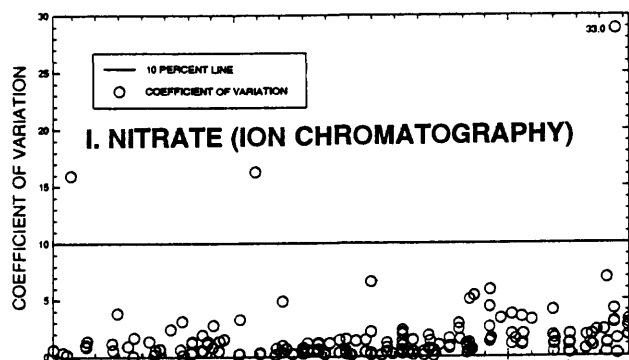
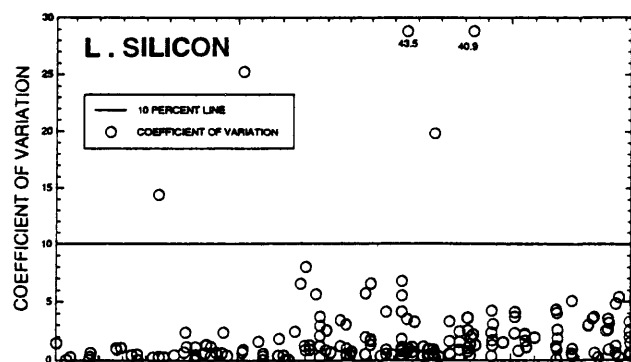
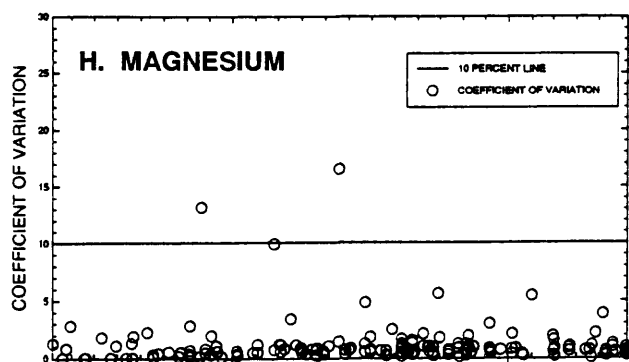


Figure 3. Duplicate and triplicate environmental samples (continued): H. Magnesium. I. Nitrate J. pH. K. Potassium. L. Silicon. M. Sodium. N.Sulfate.

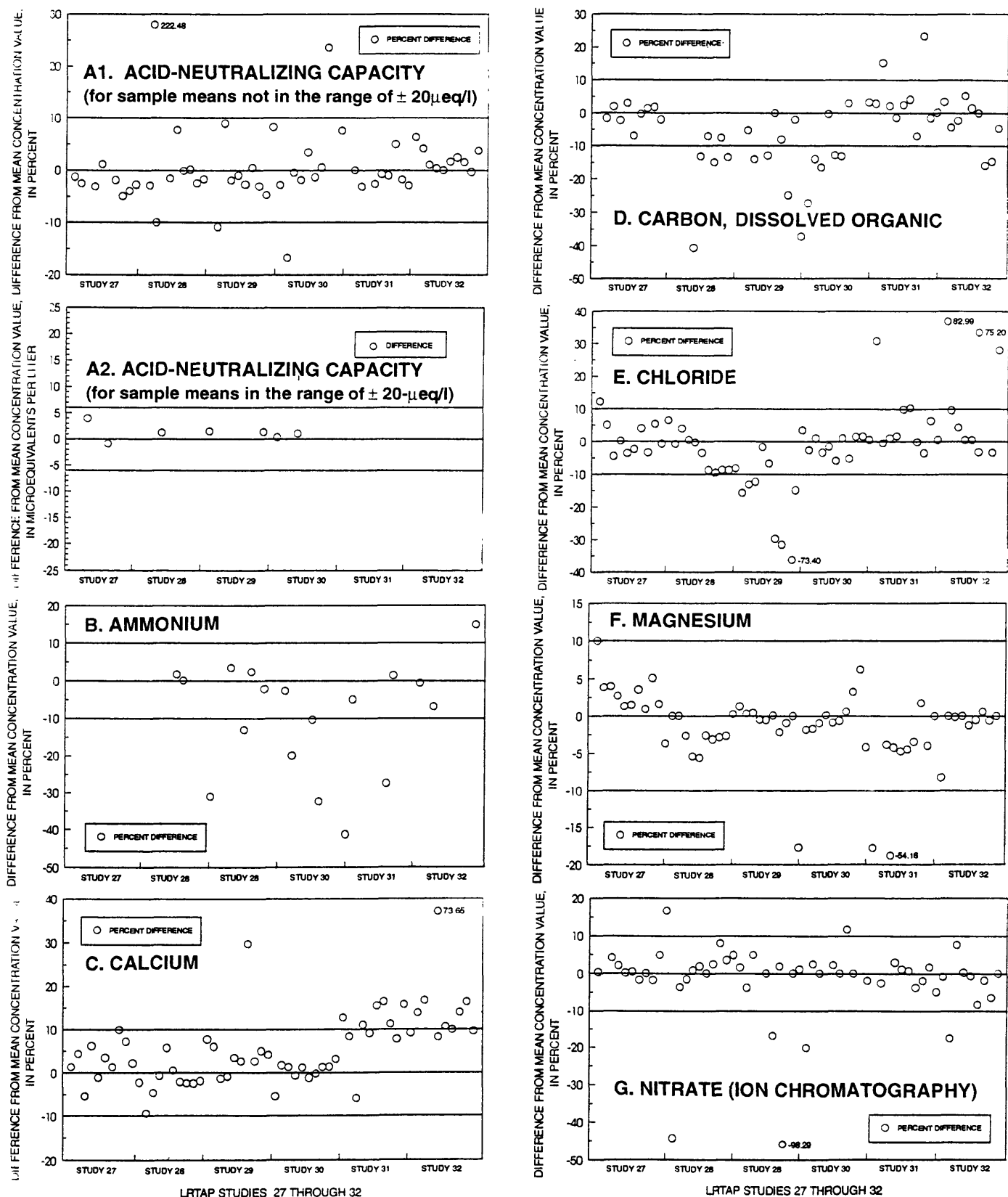
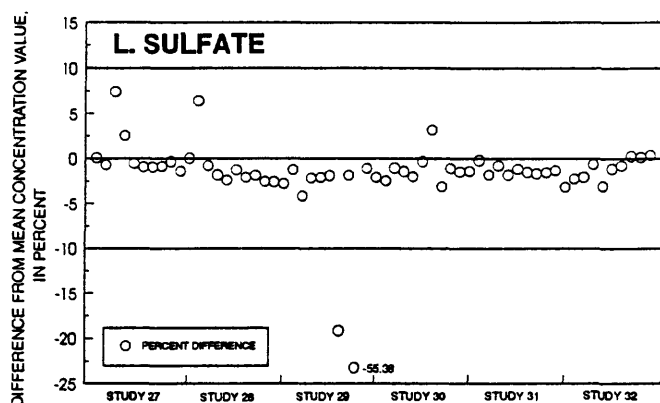
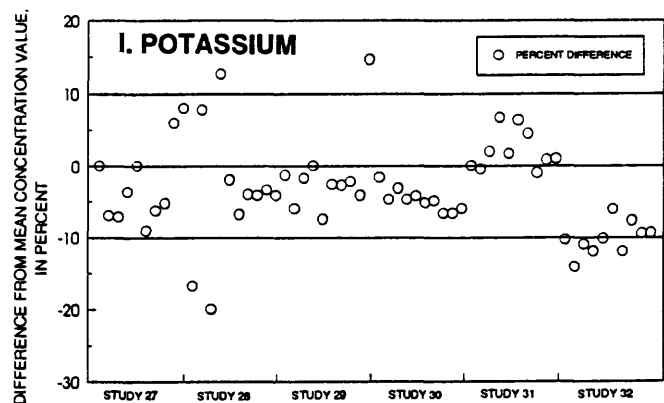
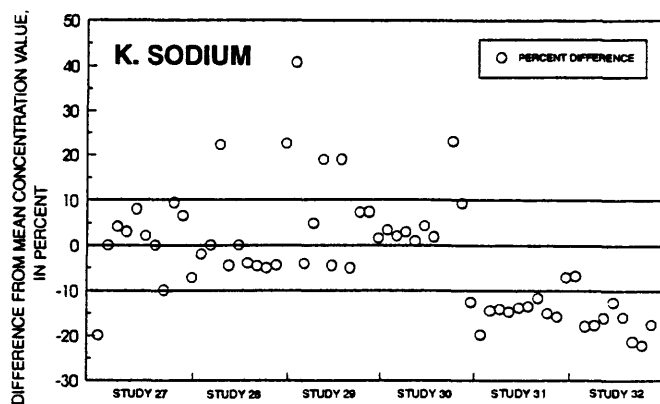
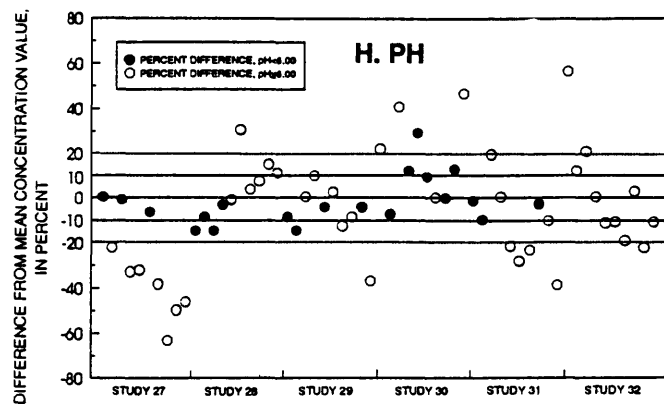


Figure 4. Environment Canada, LRTAP laboratory study: A1. Acid-neutralizing capacity (for sample means not in the range of $\pm 20 \mu\text{eq/L}$). A2. Acid-neutralizing capacity (for sample means in the range of $\pm 20 \mu\text{eq/L}$). B. Ammonium. C. Calcium. D. Carbon, dissolved organic. E. Chloride. F. Magnesium. G. Nitrate (ion chromatography.)



LRTAP STUDIES 27 THROUGH 32

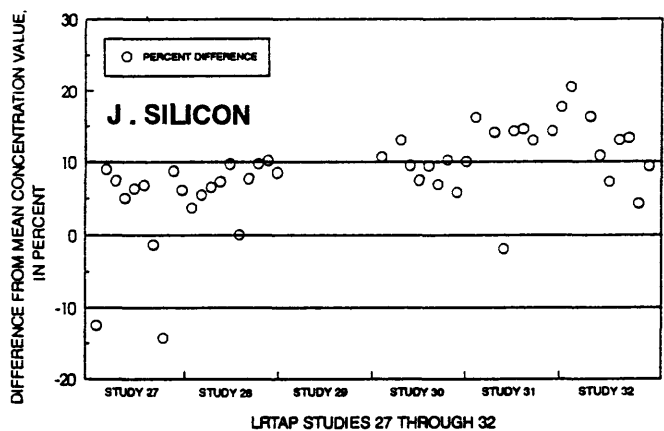


Figure 4. Environment Canada, LRTAP laboratory study (continued): H. pH. I. Potassium. J. Silicon. K. Sodium. L. Sulfate.