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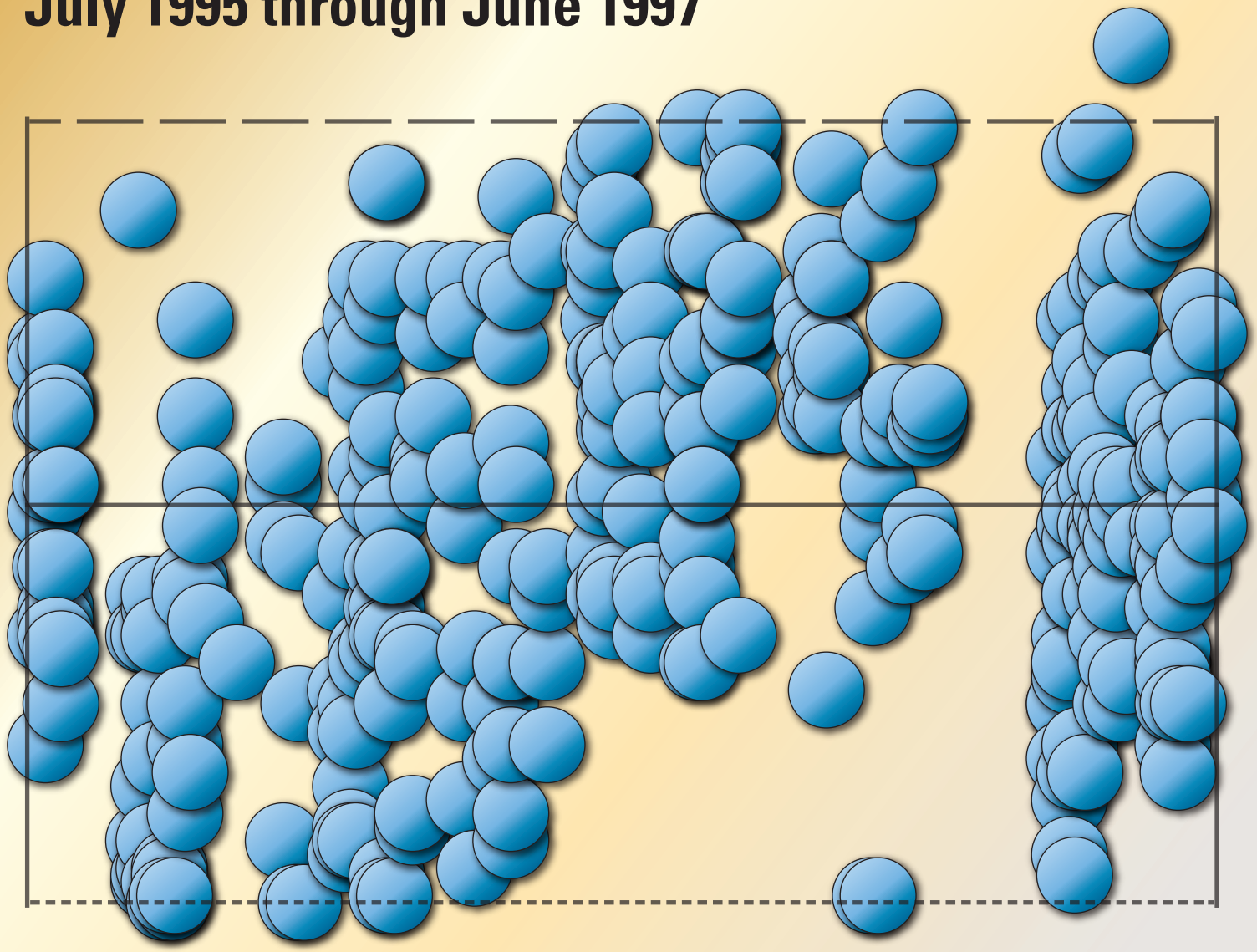
Quality-Assurance Data for Routine Water Analyses by the U.S. Geological Survey Laboratory in Troy, New York — July 1995 through June 1997



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By Tricia A. Lincoln, Debra A. Horan-Ross, Michael R. McHale, and Gregory B. Lawrence

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Gale A. Norton, Secretary

U.S. Geological Survey
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ABBREVIATED UNITS OF MEASUREMENT

mg/L	milligrams per liter
µeq/L	microequivalents per liter
µmol/L	micromoles per liter
µS/cm	microSeimens per centimeter
µg/L	micrograms 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	mean concentration value
MPV	most probable value
NWRI	National Water Research Institute
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

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By Tricia A. Lincoln, Debra A. Horan-Ross, Michael R. McHale, and Gregory B. Lawrence

Abstract

The laboratory for analysis of low-ionic-strength water at the U.S. Geological Survey (USGS) office in Troy, N.Y. analyzes samples collected by USGS projects in the Northeast. The laboratory's quality-assurance program is based on internal and interlaboratory quality-assurance samples and quality-control procedures developed to ensure proper sample collection, processing, and analysis. For the time period addressed in this report, the quality-assurance/quality-control data were stored in the laboratory's SAS data-management system, which provides efficient review, compilation, and plotting of quality-assurance/quality-control data. This report presents and discusses samples analyzed from July 1995 through June 1997.

Quality-control results for 19 analytical procedures were evaluated for bias and precision. Control charts show that data from ten of the analytical procedures were biased throughout the analysis period for either high-concentration or low-concentration samples but were within control limits; these procedures were: acid-neutralizing capacity, total monomeric aluminum, ammonium, calcium, chloride, dissolved organic carbon, magnesium, nitrate (ion chromatography), nitrate (colorimetric method), and sulfate. Four of the analytical procedures were occasionally biased but were within control limits; they were: fluoride, pH, silicon, and sodium.

Results from the filter-blank and analytical-blank analyses indicate that all analytical procedures in which blanks were run were within control limits, although values for a few blanks were outside the control limits.

Sampling and analysis precision are evaluated herein in terms of the coefficient of variation obtained for triplicate samples in 14 of the 19 procedures. Data-quality objectives (DQO's) were met by at least 92 percent of the samples analyzed in all procedures except acid neutralizing capacity (80 percent of samples met objectives), total monomeric aluminum (87 percent of samples met objectives), organic monomeric aluminum (89 percent of samples met objectives), and chloride (89 percent of samples met objectives). The data are insufficient to evaluate the DQO's for total aluminum.

Results of the USGS interlaboratory Standard Reference Sample Program indicated acceptable data quality for most constituents over the time period. The results of the P-sample (low-ionic strength constituent) analysis indicated high data quality with good ratings in all studies. The T-sample (trace constituent) had unacceptable ratings in two studies, but received satisfactory ratings in the others. The N-sample (nutrient constituent) studies had an unacceptable rating in one and an excellent rating in the other.

Environment Canada's NWRI program results indicated that at least 90 percent of the samples met data-quality objectives in 9 of the 12 analyses; exceptions were calcium, chloride, and silicon. Data-quality objectives were not met for calcium samples in two NWRI studies, but all of the samples analyzed were within control limits for the remaining studies. Data-quality objectives were not met for 32 percent of samples analyzed for chloride and 27 percent of samples analyzed for silicon.

Results from blind reference-sample analyses indicated that data-quality objectives were met by at least 90 percent of the calcium, pH, potassium, and sodium samples. Data-quality objectives were met by 77 percent of the chloride samples, 83 percent of the magnesium samples, and 80 percent of the sulfate samples. There is insufficient data to evaluate the specific conductance 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, and stream-water samples. The methods used in this laboratory are described in detail in Lawrence and others (1995). During this time period quality-assurance/quality control data were collected, stored, and reviewed using the laboratory's SAS data-management system.

Analyses done during the 2-year period (July 1995-June 1997) represented by this report were: acid-neutralizing

capacity (ANC), total monomeric aluminum, organic monomeric aluminum, total aluminum, ammonium, calcium, dissolved organic carbon (DOC), DOC (soil expulsions), chloride, fluoride, magnesium, nitrate (ion chromatograph and colorimetric method), pH, potassium, silicon, sodium, specific conductance, and sulfate.

Purpose and Scope

This report documents the quality-assurance practices and quality-control data 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, triplicate environmental samples, and blind reference samples, and (3) describes analytical biases and outliers and the corrective actions taken.

Participating Projects

The numbers and types of samples analyzed by the laboratory during the 2-year period are summarized below, by the 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: 181 samples (stream water, shallow ground water, and snow).

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: 4,385 samples (stream water, shallow ground-water, soil water solution, soil water by expulsion method, and snow).

Project: Long-Term Monitoring of Five Streams in the Catskill Mountains (NY85-152)
Cooperator: U.S. Environmental Protection Agency
Analyses: 331 stream-water samples.

Project: Forest-Floor Aluminum and Calcium Chemistry—Relations with Acid Deposition, Root Vitality, Stand Dynamics, and Red Spruce (NY92-208)
Cooperator: U.S. Forest Service
Analyses: 67 samples (stream water, soil water solution, and soil water by expulsion method).

Project: The effects of the Clean Air Act on water quality of medium-scale rivers in the Northeastern United States (NY97-322)
Cooperator: US Geological Survey, Office of Water Quality
Analysis: 22 stream samples.

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

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. The data quality objectives (DQO's) are based on (1) the precision and accuracy levels generally required in projects using the Troy Laboratory, and (2) the analytical limits of the methods used.

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 either 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 analyses; exceptions are inorganic monomeric aluminum, for which column efficiency is used to determine the acceptability of the data, and fluoride, for which only one mid-level QC sample is prepared because the concentrations encountered by the laboratory are within a narrow range.

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 (after every 17 environmental samples), and pH (after every 7 to 13 environmental samples). QC samples that do not meet 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 considered to be out-of-control data. The data 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. Analytical results of QC samples are included in this report to

indicate (1) the frequency of out-of-control data that are not rerun, and (2) biases and trends of within control data. The number of samples analyzed and a summary of the quality-assurance data are given in table 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 constituents that require filtration. Filter-blank analysis indicates whether contamination has occurred during bottle-washing procedures, filtration, sample preservation, 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.

Triplicate Environmental Samples

One set of triplicate environmental samples is included in each group of 50 samples. An environmental triplicate set consists of three consecutive samples taken from one field site. The purpose of environmental triplicate samples is to determine long-term analytical precision. Precision can be affected by bottle washing, sample-collection, sample processing procedures, and analysis. Environmental samples

Table 1. Number of environmental and quality-control (QC) samples analyzed by the Troy Laboratory, and summary of quality-control data for each constituent, July 1995 through June 1997.

[QC-high = high concentration quality-control sample. QC-low = low concentration quality-control sample.]

Constituent	Number of samples analyzed			Number of QC samples exceeding control limits where environmental sample data are not rejected		Number of QC samples exceeding control limits by more than 5 percent where environmental sample data are not rejected	
	Environmental samples	QC-high Samples	QC-low Samples	QC-high	QC-low	QC-high	QC-low
Acid-neutralizing capacity	3458	62	317	0	1	0	0
Aluminum, total monomeric	3722	548	548	0	1	0	1
Aluminum, organic monomeric*	3722	0	0	0	0	0	0
Aluminum, total	1098	140	140	0	0	0	0
Ammonium	2943	453	453	2	5	0	1
Calcium	3019	615	615	0	1	0	0
Carbon, dissolved organic	3885	535	535	2	3	0	1
Carbon, dissolved organic (soil expulsions)	67	18	18	0	0	0	0
Chloride	3937	647	647	0	0	0	0
Fluoride	1792	0	312	1	0	0	0
Magnesium	3801	601	601	0	0	0	0
Nitrate (ion chromatography)	3922	647	647	0	4	0	2
Nitrate (colorimetric method)	988	175	171	5	0	0	0
pH	3760	125	489	0	1	0	0
Potassium	3765	587	585	0	3	0	3
Silicon	3684	546	546	1	4	0	1
Sodium	836	539	539	0	0	0	0
Specific conductance	316	36	88	0	0	0	0
Sulfate	935	647	647	0	3	0	1

*Column efficiency is used to determine the acceptability of the data.

are selected for triplicate analysis on a random basis to ensure a wide range of sample concentrations from various field sites. The laboratory alternates between analyzing a triplicate set consecutively and separating the triplicate set over the day's analytical run.

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 laboratory participates in the low-ionic strength, nutrient, and trace components of this program. Typically, the reference samples consists of snow, rain, surface water, or deionized water that is collected, filtered, and possibly spiked with reagent-grade chemicals to meet the goals of the SRS program. Low-ionic strength constituent reference samples are prefixed by a P and are analyzed for calcium, chloride, fluoride, magnesium, pH, potassium, sodium, specific conductance, and sulfate. Nutrient constituent reference samples are prefixed by an N and are analyzed for ammonium. Trace constituent reference samples are prefixed by a T and are analyzed for aluminum, calcium, magnesium, potassium, silicon, and sodium. 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 after the conclusion of each study. The most probable value (MPV) for each constituent is equal to the median value. Individual laboratory performances are rated numerically; the highest score is 4.0, and the lowest is 0.0.

NWRI Ecosystem Interlaboratory QA Program

In 1996, Environment Canada changed the name of the LRTAP interlaboratory study to the NWRI Ecosystem Interlaboratory QA program. The Troy Laboratory participates in the quality-assurance program, in which a set of 10 samples is analyzed two 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. The concentrations of the constituents in the NWRI samples are similar to those of the environmental samples analyzed at the Troy Laboratory. Laboratory results are compared with a median concentration value (MCV) calculated from results from all participants in the NWRI program. Laboratory personnel are aware of the presence of NWRI samples at the time of analysis but do not know the MCV of the constituents until Environment Canada publishes a report at the conclusion of each study.

Blind Reference Samples

The Troy Laboratory disguises USGS SRS samples from previous studies as routine environmental samples. These blind reference samples are processed and analyzed as environmental samples and therefore assumed by the analyst to be a project sample. The blind reference samples have most probable values that are reported by the USGS SRS program. The SRS samples are rotated as supplies are exhausted, and periodically the identity of the blind reference sample is changed. One blind reference sample is included in each set of 50 environmental samples.

Control-Chart Development and Evaluation

Control charts (figs. 1-5) 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.

A constituent analysis is considered biased if 70 percent or more of the points on a chart are above or below the theoretical value.

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 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 and precision. All data are reported in micromoles per liter (μmol/L) except pH (pH units), ANC (microequivalents per liter, μeq/L), and specific conductance (microSeimens per centimeter, mS/cm).

During the period represented by this report, two quality-control sample concentrations were changed to reflect typical environmental-sample concentrations (see fig. 1N and 1P). The concentration changes are discussed in the summary of results.

Filter Blanks and Analytical Blanks

Results from blank analyses (fig. 2) are plotted on control charts by constituent. The control limits were established to meet project DQO's (table 2) and are represented by horizontal lines on the control charts. Data are plotted as concentration in relation to date of collection. Negative blank concentrations are encountered frequently. The standard curve is extrapolated beyond the lowest standard in order to evaluate blank samples and negative concentrations reflect the practical limitations of the extrapolation. The control charts are evaluated to identify possible contamination or positive interferences.

Table 2. Reporting limits and data-quality objectives for accuracy, precision, and blanks for solution analyses performed by the U.S. Geological Survey Laboratory in Troy, N.Y., July 1995 through June 1997.

[DQO, data-quality objective. µmol/L, micromoles per liter. CV, coefficient of variation. ANC, acid-neutralizing capacity.]

		Accuracy				Precision	
		Low-concentration quality-control sample		High-concentration quality-control sample			
Constituent or property	Reporting limit (µmol/L)	DQO (percent error)	Concentration (µmol/L)	DQO (percent error)	Concentration (µmol/L)	Environmental Triplicate Samples DQO (CV)	Filter and analytical blanks DQO (µmol/L)
Acid-neutralizing capacity [1]	none	10	(-39.9)	10	(125)	15	none
Aluminum, total monomeric	1.5	15	7.41	10	18.5	15	1.0
Aluminum, organic monomeric [2]	1.5	none	none	none	none	15	1.0
Aluminum, total	1.0	20	3.0	10	15.0	10	none
Ammonium	2.0	15	7.14	10	17.9	none	none
Calcium	2.0	10	25.0	10	99.8	10	1.0
Carbon, dissolved organic[3]	41.0	15	83.3	10	416	10	18
Carbon, dissolved organic (soil expulsions)[3]	41.0	10	416	10	1665	none	none
Chloride	3.0	10	8.47	10	84.7	10	2.0
Fluoride	0.5	15	1.58	none	none	none	none
Magnesium	1.0	10	10.3	10	41.1	10	0.5
Nitrate (ion chromatography)	2.0	10	4.84	10	48.4	10	0.3
Nitrate (colorimetric method)	5.0	15	42.9	10	100	none	none
pH[4]	none	10	(4.44)	20	(6.88)	10	none
Potassium	1.0	10	6.40	10	25.6	10	0.5
Silicon	6.0	10	35.6	10	107	10	3.0
Sodium	1.0	10	8.70	10	43.5	10	1.0
Specific conductance[5]	none	10	(17.0)	10	(39.0)	none	none
Sulfate	2.0	10	8.33	10	83.3	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.

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

[3] Concentrations are expressed as micromoles carbon per liter.

[4] pH: Percent error and coefficient of variation determined from [H+]. Values in parentheses are in pH units.

[5] Specific conductance: Values in parentheses are in microSiemens per centimeter.

Triplicate Environmental Samples

The coefficient of variation (CV) for each triplicate sample concentration 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. The DQO for all constituents is a CV of less than 10 percent, with the exception of ANC, total monomeric aluminum and organic monomeric aluminum, which are 15 percent. Each circle within the control charts represents the CV of a triplicate environmental sample.

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

where: s = standard deviation, and
x = arithmetic mean of triplicate samples

ANC triplicate sample means were plotted on two graphs. The first graph shows the CV for triplicate sample means outside the range of -20 to +20 µeq/L (fig. 3A1); the absolute value of the mean is used to calculate the CV. The second graph shows values that fall between -20 and +20 µeq/L (fig. 3A2); each symbol on the second graph represents the difference between the triplicate sample mean and the individual values of that triplicate sample.

NWRI Ecosystem Interlaboratory QA Program

Interlaboratory comparison graphs (fig. 4) are based on results from NWRI samples and represent NWRI studies from September 1995 through April 1997. Samples with MCV's less than the reporting limits were excluded from the graphs. The MCV and the control limits are represented by lines on the graphs; the percent difference (D) is calculated as:

D = [(AV - MCV)/MCV] x 100
where: AV = analyzed value, and
MCV = mean concentration value

A separate graph is shown for ANC values in the +20 to -20 µeq/L range; results for these samples are plotted as the difference between the laboratory value and the MCV (fig. 4A2). The NWRI 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 short dashed line and a long dashed line on the pH graph (fig. 4H).

Blind Reference Samples

Results from blind reference sample analyses (fig.5) are plotted on separate control charts, by constituent and date of analysis. Samples with MPV's less than the reporting limits were excluded from the graphs. The MPV and the control limits of ±10 percent are represented by lines on the graphs; the percent difference (D) is calculated as:

D = [(AV-MPV)/MPV]x100
where: AV = analyzed value, and
MPV = most probable value

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) triplicate environmental samples (fig. 3, p. 19-20), (D) SRS samples (table 3), (E) LRTAP samples (fig. 4, p. 21-22), and (F) blind samples (fig. 5, p. 23).

A. Quality-Control Samples

Acid-Neutralizing Capacity (fig. 1A).– DQO's were met by 99 percent of the samples. The QC-high sample had a negative bias during this time period. The QC-low sample had a positive bias from June through December 1996.

Aluminum, Total Monomeric (fig. 1B).–DQO's were met by 99 percent of the samples. The QC-high sample had a slight positive bias during this time period. The QC-low sample had a slight positive bias through 1996 and a slight negative bias through 1997.

Aluminum, Organic Monomeric.–A QC sample has not been developed for this analysis. Column efficiency is used to determine acceptability of the data.

Aluminum, Total (fig. 1C).–DQO's were met by 100 percent of the samples. No apparent trends or biases were evident among the QC-high and QC-low samples.

Ammonium (fig. 1D).–DQO's were met by 99 percent of the samples. No apparent trends or biases were evident among the QC-low samples. The QC-high sample had a slight positive bias during this time period.

Calcium (fig. 1E).–DQO's were met by 99 percent of the samples. A slight positive bias was observed for most analyzed QC-high and QC-low samples during this period.

Carbon, Dissolved Organic (fig. 1F).–DQO's were met by 99 percent of the samples. A positive bias was observed for the QC-high sample in 1995 which reappeared in September of 1997. The QC-low sample had a negative bias during this period.

Carbon, Dissolved Organic (soil expulsions) (fig. 1G).–DQO's were met by 100 percent of the samples. The data are insufficient for trend analysis.

Chloride (fig. 1H).–DQO's were met by 100 percent of the samples. The QC-high graph illustrates a negative bias which was due to an error in preparation of QC stock

Table 3. Results obtained by the Troy Laboratory for U.S. Geological Survey Standard Reference Sample (SRS) Program, October 1995 through April 1997.

[MPV, most probable value; TV, Troy Laboratory value. All values are in milligrams per liter except aluminum (µg/L), pH (pH units) and specific conductance (microSiemens per centimeter). Dashes indicates no results reported.]

Analyte	MPV, TV, and rating[a]	SRS sample number and date of sample distribution										
		P-25 10-95[b]	T-137 10-95[b]	P-26 4-96[c]	T-139 4-96[c]	T-141 4-96[c]	N-49 4-96[c]	P-27 9-96[d]	T-143 9-96[d]	N-51 9-96[d]	P-28 4-97[e]	T-149 4-97[e]
Aluminum	MPV	--	--	--	22.4	75.4	--	--	--	--	--	--
	TV	--	--	--	11.1	26.4	--	--	--	--	--	--
	Rating	--	--	--	0	0	--	--	--	--	--	--
Ammonium	MPV	--	--	--	--	--	0.155	--	--	0.07	--	--
	TV	--	--	--	--	--	0.269	--	--	0.10	--	--
	Rating	--	--	--	--	--	0	--	--	4	--	--
Calcium	MPV	1.67	38.1	0.450	50.3	19.1	--	2.53	53.7	--	1.64	42.3
	TV	1.68	38.2	0.280	33.9	13.0	--	1.45	55.0	--	1.64	42.9
	Rating	4	4	0	0	0	--	0	3	--	4	4
Chloride	MPV	1.30	--	7.79	--	--	--	1.20	--	--	3.30	--
	TV	1.25	--	7.46	--	--	--	1.13	--	--	3.39	--
	Rating	4	--	3	--	--	--	4	--	--	4	--
Fluoride	MPV	0.139	--	0.040	--	--	--	--	--	--	0.06	--
	TV	0.139	--	0.027	--	--	--	--	--	--	0.04	--
	Rating	4	--	3	--	--	--	--	--	--	3	--
Magnesium	MPV	0.350	10.1	0.060	10.00	5.48	--	0.461	10.4	--	0.883	13.1
	TV	0.330	9.5	0.050	8.00	4.33	--	0.450	8.3	--	0.850	12.9
	Rating	2	2	3	0	0	--	4	0	--	3	4
pH	MPV	6.52	--	4.70	--	--	--	6.92	--	--	6.75	--
	TV	6.49	--	4.78	--	--	--	7.03	--	--	6.94	--
	Rating	4	--	3	--	--	--	4	--	--	4	--
Potassium	MPV	0.55	1.19	0.146	2.73	2.32	--	--	--	--	--	2.00
	TV	0.56	1.19	0.160	2.82	2.42	--	--	--	--	--	2.31
	Rating	4	4	4	4	3	--	--	--	--	--	0
Silicon	MPV	--	6.96	--	9.31	8.70	--	--	23.4	--	--	--
	TV	--	8.01	--	10.24	9.44	--	--	25.4	--	--	--
	Rating	--	1	--	0	1	--	--	2	--	--	--
Sodium	MPV	1.28	22.0	4.40	90.9	33.0	--	1.34	34.0	--	3.25	42.8
	TV	1.27	20.6	4.28	109.3	35.1	--	1.32	33.0	--	3.20	37.1
	Rating	4	2	4	0	1	--	4	3	--	4	0
Specific conductance	MPV	20.9	--	--	--	--	--	--	--	--	--	--
	TV	20.2	--	--	--	--	--	--	--	--	--	--
	Rating	4	--	--	--	--	--	--	--	--	--	--
Sulfate	MPV	2.34	--	0.67	--	--	--	2.42	--	--	6.14	--
	TV	2.36	--	0.68	--	--	--	2.34	--	--	6.18	--
	Rating	4	--	4	--	--	--	4	--	--	4	--

[a] Laboratory rating system: 4 is highest score; 0 is lowest
[b] Sample described in Long and Farrar (1994a)
[c] Sample described in Long and Farrar (1994b)
[d] Sample described in Long and Farrar (1995a)
[e] Sample described in Long and Farrar (1995b)

solution and has been corrected. The QC-low sample shows a positive bias during this time period.

Fluoride (fig. 1I).–DQO's were met by 99 percent of the samples. The positive bias in 1995 and 1997 is attributed to the QC stock solution, which was replaced.

Magnesium (fig. 1J).–DQO's were met by 100 percent of the samples. The QC-high sample had a negative bias. The QC-low sample had a negative bias in 1995.

Nitrate (ion chromatography) (fig. 1K).–DQO's were met by 99 percent of the samples. The QC-high sample had a negative bias during this period. No apparent trends or biases were evident among the QC-low sample.

Nitrate (colorimetric method) (fig. 1L).–DQO's were met by 99 percent of the samples. The QC-high and QC-low samples appear to have a negative bias; 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. Project chiefs were notified of the negative bias; data were not changed.

pH (fig. 1M).–DQO's were met by 99 percent of the samples. The QC-high sample had a positive bias from March through August 1996. The QC-low sample had a positive bias during 1995.

Potassium (fig. 1N).–DQO's were met by 100 percent of the samples. No apparent trends or biases were evident among the QC-high and QC-low samples. The potassium QC-low concentration was decreased from 6.40 to 5.12 µmol/L in January 1996 and reverted to 6.40 µmol/L in November of 1996 to reflect typical environmental-sample concentrations.

Silicon (fig. 1O).–DQO's were met by 99 percent of the samples. The QC samples had a positive bias from June to December of 1996.

Sodium (fig. 1P).–DQO's were met by 100 percent of the samples. No apparent trends or biases were evident among the QC sample. The sodium QC-low concentration was changed periodically between 8.70 and 10.88 µmol/L to reflect typical environmental-sample concentrations. The QC-low sample had a negative bias during February of 1997 and a positive bias in May of 1997.

Specific conductance (fig. 1Q).–DQO's were met by 100 percent of the samples. The data are insufficient for trend analysis, but visual inspection appears to indicate a negative bias.

Sulfate (fig. 1R).–DQO's were met by 99 percent of the samples. No apparent trends or biases were evident among the QC-low sample. The QC-high sample had a positive bias during this time period.

B. Filter Blanks and Analytical Blanks

Acid-Neutralizing Capacity.–Blanks were not analyzed for this constituent.

Aluminum, Total Monomeric (fig. 2A).–The DQO was met by 88 percent of the samples. Although below the DQO, there is evidence of some aluminum contamination in 1996.

Aluminum, Organic Monomeric (fig. 2B).–The DQO was met by 100 percent of the samples. Although below the DQO, there is evidence of some aluminum contamination in 1996.

Aluminum, Total.–Blanks were not analyzed for this constituent.

Ammonium.–Blanks were not analyzed for this constituent.

Calcium (fig. 2C).–The DQO was met by 86 percent of the samples. No systematic trends were evident for this analysis.

Carbon, Dissolved Organic (fig. 2D).–The DQO was met by 93 percent of the samples. No systematic trends were evident for this analysis.

Carbon, Dissolved Organic (soil expulsions).–Blanks were not available for this constituent.

Chloride (fig. 2E).–The DQO was met by 67 percent of the samples. The source of chloride contamination is being investigated.

Fluoride.–Blanks were not analyzed for this constituent.

Magnesium (fig. 2F).–The DQO was met by 98 percent of the samples. No systematic trends were evident for this analysis.

Nitrate (ion chromatography) (fig. 2G).–The DQO was met by 97 percent of the samples. No systematic trends were evident for this analysis.

Nitrate (colorimetric method).–Blanks were not available for this constituent.

pH.—Blanks were not analyzed for this constituent.

Potassium (fig. 2H).–The DQO was met by 99 percent of the samples. No systematic trends were evident for this analysis.

Silicon (fig. 2I).–The DQO was met by 87 percent of the samples. No systematic trends were evident for this analysis.

Sodium (fig. 2J).–The DQO was met by 96 percent of the samples. No systematic trends were evident for this analysis.

Specific conductance.–Blanks were not analyzed for this constituent.

Sulfate (fig. 2K).–The DQO was met by 99 percent of the samples. No systematic trends were evident for this analysis.

C. Triplicate Environmental Samples

Acid-Neutralizing Capacity (figs. 3A1 and 3A2).–The DQO was met by 80 percent of the triplicate samples.

Aluminum, Total Monomeric (fig. 3B).–The DQO was met by 87 percent of the triplicate samples.

Aluminum, Organic Monomeric (fig. 3C).–The DQO was met by 89 percent of the triplicate samples.

Aluminum, Total (fig. 3D).–The data are insufficient to evaluate the DQO's.

Ammonium.–Triplicate samples were not analyzed for this constituent.

Calcium (fig. 3E).–The DQO was met by 94 percent of the triplicate samples.

Carbon, Dissolved Organic (fig. 3F).–The DQO was met by 93 percent of the triplicate samples.

Carbon, Dissolved Organic (soil expulsions).–Triplicate samples were not available for this constituent.

Chloride (fig. 3G).–The DQO was met by 89 percent of the triplicate samples.

Fluoride.–Triplicate samples were not analyzed for this constituent.

Magnesium (fig. 3H).–The DQO was met by 100 percent of the triplicate samples.

Nitrate (ion chromatography) (fig. 3I).–The DQO was met by 96 percent of the triplicate samples.

Nitrate (colorimetric method).–Triplicate samples were not available for this constituent.

pH (fig. 3J).–The DQO was met by 99 percent of the triplicate samples.

Potassium (fig. 3K).–The DQO was met by 95 percent of the triplicate samples.

Silicon (fig. 3L).–The DQO was met by 98 percent of the triplicate samples.

Sodium (fig. 3M).–The DQO was met by 98 percent of the triplicate samples.

Specific conductance.–Triplicate samples were not analyzed for this constituent.

Sulfate (fig. 3N).–The DQO was met by 100 percent of the triplicate samples.

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

The U.S. Geological's SRS Program rates laboratory performance for each analyte on a scale of 4 to 0:

Rating	Performance
4.0	Excellent
3.0-3.99	Good
2.0-2.99	Satisfactory
1.0-1.99	Marginal
0.0-0.99	Unsatisfactory

Overall laboratory mean ratings for each SRS sample were:

P-25	3.8	T-137	2.6	N-49	0.0
P-26	3.0	T-139	0.7	N-51	4.0
P-27	3.3	T-141	0.8		
P-28	3.7	T-143	2.0		
		T-149	2.0		

All analyses received an acceptable rating for each constituent with these exceptions:

Aluminum.–Due to the malfunctioning of the graphite furnace, aluminum data are erroneous. An inductively coupled plasma (ICP) spectrophotometer has been purchased and improved results are expected.

Ammonium.–SRS sample N-49 was improperly diluted leading to erroneous data.

Calcium.–In 1996, calcium data are erroneous due to a method error. The calcium method used during this period included a lanthanum chloride reagent whose concentration was too low to mask interferences. Environmental-sample data were erroneously low. The method was corrected, and project samples were reanalyzed for calcium. Initial data were flagged as erroneous, and reanalysis data were added to the database.

Magnesium.–The most probable cause of erroneous magnesium data for high concentration SRS samples is an error in dilution of the sample.

Potassium.–The cause of a zero rating for SRS T-149 is unexplained.

Silicon.–The erroneous silicon data were due to a matrix interference. All SRS T samples are acidified. An acidified sample was not compatible with the silicon method utilized during this period. SRS silicon analysis was discontinued until the purchase of an ICP.

Sodium.–The most probable cause of erroneous sodium data for high concentration SRS samples is an error in dilution of the sample.

E. NWRI Ecosystem Interlaboratory QA Program

Environment Canada's NWRI program does not audit the analysis of total monomeric aluminum, organic monomeric aluminum, dissolved organic carbon (soil expulsions), fluoride, and nitrate (colorimetric method).

The laboratory did not submit results for total aluminum or specific conductance analyses during this time period.

Acid-Neutralizing capacity (figs. 4A1 and 4A2).—The DQO was met by 100 percent of the NWRI samples. No trend or bias was evident.

Ammonium (fig. 4B).—The DQO was met by 92 percent of the NWRI samples. NWRI samples were not run for ammonium for studies 39 or 68. Environmental samples are no longer routinely analyzed for ammonium. Samples are selectively analyzed a few times yearly.

Calcium (fig. 4C).—The DQO was met by 58 percent of the NWRI samples. The calcium method used during this period included a lanthanum chloride reagent, whose concentration was too low to mask interferences. Environmental-sample data were erroneously low. The method was corrected, and project samples were reanalyzed for calcium. Initial data were flagged as erroneous, and reanalysis data were added to the database.

Carbon, dissolved organic (fig. 4D).—The DQO was met by 90 percent of the NWRI samples. The data exhibited a positive bias. A new carbon analyzer has been purchased and improved results are expected.

Chloride (fig. 4E).—The DQO was met by 68 percent of the NWRI samples. Most outliers had a positive bias.

Magnesium (fig. 4F).—The DQO was met by 95 percent of the NWRI samples.

Nitrate (ion chromatography) (fig. 4G).—The DQO was met by 90 percent of the NWRI samples.

pH (fig. 4H).—The DQO was met by 100 percent of the NWRI samples. No trend or bias was evident.

Potassium (fig. 4I).—The DQO was met by 90 percent of the NWRI samples. No trend or bias was evident.

Silicon (fig. 4J).—The DQO was met by 73 percent of the NWRI samples. An ICP was recently installed for silicon analysis, and improved results are expected.

Sodium (fig. 4K).—The DQO was met by 90 percent of the NWRI samples. No trend or bias was evident.

Sulfate (fig. 4L).—The DQO was met by 100 percent of the samples. Data indicate a slight negative bias for studies 39, 68, and 69. The cause is uncertain, but no bias is evident for study 70.

F. Blind Reference Samples

Blind reference samples are analyzed for all constituents for which the SRS program reports. The blind reference samples are not analyzed for acid-neutralizing capacity, total monomeric aluminum, organic monomeric aluminum, total aluminum, ammonium, dissolved organic carbon, fluoride, nitrate and silicon.

Calcium (fig. 5A).–The DQO for calcium was met by 95 percent of the blind reference samples. The calcium method used during this period included a lanthanum chloride reagent, whose concentration was too low to mask interferences. The method was corrected, and project samples were reanalyzed for calcium. Most blind sample data are from the time period after the error was corrected.

Chloride (fig. 5B).–The DQO was met by 77 percent of the blind reference samples.

Magnesium (fig. 5C).–The DQO was met by 83 percent of the blind reference samples.

pH (fig. 5D).–The DQO was met by 100 percent of the blind reference samples. No trend or bias was evident.

Potassium (fig. 5E).–The DQO was met by 90 percent of the blind reference samples. No trend or bias was evident.

Sodium (fig. 5F).–The DQO was met by 100 percent of the blind reference samples.

Specific conductance (fig. 5G).–There are insufficient data for DQO evaluation. The analysis appears to have a low bias which subsequent control charts may show.

Sulfate (fig. 5H).–The DQO was met by 80 percent of the samples. No trend or bias was evident.

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_____1997, Report on the U.S. Geological Survey's evaluation program for Standard Reference Samples distributed in September 1996: T-143 (trace constituents), T-145 (trace constituents), M-140 (major constituents), N-51 (nutrient constituents), N-52 (nutrient constituents), P-27 (low ionic strength constituents), and Hg-23 (mercury): U.S. Geological Survey Open-File Report 97-20, 145 p.

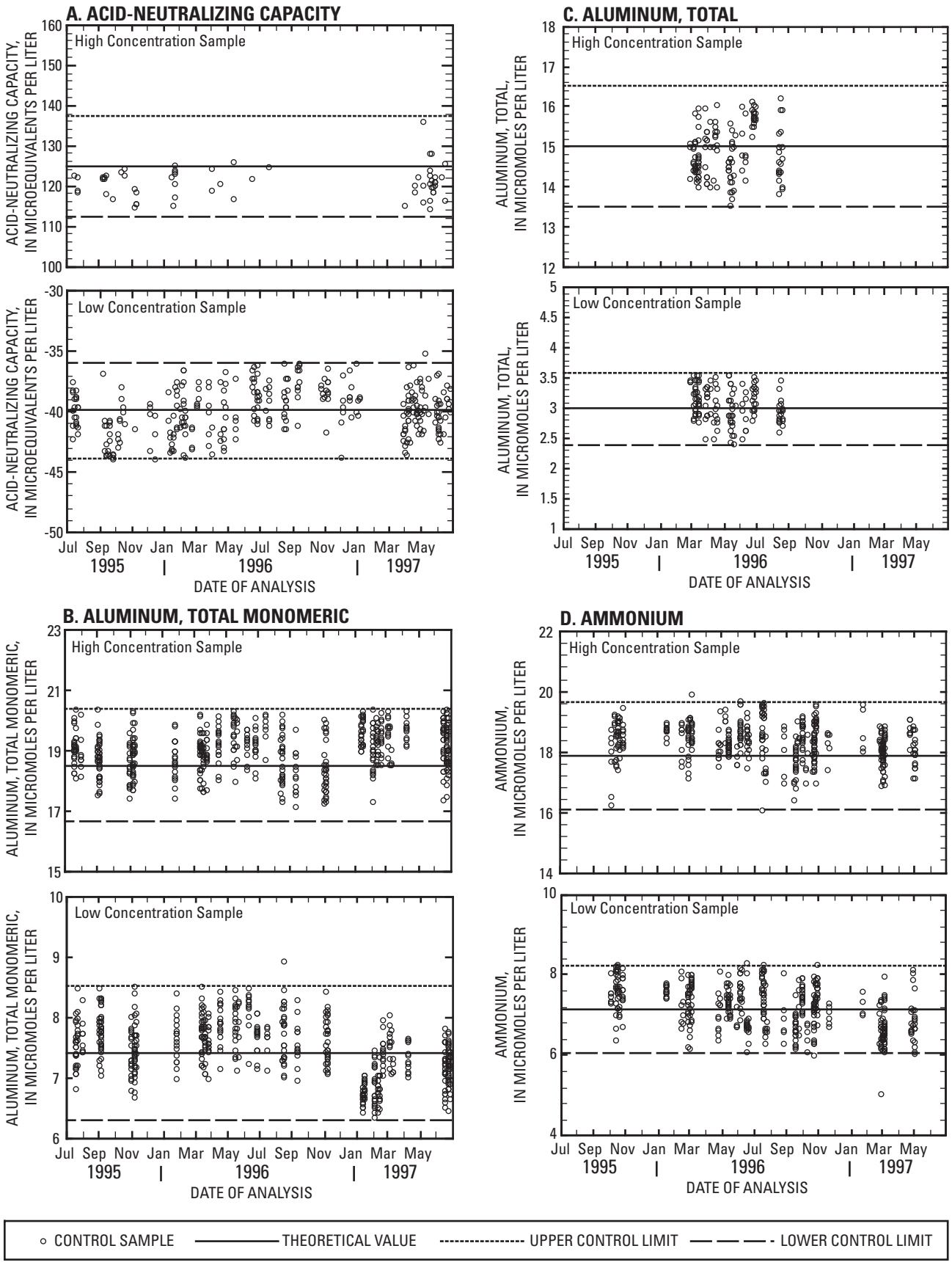
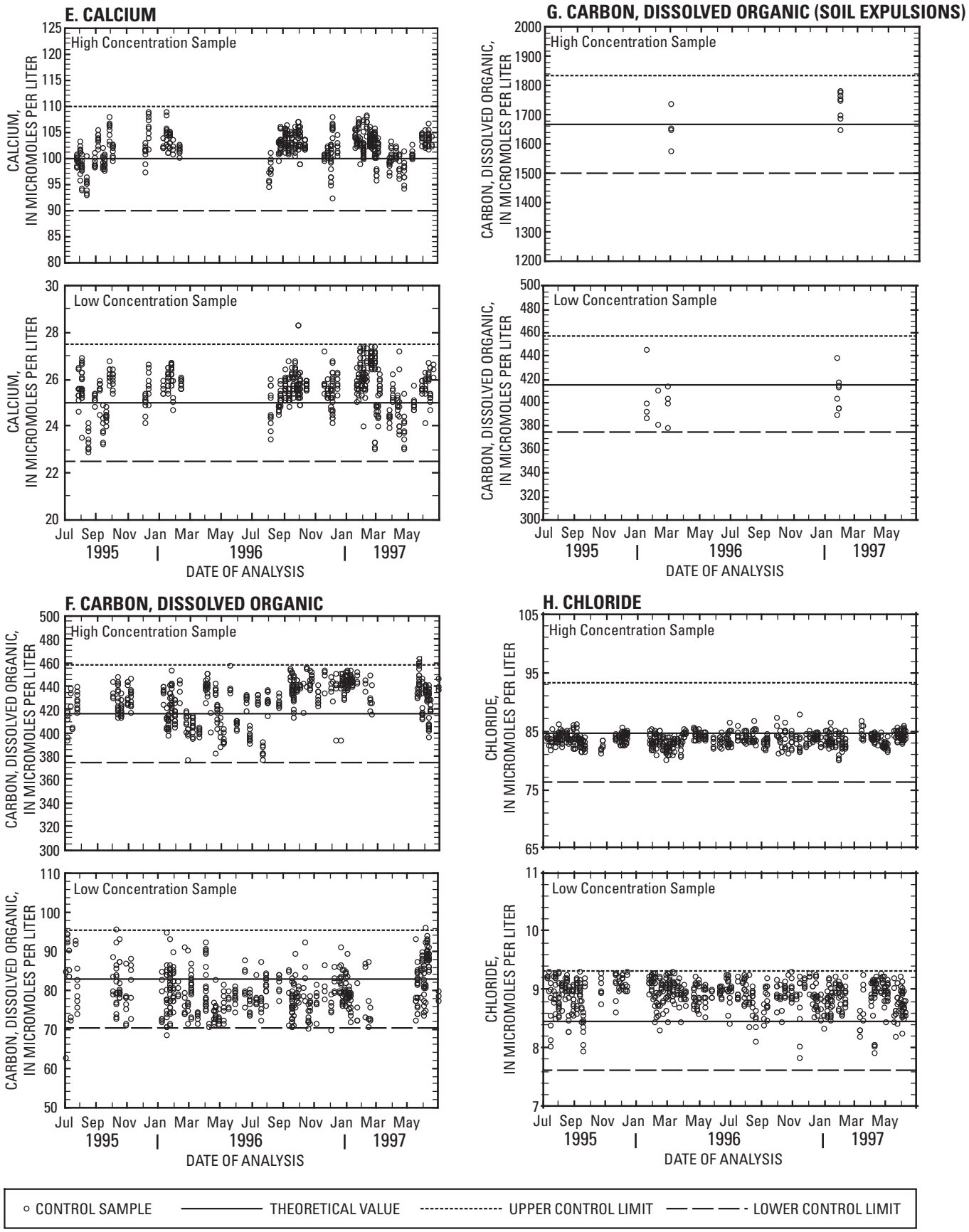


Figure 1. Results of quality-control data for high- and low-concentration quality-control samples from July 1995 through June 1997.



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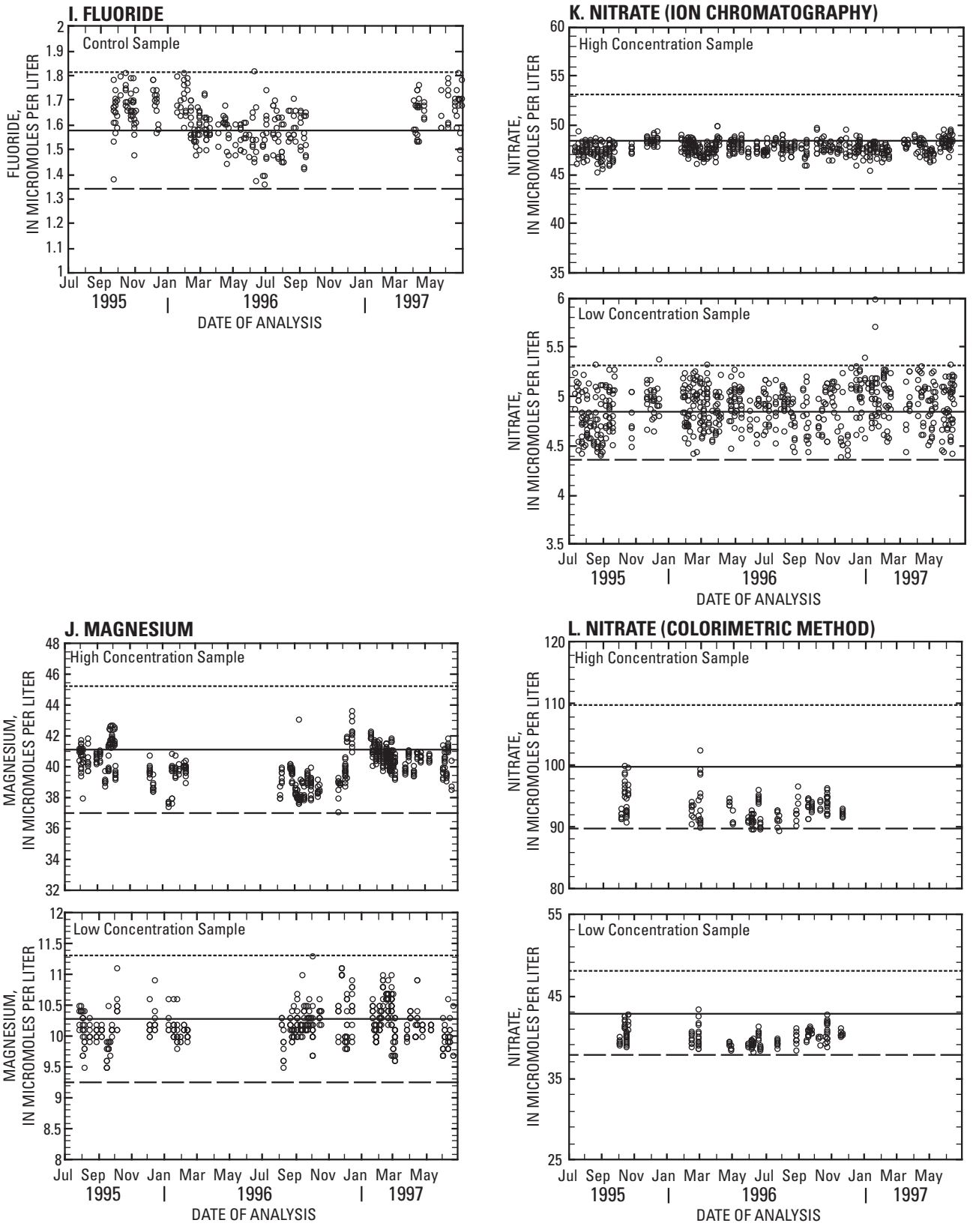

Figure 1. (continued) Results of quality-control data for high- and low-concentration quality-control samples from July 1995 through June 1997.

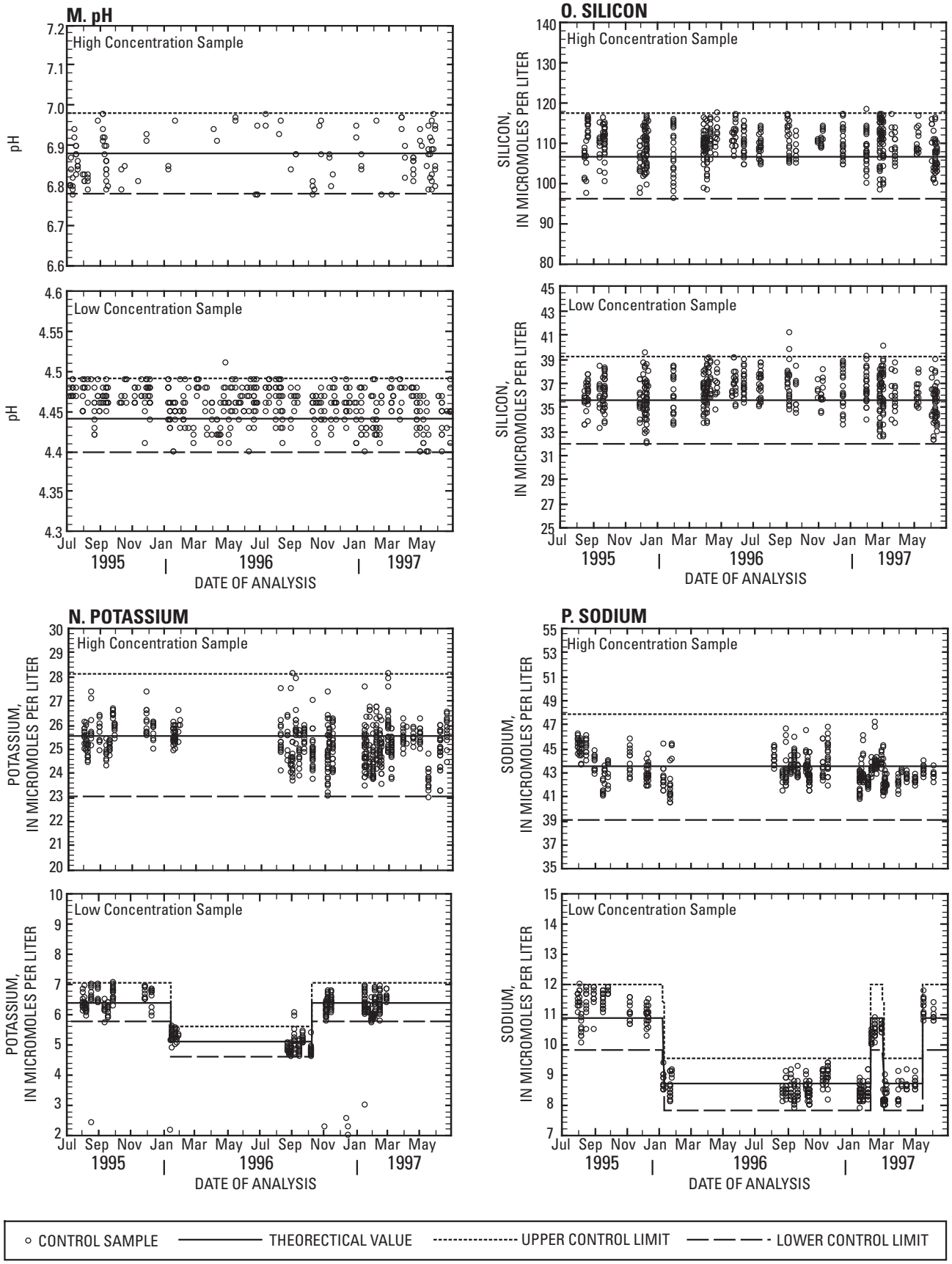

Figure 1. (continued) Results of quality-control data for high- and low-concentration quality-control samples from July 1995 through June 1997.

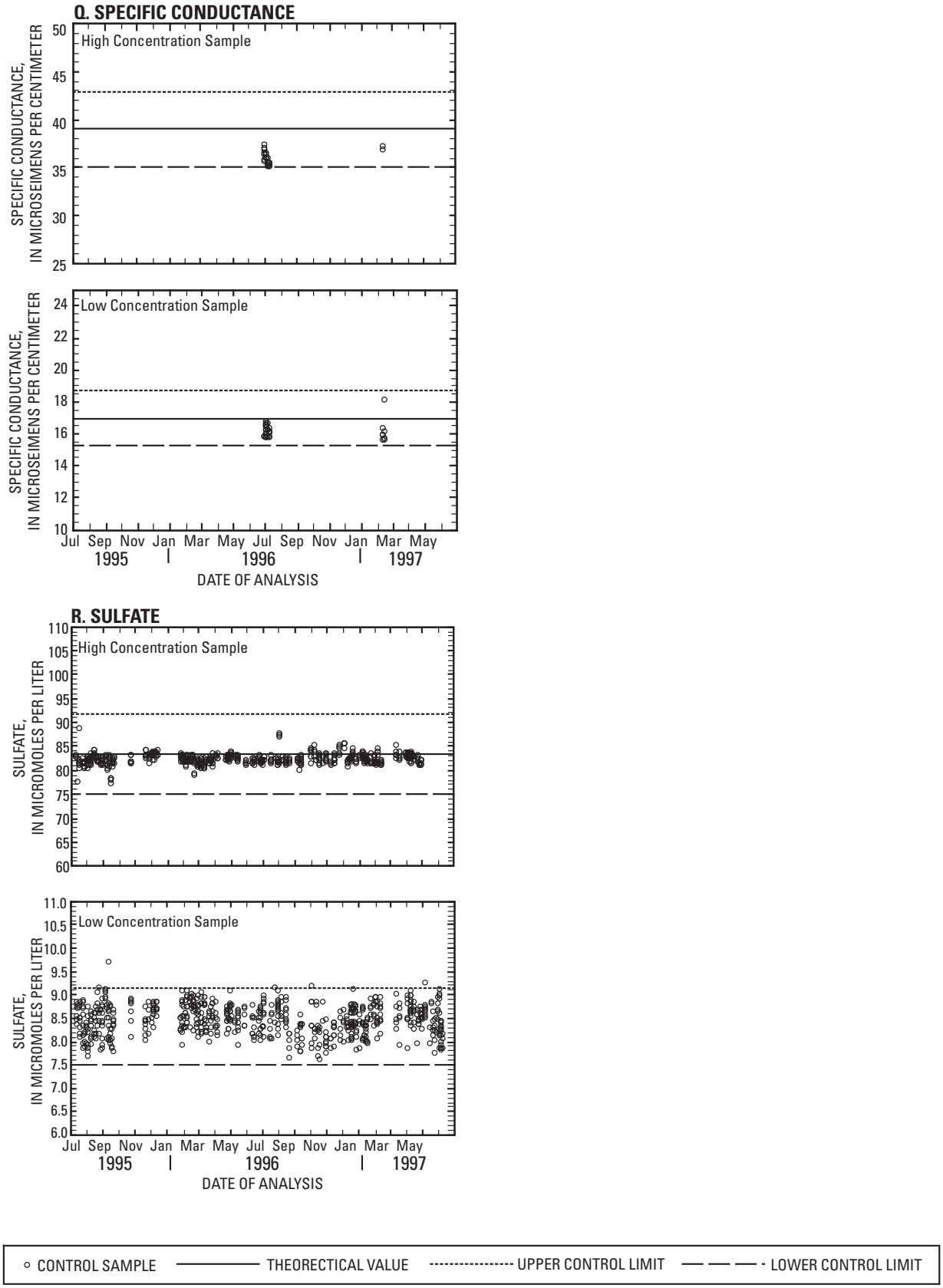

Figure 1. (continued) Results of quality-control data for high- and low-concentration quality-control samples from July 1995 through June 1997.

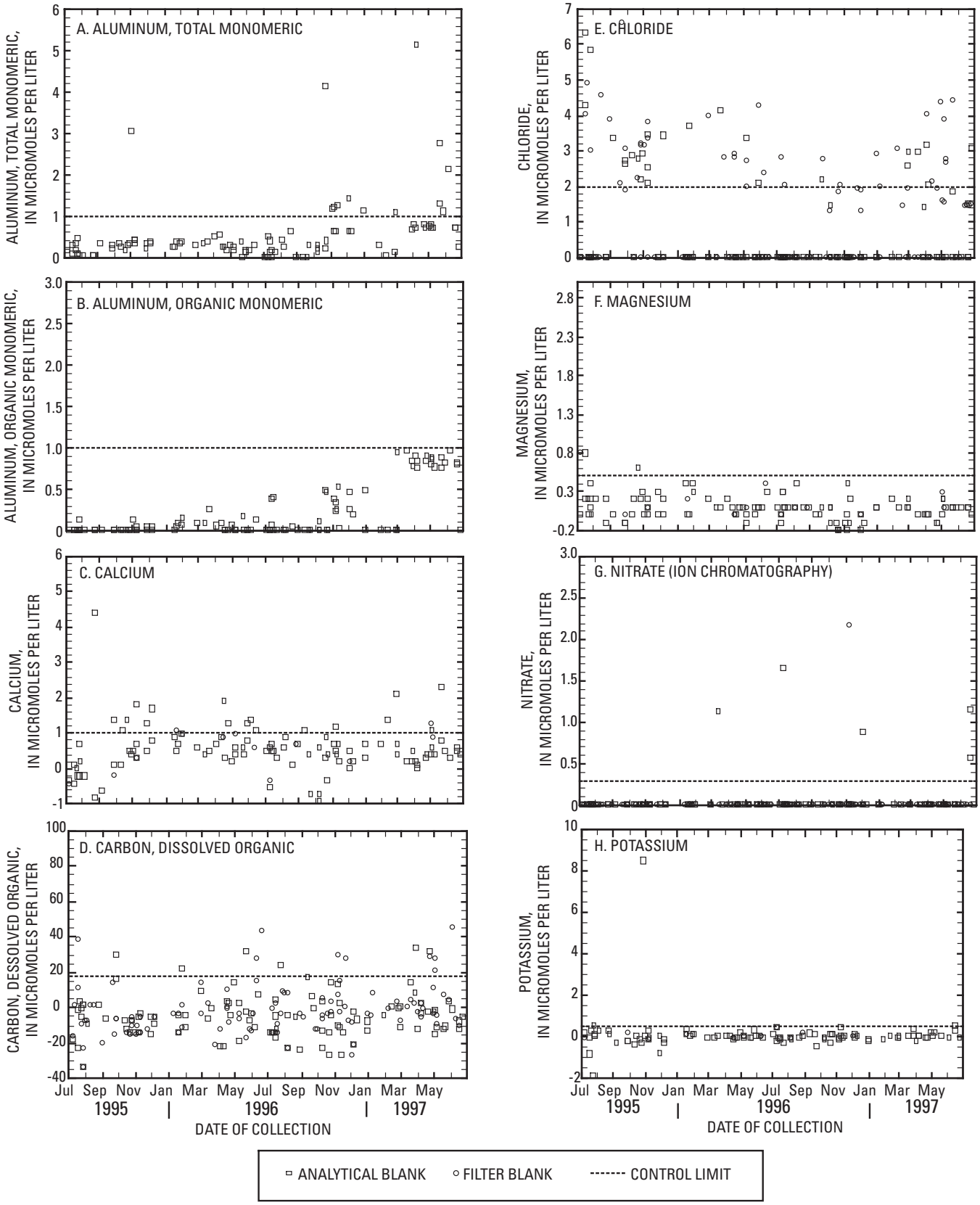

Figure 2. Results of quality-control data for filter blank and analytical blank samples from July 1995 through June 1997.

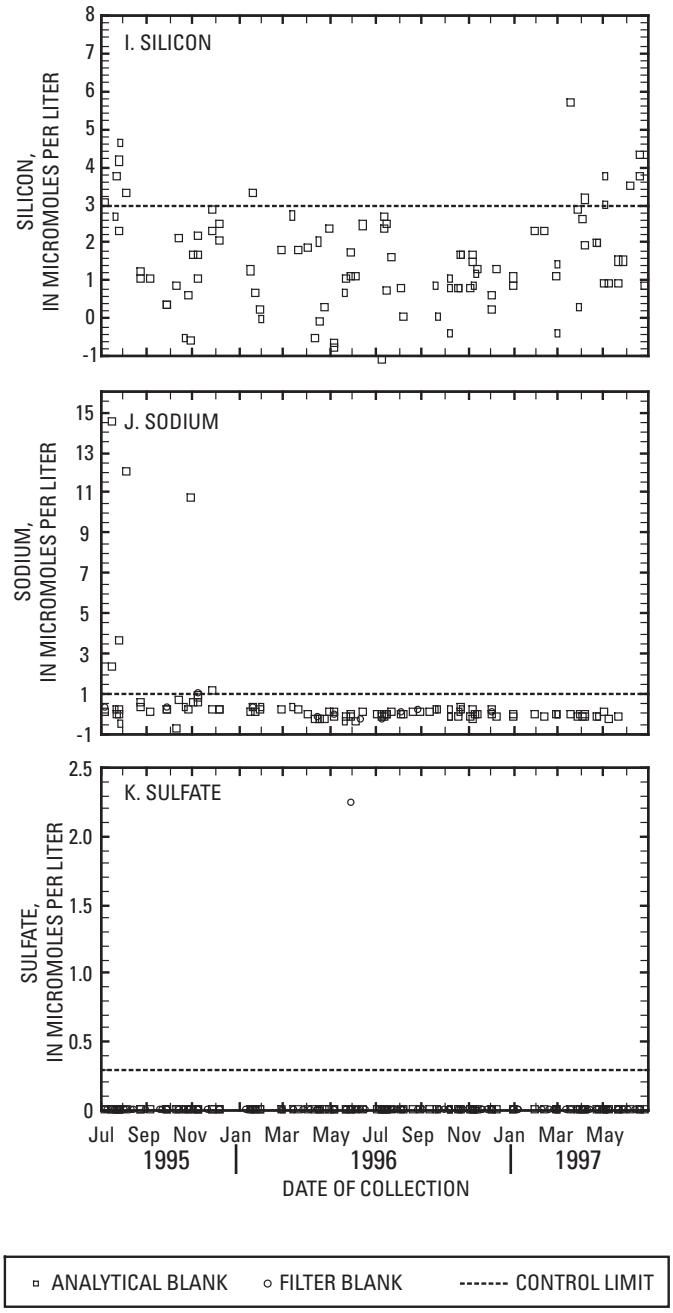

Figure 2. (continued) Results of quality-control data for filter blank and analytical blank samples from July 1995 through June 1997.

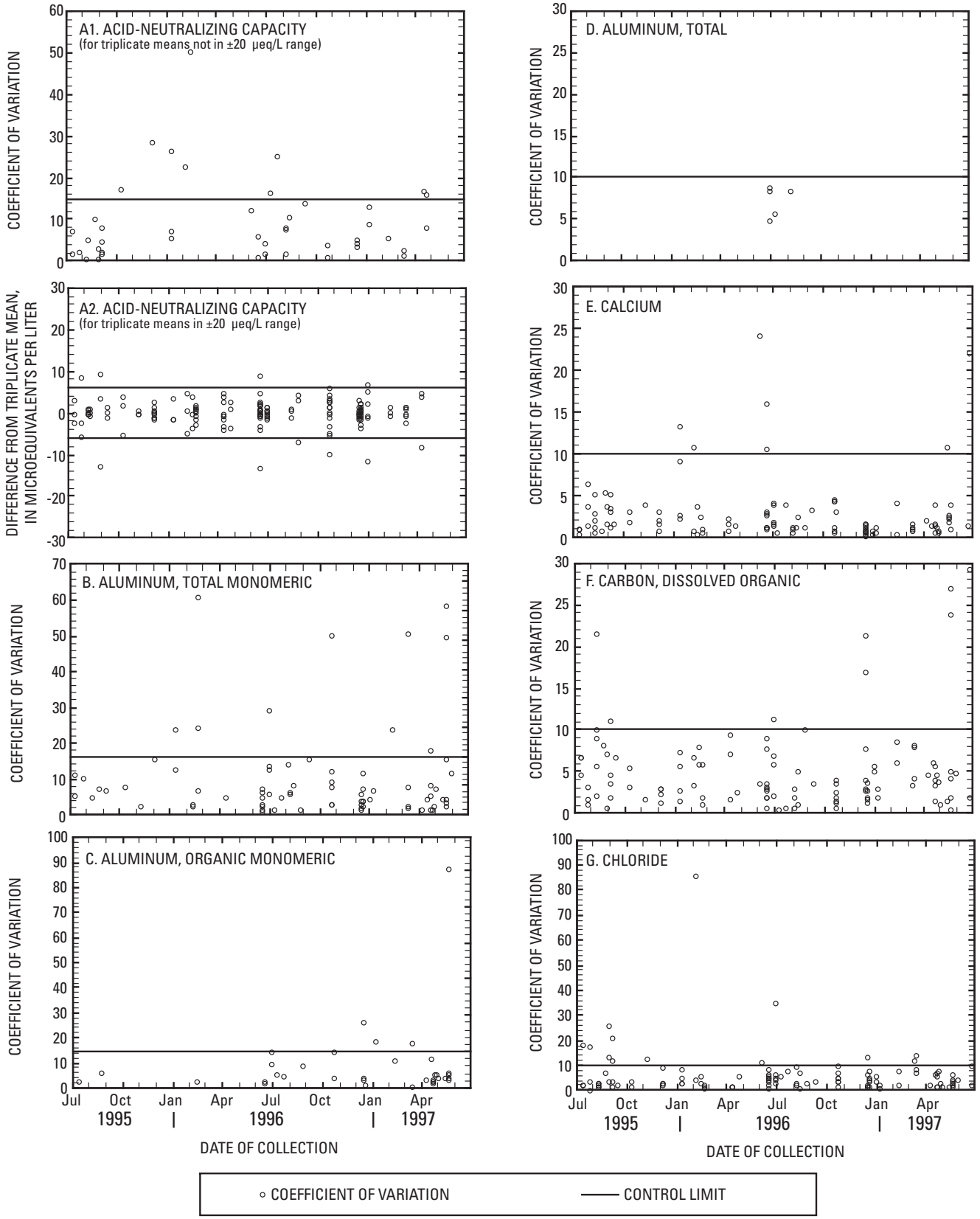

Figure 3. Results of quality-control data for triplicate environmental samples from July 1995 through June 1997.

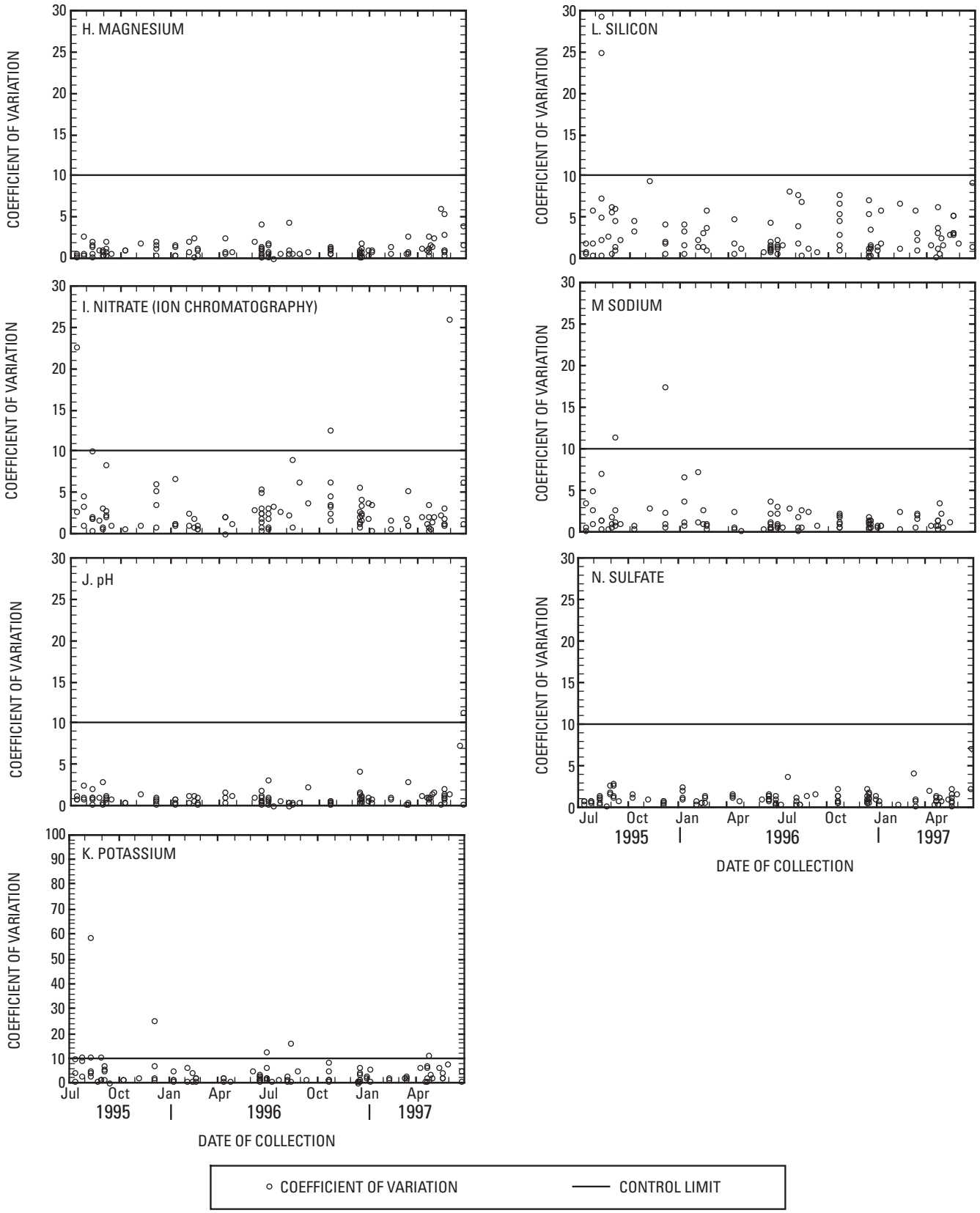

Figure 3. (Continued) Results of quality-control data for triplicate environmental samples from July 1995 through June 1997.

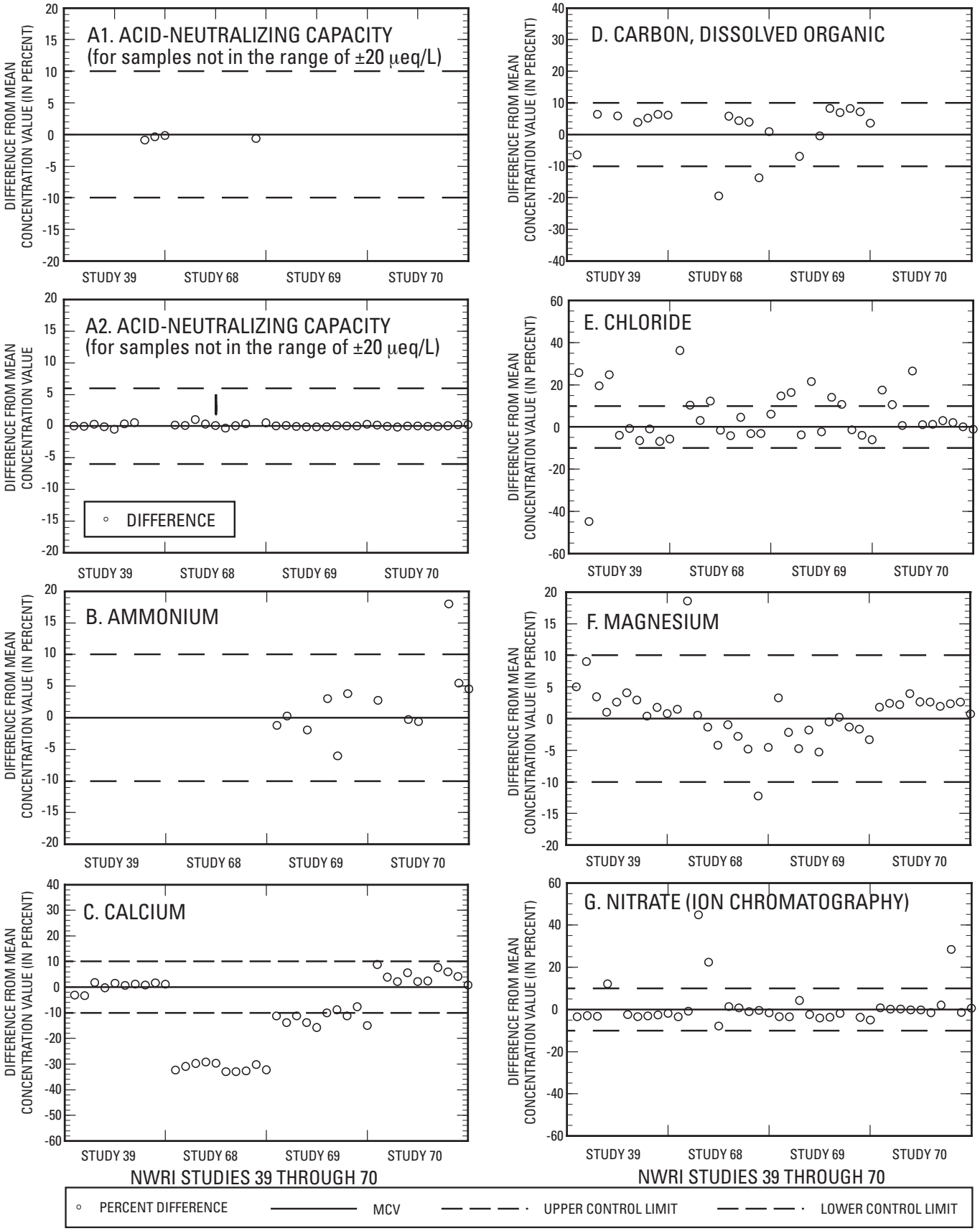

Figure 4. Results of quality-control data for NWRI Ecosystem Interlaboratory QA Program from July 1995 through June 1997.

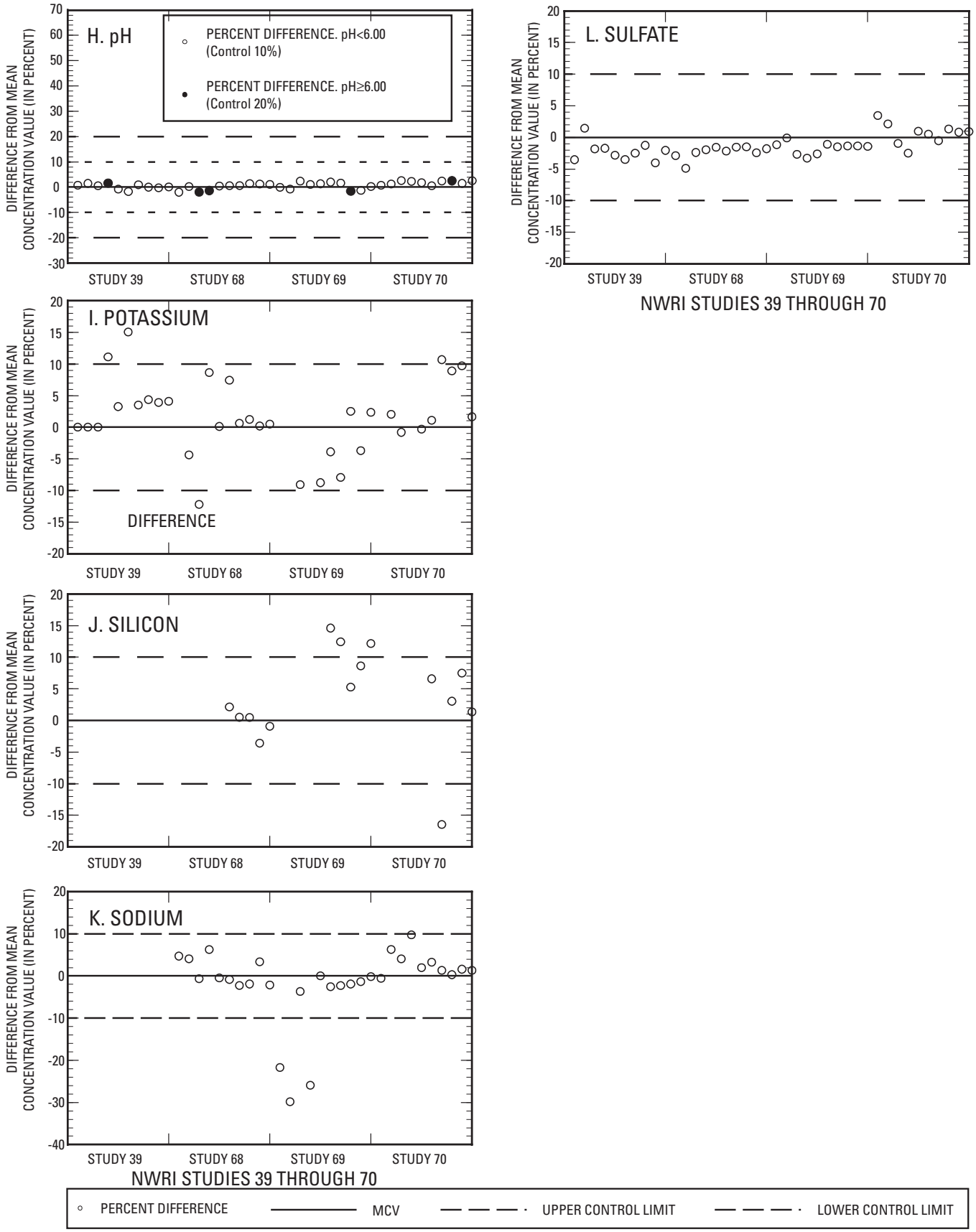

Figure 4. (Continued) Results of quality-control data for NWRI Ecosystem Interlaboratory QA Program from July 1995 through June 1997.

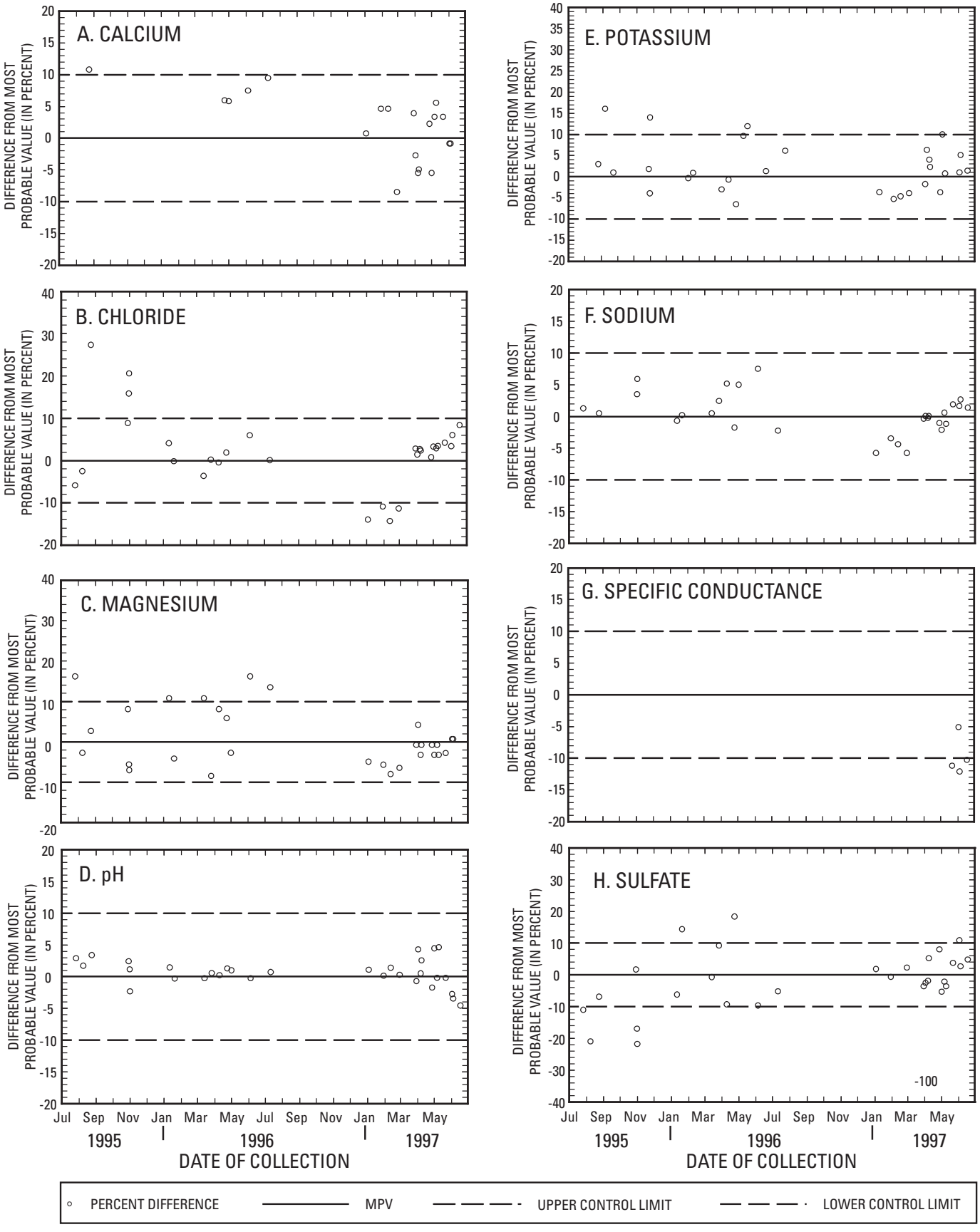

Figure 5. Results of quality-control data for blind reference samples from July 1995 through June 1997.