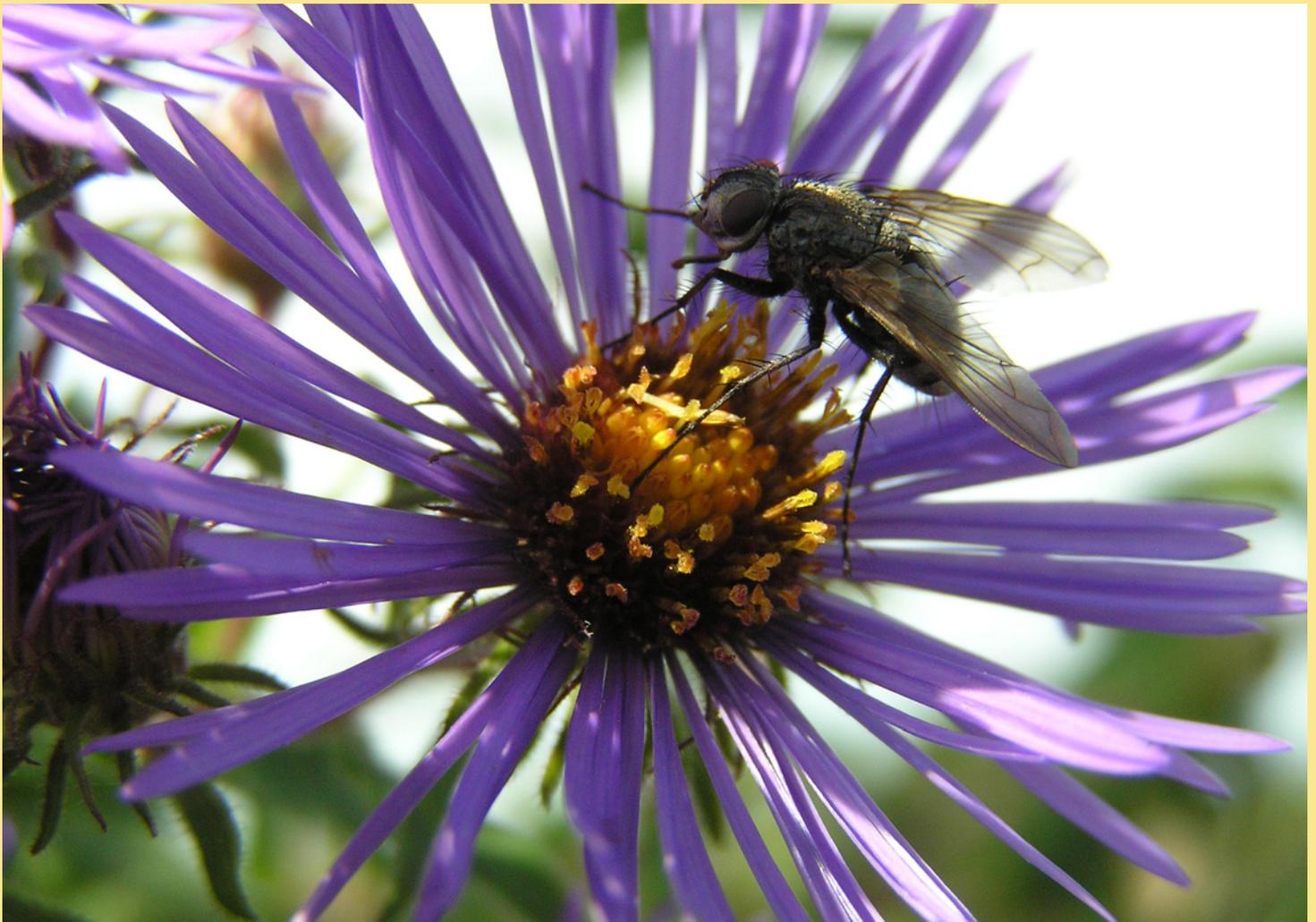


Quality-Assurance Data for Routine Water Analyses by the U.S. Geological Survey Laboratory in Troy, New York— July 1999 through June 2001



Open-File Report 2006-1246

U.S. Department of the Interior
U.S. Geological Survey

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

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**U.S. Department of the Interior
U.S. Geological Survey**

U.S. Department of the Interior
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U.S. Geological Survey
Mark D. Myers, Director

U.S. Geological Survey, Reston, Virginia: 2006

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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	microsiemens per centimeter
µg/L	micrograms per liter

Other Abbreviations

ANC	Acid-neutralizing capacity
AV	Analyzed value
CV	Coefficient of variation
D	Percent difference
DI	Deionized water
DOC	Dissolved organic carbon
DQO	Data-quality objective
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
TV	Troy Laboratory value
USGS	U.S. Geological Survey

Quality-Assurance Data for Routine Water Analyses by the U.S. Geological Survey Laboratory in Troy, New York—July 1999 through June 2001

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) Water Science Center in Troy, N.Y., analyzes samples collected by USGS projects throughout the Northeast. The laboratory's quality-assurance program is based on internal and interlaboratory quality-assurance samples and quality-control procedures that were developed to ensure proper sample collection, processing, and analysis. The quality-assurance and quality-control data were stored in the laboratory's LabMaster data-management system, which provides efficient review, compilation, and plotting of data. This report presents and discusses results of quality-assurance and quality-control samples analyzed from July 1999 through June 2001.

Results for the quality-control samples for 18 analytical procedures were evaluated for bias and precision. Control charts indicate that data for eight of the analytical procedures were occasionally biased for either high-concentration or low-concentration samples but were within control limits; these procedures were: acid-neutralizing capacity, total monomeric aluminum, total aluminum, calcium, chloride and nitrate (ion chromatography and colorimetric method) and sulfate. The total aluminum and dissolved organic carbon procedures were biased throughout the analysis period for the high-concentration sample, but were within control limits. The calcium and specific conductance procedures were biased throughout the analysis period for the low-concentration sample, but were within control limits. The magnesium procedure was biased for the high-concentration and low concentration samples, but was within control limits.

Results from the filter-blank and analytical-blank analyses indicate that the procedures for 14 of 15 analytes were within control limits, although the concentrations for blanks were occasionally outside the control limits. The data-quality objective was not met for dissolved organic carbon.

Sampling and analysis precision are evaluated herein in terms of the coefficient of variation obtained for triplicate samples in the procedures for 17 of the 18 analytes. At least 90 percent of the samples met data-quality objectives for

all analytes except ammonium (81 percent of samples met objectives), chloride (75 percent of samples met objectives), and sodium (86 percent of samples met objectives).

Results of the USGS interlaboratory Standard Reference Sample (SRS) Project indicated good data quality over the time period, with most ratings for each sample in the good to excellent range. The P-sample (low-ionic-strength constituents) analysis had one satisfactory rating for the specific conductance procedure in one study. The T-sample (trace constituents) analysis had one satisfactory rating for the aluminum procedure in one study and one unsatisfactory rating for the sodium procedure in another. The remainder of the samples had good or excellent ratings for each study.

Results of Environment Canada's National Water Research Institute (NWRI) program indicated that at least 89 percent of the samples met data-quality objectives for 10 of the 14 analytes; the exceptions were ammonium, total aluminum, dissolved organic carbon, and sodium. Results indicate a positive bias for the ammonium procedure in all studies. Data-quality objectives were not met in 50 percent of samples analyzed for total aluminum, 38 percent of samples analyzed for dissolved organic carbon, and 27 percent of samples analyzed for sodium.

Results from blind reference-sample analyses indicated that data-quality objectives were met by at least 91 percent of the samples analyzed for calcium, chloride, fluoride, magnesium, pH, potassium, and sulfate. Data-quality objectives were met by 75 percent of the samples analyzed for sodium and 58 percent of the samples analyzed for specific conductance.

Introduction

The U.S. Geological Survey (USGS) maintains a laboratory at its Water Science Center in Troy, N.Y., to analyze low-ionic-strength water for USGS watershed-research projects that require major-ion analyses of precipitation, soil-water, shallow ground-water, and

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stream-water samples. The methods used in this laboratory are described in detail in Lawrence and others (1995). The entire historical database was moved from the laboratory's SAS data-management system to a LabMaster laboratory information management system in January 2000. Quality-assurance and quality-control data were then collected, stored, and reviewed through the laboratory's LabMaster information management system for the remainder of this report period (July 1999-June 2001).

The 18 analytes represented by this study were: acid-neutralizing capacity (ANC), total monomeric aluminum, organic monomeric aluminum, total aluminum, ammonium, calcium, dissolved organic carbon (DOC), 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 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, interlaboratory quality-assurance 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.

Project: Neversink Watershed Study

Cooperator: New York City Department of Environmental Protection

Analyses: 176 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

Cooperator: New York City Department of Environmental Protection

Analyses: 2,354 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

Cooperator: U.S. Environmental Protection Agency

Analyses: 610 stream-water samples.

Project: The Effects of the Clean Air Act on Water Quality of Medium-Scale Rivers in the Northeastern United States

Cooperator: U.S. Geological Survey, Office of Water Quality

Analysis: 667 stream-water samples.

Project: Adirondack Effects Assessment Program

Cooperator: Rensselaer Polytechnic Institute

Analyses: 442 stream-water samples.

Project: Upper and Lower Node Water-Quality Operation and Maintenance in the Catskill Mountains, New York

Cooperator: New York City Department of Environmental Protection

Analyses: 735 stream-water samples.

Project: Hydrologic Geomorphology, Water Quality, and Biology of the Neversink River

Cooperator: Town of Thompson, New York

Analysis: 162 stream-water samples.

Project: Collaborative Environmental Monitoring and Research Initiative

Cooperator: U.S. Geological Survey, Office of Water Quality and U.S. Forest Service

Analyses: 32 stream-water samples.

Additional information on projects of the New York Water Science Center is given at <http://ny.water.usgs.gov>.

Quality-Assurance/Quality-Control (QA/QC) Program

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 (DQOs) are based on (1) the precision and accuracy levels generally required by projects that use the Troy Laboratory, and (2) the analytical limits of the methods used.

Quality-Control Samples

Quality-control (QC) samples are used to measure 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 lot other than the source material used to make calibration standards.

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 organic 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.

QC-high and QC-low samples are analyzed within a run for most constituents; exceptions are ANC, pH, and specific conductance. Either the QC-high sample or QC-low sample is analyzed within an ANC, pH, and specific conductance run, depending upon the expected concentration range of the environmental samples.

Quality-control samples are analyzed immediately after instrument calibration, after every 10 analyses of environmental samples, and at the end of each run. QC samples that do not meet DQOs 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, 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 use or exclude these data from their reports. The analytical results of QC samples in this report indicate (1) the frequency of out-of-control data that are not rerun, and (2) biases and trends of control data. The numbers 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 any step in sample handling, including 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 any step in sample handling, 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 collected at 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 or sample-processing procedures, and analysis. Environmental samples are selected for triplicate analysis on a random basis to ensure a wide range of sample concentrations from several field sites. The laboratory alternates between analyzing a triplicate set consecutively and separating the triplicate set over a day or multiple day's analytical runs.

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

The USGS Standard Reference Sample (SRS) Project 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 consist 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 program. Reference samples for low-ionic-strength constituents are prefixed by a P and are analyzed for calcium, chloride, fluoride, magnesium, pH, potassium, sodium, specific conductance, and sulfate. Reference samples for nutrient constituents are prefixed by an N and are analyzed for ammonium. Reference samples for trace constituents 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 calculated from the results submitted by participating laboratories. Laboratory performance is rated numerically by comparing analysis results to the MPVs for each constituent; the highest score is 4.0, and the lowest is 0.0.

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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 1999 through June 2001.

[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	5,067	161	424	0	21	0	0
Aluminum, total monomeric	4,739	623	623	1	1	0	0
Aluminum, organic monomeric ¹	4,746	0	0	0	0	0	0
Aluminum, total	5,471	718	717	0	0	0	0
Ammonium	4,521	840	837	0	2	0	0
Calcium	5,227	655	655	0	0	0	0
Carbon, dissolved organic	5,068	804	805	6	7	6	6
Chloride	5,303	861	866	0	0	0	0
Fluoride	1,384	0	174 ²	0	0	0	0
Magnesium	5,226	656	655	0	0	0	0
Nitrate (ion chromatography)	5,212	878	882	0	1	0	0
Nitrate (colorimetric method)	620	285	285	2	0	0	0
pH	5,108	233	521	3	16	0	0
Potassium	5,223	741	741	2	6	0	1
Silicon	5,228	654	655	0	1	0	0
Sodium	5,224	658	658	6	5	4	3
Specific conductance	4,054	0	479	0	6	0	0
Sulfate	5,304	1006	1011	0	0	0	0

¹Column efficiency is used to determine the acceptability of the data.

²Mid-level QC samples are used for fluoride.

NWRI Ecosystem Interlaboratory QA Program

The Troy Laboratory participates in Environment Canada's National Water Research Institute (NWRI) Ecosystem Interlaboratory QA program, in which a set of 10 samples is analyzed twice yearly. The samples are obtained from predominantly low-ionic-strength waters from several 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 appear to the analyst to be project samples. The blind reference samples have most probable values that were reported by the USGS SRS project. 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. The Troy Laboratory used SRS P-samples as the blind reference samples during the time period represented in this report.

Control-Chart Evaluation

Control charts (figs. 1–5, p. 14–27) are plots of QC data through time. This report uses control charts to (1) indicate whether the laboratory DQOs are met for individual QC samples; (2) reveal long-term biases within and outside the control limits; and (3) provide comparisons with results from other laboratories.

Each analyte has prescribed control limits that have been established to meet project DQOs (table 2). A constituent analysis is considered biased if 70 percent or more of the points on a chart are above or below the target value.

Quality-Control Samples

QC sample-analysis data are plotted on control charts (fig. 1) in which the central line is equal to the target value of the control sample. The control limits for the samples 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 ($\mu\text{mol/L}$) except for pH (pH units), ANC (microequivalents per liter, $\mu\text{eq/L}$), and specific conductance (microsiemens per centimeter, $\mu\text{S/cm}$).

Filter Blanks and Analytical Blanks

Results from the blank analyses are plotted on control charts by constituent in figure 2. The control limits 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. During analysis, the instrument calibration curve is extrapolated beyond the lowest standard in order to evaluate blank samples, and negative concentrations reflect the practical limitations of the extrapolation. An outlier on the control chart indicates possible contamination.

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, organic monomeric aluminum, total aluminum, and ammonium, for which it is 15 percent. Each circle within the control charts represents the CV of a triplicate environmental sample.

$$CV = \frac{S}{\bar{X}}(100), \quad (1)$$

where

S = standard deviation,

and

\bar{X} = arithmetic mean of triplicate samples.

The ANC data are plotted on two graphs. The first (fig. 3A1) shows the CV for triplicate sample means *outside* the range of $\pm 20\text{-}\mu\text{eq/L}$; the absolute value of the mean is used to calculate the CV . The second (fig. 3A2) shows values *within* $\pm 20\text{-}\mu\text{eq/L}$; 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 1999 through April 2001. Sample data with MCVs less than the Troy Laboratory reporting limits were excluded. The MCV and the control limits are represented by lines on the graphs; the percent difference (D) is calculated as:

$$D = [(AV - MCV)/MCV] \times 100, \quad (2)$$

where

AV = analyzed value,

and

MCV = mean concentration value.

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

Blind Reference Samples

Results from blind reference sample analyses are plotted in figure 5 by constituent and date of analysis. Sample data with MPVs less than the reporting limits were excluded. The MPV and the control limits of ± 10 percent are represented by lines on the graphs; the percent difference (D) is calculated as:

$$D = [(AV - MPV)/MPV] \times 100, \quad (3)$$

where

AV = analyzed value,

and

MPV = most probable value.

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 1999 through June 2001.[DQO, data-quality objective; $\mu\text{mol/L}$, micromoles per liter; CV, coefficient of variation; ANC, acid-neutralizing capacity]

Constituent or property	Reporting limit ($\mu\text{mol/L}$)	Accuracy				Precision	
		Low-concentration quality-control sample		High-concentration quality-control sample		Environmental triplicate samples DQO (CV)	Filter and analytical blanks DQO ($\mu\text{mol/L}$)
		DQO (percent error)	Concentration ($\mu\text{mol/L}$)	DQO (percent error)	Concentration ($\mu\text{mol/L}$)		
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	1.49	10	11.2	15	1.0
Ammonium	2.0	15	7.14	10	17.9	15	1.5
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
Chloride	3.0	10	8.47	10	84.7	10	2.0
Fluoride	0.5	15	1.58	none	none	10	0.5
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	10.9	10	43.5	10	1.0
Specific conductance ⁵	none	10	(17.0)	10	(39.0)	10	1.5
Sulfate	2.0	10	8.33	10	83.3	10	0.3

¹ANC: 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.

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

³Concentrations are expressed as micromoles carbon per liter.

⁴pH: percent error and coefficient of variation are calculated from $[\text{H}^+]$. Values in parentheses are in pH units.

⁵Specific conductance: values in parentheses are in microsiemens per centimeter.

Summary of Results

The following sections summarize the results for (A) quality-control samples (fig. 1, p. 14–18), (B) filter blanks and analytical blanks (fig. 2, p. 19–20), (C) triplicate environmental samples (fig. 3, p. 21–23), (D) SRS samples (table 3), (E) NWRI samples (fig. 4, p. 24–25), and (F) blind samples (fig. 5, p. 26–27).

A. Quality-Control Samples

Acid-Neutralizing Capacity (fig. 1A)—DQOs were met by 96 percent of the samples. The QC-high sample had a negative bias through July 2000. No apparent trends or biases were evident for the QC-low sample.

Aluminum, Total Monomeric (fig. 1B)—DQOs were met by 99 percent of the samples. The QC-low sample had a slight positive bias through 2000.

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

Aluminum, Total (fig. 1C)—DQOs were met by 100 percent of the samples. The QC-high sample had a positive bias during this period; the QC-low sample had a positive bias through May 2000.

Ammonium (fig. 1D)—DQOs were met by 99 percent of the samples. No apparent trends or biases were evident during this period.

Calcium (fig. 1E)—DQOs were met by 100 percent of the samples. The QC-high sample had a slight positive bias in 2001; the QC-low sample had a negative bias during this period.

Carbon, Dissolved Organic (fig. 1F)—DQOs 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 for the QC-low sample.

Chloride (fig. 1G)—DQOs were met by 100 percent of the samples. The QC-high sample had a negative bias from November 1999 through November 2000; the remaining time it indicated a positive bias. No apparent trends or biases were evident for the QC-low sample.

Fluoride (fig. 1H)—DQOs were met by 100 percent of the samples. No apparent trends or biases were evident during this period.

Magnesium (fig. 1I)—DQOs were met by 100 percent of the samples. The QC-high sample had a positive bias and the QC-low sample had a negative bias during this period.

Nitrate (ion chromatography) (fig. 1J)—DQOs were met by 99 percent of the samples. The QC-high sample had a negative bias from November 1999 through November 2000; the remaining time it indicated a positive bias. No apparent trends or biases were evident for the QC-low sample.

Nitrate (colorimetric method) (fig. 1K)—DQOs were met by 99 percent of the samples. The QC-high and QC-low samples had a negative bias in 2000.

pH (fig. 1L)—DQOs were met by 97 percent of the samples. No apparent trends or biases were evident during this period.

Potassium (fig. 1M)—DQOs were met by 99 percent of the samples. No apparent trends or biases were evident during this period.

Silicon (fig. 1N)—DQOs were met by 99 percent of the samples. No apparent trends or biases were evident during this period.

Sodium (fig. 1O)—DQOs were met by 99 percent of the samples. No apparent trends or biases were evident during this period.

Specific conductance (fig. 1P)—DQOs were met by 99 percent of the samples. The QC-high concentration sample was not analyzed during period. The QC-low sample had a negative bias from May 2000 through April 2001.

Sulfate (fig. 1Q)—DQOs were met by 100 percent of the samples. The QC-high sample had a negative bias from November 1999 through November 2000; the remainder of the period it indicated a positive bias. No apparent trends or biases were evident for the QC-low sample.

B. Filter Blanks and Analytical Blanks

Acid-Neutralizing Capacity—Blanks were not analyzed for this constituent during this period.

Aluminum, Total Monomeric (fig. 2A)—The DQO was met by 99 percent of the samples. No systematic trends were evident for this analysis.

Aluminum, Organic Monomeric (fig. 2B)—The DQO was met by 100 percent of the samples. No systematic trends were evident for this analysis.

Aluminum, Total (fig. 2C)—The DQO was met for 92 percent of the samples. No systematic trends were evident for this analysis.

Ammonium (fig. 2D)—The DQO was met by 91 percent of the samples. No systematic trends were evident for this analysis.

Calcium (fig. 2E)—The DQO was met by 98 percent of the samples. No systematic trends were evident for this analysis.

Carbon, Dissolved Organic (fig. 2F)—The DQO was not met for DOC. Blank data results are significantly higher in DOC concentrations since a new instrument was purchased in 1998. The current DQO is being evaluated.

Chloride (fig. 2G)—The DQO was met by 82 percent of the samples. The chloride contamination problem has continued to improve.

Fluoride (fig. 2H)—The DQO was met by 100 percent of the samples. No systematic trends were evident for this analysis.

Magnesium (fig. 2I)—The DQO was met by 100 percent of the samples. No systematic trends were evident for this analysis.

Nitrate (ion chromatography) (fig. 2J)—The DQO was met by 92 percent of the samples. No systematic trends were evident for this analysis.

Nitrate (colorimetric method)—Blanks were not available for this constituent during this period.

pH—Blanks were not analyzed for this constituent during this period.

Potassium (fig. 2K)—The DQO was met by 92 percent of the samples. No systematic trends were evident for this analysis.

Silicon (fig. 2L)—The DQO was met by 100 percent of the samples. No systematic trends were evident for this analysis.

Sodium (fig. 2M)—The DQO was met by 94 percent of the samples. No systematic trends were evident for this analysis.

Specific conductance (fig. 2N)—The DQO was met by 80 percent of the samples. No systematic trends were evident for this analysis.

Sulfate (fig. 2O)—The DQO was met by 98 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 96 percent of the triplicate samples.

Aluminum, Total Monomeric (fig. 3B)—The DQO was met by 96 percent of the triplicate samples.

Aluminum, Organic Monomeric (fig. 3C)—The DQO was met by 100 percent of the triplicate samples.

Aluminum, Total (fig. 3D)—The DQO was met by 90 percent of the triplicate samples.

Ammonium (fig. 3E)—The DQO was met by 81 percent of the triplicate samples.

Calcium (fig. 3F)—The DQO was met by 100 percent of the triplicate samples.

Carbon, Dissolved Organic (fig. 3G)—The DQO was met by 92 percent of the triplicate samples.

Chloride (fig. 3H)—The DQO was met by 75 percent of the triplicate samples.

Fluoride (fig. 3I)—The DQO was met by 91 percent of the triplicate samples.

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

Nitrate (ion chromatography) (fig. 3K)—The DQO was met by 95 percent of the triplicate samples.

Nitrate (colorimetric method)—Triplicate samples were not available for this constituent during this period.

pH (fig. 3L)—The DQO was met by 100 percent of the triplicate samples.

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

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

Sodium (fig. 3O)—The DQO was met by 86 percent of the triplicate samples.

Specific conductance (fig. 3P)—The DQO was met by 91 percent of the triplicate samples.

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

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

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

<u>Rating</u>	<u>Performance</u>
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-34	3.6	T-161	3.0	N-63	3.0
P-35	3.9	T-163	3.2	N-65	3.0
				N-67	4.0

Missing SRS results for the Troy Laboratory were due to instrument failure during the SRS study period. The laboratory did not submit results for the SRS samples distributed in April 2001.

All analyses received a satisfactory or better rating for each constituent with one exception:

Sodium—The cause of a zero rating for SRS T-161 is erroneous data entry.

Table 3. Results obtained by the Troy Laboratory for the U.S. Geological Survey Standard Reference Sample (SRS) Project, October 1999 through October 2000.

[MPV, most probable value; TV, Troy Laboratory value. All values are in milligrams per liter except aluminum ($\mu\text{g/L}$), pH (pH units) and specific conductance (microsiemens per centimeter); --, dashes indicate no results reported]

Analyte	MPV, TV, and rating ^a	SRS sample number and date of sample distribution						
		N-63 10-99 ^b	T-161 03-00 ^c	N-65 03-00 ^c	P-34 03-00 ^c	T-163 10-00 ^d	N-67 10-00 ^d	P-35 10-00 ^d
Aluminum	MPV	--	38.4	--	--	16.8	--	--
	TV	--	38.3	--	--	14.54	--	--
	Rating	--	3	--	--	2	--	--
Ammonium ^e	MPV	0.150	--	0.124	--	--	0.433	--
	TV	0.165	--	0.142	--	--	0.4466	--
	Rating	3	--	3	--	--	4	--
Calcium	MPV	--	7.17	--	1.63	6.30	--	0.541
	TV	--	7.10	--	1.58	6.45	--	0.522
	Rating	--	4	--	3	4	--	4
Chloride	MPV	--	--	--	4.18	--	--	5.31
	TV	--	--	--	4.22	--	--	5.032
	Rating	--	--	--	4	--	--	3
Magnesium	MPV	--	1.51	--	0.592	1.23	--	0.090
	TV	--	1.51	--	0.577	1.299	--	0.089
	Rating	--	4	--	4	3	--	4
pH	MPV	--	--	--	4.32	--	--	4.89
	TV	--	--	--	4.32	--	--	4.96
	Rating	--	--	--	4	--	--	4
Potassium	MPV	--	1.26	--	0.238	1.02	--	0.184
	TV	--	1.36	--	0.230	1.08	--	0.1786
	Rating	--	3	--	4	4	--	4
Silicon ^f	MPV	--	14.8	--	--	4.56	--	--
	TV	--	14.8	--	--	4.759	--	--
	Rating	--	4	--	--	3	--	--
Sodium	MPV	--	43.0	--	0.439	--	--	3.00
	TV	--	3.8	--	0.450	--	--	2.995
	Rating	--	0	--	4	--	--	4
Specific conduc- tance	MPV	--	--	--	41.8	--	--	27.0
	TV	--	--	--	39.4	--	--	26.05
	Rating	--	--	--	2	--	--	4
Sulfate	MPV	--	--	--	0.437	--	--	0.673
	TV	--	--	--	0.437	--	--	0.626
	Rating	--	--	--	4	--	--	4

^aLaboratory rating system: 4 is highest score; 0 is lowest.

^bSample described in Farrar (2000).

^cSample described in Farrar and Copen (2000).

^dSample described in Connor, Currier, and Woodworth (2001).

^eThe SRS Project reports data as "Ammonia as Nitrogen."

^fThe SRS Project reports data as "Silica."

E. NWRI Ecosystem Interlaboratory QA Program

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

Acid-Neutralizing Capacity (figs. 4A1–4A2)—The DQO was met by 90 percent of the NWRI samples. No trend or bias was evident. Data were not submitted for study 77 due to instrument failure.

Aluminum, Total (fig. 4B)—The DQO was met by 50 percent of the NWRI samples. The cause of the erratically high outliers is unknown.

Ammonium (fig. 4C)—The DQO was not met for the NWRI samples. The cause of the positive bias is currently being investigated. The reporting limit for ammonium is being reevaluated.

Calcium (fig. 4D)—The DQO was met by 98 percent of the NWRI samples. No trend or bias was evident.

Carbon, Dissolved Organic (fig. 4E)—The DQO was met by 62 percent of the NWRI samples. The data exhibited a positive bias for studies 75 and 78. The cause is unknown.

Chloride (fig. 4F)—The DQO was met by 90 percent of the NWRI samples. The data exhibited a negative bias during studies 76 and 78.

Magnesium (fig. 4G)—The DQO was met by 100 percent of the NWRI samples. The data exhibited a slight positive bias during studies 75 and 78 and a slight negative bias during studies 76 and 77.

Nitrate (ion chromatography) (fig. 4H)—The DQO was met by 89 percent of the NWRI samples. No trend or bias was evident.

pH (fig. 4I)—The DQO was met by 100 percent of the NWRI samples. No trend or bias was evident. Data were not submitted for study 77 due to instrument failure.

Potassium (fig. 4J)—The DQO was met by 98 percent of the NWRI samples. The data exhibited a positive bias during studies 75, 76, and 77.

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

Sodium (fig. 4L)—The DQO was met by 73 percent of the NWRI samples. The cause of the erratically high outliers is unknown.

Specific Conductance (fig. 4M)—The DQO was met by 97 percent of the NWRI samples. The data exhibited a negative bias during study 76. Data were not submitted for study 77 due to instrument failure.

Sulfate (fig. 4N)—The DQO was met by 98 percent of the NWRI samples. The data exhibited a slight negative bias for studies 76 and 77.

F. Blind Reference Samples

Blind reference samples (SRS low-ionic-strength constituent P-samples) are analyzed for the Troy Laboratory procedures for which the SRS project reports an analyte MPV. The blind reference samples are not analyzed for acid-neutralizing capacity, total monomeric aluminum, organic monomeric aluminum, total aluminum, ammonium, dissolved organic carbon, nitrate and silicon.

Calcium (fig. 5A)—The DQO for calcium was met by 95 percent of the blind reference samples. The data exhibited a negative bias for this period.

Chloride (fig. 5B)—The DQO was met by 100 percent of the blind reference samples. A negative bias was evident through 1999.

Fluoride (fig. 5C)—The DQO was met by 100 percent of the blind reference samples. The laboratories began fluoride analysis on blind reference samples in 2001.

Magnesium (fig. 5D)—The DQO was met by 94 percent of the blind reference samples. Most data indicated a negative bias.

pH (fig. 5E)—The DQO was met by 91 percent of the blind reference samples. A slight positive bias was evident during 1999 and again in 2001.

Potassium (fig. 5F)—The DQO was met by 93 percent of the blind reference samples. No trend or bias was evident.

Sodium (fig. 5G).—The DQO was met by 75 percent of the blind reference samples. The cause of the negative bias is unknown.

Specific conductance (fig. 5H)—The DQO was met by 58 percent of the blind reference samples. A negative bias is evident.

Sulfate (fig. 5I)—The DQO was met by 100 percent of the samples. No trend or bias was evident.

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Figures 1–5

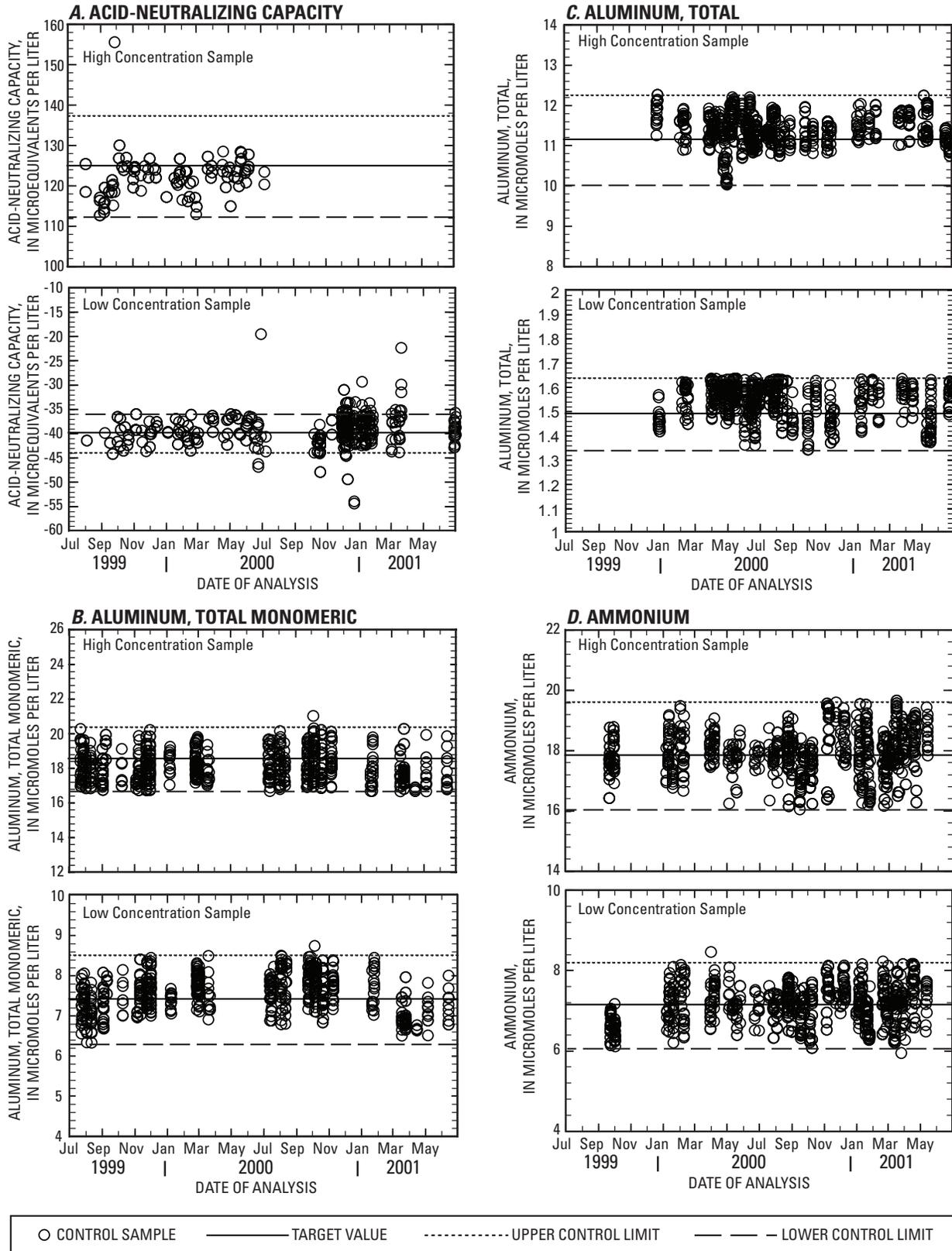


Figure 1. High- and low-concentration quality-control sample results: A. Acid-neutralizing capacity. B. Aluminum, total monomeric. C. Aluminum, total. D. Ammonium.

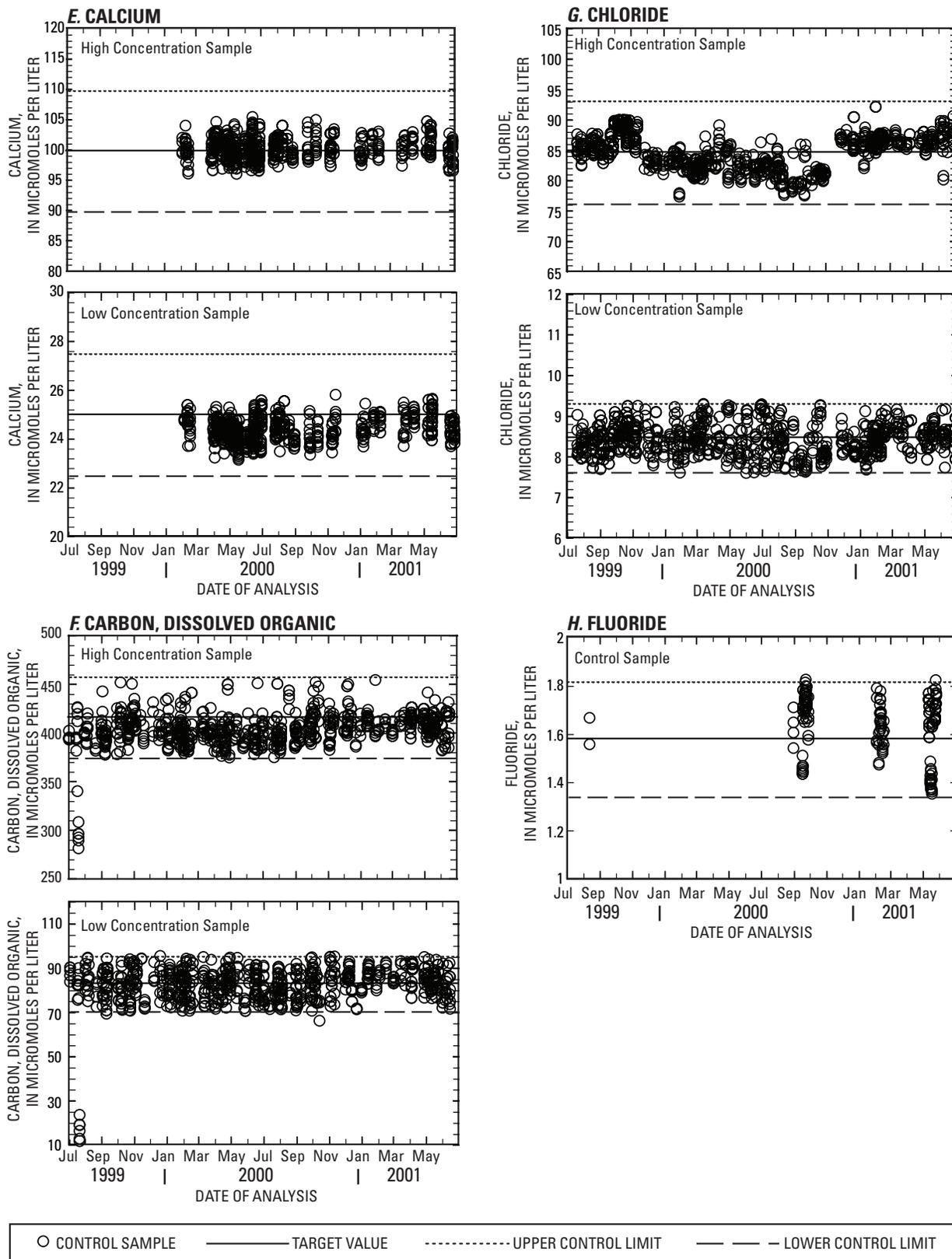


Figure 1. High- and low-concentration quality-control sample results: *E.* Calcium. *F.* Carbon, dissolved organic. *G.* Chloride. *H.* Fluoride.—Continued

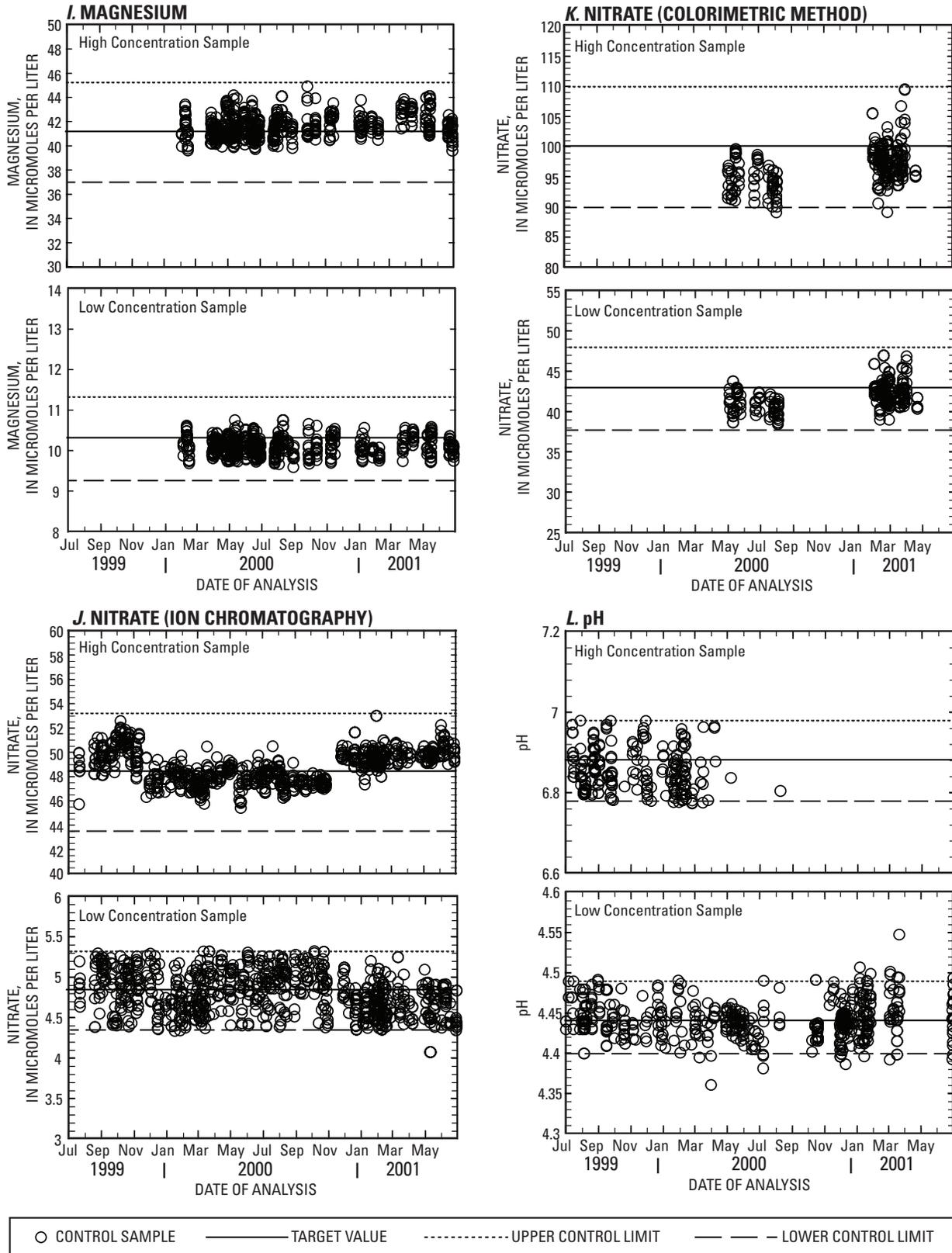


Figure 1. High- and low-concentration quality-control sample results: *I.* Magnesium. *J.* Nitrate (ion chromatography). *K.* Nitrate (colorimetric method). *L.* pH.—Continued

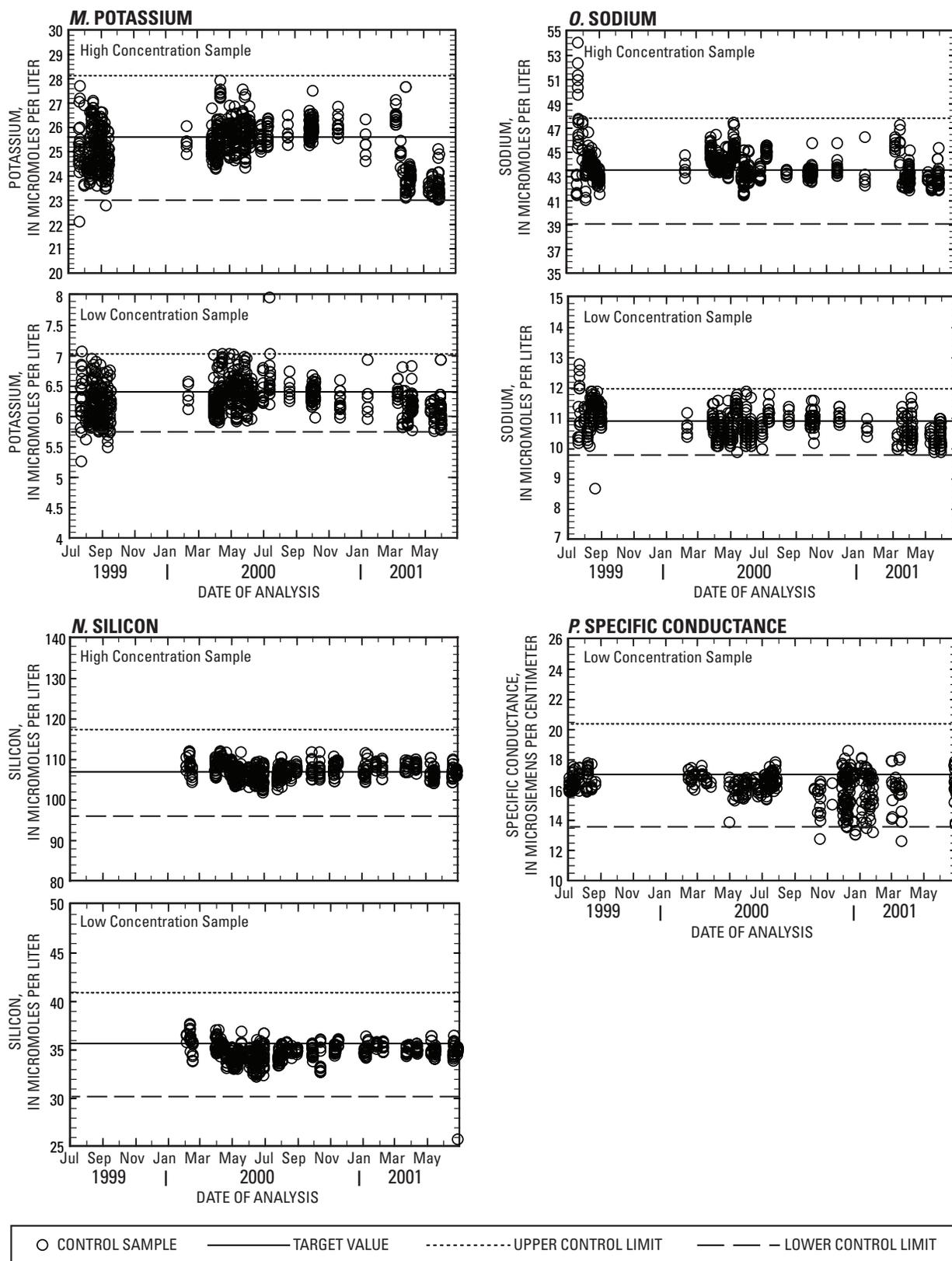


Figure 1. High- and low-concentration quality-control sample results: *M.* Potassium. *N.* Silicon. *O.* Sodium. *P.* Specific conductance.—Continued

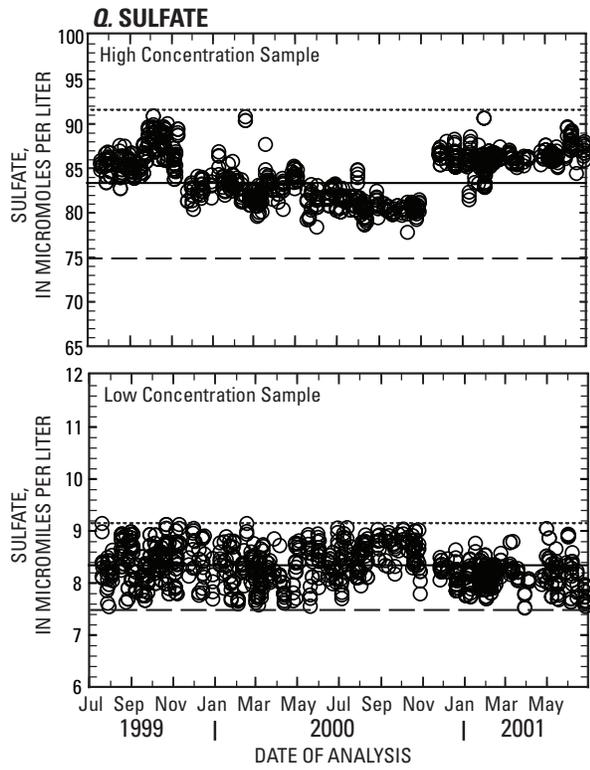


Figure 1. High- and low-concentration quality-control sample results: Q. Sulfate.—Continued

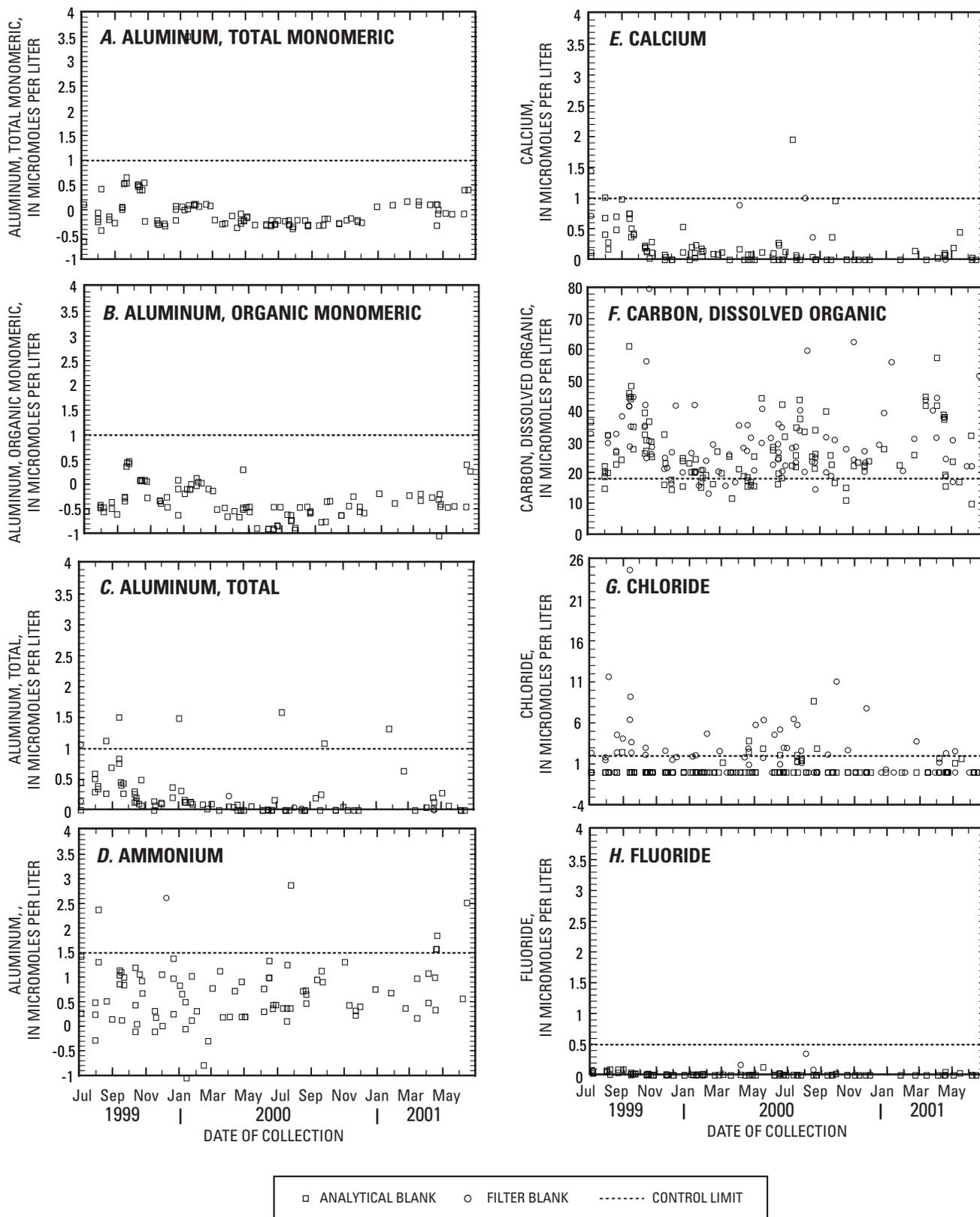


Figure 2. Filter-blank and analytical-blank sample results: A. Aluminum, total monomeric. B. Aluminum, organic monomeric. C. Aluminum, total. D. Ammonium. E. Calcium. F. Carbon, dissolved organic. G. Chloride. H. Fluoride.

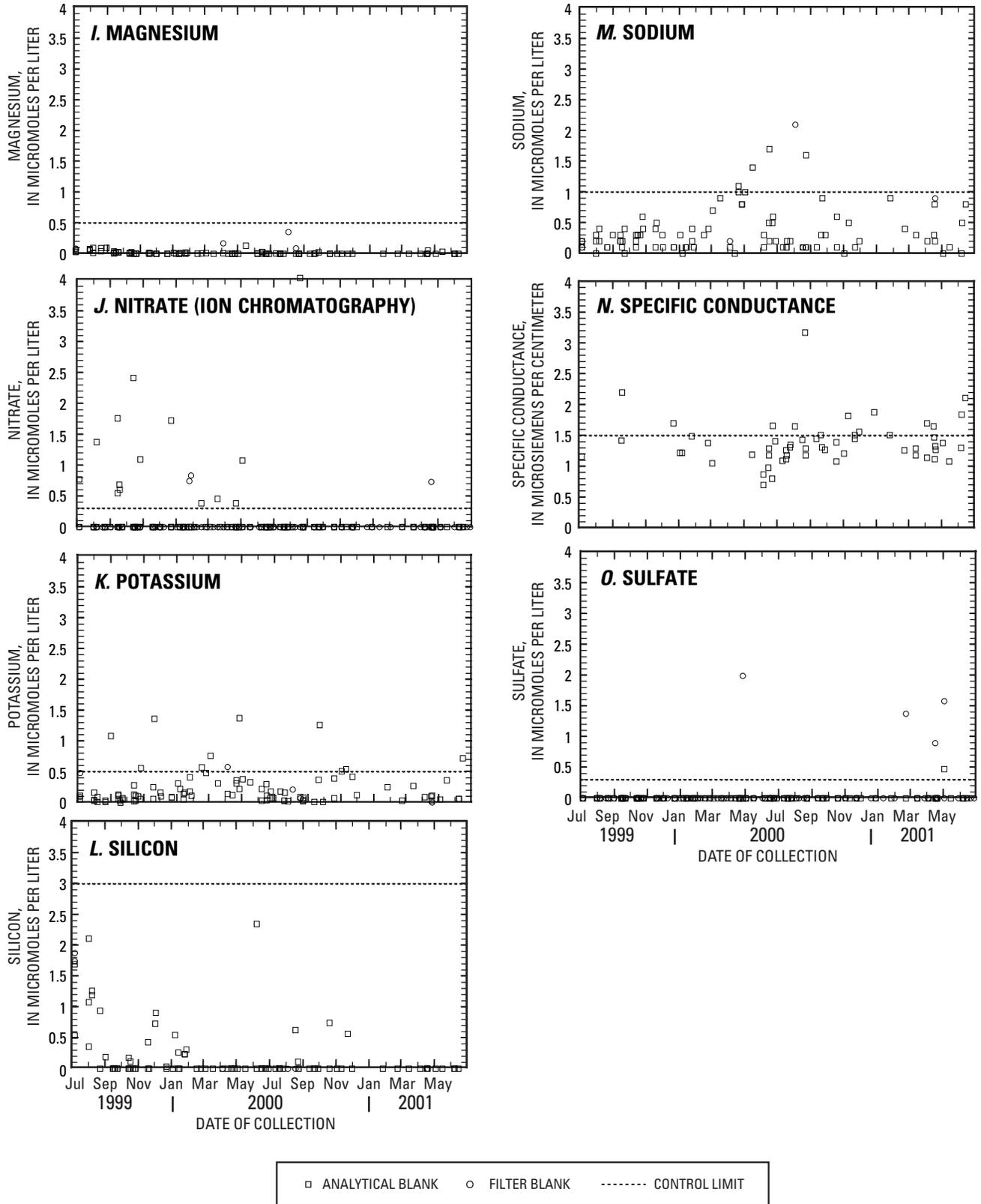


Figure 2. Filter-blank and analytical-blank sample results: I. Magnesium. J. Nitrate (ion chromatography). K. Potassium. L. Silicon. M. Sodium. N. Specific conductance O. Sulfate.—Continued

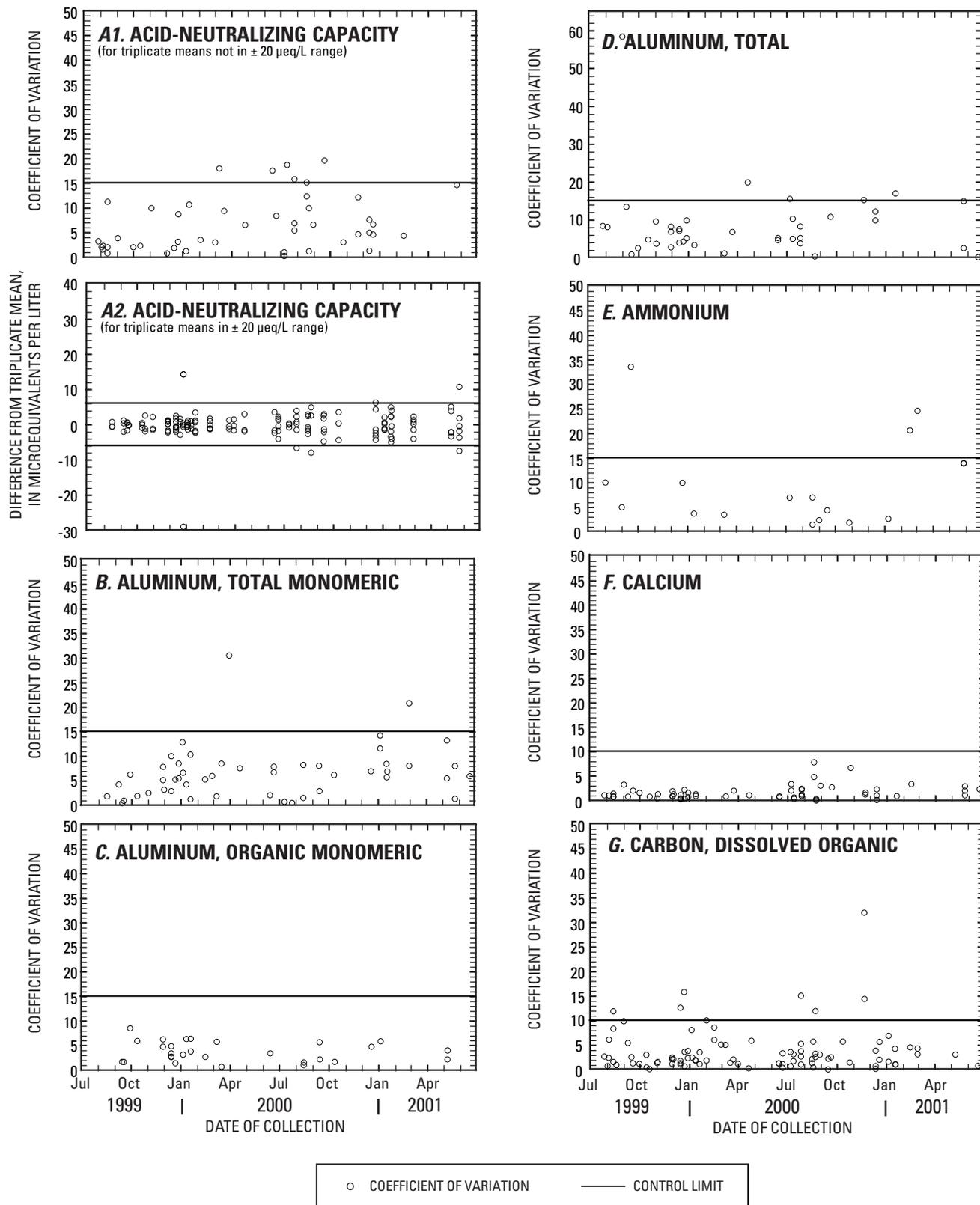


Figure 3. Triplicate environmental sample results: *A1.* Acid-neutralizing capacity (for triplicate means not in $\pm 20 \mu\text{eq/L}$ range). *A2.* Acid-neutralizing capacity (for triplicate means in $\pm 20 \mu\text{eq/L}$ range). *B.* Aluminum, total monomeric. *C.* Aluminum, organic monomeric.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

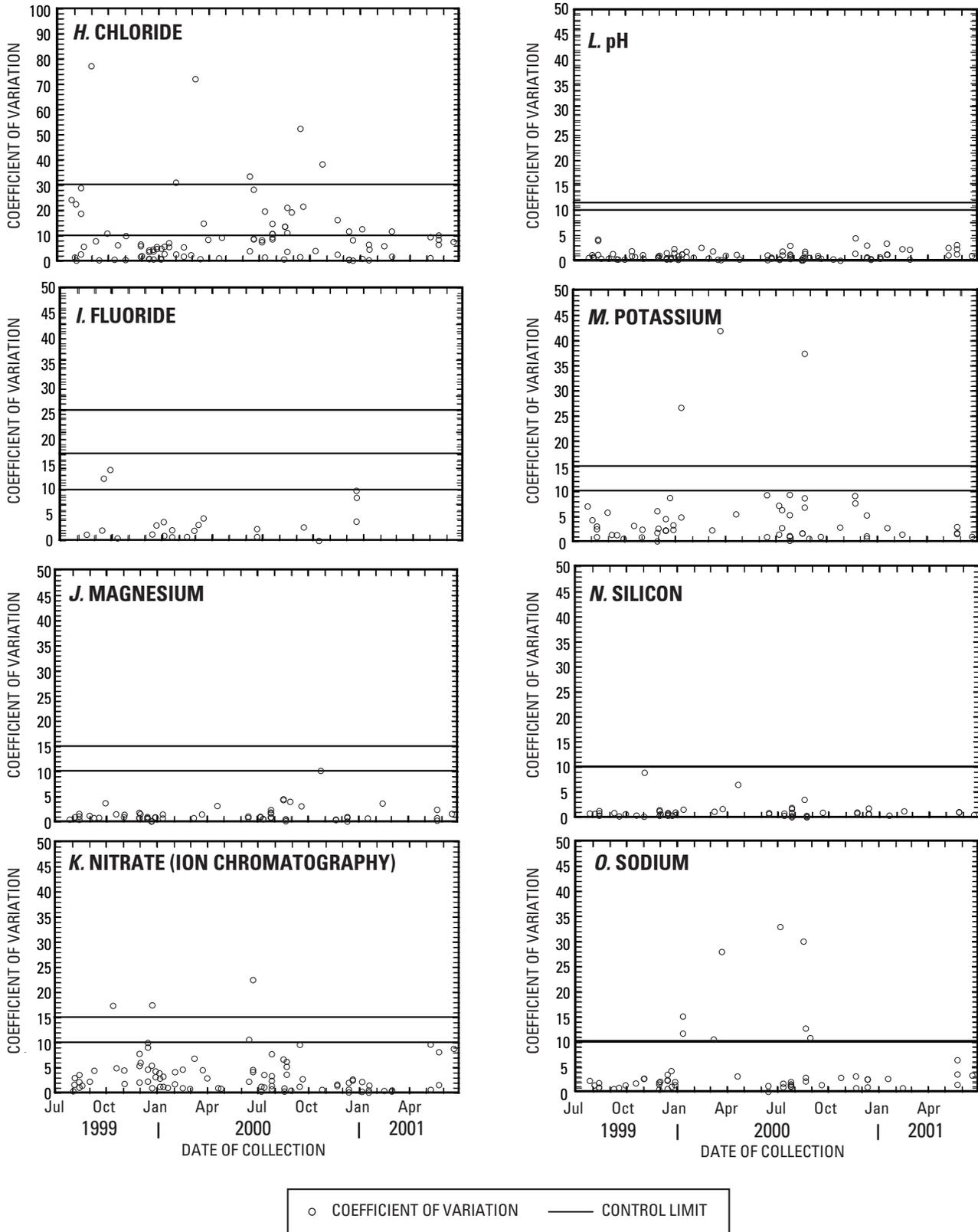


Figure 3. Triplicate environmental sample results: *H.* Chloride. *I.* Fluoride. *J.* Magnesium. *K.* Nitrate (ion chromatography). *L.* pH. *M.* Potassium. *N.* Silicon. *O.* Sodium—Continued

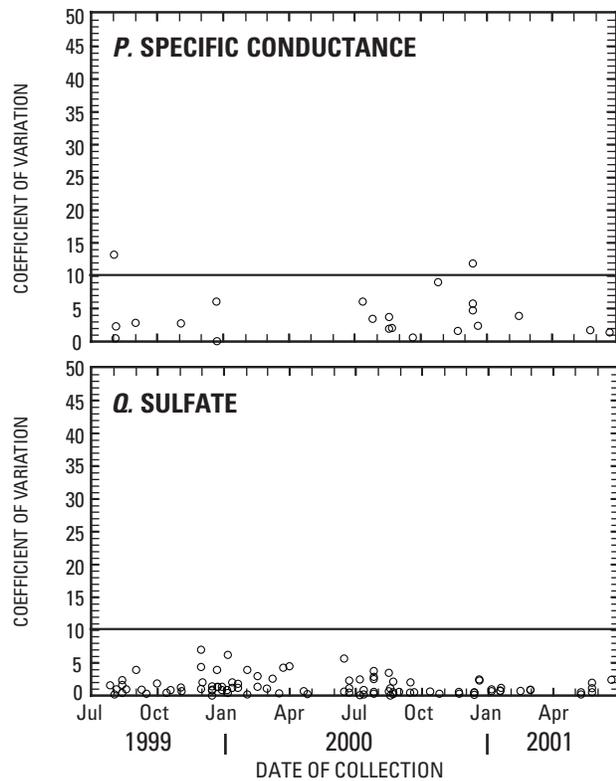


Figure 3. Triplicate environmental sample results: *P.* Specific conductance. *Q.* Sulfate.—Continued

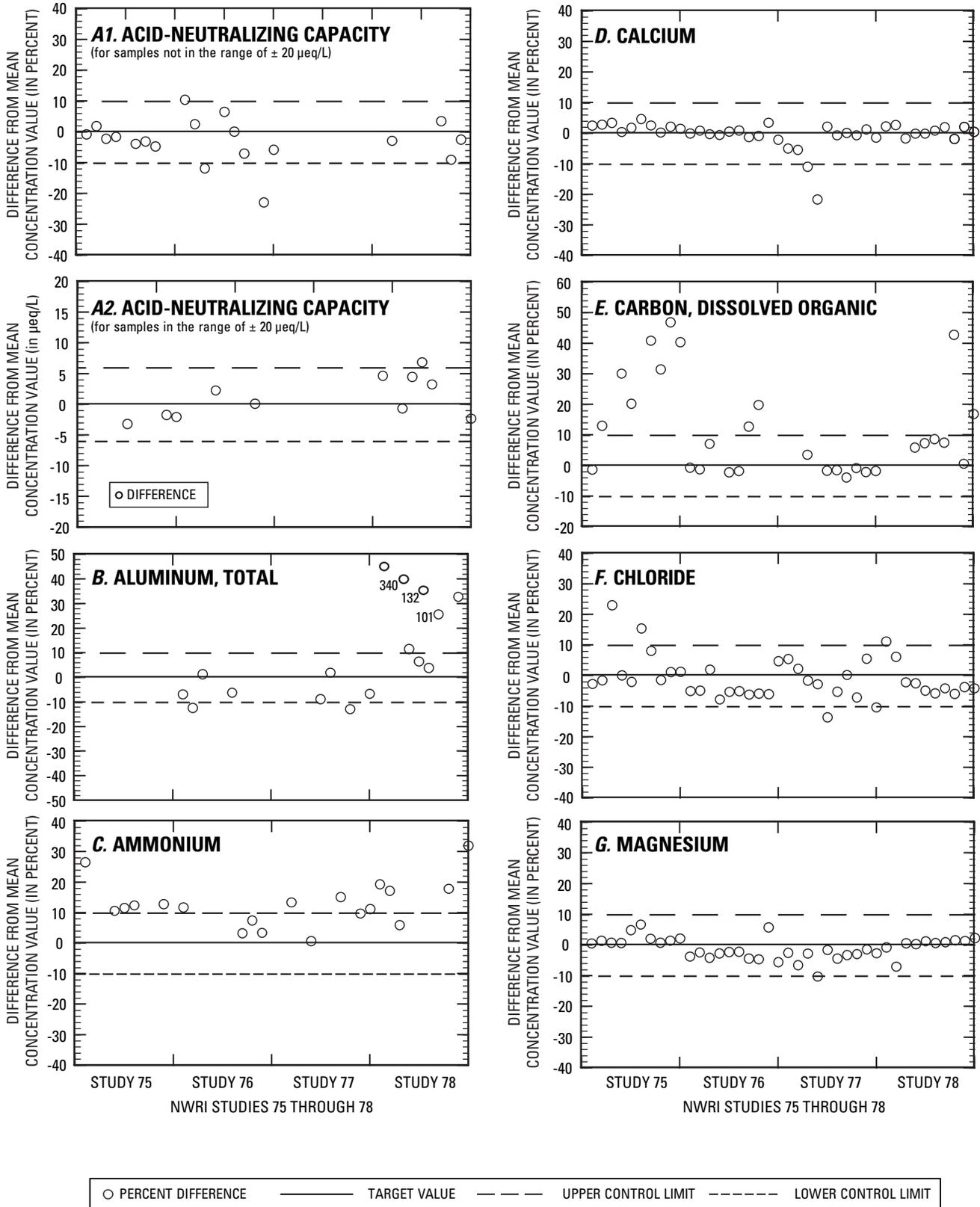


Figure 4. NWRI Ecosystem Interlaboratory QA Program results: A1. Acid-neutralizing capacity (for samples not in the range of $\pm 20 \mu\text{eq/L}$). A2. Acid-neutralizing capacity (for samples in the range of $\pm 20 \mu\text{eq/L}$). B. Aaluminum, total. C. Ammonium. D. Calcium. E. Carbon, dissolved organic. F. Chloride. G. Magnesium.

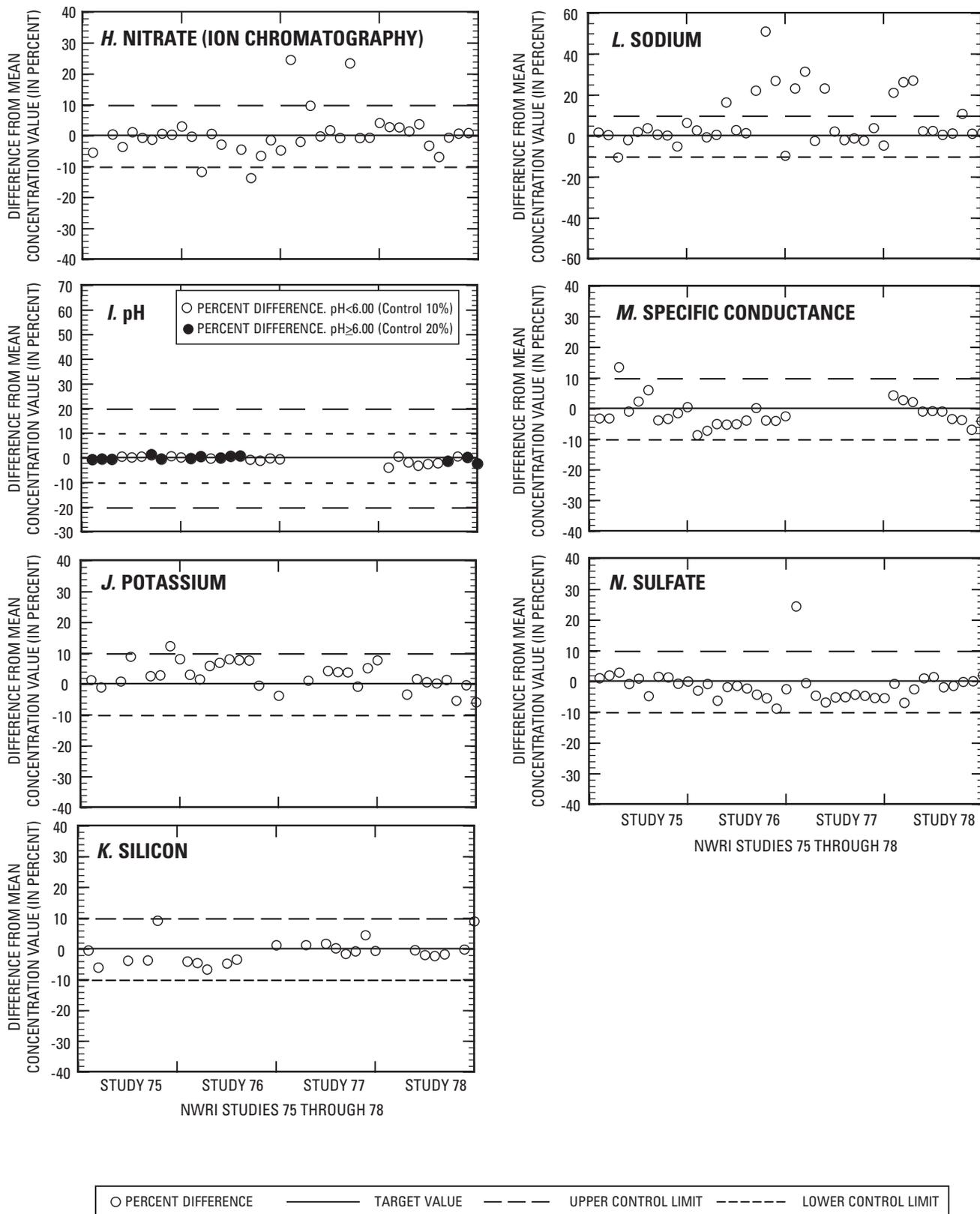


Figure 4. NWRI Ecosystem Interlaboratory QA Program results: *H.* Nitrate (ion chromatography). *I.* pH. *J.* Potassium. *K.* Silicon. *L.* Sodium. *M.* Specific conductance. *N.* Sulfate.—Continued.

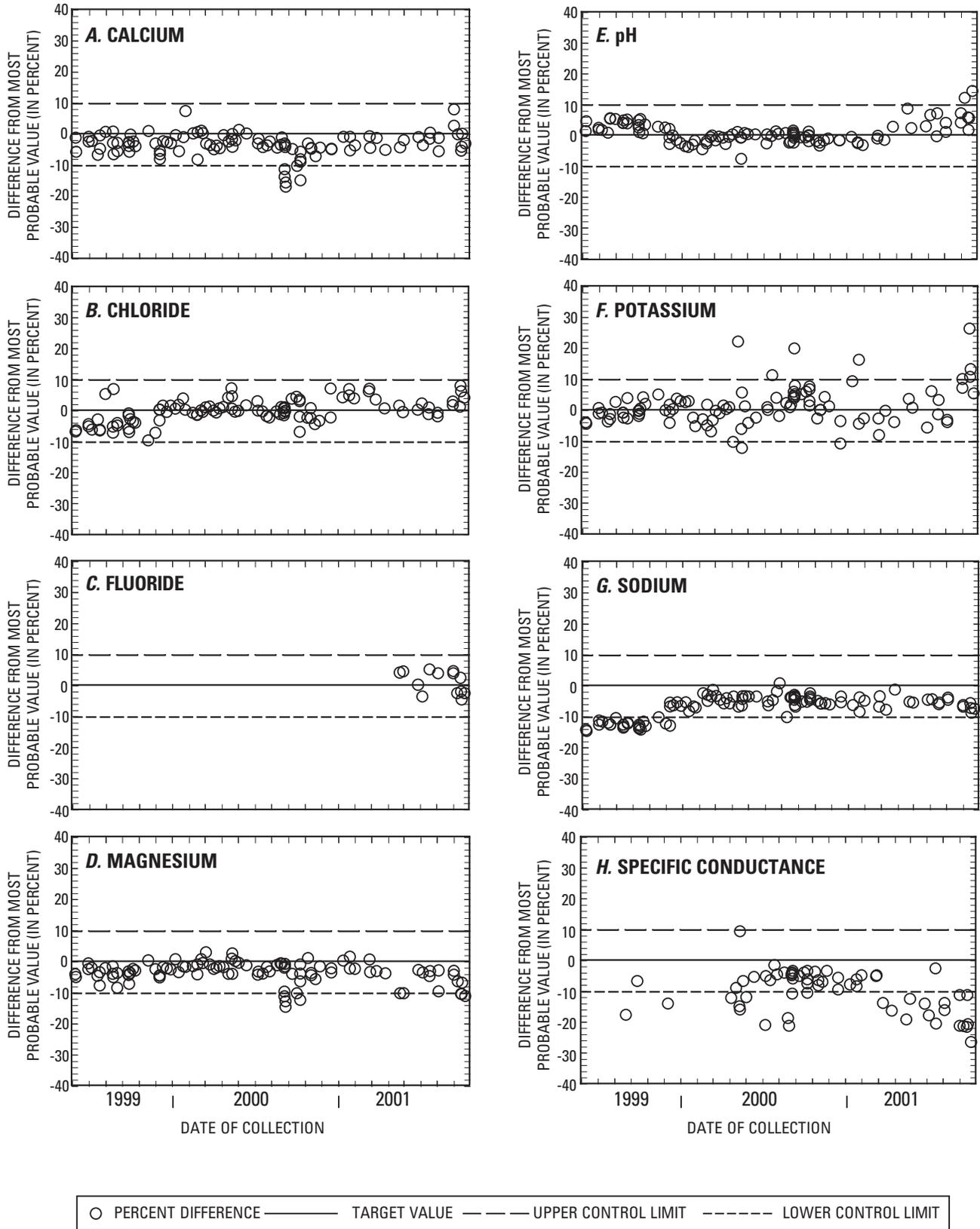


Figure 5. Blind reference sample results: A. Calcium. B. Chloride. C. Fluoride. D. Magnesium. E. pH. F. Potassium. G. Sodium. H. Specific conductance.

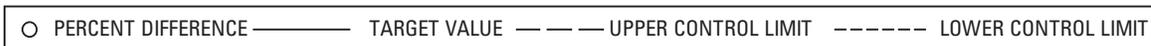
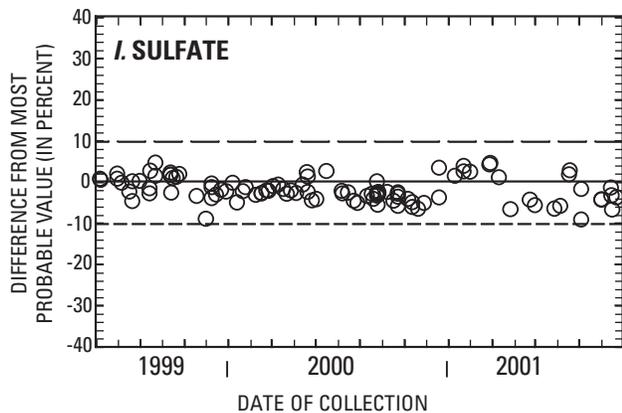


Figure 5. Blind reference sample results: *I. Sulfate*.—Continued

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