

Quality-Assurance Results for Routine Water Analyses in U.S. Geological Survey Laboratories, Water Year 1998



Water-Resources Investigations Report 00-4176

Quality-Assurance Results for Routine Water Analyses in U.S. Geological Survey Laboratories, Water Year 1998

By Amy S. Ludtke, Mark T. Woodworth, and Philip S. Marsh

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 00-4176

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

U.S. GEOLOGICAL SURVEY Charles G. Groat, Director

The use of firm, trade, and brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

For additional information write to:

Copies of this report can be purchased from:

Chief, Branch of Quality Systems U.S. Geological Survey Water Resources Division Box 25046, Mail Stop 401 Denver Federal Center Denver, CO 80225–0046

U.S. Geological Survey Information Services Box 25286 Federal Center Denver, CO 80225

CONTENTS

Abstract	
Introduction	
Program Desc	ription
	on of Sample Loads
Compar	ison of Results with the National Water Information System Water-Quality Data Bases
	luation
Control	Chart Development and Evaluation
	n Chart Development and Evaluation
Binomia	al-Probability-Distribution Technique to Assess Precision
	on Signed-Rank Procedure to Assess Bias
Quality-Assur	ance Data for Inorganic-Constituent Samples
Precisio	n
Bias	
Quality-Assur	ance Data for Nutrient-Constituent Samples
Precisio	n
Bias	
Summary	
References	
Supplemental	Data
FIGURES	
1-159. Grapl	as showing.
1-139. Grapi	· ·
1.	Display of line of relation for ordinary least-squares regression equation derived for sodium
2.	·
2	Quality Laboratory
3.	
4	the National Water Quality Laboratory
4.	, , , , , , , , , , , , , , , , , , ,
E	Water Quality Laboratory
5.	Aluminum, whole-water recoverable, (direct current plasma-atomic emission spectrometry)
6	data from the National Water Quality Laboratory
6.	J, J J
7	National Water Quality Laboratory
7.	
o	Water Quality Laboratory
0.	National Water Quality Laboratory
0	Arsenic, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry,
9.	U.S. Environmental Protection Agency) data from the National Water Quality Laboratory
10	
10.	Arsenic, whole-water recoverable, (hydride generation-atomic absorption spectrophotometry) data from the National Water Quality Laboratory
11	Barium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the
11.	
10	National Water Quality Laboratory
12.	Barium, dissolved, (inductively coupled plasma-mass spectrometry) data from the National
10	Water Quality Laboratory
13.	Beryllium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from
	the National Water Quality Laboratory
14.	Beryllium, dissolved, (inductively coupled plasma-mass spectrometry) data from the National
	Water Quality Laboratory
15.	Boron, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the
	National Water Quality Laboratory

16.	Boron, whole-water recoverable, (direct current plasma-atomic emission spectrometry)	
	data from the National Water Quality Laboratory	55
17.		
	the National Water Quality Laboratory	56
18.	Cadmium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data	
	from the National Water Quality Laboratory	57
19.	Cadmium, dissolved, (inductively coupled plasma-mass spectrometry) data from the	
	National Water Quality Laboratory	58
20.	Cadmium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry)	
	data from the National Water Quality Laboratory	59
21.		
	the National Water Quality Laboratory	60
22.	Chloride, dissolved, (ion chromatography) data from the National Water Quality Laboratory	
23.		
	Laboratory	62
24.		
	National Water Quality Laboratory	63
25.	Chromium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from	
	the National Water Quality Laboratory	64
26.	Chromium, dissolved, (inductively coupled plasma-mass spectrometry) data from the National	
20.	Water Quality Laboratory	65
27.	Chromium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry)	
21.	data from the National Water Quality Laboratory	66
28.	Cobalt, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the	
20.	National Water Quality Laboratory	67
29.	Cobalt, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from	
27.	the National Water Quality Laboratory	68
30.	Cobalt, dissolved, (inductively coupled plasma-mass spectrometry) data from the National	00
<i>5</i> 0.	Water Quality Laboratory	69
31.		03
31.	data from the National Water Quality Laboratory	70
22	Copper, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the	
32.	National Water Quality Laboratory	7 1
22		/]
<i>33</i> .	Copper, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from	70
2.4	the National Water Quality Laboratory	72
34.		7.
25	Water Quality Laboratory	7 3
<i>3</i> 3.	Copper, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry)	7
	data from the National Water Quality Laboratory	
36.	Dissolved solids, dissolved, (gravimetric) data from the National Water Quality Laboratory	/3
37.	Fluoride, dissolved, (ion chromatography, low level) data from the National Water Quality	_
	Laboratory	
38.	Fluoride, dissolved, (ion-selective electrode) data from the National Water Quality Laboratory	77
39.		
	National Water Quality Laboratory	78
40.		
	National Water Quality Laboratory	79
41.		
	National Water Quality Laboratory	80
42.	Lead, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the	
	National Water Quality Laboratory	81
43.	Lead, dissolved, (inductively coupled plasma-mass spectrometry) data from the National	
	Water Quality Laboratory	82
44.	Lead, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry)	
	data from the National Water Quality Laboratory	83

45.	Lithium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data	
	from the National Water Quality Laboratory	84
46.	Lithium, whole-water recoverable, (flame-atomic absorption spectrophotometry) data	
	from the National Water Quality Laboratory	85
47.	Magnesium, dissolved, (inductively coupled plasma-atomic emission spectrometry)	
	data from the National Water Quality Laboratory	86
48.	Manganese, dissolved, (inductively coupled plasma-atomic emission spectrometry) data	
	from the National Water Quality Laboratory	87
49.	Manganese, dissolved, (inductively coupled plasma-mass spectrometry) data from the	
	National Water Quality Laboratory	88
50.	Manganese, whole-water recoverable, (flame-atomic absorption spectrophotometry)	
	data from the National Water Quality Laboratory	89
51.	Mercury, dissolved, (cold vapor-atomic absorption spectrophotometry) data from the	
	National Water Quality Laboratory	90
52.	Mercury, whole-water recoverable, (cold vapor-atomic absorption spectrophotometry)	
	data from the National Water Quality Laboratory	91
53.	Molybdenum, dissolved, (graphite furnace-atomic absorption spectrophotometry) data	
	from the National Water Quality Laboratory	92
54.	Molybdenum, dissolved, (inductively coupled plasma-atomic emission spectrometry) data	
	from the National Water Quality Laboratory	93
55.	Molybdenum, dissolved, (inductively coupled plasma-mass spectrometry) data from the	
	National Water Quality Laboratory	94
56.	Molybdenum, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry)	
	data from the National Water Quality Laboratory	95
57.	Nickel, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the	
	National Water Quality Laboratory	96
58.	Nickel, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from	
	the National Water Quality Laboratory	97
59.	Nickel, dissolved, (inductively coupled plasma-mass spectrometry) data from the National	
	Water Quality Laboratory	98
60.	Nickel, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry)	
	data from the National Water Quality Laboratory	99
61.	Potassium, dissolved, (flame-atomic absorption spectrophotometry) data from the National	
	Water Quality Laboratory	100
62.	Potassium, dissolved, (flame-atomic absorption spectrophotometry, low level) data from	
	the National Water Quality Laboratory	101
63.	Selenium, dissolved, (hydride generation-atomic absorption spectrophotometry) data from	
	the National Water Quality Laboratory	102
64.	Selenium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry,	100
	U.S. Environmental Protection Agency) data from the National Water Quality Laboratory	103
65.	Selenium, whole-water recoverable, (hydride generation-atomic absorption spectrophotometry)	104
	data from the National Water Quality Laboratory	
66.	Silica, dissolved, (colorimetric) data from the National Water Quality Laboratory	105
67.	Silica, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the	100
- 0	National Water Quality Laboratory	106
68.	Silver, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the	105
.	National Water Quality Laboratory	107
69.	Silver, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from	100
70	the National Water Quality Laboratory	108
70.	Silver, dissolved, (inductively coupled plasma-mass spectrometry) data from the National	100
- -	Water Quality Laboratory	109
71.	Silver, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry)	
70	data from the National Water Quality Laboratory	110
72.	Sodium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from	444
	the National Water Quality Laboratory	111

73.		
	National Water Quality Laboratory	112
74.	Strontium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from	
	the National Water Quality Laboratory	
75.	Sulfate, dissolved, (ion chromatography) data from the National Water Quality Laboratory	114
76.	Vanadium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from	
	the National Water Quality Laboratory	115
77.	Zinc, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the	110
=0	National Water Quality Laboratory	116
78.	Zinc, dissolved, (inductively coupled plasma-mass spectrometry) data from the National	
70	Water Quality Laboratory	117
79.	Zinc, whole-water recoverable, (flame-atomic absorption spectrophotometry) data from	110
90	the National Water Quality Laboratory	118
80.	Ammonia as nitrogen, dissolved, (colorimetric) data from the National Water Quality	110
01	Laboratory	119
81.	Ammonia as nitrogen, dissolved, (colorimetric, low level) data from the National Water Quality Laboratory	120
92	Ammonia as nitrogen, dissolved, (U.S. Environmental Protection Agency) data from the	120
82.	National Water Quality Laboratory	121
83.	Ammonia plus organic nitrogen as nitrogen, dissolved, (micro-Kjeldahl digestion, automated	121
65.	segmented flow, colorimetric) data from the National Water Quality Laboratory	122
84.	Ammonia plus organic nitrogen as nitrogen, dissolved, (U.S. Environmental Protection Agency)	122
07.	data from the National Water Quality Laboratory	123
85.	Ammonia plus organic nitrogen as nitrogen, whole-water recoverable, (micro-Kjeldahl digestion,	123
ου.	automated segmented flow, colorimetric) data from the National Water Quality Laboratory	124
86.	Ammonia plus organic nitrogen as nitrogen, whole-water recoverable, (U.S. Environmental	12
00.	Protection Agency) data from the National Water Quality Laboratory	125
87.	Nitrate plus nitrite as nitrogen, dissolved, (colorimetric) data from the National Water Quality	
• • •	Laboratory	126
88.	Nitrate plus nitrite as nitrogen, dissolved, (colorimetric, low level) data from the National	
	Water Quality Laboratory	127
89.	Orthophosphate as phosphorus, dissolved, (colorimetric) data from the National Water Quality	
	Laboratory	128
90.	Orthophosphate as phosphorus, dissolved, (colorimetric, low level) data from the National	
	Water Quality Laboratory	129
91.	Phosphorus, dissolved, (micro-Kjeldahl digestion, automated segmented flow, colorimetric)	
	data from the National Water Quality Laboratory	130
92.	Phosphorus, dissolved, (colorimetric, low level) data from the National Water Quality	
	Laboratory	131
93.	Phosphorus, dissolved, (U.S. Environmental Protection Agency) data from the National	
	Water Quality Laboratory	132
94.	Phosphorus, whole-water recoverable, (micro-Kjeldahl digestion, automated segmented flow,	
	colorimetric) data from the National Water Quality Laboratory	133
95.	Phosphorus, whole-water recoverable, (colorimetric, low level) data from the National Water	
	Quality Laboratory	134
96.	Phosphorus, whole-water recoverable, (U.S. Environmental Protection Agency) data from the	
	National Water Quality Laboratory	135
97.	Alkalinity, whole-water recoverable, (electrometric titration) data from the Quality of Water	
	Service Unit laboratory	136
98.	Aluminum, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data	
00	from the Quality of Water Service Unit laboratory	137
99.	Aluminum, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry,	100
	U.S. Environmental Protection Agency) data from the Quality of Water Service Unit laboratory	138
100.	Aluminum, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry,	100
	trace) data from the Quality of Water Service Unit laboratory	1 <i>5</i> 9

101.	Arsenic, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory	140
102.	Arsenic, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry)	2 . 0
102.	data from the Quality of Water Service Unit laboratory	141
103.	Barium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data	1.10
	from the Quality of Water Service Unit laboratory	142
104.	Barium, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory	143
105.	Beryllium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory	144
106.	Beryllium, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry,	
	trace) data from the Quality of Water Service Unit laboratory	145
107.	Boron, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory	146
108.	Cadmium, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory	
109.	Cadmium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data	17/
	from the Quality of Water Service Unit laboratory	148
110.	Cadmium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory	149
111.	Cadmium, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry,	172
	trace) data from the Quality of Water Service Unit laboratory	150
112.	Calcium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the	
	Quality of Water Service Unit laboratory	151
113.	Calcium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data	
	from the Quality of Water Service Unit laboratory	152
114.	Chloride, dissolved, (ion chromatography) data from the Quality of Water Service Unit	152
115	laboratory	133
115.	from the Quality of Water Service Unit laboratory	154
116.	Chromium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry)	154
	data from the Quality of Water Service Unit laboratory	155
117.	Chromium, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory	
118.	Cobalt, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from	100
	the Quality of Water Service Unit laboratory	157
119.	Copper, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory	158
120.	Copper, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from	
	the Quality of Water Service Unit laboratory	159
121.	Copper, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data	1.60
100	from the Quality of Water Service Unit laboratory	160
122.	Copper, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory	161
123.	Dissolved solids, dissolved, (gravimetric) data from the Quality of Water Service Unit	
104	laboratory	162
124.	Fluoride, dissolved, (ion-selective electrode) data from the Quality of Water Service Unit laboratory	163
125.	Iron, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from	1.04
126	the Quality of Water Service Unit laboratory	154
126.	Iron, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory	165
127.	Lead, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the Quality	
	of Water Service Unit laboratory	166

128.	Lead, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from	
	the Quality of Water Service Unit laboratory	167
129.	Lead, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data	
	from the Quality of Water Service Unit laboratory	168
130.	Lead, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry,	
	trace) data from the Quality of Water Service Unit laboratory	169
131.	Magnesium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data	
	from the Quality of Water Service Unit laboratory	170
132.	Magnesium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace)	
	data from the Quality of Water Service Unit laboratory	171
133.	Manganese, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace)	
	data from the Quality of Water Service Unit laboratory	172
134.	Manganese, whole-water recoverable, (inductively coupled plasma-atomic emission	•
	spectrometry, trace) data from the Quality of Water Service Unit laboratory	173
135.	Mercury, whole-water recoverable, (cold vapor-atomic absorption spectrophotometry) data	
	from the Quality of Water Service Unit laboratory	174
136.	Molybdenum, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace)	
	data from the Quality of Water Service Unit laboratory	175
137.	Nickel, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data	
	from the Quality of Water Service Unit laboratory	176
138.	Nickel, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry)	
	data from the Quality of Water Service Unit laboratory	177
139.	Nickel, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry,	
	trace) data from the Quality of Water Service Unit laboratory	178
140.	Potassium, dissolved, (flame-atomic absorption spectrophotometry) data from the Quality of	
	Water Service Unit laboratory	179
141.	Selenium, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the	
	Quality of Water Service Unit laboratory	180
142.	Selenium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry)	
	data from the Quality of Water Service Unit laboratory	181
143.	Silica, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the	
	Quality of Water Service Unit laboratory	182
144.	Silica, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data	
	from the Quality of Water Service Unit laboratory	183
145.		
1	from the Quality of Water Service Unit laboratory	184
146.	· · · · · · · · · · · · · · · · · · ·	
1	of Water Service Unit laboratory	185
147.	Strontium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace)	
· · · ·	data from the Quality of Water Service Unit laboratory	186
148.	Strontium, whole-water recoverable, (inductively coupled plasma-atomic emission	100
170.	spectrometry, trace) data from the Quality of Water Service Unit laboratory	187
149.	Sulfate, dissolved, (ion chromatography) data from the Quality of Water Service Unit	107
147.	laboratory	100
150	Vanadium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace)	100
150.	data from the Quality of Water Service Unit laboratory	100
151	Zinc, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data	105
151.		100
150	from the Quality of Water Service Unit laboratory	190
152.	Zinc, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry,	101
150	trace) data from the Quality of Water Service Unit laboratory	
153.		192
154.		100
155	Unit laboratory	193
155.		10
	Quality of Water Service Unit laboratory	194

	156. Nitrate plus nitrite as nitrogen, dissolved, data from the Quality of Water Service Unit laboratory	195
	157. Orthophosphate as phosphorus, dissolved, data from the Quality of Water Service Unit laboratory	196
	158. Phosphorus, dissolved, data from the Quality of Water Service Unit laboratory	197
	159. Phosphorus, whole-water recoverable, data from the Quality of Water Service Unit laboratory	198
TABLE	s	
1.	Ordinary least-squares equations for determining the most probable deviation	<i>6</i>
2.	Total number of analyses from quality-assurance samples during water year 1998 with the number greater than two and six standard deviations from the most probable value and results of statistical testing for analytical precision in constituent data for the National Water Quality Laboratory	12
3.	Total number of analyses from quality-assurance samples during water year 1998 with the number greater than two and six standard deviations from the most probable value and results of statistical testing for analytical precision in constituent data for the Quality of Water Service Unit laboratory	14
4.	Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory	18
5.	Results of Wilcoxon signed-rank test for bias in constituent data for the Quality of Water Service Unit Laboratory	29

ABBREVIATIONS

Units of Measure

C Celsius

mg/L milligrams per liter

μg/L micrograms per liter

μS/cm microsiemens per centimeter at 25 degrees Celsius

Analytical Methods

ASF micro-Kjeldahl digestion, automated segmented flow, colorimetric

COL colorimetric

CV-AAS cold vapor-atomic absorption spectrophotometry
DCP-AES direct current plasma-atomic emission spectrometry

DIS dissolved ELEC electrometric

F-AAS flame-atomic absorption spectrophotometry

GF-AAS graphite furnace-atomic absorption spectrophotometry

GRAV gravimetric

HG-AAS hydride generation-atomic absorption spectrophotometry

IC ion chromatography

ICP-AES inductively coupled plasma-atomic emission spectrometry ICP-AES/T inductively coupled plasma-atomic emission spectrometry, trace

ICP-MS inductively coupled plasma-mass spectrometry

ISE ion-selective electrode

LL low level

LRL laboratory reporting limit
TITR electrometric titration

USEPA U.S. Environmental Protection Agency method

WWR whole-water recoverable

Others

BSP Blind Sample Project

 F_{σ} regression estimate of F-pseudosigma LOP statistically significant lack of precision

MPV most probable value MRL minimum reporting limit

NEG negative bias

NSD number of standard deviations NWIS National Water Information System NWQL National Water Quality Laboratory

POS positive bias

QWSU Quality of Water Service Unit RSD relative standard deviation SRWS standard reference water sample

U.S. Geological Survey

Quality-Assurance Results for Routine Water Analyses in U.S. Geological Survey Laboratories, Water Year 1998

By Amy S. Ludtke, Mark T. Woodworth, and Philip S. Marsh

Abstract

The U.S. Geological Survey operates a quality-assurance program based on the analyses of reference samples for two laboratories: the National Water Quality Laboratory and the Quality of Water Service Unit. Reference samples that contain selected inorganic, nutrient, and lowlevel constituents are prepared and submitted to the laboratory as disguised routine samples. The program goal is to estimate precision and bias for as many analytical methods offered by the participating laboratories as possible. Blind reference samples typically are submitted at a rate of 2 to 5 percent of the annual environmental-sample load for each constituent. The samples are distributed to the laboratories throughout the year. The reference samples are subject to the identical laboratory handling, processing, and analytical procedures as those applied to environmental samples and, therefore, have been used as an independent source to verify bias and precision of laboratory analytical methods and ambient waterquality measurements. The results are stored permanently in the National Water Information System and the Blind Sample Project's data base. During water year 1998, 95 analytical procedures were evaluated at the National Water Quality Laboratory and 63 analytical procedures were evaluated at the Quality of Water Service Unit.

An overall evaluation of the inorganic and low-level constituent data for water year 1998 indicated 77 of 78 analytical procedures at the National Water Quality Laboratory met the criteria for precision. Silver (dissolved, inductively coupled plasma-mass spectrometry)

was determined to be imprecise. Five of 78 analytical procedures showed bias throughout the range of reference samples: chromium (dissolved, inductively coupled plasma-atomic emission spectrometry), dissolved solids (dissolved, gravimetric), lithium (dissolved, inductively coupled plasma-atomic emission spectrometry), silver (dissolved, inductively coupled plasma-mass spectrometry), and zinc (dissolved, inductively coupled plasma-mass spectrometry).

At the National Water Quality Laboratory during water year 1998, lack of precision was indicated for 2 of 17 nutrient procedures: ammonia as nitrogen (dissolved, colorimetric) and orthophosphate as phosphorus (dissolved, colorimetric). Bias was indicated throughout the reference sample range for ammonia as nitrogen (dissolved, colorimetric, low level) and nitrate plus nitrite as nitrogen (dissolved, colorimetric, low level).

All analytical procedures tested at the Quality of Water Service Unit during water year 1998 met the criteria for precision. One of the 63 analytical procedures indicated a bias throughout the range of reference samples: aluminum (whole-water recoverable, inductively coupled plasma-atomic emission spectrometry, trace).

INTRODUCTION

The U.S. Geological Survey (USGS) performs numerous hydrologic investigations that require analyses of water for inorganic, nutrient, and low-level constituents. The National Water Quality Laboratory (NWQL) and the Quality of Water Service Unit (QWSU) laboratory are the primary sources of analytical services for many of these hydrologic investigations. The NWQL, which now occupies a new facility in Lakewood, Colorado, was located in Arvada, Colorado, during this reporting period. The QWSU is in Ocala, Florida. The NWQL provides analytical services for all national programs conducted by the USGS and also is used by USGS district offices throughout the Nation for local and regional programs. The QWSU provides analytical services to USGS district offices in the Southeastern United States.

This report describes the results of a quality-assurance program used to monitor the quality of inorganic, nutrient, and low-level analytical procedures at the NWQL and inorganic and nutrient analytical procedures at the QWSU. Previous reports (Peart and Thomas, 1983a, 1983b, 1984; Peart and Sutphin, 1987; Lucey and Peart, 1988, 1989a, 1989b; Lucey, 1989; Maloney and others, 1992, 1993, 1994; Ludtke and others, 1999) document results from February 1981 through September 1997. Some of the previous reports contain quality-assurance information for organic determinations.

The water year used by the USGS is the 12 months from October 1 through September 30 and is identified by the calendar year in which the water year ends. During water year 1998, 95 analytical procedures were evaluated for the NWQL by the Blind Sample Project (BSP). This represents about 85 percent of the inorganic and nutrient analytical procedures offered by the laboratory for water-matrix determinations. The remaining 15 percent of the water-matrix determinations offered were either infrequently requested, so that it was not feasible to include them in the BSP, or the constituents did not have a readily available, stable source of reference material. In addition, the NWQL offers analytical determinations for sample matrices other than water, such as biological tissues and sediments.

The BSP evaluated 63 analytical procedures for the QWSU during water year 1998. This represents about 75 percent of the total number of water-matrix constituents offered for analysis. The remaining 25 percent were considered to be custom determinations that were infrequently requested. In addition, some of the constituents did not have a readily available, stable source of reference material.

Laboratory users who require analyses for water-matrix constituents not offered through the BSP, or any nonwater-matrix determinations, should consider alternative procedures to measure analytical quality. The analytes included in the 1998 NWQL and QWSU BSP are listed below by constituent categories:

Inorganic constituents (NWQL and QWSU BSP's)—alkalinity, aluminum, arsenic, barium, beryllium, boron, cadmium, calcium, chloride, chromium, cobalt, copper, dissolved solids (residue on evaporation at 180°C), fluoride, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, potassium, selenium, silica, silver, sodium, strontium, sulfate, vanadium, and zinc. Constituents included only in the NWQL BSP were antimony, lithium, and specific conductance (low level). The reference materials used by the BSP are not stable for the higher specific conductance concentration range.

Nutrient constituents (NWQL and QWSU BSP's)—ammonia as nitrogen, ammonia plus organic nitrogen as nitrogen, nitrate plus nitrite as nitrogen, orthophosphate as phosphorus, and phosphorus.

PROGRAM DESCRIPTION

Standard reference water samples (SRWS) (Skougstad and Fishman, 1975; Schroder and others, 1980; Janzer, 1985; Farrar and Chleboun, 1999) are used to prepare samples for the BSP. The SRWS's are used undiluted, diluted with deionized water, or mixed in varying proportions with other SRWS's. This sample-mixing procedure produces a large number of unique samples available for quality-assurance purposes.

Reference samples for the BSP are made to appear as much like environmental samples as possible to reduce the possibility that analysts will recognize them as quality-assurance samples. Analytical request forms are completed to ensure that appropriate analyses have been requested for the samples. For the NWQL program, samples are delivered by BSP personnel directly to the sample login unit of the laboratory. Because of the great number of samples delivered to the NWQL and because the login unit is separated from the analytical operations, there is little chance that the origin of these quality-assurance samples will be detected. Because the QWSU operation is much smaller than the NWQL and the analysts have direct contact with the sample login operations, the samples and forms are sent to selected USGS

offices that use that laboratory. Throughout the year, these offices send the quality-assurance samples for the BSP to the QWSU with their regular environmental samples.

The BSP samples are subjected to laboratory handling, processing, and analytical procedures identical to processes for the environmental samples. After laboratory analysis, BSP personnel compile and review the analytical results. The resulting data are stored in a National Water Information System (NWIS) data base and the BSP's SAS[©] data base.

The SRWS's are filtered during preparation; therefore, all constituents in the Blind Reference Samples are in the dissolved phase. Constituents that are designated as whole-water recoverable in this report are from filtered reference samples that have undergone a digestion process (Fishman and Friedman, 1989, p. 87–88) rather than from unfiltered or whole-water samples. Differences that appear in this report between the dissolved (DIS) analyses and the whole-water recoverable (WWR) analyses will be due to the digestion process rather than any difference in the sample phase.

Estimation of Sample Loads

The number of quality-assurance determinations requested for each analytical procedure is proportional to the number of requests for the procedure from all environmental samples submitted. Because both laboratories have active quality-control programs, the BSP followed the guidelines of Friedman and Erdmann (1982) to set submission of these external quality-assurance samples at a rate of about 2 to 5 percent of the laboratory work for each analytical procedure. The annual workload for each analytical procedure is estimated from sample login records for the previous year. The estimate is determined by taking the difference of the total number of login records for the procedure minus the number of samples submitted by the BSP and the laboratories' quality-control program.

Comparison of Results with the National Water Information System Water-Quality Data Bases

Analytical results for environmental samples are stored in the USGS National Water Information System (NWIS) data base. The NWIS is a national

standardized data-base system that is maintained by each USGS district office nationwide. The NWIS allows users in those offices to enter, review, update, and retrieve analytical results that pertain to the field area the office serves.

The assessments presented in this report are based on analytical results released from the laboratories that have the same level of quality-control review as the data released to each USGS district office. The results presented in the report, however, provide a conservative estimate of the quality of the data stored in individual NWIS data bases because water-quality specialists and project chiefs are expected to scrutinize analytical results for discrepancies, request reruns for questionable results, and update analytical results in the NWIS data base as appropriate.

Factors that need to be considered for interpretation of results stored in NWIS data bases with relation to the results presented in this report include the following:

- 1. No effort was made to correct nonanalytical errors, even when it was obvious which corrective measures were appropriate. The data are presented as originally produced by the laboratories. Nonanalytical errors include sample login errors, transcription errors by the analyst, datatransmission errors by laboratory instruments, and manual data-entry errors. Therefore, a data reviewer that detects nonanalytical errors can make corrections to improve the quality of the NWIS data base. For example, two samples from different sites are submitted to a laboratory on the same day and are misidentified by the laboratory in a way that the analytical data reported for one actually belongs to the other. A data reviewer familiar with one of the sites or its historical data usually could detect and correct the problem with help from the laboratory.
- 2. Dilution factors that were incorrectly applied account for some analytical errors. Sample dilutions are routinely made in the laboratory to bring sample concentrations into analytical calibration range. If the dilution factor is not applied or is applied incorrectly, the reported value will be in error. For example, if a nutrient sample has a phosphorus concentration of 1.6 mg/L and an analysis is reported at 0.16 mg/L, a tenfold dilution may have been used and not applied to the

- final result. These errors are difficult to identify unless historical data for a sampling site are available for comparison.
- 3. Determinations that exceed control limits, set at ±2 standard deviations of the referencesample concentration, are typically submitted for reanalysis by the BSP. The purpose of these rerun requests is to identify reference samples that may be deteriorating or that may have been incorrectly bottled. If the BSP determines that the source of error was deterioration of the sample or a sample mixup that occurred before the sample was delivered to the laboratory, then the data are purged from the quality-assurance data base. The majority of analysis reruns indicate the source of error to be problems associated with laboratory operations, such as analytical errors, internal bottle mixups, or data-transmission errors. If a laboratory problem is indicated by the analysis rerun, the original data remain in the qualityassurance data base. If the quality-control section of the laboratory independently identifies problems with an analytical determination and requires that updated analyses be released, then the quality-assurance data base is updated with the new values.
- 4. Control charts included in this report may be used to determine analytical conditions at any given time for water year 1998. A chart may show an analytical process to be out of statistical control for a short period of time, but in statistical control for most of the year. The data for the short period may affect the statistical tests for the entire year such that they would indicate analytical imprecision or significant bias. The data for the period when the analytical process was in statistical control can be considered separately to evaluate precision and bias. An interactive quality-assurance data base is available for the retrieval and assessment of blind quality-control sample analytical results. Currently, the BSP data-base system contains more than 190,000 analyses dating from October 1984 to present (2000). New analytical data released from the laboratories are added weekly to the data base. Data retrievals can be customized to document the laboratories' analytical bias and variability relative to the time period, analytical procedures, and concentration ranges of individual water-quality

programs. Step-by-step instructions for accessing the BSP data base can be found on the internet at: http://bqs.usgs.gov/bsp/qadatanew.htm.

STATISTICAL EVALUATION

Control Chart Development and Evaluation

The SRWS's used in the BSP are analyzed through a round-robin evaluation program described by Farrar and Chleboun (1999). A statistical summary of the round-robin results is prepared for each set of samples. The SRWS Project uses median and F-pseudosigma in the summary reports as a measure of the known value and variability about the known value. The median data reported in the SRWS summaries have been referred to as most probable value (MPV). The F-pseudosigma (F_{σ}) is defined by Hoaglin and others (1983) as:

$$F_{\sigma} = \frac{data \, (Fourth-spread)}{1.349} \tag{1}$$

where the Fourth-spread is analogous to the interquartile range of the data. In addition, they show that the F-pseudosigma yields an unbiased estimate of standard deviation when the data distribution is Gaussian. However, it is recognized that some of the SRWS Project data sets may not have Gaussian data distributions. For non-Gaussian distributions, the F-pseudosigma is still a good estimate of spread and is not unduly influenced by outliers.

The SRWS Project MPV's are used to estimate the BSP mix concentrations that are based on the proportion of the SRWS's used. Likewise, if deionized water is used in the preparation of a blind sample mix, then a sample concentration of zero is applied to estimate the resultant MPV that is based on the proportion used. The resulting MPV's are used in the BSP to compare with analytical results.

For each SRWS constituent, a regression equation was used to estimate the F_{σ} over a continuous range of concentrations. The equations were derived by using ordinary least-squares and regressing the F-pseudosigma against the MPV. The ordinary least-squares regression equation derived for sodium is displayed in figure 1.

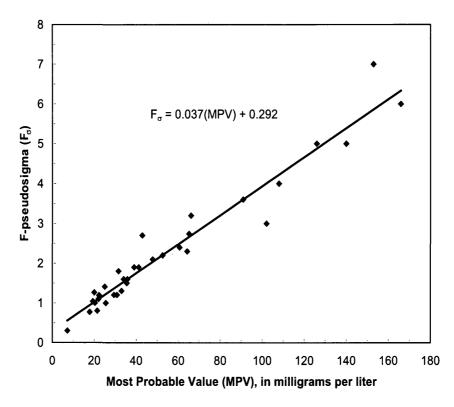


Figure 1. Display of line of relation for ordinary least-squares regression equation derived for sodium.

Helsel and Hirsch (1992) provide a general model for estimation of ordinary least-squares regression:

$$F_{\sigma_i} = \beta_0 + \beta_1 MPV_i + \varepsilon_i \qquad i = 1, 2, ...n \qquad (2)$$

where

 F_{σ_i} = the *i*th observation of the response variable, F_{σ} ;

 β_0 = the intercept;

 β_1 = the slope;

 MPV_i = the *i*th observation of the explanatory variable, Most Probable Value;

 ε_i = the random error or residual for the *i*th observation; and

n =the number of samples.

The SRWS Project summary data for semiannual round-robin sample studies conducted during the last 7 years were used to derive regression equations for each analyte. The concentration range of SRWS's used to derive the regression equations, the units of measurement, the derived F_{σ} equation, the number of samples

used to derive the equation, and the p-value indicating the level of significance associated with the derived equation are presented in table 1. P-values greater than 0.05 indicate there is less than a 5-percent chance that such a relationship would exist. The null hypothesis for the ordinary least-squares regression equation is that no relationship exists between the MPV and the F_{σ} . The authors set a significance level of 0.05. Then the null hypothesis was rejected when the probability, or p-value, was less than or equal to 0.05. Alternatively, when the p-value was less than or equal to 0.05, there is at least 95-percent chance that there is a linear relationship between the MPV and the F_{σ} .

The p-value for fluoride (DIS, IC, LL) is greater than 0.05. All of the MPV's and F_{σ} 's used in this regression equation were tightly clustered together. The errors contributed by using this regression equation are very minor, due to the samples' low MPV's. For example, the lowest concentration SRWS was 0.04 mg/L and the highest concentration SRWS was 0.139 mg/L. The F_{σ} for each of these samples would be 0.0202 and 0.0207, respectively. In the case of fluoride (DIS, IC, LL), we can conclude that the F_{σ} is close to constant for the narrow range of MPV's analyzed.

The assessment of whether an analytical measurement meets control specifications is based on the number of standard deviations (NSD) that the measured concentration differs from the MPV. In this report, the term standard deviations will be used when comparing individual determinations to the MPV. The NSD is determined by taking the difference between the analytical result and the MPV and dividing by the F_{σ} estimated by the appropriate regression equation using the MPV concentration. Taylor (1987, p. 33–34) provides a general equation that was modified to determine the NSD values for this assessment:

$$NSD = \frac{X_q - MPV}{F_{\sigma}} \tag{3}$$

where

NSD = number of standard deviations,

 X_a = value in question,

MPV = most probable value, and

 F_{σ} = regression estimate of F-pseudosigma.

Analytical results that are within two NSD's of the MPV concentration are considered acceptable; however, there have been instances where the assessment criteria, as defined above, resulted in unrealistic tolerances not related to analytical capability but rather to data-reporting criteria set for computer storage of environmental data. This primarily occurred for results near the reporting limits. The numerical precision for computer storage of environmental data is often much less than that used to calculate the MPV's of the SRWS's. For example, the criteria for NWIS data entry for many metals determined by flame-atomic absorption spectrophotometry (F-AAS) is to report values to the nearest 10 µg/L for determinations below 100 µg/L. For the SRWS project roundrobin study, however, laboratories typically report data to the nearest 1 µg/L, and the standard deviation for samples with concentrations below 100 µg/L may be only a few micrograms per liter. The regression equations used to estimate F_{σ} are based on SRWS data that are reported with more significant figures, especially at lower concentrations.

Table 1. Ordinary least-squares equations for determining the most probable deviation

Constituent and method of analysis	Concentration range	Unit	Equation to determine F_{σ}	Number of samples	p-value
	Inorganic constituen	ts			
Alkalinity (WWR, TITR)	27.0-234	mg/L	$F_{\sigma} = 0.018 \times + 0.955$	13	0.0001
Aluminum (DIS, GF-AAS)	10.0-317	μg/L	$F_{\sigma} = 0.090 \times + 6.834$	19	0.0001
Aluminum (DIS, ICP-AES)	10.0–317	μg/L	$F_{\sigma} = 0.090 \times + 6.834$	19	0.0001
Aluminum (DIS, ICP-MS)	10.0-317	μg/L	$F_{\sigma} = 0.090 \times + 6.834$	19	0.0001
Aluminum (WWR, DCP-AES)	10.0–317	μg/L	$F_{\sigma} = 0.090 \times + 6.834$	19	0.0001
Aluminum (WWR, GF-AAS, USEPA)	10.0–317	μg/L	$F_{\sigma} = 0.090 \times + 6.834$	19	0.0001
Aluminum (WWR, ICP-AES)	10.0-317	μg/L	$F_{\sigma} = 0.090 \times + 6.834$	19	0.0001
Antimony (DIS, HG-AAS)	0.55-76.3	μg/L	$F_{\sigma} = 0.109 \times + 0.559$	19	0.0001
Antimony (DIS, ICP-MS)	0.55-76.3	μg/L	$F_{\sigma} = 0.109 \times + 0.559$	19	0.0001
Arsenic (DIS, GF-AAS)	0.55-56.6	μg/L	$F_{\sigma} = 0.090 \times + 0.427$	19	0.0001
Arsenic (DIS, HG-AAS)	0.55-56.6	μg/L	$F_{\sigma} = 0.090 \times + 0.427$	19	0.0001
Arsenic (WWR, GF-AAS)	0.55-56.6	μg/L	$F_{\sigma} = 0.090 \times + 0.427$	19	0.0001
Arsenic (WWR, GF-AAS, USEPA)	0.55-56.6	μg/L	$F_{\sigma} = 0.090 \times + 0.427$	19	0.0001
Arsenic (WWR, HG-AAS)	0.55-56.6	μg/L	$F_{\sigma} = 0.090 \times + 0.427$	19	0.0001

Table 1. Ordinary least-squares equations for determining the most probable deviation—Continued

Constituent and method of analysis	Concentration range	Unit	Equation to determine \emph{F}_{σ}	Number of samples	p-value
	Inorganic constituents—Co	ntinued			
Barium (DIS, ICP-AES)	7.65–507	μg/L	$F_{\sigma} = 0.042 \times + 1.411$	19	0.0001
Barium (DIS, ICP-MS)	7.65–507	μg/L	$F_{\sigma} = 0.042 \times + 1.411$	19	0.0001
Barium (WWR, ICP-AES)	7.65–507	μg/L	$F_{\sigma} = 0.042 \times + 1.411$	19	0.0001
Beryllium (DIS, ICP-AES)	0.12-59.0	μg/L	$F_{\sigma} = 0.042 \times + 0.482$	18	0.0001
Beryllium (DIS, ICP-MS)	0.12-59.0	μg/L	$F_{\sigma} = 0.042 \times + 0.482$	18	0.0001
Beryllium (WWR, ICP-AES)	0.12-59.0	μg/L	$F_{\sigma} = 0.042 \times + 0.482$	18	0.0001
Boron (DIS, ICP-AES)	0.18-297	μg/L	$F_{\sigma} = 0.060 \times + 6.207$	33	0.0001
Boron (WWR, DCP-AES)	0.18-297	μg/L	$F_{\sigma} = 0.060 \times + 6.207$	33	0.0001
Cadmium (DIS, GF-AAS)	0.34-50.5	μg/L	$F_{\sigma} = 0.060 \times + 0.350$	19	0.0001
Cadmium (DIS, ICP-AES)	0.34-50.5	μg/L	$F_{\sigma} = 0.060 \times + 0.350$	19	0.0001
Cadmium (DIS, ICP-MS)	0.34-50.5	μg/L	$F_{\sigma} = 0.060 \times + 0.350$	19	0.0001
Cadmium (WWR, GF-AAS)	0.34-50.5	μg/L	$F_{\sigma} = 0.060 \times + 0.350$	19	0.0001
Cadmium (WWR, ICP-AES)	0.34-50.5	μg/L	$F_{\sigma} = 0.060 \times + 0.350$	19	0.0001
Calcium (DIS, ICP-AES)	4.60–154	mg/L	$F_{\sigma} = 0.054 \times -0.187$	33	0.0001
Chloride (DIS, IC)	7.60-208	mg/L	$F_{\sigma} = 0.030 \times + 0.355$	14	0.0001
Chloride (DIS, IC, LL)	0.14-7.79	mg/L	$F_{\sigma} = 0.040 \times + 0.164$	12	0.0001
Chromium (DIS, GF-AAS)	0.68-79.0	μg/L	$F_{\sigma} = 0.059 \times + 0.754$	18	0.0001
Chromium (DIS, ICP-AES)	0.68-79.0	μg/L	$F_{\sigma} = 0.059 \times + 0.754$.18	0.0001
Chromium (DIS, ICP-MS)	0.68-79.0	μg/L	$F_{\sigma} = 0.059 \times + 0.754$	18	0.0001
Chromium (WWR, GF-AAS)	0.68-79.0	μg/L	$F_{\sigma} = 0.059 \times + 0.754$	18	0.0001
Chromium (WWR, ICP-AES)	0.68-79.0	μg/L	$F_{\sigma} = 0.059 \times + 0.754$	18	0.0001
Cobalt (DIS, GF-AAS)	0.40-40.0	μg/L	$F_{\sigma} = 0.048 \times + 0.734$	17	0.0003
Cobalt (DIS, ICP-AES)	0.40-40.0	μg/L	$F_{\sigma} = 0.048 \times + 0.734$	17	0.0003
Cobalt (DIS, ICP-MS)	0.40-40.0	μg/L	$F_{\sigma} = 0.048 \times + 0.734$	17	0.0003
Cobalt (WWR, GF-AAS)	0.40-40.0	μg/L	$F_{\sigma} = 0.048 \times + 0.734$	17	0.0003
Copper (DIS, GF-AAS)	1.90-85.3	μg/L	$F_{\sigma} = 0.050 \times + 1.067$	19	0.0001
Copper (DIS, ICP-AES)	1.90-85.3	μg/L	$F_{\sigma} = 0.050 \times + 1.067$	19	0.0001
Copper (DIS, ICP-MS)	1.90-85.3	μg/L	$F_{\sigma} = 0.050 \times + 1.067$	19	0.0001
Copper (WWR, GF-AAS)	1.90-85.3	μg/L	$F_{\sigma} = 0.050 \times + 1.067$	19	0.0001
Copper (WWR, ICP-AES)	1.90-85.3	μ g/L	$F_{\sigma} = 0.050 \times + 1.067$	19	0.0001
Dissolved solids (DIS, GRAV)	88.0-1309	mg/L	$F_{\sigma} = 0.017 \times + 7.610$	13	0.0001
Fluoride (DIS, IC, LL)	0.028-0.14	mg/L	$F_{\sigma} = 0.005 \times + 0.020$	9	0.953
Fluoride (DIS, ISE)	0.23-1.23	mg/L	$F_{\sigma} = 0.061 \times + 0.012$	12	0.0001
Iron (DIS, ICP-AES)	4.30–1175	μg/L	$F_{\sigma} = 0.045 \times + 4.886$	17	0.0001
Iron (WWR, F-AAS)	4.30–1175	μg/L	$F_{\sigma} = 0.045 \times + 4.886$	17	0.0001
Iron (WWR, ICP-AES)	4.30–1175	μg/L	$F_{\sigma} = 0.045 \times + 4.886$	17	0.0001
Lead (DIS, GF-AAS)	1.00-103	μg/L	$F_{\sigma} = 0.066 \times + 0.822$	19	0.0001

Table 1. Ordinary least-squares equations for determining the most probable deviation—Continued

Constituent and method of analysis	Concentration range	Unit	Equation to determine F_{σ}	Number of samples	p-value
	Inorganic constituents—Co	ntinued			
Lead (DIS, ICP-AES)	1.00-103	μ g /L	$F_{\sigma} = 0.066 \times + 0.822$	19	0.0001
Lead (DIS, ICP-MS)	1.00-103	μ g/L	$F_{\sigma} = 0.066 \times + 0.822$	19	0.0001
Lead (WWR, GF-AAS)	1.00-103	μg/L	$F_{\sigma} = 0.066 \times + 0.822$	19	0.0001
Lead (WWR, ICP-AES)	1.00-103	μg/L	$F_{\sigma} = 0.066 \times + 0.822$	19	0.0001
Lithium (DIS, ICP-AES)	8.70–132	μg/L	$F_{\sigma} = 0.081 \times + 0.364$	19	0.0001
Lithium (WWR, F-AAS)	8.70-132	μg/L	$F_{\sigma} = 0.081 \times + 0.364$	19	0.0001
Magnesium (DIS, ICP-AES)	0.78-58.4	mg/L	$F_{\sigma} = 0.044 \times -0.003$	33	0.0001
Manganese (DIS, ICP-AES)	2.40-455	μg/L	$F_{\sigma} = 0.047 \times + 0.990$	19	0.0001
Manganese (DIS, ICP-MS)	2.40-455	μg/L	$F_{\sigma} = 0.047 \times + 0.990$	19	0.0001
Manganese (WWR, F-AAS)	2.40-455	μg/L	$F_{\sigma} = 0.047 \times + 0.990$	19	0.0001
Manganese (WWR, ICP-AES)	2.40-455	μg/L	$F_{\sigma} = 0.047 \times + 0.990$	19	0.0001
Mercury (DIS, CV-AAS)	0.34-5.04	μg/L	$F_{\sigma} = 0.110 \times + 0.075$	16	0.0001
Mercury (WWR, CV-AAS)	0.34-5.04	μg/L	$F_{\sigma} = 0.110 \times + 0.075$	16	0.0001
Molybdenum (DIS, GF-AAS)	1.25–112	μg/L	$F_{\sigma} = 0.081 \times + 0.735$	18	0.0001
Molybdenum (DIS, ICP-AES)	1.25–112	μg/L	$F_{\sigma} = 0.081 \times + 0.735$	18	0.0001
Molybdenum (DIS, ICP-MS)	1.25–112	μg/L	$F_{\sigma} = 0.081 \times + 0.735$	18	0.0001
Molybdenum (WWR, GF-AAS)	1.25–112	μg/L	$F_{\sigma} = 0.081 \times + 0.735$	18	0.0001
Nickel (DIS, GF-AAS)	1.70-71.0	μg/L	$F_{\sigma} = 0.057 \times + 1.14$	19	0.0001
Nickel (DIS, ICP-AES)	1.70-71.0	μg/L	$F_{\sigma} = 0.057 \times + 1.14$	19	0.0001
Nickel (DIS, ICP-MS)	1.70-71.0	μ g /L	$F_{\sigma} = 0.057 \times + 1.14$	` 19	0.0001
Nickel (WWR, GF-AAS)	1.70-71.0	μg/L	$F_{\sigma} = 0.057 \times + 1.14$	19	0.0001
Nickel (WWR, ICP-AES)	1.70-71.0	μ g/L	$F_{\sigma} = 0.057 \times + 1.14$	19	0.0001
Potassium (DIS, F-AAS)	0.45-13.9	mg/L	$F_{\sigma} = 0.067 \times + 0.022$	33	0.0001
Potassium (DIS, F-AAS, LL)	0.057-0.55	mg/L	$F_{\sigma} = 0.064 \times + 0.017$	12	0.0024
Selenium (DIS, GF-AAS)	2.10-21.4	μg/L	$F_{\sigma} = 0.160 \times + 0.191$	17	0.0001
Selenium (DIS, HG-AAS)	2.10-21.4	μ g /L	$F_{\sigma} = 0.160 \times + 0.191$	17	0.0001
Selenium (WWR, GF-AAS)	2.10-21.4	μg/L	$F_{\sigma} = 0.160 \times + 0.191$	17	0.0001
Selenium (WWR, GF-AAS, USEPA)	2.10-21.4	μg/L	$F_{\sigma} = 0.160 \times + 0.191$	17	0.0001
Selenium (WWR, HG-AAS)	2.10-21.4	μg/L	$F_{\sigma} = 0.160 \times + 0.191$	17	0.0001
Silica (DIS, COL)	2.46-24.0	mg/L	$F_{\sigma} = 0.061 \times + 0.007$	32	0.0001
Silica (DIS, ICP-AES)	2.46-24.0	mg/L	$F_{\sigma} = 0.061 \times + 0.007$	32	0.0001
Silver (DIS, GF-AAS)	0.90-19.8	μg/L	$F_{\sigma} = 0.049 \times + 0.568$	16	0.0043
Silver (DIS, GF-AAS, LL)	0.90-19.8	μg/L	$F_{\sigma} = 0.049 \times + 0.568$	16	0.0043
Silver (DIS, ICP-AES)	0.90-19.8	μg/L	$F_{\sigma} = 0.049 \times + 0.568$	16	0.0043
Silver (DIS, ICP-MS)	0.90-19.8	μg/L	$F_{\sigma} = 0.049 \times + 0.568$	16	0.0043
Silver (WWR, GF-AAS)	0.90-19.8	μg/L	$F_{\sigma} = 0.049 \times + 0.568$	16	0.0043
Sodium (DIS, F-AAS)	7.19–166	mg/L	$F_{\sigma} = 0.037 \times + 0.292$	33	0.0001

Table 1. Ordinary least-squares equations for determining the most probable deviation—Continued

Constituent and method of analysis	Concentration range	Unit	Equation to determine F_{σ}	Number of samples	p-value
	ic constituents—Co	ontinued			
Sodium (DIS, F-AAS, LL)	0.117-4.40	mg/L	$F_{\sigma} = 0.047 \times + 0.023$	12	0.0001
Sodium (DIS, ICP-AES)	7.19–166	mg/L	$F_{\sigma} = 0.037 \times + 0.292$	33	0.0001
Specific conductance (WWR, ELEC, LL)	7.000-44.1	μS/cm	$F_{\sigma} = 0.049 \times + 0.460$	13	0.0127
Strontium (DIS, ICP-AES)	31.9-1669	μg/L	$F_{\sigma} = 0.054 \times -0.870$	33	0.0001
Strontium (WWR, ICP-AES)	31.9-1669	μg/L	$F_{\sigma} = 0.054 \times -0.870$	33	0.0001
Sulfate (DIS, IC)	6.06-621	mg/L	$F_{\sigma} = 0.036 \times + 0.631$	14	0.0001
Vanadium (DIS, COL)	1.00-52.8	μ g/L	$F_{\sigma} = 0.047 \times + 1.343$	29	0.0001
Vanadium (DIS, ICP-AES)	1.00-52.8	μg/L	$F_{\sigma} = 0.047 \times + 1.343$	29	0.0001
Zinc (DIS, ICP-AES)	5.80-381	μg/L	$F_{\sigma} = 0.046 \times + 2.448$	19	0.0001
Zinc (DIS, ICP-MS)	5.80-381	μg/L	$F_{\sigma} = 0.046 \times + 2.448$	19	0.0001
Zinc (WWR, F-AAS)	5.80-381	μg/L	$F_{\sigma} = 0.046 \times + 2.448$	19	0.0001
Zinc (WWR, ICP-AES)	5.80-381	μg/L	$F_{\sigma} = 0.046 \times + 2.448$	19	0.0001
7	Nutrient constituen	ts	·		
Ammonia as nitrogen (DIS)	0.024-1.33	mg/L	$F_{\sigma} = 0.060x + 0.012$	25	0.0004
Ammonia as nitrogen (DIS, COL)	0.024-1.33	mg/L	$F_{\sigma} = 0.060x + 0.012$	25	0.0004
Ammonia as nitrogen (DIS, COL, LL)	0.024-1.33	mg/L	$F_{\sigma} = 0.060x + 0.012$	25	0.0004
Ammonia as nitrogen (DIS, USEPA)	0.024-1.33	mg/L	$F_{\sigma} = 0.060x + 0.012$	25	0.0004
Ammonia plus organic nitrogen as nitrogen (DIS)	0.118-2.37	mg/L	$F_{\sigma} = 0.052x + 0.113$	27	0.0069
Ammonia plus organic nitrogen as nitrogen (DIS, ASF)	0.118-2.37	mg/L	$F_{\sigma} = 0.052x + 0.113$	27	0.0069
Ammonia plus organic nitrogen as nitrogen (DIS, USEPA)	0.118-2.37	mg/L	$F_{\sigma} = 0.052x + 0.113$	27	0.0069
Ammonia plus organic nitrogen as nitrogen (WWR)	0.118-2.37	mg/L	$F_{\sigma} = 0.052x + 0.113$	27	0.0069
Ammonia plus organic nitrogen as nitrogen (WWR, ASF)	0.118-2.37	mg/L	$F_{\sigma} = 0.052x + 0.113$	27	0.0069
Ammonia plus organic nitrogen as nitrogen (WWR, USEPA)	0.118-2.37	mg/L	$F_{\sigma} = 0.052x + 0.113$	27	0.0069
Nitrate plus nitrite as nitrogen (DIS)	0.073-1.93	mg/L	$F_{\sigma} = 0.042x + 0.015$	25	0.0003
Nitrate plus nitrite as nitrogen (DIS, COL)	0.073-1.93	mg/L	$F_{\sigma} = 0.042x + 0.015$	25	0.0003
Nitrate plus nitrite as nitrogen (DIS, COL, LL)	0.073-1.93	mg/L	$F_{\sigma} = 0.042x + 0.015$	25	0.0003
Orthophosphate as phosphorus (DIS)	0.052-1.59	mg/L	$F_{\sigma} = 0.040x + 0.006$	24	0.0004
Orthophosphate as phosphorus (DIS, COL)	0.052-1.59	mg/L	$F_{\sigma} = 0.040x + 0.006$	24	0.0004
Orthophosphate as phosphorus (DIS, COL, LL)	0.052-1.59	mg/L	$F_{\sigma} = 0.040x + 0.006$	24	0.0004
Phosphorus (DIS)	0.060-1.63	mg/L	$F_{\sigma} = 0.035x + 0.009$	27	0.0001
Phosphorus (DIS, ASF)	0.060-1.63	mg/L	$F_{\sigma} = 0.035x + 0.009$	27	0.0001
Phosphorus (DIS, COL, LL)	0.060-1.63	mg/L	$F_{\sigma} = 0.035x + 0.009$	27	0.0001
Phosphorus (DIS, USEPA)	0.060-1.63	mg/L	$F_{\sigma} = 0.035x + 0.009$	27	0.0001
Phosphorus (WWR)	0.060-1.63	mg/L	$F_{\sigma} = 0.035x + 0.009$	27	0.0001
Phosphorus (WWR, ASF)	0.060-1.63	mg/L	$F_{\sigma} = 0.035x + 0.009$	27	0.0001
Phosphorus (WWR, COL, LL)	0.060-1.63	mg/L	$F_{\sigma} = 0.035x + 0.009$	27	0.0001
Phosphorus (WWR, USEPA)	0.060-1.63	mg/L	$F_{\sigma} = 0.035x + 0.009$	27	0.0001

The rounding differences between the SRWS summary results and the NWIS computer-storage criteria make the assessments at lower sample concentrations less sensitive. As a means to make the assessments more sensitive at lower concentration ranges, a correction factor has been applied to allow at least one reportable value to be within one standard deviation of the MPV. The correction is accomplished by setting a minimum F_{σ} at three-fourths of the minimum reporting limit. For example, a sample may be assigned an MPV for manganese of 13.7 µg/L; however, the laboratories can only report environmental data for manganese (WWR, F-AAS) to the nearest 10 µg/L in the NWIS data base. For the reference sample in question, a reported value of 10 or 20 would generally be expected. The regression equation for manganese ($F_{\sigma} = 0.047 \text{MPV} + 0.990$) provides an estimate that reported F_{σ} values within $\pm 1.63 \,\mu g/L$ of a sample with an MPV of 13.7 µg/L will be considered within one standard deviation. The laboratories' closest reportable values, 10 and 20 µg/L, would be -2.27 and +3.87 standard deviations, respectively, from the MPV. When a minimum F_{\odot} value of 7.5 µg/L is assigned (three-fourths of the reporting limit), then values reported at 10 and 20 µg/L would be -0.49 and +0.84 standard deviations from the MPV, respectively.

BSP mixes that had MPV concentrations less than the laboratory reporting limit (LRL) were removed from the BSP data base. The BSP mixes are not designed to quality ensure the laboratories for false positives or for how well the laboratory reports samples less than the LRL.

For each constituent, the NSD values were plotted against the date that the samples were logged into the laboratory to prepare control charts. The results for each constituent are presented as control charts, as shown in part A of figures 2 through 96 for the NWQL and figures 97 through 159 for the QWSU in the "Supplemental Data" section of this report.

Control charts for inorganic-constituent reference samples are presented in figures 2 through 79 for the NWQL and figures 97 through 152 for the QWSU. Control charts for nutrient constituents are shown in figures 80 through 96 for the NWQL and figures 153 through 159 for the QWSU. The data on control charts have been separated into quartiles on the basis of environmental sample concentrations. All environmental data released during water year 1998 by the NWQL and QWSU were obtained and used to determine the quartiles. The quartiles and their associated concentration ranges are identified in the figure explanation. The MPV's of the reference materials were examined to

determine which quartile group they represented. A different symbol was used to represent data points in each of the quartile ranges. For reference samples with MPV's in quartile 1 (up through 25 percent), the (\bigcirc) symbol has been used; reference samples in quartile 2 (25.1 through 50 percent) are represented by the (Δ) symbol; quartile 3 (50.1 through 75 percent) by the (\bullet) symbol; and quartile 4 (75.1 through 100 percent) by the (\times) symbol.

Points on the control charts that are greater than 6 standard deviations or less than -6 standard deviations have been rounded to 6 and -6, respectively, and are plotted at the top or bottom edge of the figure.

Precision Chart Development and Evaluation

Replicate determinations of reference samples were used to estimate precision. For each sample mixture having at least three determinations for water year 1998, the mean, standard deviation, and relative standard deviation (RSD) were calculated for each constituent. Taylor (1987, p. 20) defines RSD as the coefficient of variation multiplied by 100 (percent). The equation to represent this is:

$$RSD = \frac{\sigma}{X} \times 100 \tag{4}$$

where

RSD = relative standard deviation,

 σ = standard deviation, and

X = mean of replicate values reported by the laboratory.

The RSD provides an estimate of error relative to the mean of replicate values reported by the laboratory for each reference sample.

The RSD data are presented graphically as precision data charts in part B of figures 2 through 96 for the NWQL and figures 97 through 159 for the QWSU in the "Supplemental Data" section of this report. These charts were prepared by plotting the RSD for inorganic, nutrient, and low-level constituents against the mean concentration of the reference samples reported by the individual laboratories. These charts allow a data reviewer to estimate precision at any concentration shown for a constituent. For example, figure 80B shows precision data for dissolved ammonia determinations from the NWQL.

This plot shows a distribution of approximately 19 to 4 percent RSD for concentrations that range from 0.23 to 1.29 mg/L.

Precision is dependent upon the analyte of interest, the concentration range, the number of determinations, the method of determination, and the analyzing laboratory. A precision of 2 to 5 percent RSD is typical for chloride; whereas mercury's precision may vary from 10 to 40 percent RSD. Therefore, a data reviewer needs to be cognizant of the many variables contributing to a determination's precision and only compare for similar determinations.

To allow the precision charts to be used to estimate expected error of analytical results, outliers were rejected from the data set. Outliers are a rare occurrence in the data reported by the laboratories, accounting for less than 0.5 percent of all data. Outliers produce erroneous results in the use of parametric statistics such as RSD. Taylor (1987, p. 33-34) suggested NSD ≥141 as a criterion for rejection of data for a large sample set and NSD ≥161 for smaller data sets or when the standard deviation is not well established. In this report, an outlier was defined as a value greater than or equal to 6 standard deviations from the MPV. There were 48 outliers deleted from the entire data set of 11,056 analyses for the RSD procedure. Table 2 for the NWQL and table 3 for the QWSU present the total number of determinations for each constituent processed during the water year, the number of determinations that lie outside the ±2 standard deviation limits, and the number of determinations that lie outside the ±6 standard deviation limits.

The precision chart data for inorganic, nutrient, and low-level constituents have been separated into groups that are based on environmental-sample data quartiles in the same manner as explained previously in this report for the development of the control charts.

Binomial-Probability-Distribution Technique to Assess Precision

Measures of precision were determined from the control chart data by applying binomial-probability-distribution procedures described by Friedman, Bradford, and Peart (1983) and by Peart and Thomas (1983a). The precision evaluation is based on whether or not an analytical method could produce results within ±2 standard deviations of the MPV. The binomial equation identifies the maximum number of determinations that could exceed the control limit at a 0.01 significance level. A comparison

is then made between the number of analytical determinations that exceed control limits and the results of the binomial-probability-distribution equation for the total number of analytical determinations.

$$P(x) = \sum_{i=x}^{N} \frac{N!}{i!(N-i)!} (0.05)^{i} (0.95)^{N-i}$$
 (5)

where

P(x) = probability of having x or more points greater than two standard deviations,

N = number of successive points, and

i = number of points greater than two standard deviations.

Analytical procedures exhibit imprecision if they have more determinations outside the control limits than the result predicted by the binomial equation. The binomial-probability-distribution procedure to measure precision allows tracking of annual variations in the precision of analytical measurements. The binomial test can be used to evaluate analytical results for short periods that appear to indicate imprecision, but the test loses power as fewer total analytical determinations are used in the evaluation.

Wilcoxon Signed-Rank Procedure to Assess Bias

The Wilcoxon signed-rank test (Helsel and Hirsch, 1992) was used to determine whether the median difference between the laboratory determinations and the MPV of the reference samples equaled zero. An assessment of bias was made for each analyte and mix combination that had three or more observations. The null hypothesis for the bias assessment was defined as that the median difference between the laboratory determinations and the MPV equaled zero. A bias condition was assigned if the p-value of the test was less than 0.05 and the median difference was greater than the nearest reporting unit used for the analyte concentration in the mix. When the analyte concentration fell below the minimum reporting limit, bias was not stated. Whether bias is negative or positive was determined on the basis of the sign of the median difference. Data users are urged to consider the concentration level and review the magnitude of bias, which is based on the median differences, to evaluate whether a bias is of any practical concern for their particular situation.

Table 2. Total number of analyses from quality-assurance samples during water year 1998 with the number greater than two and six standard deviations from the most probable value and results of statistical testing for analytical precision in constituent data for the National Water Quality Laboratory

[>2SD, number of analyses greater than 2 or less than -2 standard deviations from the most probable value; >6SD, number of analyses greater than 6 or less than -6 standard deviations from the most probable value; WWR, whole-water recoverable; TITR, electrometric titration; --, acceptable results; DIS, dissolved; ICP-AES, inductively coupled plasma-atomic emission spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; DCP-AES, direct current plasma-atomic emission spectrometry; HG-AAS, hydride generation-atomic absorption spectrophotometry; GF-AAS, graphite furnace-atomic absorption spectrophotometry; USEPA, U.S. Environmental Protection Agency; IC, ion chromatography; LL, low level; GRAV, gravimetric; ISE, ion-selective electrode; F-AAS, flame-atomic absorption spectrophotometry; CV-AAS, cold vapor-atomic absorption spectrophotometry; LOP, statistically significant lack of precision; ELEC, electrometric; COL, colorimetric; ASF, micro-Kjeldahl digestion, automated segmented flow, colorimetric]

Constituent and	Number	Number of analyses			Results
method of analysis	Total	>2SD	>6SD	p-value	from 1998
	Inorganic constituents				
Alkalinity (WWR,TITR)	241	1	0	1.00000	
Aluminum (DIS, ICP-AES)	31	0	0	0.79609	
Aluminum (DIS, ICP-MS)	96	0	0	0.99273	
Aluminum (WWR, DCP-AES)	37	5	1	0.03593	
Antimony (DIS, HG-AAS)	12	1	0	0.45964	
Antimony (DIS, ICP-MS)	96	0	0	0.99273	
Arsenic (DIS, HG-AAS)	72	1	0	0.97511	
Arsenic (WWR, GF-AAS, USEPA)	8	0	0	0.33658	
Arsenic (WWR, HG-AAS)	41	0	0	0.87791	
Barium (DIS, ICP-AES)	97	0	0	0.99309	
Barium (DIS, ICP-MS)	96	0	0	0.99273	
Beryllium (DIS, ICP-AES)	73	0	0	0.97635	
Beryllium (DIS, ICP-MS)	96	0	0	0.99273	
Boron (DIS, ICP-AES)	161	0	0	0.99974	
Boron (WWR, DCP-AES)	12	1	0	0.45964	
Cadmium (DIS, GF-AAS)	48	1	0	0.91474	
Cadmium (DIS, ICP-AES)	62	2	0	0.82275	
Cadmium (DIS, ICP-MS)	96	0	0	0.99273	
Cadmium (WWR, GF-AAS)	73	2	1	0.88549	
Calcium (DIS, ICP-AES)	241	0	0	1.00000	
Chloride (DIS, IC)	241	4	0	0.99816	
Chloride (DIS, IC, LL)	12	1	1	0.45964	
Chromium (DIS, GF-AAS)	48	1	0	0.91474	
Chromium (DIS, ICP-AES)	59	0	0	0.95151	
Chromium (DIS, ICP-MS)	96	0	0	0.99273	
Chromium (WWR, GF-AAS)	49	0	0	0.91901	
Cobalt (DIS, GF-AAS)	8	0	0	0.33658	~-
Cobalt (DIS, ICP-AES)	29	3	0	0.17512	
Cobalt (DIS, ICP-MS)	64	0	0	0.96248	
Cobalt (WWR, GF-AAS)	25	0	0	0.72261	
Copper (DIS, GF-AAS)	37	0	0	0.85011	
Copper (DIS, ICP-AES)	49	0	0	0.91901	
Copper (DIS, ICP-MS)	64	0	0	0.96248	
Copper (WWR, GF-AAS)	54	2	1	0.75921	
Dissolved Solids (DIS, GRAV)	239	4	0	0.99801	
Fluoride (DIS, IC, LL)	13	1	1	0.48666	
Fluoride (DIS, ISE)	236	3	0	0.99950	
Iron (DIS, ICP-AES)	191	0	0	0.99994	
· · · · · · · · · · · · · · · · · · ·					

Table 2. Total number of analyses from quality-assurance samples during water year 1998 with the number greater than two and six standard deviations from the most probable value and results of statistical testing for analytical precision in constituent data for the National Water Quality Laboratory—Continued

[>2SD, number of analyses greater than 2 or less than -2 standard deviations from the most probable value; >6SD, number of analyses greater than 6 or less than -6 standard deviations from the most probable value; WWR, whole-water recoverable; TITR, electrometric titration; --, acceptable results; DIS, dissolved; ICP-AES, inductively coupled plasma-atomic emission spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; DCP-AES, direct current plasma-atomic emission spectrometry; HG-AAS, hydride generation-atomic absorption spectrophotometry; GF-AAS, graphite furnace-atomic absorption spectrophotometry; USEPA, U.S. Environmental Protection Agency; IC, ion chromatography; LL, low level; GRAV, gravimetric; ISE, ion-selective electrode; F-AAS, flame-atomic absorption spectrophotometry; CV-AAS, cold vapor-atomic absorption spectrophotometry; LOP, statistically significant lack of precision; ELEC, electrometric; COL, colorimetric; ASF, micro-Kjeldahl digestion, automated segmented flow, colorimetric]

Constituent and	Numi	p-value	Results		
method of analysis	Total	>2SD	>6SD	p-value	from 1998
_	anic constituents—Co	ntinued			
Iron (WWR, F-AAS)	73	3	0	0.71332	
Lead (DIS, GF-AAS)	48	1	1	0.91474	
Lead (DIS, ICP-AES)	10	3	0	0.01150	
Lead (DIS, ICP-MS)	96	0	0	0.99273	
Lead (WWR, GF-AAS)	73	2	0	0.88549	
Lithium (DIS, ICP-AES)	97	0	0	0.99309	
Lithium (WWR, F-AAS)	13	0	0	0.48666	
Magnesium (DIS, ICP-AES)	241	2	0	0.99994	
Manganese (DIS, ICP-AES)	191	0	0	0.99994	
Manganese (DIS, ICP-MS)	96	0	0	0.99273	
Manganese (WWR, F-AAS)	43	0	0	0.88982	
Mercury (DIS, CV-AAS)	48	3	0	0.43295	
Mercury (WWR, CV-AAS)	48	6	3	0.03171	
Molybdenum (DIS, GF-AAS)	12	0	0	0.45964	
Molybdenum (DIS, ICP-AES)	16	2	0	0.18924	
Molybdenum (DIS, ICP-MS)	96	0	0	0.99273	
Molybdenum (WWR, GF-AAS)	24	1	1	0.70801	
Nickel (DIS, GF-AAS)	24	1	0	0.70801	
Nickel (DIS, ICP-AES)	33	1	0	0.81597	
Nickel (DIS, ICP-MS)	96	0	0	0.99273	
Nickel (WWR, GF-AAS)	49	2	1	0.71012	
Potassium (DIS, F-AAS)	241	6	2	0.98243	
Potassium (DIS, F-AA, LL)	13	0	0	0.48666	
Selenium (DIS, HG-AAS)	108	2	0	0.97375	
Selenium (WWR, GF-AAS, USEPA)	8	0	0	0.33658	
Selenium (WWR, HG-AAS)	41	0	0	0.87791	
Silica (DIS, COL)	120	4	2	0.85559	
Silica (DIS, ICP-AES)	240	0	0	1.00000	
Silver (DIS, GF-AAS)	16	0	0	0.55987	
Silver (DIS, ICP-AES)	30	2	0	0.44646	
Silver (DIS, ICP-MS)	64	11	0	0.00031	LOP
Silver (WWR, GF-AAS)	33	4	1	0.08081	
Sodium (DIS, ICP-AES)	241	0	0	1.00000	
Specific Conductance (WWR, ELEC, LL)	13	1	0	0.48666	
Strontium (DIS, ICP-AES)	97	0	0	0.99309	
Sulfate (DIS, IC)	241	1	0	1.00000	
Vanadium (DIS, ICP-AES)	52	0	0	0.93056	
Zinc (DIS, ICP-AES)	53	4	0	0.27287	
Zinc (DIS, ICP-MS)	96	0	0	0.99273	
Zinc (WWR, F-AAS)	73	1	0	0.97635	

Table 2. Total number of analyses from quality-assurance samples during water year 1998 with the number greater than two and six standard deviations from the most probable value and results of statistical testing for analytical precision in constituent data for the National Water Quality Laboratory—Continued

[>2SD, number of analyses greater than 2 or less than -2 standard deviations from the most probable value; >6SD, number of analyses greater than 6 or less than -6 standard deviations from the most probable value; WWR, whole-water recoverable; TITR, electrometric titration; --, acceptable results; DIS, dissolved; ICP-AES, inductively coupled plasma-atomic emission spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; DCP-AES, direct current plasma-atomic emission spectrometry; HG-AAS, hydride generation-atomic absorption spectrophotometry; GF-AAS, graphite furnace-atomic absorption spectrophotometry; USEPA, U.S. Environmental Protection Agency; IC, ion chromatography; LL, low level; GRAV, gravimetric; ISE, ion-selective electrode; F-AAS, flame-atomic absorption spectrophotometry; CV-AAS, cold vapor-atomic absorption spectrophotometry; LOP, statistically significant lack of precision; ELEC, electrometric; COL, colorimetric; ASF, micro-Kjeldahl digestion, automated segmented flow, colorimetric]

Constituent and	Num	ber of analyses			Results
method of analysis	Total	>2SD	>6SD	p-value	from 1998
Nuti	rient constituent	s			
Ammonia as nitrogen (DIS, COL)	333	30	2	0.00153	LOP
Ammonia as nitrogen (DIS, COL, LL)	66	1	1	0.96613	
Ammonia as nitrogen (DIS, USEPA)	17	1	0	0.58188	
Ammonia plus organic nitrogen as nitrogen (DIS, ASF)	334	5	1	0.99982	
Ammonia plus organic nitrogen as nitrogen (DIS, USEPA)	34	0	0	0.82518	
Ammonia plus organic nitrogen as nitrogen (WWR, ASF)	226	1	0	0.99999	
Ammonia plus organic nitrogen as nitrogen (WWR, USEPA)	34	1	0	0.82518	
Nitrate plus nitrite as nitrogen (DIS, COL)	334	21	3	0.16875	
Nitrate plus nitrite as nitrogen (DIS, COL, LL)	66	2	1	0.84850	
Orthophosphate as phosphorus (DIS, COL)	332	52	8	0.00000	LOP
Orthophosphate as phosphorus (DIS, COL, LL)	66	3	3	0.64727	
Phosphorus (DIS, ASF)	334	21	2	0.16875	
Phosphorus (DIS, COL, LL)	33	4	2	0.08081	
Phosphorus (DIS, USEPA)	34	1	0	0.82518	
Phosphorus (WWR, ASF)	226	3	0	0.99923	
Phosphorus (WWR, COL, LL)	65	5	3	0.22479	
Phosphorus (WWR, USEPA)	34	0	0	0.82518	

Table 3. Total number of analyses from quality-assurance samples during water year 1998 with the number greater than two and six standard deviations from the most probable value and results of statistical testing for analytical precision in constituent data for the Quality of Water Service Unit laboratory

[>2SD, number of analyses greater than 2 or less than -2 standard deviations from the most probable value; >6SD, number of analyses greater than 6 or less than -6 standard deviations from the most probable value; WWR, whole-water recoverable; TITR, electrometric titration; --, acceptable results; DIS, dissolved; ICP-AES/T, inductively coupled plasma-atomic emission spectrometry, trace; GF-AAS, graphite furnace-atomic absorption spectrophotometry; USEPA, U.S. Environmental Protection Agency; ICP-AES, inductively coupled plasma-atomic emission spectrometry; IC, ion chromatography; GRAV, gravimetric; ISE, ion-selective electrode; CV-AAS, cold vapor-atomic absorption spectrophotometry; F-AAS, flame-atomic absorption spectrophotometry]

Nun	nber of analys	n volue	Results	
Total	>2SD	>6SD	- p-value	from 1998
organic constituents			-	
65	1	1	0.96435	
24	0	0	0.70801	
11	1	0	0.43120	
24	0	0	0.70801	
12	0	0	0.45964	
8	0	0	0.33658	
10	0	0	0.40126	
12	0	0	0.45964	
	Total organic constituents 65 24 11 24 12 8 10	Total >2SD	65 1 1 1 24 0 0 11 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Total >2SD >6SD

Table 3. Total number of analyses from quality-assurance samples during water year 1998 with the number greater than two and six standard deviations from the most probable value and results of statistical testing for analytical precision in constituent data for the Quality of Water Service Unit laboratory—Continued

[>2SD, number of analyses greater than 2 or less than -2 standard deviations from the most probable value; >6SD, number of analyses greater than 6 or less than -6 standard deviations from the most probable value; WWR, whole-water recoverable; TITR, electrometric titration; --, acceptable results; DIS, dissolved; ICP-AES/T, inductively coupled plasma-atomic emission spectrometry, trace; GF-AAS, graphite furnace-atomic absorption spectrophotometry; USEPA, U.S. Environmental Protection Agency; ICP-AES, inductively coupled plasma-atomic emission spectrometry; IC, ion chromatography; GRAV, gravimetric; ISE, ion-selective electrode; CV-AAS, cold vapor-atomic absorption spectrophotometry; F-AAS, flame-atomic absorption spectrophotometry]

method of analysis	Total	>2SD	>6SD	p-value	
			703D	- p-value	from 1998
Inorganic consti	ituents—Continue	ed			
Beryllium (DIS, ICP-AES/T)	10	0	0	0.40126	
Beryllium (WWR, ICP-AES/T)	12	0	0	0.45964	
Boron (DIS, ICP-AES/T)	10	0	0	0.40126	
Cadmium (DIS, GF-AAS)	11	0	0	0.43120	
Cadmium (DIS, ICP-AES/T)	10	0	0	0.40126	
Cadmium (WWR, GF-AAS)	11	0	0	0.43120	
Cadmium (WWR, ICP-AES/T)	11	1	0	0.43120	
Calcium (DIS, ICP-AES)	90	2	0	0.94327	
Calcium (DIS, ICP-AES/T)	34	0	0	0.82518	
Chloride (DIS, IC)	89	0	0	0.98959	
Chromium (DIS, ICP-AES/T)	10	0	0	0.40126	
Chromium (WWR, GF-AAS)	11	1	0	0.43120	
Chromium (WWR, ICP-AES/T)	10	1	0	0.40126	
Cobalt (DIS, ICP-AES/T)	8	0	0	0.33658	
Copper (DIS, GF-AAS)	11	0	0	0.43120	
Copper (DIS, ICP-AES/T)	8	0	0	0.33658	
Copper (WWR, GF-AAS)	9	0	0	0.36975	
Copper (WWR, ICP-AES/T)	12	0	0	0.45964	
Dissolved Solids (DIS, GRAV)	65	2	0	0.84240	
Fluoride (DIS, ISE)	76	0	0	0.97972	
Iron (DIS, ICP-AES/T)	44	1	1	0.89533	
Iron (WWR, ICP-AES/T)	45	2	0	0.66504	
Lead (DIS, GF-AAS)	10	0	0	0.40126	
Lead (DIS, ICP-AES/T)	10	0	0	0.40126	
Lead (WWR, GF-AAS)	11	2	1	0.10189	
Lead (WWR, ICP-AES/T)	11	0	0	0.43120	
Magnesium (DIS, ICP-AES)	90	0	0	0.99011	
Magnesium (DIS, ICP-AES/T)	34	1	0	0.82518	
Manganese (DIS, ICP-AES/T)	44	0	0	0.89533	
Manganese (WWR, ICP-AES/T)	35	2	0	0.52797	
Mercury (WWR, CV-AAS)	21	0	0	0.65944	
Molybdenum (DIS, ICP-AES/T)	10	0	0	0.40126	
Nickel (DIS, ICP-AES/T)	10	0	0	0.40126	
Nickel (WWR, GF-AAS)	11	0	0	0.43120	
Nickel (WWR, ICP-AES/T)	12	0	0	0.45964	
Potassium (DIS, F-AAS)	90	0	0	0.99011	
Selenium (DIS, GF-AAS)	11	0	0	0.43120	
Selenium (WWR, GF-AAS)	8	0	0	0.43120	
Silica (DIS, ICP-AES)	66	0	0		
				0.96613	
Silica (DIS, ICP-AES/T)	34	0	0	0.82518	

Table 3. Total number of analyses from quality-assurance samples during water year 1998 with the number greater than two and six standard deviations from the most probable value and results of statistical testing for analytical precision in constituent data for the Quality of Water Service Unit laboratory—Continued

[>2SD, number of analyses greater than 2 or less than -2 standard deviations from the most probable value; >6SD, number of analyses greater than 6 or less than -6 standard deviations from the most probable value; WWR, whole-water recoverable; TITR, electrometric titration; --, acceptable results; DIS, dissolved; ICP-AES/T, inductively coupled plasma-atomic emission spectrometry, trace; GF-AAS, graphite furnace-atomic absorption spectrophotometry; USEPA, U.S. Environmental Protection Agency; ICP-AES, inductively coupled plasma-atomic emission spectrometry; IC, ion chromatography; GRAV, gravimetric; ISE, ion-selective electrode; CV-AAS, cold vapor-atomic absorption spectrophotometry; F-AAS, flame-atomic absorption spectrophotometry]

Constituent and	Nun	nber of analys	ses	n velue	Results
method of analysis	Total	>2SD	>6SD	- p-value	from 1998
Inorganic constit	uents—Continu	ed		·	
Silver (DIS, ICP-AES/T)	8	0	0	0.33658	
Sodium (DIS, F-AAS)	90	0	0	0.99011	
Strontium (DIS, ICP-AES/T)	20	0	0	0.64151	
Strontium (WWR, ICP-AES/T)	12	1	0	0.45964	
Sulfate (DIS, IC)	89	0	0	0.98959	
Vanadium (DIS, ICP-AES/T)	10	0	0	0.40126	
Zinc (DIS, ICP-AES/T)	10	0	0	0.40126	
Zinc (WWR, ICP-AES/T)	22	0	0	0.67647	
Nutrient c	onstituents				
Ammonia as nitrogen (DIS)	39	2	1	0.58705	
Ammonia plus organic nitrogen as nitrogen (DIS)	41	0	0	0.87791	
Ammonia plus organic nitrogen as nitrogen (WWR)	64	0	0	0.96248	
Nitrate plus nitrite as nitrogen (DIS)	39	1	0	0.86472	
Orthophosphate as phosphorus (DIS)	39	1	0	0.86472	
Phosphorus as phosphorus (DIS)	41	1	0	0.87791	
Phosphorus as phosphorus (WWR)	64	3	1	0.62653	

There are two important factors to consider when analyzing analytical results for bias: the first is the number of observations in the subsample, and the second is the magnitude of the bias. If there are few observations in the subsample, the median difference has to be large to attain a p-value that indicates a biased condition. On the other hand, if there are many observations, a small median difference may result in a p-value that indicates bias.

The second factor used for the bias assessment is the bias magnitude. The magnitude of the bias is defined as the difference in concentration between the reported values from the laboratory and the MPV. The magnitude must be greater than one reporting unit for that MPV for the results to be considered biased. For example, 32 aluminum (DIS, ICP-MS) determinations of a sample having an MPV of 11.1 μ g/L resulted in a median difference of 0.3 μ g/L from the MPV. It is important to consider that at a concentration of 11.1 μ g/L, a laboratory would typically report data only to the nearest 1 μ g/L. The signed-rank test provided a p-value of 0.00247, which is considerably

less than the 0.05 value. If the reporting unit was not considered, this result would have been considered biased negative, even though the laboratory was reporting the sample to the best of its reporting ability. Because the median difference of 0.3 μ g/L is less than the reporting level of 1 μ g/L, the magnitude of the bias is less than the implied accuracy of the analysis; therefore, analytical bias that is based strictly on the p-value has no practical meaning.

QUALITY-ASSURANCE DATA FOR INORGANIC-CONSTITUENT SAMPLES

Precision

The results of the binomial-probability-distribution test for analytical precision for each inorganic constituent are presented in table 2 for the NWQL and in table 3 for the QWSU. These tables show either acceptable results (indicated by --) or a

statistically significant lack of precision (LOP) at a significance level of 0.01 for each constituent. The NWQL data from water year 1998 for silver (DIS, ICP-MS) indicated lack of precision. There were no inorganic methods at the QWSU that indicated imprecision.

Bias

Analytical bias for the inorganic analyses are presented in table 4 for the NWQL and in table 5 for the QWSU. These tables show the results of the Wilcoxon signed-rank test for each reference sample mix by constituent. The following discussion presents an evaluation of those analytes that show strong evidence of bias through part or all of the concentration range of reference samples submitted by the BSP. Strong evidence of bias was considered to be greater than 50 percent of the samples found to have a positive or negative bias. Frequently only one or two of the reference mixes for a constituent indicated analytical bias. In many of these cases, the median bias was only slightly greater than the reporting unit, or the data for other reference samples in the same analytical range did not indicate analytical bias.

At the NWQL, positive analytical bias was indicated throughout the range of reference samples for chromium (DIS, ICP-AES), dissolved solids (DIS, GRAV), lithium (DIS, ICP-AES), and zinc (DIS, ICP-MS). Negative analytical bias throughout the reference sample range was indicated for silver (DIS, ICP-MS). This bias was caused by mix biases in the two samples submitted. Manganese (DIS, ICP-AES) showed a negative bias only on those mixes greater than $25~\mu g/L$.

At the QWSU, positive bias was indicated throughout the range of reference samples for aluminum (WWR, ICP-AES/T). This bias was determined to be an artifact of the digestion process. Positive bias was indicated on the majority of sample mixes submitted for alkalinity (WWR, TITR) and dissolved solids (DIS, GRAV).

The statistical power of the Wilcoxon signedranks tests for analytical bias from QWSU is dependent on sample size. Tests on analytical data from the QWSU are less powerful than the same tests used at the NWQL due to the smaller sample sizes associated with the QWSU data.

QUALITY-ASSURANCE DATA FOR NUTRIENT-CONSTITUENT SAMPLES

Precision

The results of the binomial-probabilitydistribution test for analytical precision for each nutrient constituent are presented in table 2 for the NWQL and table 3 for the QWSU. These tables show either acceptable results (indicated by --) or a statistically significant lack of precision (LOP) at a significance level of 0.01 for each constituent. NWQL data from water year 1998 for ammonia as nitrogen (DIS, COL) and orthophosphate as phosphorus (DIS, COL) indicated lack of precision. The ammonia as nitrogen (DIS, COL) method experienced a period of imprecision from October 1997 to mid-January 1998. Beginning in October 1997, new analytical software was installed, and the baseline correction factor was calculated incorrectly, skewing the analytical results (J. Vasquez, U.S. Geological Survey, National Water Quality Laboratory, written commun., March 1998). All seven nutrient procedures at the QWSU displayed acceptable precision for water year 1998.

Bias

Analytical bias for the nutrient analyses are presented in table 4 for the NWQL and in table 5 for the QWSU. These tables show the results of the Wilcoxon signed-rank test for each reference sample mix by constituent. The following discussion presents an evaluation of those analytes that showed strong evidence of bias through part or all of the range of reference samples submitted by the BSP. Strong evidence of bias was indicated if more than 50 percent of the samples had a positive or negative bias. Frequently, one or two of the reference mixes for a constituent indicated analytical bias. In many of these cases, the median bias was only slightly greater or less than the reporting unit, or data for other reference samples in the same analytical range did not indicate analytical bias.

At the NWQL, two mixes submitted for ammonia as nitrogen (DIS, COL, LL) and nitrate plus nitrite as nitrogen (DIS, COL, LL) showed a negative bias. There were no nutrient procedures at the QWSU that indicated a significant bias.

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorgani	c constituents				
Alkalinity (WWR,TITR) Minimum Reporting	9.08	22	1.29	0.1	0.00000	POS
Limit 1 mg/L	18.2	30	1.0	1	0.00000	
	55.7	16	-0.1	1	0.27444	
	75.2	24	-0.2	1	0.03664	
	76.0	27	2.5	1	0.00000	POS
	88.5	18	0.0	1	0.94080	
	94.2	30	0.4	1	0.00036	
	107.5	34	2.0	1	0.00000	POS
	114.0	26	2.7	1	0.00000	POS
	129.7	14	2.8	1	0.00012	POS
Aluminum (DIS, ICP-AES) Minimum Reporting	7.63	3	3.95	0.1	0.25000	
Limit 10 μg/L	26.30	4	1.68	0.1	0.12500	
	26.45	12	0.19	0.1	0.73340	
	28.48	8	-1.95	0.1	0.03906	NEG
	33.48	4	0.91	0.1	0.37500	
Aluminum (DIS, ICP-MS) Minimum Reporting	7.6	32	0.4	1	0.00000	
Limit 1 μg/L	11.1	32	0.3	1	0.00247	
	44.9	32	-2.5	1	0.00000	NEG
Aluminum (WWR, DCP-AES) Minimum	26	4	8	10	0.62500	
Reporting Limit 10 μg/L	26	4	5	10	0.87500	
	28	8	-1	10	0.72656	
	33	4	12	10	0.37500	
	45	8	-2	10	0.71094	
	45	8	8	10	0.01563	
Antimony (DIS, HG-AAS) Minimum Reporting	12.4	4	0.5	1	0.25000	
Limit 1 μg/L	14.7	4	0.2	1	0.87500	
	16.1	4	0.0	1	0.87500	
Antimony (DIS, ICP-MS) Minimum Reporting	3.9	32	0.4	1	0.00000	
Limit 1 µg/L	8.3	32	0.4	1	0.00000	
	12.7	32	0.9	1	0.00000	
Arsenic (DIS, HG-AAS) Minimum Reporting	1.8	8	0.2	1	0.00781	
Limit 1 µg/L	3.1	12	0.3	1	0.05127	
	7.6	21	0.4	1	0.69287	
	7.9	4	1.1	1	0.12500	
	11.4	8	0.6	1	0.35938	
	12.5	14	0.0	1	0.11133	
	13.9	4	-0.9	1	0.62500	
Arsenic (WWR, GF-AAS, USEPA) Minimum	7.6	4	-0.5	1	0.12500	
Reporting Limit 1 μg/L	11.4	4	0.1	1	1.00000	

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic const	ituents—Continued				
Arsenic (WWR, HG-AAS) Minimum Reporting	1.8	8	0.2	1	0.00781	
Limit 1 μg/L	7.6	8	0.4	1	0.32031	
	7.7	8	0.3	1	0.53125	
	11.4	8	0.6	1	0.01563	
	12.5	8	1.0	1	0.13281	
Barium (DIS, ICP-AES) Minimum Reporting	32.5	8	-0.9	1	0.10938	
Limit 1 μg/L	40.6	26	-0.3	1	0.81470	
	41.0	8	0.0	1	0.84375	
	59.5	22	0.3	1	0.39316	
	59.8	24	0.1	1	0.59798	
	61.4	8	1.6	1	0.02344	POS
Barium (DIS, ICP-MS) Minimum Reporting	16.3	32	0.1	1	0.63431	
Limit 1 µg/L	41.0	32	0.8	1	0.00004	
	59.5	32	1.2	1	0.00000	POS
Beryllium (DIS, ICP-AES) Minimum Reporting	6.43	24	0.02	0.1	0.73957	
Limit 1 μg/L	8.77	22	0.03	0.1	0.06501	
	9.57	26	0.0	0.1	0.76710	
Beryllium (DIS, ICP-MS) Minimum Reporting	1.3	32	0.0	1	0.07286	
Limit 1 μg/L	4.3	32	0.0	1	0.18195	
	8.8	32	0.0	1	0.67354	
Boron (DIS, ICP-AES) Minimum Reporting	5.00	5	-0.59	0.1	0.75000	
Limit 16 µg/L	17.90	16	-1.90	0.1	0.00134	NEG
	20.70	8	0.23	0.1	0.74219	
	25.80	8	1.03	0.1	0.38281	
	37.65	18	1.50	0.1	0.36339	
	100.0	27	2.9	1	0.00000	POS
	105.0	30	-0.6	1	0.23505	
	116.9	34	0.7	1	0.02109	
	158.4	14	3.1	1	0.00037	POS
Boron (WWR,DCP-AES) Minimum Reporting	25	4	-6	10	0.37500	
Limit 10 μg/L	26	4	2	10	1.00000	
	38	4	-5	10	0.62500	
Cadmium (DIS, GF-AAS) Minimum Reporting	1.7	8	0.1	1	0.12500	
Limit 1 μg/L	3.4	8	0.0	1	0.90625	
	7.0	8	0.0	1	0.57031	
	7.2	8	0.1	1	0.56250	
	9.6	8	0.0	1	0.57031	
	14.3	8	0.5	1	0.46094	

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic const	ituents—Continued				
Cadmium (DIS, ICP-AES) Minimum Reporting	7.0	13	1.9	1	0.00439	POS
Limit 8 μg/L	8.4	26	-0.4	1	0.89085	
	14.2	22	-0.6	1	0.43919	
Cadmium (DIS, ICP-MS) Minimum Reporting	1.7	32	0.0	1	0.11706	
Limit 1 µg/L	9.6	32	0.1	1	0.23892	
	14.2	32	-0.2	1	0.00137	
Cadmium (WWR, GF-AAS) Minimum Reporting	1.7	10	0.0	1	0.81250	
Limit 1 μg/L	3.4	16	-0.1	1	0.25708	
	7.0	14	-0.1	1 .	0.51135	
	8.4	8	-0.3	1	0.08594	
	9.6	8	-0.3	1	0.14844	
	14.2	8	-0.1	1	0.38281	
	14.3	8	-0.8	1	0.19531	
Calcium (DIS, ICP-AES) Minimum Reporting	3.33	22	-0.01	0.1	0.30971	
Limit 0.02 mg/L	9.53	14	-0.06	0.1	0.46313	
	25.1	16	-0.2	1	0.10458	
	37.0	24	-1.1	1	0.00034	NEG
	40.5	26	0.3	1	0.04089	
	41.2	24	0.4	1	0.06609	
	42.2	22	0.3	1	0.07849	
	44.2	16	0.6	1	0.23120	
	45.9	18	-0.2	1	0.52261	
	47.1	26	-0.9	1	0.00056	
	52.2	18	-1.3	1	0.00560	NEG
	58.1	14	-1.3	1	0.01660	NEG
Chloride (DIS, IC) Minimum Reporting Limit	8.35	21	0.29	0.1	0.00011	POS
0.1 mg/L	16.7	30	0.1	1	0.36890	
	29.6	24	0.7	1	0.00321	
	31.5	16	0.9	1	0.01550	
	45.4	18	0.3	1	0.26453	
	46.0	27	0.2	1	0.15293	
	62.7	30	2.2	1	0.00000	POS
	69.0	26	1.6	1	0.00013	POS
	78.5	34	0.2	1	0.22678	
	85.3	14	0.6	1	0.50159	
Chloride (DIS, IC, LL) Minimum Reporting Limit	1.20	5	0.02	0.1	0.06250	
0.01 mg/L	1.30	4	-0.01	0.1	0.87500	
	7.79	3	0.34	0.1	1.00000	

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic const	ituents—Continued				
Chromium (DIS, GF-AAS) Minimum Reporting	4.85	10	0.15	0.1	0.61133	
Limit 1 µg/L	9.70	16	0.35	0.1	0.00012	POS
	16.5	6	1.5	1	0.06250	
	18.5	8	0.3	1	0.32813	
	27.8	8	-0.4	1	0.66406	
Chromium (DIS, ICP-AES) Minimum Reporting	11.5	12	3.5	1	0.00146	POS
Limit 14 μg/L	16.5	24	1.3	1	0.00074	POS
	26.2	22	1.6	1	0.00019	POS
Chromium (DIS, ICP-MS) Minimum Reporting	4.9	32	0.0	1	0.88591	
Limit 1 μg/L	18.5	32	-0.2	1	0.00024	
	26.2	32	-1.1	1	0.00000	NEG
Chromium (WWR, GF-AAS) Minimum	9.70	8	-0.05	0.1	0.67188	
Reporting Limit 1 μg/L	11.5	8	-0.1	1	0.52344	
	16.5	8	-0.6	1	0.38281	
	18.5	8	-0.4	1	0.14844	
	26.2	8	-1.3	1	0.25000	
	27.8	8	-0.9	1	0.10938	
Cobalt (DIS, GF-AAS) Minimum Reporting Limit 1 µg/L	8.5	6	0.4	1	0.18750	
Cobalt (DIS, ICP-AES) Minimum Reporting	8.4	6	1.1	1	0.31250	
Limit 12 μg/L	13.5	22	0.5	1	0.08154	
Cobalt (DIS, ICP-MS) Minimum Reporting Limit	8.5	32	0.0	1	0.26020	
1 μg/L	13.5	32	-0.1	1	0.00982	
Cobalt (WWR, GF-AAS) Minimum Reporting	2.0	8	0.0	1	0.64063	
Limit 1 μg/L	8.4	8	0.5	1	0.31250	
	13.5	8	0.5	1	0.07813	
Copper (DIS, GF-AAS) Minimum Reporting	0.95	5	0.05	0.1	0.06250	
Limit 1 µg/L	4.7	8	0.1	1	0.46094	
	7.5	8	1.0	1	0.01563	
	11.2	8	0.7	1	0.03125	
	16.7	8	0.4	1	0.05469	
Copper (DIS, ICP-AES) Minimum Reporting	12	26	0	10	0.14029	
Limit 10 μg/L	17	22	0	10	0.53920	
Copper (DIS, ICP-MS) Minimum Reporting	11.2	32	0.3	1	0.00002	
Limit 1 µg/L	16.7	32	0.0	1	0.21890	
Copper (WWR, GF-AAS) Minimum Reporting	0.95	7	0.15	0.1	0.01563	POS
Limit 1 µg/L	4.7	14	-0.2	1	0.13135	
,	11.2	8	0.0	1	0.58594	
	12.0	8	-0.1	1	0.78125	
	16.7	8	0.1	1	0.92188	
	16.7	8	0.8	1	0.07813	

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic const	ituents—Continued				
Dissolved Solids (DIS, GRAV) Minimum	37.8	22	3.3	1	0.01783	POS
Reporting Limit 10 mg/L	75.5	29	2.5	1	0.01583	POS
	208.8	16	3.3	1	0.00015	POS
	266.5	24	4.0	1	0.01043	POS
	284.0	27	5.0	1	0.00000	POS
	359.5	30	4.5	1	0.00021	POS
	376.0	17	9.0	1	0.00002	POS
	426.0	26	3.5	1	0.00583	POS
	469.0	34	6.0	1	0.00102	POS
	518.5	14	7.5	1	0.01270	POS
Fluoride (DIS, IC, LL) Minimum Reporting Limit	0.040	4	0.004	0.01	0.87500	
0.01 mg/L	0.110	5	0.005	0.01	0.81250	
	0.139	4	0.017	0.01	0.12500	
Fluoride (DIS, ISE) Minimum Reporting Limit	0.18	21	0.02	0.1	0.00155	
0.1 mg/L	0.36	29	0.03	0.1	0.00000	
	0.52	27	0.03	0.1	0.00114	
	0.55	18	0.02	0.1	0.02003	
	0.63	24	0.05	0.1	0.00001	
	0.67	15	0.04	0.1	0.00012	
	0.78	24	0.04	0.1	0.00001	
	0.80	34	0.04	0.1	0.00000	
	0.88	30	0.05	0.1	0.00000	
	0.92	14	0.05	0.1	0.00403	
Iron (DIS, ICP-AES) Minimum Reporting Limit	17.8	31	1.0	1	0.12334	
10 μg/L	35.5	16	2.5	1	0.03354	POS
	39.3	24	-3.0	1	0.00000	NEG
	54.3	26	-1.5	1	0.00119	NEG
	55.1	37	-2.0	1	0.00018	NEG
	111	8	-3	10	0.00781	
	147	18	-2	10	0.10838	
	162	22	-5	10	0.00219	
	167	8	2	10	0.25000	
Iron (WWR, F-AAS) Minimum Reporting Limit 10 μg/L	18	10	4	10	0.07617	
	36	16	5	10	0.00113	
	54	8	-2	10	1.00000	
	55	14	3	10	0.26050	
	111	8	- 6	10	0.10938	
	162	8	-9	10	0.01563	
	167	8	-2	10	0.48438	

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic const	tituents—Continued				
Lead (DIS, GF-AAS) Minimum Reporting Limit	1.6	8	0.1	1	0.55469	
1 μg/L	3.2	8	-0.3	1	0.10156	
	5.4	8	-0.1	1	0.08594	
	5.8	8	-0.1	1	0.07031	
	41.7	8	0.8	1	0.05469	
	62.6	8	3.2	1	0.00781	POS
Lead (DIS, ICP-AES) Minimum Reporting Limit 100 μg/L	48	5	2	10	0.81250	
Lead (DIS, ICP-MS) Minimum Reporting Limit	1.6	32	0.0	1	0.88342	
1 μg/L	41.7	32	0.0	1	0.89829	
	48.1	32	-0.3	1	0.21900	
Lead (WWR, GF-AAS) Minimum Reporting	1.6	10	0.1	1	0.48242	
Limit 1 μg/L	3.2	16	0.1	1	0.40942	
	5.8	14	-0.1	1	0.89050	
	8.6	8	0.2	1	0.29688	
	41.7	8	-0.2	1	0.77344	
	48.1	8	-0.3	1	0.94531	
	62.6	8	3.4	1	0.07813	
Lithium (DIS, ICP-AES) Minimum Reporting	4.4	8	1.5	1	0.01563	POS
Limit 6 μg/L	9.0	8	1.1	1	0.00781	POS
	11.2	24	2.0	1	0.00000	POS
	13.5	8	1.4	1	0.00781	POS
	22.7	22	1.4	1	0.00000	POS
	23.0	26	1.9	1	0.00000	POS
Lithium (WWR, F-AAS) Minimum Reporting	23	7	0	10	0.89063	
Limit 10 μg/L	23	4	0	10	1.00000	
Magnesium (DIS, ICP-AES) Minimum Reporting	0.925	22	-0.010	0.01	0.05983	
Limit 0.01 mg/L	2.53	14	0.01	0.1	0.79517	
	7.43	16	-0.24	0.1	0.00006	NEG
	9.34	26	-0.10	0.1	0.00537	NEG
	9.54	22	-0.10	0.1	0.25841	
	10.1	16	0.1	1	0.77225	
	10.1	24	0.0	1	0.40287	
	10.3	18	0.0	1	0.31165	
	11.2	24	-0.5	1	0.00000	
	11.5	26	-0.2	1	0.00010	
	13.9	14	-0.2	1	0.01294	
	14.2	18	-0.3	1	0.00001	

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic const	ituents—Continued				
Manganese (DIS, ICP-AES) Minimum Reporting	9.1	8	-0.2	1	0.14844	
Limit 4 μg/L	11.7	26	-0.1	1	0.39137	
	13.7	8	0.5	1	0.03906	
	19.6	22	-0.1	1	0.93754	
	24.5	31	-0.9	1	0.00000	
	49.0	16	-1.4	1	0.00003	NEG
	50.2	24	-2.2	1	0.00000	NEG
	58.1	18	-1.6	1	0.00033	NEG
	74.1	37	-2.1	1	0.00000	NEG
Manganese (DIS, ICP-MS) Minimum Reporting	9.1	32	-0.1	1	0.00112	
Limit 1 μg/L	19.6	32	-0.7	1	0.00000	
	24.5	32	-1.2	1	0.00000	NEG
Manganese (WWR, F-AAS) Minimum Reporting	12	8	2	10	0.02344	
Limit 10 μg/L	14	8	1	10	0.06250	
	20	8	-1	10	1.00000	
	49	8	-5	10	0.01563	
	74	8	- 3	10	0.04688	
Mercury (DIS, CV-AAS) Minimum Reporting	0.26	8	-0.04	0.1	0.00781	
Limit 0.1 μg/L	0.76	16	0.08	0.1	0.39642	
	0.93	8	0.08	0.1	0.93750	
	3.32	16	0.20	0.1	0.06357	
Mercury (WWR, CV-AAS) Minimum Reporting	0.26	8	-0.06	0.1	0.10938	
Limit 0.1 μg/L	0.76	8	0.00	0.1	0.82031	
	0.93	15	0.02	0.1	0.55054	
	3.32	16	0.02	0.1	0.55283	
Molybdenum (DIS, GF-AAS) Minimum	2.22	5	0.58	0.1	0.62500	
Reporting Limit 1 µg/L	11.9	5	0.5	1	0.12500	
Molybdenum (DIS, ICP-AES) Minimum	10	6	0	10	0.43750	
Reporting Limit 60 μg/L	12	4	0	10	0.62500	
	23	5	-11	10	0.62500	
Molybdenum (DIS, ICP-MS) Minimum	2.2	32	0.1	1	0.00001	
Reporting Limit 1 µg/L	18.1	32	0.6	1	0.00000	
	22.7	32	0.4	1	0.00002	
Molybdenum (WWR, GF-AAS) Minimum	10.4	8	-0.8	1	0.03906	
Reporting Limit 1 µg/L	12.1	8	-0.9	1	0.05469	
	22.7	8	0.3	1	0.94531	

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic const	ituents—Continued				
Nickel (DIS, GF-AAS) Minimum Reporting	3.8	5	0.4	1	0.06250	
Limit 1 µg/L	7.5	4	0.5	1	0.25000	
	14.1	5	0.9	1	0.06250	
	35.5	6	2.0	1	0.03125	POS
Nickel (DIS, ICP-AES) Minimum Reporting	12	4	4	10	0.02500	
Limit 40 μg/L	15	6	2	10	0.56250	
	41	22	1	10	0.03200	
Nickel (DIS, ICP-MS) Minimum Reporting Limit	3.8	32	0.3	1	0.00000	
1 μg/L	35.5	32	-0.4	1	0.01415	
	41.0	32	-1.1	1	0.00000	NEG
Nickel (WWR, GF-AAS) Minimum Reporting	7.5	8	0.7	1	0.00781	
Limit 1 μg/L	12.1	8	0.5	1	0.00781	
	14.5	8	0.6	1	0.10938	
	35.5	8	2.2	1	0.00781	POS
	41	8	1.9	1	0.01563	POS
	53.3	8	4.0	1	0.05469	
Potassium (DIS, F-AAS) Minimum Reporting	0.46	22	-0.02	0.1	0.00000	
Limit 0.1 mg/L	0.91	30	-0.03	0.1	0.00217	
	2.01	16	-0.03	0.1	0.29694	
	2.20	24	-0.04	0.1	0.41355	
	2.49	18	-0.04	0.1	0.47470	
	3.27	27	-0.01	0.1	0.36439	
	4.18	30	-0.05	0.1	0.20736	
	4.47	34	-0.05	0.1	0.36349	
	4.90	26	0.02	0.1	0.83387	
	5.50	14	0.12	0.1	0.03406	POS
Potassium (DIS, F-AAS, LL) Minimum Reporting	0.118	5	0.001	0.01	0.37500	
Limit 0.01 mg/L	0.146	4	0.003	0.01	0.25000	
	0.550	4	0.008	0.01	0.12500	
Selenium (DIS, HG-AAS) Minimum Reporting	2.2	31	-0.9	1	0.00000	
Limit 1 μg/L	3.1	12	-0.5	1	0.00049	
	4.8	8	-0.2	1	0.46094	
	5.5	4	-0.8	1	0.25000	
	7.2	8	0.3	1	0.25000	
	7.5	22	-0.1	1	0.88780	
	9.7	4	0.6	1	0.37500	
	9.9	19	0.6	1	0.91347	

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic const	ituents—Continued				
Selenium (WWR, GF-AAS, USEPA) Minimum	4.8	4	0.5	1	0.12500	
Reporting Limit 1 µg/L	7.2	4	0.6	1	0.12500	
Selenium (WWR, HG-AAS) Minimum Reporting	2.2	8	-0.9	1	0.00781	
Limit 1 μg/L	4.8	8	0.0	1	0.74219	
	7.2	8	-0.1	1	0.74219	
	7.5	8	0.0	1	1.00000	
	9.9	8	0.0	1	0.54688	
Silica (DIS, COL) Minimum Reporting Limit	2.24	22	-0.04	0.1	0.35836	
0.1 mg/L	6.35	18	-0.21	0.1	0.00011	NEG
	8.15	24	0.04	0.1	0.83553	
	8.54	16	0.15	0.1	0.19281	
	9.75	25	-0.22	0.1	0.02308	NEG
	11.1	14	-0.4	1	0.01343	
Silica (DIS, ICP-AES) Minimum Reporting Limit	1.74	14	-0.07	0.1	0.00012	
0.1 mg/L	4.47	30	-0.16	0.1	0.00000	NEG
	6.50	26	-0.22	0.1	0.00000	NEG
	7.55	24	-0.06	0.1	0.00119	
	8.14	16	-0.05	0.1	0.85034	
	9.17	34	-0.35	0.1	0.00000	NEG
	10.3	26	-0.1	1	0.00035	
	11.0	29	-0.3	1	0.00000	
	15.2	18	-0.4	1	0.00026	
	17.4	22	-0.6	1	0.00001	
Silver (DIS, GF-AAS) Minimum Reporting Limit	9.9	8	-1.1	1	0.00781	NEG
1 μg/L	14.9	8	-0.1	1	0.29688	
Silver (DIS, ICP-AES) Minimum Reporting Limit	4.9	14	-0.1	1	0.38208	
4 μg/L	13.7	14	-2.6	1	0.00012	NEG
Silver (DIS, ICP-MS) Minimum Reporting Limit	9.9	32	-1.3	1	0.00000	NEG
1 μg/L	13.7	32	-2.3	1	0.00000	NEG
Silver (WWR, GF-AAS) Minimum Reporting	4.9	8	-0.1	1	0.28906	
Limit 1 µg/L	9.9	8	-1.2	1	0.00781	NEG
	13.7	8	-2.1	1	0.00781	NEG
	14.9	8	0.3	1	0.14844	
Sodium (DIS, ICP-AES) Minimum Reporting	5.50	14	-0.05	0.1	0.42627	
Limit 0.2 mg/L	7.90	22	-0.05	0.1	0.02980	
	28.0	18	0.1	1	0.21214	
	33.5	16	0.2	1	0.70572	
	35.4	24	0.2	1	0.93384	
	37.6	22	0.0	1	0.40216	
	39.2	24	-0.1	1	0.40287	
	49.9	18	0.1	1	0.29869	
	56.5	16	1.0	1	0.05066	
	66.1	26	0.1	1	0.97050	
	81.0	26	-0.7	1	0.03564	
	96.2	14	-0.7	1	0.13525	

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic const	ituents—Continued				
Specific Conductance (WWR, ELEC, LL)	13.3	5	-0.5	1	0.43750	
Minimum Reporting Limit 0.5 μS/cm	20.9	4	0.0	1	1.00000	
	36.1	4	1.3	1	0.25000	
Strontium (DIS, ICP-AES) Minimum Reporting Limit 1 µg/L	115	8	-1	10	0.31250	
	153	8	-2	10	0.25000	
	230	8	7	10	0.03906	
	255	22	-1	10	0.56038	
	273	24	3	10	0.00634	
	302	26	4	10	0.01828	
Sulfate (DIS, IC) Minimum Reporting Limit 0.1 mg/L	7.00	21	-0.41	0.1	0.00000	NEG
	14.0	30	-0.9	1	0.00000	
	58.5	16	-1.2	1	0.00015	NEG
	75.0	27	-0.4	1	0.00218	
	89.0	54	-0.6	1	0.00862	
	113	26	0	10	0.60359	
	114	52	-1	10	0.00014	
	132	14	-1	10	0.17261	
Vanadium (DIS, ICP-AES) Minimum Reporting	8.4	5	-0.3	1	1.00000	
Limit 10 μg/L	11.8	24	0.1	1	0.78181	
	20.9	22	0.4	1	0.23168	
Zinc (DIS, ICP-AES) Minimum Reporting Limit	10.5	4	2.0	1	0.12500	
20 μg/L	15.0	15	6.7	1	0.00085	POS
	24.8	8	3.1	1	0.05469	
	39.9	24	0.8	1	0.59798	
Zinc (DIS, ICP-MS) Minimum Reporting Limit	10.0	32	1.7	1	0.00000	POS
1 μg/L	12.4	32	1.4	1	0.00000	POS
	15.0	32	2.5	1	0.00000	POS
Zinc (WWR, F-AAS) Minimum Reporting Limit	10	8	3	10	0.01563	
10 μg/L	11	8	2	10	0.00781	
	12	8	3	10	0.00195	
	15	16	4	10	0.00360	
	25	16	0	10	0.31619	
	40	14	2	10	0.01953	
		Constituents				
Ammonia as nitrogen (DIS, COL) Minimum	0.210	60	0.026	0.01	0.00001	POS
Reporting Limit 0.02 mg/L	0.240	54	-0.012	0.01	0.06591	
	0.498	60	0.004	0.01	0.41528	
	0.620	62	0.054	0.01	0.00000	POS
	1.24	96	0.05	0.1	0.00000	

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Nutrient consti	tuents-Continued				
Ammonia as nitrogen (DIS, COL, LL) Minimum	0.2100	36	-0.0140	0.001	0.00000	NEG
Reporting Limit 0.002 mg/L	0.2400	30	-0.0130	0.001	0.00000	NEG
Ammonia as nitrogen (DIS, USEPA) Minimum Reporting Limit 0.02 mg/L	0.210	3	-0.022	0.01	0.25000	
	0.240	3	-0.035	0.01	0.25000	
	0.498	6	0.002	0.01	1.00000	
	0.620	5	-0.036	0.01	0.12500	
Ammonia plus organic nitrogen as nitrogen (DIS,	0.29	60	-0.06	0.1	0.00000	
ASF) Minimum Reporting Limit 0.1 mg/L	0.30	59	-0.03	0.1	0.00047	
	0.75	60	-0.04	0.1	0.00000	
	0.86	95	0.00	0.1	0.38038	
	0.91	59	0.02	0.1	0.03868	
Ammonia plus organic nitrogen as nitrogen (DIS,	0.285	9	-0.045	0.01	0.12500	
USEPA) Minimum Reporting Limit 0.1 mg/L	0.300	7	-0.024	0.01	0.17188	
•	0.750	9	-0.012	0.01	0.44531	
	0.910	9	0.022	0.01	0.64063	
Ammonia plus organic nitrogen as nitrogen	0.29	60	-0.07	0.1	0.00000	
(WWR, ASF) Minimum Reporting Limit	0.30	46	-0.02	0.1	0.00833	
0.1 mg/L	0.75	60	-0.04	0.1	0.00000	
	0.91	59	0.00	0.1	0.69543	
Ammonia plus organic nitrogen as nitrogen	0.29	9	-0.07	0.1	0.00781	
(WWR, USEPA) Minimum Reporting Limit	0.30	7	0.00	0.1	0.81250	
0.1 mg/L	0.75	9	-0.03	0.1	0.16406	
	0.91	9	0.01	0.1	0.91016	
Nitrate plus nitrite as nitrogen (DIS, COL)	0.220	60	-0.004	0.01	0.10353	
Minimum Reporting Limit 0.05 mg/L	0.443	54	-0.008	0.01	0.11066	
	0.747	60	-0.037	0.01	0.00000	NEG
	1.01	62	-0.02	0.1	0.00016	
	1.04	96	0.03	0.1	0.00011	
Nitrate plus nitrite as nitrogen (DIS, COL, LL)	0.220	36	-0.013	0.01	0.00000	NEG
Minimum Reporting Limit 0.005 mg/L	0.443	30	-0.011	0.01	0.00000	NEG
Orthophosphate as phosphorus (DIS, COL)	0.195	60	0.005	0.01	0.05772	
Minimum Reporting Limit 0.01 mg/L	0.580	54	0.054	0.01	0.00000	POS
	0.658	59	-0.032	0.01	0.00000	NEG
	0.758	62	0.001	0.01	0.98840	
	1.01	96	0.00	0.1	0.42110	
Orthophosphate as phosphorus (DIS, COL, LL)	0.195	36	0.004	0.01	0.10731	
Orthophosphate as phosphorus (DIS, COL, LL) Minimum Reporting Limit 0.001 mg/L	0.580	30	0.007	0.01	0.00005	

Table 4. Results of Wilcoxon signed-rank test for bias in constituent data for the National Water Quality Laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Nutrient consti	tuents—Continued				
Phosphorus (DIS, ASF) Minimum Reporting	0.201	60	-0.002	0.01	0.88725	
Limit 0.05 mg/L	0.602	60	0.003	0.01	0.31645	
	0.715	60	0.008	0.01	0.00240	
	0.766	59	0.025	0.01	0.00020	POS
	1.01	95	0.02	0.1	0.00003	
Phosphorus (DIS, COL, LL) Minimum Reporting Limit 0.001 mg/L	0.201	18	0.007	0.01	0.35216	
	0.602	15	0.014	0.01	0.11029	
Phosphorus (DIS, USEPA) Minimum Reporting	0.201	9	-0.008	0.01	0.58594	
Limit 0.05 mg/L	0.602	7	0.002	0.01	1.00000	
	0.715	9	0.018	0.01	0.73438	
	0.766	9	0.022	0.01	0.12500	
Phosphorus (WWR, ASF) Minimum Reporting	0.201	60	0.003	0.01	0.32082	
Limit 0.05 mg/L	0.602	46	0.000	0.01	0.54222	
	0.715	60	0.007	0.01	0.12027	
	0.766	60	0.028	0.01	0.00000	POS
Phosphorus (WWR, COL, LL) Minimum	0.201	35	0.007	0.01	0.00239	
Reporting Limit 0.001 mg/L	0.602	30	0.019	0.01	0.17542	
Phosphorus (WWR, USEPA) Minimum Reporting	0.201	9	0.012	0.01	0.37500	
Limit 0.05 mg/L	0.602	7	-0.006	0.01	0.81250	
	0.715	9	0.007	0.01	0.67188	
	0.766	9	0.040	0.01	0.03906	POS

Table 5. Results of Wilcoxon signed-rank test for bias in constituent data for the Quality of Water Service Unit laboratory

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic	constituents				
Alkalinity (WWR, TITR) Minimum Reporting	55.7	11	1.3	1	0.00098	POS
Limit 1 mg/L	76.0	6	3.0	1	0.03125	POS
	88.5	12	-0.5	1	0.17529	
	94.2	12	0.9	1	0.02246	
	107.5	12	1.6	1	0.00049	POS
t .	129.7	12	2.3	1	0.02588	POS

Table 5. Results of Wilcoxon signed-rank test for bias in constituent data for the Quality of Water Service Unit laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic consti	tuents—Continued	·			_
Aluminum (DIS, ICP-AES/T) Minimum Reporting	28.5	8	-0.5	1	0.74219	
Limit 3 μg/L	44.9	8	0.7	1	0.08594	
	45.0	8	6.0	1	0.00781	POS
Aluminum (WWR, GF-AAS, USEPA) Minimum	28	4	2	10	0.12500	
Reporting Limit 2 μg/L	45	4	5	10	0.25000	
	45	3	5	10	0.25000	
Aluminum (WWR, ICP-AES/T) Minimum	28.5	8	5.0	1	0.03906	POS
Reporting Limit 3 μg/L	44.9	8	2.2	1	0.00781	POS
	45.0	8	15.0	1	0.00781	POS
Arsenic (DIS, GF-AAS) Minimum Reporting Limit	1.84	5	-0.54	0.1	0.12500	
1 μg/L	7.72	3	0.29	0.1	0.25000	
	12.5	4	0.0	1	0.87500	
Arsenic (WWR, GF-AAS) Minimum Reporting Limit 1 µg/L	7.60	4	-0.10	0.1	1.00000	
	11.4	4	-1.3	1	0.37500	
Barium (DIS, ICP-AES/T) Minimum Reporting Limit 0.2 μg/L	54.5	4	-0.5	1	0.62500	
	73.5	4	0.1	1	0.87500	
Barium (WWR, ICP-AES/T) Minimum Reporting	54.5	4 .	-1.5	1	0.12500	
Limit 0.2 μg/L	70.7	4	-1.7	1	0.25000	
	73.5	4	-2.0	1	0.12500	
Beryllium (DIS, ICP-AES/T) Minimum Reporting	6.85	4	-0.05	0.1	0.50000	
Limit 0.5 μg/L	7.65	4	-0.05	0.1	0.12500	
Beryllium (WWR, ICP-AES/T) Minimum	6.85	4	-0.30	0.1	0.12500	
Reporting Limit 0.5 μg/L	7.65	4	-0.25	0.1	0.12500	
	8.64	4	-0.19	0.1	0.12500	
Boron (DIS, ICP-AES/T) Minimum Reporting	25.3	4	-0.3	1	1.00000	
Limit 3 μg/L	25.8	4	-0.8	1	0.25000	
Cadmium (DIS, GF-AAS) Minimum Reporting	6.98	4	0.08	0.1	0.62500	
Limit 1 μg/L	8.42	3	0.19	0.1	0.25000	
	14.2	4	-0.2	1	1.00000	
Cadmium (DIS, ICP-AES/T) Minimum Reporting	7.15	4	-0.05	0.1	0.50000	
Limit 0.5 µg/L	13.0	4	0.1	1	1.00000	
Cadmium (WWR, GF-AAS) Minimum Reporting	3.40	3	0.10	0.1	0.75000	
Limit 1 µg/L	9.55	4	-0.50	0.1	0.12500	
	14.3	4	-0.8	1	0.37500	
Cadmium (WWR, ICP-AES/T) Minimum	6.98	4	-0.38	0.1	0.12500	
Reporting Limit 0.5 μg/L	8.42	3	-0.22	0.1	1.00000	
	14.2	4	-1.2	1	0.12500	

Table 5. Results of Wilcoxon signed-rank test for bias in constituent data for the Quality of Water Service Unit laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic consti	tuents—Continued				
Calcium (DIS, ICP-AES) Minimum Reporting	9.53	8	-0.08	0.1	0.35156	
Limit 0.02 mg/L	25.1	11	-1.1	1	0.00098	NEG
	31.4	7	-0.4	1	0.85938	
	38.1	12	-1.1	1	0.00049	NEG
	44.2	8	0.8	1	0.25000	
	45.9	8	0.1	1	0.13281	
	52.2	12	-1.2	1	0.00391	NEG
•	53.3	12	-0.3	1	0.01123	
	58.1	12	-1.1	1	0.00049	NEG
Calcium (DIS, ICP-AES/T) Minimum Reporting Limit 0.02 mg/L	40.5	8	0.5	1	0.06250	
	41.2	8	0.9	1	0.09375	
	42.2	8	0.8	1	0.01563	
	44.2	4	-0.2	1	1.00000	
	45.9	4	0.1	1	0.12500	
Chloride (DIS, IC) Minimum Reporting Limit 0.1 mg/L	8.35	8	0.05	0.1	0.00781	
	29.6	7	0.4	1	0.01563	
	31.5	11	0.5	1	0.00098	
	45.4	12	-0.4	1	0.12500	
	46.0	7	1.0	1	0.03125	
	62.7	12	2.3	1	0.00049	POS
	69.0	8	0.5	1	0.25000	
	78.5	12	1.5	1	0.00293	POS
	85.3	12	1.8	1	0.00488	POS
Chromium (DIS, ICP-AES/T) Minimum Reporting	13.6	4	-0.6	1	0.12500	
Limit 1 μg/L	28.2	4	-0.7	1	0.12500	
Chromium (WWR, GF-AAS) Minimum Reporting	9.70	3	0.30	0.1	0.75000	
Limit 1 μg/L	18.5	4	-0.5	1	0.50000	
	27.8	4	-0.8	1	0.62500	
Chromium (WWR, ICP-AES/T) Minimum	9.70	4	-0.20	0.1	0.25000	
Reporting Limit 1 μg/L	27.8	4	-1.8	1	0.12500	
Cobalt (DIS, ICP-AES/T) Minimum Reporting	3.55	4	0.05	0.1	0.75000	
Limit 1 μg/L	8.70	4	-0.05	0.1	0.75000	
Copper (DIS, GF-AAS) Minimum Reporting Limit	4.68	4	-0.13	0.1	0.50000	
1 μg/L	12.0	3	0.0	1	1.00000	
	16.7	4	0.4	1	0.12500	
Copper (DIS, ICP-AES/T) Minimum Reporting	7.45	4	0.90	0.1	0.12500	
Limit 1 µg/L	12.1	4	0.4	1	0.62500	
Copper (WWR, GF-AAS) Minimum Reporting	11.2	4	0.9	1	0.25000	
Limit 1 µg/L	16.7	4	-0.2	1	0.62500	

Table 5. Results of Wilcoxon signed-rank test for bias in constituent data for the Quality of Water Service Unit laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic consti	tuents-Continued				
Copper (WWR, ICP-AES/T) Minimum Reporting	7.45	4	-0.20	0.1	0.62500	
Limit 1 μg/L	12.1	4	-1.1	1	0.12500	
	19.5	4	0.5	1	0.75000	
Dissolved Solids (DIS, GRAV) Minimum	208.8	11	5.3	1	0.00977	POS
Reporting Limit 1 mg/L	284.0	6	7.0	1	0.03125	POS
	359.5	12	7.5	1	0.01123	POS
	376.0	12	12.0	1	0.00391	POS
	469.0	12	7.0	1	0.06055	
	518.5	12	10.5	1	0.00049	POS
Fluoride (DIS, ISE) Minimum Reporting Limit 0.1 mg/L	0.180	4	0.015	0.01	0.25000	
	0.520	7	0.010	0.01	0.56250	
	0.546	12	0.004	0.01	0.71924	
	0.673	11	0.017	0.01	0.00781	POS
	0.780	4	0.000	0.01	1.00000	
	0.800	12	0.000	0.01	0.50000	
	0.880	12	0.020	0.01	0.00098	POS
	0.920	12	-0.010	0.01	0.17188	
Iron (DIS, ICP-AES/T) Minimum Reporting Limit	35.5	4	4.5	1	0.25000	
1 μg/L	39.3	4	0.8	1	0.12500	
	54.3	8	-3.8	1	0.72656	
	55.1	8	-5.1	1	0.00781	NEG
	146.5	4	-4.5	1	0.37500	
•	161.5	8	-1.5	1	0.00781	NEG
	166.5	4	-6.5	1	0.12500	
Iron (WWR, ICP-AES/T) Minimum Reporting	35.5	7	4.5	1	0.01563	POS
Limit 1 μg/L	54.3	8	2.3	1	0.03125	POS
	55.1	8	-0.6	1	0.42188	
	111.0	6	-1.0	1	0.40625	
	161.5	8	-1.5	1	0.00781	NEG
	166.5	8	-6.5	1	0.19531	
Lead (DIS, GF-AAS) Minimum Reporting Limit	3.2	4	-0.2	1	0.12500	
1 μg/L	62.6	4	1.5	1	0.62500	
Lead (DIS, ICP-AES/T) Minimum Reporting Limit	5.39	4	-0.29	0.1	0.12500	
1 µg/L	44.9	4	0.2	1	0.75000	
Lead (WWR, GF-AAS) Minimum Reporting Limit	3.2	3	-0.2	1	0.25000	
1 µg/L	41.7	4	-1.2	1	0.25000	
	62.6	4	-7.1	1	0.37500	
Lead (WWR, ICP-AES/T) Minimum Reporting	5.84	4	-0.24	0.1	0.62500	
Limit 1 µg/L	8.59	3	-0.49	0.1	0.75000	
	48.1	4	-2.6	1	0.12500	

Table 5. Results of Wilcoxon signed-rank test for bias in constituent data for the Quality of Water Service Unit laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic consti	tuents-Continued				
Magnesium (DIS, ICP-AES) Minimum Reporting	2.53	8	0.08	0.1	0.03125	
Limit 0.01 mg/L	7.43	11	-0.23	0.1	0.00098	NEG
	7.65	7	-0.05	0.1	0.18750	
	9.50	12	-0.20	0.1	0.00098	NEG
	10.1	8	-0.1	1	0.00781	
	10.3	8	-0.3	1	0.23438	
	12.5	12	-0.5	1	0.00049	
	13.9	12	0.1	1	0.84277	
	14.2	12	-0.2	1	0.00049	
Magnesium (DIS, ICP-AES/T) Minimum	9.34	8	-0.14	0.1	0.03906	NEG
Reporting Limit 0.001 mg/L	9.54	8	0.01	0.1	0.50781	
	10.1	4	-0.1	1	0.12500	
	10.1	8	-0.1	1	0.00781	
	10.3	4	-0.3	1	0.12500	
Manganese (DIS, ICP-AES/T) Minimum Reporting Limit 0.2 μg/L	11.7	8	0.4	1	0.00781	
	13.7	4	0.4	1	0.12500	
	19.6	8	0.5	1	0.00781	
	49.0	4	0.0	1		
	50.2	4	-1.2	1	0.12500	
	58.1	4	-0.1	1	0.62500	
	74.1	8	-1.1	1	0.02344	NEG
Manganese (WWR, ICP-AES/T) Minimum	9.10	4	0.10	0.1	0.50000	
Reporting Limit 0.2 μg/L	11.7	8	-0.7	1	0.29688	
	13.7	4	-0.2	1	0.62500	
	19.6	8	-0.1	1	0.28125	
	49.0	3	-1.0	1	1.00000	
	74.1	8	-4 .1	1	0.00781	NEG
Mercury (WWR, CV-AAS) Minimum Reporting	0.26	4	-0.01	0.1	0.50000	
Limit 0.1 μg/L	0.76	8	0.09	0.1	0.06250	
	3.32	7	0.29	0.1	0.01563	POS
Molybdenum (DIS, ICP-AES/T) Minimum	11.9	4	0.1	1	0.62500	
Reporting Limit 2 µg/L	22.5	4	1.0	1	0.12500	
Nickel (DIS, ICP-AES/T) Minimum Reporting	14.1	4	0.5	1	0.50000	
Limit 1 µg/L	43.0	4	0.0	1	1.00000	
Nickel (WWR, GF-AAS) Minimum Reporting	7.50	3	0.20	0.1	0.75000	
Limit 1 μg/L	35.5	4	-1.5	1	0.50000	
	53.3	4	-3.8	1	0.12500	
Nickel (WWR, ICP-AES/T) Minimum Reporting	14.1	4	-0.1	1	0.62500	
Limit 1 µg/L	43.0	4	-1.0	1	0.12500	
ro -	56.0	4	-1.5	1	0.37500	

Table 5. Results of Wilcoxon signed-rank test for bias in constituent data for the Quality of Water Service Unit laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic consti	tuents-Continued				
Potassium (DIS, F-AAS) Minimum Reporting	0.30	8	0.00	0.1	0.00781	
Limit 0.1 mg/L	1.85	8	-0.05	0.1	0.23438	
	1.96	8	-0.06	0.1	0.00781	
	2.01	11	-0.01	0.1	0.68164	
	2.49	12	0.01	0.1	0.59912	
	3.27	7	0.04	0.1	0.48438	
	4.18	12	0.03	0.1	0.11084	
	4.47	12	-0.07	0.1	0.01904	
	5.50	12	-0.10	0.1	0.02002	
Selenium (DIS, GF-AAS) Minimum Reporting	2.18	4	-0.98	0.1	0.12500	
Limit 1 μg/L	7.47	3	-0.57	0.1	0.25000	
	9.87	4	-0.42	0.1	1.00000	
Selenium (WWR, GF-AAS) Minimum Reporting	4.82	4	0.79	0.1	0.12500	
Limit 1 μg/L	7.22	4	0.23	0.1	0.37500	
Silica (DIS, ICP-AES) Minimum Reporting Limit	6.35	12	-0.05	0.1	0.91162	
0.01 mg/L	6.50	7	-0.10	0.1	0.06250	
	8.54	11	-0.04	0.1	0.81055	
	9.17	12	-0.12	0.1	0.01123	NEG
	11.0	12	0.0	1	0.00049	
	11.1	12	-0.1	1	0.00049	
Silica (DIS, ICP-AES/T) Minimum Reporting	7.55	8	0.25	0.1	0.00781	POS
Limit 0.01 mg/L	8.14	4	0.17	0.1	0.12500	
	10.3	8	0.2	1	0.28125	
	15.2	4	-0.2	1	1.00000	
	17.4	8	-0.4	1	0.64844	
Silver (DIS, ICP-AES/T) Minimum Reporting	1.28	4	0.27	0.1	0.12500	
Limit 1 μg/L	10.1	4	-0.6	1	0.12500	
Sodium (DIS, F-AAS) Minimum Reporting Limit	5.50	8	0.15	0.1	0.37500	
0.1 mg/L	28.0	8	0.0	1	0.62500	
	33.5	11	-0.5	1	0.66309	
	49.9	12	0.1	1	0.09180	
	54.0	7	0.0	1	0.75000	
	56.4	8	0.1	1	0.78906	
	69.8	12	-0.8	1	0.09766	
	84.4	12	0.3	1	0.55078	
	96.2	12	-0.2	1	0.06055	
Strontium (DIS, ICP-AES/T) Minimum Reporting	115	4	0	10	1.00000	
Limit 0.5 µg/L	330	4	1	10	0.12500	
• •	268	4	2	10	1.00000	
	316	4	-1	10	0.50000	

Table 5. Results of Wilcoxon signed-rank test for bias in constituent data for the Quality of Water Service Unit laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Inorganic consti	tuents—Continued				
Strontium (WWR, ICP-AES/T) Minimum	268	4	-8	10	0.12500	
Reporting Limit 0.5 μg/L	280	4	-10	10	0.12500	
	316	4	- 6	10	0.12500	
Sulfate (DIS, IC) Minimum Reporting Limit 0.2 mg/L	7.00	8	-0.20	0.1	0.01563	NEG
	58.5	11	0.5	1	0.06543	
	75.0	7	1.0	1	0.01563	
	89.0	19	1.0	1	0.00046	
	113	8	-3	10	0.64844	
	114	24	6	10	0.00279	
	132	12	-2	10	0.67041	
Vanadium (DIS, ICP-AES/T) Minimum Reporting	9.5	4	-0.5	1	0.12500	
Limit 1 μg/L	22.0	4	-0.5	1	0.50000	
Zinc (DIS, ICP-AES/T) Minimum Reporting Limit	30.3	4	-0.8	1	0.37500	
1 μg/L	34.8	4	2.3	1	0.12500	
Zinc (WWR, ICP-AES/T) Minimum Reporting Limit 1 μg/L	10.0	4	1.5	1	0.12500	
	15.0	4	1.5	1	0.62500	
	17.5	4	3.0	1	0.12500	
	24.8	3	-0.8	1	1.00000	
	30.3	4	-0.3	1	1.00000	
	34.8	3	1.3	1	0.25000	
	Nutrient	constituents				
Ammonia as nitrogen (DIS) Minimum Reporting	0.210	6	0.010	0.01	0.06250	
Limit 0.01 mg/L	0.240	5	0.010	0.01	0.12500	
	0.498	4	0.052	0.01	0.12500	
	0.620	4	0.060	0.01	0.12500	
	1.24	20	0.06	0.1	0.00340	
Ammonia plus organic nitrogen as nitrogen (DIS)	0.285	6	-0.085	0.01	0.03125	NEG
Minimum Reporting Limit 0.2 mg/L	0.300	5	-0.040	0.01	0.43750	
	0.750	4	0.045	0.01	0.12500	
	0.864	22	-0.014	0.01	0.45803	
	0.910	4	-0.085	0.01	0.12500	
Ammonia plus organic nitrogen as nitrogen	0.285	14	-0.075	0.01	0.00061	NEG
(WWR) Minimum Reporting Limit 0.2 mg/L	0.300	13	0.000	0.01	0.27148	
	0.750	17	0.010	0.01	0.66849	
	0.910	20	-0.070	0.01	0.00373	NEG
Nitrate plus nitrite as nitrogen (DIS) Minimum	0.220	6	0.000	0.01	1.00000	
Reporting Limit 0.02 mg/L	0.443	5	0.017	0.01	0.06250	
	0.747	4	-0.052	0.01	0.12500	
	1.01	4	-0.05	0.1	0.12500	
	1.04	20	-0.04	0.1	0.58840	

Table 5. Results of Wilcoxon signed-rank test for bias in constituent data for the Quality of Water Service Unit laboratory—Continued

Constituent and method of analysis	Most probable value	Number of determinations	Median bias	Nearest reporting unit	p-value	Bias
	Nutrient constit	uents—Continued				
Orthophosphate as phosphorus (DIS) Minimum	0.195	6	-0.005	0.01	0.15625	
Reporting Limit 0.01 mg/L	0.580	5	0.030	0.01	0.12500	
	0.658	4	-0.013	0.01	0.62500	
	0.758	4	-0.008	0.01	0.62500	
	1.01	20	-0.01	0.1	0.00968	
Phosphorus as phosphorus (DIS) Minimum	0.201	6	-0.021	0.01	0.03125	NEG
Reporting Limit 0.02 mg/L	0.602	5	-0.022	0.01	0.37500	
	0.715	4	-0.010	0.01	0.87500	
	0.766	4	-0.006	0.01	0.12500	
	1.01	22	-0.01	0.1	0.00003	
Phosphorus as phosphorus (WWR) Minimum	0.201	14	-0.021	0.01	0.00012	NEG
Reporting Limit 0.02 mg/L	0.602	13	-0.002	0.01	0.49341	
	0.715	17	-0.005	0.01	0.61668	
	0.766	20	0.004	0.01	0.51160	

SUMMARY

A quality-assurance program was operated during water year 1998 to evaluate the quality of analytical work for inorganic, nutrient, and low-level constituents at two USGS laboratories. Reference water samples with established most probable values were disguised and submitted as routine environmental water samples to the National Water Quality Laboratory in Arvada, Colorado, and the Quality of Water Service Unit laboratory in Ocala, Florida. Reference samples were submitted at a rate of 2 to 5 percent of the laboratory work for each analytical procedure. Resulting analytical data were stored in National Water Information System and the Blind Sample Project's data base.

For each constituent, control charts were prepared on the basis of the difference between the analytical results and the most probable values of the reference samples. To allow the data for all reference mixes to be plotted on the same chart, the difference

from the above calculations was divided by each sample's F-pseudosigma, which was determined from a linear-regression technique. Replicate sample determinations allowed the preparation of precision charts for each constituent. Data for inorganic, nutrient, and low-level constituent samples were then evaluated statistically for precision by using a binomial-probability-distribution test. The Wilcoxon signed-rank test was used in the bias assessment for each constituent by quantifying the median difference between the reported values and the most probable values.

An overall evaluation of the National Water Quality Laboratory inorganic and low-level constituent data for water year 1998 indicated imprecision for silver (dissolved, inductively coupled plasma-mass spectrometry). The evaluation also indicated bias throughout the range of reference samples for chromium (dissolved, inductively coupled plasma-atomic emission spectrometry), dissolved solids (dissolved,

gravimetric), lithium (dissolved, inductively coupled plasma-atomic emission spectrometry), silver (dissolved, inductively coupled plasma-mass spectrometry), and zinc (dissolved, inductively coupled plasma-mass spectrometry).

Statistical evaluation of the National Water Quality Laboratory nutrient methods indicated a lack of precision for ammonia (dissolved, colorimetric) and orthophosphate as phosphorus (dissolved, colorimetric). Bias was indicated throughout the reference sample range for ammonia as nitrogen (dissolved, colorimetric, low level) and nitrate plus nitrite as nitrogen (dissolved, colorimetric, low level).

An overall evaluation of the Quality of Water Service Unit data for water year 1998 indicated no imprecision. Bias throughout the reference sample range was indicated for aluminum (whole-water recoverable, inductively coupled plasma-atomic emission spectrometry, trace).

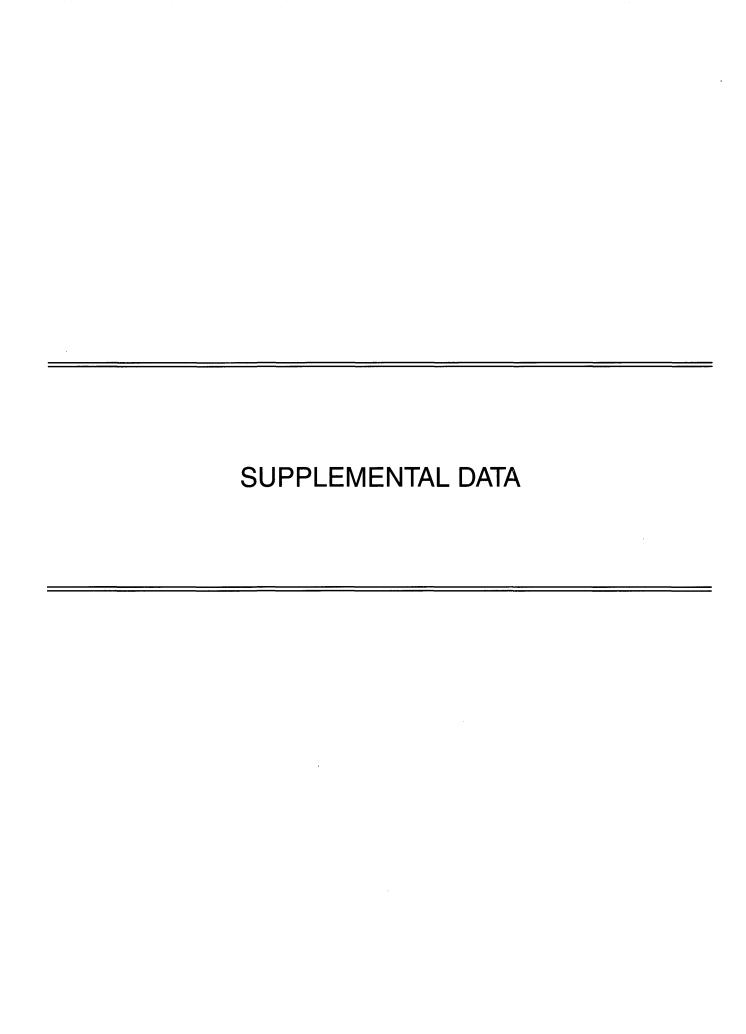
REFERENCES

- Farrar, J.W., and Chleboun, K.M., 1999, Results of the U.S. Geological Survey's analytical evaluation program for standard reference samples distributed in March 1999: U.S. Geological Survey Open-File Report 99–259, 166 p.
- Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: Techniques of Water-Resources Investigations of the U.S. Geological Survey, book 5, chap. A1, 545 p.
- Friedman, L.C., Bradford, W.L., and Peart, D.B., 1983, Application of binomial distributions to quality assurance of quantitative chemical analyses: Journal of Environmental Science and Health, v. A18, no. 4, p. 561–570.
- Friedman, L.C., and Erdmann, D.E., 1982, Quality assurance practices for the chemical and biological analyses of water and sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A6, 181 p.
- Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources—Studies in environmental science,
 v. 49: Amsterdam, The Netherlands, Elsevier Science Publishers, 522 p.

- Hoaglin, D.C., Mosteller, Frederick, and Tukey, J.W. 1983, Understanding robust and exploratory data analysis: New York, John Wiley, 447 p.
- Janzer, V.J., 1985, The use of natural waters as U.S. Geological Survey reference samples, *in* Taylor, J.K., and Stanley, T.W., eds., Quality assurance for environmental measurements, ASTM STP 867: Philadelphia, American Society for Testing and Materials, p. 319–333.
- Lucey, K.J., 1989, Quality-assurance data for routine water analysis in the National Water Quality Laboratory of the U.S. Geological Survey for water year 1988: U.S. Geological Survey Water-Resources Investigations Report 89–4166, 96 p.
- Lucey, K.J., and Peart, D.B., 1988, Quality-assurance data for routine water analysis in the laboratories of the U.S. Geological Survey for water year 1985: U.S. Geological Survey Water-Resources Investigations Report 88–4109, 121 p.
- ———1989b, Quality-assurance data for routine water analysis in the laboratories of the U.S. Geological Survey for water year 1987: U.S. Geological Survey Water-Resources Investigations Report 89–4049, 90 p.
- Ludtke, A.S., Woodworth, M.T., and Marsh, P.S., 1999,
 Quality-assurance data for routine water analysis in
 U.S. Geological Survey laboratories, water year 1997:
 U.S. Geological Survey Water-Resources Investigations Report 99–4057, 186 p.
- Maloney, T.J., Ludtke, A.S, and Krizman, T.L., 1992,
 Quality-assurance data for routine water analysis in the National Water Quality Laboratory of the U.S. Geological Survey for water year 1989:
 U.S. Geological Survey Water-Resources Investigations Report 92–4075, 99 p.
- —— 1993, Quality-assurance data for the routine water analysis in the laboratories of the U.S. Geological Survey for water year 1990: U.S. Geological Survey Water-Resources Investigations Report 93–4082, 145 p.
- ———1994, Quality-assurance results for routine water analysis in U.S. Geological Survey laboratories, water year 1991: U.S. Geological Survey Water-Resources Investigations Report 94–4046, 144 p.

- Peart, D.B., and Sutphin, H.B. 1987, Quality-assurance data for routine water analysis in the laboratories of the U.S. Geological Survey for water year 1984: U.S. Geological Survey Water-Resources Investigations Report 87–4077, 125 p.
- Peart, D.B., and Thomas, Nancy, 1983a, Quality-assurance data for routine water analysis in the laboratories of the U.S. Geological Survey 1981 annual report: U.S. Geological Survey Water-Resources Investigations Report 83–4090, 112 p.
- ————1983b, Quality-assurance data for routine water analysis in the laboratories of the U.S. Geological Survey for water year 1982: U.S. Geological Survey Water-Resources Investigations Report 83–4264, 112 p.

- ———1984, Quality-assurance data for routine water analysis in the laboratories of the U.S. Geological Survey for water year 1983: U.S. Geological Survey Water-Resources Investigations Report 84–4234, 112 p.
- Schroder, L.J., Fishman, M.J., Friedman, L.C., and Darlington, G.W., 1980, The use of standard reference water samples by the U.S. Geological Survey: U.S. Geological Survey Open-File Report 80–738, 11 p.
- Skougstad, M.W., and Fishman, M.J., 1975, Standard reference water samples: American Water Works Association Water Quality Technology Conference, Dallas, 1974, Proceedings, p. XIX-1—XIX-6.
- Taylor, J.K., 1987, Quality assurance of chemical measurements: Chelsea, Mich., Lewis Publishers, 328 p.



		•		

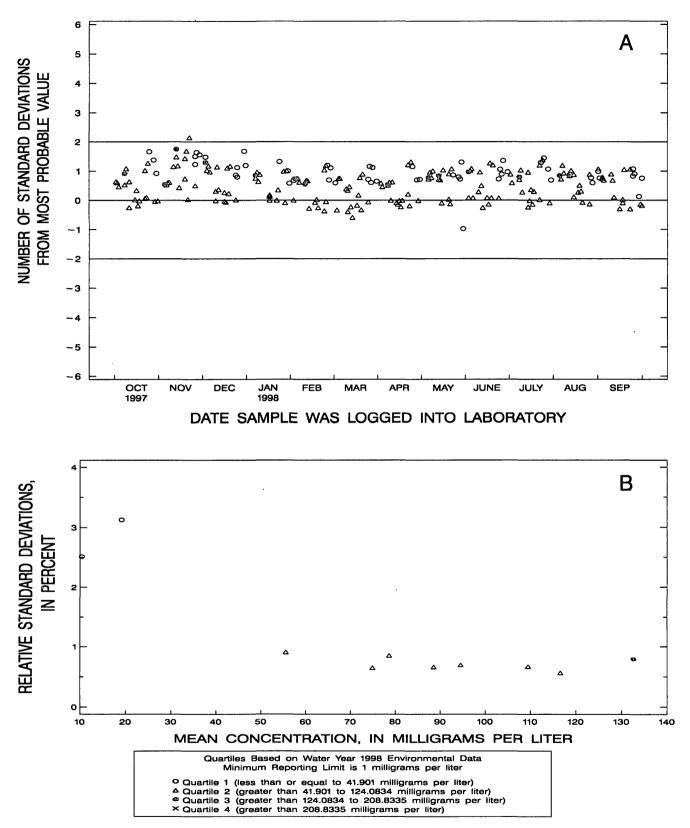


Figure 2. Alkalinity, whole-water recoverable, (electrometric titration) data from the National Water Quality Laboratory.

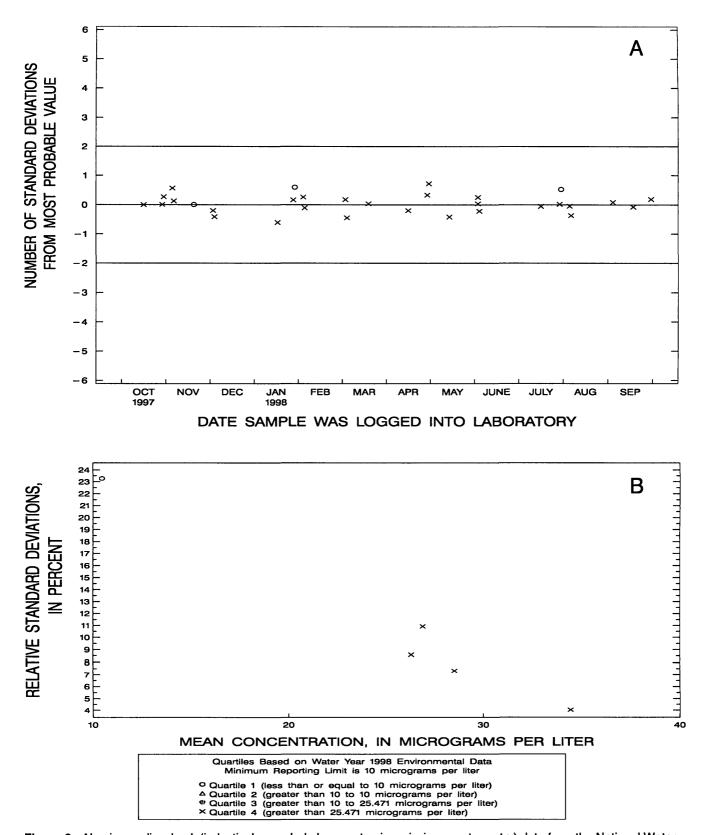


Figure 3. Aluminum, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

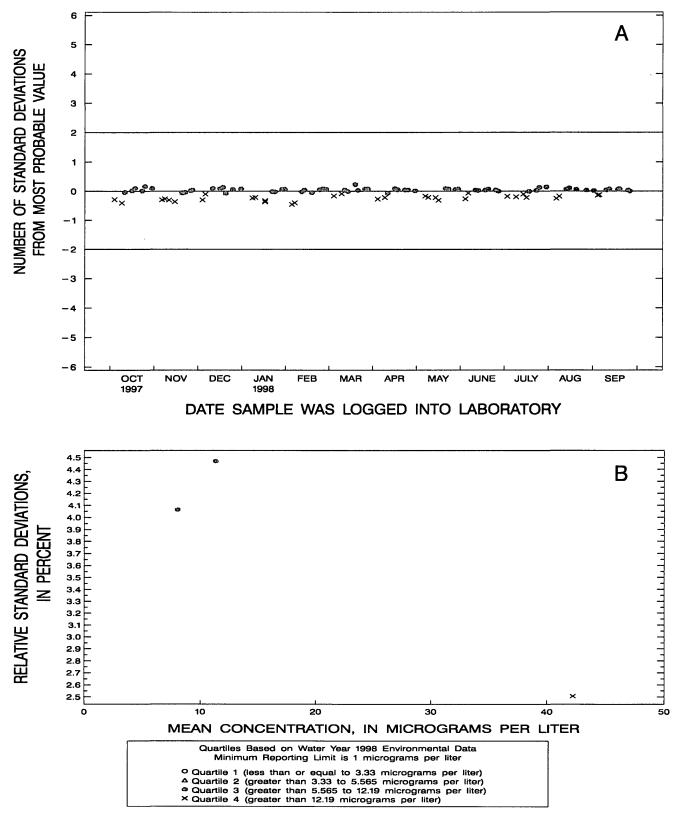


Figure 4. Aluminum, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

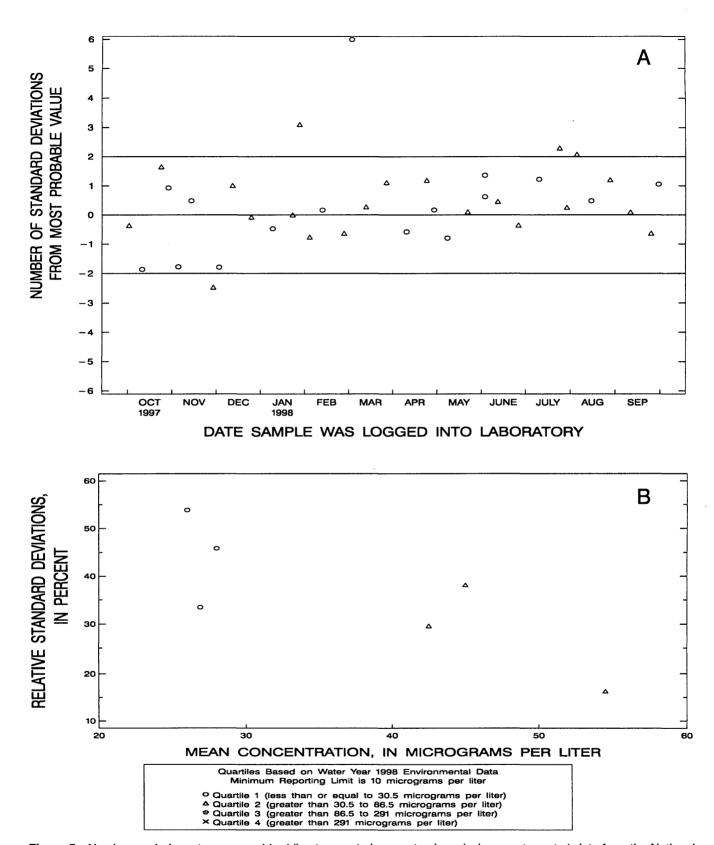


Figure 5. Aluminum, whole-water recoverable, (direct current plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

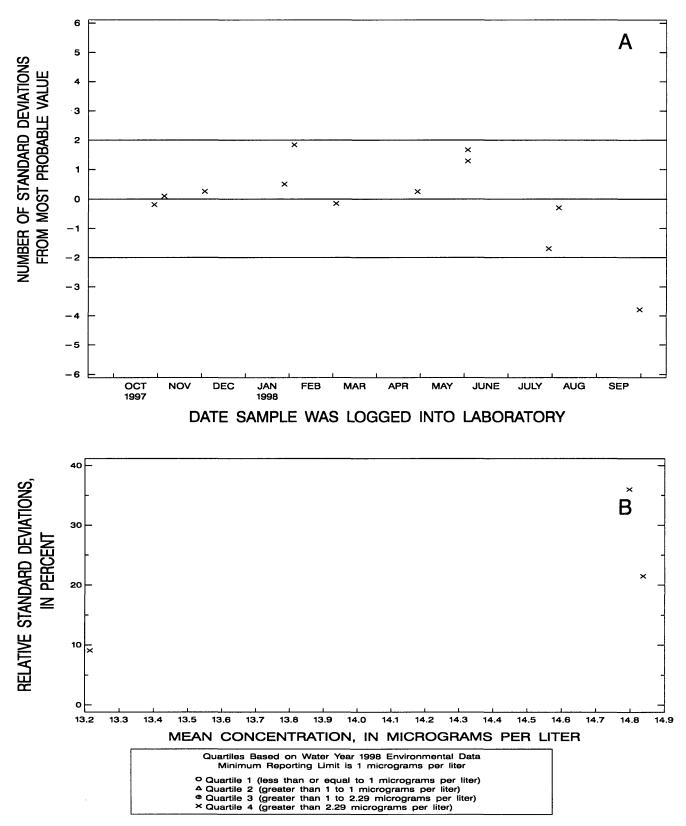


Figure 6. Antimony, dissolved, (hydride generation-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

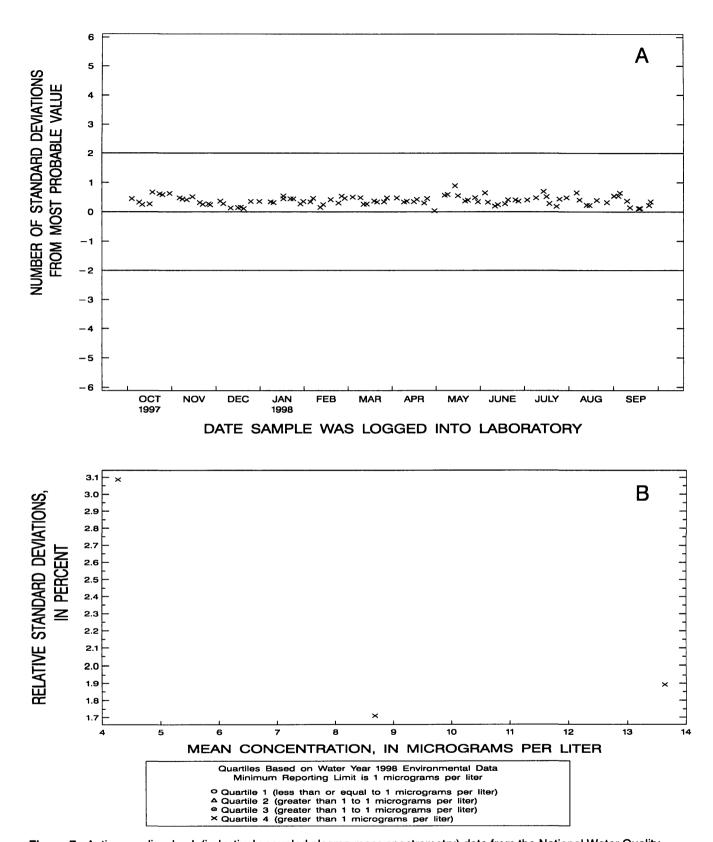


Figure 7. Antimony, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

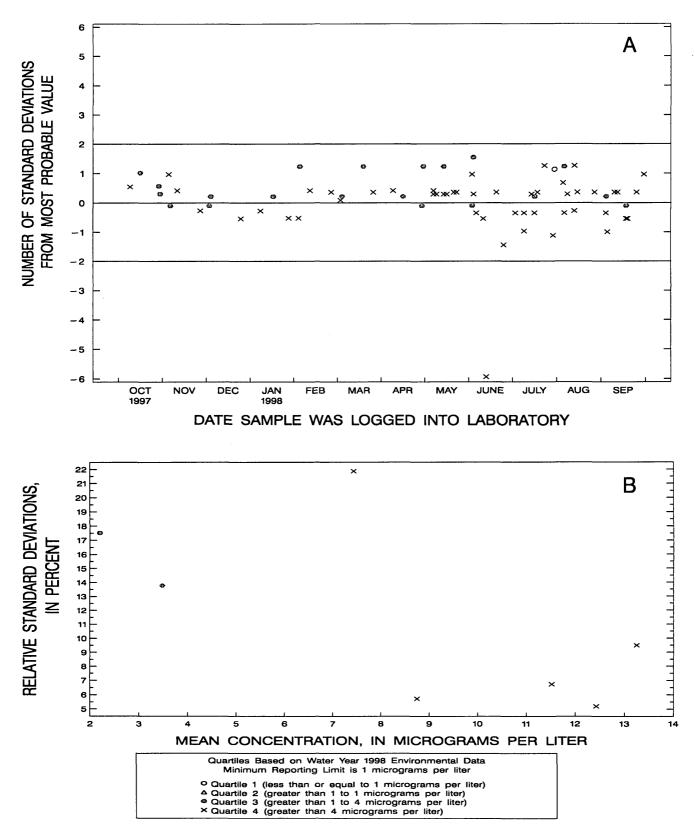


Figure 8. Arsenic, dissolved, (hydride generation-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

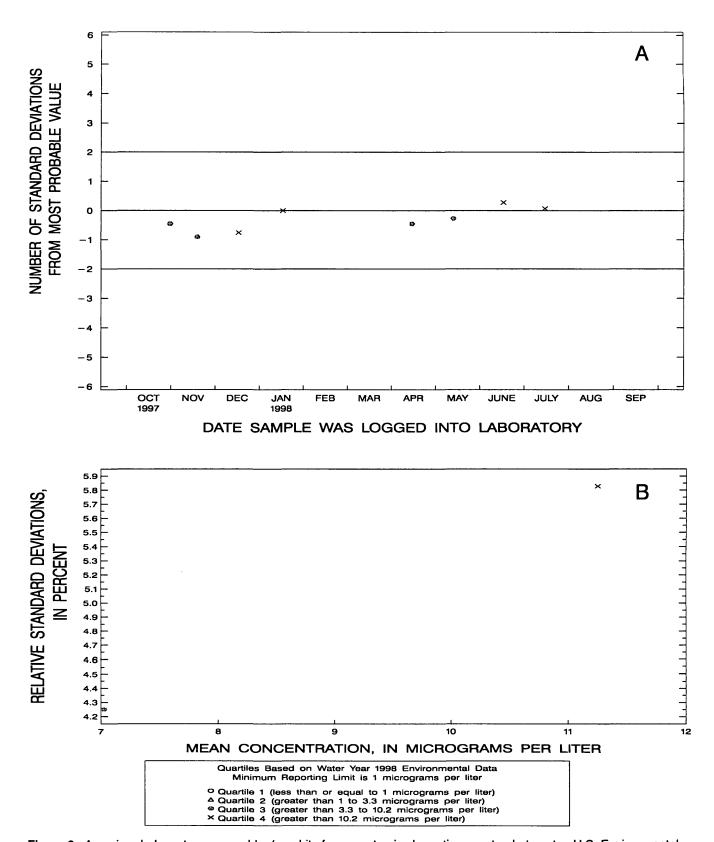


Figure 9. Arsenic, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry, U.S. Environmental Protection Agency) data from the National Water Quality Laboratory.

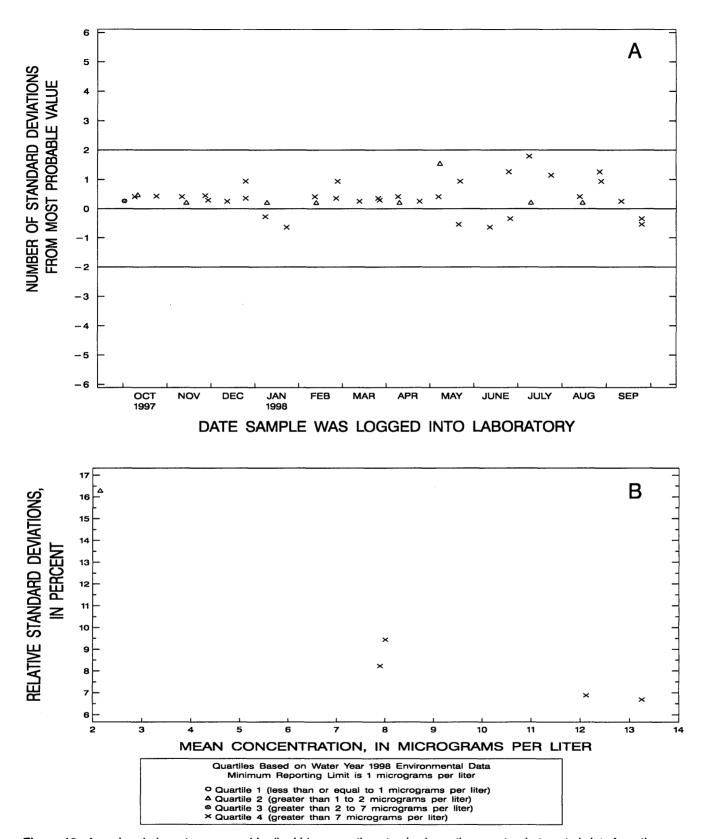


Figure 10. Arsenic, whole-water recoverable, (hydride generation-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

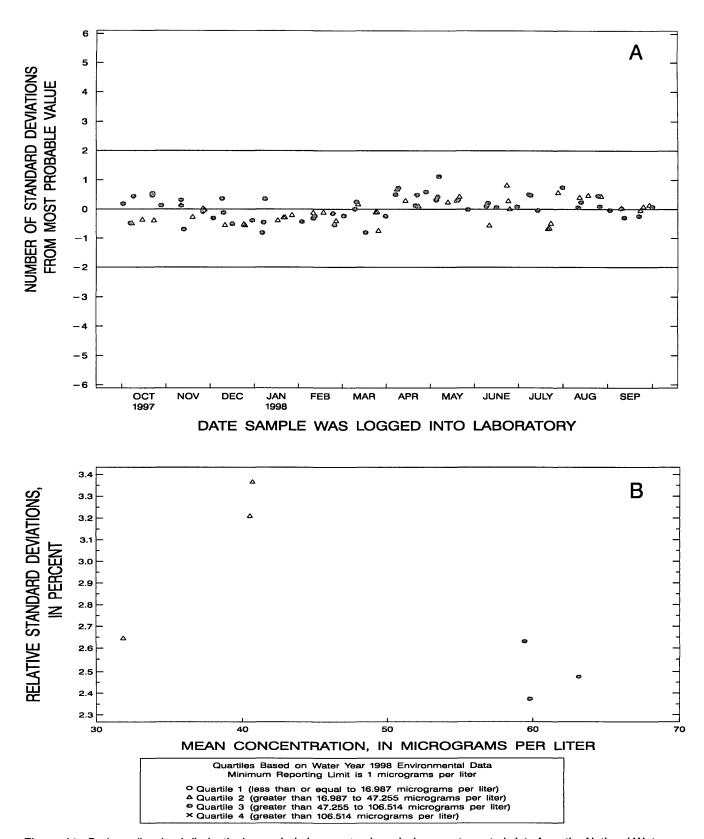


Figure 11. Barium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

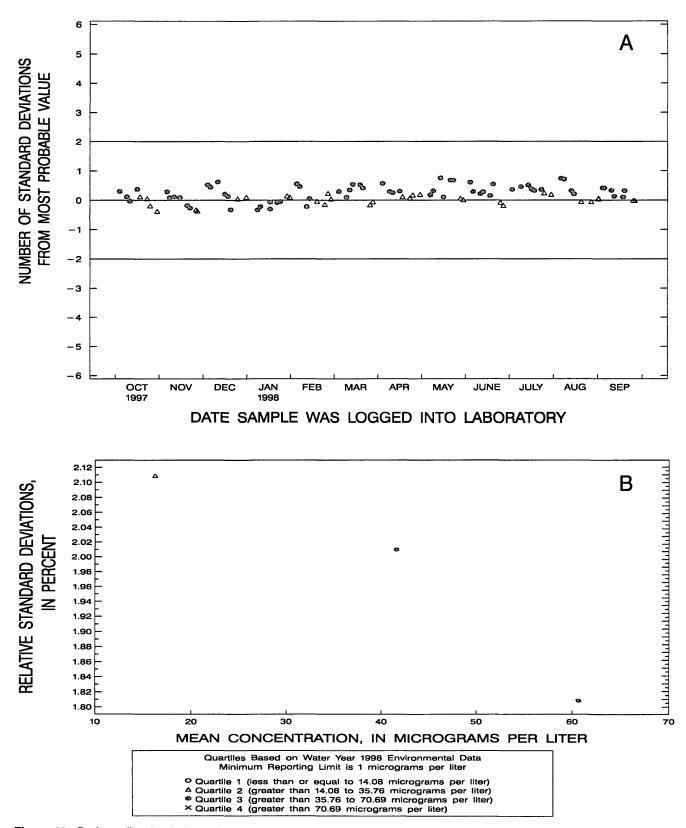


Figure 12. Barium, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

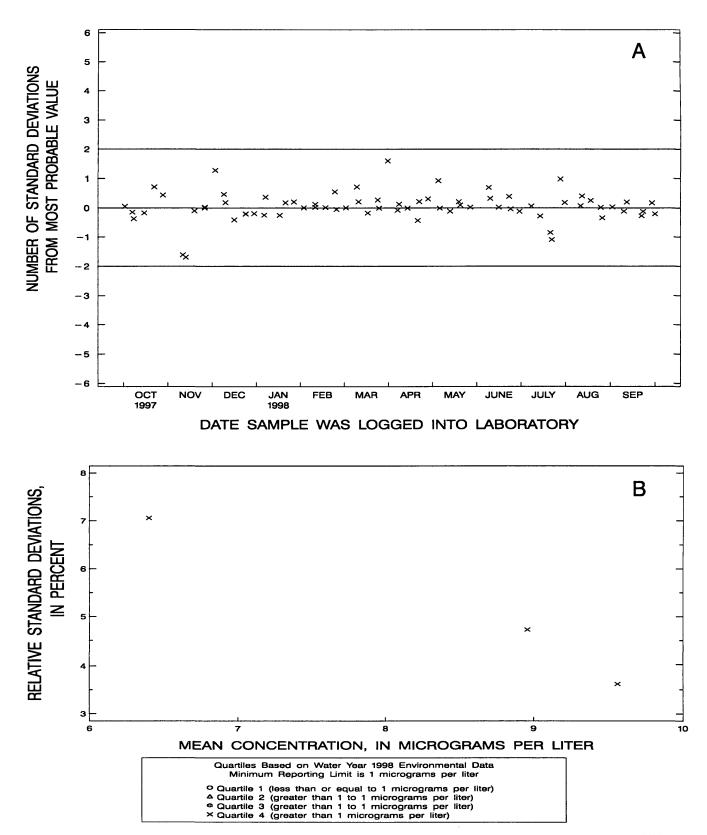


Figure 13. Beryllium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

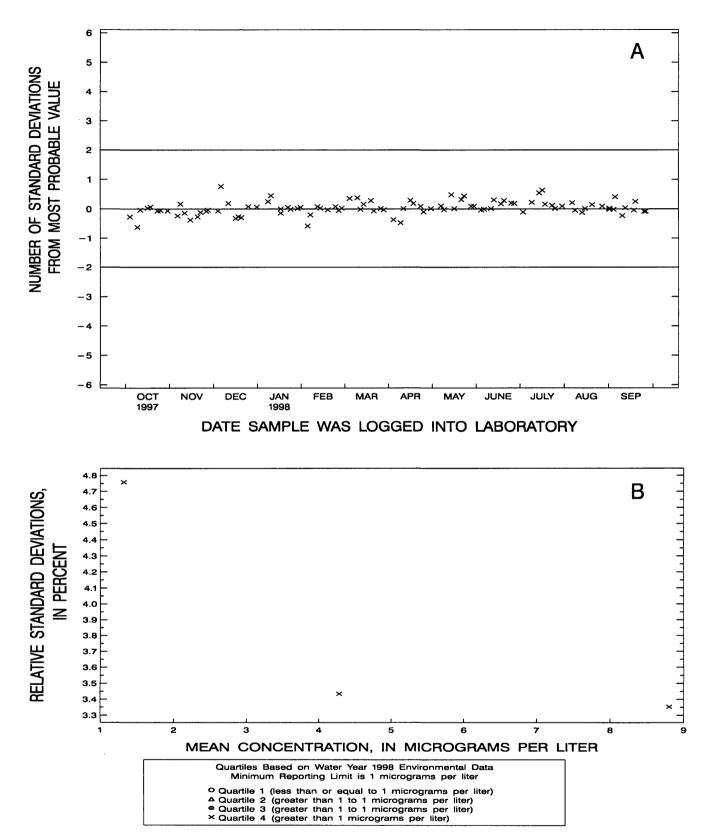


Figure 14. Beryllium, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

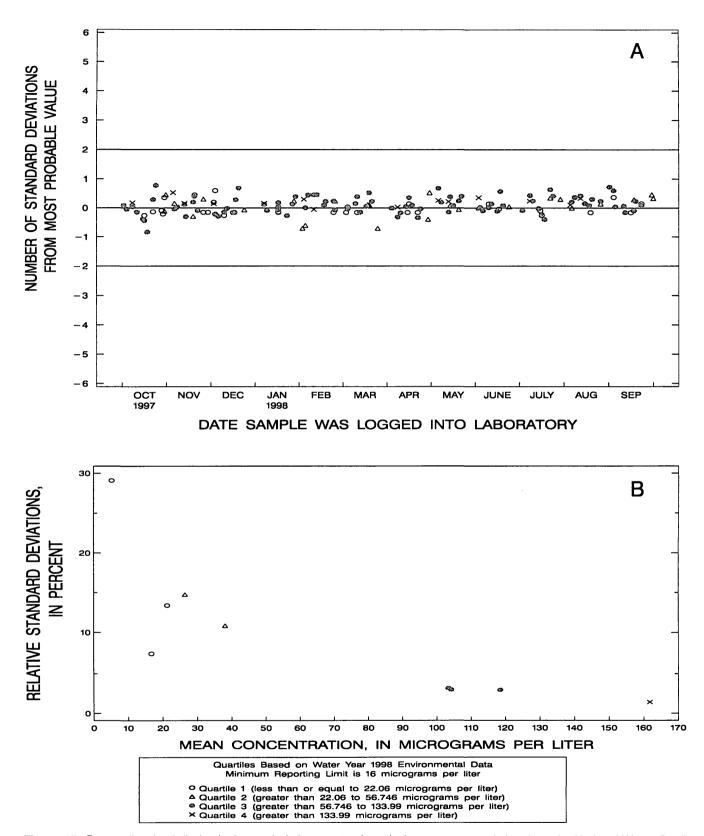


Figure 15. Boron, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

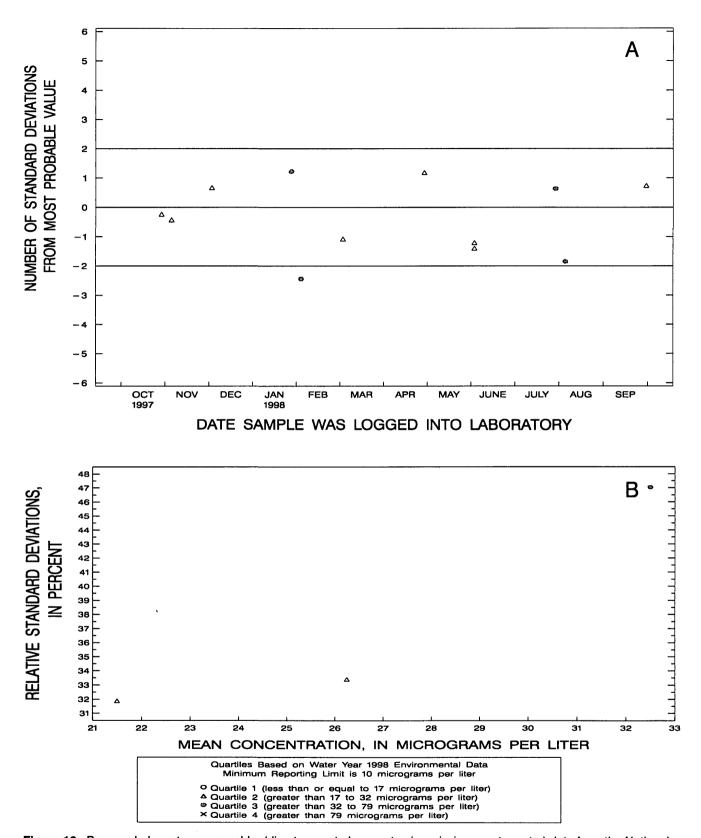


Figure 16. Boron, whole-water recoverable, (direct current plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

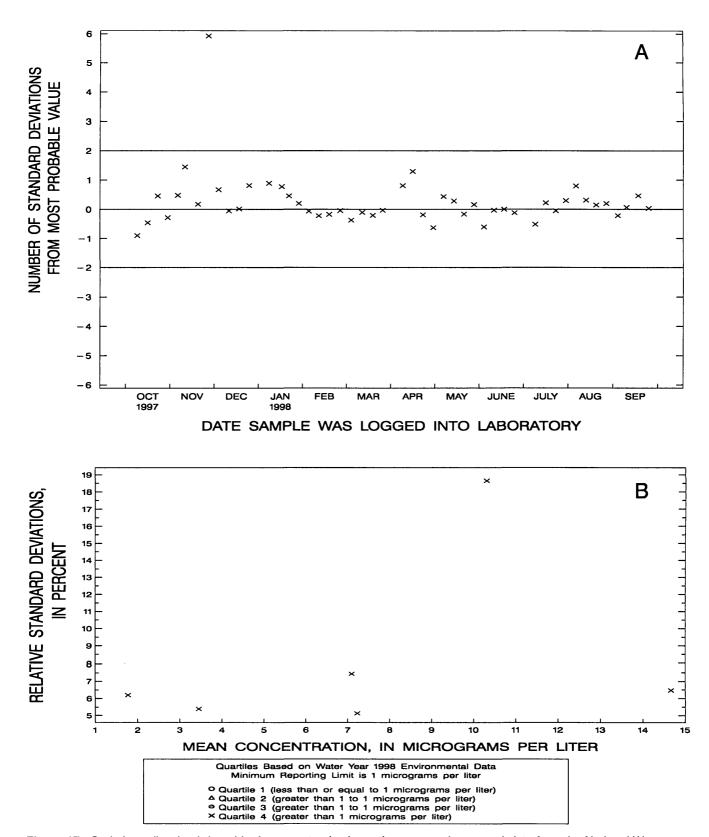


Figure 17. Cadmium, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

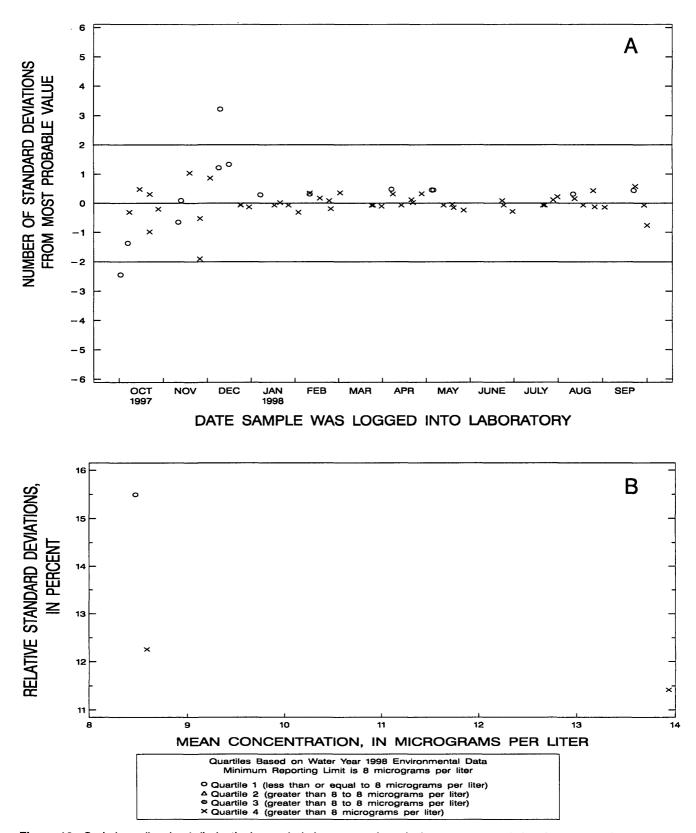


Figure 18. Cadmium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

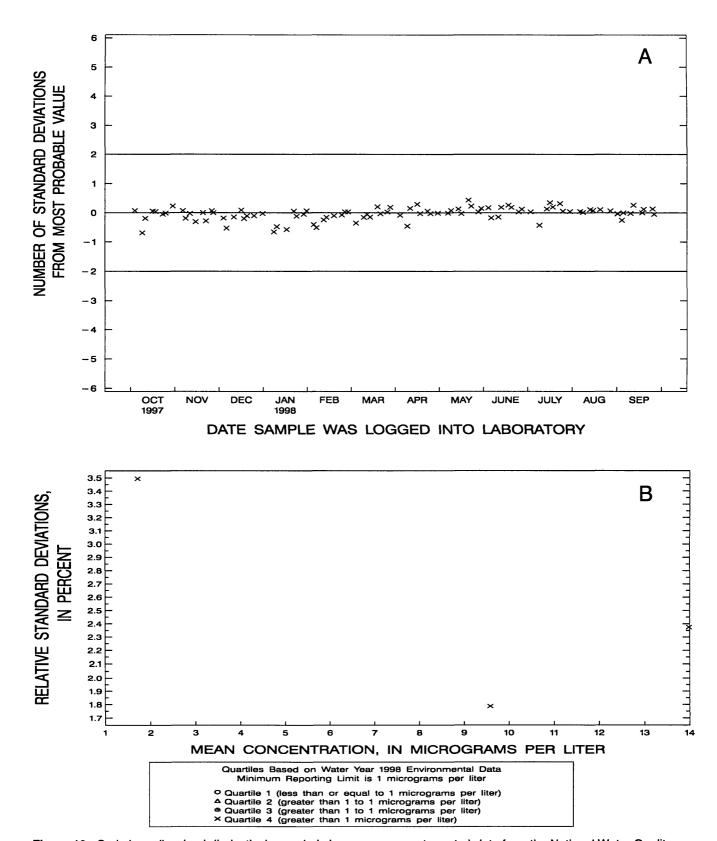


Figure 19. Cadmium, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

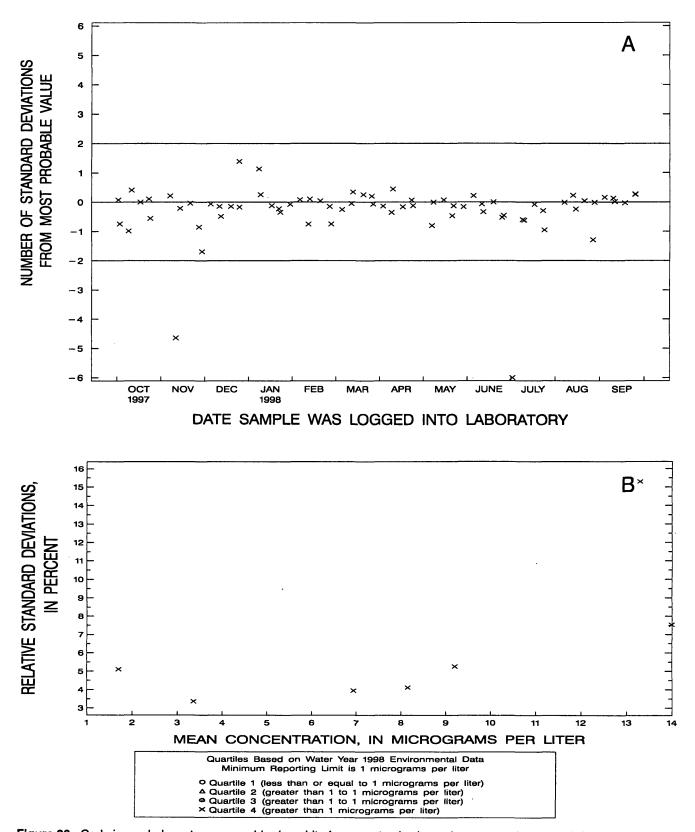


Figure 20. Cadmium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

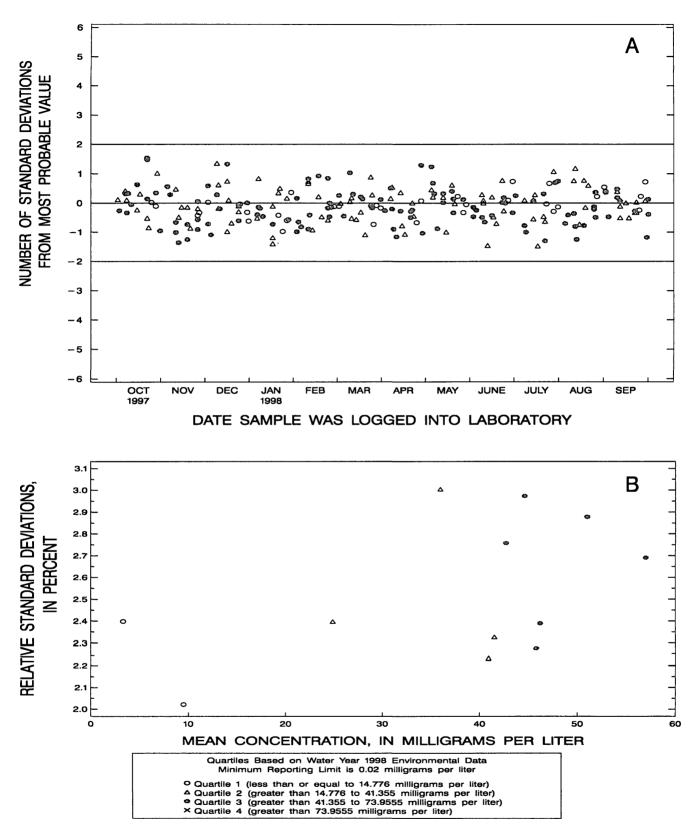


Figure 21. Calcium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

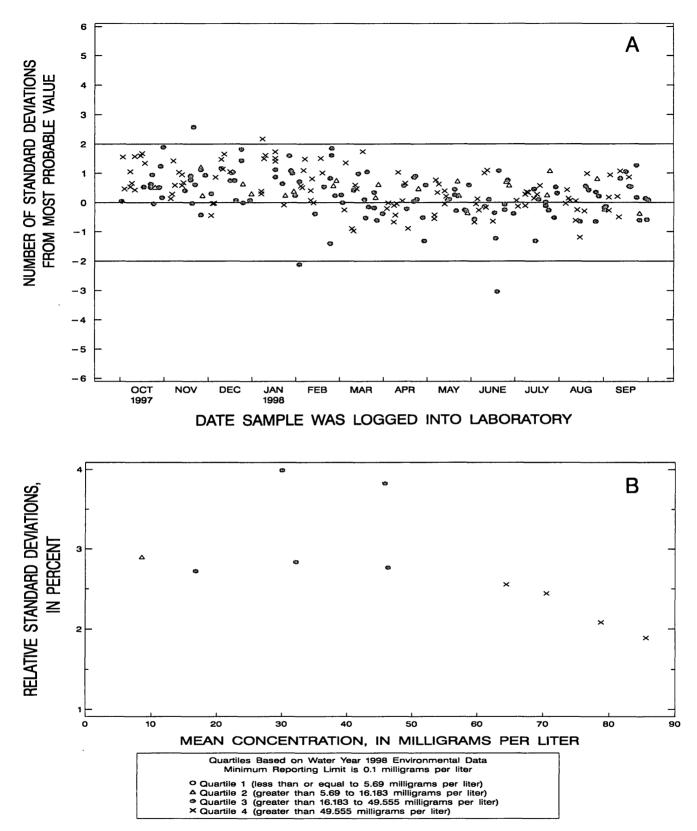


Figure 22. Chloride, dissolved, (ion chromatography) data from the National Water Quality Laboratory.

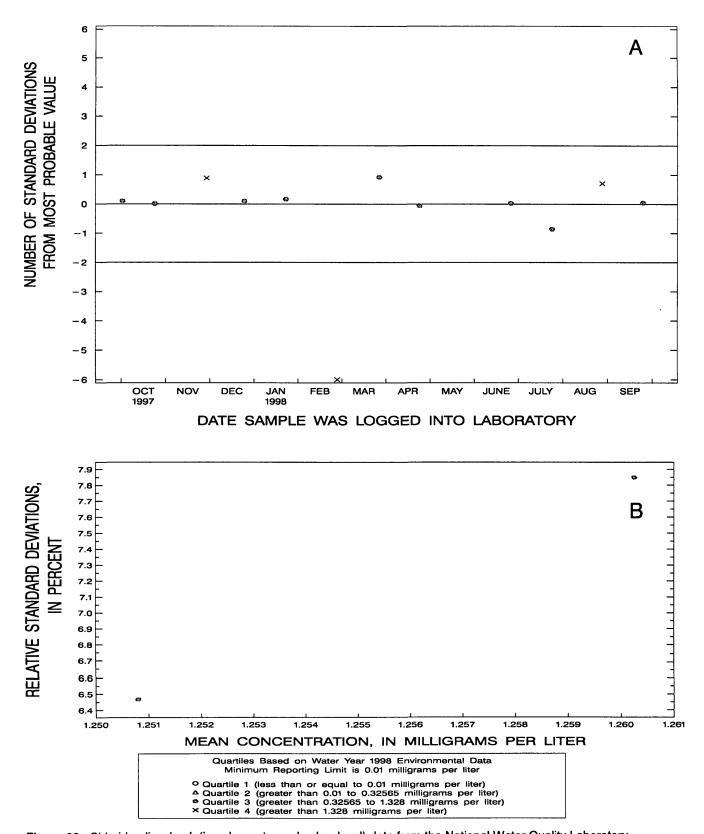


Figure 23. Chloride, dissolved, (ion chromatography, low level) data from the National Water Quality Laboratory.

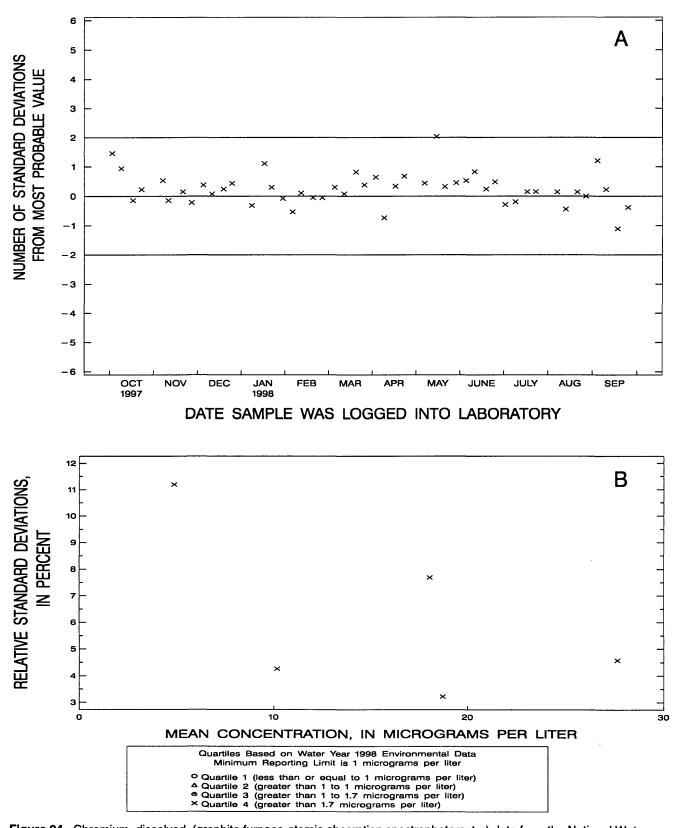


Figure 24. Chromium, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

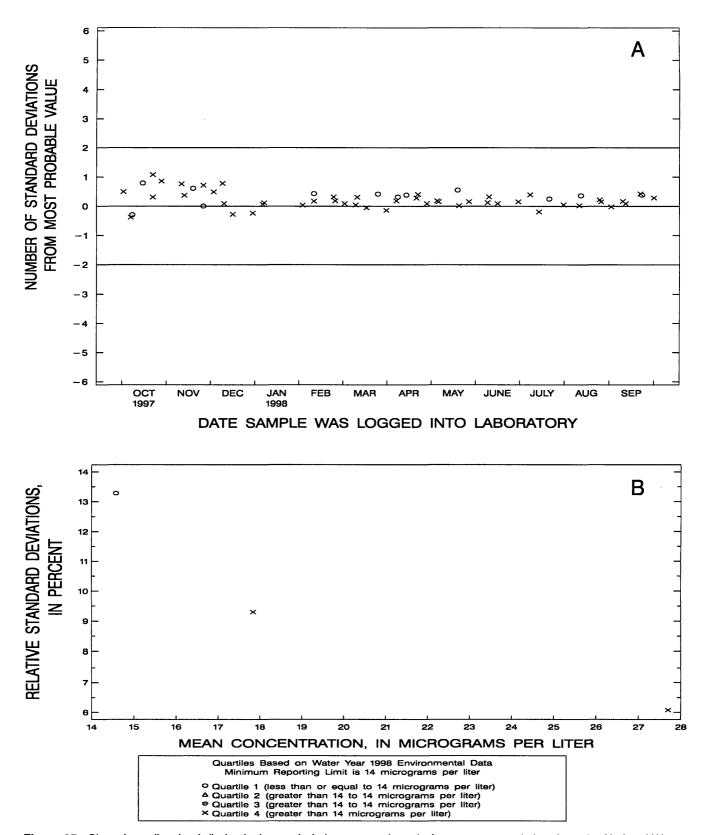


Figure 25. Chromium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

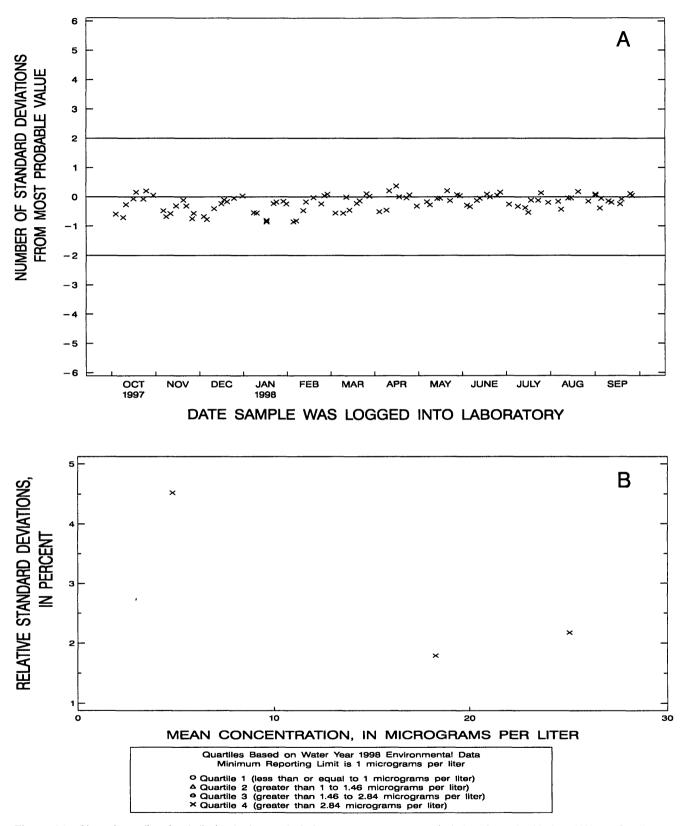


Figure 26. Chromium, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

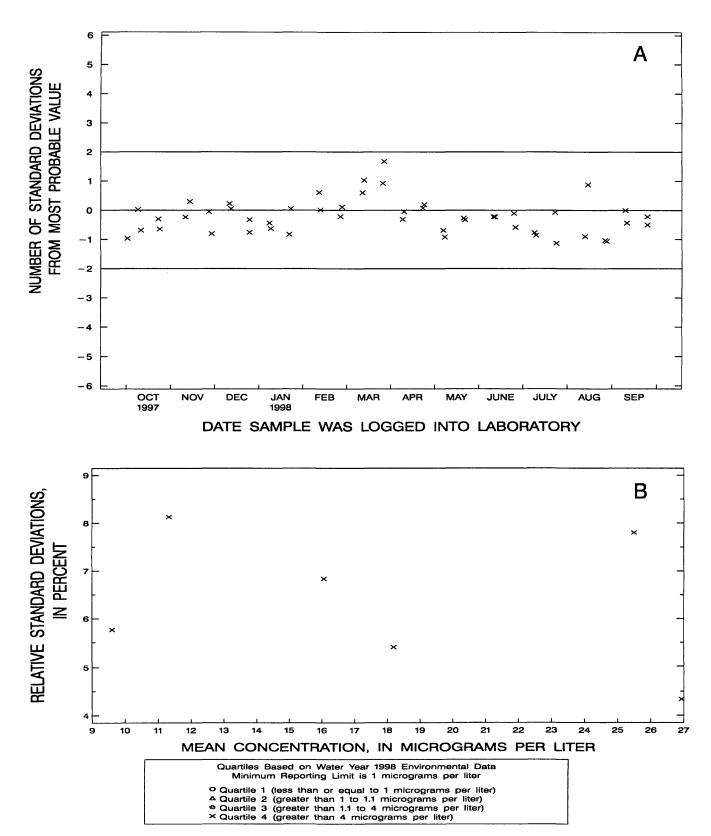


Figure 27. Chromium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

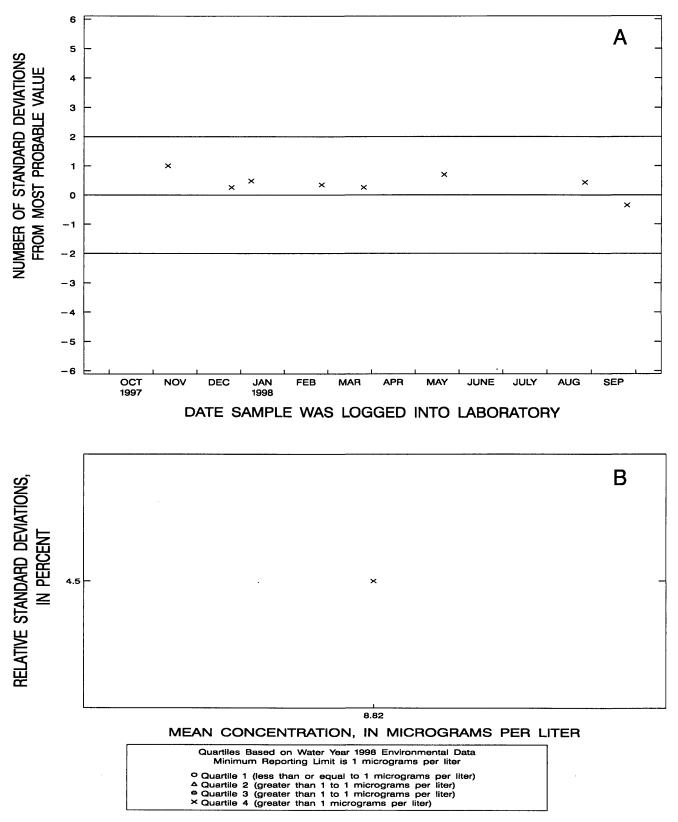


Figure 28. Cobalt, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

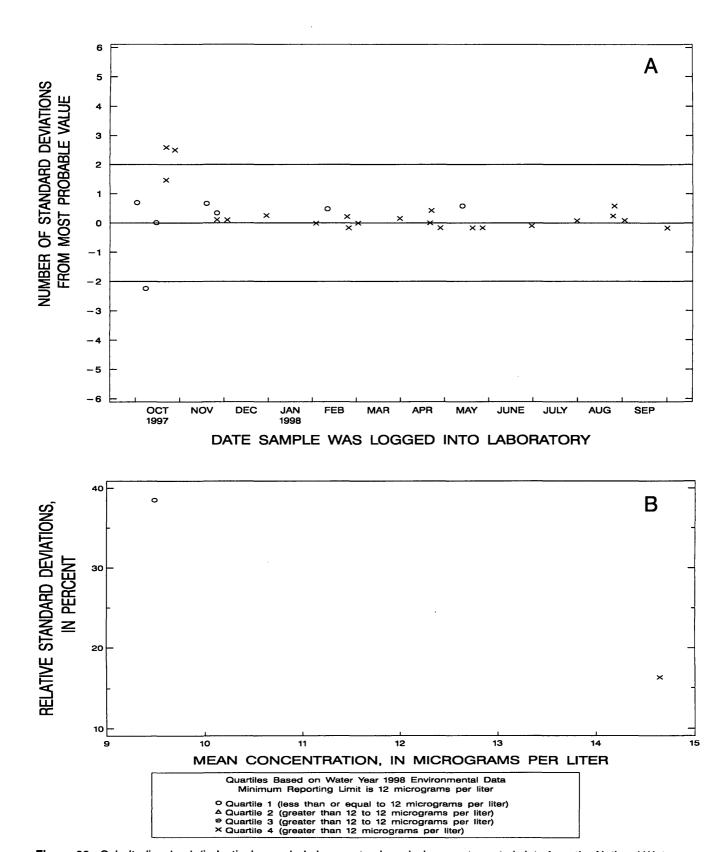


Figure 29. Cobalt, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

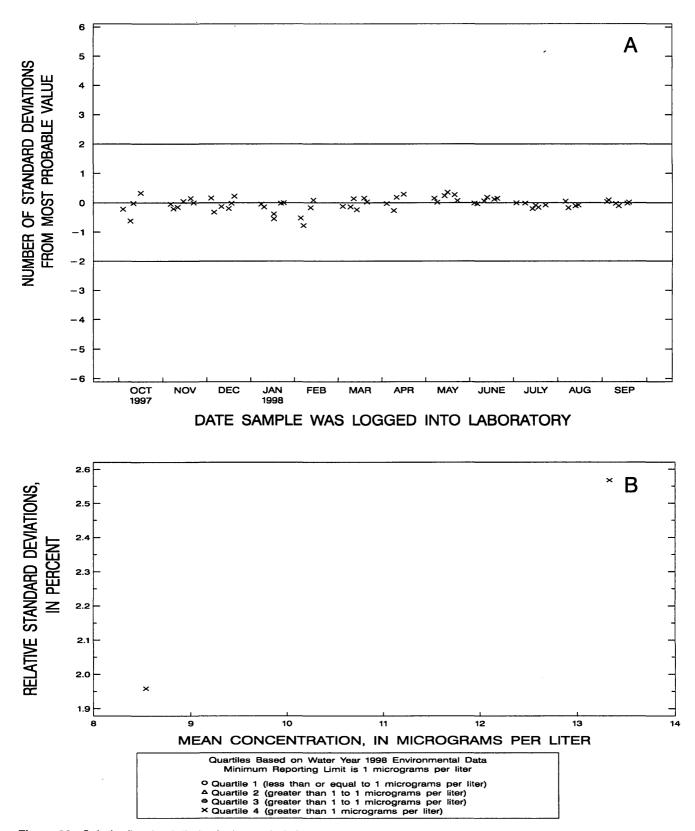


Figure 30. Cobalt, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

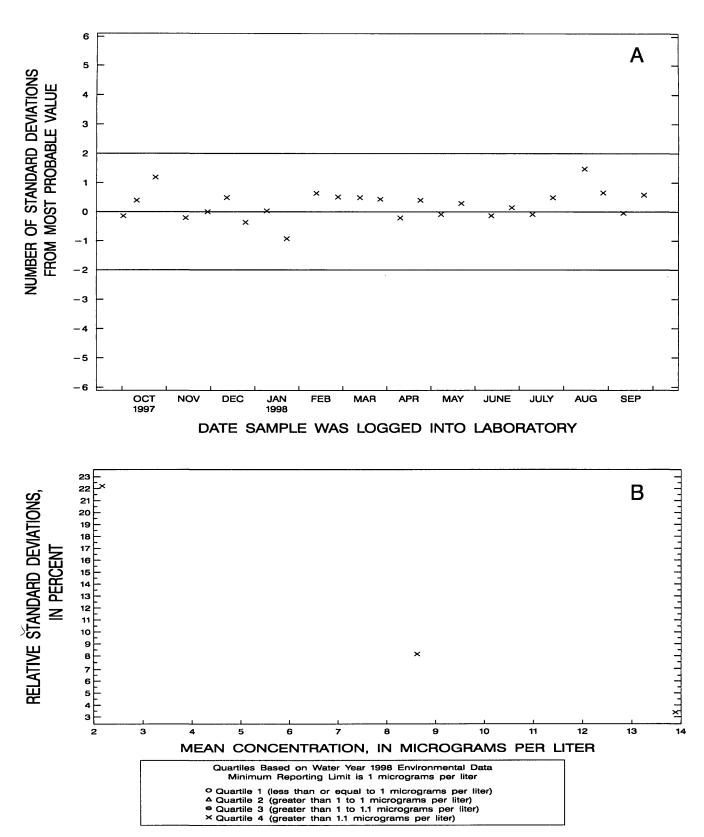


Figure 31. Cobalt, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

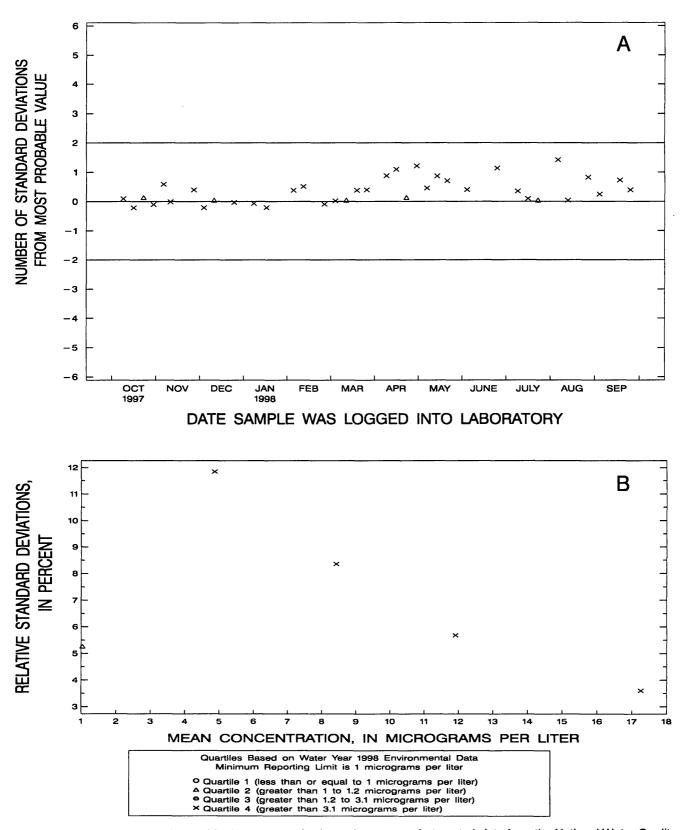


Figure 32. Copper, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

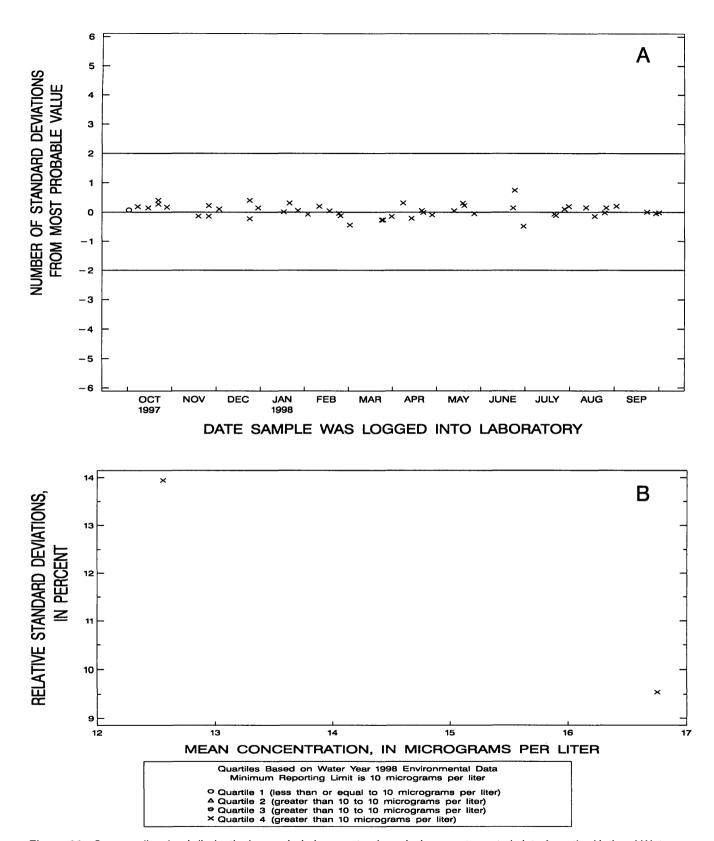


Figure 33. Copper, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

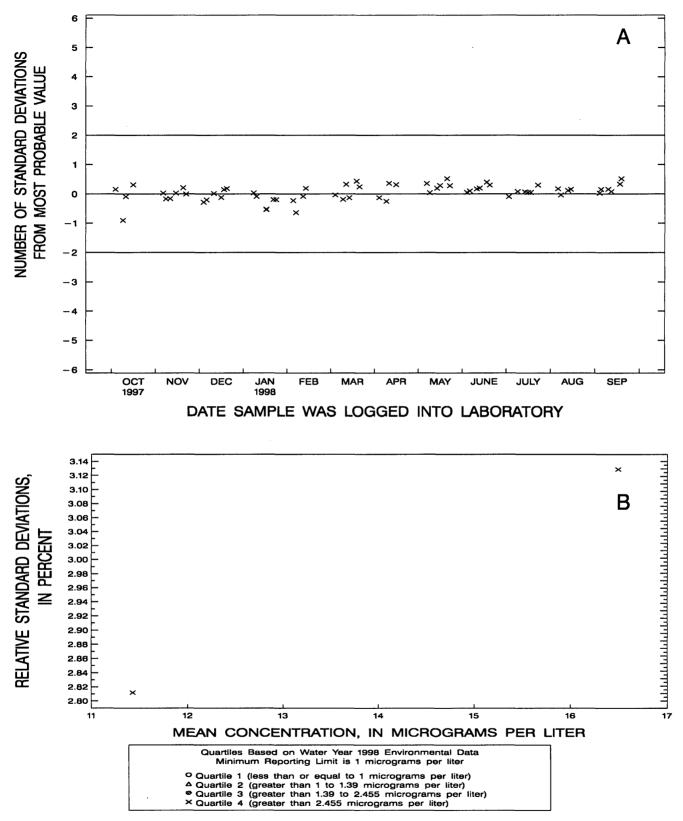


Figure 34. Copper, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

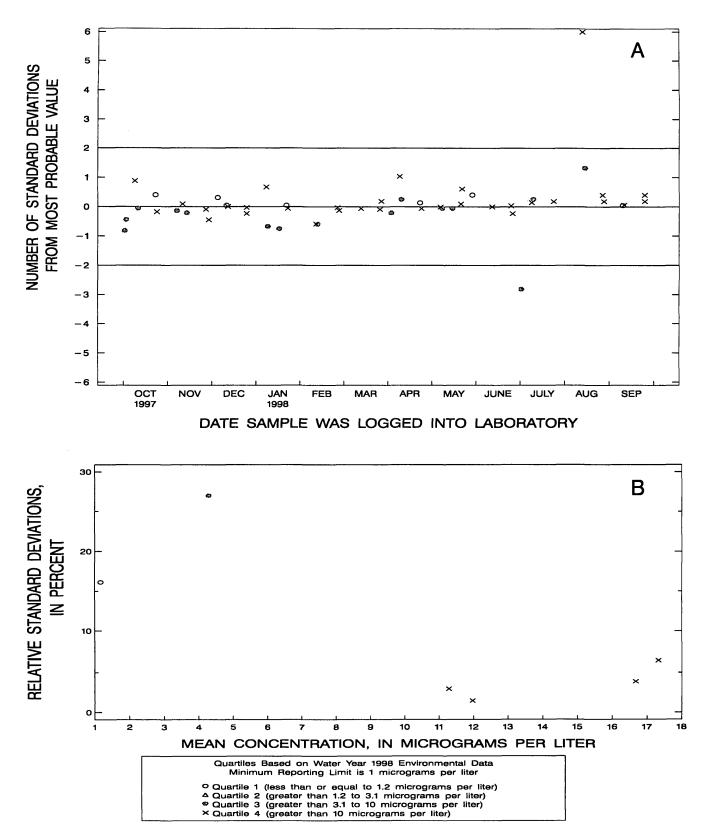


Figure 35. Copper, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

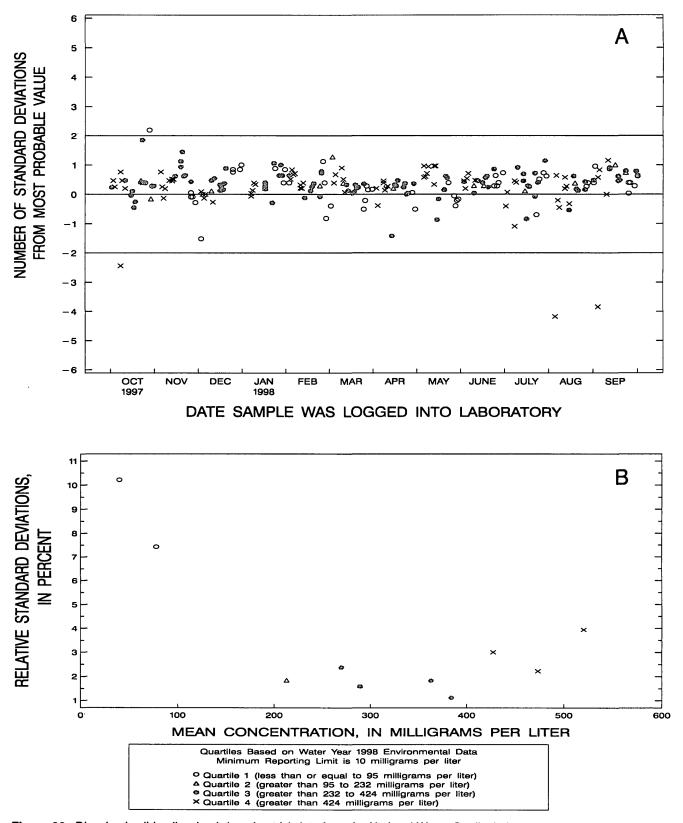


Figure 36. Dissolved solids, dissolved, (gravimetric) data from the National Water Quality Laboratory.

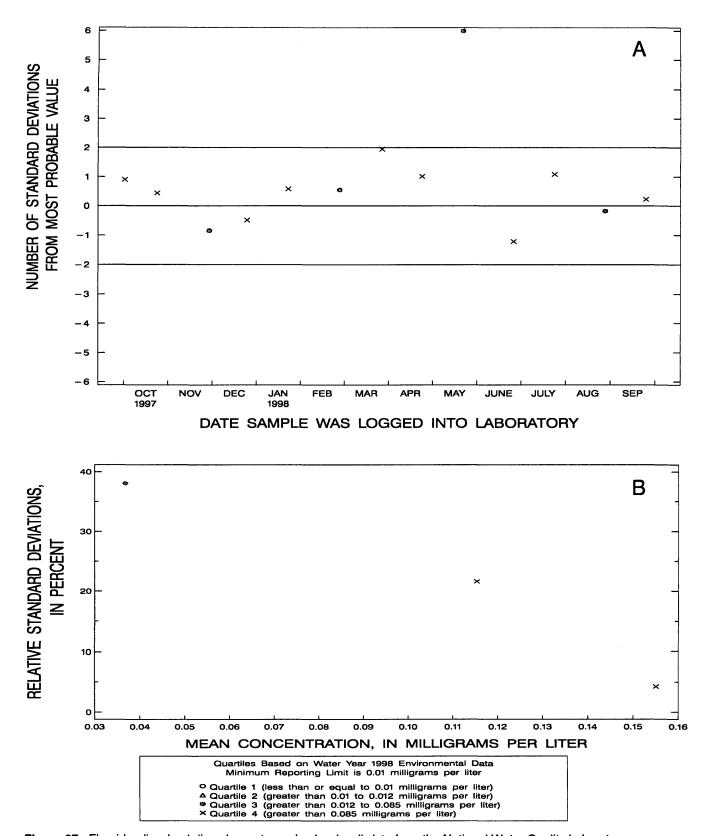


Figure 37. Fluoride, dissolved, (ion chromatography, low level) data from the National Water Quality Laboratory.

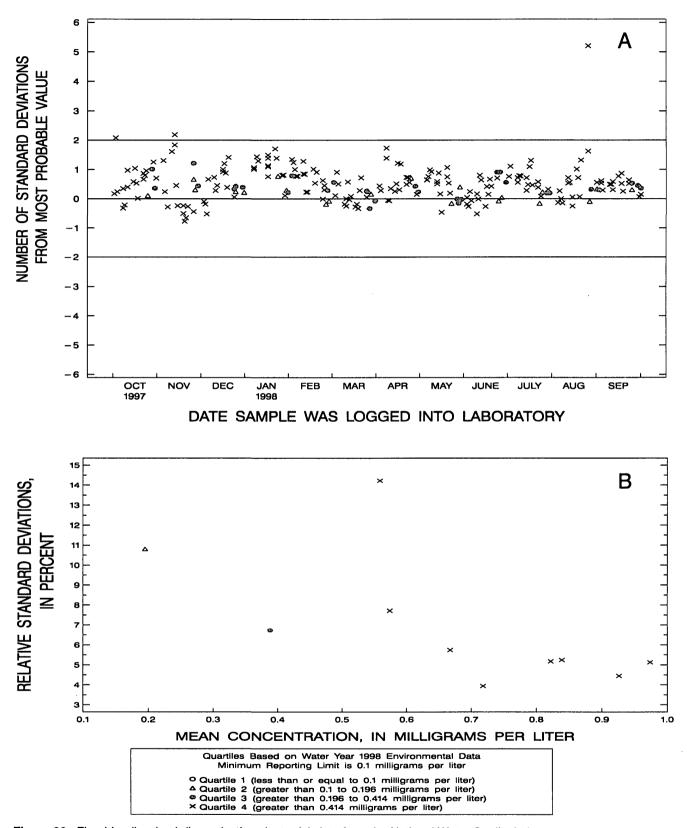


Figure 38. Fluoride, dissolved, (ion-selective electrode) data from the National Water Quality Laboratory.

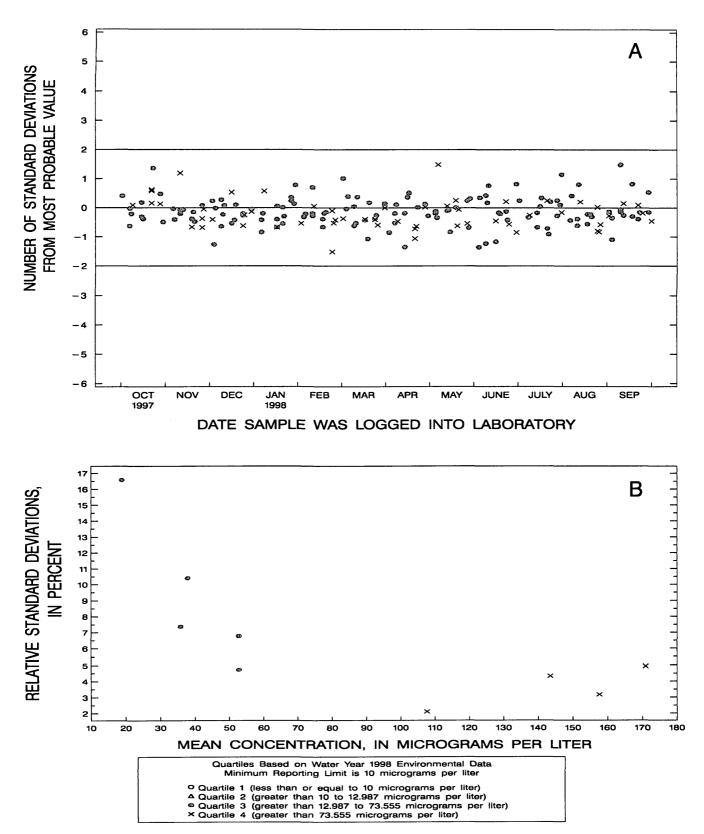


Figure 39. Iron, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

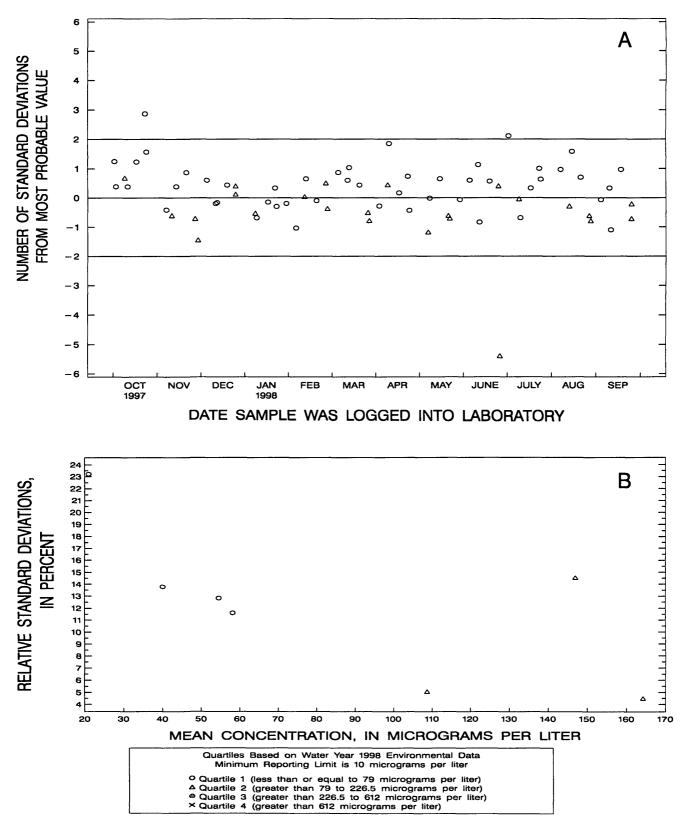


Figure 40. Iron, whole-water recoverable, (flame-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

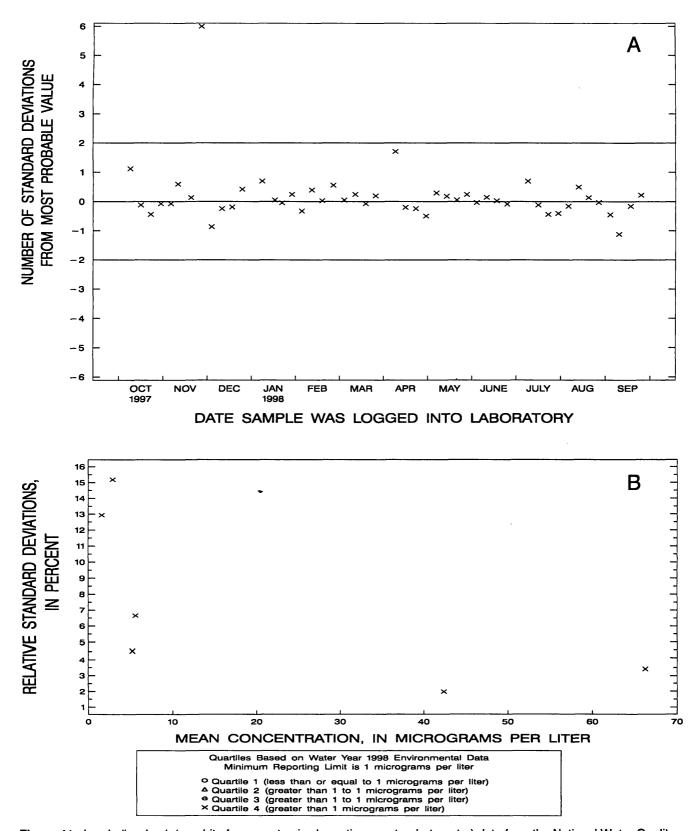


Figure 41. Lead, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

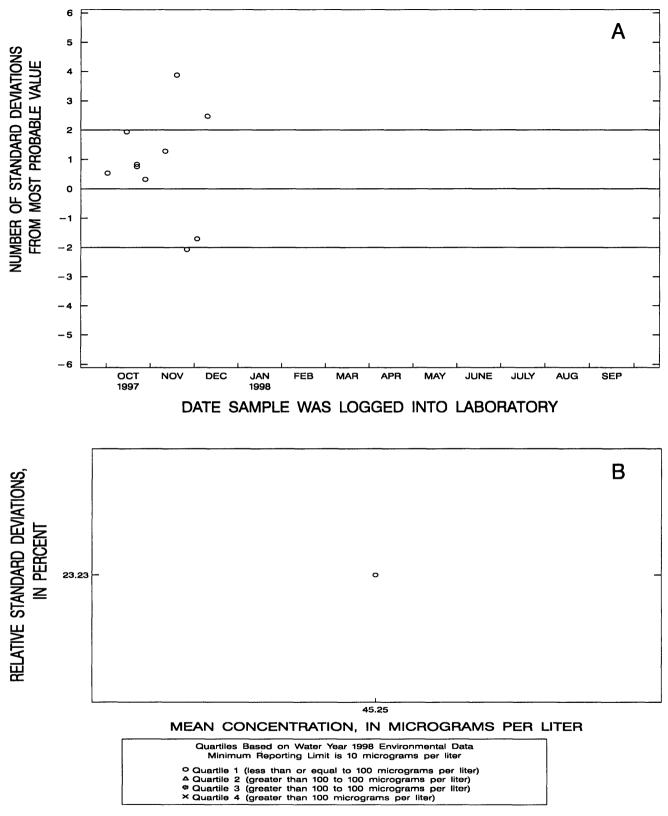


Figure 42. Lead, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

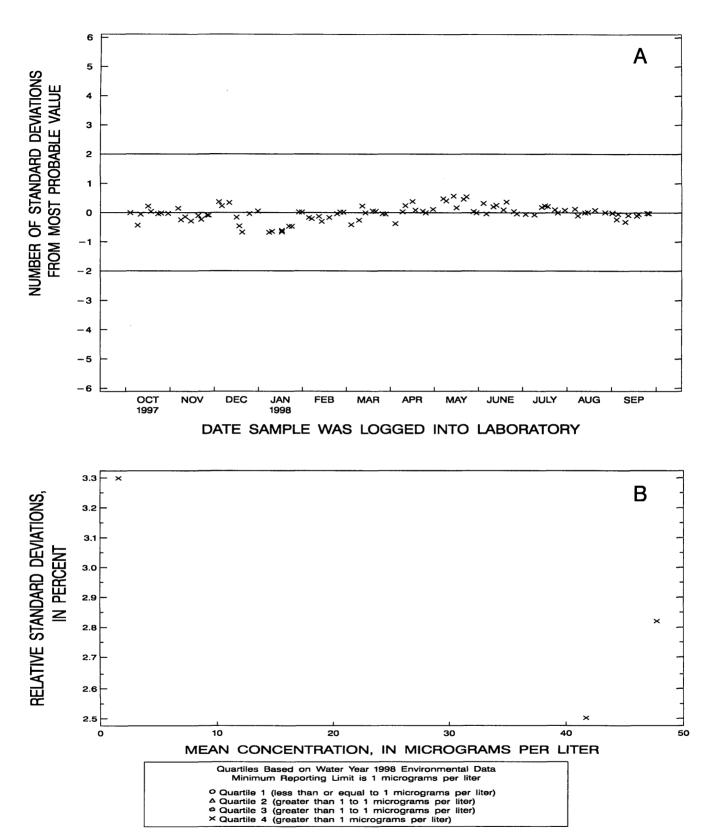


Figure 43. Lead, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

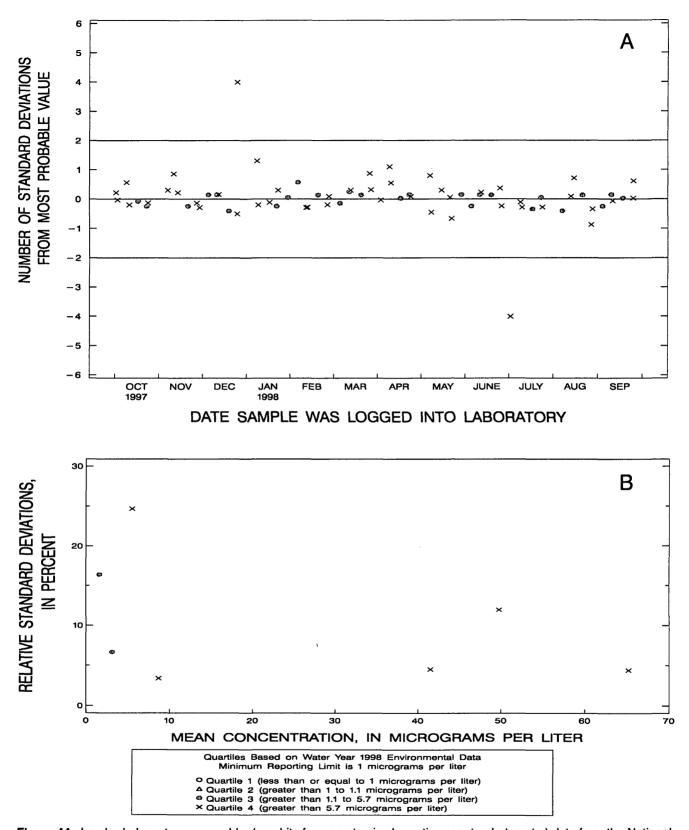


Figure 44. Lead, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

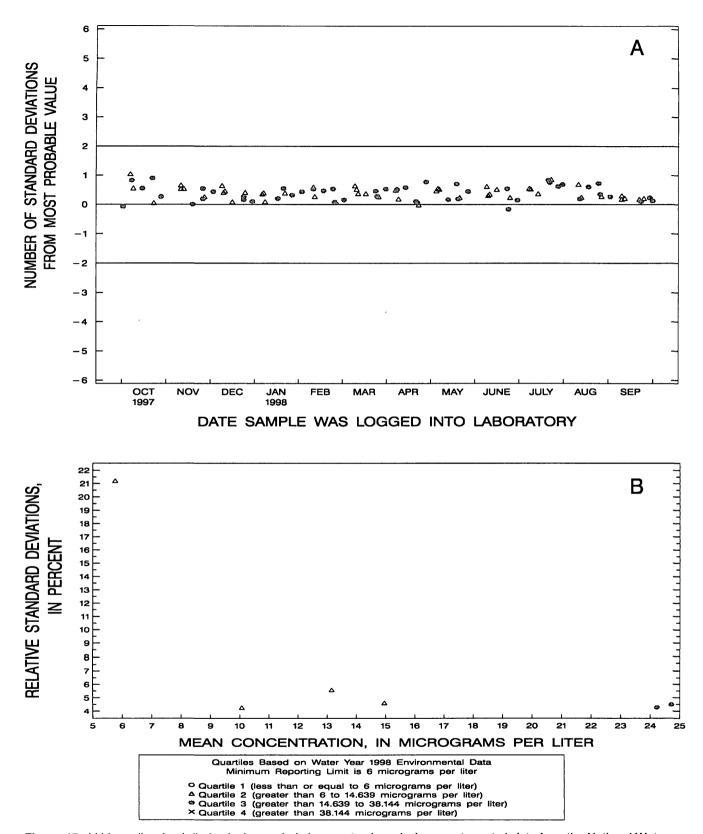


Figure 45. Lithium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

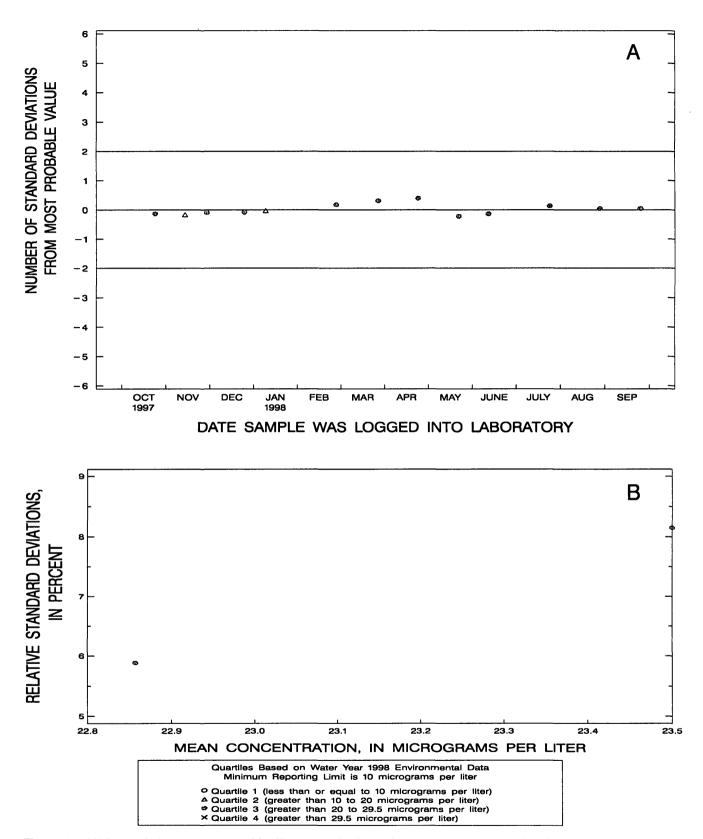


Figure 46. Lithium, whole-water recoverable, (flame-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

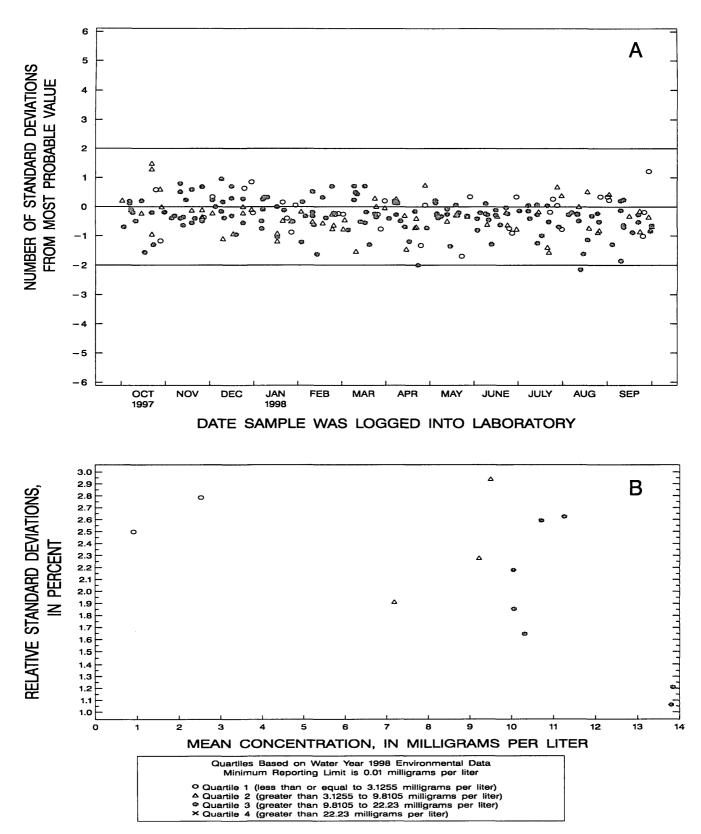


Figure 47. Magnesium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

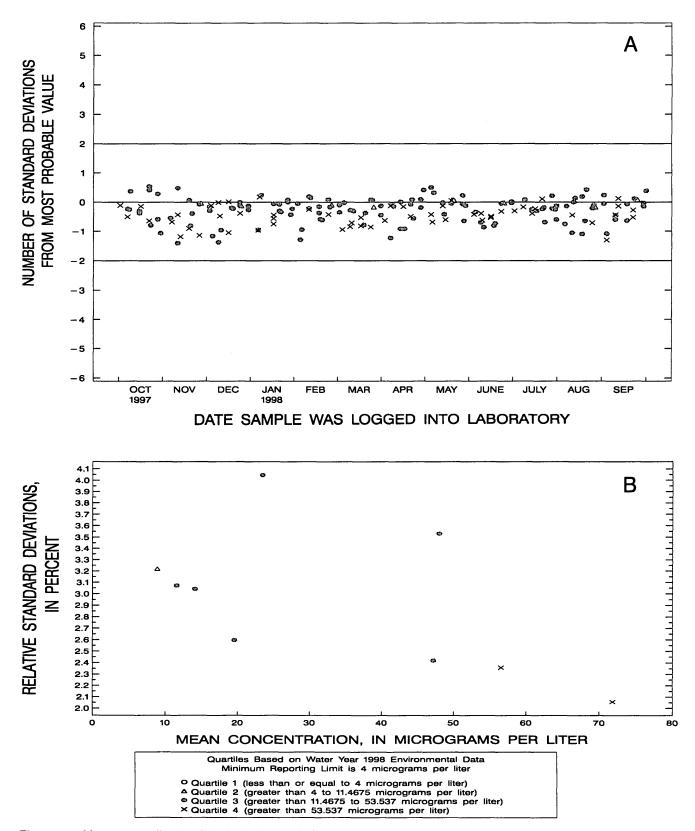


Figure 48. Manganese, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

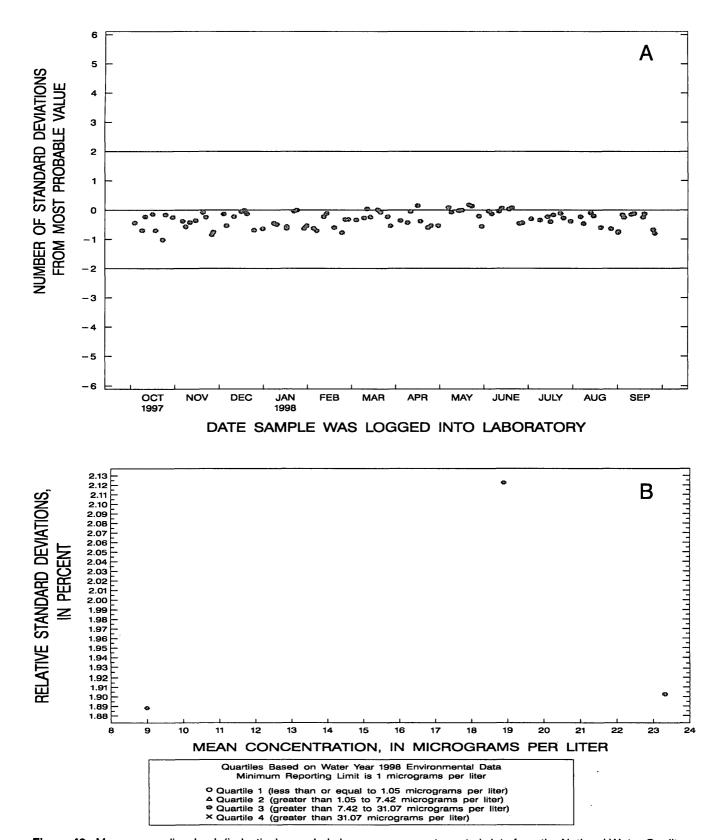


Figure 49. Manganese, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

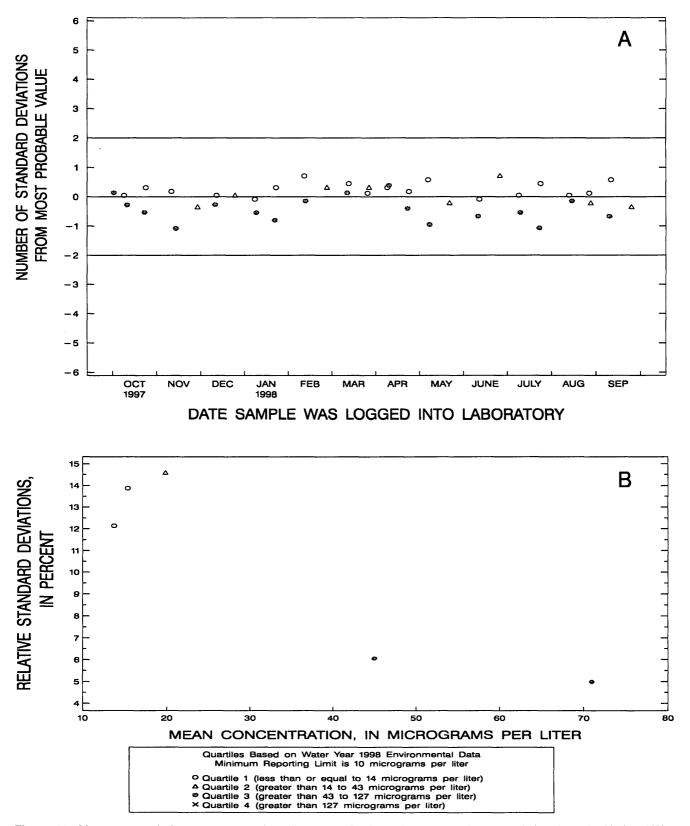


Figure 50. Manganese, whole-water recoverable, (flame-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

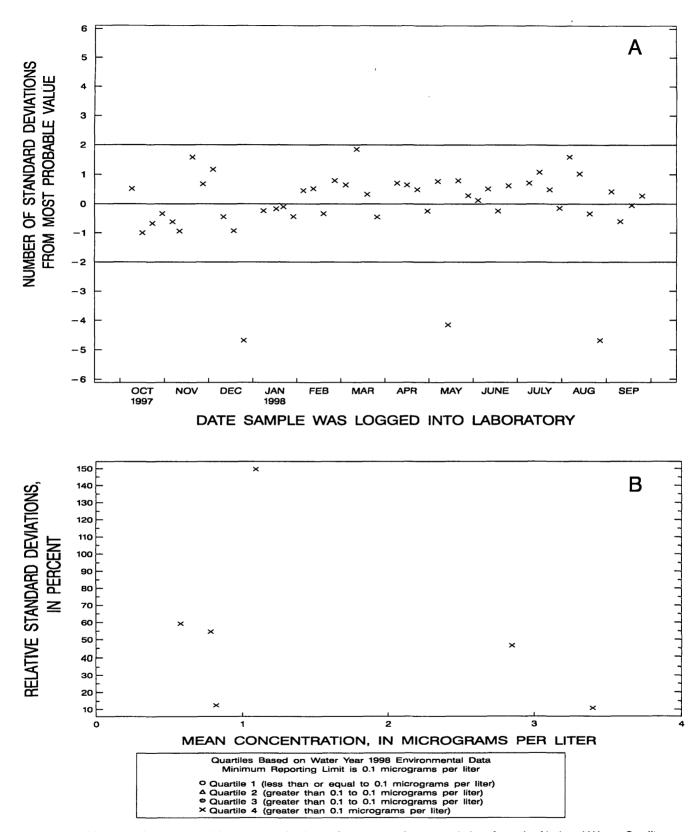


Figure 51. Mercury, dissolved, (cold vapor-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

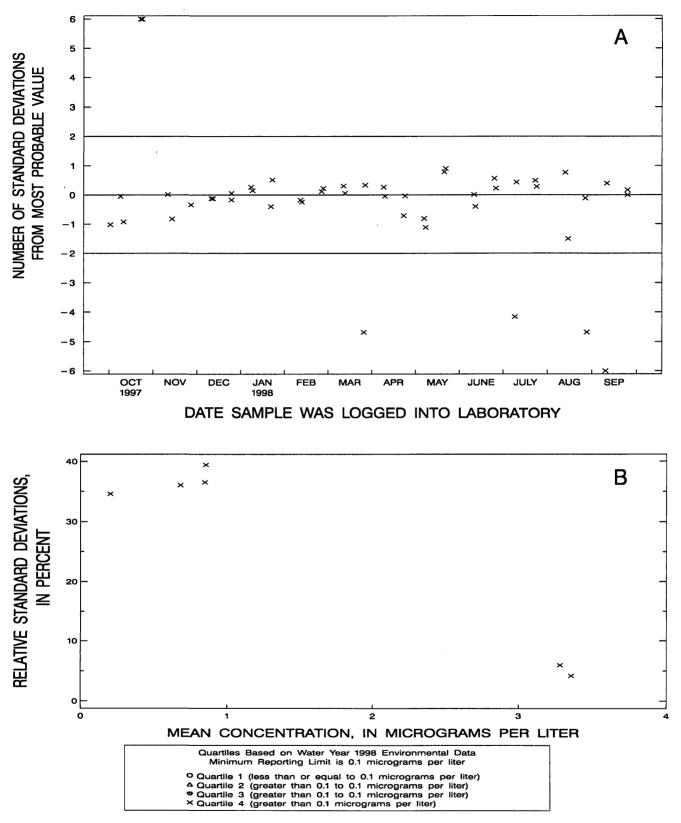


Figure 52. Mercury, whole-water recoverable, (cold vapor-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

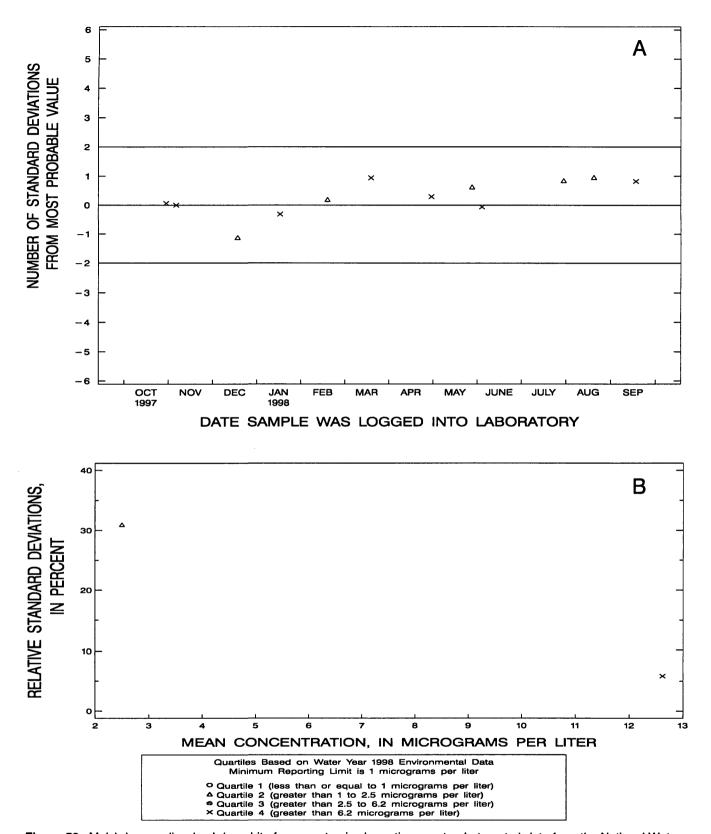


Figure 53. Molybdenum, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

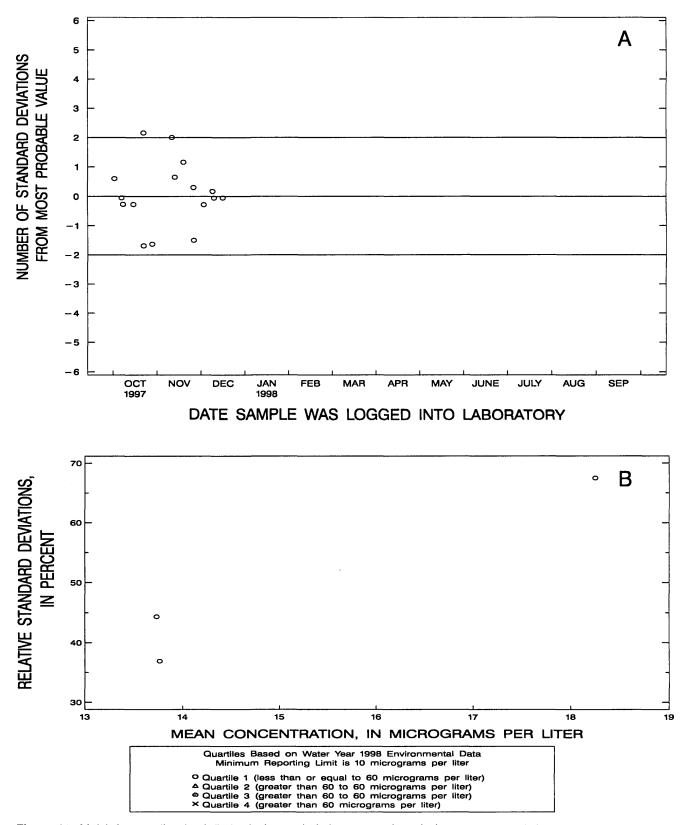


Figure 54. Molybdenum, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

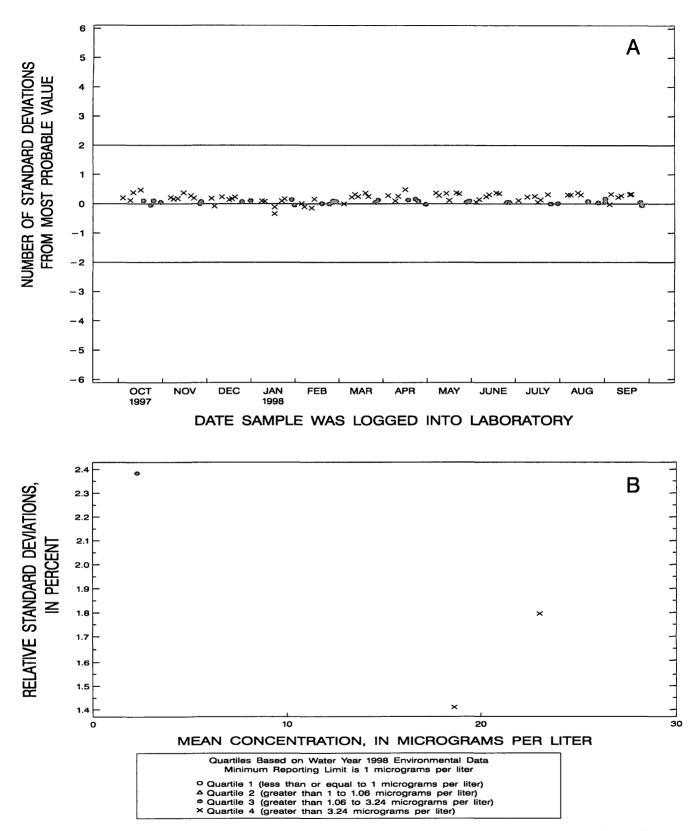


Figure 55. Molybdenum, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

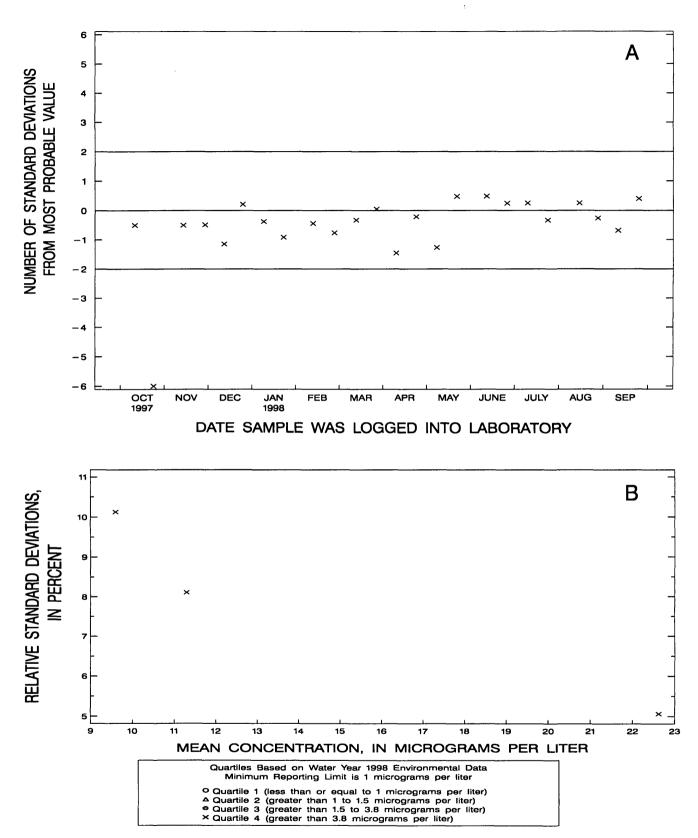


Figure 56. Molybdenum, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

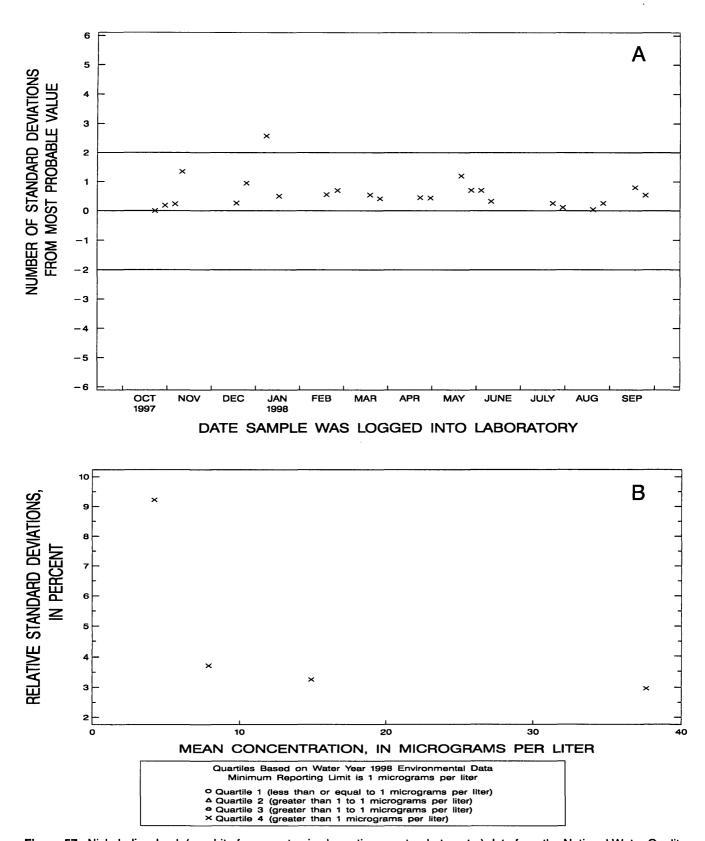


Figure 57. Nickel, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

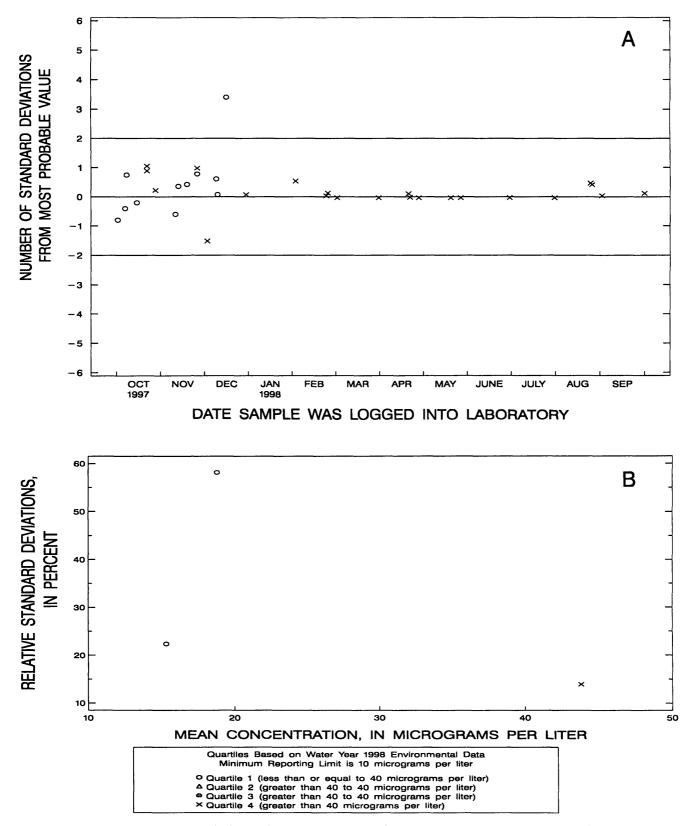


Figure 58. Nickel, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

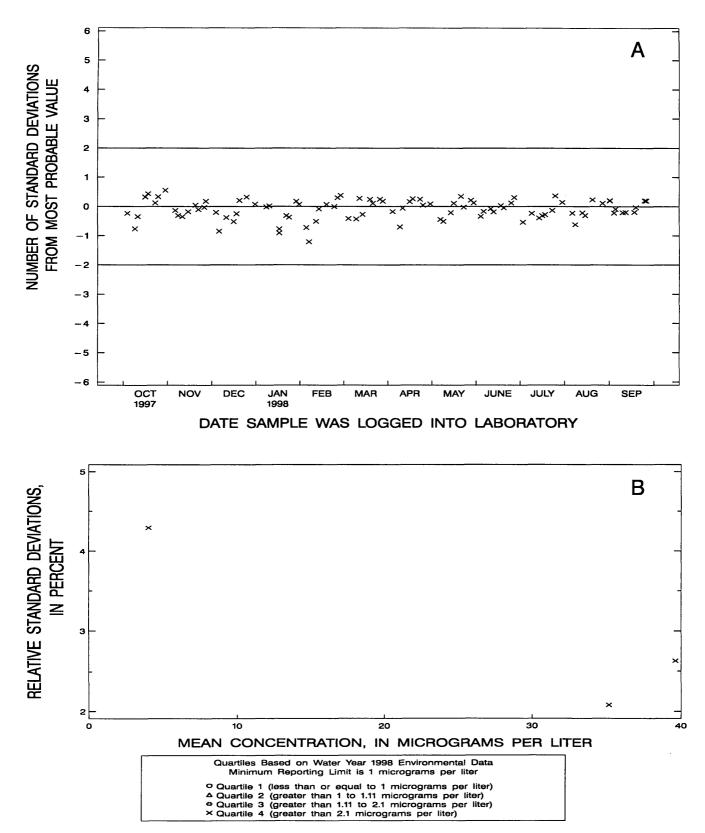


Figure 59. Nickel, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

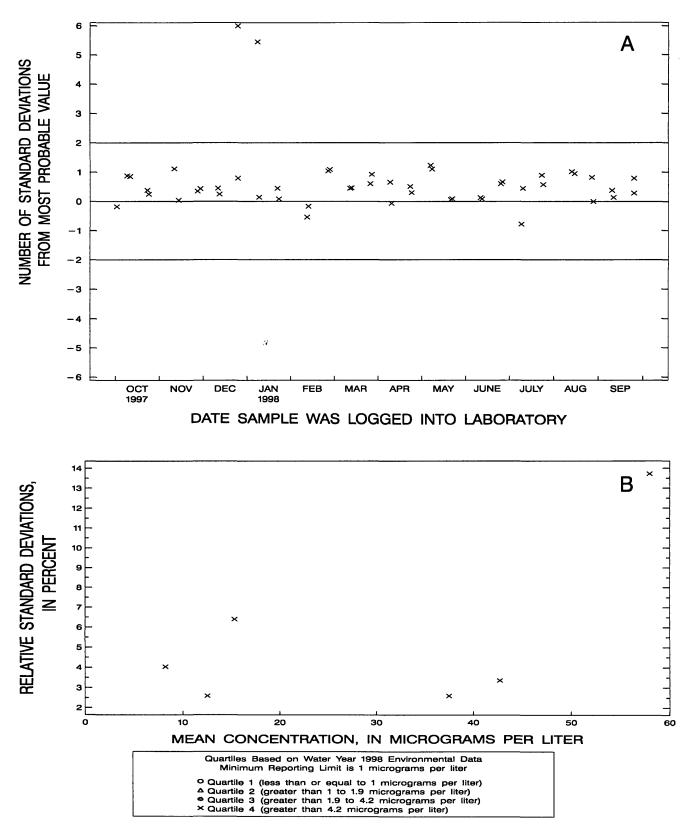


Figure 60. Nickel, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

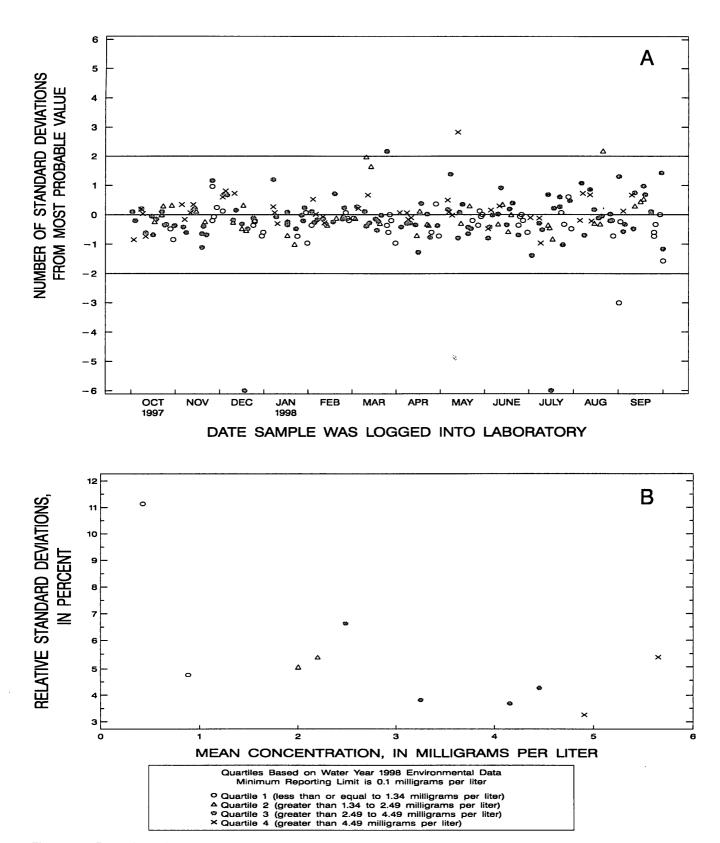


Figure 61. Potassium, dissolved, (flame-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

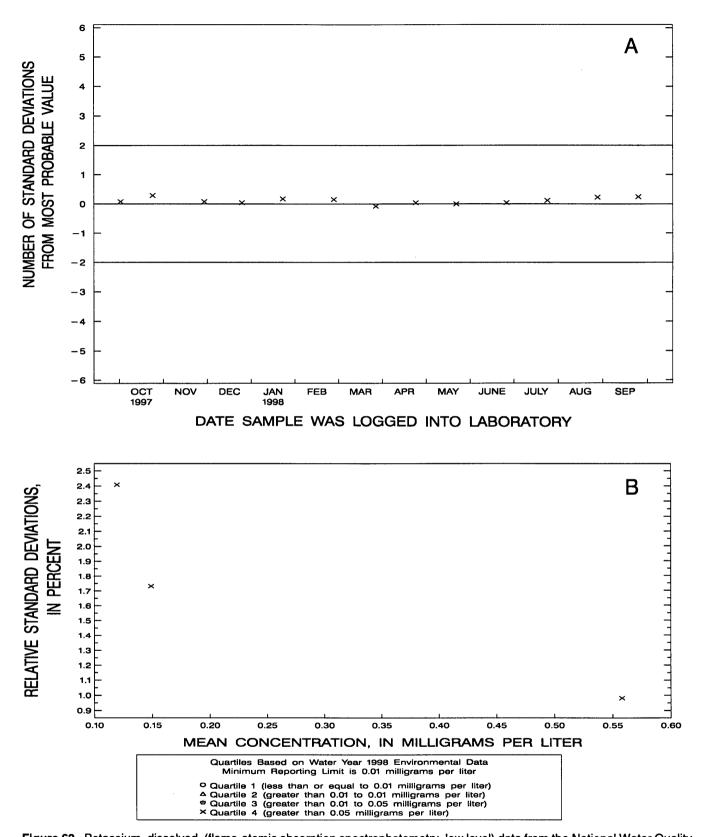


Figure 62. Potassium, dissolved, (flame-atomic absorption spectrophotometry, low level) data from the National Water Quality Laboratory.

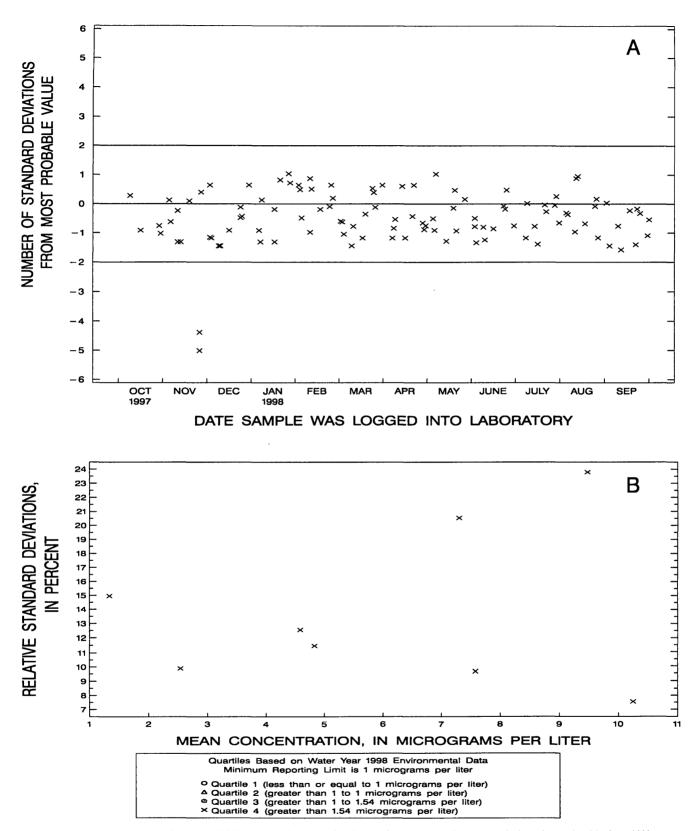


Figure 63. Selenium, dissolved, (hydride generation-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

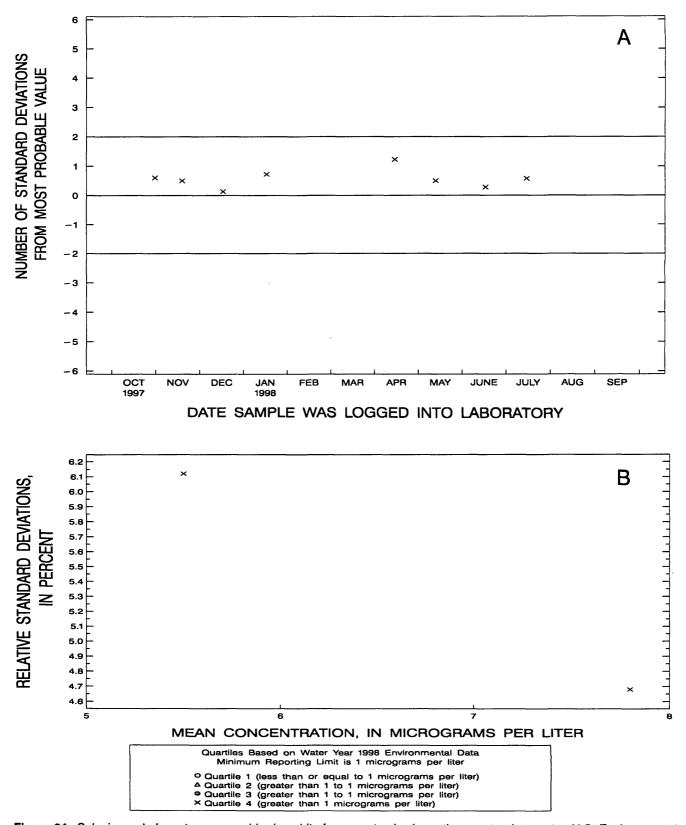


Figure 64. Selenium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry, U.S. Environmental Protection Agency) data from the National Water Quality Laboratory.

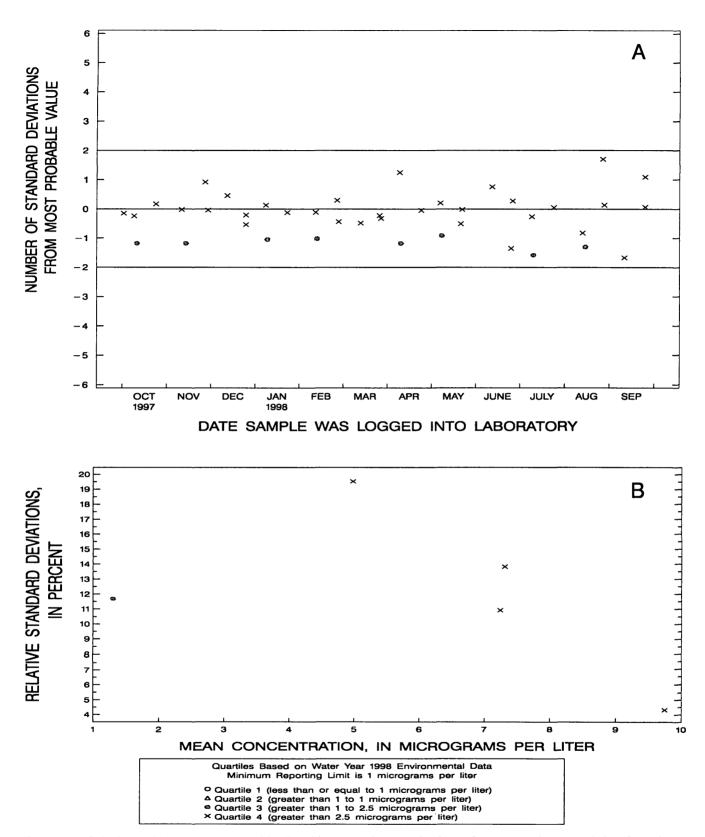


Figure 65. Selenium, whole-water recoverable, (hydride generation-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

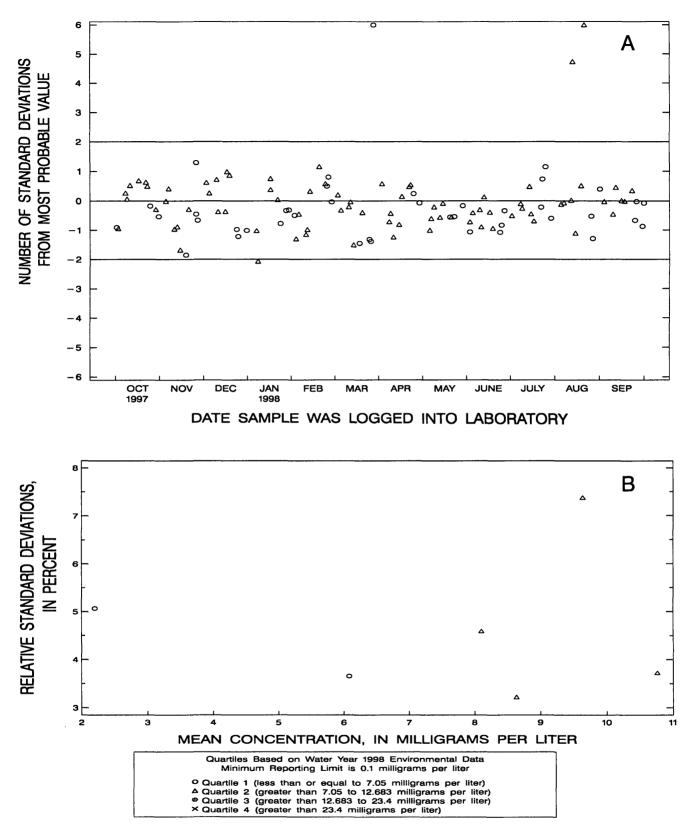


Figure 66. Silica, dissolved, (colorimetric) data from the National Water Quality Laboratory.

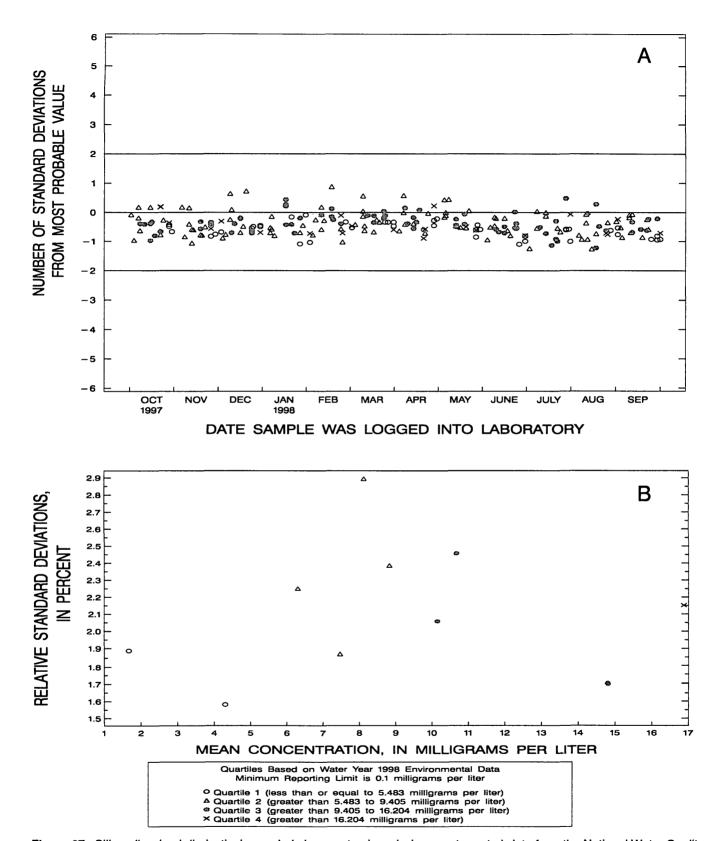


Figure 67. Silica, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

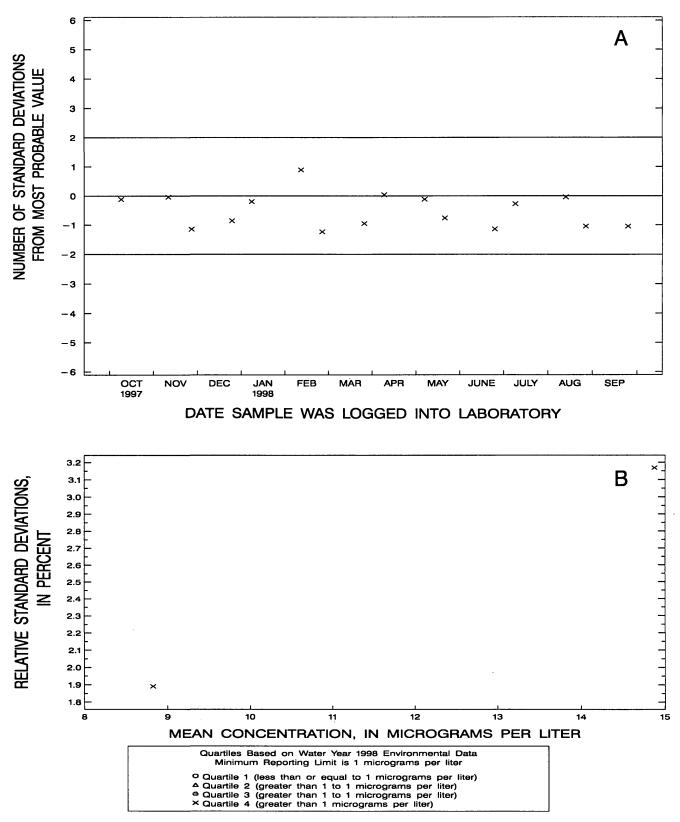


Figure 68. Silver, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

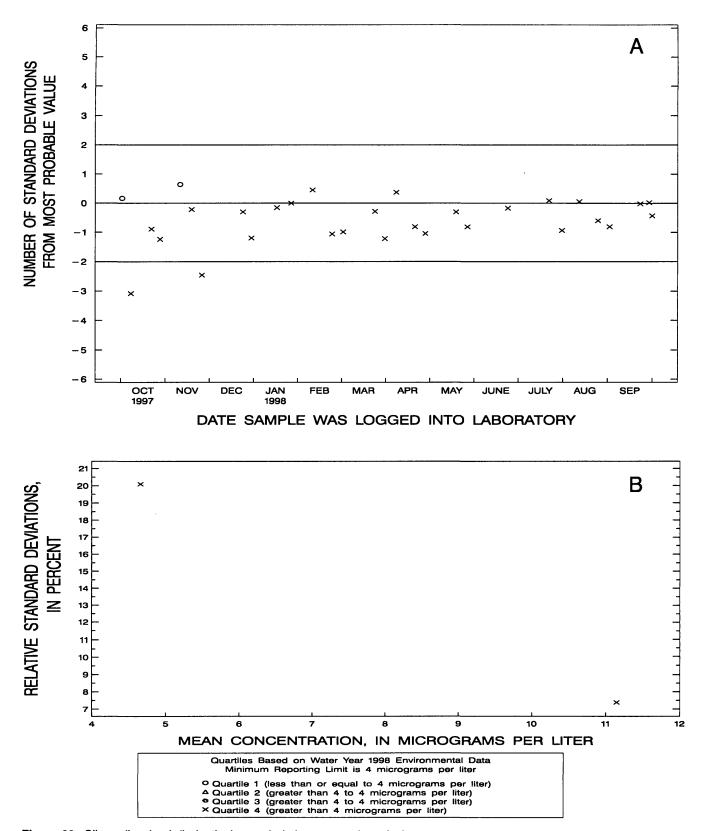


Figure 69. Silver, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

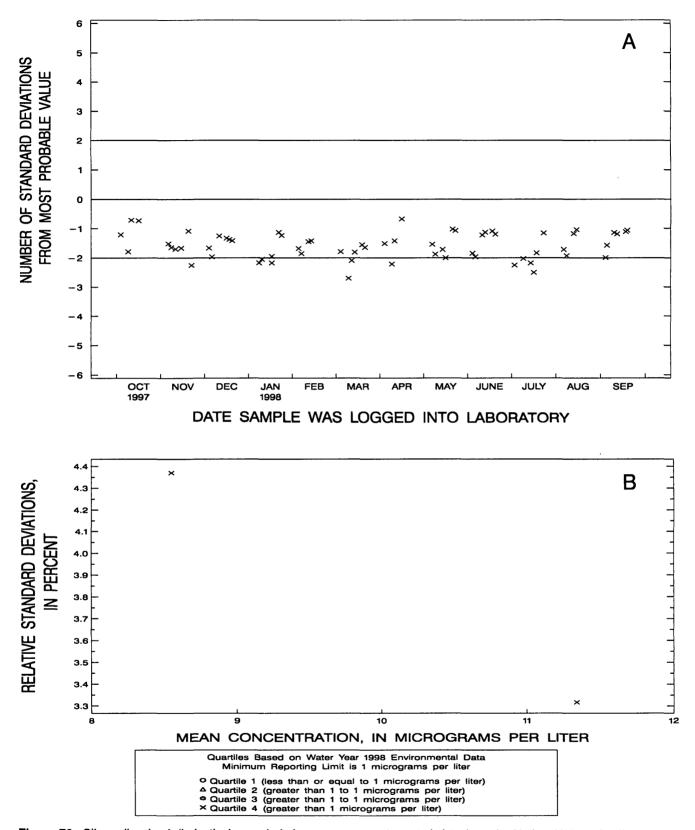


Figure 70. Silver, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

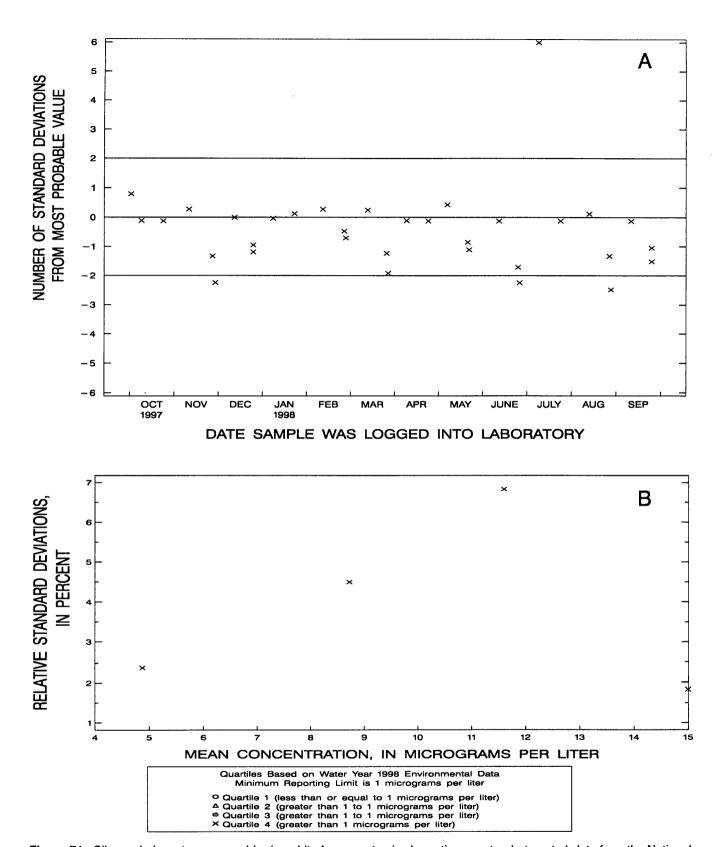


Figure 71. Silver, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

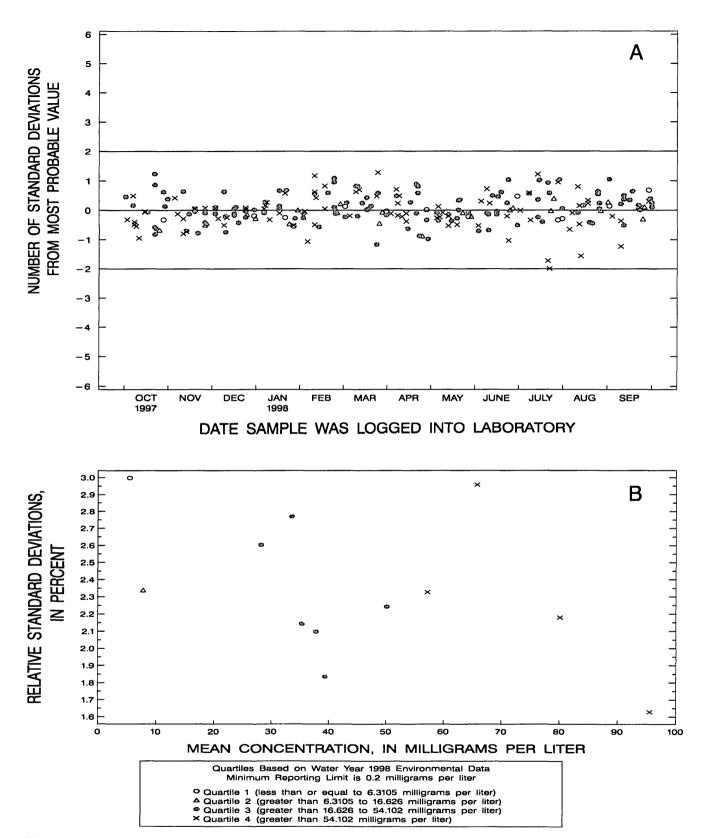


Figure 72. Sodium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

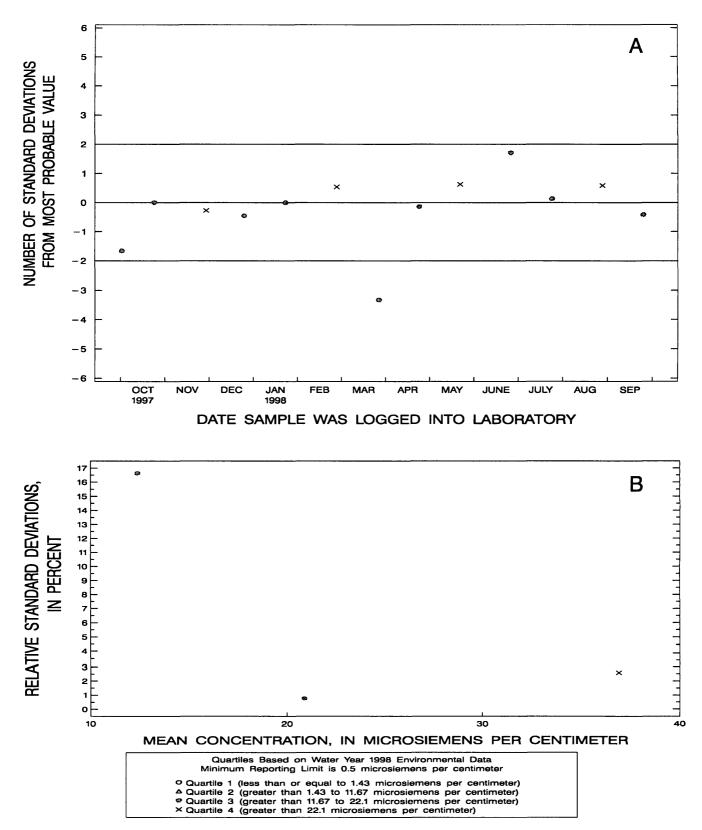


Figure 73. Specific conductance, whole-water recoverable, (electrometric, low level) data from the National Water Quality Laboratory.

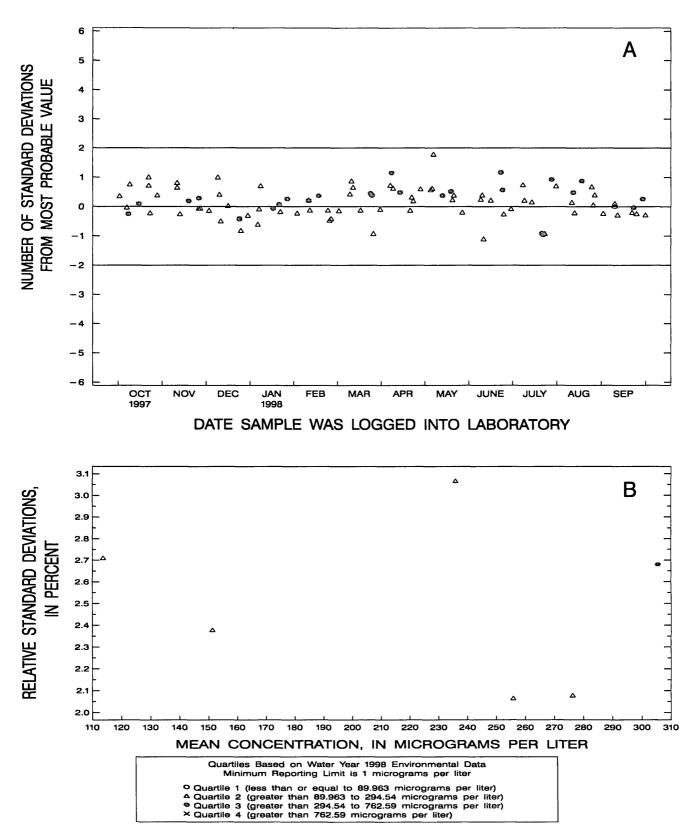


Figure 74. Strontium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

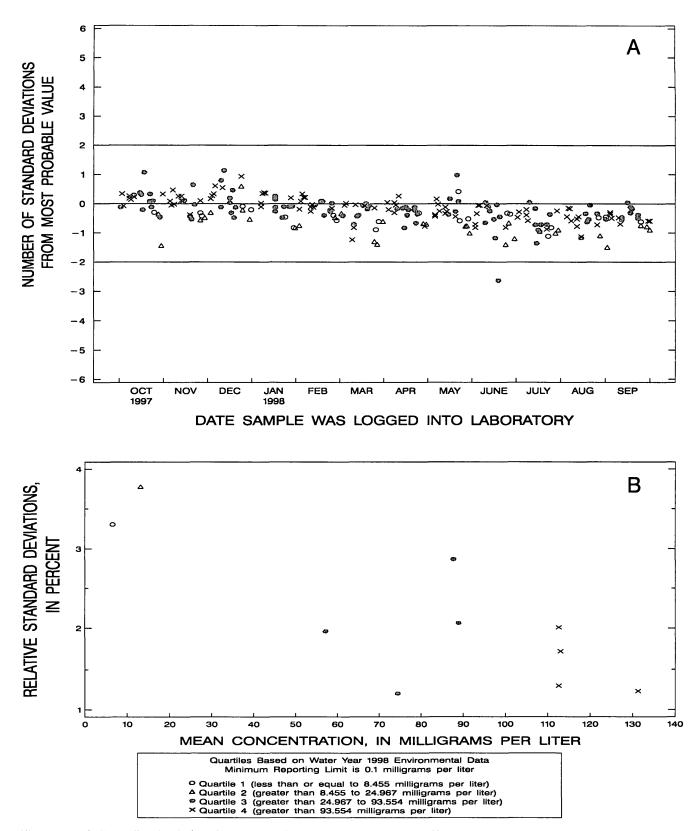


Figure 75. Sulfate, dissolved, (ion chromatography) data from the National Water Quality Laboratory.

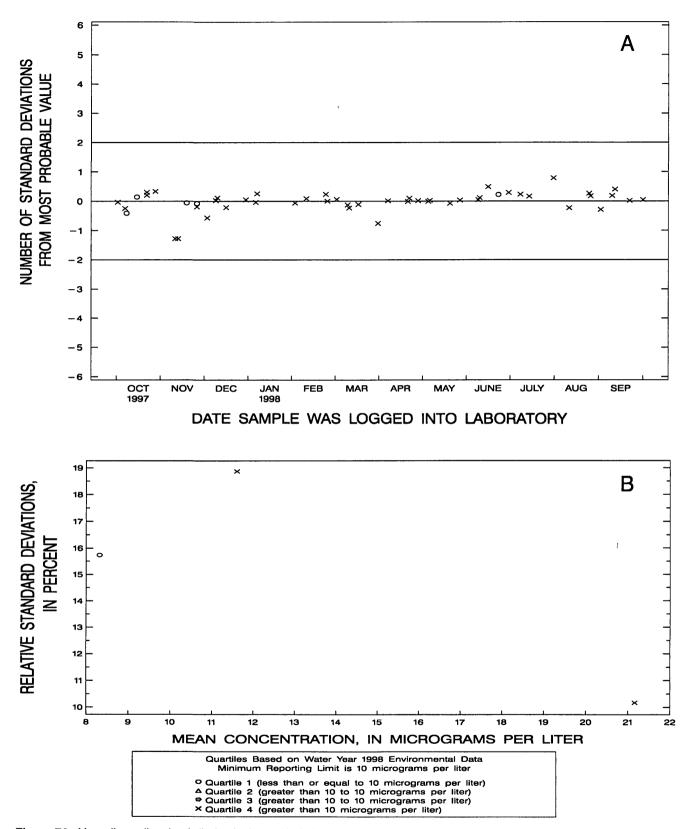


Figure 76. Vanadium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

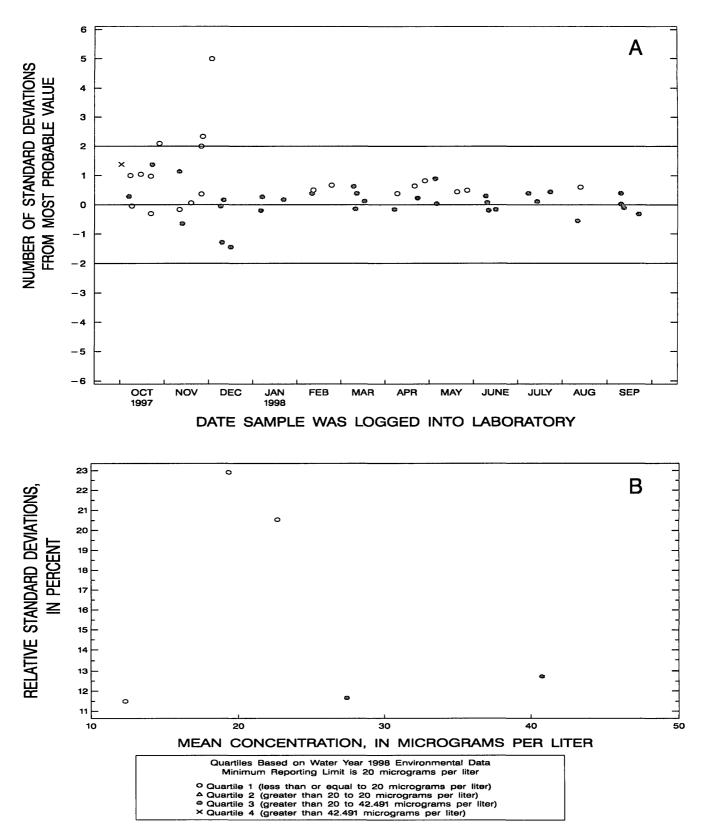


Figure 77. Zinc, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the National Water Quality Laboratory.

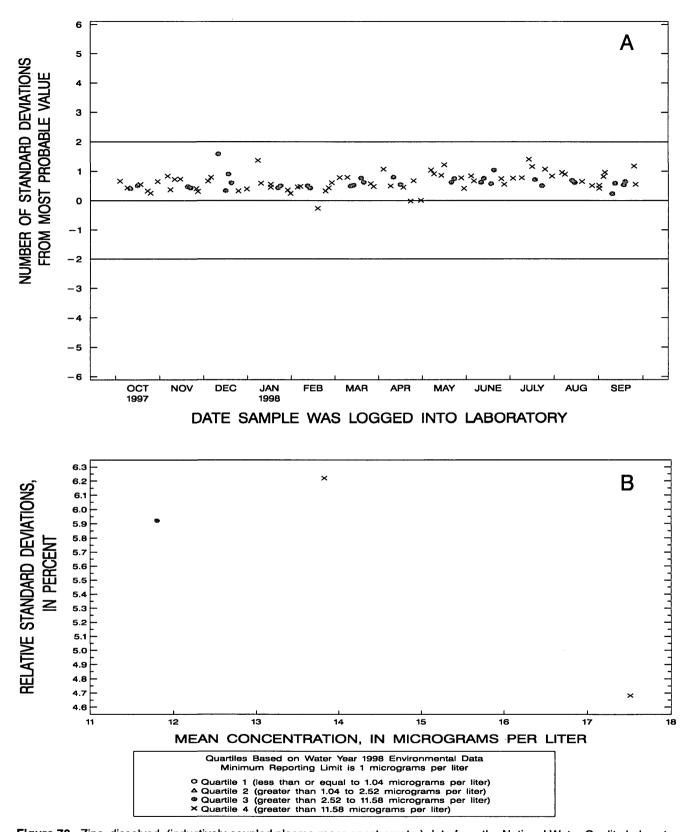


Figure 78. Zinc, dissolved, (inductively coupled plasma-mass spectrometry) data from the National Water Quality Laboratory.

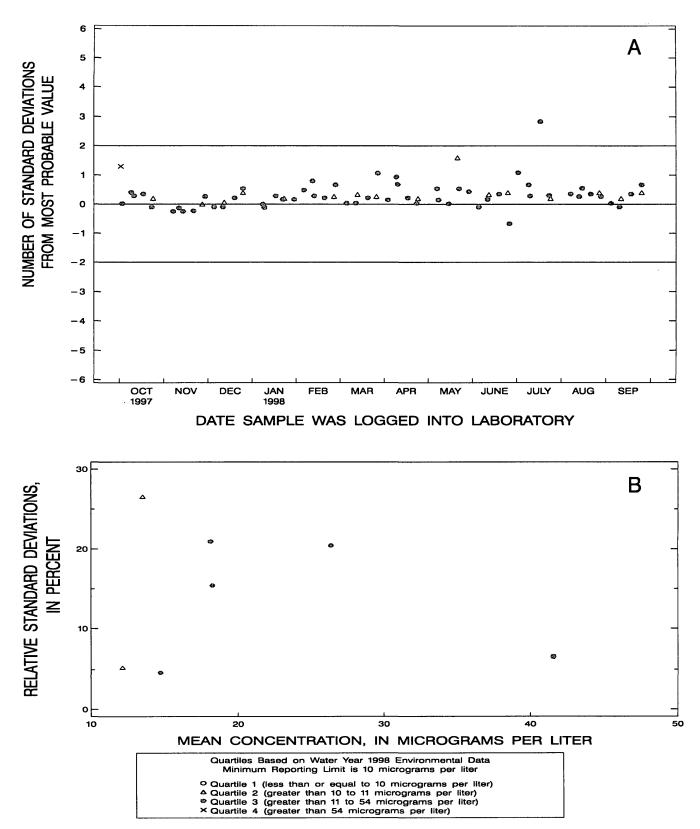


Figure 79. Zinc, whole-water recoverable, (flame-atomic absorption spectrophotometry) data from the National Water Quality Laboratory.

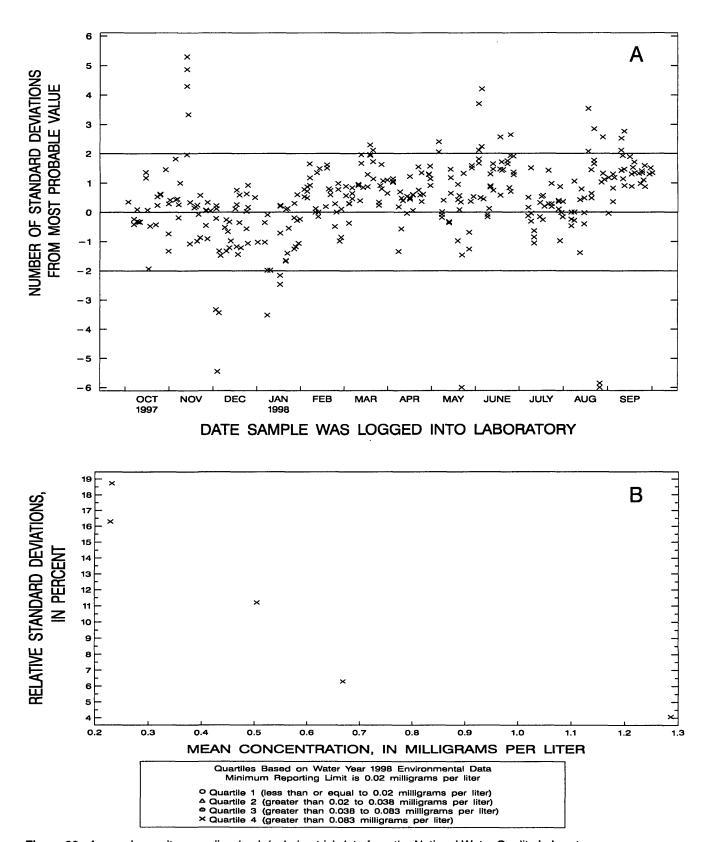


Figure 80. Ammonia as nitrogen, dissolved, (colorimetric) data from the National Water Quality Laboratory.

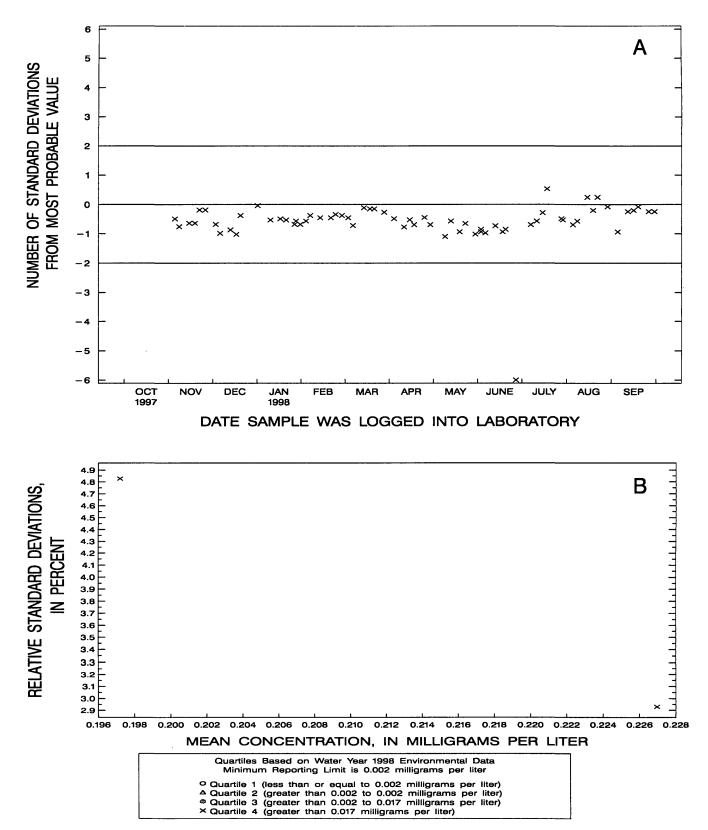


Figure 81. Ammonia as nitrogen, dissolved, (colorimetric, low level) data from the National Water Quality Laboratory.

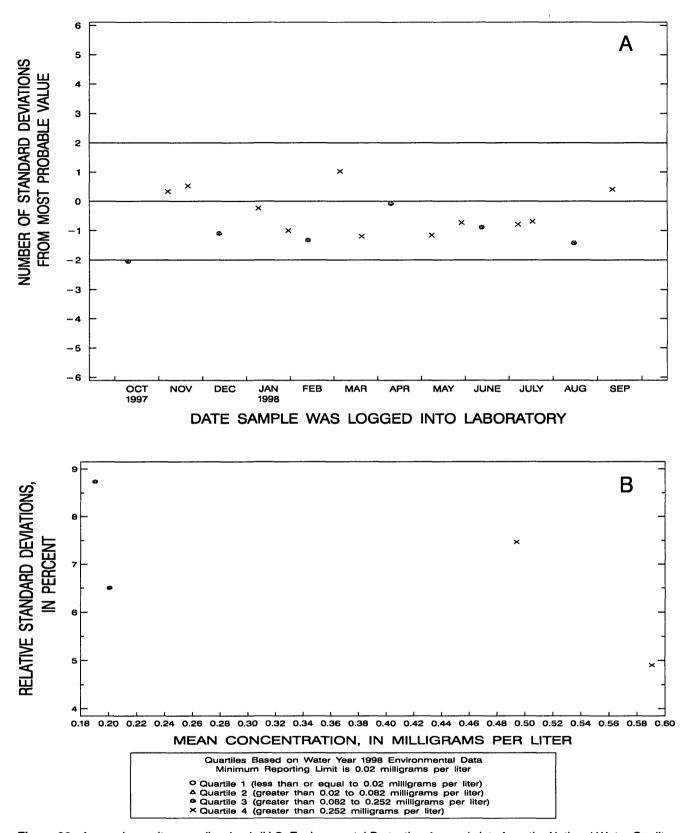


Figure 82. Ammonia as nitrogen, dissolved, (U.S. Environmental Protection Agency) data from the National Water Quality Laboratory.

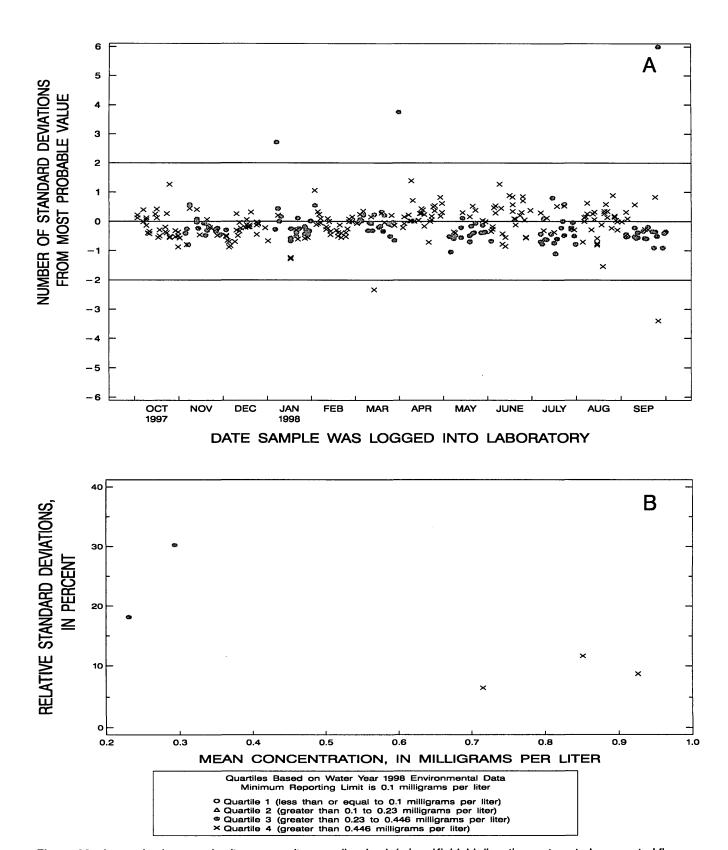


Figure 83. Ammonia plus organic nitrogen as nitrogen, dissolved, (micro-Kjeldahl digestion, automated segmented flow, colorimetric) data from the National Water Quality Laboratory.

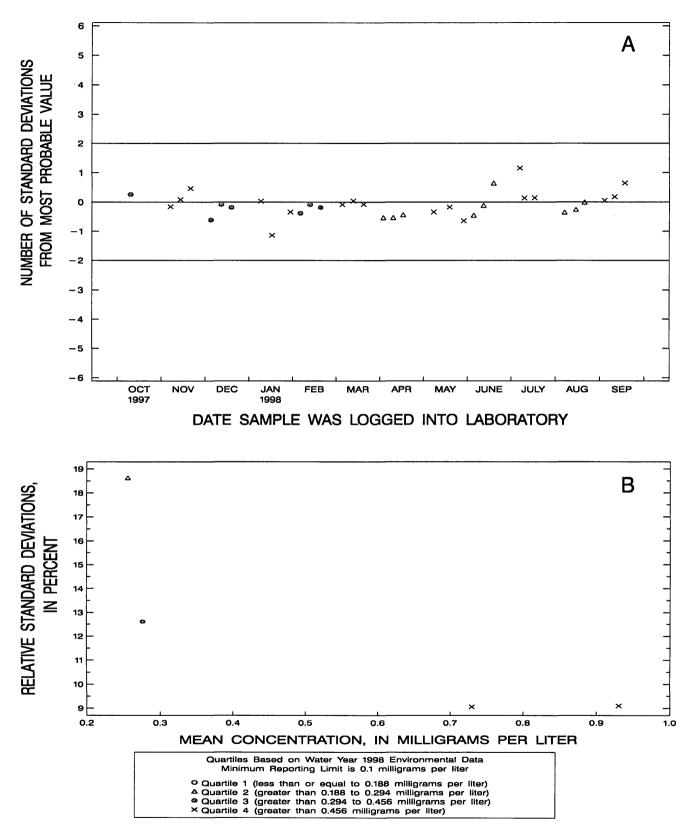


Figure 84. Ammonia plus organic nitrogen as nitrogen, dissolved, (U.S. Environmental Protection Agency) data from the National Water Quality Laboratory.

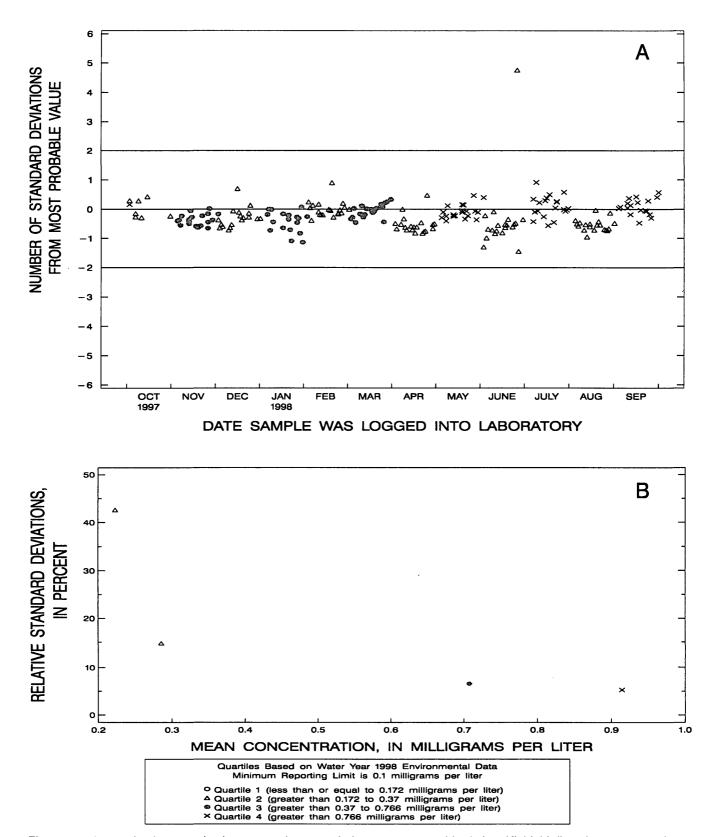


Figure 85. Ammonia plus organic nitrogen as nitrogen, whole-water recoverable, (micro-Kjeldahl digestion, automated segmented flow, colorimetric) data from the National Water Quality Laboratory.

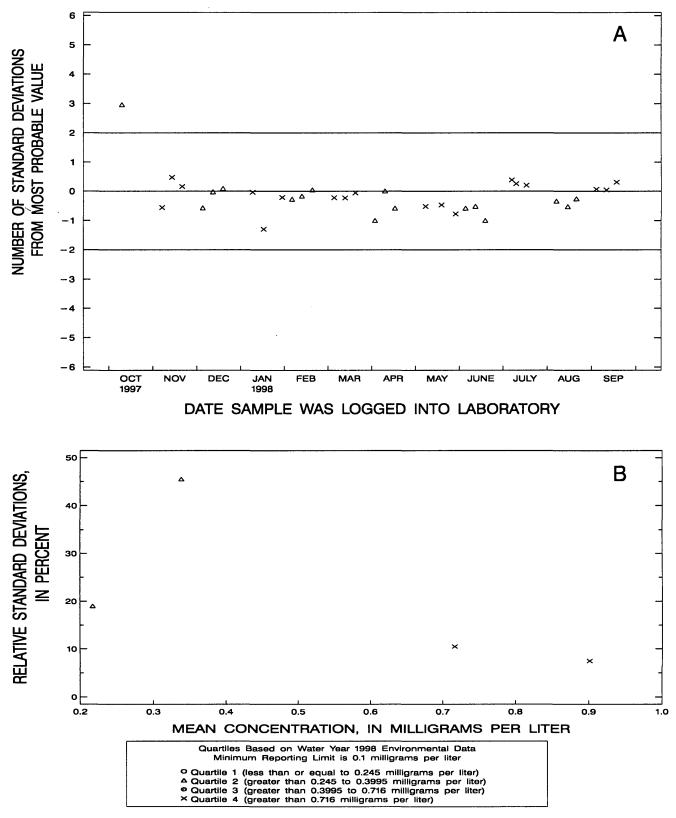


Figure 86. Ammonia plus organic nitrogen as nitrogen, whole-water recoverable, (U.S. Environmental Protection Agency) data from the National Water Quality Laboratory.

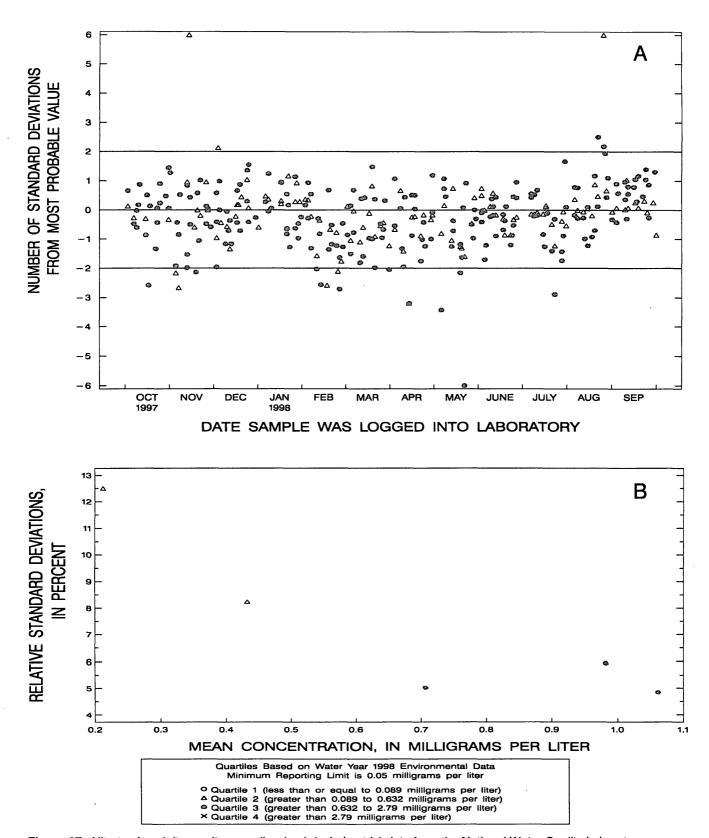


Figure 87. Nitrate plus nitrite as nitrogen, dissolved, (colorimetric) data from the National Water Quality Laboratory.

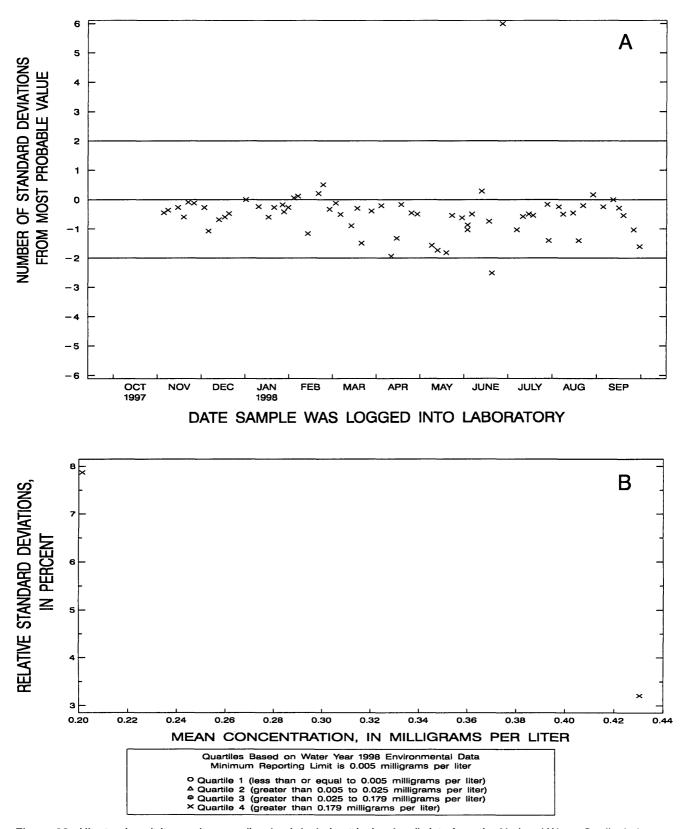


Figure 88. Nitrate plus nitrite as nitrogen, dissolved, (colorimetric, low level) data from the National Water Quality Laboratory.

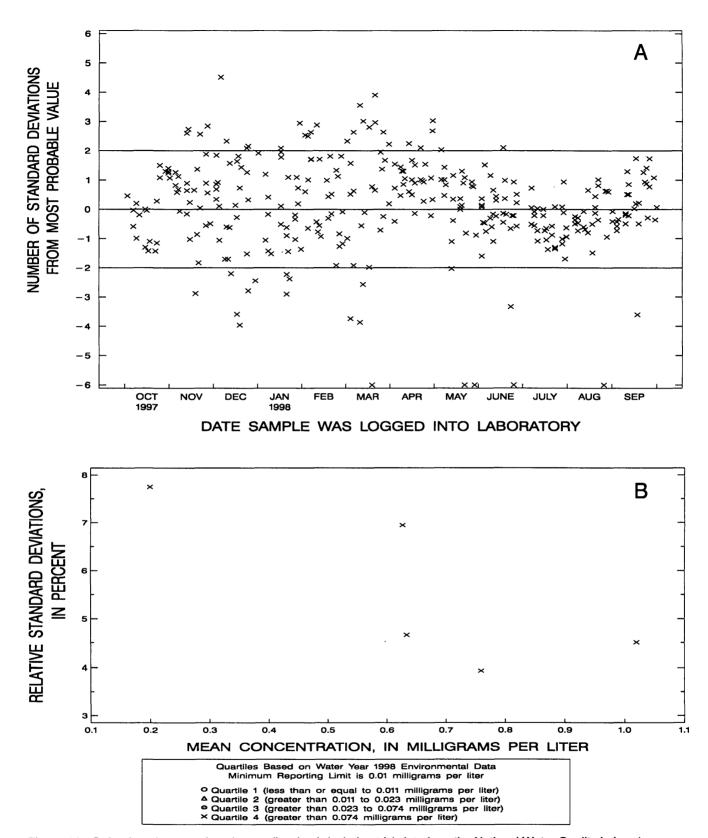


Figure 89. Orthophosphate as phosphorus, dissolved, (colorimetric) data from the National Water Quality Laboratory.

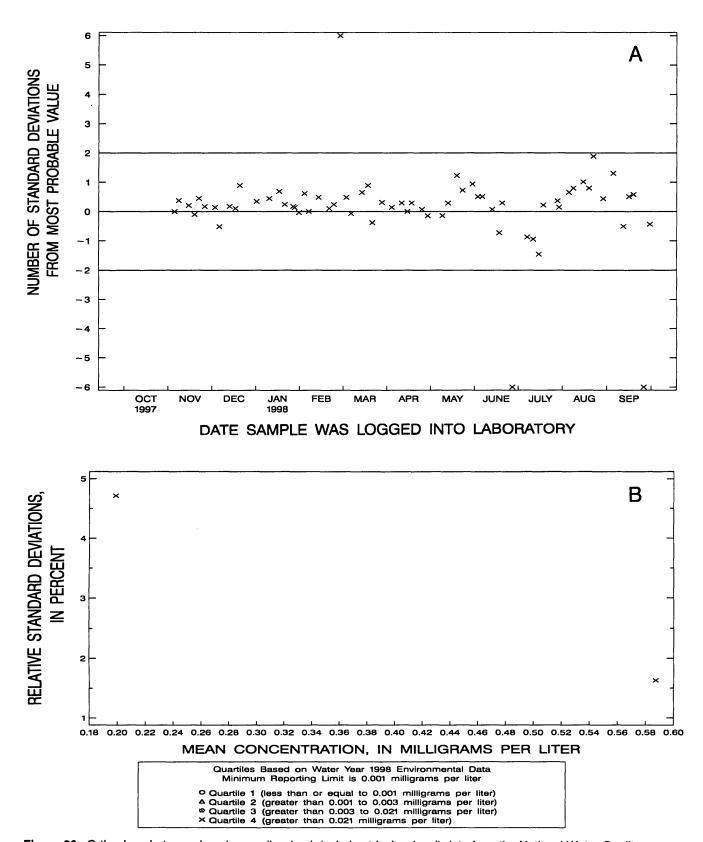


Figure 90. Orthophosphate as phosphorus, dissolved, (colorimetric, low level) data from the National Water Quality Laboratory.

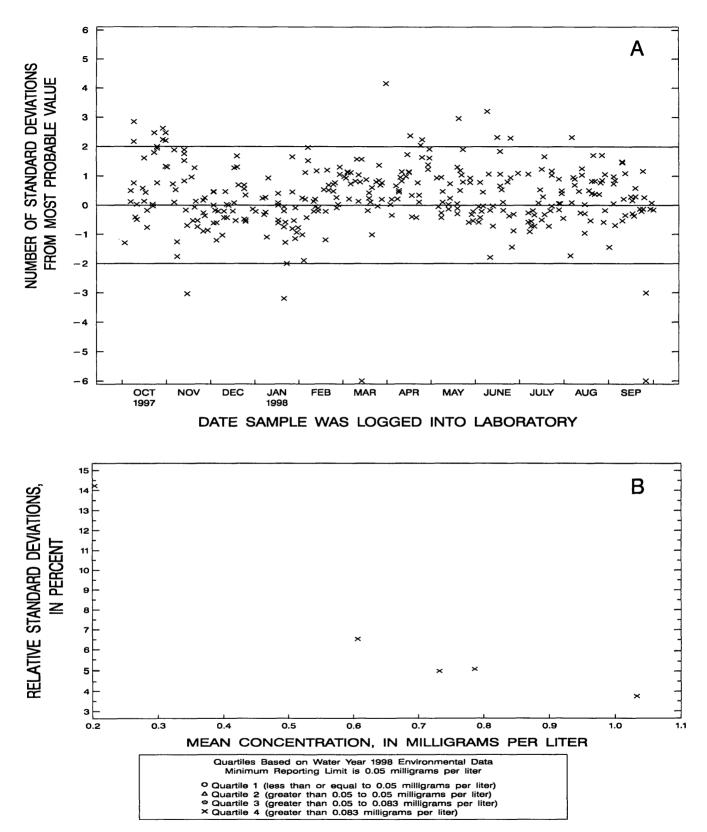


Figure 91. Phosphorus, dissolved, (micro-Kjeldahl digestion, automated segmented flow, colorimetric) data from the National Water Quality Laboratory.

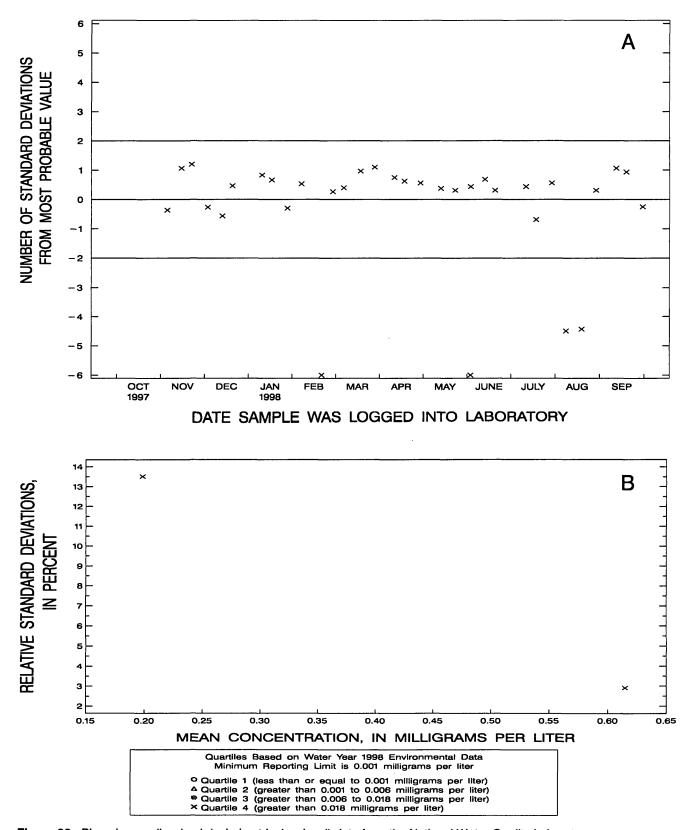


Figure 92. Phosphorus, dissolved, (colorimetric, low level) data from the National Water Quality Laboratory.

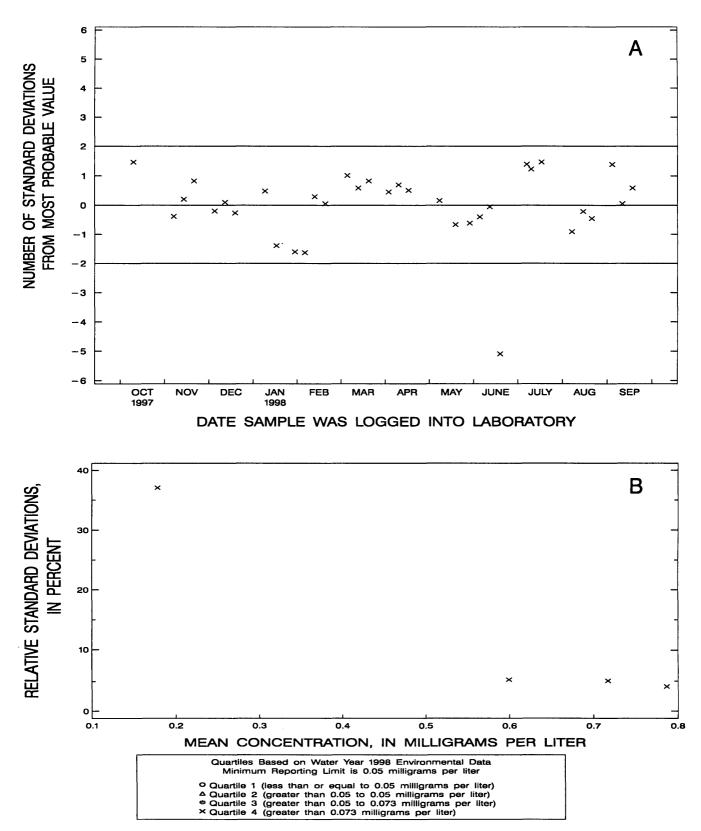


Figure 93. Phosphorus, dissolved, (U.S. Environmental Protection Agency) data from the National Water Quality Laboratory.

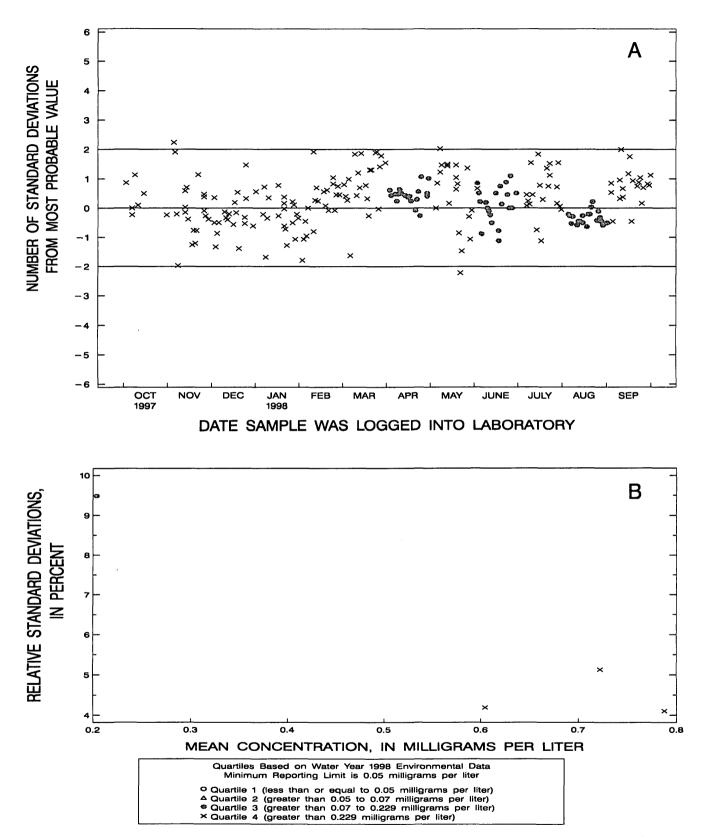


Figure 94. Phosphorus, whole-water recoverable, (micro-Kjeldahl digestion, automated segmented flow, colorimetric) data from the National Water Quality Laboratory.

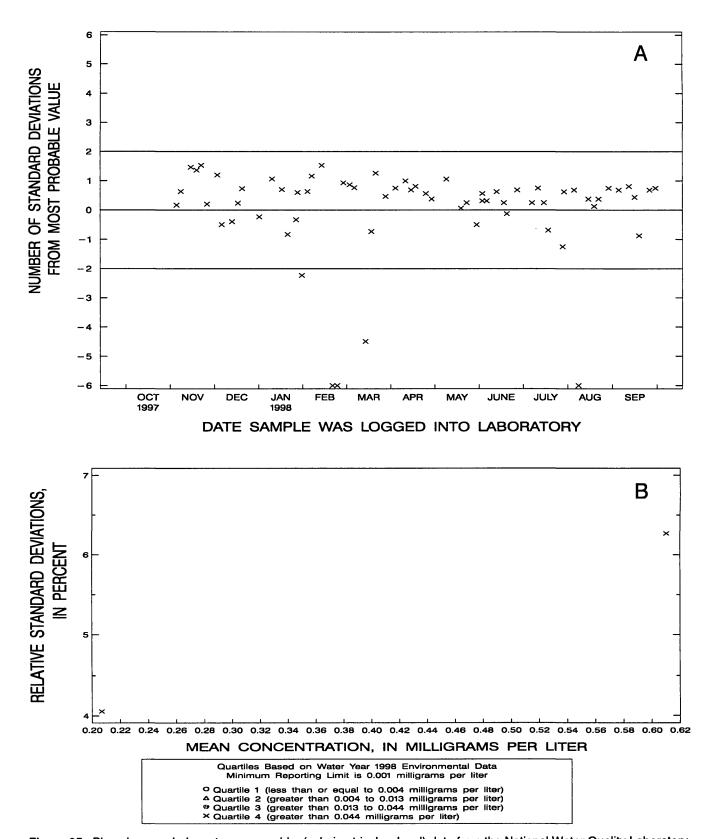


Figure 95. Phosphorus, whole-water recoverable, (colorimetric, low level) data from the National Water Quality Laboratory.

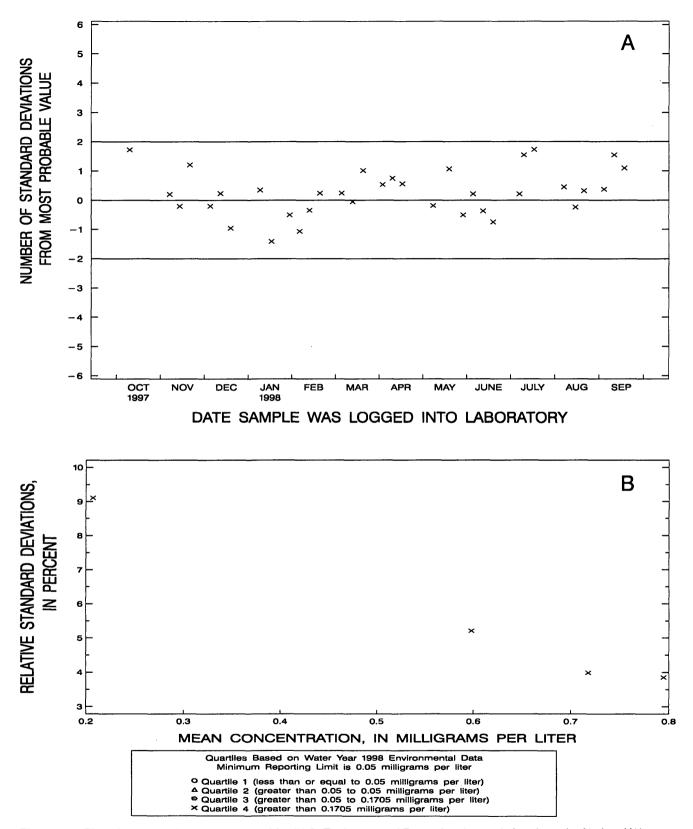


Figure 96. Phosphorus, whole-water recoverable, (U.S. Environmental Protection Agency) data from the National Water Quality Laboratory.

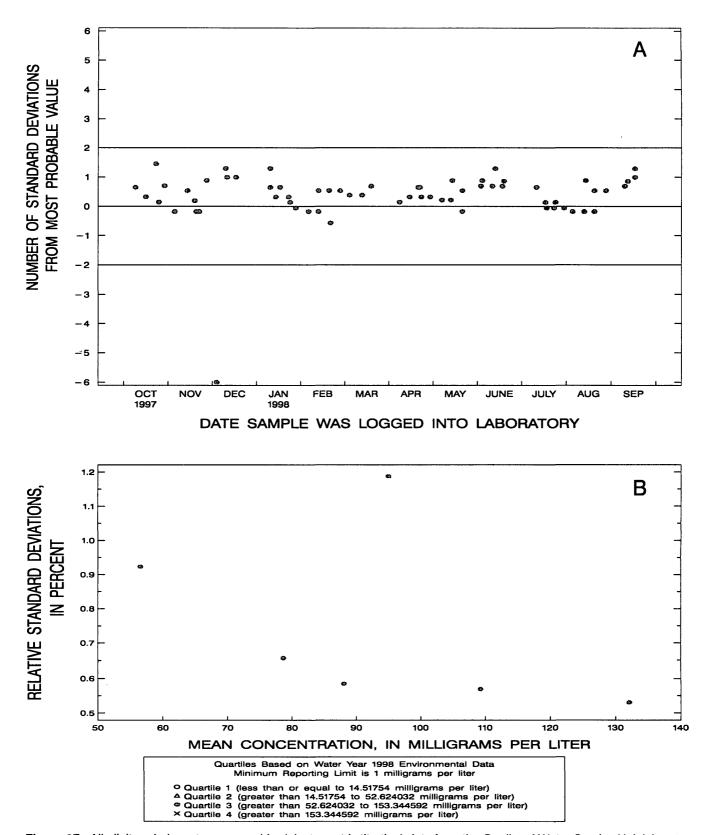


Figure 97. Alkalinity, whole-water recoverable, (electrometric titration) data from the Quality of Water Service Unit laboratory.

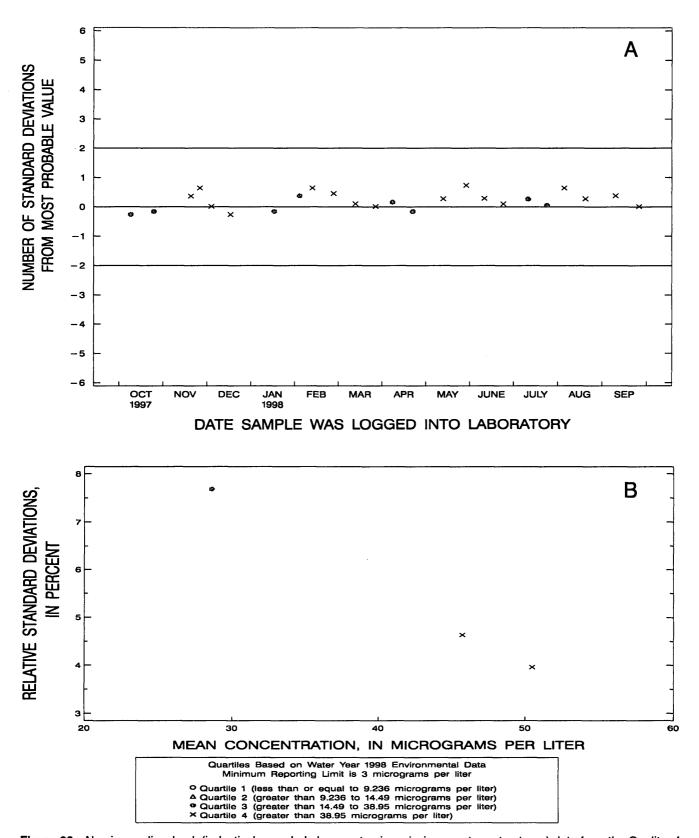


Figure 98. Aluminum, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

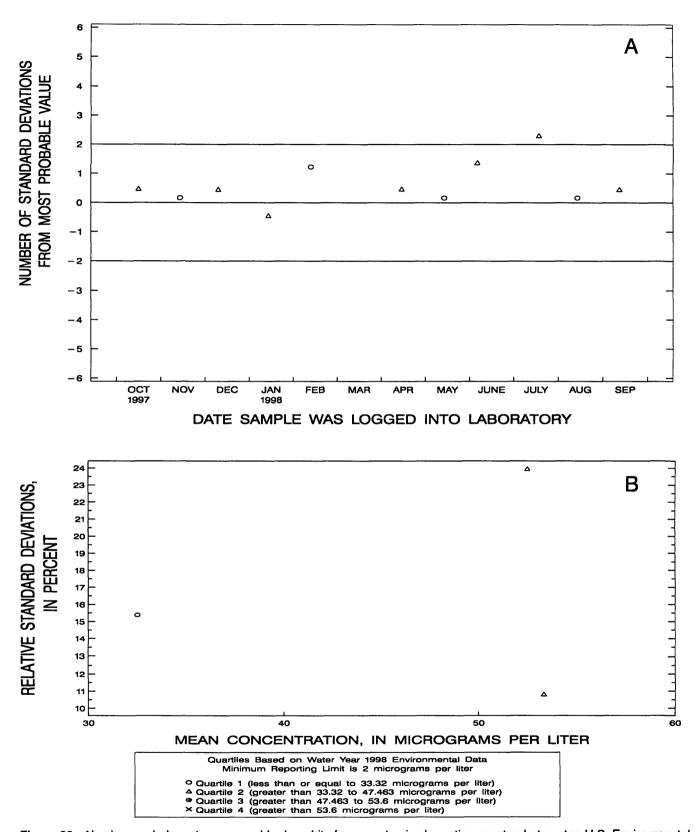


Figure 99. Aluminum, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry, U.S. Environmental Protection Agency) data from the Quality of Water Service Unit laboratory.

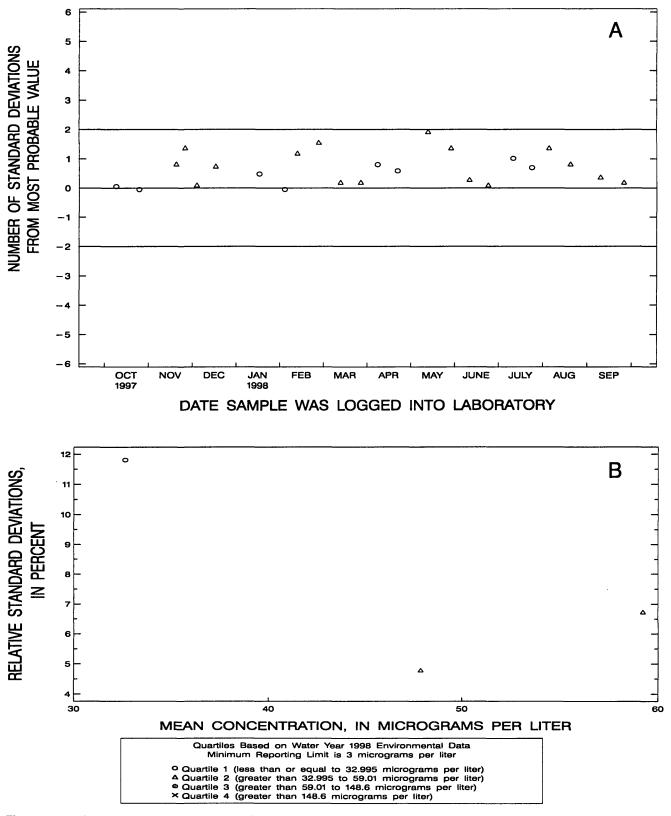


Figure 100. Aluminum, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

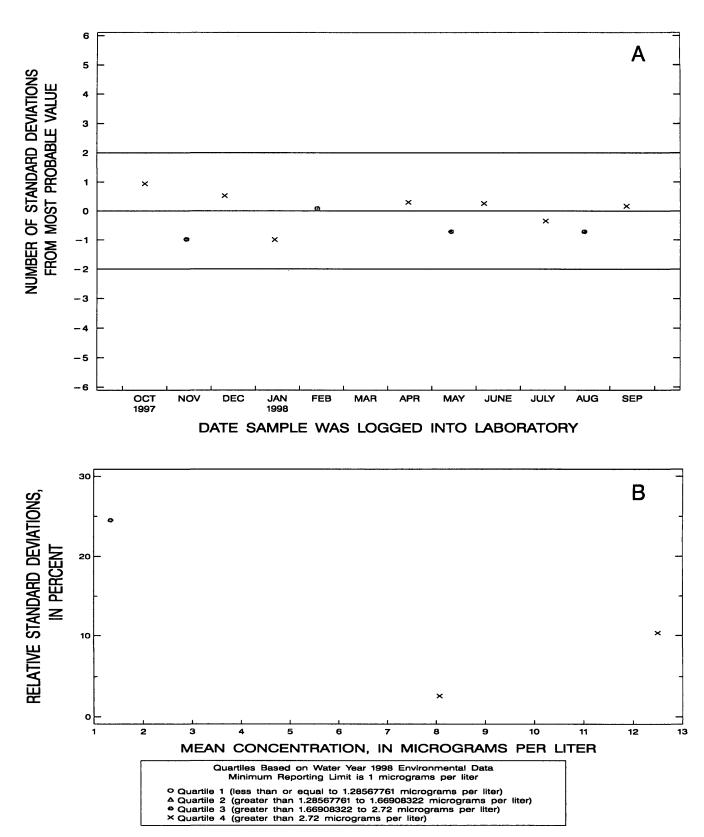


Figure 101. Arsenic, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

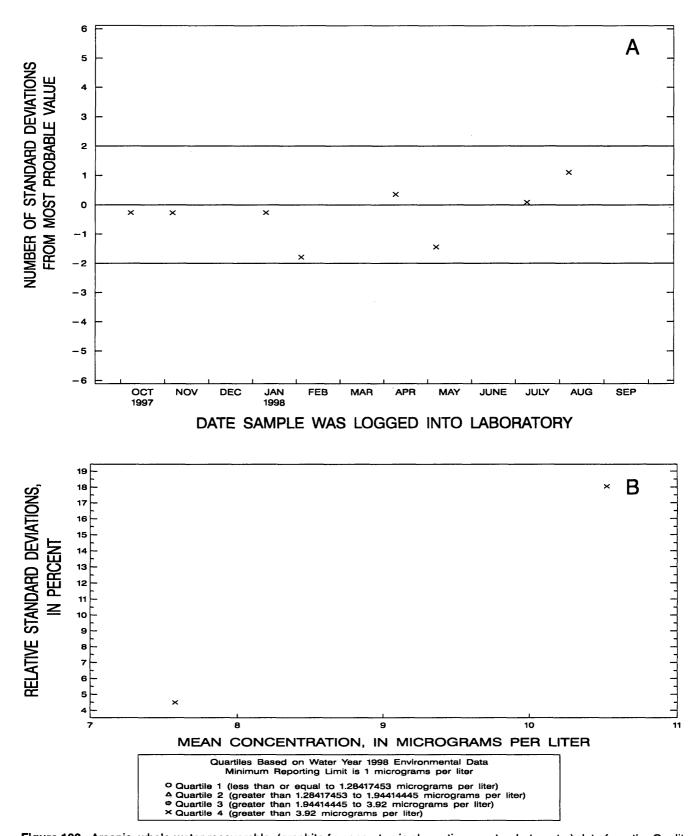


Figure 102. Arsenic, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

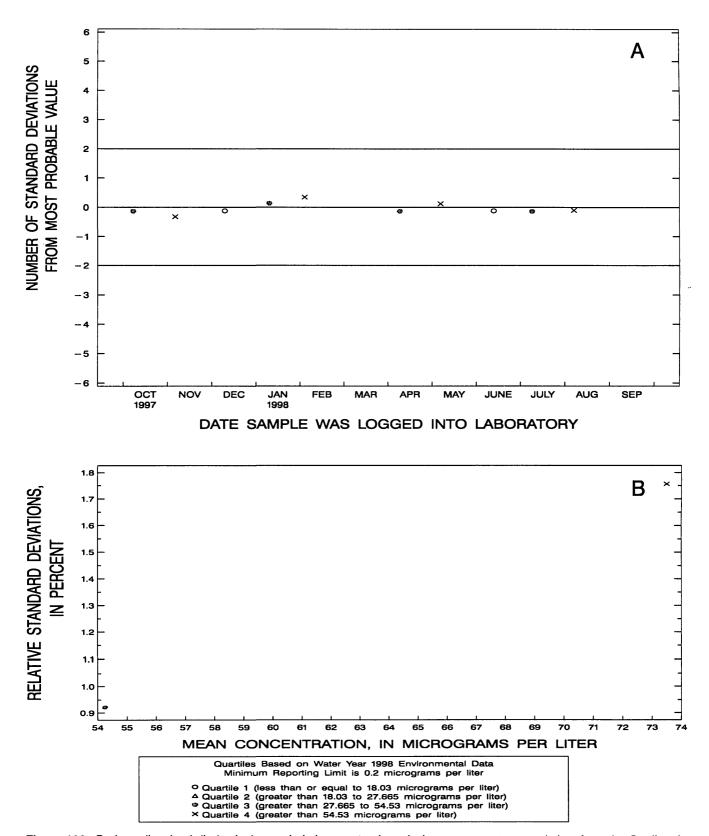


Figure 103. Barium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

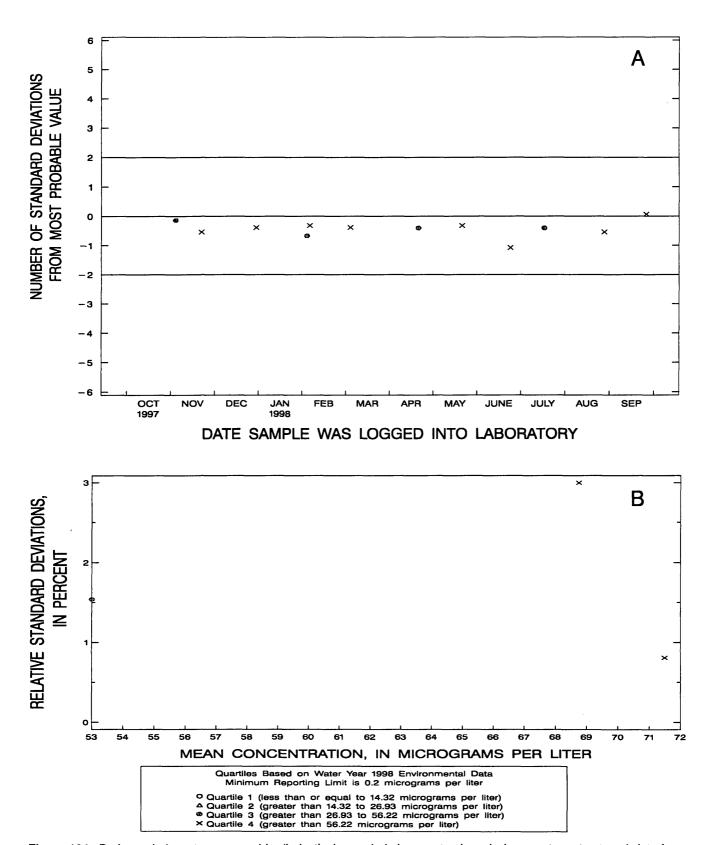


Figure 104. Barium, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

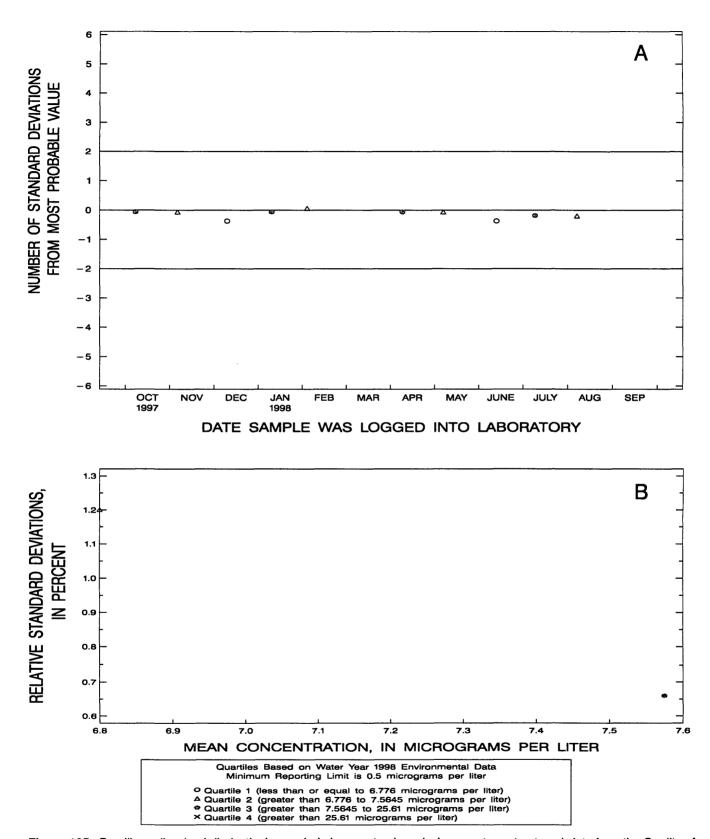


Figure 105. Beryllium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

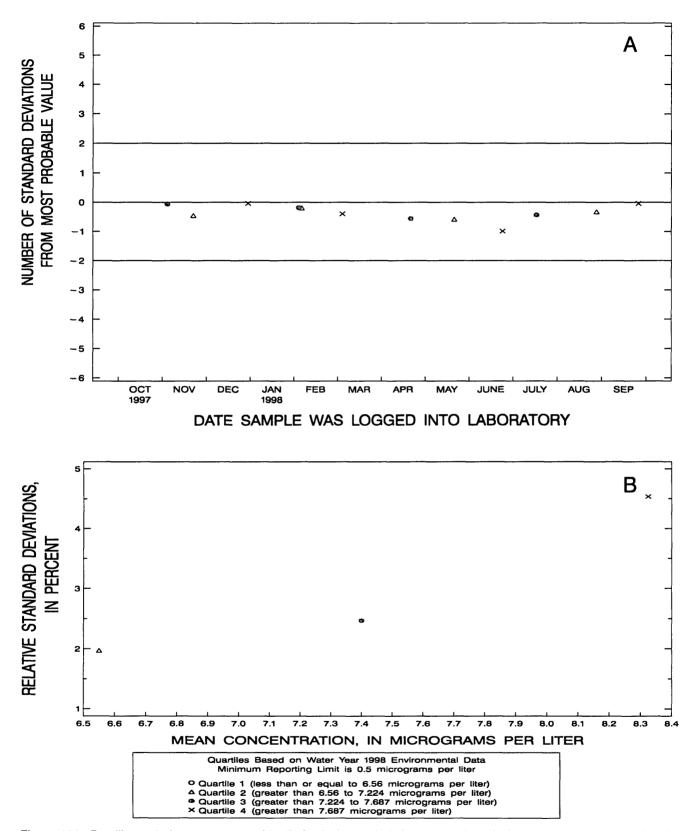


Figure 106. Beryllium, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

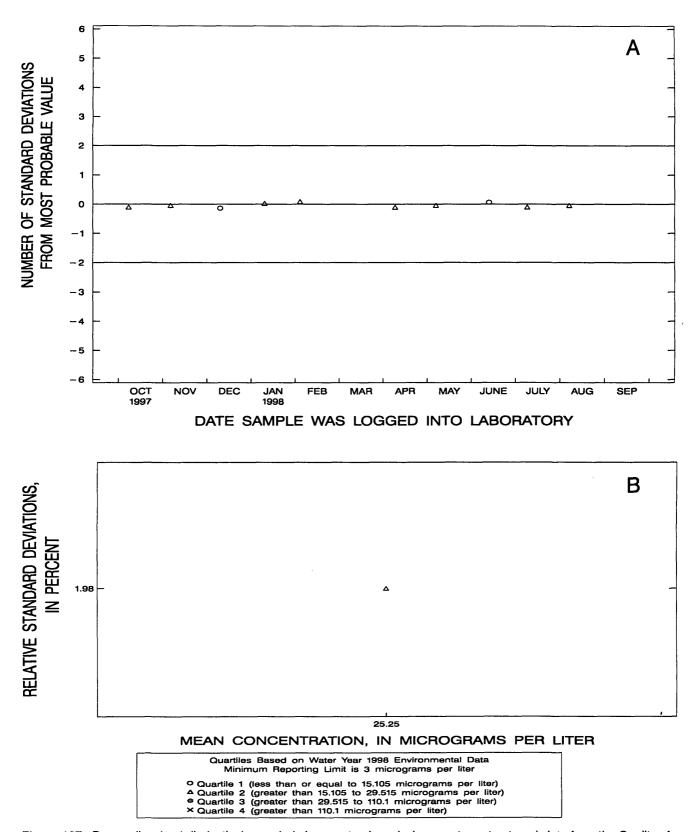


Figure 107. Boron, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

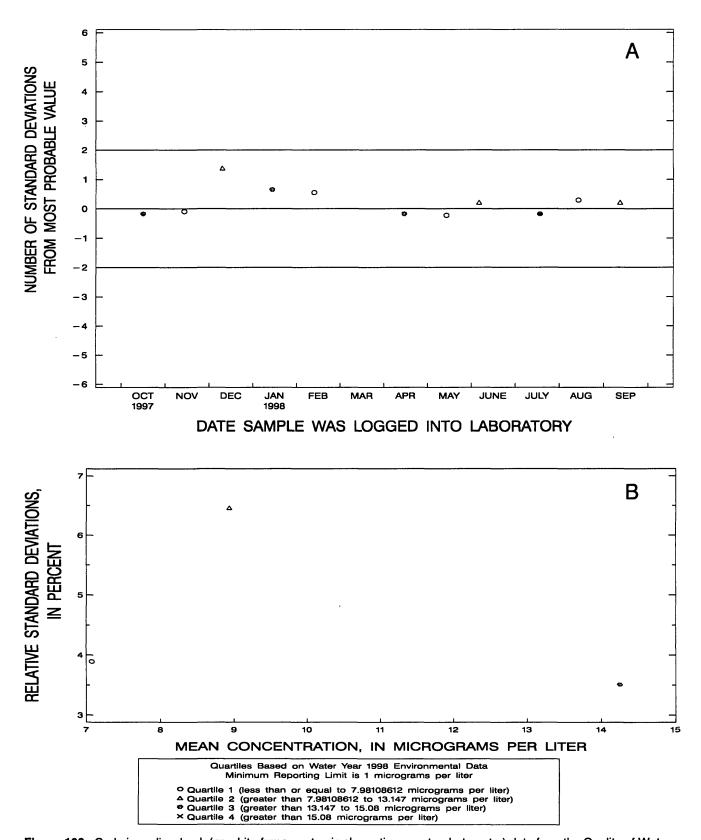


Figure 108. Cadmium, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

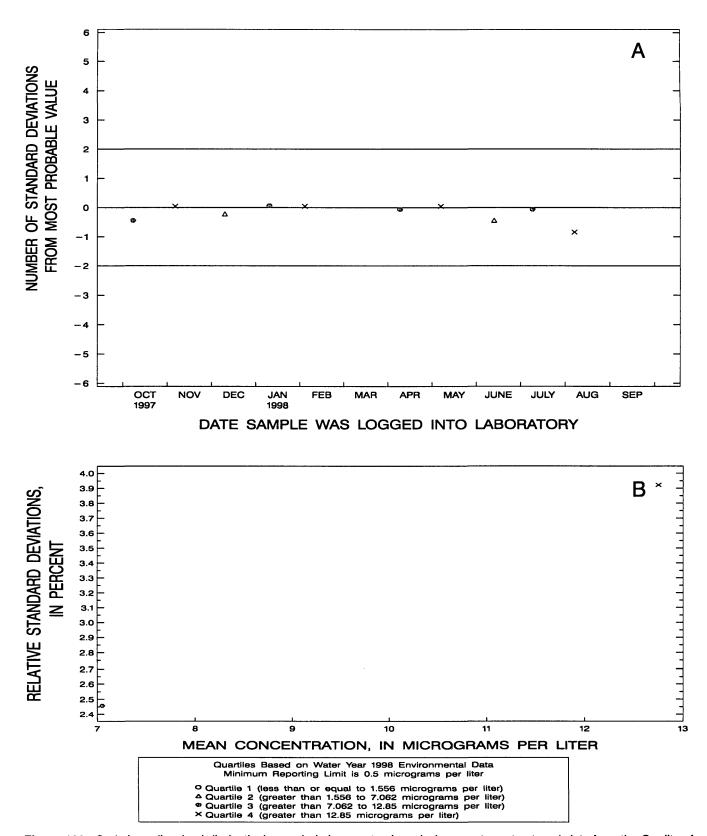


Figure 109. Cadmium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

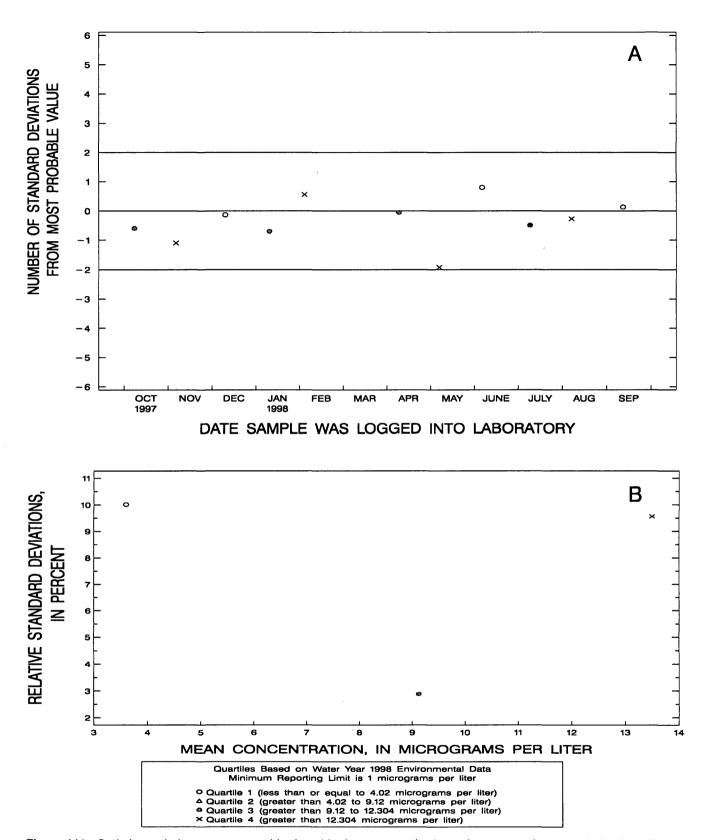


Figure 110. Cadmium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

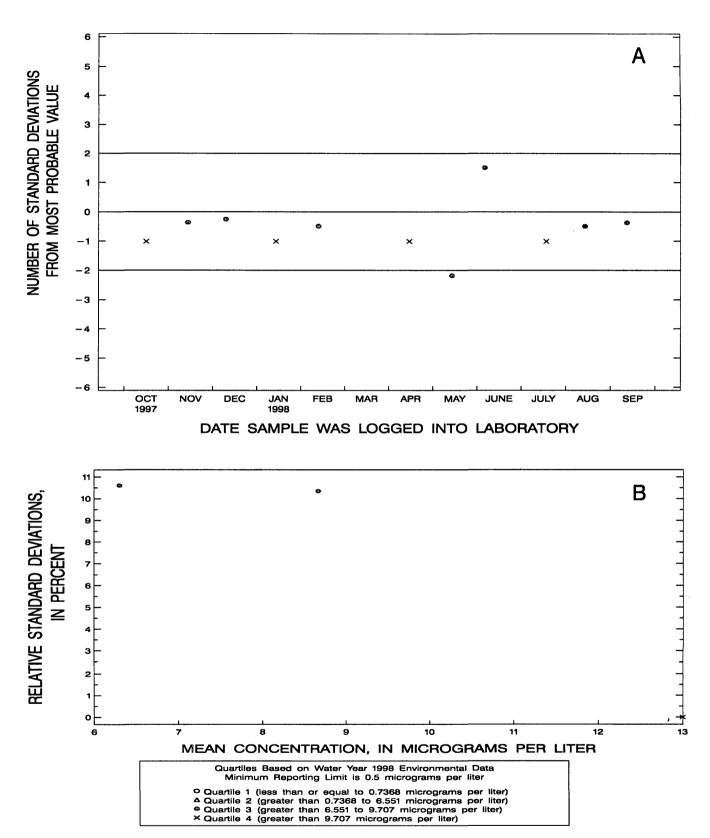


Figure 111. Cadmium, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

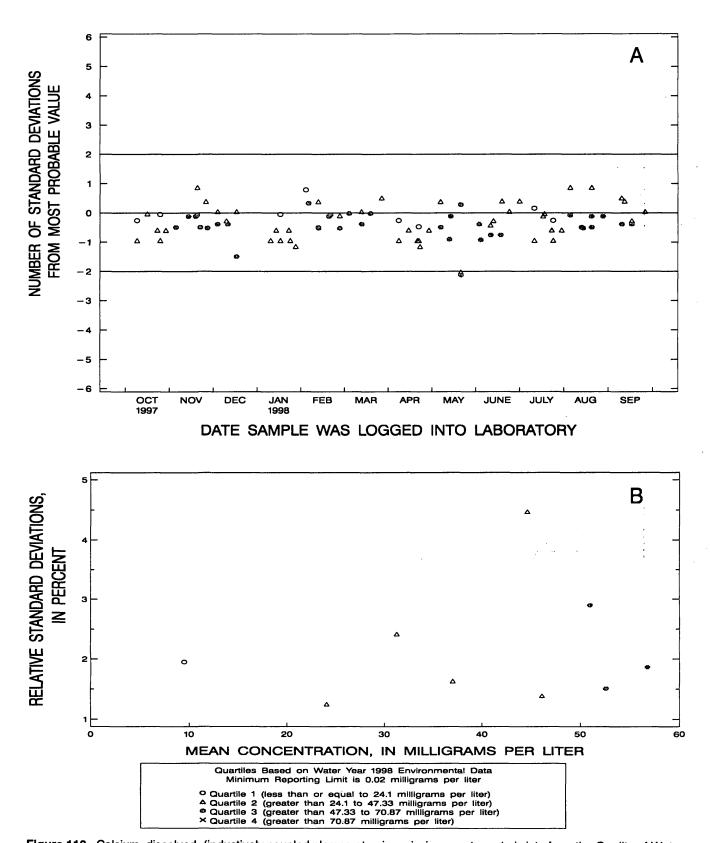


Figure 112. Calcium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the Quality of Water Service Unit laboratory.

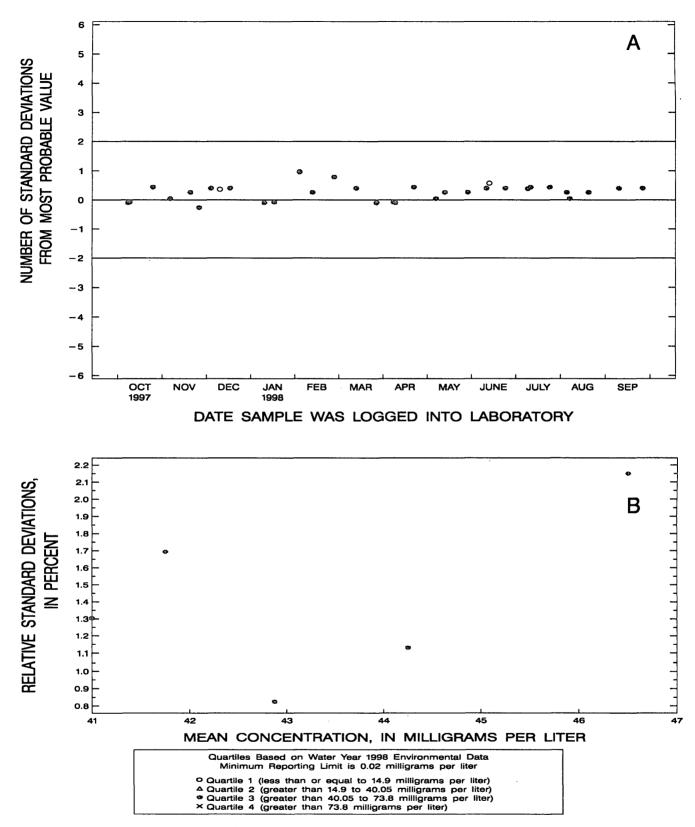


Figure 113. Calcium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

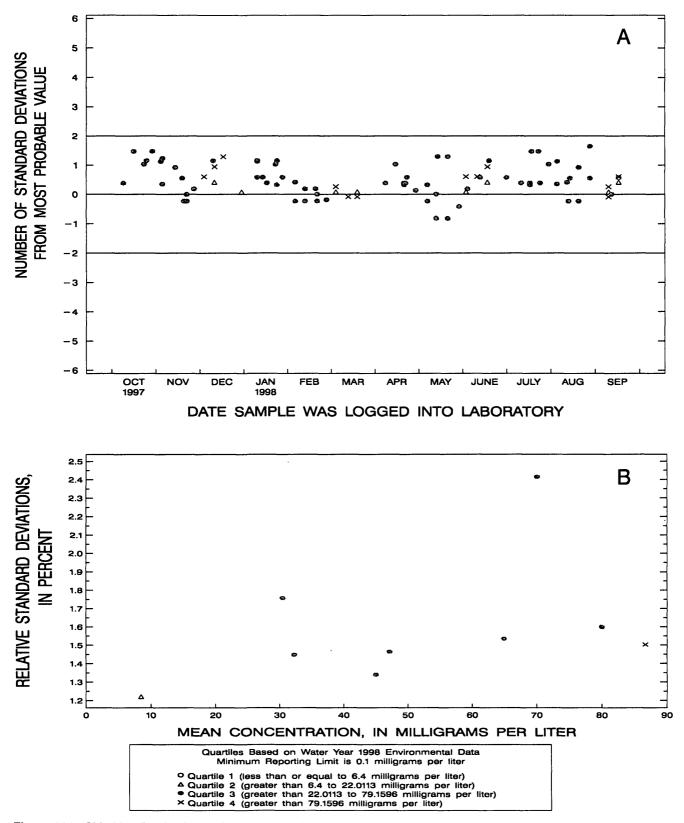


Figure 114. Chloride, dissolved, (ion chromatography) data from the Quality of Water Service Unit laboratory.

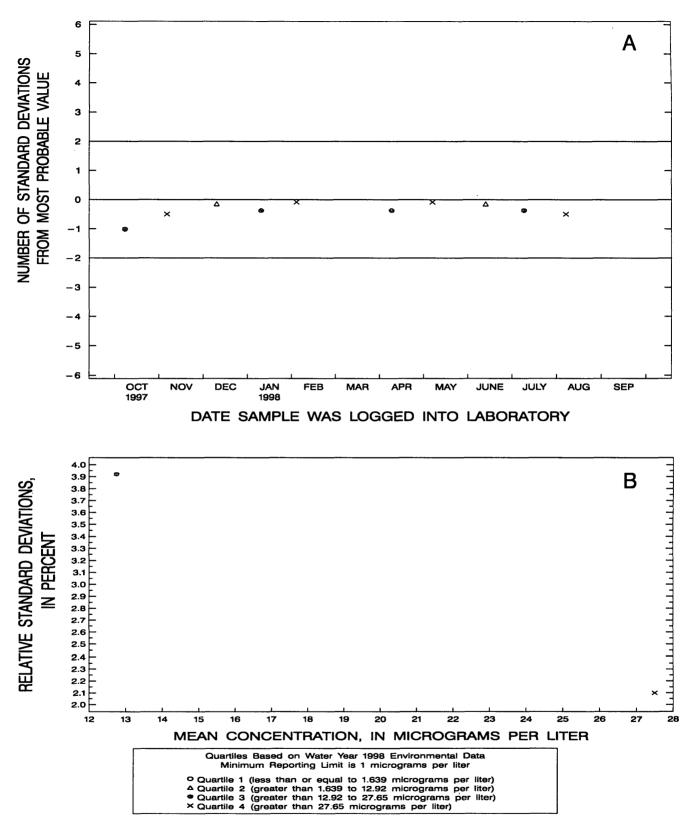


Figure 115. Chromium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

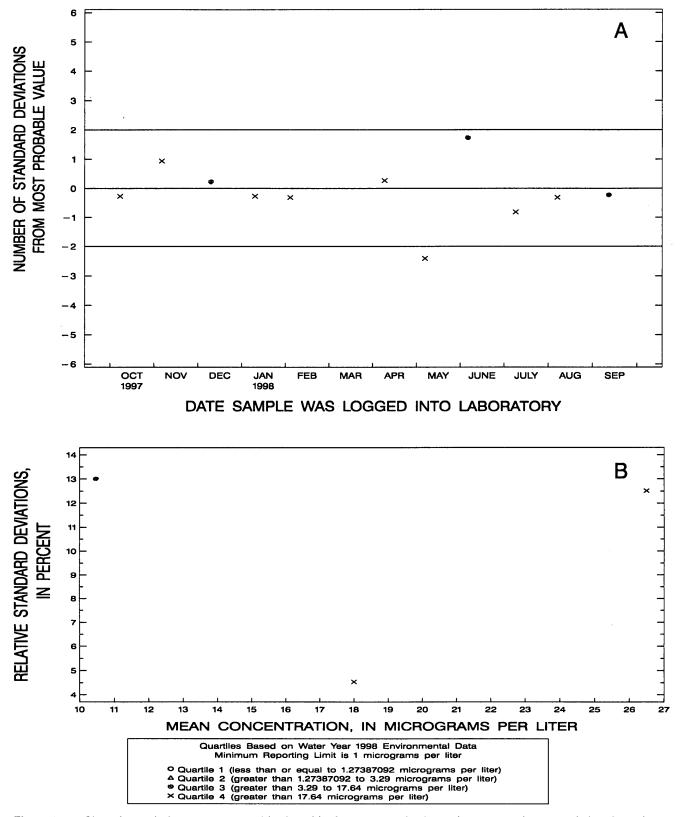


Figure 116. Chromium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

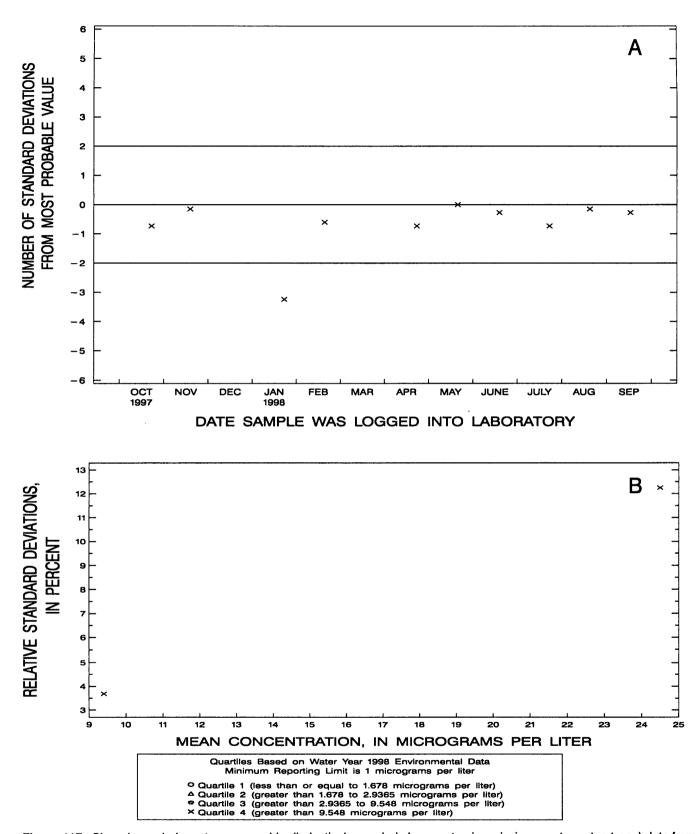


Figure 117. Chromium, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

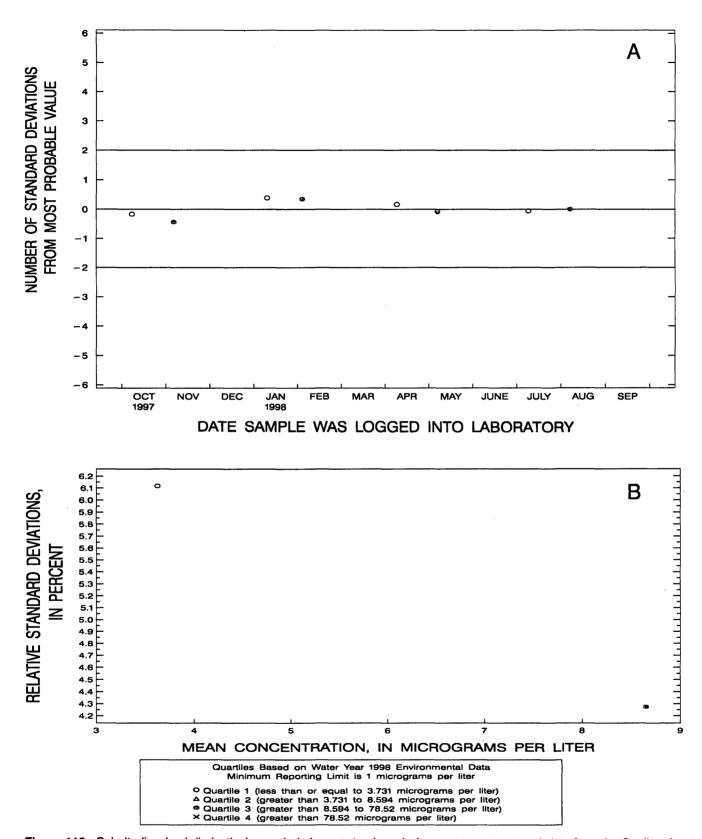


Figure 118. Cobalt, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

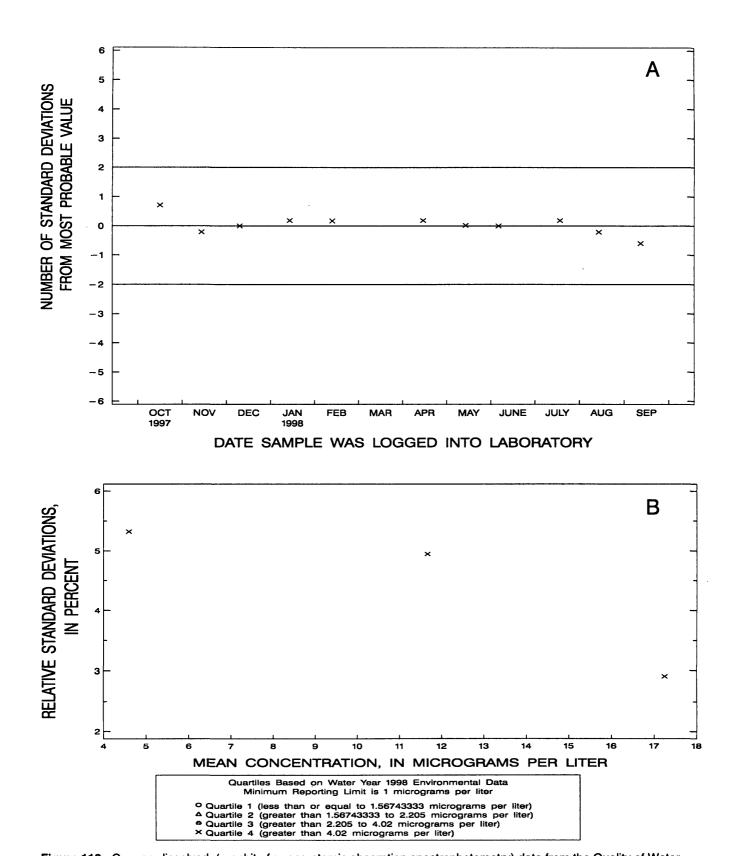


Figure 119. Copper, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

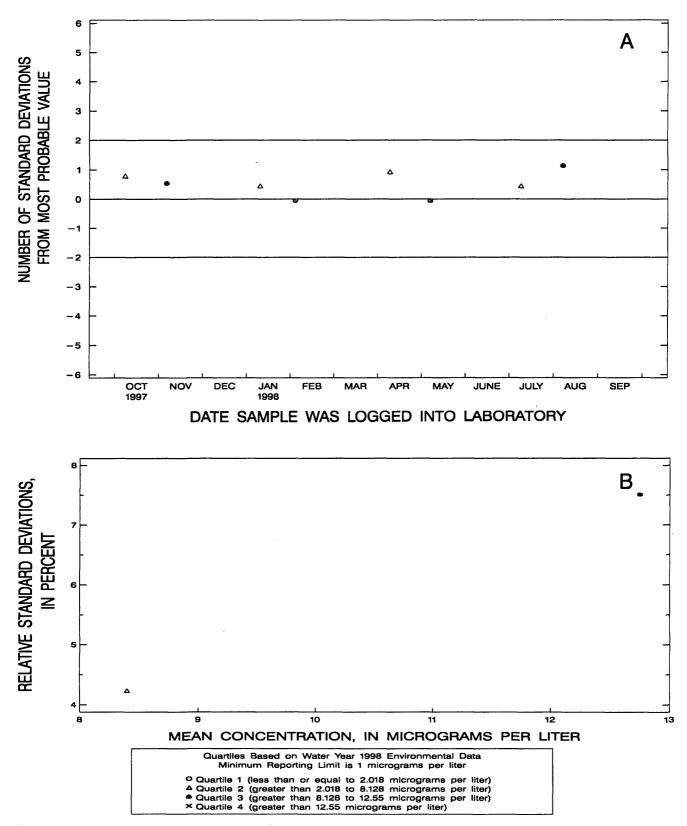


Figure 120. Copper, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

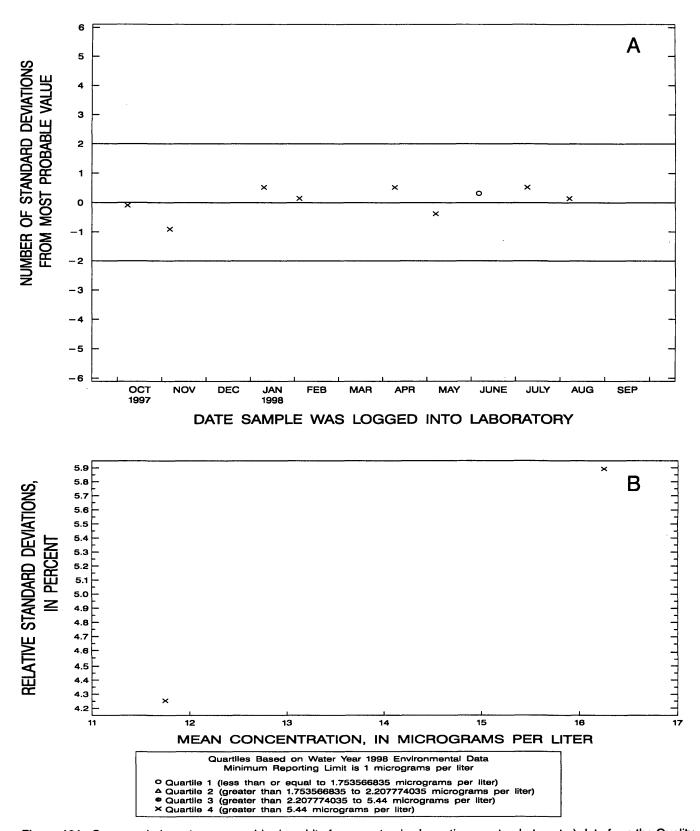


Figure 121. Copper, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

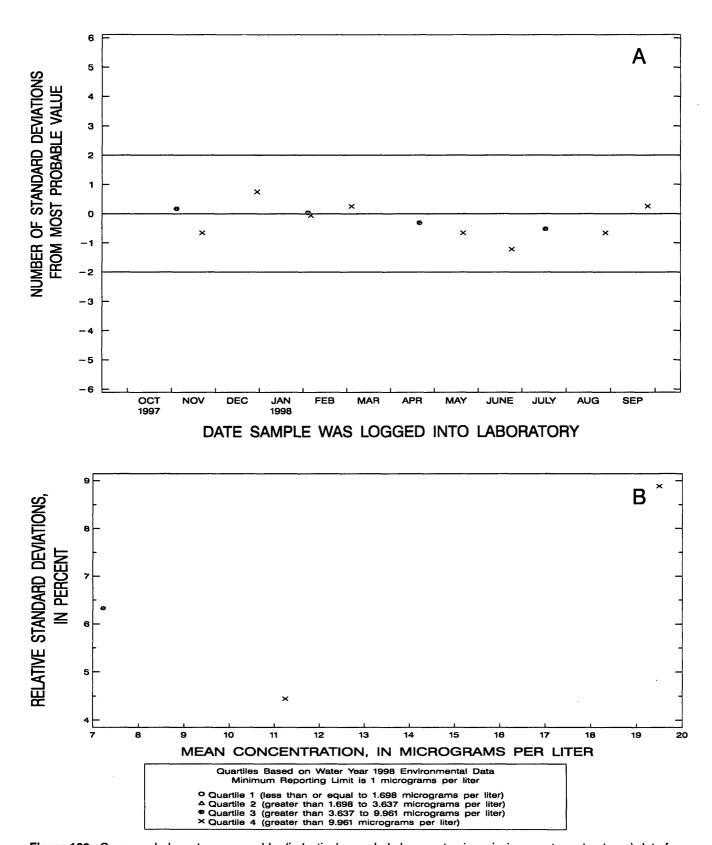


Figure 122. Copper, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

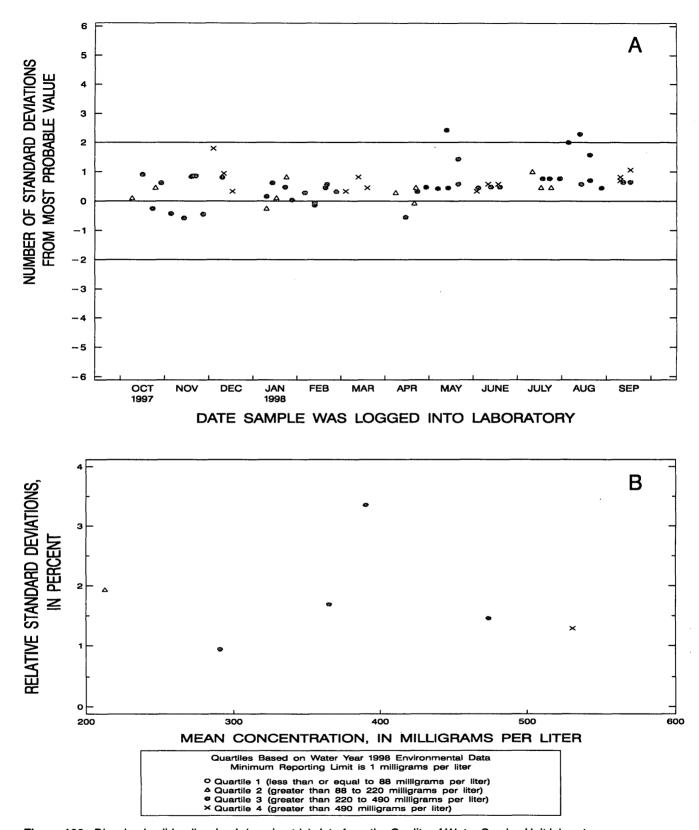


Figure 123. Dissolved solids, dissolved, (gravimetric) data from the Quality of Water Service Unit laboratory.

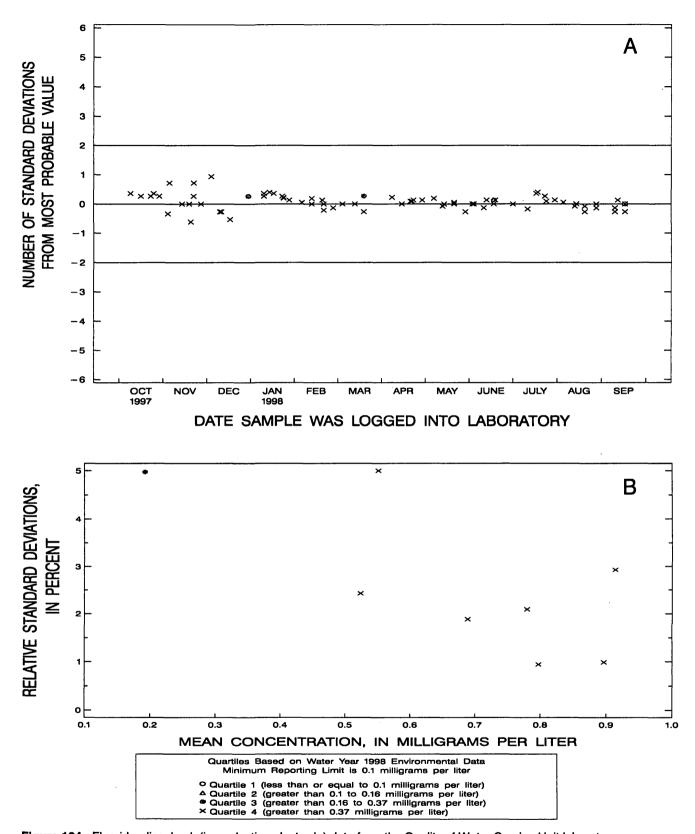


Figure 124. Fluoride, dissolved, (ion-selective electrode) data from the Quality of Water Service Unit laboratory.

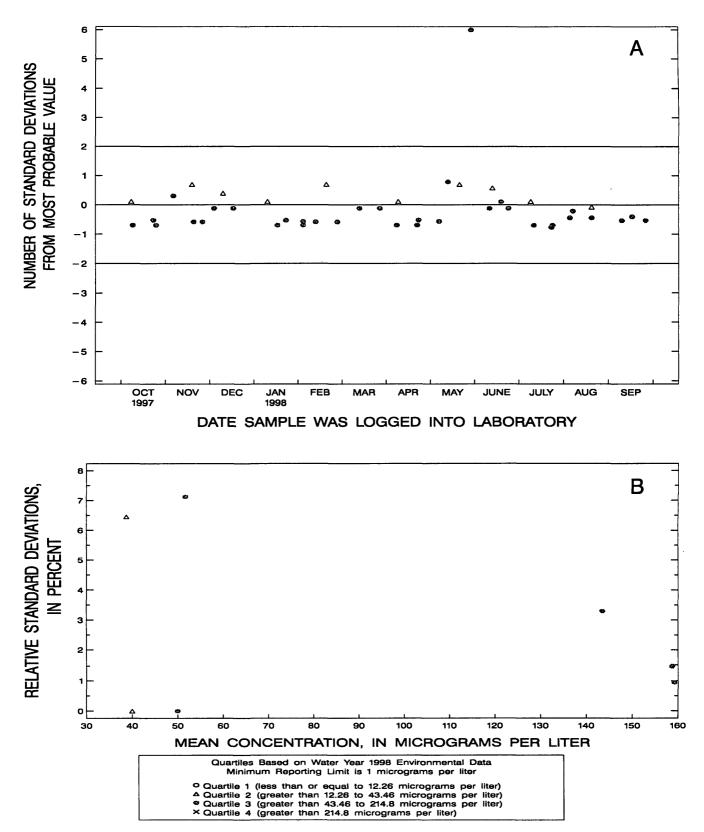


Figure 125. Iron, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

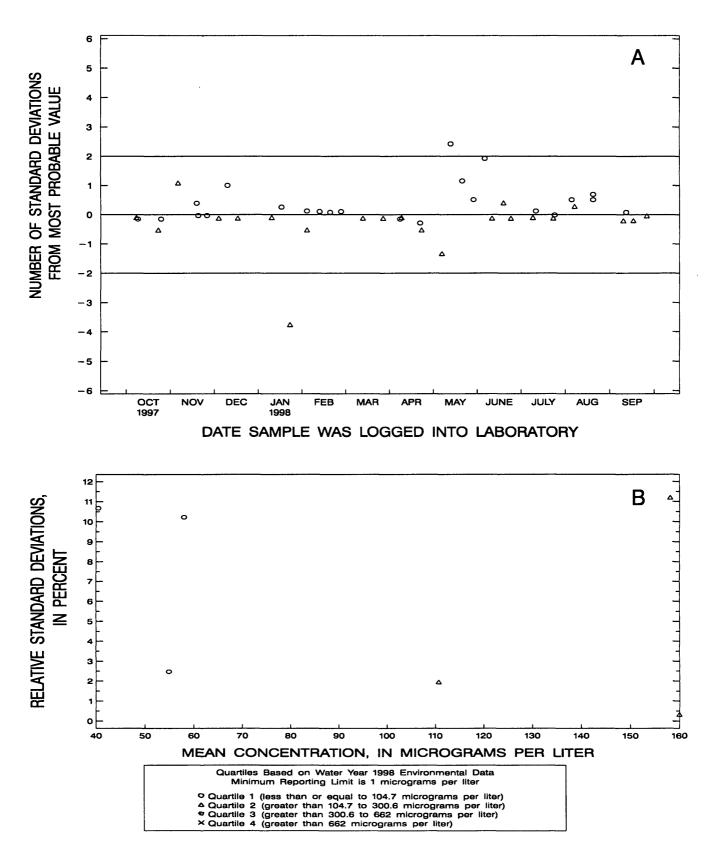


Figure 126. Iron, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

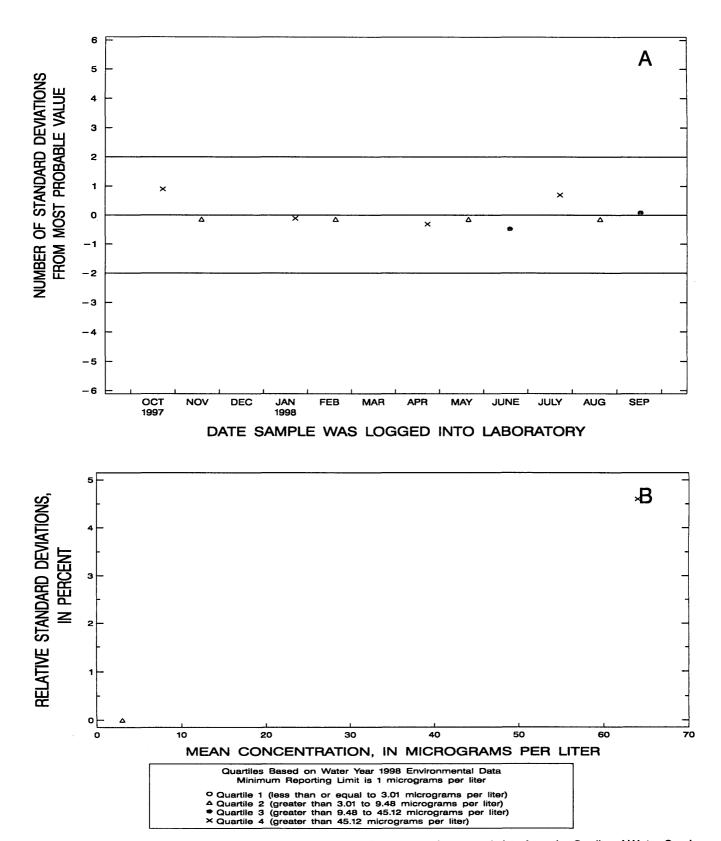


Figure 127. Lead, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

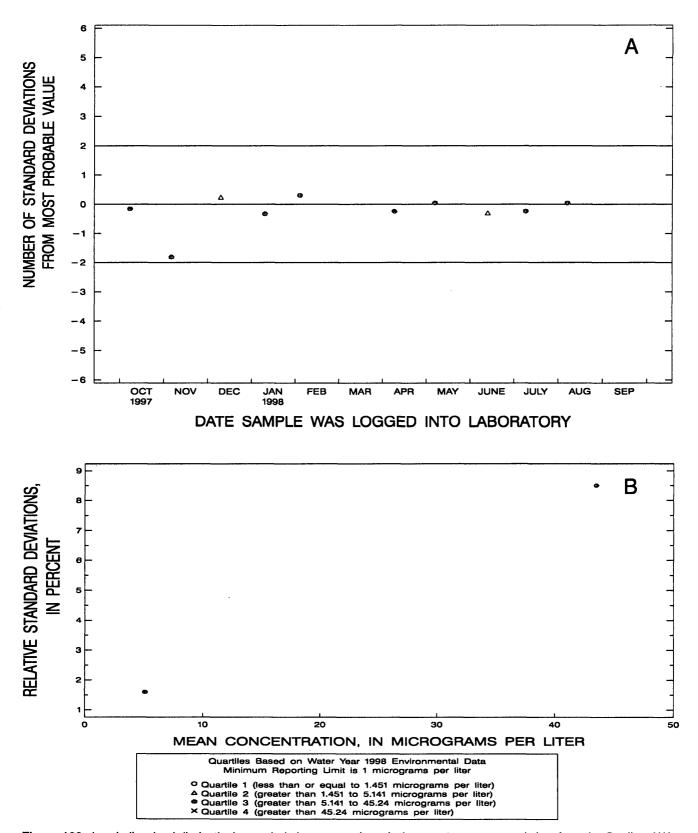


Figure 128. Lead, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

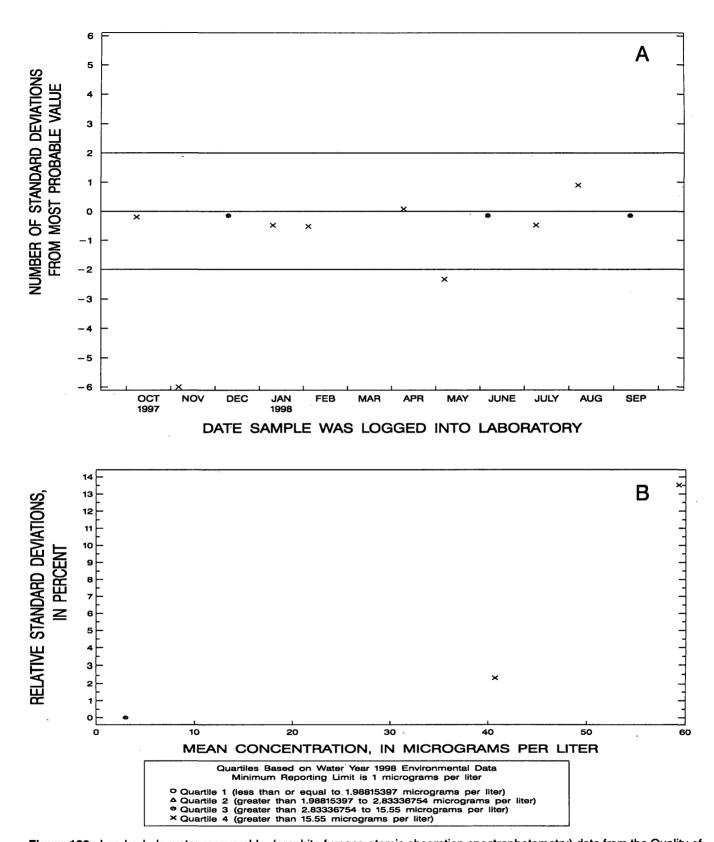


Figure 129. Lead, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

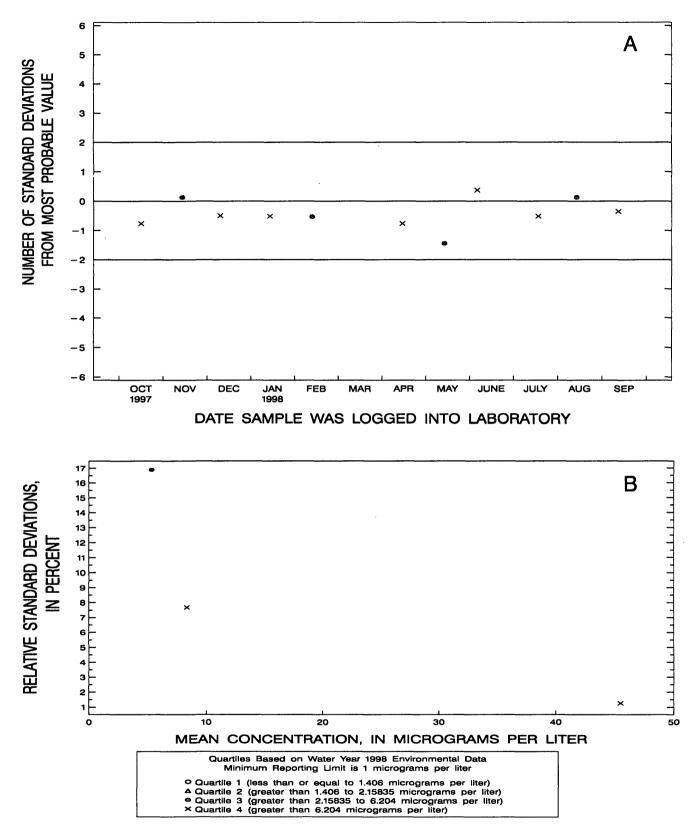


Figure 130. Lead, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

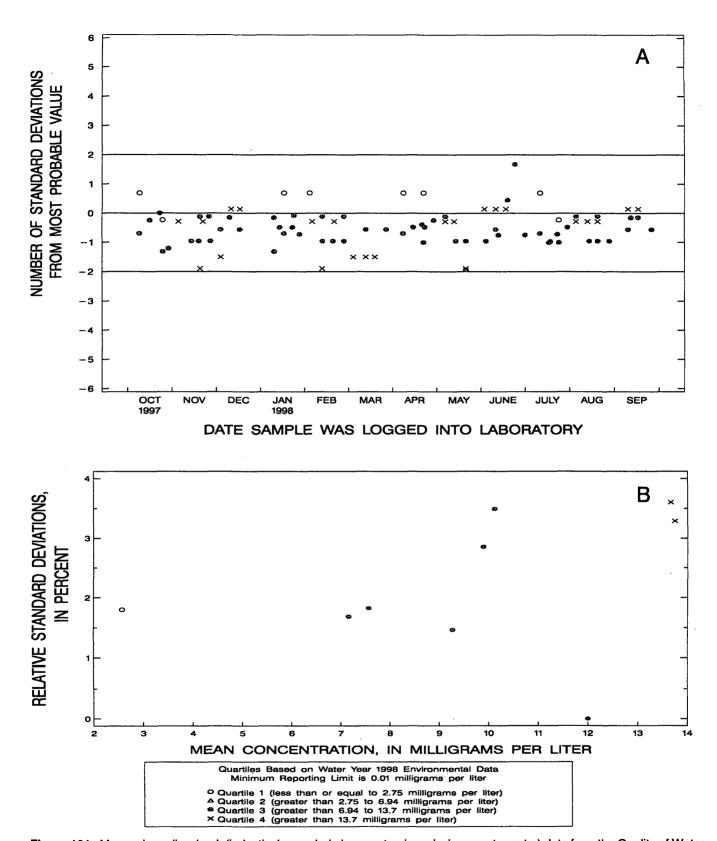


Figure 131. Magnesium, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the Quality of Water Service Unit laboratory.

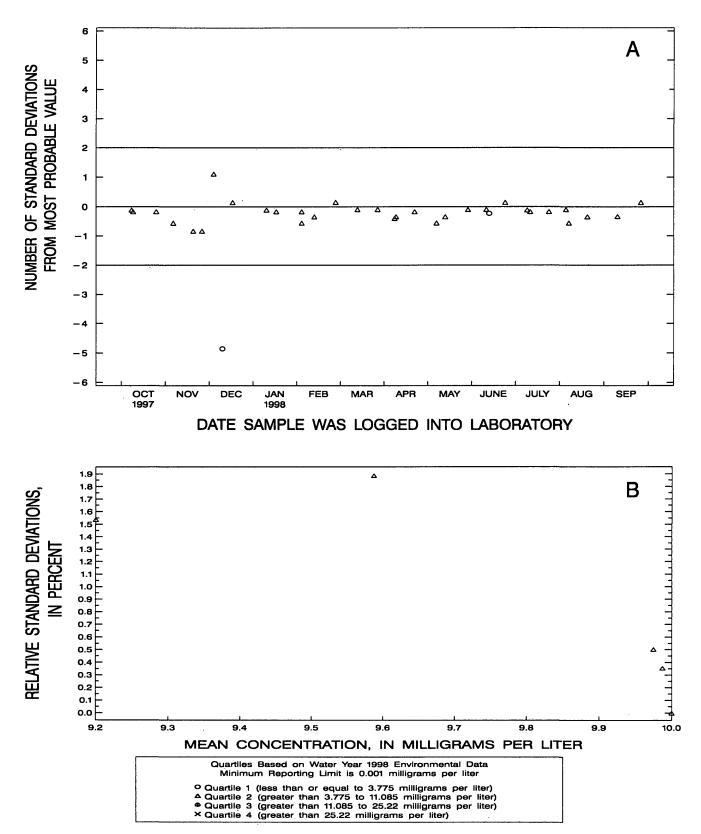


Figure 132. Magnesium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

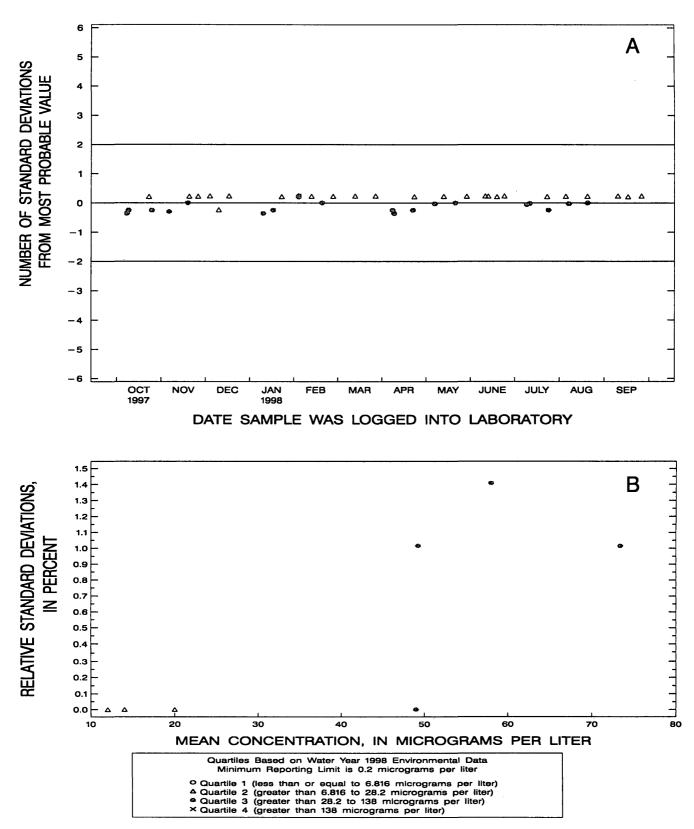


Figure 133. Manganese, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

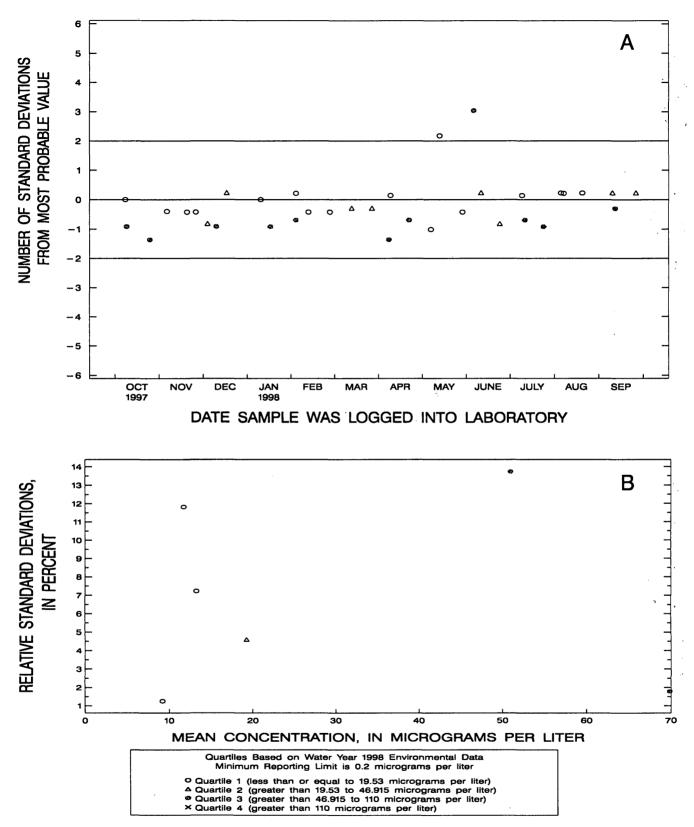


Figure 134. Manganese, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

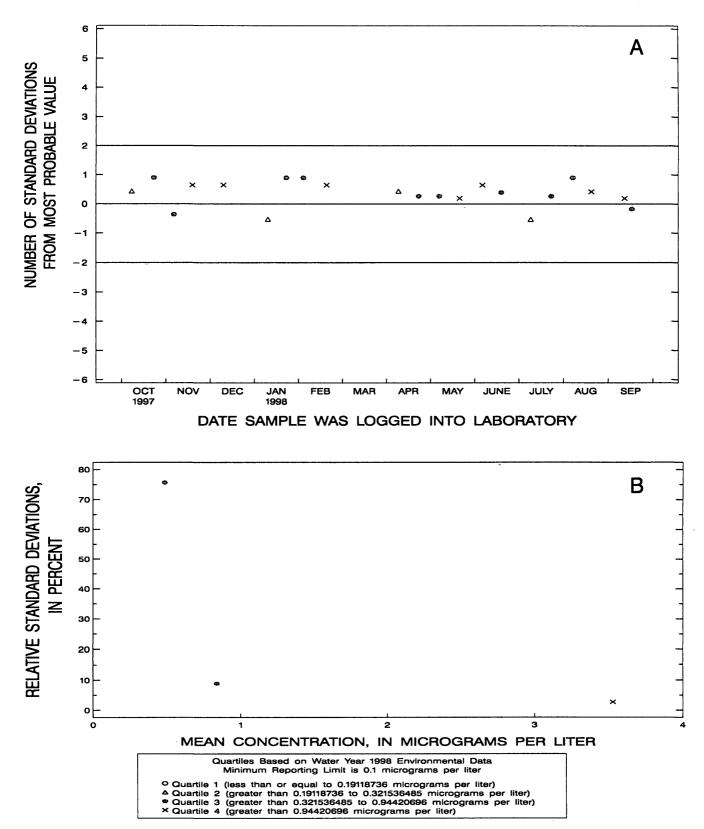


Figure 135. Mercury, whole-water recoverable, (cold vapor-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

174

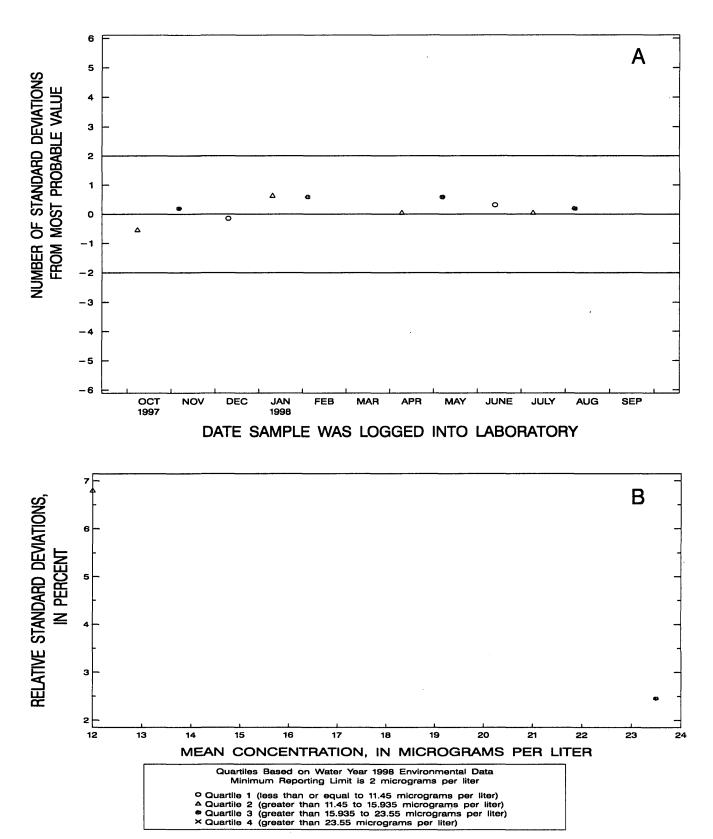


Figure 136. Molybdenum, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

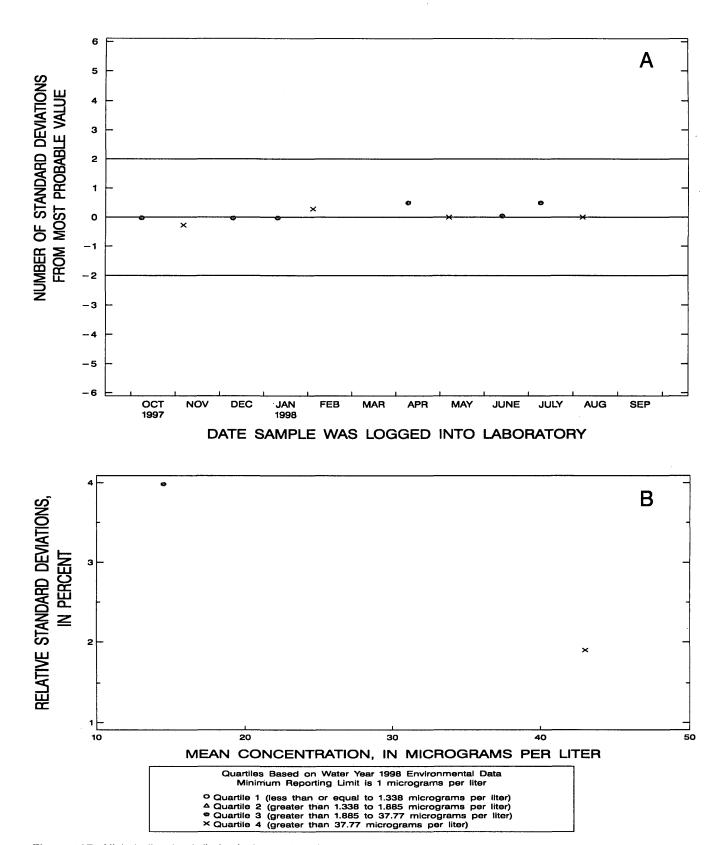


Figure 137. Nickel, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

į,

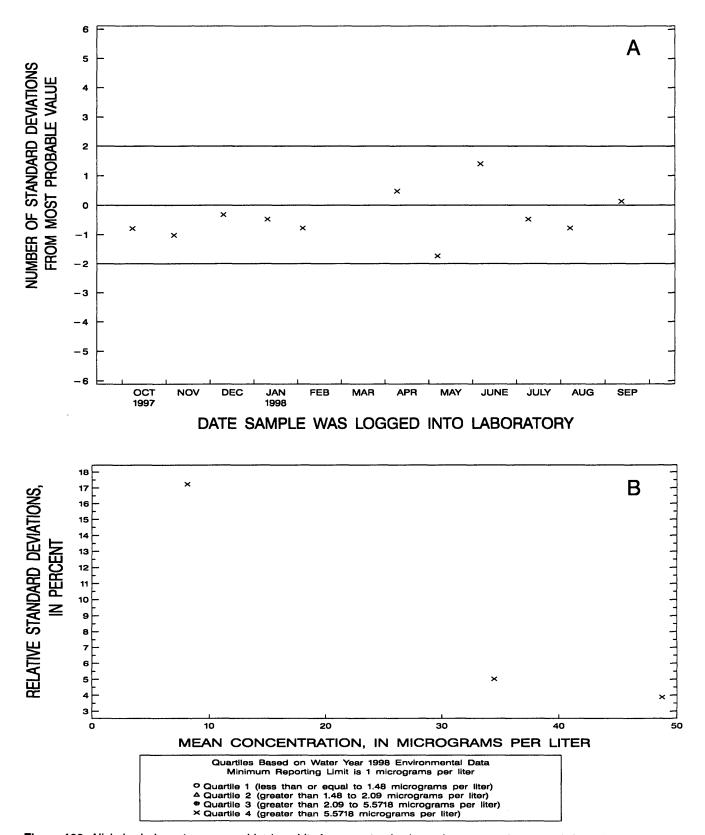


Figure 138. Nickel, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

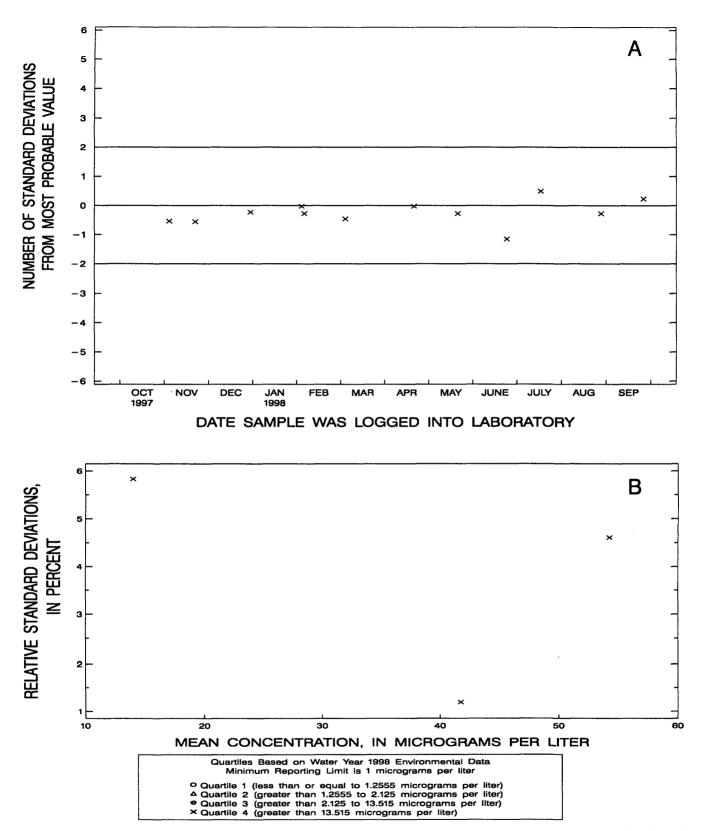


Figure 139. Nickel, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

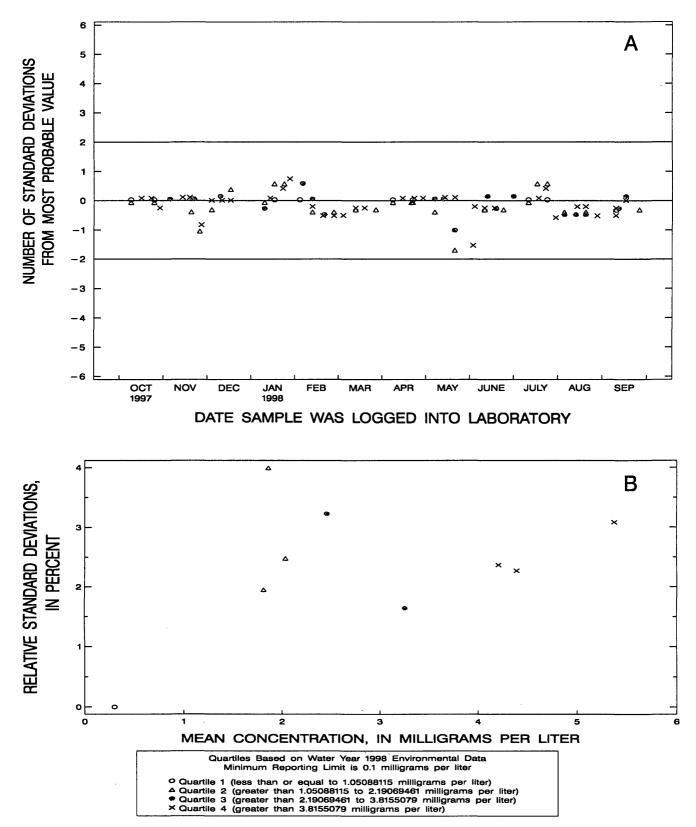


Figure 140. Potassium, dissolved, (flame-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

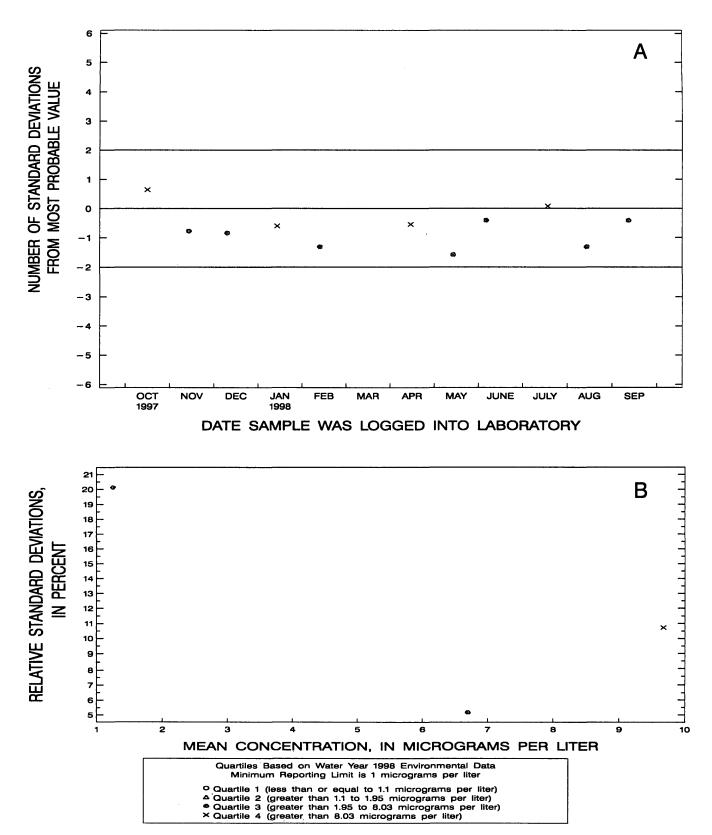


Figure 141. Selenium, dissolved, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

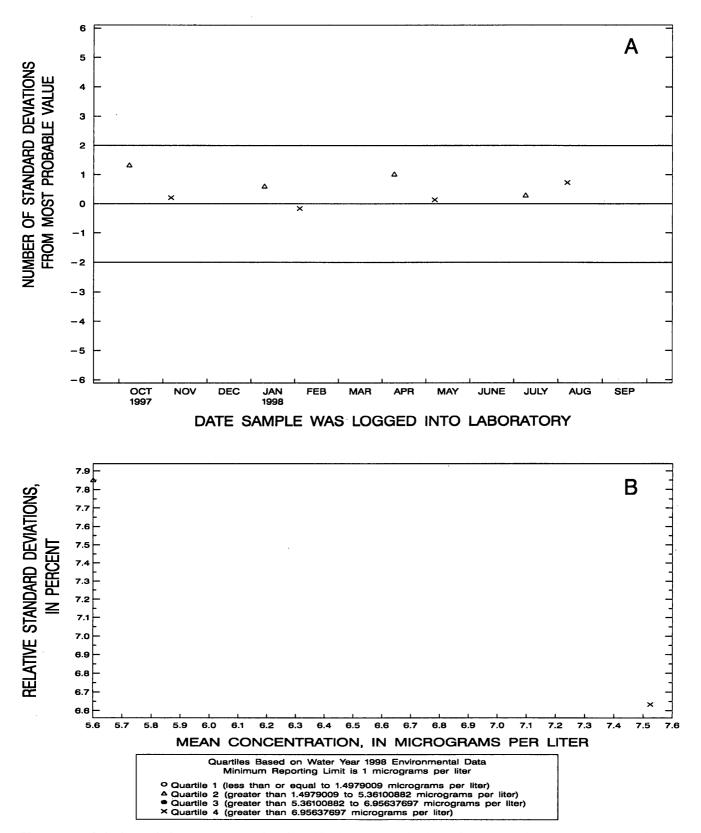


Figure 142. Selenium, whole-water recoverable, (graphite furnace-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

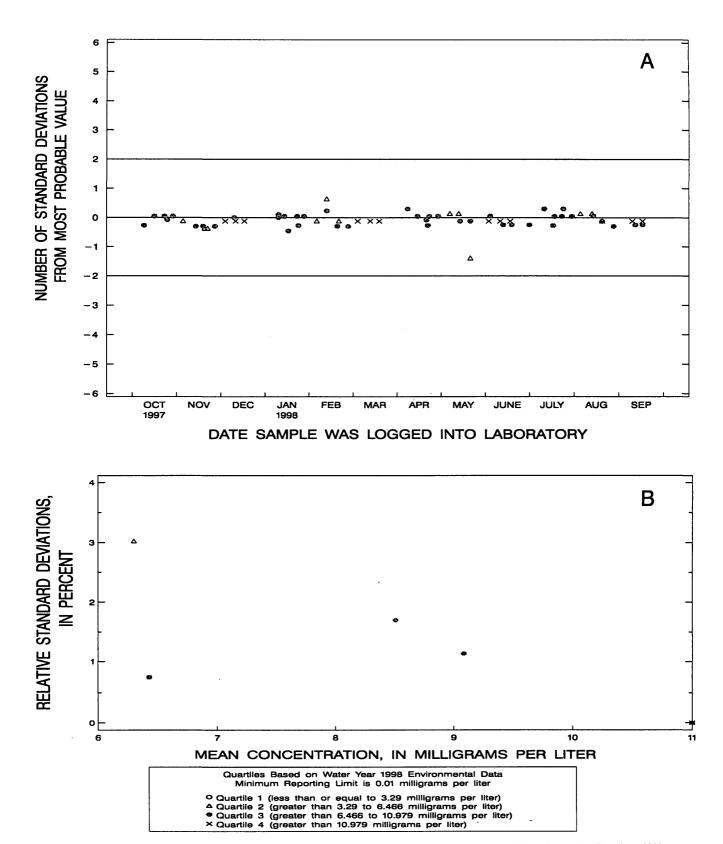


Figure 143. Silica, dissolved, (inductively coupled plasma-atomic emission spectrometry) data from the Quality of Water Service Unit laboratory.

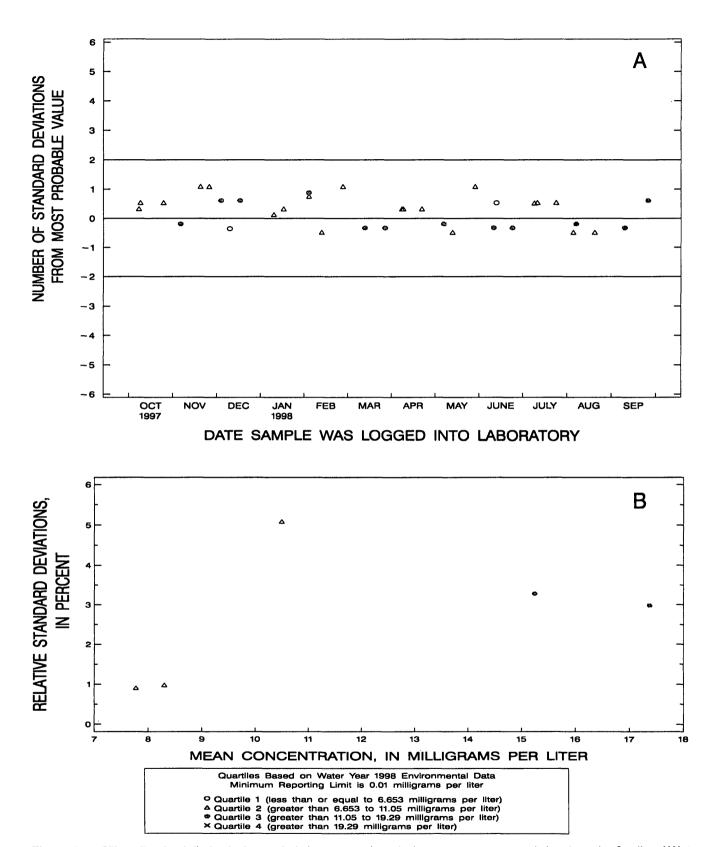


Figure 144. Silica, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

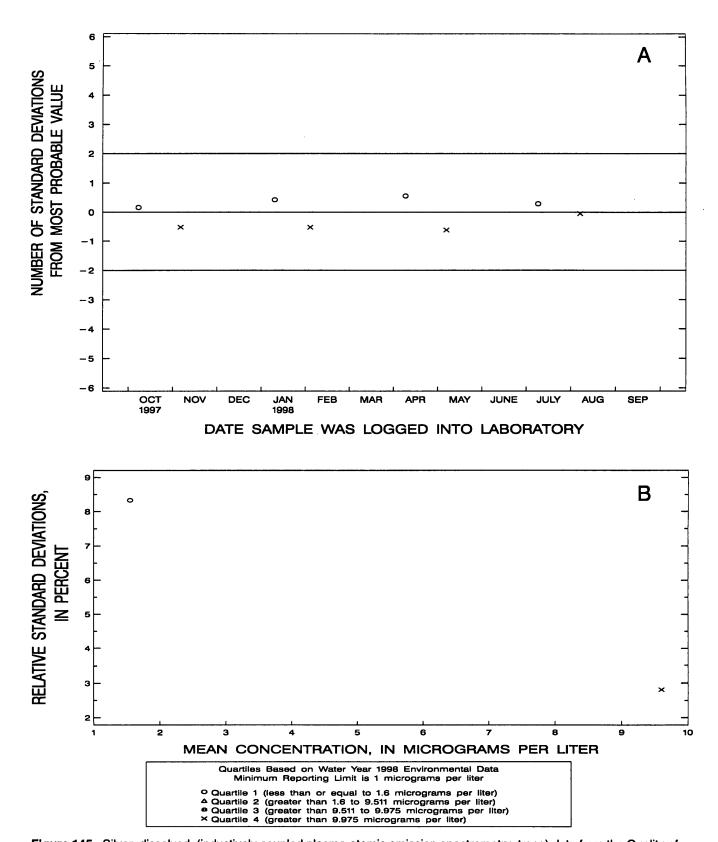


Figure 145. Silver, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

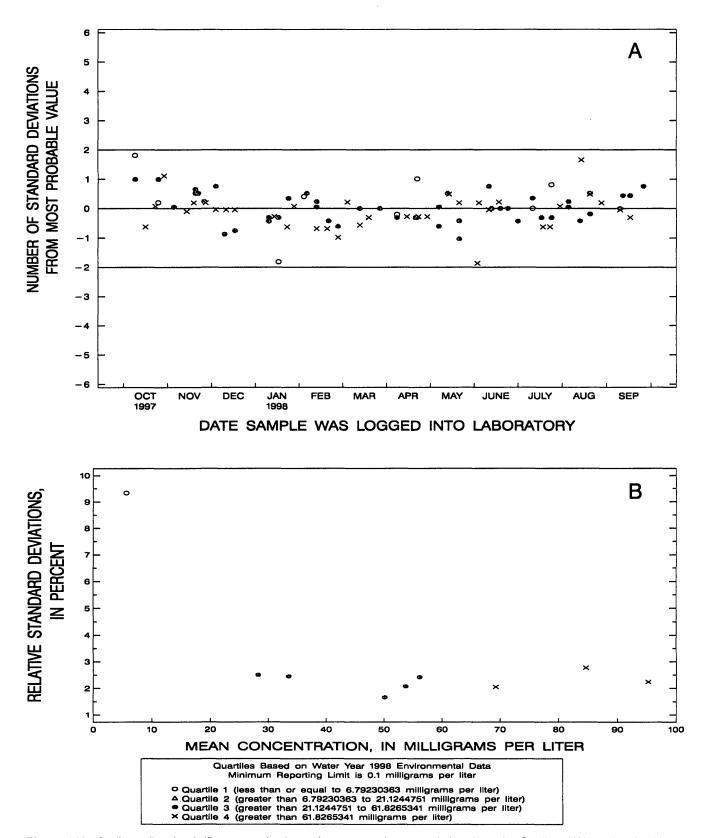


Figure 146. Sodium, dissolved, (flame-atomic absorption spectrophotometry) data from the Quality of Water Service Unit laboratory.

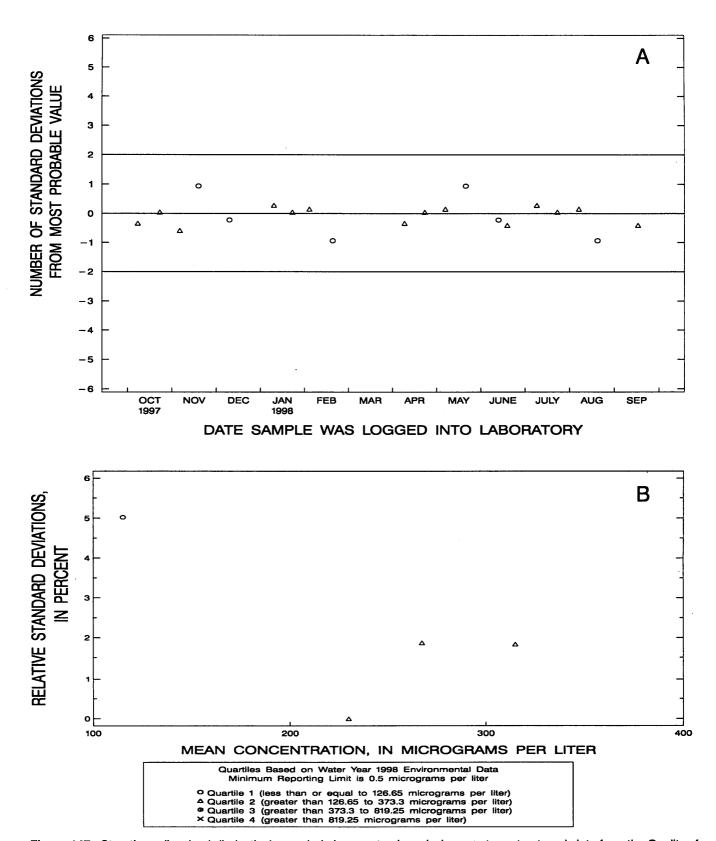


Figure 147. Strontium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

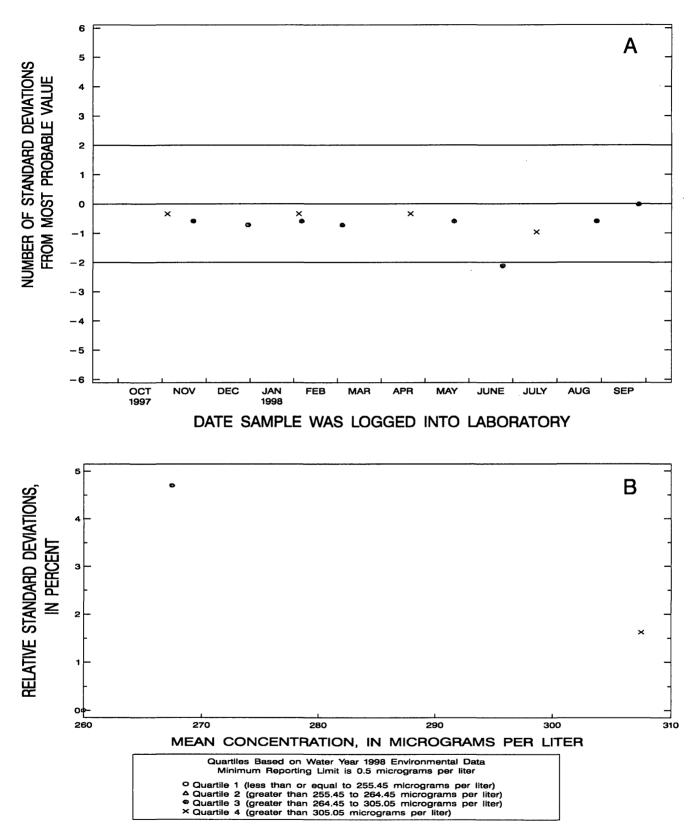


Figure 148. Strontium, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

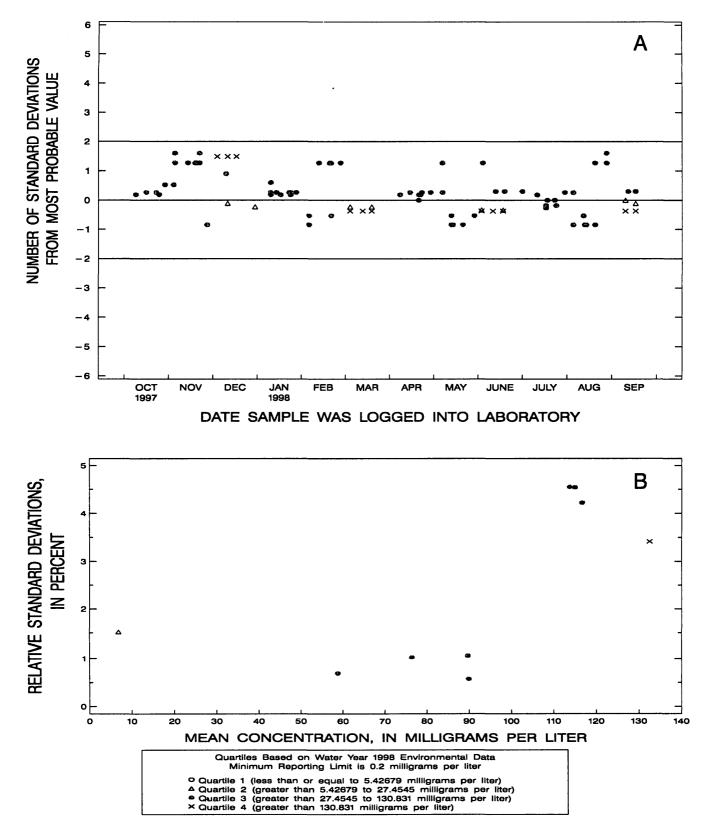


Figure 149. Sulfate, dissolved, (ion chromatography) data from the Quality of Water Service Unit laboratory.

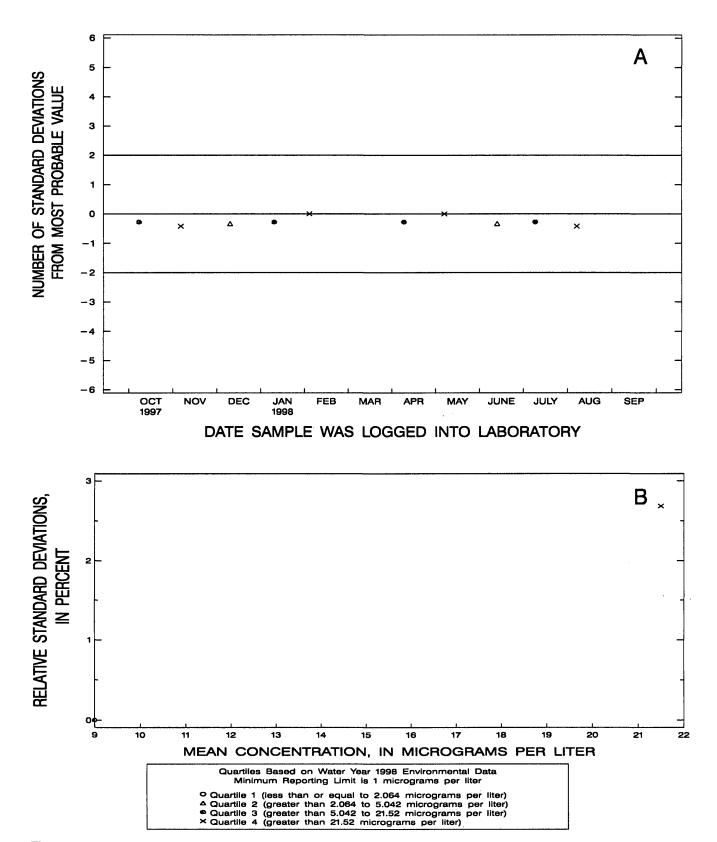


Figure 150. Vanadium, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

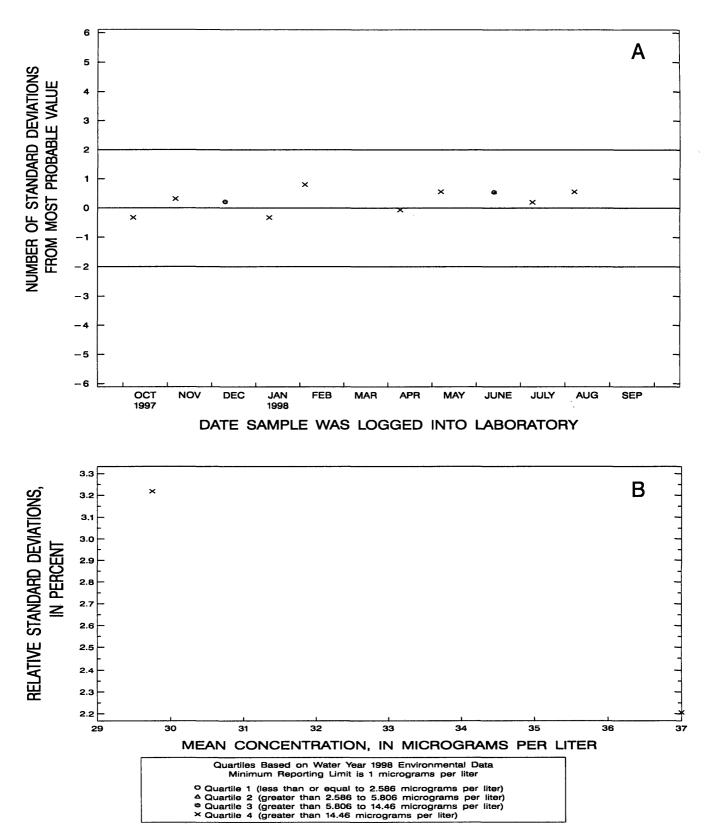


Figure 151. Zinc, dissolved, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

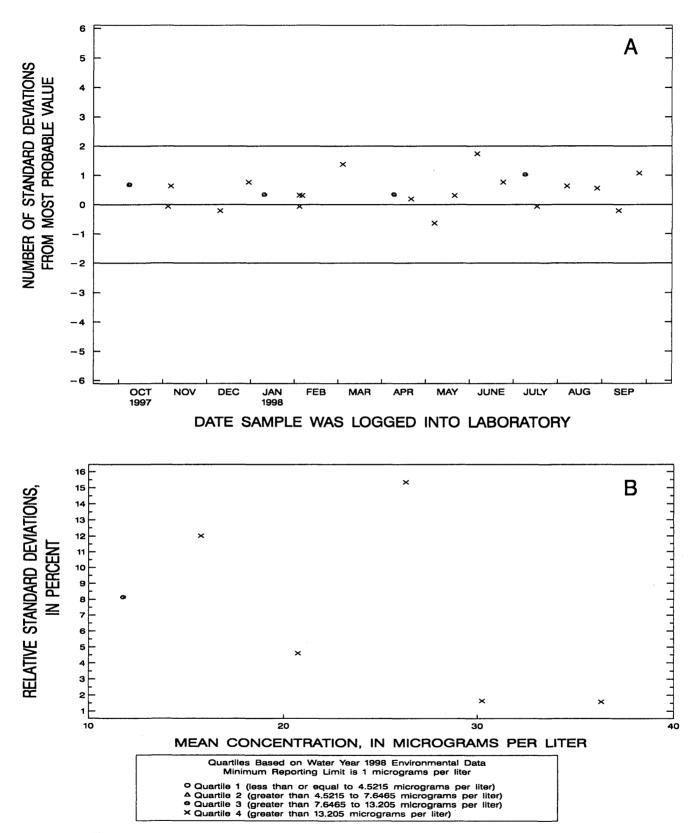


Figure 152. Zinc, whole-water recoverable, (inductively coupled plasma-atomic emission spectrometry, trace) data from the Quality of Water Service Unit laboratory.

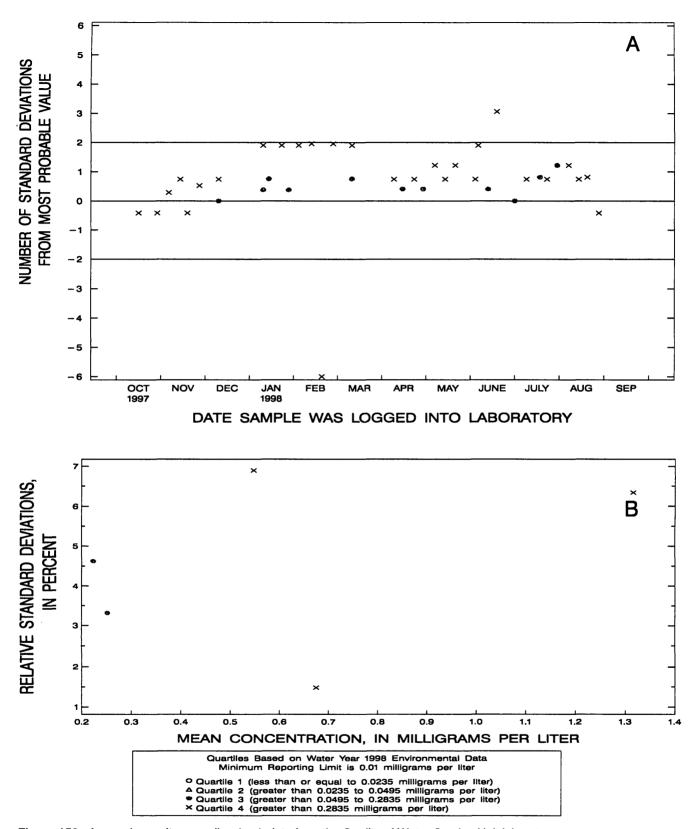


Figure 153. Ammonia as nitrogen, dissolved, data from the Quality of Water Service Unit laboratory.

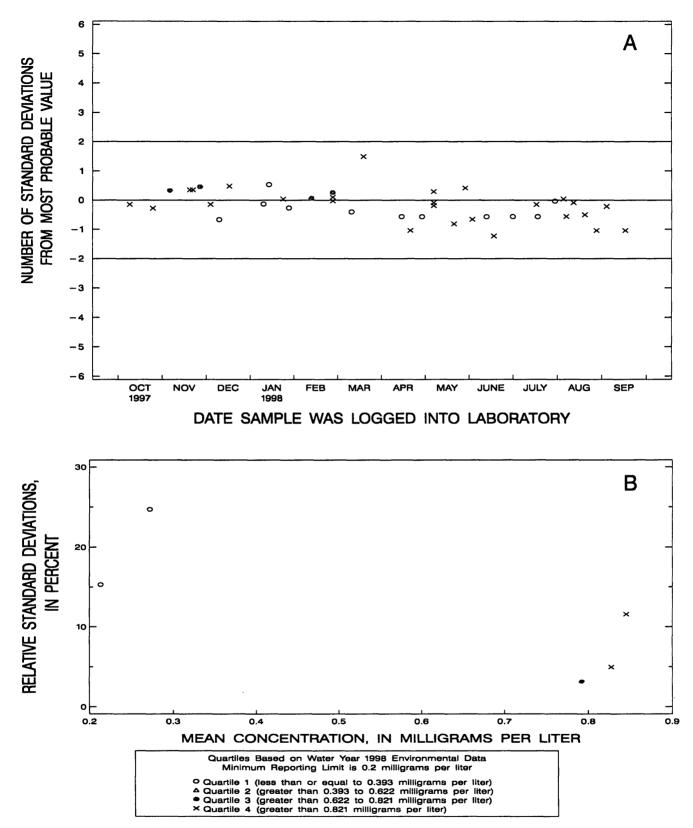


Figure 154. Ammonia plus organic nitrogen as nitrogen, dissolved, data from the Quality of Water Service Unit laboratory.

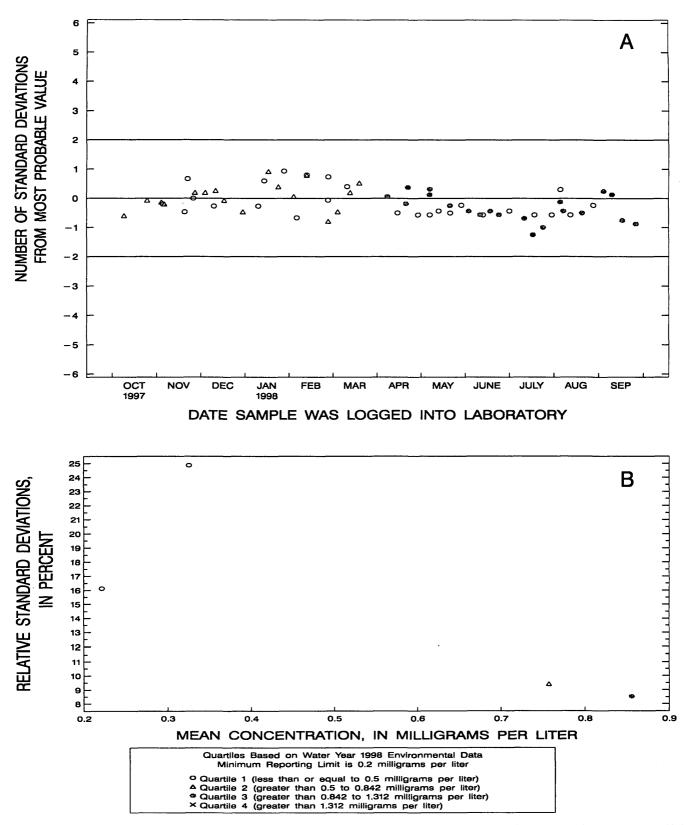


Figure 155. Ammonia plus organic nitrogen as nitrogen, whole-water recoverable, data from the Quality of Water Service Unit laboratory.

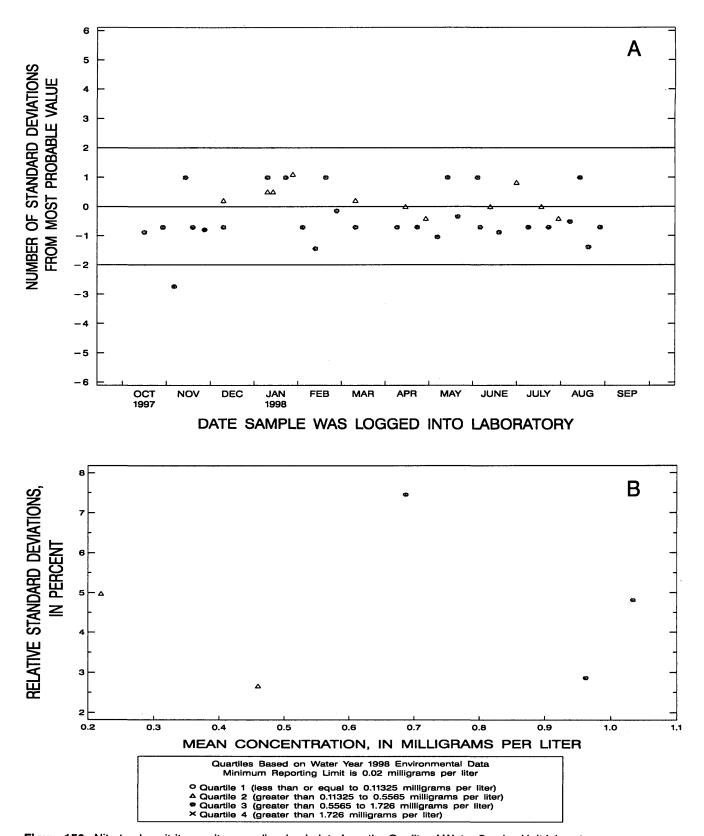


Figure 156. Nitrate plus nitrite as nitrogen, dissolved, data from the Quality of Water Service Unit laboratory.

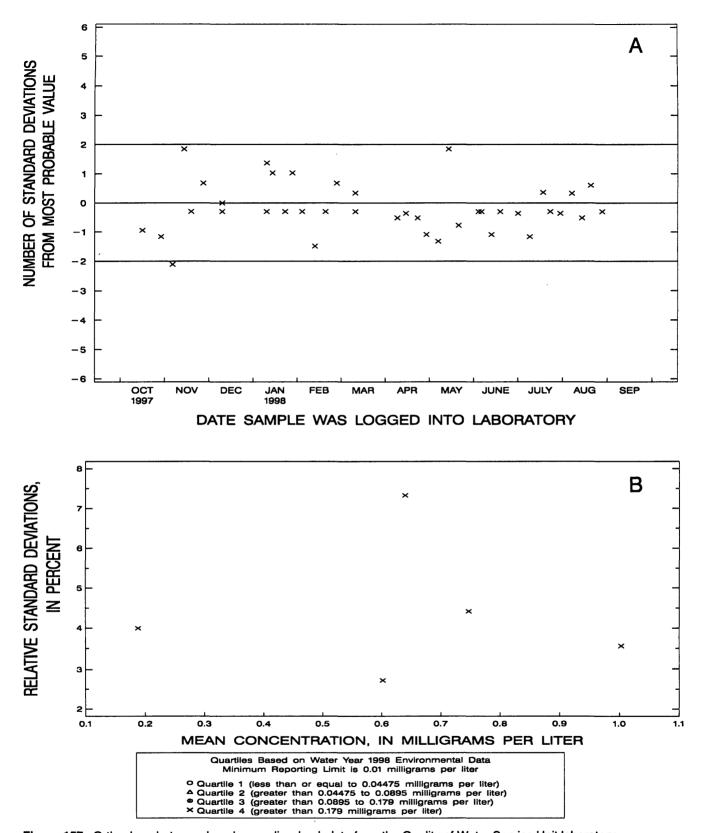


Figure 157. Orthophosphate as phosphorus, dissolved, data from the Quality of Water Service Unit laboratory.

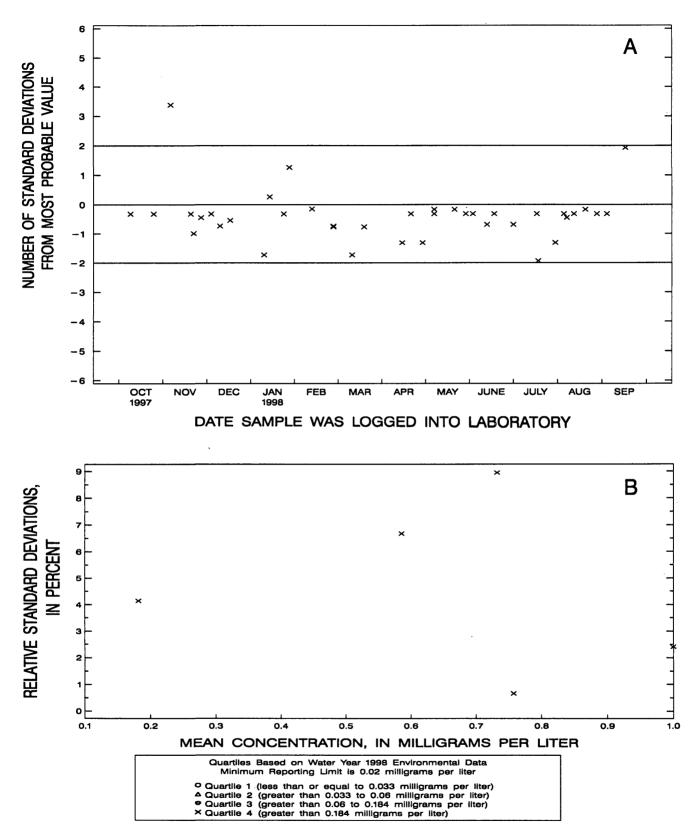


Figure 158. Phosphorus, dissolved, data from the Quality of Water Service Unit laboratory.

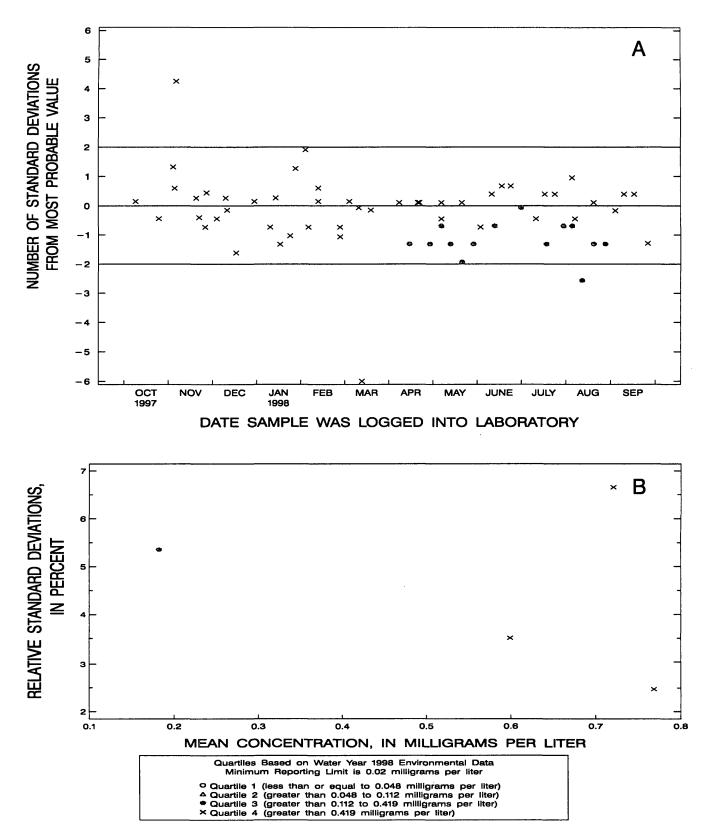


Figure 159. Phosphorus, whole-water recoverable, data from the Quality of Water Service Unit laboratory.

198



Printed on recycled paper