Quality-Assurance Results for Routine Water Analysis in U.S. Geological Survey Laboratories, Water Year 1991

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U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 94-4046



Denver, Colorado 1994

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

U.S. GEOLOGICAL SURVEY

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CONTENTS

Abstract	1
Introduction	1
Program description	2
Statistical evaluation	4
Control chart development and evaluation	4
Precision chart development and evaluation	8
Binomial-probability-distribution technique to assess precision and bias	8
Quality-assurance results for inorganic-constituent samples	12
	12
Bias	14
Quality-assurance results for nutrient constituent samples	15
Precision	15
Bias	15
Quality-assurance results for low ionic-strength samples	17
Precision	17
2.40	17
Summary	18
	18
Supplemental data	21

FIGURES

1-123.	Grapl	hs showing:	
	1.	Alkalinity, whole-water recoverable, (electrometric titration) data from the	
		National Water Quality Laboratory	22
	2.	Aluminum, dissolved, (atomic emission spectrometric, direct-current plasma) data from the	
		National Water Quality Laboratory	23
	3.	Aluminum, whole-water recoverable, (atomic emission spectrometric, direct-current plasma) data	
		from the National Water Quality Laboratory	24
	4.	Antimony, dissolved, (atomic absorption spectrometric, hydride) data from the	
		National Water Quality Laboratory	25
	5.	Arsenic, dissolved and whole-water recoverable, (atomic absorption spectrometric, hydride) data	
		from the National Water Quality Laboratory	26
	6.	Arsenic, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the	
		National Water Quality Laboratory	27
	7.	Barium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
		National Water Quality Laboratory	28
	8.	Barium, dissolved, (atomic absorption spectrometric, direct) data from the	
		National Water Quality Laboratory	29
	9.	Barium, whole-water recoverable, (atomic absorption spectrometric, direct) data from the	
		National Water Quality Laboratory	30
	10.	Beryllium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
		National Water Quality Laboratory	31
	11.	Beryllium, whole-water recoverable, (atomic absorption spectrometric, direct) data from the	
		National Water Quality Laboratory	32
	12.	Boron, dissolved, (atomic emission spectrometric, direct-current plasma) data from the	
		National Water Quality Laboratory	33
	13.	Cadmium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
		National Water Quality Laboratory	34

14.	Cadmium, dissolved, (atomic absorption spectrometric, graphite furnace) data from the	
	National Water Quality Laboratory	35
15.	Cadmium, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data	
	from the National Water Quality Laboratory	36
16.	Calcium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
	National Water Quality Laboratory	37
17.	Calcium, dissolved, (atomic absorption spectrometric, direct) data from the	
	National Water Quality Laboratory	38
18.	Chloride, dissolved, (ion-exchange chromatographic) data from the	
	National Water Quality Laboratory	39
19.	Chromium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
	National Water Quality Laboratory	40
20.	Chromium, dissolved, (atomic emission spectrometric, direct-current plasma) data from the	
	National Water Quality Laboratory	41
21.	Chromium, whole-water recoverable, (atomic emission spectrometric, direct-current plasma) data	
	from the National Water Quality Laboratory	42
22.	Cobalt, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
22.	National Water Quality Laboratory	43
23.	Cobalt, dissolved, (atomic absorption spectrometric, graphite furnace) data from the	45
25.	National Water Quality Laboratory	44
24.	Cobalt, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the	
27.	National Water Quality Laboratory	45
25.	Copper, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	45
23.	National Water Quality Laboratory	46
26.	Copper, dissolved, (atomic absorption spectrometric, graphite furnace) data from the	40
20.	National Water Quality Laboratory	47
27.	Copper, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the	47
21.	National Water Quality Laboratory	48
20	Dissolved solids, (gravimetric) data from the National Water Quality Laboratory	40 49
28.	Fluoride, dissolved, (ion-exchange chromatographic) data from the	47
29.	National Water Quality Laboratory	50
20		50
30.	Iron, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory	51
21		51
31.	Iron, dissolved, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory	50
22		52
32.	Iron, whole-water recoverable, (atomic absorption spectrometric, direct) data from the	50
22	National Water Quality Laboratory	53
33.	Lead, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	5 4
~ ~	National Water Quality Laboratory	54
34.	Lead, dissolved, (atomic absorption spectrometric, graphite furnace) data from the	
	National Water Quality Laboratory	55
35.	Lead, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the	
	National Water Quality Laboratory	56
36.	Lithium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
	National Water Quality Laboratory	57
37.	Lithium, whole-water recoverable, (atomic absorption spectrometric, direct) data from the	
	National Water Quality Laboratory	58
38.	Magnesium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
	National Water Quality Laboratory	59
39.	Magnesium, dissolved, (atomic absorption spectrometric, direct) data from the	
	National Water Quality Laboratory	60
40.	Manganese, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
	National Water Quality Laboratory	61

41.	Manganese, dissolved, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory	62
42.	Manganese, whole-water recoverable, (atomic absorption spectrometric, direct) data from the	0.
	National Water Quality Laboratory	6.
43.	Mercury, dissolved, (atomic absorption spectrometric, flameless) data from the	
	National Water Quality Laboratory	64
44.	Mercury, whole-water recoverable, (atomic absorption spectrometric, flameless) data from the	
	National Water Quality Laboratory	6.
45.	Molybdenum, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
	National Water Quality Laboratory	6
46.	Molybdenum, dissolved, (atomic absorption spectrometric, chelation extraction) data from the	
	National Water Quality Laboratory	6
47.	Molybdenum, whole-water recoverable, (atomic absorption spectrometric, chelation extraction)	
	data from the National Water Quality Laboratory	6
48.	Nickel, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
	National Water Quality Laboratory	6
49.	Nickel, dissolved, (atomic absorption spectrometric, graphite furnace) data from the	
	National Water Quality Laboratory	7(
50.	Nickel, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the	
	National Water Quality Laboratory	7
51.	Potassium, dissolved, (atomic absorption spectrometric, direct) data from the	•
	National Water Quality Laboratory	72
52.	Selenium, dissolved and whole-water recoverable, (atomic absorption spectrometric, hydride) data	
	from the National Water Quality Laboratory	73
53.	Selenium, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from	/.
55.	the National Water Quality Laboratory	74
54.	Silica, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	/-
54.	National Water Quality Laboratory	75
E E	Silica, dissolved, (colorimetric) data from the National Water Quality Laboratory	
55.		76
56.	Silver, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
57	National Water Quality Laboratory	77
57.	Silver, dissolved, (atomic absorption spectrometric, graphite furnace) data from the	
50	National Water Quality Laboratory	78
58.	Silver, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the	-
50	National Water Quality Laboratory	79
59.	Sodium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
	National Water Quality Laboratory	80
60.	Sodium, dissolved, (atomic absorption spectrometric, direct) data from the	
	National Water Quality Laboratory	81
61.	Strontium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
	National Water Quality Laboratory	82
62.	Sulfate, dissolved, (ion-exchange chromatographic) data from the National Water Quality Laboratory	83
63.	Vanadium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
	National Water Quality Laboratory	84
64.	Vanadium, dissolved, (colorimetric) data from the National Water Quality Laboratory	85
65.	Zinc, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the	
	National Water Quality Laboratory	86
66.	Zinc, dissolved, (atomic absorption spectrometric, direct) data from the National Water	
	Quality Laboratory	87
67.	Zinc, whole-water recoverable, (atomic absorption spectrometric, direct) data from the	
	National Water Quality Laboratory	88
68.	Ammonia as nitrogen, dissolved and whole-water recoverable, (colorimetric) data from the	
	National Water Quality Laboratory	89

69.	Ammonia plus organic nitrogen as nitrogen, dissolved and whole-water recoverable, (colorimetric) data from the National Water Quality Laboratory	90
70.	Nitrate plus nitrite as nitrogen, dissolved and whole-water recoverable, (colorimetric) data	
	from the National Water Quality Laboratory	91
71.	Orthophosphate as phosphorus, dissolved and whole-water recoverable, (colorimetric) data from the National Water Quality Laboratory	92
72.	Phosphorus, dissolved and whole-water recoverable, colorimetric) data from the	12
12.	National Water Quality Laboratory	93
73.	Cadmium, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data	,,,
15.	from the National Water Quality Laboratory	94
74.	Calcium, dissolved, low ionic-strength, (atomic absorption spectrometric, direct) data from the	74
,	National Water Quality Laboratory	95
75.	Chloride, dissolved, low ionic-strength, (ion-exchange chromatographic) data from the	10
	National Water Quality Laboratory	96
76.	Chromium, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data	
	from the National Water Quality Laboratory	97
77.	Cobalt, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data	
	from the National Water Quality Laboratory	98
78.	Copper, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data	
	from the National Water Quality Laboratory	99
79.	Fluoride, dissolved, low ionic-strength, (ion-exchange chromatographic) data from the	
	National Water Quality Laboratory	100
80.	Lead, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data	
	from the National Water Quality Laboratory	101
81.	Magnesium, dissolved, low ionic-strength, (atomic absorption spectrometric, direct) data from the	
	National Water Quality Laboratory	102
82.	Nickel, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data	
	from the National Water Quality Program	103
83.	Potassium, dissolved, low ionic-strength, (atomic absorption spectrometric, direct) data from the	
	National Water Quality Laboratory	104
84.	Sodium, dissolved, low ionic-strength, (atomic absorption spectrometric, direct) data from the	
	National Water Quality Laboratory	105
85.	Specific conductance, dissolved, low ionic-strength, (electrometric, Wheatstone bridge) data	
	from the National Water Quality Laboratory	106
86.	Sulfate, dissolved, low ionic-strength, (ion-exchange chromatographic) data from the	
	National Water Quality Laboratory	107
87.	Alkalinity, dissolved, (electrometric titration) data from the	
	Quality of Water Service Unit laboratory	108
88.	Aluminum, whole-water recoverable, (atomic absorption spectrometric, chelation-extraction) data	
	from the Quality of Water Service Unit laboratory	109
89.	Arsenic, dissolved and whole-water recoverable, (atomic absorption spectrometric, hydride) data	
	from the Quality of Water Service Unit laboratory	110
90.	Beryllium, whole-water recoverable, (atomic absorption spectrometric, direct) data from the	
	Quality of Water Service Unit laboratory	
91.	Boron, dissolved, (colorimetric) data from the Quality of Water Service Unit laboratory	112
92.	Cadmium, dissolved, (atomic absorption spectrometric, graphite furnace) data from the Quality of Water Service Unit laboratory	113
93.	Cadmium, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data	
	from the Quality of Water Service Unit laboratory	114
94.	Calcium, dissolved, (atomic absorption spectrometric, direct) data from the	_ •
	Quality of Water Service Unit laboratory.	115
95.	Chloride, dissolved, (ion-exchange chromatographic) data from the	
	Quality of Water Service Unit laboratory	116

96.	Chromium, whole-water recoverable, (atomic absorption spectrometric, chelation-extraction) data	
	from the Quality of Water Service Unit laboratory	117
97.	Copper, dissolved, (atomic absorption spectrometric, graphite furnace) data from the Quality of Water Service Unit laboratory	118
98.	Copper, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the	
	Quality of Water Service Unit laboratory.	119
99.	Dissolved solids, (gravimetric) data from the Quality of Water Service Unit laboratory	
100.	Fluoride, dissolved, (ion-selective electrode) data from the Quality of Water Service Unit laboratory	
101.	Iron, dissolved, (atomic absorption spectrometric, direct) data from the	
	Quality of Water Service Unit laboratory	122
102.	Iron, whole-water recoverable, (atomic absorption spectrometric, direct) data from the	
	Quality of Water Service Unit laboratory	123
103.	Lead, dissolved, (atomic absorption spectrometric, graphite furnace) data from the	
	Quality of Water Service Unit laboratory	124
104.	Lead, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the	
	Quality of Water Service Unit laboratory	125
105.	Magnesium, dissolved, (atomic absorption spectrometric, direct) data from the	
	Quality of Water Service Unit laboratory	126
106.	Mercury, dissolved, (atomic absorption spectrometric, flameless) data from the	
	Quality of Water Service Unit laboratory	127
107.	Mercury, whole-water recoverable, (atomic absorption spectrometric, flameless) data from the	
	Quality of Water Service Unit laboratory.	128
108.	Nickel, dissolved, (atomic absorption spectrometric, graphite furnace) data from the	
	Quality of Water Service Unit laboratory	129
109.	Nickel, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the	
	Quality of Water Service Unit laboratory	130
110.	Potassium, dissolved, (atomic absorption spectrometric, direct) data from the	
	Quality of Water Service Unit laboratory	131
111.	Selenium, dissolved and whole-water recoverable, (atomic absorption spectrometric, hydride) data	
	from the Quality of Water Service Unit laboratory	
112.	Silica, dissolved, (colorimetric) data from the Quality of Water Service Unit laboratory	133
113.	Sodium, dissolved, (atomic absorption spectrometric, direct) data from the	
	Quality of Water Service Unit laboratory	134
114.	Strontium, dissolved, (atomic absorption spectrometric, direct) data from the	
	Quality of Water Service Unit laboratory	135
115.	Sulfate, dissolved, (ion-exchange chromatographic) data from the Quality of Water Service	
	Unit laboratory	136
116.	Vanadium, dissolved, (colorimetric) data from the Quality of Water Service Unit laboratory	137
117.	Zinc, dissolved, (atomic absorption spectrometric, direct) data from the Quality of Water	
	Service Unit laboratory	138
118.	Zinc, whole-water recoverable, (atomic absorption spectrometric, direct) data from the	
	Quality of Water Service Unit laboratory	139
119.	Ammonia as nitrogen, dissolved and whole-water recoverable, (colorimetric) data from the	
	Quality of Water Service Unit laboratory	140
120.	Ammonia plus organic nitrogen as nitrogen, dissolved and whole-water recoverable,	
	(colorimetric) data from the Quality of Water Service Unit laboratory	141
121.	Nitrate plus nitrite as nitrogen, dissolved and whole-water recoverable, (colorimetric) data	
	from the Quality of Water Service Unit laboratory	142
122.	Orthophosphate as phosphorus, dissolved and whole-water recoverable, (colorimetric) data	
	from the Quality of Water Service Unit laboratory	143
123.	Phosphorus, dissolved and whole-water recoverable, (colorimetric) data from the	
	Quality of Water Service Unit laboratory	144

TABLES

1.	Linear least-squared equations for determining the most probable deviation	5
2.	Total number of analyses from quality assurance samples during water year 1991 with number greater than	
	two and six standard deviations from the most probable value for the National Water Quality Laboratory	9
3.	Total number of analyses from quality-assurance samples during water year 1991 with number greater	
	than two and six standard deviations from the most probable value for the	
	Quality of Water Service Unit laboratory	11
4.	Results of statistical testing for analytical precision in inorganic constituent data for the	
	National Water Quality Laboratory	12
5.		
	Quality of Water Service Unit laboratory	13
6.		
	Quality Laboratory	14
7.	Results of statistical testing for bias in inorganic-constituent data for the Quality of Water	
	Service Unit laboratory	15
8.	Results of statistical testing for analytical precision in nutrient constituent data for the	
	National Water Quality Laboratory	16
9.	Results of statistical testing for analytical precision in nutrient constituent data for the	
	Quality of Water Service Unit laboratory	16
10.	Results of statistical testing for bias in nutrient constituent data for the	
	National Water Quality Laboratory	16
11.		
	Quality of Water Service Unit laboratory	16
12.	Results of statistical testing for analytical precision in low ionic-strength data for the	
	National Water Quality Laboratory	17
13.	Results of statistical testing for bias in low ionic-strength data for the National Water Quality Laboratory	17

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation: °F = 9/5 (°C) + 32.

ABBREVIATIONS

Units of measure

C mg/L μg/L μS/cm	Celsius milligrams per liter micrograms per liter microsiemens per centimeter at 25 degrees Celsius <u>Analytical Methods</u>
AA COL CX DCP ELEC F GF GRAV H IC ICP ISE TITR TURB WWR	atomic absorption spectrometric colorimetric chelation extraction atomic emission spectrometric, direct-current plasma electrometric flameless graphite furnace gravimetric hydride ion-exchange chromatographic atomic emission spectrometric, inductively-coupled plasma ion-selective electrode electrometric titration turbidimetric whole-water recoverable
LOP MPD MPV NSD NWQL QL QWSU RSD SRWS WATSTORE - +	Others statistically significant lack of precision most probable deviation most probable value number of standard deviation National Water Quality Laboratory quantitation limit bias Quality of Water Service Unit relative standard deviation standard reference water samples National Water Data Storage and Retrieval System negative bias positive bias

Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

By Thomas J. Maloney, Amy S. Ludtke, and Teresa L. Krizman

Abstract

The U.S. Geological Survey operates a quality-assurance program based on the analyses of reference samples for the National Water Quality Laboratory in Arvada, Colorado, and the Quality of Water Service Unit in Ocala, Florida. Reference samples containing selected inorganic, nutrient, and low ionic-strength constituents are prepared and disguised as routine samples. The program goal is to determine precision and bias for as many analytical methods offered by the participating laboratories as possible. The samples typically are submitted at a rate of approximately 5 percent of the annual environmental sample load for each constituent. The samples are distributed to the laboratories throughout the year. Analytical data for these reference samples reflect the quality of environmental sample data produced by the laboratories because the samples are processed in the same manner for all steps from sample login through data release. The results are stored permanently in the National Water Data Storage and Retrieval System. During water year 1991, 86 analytical procedures were evaluated at the National Water Quality Laboratory and 37 analytical procedures were evaluated at the Quality of Water Service Unit.

An overall evaluation of the inorganic (major ion and trace metal) constituent data for water year 1991 indicated analytical imprecision in the National Water Quality Laboratory for 5 of 67 analytical procedures: aluminum (whole-water recoverable, atomic emission spectrometric, direct-current plasma); calcium (atomic emission spectrometric, direct); fluoride (ion-exchange chromatographic); iron (whole-water recoverable, atomic absorption spectrometric, direct); and sulfate (ion-exchange chromatographic). The results for 11 of 67 analytical procedures had positive or negative bias during water year 1991. Analytical imprecision was indicated in the determination of two of the five National Water Quality Laboratory nutrient constituents: orthophosphate as phosphorus and phosphorus. A negative or positive bias condition was indicated in three of five nutrient constituents.

Analytical precision was acceptable, and no bias was indicated for the 14 low ionic-strength analytical procedures tested in the National Water Quality Laboratory program and for the 32 inorganic and 5 nutrient analytical procedures tested in the Quality of Water Service Unit during water year 1991.

INTRODUCTION

The Water Resources Division of the U.S. Geological Survey (USGS) performs numerous hydrologic investigations that require analyses of water for inorganic constituents, nutrients, low ionic-strength constituents, and some physical properties. The National Water Quality Laboratory (NWQL) in Arvada, Colorado, and the Quality of Water Service Unit (QWSU) laboratory in Ocala, Florida, are the primary sources of analytical services for many of these hydrologic investigations. The NWQL provides analytical services for all national programs and many local and (or) regional programs conducted by the USGS. The QWSU provides analytical services for many USGS programs in the southeastern part of the United States.

This report describes the results of the qualityassurance programs used to monitor the quality of analytical work for inorganic constituents, nutrients, and some physical properties at the NWQL and 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) document results from February 1981 through September 1990. Some of the previous reports contain quality-assurance information for organic determinations.

During water year 1991, 86 analytical procedures were evaluated for the NWQL by the Blind Sample Program. This represents about 80 percent of

the analytical procedures offered by the laboratory for water matrix determinations. The remaining 20 percent of the water matrix determinations offered were either infrequently requested so that it was not feasible to include them into the Blind Sample Program, 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 or sediments. There are no readily available sources of stable, inexpensive, reference materials for samples other than water. Beryllium [atomic absorption spectrometric (AA)] was not evaluated during water year 1991 because all reference samples had most probable values (MPV) below the reporting limit of the method. Four analytical procedures that were added to the NWOL Blind Sample Program during the year, were for arsenic [whole-water recoverable (WWR), AA, graphite-furnace (GF)]; selenium (WWR,AA,GF); and low ionic strength determinations for chromium (AA,GF) and nickel (AA,GF).

The Blind Sample Program evaluated 37 analytical procedures for the QWSU during the water year 1991. Although this represents only about 40 percent of the total number of water matrix constituents offered for analysis, the remaining 60 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. Beryllium (AA) was not evaluated during water year 1991 because all reference samples had MPV's below the reporting limit of the method. Manganese (AA) and manganese (WWR,AA) were not included in the water year 1991 evaluation because of instability of this ion in the reference materials submitted to the laboratory.

The analytes included in the 1991 NWQL and QWSU Blind Sample Programs are listed below by constituent categories. Analytes determined by methods adapted to detect low-level concentrations are included in the low ionic-strength category.

Inorganic constituents: (NWQL and QWSU Blind Sample Programs) alkalinity, aluminum, arsenic, beryllium, boron, cadmium, calcium, chloride, chromium, copper, dissolved solids (residue on evaporation at 180°C), fluoride, iron, lead, magnesium, mercury, nickel, potassium, selenium, silica, sodium, strontium, sulfate, vanadium, and zinc. (NWQL only) antimony, barium, cobalt, lithium, manganese, molybdenum, and silver.

Nutrient constituents: (NWQL and QWSU Blind Sample Programs) ammonia as nitrogen, ammonia plus organic nitrogen as nitrogen, nitrate plus nitrite as nitrogen, orthophosphate as phosphorus, and phosphorus.

Low ionic-strength constituents and physical property: (NWQL Blind Sample Program only) cadmium, calcium, chloride, chromium, cobalt, copper, fluoride, lead, magnesium, nickel, potassium, sodium, specific conductance, and sulfate.

PROGRAM DESCRIPTION

Standard reference water samples (SRWS) (Skougstad and Fishman, 1975; Schroder and others, 1980; Janzer, 1985; Long and Farrar, 1992) are used to prepare samples for the Blind Sample Program. The SRWS are used undiluted, diluted with deionized water, or mixed in varying proportions with other SRWS. This sample-mixing procedure produces a large number of unique samples available for qualityassurance purposes. The probability that the Blind Sample Program's quality-assurance samples will be recognized in the laboratories is low because of the diversity and small percentage of samples.

Reference samples for the Blind Sample Program are made to appear as much like environmental samples as possible. Analytical request forms are completed to ensure that appropriate analyses have been requested for the samples. The samples and the forms are shipped to selected USGS offices across the Nation. Throughout the year these offices send the qualityassurance samples for the Blind Sample Programs to the laboratories with their regular environmental samples.

Quality-assurance samples pass through each laboratory as routine samples, undergoing the normal laboratory quality-control and quality-assurance procedures; thus, data from these quality-assurance samples reflect the quality of the analytical data that the laboratories produce for environmental samples. The data released by the laboratory are stored in the National Water Data Storage and Retrieval System (WATSTORE), the USGS data base for all water data.

SRWS are filtered during preparation; therefore, all constituents in the Blind Reference Samples are in the dissolved phase. Constituents that are designated as WWR in this report are from 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 analyses and the WWR analyses will be due to the digestion process rather than any difference in the sampling techniques or sample source.

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 Blind Sample Project followed the guidelines of Friedman and Erdmann (1982) to set submission of these "external" quality-assurance samples at a rate of approximately 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 Blind Sample Project and the laboratory's quality-control program.

Analytical results for environmental samples are stored by the requesting district office on the USGS National Water Information System (NWIS) data base. These results are periodically loaded onto the WAT-STORE system for national access. The NWIS is a national standardized data-base system maintained by local USGS offices. NWIS allows users in the local 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 which have the same level of quality-control review as the data released to local WRD offices. However, results presented in the report provide a conservative estimate of data stored in local NWIS data bases because water-quality specialists and project chiefs are expected to scrutinize analytical results for discrepancies, request reruns for questionable results, and make corrections to the NWIS data base as appropriate.

Factors that need to be considered for interpretation of results stored in local 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, data-transmission 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 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 the problem and make the necessary corrections.

- 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 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 detect but may be identified if historical data for a sample site are available for comparison.
- 3. Determinations that exceed control limits set at ± 2 standard deviations of the referencesample concentration are typically submitted for analysis reruns by the Blind Sample Program. The purpose of these rerun requests is to identify reference samples that may be deteriorating or that may have been incorrectly bottled. If the Blind Sample Program 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 qualityassurance 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 originally released data remain in the quality-assurance data base. However, if the quality-control section of the laboratory independently identifies problems with an analytical line 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 1991. 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 that allows laboratory users to select specific analytes and time periods of interest. Lucey (1990) described the use of the program to retrieve information from the data base.

STATISTICAL EVALUATION

Control Chart Development and Evaluation

The SRWS used in the Blind Sample Program are analyzed through a round-robin evaluation program described by Long and Farrar (1992 and 1993). A statistical summary of the round-robin results are prepared for each set of samples. Until 1988, the SRWS program used mean and standard deviation, derived by parametric statistics, in the summary reports. After 1988, the SRWS program used median and F-pseudosigma, derived by nonparametric statistics, in the summary reports. Hoaglin and others (1983), defined the F-pseudosigma as

$$F-pseudosigma = data \frac{(Fourth-spread)}{1.349}$$
 (1)

where, the *Fourth – spread* is analogous to the interquartile range of the data. In addition, they indicated that the *F-pseudosigma* yields an estimate of standard deviation when the data distribution is Gaussian. However, it is recognized that some of the SRWS program data sets may not have Gaussian data distributions. The SRWS program plans to recompile the statistical results of historical round-robin studies so that median and F-psuedosigma results will be available. Until the updated statistical summary results are available, the regression equations will be derived from a combination of parametric and nonparametric results.

The SRWS program's most probable values (MPV's) are used to estimate the MPV's of the Blind Sample Program mixes based on the proportion of the SRWS 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 based on the proportion used. The resulting MPV's are used in the Blind Sample Program to compare with analytical results.

For each SRWS constituent, a regression equation has been derived to enable estimation of the most probable deviation (MPD) at various concentrations (Table 1). The equations were derived by regressing the F-pseudosigma or standard deviation against the MPV using ordinary least-squares. Helsel and Hirsch (1992) provided a general model for estimation of ordinary least-squares regression:

$$y_i = \beta_0 + \beta_1 x_i + \varepsilon_i$$
 $i = 1, 2, ..., n$ (2)

where

 y_i = the *i*th observation of the response variable;

 x_i = the *i*th observation of the explanatory variable;

$$\beta_0$$
 = the intercept;

 β_1 = the slope;

 \mathcal{E}_i = the random error or residual for the *i*th observation; and

n =the sample size.

SRWS program-summary statistics for semiannual round-robin sample studies conducted during the last 7 years were used to account for long-term analytical improvements and to provide a statistically significant number of data points to derive the regression equations.

The assessment of whether an analytical measurement is in or out of control 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 against the MPV. The NSD is determined by taking the difference between the constituent concentration and the MPV and dividing by the MPD estimated by the appropriate regression equation for the MPV concentration. Taylor (1987, p. 33–34) provided a general equation that was modified to determine the NSD values for this assessment:

$$NSD = \frac{X_q - MPV}{MPD}$$
(3)

where

NSD = number of standard deviations;

 X_q = value in question;

MPV = most probable value; and

MPD = most probable deviation (assumed to be the standard deviation).

Analytical results that are within two standard deviations 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. This primarily occurred for results near the reporting limits set for computer storage of environmental data. The accuracy allowed for computer storage of environmental data often is much less than that assigned to the MPV's of the SRWS. For example, the criteria for NWIS and

Table 1. Linear least-squared equations for determining the most probable deviation

[MPD, most probable deviation; TTTR, electrometric titration; mg/L, milligrams per liter; MPV, most probable value; *, not applicable; DCP, atomic emission spectrometric, direct-current plasma; μ g/L, micrograms per liter; WWR, whole-water recoverable; AA, atomic absorption spectrometry; CX, chelation extraction; H, hydride; GF, graphite furnace; ICP, atomic emission spectrometry, inductively-coupled plasma; COL, colorimetric; IC, ion-exchange chromatography; GRAV, gravimetric; ISE, ion-selective electrode; F, flameless; ELEC, electrometric; μ S/cm, microsiemens per centimeter at 25 degrees Celsius]

Constituent				
(dissolved except as indicated) or physical property and analytical method	Units	Equation to determine MPD	Minimum MPE	
	GANIC CONSTITU	IENTS		
Alkalinity (TITR)	mg/L	(0.025 x MPV) + 0.83	*	
Aluminum (DCP)	μg/L	(0.022 x MPV) + 6.73	*	
Aluminum (AA,CX)	μg/L	(0.012 x MPV) + 23.5	*	
Aluminum (WWR,DCP)	μg/L	(0.022 x MPV) + 6.73	7.5	
Aluminum (WWR,AA,CX)	μg/L	(0.12 x MPV) + 23.5	*	
Antimony (AA,H)	μg/L	(0.021 x MPV) + 1.96	*	
Arsenic (AA,H)	μg/L	(0.140 x MPV) + 0.59	*	
Arsenic (WWR,AA,GF)	μg/L	(0.140 x MPV) + 0.59	*	
Barium (ICP)	μg/L	(0.051 x MPV) + 1.69	*	
Barium (AA)	μg/L	(0.190 x MPV) + 17.0	75	
Barium (WWR,AA)	μg/L	$(0.190 \times MPV) + 17.0$	75	
Beryllium (ICP)	μg/L	(0.056 x MPV) + 0.71	*	
Beryllium (WWR,AA)	μg/L	(0.056 x MPV) + 0.71	7.5	
Boron (DCP)	μg/L	(0.016 x MPV) + 5.0	7.5	
Boron (COL)	μg/L	(0.048 x MPV) + 29.9	*	
Cadmium (ICP)	μg/L μg/L	$(0.048 \times MPV) + 23.3$ $(0.090 \times MPV) + 0.68$	0.75	
Cadmium (AA,GF)		(0.090 x MPV) + 0.08	0.75	
	μg/L		0.75	
Cadmium (WWR,AA,GF)	μg/L	$(0.090 \times MPV) + 0.68$	*	
Calcium (ICP)	mg/L	$(0.043 \times MPV) + 0.23$	*	
Calcium (AA)	mg/L	(0.043 x MPV) + 0.23	*	
Chloride (IC)	mg/L	$(0.038 \times MPV) + 0.44$		
Chromium (ICP)	μg/L	(0.090 x MPV) + 1.71	3.75	
Chromium (DCP)	μg/L	(0.090 x MPV) + 1.71	*	
Chromium (WWR,DCP)	μg/L	(0.090 x MPV) + 1.71	*	
Chromium (WWR,AA,CX)	μg/L	(0.090 X MPV) + 1.71	*	
Cobalt (ICP)	μg/L	(0.150 x MPV) + 0.95	*	
Cobalt (AA,GF)	μg/L	(0.150 x MPV) + 0.95	*	
Cobalt (WWR,AA,GF)	μg/L	(0.150 x MPV) + 0.95	*	
Copper (ICP)	μg/L	(0.038 x MPV) + 2.89	7.5	
Copper (AA,GF)	μg/L	(0.038 x MPV) + 2.89	*	
Copper (WWR,AA,GF)	μg/L	(0.038 x MPV) + 2.89	*	
Dissolved solids (GRAV)	mg/L	(0.022 x MPV) + 7.4	*	
Iuoride (ISE)	mg/L	(0.083 x MPV) + 0.01	0.075	
luoride (IC)	mg/L	(0.083 x MPV) + 0.01	0.075	
ron (ICP)	μg/L	(0.087 x MPV) + 5.71	*	
ron (AA)	μg/L	(0.087 x MPV) + 5.71	7.5	
ron (WWR,AA)	μg/L	(0.087 x MPV) + 5.71	7.5	
ead (ICP)	μg/L	(0.079 x MPV) + 3.39	7.5	
ead (AA,GF)	μg/L	(0.079 x MPV) + 3.39	*	
ead (WWR,AA,GF)	μg/L	(0.079 x MPV) + 3.39	*	
ithium (ICP)	μg/L	(0.079 x MPV) + 2.56	3.0	
ithium (WWR,AA)		(0.079 x MPV) + 2.50 (0.079 x MPV) + 2.56	7.5	
	μg/L ma/l		7.5 *	
Magnesium (ICP)	mg/L	(0.041 x MPV) + 0.11		

Constituent (dissolved except as indicated) or physical property and analytical method	Units	Equation to determine MPD	Minimum MPD
	C CONSTITUENTS-	Continued	
Magnesium (AA)	mg/L	(0.041 x MPV) + 0.11	*
Manganese (ICP)	μg/L	$(0.083 \times MPV) + 1.82$	*
Manganese (AA)	μg/L	$(0.083 \times MPV) + 1.82$	7.5
Manganese (WWR,AA)	μg/L	$(0.083 \times MPV) + 1.82$	7.5
Mercury (AA,F)	μg/L	$(0.094 \times MPV) + 0.12$	*
Mercury (WWR,F)	μg/L	(0.094 x MPV) + 0.12	*
Molybdenum (ICP)	μg/L	(0.045 x MPV) + 3.46	7.5
Molybdenum (AA,CX)	μg/L	(0.045 x MPV) + 3.46	*
Molybdenum (WWR,AA,CX)	μg/L	(0.045 x MPV) + 3.46	*
Nickel (ICP)	μg/L	$(0.069 \times MPV) + 3.69$	7.5
Nickel (AA,GF)	μg/L	$(0.069 \times MPV) + 3.69$	*
Nickel (WWR,AA,GF)	μg/L	$(0.069 \times MPV) + 3.69$	*
Potassium (AA)	μg/L mg/L	$(0.009 \times MPV) + 0.10$	*
Selenium (AA,H)	μg/L	(0.210 x MPV) + 0.61	0.75
Selenium (WWR,AA,GF)	μg/L μg/L	$(0.210 \times \text{MPV}) + 0.61$	*
Silica (ICP)	μg/L mg/L	$(0.210 \times MPV) + 0.01$ $(0.062 \times MPV) + 0.13$	*
Silica (COL)	mg/L	$(0.062 \times MPV) + 0.13$	*
Silver (ICP)	μg/L	$(0.002 \times MPV) + 0.13$ $(0.140 \times MPV) + 0.88$	*
Silver (AA,GF)	μg/L μg/L	$(0.140 \times MPV) + 0.88$	*
Silver (WWR,AA,GF)		(0.140 x MPV) + 0.88	*
	μg/L ma/l	(0.140 x MPV) + 0.88 (0.040 x MPV) + 0.20	*
Sodium (ICP)	mg/L	· · · ·	*
Sodium (AA)	mg/L	(0.040 x MPV) + 0.20	*
Strontium (ICP)	μg/L	(0.059 x MPV) - 0.89	*
Strontium (AA)	μg/L	$(0.059 \times MPV) - 0.89$	*
Sulfate (IC)	mg/L	(0.041 x MPV) + 1.3	*
Vanadium (ICP)	μg/L	$(0.088 \times MPV) + 2.3$	*
Vanadium (COL)	μg/L	$(0.088 \times MPV) + 2.3$	*
Zinc (ICP)	μg/L	$(0.059 \times MPV) + 3.97$	
Zinc (AA)	μg/L	$(0.059 \times MPV) + 3.97$	7.5
Zinc (WWR,AA)	µg/L RIENT CONSTITUE	(0.059 x MPV) + 3.97	7.5
Ammonia as nitrogen (COL)		(0.088 x MPV) + 0.02	*
Ammonia plus organic nitrogen as nitrogen (COL)	mg/L	$(0.088 \times MPV) + 0.02$ $(0.120 \times MPV) + 0.11$	*
Nitrate plus nitrite as nitrogen (COL)	mg/L	$(0.120 \times MPV) + 0.011$ $(0.048 \times MPV) + 0.04$	*
Orthophosphate as phosphorus (COL)	mg/L mg/L	$(0.048 \times MPV) + 0.04$ $(0.047 \times MPV) + 0.01$	*
Phosphorus (COL)	mg/L	$(0.060 \times MPV) + 0.01$	*
LOW IONIC-STRENG			·
Cadmium (AA,GF)	μg/L	$(0.090 \times MPV) + 0.68$	*
Calcium (AA)	mg/L	$(0.059 \times MPV) + 0.04$	*
Chloride (IC)	mg/L	(0.069 x MPV) + 0.16	*
Cobalt (AA,GF)	μg/L	$(0.150 \times MPV) + 0.95$	*
Copper (AA,GF)	μg/L μg/L	$(0.038 \times MPV) + 2.89$	*
Fluoride (IC)	μg/L mg/L	$(0.038 \times MPV) + 2.89$ $(0.010 \times MPV) + 0.03$	*
Lead (AA,GF)	μg/L	(0.079 x MPV) + 3.39	*
Magnesium (AA)		(0.041 x MPV) + 0.01	*
-	mg/L		*
Potassium (AA)	mg/L	(0.100 x MPV) + 0.01	*
Sodium (AA)	mg/L	(0.045 x MPV) + 0.04	*
Specific conductance (ELEC)	μS/cm	(0.067 x MPV) + 0.37	*
Sulfate (IC)	mg/L	(0.310 x MPV) + 0.03	*

Table 1. Linear least-squared equations for determining the most probable deviation--Continued

WATSTORE data entry for many metals determined by AA is to report values to the nearest 10 μ g/L for determinations below 100 μ g/L. However, for the SRWS program, laboratories typically report data to the nearest μ g/L, and the standard deviation for samples with concentrations below 100 μ g/L may be only a few μ g/L. In addition, the MPD regression equations are based on SRWS data that are reported with more significant figures, so that the regression equations may produce MPD values, especially at lower concentrations, with tolerances too small to be met by the laboratories.

The rounding differences between the SRWS summary results and the NWIS and WATSTORE 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 MPD at three-quarters of the computer reporting level. For example, a sample may be assigned an MPV for manganese of $25.2 \,\mu g/L$; however, the laboratories can only report environmental data for manganese (AA or WWR, AA) to the nearest 10 µg/L in the NWIS and WATSTORE data bases. For the reference sample in question, a reported value of $20 \text{ or } 30 \,\mu\text{g/L}$ would generally be expected. The regression equation for manganese [MPD = (0.083 X MPV)+ 1.82] provides an estimate that reported values within \pm 3.91 µg/L of a sample with an MPV of 25.2 µg/L will be considered within one standard deviation. The laboratories' closest reportable values, 20 and 30 µg/L, would be -1.33 and +1.23 standard deviations from the MPV. When a minimum MPD value of 7.5 μ g/L is assigned (75 percent of the reporting unit) then values reported at 20 and 30µg/L would be -0.69 and +0.64 standard deviations from the MPV. The equations for determining the MPD for each constituent or property and the established minimum MPDs are listed in table 1.

For some determinations, laboratories report data as "less than" the reporting limit. This most frequently happens for samples that have MPV's near the reporting limit. For the purposes of the Blind Sample Program assessments, these "less than" values have been replaced, using simple substitution, to the reporting limit.

For each constituent, the standard deviation 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 1 through 86 for the NWQL and in figures 87 through 123 for the QWSU in the Supplemental Data section of this report.

Control charts for trace-metal and major constituent reference samples are presented in figures 1 through 67 for the NWQL and figures 87 through 118 for the OWSU. The data on control charts for inorganic constituents have been separated into quartiles based on environmental sample concentrations. All environmental data released during 1991 by the NWQL were obtained and used to determine the quartiles. The quartiles and calibration range of each analytical method is identified in the explanation of the associated figure. 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 the first quartile (up to 25 percent), the () symbol has been used; reference samples in the second quartile (25.1 to 50 percent) are represented by the (o) symbol; the third quartile (50.1 to 75 percent) are represented by the (\triangle) symbol; and reference samples in the fourth quartile (75.1 percent to upper calibration limit) are represented by the (•) symbol. If a reference sample has an MPV above the upper calibration limit, the sample would require dilution to get within calibration range. Data for all samples requiring dilution are represented by a filled in symbol for the appropriate quartile. For example, if the concentration of the reference sample was in the fourth quartile, then the (*) was used to display the data.

Control charts for nutrient constituents are shown in figures 68 through 72 for the NWQL and figures 119 through 123 for the QWSU. Control charts for NWOL low ionic-strength constituents are shown in figures 73 through 86. The calibration range of each analytical method is identified in the explanation of the associated figure. The data for all determinations with MPV's in the analytical calibration range for nutrient and low ionic-strength constituents have been plotted using the symbol (a). If the MPV of a reference mix is outside the analytical calibration range, the laboratory likely would have had to make a dilution to bring the sample into range. The data points for all nutrient and low ionic-strength constituent determinations that had MPV's above the upper limit of the calibration curve have been plotted with the symbol (=).

Points on the control charts that are greater than 6 standard deviations or less than -6 standard deviations are plotted at the top or bottom edge of the figure, and the actual number of standard deviations are indicated adjacent to the point (see fig. 1A, for example).

Precision Chart Development and Evaluation

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

$$RSD = \frac{\sigma}{MPV} \times 100 \, (percent) \tag{4}$$

where

RSD = relative standard deviation;

 σ = standard deviation; and

MPV = most probable value.

The RSD provides an estimation of error relative to the MPV of the reference samples.

The RSD data are presented graphically as precision data charts in Part B of figures 1 through 86 for the NWQL and figures 87 through 123 for the QWSU in the Supplemental Data section of this report. These charts were prepared by plotting the RSD for inorganic, nutrient, and low ionic-strength constituents against the mean concentration of the reference samples as reported by the individual laboratories. These charts allow a data reviewer to estimate precision at any concentration shown for a constituent. For example, figure 1B shows the precision data for total alkalinity determinations from the NWQL. This plot shows a distribution of approximately 4.5 percent RSD data for the entire analytical range.

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 much less than 1 percent of all data. However, outliers produce erroneous results in the use of parametric statistics such as RSD. Taylor (1987, p. 33-34), suggested $NSD \ge |4|$ as a criterion for rejection of data for a large sample set and NSD \geq |6| for smaller data sets or when the standard deviation is not well established. In this report, an outlier was defined as a value that is greater than 6 or less then -6 standard deviations from the MPV. Table 2 for the NWOL and table 3 for the OWSU present the total number of determinations for each constituent processed during the water year, the number of determinations with standard deviations greater than 2 or less than -2 from the MPV, and the number of determinations with standard deviations greater than 6 or less than -6 from the MPV.

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

Binomial-Probability-Distribution Technique to Assess Precision and Bias

Measures of precision and bias 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 theoretical values. The binomial equation identifies the maximum number of determinations that could exceed the control limit at a 99-percent confidence level. A comparison is then made between the number of analytical determinations exceeding control limits and the results of the binomialprobability-distribution equation for the total number of analytical determinations. Analytes exhibit analytical imprecision if they have more determinations outside the control limits than the result of the binomial equation. The binomial-probability-distribution procedure to measure precision allows tracking of annual variations in the precision of analytical measurements. However, this statistical test can fail to identify periods of serious imprecision of laboratory methods because it is based on MPV's from inter-laboratory testing using multiple methods rather than individual laboratories' analysis means.

The bias analysis is made by tabulating the total number of analyses and the number of determinations above, below, and at the MPV concentration. A binomial equation is used to determine the maximum number of determinations above or below the MPV at a 99-percent confidence level. Analyses exhibit a positive bias if the number of determinations above the MPV exceeded the result of the binomial equation. Likewise, analyses exhibit a negative bias if the number of determinations below the MPV exceeded the result of the binomial equation.

The constituents in the SRWS are not certified to specific values but are reported as an MPV at a 95-percent confidence interval. The 95-percent confidence interval indicates the level of certainty of the MPV, which although generally minor is still important to consider. Application of a strict bias test based only on MPV's without consideration of the associated confidence interval is questionable. Therefore, a correction has been applied to the bias analysis to allow determinations in a window from -0.25 to +0.25 standard deviations of the MPV to be considered equal to the MPV concentration.

Table 2. Total number of analyses from quality assurance samples during water year 1991 with number greater than two and six standard deviations from the most probable value 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; TITR, electrometric titration; DCP, atomic emission spectrometric, direct-current plasma; WWR, whole-water recoverable; AA, atomic absorption spectrometric; H, hydride; GF, graphite furnace; ICP, atomic emission spectrometric, inductively-coupled plasma; IC, ion-exchange chromato-graphic; GRAV, gravimetric; F, flameless; CX, chelation extraction; COL, colorimetric; ELEC, electrometric]

•

Constituent	Number of analyses		
(dissolved except as indicated) or physical property and analytical method	Total	>2SD	>6SD
INORGANIC	CONSTITUENTS		
lkalinity (TITR)	264	5	2
luminum (DCP)	72	4	0
luminum (WWR,DCP)	33	9	1
ntimony (AA,H)	39	1	0
rsenic (AA,H)	98	1	0
rsenic (AA,GF)	20	1	1
arium (ICP)	202	1	1
arium (AA)	13	0	0
arium (WWR,AA)	13	0	0
eryllium (ICP)	202	2	1
eryllium (WWR,AA)	10	0	0
oron (DCP)	177	7	2
admium (ICP)	202	0	0
admium (AA,GF)	81	8	1
admium (WWR,AA,GF)	71	4	1
alcium (ICP)	376	6	0
alcium (AA)	86	12	2
hloride (IC)	264	23	2
hromium (ICP)	167	0	0
hromium (DCP)	105	12	0
hromium (WWR,DCP)	69	2	0
obalt (ICP)	202	1	0
obalt (AA,GF)	38	1	0
obalt (WWR,AA,GF)	37	1	0
opper (ICP)	182	6	0
opper (AA,GF)	81	2	0
opper (WWR,AA,GF)	70	5	0
issolved solids (GRAV)	259	9	0
uoride (IC)	264	49	3
on (ICP)	133	0	0
on (AA)	57	6	ů 0
on (WWR,AA)	46	10	4
ead (ICP)	202	0	0
ead (AA,GF)	81	1	0
ead (WWR,AA,GF)	70	1	0
thium (ICP)	202	1	0
ithium (WWR,AA)	21	0	0
lagnesium (ICP)	376	4	0
(agnesium (AA)	86	4	2
(anganese (ICP)	67	4 0	0
(anganese (AA)	24	2	0
anganese (WWR,AA)	35	0	0

Table 2. Total number of analyses from quality-assurance samples during water year 1991 with numbergreater than two and six standard deviations from the most probable value for the National Water QualityLaboratory--Continued

Constituent	Number of analyses		
 (dissolved except as indicated) or physical property and analytical method 	Totai	>2SD	>6SD
INORGANIC CONST	TITUENTSContin	ued	· · · · · · · · · · · · · · · · · · ·
Mercury (AA,F)	81	1	0
Mercury(WWR,AA,F)	70	2	0
Molybdenum (ICP)	197	1	0
Molybdenum (AA,CX)	43	0	0
Molybdenum (WWR,AA,CX)	32	1	0
Nickel (ICP)	167	0	0
Nickel (AA,GF)	116	2	0
Nickel (WWR,AA,GF)	70	6	0
Potassium (AA)	262	0	0
Selenium (AA,H)	103	2	0
Selenium (AA,GF)	20	0	0
Silica (ICP)	132	1	0
Silica (COL)	264	1	1
Silver (ICP)	167	1	0
Silver (AA,GF)	60	0	0
Silver (WWR,AA,GF)	59	3	0
Sodium (ICP)	376	17	0
Sodium (AA)	86	1	1
Strontium (ICP)	202	0	0
Sulfate (IC)	264	35	2
Vanadium (ICP)	200	0	0
Vanadium (COL)	84	4	0
Zinc (ICP)	202	1	0
Zinc (AA)	81	1	1
Zinc (WWR,AA)	71	3	0
	ONSTITUENTS		
Ammonia as nitrogen (COL)	514	18	2
Ammonia plus organic nitrogen as nitrogen (COL)	423	18	1
Nitrate plus nitrite as nitrogen (COL)	514	13	4
Orthophosphate as phosphorus (COL)	514	68	3
Phosphorus (COL)	424	30	3
LOW IONIC-STREN	GTH CONSTITUE	NTS	
Cadmium (AA,GF)	23	4	0
Calcium (AA)	49	2	0
Chloride (IC)	49	0	0
Chromium (AA,GF)	22	3	0
Cobalt (AA,GF)	23	0	0
Copper (AA,GF)	23	2	0
Fluoride (IC)	26	1	1
Lead (AA,GF)	23	1	0
Magnesium (AA)	49	0	0
Nickel (AA,GF)	22	5	0
Potassium (AA)	49	0	0
Sodium (AA)	49	2	1
Specific conductance (ELEC)	49	2	1
Sulfate (IC)	49	0	0

Table 3. Total number of analyses from quality-assurance samples during water year 1991 with number greater than two and six standard deviations from the most probable value 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; TITR, electrometric titration; WWR, whole-water recoverable; AA, atomic absorption spectrometric; CX, chelation extraction; H, hydride; COL, colorimetric; GF, graphite furnace; IC, ion-exchange chromatographic; GRAV, gravimetric; ISE, ion-selective electrode; F, flameless]

Constituent	Number of analyses			
(dissolved except as indicated)	Total	>2SD	>6SD	
INORGANIC C	ONSTITUENTS		· · · · ·	
Alkalinity (TITR)	47	4	2	
Aluminum (WWR,AA,CX))	15	0	0	
Arsenic (AA,H)	22	0	0	
Beryllium (WWR,AA)	8	0	0	
Boron (COL)	8	0	0	
Cadmium (AA,GF)	13	0	0	
Cadmium (WWR,AA,GF)	27	0	0	
Calcium (AA)	55	0	0	
Chloride (IC)	55	2	0	
Chromium (WWR,AA,CX)	28	2	0	
Copper (AA,GF)	19	0	0	
Copper (WWR,AA,GF)	28	0	0	
Dissolved solids (GRAV)	47	0	0	
Fluoride (ISE)	47	1	0	
Iron (AA)	23	0	0	
Iron (WWR,AA)	19	4	0	
Lead (AA,GF)	20	0	0	
Lead (WWR,AA,GF)	35	0	0	
Magnesium (AA)	55	0	0	
Mercury (AA,F)	12	0	0	
Mercury(WWR,AA,F)	34	ů 0	ů 0	
Nickel (AA,GF)	13	ů 0	ů 0	
Nickel (WWR,AA,GF)	35	0	0 0	
Potassium (AA)	47	0	ů 0	
Selenium (AA,H)	18	0	ů 0	
Silica (COL)	47	ů	ů 0	
Sodium (AA)	47	ů 0	ů 0	
Strontium (AA)	27	ů 0	ů 0	
Sulfate (IC)	55	ů 0	0	
Vanadium (COL)	12	ů 0	ů 0	
Zinc (AA)	20	ů 0	0	
Zinc (WWR,AA)	28	1	0	
	20 INSTITUENTS	1	v	
Ammonia as nitrogen (COL)	89	2	0	
Ammonia plus organic nitrogen as nitrogen (COL)	74	3	1	
Nitrate plus nitrite as nitrogen (COL)	85	3	1	
Orthophosphate as phosphorus (COL)	82	4	1	
Phosphorus (COL)	86	3	2	

QUALITY-ASSURANCE RESULTS FOR INORGANIC-CONSTITUENT SAMPLES

Precision

The results of statistical testing for analytical precision for each inorganic constituent are presented in table 4 for the NWQL and in table 5 for the QWSU. These tables show either acceptable results (indicated by "--") or a significant lack of precision at the 99-percent confidence level (indicated by "LOP") for each constituent.

NWQL data for water year 1991 for aluminum [WWR, atomic emission spectrometric, direct-current plasma (DCP)], calcium (AA), fluoride [ion-exchange chromatographic (IC)], iron (WWR, AA), and sulfate (IC) indicated lack of precision. Fluoride (IC) failed the precision criterion for both water years 1990 (Maloney and others, 1993) and 1991. Iron (WWR,AA) has failed the precision criterion for 7 consecutive years (Lucey and Peart, 1988, 1989a, 1989b; Lucey, 1989; Maloney and others, 1992; Maloney and others, 1993). NWQL determinations of boron (DCP), chloride, and manganese (WWR,AA) had acceptable results during water year 1991 after failing the precision tests during water year 1990 (Maloney and others, 1993).

The QWSU had acceptable precision for all 32 inorganic analytical procedures that were tested for this report for water year 1991. QWSU determinations of aluminum (WWR,AA), copper (WWR,AA), and fluoride [colorimetric (COL) and ion-selective electrode (ISE)], which had failed precision tests during water year 1990 (Maloney and others, 1993), all passed precision tests for the water year 1991.

 Table 4. Results of statistical testing for analytical precision in inorganic constituent data for the National Water Quality

 Laboratory

[TITR, titration; --, acceptable results; DCP, atomic emission spectrometric, direct-current plasma; WWR, whole-water recoverable; LOP, statistically significant lack of precision; AA, atomic absorption spectrometric; H, hydride; GF, graphite furnace; ICP, atomic emission spectrometric, inductively-coupled plasma; IC, ion-exchange chromatographic; GRAV, gravimetric; F, flameless; CX, chelation extraction; COL, colorimetric]

Constituent dissolved except as indicated) and analytical method	Results from October 1990– September 1991	Constituent (dissolved except as indicated) and analytical method	Results from October 1990– September 1991
Alkalinity (TITR)		Copper (ICP)	
Aluminum (DCP)		Copper (AA,GF)	
Aluminum (WWR,DCP)	LOP	Copper (WWR,AA,GF)	
Antimony (AA,H)		Dissolved solids (GRAV)	
Arsenic (AA,H)		Fluoride (IC)	LOP
Arsenic (AA,GF)		Iron (ICP)	
Barium (ICP)		Iron (AA)	
Barium (AA)		Iron (WWR,AA)	LOP
Barium (WWR,AA)		Lead (ICP)	
Beryllium (ICP)		Lead (AA,GF)	
Beryllium (WWR,AA)		Lead (WWR,AA,GF)	
Boron (DCP)		Lithium (ICP)	
Cadmium (ICP)		Lithium (WWR,AA)	
Cadmium (AA,GF)		Magnesium (ICP)	
Cadmium (WWR,AA,GF)		Magnesium (AA)	
Calcium (ICP)		Manganese (ICP)	
Calcium (AA)	LOP	Manganese (AA)	
Chloride (IC)		Manganese (WWR,AA)	
Chromium (ICP)		Mercury (AA,F)	
Chromium (DCP)		Mercury (WWR,AA,F)	
Chromium (WWR,DCP)		Molybdenum (ICP)	
Cobalt (ICP)		Molybdenum (AA,CX)	
Cobalt (AA,GF)		Molybdenum (WWR,A,CX)	
Cobalt (WWR,AA,GF)		Nickel (ICP)	

¹² Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

 Table 4. Results of statistical testing for analytical precision in inorganic constituent data for the National Water Quality

 Laboratory--Continued

Constituent (dissolved except as indicated) and analytical method	Results from October 1990– September 1991	Constituent (dissolved except as indicated) and analytical method	Results from October 1990– September 1991
Nickel (AA,GF)		Sodium (ICP)	
Nickel (WWR,AA,GF)		Sodium (AA)	
Potassium (AA)		Strontium (ICP)	
Selenium (AA,H)		Sulfate (IC)	LOP
Selenium (AA,GF)		Vanadium (ICP)	
Silica (ICP)		Vanadium (COL)	
Silica (COL)		Zinc (ICP)	
Silver (ICP)		Zinc (AA)	
Silver (AA,GF)		Zinc (WWR,AA)	
Silver (WWR,AA,GF)			

 Table 5. Results of statistical testing for analytical precision in inorganic constituent data for the Quality of Water Service Unit

 laboratory

[TITR, titration; --, acceptable results; WWR, whole-water recoverable; AA, atomic absorption spectrometric; CX, chelation extraction; H, hydride; COL, colorimetric; GF, graphite furnace; IC, ion-exchange chromatographic, GRAV, gravimetric; ISE, ion-selective electrode; F, flameless]

Constituent (dissolved except as Indicated) and analytical method	Results from October 1990–September 1991	Constituent (dissolved except as indicated) and analytical method	Results from October 1990–September 1991
Alkalinity (TITR)		Lead (AA,GF)	
Aluminum (WWR,AA,CX)		Lead (WWR,AA,GF)	
Arsenic (AA,H)		Magnesium (AA)	
Beryllium (WWR,AA)		Mercury (AA,F)	
Boron (COL)		Mercury (WWR,AA,F)	
Cadmium (AA,GF)		Nickel (AA,GF)	
Cadmium (WWR,AA,GF)		Nickel (WWR,AA,GF)	
Calcium (AA)		Potassium (AA)	
Chloride (IC)		Selenium (AA,H)	
Chromium (WWR,AA,CX)		Silica (COL)	
Copper (AA,GF)		Sodium (AA)	
Copper (WWR,AA,GF)		Strontium (AA)	
Dissolved Solids (GRAV)		Sulfate (IC)	
Fluoride (ISE)		Vanadium (COL)	
Iron (AA)		Zinc (AA)	
Iron (WWR,AA)		Zinc (WWR,AA)	

Bias

Analytical bias for NWQL determinations is indicated for 11 inorganic constituents for water year 1991 compared to 13 for water year 1990 (Maloney and others, 1993). Table 6 presents the results of the binomial-probability-distribution statistical test for bias for each inorganic constituent.

Vanadium (COL) was the only NWQL constituent that showed negative bias for water years 1990 (Maloney and others, 1993) and 1991. In addition, cadmium [atomic emission spectrometric, inductivelycoupled plasma (ICP)], calcium (AA), dissolved solids (GRAV), and molybdenum (WWR,AA) had negative bias for water year 1991. Positively biased constituents for water year 1991 were: alkalinity [electrometric titration (TITR)], barium (ICP), beryllium (ICP), calcium (ICP), chloride (IC), and sodium (ICP).

Statistical tests of water year 1991 inorganic procedures at the QWSU did not indicate analytical bias, as shown in table 7.

Table 6. Results of statistical testing for bias in inorganic constituent data for the National Water Quality Laboratory

[TTTR, titration; +, positive bias; DCP, atomic emission spectrometric, direct-current plasma; 0, acceptable results; WWR, whole-water recoverable; AA, atomic absorption spectrometric; H, hydride; GF, graphite furnace; ICP, atomic emission spectrometric, inductively-coupled plasma; -, negative bias; IC, ion-exchange chromatographic, GRAV, gravimetric; F, flameless; CX, chelation extraction; COL, colorimetric]

Constituent (dissolved except as indicated) and analyticai method	Results from October 1990–September 1991	Constituent (dissoived except as indicated) and anaiyticai method	Results from October 1990–September 1991
Alkalinity (TITR)	+	Lead (WWR,AA,GF)	0
Aluminum (DCP)	0	Lithium (ICP)	0
Aluminum (WWR,DCP)	0	Lithium (WWR,AA)	0
Antimony (AA,H)	0	Magnesium (ICP)	0
Arsenic (AA-H)	0	Magnesium (AA)	0
Arsenic (AA,GF)	0	Manganese (ICP)	0
Barium (ICP)	+	Manganese (AA)	0
Barium (AA)	0	Manganese (WWR,AA)	0
Barium (WWR,AA)	0	Mercury (AA,F)	0
Beryllium (ICP)	+	Mercury (WWR,AA,F)	0
Beryllium (WWR,AA)	0	Molybdenum (ICP)	0
Boron (DCP)	0	Molybdenum (AA,CX)	0
Cadmium (ICP)	-	Molybdenum (WWR,AA,CX)	-
Cadmium (AA,GF)	0	Nickel (ICP)	0
Cadmium (WWR,AA,GF)	0	Nickel (AA,GF)	0
Calcium (ICP)	+	Nickel (WWR,AA,GF)	0
Calcium (AA)	-	Potassium (AA)	0
Chloride (IC)	+	Selenium (AA,H)	0
Chromium (ICP)	0	Selenium (AA,GF)	0
Chromium (DCP)	0	Silica (ICP)	0
Chromium (WWR,DCP)	0	Silica (COL)	0
Cobalt (ICP)	0	Silver (ICP)	0
Cobalt (AA,GF)	0	Silver (AA,GF)	0
Cobalt (WWR,AA,GF)	0	Silver (WWR,AA,GF)	0
Copper (ICP)	0	Sodium (ICP)	+
Copper (AA,GF)	0	Sodium (AA)	0
Copper (WWR,AA,GF)	0	Strontium (ICP)	0
Dissolved solids (GRAV)	_	Sulfate (IC)	0
Fluoride (IC)	0	Vanadium (ICP)	0
Iron (ICP)	0	Vanadium (COL)	-
Iron (AA)	0	Zinc (ICP)	0
Iron (WWR,AA)	0	Zinc (AA)	0
Lead (ICP)	0	Zinc (WWR,AA)	0
Lead (AA,GF)	0	-	

Table 7. Results of statistical testing for bias in inorganic-constituent data for the Quality of Water Service Unit laboratory

[TITR; titration; 0, acceptable results; WWR, whole-water recoverable; AA, atomic absorption spectrometric; CX, chelation extraction; H, hydride; COL, colorimetric; GF, graphite furnace; IC, ion-exchange chromatographic; GRAV, gravimetric; ISE, ion-selective electrode; F, flameless]

Constituent (dissolved except as indicated) and analytical method	Results from October 1990–September 1991	Constituent (dissolved except as indicated) and analytical method	Results from October 1990–September 1991
Alkalinity (TITR)	0	Lead (AA,GF)	0
Aluminum (WWR,AA,CX)	0	Lead (WWR,AA,GF)	0
Arsenic (AA,H)	0	Magnesium(AA)	0
Beryllium (WWR,AA)	0	Mercury (AA,F)	0
Boron (COL)	0	Mercury (WWR,AA,F)	0
Cadmium (AA,GF)	0	Nickel (AA,GF)	0
Cadmium (WWR,AA,GF)	0	Nickel (WWR,AA,GF)	0
Calcium (AA)	0	Potassium (AA)	0
Chloride (IC)	0	Selenium (AA,H)	0
Chromium (WWR,AA,CX)	0	Silica (AA)	0
Copper, (AA,GF)	0	Sodium (AA)	0
Copper (WWR,AA,GF)	0	Strontium (AA)	0
Dissolved Solids (GRAV)	0	Sulfate (IC)	0
Fluoride (ISE)	0	Vanadium (COL)	0
Iron (AA)	0	Zinc (AA)	0
lron (WWR,AA)	0	Zinc (WWR,AA)	0

QUALITY-ASSURANCE RESULTS FOR NUTRIENT CONSTITUENT SAMPLES

Precision

The results of statistical testing for analytical precision for each nutrient constituent are presented in table 8 for the NWQL and table 9 for the QWSU. The only nutrient constituents for either laboratory to fail the precision test for water year 1991 were the NWQL determinations for orthophosphate as phosphorus (COL) and phosphorus (COL). The control chart for NWQL orthophosphate as phosphorus determinations (fig. 71A) shows numerous points that plot outside the control limits throughout the year, whereas the control chart for OWSU orthophosphate as phosphorus determination (fig. 122A) does not show an inordinate number of points outside the control limits. Because the same six SRWS nutrient samples were used in the blind sample programs for each laboratory, comparisons were made of the data from both laboratories. The concentration of orthophosphate as phosphorus in the six reference samples ranged from 0.15 to 1.57 mg/L. The SRWS sample with the 1.57 mg/L concentration of orthophosphate as phosphorus accounted for approximately 65 percent of the out-of-control determinations at the NWQL. However, the QWSU never reported an out-of-control result for this reference sample. The techniques used by both laboratories are identical with

the upper analytical range set at 1.00 mg/L; analyses above this concentration require dilutions, including the SRWS with a concentration of 1.57 mg/L. Analytical imprecision for NWQL orthophosphate as phosphorus determinations can partly be attributed to dilution errors. The NWQL phosphorus determination failed the precision test for both water years 1990 (Maloney and others, 1993) and 1991.

Bias

Results of the statistical tests for bias are presented in table 10 for the NWQL and table 11 for the QWSU. All the QWSU nutrient determinations passed the binomial-probability-distribution bias test for water year 1991. The NWQL determinations for ammonia as nitrogen (COL), phosphorus (COL), and orthophosphate as phosphorus (COL) exhibited a bias condition for water year 1991. Both phosphorus (COL) and orthophosphate as phosphorus (COL) showed a negative bias, whereas ammonia as nitrogen (COL) had a positive bias. The orthophosphate as phosphorus (COL) negative bias can partly be attributed to dilution errors on one SRWS, as described in this report.

The NWQL determination for nitrate plus nitrite as nitrogen (COL), which had been designated as biased during water year 1990 (Maloney and others, 1993), did not show a bias condition for water year 1991.

[COL, colorime	etric;, acceptable res	ults; LOP, statistically	significant lack of precision]

Constituent (dissolved except as indicated) and analytical method	Results from October 1990– September 1991	Constituent (dissolved except as indicated) and analytical method	Results from October 1990– September 1991
Ammonia as nitrogen (COL)		Orthophosphate as phosphorus (COL)	LOP
Ammonia plus organic nitrogen as nitrogen (COL)		Phosphorus (COL)	LOP
Nitrate plus nitrite as nitrogen (COL)			

Table 9. Results of statistical testing for analytical precision in nutrient constituent data for the Quality of Water Service Unit laboratory

[COL, colorimetric; --, acceptable results]

Constituent (dissolved except as indicated) and analytical method	Results from October 1990– September 1991	Constituent (dissolved except as indicated) and analytical method	Results from October 1990– September 1991
Ammonia as nitrogen (COL)		Orthophosphate as phosphorus (COL)	
Ammonia plus organic nitrogen as nitrogen (COL)		Phosphorus (COL)	
Nitrate plus nitrite as nitrogen (COL)			

Table 10. Results of statistical testing for bias in nutrient constituent data for the National Water Quality Laboratory

[COL, colorimetric; +, positive bias; 0, acceptable results; -, negative bias]

Constituent (dissolved except as indicated) and analytical method	Results from October 1990– September 1991	Constituent (dissolved except as indicated) and analytical method	Results from October 1990– September 1991
Ammonia as nitrogen (COL)	+	Orthophosphate as phosphorus (COL)	-
Ammonia plus organic nitrogen as nitrogen (COL)	0	Phosphorus (COL)	-
Nitrate plus nitrite as nitrogen (COL)	0		

Table 11. Results of statistical testing for bias in nutrient constituent data for the Quality of Water Service Unit laboratory

[COL, colorimetric; 0, acceptable results]

Constituent (dissolved except as indicated) and analytical method	Results from October 1990– September 1991	Constituent (dissolved except as indicated) and analytical method	Results from October 1990– September 1991
Ammonia as nitrogen (COL)	0	Orthophosphate as phosphorus (COL)	0
Ammonia plus organic nitrogen as nitrogen (COL)	0	Phosphorus (COL)	0
Nitrate plus nitrite as nitrogen (COL)	0		

QUALITY-ASSURANCE RESULTS FOR LOW IONIC-STRENGTH SAMPLES

showed significant improvement in precision over the previous water year (Maloney and others, 1993).

Precision

Low ionic-strength determinations are provided by the NWQL but not by the QWSU. The results of the statistical tests of precision for each low ionic-strength analytical procedure are presented in table 12. The 14 low ionic-strength determinations all showed acceptable precision for water year 1991. Cadmium

Bias

The results of the binomial-probability-distribution statistical test of bias for each constituent in the low ionic-strength samples are presented in table 13. No low ionic-strength determinations failed the binomial-probability-distribution bias test for water year 1991.

 Table 12. Results of statistical testing for analytical precision in low ionic-strength data for the National Water Quality

 Laboratory

[AA, atomic absorption spectrometric; GF, graphite furnace; --, acceptable results; IC, ion-exchange chromatographic; ELEC, electrometric]

Constituent (dissolved except as indicated) or physical property	Results from October 1990– September 1991	Constituent (dissolved except as indicated) or physical property	Results from October 1990– September 1991
Cadmium (AA,GF)		Lead (AA,GF)	••
Calcium (AA)		Magnesium (AA)	
Chloride (IC)		Nickel (AA,GF)	
Chromium (AA,GF)		Potassium (AA)	
Cobalt (AA,GF)		Sodium (AA)	
Copper (AA,GF)		Specific conductance (ELEC)	
Fluoride (IC)		Sulfate (IC)	

Table 13. Results of statistical testing for bias in low ionic-strength data for the National Water Quality Laboratory

[AA, atomic absorption spectrometric; GF, graphite furnace; 0, acceptable results; IC, ion-exchange chromatographic; ELEC, electrometric]

Constituent (dissolved except as indicated) or physical property	Results from October 1990– September 1991	Constituent (dissolved except as indicated) or physical property	Results from October 1990– September 1991
Cadmium (AA,GS)	0	Lead (AA,GF)	0
Calcium (AA)	0	Magnesium (AA)	0
Chloride (IC)C	0	Nickel (AA,GF)	0
Chromium (AA,GF)	0	Potassium (AA)	0
Cobalt (AA,GF)	0	Sodium (AA)	0
Copper (AA,GF)	0	Specific conductance (ELEC)	0
Fluoride (IC)	0	Sulfate (IC)	0

SUMMARY

A quality-assurance program was operated during water year 1991 to evaluate the quality of analytical work for inorganic constituents, nutrients, low ionicstrength constituents, and some physical properties at two USGS laboratories. Reference water samples with established most probable values were disguised as regular samples and submitted with environmental water samples by USGS offices to the National Water Quality Laboratory (NWQL) in Arvada, Colorado, and the Quality of Water Service Unit (QWSU) laboratory in Ocala, Florida. Reference samples were submitted at a rate of approximately 5 percent of the laboratory work for each analytical procedure. Resulting analytical data were stored in the WATSTORE data base.

For each constituent, control charts were prepared based on 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 most probable deviation, 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 ionic-strength constituent samples were then evaluated statistically for precision and bias by using a binomialprobability-distribution equation.

An overall evaluation of the inorganic-constituent data for water year 1991 indicates an analytical imprecision in results from the NWQL for aluminum, (WWR,DCP), calcium (AA), fluoride (IC), iron, (WWR, AA), and sulfate (IC). All inorganic-constituent data for the QWSU during water year 1991 passed the precision test.

The water year 1991 evaluation of analytical bias for inorganic determinations indicates statistically significant bias for 11 NWQL analytical procedures: alkalinity (TITR), barium (ICP), beryllium (ICP), cadmium (ICP), calcium (ICP and AA), chloride (IC), dissolved solids (GRAV), molybdenum (WWR,AA), sodium (ICP), and vanadium (COL). None of the inorganic determinations from the QWSU showed bias results.

Statistical evaluations of nutrient procedures at the NWQL indicated that the results for phosphorus (COL) and orthophosphate as phosphorus (COL) failed the precision test. Results for ammonia as nitrogen (COL), phosphorus (COL), and orthophosphate as phosphorus (COL) showed significant bias. Evaluations of the QWSU nutrient methods did not indicate analytical imprecision or bias.

All low ionic-strength procedures at the NWQL showed adequate precision and no indication of bias.

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SUPPLEMENTAL DATA

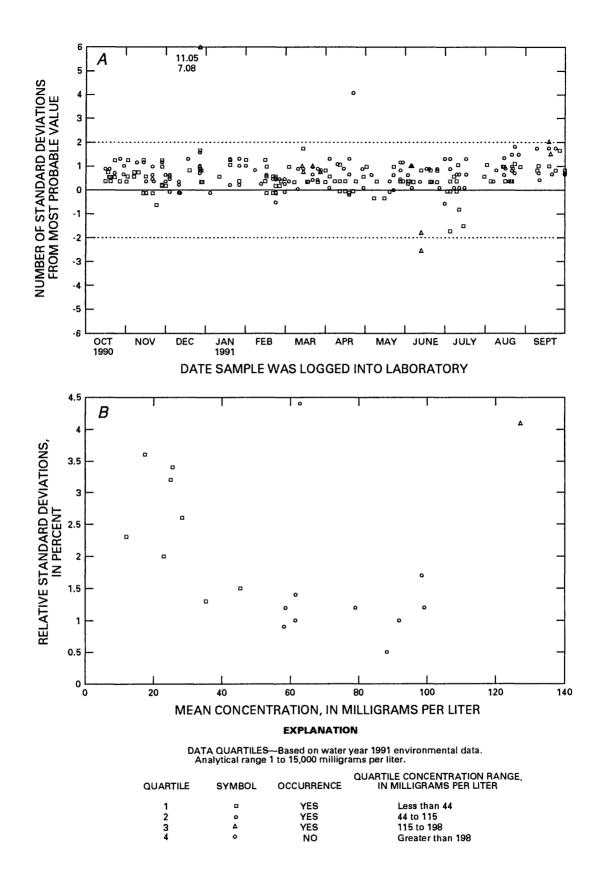


Figure 1. Alkalinity, whole-water recoverable, (electrometric titration) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

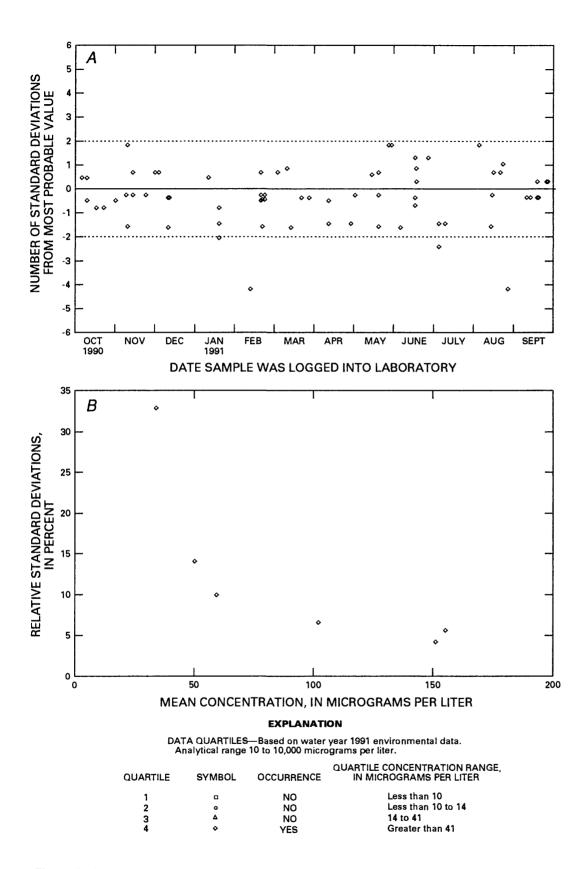


Figure 2. Aluminum, dissolved, (atomic emission spectrometric, direct-current plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

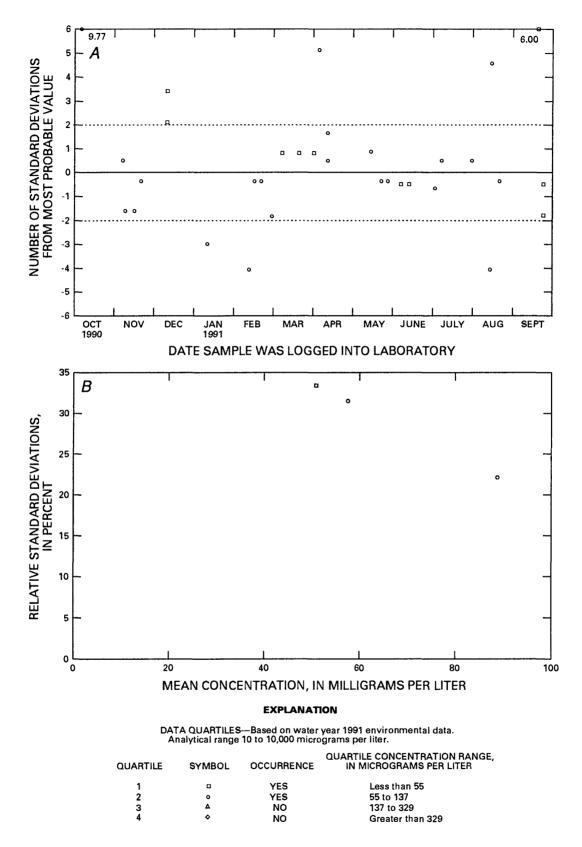


Figure 3. Aluminum, whole-water recoverable, (atomic emission spectrometric, direct-current plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

24 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

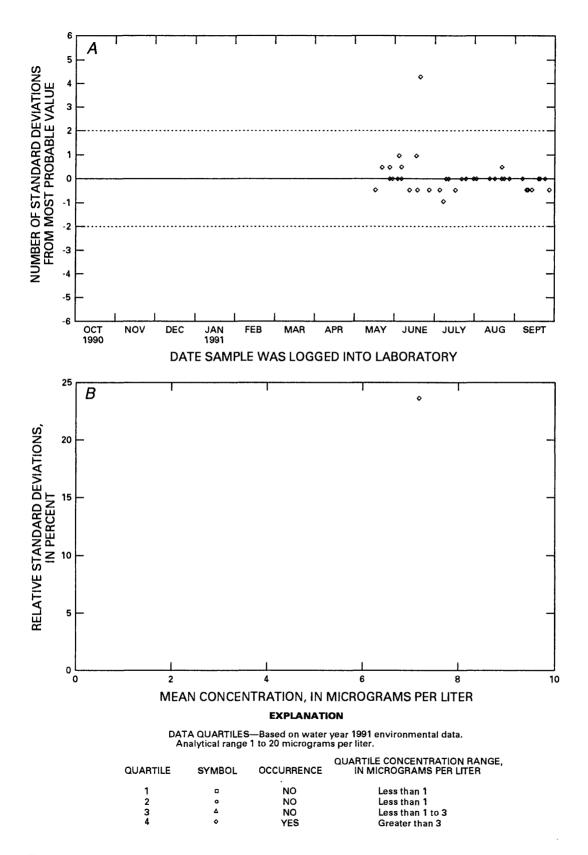


Figure 4. Antimony, dissolved, (atomic absorption spectrometric, hydride) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

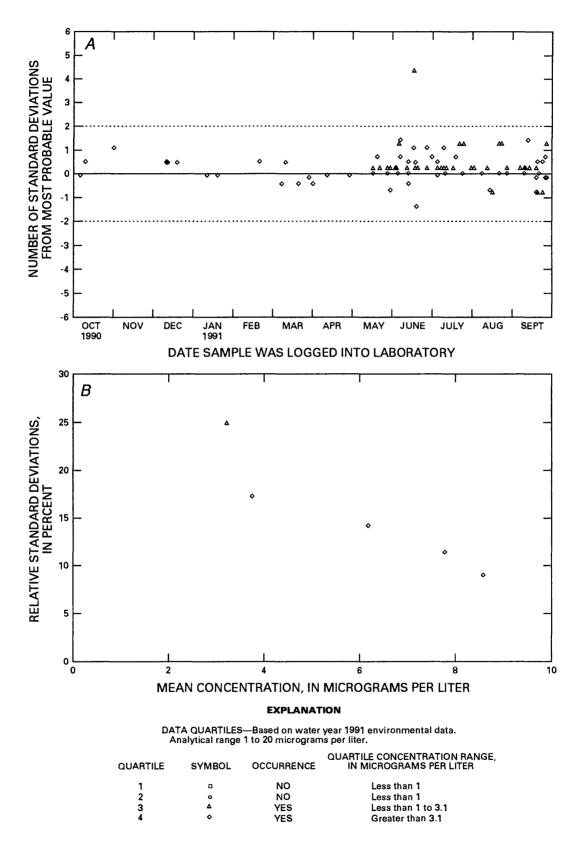


Figure 5. Arsenic, dissolved and whole-water recoverable, (atomic absorption spectrometric, hydride) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

26 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

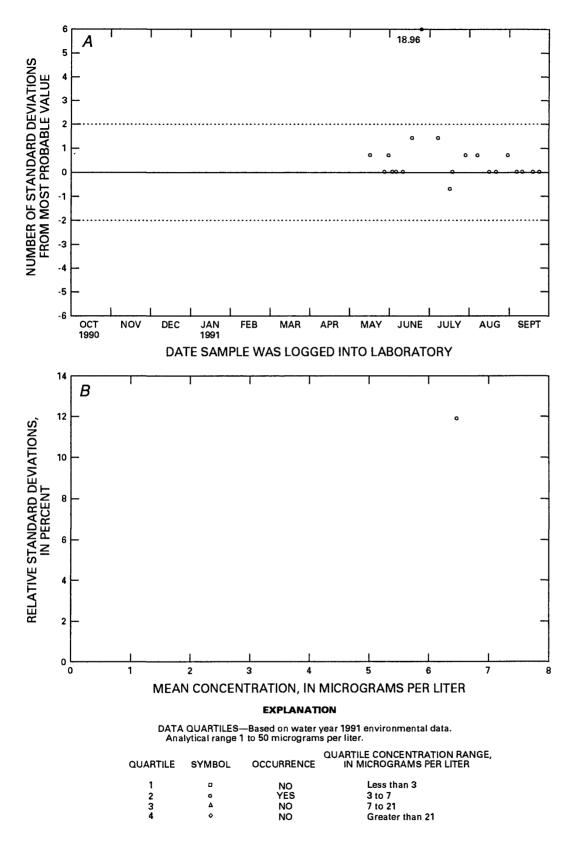


Figure 6. Arsenic, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

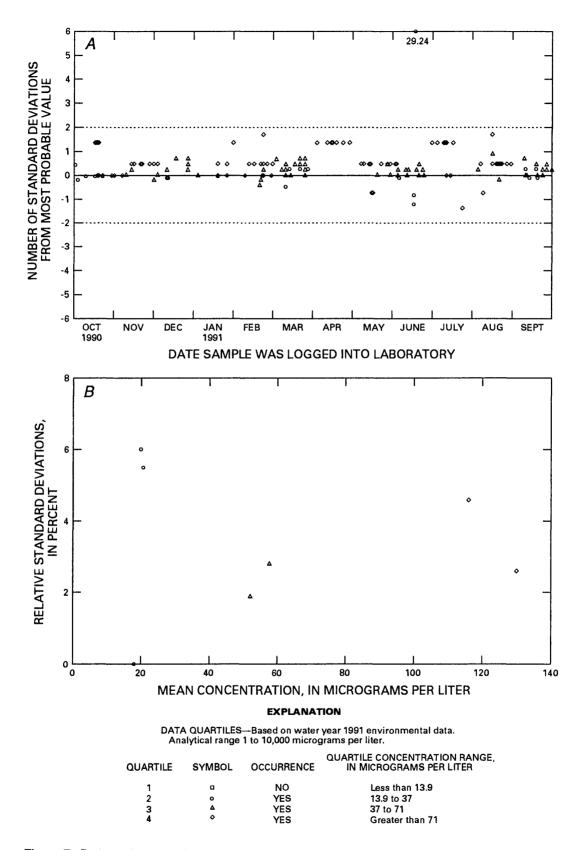


Figure 7. Barium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

28 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

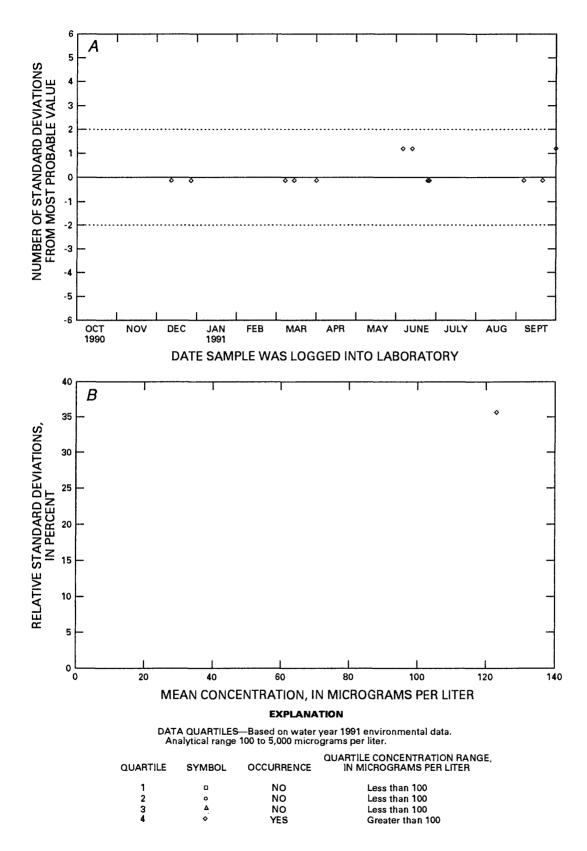


Figure 8. Barium, dissolved, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

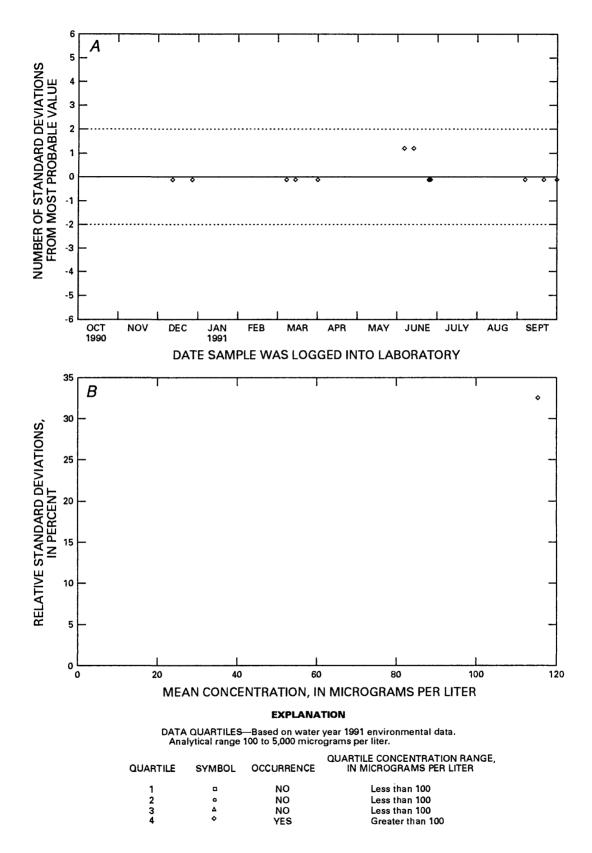


Figure 9. Barium, whole-water recoverable, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

30 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

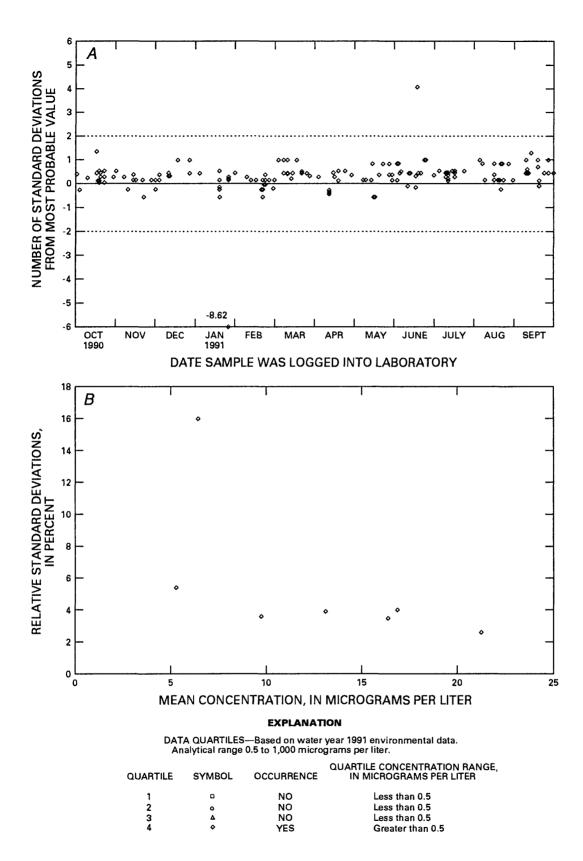


Figure 10. Beryllium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

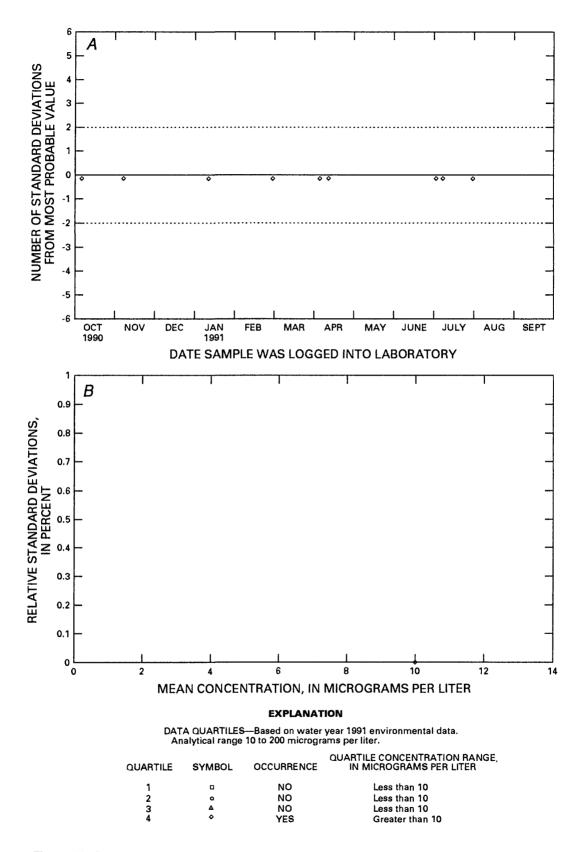


Figure 11. Beryllium, whole-water recoverable, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

32 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

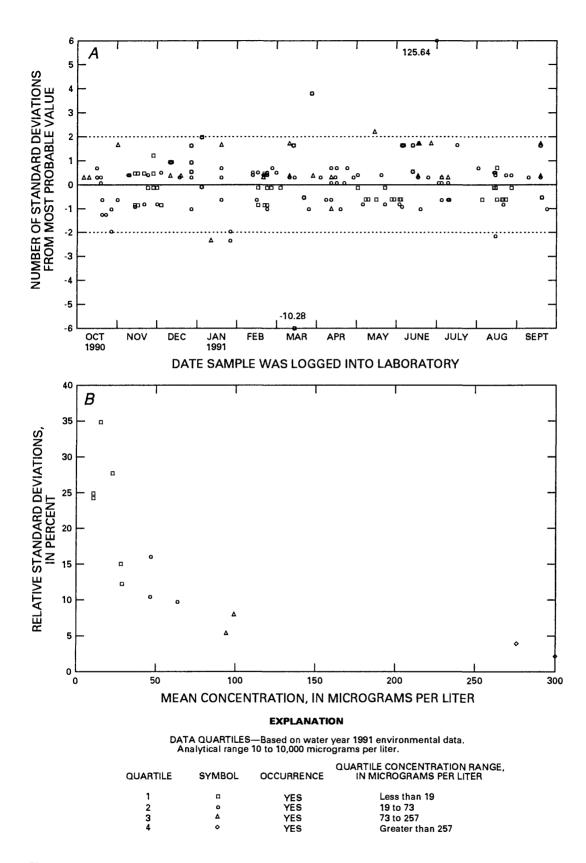


Figure 12. Boron, dissolved, (atomic emission spectrometric, direct-current plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

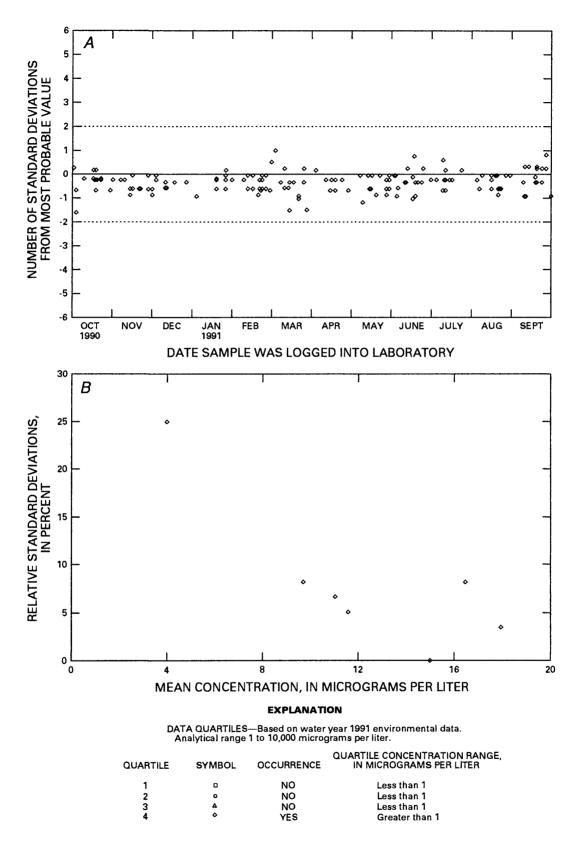


Figure 13. Cadmium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

34 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

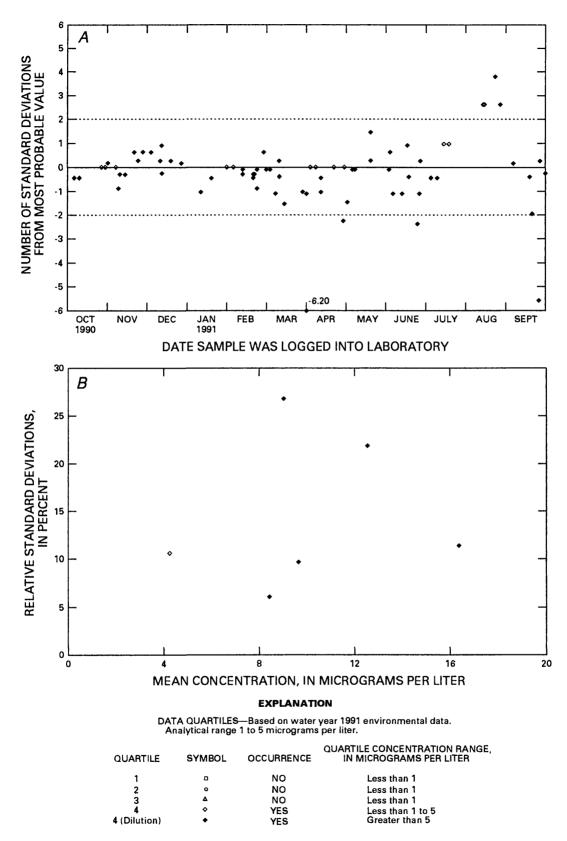


Figure 14. Cadmium, dissolved, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

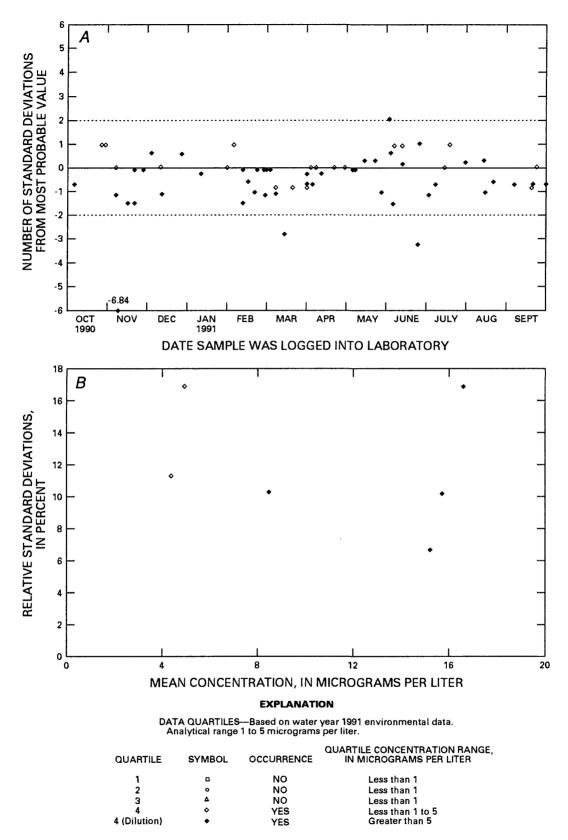


Figure 15. Cadmium, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

36 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

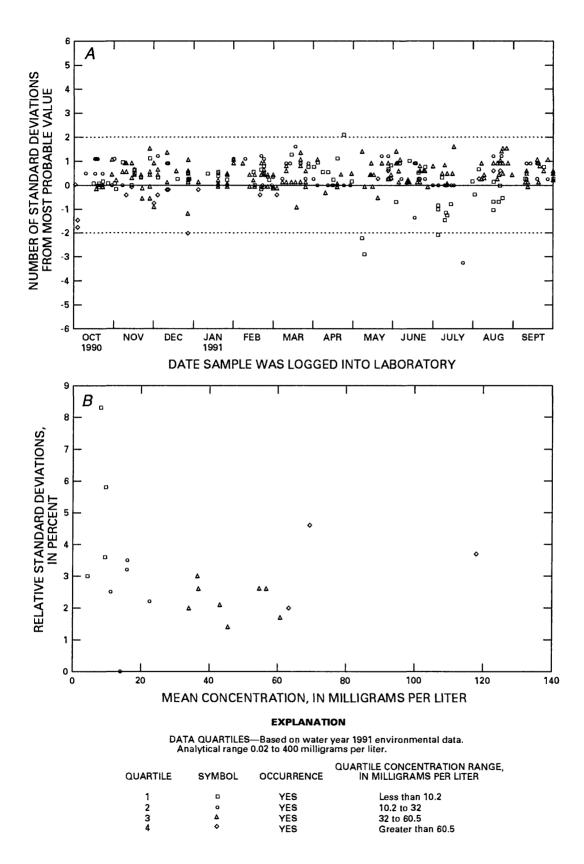


Figure 16. Calcium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

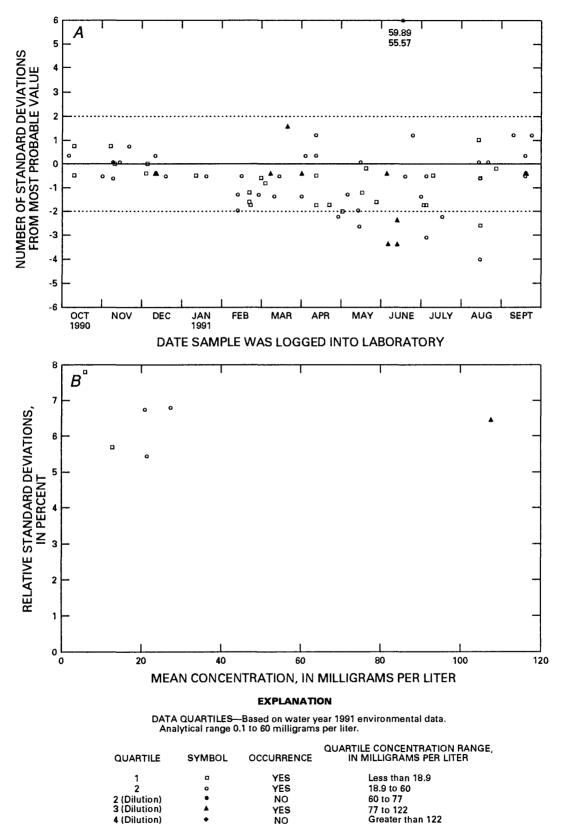


Figure 17. Calcium, dissolved, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

38 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

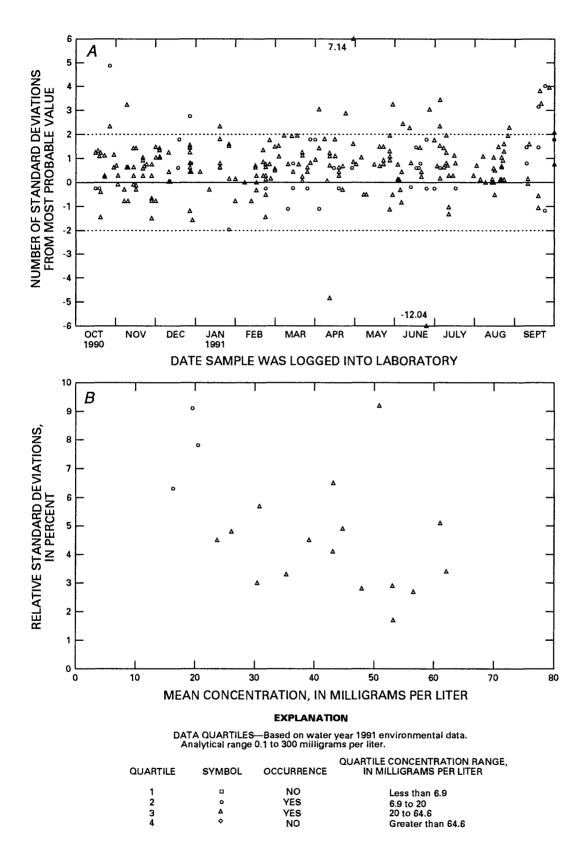


Figure 18. Chloride, dissolved, (ion-exchange chromatographic) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

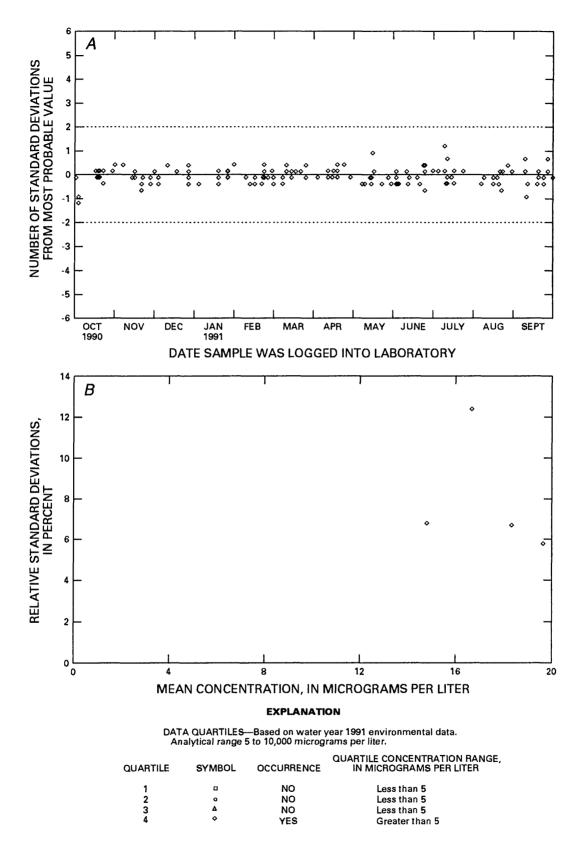


Figure 19. Chromium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

40 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

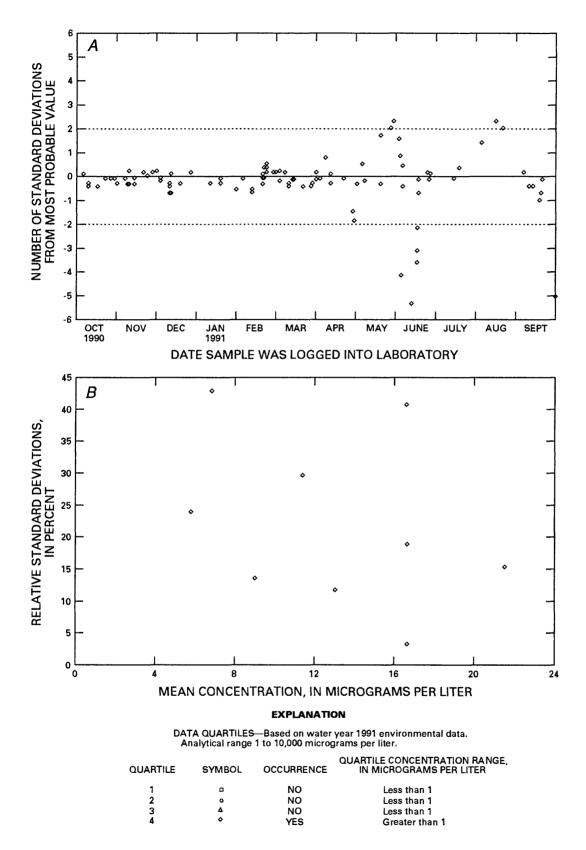


Figure 20. Chromium, dissolved, (atomic emission spectrometric, direct-current plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

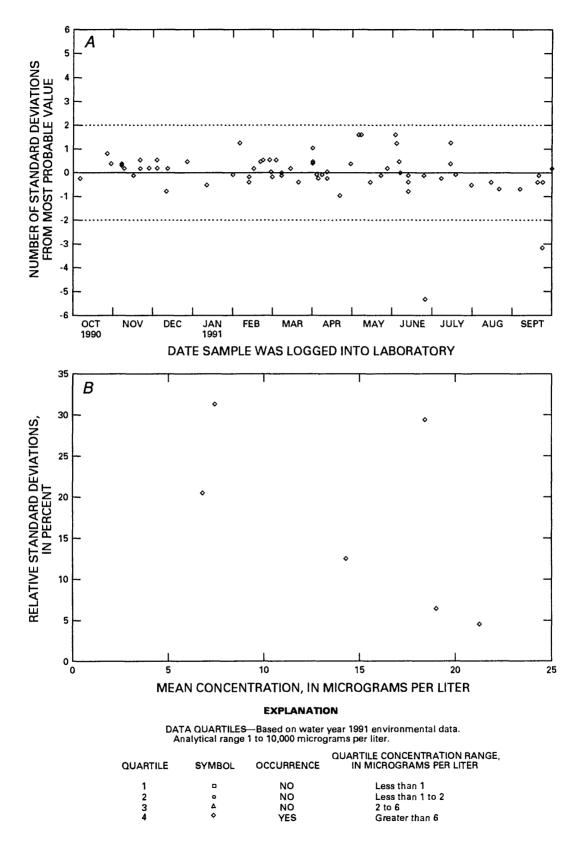


Figure 21. Chromium, whole-water recoverable, (atomic emission spectrometric, direct-current plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

42 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

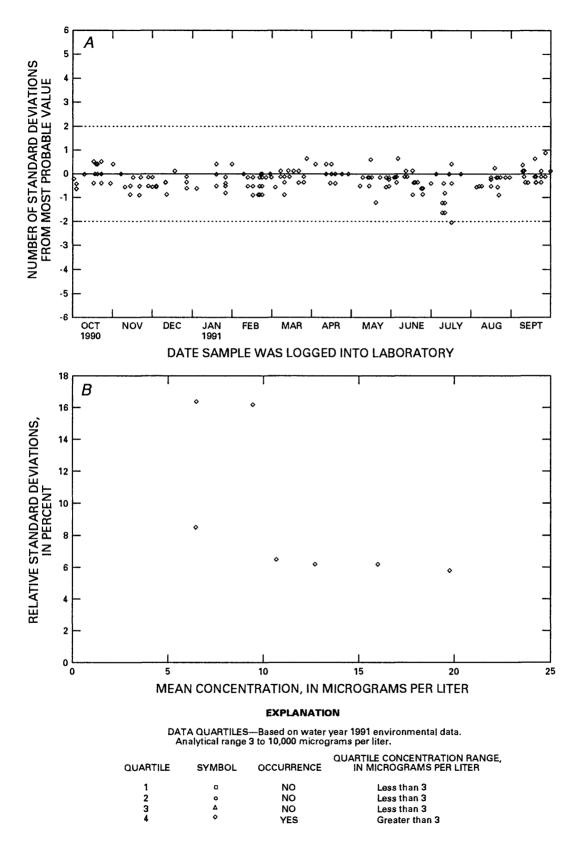


Figure 22. Cobalt, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

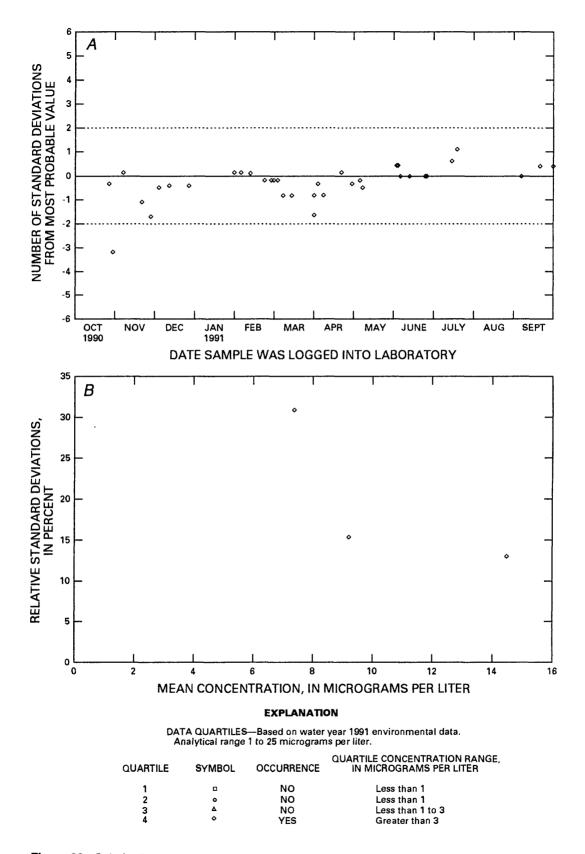


Figure 23. Cobalt, dissolved, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

44 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

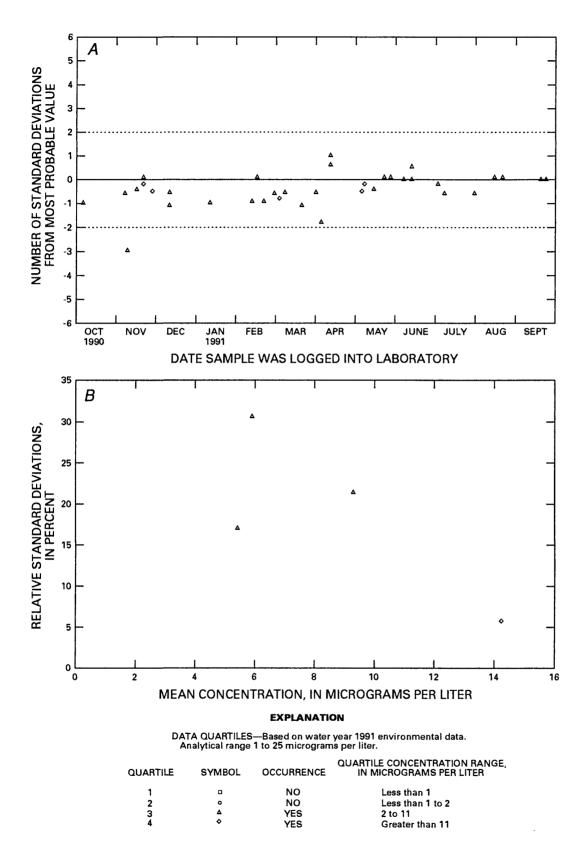


Figure 24. Cobalt, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

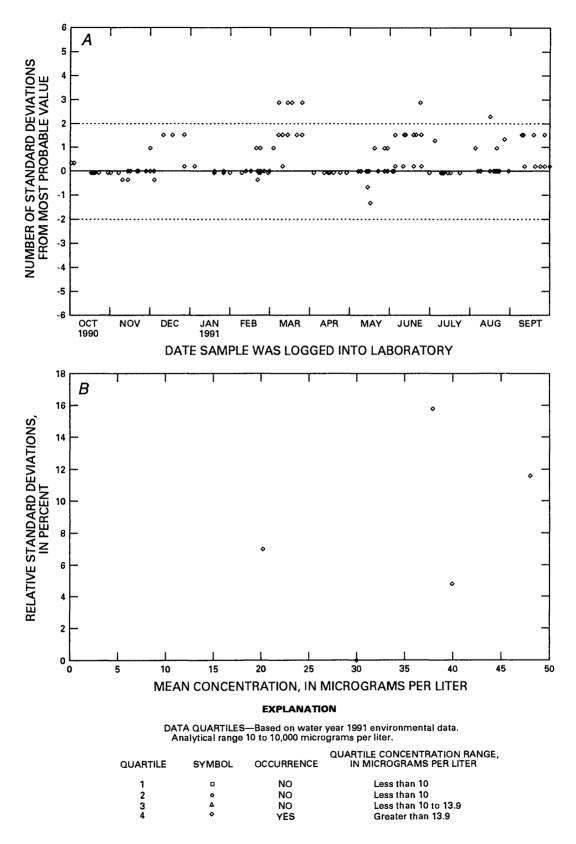


Figure 25. Copper, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

46 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

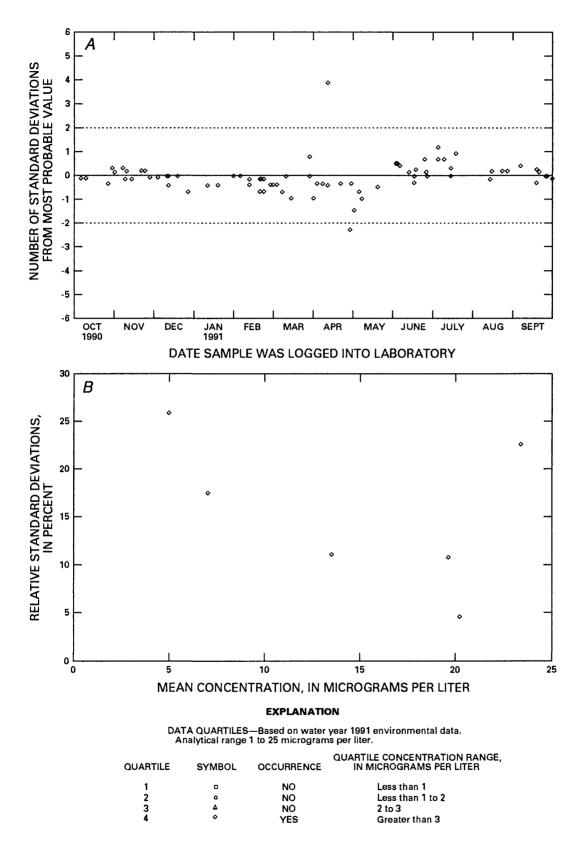


Figure 26. Copper, dissolved, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

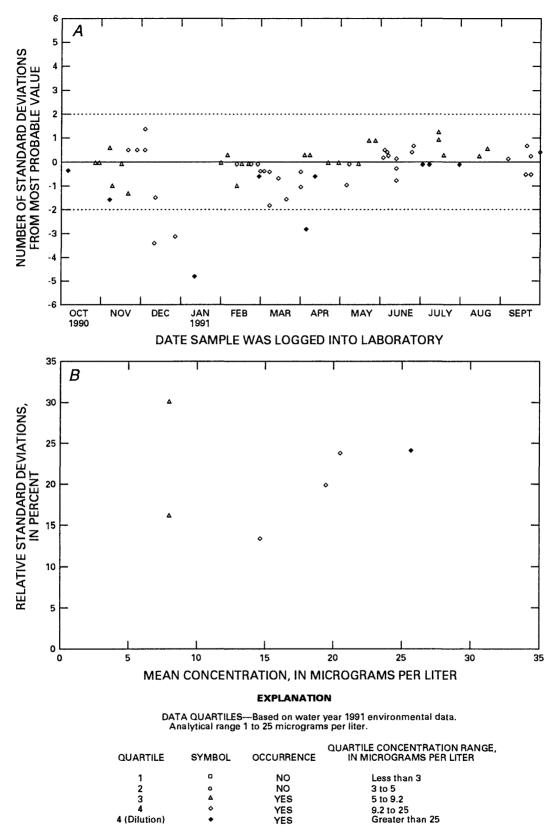


Figure 27. Copper, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

48 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

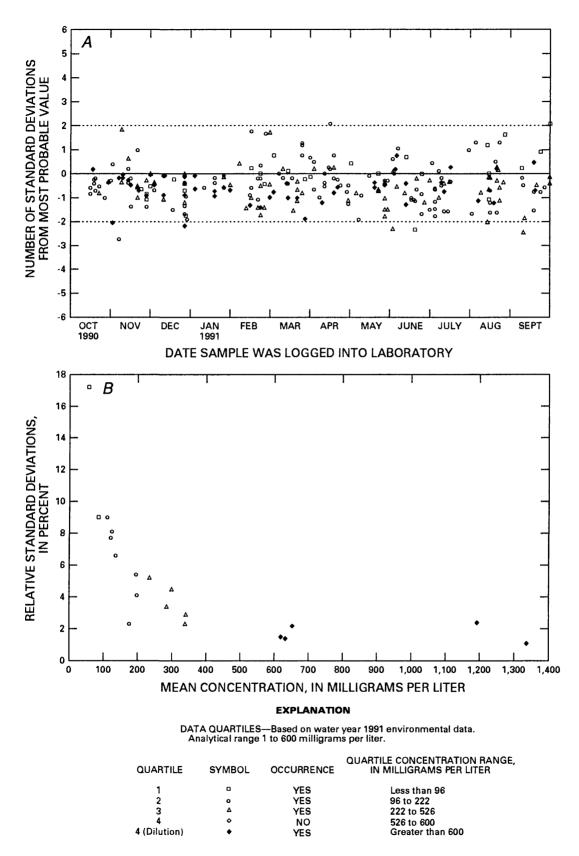


Figure 28. Dissolved solids, (gravimetric) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

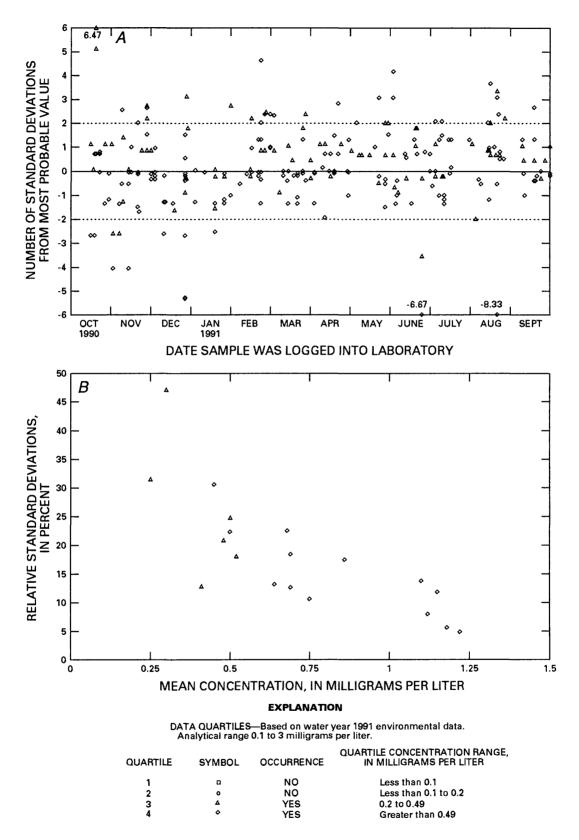


Figure 29. Fluoride, dissolved, (ion-exchange chromatographic) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

50 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

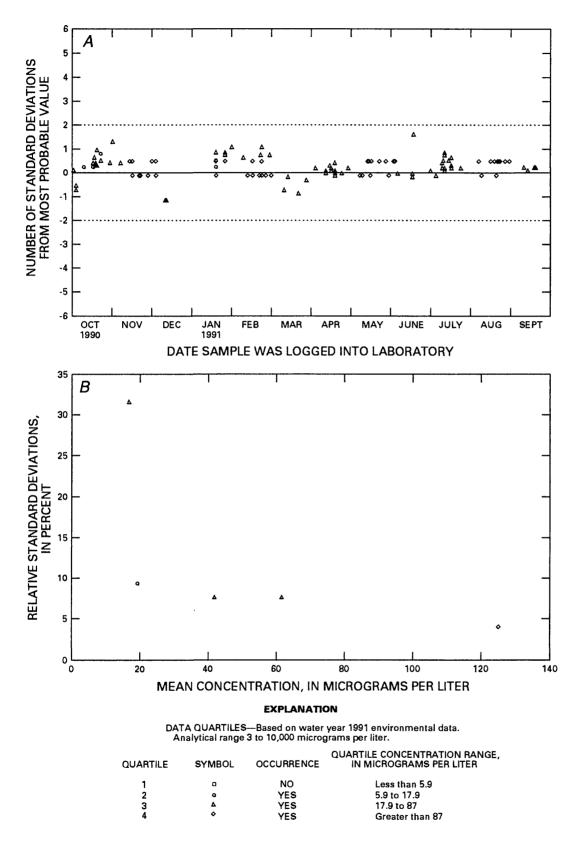


Figure 30. Iron, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

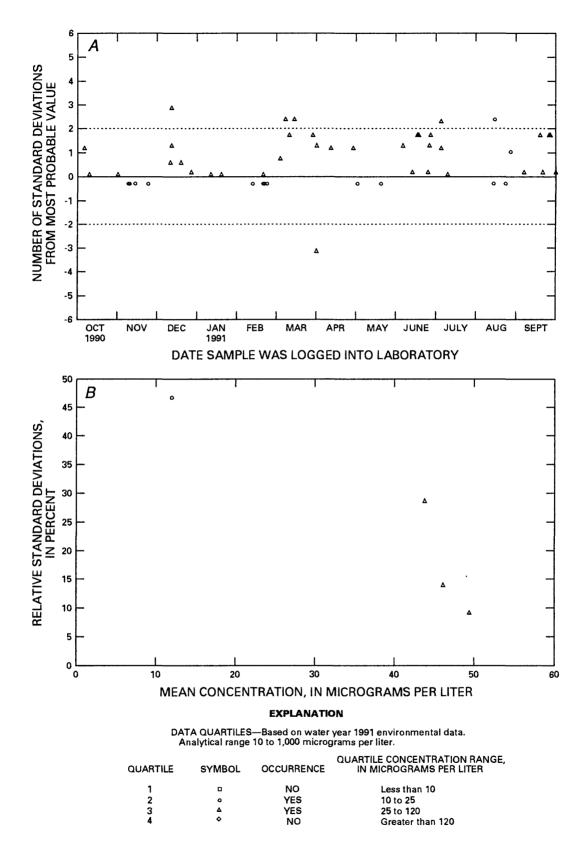


Figure 31. Iron, dissolved, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

52 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

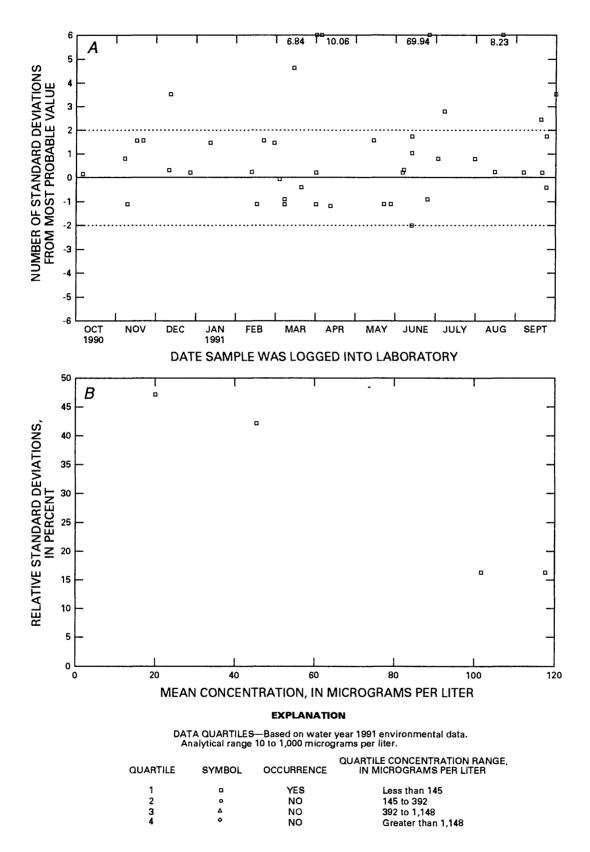


Figure 32. Iron, whole-water recoverable, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

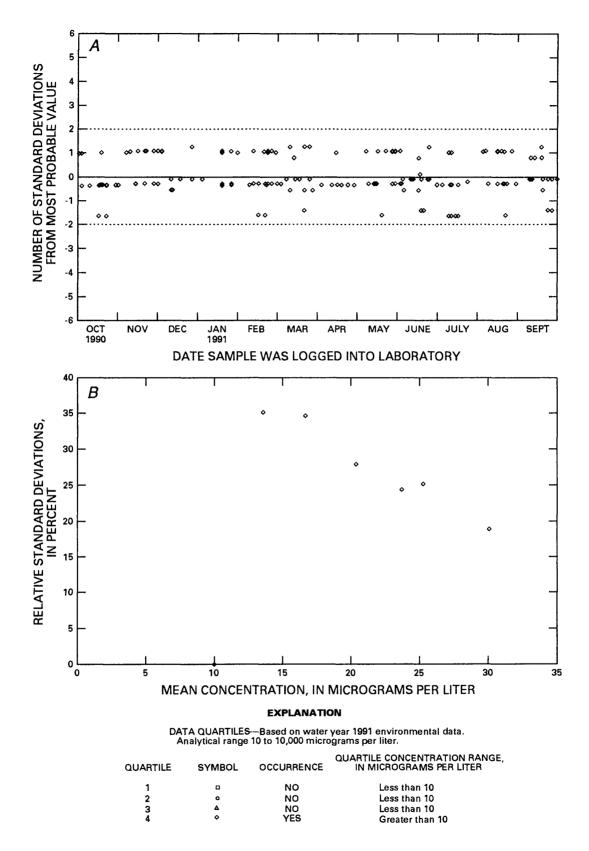


Figure 33. Lead, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

54 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

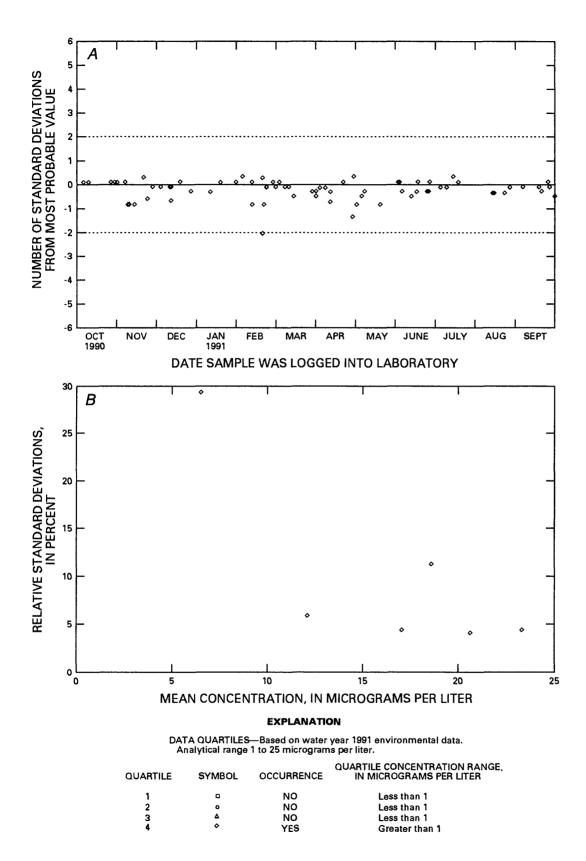


Figure 34. Lead, dissolved, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

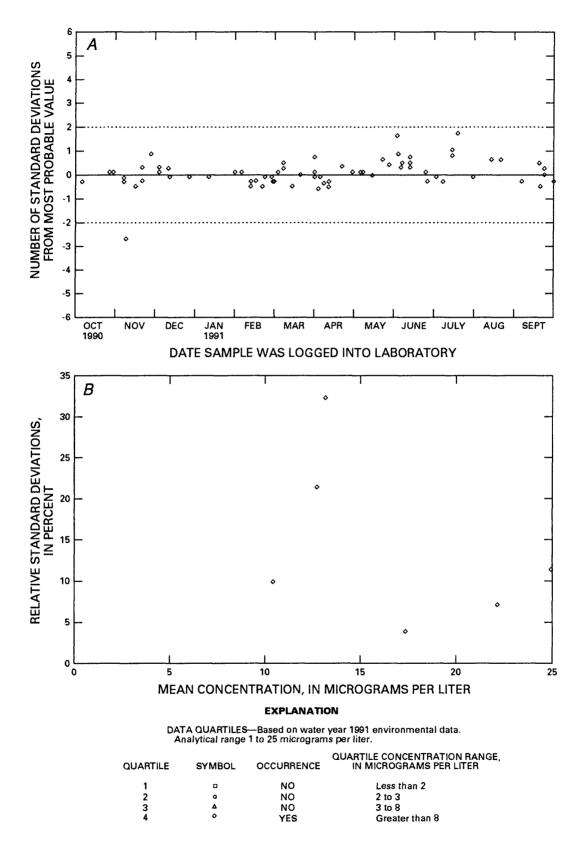


Figure 35. Lead, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

56 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

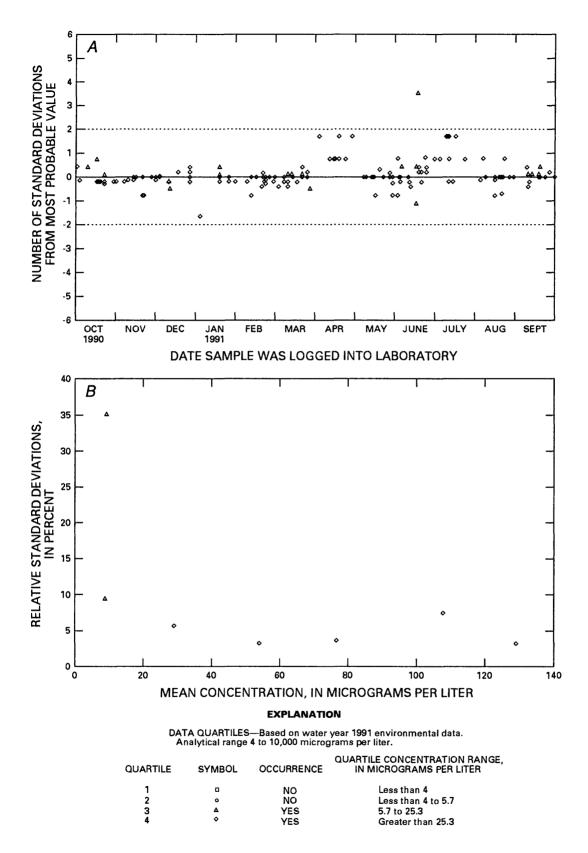


Figure 36. Lithium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

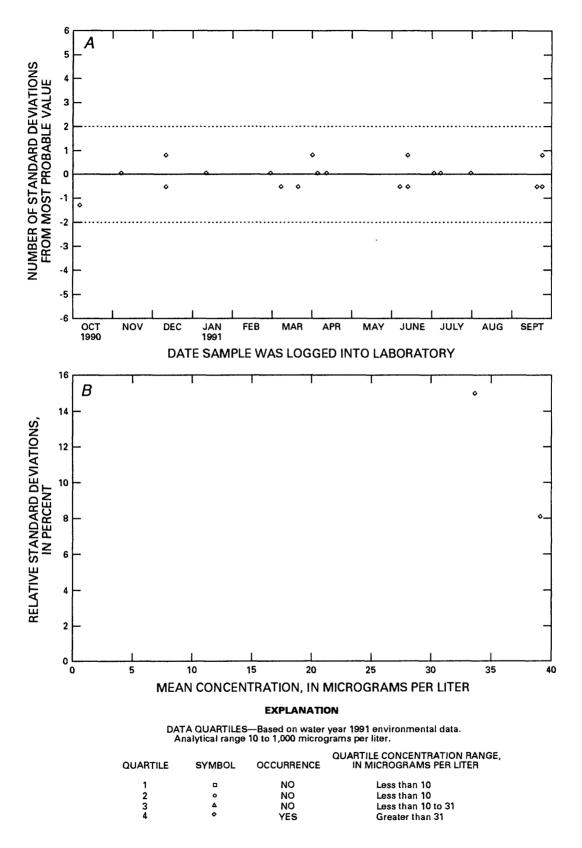


Figure 37. Lithium, whole-water recoverable, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

58 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

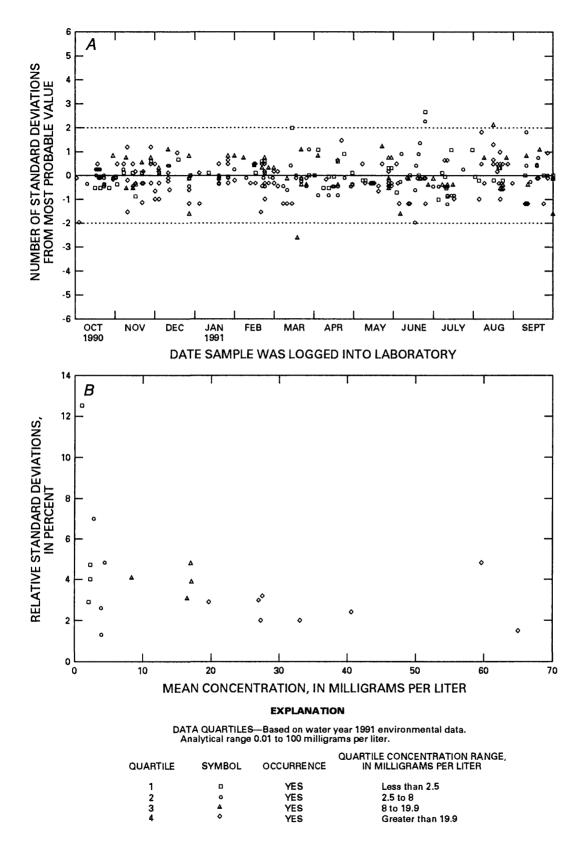


Figure 38. Magnesium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

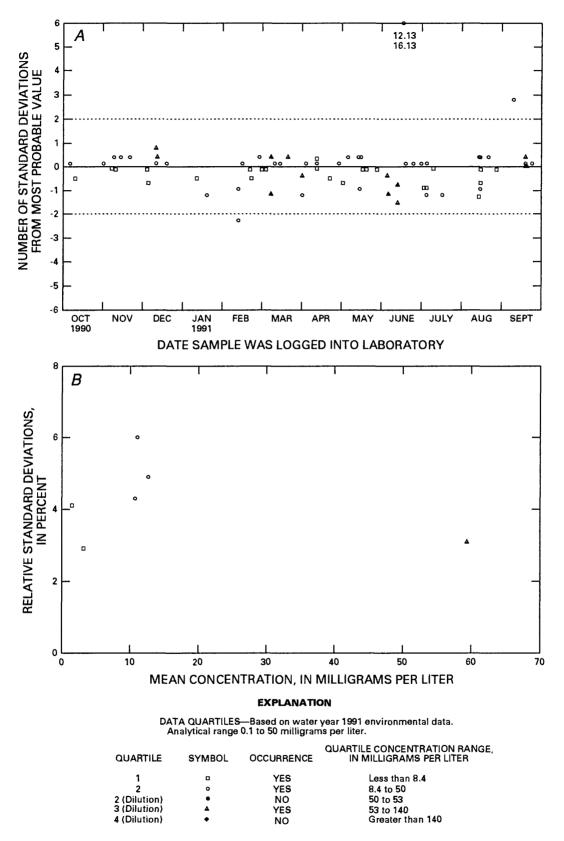


Figure 39. Magnesium, dissolved, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

60 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

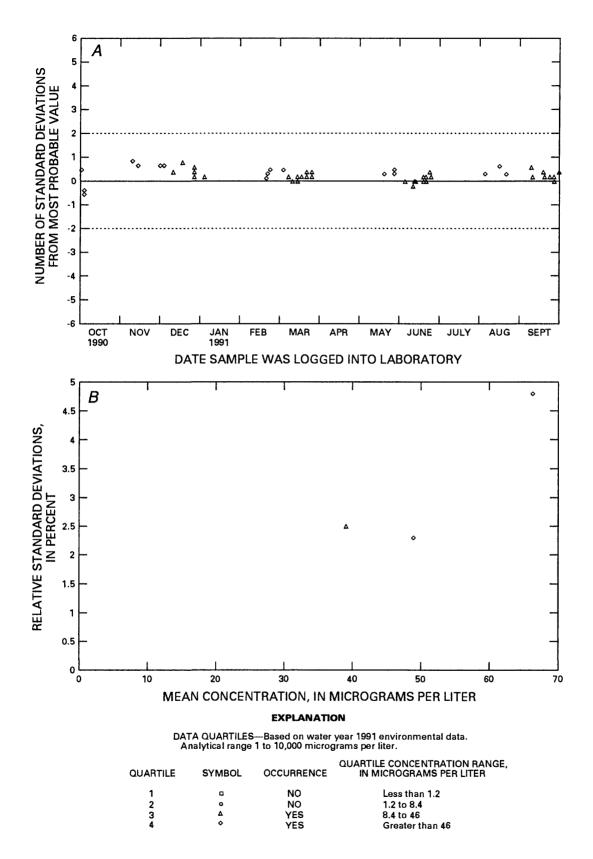


Figure 40. Manganese, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

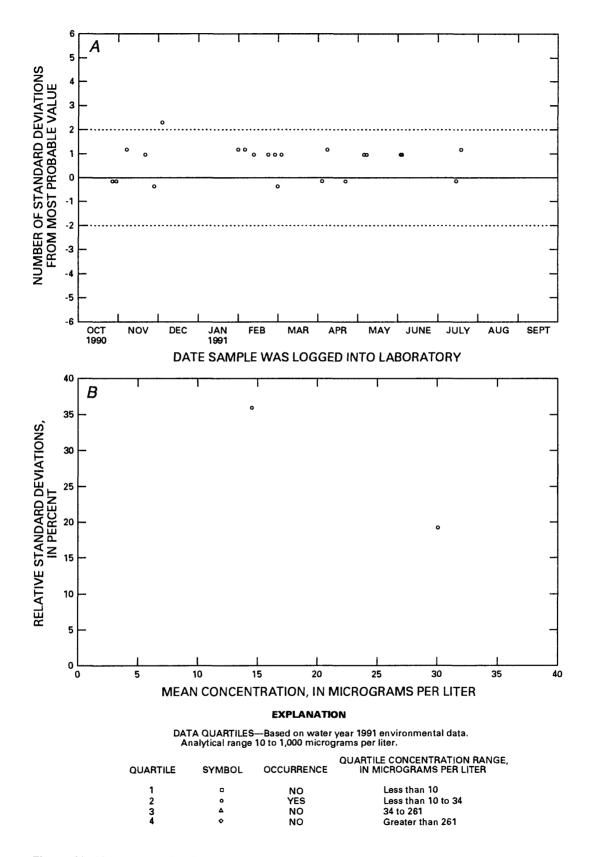


Figure 41. Manganese, dissolved, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

62 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

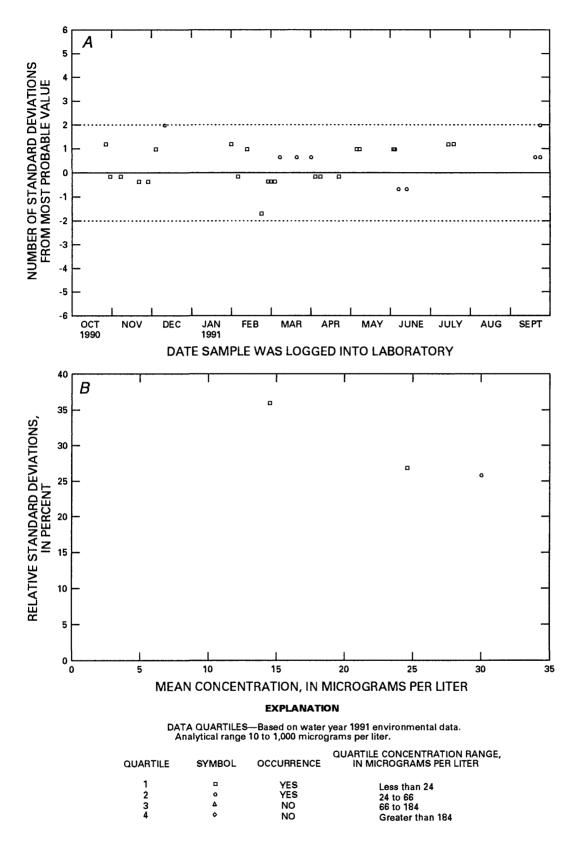


Figure 42. Manganese, whole-water recoverable, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

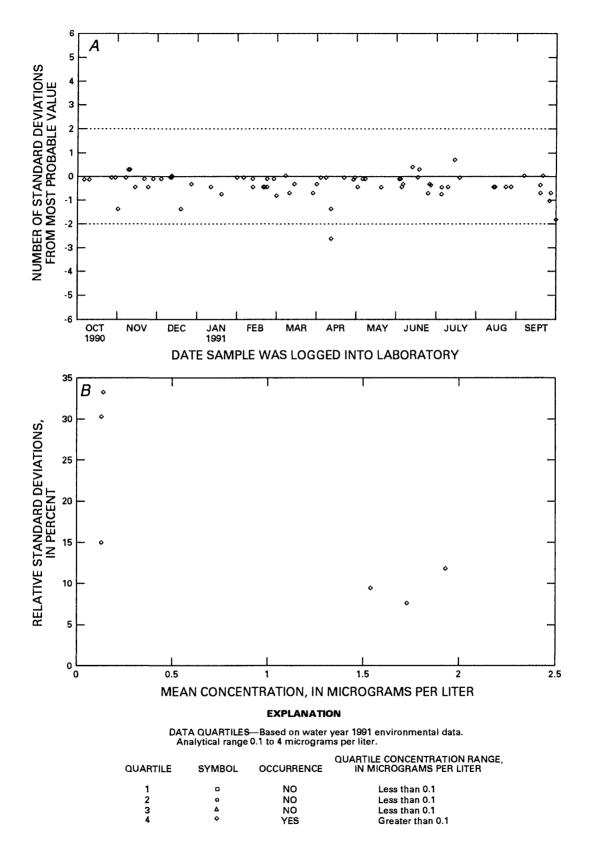


Figure 43. Mercury, dissolved, (atomic absorption spectrometric, flameless) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

64 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

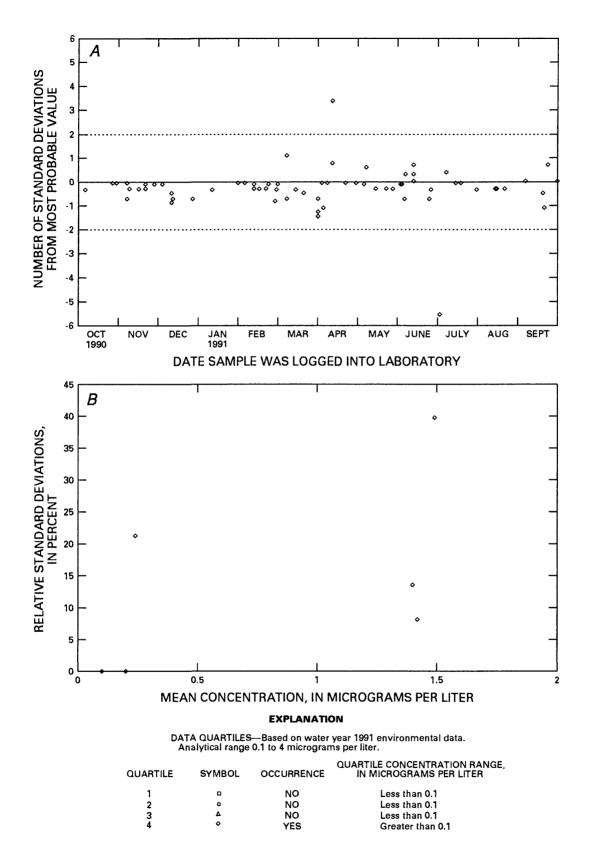


Figure 44. Mercury, whole-water recoverable, (atomic absorption spectrometric, flameless) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

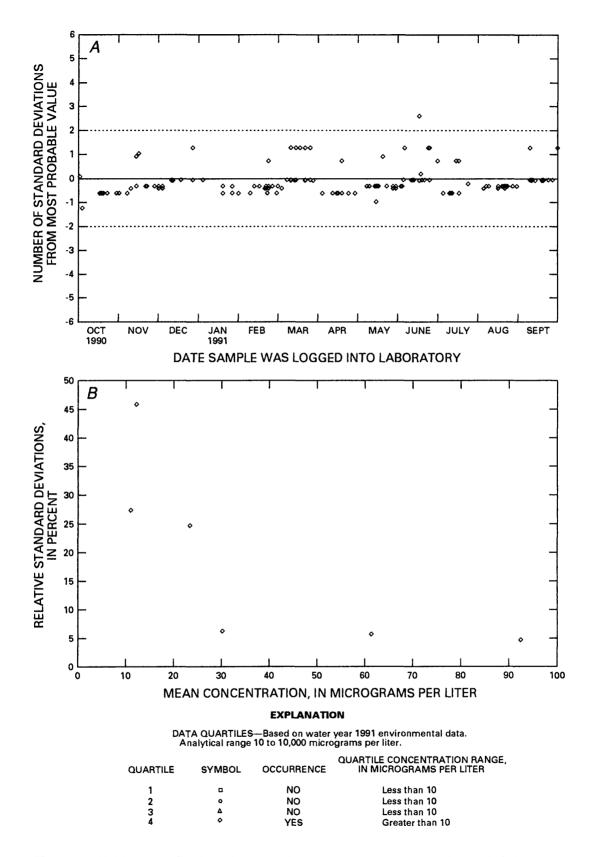


Figure 45. Molybdenum, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

66 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

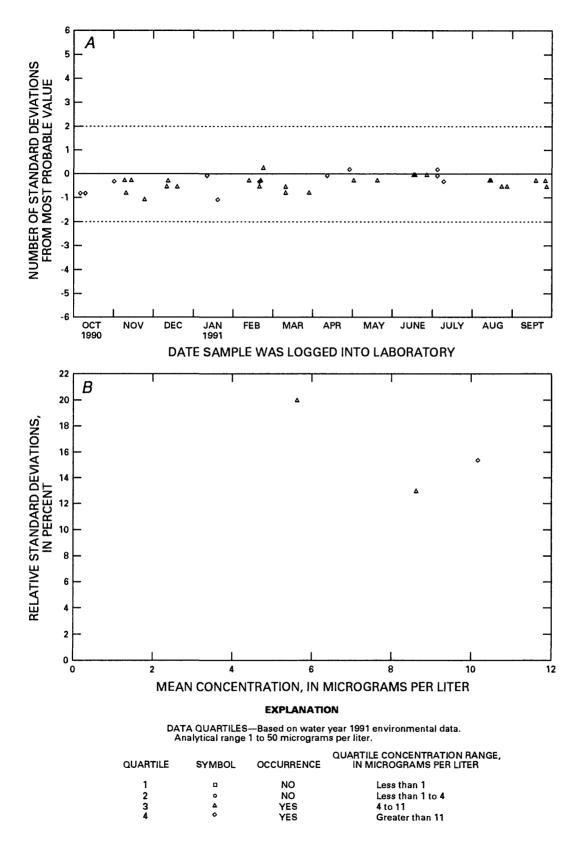


Figure 46. Molybdenum, dissolved, (atomic absorption spectrometric, chelation extraction) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

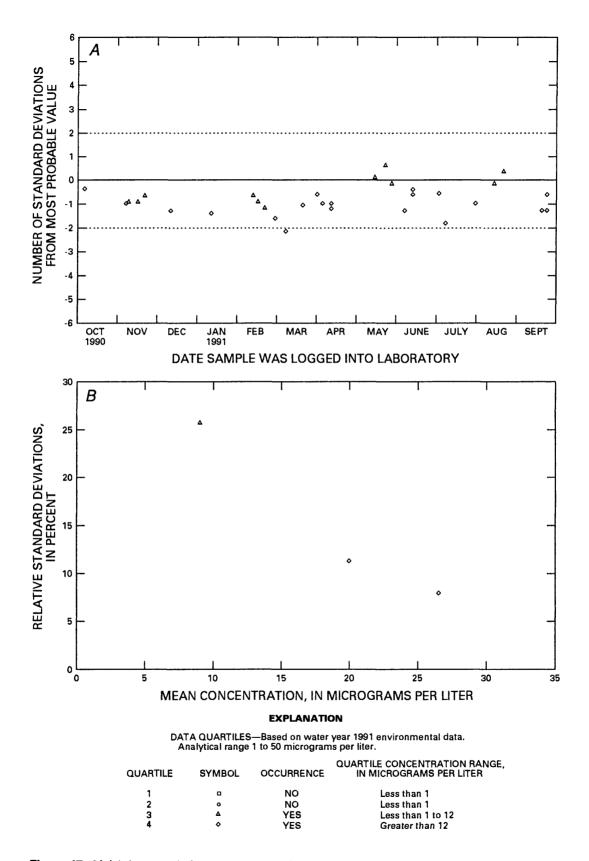


Figure 47. Molybdenum, whole-water recoverable, (atomic absorption spectrometric, chelation extraction) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

68 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

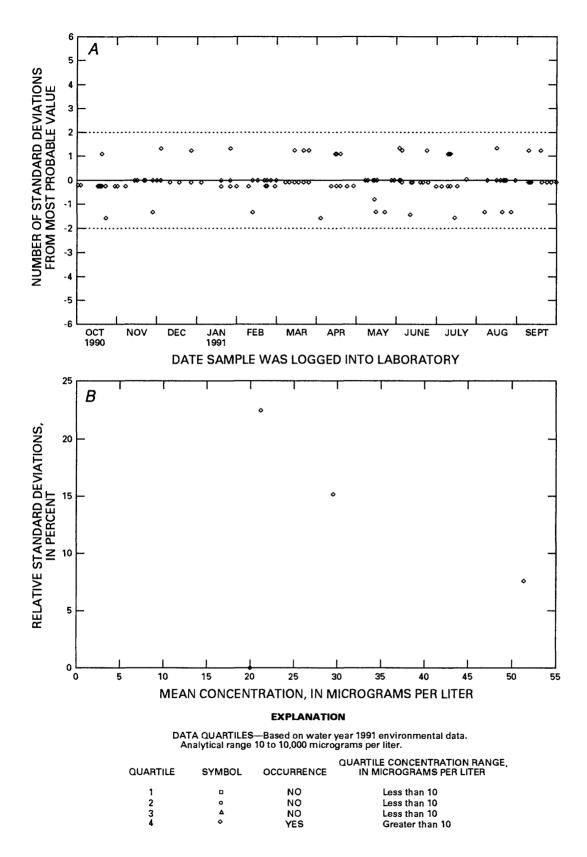


Figure 48. Nickel, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

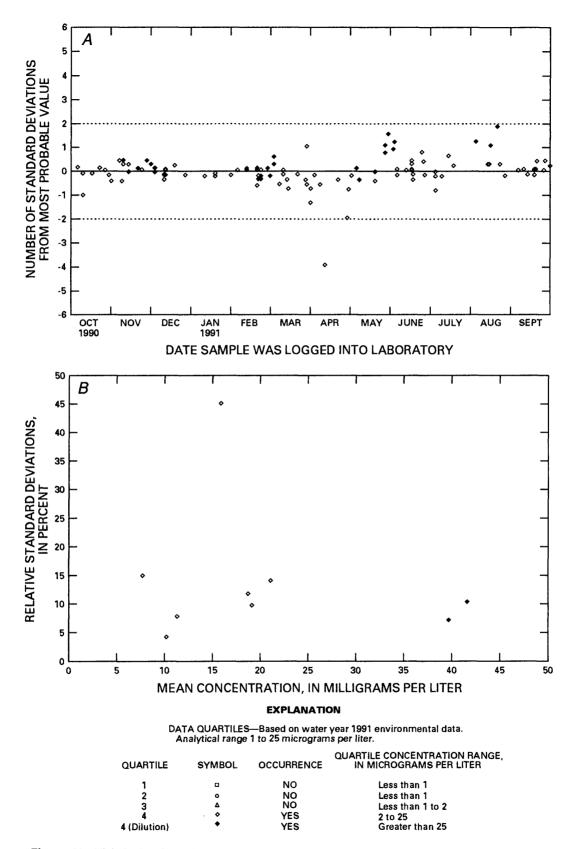


Figure 49. Nickel, dissolved, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

70 Quality-Assurance Results for Routine Water Analysis In the Laboratories of the U.S. Geological Survey for Water Year 1991

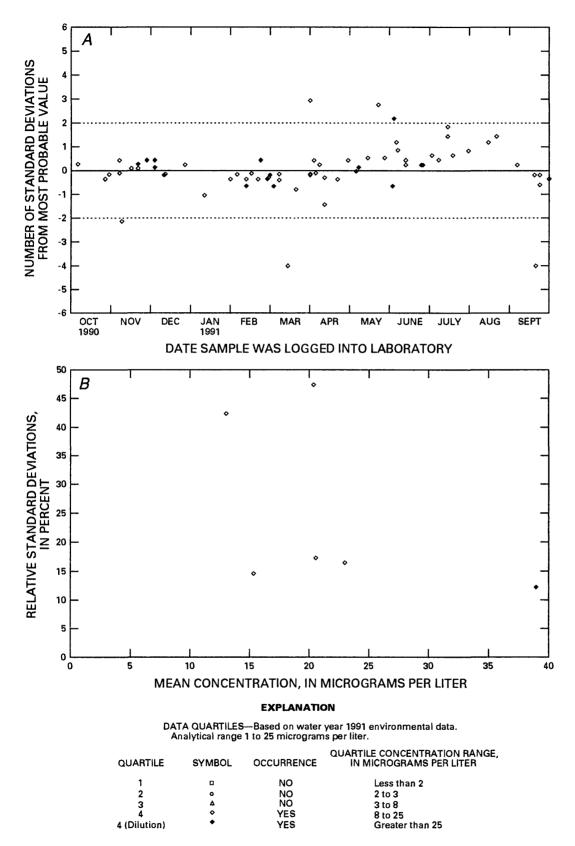


Figure 50. Nickel, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

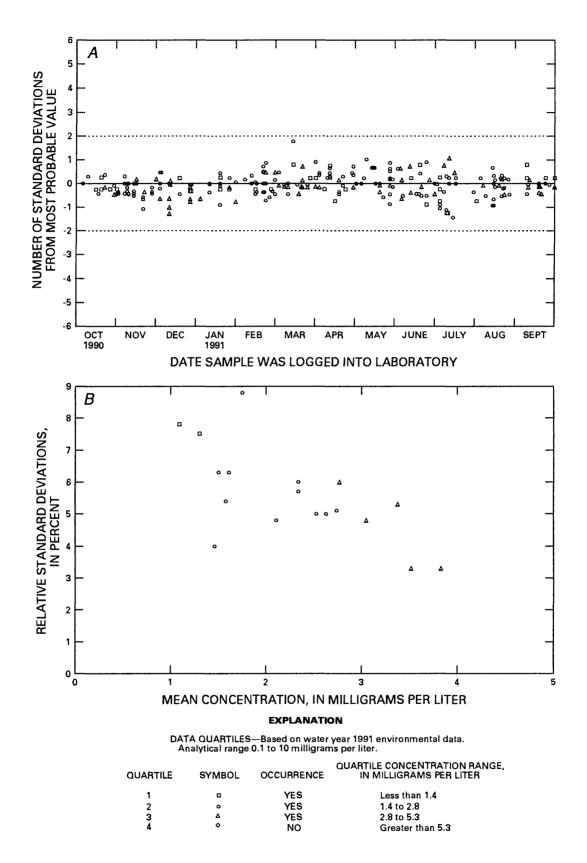


Figure 51. Potassium, dissolved, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

72 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

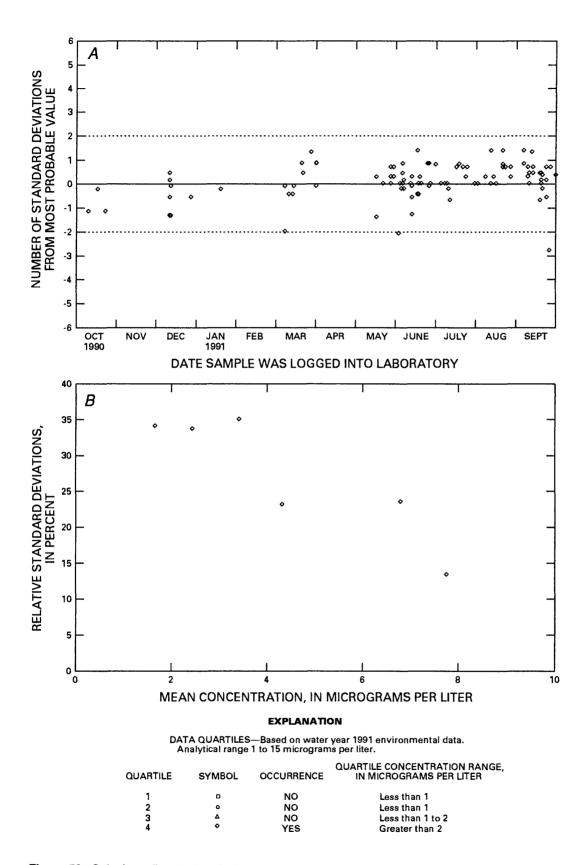


Figure 52. Selenium, dissolved and whole-water recoverable, (atomic absorption spectrometric, hydride) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

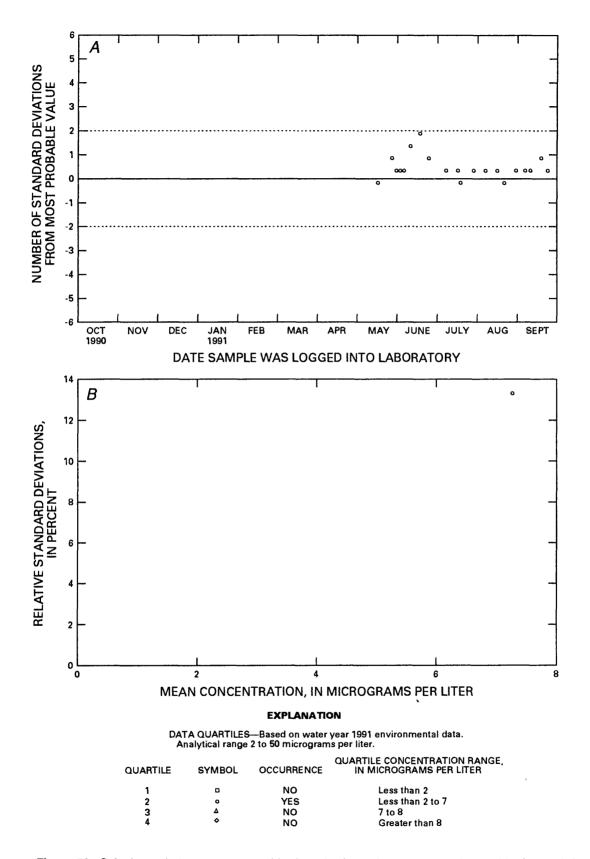


Figure 53. Selenium, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

74 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

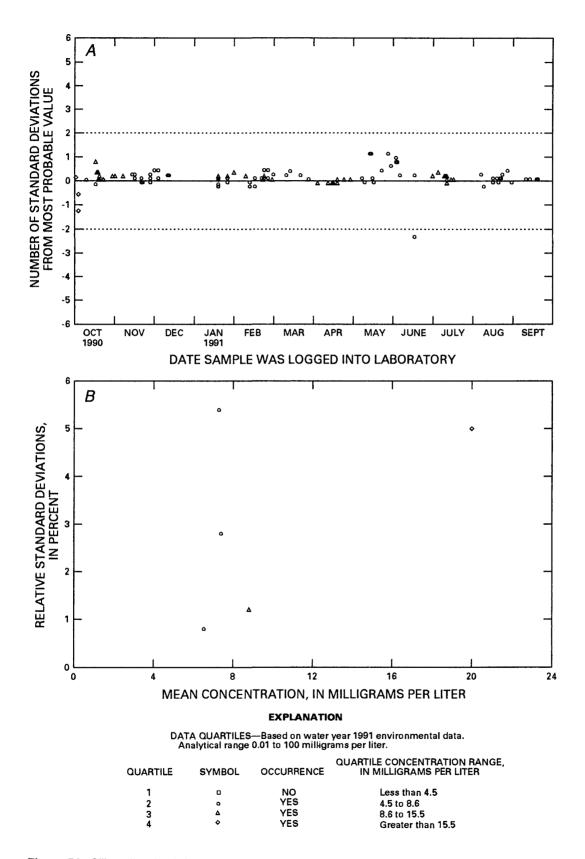


Figure 54. Silica, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

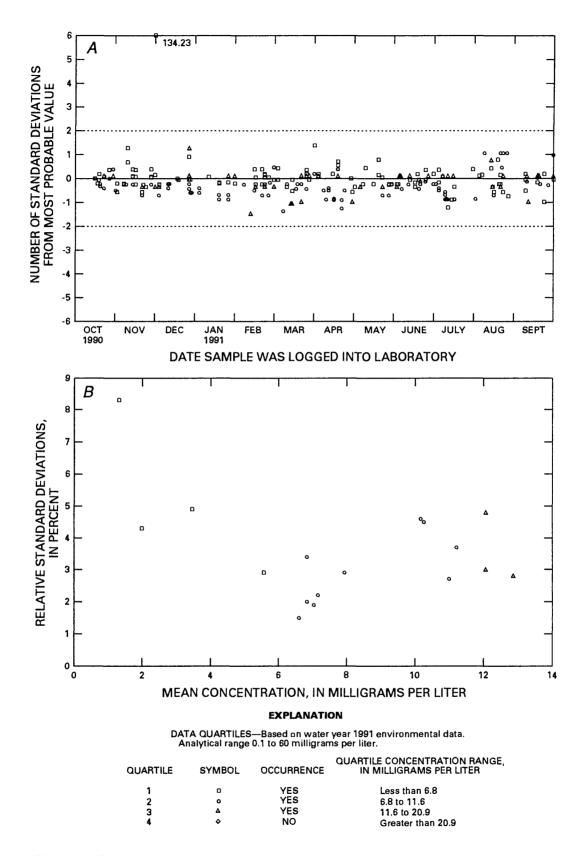


Figure 55. Silica, dissolved, (colorimetric) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

76 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

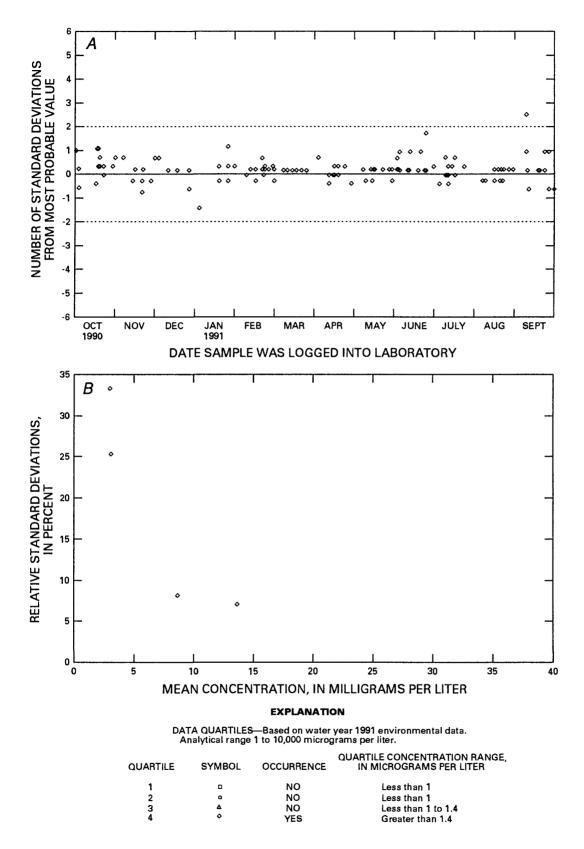


Figure 56. Silver, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

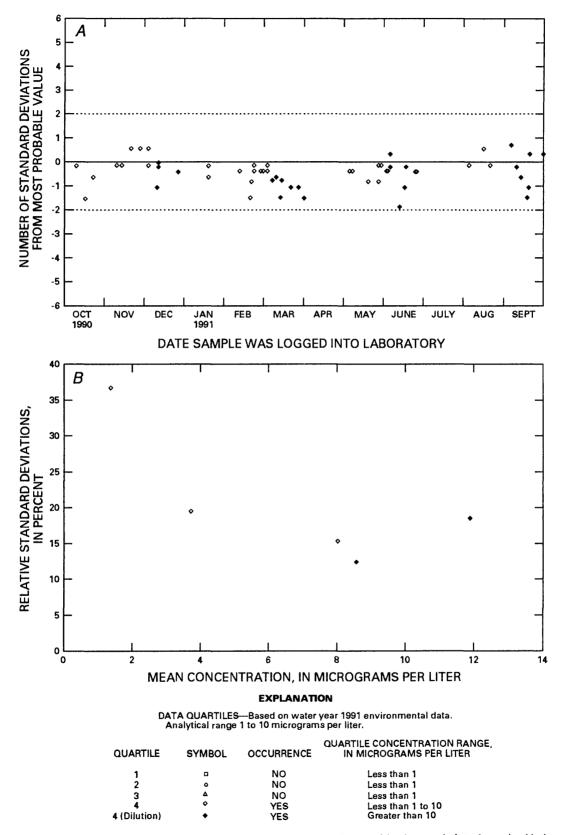


Figure 57. Silver, dissolved, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

78 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

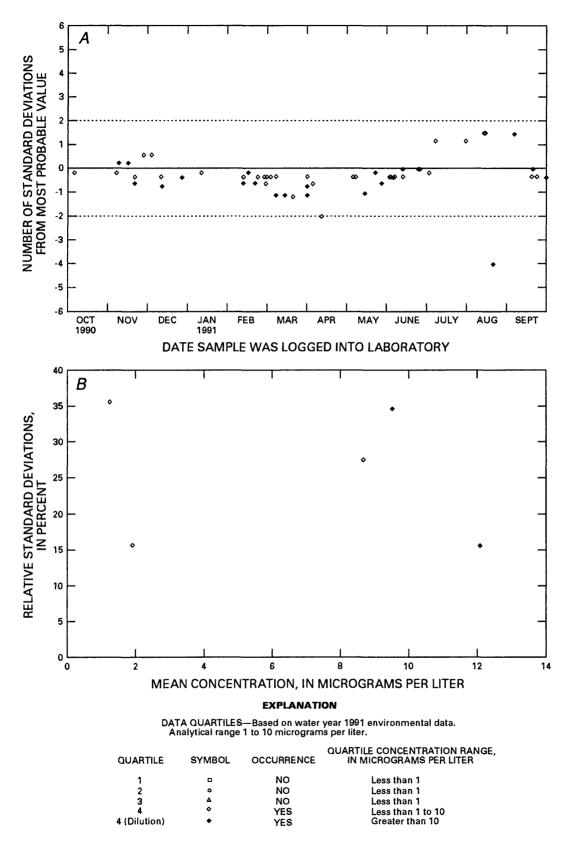


Figure 58. Silver, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

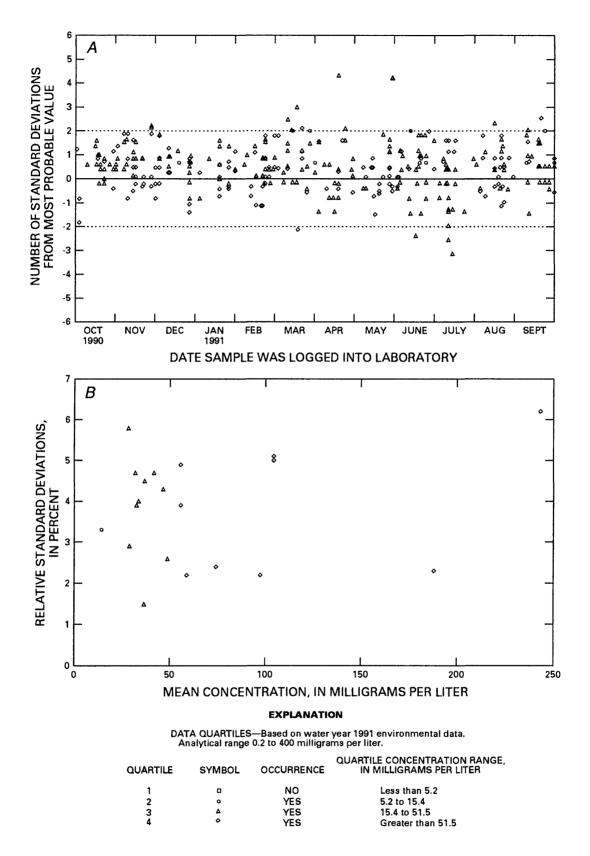


Figure 59. Sodium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

80 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

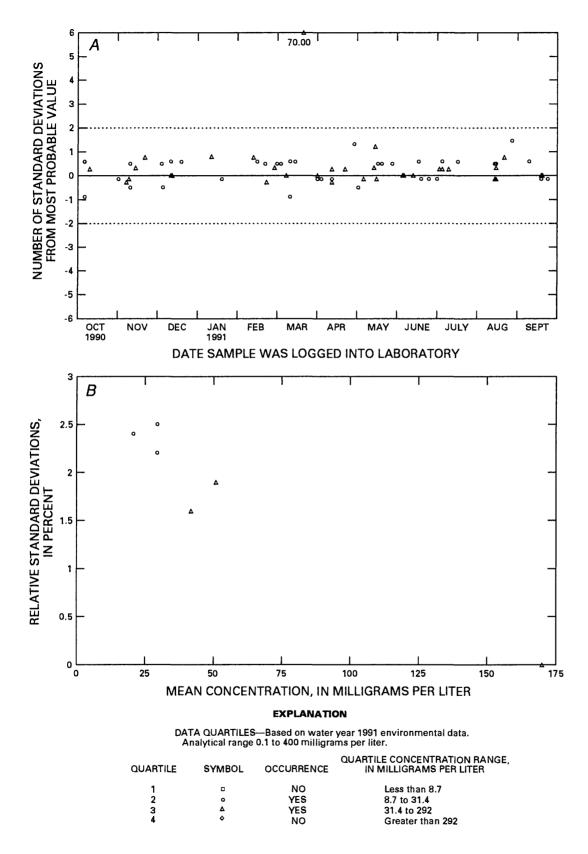


Figure 60. Sodium, dissolved, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

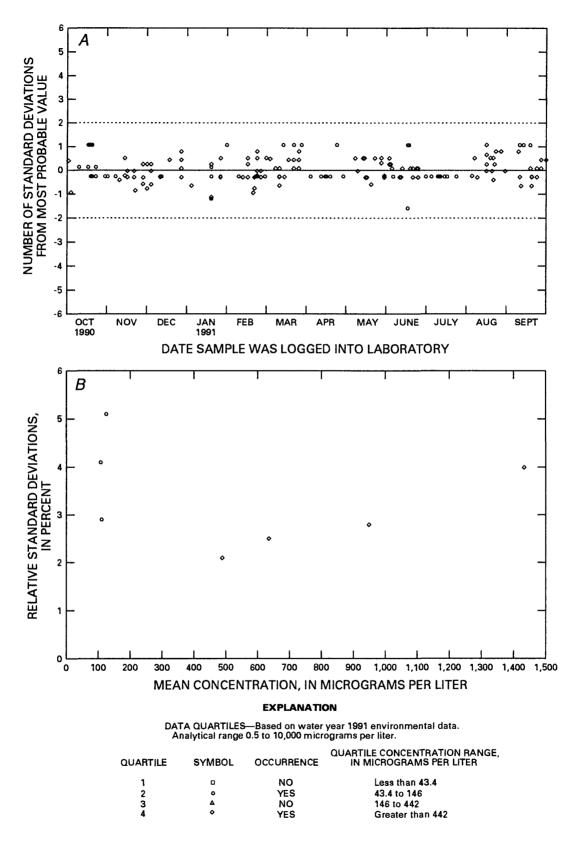


Figure 61. Strontium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

82 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

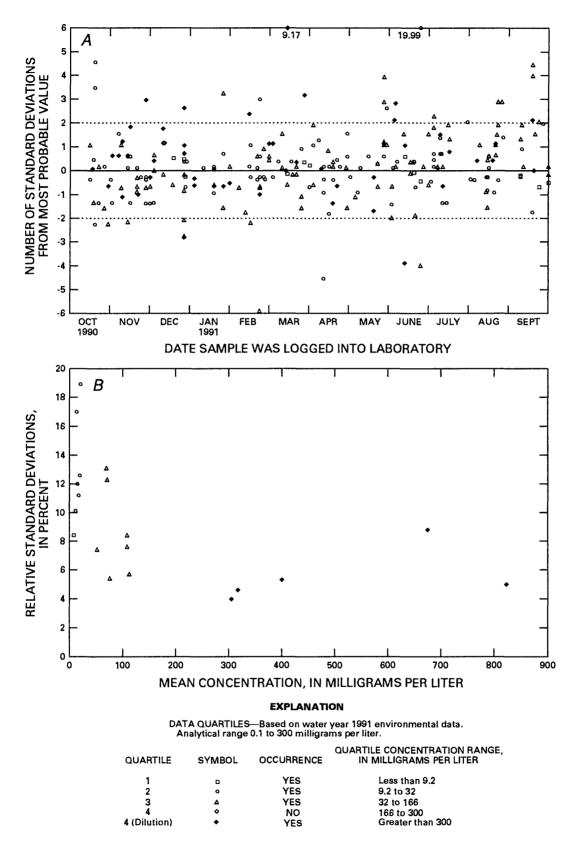


Figure 62. Sulfate, dissolved, (ion-exchange chromatographic) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

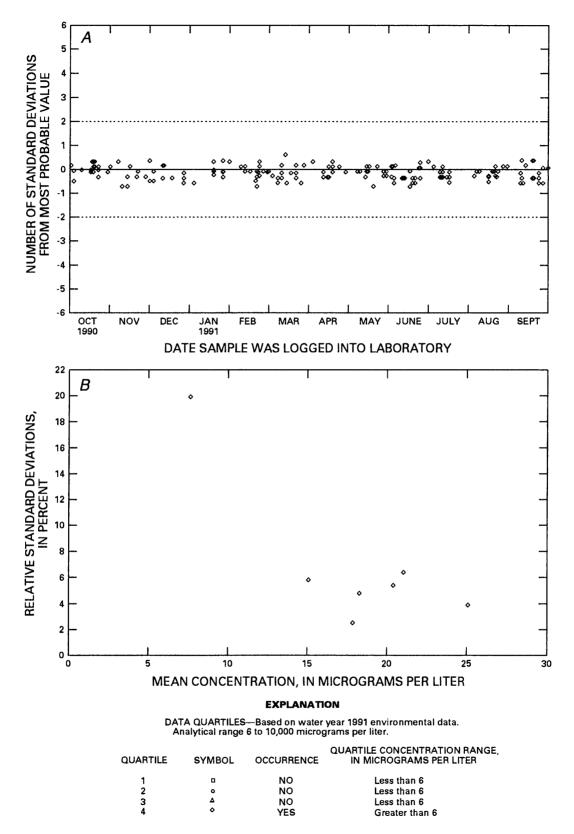


Figure 63. Vanadium, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

84 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

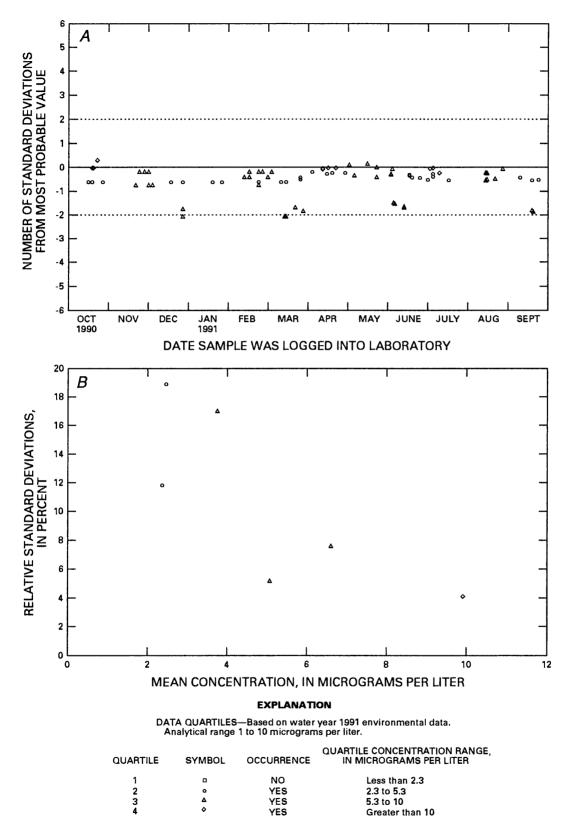


Figure 64. Vanadium, dissolved, (colorimetric) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

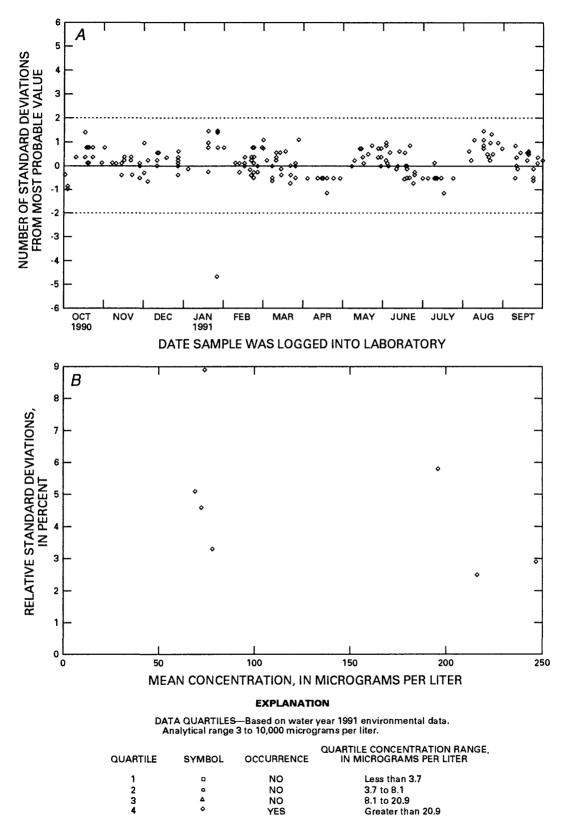


Figure 65. Zinc, dissolved, (atomic emission spectrometric, inductively-coupled plasma) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

86 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

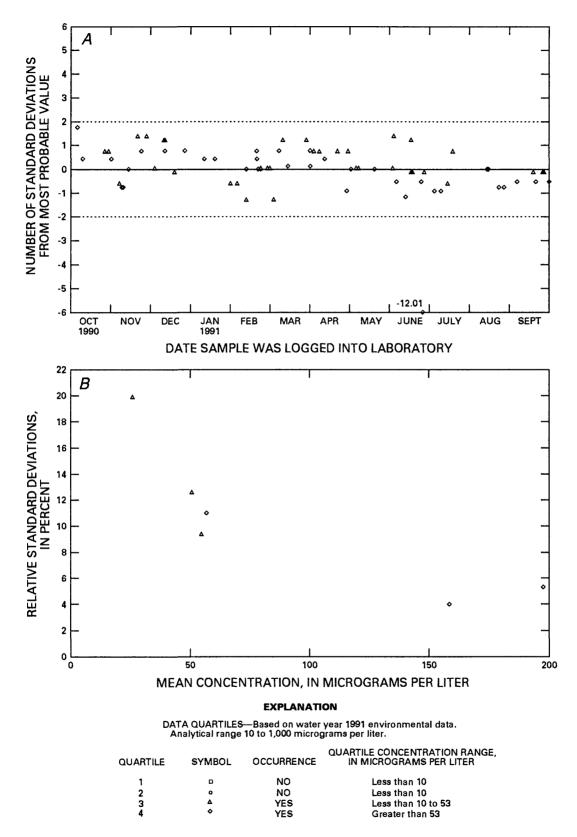


Figure 66. Zinc, dissolved, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

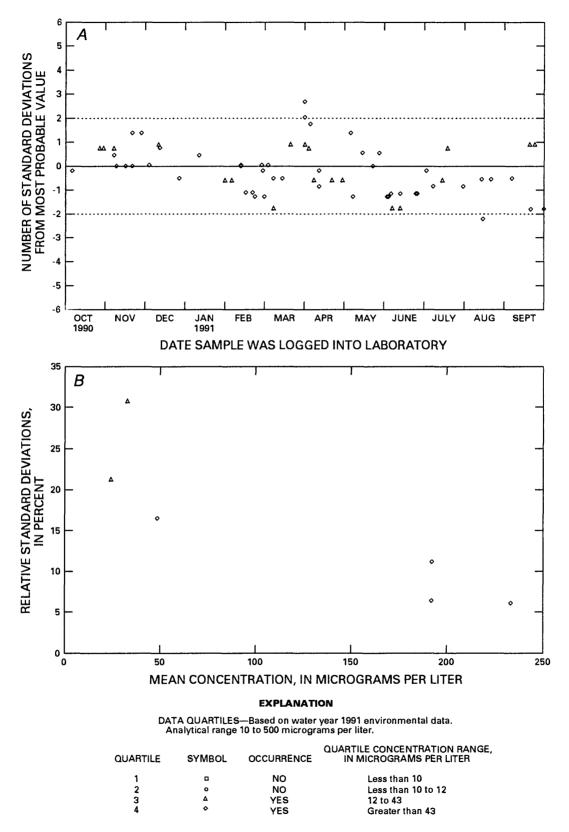


Figure 67. Zinc, whole-water recoverable, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

88 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

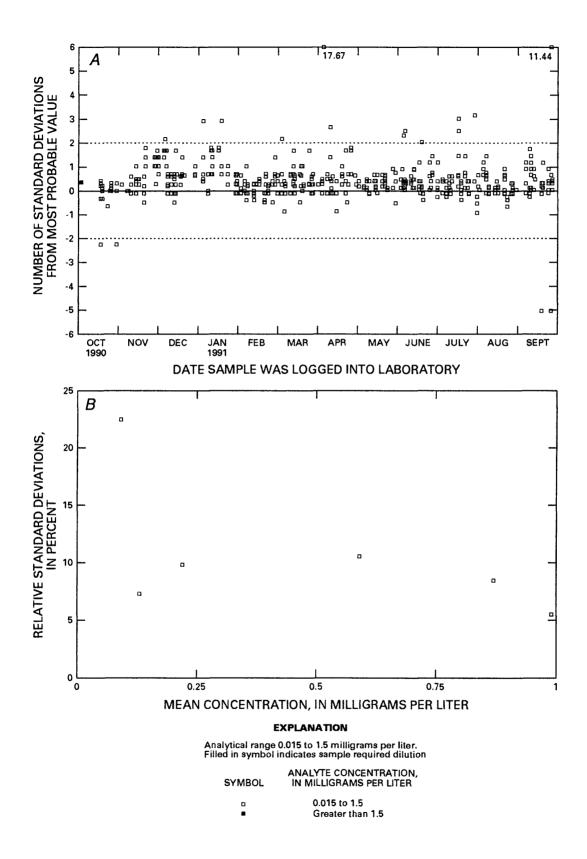


Figure 68. Ammonia as nitrogen, dissolved and whole-water recoverable, (colorimetric) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

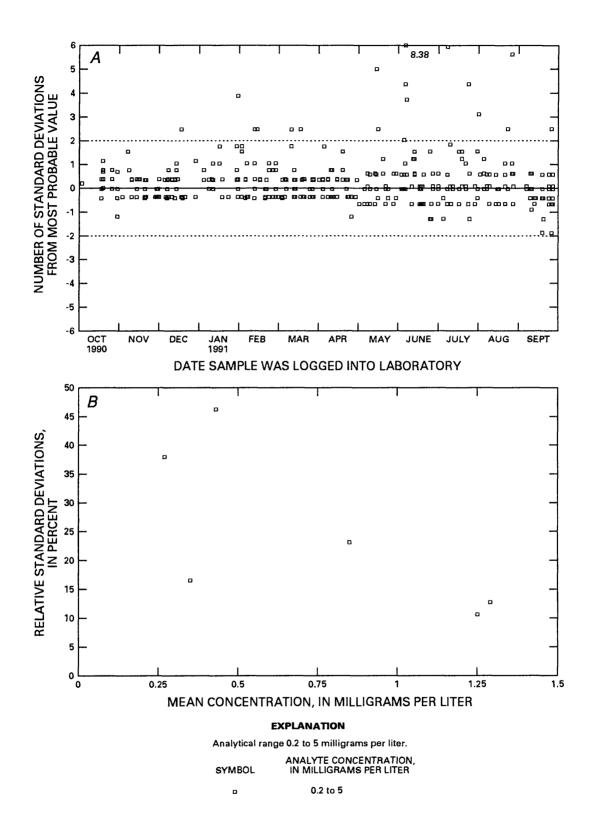


Figure 69. Ammonia plus organic nitrogen as nitrogen, dissolved and whole-water recoverable, (colorimetric) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

90 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

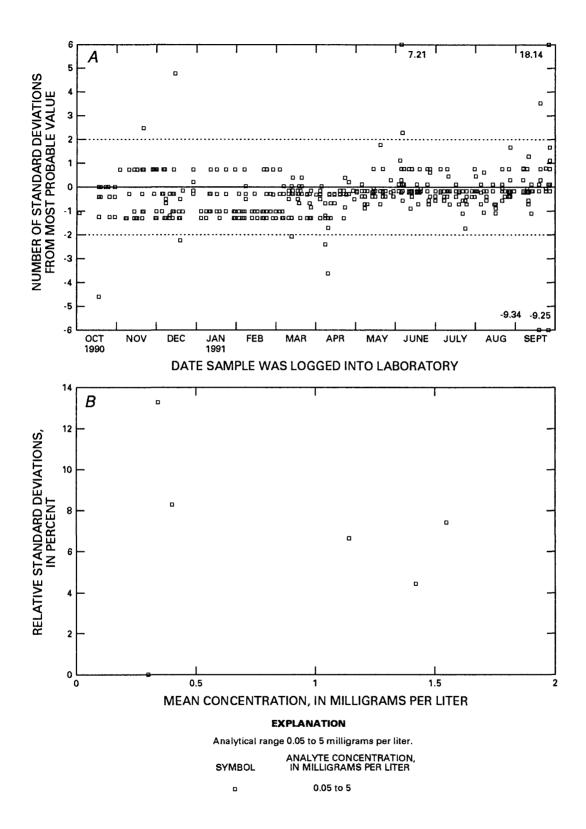


Figure 70. Nitrate plus nitrite as nitrogen, dissolved and whole-water recoverable, (colorimetric) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

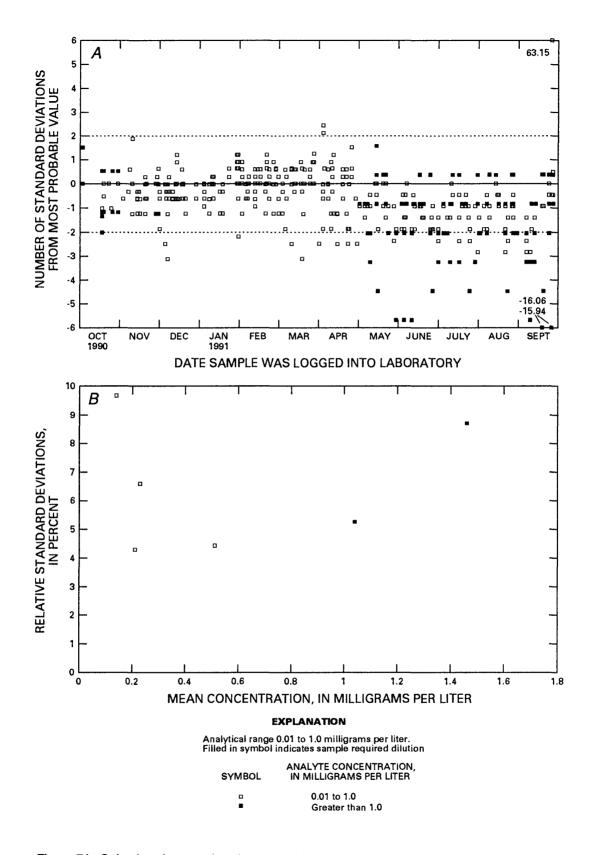


Figure 71. Orthophosphate as phosphorus, dissolved and whole-water recoverable, (colorimetric) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

92 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

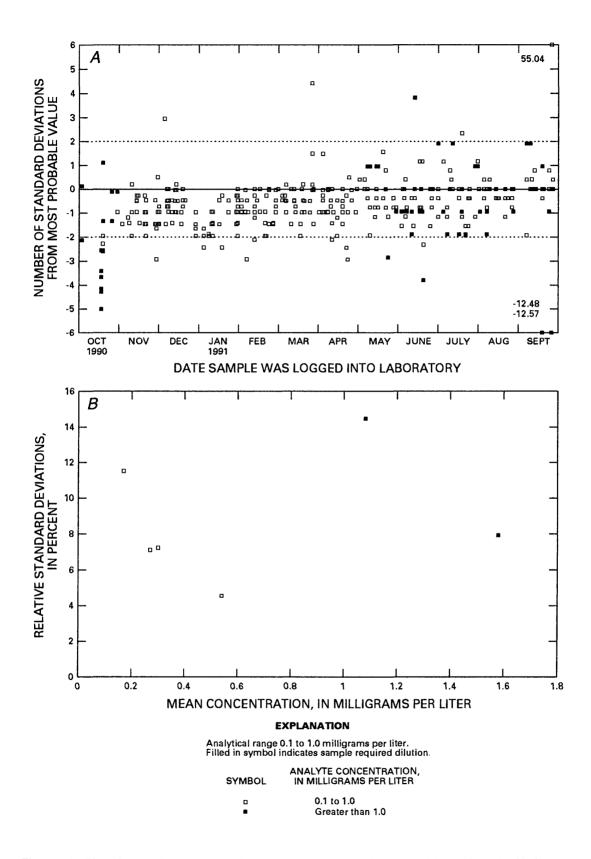


Figure 72. Phosphorus, dissolved and whole-water recoverable, (colorimetric) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

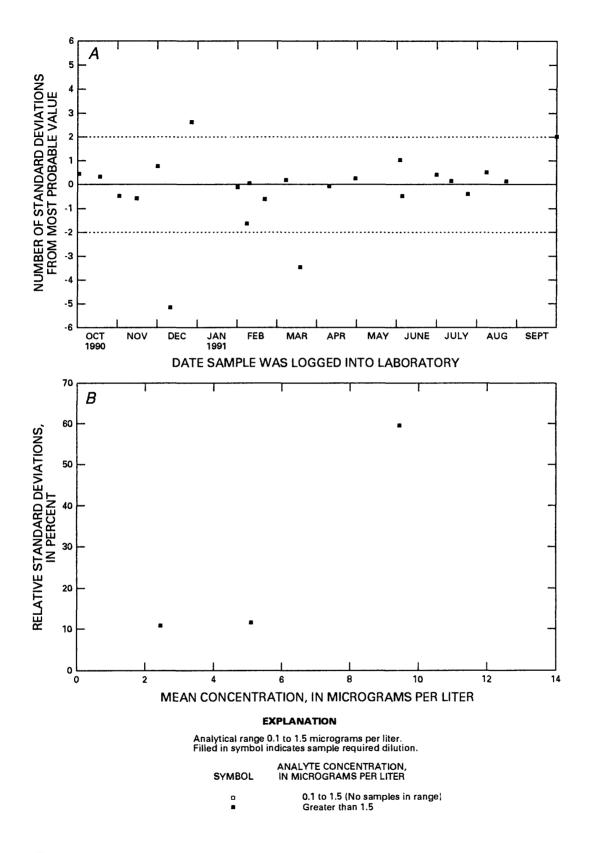


Figure 73. Cadmium, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

94 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

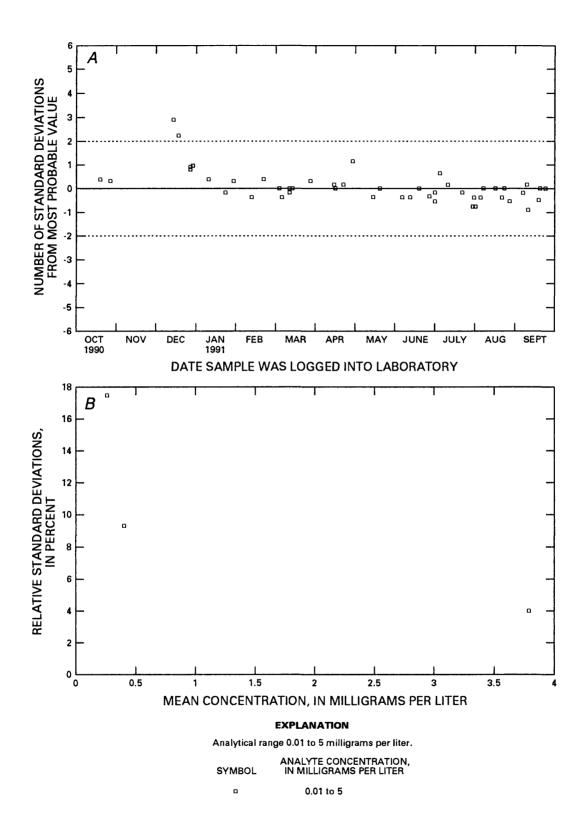


Figure 74. Calcium, dissolved, low ionic-strength, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

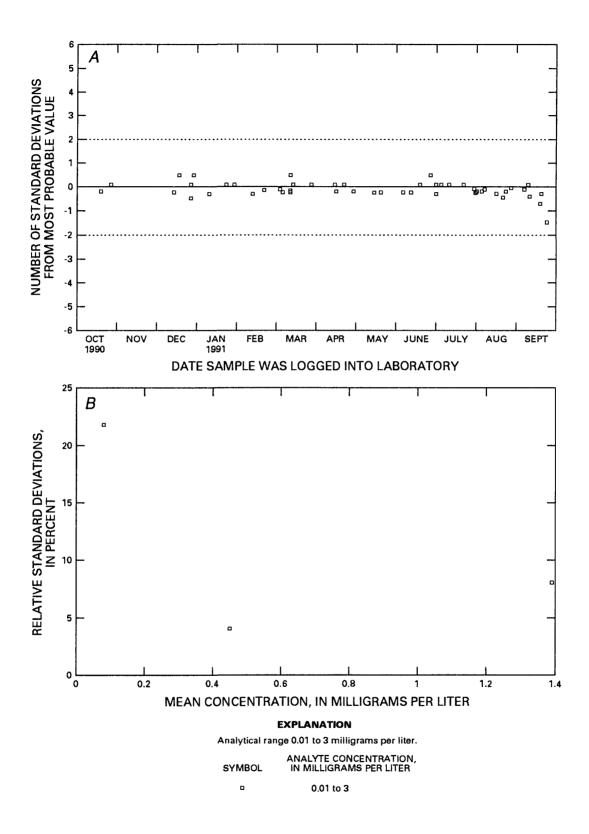


Figure 75. Chloride, dissolved, low ionic-strength, (ion-exchange chromatographic) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

96 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

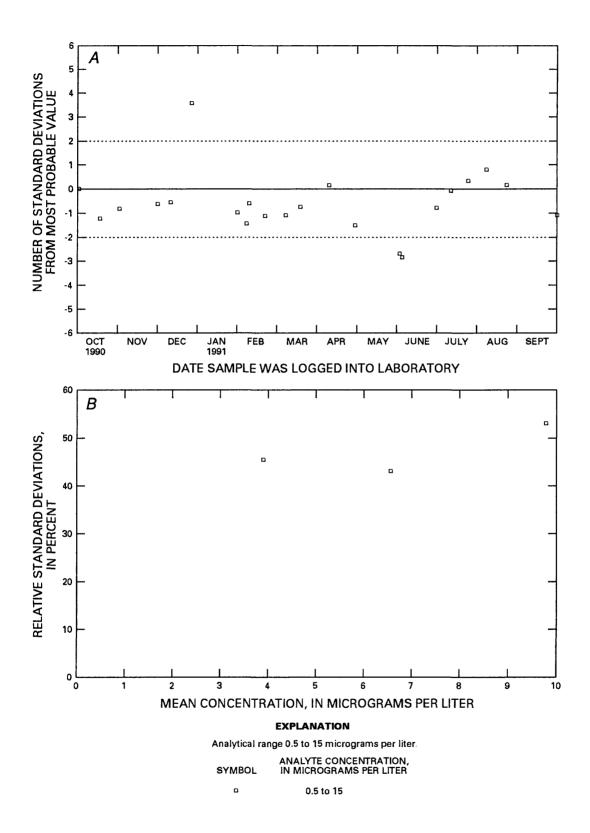


Figure 76. Chromium, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

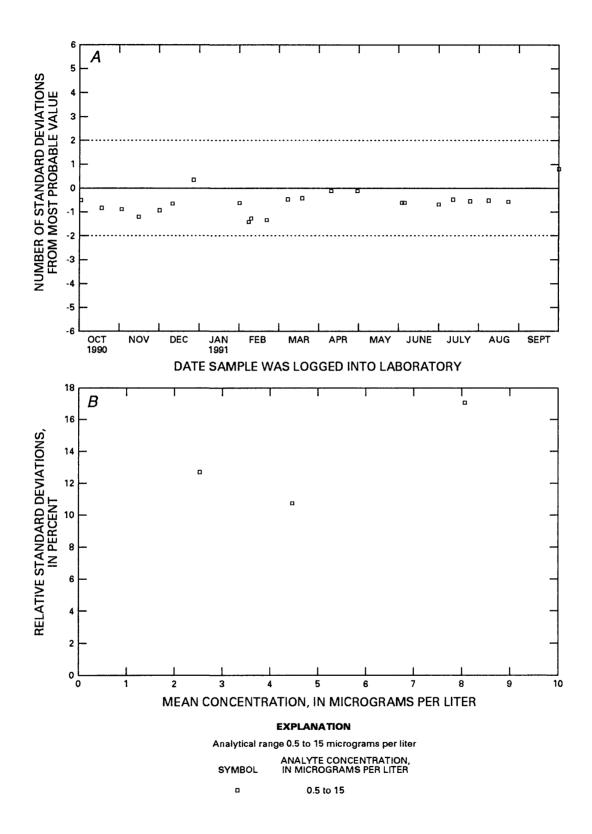


Figure 77. Cobalt, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

98 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

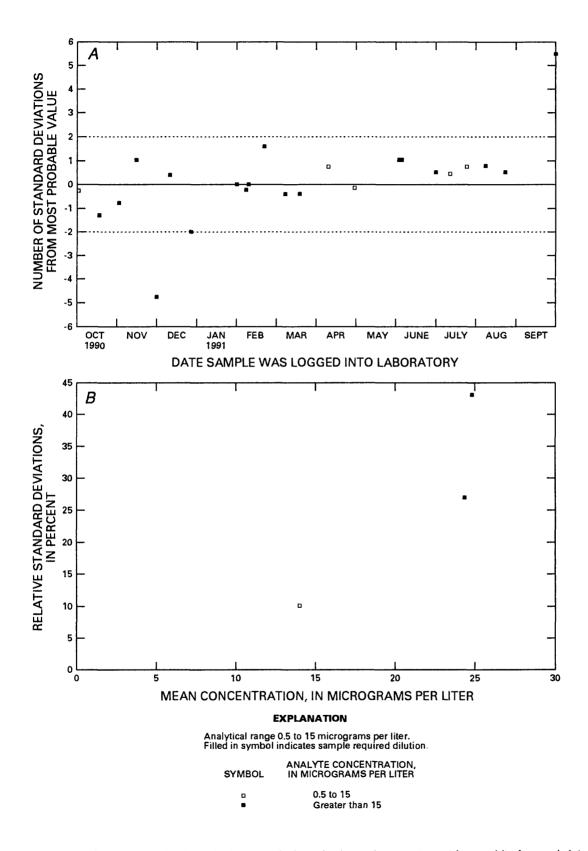


Figure 78. Copper, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

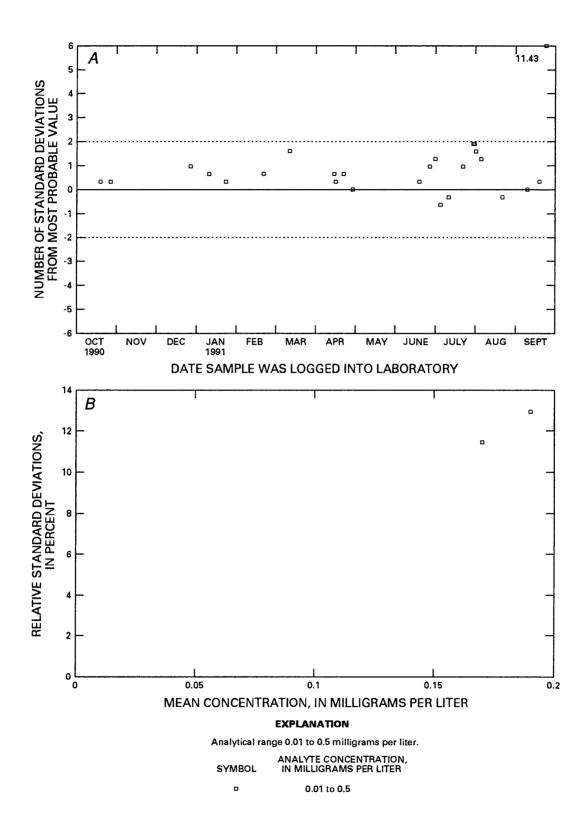


Figure 79. Fluoride, dissolved, low ionic-strength, (ion-exchange chromatographic) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

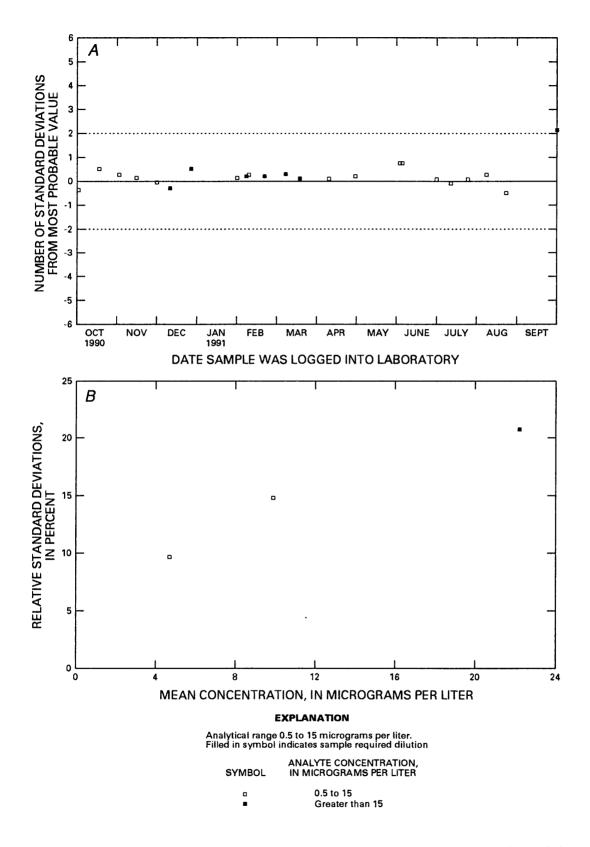


Figure 80. Lead, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

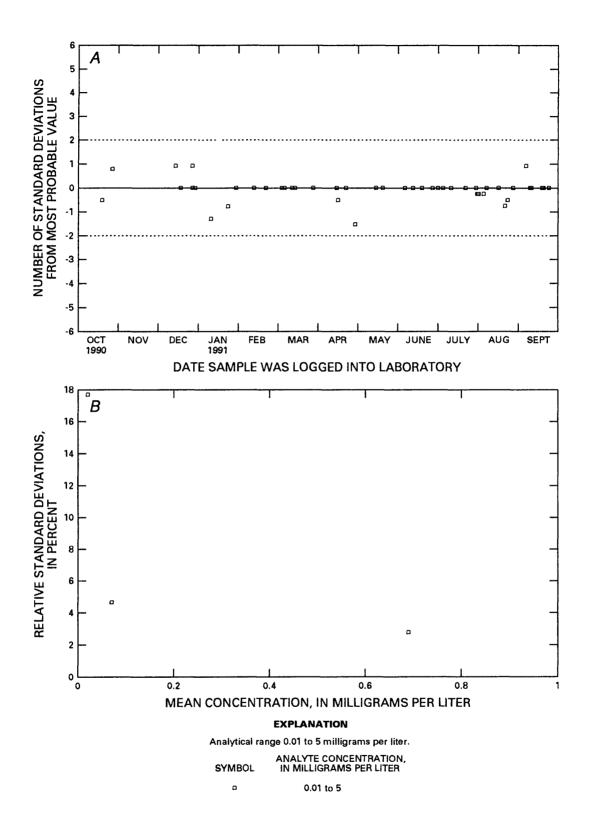


Figure 81. Magnesium, dissolved, low ionic-strength, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

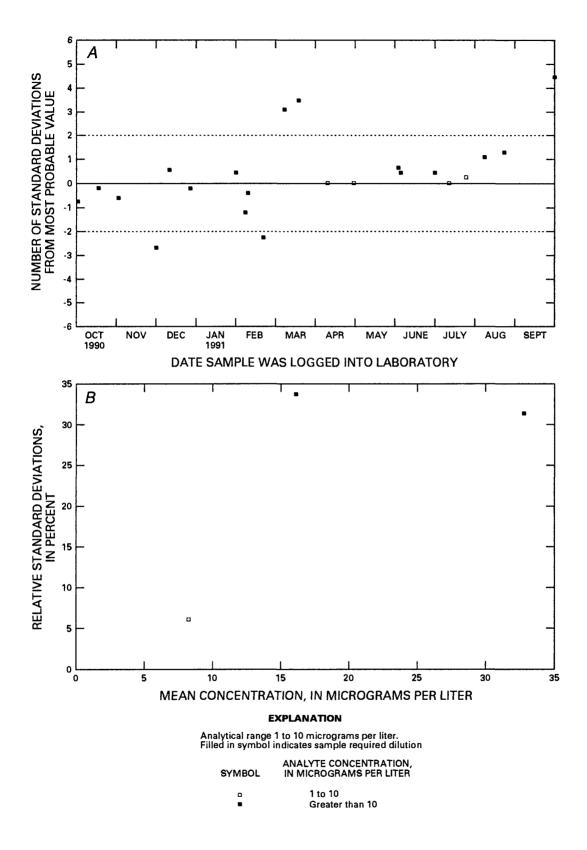


Figure 82. Nickel, dissolved, low ionic-strength, (atomic absorption spectrometric, graphite furnace) data from the National Water Quality Program. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

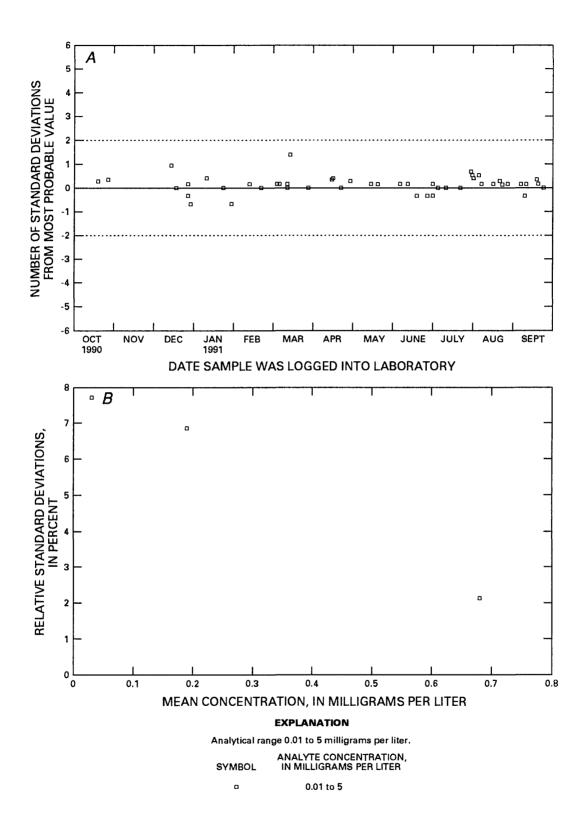


Figure 83. Potassium, dissolved, low ionic-strength, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

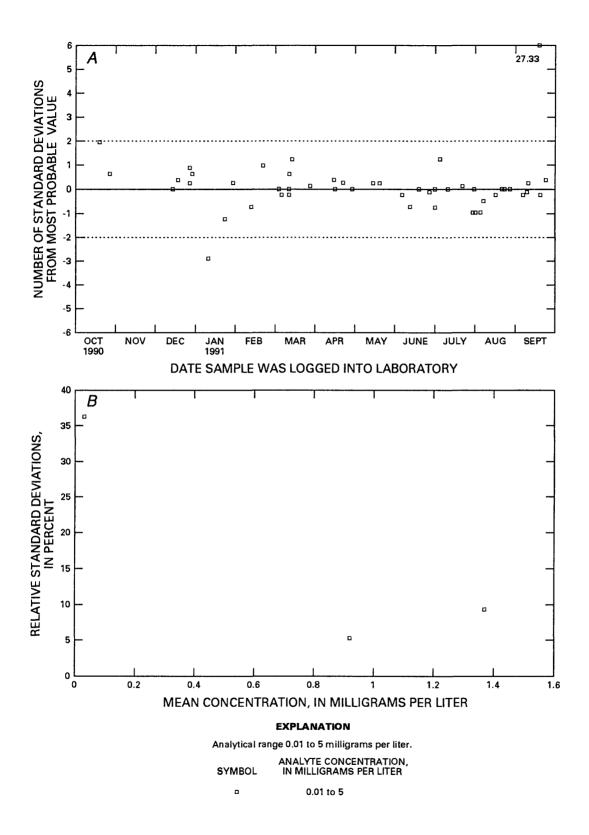


Figure 84. Sodium, dissolved, low ionic-strength, (atomic absorption spectrometric, direct) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

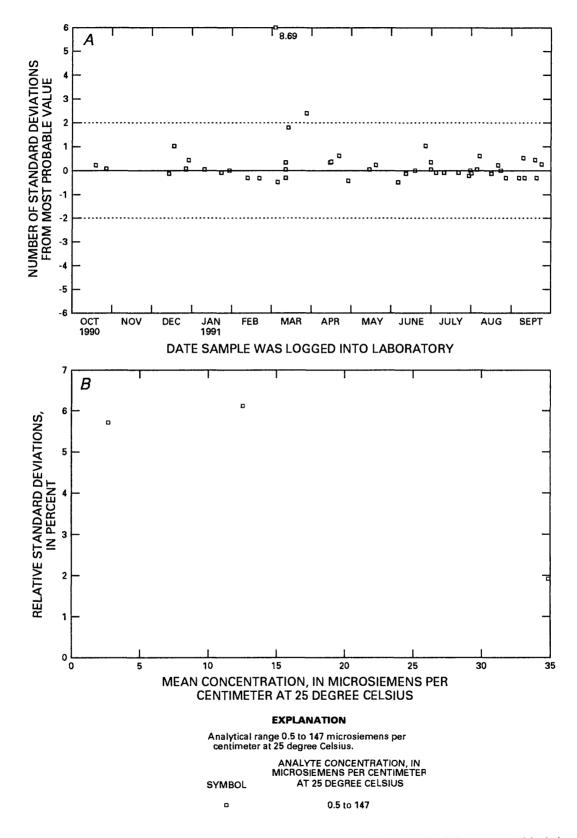


Figure 85. Specific conductance, dissolved, low ionic-strength, (electrometric, Wheatstone bridge) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

106 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

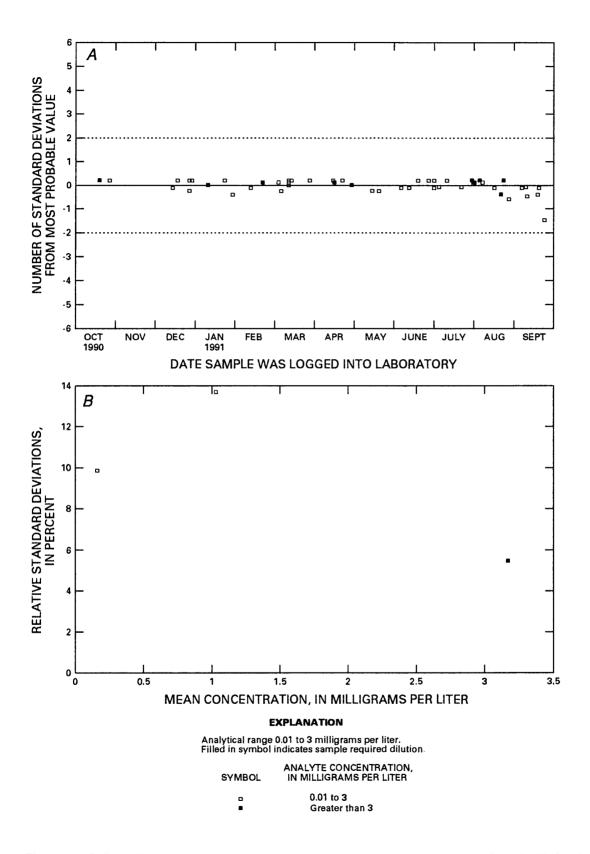


Figure 86. Sulfate, dissolved, low ionic-strength, (ion-exchange chromatographic) data from the National Water Quality Laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

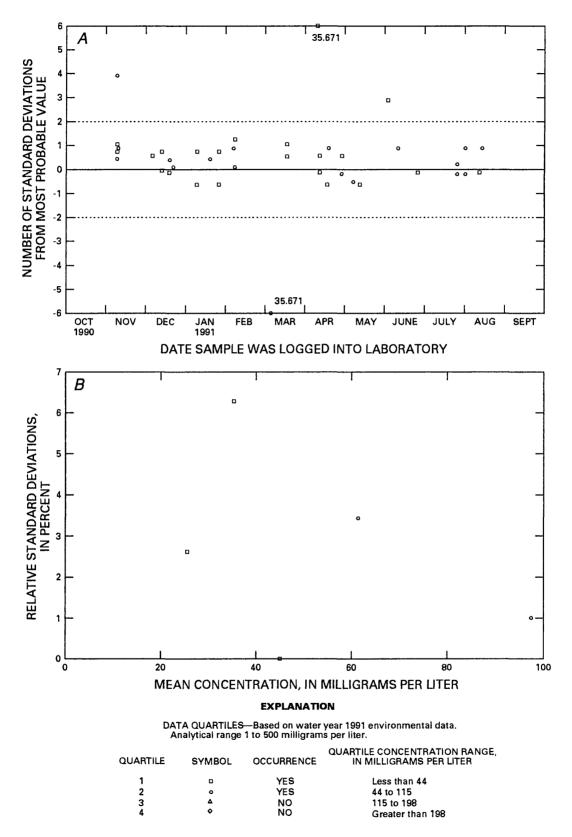


Figure 87. Alkalinity, dissolved, (electrometric titration) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

108 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

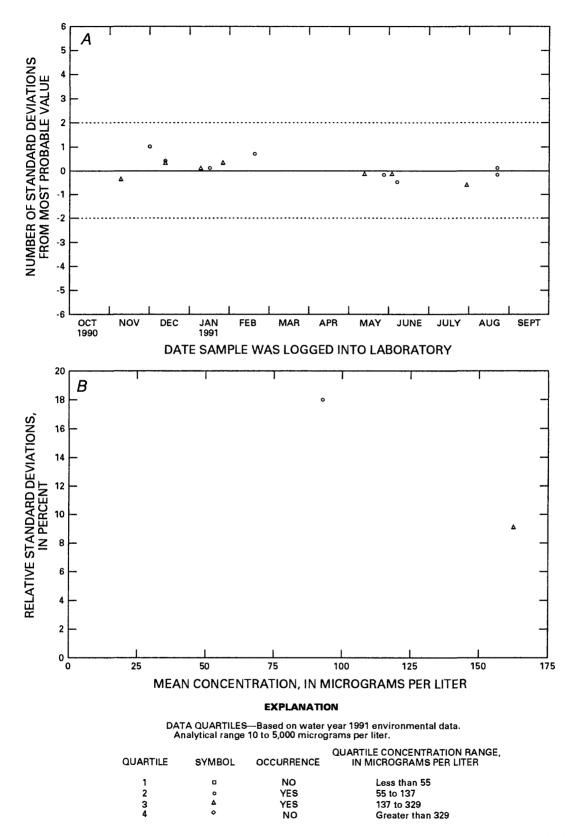


Figure 88. Aluminum, whole-water recoverable, (atomic absorption spectrometric, chelation-extraction) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

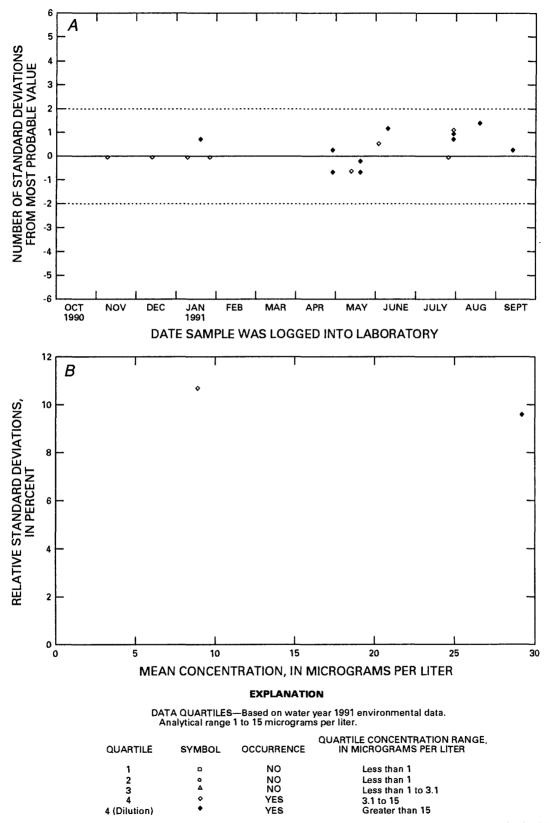


Figure 89. Arsenic, dissolved and whole-water recoverable, (atomic absorption spectrometric, hydride) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

110 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

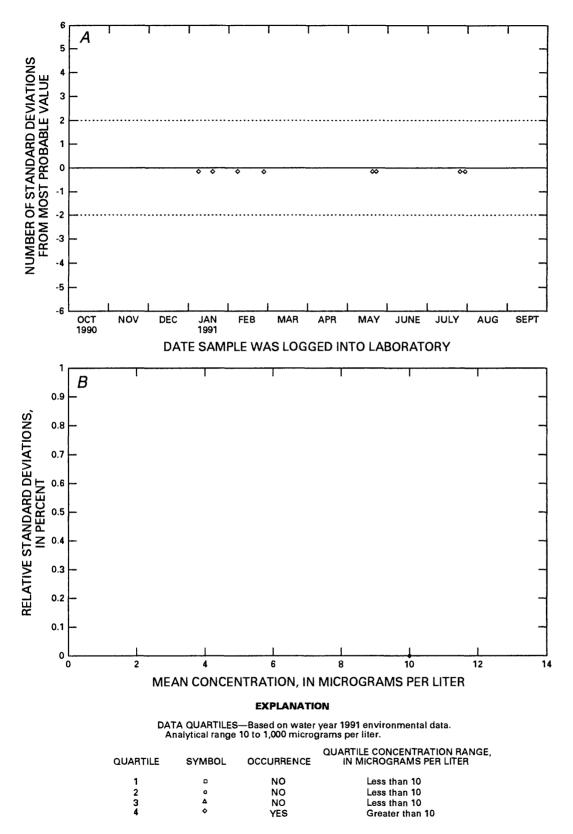


Figure 90. Beryllium, whole-water recoverable, (atomic absorption spectrometric, direct) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

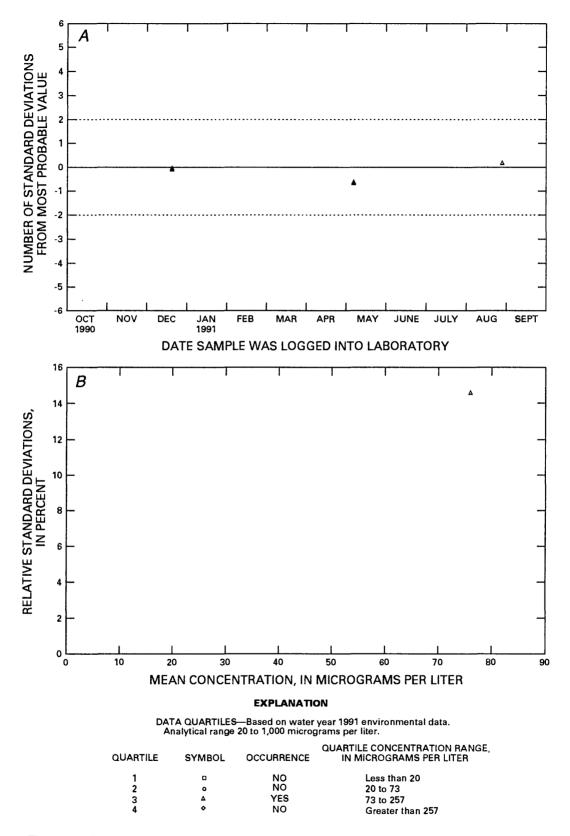


Figure 91. Boron, dissolved, (colorimetric) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

112 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geologicai Survey for Water Year 1991

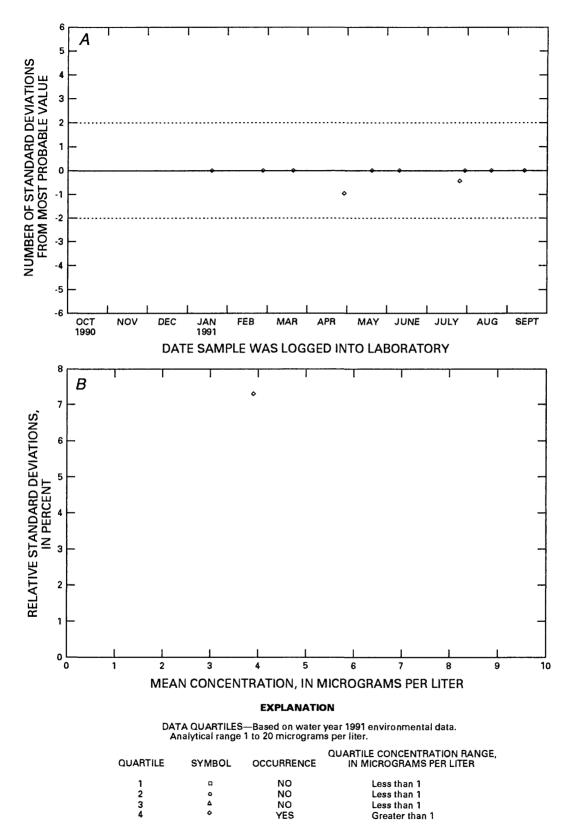


Figure 92. Cadmium, dissolved, (atomic absorption spectrometric, graphite furnace) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

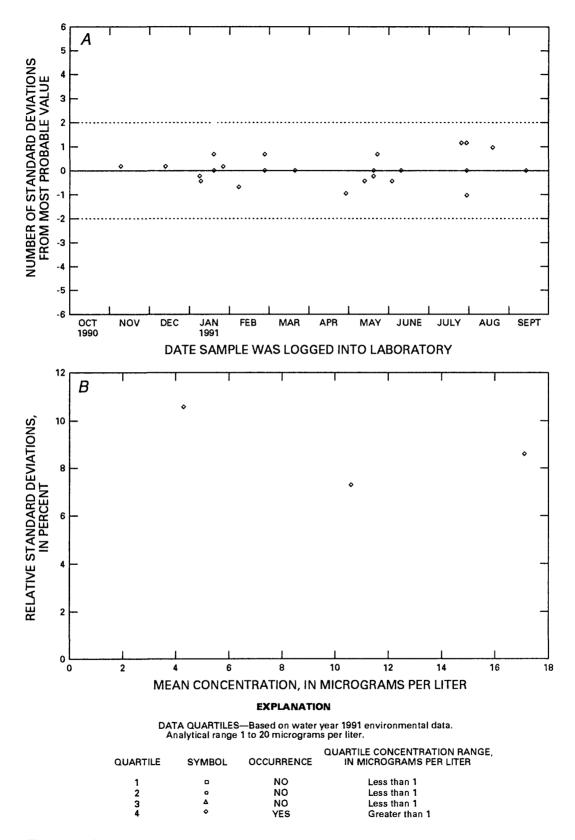


Figure 93. Cadmium, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

114 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

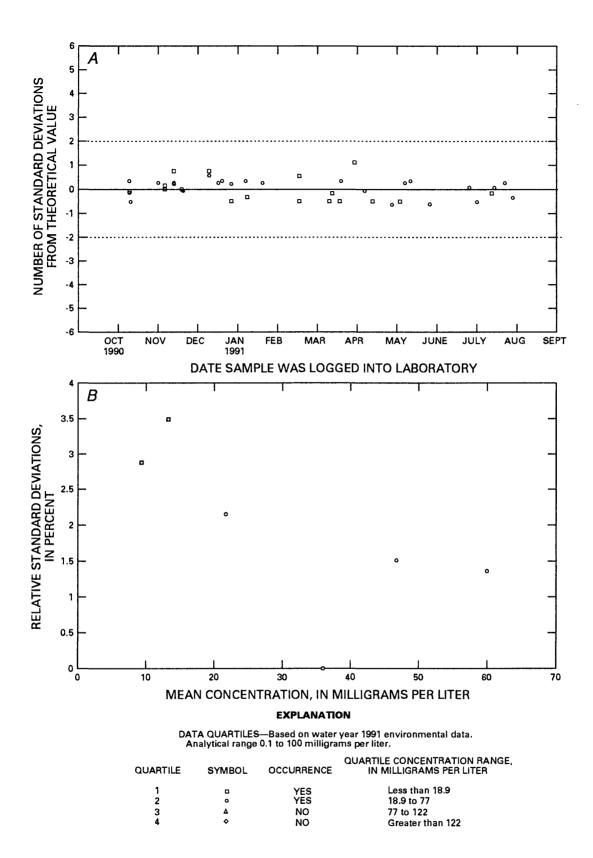


Figure 94. Calcium, dissolved, (atomic absorption spectrometric, direct) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

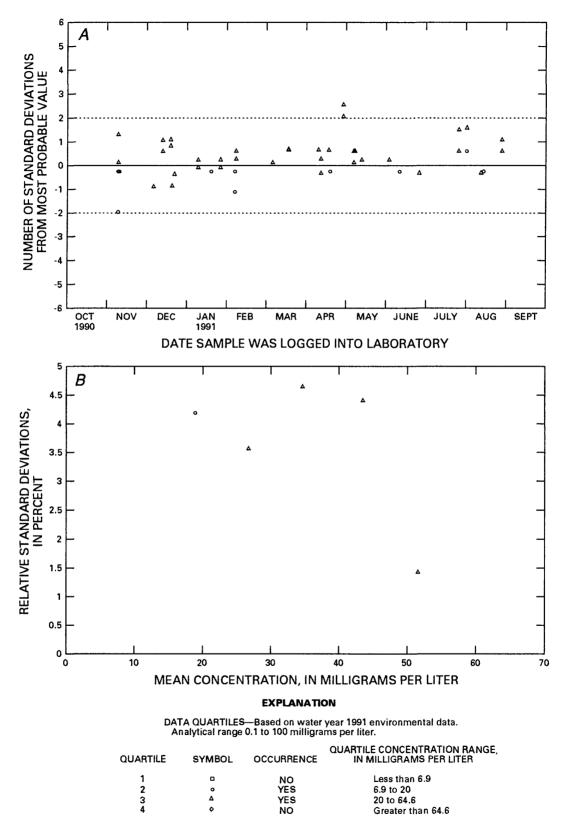


Figure 95. Chloride, dissolved, (ion-exchange chromatographic) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

116 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

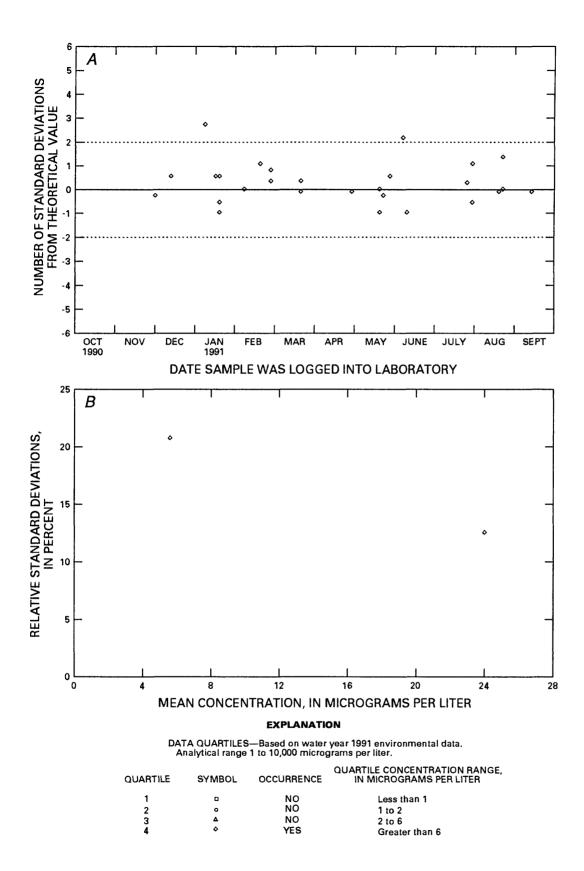


Figure 96. Chromium, whole-water recoverable, (atomic absorption spectrometric, chelation-extraction) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

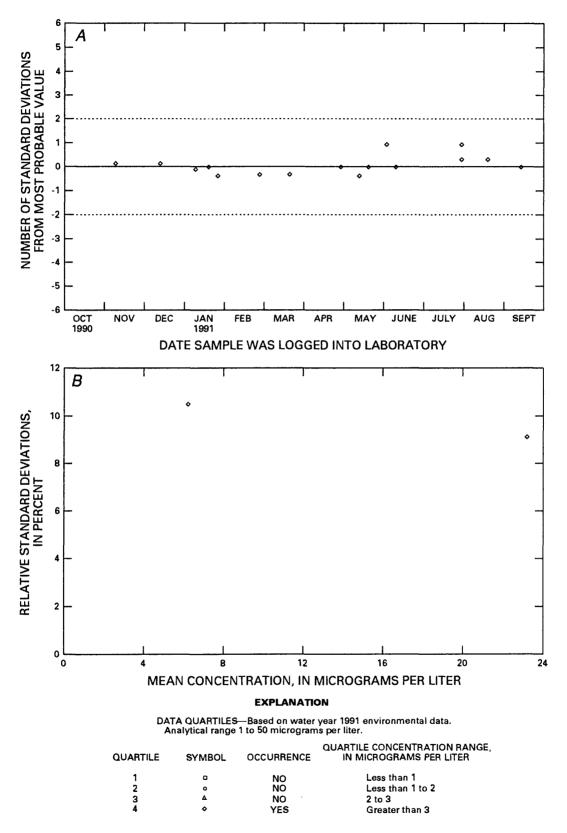


Figure 97. Copper, dissolved, (atomic absorption spectrometric, graphite furnace) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

118 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

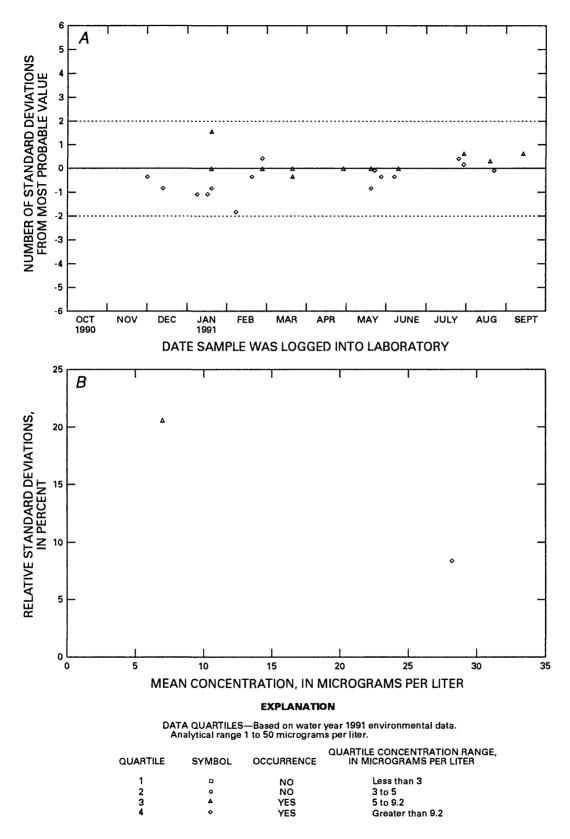


Figure 98. Copper, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

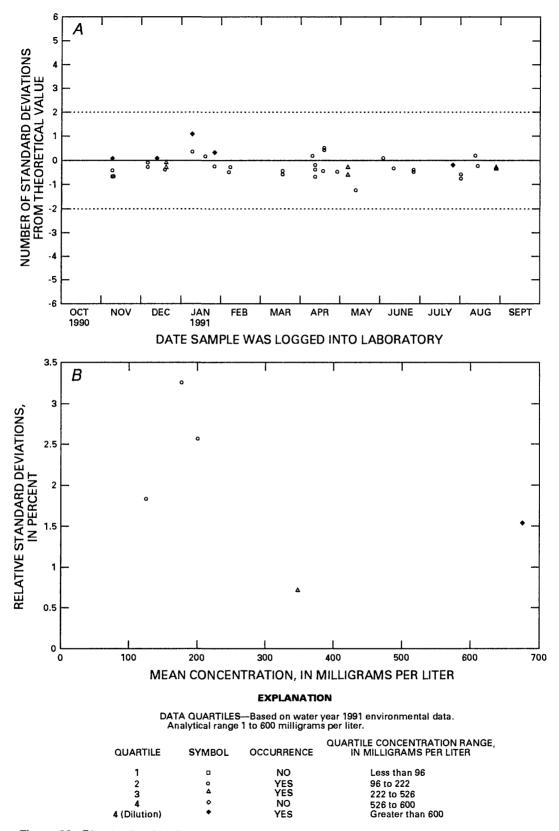


Figure 99. Dissolved solids, (gravimetric) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

120 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

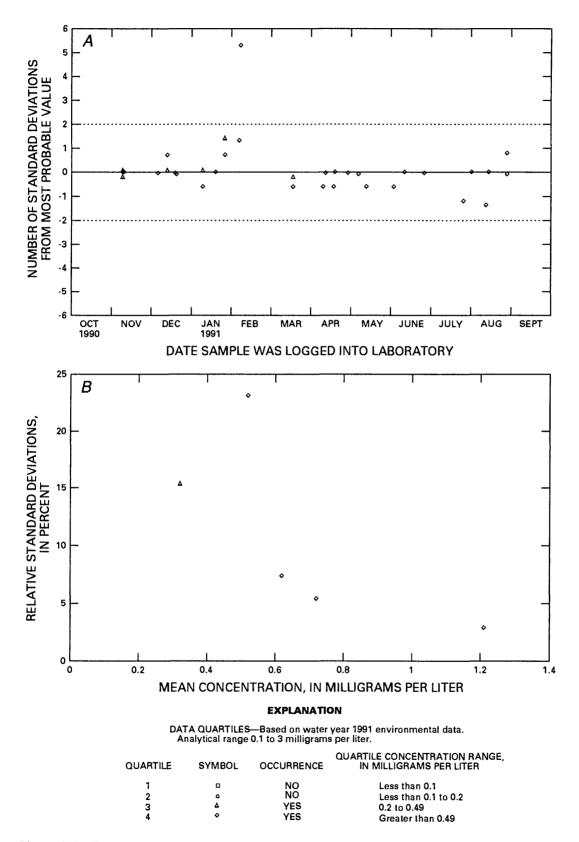


Figure 100. Fluoride, dissolved, (ion-selective electrode) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

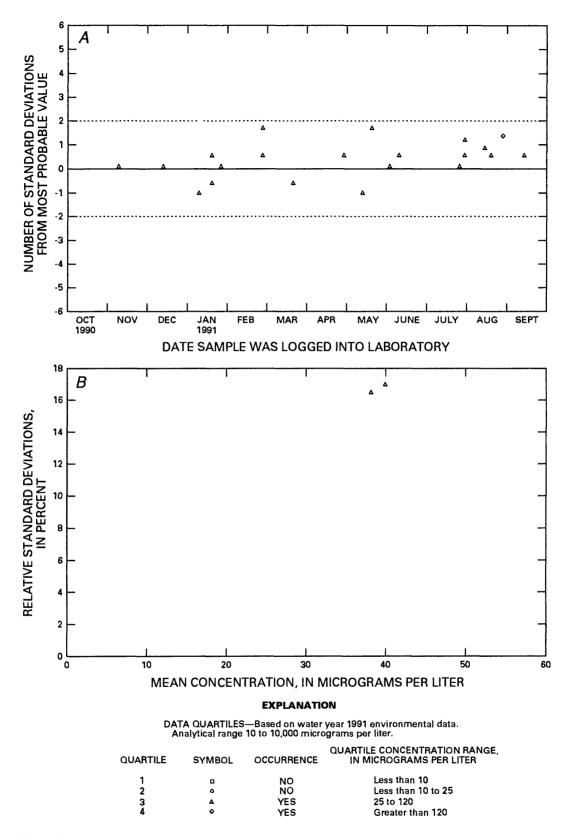


Figure 101. Iron, dissolved, (atomic absorption spectrometric, direct) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

122 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

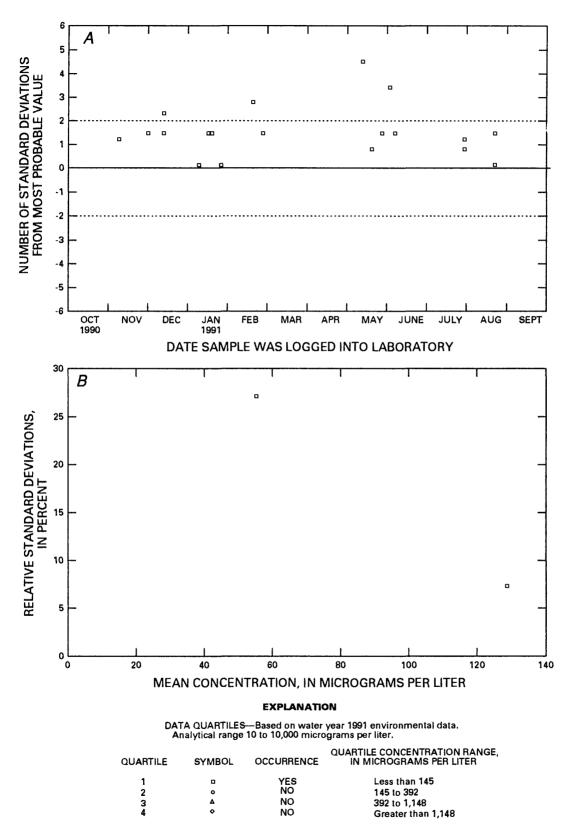


Figure 102. Iron, whole-water recoverable, (atomic absorption spectrometric, direct) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

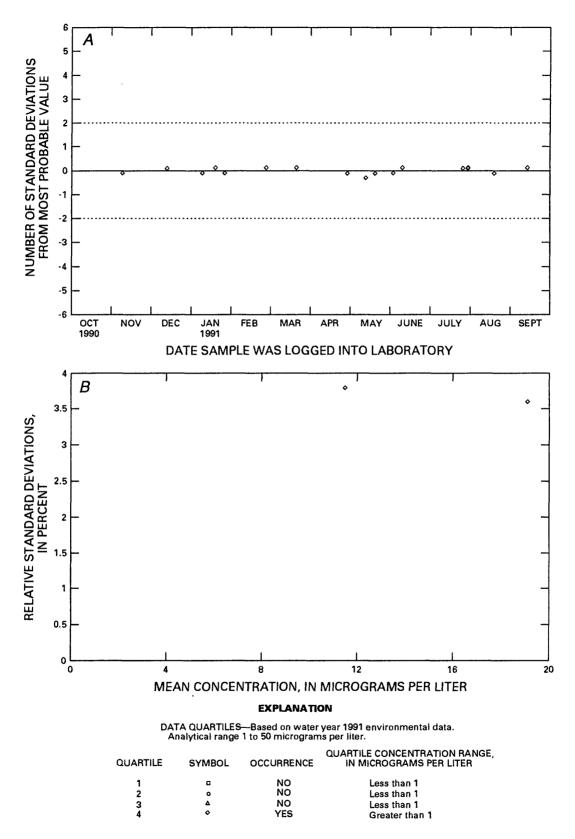


Figure 103. Lead, dissolved, (atomic absorption spectrometric, graphite furnace) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

124 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

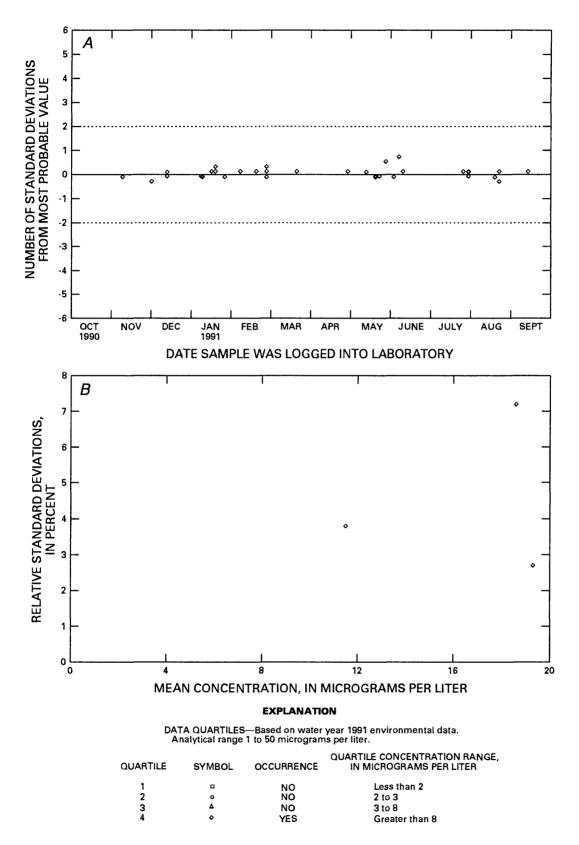


Figure 104. Lead, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

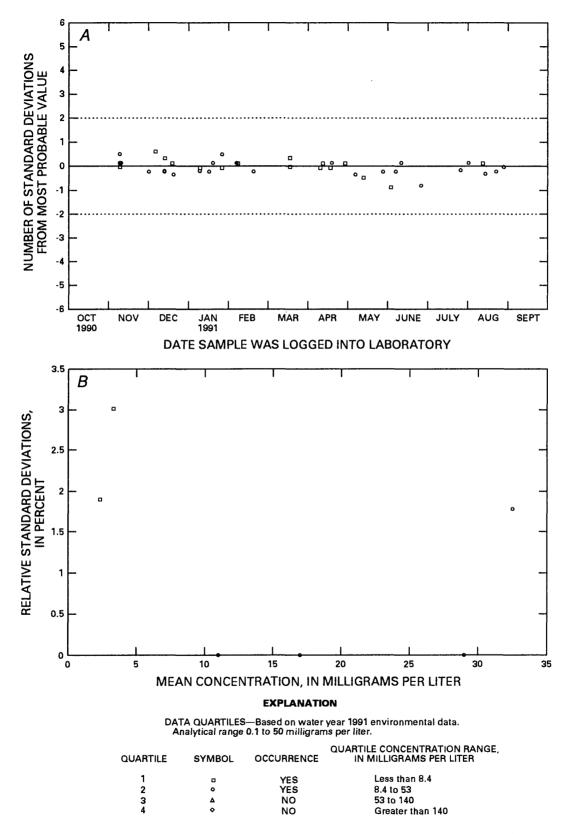


Figure 105. Magnesium, dissolved, (atomic absorption spectrometric, direct) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

126 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

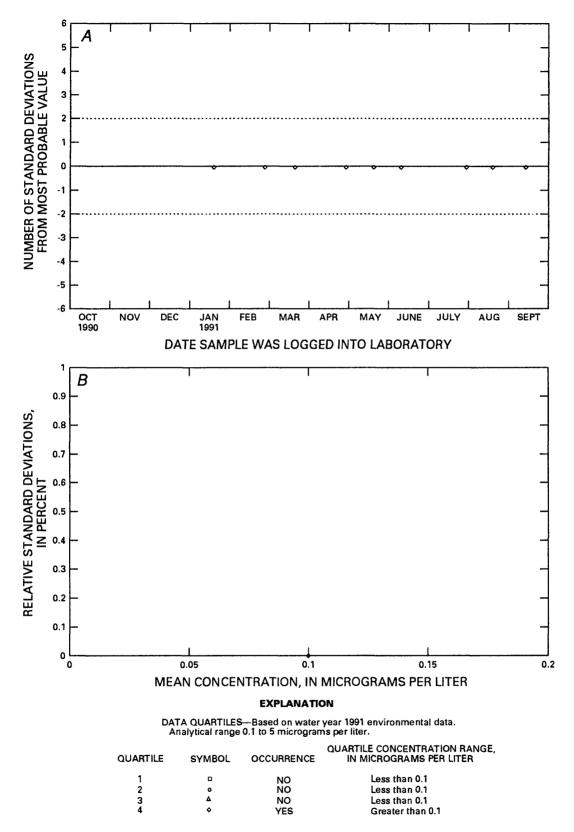


Figure 106. Mercury, dissolved, (atomic absorption spectrometric, flameless) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

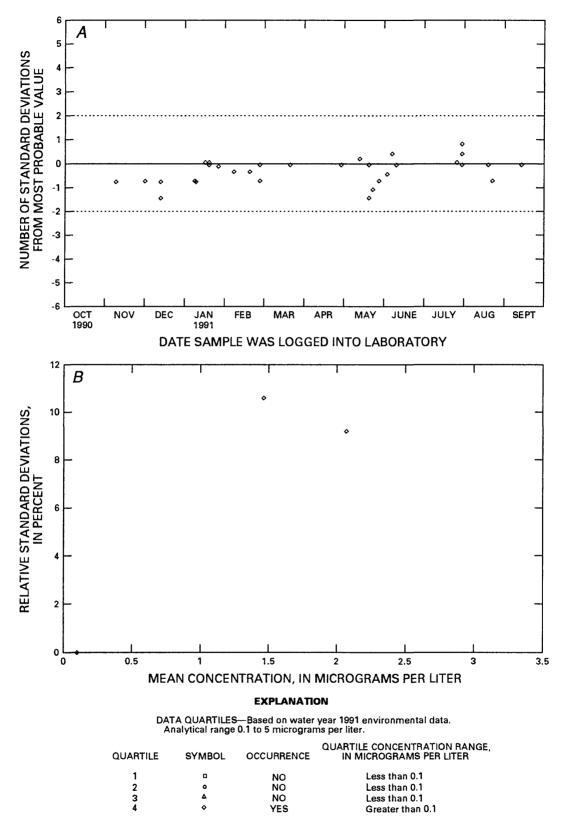


Figure 107. Mercury, whole-water recoverable, (atomic absorption spectrometric, flameless) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

128 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

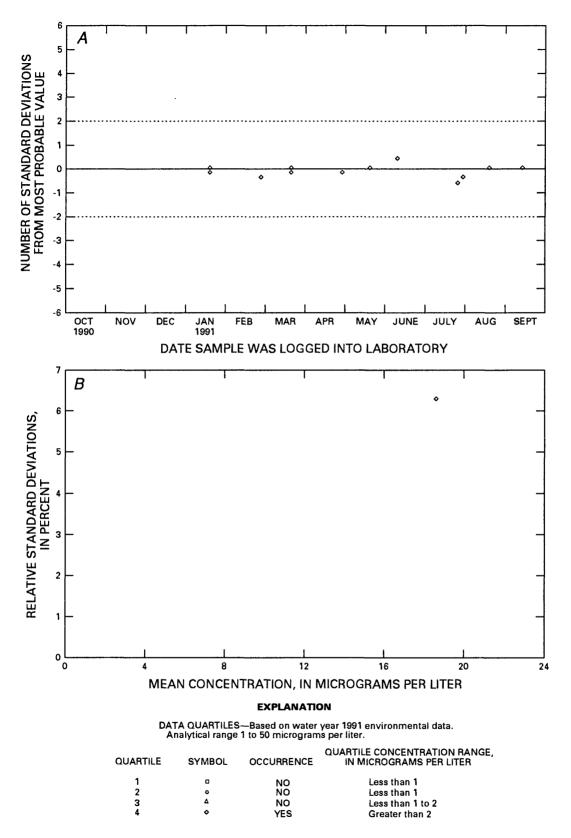


Figure 108. Nickel, dissolved, (atomic absorption spectrometric, graphite furnace) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

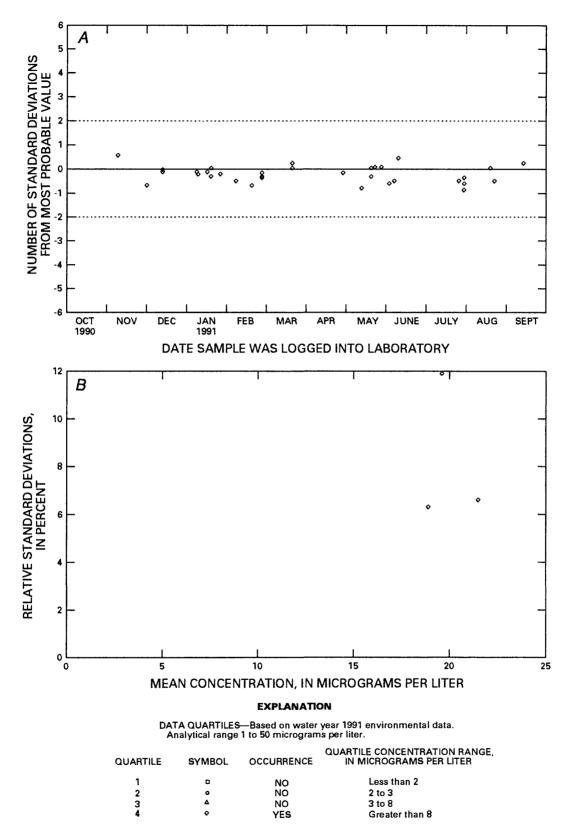


Figure 109. Nickel, whole-water recoverable, (atomic absorption spectrometric, graphite furnace) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

130 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

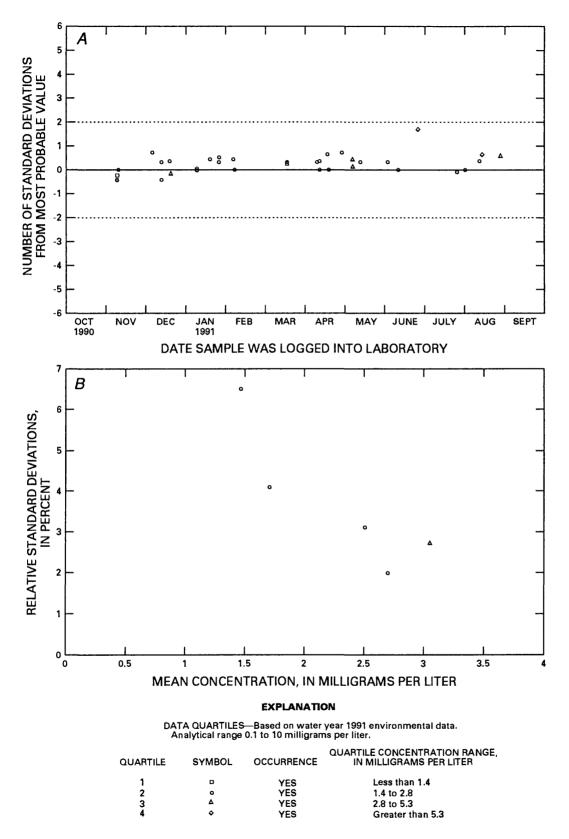


Figure 110. Potassium, dissolved, (atomic absorption spectrometric, direct) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

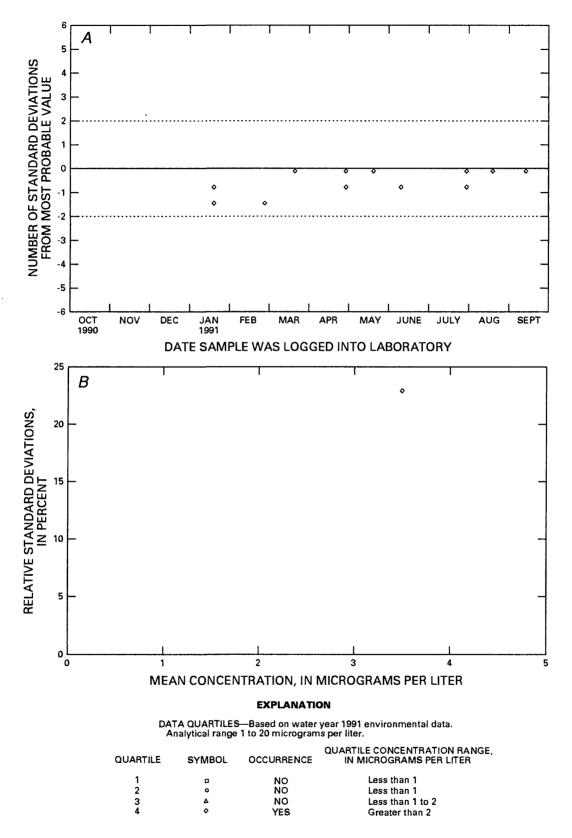


Figure 111. Selenium, dissolved and whole-water recoverable, (atomic absorption spectrometric, hydride) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

132 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

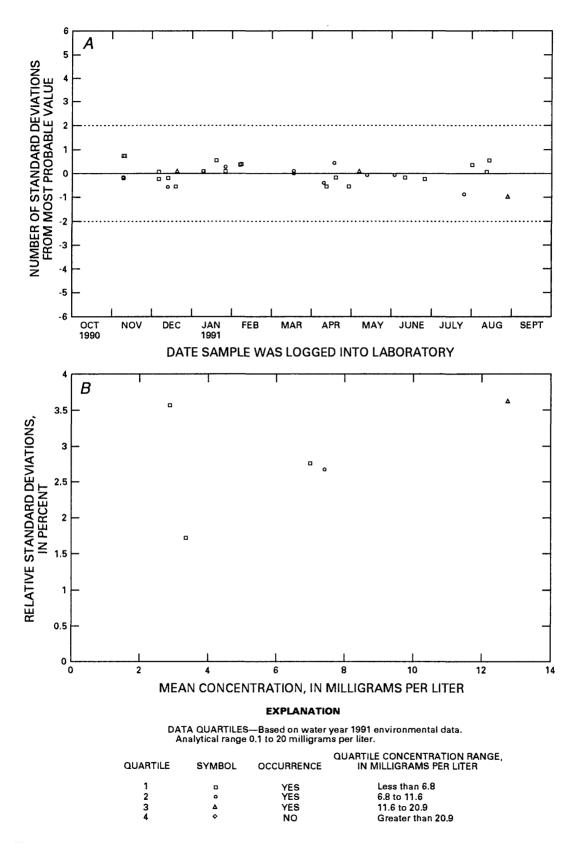


Figure 112. Silica, dissolved, (colorimetric) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

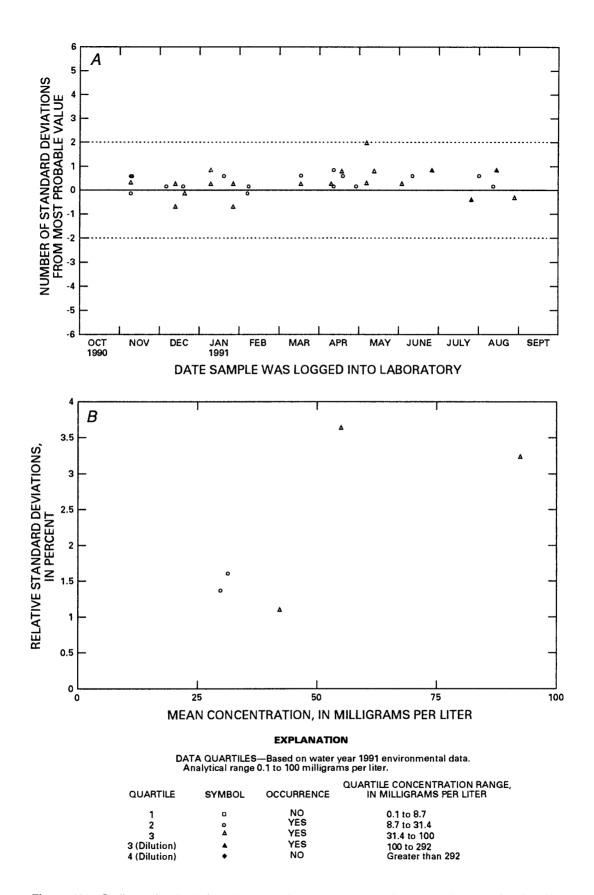


Figure 113. Sodium, dissolved, (atomic absorption spectrometric, direct) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

134 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geologicai Survey for Water Year 1991

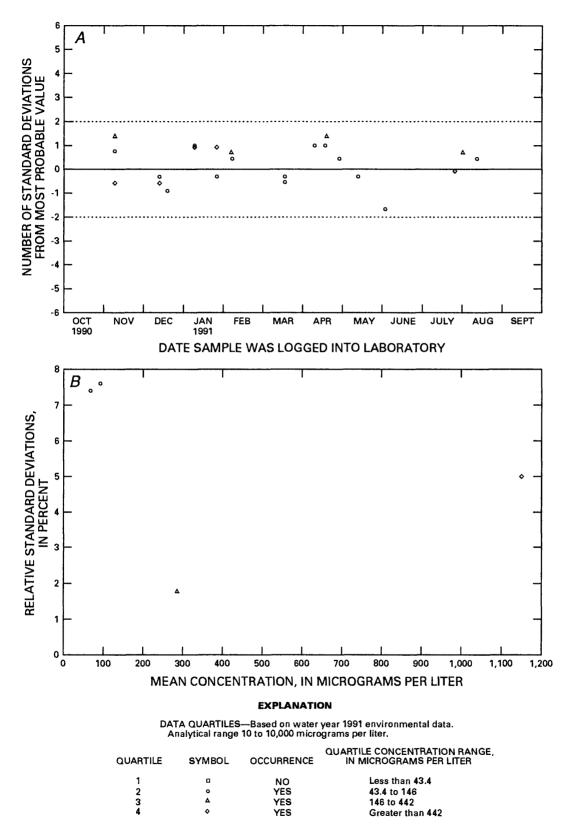


Figure 114. Strontium, dissolved, (atomic absorption spectrometric, direct) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

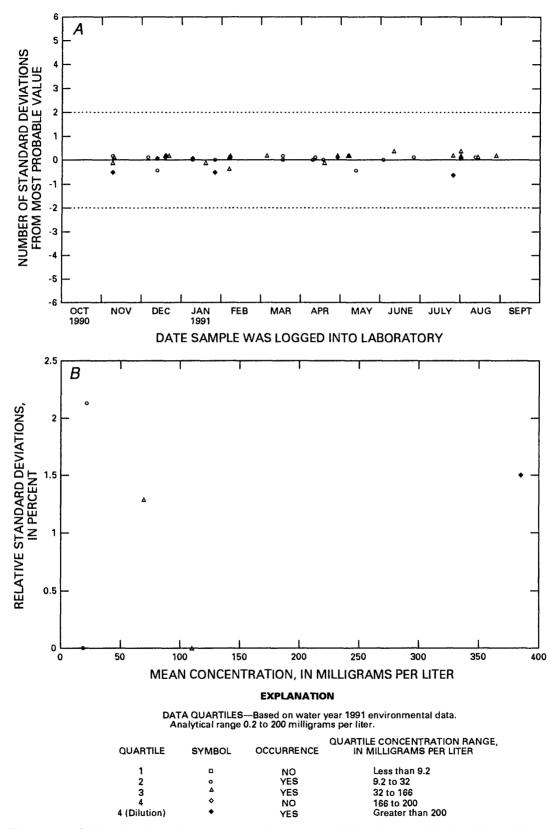


Figure 115. Sulfate, dissolved, (ion-exchange chromatographic) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

136 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

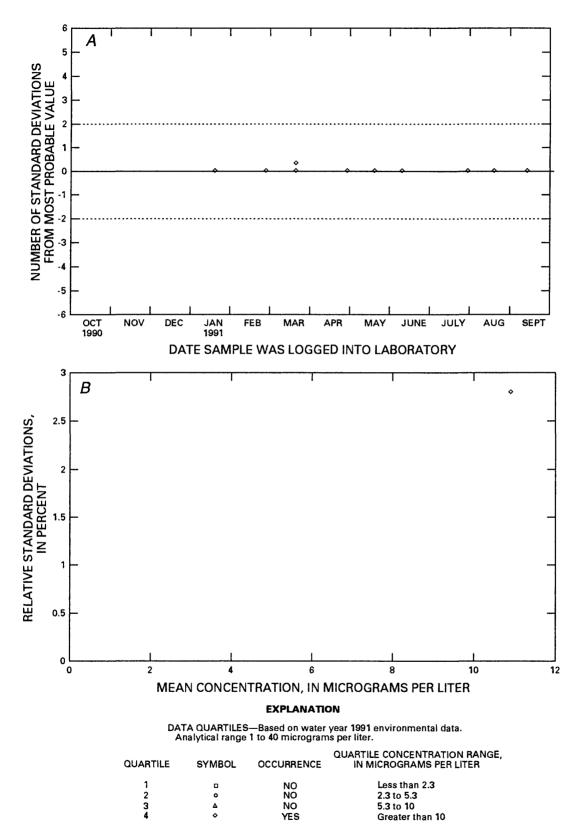


Figure 116. Vanadium, dissolved, (colorimetric) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

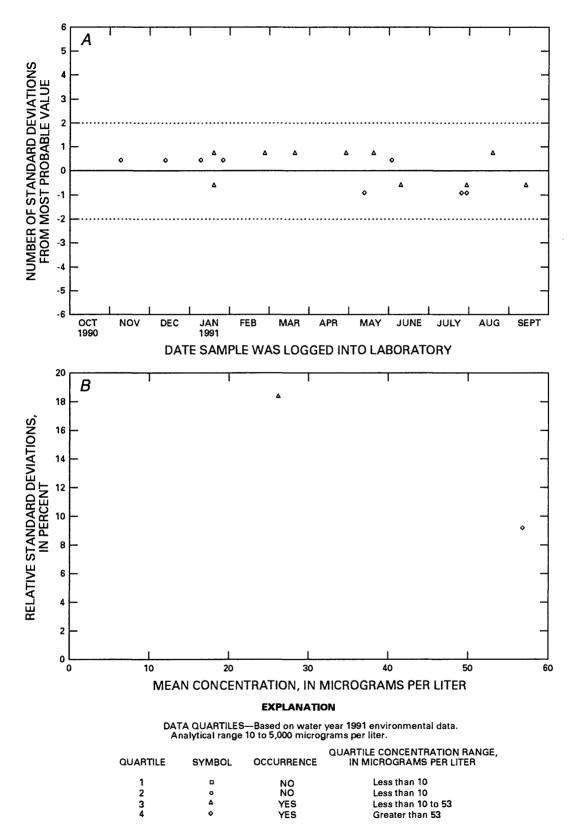


Figure 117. Zinc, dissolved, (atomic absorption spectrometric, direct) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

138 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

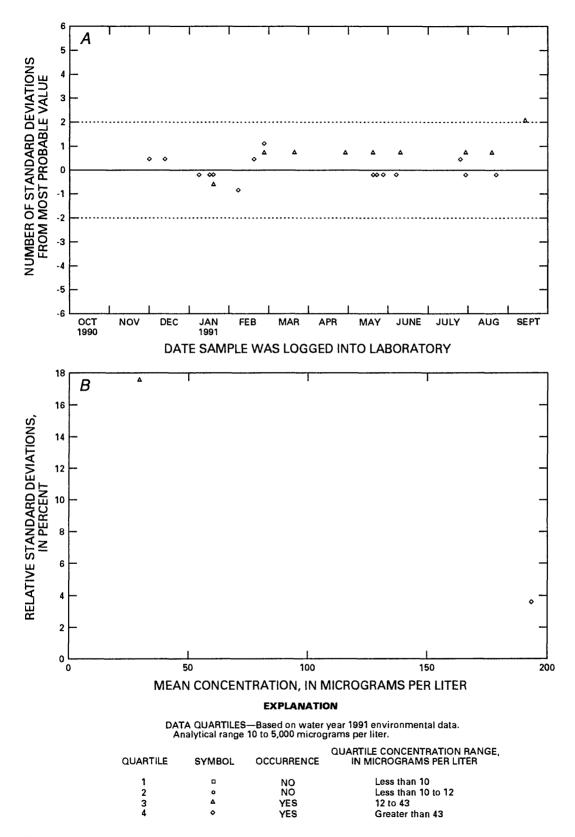


Figure 118. Zinc, whole-water recoverable, (atomic absorption spectrometric, direct) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

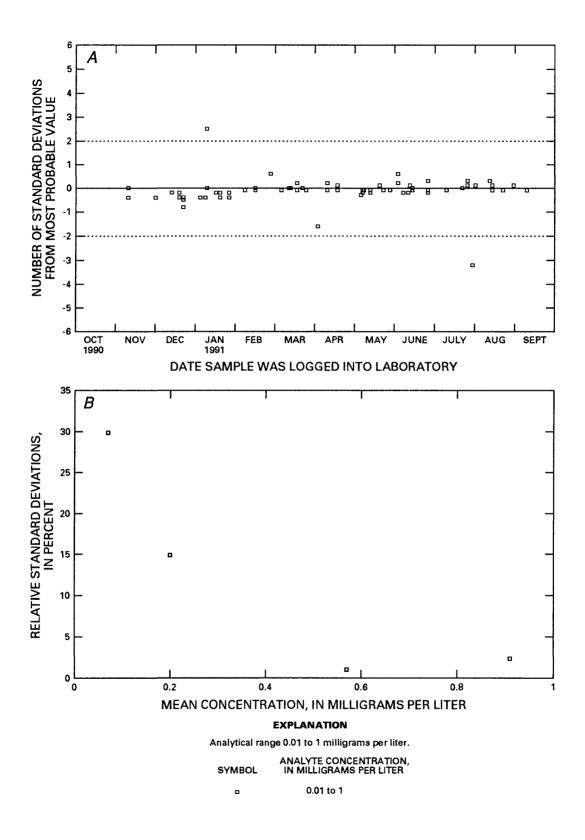


Figure 119. Ammonia as nitrogen, dissolved and whole-water recoverable, (colorimetric) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

140 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

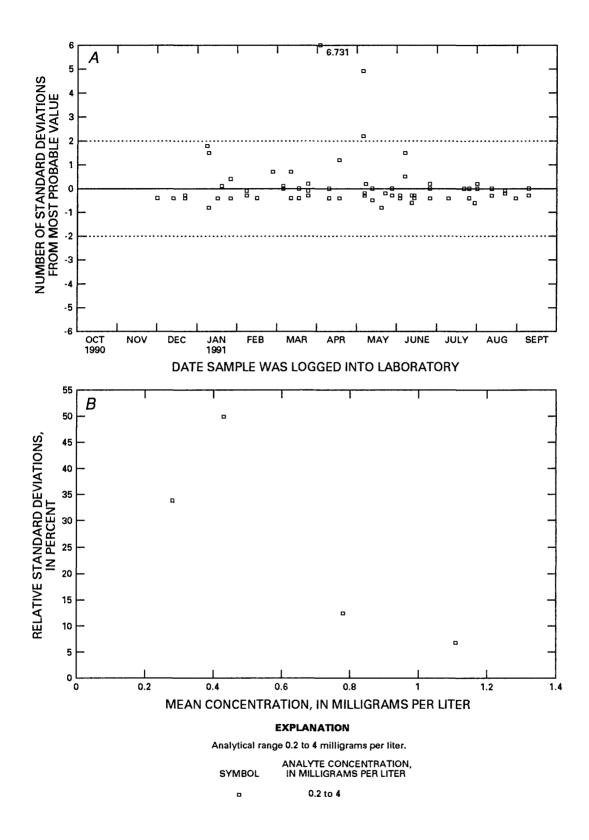


Figure 120. Ammonia plus organic nitrogen as nitrogen, dissolved and whole-water recoverable, (colorimetric) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

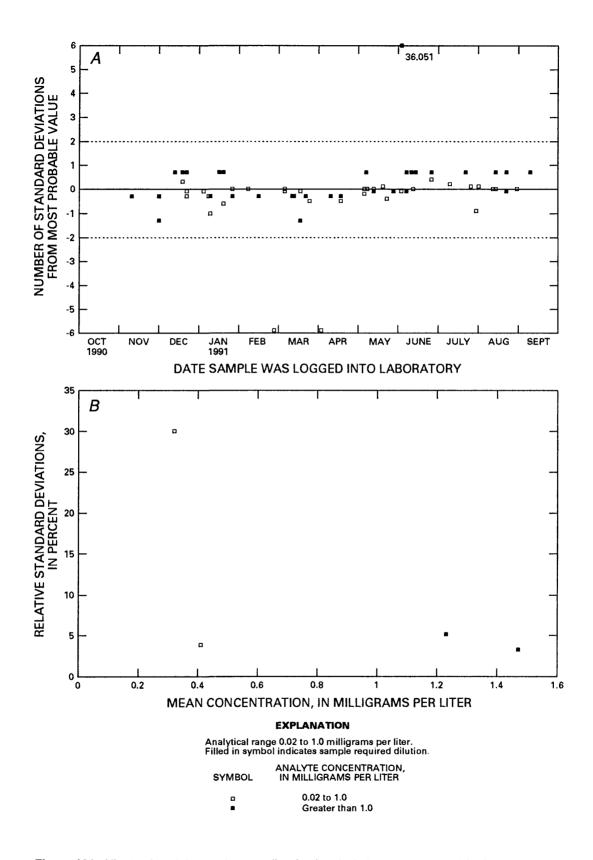


Figure 121. Nitrate plus nitrite as nitrogen, dissolved and whole-water recoverable, (colorimetric) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

142 Quality-Assurance Results for Routine Water Analysis in the Laboratories of the U.S. Geological Survey for Water Year 1991

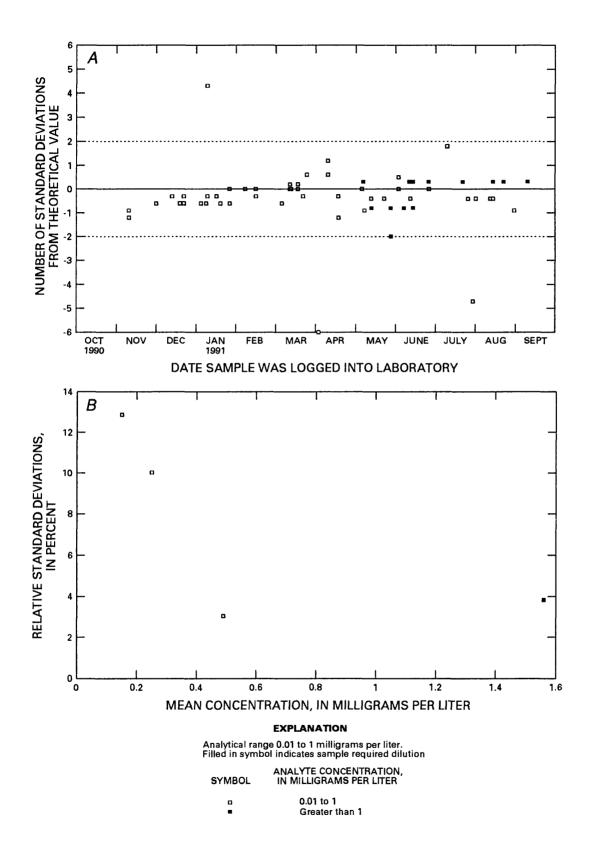


Figure 122. Orthophosphate as phosphorus, dissolved and whole-water recoverable, (colorimetric) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.

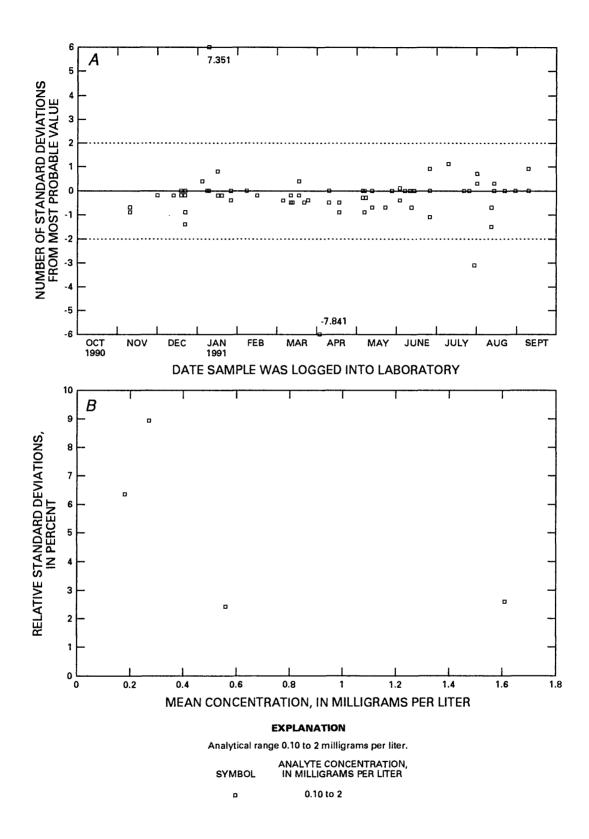


Figure 123. Phosphorus, dissolved and whole-water recoverable, (colorimetric) data from the Quality of Water Service Unit laboratory. *A*, Control chart of samples logged in during water year 1991: *B*, Precision data for sample sets submitted during water year 1991.