RESULTS OF INTERCOMPARISON STUDIES FOR THE MEASUREMENT OF pH AND SPECIFIC CONDUCTANCE AT NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/ NATIONAL TRENDS NETWORK MONITORING SITES, OCTOBER 1981-OCTOBER 1985

By LeRoy J. Schroder and Myron H. Brooks,
U.S. Geological Survey, and
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CONTENTS

FIGURES

FIGURES

TABLES

CONVERSION FACTORS

For the reader who may prefer to use inch-pound units, conversion factors for the terms used in this report are listed below:

Multiply SI units	*By*	*To obtain inch-pound units*
centimeter (cm)	0.3937	inch

Temperature can be converted from degree Celsius to degree Fahrenheit (°F) by using the following equation:

$$°F=9/5\ °C+32.$$

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ABSTRACT

Ten intercomparison studies to determine the accuracy of pH and specific-conductance measurements, using dilute-nitric acid solutions, were managed by the U.S. Geological Survey for the National Atmospheric Deposition Program and the National Trends Network precipitation networks. These precipitation networks set quality-control goals for site-operator measurements of pH and specific conductance. The accuracy goal for pH is ±0.1 pH unit; the accuracy goal for specific conductance is ±4 microsiemens per centimeter at 25 °Celsius. These intercomparison studies indicated than an average of 65 percent of the site-operator pH measurements and 79 percent of the site-operator specific-conductance measurements met the quality-control goal. A statistical approach that is resistant to outliers was used to evaluate and illustrate the results obtained from these intercomparisons.

INTRODUCTION

The precipitation monitoring network of the National Atmospheric Deposition Program (NADP) was organized in 1977 by a number of State agricultural-experiment stations to provide information on the spatial and temporal trends of atmospheric deposition in the United States. Extensive participation was obtained from other organizations, because of the broad interest in the subject. The National Trends Network (NTN) was established by the Deposition Monitoring Task Group of the Interagency Task Force on Acid Precipitaion in 1983 as a minimal network for determining spatial and temporal trends in precipitation in the United States. Both networks use identical sampling and chemical-analysis protocols; therefore, this report will consider NADP and NTN as one group known as NADP/NTN. About 195 atmospheric-deposition monitoring sites currently (1986) are being operated for the NADP/NTN.

Each sampling-site operator determines the pH and specific conductance of each weekly precipitation sample collected at the site. The NADP/NTN has set quality-control goals for the sampling-site operator measurements of pH and specific conductance. The accuracy goal for pH measurement is ±0.1 pH unit; the accuracy goal for the specific-conductance measurement is ±4 µS/cm (microsiemens per centimeter at 25 °Celsius). Ten intercomparison studies to determine the accuracy of pH and specific-conductance measurements were managed by the U.S. Geological Survey for the NADP/NTN to assist the sampling-site operators to meet the quality-control goals.

This paper describes the results obtained from these 10 intercomparison studies, from October 1981 through October 1985. A description of sample preparation and stability, analytical protocol, and sample handling was reported by Schroder and Brennan (1985).

DATA ANALYSIS

Measurements of pH and specific conductance by site operators normally uses less than 40 mL (milliliters) of an 125-mL sample. The remainder of the sample and the operator's results are returned to the U.S. Geological Survey. For the intercomparison studies from October 1981 through July 1984, the U.S. Geological Survey analyzed all returned samples for pH or specific conductance or both when: (1) Reported pH was more than ±0.4 unit from the calculated pH; or (2) reported specific conductance was more than ±20 percent from the calculated specific conductance. A new protocol implemented in January 1985 prescribed that, after outlier rejection, the standard deviation be calculated and all samples with results greater than 1.5 standard deviations from the mean be reanalyzed.

The U.S. Geological Survey analysis of the returned samples was to determine if either the pH or specific conductance had changed in the samples. The criteria used to determine that a sample had changed was described by Schroder and Brennan (1985). The pH or specific conductance was determined to have changed in 6 of 1,243 returned samples. Data for these six samples were removed from the data sets before data analysis.

The range of reported results for the individual data sets is large. For example, the reported values of specific conductance from the October 1985 study ranged from 0.9 to 550 µS/cm. Included in this range were two values of 99 µS/cm and one value of 85.4 µS/cm. The skewness caused by these outliers caused the sample dispersion and the related standard deviation to be poor measures of the dispersion of the results.

The classic statistical techniques designed to reduce the influence of outliers can follow various outlier-rejection protocols. Another technique that reduces the influence of outliers is resistant statistics (Hoaglin and others, 1983; Huber, 1981). The median is a resistant statistic. The resistant analog to the standard deviation is the F-pseudosigma. The F-pseudosigma is calculated by dividing the fourth-spread (Hoaglin and others, 1983) by 1.349. The fourth-spread is the measure of the middle one-half of the data set and is similar to the interquartile range. If the data really are Guassian, the F-pseudosigma will yield an estimate of sigma (σ), and the F-pseudosigma value usually will be similar to that of the sample standard deviation. In addition, the F-pseudosigma is resistant to outliers or to a few wild observations, that otherwise would inflate the standard deviation. Therefore, the resistant statistics eliminate the need to apply outlier-rejection techniques and the various problems related to outlier rejection.

RESULTS OF INTERCOMPARISON STUDIES

Summary statistics of the results from 10 intercomparison studies are presented in tables 1-4. The mean pH differs from the median pH by a maximum of 0.04 unit; the estimate of the sample dispersion indicated by the standard deviation commonly is more than double the estimate made by the F-pseudosigma (table 1). The indication is that the outlying pH values are not having a major influence on the mean, but that they are having a significant influence on the standard deviation. For example, the standard deviation for the October 1985 pH intercomparison is 0.36 unit, whereas the F-pseudosigma is 0.09 unit. Even though 73 percent of the reported pH values were within ±0.1 unit of the median, the calculated standard deviation is 0.36 unit (table 1). The mean standard deviation is reduced to 0.12 pH unit by trimming the data set by 2 percent indicating the effect of a few wild values. Specific-conductance data (tables 2 and 4) have the same general trends as pH.

The number of reported pH and specific-conductance values that are within the quality-control criteria of the NADP/NTN, are listed in tables 3 and 4. An average of 65 percent of the pH values are within ±0.1 pH unit of the median pH values. The percentage of reported pH results within the ±0.1 criterion appears to be independent of the median pH values ranging from 3.84 to 4.80. An average of 79 percent of the specific-conductance results is within ±4 µS/cm of the intercomparison median. The percentage of results reported within ±4 µS/cm of the median value is dependent on the median value for values ranging from 6.6 to 60 µS/cm. An average of 91 percent of the reported results is within ±4 µS/cm for median values less than 22 µS/cm. Data from the intercomparison studies indicate that the criterion of ±4 µS/cm is unobtainable by most of the site operators when specific conductance is 60 µS/cm. As indicated in table 4, only 38 percent of the reported results from the May 1983 intercomparison study were within ±4 µS/cm of the median value. These data indicate that a criterion of ±7 µS/cm would be more appropriate for samples having a specific conductance of 60 µS/cm. The NADP/NTN quality-control criterion of ±4 µS/cm probably is too large for samples having a specific conductance of 22 µS/cm or less.

Stem-and-leaf displays (Velleman and Hoaglin, 1981) are used to present the pH and specific-conductance results from each of the intercomparison studies. Stem-and-leaf displays allow every data value to be presented, as opposed to a histogram, where only data ranges are presented. Each data value is split into its leading digits and its trailing digit. For example, a value of 3.99 is displayed as 39/9 (fig. 1); a value of 14.2 is displayed as 14/2 (fig. 2). Because the location of the decimal point is lost when the data value is split, the stem-and-leaf display (fig. 1) includes a heading that declares the leaf-digit unit as the decimal place of each leaf. The leaf-digit declaration is followed by an example. Stem-and-leaf displays of the pH and specific-conductance results from the intercomparison studies are shown in figures 1-20.

Table 1.--*Summary statistics obtained from the analysis of site-operator results for pH measurements obtained from intercomparison studies*

Date of intercomparison study	Number of results	pH (units)			
		Mean	Standard deviation	Median	F-pseudosigma
October 1981	73	4.26	0.26	4.29	0.12
April 1982	78	4.58	.36	4.58	.13
November 1982	93	4.02	.19	4.03	.10
May 1983	101	3.80	.20	3.84	.10
November 1983	118	4.61	.31	4.61	.11
July 1984	119	4.12	.49	4.12	.06
January 1985	163	4.56	.26	4.55	.10
April 1985	164	4.13	.23	4.13	.07
July 1985	170	4.84	.42	4.80	.11
October 1985	164	4.64	.36	4.61	.09

Table 2.--*Summary statistics obtained from the analysis of site-operator results for specific-conductance measurements obtained from intercomparison studies*

[µS/cm, microsiemens per centimeter at 25 °Celsius]

Date of intercomparison study	Number of results	Specific conductance (µS/cm)			
		Mean	Standard deviation	Median	F-pseudosigma
October 1981	72	21.7	6.4	21.6	2.8
April 1982	78	13.9	10.7	12.4	1.5
November 1982	91	36.7	9.4	38.0	4.4
May 1983	99	57.2	11.3	60.0	7.9
November 1983	116	10.8	6.0	10.8	1.6
July 1984	119	31.0	4.8	31.8	4.1
January 1985	164	12.8	9.8	11.4	1.5
April 1985	161	29.2	4.3	30.0	3.3
July 1985	170	7.5	7.0	6.6	.9
October 1985	165	14.4	43.5	9.8	1.2

Table 3.--*Percentage of site-operator results that are within the National Atmospheric Deposition Program/National Trends Network criterion for pH measurements*

Date of intercomparison study	Number of site operators reporting	Median pH (units)	Percentage of values within criterion of ±0.1 unit	Percentage of values within outside cutoffs
October 1981	73	4.29	59	93
April 1982	78	4.58	55	90
November 1982	93	4.03	66	87
May 1983	101	3.84	64	85
November 1983	118	4.61	60	86
July 1984	119	4.12	71	87
January 1985	163	4.55	63	89
April 1985	164	4.13	73	87
July 1985	170	4.80	65	88
October 1985	164	4.61	73	94

Table 4.--*Percentage of site-operator results that are within the National Atmospheric Deposition Program/National Trends Network criterion for specific-conductance measurements*

[µS/cm, microsiemens per centimeter at 25 °Celsius]

Date of intercomparison study	Number of site operators reporting	Median specific conductance (µS/cm)	Percentage of values within criterion of 4 µS/cm	Percentage of values within outside cutoffs
October 1981	72	21.6	87	94
April 1982	78	12.4	92	95
November 1982	91	38.0	62	90
May 1983	99	60.0	38	96
November 1983	116	10.8	90	93
July 1984	119	31.8	70	97
January 1985	164	11.4	90	90
April 1985	161	30.0	77	97
July 1985	170	6.6	95	92
October 1985	165	9.8	93	92

```
  LEAF DIGIT UNIT = 0.01
  39|9 REPRESENTS 3.99

 LOW|  330,361,367,377,389,395 (OUTLIERS)

  39|9   (ONE VALUE OF 3.99 IN DATA SET)
  40|003 (TWO VALUES OF 4.00; ONE VALUE OF 4.03)
  40|
  41|0
  41|56666789
  42|00000134
  42|5555566777999
  43|000111112344
  43|555666778
  44|012
  44|59
  45|0004
  45|
  46|00

HIGH|  481,542 (OUTLIERS)
```

Figure 1.--Stem-and-leaf display of pH results, in units, from October 1981 intercomparison study.

```
  LEAF DIGIT UNIT = 0.1
  14|2 REPRESENTS 14.2

 LOW|  30,122

  14|2
  15|9
  16|9
  17|8
  18|124588
  19|0000123578
  20|00001446
  21|014556678
  22|00023335689
  23|000112234688
  24|0078
  25|04
  26|02

HIGH|  369,635
```

Figure 2.--Stem-and-leaf display of specific-conductance results, in microsiemens per centimeter at 25 °Celsius, from October 1981 intercomparison study.

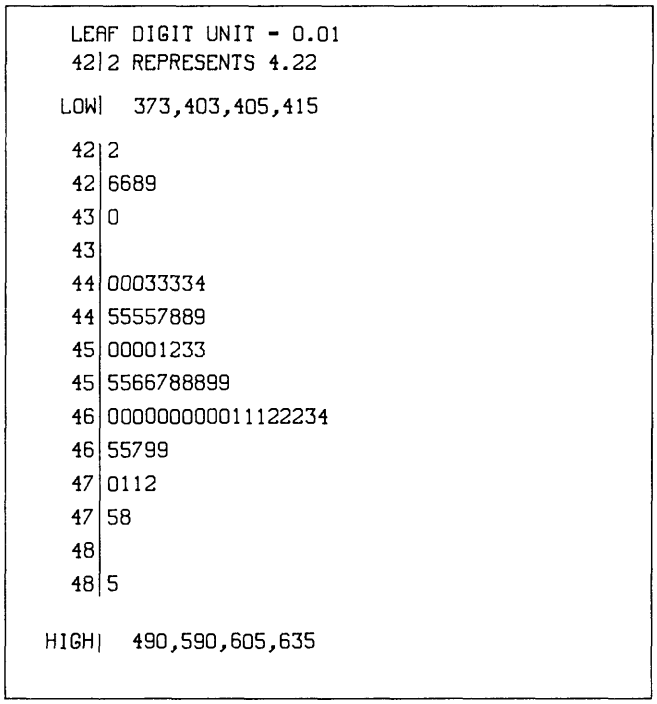

Figure 3.--Stem-and-leaf display of pH results, in units, from April 1982 intercomparison study.

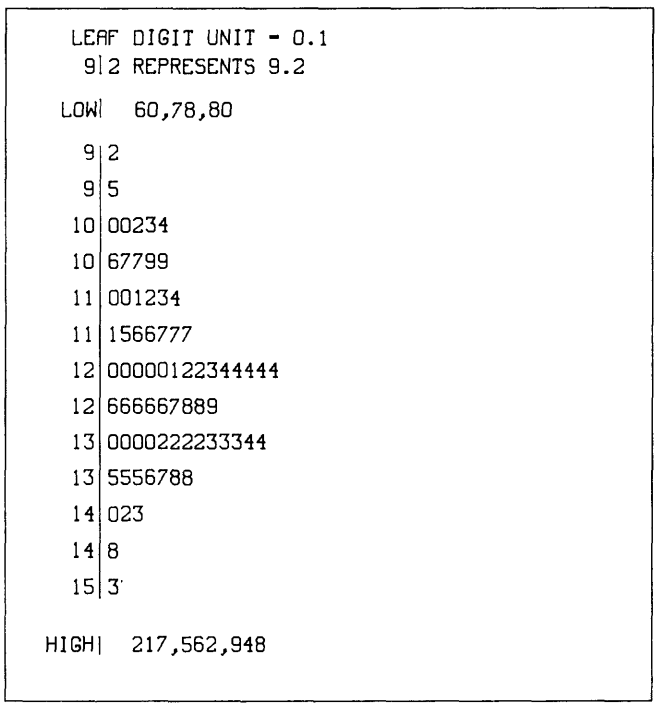

Figure 4.--Stem-and-leaf display of specific-conductance results, in microsiemens per centimeter at 25 °Celsius, from April 1982 intercomparison study.

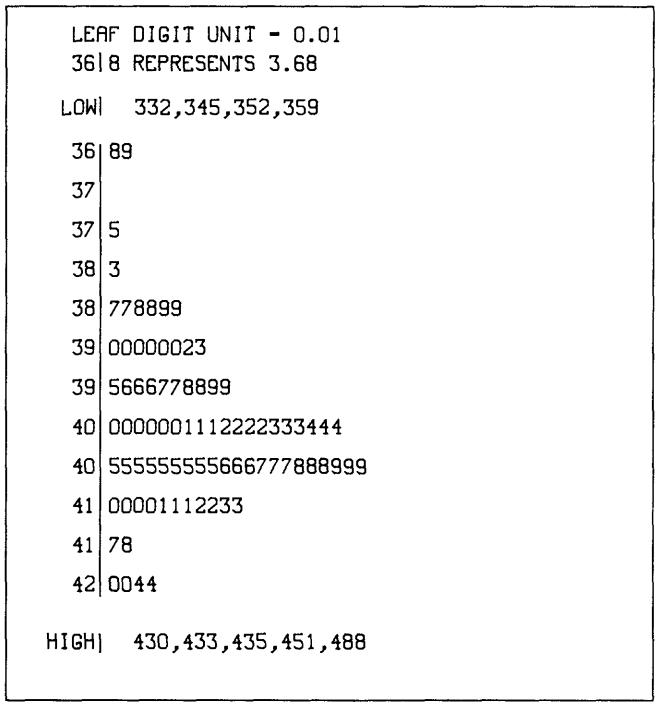

Figure 5.--Stem-and-leaf display of pH results, in units, from November 1982 intercomparison study.

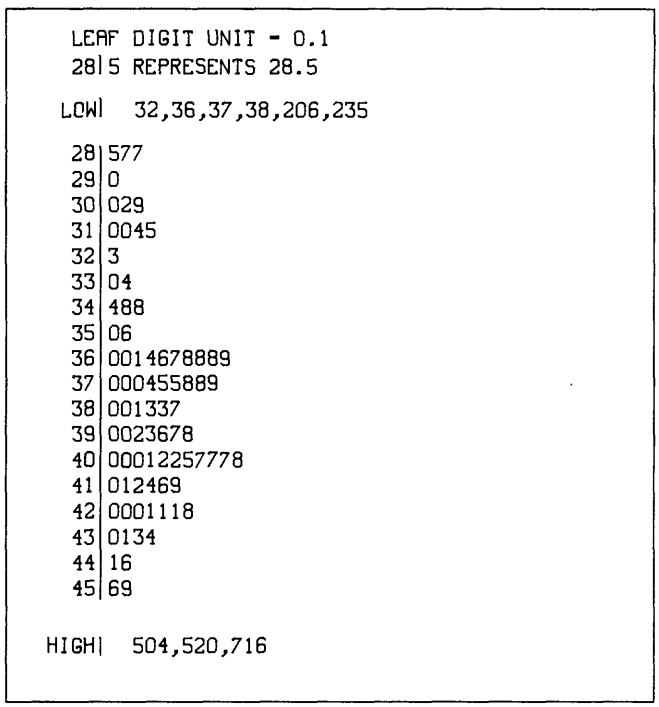

Figure 6.--Stem-and-leaf display of specific-conductance results, in microsiemens per centimeter at 25 °Celsius, from November 1982 intercomparison study.

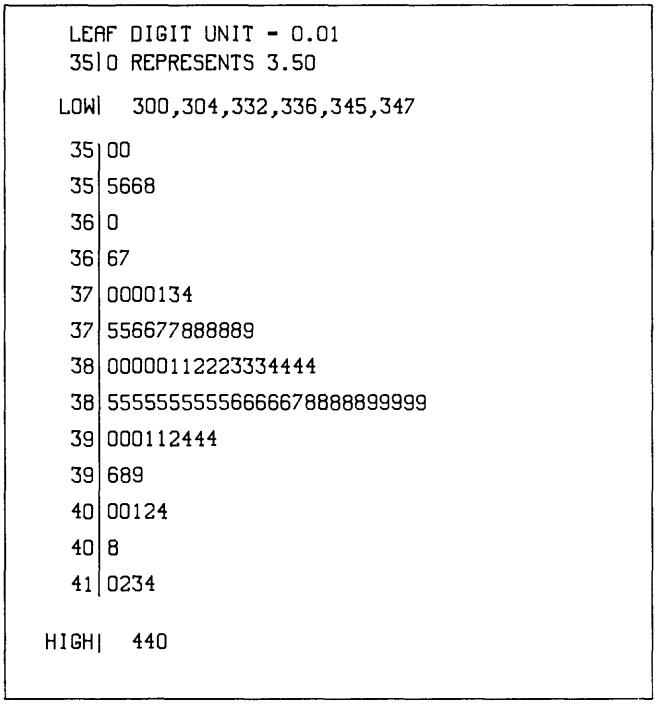

Figure 7.--Stem-and-leaf display of pH results, in units, from May 1983 intercomparison study.

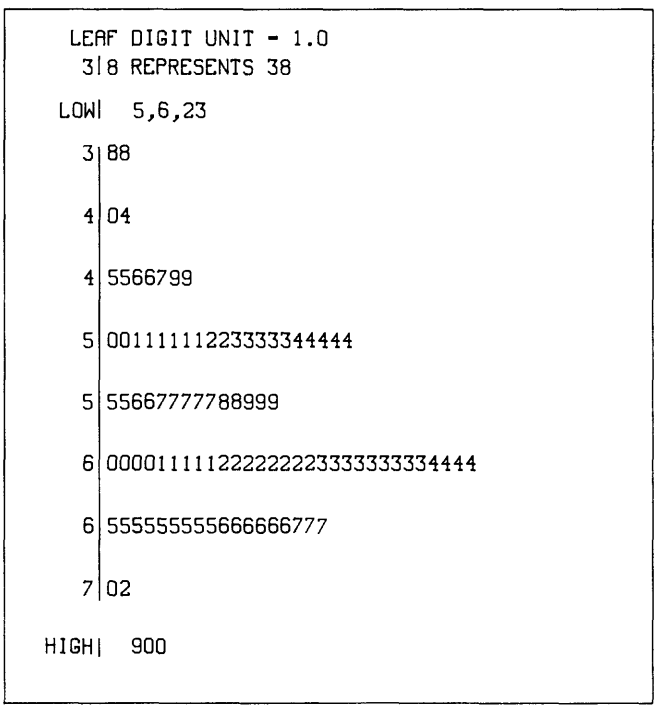

Figure 8.--Stem-and-leaf display of specific-conductance results, in microsiemens per centimeter at 25 °Celsius, from May 1983 intercomparison study.

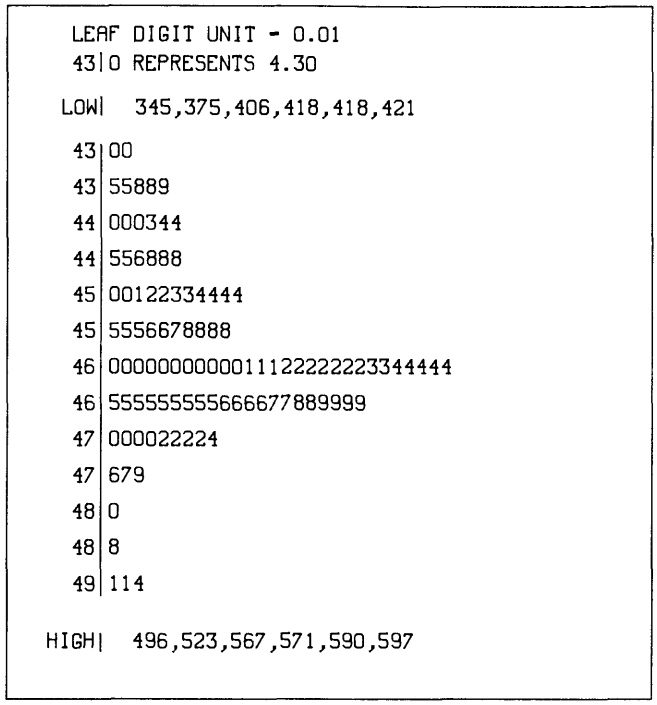

Figure 9.--Stem-and-leaf display of pH results, in units, from November 1983 intercomparison study.

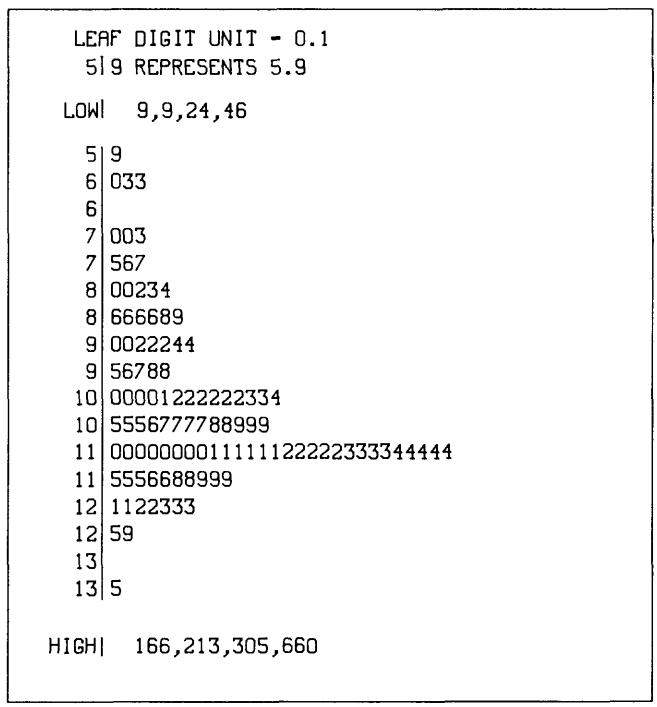

Figure 10.--Stem-and-leaf display of specific-conductance results, in microsiemens per centimeter at 25 °Celsius, from November 1983 intercomparison study.

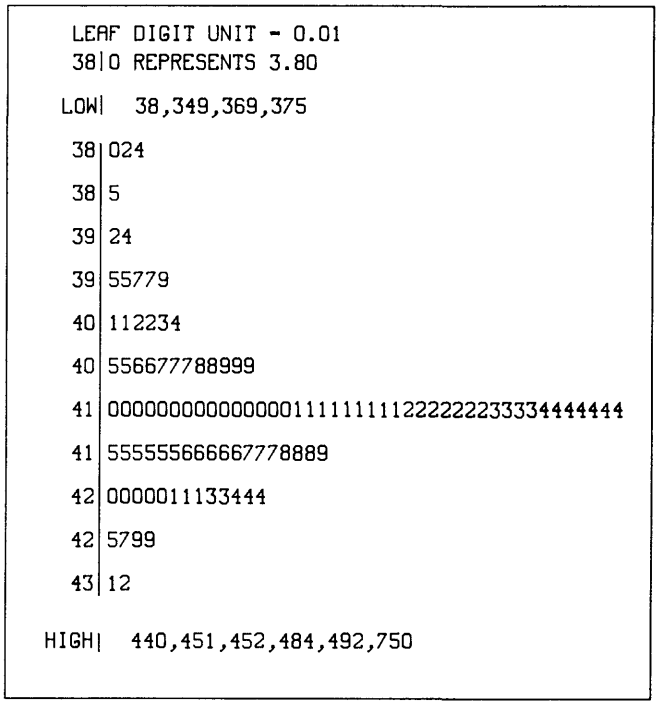

Figure 11.--Stem-and-leaf display of pH results, in units, from July 1984 intercomparison study.

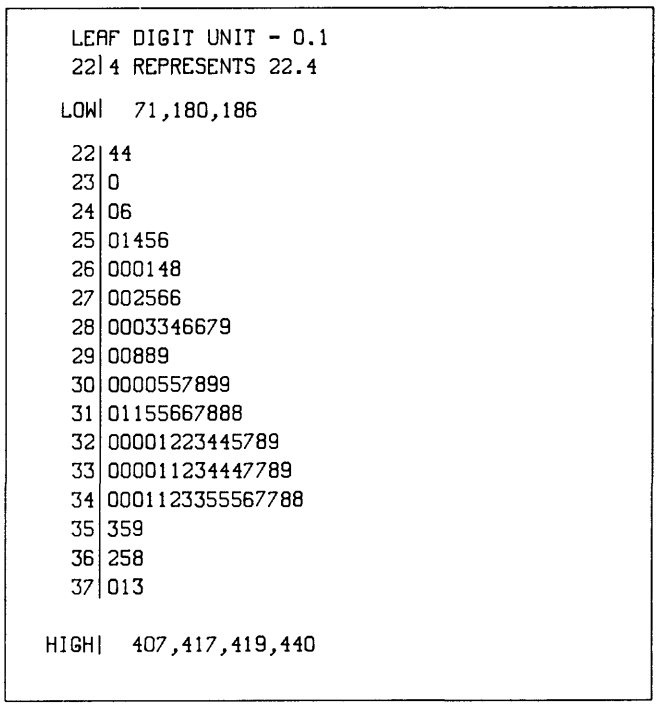

Figure 12.--Stem-and-leaf display of specific-conductance results, in microsiemens per centimeter at 25 °Celsius, from July 1984 intercomparison study.

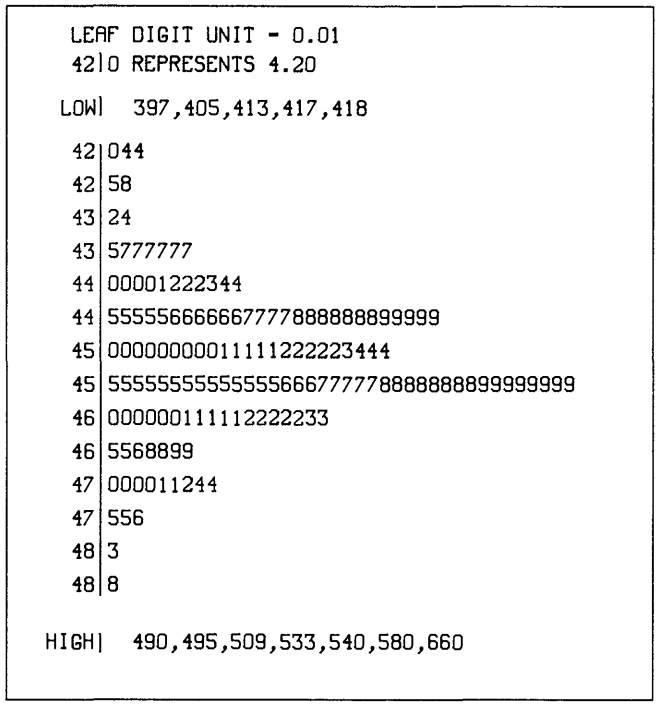

Figure 13.--Stem-and-leaf display of pH results, in units, from January 1985 intercomparison study.

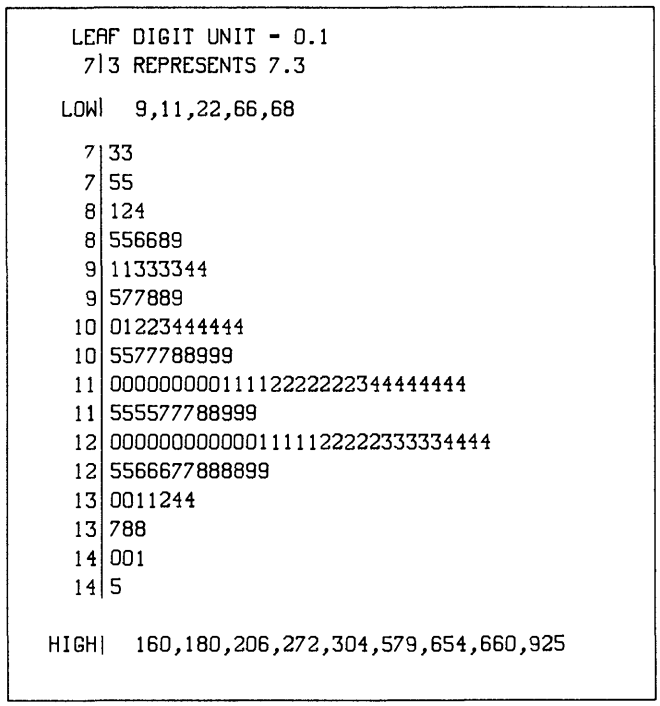

Figure 14.--Stem-and-leaf display of specific-conductance results, in microsiemens per centimeter at 25 °Celsius, from January 1985 intercomparison study.

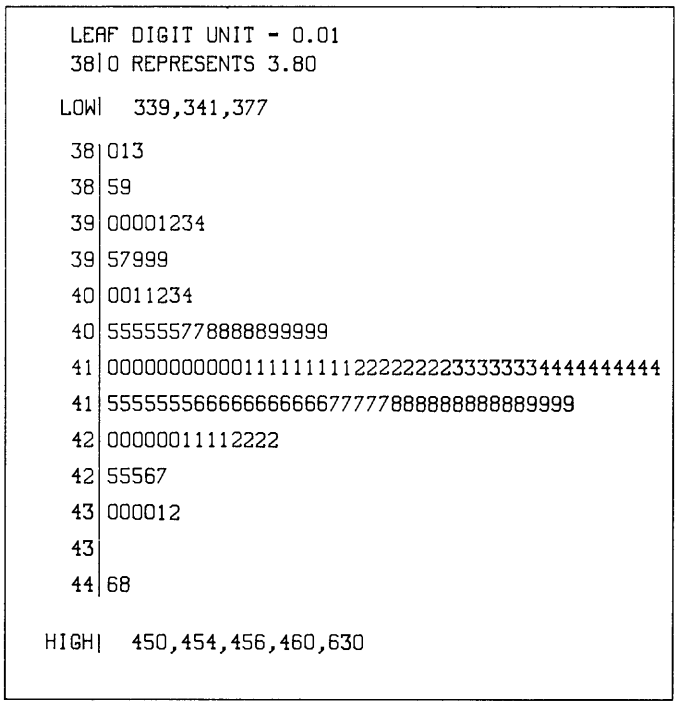

Figure 15.--Stem-and-leaf display of pH results, in units, from April 1985 intercomparison study.

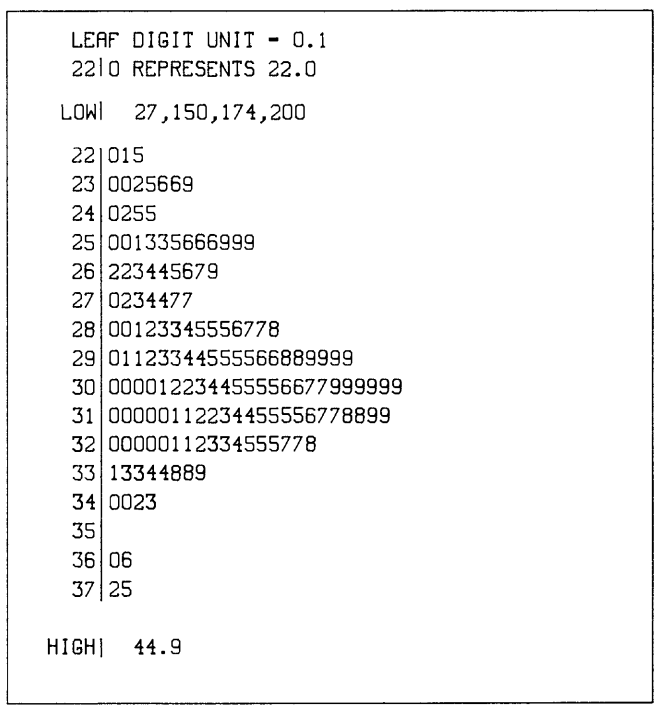

Figure 16.--Stem-and-leaf display of specific-conductance results, in microsiemens per centimeter at 25 °Celsius, from April 1985 intercomparison study.

```
  LEAF DIGIT UNIT = 0.01
  52|0 REPRESENTS 5.20

 LOW|  361,425,430

  44| 244
  44| 5789
  45| 02
  45| 5788
  46| 022334
  46| 55577799999
  47| 00000000111111122233334
  47| 55555566666677777888888999999
  48| 000000000011111111222222333333334444
  48| 5556666667777889999
  49| 001122334
  49| 578
  50| 0024
  50| 6
  51| 22

HIGH|  520,524,530,550,603,605,655,690,745,750
```

Figure 17.--Stem-and-leaf display of pH results, in units, from July 1985 intercomparison study.

```
  LEAF DIGIT UNIT = 0.1
   4|0 REPRESENTS 4.0

 LOW|  6,35,37

   4| 04
   4| 56677889999
   5| 00011122233444444
   5| 55666777778899
   6| 000000022222222333333333444444444
   6| 556666666677777777888888999999999
   7| 000000000000001111111222233444
   7| 5566788
   8| 022
   8| 5668
   9| 0

HIGH|  101,104,119,119,120,150,269,475,573,640
```

Figure 18.--Stem-and-leaf display of specific-conductance results, in microsiemens per centimeter at 25 °Celsius, from July 1985 intercomparison study.

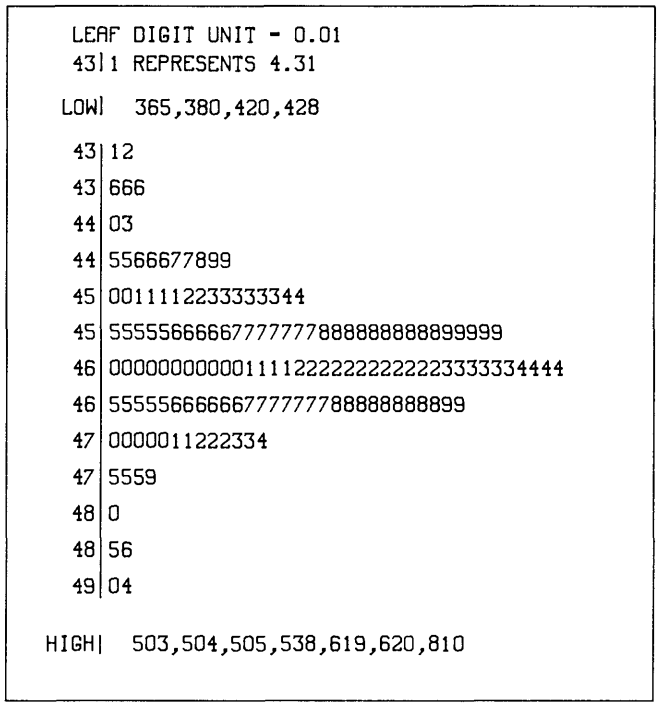

Figure 19.--Stem-and-leaf display of pH results, in units, from October 1985 intercomparison study.

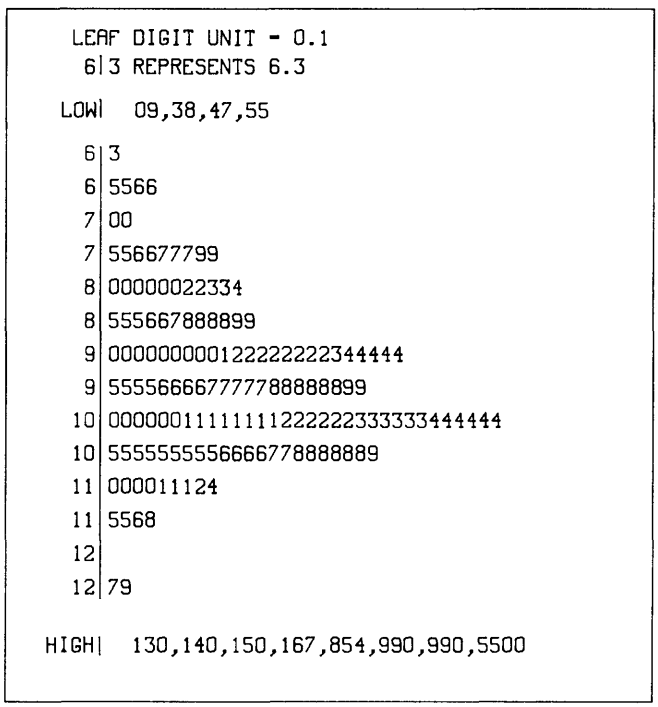

Figure 20.--Stem-and-leaf display of specific-conductance results, in microsiemens per centimeter at 25 °Celsius, from October 1985 intercomparison study.

Scatter plots of each site operator's reported pH value versus the associated reported specific-conductance value are shown in figures 21-30. Superimposed on each plot are two different rectangles that are defined by the two criteria used to accept or reject results. The NADP/NTN quality-control criteria is the smaller of the two rectangles. The larger rectangle is the outside cutoffs defined by the lower fourth minus 1.5 times the fourth-spread, and the upper fourth plus 1.5 times the fourth-spread (Hoaglin and others, 1983). Values that plot outside the larger rectangle possibly are in error, and site operators need to check their equipment and calibration procedures.

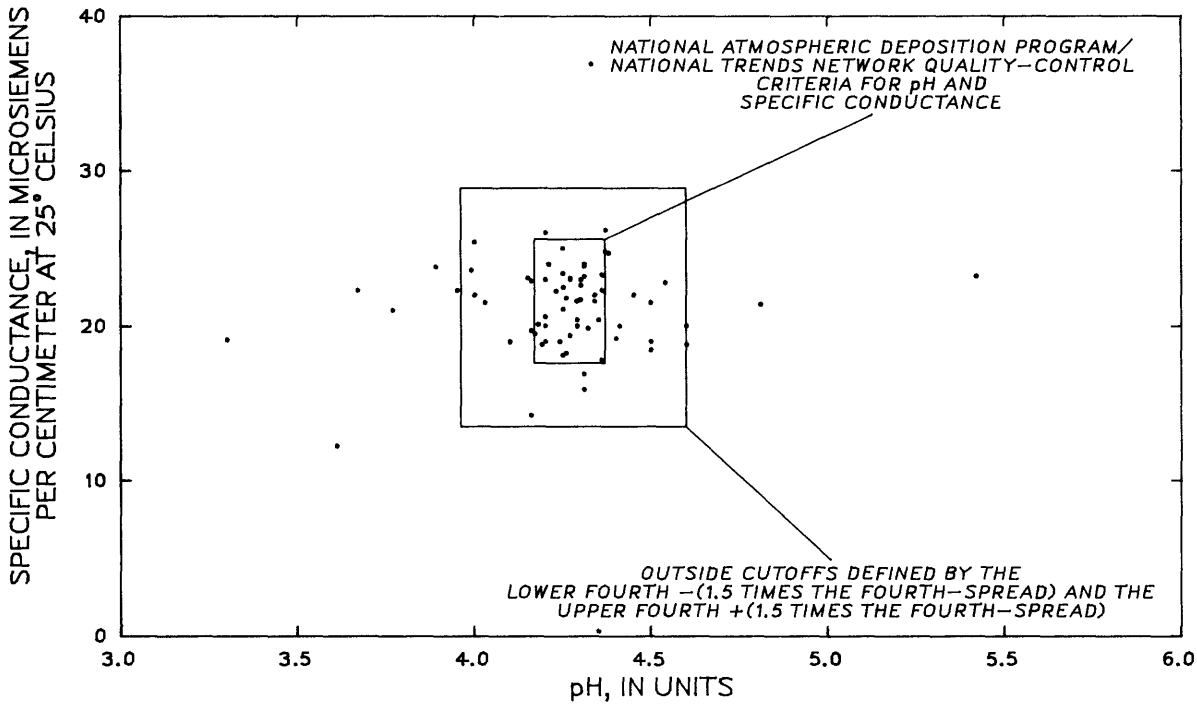

Figure 21.--Scatter plot of pH versus specific-conductance results for October 1981 intercomparison study.

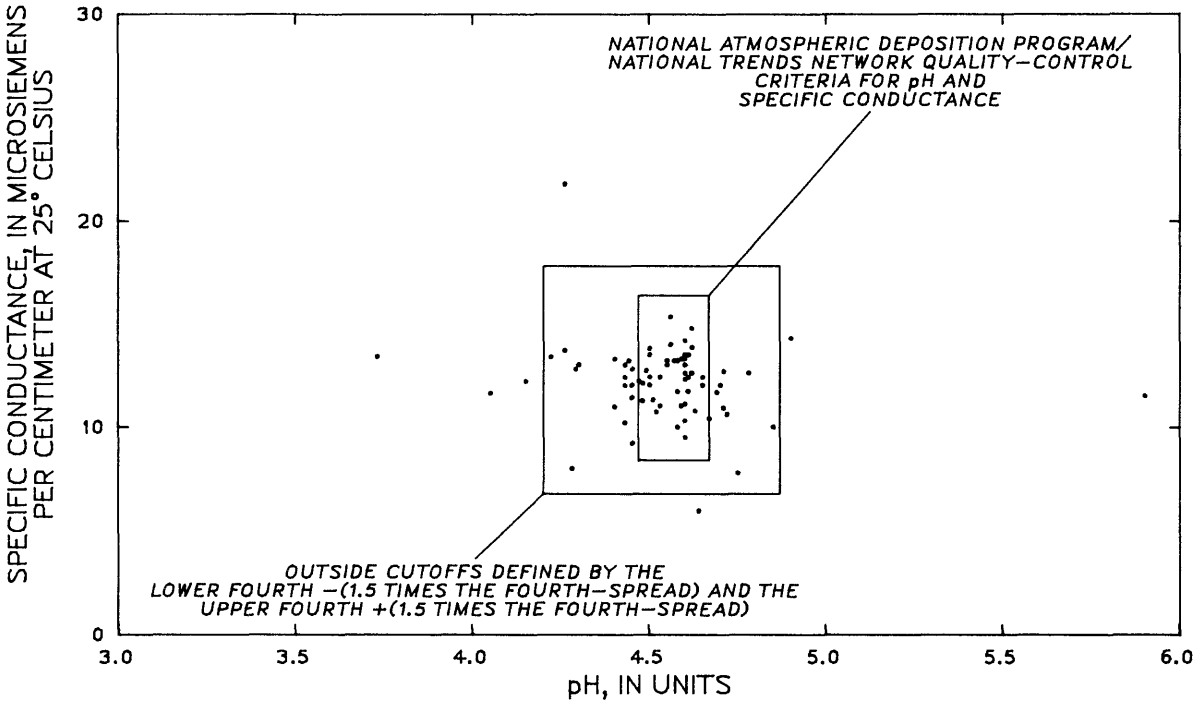

Figure 22.--Scatter plot of pH versus specific-conductance results for April 1982 intercomparison study.

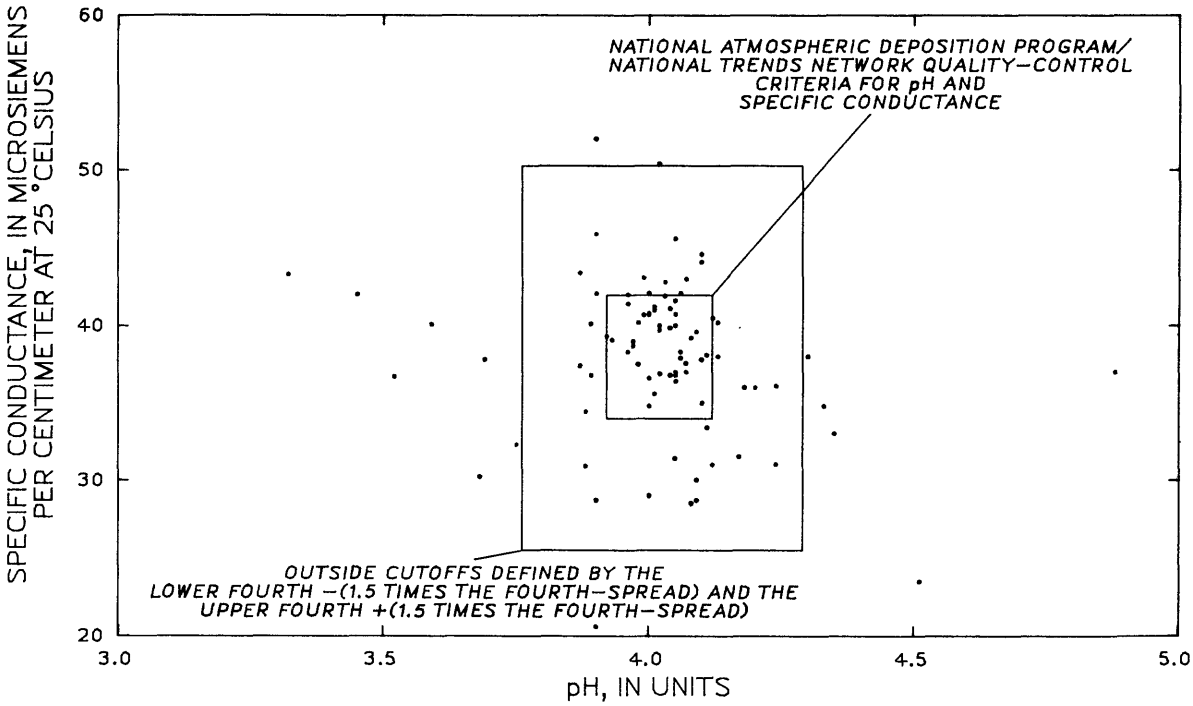

Figure 23.--Scatter plot of pH verus specific-conductance results for November 1982 intercomparison study.

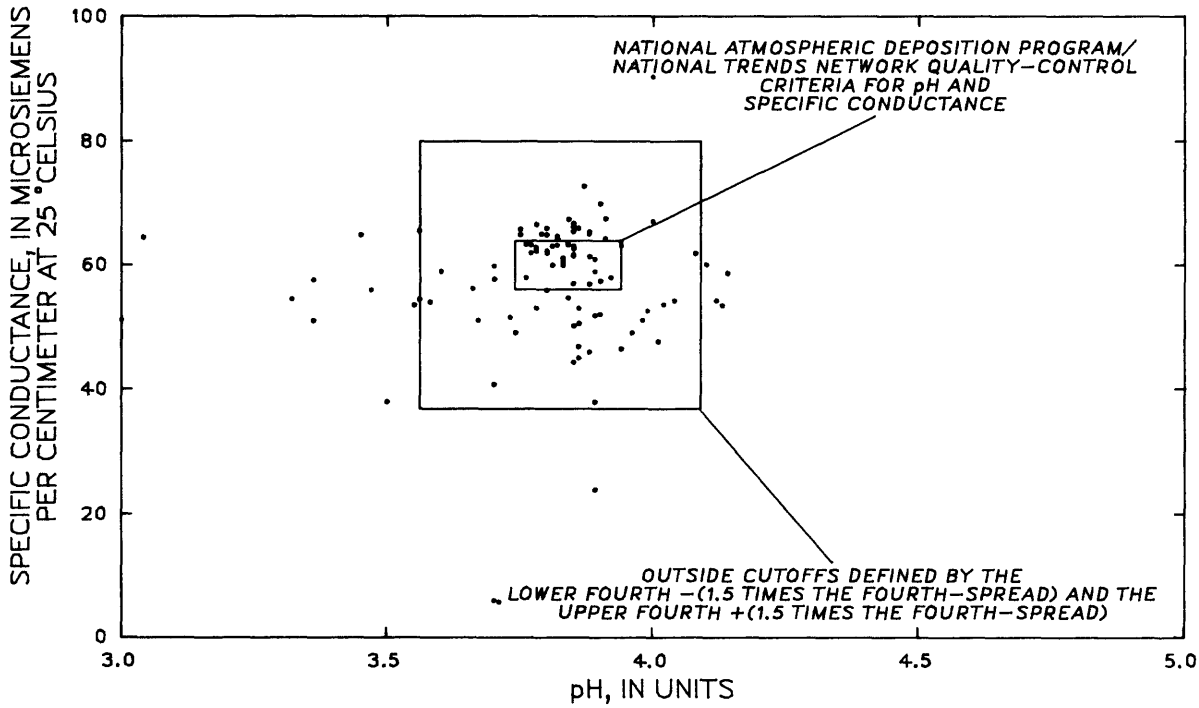

Figure 24.--Scatter plot of pH versus specific-conductance results for May 1983 intercomparison study.

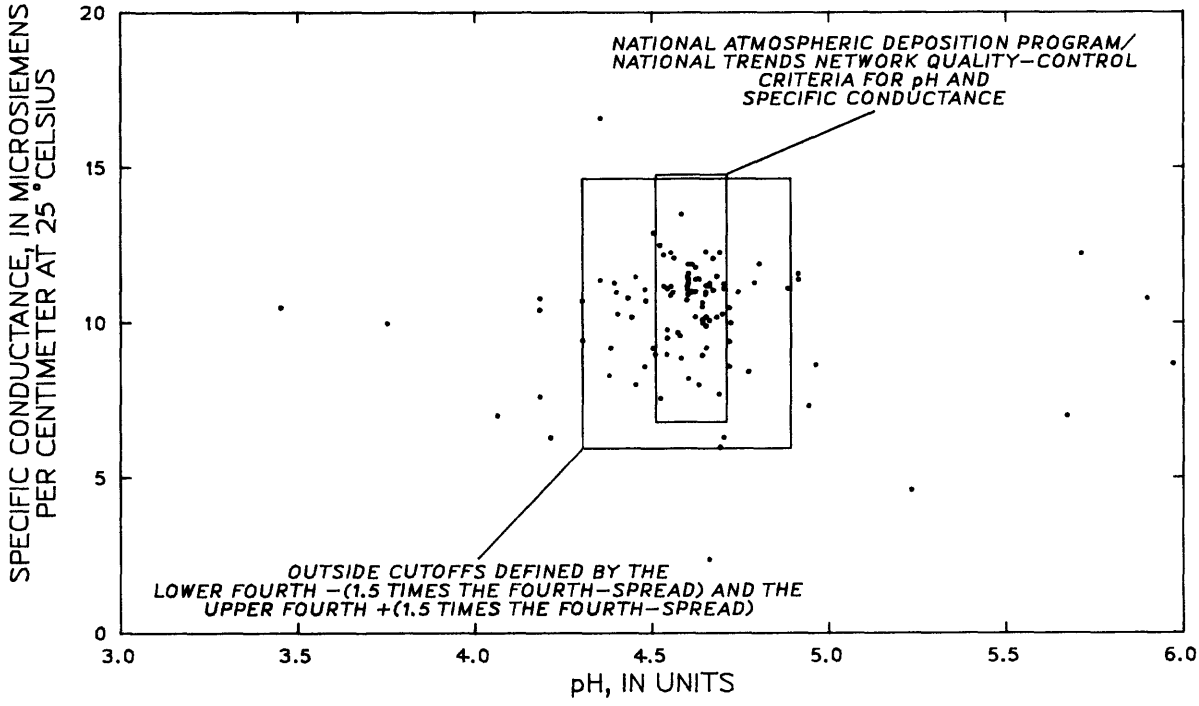

Figure 25.--Scatter plot of pH versus specific-conductance results for November 1983 intercomparison study.

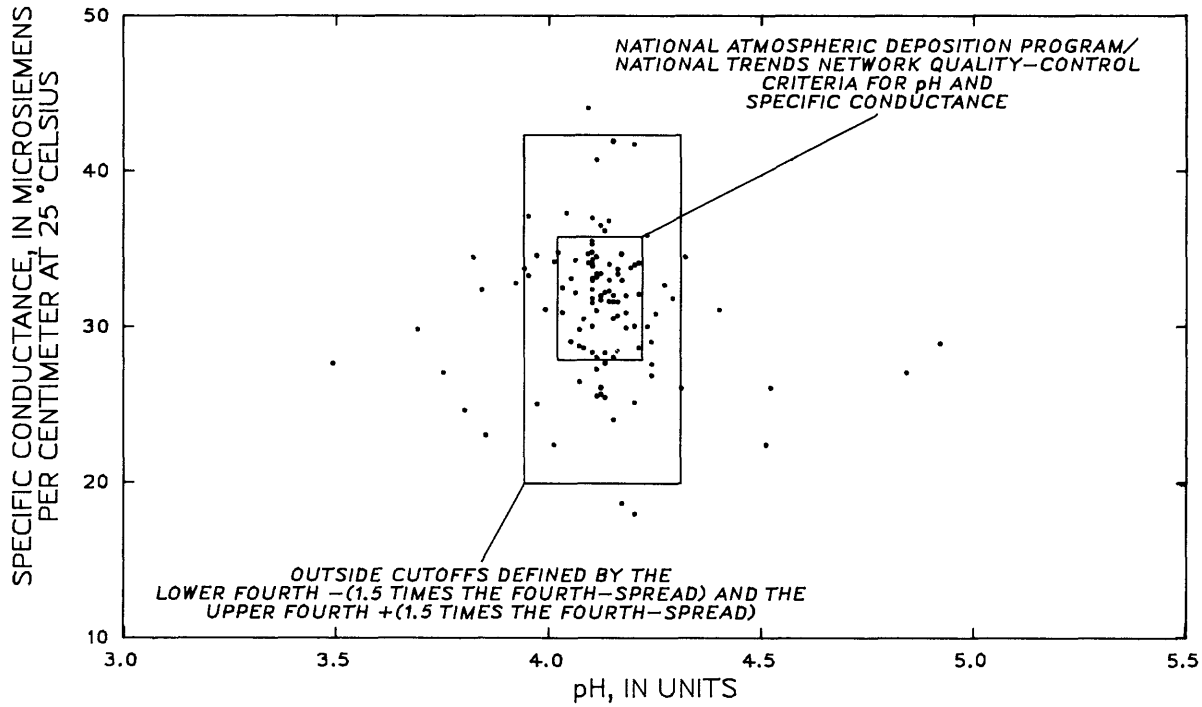

Figure 26.--Scatter plot of pH versus specific-conductance results for July 1984 intercomparison study.

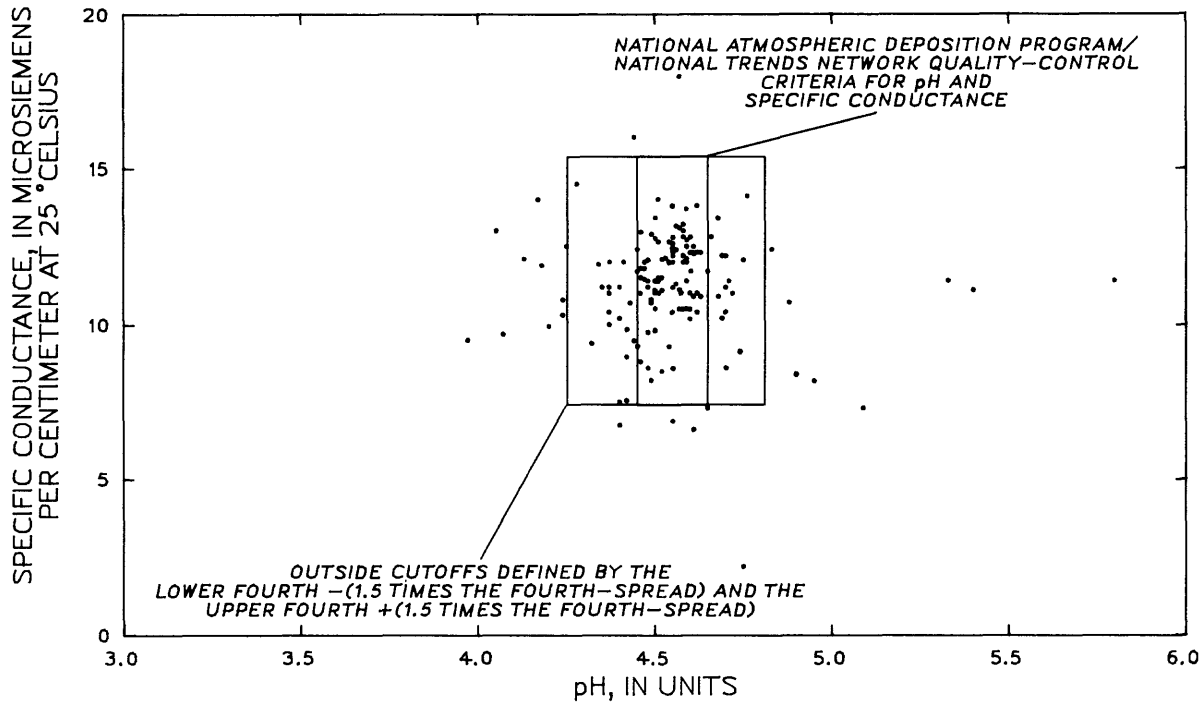

Figure 27.--Scatter plot of pH versus specific-conductance results for January 1985 intercomparison study.

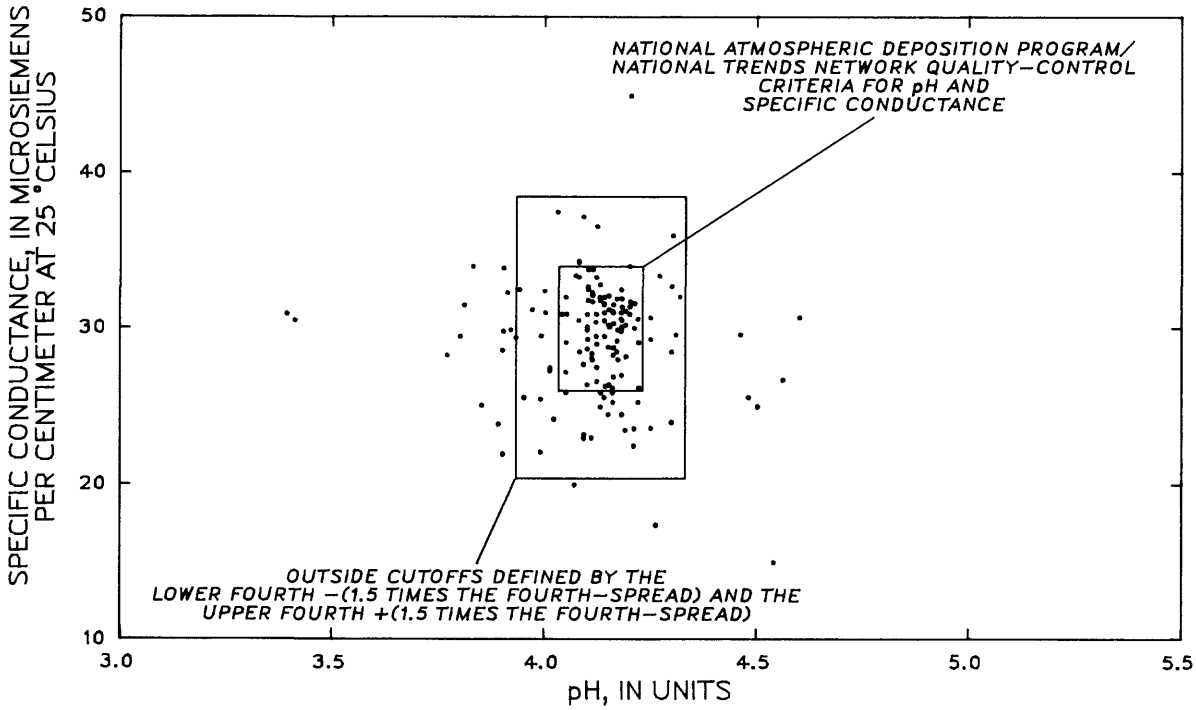

Figure 28.--Scatter plot of pH versus specific-conductance results for April 1985 intercomparison study.

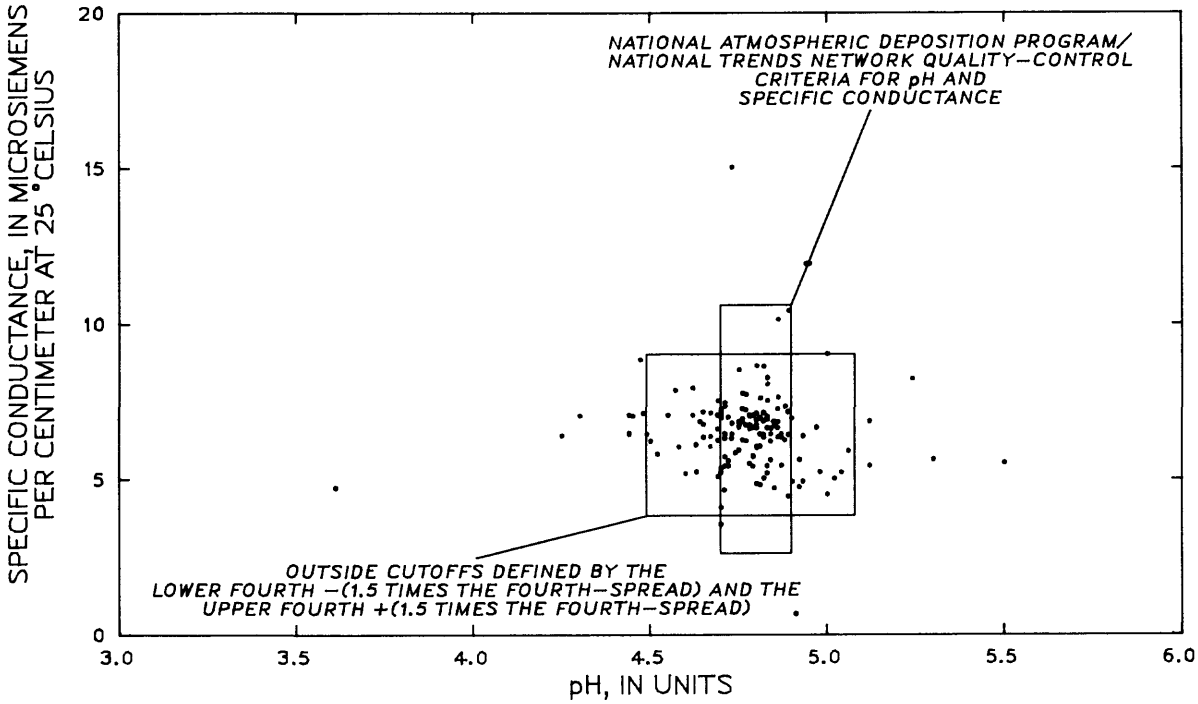

Figure 29.--Scatter plot of pH versus specific-conductance results for July 1985 intercomparison study.

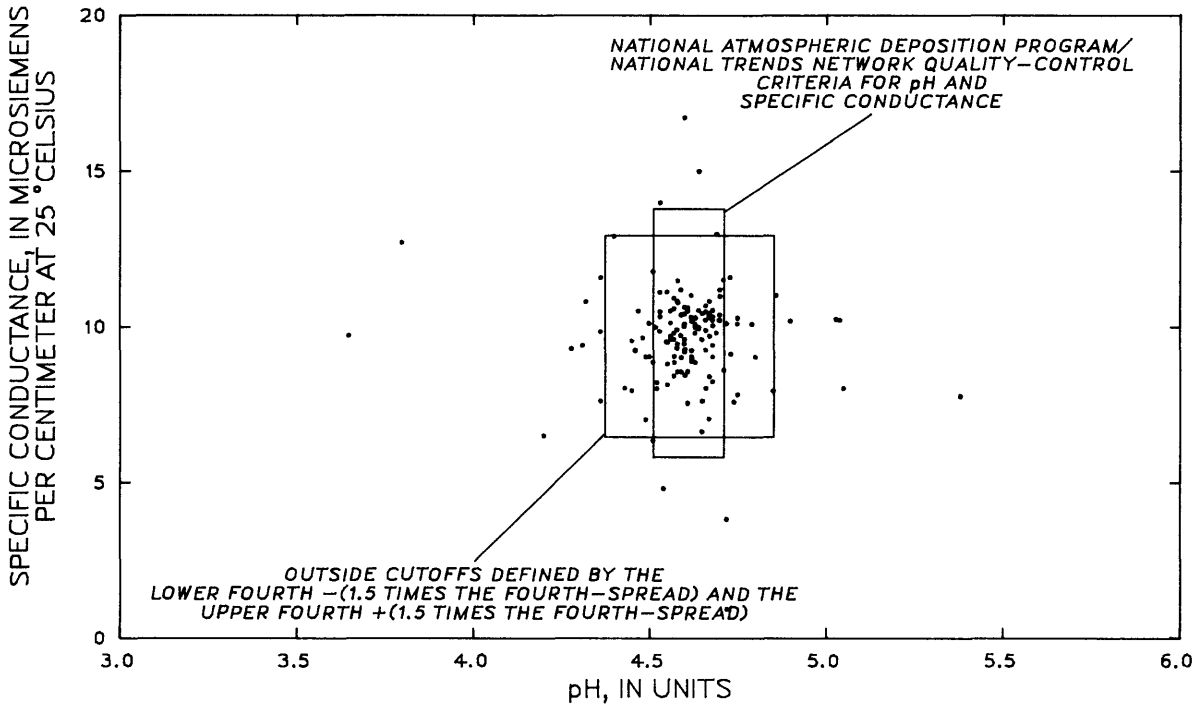

Figure 30.--Scatter plot of pH versus specific-conductance results for October 1985 intercomparison study.

CONCLUSIONS

Results from the 10 intercomparison studies managed by the U.S. Geological Survey during the past 4 years indicate than an average of 65 percent of the site operators report pH values within ±0.1 unit of the median pH; therefore, they are meeting the NADP/NTN criterion for field measurements of pH. The number of reported results that meet this criterion appears to be independent of the sample pH, and the increased frequency of testing during 1985 does not appear to increase the percentage of results that meet the pH criterion. Results of the studies also indicate than an average of 79 percent of the specific-conductance values meet the NADP/NTN criterion of ±4 µS/cm. The percentage of results meeting the criterion is dependent on the median specific conductance. The percentage decreases from an average of 91 percent if the median specific conductance is below 22 µS/cm, to a low of 38 percent, if the median specific conductance is 60 µS/cm. Data from the May 1983 intercomparison indicates that ±7 µS/cm would be a better criterion for specific-conductance values of 60 µS/cm.

Resistant statistical techniques are used to evaluate the intercomparison data, because of the influence of wild values or outliers on the mean and standard deviation. The median is used because of its resistance to wild values. The F-pseudosigma is used as a replacement for the standard deviation, and it may be used to estimate the sample dispersion of each intercomparison. The use of resistant statistical techniques eliminates the need to apply various outlier-rejection tests to data sets containing wild values.

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