Analysis of Ground Water by Different Laboratories— A Comparison of Chloride and Nitrate Data, Nassau and Suffolk Counties, New York

U.S. GEOLOGICAL SURVEY

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Nassau County Department of Public Works
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Suffolk County Water Authority

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Multiply metric units	*By*	*To obtain Inch-pound units*
meter (m)	3.281	feet (ft)
milligrams per liter (mg/L)	--	--
micrometer (μ)	--	--
degrees Celsius (°C)	1.8°C + 32	degrees Fahrenheit (°F)

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ABSTRACT

Water samples from wells in Nassau and Suffolk Counties were analyzed for chloride and nitrate. Two samples were collected at each well; one was analyzed by the U.S. Geological Survey, the other by a laboratory in the county from which the sample was taken. Results were compared statistically by paired-sample t-test to indicate the degree of uniformity among laboratory results. Chloride analyses from one of the three county laboratories differed significantly (0.95 confidence level) from that of a Geological Survey laboratory. For nitrate analyses, a significant difference (0.95 confidence level) was noted between results from two of the three county laboratories and the Geological Survey laboratory. The lack of uniformity among results reported by the participating laboratories indicates a need for continuing participation in a quality-assurance program and exercise of strong quality control from time of sample collection through analysis so that differences can be evaluated.

INTRODUCTION

Chloride and nitrate are major inorganic ions in ground water of Long Island. Both have been used extensively as indicators of water-quality degradation resulting from (1) effluent from septic systems, (2) salt-water intrusion, (3) effluent from industrial processes, and (4) runoff containing dissolved salts from fertilizers and road salts. Over the past 50 years, chloride and nitrate concentrations have been published by the U.S. Geological Survey and measured by several county and State agencies and by the U.S. Geological Survey through cooperative programs. The precision and accuracy of the older analyses have not been reported, and it has been assumed that these analyses were performed accurately.

In natural waters, chloride is a nonreactive ion, and the analysis for chloride in water is commonly assumed to be a simple and dependable procedure (Hem, 1970). The analysis for nitrate, however, is more difficult because of chemical interferences and the complexity of procedures used in the analysis (American Public Health Association and others, 1976). Nitrate is stable in water in that it is the end product of the aerobic decomposition of organic nitrogen. However, storage time and temperature of samples is critical for maintaining the integrity of samples prior to analysis (American Public Health Association and others, 1976).

As a part of a water-quality-monitoring program in Nassau and Suffolk Counties on Long Island, N.Y., the U.S. Geological Survey sampled water from selected wells for chloride and nitrate analysis from July 1975 to September 1976. By an agreement between the Geological Survey and three county-agency laboratories, two samples were collected at each site; one was sent to the Geological Survey Laboratory in Albany, N.Y., the other to a laboratory in the county from which the sample was taken. By agreement, all samples were analyzed by the Geological Survey, and no samples were analyzed by more than any one county laboratory.

The objective of this study was to investigate the uniformity of values reported by the different laboratories. Ideally, analyses of duplicate samples would produce identical results; however, differences in procedural factors such as sample-storage time and variations in analytical techniques may produce significant discrepancies. To provide a common basis for comparison of differences between laboratories, the U.S. Geological Survey data were used as a reference. This was done only for convenience of presentation, and it is emphasized that no greater accuracy is attributed to Survey analyses than to any of the others. The county laboratories that participated in the study are referred to as laboratories 1, 2, and 3.

The purpose of this report is to (1) describe the methods used by the four laboratories to analyze ground water for chloride and nitrate; (2) show in graphs and tables the degree of uniformity among laboratory results; and (3) discuss sample collection and storage procedures as possible sources of error.

PROCEDURES

Collection and Preservation Methods

Ninety wells were sampled for the study. At shallow (water-table) wells, where depth to water was less than 8 m below land surface, a rubber hose was lowered down the casing to below water level. Samples were taken by centrifugal pump after three times the volume of water in the well casing had been removed to insure a representative ground-water sample.

At the deeper wells, where depth to water was greater than 8 m below land surface, samples were taken by submersible pump lowered down the casing to between 3 and 6 m below water level. Again, samples were taken consecutively after three times the volume of water in the well casing was removed.

All samples were preserved in accordance with the established procedures outlined in Brown and others (1970). Samples to be analyzed for dissolved constituents were filtered in the field through a 0.45-µ filter. Samples for nitrate analysis (which require refrigeration) were packed with ice and maintained at about 4°C until time of analysis.

Analytical Methods

Laboratories 1 and 3 used the argentometric method to determine dissolved-chloride concentration (American Public Health Association and others, 1975), whereas the U.S. Geological Survey and Laboratory 2 used the mercuric thiocyanate method (Technicon Industrial Systems, 1974). All laboratories used the cadmium reduction method (American Public Health Association and others, 1975) to determine dissolved-nitrate concentration.

RESULTS

Graphs (figs. 1 and 2) were constructed to show (a) differences between values reported by the Geological Survey laboratory and a particular county laboratory (1, 2, or 3), and (b) systematic errors, if any. In figures 1 (chloride) and 2 (nitrate), all values reported by a particular county laboratory are subtracted from the corresponding paired value reported by the Geological Survey laboratory. These differences are plotted on the Y-axis, and the months in which the samples were collected and analyzed are plotted on the X-axis.

Ideally, if the values reported by the four laboratories were in perfect agreement, all data points would be grouped closely around the horizontal line of zero difference. Systematic errors would be seen as a grouping of data points elsewhere; for example, if a county laboratory consistently reported higher values than the Geological Survey laboratory, the differences would be clustered below the horizontal line of zero difference.

A paired-sample t-test (Campbell, 1967) was used to indicate whether the differences between county-laboratory analyses for chloride and nitrate analyses were significantly different from Geological Survey laboratory results. A confidence level of 0.95 was used. If a significant difference was found at this level, the chances are less than 5 percent that this difference was due to random factors. The mean and standard deviation of the differences are given in tables 1 and 2.

Differences between paired chloride values reported by county laboratories and the Geological Survey laboratory were generally small (fig. 1). However, a significant difference is apparent between paired chloride values reported by Laboratory 1 and the Geological Survey laboratory, and most values reported by the latter are less than those reported by laboratory 1. (See table 1.)

Differences between paired nitrate values reported by county laboratories and the Geological Survey laboratory were generally large (fig. 2). A significant difference (0.95 confidence level) is apparent between paired nitrate values reported by Laboratories 2 and 3 and those reported by the Geological Survey laboratory, and most nitrate values reported by the Geological Survey laboratory were greater than those reported by Laboratories 1 and 2. The mean and standard deviation of differences between paired nitrate values are given in table 2.

DISCUSSION

The significant differences between (1) chloride values reported by a county laboratory and the Geological Survey laboratory, and (2) nitrate values reported by two county laboratories and the Geological Survey laboratory, most likely result from variations in methods and duration of sample storage but could be due to error by analysts. Discrepancies resulting from differences in analytical methods, equipment, or interpretations are difficult to evaluate and are beyond the scope of this report.

Water samples were taken under a variety of climatic conditions throughout the study period. Because preservation of samples may be difficult in hot weather, one might expect a greater discrepancy among reported nitrate values during summer; however, no consistent relationship between time of year and uniformity of laboratory results is evident from the nitrate analyses.

Because the samples were taken consecutively from the source rather than from a large composite sample, some heterogeneity may have resulted. Ideally, all laboratories would analyze dissolved nitrate and chloride on split samples within 48 hours after sample collection. However, mailing and other delays could have caused degradation in some samples.

Table 1.--Mean and standard deviation of differences between chloride values reported by county laboratories and by U.S. Geological Survey laboratory

Comparison	Mean of differences (mg/L)	Standard deviation	Number of paired analyses
USGS and Laboratory 1	-1.36	2.64	70
USGS and Laboratory 2	-0.518	0.873	11
USGS and Laboratory 3	0.776	3.32	59

Table 2.--Mean and standard deviation of differences between nitrate values reported by county laboratories and by U.S. Geological Survey laboratory

Comparison	Mean of differences (mg/L)	Standard deviation	Number of paired analyses
USGS and Laboratory 1	0.190	1.21	63
USGS and Laboratory 2	0.561	0.821	11
USGS and Laboratory 3	0.970	3.64	58

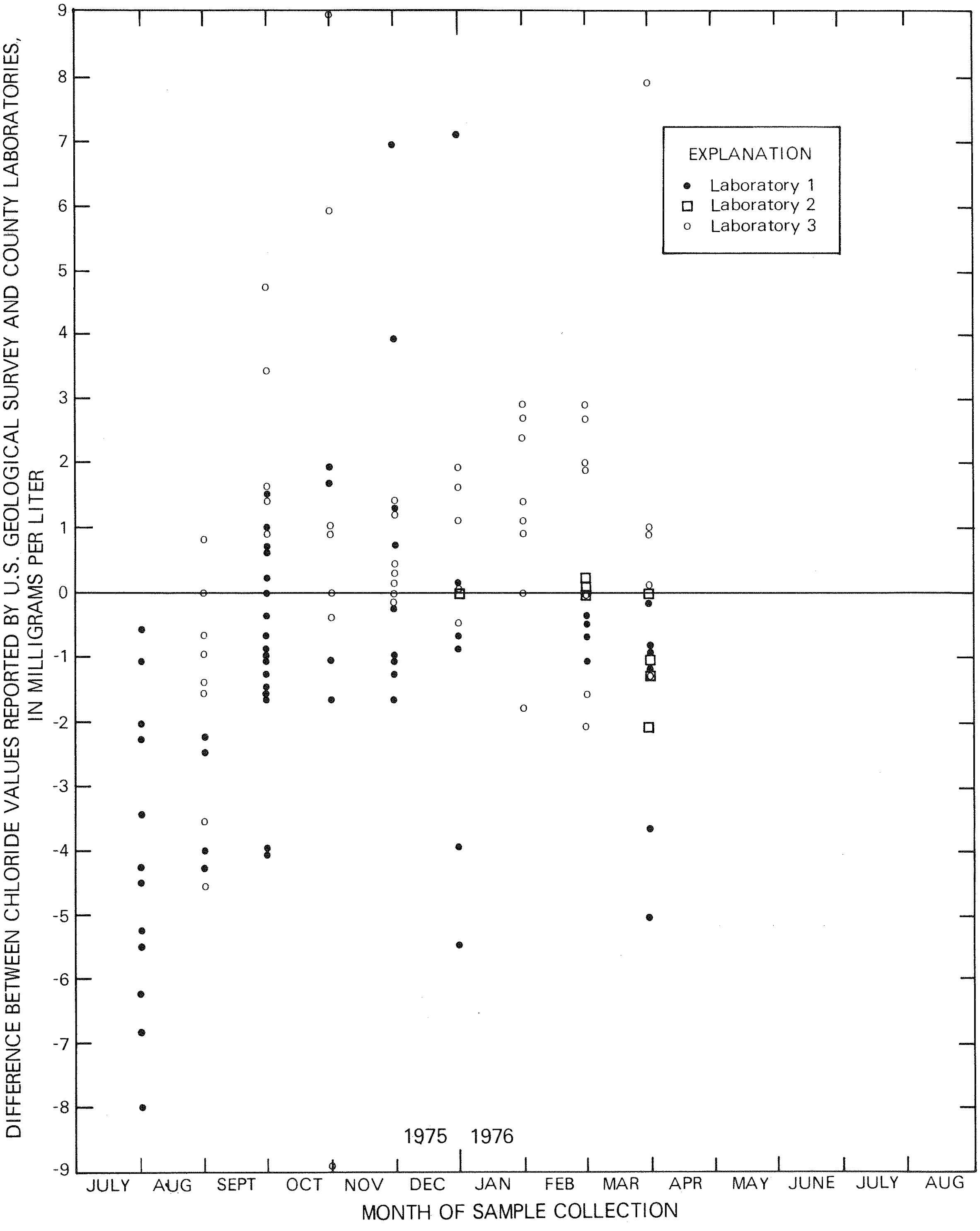

Figure 1.--Differences between paired chloride analyses determined by U.S. Geological Survey laboratory and each of three county laboratories.

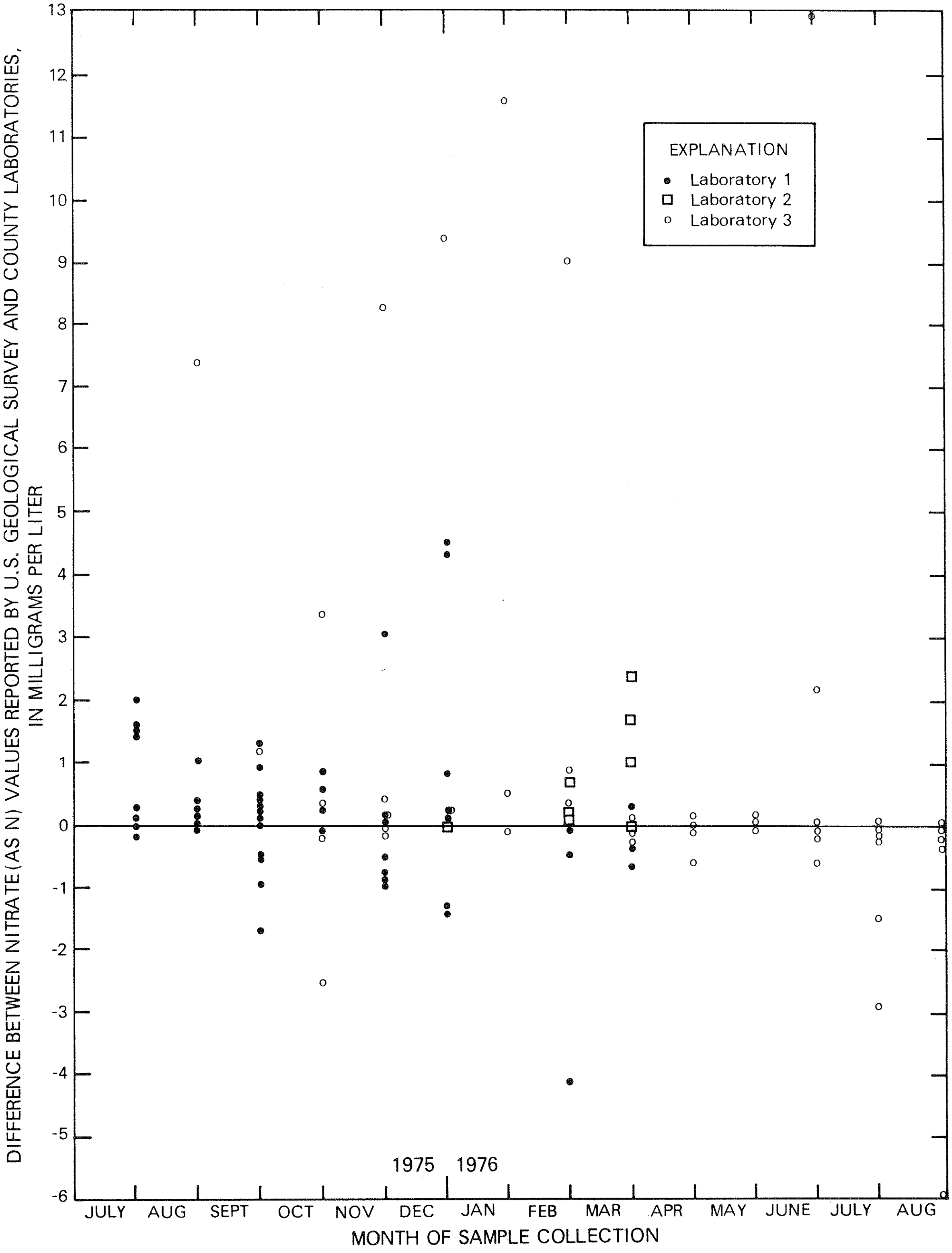

Figure 2.--Differences between paired nitrate analyses determined by U.S. Geological Survey laboratory and each of three county laboratories.

SUMMARY AND CONCLUSIONS

As part of a water-quality-monitoring program in Nassau and Suffolk Counties, water samples from selected wells were taken for chloride and nitrate analyses from July 1975 to September 1976. Two samples were collected at each site; one was sent to the U.S. Geological Survey laboratory in Albany, N.Y., the other to a laboratory in the county from which the sample was taken. Results were compared statistically with a paired-sample t-test to indicate the degree of uniformity among laboratory results.

Significant differences were noted between (1) chloride values reported by one of three county laboratories and the Geological Survey laboratory, and (2) paired nitrate values reported by two of the three county laboratories and the Geological Survey laboratory.

The lack of uniformity among laboratory results probably arises from variations in analytical methods and duration of sample storage. Delays due to mailing probably cause degradation in some samples. The considerable difference among results reported by the participating laboratories indicates a need for continuing participation in a quality-assurance program and use of firm quality control from time of sample collection through analysis so that differences can be evaluated. Because procedural and analytical effects may adversely affect the accuracy and precision of an analysis, extreme care must be exercised when using data from more than one laboratory to report areal and temporal distribution of a particular constituent.

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