

MINISTRY OF ENVIRONMENT, LANDS and PARKS  
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COMPARISON OF ANALYTICAL METHODS  
FOR pH USED IN THE LAKE TREND  
MONITORING PROGRAM

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## Executive Summary

This report describes the analytical precision of two methods of measuring pH—the Orion Ross combination pH electrode method and the Metrohm automated electrode method—in water samples collected for the Lake Trend Monitoring Program. The study involved:

- a comparison of precision measurements for each method to the Long Range Transport of Air Pollutants (LRTAP) interlaboratory acceptable error values, and to the U. S. Environmental Protection Agency intralaboratory precision objective;
- an evaluation of the effect of calibration methods on analytical variability;
- an evaluation of the change in reported pH values over time;
- a comparison of pH values reported for two sampling methods (1-L bottle and 60-mL syringe); and
- an evaluation of the data management methods for reported pH values.

We recommend that:

- the Orion Ross combination pH electrode method be used with the 60-mL syringe sampling method for data required to meet the LRTAP criterion for interlaboratory acceptable error values or the EPA intralaboratory precision objectives.
- the ionic strength of ambient water quality samples should be determined. If the ionic strength of the sample is *low*, then low ionic strength solutions should be used in the calibration procedure of the Metrohm automated electrode.
- water samples be analyzed for pH as soon as possible to minimize changes in pH values caused by gas exchange.
- reported values for pH using the two analytical methods be stored separately and evaluated separately.
- a data quality flag be associated with all values that were analyzed immediately after the Metrohm automated electrode was calibrated.
- reported values for pH using the two sampling methods should be stored separately and evaluated separately.

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## 1 INTRODUCTION

The Lake Trend Monitoring Program has used two analytical methods for measuring pH in ambient water samples and used two methods for collecting these samples. This report assesses the analytical methods and sampling methods, and recommends how future measurements of pH in ambient water samples should be sampled, analyzed, and stored in a database.

The purpose of the Lake Trend Monitoring Program is to assess the long-term effects of acid deposition on water quality and aquatic life (Swain 1991). Ambient water samples are collected monthly from four lakes located on Vancouver Island, one lake located on Saltspring Island, and one lake located on the lower mainland of B.C. The Quality Assurance and Quality Control (QA\QC) sampling portion of this program includes samples containing de-ionized water and ambient water. The de-ionized water is added to the 1-L sample bottle and sent to the laboratory for analysis. Ambient lake samples are collected from the six lakes, with the use of a 1-L sample bottle and a 60-mL syringe, and sent to the laboratory.

The monitoring program uses two analytical methods to measure pH (Dr. D. Jeffery, pers. comm.).<sup>1</sup> The Metrohm automated electrode consists of a glass indicating electrode and a platinum reference electrode. The electrodes are placed into the water sample and allowed to stabilize (i.e., allows the sample to interact with the indicating electrode and allows the electrode to compensate for the temperature of the sample) for a fixed period of time. The pH value is reported two minutes later. The electrodes are removed from the sample, rinsed in de-ionized water, and placed in the next water sample for analysis. Calibration of the reference electrode is done at the beginning of the day with solutions of pH 4 and 7. Samples with known pH values of 4, 7, and 10 are used to verify the accuracy of the readings from the electrode. Analyses of these samples are performed as required.

The Orion Ross combination pH electrode method is a manual method used to measure pH in water samples. Two aspects of this method differ from the Metrohm automated electrode method. First, the Orion Ross combination pH electrode method uses a stabilization period which varies with each sample. Second, the calibration method for the Orion Ross combination pH electrode is expanded to include pH 10.

Two methods of sample collection are used in this program. Water quality samples were collected with a 1-L sample bottle and with a 60-mL syringe. The syringe was used to minimize the amount of interaction between the sample and the atmosphere. These interactions may contribute to the variability in reported pH values.

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<sup>1</sup>. Details of the two analytical methods and calibration method were provided by Dr. D. Jeffery (Zenon Environmental Laboratories) to Mr. G. B. Holms (Water Quality Branch) on September 17, 1991 and May 20, 1992.

## 2 EXPERIMENTAL DESIGN

A "repeated measures" design was adopted to compare the two analytical methods and two sampling methods used for pH. This type of experimental design compares the difference between values that are collected sequentially. The difference may be measured within a series of values (e.g., the difference in pH values between sequential samples from a lake) or between a series of values (e.g., the difference in pH values reported over time). This assessment compared:

- the difference between reported values of pH from the two analytical methods,
- the variability in reported values of pH for each analytical method  
(i.e., standard deviation was used to express variability),
- the difference in reported values of pH over time for each analytical method, and
- the difference between reported values of pH from the two sampling methods.

The difference between reported values of pH from the two analytical methods was evaluated using a Student's paired *t-test* and the Long Range Transportation of Air Pollutants acid rain QC interlaboratory criterion for acceptable error between reported values (0.25) (Arafat and Aspila 1990). The pH values reported by the two analytical methods are considered *unique* when the *t-test* indicates that the differences are significant or when the difference exceeds the criterion.

The purpose of examining the variability within each analytical method was to determine the randomness of the error measurement. The distribution characteristics (i.e., normality, kurtosis, skewness) of repeated pH measurements were used to describe the variability in reported values of pH for each analytical method. A normal distribution is characterized by a constant mean value with no variability. If this is not the case, skewness and kurtosis are used to describe the shape of the distribution of values. This type of variability was also examined in this report using the U. S. Environmental Protection Agency intralaboratory precision objective (standard deviation for replicate samples in a laboratory should be  $\leq 0.05$  pH units) (Silverstein et al 1987) and Grubb's test for outliers (Taylor 1987). Values for pH reported by an analytical method are considered *unreliable* when the standard deviation is not normally distributed, contains outliers, or exceeds the objective.

A Student's paired *t-test* was used to evaluate the differences in pH values over time for ambient water analyzed by the two analytical methods. Values for pH reported by an analytical method are considered *unreliable* when the *t-test* indicates that the differences over time are significant.

The difference in reported pH values between the two sampling methods, for ambient water, was evaluated using a Student's paired *t-test*. Values for pH reported by a sampling method are considered *unique* when the *t-test* indicates that the differences are significant.

The purpose of using de-ionized water was to reduce the sources of variability in samples by minimizing the interactions between ions within the sample and their effect on the reported pH value. Buffering capacity of de-ionized water was not considered in the selection of this sample medium. Ten de-ionized samples (collected on September 21, 1990, and reported in Table 1 and



Figures 1 and 2) were used in these comparisons. The ionic strength of these samples and their reported pH values were lower than for the samples from ambient lakes. Therefore, additional ambient water samples were collected on four occasions to verify the results of the comparisons made using de-ionized water: September 21, 1990 (Table 1, Figures 1 and 2), November 8, 1990 (Table 2, Figures 3 to 6), and February 14 and August 2, 1990 (Table 4, Figures 7 and 8).

Samples collected from Maxwell Lake on February 14 and August 2, 1990, were used to compare the difference between sampling methods. These data are presented in Table 4 and Figures 7 and 8.

A comparison between evaluations using the reported pH values and those using an antilog transformation of the pH values indicated that the evaluations were similar. For clarity, the presentation of the comparisons uses the reported pH values.

### 3 VARIABILITY IN REPORTED pH VALUES FOR DE-IONIZED WATER

In September 1990, ten 1-L samples of de-ionized water were opened, sealed, and labelled over the course of the sampling trip: three samples at the start of the trip (labelled as "Sample 1 Day 1 Pre-Maxwell Lake"), four over the course of the sample trip (three samples were labelled as "Sample 1 Day 2 Pre-Maxwell Lake" and one sample was labelled as "Pre-Maxwell"), and three samples at the end of the sampling trip (labelled as "Sample 1 Day 1 Post Old Wolf Lake"). All the samples were analyzed for pH using the Orion Ross combination pH electrode method and the Metrohm automated electrode method. These samples were then re-analyzed three days later using the Orion Ross combination pH electrode method. The pH values reported from these samples were tabulated in Tables 1 and 3 and presented in Figures 1 and 2.

#### 3.1 Comparison of Analytical Methods

The differences in pH values between the two analytical methods are shown in Table 1 and Figure 1. Seven of the 10 samples reported higher values for pH when analyzed by the Orion Ross combination pH electrode method than when analyzed by the Metrohm automated electrode method.

The difference in pH values between the two analytical methods ranged from 0.055 to 0.623, with a mean difference of 0.147 and a standard deviation of the differences of 0.17. A paired Student's *t-test* ( $p = 0.023$ ) confirmed that the two analytical methods produced different results.

The LRTAP acid rain QC interlaboratory study lists an acceptable error of 0.25 between reported values (Arafat and Aspila 1990). This value was applied to the difference between pH values reported by the two analytical methods. In one sample, Sample 1 Day 2 Pre-Maxwell Lake, the difference (0.623) between pH values reported by the two analytical methods exceeded the acceptable error value. The influence of the difference between this one pair of pH values (6.268 measured by the Metrohm automated electrode and 5.645 measured by the Orion Ross electrode)

was sufficient for the *t-test* to conclude that the results from these analytical methods were different.

### 3.2 Variability within Analytical Methods

The variability of pH values analyzed using the Metrohm automated electrode method (standard deviation, 0.239) was greater than the variability in values analyzed using the Orion Ross combination pH electrode method (Table 1). The latter showed very little variability (standard deviation, 0.021).

A Grubb's test for outliers (Taylor 1987) identified the first value reported for the Metrohm automated electrode method as an outlier ( $T_{(10)} = 2.665$ , probability of the value not being an outlier :  $p < 0.1\%$ ).

The U.S. EPA intralaboratory precision objective (the standard deviation  $\leq 0.05$  pH units) (Silverstein et al 1987) was exceeded by values analyzed by the Metrohm automated electrode method. Even after the outlier identified by the Grubb's test was removed from the data series, the variability (0.089) remained four times greater than that found using the Orion Ross combination electrode method (0.021) and exceeded the U.S. EPA intralaboratory precision objective (the standard deviation  $\leq 0.05$  pH units). These facts suggest that the difference between pH values reported by the two analytical methods is primarily a function of the variability in values reported by the Metrohm automated electrode method.

The randomness of variability in pH values reported by each method was evaluated and presented (Table 3, Figures 1 and 2). The pH values for de-ionized water analyzed using the Orion Ross combination pH electrode method were normally distributed about the sample mean ( $p=0.44$ ). However, the shape of the distribution differed from that of a normal distribution (e.g., Bell curve) by having more values occurring in the intermediate region of the distribution than near the mean or tails ("platykurtic distribution"), and that the pH values for the intermediate region were less than the mean of the distribution ("positively skewed"). Reported values for pH using the Metrohm automated electrode method were not normally distributed about the sample mean ( $p < 0.01$ ). This reflects the influence of the first sample analyzed. This distribution differed from a normal distribution by having more reported values occurring near the mean and tails than in the intermediate regions ("leptokurtic distribution"), and were positively skewed.

### 3.3 Variability over Time

The water samples were analyzed for pH using the Orion Ross combination pH electrode method and then re-analyzed three days later (Table 1 and Figure 2). Reported pH values increased over time (mean value Day 0, 5.62; mean value Day 3, 5.64) with a mean difference of 0.021 and standard deviation of 0.017. The results of the *t-test* indicated that pH values reported on Day 0 differed from those reported on Day 3 ( $p = 0.041$ ).

#### 4 VARIABILITY IN REPORTED VALUES OF pH FOR AMBIENT LAKE WATER

Ambient water samples were analyzed for pH using the two analytical methods in 1990. A sample was collected from each of the three lakes (Maxwell Lake, Stocking Lake, and Spectacle Lake) in September, and 32 samples were collected from four lakes (Maxwell Lake, Stocking Lake, Old Wolf Lake, Spectacle Lake) in November. The pH values reported from these samples were tabulated in Tables 1 and 2 and are presented in Figures 3 to 6. The November series of samples were re-analyzed by the Metrohm automated electrode to compare changes in pH values over time. Six samples collected from one lake (Maxwell Lake) in February and in August were used to evaluate the difference between the sampling methods. The pH values reported from these samples are presented in Figures 7 and 8 and Table 4.

##### 4.1 Comparison of Analytical Methods

A comparison of analytical methods was made using pH values from 1-L bottle samples. Values for pH analyzed using the Orion Ross combination pH electrode method were consistently higher than those analyzed using the Metrohm automated electrode method for samples collected in September, November, and February. In August, values for pH using the Metrohm automated electrode method were higher than those reported using the Orion Ross combination pH electrode method. The difference in pH values between analytical methods for ambient lake samples ranged from 0.215 to 0.528 in September, from 0.027 to 0.27 in November, from 0.08 to 0.21 in August, and from 0.011 to 0.147 in February.

The results of the *t*-test indicated that the pH values reported by the two analytical methods were significantly different (November:  $p=0.0001$ ,  $p=0.007$ ; August:  $p=0.0012$ , February:  $p=0.0042$ ).

The acceptable error of 0.25 between reported values, set by the LRTAP acid rain QC interlaboratory study (Arafat and Aspila 1990), was approximated on one occasion in November and exceeded on three occasions, twice in September and once in November.

##### 4.2 Comparison of Sampling Methods

A preliminary comparison between pH values reported for the 60-mL syringe sample method and those of the 1-L bottle sample method was done at each lake in November 8, 1990 (Table 2 Figures 3 to 6). In this comparison, pH values from eight 1-L samples were compared to one value from a 60-mL syringe sample. The comparison showed that the pH from the 60-mL syringe sample:

- was approximated by the mean pH value reported using the Orion Ross combination pH electrode method for 1-L samples collected in Maxwell Lake;
- was greater than those reported using either the Orion Ross combination pH electrode method or the Metrohm automated electrode method for 1-L samples collected in Stocking Lake and in Old Wolf Lake; and
- was greater than those reported using the Metrohm automated electrode method and less than those reported using the Orion Ross combination pH electrode

method in 1-L samples collected in Spectacle Lake.

The differences between pH values reported by the two sampling methods were greatest when the samples were analyzed by both analytical methods (i.e., 1-L samples analyzed with the Metrohm automated electrode method and 60-mL syringe samples analyzed with the Orion Ross combination pH electrode method). The differences in pH values reported for 1-L bottle samples analyzed by the Metrohm automated electrode method and 60-mL syringe samples analyzed by the Orion Ross combination pH electrode method were similar to the differences reported between analytical methods for samples collected in November and for de-ionized water samples in September. These results indicate that sample method and analyzing method have a compounding effect on the reported pH values.

The pH values reported for samples analyzed using the Orion Ross combination pH electrode method were combined (eight values reported using 1-L sample method and one reported value using the 60-mL syringe sample method) and presented in Figures 3 to 6. A Grubb's test for outliers (Taylor 1987) identified the value reported using the syringe sample method from Spectacle Lake as an outlier ( $T_{(8)} = 2.31$ , risk of false rejection 5%). This preliminary comparison indicates that the sampling method has an effect on pH values.

A second comparison of the pH values reported by the two sample methods is presented in Table 4, and Figures 7 and 8. This comparison evaluates pH values reported from replicate samples using the two sample methods (1-L bottle samples and the 60-mL syringe samples). The acceptable error of 0.25 between reported values, set by the LRTAP acid rain QC interlaboratory study was exceeded by one value in August (0.27). This difference was between the value reported for a 1-L bottle sample analyzed using the Metrohm automated electrode method and the value reported for a 60-mL syringe sample analyzed using the Orion Ross combination pH electrode method. The U.S. EPA intralaboratory precision objective (the standard deviation  $\leq 0.05$  pH units) (Silverstein et al 1987) was exceeded by 1-L bottle samples analyzed using the Metrohm automated electrode method (standard deviation, 0.055) and by 60-mL syringe samples analyzed with the Orion Ross combination pH electrode method (standard deviation, 0.063) collected from Maxwell Lake in August.

The results of the paired Student's *t*-test concluded that:

- The pH values reported for 1-L bottle samples analyzed using the Metrohm automated electrode method were different than those values reported for 60-mL syringe samples analyzed by the Orion Ross combination pH electrode method (August samples,  $p=0.0001$ ; February samples,  $p=0.002$ ).
- The pH values reported for the 1-L bottle samples and the two analyzing methods were different (February samples,  $p=0.004$ ; August samples  $p=0.001$ ).
- The pH values reported for 1-L bottle samples analyzed using the Orion Ross combination pH electrode method were similar to values reported for 60-mL syringe samples analyzed using the Orion Ross combination pH electrode method in February ( $p=0.11$ ). The values reported by these sampling procedures were different in August ( $p=0.023$ ).

In the two comparisons, a larger difference between pairs of pH values was observed when both the sampling methods and the analytical methods were different. This difference is reduced when the two sampling methods are analyzed using the Orion Ross combination pH electrode method. The replicate sampling comparison indicated that the sampling method had a minor effect on reported pH values compared to the analytical method.

#### 4.3 Variability within Analytical Methods

A comparison of variability within analytical methods was made using pH values from 1-L bottle samples. The variability within analytical methods was lower in samples analyzed by the Orion Ross combination pH electrode method than in samples analyzed by the Metrohm automated electrode method (Tables 2 and 4). Variability, expressed in terms of standard deviations, ranged from 0.015 to 0.027 using the Orion Ross combination pH electrode method, and from 0.03 to 0.055 using the Metrohm automated electrode method.

The U.S. EPA intralaboratory precision objective for replicate samples analyzed in a laboratory (standard deviation of 0.05 pH units) was exceeded by values from the 60-mL syringe samples collected from Maxwell Lake in August 1990 and analyzed using the Orion Ross combination pH electrode method. The objective was also exceeded by values from replicate 1-L bottle samples collected from Maxwell Lake in August 1990 and analyzed using the Metrohm automated electrode method. However, these results were reported to one significant figure rather than two or three significant figures used for all the other analyses. For this reason the results reported for replicate 1-L bottle samples collected from Maxwell Lake in August 1990 and analyzed using the Metrohm automated electrode method have been excluded from this comparison. Factors which could cause variability to exceed this objective are:

- the low ionic strength of the lake samples,
- the calibration methods of the electrodes, and
- the period of time the indicating electrode is exposed to the sample before a reading is made (i.e., the time period is predetermined for all samples analyzed by Metrohm automated electrode method, whereas this time period varies for samples analyzed by the Orion Ross combination pH electrode method).

The ionic strength of the lake samples (Old Wolf Lake,  $2.54 \times 10^{-4}$ ; Stocking Lake,  $3.55 \times 10^{-4}$ ; Spectacle Lake,  $5.45 \times 10^{-4}$ ; Maxwell Lake,  $6.18 \times 10^{-4}$ ) were three orders of magnitude lower than the ionic strength of the buffer solutions (pH 4, 0.5; pH 7, 0.14; pH 10, 0.116) used to calibrate the electrode. This difference may contribute to a lower pH value being reported by the electrodes in two ways. First, the hydrogen ions will not dissociate as freely when in a high ionic strength solution to a weaker ionic strength solution. Second, time required for the sample to equilibrate may be greater than the predetermined time that the sample is exposed to the indicating electrode when using the Metrohm automated electrode method.

The method for analyzing pH in ambient water lake samples by the Metrohm automated electrode method was modified between the September and November 1990 samples to reduce the difference between the value reported for the first sample and those reported in subsequent

analyses. The method was modified by having two samples of de-ionized water analyzed before each series of samples was analyzed by the Metrohm automated electrode method. The purpose of the change was to extend the stabilizing period of the automated electrode after calibration.

A Grubb's test (Taylor 1987) identified several outliers:

- the first samples analyzed using the Metrohm automated electrode method from Maxwell Lake ( $T_{(8)} = 2.24$ ), Stocking Lake ( $T_{(8)} = 2.00$ ), and Old Wolf Lake ( $T_{(8)} = 2.00$ ) in November 1990 at a 5% risk of false rejection;
- the sixth 60-mL syringe sample analyzed using the Orion Ross combination pH electrode method from Maxwell Lake ( $T_{(6)} = 1.91$ ) in August 1990 at a 3% risk of false rejection; and
- the fifth 1-L bottle sample analyzed using the Metrohm automated electrode method from Maxwell Lake ( $T_{(6)} = 1.83$ ) in February 1990 at a 4 % risk of false rejection.

The first set of outliers indicate that the modification to the method of analysis using the Metrohm automated electrode method did not eliminate the bias on the first sample after calibration. Only one pH value analyzed using the Orion Ross combination pH electrode method was identified as an outlier.

The randomness of the variability in pH values reported by each analytical method was evaluated (Table 3, Figures 3 to 6). The pH values analyzed using the Orion Ross combination pH electrode method were normally distributed about the sample mean for ambient water from Old Wolf Lake ( $p=0.30$ ), Maxwell Lake ( $p=0.55$ ), and Stocking Lake ( $p=0.63$ ). The influence of the fifth sample analyzed caused the distribution of water samples from Spectacle Lake ( $p=0.03$ ) not to be normally distributed about the mean. The distribution of these values showed more reported values near the mean and tails than in the intermediate regions, and a pH value for the intermediate region that was greater than the mean of the distribution ("negatively skewed").

Values of pH reported for ambient water from Old Wolf Lake ( $p=0.354$ ) and Spectacle Lake ( $p=0.646$ ) analyzed using the Metrohm automated electrode method were normally distributed about the sample mean. The pH values for ambient water from Maxwell Lake ( $p < 0.01$ ) and Stocking Lake ( $p=0.022$ ) using the Metrohm automated electrode method were not normally distributed about the sample mean. This is attributed to the influence of the first sample analyzed. The characteristics of these latter distributions were similar to those observed using the Orion Ross combination pH electrode method for Spectacle lake.

The randomness of the variability in pH values reported, using the Metrohm automated electrode for 1-L bottle samples and the Orion Ross combination pH electrode for 1-L bottle samples and 60-mL syringe samples, was shown in Table 5 and Figures 7 and 8. The variability of pH values was normally distributed for all samples collected using:

- the 1-L bottle samples analyzed by the Orion Ross combination pH electrode method ( $p=0.813$ ,  $p=0.98$ );
- the 60-mL syringe samples analyzed by the Orion Ross combination pH electrode method ( $p=0.680$ ,  $p=0.22$ ); and

- the 1-L bottle samples analyzed by Metrohm automated electrode method ( $p=0.202$ ).

Only the samples collected in August and analyzed using the Metrohm automated electrode method were not normally distributed. A step decrease of 0.1 pH units in 1-L bottle samples was observed between samples 1, 2, 3 and samples 4, 5, 6.

#### 4.4 Variability over Time

The pH values in the November 1990 ambient lake water samples were measured by the Metrohm automated electrode. Sample analyses were then immediately repeated to evaluate changes over time (Table 2). The mean pH values were lower (mean difference values ranged from 0.04 to 0.07 pH units) in the second series for all four lakes. The standard deviations either increased over time (in samples from Maxwell Lake and Stocking Lake) or were similar over time (in samples from Old Wolf Lake and Spectacle Lake).

Both series of samples analyzed were equal to or less than the U.S. EPA intralaboratory precision objective (the standard deviation  $\leq 0.05$  pH units).

The results of the *t-test* indicated that pH values were significantly different over time in samples collected at Maxwell Lake ( $p=0.0001$ ), Stocking Lake ( $p=0.0001$ ), Old Wolf Lake ( $p=0.0002$ ), and Spectacle Lake ( $p=0.038$ ).

## 5 CONCLUSIONS

Values for pH analyzed by the Orion Ross combination pH electrode method were higher than those analyzed by the Metrohm automated electrode method in 7 of 10 de-ionized water samples and in 42 of 47 ambient lake samples. The reported pH values for each method of analysis are *unique* because:

- the differences between the values were significant; and
- the LRTAP acid rain QC interlaboratory study's acceptable error between reported values of 0.25 was exceeded by one de-ionized sample (10% of the de-ionized water samples collected) and three samples (approximately 7% of the ambient lake samples collected) from four lakes.

Reported pH values using the Metrohm automated electrode method are considered *unreliable* because the data series contained outliers and the variability was high and not always random. The first sample analyzed contributed a significant amount to this variability. Increased variability in these samples is attributed to:

- the differences in ionic strengths between the low ionic strength lake samples and the ionic strengths of the calibration solutions;
- the stabilizing period before measuring pH values; and
- the calibration procedures of the electrode.

Reported values for pH from 1-liter bottle samples using both analytical methods changed over time.

Consistent trends were absent between pH values from the two sampling methods. The two sampling methods are considered *unique* because:

- the differences between pH values from 1-L bottle samples and 60-mL syringe samples were significant;
- the variability within analytical methods were different and exceeded the U.S. EPA intralaboratory precision objective values (standard deviation  $\leq 0.05$  pH units); and
- the acceptable error of 0.25 between values, set by the LRTAP acid rain QC interlaboratory study, was exceeded.



## 6 RECOMMENDATIONS

We recommend that:

- the Orion Ross combination pH electrode method be used with the 60-mL syringe sampling method for data required to meet the LRTAP criterion for interlaboratory acceptable error values or the EPA intralaboratory precision objectives.
- the ionic strength of ambient water quality samples should be determined. If the ionic strength of the sample is *low*, then low ionic strength solutions should be used in the calibration procedure of the Metrohm automated electrode.
- water samples be analyzed for pH as soon as possible to minimize changes in pH values caused by gas exchange.
- reported values for pH using the two analytical methods be stored separately and evaluated separately.
- a data quality flag be associated with all values that were analyzed immediately after the Metrohm automated electrode was calibrated.
- reported values for pH using the two sampling methods should be stored separately and evaluated separately.

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TABLE 1: Comparison of pH values from analytical Methods for the Lake Trend Monitoring Program. Samples collected on September 21, 1990

Sample type	Samples analyzed immediately				Samples analyzed over time by the Orion Ross combination pH electrode method			
	Metohm automated electrode method	Orion Ross combination electrode method	Order of analyses for both methods	Differences between analytical methods	Order of analyses for both methods	Day 0	Day 3	Differences between analytical Days
PRE-MAXWELL	5.484	5.608	10	0.124	13	5.608	5.65	0.042
SAMPLE1 DAY1 POST OLD WOLF	5.517	5.622	6	0.105	12	5.622	5.61	0.012
SAMPLE1 DAY1 POST OLD WOLF	5.541	5.618	5	0.077	11	5.618	5.63	0.012
SAMPLE1 DAY1 POST OLD WOLF	5.704	5.604	4	0.1	10	5.604	5.62	0.016
SAMPLE1 DAY2 PRE MAXWELL LK.	5.472	5.59	9	0.118	9	5.59	5.62	0.03
SAMPLE1 DAY2 PRE MAXWELL LK.	5.531	5.602	8	0.071	8	5.602	5.66	0.058
SAMPLE1 DAY2 PRE MAXWELL LK.	5.497	5.63	7	0.133	7	5.63	5.65	0.02
SAMPLE1 DAY2 PRE MAXWELL LK.	5.593	5.648	3	0.055	6	5.648	5.65	0.002
SAMPLE1 DAY2 PRE MAXWELL LK.	5.706	5.646	2	0.06	5	5.646	5.68	0.014
SAMPLE1 DAY2 PRE MAXWELL LK.	6.268	5.645	1	0.623	4	5.645	5.65	0.005
Mean	5.6313	5.6213		0.147		5.62	5.64	0.021
Standard Deviation (A) (B)	0.239	0.021		0.170		0.021	0.018	0.017
Mean *	5.561			0.094				
Standard Deviation * (A) (B)	0.089			0.029				
Ambient lake samples								
Maxwell Lake	7.002	7.53	11	0.528	3	7.53	7.47	0.06
Stocking Lake	7.168	7.455	12	0.287	2	7.455	7.32	0.135
Spectacle Lake	7.175	7.39	13	0.215	1	7.39	7.39	0

\* Mean and Standard Deviations calculations excluding sample value 6.268.

Grubb's test for outlying values(Taylor 1987) identified this value as an outlier ( $T(10)=2.665$ ).

A. LRTAP L-24 acid rain QC interlaboratory study

use an acceptable error between reported values of 0.25 (Arafat and Aspila 1990).

B. EPA intralaboratory precision objective for pH measured in an analytical

laboratory is a standard deviation of 0.05 pH units. (Silverstein et al 1987)

TABLE 2: Comparison of pH values from analytical methods for the Lake Trend Monitoring Program. Samples collected on November 8, 1990

Sample Type: Ambient lake water Discrete water sample	1- L bottle samples analyzed immediately				1-L bottle samples analyzed over time by the Metrohm automated electrode method			
	Metrohm automated electrode method	Orion Ross combination electrode method	Order of analyses for both methods	Differences between analytical methods	Order of analyses for both methods	Run 1	Run 2	Differences between analytical Runs
Maxwell Lake  60-mL syringe sample analyzed using the Orion Ross combination electrode pH value: 7.35	7.089	7.31	1	0.221	1	7.089	7.01	0.079
	7.18	7.36	2	0.18	2	7.18	7.105	0.075
	7.194	7.36	3	0.166	3	7.194	7.124	0.07
	7.203	7.34	4	0.137	4	7.203	7.141	0.062
	7.208	7.32	5	0.112	5	7.208	7.149	0.059
	7.225	7.33	6	0.105	6	7.225	7.158	0.067
	7.22	7.36	7	0.14	7	7.22	7.167	0.053
	7.229	7.34	8	0.111	8	7.229	7.167	0.062
	Mean	7.19	7.34	0.15		7.19	7.13	0.07
	Standard Deviation	0.045	0.019	0.040		0.045	0.052	0.009
Stocking Lake  60-mL syringe sample analyzed using the Orion Ross combination electrode pH value: 7.26	6.98	7.25	9	0.27	9	6.98	6.882	0.098
	7.025	7.2	10	0.175	10	7.025	6.958	0.067
	7.06	7.21	11	0.15	11	7.06	6.977	0.083
	7.056	7.22	12	0.164	12	7.056	7.001	0.055
	7.049	7.17	13	0.121	13	7.049	6.996	0.053
	7.056	7.19	14	0.134	14	7.056	7.005	0.051
	7.061	7.2	15	0.139	15	7.061	6.998	0.063
	7.072	7.19	16	0.118	16	7.072	6.999	0.073
	Mean	7.04	7.20	0.16		7.04	6.98	0.07
	Standard Deviation	0.030	0.024	0.049		0.030	0.041	0.016
Old Wolf Lake  60-mL syringe sample analyzed using the Orion Ross combination electrode pH value: 6.92	6.708	6.93	17	0.222	17	6.708	6.677	0.031
	6.81	6.85	18	0.04	18	6.81	6.737	0.073
	6.78	6.88	19	0.1	19	6.78	6.742	0.038
	6.785	6.91	20	0.125	20	6.785	6.749	0.036
	6.839	6.91	21	0.071	21	6.839	6.784	0.055
	6.806	6.86	22	0.054	22	6.806	6.796	0.01
	6.835	6.88	23	0.045	23	6.835	6.792	0.043
	6.853	6.88	24	0.027	24	6.853	6.801	0.052
	Mean	6.80	6.8875	0.09		6.80	6.76	0.04
	Standard Deviation	0.046	0.027	0.064		0.046	0.042	0.019
Spectacle Lake  60-mL syringe sample analyzed using the Orion Ross combination electrode pH value: 7.20	7.055	7.3	25	0.245	25	7.055	7.008	0.047
	7.092	7.28	26	0.188	26	7.092	7.075	0.017
	7.103	7.31	27	0.207	27	7.103	7.094	0.009
	7.137	7.29	28	0.153	28	7.137	7.11	0.027
	7.139	7.25	29	0.111	29	7.139	7.127	0.012
	7.146	7.3	30	0.154	30	7.146	7.117	0.029
	7.148	7.3	31	0.152	31	7.148	7.061	0.087
	7.182	7.3	32	0.118	32	7.182	7.079	0.103
	Mean	7.13	7.29	0.17		7.13	7.08	0.04
	Standard Deviation	0.040	0.019	0.045		0.040	0.038	0.035
A. LRTAP L-24 acid rain QC interlaboratory study use an acceptable error between reported values of 0.25 (Arafat and Aspila 1990).				B. EPA intralaboratory precision objective for pH measured in an analytical laboratory is a standard deviation of 0.05 pH units. (Silverstein et al 1987)				

TABLE 3: Comparison of the distribution in pH values from analytical methods for the Lake Trend Monitoring Program.  
Samples collected on September 21, 1990 and November 8, 1990

Sample Type: Ambient lake water Discrete water sample Lake name	Metrohm automated electrode method 1-L bottle samples	Orion Ross combination electrode method 1-L bottle samples
Maxwell Lake November,1990	Sample #1 reported a pH value approximating (Mean - (2*STD)) Kurtosis= 5.075 Skewness= - 2.143  Quantiles 10th 25th Mean Median 75th 90th 7.089 7.184 7.194 7.206 7.224 7.229  Sample #1 reported a pH value approximating (Mean - (2*STD)) Kurtosis= 3.50 Skewness= - 1.858  Quantiles 10th 25th Mean Median 75th 90th 6.98 7.031 7.089 7.184 7.061 7.072	Sample #1 reported a pH value between (Mean - (STD)) and (Mean + (2*STD)) Kurtosis= -1.27; Skewness= - 0.319  Quantiles 10th 25th Mean/ Median 75th/90th 7.31 7.323 7.34 7.36  Sample #5 reported a pH value between (Mean - (2*STD)) and (Mean + (2*STD)) Kurtosis= 1.457 Skewness= 0.837  Quantiles 10th 25th Mean/ Median 75th 90th 7.17 7.19 7.20 7.218 7.25
Stocking Lake November,1990	Sample #1 reported a pH value approximating (Mean - (2*STD)) Kurtosis= 1.914 Skewness= - 1.234  Quantiles 10th 25th Mean Median 75th 90th 6.708 6.78 6.802 6.808 6.838 6.853	Samples #1 and #2 reported a pH value between (Mean + (STD)) and (Mean + (2*STD)) and (Mean - (STD)) and (Mean - (2*STD)) Kurtosis= - 0.888 Skewness= 0.236  Quantiles 10th 25th Mean/ Median 75th 90th 6.85 6.865 6.88 6.91 6.93
Old Wolf Lake November,1990	Samples #1 and #8 reported pH values between (Mean - (STD)) and (Mean - (2*STD)) and (Mean + (STD)) and (Mean + (2*STD)) Kurtosis= 0.166 Skewness= - 0.569  Quantiles 10th 25th Mean Median 75th 90th 7.055 7.095 7.125 7.138 7.148 7.182	Sample #5 reported a pH values approximating (Mean - (2*STD)) Sample #3 reported a pH values approximating (Mean - (STD)) Kurtosis= 3.404 Skewness= - 1.772  Quantiles 10th 25th Mean Median 75th 90th 7.25 7.285 7.291 7.3 7.3 7.31
Spectacle Lake November,1990	Sample #1 reported a pH value exceeding (Mean + (2*STD)) Kurtosis= 6.776 Skewness= 2.502  Quantiles 10th 25th Mean Median 75th 90th 5.473 5.494 5.536 5.631 5.705 6.212	Samples #1, #2, #3 reported pH values between (Mean - (STD)) and (Mean - (2*STD)) Sample #9 reported pH values between (Mean + (STD)) and (Mean + (2*STD)) Kurtosis= - 1.375 Skewness= 0.042  Quantiles 10th 25th Median/ Mean 75th 90th 5.591 5.604 5.62 5.645 5.648
De-ionized water September, 1990		

TABLE 4: Comparison of pH values from analytical Methods for the Lake Trend Monitoring Program. Samples collected on February 14, 1990 and August 2, 1990 from Maxwell Lake.

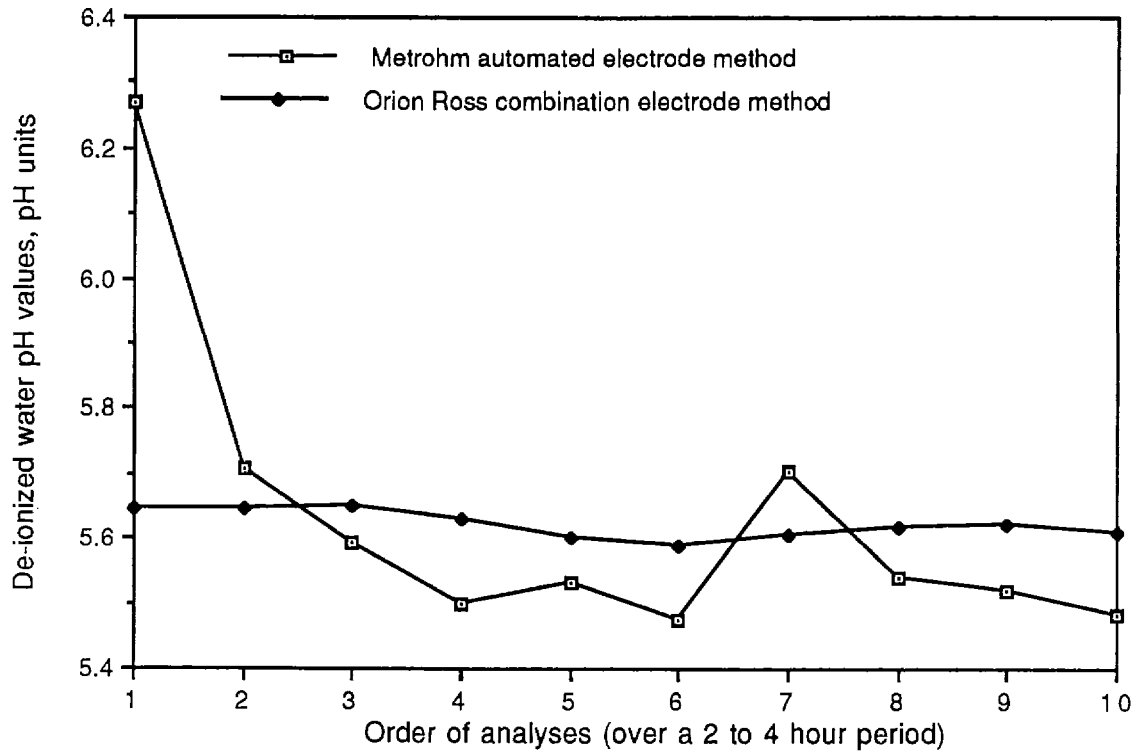
Samples collected on February 14, 1990										Samples collected on August 2, 1990											
Metrohm automated electrode method 1-L bottle sample	Orion Ross combination electrode method 1-L bottle sample			Order of analyses for all methods			Difference between analytical results from the 60-mL syringe sample and analytical results 1-L bottle sample			Metrohm automated electrode method 1-L bottle sample			Orion Ross combination electrode method 60-mL syringe 1-L bottle sample			Order of analyses for all methods			Difference between analytical results from the 60-mL syringe sample and analytical results 1-L bottle sample		
6.961	7.08	7.16	7.19	7.23	1	0.199	0.080	0.119	7.6	7.39	7.37	7.37	7.37	1	0.23	0.02	0.21				
6.973	7.12	7.12	7.12	7.12	2	0.147	0.000	0.147	7.6	7.4	7.37	7.37	7.37	2	0.23	0.03	0.2				
7.011	7.09	7.14	7.14	7.14	3	0.129	0.050	0.079	7.6	7.44	7.42	7.42	7.42	3	0.18	0.02	0.16				
7.006	7.11	7.11	7.11	7.11	4	0.094	0.104	0.104	7.5	7.41	7.34	7.34	7.34	4	0.16	0.07	0.09				
7.079	7.09	7.12	7.12	7.12	5	0.041	0.030	0.011	7.5	7.42	7.35	7.35	7.35	5	0.15	0.07	0.08				
6.977	7.1	7.11	7.11	7.11	6	0.133	0.010	0.123	7.5	7.36	7.23	7.23	7.23	6	0.27	0.13	0.14				
7.00	7.10	7.13	7.13	7.13	Mean	0.12	0.03	0.10	7.55	7.40	7.35	7.35	7.35	Mean	0.20	0.06	0.15				
0.043	0.015	0.022	0.022	0.022	Standard Deviation	0.053	0.030	0.048	0.055	0.027	0.063	0.063	0.063	Standard Deviation	0.047	0.043	0.054				

A. LRTAP L-24 acid rain QC interlaboratory study use an acceptable error between reported values of 0.25 (Aratat and Aspila 1990).

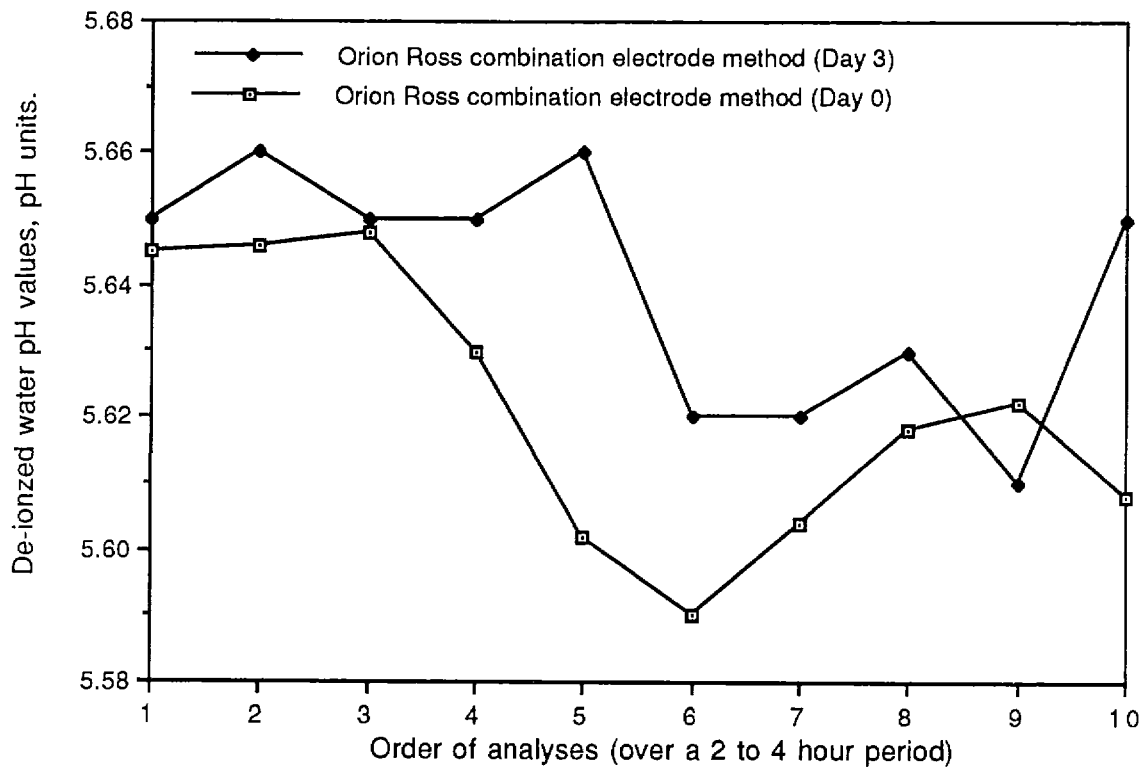
B. EPA intralaboratory precision objective for pH measured in an analytical laboratory is a standard deviation of 0.05 pH units. (Silverstein et al 1987)

TABLE 5: Comparison of the distribution in pH values from analytical methods for the Lake Trend Monitoring Program.  
Samples collected on February 14, 1990 and August 2, 1990

Sample Type: Ambient lake water Discrete water sample		Metrohm automated electrode method		Orion Ross combination electrode method	
Lake name					
1-L bottle sample Maxwell Lake February 14, 1990		Sample #5 reported a pH value approximating (Mean + (STD)) and (Mean + (2*STD)) Kurtosis= 2.136 Skewness= 1.42		Sample #2 reported a pH value approximating (Mean + (STD)) and (Mean + (2*STD)) Kurtosis= -0.859 Skewness= 0.418	
		Quantiles 10th 25th Median Mean 75th 90th 6.96 6.97 6.991 7.001 7.01 7.079		Quantiles 10th 25th Median Mean 75th 90th 7.08 7.09 7.095 7.098 7.11 7.12	
60-mL syringe sample Maxwell Lake February 14, 1990				Samples #1 reported a pH value between (Mean + (STD)) and (Mean + (2*STD)) Kurtosis= 0.068 Skewness= 0.795	
				Quantiles 10th 25th Mean/Median 75th 90th 7.10 7.11 7.12 7.14 7.16	
1-L bottle sample Maxwell Lake August 2, 1990		Kurtosis= - 3.33 Skewness= 0.00		Samples #3 reported a pH value between (Mean + (STD)) and (Mean + (2*STD)) Kurtosis= 0.586 Skewness= - 0.435	
		Quantiles 10th 25th Mean/ Median 75th 90th 7.5 7.5 7.55 7.6 7.6		Quantiles 10th 25th Median 75th 90th 7.36 7.39 7.403 7.405 7.42 7.44	
60-mL syringe sample Maxwell Lake August 2, 1990				Samples #3 reported a pH value between (Mean + (STD)) and (Mean + (2*STD)), Sample #6 reported a pH value between (Mean - (STD)) and (Mean - (2*STD)) Kurtosis= 3.02 Skewness= - 1.372	
				Quantiles 10th 25th Median 75th 90th 7.23 7.34 7.35 7.36 7.37 7.42	



**FIGURE 1: Comparison of pH values analyzed by two analytical procedures  
Samples collected September 21, 1990.**



**FIGURE 2: Comparison of pH values analyzed over time  
Samples collected September 21, 1990.**



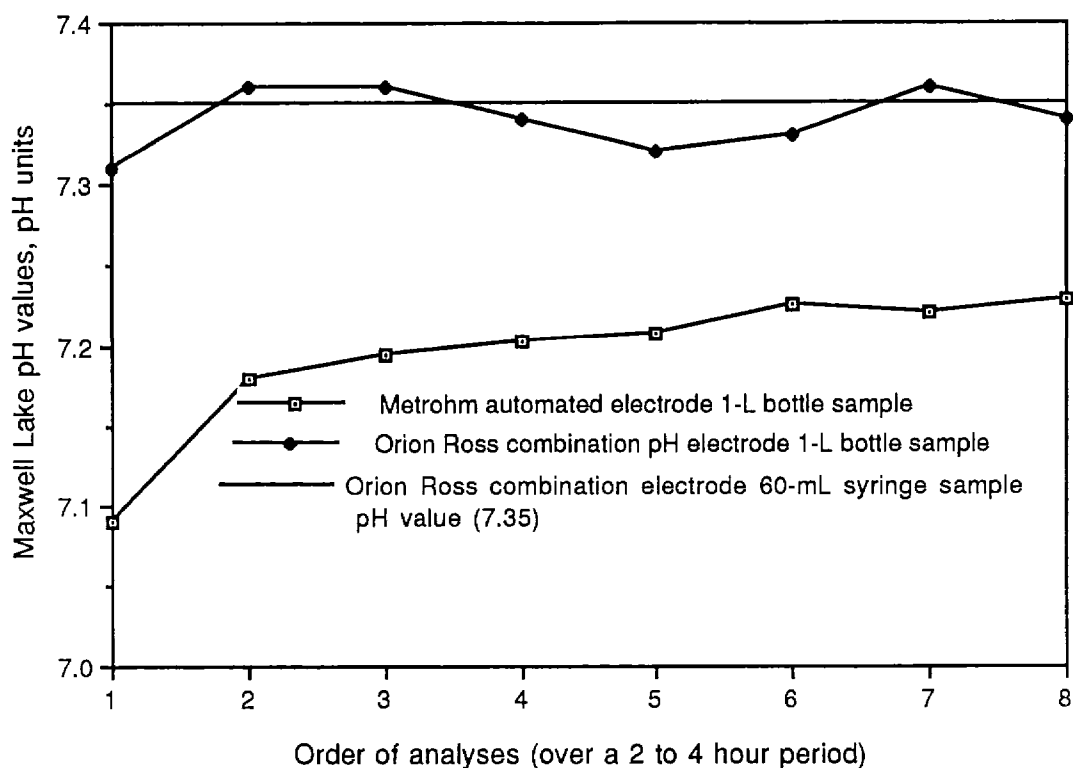


FIGURE 3: Comparison of pH values analyzed by two analytical methods and two sampling methods for Maxwell Lake samples, November 8, 1990.

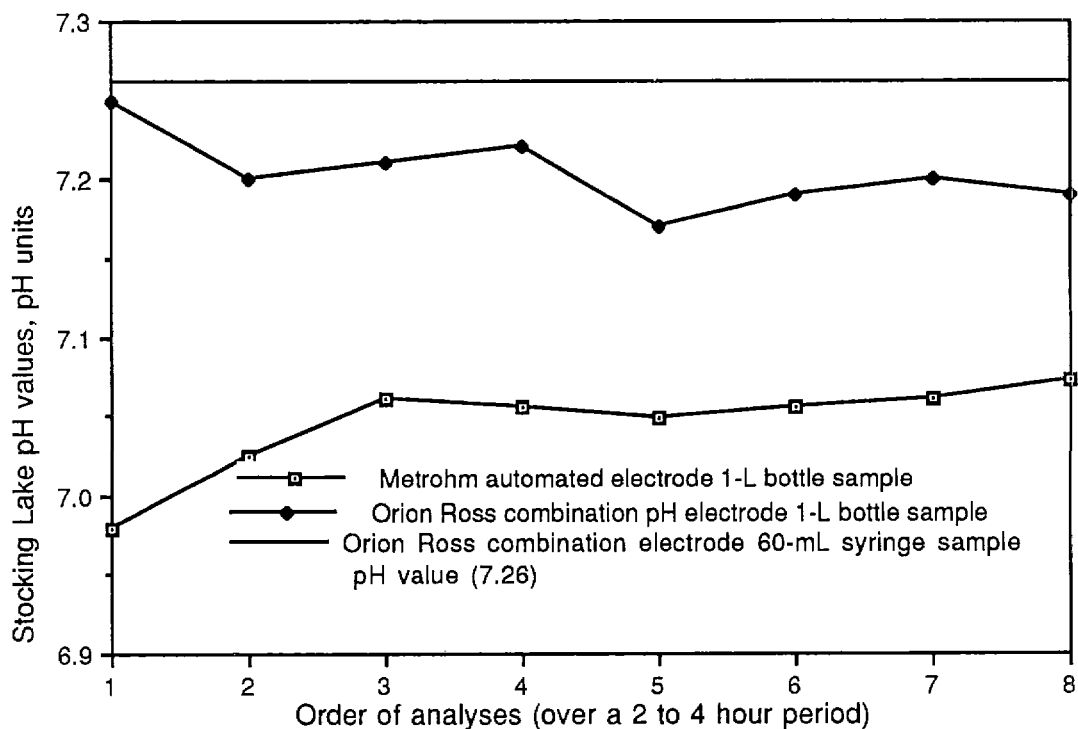


FIGURE 4: Comparison of pH values analyzed by two analytical methods and two sampling methods for Stocking Lake samples, November 8, 1990.

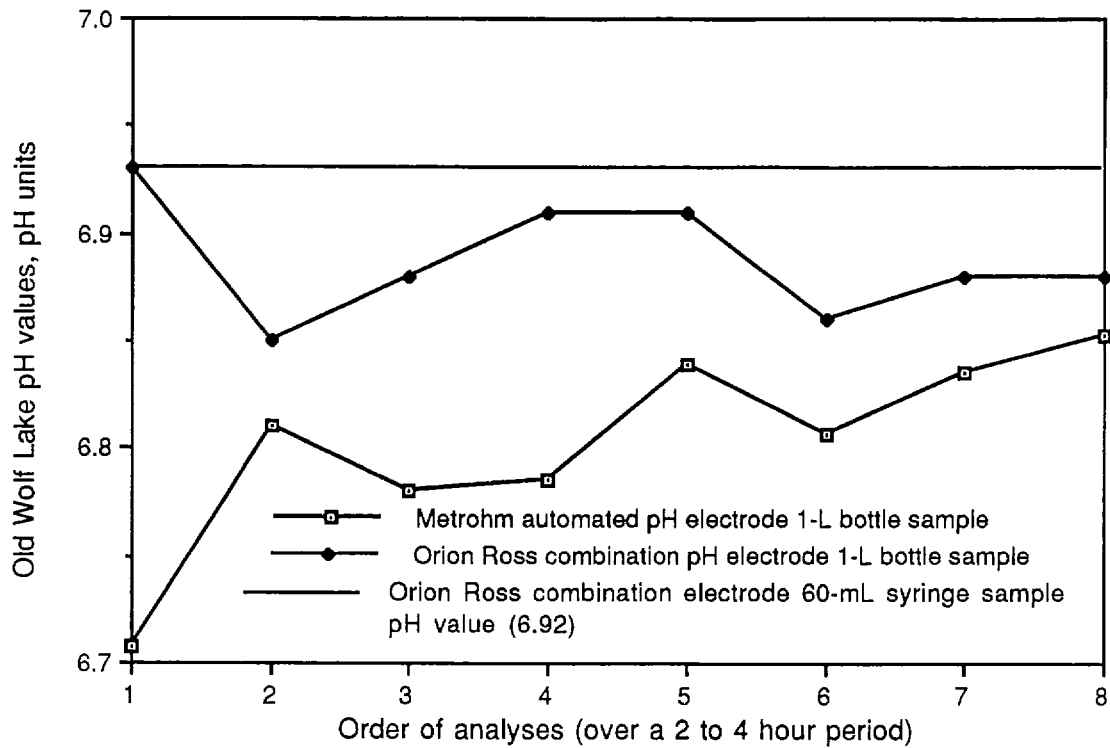


FIGURE 5: Comparison of pH values analyzed by two analytical methods and two sampling methods for Old Wolf Lake samples, November 8, 1990.

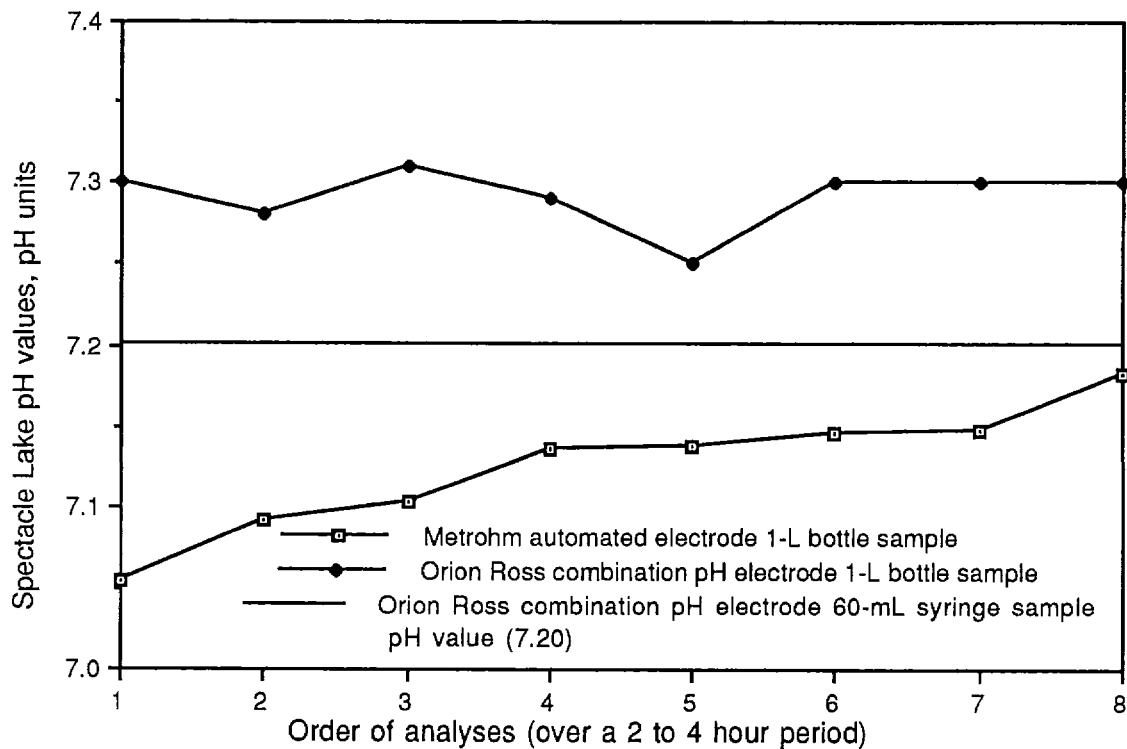
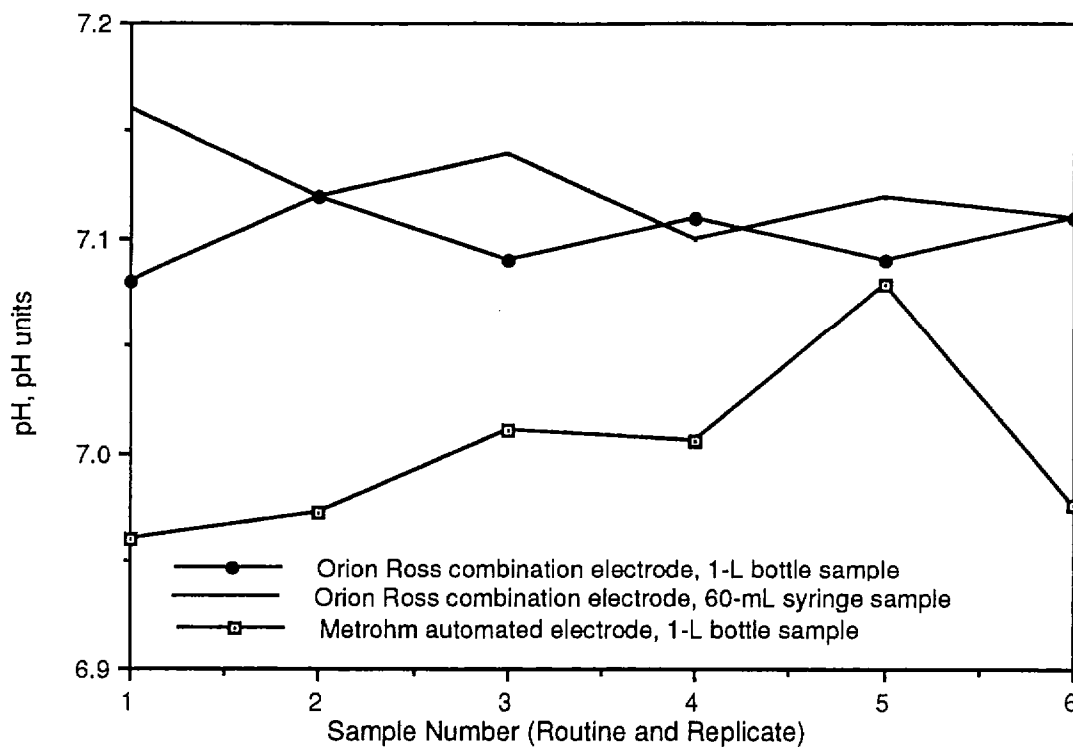
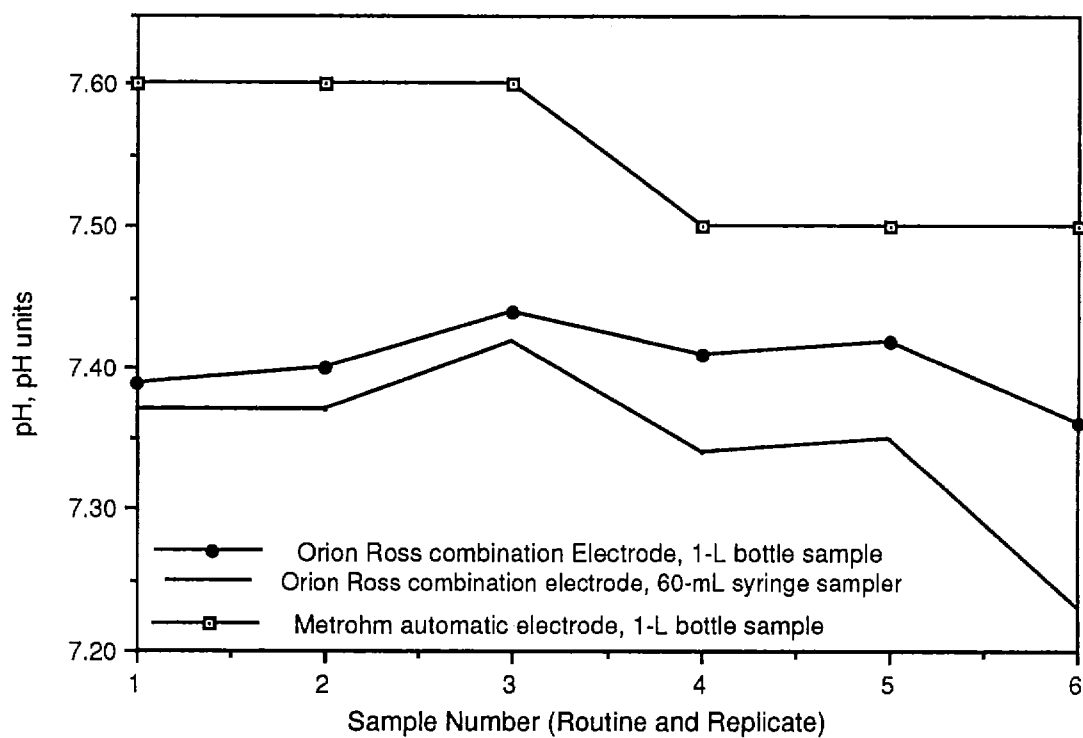


FIGURE 6: Comparison of pH values analyzed by two analytical methods and two sampling methods for Spectacle Lake samples, November 8, 1990.



**Figure 7: Values for pH reported for two sampling methods and analyzed using the Metrohm automated electrode and the Orion Ross combination electrode**  
**Sample date February 14, 1990, Maxwell Lake**



**Figure 8: Values for pH reported for two sampling methods using the Metrohm automated electrode and the Orion Ross combination electrode**  
**Sample date August 2, 1990, Maxwell Lake**

