Identification of Native Brook Trout Streams That Are Impaired by Acidification

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Abstract

Although it is well established that many of Virginia’s native brook trout streams have been acidified as a consequence of atmospheric deposition (acid rain), relatively few of these streams have been included in the impaired streams listings developed by the Virginia Department of Environmental Quality to satisfy the reporting requirements of Section 303(d) of the Clean Water Act. Whereas most of the available pH data for Virginia’s native brook trout streams have been obtained by lab analysis, the U.S. Environmental Protection Agency effectively requires field analysis of pH for purposes of water quality assessment. Most of Virginia’s acidification-impaired brook trout streams are thus not subject to the potential benefits of the TMDL (Total Maximum Daily Load) development process, which involves study to identify sources of pollution and implementation of a plan to achieve water quality improvements. This project obtained one year of monthly pH measurements in the field by approved methods from 20 of Virginia’s most acidic native brook trout streams. Examination of these pH data indicate that 19 of the studied streams meet the criteria for impaired streams listing. Another component of the project examined differences between field and lab measurements of pH to evaluate the use of lab pH to predict violations of the general statewide minimum pH standard of 6.0. For the type of streams included in this study, and for analysis up to 29-30 days following sampling, it can be predicted with at least 99% certainty that field pH is <6.0 when lab pH is ≤5.79, and that field pH is >6.0 when lab pH is ≥6.33. Recommendations include: (1) development of a screening tool for use of lab pH for preliminary evaluation of stream impairment and prioritization of follow-up data collection; and (2) development of water quality standards, in addition to standards based on pH and benthic data, for the specific identification and assessment of atmospheric deposition as an impairment source.

Introduction

The small headwater streams in the mountains of western Virginia that provide habitat for our native brook trout (Salvelinus fontinalis) are among the most highly valued of the Commonwealth’s surface water resources. Many of these streams are associated with the remnant wild lands that have been set aside as National Forest, National Park, and Wilderness. Although these streams are generally protected from degradation that can be characterized as
direct anthropogenic impact, it is well documented that water quality and faunal diversity in a substantial number of these streams have been altered by acidification related to atmospheric deposition (Webb et al. 1989; Cosby et al. 1991; Bulger et al. 2000). It is also apparent that current efforts to control air pollution are insufficient to achieve significant improvement in the condition of these streams. A recent report to Congress (Stoddard et al. 2003) established that, although reductions in acidic emissions mandated by the Clean Air Act Amendments of 1990 have resulted in recovery of acidified surface waters in other regions of the United States, surface waters in the region that includes western Virginia have shown limited or no recovery. Additional studies specific to the western Virginia area (e.g., Webb et al. 2004) document the fact that the limited recovery that has occurred in some streams in the area is minor in relation to historic acidification and in relation to recovery observed in other areas. However, the effects of atmospheric deposition have only recently been recognized in regional water quality assessments and listings of impaired streams prepared by the Virginia Department of Environmental Quality (DEQ) to satisfy reporting requirements of the Clean Water Act.

The 2002 Report on Impaired Waters in Virginia (DEQ 2002) identified eight streams for which the source of impairment is believed to be atmospheric deposition. The more-recent 2004 Combined Water Quality Assessment and Impaired Streams Report (DEQ 2004a) identified an additional 12 streams for which the source of impairment is believed to be atmospheric deposition.\(^1\) Available data indicate that the actual number of Virginia streams that are impaired due to atmospheric deposition is much higher.

For example, the Shenandoah Watershed Study and the Virginia Trout Stream Sensitivity Study (SWAS/VTSSS) provide water quality data for most of the streams in western Virginia that support reproducing populations of native brook trout.\(^2\) Among 450 stream sites sampled through surveys and routine monitoring conducted by the SWAS/VTSSS program, pH values of <6.0 have been observed at 100 sites or 22.2% of the total number of sampled sites. Although pH values <6.0 violate the general statewide pH standard of 6.0-9.0 (Virginia Water Quality Standards; 9 VAC 25-260), the SWAS/VTSSS pH data do not comply with methods requirements established by the U.S. Environmental Protection Agency (EPA) as published in 40 CFR 136. The specific requirement is that analysis must be performed immediately, which is defined to mean within fifteen minutes of water sample collection. This effectively requires analysis in the field. The pH measurements obtained through the SWAS/VTSSS program have been obtained by analysis of samples in the lab. Thus, the extensive pH data obtained by the

\(^1\) Of the 20 streams for which impairment is attributed to atmospheric deposition in the Final 2004 305(b)/303(d) Water Quality Assessment Integrated Report (DEQ 2004a), the determination of impairment was based on evaluation of benthic data for 13 streams and on pH data for seven streams.

\(^2\) The Shenandoah Watershed Study and the Virginia Trout Stream Sensitivity Study are conducted by the Department of Environmental Sciences at the University of Virginia in cooperation with the National Park Service, the U.S. Environmental Protection Agency, The USDA Forest Service, the Virginia Department of Game and Inland Fisheries, and Trout Unlimited. See http://swas.evsc.virginia.edu.
SWAS/VTSSS program have not been used by the DEQ in the performance of federally mandated water quality assessment activities. The DEQ is similarly constrained from relying on lab pH measurements obtained through other sampling and analysis programs.

The stipulation that only field measurements of pH are acceptable for required water quality assessments may be overly restrictive. Collection of reliably accurate pH measurements in the field is time-consuming and therefore difficult in a context of limited resources for data collection. Previous work involving relatively low-ionic strength surfaces waters of the type represented by Virginia’s brook trout streams has shown that the in situ pH for most waters is lower than the value measured in the lab (Kaufmann et al. 1988). Thus, for those Virginia brook trout streams for which lab pH values are less than a minimum criterion value, the actual stream pH is probably as low or lower.

Regardless of the actual significance of differences in pH analysis methods, the DEQ adheres to methods requirements. Consequently, most of the brook trout streams that are impaired by acidification have not been included in the DEQ listings of impaired waters. These streams are thus not subject to the TMDL (Total Maximum Daily Load) process. Streams that are listed as impaired should benefit from the TMDL process, which involves study to identify the sources of pollution and implementation of a plan to achieve water quality improvements.3

Objectives

The major goal of the project was to better establish the extent of the acidification problem in the class of headwater streams that provides habitat for the native brook trout in the mountainous region of Virginia. The first objective was to obtain pH data for a number of these streams using methodology that conforms to EPA and DEQ requirements for identification of surface waters impaired by acidification. The second objective was to examine pH stability or differences between field and lab pH measurements.

Procedures

Field pH Component

The streams that have been studied through the SWAS/VTSSS programs were ranked based on pH values previously determined by measurement in the lab. Those streams with the lowest pH values (most acidic) were selected as candidate study sites for measurement of pH in the field. Based on the available funding and logistical considerations, including travel, site access, and analysis time, it was decided to select sites grouped in a four-county area (Rockingham, Augusta, Bath, and Rockbridge Counties). Figure 1 indicates the locations of the selected sites (n = 20). Table 1 provides site-location information. All of the sites were located on public land, including the Shenandoah National Park, the George Washington National Forest, and the Goshen Wildlife

3 The earliest date set for TMDL development for any Virginia stream for which impairment is associated with atmospheric deposition is 2014 (DEQ 2004a).
Figure 1. Native brook trout stream data collection sites in western Virginia. This project obtained one year of monthly pH measurements in the field by approved methods from these sites.
Table 1. Location data for study streams.

<table>
<thead>
<tr>
<th>Site</th>
<th>Stream</th>
<th>COUNTY</th>
<th>UTM</th>
<th>ELEVATION</th>
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<td>Bath</td>
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</tr>
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<td>0667893</td>
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<td>Rockingham</td>
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</table>

Note: Elevation is reported as feet above mean sea level.
Management Area. Nine of the twenty streams selected for study are included in the long-term stream monitoring program maintained by the SWAS/VTSSS program. For these nine streams, lab pH and other analyses of stream water composition are routinely obtained on at least a quarterly basis. For the other eleven streams selected for study, stream water composition data were obtained through regional synoptic sampling surveys conducted by the SWAS/VTSSS program in 1987 and in 2000.

Sampling for the current project was organized by assigning the selected study streams to four “routes” that were each followed at roughly four-week intervals during a period of twelve months (Water Year 2004; October 2003 – September 2004). Two students in the Department of Environmental Sciences at UVA, Douglas Tobias and Adam Humphries, conducted the weekly field trips, kept records, and performed the pH analysis in the field and in the lab. SWAS/VTSSS staff provided training prior to initiation of the project and provided oversight during the project.

The analysis method for collection of field pH data conformed to the requirements established by EPA as published in 40 CFR 136. Data quality assurance was provided by calibration with NIST traceable buffers at each data collection site and by adherence to a strict protocol involving analysis of multiple aliquots and application of stability criteria (see Appendix 1).

We also worked with the DEQ in planning and executing the field project. Prior to initiation of the field work we consulted with Mr. Gary Du, with the DEQ Water Quality Assessment section, who conducted a QA/QC review of our protocol for pH measurement in the field (see Appendix 2). In addition, we consulted with Mr. Harry Augustine, Water Quality Assessment Coordinator for the DEQ, concerning the appropriate number of pH measurements for purposes of impaired waters identification. Mr. Augustine indicated that the DEQ would prefer that we obtain 12 measurements of pH during the course of the year for each study site.

**pH Stability Component**

The secondary study of differences between field and lab pH measurements involved field measurement of pH and collection of samples for pH measurement in the lab. Lab measurements were obtained at four points in time, including 1-2, 8-9, 15-16, and 29-30 days after field measurement and sample collection. The samples for lab analysis were collected at the same sites and at the same times that field pH measurements were obtained, with separate samples collected for each of the subsequent lab analyses. The stability study was conducted on a quarterly basis, with three different sites selected for both field and lab measurements in each of four quarters, involving a total of 12 sites during the course of the project. The samples were collected in prewashed 500 ml LDPE Nalgene bottles. Immediately upon collection, the samples were placed in insulated containers with refrigerant and then placed in a refrigerator upon return to the project lab. Prior to analysis in the lab, the individual samples to be analyzed were removed from the refrigerator and allowed to attain room temperature. The protocol used for lab analysis of pH was the same as the protocol used for field analysis with respect to calibration, analysis of multiple aliquots, and application of stability criteria. Both protocols can be accessed by linking to the methods page on the SWAS/VTSSS website: [http://swas.evsc.virginia.edu](http://swas.evsc.virginia.edu).
Results

Field pH Component
The project provided sufficient data to evaluate 20 of Virginia’s native brook trout streams in relation to the pH criteria established for identification of impaired surface waters. The number of monthly values obtained per stream ranged from 10 to 14, with at least 12 monthly values obtained for 19 of the streams. The monthly pH values obtained for the 20 streams are provided in Table 2. Time series plots of the monthly pH values obtained for the 20 streams are provided in Figure 2.

A stream is considered impaired if the values of 10.5% or more of the available data violate the applicable water quality standard and there are at least two violations (DEQ 2004a). The general statewide pH standard is 6.0-9.0, with 6.5-9.5 specified for certain streams, including many native brook trout streams (Virginia Water Quality Standards; 9 VAC 25-260). The following results are presented in reference to these criteria.

• The applicable pH standard for 16 of the 20 study streams is 6.5-9.5. All 16 of these streams met the criteria for designation as impaired by acidification.
  o For each of these 16 streams there were more than two measurements with pH <6.5 and the pH was <6.5 for more than 10.5% of all the measurements.
  o The median pH values for these 16 streams ranged from 5.02 to 6.38.
  o For 15 of these 16 streams, 100% of the measured pH values were less than 6.5.

• The applicable pH standard for four of the 20 streams is 6.0-9.0. Three of these streams met the criteria for designation as impaired by acidification.
  o For each of these three streams there were more than two measurements with pH <6.0 and the pH was <6.0 for more than 10.5% of all the measurements.
  o The median pH values for these three streams ranged from 5.04 to 6.12.
  o For one of these three streams, 100% of the measured pH values were less than 6.0.
  o The median pH for the one stream that did not meet the criteria for impairment was 6.17.

Stability Component
The data obtained during the stability component of the project are presented in Table 3. Time series plots of the data are provided in Figure 3. Time series analysis indicated no significant difference in pH related to the timing of lab analysis. Thus, for the following summary of observed results, no distinction is made among the lab data based on the length of the delay following field measurement and sampling.

• Difference in pH values between lab pH and field pH (lab value minus field value):
  o The total range of the deviations for all 12 streams was about 0.3 pH units, or -0.09 to +0.20 pH units.
Table 2. Monthly field pH values for study streams.

### ROUTE 1

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<tr>
<th>Site</th>
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<th>10/11</th>
<th>11/8</th>
<th>12/16</th>
<th>1/6</th>
<th>1/31</th>
<th>2/18</th>
<th>3/12</th>
<th>4/7</th>
<th>5/9</th>
<th>6/4</th>
<th>7/1</th>
<th>8/5</th>
<th>9/2</th>
<th>9/23</th>
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<th>% &lt; 6.0</th>
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<td>5.13</td>
<td>5.20</td>
<td>5.16</td>
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### ROUTE 2

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Notes: - empty cells indicate missing data
- measurement not obtained within 15 minutes of sample collection: OB01 1/21/03
Table 2. Monthly field pH values for study streams. (continued)

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Notes  - measurement not obtained within 15 minutes of sample collection: RH52 12/15/03, 1/18/04, 2/11/04, 3/19/04
- quality control criteria not met: RH52 2/11/04
Figure 2. Field pH. The stream-specific minimum pH criteria for impairment (6.0 or 6.5) are indicated by the red lines.
Table 3. pH values for stability study.

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<tr>
<th>Site</th>
<th>Stream</th>
<th>Sample Date</th>
<th>Field Value</th>
<th>Day 2</th>
<th>Day 9</th>
<th>Day 16</th>
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<td>05/02/04</td>
<td>5.07</td>
<td>5.06</td>
<td>5.05</td>
<td>5.05</td>
<td>5.06</td>
<td>- 0.02</td>
</tr>
<tr>
<td>VT36</td>
<td>Meadow Run</td>
<td>07/29/04</td>
<td>5.41</td>
<td>5.47</td>
<td>5.49</td>
<td>5.45</td>
<td>5.49</td>
<td>+ 0.08</td>
</tr>
<tr>
<td>PAIN</td>
<td>Paine Run</td>
<td>07/29/04</td>
<td>5.97</td>
<td>6.17</td>
<td>6.16</td>
<td>6.11</td>
<td>6.13</td>
<td>+ 0.20</td>
</tr>
<tr>
<td>VT53</td>
<td>Two Mile Run</td>
<td>07/29/04</td>
<td>6.03</td>
<td>6.11</td>
<td>6.14</td>
<td>6.13</td>
<td>6.22</td>
<td>+ 0.19</td>
</tr>
</tbody>
</table>
Figure 3. Stability test results. Initial (field) pH values are indicated by the blue lines.
The range of the deviations for six streams with field pH measurements less than 6.0 was -0.02 to +0.20 pH units.

The range of the deviations for six streams with field pH measurements greater than 6.0 was -0.09 to +0.19 pH units.

For five streams for which any lab measurements were lower than the field measurement, the maximum decrease (field value minus lab value) ranged from 0.02 to 0.09 pH units.

For eight streams for which any lab measurements were higher than the field measurement, the maximum increase (lab value minus field value) ranged from 0.03 to 0.20 pH units.

Simple linear regressions were performed to examine the use of lab pH for prediction of field pH. Figure 4 provides the regression equations for field pH with lab pH obtained 1-2, 8-9, 15-16, and 29-30 days after field measurement and sample collection. Based on these results we examined the uncertainty (prediction error) associated with predictions centered on pH 6.0, the general statewide criterion value for impairment due to acidification.

For lab analysis conducted 1-2 days following field measurement and sampling:
  o The lab pH value at or below which there is at least a 99% certainty that the field pH is <6.0 is 5.79.
  o The lab pH value at or above which there is at least a 99% certainty that the field pH is >6.0 is 6.27.

For lab analysis conducted 8-9 days following field measurement and sampling:
  o The lab pH value at or below which there is at least a 99% certainty that the field pH is <6.0 is 5.79.
  o The lab pH value at or above which there is at least a 99% certainty that the field pH is >6.0 is 6.28.

For lab analysis conducted 15-16 days following field measurement and sampling:
  o The lab pH value at or below which there is at least a 99% certainty that the field pH is <6.0 is 5.80.
  o The lab pH value at or above which there is at least a 99% certainty that the field pH is >6.0 is 6.26.

For lab analysis conducted 29-30 days following field measurement and sampling:
  o The lab pH value at or below which there is at least a 99% certainty that the field pH is <6.0 is 5.79.
  o The lab pH value at or above which there is at least a 99% certainty that the field pH is >6.0 is 6.33.
Discussion

The problem of stream acidification due to atmospheric deposition in Virginia’s mountain streams has not been effectively addressed in previous water quality assessments prepared by the DEQ to satisfy reporting requirements of the Clean Water Act. The most-recent impaired streams listing identified only 20 streams that are impaired by acidification believed to be associated with atmospheric deposition (DEQ 2004a). This is despite the well-documented problem of stream acidification in the mountains of western Virginia (Webb et al. 1989; Cosby et al. 1991; Bulger et al. 2000) and in the central Appalachian region (Kaufmann et al. 1988; Herlihy et al. 1993; Sullivan et al. 2000).

A principal reason that the DEQ water quality assessments do not effectively account for stream acidification due to atmospheric deposition in Virginia’s mountain streams is a lack of approved pH data. Of the 20 streams identified as impaired by acidification due to atmospheric deposition in the most-recent impaired streams listing, 13 were identified as impaired based on benthic sampling data. Only seven were identified as impaired based on measurement of stream water pH. For these seven streams, the identification of impairment was based on only two pH measurements, and for five of the seven streams, only two pH measurements were available for the reporting period. It is apparent that very few pH data are being obtained for Virginia mountain streams by methods that satisfy the DEQ and EPA requirements.

This project addressed this data deficiency with two objectives: (1) collection of pH data by approved methods to support the listing of additional native trout streams as impaired; and (2)
evaluation of differences between approved field measurements of pH and commonly obtained, but unapproved, lab measurements.

In order to meet the first objective, the monthly data obtained through the field pH component of the project were submitted on April 14, 2005 to Mr. James Beckley, Water Quality Liaison for the DEQ. These data will be reviewed by the DEQ staff as water quality assessment and impaired streams reports are prepared for the time period of the data collection. The submitted data support the listing of 19 native brook trout streams as impaired by acidification, including 14 streams that have not been listed as impaired by acidification in previous impaired streams reports. For the five streams listed as impaired in previous reports, the data provide a stronger basis for assessment, increasing the number of available pH measurements from two to 12 for three streams and providing 12 pH measurements for each of two streams for which benthic data, but no pH data, were previously available.

In order to meet the second objective, we examined the data obtained through the stability component of the project to obtain information related to the potential use of lab pH to estimate field pH. We were primarily concerned with differences between field and lab pH that would result in errors of two types, either failure to identify an impaired stream or incorrect identification of an impaired stream. Failure to identify an impaired stream would result if the lab pH was above the standard for impairment, when the field pH was below the standard. Incorrect identification of an impaired stream would result if the lab pH was below the standard for impairment, when the field pH was above the standard. In order to avoid these errors, we evaluated the uncertainty associated with the use of lab pH to predict field pH. For the type of streams examined in this study, and for lab analysis conducted up to 29-30 days following sampling, we conclude with a high degree of confidence that field pH is less than the general statewide standard of 6.0 if the lab pH is 5.79 or lower, and that field pH is greater than 6.0 when the lab pH is 6.33 or higher.

These results suggest that a reliable screening tool can be developed to allow preliminary evaluation of stream impairment based on lab pH measurement. However, the development of a broadly useful screening tool would require more information than provided by the current study, which involved a small sample size (n = 12) and a relatively narrow pH range. Only one of the streams included in the study had pH values greater than 6.5, which is the special standard established for many of Virginia’s native brook trout streams. Thus, even the development of a

4 The DEQ is currently developing the 2006 Integrated Report (305(b) Water Quality Assessment /303(d) Impaired Waters). The data window for this report is January 1, 2000 through December 31, 2004 (DEQ 2004b).

5 The utility of such a screening tool is suggested by the description of the Virginia Water Quality Assessment Category 3C: “... for data collected by a citizen monitoring or other organization indicating water quality problems may exist but the methodology and/or data quality has not been approved for a determination of attainment of designated uses. These waters are considered as having insufficient data with observed effects. Such waters will be a prioritized for follow up monitoring.” (DEQ 2004a)
screening tool specifically designed for native brook trout streams would require information based on streams representing a broader range of pH.

The collection of approved pH data from additional streams, as well as the development of an effective screening tool for prioritizing such data collection, would address a significant data deficiency and thereby contribute to consideration of atmospheric deposition effects in Virginia’s water quality assessment program. However, it should be recognized that assessments based on reference to a pH standard are inherently limited. We note that for those streams identified in the DEQ assessments as impaired by acidification caused by atmospheric deposition, the attribution of cause is not definitive. This is reflected in stream-specific fact sheets, which indicate that the impairment source for these waters is “believed to be” atmospheric deposition (DEQ 2004a). It may also be reflected by a concern that apparent impairment of native trout streams is due to natural conditions (DEQ 2004b). The underlying problem is that neither low pH, nor evidence for acidification-related impairment of the benthic community, provide sufficient basis for identification or assessment of atmospheric deposition effects.

The primary pollutants associated with atmospheric deposition are acidic sulfur and nitrogen compounds, and water quality effects are determined by watershed conditions and processes that govern the transport and neutralization of these compounds (see Galloway et al. 1983; Cosby et al. 1991; Webb 2004). The impact of atmospheric deposition and the mitigating effects of these watershed factors are indicated in surface waters by the concentrations and ratios of solutes derived from the atmosphere (e.g., sulfate and nitrate) and solutes derived from watersheds (e.g., calcium ion and magnesium ion). We propose that reliable identification and assessment of impairment due to atmospheric deposition will need to consider the relative concentrations of such solutes, as well as pH or evidence of biological impairment.

Conclusions

1) Although acidification due to atmospheric deposition is a well-documented problem for Virginia’s native brook trout streams, it is a problem that has not been effectively addressed in Virginia’s water quality assessment reports and impaired streams listings.

2) Although pH standards have been established for identification of surface water acidification, very little pH data has been collected for Virginia’s native brook trout streams by methods that are approved by the EPA and the DEQ.

3) Although collection of pH data by approved methods is time-consuming and logistically difficult, such data collection is feasible as demonstrated by collection of pH data on an approximately monthly basis during a one-year period for 20 native brook trout streams in western Virginia.

4) Although lab measurement of pH is not approved for use in Virginia’s water quality assessment program, a study of differences between field and lab measurements suggests that lab measurement can be used to estimate field pH.
5) Although impairment due to acidification may be identified based on pH or benthic data, additional information is needed for identification of atmospheric deposition as an impairment source.

**Recommendations**

1) A screening tool should be developed to allow use of lab pH measurement for preliminary evaluation of stream impairment and prioritization of follow-up data collection.

2) Water quality standards, in addition to standards based on pH and benthic data, should be developed for the specific identification of surface waters that are impaired due to atmospheric deposition.

**Acknowledgement**

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Appendix 1. Determination of pH in the Field.

Shenandoah Watershed Study/Virginia Trout Stream Sensitivity Study

Equipment and Materials:
Thermo Orion model 290Aplus portable pH meter with model 9107BN 3-in-1 pH/ATC probe in field kit
Deionized water rinse bottle
Stopwatch
pH 4.0 and 7.0 buffers (NIST traceable)
pH 4.60 Quality Control Sample (QCS)
Kimwipes

Quality Control Criteria (Definitions):
(Meter should be set to read measurements to 2 decimal places.)
a) Within-aliquot stability criterion - drift in pH value is 0.01 units or less over 60 seconds
b) Sequential-aliquot stability criterion - difference in obtained pH values between sequential aliquots is 0.03 units or less
c) Buffer agreement criterion - pH determined for each buffer differs by no more than 0.02 units from true value of the buffer at operating temperature
d) QCS agreement criterion - pH determined for the QCS differs from prepared value (4.60) by no more than 0.10 units

Quality Assurance:
The meter is calibrated when unpacked at each field site using pH 7.0 and 4.0 buffer solutions.
The calibration of the meter is checked by determining the pH of the 7.0 and 4.0 buffer solutions. If either value exceeds the “c” criterion, the meter is recalibrated. If agreement cannot be obtained in two attempts, the electrode is replaced. The calibration check should be performed in the following situations.
• whenever the meter is calibrated
• after an interruption in the analysis session of greater than 1 hour

The pH of the QCS is measured in the following situations.
• after the pH of the sample is obtained (if only one sample is to be measured)
• after the last sample in the analysis session
• after every 8 samples (if more than 8 samples are to be measured)
• after an interruption in the analysis session of less than one hour
• whenever the “a” criterion is not met in 15 minutes
• whenever the “b” criterion is not met after 4 aliquots (not including the rinse aliquot)

If the “d” QCS agreement criterion is not met, the meter must be recalibrated, and all samples since the last agreement must be reanalyzed.

**Procedure:**

**A. Calibration**

Remove pH meter and electrode from the carrying case and set it up in as dry and level an area as possible considering field conditions.

Press the **power** key to turn the meter on and wait a few seconds.

Make sure the meter is in pH mode by checking the screen. If not, push the **mode** key until the screen indicates pH.

Place the electrode in the holder. Using a DI water squirt bottle and a plastic waste beaker to catch the rinse water, rinse the electrode well. Blot dry with a Kimwipe (do not wipe).

Place electrode in pH 7 buffer, swirl for 5 seconds, and then allow the buffer to become quiet.

Press the **2nd** then the **cal** keys. (CALIBRATE and the time and date of the last calibration will briefly be displayed.)

After a few seconds, P1 will be displayed meaning the meter is ready for the first buffer. When the word READY is displayed and the meter beeps, press the **yes** key.

Wait until P2 appears in the display.

Using a DI water squirt bottle and a plastic waste beaker to catch the water, rinse the electrode well. Blot dry with a Kimwipe (do not wipe).

Place electrode in pH 4 buffer, swirl for 5 seconds, and then allow the buffer to become quiet.

When the word READY is displayed and the meter beeps, press the **yes** key.

Wait until P3 appears in the display.

Press the **measure** key. The slope will be briefly displayed as a percent of theoretical. The meter is now ready to begin measurements.
**B. Calibration Check**

Rinse electrode with DI water and blot *(do not wipe)* dry with a Kimwipe. Immerse in pH 7.0 buffer. Swirl briefly and allow to settle down (approximately 30 seconds).

Record pH value at 60 second intervals until “a” criterion is met. If measured value differs from true value by more than 0.02 units (“c” criterion), recalibrate electrode.

Rinse electrode with DI water and blot dry with a Kimwipe. Immerse in pH 4.0 buffer. Swirl briefly and allow to settle down (approximately 30 seconds).

Record pH value at 60 second intervals until “a” criterion is met. If measured value differs from true value by more than 0.02 units (“c” criterion), recalibrate electrode.

After doing this, be sure to rinse the electrode well to remove any remaining buffer: Use a DI water squirt bottle and a plastic waste beaker to catch the water to rinse the electrode. Then fill a small beaker with DI water, lower the electrode into it, and swirl it around.

**C. Sample and QCS analysis**

Rinse sample beaker with DI water. Add approximately 5 mL of sample, swirl, and discard. Add approximately 25 mL of sample to beaker.

Rinse electrode with DI water, return it to the electrode holder and blot *(do not wipe)* dry with a Kimwipe.

Immerse electrode in sample. (Never allow electrode to touch the sides or bottle of the beaker.) Swirl sample for approximately 5 seconds. Wait at least 30 seconds, then lift out electrode gently. **Do not** rinse or blot electrode.

Discard sample in beaker, and then add a fresh 25 mL aliquot of the same sample to the beaker. (Do not rinse beaker with DI water between successive aliquots.)

Immerse electrode in sample and do **not** swirl.

Record pH readings at 60 second intervals. When “a” criterion is met, gently lift electrode from sample. **Do not** rinse electrode.

Repeat steps 4 – 6 for another fresh 25 mL aliquot of sample.

Compare the final pH value obtained for the aliquot with the final value obtained for the previous aliquot. Determine if difference in values is 0.03 units or less ("b"). If "b" criterion has not been met, repeat steps 4 - 6 using additional aliquots as needed until criterion is met. When “b” criterion has been met, this value is the pH measurement of the sample. Record the temperature from the meter.
The results of my QA/QC review of the procedure used by UVA's laboratory to monitor field pH are as follows:

I went out for the field audit with Susie Maben, UVA's lab manager, on Jan. 21. The lab utilizes an Orion pH meter. The meter was calibrated in the field with NIST traceable pH 4.0 and 7.0 buffers. Each sample was measured twice until certain criteria are met. A QC sample is utilized after obtaining the measurements to check for drift of the calibration.

Ms. Maben is very knowledgeable of the testing procedure. The lab has an acceptable procedure, very good QC protocols and record documentation. I am very pleased, impressed and satisfied with the lab procedure.