**pH Meter QA/QC Report- 2011**

**History**

Since October of 2000, SYRCL’s monitoring program has collected pH data at 62 sites throughout the Yuba watershed. For the first 3 years of the program SYRCL used Oakton brand pH meters to measure pH in the field. In 2004 many of the Oakton meters were discarded and replaced by Hanna brand pH meters. A complete switch was made to Hanna Meters by 2005 and they have been used exclusively ever since.

In 2010 an analysis of ten years of data revealed a trend throughout the watershed of declining pH over time. It was suggested by BJ Schmitt, a TAC member from Wolf Creek Community Alliance (WCCA) that this trend may be reflecting the increasing age of our pH meters and their resulting inability to measure accurately, and not a decline of pH in the field. To test this hypothesis a series of experiments were conducted.

**Methods**

On September 9 and October 1, 2010 six new Hanna meters were calibrated along side SYRCL’s pH meters using identical pH buffers and calibration protocols. These six meters, borrowed from WCCA, were sent into the field with SYRCL meters on regular monitoring days. Both meters were used to collect pH and water temperature data from the same location in the channel at the same time.

It was also suggested that SYRCL volunteers were not pre-soaking there meters long enough prior to use and that this practice could skew pH results. To eliminate this possible variable, all SYRCL volunteers were asked to soak their pH meters in at least one inch of river water for a minimum of 15 minutes prior to taking measurements.

To test if SYRCL and WCCA meters were staying properly calibrated those meters involved in the field comparison were tested in pH 7 and pH 4 buffer solutions upon return to the office the day of sampling. On average meters were tested within 3 hours of taking field measurements.

**Results**

The results of the September and October tests are summarized in Figure 1 and Figure 2.

*Figure 1: Chart showing results of September comparison of SYRCL meters and WCCA meters at 4 different sites.*

*Figure 2: Chart showing results of October comparison of SYRCL meters and WCCA meters at 5 different sites.*

On all occasions:

* SYRCL meters yielded lower pH values than WCCA meters in the field
* Both SYRCL and WCCA meters calibrated properly prior to sampling
* Both SYRCL and WCCA meters gave results within 0.1 unit of the true values of the buffer solutions in the post-field sampling tests.

Because meter age was the only known difference between SYRCL meters and WCCA meters these data indicate that meter age is affecting SYRCL’s pH measurements. To prevent further skewing the pH data, November 2010 pH testing was only conducted on water samples that were returned to the office and tested with a single new meter of known quality.

**Determining Reliability of Past pH Data**

The manufacturer was contacted to determine how long pH meter probes should be used and the following questions addressed.

* How long may pH probes be used before they are too old to collect accurate data?
* Hanna Meters: Probes should be replaced every 6-12 months.
* Oakton: Probes should be changed every 6-18 months.
* Is the age at which pH meter probes should be replaced dependant on the number of uses and calibration frequency?
* Hanna Meters: Probes that are used more frequently are less likely to dry out and so they tend to last longer. Same for the frequency of calibration. Meters should always be calibrated prior to use.
* How does storage affect pH probe life length?
* Hanna Meters: Meters should be stored upright with the probes in a storage solution or pH 4 buffer solution. Probes that are allowed to dry out will have a shorter life.
* Why do our meters calibrate correctly but yield more acidic results in the field when compared to newer meters?
* Hanna Meters: Probes that are too old should not calibrate properly. Manufacturer had no explanation for this.
* John Vanderveen: The chemist from Friends of Deer Creek has suggested that since pH buffers are strong solutions that are easily recognized, the meters are able to calibrate properly but are less able to detect the pH of river water. He hypothesizes that if the meter were left in river water for many hours it would eventually arrive at the correct pH value.
* Will our pH meters still give us the correct water temperature despite aging pH probes?
* Hanna Meters: The temperature sensor in the pH meters are completely independent of the pH probe and are unaffected by aging.

Based on this input from the manufacturer it was decided that *any data generated by a probe greater than one year in age would not be considered valid*.

**Analysis of pH and Meter Age**

To evaluate the true pH conditions in the Yuba watershed over the past ten years it is necessary to remove inaccurate data from the River Monitoring Database (RimDB). The following steps were taken to determine what data was not usable.

1. Meter age and frequency of use was determined by compiling information from calibration logs (which dated back to 2004), purchase records, and the meter type and ID number recorded in RimDB for every sampling occasion.
2. For each year, the ages of the meters used for each sampling occasion were found by subtracting the sample date from the first known date of use.
3. Any data collected by a meter one year older than the sample date was flagged as invalid and deleted from RimDB. All old pH data was backed up before deletion and is saved for future use.

**Invalid Data Results**

Table 1 below summarizes the percentage of pH data per year that does not meet the meter age standard of one year or less.

Table 1: Percent invalid pH data by year.

|  |  |
| --- | --- |
| Year | Percent Invalid Data |
| 2000 | 0% |
| 2001 | 5.5% |
| 2002 | 46.6% |
| 2003 | 70.3% |
| 2004 | 19.1% |
| 2005 | 38.6% |
| 2006 | 89.4% |
| 2007 | 88.8% |
| 2008 | 91.4% |
| 2009 | 91.9% |
| 2010 | 83.3% |

**Meter Age and pH**

To determine if there is any relationship between the age of a meter and the pH it yielded reflected in the data, the average pH from every sampling occasion in a given year was charted with the age of its meter. A best fit line was generated and the R squared value calculated for each year. The expected result, if the meters are working properly, is no correlation between age and pH (an R squared close to zero).

Four of the years analyzed showed an R squared value greater than 0.10 (10%) indicating a possible correlation between meter age and pH. 2009 has the largest R squared value of 0.3222 (32.22%) while conversely, 2002 has the smallest R squared value of 0.0023 (0.23%). Figures 3 and 4 show the resulting graphs for both these extremes. Results for all years are summarized in Table 2.

**Results**

*Figure 3: Average pH values for all sampling occasions in 2009 organized by meter age.*

*Figure 4: Average pH values for all sampling occasions in 2002 organized by meter age.*

Figure 3 shows that in 2009 older meters tended to yield more acidic pH readings than newer meters. This relationship is not observed in 2002 where the oldest meter is 2.16 year old. Those years that show the greatest correlation (at least 0.10) between meter age and pH are those years where a subset of pH meters are at least 3.33 year old.

Table 2: Summary of meter age and R squared value for each year. Year 2000 had too small a sample size to be included.

|  |  |  |
| --- | --- | --- |
| Year | Oldest Meter Age (years) | R Squared |
| 2010 | 6.8 | 0.2561 |
| 2009 | 5.31 | 0.3222 |
| 2008 | 4.32 | 0.192 |
| 2007 | 3.47 | 0.0936 |
| 2006 | 2.4 | 0.0313 |
| 2004 | 3.33 | 0.149 |
| 2003 | 2.98 | 0.071 |
| 2002 | 2.16 | 0.0023 |
| 2001 | 1.16 | 0.0223 |
|  |  |  |

To further investigate the relationship between the meter age and correlation (R squared) the age of the oldest meters from each year were plotted against the respective year’s R squared value.

*Figure 5: Chart showing the relationship between greatest meter age for each year and R squared value for each year.*

**Discussion**

Meter age is more strongly correlated with pH value as the meter age increases. These results suggest that at a certain age a meter does affect the reported pH and that the severity of this effect increases with the age of the meter. The low R squared value in 2002 is likely explained by the fact that over half of the pH readings were taken with meters a year old or younger and that almost all meters used in 2002 were under 2 years of age. The large R squared for 2009 occurred when meters had aged several years and were less accurate as a result.

These results indicate that increasingly old meters, especially those older than 2 years, influence pH and do not report the true value of pH in the field. Stopping a meter’s use after one year appears to be a meaningful way to prevent inaccuracy in future measurements. Removing pH values given by meters older than a year also appears to be a reasonable way to cull inaccurate data from the database.