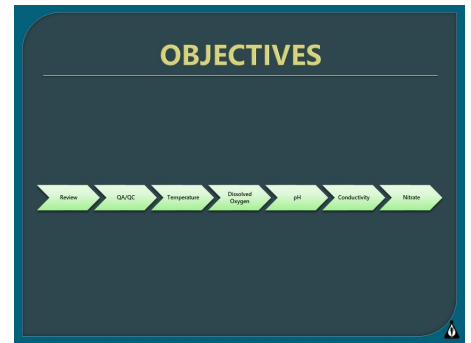


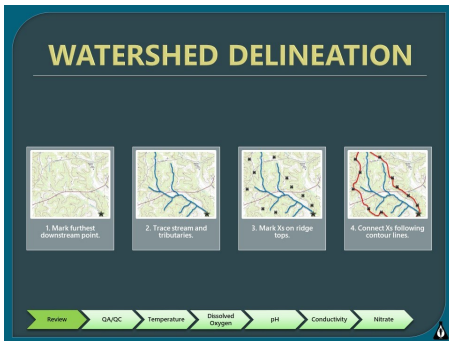
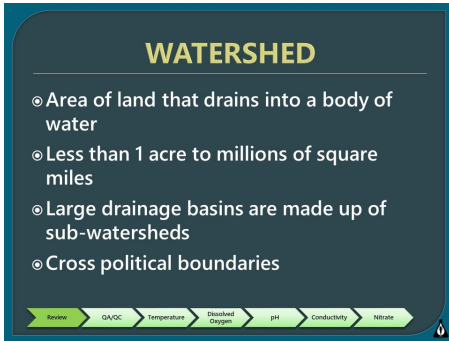
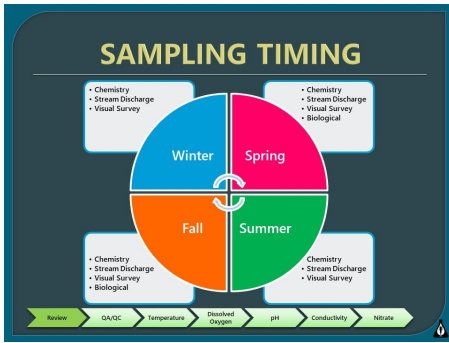
Water Chemistry



Several factors can affect the accuracy of data. During the water chemistry QA/QC portion of the workshop, the reliability of equipment and viability of reagents will be checked. Proper sampling technique will also be assessed. In this section we will cover:

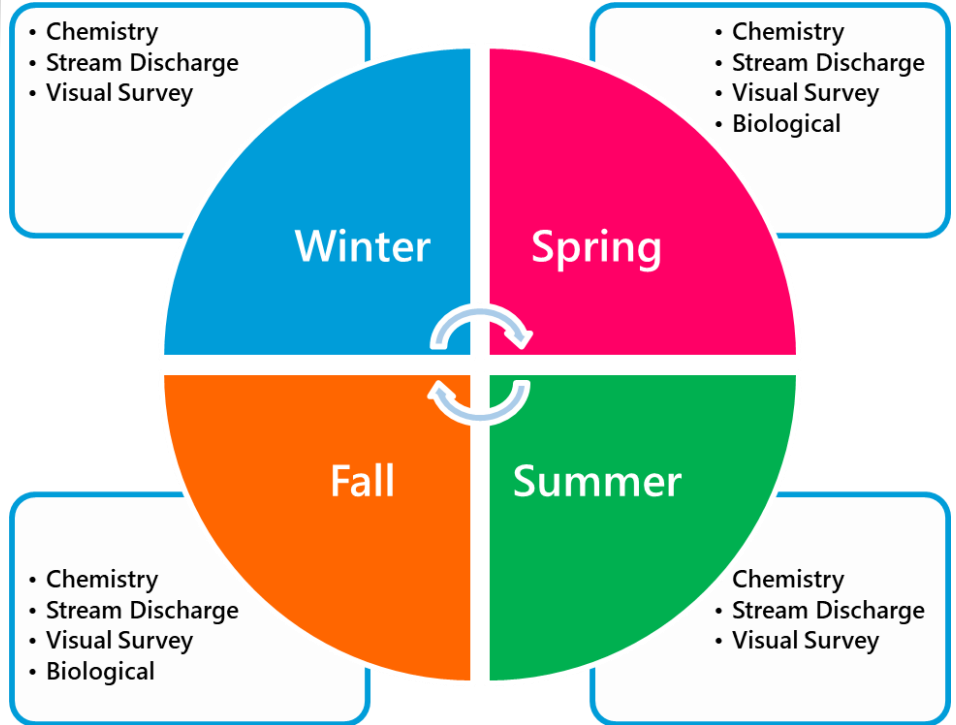
- QC Level 1 review
- QA/QC requirements and chemical disposal
- Temperature QC
- Dissolved oxygen QC
- pH QC
- Conductivity QC
- Nitrate QC





Sampling Timing

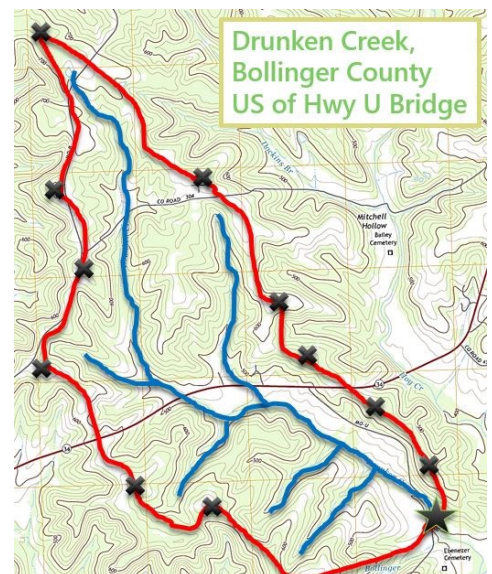
The frequency of monitoring is dependent on your goals or project. The VWQM program recommends monitoring at least four times a year, but no more than twice per year for biological monitoring at a given site. The most meaningful data is collected consistently over a long period of time.

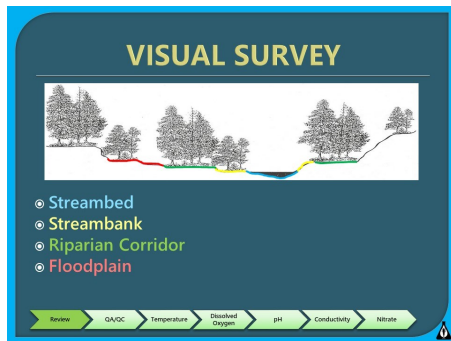


Watersheds

A watershed is a topographically defined area that drains into a body of water. Watersheds can range in size from less than an acre to millions of square miles. To delineate the watershed for your monitoring site, follow these steps:

1. Mark your monitoring site on a topographic map, which is the furthest downstream point you will evaluate.
2. Trace the stream and all tributaries upstream from your site.
3. Mark an X on all ridge tops surrounding the stream(s).
4. Connect these Xs while following the contour lines.





Visual Survey

Visual Survey is the physical assessment of your monitoring site. Since this is a collection of observations, it can be subjective. The Visual Survey datasheet should be completed by the same monitor at a given site to reduce variation based on opinion. It's most beneficial to collect this data at least twice a year, once with foliage absent and once with foliage present.

Observations in Visual Survey cover the following watershed components:

- **Streambed**—The area where a natural stream runs, or may run, depending on precipitation. This is the area between the streambanks in which substrate is deposited or removed by the energy of moving water. The streambed may be dry during times of the year, especially in the upper stream reaches.
- **Streambank**—The area of land that rises from the streambed and reaches a crest. Such crests are most noticeable when looking at the outside bend of a stream meander. If, and only if, there is no marked change or obvious crest, consider the bank to extend no further than 50 feet away from the streambed.
- **Riparian corridor**—The linear strip of land adjacent to the stream that is within the floodplain. There is variation in the definition of the riparian corridor, particularly related to stream width. VWQM protocol measures riparian corridor from the top of the streambank to 100 feet away from the stream.
- **Floodplain**—The flattened portion of the stream valley susceptible to large floods.

Quality Assurance / Quality Control

Quality assurance (QA) is a set of activities that ensures processes are adequate in order for a system to meet its objectives. An example of this would be sampling protocols that monitors must follow. Quality Control (QC) is a set of activities designed to evaluate the developed products. Verifying the accuracy of a chemical test kit would be a QC measure.

To be considered accurate, the data produced from your analyses must meet the following acceptability limits:

Parameter	QC Limits
Temperature	$\pm 2^{\circ}$ C of meter
Dissolved Oxygen	± 1 mg/L of meter
pH	± 0.2 pH units of standard
Conductivity	$\pm 10\%$ of standard
Nitrate	± 1.0 mg/L of standard

Common Sources of Error

If a monitor does not meet the acceptability limits on the analyses, possible sources of errors must be systematically eliminated. The following is a list of possible problems:

1. **Reagents no longer viable**—Analysis should be repeated using viable reagents. Reagents should be stored in a low-moisture, temperature controlled environment.
2. **Equipment malfunction**—Troubleshoot following manufacturer's instructions and replace any damaged equipment.
3. **Analyst error**—An instructor should observe the analyst's technique.

QA/QC

Quality Assurance

- Prevent defects
- SOPs

Quality Control

- ID and correct defects
- QC of equipment

Review → QA/QC → Temperature → Dissolved Oxygen → pH → Conductivity → Nitrate

QA/QC

- Assures data validity
- Higher confidence in information generated
- Participation in QA/QC workshops demonstrates data meet specific criteria
 - Data can be used for a variety of purposes

Review → QA/QC → Temperature → Dissolved Oxygen → pH → Conductivity → Nitrate

ACCEPTABLE QC LIMITS

To be considered accurate, the data produced from your analyses must meet the following QC limits:

Parameter	QC Limits
Temperature	$\pm 2^{\circ}$ C of meter
Dissolved Oxygen	± 1 mg/L of meter
pH	± 0.2 pH units of standard
Conductivity	$\pm 10\%$ of standard
Nitrate	± 1.0 mg/L of standard

Review → QA/QC → Temperature → Dissolved Oxygen → pH → Conductivity → Nitrate

SOURCES OF ERROR

- Reagents no longer viable
 - Expired
 - Improper storage
- Equipment malfunction
 - Electronic malfunction
 - Dirty or damaged glassware
- Analyst error

Review → QA/QC → Temperature → Dissolved Oxygen → pH → Conductivity → Nitrate

CHEMICAL WASTE	
Chemical	Disposal
DO 1 packet	Dispose of packets unopened in trash
DO 2 packet	
DO 3 powder pillow	
Nitrate tablet #1	
Nitrate tablet #2	
pH 7 buffer solution	Flush down drain with ample cold water
pH 10 buffer solution	
Sodium or potassium chloride	
Sodium thiosulfate	

Chemical Waste

The table below gives proper disposal instructions for commonly used VWQM chemicals:

Chemical	Disposal
DO 1 packet	Dispose of packets unopened in trash
DO 2 packet	
DO 3 powder pillow	
Nitrate tablet #1	
Nitrate tablet #2	
pH 7 buffer solution	Flush down drain with ample cold water
pH 10 buffer solution	
Sodium or potassium chloride	
Sodium thiosulfate	

Replacement equipment and reagents can be ordered at www.mostreamteam.org or by scanning the QR code below.



Water Chemistry QC

Each monitor's chemistry test equipment and reagents will go through QC analysis during this training. The results will be recorded on the provided answer sheet and will be kept on file with program staff for three years until the next QC is required.

Program staff will provide standards and samples to measure. Each chemical parameter is analyzed as a group. Please do not work ahead.

WATER CHEMISTRY QC

⊗ Each chemical parameter will be analyzed as a group -- Please do not work ahead

VWQM LEVEL 2 WORKSHEET

Name: _____ Location: _____

PARAMETER	RESULT	RANGE	ANALYST	DATE
Temperature (°C)		± 0.2°C		
pH		± 0.1 pH		
Dissolved Oxygen		± 0.2 mg/L		
Conductivity		± 0.2 µS/cm		
Ammonia-N (NH ₃ -N)		± 0.02 mg/L		
Nitrite-N (NO ₂ -N)		± 0.02 mg/L		
Nitrate-N (NO ₃ -N)		± 0.2 mg/L		

Review
QA/QC
Temperature
Dissolved Oxygen
pH
Conductivity
Nitrite

Measuring Temperature

TEMPERATURE QC

1. Measure the temperature of the sample water on the table
2. Record result on the answer sheet

PARAMETER	RESULT	RANGE
Temperature (°C)		± 0.2°C

Review
QA/QC
Temperature
Dissolved Oxygen
pH
Conductivity
Nitrite

VWQM data sheets include air and water temperature, which should be measured in the shade. Measure air temperature first to avoid residual water on the thermometer affecting the temperature reading. When measuring water temperature, read the temperature while the thermometer is still submerged. Always allow several minutes for the thermometer to acclimate, especially in extreme temperatures.

Temperature QC

1. Using your thermometer(s), measure the temperature of the sample water on the table.
2. Record result on the answer sheet.

DISSOLVED OXYGEN (DO)

- Includes concentration of DO (mg/L) and oxygen saturation (%)
- Oxygen saturation is temperature dependent
- Oxygen is more easily dissolved in colder water

Review OA/OC Temperature Dissolved Oxygen pH Conductivity Nitrate



INFLUENCES ON DO

Natural	Anthropogenic
Temperature	Removal of Vegetation
Flow	Dams
Suspended Solids	Organic Waste
Aquatic Plants	Temperature

Review OA/OC Temperature Dissolved Oxygen pH Conductivity Nitrate




DO PERCENT SATURATION

General rule for healthy streams

 Ozark Streams	> 80% DO Saturation
 Prairie or Lowland Streams	> 60% DO Saturation

Review OA/OC Temperature Dissolved Oxygen pH Conductivity Nitrate

DISSOLVED OXYGEN KIT

-  Kit waste may be discarded on ground away from stream
-  If floc does not settle, wait 10 minutes and shake bottle again
-  Return unused, unopened DO 2 packets to Stream Team program

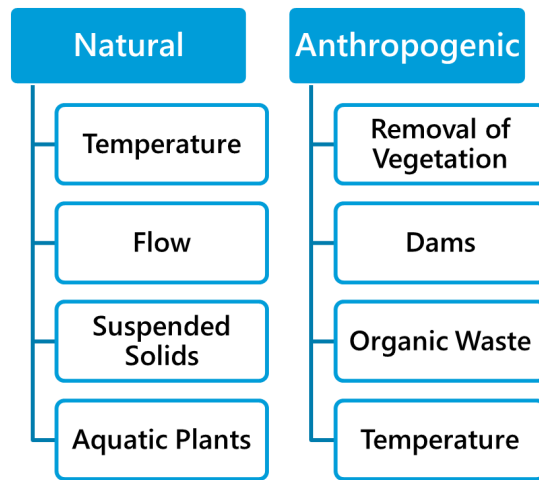
Review OA/OC Temperature Dissolved Oxygen pH Conductivity Nitrate

Dissolved Oxygen

Under natural conditions, water generally can hold more than 5 mg/L of dissolved oxygen (DO). To determine what your DO reading means you should calculate percent saturation, which is temperature dependent. Oxygen is more easily dissolved in cold water than in warm water. Slow-moving warm-water prairie streams will have a much lower saturation point than a fast-moving cool-water Ozark stream.

As a general rule, a healthy Ozark stream has greater than 80% DO saturation, while a healthy prairie or lowland stream will have greater than 60% DO saturation.

There are many influences on stream DO levels. Some of these are natural and some are anthropogenic, or human influenced:

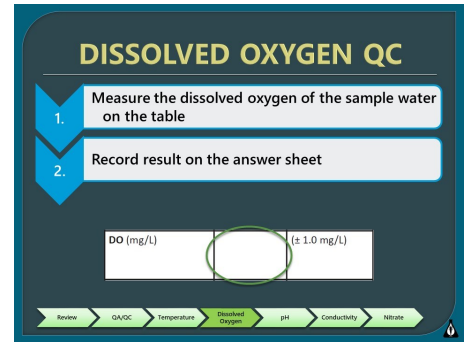


DO Troubleshooting

- Air bubble in sample bottle**—Try one of two methods to collect a sample:
 - Fill the sample bottle slightly into the frosted neck line. Add the DO 1 and 2 reagents, then stopper the bottle. This will result in a little spill-over but will not affect the test.
 - Place the sample bottle in the stream and stopper it while still under water. Remove the sample bottle from the stream and lift the stopper to add DO 1 and 2. A small amount of water that was pooled around the stopper will enter the sample bottle. This should be just enough water to prevent the air bubble when returning the stopper.
- Flocculant slow to settle**—Extremely cold water or high chloride levels will affect how the floc settles. If floc does not settle after 10 minutes, shake the bottle once more and continue with the test.
- Titration drops are small or inconsistent in size**—Hold dropper vertical and give confident, firm squeezes to ensure full drops. Release dropper bulb between drops. Do not allow drops to run down the side of the titration bottle.

Measuring DO

1. Fill the dissolved oxygen bottle with sample water to the middle of the frosted area by submerging it in the stream.
2. Add the contents of one Dissolved Oxygen Reagent 1 packet and one Dissolved Oxygen Reagent 2 packet.
3. Stopper the bottle without trapping air bubbles.
4. Shake the bottle vigorously to mix.
5. Wait for flocculent to settle to approximately half the bottle volume.
6. Shake the bottle vigorously again.
7. Wait for the flocculent to settle to approximately half the bottle volume.
8. Remove the stopper and add the contents of one Dissolved Oxygen 3 Reagent powder pillow.
9. Stopper the bottle and shake the bottle vigorously (flocculent will dissolve and sample will turn yellow if oxygen is present).
10. Fill the plastic tube to the top with sample from dissolved oxygen bottle.
11. Place the square bottle over the full plastic tube and invert to pour the contents into the square bottle.
12. Add Sodium Thiosulfate Standard Solution one drop at a time to the mixing bottle (making sure to hold the dropper vertical). Count each drop. Swirl to mix after each drop. Add drops until the sample becomes colorless.
13. Record the number of drops used in Step 12. One drop equals one mg/L.



DO QC

1. Measure the dissolved oxygen of the sample water on the table.
2. Record result on the answer sheet.

PH

The measure of hydrogen ion (H⁺) concentration

Base
• More OH⁻
• pH > 7

Acid
• More H⁺
• pH < 7

Review QA/QC Temperature Dissolved Oxygen pH Conductivity Nitrate

PH VALUES

- ⊙ Missouri streams should have a range of 6.5 to 9.0
- ⊙ VWQM uses two-point calibration with 7.01 and 10.01 calibration solutions
- ⊙ If your stream is typically below 7.0, contact staff for an alternative calibration solution

Review QA/QC Temperature Dissolved Oxygen pH Conductivity Nitrate

PH METER

If probe has white residue, soak in water several minutes to dissolve potassium chloride

Never submerge meter over cap line

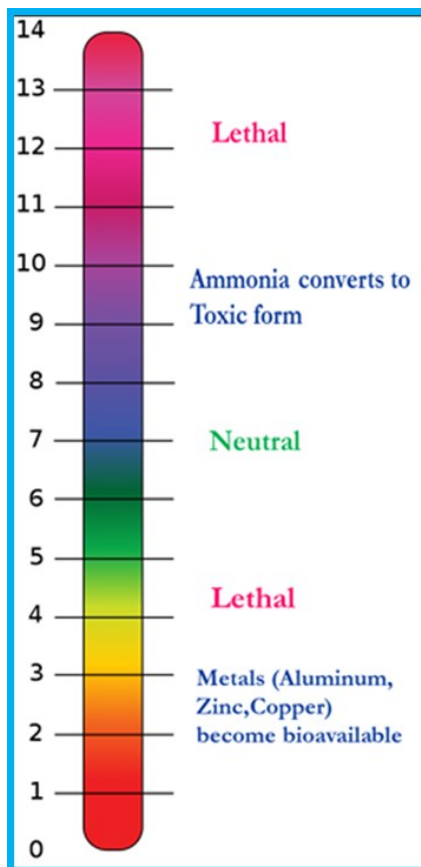
Discard used calibration solutions

Review QA/QC Temperature Dissolved Oxygen pH Conductivity Nitrate

pH

The pH levels of most Missouri streams should range from 6.5 to 9.0. Since the average pH of Missouri streams is slightly basic, we use a two-point calibration of 7.0 and 10.01. If typical pH readings for your stream site are below 7.0, please contact VWQM program staff for an alternative calibration solution.

pH levels above 10 and below 6 can be lethal to aquatic life. Lower pH allows sediments to release metals into the water, which can disrupt biological functions or cause deformities in fish.






pH Troubleshooting


- **White residue buildup on meter probe**—This white residue is potassium chloride. These meters are designed to slowly release potassium chloride to measure pH. To remove a buildup of residue from the meter, simply soak the meter in tap water or buffer solution and swirl. After calibration or measurement, store the meter in the cap with residual tap water or buffer solution. Do not store the pH meter in DI water.
- **Air bubble in glass bulb**—The glass bulb is filled with an electrolyte solution. The electrolyte can move and shift during transport or horizontal storage. If an air bubble appears, shake the meter in a downward motion to force the bubble out of the glass bulb. Inspect the bulb for cracks and air bubbles prior to calibration.

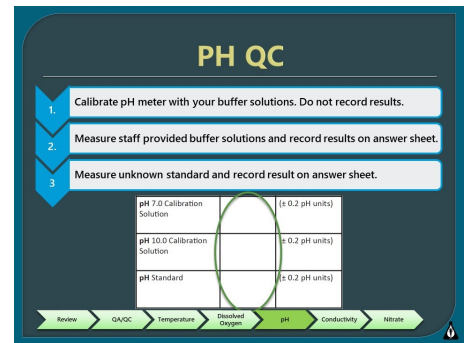
Measuring pH

Calibration (within 12 hours prior to monitoring):

1. Set the power to on and remove the cap from the sensor.
2. Push  to go to calibration mode. The auto-recognition standard (7.00) the tester expects will display at the bottom of the screen..
3. Pour the yellow pH 7.00 buffer solution into the cap to the fill line.
4. Put the sensor fully into the cap.
5. When the measurement is stable, push  to save the measurement. The measured value flashes three times.
6. Repeat steps 3-5 with blue pH 10.01 buffer solution.
7. Push and hold  to go to continuous measurement mode. "END" shows on the display.
Note: "ECAL" shows on the display if the calibration was not successful.
8. Rinse the sensor and cap with deionized water and blot dry.

Measurement:

1. Set the power to on.
2. Remove the cap from the sensor.
3. If the lock icon shows on the display, push  to go to continuous measurement mode.
4. Place meter sensor in flowing stream water until reading is stable.
5. The measured value shows on the top line.



pH QC

1. Calibrate your pH meter with your pH 7 and pH 10 buffer solutions. Do not record these results from calibration.
2. Measure the staff provided pH 7 and pH 10 buffer solutions. Record these results on the answer sheet.
3. Measure the unknown standard. Record this result on the answer sheet.

CONDUCTIVITY

- ⦿ Measures how well an electrical current passes through water
- ⦿ Dependent on amount of dissolved solids in water
 - Conductivity increases with increased ions (chloride, calcium, bicarbonate, etc.)
- ⦿ Essential for biological functions

Review OA/OC Temperature Dissolved Oxygen pH Conductivity Nitrate

AVERAGE CONDUCTIVITY

St. Francis mountains	30 – 150 $\mu\text{S/cm}$
Bootheel region	100 – 500 $\mu\text{S/cm}$
Ozark streams	150 – 500 $\mu\text{S/cm}$
Northern Missouri	300 – 800 $\mu\text{S/cm}$
Missouri/Mississippi River	500 – 800 $\mu\text{S/cm}$
Wastewater effluent	800 – 2000 $\mu\text{S/cm}$

Review OA/OC Temperature Dissolved Oxygen pH Conductivity Nitrate

CONDUCTIVITY METER

If meter does not calibrate, soak in water with one drop of dish soap

Calibrate within 12 hours of sampling

If "----" displays, the sample is over range

Review OA/OC Temperature Dissolved Oxygen pH Conductivity Nitrate

Conductivity

Conductivity is the measurement of electrical current that can pass through water. This is dependent on dissolved solids, such as calcium, sodium, iron, and chloride. These dissolved solids form ions, which allow water to conduct electricity. Large amounts of dissolved solids in the stream results in higher conductivity readings.

Conductivity varies greatly from stream to stream. Below is a table of average conductivity readings in Missouri:



Stream location	Average conductivity
St. Francis mountains	30—150 $\mu\text{S/cm}$
Bootheel region	100—500 $\mu\text{S/cm}$
Ozark streams	150—500 $\mu\text{S/cm}$
Northern Missouri	300—800 $\mu\text{S/cm}$
Missouri/Mississippi River	500—800 $\mu\text{S/cm}$
Wastewater effluent	800—2000 $\mu\text{S/cm}$

Conductivity Troubleshooting


- **Unable to calibrate**—The electrodes probably need cleaned. These black platinum coated silver electrodes have a film coating from the manufacturer. Until the meter is well conditioned, this can interfere with calibration. Soak the meter in tap water with one drop of dish soap for several minutes, occasionally swirling. Do not wipe, rub or use abrasives on the probes.
- **Meter displays “----” while measuring conductivity**—Measurement is out of range. Low range conductivity meters can only measure up to 1990 $\mu\text{S/cm}$. Conductivity measurements exceeding 1990 $\mu\text{S/cm}$ can be expected in large cities, such as St. Louis, Kansas City, and Springfield, during winter after road salt applications. If an out of range reading occurs and is unexpected for your stream site, contact VWQM program staff to report the high conductivity reading.

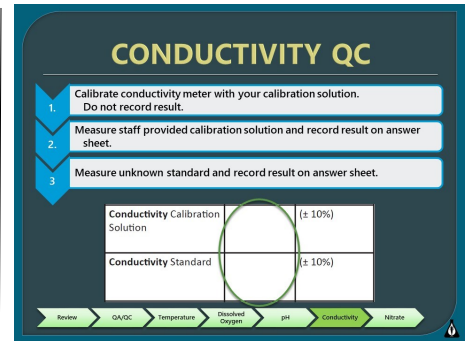
Measuring Conductivity

Calibration (within 12 hours prior to monitoring):

1. Set the power to on and remove the cap from the sensor.
2. Push  to go to calibration mode. The auto-recognition standard (1413 or 147 $\mu\text{S}/\text{cm}$) the tester expects will display at the bottom of the screen.
3. Pour the 1413 $\mu\text{S}/\text{cm}$ calibration standard shown into the cap to the fill line.
4. Put the sensor fully into the cap.
5. When the measurement is stable, push  to save the calibration and go to continuous measurement mode. The measured value will flash 3 times and then stop. Then, "END" shows on the display.
6. Rinse the sensor and cap with deionized water and blot dry.

Measurement:

1. Set the power to on.
2. Remove the cap from the sensor.
3. If the lock icon shows on the display, push  to go to continuous measurement mode.
4. Place meter sensor in flowing stream water until reading is stable.
5. The measured value shows on the top line.



Conductivity QC

1. Calibrate your conductivity meter with your calibration solution. Do not record this result from calibration.
2. Measure the staff provided calibration solution. Record this result on the answer sheet.
3. Measure the unknown standard. Record this result on the answer sheet.

NITRATE

- ◉ Nitrogen measured as nitrate-nitrogen
- ◉ Occurs naturally and required by all organisms
- ◉ Excessive amounts overstimulates plant and algae grow

Review → OA/OC → Temperature → Dissolved Oxygen → pH → Conductivity → Nitrate

NITRATE TEST KIT



Do not perform this test if pregnant



Always wear gloves and safety goggles



Containerize waste in a cubitainer

Review → OA/OC → Temperature → Dissolved Oxygen → pH → Conductivity → Nitrate

Nitrate

VWQM measures nitrate as nitrogen (NO₃-N). Nitrate levels are dependent on season, organic breakdown, and organic loading. Seasonally, nitrates are higher in the fall due to the organic breakdown of leaves and algae. Septic tanks, wastewater treatment plants, storm drains, feedlots, crop fields, and fertilized lawns can cause elevated nitrate levels. Average nitrate levels in Missouri range from less than 0.25 mg/L to 2.0 mg/L.

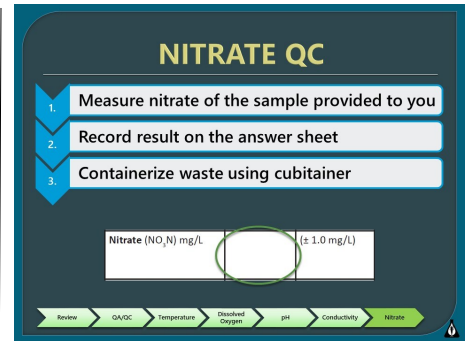


Nitrate Troubleshooting

- **The solution looks yellow after completing the test** — Nitrate tablet #2 is sensitive to sunlight. Keep the test in the foil sleeve from the time tablet #2 is added until the test is complete. Exposing the test tube to sunlight will result in a yellow solution. A yellow solution may also be observed if nitrate is very low, despite not being exposed to sunlight. If you know your test tube was not exposed to sunlight during while running the test and you got a yellow solution, record your value as < 1 mg/L. If you think you may have exposed it to sunlight, rerun the test using the foil sleeve.
- **The solution looks stratified or cloudy after completing the test**—The tablets may not have dissolved. Be sure to shake the test tube vigorously with tablet #1 and tablet #2.
- **The reading is between two values on the colorimeter**—Record the nitrate reading as a range on the data sheet. For example, if the nitrate reading looks to be between 6 and 8 on the colorimeter, record this as, “>6 , <8.”

Measuring Nitrate

1. Rinse the sample bottle three times with stream water.
2. Fill sample bottle with sample water.
3. Fill one test tube to the 5.0 mL line with water from the sample bottle.
4. Add one Nitrate #1 Tablet.
5. Cap and mix until the tablet disintegrates.
6. Place the test tube in foil protective sleeve.
7. Add one Nitrate #2 Tablet.
8. Cap the test tube and mix for (2) minutes to disintegrate the tablet.
9. Set a timer and wait (5) minutes
10. Remove the test tube from the foil protective sleeve
11. Inset the test tube into the Octa-Slide 2 Viewer (color comparator).
12. Hold the Viewer so that non-direct light enters through the back.
13. Match the sample color to a color on the Viewer.
14. Record the result on the data form as: NO₃-N mg/L.
15. Record a range or number on the data form at NO₃-N mg/L. *Do not use the multiplier on the instructions.*
16. Containerize the liquid waste in a waste container and pour down the drain after returning home.



Nitrate QC

1. Measure the nitrate of the sample provided to you.
2. Record result on the answer sheet.