Chemical parameters play an important role in the health, abundance, and diversity of aquatic life. Excessive amounts of some constituents such as nutrients, or the lack of others can result in imbalances in water chemistry. In this chapter, we will discuss:

- Understanding Water Chemistry
- Temperature
- Dissolved Oxygen
- pH
- Dissolved Solids
- Nutrients
- Transparency
Why monitor chemical parameters?

Water carries needed nutrients and minerals to aquatic life and carries waste. Chemical parameters play an important role in:

- **Health**: of the stream
- **Abundance**: of aquatic insects
- **Diversity**: of aquatic organisms
- **The life within the stream**

Remember that changes in many of the following parameters can affect other chemical parameters.

Toxicity Definitions

**Toxicity**: A measurement of how poisonous or harmful a substance is to plants and animals

<table>
<thead>
<tr>
<th>Acute Toxicity</th>
<th>Chronic Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short term (2-4 days)</td>
<td>Longer-term (1/10 of life span or more)</td>
</tr>
<tr>
<td>Lethal/Serious harm</td>
<td>Harmful but usually not lethal (affects growth, reproduction)</td>
</tr>
</tbody>
</table>

Water Quality Standards (WQS) are set to protect human health and animal life. These standards can be found on the Missouri Department of Natural Resources website.

Monitoring Water Chemistry

Water chemistry should be monitored at least four times per year, once every season. Some monitors may have specific project goals which require monitoring more frequently. Since stream flow affects water chemistry, also measure stream discharge while collecting water chemistry data.
The amount of dissolved oxygen in the water, the rate of photosynthesis by algae and other aquatic plants, and the rate of plant growth are all affected by temperature. Plant growth increases with warmer temperatures. When plants die, they are decomposed by bacteria, which use up oxygen. Increased plant growth means more oxygen being removed from the water during the decomposition process.

The metabolic rates of organisms increase with higher temperatures. As respiration and digestion rates increase, fish, aquatic insects, and aerobic bacteria require more oxygen to survive.

The sensitivity rates of organisms is also affected by temperature. Many organisms require a specific temperature range, and changing that range may eliminate some organisms from the ecosystem. Under temperature extremes, organisms may become stressed, which makes them more vulnerable to toxic wastes, parasites, and disease.

## Effects on Temperature

- **Riparian cover removal**: What if the trees in the riparian zone were removed from a cold-water trout stream? It is likely that our cold-water stream would not remain cold as long, because there would no longer be any shade.

- **Soil Erosion**: increased turbidity

- **Thermal Pollution**: Sources of thermal pollution include warm or hot water from a power plant or industrial discharge and runoff from impervious surfaces such as parking lots and streets.

- **Impervious Surfaces**: Impervious surfaces are anything that does not absorb water such as concrete, asphalt, roof tops and compacted soils. Impervious surfaces get very hot in the summer and stormwater runoff from these surfaces can reach as much as 120°F Fahrenheit.
Missouri Stream Team: Introduction to VWQM

Dissolved Oxygen

*Dissolved oxygen (DO)* is essential for the maintenance of healthy waterways. Aquatic life needs a certain level of dissolved oxygen for survival and a depletion of DO can cause a major shift in the organisms present in a stream. Dissolved oxygen comes from 3 major sources:

- **Atmosphere**: The air we breathe contains approximately 21% oxygen, which equates to 210,000 ppm oxygen. Some of this oxygen diffuses into streams. Most surface waters contain between 5 and 15 ppm dissolved oxygen.
- **Aeration**: Waves and tumbling saturate water with oxygen from the atmosphere like an aquarium aerator.
- **Photosynthesis**: Algae and other aquatic plants deliver oxygen to water. Waters with consistently high D.O. are considered healthy and stable aquatic systems – a positive sign. Absence of D.O. is a sign of severe pollution.

**Water Quality Standard for Dissolved Oxygen**

*The Water Quality Standard for D.O. is no less than 5 mg/L (5 ppm)*

**Influences and Impacts on Dissolved Oxygen**

Natural Influences:
- Temperature
- Flow
- Dissolved and Suspended Solids
- Aquatic Plants

Human influences:
- *Removal of Riparian Corridor Vegetation*
- *Dams*
- *Organic Waste*
- *Urban Runoff*
Diel Fluctuation in Dissolved Oxygen

Dissolved oxygen fluctuates throughout the day. It is natural to be lowest just before sunrise and peak during the middle of the day. This is because algae and other aquatic plants switch from photosynthesis to respiration at night and are therefore using oxygen, not producing it.

Some of the factors that can cause extreme fluctuations in DO include:

- Removal of trees
- Excess nutrients

It’s best to sample water quality first thing in the morning to measure the lowest dissolved oxygen for your stream.

Dissolved Oxygen Percent Saturation

*Dissolved Oxygen Saturation* is the maximum level of dissolved oxygen that would be present in the water at a specific temperature, in the absence of other influences.

*Percent Saturation* is the percentage of dissolved oxygen concentration relative to that when completely saturated. This tells us whether a DO measurement is good or bad.

As water temperature increases, DO saturation decreases, and as water temperature decreases, DO saturation increases. Therefore, cold water will hold more DO than warm water.

### Acceptable D.O. Percent Saturation Levels

<table>
<thead>
<tr>
<th>Ozark Stream (high gradient, rocky bottom)</th>
<th>&gt;80% D.O. Saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prairie Streams (Low-gradient or slow moving)</td>
<td>&gt;60% D.O. Saturation</td>
</tr>
</tbody>
</table>

D.O. Percent Saturation

- D.O. concentration tells us how much oxygen is in the water.
- How do we know whether there is enough oxygen in the water?
- **D.O. Percent Saturation**: Ratio of amount of oxygen present in water to the maximum the water could hold at that temperature in the absence of other influences.
- More meaningful indicator than a D.O. reading alone.

**D.O. Saturation**

- As water temperature increases, the amount of oxygen it takes to saturate the water decreases.
- Cold water can hold more oxygen than warmer water.

**D.O. Percent Saturation**

- Example: D.O. of 8 mg/L
- In the summer, when water temperatures are high, could be an excellent result
- In winter, when water temperatures are low, could indicate problems
- D.O. Saturation takes the guesswork out of interpreting D.O. measurements
Normal stream water pH ranges from 6.5 to 8.0. Most organisms have adapted to life in water of a specific pH and may die if that fluctuates even slightly. At extremely high or low pH values (11.0 or 4.5) the water becomes lethal to most organisms.

Waters that are acidic can cause metals such as zinc, aluminum, and copper to be released into the water column and accumulate in the food chain. Copper and aluminum can accumulate on fish gills and cause deformities in young fish, reducing their chance of survival. Ammonia compounds convert to a toxic form in basic water. The more basic the water, the more toxic the ammonia that is present.

**Water Quality Standard for pH**

The Water Quality Standard in Missouri for pH is a range of 6.5–9.0
Conductivity

**Conductivity** is a measure of the electrical current passing through water. It is a general indicator of water quality trends because it tells us the amount of dissolved solids are in the water. **Conductivity measurements do not tell us which dissolved substances are in the water, only how much.** Small amounts of certain dissolved solids, such as some metals, can cause significant changes in conductivity.

Common dissolved solids which influence conductivity:

- Bicarbonate
- Calcium
- Magnesium
- Sulfate
- Chloride
- Sodium
- Potassium

Sources of dissolved solids in streams include: rainfall, vegetation, rocks, soil, and groundwater. The three most abundant dissolved substances come from the dissolution of limestone and dolomite. The remaining one percent of dissolved solids can vary considerably, but can include nitrates, metals, ammonia, phosphorus, and manmade compounds such as pesticides and fuel.

**Water Quality Standards for Chlorides**

There is currently no Water Quality Standards for conductivity in Missouri.

## Conductivity Ranges in Missouri

<table>
<thead>
<tr>
<th>Stream</th>
<th>Conductivity Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pickle Creek</td>
<td>40 – 60 μS/cm</td>
</tr>
<tr>
<td>Big Piney River</td>
<td>200 – 350 μS/cm</td>
</tr>
<tr>
<td>Grand River</td>
<td>350 – 550 μS/cm</td>
</tr>
<tr>
<td>Missouri River</td>
<td>400 – 750 μS/cm</td>
</tr>
<tr>
<td>Wastewater Effluent</td>
<td>800 – 2000 μS/cm</td>
</tr>
<tr>
<td>N. MO Groundwater</td>
<td>800 – 2000 μS/cm</td>
</tr>
</tbody>
</table>
Chlorides

Chlorides are salts resulting from the combination of chlorine gas and various metals. Most chlorides come from sodium chloride (NaCl) applied to roads and sidewalks to melt ice.

Application of these road salts has drastically increased since the 1970s. These salts can travel up to 130 ft from the roadway and often have heavy metal additives, so other harmful substances may be present.

High levels of chlorides are toxic to aquatic life. They interfere with osmoregulation in freshwater organisms and can lead to fish kills.

Some invasive species (e.g. Eurasian water milfoil) are more tolerant to chloride and can outcompete the native species of the area.

Spikes can occur during the summer during low flows and during the spring and fall after fertilizer applications.

Water Quality Standards for Chlorides

<table>
<thead>
<tr>
<th>Designated Use</th>
<th>Chronic</th>
<th>Acute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquatic Life</td>
<td>230 mg/L</td>
<td>860 mg/L</td>
</tr>
<tr>
<td>Drinking Water</td>
<td>250 mg/L</td>
<td></td>
</tr>
</tbody>
</table>

Best Management Practices for ROAD SALT

- Rate adjustments on salt spreaders
- Brine pre-treatment
  (St. Louis University research project)

**Not a problem for all streams; must be Level 2 to monitor**
Nitrogen

**Nitrogen** is an essential plant nutrient required by all living plants and animals for building protein. All living, organic matter contains nitrogen. As aquatic plants and animals die, bacteria break down the organic matter. Ammonia (NH₃) is oxidized (combined with oxygen) by bacteria to form nitrates (NO₂) and nitrates (NO₃).

![Nitrogen Cycle Diagram]

**What affects nitrogen levels?**

- Leaf fall
- Organic decay
- Anthropogenic impacts:
  - Poorly functioning septic systems
  - Wastewater from treatment plants
  - Runoff from animal production
  - Runoff from fields and lawns
  - Storm drains
  - Combined sewer overflows (CSO)

**Nitrate**

VWQMs measure nitrate. It is expressed at nitrate-nitrogen (NO₃-N), which means nitrogen in the form of nitrate. Nitrate is the most stable nitrogen compound and is an indicator of excess nitrogen loading.

Here are average nitrate readings in Missouri streams:

<table>
<thead>
<tr>
<th>Stream</th>
<th>Average Value</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mississippi</td>
<td>2.39</td>
<td>0.56 – 4.53</td>
</tr>
<tr>
<td>Chariton</td>
<td>0.73</td>
<td>0.38 – 1.43</td>
</tr>
<tr>
<td>Pomme de Terre</td>
<td>0.15</td>
<td>0.02 – 0.81</td>
</tr>
<tr>
<td>Jacks Fork</td>
<td>0.35</td>
<td>0.31 – 0.39</td>
</tr>
</tbody>
</table>

**Water Quality Standard for Nitrate**

There is a nitrate Water Quality Standard criterion of 10 mg/L only for Missouri streams that have a designated use as a drinking water source.
Ammonia

*Ammonia (NH₃) is the only nutrient that is directly toxic to aquatic life.*

However, the toxicity of ammonia is dependent on the pH and the temperature of the water.

Ammonia levels are not usually a problem in most Missouri streams. Ammonia is only monitored by Level 2 VWQM certified monitors when a need is determined.

Phosphorus

*Phosphorus* is also a plant nutrient. It is most readily available to plants as orthophosphate, a reactive form of phosphorus commonly referred to as “phosphate” (PO₄). Phosphorus occurs naturally in rocks and enters the water column through the weathering of rock. When additional phosphorus enters an aquatic system, even very small amounts (0.01 mg/L) can cause large algal blooms.

In Missouri, phosphate is the nutrient that limits plant growth in a body of water in a process called “primary productivity.”

**Natural:**

- **Rocks and soil**
- **Breakdown of organic matter**

**Anthropogenic:**

- **Runoff from animal production:** especially from poultry litter
- **Wastewater from treatment plants**
- **Poorly functioning septic systems**
- **Runoff from fields and lawns:** Many people fertilize their lawns in urban areas. Runoff from rainfall events following application can cause high phosphorus levels after storm events.
- **Storm drains** - Storm drains may carry waste from pets, lawn fertilizer, broken wastewater lines and septic systems.
- **Combined sewer overflows (CSO)** - These systems caused excessive algae blooms in Lake Erie in the 1960’s. Starting in 2011, projects began to reduce the volume of discharges by CSOs around Lake Erie.

Phosphate is only monitored by Level 2 VWQM certified monitors when a need is determined.
**Transparency**

*Transparency* is a measure of water clarity. It measures the depth in centimeters that light can penetrate the water. Suspended matter and plankton can cause cloudy, murky, or green water. A larger reading means the transparency is higher, thus the water is clearer.

Having a low transparency is detrimental to aquatic life. Sediment can block out light needed for vegetation, and it can bury fish eggs and benthic invertebrates. Suspended particles can also absorb heat and increase the water temperature.

**Monitoring transparency can be particularly valuable:**

- In areas being developed
- Agricultural areas not adopting best management practices to prevent soil erosion
- Downstream from quarries and gravel mining operations
Water Chemistry Reference Table

The Water Chemistry Reference Table can be found on the Missouri Stream Team website. This provides natural readings for Missouri streams, cautionary readings, possible sources affecting readings, and remedies. This resource should only be used as a guide. If there are concerns at your site, please contact Missouri Stream Team staff or Department of Natural Resources Environmental Response in case of emergency.

Water Chemistry Data Sheet

- **Header:** This section includes required information such as stream name, site number, site description, date and time monitored, name of trained volunteer, and Stream Team number. Additionally, it asks for the amount of rainfall in the last seven days, water temperature (in Celsius), and the name of any other participants assisting you.

- **Weather Conditions:** Record the weather conditions on the date you monitored your stream. You will also need to take an air temperature reading (in Celsius). Be sure to take the air temperature reading in the shade and before taking a water temperature reading.

- **Nitrate**
- **Dissolved Oxygen**
- **pH**
- **Conductivity**
- **Transparency**
- **Chlorides**
- **Hardness**
- **Alkalinity**
- **PO₄**
- **Ammonia**

*Not standard issued chemical monitoring kits. This parameters are not commonly measured. If you have a need to monitor these parameters, contact Missouri Stream Team staff.*

Definitions for Water Chemistry

- **Reagent**
  - A substance used in chemical analysis

- **Meniscus**
  - The curve in the upper surface of a liquid
  - Read the level from the bottom of a concave curve within a container
Measuring Temperature

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 Tips

- **Temperature should be measured with the program provided liquid-in-glass thermometer.**

  *Do not measure temperature using the pH or conductivity meters.*

- **Routinely inspect your thermometer for air bubbles in the liquid column. If liquid becomes separated, request a new thermometer from Missouri Stream Team.*
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. Insert 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 Tips

- Nitrate Tablet #2 is sensitive to sunlight. The test tube must be kept in the kit provided foil sleeve when adding the tablet and while the chemical reaction is processing. If exposed to sunlight the reaction will be yellow.
- A yellow color may also be observed at very low levels, even when not exposed to sunlight. If your reaction is yellow and you did not expose it to sunlight, record nitrate as <1 mg/L.
- Waste from the nitrate tablet kit may be containerized, taken home, and poured down the drain while flushing with cold water.
- If your nitrate reading appears to be between two values on the color comparator, 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 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 Tips

- Routinely inspect the bulb on the pH meter for cracks or air bubbles. If the bulb has an air bubble, hold the meter in your hand firmly with the bulb facing the ground. Give the meter a quick fling downwards as if you are flinging water from the meter. This should force the air bubble out.
  If meter bulb is cracked or dry, contact Missouri Stream Team for a replacement.
- After storage you may see a white crystallization around the bulb. This is potassium chloride and completely normal. Soak the meter bulb in tap water for a few minutes to rinse.
- The PocketPro pH meter is designed to be stored with residual water on the bulb. Do not pat dry. Do not store in DI water.
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 μS/cm) the tester expects will display at the bottom of the screen.
3. Pour the 1413 μS/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 Tips**

- The PocketPro conductivity meter is prone to calibration challenges until it is well conditioned. There is a protective coating on the meter electrodes. Do not wipe these, but they should be cleaned by soaking in a cap of tap water with a drop of dish soap. Rinse well before calibrating. An indicator that the electrodes need to be cleaned is if the meter is reading too low to be calibrated successfully.
- Hold the conductivity meter by the top while measuring. Holding it by the cap or setting it on a metal surface will affect the reading.
- If your meter displays “- - - -“ while measuring conductivity, the measurement is out of range. Low range conductivity meters can only measure up to 1990 μS/cm. Conductivity measurements exceeding 1990 μS/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 Dissolved Oxygen

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.

Dissolved Oxygen Tips

- If an air bubble is observed in the sample vial while adding DO 1, 2, or 3, please start over. The air bubble will affect the chemical reaction. If there is a residue on the bottom of the sample bottle after restarting a test, add DO 3 to complete the chemical reaction and break apart the residue.
- Waste from the DO kit can be containerized and taken home to be poured down the drain while flushing with cold water.
- 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.
- Hold sodium thiosulfate 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.
Water Chemistry Reminders

- Check expiration dates of reagents well before monitoring. Equipment orders take 2-4 weeks to arrive.
- Double check data sheet and online data entry for errors
- Save a copy of your data collected in case of follow-up questions or errors
- When adopting a new monitoring site, submit site map to StreamTeam@dnr.mo.gov
- Liquid waste can be poured down the drain while flushing with cold water. Containers for liquid waste can be requested through Missouri Stream Team staff.
- Dry waste can be kept in original packaging and discarded in trash
- Keep all chemicals and waste out of reach from children and pets.

Next Steps

After completion of the virtual trainings, you are eligible to attend the field certification. Check mostreamteam.org for field certification opportunities. Individuals that complete the field training are VWQM Level 1 certified and are eligible to receive the following monitoring equipment:

Stream Discharge
- Flow balls
- Measure tape

Biological Monitoring
- Kick net
- Vials
- Magnifiers
- Forceps

Water Chemistry
- Thermometer
- Transparency tube
- DO kit
- Nitrate kit
- Conductivity meter
- pH meter