Why Monitor 101

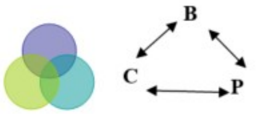
Monitoring can tell us how well a river is functioning and if it is healthy or at risk. Understanding how monitoring fits into the bigger picture is essential in implementing a River Watch monitoring program. One way to assess the health of an aquatic ecosystem is to categorize monitoring parameters into three areas **chemical**, **physical**, or **biological**. The River Watch program measures parameters in each of these three categories. When assessing the health or status of a system, like your body or a stream, you want to measure the **stress, exposure** and **responses** to possible pollutants. A comprehensive watershed monitoring plan would incorporate all six of these elements as much as resources allow.

Furthermore, all three areas can be a stressor, exposing harm to organism who live or use the river and they are indicator species. Exposure causes a response in these species .That response can be **chronic** or **acute**. To characterize or quantify exposure a monitoring program's study design will include ways to measure **magnitude, frequency and duration** of exposure to determine if it is at a level to cause a chronic or acute impact. That impact will also depend upon the organism, the size, age, species, ability to move, time of year, path of exposure (ingestion, physical, etc.). **Magnitude** is the degree of exposure above a threshold, large or small. **Frequency** is how often the organism is exposed, every day or once year or once a life time. **Duration** is how long an exposure occurs, if every day maybe all day or only for five minutes, if once a year for one day, etc. If the exposure is of sufficient magnitude, frequency and duration and the organism dies, that is considered an **acute exposure** (often high magnitude, not frequent and short duration think of being in the building during the 1986 Chernobyl nuclear plant breakdown). If the exposure causes anything from a skin condition to death, that is considered **chronic exposure** (lower magnitude, very frequent and longer duration think second hand smoke). Clean Water Act standards include an acute and chronic level when data is available.

Monitoring stressors provide information on stressors and exposure. Conclusions may or may not support the same conclusion if monitoring response communities exposed to those stressors. The response community would include monitoring the plants, animals and/or humans directly. Humans are difficult to monitor directly but patterns if disease, sickness or other conditions, can be monitored, that is the science of epidemiology. Bacteria like E.coli provide an indicator of health and is often the parameter used to protect recreation standards in many states clean water acts. All waters have **bacteria** to break down organic material for food like your stomach, some are good and some are harmful like some cyanobacteria. As an example, **aquatic vegetation** can be an indicator for excess nutrient loading along with chlorophyll and direct measurements of phosphorus and nitrogen. **Macroinvertebrates are an effective indicator species** because they spend most of their life cycle in the water, live a year or less, are not that mobile relative to fish, easy and feasible to collect, occupy diverse habitats, have diverse life cycles, are not artificially managed, differ in their tolerance to different pollutants (stressors) and respond to human disturbances in predictable ways. **Fish** are also good indicators as they are further up the food chain, reside in different habitats, do have different tolerances to pollutants and their response is predictable for some human disturbances. However, fish are more expensive and difficult to collect, there are fewer of them and they can be managed (stocked, etc.). Each biological community provides a unique line of evidence for impairment or health that adds to information from chemical and physical habitat monitoring.

Examples of a chemical indicator include pH, dissolved oxygen or cadmium. An example of a physical habitat indicator includes the amount of flow, stream width and depth, bank stability and substrate composition. An example of a biological indicator includes fish, macroinvertebrates, algae, daphnia and bacteria. An example indicator of a stress could be chemical pollutants or toxicant substances such as the heavy metal cadmium. An example indicator of exposure would be to test the exposure of an organism to a specific pollutant as laboratory experiments often do to produce a concentration that kills 50% of the organisms, called the LC50. An example indicator of a response is to measure the community structure of an aquatic system such as the species composition of the macroinvertebrate community or a diversity index. River Watch includes indicators in all three media's and for stress, and response to organisms. Exposure is difficult to measure because it is very resource intensive and not scalable. Indirectly, exposure limits drive water quality standards to protect uses such as drinking water and aquatic life.

Biological Integrity is where the chemical, physical habitat and biological components and in their healthy condition overlap, see the Venn diagram below. Stressors in any area can result in stress to another area as they are all connected. Stresses include pollutants (chemical), physical habitat (flow for e.g.) or biological (invasive species for e.g.). You can identify a stressor in one area and identify possible stressors in other areas. For example, a physical habitat stressor such as poor riparian and bank condition (perhaps due to overgrazing or a bike path), causes the bank to slough into the river. This results in a chemical stressor, sedimentation, which then buries substrate, macroinvertebrate and spawning habitat impacting those biological communities. The exposure to the stressor is covered in detail in the metals section. Response is measuring the actual plant, animal or human condition, in response to being exposed to a stressor.



Environmental Protection Agencies' top three pollutants for the nation are nitrogen, phosphorus and sediment. In Colorado, due to the precious metal mining legacy the top pollutant is metals. What comes next depends on the area and waterbody type, sediment, nutrients (N and T), algal blooms and cyanobacteria are some examples and impact lakes and reservoirs differently. The extent of new chemicals such as plastics, endocrine disruptors, forever chemicals (including fire retardant, water proofing and deicing chemicals). Often flow and physical habitat are more or as limiting for aquatic life as chemical stressors.

For metals, nutrients and sediment, it is important to distinguish the difference between *natural/background and human caused (anthropogenic) reversible* and *pollution and pollutant*. These things occur naturally and are often needed. It is the role of streams to carry sediment from eroding mountains to the ocean and that sediment often carries necessary nutrients for organism. As rivers flood they bring in more nutrients and flush out the system and move material downstream. These become pollutants when they exceed a threshold, biological or physical. Pollution is the introduction of harmful materials into the environment. Those harmful materials are called pollutants. Pollutants can be natural, like volcanic ash or man-made like plastics, pesticides or hormones. A river that receives too much sediment for its discharge, hydrology and physical capacities will “fill up” in a sense and sediment becomes a pollutant causing pollution (impact). Same with metals and nutrients.

Following how a pollutant behaves and changes as it enters the soil, the water or the air is called **fate** and **transport**. Many chemicals break down into numerous pollutants as part of fate and transport, and that one product produces 17 pollutants to monitor and analyze. A metal may change form and become bioavailable or unavailable. This presents an additional challenging for monitoring as well as developing policies that protect all beings.

Systems have varying degrees of what is natural or background levels occurring based on many factors; region, elevation, geology, climate, etc. Often in an unnatural way or rate, human uses over time introduce, metals, nutrients and sediment, in this example and that is called an anthropogenic source. Different systems have different capacities to assimilate and process these exposures or additions, just like humans. The Clean Water Act attempts to minimize impacts from human sources and has many programs to protect and restore waters. The primary philosophy is that if a human source can be “fixed” it will be. In some cases, the system cannot be returned to its natural or previous condition and that is termed irreversible and efforts focus on reaching the ‘new’ potential, even if altered from the natural state. In some cases, the altered condition can be perceived as better than the natural condition. For example, some braided flashing streams or ephemeral streams (streams that don’t flow all year) are altered into contained cold water, year round flows that support trout; or some rivers are dammed and now support a reservoir fishery. These may be irreversible changes. Restoration strategies have to discern between these areas.

Monitoring is a necessary component in understanding the function and health of river ecosystems, but only a means to an end, not the end. Monitoring generates **data;** numbers, ratings, and descriptions, but that data still needs to translation into **usable information,** used by decision makers, even if that decision maker is you, for a desired action, change, impact or result. The decision and actions taken because of the information generated by the data is the end. In order to have your monitoring efforts produce a measurable result, you start with the end in mind. You ask, what is the desired action, result or change and work backwards to what you do not know and data will help you answer. These questions are often called monitoring objectives.

Steps to identifying the monitoring objectives include, who will use the data, how they will use the data, what decision they are trying to make, and what information needs generating to make those decisions. Information needs of the data user, decision maker and uses that should determine what, where, when, and how the data is collected. As well as the quality of the data and how rigorous the data collection needs to be.

Finally, a plan to manage the monitoring results (data management) and translate the data into information (information products) is essential. This includes a plan to implement the monitoring, manage raw data, perform data analysis, derive findings, interpret the results, make recommendations, and deliver the results to data users. Then circulate back, evaluate and adjust the monitoring plan (asking questions: what, when, where, how, data quality, etc.).

Together the steps and approaches listed above make up the bigger picture of an effective study design or monitoring plan and thus monitoring program. Many of the components of an effective monitoring program (or watershed assessment) are in place with the River Watch program for the participants.

A primary River Watch data use is to provide a voice for aquatic life through the implementation of the **Colorado's Clean Water Act**. A primary user of this data is the organization that administers the Clean Water Act; the Colorado Department Public Health and Environment's (CDPHE) Water Quality Control Division (WQCD) and appointed Commission. This Water Quality Control Commission (WQCC) is responsible for determining water quality standards or how much pollution is allowed in our waterways, if a waterbody is not meeting a designated use (like drinking water or supporting aquatic life) and is impaired and how restoration will happen.

CDHPE receives funding from the Environmental Protection Agency (EPA) to implement Colorado's Clean Water Act. Those policies and regulations require clean water act agencies to utilize all data of a known quality for the Act's programs and decisions. This is why it is so important to include information about the data so decision makers can determine the quality. This is also what drives the level of rigor and quality of data required for these decisions. The result is River Watch is transparent about our methods, provides information about the data (station location as an example) and why we ask River Watch Volunteers to do things like unknowns, blanks and dups and only use the equipment we provide.

You, the volunteer or data generator are a primary user. You can conduct your own data analysis and data interpretation and decide for yourself the health of your river. Other primary users of RW data include Colorado Parks & Wildlife biologists, the Environmental Protection Agency and various watershed groups.

What to Monitor

Monitoring can tell us how our river is functioning and if it is healthy or at risk. Monitoring can be categorized into chemical, physical and biological variables. RW monitors for variables in each of these areas. Monitoring can occur in the water column, substrate/soil, below substrate, on the bank, in the groundwater, on the riparian zone or flood plain. RW focuses primarily in the water column, substrate in riparian zone. Finally, a comprehensive watershed assessment program would monitor variables that included indicators of stressors, exposure and response. An example indicator of a stressor could be chemical pollutants or a toxicant such as cadmium. An example indicator of exposure would be tests that measure the exposure of an organism to a specific pollutant. An example indicator of a response measurement would be to monitor the function or structure of an aquatic community, such as fish, macroinvertebrates, bacteria/coliform or periphyton/algae. RW includes indicators for stressors and response organisms as well as background indicators such as temperature and dissolved oxygen.

How does monitoring fit into the bigger picture?

Monitoring is a necessary component to understanding the function and health of our river ecosystems, but monitoring alone cannot do it. Monitoring generates data, numbers, ratings, descriptions, but does not necessarily produce information. Monitoring needs to be accompanied with identifiable questions that you are asking the numbers or data to answer. These questions are often called monitoring objectives. In addition, identifying who will use the data, how they will use the data and what information they need to make decisions is an important component. It is the information needs of the data user and uses that should determine what is collected, where, when and how it is collected as well as the level of quality control and assurance needed. Finally, a plan to manage the results and turn the data into information is essential. This includes a plan to determine findings, conduct data analysis, complete interpretation, develop conclusions, make recommendations, take action and deliver data to the data users. Finally, data management needs to be planned and an evaluation of the monitoring design should be conducted. All of these components take monitoring to an endpoint.

All the components of an effective watershed assessment program have been pre-designed for River Watch participants. The CPW targets the Colorado's Clean Water Act, administered by the Colorado Department Public Health and Environment Water Quality Control Division (WQCD) and appointed Water Quality Control Commission (WQCC). The WQCC and CPW biologists are the primary data users in addition to their own biologists and goals of individual groups. All the protocols, what, where, when and how you collect data are directly related to these target data users. The level of quality control and assurance, type of chemicals, number of blanks and site visits are designed to meet the data quality needs of these users. Since all this is rigorous RW data meets many other monitoring objectives and data uses as well.

The reason for you to participate in River Watch is for you to decide. CPW started RW to provide more and higher quality data in decision-making processes to protect aquatic life. CPW delivers RW data to the WQCC, WQCD biologists and any interested entity to determine the health of our rivers. You, the data generator, can conduct your own data analysis and interpretation and decide for yourself the condition of your river.

pH

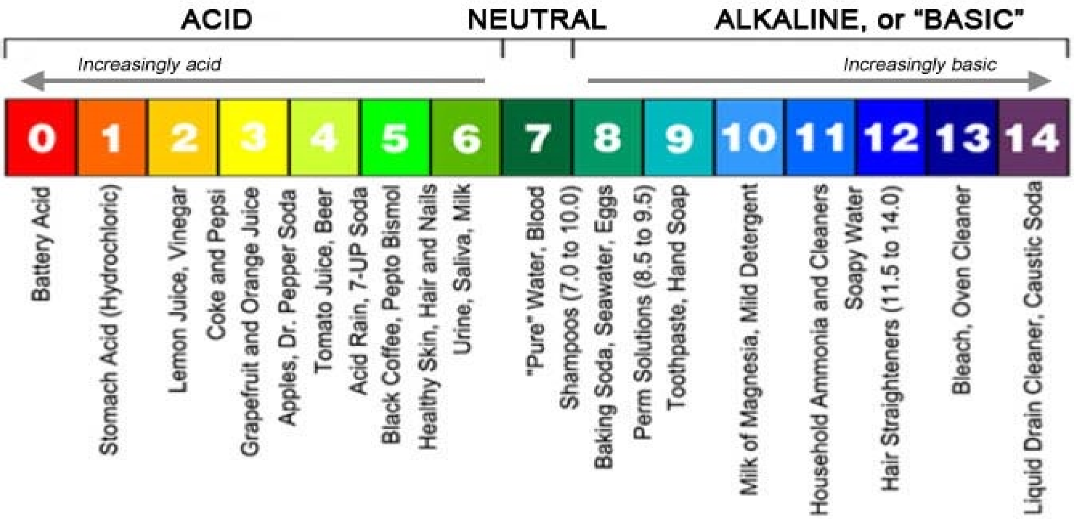
What is pH?

pH is a measure of the acidity of water and varies on a scale from 0 to 14 units. The acidity of water increases as the pH gets lower. Acids release hydrogen ions (H+); bases dissociate in water to produce hydroxide ions (OH-). A pH of 7 has equal amounts of hydrogen ions (H+) and hydroxide ions (OH-) and is considered neutral. Water with a pH less than 7 is acidic, and has more H+ ions. Water with a pH greater than 7 is basic and has more OH- ions. The lower the number (below 7), the stronger the acid. The higher the number (above 7), the stronger the base.

Even water from rain can be acidic. Normal rainwater has a pH of 5.6 (slightly acidic). This is because it is exposed to the carbon dioxide in the atmosphere. The carbon dioxide gets dissolved in the rainwater and forms carbonic acid, a weak acid.

Rainwater with pH value below 5.6 is considered acid rain. There are both natural and non-natural sources of materials that can cause pH of rainwater to change.

<u>Chart 1</u>



pH scale and pH of selected liquids. (EPA, 2022)

pH is measured on a negative logarithmic scale. A drop in the pH of a water sample by 1.0 unit is equivalent to a 10 fold increase in acidity. This means a river with a pH of 5.0 is 10 times as acidic as one with a pH of 6.0 and a waterbody of pH 4.0 is 100 times more acidic than one with a pH 6.0.

Why do we care about pH?

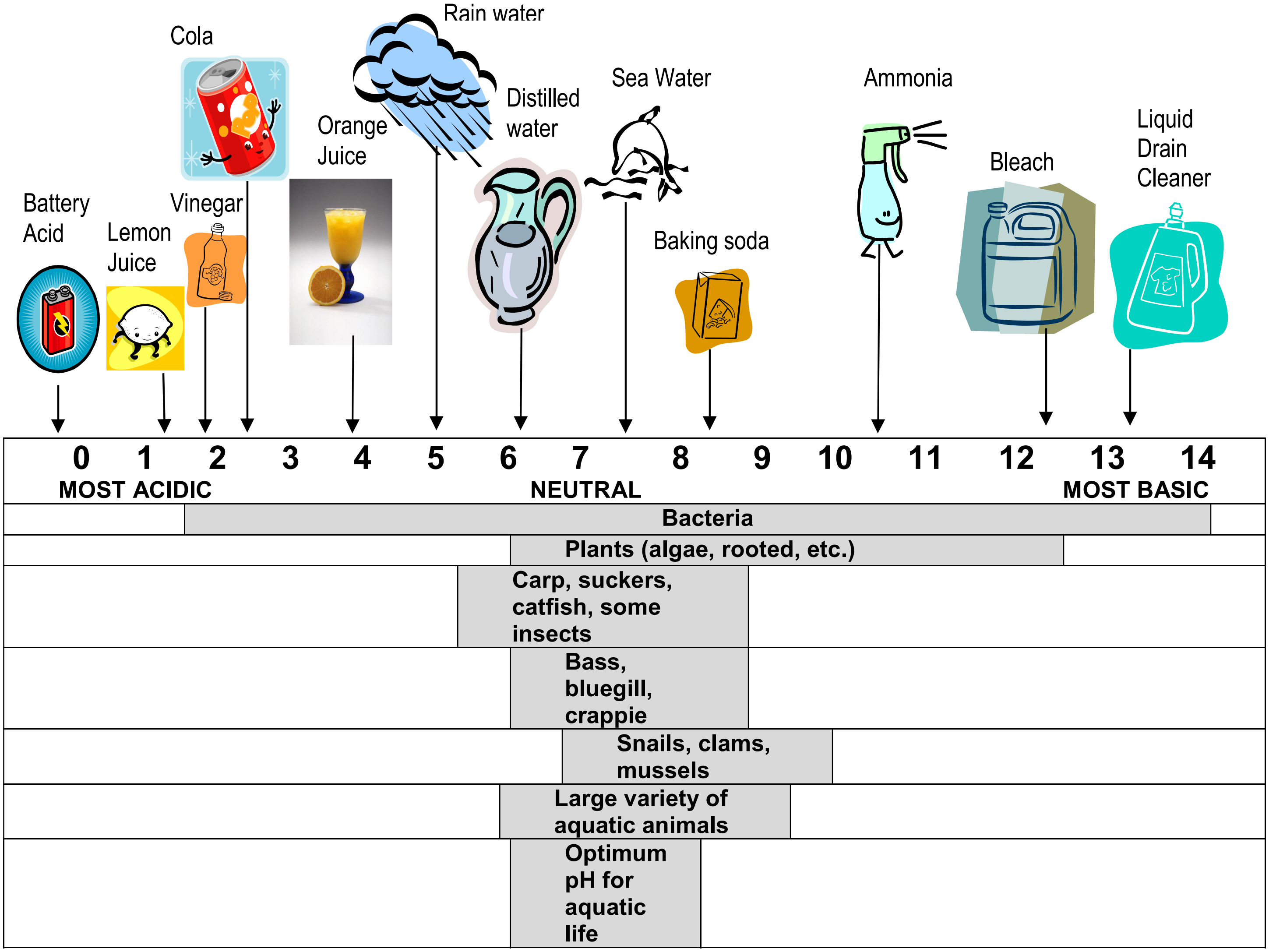
Reason 1: pH will affect what can live in a body of water

All animals and plants are adapted to a certain pH range but most prefer a circumneutral pH of 6.5-8.5. An increase or decrease in pH outside the normal range of a waterbody can stress an organism's system. This could lead to reduced hatching and survival rates. This could cause problems and possibly death of the aquatic organism depending on their sensitivity; the further outside the optimum range of preferred pH, the higher the mortality rate.

pH can also affect what can live in water by influencing the blood's ability to hold oxygen.

Chart 2

pH scale



Reason 2: pH can affect a certain life stage of an organism

Rapid changes in pH, even within an optimal range, can be fatal to fish. While fish can adjust their body chemistries as pH changes in the water, this takes energy, which could instead be used for growth and reproduction. Extreme pH levels can kill adult fish and can damage developing juvenile fish. Maintaining a constant internal pH in an extreme environment causes stress, making the fish susceptible to disease and parasites.

The most serious chronic effect of increased acidity in surface waters appears to be interference with the fish' reproductive cycle. Calcium levels in the female fish may be lowered to the point where she cannot produce eggs or the eggs fail to pass from the ovaries or if fertilized, the eggs and/or larvae develop abnormally (EPA 1980). Below a pH of 4.5, the water is essentially devoid of most fish. (There are a few fish that are able to survive and reproduce in water below pH 4.5 (e.g. central mudminnow, yellow perch).

Macroinvertebrates are also affected by pH levels. At a pH between 5.0 and 5.5, there is a shift in species composition and a decline in species richness. There is also a decrease in total abundance and biomass of benthic invertebrates and zooplankton that could occur. Acidic water (where pH is below 5.5) dissolves the exoskeletons of macroinvertebrates, shellfish, and zooplankton causing a shift in species composition. Their exoskeletons and shells are primarily composed of calcium carbonate which dissolves and dissociates in acidic water.

High pH levels occur when hydroxide ion concentrations are high and hydrogen ions are scarce. Although acidic conditions more commonly result from human activities, alkaline conditions also can occur and adversely affect aquatic biota. Certain human activities and associated sources can result in increased pH in aquatic systems. These include stormwater runoff from sources associated with agriculture (e.g., lime-rich fertilizers) and urbanization (e.g., asphalt roads) and effluents and leachate from sources associated with industry (e.g., soap manufacturing plants) and mining (e.g., oil and gas brine mining wastes). Atmospheric emissions and deposition generally do not contribute to high pH conditions, a marked difference from low pH conditions.

There are also natural sources which can result in high pH conditions, such as naturally alkaline geologies and lithologies and high levels of photosynthesis. Because photosynthesis produces hydroxide ions and consumes carbon dioxide (carbonic acid) elevated nutrient concentrations which promote plant growth may contribute to pH increases.

Ultimately, these effects may result in increased mortality, decreased reproductive success and changes in population and community structure and ecosystem function. For example, taxa sensitive to high pH (e.g., perciform fishes) may decrease, while more tolerant taxa (e.g., cypriniform fishes, *Cladophora*) may increase. These changes may result in reduced taxa richness or diversity. (EPA 2022)

Chart 3

River Parameter pH Values for Brown Trout Life Cycle.

	Egg	Fry	Juvenile	Adult
Tolerant pH	5.0-9.5	5.0-9.5	5.0-9.5	5.0-9.5
Optimal pH	6.8-7.8	6.8-7.8	6.8-7.8	6.8-7.8

Reason 3: pH can influence the state of metals in water and buffering capacity (alkalinity) of water. For example: at a pH of 3, Iron is Fe^{2+} but at a pH of 7 it changes to Fe^{3+}. Low pH water (below 3.3) dissolves metals (such as zinc and cadmium) and makes them more bioavailable allowing fish and insects to uptake the excess metals. These metals are present in rocks within the watershed and river in a solid form and are benign, but when they are dissolved in water they can be present in concentrations that are toxic to fish and wildlife.

How do we measure pH?

pH can be analyzed using litmus paper, a colorimetric test, pH pen or a pH meter. River Watch uses a pH meter with at least two calibration standards because it will produce more precise, accurate, consistent and comparable results or data quality required by our data users.

What influences pH?

Respiration and photosynthesis

Respiration and the photosynthetic activities of aquatic plants and algae can cause large changes in pH. Carbon dioxide (CO_2) is produced during respiration by both plants and animals 24 hours a day. It is also consumed by plants during photosynthesis in the daylight hours. Carbon dioxide dissolves in water to form carbonic acid (H_2CO_3).

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

Carbonic acid is a weak acid. Some of these molecules ionize to make hydrogen ions H+.

$$H_2CO_3 \leftrightarrow HCO_3- + H^+$$

Some of the hydrogen carbonate ions (HCO_3^-) ionize further to produce more hydrogen.

$$HCO_3{}^2- \leftrightarrow CO_3- + H^+$$

Therefore, adding more carbon dioxide to water, e.g. by respiration, will increase the number of hydrogen ions and lower the pH. On the other hand, removing carbon dioxide, e.g. by photosynthesis, will increase the pH. A cyclic pattern of addition and removal of carbon dioxide takes place over a 24 hour period due to photosynthesis during the day. The highest pH values usually occur at mid-afternoon.

Temperature

Temperature directly influences pH measurements. The pH of a solution is inversely proportional to the temperature. When the temperature of a solution rises, molecular vibrations increase which results in the ability of water to ionize and form more hydrogen ions. As a result, the pH value will drop. This is why the RW pH meter has a thermometer (ATC or Automatic

Temperature Compensator) attached. When the ATC probe is plugged into the meter and placed in the sample you are testing, the meter is automatically adjusting the pH measurement with the temperature it is reading before showing you a pH reading. If you unplug the ATC probe, you will see a temperature of 25 degrees Celsius. The meter is adjusting your pH measurement to 25 degrees Celsius. As a general rule, when water temperature drops (gets colder), chemical reactions occur more slowly.

Buffering capacity

Buffering capacity is defined as the ability of water to remain neutral with the addition of an acid or a base without changing overall pH. Alkalinity is a measurement of a water body's buffering capacity.

Water containing low concentrations of ions, e.g. calcium, magnesium, sodium, chloride, sulfate and carbonate, tend to be poorly buffered. The more of these ions are present in the water body, the better able the water body is to accept acidic or basic inputs with little change to the overall pH. This is because the various ions bind with the added H^+ (Acid) or OH^- (Base) to neutralize their effects. The impact of the carbonate equilibrium and the buffering capacity of a water body are linked mainly to pH. Poorly buffered waters are more likely to have large fluctuations in measured pH than more strongly buffered waters. In general, small streams in pristine areas tend to be poorly buffered, whilst larger lowland rivers are normally well buffered. Large variations in pH readings may not necessarily indicate problems with the testing procedure, rather the normal variation at that site.

Watershed geology

Wide variations in pH can also occur because of watershed geology. Even under natural conditions, the animal and plant communities of acidic streams contain many different species from those in alkaline streams. Mineralized areas might have lower pH values and limestone might have higher pH values. The pH of natural waters is largely determined by the geology and soils of the watershed.

Water running off limestone dissolves calcium carbonate. Therefore, a limestone dominated area would have relatively high pH value. However, streams and lakes that drain wetland bogs may have very low pH values (sometimes less than 5) due to the presence of humic acids derived from the slow breakdown of organic matter. Humic acids are a brown or black organic substance consisting of partially or wholly decayed vegetable or animal matter.

Human caused changes in pH

The most common cause of unnatural changes to pH occurs in catchments where certain types of soils (acid sulfate soils) or sulfate containing rocks have been disturbed and exposed to the atmosphere. Such disturbance may occur naturally or be the result of mining or agricultural practices. The exposure of these sulfate containing rocks and soils to oxygen and water can cause sulfuric acid to be formed. These acids can then be washed into streams where they can cause dramatic decreases in pH. Fish and other aquatic animals can suffer from skin irritations, tumors, ulcers and impaired gill functioning due to metal toxicity in acidic water.

Lower pH levels (below pH 5.5) particularly affect the immature stages of aquatic insects and fish by dissolving (leaching) heavy metals such as zinc, copper, lead, and cadmium into the water. These low pH and high metal concentration conditions are often toxic to aquatic life, particularly for sensitive species such as trout.

Some industrial wastes have pH values outside the normal range and thus have the potential to affect pH in receiving waters. However, in Colorado, discharge of highly acid or alkaline waste water is rarely, if ever, permitted. Such wastes are required to have pre-treatment to correct the pH balance before discharge is allowed.

Changes in pH can be caused by atmospheric deposition (acid rain, dry particle deposition) and from the burning of fossil fuels by cars, factories, and smelters, lowering pH values in rivers.

Fluctuation Expectations can be expected:

- **Daily** – due to photosynthesis, respiration, temperature and discharges
- **Seasonally** – due to temperature and associated biological activity
- **River, Lake/Reservoir, Groundwater Concentrations** – rivers will generally have lower pH values than the other water types due the minimal contact to surroundings. However, certain geology, discharges and land uses can change pH (high or low), such as acidic mine drainage, a naturally mineralized drainage, an organic load from a wastewater treatment plan or significant wetland. Lakes and reservoirs will generally have a higher pH due to the residential time of water in relation to biological activity and the environment. Groundwater will depend upon the geology of the area. Groundwater can increase slightly downstream, but the pH usually stays in between 6.5-9.5.
- **River Continuum** – can decrease due to more acid rain/snow in high mountains or naturally mineralized areas and increase if geology changes, or from urban or agriculture practices, and pH may increase due to more exposure and dissolution of limestone as the river moves down the watershed.

How an electronic pH meters works

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Let's start off with a little experiment.

1. Take two uncooked grocery store chicken eggs and place each in a glass full of vinegar for two days to dissolve the outer calcium shell, leaving only a thin "skin membrane" where the shell used to be.
2. Carefully remove one egg from the vinegar and place it in a glass of water.
3. Carefully remove the second egg and place it in a glass of corn syrup.

What happens to the eggs?

This experiment is a demonstration of the process of **osmosis**. Once the outer shell of the eggs dissolves the eggs insides are left with only a thin membrane between them and the outside world. This membrane is an **osmotic membrane.** This membrane allows water to pass **ALMOST** freely through it, however many other materials, like the eggs innards and corn syrup cannot.

The egg in the water will grow larger as it continues to sit in the water because there is a high concentration of water outside the egg and much less water inside. Since water can freely pass through the membrane, it will flow into the egg trying to equalize the water concentration on both sides of the membrane. Likewise, the egg innards will want to flow out into the water. However, the membrane does not let the innards pass through, so the whole egg will expand as it takes on more water.

The egg in the corn syrup (a form of sugar) will do the opposite: it will shrink. Why? Because in this case there is more water inside the egg membrane that outside in the sugar solution. So the water will flow out of the egg through the membrane into the sugar solution. The sugar solution will want to flow into the egg, but it will be unable to penetrate through the membrane, so the egg will shrink.

In both cases, the eggs will not continue to expand until it explodes, or shrinks until there is nothing left. At some point the osmotic process will stop even though the water concentrations inside and outside the eggs are not equal. This is because the membrane has osmotic pressure. Remember that the water can pass **ALMOST** freely through the membrane. The **ALMOST** part is the osmotic pressure. There has to be enough difference in water concentration between the inside and outside of the egg to make the water want to go through the trouble of squeezing through the membrane - just like squeezing tooth paste out of a tube.

Osmosis also happens to be how cells in your body take nutrients and oxygen in from your blood and pass waste and carbon dioxide back out to your blood. Osmosis is how your lungs take oxygen in to your blood from the air and pass carbon dioxide back out. Osmosis is very popular in nature!

So this is very cool, but what does it have to do with a pH meter?

pH is the measure the of how many free hydrogen ions there are in a solution compared to how many hydrogen ions are bound into molecules. In a glass of drinking water, most of the molecules are positively charged hydrogen ions (H+) bound together with negatively charged hydroxide ions (OH-) to form water molecules. Together, the positive and negative charges cancel, which is why they want to be together in the first place. If you dissolve other chemicals, like table salt, calcium, or iron, in the water, then some of the water molecules will break apart into their H+ and OH- ions and some of these ions will bond with the new chemical to form other molecules. So some of your drinking water has free hydrogen ions floating around with the water molecules. But for every free H+ ion there will always be a free OH- floating around, so the solution will, as a whole, have a neutral electrical charge.

A pH meter uses a form of osmosis to figure out what percentage of the hydrogen ions in a solution is free. The glass casing of the pH meter probe is a particular type of glass, which is an osmotic membrane that passes hydrogen ions (H+), but not water molecules, hydroxide ions (OH-), or most other molecules. Inside the glass of the probe is a metal wire and potassium chloride solution. The potassium chloride on the inside contains almost no hydrogen ions. If you place the probe in pure water where all the hydrogen ions are bound to hydroxide ions, then there will be no free hydrogen ions in the water. Since there are almost no free hydrogen ions inside the probe either, everything is in balance and nothing happens. If you put the probe in an acid that contains some hydrogen ions freely floating around, the ions will want to get inside the probe through the glass to balance out the ion concentration on both sides of the glass. Ions will pass through the glass into the potassium chloride solution inside the probe until the difference in concentration between the inside and outside has drop below the osmotic pressure point of the glass, just like the egg in the water glass.

Since only the positively charged hydrogen ions can get in, the negatively charged hydroxide ions have to park themselves just outside the glass. They want to get in too, (like the corn syrup and the egg) since potassium chloride contains almost no hydroxide ions, but the glass won't let them pass. So now the glass has positive charged ions inside and negative charged ions lined up on the outside. This creates and electrical voltage across the glass. By measuring the voltage between the wire inside the probe and the outside surface of the glass, the meter knows how many hydrogen ions have made it through the glass. If you place the probe in a very strong solution of hydrochloric acid, with a huge concentration of free hydrogen ions, then the probe will take on a whole lot of hydrogen ions, just like the egg in the glass of water, and the voltage across the glass will go up proportionally. The higher the voltage, the higher the free hydrogen ion concentration, and the lower the pH of the solution.

So why does the pH meter need to know the temperature of the solution being measured? Because the osmotic pressure point of the glass changes with temperature. If you heat the outside solution up, the hydrogen ions are more energized, and will be able to keep passing through the glass with less concentration difference between the sides then when the solution is colder. If the pH meter knows the temperature of the outside solution, it also knows the osmotic pressure point of the glass and can calibrate out extra ions that it will measure passing through at that temperature.

Finally, why does the probe need to be soaked in potassium chloride before using it? That’s easy; since the inside of the probe contains potassium chloride too, soaking the probe in the same solution will cause any hydrogen ions trapped inside from previous use to come out, just like the egg in the corn syrup solution.

Worksheet - pH

What: ______________________________

Why: ______________________________

How: ______________________________

Influences: ______________________________

Alkalinity

What is alkalinity?

Alkalinity can be defined as the capacity of water to neutralize acids; the buffering capacity of a water body; the measure of the ability of water to keep a stable pH.

More precisely, alkalinity is the balance of carbon dioxide in the river. Specifically, alkalinity is the amount of HCO_3^-(bicarbonates) + CO_3^{2-} (carbonates) present. These bicarbonates and carbonates are anions. The dynamic equilibrium that exists in water is the following:

CO_2 + H_2O = CO_2 (dissolved) + H_2O = H_2CO_3 (carbonic acid)

H_2CO_3 = HCO_3- (bicarbonate) + H^+

HCO_3- = CO_3^2- (carbonate) + H^+

Geology plays a big role in where both alkalinity and hardness come from. Geology is the PRIMARY source of alkalinity and hardness (there are minor secondary sources of each, which will be discussed later). Bicarbonates get into water when it passes through a calcium carbonate or magnesium carbonate (limestone or dolomite) rock formation.

As rivers travel downstream, they become larger, deeper, and wider and both alkalinity and hardness increase. Why does hardness increase more than alkalinity? Since the alkalinity concentration is measuring <u>one specific</u> anion that comes from <u>one primary</u> source; that concentration will almost always be LESS than the hardness concentration which is coming from the calcium carbonate with the addition of other cations. The farther a stream moves downstream the greater the difference between these two concentrations can increase.

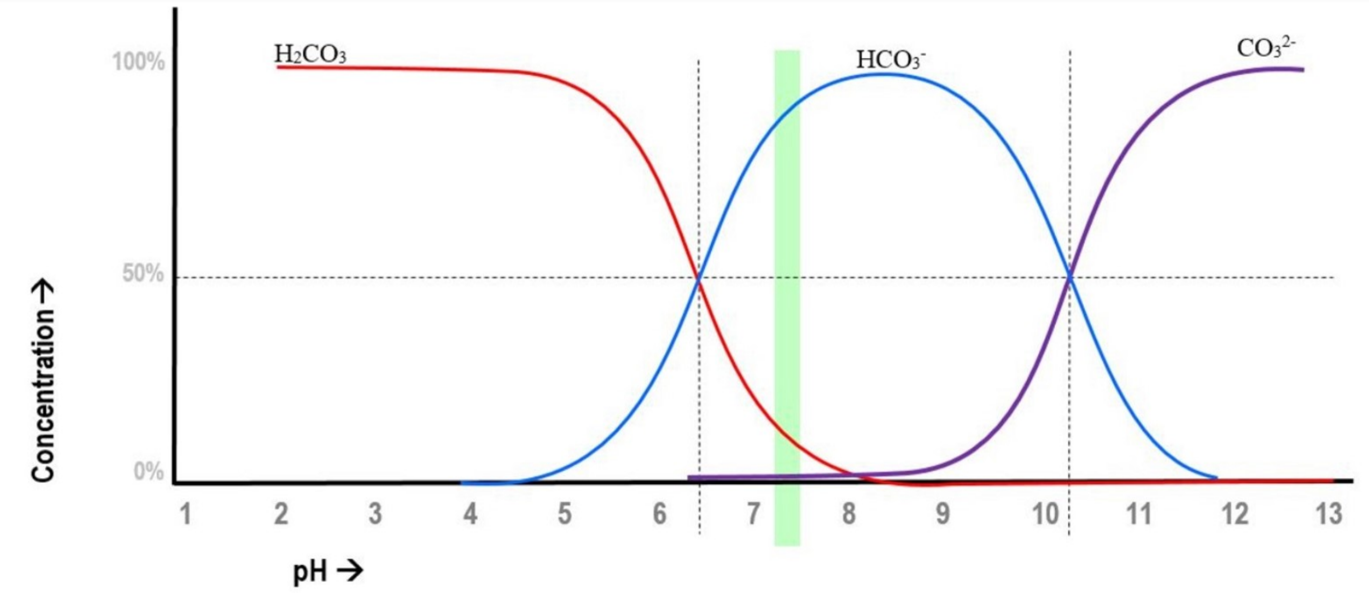
Both hardness and alkalinity measure the cations (H) and anions (A) that (in general) come from $CaCO_3$ (calcium carbonate). IF the only source of these two cations and anions is $CaCO_3$ (which is generally LIMESTONE) then these two would be equal in concentration. This is why we generally see very low concentrations of alkalinity and hardness in the high mountain reaches of streams in Colorado and they will be close to equal concentrations in these instances. The streams have little time to pick up (dissolve) hardness and alkalinity. As streams move downstream they have an opportunity to dissolve more of the cations and anions, so hardness AND alkalinity will increase.

Why do we care about alkalinity?

In equilibrium, all these reactions are happening. When pH is pushed toward the basic end (above seven), all these reactions go to the right until all H_2CO_3 or CO_2 is converted to CO_3^{2-}. Conversely, when pH is pushed below seven or to the acidic end, all these reactions go to the left until all CO_3^{2-}, HCO_3^- or CO_2 is in the H_2CO_3 form. Thus, alkalinity, or the amount of HCO_3^- + CO_3^{2-}, present in your river is a function of pH.

See chart 4 for alkalinity’s relationship to pH.

Chart 4



Alkalinity is measured as mg/l $CaCO_3$. Think of the CO_3^{2-} part of the unit as alkalinity. Water does not contain mg/l of $CaCO_3$ but behaves as if it does because CO_3^{2-}+ HCO_3^- are the main anions that neutralize acid (H^+) in natural waters. An acid (H^+) in water can be neutralized by carbonates CO_3^{2-} to form bicarbonate HCO_3^-, or by HCO_3^- to form H_2CO_3.

Reason 1: Buffering Capacity

Alkalinity is sometimes referred to as buffering capacity. Buffering capacity is the ability of water to resist a change in pH when an acid (H^+) or a base (OH^-) is added. When many HCO_3^- or CO_3^{2-} ions are present, they can bind with additional H^+'s to the system and thus overall pH will not change. When there are no HCO_3^- or CO_3^{2-} left to bind with additional H^+'s, the free H^+'s will lower overall pH of the water body. It is also possible to add H^+'s faster than the available HCO_3^- or CO_3^{2-} can bind, creating a short term lowering of pH. Technically, below pH 4.5, no alkalinity can be measured—there is no HCO_3^- + CO_3^{2-} present. When an H^+ is added, it will hook up with a HCO_3^- and make H_2CO_3 or CO_3^{2-} and make HCO_3^- and pH will not change. If H^+ is added faster than HCO_3^- or CO_3^2- can react or if there is no HCO_3^- + CO_3^2 left, the pH of your system **will** decrease. This is what happens in an acid rain/snow situation.

Reason 2: Mitigation or relief from elevated levels of metals

Ample documentation exists to demonstrate that when fish are in high alkalinity waters, they can withstand higher concentrations of metals given equal water volumes. It is not known exactly how alkalinity mitigates toxic impacts from elevated metals. It is thought that the available HCO_3^- and CO_3^{2-} can bind with dissolved metals, such as Cd^{2+} or Fe^{2+} and "take them out of action" much like when two single people become a couple, neither is "available" for others to pair with. It is the dissolved or free form of the metal that harms aquatic life. Thus, alkalinity is inversely related to metal toxicity.

How do we measure alkalinity?

Acid/base titration with sulfuric acid (H_2SO_4) as a titrant, and using phenolphthalein and BGMR as indicators.

Chemical reactions: $H^+ + IN^- \Leftrightarrow HIN$

Where H^+ is the acid you are titrating with: H_2SO_4. IN^- is the color indicator and HIN is the color of the endpoint solution.

If the pH sample is above 8.3, your CO_2 is in the form of CO_3^{2-} plus some HCO_3-, and your color indicator (IN^-) will be pink after adding 15 drops of phenolphthalein. When you add H_2SO_4 (an acid) eventually the solution turns clear. This is the endpoint solution (HIN) color.

If the pH sample is below 8.3 your CO_2 is all in the form of HCO_3-. Your color indicator (IN^-) will be turquoise after adding six drops of BGMR. When you add H_2SO_4 eventually the solution turns pink-gray-blue. That is the endpoint solution (HIN) color.

As the buffer capacity is consumed adding H^+, it will cause CO_3^{2-} to be converted to H_2CO_3 (carbonic acid).

With a pH below 4.5, there is no more HCO_3- left; all CO_2 is in H_2CO_3 form. Thus, the endpoint solution (HIN) can’t get any more pink. You have used up all the solutions buffering capacity.

What Influences alkalinity?

Watershed geology

Variations in alkalinity can be attributed to the substrate and soils the water runs over and through. Limestone has higher alkalinity waters, granite has lower.

Climate and precipitation

Wetter and warmer climates have different soil types and different vegetation. Alkalinity will vary among warmer and cooler climates; areas that freeze and have snow versus those that receive primary precipitation via rain. Alkalinity is typically higher in warmer and more productive climates.

Land use activities

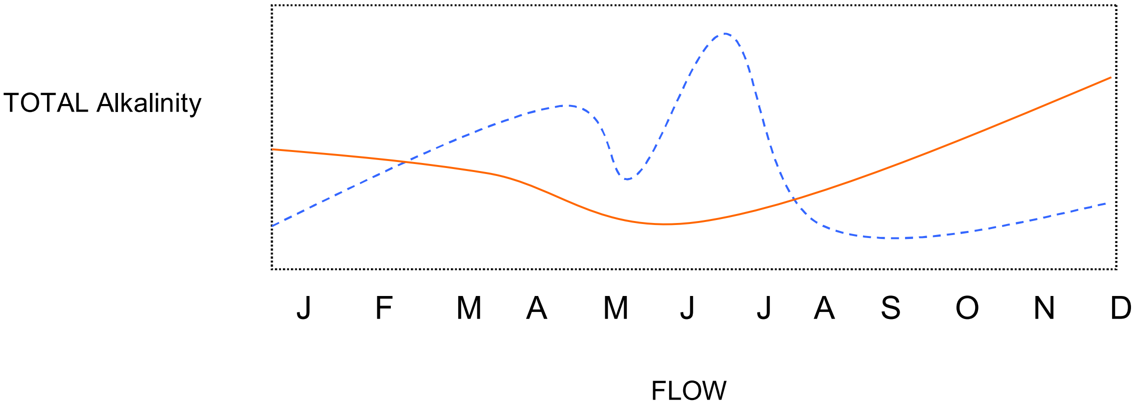
Land use activities that disturb enough soil that makes its way to the surface or groundwater can increase alkalinity concentrations. Some examples include water applied to land, such as flood irrigation. This practice can artificially increase alkalinity in waterways through irrigation return flows for example. Certain industrial processes could also increase alkalinity. Groundwater pumped and applied on land which later flows into surface waters can increase alkalinity.

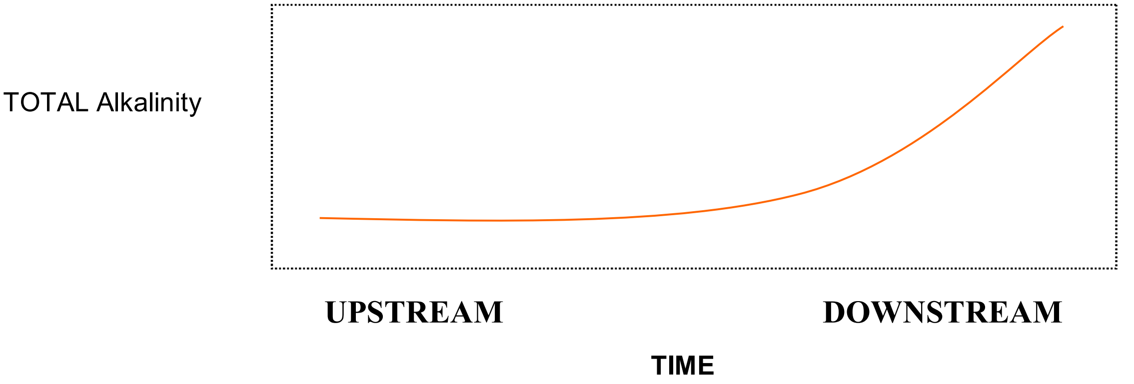
Fluctuation Expectations can be expected:

- **Daily** – not much, but can fluctuate below an organic discharge like a relatively large waste water treatment plant.
- **Seasonally – lower in runoff due to dilution, higher in low flow**
- **River, Lake/Reservoir, Groundwater Concentrations** – rivers will generally have the lowest values, next higher is lakes and reservoirs. More bicarbonate and carbonates available in lakes and reservoirs, more surface area, retention, more species so more

biological processes such as photosynthesis, respiration, decomposition, etc. Groundwater will depend if it is calcium carbonate dominated geology or sodium and potassium dominated.

- **River Continuum – increases downstream due to more water draining more area; alkalinity will not** increase as much as hardness in most areas of Colorado. High in the mountains, alkalinity and hardness can be equal. Furthermore, alkalinity can be consumed in solution (i.e. utilized to assist with buffering in the presence of an acid or a base for example). Generally Mg, and Ca are conserved.





Worksheet - Alkalinity

What: ______________________________

Why: ______________________________

How: ______________________________

Influences: ______________________________

Hardness

What is hardness?

Hardness is a measure of all multivalent cations (ions with a positive charge greater than +1) present in solution. Ca^{2+} (calcium) and Mg^{2+} (magnesium) are the most common multivalent cations in fresh water. A simplified definition of hardness is the amount of dissolved calcium and magnesium in the water.

Geology is the **PRIMARY** source of alkalinity and hardness in a river. Hardness gets into the groundwater and rivers when water percolates through rocks or deposits of limestone, chalk or gypsum, which are largely made up of calcium and magnesium carbonates, bicarbonates and sulfates.

IF the only source of hardness and alkalinity came from $CaCO_3$ (which is the predominant mineral in LIMESTONE, common in Colorado geology) then these two would be equal in concentration; hardness (Ca^{2+}) would equal alkalinity (CO_3^{2-}). In high mountain streams in Colorado, we generally see very low concentrations of alkalinity and hardness and the concentration of each is similar. The streams have little time to pick up (dissolve) hardness (cations) and alkalinity (anions) from rocks. As streams move downstream they have an opportunity to dissolve more of the cations and anions, so hardness AND alkalinity will increase.

Aquatic systems with hard water often have other elements like salts, suspended solids, nutrients, iron and/or sulfur. Harder water is often more biologically productive, has greater biomass and greater species diversity than soft water. These increases are a result of hardness, but also because of these other associations. Hard water can leave a crust or white film when it evaporates, (sometimes found around faucets), a yellow stain, smell, create a tannin color or have other effects – not all these affects are from the Ca^{2+} or Mg^{2+} present in water, but come from other elements prevalent in water. Soft water is less productive in terms of primary productivity, species diversity and total biomass.

Hardness is a widely used term, often confused by the use of water softeners. Hard water makes using soap difficult because it won't lather. Water softeners make hard water functional or able to lather up and clean our bodies, clothes or cars. In general, water softeners work by replacing Ca^{2+} and Mg^{2+} with Na^+ (sodium) K^+ (potassium) ions. Soft water has a slimy feeling but does lather well.

There will always be some amount of hardness and alkalinity in any river because there is always some geology that water flows over/through to get to the surface. In regards to rivers, hardness cannot be too high but other elements often associated with hard water can be harmful to aquatic life and productivity at some point.

Chart 5 defines the Environmental Protection Agencies range for hardness levels.

Chart 5

Levels of Water Hardness mg/L $CaCO_3$ (Environmental Protection Agency 1976)

Soft	0-75
Moderate	75-150
Hard	150-300
Very Hard	300

Hardness is measured in mg/L $CaCO_3$ (like alkalinity). Water does not contain X mg/L of $CaCO_3$, but behaves as if it does contain X mg/L of $CaCO_3$. Think of the Ca^{2+} part of the $CaCO_3$ equation as units of hardness. This unit provides a common language to compare hardness and alkalinity results across waterbodies. The River Watch hardness titration measures NOT ONLY the Ca (Calcium) half of Calcium Carbonate but also measures other cations that are present in the water, including Mg^{2+}. In headwater (high mountain) waters there is less opportunity to dissolve these cations, therefore these systems typically have low hardness numbers. As the stream flows downstream it interacts with more geology that not only has limestone but other rocks that add other cations to the mix. These are primarily Mg (Magnesium) and Fe (Iron) and others too, but to a much lesser extent. So hardness will increase as the stream moves downstream.

Therefore, a good general statement is that there are more cations contributing to the hardness number than just calcium from limestone. As rivers travel downstream, they become larger, deeper, and wider and both alkalinity and hardness increase. Why does hardness increase more than alkalinity? Since the alkalinity concentration is measuring one specific anion that comes from one primary source; that concentration will almost always be LESS than the hardness concentration which is coming from the calcium carbonate with the addition of other cations. The farther a stream moves downstream the greater the difference between these two concentrations increases.

Why do we care about hardness?

For aquatic life, hardness mitigates the toxicity from elevated levels of metals; hardness reduces the impact of harmful metals in water.

Ample documentation exists that demonstrates when fish reside in high hardness waters, they can withstand higher concentrations of metals compared to the same metal concentration in a low hardness environment. The hardness appears to “protect” fish from the effects of elevated metals. It is not known exactly how hardness mitigates toxic impacts from elevated metals. It is thought that the available Ca^{2+} and Mg^{2+} out compete the dissolved metals, such as Cd^{2+} or Fe^{2+} on the gill sites of fish. Gills are physically damaged and also functionally impaired in water with elevated metals. The more calcium and magnesium present, the better the odds of those ions being on the gill uptake sites than a harmful metal. Additionally, the presence of cations such as Ca^{2+} and Mg^{2+} physically repel other positively charged metals, such as Cd^{2+} or Fe^{2+}. Generally the dissolved ion, or free form of the metal harms aquatic life. Thus, hardness is inversely related to metal toxicity.

How do we measure hardness?

River Watch measures hardness with an acid based titration method, using EBT (Erichrome black T powder) and ammonia buffer as indicators. This is known as a complexation reaction. EBT binds to Mg^{2+} ions at high (basic) pH value. This EBT-Mg^{2+} complex is magenta. We then slowly titrate the sample from magenta to blue using EDTA (ethylene diamine tetra acetic acid). The first drop of EDTA added that maintains a blue color in your sample is equivalent to the concentration of multivalent cations present in solution – the hardness.

How does this work? Initially we add 15 drops of ammonia buffer to our river water sample. This raises the pH of the sample above 10 and holds it at that pH (buffers the sample; **remember** a buffer is something that will resist a change in pH). Ammonia buffer will not change the color of your sample, however, if you were to measure the pH change, you would see it rise rapidly to above 10. Next we add a small amount of the EBT powder to the solution and swirl, at this elevated pH, the EBT binds all of the Mg^{2+} present in solution and this complex is magenta. If you add in the EBT before the ammonia buffer, you can make the sample turn purple. However, when you add the ammonia buffer, the sample will be too dark to titrate. Your sample can be too light (not enough EBT) or too dark (too much EBT), which may cause you to underestimate or overestimate the hardness. The goal is a consistent density magenta that you could ‘read” words through if you set the flask on your instructions.

Then, after zeroing the burette, we slowly add EDTA to the solution. EDTA is a chelator, a chemical term meaning it binds metals. EDTA is one of the BEST chelators out there and has effectively 6 teeth to envelop metals. At this point EDTA begins to envelop multivalent metals present in solution, most of these are Mg^{2+} and Ca^{2+}, but EDTA also binds Pb, Zn, Cu, Mn etc. (just remember these are FAR less abundant than Mg and Ca). Initially, EDTA chooses Ca over Mg because the Mg is bound up with EBT (causing your solution to be magenta) so the EDTA, drop by drop, begins to bind to calcium until all the calcium is bound, still you will see no color change, your solution will remain magenta. Once the Ca has been consumed, the EDTA, starts to outcompete EBT for Mg, stealing Mg from the EBT-Mg complex. This is where you slowly see the color change from magenta to purple. Drop by drop EDTA is added until all the Mg is bound up. At this point the solution turns blue. If you continue to add EDTA, the color will remain blue, as there are no more metals cations to bind in solution. For this reason, the last drop of EDTA added that maintains a blue color is your endpoint and equivalent to the hardness is solution.

Chemical reactions:

[EBT + ammonia buffer] = (blue) + Mg^{2+} $\Leftrightarrow$ MgEBT (magenta)

EDTA + Ca^{2+} $\Rightarrow$ CaEDTA

EDTA + Mg^{2+} $\Rightarrow$ MgEDTA

EDTA + MgEBT (magenta)   MgEDTA + EBT (blue)

What Influences hardness?

Watershed geology

Variations in hardness can be attributed to the substrate and soils the water runs over and through. More limestone yields higher hardness than silica rock. On a side note, this is also why alkalinity and hardness typically increase during low flow months. The primary source of these constituents are geology and groundwater (these remain relatively constant over the course of a year). When river flows increase (spring runoff), these concentrations are diluted by runoff. This is also why we see a seasonal fluctuation in metals concentration (lower during runoff). Despite lower metal concentrations that can occur during spring runoff, when hardness also is diluted, the protection offered to aquatic life from hardness is reduced. For these reasons aquatic life are more threatened by metals in the spring high flow months than at other times of the year when hardness offers better protection.

Climate and precipitation

Wetter and warmer climates have different soil types and vegetation. Likewise, hardness will vary depending on precipitation. Typically high water flows in Colorado result in lower hardness due to dilution.

Land use activities

Land use activities that disturb enough soil that makes its way to the surface or groundwater can increase hardness concentrations. Some examples include water applied to land. Flood irrigation can artificially increase hardness in waterways through irrigation return flows for example. Certain industrial processes could also increase hardness. When groundwater is pumped to the surface for agricultural or industrial needs and later reaches the stream, it may increase the hardness. Finally construction activities in or near streams can disturb soil causing increased hardness concentrations.

How does hardness fluctuate?

- **Daily** – hardness does not fluctuate much; it is difficult to measure if it does, because sources do not change daily
- **Seasonally** – typically hardness is lower during runoff due to dilution, and higher in low flow
- **River, Lake/Reservoir, Groundwater Concentrations** – rivers will generally have the lowest values, next higher is lakes and reservoirs and groundwater will depend if it is calcium carbonate dominated geology or sodium and potassium dominated geology.
- **River Continuum** – High in the mountains, alkalinity and hardness are typically low and can be close in concentration. As you move down in a watershed both alkalinity and hardness INCREASE, though typically hardness increases more rapidly than alkalinity.

A deeper dive:

Why does hardness increase more than alkalinity as you move downstream? One reason is that alkalinity can be consumed in solution (i.e. utilized to assist with buffering in the presence of an acid or a base for example). Generally Mg, and Ca (simplified, this is hardness) are conserved. Furthermore, since the alkalinity concentration is measuring one specific anion (HCO_3^- or CO_3^{2-} depending on the pH) that comes from one primary source (geology), that concentration will almost always be LESS than the hardness concentration which is coming from the calcium carbonate with the addition of other cations. The farther a stream moves downstream the greater the difference between these two concentrations increases.

WHY? HOW do they buffer/mitigate metal toxicity?
Hardness and alkalinity “BUFFER” a stream from insults (toxicity) caused by dissolved (free radical) metals concentrations. To account for this many metals standards in Colorado are calculated using the HARDNESS concentration. The higher the hardness, the more metals a stream can contain before they become toxic.

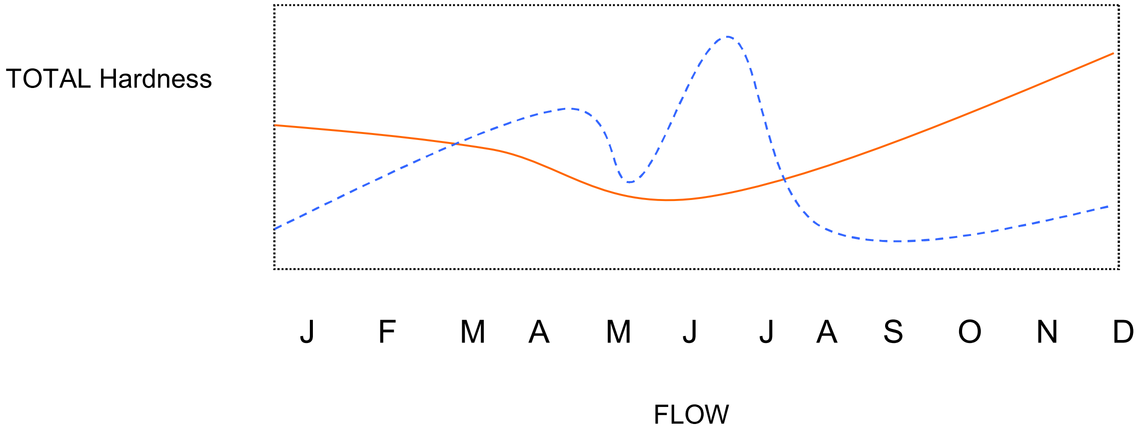
What is the relationship between hardness and alkalinity concentrations and the metals standards? First and foremost, hardness and alkalinity concentrations INCREASE as you travel downstream. Second, hardness and alkalinity "BUFFER" a stream from insults (toxicity) caused by dissolved (free radical) metals concentrations. Third, metals concentration standards are calculated using the HARDNESS concentration. The higher the hardness, the more metals a stream can contain before they become toxic.

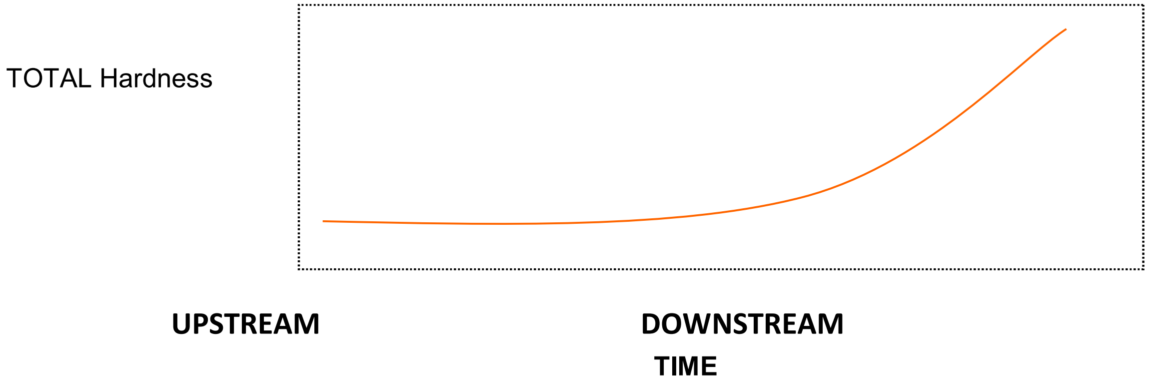
Metals, in their dissolved state, are either absorbed through the gills or ingested by aquatic organisms through their gills and through ingestion. Many of these metals are then concentrated in the organism and at some point will become toxic (ex. Mercury, selenium).

Alkalinity (anions, negative charged ions HCO_3^- and CO_3^{2-}) buffers or mitigates toxicity by **BINDING** with free radicals (cations, positively charged elements, Cd^{2+}, Fe^{2+}, Zn^{2+}, Pb^{2+} etc.) that is the dissolved metal. This takes the metal from its "toxic" state to a bonded state that is no longer reactive and is now non-toxic. These often precipitate (fall out) of solution and are deposited in the sediment where they are less bioavailable to aquatic life.

Hardness (the cation, positive charge, Ca^{2+}, Mg^{2+}) buffers or mitigates toxicity by **COMPETITION**. An aquatic organism will naturally pick up "X" amount of these cations from its environment. These cations can be loosely divided into the "good guys" (hardness cations) and the "bad guys" (metals). The "good guy" to "bad guy" ratio in a headwater high-mountain stream is very low (low hardness, potentially high metals), therefore the organism will tend to pick up more "bad guys." As you move downstream the stream picks up more and more "good guys" while the "bad guys" remain relatively constant or increase very little.

A headwater (high mountain) stream near a town like Fairplay will have very low hardness and alkalinity and therefore have very little capacity to "BUFFER" against insults from even very low metals concentrations. A river near Sterling will have extremely high hardness and alkalinity and therefore can "BUFFER" against a fairly high metal concentration.


TOTAL Hardness
J
F
M
A
M
J
J
A
S
O
N
D
FLOW


TOTAL Hardness
UPSTREAM
DOWNSTREAM
TIME

Worksheet - Hardness

What: ______________________________

Why: ______________________________

How: ______________________________

Influences: ______________________________

Temperature

What is temperature?

Degree of hotness or coldness measured on a definite scale.

Why do we care about temperature?

Reason 1: Water temperature is important because it affects the rate of many biological and chemical processes in the waterway and the amount of oxygen gas that can dissolve in the water. The well-being of aquatic life, from bacteria to fish, are influenced by temperature. In general, increasing temperature tends to speed up the rate of chemical reactions, including those that occur in the body. At higher temperatures, the rate of energy production in the body rises and more oxygen is consumed. At low temperatures, cold blooded animals tend to be more sluggish.

Reason 2: Affects what organisms can live in water:

Chart 6

Temperature	Examples of Life
Greater than 68° F, 20° C	Much plant life, many warm water fish diseases. Most bass, crappie bluegill, carp and catfish.
Upper range (55-68° F) (13-20° C) Less than 68° F or 20° C (Cold water)	Some plant life, some fish diseases. Salmon, trout. Stonefly nymphs, mayfly nymphs, caddis fly larvae, water beetles and water striders.
Lower range (Less than 55° F)	Trout, caddisfly larvae, stonefly nymphs and mayfly nymphs.

Reason 3: Different life stages might have different temperature requirements as well:

Chart 7

	Egg	Fry	Juvenile	Adult
Tolerant Temperature (°C)	0-15	5-25.5	0-27	0-27
Optimal Temperature (°C)	2-13	7-15	7-19	12-19

Reason 4: Temperature affects the ability of water to hold oxygen or the solubility of O_2.

Refer to the dissolved oxygen saturation charts on page 102-103. Temperature also affects pH levels.

How do we measure temperature?

The alcohol (red) or mercury (silver) liquid in a thermometer expands or contracts in a predictable manner as the temperature rises or falls respectively. In the Celsius scale there is 100 degrees between water freezing and water boiling. The thermometer is calibrated to the amount of expansion or contraction relative to the Celsius scale.

What influences temperature?

Water temperature is affected by a number of factors which can include:

- temperature of the air
- groundwater inflows to the river
- stormwater runoff, urban, forest
- industrial discharge from cooling towers
- removing trees or riparian vegetation/shade
- cloudiness of the water or air
- amount of shading
- warm or cold water discharges
- soil erosion
- improper logging practices

Some human activities can have significant effects on the temperature of water. These can include industrial discharge to surface water bodies, removal of large number of trees, soil erosion from farming or construction activities.

Fluctuation Expectations

- **Daily** – Yes, with the rising and setting of the sun. Fluctuations can be large, not as large as air temperature (sometimes 50 degrees w/in one day) but varies, depending upon the season, elevation and amount of water (mass) heating or cooling.

  Water temperature of streams change over time. Daily changes may be significant in smaller streams (as much as 6°C), with the warmest temperatures in the afternoon and the coolest at night. Streams that are deep, spring-fed, and shaded streams do not heat up as quickly. The temperature of larger streams does not change as rapidly because of the larger volume of the water.

- **Seasonally** – Temperatures will be colder in winter and warmer in summer in general (maximums, minimums and averages), temperatures will decrease from snow melt in mountain rivers or foothill areas. Temperature may increase if flow is significantly lowered due to irrigation withdrawals or return flows, or ground water is significant in plains areas. In addition, temperatures are also often altered below reservoirs and are a function of where the water is released from the reservoir water column often eliminated a natural seasonal temperature variation.

- **River Continuum** – In general, temperature increases in a downstream direction due to elevation and the influence of ground water, increased volume of water and land being "drained." Reservoirs, diversions, discharges can all interrupt this natural continuum.

- **River, Lake/Reservoir, Groundwater Concentrations** – there is no pattern here, it will depend upon time of day, year, climate, etc.

Worksheet - Temperature

What: ______________________________

Why: ______________________________

How: ______________________________

Influences: ______________________________

Dissolved Oxygen

What is dissolved oxygen?

Dissolved oxygen (DO) is the amount of oxygen (O_2) dissolved in the water. When O_2 is present in water, it is in a dissolved form. We are looking at the concentration of dissolved oxygen in water. This does not include air bubbles, but oxygen at the molecular level dissolved in the water. Oxygen in the water comes from the atmosphere and aquatic plants.

DO saturation or solubility is the relative measure of the concentration of oxygen that is dissolved or carried in a given medium (water here) as a proportion of the maximum concentration that can be dissolved in that medium (water here). When water holds all the dissolved oxygen it can at a given temperature, it is said to be 100 percent saturated with oxygen.

Oxygen can be both added and removed from water. Water gains oxygen from the atmosphere, from plants as a result of photosynthesis and the churning of running water adds dissolved oxygen. Respiration (breathing) by aquatic animals, decomposition, and various chemical reactions, consume oxygen from the waterbody. If more oxygen is consumed than produced, dissolved oxygen levels decline and some sensitive animals may move away, weaken or die.

Why do we care about dissolved oxygen?

Reason 1: Oxygen is necessary for all living things and for many of the chemical processes that take place in water. Most aquatic animals breathe the oxygen dissolved in water. Waters with consistently high dissolved oxygen levels are capable of supporting a myriad of aquatic animals. Fish, plants, algae, and macroinvertebrates that live in the river all depend on dissolved oxygen to survive. The necessary amount of dissolved oxygen varies with species, age and activity. Low oxygen levels greatly affect salmon and trout and these fish will generally attempt to avoid areas where the dissolved oxygen is less than 5 mg/L and if exposed to levels lower than 3 mg/L will begin to die off.

Chart 8 **Dissolved O_2 Values for Brown Trout Life Cycle**

	Egg	**Fry**	**Juvenile**	**Adult**
Tolerant for O_2	3-25	3-25	3-25	3-25
Optimal for O_2	9-12	9-12	9-12	9-12

Reason 2: Oxygen levels can affect metals or other chemical changes through oxidation or reduction, like the creation of rust. In anaerobic environments (no oxygen) chemical reactions can release organic and inorganic elements into the water. Most rivers in Colorado are not anaerobic.

Dissolved oxygen levels vary with water temperature, altitude, depth, daily and seasonal cycles, and discharge. For example, water at high altitudes holds less oxygen due to lower atmospheric pressure. Warm water holds less oxygen than cold water. Dissolved oxygen levels change with the seasons as the temperature of the water changes.

Saturation/Solubility of Oxygen Exposed to Water

The charts below illustrate the influence of temperature and elevation on dissolved oxygen saturation (solubility).

To illustrate the relationship between temperature, altitude and their influence on dissolved oxygen saturation, find your river temperature and solubility level on Table A (e.g. 5°C =12.77mg/L). Find your altitude and corresponding calibration value (saturation value) on the Table B (e.g. 5,067 feet = 83%). If you take 83 percent of 12.77 mg/L you get 10.6 mg/L. This is what the results of a dissolved oxygen test would be for that temperature and altitude if the water was completely saturated.

(Table A)

Saturation / Solubility of Oxygen Water Exposed to Water

SATURATED AIR AT 760 mm Hg PRESSURE

Temp ºC	Solubility mg/L	Temp ºC	Solubility mg/L	Temp ºC	Solubility mg/L
0	14.62	16	9.87	32	7.31
1	14.22	17	9.67	33	7.18
2	13.83	18	9.47	34	7.07
3	13.46	19	9.28	35	6.95
4	13.11	20	9.09	36	6.84
5	12.77	21	8.92	37	6.73
6	12.45	22	8.74	38	6.62
7	12.14	23	8.58	39	6.52
8	11.84	24	8.42	40	6.41
9	11.56	25	8.26	41	6.31
10	11.29	26	8.11	42	6.21
11	11.03	27	7.97	43	6.12
12	10.78	28	7.83	44	6.02
13	10.54	29	7.69	45	5.93
14	10.31	30	7.56	46	5.84
15	10.08	31	7.43	47	5.74

Calibration Values – Atmospheric Pressures and Altitudes

Inches	mm		Altitude		Calibration
Hg	Hg	kPa	Ft.	m	Value (%)
30.23	768	102.3	-276	-84	101
29.92	760	101.3	0	0	100
29.61	752	100.3	278	85	99
29.33	745	99.3	558	170	98
29.02	737	98.3	841	256	97
28.74	730	97.3	1126	343	96
28.43	722	96.3	1413	431	95
28.11	714	95.2	1703	519	94
27.83	707	94.2	1995	608	93
27.52	699	93.2	2290	698	92
27.24	692	92.2	2587	789	91
26.93	684	91.2	2887	880	90
26.61	676	90.2	3190	972	89
26.34	669	89.2	3496	1066	88
26.02	661	88.2	3804	1160	87
25.75	654	87.1	4115	1254	86
25.43	646	86.1	4430	1350	85
25.12	638	85.1	4747	1447	84
24.84	631	84.1	5067	1544	83
24.53	623	83.1	5391	1643	82
24.25	616	82.1	5717	1743	81
23.94	608	81.1	6047	1843	80
23.62	600	80	6381	1945	79
23.35	593	79	6717	2047	78
23.03	585	78	7058	2151	77
22.76	578	77	7401	2256	76
22.44	570	76	7749	2362	75
22.13	562	75	8100	2469	74
21.85	555	74	8455	2577	73
21.54	547	73	8815	2687	72
21.26	540	71.9	9178	2797	71
20.94	532	70.9	9545	2909	70
20.63	524	69.9	9917	3203	69
20.35	517	68.9	10293	3137	68
20.04	509	67.9	10673	3253	67
19.76	502	66.9	11058	3371	66

How is dissolved oxygen measured?

The Winkler method indirectly measures dissolved oxygen by taking advantage of how iodine reacts with an acid and using starch indicator to more precisely and consistently see the color change. This method measures all and low DO levels more accurately than many kits (Hach, LaMotte as examples) because it uses starch indicator, fixes 300 mLs vs 60 mLs of sample and measures samples with class A measuring device.

The chemical reactions that take place in the Winkler test are described in the following:

In the presence of a base (OH^-), dissolved oxygen reacts with manganous ion (Mn^{+2}) to form manganese dioxide (equation 1)*. When you add acid (H^+ or sulfamic acid) the manganese dioxide will react with iodide to form iodine (equation 2 + 3)*. The amount of iodine formed is exactly twice the amount of dissolved oxygen originally present in the water. So, if you know the amount of iodine, you can determine the amount of dissolved oxygen originally present. The amount of iodine can be determined by titration with sodium thiosulfate (NaS_2O_3) (equation 4)*. Starch is used as the final indicator to assist making the endpoint more consistent and reliable to see. Starch turns blue if iodine is present but turns colorless after all the iodine has reacted with the sodium thiosulfate.

*Chemical reactions:

1. $Mn^{+2} + 2OH^- + O2 \Leftrightarrow MnO_2 + H2O$
2. $MnO_2 + 2I^- + 4H^+ \Leftrightarrow Mn^{+2} + I_2 + H_2O$
3. $I_2 + I^- \Leftrightarrow I_{3-}$
4. $I_{3-} + 2S_2O_{3-}2 \Leftrightarrow S_4O_{6-}2 + 3I^-$

For simplicity, you may want to combine reactions:

$$I_2 + 2S_2O_3^{-2} \Leftrightarrow S_4O_6\text{-}^2 + 2I^-$$

What influences dissolved oxygen?

- Temperature – cold water holds more oxygen than warm, saturation/solubility; see chart above
- Elevation, atmospheric pressure, altitude – higher elevations have less atmospheric pressure, water will hold less oxygen (much like how it is hard to breath above timberline)
- Velocity – faster water has higher oxygen levels than still water
- Biological activity – Organic wastes from wastewater treatment, industry and runoff can decrease oxygen concentration. Bacteria consume O_2 while decomposing organic material, respiration/decomposition.

Fluctuation Expectations

- **Daily** – Yes, with the rising and setting of the sun changes temperature, decreasing at warmer times, or as biological activity varies, decreasing with more activity.
- **Seasonally** – Yes, can as temperature varies seasonally or as water management regimes change, such as irrigation diversions or return flows, usually decreasing with more sedimentation, increases temperature.
- **River, Lake/Reservoir, Groundwater Concentrations** – There is no pattern here other than these observations. Rivers will have higher concentrations when gradients are greater but can be anaerobic (no oxygen) in slow gradient back waters or large rivers near the bottom. Lakes and Reservoirs can stratify where oxygen levels will vary from top to bottom. Groundwater will concentrations will vary with source, retention time and other variables.
- **River Continuum** – In general, decreases downstream with lower elevations, gradients and velocities, larger volumes, warmer temperatures and increased biological activities.

Worksheet – Dissolved Oxygen

What: ______________________________

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Why: ______________________________

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How: ______________________________

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Influences: ______________________________

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Metals

What are metals?

Source All the metals on the earth are here to stay, we can't get rid of them; in fact we need them. The key is sustainable use and practices that minimizes releasing forms of metals into the environment that could potentially cause harm to any or all life. Almost all metals present in the environment have been bio-geochemically cycled since the formation of the Earth. Human activity has introduced additional processes that have increased the rate of redistribution of metals between environmental compartments, particularly since the industrial revolution. However, over most of the Earth's land surface the primary control on the distribution of metals is the geochemistry of the underlying and local rocks except in all but the worst cases of industrial contamination and some particular geological situations.

Fundamental links between chemistry and mineralogy lead to characteristic geochemical signatures for different rock types. As rocks erode to form soils and sediments, chemistry and mineralogy again influence how much metal remains close to its source versus how much is translocated greater distances, and how much is transported in solutions that replenish ground and surface water supplies. In addition, direct processes such as the escape of gases and fluids along major fractures in the Earth's crust, and volcanic related activity, locally can provide significant sources of metals to surface environments, including the atmosphere and the sea floor. As a result of these processes, the Earth's surface is geochemically inhomogeneous. Regional scale processes lead to large areas with enhanced or depressed metal levels that can cause biological effects due to either toxicity or deficiency if the metals are, or are not, transformed to bioavailable chemical species. Industrial process that allow humans to use metals such as extraction (mining) bring metals to the surface, change their native composition, fate and transport.

Total (Not Filtered) and Dissolved (Filtered) Sample In general, most metals are normally present in trace amounts in rivers. Metals can be present in two different forms that make them bioavailable to aquatic wildlife. Some metals are present in an ionic, free or dissolved form and will have an associated charge. Think of this "free" form as being like a single person, free and available to join with something, like Fe^{2+} (iron with a two plus ionic charge). A water sample that is "filtered" is analyzed for the dissolved, free or bioavailable metal form. The size of the filter only allows these "single" metals to pass through creating the dissolved or filtered River Watch metal sample. Bioavailable means the metal is available biologically to an organism who may need it in certain amounts and in excessive amounts causes harm. It this form of metal this is most harmful to aquatic life in excess.

A free, ionic form of metal can "join" with an equivalent negative charged element like iron, Fe^{2+}can combine with Sulfate, SO_4^{2-} to create a compound $FeSO_4$. Chemical, physical and biological processes can cause the "combining" or "release" metals. Iron, when bound up like this is less available and less toxic to aquatic life than when in single or ionic form. A total sample, (not filtered sample), includes both free/ionic metals and combined metals. Like a dance hall will have both singles and couples on the dance floor and the filter is akin to creating a singles bar or a door where only single or free metals can enter. ***In theory, results for a total/not filtered metals sample will always be greater or equal to results for its paired dissolved/filtered sample, if neither sample is contaminated.*** Metals blank and duplicate quality assurance and control samples test for this type of field contamination. It is helpful to know both total (not filtered) and dissolved (filtered) amounts to assess potential impact of elevated metals. For example, if 100 units of zinc are total and 99 units are dissolved, that means most of the zinc present is in the bioavailable form. If 100 units of total zinc are measured and 5 units are dissolved, then most of the zinc is not bioavailable.

Concentrations of chemicals in water are typically measured as the mass of the chemical (often in milligrams (mg) or micrograms (µg)) in the total volume of water (liter (L)) where:
1 milligram (mg) = 1/1,000 gram = 0.001 gram
1 microgram (µg) = 1/1,000,000 gram = 0.000001 gram

Chemical concentration may also be expressed as parts per million (ppm) or parts per billion (ppb). A way to visualize one part per billion (ppb) in water is to think of it as one drop of water in one billion drops, or about one drop of water in a swimming pool!!! One part per million is about 1 cup of water in a swimming pool. In water samples, 1 ppm = approximately 1 mg/L of chemical in water, and 1 ppb = 1 µg/L chemical in water. Studies have shown that aquatic life can be sensitive to certain chemicals at VERY low concentrations. Lead for example is acutely toxic to rainbow trout eggs at a concentration of 4.1 µg/L in soft water (28 mg $CaCO_3$/L).

Reference
1. P.H. Davies, J.P. Goettl, J.R. Sinley, N.F. Smith, Acute and chronic toxicity of lead to rainbow trout salmo gairdneri, in hard and soft water, Water Research, Volume 10, Issue 3, 1976, Pages 199-206
(Fishery Research Centre, P.O. Box 2287, Fort Collins, CO 80522, U.S.A.) **This is our Ft. Collins LAB!!**

River Watch Metals River Watch analyzes these metals (both total and dissolved): aluminum (Al), arsenic (As), calcium (Ca), magnesium (Mg), selenium (Se), sodium (Na), potassium (K), zinc (Zn), cadmium (Cd), copper (Cu), lead (Pb), iron (Fe), and manganese (Mn). River Watch reports the concentrations of metal amounts in parts per billion (ppb).

Why do we care about metals?

Excess amounts of metals, especially in the dissolved form, can cause subtle impacts (chronic) to aquatic life, from stunted growth to inability to reproduce all the way to death (acute). High metal concentrations may also limit the functionality of water. How a metal, substance or pollutant moves through soil, water, air and systems and changes is the process of identifying the fate and transport, revealing the exposure paths along that journey.

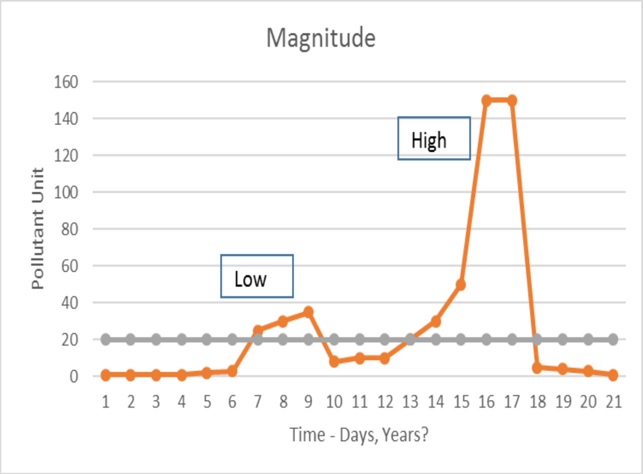
Exposure An organism's exposure to excess metals can be characterized or quantified by the duration, frequency and magnitude of an "event". Chronic exposure (long in duration, very frequent but small magnitude) can result in a small impacts like a skin rash to deadly impact: death (think of impact from being around second hand smoke for 20 years). Acute exposure (short in duration, one or few times and high in magnitude) can result in quicker death (think Chernobyl nuclear accident for those in proximity). Different organisms and life stages have different tolerances to each metal. The Clean Water Act standards are developed based on toxicity studies that integrate these concepts providing where data supports chronic and acute standards.

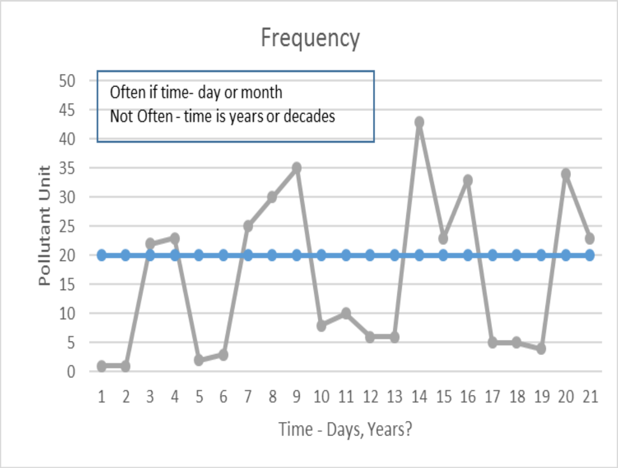
Magnitude – the amount a metal is elevated is above a specific threshold

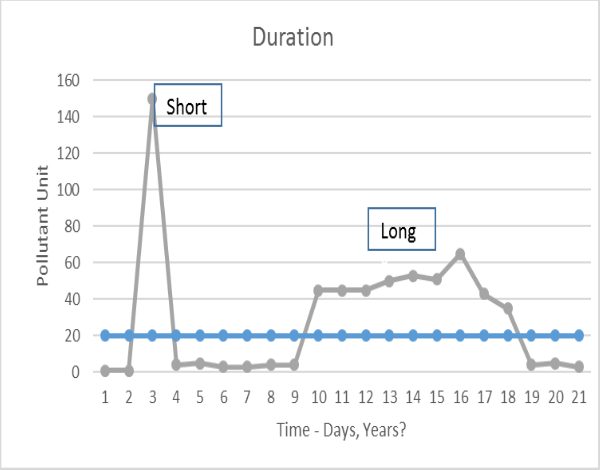
Duration – the length of time a metal is elevated above a specific threshold

Frequency – the number of times or events that occur where the metal is elevated above a specific threshold

The best study designs attempt to capture a particular pollutants behavior in a river (system) naturally or altered by human influence to assess magnitude, duration and frequency along with sources and extent. This is difficult to accomplish, but also why River Watch collects monthly metals.







The Colorado Department of Public Health and Environment administers the Colorado Clean Water Act and implements standards to protect aquatic life from two types of exposure, *acute and chronic.* Two definitions of acute and chronic exposure exists: *biological and regulatory*. The regulatory definition is necessary to take something that varies widely across organisms (biology) and translate it into an enforceable and protective standard that provides predictability and certainty for industries, water managers and regulators who make significant investments into treatment systems.

Biological acute – the magnitude is high, duration relatively short and frequency often only once, all sufficient to cause death. Think Chernobyl radiation explosion.

Regulatory acute – threshold acute standard cannot be exceeded more than one time in a three year period.

Biological chronic – the magnitude is lower but exceeds a threshold, duration is long and frequency is numerous all causing impacts from say a skin condition to death, but doesn't have to result in death. Think second hand smoke, lead in drinking water, eating a high fat diet.

Regulatory chronic – threshold acute standard cannot be exceeded more than one time in a three year period.

The above values for each metal are the biological thresholds for aquatic life. Primarily generated from toxicity studies where fish are put into tanks with the same alkalinity, hardness and pH, with each tank receiving a larger dose of one metal. The tank or concentration where 50% of the organism dies (called an LC50 or lethal concentration of 50%) is the threshold. The Clean Water Act will take a number (say 8-12) of these LC50's for the most sensitive species that data exists, combine them and you get an equation, which hardness is part of that becomes the standard for most metals, like for zinc $0.978 * e(0.9094[\ln(\text{hardness})]+0.9095)$. This is the case in most state's Clean Water Acts.

Just because a standard is exceeded and an organism is exposed, doesn't mean it will suffer an acute or chronic effect. That depends on the species, age, and other environmental, physiology or health factors for example. As in humans a virus effects people differently. Look at graphs below and make statements about standard, metal concentration and time, up/downstream patterns.

The following list provides some information about what each metal is and why River Watch analyzes these metals. The ICP technology allows River Watch to analyze all these metals for the same cost and level of effort (unlike nutrients). It is also why River Watch doesn't analyze mercury or other metals that are harder to collect and require a different analytical method.

Metals that River Watch Analyze:

Aluminum occurs naturally and makes up about 8% of the surface of the earth. It is used in many forms including antacids, deodorant, paint, and fireworks. Aluminum will leave a white precipitate stain on river substrate. It's also used to treat drinking water (aluminum sulfate) to remove silts, clays and viruses. Low levels of aluminum are not thought to be harmful. Studies have attempted to link birds eating insects with high aluminum content to produce fragile eggs reflecting disturbance of calcium metabolism. The Colorado Department of Public Health and Environment Basic Standards applied to most waters list aluminum at 750 µg/l (ppb) acute and 87 µg/l (ppb) chronic thresholds to protect aquatic life. *Aluminum toxicity is affected by pH levels*.

Arsenic can be found in fresh water environments and soils. Arsenic can *bioaccumulate*, which means the level of metal in one organism is passed to an organism that consumes it, accumulating in species higher up the food chain, while it may not appear to magnify within a food web. Arsenic rarely occurs by itself in the environment and other agents such as metals, chlorinated organics and sulfates influence availability and toxicity for both humans and aquatic organisms. Arsenic is toxic to aquatic life 2-9 µg/l (ppb) for freshwater shellfish and yet, in one study, concentrations of 50 µg/l (ppb) didn't harm rainbow trout. Colorado Department of Public Health and Environment Basic Standards applied to most waters list 360 µg/l (ppb) acute and 150 µg/l (ppb) chronic thresholds for arsenic to protect aquatic life. USEPA recommends levels of 50 µg/l (ppb) for drinking water and 100 µg/l (ppb) for agriculture use.

Cadmium is nonessential. Concentrations of cadmium are toxic to trout at around 1.4 µg/L (ppb).

Copper is essential and is used in cellular metabolism and oxygen transport as well as is in some enzymes. Concentrations of copper are toxic to trout, depending on the water quality, around 20 µg/L (ppb). Copper and zinc tend to stay in a river system longer than other metals in time and space (fate and transport).

Iron is necessary is small amounts. Iron is usually indirectly toxic before directly toxic, meaning as it precipitates out of the water column and onto substrate it leaves a yellow stain and can harden the substrate (embeddeness) reducing macroinvertebrate and fish egg habitat before it ever reaches toxic concentrations in the water column itself. A relatively short fate and transport. Iron is toxic above 1,000s µg/L (ppb). Iron precipitates may cover spawning habitat and eggs as well as macroinvertebrate habitat.

Manganese is essential to many bodily functions, metabolism of amino acids, cholesterol, glucose and carbohydrates, bone formation, blood clotting and reducing inflammation. The human body cannot produce manganese but can store it the liver, pancreas, bones, kidney and brain. It is never found as a free metal but in a number of minerals, a primary one is pyrolusite. Manganese is essential to iron and steel production. The U.S.A., Japan and Western Europe are nearly deficient in economically mineable manganese. It makes a black stain on rocks when it precipitates out of the water column.

Lead is nonessential and toxic to aquatic life in the 10-100 µg/L (ppb) range. There is not much research regarding lead toxicity in aquatic systems due to its low solubility, although extensive work has been done on lead toxicity in humans.

Selenium is needed by aquatic organisms and humans in very small amounts, but in higher concentrations it is a neurological poison. High concentrations of selenium can cause birth defects and other impairments in birds, fish, and humans. In Colorado, there are two natural significant sources of selenium, the Mancos shale, and the Pierre shale. In the lower Gunnison and lower Colorado River basins, the Mancos shale underlies the soils and in some places is exposed to the surface. The Pierre shale, though not prevalent, is found in places along the Front Range. Naturally high concentration of selenium exists in the places where the shale is present. Irrigated agriculture increases the amount of selenium by leaching it from the soils and shale. This has led to levels of selenium in the Colorado and Gunnison basins that are higher than the water quality standards. There are “Selenium Task Forces” in the two basins that have been working to reduce the amount of selenium that go in to the rivers. This effort is proving to be a very costly and time intensive, involving many agriculture producers, water providers and government agencies. Selenium is exceeding stream standards in every basin in the state around 4-20 ug/L.

Sodium and Potassium are both essential for aquatic life. They are usually less than calcium and magnesium in an aquatic environment but behave similar. They are not traditionally of concern in legacy mining areas. Rivers with a large ground water influence can have high sodium or potassium, this is especially important in areas where natural gas is extracted how water is managed. A Sodium Adsorption Ratio (SAR) helps reflect the infiltration rate of soil, more a physical measurement than toxicity.

Zinc is essential for cell differentiation and growth. It is also used in enzymes and DNA. Zinc is toxic to aquatic life at about 50-200 µg/L (ppb). Zinc can have synergistic effects when occurs with copper, meaning the toxicity of both zinc and copper together is as bad or worse than either of those alone, depending on the concentrations.

Aquatic organism needs **calcium** and **magnesium** for the same biological function and health reasons as humans. Calcium and magnesium are measured with the hardness titration and calculated in the River Watch lab through the ICP. The titration doesn't work well when high concentrations of iron or other anions and cations are present, usually from detergents or other substances in the water. The ICP metals analyses can see through those interferences. Neither calcium nor magnesium is thought to be toxic. Hardness actually helps mitigate elevated metal levels. In fact, many metal standards employ an equation where hardness levels are inserted and the resulting calculation becomes the standard. The higher the hardness the higher the metals standard or the more metals can be in a system before harm might occur. This table is an illustration of hardness influence on metal standards.

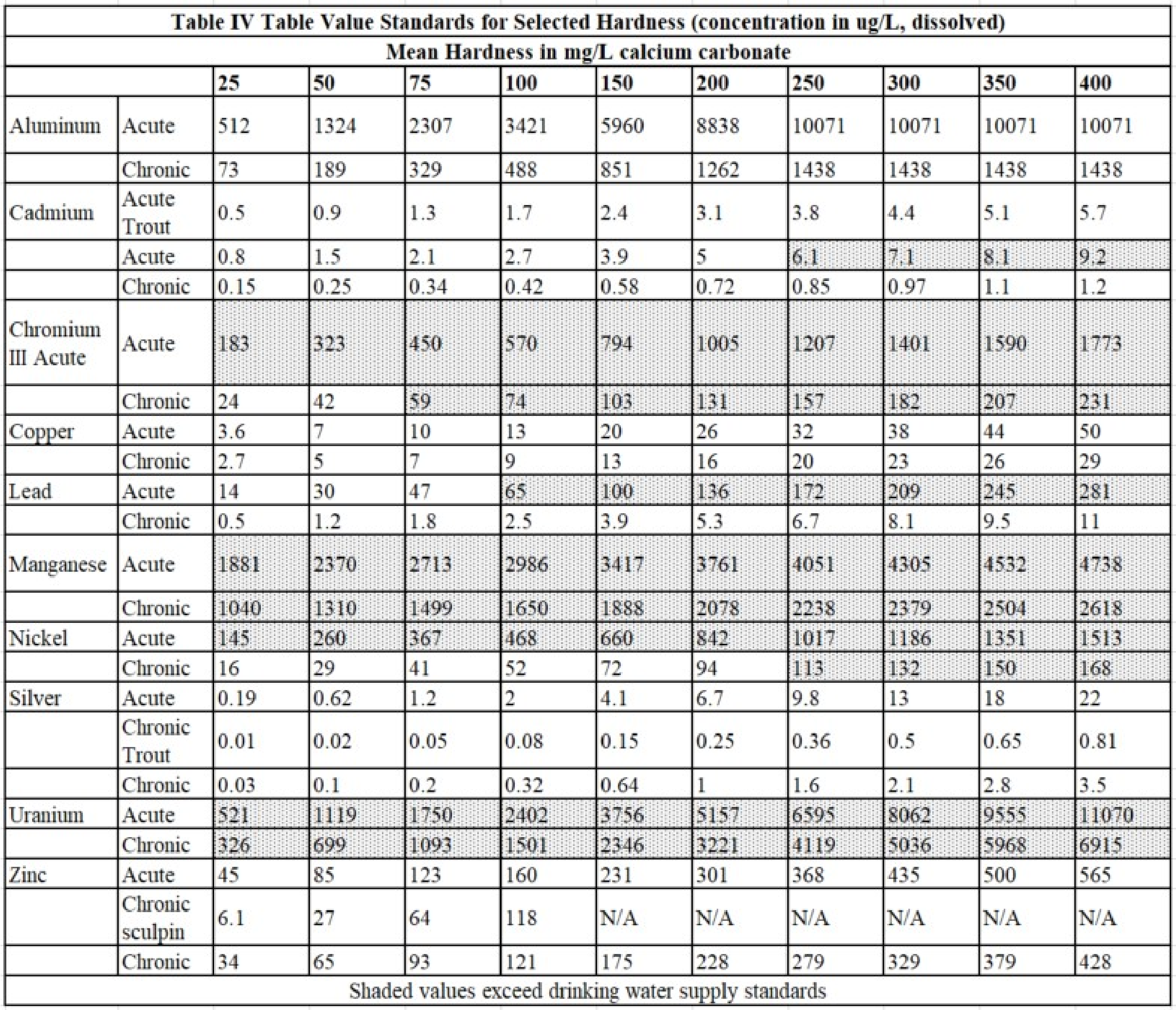


Table IV Table Value Standards for Selected Hardness (concentration in ug/L, dissolved)

Mean Hardness in mg/L calcium carbonate

		25	**50**	**75**	**100**	**150**	**200**	**250**	**300**	**350**	**400**
Aluminum	Acute	512	1324	2307	3421	5960	8838	10071	10071	10071	10071
	Chronic	73	189	329	488	851	1262	1438	1438	1438	1438
Cadmium	Acute Trout	0.5	0.9	1.3	1.7	2.4	3.1	3.8	4.4	5.1	5.7
	Acute	0.8	1.5	2.1	2.7	3.9	5	6.1	7.1	8.1	9.2
	Chronic	0.15	0.25	0.34	0.42	0.58	0.72	0.85	0.97	1.1	1.2
Chromium III Acute	Acute	183	323	450	570	794	1005	1207	1401	1590	1773
	Chronic	24	42	59	74	103	131	157	182	207	231
Copper	Acute	3.6	7	10	13	20	26	32	38	44	50
	Chronic	2.7	5	7	9	13	16	20	23	26	29
Lead	Acute	14	30	47	65	100	136	172	209	245	281
	Chronic	0.5	1.2	1.8	2.5	3.9	5.3	6.7	8.1	9.5	11
Manganese	Acute	1881	2370	2713	2986	3417	3761	4051	4305	4532	4738
	Chronic	1040	1310	1499	1650	1888	2078	2238	2379	2504	2618
Nickel	Acute	145	260	367	468	660	842	1017	1186	1351	1513
	Chronic	16	29	41	52	72	94	113	132	150	168
Silver	Acute	0.19	0.62	1.2	2	4.1	6.7	9.8	13	18	22
	Chronic Trout	0.01	0.02	0.05	0.08	0.15	0.25	0.36	0.5	0.65	0.81
	Chronic	0.03	0.1	0.2	0.32	0.64	1	1.6	2.1	2.8	3.5
Uranium	Acute	521	1119	1750	2402	3756	5157	6595	8062	9555	11070
	Chronic	326	699	1093	1501	2346	3221	4119	5036	5968	6915
Zinc	Acute	45	85	123	160	231	301	368	435	500	565
	Chronic sculpin	6.1	27	64	118	N/A	N/A	N/A	N/A	N/A	N/A
	Chronic	34	65	93	121	175	228	279	329	379	428

Shaded values exceed drinking water supply standards

How do we measure for metals?

Each collected sample is preserved in pure nitric acid to “freeze” all metals in their current form. This will ensure metals that are dissolved stay dissolved and those are bound (or those that have mates) stay bound. River Watch uses an Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP) for analysis of metals. This technology is necessary to measure low levels of metals, low enough to ensure we are able to assess the results against Clean Water Act standards. Initial technology was an atomic absorption spectrometry. The ICP is used to analyze each metal which emits a specific wavelength of light when ionized. This result is compared to a standard curve and the concentration determined. Due to shifts in technology, not all stations have all metals or data for both total and dissolved samples. The RW Data FAQ (www.coloradoriverwatch.org) provides more information on what data is available. River Watch follows the same analytical methods as the Colorado Department of Public Health and Environment.

What influences metal concentrations?

Metals can enter waterways in excessive amounts through:

Natural	Anthropogenic (Manmade)
Geology	Abandoned mines, tailing or waste piles
Mineralized Geological Areas	Industry by-products, landfills
Volcanos	Urban runoff (parking lots, streets, industrial areas)
Hot springs	Agriculture runoff
Some wetlands	Other activities that expose soil and/or facilitate movement of soil from the land to water (erosion), that becomes a non-point source (not from a discrete pipe or outflow) of runoff
Natural Disasters and climate	Emissions into the air from all sources

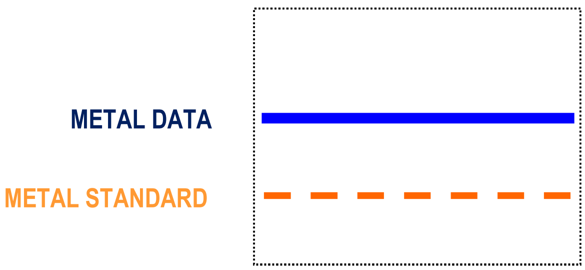
Fluctuation Expectations

- **Daily** – not naturally in most cases, can change daily with unnatural point or non-point discharges.
- **Seasonally** – not naturally, however if water body is naturally mineralized or has a loading source (non-point from soil or in water from discharge for example), it can increase with snowmelt or storm events if the runoff moves metals into the water, or can decrease due to dilution.
- **River, Lake/Reservoir, Groundwater Concentrations** – No general pattern exists. Concentrations will be a function of all variables discussed in this section.
- **River Continuum** – generally remains natural within background or natural levels, human activity on the land and with the water can increase metals levels in a downstream direction, especially metals that are conservative and stay dissolved in the water for a time or space duration.

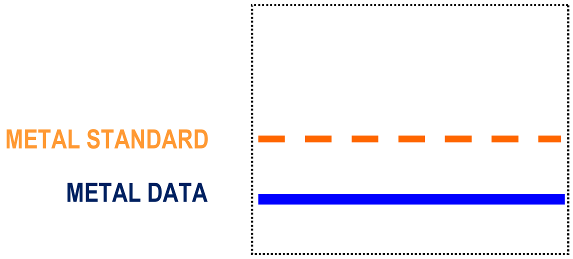
CHANGE WITH TIME (X-axis)

TIME

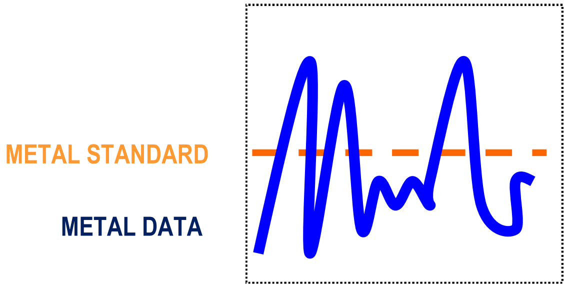
Graph 1



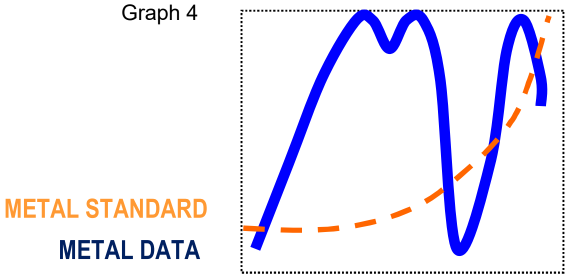
Graph 2



Graph 3



Graph 4

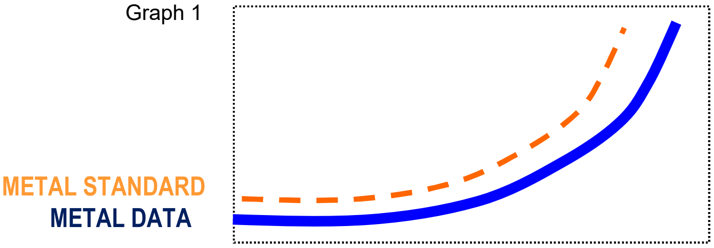


TIME

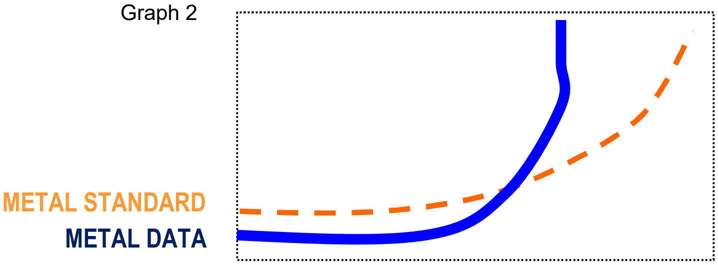
CHANGE WITH SPACE

UPSTREAM to DOWNSTREAM

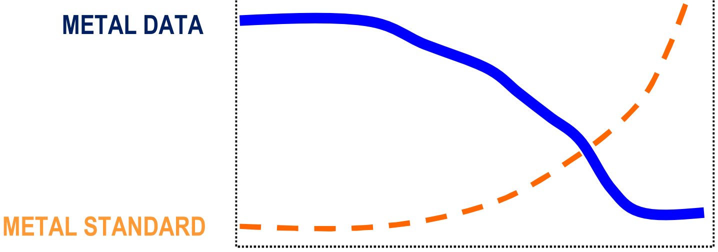
Graph 1



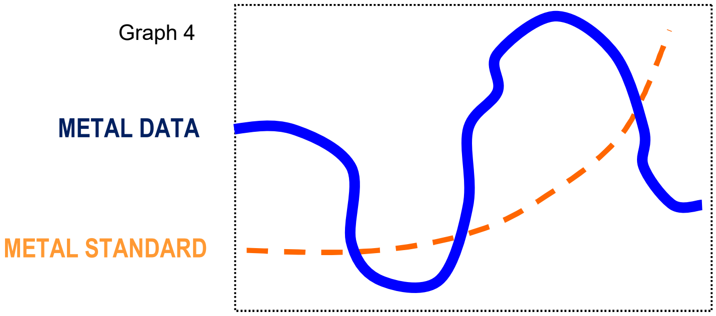
Graph 2



Graph 3



Graph 4



UPSTREAM to DOWNSTREAM

Worksheet – Metals

What: ______________________________

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Why: ______________________________

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How: ______________________________

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Influences: ______________________________

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Nutrients

What are nutrients?

Nutrients are chemicals that are essential for plant growth.

Nitrogen (Nitrate, Nitrite, Nitrate-Nitrite and Ammonia)

Gaseous nitrogen (N_2) forms the major portion of the earth's atmosphere (about 80%).

Nitrogen can be found in water in several different combinations with oxygen. River Watch analyzes four forms of nitrogen: ammonia (NH_3), nitrite + nitrate (NO_3^-) as well as total nitrogen (TN).

Why do we care about nitrogen?

Nitrogen is a necessary element for all forms of life. Its electronic configuration makes it uniquely suited to form the long chain-like structures of proteins and nucleic acids. Proteins make up the building blocks for all cell structure and enzymes that carry on energy transformations within cells. Proteins also comprise the mass of muscle tissue that allows animals to carry out movement. Nucleic acids carry the genetic information as the genetic code from generation to generation for the making of all these proteins.

Gaseous nitrogen is not available for most living organisms to take up and use. Some microorganisms are able to chemically transform it and incorporate it into living cells to build proteins. The series of nitrogen transformations bacteria carries out in soil and water is called the "nitrogen cycle."

A simplified outline of the nitrogen cycle follows:

Nitrification from air to soil and water →

$$N_2 \leftrightarrows NH_3 \leftrightarrows NO_2^- \leftrightarrows NO_3^-$$

nitrogen (in air) ammonia nitrite nitrate

← Denitrification from organic matter to the air

Plants take up the nitrate bacteria and assimilate it into their tissue. Animals must obtain their nitrogen from either plants or consumption of other animals.

Cells must also have an effective manner to get rid of nitrogen wastes (mainly ammonia) after the breakdown of old and replaced cell components. Too much ammonia in the bloodstream causes brain damage. In fish, ammonia is carried either free or as a complex to the gills where it is swept away by water. High concentrations of ammonia in water inhibit their ability to excrete their own ammonia. Most terrestrial vertebrates convert ammonia to urea in the liver and then excrete it by means of the kidneys. Birds and snakes excrete ammonia wastes as uric acid--a compound with four nitrogen molecules.

High concentrations of nitrite and nitrate in water can cause oxidation of the iron molecule in hemoglobin, especially in human infants. Oxidized hemoglobin cannot carry oxygen thereby causing "blue baby syndrome."

How do we measure for nitrogen?

The sample is preserved with sulfuric acid prior to collection. All nitrogen components are measured by the River Watch analyst using a Lachat auto-analyzer. This machine carries out a series of chemical reactions with the nitrogen to form a color unique to that form of nitrogen, and measures the intensity of that color through a spectrophotometer. The more intense the color, the more the nitrogen compound is present. The intensity is correlated with known samples to develop a relationship to calculate the concentration of the unknown sample.

What influences nitrogen?

- Fertilizers
- Untreated human and animal wastes
- Domestic treated water, large plants to failed septic systems
- Breakdown of organic material in standing water
- Irrigation runoff
- pH
- Hydrology
- Concentrations in the air

<u>Fluctuation Expectations</u>

- **Daily** – will depend on background levels, climate and land/water use
  Seasonally – will depend on background levels, climate and land/water use
- **River Continuum** – in general increase in a downstream direction, more land, use, water, etc.
- **River, Lake/Reservoir, Groundwater Concentrations** – No general pattern exists. Concentrations will be a function of all variables discussed in this section.

Phosphorus (phosphates)

What is phosphorus?

Phosphorus is the 15th element in the periodic table. Most phosphorus is found in marine rocks. The ocean is saturated with respect to phosphorus and it precipitates as phosphate rocks where colder water is brought to the surface and warmed by ocean currents.

Phosphate in water is found mostly as single anions (PO_4^{3-}), but may condense into “poly” phosphates or become bound to organic matter.

Why do we care about phosphorus?

Like nitrogen, phosphorus is an essential nutrient for plants and animals. Living cells require phosphorus for nucleic acid production and energy transformations. Adenosine triphosphate (ATP) is the major compound in cells that stores energy in molecular bonds. When these high-energy bonds are broken, other cellular compounds can be built up.

Phosphorus is the major limiting element in water for algal growth. In standing waters where phosphorus accumulates, algal blooms proliferate and reduce the concentrations of dissolved oxygen. As oxygen concentrations decrease, less desirable organisms flourish.

How do we measure phosphorus?

The same samples that are preserved with sulfuric acid for nitrogen analyses are used to quantify total phosphorus.

The water is digested with concentrated acids and high temperatures to break down all forms of phosphorus into its simplest form (PO_4^{3-}).

A soluble form of the element molybdenum (Mo) is added which combines with the phosphate to produce a yellow color. This color is converted to a blue color by the addition of ascorbic acid (vitamin C).

The amount of light that is absorbed by the blue color is measured by a spectrophotometer. This is directly proportional to the amount of total phosphorus in the solution in mg/L.

What influences phosphorus?

- Domestic wastewater containing phosphate detergents
- Fertilizers
- Irrigation runoff
- Soil type

<u>Fluctuation Expectations</u>

- **Daily** - will depend on background levels, climate and land/water use
  Seasonally – will depend on background levels, climate and land/water use
- **River Continuum** – in general increase in a downstream direction, more land, use, water, etc.
- **River, Lake/Reservoir, Groundwater Concentrations** – No general pattern exists. Concentrations will be a function of all variables discussed in this section

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Sulfur (sulfates)

What is sulfur?

Sulfur is brought to the earth’s surface by volcanoes where it reacts with metals, hydrogen and oxygen to form various minerals. In water, sulfur is found mostly in the combined form with oxygen as the anion sulfate (SO_4^{2-}).

Why do we care about sulfur?

Sulfur is essential to all living things. Cells require sulfur to make protein compounds responsible for energy transformations. When sulfur that is combined or reacts with oxygen in water to make the sulfate ion, the pH of the water lowers (becomes acidic). When that acidic water is exposed to earth inside mines or tailing piles it will release metals into the environment.

This is often what causes acid mine drainage. This low pH or acidic water can be harmful to living organisms.

How do we measure for sulfur?

The compound barium chloride (BaCl) is added to water and forms the insoluble compound barium sulfate ($BaSO_4^2$) according to the reaction:

$BaCl + SO_4^{2-} \Longrightarrow BaSO_4^2 + Cl^-$ precipitate

The precipitate absorbs light in a spectrophotometer in direct proportion to the sulfate concentration in mg/L.

What influences sulfur?

- Volcanic eruptions
- Mining and processing of mineral deposits
- Mining and burning fossil fuels
- Soil type
- Industry

Fluctuation Expectations

- **Daily** - will depend on background levels, climate and land/water use
  Seasonally – will depend on background levels, climate and land/water use
- **River Continuum**– in general increase in a downstream direction, more land, use, water, etc. but may not if treated
- **River, Lake/Reservoir, Groundwater Concentrations** – No general pattern exists. Concentrations will be a function of all variables discussed in this section.

Chlorine (chloride)

What is chlorine?

Chlorine is very reactive and strongly attracts electrons from other elements in water to become the anion chloride (Cl^-).

Why do we care about chlorine?

In living cells, chloride ions act primarily to regulate osmotic pressure and maintain cell membrane integrity. High chloride concentrations most often indicate large amounts of water evaporation or exposure to sources of salt. High chloride concentrations make it difficult for aquatic insects and fish to regulate their cellular ionic balance.

How do we measure for chlorine?

Thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ion, free thiocyanate ion forms the highly colored ferric thiocyanate, of which the absorbance is proportional to the chloride concentration. This absorbance is measured at a wavelength of 480 nanometers.

$$\mathbf{Hg\ (SCN)_2 + 2Cl^- \longrightarrow HgCl_2 + 2(SCN)^- (SCN)^- + Fe^3 \longrightarrow (Fe\ [SCN])\ {+2}}$$

What influences chlorine?

- Salt drainage from roads
- Evaporation of large areas of standing water
- Water treatment, large plants to septic systems
- Water and ditch treatment for excess algae growth
- Geology
- Industry

Fluctuation Expectations

- **Daily** - will depend on background levels, climate and land/water use
  Seasonally – will depend on background levels, climate and land/water use
- **River, Lake/Reservoir, Groundwater Concentrations** – No general pattern exists. Concentrations will be a function of all variables discussed in this section.
- **River Continuum**– in general increase in a downstream direction, more land, use, water, etc. but may not if treated

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Total Suspended Solids

What are total suspended solids?

Total suspended solids are the mineral materials and sediment that are kept in suspension in the water column. Some of this suspended material is dissolved, like sugar in hot water and some of the suspended material is not dissolved. The sum of dissolved solids is called **Total DISSOLVED Solids** and non-dissolved suspended material is **Total SUSPENDED Solids**. When the water slows or ceases to flow, the suspended matter is deposited on the bottom of the lakes or stream. Faster flowing water can transport more suspended solids as well as carry a suspended solids load further downstream. Coarse material settles out first, followed by finer material. Some material may always remain in suspension. The river is always trying to maintain equilibrium between how much material it can "hold" and transport with its velocity (speed) and discharge (volume).

Why do we care about total suspended solids?

Suspended material can clog or abrade fish and insect gills, and can cover spawning beds thereby inhibiting reproduction, and can even smother a macroinvertebrate habitat. Suspended solids may cause the color of water to become darker and thus cause an increase the water temperature and possibly lower the dissolved oxygen concentrations. The darker colored water can inhibit visibility for trout and make it difficult for them to find the macroinvertebrates they consume for food.

How do we measure total suspended solids?

A glass fiber filter is washed, dried and weighed. A known volume of mixed water sample is filtered through the filter. The filter plus suspended material is dried and re-weighed, and weight of the suspended material in mg/L is obtained by subtraction.

Measuring TSS or TDS does not tell you what is in those solids. In that regard this is similar to conductivity, specific conductance, turbidity and clarity. Standards for these parameters are difficult because they indicate a problem but not enough information to know what is in the water, where it came from or how it is tied to a land or water use or practice. In addition, it is a rivers role to move sediment and nutrients from the mountains to the ocean, and it is natural for certain times of the year and events to increase TSS. Every river will have its own “bed load” that its flows can carry. Above that bed load the river will begin to drop the sediment and create a braided channel and aquatic life will be impacted directly or their habitat. TSS can be an effective screening indicator and illustrate patterns in water ways or watersheds.

What Influences total suspended solids?

- Sediment, dirt and minerals not contained on the land from inappropriate land use practices creates non-point source runoff from logging, agriculture, ranching, construction, development, pavement, dirt roads, construction of or failing culverts, channelization, etc.
- Geology
- Natural disasters like floods or fires and associated floods
- Changes in channel morphology, natural or unnatural
- Road construction, maintenance or lack of maintenance
- Destruction of riparian buffer along river corridor
- Reservoir releases

Fluctuation Expectations

- **Daily** - Could if a large sediment load was introduced, but typically not much daily fluctuation.
- **Seasonally** - Yes, can with snowmelt, large storm events, irrigation diversions/return flows, managed rivers (reservoirs).
- **River Continuum** - Generally increases downstream with more land 'drained' into the system.
- **River, Lake/Reservoir, Groundwater Concentrations** – No general pattern exists. Concentrations will be a function of all variables discussed in this section.

Worksheet – Nutrients

What: ____________________

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Why: ____________________

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How: ____________________

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Influences: ____________________

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Freshwater Macroinvertebrates

What are freshwater macroinvertebrates?

Freshwater environments are generally considered to include inland waters not influence by tides from the ocean or natural salty waters. Invertebrates are all the animals that do not have an internal skeleton of cartilage or bone. Macroinvertebrates are large enough to see with a naked eye. In rivers, these organisms are benthic (live on the bottom), on, between and under the substrate. They have an enormous range of morphological adaptations, feeding niches, life cycle variations, habitat niches and movement variations.

Why do we care about macroinvertebrates?

Reason 1:

Invertebrates are some of the oldest organism on the planet. Invertebrates account for 70% of all known species of living organisms including microbes, plants and animals. They are fun to collect, identify, grow, watch and observe. Within the animal group alone, 96% of known species are invertebrates. This percentage is as high or higher in freshwater environments. Freshwater invertebrates have unique adaptations that make them successful in water and on land. For River Watch, macroinvertebrates provide the “response” organism for our holistic sampling, while the chemical parameters help measure “stressors”. River Watch cares about macroinvertebrates; our primary goal is to compile a species list over space and time to identify missing, additional and indicator species that might signify changes in community structure or function. Fish are indicators too but are more expensive and difficult to collect and sometimes can move away from stressors avoiding exposure.

Reason 2:

They serve an important role in the food change for fish, amphibians and water birds.

Reason 3:

They are involved in ecological processes such as decomposition of organic material and nutrients, and the recycling of nutrients.

Reason 4:

We eat some macroinvertebrates such as crayfish or shrimp.

Reason 5:

They help assess the health of a water body because they occupy the same narrow habitat, some are sensitive to stress produced by pollution, habitat modification, natural events, some have high tolerance to these items, and they have varying life cycles and are easy to collect.

How do we measure macroinvertebrates?

River Watch uses 2 distinct methods for collecting macroinvertebrates. We have protocols for Sandy bottom substrate and Rocky bottom substrate. See the Macroinvertebrate manual for instructions on these collection methods.

What Influences macroinvertebrates?

- Elevation
- Temperature
- Hydrology
- Substrate type
- Coarse or fine particulate matter
- Water quality
- Duration and magnitude of natural or human stressors

Fluctuation Expectations

Macroinvertebrate community structure and function is primarily influenced by elevation and climate, but also hydrology, temperature, water quality and frequency, duration and magnitude of natural or human stressors.

Benthic diversity has been used for years as an indication of stressors, including water quality. Diversity measures are founded on the concept that higher quality waters support a greater diversity of organisms than poor quality waters. In general, this is true, but diversity also changes along the river continuum.

According to the River Continuum Concept (Vannote et al., 1980):

- heterotrophic headwater streams (stream orders 1-3) support a less diverse benthic community than the mid-reaches;
- autotrophic mid-reaches of rivers (stream orders 4-6) support the highest diversity of macroinvertebrates found along the river continuum;
- heterotrophic lower reaches (stream orders 7) support a lower diversity of benthic macroinvertebrates than the mid-reach.

Changes in diversity along the river continuum are a result of alterations in the magnitude and pattern of physical stream/river parameters along the river continuum. The River Continuum Concept, however, is based on river ecosystems relatively undisturbed by pollution and unwise land use practices.

Many river ecosystems, however, are impacted by point and nonpoint sources of pollution and by land use practices that alter the river environment. It is important to recognize factors that may impact benthic diversity when designing a benthic collecting program.

Physical Habitat

What is physical habitat?

Physical habitat is literally the house and home for aquatic animals. Like humans, we have all kinds of houses and homes, sizes and types. Our habitats include where we sleep, eat, acquire food, reproduce and raise families. These habitats are the same for animals. Features in the stream ecosystem provide houses and homes, places to find food, reproduce and raise families. Animals also have features that help them adapt and navigate to their habitat; is the water is fast or slow, deep or shallow, cold or warm? The type of substrate, seasons, food availability and other organisms all contribute to physical habitat or home for an organism.

Physical habitat can be defined as micro (within the stream) or macro defined by scale stream reach, watershed, riparian zone, floodplain. Physical habitat includes objective and subjective measurements, rankings, observations, etc. of physical features in the stream ecosystem that provided habitat for macroinvertebrates, microorganisms, fish, plants and other animals.

Physical habitat features include micro habitat like substrate composition, embeddedness, sedimentation, organic debris, width, depth, bank stability and vegetation. These features can be assessed in a reach or segment along with riffle/pool ratio, stream cover, meander ratio, etc.

Velocity is the speed at which water flows and discharge measures the volume (how much) water is traveling down a stream.

Station photograph is ideally a photo from the same location and perspective over time. A stream selfie, is a way to engage citizens and join a network of groups protecting streams, http://www.streamselfie.org/

Why do we care about physical habitat?

River watch desires to provide data in all three stream ecosystem areas, chemical, physical and biological. Physical habitat integrity or lack thereof will influence changes in either or both biological communities or chemical concentrations. Physical habitat itself can be degraded beyond a point where it will no longer support aquatic life. It is an essential component to monitor to determine the health of a stream or changes in the health.

Velocity and discharge are important to know how much water is diluting a pollutant and to translate from concentrations of standards to loadings of reduction strategies.

Station photos document conditions of a river overtime that provide a visual of condition and tell a story in a way chemistry does not.

How do we measure physical habitat?

See Physical Habitat section of the Macroinvertebrate Sampling Manual for River Watch required physical habitat assessment and for velocity and discharge what and why’s. See the optional section of this manual for Photographic record of stream site.

What Influences Physical Habitat?

Any alterations to the stream channel morphology like channel, substrate, bank, meander ratio, natural pool riffle ration or riparian zone can affect the biological or chemical components of the river ecosystem. Activities that cause channelization that straighten stretches of river, dewatering, diversions, return flows, flows from trans-mountain diversions, culverts, road crossings/bridges and the like can influence physical habitat changes.

Fluctuation Expectations

- **Daily** – not many features change daily naturally, flow, velocity, width and depth might change due to a discharge, especially if the discharge is larger in volume than the receiving waters.
- **Seasonally** – some features do naturally or human induced, such as flow, pool/riffle habitat, width and depth, discharge and velocity, etc.
- **River Continuum** – change in physical habitat features can be predicated in downstream direction, barring human disturbances or changes. For example, substrate changes in dominant size, stream width, depth, flow increases, velocity decreases, elevation decreases, etc.

Worksheet – Macroinvertebrate & Physical Habitat

What: ____________________

Why: ____________________

How: ____________________

Influences: ____________________

Data Interpretation 101

Data interpretation refers to **the process of using diverse analytical methods to review data and arrive at relevant conclusions**. The interpretation of data helps researchers to categorize, manipulate, and summarize the information in order to answer critical questions. At this point in a study design the monitoring questions have been determined, who is using the data for what purposes and uses is determined driving the information that needed to be collected. Data is just data and means nothing until it is translated into information. This is the information design or turning that data into information which includes the act of discovering findings in the data, conducting data analyses, interpreting that analyses and making recommendations or conclusions. Often in this workflow it is discovered the limitations of the data collected and that should be noted. Perhaps more stations or more sample events would help answer the questions. The task is to play with the data and find the story in the data.

After you become familiar with RW protocols and equipment, what RW monitors and why, you might wonder what all the results mean. As stated before, monitoring activities generate data, numbers, ratings, descriptions and the like but does not necessarily produce information. In addition to identifying your monitoring questions and data user/use endpoints, in order to turn data into information we will go through some version of the following process:

1) Determine findings and analysis (objective such as summary statistics, comparison to criteria, benchmarks, pre/post or historic conditions).
2) Interpretation and conclusions from the findings and analyses (subjective).
3) Make recommendations and/or take action.
4) Data utility, reporting or delivery to the identified decision makers. An effective study design would have planned these steps as best as possible based on the information needs of the target data users and their data uses and identified monitoring objectives.

Findings and Analyses

This step involves data management and playing with the data in order to find or tell a story and as the first step to see if the data answered your monitoring questions. It may involve getting data from other sources, simplifying or reducing the current data set by simple statistics (means, medians, percentiles, maximums, minimums, standard deviations, etc.). It may include graphing of variables through space (upstream to downstream) or through time. It might be best to graph variables that are related like dissolved oxygen and temperature. Look for outliers, patterns and the like. If relevant to your data objectives, compare results to pre/post data, historic data, benchmarks or reference sites or criteria. This step is objective, working the data to see what it can tell you and what it can't, recognizing the limitations becomes the stepping stone for recommendations and action as well. CPW biologist work with RW data for the next processes. You can work on your own data set or others from the RW database. Findings and analyses can be repeated by anyone and is not subjective in that sense, methods should be communicated and transparent.

Interpretation and Conclusions

Data interpretation and conclusions are both subjective and the task most people want someone else to do, but you can do it with River Watch or any other data. Interpreting the data is in essence answering the question from your analyses and findings: did the data you collected answer the questions you were asking? For example, your question might be: what are the metal levels in my stream? Are they safe for humans and fish? When you answer the question you asked with the data you are interpreting the data. You can further that interpretation and make a conclusion or two. In the above example, if you interpret your data to illustrate the metal levels in your stream and use brown trout toxicity thresholds (levels below these thresholds mean brown trout are safe), to compare data with, you may conclude brown trout are safe or not safe. Another example is how CPW and the WQCD use RW data to determine if stream standards (limits on pollutants such as zinc) are in at acceptable levels. If the data shows that the standards are being exceeded, that could mean the aquatic life is being exposed to toxic conditions. The conclusion might be that they are unsafe or might be simply that we need more data at a station or frequency to answer that question.

Recommendations and Action

If appropriate, determine the recommendations for future information, changes in study design and for action. Recommendations and action usually come from the conclusion of whether the initial monitoring objectives or questions were answered or not. Action can take many forms. If CPW and WQCD determine a stream is in attainment, we work for protection, if it is impaired, we work toward restoration.

Data Utility or Reporting

Data utility is how data will be used, and reporting is defined as how the data will get to the user.

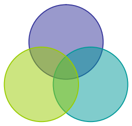
A data user is the intended audience for whom the data being generated. For River Watch, the data users are primarily the volunteers, CPW biologists and the WQCC and secondarily any other interested party. From a data users perspective, data is “put to use” or utilized for some decision making process after it is received or “reported”. It is important to understand how and when each decision maker needs the data you have generated.

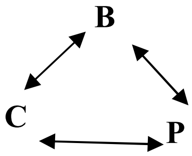
Since data users’ needs vary, data delivery can take many forms but in theory meets the information needs of the data user, format, type, variables, etc. It can be raw data, a fancy report or a verbal presentation. Use graphs, tables, pictures and summaries. The needs of the target audience must be considered. For RW, the CPW submits data to the WQCC in every triennial basin review of standards and water body use designations in order to protect aquatic life uses. CPW also submits data to other agencies, institutions, watershed groups, work groups and individuals for their purposes; they decide if the study design will answer their monitoring objectives. In addition, CPW biologists use RW data for management decisions.

Helpful tips

1. Know what you are monitoring or measuring. What is dissolved oxygen, what is alkalinity, what is physical habitat substrates ecological contribution, what are macroinvertebrates?
2. Know how your variable is “suppose” to behave, daily, seasonally, upstream to downstream (river continuum concept), with the groundwater, with the floodplain, etc.
3. Know why we care about this variable, what is the ecological contribution and associated monitoring question?
4. Remember the triangle relationship between physical, chemical and biological attributes of a stream? For example, how do the physical parameters affect chemical and biological parameters? A specific example might be when a bank is overgrazed and becomes unstable (physical), it sluffs into the stream and causes sedimentation and turbidity

(chemical) and the fish can't spawn or the macroinvertebrates lose their habitat (biological). The intersection of all three areas creates an environment for maximum biodiversity.





That example has a physical starting point. An example using a chemical starting point is the effect an abandoned mine has on a waterbody. Water running through a mine, exposed to air, becomes acidic and causes a reduction in pH and an elevation in metals (chemical); iron precipitates out and smothers habitat (physical) eradicating all fish, leaving only tolerant macroinvertebrates and algae (biological, low diversity).

5. Employ criteria and or benchmarks for comparison. These can be in the form of WQCC Clean Water Act Stream standards, biological or toxicity thresholds, historic data, pre/post, upstream downstream (control, impact, recovery zones), and reference or least impacted sites. An example is provided above in the metals "why" section.
6. What other variables might influence this parameter, did I measure it? For example, dissolved oxygen fluctuates with temperature; you have a better story if you collect both. Flow or discharge can dilute or concentrate some pollutants.
7. Land or water uses, precipitation, geology, stream morphology, hydrological modifications and natural events can influence results. Where are point sources and non-point sources of pollutants in your watershed?
8. What are you measuring, stressors (chemical variable for example a concentration), response (macroinvertebrate assemblages or pounds per acre of fish) or exposure? With exposure, what can you say about magnitude, duration or frequency in relationship to thresholds? Are you trying to make an interpretation about the response community based on stressor data or vice versa?
9. Worksheet 6 provides a teacher's guide and student worksheet to go through these steps.
10. It will help to have these resources:
    a. The "why's and what's" of parameters earlier in this chapter.
    b. Characterization of exposure, the beginning of this chapter.
    c. Excel, google sheets or equivalent. Software can calculate some metrics automatically thus and effort must be made to ensure the student understands what the metric is and characterizes.
    d. How to export data from the RW database (Chapter 1 here, FAQ on RW Website all have instructions).
    e. How to access Colorado Department of Public Health and Environment, Water Quality Control Commission standards (look for the CO Clean Water Act Tutorial).
    f. Any parameter will likely have a relationship with flow, you can get flow data following instructions in the Sample Plan or USGS site. Ensure the flow data aligns with time

period and location of the data, if not make qualifying statements. Even if alignment is not perfect it is a great educational exercise.

   g. This tutorial assigns two parameters and two locations to each student. Modify as needed.

11. If you want some data sets to work with as an example here are a few with ample data that align in space and time:
   a. Dissolved Oxygen and Temperature from: **Buena Vista HS, Arkansas River, Stations 27 and 28**
   b. Alkalinity and Hardness from: **Multiple Groups, Animas River, Stations 103 and 93**
   c. Cadmium, copper and zinc from: **Same stations or, Cement Cr and Mineral Cr, stations 323 and 104**
   d. Nutrients from: **CPW, Long Hollow and La Plata, Stations 341, 85 and 902**

Worksheet 6 – Teachers Guide to Data Interpretation

Teachers Guide
Data Interpretation Outline

1. Teacher determines the data set and objectives. Make up a date; use your data, others or a combination. You need to determine if you have multiple stations or just one. The tasks 2-7 should be done for each station, looking through time. Step 8 has an exercise to look at multiple stations, or data through space.

2. Homework. Teacher will tally the years' worth of data (or some time and location data), assign teams to data sets and provide them with the raw data. The overall objective of the homework is to have the students play with the data and see what story it tells, or doesn't, and make recommendations. If you have multiple years of data you might need to summarize using averages or other statistics. The activities to achieve this include:

   a. Complete the inquiry questions on the homework regarding the parameter they are assigned, what is the parameter, why do we care about it, etc.
   b. Assess results in context with River Continuum Concept
   c. Assess results in context with one years' seasons (or given time)
   d. Bonus if you have more than one station's data-assess results through space
   e. Graph the data over time and space
   f. Compare the values to a benchmark (standard) if it exists
   g. Calculate summary statistics, max, min, range, mean
   h. Identify median and interquartile ranges
   i. Record findings and analyses
   j. Conduct interpretation and draw conclusions
   k. Provide recommendations and action
3. Class Time. Each parameter group (like temperature and DO) will present their conclusions and recommendations. Discussion will follow. Weave in concepts such as:

   - Stressor, exposure, response
   - Exceedance related to frequency, duration, magnitude (just because exceed may not cause harm function of [frequency, duration and magnitude])

4. Some ideas on how to break up the parameters to tell a story:

   - Temperature and dissolved oxygen (temperature influences DO)
   - Temperature and pH
   - Alkalinity and hardness
   - Copper, zinc, aluminum
   - A metal and hardness
   - TSS
   - Nitrogen and Total Phosphorus
   - Nitrogen and Ammonia
   - Any variable and flow (if have data)

   Develop presentation format, verbal or written. Have class discussion.

Data Interpretation Worksheet

Worksheet 6

1. What locations is your data from? Look up on a map the stations. Get a clear picture of their relationship to each other. Explore what else is in the basin and what you know about the area currently and historically. Take notes and provide findings here.

2. a. What parameter(s) were you assigned (for example temperature, dissolved oxygen, etc.)? For each parameter what are you specifically measuring? Do you have more than one station Yes or No?

b. For each parameter, list one reason it is important to measure for aquatic life or human health.

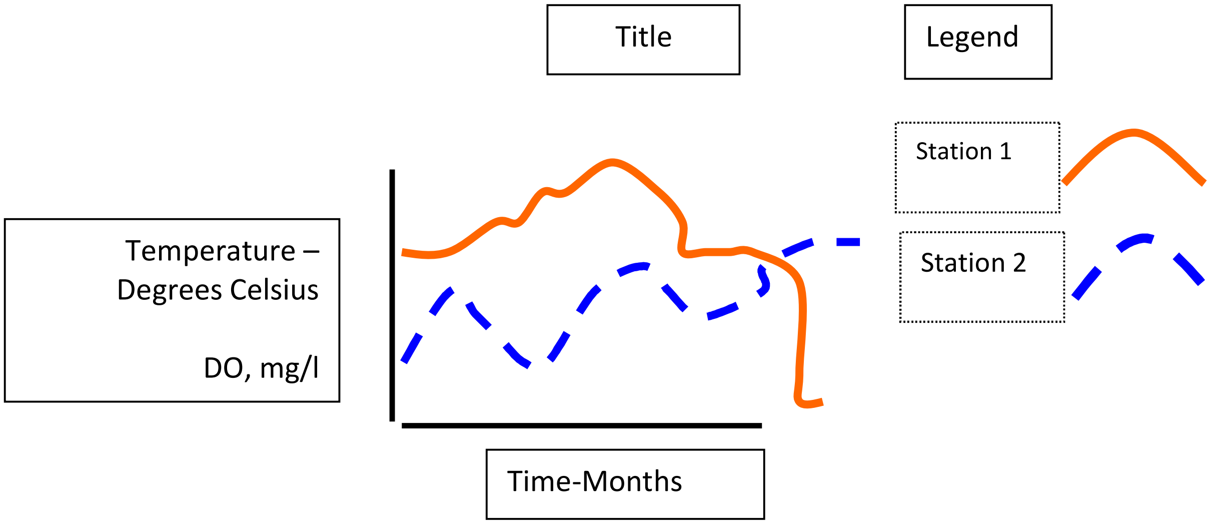
3. For each parameter, record how you predict this parameter changes from upstream to downstream, the River Continuum Concept? This tells you how the parameter typically behaves up to downstream, once you graph it you can determine if it is ‘behaving’ as expected, if have enough data to make that interpretation or hypothesize why it is not following an expected pattern

Parameter	**Change Upstream to Downstream?**	**Why?**

4. For each parameter, record how you predict this parameter changes daily or seasonally (summer, fall, winter, spring) and why? This tells you how the parameter typically behaves up to seasonally, once you graph it you can determine if it is ‘behaving’ as expected, if have enough data to make that interpretation or hypothesize why it is not following an expected pattern.

Parameter ↓↑	**Daily OR Neutral Change?** ↓↑	**Seasonal OR Neutral Change?**	**Why?**

5. On another sheet of paper, in Excel, Google sheets or equivalent, graph all your parameters against **time**. And because you are graphing two stations you are also graphing data over **space.** This displays changes over time, depending on your data set that could be days, weeks, months, years or decades. Put time (monthly sampling dates) on the x-axis and your parameters on the y-axis. Connect each point to make a line. Give the graph a title that tells the reader where, when and what is being illustrated. Label each axis appropriately with name and units. Include a legend for stations. Graphing two parameters helps you see their relationship. Looking at changes between stations tells a story over space. A graph should stand on its own and not need someone to explain it. See example below.



6. Let's start to look for a story. First between the two parameters. Do they have relationship, like DO and temperature, pH and temperature, alkalinity and hardness, a metal with flow, a metal with hardness? If so can you see it? Do you have enough data? What is the relationship over time? This is the first set of notes in your findings, analyses worksheet.
   - Each parameter over time?
   - Between parameters over time?

7. Next story is about changes or not over time, but over space, between each station. Do you have enough data or is it a comparable data set? If do what are your findings and then interpretation? How does your parameters vary between each station? What is your interpretation of that difference or no difference? Look for the finding, then the interpretation and next the conclusion, naming limitations with the data or information. Add to your findings, analyses worksheet:

   - Differences or not between stations over time?
   - Statement about the data?

8. Let us look at more information. For each parameter, is there a standard or benchmark that should not be exceeded? See the reference to where the standards are above and ask for help to find your segment or water body Id and the standards, especially if they are "TVS" or a table value standard. If you have a benchmark, add it to your graph above. Ask your teacher for assistance if needed. Note if you selected hardness, in the "what is it" column characterize hardness role or influence on metals standards.

Parameter	Benchmark Y or N	If Benchmark what is it?

9. Add benchmarks to your graph(s). Observe if there is a station and/or time that the standard is exceeded. This is a finding. Calculations or estimations about how long (duration), how often (frequency) and how much (magnitude) the exceedance occurs help determine if organisms exposed to this standard could be harmed. This explores exposure and how the Clean Water Act tries to address a biological, toxicological and ecosystem phenomena in the policy and regulatory world. To interpret your finding review the beginning of the Chapter 3, Monitoring. Then make an interpretation based on your parameters and graphs. Is aquatic life potentially exposed and or not? Make a statement about each station and topic (2 points per station, 5 topics).
   - Exposed or not at each station?
   - Duration
   - Frequency
   - Magnitude
   - Statement about the data

10. For each parameter, calculate the following summary statistics and put the results in the following table.

    Maximum data point (highest value in dataset)
    Minimum data point (lowest value in dataset)
    Range (maximum to minimum values)
    Mean (average of all results)

Parameter	Max	Min	Range	Mean

11. For each parameter identify the Median, Interquartile and IQ Range. These summary statistics help us identify the variation in our data set. If the IQ Range is large, this indicates we have large variation in our dataset. Large variation may be due to sampling or analytical error, a limited data set or expected. If the IQ Range is small it means our results are relatively consistent, similar and clustered around the median, perhaps in a more predictable occurrence. If you have more data than the lines allow, create another sheet. If you have tons of data do this with summary statistics like the mean or median.

    - The median is the result that falls exactly in the middle of the dataset and is the same as the 50th percentile. Half of the results are above the median and half are below.
    - The 25th and 75th quartile represent the result where respectively ¼ of the data are above or below.
    - The IQ range is the difference between the 25th and 75th quartiles.

To accomplish this complete the following, see the provided example table:

a. For each parameter rank your results (list the results) and corresponding collection date from low to high in the following table.
b. Find the median value, 50th percent quartile. Record it on the table.
c. Find the 25th and 75th percent quartiles. Record on the table.
d. Take the difference between the results for the 25th and 75th percentile, this is the IQ Range. Shade this area in on the table.

EXAMPLE TABLE:

Mark IQ Range	**Mark 25th, 50th, 75th quartile**		**Results to rank (low to high)**	**Corresponding collection date**
			10.5	1/6/04
			10.8	2/6/04
IQ Range Shaded	25th		11.5	3/9/04
Difference is			12.6	12/6/04
25th – 75th =	Median-50th		13.5	4/9/04
14.2-11.5 = 2.7			13.6	11/5/04
IQ=2.7	75th		14.2	5/10/04
			15.7	10/5/04
			22.3	9/4/04

PARAMETER 1, Station 1:

Mark IQ Range	Mark 25th, 50th, 75th quartile		Results to rank (low to high)	Corresponding collection date

PARAMETER 2, Station 1:

Mark IQ Range	Mark 25th, 50th, 75th quartile		Results to rank (low to high)	Corresponding collection date

PARAMETER 2, station 2:

Mark IQ Range	Mark 25th, 50th, 75th quartile		Results to rank (low to high)	Corresponding collection date

PARAMETER 2, station 2:

Mark IQ Range	Mark 25th, 50th, 75th quartile		Results to rank (low to high)	Corresponding collection date

Parameter	Station	Median	25th / 75th	IQ Range
1	1			
2	1			
1	2			
2	2			

12. What can you say about these metrics (findings) at each station? Is the data tight, not large differences between 25, 50 and 75th? Or is it large? Does the data cover expected changes daily, seasonally or over multiple years? What are differences between stations? The interpretation helps determine how variable the parameter is in this river, what variability is acceptable given management goals and relationships with other factors out of your control?
    - Median, 25 and 75th Spread at each station?
    - Between each station
    - Statement about the data

13. You now have multiple interpretations and statements about the data (what more would be helpful or is there enough?). Take your interpretations from the findings and make some conclusions, listing any data limitations. Your goal is to conclude if the stream will support aquatic life or not. Make conclusions about both stations, providing the case or the why from your findings and analyses.
    - Conclusions station 1
    - Why Station 1
    - Conclusions station 2
    - Why Station 2

14. Now from your conclusions, use your imagination and resourcefulness, make a recommendation to the client as if the client is has resources to apply to the project. For example, if conditions support trout you will recommend _________. If conditions don't support trout you recommend _________. If there is not enough data what specifically do you recommend be collected, when and where?
    - Recommendation station 1
    - Recommendation station 2
    - Recommendation on data collection:

15. Present your recommendations and conclusions to the client. Provide the interpretation, analyses and findings as foundation the foundation. You have five minutes. Include recommendations about the data set itself. Pretend the class is the client you have been hired to evaluate this data set, what would you tell them?