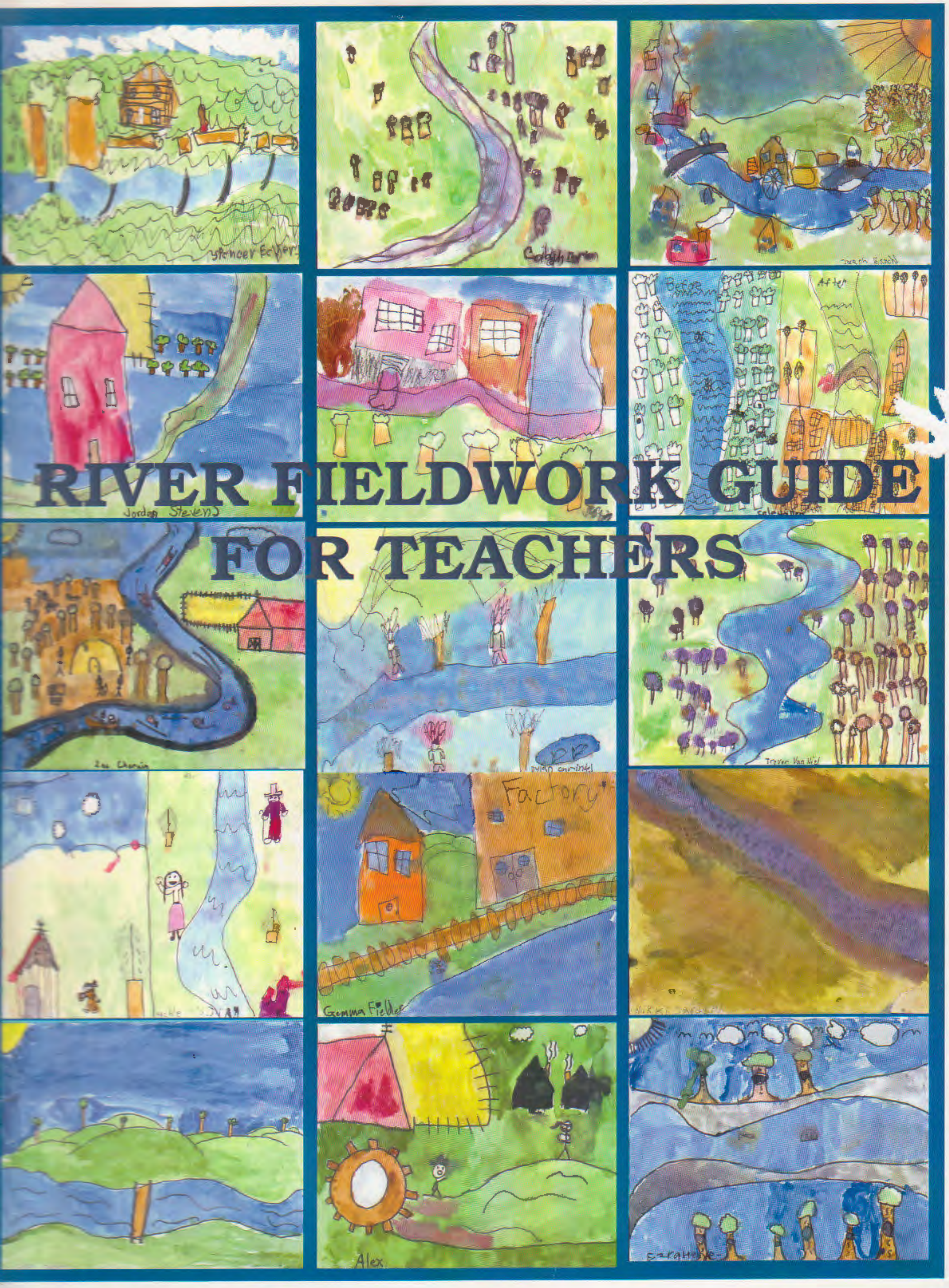
RIVER FIELDWORK GUIDE FOR TEACHERS



RIVER FIELDWORK GUIDE
For Teachers

A unit of
Environmental Citizenship:
Learning to Make Informed Decisions

June 2006

June 2006 Edition *"River Fieldwork Guide for Teachers"* developed by Kimberly Jensen and edited by Mike Muller. Contributing authors were Caitrin Noel, Jenna Guarino, Kimberly Jensen, Lori Barg and Matt Bratner. Special thanks to Kari Dolan. Illustrations were produced by Susan Sawyer. Funding was made possible by generous grants from The Wellborn Ecology Fund of the Upper Valley Community Foundation dedicated to increasing awareness of environmental and ecological issues in the Upper Valley of the Connecticut River.

What is Environmental Citizenship?

Environmental Citizenship (EC) is an educational program for middle school students focused on balancing the needs of humans and wildlife through informed decisions. Students learn about natural systems, conduct outdoor scientific investigations, and contribute to community environmental health through educational activities and citizenship projects.

The Five EC Units

- Atlantic Salmon: A Watershed-Wide View
- Trout: A Watershed-Wide View
- Bobcats: Predators in a Changing Landscape
- Vernal Pools: Life in Temporary Ponds
- Thrushes: Migrant Songbirds of the Forest

Note: Each unit has an accompanying TEACHING KIT that is available from VINS.

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V. The Chemical Interactions of a River

In this chapter, we will explore the chemistry picture of a "healthy" river. To do this, we will first take a step back and look at the unique properties of water which direct and affect river chemistry. Then we will move through a more detailed exploration of the relevant chemical parameters in river, the internal and external factors affecting these parameters, as well as the interaction of the parameter with the physical and biological components of a river.

Water is Magic: The Unique Properties of Water

Water is essential to life; most living things are composed of a significant percentage of water. Not only is it essential, it is also a very unique substance. While it is a common substance, it has unusual physical and chemical properties. These properties, explained in the following section, are interrelated and define how water acts in the environment. A basic understanding of the physical and chemical properties of water is essential to explore the chemistry of rivers.

Phases of Water

Water is the only substance common on earth that is present in all three states of matter (solid, liquid, gas) within the natural range of temperature and pressure. Whether water exists as a solid, liquid, or gas depends on its temperature and the pressure of the surrounding environment. Change the temperature or pressure, and water may undergo a phase change. At sea level, it typically freezes at 0° C and boils at 100 0° C.

At the boundary line between two phases, determined by temperature and pressure, two phases are in equilibrium with one another – the rate of molecules leaving a phase equals the number returning. The inclination of a molecule to change phase and establish equilibrium is defined as its vapor pressure. Vapor pressure increases with increasing temperatures. At higher temperatures, a particle's kinetic energy is higher, and, with more energy available at higher temperatures, it is easier for particles to change phase. Even solids such as ice have a vapor pressure and can sublimate directly to the vapor phase.

Very near 0° C (0.0098 0° C), all three phase boundary lines meet at a point called the triple point. At this temperature and pressure, all three phases are in equilibrium with one another. In other words, at the triple point, vapor sublimates to ice and condenses to liquid, liquid evaporates to vapor and freezes to ice, and ice melts to liquid and sublimates to vapor all the same rate.

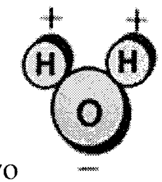
Heat and Energy

Water has a high heat capacity, absorbing and releasing heat slowly. It takes one calorie to raise the temperature of one cubic centimeter of water one degree (at 20°C). When a cubic centimeter of water drops one degree, one calorie of energy is released. 1 million calories are required to raise the temperature of one cubic meter of water by one degree (Celsius), if no changes of state are involved. Because it absorbs, stores, moves and releases heat, it shapes climate and weather. Water temperature, a function of heat capacity, directly affects a number of physical and chemical characteristics of river water, including density, dissolved oxygen levels, and electrical conductivity.

Water also absorbs and releases heat during the water cycle. Latent heat (or energy) is the amount of heat released from or absorbed by a substance when it undergoes a change of state. For water, latent heat is very high, about 600 calories/gm. This is the amount of heat energy required to evaporate water into the atmosphere, or the amount of heat lost to the atmosphere in precipitation of vapor to liquid water.

Molecular Structure

Water molecules are composed of hydrogen and oxygen, with one atom of oxygen bound to two atoms of hydrogen. Water is a dipolar molecule because of the arrangement of the hydrogen atoms (which meet at a 105° angle across the oxygen atom), with a slight positive charge on the hydrogen side and a slight negative charge on the oxygen side. The charges do not cancel one another out but create two separate poles (Figure 7 [1]).



Water is an excellent solvent due to its polarity and small size. It dissolves most things: 72% of known substances are water soluble. As a nearly universal solvent, water dissolves and transports many surface materials, including chemicals, minerals, and nutrients important to the functioning of rivers.

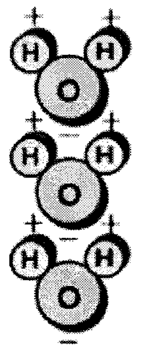


Figure 7: Since opposite electrical charges attract, water molecules tend to attract each other. The positive charge on the hydrogen pole of one water molecule is attracted to and forms a bond with the negative charge on the oxygen pole of a different water molecule. Figure 2: A chemical bond caused by electromagnetic forces is known as a hydrogen bond. In liquid water, hydrogen bonds are constantly broken and reformed, allowing water molecules to move.

This attraction among water molecules causes them to tend to clump together. This electrical attraction causes water to form drops (drop of water on wax paper beads up), flow as a discrete and defined stream (pour slow stream of water across a an inclined smooth impervious surface – plastic sheet), and allows siphons and pumps to function (a towel or other fairly absorbent cloth draped over the edge of a basin of water will rapidly cause water to travel up and over the rim).

[1] Figures 1 and 2 from USGS Water Science for Schools, http://ga.water.usgs.gov/edu/waterproperties.html

Density

Liquid water has a density (mass/unit volume) of 1 gm/cm³ at standard temperature and pressure. The high density of liquid water is due to the cohesive nature of the hydrogen-bonded network. This reduces the free volume and ensures a relatively high density. For pure water, the density will change as a result of temperature change. The quantity of dissolved solids or suspended material may also affect density of naturally occurring waters.

Temperature and Density

As a substance loses heat energy, molecular motion slows and the atoms come closer together. This results in a higher density. As a liquid cools its density increases, becoming most dense at the point of phase change from liquid to solid. All known substances abide by this rule, except for water.

The density of water does increase as it cools, but at 4°C the density vs. temperature relationship goes the other way and the density actually begins to decrease. This density decrease continues until the solid state is achieved at 0° C. At 4° C the water molecules have very little energy, and the strong hydrogen bonds hold them close together, making water very dense. When water is cooled below 4° C, the water molecules have even less energy and are no longer able to break the hydrogen bonds. This causes the molecules to start to stack in a crystalline lattice configuration, the structure of ice.

Stacking stretches the hydrogen-oxygen bonds, so the water molecule takes up more space and lowers the density. At 0° C the crystalline lattice structure fully forms and the phase change from liquid water to solid ice occurs.

Solids of most substances are denser than when they are in their liquid form. The opposite is true of water. Because of the way water molecules are arranged, with longer intermolecular bonds, water molecules in ice take up more space and make it less dense. In ice, all the water molecules are arranged in four straight tetrahedrally-oriented hydrogen bonds. This creates an open structure of space within the crystalline lattice. When water freezes at 0°C, at atmospheric pressure, its volume (as ice) increases by about 9%. Less dense than water, ice floats. Preventing the expansion in volume during freezing may generate pressures of up to 25 MPa (megapascal units), easily capable of bursting pipes.

Solutions

When a substance dissolves in water the mixture is called a solution. A substance dissolved in water may be dramatically changed, but its basic characteristics remain constant. As a result, substances in solution can be separated out by physical means, such as evaporation to separate salts from water or distillation to remove alcohol.

What is dissolved in the water is one of the defining characteristics of river waters. Nitrates occur in water as a result of seepage through nitrate bearing rocks or soils. High levels of fluoride (over 2 mg/L) are common in the Pecos River of West Texas, and elevated levels of arsenic are found in the Rio Grande. Rivers flowing over limestone are often quite alkaline, containing high levels of carbonates and bicarbonates.

Many of the parameters measured in water quality testing are measurements involving solutions. Some of the more common parameters, and the dissolved materials they measure, are explained in the next section.

Environmental Chemistry

Dissolved Oxygen: The Breath of Life

As our circulatory system and blood carry oxygen to our various systems, river water carries *dissolved oxygen* (DO or O_2) to aquatic organisms. Since sufficient oxygen is essential to the well being and survival of the organisms living in a river system, it is arguably the most important chemical factor in a river system. Oxygen is necessary for decomposition, respiration, the conversion of nutrients, and other essential functions.

Dissolved oxygen measures the concentration of free (not chemically combined) molecular oxygen gas dissolved in water, usually expressed in milligrams per liter, parts per million, or percent of saturation.

Aquatic organisms require a minimum level of dissolved oxygen to survive, and certain sensitive organisms require still more. DO is considered the most important and commonly employed measurement of water quality, and it is an indicator of a river's ability to support aquatic life. Levels above 5 milligrams per liter (mg O_2/L) are considered optimal, and most fish cannot survive for prolonged periods at levels below 3 mg O_2/L. Levels below 1 mg O_2/L are often referred to as *hypoxic.*When O_2 is totally absent, water is *anoxic* (or anaerobic which technically means *without air*).

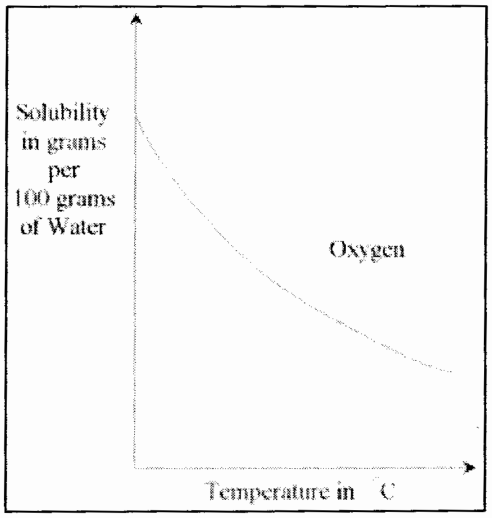


Figure 8: Solubility of oxygen in water at various temperatures

Oxygen becomes dissolved in water at varying levels depending on water temperature (Figure 8), atmospheric pressure, and other factors. As water temperature increases, the amount of dissolved oxygen (DO) in water decreases. Water temperature can be increased by thermal pollution, runoff from paved surfaces, and the loss of riparian vegetation and/or canopy cover.

Other factors which influence water temperature are physical mixing, time of day, organic matter inputs, and number of aerobic bacteria present. (**Table 3**) Physical mixing increases the amount of DO, and occurs when water is churned, for example when it passes over a waterfall.

The time of day is important when measuring dissolved oxygen because DO levels tend to be lowest in the early morning hours, then increase throughout the day. This is because there is a lack of photosynthesis during the night, while aerobic organisms are still respiring throughout this period. Increased organic inputs can lower DO levels since aerobic bacteria inhabit the matter, using oxygen as they facilitate decomposition. Eutrophication, caused by increase in nutrient levels, can also dramatically reduce DO levels; in extreme cases eutrophication can cause anoxic conditions and result in large fish kills (see Nutrients section). A common source of organic matter in rivers is wastewater treatment plants. Secondary and advanced wastewater treatment systems are now generally designed to degrade organic matter prior to discharge to ensure adequate dissolved oxygen in receiving waters.

Table 3: Various factors which influence dissolved oxygen levels

Factor	Mechanism	Outcome
Loss of Riparian Vegetation/Canopy Cover	Radiation from sun heats stream water	Increased temperature, Decreased DO levels
Increased impervious surface in watershed	Radiation from sun superheats runoff from impervious surfaces	Increased temperature, Decreased DO levels
Industrial use of stream water	Industrial cooling process returns warmer water to stream	Increased temperature, Decreased DO levels
Physical mixing	Riffles and waterfalls create optimal mixing	No change in temperature Increased DO levels
Increased amounts of organic matter	Excessive algae or organic matter inputs create increase in aerobic bacteria associated with decomposition	No change in temperature, Decreased DO levels
Time of day	Lower dissolved oxygen levels in morning due to lack of photosynthesis overnight	May be decreased temperature, Decreased DO levels

Phosphorus: Too much of a good thing?

Phosphorus is a nutrient essential to the growth and survival of all living things. One of the many nutrients in food we eat every day, phosphorus is also essential for plant growth. Phosphorus exists in several forms in the environment. In aquatic systems, phosphorus exists in a dissolved form (orthophosphate, available to plants) as well as in an organic form (unavailable to plants without being converted to the inorganic form). While plants need phosphorus to photosynthesize, additional phosphorus can create conditions of excessive plant growth and lead to eutrophication.

Eutrophication happens when excessive nutrients cause excessive plant growth and subsequently anoxic conditions (when the plants die, aerobic bacteria take in large amounts of dissolved oxygen from the water). Eutrophication is NOT a desirable condition, whether you are a fish, a fisherman, swimmer, boater, or otherwise interact with a lake.

In the northeast, eutrophication is a major concern in many watersheds. Excess phosphorus comes from fertilizers, manure, and soils which are washed into waterways everyday. However, while most folks believe farms are part of the problem, studies have shown that urban areas add significantly more phosphorus per acre than farmland.

Most streams in the northeast have natural levels of phosphate less than 0.05 mg/L. When levels are between 0.05 and 0.10 mg/L, the stream is "likely impacted" When levels reach greater than 0.10mg/L, the stream is considered "certainly impacted".

**Kit Tip:* It is difficult to test for phosphate with simple kits, as the sensitivity of many of these kits is insufficient; many kits cannot detect levels below 1.0 mg/L. Before purchasing a test kit, be sure that the sensitivity is sufficient. Kits using an electronic colorimeter are usually sufficient. Also remember to acid wash glassware as phosphates are very "sticky" and can cling to the inside of testing vessels.

Nitrogen

Nitrogen exists in aquatic systems mainly as nitrate, with small amounts of nitrite, ammonium and ammonia (these forms are quickly converted to nitrate or returned to the atmosphere). Like phosphorus, nitrogen is essential for plant growth. The sources of nitrates are the same as for phosphates—animal wastes, soil and decomposing plant material. Most scientists believe that phosphorus is the limiting nutrient in freshwater ecosystems, and nitrogen is the limiting nutrient in marine and estuarine environments. Therefore, human inputs of nitrogen into marine or estuarine system can also cause eutrophication, such as red tide outbreaks. In the northeast's freshwater watersheds, many efforts focus on controlling phosphorus levels; in coastal areas, the focus is on controlling nitrate levels.

**Kit Tip:* If you live in an area where there is concern about rising nitrate levels, such as a coastal or estuarine area, please use caution when testing. Many of the common inexpensive kits produce cadmium waste, which is highly toxic. Those not living in coastal areas should consider only testing for phosphorus, as the test kits produce much less toxic waste.

Conductivity

Conductivity (electrical conductivity and specific conductance) measures the water's ability to conduct an electric current and is directly related to the total dissolved salts (TDS) in the water. Conductivity increases as the salt/ion concentration in water increases. Conductivity is a general, non-specific measure of water quality because it is an aggregate of all ions, and one does not know which ions are responsible for increased conductivity.

The primary inorganic ions that make up TDS are Calcium Ca++, Magnesium Mg++, Sodium Na+, Iron Fe++, Manganese Mn++, Bicarbonate HCO3-, Chloride Cl-, Sulfate SO4--, Nitrate NO3-, Carbonate CO3--. When the conductivity of a lake or river changes, it indicates there has been some sort of disturbance. The disturbance might result from natural or human activities and might be involve physical, chemical, or biological factors. In Vermont and New Hampshire, the most common cause of rapid conductivity changes in rivers is the introduction of salt (NaCl) from road salt in runoff.

Electrical conductivity (EC) is reported in micromhos per centimeter (umhos/cm) which has been recently renamed as uS/cm (microSiemans per centimeter). EC is temperature sensitive and increases with increasing temperature. A simple inexpensive probe can be used to measure conductivity. Most modern probes automatically correct for temperature by standardizing all readings to 25°C then refer to the data as *specific* EC.

There are expected natural ranges (background levels) for conductivity, but these vary regionally due to differences in geology and soils. Therefore it can be difficult to interpret your results unless you know the background levels in your area. It is helpful to consult with a local geologist to determine the natural ranges of conductivity in your area. Changes in conductivity can affect freshwater biological life in the same way as salinity (see salinity section).

Alkalinity

Alkalinity is the acid neutralizing or buffering capacity of water. It is a measure of the ability of water to resist changes in pH due to the addition of acids or bases. It is a principal indicator of susceptibility to acid rain. Alkalinity is expressed in units of milligrams per liter (mg/l) of $CaCO_3$ (calcium carbonate), or as microequivalents per liter (ueq/l) where 20 ueq/l = 1 mg/l of $CaCO_3$.

Watershed geology is one determinant for the buffering capacity of a given stream. For instance, watersheds with predominantly alkaline soils and geology, such as limestone and dolomite, increase the buffering capacity of streams. These rocks contain carbonates and when the rocks erode, these materials are released into the water column. The carbonates bond with excess hydrogen atoms, thus "locking up" the hydrogen and increasing the pH (remember pH measures the concentration of hydrogen atoms present). A solution having a pH below about 5 contains no alkalinity.

The terms "hard" and "soft" are sometimes used to identify water with high and low calcium carbonate concentrations, respectively. Hard waters have dissolved salt concentrations greater than 120 mg/L and are resistant to pH changes. Soft waters have low concentrations and low buffering capacity. CaCo3 can be measured with inexpensive kits with reasonable reliability and accuracy.

Acidity

Acidity is indicated by pH. The pH is a measure of the concentration of hydrogen ions: it is the negative logarithm of the hydrogen ion (H^+) concentration. At higher pH levels, there are fewer free hydrogen ions, and a change of one pH unit reflects a tenfold change in the concentrations of the hydrogen ions. For example, there are 10 times as many hydrogen ions available at a pH of 7 than at a pH of 8. The scale ranges from 1-14 with 1 being the most acidic and 14 the most basic. A pH of 7 is considered to be neutral. A solution with a pH of less than 7.0 is considered acidic, and substances with pH greater than 7.0 are basic.

The pH of natural waters can vary. The pH scale may go from 0 to 14, but the pH of natural waters hovers between 6.5 and 8.5. Pure water is neutral with a pH of 7. Most commonly, pH may be affected by the concentration of carbon dioxide. In water, dissolved carbon dioxide (CO_2) gas acts like carbonic acid (H_2CO_3). Plant respiration and decomposition increase CO_2 concentrations, thus increasing acidity and decreasing pH. The pH of water samples is likely to be highest when photosynthesis is greatest, during daylight hours and during the growing season. The buffering capacity of water, measured by the alkalinity affects the overall range of pH change under natural conditions.

Salinity

Salinity refers to the amount of sodium chloride (NaCl) found in a given volume of water. This manual is designed for the study of freshwater rivers, which naturally have no salinity, so why include salinity as a water quality parameter? Since the 1940's, highway crews have been spreading road salt on our highways in an effort to deice roads and improve winter driving conditions. In fact, each winter Vermont road crews spread more than 34 tons per mile of salt throughout the more than 3200 miles of highway. That adds up to more than 108,000 tons of salt used annually in Vermont alone!

So what? Is this a problem? The answer is *maybe*. There is conflicting scientific evidence on the issue; studies done by several organizations in several countries are split. Some studies suggest that road salt as currently used is not ecologically harmful and is the best of available options, while others claim negative water quality effects and call for drastic reductions in salt application and changes in winter road management. While there is debate about salt use and ecological impacts, all parties agree that salt storage has been and continues to be a problem. Many towns in Vermont and New Hampshire lack the resources to build covered storage spaces for road gravel and salt, and the uncovered piles (many located by necessity in valley locations, unfortunately also near streams) are a significant source of pollution.

**Kit Tip:* Salinity is measured in parts per million (ppm) or milligrams per liter (mg/L), and can be tested with a simple, inexpensive kit to obtain reasonably valid and reliable results. However, salinity tests done well after the spring runoff may be misleading, as most of the road salt runoff is long gone!

Measuring Chemistry in a Stream Near You

In the previous sections, the basic factors which explain and influence stream chemistry were explored. Now students should be ready to collect, analyze and interpret data in a local stream.

The first step to sampling water chemistry is to design an appropriate study. This includes deciding what, where, when, how and why you are testing. For more information on preparing a stream study, please refer to the Vermont Volunteer Surface Water Monitoring Guide. You can also contact the University of Vermont Watershed Alliance coordinator for assistance, equipment, and to find out about the interns-in-the-classroom program (See ***Diving Deeper*** below).

After you have designed your study, prepare students for the field by checking maps of the sampling area, making sure they are aware of safety issues, and are dressed appropriately for field work.

Limitations of Studying Stream Chemistry

While biological and physical factors tend to be more stable in a stream, stream chemistry can change in hours or even minutes. Therefore, chemistry studies done on one or two or even twelve days a year are merely snapshots of the conditions in a river. An ideal chemical monitoring program would test each parameter in every site at every moment, but obviously this is impractical. Stream studies are ALWAYS less than ideal; there is no perfect information. However, we can still use data to make estimations about general conditions in the stream or watershed. Even better, we can look at data trends over years to track long term shifts in water quality. When designing a monitoring study with students, it is important to acknowledge that this data is limited, but nonetheless it is a useful and necessary piece of the puzzle.

Diving Deeper

UVM Watershed Alliance: 655 Spear Street, Burlington, VT 05405; Tel: (802) 656-5428; E-mail: caitrin.noel@uvm.edu; http://www.uvm.edu/~watershd

Vermont Department of Environmental Conservation - Water Quality Division. A complete list of publications and videos are available by request from their website: http://www.anr.state.vt.us/dec/waterq/cfm/ref/Ref_Result.cfm