The River Mile
Water Quality

Lesson # 6

Water Quality: Nutrient Loading & Dissolved Oxygen

Developed by the Lake Roosevelt Forum to support "The River Mile" National Park Service Program

Suggested duration:
90 minutes
Inquiry Question:
How do excess nutrients affect dissolved oxygen levels and impact water quality?

Inquiry Process:
Synthesizing information
Compare & contrast data

Standards:
PS2, Ls1, LS2, LS3

Assessment:
Analyze data, make inferences and draw data based conclusions

Materials:
Nutrients & DO PPP
Computer
LCD projector
WQ CD

Handouts:
Student Handout
DO Data tables from ECY reports on Hawk Creek Grand Coulee & North Port

Credits/Citations:
BPA
EPA
GLOBE
MEEC
Nature Mapping
USGS
WA Dept of Ecology

LESSON #6

Water Quality: Nutrient Loading and Dissolved Oxygen

INTRODUCTION:

Dissolved oxygen is molecular oxygen freely available in water and necessary for the respiration of aquatic life and the oxidation of organic material. **Nutrients** are beneficial but too much of anything is a problem especially when aquatic plants & microorganisms take over. **Sources of nitrogen and phosphorus** include discharge (effluent) from waste water treatment plants, runoff from municipal and agricultural fertilizer, livestock manure and leaky septic systems. The excess nutrients support the rapid growth of an overabundance of aquatic plants and subsequent death. Plant decomposition uses oxygen and reduces the dissolved oxygen available to support other aquatic inhabitants. Algae tend to grow and decompose faster in warm water.

STUDENT WORK AND ASSESSMENT

Analyze data on nitrogen, phosphorus, and dissolved oxygen levels provided by the Washington Department of Ecology Water Quality tests at Grand Coulee, Hawk Creek and North Port. Make inferences and draw data based conclusions about the relationship between nutrient levels and available dissolved oxygen.

QUESTIONS TO EXPLORE/INSTRUCTIONS/PROCEDURE

1. Introduce Nutrient Loading and Dissolved Oxygen by viewing the power point presentation which incorporates resources from EPA, WA Dept of Ecology, and the United States Geological Society. Source documents are provided for each agency resourced
2. Students analyze Department of Ecology data to determine relationships.
3. Prepare for TRM visit by testing various water samples using the YSI probe (Probe is obtained from NPS Ranger and Education Specialist Janice Elvidge. See lesson 12 for probe operating instructions.
4. Test dissolved oxygen from two sources. The first source is a clean bucket of water, which has been sitting at room temperature for 1 week. The second source could be a bucket with decomposing plant matter (leaves, algae etc.) This bucket would also be setup a week prior to the experiment. Is there a difference? Why?

Additional Resources: DO, Nitrogen & Phosphorus testing protocols on CD; BPA Kids in the Creek DO testing; GLOBE Nitrogen and DO protocols; and EPA Phosphorus Monitoring protocol.

DISCUSSION:

What can the general public do? What are citizen scientists? Who is monitoring and removing excess aquatic weeds? What can the government do?

WATER QUALITY: NUTRIENT LOADING & DISSOLVED OXYGEN

Name: _____Date: _____

Essential Questions:

How do excess nutrients affect dissolved oxygen levels & impact water quality?

Inquiry Questions:

How can dissolved oxygen data predict species survival in Lake Roosevelt and its tributaries?

Objective:

You will:

- Analyze Ecology dissolved oxygen data and predict the impact on aquatic species
- Understand natural and human factors that impact water dissolved oxygen

Think Time:

Things I already know about dissolved oxygen and some questions running around in my mind....

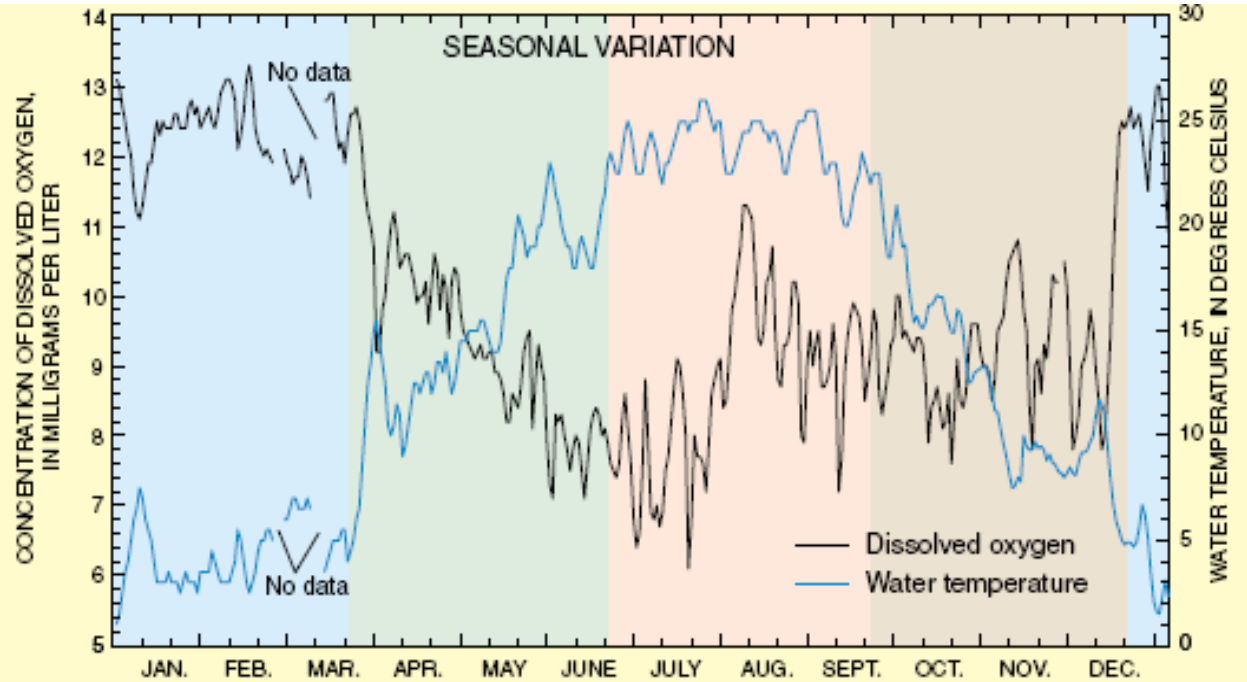
Notes: As you watch the power point presentation, identify key points about nutrients and dissolved oxygen.

Why is dissolved oxygen important?

How do phosphorus & nitrogen (nutrients) impact water quality & dissolved oxygen levels?

In what ways are aquatic organisms impacted by dissolved oxygen?

How do dissolved oxygen levels differ between various locations along the Columbia River and throughout Lake Roosevelt?



Credits: USGS *http://ga.water.usgs.gov/edu/dissolvedoxygen.html*

Describe the relationship between water temperature and dissolved oxygen.

Table 200 (1)(d) Aquatic Life Dissolved Oxygen Criteria in Fresh Water

Fish Category	Lowest 1-Day Minimum
Char Spawning and Rearing	9.5 mg/L
Core Summer Salmonid Habitat	9.5 mg/L
Salmonid Spawning, Rearing, and Migration	8.0 mg/L
Salmonid Rearing and Migration **Only**	6.5 mg/L
Non-anadromous Interior Redband Trout	8.0 mg/L
Indigenous Warm Water Species	6.5 mg/L

(d) Aquatic life dissolved oxygen (D.O.) criteria. The D.O. criteria are measured in milligrams per liter (mg/L). Table 200 (1)(d) lists the 1-day minimum D.O. for each of the aquatic life use categories. **Washington State Legislature** http://apps.leg.wa.gov/WAC/default.aspx?dispo=true&cite=173-201A-200

Use the data table **above** to identify locations **below** where the Dissolved Oxygen is below the minimum level for survival. Highlight each month and the locations with acceptable DO levels. In the last column **name the fish(es) that would not survive**.

date	GC O2 (mg/L)	HC O2 (mg/L)	KB O2 (mg/L)	NP O2 (mg/L)		Endangered Fish due to low oxygen levels
10/6/2008	7.9	10.1	10.5	9.3		
11/3/2008	8.8	10.8	10.4	9.9		
12/1/2008	9.69	11.9	13.2	10.9		
1/5/2009	11.4	11.9				
2/2/2009	12.76	12.46				
3/2/2009	13.36	11.55	13.86	13.46		
4/6/2009	13.1	10.19				
5/4/2009	12.7	10.04	11.3	11.65		
6/1/2009	11	9.5	11.7	11.9		
7/6/2009	10	9.3	9.19	9.8		
8/3/2009	8.3	9	8.4	8.8		
9/14/2009	7.8	9	9.4	8.6		

Reflections, thoughts, and new questions about the role of dissolved oxygen in water quality

Read the background information below and consider one thing our class, school or community could do to help maintain healthy dissolved oxygen levels for aquatic organisms?

One Idea I have for a community action project that would improve oxygen levels at our River Mile is...

Background Information:

http://scorecard.goodguide.com/env-releases/def/cwa_cause_class_def.html#diss_oxygn

Low Dissolved Oxygen / Organic Enrichment: Dissolved oxygen is a basic requirement for a healthy aquatic ecosystem. Most fish and beneficial aquatic insects "breathe" oxygen dissolved in the water column. Some fish and aquatic organisms (such as carp and sludge worms) are adapted to low oxygen conditions, but most desirable fish species (such as trout and salmon) suffer if dissolved oxygen concentrations fall below 3 to 4 mg/L (3 to 4 milligrams of oxygen dissolved in 1 liter of water, or 3 to 4 parts of oxygen per million parts of water). Larvae and juvenile fish are more sensitive and require even higher concentrations of dissolved oxygen. Many fish and other aquatic organisms can recover from short periods of low dissolved oxygen availability.

Prolonged episodes of depressed dissolved oxygen concentrations of 2 mg/L or less can result in "dead" waterbodies. Oxygen concentrations in the water column fluctuate under natural conditions, but severe depletion usually results from human activities that introduce large quantities of biodegradable organic materials into surface waters. In polluted waters, bacterial degradation of organic materials can result in a net decline in oxygen concentrations in the water. Oxygen depletion can also result from chemical reactions place a chemical oxygen demand on receiving waters. Other factors (such as temperature and salinity) influence the amount of oxygen dissolved in water. Prolonged hot weather will depress oxygen concentrations and may cause fish kills even in clean waters because warm water cannot hold as much oxygen as cold water.

Investigating Water Quality

How do excess nutrients affect dissolved oxygen levels & impact water quality?

Water Quality: Dissolved Oxygen

Below is what water looks like when the oxygen level is too low for the number of plants and animals using the aquatic habitat.

- **Dissolved oxygen** is molecular oxygen freely available in water and necessary for the respiration of aquatic life and the oxidation of organic material.

Water Quality: Nutrients and Nutrient loading

- **Nutrients** are elements or compounds essential to life, including but not limited to oxygen, carbon, nitrogen, and phosphorus.
- **Nutrient loading** is the addition of nutrients, usually nitrogen or phosphorus, to a water body (often expressed as g/m2 of lake surface area per year) . The majority of nutrient loading in a lake usually comes from its tributaries.

- **Nutrients** are supposed to be good but too much of anything is a problem especially when aquatic plants & microorganisms take over.
- **Sources** include agricultural runoff with nitrogen rich fertilizers, waste water treatment plants, septic systems, and detergents using phosphates.

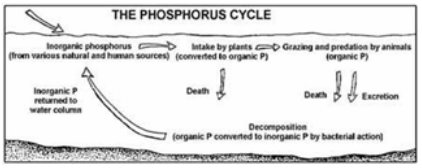
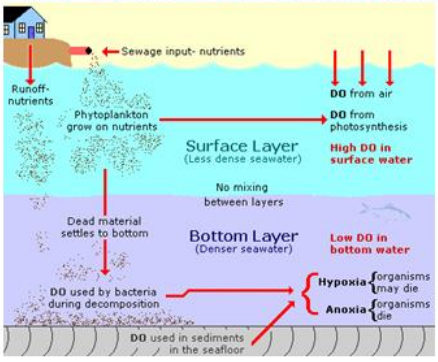


Fig 5.12 EPA

- Phosphorus cycles through the environment, changing form as it does so (Fig. 5.12). Aquatic plants take in dissolved inorganic phosphorus and convert it to organic phosphorus as it becomes part of their tissues. Animals get the organic phosphorus they need by eating either aquatic plants, other animals, or decomposing plant and animal material.
- As plants and animals excrete wastes or die, the organic phosphorus they contain sinks to the bottom, where bacterial decomposition converts it back to inorganic phosphorus

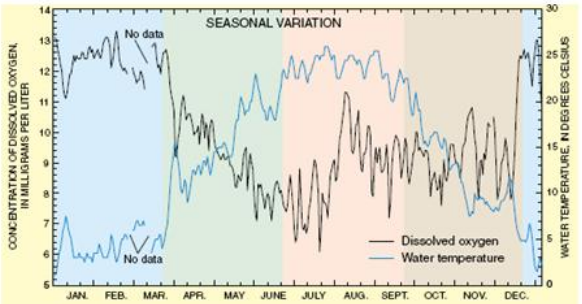
Environmental Protection Agency

http://omp.gso.uri.edu/ompweb/doee/science/physical/choxy2.htm



- Water becomes stratified
- The bottom layer becomes toxic
- Aquatic organisms compete for DO in warmer & vulnerable surface waters.

What is the relationship between water temperature and dissolved oxygen?



MEAN DAILY DISSOLVED-OXYGEN CONCENTRATION AND WATER TEMPERATURE, PASSAIC RIVER BELOW POMPTON RIVER AT TWO BRIDGES, N. J., JANUARY-DECEMBER 1998 http://ga.water.usgs.gov/edu/dissolvedoxygen.html

WA Department of Ecology

2008-2009 Water Quality Testing Data

Phosphorus, Nitrogen & Dissolved Oxygen

Columbia River @ Grand Coulee
Hawk Creek
Kettle River near Barstow
North Port

http://www.ecy.wa.gov/programs/eap/fw_riv/rv_main.html

61A070 - Columbia R @ Northport

LOCATED AT THE BRIDGE CROSSING THE COLUMBIA RIVER ON STATE HIGHWAY 25, IMMEDIATELY NORTHEAST OF NORTHPORT

Overall water quality at this station is of moderate concern. (based on water-year 2008 summary)

60A070 - Kettle R nr Barstow

LOCATED 10.9 MILES FROM THE MOUTH OF THE KETTLE RIVER, .75 MILES EAST OF BARSTOW ON THE FERRY-STEVENS COUNTY LINE

Overall water quality at this station is of moderate concern. (based on water-year 2008 summary)

53A070 - Columbia River @ Grand Coulee

LOCATED AT THE COULEE DAM BRIDGE .5 MILES BELOW GRAND COULEE DAM
Data years 1949 - 2010

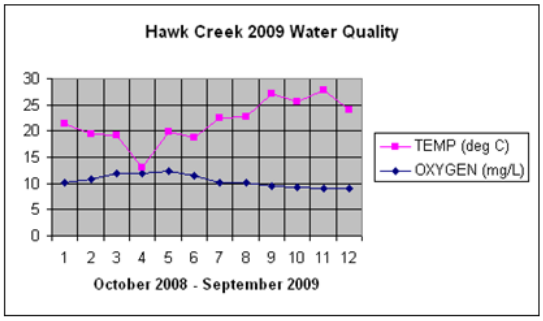
Overall water quality at this station met or exceeded expectations and is of lowest concern. (based on water-year 2009 summary)

53C070 - Hawk Creek @ Miles-Creston Rd.

Location: From Grand Coulee: Head southwest on Hwy 174 towards Wilbur. Turn left onto Hwy 2 heading towards Wilbur/Creston. After traveling past Creston ~6 miles, turn left onto Miles-Creston Rd. Follow until the road crosses Hawk Creek. Park on the near side of the bridge on the left hand side of the road.

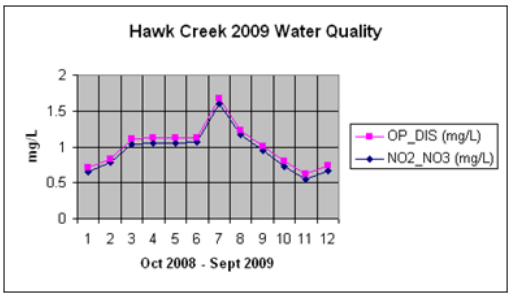
Overall water quality at this station did not meet expectations and is of highest concern. (based on water-year 2009 summary)

Hawk Creek 2008 -2009 WQ Data

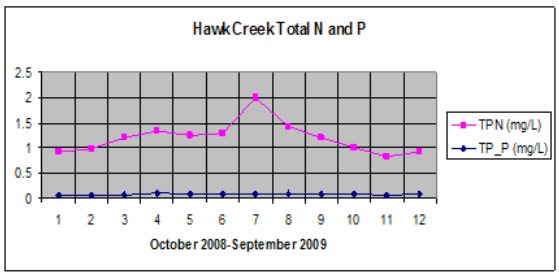


What does the data show about the relationship between temperature and oxygen?

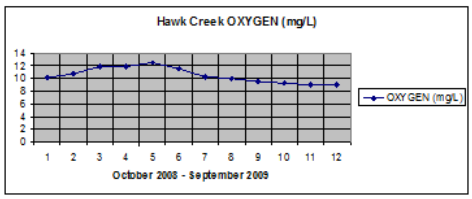
Hawk Creek 2008 -2009 WQ Data

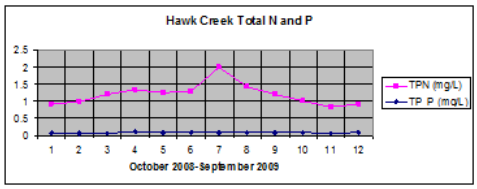


Hawk Creek 2008 -2009 WQ Data



Hawk Creek 2008 -2009 WQ Data





Compare the graphs for Oxygen and total nitrogen & phosphorus

Explain the data trends for columns 6-8

Feb - April

Hawk Creek 2008 -2009 WQ Data

date	OXYGEN (mg/L)	TP_P (mg/L)	TPN (mg/L)
10/6/2008	10.1	0.062	0.869
11/3/2008	10.8	0.068	0.908
12/1/2008	11.9	0.0723	1.13
1/5/2009	11.9	0.102	1.24
2/2/2009	12.46	0.0799	1.16
3/2/2009	11.55	0.0976	1.2
4/6/2009	10.19	0.0964	1.9
5/4/2009	10.04	0.0848	1.33
6/1/2009	9.5	0.0867	1.13
7/6/2009	9.3	0.0882	0.915
8/3/2009	9	0.0758	0.748
9/14/2009	9	0.0796	0.851

For which months is
- Total Phosphorus highest?
- Total Nitrogen highest?
- Oxygen Lowest?

- What is happening in June that explains the data trends?

Do the data show patterns or local circumstances?

- Analyze the WQ data for
  - Grand Coulee
  - Kettle River and
  - North Port
- Compare the three locations to Hawk Creek? Find any similarities & differences.

Nutrients: The addition of nutrients to surface waters has the effect of stimulating biological activity. While some fertilization may have positive effects (e.g. better fishing), too much leads to water quality problems. Nutrients fall into two categories, inorganic chemicals such as nitrogen and phosphorus which stimulate plant growth and organic matter which stimulates bacterial growth.

Inorganic Nutrients: The sun is the primary source of energy for all life on earth. The sun's energy is stored in the bonds of carbon-based chemicals (organic matter) produced by plants through the process of photosynthesis:

The energy is stored in chemical bonds of the organic matter, $C(H_20)$, and can later be released for use by microbes and higher plants and animals through the process of respiration.

Plants are called autotrophs (or self-feeders) because they produce their own organic matter. They also require inorganic nutrients such as nitrogen and phosphorus, the fertilizing chemicals that we apply to farm fields, gardens and lawns. There is often one special nutrient that is needed for growth--the limiting nutrient. In freshwater ponds, lakes and rivers, that nutrient is phosphorus.

Consider this animation: in order to build an 'item' (an algal cell or a higher aquatic plant), we might need 4 units of oxygen, 3 units of carbon and 2 units of phosphorus. The 'supplies' available in a lake are shown on the left. We can build 2 'items' from the 'supplies' and then we run out of phosphorus. Even though we have some carbon and oxygen left, growth stops because it is limited by the availability of phosphorus.

Eutrophication: When excessive phosphorus is added to lakes it stimulates the growth of algae and higher aquatic plants. This 'over-feeding' is called eutrophication and leads to water that can be 'pea soup green' with algae and overcrowded with macrophytes. These turbid, often foul smelling waters are unpleasant and even dangerous for swimming and other forms of recreation. The plants eventually settle to the bottom of the lake and decompose, consuming oxygen. The loss of oxygen can lead to fish kills.

Phosphorus: Sources and Control: Phosphorus is found in fertilizer and in animal (including human) wastes and is discharged to lakes and rivers from point (single origin such as a pipe) and nonpoint (diffuse origin such as a field) sources. In the Great Lakes region, we have reduced point sources by banning the use of phosphorus in laundry detergents and by limiting the amount of phosphorus which can be discharged by wastewater treatment plants. Nonpoint sources can be controlled by managing the way farmers apply manure and plow their fields to minimize phosphorus runoff to lakes

Phosphorus and Transparency:

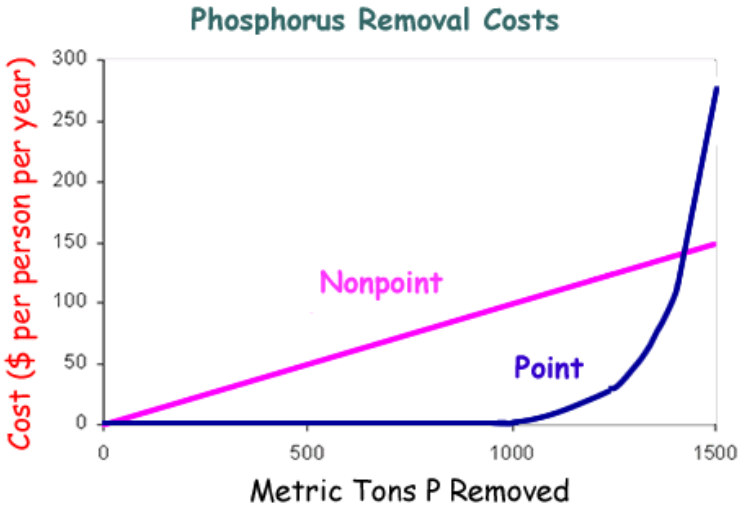
Water clarity or transparency is an important indicator of water quality in lakes. Clarity is measured using a Secchi disk, a white (or black and white) plate which is lowered into the water until it can no longer be seen: the deeper you can see it, the better the transparency. The Secchi disk depth can range from less than 1m in highly eutrophic lakes to more than 20m in Lake Superior.

The addition of excess phosphorus to lakes stimulates algal growth (eutrophication) and the water becomes green and turbid (low transparency, shallow Secchi disk depth). Transparency can be improved by reducing phosphorus inputs to the lake.

Reducing Phosphorus Inputs: Phosphorus management focuses on both point and nonpoint sources.

Phosphorus inputs from point sources such as wastewater treatment plants can be reduced by adding chemicals (e.g. iron chloride or aluminum sulfate). The cost to each person living in the watershed might range from < 1¢ to >45¢ per year for each metric ton of phosphorus removed. The cost varies because as phosphorus is removed it gets harder and harder to get the last little bit. This is shown in the cost curve at the right.

Phosphorus inputs from nonpoint sources such as agricultural land can be reduced by paying farmers to use manure management and conservation tillage methods. The cost to each person living in the watershed might be about 10¢ per year for each metric ton of phosphorus removed.

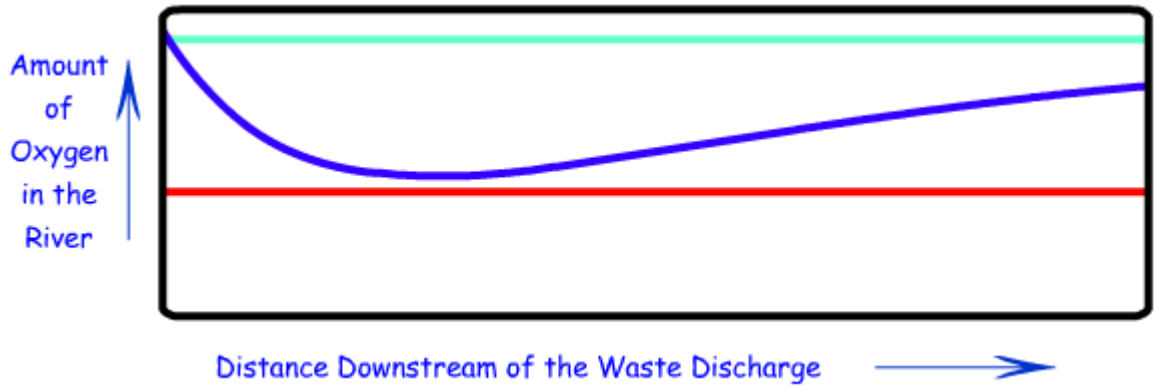


Oxygen Depletion: Microbes and higher plants and animals obtain the energy stored in the chemical bonds of organic matter, $C(H_2O)$, through the process of respiration:

$$C(H_2O) + O_2 \longrightarrow CO_2 + H_2O + \text{Energy}$$

Organisms that depend on others to produce that organic matter are called heterotrophs (or other-feeders). Examples of heterotrophs include bacteria, fungi and even people! We tap into the sun's energy when we eat organic matter (e.g. pizza) and breathe in oxygen and then breathe back out carbon dioxide and water vapor.

If there is too much organic matter in a lake or river, oxygen can be consumed by bacterial respiration faster than it is re-supplied from the atmosphere. This can lead to oxygen depletion and fish kills. In rivers, oxygen depletion takes a special form called the dissolved oxygen sag curve. The oxygen concentration in the river drops rapidly following the discharge of a waste containing organic matter. Later, as the organic matter becomes used up, the oxygen resources of the river are replenished.



Organic Matter: Sources and Control: Earlier, we learned that the addition of phosphorus to lakes stimulated the growth of algae and higher plants which settle to the bottom and use up oxygen when they are decomposed.

In rivers, the primary source of oxygen-consuming organic matter is the effluent from municipal and industrial wastewater treatment plants. The animation shows how the level of treatment influences the dissolved oxygen sag curve. You can estimate the level of wastewater treatment (percent organic matter removed) required to meet the oxygen standard (red line) which protects aquatic life. Note that less treatment is required in winter because bacteria respire more slowly when it is cold. Cost is always a consideration in pollution control. How do you think families would react to having to pay the cost of protecting the river?

USGS Water measurements: Temperature, pH, Specific conductance, Turbidity, Dissolved oxygen, Hardness, Suspended sediment, All water measurements

Water properties: Dissolved oxygen

The U.S. Geological Survey (USGS) has been measuring water for decades. Millions of measurements and analyses have been made. Some measurements, such as temperature, pH, and specific conductance are taken almost every time water is sampled and investigated, no matter where in the U.S. the water is being studied. Another common measurement often taken is dissolved oxygen (DO), which is a measure of how much oxygen is dissolved in the water - DO can tell us a lot about water quality.

Dissolved oxygen

You can't tell by looking at water that there is oxygen in it (unless you remember that chemical makeup of a water molecule is hydrogen and oxygen). But, if you look at a closed bottle of a soft drink, you don't see the carbon dioxide dissolved in that - until you shake it up and open the top. The oxygen dissolved in lakes, rivers, and oceans is crucial for the organisms and creatures living in it. As the amount of dissolved oxygen drops below normal levels in water bodies, the water quality is harmed and creatures begin to die off. Indeed, a water body can "die", a process called eutrophication.

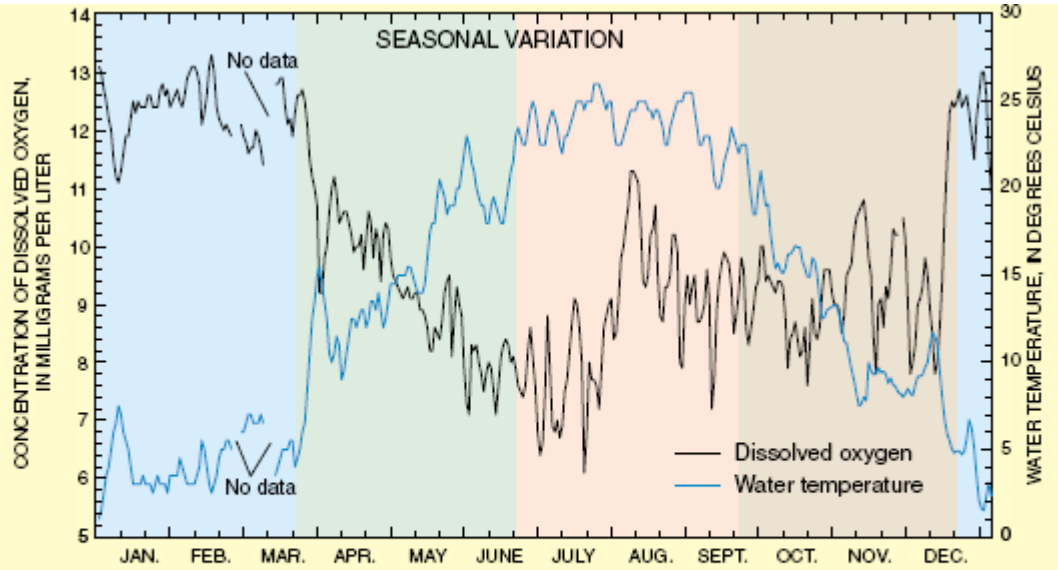
Although water molecules contain an oxygen atom, this oxygen is not what is needed by aquatic organisms living in natural waters. A small amount of oxygen, up to about ten molecules of oxygen per million of water, is actually dissolved in water. Oxygen enters a stream mainly from the atmosphere and, in areas where ground-water discharge into streams is a large portion of stream flow, from ground-water discharge. This dissolved oxygen is breathed by fish and zooplankton and is needed by them to survive.

Dissolved oxygen and water quality

Eutrophic conditions, Hartbees River, South Africa
Credit: National Eutrophication Monitoring Programme

Rapidly moving water, such as in a mountain stream or large river, tends to contain a lot of dissolved oxygen, whereas stagnant water contains less. Bacteria in water can consume oxygen as organic matter decays. Thus, excess organic material in lakes and rivers can cause eutrophic conditions, which is an oxygen-deficient situation that can cause a water body "to die." Aquatic life can have a hard time in stagnant water that has a lot of rotting, organic material in it, especially in summer (the concentration of dissolved oxygen is inversely related to water temperature), when dissolved-oxygen levels are at a seasonal low. Water near the surface of the lake (the epilimnion) is too warm for them, while water near the bottom (the hypolimnion) has too little oxygen. Conditions may become especially serious during a spate of hot, calm weather, resulting in the loss of many fish. You may have heard about summertime fish kills in local lakes that likely result from this problem. ((Source: A Citizen's Guide to Understanding and Monitoring Lakes and Streams)

Dissolved oxygen, temperature, and aquatic life



MEAN DAILY DISSOLVED-OXYGEN CONCENTRATION AND WATER TEMPERATURE, PASSAIC RIVER BELOW POMPTON RIVER AT TWO BRIDGES, N. J., JANUARY-DECEMBER 1998

As this chart shows, the concentration of dissolved oxygen in surface water is controlled by temperature and has both a seasonal and a daily cycle. Cold water can hold more dissolved oxygen than warm water. In winter and early spring, when the water temperature is low, the dissolved oxygen concentration is high. In summer and fall, when the water temperature is high, the dissolved-oxygen concentration is low.

Dissolved oxygen in surface water is used by all forms of aquatic life; therefore, this constituent typically is measured to assess the "health" of lakes and streams. Oxygen enters a stream from the atmosphere and from ground-water discharge. The contribution of oxygen from ground-water discharge is significant, however, only in areas where ground water is a large component of stream flow, such as in areas of glacial deposits. Photosynthesis is the primary process affecting the dissolved-oxygen/temperature relation; water clarity and strength and duration of sunlight, in turn, affect the rate of photosynthesis. Dissolved-oxygen concentrations fluctuate with water temperature seasonally as well as diurnally (daily).

Measuring dissolved oxygen

Field and lab meters to measure dissolved oxygen have been around for a long time. As this picture shows, modern meters are small and highly electronic. They still use a probe, which is located at the end of the cable. Dissolved oxygen is dependent on temperature (an inverse relation), so the meter must be calibrated properly before each use.

Sources and more information

- USGS field manual for dissolved oxygen

Do you want to test your local water quality?

Water test kits are available from World Water Monitoring Day (WWMD). Teachers and water-science enthusiasts: Do you want to be able to perform basic water-quality tests on local waters? WWMD offers inexpensive test kits so you can perform you own tests for temperature, pH, turbidity, and dissolved oxygen.

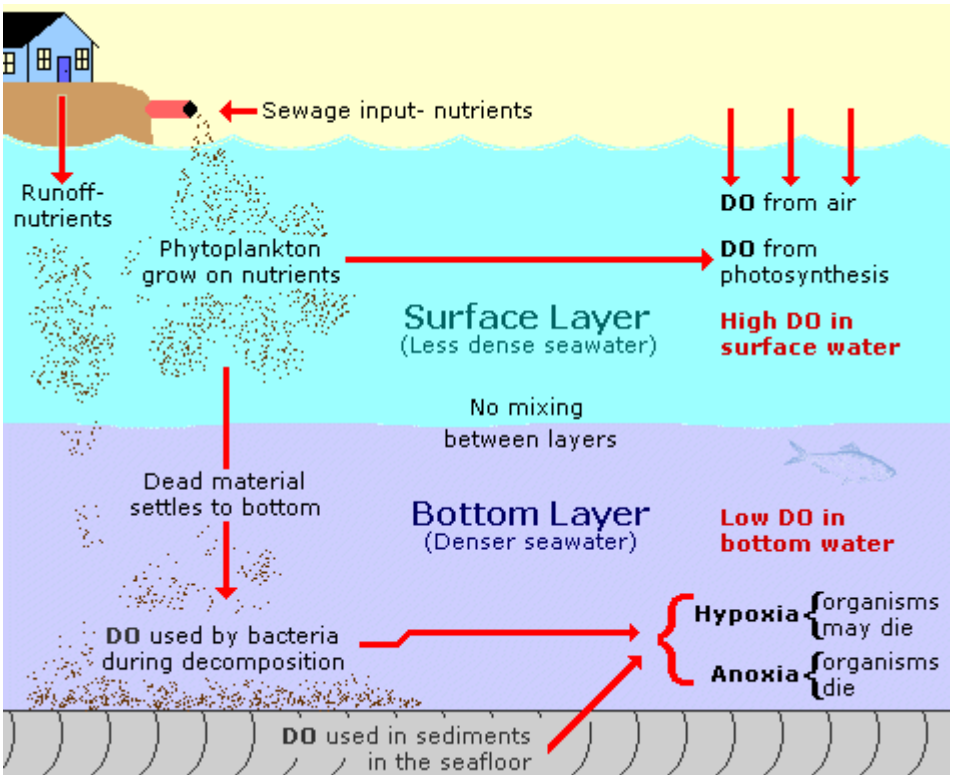
World Water Monitoring Day is an international education and outreach program that

What is dissolved oxygen?

Dissolved oxygen (DO) is the amount of oxygen (O2) dissolved in the water. Dissolved oxygen is one of the best indicators of water quality. People need oxygen in the atmosphere to survive and animals that live in the ocean, like fish, need dissolved oxygen in the water to survive.

The amount of dissolved oxygen that the water can hold depends on the temperature and salinity of the water. Cold water can hold more dissolved oxygen than warm water and fresh water can hold more dissolved oxygen than salt water. So the warmer and saltier the water, the less dissolved oxygen there can be. The maximum amount of dissolved oxygen that the water can hold is called the saturation value. Dissolved oxygen measurements are given as a percent of saturation (%) or in units of milligrams per liter (mg/l).

Oxygen enters the water at the surface of the water where exchange between the atmosphere and the water can take place. Waves and wind help put oxygen into the water. Dissolved oxygen is also put into the water as a byproduct of phytoplankton photosynthesis. The oxygen found in the deeper water comes from mixing with surface water. Photosynthesis can cause the water to have more dissolved oxygen than the saturation amount. When that happens it is called supersaturation.



Animals, such as fish, breathing in the water consume dissolved oxygen. It is also used in the break down of organic matter. As organic matter sinks to the sea floor it begins to decompose. Bacteria in the water use oxygen to break down this organic material.

When there is a lot of organic debris, the dissolved oxygen in the deeper water can be used up. If the water at the surface (which has plenty of dissolved oxygen) is not mixed with the deeper water layers form and the water becomes stratified. Then there is no new dissolved oxygen for the deep water. When this happens, the deep water can become unhealthy.

Above 5 mg/l dissolved O2, most marine plants and animals have plenty of oxygen. When the dissolved oxygen is low, below 3 mg/l, the water is called hypoxic. If all the dissolved oxygen is used up, below 0.5 mg/l, the water is called anoxic. Under hypoxic conditions, many marine plants and animals may not survive. No marine plants and animals that require oxygen can survive in anoxic conditions.

Approximate dissolved oxygen saturation values (At a salinity of 30ppt):

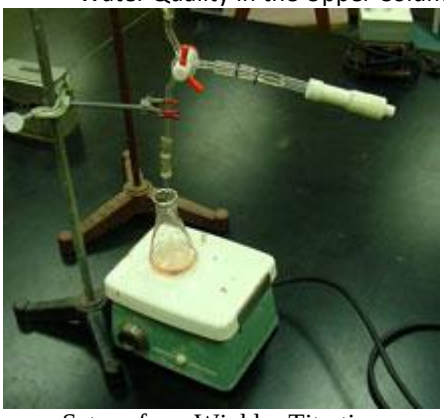
Temperature (°C)	Dissolved oxygen (mg/l)
30	6.4
25	7.0
20	7.6
15	8.4
10	9.3
5	10.5

1. What is dissolved oxygen?
2. How do we measure dissolved oxygen?
3. How much dissolved oxygen is in Narragansett Bay?
4. What can we learn about Narragansett Bay by measuring dissolved oxygen?

to Water Chemistry to Water Properties

How do we measure dissolved oxygen?

Dissolved oxygen is measured two different ways. The first method is the Winkler titration, a chemical measurement of dissolved oxygen. The Winkler titration has been used for a long time and can give very good results if done carefully. Field test kits are based on the Winkler titration.



Set-up for a Winkler Titration
(Click for larger image)

The second method is using an electronic oxygen meter. The oxygen meter is generally fairly expensive (several hundred dollars) and requires proper care and calibration. Oxygen meters give good results and are often the best option for looking through the water column and continuous measurements. Oxygen meters are commonly used on research buoys and oceanographic research vessels.

Sensors used on the RI/MA EMPACT Buoys. If you were looking straight at the end on the instrument, the probe in the 3 o'clock position with the brown end is an oxygen sensor.
(Click for larger image)

For further explanation of the Winkler titration see the web page:
<http://water.usgs.gov/owq/FieldManual/Chapter6/6.2.1.html#HDR6.2.1.CAL4>

For further explanation of how an oxygen meter works see this web site:
<http://www.vernier.com/probes/do.html>

5.6 Phosphorus

Why is phosphorus important?

Both phosphorus and nitrogen are essential nutrients for the plants and animals that make up the aquatic food web. Since phosphorus is the nutrient in short supply in most fresh waters, even a modest increase in phosphorus can, under the right conditions, set off a whole chain of undesirable events in a stream including accelerated plant growth, algae blooms, low dissolved oxygen, and the death of certain fish, invertebrates, and other aquatic animals.

There are many sources of phosphorus, both natural and human. These include soil and rocks, wastewater treatment plants, runoff from fertilized lawns and cropland, failing septic systems, runoff from animal manure storage areas, disturbed land areas, drained wetlands, water treatment, and commercial cleaning preparations.

Forms of phosphorus

Phosphorus has a complicated story. Pure, "elemental" phosphorus (P) is rare. In nature, phosphorus usually exists as part of a phosphate molecule (PO_4). Phosphorus in aquatic systems occurs as organic phosphate and inorganic phosphate. Organic phosphate consists of a phosphate molecule associated with a carbon-based molecule, as in plant or animal tissue. Phosphate that is not associated with organic material is inorganic. Inorganic phosphorus is the form required by plants. Animals can use either organic or inorganic phosphate.

Both organic and inorganic phosphorus can either be dissolved in the water or suspended (attached to particles in the water column).

The phosphorus cycle

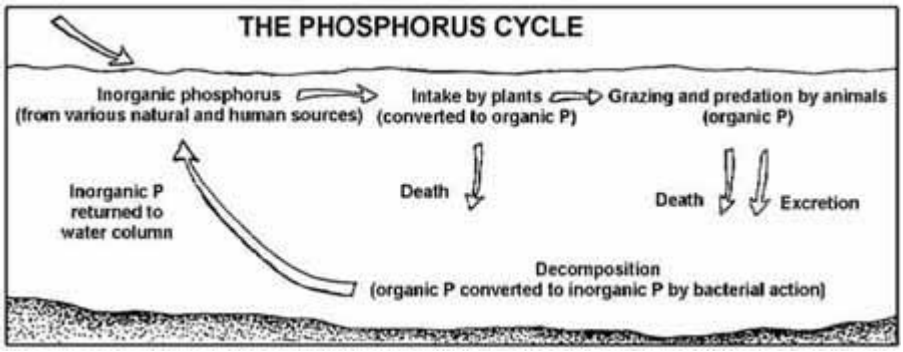


Figure 5.12

The phosphorus cycle
Phosphorus changes form as it cycles through the aquatic environment.

Phosphorus cycles through the environment, changing form as it does so (Fig. 5.12). Aquatic plants take in dissolved inorganic phosphorus and convert it to organic phosphorus as it becomes part of their tissues. Animals get the organic phosphorus they need by eating either aquatic plants, other animals, or decomposing plant and animal material.

As plants and animals excrete wastes or die, the organic phosphorus they contain sinks to the bottom, where bacterial decomposition converts it back to inorganic phosphorus, both dissolved and attached to particles. This inorganic phosphorus gets back into the water column when the bottom is stirred up by animals, human activity, chemical interactions, or water currents. Then it is taken up by plants and the cycle begins again.

In a stream system, the phosphorus cycle tends to move phosphorus downstream as the current carries decomposing plant and animal tissue and dissolved phosphorus. It becomes stationary only when it is taken up by plants or is bound to particles that settle to the bottom of pools.

In the field of water quality chemistry, phosphorus is described using several terms. Some of these terms are chemistry based (referring to chemically based compounds), and others are methods-based (they describe what is measured by a particular method).

The term "orthophosphate" is a chemistry-based term that refers to the phosphate molecule all by itself. "Reactive phosphorus" is a corresponding method-based term that describes what you are actually measuring when you perform the test for orthophosphate. Because the lab procedure isn't quite perfect, you get mostly orthophosphate but you also get a small fraction of some other forms.

More complex inorganic phosphate compounds are referred to as "condensed phosphates" or "polyphosphates." The method-based term for these forms is "acid hydrolyzable."

Monitoring phosphorus

Monitoring phosphorus is challenging because it involves measuring very low concentrations down to 0.01 milligram per liter (mg/L) or even lower. Even such very low concentrations of phosphorus can have a dramatic impact on streams. Less sensitive methods should be used only to identify serious problem areas.

While there are many tests for phosphorus, only four are likely to be performed by volunteer monitors.

1. The *total orthophosphate* test is largely a measure of orthophosphate. Because the sample is not filtered, the procedure measures both dissolved and suspended orthophosphate. The EPA-approved method for measuring total orthophosphate is known as the ascorbic acid method. Briefly, a reagent (either liquid or powder) containing ascorbic acid and ammonium molybdate reacts with orthophosphate in the sample to form a blue compound. The intensity of the blue color is directly proportional to the amount of orthophosphate in the water.
2. The *total phosphorus* test measures all the forms of phosphorus in the sample (orthophosphate, condensed phosphate, and organic phosphate). This is accomplished by first "digesting" (heating and acidifying) the sample to convert all the other forms to orthophosphate. Then the orthophosphate is measured by the ascorbic acid method. Because the sample is not filtered, the procedure measures both dissolved and suspended orthophosphate.
3. The *dissolved phosphorus* test measures that fraction of the total phosphorus which is in solution in the water (as opposed to being attached to suspended particles). It is determined by first filtering the sample, then analyzing the filtered sample for total phosphorus.
4. *Insoluble phosphorus* is calculated by subtracting the dissolved phosphorus result from the total phosphorus result.

All these tests have one thing in common they all depend on measuring orthophosphate. The total orthophosphate test measures the orthophosphate that is already present in the sample. The others measure that which is already present and that which is formed when the other forms of phosphorus are converted to orthophosphate by digestion.

Sampling and equipment considerations

Monitoring phosphorus involves two basic steps:

- Collecting a water sample
- Analyzing it in the field or lab for one of the types of phosphorus described above. This manual does not address laboratory methods. Refer to the references cited at the end of this section.

Sample Containers

Sample containers made of either some form of plastic or Pyrex glass are acceptable to EPA. Because phosphorus molecules have a tendency to "adsorb" (attach) to the inside surface of sample containers, if containers are to be reused they must be acid-washed to remove adsorbed phosphorus. Therefore, the container must be able to withstand repeated contact with hydrochloric acid. Plastic containers either high-density polyethylene or polypropylene might be preferable to glass from a practical standpoint because they will better withstand breakage. Some programs use disposable, sterile, plastic Whirl-pak® bags. The size of the container will depend on the sample amount needed for the phosphorus analysis method you choose and the amount needed for other analyses you intend to perform.

Dedicated Labware

All containers that will hold water samples or come into contact with reagents used in this test must be dedicated. That is, they should not be used for other tests. This is to eliminate the possibility that reagents containing phosphorus will contaminate the labware. All labware should be acid-washed. The only form of phosphorus this manual recommends for field analysis is total orthophosphate, which uses the ascorbic acid method on an untreated sample. Analysis of any of the other forms requires adding potentially hazardous reagents, heating the sample to boiling, and using too much time and too much equipment to be practical. In addition, analysis for other forms of phosphorus is prone to errors and inaccuracies in a field situation. Pretreatment and analysis for these other forms should be handled in a laboratory.

Ascorbic Acid Method

In the ascorbic acid method, a combined liquid or prepackaged powder reagent, consisting of sulfuric acid, potassium antimonyl tartrate, ammonium molybdate, and ascorbic acid (or comparable compounds), is added to either 50 or 25 mL of the water sample. This colors the sample blue in direct proportion to the amount of orthophosphate in the sample. Absorbance or transmittance is then measured after 10 minutes, but before 30 minutes, using a color comparator with a scale in milligrams per liter that increases with the increase in color hue, or an electronic meter that measures the amount of light absorbed or transmitted at a wavelength of 700 - 880 nanometers (again depending on manufacturer's directions).

A color comparator may be useful for identifying heavily polluted sites with high concentrations (greater than 0.1 mg/L). However, matching the color of a treated sample to a comparator can be very subjective, especially at low concentrations, and can lead to variable results.

A field spectrophotometer or colorimeter with a 2.5-cm light path and an infrared photocell (set for a wavelength of 700-880 nm) is recommended for accurate determination of low concentrations (between 0.2 and 0.02 mg/L). Use of a meter requires that you prepare and analyze known standard concentrations ahead of time in order to convert the absorbance readings of your stream sample to milligrams per liter, or that your meter reads directly as milligrams per liter.

How to prepare standard concentrations

Note that this step is best accomplished in the lab before leaving for sampling. Standards are prepared using a phosphate standard solution of 3 mg/L as phosphate (PO4). This is equivalent to a concentration of 1 mg/L as Phosphorus (P). All references to concentrations and results from this point on in this procedure will be expressed as mg/L as P, since this is the convention for reporting results.

Six standard concentrations will be prepared for every sampling date in the range of expected results. For most samples, the following six concentrations should be adequate:

0.00 mg/L	0.12 mg/L
0.04 mg/L	0.16 mg/L
0.08 mg/L	0.20 mg/L

Proceed as follows:

1. Set out six 25-mL volumetric flasks one for each standard. Label the flasks 0.00, 0.04, 0.08, 0.12, 0.16, and 0.20.
2. Pour about 30 mL of the phosphate standard solution into a 50 mL beaker.
3. Use 1-, 2-, 3-, 4-, and 5-mL Class A volumetric pipets to transfer corresponding volumes of phosphate standard solution to each 25-mL volumetric flask as follows:

Standard Concentration	mL of Phosphate Standard Solution
0.00	0
0.04	1
0.08	2
0.12	3
0.16	4
0.20	5

Note: The standard solution is calculated based on the equation: A = (B x C) ö D

Where:
A = mL of standard solution needed
B = desired concentration of standard
C = final volume (mL) of standard
D = concentration of standard solution
For example, to find out how much phosphate standard solution to use to make a 0.04-mg/L standard:

A = (0.04 x 25) ö 1 A = 1 mL

Before transferring the solution, clear each pipet by filling it once with the standard solution and blowing it out. Rinse each pipet with deionized water after use.

4. Fill the remainder of each 25 mL volumetric flask with distilled, deionized water to the 25 mL line. Swirl to mix.
5. Set out and label six 50-mL Erlenmeyer flasks: 0.00, 0.04, 0.08, 0.12, 0.16, and 0.20. Pour the standards from the volumetric flasks to the Erlenmeyer flasks.
6. List the standard concentrations (0.00, 0.04, 0.08, 0.12, 0.16, and 0.20) under "Bottle #" on the lab sheet.
7. Analyze each of these standard concentrations as described in the section below.

How to collect and analyze samples

The field procedures for collecting and analyzing samples for phosphorus consist of the following tasks:

TASK 1 Prepare the sample containers

If factory-sealed, disposable Whirl-pak® bags are used for sampling, no preparation is needed. Reused sample containers (and all glassware used in this procedure) must be cleaned (including acid rinse) before the first run and after each sampling run by following the procedure described in Method B on page 128. Remember to wear latex gloves.

TASK 2 Prepare before leaving for the sample site

Refer to section 2.3 - Safety Considerations for details on confirming sampling date and time, safety considerations, checking supplies, and checking weather and directions. In addition to sample containers and the standard sampling apparel, you will need the following equipment and supplies for total reactive phosphorus analysis:

- Color comparator or field spectrophotometer with sample tubes for reading the absorbance of the sample

- Prepackaged reagents (combined reagents) to turn the water blue
- Deionized or distilled water to rinse the sample tubes between uses
- Wash bottle to hold rinse water
- Mixing container with a mark at the recommended sample volume (usually 25 mL) to hold and mix the sample
- Clean, lint-free wipes to clean and dry the sample tubes

Note that prepackaged reagents are recommended for ease and safety.

TASK 3 Collect the sample

Refer to Task 2 in the Introduction to Chapter 5 for details on how to collect water samples using screw-cap bottles or Whirl-pak® bags.

TASK 4 Analyze the sample in the field (for total orthophosphate only) using the ascorbic acid method.

If using an electronic spectrophotometer or colorimeter:

1. "Zero" the meter (if you are using one) using a reagent blank (distilled water plus the reagent powder) and following the manufacturer's directions.
2. Pour the recommended sample volume (usually 25 mL) into a mixing container and add reagent powder pillows. Swirl to mix. Wait the recommended time (usually at least 10 minutes) before proceeding.
3. Pour the first field sample into the sample cell test tube. Wipe the tube with a lint-free cloth to be sure it is clean and free of smudges or water droplets. Insert the tube into the sample cell.
4. Record the bottle number on the field data sheet.
5. Place the cover over the sample cell. Read the absorbance or concentration of this sample and record it on the field data sheet.
6. Pour the sample back into its flask.
7. Rinse the sample cell test tube and mixing container three times with distilled, deionized water. Avoid touching the lower portion of the sample cell test tube. Wipe with a clean, lint-free wipe. Be sure that the lower part of the sample cell test tube is clean and free of smudges or water droplets.

Be sure to use the same sample cell test tube for each sample. If the test tube breaks, use a new one and repeat step 1 to "zero" the meter.

If using a color comparator:

1. Follow the manufacturer's directions. Be sure to pay attention to the direction of your light source when reading the color development. The light source should be in the same position relative to the color comparator for each sample. Otherwise, this is a source of significant error. As a quality check, have someone else read the comparator after you.
2. Record the concentration on the field data sheet.

TASK 5 Return the samples (for lab analysis for other tests) and the field data sheets to the lab/drop-off point.

Samples for different types of phosphorus must be analyzed within a certain time period. For some types of phosphorus, this is a matter of hours; for others, samples can be preserved and held for longer periods. Samples being tested for orthophosphate must be analyzed within 48 hours of collection. In any case, keep the samples on ice and take them to the lab or drop-off point as soon as possible.

TASK 6 Analyze the samples in the lab.

Lab methods for other tests are described in the references below (APHA. 1992; Hach Company, 1992; River Watch Network, 1992; USEPA, 1983).

TASK 7 Report the results and convert to milligrams per liter

First, absorbance values must be converted to milligrams per liter. This is done by constructing a "standard curve" using the absorbance results from your standard concentrations.

1. Make an absorbance versus concentration graph on graph paper:
    - Make the "y" (vertical) axis and label it "absorbance." Mark this axis in 0.05 increments from 0 as high as the graph paper will allow.
    - Make the "x" (horizontal) axis and label it "concentration: mg/L as P." Mark this axis with the concentration of the standards: 0, 0.04, 0.08, 0.12, 0.16, 0.20.
2. Plot the absorbance of the standard concentrations on the graph.
3. Draw a "best fit" straight line through these points. The line should touch (or almost touch) each of the points. If it doesn't, make up new standards and repeat the procedure.

Example: Suppose you measure the absorbance of the six standard concentrations as follows:

Concentration	Absorbance
0.00	0.000
0.04	0.039
0.08	0.078
0.12	0.105
0.16	0.155
0.20	0.192

The resulting standard curve is displayed in Fig. 5.13.

4. For each sample, locate the absorbance on the "y" axis, read horizontally over to the line, and then more down to read the concentration in mg/L as P.
5. Record the concentration on the lab sheet in the appropriate column. NOTE: The detection limit for this test is 0.01 mg/L. Report any results less than 0.01 as "<0.01." Round off all results to the nearest hundredth of a mg/L.

Results can either be reported "as P" or "as PO4." Remember that your results are reported as milligrams per liter weight per unit of volume. Since the PO4 molecule is three times as heavy as the P atom, results reported as PO4 are three times the concentration of those reported as P. For example, if you measure 0.06 mg/L as PO4, that's equivalent to 0.02 mg/L as P. To convert PO4 to P, divide by 3. To convert P to PO4, multiply by 3. To avoid this confusion, and since most state water quality standards are reported as P, this manual recommends that results always be reported as P.

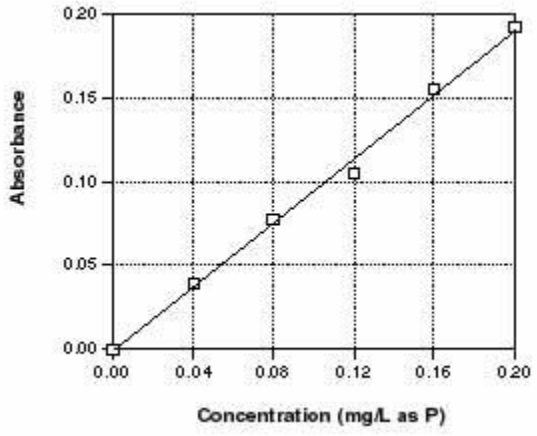


Figure 5.13

Absorbance of standard concentrations, when plotted, should result in a straight line

References

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Dissolved Oxygen

173-201A-200
Fresh water designated uses and criteria.

Statutory Authority: Chapters 90.48 and 90.54 RCW. 03-14-129 (Order 02-14), § 173-201A-200, filed 7/1/03, effective 8/1/03.

Table 200 (1)(d) Aquatic Life Dissolved Oxygen Criteria in Fresh Water

Category	Lowest 1-Day Minimum
Char Spawning and Rearing	9.5 mg/L
Core Summer Salmonid Habitat	9.5 mg/L
Salmonid Spawning, Rearing, and Migration	8.0 mg/L
Salmonid Rearing and Migration **Only**	6.5 mg/L
Non-anadromous Interior Redband Trout	8.0 mg/L
Indigenous Warm Water Species	6.5 mg/L

(d) Aquatic life dissolved oxygen (D.O.) criteria. The D.O. criteria are measured in milligrams per liter (mg/L). Table 200 (1)(d) lists the 1-day minimum D.O. for each of the aquatic life use categories.

i. When a waterbody's D.O. is lower than the criteria in Table 200 (1)(d) (or within 0.2 mg/L of the criteria) and that condition is due to natural conditions, then human actions considered cumulatively may not cause the D.O. of that water body to decrease more than 0.2 mg/L.

ii. For lakes, human actions considered cumulatively may not decrease the dissolved oxygen concentration more than 0.2 mg/L below natural conditions.

iii. Concentrations of D.O. are not to fall below the criteria in the table at a probability frequency of more than once every ten years on average.

iv. D.O. measurements should be taken to represent the dominant aquatic habitat of the monitoring site. This typically means samples should:

   A. Be taken from well mixed portions of rivers and streams.

   B. Not be taken from shallow stagnant backwater areas, within isolated thermal refuges, at the surface, or at the water's edge.

Dissolved Oxygen

Procedure

Read LaMotte Direct Reading Titrator Manual before proceeding. The Titrator is calibrated in parts per million (ppm) dissolved oxygen.

Steps 1 through 4 below describe proper sampling techniques in shallow water. For collection of samples at depths beyond arm's reach, special water sampling apparatus is required (e.g., the LaMotte Water Sampling Chamber, Code 1060; Model JT-1 Water Samplers, Code 1077; or Water Sampling Outfit, Code 3103).

1. To avoid contamination, thoroughly rinse the Water Sampling Bottle (0688-DO) with sample water.
2. Tightly cap the bottle and submerge to the desired depth. Remove cap to allow the bottle to fill.
3. Tap the sides of the submerged bottle to dislodge any air bubbles clinging to the inside. Replace the cap while the bottle is still submerged.
4. Retrieve the bottle and examine it carefully to make sure that no air bubbles are trapped inside. Once a satisfactory sample has been collected, proceed immediately with Steps 5 & 6 to "fix" the sample.
    - **NOTE:** Be careful not to introduce air into the sample while adding the reagents in Steps 5 & 6. Simply drop the reagents into the sample. Cap carefully and mix gently.
5. Add 8 drops of *Manganous Sulfate Solution (4167) and 8 drops of *Alkaline Potassium Iodide Azide (7166). Cap and mix by inverting several times. A precipitate will form. Allow the precipitate to settle below the shoulder of the bottle before proceeding.
6. Use the 1.0 g spoon (0697) to add one level measure of *Sulfamic Acid Powder (6286). Cap and gently shake until the reagent and the preciptate have dissolved. A clear-yellow to brown-orange color will develop, depending on the oxygen content of the sample.
    - **NOTE:** Following the completion of Step 6, contact between the water sample and the atmosphere will not affect the test results. Once the sample has been "fixed" in this manner, it is not necessary to perform the actual test procedure immediately. Thus, several samples can be collected and "fixed" in the field, and then carried back to a testing station or laboratory where the test procedure is to be performed.
7. Fill the titration tube (0299) to the 20 ml. line with the "fixed" sample and cap.
    - **NOTE:** If the color of the "fixed" sample is already a very faint yellow, skip to Step 9.
8. Fill the Direct Reading Titrator (0377) with *Sodium Thiosulfate, 0.025N (4169). Insert the Titrator into the center hold of the titration tube cap. While gently shaking the tube, slowly press the plunger to titrate until the yellow-brown color is reduced to a very faint yellow.

9. Remove the Titrator and cap. Be careful not to disturb the Titrator plunger, as the titration begun in Step 2 will be continued in Step 10. Add 8 drops of Starch Indicator Solution (4170WT). The sample should turn blue.

10. Replace the cap and Titrator. Continue titrating until the blue color just disappears. Read the test result where the plunger tip meets the scale. Record as ppm Dissolved Oxygen.

    - **NOTE:** Each minor division on the Titrator scale equals 0.2 ppm.

    - **NOTE:** If the plunger tip reaches the bottom line on the Titrator scale (10 ppm) before the endpoint color change occurs, refill the Titrator and continue the titration. When recording the test results, be sure to include the value of the original amount of reagent dispensed (10 ppm).

***WARNING:** Reagents marked with a * are considered hazardous substances. Material Safety Data Sheets (MSDS) are supplied for these reagents. For your safety, read the label and the accompanying MSDS before using.

11/95
