

Dissolved Oxygen (DO or Dissolved O₂)

Among the most important variables affecting stream health is the concentration of dissolved oxygen present in the water. It is essential to numerous life forms and is readily affected by many human activities. In this activity, students will measure the amount of dissolved oxygen in a water sample from the Huron River watershed.

Although the pre and post discussions are necessary to provide important information about each topic, it is the activity that is most vital to this unit. Be sure to allow plenty of time to complete the activity.

Pre-Activity Discussion (Answers can be found in the Background Information section below)

Before beginning the experiment ask the students:

- 1) What is dissolved oxygen and why is it important? How does it differ from the combined oxygen in H₂O?
- 2) What are some natural sources of dissolved oxygen in water?
- 3) What natural phenomena affect the level of dissolved oxygen in stream water?
- 4) What human activities affect the level of dissolved oxygen in stream water?

The Activity

Equipment

- Hach field test kit for dissolved oxygen: Azide-modified Winkler method
- Scissors to open powder pillows in Hach kit
- Small table
- Long-handled dipper (if you need to sample water from a steep bank)
- Display board
- Data sheets and clipboard
- Wastewater jug for disposal of spent solutions
- Safety glasses

The Process

You will be using a Hach portable field test kit for this measurement. The procedure is below and is easy to follow if you do each step carefully. The chemistry, however, is complicated.

In brief, you will be removing interfering NO₂ (nitrite ion) from the water sample with alkaline sodium azide. Manganous sulfate (MnSO₄) and potassium iodide (KI) are then added to the sample. A white precipitate of manganous hydroxide (MnOH₂) is formed which rapidly reacts with any dissolved oxygen present to form brown manganese dioxide (MnO₂). The solution is then made acid by adding sulfamic acid (H₃NSO₃). In this acidic solution the manganese dioxide reacts with iodide ion (from the potassium iodide added earlier) to form an amount of iodine (I₂) chemically equivalent to the amount of dissolved oxygen originally present in the sample. Lastly, the released I₂ is titrated using

a carefully measured amount of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution. This converts the brown I_2 to colorless I^- leaving a colorless solution. The amount of sodium thiosulfate needed to turn the water colorless is proportional to the concentration of dissolved oxygen in the original sample.

Toxicity and Disposal Information for Activity Leaders and Students

These chemicals are toxic (some quite toxic) and very irritating to the eyes. Wear safety goggles, avoid spills, DO NOT TASTE ANY OF THE CHEMICALS, and rinse your hands well with water after completing the activity. If you get any of these chemicals in an eye, wash the eye with clean water (such as drinking water) for 5 minutes and then seek medical attention at once. Dispose of liquid wastes from the activity in the jug provided for later disposal in a sink or toilet.

Set-up

Select a site with space for a small table and easy access to the stream. You will need to be upstream from activities that may cause a lot of turbidity (macroinvertebrate collection, stream speed). The water should be deep enough to allow you to hold the sample bottle 6-12 inches under the surface of the water while filling it.

Procedure (Technical information is in parentheses)

1. Fill the glass-stoppered bottle with sample, allowing the sample water to overflow for a minute and making sure there are no bubbles in the bottle. If possible, fill this bottle by holding it 6-12 inches below the surface of the water in the stream.
2. Tip the bottle slightly and stopper it WITHOUT trapping any air bubbles. The concentration of oxygen in air is roughly 30 times its concentration in water so a small air bubble can throw off your results, making them high.
3. Remove stopper and add the contents of a DO 1 reagent envelope. (This envelope contains sodium azide that will prevent nitrite interference, and sodium hydroxide to make the solution alkaline.) Also add a DO reagent 2 envelope. (This envelope contains manganous sulfate and potassium iodide.) Stopper the bottle carefully to avoid trapping any bubbles.
4. Invert the bottle several times to dissolve the powders. A precipitate (floc) will form. It will be brown if oxygen is present. (The floc is a mixture of white manganous hydroxide and dark brown manganese dioxide.) Let the floc settle to about half the bottle volume.
5. Invert the bottle once more to mix and again let the floc settle to about half the bottle volume. This gives time for the reaction between manganous hydroxide and dissolved oxygen to go to completion.
6. Remove the stopper and add the contents of one DO 3 reagent powder pillow. (This pillow contains sulfamic acid. It is much safer than sulfuric acid and just as effective). Invert the bottle several times to mix. The sample will turn clear yellow-brown if oxygen

was present.

7. Add one full measuring tube- the small round tube- of the sample to the square bottle.

8. Add sodium thiosulfate solution one drop at a time to the square bottle, swirling it after the addition of each drop and counting the number of drops added. Stop when the color of the solution changes from yellow to colorless. This is easiest to see if done on a white background. A piece of white paper is fine. (The thiosulfate reacts with the colored iodine to produce colorless iodide ion.)

9. The number of drops of thiosulfate solution added to the sample is equal to the DO concentration in the water in mg/L. (milligrams per liter)

10. Optional: If you wish, you can check your accuracy by discarding the solution in the square bottle, rinsing it, and then adding **two** full measuring tubes of sample from the glass-stoppered bottle to the square bottle. Then add sodium thiosulfate one drop at a time as in Step 8, swirling and counting drops as before until the solution becomes colorless. Here the DO concentration is **half** the number of drops added.

11. If time permits, rotate assignments among the students and make a second run, repeating Steps 1 through 9 above.

Examining the Results

Compare the results of the testing to the chart below.

Table 1: Minimum DO requirements for some aquatic organisms

<u>Organism</u>	<u>Minimum D.O. requirement (mg/L)</u>
Trout	6.5
Smallmouth bass	6.5
Caddisfly larvae	4.0
Mayfly larvae	4.0
Catfish	2.5
Carp	2.0
Mosquito larvae	1.0

Note: Fish requirements for DO depend on a number of factors, so the numbers in Table 1 are not precise, and other sources may give slightly different figures. Nevertheless Table 1 provides useful approximate information about the DO needs of aquatic life.

Post-activity discussion questions:

- 1) What do our results tell us about the stream water?
- 2) Are there any conditions nearby that might affect the amount of dissolved oxygen concentration in the portion of the stream being sampled?

- 3) The chart below shows how the ability of water to hold dissolved oxygen decreases as water temperature rises. What are some things that can cause water temperatures to rise? What can we do to prevent the warming of stream waters?
- 4) What other things can be done to protect against low levels of dissolved oxygen?

Table 2: Oxygen solubility in water at 1 atmosphere (760 mm Hg) pressure of air

<u>Temperature °C</u>	<u>Temperature °F</u>	<u>Oxygen solubility: mg/L</u>
10	50	11.28
20	68	9.09
30	86	7.56
40	104	6.41

Background Information

Dissolved oxygen is essential for fish, benthic macroinvertebrates and plants to live. When there is not enough oxygen, the food web for the whole ecosystem is affected. It must be remembered that the oxygen that hooks up with hydrogen to make water is not available for respiration. Although the concentration of oxygen in the air is quite high, O₂ is not very soluble in water. At a pressure of one atmosphere (atm) of air, the oxygen concentration in water at room temperature is about 8.2 mg/L or 8.2 parts per million (ppm) at saturation level.

Aquatic organisms do not get their oxygen through breathing. In fish, oxygen that is dissolved in water moves over gills, and is diffused into their bloodstreams. Other aquatic organisms also take dissolved oxygen directly into their bodies. Organisms need oxygen to use food energy to perform cell functions. When there is not enough oxygen for the cells to function, death occurs.

Levels of DO are affected by discharges from industrial facilities and water treatment plants. They are also affected by water released from dams. DO concentrations in Michigan waters are monitored by the Michigan Department of Natural Resources. Violations are investigated and corrective action is taken. According to the laws of the State of Michigan, the minimum permissible DO in most Michigan streams is 5.0 mg/L. This is enough to support most aquatic life (but not trout or small-mouth bass) however the margin is not large. Another reason that the DNR monitors DO levels is to determine where to stock fish and the kind of fish to stock.

Dissolved oxygen can enter stream or lake water in many ways. Below are some common sources.

- 1) Diffusion from the atmosphere
- 2) Aeration as water moves over rocks and debris, riffles, rapids, waterfalls, etc.
- 3) Aeration from wind and waves
- 4) Photosynthesis of aquatic plants

There are a number of factors that affect the DO concentration including:

1. Efficiency of re-aeration from the atmosphere: Oxygen is easily transported from air to water in shallow, turbulent streams. It is poorly transported in deep, slow-moving or stagnant streams.
2. Organic materials in water material such as food processing wastes, human and animal feces and urine, paper mill wastes, dead and decomposing algae and leaves, etc. can affect the levels of DO in water. These materials when present in water are referred to as Biochemical (or Biological) Oxygen Demand (BOD) and can be used as food by bacteria naturally present in surface waters. As the bacteria feed upon these materials, they use oxygen. They also multiply. If there is sufficient BOD present, its metabolism by the stream bacteria will use up all of the dissolved oxygen in the water. At this point fish and most benthic macroinvertebrates die of suffocation.
3. Temperature: The solubility of oxygen in water decreases with increasing temperature. In other words, colder water is capable of holding more dissolved oxygen than warmer water. For example, at 14°C the solubility of oxygen in pure water (no dissolved salts) is 10.30 mg/L, while at 30°C it is only 7.56 mg/L.

There are a number of human-caused conditions that can cause stream temperature to rise. Some strategies for remediation for each of these are listed.

- 1) Runoff: Impervious surfaces, cultivated fields and lawns cause water to run into lakes and streams quickly. When this happens, the water is much warmer than if it soaks into the ground and then slowly moves as groundwater to enter streams and lakes. Buffer zones, retention ponds, rain barrels and water gardens can be helpful. Greater use of permeable asphalt that allows water to penetrate through to the soil beneath would also reduce runoff.
- 2) Discharged water: Water that is discharged from industrial operations or water treatment plants is generally warmer than the bodies of water it is discharged into. Here, too, retention ponds for cooling could be helpful.
- 3) Health of Riparian Zones: Water that is shaded is cooler than water that is exposed to sunlight. When trees and shrubs that shade stream and rivers are removed, the increase in direct sunlight warms the water. Restoring streamside vegetation with a mix of trees, shrubs, grass and other plants will create more shade and also reduce erosion of stream banks.
- 4) Erosion: When soil enters the water through erosion, the increased concentration of

sediment (dirt in the water) increases turbidity. Water heats up more quickly when it has high turbidity. Good vegetation buffer zones to prevent soil from entering streams will improve stream health in many ways.

For this and all other units, advanced level information is available if desired. Contact the HRWC and request an electronic version of the unabridged manual.

Dissolved Oxygen (DO) Data Sheet

<p>First run: Drops of thiosulfate solution added to decolorize one measuring tube of sample:</p> <p>_____ DO concentration = _____ mg/L</p> <p>Drops of thiosulfate solution added to decolorize two measuring tubes of sample: (DO concentration = half # drops added)</p> <p>_____ DO concentration = _____ mg/L</p> <p>Second run: Drops of thiosulfate solution added to decolorize one measuring tube of sample:</p> <p>_____ DO concentration = _____ mg/L</p> <p>Drops of thiosulfate solution added to decolorize two measuring tubes of sample: (DO concentration = half # drops added)</p> <p>_____ DO concentration = _____ mg/L</p>	<p>Minimum DO requirements for some aquatic organisms</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 70%;">Trout</td> <td style="text-align: right;">6.5 mg/L</td> </tr> <tr> <td>Smallmouth bass</td> <td style="text-align: right;">6.5 mg/L</td> </tr> <tr> <td>Caddisfly larvae</td> <td style="text-align: right;">4.0 mg/L</td> </tr> <tr> <td>Mayfly larvae</td> <td style="text-align: right;">4.0 mg/L</td> </tr> <tr> <td>Catfish</td> <td style="text-align: right;">2.5 mg/L</td> </tr> <tr> <td>Carp</td> <td style="text-align: right;">2.0 mg/L</td> </tr> <tr> <td>Mosquito larvae</td> <td style="text-align: right;">1.0 mg/L</td> </tr> </table>	Trout	6.5 mg/L	Smallmouth bass	6.5 mg/L	Caddisfly larvae	4.0 mg/L	Mayfly larvae	4.0 mg/L	Catfish	2.5 mg/L	Carp	2.0 mg/L	Mosquito larvae	1.0 mg/L
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1. Does this water meet the Michigan state requirement of 5.0 mg/L as the minimum acceptable DO concentration?

2. Could trout and smallmouth bass live in this stream?

3. Name 3 factors that affect Dissolved Oxygen concentration.

4. What can people do to improve the DO concentration in our watershed?

5. KEY Dissolved Oxygen Student Page

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Answers will vary

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3. Name 3 factors that affect Dissolved Oxygen concentration

a. Efficiency of re-aeration from the atmosphere. Efficiency of oxygen transport from air to water is high in shallow, turbulent streams; it is poor in deep, slow-moving or stagnant streams.

b. Temperature. The solubility of oxygen in water decreases with increasing temperature. For example, at 14°C the solubility of oxygen in pure water (no dissolved salts) is 10.30 mg/L, while at 30°C it is only 7.56 mg/L.

c. Presence of Biochemical (Biological) Oxygen Demand, BOD. BOD consists of organic material (food processing wastes, human and animal feces and urine, paper mill wastes, dead and decomposing algae and leaves, etc.) that can be used as food by bacteria naturally present in surface waters. As the bacteria feed upon the BOD, they use oxygen. They also multiply. If there is sufficient BOD present, its metabolism by the stream bacteria will use up all of the dissolved oxygen in the water. At this point fish and most benthic macro-invertebrates die of suffocation.

4. What can people do to improve the DO concentration in our watershed?
 - a. **Help maintain natural streambanks by limiting erosion, leaving rocks in river bottoms. Remove un-needed dams.**
 - b. **Limit erosion, since sediments can increase stream temperatures.**
 - c. **Clean up after pets, limit discharge of biological wastes into streams.**