

## Water Quality Notes: Dissolved Oxygen<sup>1</sup>

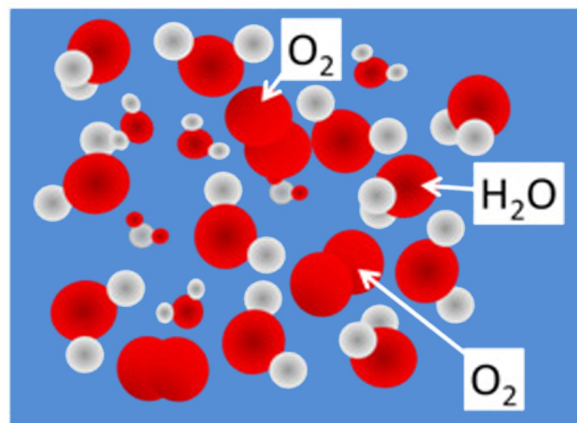
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### Objective

The objectives of this document are to provide readers with: 1) an overview of dissolved oxygen (DO) from a chemical, physical, and ecological perspective, 2) a summary of two of the most common analytical methods for measuring DO, and 3) the current state regulations for DO in public waters in Florida and 4) opportunities for managing dissolved oxygen in aquatic systems. A glossary is provided at the end of this document for terms that are in bold in the text.

### Description

Fish and other aerobic aquatic organisms require oxygen to live and reproduce. For those that cannot obtain oxygen directly from the atmosphere, the amount dissolved in the water is critical. On the molecular scale, DO molecules can be illustrated as fitting in the spaces between adjacent water molecules (Figure 1). Dissolved oxygen is typically measured and reported as concentrations using either mg-DO/L of water (mg/L) or percent saturation as the units.



**Figure 1.** Molecular view of dissolved oxygen occupying spaces between water molecules. Credit: Chris Wilson

## Factors Affecting Dissolved Oxygen Concentrations in Water

### *Abiotic Factors*

The amount of oxygen that can be dissolved in water depends on several factors, including: water temperature, the amount of dissolved salts present in the water (salinity), and atmospheric pressure (Tables 1 and 2). On a relative scale, the amount of oxygen dissolved in saturated water will be greater in cooler waters than in warmer ones. Higher water temperatures result in increased molecular vibrations,

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essentially reducing the amount of space available between water molecules. The capacity of water to hold DO also decreases as the salinity increases. This results from more effective competition of the salts for intermolecular spaces due to their ionic charges. Altitude also affects the amount of DO in water due to differing densities of O<sub>2</sub> available for dissolution. Since atmospheric O<sub>2</sub> is less dense at higher altitudes, saturation DO concentrations will be lower than in water at sea level where atmospheric O<sub>2</sub> is more dense.

Oxygen enters water bodies primarily by transfer from the atmosphere across the air-water interface and to a lesser extent by the action of photosynthetic organisms (See **Biotic Factors** for explanation). Transfer of oxygen across the air-water interface is facilitated by increasing the surface area exposed to the atmosphere. The surface area of a water body in contact with the atmosphere is increased by wind-driven waves and ripples, as well as by forcing water into droplets by splashing over obstacles or forcing through a fountain. Given that atmospheric transfer is the dominant mechanism for infusing O<sub>2</sub> into an aquatic system, the surface area to volume ratio is very important for establishing the baseline oxygen status for a given water body. Deep water bodies with relatively low surface area will have less opportunity for O<sub>2</sub> transfer into the water compared to shallow water bodies with a larger surface area exposed to the atmosphere.

**Table 1.** Influence of temperature and salinity on saturated dissolved oxygen concentrations (mg/L) in water. PPT = parts per thousand.

Temperature °C / °F	Salinity		
	0 PPT	18 PPT	36 PPT
10/50	11.3	10.7	9.5
15/59	10.1	9.3	8.3
20/68	9.1	8.2	7.6
25/77	8.3	7.5	6.7
30/86	7.6	6.9	6.2
35/95	7.0	6.3	5.7

**Table 2.** Influence of temperature and elevation on saturated dissolved oxygen concentrations in water.

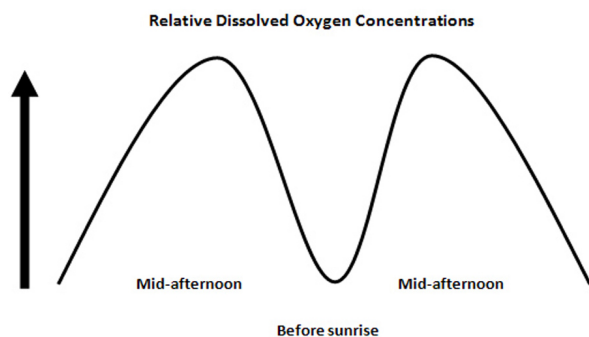
Temperature °C/°F	Elevation (Feet)		
	Sea	1000	5000
5/41	12.8	12.3	11.0
10/50	11.3	10.9	9.4
15/59	10.1	9.7	8.4
20/68	9.1	8.9	7.6
25/77	8.3	8.1	6.9
30/86	7.6	-	-

### **Biotic Factors**

Aquatic plants and algae also contribute dissolved oxygen to water bodies during daylight hours through **photosynthesis**. The very first step of photosynthesis splits two water molecules (H<sub>2</sub>O) into two hydrogen (H<sub>2</sub>) molecules and one oxygen (O<sub>2</sub>) molecule; where the O<sub>2</sub> is released into the water for underwater photosynthetic organisms. While this does represent O<sub>2</sub> input into the water, the net effect on DO concentrations is usually very small or neutral since comparable amounts of DO are consumed by these same organisms at night through **respiration**, when photosynthesis is not actively occurring. Aerobic respiration consumes oxygen to extract energy from energy-rich carbon compounds needed for sustaining life, ultimately oxidizing the carbon to carbon dioxide (CO<sub>2</sub>) and reducing the O<sub>2</sub> to H<sub>2</sub>O. Thus, dissolved oxygen concentrations will typically be highest in the mid- to late afternoon when photosynthesis rates are greatest, and will reach the lowest concentrations just before the sun rises the next morning due to respiration needs. This fluctuation pattern is referred to as the "diurnal oxygen cycle" (Figure 2).

In addition to the respiration needs of photosynthetic organisms during darkness, oxygen within the system is also consumed through aerobic respiration by other organisms including: aquatic **vertebrates** and **invertebrates**, and bacterial and fungal communities involved in degrading dead plants and animals. Biological Oxygen Demand (BOD) is a measure of the potential for DO within a water body to become depleted and possibly become anaerobic due to the biodegradation of organic matter by microbial organisms. BOD considerations are

especially important when management activities will increase the available carbon within a system, such as with aquatic weed management using aquatic herbicides. The plants killed will become a source of BOD within the system as they are degraded by microbial organisms. Another indirect source of BOD to a water body is nutrient runoff from surrounding land and drainage systems. Nutrient enrichment often results in increased algae production, or algae blooms. Once these algal populations die, BOD will increase significantly as microbes degrade them.



**Figure 2.** Dissolved oxygen concentrations are lowest just before the sun rises and highest when photosynthesis rates are the greatest (i.e. the sun is closest to the photosynthesizing organisms). Credit: Chris Wilson

### Consequences of Low DO Concentrations

DO requirements for maintenance of health and reproduction differ for different fish and invertebrate species. Prolonged exposure to low DO levels may not directly kill an organism, but may significantly increase its susceptibility to other environmental stresses and diseases. Most data related to low DO tolerance is available from the aquaculture industry; less data are available for natural systems. Exposure to less than 2 mg/L oxygen for one to four days may kill most of the biota in a system, leaving behind low-DO tolerant fish, air-breathing insects and anaerobic (not requiring oxygen) bacteria and fungi (microflora). Table 3 lists reported lethal minimum DO concentrations for several species common to the natural environment and the aquaculture industry. Generally, the lethal DO concentrations for fish are between 1 and 3 mg/L. At these levels, fish activity is minimal. For normal levels of activity, DO concentrations above 3 mg/L generally seem sufficient for many species.

**Table 3.** Minimum dissolved oxygen concentrations for sustaining life of several aquatic species. LC50 is the concentration at which 50% of the organisms die. Data adapted from Avault, Jr. 1996.

DO Concentration (mg/L)	Organism	Effect
1-1.1	Juvenile catfish	Death
1-2	Catfish	Reduced food intake
1.3-1.6	Rainbow trout (6-months old)	Death (LC50)
1.3-2.5	Rainbow trout (Yearlings)	Death (LC50)
< 3.0	Salmonids	Death
0.49-1.1	Red Swamp crawfish	Death (LC50)
< 0.7	Brown shrimp (sub-adults)	Death

### Adaptations to Low DO Conditions

The presence of aquatic organisms in a given water body may not be indicative of DO concentrations that are adequate for all aquatic life. Many aquatic organisms (vertebrates and invertebrates) require different amounts of DO for normal respiration. Survival of these organisms decreases when DO concentrations are depressed lower than organism-specific critical levels for extended periods of time. However, this generalization does not hold for all aquatic organisms. Some fish species such as gar and bowfin can live in low DO environments by breathing at the surface. Other species such as the mosquito fish have upward-pointing mouths that are well adapted to obtain oxygen from the air-water interface. In addition, many fish species can physiologically acclimate to low DO conditions by increasing the amount of water flowing over their gills, lowering metabolic oxygen demand, and by increasing hemoglobin (oxygen-carrying component of blood) and hematocrit levels. With the exception of increasing gill activity, these adaptations generally require long-term exposure to low, sublethal DO levels. Aside from the obvious presence of dead fish, one of the most common symptoms of low DO within a system before a fish kill occurs is the presence of fish gulping for air at the water surface.

Aquatic invertebrates also differ widely in where and how they obtain oxygen. **Table 4** lists several common orders of aquatic insects and their sources of oxygen and respiratory options. Some aquatic insects are capable of obtaining oxygen directly from the atmosphere or from plants. Dissolved oxygen concentrations in water are of little consequence to these organisms. Others have **cutaneous** respiratory systems, **gills**, or **hemoglobin** that transfers dissolved oxygen from the water column into their bodies for respiration. The amount of oxygen dissolved in the water is important for these species. In addition, these organisms vary in their abilities to adapt to- and in their tolerance of- low DO conditions. Many of the sediment dwelling chironomid larvae and polychaete/oligochaete worms are commonly found in areas with very low DO concentrations.

**Table 4.** Several common orders of aquatic insects and their modes of obtaining- and sources of- oxygen for respiration.

Order	Respiratory Option	Oxygen Source
Diptera Coleoptera Hemiptera	Atmospheric breathers. Spiacles in contact with the atmosphere continuously or periodically.	Atmosphere
Coleoptera Diptera	Plant breathers. Spiracles modified to pierce submerged portions of aerenchyma tissue in wetland plants.	Plants
Coleoptera Diptera Lepidoptera	Use air-storage organs. This is typically a gas bubble that is transported with the organism.	Atmosphere or dissolved
Coleoptera Diptera Ephemeroptera Odonata Plecoptera, Lepidoptera Megaloptera Neuroptera Tricoptera	Breathe through gills, physical structures that facilitate O <sub>2</sub> transfer from the water.	Dissolved oxygen

**Table 4.** Several common orders of aquatic insects and their modes of obtaining- and sources of- oxygen for respiration.

Order	Respiratory Option	Oxygen Source
Diptera Lepidoptera Plecoptera Tricoptera	Diffusion of O <sub>2</sub> through the cuticle. Because of respiration needs, only practical for organisms with a high surface area to volume ratio.	Dissolved
Hemiptera Diptera	Hemoglobin. Specialized form of hemoglobin that releases O <sub>2</sub> at low external O <sub>2</sub> pressures, such as found in low DO waters and mud.	Atmosphere or dissolved

### Measurement Timing and Methods

Dissolved oxygen measurements are especially useful when fish kills are first detected, or when fish are seen gulping for air at the water surface. Timely measurements of this type are often indispensable in determining the cause of death (i.e. lack of DO versus poisoning, etc.). In addition to helping define cause and effect associated with fish kills, monitoring of DO is often necessary for managing aquatic systems for their intended use. Dissolved oxygen concentrations taken at sporadic intervals of time are difficult to interpret due to the diurnal oxygen cycle. For this reason, a DO monitoring program should be tailored for individual needs. Since the lowest DO levels typically influence what species can live in a given waterbody, one might be interested in determining the lowest DO concentrations over a span of time by taking measurements before dawn every morning or over a series of mornings. Conversely, taking samples throughout the day will give an idea of the daily fluctuations in DO concentrations (minimum, maximum, mean, median), which are related to photosynthetic activity, respiration, and atmospheric transfer of oxygen. Measurements taken in the early afternoon will likely represent the highest achievable DO concentrations in

a given water body with regard to photosynthetic organisms.

Dissolved oxygen can be measured by two common techniques, each with advantages and disadvantages. The first method is called an iodometric method or Winkler titration and the second method uses a gas-permeable membrane electrode. These methods are discussed in the following sections.

### Iodometric Method

The description of this method was taken from *Standard Methods for Examination of Water and Wastewater* (APHA et. al, 1995). This reference should be consulted for more detailed information when needed. The iodometric method can be one of the most precise and reliable procedures for DO analysis. This is a **titration**-based method based on the reaction of DO with divalent manganese ( $Mn^{++}$ ) ions. Briefly, after adding a known amount of dissolved divalent manganese ions and iodide to a known volume of sample, the pH is increased by adding base and the bottle is then stoppered. An insoluble **precipitate** of manganous hydroxide forms. Dissolved oxygen present in the sample oxidizes an equivalent amount of the manganous hydroxide precipitate, forming chemically different hydroxides. The sample is next acidified, which causes the precipitate to dissolve, releasing the iodide originally consumed in the solution. The amount of iodine released is then measured by titration with a standard solution of thiosulfate ( $Na_2S_2O_3$ ) and a starch indicator. The solution is blue as long as  $I_2$  is present. When all of the  $I_2$  has been removed from solution by thiosulfate, the solution clears. The volume of thiosulfate used to clear the solution is then used to calculate the concentration of DO in the sample (1 mL of 0.025M  $Na_2S_2O_3$  = 1 mg-DO/L for a 200 mL sample). The DO concentration can also be determined directly using an absorption spectrophotometer.

### Advantages

1. Can be very accurate and precise.
2. Relatively inexpensive (only requiring titration burets, sample bottles, and chemicals)

3. Available in kits from several manufacturers.

### Disadvantages

1. Cannot monitor DO instantaneously or continuously.
2. More time consuming than membrane electrode methods.
3. Nitrite, iron (ferrous and ferric), suspended solids, and color in the sample can interfere with accurate measurement. Modifications to the method can be made to remove these interferences.

### Membrane Electrode Methods

The membrane electrode method uses a submersible, membrane-covered electrode that is attached to a meter that gives direct readings in mg/L (parts-per-million, PPM) or percent saturation. There are a variety of membrane electrodes that are commercially available and that provide an excellent method for DO measurement in highly polluted and/or highly colored waters, as well as in strong waste effluents. They are especially useful under conditions that are not favorable for use of the iodometric methods and for *in situ* measurements in the field. Two basic types of membrane electrodes exist, polarographic and galvanic. The following description is for the more common polarographic models.

The electrode itself is composed of a physically separated metal **anode** and **cathode** (Figure 3). An **electrolyte** solution provides connectivity between the two. A thin, oxygen-permeable membrane is stretched over the sensor isolating the anode, cathode, and electrolyte solution from the environment, while allowing oxygen to enter. This membrane is typically composed of polyethylene or fluorocarbon materials because of their relative ruggedness and permeability to molecular oxygen.

When this type of meter is switched ON, a background electrical current is established through the anode-electrolyte-cathode-meter circuit. Oxygen passes through the membrane at a rate proportional to its concentration in the water. Oxygen, which has passed through the membrane, reacts at the cathode

causing a change in the current flow in the anode-electrolyte-cathode-meter circuit when the meter is turned on. The probe current (reading) changes proportionally to the amount of  $O_2$  diffusing through the membrane and reacting at the cathode. The oxygen concentration inside the membrane can be assumed to be zero since it is readily consumed at the cathode.

### Advantages

1. Field portable.
2. Easy to calibrate and use.
3. Can instantaneously and continuously monitor DO concentrations.
4. Do not need sampling equipment, bottles, or storage facilities.

### Disadvantages

1. Difficulties associated with instrument calibration and maintenance.
2. Relatively expensive. Typical DO meters range in cost from \$600 to \$1,500.
3. Hydrogen sulfide gases tend to reduce the sensitivity of membrane electrodes. Frequent use in environments where these gases are common will require more frequent cleaning of electrodes and replacement of membranes.

## State Surface Water Quality Criteria

It is important to recognize that the most desirable DO concentrations for one water body may not be the same as for others. The desired concentration range ultimately depends on the desired use for the water body. The lowest desired concentration should support desirable species at the lowest point of the diurnal DO profile (just before dawn).

The Florida Department of Environmental Protection (FDEP) is charged with protecting water quality within State-owned surface water bodies for their respective designated uses. To accomplish this



**Figure 3.** Typical membrane electrode used for measuring dissolved oxygen. A gas-permeable membrane covers the gold cathode and anode. The electrode is attached to an electronic meter that gives direct readings in mg/L or percent saturation.

goal, FDEP defined criteria for DO concentrations in State surface water bodies. Table 5 lists the designated uses for each surface water classification group. Water quality restrictions are greater for numerically lower classes of water (i.e. I > II > III > IV > V). Water flowing from a numerically higher class of water (for example class IV) into a more restrictive class (i.e. numerically lower class) may be required to meet standards for the lower class. A listing of the FDEP guidelines for surface water DO concentrations is also shown in Table 5.

## Dissolved Oxygen Management Opportunities

1. When designing and constructing ponds, maximize the surface area exposed to the atmosphere and limit the depth to facilitate atmospheric transfer and to encourage natural mixing by wind and wave action.
2. While not as environmentally sustainable as natural atmospheric transfer, blowers and fountains can be used to increase DO levels.
3. Minimize input of additional Biological Oxygen Demand into aquatic systems. Always follow the instructions on the herbicide label when controlling weeds within an aquatic system. If allowed, consider treating large water bodies in sections over time to prevent the entire water body from becoming anaerobic when the plant material begins to degrade by microbial action.

4. Minimize nutrient inputs into the aquatic systems from surrounding land and drainage systems to reduce risks of stimulating algal blooms. Limitation of all nutrients may not be necessary since algal blooms are often limited by a single nutrient (typically nitrogen or phosphorus). Determine the limiting nutrient and target best management practices that minimize export of that nutrient into the aquatic system.

## References for More Information

American Public Health Association (APHA), American Water Works Association (AWWA), and the Water Environment Federation (WEF). Standard Methods for Examination of Water and Wastewater. United Book Press, Inc. Baltimore, MD.

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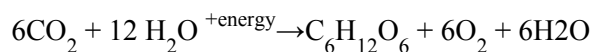
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## Glossary

**Photosynthesis** - The assimilation of carbon dioxide by green plants and by pigmented, photosynthetically active prokaryotes, and its conversion into carbohydrate, using energy from the sun. This conversion can be described by the following equation:



**Respiration** – Metabolic process in which stored energy is released with the oxidation of reduced organic carbon compounds. The ultimate by-products of respiration are often carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O).

**Vertebrate** - Organism possessing a distinct cartilaginous or bony axial endoskeleton, consisting of a skull and vertebral column.

**Invertebrate** - Animals not possessing a distinct cartilaginous or bony axial endoskeleton.

**Titration** – Procedure used to quantitatively analyze the amount of a substance by means of an essentially complete reaction in a solution with a reagent of known concentration (Kotz and Purcell, 1987).

**Anode** – Within the context of oxidation-reduction reactions, electrons are produced at the anode (- terminal) where oxidation occurs.

**Cathode** - Within the context of oxidation-reduction reactions, electrons produced at the anode move toward the cathode (+ terminal) where reduction occurs.

**Electrolyte** – A substance that dissolves in water to form an electrically conducting solution (Kotz and Purcell, 1987).

**Precipitate** – An insoluble salt (Kotz and Purcell, 1987).

**Cutaneous** – of, pertaining to, or affecting the skin.

**Gills** – Respiratory organs present in many aquatic animals. Gills are the structures used to transfer dissolved oxygen from the water into the organism for aerobic metabolism.

**Hemoglobin** – Component of blood responsible for transport of O<sub>2</sub> from respiratory gas exchange organs to respiring cells and transport of CO<sub>2</sub> from respiring cells to gas exchange organs.

**Table 5.** Designated water-use groups and dissolved oxygen (DO) criteria for surface waters of the state of Florida. Source: Florida Department of Environmental Protection; <http://www.dep.state.fl.us/water/wqssp/classes.htm#criteria> and <http://www.dep.state.fl.us/legal/Rules/shared/62-302/302-Table.doc>.

Surface Water Classification	Designated Use(s)	State Criteria for Dissolved Oxygen	Biochemical Oxygen Demand
I	Potable water supply. Rivers, lakes, etc. used as a drinking water supply.	Shall not be less than 5 mg/L. Normal daily and seasonal fluctuations above this level shall be maintained.	Shall not be increased to exceed values which would cause dissolved oxygen to be depressed below the limit established for each class and, in no case, shall it be great enough to produced nuisance conditions.
II	Shellfish propagation or harvesting. Coastal areas where shellfish harvesting occurs.	Shall not average less than 5 mg/L in a 24-hour period and shall never be less than 4 mg/L. Normal daily and seasonal fluctuations above this level shall be maintained.	
III: Fresh	Recreation, propagation and maintenance of a healthy, well-balanced population of fish and wildlife in predominantly fresh waters. Most surface waters of the State are Class III, unless otherwise designated.	Shall not be less than 5 mg/L. Normal daily and seasonal fluctuations above this level shall be maintained.	
III: Marine	Recreation, propagation and maintenance of a healthy, well-balanced population of fish and wildlife in predominantly marine waters.	Shall not average less than 5 mg/L in a 24-hour period and shall never be less than 4 mg/L. Normal daily and seasonal fluctuations above this level shall be maintained.	
IV	Agricultural water supplies. Primarily agricultural areas located around Lake Okeechobee.	Shall not average less than 4 mg/L in a 24-hour period and shall never be less than 3 mg/L.	
V	Navigation, utility, and industrial use. No Class IV waters currently in FL.	Shall not be less than 0.3 mg/L, 50% of the time on an annual basis for flows greater than or equal to 250 cubic feet per second and shall never be less than 0.1 mg/L. Normal daily and seasonal fluctuations above this level shall be maintained.	