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Dissolved Oxygen and The Three S's

Sources, Sinks, and Solubility

Some DO Chemistry

"Dissolved oxygen", abbreviated as "DO", is simply oxygen gas dissolved in water. Note that this refers to the free oxygen **molecule** (O_2), rather than the oxygen **atom** bound to hydrogen in a water molecule (H_2O). An easy way to distinguish them is to recall that a fish "breathes" by swimming and passing water over its gills, extracting free oxygen gas **molecules** for absorption into its blood. If a fish instead wished to pry oxygen **atoms** from water molecules, it would require something a bit more elaborate (like Fermi Lab).

Therefore, we are interested in the concentration of oxygen **molecules** in river water, and that is what we will be measuring with the Hach kit. There is no need for us to measure the concentration of oxygen **atoms** in water - we already know it! Since the chemical formula for water is H_2O, the concentration of oxygen atoms in (pure) water is always 33% (i.e. one O atom for every two H atoms).

One way to visualize dissolved oxygen is to picture the bubbles in soda pop, beer, or champagne. The only difference is that these liquids contain super-high concentrations of dissolved carbon dioxide gas, rather than oxygen gas (which explains why they are called "carbonated", not "oxygenated").

Dissolved oxygen may be thought of as "free oxygen", because the gas is not chemically bound to the water. It freely moves into and out of the water ("diffusion"), maintaining a constant concentration. The concentration at any given moment depends on three factors:

1. Oxygen Sources - the external & internal sources which deliver oxygen to the water
2. Oxygen Sinks - the water's inhabitants which consume the oxygen
3. Oxygen Solubility - the extent to which oxygen is able to dissolve in the water

Mathematically, this could be roughly expressed as:

$$DO = (O_{sources} \times solubility) - O_{sinks}$$

While systems in nature appear simple on the surface, we know they are quite complicated when examined closely. Dissolved oxygen is no exception, and the three factors which govern its concentration in a pond or river will now be presented in detail.

The Three S's of Dissolved Oxygen: Sources, Sinks, and Solubility

Oxygen Sources

A body of water has two sources of oxygen: an external source (the atmosphere) and an internal source (photosynthesis).

Atmosphere

Water can absorb different types of gasses, each to a different extent. "Air" is simply a mixture of many different gasses, so when water absorbs air from the atmosphere, it absorbs many different gasses. We are only concerned with oxygen, because it is crucial for aquatic health.

Water's surface area influences the amount of air it can absorb, so, increasing its surface area increases the amount of air it can absorb. Thus, a larger surface area enhances water's ability to "breathe". How can the surface area of water be enlarged? Through agitation.

Agitating water increases its exposed surface area, allowing it to "inhale" more oxygen. In this way, agitation increases the concentration of dissolved oxygen in water. Examples of agitation in nature are waterfalls, currents, and waves, whereas manmade examples are fountains in retention ponds and aerators in fish aquariums. Without agitation, still water in a fish tank or pond will turn stagnant from oxygen depletion and become unhealthy for its inhabitants.

Note that agitation passively enables water to increase its absorption - it does not force additional air into the water like a compressor. Thus, regardless of whether agitation is present or not, atmospheric oxygen enters water through the process of diffusion, and at that point, becomes dissolved oxygen.

A Word on Diffusion and Equilibrium

Oxygen diffuses from the atmosphere through the water's surface, until the water is able to absorb no more oxygen. At this point, the water and surrounding air are said to be in "equilibrium" (balance), and the concentration of DO stabilizes. (However, the system is not "frozen" - new oxygen is continually exchanged between the air and water's surface. But, the overall amount of DO does not change, because the amount of O_2 diffusion from water to air equals that from air to water.) This theory is so solid, you can actually calculate the amount of DO in a liquid for a given O_2 concentration, barometric pressure, and temperature. More on this shortly.

On the other hand, if you change any of the three factors, the fine balance (equilibrium) between air and liquid will be upset, and they will begin to adjust themselves to the new conditions. In the process of doing so, the liquid will slowly move back into equilibrium with the air (via diffusion), resulting in a new level of DO.

Note that a system in equilibrium will tend to stay that way (i.e. at rest). Thus, if additional oxygen is somehow forced into the liquid, the excess will simply bubble off, and the system will return to equilibrium.

Diffusion and equilibrium are not limited to water absorbing air - air also absorbs water (although this is normally referred to as evaporation, rather than diffusion), and does so until it can absorb no more.

In nature, these changes occur very slowly, so our DO analysis assumes the air and water are in equilibrium.

Photosynthesis

Water also absorbs oxygen from the algae (and to a lesser extent, plants) within it. Through the action of photosynthesis, they release pure O_2 directly into the water during daylight hours.

In fact, of the two oxygen sources, photosynthesis has a greater effect on DO than does atmospheric diffusion, because the oxygen produced by algae (and aquatic plants) is 100% O_2, whereas the air absorbed from the atmosphere contains only 20% O_2. And, even though algae are microscopic single-celled organisms, don't assume their influence is insignificant - in a pond, they comprise the single largest biomass.

Oxygen Sinks

Regardless of where it came from, dissolved oxygen in the water is steadily consumed by aquatic respiration - the "breathing" of all living organisms in the water - fish, plants, algae, bacteria, and other microorganisms, collectively known as "O_2 sinks".

Like mammals, they breathe, inhaling oxygen and exhaling carbon dioxide, twenty four hours a day. In most bodies of water, then, the level of dissolved oxygen increases during the day (as algal photosynthesis outpaces fish respiration) and then decreases at night as photosynthesis falls off but organisms continue to breathe. This variation is known as a "diurnal cycle" and is illustrated in Appendix A.

Like animals, algae respirate by absorbing oxygen and expelling carbon dioxide; like plants, they photosynthetically release oxygen by day. Thus, algae are both a source and sink, and thus affect dissolved oxygen and its measurement in two ways:

- Algae account for the diurnal cycles of dissolved oxygen concentration, which will vary by as much as 50% over the course of a day, although the actual amount of fluctuation depends on the body of water. See Appendix A for an example of typical 24-hour variation.

- Although algae produce oxygen via photosynthesis, they also consume it while "breathing". If the algae population becomes excessive (called a bloom), they will consume more than their share of oxygen, suffocating other organisms, such as fish (this explains why stagnant ponds, streams, and even some ocean bays, have low or no fish populations). Such oxygen depletion is known as *eutrophication,* and is normally triggered by the accumulation of manmade nutrients: phosphorus and nitrogen are broad fertilizers, and just as they will accelerate crop and lawn growth, so too will they accelerate algae growth when washed into a watershed.

In a healthy body of water, organisms exist in harmony, and the oxygen consumed by its sinks is replenished by its sources. Low DO levels indicate that demand has outstripped supply, suggesting that some external influence has pushed the system out of balance. This explains why DO is a useful gauge for determining aquatic health.

Oxygen Solubility

"Solubility" describes a liquid's propensity for absorbing gasses. Thought of in a different way, it is a measure of the ease with which gas can dissolve in a liquid - and remain dissolved. Three factors affect solubility, and unlike the first two S's, none are influenced by the water's inhabitants:

1. **Pressure.** Gas solubility increases with pressure. This means water at low elevations holds more O_2 than at high elevations, because the greater barometric pressure at low elevations exerts a force on the water's surface which prevents more of the dissolved gasses from escaping. (We all know that soda pop must remain pressurized and tightly capped, or the carbonization will slowly bubble out and you'll be left with flat Pepsi!)
2. **Salinity.** Gas solubility increases as salinity decreases. This means freshwater holds more O_2 than saltwater.
3. **Temperature.** Gas solubility increases as temperature decreases. This means cold water holds more O_2 than warm water; to illustrate, think of two extreme cases: ice cubes trap so much oxygen you can see it (in its frosty interior and bubbles), whereas boiling water violently sheds its gas bubbles. (And again, we all know that cold soda pop loses some of its fizz after it warms up.)

Since the first two are fixed in a geographic area, the only factor which varies is temperature. Thus, the only influence on gas solubility with which we are concerned is **temperature**[1]**.**

1. In sufficiently high concentrations, certain pollutants can also affect solubility, but our rivers are relatively clean in this respect, and so, we disregard their contribution. Salinity, too, is disregarded here, as it achieves prominence only sporadically, and is monitored in a separate test battery.

To summarize the three S's of dissolved oxygen:

- the sinks consume DO, the sources replenish it, and solubility determines the amount of it that doesn't bubble off
- DO in lakes and streams is influenced by surface area (including agitation), algae, water temperature, and time of day
- the three S's are also responsible for the variation of DO with depth. DO measurements taken near the surface will be different from those taken 3 feet below, which in turn, will be different from those taken 8 feet below. This is called *stratification.*

Measuring DO

Why measure DO?

Dissolved oxygen is essential to life in an aquatic system. As such, it provides an indication of the overall health of a water body, in the same way that a child's temperature provides an indication of his/her overall health. In fact, much of the information on DO you will encounter on the Internet will be on fishery websites, because their business hinges on healthy water.

Measuring DO

Because DO is highly influenced by agitation and temperature, testing is performed in the field immediately after the water sample is retrieved from the river, to achieve accurate results. For reasons already mentioned, the sample must be retrieved from the same location and the same depth, at the same time of day, as the previous test sample. Also, the water temperature must be recorded.

Units of Measurement

Dissolved Oxygen concentration is specified in one of three ways. The first two specify absolute quantity and are identical, while the third specifies a relative value.

mg/L

This is the same unit used in our tests for Nitrate, Chloride, etc., except that here it refers to **mg O_2/L H_2O**. This difference is important because, unlike those other tests, mg/L here represents milligrams of **gas** per liter of H_2O. For example, a DO measurement of 9 mg/L means "9 milligrams of O_2 per liter of H_2O". This is larger than it seems, as gas comprises a much larger volume than an equivalent weight of solid. For example, two grams of a solid might be the size of a marble, whereas two grams of oxygen is (approximately) the size of a 2 liter bottle of soda pop!

PPM ("parts per million")

Just as the name says, PPM specifies the number of O_2 molecules per million molecules (most of which are H_2O). For example, a DO measurement of 9 ppm means "for every million molecules, nine are O_2". More precisely, for every 1,000,000 molecules, 9 are O_2 and 999,991 are H_2O (assuming ideal laboratory conditions).

Note that PPM is grammatically similar to %, which, of course, represents "per cent" ("cent" means "hundred", so while PPM means "per million", % means "per hundred"). Percent is not convenient for DO measurement, because the quantities are too small - the previous example would be represented as 0.0009% O_2, so PPM is used instead.

When reporting DO data, note that mg/L = PPM!! DO analyzers will always display their results in one of these two units, and you can use whichever you like.

Percent Saturation

The previous two units indicate DO concentration in absolute terms. However, absolute units sometimes aren't enough, because they don't convey the conditions under which the measurement was made. For example, let's say you loan your car to your teenager for the evening, with the understanding that he brings it back with a full tank. When he returns, you ask him if he filled it up, and he says, "I added 5.18 gallons". While that may be a precise number, it doesn't answer your question. You were looking for a relative measurement.

Recall from the "Gas Solubility" section that water's ability to trap oxygen is affected by pressure, salinity, and temperature, but only the latter varies in a lake or stream. So, while temperature influences the amount of oxygen that water can hold, what is the maximum it can hold?

"Saturation" refers to the maximum amount of O_2 that water can hold. I.e., it is the equilibrium point at which water becomes saturated (soaked) with O_2 gas; at this point, the water can hold no more O_2, and any additional will just bubble off. (As an analogy, think of a kitchen sponge that is completely saturated - adding additional water to one part just causes it to drip out from another part.) However, since water's ability to trap oxygen is dependent on temperature, its maximum capacity (saturation) also depends on temperature: 40°F water with a DO of 13ppm is considered saturated ("up to its ears") in O_2, whereas 80°F water with a DO of 8ppm is also considered to be saturated (again, "up to its ears") in O_2. In both cases, any more would just bubble out.

"Percent saturation" is a relative figure in which the DO concentration is expressed as a percentage of saturation[1] (that is, as a percentage of maximum). As the borrowed car example illustrated, percent saturation tells us how close to "full" the water is. Just as the fuel gauge on your car's dashboard is a "percent saturation" meter (in which 50% saturation represents ½ tank of gasoline), percent saturation in the DO world tells us how close to ideal the water is. So, a more useful answer from your teenager would have been, "It's ¾ full."

Percent saturation is a relative measurement that is derived by taking an absolute quantity (PPM or mg/L) and adjusting it for temperature. So, how do you go about do this? The equation is too complex to perform, so a special graph called a "nomogram" is used.

1. Saying that water is "saturated" is the same as saying it is "100% saturated", just as saying your car's fuel tank is "full" is the same as saying it is "100% full".

A nomogram is a special graph which contains three[1] lines of data: water temperature, % saturation, and DO ppm (or mg/L); see Appendix B. If you know two of those pieces of data, you can derive the third by simply drawing a straight line (use a ruler!) through them, and the line will intersect the third. Bingo!

When we test for DO, the two known pieces of data will be water temperature and DO (in ppm or mg/L). Thus, drawing a line between them will yield the corresponding percent saturation value; an example is given in Appendix C. At that date and time, the water held only 70% of the DO that it was capable of holding (i.e. it was nearly ¾ full).

What would cause a body of water to fall short of saturation? Primary, unbalance - the water's sinks are consuming more oxygen than its sources can replenish.

The Hach test kit is based on titration, and the final test result is obtained by dividing the titrator dial indicator by ten. For example, a dial indication of 116 equates to 11.6ppm O_2 (or equivalently, 11.6mg/L).

DO Standards

There is no one EPA standard for DO (although the State of Illinois has specified a minimum of 5ppm for rivers). DO requirements depend on the type of water body (river or lake), and the type of life it is expected to support. For example, trout have much higher metabolism than catfish, and thus, a cold, fast moving trout stream has a much higher DO requirement than a murky catfish pond. Some general guidelines are:

DO (ppm)	Interpretation
9-10	very healthy for all aquatic life
5-6	minimum level for healthy fish
2-4	fish are stressed
1-2	fish die (even if it occurs for only a few hours)

Too Much of a Good Thing?

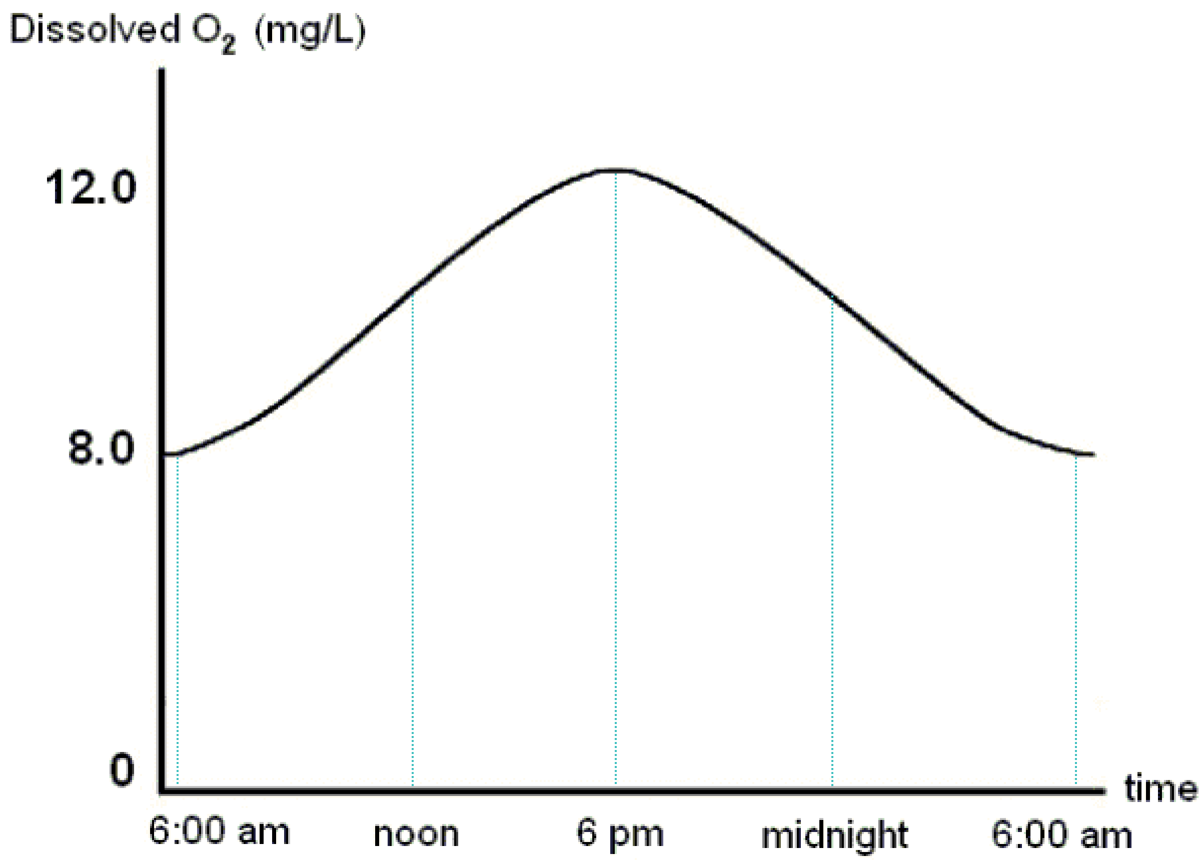
If a little oxygen is good, then a lot is better, right? Wrong! In some situations, it is possible for water to become oversaturated, such as when excess O_2 becomes "trapped" in a layer of water and can't bubble out. When water is more than 110% saturated, bubbles of O_2 may pass through the gills of fish and cause a fatal embolism, just as a bubble in the artery of a mammal will kill it.

1. It is impossible to draw a two-dimensional nomogram which accounts for all three Gas Solubility factors (pressure, salinity, and temperature), so the graph is custom drawn for a specific pressure (elevation) and salinity. The nomogram in the appendix is designed for fresh water at sea level; the error in using it for northern Illinois (elevation = ~ 600 ft) is that the percent saturation values in the graph will read approx. 2.5% lower that actual.

Appendix A

Example Illustration

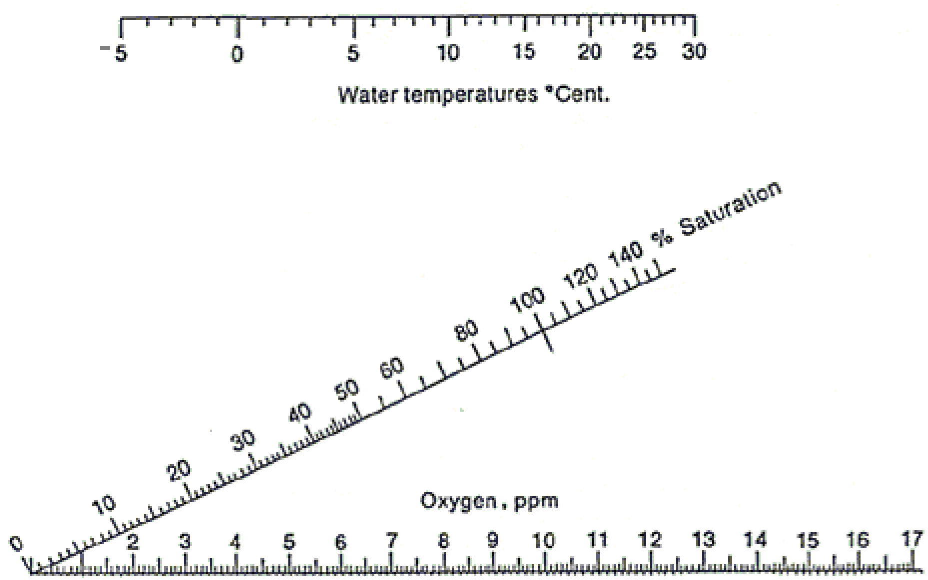
Diurnal Cycle of Dissolved Oxygen



Appendix B

Nomogram

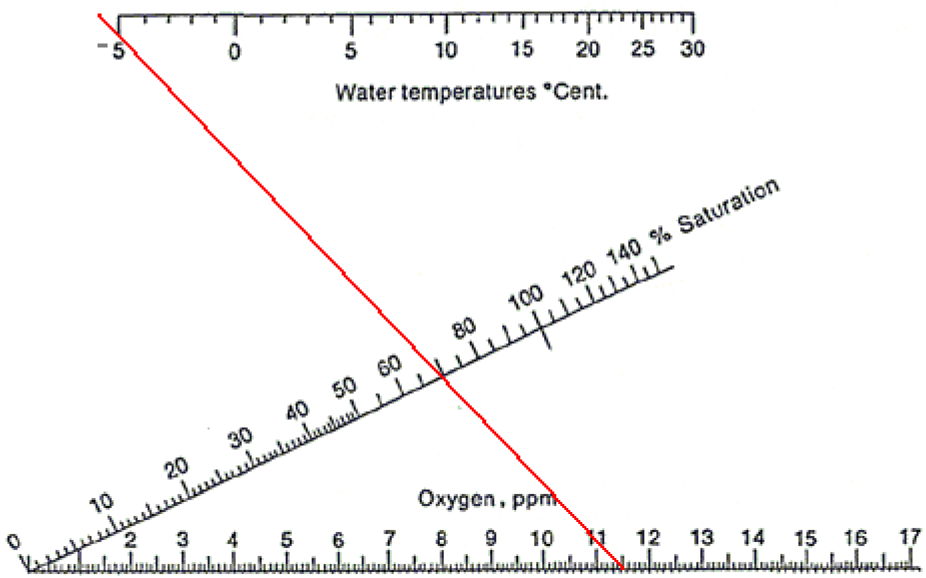
calibrated for fresh water @ sea level



Appendix C

Nomogram Example

using Klein Creek data from Jan 4 2003
DO = 11.5, Temp = -6 Celsius



Result: from graph, water's saturation level = 70%