Dissolved Oxygen Measurement Overview

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Background information:
Oxygen saturation generally refers to the amount of oxygen dissolved in bodies of water. Dissolved oxygen can be important to the sustainability of a particular ecosystem. Insufficient oxygen (environmental hypoxia) may occur in bodies of water such as ponds and rivers, tending to suppress the presence of aerobic organisms such as fish. De-oxygenation increases the relative population of anaerobic organisms such as plants and some bacteria, resulting in fish kills and other adverse events. The net effect is to alter the balance of nature by increasing the concentration of anaerobic over aerobic species. Many factors can affect DO levels, and an understanding of these levels in order to make informed decisions concerning wastewater treatment operations, hypoxic zones, aquaculture facilities or large-scale ecosystems is essential.

Standards:
At the time of writing NEMS (National Environmental Monitoring Standards) for dissolved oxygen are in the final stages of being approved. Horizons procedures are intended to comply with the NEMS Dissolved Oxygen standard.

Approved Instrumentation for Dissolved Oxygen testing at Horizons:

Spot measurements:
- YSI Pro Galvanic Probe
  - **Must be stirred** (With barometer and salinity corrections)

Continuous Instruments:
- WTW FDO 700IQ sensor –[Suitable for long term deployment]
  - Must be used in conjunction with a barometer
- YSI/WTW EXO Optical DO probe –[Suitable for long term deployment]
  - Must be used in conjunction with a barometer
- D – Opto Self logging sensor –[Suitable for short term investigation work <3 weeks]
  - Must be used in conjunction with a barometer

How to we test for dissolved oxygen? Winkler titrations:
Considered the benchmark test for dissolved oxygen. However the test is limited by operational / field procedures and the potential errors during the test. There is also a lot of variation in the “standard method” depending on which organisation you go to. We need to be careful when looking at titration results. It is very easy to incorporate extra oxygen into the sample with poor sampling techniques or not locking the oxygen in the sample correctly. Also the time between collecting the sample and testing the sample has a negative effect on the titration result. Winkler titrations are also best done in the range of 5 mg/l to 100% saturation. Saturated water is easily visible when sampling (air bubbles attach to container). At this point the errors will be high. The limited range of the Winkler titration at the high end (>100%) is a problem as our rivers routinely are over 100% saturated. The Winkler titration measures concentration and saturation values need to be calculated.

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What does a DO sensor actually measure?
Electrochemical and optical sensors do not measure dissolved oxygen concentration or saturation. They actually measure the pressure of oxygen that is dissolved in the sample. The pressure of dissolved oxygen is expressed in terms of DO % Saturation.

$$\text{Basic DO \% Saturation} = \frac{\text{Sensor output (Pressure mmHg)}}{160} \times 100$$

**Note the pressure of oxygen at sea level is 160 mmHg (0.21 x 760 mmHg)

$$\text{Or} \quad \text{DO \% Saturation} = \frac{\text{Sensor output (Pressure mbar)}}{212.78} \times 100$$

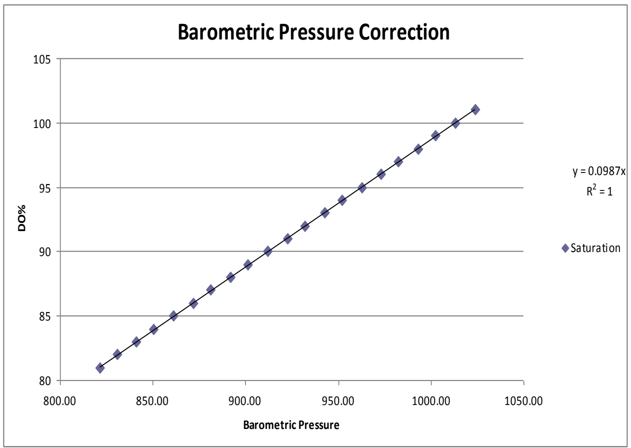
**Note the pressure of oxygen at sea level is 212.78 mbar (0.21 x 1013.25 mbar)

DO concentration (mg/l or ppm) is calculated typically by lookup table or by calculation in the sensor.

Major factors which affect dissolved oxygen measurements:

Barometric pressure: Barometric pressure affects the pressure of oxygen in a sample of air or water at sea level. The barometric pressure needs to be known at the time of calibration. After calibration changes in barometric pressure are linear but many sensors do not measure barometric pressure so no correction is carried out. Note: D Optos & WTW sensors do not measure barometric pressure.

Constants:		
One atmosphere	1013.25	mbars (760 mmHg)
Oxygen content in air	21	%
Pressure correction factor	0.0987	(mbars) [100/1013.25]



Uncorrected DO Saturation:

$$\text{DO \%} = \frac{\text{Sensor output (}O_2\text{ Pressure mbar)}}{0.21 \times 1013.25} \times 100$$

Altitude Corrected DO Saturation:

$$\text{DO \%} = \frac{\text{Sensor output (}O_2\text{ Pressure mbar)}}{0.21 \times 1013.25} \times (99.4 - \text{elevation}_{meters} \div 100)$$

Barometric Pressure Corrected DO Saturation:

$$\text{DO \%} = \frac{\text{Sensor output (}O_2\text{ Pressure mbar)}}{0.21 \times 1013.25} \times \text{Barometric (mbar)} \times 0.0987$$

Notes: Most instruments use mmHG, The units and equations have been converted to mbars. The equations above have not been supplied by equipment manufactures. The errors associated with not doing barometric pressure corrections are significant.

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Some dissolved oxygen sensors measure barometric pressure and correct for changes in barometric pressure. The YSI Pro's which Horizon's use do use barometric correction. When taking DO readings with a YSI, the barometer must have been calibrated to sea level. Any altitude correction will adversely affect the calibration and readings. Some instruments have "Altitude Correction" like the WTW sensors. This form of correction is not as good as barometric pressure as it sets the correction factor as a constant. For best quality data, barometric pressure needs to be measured and corrected for.

Temperature: There are two effects:

Membrane Permeability: The permeability of the membrane changes with temperature. Dissolved oxygen sensors therefore need to apply a temperature correction to allow for changes in the membrane. Most sensors that describe having temperature correction are referring to the membrane. This should not be confused with temperature correction required for saturation calculations. Some dissolved oxygen sensors have two temperature probes, one measuring the temperature of the membrane, and one measuring the water temperature.

Solubility of oxygen in water changes with temperature. Temperature is the most significant variable and is often the only one taken into account when calculating concentration from saturation or vice versa. Temperature correction is empirically derived at the time of the sample.

How temperature compensation is applied:

$$\text{DO Concentration} = \frac{\text{DO\% Saturated}}{\text{DO Saturation Value}}$$

*Note: for titrations a look up table is normally used to look up the DO saturation value.

The DO saturation value varies with temperature and salinity. Most manufactures only use temperature correction:

$$\text{DO Concentration} = \frac{\text{DO\% Saturation}}{(C + M_1 \times T + M_2 \times T^2 + M_3 \times T^3 + M_4 \times T^4)}$$

Where: T = Temperature

C, M_1, M_2, M_3 & M_4 are constants which change with salinity.

For fresh water the constants are C = 14.621, M_1 = -0.4094, M_2= 0.0087, M_3 = -0.0001, M_4 = 0.0000002

The above equation was calculated from data supplied by YSI.

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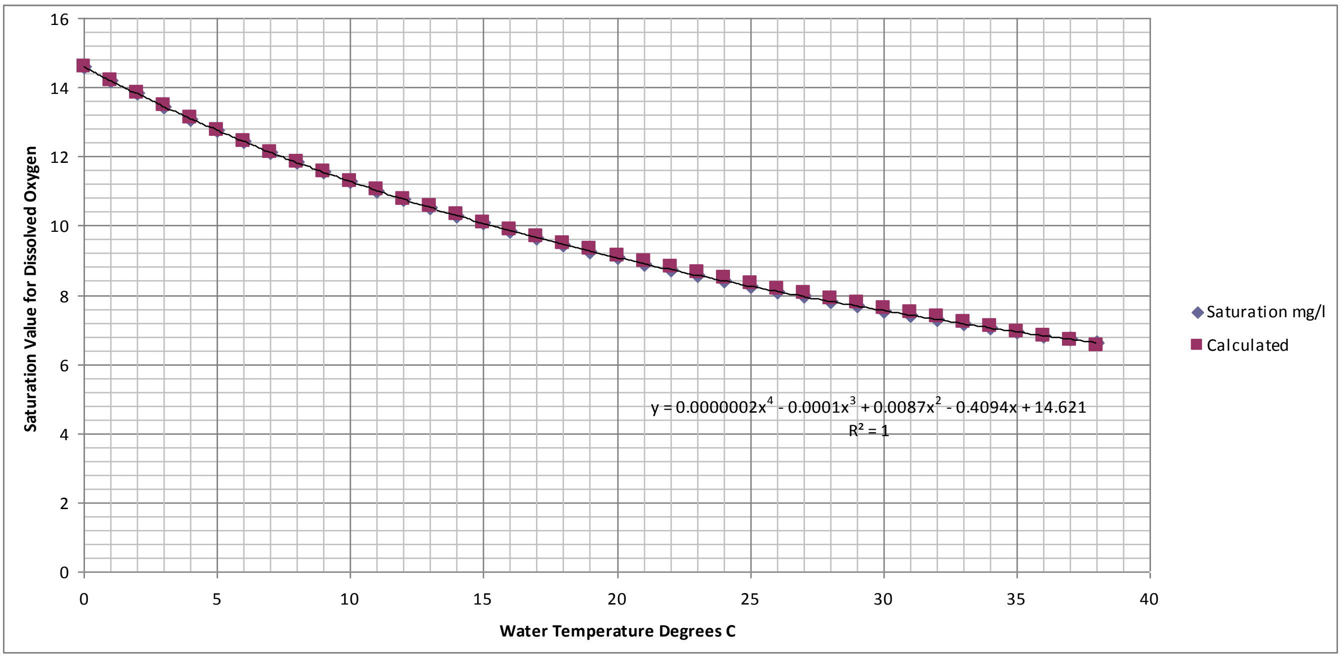

Salinity: The salinity of the water does not affect the dissolved oxygen saturation. It does have an effect on concentration readings. This needs considering when measuring different water sources (fresh water, brackish water, sea water). The salinity correction is normally taken into account (if at all) within the firmware of the instrument. For YSI instruments like our YSI Pro's that measure conductivity, salinity is measured and compensated for. This means the conductivity also needs calibrating daily on the YSI's prior to use. (The WTW sensors do not measure salinity and cannot compensate for salinity changes). If WTW sensors are to be deployed in a salt water environment or a tidal or brackish water environment then further corrections will be required.

Other factors that affect dissolved oxygen readings:

Membrane:
Life: The membrane life deteriorates over time and also deteriorates (slightly) each time a sample is taken. YSI's membranes should be replaced every month, in river sensors normally can last for two years with reduced sampling (WTW Signal average of T=360 seconds = 2 year membrane life).

Steady state polarographic (Clark) sensors: This method uses an electrochemical sensor element with a membrane. Polarographic sensors last longer than the galvanic sensors but require a 5 – 15 minute warm up period. (Dr Clark worked for YSI). YSI 556's used polarographic sensors.

Steady state galvanic sensors: Similar to the polarographic sensors, however they are "instant on" (55 seconds response time still applies). As with the polarographic sensors they are an electrochemical sensor with an electrolyte, cathode, anode, and a membrane. (YSI Pro uses these) They are also suitable for short term deployment.

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Early Optical Sensors: (D Opto's) use a blue light. They are prone to drifting and fouling. They require regular calibrations (fortnightly / monthly). Calibration methods need careful consideration when considering deployment of these sensors. Not recommended

Optical Sensors: Use a green light attenuated fluorescent signal. They have a permeable membrane (which degrades over time with each measurement). The WTW sensor has a membrane at 45 degrees which eliminates the problem of air bubbles seen in early designs. The sensor optics are calibrated to the speed of light and as this is a constant, the WTW sensor should not require any further calibration. User calibrations can be performed if required.

Response time: The response time needs to be taken into consideration when taking DO readings. Response time is the time for the sensor to respond to a change in oxygen levels not including any warm up time).
-WTW FDO 700IQ sensors have a 360 'signal averaging'. The response time is typically 60 seconds. When calibrating these units this means we need to keep the sensors in the 100% saturated environment for 7 minutes (360 + 60 seconds).
-YSI Pro Typical response time of 55 seconds.

Flow dependence:
Electrochemical sensors (like YSI's) require flow past the sensor, optical sensors do not. Electrochemical sensors will artificially read low when there is no flow, and will drop over time. The minimum flow for an electrochemical probe is 0.3 $m.s^{-1}$. This means the YSI's need to be in the flow or stirred to maintain flow across the membrane. This is particularly important when measuring lakes or wells or slow moving rivers.

Warm up time:
Polarographic sensors require 5 – 15 minute warm up time prior to a calibration and prior to a reading as the electrodes have to polarize. Galvanic sensors and optical sensors can be turned on and used immediately. (Sensor still requires time to stabilise ~55 seconds, best to leave in the solution for a good five minutes)

Calibration frequency:
Optical sensors require little to no calibration. Both types of electrochemical sensor require a calibration every day before use. If the sensors have conductivity and barometric pressure compensation (YSI Pro's) then the barometer needs calibration at sea level and the conductivity probe also requires calibration.

Other Dissolved gasses:
Optical sensors do not detect other dissolved gasses; however electrochemical sensors will detect some other gasses including hydrogen sulphide. (Full list is available in YSI's manual)

Depth / Stratification:
Dissolved oxygen changes with depth in stratified water ways like lakes. The temperature can vary at different depths and so can the oxygen levels. In lakes the oxygen levels will typically be lower as the depth increases. Similar effects could be seen in rivers to a lesser extent, as turbulent flow should see much more mixing. In deeper slow moving sections the effects could be greater.

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Quick Comparison Table:

	Winkler Titration	YSI 556 / Pro	WTW Trioxmatic 700IQ	Zebra Tech D opto
Method:	Chemical	Electrochemical	Optical -Green Light	Optical -Blue Light
Measures:	-Concentration	-Oxygen Pressure -Temperature -Salinity (Conductivity) -Barometric Pressure	-Oxygen Pressure -Temperature	-Oxygen Pressure -Temperature
Calculates	-Saturation Has been by lookup table but should be by the following formula: $DO\% = (DO\ Mg/l) \times (C + M_1 \times T + M_2.T^2 + M_3.T^3 + M_4.T^4)$ *Where:* *T = Temperature* C, = 14.611 M_1,= -0.407 M_2= 0.0085 M_3 = -0.0001 M_4 = 0.0000006 *Calculated by D. Brown	-Saturation (Barometric Correction) $DO\ \% = \frac{Sensor\ (O_2\ mbar)}{0.21 \times 1013.25} \times P_{air}\ (mbar) \times 0.0987$ Where: P_{air} = Barometric Pressure in mbars *Assumed correction method	-Saturation (Altitude Correction available) $DO\ \% = \frac{Sensor\ (O_2\ mbar)}{0.21 \times 1013.25} \times 100$ Where: A = elevation in meters *Assumed correction method	-Saturation (Uncorrected) $DO\ \% = \frac{Sensor\ (O_2\ mbar)}{0.21 \times 1013.25} \times 100$ *Assumed correction method
Calculates	N/A	-Concentration (Temperature, barometer, and salinity corrections) $DO\ Mg/l = \frac{DO\%\ Saturation}{(C + M_1 \times S + M_2 \times S^2 + M_3 \times S^3 + M_4 \times S^4)}$ *Where:* *S = Temperature x Salinity Correction* *Fresh Water Salinity correction = 1* C, = 14.611 M_1,= -0.407 M_2= 0.0085 M_3 = -0.0001 M_4 = 0.0000006 *Assumed correction method calculated by D. Brown	-Concentration (Temperature corrected) $DO\ Mg/l = \frac{DO\%\ Saturation}{(C + M_1 \times T + M_2 \times T^2 + M_3 \times T^3 + M_4 \times T^4)}$ *Where:* *T = Temperature* C, = 14.611 M_1,= -0.407 M_2= 0.0085 M_3 = -0.0001 M_4 = 0.0000006 *Assumed correction method calculated by D. Brown	-Concentration (Temperature corrected) $DO\ Mg/l = \frac{DO\%\ Saturation}{(C + M_1 \times T + M_2 \times T^2 + M_3 \times T^3 + M_4 \times T^4)}$ *Where:* *T = Temperature* C, = 14.611 M_1,= -0.407 M_2= 0.0085 M_3 = -0.0001 M_4 = 0.0000006 *Assumed correction method calculated by D. Brown
Flow required	no	Yes	No	No
Barometer correction	N/A -Calculated	Yes	No	No
Salinity Correction	Yes	Yes	No	No
Temperature Correction	Yes by calculation	Yes	Membrane and modified concentration calculation	Membrane and modified concentration calculation
Affected by other gasses	Yes	Yes	No	No
Calibration Frequency	N/A	Daily –Also requires barometer and conductivity calibration	Not Required	Fortnightly
Stable Time	N/A	55 seconds	360 seconds	155 seconds check

As can be seen above we do not have any real direct correlation in the methods. Ideally we should measure saturation using a similar technology (optical) for the check data.

Measurement Selected:

Horizons Regional Council has opted to use saturation as the primary measurement source for all data after 01/09/11. Barometric pressure correction is to be applied to all data.