

National Environmental Monitoring Standard

Dissolved Oxygen

Measuring, Processing and Archiving of
Dissolved Oxygen Data

Version: 2.0

Date of Issue: July 2016



The National Environmental Monitoring Standards

The following National Environmental Monitoring Standards (NEMS) documents can be found at www.lawa.org.nz:

Standards

- **Dissolved Oxygen (this Standard)**
Measuring, Processing and Archiving of Dissolved Oxygen Data
- **Open Channel Flow**
Measuring, Processing and Archiving of Open Channel Flow Data
- **Rainfall**
Measuring, Processing and Archiving of Rainfall Intensity Data for Hydrological Purposes
- **Rating Curves**
Construction of Stage-Discharge and Velocity-Index Ratings
- **Soil Water**
Measuring, Processing and Archiving of Soil Water Content Data
- **Turbidity**
Measuring, Processing and Archiving of Turbidity Data
- **Water Level**
Measuring, Processing and Archiving of Water Level Data
- **Water Meter Data**
Measuring, Processing and Archiving of Water Meter Data for Hydrological Purposes
- **Water Temperature**
Measuring, Processing and Archiving of Water Temperature Data

Codes of Practice

- Hydrological and Meteorological Structures
- Safe Acquisition of Field Data In and Around Fresh Water
- Site Surveys

Supplementary Material

- **Glossary**
Terms, Definitions and Symbols

NEMS Dissolved Oxygen Recording | Date of Issue: July 2016

- National Quality Code Schema

Implementation

When implementing the Standards, current legislation relating to health and safety in New Zealand and subsequent amendments and the NEMS Codes of Practice shall be complied with.

Limitations

It is assumed that as a minimum the reader of these documents has undertaken industry-based training and has a basic understanding of environmental monitoring techniques. Instructions for manufacturer-specific instrumentation and methodologies are not included in this document.

The information contained in these NEMS documents relies upon material and data derived from a number of third-party sources.

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Development

The National Environmental Monitoring Standards (NEMS) steering group has prepared a series of environmental monitoring standards on authority from the Regional Chief Executive Officers (RCEOs) and the Ministry for the Environment (MfE). The strategy that led to the development of these Standards was established by Jeff Watson (Chairman) and Rob Christie (Project Director). From 2014, the implementation of the strategy has been overseen by a steering group, and the current steering group comprises Phillip Downes, Martin Doyle, Michael Ede, Glenn Ellery, Nicholas Holwerda, Jon Marks, Charles Pearson, Jochen Schmidt, Alison Stringer, Raelene Mercer (Project Manager) and Jeff Watson.

The development of this Standard involved consultation with regional and unitary councils across New Zealand, major electricity-generation industry representatives and the National Institute for Water and Atmospheric Research Ltd (NIWA). These agencies are responsible for the majority of hydrological and continuous environmental-related measurements within New Zealand. It is recommended that these Standards are adopted throughout New Zealand and all data collected be processed and quality coded appropriately to facilitate data sharing. The degree of rigour with which the Standards and associated best practice may be applied will depend on the quality of data sought.

This document has been prepared by the Local Authorities Environmental Monitoring Group (LAEMG) to help provide consistency in the application of work practices specific to environmental monitoring and data collection across New Zealand. The input of NEMS members into the development of this document is gratefully acknowledged; in particular, the review undertaken by the NEMS steering group and non-technical editing by writer Chris Heath of Heath Research Services.

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- Northland Regional Council
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- Taranaki Regional Council
- Tasman District Council
- West Coast Regional Council
- Waikato Regional Council.

Review

This document will be reviewed by the NEMS steering group in February 2018, and thereafter once every two years. Further details on the review process can be found at www.lawa.org.nz.

Signatories

NEMS Project Director	NEMS Chair	MfE
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Terms, Definitions and Symbols

Relevant definitions and descriptions of symbols used in this Standard are contained within the NEMS *Glossary* available at www.lawa.org.nz.

Normative References

This Standard should be read in conjunction with the following references:

- NEMS *Glossary*
- NEMS *Quality Code Schema*
- NEMS *Water Temperature*
- NEMS Code of Practice *Safe Acquisition of Field Data In and Around Fresh Water*.

About this Standard

Introduction

A dissolved oxygen (DO) record often gives a measure of aquatic ecosystem health because it measures an important quality of the life-supporting capacity of natural waters.

DO is subject to many influences. These include wastewater discharges, plant (including algae) growth and respiration, and urban run-off. DO data can provide information about organic inputs to water bodies and their capacity to cope with them. DO is a key water-quality descriptor that is included in most monitoring programmes. Each monitoring situation provides its own challenges and it is important that the measured data are 'fit for purpose'. The monitoring Standard set out in this document is accompanied by a set of working guidelines on how to achieve the Standard. By following the guidelines, the vast majority of pitfalls and challenges can be overcome to achieve consistency between regions and consistency over time.

The systematic measurement of DO in water became a much easier task when portable electrodes became readily available in the 1970s. Prior to that, water samples were collected and titrated either in the field, or stabilised and then brought back to a laboratory for titration. The advent of portable electrode-meter systems enabled spot measurements to be made, particularly where large wastewater discharges were causing depletion in DO which threatened the survival of aquatic ecosystems. The larger wastewater sources were meat works, municipal sewage treatment plants and dairy factories, whereas the small discharges mainly comprised farm wastes and community sewage schemes.

Continuously monitoring electrodes with data loggers (sondes) were introduced to New Zealand in the 1990s and were initially used by researchers studying 24-hour (diel) variations in DO. Councils used them widely for monitoring compliance of water rights and for characterising water quality. These early sondes had membrane electrodes which required regular maintenance checks. The development and wide-scale availability of optical electrodes (commonly called optodes) since c. 2006 has resulted in much more reliable devices for continuous measurement and greatly aided monitoring agencies in understanding DO variation throughout the year. Modern sondes using optode technology are now routinely used by water monitoring agencies. Key to planning, maintaining and recording DO is understanding and catering for stationarity.

When measuring DO, attention should also be drawn to NEMS *Water Temperature – Measuring, Processing and Archiving of Water Temperature Data*.

Objective

The objective of this Standard is to ensure that continuous measurement of DO data is gathered, processed, archived and quality assured consistently across New Zealand. This document is made up of two parts: the first part is the Standard and the second part contains supporting information that practitioners are required to implement in order to achieve the Standard.

Scope

The scope of the Standard covers all processes associated with:

- site selection in rivers, groundwater, lakes and saline waters
- types of measuring devices
- calibration
- deployment and maintenance of field equipment
- the acquisition of continuous DO data
- validation of field measurements
- data processing, and
- quality assurance (QA) that is undertaken prior to archiving the data.

Data fit for purpose

This Standard requires all collected data to be assigned a quality code.

Data that are collected, processed and archived in a verifiable and consistent manner according to this Standard can meet the highest quality code (QC 600).

Data that do not meet QC 600 shall be coded appropriately. This allows monitoring to be carried out that is 'fit for purpose', and these data can be coded as QC 500 (Fair), or QC 400 (Poor). These data are deemed acceptable for specific, often secondary, purposes that only require data of a lesser quality.

Note: Enduring use – It is important to note that data that are coded QC 500 or QC 400 may be restricted in their use for a wide range of (yet unknown) purposes sometime in the future.

The Standard – Dissolved Oxygen

For data to meet the Standard, the following shall be achieved:

Accuracy	Deviation from primary reference when measuring concentration	$\pm (0.3 \text{ mg l}^{-1} + 5\% \text{ of the reference value})$
	Deviation from primary reference when measuring saturation	$\pm (3\% + 5\% \text{ of the reference value})$
Stationarity	Stationarity of record shall be maintained.	

Requirements

As a means of achieving the Standard (QC 600), the following requirements apply:

Units of Measurement	Concentration		mg l^{-1} (mg/l) <i>Note: This is equivalent to g m^{-3} or g/m^3, and parts per million (ppm).</i>
	Saturation		% saturation
	Barometric pressure		hectopascals (hPa), or millibars (mb)
	Temperature		$^{\circ}\text{C}$
	Salinity		parts per thousand
Precision	Concentration	<i>Measurements less than 1 mg l^{-1}</i>	$\pm 0.05 \text{ mg l}^{-1}$
		<i>Measurements in the range 1 to 10 mg l^{-1}</i>	$\pm 0.10 \text{ mg l}^{-1}$

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Precision (con.)	Concentration (con.)	<i>Measurements greater than 10 mg l⁻¹</i>	± 1 mg l ⁻¹
	Saturation	<i>Measurements less than 10%</i>	± 0.5%
		<i>Measurements in the range 10% to 100%</i>	± 1%
		<i>Measurements greater than 100%</i>	± 10%
Timing of Measurements	Maximum recording interval		15 min
	Measurement		Instantaneous value as defined by the response time of the sensor.
	Resolution		1 s
	Accuracy		± 90 s/month
	Time zone		Express time as New Zealand Standard Time (NZST). <i>Note: Do not use New Zealand Daylight Time (NZDT).</i>
Supplementary Measurements	Temperature		Shall be recorded at all times to a precision of ± 0.5 °C.
	Salinity		Required when salinity is at least 8 parts per thousand, and where salinity may vary.
	Barometric pressure		Barometric pressure shall be recorded for all deployments. Measured using a reference sensor or continuously deployed barometer within 30 km from the site.

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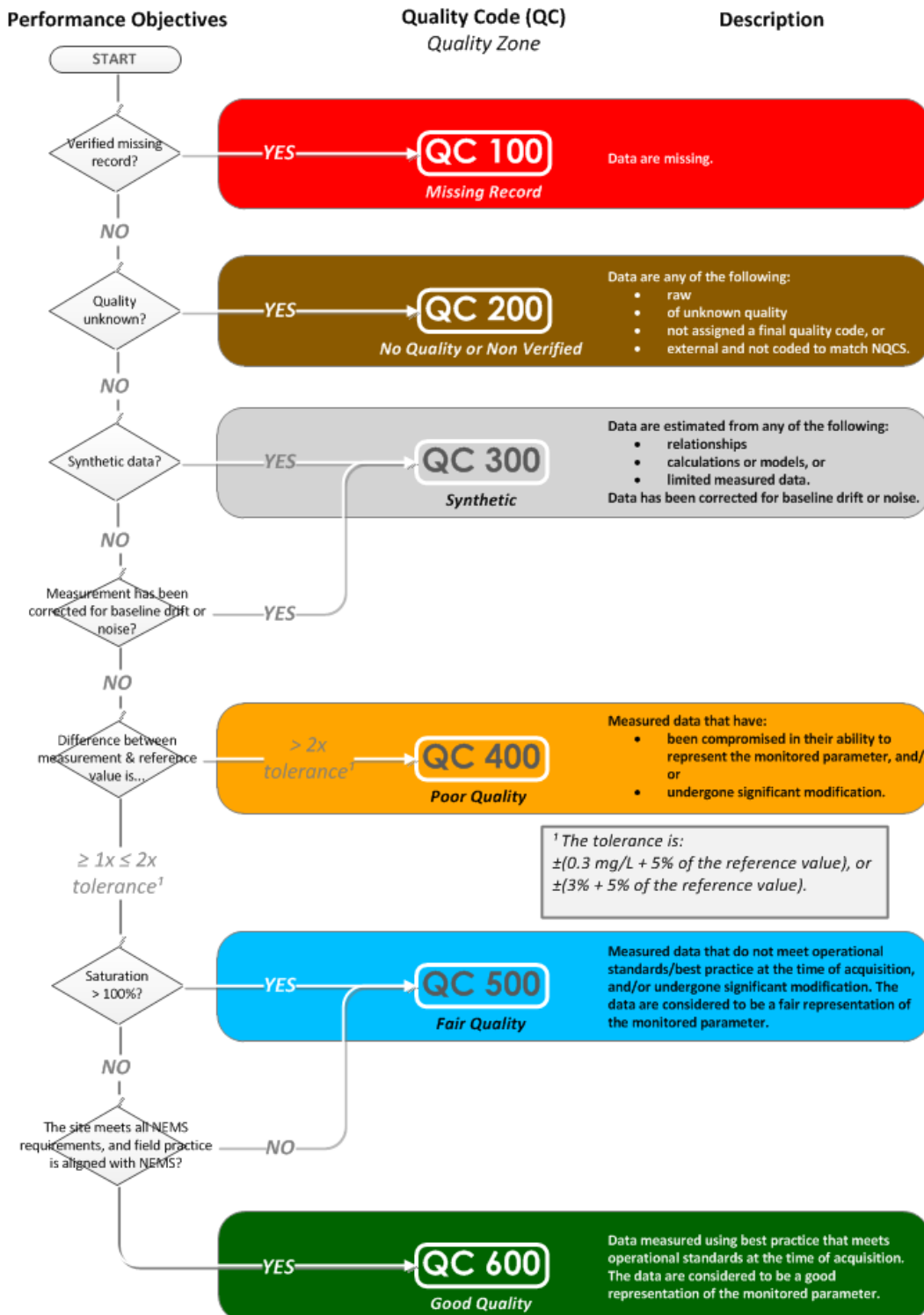
Supplementary Measurements (con.)	Altitude	Altitude shall be recorded for all deployments.
Validation	Frequency	In situ sensor: at a frequency determined by the risk and impacts of losing data. <i>Note: Validation measurements are undertaken using a calibrated handheld instrument.</i>
	Tolerance	See Table 2.
Calibration	Frequency	<ul style="list-style-type: none"> • In situ sensor: calibration shall occur when validation confirms that the in situ sensor is not conforming to the accuracy of the Standard (QC 600). • In situ sensors: shall be calibrated at least once a year (annually). • Handheld primary reference meter: calibration confirmed every day they are used.
	Method	As per manufacturer's specification for each instrument, or as a reliable default. <ul style="list-style-type: none"> • The preferred method is a 2-point calibration as defined within this Standard.
Metadata		Metadata shall be recorded for all measurements.
Quality Assurance		<i>Quality assurance requirements are under development.</i>
Processing of Data		All changes shall be documented. All data shall be quality coded as per Quality Codes Flowchart.

The following summarises best practice:

Validation Methods	Inspection of recording installations	Sufficient to ensure the data collected are free from error and bias, both in dissolved oxygen and time.
Archiving	Original and final records	File, archive indefinitely, and back up regularly: <ul style="list-style-type: none"> • raw and processed records • primary reference data • supplementary measurements • validation checks • smoothing or baseline adjustments • site inspections • calibration results, and • metadata.
Auditing		<i>Quality assurance requirements are under development.</i>

Quality Codes – Dissolved Oxygen

All data shall be quality coded in accordance with the National Quality Coding Schema. The schema permits valid comparisons within and across multiple data series. Use the following flowchart to assign quality codes to all continuous dissolved oxygen data.



Note: For an example of how the quality codes are applied to freshwater measurements at 15 °C, see Table 3 and Table 4.

1 Site Selection and Deployment

1.1.1 In this Section

This section contains a set of Standards that can be used to ensure that dissolved oxygen (DO) sensors provide useful information about the water body they are placed in.

The water bodies covered in this Standard are:

- rivers
- lakes and coastal waters, and
- groundwaters.

1.2 Stationarity of Record

Stationarity of record:

- is maintained when variability of the parameter being measured is only caused by the natural processes associated with the parameter, and
- ceases when variability is caused or affected by other processes; for example, moving the location of the sensor within the site so that it may not characterise the same water as before.

Without stationarity, a data record cannot be analysed for changes over time (such as climate change). While the accuracy of collection processes may change, it is critical that the methods and instruments (both primary instrumentation and those for measuring supplemental data) used to continuously record DO remain without bias over the lifetime of the record. For example, errors in temperature measurements may give a false impression about trends in DO percentage saturation values.

Because the methods of collecting continuous environmental data do change over time, external reference checks should always be used to compare and, if necessary, adjust continuous measurements. In the case of DO, the external reference is another device that has been recently calibrated or validated under optimal conditions.

1.3 Practical Controls

1.3.1 Site Access

Site access shall be secure and safe for the complete period of deployment.

A long-term access agreement with any landowners whose land must be crossed to gain access to the site is recommended.

1.3.2 Safety

Hazards (for observers, the public, livestock, and wildlife) related to the location and the measurement activity shall be identified and minimised.

1.3.3 Hazard Review

On selection of a final site, a hazard review shall be carried out in accordance with relevant guidelines or best practice.

The potential for human activity affecting the measurement, e.g. vandalism, shall be minimised.

1.3.4 Different Water Environments

The following special features of different water environments shall be considered:

- **rivers have highly variable flows (viz. floods)**
Note: Extra care should be given to ensuring the stability and security of monitoring equipment.
- **stratification**
Note: Consider the sensor location in terms of both the depths of sampling when lakes and bores stratify, and the influence of any saltwater–freshwater interface.
- **tidal influence**
Note: Coastal and estuarine waters may vary in salinity and water quality according to the tidal influence.
- **groundwater aeration**
Note: Special measuring techniques are required for groundwaters to avoid errors caused by surface aeration within a well.

1.4 Rivers

When deploying a sensor in a river, both DO and temperature shall be measured.

1.4.1 Selecting a Site

Consideration shall be given to the objective of the study prior to site selection.

When selecting a site on a river, the site shall be representative of the upstream reach that is to be characterised.

1.4.2 Site Metadata

All information about the site shall be recorded in a recognised database or time-series management system. These data shall include the date and times of each measurement in the format prescribed by the database.

The location of the selected site shall be recorded using GPS coordinates and WGS84 datum.

The altitude of the site shall be recorded in metres above sea level.

Note: A 20-metre change in altitude equates to approximately 0.25% DO.

1.4.3 Deploying Sensors

When deploying a sensor, the sensor shall:

- be placed in open water
- always be submerged
- be securely mounted, and
- be accessible for maintenance.

Do not place the sensor:

- in a weed bed
- where it is a navigational hazard
- where it is oriented towards a strong light source, or
- where it is at risk; for example, from vandalism or theft.

Electrochemical electrodes shall not be deployed where water velocity is less than 0.3 m/s unless a stirrer is used.

1.5 Lakes, Estuaries and Coastal Waters

When deploying a sensor in coastal waters, DO, temperature and salinity shall be measured.

1.5.1 Selecting a Site

When selecting a site, the site shall best represent the water body being monitored. For a lake, this may be a position away from the margins.

The sampling site must be fit for purpose and enable measurements that meet the objective of the monitoring programme.

Do not select a site that:

- is a navigational hazard, or
- puts the monitoring equipment at risk; for example, from vandalism or theft.

In estuarine waters:

- where water flows change with time, or there are freshwater inputs, a continuous record of river flow and/or stage may be required.
- where water salinity changes occur, salinity shall be measured.

Note: Salinity may vary with tidal motion and subsequent measurements will alter between freshwater and saline water sources. Salinity affects DO measurements.

1.5.2 Site Metadata

All information about the site shall be recorded in a recognised database or time-series management system. These data shall include the date and times of each measurement in the format prescribed by the database.

The location of the selected site shall be recorded using GPS coordinates and WGS84 datum.

1.5.3 Deploying Sensors

When deploying a sensor, the sensor shall:

- be placed in open water
- always be submerged
- be securely mounted, and
- be accessible for maintenance.

Do not place the sensor:

- in a weed bed
- where it is a navigational hazard
- where it is oriented towards a strong light source, or
- where it is at risk; for example, from vandalism or theft.

Electrochemical electrodes shall not be deployed where water velocity is less than 0.3 m/s unless a stirrer is used.

If stratification is suspected in a lake or saltwater-freshwater interface, the DO may be measured at a number of depths to provide a depth profile. In all cases, the depth of the sensor shall be specified as metadata in lakes and other impounded waters (dams and reservoirs).

Note: The quantity of DO may vary with depth (because of stratification) in lakes and reservoirs.

1.6 Groundwater

1.6.1 Selecting a Site

When choosing a groundwater site for DO sampling, careful consideration must be given to the sampling techniques to be used. This will in part be determined by the:

- sampling programme requirements, and
- type of aquifer (artesian/non-artesian).

If there is saltwater intrusion, then salinity must also be measured.

1.6.2 Site Metadata

Site information shall be recorded in a recognised database or time-series management system, including:

- bore ID
- bore location
 - Note: Use GPS coordinates and WGS84 datum.*
- height of bore cap above sea level
- bore depth
- radius of bore casing
- static water level
- sampling method
- instruments used
- purging calculations
- sensor depth
- whether the bore is in use (i.e. water is regularly pumped from the bore)
- salinity of the water, and
- whether the site is affected by tides.

1.6.3 Deployment of Sensors in a Groundwater Bore

When deploying a sensor in a groundwater bore, both DO and temperature, shall be measured. Salinity measurements may also be required.

For more information, see the following in Section 2: 'Data Acquisition':

- 2.2.5: 'Water Pumped to Surface'
- 2.2.6: 'Sub-Surface Measurements', and
- 2.2.7: 'Low Flow Measurements'.

1.7 Sensors

- 1.7.1 Some sensors measure DO and/or some of the following parameters concurrently and calculate DO values to compensate for:
- temperature
 - salinity, and
 - barometric pressure.

2 Data Acquisition

2.1.1 In this Section

This section focuses on mitigating errors associated with data acquisition; in particular, errors associated with:

- methods of measurement, and
- instrument validation and calibration.

2.2 Measurement

All dissolved oxygen (DO) measurements are affected by:

- temperature
- barometric pressure, and
- altitude.

Some DO measurements are affected by salinity.

2.2.1 Temperature

Temperature shall be measured in situ at the same frequency and times as DO measurements to an accuracy of ± 0.5 °C.

2.2.2 Barometric Pressure

Barometric pressure is preferably recorded continuously throughout the DO data record (at the same frequency as the DO data).

Barometric pressure shall be recorded:

- at the start of in situ sensor continuous-deployment periods
- at the end of the record, and
- when validation measurements are made with reference sensors from a local barometer within 30km from the site.

Note: Barometric pressures are normally within the range of 95 to 105 kPa (950 millibar to 1050 millibar) corresponding to a saturation DO variation of $\pm 5\%$ (i.e. from 95% to 105% of the value at the standard atmospheric pressure of 1013 millibar).

2.2.3 Altitude

The altitude shall be recorded for all in situ deployments of DO sensors. The effects of low altitude (400 m above sea level or less) have a minimal effect on the accuracy of the measurement. Saturation DO decreases by about 1% for every 100-m increase in altitude above sea level. For more information, see Table 9 (page 55), and subsection 2.2: **'Error! Not a valid bookmark self-reference.'**

2.2.4 Salinity

Measurements made in coastal and estuarine waters may have varying salinity according to the tidal stage. In which case, salinity, temperature and DO measurements shall all be logged simultaneously.

Salinity shall be recorded for every DO measurement when:

- salinity is at least 8 parts per thousand, and
- is in a site where salinity may vary because of mixing of different waters.

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Note: Estuarine and harbour waters are likely to have variable amounts of freshwater and saltwater depending on the tide and sensor location. At a salinity of 8 parts per thousand, saturation DO concentration are 5% to 6% lower than in freshwater at 5 °C to 20 °C.

2.2.5 Water Pumped to Surface

For measurements made on groundwater that is pumped to the surface:

- only constantly pumped sites shall be monitored continuously
- continuous measurements shall be taken using optode sensors
- electrochemical sensors (without a stirrer) may be only used when flow velocities are at least 0.3 metre per second
- for intermittent measurements, bores shall be purged of standing water by pumping out at least three times the standing bore volume prior to making measurements of DO

Note: The formula to calculate standing bore volume is:

$$\text{Standing water volume (in litres)} = ((\pi \times r^2) \times L) \times 1000$$

where: r = radius of bore casing (in metres)

L = depth of the water column (in metres).

- DO measurements in purged samples shall comprise three consecutive stable readings made three to five minutes apart, and
- the pumping shall be smooth and shall not allow entrainment of air; preferably a flow-cell is utilised to avoid exposing the pumped water to air.

Note: If aerated as a result of extraction, the DO concentration may be artificially high.

2.2.6 Sub-Surface Measurements

Optode sensors shall be deployed as close to the bore screen as possible to avoid the stagnant water within the bore.

Sensor depth shall be recorded for each deployment.

2.2.7 Low Flow Measurements

In order to minimise the drawdown on an aquifer during purging and sampling, the technique of low flow sampling is recommended.

Low flow sampling is typically done through the use of an adjustable rate pump to remove water from the screened zone of a bore at a rate that will cause minimal drawdown of the water level in the bore.

Drawdown is measured in the bore concurrent with pumping using a water level sensor. Low flow sampling does not require a specific flow rate or purge volumes.

Note: 'Low flow' refers to the velocity at which water enters the sampling pump intake.

The water that is sampled shall be the water in the immediate vicinity of the bore screen.

Note: Water level drawdown provides the best indication of the stress imparted by a given flow rate for a given hydrological situation. Typical flow rates of the order of 0.1 to 1.0 litres per minute are normally used.

After purging the pump tubing, DO measurements shall comprise three consecutive stable readings made 3 to 5 minutes apart.

2.2.8 Optodes

Optodes provide accurate data in rivers, groundwater, lakes and reservoirs, and saline waters.

Optodes are preferred for deployment where:

- long-term continuous measurement is required
- water flow is less than 0.3 metres per second
- water contains hydrogen sulphide, and

Note: Optodes are not sensitive to hydrogen sulphide and are therefore better than electrochemical electrodes in anaerobic or highly organic conditions (e.g. sewage ponds).

- fouling is likely.

Note: Optodes are less affected by fouling than electrochemical electrodes because they do not rely on diffusion of DO from the water into the sensor.

Optodes are suitable for reference checking of in situ meters.

Note: This requires the optode to respond quickly to temperature.

When choosing an appropriate sensor, the following comparison (Table 1) shall be considered.

Table 1 – Sensor comparison

	Electrochemical Sensors	Optodes (Optical Sensors)
Suitable For	<p>Sampling situations that require a rapid response time (e.g. swift-flowing rivers)</p> <p>Where a lot of measurements have to be made in a short time</p> <p>Short-term deployments of 1-2 weeks</p>	<p>In situ deep-water profiling (e.g. stratified lakes and ground waters)</p> <p>Shallow, still waters where it may be difficult to maintain stirring</p> <p>Rivers with very low velocities</p> <p>Where the water volume is small or hydrogen sulphide may be present</p> <p>Continuous long-term deployments</p>
Response Time	Generally faster	<p>Some optodes have the thermistor mounted within the casing, so temperature equilibrium takes a considerably long time.</p> <p><i>Note: Thermal response is very important because measurements that are not matched correctly to the water temperature may be considerably in error.</i></p> <p><i>This is especially so for percentage saturation data, where the measured concentration is divided by the saturation DO at that temperature.</i></p>
Warm Up	Up to 15 minutes	Instant on – no warm-up time needed
Power Consumption	Generally lower	<p>Generally higher</p> <p><i>Note: Some optodes have higher power consumption than many electrochemical electrodes.</i></p>
Water Movement Required?	Yes – at least 0.3/s unless a stirrer is used	No

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	Electrochemical Sensors	Optodes (Optical Sensors)
Frequent Calibrations Required?	<p>Yes</p> <p><i>Note: The external membranes of electrochemical sensors are prone to being damaged in some harsh environments, requiring more frequent calibration and maintenance checks of these sensors.</i></p>	<p>No</p> <p><i>Note: Optodes exhibit very little calibration drift and can hold a calibration for several months.</i></p> <p><i>Note: Some optodes have demonstrated erratic behaviour in harsh environments, which includes baseline drift and a noisy signal, but this is also likely to be true of electrochemical electrodes.</i></p>
Susceptible to Gases such as Hydrogen Sulphide?	<p>Yes</p> <p><i>Note: Some gases cause erratic measurements.</i></p>	No
Maintenance	The electrodes require periodic maintenance and new electrolyte solution.	Optodes require less maintenance than electrochemical sensors.
Durability	Subject to regular maintenance	Unknown

2.2.9 Required Precision

For measuring concentration, the required precision of a (electrochemical or optode) DO sensor shall be at least:

- $\pm 0.05 \text{ mg l}^{-1}$ for measurements less than 1 mg l^{-1}
- $\pm 0.10 \text{ mg l}^{-1}$ for measurements in the range 1 to 10 mg l^{-1} , and
- $\pm 1\%$ for measurements greater than 10 mg l^{-1} .

For measuring saturation, the required precision of a (electrochemical or optode) DO sensor shall be at least:

- $\pm 0.5\%$ for measurements less than 10%
- $\pm 1\%$ for measurements in the range 10 to 100% , and
- $\pm 10\%$ for measurements greater than 100% .

Note: The percentage values above are stated in relation to the measured value.

Only sensors that measure at least up to 200% saturation (20 mg l^{-1}) with the above precision shall be used for continuous in situ monitoring of DO. It is assumed by

manufacturers that DO sensors behave linearly above 100% saturation just as they do between 0 and 100% saturation.

Note: Some claim to be able to accurately measure up to 250%, or even 500% but offer no evidence that optodes have been calibrated above 100% saturation.

Note: There are many different makers of DO sensors. In this document we have concentrated on those most widely used in New Zealand, viz. Hach, WTW, YSI and Zebra-Tech (supporting documents are listed in the references). Each model has its own distinct sensitivity, accuracy, precision and ranges of operation. For more information, see Annex D – Dissolved Oxygen Tables', Table 8.

2.3 Calibration

2.3.1 Factors to Consider When Calibrating

The following factors shall be taken into account when calibrating a sensor:

- temperature
- barometric pressure & altitude
- salinity.

2.3.2 Temperature

DO saturation varies with temperature.

Temperature shall always be recorded when calibrating DO sensors.

The temperature sensor shall be accurate to within ± 0.5 °C.

Note: Accuracy can be determined by comparing the sensor temperature readings with a calibrated (reference) thermometer and recording the difference.

2.3.3 Barometric Pressure and Altitude

DO is affected by barometric pressure and altitude. These effects are generally quite small; however, adjustments are required for these parameters.

The manufacturer's documentation shall be followed when making corrections for one or both of the following factors:

- barometric pressure, and/or
- altitude.

Standard barometric pressure corresponding to sea level is 1013 millibar (or 101.3 kPa). Many instruments do not compensate for the local barometric pressure or altitude and calibrate the percentage reading to a value corresponding to the current barometric pressure (altitude). Therefore, the calibration value of 100% only corresponds to tabulated values that are based on standard atmospheric pressure when at a barometric pressure of 1013 millibar (sea level).

To determine the DO percentage calibration value for other barometric pressures/altitudes:

- refer to the operation manuals
For an example, see Annex E – Options for Editing Data'.
- divide the actual barometer reading by 1013 and then multiply that number by 100.

Examples:

For a barometric pressure of 987 millibars, the saturation DO (mg l^{-1}) = $987/1013 \times 100\% = 97.4\%$ of the sea-level value.

If the sea-level saturation value is 10 mg l^{-1} , then saturation at 987 millibars is 9.74 mg l^{-1} (or about 2.6% lower).

Barometric pressure (p) change with altitude (h) is given by:

$$p = 1013 \times (1 - 2.25577 \times 10^{-5} h)^{5.25588}$$

Therefore, at an altitude of 400 m, the pressure is 95% of sea level, and at 1000 m, saturation DO is 87% of the sea-level value.

Ways to correct DO percentage saturation for altitude and barometric pressure are given in Annex D – ‘DO Tables’, Table 7.

2.3.4 Salinity

DO is affected by salinity. Manufacturers’ user guides explain how this should be allowed for when calibrating a sensor.

Correcting DO saturation values for salinity shall be made with accurately measured salinity measurements, or by using tables that are in most DO instrument handbooks. For more information, see Annex D – Dissolved Oxygen Tables’. An equation for calculating DO saturation values for all commonly encountered temperatures and salinities is given in Quality Codes – Dissolved Oxygen ’.

Note: Oxygen solubility is lower in saline waters than freshwater. For example, saturation DO at 15 °C in seawater is 7.9 mg l^{-1} compared with 10.1 mg l^{-1} in freshwater.

2.3.5 Where to Calibrate

2.3.5.1 Indoors

Where practicable, sensors shall be calibrated in a stable environment, such as a laboratory or office.

2.3.5.2 In the Field

When calibrating a sensor in the field, the sensor shall be calibrated in a sheltered location out of the wind; for example, inside a vehicle.

2.3.6 Calibration Frequency

In situ sensors shall be calibrated at least annually or more frequently if sensor drift is suspected.

The primary reference sensor shall be calibration checked every day it is used.

The in situ sensor shall be calibrated when validation confirms that it is not conforming to the accuracy of the Standard (QC 600).

2.3.7 Methods

Calibration shall be carried out:

- as per the manufacturer's specification for each instrument, or
- with a 2-point calibration using air-saturated water or saturated air for 100% and a deoxygenated solution for the zero.

When calibrating a DO sensor, any one of the following three calibration methods may be considered valid:

- the Winkler method
- air-saturated water, or
- water-vapour-saturated air.

For any of these three methods, the manufacturer's recommended method shall be followed.

Note: Some optode sensors should be calibrated using the water-vapour-saturated air method at temperatures above 5 °C, and the air-saturated water method at temperatures below 5 °C. By contrast, other optodes shall only be calibrated by the air-saturated water method.

Calibrations may be 'one point', when only one experimental value is used to calibrate the sensor, or 'two point', when two experimental data points are used. The manufacturer's recommended method shall be followed.

One-point calibrations are the most common and are usually conducted with water that is 100% saturated with DO. Two-point calibrations mostly use water with zero DO (made by treating the test water with sodium sulphite, and cobalt chloride as a catalyst), and 100% saturated water. Alternatively, nitrogen gas (or argon) may be used to produce a zero DO test solution.

2.3.7.1 The Winkler Method

The Winkler method calibrates the mg l⁻¹ concentration value; the air-saturated water and water-saturated air methods both calibrate the percentage saturation reading.

The Winkler method is an accurate but time-consuming way of analysing DO in water by chemical titration. It is best suited to the laboratory. Sensors are calibrated by being adjusted to agree with accurately known DO concentrations.

2.3.7.2 Air-Saturated Water Method

The air-saturated water method entails:

- saturating water with air at a known temperature
- placing the sensor in the water, and
- when the reading has stabilised, setting the DO to 100% saturation.

Stirring may be required for electrochemical electrode sensors.

Methods for ensuring that water is saturated with air (100%) include:

- using an aquarium pump and aeration stone, or
- pouring a fixed volume of water, e.g. 2 litres, from one bucket to another 10 to 20 times.

Note: The WTW and YSI sensor guides state that: "You obtain air-saturated water by pouring water several times in and out of two vessels so that it sparkles."

2.3.7.3 Water-Vapour-Saturated Air Method

The water-vapour-saturated air method is the quickest calibration procedure and may only take a few minutes to perform. It entails:

- placing a clean dry sensor in a vented vessel containing air
- placing a small amount of water in a sponge, and
- when the reading has stabilised, setting the DO to 100% saturation.

Note: Response times vary with sensors. For example, some sensors (once temperature equilibrium has been achieved) reach 90% of the final value within 360 seconds and other sensors within 60 seconds.

2.4 Validation

The purpose of validation is to ensure that in situ sensor measurements are reliable.

Routine checks on the in situ performance of DO sensors can prevent loss of data by identifying faulty field equipment. Steps can then be taken to rectify the problem.

While undertaking a validation on site between the primary reference sensor and the in situ sensor all supplementary measurements should be considered; i.e. barometric pressure, temperature, altitude and salinity. Corrections during the validation should be resolved according to the equations in Annex D - 'DO Tables', Table 7.

2.4.1 Reference Sensors

Reference sensors are reliable, well-calibrated instruments used to validate in situ sensors. They are most often handheld instruments and can have optodes or electrochemical sensors.

Reference sensors shall be calibrated or validated:

- every day they are used, and
- in a stable temperature environment.

2.4.1.1 Log

A log shall be kept that records:

- each time reference sensors are calibrated or validated
- the temperature, and
- barometric pressure.

2.4.1.2 Response Time

The response time of the reference sensor and any other important features, e.g. the time it takes to reach the ambient temperature, shall be logged with the instrument.

2.4.1.3 Proximity to Field Sensor

When using the reference sensor, it shall be located as close as possible to the in situ sensor.

Note: Because DO may vary spatially in a water body, reference sensor readings should be made as near as possible at the same horizontal and vertical position as the in situ recording sensor.

2.4.1.4 Frequency of Measurements

All reference sensor measurements shall be:

- made at the same time as in situ measurements
- made at the start and finish of the deployment
- recorded, and
- performed at a frequency determined by the risk and impacts of losing data.

Note: Also take into account the manufacturer's recommendations, unless observations suggest it should be more frequent.

If cleaning is required, a pre- and post-validation measurements shall be undertaken.

If the in situ device is deviating more than acceptably from the reference checks (as defined by the accuracy statement in the Standard), then the frequency of maintenance visits should be increased.

2.4.2 Validating In Situ Measurements

Differences between recorded field measurements and values given by the reference check instrument are used to assess the extent to which field data meets the Standard.

Calibration shall occur when validation confirms that the in situ sensor does not conform to the accuracy of the Standard.

If tolerance is 'poor' (QC 400), the field sensor system shall be serviced. This may entail cleaning, replacement of parts, validation and recalibration if necessary.

Once this is done, further agreement with the reference sensor should then be 'good' (QC 600). If not, a replacement sensor may need to be deployed that agrees better with the reference measurements.

2.4.3 Temperature

The temperature shall be recorded using a reference thermometer. For more information, refer to the NEMS *Water Temperature – 'Measuring, Processing and Archiving of Water Temperature Data'*.

2.4.4 Barometers and Salinity Meters

Barometers and salinity meters shall be routinely checked against calibrated standards according to the manufacturer's recommendations, and any differences shall be logged.

2.4.5 Operational Standard for Dissolved Oxygen Measurements

2.4.5.1 Concentration

When DO is measured in concentration units, agreement between the measurement and the reference value shall be within $\pm (0.3 \text{ mg l}^{-1} + 5\%$ of the reference value).

For example, when the reference value is 5 mg l^{-1} , the field sensor shall be within $\pm 0.55 \text{ mg l}^{-1}$ of this value to be considered reliable. That is, any measurement within the range 4.45 to 5.55 mg l^{-1} is deemed to have passed the validation check.

2.4.5.2 % Saturation

When DO is measured in percentage saturation units, agreement between the measurement and the reference shall be within $\pm (3\% + 5\%$ of the reference value).

For example, when the reference value is 50% saturation, the field sensor shall be within $\pm 5.5\%$ of this value to be considered reliable. That is, any measurement within the range 44.5 to 55.5% is deemed to have passed the validation check.

Table 2 provides information on validation tolerances for DO measurements in freshwater.

Table 2 – Example of DO data tolerances and measured ranges used to pass validation checks

Reference DO (% Sat)	Tolerance (% Sat)	Range (% Sat)	Reference DO (mg l ⁻¹)	Tolerance (mg l ⁻¹)	Range (mg l ⁻¹)
10	3.5	6.5 to 13.5	1	0.35	0.65 to 1.35
20	4.0	16 to 24	2	0.40	1.6 to 2.4
30	4.5	25.5 to 34.5	3	0.45	2.55 to 3.45
40	5.0	35 to 45	4	0.50	3.5 to 4.5
50	5.5	44.5 to 55.5	5	0.55	4.45 to 5.55
60	6.0	54 to 66	6	0.6	5.4 to 6.6
70	6.5	63.5 to 76.5	7	0.65	6.35 to 7.65
80	7.0	73 to 87	8	0.7	7.3 to 8.7
90	7.5	82.5 to 97.5	9	0.75	8.25 to 9.75
100	8.0	92 to 108	10	0.8	9.2 to 10.8

Note: Examples of data tolerances for DO concentrations above 100% saturation are not shown because calibration procedures have not been verified for these high levels. Manufacturers assume that sensors behave linearly throughout their specified ranges (e.g. 0% to 250% saturation).

2.5 Maintenance

2.5.1 Manufacturer's Recommendations

The manufacturer's recommendations shall be the starting point for routine maintenance and inspection of equipment.

2.5.2 Maintenance Considerations

Routine maintenance shall include:

- cleaning sensors (removing debris and organic films)
- checking for physical damage, making necessary repairs and/or replacements as recommended by the manufacturer, and
- validation checks against a reference DO sensor.

Maintenance may also include checking power supply status.

Carry spare equipment in the field in case you need to replace membranes or electrolyte on electrochemical sensors.

2.5.3 Frequency

Routine maintenance shall be at a frequency determined by the risk and impacts of losing data, also taking into account the manufacturer's recommendations.

Note: Based on observation of condition of the equipment, maintenance may need to be performed more often.

If a lot of cleaning is required, or the in situ sensor is deviating more than is acceptable from the reference checks, then maintenance shall be performed more often.

2.5.4 Telemetered Systems

Daily checks of data through telemetered systems allows for early detection of sensor drift, fouling, malfunction or failure.

Daily data checks can be used to manage the frequency of site visits.

2.5.5 Event-Based Maintenance

Maintenance may be required immediately after an event; for example, a flood, tsunami or pollution event.

The sensor's performance shall be checked.

2.5.6 Biofouling

Unmonitored or unmanaged biofouling may degrade or even ruin much of a DO record.

Sites are prone to biofouling during summer and where the water has high nutrient concentrations.

At sites prone to biofouling, a biofouling management plan shall be devised and operated.

Note: It is recommended that all sites prone to biofouling be equipped with telemetry so that the early signs of biofouling can be checked in the office on a regular (e.g. even daily) basis, and appropriate measures taken to clean the sensor before the record deteriorates to the point of losing data.

2.5.7 Chemical Interferences

Electrochemical sensors fitted with gas-permeable membranes are subject to interferences caused by gases reacting with the electrodes. Of particular concern are hydrogen sulphide and ammonia, both present in anaerobic environments, such as waste-treatment ponds.

Optodes are not affected by gases other than oxygen.

2.5.8 Inhibitors

Sensors deployed in situ for continuous monitoring may include mechanisms for continuously inhibiting the growth of biofilms on the sensor lens.

Mechanisms may consist of a:

- mechanical wiper
- mechanical shutter
- ultra-sonic vibrator, or
- copper ring

Note: Lens biofouling may also be inhibited by specialised factory-applied polymer coatings.

2.5.9 Sensor Storage

The sensor manufacturer's guide for storing sensors when not in use shall be followed. Some electrochemical sensors should be emptied of electrolyte solution, cleaned and stored dry, but some need to be stored moist.

3 Data Processing and Preservation

3.1.1 In this Section

This section contains information on the handling of data from the field, in its original form, and data processing, editing, final archiving and auditing.

Essential information that needs to be collected comprises 'metadata' (information about where and when the dissolved oxygen (DO) measurements were made), as well as the actual measured data.

Multiple data sets shall be required. This ensures that data can be tracked back to the original values. Interpreted data shall be kept separate from the raw data.

3.2 Field Data

Data shall be stored in a recognised time-series manager.

3.3 Data Processing

Data processing includes:

- assignment of quality codes
- adjustment of data based on additional environmental parameters such as temperature, barometric pressure and salinity
- data editing, to cater for step-changes or data deviations as a result of sensor recalibration, baseline drift, fouling or sensor maintenance.

Note: For suggestions on possible options for editing data, see Annex E – Options for Editing Data’.

3.4 Quality Coding

3.4.1 Performance

All data shall be quality coded in accordance with the National Quality Coding Schema.

Note: The National Quality Coding Schema permits valid comparisons within a data series and across multiple data series.

3.4.2 Considerations

The following points shall be considered when quality coding data:

- whether the recording deployment as a whole meets one or both of the following criteria:
 - operational Standards, and/or
 - best practice at the time of data acquisition
- the instrument calibration status at the time of data acquisition
- the editing of data
- the occurrence and quality of synthetic data, and
- the processing Standards at the time of archiving.

3.4.3 Data that Do Not Meet the Standard

Any data that are collected from equipment that do not meet this best practice Standard shall be assigned a quality value from QC 100 to QC 500.

Note: A quality value of QC 600 shall only be assigned where this Standard and associated best practice is achieved.

3.4.4 Measurements Above 100% Saturation

Calibration can be accurately achieved to 100%, and values up to 100% are within the acceptable range for the quality code schema. For a list of quality codes, see 'Quality Codes – Dissolved Oxygen Measurement', earlier in this document.

The quality code schema allows for increasing uncertainty at higher DO levels.

Methods for calibrating sensors for DO concentrations above 100% are not yet available, and there is some uncertainty about applying quality codes for such data.

Note: Manufacturers assume that calibrations apply over the whole measurement range. Upper 'measurable' values may be 200% to 600% saturation depending on the brand of DO sensor.

Table 3 and Table 4 show quality codes (QC 400 to QC 600) assigned for DO concentrations up to 100% saturation, based on how well it falls within the tolerance criteria.

Note: A maximum quality code of 500 shall be applied to DO data over 100%.

Table 3 – Example: Dissolved oxygen expressed as % saturation
Quality codes (QC 600, QC 500 and QC 400) assigned to freshwater data.

DO (% sat)	Less than Standard	Within Range	Greater than Standard
	QC 600	QC 500	QC 400
10	3.5	(3.5 to 7.0)	7
20	4.0	(4.0 to 8.0)	8
30	4.5	(4.5 to 9.0)	9
40	5.0	(5.0 to 10.0)	10
50	5.5	(5.5 to 11.0)	11
60	6.0	(6.0 to 12.0)	12
70	6.5	(6.5 to 13.0)	13
80	7.0	(7.0 to 14.0)	14
90	7.5	(7.5 to 15.0)	15
100	8.0	(8.0 to 16.0)	16

Note: For these examples (Tables 3 & 4), it is assumed that all measurements are made in freshwater at 15 °C and standard barometric pressure (1013 mbar) and at sea level.

Note: Quality codes are assigned according to how well measured values agree with reference checks (left column). Good quality data (QC 600) differ by less than Standard. Fair quality data (QC 500) differ by 1 to 2 times the Standard. Poor quality data (QC 400) differ from the reference value by more than twice the Standard. The same is true for concentration values (mg l-1).

Table 4 – Example: Dissolved oxygen expressed in milligrams per litre
Quality codes (QC 600, QC 500 and QC 400) assigned to freshwater data.

DO (mg l ⁻¹)	Less than Standard	Within Range	Greater than Standard
	QC 600	QC 500	QC 400
1	0.35	(0.35 to 0.70)	0.70
2	0.40	(0.40 to 0.80)	0.80
3	0.45	(0.45 to 0.90)	0.90
4	0.50	(0.50 to 1.00)	1.00
5	0.55	(0.55 to 1.10)	1.10
6	0.60	(0.60 to 1.20)	1.20
7	0.65	(0.65 to 1.30)	1.30
8	0.70	(0.70 to 1.40)	1.40
9	0.75	(0.75 to 1.50)	1.50
10	0.80	(0.80 to 1.60)	1.60

Note: Refer to footnote under Table 3 for an explanation of the QC codes.

3.5 Metadata and Comments

Metadata describes the type of data, where it has been measured, length of record and other information relevant to the data set.

Comments are very useful to explain unusual features or events in the record that users of the data should be aware of. In addition, routine comments are required for key information.

Comments should describe in time-stamped text format and include but not be limited to:

- information about the site, station and characteristics of the data
- alerts and supporting information intended for end users of the data, and
- aspects not easily quality coded or otherwise quantified in point detail.

Note: Current software packages provide several ways to build a database of comments. Comments can be entered into an unstructured file of text. If the comments are entered into an ODBC (Open Database Connectivity) database, they can be accessed by any ODBC compliant software. Therefore this method is recommended.

3.5.1 Metadata – Site Details

Adequate mechanisms shall be put in place to store all relevant site-related metadata with the actual data records including, but not limited to:

- site purpose
- recording agency/ies
- site location

For example, GPS coordinates, Spatial Reference System (SRS), and triangulation information.

- site altitude
- location of nearest barometer
- site name and past and present aliases
- names and/or indices of relevant environmental features

For example, river, lake or estuary.

Note: Latitude/longitude coordinates, e.g. WGS84, must be expressed to a minimum of 6 decimal places.

- start and end date of site and record

Note: Recorded using New Zealand Standard Time (NZST).

- related sites and records, and
- reference to the Standard and version used.

3.5.3 Metadata – Other Details

Adequate mechanisms shall be put in place to store all non-site-related metadata with the actual data records including, but not limited to:

- sensor details

Note: Preferably through an agency instrument management system.

- original format details

For example, chart or digitised format details.

- logger and telemetry details

- calibration records

Note: It is preferable to use an agency instrument/asset management system.

- any relevant comments in document vocabularies that future users will understand, and

For example, terms shall be defined and instrument types referred to, not brands.

- information about:

- legal requirements
- confidentiality agreements
- intellectual property, and
- any other restrictions related to data access.

3.6 Data Storage

3.6.1 Storage

Data shall be stored within a recognised time-series manager.

3.6.2 Data Files

All of the following three versions of DO data shall be retained and maintained:

- raw data
- adjusted data set, and
- edited data set.

3.6.2.1 Raw Data

Raw data is defined as ‘unadjusted data’ taken directly from the reference and in situ sensors. The raw data are useful for tracking sensor deterioration over time and provides the means of revisiting data for reprocessing.

Note that raw data may include DO data that has been corrected by the sensor for some or all of the following:

- temperature
- barometric pressure
- salinity, and/or
- altitude.

3.6.2.2 Adjusted Data Set

The adjusted data set shall take into account the relevant temperature, salinity and barometric pressure adjustments. For an explanation of how this may be done see subsection 2.3.3: ‘Barometric Pressure and Altitude’ and Annex D – Dissolved Oxygen Tables’.

3.6.2.3 Edited Data Set

Edits may include one or both of the following:

- changes in baseline due to sensor drift and/or ramping, and/or
Note: That is, where the baseline drifts steadily up or down.
- smoothing of noisy data.

Any data edits, e.g. edits due to calibration, shall be recorded.

Such adjustments are subjective, and while suggestions for addressing this are given in this document (see Annex E – Options for Editing Data’), they must be treated with caution.

Edited data shall be accorded a quality code of less than 500.

3.6.2.4 Supporting Data

In addition to the three DO data sets, supporting data used to make adjustments, e.g. temperature, and when essential, barometric pressure and salinity data, will also be stored or referenced.

3.7 Preservation of Record

3.7.1 Storage

The following data shall be archived and retained indefinitely:

- final checked and verified data – whether primary or backup
- unedited raw primary and backup data
- associated metadata, including
 - data comments
 - site details
 - recording accuracy and resolution
 - site/station inspections
 - equipment calibration history, and
 - any other factors affecting data quality.

All original records shall be retained indefinitely by the recording agency.

Note: The original raw data may be required at a later date should the archive data:

- *be found to be in error*
- *become corrupted, or*
- *be lost.*

3.7.2 Data Archiving

The archiving procedures, policies and systems of the archiving body shall consider:

- future data-format changes
- off-site duplication of records, and
- disaster recovery.

3.8 Quality Assurance

The information on quality assurance below is considered to be best practice. All agencies should implement a standard methodology for data audit and review.

Note: This is to ensure standardisation of data sets that enable meaningful analyses and comparison of DO data within regions, across regions and nationally.

3.8.1 Audit Cycle

Quality assurance processes shall include an audit of the data:

- at a frequency appropriate to the organisation's and users' needs, or
- as defined by the organisation's quality management systems documentation or documented procedures.

This work shall be undertaken by a suitably qualified and experienced practitioner.

Unaudited data that are released for use shall be identified as being unaudited.

Note: Stations other than those under review may be included in the audit to help with comparisons. Where available, reliable records from stations operated by other agencies may be used.

3.8.2 Minimum Audit Report Requirements

As a minimum, analyses and information required for an audit report for DO sites shall cover:

- site and deployment metadata details, including catchment (if applicable) and site details
- comments and quality coding attached to the records
- data tabulations, and
- data plots.

3.8.2.1 Catchment and Site Details

The following shall be included in the audit report:

- a site details summary, and
- a location map, with locations of in situ DO sensors identified.

The site details summary shall:

- identify the water body and catchment
- identify other DO data utilised in the audit report for comparison purposes or for generating missing records
- for each DO record, identify:
 - the period of record covered
 - the site name and number
 - the map reference
 - altitude, and
 - sensor type.

3.8.2.2 Comments and Quality Coding

The following shall be included in the audit report:

- for each DO record being reviewed, a copy of the filed comments for the total record periods, and
- a copy of the quality codes of all of the data being audited.

3.8.3 Other Requirements

3.8.3.1 Outputs

Recommended report outputs include:

- a hard copy report
- an electronic report, or
- at a minimum, an electronic document that only identifies which record periods have passed audit.

3.8.3.2 Audit Certification

The completed audit shall contain the name and signature of the auditor and the date that the audit was completed.

3.8.4 Comments and Quality Coding

The following shall be included in the audit report:

- for each abstraction being reviewed, a copy of the filed comments for the total recorded period, and
- a copy of the quality codes that have been applied to the data being audited.

Annex A – List of Referenced Documents

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Annex B – Measuring Devices

The following sensors are acceptable for the purpose of measuring dissolved oxygen (DO):

- electrochemical sensors, and
- optical sensors (optodes).

Purpose

The purpose here is to describe the major types of DO measuring instruments in use. It is expected that most agencies will use optical sensors for routine and continuous measurement of DO. Electrochemical sensors are still widely used, especially for handheld meters and check measurements.

Electrochemical Sensors

How They Work

Oxygen in the water diffuses across a permeable membrane and causes chemical reactions that are measured electrically inside the sensor.

DO is consumed by the electrode reactions within the sensor.

Additional stirring or a minimum water velocity is needed to maintain a fresh supply of test water at the surface of the sensor.

Electrochemical sensors are either 'galvanic' or 'polarographic' depending upon whether they measure a voltage change or a current.

The polarographic sensors are more likely to require stirring or running water for accurate measurement. A minimum velocity of 0.3 metres per second is usually required unless a stirrer is used.

Galvanic electrochemical sensors require a much smaller minimum flow rate, commonly 0.05 metres per second (50 centimetres per second).

Response times for electrochemical electrodes are 30 to 180 sec to reach 90% of the final value, depending on the sensor model. When response time increases it often means that the electrolyte should be replaced.

Optical Sensors (Optodes)

Optical sensors have a specially coated lens that produces different amounts of fluorescence relative to the DO concentration, when excited by a laser. They are also called luminescence sensors.

The DO signal is proportional to the amount of reflected light relative to a reference laser.

Optodes do not consume DO during measurements and don't require stirring or a minimum water velocity.

Unlike electrochemical sensors, optodes require little maintenance other than being kept clean and free of debris.

Response times for optodes vary between models and makes and are typically 60 to 150 seconds to reach 90% of the final value, depending on the sensor model.

Important Points to Consider

Follow the manufacturer's recommended maintenance requirements and procedures, in the first instance.

Routine checks should be carried out to keep sensors clean and free of debris. This will vary according to site.

All sensors shall be validated routinely to ensure they are performing accurately.

When considering prices of different sensors, the cost of not getting reliable data should also be taken into account. The costs of optode and electrochemical sensors are similar.

Some instruments have better stability and less drift of the DO signal than others.

Instrument performance may deteriorate depending on environmental factors.

Different uses include:

- deployment at a site for continuous measurement
- validation checks on continuous sensors using a calibrated DO sensor, and
- spot measurements made with handheld meters.

Optical Dissolved Oxygen

Figure 1 (right) shows a sensor manufactured by WTW. Other types of optode work in a similar way but may have different geometric configurations or use different wavelength reference lasers.

EPRS = Equal Path Reference System

The natural aging processes of the optical components can be compensated for by measuring the reference path and optical components and compensating in the measuring path. See (a), Figure 1.

Measuring the reference path as well as optical components allows natural aging processes of the optical components to be compensated for by measuring the reference path and compensating in the measuring path. See (a), Figure 1.

Green Light Technology

Bleaching of the fluorescent dye in the sensor electrochemical is avoided by stimulating the fluorescent reaction in the electrochemical with low-energy green light.1.

45 degree Technology

A horizontal slope of 45 degrees prevents a congestion of air bubbles in front of the electrochemical (a problem on first-generation optical probes). See (c), Figure 1.

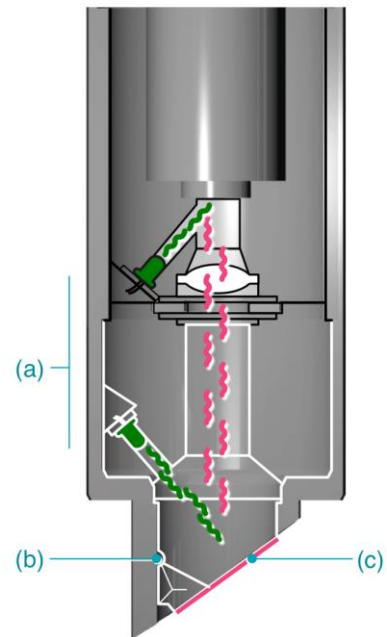


Figure 1 – Optical dissolved oxygen (luminescent or fluorescent method)

Illustration: Chris Heath.
(Based on an illustration from www.wtw.de)

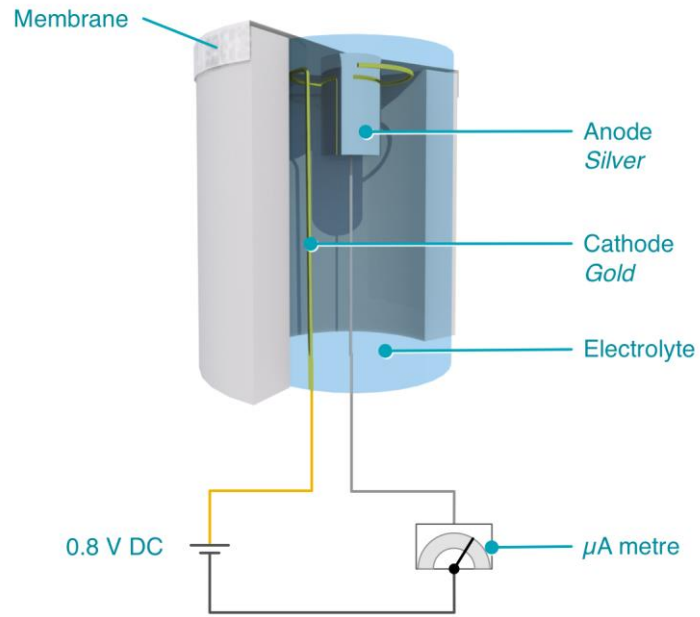


Figure 2 – Cutaway diagram showing the electrochemical (either galvanic or polarographic) method

Illustration: Chris Heath.

Clark Electrode

Oxygen is:

- diffused through a Teflon membrane, and
- reduced at a gold cathode.

The electrons flow equals the electrical signal. Oxygen concentration is proportional to signal level.

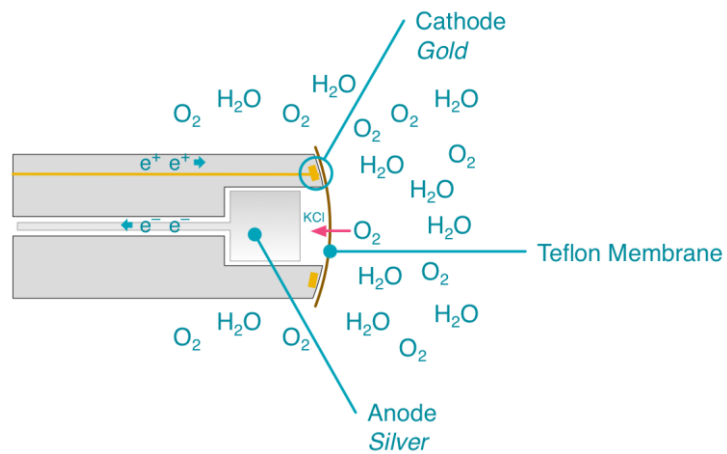


Figure 3 – How the Clark electrode works

Illustration: Chris Heath.


(Based on an illustration from YSI 556, YSI Pro Handheld brochures.)

Annex C – Sensor Calibration Table

Adapting Programme Design

To obtain data that are fit for purpose, adapt the programme design.

Table 5 – Higher-quality data versus lower-quality data

Higher-Quality Data		Lower-Quality Data
Frequent	Validation	Nil
Two Point	Calibration	Single Point
Yes	Calibrate at Field Temperature?	No
Available	Calibration System in the Field	Not Available
Regular	Checks via Telemetry or Field Visits	Nil
Yes	Event-Based Checks?	No

Annex D – Dissolved Oxygen Tables

Table 6 – Percentage change in saturation dissolved oxygen (DO)

With unit change in temperature, atmospheric pressure and salinity, at different temperatures.

Variable	Change in saturation DO (%)		
	5°C	10°C	20°C
Temperature (°C)	-2.24	-2.27	-1.94
Barometric Pressure (kPa) ¹	1.02	0.98	0.98
Salinity (‰)	-0.59	-0.56	-0.52

¹1013.25 millibar = 101.325 kPa = standard atmospheric pressure.

Note: An error of +1 °C in the water temperature reading results in an error of about -2% in the DO (percentage saturation) reading. The effect is slightly greater at cooler temperatures.

An error of +1 kPa in the barometric pressure reading corresponds to an error of about 1% in DO saturation.

An error of +1‰ in the salinity reading corresponds to an error in the percentage saturation DO of 0.5 to 0.6%. This effect lessens as water temperature increases.

**Table 7 – Corrections in saturation dissolved oxygen (DO)
for atmospheric pressure and altitude**

All pressures are in millibars.

<p>Barometric Correction – On Site</p> <p><i>Recommended</i></p>	$DO\%_{(\text{corrected})} = DO\%_{(\text{raw})} \times \frac{1013.25}{\text{Barometer}}$ <p>where:</p> <ul style="list-style-type: none"> • barometer = reading (mbar) not reduced to mean sea level.
<p>Barometric Correction – Nearby Site</p> <p><i>Recommend that barometer be within 30 km.</i></p>	$DO\%_{(\text{corrected})} = DO\%_{(\text{raw})} \times \frac{1013.25}{\text{Barometer} \times (1 - 2.25577 \times 10^{-5} h)^{5.25588}}$ <p>where:</p> <ul style="list-style-type: none"> • barometer = reading (mbar) of the nearest barometer not reduced to mean sea level, and • h = height above sea level of the monitoring site – height of the nearby barometer, in metres.
<p>Altitude Only Correction</p>	$DO\%_{(\text{corrected})} = DO\%_{(\text{raw})} \times \frac{1}{(1 - 2.25577 \times 10^{-5} h)^{5.25588}}$ <p>where:</p> <ul style="list-style-type: none"> • h = height above sea level of the monitoring site, in metres.

Note: These corrections are to be applied when the reference sensor has initially been calibrated at standard atmospheric pressure, or at sea level.

Table 8 – Comparison of detection levels and precisions for different dissolved oxygen (DO) measurement methods

Concentrations and specifications are cited from manufacturers' websites accessed in December 2010.

Method	Precision (mg l⁻¹)	Detection level (mg l⁻¹)	Range¹ (% saturation)	Reference
Winkler titration	± 0.05	0.01	0 to 100	APHA (2005), Environment
YSI Pro2030 handheld meter (galvanic or polarographic)	± 0.20	0.01	0 to 500	www.yisi.com
YSI Optical ODO probe	± 0.10	0.01	0 to 500	www.yisi.com
YSI ROX optode for sondes	± 0.10 (0 to 10) ± 3 to 5 (20 to 50)	0.01	0 to 500	www.yisi.com
Aanderaa 4835 optode	± 0.15	0.02	0 to 150	www.aadi.no
Hach LDO luminescent DO sensor	<1 mg l ⁻¹ : ± 0.1 mg l ⁻¹ ≥ 1 mg l ⁻¹ : ± 0.2 mg l ⁻¹	< 10 mg l ⁻¹ : ± 0.01 mg l ⁻¹ or ± 0.1% sat. ≥ 10 mg l ⁻¹ : ± 0.1 mg l ⁻¹ or ± 0.1% sat.	0 to 200	www.hach.com
Zebra-Tech D-opto optode	± 0.02 or 1%, whichever is greater	0.02	0 to 250	www.D-opto.com
WTW FDO® 700IQ (SW)	± 0.01	0.01	0 to 200	www.WTW.com
Eureka Manta 2 optode	±0.1 mg l ⁻¹ for <8 mg l ⁻¹ ±0.2 mg l ⁻¹ for 8 to 25 mg l ⁻¹	0.01 mg l ⁻¹	0 to 250	www.eurekaenviro nmental.com

¹Based on a saturation DO concentration of 10 mg l⁻¹ (i.e. at 15 °C).

Annex E – Options for Editing Data

Purpose

This annex is provided for information purposes only, and is not intended to constitute a standard. All data edited in this way shall be assigned a quality code QC 500 or less.

Note: The methods below are in a report by Wilcock et al. (2011).

Data Offset

Data offset occurs when the continuously recorded data differs from a reference measurement, usually made with a recently calibrated handheld dissolved oxygen (DO) meter.

Such data should be edited by adding or subtracting appropriately to get agreement with the reference (i.e. the most recently calibrated instrument; commonly a handheld meter).

If the amounts are different at the start and end of a data series, e.g. 5% at the start and 15% at the end, then first check if a continuous and linear correction can be made throughout the data set or if the edits should be from a particular time only. A linearly increasing offset of the DO data can be edited as follows:

$$DO_{\text{adjusted}} = DO_{\text{measured}} - \alpha$$

$$\alpha = \frac{\Delta_2 - \Delta_1}{t_2 - t_1}$$

Here, t_1 and t_2 are the start and end times corresponding to the respective differences, Δ_1 and Δ_2 , between measured and reference dissolved oxygen (DO) concentrations. See, for example, Figure 4.

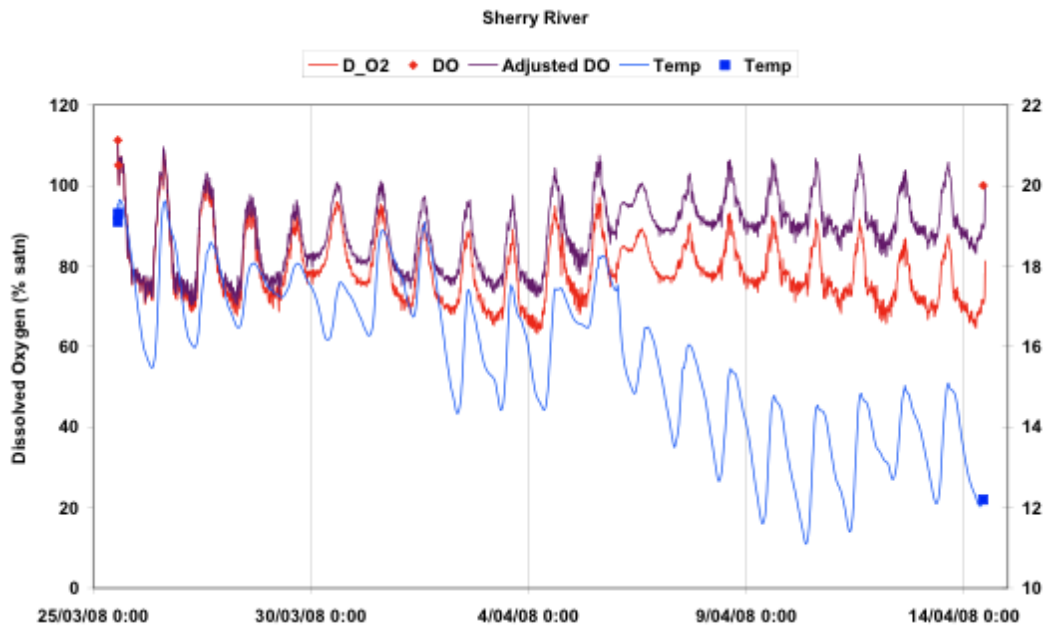


Figure 4 – Example of an edited dissolved oxygen (DO) time series

From a sonde deployment showing the original and edited DO data. Spot measurements for checking sonde data are shown as dark blue squares (temperature) and red diamonds (DO).

Source: Wilcock et al., 2011.

If the drift occurs sometime after the start of the record then the offset may be a constant value for the first part of the data set and vary according to the equations above for the second part. Stepwise linear edits may be made if three or more comparisons are made with reference devices that show that the drift is variable.

For any given data logger, this requirement may be reduced by performing regular checks with reference instruments and recalibrating as necessary until a safe period for reliable data acquisition is established. Historical data sets may be edited using this procedure provided suitable reference data exists.

Noise may be a response to environmental conditions, i.e. real, such as intermittent cloud cover, turbidity or something affecting the sensor like filamentous green algae, or it may be an artefact caused by sensor malfunction. The latter is usually characterised by increasingly poor performance that eventually provides unreadable data, whereas the former is often usable and can be analysed by smoothing diel data sets and ignoring spikes and troughs that deviate from the main curve (Figure 5).

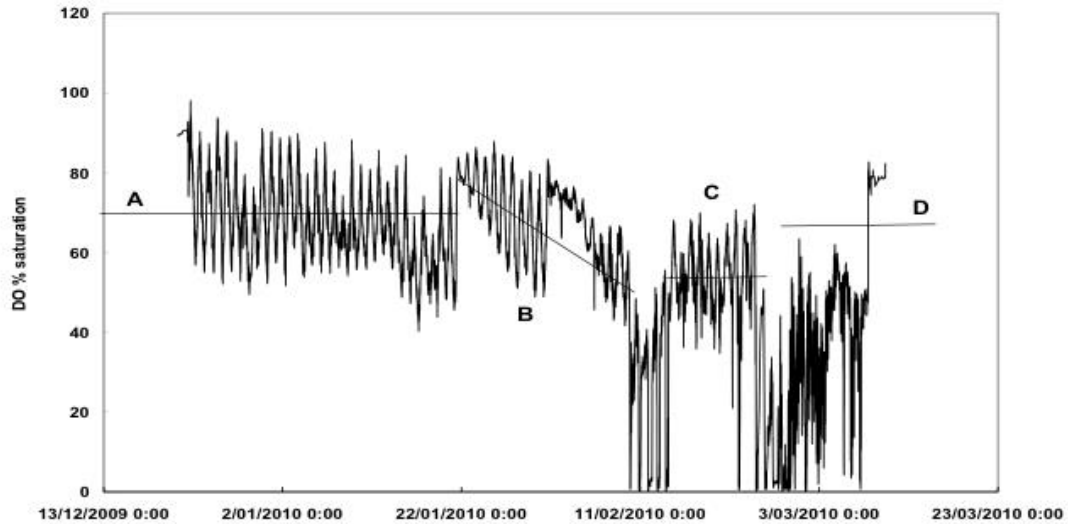


Figure 5 – Example of a dissolved oxygen (DO) Sonde time series
Showing good data (A), baseline drift (B), noisy data (C) and unusable noise (D).

Source: Wilcock et al., 2011.

To distinguish between real data and sensor failure, the noise associated with real data has a pattern that is ecologically feasible as a photosynthesis response by in-stream algae to a changing light regime. The noise should not be present on a clear day. It will never exceed the clear-day maximum and will have variable periods of high DO in bright sunshine with a lag in the DO reduction as cloud cover reduces the photosynthesis response. This pattern also includes low noise in the mornings and evenings, and no noise at night. Conversely, sensor failure noise can have rapid swings between high or low around the diel light cycle and at night.

Peak clipping occurs when in situ DO concentrations exceed the operational maximum of the instrument. Nothing can be done to improve data but there are usually diel curves within any given period that are not affected by clipping (Figure 6).

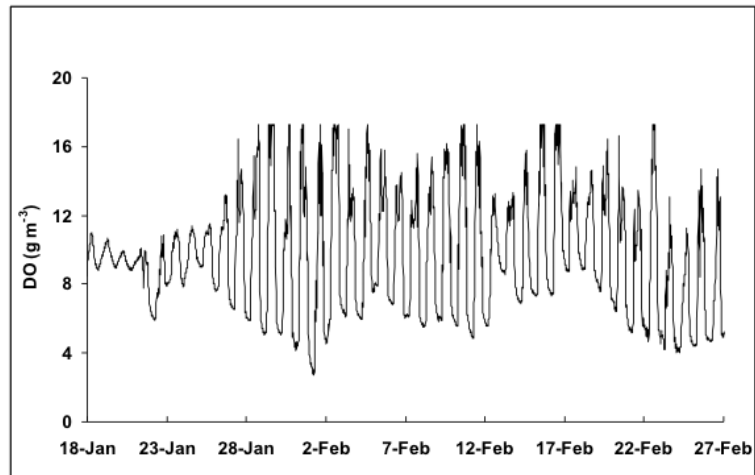


Figure 6 – Shag River dissolved oxygen (DO) time series

Collected with an optode in 2008. Note the clipping of peaks when DO concentration exceeds the instrument maximum of 17 g m⁻³.

Source: Wilcock et al., 2011.

Annex F – Data Tables

Table 9 – Variation of (%) saturation DO with barometric pressure and altitude

Source: YSI. (2009). *The dissolved oxygen handbook: A practical guide to dissolved oxygen measurements.*

Pressure		Altitude	Calibration Value
kPa	mbar	Meters	% Saturation
102.4	1023	-84	101
101.3	1013	0	100
100.3	1002	85	99
99.3	993	170	98
98.3	983	256	97
97.3	973	343	96
96.3	963	431	95
95.2	952	519	94
94.2	944	608	93
93.2	932	698	92
92.3	923	789	91
91.2	912	880	90
90.1	901	972	89
89.2	892	1066	88
88.1	881	1106	87
87.2	872	1254	86
86.1	861	1350	85

Pressure		Altitude	Calibration Value
kPa	mbar	Meters	% Saturation
85.1	851	1447	84
84.1	841	1544	83
83.1	831	1643	82
82.1	821	1743	81
81.1	811	1843	80
80.0	800	1945	79
79.1	791	2047	78
78.0	780	2151	77
77.1	771	2256	76
76.0	760	2362	75
74.9	749	2469	74
74.0	740	2577	73
73.0	729	2687	72
72.0	720	2797	71
71.0	709	2909	70
70.0	699	3023	69
69.0	689	3137	68
67.9	679	3371	67
66.9	669	3371	66

Table 10 – Solubility of oxygen in mg/l in water exposed to water-saturated air at 1013 mbar atmospheric pressure

Source: from YSI, 2009.

Temp °C	Chlorinity: 0	5.0 ppt	10.0 ppt	15.0 ppt	20.0 ppt	25.0 ppt
	Salinity: 0	9.0 ppt	18.1 ppt	27.1 ppt	36.1 ppt	45.2 ppt
0.0	14.621	13.728	12.888	12.097	11.355	10.657
1.0	14.216	13.356	12.545	11.783	11.066	10.392
2.0	13.829	13.000	12.218	11.483	10.790	10.139
3.0	13.460	12.660	11.906	11.195	10.526	9.897
4.0	13.107	12.335	11.607	10.920	10.273	9.664
5.0	12.770	12.024	11.320	10.656	10.031	9.441
6.0	12.447	11.727	11.046	10.404	9.799	9.228
7.0	12.139	11.442	10.783	10.162	9.576	9.023
8.0	11.843	11.169	10.531	9.930	9.362	8.826
9.0	11.559	10.907	10.290	9.707	9.156	8.636
10.0	11.288	10.656	10.058	9.493	8.959	8.454
11.0	11.027	10.415	9.835	9.287	8.769	8.279
12.0	10.777	10.183	9.621	9.089	8.586	8.111
13.0	10.537	9.961	9.416	8.899	8.411	7.949
14.0	10.306	9.747	9.218	8.716	8.242	7.792
15.0	10.084	9.541	9.027	8.540	8.079	7.642
16.0	9.870	9.344	8.844	8.370	7.922	7.496
17.0	9.665	9.153	8.667	8.207	7.770	7.356

Temp °C	Chlorinity: 0	5.0 ppt	10.0 ppt	15.0 ppt	20.0 ppt	25.0 ppt
	Salinity: 0	9.0 ppt	18.1 ppt	27.1 ppt	36.1 ppt	45.2 ppt
18.0	9.467	8.969	8.497	8.049	7.624	7.221
19.0	9.276	8.792	8.333	7.896	7.483	7.090
20.0	9.092	8.621	8.174	7.749	7.346	6.964
21.0	8.915	8.456	8.021	7.607	7.214	6.842
22.0	8.743	8.297	7.873	7.470	7.087	6.723
23.0	8.578	8.143	7.730	7.337	6.963	6.609
24.0	8.148	7.994	7.591	7.208	6.844	6.498
25.0	8.263	7.850	7.457	7.093	6.728	6.390
26.0	8.113	7.711	7.327	6.962	6.615	6.285
27.0	7.968	7.575	7.201	6.845	6.506	6.184
28.0	7.827	7.444	7.079	6.731	6.400	6.085
29.0	7.691	7.317	6.961	6.621	6.297	5.990
30.0	7.559	7.194	6.845	6.513	6.197	5.896
31.0	7.430	7.073	6.733	6.409	6.100	5.806
32.0	7.305	6.957	6.624	6.307	6.005	5.717
33.0	7.183	6.843	6.518	6.208	5.912	5.631
34.0	7.065	6.732	6.415	6.111	5.822	5.546
35.0	6.950	6.624	6.314	6.017	5.734	5.464
36.0	6.837	6.519	6.215	5.925	5.648	5.384
37.0	6.727	6.416	6.119	5.835	5.564	5.305

Temp °C	Chlorinity: 0	5.0 ppt	10.0 ppt	15.0 ppt	20.0 ppt	25.0 ppt
	Salinity: 0	9.0 ppt	18.1 ppt	27.1 ppt	36.1 ppt	45.2 ppt
38.0	6.620	6.316	6.025	5.747	5.481	5.228
39.0	6.515	6.217	5.932	5.660	5.400	5.152
40.0	6.142	6.121	5.842	5.576	5.321	5.078
41.0	6.312	6.026	5.753	5.493	5.243	5.005
42.0	6.213	5.934	5.667	5.411	5.167	4.993
43.0	6.116	5.843	5.581	5.331	5.091	4.861
44.0	6.021	5.753	5.497	5.252	5.017	4.793
45.0	5.927	5.665	5.414	5.174	4.994	4.724
46.0	5.835	5.578	5.333	5.097	4.872	4.656
47.0	5.744	5.493	5.252	5.021	4.801	4.589
48.0	5.654	5.408	5.172	4.947	4.730	4.523
49.0	5.565	5.324	5.094	4.872	4.660	4.457
50.0	5.477	5.242	5.016	4.799	4.591	4.392

Annex G – Dissolved Oxygen Saturation Calculations

A widely used equation relating equilibrium (saturation) dissolved oxygen (C_s) to temperature (T in K = °C + 273.15) and salinity (S) is given by APHA (2005), as follows:

$$\ln C_s = -139.344 + (1.575701 \times 10^5 / T) - (6.642308 \times 10^7 / T^2) + (1.243800 \times 10^{10} / T^3) - (8.621949 \times 10^{11} / T^4) - S[(1.7674 \times 10^{-2}) - (1.0754 \times 10^1 / T) + (2.1407 \times 10^3 / T^2)]$$

where: $\ln C_s$ is the natural logarithm (base e) of C_s .

For example, when the temperature is 20 °C ($T=293.15$ K) and salinity is 0 ppt, C_s is 9.09 mg/l; and at 20 °C and a salinity of 30 ppt, C_s is 7.62 mg/l.

Conversion Calculations

The following are conversion calculations:

$$\text{DO mg/l} = \text{DO\%} / 100 * (14.621 + (-0.4094 * t) + (0.0087 * t^2) + (-0.0001 * t^3) + (0.0000002 * t^4))$$

$$\text{DO\%} = \text{DO mg/l} * 100 / (14.621 + (-0.4094 * t) + (0.0087 * t^2) + (-0.0001 * t^3) + (0.0000002 * t^4))$$

where: t = temperature in degrees Celsius.



NEMS

