

National Environmental Monitoring Standards

Dissolved Oxygen Recording

Measurement, Processing and Archiving of
Dissolved Oxygen Data

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NEMS

NEMS Standards Documents

The following standards can be found at www.landandwater.co.nz.

- National Quality Coding Schema
- Safe Acquisition of Field Data In and Around Fresh Water
Code of Practice
- Dissolved Oxygen Recording
Measurement, Processing and Archiving of Dissolved Oxygen Data
- Open Channel Flow Measurement
Measurement, Processing and Archiving of Open Channel Flow Data
- Rainfall Recording
Measurement, Processing and Archiving of Rainfall Intensity Data
- Soil Water Measurement
Measurement, Processing and Archiving of Soil Water Content Data
- Turbidity Recording
Measurement, Processing and Archiving of Turbidity Data.
- Water Level Recording
Measurement, Processing and Archiving of Water Level Data
- Water Meter Data
Acquisition of Electronic Data from Water Meters for Water Resource Management
- Water Temperature Recording
Measurement, Processing and Archiving of Water Temperature Data

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.

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When implementing these standards, the following act, regulations and code of practice shall be complied with:

- Health and Safety in Employment Act 1992
- Health and Safety in Employment Regulations 1995
- NEMS Safe Acquisition of Field Data In and Around Fresh Water, Code of Practice 2012

National Environmental Monitoring Standards (NEMS)

The National Environmental Monitoring Standards steering group (NEMS) has prepared a series of environmental monitoring standards on authority from the Regional Chief Executive Officers (RCEO) 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). The implementation of the strategy has been overseen by a steering group consisting of Jeff Watson, Rob Christie, Jochen Schmidt, Martin Doyle, Phil White, Mike Ede, Glenn Ellery, Lian Potter, Lucy Baker, Eddie Stead and David Payne.

The development of these standards involved consultation with regional and unitary councils across New Zealand, 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.

The lead writer of this document was Bob Wilcock of the National Institute of Water and Atmospheric Research Ltd, with workgroup members, David Brown of Horizons Regional Council, Mike McMurtry and Phil White of Auckland Council. 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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- Tasman District Council
- West Coast Regional Council
- Waikato Regional Council

Review

This document will be reviewed by the NEMS steering group in February 2014, and thereafter once every two years.

Signatories

NEMS Project Director	NEMS Chairman	MFE	NIWA	Workgroup Leader
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TABLE OF CONTENTS

Definitions	iii
About this Standard	v
The Standard – Dissolved Oxygen Recording.....	vii
Quality Codes – Dissolved Oxygen Recording	x
1 Site Selection and Deployment.....	1
1.2 Practical Controls	2
1.3 Rivers	3
1.4 Lakes, Estuaries and Coastal Waters	4
1.5 Groundwater	6
1.6 Sensors	7
2 Data Acquisition.....	11
2.2 Measurement	12
2.3 Calibration	14
2.4 Validation	18
2.5 Maintenance.....	21
3 Data Processing and Preservation	23
3.2 Quality Coding Dissolved Oxygen Data	24
3.3 Data Storage	27
3.4 Preservation of Record	28
3.5 Quality Assurance.....	30
Annex A – List of Referenced Documents	33
Annex B – Measuring Devices.....	34
Annex C – Sensor Calibration Table	38
Annex D – Dissolved Oxygen Tables.....	39
Annex E – Options for Editing Data	41
Annex F – Data Tables	44

Annex G – Dissolved Oxygen Saturation Calculation	48
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Definitions

accuracy The degree of closeness of a measurement to the actual value.

adjusted data Data that takes into account the effects of temperature, salinity, altitude and barometric pressure.

barometric pressure The current pressure of the atmosphere, measured in hectopascals (hPa) or millibars (numerically the same).

calibration The process of determining, checking, or rectifying the quantitative measurements of any instrument.

comments file A metadata file associated with the data file. The metadata provides relevant information about the site and data.

concentration Dissolved oxygen is expressed either as milligrams per litre (mg L⁻¹, mg/L), or as % saturation (the % ratio of the concentration to that in equilibrium with the atmosphere).

DO Acronym for dissolved oxygen

edited data Data that may have been altered to correct for changes in baseline (drift), or been smoothed, or changed as a result of calibration or validation checks

flow cell An enclosed vessel into which groundwater is pumped, which also houses water quality sensors, to isolate the fluid from the surface environment, and ensure minimal aeration.

instantaneous measurement A measurement or average of a series of measurements spanning a period defined by the response time of the sensor. This may be up to 360 seconds per measurement.

in situ sensor A sensor that is mounted 'permanently' for measuring DO, as opposed to a hand held sensor.

metadata Information about the data that may describe the content, quality, condition and/or other characteristics of the data.

optode An optical electrode device for measuring dissolved oxygen in water. They are also called luminescence sensors.

QC Abbreviation for quality code. For example, a quality code of 600 may be referred to as QC 600

quality codes An overlying set of associated information that provide the end user with information about the quality of the data.

precision The degree to which repeated measurements under unchanged conditions show the same results.

resolution The smallest increment that is measurable by a scientific instrument.

response time The time required, by the instrumentation, for a measurement.

salinity The total amount of solids dissolved in one kilogram of water, expressed in parts per thousand (‰)

saturation The concentration of dissolved oxygen in equilibrium with the atmosphere.

site The geographical location of the measurement.

stationarity of record The quality of a process in which the statistical parameters of the process do not change with time. Stationarity of record is maintained when variability, of the parameter being measured, is only caused by the natural processes associated with the parameter. Stationarity of record ceases when variability is caused or affected by other processes.

supersaturation Where the oxygen content in the water body is greater than for atmospheric equilibrium.

tolerance The range of variance between two measurements that is permitted or which defines agreement.

validation A check to determine if the device or procedure conforms to specifications.

About this Standard

Introduction

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

Dissolved oxygen is subject to many influences. These include wastewater discharges, plant (including algae) growth and respiration, and urban runoff. Dissolved oxygen data can provide information about organic inputs to water bodies and their capacity to cope with them. Dissolved oxygen 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 is '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 dissolved oxygen (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 that 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 dissolved oxygen. Councils used them widely for monitoring compliance of water rights and for characterising water quality. These early sondes had membrane electrodes that 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 dissolved oxygen variation throughout the year. Modern sondes using optode technology are now routinely used by water monitoring agencies. Key to planning, maintaining and recording dissolved oxygen is understanding and catering for stationarity.

When measuring DO attention should also be drawn to the NEMS Water Temperature Recording Standards.

Objective

The objective of this standard is to ensure that continuous measurement of dissolved oxygen data, is gathered, processed, archived and quality assured consistently across New Zealand

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 dissolved oxygen data
- validation of field measurements
- data processing, and
- quality assurance (QA) that is undertaken prior to archiving the data.

The Standard – Dissolved Oxygen Recording

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		$\text{mg L}^{-1} (\text{mg/L})$ <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		°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>	$\pm 0.10 \text{ mg L}^{-1}$
		<i>Measurements greater than 10 mg L^{-1}</i>	$\pm 1 \text{ mg L}^{-1}$
	Saturation	<i>Measurements less than 10%</i>	$\pm 0.5\%$
		<i>Measurements in the range 10% to 100%</i>	$\pm 1\%$
		<i>Measurements greater than 100%</i>	$\pm 10\%$

Continued on next page...

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>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	Recommended for high precision measurements.
	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	- 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 manufacturers' specification for each instrument, or as a reliable default: The preferred method is a 2-point calibration as defined within this standard.

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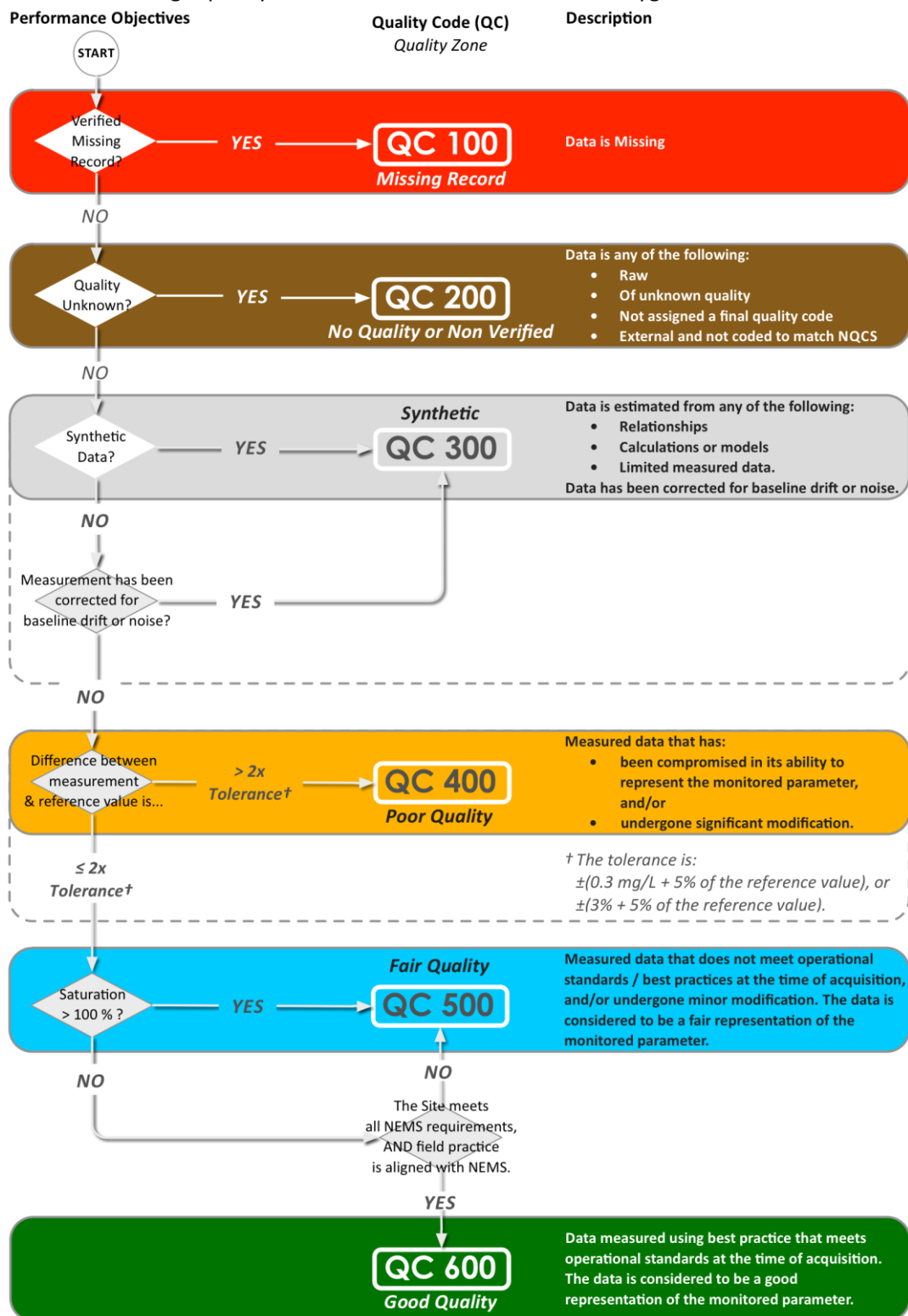
Metadata		Metadata shall be recorded for all measurements.
Quality Assurance		<i>Quality assurance requirements are under development</i>
Processing of Data		All changes shall be documented. All data shall be quality coded as per Quality Flowchart.

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: • Raw and processed records • Primary reference data • Supplementary measurements • Validation checks • Smoothing or baseline adjustments • Site inspections • Calibration results • Metadata
Auditing		<i>Quality assurance requirements are under development.</i>

Quality Codes – Dissolved Oxygen Recording

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 (Page 26).

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
- ground waters.

1.1.2 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, e.g., 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 dissolved oxygen remain without bias over the lifetime of the record. For example, errors in temperature measurements may give a false impression about trends in dissolved oxygen per cent 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 dissolved oxygen, the external reference is another device that has been recently calibrated or validated under optimal conditions.

1.2 Practical Controls

1.2.1.1 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.

1.2.1.2 Safety

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

1.2.1.3 Hazard Review

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

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

1.2.1.4 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.

1.3 Rivers

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

1.3.1 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.

1.3.2 Selected Site

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.

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% dissolved oxygen.

1.3.3 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, nor
- where it is at risk, e.g., 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.

1.4 Lakes, Estuaries and Coastal Waters

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

1.4.1 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, e.g. 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 dissolved oxygen measurements.

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.

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, nor
- where it is at risk, e.g., 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 dissolved oxygen 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 dissolved oxygen may vary with depth (because of stratification) in lakes and reservoirs.

1.5 Groundwater

1.5.1 Selecting a Site

When choosing a groundwater site for dissolved oxygen 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 salt-water intrusion, then salinity must also be measured.

1.5.2 Selected Site

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 (water is regularly pumped from the bore)
- salinity of the water, and
- whether the site is affected by tides.

1.5.3 Deployment of Sensors in a Groundwater Bore

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

For more information, see: '2 Data Acquisition':

- 'Water Pumped to Surface'
- 'Sub-Surface Measurements', and
- 'Low Flow Measurements'.

1.6 Sensors

1.6.1 Some sensors measure dissolved oxygen and or some of the following parameters concurrently and calculate dissolved oxygen values to compensate for:

- temperature
- salinity, and
- barometric pressure.

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

Continued on next page...

	Electrochemical Sensors	Optodes (Optical Sensors)
Susceptible to gases such as hydrogen sulphide?	Yes <i>Note: Some gases cause erratic measurements</i>	No
Maintenance	The electrodes require periodic maintenance and new electrolyte solution.	Requires less maintenance than electrochemical sensors.
Durability	Subject to regular maintenance.	Unknown.

1.6.3 Required Precision

For measuring concentration, the required precision of a (electrochemical or optode) dissolved oxygen 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 $1\text{-}10 \text{ mg L}^{-1}$, and
- $\pm 1\%$ for measurements greater than 10 mg L^{-1} .

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

- $\pm 0.5\%$ for measurements less than 10%
- $\pm 1\%$ for measurements in the range 10-100%, 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 dissolved oxygen. It is assumed by manufacturers that dissolved oxygen 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 dissolved oxygen 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 '.

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 measurements are affected by:

- temperature
- barometric pressure, and
- altitude.

Some dissolved oxygen measurements are affected by salinity.

2.2.1 Temperature

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

2.2.2 Barometric Pressure

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

Note: Barometric pressures are normally within the range of 95-105 kPa (950 millibar to 1050 millibar) corresponding to a saturation dissolved oxygen 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 dissolved oxygen decreases by about 1% for every 100 m increase in altitude above sea level. For more information, see Table (Page 44), and '2.3 Calibration').

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 dissolved oxygen measurements shall all be logged simultaneously.

Salinity shall be recorded for every dissolved oxygen 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.

Note: Estuarine and harbour waters are likely to have variable amounts of freshwater and salt water depending on the tide and sensor location. At a salinity of 8 parts per thousand, saturation dissolved oxygen 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 dissolved oxygen.

Note: The formula to calculate standing bore volume is:

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

where r = radius of bore casing (in metres)

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

- dissolved oxygen measurements in purged samples shall be 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 dissolved oxygen 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 0.1-1.0 litres per minute are normally used.

After purging the pump tubing, dissolved oxygen measurements shall be comprise three consecutive stable readings made three to five minutes apart.

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

Dissolved oxygen saturation varies with temperature.

Temperature shall always be recorded when calibrating dissolved oxygen sensors.

The temperature sensor shall be accurate to within $\pm 0.5^{\circ}\text{C}$.

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 & Altitude

Dissolved oxygen 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
- 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 % 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 % 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.

Example:

For a barometric pressure of 987 millibar, 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 % saturation for altitude and barometric pressure are given in .

2.3.4 Salinity

Dissolved oxygen is affected by salinity. Manufacturers' user guides explain how this should be allowed for when calibrating a sensor.

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

Note: Oxygen solubility is lower in saline waters than freshwater. For example saturation dissolved oxygen 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 manufacturers' specification for each instrument, or
- a 2-point calibration using air saturated water or saturated air for 100% and a deoxygenated solution for the zero.

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

- Winkler method
- Air-saturated water

– 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 most common and are usually conducted with water that is 100% saturated with dissolved oxygen. Two-point calibrations mostly use water with zero dissolved oxygen (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 dissolved oxygen test solution.

2.3.7.1 Winkler Method

The Winkler method calibrates the mg L^{-1} concentration value; the air-saturated water and water-saturated air methods both calibrate the % saturation reading.

The Winkler method is an accurate but time-consuming way of analysing dissolved oxygen in water by chemical titration. It is best suited to the laboratory. Sensors are calibrated by being adjusted to agree with accurately known dissolved oxygen 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 dissolved oxygen 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., two litres, from one bucket to another for ten to twenty 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
- a small amount of water in a sponge, and
- when the reading has stabilised, setting the dissolved oxygen 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 dissolved oxygen sensors, can prevent loss of data by identifying faulty field equipment. Steps can then be taken to rectify the problem.

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 dissolved oxygen 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 manufacturers recommendations, unless observations suggest it should be more frequent.*

If cleaning is required, a pre and post validation 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 re-calibration 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: 'NEMS Water Temperature Recording – Measurement, 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 manufacturer's recommendations, and any differences shall be logged.

2.4.5 Operational Standard for Dissolved Oxygen Measurements

2.4.5.1 Concentration

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

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 4.45-5.55 mg L^{-1} is deemed to have passed the validation check.

2.4.5.2 % Saturation

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

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 44.5-55.5% is deemed to have passed the validation check.

Table 2 provides information on validation tolerances for dissolved oxygen 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 dissolved oxygen 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 dissolved oxygen 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 acceptably 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, e.g., 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
- a 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, data processing, editing, final archiving and auditing.

Essential information that needs to be collected comprises 'metadata' (information about where and when the dissolved oxygen 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.

3.1.2 Field Data

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

3.1.3 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'.

3.2 Quality Coding Dissolved Oxygen Data

3.2.1 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.

3.2.2 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
 - 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.

3.2.3 Data that Does Not Meet the Standard

Any data that is collected from equipment that does 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.

3.2.4 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 Recording', earlier in this document.

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

Methods for calibrating sensors for dissolved oxygen 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 'measureable' values may be 200% to 600% saturation depending on the brand of dissolved oxygen sensor.

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

A maximum quality code of 500 shall be applied to dissolved 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

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)	0.7
2	0.40	(0.40 to 0.80)	0.8
3	0.45	(0.45 to 0.90)	0.9
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: 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) differs by less than standard. Fair quality data (QC 500) differs by 1-to-2 times the standard. Poor Quality data (400) differs from the reference value by more than twice the standard. The same is true for concentration values (mg L⁻¹) in the last four columns.

3.3 Data Storage

3.3.1 Storage

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

3.3.2 Data Files

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

- raw data
- adjusted dataset
- edited dataset.

3.3.2.1 Raw Data

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

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

- Temperature
- Barometric pressure
- Salinity
- Altitude.

3.3.2.2 Adjusted Dataset

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

3.3.2.3 Edited Dataset

Edits may include one or both of the following:

- Changes in baseline due to sensor drift and/or ramping.
That is, where the baseline drifts steadily up or down.
- Smoothing of noisy data.
- Any data edits, for example, 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.

3.3.2.4 Supporting Data

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

3.4 Preservation of Record

3.4.1 Performance

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*
- *becomes corrupted, or*
- *be lost.*

3.4.2 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.

3.4.2.1 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
 - Standard and defined coordinate system (preferably WGS 84) shall be used.*
- 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.*
- start and end date of site and record
 - Recorded using New Zealand standard time (NZST)*
- related sites and records, and
- reference to the standard and version used

3.4.2.2 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
Preferably through an agency instrument management system.
- original format details
For example: chart or digitised format details.
- logger and telemetry details
- calibration records
Preferably through 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.

3.5 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 dissolved oxygen data within regions, across regions and nationally.

3.5.1 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 is released for use shall be identified as being unaudited.

Where available, reliable records of dissolved oxygen reported from other sites may be used.

3.5.2 Minimum Audit Report Requirements

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

- site details
- comments and quality coding
- data tabulations, and
- data plots.

3.5.2.1 Catchment and Site Details

The following shall be included in the audit report:

- Site Details Summary
- A location map, with locations of in-situ dissolved oxygen sensors identified.

The location details summary shall:

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

3.5.2.2 Comments and Quality Coding

The following shall be included in the audit report:

- For each dissolved oxygen record being reviewed, a copy of the filed comments for the total record periods.
- A copy of the quality codes of all of the data being audited.

3.5.3 Other Requirements

3.5.3.1 Outputs

Recommended report outputs include:

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

3.5.3.2 Audit Certification

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

Annex A – List of Referenced Documents

APHA, AWWA, WEF (2005). *Standard methods for the examination of water and wastewater*, 21st ed. Water Environment Federation, Alexandria, VA, USA.

Eureka (2007). Manta2 Optical Dissolved Oxygen Sensor data sheet.

http://eurekaenvironmental.com/Dissolved_Oxygen_Optical.html

Hach (2007). Hach LDO dissolved oxygen data sheet.

http://www.wastewatercanada.com/Products/Hach/Parameters_Process/LDO-Spec.pdf

Lewis ME (2006). USGS Field Manual Version 2.1. Chapter A6 Field Measurements, Section 6.2 Dissolved Oxygen. US geological Survey, 48pp.

http://water.usgs.gov/owq/FieldManual/Chapter6/6.2_v2.1.pdf

WTW (2012). WTW laborprodukte und on-line messtechnik – dissolved oxygen.

<http://www.wtw.de/us/products/lab/dissolved-oxygen.html>

Wilcock B, Gibbs M, McBride G, Young R (2011). *Continuous measurement and interpretation of dissolved oxygen data in rivers*. Prepared for Horizons Regional Council. NIWA Client Report HAM2011-010.

YSI (2009). *The Dissolved Oxygen Handbook: a practical guide to dissolved oxygen measurements*. Yellow Springs Instruments Inc. www.ysi.com. 76pp.

YSI (2010). YSI 556 MPS Multi Probe System – Operations Manual. Yellow Springs Instruments Inc. 120pp.

Zebra-Tech (undated). D-Opto Dissolved Oxygen Sensor Operation Manual.

<http://www.globalw.com/downloads/WQ/D-OptoManual.pdf>

Annex B – Measuring Devices

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

- Electrochemical sensors
- 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 dissolved oxygen. Electrochemical sensors are still widely used, especially for hand-held 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.

Dissolved oxygen 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 30-180 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 dissolved oxygen concentration, when excited by a laser. They are also called luminescence sensors.

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

Optodes do not consume dissolved oxygen 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 dissolved oxygen 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 dissolved oxygen sensor, and
- spot measurements made with hand-held 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

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

By stimulating the fluorescent reaction in the electrochemical with low energy green light, a bleaching of the fluorescent dye in the sensor electrochemical is avoided. See (b), Figure 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.

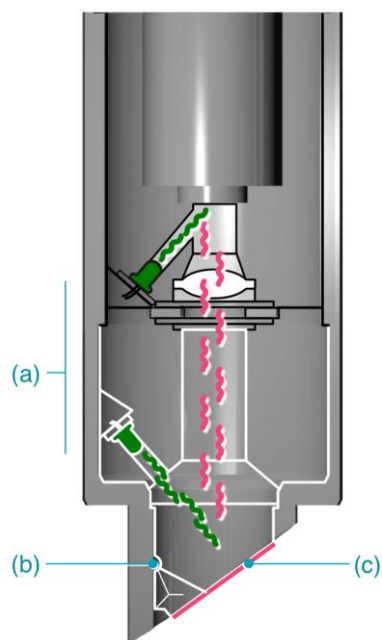


Figure 1 – Optical Dissolved Oxygen (luminescent or fluorescent method).

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

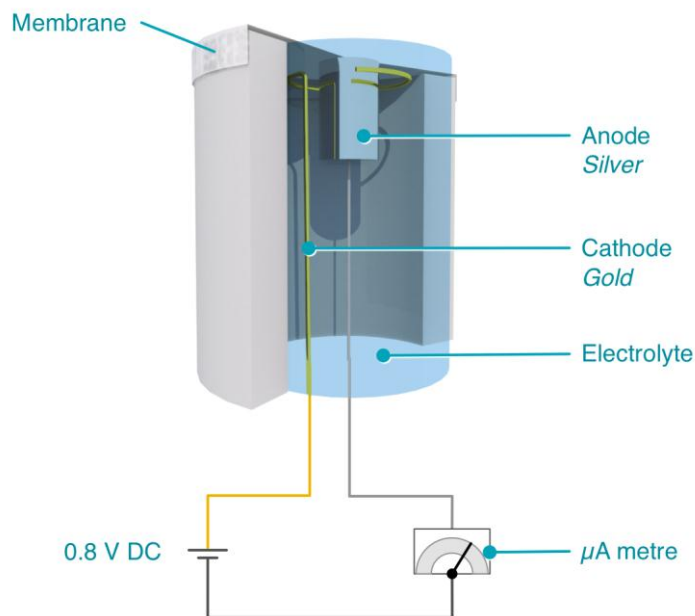


Figure 2 – Cutaway Diagram Showing the Electrochemical (either galvanic or polarographic) method.

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.

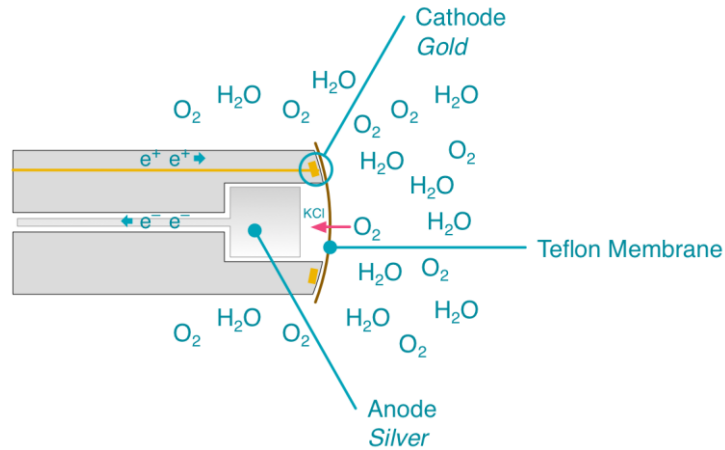


Figure 3 –How the Clark Electrode Works

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 is fit for purpose, adapt the programme design.

Table 5 – High Quality Data vs. Low 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 (% 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 % saturation DO of 0.5-0.6%. This effect lessens as water temperature increases.

Table 7 – Corrections in Saturation Dissolved Oxygen (DO) for Atmospheric Pressure and Altitude.

All pressures are in millibar.

Barometric Correction - On Site <i>Recommended</i>	$DO\%_{(corrected)} = DO\%_{(raw)} \times \frac{1013.25}{\text{Barometer}}$ Where: Barometer = reading (mbar) not reduced to mean sea level
Barometric Correction Nearby Site <i>Recommend that barometer be within 30 km.</i>	$DO\%_{(corrected)} = DO\%_{(raw)} \times \frac{1013.25}{\text{Barometer} \times (1 - 2.25577 \times 10^{-5} h)^{5.25588}}$ Where: - 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.
Altitude Only Correction	$DO\%_{(corrected)} = DO\%_{(raw)} \times \frac{1}{(1 - 2.25577 \times 10^{-5} h)^{5.25588}}$ Where: h = height above sea level of the monitoring site, in metres

Note: These corrections are to be applied when the 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)	Range ¹ (% 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.ysi.com
YSI Optical ODO probe	± 0.10	0.01	0 to 500	www.ysi.com
YSI ROX optode for sondes	± 0.10 (0 to 10) ± 3 to 5 (20 to 50)	0.01	0 to 500	www.ysi.com
Aanderaa 4835 optode	± 0.15	0.02	0 to 150	www.aadi.no
Hach LDO luminescent DO sensor	Below 1 mg L ⁻¹ : ± 0.1 mg L ⁻¹ Above 1 mg L ⁻¹ : ± 0.2 mg L ⁻¹	Below 10 mg L ⁻¹ : ± 0.01 mg L ⁻¹ or ± 0.1% sat. Above 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 8-25 mg L ⁻¹	0.01 mg L ⁻¹	0 to 250	www.eurekaenvironmental.com

¹Based on a saturation dissolved oxygen 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 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 concentrations, e.g., Figure 4.

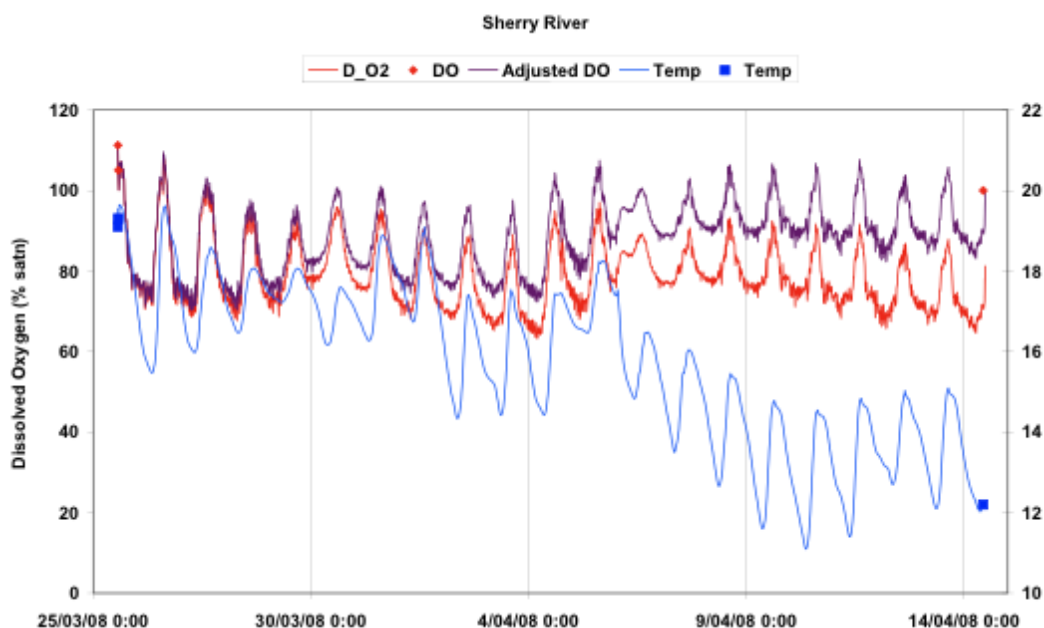


Figure 4 – Example of an Edited Dissolved Oxygen (DO) Time Series

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) (taken from 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 datalogger, 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 exist.

Noise may be a response to environmental conditions, i.e., real; such as intermittent cloud cover, turbidity or something affecting the sensor, e.g., 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).

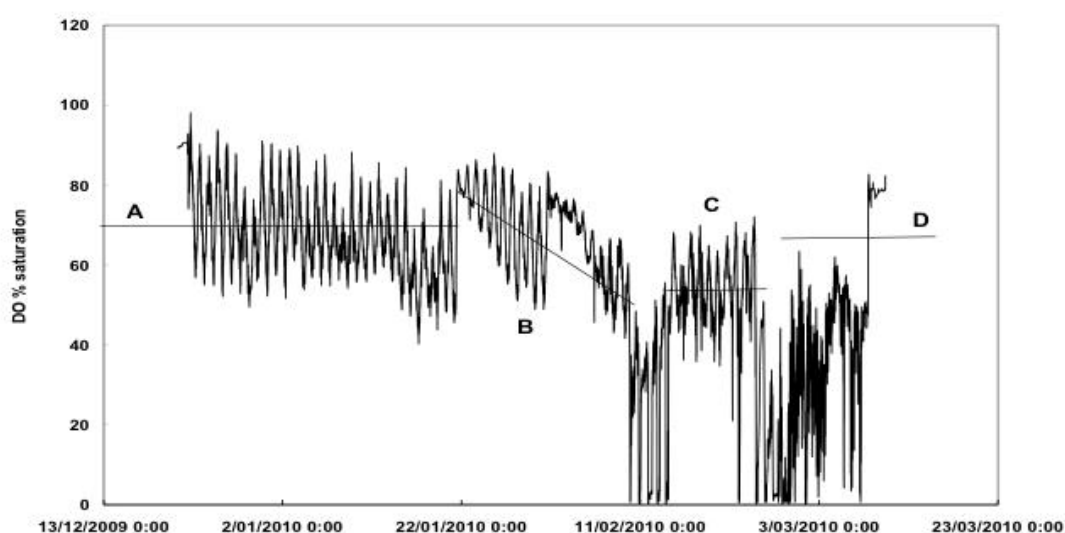


Figure 5 – Example of a Dissolved Oxygen (DO) Sonde Time-Series
Showing good data (A), baseline drift (B), noisy data (C) and unusable noise (D)
(taken from Wilcock et al. 2011).

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).

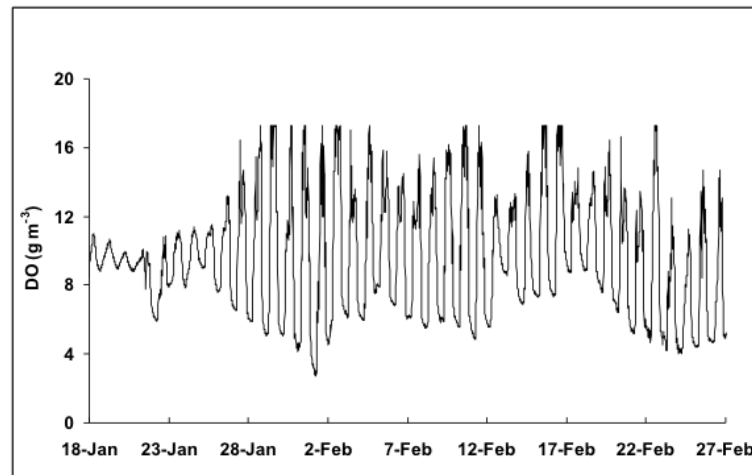


Figure 6 – Shag River Dissolved Oxygen (DO) Time-Series.

Collected with an optode in 2008. Note the clipping of peaks when DO concentration exceeds the instrument maximum of 17 g m^{-3} (taken from Wilcock et al. 2011).

Annex F – Data Tables

Table 9 –Variation of (%) saturation DO with barometric pressure and altitude (from YSI 2009).

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	913	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
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

Pressure		Altitude	Calibration Value
kPa	mbar	Meters	% Saturation
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 (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	10.027	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
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

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
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
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 Calculation

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

$$\ln C_s = -139.344 + (1.575701 \times 10^5 / T) - (6.642308 \times 10^7 / T^2) + (1.243800 \times 10^{10} / T^3) - (8.621949 \times 10^{11} / T^4) \\ - S[(1.7674 \times 10^{-2}) - (1.0754 \times 10^{-5} / T) + (2.1407 \times 10^{-8} / T^2)]$$

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

For example, when the temperature is 20°C ($T=293.15^{\circ}\text{K}$) and salinity is 0 ppt, C_s is 9.09 mg/L. At 20°C and a salinity of 30 ppt, C_s is 7.62 mg/L.



NEMS

