Continuous measurement & interpretation of dissolved oxygen data in rivers

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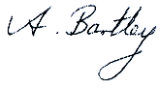

1. Executive summary

This report addresses a number of questions raised at a meeting convened by Horizons Regional Council (HRC) in 2010 regarding the measurement of dissolved oxygen (DO) in rivers and the interpretation of DO data. In particular, requirements for sound protocols regarding the deployment of continuous DO datalogging equipment, quality assurance and control methods to ensure that recorded data was of suitable quality, and for some discussion of how that data might be analysed to describe ecosystem state in rivers were identified. The emphasis of the report has been on equipment currently used by HRC and on their use for continuous monitoring of DO. Full answers to these questions are given throughout the report and are summarised in section 10, Conclusions and Recommendations. The following is a list of key points from the report:

- Dissolved oxygen (DO) is a key water quality variable that describes the suitability of a given water body for supporting a healthy ecosystem. Trout are the most sensitive of fish common to the Horizons region and may exhibit moderate-severe impairment when DO is 40-80% saturation, or less. Acute toxicity DO limits are usually set at 3-6 mg/L (30-60% saturation at 15°C).
- New Zealand native species are generally less sensitive to DO concentrations than trout, but stream invertebrates may show adverse effects at concentrations below 50% saturation.
- Cyanobacteria mats are thought to behave like other forms of periphyton causing similar diel changes in DO.
- Research over 25-30 years has shown that the Manawatu River has been subjected to pollutant inputs that have affected its DO regime. The latest ecosystem metabolism studies show that it is in poor condition.
- We recommend that year-round continuous measurement of DO be discontinued. This is justified because (a) the primary interest is in extreme values that mainly occur in late summer-early autumn during times of low flow, warm water temperature and the occurrence of periphyton and cyanobacteria blooms, (b) flood flows and vandalism may result in increased risk of damage to deployed equipment, (c) considerable effort with equipment maintenance and calibration is required to maintain accurate data collection on a continuous basis under all flow conditions. We recommend that continuous DO monitoring be carried out in intense surveys of about 2 weeks duration (e.g., during periphyton blooms), with considerable effort being placed on equipment maintenance and calibration to ensure good quality data are collected over the intense monitoring period.
- We recommend that continuous monitoring by HRC be carried out primarily in summer-autumn, during periods of stable flow that are not greater than the 25th percentile, and for periods not exceeding two weeks. This would enable greater attention to be given to calibration, maintenance and independent check measurements made using other instruments, and to gathering supporting data (standard water quality information). Dissolved oxygen data of interest would be

concentrations that are less than 50% or greater than 120% saturation, and diel ranges of at least 2 mg/L (or, 20% saturation).

- The WTW optode sensors used by HRC are claimed by the manufacturers to be inherently more stable and more accurate than most membrane electrodes and many other optode systems, because of the green light fluorescence system, but are still liable to being damaged and producing erroneous signals at times.
- There can be wide divergences between DO measuring devices at concentrations >100% saturation because routine DO calibration is restricted to the range between 0 and 100% saturation. Calibration of instruments for values >100% saturation is very complicated. The sensitivity of optical DO sensors is also reduced at very high DO saturation values because of the immediate quenching of luminescence. Regular sensor maintenance and calibration checks with other instruments is currently the only way to improve the accuracy of measurements >100% saturation. However, at least one manufacturer of optical sensors (D-opto) is currently developing a special calibration tank to test the sensor response at DO concentrations above 100% saturation.
- We recommend that HRC calibrate handheld meters and fluorescent optode equipment at the start of each field trip or *in situ* deployment. In addition, it would be prudent to check meter performance against a recently calibrated instrument at the end of each sampling event and note any differences so that baseline drift may be adjusted if necessary. We think that ±5% (roughly 0.5 mg/L at 100% saturation) is an acceptable level of precision.
- The Winkler titration method remains the 'gold standard' for measuring DO in clean waters in the 0-10 mg/L range, but cannot be used to resolve the uncertainty in measurements substantially greater than 100% saturation.
- Membrane electrode systems, such as the YSI Pro series meters, are well suited to a wide range of applications provided they are well maintained and calibrated regularly. They are subject to gaseous interferences in some polluted situations (notably by H_2S and NH_3).
- The WTW manufacturers claim their optode sensors (used by HRC) operate with green light excitation that is less damaging to the sensor window, hold calibration longer and are more durable than those using blue light excitation.
- Data quality is maximised by regular checking of field equipment and regular calibration. Drift in sensor response may be reduced by undertaking continuous logging over relatively short duration periods.
- Ecosystem metabolism is a useful functional indicator of river ecosystem health. This is characterised by parameters describing the capacity of a river for gas exchange through the water surface (the reaeration coefficient, k_a), the rate of gross primary productivity (GPP or *P*) and the rate of ecosystem respiration (ER or *R*).

- Ecosystem metabolism calculations can be carried out by the night-time regression method or the Approximate Delta Method (ADM).
- The two methods were compared on five river data sets and agreed well when DO maximum concentrations occurred at least one hour after solar noon (the midpoint between sunrise and sunset). At reaeration rates greater than 25 /d, the maximum DO is likely to be close to solar noon and only the night-time regression method will give satisfactory answers. The ADM precision increases as the reaeration coefficient decreases below 20 /d.
- We found no protocols for routine, continuous measurement of DO used by other agencies. The Auckland Regional Council has had experience with continuous DO monitoring going back to 2003. DO concentration was measured at ARC sites using an independent calibrated meter and logger data collected over the preceding period was classified according to the deviation from the independent meter. Data from a logger that was within 0.5 mg/L of the independent measurement was considered ‘High Quality’, data between 0.5 and 1 mg/L of independent measurements was considered ‘Good Quality’, and data more than 1 mg/L from the independent measurements was considered ‘Poor Quality'.

2. Report brief

At a workshop convened by Horizons Regional Council on 20 August 2010, Council staff and the authors addressed issues relating to the continuous measurement of dissolved oxygen (DO) and use of that data for productivity analysis that had arisen during the One Plan Water Hearing. This report is an outcome of that workshop with the following key objectives:

- to improve understanding of the measurement and interpretation of continuous DO concentrations in rivers, and
- to establish agreed protocols for measurement and processing of continuous DO data by Horizons Regional Council and provide advice on interpretation of DO data.

To achieve the key outputs, the project sought to address the following questions and provide a clear set of recommendations, namely:

1. How to achieve accurate and precise measurement of dissolved oxygen data? This will necessitate investigating items such as:
   - calibration procedures
   - checks on linearity in the measurements of the sensor
   - inter-method comparisons and use of the Winkler titration method as a standard
   - adjustments for barometric pressure and altitude
   - comparison of available instrument performance, and
   - early detection of instrument malfunction and identification of appropriate remedial action.
2. What QA procedures should be implemented and what is the best way to correct datasets when required?
3. Which is the primary measurement? Is it concentration or percent saturation?
4. Use of data, including models - what degree of accuracy and precision is required? If models are used to quantify processes, what criteria are required to establish monitoring sites and reaches?
5. How do methods used for productivity analysis compare? A comparison will be made using shared data sets to compare the slope regression and approximate Delta methods.
6. Should experimental approaches be investigated? These would include chamber methods, and the use of gas tracers to quantify the reaeration coefficient. If so, direction on how to undertake such work will be provided.
7. What do the historic Manawatu River data sets (e.g., PhD thesis by John Quinn and Mike Freeman PhD, and any other material) provide in terms of insights into respiration and productivity rates?

8. Comment on any protocols that have been developed overseas?

9. What influence (if any) do cyanobacteria have on the measurement of DO concentration?

In addition to these core questions, the following additional points emerged in subsequent discussions:

10 Should Horizons Regional Council be making continuous measurements of DO concentration, year-round, and if not what is recommended?

11. When and at what level are discrepancies between measurements of DO important?

12. Are Horizons Regional Council's protocols for continuous DO measurement and processing of data adequate and appropriate for their purposes?

3. Introduction

3.1 The importance of dissolved oxygen

The concentration of dissolved oxygen in water is a critical component affecting the life supporting capacity of a river system. Dissolved oxygen concentrations are affected by three key processes – 1) oxygen production associated with photosynthesis of algae and other aquatic plants, which raises the oxygen concentrations within the water, 2) oxygen uptake associated with respiration of all river life including fish, invertebrates, algae, aquatic plants and microbes, which lowers the oxygen concentrations in the water, and 3) oxygen diffusion through the water surface, which can either raise or lower oxygen concentrations.

Ecosystem metabolism – the combination of algal productivity or photosynthesis (GPP) and ecosystem respiration (ER) – is a measure of the main factors controlling dissolved oxygen dynamics in rivers, and indicates how much organic carbon is produced and consumed in river systems. Recent research has shown that ecosystem metabolism is a useful indicator of river ecosystem health and complements traditional monitoring tools such as water quality analysis, periphyton assessments, and invertebrate community composition. Ecosystem metabolism is influenced by a wide variety of factors such as nutrient inputs, organic waste discharges, shading, river flow and water temperature.

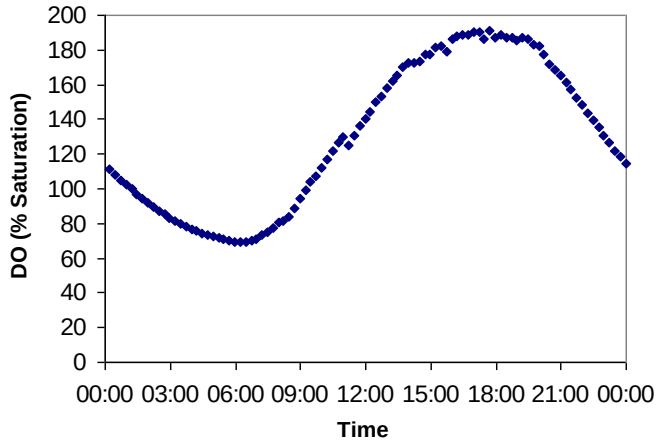

Figure 1: Example of 24-hr (diel) variation in dissolved oxygen in a river. (Provided by Roger Young, Cawthron Institute).

Ecosystem metabolism can be measured by monitoring the daily changes in oxygen concentration at a site. Dissolved oxygen (DO) concentrations rise during the daytime when sunlight facilitates photosynthesis and then decline during the night when only respiration occurs (Figure 1). The size of the daily fluctuations depends on the amount of photosynthesis and respiration occurring within the river and also the flux of oxygen through the river surface.

Sites with high rates of ER are normally characterised by large inputs of organic matter from point source discharges of sewage/waste water, or large diffuse inputs from sources such as deciduous trees. High biomasses of algae and other aquatic plants are also often associated with high rates of ecosystem respiration. Sites with high rates of ER will be prone to low dissolved oxygen concentrations and have the potential to kill fish and other aquatic life.

3.1.1 Dissolved oxygen and aquatic life

Data regarding tolerance and mortality associated with DO concentrations are available for trout and some native fish, and aquatic invertebrates (Dean & Richardson 1999; Connolly et al. 2004; Landman et al. 2005; Franklin 2010). Criteria for protecting different species and life stages are given in terms of DO concentrations in mg/L (g m^{-3}) by these authors and are summarised in Table 1). It should be noted that because it influences metabolic rates, water temperature affects the sensitivity of aquatic animals to low DO. For example, as temperature rises, metabolic rates of fish increase and more oxygen is needed (Dean & Richardson 1999). Salmonids (viz. trout) are regarded as the most sensitive coldwater fish species to low DO (USEPA 1986), whereas most native New Zealand species are quite tolerant of low DO concentrations. A further complication is the length of the exposure period to low DO and the distinction between acute (up to 48 hr) and chronic (longer times) exposure (Landman et al. 2005). Chronic effects occur at much lower DO concentrations than acute affects.

Table 1: Effect of dissolved oxygen concentrations on some freshwater species. A temperature of 15°C is assumed.

Species protected	Dissolved oxygen		Degree of impairment	Comment
	mg/L	% sat.		
Trout (all life stages)	8-11	80-110	Moderate-none	Higher numbers of each range refer to early life stages and lower numbers refer to other life stages (USEPA 1986).
	4-8	40-80	severe-moderate	
	3-6	30-60	Acute limit	
New Zealand native fish	5	50	None	From experiments by Dean & Richardson (1999)
	3	30	Some surfacing breathing	
	1	10	Significant mortality	
Stream invertebrates	5-10	50-100	Mostly none – but some sensitive species affected below 50%	Data summarised by Connolly et al. (2004)
	4-5	40-50	50% mortality for a few species	
	1-2	10-20	50% mortality for most species	
	0-1	0-10	High mortality for all species within 2 days	

The USEPA (1986) report states that “although the acute lethal limit for salmonids is at or below 3 mg/L, the cold water minimum has been established at 4 mg/L because a significant proportion of the insect species common to salmonids’ habitats are less tolerant of acute exposures to low dissolved oxygen than are salmonids.” The USEPA (1986) water quality criterion for DO is a 1-day minimum concentration of 4 mg/L for adult and juvenile salmonids older than 30 days following hatching. By contrast, the Canadian water quality guidelines for the lowest acceptable DO concentrations are 6 and 5.5 mg/L for the protection of early and other life stages, respectively, in warm-water ecosystems, and 9.5 and 6.5 mg/L for the early and other life stages, respectively, in cold-water ecosystems (CCME 1999).

Dissolved oxygen maxima up to 150% saturation are reasonably common in lowland streams (e.g., Wilcock et al. 1998) without apparent ill-effect on aquatic life. However, a Chinese study has reported that Juvenile rock carp exposed to water with different levels of supersaturation at a depth of 0.20 m, at 25 °C for 60 h, showed negligible effects at DO concentrations below 115%, and mortalities of 50% or more when DO was greater than 120% for 60 hours (Huang et al. 2010). It is most unlikely that these conditions will occur in New Zealand rivers, where there is a pronounced diel pattern in DO (Fig. 1) so that there is uncertainty about short-term (2-4 hour) exposure to very high DO concentration (>150% saturation).

3.1.2 Cyanobacteria blooms

Sudden blooms of benthic cyanobacteria are reasonably common, and appear to be becoming more common, with some sites going from 5-10% coverage to 80-100% coverage within just a few days. During this rapid growth phase it is likely that the benthic cyanos are making a major contribution to the diel fluctuations in DO.

3.2 Ecosystem metabolism in the Manawatu River

As part of a study on the ecosystem integrity of New Zealand's large rivers, ecosystem metabolism was measured at 16 sites throughout the country. The results showed that rates of GPP and ER in the lower Manawatu River at Opiki were among the highest ever reported internationally and well above the thresholds considered to represent the transition from satisfactory to poor ecosystem health – GPP values above 7 g O_2/m^2/day and ER values above 10 g O_2/m^2/day are considered to indicate poor ecosystem health (Young et al. 2008). The outcome from the national survey work has been three reports (Collier et al. 2009; Clapcott & Young 2009, Young & Clapcott 2010) that are described in more detail in section 3.2.2, and a focus on establishing good quality assurance around the measurement of DO and subsequent presentation of DO data.

> The research results indicated that the Manawatu River was very unhealthy. Other indicators of river health such as nutrient concentrations, water clarity, faecal bacteria, and stream invertebrates also indicated the poor status of the Manawatu River (http://www.mfe.govt.nz/environmental-reporting/freshwater/river/league-table/river-water-quality-league-tables.html).

Typically, agencies collect dissolved oxygen data either by making spot measurements or by temporarily deploying sensors (sondes or datasondes). Horizons have invested in monitoring dissolved oxygen concentrations on a continuous (15 minute interval) basis. Sensors are permanently located at five sites as part of Horizons' water allocation and state of environment monitoring programmes and there is presently approximately four years of record for each of the five sites (i.e., 2006-2010).

3.2.1 Studies in the 1980s

Primary production analysis were carried out during March 1983, at Manawatu River sites 2-5 km upstream of major point source inputs of organic waste from the Palmerston North City Council sewage treatment plant, a dairy factory and a freezing works. The analysis yielded maximum rates of about 13 g O_2/m^3/day (22 g O_2/m^2/day) for gross primary production (GPP)

and 18 g O_2/m^3/day (29 g O_2/m^2/day) for ecosystem respiration (ER) (Freeman 1983). The dominant periphyton species at the upstream sites was *Cladophora* with a biomass of 41 g DW/m^2, or approximately 16 g ash-free dry weight per m^2 (g AFDW/m^2) at the time measurements were made; river flow was 24 m^3/s (Freeman 1983). The single-station productivity analysis method used by Freeman (1983) entailed calculating the reaeration coefficient (k_a) using river velocity-depth data and the O'Connor-Dobbins equation (Table 3), and calculating gross primary production and total respiration rates from time-dependent DO data for given 24-hr periods. By contrast Quinn (1985) used 2-station diurnal curve analysis method and recirculating chambers to estimate productivity parameters at sites downstream of the major discharges to the Manawatu River during summer of 1983-84 when there was abundant sewage fungus growth. Quinn (1985) reported maximum values of 34.7 g O_2/m^3/day (or 34.2 g O_2/m^2/day) for GPP and 36.9 g O_2/m^3/day (37.6 g O_2/m^2/day) for ER, corresponding to flows of 15-19 m^3/s and a periphyton biomass of 70-150 g AFD/ m^2, or 175-375 g DW/m^2. These results indicated that fairly polluted conditions existed in the Manawatu River before major reductions of point source discharges occurred and can be contrasted with recent measurements made in the Manawatu River (Collier et al. 2009; Clapcott & Young 2009; Young & Clapcott 2010).

3.2.2 Recent studies

Collier et al. (2009) investigated dissolved oxygen concentrations at a range of rivers across New Zealand and calculated rates of ecosystem metabolism from the DO data. The results showed the Manawatu River Opiki site (5-10 km downstream of those cited by Quinn (1985)) had very poor ecosystem health. Horizons Regional Council (HRC) subsequently engaged Cawthron to look further into these measures of ecosystem health using the data from Horizons' five continuous DO monitoring sites. This work (Clapcott and Young 2009) was subsequently updated in 2010 because of errors in the data sets originally provided (Young and Clapcott 2010). These errors related to the calculation of saturation values from concentration data and from sensor damage during floods at one of the sites.

Gross primary production (GPP) values calculated by Young and Clapcott (2010) ranged from <0.1 g O_2/m^2/day (in the Rangitikei at Onepuhi in winter) to 24.5 g O_2/m^2/day (Manawatu at Hopelands in spring). The Hopelands GPP value is similar to that measured by Quinn (1985), (34.2 g O_2/m^2/day) during a period when sewage fungus was very evident in the river as a result of the discharges of PNCC sewage effluent and industrial waste downstream of Palmerston North City. Ecosystem (ER) respiration values calculated by Young and Clapcott (2010) ranged from 0.1 g O_2/m^2/day (Manawatu at Teachers College in winter) to 32.8 g O_2/m^2/day (Manawatu at Hopelands in spring). Again, these can be compared with the 36.9 g O_2/m^2/day measurement from Quinn (1985). Thus, in 2007 the Manawatu River Hopelands site, affected largely by diffuse source pollution from agriculture and a few consented point sources (brewery wastes, community sewage pond discharges) had similar levels of GPP and ER to those in the Manawatu River immediately downstream of major point source discharges in the 1980s.

The work of Young and Clapcott (2010) provided results indicating poor ecosystem health at the Manawatu River Hopelands site (in the upper catchment of the Manawatu River). Data reported in a peer reviewed scientific journal article (Young et al. 2008) were used to compare measurements made elsewhere with the values measured in the Manawatu River. Measurements at the Manawatu River Opiki site were the highest (worst) of the

approximately 300 measurements that were reviewed in this paper. The GPP and ER values were 107.1 and 65.2 g O_2/m^2/day, respectively (Collier et al. 2009), and made independently of the Horizons measurements. Some media when interpreting this information wrongly dubbed the Manawatu River as having the "worst water quality in the western world". Ecosystem metabolism in the Manawatu River at different sites over the period from 1982-2008 are compared in Table 1 and indicate a possible worsening of river conditions despite the removal of, or substantial reduction in, point source loadings of organic wastewater. Agricultural intensification particularly expansion and intensification of dairying is a likely cause for the increase in diffuse source pollution.

Table 2: Maximum rates of ecosystem metabolism recorded in the Manawatu River using diel dissolved oxygen data. .Key: PN = Palmerston North; GPP = gross primary production, g O_2/m^2/day; ER = ecosystem respiration, g O_2/m^2/day.

Site (year)	GPP	ER	Reference
2-5 km upstream of PN (Feb 1983)	22	29	Freeman (1983)
Downstream of PN (1983-84)	34.2	37.6	Quinn (1985)
Hopelands (spring 2007)	24.5	32.8	Young & Clapcott (2010)
Opiki (summer 2008)	107.1	65.2	Collier et al. (2009)

The parameters estimated in Table 1 were based on continuously recorded DO data. The magnitudes of these parameters are dependent on the difference between minimum and maximum dissolved oxygen (Delta) and the amount of gas exchange through the water surface (Chapra & Di Toro 1991). Given the publicity that analyses based on DO measurements sometimes attract, there is a greater need than ever to ensure that the primary data, which usually comprises time-series of DO concentrations, is accurate and reliable, particularly when Delta is very large.

3.2.3 Horizons Regional Council DO monitoring

Dissolved oxygen standards for Water Management Sub-zones in the One Plan (Schedule AA) vary between minimum values of 60% and 80% saturation, depending upon the aquatic ecosystem values being protected (Figure 2). A list of sites currently being monitored for DO by HRC, is given in Tables 3 (provided by Brent Watson, HRC). Previously HRC used Zebra-tech D-opto optodes but are now using the WTW FDO green light optical sensors (specifications for these are in Appendix 1). DO concentration and saturation values measured by five YSI membrane sensors systems (YSI Pro1, YSI Pro 2, YSI Pro 4, YSI Pro 5 and YSI 556) and D-opto DO sensors were compared by HRC using the Winkler method as a reference (Clark et al. 2010). The study concluded that the YSI Pro 1 was the meter system most consistently within range of acceptable error from the titration when carried out using a progressively oxygenated water sample. The D-opto system consistently read at a lower concentration than all of the other meters either on water samples with fixed DO concentrations or on progressively oxygenated water samples (Clark et al. 2010).

The remainder of this report will relate to the WTW FDO green light optical sensors currently used by HRC, and to various handheld instruments that use either membrane or optode sensor technologies. An explanation of the working principles of these different sensors is given in Section 6 of this report.

3.2.4 Summary of key points

- Dissolved oxygen (DO) is an important water quality variable that can affect aquatic species at different threshold values, according to species and life stage.
- Most adult fish can tolerate DO concentrations down to 30-40% saturation for short periods, but for longer periods of exposure higher DO values (60-95% saturation) are necessary for the protection of aquatic life.
- Little is known about the effects of very high DO levels (greater than 200%) on aquatic species for exposure periods of a few hours.
- Recent (2009-10) ecosystem metabolism studies based on diel DO profiles showed the Manawatu River to be in poor condition. Calculated GPP and ER rates are among the highest reported and are attributed to diffuse source pollution from agriculture and nutrients associated with point source discharges.
- Horizons has set DO standards for Water Management Sub-zones in the One Plan that vary between minimum values of 60% and 80% saturation, depending upon the aquatic ecosystem values being protected.

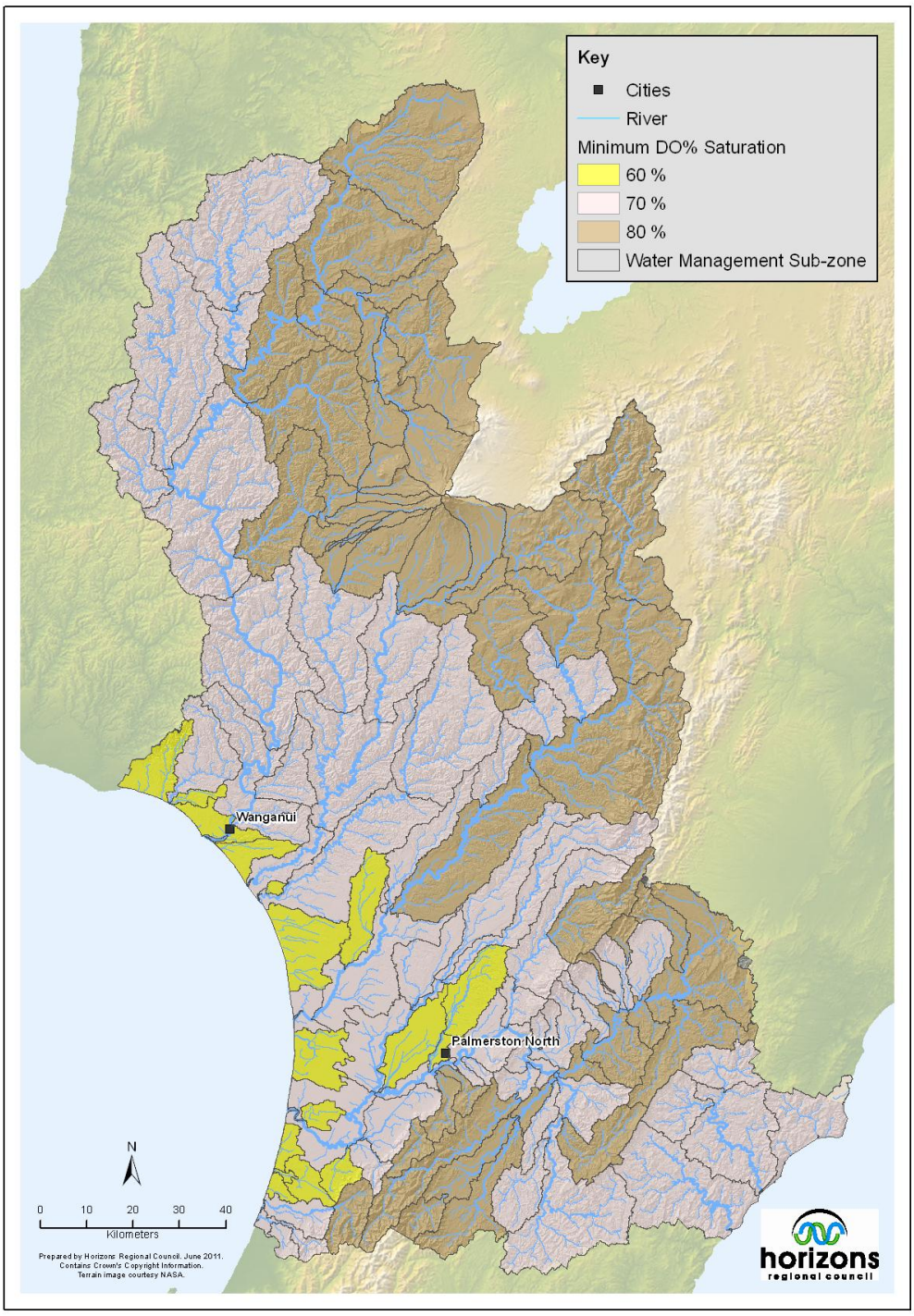

Figure 2: Dissolved oxygen standards for Water Management Sub-zones in the Horizons Regional Council One Plan.

Table 3: Current Horizons Regional Council dissolved oxygen monitoring sites.

File site name	Metric map reference	Altitude	River Number	Easting	Northing	HRC Lat	HRC Long	Catchment Area
Manawatu at Hopelands	T24:616899	109	325000	2761600	6089900	-40.35886	175.96286	1247
Manawatu at Teachers College	T24:331892	34	325000	2733100	6089200	-40.37329	175.62773	3900
Manawatu at Weber Road (New 2011)	U23:751027	160	325000	2775100	6102700	-40.23947	176.11638	713
Mangatainoka at Pahiatua Town Bridge	T24:501802	107	325201	2750100	6080200	-40.44957	175.83121	395
Rangitikei at Mangaweka	T22:504513	257	327000	2750400	6151300	-39.80942	175.80811	2787
Rangitikei at Onepuhi	S23:201222	78	327000	2720100	6122200	-40.07957	175.46384	3420

HRC do not use self –logging sondes; all sites are configured with sensors connected/logged onto Campbell dataloggers, with near real-time telemetry (Brent Watson, HRC pers. comm.).

4. Continuous measurement of DO

Horizons Regional Council continuously monitors DO at six sites (Table 3) using WTW optodes connected to Campbell loggers, providing near real-time data via telemetry (Brent Watson, HRC, pers. comm.). Given the interest that these data and their subsequent analysis have attracted, it is of great importance that the primary data collected from instruments deployed for continuous data collection is robust and defensible and provides a sound basis for ecosystem metabolism calculations. In order for this to happen there should be sound calibration and maintenance procedures with appropriate quality assurance and control (QA/QC). Methods used for data manipulation to correct artefacts of measurement, instrument malfunction and human errors should be transparent and auditable if necessary. The following sections relate to the WTW FDO® 700 IQ optical sensors currently used by HRC.

4.1 Routine measurements

4.1.1 When to monitor DO

A key question is “should DO be monitored continuously, year round?” Most DO measurements made throughout the year are unremarkable, especially if made during median or higher flows when concentrations are not likely to vary greatly from 80-100% saturation. It is normally the extreme DO concentrations occurring during summer low flows, or other times of special interest (e.g., during algal blooms) that are of interest. Thus, there may only be a need for continuous DO data for a relatively small proportion of the year. Secondly, data sets collected from sondes deployed continuously may often need to be corrected for baseline drift and noise (section 7) and have associated uncertainties that reduce their usefulness and robustness.

Minimum DO concentrations are usually of greater concern than maximum values because of the suffocating effects of low DO on fish and invertebrates (Table 1). However, the diel range between the minimum and maximum DO concentrations in any 24-hr period is important for ecosystem metabolism calculations that may be used as an index of river condition (Sections 3 and 8). Minimum DO concentrations may be roughly correlated, negatively, with maximum temperature (Fig. 3), reflecting the underlying common conditions of summer low flows – viz. warm stream temperatures and vigorous plant growth in pastoral streams (Wilcock et al. 1998). A similar relationship would be expected in the Horizons region, where low flows during warm weather would coincide with the maximum occurrence of periphyton blooms, and extreme diel DO variation. Supersaturation of DO above 120% generally occurs at very low flows when reaeration rate coefficients may be low and exchange of DO with the atmosphere relatively weak. As flow increases so does the tendency of DO to reach equilibrium with the atmosphere, and 100% saturation. At median or higher flows there may be little diel variation in DO in some river systems.

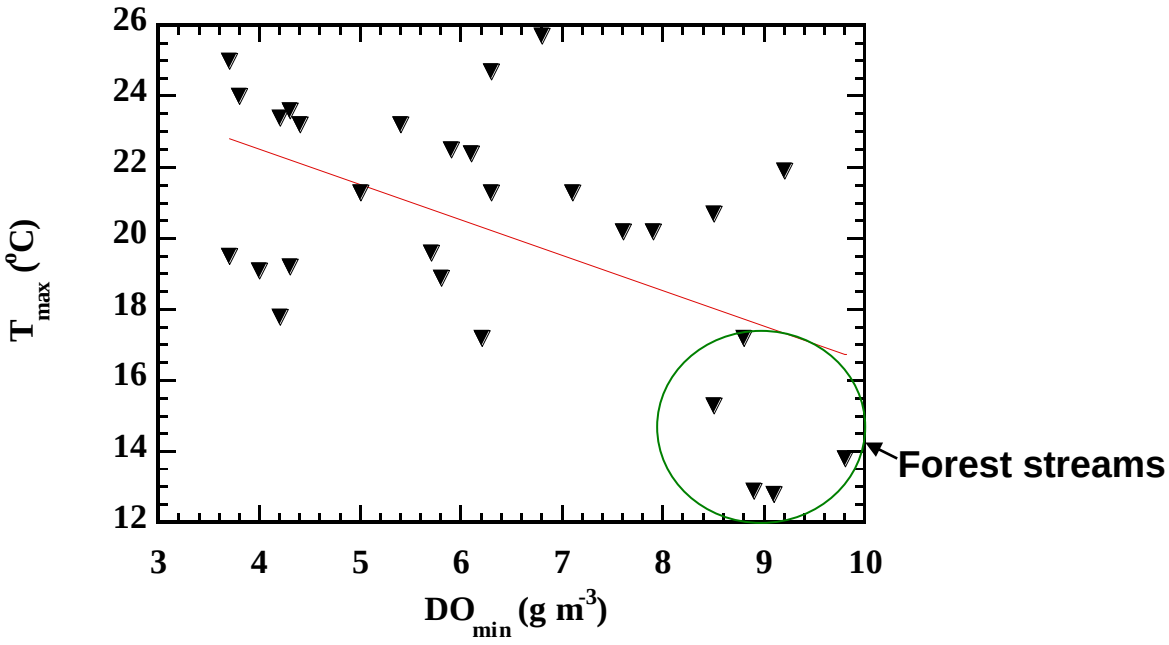

Figure 3: Comparison of diel minimum dissolved oxygen (DO) concentrations and maximum water temperatures measured in Waikato streams. (Wilcock et al. 1998).

Recommendation:

It is difficult to recommend precisely when it would be best to monitor DO to capture extreme diel variation in the Horizons region. One way to do this would be to analyse existing data held by HRC and derive a relationship between diel range and flow statistics such as the median, lower percentiles (10 and 25%-ile) and Q_5. The occurrence of these flows would also indicate when continuous monitoring should occur.

As a starting point, we recommend that continuous monitoring by HRC be carried out only in summer-autumn, during periods of stable flow that are not greater than the 25th percentile, and for periods not exceeding two weeks. This would enable greater attention to be given to calibration, maintenance and check measurements with other instruments, and to gathering supporting data (standard water quality information). Dissolved oxygen data of interest are concentrations that are less than 50% or greater than 120% saturation, and diel ranges of at least 2 mg/L (or, 20% saturation). It is worth noting that some elements of the aquatic ecosystem are adversely affected once DO drops below 80% (see Section 3.1.1), which may have a bearing on the DO range of interest.

4.1.2 Maintenance and deployment

Of primary importance is that care should be taken in cleaning sensors between field deployments and in taking pains to get calibrations done correctly before each deployment. When determining how long the equipment may be left to reliably gather field data, consideration must be given to the environment where it is deployed and the instrument stability.

Sondes tend to be deployed either in an ad hoc way in sites chosen for particular studies, or in specially chosen sites used in ongoing, long-term monitoring (e.g., the HRC sites listed in Table 1). Hydrolab datasondes fitted with Clark membrane electrodes were deployed satisfactorily for 3-4 day periods in a NIWA study of DO in 23 lowland Waikato streams during summer low-flow conditions (Wilcock et al. 1998). Longer deployments of these sondes have sometimes produced unreliable data.

The WTW sondes used by HRC use optode technology (section 6) are inherently more stable than membrane electrodes, are externally powered, and should be able to be deployed for several weeks and yield reliable data. However, fouling of the sensors by weed, algae and other debris, falling water levels and security of the equipment may warrant fortnightly inspection. The only way to be sure that the data collected is useful is to monitor sensor performance carefully in each site, under a range of flows.

DO sensors are usually located in secure sites. Deployment must ensure that they are always immersed in water, whatever the flow (stage height). Shading of sensors from the sun, either by the sonde itself or by placement in shaded locations reduces the chances of thermal variation of the sonde affecting measurements, or of problems caused by thermal expansion. Pumping of water to sensors is not recommended because of the risk of stripping oxygen from supersaturated waters, or aerating undersaturated waters. Ultimately, the best test is to check performance against external references, such as reliably calibrated handheld meters (e.g., YSI Pro series used by HRC) under typical or representative conditions.

DO concentrations in most rivers are uniform although small gradients may occur where there are extensive macrophytes beds in very slow moving low gradient streams (Wilcock et al. 1999). There is also the possibility that periphyton may become attached to sensor heads and cause anomalously high readings, or that bubbles may give rise to localised very high concentrations of DO. Although DO concentrations of 20-25 mg/L (i.e., >200% saturation) have recently been reported in a nutrient-rich South American stream (Acuña et al. 2011) river DO concentrations above 200% saturation are a rarity in the scientific literature.

Clearly, sonde reliability is influenced by site-specific conditions and there may be situations where fouling of the membrane occurs after a few days (Fig. 4). Routine inspections should include comparison with a calibrated portable sensor, and sensor maintenance and recalibration if necessary. These measures would ensure that at most only two weeks of data would be lost and, for minor baseline drift, would provide a reasonable basis for retrospective adjustments of data that had already been collected. The alternative might be to discover after a longer period between inspections (say, 1 month) that 3 weeks of data was lost because of sensor malfunction or fouling, battery failure or some other reason.

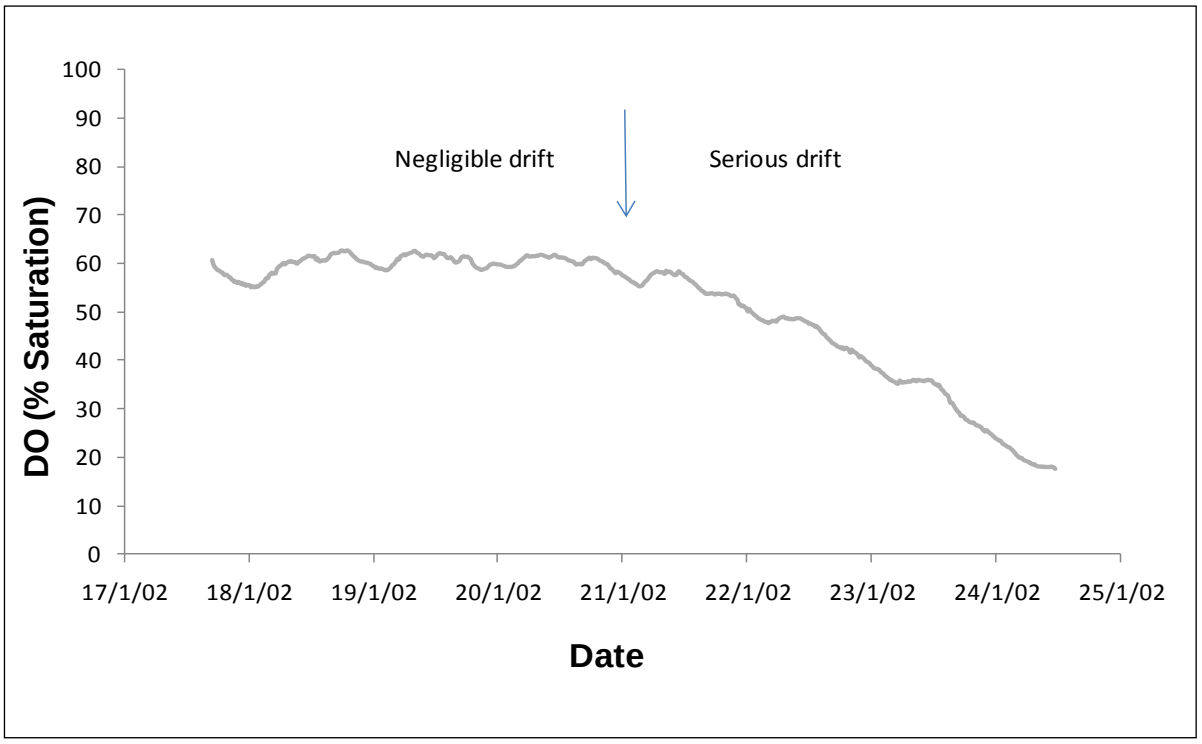

Figure 4: Continuous DO profile recorded in Pa Stream, Marlborough, using a pulsed Clark sensor over the period from 17th January 2002 to 24th January 2002. .Serious drift began after three days of deployment. Independent measurements with a handheld meter were close to 60% saturation throughout the deployment period.

Sondes with optode sensors will also need to be cleaned and their calibration and performance checked *in situ* against a calibrated field instrument after a period of field deployment. An external power source obviates reliance upon internal batteries. In any case a maximum period of 2 weeks between field reliability (QA/QC) checks is recommended initially for any DO sonde device (optode or membrane), at least until it is proven that servicing can be at longer time intervals. Obvious signs that the sonde is awry can be seen in the output - drifting baseline, increasing diel range, daily minimum DO saturation >100% and noisy signals indicate that the data produced by the sonde may be unreliable and that the instrument needs maintenance. Analysis of continuous DO concentration data is discussed in section 8 of this report. It entails using 24-hr data sets to calculate values for parameters characterising photosynthetic production and respiration, and reaeration caused by turbulent mixing. These parameters are often used to characterise river condition and assist evaluations (i.e., “good” and “bad” river state). Erroneously wide DO ranges used for primary production analysis generate very large values for rates of photosynthetic production, ecosystem respiration and the reaeration coefficient that can be quite misleading. The DO profile in Figure 5 shows some of these characteristics (viz. widening DO range and increasingly noisy signal). We have noticed in some cases that optode membranes delaminate, possibly as a result of physical abrasion under harsh conditions (e.g., flood flows carrying suspended sediment and debris). This is likely to give rise to noisy, unreliable signals and may be something that HRC should look out for.

Baseline drift can be corrected provided the DO time-series is acceptable in all other aspects (not too noisy and no sudden amplitude changes). The only sure way to validate the reliability of a sonde deployed in the field is to inspect the sonde and compare its performance with a reliably calibrated handheld instrument. Time spent servicing and recalibrating sondes is a necessary but valuable cost of ensuring against lost monitoring data from un-serviced sonde deployments: better safe than sorry.

4.2 Spot measurements with hand-held meters

Spot measurements provide useful information about the state of water bodies and allow comparisons with deployed sondes (dataloggers) as a form of QA/QC, but only if they are properly calibrated. Recently, a joint study by Cawthron and NIWA deploying optode sondes in the Tukituki River showed that agreement between measurements made soon after field deployment were within 5-10% saturation but that agreement was not as good at the end of a 4-day deployment, where there was a disparity of nearly 70% saturation between the hand-held meter and the deployed optode sonde when DO saturation was very high (Fig. 5). It is possible that periphyton that was abundant in the river at the time grew on the surface of the optode membrane, giving an enhanced DO response relative to ambient river concentrations, although this has not been verified. However, uncertainties with sensor response for dissolved oxygen measurements >100% saturation are similar for both the hand-held meter and the optode sonde, so it is not clear which type of instrument provided the more accurate measurement. There is the possibility that DO sensors (including those used by HRC) do not perform reliably when DO reaches high levels (say, >150%).

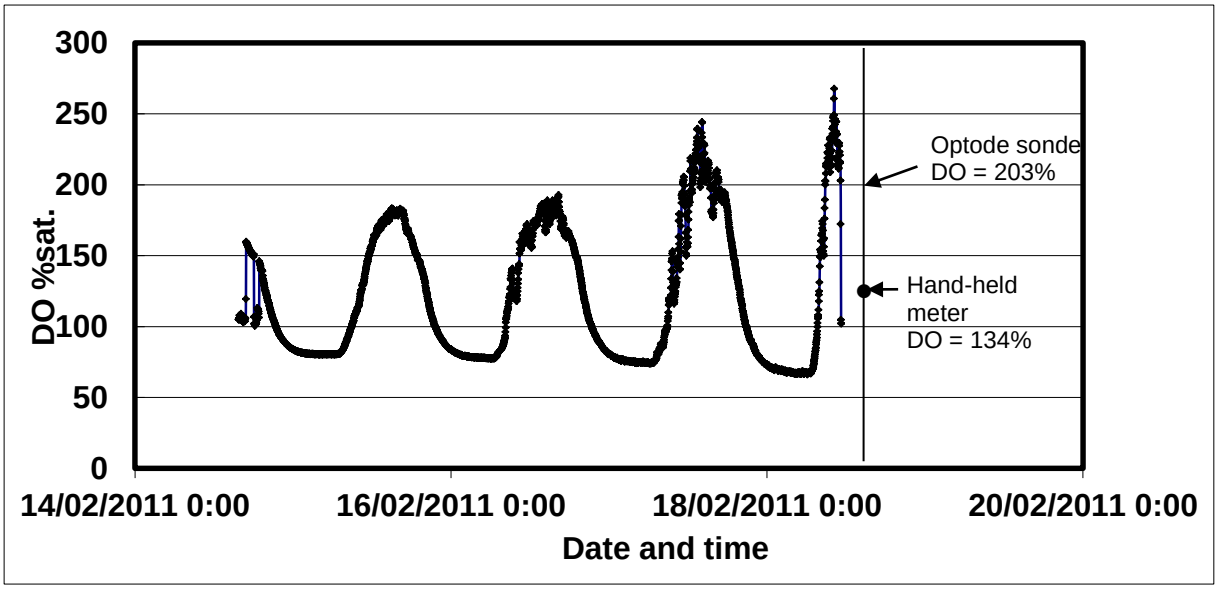

Figure 5: Continuous DO time-series recorded at site T5, Tukituki River above the Waipawa confluence during 14-18 February 2011.

4.3 Very high DO levels

Recent studies have highlighted the occurrence of DO concentrations greater than 150% saturation in wide, highly productive, gravel-bed rivers with abundant periphyton biomass. In studies conducted by the authors on the Tukituki River, Hawke's Bay, in January and February 2011, a number of comparisons were made between optodes and hand-held meters fitted with membrane electrodes or optode sensors. Comparison between results showed there was widespread divergence between measurements of DO concentrations above 130%, where the overall spread was about ±20% (Fig. 6). It is not entirely clear why there should be such differences, especially when care was taken with calibrating the instruments prior to their deployment. Until this matter is resolved we urge caution when recording very high DO concentrations (say, >150% saturation) and in using this data for calculating rates of ecosystem metabolism, given the large uncertainty associated with these data.

> We note that the manufacturers of WTW FDO 700 IQ sensors, used by HRC, claim that the sensors are less sensitive to error caused by bubbles than are other optodes (presumably based on blue light stimulation, rather than the green light method used by WTW). We would recommend verifying this claim through paired comparison with other instruments that have been reliably calibrated.

[1]

Perhaps of even greater importance is whether it matters if meters disagree by ±20% when DO is >150%. Clearly, low DO concentrations are of great importance to aquatic life, particularly below 6 mg/L (approximately 60% saturation at 15°C) (Table 1). Given that there may also be adverse effects on fish and other stream life when DO is above 120% for lengthy periods, it would be preferable to have a precision of at least ±10% (say over a range from 40 to 120% saturation), possibly by taking the mean of several different instrument values and omitting outlier results.

[1] http://www.wtw.de/us/products/online/dissolved-oxygen/optical-sensors.html

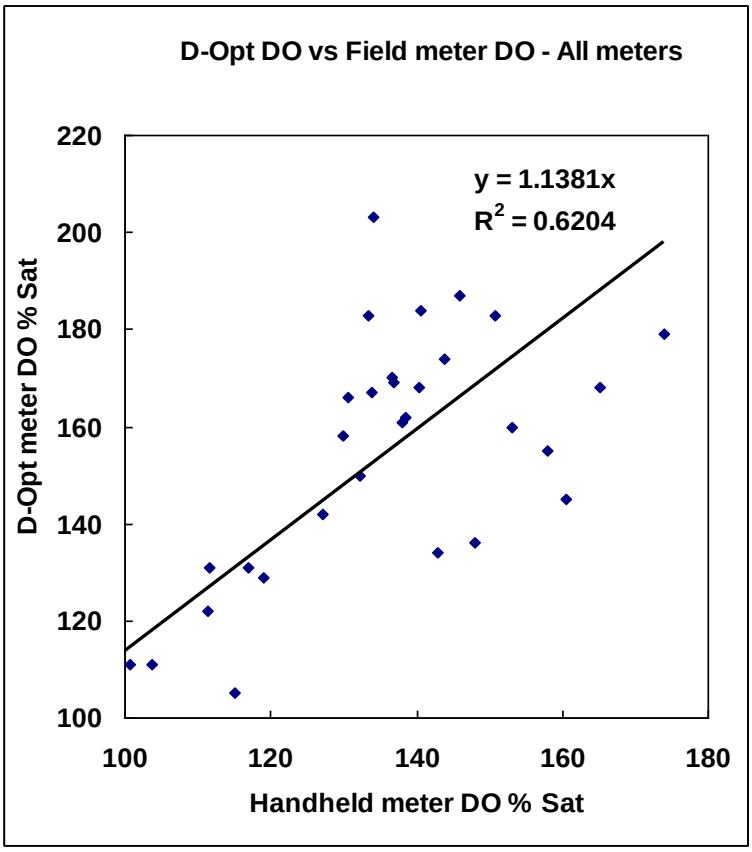

Figure 6: Comparison of dissolved oxygen (DO) measurements made in the Tukituki River in February 2011, using several calibrated optodes and handheld meters. (Roger Young, Cawthron).

4.4 Summary of key points about *in situ* measurement

- We recommend against conducting year-round continuous monitoring of DO and suggest that monitoring be confined to periods of stable low-flow (less than 25th percentile as an initial guideline), during summer-autumn, and for periods not exceeding 2-weeks.
- These guidelines should be refined for specific locations and be governed by the observed stability of the DO records (viz. lack of baseline drift and noise).
- According to the manufacturer, the WTW optode sensors used by HRC are inherently more stable and more accurate than membrane electrodes and many other optode systems, because of the green light fluorescence system, but are still liable to being damaged and producing erroneous signals at times.
- Auditing of data sets is recommended to establish sites and conditions where an acceptable signal is recorded, indicating reliable sonde performance.
- Signs of sensor malfunction include: baseline drift and ramping, noisy signals and widening amplitude in DO concentration.

- There are often wide divergences between DO measuring devices at concentrations >100% saturation. These could be caused by specific local conditions (e.g., bubbles, DO gradients). Regular calibration checks with other instruments, and sensor maintenance is probably the only way to reduce such discrepancies.

5. Calibration

5.1 Air-water equilibrium

There are two standard ways of calibrating oxygen sensors: immersion of the probe in 100% air-saturated water; and surrounding the probe with moist (water saturated) air. Oxygen in contact with water will tend to an equilibrium position in which the DO concentration is directly proportional to the partial pressure of atmospheric oxygen at any given temperature. This is Henry's Law and may be expressed by Eq. 1, where p_{O_2} is the partial pressure of oxygen in the atmosphere, $C^s_{O_2}$ is the saturation DO concentration, and K_H, is the Henry's law constant which varies with temperature (Hitchman 1978).

$$p_{O_2} = K_H C^s_{O_2} \quad (1)$$

The partial pressure of oxygen is the fraction of the total atmospheric pressure for all gasses other than water vapour and is usually taken as being 0.2094(P-v), where P is the atmospheric or barometric pressure and v is the saturation vapour pressure of water at a given temperature. The DO saturation values given in handbooks and manufacturer's tables are for a reference atmospheric pressure of 1013.25 millibar (101.325 kPa). The variation of $C^s_{O_2}$ with atmospheric pressure under conditions of water vapour saturation (as occurs with moist-air calibrations) is given by Eq. 2, where $C^\circ_{O_2}$ is the DO concentration at a barometric pressure of 1013.25 millibar and v is the vapour pressure of water at the given temperature. Water vapour pressures at 15, 20 and 30ºC are 12, 23 and 42 millibar, respectively.

$$C^s_{O_2}(P) = \frac{C^\circ_{O_2}(P - v)}{1013.25 - v} \quad (2)$$

or less precisely

$$C^s_{O_2}(P) = \frac{C^\circ_{O_2} P}{1013.25 - v} \quad (3)$$

Equations 2 and 3 show why it is important to have saturated air when carrying out moist-air calibrations.

The sensor response to zero DO concentration is ascertained by immersing the probe in water that has been deoxygenated with sodium sulphite (Na_2SO_3), facilitated by the addition of 1.1 mg/L cobalt chloride ($CoCl_2$) catalyst (Wilcock 1984). A feature of many membrane electrodes is their poor response to very low levels of DO (say, <1 mg/L) and it is worth noting (1) whether the sensor being tested is capable of giving a true 'zero' response, and (2) if it is, what time is needed to get an accurate reading. It is most important to clean sensors adequately after immersion in Na_2SO_3 solutions to prevent carry-over to subsequent measurements and subsequent 'low' measurements of DO concentration.

It is widely observed, and claimed by manufacturers, that optodes require less frequent calibration than membrane electrodes (galvanic or polarographic), because they are less likely to exhibit electrode drift (no metal electrodes to react with dissolved gases, lasers isolated from external environment). However, regular calibration is still recommended given

the small cost in time relative to the potential loss of data from a wrongly calibrated instrument.

The question is often asked “which is the better method of calibrating a DO sensor; moist-air or saturated water?” Given their equivalence (Eqs. 1-3), it could be said that both are equally good. In practice, however, a major source of error with field measurements is not having the sensor at the temperature used for calibration. This is most likely for moist-air calibrations carried out, for example, when probes stored in a vehicle may be at markedly different temperature from outside ambient temperature where the calibration may be carried out. Immersing the probe in saturated water overcomes that problem by ensuring that water and sensor are at the same temperature. The recommended method for calibrating the Hach model HQ40d portable DO meters fitted with optode sensors, used in the National River Water Quality Network, makes use of natural saturated water solutions (Appendix 2). Saturation is achieved by pouring water back and forth between containers and has been verified by NIWA.

The FDO 700 IQ (SW) sensors used by HRC specify that when air temperature is over 5°C, calibration should take place in water vapor-saturated air with the sensor approx. 2 cm above a water surface, for example in a narrow bucket. When air temperature is below 5°C, WTW recommend calibration in air-saturated water that has a higher temperature. “You obtain air-saturated water by pouring water several times in and out of two vessels so that it sparkles.” This latter method is similar to the NIWA method (Appendix 2).

WTW FDO 700 IQ (SW) sensors are factory calibrated and the manufacturers claim that “measuring characteristics of the sensor cap remain stable for the specified service life. Thus, a user calibration is not usually required.” They also specify that water vapour saturated air (i.e., moist-air) calibration be used to check if the “service life of the sensor cap is over”. These claims should not be accepted without verification.

[2]

5.2 Calibration at 0% saturation

Mention is sometimes made in the scientific literature of using inert gases, such as nitrogen or argon, to deoxygenate water and produce a 0% DO concentration for checking the instrument’s zero response. This is based on Henry’s law (Eq. 1) whereby the partial pressure of oxygen in equilibrium with the water is reduced to zero by displacement with another gas. In practice, it is quite difficult to achieve $p_{O_2} = 0$ and, in addition, it can be unsafe to undertake this procedure in confined spaces. The best way to obtain a solution with a DO concentration of zero mg/L is to add sodium sulphite, Na_2SO_3, with $CoCl_2$ catalyst. This may not be necessary for modern optode sensors but may be worth doing to determine how well any given sensor is behaving at very low DO levels. It is a relatively simple check that can be done occasionally, say once a year. It is most important to wash sensors well after they have been immersed in Na_2SO_3 solutions to avoid getting artificially low DO values from subsequent measurements.

[2] http://www.wtw.com/downloads/manuals/ba75586e03_FDO_700_%20IQ_SW.pdf

5.3 Calibrations above 100% saturation

Membrane sensors and optodes are assumed to have linearised responses to DO concentration (and p_{O2}) over their operating range (Table 5). Given the current interest in very high DO concentrations in the Manawatu River and others like it, it is possible to conduct calibrations of sensors at p_{O2} values greater than 0.21, i.e., for saturation values >100%. This may be possible using "moist-air" calibrations with mixtures of pure oxygen instead of air. Thus, pure oxygen would give a calibration value of 100% X 1/0.21=476%, and a 50:50 nitrogen/oxygen mixture would give 100% X 0.5/0.21=238% saturation (Eq. 1). Before attempting calibrations with gas mixtures or pure oxygen it would be advisable to carry out a normal calibration (moist-air or saturated water) to establish the 100% saturation, as usual, before looking at the meter's response to saturation levels above this value (say, 200% for the WTW optode and >250% for the YSI Pro series handheld meters, that are used by HRC)). If a zero check were also performed with deoxygenated water (using Na_2SO_3 and $CoCl_2$) then sensor linearity could be checked using a three point scale.

5.4 Barometric pressure, elevation and salinity

Atmospheric pressure decreases with increasing altitude so that saturation DO at 15º C decreases by about 1 mg/L per 1000 m. Calibrations made using saturated sea-level concentrations in units of mg/L can be compensated for altitude (A, m) by applying a correction factor (CF)

$$\mathrm{CF} = 0.994 - \frac{\mathrm{A}}{10{,}000} \qquad (4)$$

$DO_A = DO_{sea\text{-}level}$ X CF (5)

Because the % saturation scale is the ratio of two concentrations, each affected by the barometric pressure correction factor, the scale values made at a given altitude (or pressure) hold true and can be converted to mg/L if $C^s_{O_2}$ is known. This can be calculated by multiplying the saturation DO at standard atmospheric pressure (1013.25 mbar), $C^\circ_{O_2}$, by the correction factor (Eq. 4). Thus, for accurate measurements it is important to know the altitude and/or the barometric pressure at the place of measurement.

Salinity affects the saturation of DO according to the Setschenow equation (Eq. 6) and is important in coastal, estuarine and marine waters likely to have significant salinity (Battino et al. 1983).

$$\log_{10}\frac{C^{purewater}_{sat}}{C^{saltsolution}_{sat}} = k_S[\text{salt concentration}] \qquad (6)$$

Instrument manufacturers usually provide tables for correcting saturation DO concentrations in different salinities and, as well, there are many published empirical methods for calculating $C^s_{O_2}$ at any given salinity (S) or chlorinity, and temperature (NB salinity, ‰ = 1.80655 X chlorinity, mg g^{-1}; a measure of the total chloride and other halides in salt waters and a good approximation to the chloride concentration) (NCASI 1985). An example follows (Eq. 7) of an expression cited in NCASI (1985) that enables calculation of $C^\circ_{O_2}$ in mg/L as a function of

salinity (S, ‰) and temperature (TºC). There are many others expressions like Eq. 7 in the literature that are equally reliable.

$$C_{O_2}^{s} = 14.6244 - 0.367134T + 0.0044972T^2 - 0.0966S + 0.00205ST + 0.0002739S^2 \quad (7)$$

A summary of the effects of temperature, atmospheric pressure, altitude and salinity is given in Table 4. For example, if the actual temperature is 11˚C but is recorded as 10˚C, the actual saturation DO will be 2.4% lower than it is assumed to be.

Table 4: Percentage change in saturation dissolved oxygen (DO) with unit change in temperature, atmospheric pressure, altitude and salinity, at different temperature. .

Variable	Change in saturation DO (%)		
	5°C	10°C	20°C
Temperature (°C)	-2.50	-2.41	-2.06
Barometric pressure (kPa)[1]	1.02	0.98	0.98
Altitude (masl)	-0.012	-0.012	-0.012
Salinity (‰)	-0.74	-0.71	-0.67

[1]1013.25 millibar = 101.325 kPa = standard atmospheric pressure

5.5 Units and conversions

The question was asked: which is the more fundamental measurement of DO concentration, mg/L or % saturation? Mass per unit volume (mg/L) can be related to other solution concentration scales like molarity (moles solute per unit volume of solution) by giving a direct indication of the amount of dissolved oxygen (solute) in water (solvent), without reference to saturation conditions that vary with temperature, or equilibrium with the atmosphere under specified conditions. In this sense it is a more fundamental measure than % saturation.

Percent saturation is a dimensionless metric that relates measurements to a reference equilibrium value (typically p_{O_2} = 0.2094) and, because saturation concentrations relate to local conditions of temperature and barometric pressure, gives a relative measure of the degree of saturation at different locations and different ambient conditions.

To convert between mg/L (ppm) and % saturation requires knowledge of the water temperature, assuming that salinity, barometric pressure and altitude corrections are not required – that is, in freshwaters that are no more than 500 m above sea level where saturation DO is decreased by about 5%. Temperature is used to calculate the saturation DO concentration $(C_{O_2}^{s})$ either using Eq. 7, or the simpler formula (Eq. 8), and thus relate % saturation to the measured concentration $(C_{O_2}, \text{mg/L})$ (Eq. 9).

$$C_{O_2}^{s} = \frac{468}{(T + 31.56)} \times CF \quad (8)$$

where T is the temperature (ºC) of the water being measured and CF is the altitude correction factor (Eq. 4).

$$\%\,\text{Saturation DO} = \frac{100}{1} \times \frac{C_{O_2}}{C^{s}_{O_2}} \qquad (9)$$

5.6 Calibration of Horizons equipment

5.6.1 Handheld meters and sensors

Horizons currently use YSI Pro handheld meters fitted with membrane electrodes. In addition to the manufacturer's recommendations we would emphasise that electrodes be calibrated before each field trip in a stable environment like an office or laboratory, as well as in the field if they are used in several locations over the day. It would be good to compare the meter at the end of a field trip with a measurement made using a calibrated (reference) laboratory instrument. That way, any discrepancies could be used to proportionately adjust data, assuming that the initial measurements are accurate.

Laboratory dissolved oxygen meters can be calibrated when they are used (but no less often than once a week) because they are in a stable-temperature environment. Usual practice is to let instruments warm up for 15 minutes before performing calibration using accurate temperature and barometric pressure data to calibrate the instrument (mg/L scale).

Maintenance should include cleaning and replacement of sensor membranes and electrolyte as recommended by the manufacturer (Yellow Springs Instrument Co.).

5.6.2 Continuously logging sondes

Horizons currently use WTW FDO 700IQ meters with optical fluorescence sensors (optodes) that are factory calibrated prior to sale. Nonetheless, we recommend calibration at the start and end of each two-week deployment period. We further recommend that calibration be carried out every two weeks and the data compared with that from a reference DO meter if instruments are deployed for longer periods.

Initial calibrations should be carried out in a (near) constant temperature environment, such as an office or laboratory, using the % saturation scale. Given that the acceptable accuracy for these sensors is ±5% (roughly 0.5 mg/L at 100% saturation) and most of HRC's sites are less than 500 m above sea level this probably an acceptable precision level. Adverse effects of low DO concentrations on aquatic life probably entail measurements that are within 0.5 mg/L. Any changes in instrument calibration (i.e., baseline drift) can be compensated for as described in section 7 of this report.

5.7 Summary of key points about calibration

- Moist-air and saturated water calibration methods are equivalent in principle but calibrations in saturated water are more reliable in practice because they are less likely to be affected by temperature differences.
- Regular cleaning and calibration checks are strongly recommended. Sensor probes should be calibrated before every field deployment or at least at monthly intervals.

- Checks on sensor response to zero DO may be done occasionally using Na_2SO_3 solutions.
- Optodes require less frequent calibration because they are less likely to exhibit electrode drift. They still should be calibrated and any deviations logged.
- Field checks of sondes should be made with reliably calibrated handheld instruments. If DO (in the range 0-150% saturation) differs by more than 5% it is likely that the sonde needs recalibrating. For higher DO values there is often wide divergence between measuring systems and it may only be possible to determine which, if any, is giving the most accurate reading after inspection of the site and use of other meters.
- It may be possible to calibrate instruments at DO concentrations above 100% using gas mixtures (e.g., a 50:50 oxygen:nitrogen mixture for 238% saturation). Normal calibration with 100% saturated water is still recommended. The need for this is contingent on the importance of the data. If DO concentrations > 200% are recorded and used for ecosystem metabolism calculations that describe waterbody quality it may be important to conduct such extra calibrations in order to validate the primary data.
- Correction must be made for altitude, barometric pressure and salinity; where relevant (the precision may not be warranted if you only want to know the DO within 1 mg/L).
- As a rule, a 1°C increase in temperature decreases saturation DO ($C^s_{O_2}$) by about 2-3%; an increase in altitude of 100 m decreases $C^s_{O_2}$ by about 1%; and an increase in salinity of 1‰ causes decrease in $C^s_{O_2}$ of about 0.7%.
- Results can be equivalently expressed as concentration (mg/L) or % saturation units, but water temperature must also be recorded for conversion between units. Concentration units are not affected by temperature and might therefore be considered ‘more fundamental’.

6. Methods for measurement of dissolved oxygen

6.1 Winkler method

The Winkler titration method is widely adopted as a standard reference method by manufacturers like Aanderaa[3] and Yellow Springs Instrument Co.[4], and environmental agencies such as the USEPA and the American Public Health Association (APHA et al. 2005). The method is based upon the addition of divalent manganese solution followed by strong alkali, to the sample in a glass-stoppered bottle. DO rapidly oxidises an equivalent amount of dispersed manganous hydroxide precipitate to hydroxides of higher valency states (notably III). In the presence of iodide ions under acidic conditions, the oxidised manganese reverts to the divalent state (II), with liberation of an amount of iodine equivalent to the original DO content as outlined in the following sequence of chemical reactions. The iodine is titrated with a standardised solution of sodium thiosulphate to determine the initial DO concentration (APHA 2005). The sample may be acidified and titrated in the field at the sample site, but it is more usual to deliver it to a laboratory for titration after acidification of the sample in the field (USEPA 1997). Because it is a quantitative titrimetric method, the Winkler method provides a measure of the oxygen present in a sample without reliance on diffusion across membranes or electrode response. Key reactions are as follows:

Step 1. Reaction of manganous ions with oxygen

$$4Mn^{2+} + 8OH^{-} + O_2(aq) \rightarrow 4MnO(OH) + 2H_2O$$

Step 2. Acidification to give manganic ions

$$MnO(OH) + 3H^{+} \rightarrow Mn^{3+} + 2H_2O$$

Step 3. Production of iodine

$$2\ Mn^{3+} + 2I^{-} \rightarrow 2Mn^{2+} + I_2$$

Step 4. Titration of iodine with thiosulphate

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^{-}$$

Oxidising and reducing agents that may interfere with the method include ferrous and ferric salts, chromate, nitrite, residual chlorine, sulphite, sulphides and readily oxidisable organic matter. As the DO concentration falls below 5 mg/L, manganous ions may appear in the water column. Below 2 mg/L, ferrous ions may appear in the water. Concentration of both metal ions increase as the oxygen falls to zero, when sulphide may be released into the water. These three DO-dependent reactions have the potential to interfere with the Winkler method and produce errors. Consequently, the error free useable range of DO for the Winkler method is between 5 mg/L and 100% saturated, when iron (Fe) and manganese (Mn) are present. This not usually a problem in rivers or wastewaters, but does manifest itself in lake sampling and/or where there are groundwater inputs having Fe and Mn.

[3] http://www.act-us.info/Download/Do_Evaluations/ACT_VS04-01_Aanderaa_DO.pdf
[4] http://www.ysi.com/index.php

Nitrite is the commonest of interference for the Winkler method in natural waters and is eliminated by reaction with sodium azide (NaN_3) according to the following reaction (the Alsterberg or azide modification of the Winkler method) (APHA 2005).

$$N_3^- + NO_2^- + 2H^+ \rightarrow N_2 + N_2O + H_2O$$

Water samples are commonly collected or transferred to a glass BOD bottle having a special stopper that displaces any residual air bubble. Samples can be treated *in situ* by firstly adding a solution of (pink) $MnSO_4$ followed by the alkaline-iodide-azide solution, to give a brownish precipitate. Concentrated H_2SO_4 may be added to dissolve the precipitate and produce manganic ions. At this point the sample is stable and can be safely transported back to the laboratory to complete the analysis. Alternatively, samples collected in standard (300 ml) BOD bottles can be transported to the laboratory and analysed within a few hours, so long as the samples are kept at an even temperature and are not shaken excessively (particularly for supersaturated samples).

Carpenter (1965) reviewed the Winkler method and identified the key source of error as iodine loss during titration. Experienced analysts can maintain a precision of ±0.05 mg/L with visual end-point detection and a precision of ±0.005 mg/L with electrometric end-point detection (APHA 2005). This is much better than can be achieved with most optical and membrane electrode methods. The Winkler method is labour intensive and best suited to laboratory measurements on relatively clean samples with little or no colour. Although the Winkler method may in principle be used for the analysis of supersaturated samples, its accuracy is likely to be greatly reduced as DO increases above 100% saturation because of the possibility of bubble formation and gas loss when manipulating such water samples for *in vitro* measurement. For this reason, sensors that make measurements *in situ* are preferred when DO concentrations exceed 100% saturation. A detailed description for the Winkler method is given in “Standard Methods” (APHA 2005), held in most water quality laboratories. The remainder of this report deals with electrode methods for measuring DO concentration.

6.2 Membrane electrodes

Membrane electrodes are of two kinds: galvanic (potentiometric) and polarographic (amperometric). Both types comprise two solid metal electrodes in contact with an aqueous salt solution (electrolyte), separated from the water being tested by a gas permeable membrane made of either Teflon® or polyethylene. Membrane electrodes have a high sensitivity to temperature largely because of changes in membrane permeability with temperature. Temperature compensation is made automatically with thermistors in the electrode circuit (APHA 2005). Because the membranes are permeable to gases other than oxygen, membrane electrodes may be poisoned by hydrogen sulphide – often produced under reducing conditions in highly polluted waters (e.g., sewage effluents and processing wastes). Manufacturers’ manuals describe ways of rejuvenating electrodes that have been ‘poisoned’ (e.g., gentle buffing or chemical treatment to remove surface films, such as the use of strong ammonium solution to dissolve the silver sulphide from the porous silver anode in the electrode).

Horizons Regional Council uses YSI Pro (since 2009) and YSI 556 (before 2009) handheld meters fitted with galvanic membrane electrodes.

6.3 Polarographic electrode

Polarographic (Clark) electrodes, such as those made by YSI, have a gold cathode, a silver anode at which oxygen is consumed/reduced and a solution of KCl for the electrolyte (Fig. 7). The current produced is proportional to the oxygen flux across the membrane and hence, the external DO concentration. Stirring is important for accurate readings because the oxygen concentration outside the membrane over the cathode becomes depleted as oxygen molecules move through the membrane, causing a lower-than-true reading unless fresh sample water is brought in front of the membrane. YSI membrane sensors require a stirring rate of 30 cm/s for adequate stirring. Stirring is not required in a gaseous sample, such as when calibrating in moist air.

Clark electrodes are generally fast-responding with measurements taking typically 30 seconds to 2 minutes. However, they can be slow to warm up when turned on and up to 10 minutes may be needed for the sensor electrodes to be polarised (i.e., for the current loop to be stabilised). Measurements made during this time may be higher than the true values. The time taken to reach a stable reading is largely a function of the temperature of the probe. The temperature sensor in a standard YSI electrode is a slow response thermistor. The use of the same YSI electrode in an instrument fitted with a high speed temperature sensor can reduce the time to stability to less than 15 seconds. It is recommended best practice to store the electrode in a container of the sample site water and out of direct sunlight if multiple readings are being made, to reduce the range of the temperature compensation required.

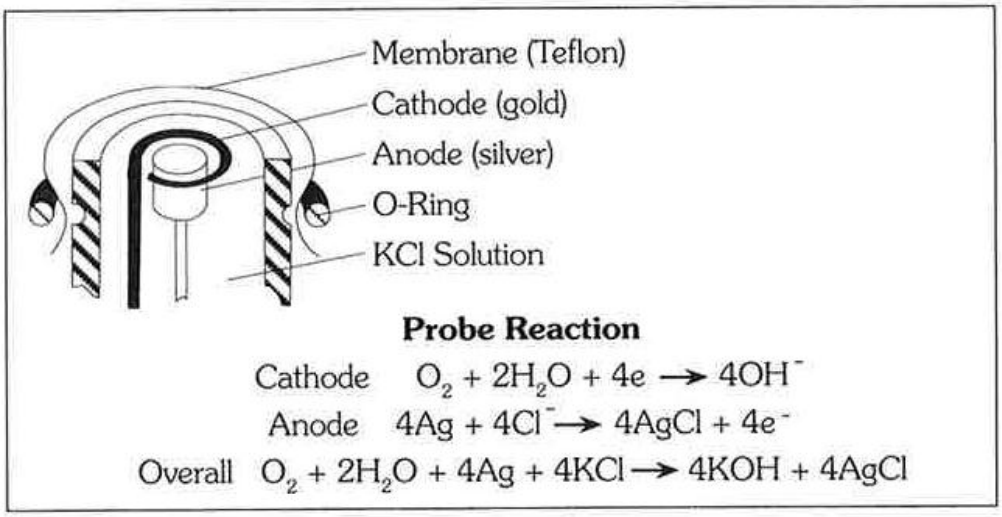

Figure 7: Schematic of Clark electrode and chemical reactions. (From: Making Dissolved Oxygen Measurements, Yellow Springs Inc.).

Apart from interferences, there are some other limitations to the use of Clark electrodes, viz:

- Build-up of silver chloride (AgCl) on the anode (remedied by cleaning the anode).
- Accumulation of base (OH^-) causing the zero to shift over time (remedied by changing the electrolyte solution). This can be compensated for on some instruments.
- Depletion of chloride (remedied by changing the electrolyte).

6.4 Galvanic electrode

The galvanic (Mackereth) sensors produce a millivolt output proportional to the oxygen concentration surrounding the sensor. They commonly have a zinc or lead anode, an inert cathode (e.g., platinum) and a potassium hydroxide solution as the electrolyte. Galvanic electrodes generate their own polarizing voltage and can operate independently of the electronic circuit. Key reactions are as follows:

Anode reaction for zinc anode (lead anode)	$Zn \rightarrow Zn^{2+} + 2e^-$ $(Pb + 2OH^- \rightarrow PbO + H_2O + 2e^-)$
Cathode reaction	$2e^- + (½)O_2 + H_2O \rightarrow 2OH^-$
Net reactions Overall	$Zn + (½)O_2 + H_2O \rightarrow Zn^{2+} + 2OH^-$ $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$ $Zn(OH)_2 \rightarrow ZnO + H_2O$ $Zn + (½)O_2 \rightarrow ZnO$ (white precipitate) $(Pb + (½)O_2 \rightarrow PbO)$

The overall reactions show that because only oxygen and the anode are consumed the sensor can continue being used so long as there is anode material and it is not coated or blocked by metal oxide. Galvanic sensors consume less oxygen than Clark sensors and therefore require less stirring to maintain equilibrium between the electrolyte and the sample water. The response times of polarographic and galvanic sensors are similar; both taking a minute or two to stabilise. Like the Clark electrode, galvanic sensors are also susceptible to chemical interferences and corrosion but this varies a lot with manufacturer design.

6.5 Interference **from other gases**

Gas permeable membranes allow any passage of any gas, some of which may interfere with measurements of DO concentration or damage electrodes within the sensor.

Hydrogen sulphide, H_2S, is produced in anaerobic environments and marine sediments. When H_2S diffuses across a membrane it undergoes hydrolysis to produce sulphide and bisulphide, S^{2-} and HS^-, and attack silver (Ag). In the Clark sensor the silver anode is positively charged to produce Ag^+ ions and is especially susceptible to attack by H_2S.

$$H_2S + OH^- \rightarrow HS^- + H_2O$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O$$

$$S^{2-} + 2Ag^+ \rightarrow Ag_2S \text{ (black precipitate, tarnish)}$$

Dissolved ammonia, at high pH (>10) is mainly in the un-ionised form and can diffuse across gas permeable membranes. This is a problem with galvanic sensors having alkaline (NaOH) electolytes where the ammonia may attack the lead anode. This may be a potential problem if a galvanic membrane sensor was deployed in a dairy farm effluent oxidation pond where NH_4-N concentrations of up to 200 mg/L occur (Craggs et al. 2004).

6.6 Optodes

The principle of measurement for optical DO electrodes, or optodes, is based on luminescent quenching by molecular oxygen (Fig. 8). A fluorescent indicator is embedded in a gas permeable foil that is exposed to the surrounding water. The foil is excited by a modulated blue light, and the phase of a returned red light is measured. The significant advantage of optodes is that oxygen is not consumed during the measurement and therefore there is no need to stir the water surrounding the probe, as is the case for membrane electrodes.

Manufacturers also claim that fouling and instrument drift is minimal compared to other oxygen measurement systems, so calibration is not required so regularly. Another advantage of optodes over membrane electrodes is their rapid response. Response times of <8 seconds (for 63%) have been claimed (Aanderaa 4835). The Zebra-tech D-opto optode response time is “90% in less than 60 seconds”.

WTW optodes sensors presently used by HRC for continuous monitoring of DO) model FDO 700 IQ) utilise a fluorescent dye that is stimulated in the membrane by a short wave length light source (see diagram in Appendix 1). By falling back into the passive state, long wave light is emitted, which is recorded as a measurement signal. If oxygen contacts the dye by diffusing through the membrane the period of back scattering light is shortened according to the oxygen concentration of the sample. In principle the measurement of the fluorescent signal come back to a highly precise time measurement.

The WTW FDO 700 IQ sensors have a stated 90% response time of 150 seconds (Appendix 1) and use a green light that has a longer wavelength than the standard blue light (Fig. 8) and is less likely to bleach the photosensitive pigment in the sensing foil, giving them a longer user-life than other makes that use blue light (Appendix 1).

Optode windows may delaminate, particularly when exposed to harsh conditions (e.g., during flood flows in a river deployment) or when their depth rating is exceeded. The results of this are an increasingly noisy signal and baseline drift, performance that is also manifested by membrane electrodes in such conditions. Similarly, anything affecting the external optical pathway (e.g., sediment accumulation or detritus) is likely to cause the optode to produce spurious data. A field evaluation of two new dissolved-oxygen sensing technologies, the Aanderaa Instruments AS optode model 3830 and the Sea-Bird Electronics, Inc., model SBE43, was carried out at about 32 m water depth in western Massachusetts Bay. Optode measurements degraded when fouling was severe enough to block oxygen molecules from entering the sensing foil over a significant portion of the sensing window. Minimal drift was observed in the two optodes until about 225 and 390 days of deployment, and was attributed to degradation of the sensing foil (Martini et al. 2007).

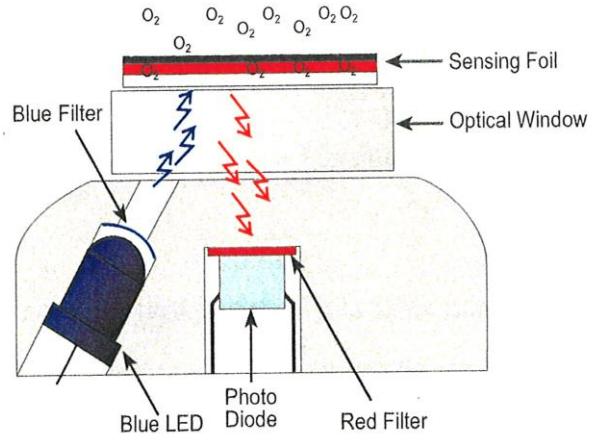

Figure 8: Conceptual diagram of a dissolved oxygen optode. (From: Aanderaa Data Sheet D355, October 2004).

Detection levels (DL) and precisions for different methods of measuring DO concentration in water are given in Table 5. The claims of manufacturers regarding precision and detection levels are sometimes not supported by the field experience of users. There are few DO methods or instruments that can measure accurately below around 0.1-0.2 mg/L, but some can discriminate to the second decimal place. Since the reported DL is 10% of the precision, the DL is essentially meaningless.

Table 5: Comparison of detection levels and precisions for different dissolved oxygen (DO) measurement methods. Concentrations are mg/L and specifications are cited from manufacturer's websites accessed in December 2010.

Method	Precision (mg/L)	Detection level (mg/L)	Range[1] (% saturation)	Reference
Winkler titration	±0.05	0.01	0-100[2]	APHA (2005), Environment Canada (1974)
YSI Pro2030 handheld meter (galvanic or polarographic)	±0.20	0.01	0-500	www.ysi.com
YSI Optical BOD probe	±0.10	0.01	0-500	www.ysi.com
YSI ROX optode for sondes	±0.10 (0-10) ±3-5 (20-50)[5]	0.01	0-500	www.ysi.com
Aanderaa 4835 optode	±0.15	0.02	0-150	www.aadi.no
Zebra-tech D-opto optode[3]	±0.02 or 1%, whichever is greater	0.02	0-250	www.D-opto.com
WTW FDO® 700IQ (SW)[4]	±0.01	0.01	0-200	www.WTW.com

[1] Note comments in text about responses to DO concentrations of zero mg/L. Actual minimum values are more likely to be 0.1-0.2 mg/L.

[2] It may be possible to measure DO concentrations of up to 150% saturation using the Winkler method, taking great care when transferring samples to the initial reaction vessel.

[3] Instrument used by Horizons Regional Council up to 2009.

[4] Instrument used by Horizons Regional Council since 2010. Note the manufacturers claim that WTW's FDO 700 IQ belongs to a new generation of optical D.O. sensors that eliminate the shortcomings of former instruments. The membrane geometry has been optimized to avoid accumulations of air bubbles on the membrane surface that might give incorrect measurement results.

[5] http://www.ysi.com/media/pdfs/E32-6150-ROX-DO-Sensor.pdf

Handheld DO meters used by: Horizons Regional Council: YSI Pro (since 2009); YSI 556 (before 2009). Both have membrane electrodes.

Inter-method comparisons generally show good agreement between laboratory measurements made by membrane electrodes and the Winkler method, and between membrane and optical electrodes for DO levels in the range 0-10 mg/L.

7. QA/QC

As stated previously, calibration should always be carried out at the start of a sonde field deployment and comparisons made with calibrated field (handheld) meters during and after the deployment. All calibration and check comparisons should be recorded to keep a running log of sonde performance and maintenance. Comparisons between instruments and with Winkler titrations may also be useful.

7.1 Ways to recover data

Data offset occurs when the continuously recorded data differs from a reference measurement, usually made with a recently calibrated handheld DO meter. Such data should be adjusted 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 adjustment should be from a particular time only. A linearly increasing offset of the DO data can be adjusted as follows

$$\mathrm{DO}_{\mathrm{adjusted}} = \mathrm{DO}_{\mathrm{measured}} - \alpha \qquad (10)$$

$$\alpha = \frac{\Delta_2 - \Delta_1}{t_2 - t_1} \qquad (11)$$

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 DO concentrations (e.g., Fig. 9). 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 Equation 10 for the second part. Stepwise linear adjustments may be made if three or more comparisons are made with reference devices that show that the drift is variable. This requirement may be reduced by having regular checks with reference instruments, and recalibrating as necessary until a safe period for reliable data acquisition is established for any given datalogger. Historical data sets may be corrected 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 (Fig. 10). To distinguish between real data and sensor failure, the noise associated with real data has a pattern which 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. For example, in Figure 5, data on 15/16th are consistent with bright sunny days and little or no clouds. The small step reduction after the midday peak may reflect bank shading of the river bed at that time. Data

on 16/17th are also acceptable because the noise is below the expected DO curve based on the cloudless day data and the step due the bank shadow is present. The data on 17/18th is not acceptable because the noise is above the expected DO curve for a sunny day with a few of the "low" data points falling in the region of the expected DO curve for that time of day.

In Figure 9, there is substantial noise during the dark periods of the diel cycle (upper curves). Because photosynthesis should be near zero in the dark, that noise suggests sensor malfunction.

Peak clipping occurs when *in situ* DO concentrations exceed the operational maximum of the instrument. Nothing can be done to restore data but there are usually diel curves within any given period that are not affected by clipping (Fig. 11).

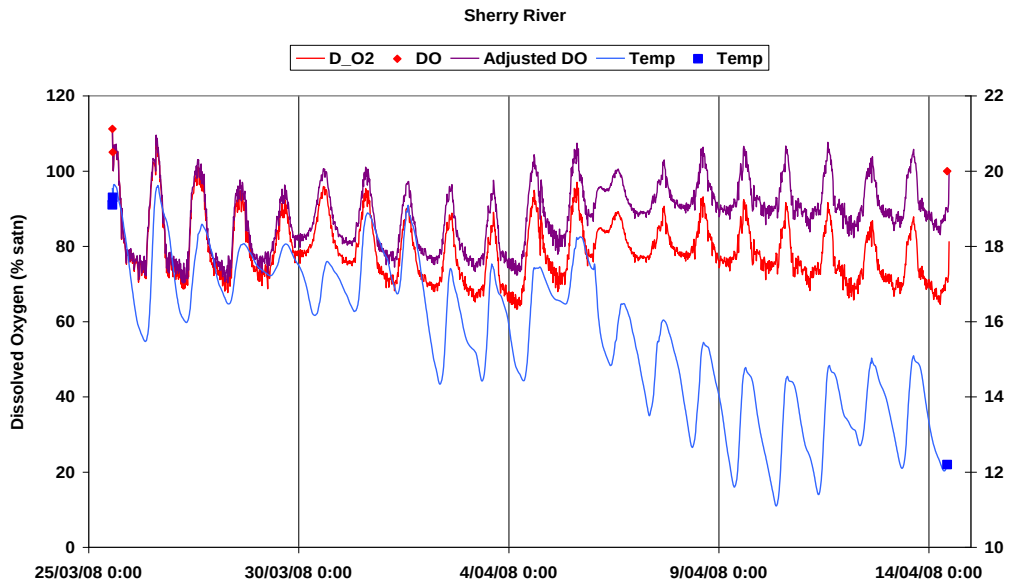

Figure 9: Example of an adjusted dissolved oxygen (DO) time series from a sonde deployment showing the original and adjusted DO data. Spot measurements for checking sonde data are shown as dark blue squares (temperature) and red diamonds (DO). (John Nagels, NIWA).

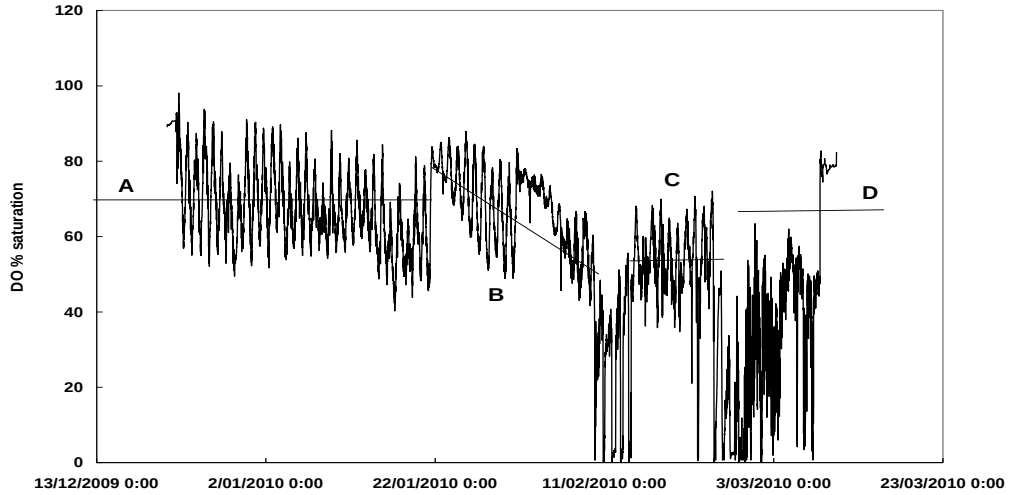

Figure 10: Example of a dissolved oxygen (DO) sonde time-series showing good data (A), baseline drift (B), noisy but usable data (C) and unusable noise (D). . (John Nagels, NIWA).

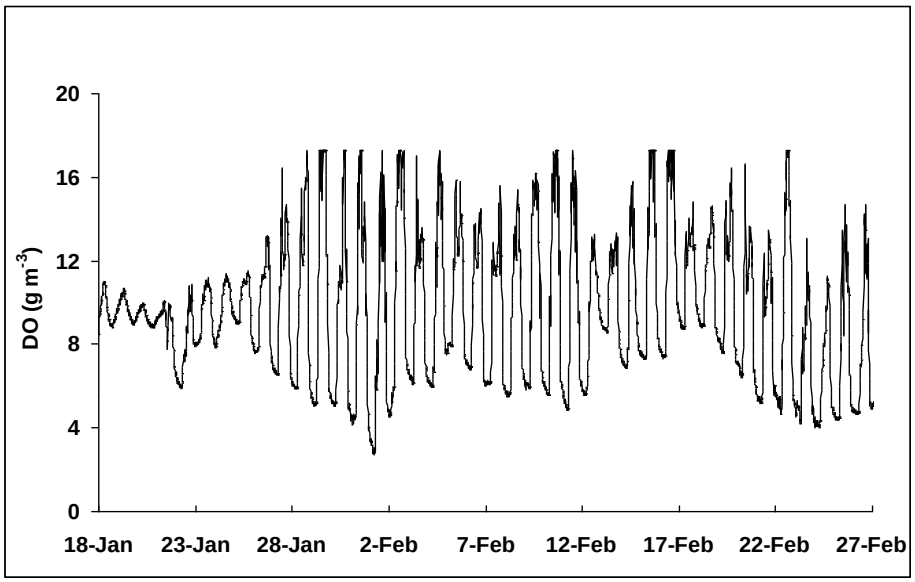

Figure 11: Shag River dissolved oxygen (DO) time-series collected with an optode in 2008. Note the clipping of peaks when DO concentration exceeds the instrument maximum of 17 g/m^3. (Bob Wilcock, NIWA).

7.2 Summary of key points for QA/QC

- Regular checking of field DO measurements with freshly calibrated, handheld DO meters allows early detection of sonde malfunction (drift, noise).
- It is recommended that calibration offsets and check comparisons be logged for each (optode) sonde deployed by HRC.

- Simple offsets between reference devices and field instruments can be adjusted by assuming a linear rate of baseline drift.
- Noise may be real (intermittent light conditions) or an artefact of sensor malfunction.
- DO time-series should not have noisy signals (under steady flow conditions) during bright sunny days or at night.
- Peak clipping occurs either when real DO exceeds the instrument limit, or as a result of sensor malfunction (detectable by comparison with a check instrument).

8. Calculating ecosystem metabolism from DO data

Ecosystem metabolism - the combination of rates of primary production (photosynthesis) and rates of ecosystem respiration - is a measure of the main biological factors controlling dissolved oxygen dynamics in rivers and indicates how much organic carbon is produced and consumed in river systems. Concentrations of DO in the water are critical components affecting the life supporting capacity of a river system. DO concentrations are affected by three key processes: (1) oxygen production associated with photosynthesis of algae and aquatic plants, which raises the oxygen concentrations within the water, (2) oxygen uptake associated with respiration of all river life including fish, invertebrates, algae, aquatic plants and microbes, which lowers the oxygen concentrations in the water, and (3) oxygen transfer across the air-water interface, which enhances equilibrium between water and atmosphere and can either raise or lower oxygen concentrations. Oxygen transfer across the air-water interface, or reaeration, is a wholly physical process that causes a rise in DO for under-saturated water, and vice versa. That is, reaeration 'pushes' DO towards equilibrium (100% saturation) with the atmosphere.

Research has shown that ecosystem metabolism is a useful functional indicator of river ecosystem health (Bunn et al. 1999; Fellows et al. 2006; Young et al. 2008; Clapcott et al. 2010). Sites with high rates of ecosystem respiration (ER) are normally characterised by high biomass of algae and other aquatic plants, and/or large inputs of organic matter from point source discharges of sewage/waste water, and/or large diffuse inputs from sources such as agricultural run-off. Such sites will be prone to low minimum dissolved oxygen concentrations (especially when reaeration rates are low), which have the potential to kill fish and other aquatic life. Sites with high rates of gross primary production (GPP) will normally be characterised by a river bed covered with a high biomass of periphyton (algae and other slimes growing on the substrate) or other aquatic plants. The highest rates of GPP will occur *in situ*ations where there is plenty of light and nutrients available to support plant growth. Sites with high GPP are likely to experience algal and cyanobacterial blooms that can degrade aquatic ecosystems and aesthetic and recreational values, and have potential health implications for humans and animals (Table 6).

Table 6: Framework for assessing river health using gross primary productivity (GPP) and ecosystem respiration (ER) data. The scores indicate the health of the test site: 2, no evidence of an impact on ecosystem functioning; 1, mild effect on ecosystem functioning; 0, severely impaired ecosystem functioning. (From Young et al. 2008)

Method	Assessment parameter	Criterion	Score
Comparison with reference	Ratio of GPP at test (GPP_t) and reference (GPP_r) sites	GPP_t:GPP_r <2.5	2
		GPP_t:GPP_r = 2.5-5.0	1
		GPP_t:GPP_r >5.0	0
	Ratio of ER at test (ER_t) and reference (ER_r) sites	ER_t:ER_r = 0.4-1.6	2
		ER_t:ER_r = 0.2-0.4 or 1.6-2.7	1
		ER_t:ER_r <0.2 or >2.7	0
Absolute value	GPP at test site ($g\ O_2/m^2/day$)	GPP_t <3.5	2
		GPP_t = 3.5-7.0	1
		GPP_t >7.0	0
	ER at test site ($g\ O_2/m^2/day$)	ER_t = 1.6-5.8	2
		ER_t = 0.8-1.6 or 5.8-9.5	1
		ER_t <0.8 or >9.5	0

8.1 Open-system measurements or chambers

Metabolism can be estimated by measuring natural changes in oxygen concentration within river systems, or alternatively by enclosing part of the ecosystem within an air-tight chamber and measuring oxygen changes within the chamber. Open-system methods have the advantage that they include the whole ecosystem and in many situations measurements are relatively simple and require just one oxygen logger (Young & Huryn 1996). Oxygen concentrations are measured at regular intervals over at least one 24 hour period and changes in concentration are related to oxygen inputs due to photosynthesis and removal via respiration. The main difficulty with open-system measurements is that they require an estimate of the rate of oxygen exchanging between the air and the water. Reaeration can be easily estimated in most rivers and streams (see Section 8.2). However, more complicated techniques are required in small, very turbulent streams with low primary productivity (Marzolf et al. 1994, 1998; Young & Huryn 1998, 1999; Roberts et al. 2007). The extra equipment and effort required to estimate oxygen exchange rates probably limits the feasibility of open-system measurements to routine stream health monitoring in these types of streams.

Measurements of metabolism made within chambers usually also use changes in oxygen concentration in chambers over a period of at least 24 hours (Bott et al. 1978). However, respiration rates and maximum photosynthesis rates can be estimated over shorter periods by comparing oxygen changes in chambers exposed to high light intensities with those in artificially darkened chambers (Hickey 1988). Chamber measurements have been useful to assess the contribution of different components of river ecosystems to overall metabolism (Naiman 1983; Mulholland et al. 1997; Naegeli & Uehlinger 1997). Since the oxygen changes are measured within an airtight chamber, estimates of metabolism can be made without measurements of reaeration. DO loggers and stirrers that can be installed inside the

chamber or through a port in the side of the chamber are now available. However, there are many limitations of using chambers which include:

- Material placed within the chamber is invariably disturbed during the process.
- Water velocity, light and temperature within the chamber will differ from natural conditions experienced in the river.
- Errors may occur when trying to relate measurements from different components of the ecosystem determined at a small spatial scale to what is occurring at the scale of a whole reach.
- Nutrients can become depleted within chambers, resulting in artificially low metabolism measurements.
- During periods of peak photosynthesis, oxygen may diffuse out of the water within the chamber forming bubbles which are not included in subsequent measurements of dissolved oxygen.
- Metabolic processes within important components of river ecosystems, such as the hyporheic zone (the habitat connected to the river but beneath the stream bed), are difficult or impossible to measure using chambers.
- Chamber design and construction is not easy and is relatively expensive.
- A large amount of equipment (chambers, pumps, hoses, power supply) is needed, because at least 3 separate chambers are required for replicate measurements at each site. There is also a risk of losing large amounts of equipment and data with unexpected rises in flow (or theft). In practice, deployment of several chambers or light and dark paired chambers may be better served by sampling via a narrow bore tube, drawing the water into a 60ml syringe and using a calibrated BOD probe to measure the DO. This water sample can then be used to measure nutrient changes in the chamber (e.g., Gibbs et al. 2005).

Considerable effort has been made to overcome some of these disadvantages (Bott et al. 1997; Dodds & Brock 1998; Bunn et al. 1999; Uzarski et al. 2001). However, many of the problems cannot be solved simply by adjustments to chamber design. Therefore, we do not recommend chambers for use in routine measurements of river ecosystem health. However, chambers have an important role in specific non-routine and compliance investigations.

8.2 Estimating reaeration

As mentioned above, open-system measurements of metabolism require an estimate of the amount of oxygen transferring between the water and the atmosphere. The easiest way to do this is to use measurements of changes in oxygen concentration, which are required for the metabolism measurements anyway. There are two techniques for using the oxygen record to estimate oxygen exchange rates. They are both “single-station analyses”, which ignore any longitudinal gradients of oxygen concentration — only variations with time-of-day are accounted for. Therefore, if these techniques are to be employed, the assumption that

longitudinal DO gradients can be ignored at the monitoring site must be justified.[5] As a rule of thumb for single-station diel curve analysis, river conditions should be the same for a distance of $3U/k_a$ where U is the reach-average velocity and k_a is the stream reaeration coefficient. This may be done by visual inspection of the reach upstream of the selected station.

The first method (the night-time regression method), used by Young & Clapcott (2010) to analyse HRC data, uses information on changes in oxygen concentration through the night and also simultaneously calculates the respiration rate (Hornberger & Kelly 1975; Kosinski 1984). During the dark, photosynthesis stops and so any changes in oxygen concentration are due to either uptake by respiration within the river, or diffusion of oxygen through the river surface, as represented in the following simple ordinary differential equation:

$$\frac{\mathrm{d}O}{\mathrm{d}t} = -R + k_a D \qquad (12)$$

where O is the dissolved oxygen concentration (mg/L), t is time-of-day (day fraction), R is the rate of oxygen uptake by respiration (mg/L/day), k_a is the stream reaeration coefficient (base e, day^{-1}) and D is the dissolved oxygen deficit (mg/L), such that $D = O_{sat} - O$ where O_{sat} is the saturation concentration of dissolved oxygen at the monitoring site (mg/L). The term k_aD represents the rate of oxygen transfer across the river surface. R has a negative sign in front of it because respiration always involves oxygen uptake. The k_aD term can be either positive (oxygen transfer into the river) or negative (oxygen transfer out of the river) depending on whether the water is under-saturated or over-saturated.

The rate of change of oxygen concentration ($\mathrm{d}O/\mathrm{d}t$) and D are known from the oxygen record. Therefore, using a simple linear regression on data points collected throughout the night it is possible to estimate R and k_a as the y-intercept and slope of the regression line, respectively (Fig. 12).

[5] Chapra & Di Toro (1991) note that there needs to be a uniform distribution of plants a distance of at least $3U/k_a$ upstream of the monitoring site for this assumption to be valid, where U is cross-section average velocity and k_a is the reaeration coefficient; U and k_a must have consistent units (e.g., if U is in m day^{-1} then k_a must be in day^{-1}).

“

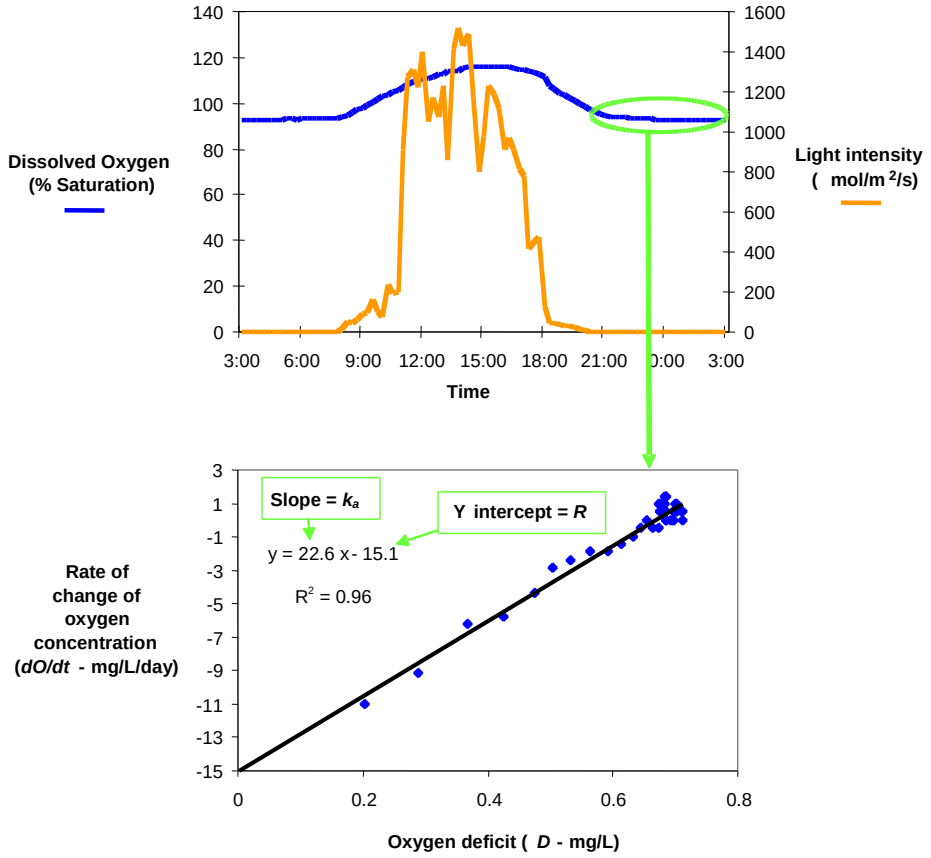

Figure 12: Typical changes in dissolved oxygen over a 24-hour period and a demonstration of how the oxygen record is used to calculate the respiration rate, *R*, and the reaeration coefficient, k_a.

A second method to calculate the reaeration coefficient using the oxygen record (the Approximate Delta Method, or ADM, where Delta is the maximum DO difference in a 24 hour period) relies on a mathematical solution of the equation describing changes in dissolved oxygen concentration at a site over a 24 hour period, assuming clear skies (Equation 14 in the next section). This mathematical solution shows that the reaeration coefficient is dependent on only two variables; the time lag between solar noon and when the minimum dissolved oxygen deficit occurs, and the length of the daylight period (Chapra & DiToro 1991). McBride (2002) has provided a logistic equation to describe this relationship.

$$k_a = 7.5\left(\frac{5.3\eta - \phi}{\eta\phi}\right)^{0.85} : \eta = \left(\frac{f}{14}\right)^{0.75} \qquad (13)$$

where ϕ is the time lag between solar noon and maximum DO (day fraction), η is the dimensionless photoperiod correction factor, and f is the photoperiod or day length (day fraction). This procedure seems to work well in rivers with a low reaeration coefficient, but is very sensitive to error in the calculation of the time lag in streams with higher reaeration coefficients, which will have short time lags (but may not exhibit pronounced diel DO variations). For example, using the example presented in Figure 12, the peak light intensity occurred at 13:45 NZDT. The highest oxygen saturation was 116% and was constant at this level from 14:30 NZDT to 16:00 NZDT. Therefore the time lag was somewhere between 0.75 and 2.25 hours. Assuming a day length (photoperiod) of 12 hours, the reaeration coefficient estimated using this approach (Equation 13) varies from 9-33 day^{-1}, which is substantial variability. If an average time lag of 1.5 hours is assumed, the reaeration coefficient is estimated to be 15.8 day^{-1}, which is reasonably close to the value (22.6 day^{-1}) calculated using the night time regression method presented in Figure 12. The Delta method for estimating the reaeration coefficient is used in WAIORA, a low-flow decision support system developed by NIWA (McBride et al. 1998).

An alternative approach to estimating the reaeration coefficient is to use empirical and theoretical equations from the literature which use mean reach depth and mean velocity. A variety of equations have been suggested in the past (Wilcock 1982). If this approach is used then we recommend the modified O'Connor-Dobbins, Owens-Edwards-Gibbs, or Bennett-Rathbun equations (Table 5); these appear to perform reasonably well at sites with reaeration coefficients up to 50 day^{-1}, but not so well in small turbulent streams (Young & Huryn 1999).

Table 7: Empirical velocity depth equations for calculating k_a (base e, day^{-1}). U is mean stream velocity (m s^{-1}) and H is mean stream depth (m) (modified O'Connor-Dobbins from Wilcock 1982).

Authors	Formulae
O'Connor-Dobbins	$3.74\ U^{0.5} / H^{1.5}$
Modified O'Connor-Dobbins*	$5.24\ U^{0.5} / H^{1.5}$
Churchill-Elmore-Buckingham	$5.01\ U^{0.969} / H^{1.673}$
Isaacs-Gaudy	$4.75\ U / H^{1.5}$
Langbein-Durum	$5.13\ U / H^{1.33}$
Negulescu-Rojanski	$10.9\ (U / H)^{0.85}$
Owens-Edwards-Gibbs	$5.33\ U^{0.67} / H^{1.85}$
Bennett-Rathbun	$5.59\ U^{0.607} / H^{1.689}$

*Developed for a range of New Zealand rivers (Wilcock 1984)

The most accurate method of estimating the reaeration coefficient is to directly measure the loss of a purposefully added inert tracer gas (e.g., propane, methyl chloride, SF_6) in a study reach (Wilcock 1984; Wanninkhof et al. 1990; Marzolf et al. 1994; Young & Huryn 1999). This method is necessary in small turbulent streams where the other techniques work poorly.

However, it requires a significant amount of effort and equipment and therefore is probably outside the scope of most regular stream health monitoring programmes.

8.3 Summary of key points for estimating of reaeration

- The reaeration coefficient (k_a) is a crucial parameter for describing diel changes in DO concentration. It characterises oxygen transfer across the air-water interface and is a wholly physical process.
- Two ways of estimating k_a using single-station DO time-series are: the night-time regression method and the Approximate Delta Method (ADM). Both methods agree well at low-moderate values of k_a, (say 0-30 d^{-1}).
- Simple linear regression of the rate of change of night-time DO concentration with time against the DO deficit (difference between saturation and actual DO concentration) yields a straight line with slopes k_a and intercept R (the average rate of community respiration).
- The ADM is based on Delta, the maximum DO difference in a 24 hour period and relies on a mathematical solution of the equation describing changes in dissolved oxygen concentration at a site over a 24 hour period, assuming clear skies.
- Values of k_a may also be calculated from empirical and theoretical equations using hydraulic data (depth, velocity, slope etc.). Each equation should only be used in conditions similar to that used to calibrate it.
- The most accurate method of estimating the reaeration coefficient is to directly measure the loss of a purposefully added inert tracer gas (e.g., C_3H_8, SF_6).
- We recommend that analysis of HRC data for parameterisation of DO data and classifying ecosystem pollution and stress, be carried out using either night-time regression or ADM approaches.

8.4 Estimating ecosystem metabolism components

Here we compare results obtained from the night-time regression approach and the ADM for single-station ecosystem metabolism analyses. In doing so we need estimates of P (for the night-time regression method) and for both R and P (for the ADM method), where P is the the photosynthetic production rate. To do so we note that during daylight hours that oxygen production also occurs and so the governing equation becomes a little more complex than Equation (12):

$$\frac{dO}{dt} = P(t) - R + k_a D \qquad (14)$$

where $P(t)$ is the time-varying photosynthetic production rate (mg/L/day). The night-time regression method calculates P by rearranging Equation (14) to give:

$$P(t) = \frac{dO}{dt} + R - k_a D \qquad (15)$$

For each interval over the 24 hour period *P(t)* is calculated using Equation (15), since d*O*/d*t* and *D* are known from the DO measurements and *R* and k_a were calculated from the night-time regression mentioned above. This approach assumes that *R* and k_a are constant throughout the 24 hour period, which is a relatively weak assumption since they are expected to vary with diel changes in temperature. To address this, temperature compensated rates of *P* can be calculated assuming that *R* will double with a 10°C increase in temperature (7.18% per degree; Phinney & McIntire 1965) and k_a will increase by 2.41% per degree (Kilpatrick et al. 1989). Temperature compensated values of *P(t)* for each interval during daylight hours are then summed to give the *P* (or GPP) for the day.

In the ADM method (McBride & Chapra 2005), having first calculated k_a as in the previous section, the 24-hour average value of *P* (i.e., "P_{av}") is then calculated under the assumption that the time-variation of its magnitude can be expressed as a half-sinusoid during daylight hours. Its daily-average value is calculated as

$$P_{av} = \left(\frac{\eta\Delta}{16}\right)\left(33 + k_a^{1.5}\right) \qquad (16)$$

where η is defined in Equation 16) and Δ is the magnitude of the diel variation in DO mg/L (hence the name "Delta Method"). The respiration term is then simply calculated as

$$R = P_{av} + k_a \overline{D} \qquad (17)$$

where $\overline{D}$ is the average DO deficit over 24 hours.

Note that the fundamental form of P_{av} and *R* in these equations is necessarily in terms of volumetric rates (mg/L/day or, equivalently, g/m^3/day). However in practice they are often transformed to areal rates (g O_2/m^2/day, e.g., Young et al. 2008). These are obtained by multiplying the volumetric rates by average reach depth, facilitating the comparison between sites with different depths (Young & Collier 2009). Thus, knowing reach-average depths it is possible to compare measurements quoted volumetrically or areally at different locations.

8.5 A comparison of measurement approaches

All approaches for calculating metabolism are dependent on accurate dissolved oxygen data collected when photosynthesis, respiration and reaeration are the main mechanisms driving variability in dissolved oxygen concentrations. In some situations inputs of groundwater containing low concentrations of dissolved oxygen will strongly influence in-stream DO and therefore bias metabolism calculations (McCutchan et al. 2002; Hall & Tank 2005; Demars et al. 2011). Similarly, if significant rainfall occurs during the monitoring period, resulting in sharp increases in flows, then oxygen concentrations in the river water will reflect rainwater composition (i.e., close to 100% DO saturation) rather than in-stream ecological processes. Calculations should not be attempted on data affected by significant rainfall. What is most

important is that flows are steady and we recommend that metabolism analysis not be conducted with data collected when flows vary by more than 30%.

Comparisons of metabolism calculations conducted using open-system and chamber methods are relatively common (e.g., Marzolf et al. 1994; Mulholland et al. 1997; Uzarski et al. 2004). However, comparisons of metabolism estimates conducted using different open-system measurements are relatively rare (but see Kosinski 1984; Young & Huryn 1999).

In order to make comparisons between the night-time regression approach (Equations 12 & 15, Fig. 13) and the approximate Delta method (Equations 13, 16 & 17), data from five sites were collated and ecosystem metabolism calculated independently using each method. Sites were chosen to cover a range of ecosystem metabolism rates and low, medium and high reaeration coefficients. A comparison of results produced by the night-time regression and ADM methods is given in Table 8.

Table 8: Comparison of single-station productivity analysis parameters derived from the night-time regression method and the approximate Delta method (ADM). Key: k_a (d^{-1} base e) is the reaeration coefficient, P_{av} (mg/L/d) is the 24-hr average rate of gross photosynthetic production, and R (mg/L/d) is the 24-hr average rate of ecosystem respiration. The R^2 value for the night-time regression method gives an indication of the confidence that can be given to the metabolic parameters – little confidence should be given to values when R^2 is <0.4. (Data provided by Roger Young, Cawthron Institute).

River	Night-time regression method					ADM method			
	k_a	P_{av}	R	P_{av}/R	R^2	k_a	P_{av}	R	P_{av}/R
Tukituki T9	13.4	38.8	10.7	3.62	0.83	8.44	23.6	6.18	3.82
Meadow Burn 3*	7.73	3.6	10.3	0.346	*0.83*	*45.2***	*21.5***	*60.0***	*0.357*
Mangaokewa 1	18.1	1.5	8.0	0.194	0.91	NC	NC	NC	NC
Tukituki T12*	7.35	11.4	7.5	1.52	0.91	4.09	9.47	7.45	1.27
Motueka Woodstock	21.0	6.7	4.7	1.44	0.95	37.0	13.0	9.35	1.39

*Data smoothed using a five-point moving average to give better r^2 values
**Not a good fit because of cloud after midday; indicative results only
NC=not able to be computed because the DO maximum preceded solar noon, cloudy afternoon or longitudinal gradients

The comparison of results (Table 8) shows good agreement where conditions are suitable for analysis, viz. Tukituki T9 and T12, and Motueka Woodstock. Of note is the excellent agreement between the methods for *P/R*.

Another way of testing the parameter results is to use them to generate 24-hr DO diel curves that can be compared with the original data; i.e., a test of self-consistency (Fig. 13). This shows good agreement where (a) the DO peak occurs well after solar noon; (b) diel curves are not badly affected by cloudiness (interrupted light) and criteria for single-station curve analysis are complied with. From this it may be concluded that both methods are suitable where conditions permit, with the night-time regression method being more suitable when reaeration coefficients are high and DO peaks occur less than 1 hour after solar noon.

We caution against only using single-station primary productivity analysis and respiration rates to determine ecosystem health of rivers, and strongly recommend that these be part of

a package of monitoring tools (e.g.,, MCI scores, periphyton cover, water quality data other than DO) used to assess river condition (Young & Collier 2009). When productivity analysis is used we recommend that the DO profiles used in the analysis be displayed along with values for the productivity analysis parameters and some assessment of the credibility of their values (e.g., use R^2 values to determine the strength of the night-time regression, and possibly empirical depth velocity relationships (Table 2) is made to validate the reaeration coefficient, k_a values (Wilcock et al. 1998).

8.6 Summary of key points on estimating ecosystem metabolism

- The ADM and night-time regression methods give similar results for estimating productivity analysis parameters (P_{av}, R and k_a) provided:
  - Peak DO occurs at least 1 hr after solar noon.
  - Diel curves are not badly affected by cloudiness.
  - Criteria for single-station curve analysis are complied with.
- The night-time regression method is more flexible than the ADM method and still works when reaeration coefficients are high and DO peaks occur less than 1 hour after solar noon (the midpoint between sunrise and sunset).
- Calculations should not be attempted using data affected by significant rainfall. We recommend that metabolism analysis not be conducted with data collected when flows vary by more than 30%.
- We caution against only using single-station primary productivity analysis and respiration rates to determine ecosystem health of rivers, and strongly recommend that these be part of a package of monitoring tools to assess river condition.

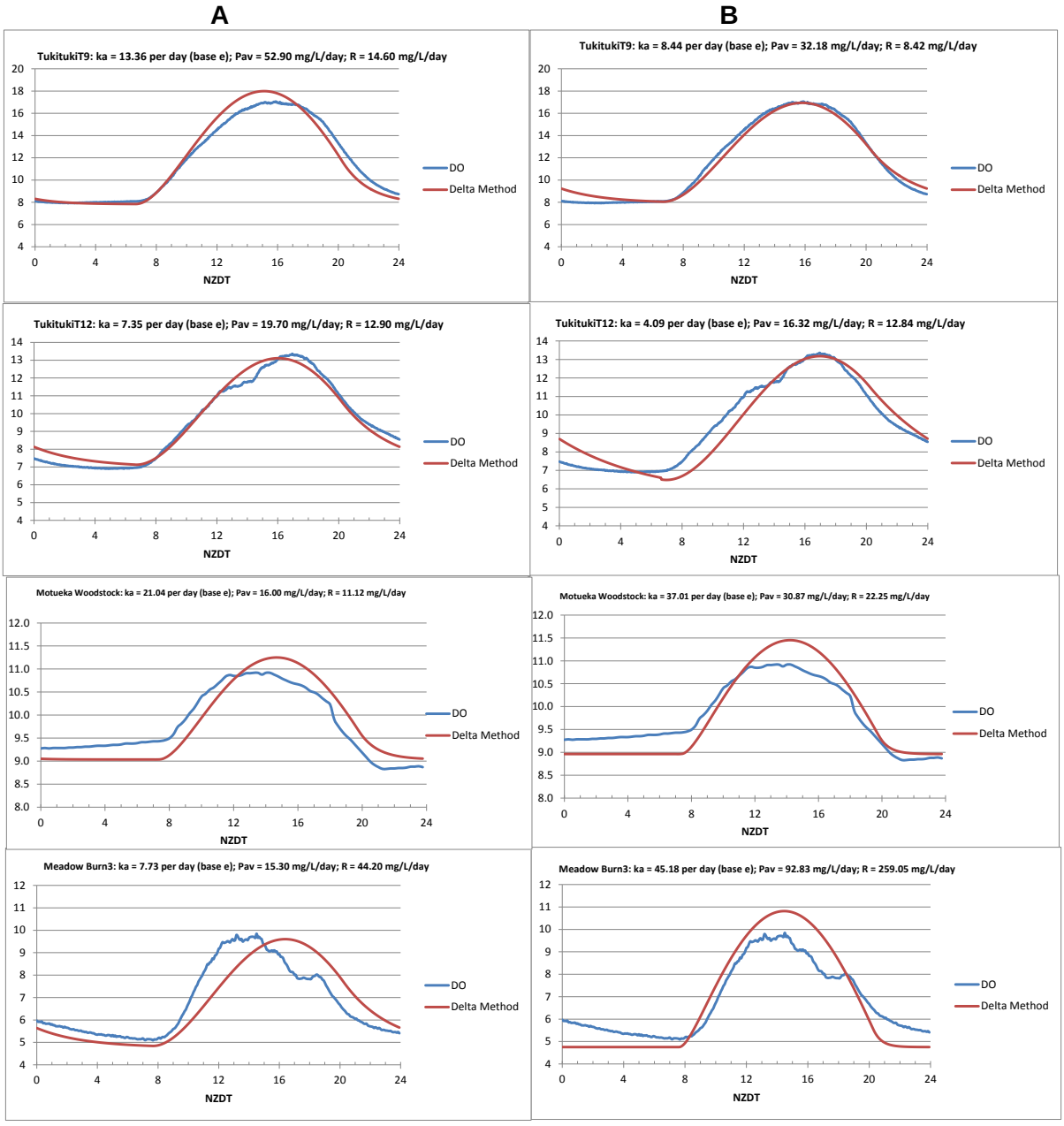

Figure 13: Comparison of diel curve predictions (red line) with field data (blue line). Two parameter estimation methods for the reaeration, production and respiration parameters (k_a, P_{av} and R): Column A—night-time regression method; Column B—Approximate Delta Method. *

*Notes: Order of curve fits (top-to-bottom): Tukituki T9, Tukituki T12, Motueka Woodstock, Meadow Burn 3. Data for the parameters are given in Table 4. The Mangaoweka site data could not be compared because the ADM method requires that the maximum DO occurs after solar noon (considerable cloud cover occurred after midday at this site).The predictions have been made using the exact "Delta Method" analytical solutions to Equation (14) (Chapra & Di Toro 1991, McBride & Chapra 2005), which assumes that photosynthesis varies during daylight hours as a half-sinusoid, with maximum at solar noon.

9. Protocols used elsewhere

We are aware of only four studies that have reported ecosystem metabolism results derived from long-term continuous monitoring of dissolved oxygen concentrations (Uehlinger 2000; Uehlinger 2006; Roberts et al. 2007; Izagirre et al. 2008).

For the Uehlinger studies, dissolved oxygen was measured quasi-continuously by the Swiss National Hydrological and Geological Survey using a Mipex 0 probe (Endress and Hauser, Switzerland) for 12+ years. These probes are no longer available, but updated models include both galvanic and optical technology so it's not clear what sort of measurement technology was used for Uehlinger's studies. Water was pumped from the river up to a flow-through chamber fitted with the DO probe. The DO probe was checked monthly and re-calibrated if necessary – deviations averaged 0.13 mg/L. Barometric pressure was monitored continuously and DO measurements corrected for changes in barometric pressure. The night time regression method was used to calculate ecosystem metabolism, although problems with this approach were evident at flows >60 m^3/s when daily changes in the oxygen deficit were too small to enable estimation of the reaeration coefficient.

Roberts et al. (2007) recorded DO every 15 minutes over a 2 year period using a YSI 6920 sonde equipped with a YSI 6562 DO probe. This probe is a pulsed Clark electrode that is designed to give stirring-independent DO measurements. The probe was deployed within the stream and was recalibrated every 7-14 days. Measurements were corrected for changes in barometric pressure, which was also measured every 15 minutes. Any instrument drift was determined from subsequent calibrations. Ecosystem metabolism was calculated using a single station approach, but reaeration coefficients were determined using tracer gas injections because the study site was a small 1^{st} order stream with a very high reaeration coefficient (70-170 day^{-1}). Thirty six propane injections were conducted across a range of flows to develop an empirical relationship between flow and reaeration coefficient values.

Izagirre et al. (2008) used dissolved oxygen data collected every 10 minutes over nine years by the Guipuscoa Provincial government using a Neurtek MP2000 logger. The sensors were housed beside the river and water was pumped up to them in a similar fashion to the approach used by Uehlinger (2000; 2006). The sensors were checked and calibrated on a weekly basis. Ecosystem metabolism and the reaeration coefficient were calculated using the night-time regression method, although this approach struggled during high flows when daily changes in the oxygen deficit were too small. An empirical relationship between flow and reaeration coefficient was used to estimate the reaeration coefficient under these conditions.

Staff at the (former) Auckland Regional Council have possibly had the most experience with continuous DO monitoring in New Zealand, with records at some sites beginning in 2003. They currently use D-opto optical probes installed directly within the streams and calibrate and maintain them at least every 6 weeks. DO concentration is measured at the site during the maintenance visit using an independent calibrated meter. Logger data collected over the preceding period is then classified according to the deviation from the independent meter. Data from a logger that is within 0.5 mg/L of the independent measurement is considered 'High Quality' (named QC 10), data between 0.5 and 1 mg/L of independent measurements is considered 'Good Quality' (QC 20), and data differing more than 1 mg/L (QC 43) from the

independent measurements is considered ‘Poor Quality'. We are aware, too, that Bay of Plenty Regional Council has deployed DO sondes continuously in the Tarawera River since approximately 2003.

10. Conclusions and Recommendations

The following sections address the nine specific questions posed by Horizons Regional Council to the authors of this report at the meeting in 2010, regarding the measurement of dissolved oxygen (DO) in rivers and the interpretation of DO data.

10.1 Achieving accurate and precise measurement of dissolved oxygen concentration

10.1.1 Calibration procedures

- We strongly recommend regular calibration of DO measuring devices with results logged to keep a record of instrument performance and stability. Monthly calibration would be appropriate until it is demonstrated that less frequent calibration is necessary.
- Optodes generally require less frequent calibration than membrane electrodes but are still subject to damage to the external window that may result in noisy or erroneous signals.
- Maintenance of calibrated sensor probes is crucial for DO measurements. Calibration may be done using either the moist air or saturated water methods (depending on manufacturer's specifications), but care must be taken to ensure that sensors are at thermal equilibrium so that the recorded temperature accurately reflects the test conditions. We prefer the saturated water method for calibrating DO sensors because the risk of errors from temperature differences between sensor and the test environment is much less than with moist-air calibrations.
- For the WTW optodes used by HRC, moist air calibration is recommended when air temperature is above 5°C, and saturated water calibration recommended when air temperature is below 5°C.
- We recommend the saturated water method when calibrating DO sensors outdoors because the risk of errors from temperature differences between sensor and the test environment is much less than with moist-air calibrations.

10.1.2 Checks on linearity in the measurements of the sensor

- Regular calibrations with air-saturated water or moist air, taking care to maintain thermal equilibrium between sensor and calibration environment, will provide a 2-point calibration, given that instruments are meant to have a zero response to 0% DO. The instrument zero response can be checked using water deoxygenated with Na_2SO_3, although some electrodes have a poor response to DO concentrations below 1 mg/L.
- Calibrations may be done at DO concentrations above 100% with instruments having appropriate scales (say, 0-250% saturation). We suggest that gas mixtures be used to validate the linearity of optodes and membrane sensors. For example, a 50:50 oxygen:nitrogen mixture would correspond to 238% saturation. This may be necessary where data are used to generate ecosystem

metabolism parameters that describe general waterbody condition. That is, the importance of the data will determine the calibration required to validate the data.

- Coupled with checks at zero and 100% saturation, calibration at DO concentrations above 100% would give a 3-point check on instrument linearity.

10.1.3 Inter-method comparisons and use of the Winkler titration method as a standard

- The Winkler titration method is a highly reliable and well-tested titrimetric method that may be a useful check on sensor performance. It is particularly suited to DO concentrations below 100% saturation.
- Inter-method comparisons generally show good agreement between laboratory measurements made using membrane electrodes and the Winkler method, and between membrane and optical electrodes for DO levels in the range 0-10 mg/L.
- Agreement between different sensors (membrane and optode) is often not good when *in situ* DO concentrations are >150% saturation. In such cases we recommend that freshly calibrated handheld instruments be used to provide reference checks and that these instruments be recalibrated in a stable environment after making field measurements as a check on their stability.
- We urge frequent calibration checks be made when such high concentrations of DO are observed. Care should also be taken to ensure sensors are clean and free of adhering material (especially periphyton).

10.1.4 Adjustments for barometric pressure and altitude

- Saturation DO is affected by temperature, atmospheric pressure, altitude and salinity.
- Calibrations made using saturated sea-level concentrations in units of mg/L can be compensated for altitude (A, masl) by applying a correction factor (CF)

$$CF = 0.994 - \frac{A}{10{,}000}$$

$DO_A = DO_{sea\text{-}level} \times CF$

- An empirical equation for calculating saturation DO concentration $(C^S_{O_2})$ as a function of temperature (T°C) and salinity (S‰) is:

$$C^S_{O_2} = 14.6244 - 0.367134T + 0.0044972T^2 - 0.0966S + 0.00205ST + 0.0002739S^2$$

- As a rule, a 1°C increase in temperature decreases saturation DO ($C^S_{O_2}$) by about 2-3%; an increase in altitude of 100 m decreases $C^S_{O_2}$ by about 1%; and an increase in salinity of 1‰ causes decrease in $C^S_{O_2}$ of about 0.7%.

10.1.5 Comparison of available instrument performance

- Instrument performance and reliability is variable, as HRC have discovered with different types of field-deployed optode sondes.
- Horizons compared several meter-sensor systems and found that the YSI Pro1 was most consistently within the range of acceptable error, and that the D-opto sensors consistently read lower than all of the other meters.
- Horizons currently use YSI Pro handheld instruments and WTW FDO sensors for continuous logging. We recommend that the WTW sensors be subjected to the same comparison that was carried out for the D-opto probes.
- Our advice is to continue to consult widely with other councils, Cawthron Institute and NIWA to compare experiences with different instrument performances in the laboratory and field.

10.1.6 Early detection of instrument malfunction and appropriate action

- Spot measurements with calibrated handheld DO meters provide useful checks on continuously logged data collected by sondes and can be a spur to undertake sonde recalibration.
- Data reliability is affected by location and sonde type. Abrasion by sediment and water-borne debris may affect DO sensors. Optode sondes should be located in sheltered places, out of direct sunlight, that represent site conditions. DO is generally uniform over the entire cross-section of river sites.
- Signs of sensor malfunction include: baseline drift and ramping, noisy signals and widening amplitude in DO concentration.
- It is appropriate to establish the safe period during which sondes (viz. optodes) may be deployed without maintenance/calibration checks. We recommend that the maximum period between checks on performance (drift, noise in data records) be less than two weeks until a longer period is established.
- There can be wide divergences between DO measuring devices at concentrations >100% saturation. Regular calibration checks and cleaning of sensors is probably the only way to reduce such discrepancies.

10.2 What QA procedures should be implemented and what is the best way to correct datasets when required?

- Regular checking of field DO measurements with recently calibrated, handheld DO meters allows early detection of sonde malfunction (drift, noise).
- It is recommended that calibration offsets and check comparisons be logged for each (optode) sonde deployed by HRC.
- Differences between portable and fixed sensors indicate offsets, which may be eliminated by adjustment of continuously recorded data.

- Noise may be real (intermittent light conditions) or an artefact of sensor malfunction.
- DO time-series should not have noisy signals (under steady flow conditions) during bright sunny days or at night.
- Peak clipping occurs either when real DO exceeds the instrument limit (very supersaturated conditions), or as a result of sensor malfunction (detected by comparison with a check instrument).

10.3 Which is the primary measurement? Is it concentration or percent saturation?

- Results can be expressed either as concentration (mg/L) or % saturation units because these values are interconvertible. Water temperature must also be recorded for conversion between units. Concentration units are not affected by temperature and might therefore be considered 'more fundamental'.

10.4 Use of data, including models - what degree of accuracy and precision is required? If models are used to quantify processes, what criteria do we need to establish monitoring sites and reaches?

- Single-station diel curve analysis (ecosystem metabolism analysis) is commonly used to parameterize DO data. This entails use of 24-hr continuous record of DO and temperature under steady flow conditions. This method assumes that there are no spatial gradients (only temporal changes) and that uniform plant growth, light and shade conditions exist.
- DO concentrations are affected by three key processes: (1) oxygen production associated with photosynthesis of algae and aquatic plants (gross primary production), (2) oxygen uptake associated with respiration of all river life including fish, invertebrates, algae, aquatic plants and microbes (ecosystem respiration), and (3) oxygen transfer across the air-water interface (reaeration). GPP, ER and k_a are rate coefficients characterising each process.
- As a rule of thumb for diel curve analysis, river conditions should be the same for a distance of $3U/k_a$ where U is the reach-average velocity.
- If these conditions are not met then it may be more appropriate to use a more complex model.
- The reaeration coefficient (k_a) is a crucial parameter for describing diel changes in DO concentration. It characterises oxygen transfer across the air-water interface and is a wholly physical process.
- Two methods exist for estimating k_a using single-station DO time-series data: the night-time regression method and the Approximate Delta Method (ADM).
- The night-time regression method uses simple linear regression of the rate of change of night-time DO concentration with time against the DO deficit

(difference between saturation and actual DO concentration). This yields a straight line with slope k_a and intercept R (the average rate of community respiration).

- The ADM is based on Delta, the maximum DO difference in a 24 hour period and relies on a mathematical solution of the equation describing changes in dissolved oxygen concentration at a site over a 24 hour period, assuming clear skies and constant water temperature.
- Values of k_a may also be calculated from empirical and theoretical relationships using hydraulic data (depth, velocity, slope etc.). Each equation should only be used in conditions similar to those used in their calibration.
- The most accurate method for estimating the reaeration coefficient is to directly measure the rate of loss of an inert tracer gas (e.g., C_3H_8, SF_6).
- We recommend that analysis of HRC data for parameterisation of DO data and classifying ecosystem pollution and stress, be carried out using either night-time regression or ADM approaches.

10.5 How do methods used for productivity analysis compare?

- Comparison of the night-time regression and ADM productivity analysis methods was carried out using five shared data sets.
- The ADM and night-time regression methods give similar results for estimating productivity analysis parameters (P_{av} (also called GPP), R (ER) and k_a) provided:
  - peak DO occurs at least 1 hr after solar noon
  - diel curves are not badly affected by cloudiness
  - criteria for single-station curve analysis are complied with.
- The night-time regression method is more suitable when reaeration coefficients are high and DO peaks occur less than 1 hour after solar noon.
- Calculations should not be attempted using data affected by significant rainfall. We recommend that metabolism analysis not be conducted with data collected when flows vary by more than 30%.
- We caution against only using single-station primary productivity analysis and respiration rates to determine ecosystem health of rivers, and strongly recommend that these be part of a package of monitoring tools used to assess river condition.

10.6 Should we investigate experimental approaches?

- Ecosystem metabolism can be estimated using either directly measured river DO and temperature data or using data collected from closed chambers.

- Chamber methods have advantages (e.g., simplicity, absence of reaeration) and disadvantages (e.g., artefacts of measurement, matching conditions within the chamber to those in the river, nutrient limitation).
- We recommend that advice be sought from experts at Cawthron Institute and NIWA with regard to setting up chamber experiments for ecosystem metabolism measurements.
- Gas tracers (e.g., propane, SF_6) provide the most accurate way of measuring the river reaeration coefficient, k_a. They require access to specialized equipment (viz. gas chromatography) and experience in sampling for dissolved tracer gases. Again, we recommend that specialist advice be sought.

10.7 Historic Manawatu River data sets

- Studies by Freeman (1983) and Quinn (1985) focused on the impacts of three major point source discharges from Palmerston North (treated sewage effluent, and effluents from a freezing works and a large dairy factory) on the Manawatu River.
- Productivity analysis using diel DO data showed that upstream of the discharges, maximum rates of gross primary production (GPP) and ecosystem respiration (ER) were 13 and 18 g O_2/m^2/day, respectively.
- Downstream of the discharges the corresponding rates were 34.2 and 37.6 g O_2/m^2/day for GPP and ER, respectively. The rates were indicative of fairly badly polluted conditions at the time when there was abundant sewage fungus growth. Since then, there have been major reductions in organic waste from these point source discharges.
- Recent measurements (Young & Clapcott 2010) indicated maximum GPP and ER values for the Hopelands site of 24.5 and 32.8 g O_2/m^2/day, respectively. This site is affected by diffuse source agricultural pollution and a few consented point source discharges.
- Results from a study by Collier et al. (2009) gave maximum GPP and ER values of 107.1 and 65.2 g O_2/m^2/day, respectively, for the lower Manawatu River at Opiki. This suggests a possible worsening of conditions in the Manawatu River despite the management and/or removal of organic waste from major point source discharges.
- The Manawatu River productivity analyses are based upon continuous records of diel DO concentration, some of which have very high maximum values. There is some uncertainty of the reliability of very high (say, > 200% saturation) DO data, which is a cause for concern and requires further investigation.

10.8 Comment on any protocols that have been developed elsewhere?

- We are aware of only four studies that have reported ecosystem metabolism results from long-term continuous monitoring of dissolved oxygen data.

- We are not aware of published protocols for DO measurement developed overseas that are particularly relevant to Horizons Regional Council.
- Auckland Regional Council (now Auckland Council) developed protocols for DO monitoring with D-opto optical probes that were calibrated at 6-weekly intervals. DO concentration is independently measured at the site using a calibrated meter. Logger data collected over the preceding period is classified according to the deviation from the independent meter. Data from a logger that is within 0.5 mg/L of the independent measurement is considered 'High Quality' (named QC 10), data between 0.5 and 1 mg/L of independent measurements is considered 'Good Quality' (QC 20), and data more than 1 mg/L (QC 43) from the independent measurements is considered 'Poor Quality'.
- The Auckland protocols could be used in the Horizons region, but calibrations and instrument checks are required more regularly than at 6-weekly intervals because the large size and mobile substrate of the Horizons rivers means that damage to sensors during high flows is more likely. 10.9What influence (if any) do cyanobacteria have on the measurement of dissolved oxygen?
- Sudden blooms of benthic cyanobacteria are reasonably common, and appear to be becoming more common, with some sites going from 5-10% coverage to 80-100% coverage within just a few days. During this rapid growth phase it is likely that the benthic cyanos are making a major contribution to the diel fluctuations in DO.
- DO bubbles are sometimes trapped within the benthic cyanobacteria mats, which is common to algal mats as well. We are not aware of any evidence suggesting that cyanos are more or less capable of trapping DO.

11. Acknowledgements

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12. References

Acuña, V.; Vilches, C.; Giorgi, A. (2011). As productive and slow as a stream can be – the metabolism of a ZPampean stream. *Journal of the North American Benthological Society 30*: 71–83.

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

Battino, R.; Rettich, T.R.; Tominaga, T. (1983). The solubility of oxygen and ozone in liquids. *Journal of Physical and Chemical Reference Data 12*: 163–178.

Bott, T.L.; Brock, J.T.; Baattrup-Pedersen, A.; Chambers, P.A.; Dodds, W.K.; Himbeault, K.T.; Lawrence, J.R.; Planas, D.; Snyder, E.; Wolfaardt, G.M. (1997). An evaluation of techniques for measuring periphyton metabolism in chambers. *Canadian Journal of Fisheries and Aquatic Sciences 54*: 715–725.

Bott, T.L.; Brock, J.T.; Cushing, C.E.; Gregory, S.V.; King, D.; Petersen, R.C. (1978). A comparison of methods for measuring primary productivity and community respiration in streams. *Hydrobiologia 60*: 3–12.

Bunn, S.E.; Davies, P.M.; Mosisch, T.D. (1999). Ecosystem measures of river health and their response to riparian and catchment degradation. *Freshwater Biology 41*: 333–345.

Carpenter, J.H. (1965). The accuracy of the Winkler method for dissolved oxygen analysis. *Limnology and Oceanography 10*: 135–140.

CCME (1999). Canadian water quality guidelines for the protection of aquatic life: dissolved oxygen (freshwater). In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Chapra, S.C.; Di Toro, D.M. (1991). Delta method for estimating primary production, respiration, and reaeration in streams. *Journal of Environmental Engineering ASCE 117*: 640–655.

Clapcott, J.E.; Young, R.G. (2009). Temporal variability in ecosystem metabolism of rivers in the Manawatu-Wanganui Region. Prepared for Horizons Regional Council*. Cawthron Report No. 1672*. 31 p.

Clapcott, J.E.; Young, R.G.; Goodwin, E.; Leathwick, J.R. (2010). Exploring the response of functional indicators of stream ecological integrity to land-use pressure gradients. *Freshwater Biology 55*: 2181–2199.

Clark, M.; McArthur, K.; Watson, B.; Swanney, A.; Roygard, J. (2010). Testing dissolved oxygen concentration and saturation measured by YSI Pro meters and D-opto dissolved oxygen sensors using chemical titrations. Draft report prepared for Horizons Regional Council.

Collier, K.J.; Clapcott, J.E.; Young, R.G. (2009). Influence of human pressures on large river structure and function. Prepared for Department of Conservation.

Centre for Biodiversity and Ecology Research, University of Waikato, *Contract Report 95*. 38 p.

Connolly, N.M.; Crossland, M.R.; Pearson, R.G. (2004). Effect of low dissolved oxygen on survival, emergence, and drift of tropical stream macroinvertebrates. *Journal of the North American Benthological Society 23*: 251–270.

Craggs, R.J.; Sukias, J.P.; Tanner, C.T.; Davies-Colley, R.J. (2004). Advanced pond systems for dairy-farm effluent treatment. New Zealand Journal of Agricultural Research 47: 449–460.

Dean, T.L..; Richardson, J. (1999). Responses of seven species of native freshwater fish and a shrimp to low levels of dissolved oxygen. *New Zealand Journal of Marine and Freshwater Research 33*: 99–106.

Franklin, P. (2010). Dissolved oxygen criteria for fish and the determination of ecological flows. *NIWA Internal report 146.*

Demars, B.O.L.; Manson, J.R.; Olafsson, J.S.; Gislason, G.M.; Gudmundsdottir, R.; Woodward, G.; Reiss, J.; Pichler, D.E.; Rasmussen, J.J.; Friberg, N. (2011). Temperature and the metabolic balance of streams. *Freshwater Biology 56*: 1106–1121.

Dodds, W.K.; Brock, J. (1998). A portable flow chamber for *in situ* determination of benthic metabolism. *Freshwater Biology 39*: 49–59.

Environment Canada (1974). Analytical Methods Manual. Water Quality Branch, Environment Canada, Ottawa.

Fellows, C.S.; Clapcott, J.E.; Udy, J.W.; Bunn, S.E.; Harch, B.D.; Smith, M.J.; Davies, P.M. (2006). Benthic metabolism as an indicator of stream ecosystem health. *Hydrobiologia 572*: 71–87.

Freeman, M.C. (1983). Periphyton and water quality in the Manawatu River, New Zealand. PhD thesis Massey University.

Gibbs, M.; Funnell, G.; Pickmere, S.; Norrko, A.; Hewitt, J. (2005). Benthic nutrient fluxes along an estuarine gradient: influence of the pinnid bivalve, *Atrina zelandica*, in summer. Marine Ecology progress Series 288: 151–164.

Hall, R.O.; Tank, J.L. (2005). Correcting whole-stream estimates of metabolism for groundwater input. *Limnology and Oceanography Methods 3*: 222–229.

Hickey, C.W. (1988). Benthic chamber for use in rivers: testing against oxygen mass balance. *Journal of Environmental Engineering ASCE 114*: 828–845.

Hitchman, M.L. (1978). Measurement of dissolved oxygen. John Wiley and Sons Inc., NY. 255 p.

Huang, X.; Li, K.; Du, J.; Li, R. (2010). Effects of gas supersaturation on lethality and avoidance responses in juvenile rock carp (*Procypris rabaudi* Tchang). Journal of Zhejiang Univ Sci B. 2010 October; 11(10): 806–811.

Hornberger, G.M.; Kelly, M.G. (1975). Atmospheric reaeration in a river using productivity analysis. *Journal of Environmental Engineering ASCE 101*: 729–739.

Izagirre, O.; Agirre, U.; Bermejo, M.; Pozo, J.; Elosegi, A. (2008). Environmental controls of whole-stream metabolism identified from continuous monitoring of Basque streams. *Journal of the North American Benthological Society 27*: 252–268.

Kosinski, R.J. (1984). A comparison of the accuracy and precision of several open-water oxygen productivity techniques. *Hydrobiologia 119*: 139–148.

Kilpatrick, F.A.; Rathbun, R.E.; Yotsukura, N.; Parker, G.W.; DeLong, L.L. (1989). Determination of stream reaeration coefficients by use of tracers. USGS. Denver.

Landman, M.J.; Van den Heuvel, M.R.; Ling, N. (2005). Relative sensitivities of common freshwater fish and invertebrates to acute hypoxia. . *New Zealand Journal of Marine and Freshwater Research 39*: 1061–1067.

Martini, M.; Butman, B.; Mickelson, M.J. (2007). Long-term performance of Aanderaa Optodes and Sea-Bird SBE-43 dissolved-oxygen sensors bottom mounted at 32 m in Massachusetts Bay. *Journal of Atmospheric and Oceanic Technology 24*: 1924–1935.

Marzolf, E.R.; Mulholland, P.J.; Steinman, A.D. (1994). Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams. *Canadian Journal of Fisheries and Aquatic Sciences 51*: 1591–1599.

Marzolf, E.R.; Mulholland, P.J.; Steinman, A.D. (1998). Reply: Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams. *Canadian Journal of Fisheries and Aquatic Sciences 55*: 1786–1787.

McBride, G.B. (2002). Calculating stream reaeration coefficients from oxygen profiles. *Journal of Environmental Engineering ASCE 128*: 384–386.

McBride, G.B.; Jowett, I.; Rutherford, J.; Pearson, C. (1998). Water allocation impacts on river attributes: technical report on modelling. *NIWA client report ARC70214/1.*

McBride, G.B.; Chapra, S.C. (2005). Rapid calculation of oxygen in streams: Approximate Delta method. *Journal of Environmental Engineering 131*: 336–342.

McCutchan, J.H.; Saunders, J.F.; Lewis, W.M.; Hayden, M.G. (2002). Effects of groundwater flux on open-channel estimates of stream metabolism. *Limnology and Oceanography 47*: 321–324.

Mulholland, P.J.; Marzolf, E.R.; Webster, J.R.; Hart, D.R.; Hendricks, S.P. (1997). Evidence that hyporheic zones increase heterotrophic metabolism and phosphorus uptake in forest streams. *Limnology and Oceanography 42*: 443–451.

Naegeli, M.W.; Uehlinger, U. (1997). Contribution of the hyporheic zone to ecosystem metabolism in a prealpine gravel-bed river. *Journal of North American Benthological Society 16*: 794–804.

Naiman, R.J. (1983). The annual pattern and spatial distribution of aquatic oxygen metabolism in boreal forest watersheds. *Ecological Monographs 53*: 73–94.

NCASI (1985). A compilation of surface water quality modelling formulations, rate constants and kinetic coefficients. *National Council of the Paper Industry for Air and Stream Improvement Technical Bulletin No. 473,* NY.

Phinney, H.K.; McIntire, C.D. (1965). Effect of temperature on metabolism of periphyton communities developed in laboratory streams. *Limnology and Oceanography 10*: 341–344.

Quinn, J.M. (1985). Wastewater effects on epilithon, particularly sewage fungus, and water quality in the Manawatu River, New Zealand. PhD thesis Massey University.

Roberts, B.J.; Mulholland, P.J.; Hill, W.R. (2007). Multiple scales of temporal variability in ecosystem metabolism rates: results from 2 years of continuous monitoring in a forested headwater stream. *Ecosystems 10*: 588–606.

Uehlinger, .U (2000). Resistance and resilience of ecosystem metabolism in a flood-prone river system. *Freshwater Biology 45*: 319–332.

Uehlinger, U. (2006). Annual cycle and inter-annual variability of gross primary production and ecosystem respiration in a floodprone river during a 15-year period. *Freshwater Biology 51*: 938–950.

USEPA (1986). Ambient water quality criteria for dissolved oxygen. Office of Water Regulations and Standards, Criteria and Standards Division report EPA 440/5-86-003. United States Environmental protection Agency, Washington DC.

USEPA (1997). Volunteer stream monitoring: A methods manual. Chapter 5.2 Dissolved oxygen and Biochemical Oxygen Demand. Office of Water report EPA 841-B-97-003. United States Environmental protection Agency, Washington DC.

Uzarski, D.G.; Burton, T.M.; Stricker, C.A. (2001). A new chamber design for measuring community metabolism in a Michigan stream. *Hydrobiologia 455*: 137–155.

Uzarski, D.G.; Stricker, C.A.; Burton, T.M.; King, D.K.; Steinman, A.D. (2004). The importance of hyporheic sediment respiration in several mid-order Michigan rivers: comparison between methods in estimates of lotic metabolism. *Hydrobiologia 518*: 47–57.

Wanninkhof, R.; Mulholland, P.J.; Elwood, J.W. (1990). Gas exchange rates for a first-order stream determined with deliberate and natural tracers. *Water Resources Research 26*: 1621–1630.

Wilcock, R.J. (1982). Simple predictive equations for calculating stream reaeration rate coefficients. *New Zealand Journal of Science 25*: 53–56.

Wilcock, R.J. (1984). Reaeration studies on some New Zealand rivers using methyl chloride as a gas tracer. *In:* Gas Transfer at Water Surfaces, edited by W. Brutsaert & G.H. Jirka. D. Reidel Publishing Co., Dordrecht, Holland. Pp 413–420.

Wilcock, R.J.; Nagels, J.W.; McBride, G.B.; Collier, K.J.; Wilson, B.T.; Huser, B.A. (1998). Characterisation of lowland streams using a single–station diurnal curve analysis model with continuous monitoring data for dissolved oxygen and temperature. *New Zealand Journal of Marine and Freshwater Research 32*: 67–79.

Wilcock, R.J.; Champion, P.D.; Nagels, J.W.; Croker, G.F. (1999). The influence of aquatic macrophytes on the hydraulic and physico-chemical properties of a New Zealand lowland stream. *Hydrobiologia 416*: 203–214.

Young, R.G.; Clapcott, J.E. (2010). Temporal variability in ecosystem metabolism of rivers in the Manawatu-Whanganui Region – Updated. Prepared for Horizons Regional Council. *Cawthron Report No. 1791*. 25 p.

Young, R.G.; Collier, K.J. (2009). Contrasting responses to catchment modification among a range of functional and structural indicators of river ecosystem health. *Freshwater Biology 54*: 2155–2170.

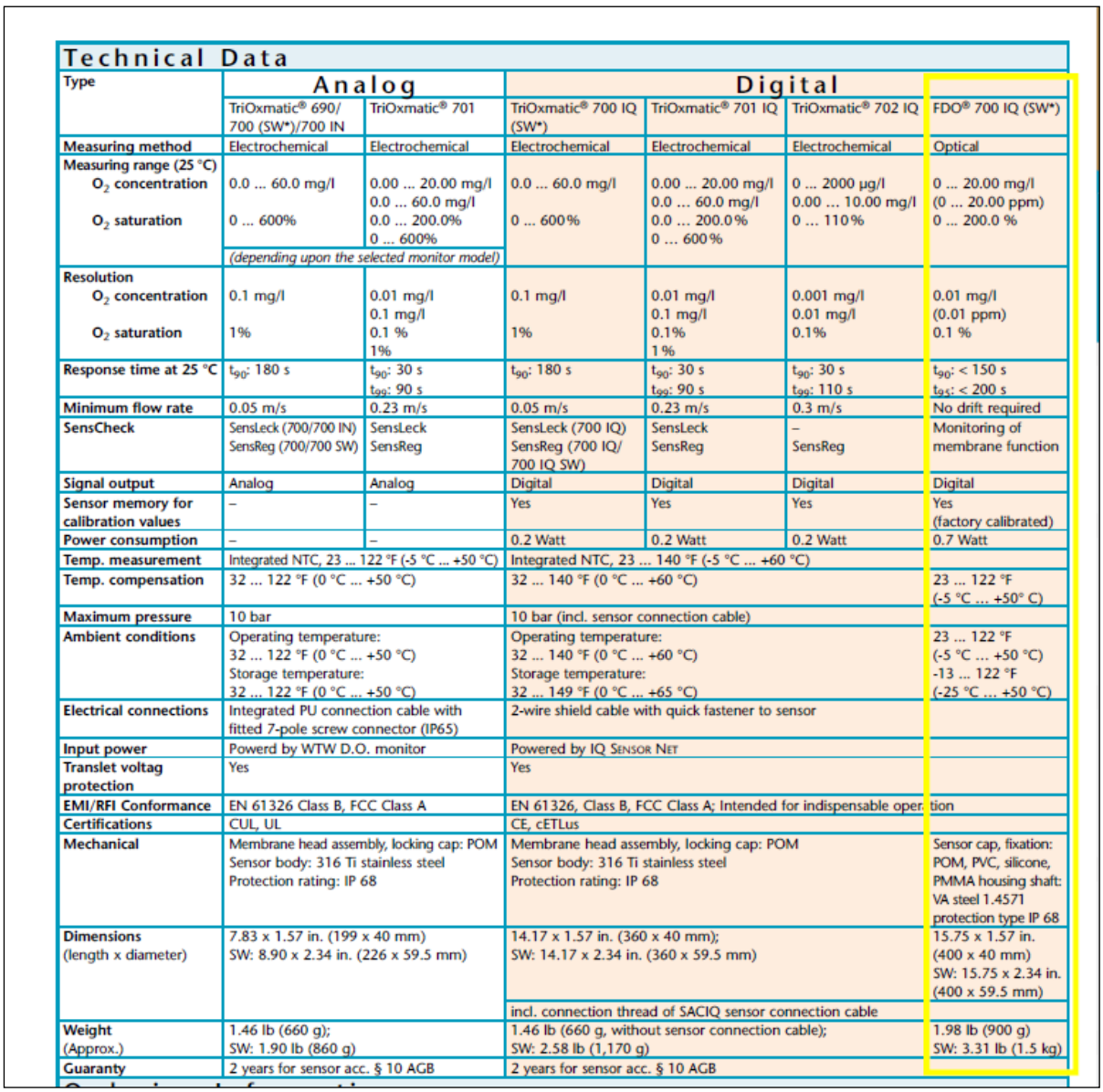
Young, R.G.; Huryn, A.D. (1996). Interannual variation in discharge controls ecosystem metabolism along a grassland river continuum. *Canadian Journal of Fisheries and Aquatic Sciences 53*: 2199–2211.

Young, R.G.; Huryn, A.D. (1998). Comment: Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams. *Canadian Journal of Fisheries and Aquatic Sciences 55*: 1784–1785.

Young, R.G.; Huryn, A.D. (1999). Effects of land use on stream metabolism and organic matter turnover. *Ecological Applications 9*: 1359–1376.

Young, R.G.; Matthaei, C.D.; Townsend, C. (2008). Organic matter breakdown and ecosystem metabolism: functional indicators for assessing river ecosystem health. *Journal of the North American Benthological Society 27*: 605–625.

Appendix 1. Specifications for the WTW green light sensors currently used by Horizons Regional Council



Technical Data

Type	Analog		Digital			
	TriOxmatic® 690/ 700 (SW*)/700 IN	TriOxmatic® 701	TriOxmatic® 700 IQ (SW*)	TriOxmatic® 701 IQ	TriOxmatic® 702 IQ	FDO® 700 IQ (SW*)
Measuring method	Electrochemical	Electrochemical	Electrochemical	Electrochemical	Electrochemical	Optical
Measuring range (25 °C)						
O_2 concentration	0.0 ... 60.0 mg/l	0.00 ... 20.00 mg/l 0.0 ... 60.0 mg/l	0.0 ... 60.0 mg/l	0.00 ... 20.00 mg/l 0.0 ... 60.0 mg/l	0 ... 2000 µg/l 0.00 ... 10.00 mg/l	0 ... 20.00 mg/l (0 ... 20.00 ppm)
O_2 saturation	0 ... 600%	0.0 ... 200.0% 0 ... 600%	0 ... 600%	0.0 ... 200.0% 0 ... 600%	0 ... 110%	0 ... 200.0 %
	(depending upon the selected monitor model)					
Resolution						
O_2 concentration	0.1 mg/l	0.01 mg/l 0.1 mg/l	0.1 mg/l	0.01 mg/l 0.1 mg/l	0.001 mg/l 0.01 mg/l	0.01 mg/l (0.01 ppm)
O_2 saturation	1%	0.1 % 1%	1%	0.1% 1 %	0.1%	0.1 %
Response time at 25 °C	t_{90}: 180 s	t_{90}: 30 s t_{99}: 90 s	t_{90}: 180 s	t_{90}: 30 s t_{99}: 90 s	t_{90}: 30 s t_{99}: 110 s	t_{90}: < 150 s t_{95}: < 200 s
Minimum flow rate	0.05 m/s	0.23 m/s	0.05 m/s	0.23 m/s	0.3 m/s	No drift required
SensCheck	SensLeck (700/700 IN) SensReg (700/700 SW)	SensLeck SensReg	SensLeck (700 IQ) SensReg (700 IQ/ 700 IQ SW)	SensLeck SensReg	– SensReg	Monitoring of membrane function
Signal output	Analog	Analog	Digital	Digital	Digital	Digital
Sensor memory for calibration values	–	–	Yes	Yes	Yes	Yes (factory calibrated)
Power consumption	–	–	0.2 Watt	0.2 Watt	0.2 Watt	0.7 Watt
Temp. measurement	Integrated NTC, 23 ... 122 °F (-5 °C ... +50 °C)		Integrated NTC, 23 ... 140 °F (-5 °C ... +60 °C)			
Temp. compensation	32 ... 122 °F (0 °C ... +50 °C)		32 ... 140 °F (0 °C ... +60 °C)			23 ... 122 °F (-5 °C ... +50° C)
Maximum pressure	10 bar		10 bar (incl. sensor connection cable)			
Ambient conditions	Operating temperature: 32 ... 122 °F (0 °C ... +50 °C) Storage temperature: 32 ... 122 °F (0 °C ... +50 °C)		Operating temperature: 32 ... 140 °F (0 °C ... +60 °C) Storage temperature: 32 ... 149 °F (0 °C ... +65 °C)			23 ... 122 °F (-5 °C ... +50 °C) -13 ... 122 °F (-25 °C ... +50 °C)
Electrical connections	Integrated PU connection cable with fitted 7-pole screw connector (IP65)		2-wire shield cable with quick fastener to sensor			
Input power	Powerd by WTW D.O. monitor		Powered by IQ Sensor Net			
Translet voltag protection	Yes		Yes			
EMI/RFI Conformance	EN 61326 Class B, FCC Class A		EN 61326, Class B, FCC Class A; Intended for indispensable oper tion			
Certifications	CUL, UL		CE, cETLus			
Mechanical	Membrane head assembly, locking cap: POM Sensor body: 316 Ti stainless steel Protection rating: IP 68		Membrane head assembly, locking cap: POM Sensor body: 316 Ti stainless steel Protection rating: IP 68			Sensor cap, fixation: POM, PVC, silicone, PMMA housing shaft: VA steel 1.4571 protection type IP 68
Dimensions (length x diameter)	7.83 x 1.57 in. (199 x 40 mm) SW: 8.90 x 2.34 in. (226 x 59.5 mm)		14.17 x 1.57 in. (360 x 40 mm); SW: 14.17 x 2.34 in. (360 x 59.5 mm)			15.75 x 1.57 in. (400 x 40 mm) SW: 15.75 x 2.34 in. (400 x 59.5 mm)
			incl. connection thread of SACIQ sensor connection cable			
Weight (Approx.)	1.46 lb (660 g); SW: 1.90 lb (860 g)		1.46 lb (660 g, without sensor connection cable); SW: 2.58 lb (1,170 g)			1.98 lb (900 g) SW: 3.31 lb (1.5 kg)
Guaranty	2 years for sensor acc. § 10 AGB		2 years for sensor acc. § 10 AGB			

Next Generation...

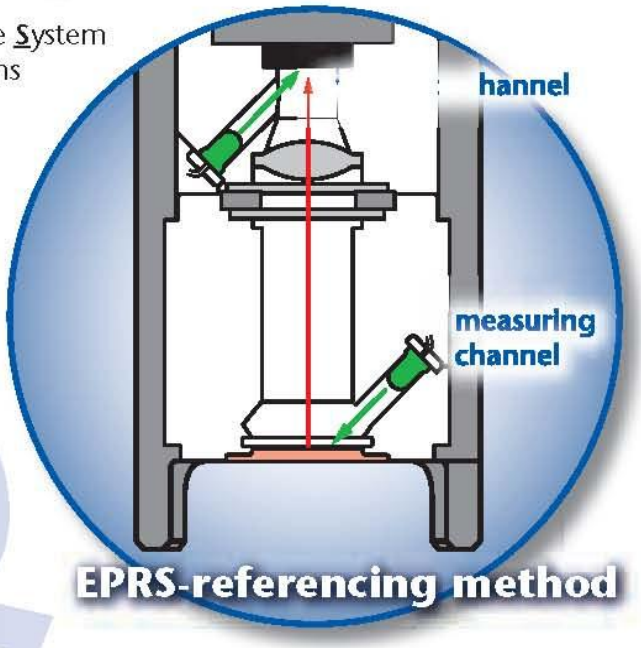
High stability – Low maintenance

...through EPRS-referencing method

EPRS stands for Equal Path Reference System
= Equal excitation and reference paths

- Identical optical paths for measuring and reference channel
- Identical components for measuring and reference channel
- Same wavelength

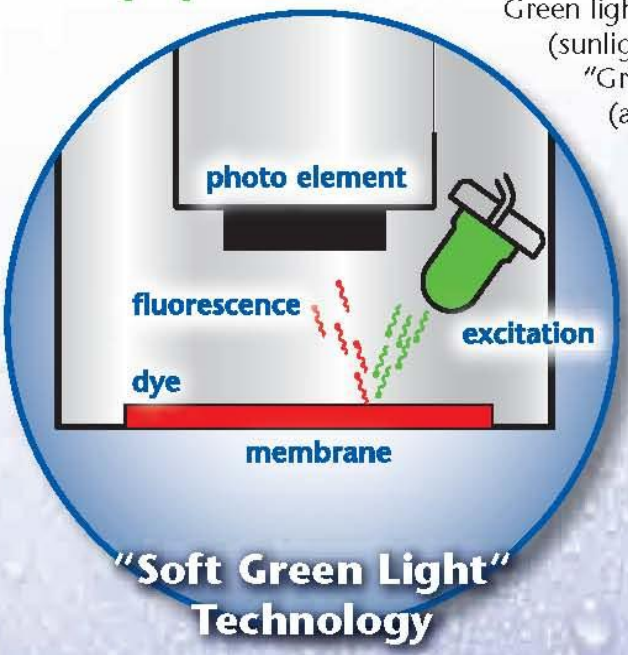
This means:
Minimum of drift for the optical system **through the whole life-time.**



...through "Soft Green Light" Technology

Green light is in comparison with UV light (sunlight / blue light) a **"soft" light.**
"Green light technology" **prevents early bleaching** (aging) of the dye.

Thus **extreme long-life stability** is achieved which provides **high accuracy and low drift** over a very long period of time.



Appendix 2. Calibration of DO sensors used in the National River Water Quality Network

For calibration purposes, two buckets are required (4 litre minimum). Collect water in one bucket and pour from a short height (e.g., 50cm) into the second bucket. Repeat this pouring back and forth between buckets 20 times. This should ensure 100% saturation at whatever temperature the water is at. A large volume is needed to ensure the probe is completely immersed for effective thermal equilibrium to occur.

NOTE – while a simple **air calibration** may be recommended in the HACH Manual, this is really only applicable to a controlled indoors type environment where there are no temperature extremes to which the probe will be subjected to as in the field environment. That is, the HACH probe is of solid metallic construction, and it takes 3-4 minutes of immersion in water medium for thermal equilibrium to occur. Such equilibrium will therefore take much longer to occur for any changes in air temperature if air calibration in the field is attempted. This may lead to results that could be several percent in error. Evaporation of water from the probe membrane or body can lower the probe temperature relative to the thermistor temperature. Similarly direct sunlight can alter the local temperature and cause an error.

Water temperature (± 0.1°C)
Instruction: Leave probe body fully immersed in river water for 3-5 minutes to equilibrate temperature. Check meter readings at least twice for stability before recording temp value. If measuring sample in a bucket, then collect a fresh bucketful for the reading.

Measured value .....°C [Correction ..... ± °C]
Final Value .....°C
If other than HACH probe used, then specify:
Pre-run calibration check OK? (tick):

Dissolved oxygen (both percentage, % , and mg/L**, required if using HACH meter)**
Instruction: At first site carry out 100% air saturated water calibration (using shaken river water, tipped 20x between two large buckets) and set meter to 100%. This should hold for rest of the run day. At LAST sampling site, recheck calibration. If less than 2% difference, then OK, no further action required. If difference > 2% then calculate the proportional difference between sites and apply an appropriate correction to sample measurements e.g., 5 sites, 4% positive drift, add 1% to values for sites 2, 3, & 4.

Sondes are water quality loggers used for continuous recording of many water quality variables, including DO. Sonde DO probes may be either the older membrane type or optodes. The NIWA procedure for deployment of Hydrolab sondes entails the following preparation in the laboratory:

Sondes should be cleaned prior to use in the field with water and dishwashing detergent. Use a soft brush to clean sonde body, protective caps and sensor trunks. Gently wipe the DO membrane or optode sensor with a cotton swab to remove any residue or oily build-up.

Sondes may be calibrated either with moist air or using saturated water.

Air calibration - Fill the sonde cup with air saturated tap water to just under the DO probe o-ring. Gently dry off the DO membrane with a cotton swab or soft cloth if necessary, and set the cap on top – don't screw it on. Wait for readings to stabilise; this can take up to five minutes. If the membrane has just been changed, it can take up to 2 hours to reach stability. Choose window SOM>calibration>oxy> %saturation. You will be asked to enter the barometric pressure (default for Hamilton 1013 mbar / 760 mm Hg). If you are calibrating in a location that is several hundred metres above sea level, make sure you are using the true local barometric pressure and not barometric pressure at sea level. After entering the barometric pressure, press enter to calibrate the DO % saturation to 100 %. The calibration can be considered successful if the reading does not fluctuate outside a band from 99.5% to 100.5% in the next 2 minutes. If you are calibrating a new membrane, repeat this procedure a second time, at least 2 hours after the first calibration.

Water calibration - Use tap water which has been aerated for at least 24 hours in an open 5 L container. Alternatively, shake a half-full 5 L sealed container vigorously for 3-5 minutes to get air saturated water. Confirm oxygen saturation by using an independently calibrated meter. Turn on the sonde and allow the DO sensor to equilibrate. Wait for readings to stabilise on the SOM screen; this can take up to five minutes. If the membrane has just been changed, it can take up to 2 hours to reach stability. Choose window SOM>calibration>oxy> %saturation. You will be asked to enter the barometric pressure (default for Hamilton 1013 mbar / 760 mmHg). If you are calibrating in a location more that several hundred meters above sea level, make sure you are using the true local barometric pressure and not barometric pressure at sea level. After entering the barometric pressure, press enter to calibrate the DO % saturation to 100%. The calibration can be considered successful if the reading does not fluctuate outside a band from 99.5% to 100.5% in the next 2 minutes. If you are calibrating a new membrane, repeat this procedure a second time, at least 2 hours after the first calibration.

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