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Measurement of dissolved oxygen using optodes in a FerryBox system

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ABSTRACT

Optode sensors can provide detailed information on concentrations of dissolved oxygen, which in turn may be used to quantify variations in net primary productivity. Throughout 2005 and 2006 the performance of commercially available oxygen optodes was examined, one in each year. The optode was part of an autonomous measurement system (FerryBox) on a ferry operating between Portsmouth (UK) and Bilbao (Spain). On crossings during which water samples were collected manually, the optode outputs were compared to measurements of dissolved oxygen made by Winkler titrations. The optodes maintained good stability with no evidence of instrumental drift during the course of a year. Over the observed concentration range (230–330 mM m^{-3}) the optode data were approximately 2% low in both years. By fitting the optode data to the Winkler data the median difference between the optode and Winkler measurements is reduced to less than 1 mM m^{-3} (0.3%) in both years. The most appropriate calibration factor for 2005 was *corrected* O_2 = Optode $O_2 \times 1.018$ and for 2006 the corresponding equation is *corrected* O_2 = Optode $O_2 \times 0.884 + 36.8$. The standard deviation (95%) of the difference between the individual Winkler measurements was 5 mM m^{-3} and 3 mM m^{-3} in 2005 and 2006 respectively. Calculation of the oxygen saturation anomaly is required for calculation of the air sea exchange of oxygen and net biological production. This calculation requires the use of both salinity and temperature data. Salinity is measured to better than 0.1 so the corresponding error in anomaly is less than 0.2 mM m^{-3}. Distortion of the temperature data is present due to warming of the water pumped to the optode. In winter this warming at the optode may be as great as 0.4 °C. The difference in the pumped water temperature can be corrected for by reference to other measurements of sea surface temperature reducing the error to less than 1 mM m^{-3}.

1. Introduction

Following on from earlier work (Redfield, 1948; Jenkins and Goldman, 1985; Emerson, 1987; Najjar and Keeling, 2000; Garcia and Keeling, 2001), Bargeron et al. (2006) demonstrated that regular measurements of oxygen concentration made in conjunction with a FerryBox system could be used to estimate net biological productivity. These estimates provided insight into the variations within the different regions along the track of the ferry. Taking the Bargeron et al. (2006) approach forward to provide more detailed information on net biological productivity in relation to driving processes and seasonal and inter-annual variability requires autonomous instrumentation that can produce reliable long-term data sets. Recent developments can make this possible (see for example Kaiser et al., 2005; Emerson et al., 2008). Oxygen optodes as described by Tengberg et al. (2006) offer the potential to develop continuous measurements of oxygen as an integrated part of FerryBox type observing systems (Petersen et al., 2008). Other recent papers have evaluated the use of the oxygen optodes in other types of installations – Argo floats (Koertzinger et al., 2005); moorings (Martini et al., 2007); CTD profilers (Uchida et al., 2008).

The European FerryBox project 2002–2005 demonstrated that where suitable sensors are available autonomous measurements can be made reliably from commercial ships (Petersen et al., 2007). This provides the potential for cost effective collection of consistent long-term data sets which in turn promises a better understanding of ecosystem processes and ecosystem change, beyond that which has already been demonstrated by systems such as the continuous plankton recorder CPR (Stevens et al., 2006). The wide range of measurements possible with FerryBox systems enables observations of biological processes to be quantitatively linked to chemical and physical driving forces (Kelly-Gerreyn et al., 2006; Fleming-Lehtinen et al., 2008; Petersen et al., 2008).

An evaluation of the quality of the data obtainable from optode systems is required before they are used for estimation of changes in net primary production. The oxygen flux method requires the oxygen

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saturation anomaly to be calculated. The oxygen anomaly is the difference between the actual *in-situ* oxygen concentration and the saturation concentration at the *in-situ* temperature, salinity and air pressure. This requires that good quality data be achieved in the FerryBox system for salinity and sea surface temperature (for this work data on air pressure and wind speed are provided by the UK MetOffice). In 2005, an oxygen optode was added to the Portsmouth–Bilbao FerryBox system (Hydes et al., 2003). In this paper we discuss the results gathered from operating the system over a two-year period from early 2005 to the end of 2006. We consider: (1) The quality of the data that the optode produced, relative to calibrations of the optode based on Winkler titration data collected onboard the ferry. (2) The magnitude of anomalies in oxygen saturation compared the identifiable errors in the data used to calculate those anomalies.

2. Methods

2.1. Sampling platform

The data presented here were obtained from surface water collected between February 2005 and December 2006 on P&O European Ferries Ltd ship "MV Pride of Bilbao". She operates between Portsmouth (UK, 50.8 °N, 1.1 °W) and Bilbao (Spain, 43.4 °N, 3.0 °W) making two crossings weekly between these ports. The distance is approximately 1000 km and the journey time is about 35 h each way. The service operates all year round except during January when the ship is in dry dock for its annual refit. The ferry route crosses a range of water types from eutrophic harbours to deep ocean waters in the central Bay of Biscay (see Bargeron et al., 2006).

2.2. Oxygen optode

Tengberg et al. (2006) described both the development of the oxygen optode and its application in a number of environments. Optode technology is based on dynamic fluorescence quenching. If certain metal complexes are excited with a blue light they will emit a red luminescence, the intensity and lifetime of which depends on the ambient oxygen concentration. The Aanderaa Instruments Oxygen Optode is based on oxygen luminescence quenching of a platinum porphyrin complex, coated onto a gas permeable foil. The complex is excited with a blue-green light modulated at 5 kHz. Measurements of oxygen are made by detection of the phase shift in the returning oxygen quenched red luminescence. The optode housing includes the optical part plus a temperature sensor and signal processing electronics. The data outputs from the optode are temperature and temperature compensated oxygen values in terms of concentration (mM m^{-3}) and percent saturation.

The manufacturer's specifications of the optode suggest they have a resolution of less than 1 mM m^{-3} and an accuracy of 8 mM m^{-3}, or 5% which ever is the greater (Aanderaa, 2005). This degree of resolution is inadequate for use in pristine waters where oxygen saturation may only vary by less than 10% over an annual cycle. However Tengberg et al. (2006) considered that levels of accuracy better than the specification would be achieved in practice. They also suggested that optodes would be stable for more than one year and evidence is accumulating that this is the case (Koertzinger et al., 2005; Martini et al., 2007).

2.3. Fitting in the NOC FerryBox system

Two optodes were purchased in 2004. The first unit (optode serial number 3835-34) was run continuously through 2005, and the second unit (optode serial number 3835-33) was used through 2006. Each optode was run at a sampling rate of one measurement every 30 s. The version of the optode with a protective Teflon coating on the foil was chosen as it was expected to be more durable for long-term deployments than an uncoated foil. The optodes were mounted in a cylindrical flow through chamber. The housing followed in series with a Chelsea Technology Group Minipack CTG CTD-F the data from which was logged at 1 Hz (Hydes et al., 2003). The seawater flow rates through the system were 12 and 20 l/min in 2005 and 2006 respectively. The chamber has water volume of 110 ml. It is made of PVC of which insulates the temperature sensor of the optode which is attached to the metal base of this early design of optode from the relatively high ambient temperatures of the engine room. Drawings and photographs are presented in Hydes et al. (2007). In this system the water is at pressure of 2 bar as it passes through the system. This prevents the water from degassing so that the measured concentrations represent those *in-situ* outside the ship.

Tengberg et al. (2006) found the time for a 90% change in the output of an optode following a step change in concentrations was 47 s for an optode fitted with a the Teflon coated membrane. In the FerryBox system data from the optode were recorded every 30 s. The water measured by the CTD-F and the optode was pumped into the ship via a sea-chest. Mixing in the chest was observed to produce "smoothing" of the temperature signal recorded by the CTD-F relative to external measurements of temperature (see Section 4.2.3). This "smoothing" resulted in there being no discernable lag between the optode and temperature data from the CTD-F when frontal features were crossed.

The optode was cleaned approximately every 9 days each time the FerryBox units were serviced. Cleaning consisted of wiping the surfaces of the optode and the inside of the flow through housing with wet paper towel. The window of the optode was cleaned with light pressure from a wet cotton wool bud. No jumps in sensor output were detected coinciding with cleaning of the membrane. The optodes performed reliably in 2005 and 2006 and the amount of data recorded was 100% of what was possible.

Five measurements of the seawater temperature are made on the Pride of Bilbao these were from (a) the CTD-F, (b) the optode, (c) a hull mounted temperature sensor Seabird 48, (d) a sea surface radiometer mounted above the ship's bridge wing (Donlon et al., 2008), and (e) monthly tows of a CPR unit fitted with a temperature sensor (RBR 1050, Werenfrid Wimmer, pers. comm.).

2.4. Winkler calibrations

Titrations (Winkler, 1888) to determine the concentration of oxygen in samples of water were done onboard the ferry during "calibration crossings" between Portsmouth and Bilbao and Portsmouth. Samples for oxygen determinations were collected on 8 crossings in 2005 and 4 crossings in 2006; two (duplicate) samples were collected at hourly intervals. Water, diverted from one of the ships cooling water intakes (pumping at a rate of 4 m^3 min^{-1}) supplied the autonomous sensors. At this junction water samples were taken from a tap that was mounted in the supply line. The accuracy and precision of the Winkler titrations were dependent on careful collection of water samples (Culberson et al., 1991; Joyce et al., 1992). Samples were titrated when possible an hour after sampling using a variation of the Winkler method which used a programmed Metrohm Titrino and potentiometric end point detection as described in Grasshoff et al. (1983). The thiosulphate solution used in the titration was standardised against an iodate solution (0.3567 g l^{-1} KIO_3) at the start of each calibration crossing. To determine the oxygen concentration in the samples a "whole-bottle" titration was done. The bottles were cooled in the seawater being sampled before being filled. The temperature of the water at the time of sampling was recorded and was used to correct the bottle volume in the calculation of the oxygen concentration after the titration. The titrations were carried out in an air-conditioned store room with a temperature of approximately 25 °C.

The room temperature tended to vary during crossings. The maximum error a sustained temperature change of 10 °C could have produced from a shift in the apparent concentration of the thiosulphate solution would have been about 0.15% or 0.5 mM m^{-3} and was likely to have been less than this. A standardised Microsoft Excel work sheet was used to calculate the results by entering the titration values, the bottle volume and the temperature of the water at sampling.

2.5. Automated data collection and initial processing

The output from the optode was logged along with the data for conductivity, temperature and fluorescence output by the CTG CTD-F, GPS position and time (Hydes et al., 2003). The data from the optode were processed to calculate the oxygen concentration in mM m^{-3} at the time of sampling. The internal processing in the optode works with a default value for salinity of zero and the temperature recorded by the optode itself (it is this temperature that was used in the factory calibration of the instrument so at this stage of processing no adjustment for temperature was made). The salinity data were calculated from the output from the CTG CTD-F. The CTD-F salinities were corrected to true salinity by comparison with measurements made from water samples. During the calibration crossing samples for the determination of salinity were collected every two hours. These samples and samples collected when the equipment was cleaned were analysed on shore with a Guildline Salinometer and standardised against OSI Standard Seawater. The accuracy of the salinity measurements was ±0.05 based on the consistency of the data from the CTD-F and salinity of the water samples. The CTD-F units were returned to CTG for calibration each year. The accuracy and precision of the temperature measurements were ±0.003 and ±0.0005 °C respectively.

2.6. Assembly of data for comparison

The procedure that has evolved for analysis and display of the large amounts of data from the FerryBox system is to reduce the size of the data sets (which is mostly collected at rate of 1 Hz) by binning them into 5-min time intervals. For the oxygen data this is a mean of 10 readings. The collection of the oxygen samples normally takes 3 min. For the comparison of the two data sets optode data were binned for a period of 5 min around the time logged for the collection of the Winkler samples. The range of values obtained in all of the 5-min bins was examined. The median value of the ranges between the minimum and maximum value was 0.3 mM m^{-3} in autumn and 0.5 mM m^{-3} in spring, reflecting higher spatial gradient in spring relating to patchiness of biological production. The range was greater than 1 mM m^{-3} in 25% of the cases and the maximum range was 7 mM m^{-3}. The standard deviation in the value of the ranges was 0.8 mM m^{-3}.

3. Results

3.1. Comparison with Winkler measurements

In 2005 and 2006, 562 pairs of Winkler titrations were performed successfully. The median difference between duplicate observations in 2005 ($n = 348$) was 1.5 mM m^{-3} with a standard deviation of 2.2 mM m^{-3}. In 2006 ($n = 214$) the corresponding values were 1.0 and 1.5 mM m^{-3}. This level of precision was not as high as the value Culberson (1991) suggested could be achieved for Winkler measurements, for example Uchida et al. (2008) reported a standard deviations on replicates of 0.13 and 0.24 μM kg^{-1} for Winkler titration carried out on two cruises during which optodes were calibrated on CTD package. The lower precision reflects working conditions on the ship and particularly the relatively short period of time that the equipment could be operated for on each crossing and the limited experience of most of the operators. An air bubble as small as 50 μl would have given an error of 4.5 mM m^{-3}. Other errors resulting from inexperience such as not closing the bottles tightly enough and making a slow start of the titration after opening the bottles would also tend to give high values. Each of these potential contamination processes allows extra oxygen to be scavenged from solution by the Winkler reagents. Therefore to derive calibration information, we used the lower titration value in each pair, as it was likely to be the more accurate.

To assess the quality and stability of the optode calibrations, data from the optodes were plotted against the Winkler titration result. This was done for each set of crossing data. For each data set a calibration equation was calculated in Excel for firstly, a least squares fit of the data forced through the origin and secondly, without forcing the regression through the origin (free fit). The resulting plots for 2005 and 2006 are presented in Figs. 1 and 2 respectively. Information from linear regression analysis for each individual calibration and for the combined annual data sets for 2005 and 2006 is shown in Table 1. Figs. 1 and 2 and Table 1 illustrate and quantify the spread in the data between the different calibrations exercises. The regression data in Table 1 do not indicate any progressive changes the calibration of the optodes with the time of year or with the length of use.

3.2. Deriving a calibration constant for each year

The purpose behind the repeated calibrations was to find out what adjustments might need to be made to the full continuous record of observations to improve the accuracy of the reported data set. For each year an equation was required that could be applied throughout the year. The evidence discussed above is insufficient to support an approach other than to produce a calibration factor by combining all the calibration data over the year. When a free fit and one forced through the origin were applied to the data from 2005 the resulting equations ((E1)–(E4)) were

$$\textit{corrected}\ O_2 = \text{Optode}\ O_2 \times 1.018(\pm 0.001) \quad \text{E1}$$

$$\textit{corrected}\ O_2 = \text{Optode}\ O_2 \times 0.989(\pm 0.013) + 8.0(\pm 3.5) \quad \text{E2}$$

and for 2006 the corresponding equations were

$$\textit{corrected}\ O_2 = \text{Optode}\ O_2 \times 1.021(\pm 0.001) \quad \text{E3}$$

$$\textit{corrected}\ O_2 = \text{Optode}\ O_2 \times 0.884(\pm 0.009) + 36.8(\pm 2.3) \quad \text{E4}$$

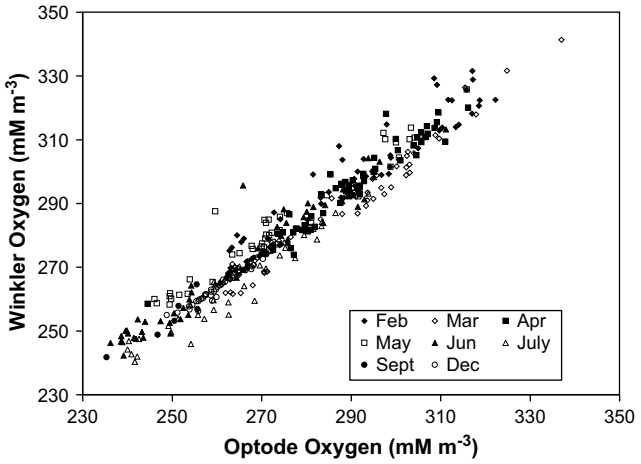

Fig. 1. Lower Winkler titration value plotted against the corresponding value for the optode in 2005. The data from the different calibration crossing are distinguished in the plots.

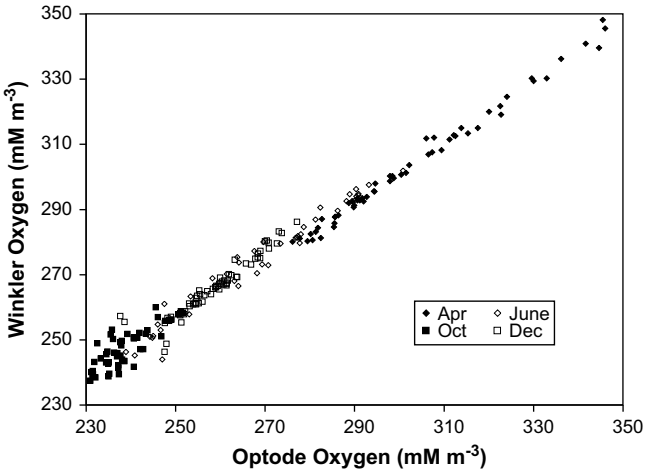

Fig. 2. Lower Winkler titration value plotted against the corresponding value for the optode in 2006. The data from the different calibration crossing are distinguished in the plots.

When the residual differences between the observed Winkler values and the optode data corrected by the forced and unforced fits were compared for the 2005 data there, was little difference between the results generated by application of the two equations. The median difference between the Winkler and optode data without correction was 4.2 mM m^{-3} (median Winkler concentration 279.5 mM m^{-3}) and reduced to −0.5 mM m^{-3} when the forced fit was applied and −0.7 mM m^{-3} for the free fit (Table 2). In 2005 the Winkler optode difference was effectively independent of the oxygen concentration. The standard deviation of the difference was unchanged by the adjustments and remained 5.0 mM m^{-3} (Table 2). However the free fit (E4) is the more appropriate one to apply to 2006. Fig. 3 shows that the Winkler optode difference was not independent of the oxygen concentration. For the 2006 data the median difference reduced from 6.4 for the uncorrected data to 1.1 with the forced fit and −0.2 mM m^{-3} with the free fit (Table 2). The standard deviation of the difference was reduced by application of the free fit equation from 4.2 to 2.9 mM m^{-3} (Table 2 cf. Figs. 3 and 4).

Table 1
Summary of the data from the individual calibrations and for the combined data sets for each year. N = numbers of pairs of duplicate samples on each crossing, b = linear fit forced through the origin calibration constant, r^2 = corresponding linear regression coefficient, b' calibration constant linear fit not forced through the origin, c = corresponding intercept, r'^2 = corresponding linear regression coefficient. Note: that b' for all the 2006 data is lower than that for each of the individual months is product of how the ranges of data for the individual months interact when b' is calculated across the full range of concentrations for the year.

date	N	b	r^2	b′	c	r'^2
2005						
feb	61	1.026	0.922	0.976	14.4	0.925
mar	60	1.005	0.963	0.995	3.1	0.964
apr	61	1.017	0.919	0.994	6.8	0.920
may	47	1.033	0.929	0.920	31.1	0.944
jun	52	1.023	0.936	0.948	20.0	0.942
jul	35	1.000	0.932	0.935	17.2	0.937
sep	8	1.017	0.943	0.960	14.6	0.946
dec	41	1.013	0.959	0.940	19.1	0.965
all 2005		1.018	0.943	0.989	8.0	0.944
2006						
apr	57	1.003	0.988	0.946	17.3	0.992
jun	43	1.021	0.958	0.935	23.3	0.966
oct	58	1.037	0.720	0.896	33.7	0.738
dec	62	1.030	0.888	0.970	15.5	0.892
all 2006		1.021	0.964	0.884	36.8	0.986

Table 2
Summary statistics of Winkler and optode data and the difference between the Winkler value and the corresponding optode value before and after adjustment of the optode value by equations (E1)–(E4). (n is number of Winkler samples).

	2005 Opt	Winkler	W-Opt	2006 Opt	Winkler	W-Opt
n	361			219		
median	274	280	4.2	261	268	6.4
mean	277	281	4.9	267	273	5.9
max	337	341	29.8	346	348	20.0
min	235	24	−8.9	229	237	−5.0
stdev	20.5	20.9	5.0	27.5	24.6	4.2
			E1			**E3**
median	279		−0.5	267		1.1
mean	281		0.2	272		0.4
max	343		25.3	353		15.1
min	239		−13.5	234		−12.1
stdev	20.8		5.0	28.0		4.7
			E2			**E4**
median	279		−0.7	268		−0.2
mean	281		0.0	273		0.0
max	341		24.9	343		10.8
min	241		−13.8	239		−10.8
stdev	20.3		5.0	24.4		2.9

4. Discussion

4.1. *Limitation of the* in-situ *calibrations*

Above, the adjustment of the calibration for the optode in 2006 was made relative to the measured concentration. However the measurement inaccuracy could also be due an inaccuracy in the optodes internal processing of its temperature corrections. In this work, as temperature and oxygen concentrations co-vary, we cannot distinguish between the two. Taking this aspect of optode calibration work further requires controlled laboratory conditions where the oxygen concentration and temperature can be modified independently. Currently as part of the preparation of oxygen optodes for use in the Argo Float programme Craig Neil and Kelly Brown at the Bjerknes Centre, Bergen, Norway (Craig Neil, pers. comm.) are doing detailed multipoint calibrations of optodes. These calibrations indicate that the standard calibration of optodes, as supplied, has errors in the calibration which vary from optode to optode as we demonstrated here. By working over a range of carefully independently controlled oxygen concentrations and

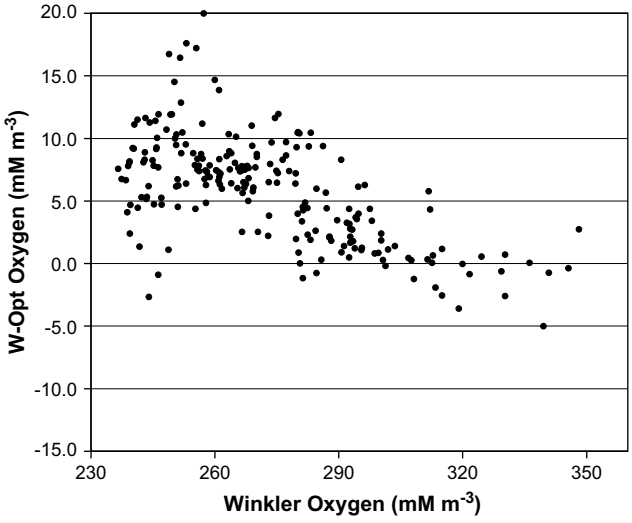

Fig. 3. Plot of the difference between the Winkler titration value and the corresponding optode value (before adjustment of the optode values) for the data from 2006.

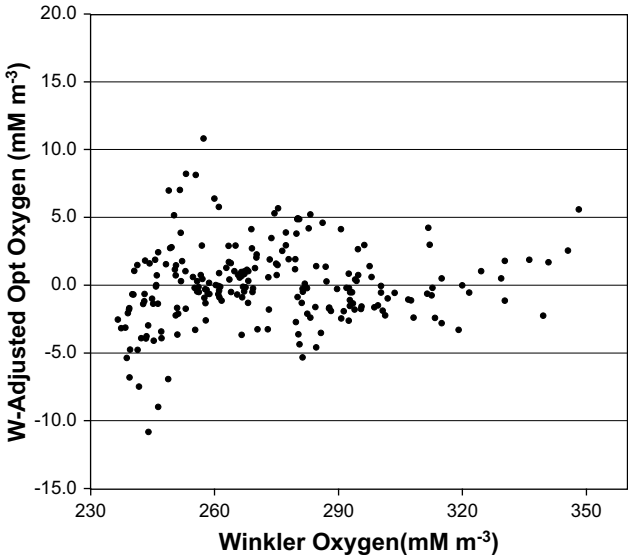

Fig. 4. Plot for the same data as in Fig. 3 after the optode data has been adjusted by equation (E4) (*corrected* O_2 = Optode $O_2 \times 0.884 + 36.8$) before subtraction from the corresponding Winkler value.

temperatures, Neil and Brown can distinguish the errors in the calibration produced from both parameters.

4.2. Errors in estimation of the oxygen anomaly

At a given salinity and temperature the saturation concentration of a seawater can be determined using the equations in Garcia and Gordon (1992) based on Benson and Krause (1984). The requirements for accurate calculations of the anomaly in concentration of oxygen are that: (1) Measurements of temperature and salinity accurately represent *in-situ* conditions at the sea surface (2) Water reaching the optode has the same concentration as water *in-situ*, outside of the ship. The latter is probable because (a) the water flowing over the optode was in a closed system at pressure of 2 bar and cannot degas, (b) sampling of the water for Winkler titrations showed no evidence of bubbles in the water stream, and (c) Bargeron et al. (2006) demonstrated that the data achieved from the Winkler titrations was oceanographically consistent. An error of 1 mM m^{-3} occurs in the calculation of the anomaly when at a temperature of 15 °C and a salinity of 35.0 the error in the temperature measurement is 0.2 °C or the error in salinity is 0.65. We now consider the likely size of error in the calculated oxygen anomaly resulting from errors in the measurement of salinity and temperature.

4.2.1. Salinity error

The CTG CTD-F measured conductivity, temperature and pressure from which salinity was calculated. The proximity of the walls of the flow housing to the conductivity sensing head on the CTD-F produced distortions of the electromagnetically induced field round the head. Variations in this distortion could occur each time it was cleaned and the CTD-F was replaced into the housing. This required repeated calibrations of the CTD-F salinity measurements to be made against samples that were collected on the calibration crossings and before and after cleaning. The procedure used produced salinity data which were oceanographically consistent to better than ±0.05 in salinity. This error in salinity (0.1) was equivalent to an error in the calculated oxygen saturation of 0.16 mM m^{-3} at 15 °C.

4.2.2. Optode temperature error

As noted in Section 2.2, systems on the Pride of Bilbao generated 5 sources of data relating to sea surface temperature (SST), including the optode temperature measurement. The most appropriate way of assessing the *in-situ* temperature needed to be decided on before calculating the oxygen anomaly. An optode includes a temperature sensor which has an accuracy of ±0.05 °C (Aanderaa, 2005). The temperature calibration of the optodes was checked by the Calibration Laboratory at NOCS and found to be better than ±0.02 °C (David Childs, pers. comm.). The consequent potential error in the calculation of the concentration of oxygen by the optode software was ±0.1 mM m^{-3}. The temperature measured by the optode is the one used in the calibration of the optode output so that the output of the optode in terms of oxygen concentration is independent of the absolute accuracy of the optodes temperature sensor. Problems may arise from differences in the response time of the temperature sensor and the oxygen detector foil (Koertzinger et al., 2005) or if the optode is mounted in away that temperature measured is different from the actual temperature of the water at the detector foil. In our installation we sought to minimise this by isolating the optode from the high temperatures of the engine room in a PVC hosing (see Section 2.3 above).

4.2.3. In-situ temperature error

Inside the ship are the optode, CTG CTD-F and a hull mounted temperature sensor (Seabird 48). Outside the ship is the ISAR sea surface radiometer and during one crossing per month an RBR 1050 is towed on the CPR. When the outputs from these different sensors were compared over the course of a year, patterns of consistent offsets were identified. These were associated with (1) warming of the water pumped into the ship and (2) delays and mixing in the water reaching the CTD-F and optode temperature sensors. [To reduce the number of channels of data being processed the temperature data from the optode is not worked up independently, so SST is estimated from the CTD-F temperature measurements taking into account the considerations discussed below.]

The CTG CTD-F temperature sensor tended to read higher than the Seabird 48 hull mounted temperature sensor. This relationship changed as the seawater temperature and the internal temperature of the ship changed relative to one another through the year. Fitting trend lines by linear regression to the data sets collected during the oxygen calibration crossings results in equations for the relationship between the MiniPack and Seabird 48 temperatures of -

$$T_{minipack} = T_{hull} \times 0.96(\pm 0.01) + 0.77(\pm 0.01) \text{ (in 2005)}$$

$$T_{minipack} = T_{hull} \times 0.98(\pm 0.01) + 0.37(\pm 0.01) \text{ (in 2006)}$$

The discrepancy was greater at lower temperatures. At about 20 °C the two temperatures agree most closely. The minimum temperature observed on the route was 5 °C in 2005. The offsets at 5 °C were 0.6 °C and 0.3 °C in 2005 and 2006 respectively. The lower off set in 2006 is consistent with the higher rate of water flowing through the system in that year. The good correlation of the hull and water stream temperatures suggested that the CTG CTD-F measurement could be corrected to take account of the heating by applying the linear correction factor from the above equations. A second factor that needed to be taken into account was that the internal temperature of the ship also influenced measurements made by the Seabird 48. The ISAR unit provided ship-based *in-situ* skin sea surface temperature measurements, the accuracy of which were considered to be ±0.1 °C (Donlon et al., 2008). ISAR temperatures and the temperatures from the RBR 1050 on the CPR tend to agree to within 0.1 °C and tend to read colder than the hull sensor (Werenfrid Wimmer, pers. comm.) by an average of 0.2 °C. [When CTD-F and the RBR 1050 were immersed in the same bath of water on the ship prior to use the temperatures that were recorded agreed to better than 0.05 °C.]

For calculating the *in-situ* equilibrium oxygen concentration the *in-situ* temperature was taken to be the CTD-F temperature adjusted for

hull temperature and ISAR offsets. The CTD-F data were adjusted rather than using ISAR data directly because the CTD-F was measuring the same water as the optode at the same time. Changes in temperature across temperature fronts were resolved to a similar degree of precision in both time and space by the ISAR, hull and CPR sensors. In contrast offsets of up to 1.0 °C between the CTD-F and hull temperature data sets occurred and the CTD-F temperatures appear smoothed. This was because water reaching the optode and CTD-F was pumped into the ship via a sea-chest; its passage through and mixing in the chest generated a delay in measurement relative to the external sensors and a "smoothing" of the temperature signal. Consequently the water for which the *in-situ* equilibrium concentration of oxygen had to be calculated was this ship mixed water. This avoided introducing noise in the calculated anomaly due to offsets in temperature between the internal and external measurements of temperature at fronts.

4.3. Summary – optode accuracy

Over the observed range concentration of oxygen (230–330 mM m^{-3}) the optode data before adjustment read about 2% low in both years. This level of accuracy was better than the value advertised by Aanderaa of "8 μM or 5%". Fitting the optode data to Winkler measurements improved the accuracy and reduced the median difference to less than 1 mM m^{-3} (0.3%) in both years.

One of the two optodes was well within the manufacturer's specifications over the range of the observations. The other was still within specification but not as accurate at lower concentrations of oxygen. Both optodes appeared to be stable over the course of a near year long deployment. The accuracy of the data achieved can be improved by user calibration. Ideally this should be done both in the laboratory and the field to take account of change in the optode output with oxygen concentration and temperature.

4.4. Summary – errors in the calculation of oxygen anomaly

Salinity is measured to better than 0.1 so the contribution to the oxygen concentration anomaly error is small, less than 0.2 mM m^{-3}. Estimation of the relevant *in-situ* temperature is more problematic. Thus for calculating the *in-situ* equilibrium oxygen concentration the temperature of the water stream flowing past the FerryBox sensors has to adjusted by a factor based on comparison temperatures measured by the CTD-F and the ISAR unit. Considering the above points discussed in Section 4.2.2, after correction of the CTD-F temperature for ship induced heating the accuracy of the estimated SST is probably better than ±0.2 °C which adds an error of ±1 mM m^{-3}, to the estimation of the oxygen anomaly.

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