NOAA Technical Memorandum, OAR AOML-99

OXYGEN WINKLER TITRATIONS BY NOAA/AOML IN SUPPORT OF DEEPWATER HORIZON SPILL MONITORING

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UNITED STATES DEPARTMENT OF COMMERCE

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The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the funding agency.

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List of Acronyms and Pertinent Web Sites

AOML	Atlantic Oceanographic and Meteorological Laboratory of NOAA http://www.aoml.noaa.gov
CIMAS	Cooperative Institute for Marine and Atmospheric Studies http://cimas.rsmas.miami.edu/
CTD	Conductivity, temperature, and depth profiling device http://www.windows2universe.org/earth/Water/CTD.html
DWH-252	Deepwater Horizon drilling platform (also referred to as the DWH MC 252 where MC stands for Mississippi Canyon)
GERG	Geochemical and Environmental Research Group of Texas A&M University http://gerg.tamu.edu/
JAG	Joint Analyses Group. JAG reports can be found at http://ecowatch.ncddc.noaa.gov/JAG/reports.html
NODC	National Oceanographic Data Center of NOAA http://www.nodc.noaa.gov/
NOS	National Ocean Service of NOAA http://oceanservice.noaa.gov/
O_2	Oxygen
SBE-43	Sea-Bird Electronics model 43 polarographic oxygen sensor http://www.seabird.com/pdf_documents/datasheets/43brochureMay09.pdf

Web Sites for Further Ship Information

Nancy Foster	http://www.moc.noaa.gov/nf/index.html
Ocean Veritas	http://www.stabbertmaritime.com/commercial_vessels/
Brooks McCall	http://www.tdi-bi.com/vessels/BrooksMcCall.htm
Henry B. Bigelow	http://www.moc.noaa.gov/hb/index.htm
Pisces	http://www.moc.noaa.gov/pc/index.html

Oxygen Winkler Titrations by NOAA/AOML in Support of Deepwater Horizon Spill Monitoring

Abstract

This report details the measurement of oxygen (O_2) by the Winkler method on the ships *Nancy Foster*, *Ocean Veritas*, *Brooks McCall*, *Henry B. Bigelow*, and *Pisces* in response to the oil spill of the Deepwater Horizon 252 well. Most of the data are from near the well and were obtained from July 1, 2010 to August 30, 2010. The purpose of these measurements was to assess the accuracy of the oxygen sensors on a conductivity-temperature-depth (CTD) sensor, henceforth referred to as CTD/O_2, and to determine if the CTD/O_2 sensor provided (low) biased readings in the presence of oil. Based on the analyses, we believe that the O_2 analyses from the CTD/O_2 and Winkler systems on the ships were accurate to within 2% (≈4 μmol/l, ≈0.1 ml/l, or ≈0.15 ml/l),[1] with exceptions listed in the following paragraph. The depression in O_2 values observed by the CTD/O_2 at depths of 1000-1300 m in the layer with diffuse oil were verified by the Winkler measurements and are attributed to oxidation of the oil and associated gas.

Based on the Winkler measurements, we cannot conclusively recommend adjustments to the CTD/O_2 data. A qualitative assessment suggests that the output of CTD/O_2 sensors on the *Brooks McCall* and *Ocean Veritas* agreed with each other and with the Winkler measurements to within 2%. The CTD/O_2 sensor on the *Pisces* appeared to read low by about 3% when compared with the *Henry B. Bigelow* CTD/O_2 and Winkler O_2 values that agreed well with each other. The *Nancy Foster* had the largest dataset of Winkler O_2 values for comparison. These values were about 2.6 ± 2% higher than the CTD/O_2 values in water depths of 100-1000 m but showed larger positive deviations of up to 10% at the surface and in deep water which we cannot explain.

1. Introduction

After the explosion and rupture of the pipe at the wellhead of the Deepwater Horizon 252 well (DWH-252), a total of 200 million gallons of oil and gas entered the ocean at about 1400 m depth over the time period from April 20, 2010 to July 15, 2010. Approximately 25% of the oil and associated gas released, or about 50 million gallons of oil, dispersed and remained at a depth of 1100 to 1300 m. Much of this oil degraded by microbial activity, which caused a decrease of oxygen at these depths (Kessler *et al.,* 2011; JAG, 2010).

As part of the compliance monitoring, oxygen levels were determined from oxygen (O_2) sensors connected to CTD sensors on the ships surveying the impact of the spill. A model SBE-43 Clark polarographic membrane-type sensor from Sea-Bird Electronics, Inc. provided full water-column O_2 values with a resolution of 1-m intervals. This model sensor was used on

[1] Various units for oxygen concentration are commonly used. In this report we use μmol/l. The conversions to other common units are: 1 μmol/kg = 1(μmol/kg)*(density of seawater (kg/l)) ≈1.02 μmol/l; 1 ml/l = 44.66 μmol/l; and 1 mg/l = 31.23 μmol/l.

all the ships described in this report and appears to have faithfully reproduced small-scale (< 20 m) variations in O_2 concentrations. At the onset of the study, however, it was not clear if there were interferences and artifacts caused by the presence of oil.

To generate high precision observations from the CTD/O_2 sensor, adjustments for generally small offsets of the sensor are required. These offsets are caused by pressure and temperature sensitivity of the sensor. Software is available from Sea-Bird to perform these adjustments that empirically account for upcast and downcast offsets in CTD/O_2 due to sensor lag and hysteresis. All CTD/O_2 data were reduced using the same routines with the latest software package (application note 64-3 from http://www.seabird.com/products/Modular.htm). The CTD/O_2 profiles that are provided after adjustments are the downcast values.

To obtain accurate measurements, the sensor data need to be verified during the cast. A common protocol for accurate oxygen measurements is to standardize the CTD/O_2 trace with discrete samples taken throughout the water column and analyzed by the Winkler technique (Carpenter, 1965) using water from Niskin sample bottles that are lowered with the CTD/O_2 on a Rosette package. Samples are taken at 10 to 24 depths throughout the water column. These adjustments to the Winkler values were not performed for the CTD/O_2 data mentioned in this report. Rather, the approximate differences between the Niskin Winkler O_2 values and the CTD/O_2 values are presented.

Since the initial requirements for oxygen monitoring were not too stringent and, because of the need to get the measurement campaigns underway as soon as possible, the Winkler calibration requirement was not instituted at the onset for all cruises. However, due to concerns about sensor biases in the presence of oil and to validate the measurements, Winkler O_2 analyses were initiated later for many of the ships monitoring the water column properties near the DWH-252 well. This report provides the description of the O_2 Winkler analyses made shipboard and at the shore-based laboratory by the Oxygen Group at NOAA's Atlantic Oceanographic and Meteorological Laboratory (AOML) in Miami, Florida. It includes measurements on samples taken from the following ships: NOAA research vessel *Nancy Foster*, the NOAA fisheries ships *Pisces* and *Henry B. Bigelow*, and the commercial research vessels *Brooks McCall* and *Ocean Veritas* covering the time period from July 1, 2010 to August 30, 2010.

During the initial response phase, few ships monitoring the environment of the well were equipped to perform O_2 Winkler titrations. The Oxygen Group at AOML was asked to provide Winkler support in large part because of their experience in providing accurate analyses on the CLIVAR/CO_2 Repeat Hydrography Program cruises. During the June-August 2010 time frame, the group performed Winkler O_2 measurements on the *Nancy Foster* (cruise 10-13), the *Ocean Veritas* (cruise 12), and the *Brooks McCall* (cruises 16 and 17). The group also supported O_2 measurements on the *Henry B. Bigelow* and *Pisces,* including shore-based O_2 analyses. As described in this report, the different systems and different levels of experience of the personnel involved in sampling and analyses contributed to variations in the quality of the data. A summary of results is provided in Table 1. A description of operations, and pre- and post-cruise calibrations and checks is presented for each ship.

Table 1: Summary of sampling results.

Ship	Cruise Number	Number of Samples[a]	Number of Duplicates[b]	Precision[c] (µmol/l)	Winkler-CTD/O_2[d] (µmol/l)	Count[e]
Nancy Foster	10-13	594	13	0.2 ± 0.2	6.7 ± 7.8	567
Ocean Veritas	12	85			-1.9 ± 4.0	70
Brooks McCall	16	51	3	4.3 ± 4.0	-4.1 ± 6.1	35
Brooks McCall	17	42			-4.2 ± 8.9	28
Henry B. Bigelow	10-06	87	20	2.6 ± 2.7	3.4 ± 4.2	66
Pisces		88	1	0.7	12.3 ± 2.2	6

[a]Number of Winkler samples analyzed.

[b]Number of duplicates taken from Niskin bottles.

[c]Average difference of the duplicates and the standard deviation of the average difference.

[d]Average difference and standard deviation of the average difference between the Winkler values and the CTD/O_2 sensor values at the bottle trip depth. All Winkler values considered questionable (quality control [QC] flag = 3) or bad (QC flag = 4) were not used.

[e]Number of samples used in the comparison.

2. *Nancy Foster*

Operator: Andrew Stefanick, AOML
Dates of O_2 Sampling: July 1-18, 2010

The *Nancy Foster* completed a two-leg cruise from Key West, Florida to Pascagoula, Mississippi with a port stop in Tampa, Florida. The chief scientist of the cruise, designated as *Nancy Foster* cruise 10-13, was Ryan Smith of NOAA/AOML. Andrew Stefanick of AOML performed oxygen analyses with assistance from Pedro Pena of AOML. The oxygen titrator was an automated system with colorimetric endpoint detection (Friederich *et al.*, 1984). Five standardization runs were performed using a 0.01 N potassium iodate (KIO_3) standard. Standardization was performed by titrating 2, 4, 6, 8, and 10 ml aliquots of iodate. The slope and intercept were used to quantify the thiosulfate concentration and to determine the blank, respectively. Reproducibility of the blank and slope (Table 2) were excellent throughout the cruise, suggesting stable instrumentation and good operator protocols. The thiosulfate disperser (Methrohm) was replaced towards the end of the cruise because of a small leak in the system. The standardization curves before and after the replacement were very similar, suggesting that the leak had no discernable impact on the results. No duplicates were measured except at the end of the cruise near the DWH-252 wellhead where all samples at depth were duplicated. Reproducibility of these samples was excellent (see Table 1).

Table 2. Standardization of the Winkler O_2 system with colorimetric end-point detection on the *Nancy Foster*.

Date	Standard Name	Slope[a]	Intercept[a]	R^2
7/04/10	nf1013a.std	25.087	-0.0003	0.9999
7/07/10	nf1013b.std	24.978	-0.0007	0.9999
7/11/10	nf1013c.std	25.118	-0.0025	0.9999
7/15/10	nf1013d.std	25.152	-0.0013	0.9999
7/18/10	nf1013e.std	24.844	0.0097	0.9999

[a]The standardization was performed by titrating 2, 4, 6, 8, and 10 ml aliquots of iodate. The ml of aliquot versus thiosulfate titrated provides the slope and intercept values given above. For the standard calibrations nf1013a and nf1013d, the 10 ml aliquot value was not used, and for the standard calibration nf1013c, the 2 ml aliquot was not included in the linear regression.

Two independent SBE-43 oxygen sensors from Sea-Bird Electronics, Inc. were used on the CTD, and data were processed according to protocols outlined in the appropriate Sea-Bird Electronics application manuals. The two sensors yielded identical data (to better than 1 µmol/l). Pre- and post-cruise calibrations were performed at Sea-Bird Electronics with one sensor showing no drift and the other showing a small change in calibration coefficients, suggesting a drift of about 1 µmol/l (@ 150 µmol/l). The comparison with the CTD/O_2 data yielded some puzzling results as shown in Figure 1. The ratio of Winkler O_2 and CTD/O_2 values is about 1.03 but shows strong positive deviations in surface water and in deep water. No explanations for these trends are offered despite discussions and checks by an application specialist at Sea-Bird Electronics of the data. The correspondence of the two CTD/O_2 sensors suggests that the processed CTD/O_2 values are correct. While CTD/O_2 data are commonly corrected to the Winkler values, we do not recommend this procedure in this instance since the duplicate and independent SBE-43 sensors provided such close correspondence.

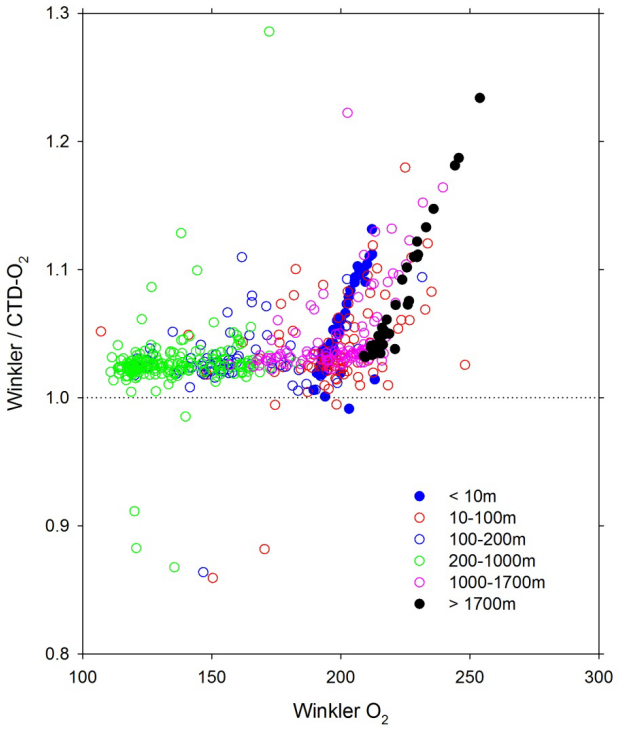

Figure 1. Ratio of Winkler O_2 analyses to the corresponding CTD/O_2 values for the *Nancy Foster* cruise 10-13. The trends at surface and at depth are unexplained.

3. *Ocean Veritas*

Operator: George Berberian, AOML/CIMAS
Dates of O_2 Sampling: August 1-2, 2010 (cruise 12)

The *Ocean Veritas* and *Brooks McCall* operated southwest of the DWH-252 wellhead for the cruises described. The *Ocean Veritas* data were obtained using an automated titrator with an amperometric endpoint detection system (Langdon, 2010). The system was standardized using a single aliquot of iodate rather than a five-point calibration as performed on the *Nancy Foster*. Four standards were run on August 1st, with an average endpoint for the 0.01 N KIO_3 solution of 701.75 ± 0.66.

The data quality was satisfactory. Fifteen of the 85 samples that were submitted to the National Oceanographic Data Center (NODC) had a quality control (QC) flag of 3 or 4, which refer to questionable or bad data, respectively.

The agreement between the Winkler analyses and the CTD/O_2 (SBE-43) was -1.9 ± 4.0 µmol/l (n=70).

4. *Brooks McCall*

Operator: George Berberian, AOML/CIMAS
Dates of O_2 Sampling: August 4-7, 2010 (cruise 16)
August 10-11, 2010 (cruise 17)

The amperometric oxygen titrator was transferred from the *Ocean Veritas* to the *Brooks McCall* for cruise 16 in Port Fourchon, Louisiana on August 3, 2010. The system was standardized using a one-point calibration method with a single 10-ml aliquot of KIO_3. Six standard runs were performed on August 4th with three values omitted. The average endpoint for the 0.01 N KIO_3 solution for the three remaining standards was 703.64 ± 0.51. The three omitted standard values had endpoints that were about 3 higher. Three duplicate samples were taken that had an average difference of 4.3 ± 4.0 µmol/l. For cruise 16, 16 samples were flagged as questionable or bad (3 or 4) based on comparisons with the CTD/O_2. For the remaining samples, the agreement between the Winkler O_2 and CTD/O_2 was -4.1 ± 6.1 µmol/l (n=35). Six aliquots of KIO_3 were analyzed on August 6th with three results omitted. The average endpoint for the 0.01 N KIO_3 solution for the three remaining standards was 701.23 ± 0.49.

For cruise 17, the system was standardized using 10-ml aliquots of KIO_3 as well. Eight standards were run on August 9th with the first five values omitted. The average endpoint for the 0.01 N KIO_3 solution for the three remaining standards was 700.64 ± 0.77. The five omitted values had endpoints ranging from 2 to 50 higher. For cruise 17, 14 samples were flagged as questionable or bad (3 or 4) based on comparisons with the CTD/O_2. For the remaining samples, the agreement between the Winkler O_2 and CTD/O_2 was -4.2 ± 8.9 µmol/l (n=28). The entire last cast (station 172) was flagged as 4 because of a large offset between the Winkler O_2 and CTD/O_2 (≈ -27 µmol/l, with the Winkler O_2 being lower than the CTD/O_2). This is attributed to analyzing the samples too soon after adding the reagents. The ship was heading into port to avoid inclement weather and samples had to be analyzed very soon after sampling.

5. *Henry B. Bigelow*

Operators: Liza Baskin, NOAA/Northeast Fisheries Science Center, Narragansett, RI
Chris Sumner, NOAA/Northeast Fisheries Science Center, Narragansett, RI

Cruise No. HB 10-06: Subsurface Oil and Ecological Impacts (Gulf of Mexico)

Dates of O_2 Sampling:

Leg 1:	July 28-August 10, 2010	Key West, Florida to Pascagoula, Mississippi
Leg 2:	August 13-22, 2010	Pascagoula, Mississippi to Key West, Florida

The *Henry B. Bigelow* worked primarily within 10 km of the DWH-252 wellhead for Leg 1. During Leg 2, work was performed in the vicinity of the wellhead but also up to 60 km from the wellhead. An amperometric O_2 system from AOML (Langdon, 2010) was installed on the *Henry B. Bigelow* in Key West, Florida. Liza Baskin collected approximately 30 samples for Winkler titrations on board. The auto-titrator was damaged on August 8th (station 33), towards the end of the first leg of the cruise, possibly because it was connected to the wrong power source. Subsequent to the failure, the samples were preserved ("pickled") at sea for analysis on shore by George Berberian of NOAA/AOML.

For the second leg, all samples were stored according to protocol (Zhang *et al.,* 2002) and analyzed on shore. In particular, a water seal was maintained on all samples, and all the samples were returned to AOML with analyses performed on the same amperometric system that was used for the analyses of the *Brooks McCall* and *Ocean Veritas* data.

The results of the duplicate analyses are presented in Table 3, and a comparison with CTD/O_2 values is shown in Table 4.

Standards:	shore based
August 28, 2010:	standard average = 703.00 ± 0.60
September 2, 2010:	standard average = 704.60 ± 0.52

There is no significant difference in the CTD/O_2 and Winkler O_2 values such that no adjustments are recommended to the CTD/O_2 data from the *Henry B. Bigelow*.

Table 3. Winkler O_2 duplicate analysis results for the *Henry B. Bigelow*.

Key Number[a]	Date	Depth (m)	O_2 (µmol/l)	O_2 (µmol/l)	Difference (µmol/l)
Ship					
211	8/3/10	64.5	213.2	211.7	1.5
408	8/4/10	504.4	123.4	124.1	0.8
607	8/5/10	403.5	125.5	125.0	0.5
903	8/7/10	1146.4	185.2	190.3	5.1
1002	8/7/10	1312.9	206.6	208.9	2.4
1105	8/7/10	1159.0	169.9	172.0	2.1
Shore					
1510	8/7/10	100.4	185.8	185.5	0.3
1607	8/8/10	705.2	138.8	142.1	3.3
1701	8/8/10	1584.1	213.9	213.4	0.5
1805	8/8/10	604.1	128.2	127.3	0.9
2006	8/8/10	704.5	140.2	141.1	0.9
2106	8/8/10	807.9	154.2	154.3	0.0
2309	8/9/10	201.0	155.4	163.4	8.0
3306	8/15/10	504.7	119.1	123.0	3.8
3403	8/15/10	908.6	169.3	164.4	5.0
3503	8/15/10	1109.5	190.5	191.5	1.0
4705	8/17/10	605.4	137.1	128.5	8.6
5306	8/18/10	503.9	135.4	134.2	1.3
5706	8/18/10	416.6	120.8	127.4	6.6
5807	8/19/10	403.7	128.3	128.8	0.5

	Average Difference[b]	*Standard Deviation*[c]	*Count*[d]
All	2.6	2.7	20
Ship	2.1	1.7	6
Shore	2.9	3.0	14

[a]Station number × 100 + Niskin position.

[b]Absolute average difference for samples run on ship and on shore.

[c]Standard deviation of the difference.

[d]Number of duplicates.

Table 4. Comparison of Winkler O_2 and CTD/O_2 values for the *Henry B. Bigelow.*

Key Number	Date	CTD/O_2 (µmol/l)	O_2 Winkler (µmol/l)	Winkler−CTD/O_2 (µmol/l)	Key Number	Date	CTD/O_2 (µmol/l)	O_2 Winkler (µmol/l)	Winkler−CTD/O_2 (µmol/l)
202	8/3/10	146.9	140.0	-7.0	2002	8/8/10	194.3	213.7	19.3
211	8/3/10	213.6	213.2	-0.4	2006	8/8/10	138.2	140.2	2.0
307	8/3/10	156.6	158.4	1.8	2106	8/8/10	151.9	154.2	2.4
312	8/3/10	226.0	223.2	-2.7	2112	8/8/10	198.5	200.0	1.5
405	8/4/10	187.9	192.9	5.0	2307	8/9/10	125.0	127.7	2.7
408	8/4/10	121.5	123.4	1.9	2309	8/9/10	154.1	155.4	1.3
601	8/5/10	179.7	182.6	2.9	2311	8/9/10	209.6	207.6	-2.0
607	8/5/10	124.8	125.5	0.7	2402	8/9/10	189.1	192.7	3.7
610	8/5/10	151.4	151.1	-0.3	2407	8/9/10	118.8	121.7	2.9
611	8/5/10	224.0	220.8	-3.2	3301	8/14/10	206.9	211.0	4.1
703	8/5/10	156.5	157.4	0.9	3306	8/15/10	117.6	119.1	1.6
705	8/5/10	130.1	130.0	-0.1	3312	8/15/10	201.8	206.0	4.2
901	8/7/10	207.0	213.3	6.3	3403	8/15/10	163.2	169.3	6.2
903	8/7/10	186.7	185.2	-1.5	3413	8/15/10	146.6	152.2	5.5
905	8/7/10	166.3	169.1	2.8	3414	8/15/10	184.8	185.2	0.4
907	8/7/10	121.9	124.1	2.1	3503	8/15/10	182.4	190.5	8.1
1002	8/7/10	202.1	206.6	4.5	3505	8/15/10	149.3	153.8	4.4
1005	8/7/10	186.9	190.5	3.5	3507	8/15/10	119.9	128.9	9.1
1011	8/7/10	153.1	155.3	2.3	4705	8/17/10	125.5	137.1	11.6
1101	8/7/10	205.5	210.4	4.9	4706	8/17/10	118.3	123.5	5.2
1105	8/7/10	169.8	169.9	0.1	4708	8/17/10	122.7	127.4	4.7
1108	8/7/10	153.0	157.6	4.6	5306	8/18/10	121.0	135.4	14.4
1510	8/7/10	184.9	185.8	0.9	5309	8/18/10	137.9	150.9	13.0
1604	8/8/10	172.6	179.4	6.8	5310	8/18/10	182.8	186.1	3.4
1607	8/8/10	136.4	138.8	2.3	5704	8/18/10	166.9	169.7	2.8
1612	8/8/10	198.6	200.8	2.1	5706	8/18/10	120.3	120.8	0.4
1701	8/8/10	208.5	213.9	5.4	5708	8/18/10	120.8	129.2	8.3
1704	8/8/10	187.7	192.8	5.1	5801	8/19/10	215.2	220.1	4.9
1709	8/8/10	144.7	147.0	2.3	5807	8/19/10	119.1	128.3	9.2
1711	8/8/10	206.0	205.0	-1.0	5818	8/19/10	227.4	223.9	-3.5
1802	8/8/10	185.9	189.0	3.1	6202	8/19/10	209.9	208.8	-1.1
1805	8/8/10	125.8	128.2	2.4	6206	8/19/10	126.4	139.7	4.1
1812	8/8/10	198.7	201.4	2.7	6211	8/20/10	230.4	235.7	5.3

Winkler-CTD[a]	*Average Difference*[b]	*Standard Deviation*[c]	*Count*[d]
All	4.0	3.5	66
Ship	1.3	3.1	23
Shore	4.4	4.3	43

[a]Winkler O_2 value minus CTD/O_2 value.

[b]Absolute average difference for Winkler O_2 and CTD/O_2.

[c]Standard deviation of the difference.

[d]Number of duplicates.

6. *Pisces*

O_2 Analyst on Shore: George Berberian, AOML/CIMAS
Dates of O_2 Sampling: August 18-September 1, 2010

The *Pisces* spent much of its time southwest of the DWH-252 wellhead. For the *Pisces,* O_2 was sampled and preserved by inexperienced operators. Samples were shipped from Pascagoula, Mississippi to Miami, Florida after the cruise. Upon arrival, most samples were lacking a water seal and many samples had bubbles in the bottles. While the integrity of the samples containing bubbles was compromised, it was decided to run all samples. As expected, samples appeared to be biased high due to the likely diffusion of air into the bottles as manifested by the bubbles. In Table 5 below, the samples were differentiated based on approximate bubble diameter. The difference between Winkler O_2 and CTD/O_2 values increased with bubble size, indicative of ambient air diffusing into the sample.

Standards:	shore based
September 1:	standard = 707.30 ± 0.16 (n=5; blank = 1.7)
September 7 with new thiosulfate:	standard = 707.70 ± 0.16 (n=5; blank = 1.7)

Table 5. Comparison of Winkler O_2 and CTD/O_2 values for the *Pisces*.

	Diameter	Average Difference[a]	Standard Deviation[b]	Count[c]
No bubble		12.3	2.2	6
Small bubble	0.3 cm	13.1	1.6	29
Medium bubble	0.8 cm	16.0	4.6	44
Large bubble	1.3 cm	16.6	3.9	12
All		15.0	4.0	91

[a]Average difference for the Winkler O_2 and CTD/O_2 values (Winkler O_2 values are higher).
[b]Standard deviation of the difference.
[c]Number of duplicates.

While the quality of samples precluded a definitive recommendation on possible offsets, a comparison of CTD/O_2 traces from the *Pisces* and *Henry B. Bigelow* at a similar sampling location suggests that the CTD/O_2 sensor on the *Pisces* was reading approximately 7 µmol/l low (Figure 2). This offset is slightly smaller than the corresponding offset for the few Winkler O_2 analyses on bottles without bubbles, but the difference between CTD/O_2 traces for the *Pisces* and *Henry B. Bigelow* varies with concentrations from 3 to 12 µmol/l (Figure 2).

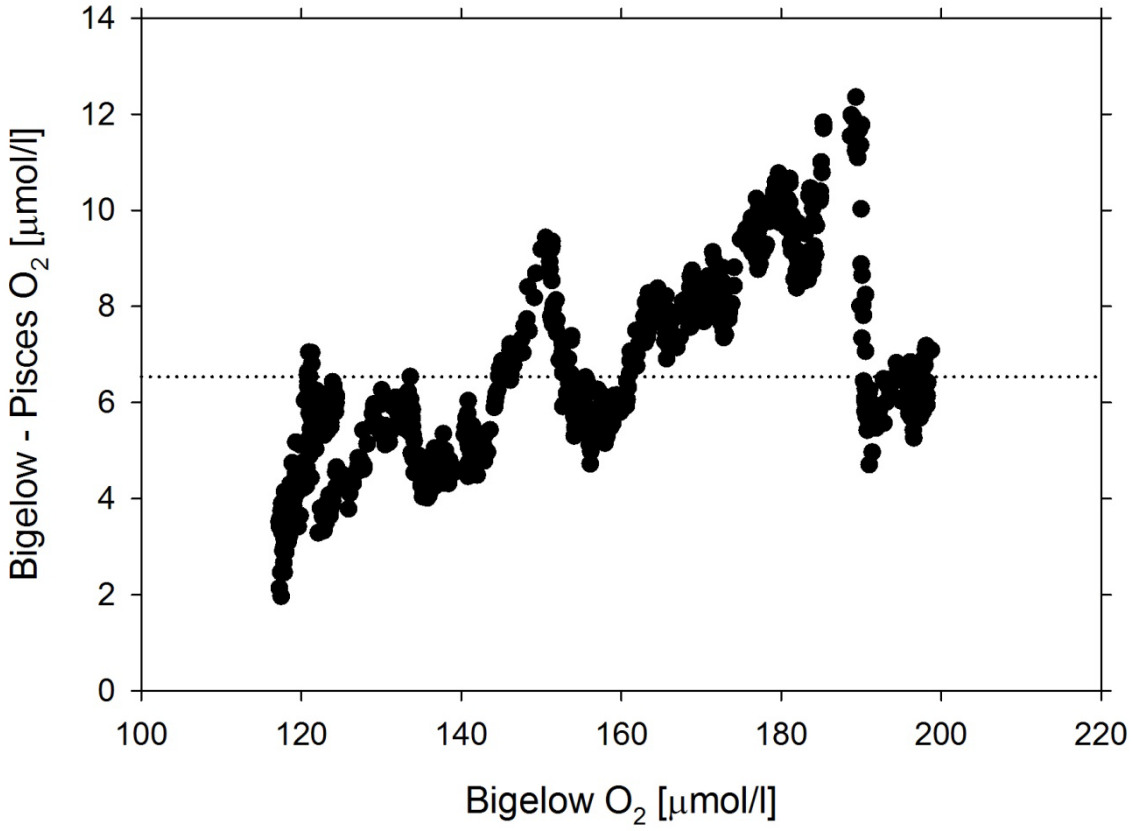

Figure 2. Comparison of CTD/O_2 values for *Henry B. Bigelow* station 34 (28.67°N, 88.44°W) on August 15, 2010 and *Pisces* station 75 (28.65°N, 88.48°W) on August 20, 2010. The figure suggests that the CTD/O_2 sensors on the *Pisces* were reading, on average, about 7 µmol/l (≒0.2 ml/l) too low. The CTD/O_2 profiles with depth for these two stations are shown in Figure 5, while their location in relationship to the DWH-252 well is shown in Figure 3.

7. Equipment and Standard Checks

Biases in burette volume and iodate standard concentration will directly impact the determination of the results. These were checked after field and laboratory analyses. The Wheaton burette used to dispense the iodate standards had not changed its assigned value appreciably since the previous check as indicated in Table 6:

Table 6. Pre- and post-cruise burette calibrations used for standards.

Burette Number[a]	Pre-cruise volume (ml)[b]	Post-cruise volume (ml)
AOML-3	9.953	9.965
AOML-4	9.975	9.977

[a]Burette number with the volume at 20°C.

[b]The pre-cruise volume was used for all calculations of standard values. The difference in volume delivered for AOML-3 pre- and post-cruise translates into a difference of 0.2 µmol/l (@ 150 µmol/l).

The KIO_3 standard was (inadvertently) left on the *Pisces* and cross-calibrated with the standard prepared by Eric Quiros of Texas A&M University's Geochemical and Environmental Research Group (GERG), who operated a similar amperometric system as used in our analyses on the *Pisces*. This cruise was also in support of monitoring impacts of the DWH-252 spill (Kessler *et al.,* 2011). It took place in September 2010 immediately after the cruise for which the samples listed previously for the *Pisces* were taken.

Both the Texas A&M standard and that used by AOML were 0.01 N KIO_3 solutions. The calibration of the standards by Eric Quiros on the *Pisces* was as follows (Table 7).

Table 7. Comparison of the AOML and Texas A&M titrations for 10-ml aliquots of independently prepared 0.01 N potassium iodate (KIO_3) solution.

	AOML Standard (µl thiosulfate)	Texas A&M Standard (µl thiosulfate)
	700.37	706.13
	700.24	705.75
	700.16	705.59
	699.00	706.12
Average:	**699.94**	**705.90**
Standard deviation:	**0.63**	**0.27**

This means that all AOML analyzed O_2 Winkler values will be 0.8% higher than comparable values provided by GERG. While the value of the µl thiosulfate titrated for 10-ml, the 0.01 N KIO_3 solution, can change over time, the trends and deviations are indicative of instrument environmental stability.

For the samples run by AOML, the same titrator was used, the "Wilson unit," provided by D. Wilson of NOAA's National Ocean Service in Charleston, South Carolina. A summary of the results of all the titrations of iodate standards for all the AOML cruises and shore-based analyses are provided in Table 8.

Table 8. Summary of standardization of units using 10 ml of KIO_3 as the standard.

Date	Ship	Titrant Delivered[a]	Number of Standards Run	Number of Standards Retained[b]
8/1/10	*Ocean Veritas*	701.75 ± 0.66	4	4
8/4/10	*Brooks McCall* (cruise 16)	703.64 ± 0.51	6	3
8/6/10	*Brooks McCall* (cruise 16)	701.23 ± 0.49	6	3
8/9/10	*Brooks McCall* (cruise 17)	700.64 ± 0.77	8	3
8/28/10	*Henry B. Bigelow*	703.00 ± 0.60	5	5
9/2/10	*Henry B. Bigelow*	704.60 ± 0.52	5	5
9/1/10	*Pisces*	707.30 ± 0.16	5	5
9/7/10	*Pisces*	707.70 ± 0.16	5	5
9/15/10	*Pisces*	699.94 ± 0.63	4	4

[a]Amount of thiosulfate titrated with standard deviation based on the number of standards retained.

[b]Standards used to determine the average titrant delivered. Values obtained when there were problems with the delivery system or values far from the mean were not used.

8. Assessment of CTD/O_2 and Winkler O_2 Values Obtained during the AOML Campaign

The main objectives of the AOML O_2 sampling and analysis campaign were to:

1. Estimate the overall accuracy of the CTD/O_2 trace and to determine ship-to ship differences in CTD/O_2 sensors.
2. Determine if there were sensor artifacts due to the presence of oil.

The results presented in this report suggest that the CTD/O_2 values agreed with the Winkler O_2 values to within 14 µmol/l (≈0.3 ml/l or 0.4 mg/l) for all cruises. Moreover, for the stations where the CTD/O_2 showed a decrease associated with the presence of oil, as indicated by a fluorometer response, the Winkler results confirmed an O_2 decrease as well. This suggests that there were no appreciable CTD/O_2 artifacts and that the observed decreases in the CTD/O_2 values were caused by oxidation of oil.

Some graphical assessments are presented in Figures 3-5. These provide a visualization of the differences between CTD/O_2 and Winkler O_2 values, as well as some comparisons of CTD/O_2 traces for the different ships.

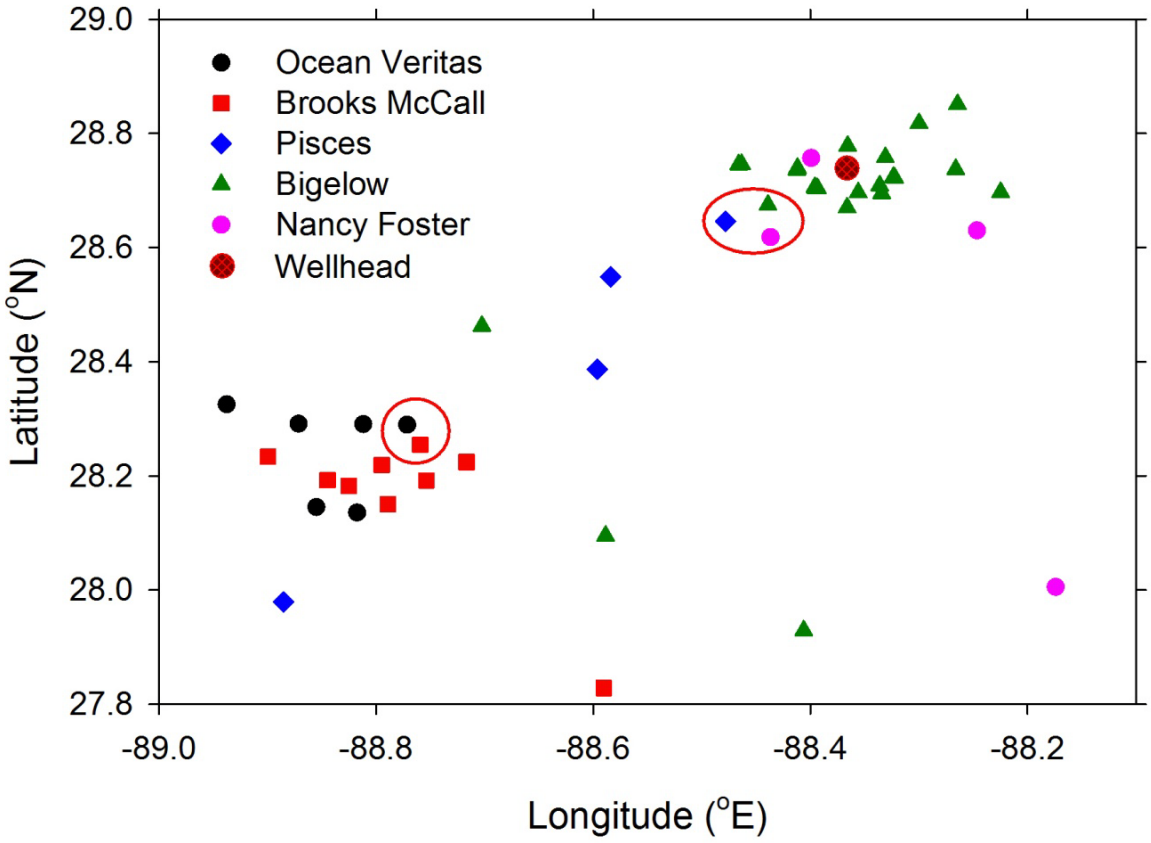

Figure 3. Distribution of stations near the wellhead of the DWH-252 well. The circle in the upper right portion of the figure shows the location of *Nancy Foster* station 71, *Pisces* station 75, and *Henry B. Bigelow* station 34. The circle in the lower left portion of the figure shows the location of *Ocean Veritas* station 153 and *Brooks McCall* station 161.

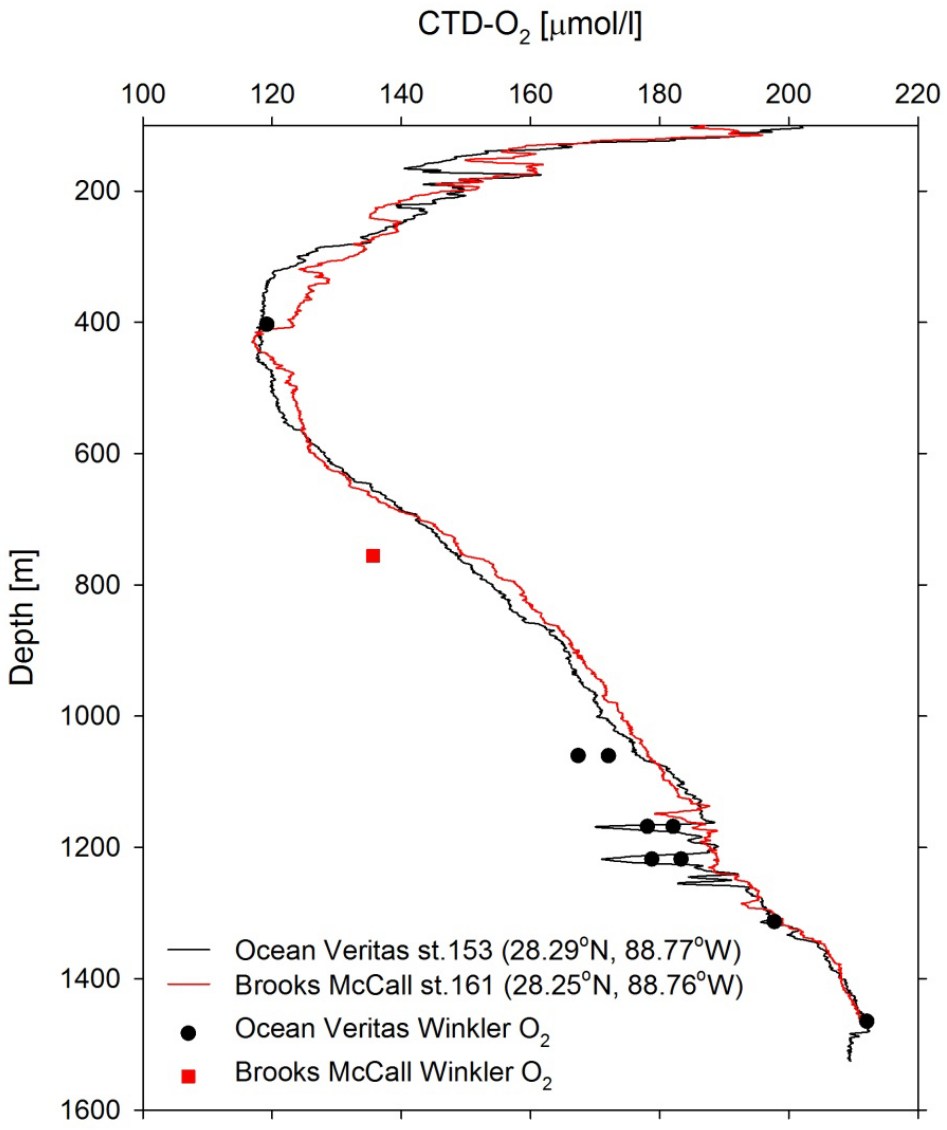

Figure 4. Comparison of CTD/O_2 and Winkler O_2 values for *Ocean Veritas* station 153 (occupied on August 2, 2010) and *Brooks McCall* station 161 (occupied on August 5, 2010). The figure and other analyses suggest that the CTD/O_2 sensors on both ships were comparable and within 4 µmol/l (0.1 ml/l) of the Winkler O_2 analyses. The location of these two stations is circled in the lower left portion of Figure 3.

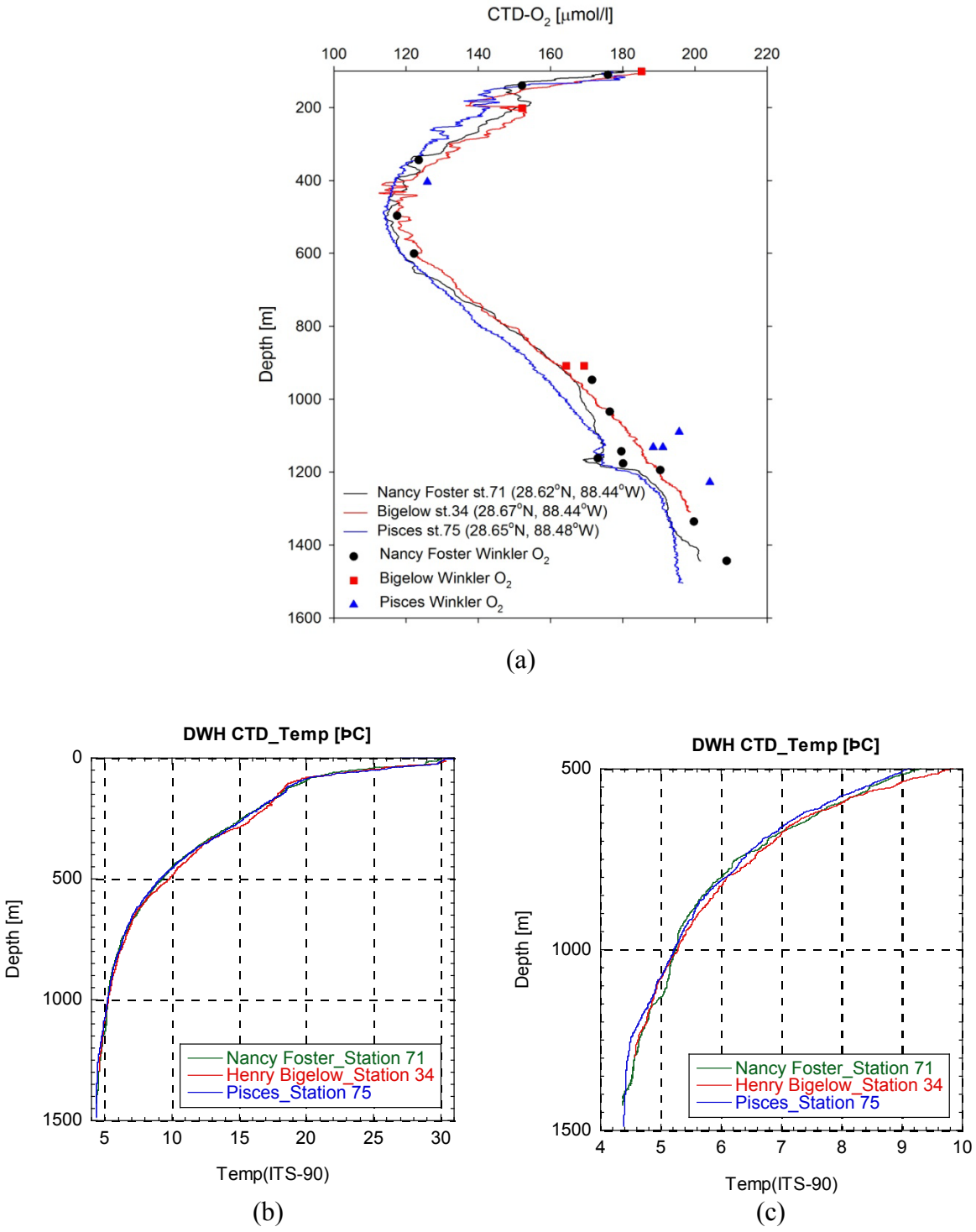

Figure 5. (a) Comparison of CTD/O_2 and Winkler O_2 titrations for *Nancy Foster* station 71 (occupied on July 17, 2010), *Henry B. Bigelow* station 34 (occupied on August 15, 2010), and *Pisces* station 75 (occupied on August 20, 2010). The figure and other analyses suggest that the CTD/O_2 sensors on the *Pisces* were reading about 7 µmol/l (≈0.2 ml/l) lower when compared to the actual values. The Winkler O_2 values from the *Pisces* (blue triangles in Figure 5a) are not deemed accurate. (b) Corresponding temperature profiles. (c) Temperature profiles for >500 m to illustrate the fine scale differences in water structure. The location of these three stations is circled in the upper right portion of Figure 3.

9. Acknowledgments

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