WASHINGTON STATE
DEPARTMENT OF
ECOLOGY

Dissolved Oxygen Measurements in Oakland Bay (Mason County)

September 2004

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Dissolved Oxygen Measurements in Oakland Bay (Mason County)

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by
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Abstract

Previous to this study, there had been a lack of data on dissolved oxygen in Oakland Bay in Mason County, particularly in the upper region of the bay. A study was undertaken in September 2003 to measure vertical dissolved oxygen profiles at several locations within the bay. The vertical profiles were measured using a Seabird™ CTD instrument, while instantaneous measurements were made with a Hydrolab™ multi-probe meter and with Winkler titration.

Data in general show compliance with Washington State's water quality standard for dissolved oxygen. There was one instance of an inconclusive exceedance of the standard. The Winkler data showed better correlation with CTD data than with Hydrolab™ data.

Further monitoring is recommended.

Acknowledgements

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- Kim Lincoln, Mason County, for providing help during sampling
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    - Joan LeTourneau for editing and formatting the final report

Introduction

Washington Administrative Code (WAC) Chapter 173-201A designates Oakland Bay and Hammersley Inlet, east of longitude 123.0834W, as Class A marine waters (Figure 1) with a dissolved oxygen (DO) standard of 6 mg/L. Oakland Bay and Hammersley Inlet are not on the 303(d) list for DO.

Inner Shelton Harbor, located in the lower Oakland Bay, west of longitude 123.0834W, is designated as Class B marine waters with a DO standard of 5 mg/L.

Available data at Ecology's station (http://www.ecy.wa.gov/apps/eap/marinewq/mwdataset.asp?staID=81) near Munson Point (Figure 1) in Oakland Bay suggest that 97% of the DO data (1974-2000) was greater than 6 mg/L. No DO measurement was observed below 6 mg/L since 1997. DO measured in May 1999 (Norton et al., 2000) in the Inner Shelton Harbor (near the mouths of Shelton and Goldsborough creeks, Figure 1) indicated a range of 12.7 – 16.3 mg/L at the surface and 7.9 – 10 mg/L at the near-bottom waters.

Dissolved oxygen in Hammersley Inlet is not perceived to be low due primarily to the swift currents, shallow depths, and rapid flushing that occur in the narrow inlet.

Albertson (2004) indicated that Oakland Bay is likely to have the lowest flushing rate in late summer and early fall. It was hypothesized that DO in the upper reaches of Oakland Bay could be lower due to poor flushing. This study was undertaken to research this hypothesis by measuring DO at various locations in Oakland Bay, particularly the upper reaches.

Project goal

The goal of this study was to produce verifiable records of DO concentrations at several locations in Oakland Bay.

Project objectives

The objective of this project was to study the vertical DO profile in Oakland Bay using both Hydrolab™ (Hach Company) and Seabird™ CTD (conductivity, depth, and temperature) corrected with discrete DO samples analyzed using a modified Winkler method (Appendix A) based on the method of Carpenter (1964).

Study design

This study was completed by the Washington State Department of Ecology (Ecology) in conjunction with the Squaxin Island Tribe. Sample locations were chosen to best represent the aerial extent of Oakland Bay.

The sampling locations were as follows (Figure 1):

- Three locations were along a horizontal transect from the mouth of Malaney Creek (on the south shore of Oakland Bay) to the north shore of Oakland Bay.
- Two locations were along a horizontal transect from the mouth of Johns Creek on the north shore to the south shore of Oakland Bay.
- Four locations were along a horizontal transect from Chapman Cove near the mouth of Campbell/Uncle John Creek to the other side of Oakland Bay.
- Three locations were along a horizontal transect from Munson Point to a point near the mouths of Goldsborough and Shelton creeks.

The sampling boat was provided by the Squaxin Island Tribe. The GIS data on sampling locations was also provided by the Tribe.

The Hydrolab™ was connected to the cage of the CTD. CTD casts were conducted by hand. Depth was measured using a measuring rope tied to the end of the Niskin bottle. Two grab samples at each station were collected near the bottom of the water column for DO analysis using a modified Winkler method (see Appendix A).

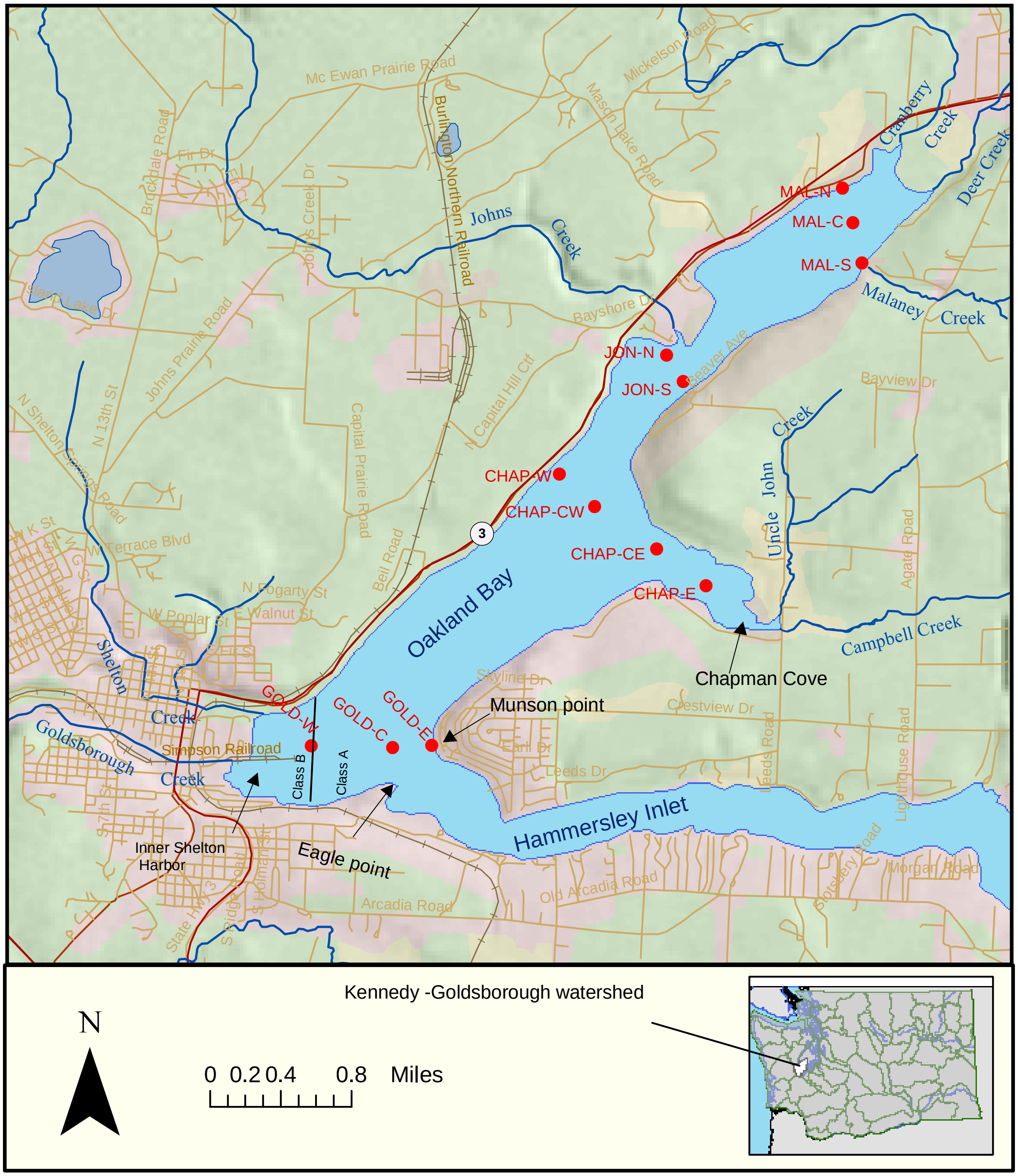

Figure 1. Sampling locations in Oakland Bay.

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Results and Discussion

Appendix B contains all DO data collected in Oakland Bay on September 29, 2003. Dissolved oxygen was measured using three methods: discrete samples using the modified Winkler method, CTD, and Hydrolab™. Data from these methods are discussed and analyzed below.

Winkler titration

Dissolved oxygen concentrations measured at the bottom of the water column at each of the 12 stations, using a modified Winkler titration method, are shown in Figure 2. All data show DO concentrations in excess of 6.5 mg/L indicating that the bay is meeting the Washington State water quality standard of 6 mg/L. Figure 2 also shows that the duplicates are in good agreement with each other, with an average difference between the duplicates of approximately 0.05 mg/L.

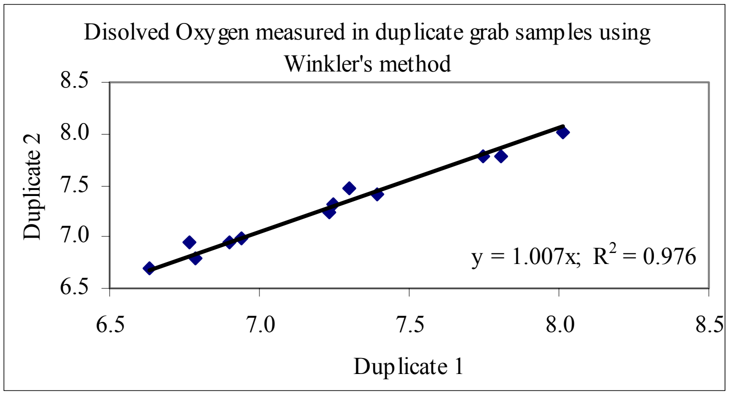

Figure 2. Dissolved oxygen measured in duplicate samples at each station using the Winkler titration method.

CTD data

In general, the CTD data were lower than those obtained with the modified Winkler method (i.e., titration) for the same depth within the water column. Thus, the CTD data were corrected using the titration data based on the relationship shown in Figure 3.

CTD measurements at the mouth of Malaney Creek (station MAL-S) were rejected based on the significant difference between CTD dissolved oxygen measurements and discrete sample results. The DO profile, based on corrected CTD data, at various locations (see Figure 1) in Oakland Bay are shown in Figures 4, 5 and 6. All DO profiles show concentrations above the state water quality standard of 6 mg/L, except for MAL-C which showed a concentration of 5.9 mg/L at the bottom of the water column, at a depth of 4 meters. However, it should be noted that the Winkler DO concentration at this location is higher than the corrected CTD data by

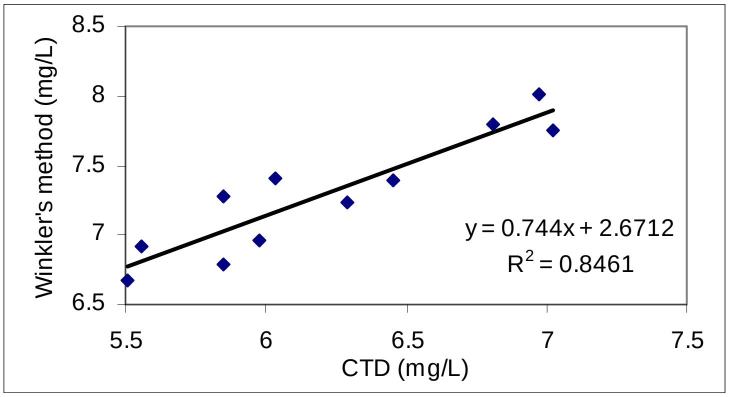

Figure 3. Comparing dissolved oxygen concentrations measured with Winkler titration method and CTD.

approximately 0.11 mg/L. Therefore, the DO standard excursion is not conclusive. The DO profiles at MAL-C and CHAP-E showed sharp reduction in DO in the bottom layers. Such stratification was not observed in any of the other stations. It is likely that the reduced DO near the bottom of the water column was due to sediment oxygen demand. Decay of large phytoplankton blooms in combination with stratification during the summer and early fall can also cause low DO in near-bottom waters. This was reported as a likely cause of low DO in near-bottom waters in Budd Inlet (Eisner, 1997).

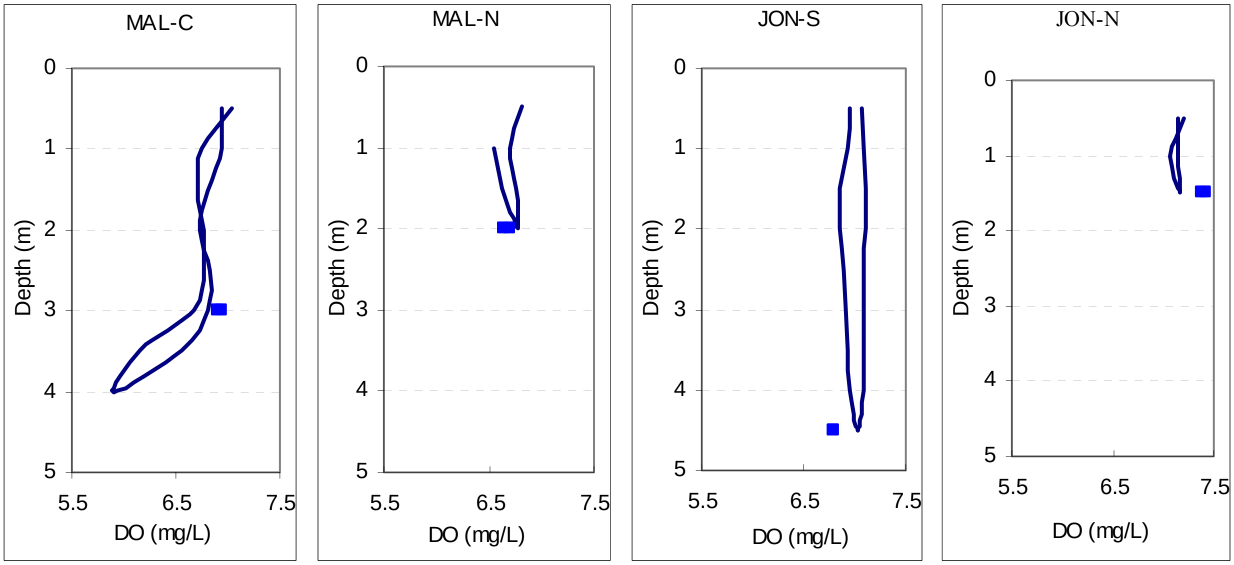

Figure 4. Dissolved oxygen profiles (— CTD) and discrete data (■) at stations in Oakland Bay, near the mouths of Malaney and Johns creeks.

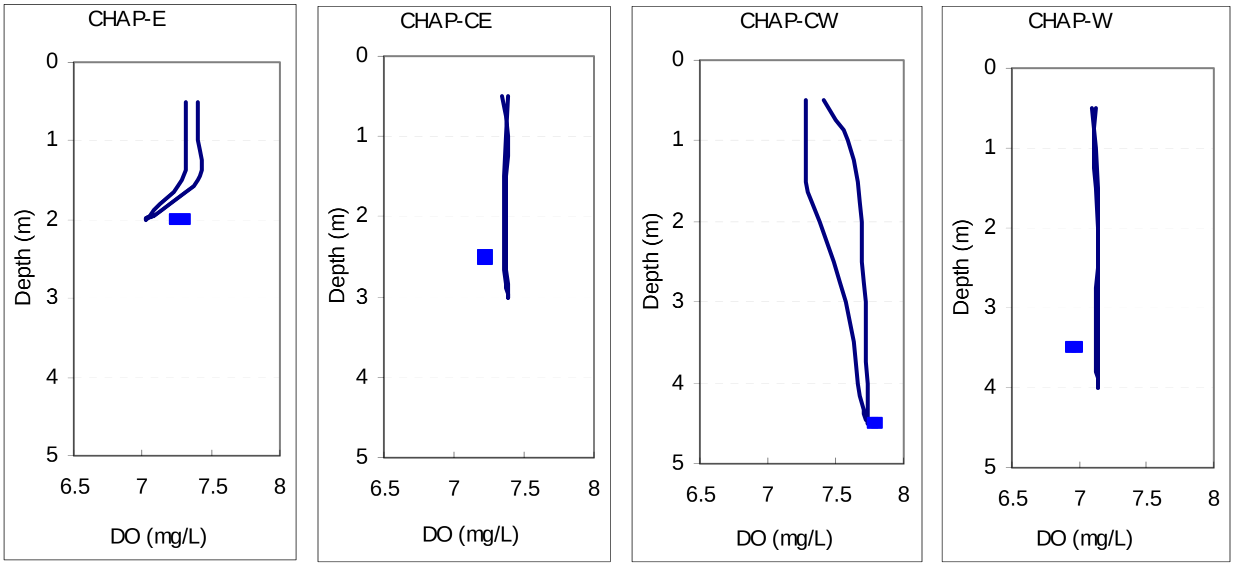

Figure 5. Dissolved oxygen profiles (— CTD) and discrete data (■) at stations in Oakland Bay off Chapman Cove.

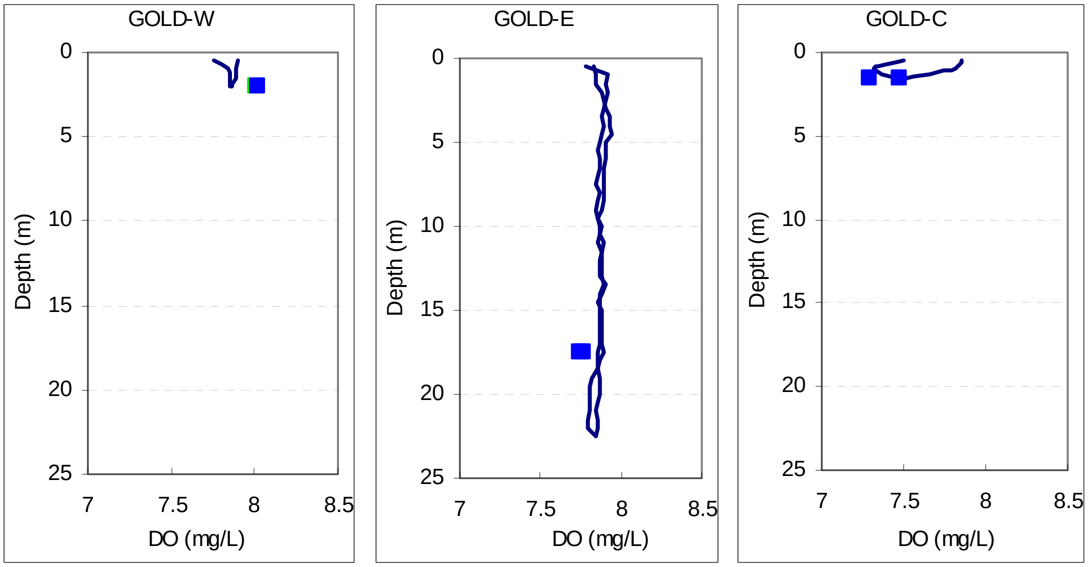

Figure 6. Dissolved oxygen profiles (— CTD) and discrete data (■) at stations in Oakland Bay from Munson Point to Shelton.

Hydrolab™ data

In general, the Hydrolab™ data were lower than those obtained with the modified Winkler method (i.e., titration) for the same depth within the water column. Thus, the Hydrolab™ data were corrected using the titration data based on the relationship shown in Figure 7.

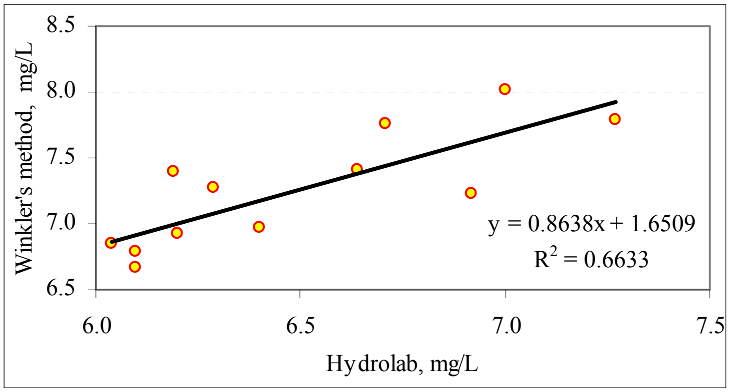

Figure 7. Comparison of dissolved oxygen concentrations measured with Winkler titration method and Hydrolab.

Dissolved oxygen measurements with the Hydrolab™ were taken only at depths where discrete samples were collected. Table 1 shows the corrected Hydrolab™ data. All DO concentrations were above the state water quality standard for DO of 6 mg/L.

Table 1. Dissolved oxygen concentrations measured by Hydrolab™ at various locations within Oakland Bay.

Station	Hydrolab DO mg/L
Mal-S	6.87
Mal-N	6.92
Mal-C	7.01
Jon-N	7.39
Jon-S	6.92
Chap-E	7.08
Chap-CE	7.63
Chap-CW	7.93
Chap-W	7.18
Gold-W	7.70
Gold-E	7.45
Gold-C	7.00

Comparison of dissolved oxygen data

Figure 8 shows a comparison of the Winkler DO data and the raw data collected with CTD and Hydrolab™. The DO concentration measured with the modified Winkler titration method was always greater than both the CTD and Hydrolab™ data. In general, the Hydrolab™ data were higher than the CTD data, except towards the end of the day, when Hydrolab™ tended to be lower than the CTD values. The CTD data had a stronger correlation to the discrete samples (R^2= 0.85) than the Hydrolab™ data (R2 = 0.66) as shown in Table 2.

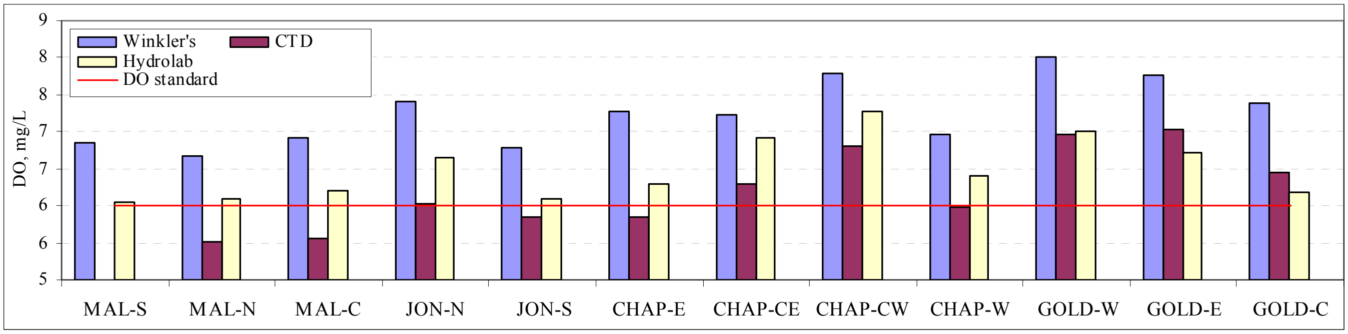

Figure 8. Raw data from modified Winkler method, CTD, and Hydrolab.

Table 2. Comparison of raw data from CTD and Hydrolab™ with titration data**.**

Linear Regression	Linear Regression Equation	R^2
Hydrolab™-Winkler	$DO_{actual} = 0.864\ DO_{hydro} + 1.65$	0.66
CTD-Winkler	$DO_{actual} = 0.74\ DO_{CTD} + 2.67$	0.85

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Conclusions and Recommendations

Conclusions

In general, the corrected vertical dissolved oxygen profiles showed compliance with the state water quality standard of 6 mg/L. There was one instance of a dissolved oxygen concentration of 5.9 mg/L observed at the bottom of the water column at station MAL-C near Malaney Creek. However, this violation of the dissolved oxygen standard was inconclusive since the Winkler data showed a higher concentration than the corrected CTD data at this location.

Lowest dissolved oxygen concentrations were observed in the upper end of Oakland Bay (e.g., near Malaney Creek), whereas concentrations were high throughout the water column for stations in the lower end of Oakland Bay, towards Hammersley Inlet.

The Winkler data showed good reproducibility. This reaffirms the use of the Winkler method for reliable dissolved oxygen data.

The Winkler data showed a relatively weak correlation with Hydrolab™ data compared to correlation with CTD data. In an earlier study (Cusimano, 2004), Hydrolab™ data collected in the Snohomish River estuary in 1993 and 1996, from areas that experienced large tidal salinity changes, were not useable because of poor agreement with Winkler data. However, in an earlier study (Norton et al., 2000), CTD data collected in the Inner Shelton Harbor compared well ($R^2 = 0.9$) with Winkler data.

A discrepancy of almost 1 mg/L existed between the raw CTD data and Winkler data. Since data showed dissolved oxygen to be at or near the state standard, the CTD and Hydrolab™ results should be viewed with some skepticism due to reasons discussed above.

Recommendations

It is recommended that further dissolved oxygen monitoring be conducted in upper Oakland Bay, particularly in late summer or early fall. The monitoring should be conducted early in the morning, when low dissolved oxygen is likely to exist in the near-surface water due to phytoplankton respiration. Additional Winkler samples should be collected from near-bottom waters in selected locations to more accurately measure dissolved oxygen.

Dissolved oxygen also should be monitored in Inner Shelton Harbor in the late summer or early fall season. Available data, which showed no violations of the dissolved oxygen standard, are limited to one survey conducted in 1999 (Norton et al., 2000).

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Appendix A

Carpenter method for determination of dissolved oxygen in marine water using modified Winkler titration

Sampling protocol

Water samples were first collected near the bottom of the water column at each location using the Niskin bottle sampler attached to the end of a rope. The water from the sampler is then transferred to a 130 mL DO-flask allowing it to overflow by 2– 3 times its volume and making sure no air bubbles are trapped or produced. Two chemicals are then added: 1 mL manganous chloride solution (3 M), followed by 1 mL of alkaline sodium hydroxide-sodium iodide reagent (8 N). Care must be taken to seal the sample bottle(s), excluding all air bubbles. Prior to titration, 1 mL of sulfuric acid (10 N H_2SO_4) is added. If samples are expected to be low in oxygen (<2 mg/L), then sodium azide should be added to the alkaline sodium hydroxide-sodium iodide reagent.

Analytical protocol

Cleaning

This is an analytical chemistry technique. The glassware and equipment -- standard and sample bottles, pipettes, stir bars, and buret tip -- must be kept scrupulously clean. Thoroughly rinse the glassware with clean hot water before and after every analysis. Clean every three months using Liqui-Nox® and water. Clean the buret as needed.

To turn on the Dosimat

a. Press the **FILL** button at the same time you turn on the **POWER** button (the red button in back).
b. Press **GO**.
c. Press **CLEAR**. The display should read **DOS 0.000 ml**.

To prepare to titrate

a. Gently lift the amber bottle of thiosulfate ($Na_2S_2O_3$ 0.01 N). Shake, then replace in the Dosimat.
b. Turn the dispense speed knob to 10. Dispense 15 ml of thiosulfate to flush out the buret (3-5 ml aliquots) by pressing the hand control button.
c. Turn the dispense speed knob to 1.
d. Press the **CLEAR** button.
e. Rinse off the buret tip with deionized water.
f. Make sure there are no bubbles in the buret or moving bubbles in the line leading to the buret tip. (Some tiny bubbles may cling to tubing but, if not moving, can be ignored.)
g. Turn on the stirrer to 4.

Preparing and running O2 standards

a. Fill clean standard sample bottle ¾ full of distilled water.
b. Add 1 ml H_2SO_4 and mix well.
c. Slowly add 1 ml of NaOH-NaI (8 N) solution. Mix well.
   -- If sample is not clear, discard and start again.
d. Using a 10 ml volumetric pipette, add 10 ml of the KIO_3 (0.01 N) standard.
   -- Always shake the standard before pipetting.
   -- Draw standard from the small bottle.
   -- Draw standard past the volume line of the pipette.
   -- Remove the pipette from the bottle.
   IMPORTANT: NEVER DRAIN LIQUID BACK INTO THE STANDARD BOTTLE.

-- Wipe down the tip of the pipette with a kim-wipe.
-- Bring the meniscus of the liquid even with the calibration line of the pipette.
-- Dispense into the sample bottle. Do not put the tip of the pipette against the wall of the sample bottle. This will cause excess standard to be delivered from the pipette.
The O_2 standard is now ready for titration.

e. Run at least 3 standards; at least 2 out of 3 should agree to ± 0.001 ml.
f. After analysis, rinse the bottles with hot water and store filled with distilled water.
g. Rinse the 10 ml volumetric pipette.

Blanks

a. Fill a standard sample bottle ¾ full of distilled water.
b. Add 1 ml H_2SO_4 and mix well.
c. Slowly add 1 ml of NaOH-NaI solution. Mix well.
d. Add 1 ml $MnCl_2$. Mix well.
e. Using an automatic pipette, add 1.0 ml KIO_3 standard.
f. Titrate sample to the endpoint.
   -- Add starch immediately (because the sample is light yellow.)
   -- Titrate slowly. Remember this is only 1/10 as strong as the standard.
g. Record endpoint #1; this is <u>Blank1</u>.
h. Add 1.0 ml more of KIO_3 standard.
i. Titrate to endpoint #2.
   -- (Endpoint #2) - (Endpoint #1) = <u>Blank2</u>.
j. (Blank1) - (Blank2) = <u>Correction blank</u>
k. Definitions:
   Blank1 (in ml) = volume of thiosulfate needed to titrate the first 1 ml KIO_3 + reagents
   Blank2 (in ml) = volume of thiosulfate needed to titrate the second 1 ml KIO_3
   Therefore, Blank1 - Blank2 = volume of thiosulfate needed to titrate reagents.
   This value may be negative or positive or zero.

Titrating samples or standards

a. If titrating a sample, carefully remove the cap, and rinse the glass bar.
b. Add a clean stir bar.
c. Position the sample bottle on the stirrer; make sure the buret tip is under the surface of the sample.
d. Make sure that the Dosimat reads 0.000 ml (press **CLEAR** to zero).
e. Titrate sample by dispensing thiosulfate in the sample.
   -- Use the thumb button gizmo to dispense thiosulfate.
f. When the sample is light yellow in color, add 1 ml of starch indicator.
g. Titrate to endpoint.
   -- Endpoint is when <u>all</u> color is gone. Watch the vortex in the upper half of the bottle.
   -- The endpoint is subtle -- the difference between clear and sparkling clear.
h. Record endpoint.
i. Remove sample bottle; dispense a few drops of thiosulfate through the buret tip to flush out any sample residue.
j. Rinse down the buret tip with deionized water.
k. Press **CLEAR** to zero the Dosimat.

Disposal

The titrated sample, as well as the excess sample in the D.O. bottle, is rinsed down the drain with copious amounts of tap water. The solution is acidic so it must be diluted as much as possible to reduce any impact on the wastewater treatment plant. Do not pour down the “live” sink.

Appendix B

Dissolved oxygen data collected in Oakland Bay using Hydrolab, CTD, and Winkler method, September 29, 2003

Description	Site Name	Latitude	Longitude	Time	Depth (m)	Hydrolab DO (mg/L)	CTD DO (mg/L)	Winkler bottle no.	Winkler DO (mg/L)
Transect near Malaney Creek	MAL-S	47.2518	-123.02058	9:41 am	1.50	6.04	***8.3**	145	6.77
								146	6.94
	MAL-N	47.2579	-123.02321	10:11 am	2.00	6.10	5.51	147	6.63
								148	6.70
	MAL-C	47.2551	-123.02179	10:29 am	3.00	6.20	5.56	149	6.90
								150	6.94
Transect near Johns Creek	JON-N	47.2437	-123.04372	10:55 am	1.80	6.64	6.04	151	7.39
								152	7.42
	JON-S	47.2416	-123.04164	11:12 am	4.50	6.10	5.85	153	6.78
								154	6.80
Transect Near Chapman Cove	CHAP-E	47.225	-123.03811	11:38 am	2.00	6.29	5.85	155	7.24
								156	7.31
	CHAP-CE	47.2279	-123.04416	12:05 pm	2.50	6.92	6.29	157	7.23
								158	7.23
	CHAP-CW	47.2311	-123.05178	12:20 pm	4.80	7.27	6.81	159	7.80
								160	7.78
	CHAP-W	47.2337	-123.05612	12:38 pm	3.50	6.40	5.98	161	6.94
								162	6.98
Transect near Munson Point	GOLD-W	47.2108	-123.0849	1:03 pm	2.30	7.00	6.97	163	8.01
								164	8.02
	GOLD-E	47.2112	-123.07042	1:23 pm	17.50	6.71	7.02	165	7.75
								166	7.77
	GOLD-C	47.2109	-123.07511	1:49 pm	2.50	6.19	6.45	167	7.30
								168	7.48

***** data rejected