

**LAVACA BAY TMDL
DISSOLVED OXYGEN
ASSESSMENT REPORT**

**Final Report Submitted To:
Texas Commission On Environmental Quality**

**Project Title:
Lavaca Bay Mercury and Dissolved Oxygen
Total Maximum Daily Load (TMDL) Assessment**

**Umbrella Contract No. 582-1-30479 (UTMSI)
Total Maximum Daily Load Research Support
Work Order No. 582-1-30479-04**

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December 15, 2003

UTMSI Technical Report Number TR/03-002

TABLE OF CONTENTS

LIST OF TABLES	iii
LIST OF FIGURES	iv
EXECUTIVE SUMMARY	v
INTRODUCTION	1
HISTORICAL DATA REVIEW	2
Aquatic Life Use	2
Dissolved Oxygen Dynamics	4
Data Sets	8
Seasonal Patterns	11
Surface Patterns	11
24-hr DO	23
Texas Parks and Wildlife Data	23
Formosa Plastics, Corp, Texas Data	24
UTMSI Data	24
Alcoa Data	24
TWDB Data	25
Summary	28
Possible Causes of Dissolved Oxygen Depletion in Lavaca Bay	28
DISSOLVED OXYGEN MONITORING AND ASSESSMENT	30
Methods	30
10 Measurement Requirement	30
Spatial Requirement	30
Critical Period Requirement	30
Annual and Monthly Sampling Requirement	30
Sonde Depth Requirement	31
Measurement Interval Requirement	31
Duplicate Sonde Requirement	31
Data Analysis	31
Results	34
Average DO Measurements	34
Minimum DO Measurements	35
Temporal Results	36
Spatial Results by Assessment Unit	39
Conclusions	48
RECOMMENDATIONS	49
REFERENCES	50

APPENDIX A: 24-Hour DO Monitoring Fact Sheet 52

APPENDIX B: YSI Sonde Methods 54

APPENDIX C: Lavaca Bay Mercury TMDL Project 63

LIST OF TABLES

Table 1: Aquatic life use categories with dissolved oxygen criteria and attributes describing each category	3
Table 2: Parameters reviewed for the Lavaca Bay/Chocolate Bay (Segment 2453)	9
Table 3: Number (and percent) of observations at each station indicative of low oxygen	22
Table 4: TCEQ 24-hr DO data	23
Table 5: Texas Water Development Board 24-hr DO data	27
Table 6: Stations sampled for dissolved oxygen assessment	31
Table 7: Number and percent of sample periods within the index and critical periods	33
Table 8: Twenty four hour average dissolved oxygen measurements (mg O ₂ / L)	34

LIST OF FIGURES

Figure 1: Major biological pathways of photosynthesis and respiration	4
Figure 2: Interaction between temperature and salinity on dissolved oxygen	6
Figure 3: Ecosystem model of oxygen dynamics in an estuary	7
Figure 4: Movements of dissolved oxygen in an aquatic ecosystem	8
Figure 5: Map of TCEQ stations in Segment 2453 used for historical data review	10
Figure 6: Hydrographic parameter values plotted by the Julian date of the year	13
Figure 7: Nutrient parameter values plotted by the Julian date of the year	14
Figure 8: Frequency of dissolved oxygen values	15
Figure 9: Frequency of conductivity values	15
Figure 10: Frequency of salinity values	16
Figure 11: Frequency of temperature values	16
Figure 12: Frequency of ammonia values	17
Figure 13: Frequency of phosphate values	18
Figure 14: Frequency of nitrate+nitrite values	19
Figure 15: Frequency of chlorophyll values	21
Figure 16: Frequency of biological oxygen demand values	21
Figure 17: Dissolved oxygen data from Texas Water Development Board, Station 13383	26
Figure 18: Map of stations used for the 24-hour data sonde deployment in Segment 2453	32
Figure 19: Average 24-hour dissolved oxygen concentrations for all samples taken from 2000 through 2003	36
Figure 20: Minimum 24-hour dissolved oxygen concentrations for all samples during 2000 through 2003	37
Figure 21: Bay-wide 24-hour dissolved oxygen concentrations each sampling period	38
Figure 22: Dissolved oxygen assessment data for Station 13383	41
Figure 23: Dissolved oxygen assessment data for Station 13384	42
Figure 24: Dissolved oxygen assessment data for Station 13385	43
Figure 25: Dissolved oxygen assessment data for Station 17552	44
Figure 26: Dissolved oxygen assessment data for Station 17553	45
Figure 27: Dissolved oxygen assessment data for Station 17554	46
Figure 28: Dissolved oxygen assessment data for Station 17555	47

EXECUTIVE SUMMARY

This project provides technical support to the Texas Commission on Environmental Quality (TCEQ) for the development of a Total Maximum Daily Load (TMDL). The TCEQ will lead an effort to assess the causes and sources of the following water quality problems identified in the Texas 2000 Clean Water Act 303(d) list for Lavaca Bay/Chocolate Bay (Segment 2453). The segment is located in Calhoun county in southeast Texas near the Cities of Point Comfort and Port Lavaca. The TCEQ water quality segment 2453 (Lavaca Bay/Chocolate Bay) currently has aquatic life closure for 2.5 square miles of the segment because of elevated mercury (Hg) levels in fin fish and crabs. In the Alcoa Ship Channel, the average Hg concentration in water exceeds the human health criterion for saltwater fish. In a 13.7-square mile area near Alcoa Ship Channel, dissolved oxygen (DO) concentrations are occasionally lower than the criteria established to assure optimum conditions to support exceptional aquatic life use.

This document reports on the monitoring and assessment activities for DO conditions. Based on the historical data review, the area within Segment 2435 with low DO is primarily in deeper navigation channels and it occurs primarily in summer. The goal of the current project was to collect sufficient data to perform an assessment of DO conditions in Lavaca Bay to determine if this segment should remain on the 303d list and if a TMDL process is required for these two characteristics of water quality. A separate report (entitled "Lavaca Bay Mercury TMDL Project," November 2003, and attached as Appendix C) was prepared for the mercury sampling and assessment.

The DO assessment was completed using a 24-hour dissolved oxygen monitoring plan. The monitoring plan was based on the requirements for a dissolved oxygen assessment as stated in the TCEQ 24-Hour DO Monitoring Fact Sheet, which requires 10 or more 24-hour samples within a two to five year period. Seven different stations, grouped in four assessment units, were sampled to provide spatial coverage of segment 2453. The stations were grouped into assessment units as follows: 17552 and 17553 comprise the Upper bay, 13383 and 17554 comprise the Gallinipper Point to SH 35, 13385 comprises the Point Comfort area, 13384 and 17555 comprise the Mouth of bay to Gallinipper Point. All samples were taken during the required index period of March 15 - October 15. The critical period sampling requirements were met, where between half and two-thirds of a year's samples must be taken between July 1 - September 30 in each of the assessment units. All DO methods are described in detail in standard operating procedures in the 2003 Annual update of the Quality Assurance Quality Control Project Plan (QAPP).

Dissolved oxygen concentrations in Lavaca Bay meet the standard that TCEQ uses to define an impaired estuary most of the time. Average 24-hour DO concentrations were below the 5 mg/L standard for exceptional aquatic life use only 2.6% of the time and minimum 24-hour DO concentrations were below the 4 mg/L standard only 6.5% of the time. These occurrences are well below the 10% limits set by TCEQ. When low DO conditions did occur, the spatial extent was confined.

The majority of occurrences of low dissolved oxygen are located at station 13385, the Alcoa ship dock. Water depth is increased by the shipping channel and water currents may be reduced by the physical structure of the docks. The increased depth may increase the likelihood of a stratified boundary layer above where dissolved oxygen measurements were taken. This could have led to

reduced oxygen concentrations as the bottom water becomes unable to replenish oxygen from the atmosphere that is being used up by benthic processes. Decreased current speed results in water remaining in this area longer than in less restricted areas. Thus, processes that reduce or consume oxygen in this water occur over longer periods of time than processes that increase or produce dissolved oxygen.

Overall, Lavaca Bay segment 2453 does not currently appear to suffer from dissolved oxygen impairment. Segment 2453 dissolved oxygen concentrations are unimpaired for its exceptional aquatic life use designation. Based on the data presented in this report it is recommend that the segment be removed from the 303(d) list for dissolved oxygen.

INTRODUCTION

This project provides technical support to the Texas Commission on Environmental Quality (TCEQ) for the development of a Total Maximum Daily Load (TMDL). The TCEQ will lead an effort to assess the causes and sources of the following water quality problems identified in the Texas 2000 Clean Water Act 303(d) list for Lavaca Bay/Chocolate Bay (Segment 2453). The segment is located in Calhoun county in southeast Texas near the Cities of Point Comfort and Port Lavaca. The TCEQ water quality segment 2453 (Lavaca Bay/Chocolate Bay) currently has aquatic life closure for 2.5 square miles of the segment because of elevated mercury (Hg) levels in fin fish and crabs. In the Alcoa Ship Channel, the average Hg concentration in water exceeds the human health criterion for saltwater fish. In a 13.7-square mile area near Alcoa Ship Channel, dissolved oxygen (DO) concentrations are occasionally lower than the criteria established to assure optimum conditions to support exceptional aquatic life use.

The total load of materials from external sources is the main concern in a typical TMDL project. In Lavaca Bay however, the concentrations, or assimilative capacity, of Hg and DO is controlled by internal processes. Therefore, two kinds of studies are needed: one study would monitor the concentrations of these materials, and the second study would identify the processes controlling change in concentrations and the relative rates of those processes.

The main source of Hg is known to be the Superfund site adjacent to the Alcoa Plant in Point Comfort. The main question therefore is how future concentrations in surface water will be affected by the current mitigation efforts.

The area with low DO is primarily in deeper navigation channels. It is possible these areas are suffering only temporally dynamic periods of low DO because of localized water column stratification. Low DO can occur when DO saturation is high, because oxygen has low solubility in sea water when temperatures and salinities are high. The main questions therefore are during what periods and for how long does low DO occur, and how far is the spatial extent of DO.

The goal of the current project was to collect sufficient data to perform an assessment of Hg in surface water and DO conditions in Lavaca Bay to determine if this segment should remain on the 303(d) list and if a TMDL process is required for these two characteristics of water quality.

The assessments for Hg and DO will be provided in separate assessment reports. The current report is for DO.

HISTORICAL DATA REVIEW

A complete historical data review for dissolved oxygen (DO) data in the Lavaca Bay/Chocolate Bay Segment 2453 has already been completed (Ritter et al., 2002). The data review was used to identify areas within the segment for further investigation, perform a preliminary assessment of the segment for DO exceedences, and support the development of a TMDL for DO. Segment 2453 was listed on the 305(d) list because DO concentrations are occasionally lower than the criterion established to assure optimum conditions for aquatic life in a 13.7-square mile area near the Alcoa Ship channel. Thus, the literature and data review focused on that part of Lavaca Bay.

Dissolved oxygen is expressed in a variety of units. The preferred unit is mg L^{-1} , which is mass per unit volume of a liquid. At 20 ‰ salinity, 25 °C temperature, and 1 atmosphere pressure, a DO concentration of $1 \text{ mg/L} = 1 \text{ ppm} = 0.7 \text{ m/L} = 32 \text{ }\mu\text{M} = 62.5 \text{ }\mu\text{g at/L} = 3\% \text{ O}_2 \text{ by volume} = 14\% \text{ saturation}$ (Diaz et al. 1992).

The following section is a brief summary of the major findings of the historical data review performed by Ritter et al. (2002).

Aquatic Life Use

“Aquatic life use” is a term used in Texas water resource management to characterize water bodies and specify water quality criteria for those bodies. The Texas Commission on Environmental Quality (TCEQ) has identified four aquatic life use categories: exceptional, high, intermediate, and limited. The TCEQ criteria for DO varies with the aquatic life use designation of a water body (Table 1). For Texas estuaries fully supporting the exceptional aquatic life use, DO criteria are 24-hr mean $\geq 5.0 \text{ mg/L}$ and 24-hr minimum $\geq 4.0 \text{ mg/L}$. Lavaca Bay (segment 2453) is designated for exceptional aquatic life use.

Dissolved oxygen is a parameter used to evaluate aquatic ecosystem health. Dissolved oxygen is a useful indicator because it is required for organism respiration and microbial sediment decomposition processes (Strobel and Heltshe 2000). In addition, low DO (i.e., hypoxia) can be caused by excess nutrient inputs into the aquatic system (e.g., sewage outfalls, non-point source pollution, etc.).

In the scientific literature, low oxygen is referred to as hypoxia and is typically defined as occurring when instantaneous (or grab sample) measurements of DO are $< 2 \text{ mg O}_2/\text{L}$ (Ritter and Montagna 1999). Other common definitions in the scientific literature are $< 2 \text{ ppm}$ (Dauer et al. 1992) and $< 2 \text{ ml O}_2/\text{L}$ (Diaz and Rosenberg 1995). Hypoxic conditions create stress on biotic communities, and can lead to reduction in populations and biomass of aerobic organisms.

Table 1: Aquatic life use categories with dissolved oxygen criteria and attributes describing each category (copied from Texas Surface Water Quality Standards, 2000).

Aquatic Life Use	Dissolved Oxygen Criteria, mg/L			Aquatic Life Attributes					
	Freshwater mean/ minimum	Freshwater in Spring mean/ minimum	Saltwater mean/ minimum	Habitat Characteristics	Species Assemblage	Sensitive Species	Diversity	Species Richness	Trophic Structure
Exceptional	6.0/4.0	6.0/5.0	5.0/4.0	Outstanding natural variability	Exceptional or unusual	Abundant	Exceptionally high	Exceptionally high	Balanced
High	5.0/3.0	5.5/4.5	4.0/3.0	Highly diverse	Usual association of regionally expected species	Present	High	High	Balanced to slightly imbalanced
Intermediate	4.0/3.0	5.0/4.0	3.0/2.0	Moderately diverse	Some expected species	Very low in abundance	Moderate	Moderate	Moderately balanced
Limited	3.0/2.0	4.0/3.0		Uniform	Most regionally expected species absent	Absent	Low	Low	Severely imbalanced

Although the presence of hypoxia is typically used as an indicator of water quality in scientific papers, it is not used as a regulatory indicator. A variety of standards for low oxygen criteria exist, each developed to fit the specific mission of the regulatory agency and that agency's sampling program. The TCEQ has established DO criteria based on 24-hr average DO that varies with the aquatic life designation of a water body (Table 1). For Lavaca and Chocolate Bays (Segment 2453), the criteria for exceptional aquatic life require minimum 24-hr DO measurements to be greater than 4 mg/L and average 24-hr DO measurements to be greater than 5 mg/L. If these criteria are not met, the measurements are called exceedences and could be listed as impaired.

Dissolved Oxygen Dynamics

Dissolved oxygen concentration in an aquatic ecosystem is a function of biotic (living) and abiotic (non-living) components. Major biotic components include photosynthesis, the production of sugars and other organic molecules by photoautotrophs using the energy from sunlight, and respiration, the breakdown of these same molecules by heterotrophs for energy (Fig. 1). A byproduct of photosynthesis is the production of O₂ while respiration requires the consumption of O₂ to harness chemical bond energy. Abiotic components have both direct and indirect effects on dissolved oxygen concentrations. Temperature, salinity, and pressure all affect the solubility of oxygen in water. A driving force of the ecosystem, photosynthesis, is limited by nutrients in the water. Combining major biotic and abiotic components yields a highly dynamic picture of dissolved oxygen concentrations over space and time.

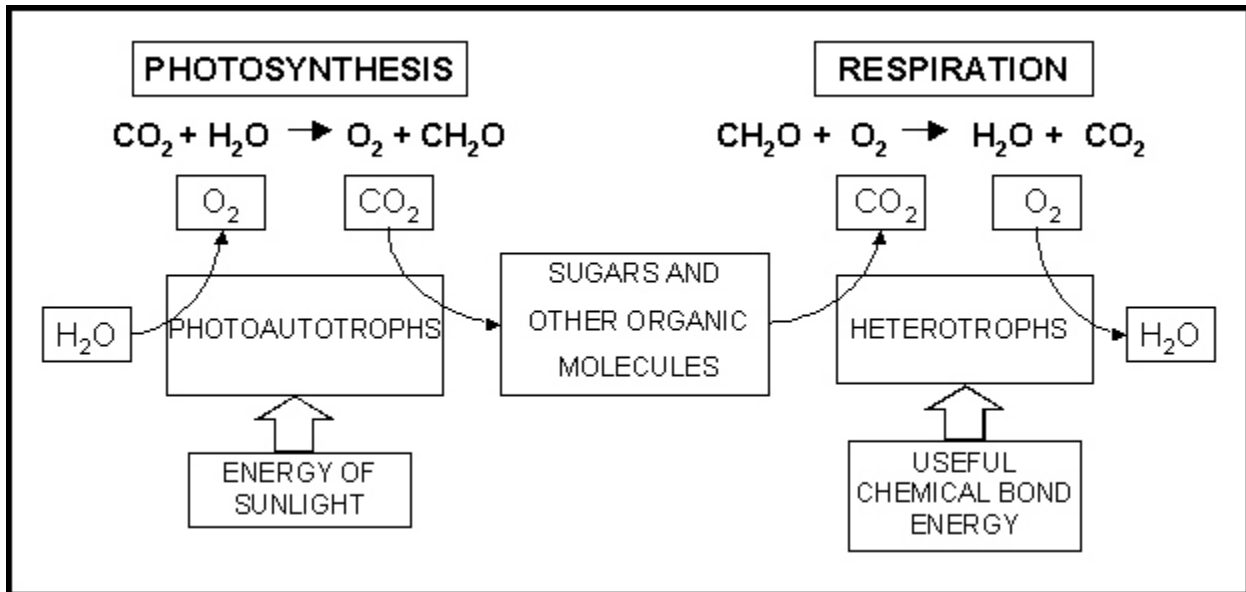


Figure 1: Major biological pathways of photosynthesis and respiration. Photosynthesis uses energy from sunlight to produce sugars and other organic molecules, which in turn serve as food for other organisms.

Aquatic plants and animals live in a more dynamic environment compared to their terrestrial relatives who enjoy a relatively stable 20% concentration of O₂ in the air. Phytoplankton, photosynthetic organisms in the water column, may have insufficient light because they live in a turbid water column (Ragotzkie, 1960). Phytoplankton must have enough sunlight to have a photosynthetic rate above their respiration rate in order for them to have net production of O₂. If non-photosynthetic organisms, located in the same water column, are using more O₂ than the net production of their photosynthetic counterparts there will be a decrease in the dissolved oxygen present in that part of the water column. The position in the water column, and subsequent light intensities, are not static like in terrestrial environments but change as a result of dynamic abiotic factors.

Highly dynamic aquatic environments are a result of changes and gradients that take place over varied time and space scales. Interfaces at the surface and at the benthos represent areas that have large gradients over small spatial scales. These interfaces dictate how much oxygen moves into and out of the water column.

The water-atmosphere interface is the site of transfer of O₂ from its' gaseous state in the air to its' dissolved state in the water. The more turbulent this interface is the deeper bubbles of air will be forced. Henry's Law predicts that as a bubble travels into deeper waters increasing pressure will cause more gas to dissolve in the water. Turbulence also plays an indirect role in dissolved oxygen concentrations by causing vertical mixing of organisms in shallow waters. Vertical mixing can take place at different rates depending on things such as wind speed over the surface and degree of stratification of the water column. The movement of O₂ (dQ/dt, mg/m/hr) across the water-atmosphere interface is given by $dQ/dt = A(D)(1/dz)(C-C_s)$, where A is the surface area, dz is the thickness of the hypothetical film separating gas and liquid, D is the molecular diffusivity, and C is the aqueous gas concentration. The term dz is inversely proportional to water turbulence and wind speed (Day et al, 1989).

The sediment-water interface is the site of O₂ transfer to and from the benthic organisms and the water column. If sunlight penetrates to the bottom then photosynthetic benthic organisms such as micro-algae and sea grasses may produce excess dissolved oxygen. These organisms usually inhabit a very thin layer of surface sediment under which dissolved oxygen concentrations decline to zero as it is used by organisms within the sediments (Fenchel and Riedl, 1970). The majority of sediments are thus devoid of oxygen, a condition termed anoxic.

Solubility of Oxygen in Surface Waters (760mm Hg)

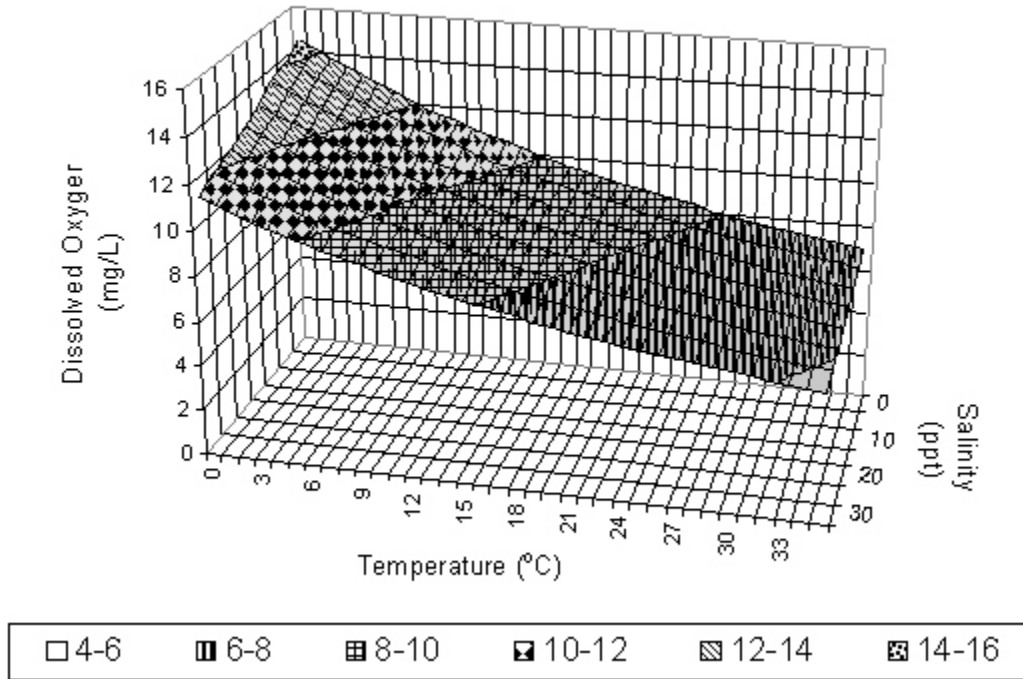


Figure 2: Interaction between temperature and salinity on dissolved oxygen. Graph developed from data compiled by Colt (1984).

Larger scale gradients and longer time span components also affect dissolved oxygen concentrations in estuaries. Temperature affects the solubility of gases in aquatic media, and is dynamic from hourly to geologic time scales. Temperature has an indirect relationship with the solubility of gas in a liquid (Fig. 2). Relatively shallow waters heated by the summer sun can become so hot that their dissolved oxygen content becomes dangerously low for aquatic life during the night-time when community respiration is greater than photosynthesis (Park et al., 1958). Salinity, the concentration of salts in the water, interacts with temperature to dictate the solubility of oxygen. This makes fresh water and oceanic water flux another very important abiotic factor. Aquatic environments not only flow vertically, which brings organisms from the surface to the benthos, but also flow horizontally. Large fresh water fluxes into an aquatic environment from direct precipitation or from stream flow, for example, can bring with it waters relatively high in dissolved oxygen. Horizontal flows from fresh water or oceanic waters also have an indirect effect on dissolved oxygen by displacing the organisms normally associated with a water body. If the above fresh water example flushes into a coastal region such as an estuary, the organisms needing higher salinities will be displaced by lower salinity tolerant species (Welsh et al, 1972). These organisms will produce or consume more dissolved oxygen. Pressure has a direct relationship with the solubility of oxygen in water. Pressure change is an example of a mesoscale gradient. The values presented in Figure 2 are only valid at the surface of the water column, which has a pressure of 760 mm Hg. Increases in depth cause the pressure to increase around a bubble of air, and more oxygen is forced into solution. This manifests

itself as an upward shift of the area in Figure 2. Temperature, salinity, and pressure interact over varying time and space scales, which result in a highly dynamic physical environment.

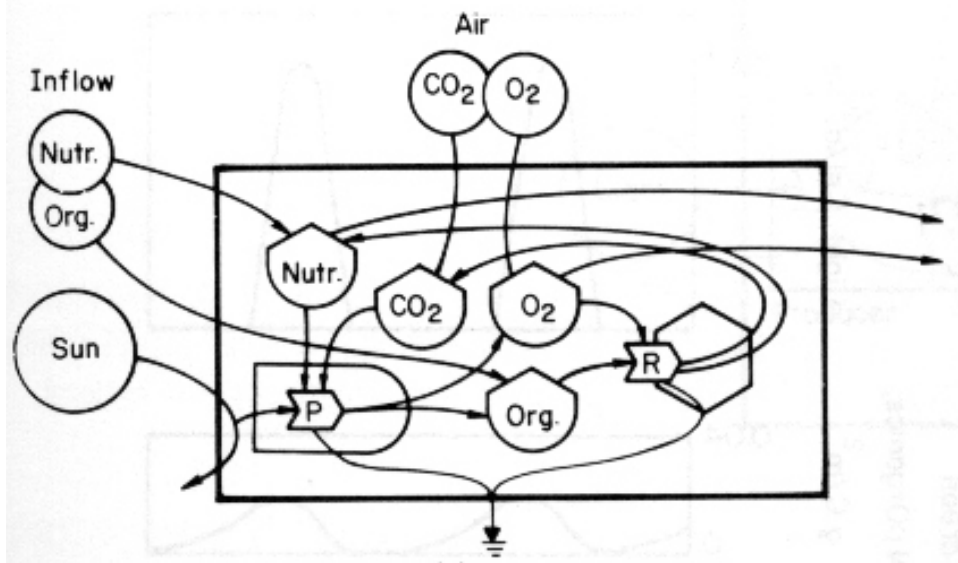


Figure 3: Ecosystem model of oxygen dynamics in an estuary. Nutrients (Nutr.) from inflow are a direct limiting factor on photosynthesis (P) and an indirect limiting factor on the production of dissolved oxygen (O₂) (Odum, 1983).

At the ecosystem level, photosynthesis is limited primarily by the amount of available nutrients (Fig. 3). In estuarine systems, the limiting nutrient is often nitrogen (Thayer, 1974). Nitrogen enters estuarine systems via streams, rivers, or runoff from the land. Characteristics of watersheds and climatic influences regulate nutrient loading rates. Anthropogenic nutrient sources can be large in some estuaries adjacent to areas with high population densities or high intensity agriculture. Nutrients are constantly cycling between organic and inorganic forms because of biological uptake and regeneration. Thus, nutrient concentration and speciation dynamics can control dissolved oxygen concentrations

Circulation and mixing in estuaries are spatially and temporally dynamic. Stratification is variable and ephemeral (Ritter and Montagna, 1999) so concentrations of nutrients (e.g. nitrate, nitrite, and ammonia) change dramatically with depth. Stratification can result in rapidly increasing ammonia concentrations with increasing depth (Webb and D'Elia, 1980). Dissolved oxygen concentration can decrease below the stratification barrier. Estuaries can change from well mixed to stratified and back again in less than two days or stratification can last through entire seasons. During extended periods of stratification, dissolved oxygen concentrations can become dangerously low in deeper waters (Rabalais and Turner, 2001). The net result is that stratification dynamics can be an important factor controlling dissolved oxygen concentrations.

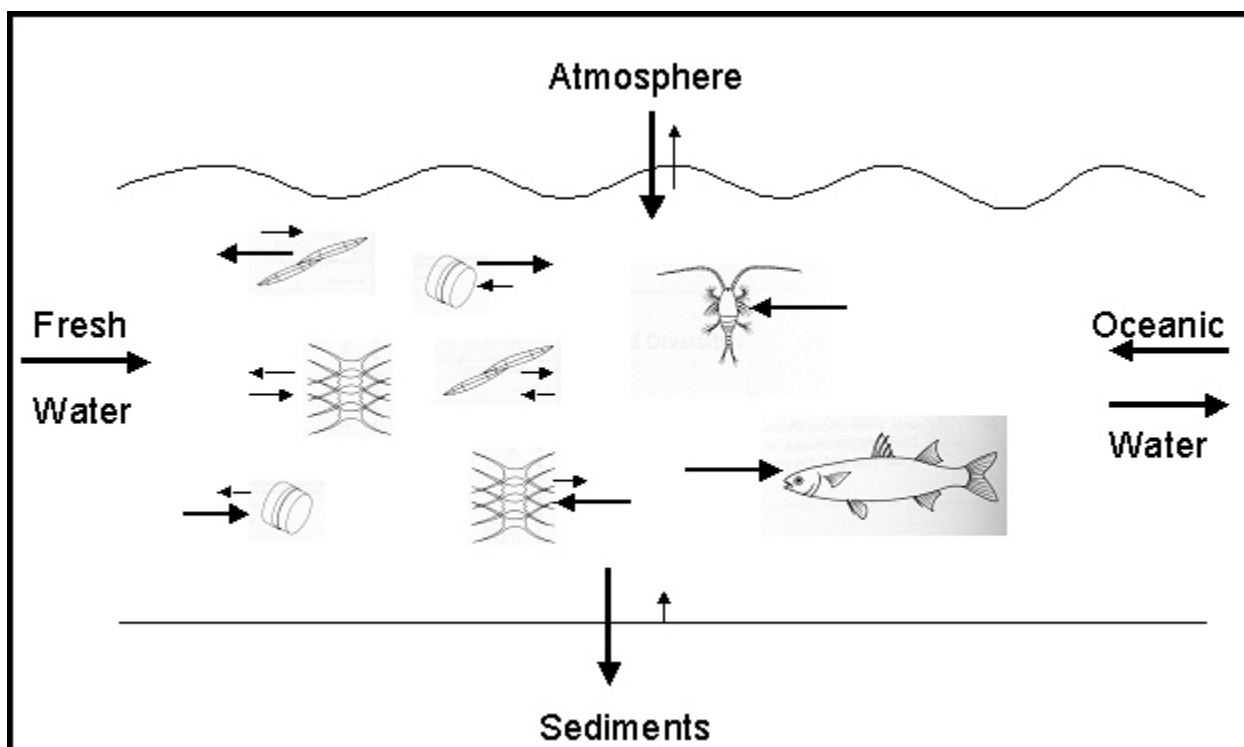


Figure 4: Movements of dissolved oxygen in an aquatic ecosystem based on biotic and abiotic components. Sizes of arrows indicate relative flux of dissolved oxygen for that pathway.

Interactions between biotic and abiotic components that regulate dissolved oxygen are highly dynamic spatially and temporally (Fig. 4). Photosynthesis and respiration, the two main biotic components, are influenced by many abiotic factors. Vertical mixing will cycle photoautotrophs from high intensity light at the surface to low intensity light near the benthos. Turbidity of the water regulates the degree of attenuation of light as it travels through the water column. Horizontal flow can displace volumes of water and their biotic inhabitants. Nutrient uptake and regeneration cycles take place on different spatial and temporal scales. Temperature, salinity, and pressure changes have direct influences on dissolved oxygen concentrations in water. Diurnal, seasonal, and geologic climatic events influence the rates of many of these abiotic and biotic processes. An understanding of estuarine dissolved oxygen dynamics must include all of these components.

Data Sets

Data from TCEQ for the historical review were obtained for the period 16 July 1969 to 13 November 2001. Data was available for 21 parameters, which are listed in Table 2. Stations for which data were available are plotted in Figure 5. Most TCEQ hydrographic measurements were from grab samples. Grab samples are samples, or composite samples (i.e., depth profiles) taken at a single point in time. The data also contained 24-hr minimum DO and 24-hr average DO values; 24-hr average DO is calculated as the average DO over a continuous 24-hr period and 24-hr minimum DO is the minimum DO over the same 24-hr period (Appendix A; DO Fact Sheet).

Grab-sample data available from Formosa, Alcoa, the University of Texas Marine Science Institute (UTMSI), and Texas Parks and Wildlife Department (TPWD) were also obtained. 24-hr DO data was available only from the Texas Water Development Board (TWDB). TWDB and TPWD conduct a joint ambient water quality monitoring program by which DO is monitored continuously for roughly one month. This data was downloaded from the internet: http://hyper20.twdb.state.tx.us/data/bays_estuaries/datasonde/Lavaca/. Only the first 24 hours of each deployment was used in this review to be consistent with the TCEQ QA requirements for DO data reporting (see Appendix A). 24-hr average, minimum, and maximum DO were determined for each observation. These datasets were reviewed separately and none of the data was included in the review of TCEQ's dataset. Each dataset was collected under a QAPP.

Table 2: Parameters reviewed for the Lavaca Bay/Chocolate Bay (Segment 2453). Abbreviations: Avg. = average, min. = minimum, max. = maximum.

Parameter	Units	Storet
24-hr number of observations	no units	89858
24-hr avg. DO	mg/L	89857
24-hr min. DO	mg/L	89855
24-hr max DO	mg/L	89856
DO	mg/L	00300
Conductivity	uS/cm	00094
Salinity	‰	00480
Temperature	°C	00010
Cholorophyll <i>a</i>	mg/L	13855
Days Since Last Significant Rainfall	days	72053
Sediment TOC	mg/kg	81951
Sediment Clay Content	% dry wt	82009
Sediment Silt Content	% dry wt	82008
Sediment Sand Content	% dry wt	89991
Sediment Gravel Content	% dry wt	80256
Total Nitrogen Ammonia	mg/L	00610
O-phosphorus	mg/L	00671
nitrate+nitrite	mg/L	00631
Chlorophyll <i>a</i>	ug/L	32211
Biological Oxygen Demand	mg/L	00310
Chemical Oxygen Demand	mg/L	00340

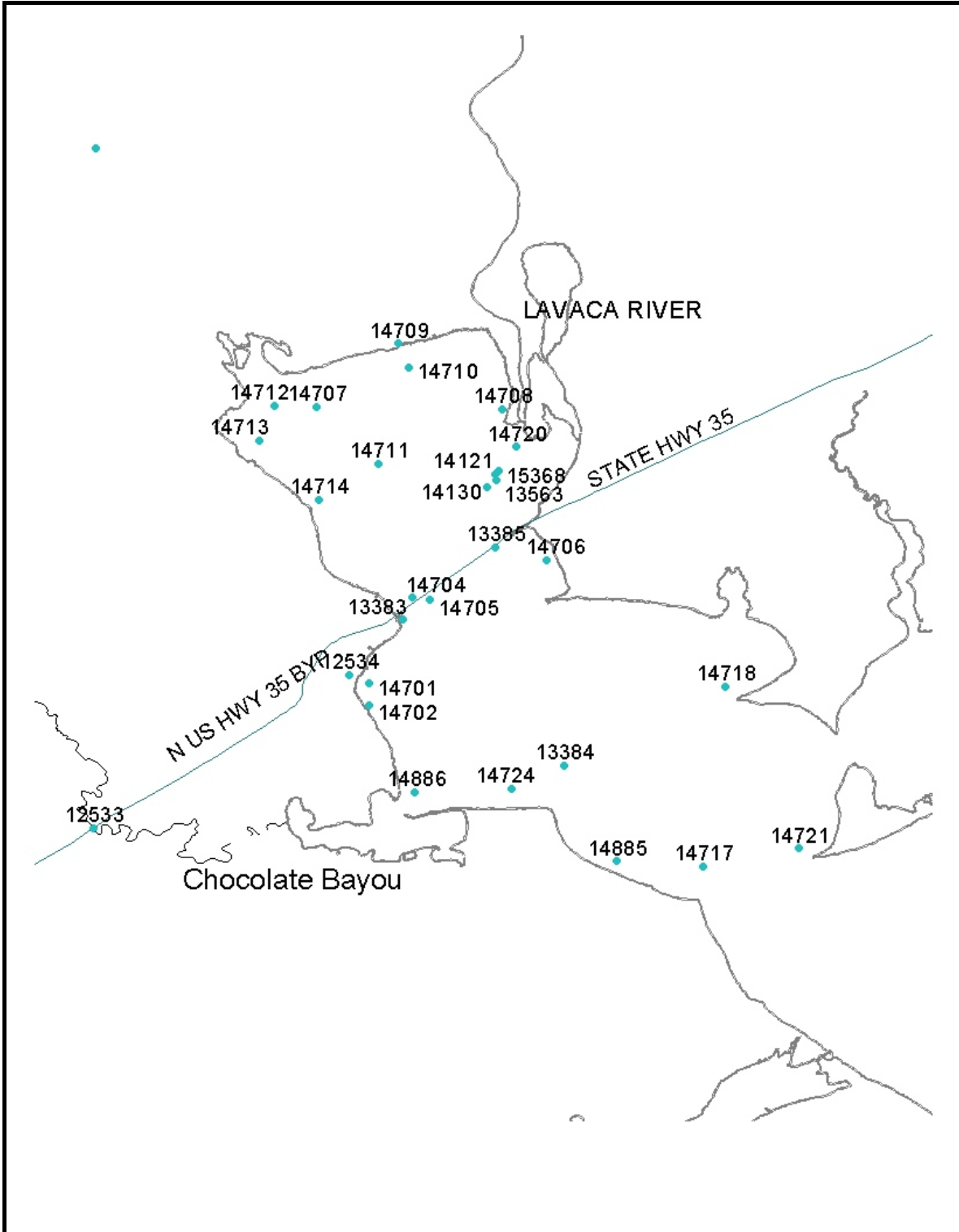


Figure 5: Map of TCEQ stations in Segment 2453 used for historical data review.

Seasonal Patterns

The entire TCEQ data set was plotted over the Julian date (i.e., serial day of the year) to discover seasonal patterns (Fig. 6). Only water temperature (Fig. 6a) and DO (Fig. 6d) demonstrated a seasonal trend. Water temperature increased during the summer, whereas DO decreased during the summer. No discernable trend was found for ammonia, nitrate+nitrite, or ortho-phosphate (Figs. 7a, 7b, and 7c) for which values were mostly < 1 mg/L. Chlorophyll *a* (Fig. 7d) may have a summer signature, but there are only a few observations indicating such a relationship.

Surface Patterns

The distribution of surface, grab-sample DO values (Fig. 8) follows a normal distribution. Roughly 77% of observed values fall within the range of 5 - 10 mg/L. More than 90% of the observations are below 10 mg/L. Dissolved oxygen values ranged 1 - 14.35 mg/L.

The distribution of conductivity values (Fig. 9) is bi-modal and skewed toward lower values of conductivity. Roughly 42% of conductivity observations were less than 6000 uS/cm. The remaining observations are roughly normally distributed between 6000 - 54000 uS/cm.

The distribution of salinity values (Fig. 10) appears to be bimodal though the plot of cumulative frequency indicates a normal distribution. The distribution peaks at 0 - 2.5 ‰ and 20 - 22.5 ‰. Only 7% of the observations are greater than 30 ‰, and roughly 30% of the values are lower than 10 ‰.

Water temperature ranged between 5.5 and 34.0 °C (Fig. 11). The Texas water quality standard for temperature is 35 °C, and all samples met the standard. The distribution is skewed to the right; 71% of the values are higher than 20 °C.

Ammonia values ranged between 0.01 and 16.6 mg/L (Fig. 12a). The distribution is skewed to the left with 96% of the values being less than 1 mg/L. Of note are the outlier values that are clear indicators of nutrient enrichment, which could contribute to DO depletion. Of 426 observations, more than 59% are less than 0.08 mg/L (Fig. 12b). The distribution of data peaked at between 0.04 and 0.06 mg/L with 25% of observations falling in this range. The TCEQ screening criteria for ammonia is 0.10 mg/L, and about 25% of the measurements were above this value.

Ortho-phosphate values ranged between 0.002 and 2.941 mg/L (Fig 13a). The distribution was skewed to the left with 96% of the observations being < 0.5 mg/L and 25% being < 0.02 mg/L. The TCEQ screening criteria for ortho-phosphate is 0.16 mg/L, and about 10% of the measurements were above this value.

Very few observations of nitrate+nitrite were available for analysis. As with the other nutrient distribution, nitrate+nitrite distribution appears to be skewed left. Of the 9 observations, 1 was > 3 mg/L, and the remaining 8 were < 1mg/L (Fig. 14). The TCEQ screening criteria for nitrate+nitrite is 0.26 mg/L, and about 22% of the measurements were above this value.

Chlorophyll *a* values ranged between 1 and 211 ug/L. The distribution of observations was skewed left with 94% of the observations being < 30 ug/L (Fig. 15a) and 74% being < 10 ug/L (Fig. 15b).

The TCEQ screening criteria for chlorophyll *a* is 11.5 mg/L, and about 24% of the measurements were above this value.

Biological oxygen demand (BOD) was measured using 5-day, 20 °C incubations. The range of BOD values was 0.5 to 16.0 mg/L (Fig. 16). The distribution of BOD values was skewed left, peaking between 1 and 2 mg/L. However, four outlier values were higher than 8, and one was as high as 16 mg/L.

Higher nutrient concentrations are associated with lower salinities (Fig. 17). Conservative mixing diagrams for ammonia and ortho-phosphate indicate that the Lavaca Bay estuary is a net sink for nutrients.

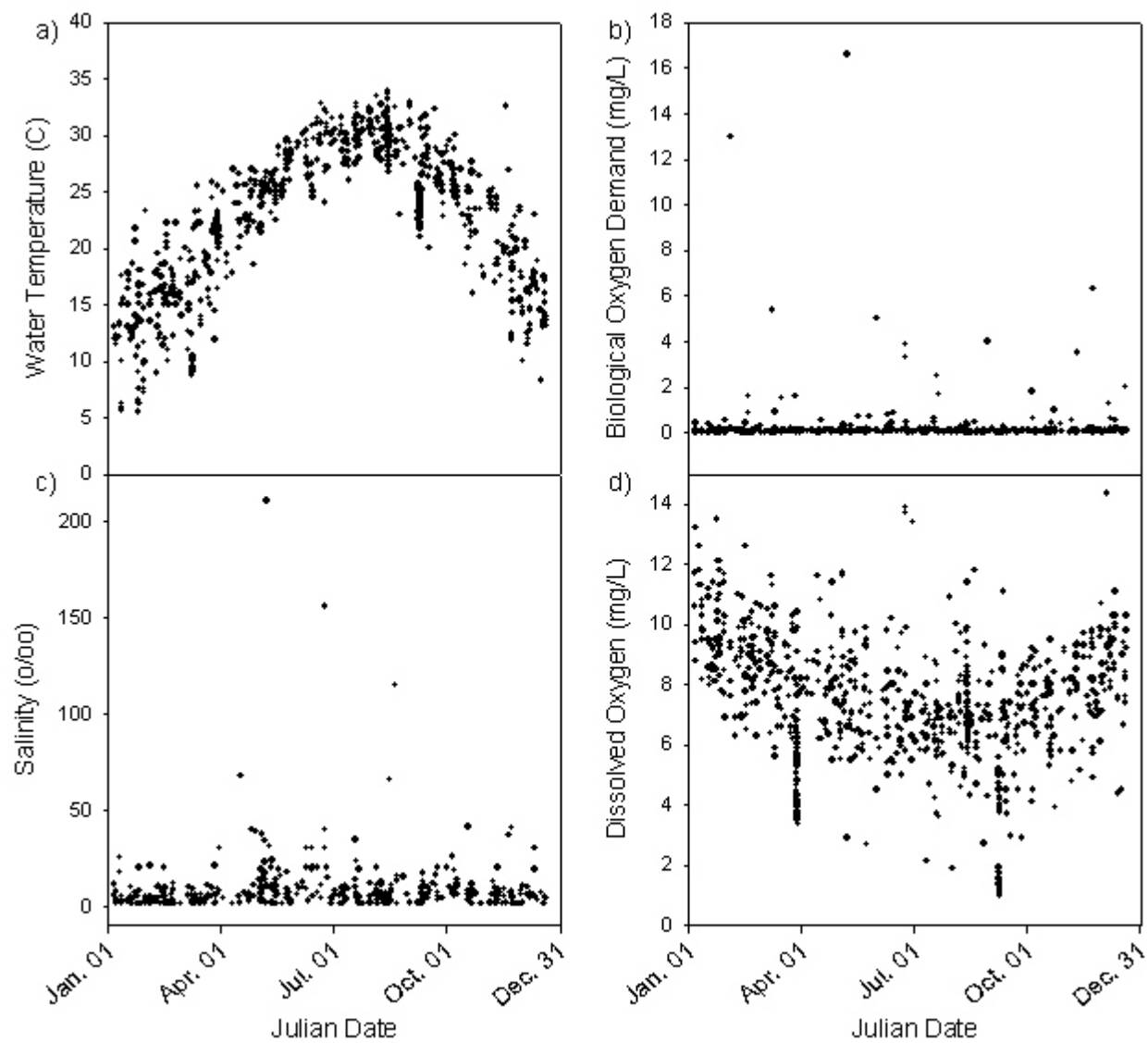


Figure 6: Parameter values plotted by the julian day of the year. a) Water temperature, b) biological oxygen demand, 3) salinity, and d) dissolved oxygen.

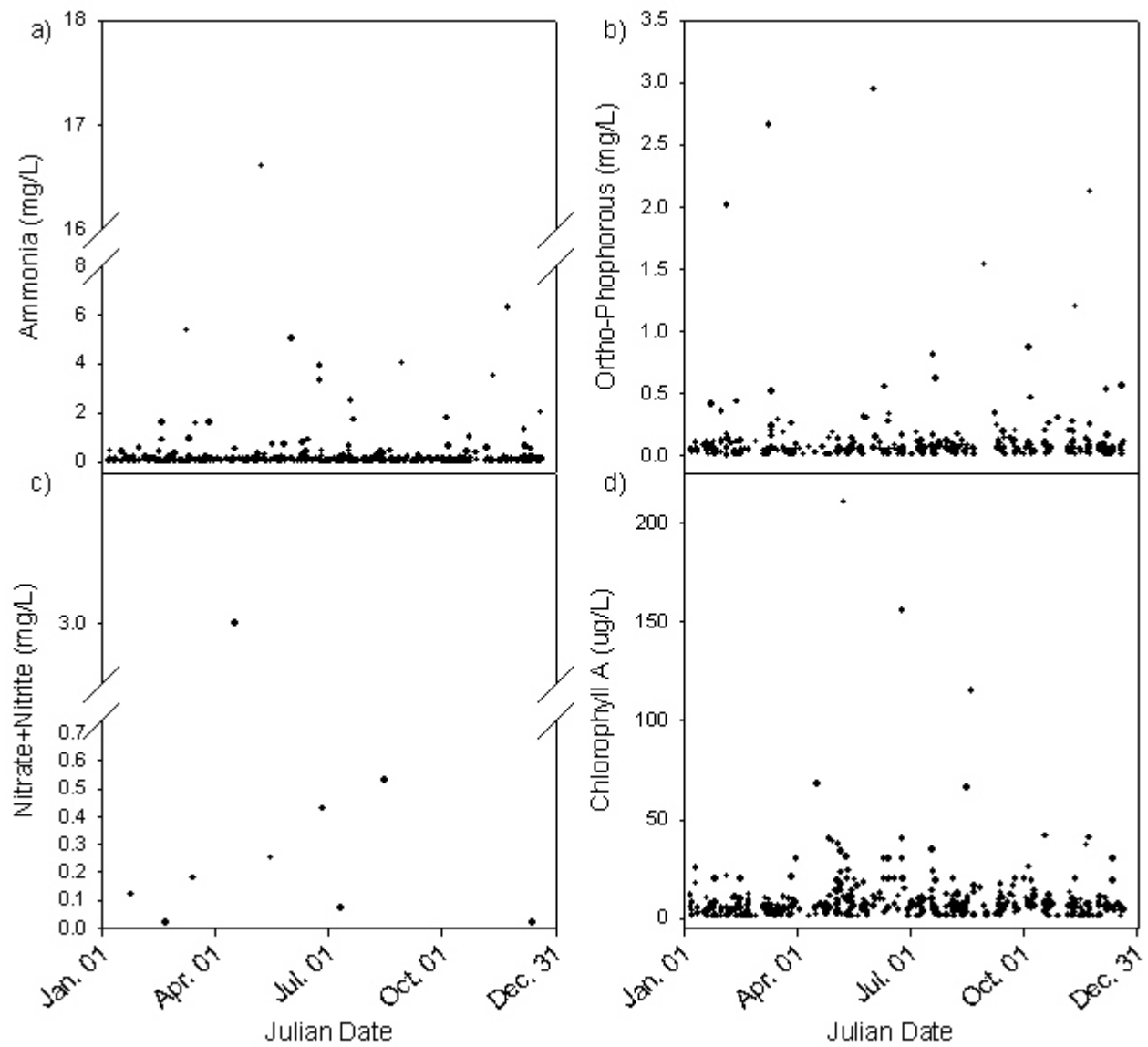


Figure 7: Parameter values plotted by the Julian day of the year. a) ammonia, 2) ortho-phosphate, 3) nitrate+nitrite, and 4) chlorophyll *a*.

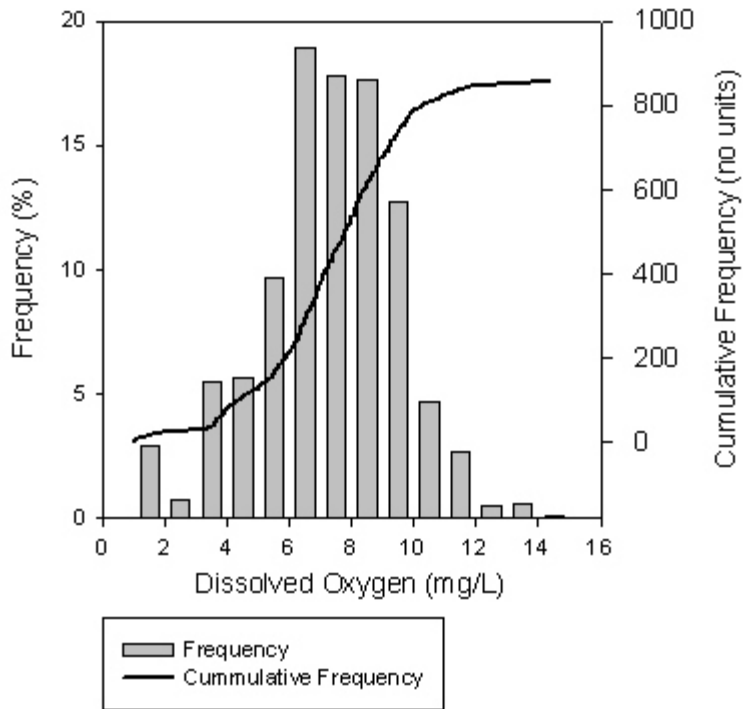


Figure 8: Frequency of dissolved oxygen values (mg/L). N = 856, mean = 7.24, std. dev. = 2.23, min. = 1.00, and max. = 14.35.

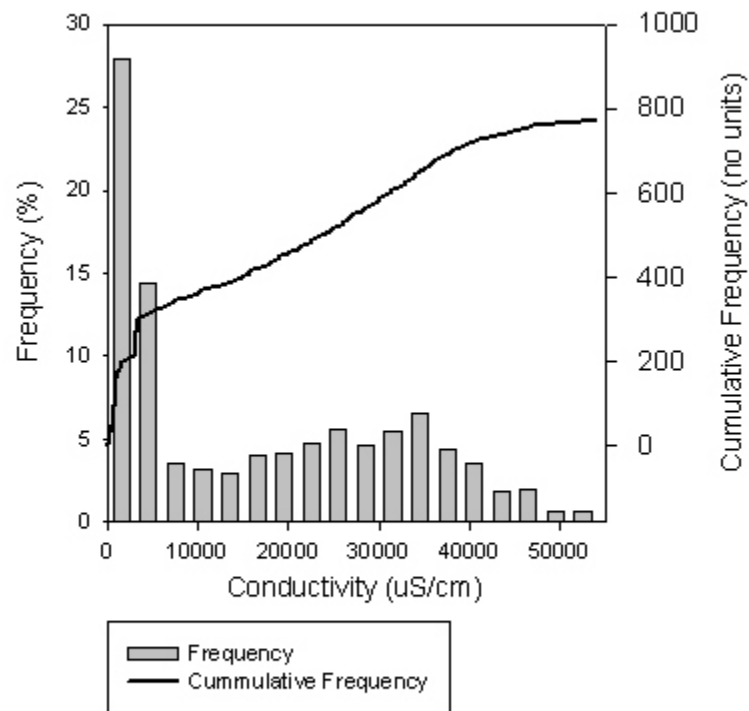


Figure 9: Frequency of conductivity values (uS/cm). N = 771, mean = 16310, std. dev. = 15081, min. = 55, and max. = 53900.

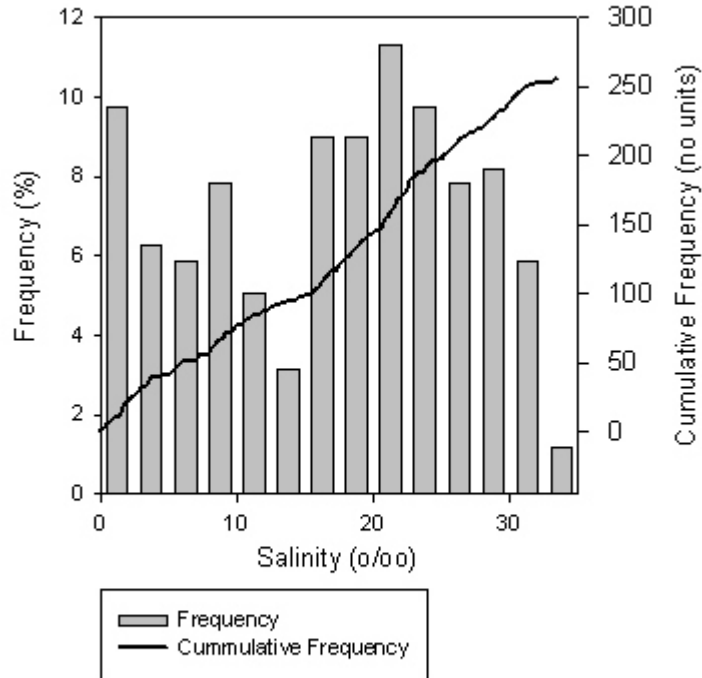


Figure 10: Frequency of salinity values (o/oo).
 N = 256, mean = 16.77, std. dev. = 9.45,
 min. = 0, and max. = 33.5.

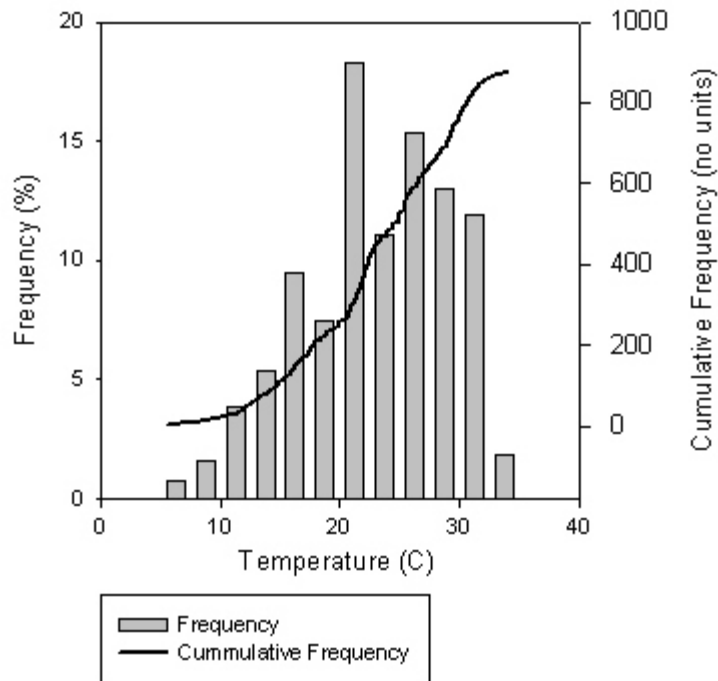


Figure 11: Frequency of temperature values (C).
 N = 875, mean = 22.82, std. dev. = 6.08,
 min. = 5.50, and max. = 33.97.

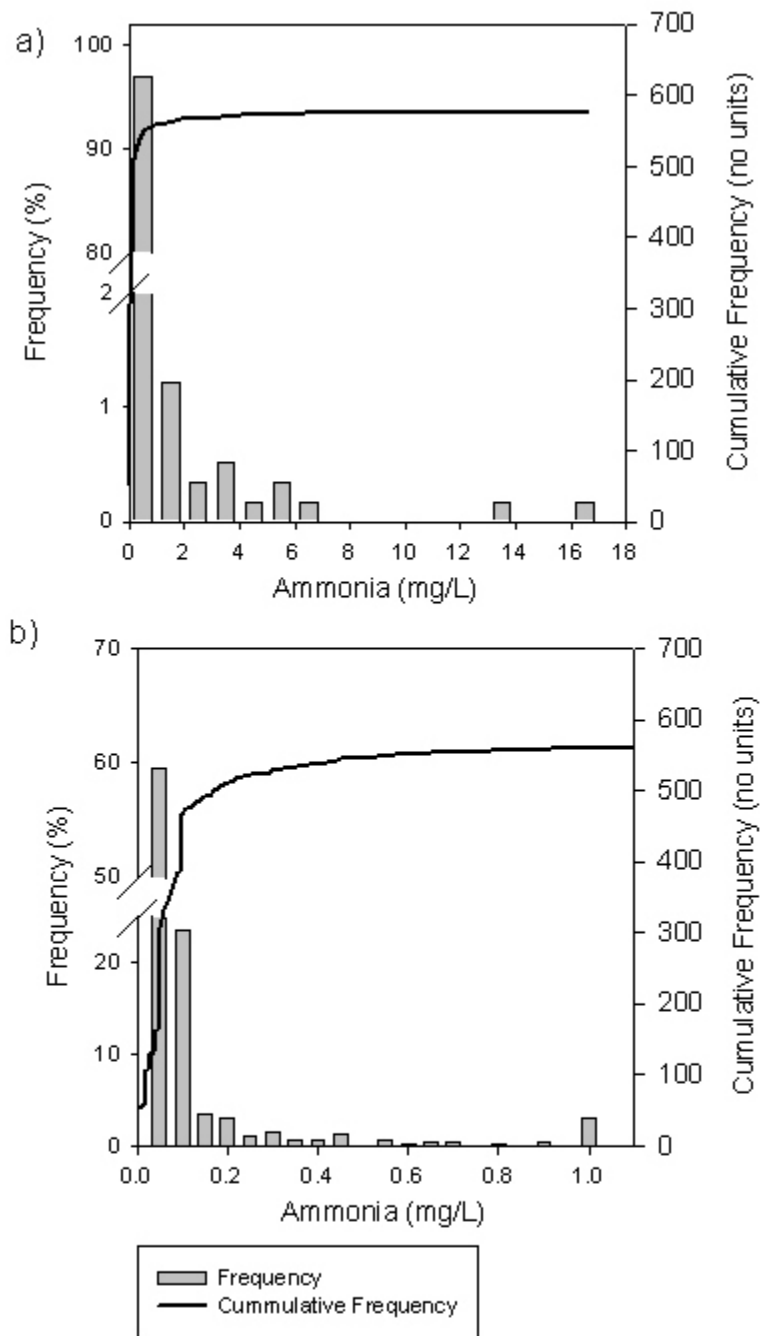


Figure 12: Frequency of ammonia values (mg/L). N = 582, mean = 0.22, std. dev. = 1.02, min. = 0.01, and max. = 16.6. a) covers the range 0 - 18 mg/L. b) covers the range 0 - 1 mg/L. Note: all values > 1.0 mg/L are lumped into the last category.

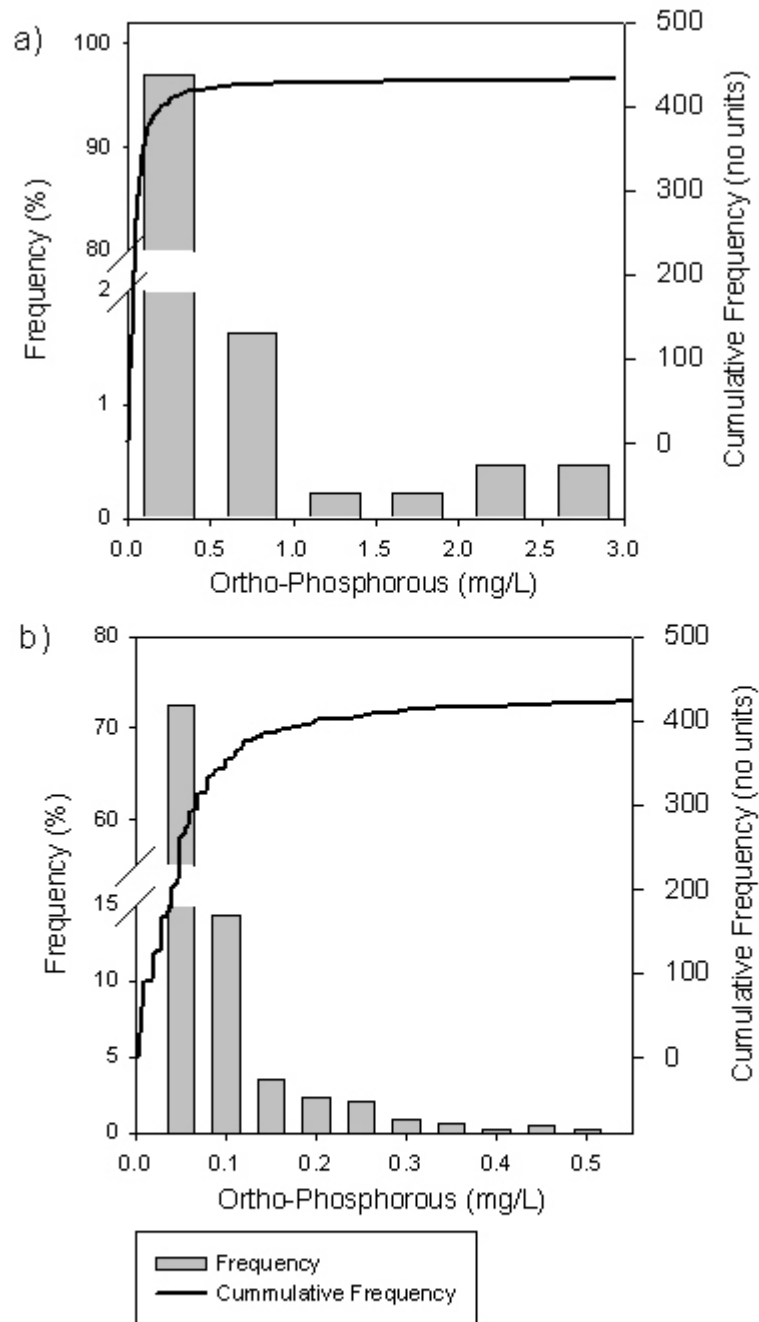


Figure 13: Frequency of ortho-phosphate values (mg/L). N = 452, mean = 0.098, std. dev. = 0.260, min. = 0.002, and max. = 2.941. a) covers the range 0 - 3 mg/L. b) covers the range 0 - 0.55 mg/L. Note: all values > 0.55 mg/L are lumped into the final category.

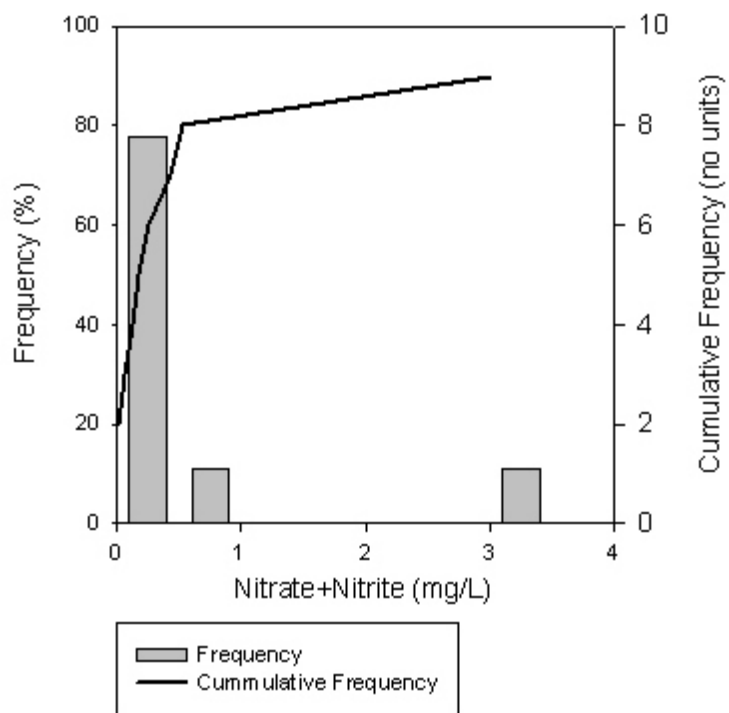


Figure 14: Frequency of nitrate+nitrite values (mg/L). N = 9, mean = 0.51, std. dev. = 0.95, min. = 0.02, and max. = 3.00.

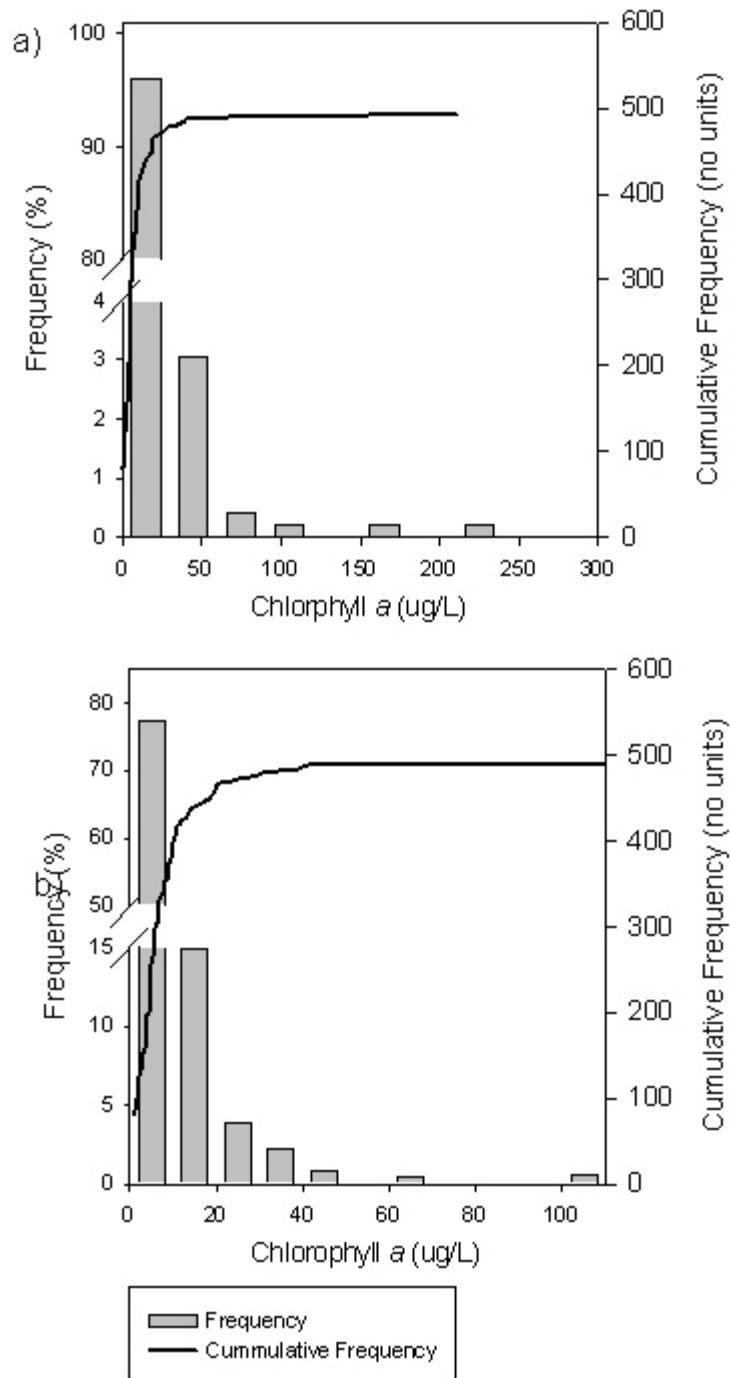


Figure 15: Frequency of chlorophyll *a* values (ug/L). N = 496, mean = 8.27, std. dev. = 14.66, min. = 1, and max. = 211. a) covers the range 0 - 300 ug/L. b) covers the range 0 - 110 ug/L. Note: All values > 110 ug/L are lumped into the final category.

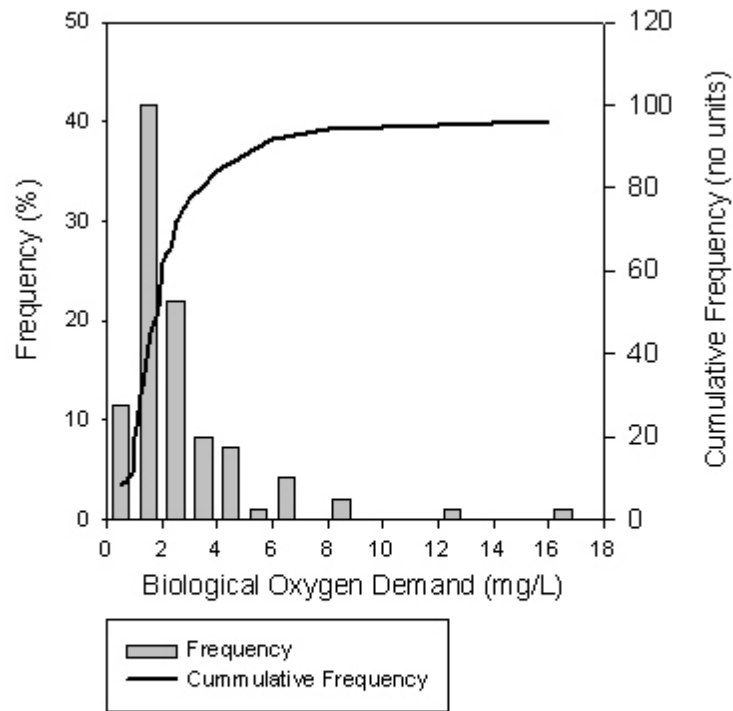


Figure 16: Frequency of biological oxygen demand values (mg/L). N = 96, mean = 2.44, std. dev. = 2.33, min. = 0.5, and max. = 16.0. BOD was measured using 5-day, 20 °C incubations.

Table 3: Number (and percent) of observations at each station indicative of low oxygen during the period 16 July 1969 to 13 November 2001. Stations with no dissolved oxygen (DO) data have been omitted. Station = TCEQ station ID. N = total number of DO observations. Observations based on grab-sample data; 24-hr time series and depth profile data are considered as single observations.

Station	N	Number of obs. where DO < 5 mg/L	Number of obs. where DO < 4 mg/L	Number of obs. where DO < 2 mg/L
12533	27	1 (4%)	-	-
12534	62	17 (27%)	9 (15%)	4 (6%)
13289	50	7 (14%)	5 (10%)	1 (2%)
13290	2	-	-	-
13291	54	2 (4%)	-	-
13292	2	-	-	-
13383	154	4 (3%)	1 (1%)	-
13384	128	36 (28%)	17 (13%)	7 (5%)
13385	100	49 (49%)	33 (33%)	17 (17%)
13563	30	1 (3%)	-	-
14701	2	-	-	-
14702	5	-	-	-
14703	4	-	-	-
14704	6	-	-	-
14705	5	-	-	-
14706	2	-	-	-
14707	6	-	-	-
14708	4	-	-	-
14709	4	-	-	-
14710	6	-	-	-
14711	5	-	-	-
14712	5	-	-	-
14713	5	-	-	-
14714	6	-	-	-
14717	3	-	-	-
14718	4	-	-	-
14720	49	1 (2%)	-	-
14721	4	-	-	-
14724	4	-	-	-
14885	4	-	-	-
14886	5	-	-	-
15368	24	1 (4%)	-	-

Table 4: TCEQ 24-hr DO data. The criteria for 24-hr average and 24-hr minimum DO are 5 mg/L and 4 mg/L respectively. Values lower than these are considered exceedences and are bold.

Date	TCEQ Stations					
	13385		13383		13384	
	24-hr average	24-hr minimum	24-hr average	24-hr minimum	24-hr average	24-hr minimum
03 May 2002	5.92	5.37				
24 August 2001			5.00	3.46		
08 August 2001	5.73	4.97	5.14	4.52	6.05	5.10
03 May 2001	6.44	5.91			6.79	6.49
28 June 2000	5.90	4.30	6.80	5.00	6.00	4.60

24-hr DO

A total of 10 24-hr DO observations were available from the TCEQ (Table 4). Of these observations, only one exceeded the TCEQ criteria of high aquatic life use. On August 24, 2001, the observed 24-hr DO minimum was 3.46 mg/L, lower than the DO minimum criteria of 4 mg/L.

Texas Parks and Wildlife Data

The Texas Parks and Wildlife Department's (TPWD) Lavaca Bay grab-sample data covered the period September 1975 - December 1999 and included 3576 grab-sample observations. Dissolved oxygen data was available for 3074 of these observations. Only two observations were hypoxic (i.e., DO < 2 mg/L). One hypoxic observation was not stationed in Lavaca Bay, but above it, as part of the TPWD's Lake Texana hydrographic survey conducted in 1984. The other hypoxic observation occurred in 1992 and was located at 28 40'20"N -96 38' 20"W in the western part of upper Lavaca Bay, south of Garcitas Cove. Only 118, roughly 4% of total DO observations, were < 5 mg/L DO and 0.8% were < 4 mg/L DO.

Of the 3576 hydrographic observations available, 975 were taken at the surface (depth = 0.3 m) with 962 observations including DO. The total range of DO values was 0.7 - 16.7 mg/L. Approximately 84% of DO values were in the range 5.4 - 10.2 mg/L. Only one observation (0.1% of DO observations) was hypoxic; it was mentioned previously. Only 33 DO observations, roughly 3.4% of total DO observations, were < 5 mg/L DO and 5, or 0.5%, were < 4 mg/L DO.

Surface salinity observations ranged 0 - 37 ‰. The frequency distribution of salinity values is irregular, but demonstrates that Lavaca Bay is as frequently fresh as it is saline up to 31.5‰. Roughly 2.3% of salinity observations were > 31.5‰. The average salinity in Lavaca Bay is 15.91 ‰.

Surface temperature observations ranged between 2.1 and 35 °C. Approximately 80% of these observations were in the range 16 - 32 °C. The mean temperature was 23.25 °C.

Formosa Plastics, Corp, Texas Data

Sixteen stations were represented in the Formosa data set. Hydrographic data obtained from Formosa Plastics, Corp, Texas (Formosa) covered the period May 1993 - January 2002. A total of 19 stations were represented in the dataset. Fifteen of these stations radiated out from around the diffuser (near TCEQ station 13563), the remaining 4 stations were scattered in upper Lavaca Bay (north of Hwy 35).

Nutrient data was obtained from Formosa for the period July 1998 - April 2001. Nutrient parameters included in this dataset are: ammonia nitrogen, nitrite nitrogen, nitrate nitrogen, total phosphorous, and ortho-phosphorous. When data for these parameters are plotted across the Julian year, no annual trends are discernable.

The Formosa dataset also included a total of 674 grab-sample observations. The variables collected are conductivity, salinity, temperature, pH, and DO; not all variables were collected for each observation. No incidences of hypoxia were observed in Formosa's dataset. Four DO observations (0.6%) were < 5 mg/L DO, but none of these were < 4 mg/L DO.

UTMSI Data

Discrete, grab-sample DO data was available from UTMSI for the period April 1988 - July 2001 for two stations in Lavaca Bay. Of a total of 240 hydrographic observations that were recorded during this period, 195 contained DO data. Only one DO observation was less than 5 mg/L. It was taken on July 9, 1996 at station B (TCEQ station 17554), at a depth of 1.6 m.

Sediment TOC was measured for stations A and B (TCEQ stations 17553 and 17554 respectively) on three dates: 14 October 1996, 17 October 1997, and 21 October 1999. At station A, sediment TOC ranged between 0.34 and 1.37 in the 0 - 1 cm section, and 0.66 - 0.78 in the 2 - 3 cm section. At station B, sediment TOC ranged between 0.71 - 1.00 in the 0 - 1 cm section, and 0.75 - 0.84 in the 2 - 3 cm section.

Surface (0 - 3 cm) sediment N was measured as part of CHN analysis for stations A and B on three dates: 14 October 1996, 17 October 1997, and 21 October 1999. Sediment N in deeper sediment layers is also available for these and other dates. At station A, sediment N ranged 0.075 - 0.110 in the 0 - 1 cm section, and 0.070 - 0.084 in the 2 - 3 cm section. At station B, sediment N ranged 0.077 - 0.115 in the 0 - 1 cm section, and 0.073 - 0.087 in the 2 - 3 cm section.

Alcoa Data

Alcoa collected hydrographic and TOC data from ten stations during the period 02 July 1996 - 04 December 1996. All of these stations were within the Superfund Site and most were within the region closed by the Texas Department of Health. Hydrographic data collected were: salinity, temperature, DO, and Redox potential (Eh). All DO measurements were > 6 mg/L. Filtered TOC

measurements ranged between 1.86 - 2.81 mg/L. Unfiltered TOC measurements ranged between 1.95 - 9.23 mg/L.

TWDB Data

24-hr DO data was available on the internet from the TWDB for the period December 1986 - March 21 2002 at the time of dat base query. The TWDB makes no warranties concerning this data stating on the website: “These data are raw, uncorrected, and may contain errors. The Board makes no warranties (including no warranties as to merchantability or fitness) either expressed or implied with respect to the data or its fitness for any specific application.” However, the TWDB has written a quality assurance (QA) document that documents their methodology and QA procedures entitled, *TWDB Ambient Water Quality Monitoring Program, Quality Assurance Project Plan*, Revision No. 1, September 2002 (David Brock, TWDB, personal communication)..

TWDB data was collected at only one station that is very nearly the same location as where TCEQ’s station 13383 is sampled. The sonde was placed at mid-water which, assuming a well-mixed estuary, is $\frac{1}{2}$ the depth of the mixed surface layer. The actual depth of deployment varied through the period evaluated, ranging from 2.32 to 6.98 ft from the water surface. The typical depth of sonde deployment was between 4 and 5 ft.

Only data dating back to September of 1997 was evaluated (Fig. 17, Table 6). A total of 41 24-hr observations were available for the period spanning September 1997 to the present. Of these, 8 observations (20%) exceeded the TCEQ criteria for 24-hr DO average (5 mg/L), and 14 observations (34%) exceeded the TCEQ criteria for 24-hr DO minimum (4 mg/L). Only 2 observations were hypoxic. Seventy-five percent of 24-hr minimum DO observations were in the range 3 - 7 mg/L. Eighty-three percent of 24-hr average DO observations were in the range 4 - 8 mg/L. Eighty-three percent of 24-hr maximum DO observations were in the range 4 - 9 mg/L.

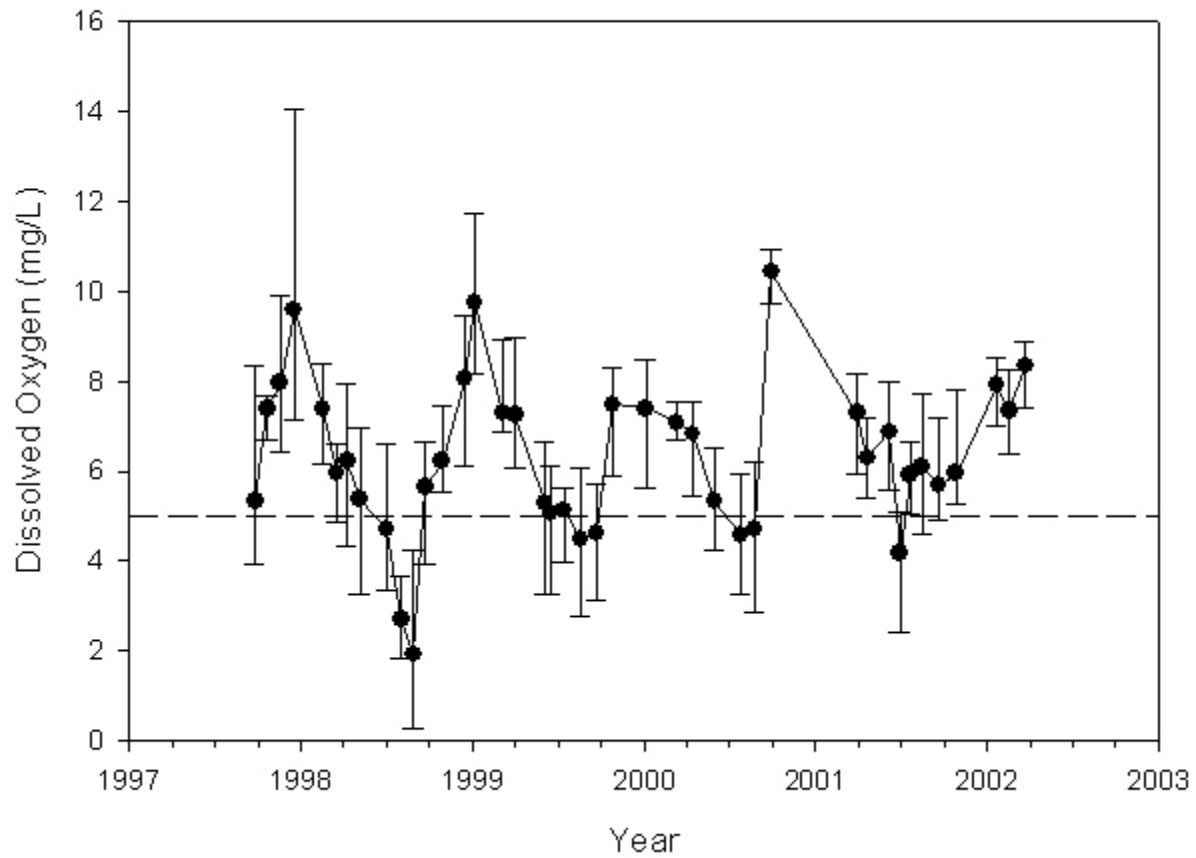


Figure 17: Dissolved oxygen data from Texas Water Development Board, Station 13383. Average 24-hour values (symbol), minimum 24-hour values (lower tick), and maximum 24-hour values (upper tick) of 24 samples for each sampling period. Dashed reference line at 5 mg/L.

Table 5: Texas Water Development Board 24-hr DO data. Sonde deployed near TCEQ station 13383. The criteria for 24-hr average and 24-minimum DO are 5 mg/L and 4 mg/L, respectively. Values lower than these are exceedences. Exceedences of TCEQ criteria are in bold typeface.

Begin Date	Min. DO	Avg. DO	Max DO	n
3/21/02	7.41	8.34	8.87	24
2/18/02	6.4	7.32	8.26	24
1/21/02	7.02	7.9	8.5	24
10/26/01	5.25	5.94	7.82	24
9/19/01	4.9	5.68	7.18	24
8/15/01	4.6	6.1	7.72	24
7/20/01	5.03	5.91	6.63	24
6/28/01	2.4	4.18	5.07	24
6/6/01	5.57	6.87	7.98	24
4/19/01	5.38	6.29	7.18	24
3/29/01	5.94	7.29	8.15	24
9/29/00	9.72	10.44	10.94	24
8/23/00	2.88	4.71	6.22	24
7/24/00	3.26	4.58	5.93	24
5/30/00	4.26	5.33	6.52	24
4/13/00	5.46	6.82	7.55	24
3/10/00	6.68	7.08	7.55	24
1/5/00	5.62	7.39	8.47	24
10/25/99	5.89	7.48	8.31	24
9/22/99	3.13	4.62	5.71	24
8/18/99	2.75	4.47	6.07	24
7/13/99	3.98	5.13	5.61	24
6/15/99	3.25	5.05	6.1	24
6/3/99	3.26	5.29	6.66	24
4/1/99	6.08	7.25	8.97	24
3/4/99	6.89	7.28	8.94	24
1/6/99	8.18	9.76	11.71	24
12/15/98	6.12	8.04	9.46	24
10/28/98	5.55	6.21	7.43	24
9/23/98	3.91	5.63	6.65	24
8/27/98	0.29	1.92	4.23	24
7/31/98	1.84	2.71	3.64	24
7/1/98	3.33	4.7	6.62	24
5/5/98	3.25	5.37	6.98	24
4/8/98	4.33	6.21	7.95	24
3/16/98	4.87	5.94	6.61	24
2/17/98	6.16	7.39	8.37	24
12/17/97	7.13	9.59	14.05	24
11/18/97	6.44	7.95	9.88	24
10/21/97	6.67	7.39	7.69	24
9/25/97	3.94	5.33	8.34	24

Summary

Low DO (i.e., $DO < 5$ mg/L) appears to be a rare occurrence in Lavaca and Chocolate Bays (Segment 2453). In the TCEQ data set, less than 10 observations for 24 stations, out of a total of 35 stations in Lavaca Bay, analyzed for DO, had low dissolved oxygen values (Table 3). Grab-sample data for only 11 stations indicated possible low DO (i.e., < 5 mg/L). These stations are: 12533, 12534, 13288, 13289, 13291, 13294, 13295, 13383, 13384, 13385, and 13563. In Lavaca Bay, 3% of TCEQ's surface DO grab-sample data were hypoxic (Fig. 8).

Although they are designated in the dataset as being within the confines of segment 2453, five of these stations (i.e., 13288, 13289, 13291, 13294, 13295) are not covered under the Lavaca Bay TMDL project because they are designated as tidal streams (i.e., tributaries to Lavaca Bay). Four of these stations had low surface water oxygen (i.e., grab-sample $DO < 5$ mg/L; Fig. 18). The remaining six stations are: 12533, 12534, 13383, 13384, 13385, and 13563. Of these, three stations (i.e., 13383, 13384, and 13385) were sampling locations in the Lavaca Bay TMDL QAPP and Field Monitoring Plan.

Possible Causes of Dissolved Oxygen Depletion in Lavaca Bay

Several natural factors may contribute to the depletion of DO in Lavaca Bay. The saturation concentration of DO varies inversely with temperature and salinity (Fig. 2). When temperature and/or salinity are high, the water will contain less DO than when temperature and/or salinity are low. In Lavaca Bay, surface DO (depth < 0.3 m) was lowest during summer months when temperatures peaked (Fig. 6).

Water column stratification is another natural factor that may contribute to the depletion of DO in Lavaca Bay. In estuaries, water column stratification can be induced by the influx of freshwater which overlies a layer of much saltier water. Water column stratification inhibits the mixing of oxygenated surface waters to deeper waters; the larger the surface to bottom salinity difference, the more mixing is inhibited. In shallow areas, low bottom DO may not be induced because of benthic photosynthesis (e.g., benthic diatoms), however, water turbidity may inhibit DO production by photosynthesis.

Inhibition of mixing processes that give rise to water column stratification may also be caused by anthropogenic alterations to the bay, such as the presence of a man-made channel, harbor, or island. Stations 13385 and 13384 are both located in channels. Both stations have had multiple incidences of low DO (Tables 3 and 4). Depth profiles of these stations indicate stratification is common because 20% of observations at stations 13385 and 13384 show that the difference between surface and bottom water salinities were greater than 10 ‰, and some observations were greater than 20 ‰. In addition to stratification, DO depletion in excess of 4 mg/L was also found at these stations.

Another factor that may contribute to DO depletion in Lavaca Bay is nutrient loading. Ammonia and ortho-phosphate concentrations were higher with lower salinity (Fig. 13) indicating possible non-point source nutrient contributions to Lavaca Bay. Based on data available, it is not possible to distinguish if nutrient influx is from natural or anthropogenic sources. Nutrients contribute to DO depletion via eutrophication processes (Fig. 3). Eutrophication can lead to increased phytoplankton

production followed by increased consumer production. The wastes of this productivity (e.g., dead cells, excrement, exudates) can settle to the benthos where decomposition processes occur and microbial respiration depletes the surrounding water of DO. In some cases benthic DO can be replenished via mixing processes or benthic primary production, however, if mixing processes are inhibited by stratification or the presence of man-made structures (e.g., channels, harbors) DO may be depleted to the point of hypoxia. Eutrophication is not in itself harmful to the ecosystem; it can boost production without causing DO depletion under some conditions. Where excess nutrients are associated with low DO, nutrient controls are needed to increase DO levels.

DISSOLVED OXYGEN MONITORING AND ASSESSMENT

Methods

10 Measurement Requirement

The dissolved oxygen impairment assessment for Lavaca Bay (segment 2453) was completed through a 24-hour dissolved oxygen monitoring plan. The monitoring plan was based on the requirements for a dissolved oxygen assessment as stated in the TCEQ 24-Hour DO Monitoring Fact Sheet (Appendix A), which requires 10 or more 24-hour samples over a two to five year period. All DO methods are described in detail in standard operating procedures in the 2003 Annual update of the Quality Assurance Quality Control Project Plan (QAPP) submitted to TCEQ (Appendix B).

Twenty-four hour parameter measurements were taken using YSI6920 and YSI600XLM data sondes at seven sites (Figure 18). The parameters have the following accuracy and units: temperature (± 0.15 °C), pH (± 0.2 units), dissolved oxygen ($\text{mg/l} \pm 0.2$), dissolved oxygen saturation ($\% \pm 2\%$), specific conductivity ($\pm 0.5\%$ of reading depending on range), redox potential (± 20 mV), depth (± 0.2 m), and salinity ($\pm 1\%$ of reading or 0.1 ppt, whichever is greater). Salinity is automatically corrected to 25°C.

Spatial Requirement

Assessment occurs at each station that is representative of 25% of the total estuary square miles, but not more than 5,120 acres or 8 square miles. These areas are called assessment units. Based on the area of Lavaca Bay there are four assessment units (Table 6). The stations sampled are thus grouped into assessment units as follows: 17552 and 17553 comprise the Upper bay, 13383 and 17554 comprise the Gallinipper Point to SH 35, 13385 comprises the Point Comfort area, 13384 and 17555 comprise the Mouth of bay to Gallinipper Point.

Critical Period Requirement

All samples were taken during the required index period of March 15 - October 15. The critical period sampling requirements, between half and two thirds of a year's samples within an assessment unit must be taken between July 1 - September 30, were met in every year except 2002 when 49% of samples were taken during the critical period (Table 7). The three measurements in 2000 were taken on June 27 and 28, only a few days before the beginning of the critical period, but will be considered as being within the critical period although they do not strictly meet the definition.

Annual and Monthly Sampling Requirement

The DO Monitoring Fact Sheet states: "No more than 2/3 of the samples should be taken in the same year" and that "Sampling events should be more than one month apart." The first of these requirements was met for all years (Table 7). The second requirement was not met for 8 out of a total of 92 samples. This is due to incorporation of data from TCEQ and UTMSI sampling which was done to provide better temporal and spatial coverage.

Sonde Depth Requirement

The DO Monitoring Fact Sheet states that sondes are to be deployed “...between a depth of 1 foot and a depth of ½ the mixed surface layer.” Assuming that Lavaca Bay is well mixed, because it is shallow and subjected to tidal and wind mixing forces, all samples were taken within a depth of 1 ft and ½ the total depth of the station. This requirement is met for all data.

Measurement Interval Requirement

The DO Monitoring Fact Sheet requires that sondes record data at least once per hour and no more frequently than every 15 minutes. This requirement is met for all data.

Duplicate Sonde Requirement

Following the 24-hr DO Monitoring Fact Sheet, two sondes were deployed in the same general area at least 20% of the time to check spatial variability at deployment sites. Thus, replicate samples were taken at sites 15 out of 77 deployments or 20% of the time.

Data Analysis

The complete data set was then analyzed to determine the percentage of 24-hour observations that were below minimum requirements for average and minimum dissolved oxygen measurements.

Table 6: Stations sampled for dissolved oxygen assessment. TCEQ descriptions and locations.

Assessment Unit	Station No.		Short Description	Latitude (N)	Longitude (W)
	TCEQ	UTMSI			
Mid-Bay	13383	15	Lavaca Bay at SH 35	28.63888931	96.60916901
Lower-Bay	13384	5	Lavaca Bay at 'Y' at CM 66	28.59583282	96.56250000
Pt. Comfort	13385	3	Alcoa Ship Dock	28.64444444	96.55666667
Upper-Bay	17552	1	Lavaca Bay So. of Garcitas Cove	28.69683456	96.64499664
Upper-Bay	17553	2	Lavaca Bay West of Point Comfort	28.67436218	96.58280182
Mid-Bay	17554	4	Lavaca Bay East of Noble Point	28.63933372	96.58449554
Lower-Bay	17555	6	Lavaca Bay South of Rhodes Pt.	28.59769440	96.51602173

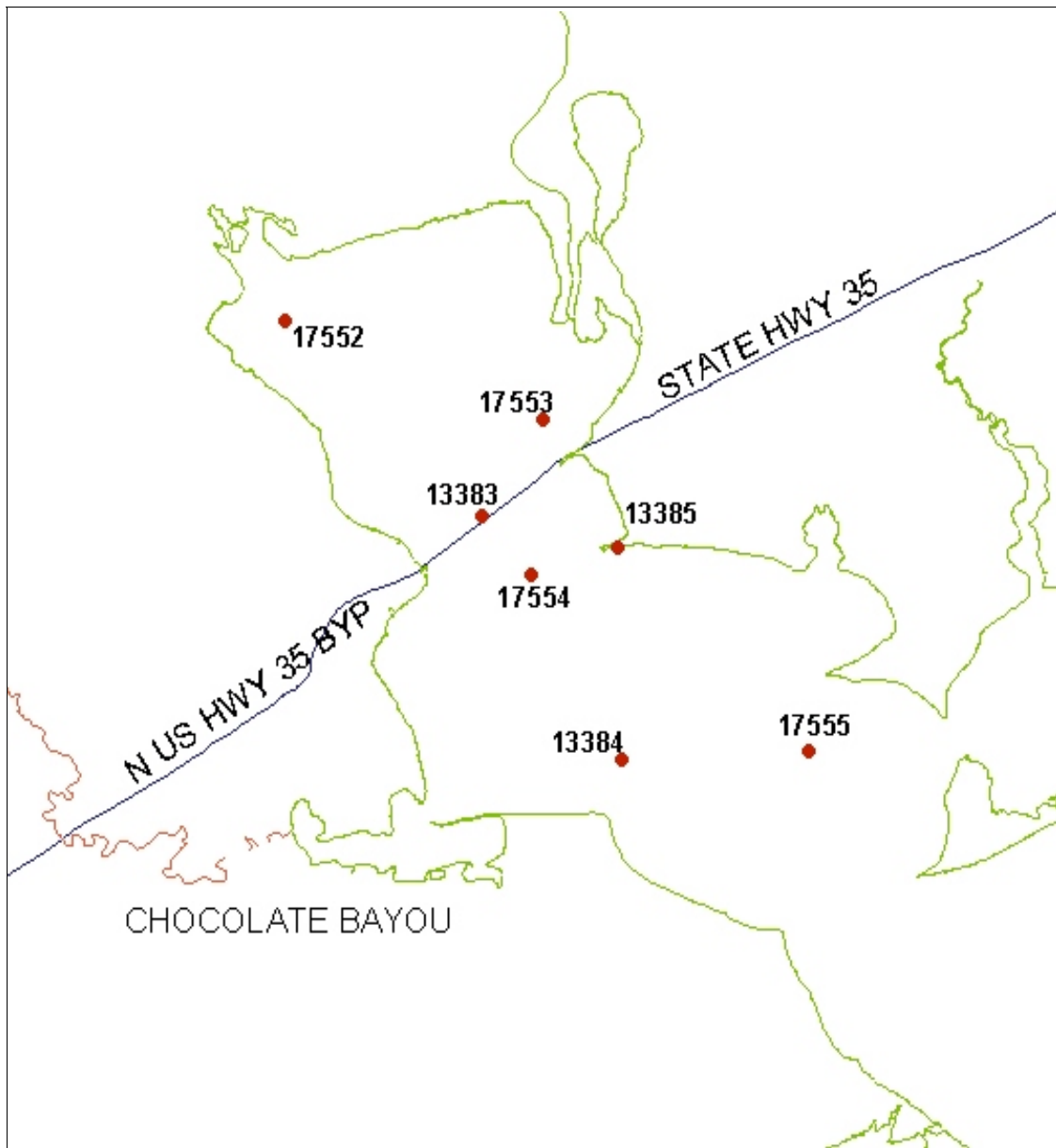


Figure 18: Map of stations used for the 24-hour data sonde deployment in Segment 2453. Stations numbers are assigned by TCEQ.

Table 7: Number and percent of sample periods within the index and critical periods.

Date	Samples in Index Period	Samples in Critical Period	% Samples in one Year	% Samples in Index Period	% Samples in Critical Period
6/29/2000	3	3	3	100	100
5/3/2001	2				
8/8/2001	3	3			
8/24/2001	1	1	7	100	67
4/24/2002	6				
5/4/2002	1				
5/22/2002	6				
7/24/2002	8	8			
7/27/2002	1	1			
8/1/2002	1	1			
8/21/2002	8	8			
8/27/2002	1	1			
10/9/2002	7		42	100	49
3/18/2003	4				
4/15/2003	6				
5/28/2003	9				
7/22/2003	5	5			
7/31/2003	3	3			
8/14/2003	1	1			
8/19/2003	7	7			
8/28/2003	1	1			
9/23/2003	8	8	48	100	57
Total Obs.	92	51		100	55

Results

Average DO Measurements

Only two out of 77 sampling measurements (i.e., 2.6%) had average dissolved oxygen concentrations of less than the required 5.0 mg/L (Table 8). Both of these occurred in late summer and were located either in deeper enclosed areas or near river mouths. Replicate measurements were used to check the quality of the data. The mean square error for 15 paired replicate average DO measurements was 0.09933 and the coefficient of variation was 4.7%. The standard deviation of the average DO measurements are within ± 0.32 mg/L, which is just over the instrumentation accuracy of ± 0.2 mg/L.

Table 8: Twenty four hour average dissolved oxygen measurements (mg O₂ / L). Exceedences of 24 hour average dissolved oxygen requirement shown in bold. Average value of two replicates denoted by *.

Date	Assessment Unit and TCEQ Station Number						
	Upper-Bay		Mid-Bay		Pt. Comfort	Lower-Bay	
	17552	17553	13383	17554	13385	13384	17555
6/29/2000			6.8		5.9	6.0	
5/3/2001					6.4	6.8	
8/8/2001			5.1		5.7	6.1	
8/24/2001			5.0				
4/24/2002	6.9	7.6		7.2	6.2	7.2	6.7
5/4/2002					5.9		
5/22/2002	7.5			7.4	7.7	7.5*	7.2
7/24/2002	7.0	7.9		7.0	5.5*	7.1	6.8*
7/27/2002					6.3		
8/1/2002			6.3				
8/21/2002	6.8	6.9*		7.0*	6.0	6.6	6.7
8/27/2002					5.9		
10/9/2002	7.6*	7.4		7.2	7.0	7.2	6.9
3/18/2003	7.8	8.8	8.3				8.7
4/15/2003	7.7	7.7*	7.4	7.2			7.6
5/28/2003	6.9*	6.9	6.3	6.5*	5.2	6.4	6.6
7/22/2003		7.0	6.6	6.8*			7.3
7/31/2003			6.6		3.9	6.3	
8/14/2003					5.0		
8/19/2003	6.7*	4.9		5.5*		6.6	6.5
8/28/2003					5.5		
9/23/2003	6.1*	5.8*	6.8	6.7*			7.9
Total Obs.	10	10	10	10	15	11	11

Minimum DO Measurements

Only five out of 77 sampling periods (i.e., 6.5%) had minimum dissolved oxygen measurements of less than the required 4.0 mg O₂ / L (Table 9). Four out of five of these low values were located at station 13385. Again all of the low values occurred during late summer. Replicate measurements were used to check the quality of the data. The mean square error for 15 paired replicate minimum DO measurements was 0.09361 and the coefficient of variation was 5.2%. The standard deviation of the minimum DO measurements are within ± 0.31 mg/L, which is just over the instrumentation accuracy of ± 0.2 mg/L.

Table 9: Twenty four hour minimum dissolved oxygen measurements (mg O₂ / L). Exceedences of 24 hour minimum dissolved oxygen requirement shown in bold. *Average value of two replicates.

Date	Assessment Unit and TCEQ Station Number						
	Upper-Bay		Mid-Bay		Pt. Comfort	Lower-Bay	
	17552	17553	13383	17554	13385	13384	17555
6/29/2000			5.0		4.3	4.6	
5/3/2001					5.9	6.5	
8/8/2001			4.5		5.0	5.1	
8/24/2001			3.5				
4/24/2002	6.3	6.7		6.7	5.5	6.7	6.4
5/4/2002					5.4		
5/22/2002	7.2			6.8	7.1	7.2*	7.0
7/24/2002	6.1	6.4		5.3*	2.5*	3.8	5.0
7/27/2002					5.4		
8/1/2002			5.2				
8/21/2002	6.3	6.2*		6.2*	4.7	6.0	6.2
8/27/2002					3.9		
10/9/2002	7.0*	6.9		6.7	6.1	6.5	6.4
3/18/2003	7.3	8.3	7.5				7.8
4/15/2003	7.5	7.5*	7.0	6.9			7.2
5/28/2003	6.6*	6.3	6.0	6.1*	4.8	6.2	6.3
7/22/2003		6.1	5.6	5.8*			6.8
7/31/2003			5.9		3.3	5.1	
8/14/2003					2.9		
8/19/2003	5.7*	4.1		4.8*		5.3	5.8
8/28/2003					4.4		
9/23/2003	5.7*	5.3*	5.2	6.0*			6.4
Total Obs.	10	10	10	10	15	11	11

Temporal Results

All exceedences of average and minimum requirements took place during the critical period from July 1 - September 30 when the largest 24 hour range of dissolved oxygen measurements occurred (Figs. 19 and 20). Out of 77 total measurements, only 2 (about 3%) were below the 24-hour average standard of 5 mg/L (Fig. 19) and only 5 (about 7%) were below the 24-hour minimum standard of 4 mg/L (Fig. 20). Lowest DO concentrations occurred in the summer, but the bay-wide average 24-hour concentration never went below the standard (Figure 21).

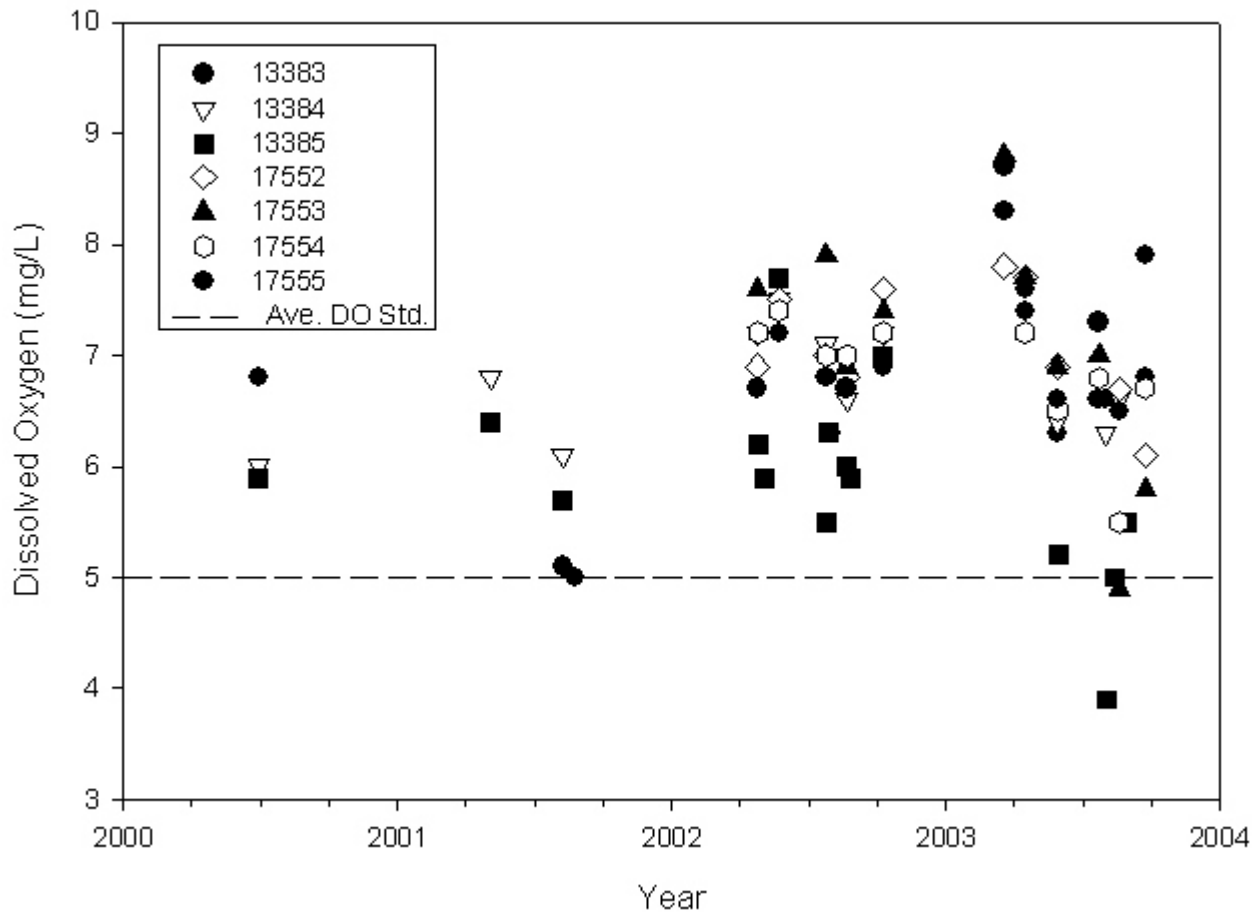


Figure 19: Average 24-hour dissolved oxygen concentrations for all samples taken from 2000 through 2003.

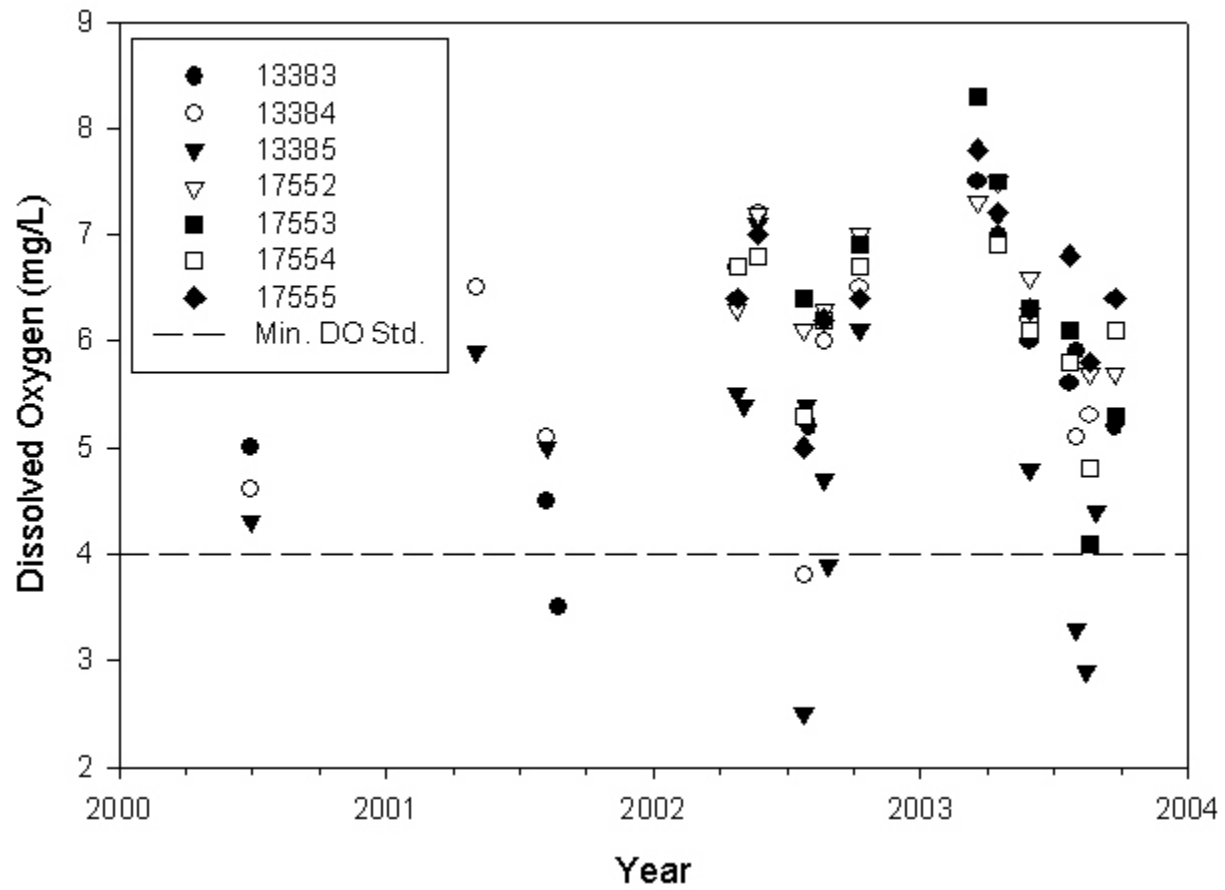


Figure 20: Minimum 24-hour dissolved oxygen concentrations for all samples during 2000 through 2003.

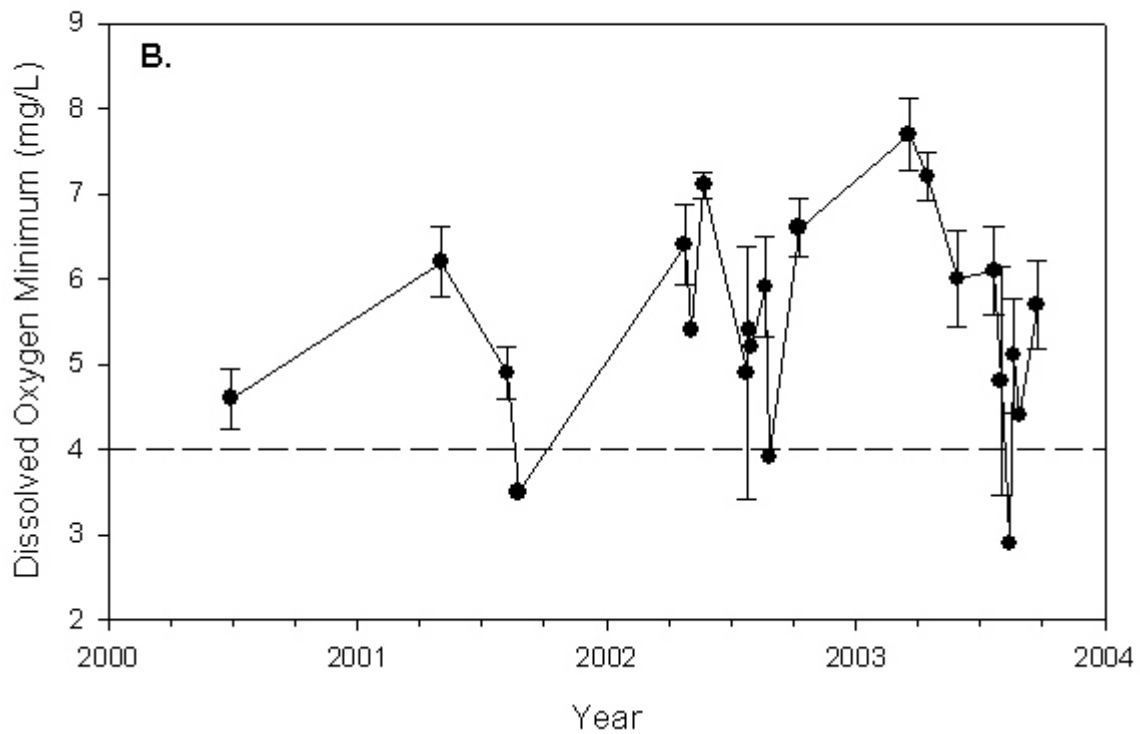
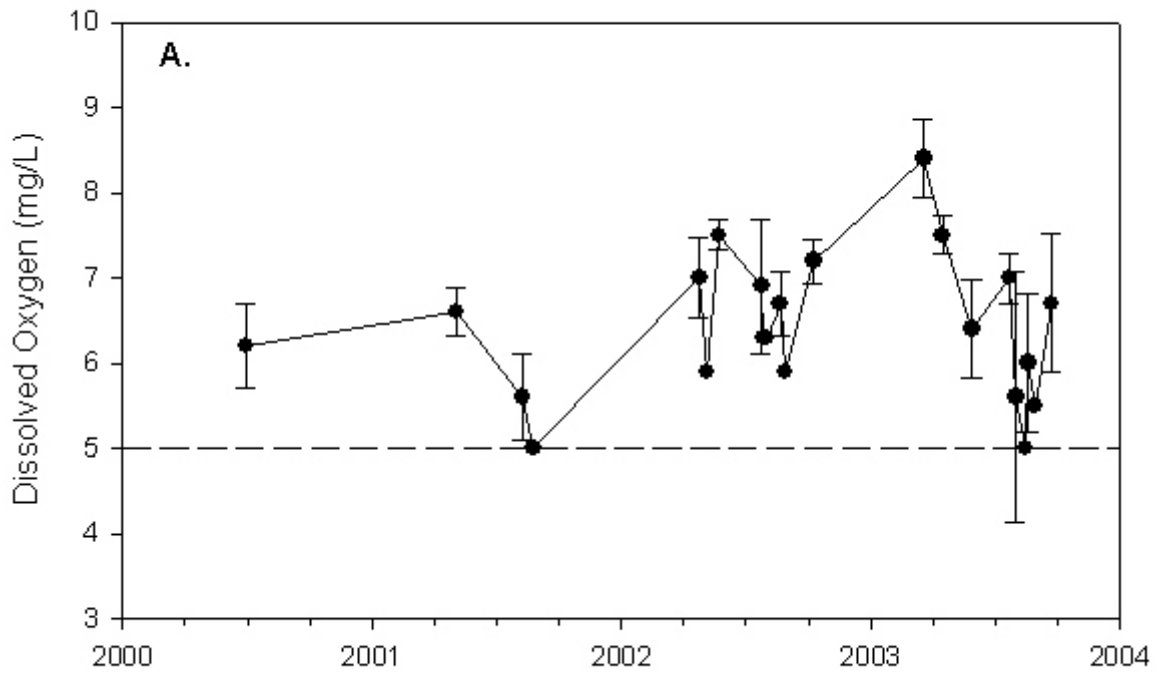


Figure 21. Bay-wide 24-hour dissolved oxygen concentrations each sampling period. A) Average 24-hour DO, and B) minimum 24-hour DO. Mean and standard deviation and reference line at standard.

Spatial Results by Assessment Unit

Point Comfort

Nearly all exceedences of average and minimum requirements occurred in the Point Comfort Assessment Unit at station 13385 near the Alcoa Ship dock (Figs. 22 - 28). At this station, the exceedences occurred during the critical period from July 1 - September 30. Still, 14 of 15 samples (i.e., 93%) were above the average 24-hour DO standard of 5 mg/L. However, only 11 of 15 samples (i.e., 73%) were above the minimum 24-hour DO standard of 4 mg/L.

It is interesting to compare Stations 13385 (Fig. 24) and 17554 (Fig. 27), which had different trends in DO concentration and variability because station 13385 is located in the Alcoa Ship Channel and station 17554 is located nearby, but in the middle of the open bay. Station 13385 is responsible for four out of five exceedences of average and minimum DO requirements. These exceedences occurred during the critical period from July 1 - September 30. The greater daily variability in DO concentrations seen at station 13385 as compared to station 17554 may arise when the stratified boundary layer moves over the sondes depth in the water column as water heats up during summer months. Station 13385 does not appear to be representative of ambient conditions of Lavaca Bay.

Upper-Bay

The Upper-Bay Assessment Unit was the only other unit to have an exceedence of the DO standard. However, 19 of 20 (i.e., 95%) samples were above the average 24-hour DO standard of 5 mg/L and all of the minimum DO values were above the 24-hour minimum standard. Stations 17552 (Fig. 25) and 17553 (Fig. 26) had similar seasonal trends in DO concentrations with lower values during mid to late Summer and higher values in Spring. The major difference occurs in late summer of 2003 when the DO dropped at station 17553, which is located at the mouth of Lavaca River, and not at station 17552. Daily variation in DO concentrations at upper bay stations remains relatively stable throughout the year with slightly larger daily variation during summer months. This implies a control by a non-seasonal forcing variable such as freshwater inflow and not by a seasonal forcing variable such as sunlight intensities and duration.

Mid-Bay

The Mid-Bay Assessment Unit had 100% of samples above the average 24-hour DO standard of 5 mg/L and 19 of 20 (i.e., 95%) minimum DO values were above the 24-hour minimum standard of 4 mg/L. The one case where the minimum DO standard was not attained was at Station 13383 in August 2001. Station 13383 (Fig. 22), located close to the causeway. The DO trend over time at Station 13383 is similar to the trend seen at station 17553 implying that it receives more input from Lavaca River.

Lower-Bay

The Lower-Bay Assessment Unit had 100% of samples above the average 24-hour DO standard and the 24-hour minimum standard. Stations 13384 (Fig. 23) and 17555 (Fig. 28) show similar trends during the period of time when sampling overlapped. They both show a tight range in DO

concentrations except during late summer months when daily variability increases dramatically. Thus daily variability at lower bay areas may be controlled by a seasonal forcing variable such as sunlight or temperature. This also implies less control of DO concentrations by river inflow events.

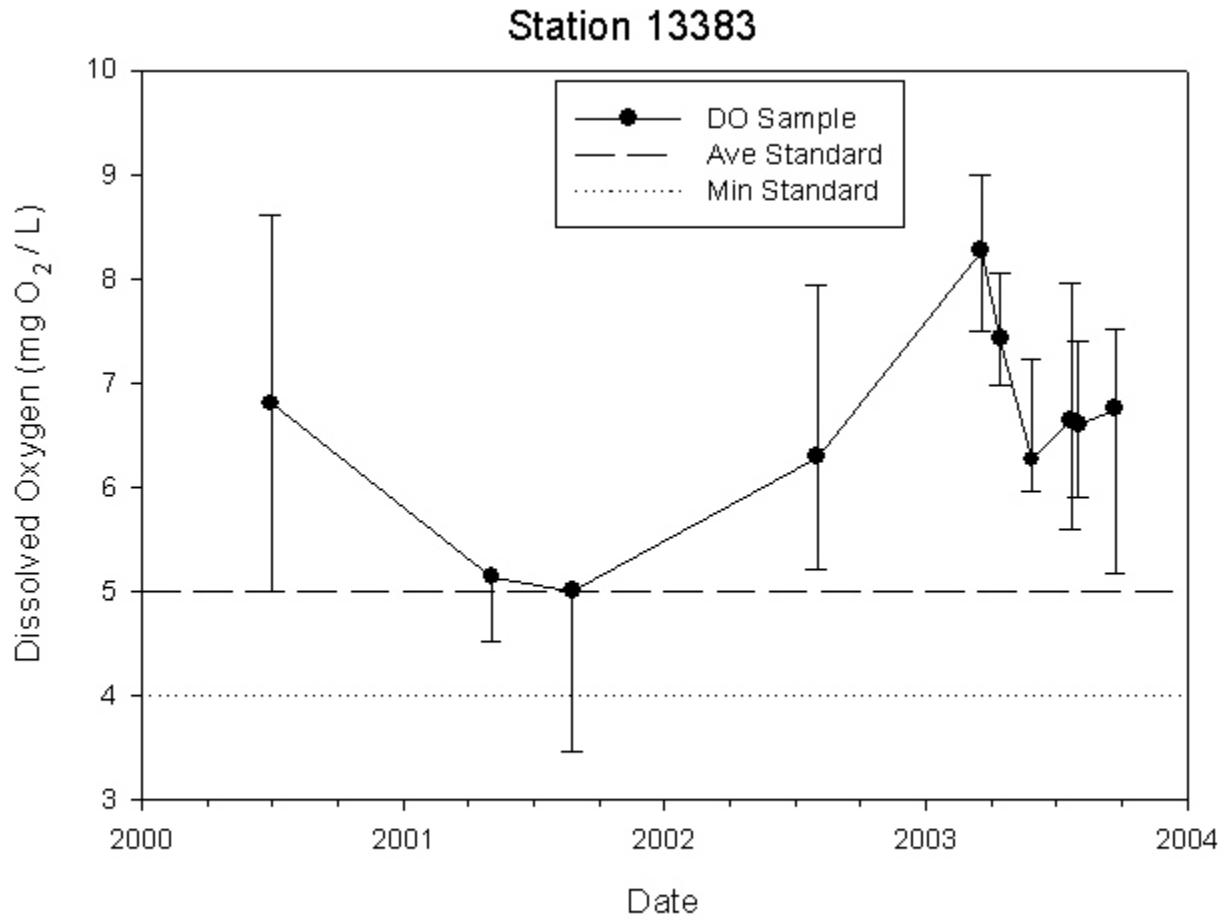


Figure 22: Dissolved oxygen assessment data for Station 13383. Average 24-hour values (symbol), minimum 24-hour values (lower tick), and maximum 24-hour values (upper tick). Dashed reference line is at the 24-hour average standard (5 mg/L) and dotted reference line is at the 24-hour minimum standard (4 mg/L).

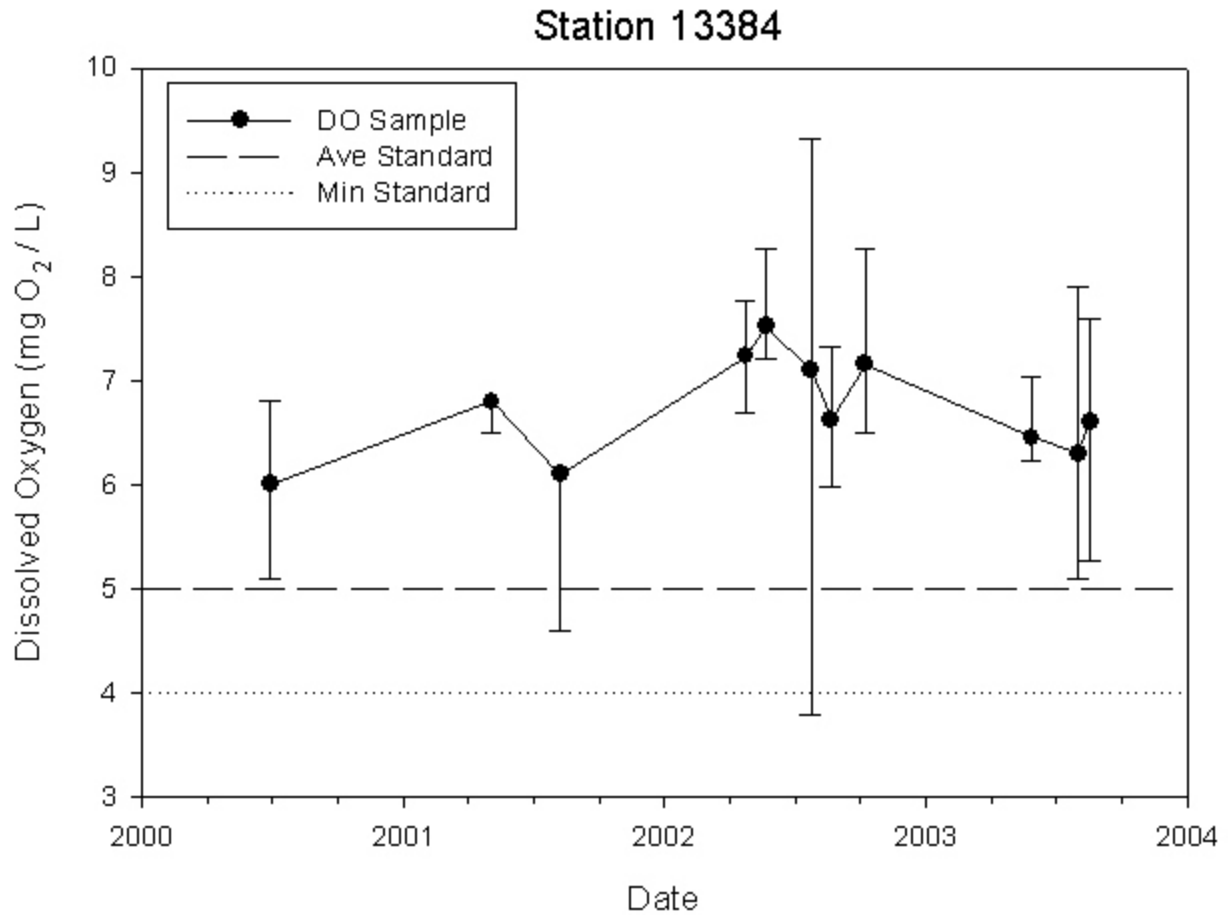


Figure 23: Dissolved oxygen assessment data for Station 13384. Average 24-hour values (symbol), minimum 24-hour values (lower tick), and maximum 24-hour values (upper tick). Dashed reference line is at the 24-hour average standard (5 mg/L) and dotted reference line is at the 24-hour minimum standard (4 mg/L).

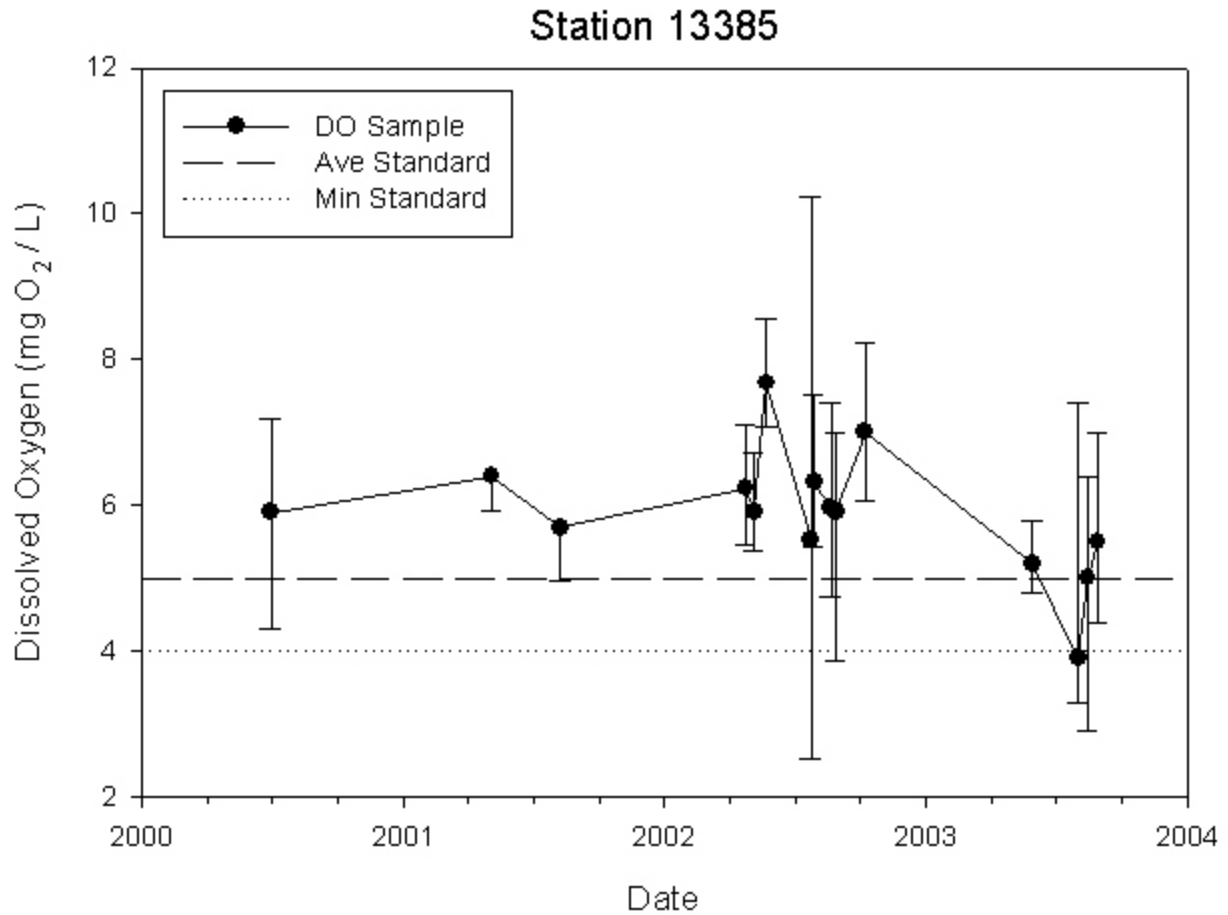


Figure 24: Dissolved oxygen assessment data for Station 13385. Average 24-hour values (symbol), minimum 24-hour values (lower tick), and maximum 24-hour values (upper tick). Dashed reference line is at the 24-hour average standard (5 mg/L) and dotted reference line is at the 24-hour minimum standard (4 mg/L).

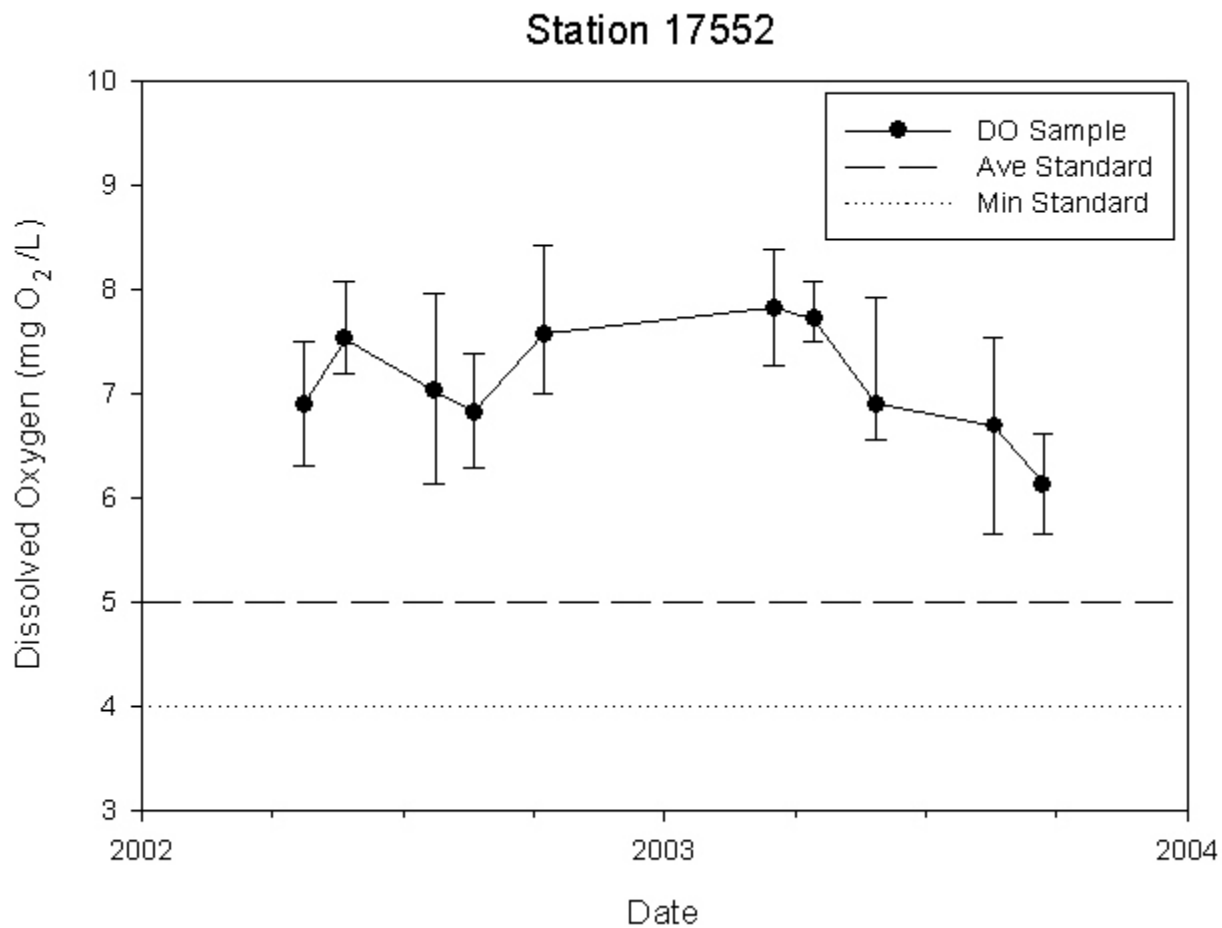


Figure 25: Dissolved oxygen assessment data for Station 17552. Average 24-hour values (symbol), minimum 24-hour values (lower tick), and maximum 24-hour values (upper tick). Dashed reference line is at the 24-hour average standard (5 mg/L) and dotted reference line is at the 24-hour minimum standard (4 mg/L).

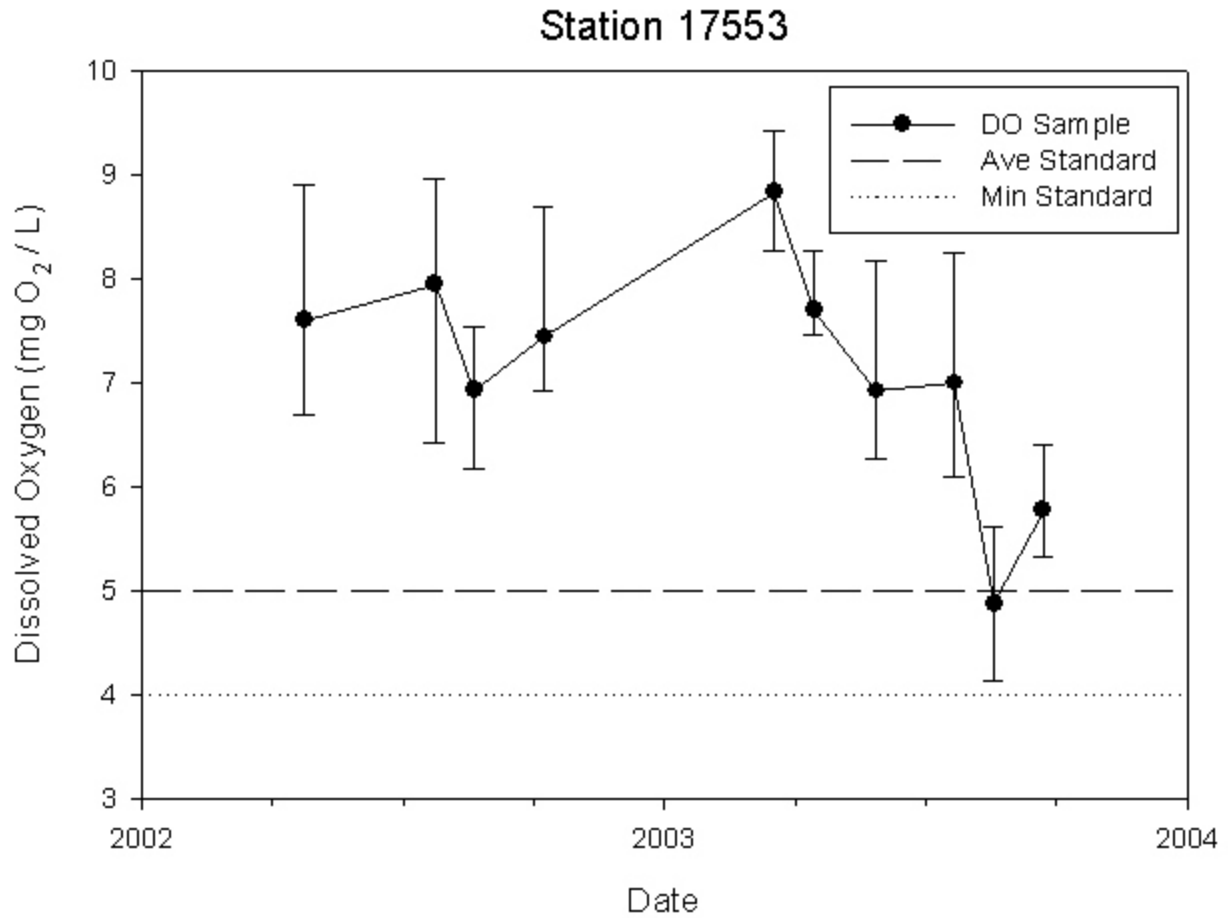


Figure 26: Dissolved oxygen assessment data for Station 17553. Average 24-hour values (symbol), minimum 24-hour values (lower tick), and maximum 24-hour values (upper tick). Dashed reference line is at the 24-hour average standard (5 mg/L) and dotted reference line is at the 24-hour minimum standard (4 mg/L).

Station 17554

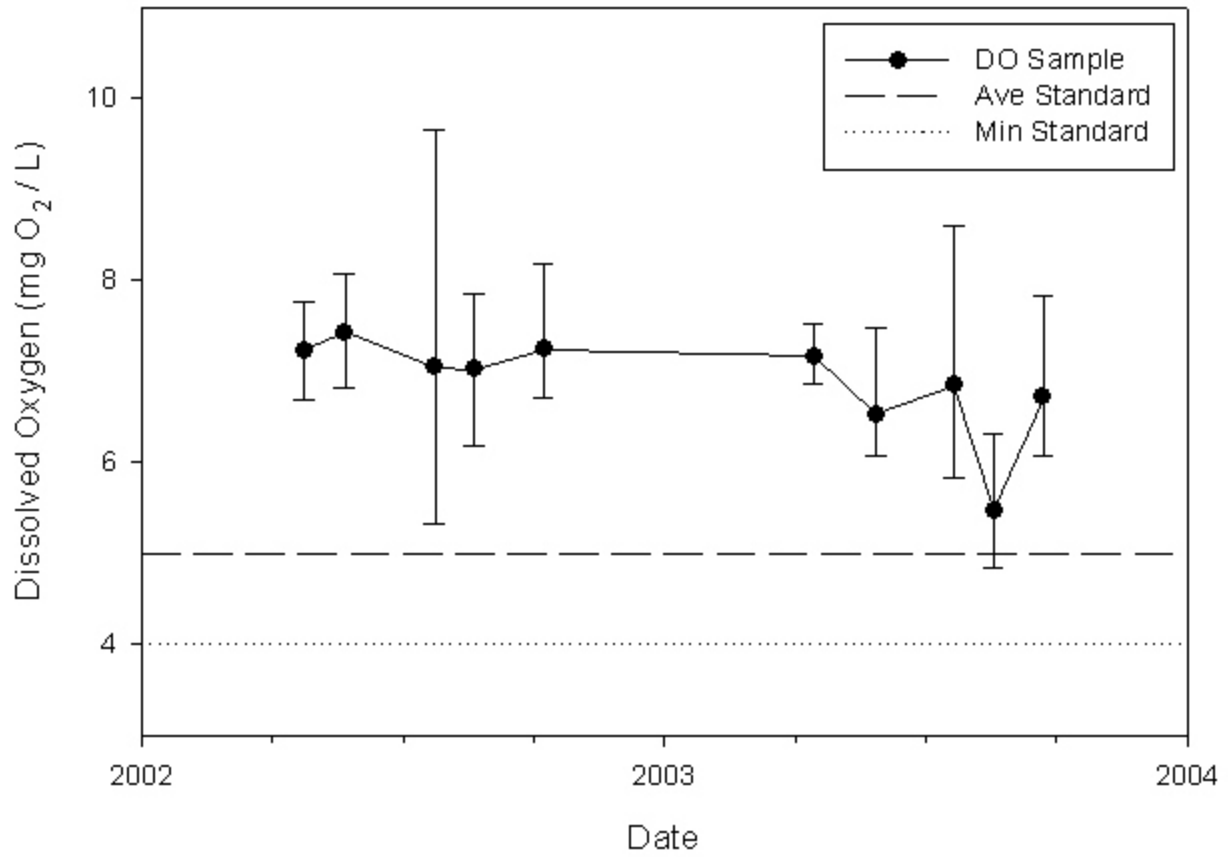


Figure 27: Dissolved oxygen assessment data for Station 17554. Average 24-hour values (symbol), minimum 24-hour values (lower tick), and maximum 24-hour values (upper tick). Dashed reference line is at the 24-hour average standard (5 mg/L) and dotted reference line is at the 24-hour minimum standard (4 mg/L).

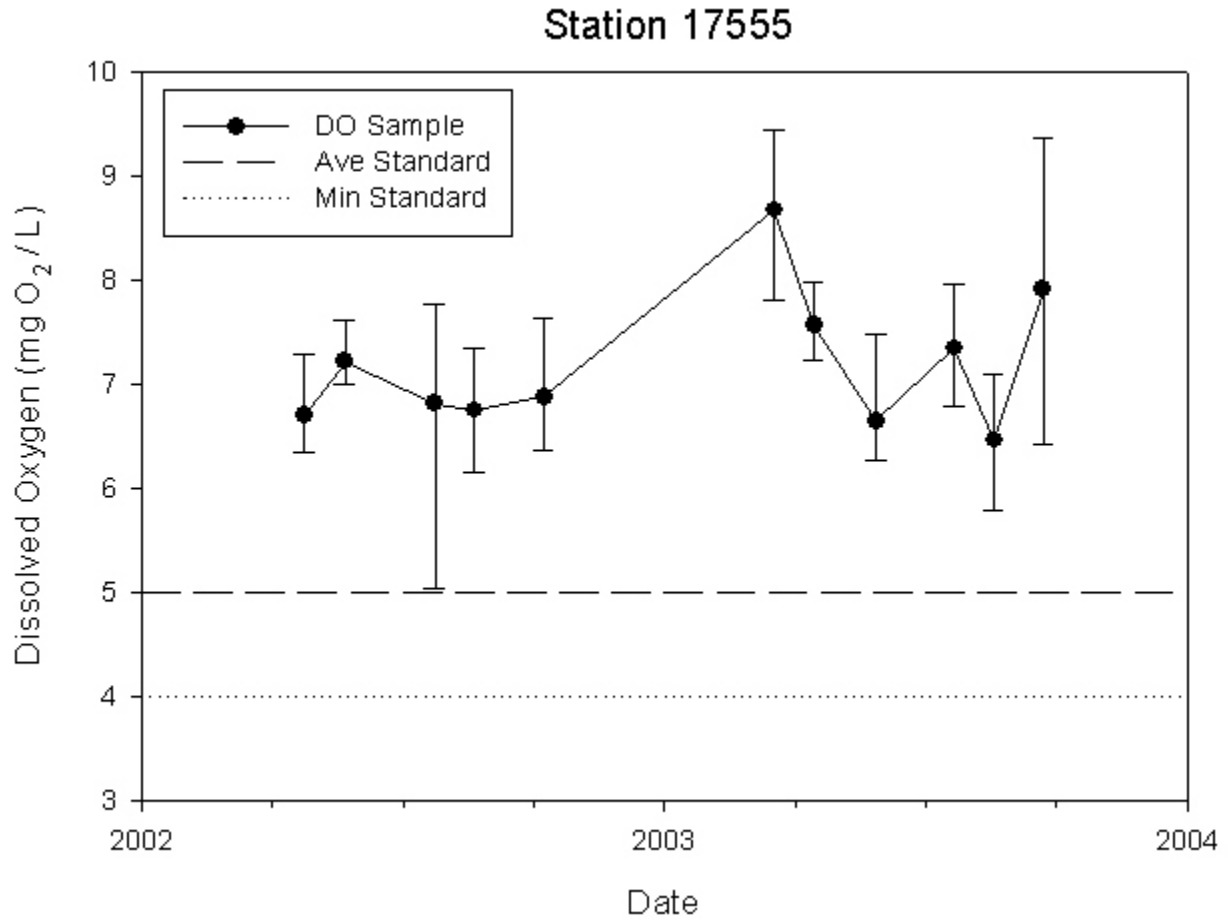


Figure 28: Dissolved oxygen assessment data for Station 17555. Average 24-hour values (symbol), minimum 24-hour values (lower tick), and maximum 24-hour values (upper tick). Dashed reference line is at the 24-hour average standard (5 mg/L) and dotted reference line is at the 24-hour minimum standard (4 mg/L).

Conclusions

The Texas Clean Water Act 303(d) list identifies Lavaca Bay/Chocolate Bay (TCEQ Segment 2453) as having dissolved oxygen concentrations that occasionally exceed the criteria established to support the segment's exceptional aquatic life designation. The spatial extent of this impairment centers around the Alcoa Ship Channel and extends out to cover a 13.7-square mile area. The historical data review identified that low DO conditions are primarily in deeper navigation channels and occurs primarily in summer. A DO monitoring plan was completed to assess the spatial and temporal occurrences of DO exceedences in segment 2453.

Dissolved oxygen concentrations in Lavaca Bay segment 2453 were found to be a function of physical conditions, such as temperature and salinity, and biological factors that use or produce oxygen, such as organic carbon remineralization and primary production. The physical conditions in segment 2453 when taken alone result in average dissolved oxygen concentrations from around 7 to 8 mg O₂ / L. The biological component of the ecosystem has a large influence on these averages, however, under various special conditions. Dissolved oxygen concentration may increase on sunny days when water current velocities are low. This production of oxygen is done by photosynthetic organisms and can be increased by recent influxes of nutrients limiting to photosynthesis. These influxes often come from freshwater inflow. Freshwater inflow, however, can also be responsible for decreasing oxygen concentrations when they bring with them or cause the production of organic matter. Oxygen is consumed as this organic matter is remineralized by organisms. The combination of physical and biological factors in segment 2453 result in spatial and temporal trends in DO concentration and variability

If physical conditions are taken alone, average and minimum dissolved oxygen concentrations in segment 2453 would be above the lower limits that TCEQ uses to define an impaired exceptional aquatic use designated estuary. Biological processes, even though sometimes producing large daily variability in daily dissolved oxygen concentrations, when coupled with physical conditions are only responsible for lower than required average dissolved oxygen concentrations 2.6% of the time and minimum requirements 6.5% of the time. These occurrences are well below the 10% limits set by TCEQ. The spatial extent of exceedences is small with the majority of occurrences of low dissolved oxygen located at site 13385, the ALCOA ship docks. Here water depth is increased by the shipping channel and water currents may be reduced by the physical structure of the docks. The increased depth may increase the likelihood of a stratified boundary layer above where dissolved oxygen measurements were taken. This could have led to reduced oxygen concentrations as the bottom water becomes unable to replenish oxygen from the atmosphere that is being used up by benthic processes. Decreased current speed results in water remaining in this area longer than in less restricted areas. Processes that reduce oxygen in this water thus have longer to act upon its dissolved oxygen concentrations. The temporal extent of exceedences is also small with all occurrences taking place during late summer months when higher temperatures and sunlight intensities may drive both physical and biological processes to lower oxygen concentrations. Different forcing factors may drive DO concentrations in the upper and lower bay areas. The upper bay DO concentrations follow a non-seasonal pattern and may be controlled by freshwater inflow events. The lower bay follows a more seasonal pattern. Overall Lavaca Bay segment 2453 dissolved oxygen concentrations are unimpaired for its exceptional aquatic life use designation.

RECOMMENDATIONS

Lavaca Bay segment 2453 does not currently appear to suffer from dissolved oxygen impairment. Segment 2435 supports exceptional aquatic life use. Based on the data presented in this report it is recommend that the segment be removed from the 303(d) list for dissolved oxygen.

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APPENDIX A: 24-Hour DO Monitoring Fact Sheet

<p>Index period for sampling:</p>	<p>March 15 - October 15. All sampling events must occur within the index period. However, at least one sample and between half and two thirds of each year's samples must be taken during the critical period of July 1 - September 30. No more than 2/3 of the samples should be taken in the same year. Sampling events should be more than one month apart. A total of ten 24-hour measurements within a two to five year period is required to provide assessment of the aquatic life use. For perennial streams, in order to determine criteria support, all ten measurements must be at or above the 7Q2, so more than ten sample-collection events may be needed. The 7Q2 for classified segments is listed in Appendix B of the TSWQS. For unclassified waterbodies, contact Suzanne Vargas: svargas@TCEQ.state.tx.us; (512) 239-4619, of the Modeling and Assessment Team to determine 7Q2. To avoid collecting samples below the 7Q2, it is recommended that flow be determined before beginning a 24-hr sampling run.</p>
<p>Depth on streams, reservoirs, or estuaries:</p>	<p>Deploy sonde at a point between a depth of 1 foot and a depth of ½ the mixed surface layer.</p>
<p>How often to record:</p>	<p>Measurement interval should be no more frequently than once per 15 minutes and no less than once per hour. Four or more dissolved oxygen measurements may also be made manually at even intervals over one 24-hour period at a site, as long as one is made near sunrise to approximate the daily minimum.</p>
<p>Data reporting:</p>	<p><u>Parameter Codes</u></p> <ul style="list-style-type: none"> • 24-hour averages DO: 89857; temperature: 00209; specific conductance: 00212; pH n/a • # of measurements over a 24-hour period: 89858 • Minimum values DO: 89855; temperature: 00211; specific conductance: 00214; pH: 00216 • Maximum values DO: 89856; temperature: 00210; specific conductance: 00213; pH: 00215 <p><u>Program Codes</u></p> <ul style="list-style-type: none"> • Diel sampling (multiple field measurements conducted over a 24 hr period and/or summary 24 hr D.O. statistics), not conducted under the scope of a TMDL QAPP: DI • Diel sampling conducted under the scope of a TMDL QAPP: TI

<p>QA requirements:</p>	<ul style="list-style-type: none"> • If sampling is multiday, the measurement (average) used for the assessment will be the first 24-hour period recorded during the deployment. Following multiday deployments, evaluate and report only creditable data (free from drift). • During initial multiday sampling, drift must be checked each day with a recently calibrated separate instrument, until it is known how long the multiprobe can be deployed before significant drift occurs. • Reference checking of the multiprobe will generally be required at 3-7 day intervals. • When setting up a YSI, ensure that the warm up time is set at 90 seconds, rather than the instrument default. • Twenty percent of the time, deploy two sondes in the same general area as a test of how spatially variable conditions are at deployment sites. This QA check may be revised after we have gained some experience.
<p>When to collect other routine field measurements and water samples:</p>	<p>Should collect at either the time of deployment, reference check, or retrieval of 24-hour monitoring multiprobe. Flow must be measured at site unless it is not possible to do so.</p>
<p>Priority for scheduling 24-hour sampling:</p>	<ol style="list-style-type: none"> 1. 303d listed waterbodies 2. Waterbodies with Concerns for DO problems (too few samples available for full use assessment). 3. Occurrence of low DO concentrations observed during the day 4. Waterbodies with trends indicating declining concentrations 5. Waterbodies which would contribute to Eco-region data set

APPENDIX B: YSI Sonde Methods

Standard Operating Procedure: SOP UT03

Pre-Deployment Calibration Preparation For Deployment Field Work Post-Deployment Calibration Maintenance and Storage

1. Introduction

1.1. This SOP describes the laboratory and field procedures used to determine water quality measurements from field deployments of a YSI 6-series Multi-parameter Water Quality Monitors. Models used are 6920-S and 600XLM data sondes with 610-DM and 650 MDS display loggers. These units can be used for hand-held discrete sampling and unattended continuous sampling. Parameters measured are date, time, depth, temperature, conductivity, salinity, pH, oxygen, and chlorophyll. Calibration is performed prior to, and after, sampling to assure data quality. The recommended order of calibration is conductivity, pH, oxygen, chlorophyll, and depth. A “Calibration Tips” handout was obtained from Michael Lizotte, YSI Applications Engineer, at the March 2001, YSI training seminar. The procedures below are derived from this training and from the YSI Environmental Operations Manual (1999).

1.2. The approach to obtaining high quality data from sondes is to ensure that calibrated values are repeatable at the end of the measurement period. The steps are to: 1) calibrate the sondes before field measurements (pre-deployment calibration), 2) start data logging, 3) log for a latent period in 100% saturated environment with stable temperature and pressure, 4) make field measurements, 5) log for post-deployment period in 100% saturated environment with stable temperature and pressure, 6) stop logging, download data, and 7) calibrate probes. Data is of acceptable quality when: 1) the pre- and post-deployment latent period data equilibrate to the same levels, and 2) pre- and post-deployment calibration values are the same within acceptable ranges.

2. Pre-Deployment Calibration

2.1. Conductivity. This procedure calibrates conductivity, specific conductance, salinity, and total dissolved solids. This parameter is measured with the sonde upright. The conductivity probe is pre-rinsed with conductivity standard and the rinse is disposed. Clean conductivity standard is used to fill the calibration cup to the appropriate volume listed in the table below. Volumes of standard required will vary depending on model used. For maximum accuracy, the conductivity standard used should be within the same conductivity range as the water sampled. For example: 1 mS/cm is used for fresh water, 10 mS/cm for brackish water, and 50 mS/cm for seawater. Error messages are usually caused by incorrect entries, for example, entering 50,000 micro-Siemens per cm (μS) instead of 50.0 milli-Siemens per cm (the sonde requires input in mS). Connect sonde to the PC with a field cable, access EcoWatch for Windows, proceed to Main menu, and select **2-Calibrate**. Immerse probe and rotate up and down to insure that vent hole is covered and no bubbles are present. Allow one minute for temperature equilibration, select **1-Conductivity, 1-SpCond**, enter calibration value,

and press **Enter**. When Specific Conductance or Conductivity readings show no significant change for ~ 30 seconds, press **Enter**, and the screen will indicate that calibration has been accepted, then press **Enter** again to return to Calibrate menu. Following calibration, conductivity should read the same as the standard used, and the conductivity cell constant should read ~ 5.0 (± 0.45). The standard is then recycled and used as probe rinse for the next calibration.

6920 Sondes

Probe to Calibrate	Upright	Upside Down
Conductivity	200ml	200ml
pH/ORP	100ml	250ml
Ion-Selective Electrodes (ISE)	125ml	275ml
Turbidity or Chlorophyll	25ml	N/A

600XLM Sondes

Probe to Calibrate	Upright	Upside Down
Conductivity	50ml	50ml
pH/ORP	25ml	50ml

All calibration data is written on the calibration form (Appendix A).

2.2. pH. A 2-point calibration is performed for pH with the sonde in the upright position using pH buffer solutions 7 and 10. The pH probe is pre-rinsed with the pH buffers 7 and 10 at the appropriate calibration times. The cup marked “pH 7 Buffer” is filled with the appropriate volume of buffer, one minute is allowed for temperature equilibration, select **4-ISE1 pH**, and then press **2- 2-point**. Press **Enter**, type in the value of the buffer, and press **Enter** again. Observe the pH readings and when they show no significant change for ~ 30 seconds, press **Enter**, and calibration is accepted. A millivolt (mV) reading is also taken by going to the Main Menu, selecting **Report**, and making sure “**pH mV**” is highlighted (buffer 7 should read $\sim 0 \pm 50$ mV). The buffer is then recycled. The cup marked “pH 10 Buffer” is filled to the appropriate volume, and the sonde is calibrated for the second pH using the steps stated above. Once again, a mV reading is obtained (buffer 10 should read $\sim -180 \pm 50$ mV) and the buffer is recycled. After recording the pH (mV), the slope of the sensor is determined by calculating the difference between the two calibration points that are used, for example:

$$\begin{array}{r}
 -177 \text{ mV} \quad \text{recorded for buffer 10} \\
 - \quad 3 \text{ mV} \quad \text{recorded for buffer 7} \\
 \hline
 -180 \text{ mV} \quad \text{slope of the sensor}
 \end{array}$$

*Note: The acceptable range of the absolute value of the slope is between 165 to 180. If the absolute value of the slope falls below 165, the sensor should be taken out of service.

2.3. Dissolved Oxygen. Before complete DO pre-calibration, the DO membrane should be checked and changed if it appears punctured, torn, or if a bubble is present. While holding the probe in a vertical position, apply enough KCl solution to form a meniscus, and secure a membrane between your left thumb and the probe body. With the thumb and forefinger of your right hand, grasp the free end of the membrane, and in one continuous motion, gently stretch it up, over, and down the other side of the sensor. Secure the end of the membrane under the forefinger of your left hand, and roll the O-ring over the end of the probe, being careful not to touch the membrane surface with your fingers. Small wrinkles may be removed by lightly tugging on the edges of the membrane. If bubbles are present, remove the membrane and repeat steps above. Trim off any excess membrane with a scalpel or scissors. Membranes may be considered slightly unstable during the first 3 to 6 hours after installation and complete DO pre-calibration should not take place until after this time period.

Use tap water in the calibration cup to rinse probe and discard of water after use. For calibration, place approximately 3 mm of tap water in the calibration cup and tighten cup onto sonde. Then turn sonde upside-down, secure support stand, loosen lid of calibration cup, and let the probe sit for 10 minutes to allow the air to saturate before proceeding. From the Calibrate menu, select **2-Dissolved Oxy**, then **1-DO%**, and enter current barometric pressure in mm of Hg into computer (Inches of Hg X 25.4 = mm Hg). Press **Enter**, observe the DO% readings, and when they show no significant change for ~ 30 seconds, press **Enter**. The screen will indicate the calibration has been accepted, press **Enter** again to return to the Calibrate menu. The DO % should read ~ 100.0 % and after five minutes, the DO Charge should read ~ 50 (\pm 25).

*Note: while waiting for DO % value to stabilize, the value should always start high and decrease to 100.0 %, it should never start low and increase to 100.0 %. If this occurs, probe should be rejected and not deployed.

2.4. Depth. Sonde is set up the same way as for dissolved oxygen, in water-saturated air. From the Calibrate menu, select **3-Pressure-Abs**, input 0.00, and press **Enter**. When no significant change occurs for ~ 30 seconds, press **Enter** for confirmation, and **Enter** again to return to the Calibrate menu.

2.5. Chlorophyll. A 1-point ($\mu\text{g/l}$) calibration is performed by filling the calibration cup with the appropriate volume of DI water listed in the table above. Input the value 0 $\mu\text{g/L}$, press **Enter**, and the screen will display real-time readings to monitor stabilization. The wiper is activated 1-2 times by pressing **3-Clean Optics** to remove bubbles from the sensor. Calibration is completed by pressing **Enter** for confirmation, and then **Enter** again to return to the Calibrate menu.

There are two ways to calibrate the YSI chlorophyll system: 1. dye solutions (Acridine Orange and Rhodamine B & WT) and 2. algal suspensions (water samples). As illustrated in the Calibration Tips handout, Acridine Orange and Rhodamine B or WT dyes may be used to calibrate the chlorophyll sensors, but both of these standards will almost certainly be less accurate than using samples of algae whose chlorophyll has been pre-determined by extractive analysis. Neither of the dyes directly correlates to Chlorophyll *a*, *b*, *c*, or *d* units. Dye standards should only be used as an

approximation that can be confirmed or adjusted later using the extractive analysis data from the water samples acquired during the study. For best results, use only freshly analyzed or prepared chlorophyll standards. Dyes may also be harmful to one's health; the algal suspensions pose no threat.

2.6. Battery Voltage. Batteries in the sonde are checked to ensure sufficient voltage is present to last through an entire deployment period. The amount of voltage required depends on how often measurements are taken. For instance, taking a reading every 15 minutes allows the sonde to be deployed for a longer period of time compared to a reading taken every 2 minutes (depending on model). Select **2-Unattended Sampling** from the Run menu, then **7-Battery** to make sure the battery voltage is suitable for the length of study, and option **8-Battery life** will calculate the approximate number of days that the batteries will last. The sonde software automatically calculates the battery life and the time it takes for the sonde memory to become filled based on duration and interval of the study.

3. Preparation for Deployment

3.1. Discrete Sampling (spot-checking). All equipment is prepared the day before use. Membranes are changed if needed. The sonde is wrapped entirely in wet, white towels and placed in a plastic graduated cylinder for stabilization and transport. This serves three main purposes: it produces a constant environment of saturation for the sonde, functions as a shock absorber against vibrations, and reduces extreme temperature changes that may occur in the field.

3.2. Unattended monitoring. As with discrete sampling, all equipment is prepared the day before and membranes are changed as needed. Select **2-Unattended Sampling** from the Run menu, **1-Interval** to enter the desired time between samples, **2-Start Date** and **3-Start Time** to set the time that data will begin to log to the sonde memory. The date and time can be verified and/or corrected any time using options **4-Status** or **5-System menu** from the Main menu. Enter **4-Duration** to set the length of study in days, **5-File** to enter a name of no more than 8 characters, and **6-Site** to enter a site name of no more than 31 characters. This filename will appear in the sonde file directory, but will not be used to identify the file after transfer to the computer. When all information has been entered for unattended setup, press **C-Start Logging**, a confirmation screen will appear, select **1-Yes** and the display will show the next date and time that a reading will be logged in addition to the stop date and time ending the study. Note the bottom command will show **B-Stop Logging**, a confirmation that the logging has been initiated.

The sonde is protected against bio-fouling organisms (barnacles and algae) by wrapping it in plastic food wrap covered with duct tape being sure to leave the depth/pressure sensors uncovered (the 2 cm circle on the side of the sonde just above the grooves where the storage cup is affixed). The sonde is left overnight wrapped in damp, white towels so that DO data remains constant and forms a pre-calibration line prior to deployment.

4. Field Work

4.1. Discrete Sampling. The sonde is wrapped in towels during transit. Upon arrival at the site, the boat is anchored and the following information is recorded at every station just prior to placing the sonde in the water: station number, date, time, refractometer/salinity, wind speed and direction, a

calibration reading for DO % and DO charge (see Appendix B, Field Data Form). The sonde is then lowered into the water at project specific depths. For example, if a project calls for depth profiles, the sonde will initially be deployed at 0.00m (surface) and successively lowered 0.50m until the bottom is reached. Parameters measured during deployment are depth (suggested at 0.5 m intervals starting with surface), temperature (°C), salinity (ppt), D.O. (mg/l), D.O. saturation (%), conductivity (mV), and pH. Once data is collected from a site, the sonde is placed back into the graduated cylinder for transport to the next station. This process is repeated until data from all sites have been recorded. Upon arrival to the lab, the sonde and probes are rinsed thoroughly with tap water and the calibration cup, containing ~ 25 ml of tap water, is fastened to the sonde for storage.

4.2. Unattended Monitoring. Sondes (covered in plastic food wrap and duct tape to prevent bio-fouling) are wrapped in damp towels during transit. Upon arrival at the site, the boat is anchored with a 3-point mooring; one off the bow, and one off each side of the stern (Figure 1). The main PVC pole measures approximately 20 ft in total length with 10 ft in the sediment and 10 ft throughout the water column. It is jettied into the sediment off the center of the stern using a gasoline-powered 2 in. centrifugal water pump. Signs denoting the area as a University of Texas experimental site are tied to a 2 m long, 2 in diameter pvc pole that is driven ~ 1 m into the sediment making sure to leave enough slack allowing for floatation. Each floating sign is placed about 15 - 20 ft from the main pole situated at 90° angles. Location of the signs should form a large triangle off the stern of the boat (Figure 1). Since the exact location of the sondes cannot be detected from the surface, three 1/8 inch nylon safety lines are tied from the main pole along the bottom to each of the 2 m poles securing a sign. This allows divers to locate the sondes starting from any of the three floating signs. This distance measures ~ 15 - 20 ft. from pole to pole (from each sign to the sondes). Sondes are secured with stainless steel hose clamps to the main pole using a 5/16 screwdriver. The depth at which sondes are deployed is project specific. For example, if a project requires that bottom dissolved oxygen be monitored, the sonde will be deployed within 25cm of the benthos. A final line is attached from each of the metal ring handles of each sonde to 1m long, 1 in pvc poles adjacent the main pole for additional security (inset of Figure 1). It is important that the probes are not exposed to air or left out of the water for any period of time during deployment; therefore, changes in the tides are accounted for when these instruments are mounted.

The length of all lines and pvc poles depends on depth of the water that is sampled, which varies at each site.

4.3 Retrieval of Sondes after Unattended Monitoring. The sondes are removed from the water, the time is recorded, and the sondes are wrapped entirely in damp, white towels and placed in the plastic graduated cylinder. As soon as sonde probes acclimate to the damp environment in the cylinder, a post-deployment calibration begins. This is a critical time, so the sondes are left overnight and untouched in the cylinder to ensure a stable environment. During this period, parameters are allowed to restabilize to their original pre-deployment measurements; creating post-deployment calibration data to compare to the pre-deployment calibration data. The unattended monitoring terminates when the duration specified has expired or the battery life has ended. The logging period may be stopped before the specified duration has expired or the batteries are expended by selecting **2-Unattended** sample from the Run menu, then **B-Stop Logging**, and **1-Yes** to return to the Unattended setup menu.

4.4 Downloading/Uploading Data. After probes have stopped logging and a post-deployment calibration period has occurred, the data is downloaded from the sonde to a windows compatible computer using Ecowatch Software (Sections 2 & 4, YSI, 1999).

5. Final Post-Deployment Calibration

5.1. Conductivity. Repeat steps from complete pre-calibration, but do not recycle the standard.

Record all calibration values on a second calibration form (Appendix A).

5.2. pH. Repeat steps from complete pre-calibration, but do not recycle the buffers.

5.3. DO. DO membranes are not changed until after the complete post-deployment calibration is performed and recorded. All other steps from the complete pre-calibration are then repeated.

5.4. Chlorophyll. Repeat steps from complete pre-calibration.

5.5. Depth. Repeat steps from complete pre-calibration.

6. Clean-up and Maintenance of Sondes for Long-Term Storage

The plastic/duct tape wrap is carefully removed and the sonde is rinsed with tap water and dried. The sensor guard is carefully removed, the sensors are cleaned, and DO membrane is replaced. The storage cup is filled with ~ 25 ml of tap water and affixed tightly onto the sonde. The batteries in the sonde are replaced if needed. Barnacles and algae are removed from the sensor guard using a 2 normal HCl acid solution. The sensor guard is allowed to soak for ~ 30 minutes (as needed) and then brushed with a toothbrush. A mild detergent is used as a final wash and the guard is rinsed once again with water and dried.

7. Bibliography

YSI Inc. 1999. Environmental Monitoring Systems Operations Manual. Publication number 1700/1725 6-Series Sondes, Item # 069300, Drawing # A69300, Revision A. YSI Inc., Brannum Lane, Yellow Springs, Ohio 45387 USA.

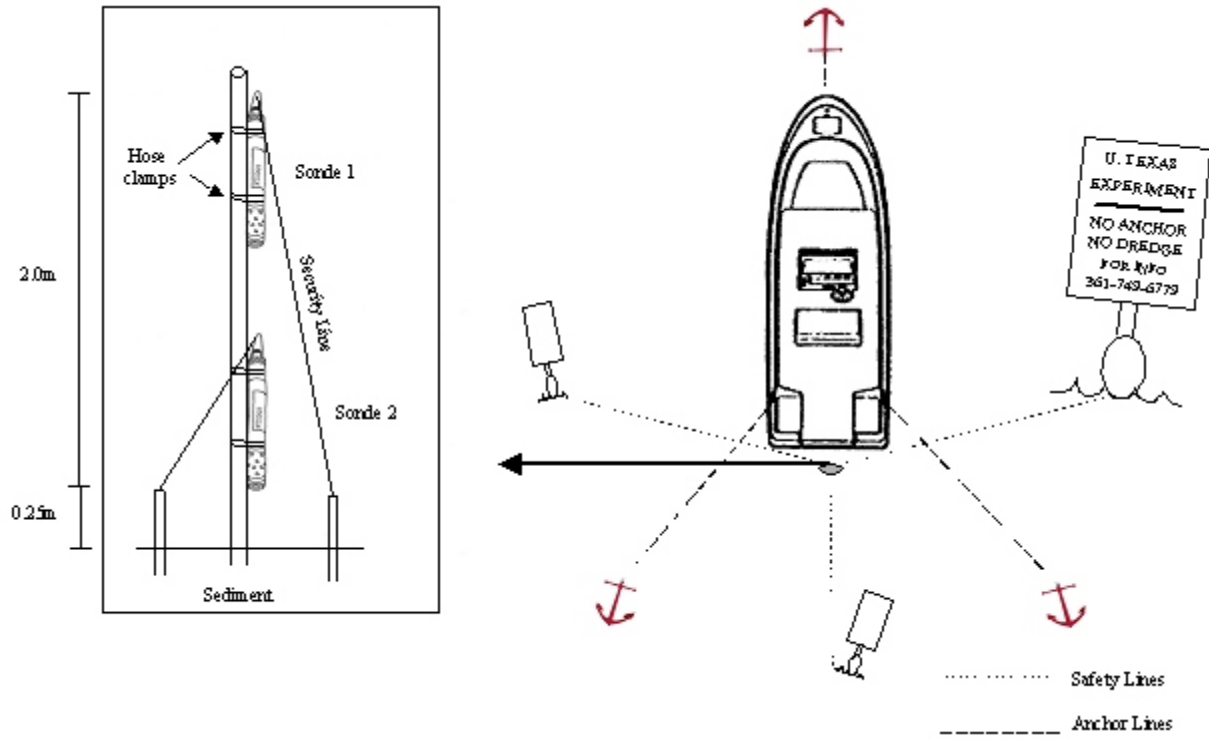


Figure 1: Deployment of continuously recording data sondes. Sondes are mounted on a pvc pole using a small boat. The pole location is fixed using a three-point mooring system (plan view shown on right). The location is marked using signs anchored to pvc poles. Inset on left shows vertical detail of an example of a placement and mounting of sondes on the pvc pole; number and depth of sondes deployed is project specific.

APPENDIX A: YSI CALIBRATION FORM

Sonde Unit id: _____ Date of Calibration: _____ Technician: _____

Calibration type: _____ Pre-deployment _____ Post-deployment

DO membrane changed? Y N *Note: Should wait 6 to 8 hours before final DO calibration, run sensor for 15 minutes in Discrete Run to accelerate burn-in.*

Date membrane changed: _____

Turbidity wiper changed? Y N Wiper parks ~ 180° from optics? Y N *Note: Change wiper if probe will not park correctly*

Chlorophyll wiper changed? Y N Wiper parks ~ 180° from optics? Y N *Note: Change wiper if probe will not park correctly.*

Record battery voltage: _____

Record the following diagnostic numbers after calibration. Record Calibration Values
Actual Sonde after cal

Conductivity cell constant _____	Range 5.0	+ 0.5	Conductivity	_____	_____
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pH MV Buffer 4 _____	Range +180	+ 50 MV	pH 4	_____	_____
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pH MV Buffer 7 _____	Range 0 MV	+ 50 MV	pH 7	_____	_____
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pH MV Buffer 10 _____	Range -180	+ 50 MV	pH10	_____	_____
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Note: Span between pH 4 and 7, and 7 and 10, milli-volt numbers should be ~ 170 to 180 MV

	ORP	_____	_____
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	Depth	_____	_____
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DO charge _____	Range 50	+ 25	Turbidity	_____	_____
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DO gain _____	Range 1.0	-0.3 to +0.4	Chlorophyll	_____	_____
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	DO	_____	_____
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Filename: _____ Site: _____

DISSOLVED OXYGEN SENSOR OUTPUT TEST (after DO calibration probe in saturated air)

The following tests will confirm the proper operation of your DO sensor. The DO charge and gain must meet spec before proceeding.

610/650 - Turn off the 610/650, wait 60 seconds. Power up 610/650 and go to the Run mode, watch the DO %output; it must display a positive number and decrease with each 4 second sample, eventually stabilizing to the calibration value in approximately 60 to 120 seconds. *Note: You can disregard the first two samples, they can be affected by the electronics warm-up.*

PC - Stop discrete and unattended sampling. Confirm that auto-sleep RS-232 is enabled (found in Advanced Menu under Setup). Wait 60 seconds. Start discrete sampling at 4 seconds. Watch the DO % output, it must display a positive number and decrease with each 4 second sample, eventually stabilizing to the calibration value in approximately 40 to 60 seconds. *Note: You can disregard the first two samples, they can be affected by the electronics warm-up.*

ACCEPT/REJECT criteria is as follows: The DO output in % must start at a positive number and decrease during the warmup. Example: 117, 117, 114, 113, 110, 107, 104, 102, 101, 100, 100. Should the output display a negative number or start at a low number and climb up to the cal point, the probe is rejected and must not be deployed.

_____ ACCEPT _____ REJECT

Notes: _____

APPENDIX B: HYDROGRAPHY FIELD DATA FORM

DATE _____ LOCATION _____ STATION _____

TIME _____ WIND DIR. _____ WIND SPEED _____

CLOUD COVER _____ WAVE HEIGHT _____ REFRACTOMETER _____

PERSONNEL _____

SAMPLES: MACROFAUNA _____ MEIOFAUNA _____

 SEDIMENTS _____ OTHER _____

NUTRIENTS: SURFACE _____ BOTTOM _____

CHLOROPHYLL: SURFACE _____ BOTTOM _____

CALIBRATION

%DO: _____

DO charge: _____

MULTIPROBE READINGS:

DEPTH (m)	TEMP (°C)	SALINITY (ppt)	DO (mg/l)	COND. (µS/cm)	DO (%)	pH	ORP (mV)

COMMENTS: _____
