WATER RECLAMATION
SOLID WASTE MANAGEMENT

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OF LOS ANGELES COUNTY

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GRACE ROBINSON HYDE
Chief Engineer and General Manager

May 15, 2019
File No: 31-300.25

VIA ELECTRONIC MAIL
Ms. Renee Purdy, Executive Officer
California Regional Water Quality Control Board
Los Angeles Region
320 W. 4th St., Suite 200
Los Angeles, CA 90013

Attn: Information Technology Unit

Joint Water Pollution Control Plant
CI No. 1758; Resolution R016-002; NPDES No. CA0053813
Special Study Final Report Submission

As required under Resolution R016-002, please find enclosed the final report for the following special study:

1) Baseline Assessment of Hypoxia and Ocean Acidification Events near the Seafloor in Santa Monica Bay (JWSS-16-002).

Unless otherwise instructed by the Regional Board or Regional Board staff, this will be the final submission associated with this Special Study. However, any other reports or peer-reviewed publications resulting from these studies will also be provided to Regional Board staff as they become available.

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

Very truly yours,

Philip Markle BCES
Senior Environmental Scientist
Reuse and Compliance Section
Technical Services Department

cc: Jeong-Hee Lim, Elizabeth Erickson, LA Regional Water Board
NM:AS:nm
Enclosure

DOC# 4911406

Baseline Assessment of Hypoxia and Ocean Acidification Events near the Seafloor in Santa Monica Bay (JWSS-16-002)

Final Report May 15, 2019

BACKGROUND

There are growing concerns that Ocean Acidification and Hypoxia (OAH), which is driven primarily by global carbon dioxide (CO_2) emissions (Chan *et al*., 2016), may decrease the aragonite saturation state (Ω_{arag}) and negatively impact marine shelled species. To properly characterize carbonate chemistry and determine Ω_{arag}, the California Current Acidification Network (C-CAN) recommends high frequency sampling of at least two carbonate chemistry parameters (e.g., pH and pCO_2); very precise pH measurements are needed to detect the small changes in pH and the corresponding changes in Ω_{arag} associated with OAH.

Under the current NPDES permit for the Joint Water Pollution Control Plant (JWPCP), conductivity, dissolved oxygen (DO), and pH are monitored quarterly. To augment this monitoring program and better assess OAH conditions, the Los Angeles County Sanitation Districts (Sanitation Districts) submitted a special study proposal to the Los Angeles Regional Water Quality Control Board (LARWQCB) staff on February 3, 2016. This study was subsequently approved by the LARWQCB on April 14, 2016 (Resolution R16-002). The primary purpose of this special study was to characterize oxygen and acidification in the coastal ocean off Santa Monica Bay (SMB) and Palos Verdes, using state-of-the-art sensors on a fixed mooring configured to record continuously, and remain in service for two years. The study was a collaborative effort with the Santa Monica Bay Restoration Commission (SMBRC), the Southern California Coastal Water Research Project (SCCWRP), and the City of Los Angeles (City of LA). Interest in the data from this study has come from the California Current Acidification Network (C-CAN), Ocean Acidification and Hypoxia (OAH) modelers at the University of California Los Angeles, and the National Oceanic and Atmospheric Administration's National Estuary Program (NOAA NEP).

In partnership with the SMBRC, who provided for the purchase of sensors to monitor OAH through a grant from the NOAA NEP, the Sanitation Districts provided support for the deployment and maintenance of these instruments and for all data collection and management associated with this Special Study. The study design was developed and implemented to support the following objectives;

1. Establish a baseline dataset to assess and track OAH in the SMB
    a. Collect continuous, high quality data to identify variability patterns in oxygen, pH, and CO_2 using state-of-art sensors to:
        i. Identify seasonal, event scale and instantaneous extremes
        ii. Contribute to trends analyses
        iii. Support a variety of biogeochemical assessment studies
2. Provide data for validation of models being developed to assess the contribution of local anthropogenic nutrients sources to OAH and inform restoration efforts by the SMBRC
3. Contribute to the development of a long-term, high frequency coastal water quality monitoring network to assess spatial and temporal trends in OAH and high chlorophyll or harmful algal bloom (HABs) events and their associated impacts within coastal waters of Los Angeles County and beyond
4. Develop expertise in the operation and maintenance of moorings equipped with next generation oxygen and acidification sensors

Benefits of this study include the contribution of high-precision, time-series data on pH and pCO_2 to monitoring programs in SMB. Although this study was the Sanitation Districts initial effort to measure continuous OAH measurements, and had limited temporal and spatial extent, ultimately such data sets of high frequency changes in OAH within SMB are anticipated by both dischargers and regulatory agencies to be valuable for making management decisions. Incorporation of pH, pCO_2 and dissolved oxygen sensors will bring monitoring in SMB in-line with the West Coast-wide monitoring strategy proposed by the C-CAN. The Special Study also provides a proof of concept for using state of science instruments (pH, pCO_2, and oxygen) deployed to collect high frequency time-series data at representative locations on the shelf in the SMB. The collected data will be made available in support of ongoing research on OAH in SMB, including model validation, and C-CAN applications. These efforts are consistent with the objectives of the SMBRC Pelagic Ecosystem Comprehensive Monitoring Program and the data will also be presented and analyzed in future State of the Bay Reports.

METHODS

Figure 1 shows the location of the first year and second year moorings, as well as the locations of 48 CTD profiling sites that are sampled quarterly. During the first year the Sanitation Districts modified an existing thermistor string mooring located offshore of Palos Verdes Point in 26m water depth to accommodate the OAH sensors suspended at 15m depth. During the second year, the OAH sensors were relocated by adding a new mooring near the outer edge of the Palos Verdes shelf at a depth of 70m. The OAH sensors themselves were attached on the second year mooring at a depth of 60m. The first year mooring was closest to CTD site 3102, and the second year mooring was nearest to CTD site 3003.

To evaluate the comparability between the CTD measurements, and the OAH moored sensors, pH and oxygen data from the CTD profile site nearest the OAH mooring, and sampled at the at the same depth as the OAH sensors, were directly compared with the OAH sensor data collected simultaneously. To illustrate the spatial variability within the area covered by the CTD survey grid, pH and oxygen from all the CTD sites at the same depth as the OAH sensors were overlaid on plots of the OAH mooring results.

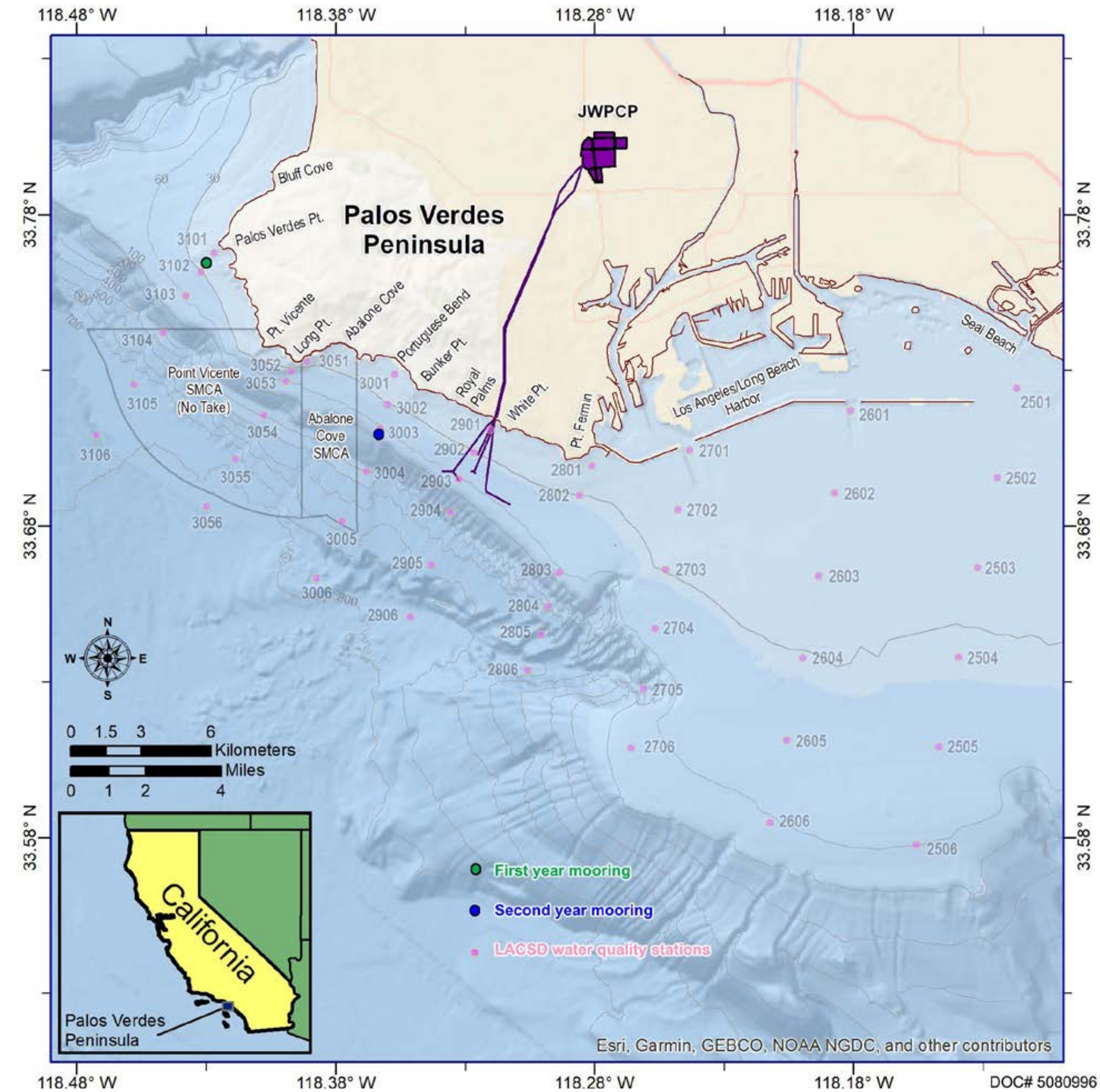

Figure 1 Map showing the First Year and Second Year OAH mooring locations. The map also shows locations of 48 CTD profiling sites sampled quarterly by the LACSD.

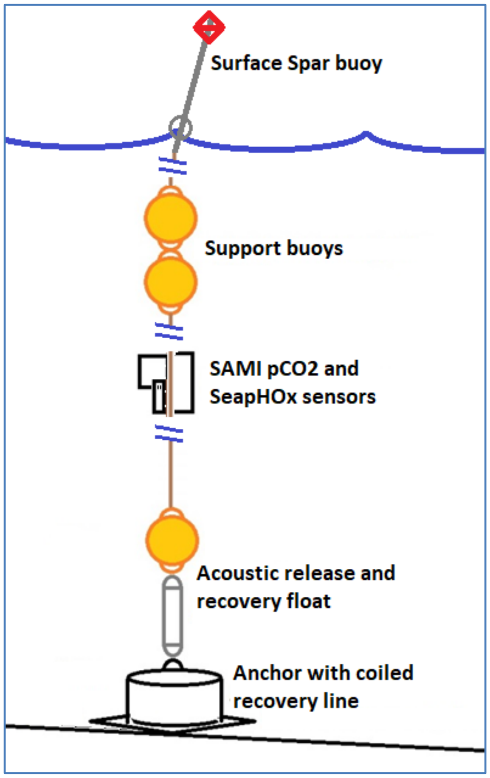

Figure 2 OAH mooring schematic

Figure 2 shows a schematic of the mooring arrangement. A surface spar buoy equipped with a radar reflector, and reflective tape marks the mooring location. The Sanitation Districts filed each mooring location with the Coast Guard and the mooring was listed on the Notice to Mariners.

Located several meters below the surface, support buoys keep the mooring line taut and vertical. The OAH sensors were located at 15m (first year) or 60m (second year), and in both cases, were suspended roughly 10m above the seafloor. A 180 kg anchor kept the mooring in place. An acoustic release and recovery float attached to this anchor were used to bring a recovery line to the surface for maintenance and data downloading.

Figure 3 SAMI pCO_2 sensor

The full characterization of seawater carbonate chemistry requires measurement of at least two independent parameters. In this case, the decision was made to deploy sensors to measure pCO_2 and pH. Additional sensors to measure oxygen, temperature and salinity were also incorporated. Descriptions of the selected sensor systems are listed below. Data for pCO_2 were collected using a SAMI Ocean CO_2 Sensor package (**Figure 3**) which measures the partial pressure of carbon dioxide in water. The sensor uses a highly precise and stable colorimetric reagent method, and provides in-situ time series data. The sensor is deployable to depths up to 600 meters and can be utilized for long-term deployments – a single reagent bag allows the unit to run for more than a year taking hourly measurements. The sensor is protected with a Biofouling Package to protect it in the highly productive environment off the Palos Verdes coast. The SAMI instrument also included a temperature probe.

The pH was collected with a Sea-Bird Scientific Deep SeapHOx™ (**Figure 4**) that combines the Deep SeaFET™ pH sensor with the SBE 37-SMP-ODO MicroCAT CTD+DO sensor. The Deep SeaFET adapts the MBARI/SIO/Honeywell Deep-Sea DuraFET technology to measure pH in a deep moored package. The MicroCAT CTD measures temperature and conductivity.

Figure 4 SeapHOx + CTD sensors

Field Operations – First Year

Due to a time constraint on the reagent pre-loaded in the SAMI instrument, and a delay in delivery of the SeapHOx instrument, the OAH sensors were not deployed together at the start of the study. The pCO_2 sensor was initially deployed at the first year mooring site on July 25, 2016, and the SeapHOx sensor package was added to the mooring on November 3, 2016. On December 4, 2016 Sanitation Districts' staff determined that the surface spar buoy was missing. Immediate investigation determined that the mooring cable had failed and without the subsurface floatation, the OAH sensors had sunk to the bottom. After recovery from the sea floor by Sanitation Districts dive team members, the sensors were redeployed on the repaired mooring on December 9, 2016. On January 24, 2017 the mooring was removed for 24 hours for additional modifications to the attachment system, before being redeployed on January 25, 2017. Subsequently, the mooring was serviced on April 6, 2017 and then on July 6, 2017. On September 1, 2017, the first year field work was completed, and the OAH sensors were removed for annual factory refurbishing and calibration.

Field Operations – Second Year

On January 26, 2018, the OAH sensors were redeployed at the second year mooring site at a depth of 60 m. A successful servicing and data recovery was completed on April 4. On May 9, 2018, Sanitation

Districts' staff noted that the surface spar buoy was missing. Using the bottom mounted acoustic release the mooring was recovered, repaired, and redeployed the same day. During the repair, inspection of the mooring suggested a vessel probably struck the surface spar buoy. The second routine servicing event was completed on July 10, however, after redeploying, staff noted that strong currents were submerging the spar buoy, so on July 11, 2018 the mooring was briefly released to add additional buoyancy on the buoy. The third mooring servicing event occurred on October 2, 2018 and the final recovery of the mooring was made on January 29, 2019. The Sanitation Districts maintains a detailed field log noting all activities and observations on every field activity (**Table 1**).

Table 1 – OAH Mooring Service Log (OAH SAMI and SeapHOx sensors)

Date	Mooring Release Time (PST)	Mooring Deploy (on bottom) Time (PST)	SAMI data logging start time (PST)	SeapHOx data logging start time (PST)	NOTES
First Year					
7/25/2016	-	1201	1300	-	Mooring deployed at first year site with SAMI pCO_2 but no SeapHOx
10/3/2016	0809	1038	1100	-	Recovery and servicing
11/3/2016	0832	1000	1000	1000	SeapHOx added to array; Did NOT turn SAMI off during the SeapHOx installation
12/4/2016*	1101	-	-	-	*Cable failure 12/4/16 last valid data point 11:00
12/9/2016	-	1338	1400	1400	Redeployed
1/24/2017*	0900	-	-	-	*Pulled sensor out of water overnight, modifications made to strongback
1/25/2017	-	1030	1000	1100	
4/6/2017	0813	1053	1000	1100	
7/6/2017	0759	1052	1000	1100	
9/1/2017					OAH sensors recovered for calibration
Second Year					
1/26/2018	-	1003	1100	1100	Mooring deployed at second year site
4/24/2018	0744	1125	1200	1200	First recovery and servicing
5/9/2018	1108	1235	1300	1300	Mooring strike; released gear & redeployed at nominal station location
7/10/2018	0730	1238	0900	~1215	Second recovery and servicing
7/11/2018	0808	1005	-	-	Mooring released to improve floatation on spar buoy
10/2/2018	0740	1019	1000	1000	Third recovery and servicing
1/29/2019	0800	-	-	-	OAH sensors recovered

During each maintenance/servicing event all mooring hardware and sensors were cleaned, thoroughly inspected, data were downloaded and checked in the field for acceptability, and the sensors were then configured to record data and the mooring redeployed. Typical servicing time was approximately 3 hours.

Throughout the study, the OAH sensors were configured to record data at one hour intervals. This was determined to be the most suitable time interval to balance battery life and reagent supplies against frequency of servicing, total duration of study, and expected scales of temporal variability in the data.

During the first and second years of the study a total of 6 and 9, respectively, discrete water samples were collected, either when the mooring was being serviced or during quarterly CTD surveys. Discrete samples were collected directly adjacent to the mooring, at the same water depth as the OAH sensors. These samples were delivered to the City of Los Angeles Environmental Monitoring Division (CLAEMD) Laboratory for alkalinity and pH analysis.

During the first year of the study, CTD casts were conducted directly adjacent to the mooring on six occasions (**Figure 5**). During the second year, CTD casts were made either at the mooring site or at the existing receiving water station 3003 (less than 100m from the mooring site) on four occasions. The Sanitation Districts uses a Sea-Bird SBE 9+ CTD with a glass electrode pH sensor, which is calibrated prior to each field use. The processed CTD data are stored at one meter intervals, and allow for direct comparison of pH, oxygen, temperature and salinity data at the same depth where the OAH sensors are attached.

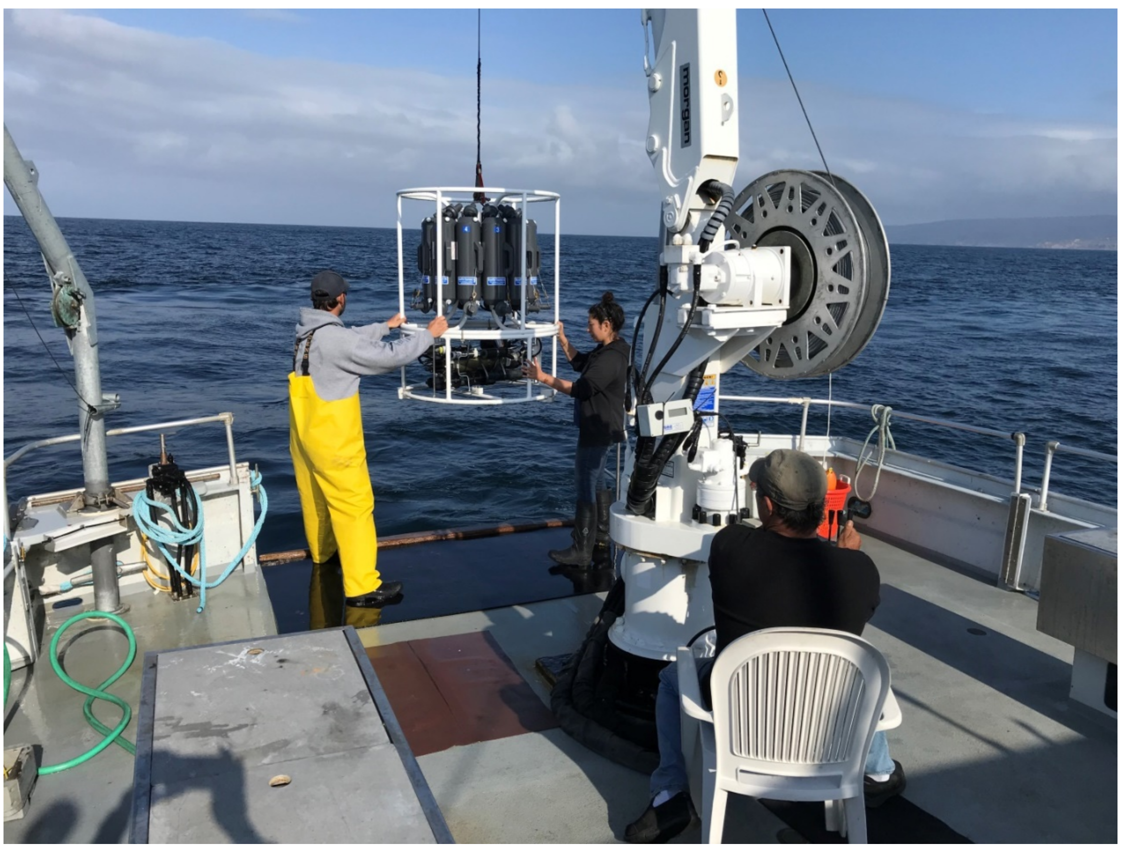

Figure 5 Sanitation Districts staff deploy the CTD

The Sanitation Districts developed a final data file formatted in Excel to hold integrated processed data from the OAH sensors. After each mooring servicing event, this file was appended with data from the most recent recovery. Other worksheets in this file tracked results from discrete sampling, and results from CTD casts made adjacent to the mooring during quarterly offshore water column monitoring cruises. Final data were distributed to SCCWRP and the SMBRC.

An Excel spreadsheet and Macro utility CO2SYS (Lewis and Wallace, 1998) were used to calculate the Ω_{arag} levels for every data record with a valid pH and pCO_2 reading.

RESULTS AND DISCUSSION

First Year Data Completeness

Data were compiled and reviewed after the OAH sensors were recovered on September 1, 2017; the verified data consisted of 8,389 hourly pCO_2 observations, for a data completeness rate of 87%. The majority of missing CO_2 data was due to the depletion of reagent and heavy biofouling during the last weeks of the deployment (**Figure 6**). The SeapHOx pH and oxygen sensors were delayed in deployment, but once in the water recorded 7,082 hours of good data, and achieved a data return rate of 98%.

Figure 6 After final recovery from the First Year mooring biofouling on the SAMI pCO_2 sensor was significant

Overall, acceptable CO_2 data were collected for 96% of the planned year-long deployment, and pH data were collected for 81% of a year-long period. However, because the sensors did not go into the water at the same time, and because the CO_2 sensor failed before the last deployment was completed, the overlapping period of simultaneous observations covers 5,986 hours, or 68% of the year-long period. Without both CO_2 and pH it is not possible to calculate the Aragonite saturation state.

Table 2. First Year at 15m Depth - Summary of Collected Data

Instrument	SAMI PCO_2		SeapHOx			
Dates deployed	7/25/2016 to 9/1/2017		11/3/2017 to 9/1/2017			
Parameter	Temperature	pCO_2	Temperature	Salinity	Oxygen	pH
Number of records	9515	8389	7082	7082	7082	7082
Percent complete	98%	87%	98%	98%	98%	98%
Minimum	10.02	306	10.09	32.571	3.68	7.64
Maximum	22.51	1417	21.85	33.604	11.50	8.20
Average	14.22	548	13.99	33.306	7.15	7.96

Second Year Data Completeness

Data were compiled and reviewed after the OAH sensors were recovered on January 29, 2019; the verified data covered 8,714 hourly pCO_2 observations, for a data completeness rate of 99%. The minimal missing CO_2 data were due to periods when the mooring was being serviced and when reagent blanks were being run through the system. The SAMI temperature, and SeapHOx temperature, salinity, and oxygen sensors recorded 8,815 hours of good data, and achieved a data return rate of almost 100%. However, a review of the final pH data, including discussion with the manufacturer, determined that the pH data from the later part of the study were invalid, probably due to sensor fouling that was only identified after the SeapHOx was returned to the factory for calibration. As a result, the acceptable pH data spanned only 65.9% of the deployment.

The OAH sensors were deployed and recovered simultaneously during the second year, and recorded for 100% of the yearlong period. However, due to the pH sensor fouling, the period of simultaneous observations covers 5,752 hours or approximately 66% of the year. Without both CO_2 and pH it is not possible to calculate the Ω_{arag} state.

Table 3. Second Year at 60m Depth - Summary of Collected Data

Instrument	SAMI PCO_2		SeapHOx			
Dates deployed	1/26/2018 to 1/29/2019		1/26/2018 to 1/29/2019			
Parameter	Temperature	pCO_2	Temperature	Salinity	Oxygen	pH
Number of records	8815	8714	8815	8815	8815	5819
Percent complete	99.8%	98.7%	99.8%	99.8%	99.8%	65.9%
Minimum	9.29	382	9.40	33.229	3.26	7.71
Maximum	16.84	1028	17.02	33.967	8.18	8.01
Average	11.88	694	11.99	33.576	5.64	7.82

Comparing the average levels between the first year (**Table 2**) and second year (**Table 3**), the key differences are related to the significantly deeper siting of the sensors in the second year. The average temperature, pH, and oxygen are lower at 60m than at 15m, while pCO_2 and salinity are higher at 60m than at 15m.

Time Series Analysis

For the following discussions, time series graphs of data from both the first year and second year moorings use a consistent x-axis of 410 days, on every graph, with the data collection period centered in the graphs. For the first year graphs, the 15m depth OAH sensor results are plotted using an x-axis that spans from 7/22/2016 to 9/5/2017. For the second year, with OAH sensors at 60m, the x-axis spans 1/5/2018 to 2/19/2019. Comparable y-scaling is used for first year and second year results to allow comparison of all parameters.

First Year

Figure 7 contains the temperature and salinity recorded at 15m water depth during the first year. Temperature data were recorded by the SAMI instrument which was deployed continuously, starting on July 25, 2016, while salinity data are from the SeapHOx instrument, which was deployed on November 4, 2016. The temperature data show a great deal of high frequency variability, especially during summer months when there was stronger stratification. Much of this variability is due to the summer season mixed layer depth being near the 15m depth where the OAH sensors were located on the mooring. As the pycnocline moved above and below the sensors large changes in temperature were observed. Both temperature and salinity also have a seasonal signal, with lowest temperature and highest salinity observed in the spring when upwelling is strongest. Salinity also shows several brief drops in January and February due to winter storms and runoff.

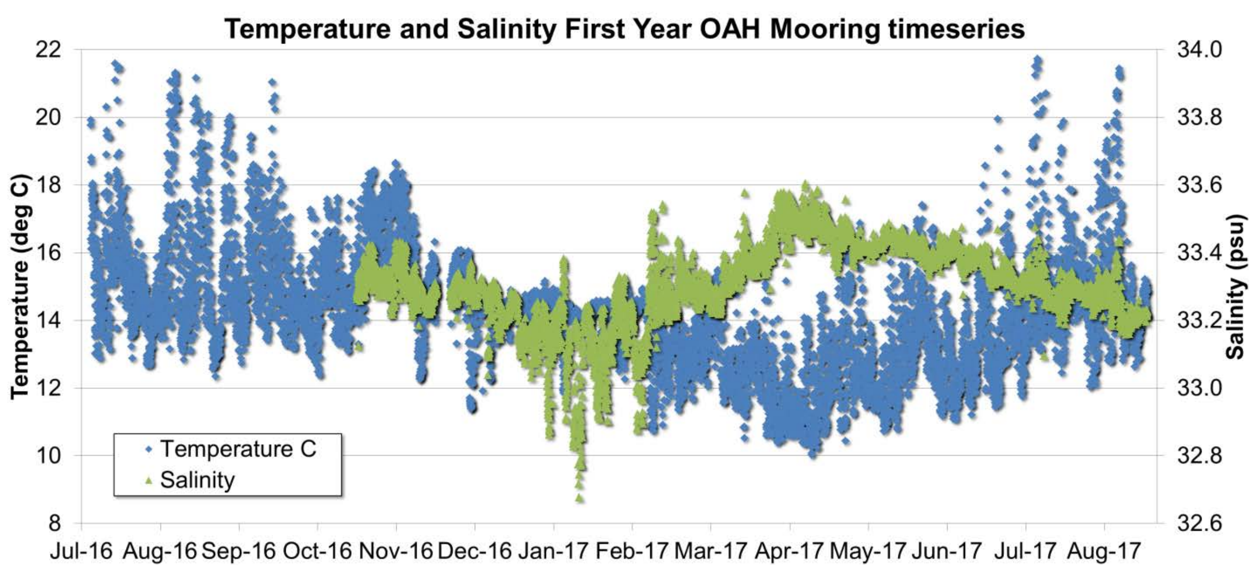

Figure 7 First Year temperature and salinity time series

Figure 8 shows the oxygen time series recorded at the first year site in 15m water. Overlaid on the graph are selected oxygen results from quarterly CTD surveys. The red symbols show the measured level of oxygen at 15m depth at the nearest adjacent CTD site (3102). The mooring oxygen levels very closely matched the adjacent CTD data, and suggest that both types of measurements are accurately quantifying oxygen levels. The blue symbols show the 15m depth oxygen from all the CTD sites, and illustrate the range of oxygen levels across the CTD sampling grid during a single survey (typically all CTD sites are sampled within a two day period). This range of CTD oxygen levels is comparable with the corresponding range of moored observations at the time the CTD survey was completed. This suggests that high frequency changes in oxygen observed at the mooring could be due to either horizontal water movements past the mooring, or vertical movements of the stratified water column at the mooring, or a combination of both.

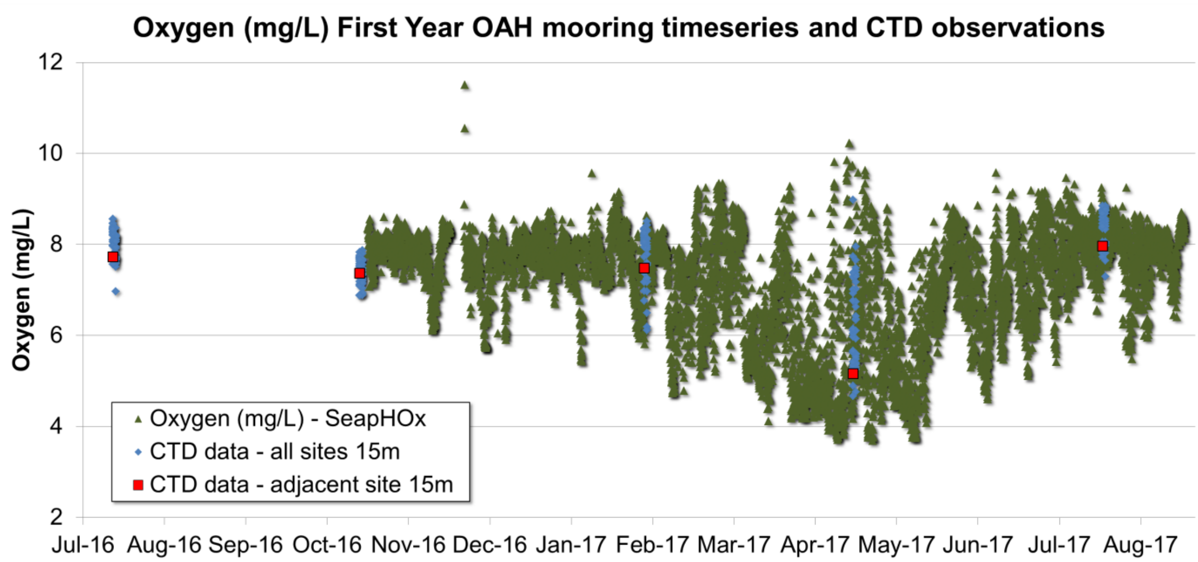

Figure 8 First year oxygen time series

Figure 9 contains the pH time series from the OAH mooring during the first year. Overlaid on the moored data, red symbols show the pH recorded at the nearest adjacent CTD site (3102) at 15m depth. There was generally close agreement between the mooring pH and the CTD pH at the same depth at the adjacent CTD site. The blue symbols show the 15m depth pH from all the CTD sites, and illustrate the range of levels across the CTD sampling grid during a single survey, completed in less than two days. These CTD data illustrate the significant spatial variability in pH at the fixed depth of 15m. As with the oxygen data, they confirm that horizontal water movements past the mooring are likely to be responsible for much of the observed variability in pH at the mooring. In offshore waters, a subsurface phytoplankton layer is commonly observed, which often will overlap with the 15m depth. Some of the higher CTD pH observations may reflect the increased pH associated with phytoplankton growth and resultant uptake of CO_2. The yellow symbols show the pH levels from discrete water samples collected at the 15m depth immediately adjacent to the mooring, and analyzed at the CLAEMD lab. These results match reasonably closely to the mooring measurements, with the remaining small offsets potentially due to small scale spatial and temporal variability between time and location of the discrete sample collection and the nearest hourly OAH mooring measurement.

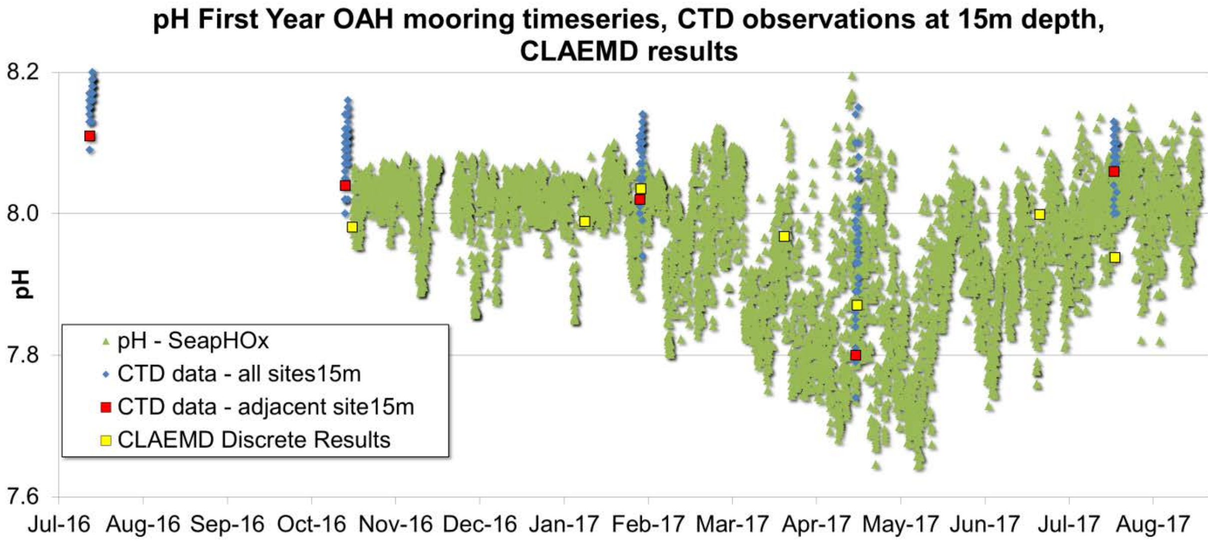

Figure 9 First Year pH time series. CLAEMD results are adjusted for temperature and pressure.

A summary of the CLAEMD analyses of discrete water samples collected during the first year is shown in **Table 4**. To compare with the moored pH the CLAEMD results were adjusted to the temperature and pressure conditions at the mooring when the sample was collected.

Table 4. First Year 15m Depth - Summary of CLAEMD discrete analyses

Date/Time	CLAEMD adjusted pH	SeapHOx Mooring pH	CLAEMD Alkalinity	Notes
11/3/2016 12:00	7.981	NS	2237	Sample ID: HT223619
1/25/2017 11:00	7.989	8.04	2214	Sample ID: 695401
2/14/2017 9:03	8.035	8.03	2313	Sample ID: 695402
4/6/2017 11:00	7.968	8.13	2247	Sample ID: 957301
5/2/2017 9:19	7.871	7.83	2261	Sample ID: 1046001
7/6/2017 11:00	7.999	8.09	2220	Sample ID: 1270501
8/2/2017 11:00	7.938	8.01	2259	Sample ID: 1370001

Figure 10 compares the First Year CLAEMD pH results to the SeapHOx mooring pH measurements made at the same location, depth, and time that the discrete samples were collected.

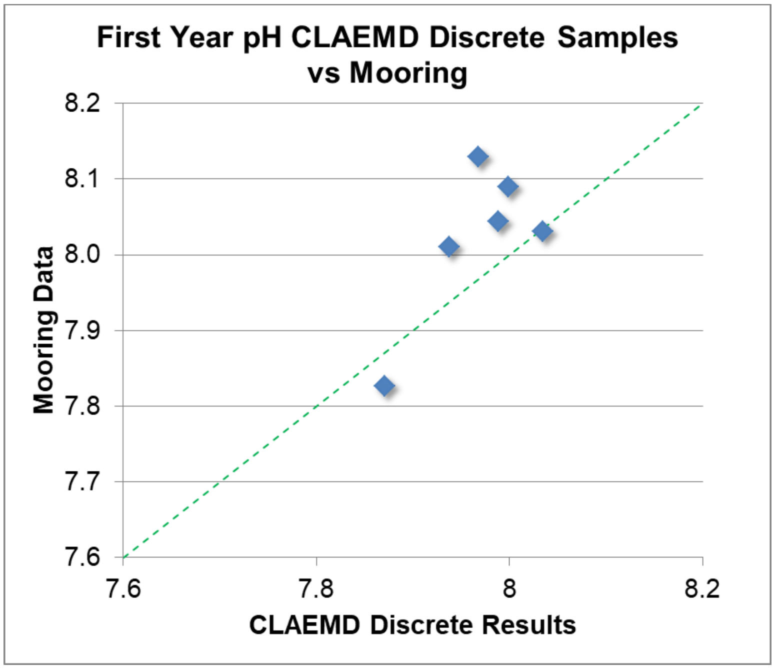

Figure 10 First Year moored pH versus CLAEMD analyses

Figure 11 is the time series of pCO_2 at the first year mooring location in 15m water depth. The data from July 20 to September 1, 2017 were censored after it was determined that the reagent had been depleted. During the first period of the deployment, values were relatively constant, but during the spring upwelling season (March through May), the pCO_2 levels rose considerably, and more high frequency variability was observed.

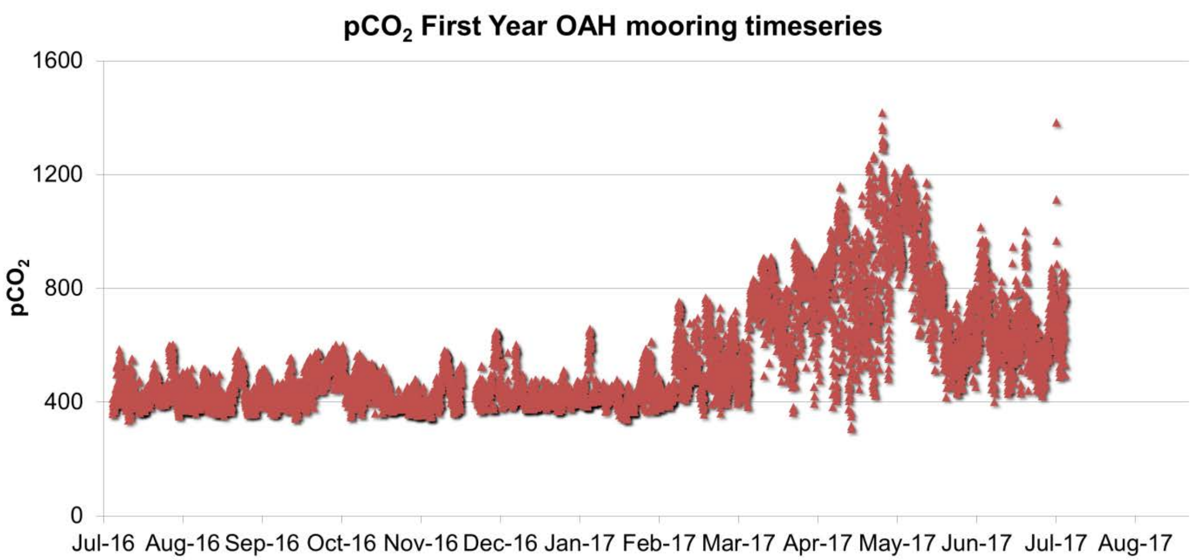

Figure 11 First Year pCO_2 time series

Figure 12 contains the Ω_{arag} time series for the first year. Ω_{arag} was derived using the Excel utility/macro PCO2SYS with the measured pH and the pCO_2 values. During the later period of the deployment, and during the spring upwelling period, the Ω_{arag} level drops, and high frequency variability increases. Lower values of Ω_{arag} are a concern because they may inhibit the formation and maintenance of calcium carbonate shells by a wide range of marine organisms. Derived Ω_{arag} values decrease as pH declines and pCO_2 increases. Based on the collected mooring data, the lowest Ω_{arag} values occurred in the spring, and were likely due to upwelling, which pushes colder water with lower pH and higher pCO_2 towards the surface, thereby decreasing Ω_{arag}.

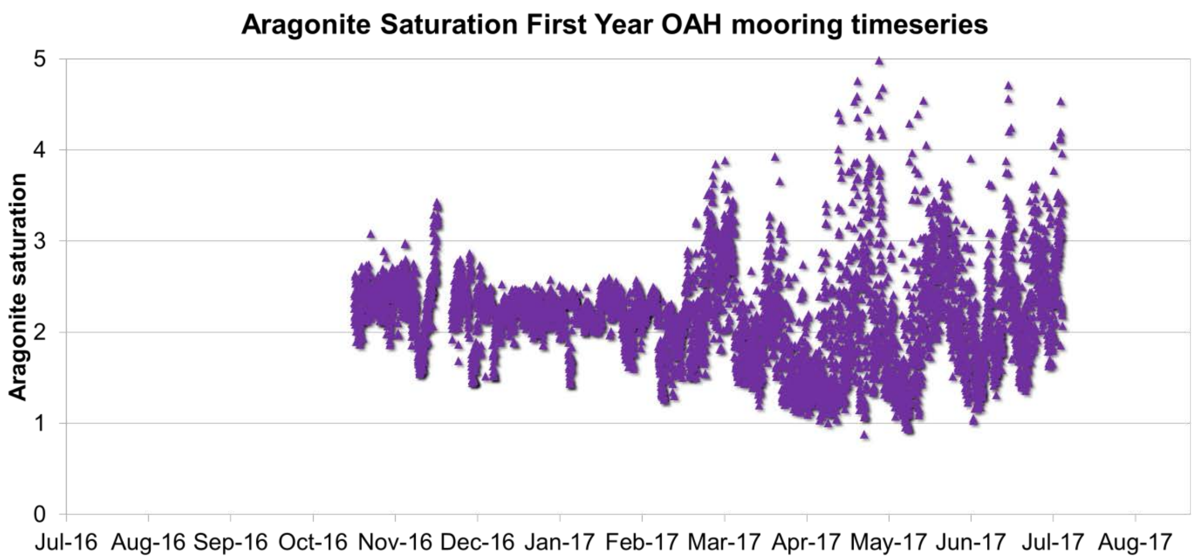

Figure 12 First Year Aragonite saturation time series

Second Year

Figure 13 contains the temperature and salinity recorded at 60m water depth during the second year. Notably, the temperature data exhibit much less variability than the shallower first year data, because the OAH mooring at 60m was always deeper than the pycnocline. The lowest temperature and highest salinity are both associated with the spring season. Winds favorable to upwelling peak in the spring, and increase the offshore displacement of surface waters; as a result, deeper waters with naturally lower temperatures and higher salinities are deflected upward in the water column. Oxygen and pH are also strongly stratified in local coastal ocean waters, and their levels decrease with increasing depth. As a result, oxygen and pH levels are lowest during the spring season below the surface mixed layer.

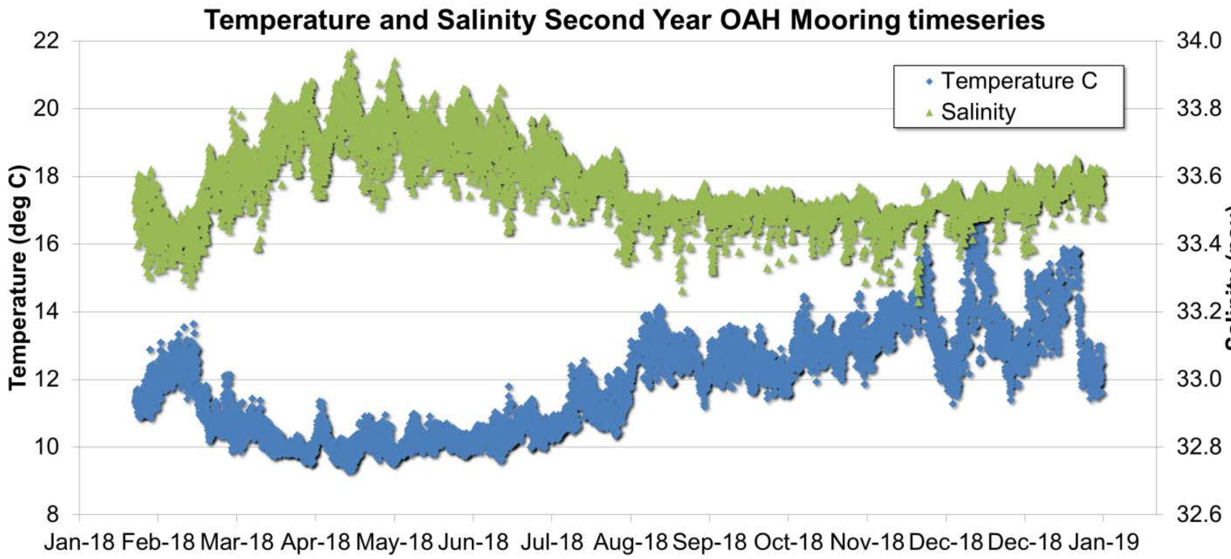

Figure 13 Second Year temperature and salinity time series

Figure 14 is the oxygen time series recorded at the second year site in 60m water. Overlaid on the graph are selected oxygen results from quarterly CTD surveys. The red symbols show the measured level of oxygen at 60m depth at the nearest adjacent CTD site routinely sampled to 60m (3004). The blue symbols show the 60m depth oxygen from all the CTD sites, and illustrate the range of oxygen levels across the CTD sampling grid during a single survey conducted within two days. This range of CTD oxygen levels is comparable with the corresponding range of moored observations at the time the CTD survey was completed

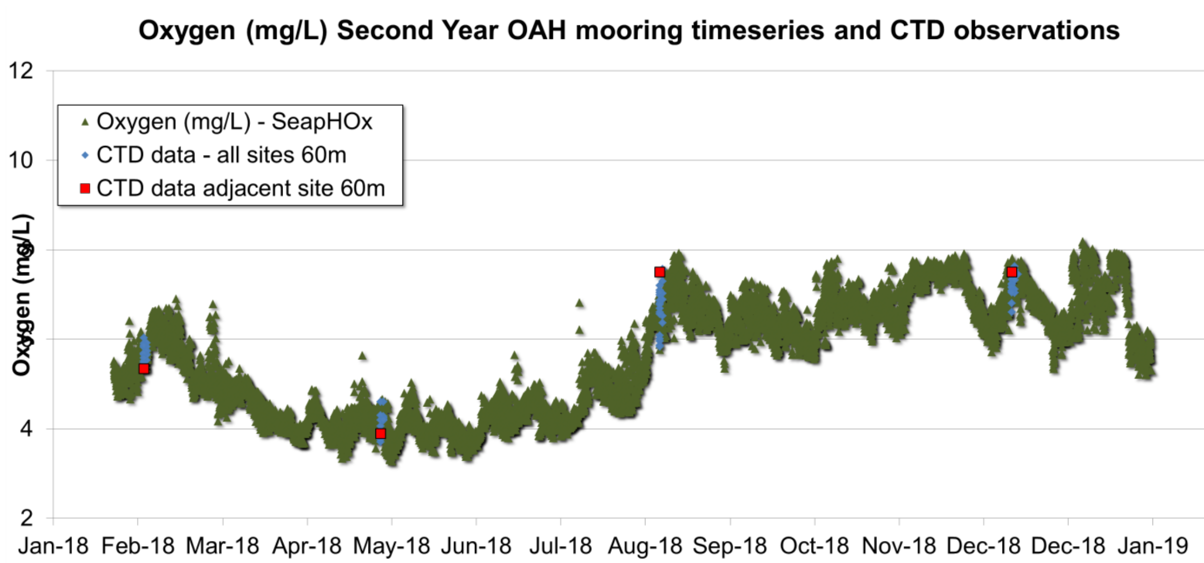

Figure 14 Second Year Oxygen time series

Figure 15 is the pH time series from the OAH mooring during the second year. Overlaid on the moored data, red symbols show the pH recorded at the nearest adjacent CTD site routinely sampled to 60m (3004). There was generally close agreement between the mooring pH and the CTD pH at the same depth at the adjacent CTD site. The blue symbols show the 60m depth pH from all the CTD sites, and illustrate the range of levels across the CTD sampling grid during a single survey, completed in less than two days. These CTD data illustrate the significant spatial variability in pH at the fixed depth of 60m. As with the oxygen data, they confirm that horizontal water movements past the mooring are contributing to the observed variability in pH at the mooring. The yellow symbols show the pH levels from discrete water samples collected at the 60m depth immediately adjacent to the mooring, and analyzed at the CLAEMD lab. Similar to the first year data, these results match reasonably closely to the mooring measurements.

Approximately one week prior to the mooring servicing on September 26, 2018 the pH signal from the SeapHOx sensor on the mooring began to decline. A quick assessment of the data in the field during that servicing did not indicate the severity of the problem. The mooring was redeployed, and recovered in late January of 2019. When the data were downloaded at that time, it was clear the sensor had not been working correctly. During October and November, the pH dropped to levels below 7.6, and yet the mooring recorded no associated change in temperature, salinity or oxygen. The pH returned to more "normal" levels in December, but remained below the CTD and CLAEMD discrete analysis levels measured in December and January. During factory refurbishment, after the second year concluded, the manufacturer found significant fouling of the sensor. The source of the fouling has not been determined, but the manufacturer has provided some additional guidance on cleaning of the sensor that will be implemented during future field servicing activities. The censored pH data represent the period when the data are not valid. The lowest valid pH measurements were observed during the spring upwelling period.

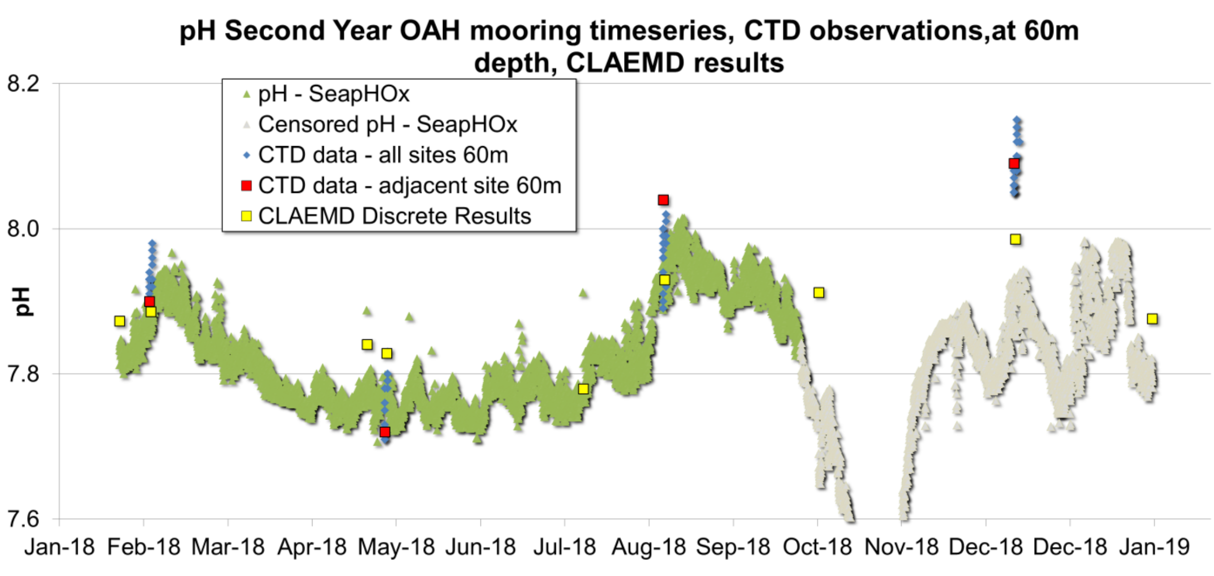

Figure 15 Second Year pH time series. CLAEMD results are adjusted for temperature and pressure.

Table 5. Second Year 60m Depth - Summary of CLAEMD discrete analyses

Date/Time	CLAEMD adjusted pH	SeapHOx Mooring pH	CLAEMD Alkalinity	Notes
1/26/2018 12:20	7.873	7.833	2368	Sample ID: 2149601
2/6/2018 12:08	7.887	7.862	2353	Sample ID: 2202501
4/24/2018 14:00	7.842	7.783	2251	Sample ID: 2554701
5/1/2018 12:30	7.828	7.756	2241	Sample ID: 2590201
7/10/2018 14:00	7.780	7.814	2249	Sample ID: 2909601
8/8/2018 12:08	7.929	7.935	2260	Sample ID: 3053201
10/2/2018 12:00	7.912	7.690	2239	Sample ID: 3317101
12/11/2018 12:50	7.986	7.856	2248	Sample ID: 3654101
1/29/2019 8:00	7.876	7.790	2283	Sample ID: 3845401

Figure 16 plots the Second Year CLAEMD pH results versus the SeapHOx mooring pH measurements made at the same location, depth, and time that the discrete samples were collected.

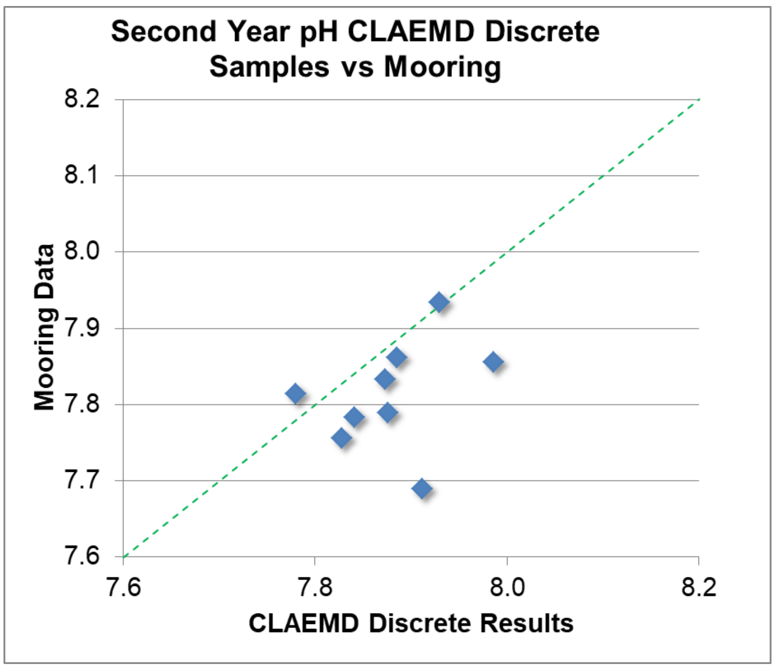

Figure 16 Second Year Moored pH versus CLAEMD analyses

Figure 17 is the time series of pCO_2 at the second year mooring location, in 60m water depth. Relative to the shallower first year data there is less variability in the pCO_2 measured at this deeper depth. Levels are generally higher than those observed during the first year which was expected because this deeper location was consistently below the pycnocline. Consistent with extreme values of other parameters, pCO_2 levels were highest during the spring upwelling period.

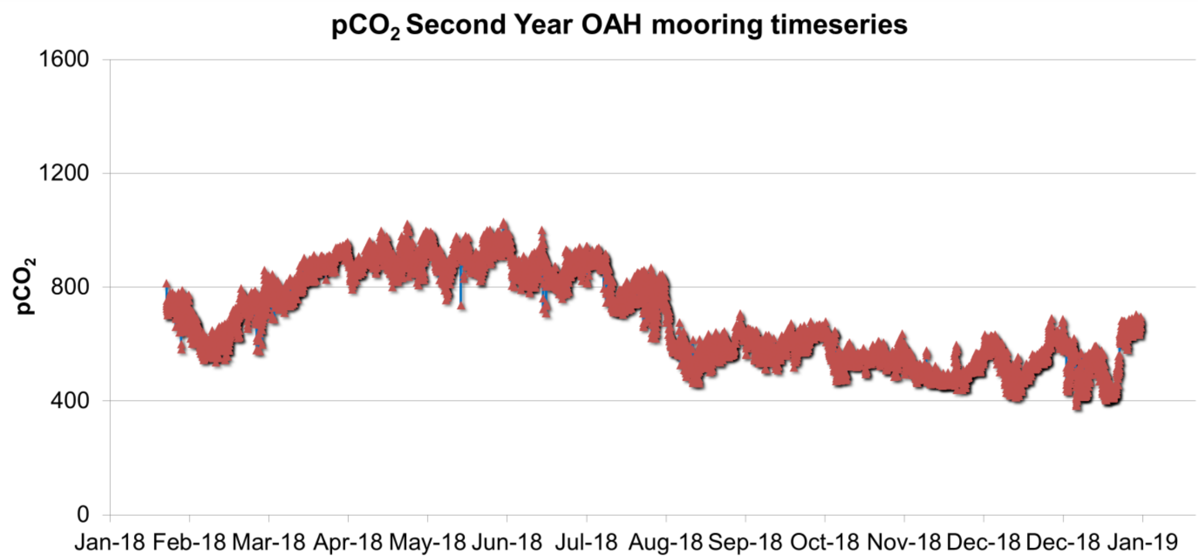

Figure 17 Second Year PCO_2 time series

Figure 18 contains the Ω_{arag} time series for the second year. Ω_{arag} was derived from the Excel utility/macro PCO2SYS by entering both the pH and the pCO_2 values. Levels were far less variable than the first year, since the mooring at 60m was below the pycnocline at all times. Lowest levels were seen during the spring upwelling period. The Ω_{arag} could not be calculated for the period from September 26 to January 29 where the pH data were invalid.

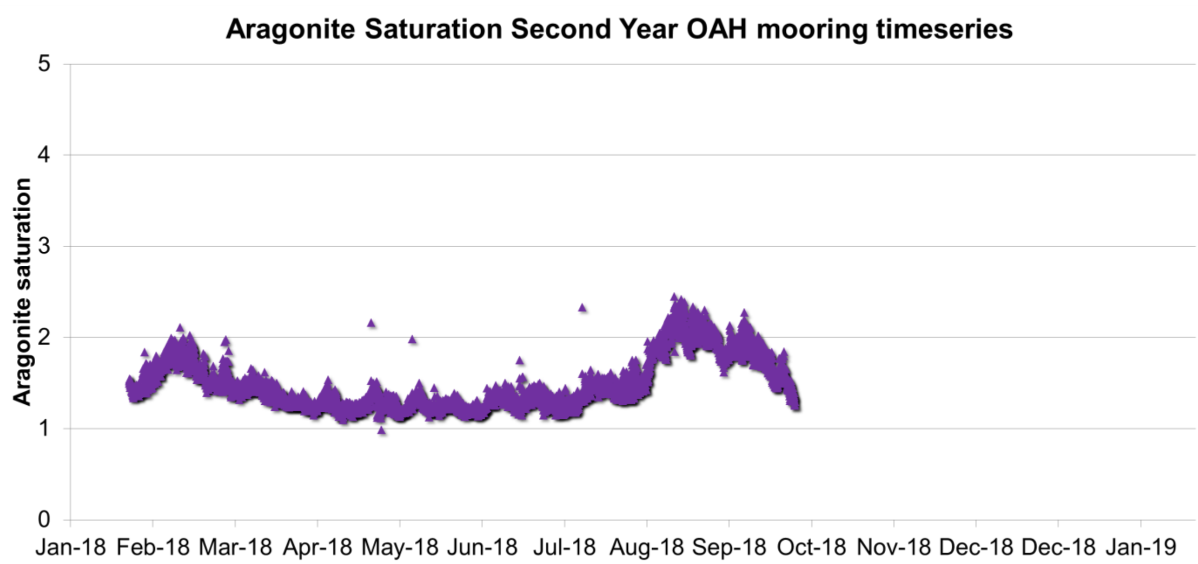

Figure 18 Second Year Aragonite saturation time series

Seasonal Patterns

The derived Ω_{arag} and the other directly measured OAH parameters were assessed by season for the first year and second year, using all data, and dividing data into three month long seasons. **Table 6** summarizes the results for the first year, and **Table 7** summarizes the results for the second year.

Table 6 - First Year – Parameter distributions by season					
	ALL	**Fall**	**Winter**	**Spring**	**Summer**
Aragonite Saturation		(Oct-Dec)	(Jan-Mar)	(Apr-Jun)	(Jul-Sept)
AVG	2.17	2.30	2.19	2.03	2.45
MIN	0.88	1.44	1.20	0.88	1.35
MAX	6.41	3.43	3.89	6.41	5.85
<1	0.12%	0.00%	0.00%	0.32%	0.00%
1-1.4	7%	0.00%	1%	19%	0.43%
1.4-1.7	13%	6%	10%	20%	9%
>1.7	80%	94%	88%	61%	91%
Salinity	33.31	33.29	33.20	33.43	33.28
Temperature	14.22	15.14	13.70	12.64	14.64
pH	7.96	8.02	7.99	7.88	7.99
pCO_2	548	447	495	767	642

Table 7 - Second Year – Parameter distributions by season					
	ALL	**Fall**	**Winter**	**Spring**	**Summer**
Aragonite Saturation		(Oct-Dec)	(Jan-Mar)	(Apr-Jun)	(Jul-Sept)
AVG	1.49		1.52	1.28	1.70
MIN	0.99		1.19	0.99	1.15
MAX	2.45		2.11	2.16	2.45
<1	0.02%		0.00%	0.05%	0.00%
1-1.4	49%		26%	93%	19.74%
1.4-1.7	28%		55%	6%	30%
>1.7	24%		19.66%	0%	51%
Salinity	33.58	33.50	33.57	33.71	33.53
Temperature	11.88	13.32	11.91	10.20	12.06
pH	7.82		7.84	7.77	7.88
pCO_2	694	536	677	893	671

Figure 19 is a plot of the seasonal distribution of Ω_{arag} relative to significant biological levels during the first year of monitoring. In all seasons, the Ω_{arag} was generally above 1.7, and unlikely to be a concern for

shell building organisms. Biologically significant levels of saturation below 1.7 and 1.4 were only observed during the spring upwelling periods and were almost never below 1.

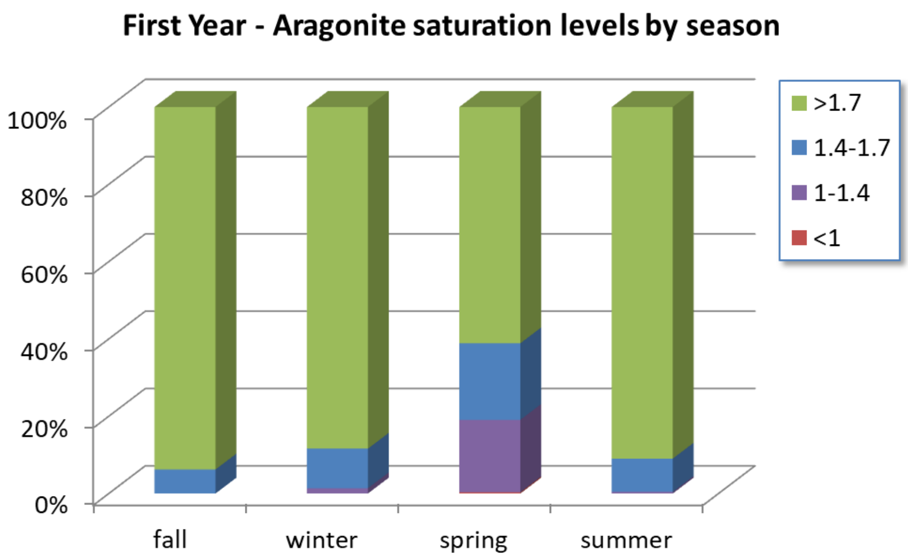

Figure 19 First Year seasonal distribution of Ω_{arag} values

In the second year, at the significantly deeper location on the outer edge of the shelf, the Ω_{arag} was lower in each of the seasons as would be expected (**Figure 20**). Due to the pH sensor failure, there was insufficient valid data to assess the Fall season. Similar to the more shallow Year 1 deployment, Spring had the greatest frequency of low Ω_{arag} due to seasonal upwelling.

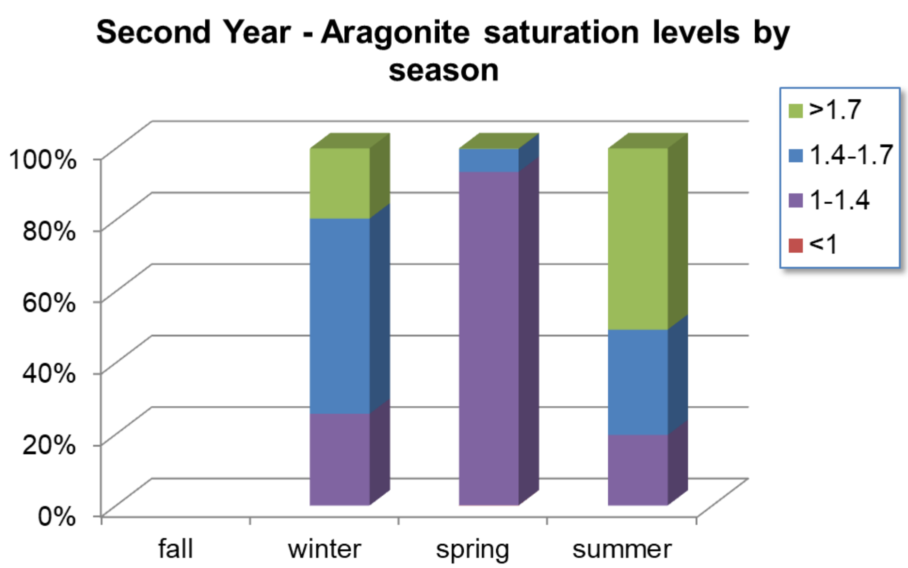

Figure 19 Second Year seasonal distribution of Ω_{arag} values

Regressions

Figures 21 and 22 plot the relationships between parameters measured on the OAH mooring during the first and second year. Consistent with expected oceanographic stratification, the pH and temperature correlate quite closely, pCO_2 is roughly inversely correlated with temperature, pH and pCO_2 are inversely correlated, and oxygen and pH are strongly correlated. The relatively strong relationships between parameters suggest that it may be possible to directly compute pH or pCO_2 using temperature, salinity, and oxygen. This could provide a simple way to estimate Ω_{arag}, and could be used to check and confirm that directly measured pH and pCO_2 values were valid.

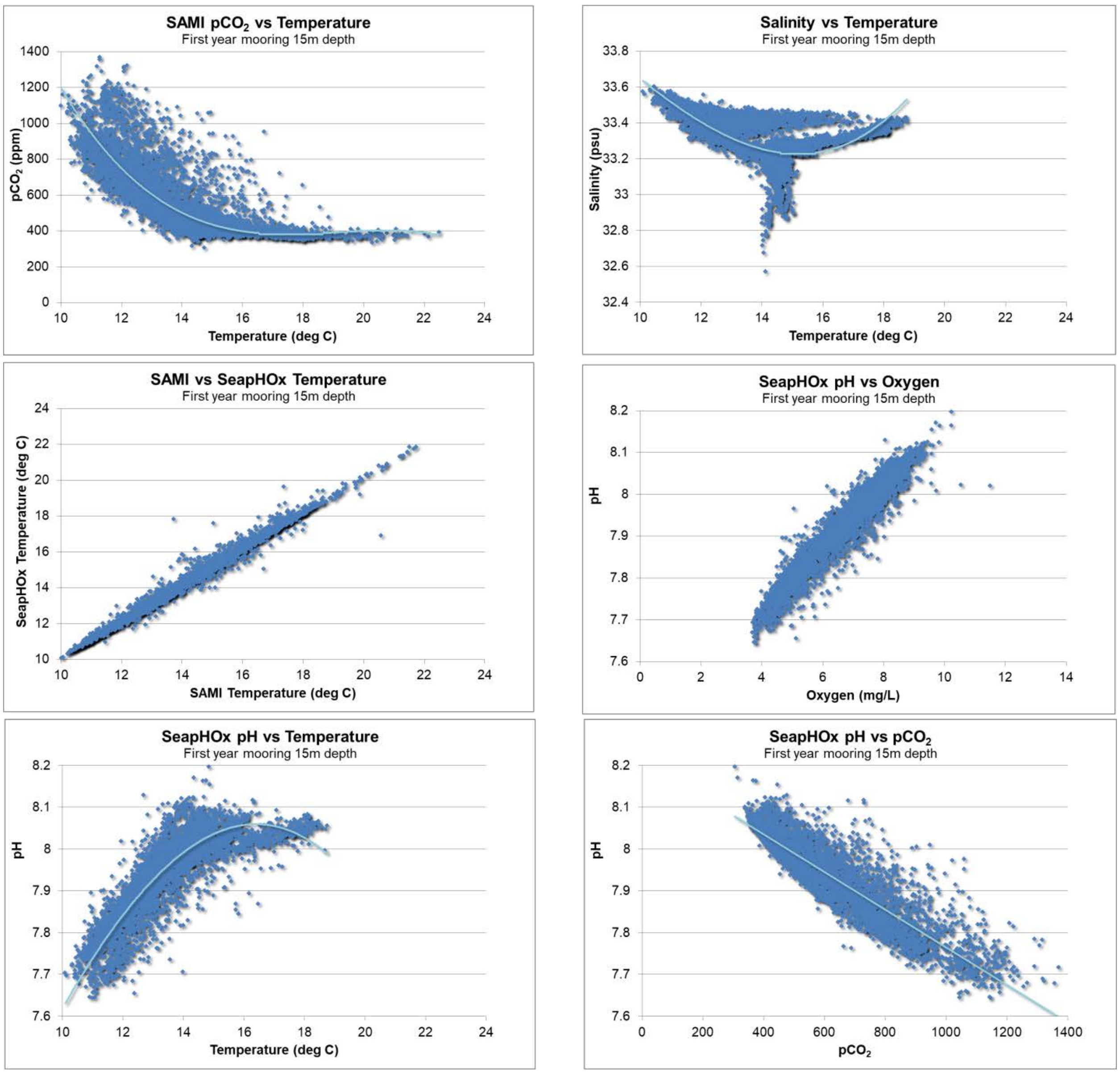

Figure 20 First Year regressions between OAH mooring parameters

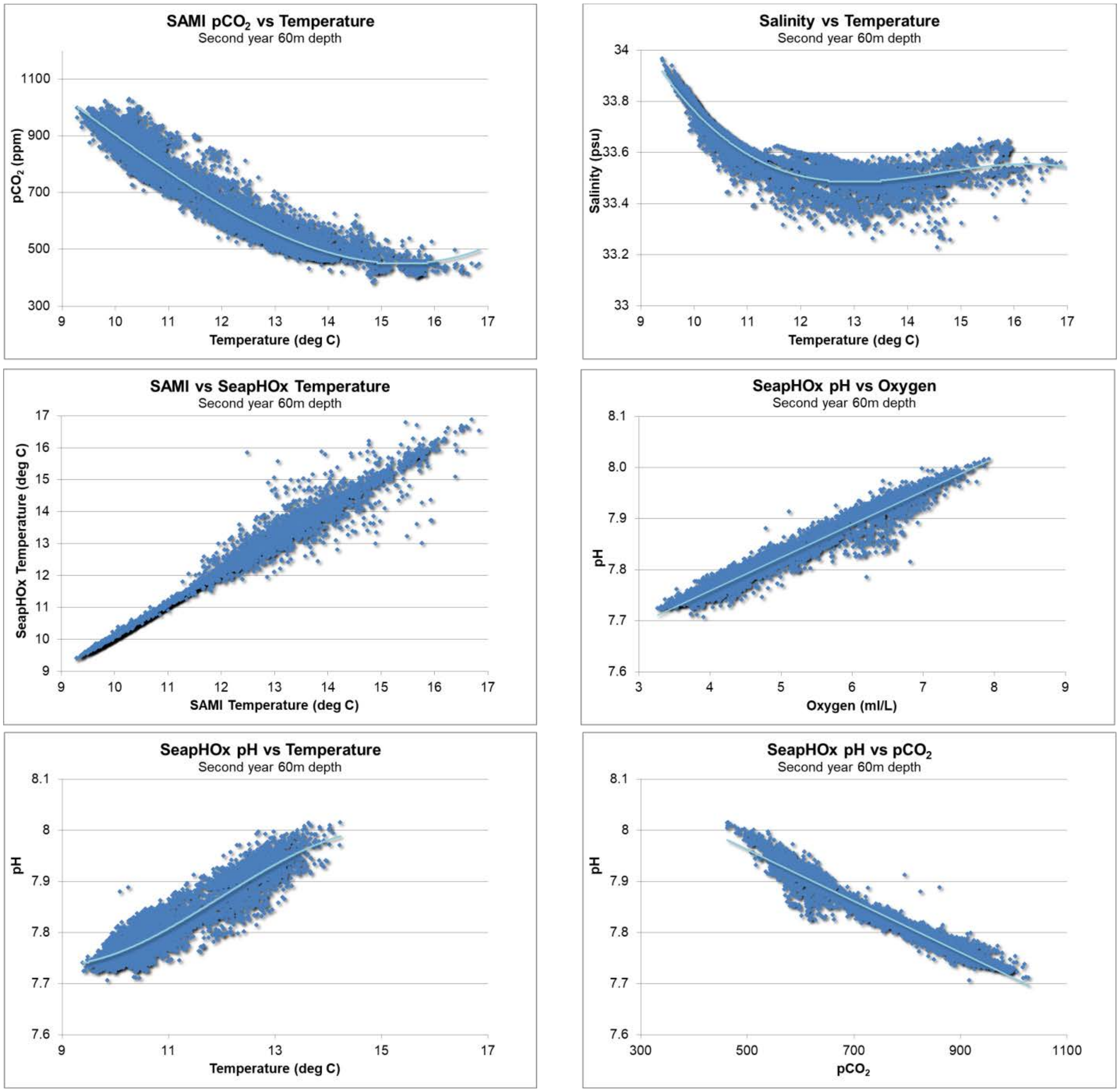

Figure 21 Second Year regressions between OAH mooring parameters

Long Term Trends versus OAH mooring results

The Sanitation Districts have sampled the pH and oxygen through the water column directly adjacent to both OAH mooring sites using a CTD at monthly or quarterly frequencies since the early 1980s. The CTD measurements at the 15m depth are plotted together with the first year moored OAH data. **Figure 23** contains the historical pH data measured by CTD (blue) and specifically at site 3102 directly adjacent to the first year mooring. The green trace of the OAH mooring data can be seen near the right end of the graph. **Figure 24** provides a similar plot of the CTD oxygen data.

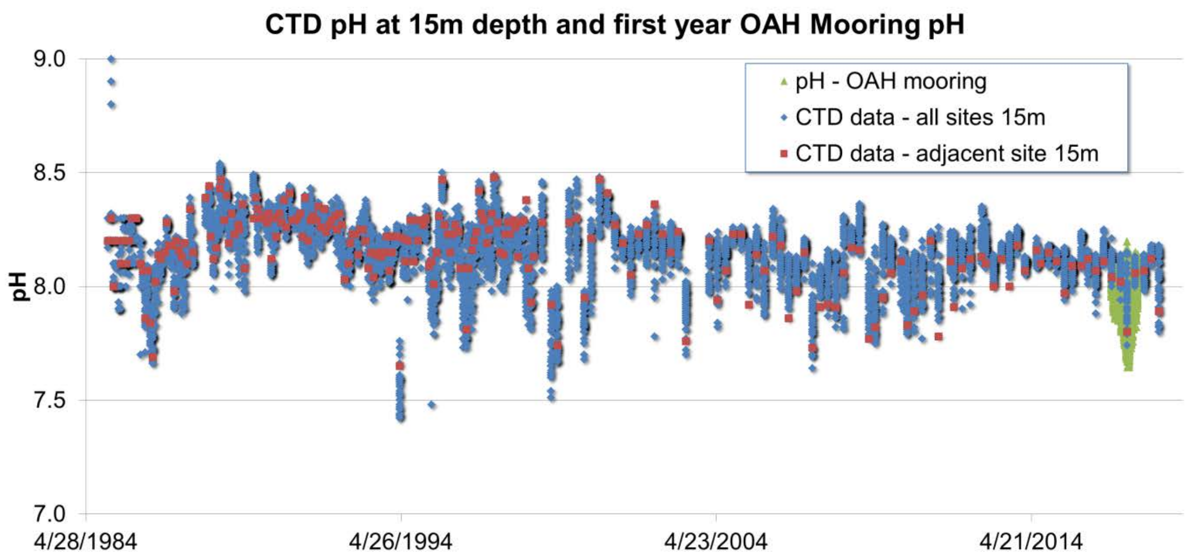

Figure 22 35 year (1984 to 2018) time series of 15m depth CTD pH data and First Year OAH mooring (November 2016 through August 2017) pH data

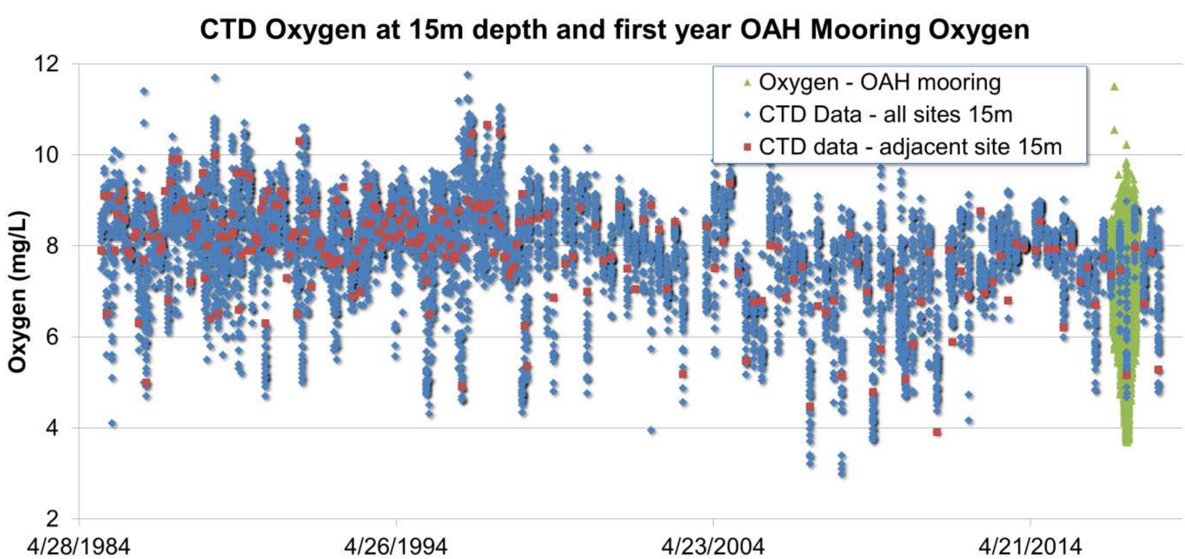

Figure 23 35 year (1984 to 2018) time series of 15m depth CTD oxygen data and First Year OAH mooring (November 2016 through August 2017) oxygen data

The CTD measurements at the 60m depth are plotted together with the second year moored OAH data. **Figure 25** shows all the historical pH data measured by CTD (blue) and specifically at site 3004, nearby to the second year mooring. The green trace of the OAH mooring data can be seen near the right end of the graph. **Figure 26** provides a similar plot of the CTD oxygen data.

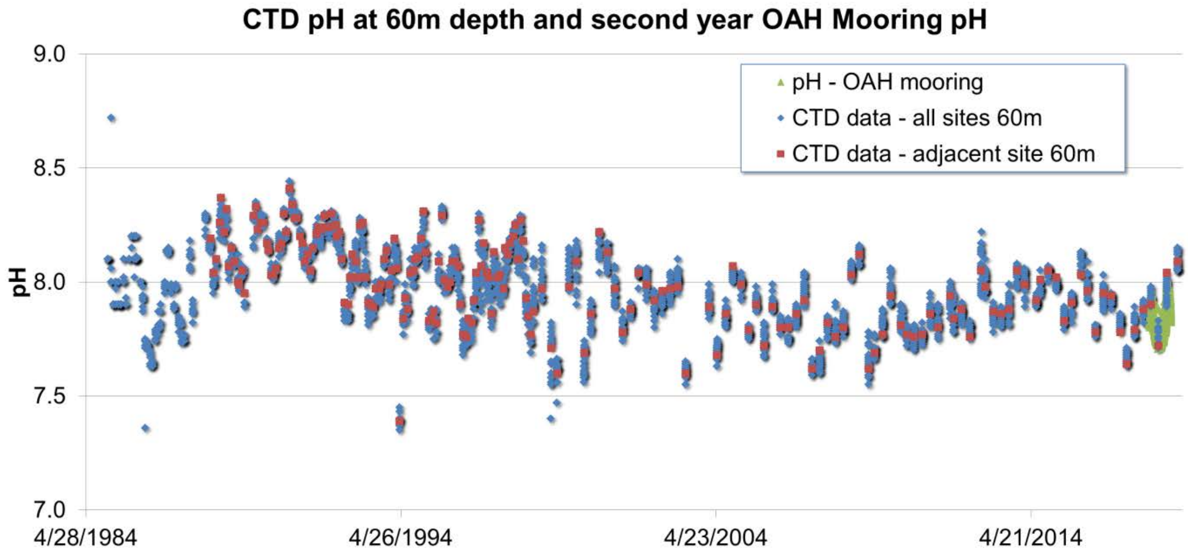

Figure 24 35 year (1984 to 2018) time series of 60m depth CTD pH data and Second Year OAH mooring (January 2018 through September 2018) pH data

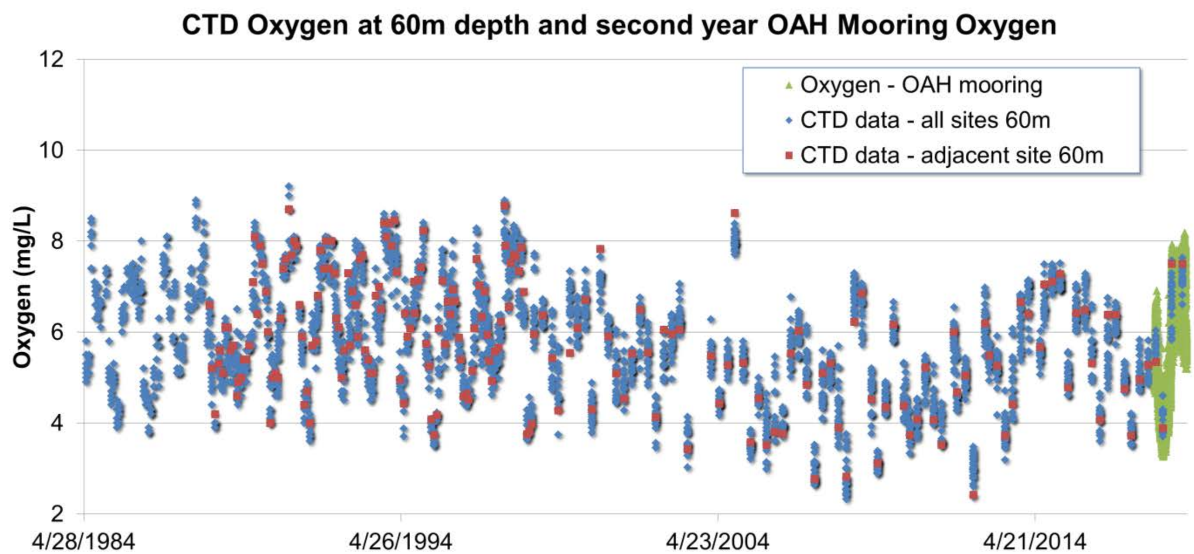

Figure 25 35 year (1984 to 2018) time series of 60m depth CTD oxygen data and Second Year OAH mooring (January 2018 through January 2019) oxygen data

A qualitative examination of these overlapped data sets (CTD and OAH mooring) suggests that CTD monitoring, despite being conducted less frequently, may be sufficient to assess local OAH conditions. For all of these OAH parameters at both depths, the overlap of the moored data shows close agreement with the CTD results.

Conclusions

The study successfully achieved the goal to deploy a mooring and continuously collect oxygen, pH and pCO_2 data at two locations for two years. However, the full data record with all sensors was not complete in either year due to issues with the sensors. During the first year, the delivery of one sensor was delayed, and as a result, the sensor that was deployed first ran out of reagent. During the second year, drift in the pH signal, apparently due to fouling, invalidated nearly four months of pH results. Nonetheless, roughly eight months of complete, continuous data were collected in each year, and allowed the determination of hourly values of Ω_{arag} as well as seasonal averages.

The moored pH results from this study were consistent with pH results from the calibrated glass electrode sensors on the Sanitation Districts CTD, and with the discrete water samples analyzed in the CLAEMD laboratory. The close comparability of pH increases confidence that the multi-decadal CTD pH data set is acceptably accurate to be used for long term trends assessment, and potentially to tease out the el Nino, years, Pacific Decadal Oscillations, and global climate change trends.

A total of nearly two years of continuous hourly observations with temperature, salinity, oxygen, pH, and pCO_2 were made over the course of this study. The Sanitation Districts leveraged previous experience with thermistor and ADCP current meter moorings and successfully achieved expertise in the operation and maintenance of moorings equipped with state-of-art OAH sensors. Valuable lessons were learned about the OAH instrumentation that may allow even higher rates of data return in future. The combined results from two sensor packages were used to determine Ω_{arag} state, and provide a valuable baseline data set for OAH in SMB.

Seasonal levels and instantaneous extremes are documented for Ω_{arag} at each site relative to biologically significant saturation levels. In both years almost all Ω_{arag} values were greater than the biologically important threshold of 1.0, and most Ω_{arag} values were higher than 1.4, a level believed to be adequate for maintaining ecosystem health. In both the first and second year, the spring upwelling season had the lowest Ω_{arag}. As expected Ω_{arag} levels were lower at 60m depth than at 15m. These observations show how future measurements could be used in support of biogeochemical assessment studies.

During both years of the study the lowest oxygen levels were observed during the spring season. At the first year mooring site, in 15m water depth, oxygen levels ranged from 3.68 to 11.50, and averaged 7.15 mg/L. At the second year site, in 60m of water, oxygen levels ranged from 3.26 to 8.18 and averaged 5.64 mg/L. No hypoxic events (oxygen <2 mg/L) were observed during this study.

An original intent of the study was to quantify the frequency, magnitude, and duration of OAH events. Review of the data suggests the variability in the Ω_{arag} at the nearshore site in the first year was primarily due to the natural vertical movement of the pycnocline passing above and below the fixed depth of the sensors, rather than OAH events. In the second year the sensor package was located at 60m, below the deepest depth reached by the pycnocline, and was therefore only recording changes in the OAH of the sub-pycnocline water. In this data set there did not seem to be significant "event" scale variability. Based on assessment of the data collected during this two year study, Ω_{arag} can be significantly variable at higher frequencies within the depth range of the pycnocline, however below the pycnocline, high frequency variability in Ω_{arag} was reduced. In both years, the lowest values of Ω_{arag} were observed over an extended period during the spring upwelling season. These observations may have relevance in assessing the OAH tolerance of ecosystems between these two depth regimes.

The Sanitation Districts, encouraged by the success of this study, proposed a follow-on special study that was approved by the Regional Board in 2019. The new study will add a vertical element by refurbishing a CLAEMD wire-walker and adding a pH sensor that will continuously profile the top 100m of the water column, at the same time that the original OAH sensors are redeployed to record data at the 100m depth. If deployment of the wire-walker is successful, this project will characterize OAH levels and variability in the upper 100m of the Santa Monica Bay. Specifically, data from the wire-walker will be used to characterize OAH levels and variability in the upper 100m of the Santa Monica Bay by assessing vertical distributions of all parameters at scales from minutes to seasons, and by evaluating relationships between key parameters such as chlorophyll levels and oxygen. The high frequency OAH sampling through the upper water column, with simultaneous chlorophyll and density measurements, will be valuable for calibration and assessment of the output from physical-biogeochemical models.

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