NOAA's Recent Field Testing of Coastal Water Quality Monitoring Systems – Quantifying Impacts of Biofouling and Investigating Chloride Measurement Techniques

Grace Browder Gray
Robert Heitsenrether

National Oceanic and Atmospheric Administration
Center for Operational Oceanographic Products and Services
Chesapeake, VA

***Abstract*— The National Oceanic and Atmospheric Administration (NOAA) Center for Operational Oceanographic Products and Services (CO-OPS) maintains and continues to develop over 300 hundred coastal observatories throughout the United States, which make up the National Water Level Observation Network (NWLON), and 22 integrated Physical Oceanographic Real-Time Systems (PORTS). In-situ, real-time observations of various water quality parameters, including dissolved oxygen, pH, turbidity, chloride, conductivity and temperature, have been identified as measurements of critical interest in many coastal regions where CO-OPS' real-time infrastructure exists. Of these parameters, only conductivity and temperature are collected at a limited number of CO-OPS' existing stations. CO-OPS has recently begun development and testing of real-time water quality systems that could be integrated with existing NWLON and PORTS stations, thereby leveraging infrastructure and enhancing the data available at locations with rich records of historical oceanographic and meteorological data.**

Field tests of multiple real-time water quality measurement systems were conducted at sites collocated with existing operational water quality sondes maintained by the Chesapeake Bay National Estuarine Research Reserve in Virginia (CBNERR-VA). One site was located in a polyhaline environment, a salinity regime typical of most CO-OPS observatories, and a separate freshwater site was chosen in order to test the performance of in-situ chloride probes. In addition to evaluating instrument performance and demonstrating system integration, these tests focused on two unique aspects of particular interest to CO-OPS: 1) assessing calibration and maintenance requirements through the side by side comparison of three multi-sonde water quality systems, one with a rigorous and routine maintenance program, and two others with sensors intentionally unmaintained; and 2) a comparison of chloride measurements obtained using three different methods: laboratory analysis, derivation from conductivity, and direct, automated measurement from an ion-selective electrode (ISE) sensor. This paper includes a brief description of test system design, a summary of system integration efforts, results of test data analysis, and plans for continuing work driven by the results of this study.

I. INTRODUCTION

The National Oceanic and Atmospheric Administration (NOAA) Center for Operational Oceanographic Products and Services (CO-OPS) supports real-time oceanographic and meteorological measurements throughout all of the United States coastal regions. Since users' critical needs continue to grow and evolve along with the advancement of environmental measurement technology, one important objective of CO-OPS is to identify potential system improvements. Currently, there are multiple real-time water quality monitoring networks throughout the Nation's coasts, including those maintained by the United States Geological Survey (USGS) [1], the Environmental Protection Agency (EPA) [2], the National Estuarine Research Reserve System (NERRS, a partnership program funded by NOAA) [3], and by various Integrated Ocean Observing System (IOOS)-supported regional associations [4]. Still, many spatial gaps remain in the coverage of real-time water quality observations, including areas where there is a critical need. In some cases, these are regions where CO-OPS real-time observatory infrastructure exists. As a result, CO-OPS has begun an effort to develop, test, and evaluate a real-time water quality measurement system, with the objective of eventual integration into its existing coastal observatories [5].

Initial development has involved evaluating various commercial-off-the-shelf (COTS) multi-probe water quality sondes and integrating them into the standard design system of NWLON/PORTS® stations. Field testing has involved the deployment of prototype real-time water quality systems at sites on the York and Pamunkey Rivers, tributaries to the southern Chesapeake Bay in eastern Virginia. The first test was carried out in a polyhaline environment near the mouth of the York River. The second test was carried out approximately 50 miles upriver in a tidal freshwater location. At each site, two different test systems were installed alongside existing operational stations, each employing a different model multisensor water quality sonde. The parameters measured at both sites included: pH, conductivity, temperature, dissolved oxygen (DO), and turbidity. At the tidal freshwater site, chloride ion-selective electrode (ISE) sensors were added to both test sondes.

The initial goal of the field testing effort was the successful integration of the test sensors with CO-OPS' real-time data collection system. While instrument performance was important, initial emphasis was placed on familiarization with the intricacies of the multi-probe sondes (calibration, sampling options, data transfer protocols, etc.) and their successful integration with CO-OPS' standard design coastal observatory systems.

Once system integration was successfully completed, the first test objective was to collect data that could support assessment of sensor maintenance requirements. Instrumentation for in-situ, automated water quality monitoring is especially prone to biofouling and can require routine service visits up to once a week in the summer months in certain locations. Given that the majority of NWLON stations are more than a day's drive away from a field office, CO-OPS has a special interest in maximizing the time required between servicing trips. The test systems were collocated next to Chesapeake Bay National Estuarine Research Reserve (CBNERR) sensors that were subject to a rigorous maintenance schedule (replaced with a newly-calibrated sensor every 1-2 weeks). By leaving the test instruments to collect data undisturbed next to a routinely maintained reference sensor, the goal was to get a sense of the data degradation rates of each sonde's individual probes, due either to biofouling or to sensor drift. Impacts of biofouling and water quality instrumentation maintenance requirements may vary widely for different locations and seasons; data reported in this study are merely intended to provide a starting point for an initial evaluation and discussion about required servicing intervals.

A second objective of this study was to explore and evaluate techniques for measuring chloride. Chloride is an effective tracer for pollution from chemicals moving from anthropogenic sources into natural water bodies or for salt water intrusion [6]. One application of interest for monitoring chloride real-time is detecting salinity intrusions at municipal raw water intake sites; chloride levels of 500 mg/L will cause water treatment plants to suspend operations [7]. Additionally, the need for chloride monitoring may become more prominent as more public water systems become vulnerable to salinity intrusions with rising sea levels [8]. Recent studies have sought to model the impact of climate change on salinity intrusion in the coastal zone; the duration of salinity intrusions can be expected to increase with an incremental rise in sea level [7, 9].

At the time this test was conducted, research into chloride monitoring methods provided a broad range of information and user opinions, and no clear reported evidence of the effectiveness and performance of in-situ, automated sensors. Chloride can act as a proxy for chloride, but grab samples analyzed in a laboratory are often preferred. For this study, several different methods of chloride quantification in a tidal freshwater environment were compared.

II. Test System Design

Based on a CO-OPS market survey of available COTS instruments, two water quality sondes were selected for this test and evaluation: a YSI 6600 EDS [10] and a Hydrolab DS5x [11], referred to hereafter as "test YSI" and "test Hydrolab". Both sensors have wipers that clean sampling probes between measurements, thereby extending deployment length. The probes on each sonde were similar in design and accuracy specifications, except for the DO probe used in the first phase of field testing. The YSI was outfitted with a Rapid Pulse DO sensor (YSI6562) and the Hydrolab had an optical DO sensor (Hach LDO). During the second phase of field testing, an optical DO sensor was added to the YSI (YSI ROX). The chloride ISE probes added to each sonde for the second phase of field testing were similar in operational theory—both measure the electrical potential across a membrane created by excess chloride ions in the sample water [6,12]—but the Hydrolab's operational range is higher than that of the YSI, as is its manufacturer-specified accuracy [10,11] .

At both field sites, an operational CBNERR sensor was used as the reference for both test sensors for the data analysis presented in Section IV (except in the case of the chloride, which is not measured by CBNERR). These operational sensors are YSI 6600V2s and use the same probes as the test YSI (ROX for DO). The instruments are deployed 30 cm off the bottom and replaced with newly cleaned and calibrated sensors as often as every week during the summer months. The operational sensors collect data every 15 minutes. After a process of QAQC, data are available for download at the Virginia Institute of Marine Science (VIMS) Virginia Estuarine and Coastal Observing System (VECOS) website [12] and NERRS' Centralized Data Management Office (CDMO) website [3].

Both test sondes were incorporated into a typical CO-OPS real-time measurement system (Fig. 1). Such a system is standalone and powered by solar panels and rechargeable batteries. The infrastructure consists of an electronics enclosure housing batteries, a Sutron data collection platform (DCP), a Sutron Satlink Geostationary Operational Environmental Satellite (GOES) transmitter, and an IP modem. Masts containing solar panels and antennas for GOES and GPS are mounted to the enclosure. Each test sensor was polled by its own DCP every six minutes and the data were transmitted via GOES. Both systems were also equipped with IP modems to enable two-way communication and back-up data download capability.

Fig. 1. Test water quality system on the VIMS Pier at Gloucester Point, Va., consisting of an electronics enclosure and mast with antennas and solar panels. The two PVC wells house the test instruments. The CBNERR reference sensor is deployed in the PVC well on the piling to the right of the test system.

Each test sensor was housed in a 4-inch PVC well based on the CBNERR design, with holes drilled to allow sufficient water flow while still affording protection from debris in the water column (Fig. 2). The wells were painted with antifouling paint. Other antifouling measures included copper tape on the water quality sonde probes and a brass probe guard on each sonde (Fig. 3).

Fig. 2. One of the PVC wells that house the test sensors shown here during fabrication. The base of the water quality sonde rests against the bolt and the large holes allow sufficient water to flow past the probes.

Fig. 3. The test Hydrolab (left) and test YSI (right) before deployment at Gloucester Point, Va. for the first phase of field testing.

III. Field Tests

Starting in November 2012, two field tests with real-time water quality systems were conducted on the York and Pamunkey Rivers in eastern Virginia (Fig. 4). In collaboration with CBNERR and VIMS, the sites were selected to allow collocation of test systems with long-term water quality stations that are part of the CBNERR network. The first test site was Gloucester Point, Va., a polyhaline (salinity = 18 – 30 ppt) environment near the Chesapeake Bay entrance, and the second site was While House Landing, a tidal freshwater (salinity = 0 – 0.5 ppt) environment approximately 50 miles upriver (Fig. 4).

Fig. 4. Map showing the field test locations.

A. Gloucester Point

For the first phase of the field test, the sondes were deployed on a pier at VIMS on the York River in Gloucester Point, Va. (Fig. 4). The main focus of this phase of the field test was initial familiarization with sensor types new to CO-OPS and the successful integration of the two selected water quality sondes with a Sutron Xpert DCP and GOES transmitter to enable real-time transmission of 6-minute values. Additionally, in order to gather useful information about the frequency of servicing required (CBNERR sensors are replaced with newly calibrated instruments every one-to-two weeks), CO-OPS did not clean or calibrate the test sensors during the six-month deployment (November 2012 through May 2013).

Operational issues were encountered with the YSI Rapid Pulse DO probe used in the first phase of the field study. Because this is an older technology, it is acknowledged that users may not have had the skill and experience necessary to correctly service the probe. For the second field test, an optical YSI ROX was installed and used for the comparison of DO data.

B. White House Landing

The tidal freshwater test site, White House Landing (Fig. 4), was used to test and compare different methods for measuring chloride. Since chloride is not a parameter measured by the reference CBNERR sensor at this site, grab samples were collected once a week for the first month of the study and analyzed by the laboratory at the Hampton Roads Sanitation District (HRSD). The grab samples were analyzed using Standard Method 4500-Cl-B, 1997, and the lab results were used as the reference against which to compare the test data.

The test instruments were installed in May 2013 and removed nine weeks later. Results from the first 41 days of the study are reported here (the remainder of the reference data were not available at press time). As in the first phase of the field test, the test instruments were not cleaned or calibrated during the test.

C. River Transect

Unfortunately, the results from the first four weeks of the study showed the chloride levels to be much lower than expected and too close to the lower measurement threshold of the water quality sondes to provide much useful data. For that reason, the water quality sondes were moved down river to another CBNERR site, Sweet House Landing (Fig. 4), and allowed to collect data over a complete tidal cycle in order to capture higher chloride levels. Additionally, the sondes were deployed at several locations along a short stretch of the Pamunkey River between Sweet Hall Landing and West Point (Fig. 5). At each station, the instruments were lowered over the side of an anchored vessel and allowed to collect data for one hour. Grab samples for laboratory analysis were also collected.

Fig. 5. Satellite imagery (*source: Google Earth Pro*) shows the chloride sampling sites along the Pamunkey River.

IV. Results

A. Impacts of Biofouling on Specific Conductance and Dissolved Oxygen Measurements

Data collected at both the Gloucester Point and White House Landing field test sites provide interesting examples of the impacts of biofouling on sensors that were intentionally left unserviced. Fig. 6 (a) and (b) show unmaintained test sensors after recovery from the Gloucester Point site after 167 days of operation; (a) shows the test YSI and (b) the test Hydrolab.

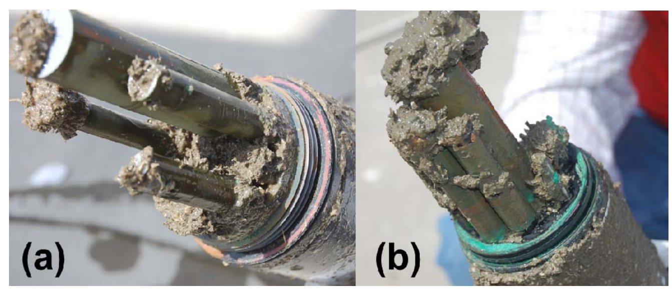

Fig. 6. The (a) test YSI and (b) test Hydrolab after a six-month deployment at Gloucester Point, during which neither sensor was serviced. The Hydrolab may have been at a disadvantage; underwater video taken at recovery revealed a mound of sediment and vegetation directly below its PVC well.

As previously stated in Section I, for NOAA CO-OPS objectives, the series of field tests reported here was conducted in part for initial familiarization with automated water quality sensors and preliminary experimentation to assess biofouling impacts and system maintenance requirements. Although long-term data sets collected with intentionally unmaintained sensors alongside rigorously maintained sensors are unique and potentially very useful, it is acknowledged that biofouling impacts (or lack thereof) presented in the data below are specific to each field site, season, conditions during the particular year tested, and installation configuration.

1) Gloucester Point

Gloucester Point is a significantly more saline location than White House Landing and presents a more challenging environment for long-term maintenance of ocean sensors. However, as compared to White House Landing, test data presented here began during a season with lower biological activity for the Chesapeake Bay tributary, mid-fall to winter. Due to uncertainty in results collected from the YSI sensor at the time this paper was written, only results for the test Hydrolab sensor are shown here. (It was learned post-test that the sensor operation may have been negatively impacted due to configuration errors).

Fig. 7 (a) shows 15-minute DO measurements from the test Hydrolab (blue) and CBNERR reference (black); (b) shows differences between test and reference sensors' 15-minute values. Measurements compared very well over the first 100 days of testing, November 11, 2012 to February 24 2013; after this time the test Hydrolab's measurements began to show a gradual decrease relative to the reference sensor, followed by a severe drop off in early March.

Fig. 8 shows daily average differences between the test Hydrolab and reference CBNERR sensors. Times of CBNERR sensor replacements are marked by red arrows. Note that the range of the axis in Fig. 8 covers times of good measurements, November 16, 2012 to February 24, 2013. Daily differences remained within the reference sensor's accuracy specification of ± 0.2 mg/L until a CBNERR sensor replacement in early January appears to have caused a sudden increase in difference value. The next time the CBNERR reference sensor is swapped on January 14, the difference with the test Hydrolab becomes smaller again. The reason for these shifts is presently under investigation. Daily average differences between the test Hydrolab and reference sensor's DO remained less than 0.3 mg/L from January 14 through February 24, 2013.

Fig. 9 (a) and (b) show the same 15-minute average and difference plots for the test Hydrolab and reference sensor's specific conductance measurements. Similar to DO, specific conductance values compare very well for the first 100 days of testing, followed by a gradual increase in difference in late February and a drop off of data values in March.

These results show one specific example of the test Hydrolab's DO and conductivity/temperature probes measuring within reasonable accuracy for 100 days while remaining completely unmaintained (repeated for emphasis: these data were collected during a less challenging biofouling season for the site). However, it should be noted that the test Hydrolab may have been at a deployment disadvantage; underwater video taken at recovery revealed that its PVC well was resting in a mound of sediment and vegetation. This could have hastened the rate of fouling experienced by the sonde.

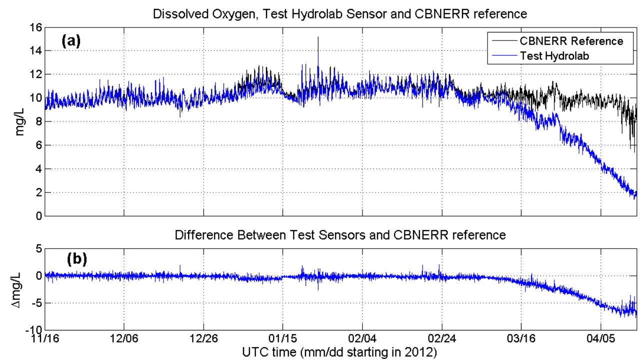

Fig. 7. (a) Fifteen-minute average DO measured by the test Hydrolab (blue line) and the CBNERR reference, (b) 15-minute differences between test sensors and reference.

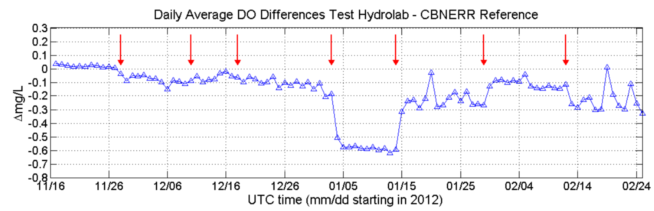

Fig. 8. Daily average differences between test Hydrolab and CBNERR reference DO sensors.

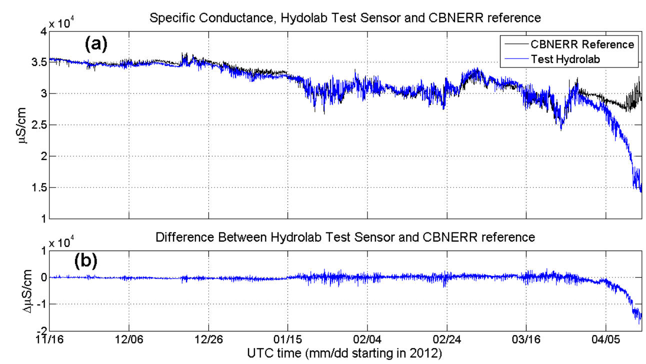

Fig. 9. (a) Fifteen-minute average specific conductance measured by the test Hydrolab (blue line) and the CBNERR reference, (b) 15-minute differences between test sensors and reference.

2) White House Landing

Data presented from the White House Landing experiment cover a 41-day period, from May 16 through June 26, 2013. In general, both test sensors' measurements of DO and specific conductance compared well to those from the CBNERR reference, considering no cleaning or maintenance was conducted over the entire measurement period.

Fig. 10 (a) shows a times series of 15-minute average DO values collected over the 41-day test period by the CBNERR reference sensor (black line) and the test Hydrolab (blue) and YSI (red) sensors; (b) shows 15-minute measurement differences between both test sensors and the CBNERR reference; and c) shows daily average differences between test and reference sensors. Fig. 11 shows the same series of plots for specific conductance measured by the three sensors. In both figures, 10 (c) and 11 (c), red arrows mark the times when the CBNERR sonde was exchanged with a newly calibrated and cleaned sonde.

Fig. 10 (c) shows that the test Hydrolab's daily average differences from reference remained within the reference's expected accuracy, ± 0.2 mg/L, for the entire 41-day test period, while the test YSI's daily average differences from reference remained within the reference's expected accuracy for only 14 days; for the rest of the test period, the test YSI differences from the reference remained < 0.35 mg/L. Both sensors showed a roughly linear drift over the duration of the measurement period: for the test Hydrolab -0.003 mg/L per day and for the test YSI 0.005 mg/L per day. These results provide an example of the test Hydrolab sensor measuring within accuracy specifications for a 41-day period with no maintenance or calibration, for this particular field location (tidal fresh water), season (spring to summer), and installation configuration.

Fig. 11 (a) shows the expected variation of specific conductance at the M2 semidiurnal tidal frequency with a significant specific conductance drop starting on June 9. Fig. 11 (b) and (c) show that both test sensors' measured specific conductance varies from the reference more than the reference sensors specified accuracy (approximately 1.5 μ/cm), but differences are still much less than accuracy requirements specified for CO-OPS applications. Daily average specific conductance of the test Hydrolab sensor remained within 6 μS/cm of the reference, and the test YSI remained within 8 μS/cm for the entire test period.

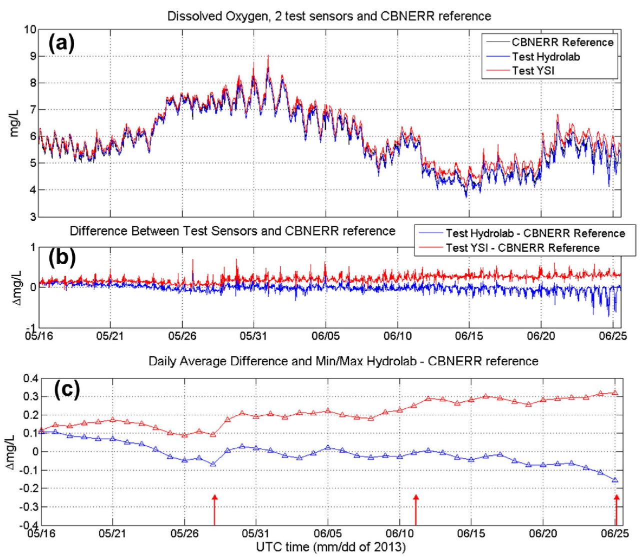

Fig. 10. (a) Fifteen-minute average DO measured by the test Hydrolab (blue line) and YSI (red line) sensors and the CBNERRS reference, (b) 15-minute differences between test sensors and reference, (c) daily average differences between test sensors and reference.

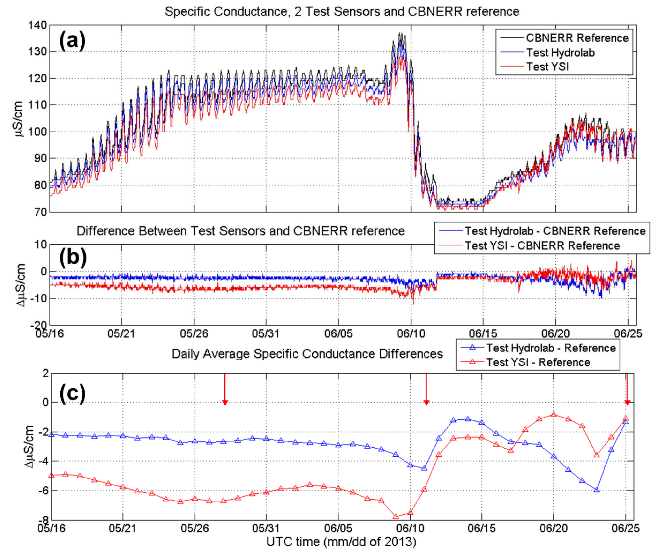

Fig. 11. (a) Fifteen-minute average specific conductance measured by the test Hydrolab (blue line) and YSI (red line) sensors and the CBNERRS reference, (b) 15-minute differences between test sensors and reference, (c) daily average differences between test sensors and reference.

After specific conductance began to return to higher values near June 17-18, differences between test sensors and reference sensor began to grow; however, differences still remained relatively small and within CO-OPS' specific conductance accuracy requirements. Similar to the DO results, these data show one specific example of two different conductivity sensors continuing to measure within reasonable accuracy for 41 days with no maintenance.

3) Comparison of Chloride Measurement Methods

As previously stated, both specific conductance and chloride measurements at the second field test site, White House Landing, were lower than expected over the first 41 days of data collection. Still, measurements from the conductivity and chloride sensor, along with chloride measurements from grab samples, provide some interesting results.

Fig. 12 shows (a) 15-minute specific conductance measurements from the CBNERR reference sensor, (b) 15-minute chloride measurements from both test sensors and grab samples, and (c) difference between the two test sensors' chloride measurements. Although the four grab samples indicated that chloride levels were very close to, or below, the detectable threshold value of 5 mg/L, both test sensors' readings were approximately 7-21 mg/L. This may be an indication of sensor noise floor. Fig. 12 (c) shows that the two sensors' readings were within ± 5 mg/L of one another, which is within the manufactures' accuracy specification.

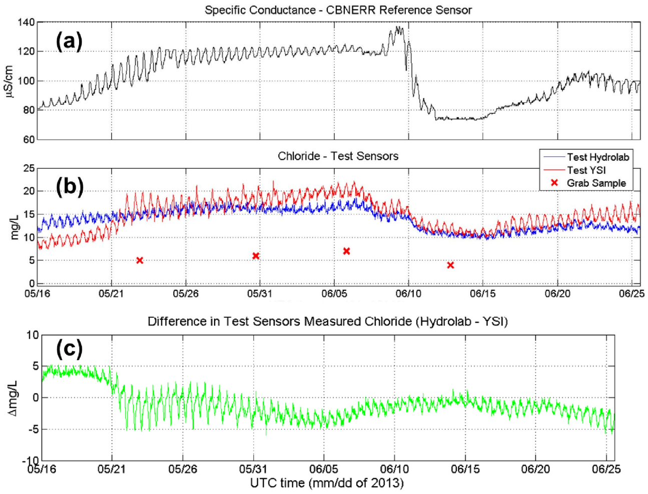

Fig. 12. (a) Specific conductance measurements from the CBNERR reference sensor, (b) chloride measurements from both test sensors and grab samples, and (c) difference between to test sensors' chloride measurements.

As expected, the scatter plot in Fig. 13 shows that the signals from both test sensors' chloride probes were strongly correlated with the reference sensor's specific conductance signal. A first order least squares fit for each yielded the following:

Test Hydrolab:

Chloride = 0.112*(Specific Conductance) + 2.356

Test YSI:

Chloride = 0.168 *(Specific Conductance) - 2.443

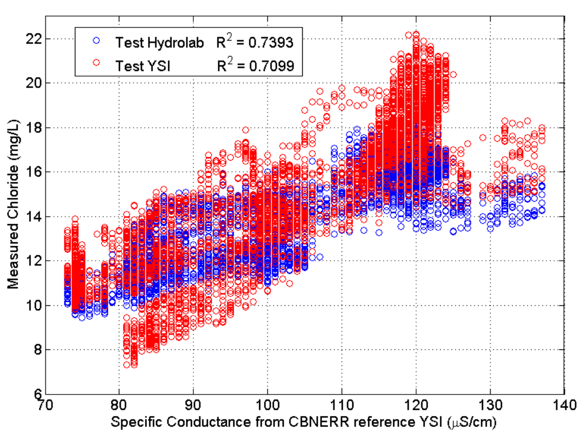

Fig. 13. Measured chloride from both test sensors versus reference sensor's specific conductance.

The data obtained during the river transect sampling are shown in Fig. 14 and Table 1. The sampling location names correspond to those shown in Fig. 5. The first sample was collected near West Point. Sampling proceeded upriver to progressively fresher sites, and the final sample was collected at Sweet Hall Landing. Samples RT_3, RT_4, and RT_5 are of the most interest since they fall near or below 500 mg/L (the cut-off for water treatment plants). Table 1 shows two additional samples collected at Sweet Hall Landing during the hours leading up to the river transect.

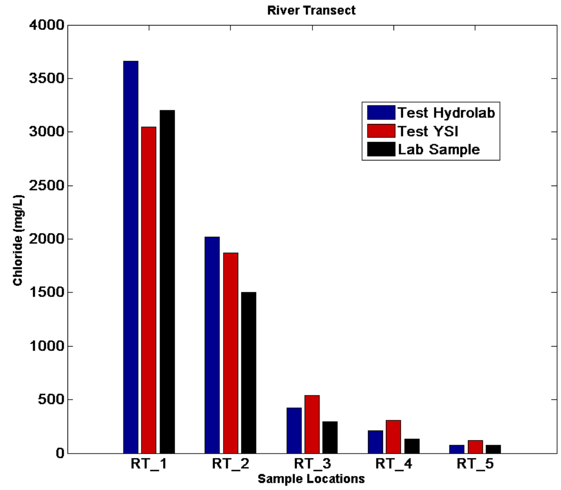

Fig. 14. Chloride data from the river transect sites shown in Fig. 5. The samples were collected moving upriver, from high to low salinity.

TABLE I. RIVER TRANSECT CHLORIDE LEVELS

		Hydrolab	YSI	Grab Sample
Chloride (mg/L)	SH_1	43.64	69.44	<5
	SH_2	45.09	63.3	27
	RT_1	3662	3044	3200
	RT_2	2017	1869	1500
	RT_3	424.4	540.6	295
	RT_4	207.7	309.1	130
	RT_5	75.51	116.8	73

In Fig. 15, the chloride differences between each test sensor and the reference grab sample at each river transect site are plotted against the grab sample value. For the three river transect samples of most interest (< 500 mg/L), along with the two Sweet Hall Landing samples taken previously, the test sensors remain within 250 mg/L of the reference samples. The differences increase with increasing chloride levels. At these lower chloride levels, the test Hydrolab measures closest to the reference grab samples in all five cases.

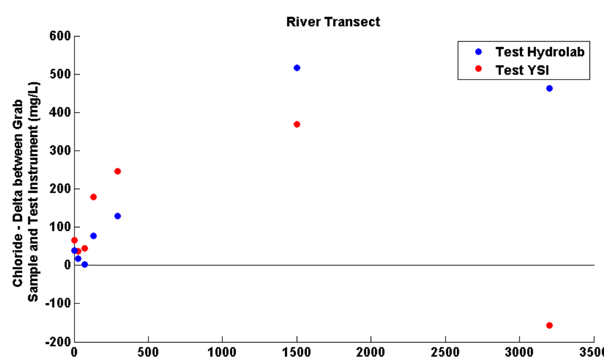

Fig. 15. Differences between chloride measured by test sensors and grab samples, plotted against grab samples. The black line represents no difference between the test sensor and reference.

In Fig. 16, the three sources of chloride data from the river transect (two test sensors and grab sample data) are plotted against measured specific conductance. The relationship between chloride and specific conductance for all three measurement sources compared very well. A first order least squares fit yields the following rate of change (slopes - mg/L per µS/cm) for each source: Hydrolab 0.377, YSI 0.349, Grab 0.324 (mg/L per µS/cm).

The 2010 South Florida Environmental Report [14] presents an application of such a regression analysis. A first order least squares fit was performed on measured chloride and specific conductance data in a fresh water environment. The resulting equation was then used to calculate chloride from measured specific conductance during subsequent monitoring efforts.

The rates of change for the data in Fig. 15 for all three sources are higher than the rate of change in the empirical formula from the South Florida Environmental Report noted in the previous paragraph (rate of change = 0.218). Also, all three are higher than the rates of change for the fit of data shown in Fig. 13 from White House Landing (rates of change = 0.112 and 0.168). This suggests that a reference expression may miss critical detections that automated sensors may detect. However, higher chloride values measured by in-situ sensors may indicate that they are more likely to be more prone to false detection.

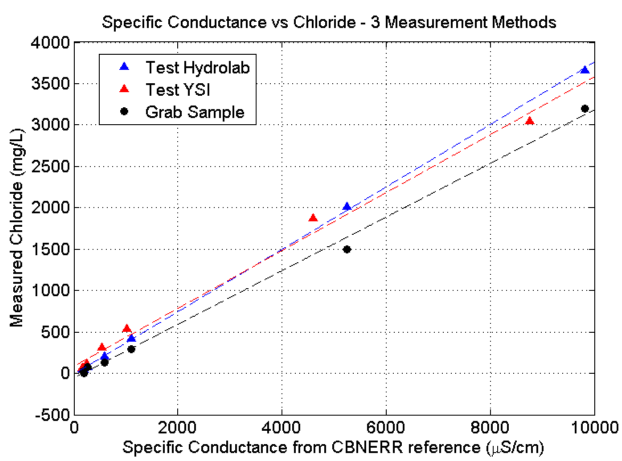

Fig. 16. Measured chloride from both test sensors and grab samples versus specific conductance for data collected over the river transect.

V. Summary

The initial goal of this study was the successful integration of two water quality sensors with CO-OPS' standard real-time system. This goal was met with the successful transmission of 6-minute water quality data via GOES for the entire 8-month study period.

Both of the test water quality sondes performed remarkably well given the complete absence of maintenance during either phase of the field test. At Gloucester Point, the test Hydrolab's DO and conductivity/temperature probes measured within reasonable accuracy for 100 days. While this test occurred during the late fall and winter months, a period of low biofouling, it is a nonetheless encouraging result that introduces the possibility of maintenance intervals longer than the typical 1-2 weeks. At White House Landing, the test Hydrolab sensor measured DO within accuracy specifications for the entire 41-day analysis period with no maintenance or calibration. Both the test Hydrolab and test YSI remained within specification for specific conductance measurements for the same period. These results are very promising, but admittedly specific to this particular site, season, and set of deployment circumstances.

The comparison of techniques for determining chloride yielded interesting results. The in-situ chloride probes measured consistently higher than the laboratory-analyzed grab samples. For the levels of interest in this study (< 500 mg/L), the test Hydrolab chloride data agreed better with the reference grab samples. Regression analysis of various sets of measured specific conductance and chloride data suggests that deriving chloride from measured conductivity is site-specific and may vary widely with changing conditions (e.g., seasons, rainfall, etc.). While the in-situ ISE sensors may not be as accurate as grab samples, they may represent a good middle ground between the two previous methods. Operating in a real-time capacity, they might serve as an early warning system for salinity intrusions, especially if ground-truthed periodically with grab samples.

As mentioned previously, CO-OPS is especially interested in prolonging the time required between servicing visits for water quality sensors. In addition to further exploring the encouraging results of the unmaintained sensors in this study, CO-OPS is investigating other methods of extending deployment times. These methods include using several sensors with more advanced technology for antifouling (a YSI EXO2 and a Sea-Bird 37SM MicroCAT); exploring the design of pumped water quality systems in which contact between sensor and sample water is minimized; and testing a GreenEyes Probe Guard (keeps probes protected between samples and periodically administers a biocide) on one of the test sensors used in this study.

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