Technical Capabilities, Limitations and Needs

Todd Martz

OAPI Meeting, 18 Sep 2013

Breakout Group #3

Technical developments Leads: Kendra Daly (USF), Todd Martz (SIO)

- Discussants will begin by reviewing the results of a brief community survey focusing on usage trends and challenges associated with sensors and carbonate chemistry equipment.
- Then, the discussion will explore :
    1) needs associated with development of new techniques, sensors, and equipment.
    2) possibilities of developing or enhancing sensor networks, particularly with an eye toward coordination and intercomparison.
    3) additional tools needed, such as analytical facilities, shared instrument repositories, or computing tools. In each case, identified needs will be matched with estimates of the type and magnitude of obstacles (e.g., time, cost, manpower, etc.) facing them.

Capabilities

- Methods are highly refined for bottle measurements.
- Commercially available bench top instruments available for all four CO_2 parameters.
- Commercially available systems available for autonomous in situ pCO_2 and pH.
- Custom underway & in situ systems have been developed for A_T and C_T.

ALLIANCE FOR COASTAL TECHNOLOGIES

SUPPORTING INNOVATION TO BETTER UNDERSTAND, PREDICT AND MANAGE COASTAL, OCEAN AND GREAT LAKES ENVIRONMENTS.

http://www.act-us.info/

INTERNATIONAL OCEAN CARBON COORDINATION PROJECT

IOCCP

http://www.ioccp.org/instruments-and-sensors

Needs

- "Recent" reviews in OceanObs'09 Community White Papers summarize the state of the art and outline needs. Workshops since OceanObs have echoed similar information.
- Several papers out in 2013 on technology developments!
- In addition to sensors, more nebulous needs include networks & facilities.

A GLOBAL SEA SURFACE CARBON OBSERVING SYSTEM: INORGANIC AND ORGANIC CARBON DYNAMICS IN COASTAL OCEANS

A.V. Borges [1], S.R. Alin [2], F.P. Chavez [3], P. Vlahos [4], K.S. Johnson [3], J.T. Holt [5], W.M. Balch [6], N. Bates [7], R. Brainard [8], W.-J. Cai[9], C.T.A. Chen [10], K. Currie [11], M. Dai [12], M. Degrandpre [13], B. Delille [14], A. Dickson [15], W. Evans [16], R.A. Feely [2], G.E. Friederich [5], G.-C. Gong [17], B. Hales [17], N. Hardman-Mountford [18], J. Hendee [19], J.M. Hernandez-Ayon [20], M. Hood [21], E. Huertas [22], D. Hydes [23], D. Ianson [24], E. Krasakopoulou [25], Litt E.[26], A. Luchetta [27], J. Mathis [28], W.R. McGillis [29], A. Murata [30], J. Newton [31], J. Ólafsson [32], A. Omar [33], F.F. Perez [34], C. Sabine [2], J.E. Salisbury [35], R. Salm [36], V.V.S.S. Sarma [37], B. Schneider [38], M. Sigler [39], H. Thomas [40], D. Turk [41], D. Vandemark [40], R. Wanninkhof [23], B. Ward [42]

TOWARD AN INTEGRATED OBSERVING SYSTEM FOR OCEAN CARBON AND BIOGEOCHEMISTRY AT A TIME OF CHANGE

Final version August 6, 2010

Nicolas Gruber [1], Arne Körtzinger[2], Alberto Borges[3], Hervé Claustre [4], Scott C. Doney [5], Richard A. Feely [6], Maria Hood [7], Masao Ishii [8], Alexander Kozyr [9], Pedro Monteiro [10], Yukihiro Nojiri [11], Christopher L. Sabine [6], Ute Schuster [12], Douglas W.R. Wallace [2], and Rik Wanninkhof [13]

AN INTERNATIONAL OBSERVATIONAL NETWORK FOR OCEAN ACIDIFICATION

R. A. Feely [1], V. J. Fabry [2], A. G. Dickson [3], J.-P. Gattuso [4], J. Bijma [5], U. Riebesell [6], S. Doney [7], C. Turley [8], T. Saino [9], K. Lee [10], K. Anthony [11], J. Kleypas [12]

SENSORS AND SYSTEMS FOR IN SITU OBSERVATIONS OF MARINE CARBON DIOXIDE SYSTEM VARIABLES

Robert H. Byrne [1], Michael D. DeGrandpre [2], R. Timothy Short [3], Todd R. Martz [4], Liliane Merlivat [5], Craig McNeil [6], Fred L. Sayles [7], Ryan Bell [8], Peer Fietzek [9]

Environmental Science & Technology

Article

pubs.acs.org/est

High-Frequency Spectrophotometric Measurements of Total Dissolved Inorganic Carbon in Seawater

Zhaohui Aleck Wang,* Sophie N. Chu, and Katherine A. Hoering

Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, McLean 203, MS no. 8, 266 Woods Hole Road, Woods Hole, Massachusetts 02543, United States

In situ Spectrophotometric Measurement of Dissolved Inorganic Carbon in Seawater

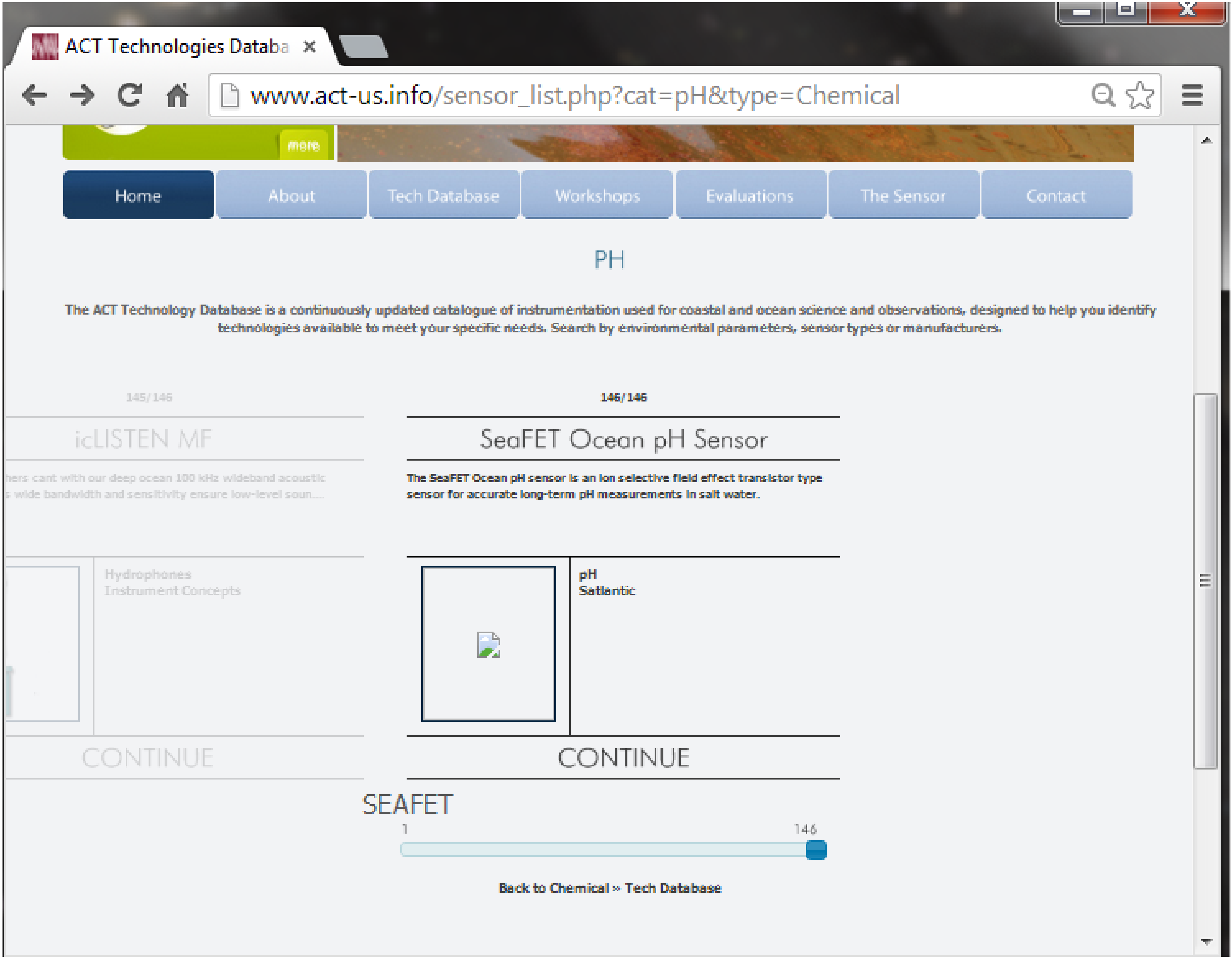
Xuewu Liu, Robert Byrne, Lori R Adornato, Kim Yates, Eric Kaltenbacher , Xiaoling Ding, and Bo Yang

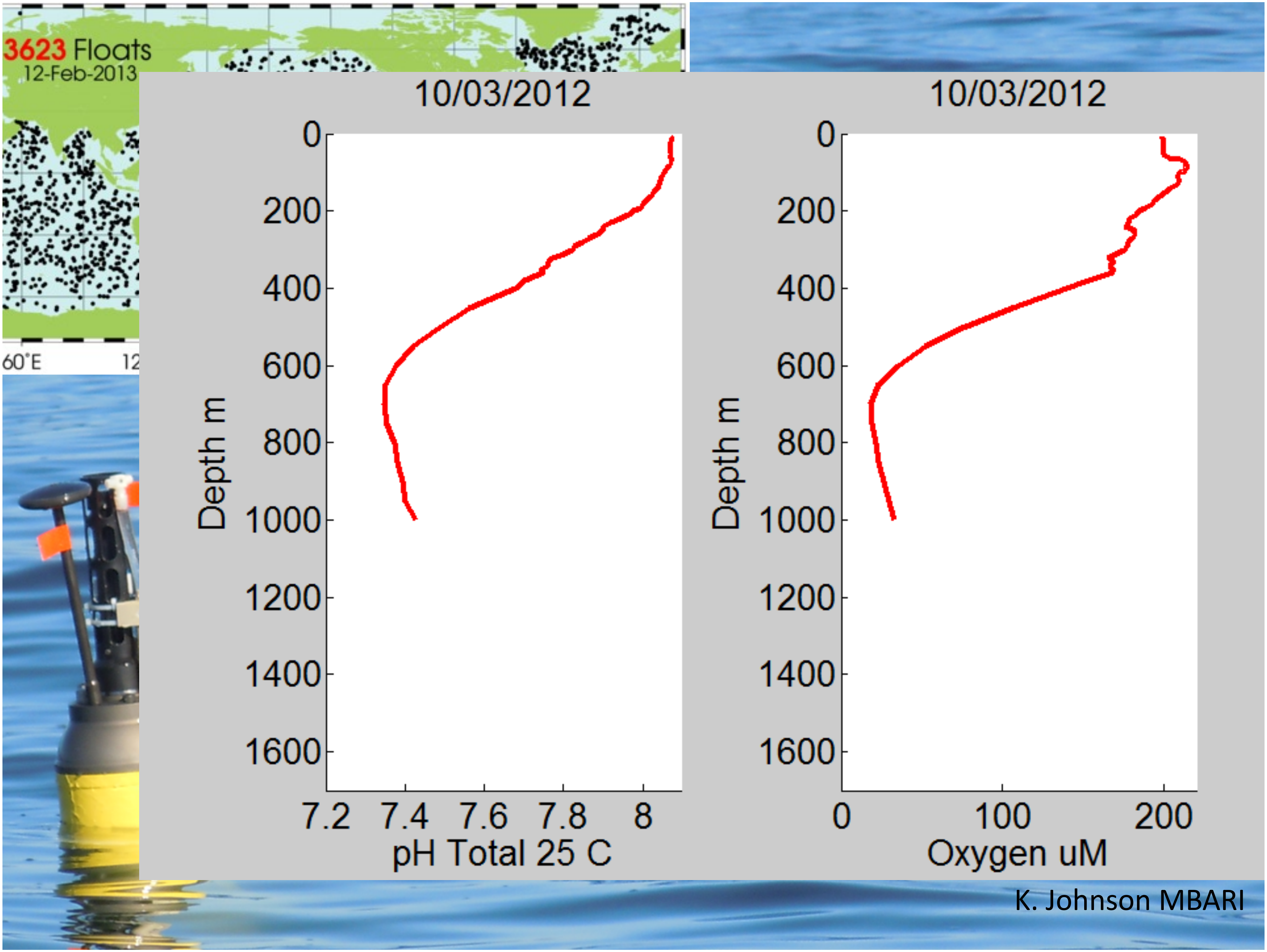
Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/es4014807 • Publication Date (Web): 30 Aug 2013

An Automated Spectrophotometric Analyzer for Rapid Single-point Titration of Seawater Total Alkalinity

Quanlong Li, Fengzhen Wang, Zhaohui Aleck Wang, Dongxing Yuan, Minhan Dai, Jinshun Chen, Junwei Dai, and Katherine Hoering

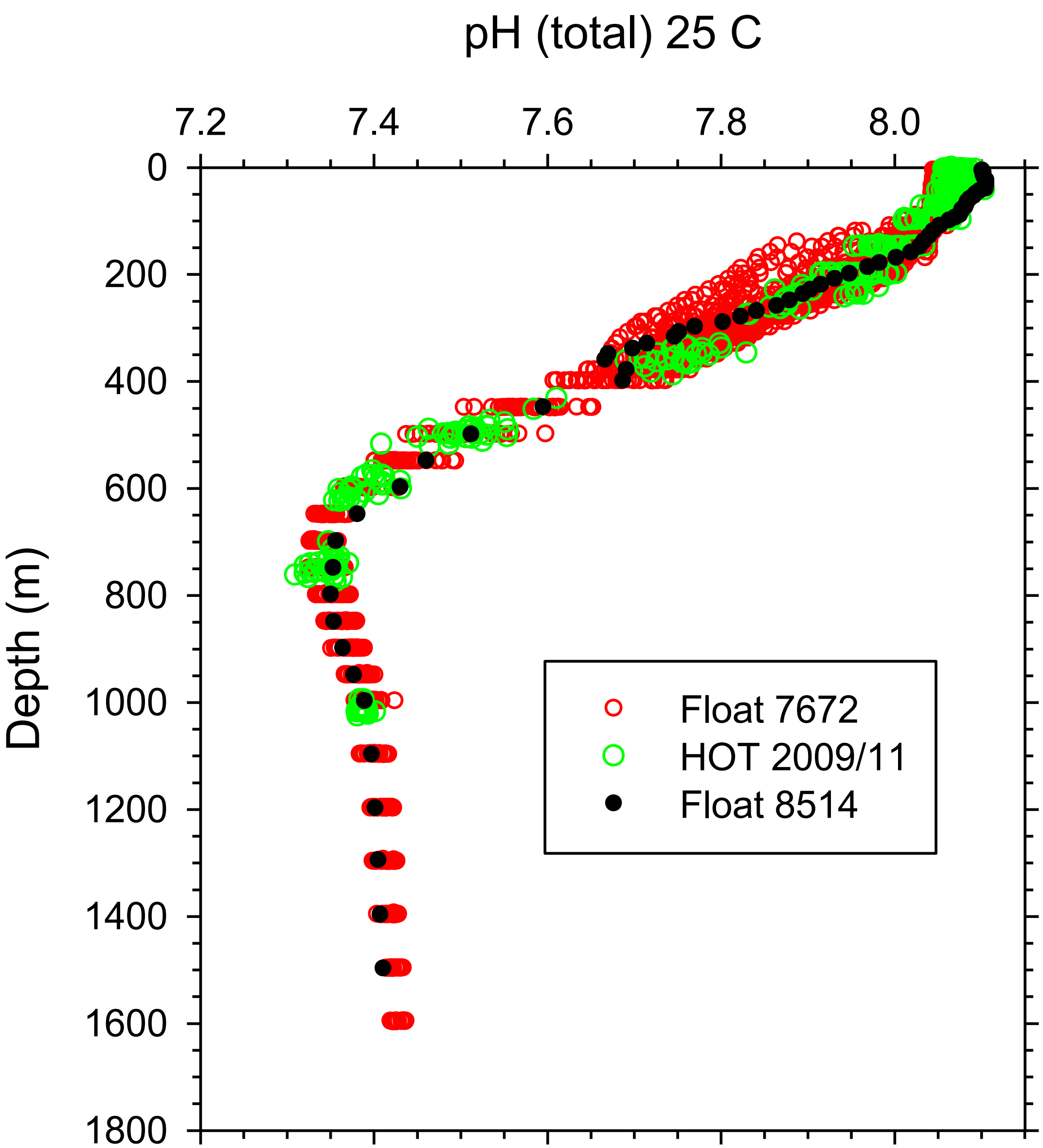
Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/es402421a • Publication Date (Web): 22 Aug 2013


ACT Technologies Databa
www.act-us.info/sensor_list.php?cat=pH&type=Chemical
more
Home
About
Tech Database
Workshops
Evaluations
The Sensor
Contact
PH
The ACT Technology Database is a continuously updated catalogue of instrumentation used for coastal and ocean science and observations, designed to help you identify technologies available to meet your specific needs. Search by environmental parameters, sensor types or manufacturers.
145/146
icLISTEN MF
hers cant with our deep ocean 100 kHz wideband acoustic
wide bandwidth and sensitivity ensure low-level soun....
Hydrophones
Instrument Concepts
CONTINUE
146/146
SeaFET Ocean pH Sensor
The SeaFET Ocean pH sensor is an Ion selective field effect transistor type sensor for accurate long-term pH measurements in salt water.
pH
Satlantic
CONTINUE
SEAFET
1
146
Back to Chemical » Tech Database


3623 Floats
12-Feb-2013
60°E
10/03/2012
Depth m
0
200
400
600
800
1000
1200
1400
1600
7.2
7.4
7.6
7.8
8
pH Total 25 C
10/03/2012
Depth m
0
100
200
Oxygen uM
K. Johnson MBARI

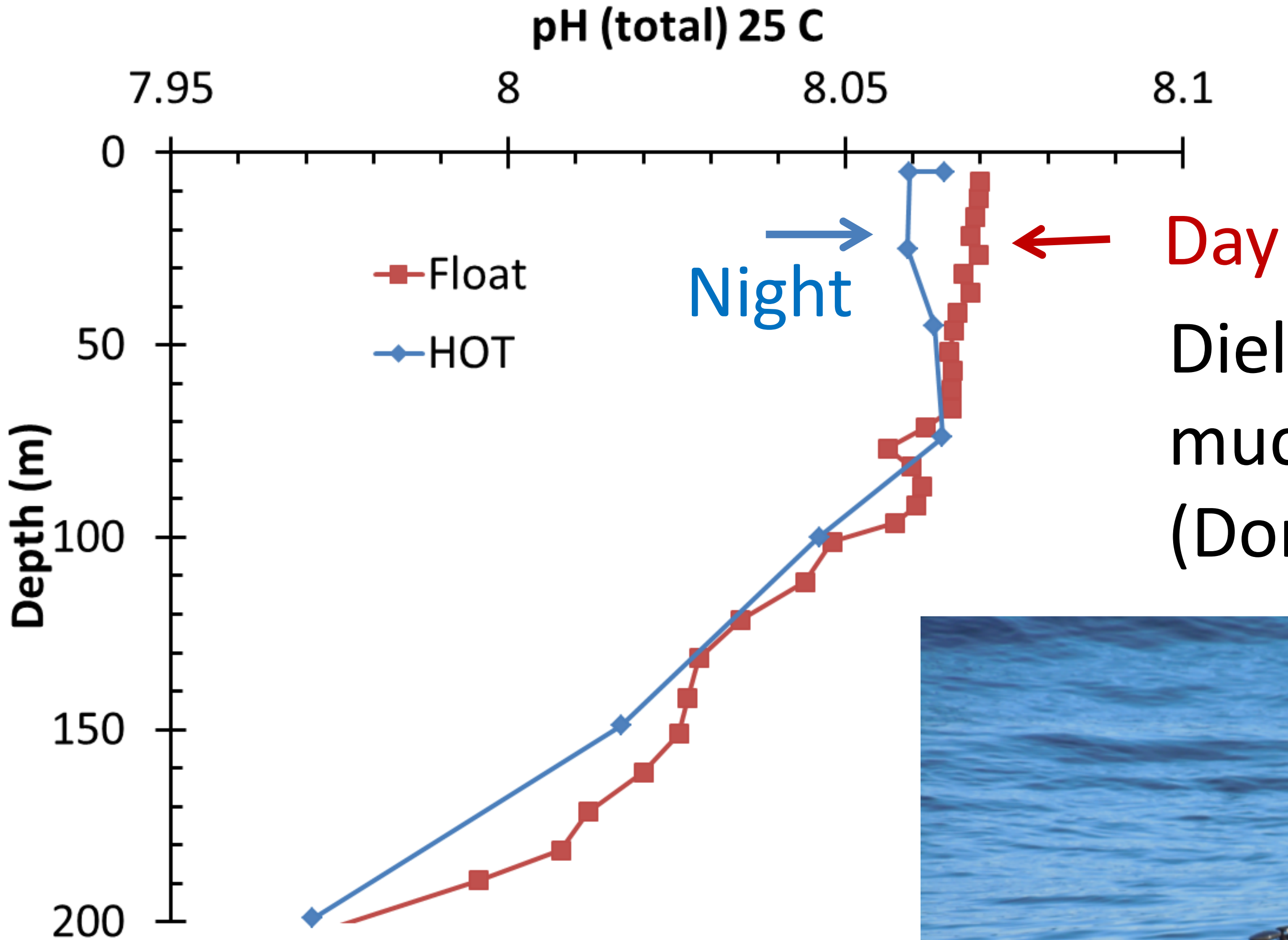
Towards a global ocean pH observing system: First measurements with Deep-Sea DuraFET pH sensors on profiling floats

K. S. Johnson, L. J. Coletti, H. W. Jannasch (MBARI), T. R. Martz, Y. Takeshita (SIO), R. Carlson, T. Nohava, G. Brown, J. Connery (Honeywell), S. Riser, D. Swift (University of Washington)



- HOT pH in 2009 to 2011.
- Float 7672 operated Oct, 2012 to April 2013
- Float 8514 launched this weekend, showing excellent agreement.

The slightly lower float pH at the surface for float 7682 vs HOT is consistent with the ocean acidification signal (-0.0017 pH/y). (8514 is high now due to the annual pH cycle at HOT).

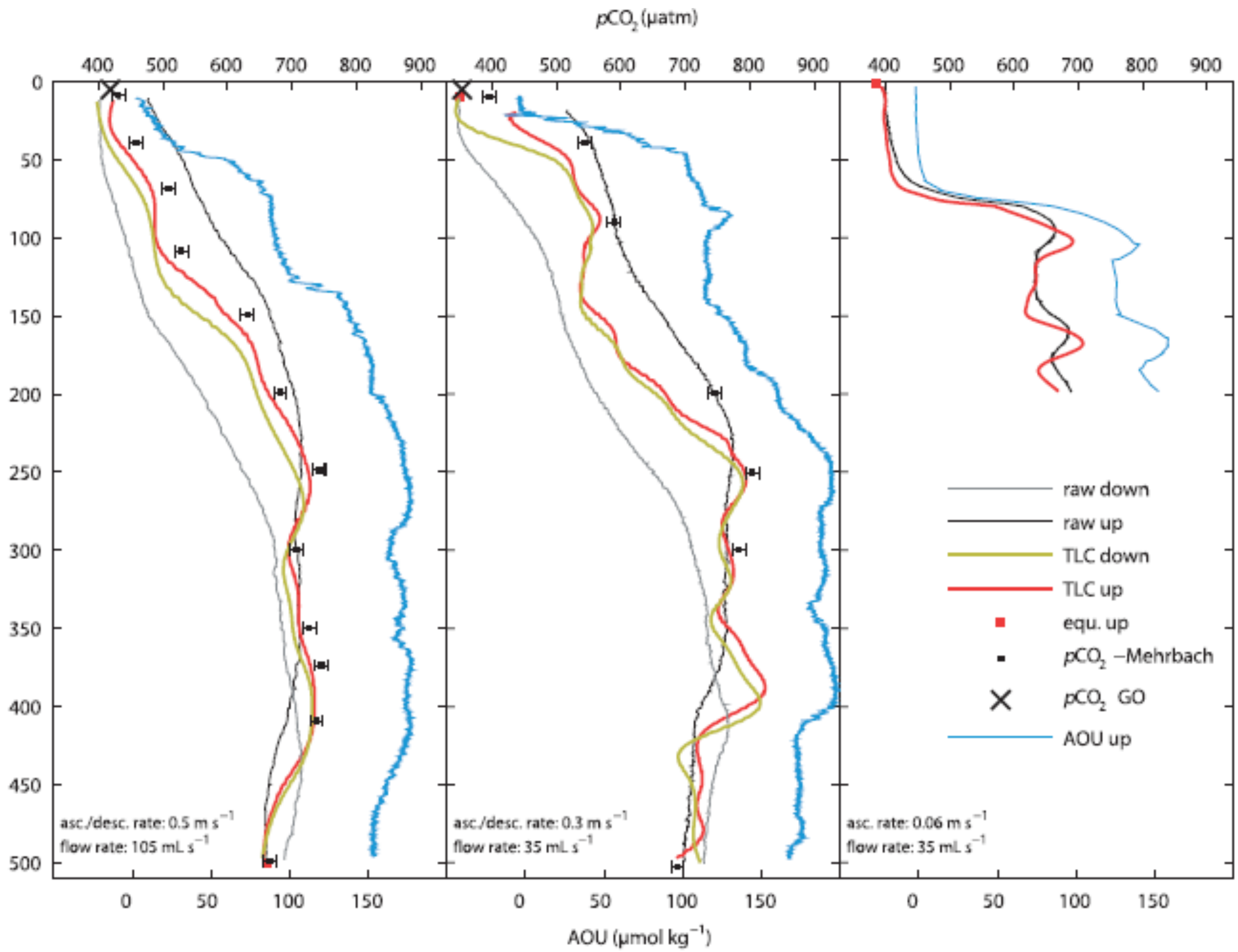


Diel cycle at HOT “as much as 0.01 in pH” (Dore et al. 2009)

K. Johnson MBARI

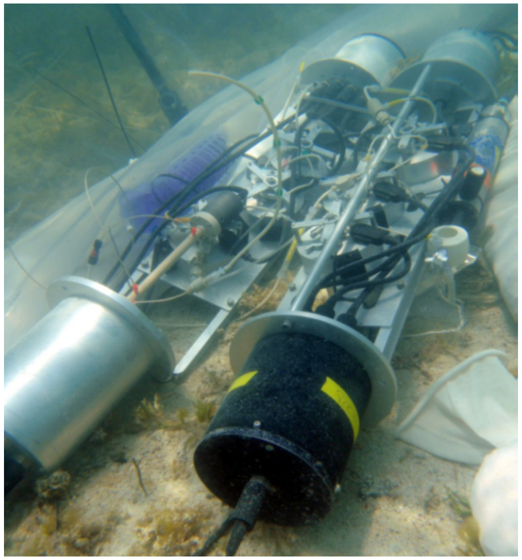
In Situ CO_2 and O_2 Measurements on a Profiling Float

Fiedler, B., P. Fietzek, N. Vieira, P. Silva, H. C. Bittig, and A. Körtzinger (2012), In Situ CO2 and O2 Measurements on a Profiling Float, *Journal of Atmospheric and Oceanic Technology*, *30*(1), 112-126.

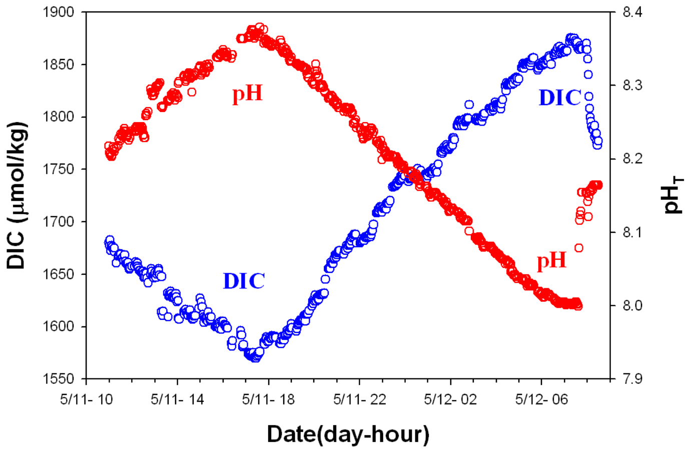


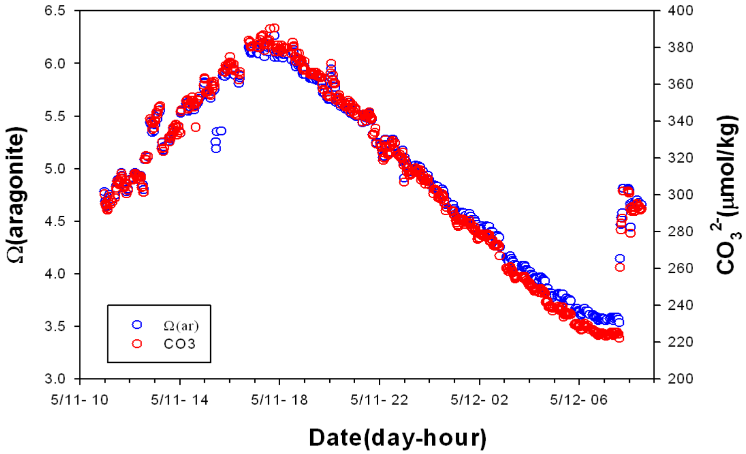
SEAS in situ DIC and pH instrumentation

Bob Byrne, Lori Adornato, Eric Kaltenbacher, Sherwood Liu



- Modular
  - Spectrometer
  - Three two-channel pumps
  - Internal or external lamp options
  - Configurable optical cell
  - Data collection from up to four peripheral sensors (e.g., CTD, fluorometer, transmissometer, second SEAS instrument)
  - Battery or externally powered
  - Heater option
- Sampling rate (pH = 1 Hz, DIC = 1 per minute)
- Ambient temperature pH and DIC measurements
- Rated to 1,000 meters depth
- Configurable for carbon system, nutrient or trace metal analysis

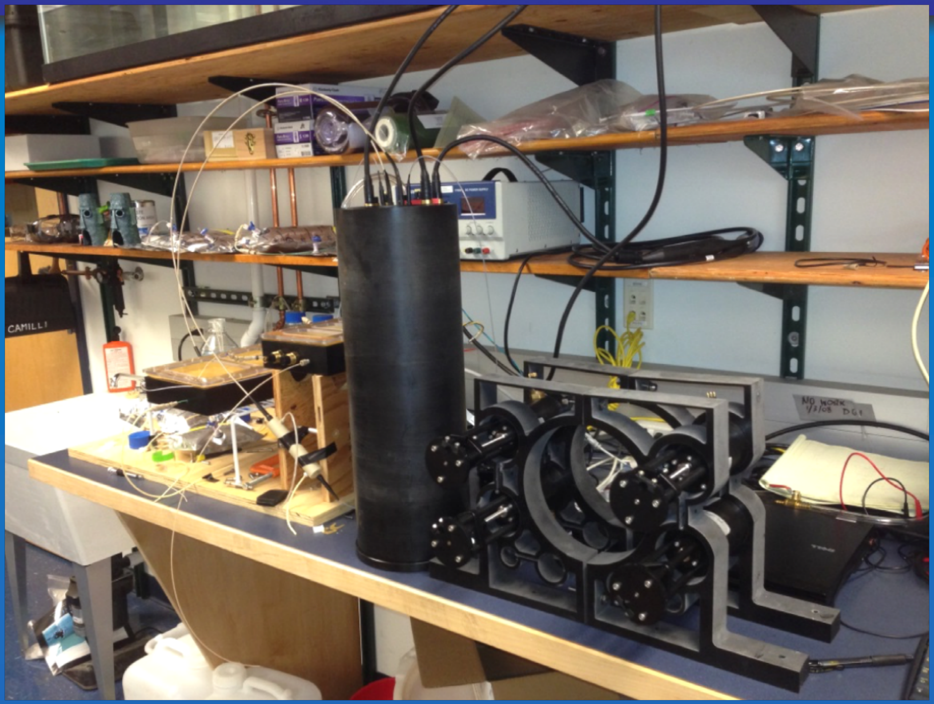




UNIVERSITY OF SOUTH FLORIDA
COLLEGE OF MARINE SCIENCE

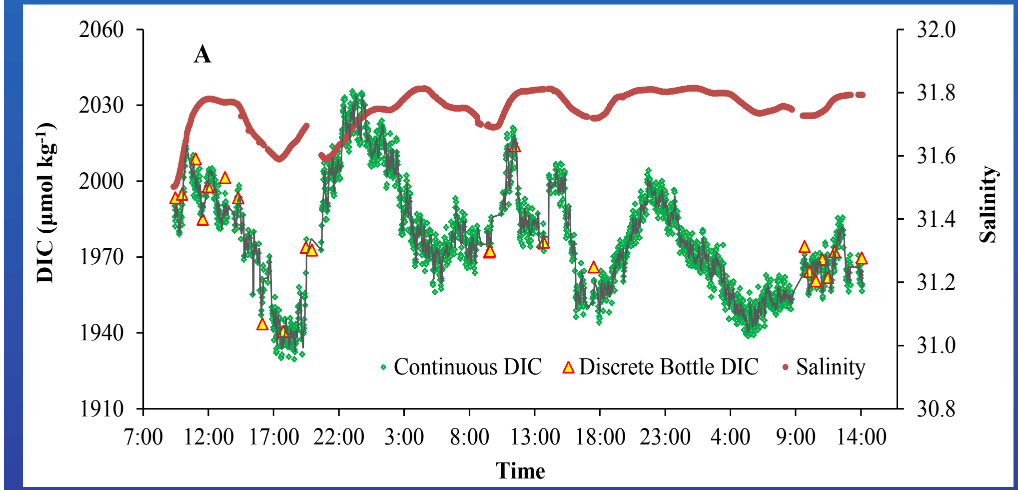
In-situ Carbon Sensing

(Aleck Wang, WHOI)



Type I: Buoy-based in-situ DIC-pH Sensor (In testing)

- Method: Concurrent, spectrophotometric
- Deployment depth: surface – 50 m
- Measurement frequency: every 10 mins
- Precision: pH ±0.001 pH, DIC ±3 μmol/kg
- In-situ calibration of DIC



Continuous DIC analysis (Wang et al. 2013)

Type II: DIC sensor for mobile platforms (AUV, ROV, and CTD) (In development)

- Method: Spectrophotometric
- Deployment depth: surface – 2000 m
- Measurement frequency: ~1 Hz
- Precision: DIC ±3 μmol/kg

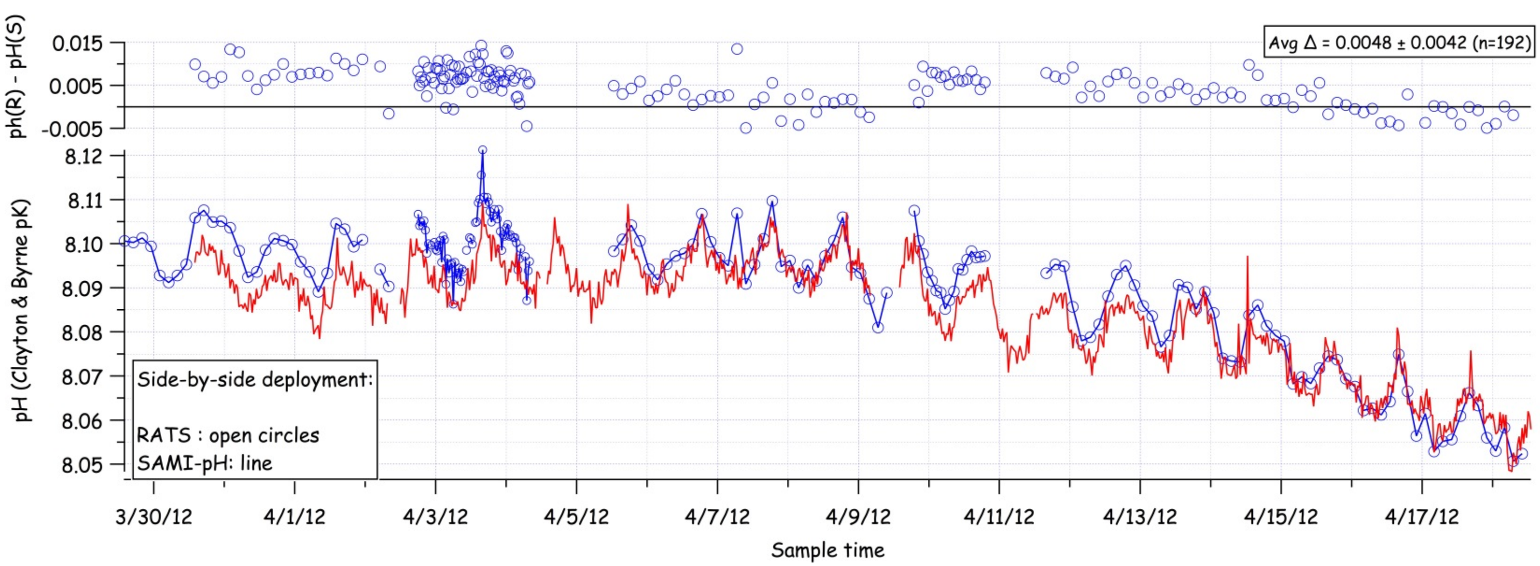
RATS : The Robotic Analyzer for the TCO_2 system in Seawater
Sayles, Martin, and McCorkle (WHOI)

<u>RATS Methods:</u> TCO_2 : Conductimetry (Sayles & Eck, 2009) : +/- 3.6 µmol/kg
pH : Spectrophotometry (Seidel et al., 2008) : +/- 0.004

Comparison 1: autonomous, in situ RATS vs. discrete (bottle) samples (n=14):

	RATS - DM lab	RATS - AW lab	RATS - SAMI-pH	
TCO2	-0.8 ± 4.7	-0.6 ± 5.7		Difference in µmol/kg
Talk	1.9 ± 4.5	2.7 ± 4.8		calc. for RATS
pH	0.0056 ± 0.0067	0.0097 ± 0.0029 (large temperature correction)	0.0048 ± 0.0042	calc. for DM SAMI and RATS co-deploy, 19 days

Comparison 2: RATS pH (Sayles et al.) and SAMI-pH (M. DeGrandpre)



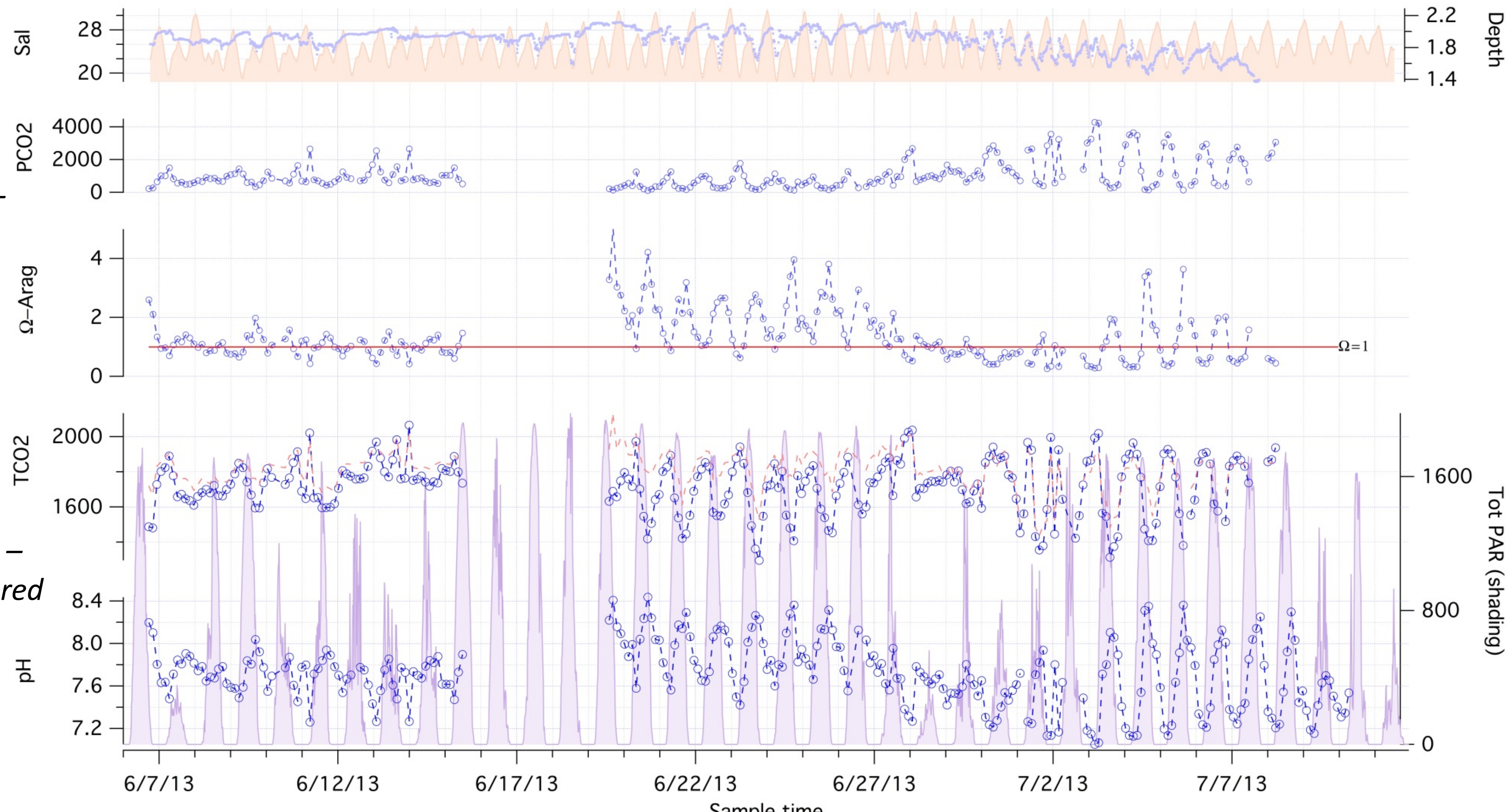
RATS : The Robotic Analyzer for the TCO_2 system in Seawater
Sayles, Martin, and McCorkle (WHOI)

35-day deployment in Waquoit Bay, MA: RATS with ancillary data from the Waquoit Bay National Estuarine Research Reserve

A eutrophic estuary with a strong diurnal cycle and tidal influence

RATS – calc.

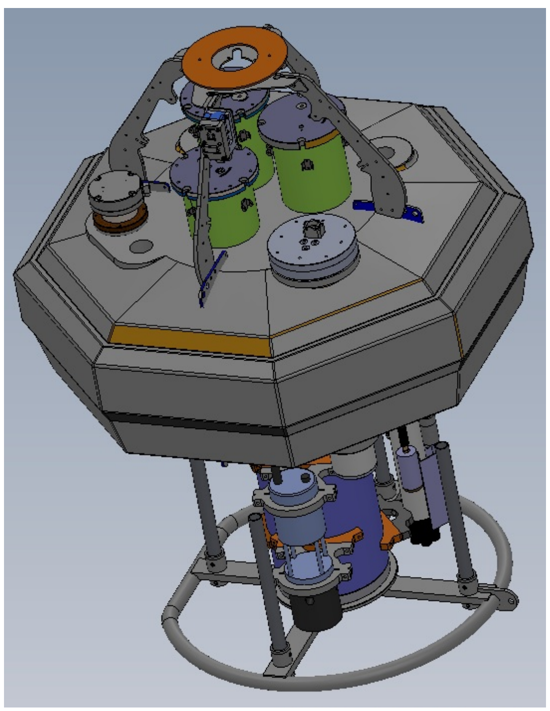
RATS – measured



Moored Autonomous Total CO2 (MAPTCO2)

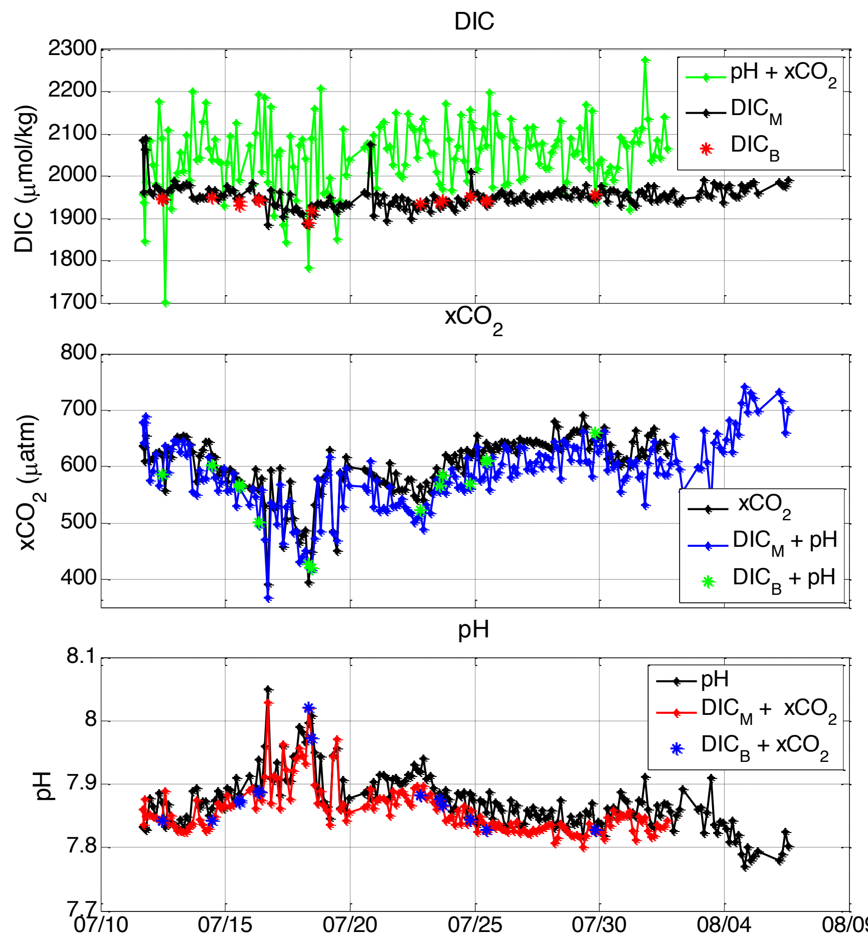
Andrea J. Fassbender, Christopher L. Sabine, Chris Meinig, Noah Lawrence-Slavas, Patrick McLain, Cathy Cosca, Geoff Lebon, Joe Resing

Instrument Goals:
Endurance of up to 1 year unattended
Measurement range of 1800 – 2250 µmol kg^{-1}
Measurement precision of ±5 µmol kg^{-1}



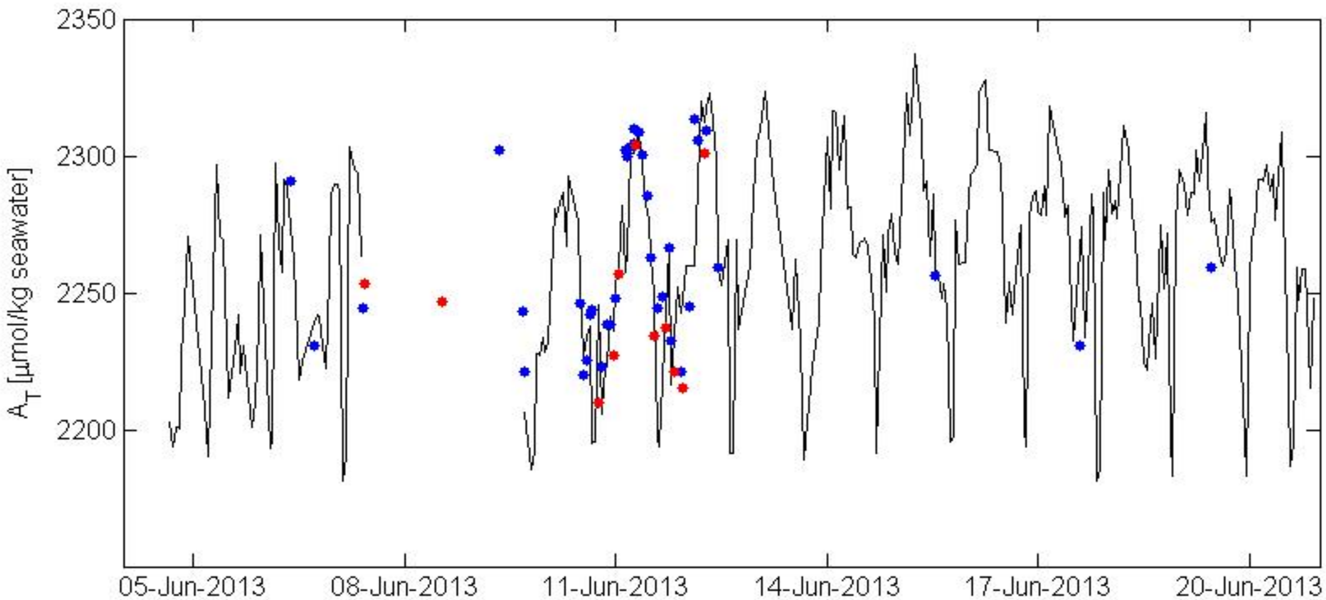
Initial testing at Seattle Aquarium

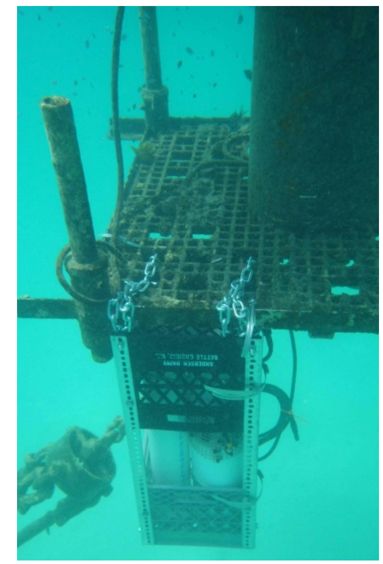
To be deployed off Hawaii next month for first fully operational use.



In situ alkalinity measurements on a coral reef

R. Spaulding (Sunburst Sensors)
M. DeGrandpre (U. Montana)





A 15-day June 2013 in situ alkalinity time-series recorded with a novel autonomous analyzer (SAMI-alk) in Kaneohe Bay, Hawaii in collaboration with Eric DeCarlo (U. Hawaii) (Black line). Alkalinity from Gran titrations (blue symbols) and calculated from pH and DIC measurements (red). The instrument uses a pH indicator for both pH measurements and to quantify the titrant added (Tracer Monitored Titration methodology, Martz et al. 2006). The gap is due to faulty initiation of the instrument program during data download.

ΔA_T SAMI vs. bottle = 0.8 ± 17.8 µmol kg sw^{-1}(n=28)
ΔA_T SAMI vs. SAMIpH+bottle DIC = 1.6 ± 27.8 µmol kg sw^{-1}(n=11)
Accuracy/Error of CRMs titrated: 1.6 +/- 3.3 (Sunburst, N=15); 5.1 +/- 9.0 (UHI, N=13)

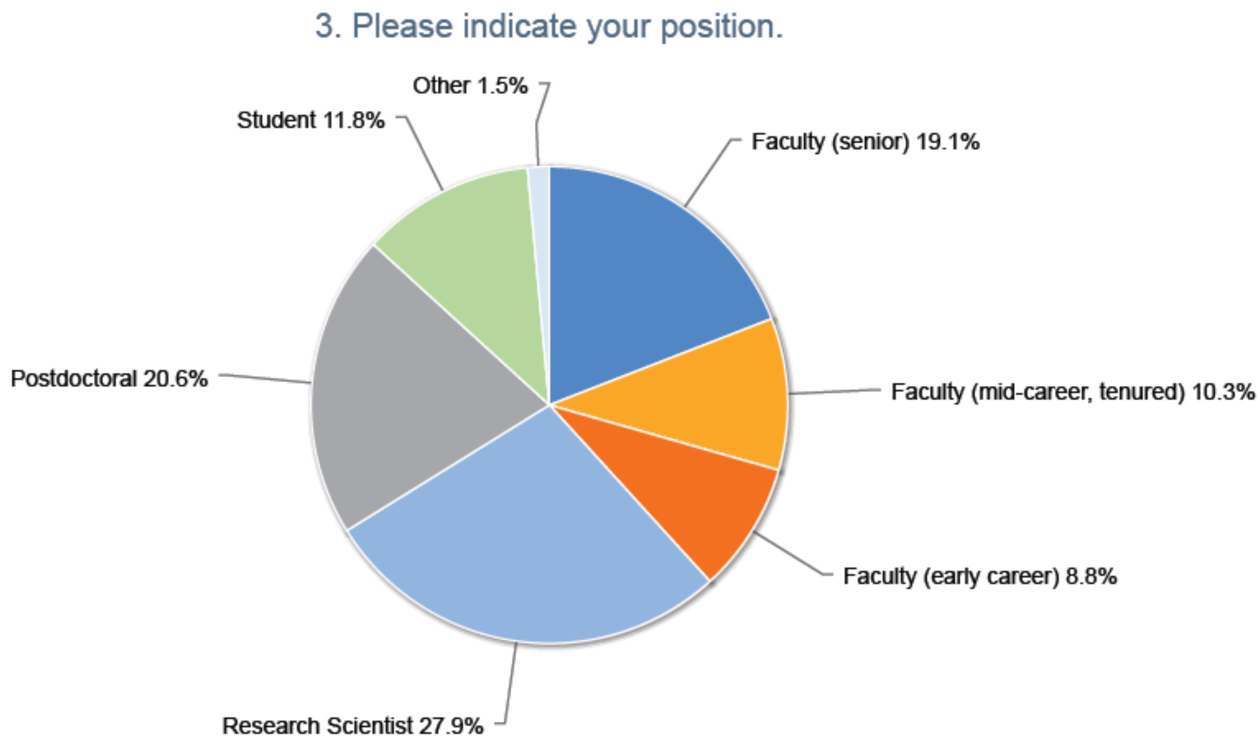
Breakout Group #3

Technical developments Leads: Kendra Daly (USF), Todd Martz (SIO)

Room 2 (2nd floor)

- Discussants will begin by reviewing the results of a brief community survey focusing on usage trends and challenges associated with sensors and carbonate chemistry equipment.
- Then, the discussion will explore :
  1) needs associated with development of new techniques, sensors, and equipment.
  2) possibilities of developing or enhancing sensor networks, particularly with an eye toward coordination and intercomparison.
  3) additional tools needed, such as analytical facilities, shared instrument repositories, or computing tools. In each case, identified needs will be matched with estimates of the type and magnitude of obstacles (e.g., time, cost, manpower, etc.) facing them.

Results of OCB Survey



3. Please indicate your position.

Value	Count	Percent %
Faculty (senior)	13	19.1%
Faculty (mid-career, tenured)	7	10.3%
Faculty (early career)	6	8.8%
Research Scientist	19	27.9%
Postdoctoral	14	20.6%
Student	8	11.8%
Other	1	1.5%

Statistics	
Total Responses	68

25/68 attending OAPI
42/68 US Investigators

Results of OCB Survey

1. Which types of carbonate system sensors and instruments do you currently use?

	Autonomous	Underway	Benchtop	Responses
Dissolved Inorganic Carbon (DIC)	**9.8%** 5	**13.7%** 7	**96.1%** 49	51
Total Alkalinity (TA)	**0.0%** 0	**7.8%** 4	**96.1%** 49	51
pH	**52.6%** 30	**24.6%** 14	**70.2%** 40	57
pCO2	**53.2%** 25	**51.1%** 24	**25.5%** 12	47

2. Please list the make and model of these sensors.
68 unique responses with many overlapping.

7. How long have your autonomous/underway sensors been deployed?

	Hours-Days	Days-Weeks	Weeks-Months	Months-Seasons	Seasons-Years	Many years	Responses
DIC	**18.2%** 2	**45.5%** 5	**18.2%** 2	**9.1%** 1	**0.0%** 0	**9.1%** 1	**11**
TA	**0.0%** 0	**60.0%** 3	**20.0%** 1	**0.0%** 0	**0.0%** 0	**20.0%** 1	**5**
pH	**8.1%** 3	**18.9%** 7	**27.0%** 10	**10.8%** 4	**24.3%** 9	**10.8%** 4	**37**
pCO2	**7.5%** 3	**15.0%** 6	**25.0%** 10	**7.5%** 3	**25.0%** 10	**20.0%** 8	**40**

8. What has been the failure rate? (e.g., no data collected after deployment or a typical run?)

	0-20%	20-40%	40-60%	60-80%	80-100%	Responses
DIC	**84.4%** 27	**9.4%** 3	**3.1%** 1	**0.0%** 0	**3.1%** 1	**32**
TA	**82.8%** 24	**10.3%** 3	**0.0%** 0	**3.4%** 1	**3.4%** 1	**29**
pH	**53.1%** 26	**30.6%** 15	**6.1%** 3	**6.1%** 3	**4.1%** 2	**49**
pCO2	**71.1%** 32	**22.2%** 10	**2.2%** 1	**2.2%** 1	**2.2%** 1	**45**

9. What percent of the total data collected has been usable?

DIC	**9.4%** 3	**0.0%** 0	**6.3%** 2	**15.6%** 5	**68.8%** 22	**32**
TA	**10.7%** 3	**7.1%** 2	**7.1%** 2	**3.6%** 1	**71.4%** 20	**28**
pH	**12.5%** 6	**6.3%** 3	**14.6%** 7	**22.9%** 11	**43.8%** 21	**48**
pCO2	**4.4%** 2	**11.1%** 5	**4.4%** 2	**28.9%** 13	**51.1%** 23	**45**

10. What methods have been used for data quality control?

	Comparison to standard reference material	Comparison to bottle samples	Comparison to climatology	Comparison to co-located sensor	Data inspection by expert/manufacturer	No QC performed	Response
DIC	**95.6%** 43	**31.1%** 14	**13.3%** 6	**8.9%** 4	**6.7%** 3	**2.2%** 1	**45**
TA	**97.7%** 42	**27.9%** 12	**9.3%** 4	**7.0%** 3	**4.7%** 2	**2.3%** 1	**43**
pH	**68.5%** 37	**46.3%** 25	**14.8%** 8	**27.8%** 15	**11.1%** 6	**5.6%** 3	**54**
pCO2	**45.2%** 19	**45.2%** 19	**23.8%** 10	**38.1%** 16	**21.4%** 9	**2.4%** 1	**42**

11. Did you calibrate the instrument/sensor yourself or rely on factory calibration?

	Self	Factory	Other	Responses
DIC	**86.4%** 38	**6.8%** 3	**6.8%** 3	44
TA	**95.1%** 39	**0.0%** 0	**4.9%** 2	41
pH	**87.5%** 49	**10.7%** 6	**1.8%** 1	56
pCO2	**59.2%** 29	**38.8%** 19	**2.0%** 1	49

12. Did the instrument or sensor's performance match the manufacturer's specifications?

	Range: Yes	Range: No	Accuracy: Yes	Accuracy: No	Precision: Yes	Precision: No	Responses
DIC	**97.1%** 33	**0.0%** 0	**85.3%** 29	**2.9%** 1	**73.5%** 25	**5.9%** 2	**34**
TA	**89.7%** 26	**3.4%** 1	**79.3%** 23	**6.9%** 2	**75.9%** 22	**6.9%** 2	**29**
pH	**90.9%** 40	**4.5%** 2	**61.4%** 27	**25.0%** 11	**61.4%** 27	**18.2%** 8	**44**
pCO2	**95.1%** 39	**2.4%** 1	**80.5%** 33	**12.2%** 5	**78.0%** 32	**0.0%** 0	**41**

Results of OCB Survey

13. If instrumental drift occurred, was the source identified? If so, how?

14. Please comment on any other problems, development needs, or other aspects of owning and operating these sensors and instruments.

All/Most of 68 responded with unique answers to the questions above. Some frequently mentioned issues include:

- CRMs are critical for identifying drift in benchtop instrumentation.
- Biofouling needs to be addressed.
- International inter-calibration exercises are needed.
- Responses in every category reported difficulty/frustration with their instrument.

Other good points raised:

- Purified m-cresol purple is needed
- CRMs with a broaer range would be helpful (e.g. for estuarine work).