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Ten Years of pCO₂ and pH Measurements on the NSF OOI Regional Cabled and Endurance Arrays: Techniques, Validation, and Science Opportunities

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OOI Science User Group 8 December 2024



Outline

- Measurement Technologies, Locations and Sampling
- Quality Assessment and Control
- Data Examples
- Comparisons to Regional Historical Data
- Summary



Representative OOI Biogeochemical Measurements

Quality Control (QC) Notes:

- HITL Human in the Loop, review by an OOI data team member (now weekly)
- Automated QC flags are based on IOOS QARTOD
 - Global range
 - Climatology
 - *Stuck values, etc. (pending)*

Measurement	Instrument	Remarks
Dissolved oxygen	Aanderaa Optode 4831, Sea-Bird SBE 43	Multi-point calibrations, UV light biofouling mitigation since 2018, HITL annotations current, historical annotations current, automated QC tests active
Chl-a, CDOM, OBS	WET Labs (Sea-Bird) ECO triplet-w	HITL annotations current, historical annotations current, automated QC tests active
Downward irradiance	Satlantic (Sea-Bird) OCR507 ICSW	UV light biofouling mitigation since fall 2019, HITL annotations current, historical annotations and automated QC tests in development (release early 2025)
nitrate	Satlantic (Sea-Bird) SUNA V2	ISUS replaced by SUNA in 2018, HITL annotations current, historical annotations in development, automated QC tests active
Spectrophotometer (Optical attenuation and absorption)	WET Labs (Sea-Bird) AC-S	HITL annotations current, historical annotations and automated QC tests pending
pH	Sunburst SAMI pH	HITL annotations current, historical annotations in development, automated QC tests active
pCO2 water	Sunburst SAMI pCO2	HITL annotations current, historical annotations in development, automated QC tests active
pCO2 air-sea	Pro-Oceanus pCO2-pro (uncabled)	HITL annotations current, historical annotations current, automated QC tests active
Bio-acoustic sonar	ASL AZFP (uncabled) Kongsberg EK-60/80 (cabled)	Raw data available with standardized plots using Echopype to create echograms available with Data now being added to Data Explorer.



OOI Regional Cabled Array Sites

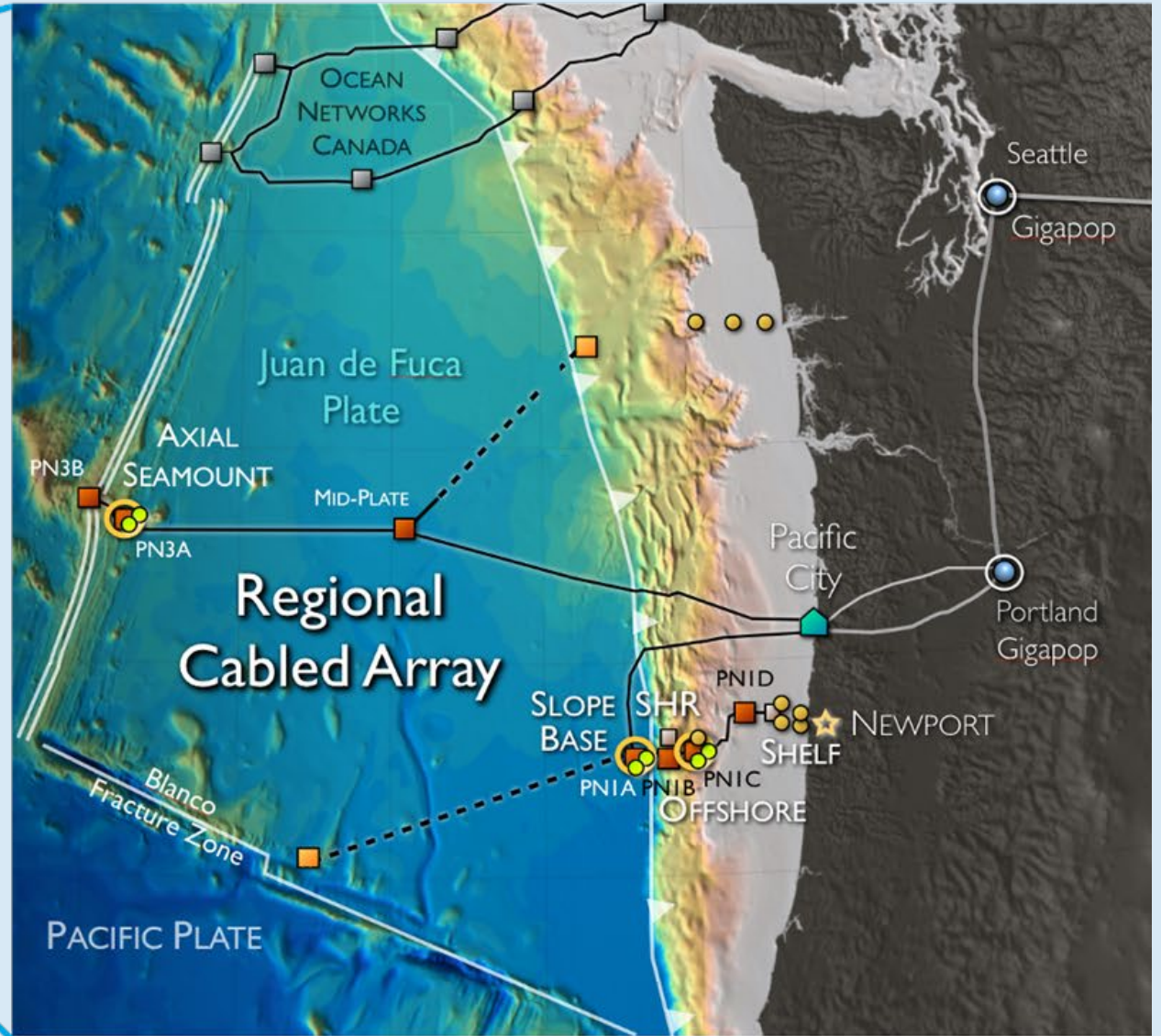
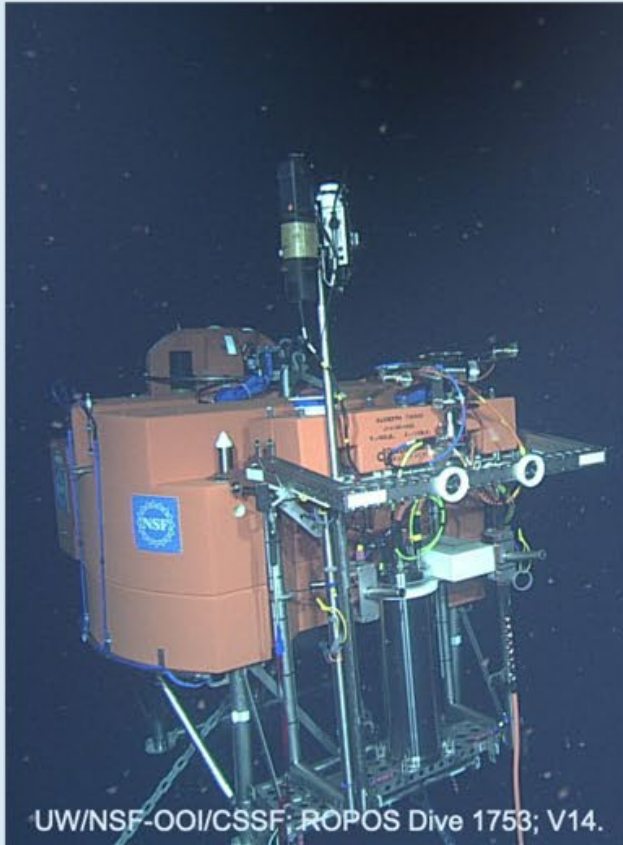


Image Credits CEV, UW, RCA



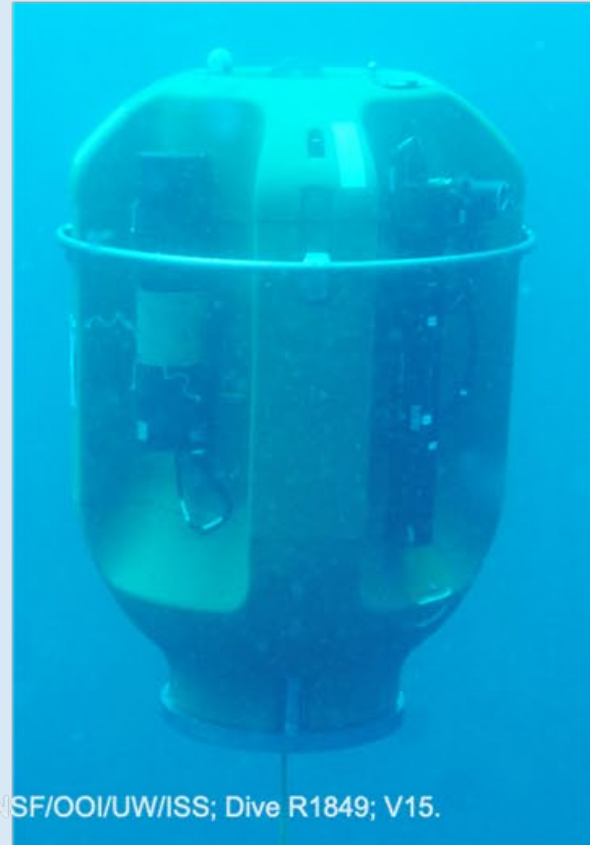
RCA pH and pCO₂ instruments



UW/NSF-OOI/CSSF; ROPOS Dive 1753; V14.

200-meter Shallow Profiler Platform:

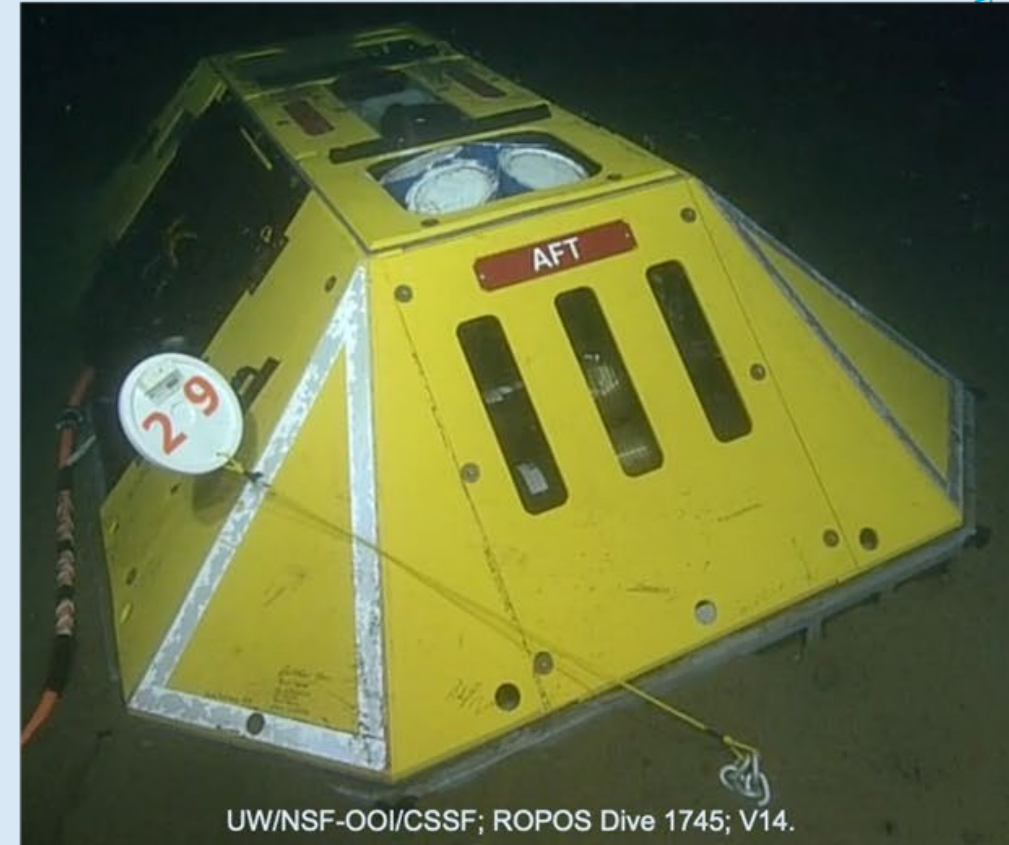
- Oregon Offshore: pCO₂ + pH
- Slope Base: pH
- Axial Base: pH



NSF/OOI/UW/ISS; Dive R1849; V15.

Shallow Profiler Science Pod:

- Oregon Offshore: pCO₂ + pH
- Slope Base: pCO₂ + pH
- Axial Base: pCO₂ + pH



UW/NSF-OOI/CSSF; ROPOS Dive 1745; V14.

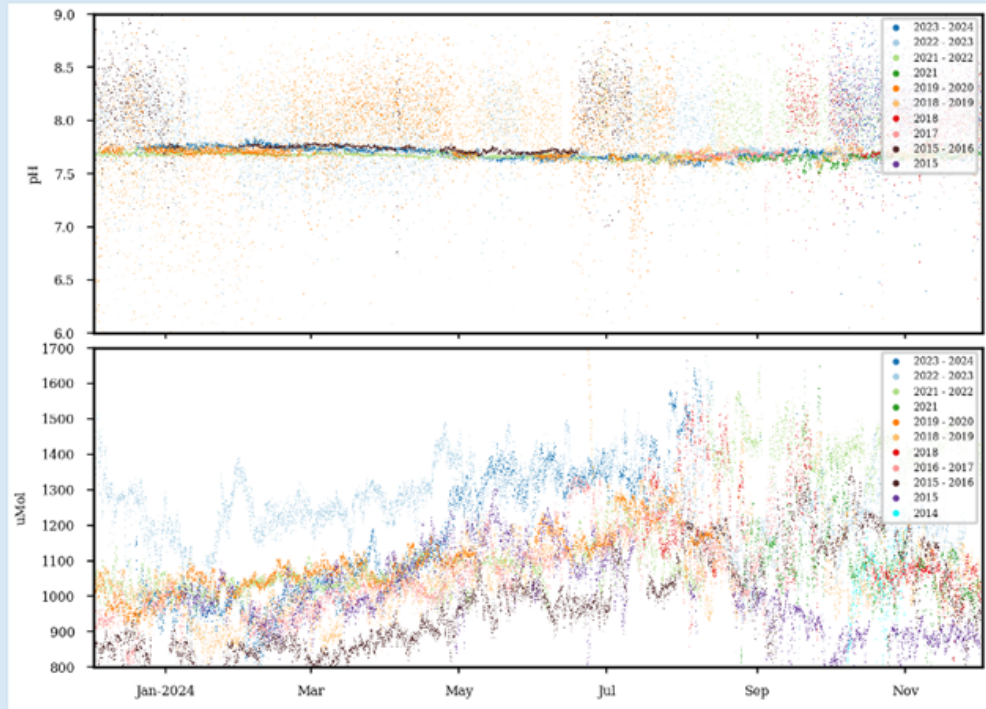
Benthic Experiment Package:

- Oregon Shelf, 80 meters: pCO₂ + pH
- Oregon Offshore, 600 meters: pCO₂ + pH

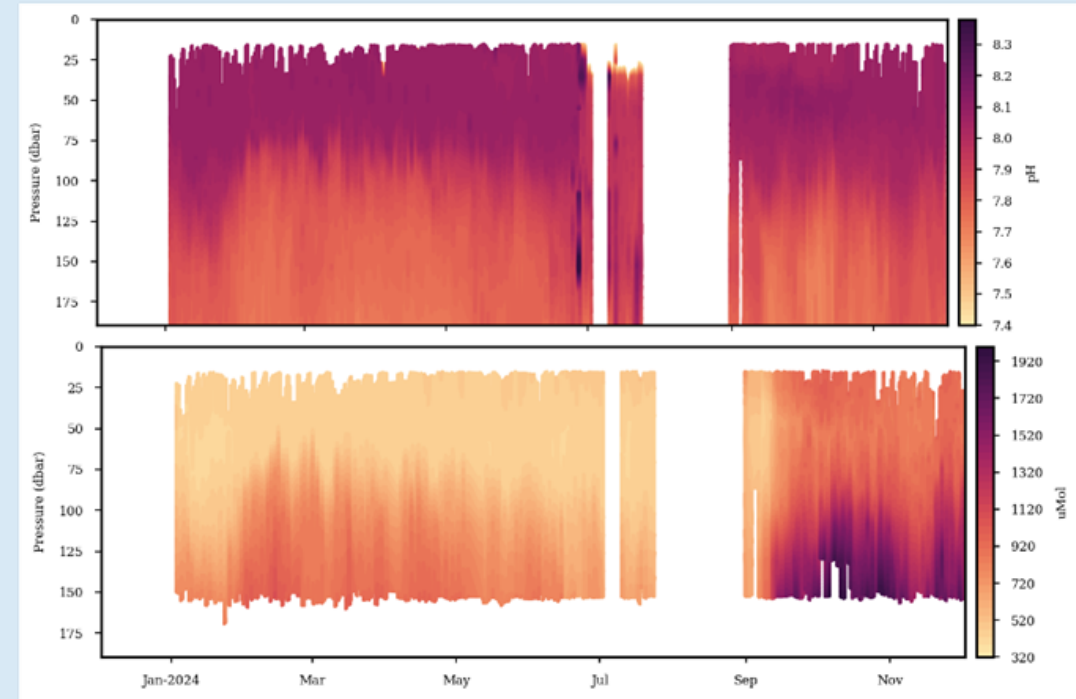


RCA pH and pCO₂ data

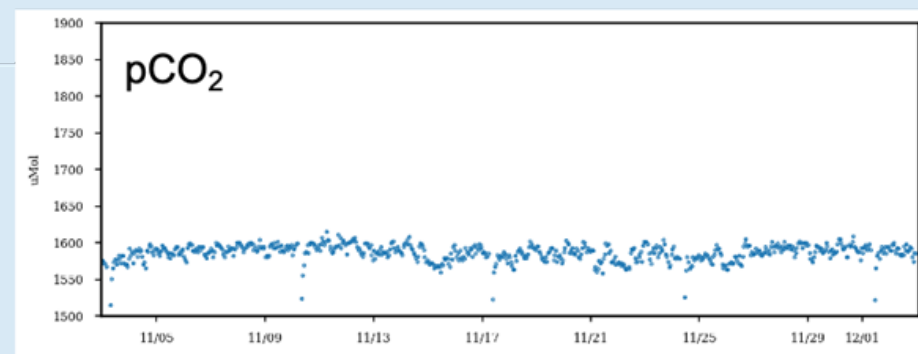
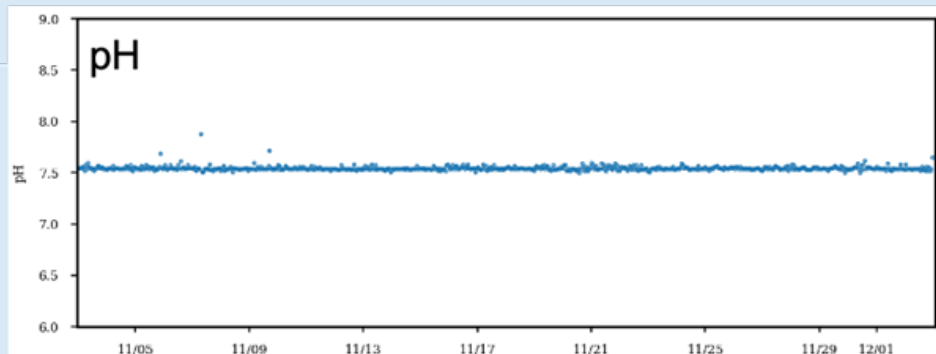
2014 – 2024, Oregon Offshore 200-meter Shallow Profiler Platform



2024, Axial Offshore Shallow Profiler

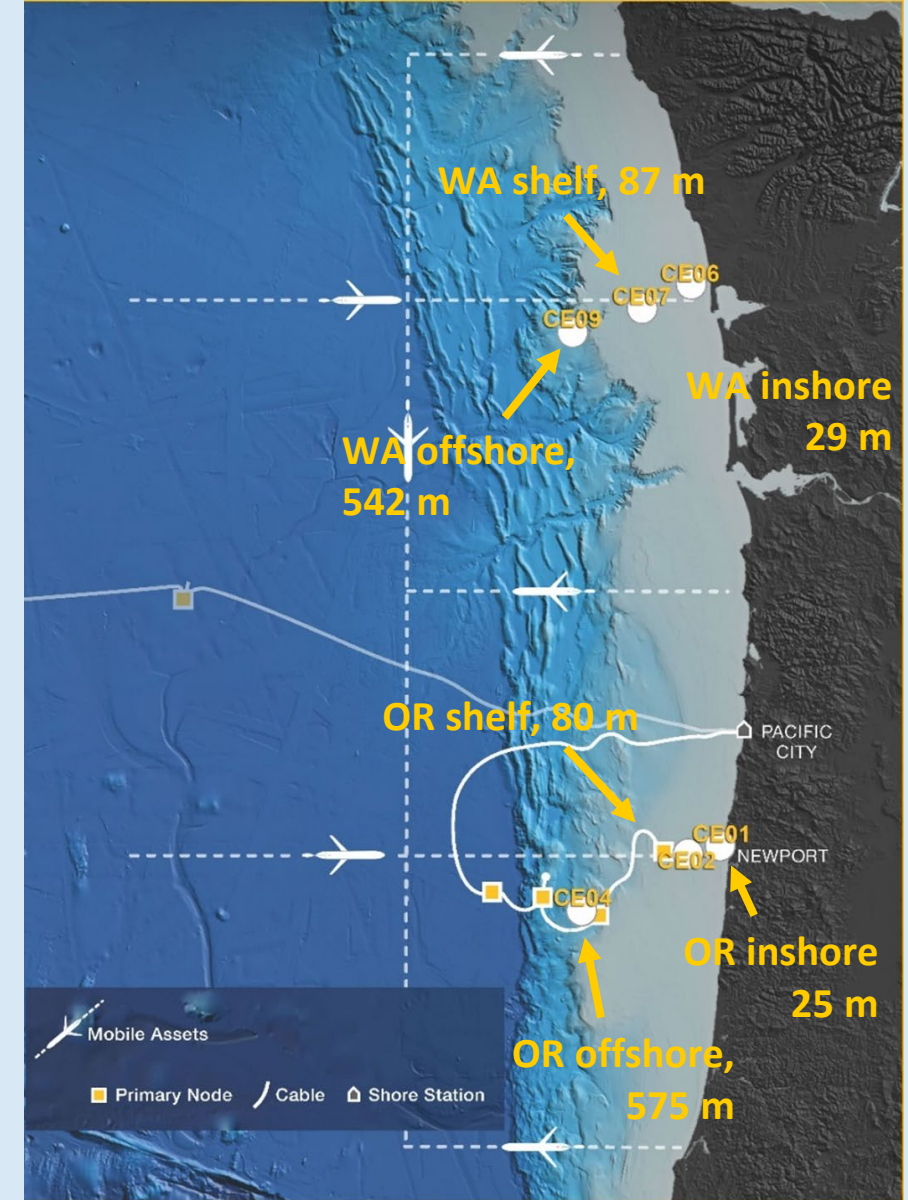


Nov 2024 Oregon Offshore Benthic Experiment Package, 600 meters



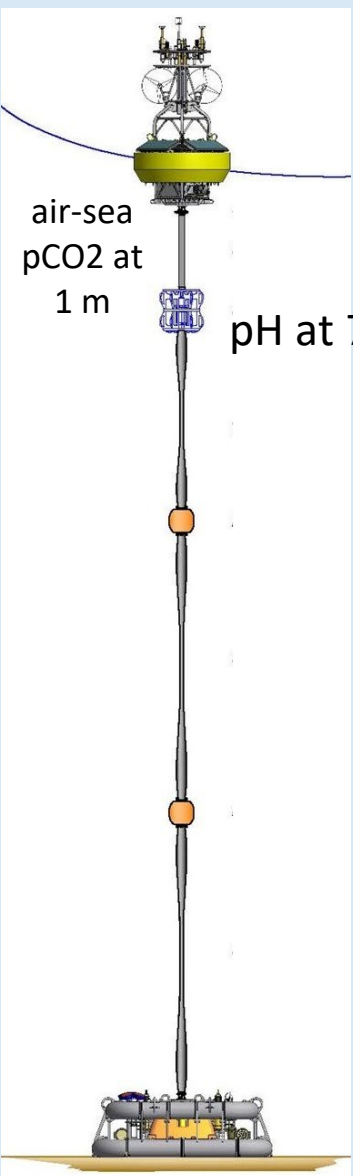
Endurance Array fixed depth carbonate system measurements

- Endurance moorings have carbonate system measurements on the buoy, at the near-surface instrument frame, and near the bottom (off WA).
- Hourly pH and pCO₂ measurements are accompanied by meteorological, physical, chemical, and bio-optical measurements.
- 2014-present records allow insights into impacts of Columbia River, California Current System variability, wind, and marine heat waves.
- Near-surface measurements have a much better data return than near bottom measurements due to sediment resuspension etc.



Pro-Oceanus CO₂-Pro air-sea pCO₂ system

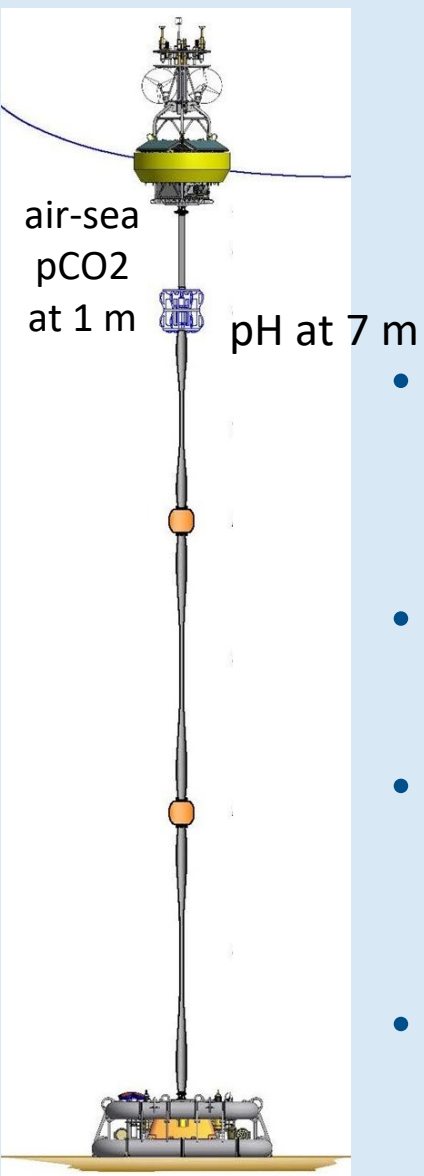
- Mounted at base of buoy at Oregon and Washington shelf and offshore buoys and at Pioneer and OOI global sites
- Other buoy measurements include full bulk mets, radiation, CTD, point velocity
- Other buoy mounted air-sea pCO₂ systems (NOAA buoys) tend to be the PMEL/Battelle M_ApCO₂ system.
- Data from the Pro-Oceanus system is consistent with shipboard underway and bottle sample measurements and land-based atmospheric measurements by Wingard *et al.* 2020 (see also [OOI website article](#))



WA shelf
87 m depth
(not to scale)

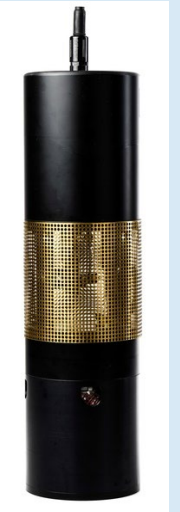
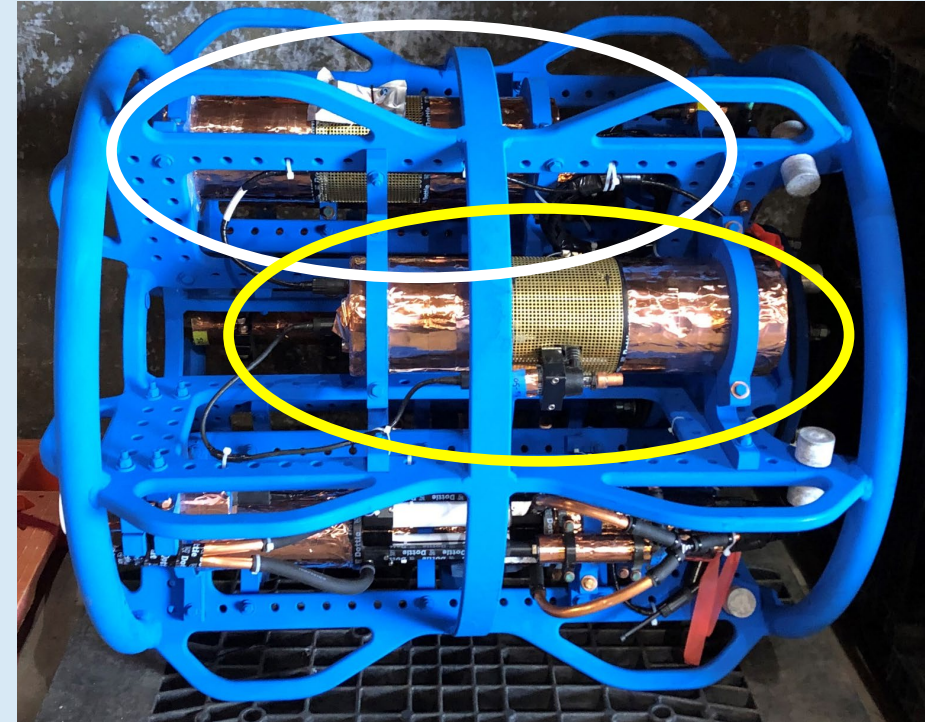


pH and pCO₂ water measurements



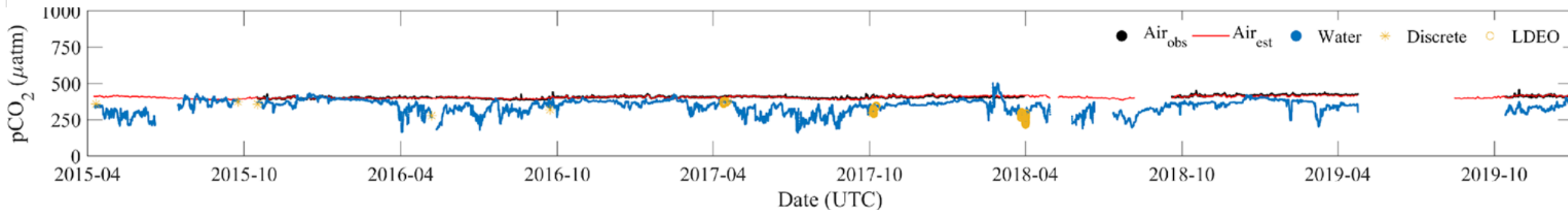
- Sunburst SAMI pH and pCO₂ mounted on a near-surface instrument frame (7 m depth).
- pH sensors are mounted on all near-surface frames.
- pCO₂ are on inshore mooring near-surface instrument frames.
- Currently implementing data quality control annotations and procedures across OOI.

WA shelf
87 m depth
(not to scale)



Initial Pro-Oceanus pCO₂ assessment

Washington Offshore Surface Mooring air-sea pCO₂ (**black, blue**) in comparison to independent measurements (**yellow, red**)
Measurements now extend through 2020 to 2021

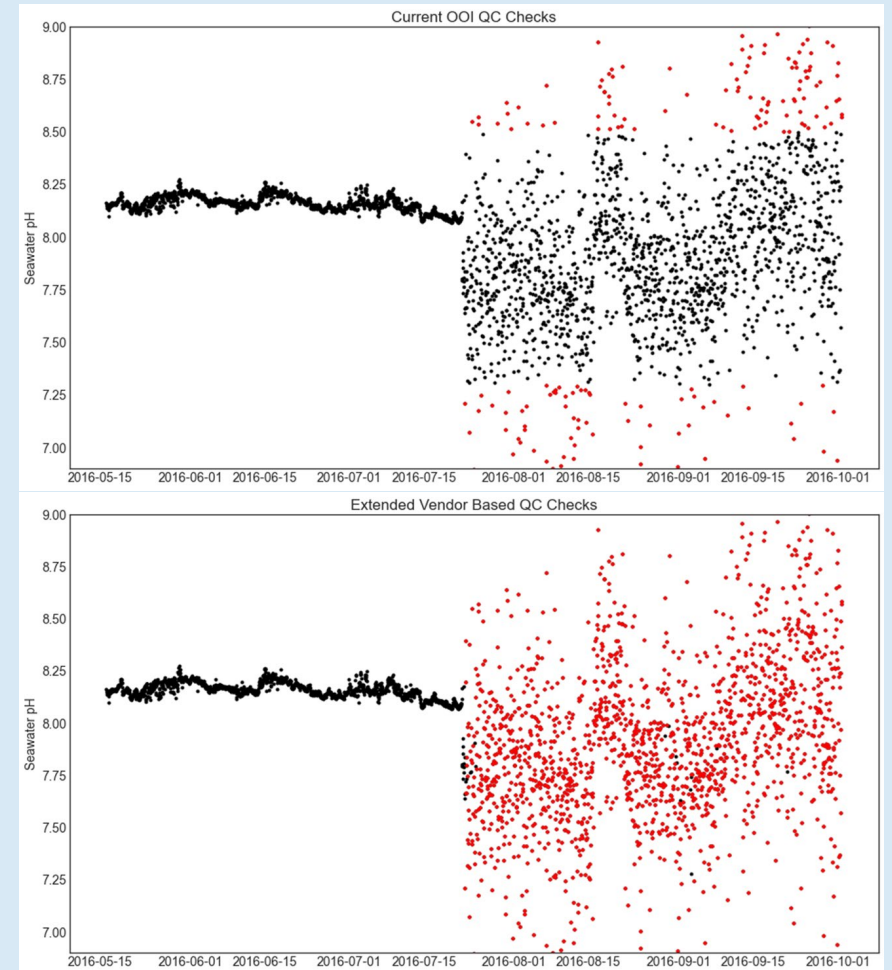


Wingard (2020) compared OOI mooring air-sea pCO₂ to land-based atmospheric pCO₂ and underway ship-based surface pCO₂ and bottle pCO₂ with good results (WA offshore shown)



Post-Processed Data Sets

- Automated QC checks to remove data points marked as fail
 - OOI Gross Range and Stuck Value tests
 - QARTOD Gross Range and Climatology tests
- Vendor-defined QC checks to remove additional failed data points
 - Example at right using Sunburst Sensors, Inc. defined flags (based on raw measurements) of failed pH data
- Annotations to remove data points marked as fail
- Validate using data from overlapping deployments and discrete samples (where available)
- Combine different data delivery methods, and resample to desired time resolution and output in user preferred format (e.g. NetCDF or CSV)

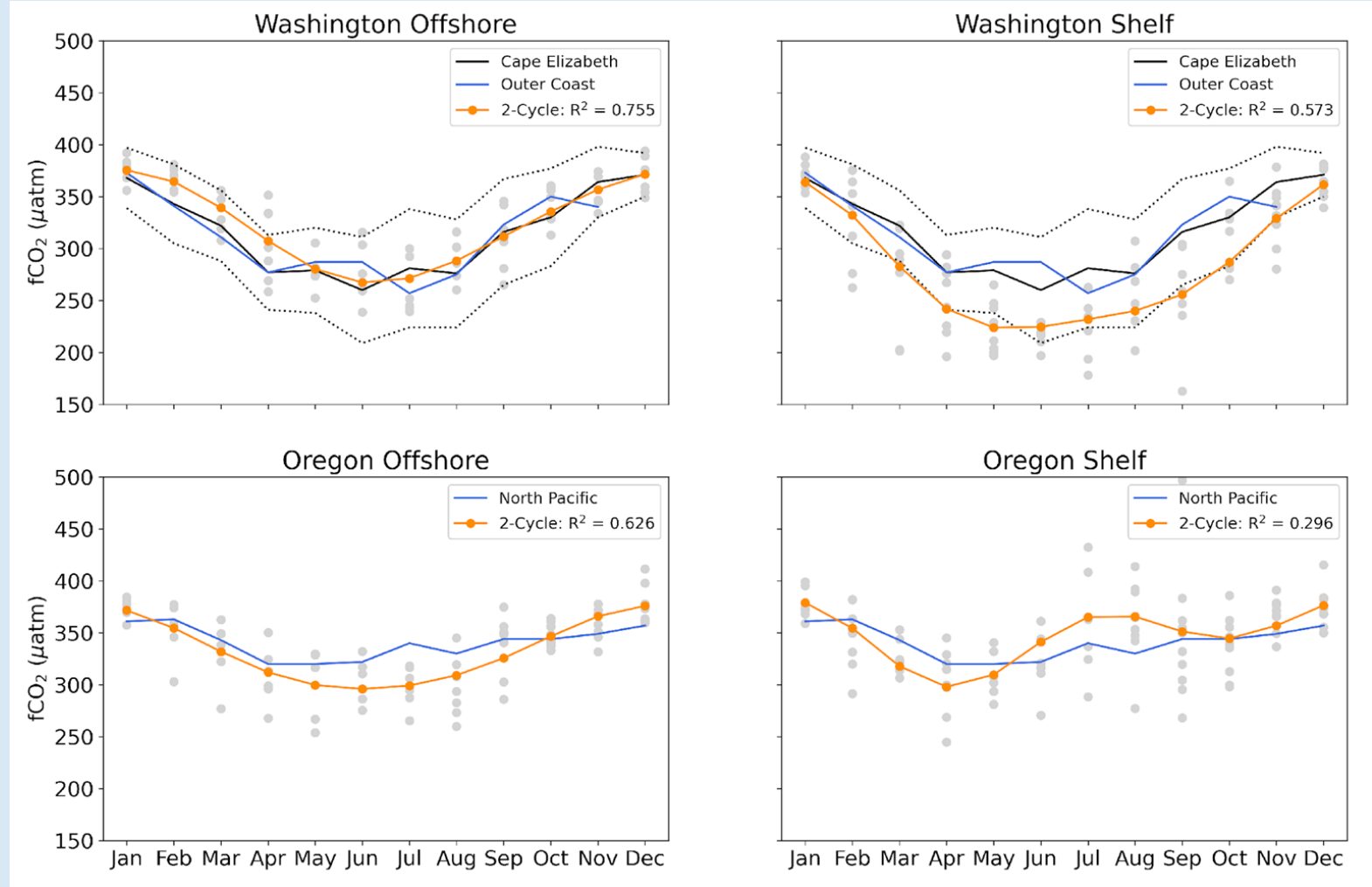


Identification of failed pH data (red) based on automated QC checks (top plot) and additional vendor defined checks (bottom plot). HITL annotations used to identify and exclude the few remaining points.



fCO₂ comparison

- Amplitude and timing of seasonal cycle between CE and WA offshore and shelf buoys reasonable*
- North Pacific and OR offshore and shelf comparisons qualitatively good
- Geographic variability in OOI data
- Seasonal cycle fit is poorest at OR shelf (gray dots represent individual monthly averages)



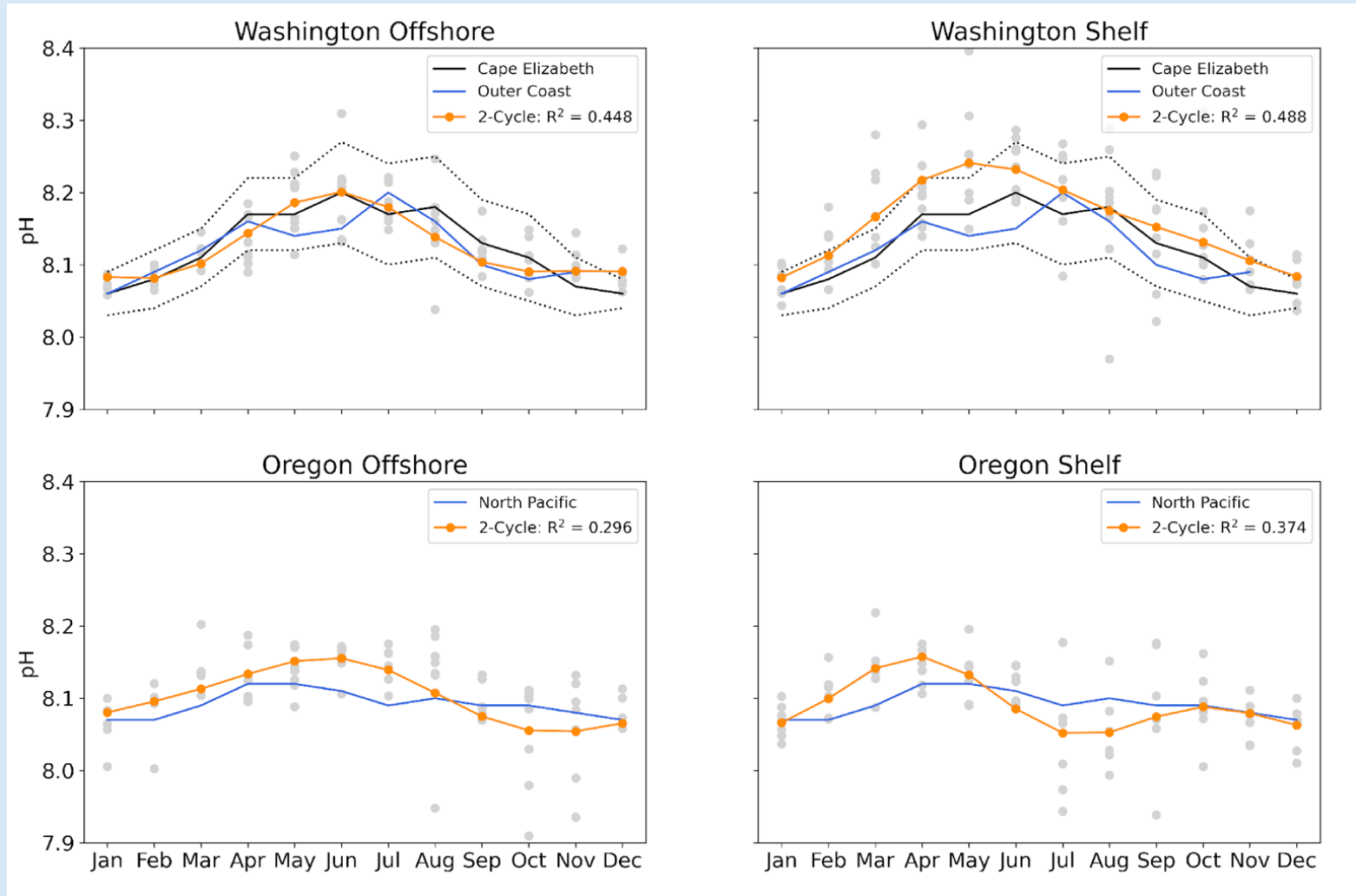
*Fassbender et al. estimate 1.5 µatm/yr upward trend. OOI mooring data adjusted to 2010. pCO₂ converted to fCO₂ using PyCO₂SYs.





pH comparison

- Amplitude and timing of seasonal cycle between CE and WA offshore and shelf buoys reasonable, some offset at WA shelf
- North Pacific and OR offshore and shelf comparisons qualitatively good
- Geographic variability in OOI data
- Seasonal cycle fit is poorest at OR offshore and shelf (gray dots represent individual monthly averages)



Cape Elizabeth NDBC buoy (2006-2013) pH estimated



Summary

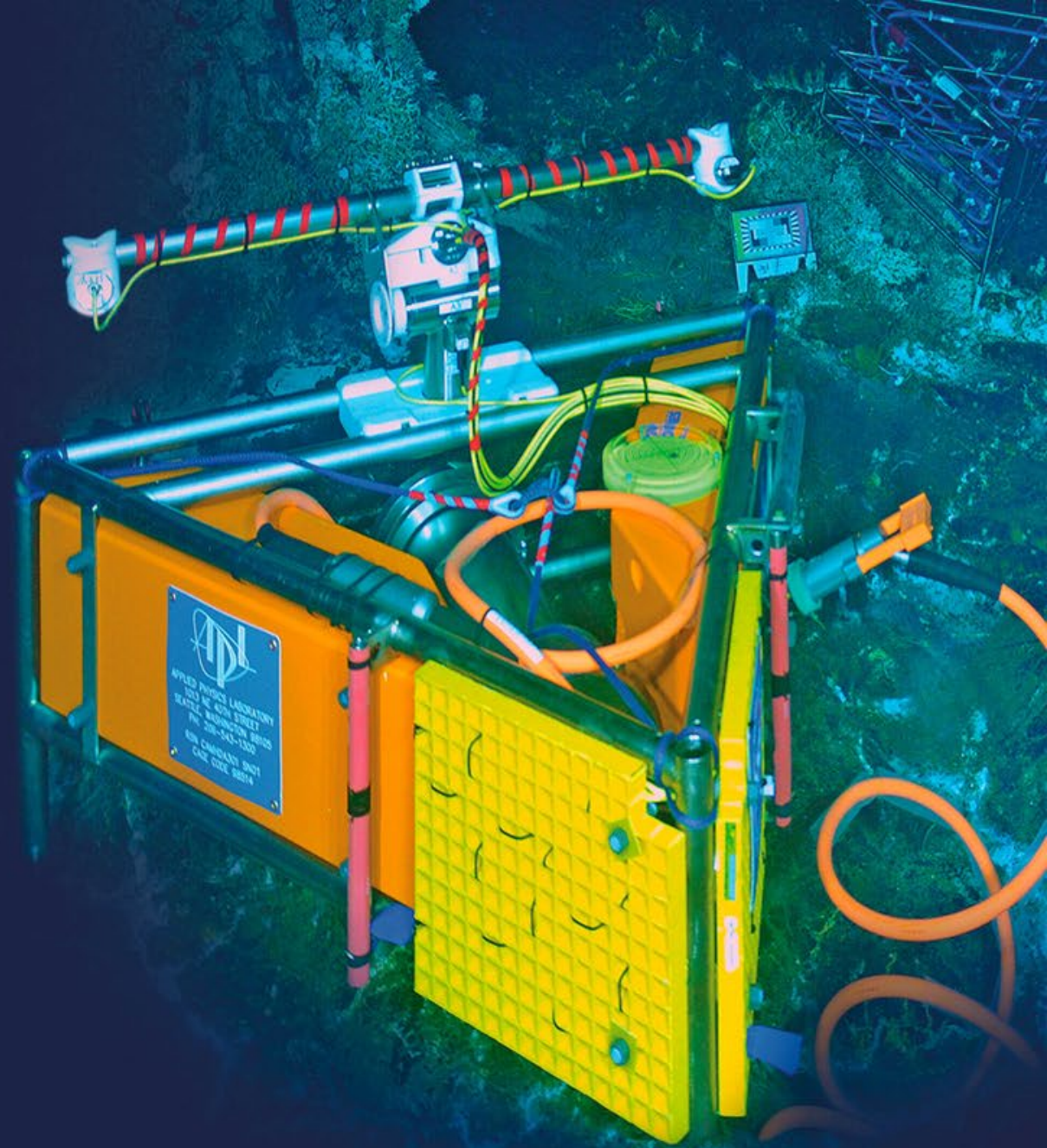
- OOI pCO₂ (fCO₂) and pH data are consistent with bottle samples, published regional measurements and (for surface pCO₂) shipboard underway measurements.
- RCA summary points
- Endurance Array data show geographic variability in the timing and magnitude of the seasonal cycle. Shelf seasonal variability precedes offshore and OR precedes WA. Monthly averages show significant year-to-year variability.
- Subsurface data, long term trends, diurnal variability and relationships to other biologically important variables (*e.g.*, NO₃) are largely unexplored in these data.





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Questions?



Back Pocket slides under development for the 1335 and 1400 discussion slots

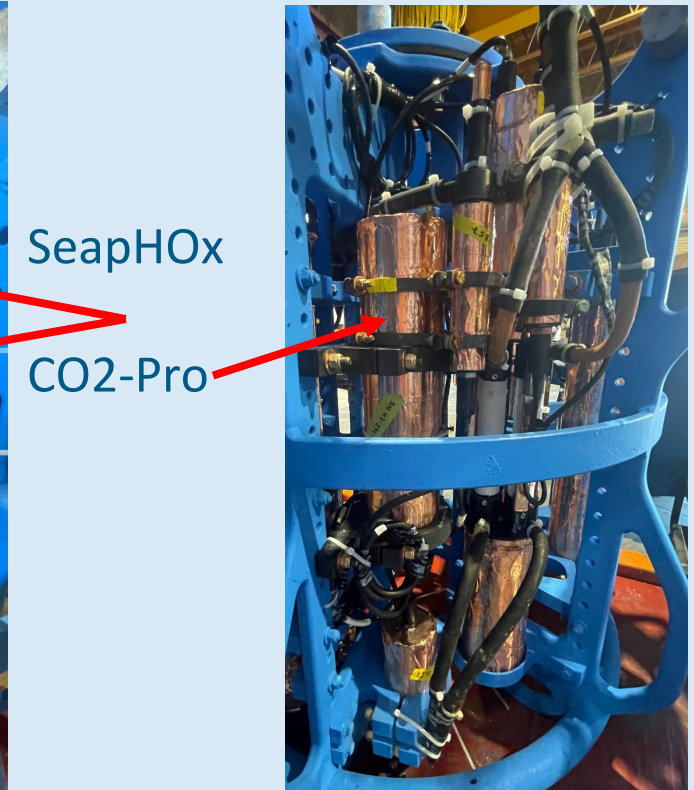
- SeapHOx, AnB and Idronaut pH tests
- OOI bottle data, PyCO2SYS use and programs
- SeapHOx testing and status
- Pro-Oceanus CO2pro CV testing



Alternate pH and pCO₂ sensor testing – Spring 2024

Instrument Testing

- Candidate PHSEN replacement on Oregon Shelf 7 m frame (SeaBird SeapHOx)
- Candidate PCO₂W replacement on Oregon Shelf 7 m frame (Pro-Oceanus CO₂-Pro CV)
- Recovered candidate PHSEN (ANB)
- Previously tested Idronaut and the previous generation SeapHOx



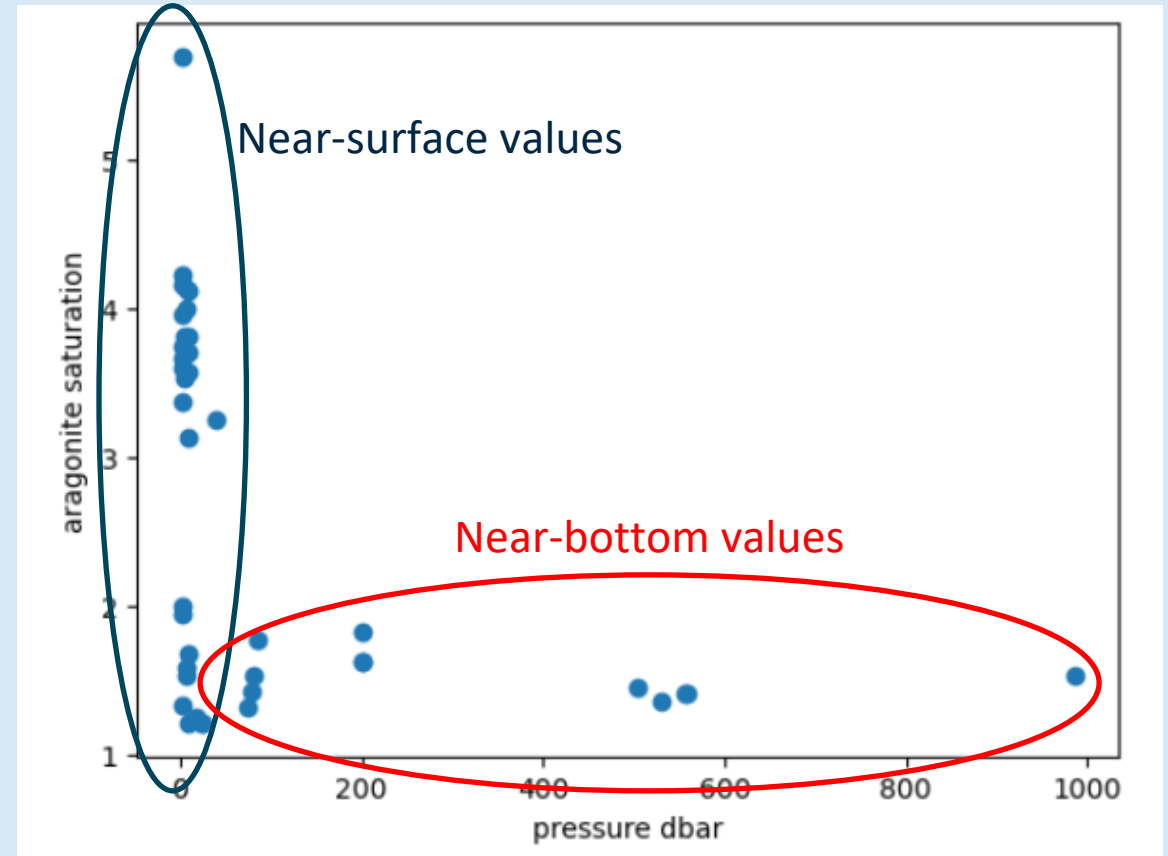
PyCO2SYS

- PyCO2SYS Python toolbox for the marine carbonate system related seawater properties.

(<https://pyco2sys.readthedocs.io/en/latest/>)

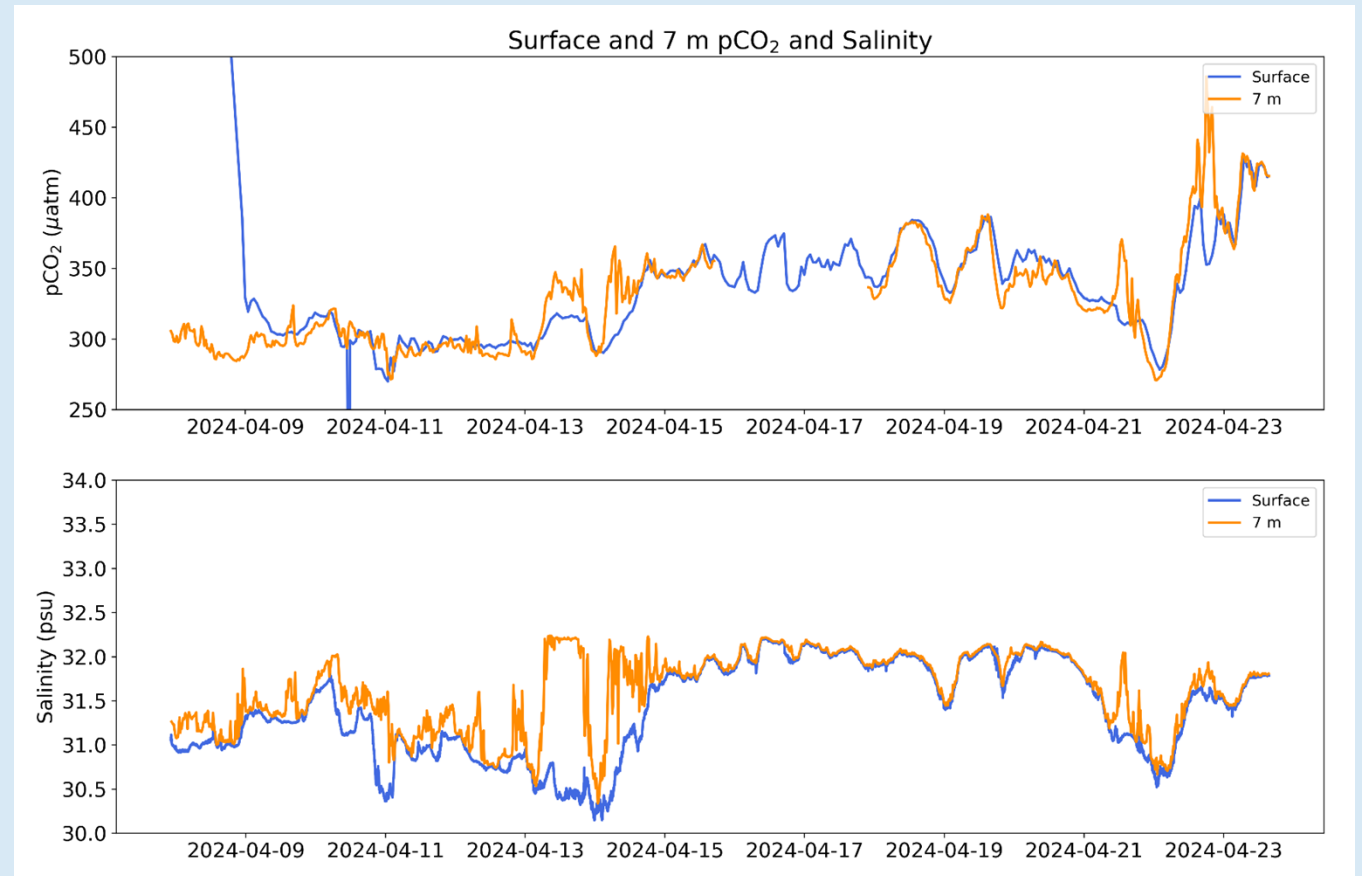
- Humphreys, M. P., Lewis, E. R., Sharp, J. D., and Pierrot, D. (2022). PyCO2SYS v1.8: marine carbonate system calculations in Python. *Geoscientific Model Development* 15, 15-43. doi:10.5194/gmd-15-15-2022.
- Anticipated uses:
 - Data quality control (estimation of missing parameters and validation of measured parameters)
 - Calculation of secondary data products (aragonite saturation etc.)
- Applied to bottle samples
- Started to apply to time series

Aragonite Saturation calculated from July 2020 Endurance 13 cruise (TN380)



pCO₂ Sensor Tech Refresh (Spring 2024)

- Instruments
 - Surface: Pro-Oceanus CO₂-Pro ATM (measures both air and surface water pCO₂). Surface intake 1 m depth, sampled hourly
 - 7 m: Pro-Oceanus CO₂-Pro CV, sampled every 30 minutes
- Salinity data from co-located CTD sensors (surface: sampled every minute, 7 m: sampled every 15 minutes)
- *Good qualitative agreement, with some water mass related differences*



CO₂-Pro CV mounted on the 7 m platform (Near-Surface Instrument Frame, NSIF) showing intake plumbing and exhaust.

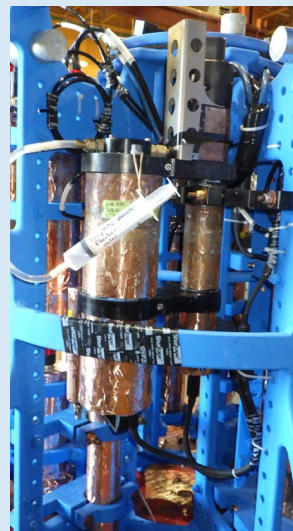
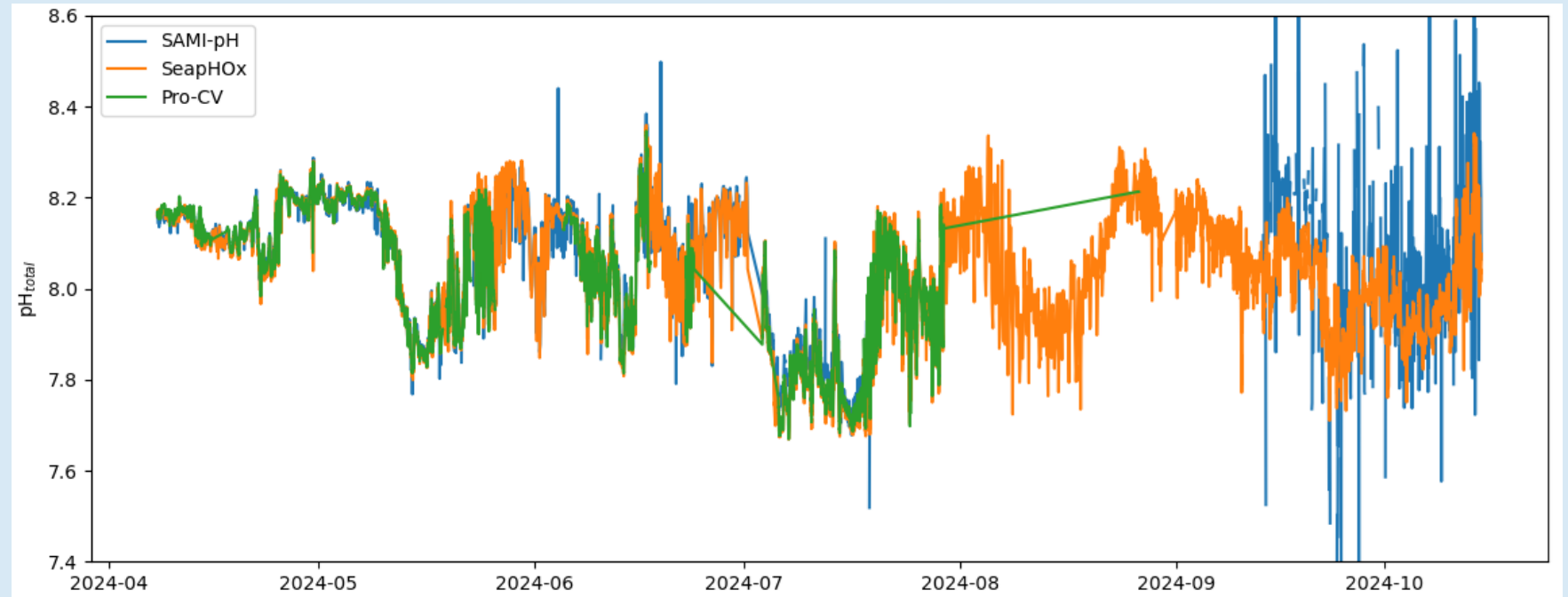


CO₂-Pro ATM on the subsurface instrument plate just above the SBE 37 CT sensor. Water intake is at 1 m nominal depth.



pH Sensor Tech Refresh (Spring 2024 deployment)

- *Sea-Bird Electronics Deep SeapHOx V2* deployed at 7 m alongside a Sunburst Sensors SAMI-pH sensor
- Estimated pH calculated using PyCO2SYS with total alkalinity derived from the *SeapHOx T/S* measurements (Lee et al. 2006, Zone 4) and the CO₂-Pro CV
- Estimated pH and SAMI-pH agree quite well, while the *SeapHOx pH* showed negative offset of ~0.08 (corrected here)



Deep SeapHOx installed in the 7 m instrument frame (NSIF)



SAMI-pH sensor installed in the 7 m instrument frame (NSIF)

Accessing OOI Data

More information at: oceanobservatories.org/data/



OOI Data Bus

More information and URLs can be found at: oceanobservatories.org/data-access/

Data Type / Source	Raw Data Archive	Thredds	DataExplorer	ERDDAP	M2M	OOI Website	Alfresco	Jupyter Hub	DataExplorer Media	OOINET
<ul style="list-style-type: none"> ● Current best method ○ Coming soon ◐ Phasing out 	Raw instrument and engineering datasets presented in an Apache file system structure for download.	Pre-computed scientific numerical data products with calibrations applied alongside engineering data. Full resolution datasets are accessible by deployment and stream.	Primary gateway to visualize and access OOI data. Search across data points, download full datasets using ERDDAP, compare datasets across regions and disciplines, and generate shareable custom data views.	Underlying data server for Data Explorer providing access to ~600 datasets organized by OOI arrays. Download datasets in common file formats and make graphs and maps.	Access to science and engineering data using both synchronous and asynchronous interfaces. NetCDF and JSON files are the standard outputs.	Oceanobservatories.org provides access to datasets compiled by Principal Investigators who have added instruments onto OOI arrays.	Document repository for instrument vendor information including calibrations.	Hosted by OOI, this hub provides access to full resolution datasets and raw data server, allowing users to share notebooks and process data in a larger server environment.	Preview HD Photo, HD Video, visualized Hydrophone and ZPLS data along side science data in the Data Explorer tool.	Legacy access to scientific and engineering data with the ability to search and plot data for review. Download requests are queued for system processing. User will be notified when download is ready. This interface will be slowly phased out.
Numerical Raw Data	●		○					●		
Processed Data Sets (NetCDF)		●	●	●	●			●		◐
Provenance data (JSON)		●	●		●			●		◐
Asset information						●	●			
Hydrophone	●							●	○	
Realtime data plots			●							◐
ZPLS data	●							●	●	
PI Data			●			●				
HD Video	●							●	●	
HD Photo	●							●	●	

