OSU
Oregon State
UNIVERSITY

College of Earth, Ocean,
and Atmospheric Sciences

SOCCOM
Southern Ocean Carbon and Climate Observations and Modeling

Southern Ocean carbon from profiling floats equipped with pH

Nancy Williams, Laurie Juranek, Richard Feely

Ken Johnson, Jorge Sarmiento, Lynne Talley, Joellen Russell, Steve Riser, Rik Wanninkhof, Alison Gray, Andrew Dickson, and all SOCCOM contributors

nancy.williams@oregonstate.edu

http://soccom.princeton.edu

ARCS ADVANCING SCIENCE IN AMERICA

Carbonate Chemistry Review

Four measurable variables:

1. Total Alkalinity (**TA**)
2. Total Dissolved Inorganic Carbon (**DIC**)

   DIC = $CO_{2(aq)}$+HCO_3^- + CO_3^{2-}
3. **pH_{Total}** = Free hydrogen ions plus sulfate ions
4. Partial pressure of carbon dioxide (**pCO_2**)

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- CO2SYS(**TA**, **DIC**, T, S, P) → **pH**, **pCO_2**, $\Omega_{Aragonite}$
- CO2SYS(**pH**, **TA**, T, S, P) → **DIC**, **pCO_2**, $\Omega_{Aragonite}$

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CO2SYS Program: *Lewis and Wallace*, 1998; *van Heuven et al.*, 2011

Bottle vs. float data

Shipboard Bottle data

- T, S, P
- Oxygen
- Nitrate
- pH
- DIC
- TA

} pCO_2, Ω_{Ar}

SOCCOM Float Sensors

- T, S, P
- Oxygen (Aanderaa Optode)
- Nitrate (ISUS or SUNA)
- pH (Deep-Sea DuraFET)

↓ ?

Full carbonate system

Two ways…

1. Float pH + TA estimate:

(e.g. Carter et al., 2016, Williams et al., in prep)

DIC

pCO_2

$\Omega_{Aragonite}/\Omega_{Calcite}$

2. No pH sensor? Use MLR algorithms:

Use high-quality bottle data to train algorithms for carbonate system parameters based on T, S, P, O_2, Nitrate

$$pH^{\mathbf{N}} = \beta_0 + \beta_1 S + \beta_2 T + \beta_3 P + \beta_4 \mathbf{N}$$

(Juranek et al., 2009, 2011, Williams et al., 2016)

Two ways… pros and cons

1. Float pH + TA estimate:

- Relies on **quality controlled** float pH sensor
- Relies on high-quality bottle data for carbon and oxygen

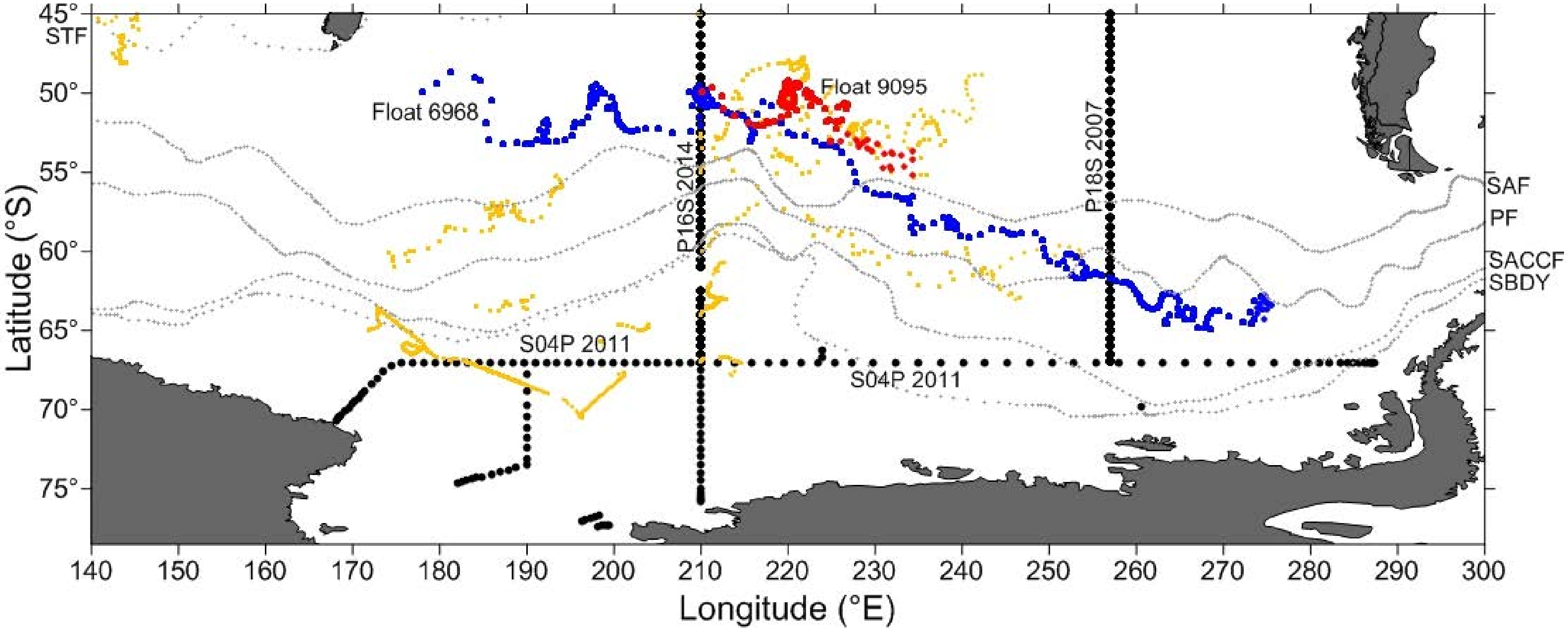
2. MLR algorithms:

- Independent of pH sensor
- Not perfect at frontal zones or at the surface
- Rely on high-quality bottle data for carbon and oxygen
- Cannot account for anthropogenic changes

pH MLR Algorithm for quality control

$$pH^{Ox}_{Deep} = \beta_0 + \beta_1 S + \beta_2 T + \beta_3 P + \beta_4 O_2$$

RMSE= 0.004, trained South of 45 °S between 1000 and 2100 m



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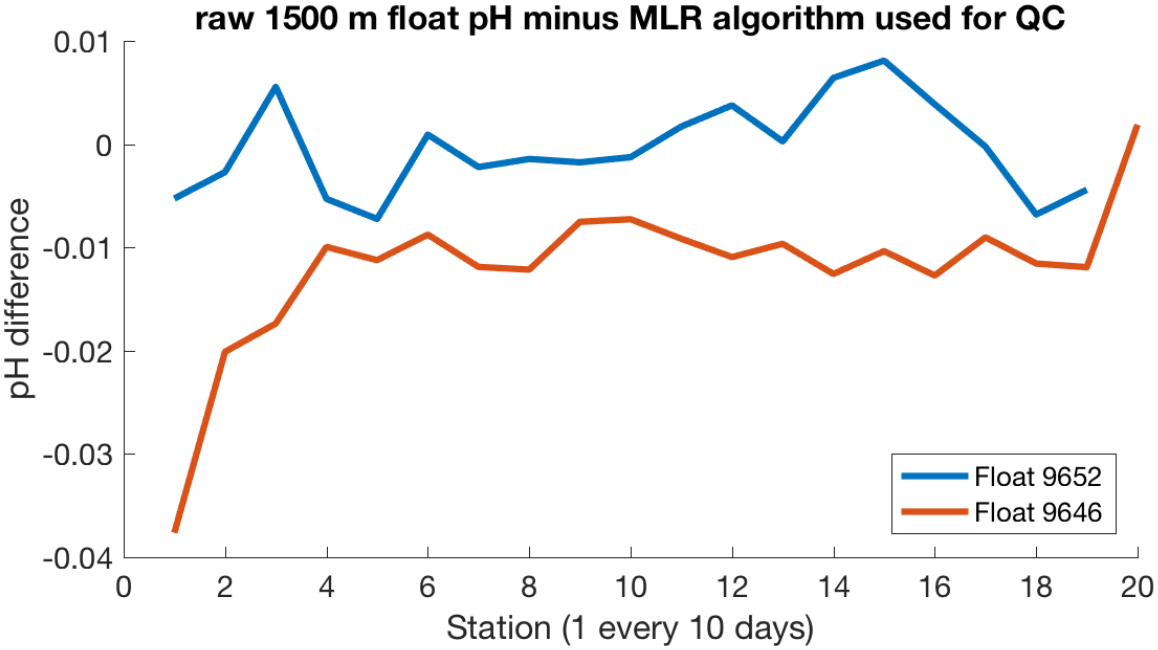
See Juranek et al., 2009, 2011, Williams et al., 2016 (*GRL*)

2015-2016 pH sensor performance



pH sensors equilibrated in flowing natural seawater for ~2 weeks before deployment are stable and accurate.

Drift rate = 0.001 yr^{-1}

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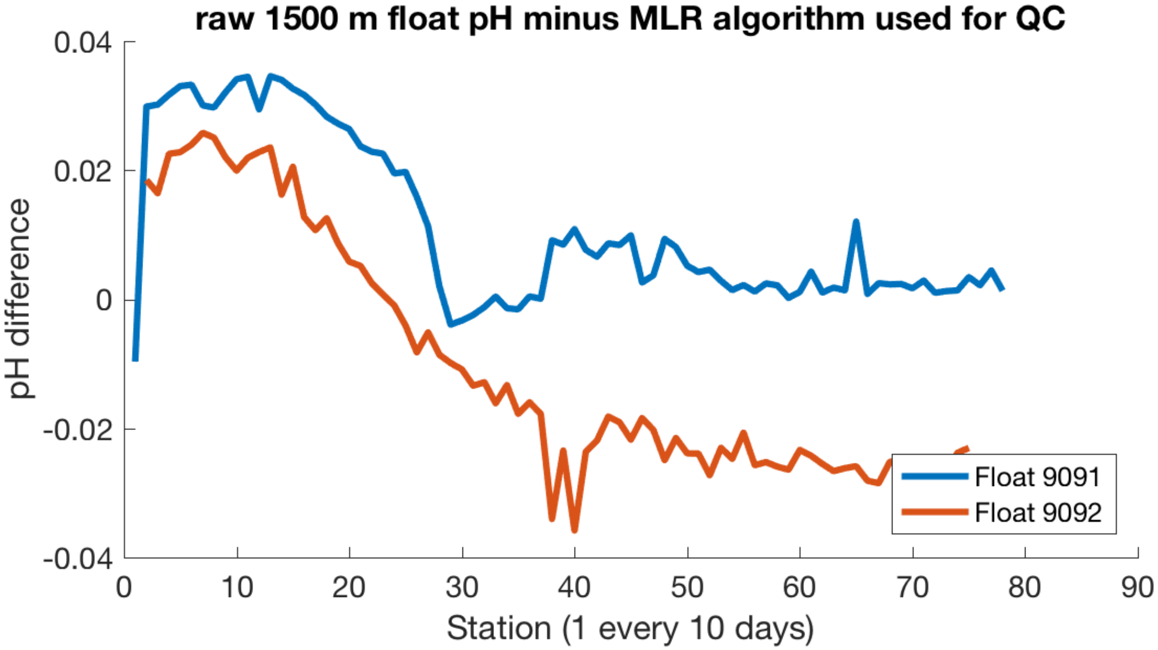
EAGER (2014) pH sensor performance



pH sensors **not** equilibrated with seawater prior to deployment show a drift in the reference potential (k_0) over time until the float stabilizes after ~1 year.

MLR is used to quality control data for these unconditioned sensors.

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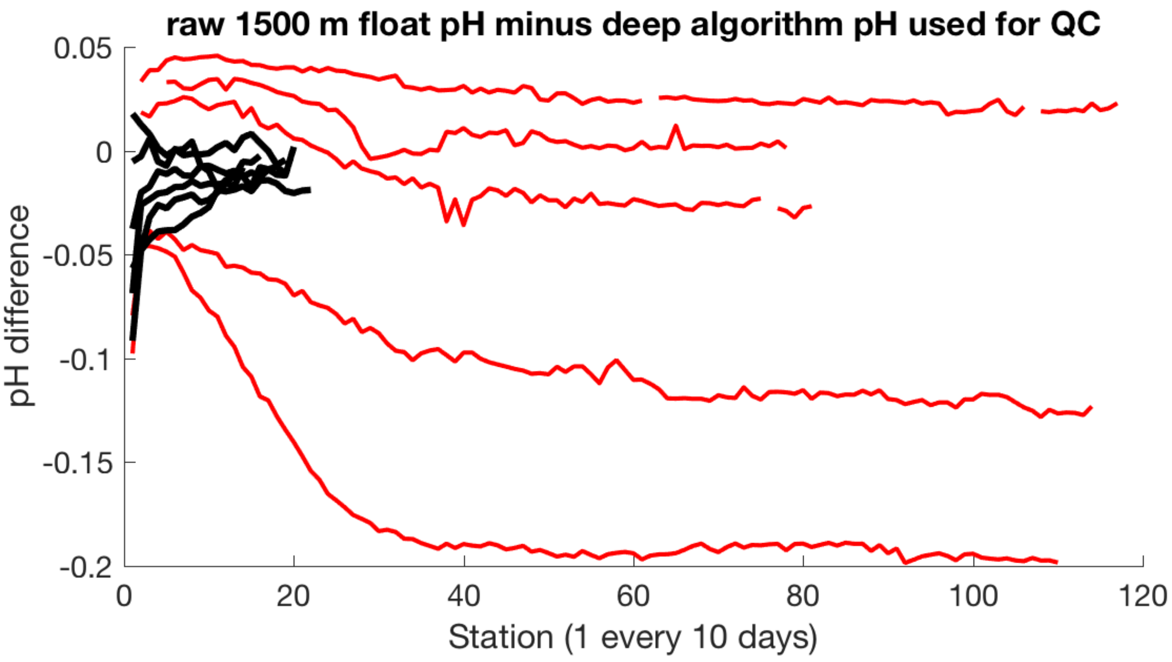
Year 2 pH sensor performance

--2014 EAGER deployments

--2015-2016 deployments equilibrated in flowing natural seawater



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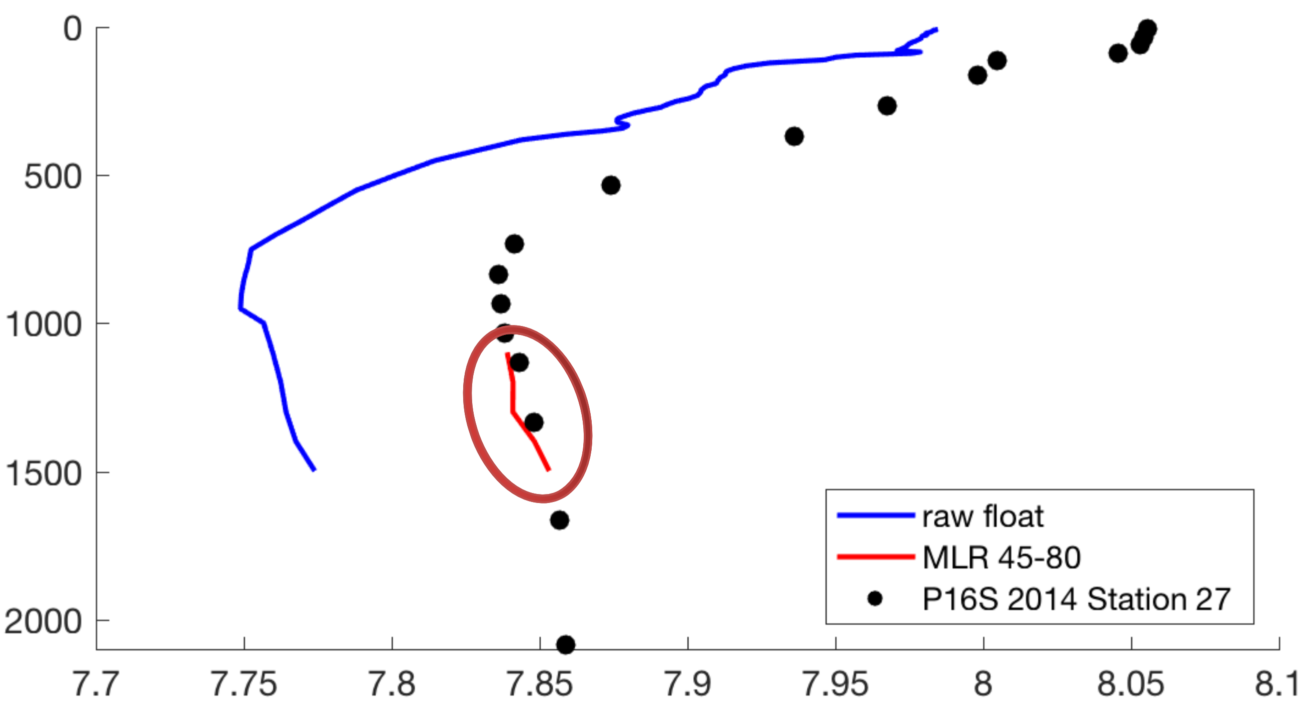
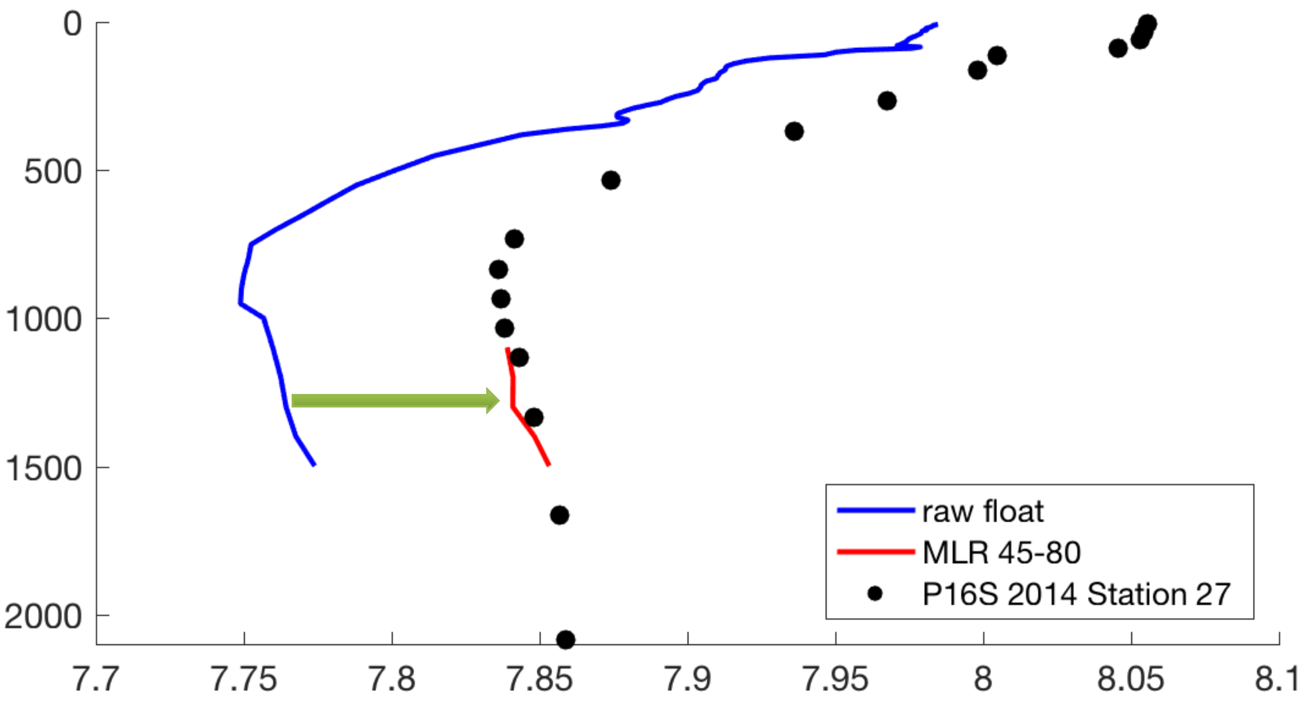
QC process



1. Calculate float MLR pH using float T, S, P, and O_2 at 1500 m

See Johnson et al., 2016, Williams et al., 2016 (*GRL*)

QC process



1. Calculate float MLR pH using float T, S, P, and O_2 at 1500 m

2. Adjust sensor reference potential (k_0) to match 1500 m sensor pH to algorithm pH

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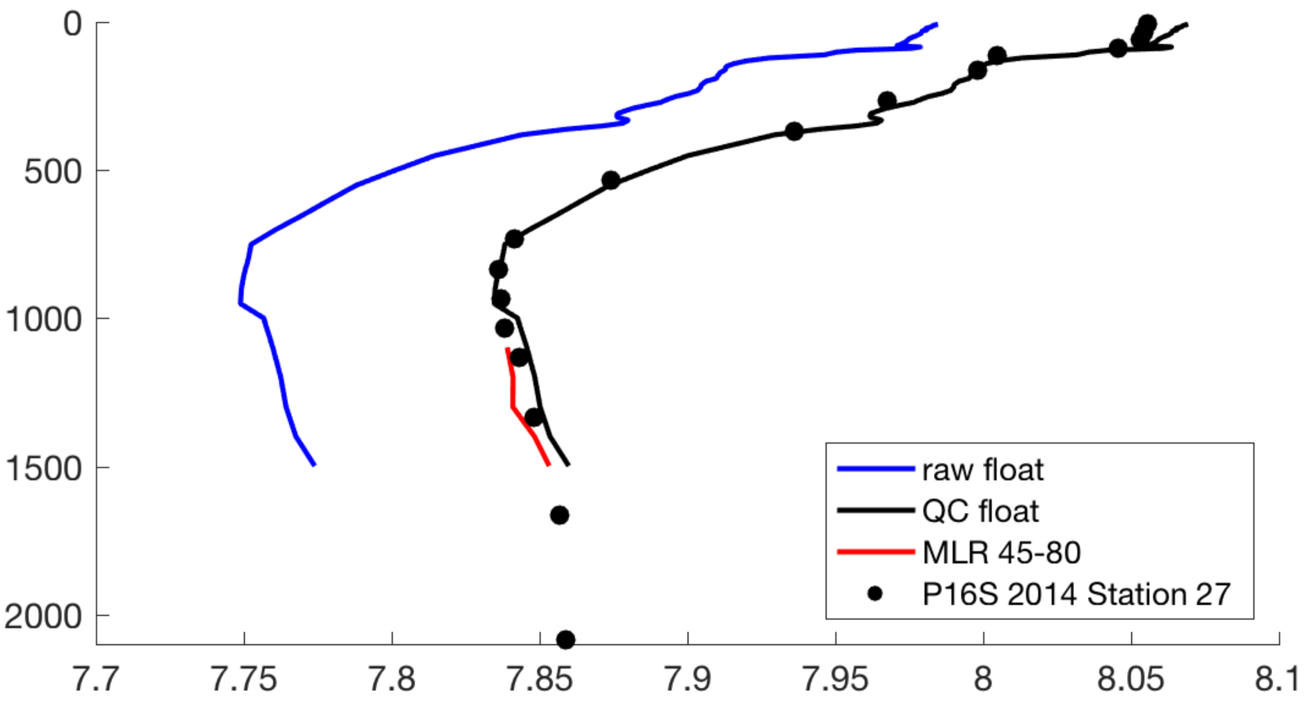
See Johnson et al., 2016, Williams et al., 2016 (*GRL*)

QC process



1. Calculate float MLR pH using float T, S, P, and O_2 at 1500 m

2. Adjust sensor reference potential (k_0) to match 1500 m sensor pH to algorithm pH

3. Apply new reference potential to entire profile

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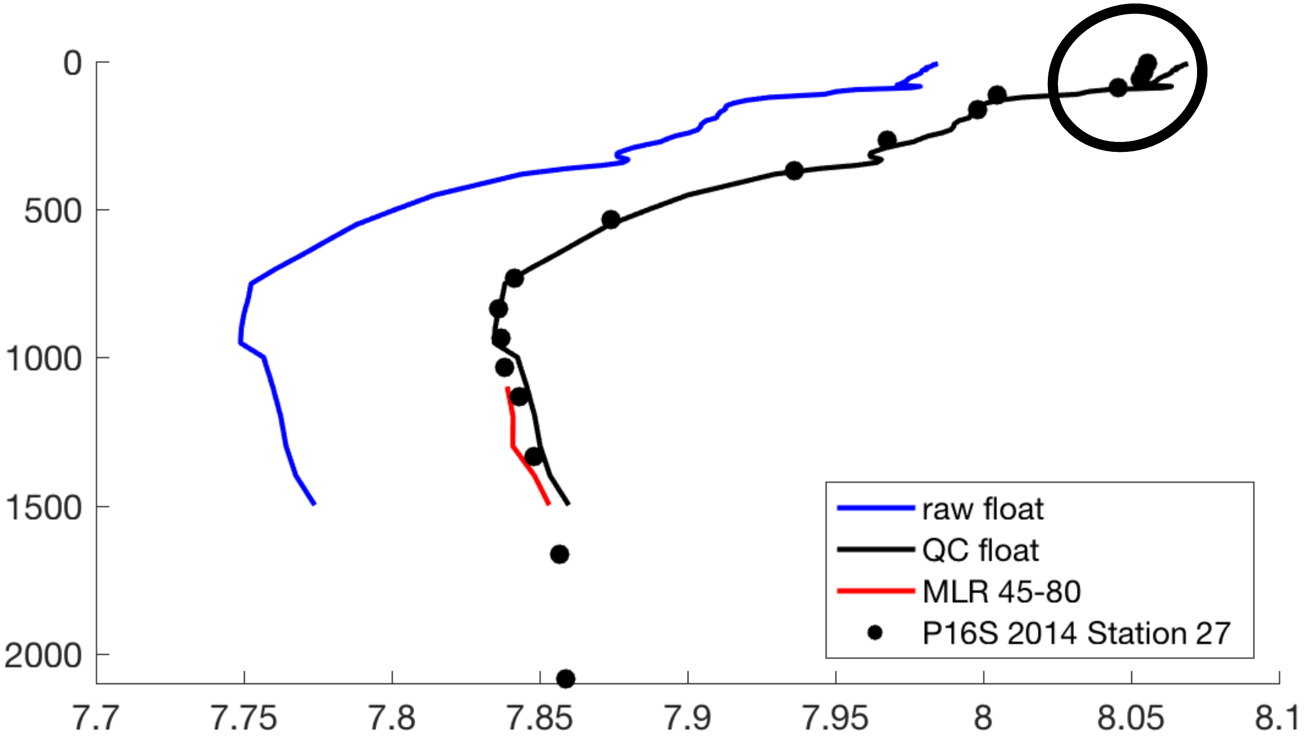
See Johnson et al., 2016, Williams et al., 2016 (*GRL*)

QC process



1. Calculate float MLR pH using float T, S, P, and O_2 at 1500 m

2. Adjust sensor reference potential (k_0) to match 1500 m sensor pH to algorithm pH

3. Apply new reference potential to entire profile

As a check: Does float pH (adjusted using 1500 m data) match the calibration bottle data at the surface? **YES!** Within reason. There are 18 hours between first profile and the calibration cast.

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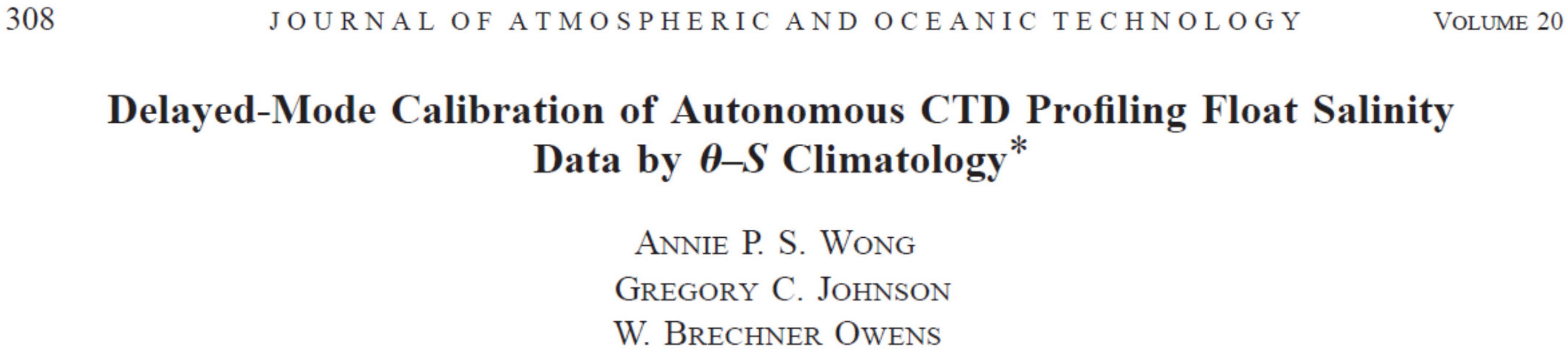
See Johnson et al., 2016, Williams et al., 2016 (*GRL*)



308 JOURNAL OF ATMOSPHERIC AND OCEANIC TECHNOLOGY VOLUME 20

Delayed-Mode Calibration of Autonomous CTD Profiling Float Salinity Data by θ–S Climatology*

ANNIE P. S. WONG
GREGORY C. JOHNSON
W. BRECHNER OWENS

“These floats give good measurements of temperature and pressure, but **salinity measurements may experience significant sensor drifts with time**. The moving nature of these floats means that it is too expensive to retrieve them regularly for physical calibrations. Thus a system has been set up to **correct the drift in these profiling float salinity data by using historical hydrographic data**.”

Estimating pCO_2

Float-
measured

Algorithm
TA (T,S,P,O_2,location)

CO2SYS(**pH_{Total}**, **TA**, T, S, P) → **pCO_2**

What is the uncertainty in calculated pCO_2?

Williams et al., in prep

Estimating pCO_2

Float-measured

Algorithm
TA (T, S, P, O_2, location)

CO2SYS(pH_{Total}, TA, T, S, P) → pCO_2

Possible sources of uncertainty:

pH:

- ☐ pH sensor precision
- ☐ Quality control process
  - ☐ Standard error of MLR
  - ☐ In situ pH calculation

TA:

- ☐ Standard error of algorithm estimate
- ☐ Seasonal application

Carbonate system equilibrium constants:

- ☐ K_0, K_1, K_2

Williams et al., in prep

Estimating pCO_2

Float-measured

Algorithm
TA (T,S,P,O_2,location)

CO2SYS(pH_{Total}, TA, T, S, P) → pCO_2

Possible sources of uncertainty:

pH:

☑ pH sensor precision 0.003
☐ Quality control process
    ☐ Standard error of MLR
    ☐ In situ pH calculation

TA:

☐ Standard error of algorithm estimate
☐ Seasonal application

Carbonate system equilibrium constants:

☐ K_0, K_1, K_2

Williams et al., in prep

Estimating pCO_2

Float-measured

Algorithm
TA (T,S,P,O_2,location)

CO2SYS(**pH_{Total}**, **TA**, T, S, P) → **pCO_2**

Possible sources of uncertainty:

pH:

- ☑ pH sensor precision
- ☑ Quality control process 0.007
  - ☑ Standard error of MLR 0.004
  - ☑ In situ pH calculation 0.005

TA:

- ☐ Standard error of algorithm estimate
- ☐ Seasonal application

Carbonate system equilibrium constants:

- ☐ K_0, K_1, K_2

Williams et al., in prep

Estimating pCO_2

Float-measured

Algorithm
TA (T,S,P,O_2,location)

CO2SYS(pH_{Total}, TA, T, S, P) → pCO_2

Possible sources of uncertainty:

pH:
- ☑ pH sensor precision
- ☑ Quality control process
  - ☑ Standard error of MLR
  - ☑ In situ pH calculation

TA:
- ☑ Standard error of algorithm estimate 5.6 μmol kg^{-1}
- ☑ Seasonal application May be larger in winter, but not significant

Carbonate system equilibrium constants:
- ☐ K_0, K_1, K_2

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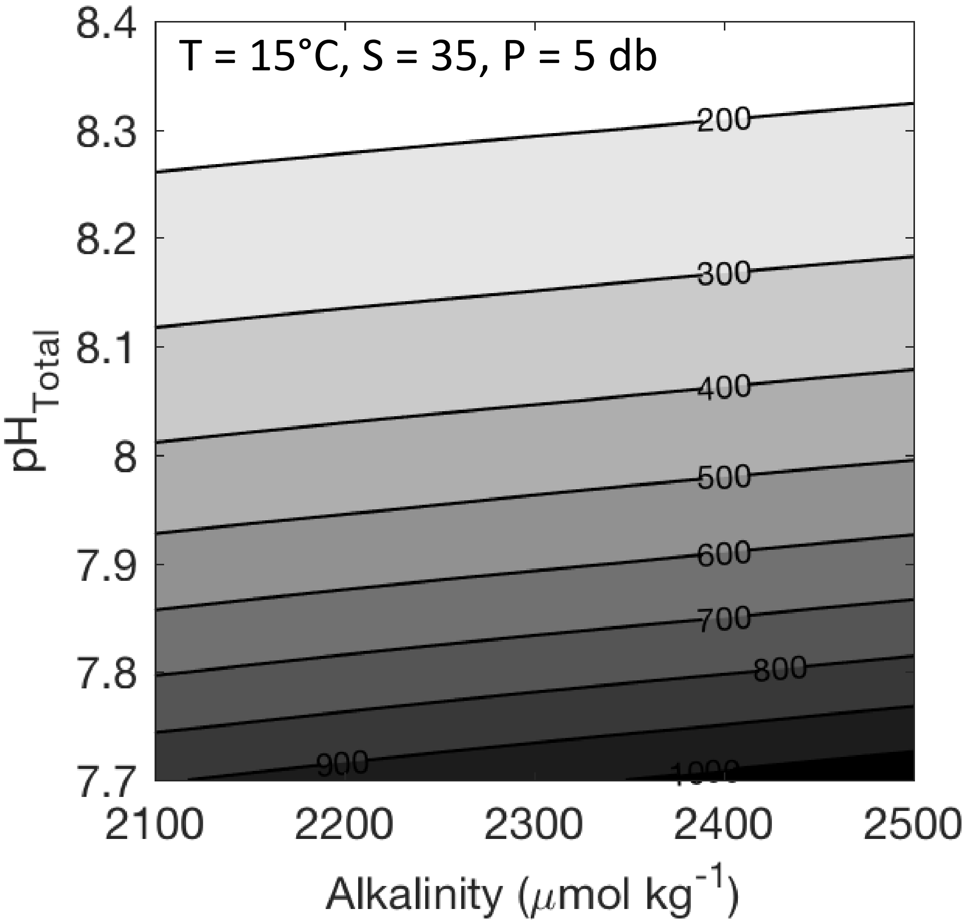
Williams et al., in prep

pCO_2 (pH, TA)



pCO_2(pH, TA) at a given T, S, and P depends mostly on the pH value

Dickson and Riley (1978):

1% uncert. in TA → 1% uncert. in pCO_2

0.2% absolute uncertainty in TA estimates → 0.2% relative uncertainty in pCO_{2sw} is **0.9 µatm at 400 µatm**

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Dickson and Riley, 1978, Williams et al., in prep

Estimating pCO_2

Float-measured → pH_{Total}

Algorithm TA (T,S,P,O_2,location) → TA

$$\text{CO2SYS}(pH_{Total},\ TA,\ T,\ S,\ P) \rightarrow pCO_2$$

Possible sources of uncertainty:

pH:

- ☑ pH sensor precision
- ☑ Quality control process
  - ☑ Standard error of MLR
  - ☑ In situ pH calculation

TA:

- ☑ Standard error of algorithm estimate
- ☑ Seasonal application

Carbonate system equilibrium constants:

- ☑ K_0, K_1, K_2 Dickson and Riley, 1978

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Williams et al., in prep

Float-based pCO_2 uncertainty

Table 2. Relative uncertainty in pCO_{2sw} from all sources

		absolute uncertainty in parameter	relative uncertainty in pCO_{2sw}	Total relative uncertainty in pCO_{2sw}
pH	sensor precision	0.003	0.83%	2.5%
	QC process	0.007	1.89%	
Alkalinity	standard error in algorithm	5.6 µmol kg^{-1}	0.24%	
Equilibrium Constants	K_0	0.50%	0.50%	
	K_1	1.27%	1.25%	
	K_2	2.30%	0.48%	

Relative uncertainties in direct underway pCO_2 measurements around **1%**

Improving pH sensors will help but still 1.43% uncertainty from equilibrium constants

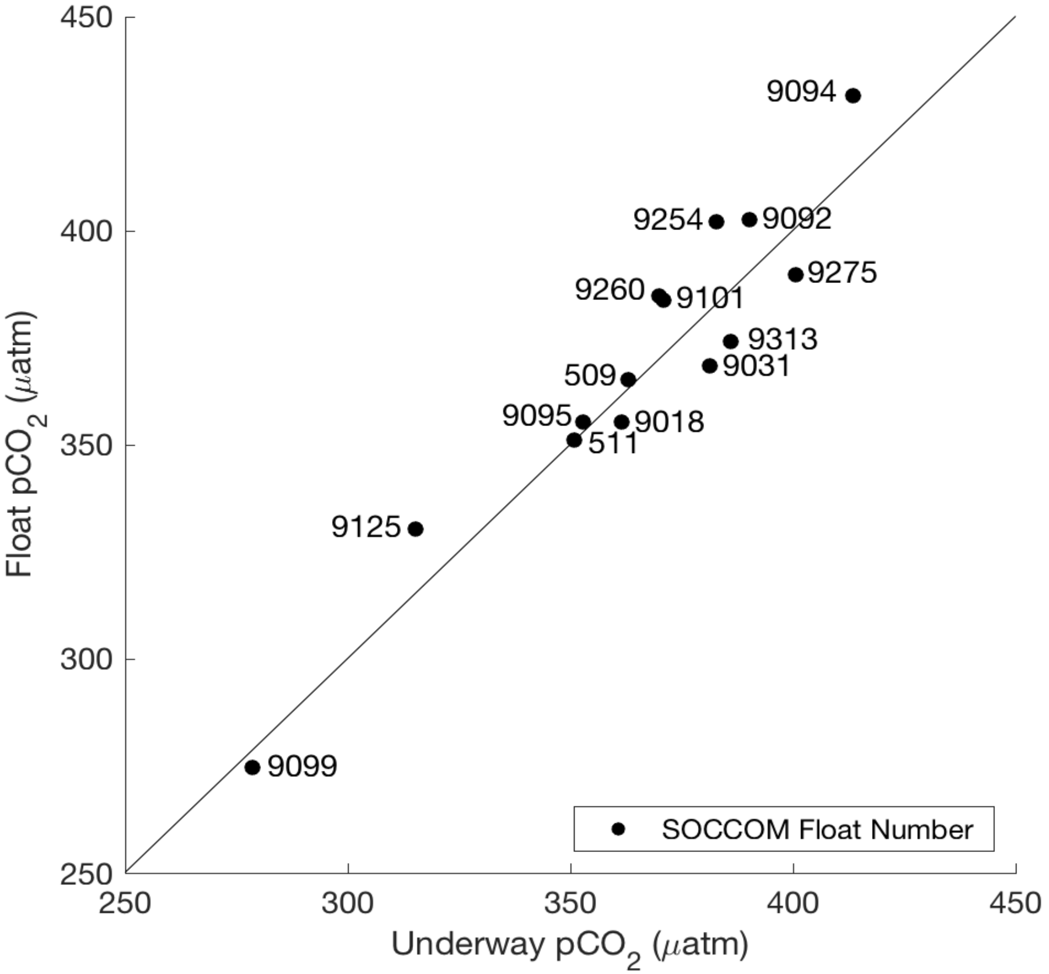
Williams et al., in prep

Underway pCO_2 matchup

Underway data are completely independent from bottle and float data

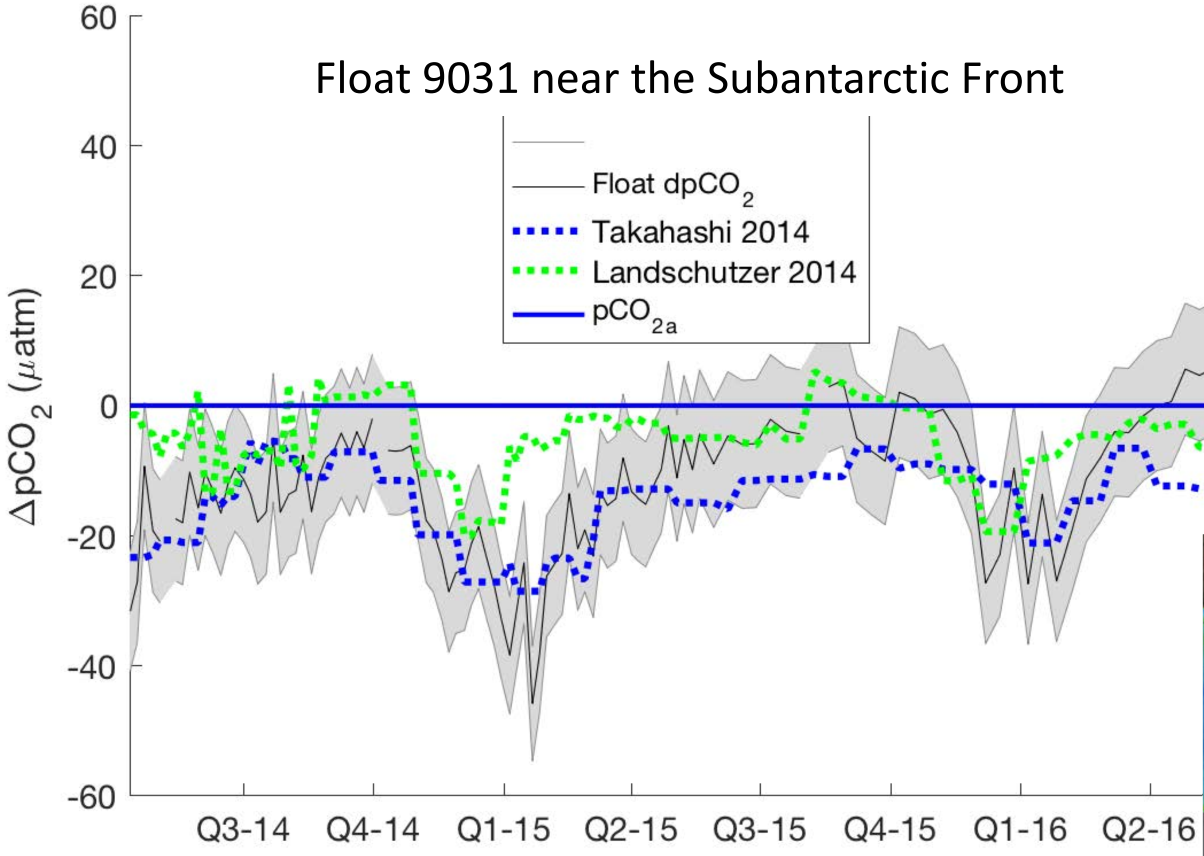
Standard deviation of the difference = **11.7 µatm (3.2%)**

The first float profile is ~18 hours after deployment. This may explain why this standard deviation is larger than our 2.5% estimate



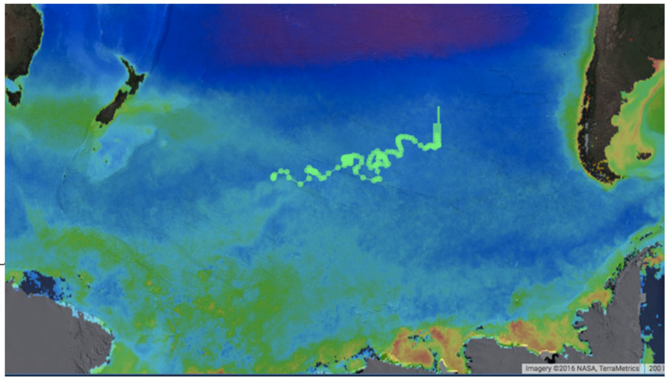
Williams et al., in prep

Complementing pCO_2 climatologies


Float 9031 near the Subantarctic Front

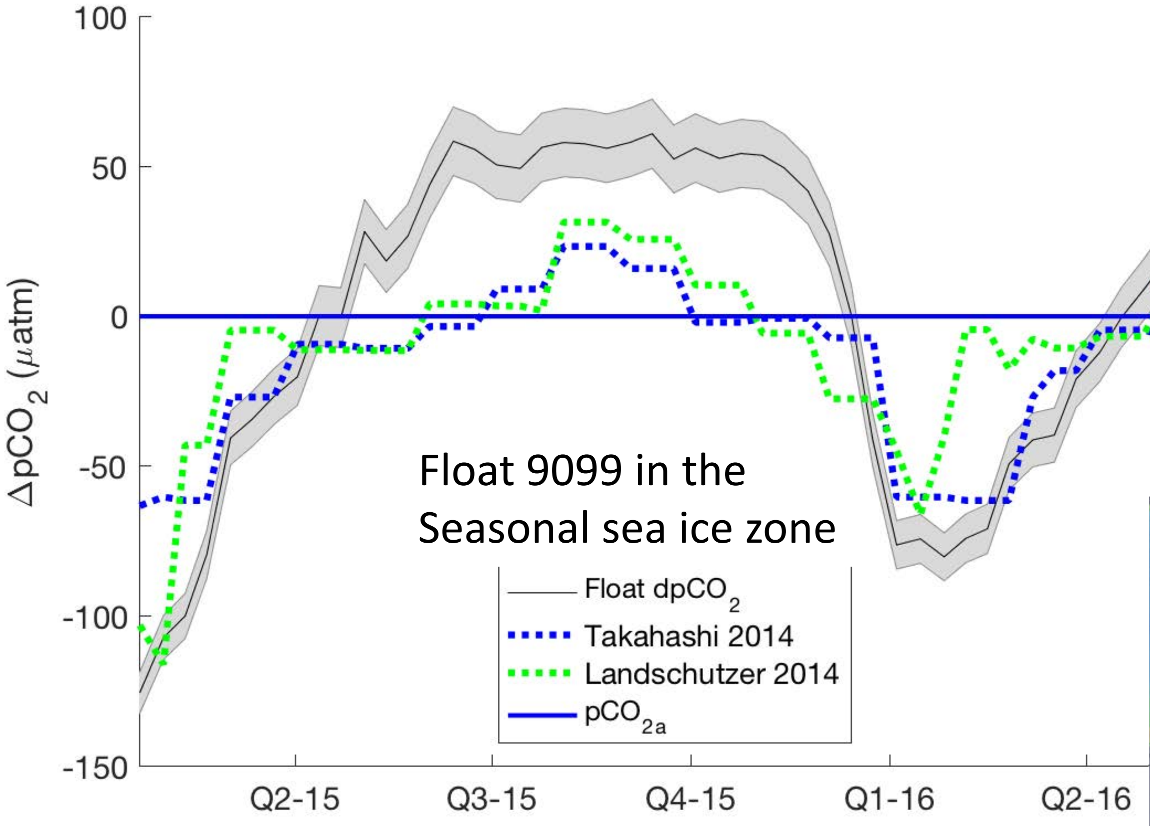
$\Delta pCO_2 = pCO_{2sw} - pCO_{2atm}$

The sign is important for flux calculations



Williams et al., in prep

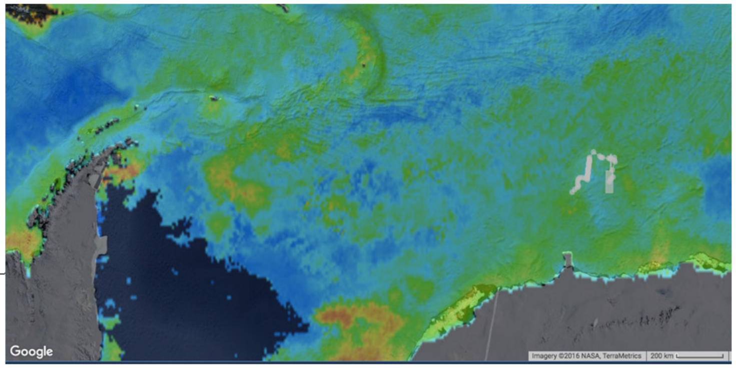
Complementing pCO_2 climatologies



Float 9099 in the Seasonal sea ice zone

$\Delta pCO_2 = pCO_{2sw} - pCO_{2atm}$

The sign is important for flux calculations



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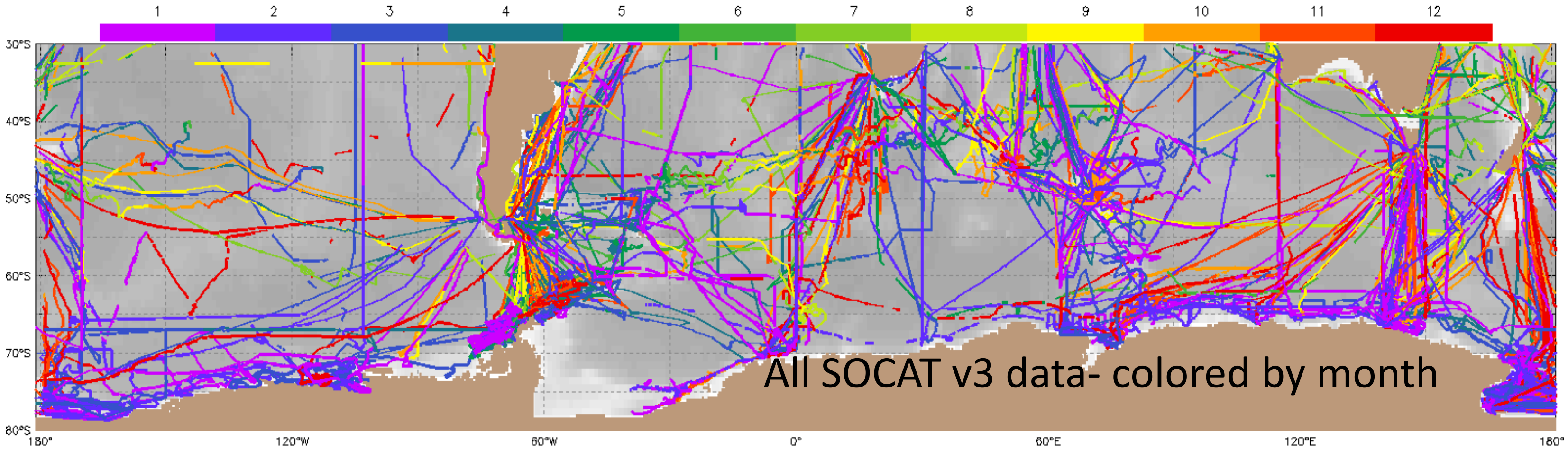
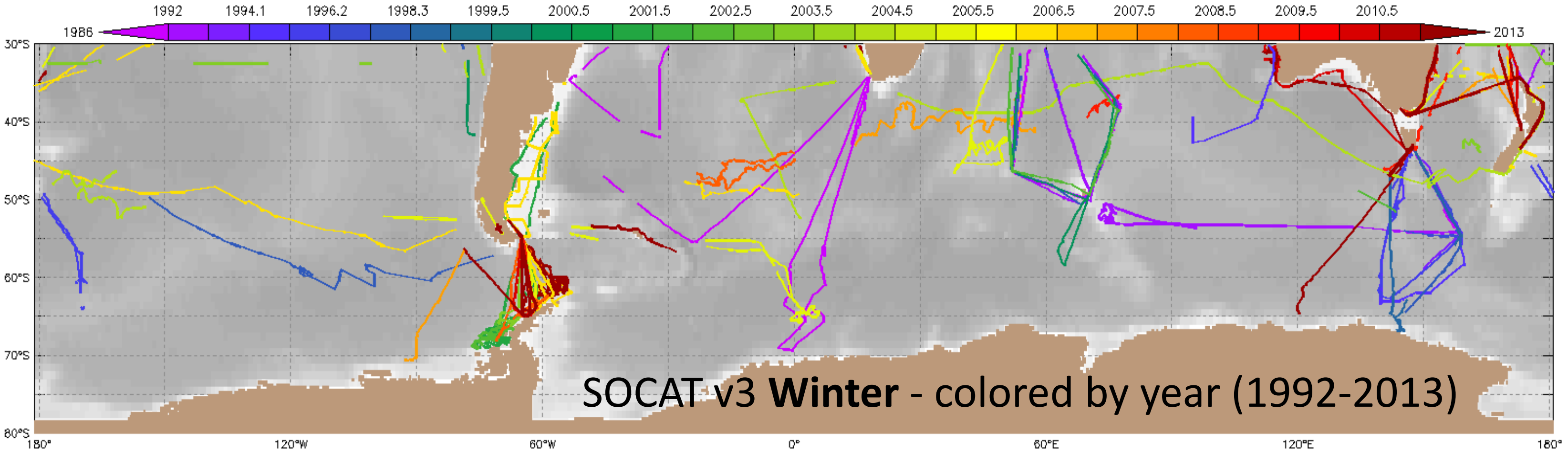
Williams et al., in prep

Why is there sometimes disagreement?



All SOCAT v3 data- colored by month



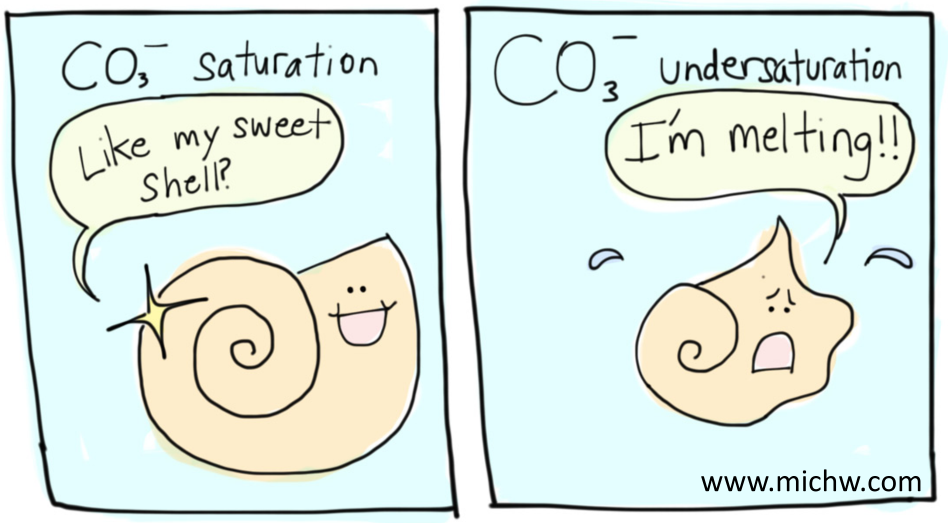
SOCAT v3 **Winter** - colored by year (1992-2013)

SOCAT does not include calculated pCO$_{2sw}$, only direct measurements

Bakker et al., 2016

Saturation state of aragonite (Ω_{Ar})

$$\Omega_{Aragonite} = \frac{[Ca^{2+}][CO_3^{2-}]}{K'_{sp}}$$



$\Omega_{Aragonite} > 1$
Aragonite is stable

$\Omega_{Aragonite} < 1$
Dissolution is favorable

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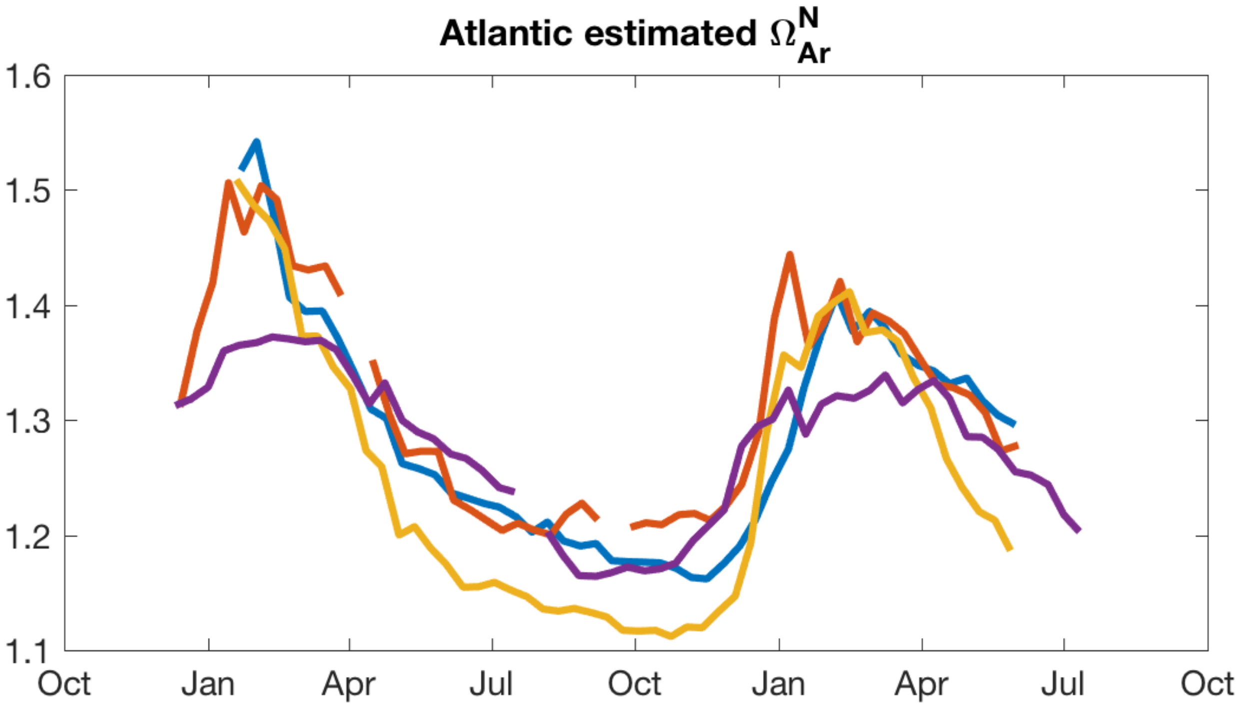
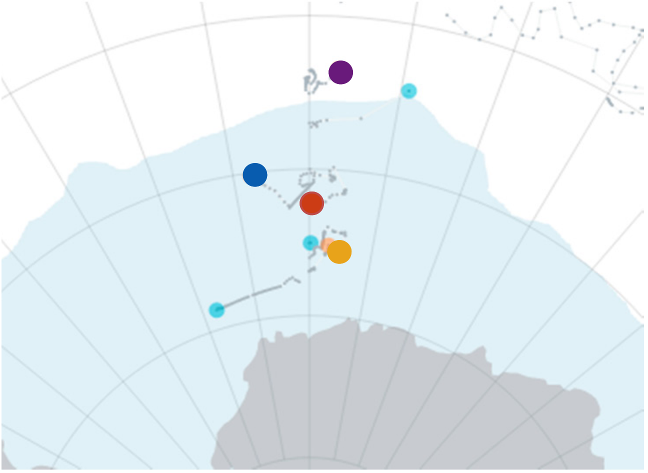
Estimated Ω_{Ar}

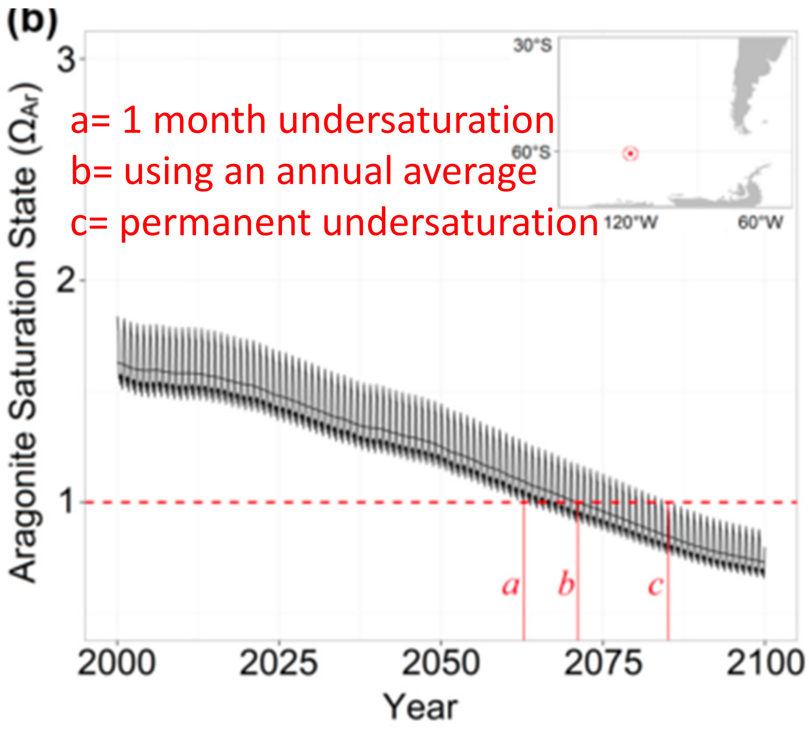




- Seasonal cycle larger in floats that go under ice
- We are observing full seasonal cycles and inter annual variability
- Some of these floats have pH sensors, some do not

Williams et al., in prep (*JGR special issue*)

Why is the seasonal cycle important?



a= 1 month undersaturation
b= using an annual average
c= permanent undersaturation

Sasse et al., 2015
Under RCP8.5 (business as usual) projection

- Knowing the magnitude of the seasonal cycle in Ω_{Ar} is important for projections of future ocean conditions
- Duration of exposure to waters with $\Omega<1$ is important! Even short-term exposure to undersaturated waters can have negative impacts

Summary

- DuraFET pH sensors conditioned in natural flowing seawater are stable
- Unconditioned sensors (2014-2015) are quality controlled using the MLR algorithm

- Float-based estimates of pCO_{2sw} have a relative standard uncertainty of 2.5% (absolute uncertainty of 10 µatm at a pCO_2 of 400 µatm)
- pCO_2 does not depend heavily on TA estimate

- We are observing the seasonal cycle and inter annual variability in $\Omega_{Aragonite}$ for the first time on floats both with and without pH sensors

THANKS!

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Nancy.williams@oregonstate.edu

Equilibrium constants uncertainty details

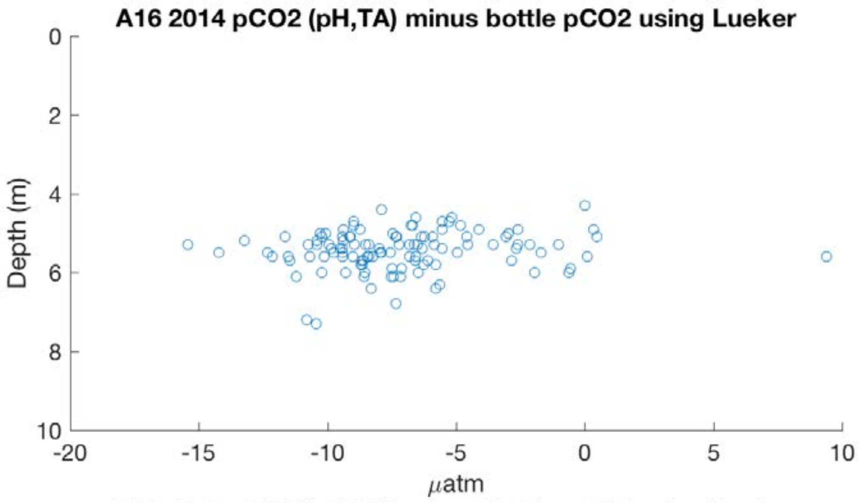
Table 1. Uncertainty in carbonate system equilibrium constants

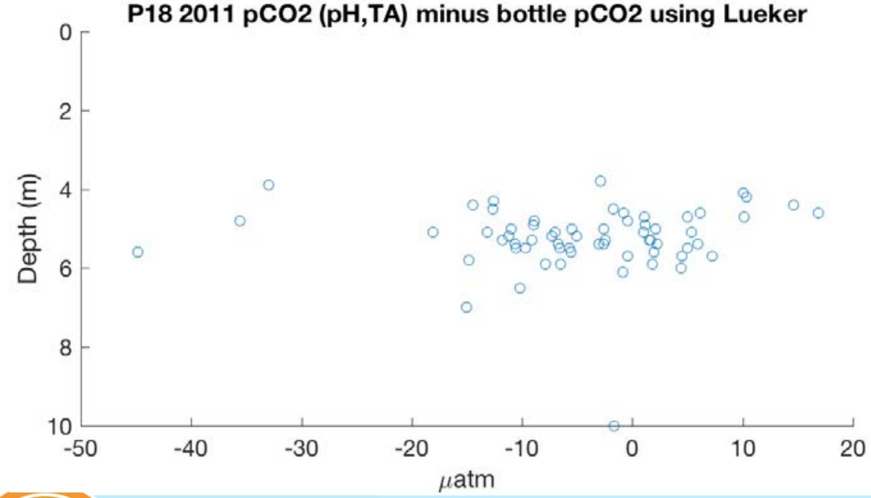
	K_0	K_1	K_2
$\%\delta pCO_2/\%\delta K^{a}$	-0.99	-0.99	-0.21
absolute uncertainty in pK^{ab}	0.002	0.0055	0.01
relative uncertainty in K^{ab}	0.50%	1.27%	2.30%
relative uncertainty in pCO_{2sw}	0.50%	1.25%	0.48%
TOTAL		1.43%	

[a] from Dickson and Riley [1978]

[b] from Lueker et al. [2000]

pCO_2(pH, TA) minus bottle pCO_2

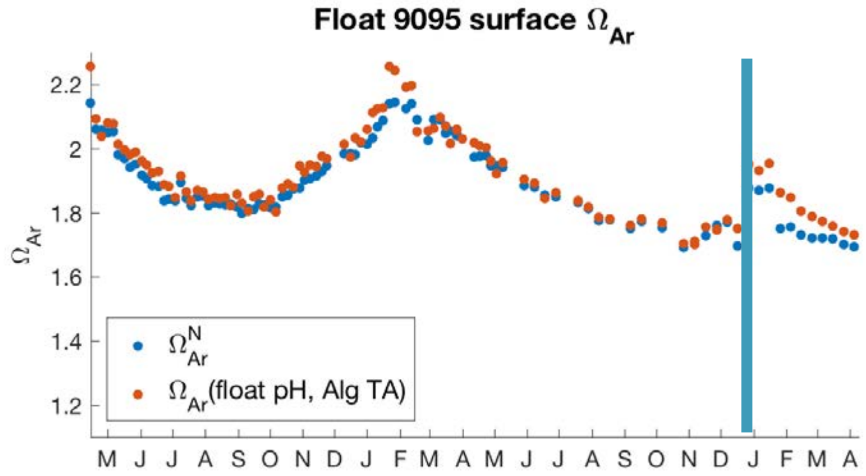




Choice of Lueker et al., 2000 (as per Dickson, Wanninkhof et al., 2016) has no significant bias in pCO2 calc minus measured at the surface

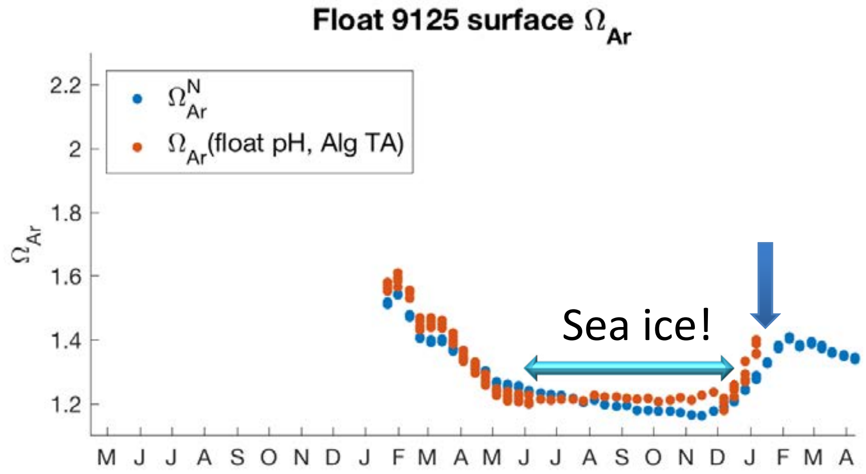
Surface Ω_{Ar} Algorithm (Ω_{Ar}^{N})

$$\Omega_{Ar}^{\mathbf{N}} = \beta_0 + \beta_1 S + \beta_2 T + \beta_3 P + \beta_4 \sigma_\Theta + \beta_5 \mathbf{N} \qquad \text{rmse} = 0.03$$


Float 9095 surface Ω_{Ar}

North of the ACC in the Pacific near the Subantarctic Front (SAF)

Surface $\Omega_{Aragonite}$ range: 1.8 →2.3


Float 9125 surface Ω_{Ar}

South of the ACC in the Atlantic seasonal sea ice zone (SSIZ)

Surface $\Omega_{Aragonite}$ range: 1.1 →1.6

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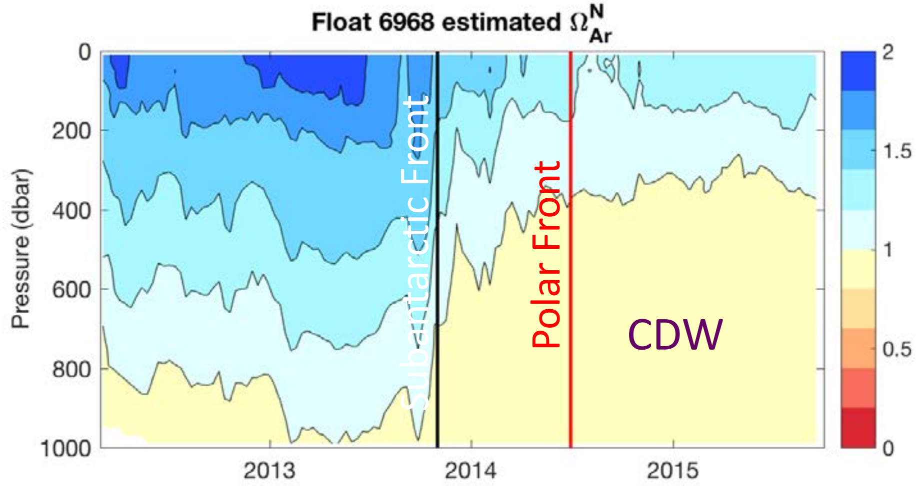
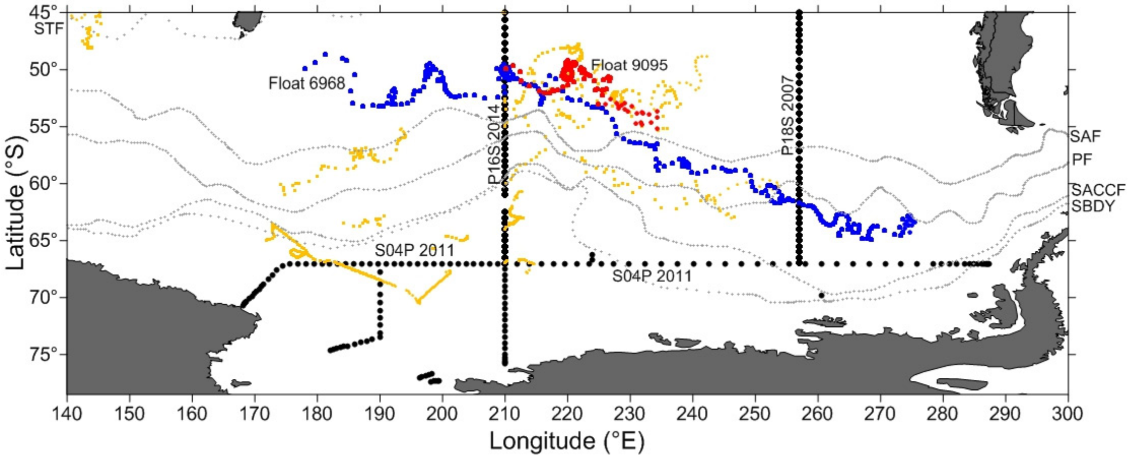
Williams et al., in prep

Estimated Ω^{N}_{Ar}





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Williams et al., in prep