An updated temperature correction for UV nitrate sensors

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&
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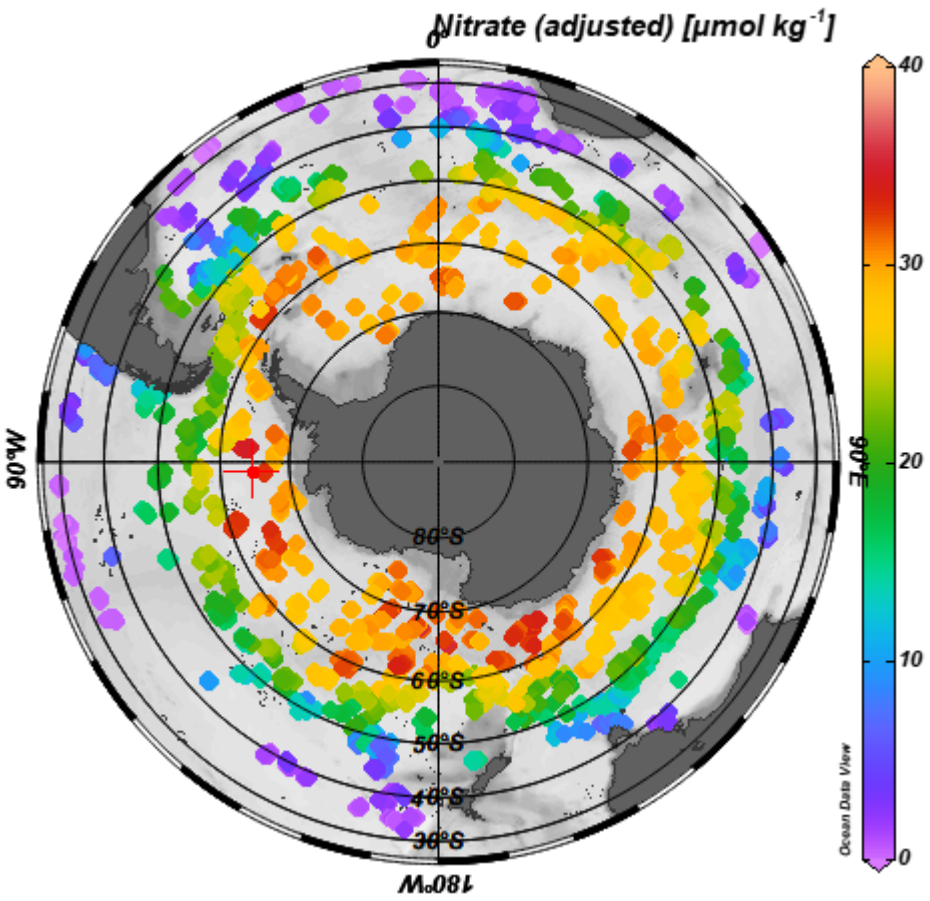
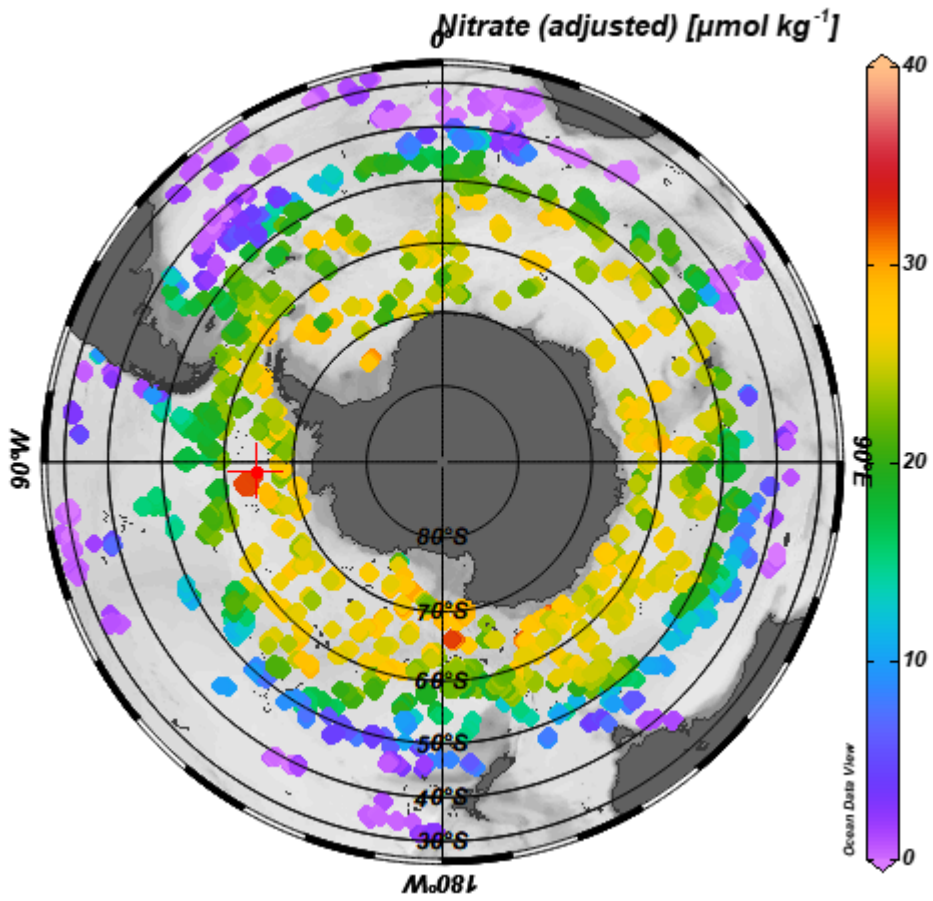
9th BGC Argo Meeting, ADMT 21
November 30 – December 1, 2020
Virtual

- Year around coverage of nitrate across the Southern Ocean
- Clearly see seasonal drawdown/ recharge
- Enables comprehensive estimates of Net Community Production (NCP)
- All due to BGC Argo!

July - August



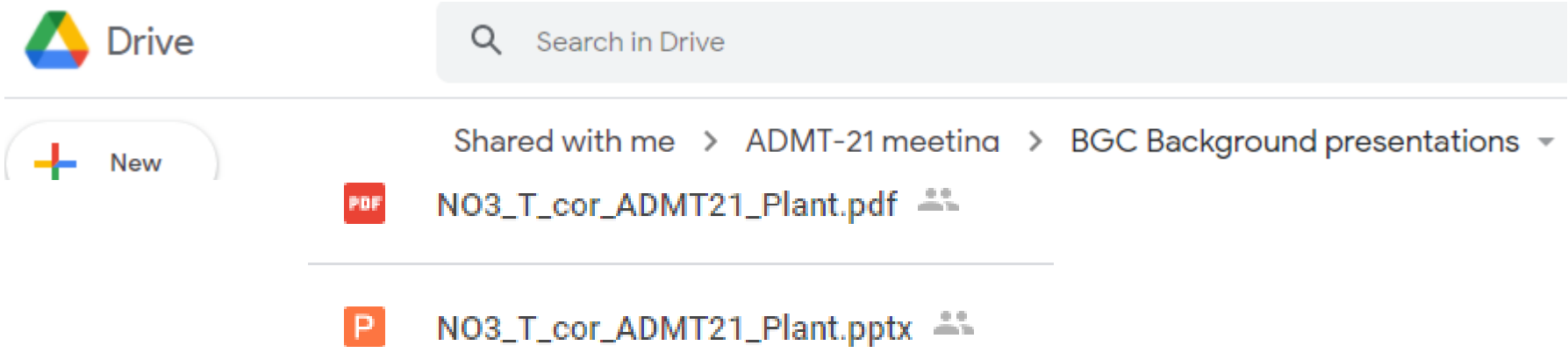
January - March



Outline

1. Need for an updated correction
2. UV nitrate method review
3. Existing temperature correction
4. New temperature correction
5. Comparison
6. Caveats
7. Conclusions – **use new T correction!**

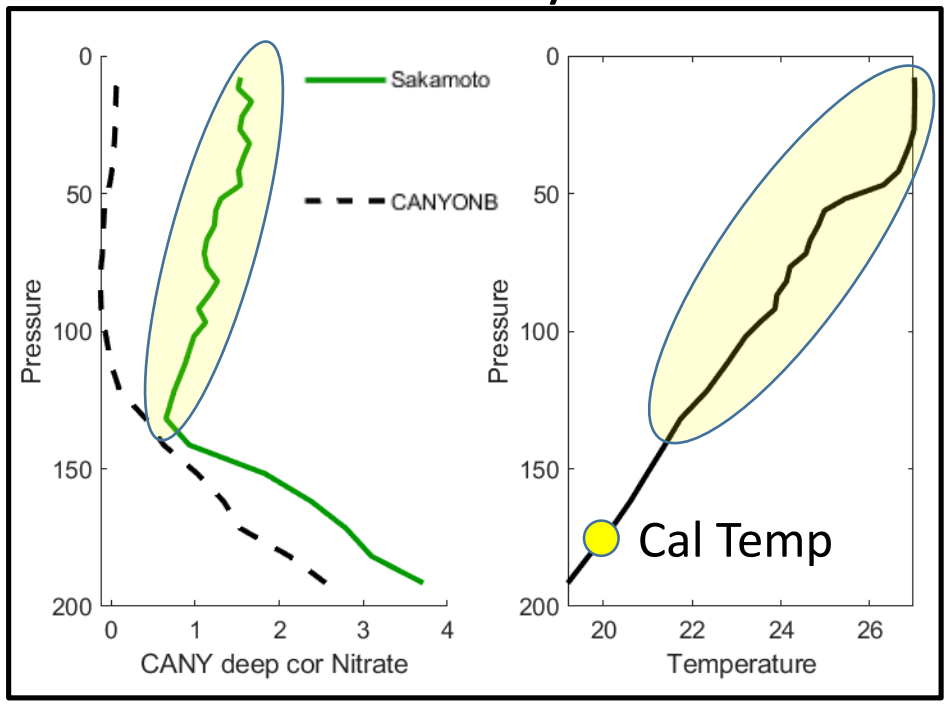
Please see detailed presentation in google drive folder:

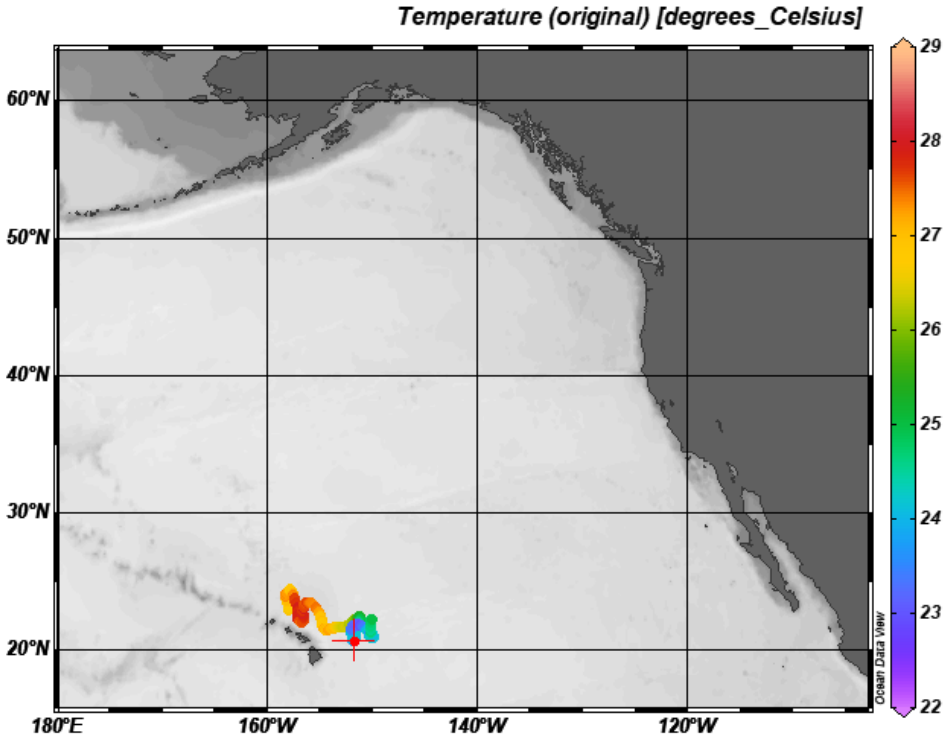


Warm water bias

- Warm tropical surface waters should have zero nitrate
- Often see an artificial increase in nitrate coincident with increasing temperature (1-2 µmol/kg)
- Likely an issue with the current temperature correction method
- 2nd order problem but it would be nice to understand & fix
- Tropical surface waters become good validation data sets to test improvements

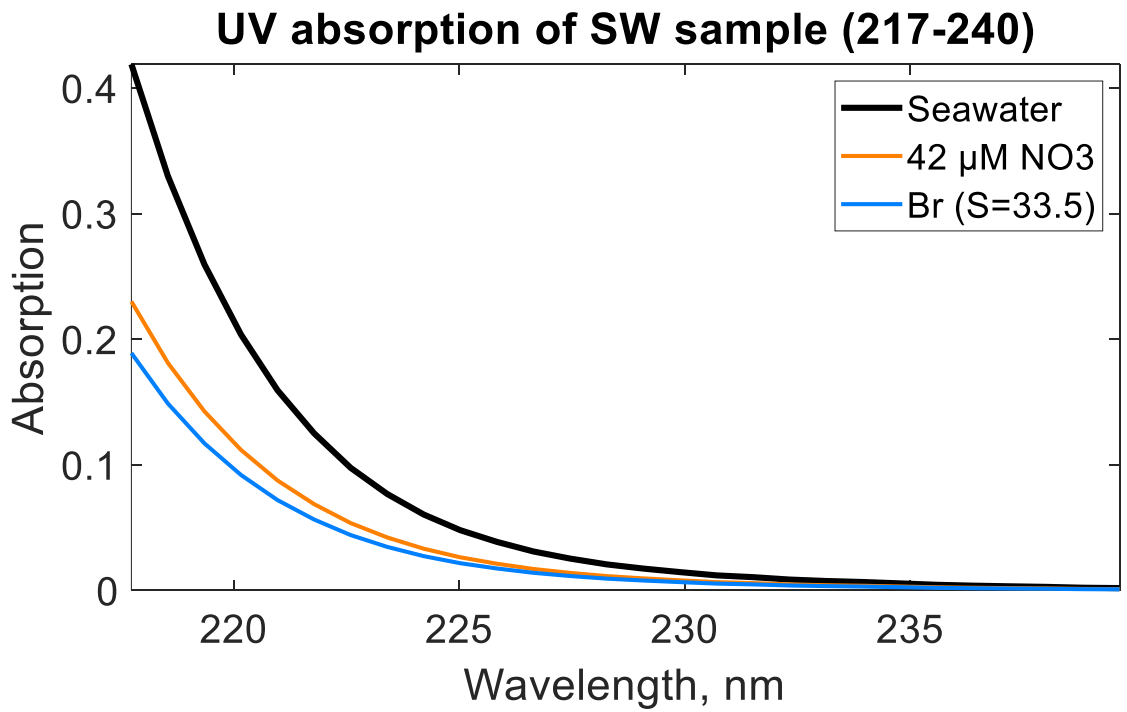
17267HOT cycle 15





Calculating Nitrate

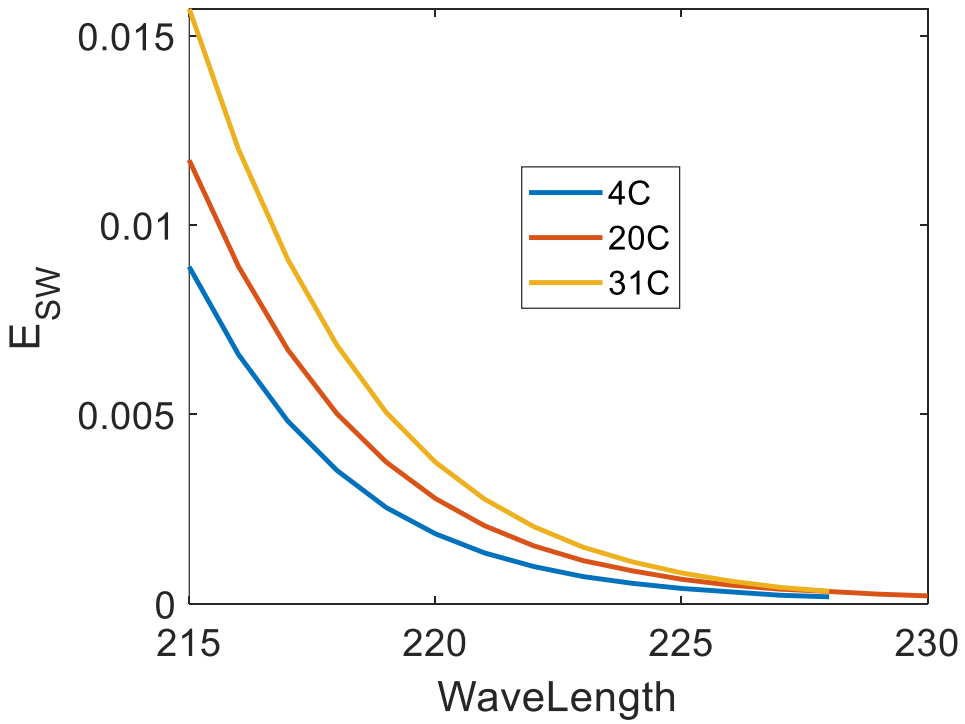
- In open ocean waters Br^- & NO_3^- dominate the UV absorption spectrum (217 – 240 nm)
- Br^- a function of salinity
- **Br^- absorption is temperature dependent!**
- Deconvolve the seawater absorption spectrum to determine nitrate
- Need accurate extinction coefficients.



Typical deep water UV absorption spectrum near Hawaii

ε_{SW} Temperature Correction

- ε_{SW} = seawater extinction coefficient (mostly due to bromide)
- Most sensors are calibrated in the lab at 20C
- ε_{SW} is a function of temperature (& pressure)
- ε_{SW} must be adjusted to in situ temperature before absorbance due to salinity can be removed from the seawater spectrum

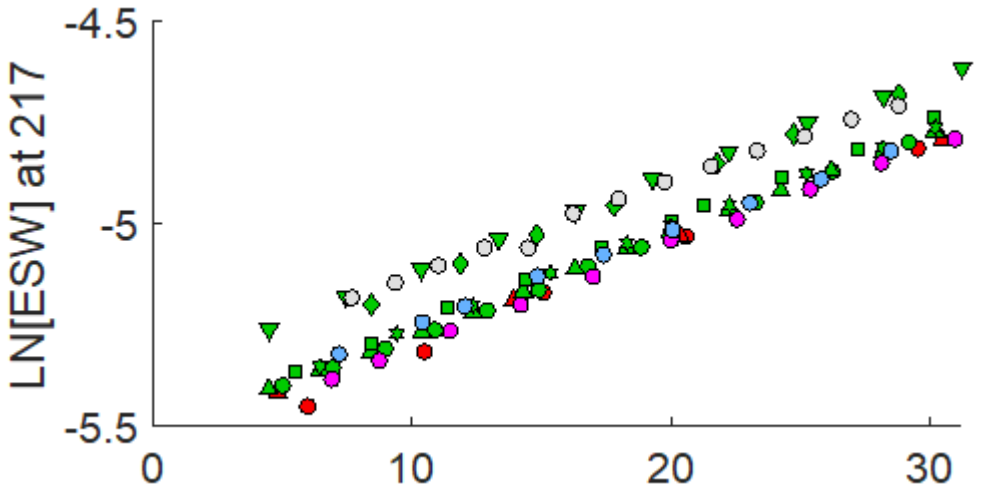


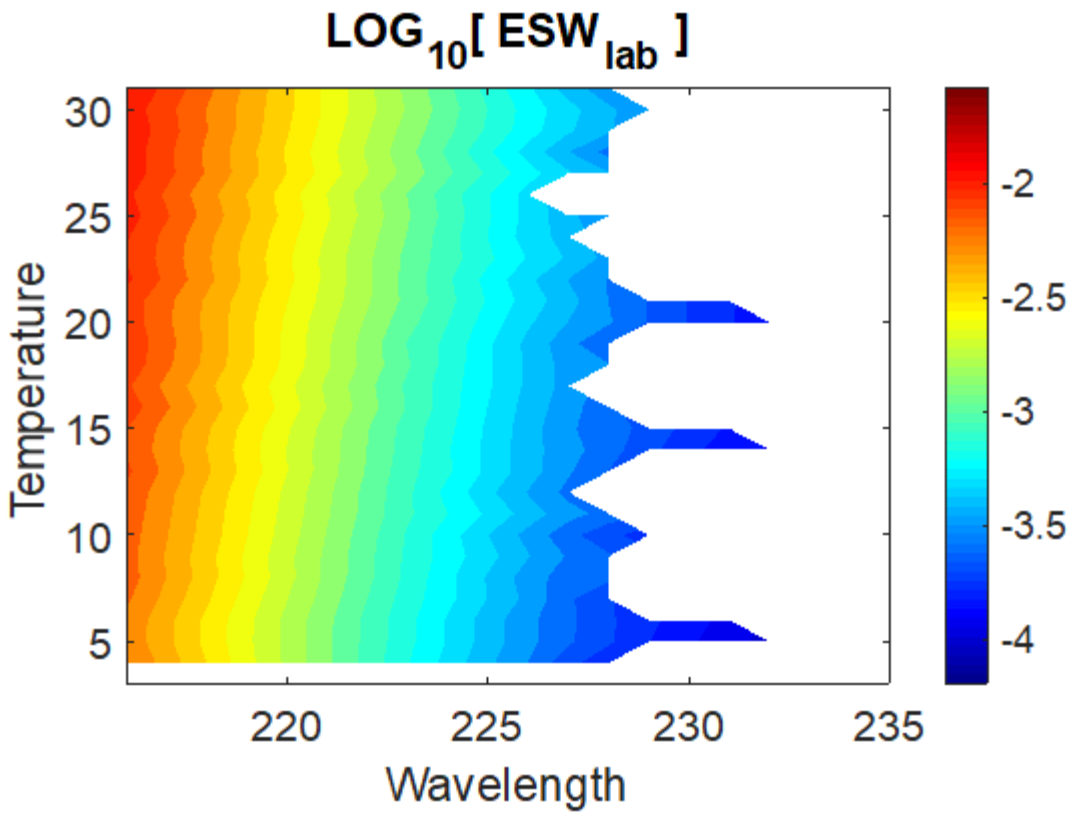
- Increasing temperature causes salinity (bromide) to absorb more UV light

- All corrections used here take the form of: $\varepsilon_{SW\,T} = \varepsilon_{SW\,CALT} * GAIN$

Proposed new ε_{SW} Temperature Correction

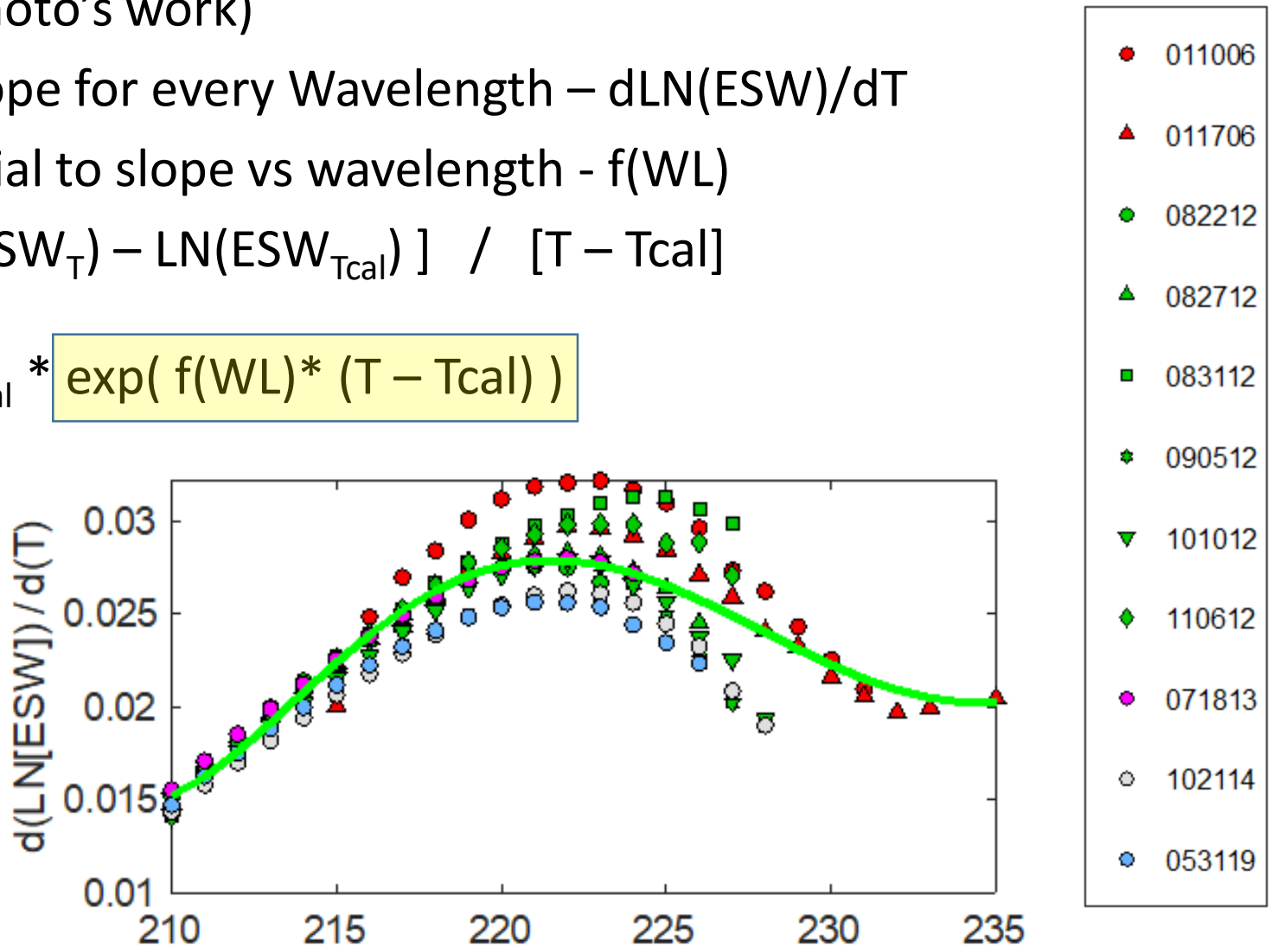
- LN(seawater absorbance) or LN(seawater extinction coefficient) is a linear function of temperature
- **For a given wavelength dLN(ϵ_{SW})/dT = constant**



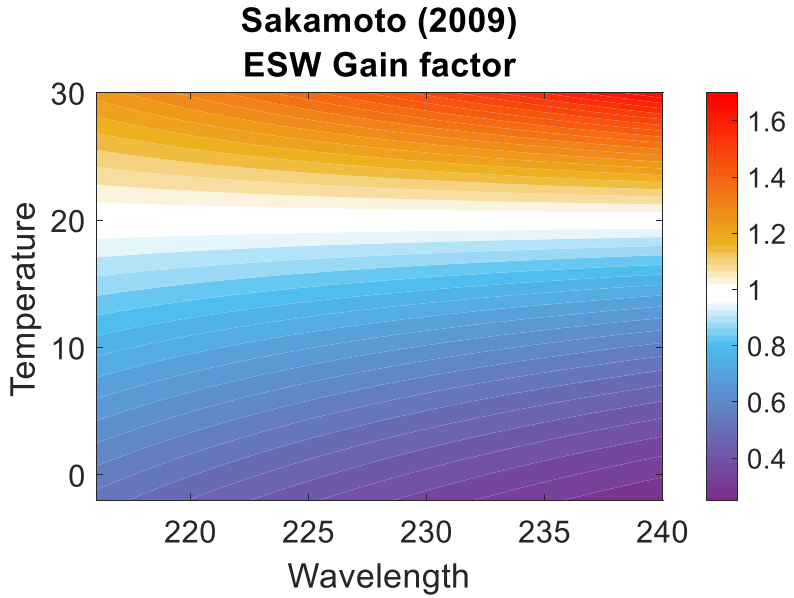


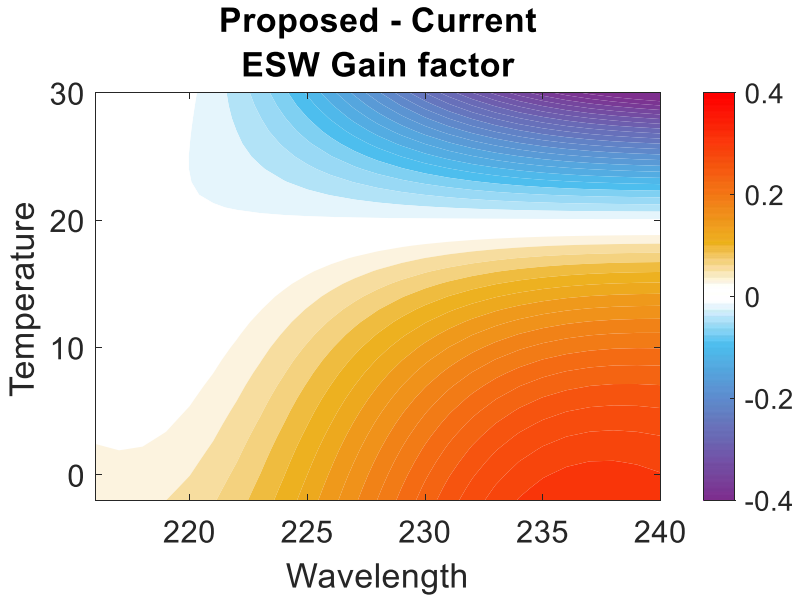
Proposed new ε_{SW} Temperature Correction

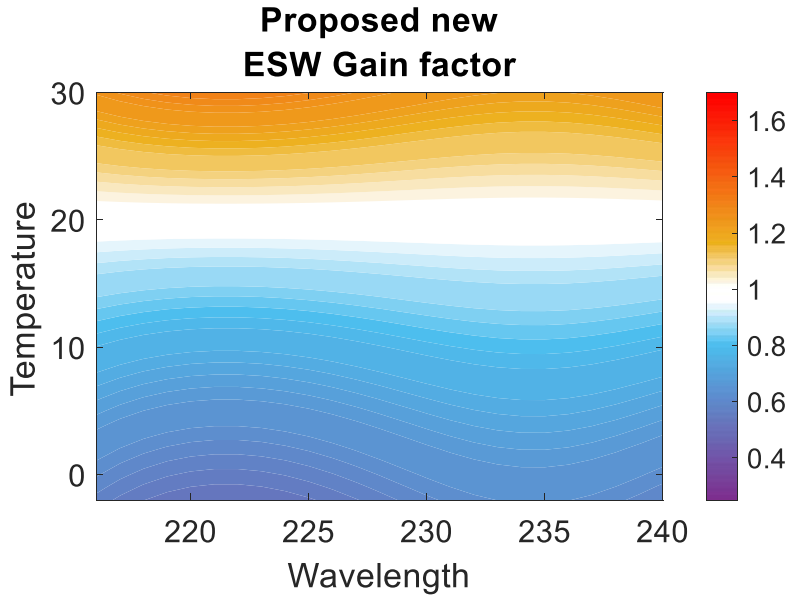
- Use select ESW lab temperature experiments 2006 – 2019 (Carole Sakamoto's work)
- Calculate a slope for every Wavelength – dLN(ESW)/dT
- Fit a polynomial to slope vs wavelength - f(WL)
- $f(WL) = [\ LN(ESW_T) - LN(ESW_{Tcal})\ ]\ \ /\ \ [T - Tcal]$
- $ESW_T = ESW_{Tcal} * \exp(\ f(WL) * (T - Tcal)\ )$



Proposed new ε_{SW} Temperature Correction







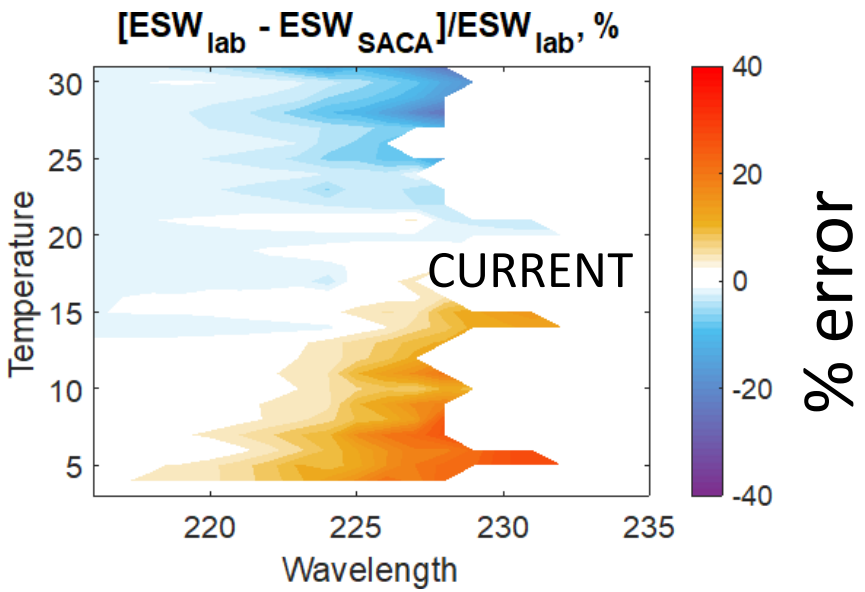
$$\varepsilon_{SW\ T} = \varepsilon_{SW\ CALT} * GAIN$$

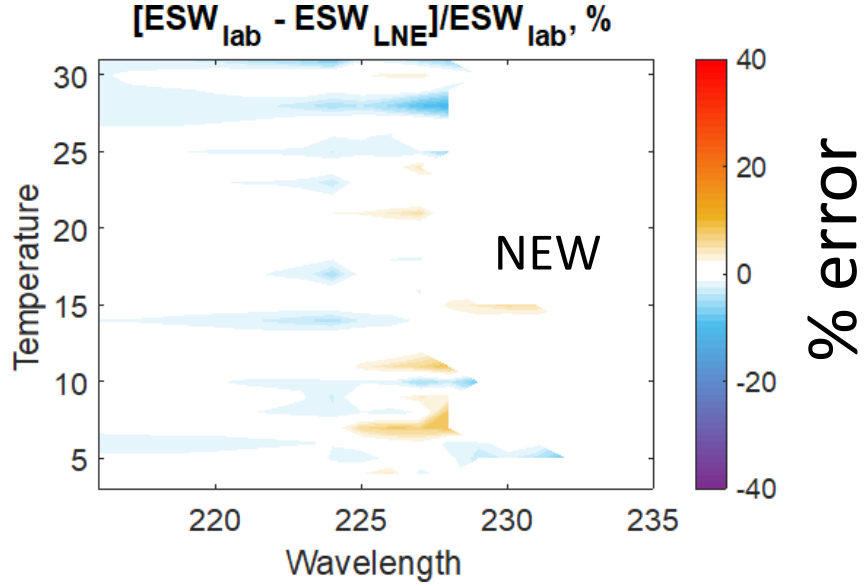
- Gain values for current & proposed temperature correction
- >1 increase ESW & < 1 decrease ESW
- New correction less aggressive
- Biggest difference at WL's > 225

Proposed new ε_{SW} Temperature Correction

How well do the temperature correction models behave?

- Take 20C lab data (Cal T = ESW_{20C}) & use T corrections to generate ESW values at all experimental T's
- Compare to lab data
- New method has much lower % error across T & WL!

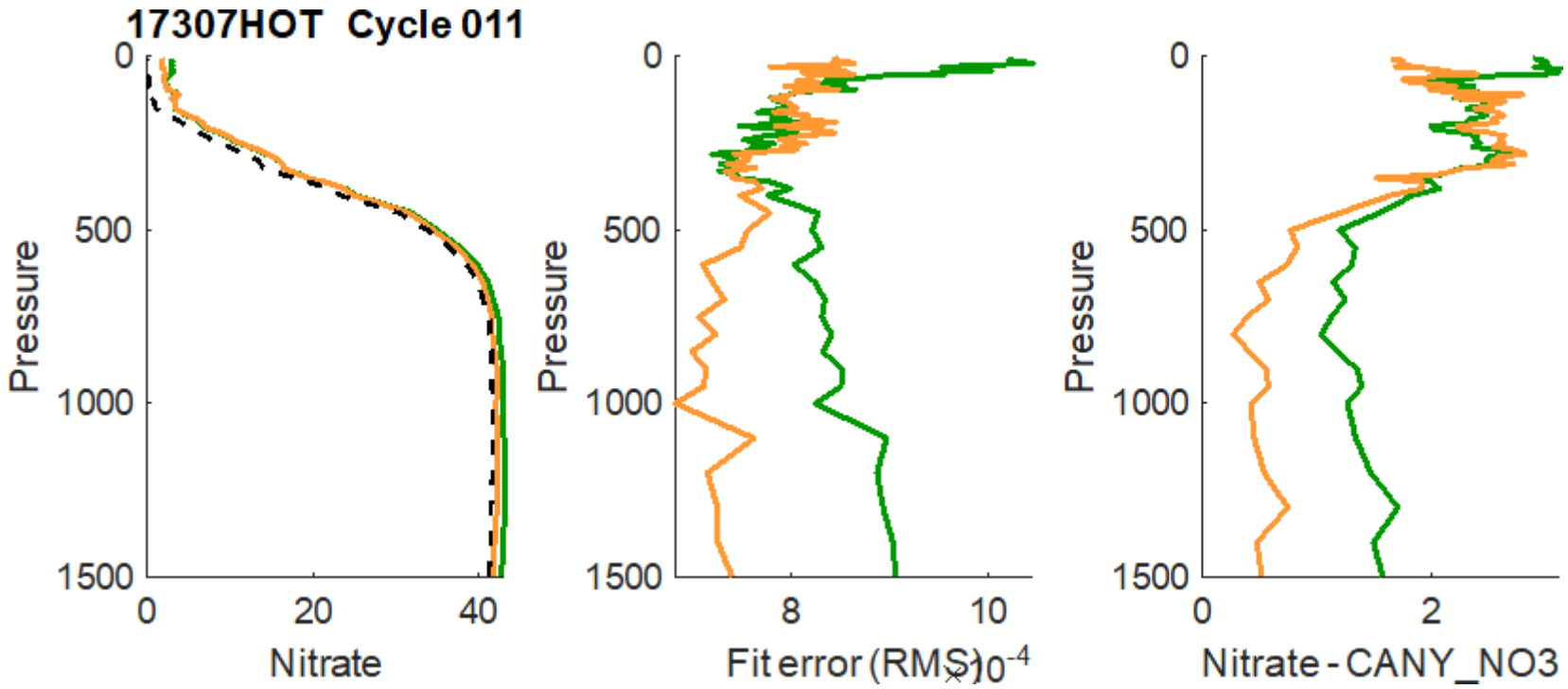




Proposed new ε_{SW} Temperature Correction

How well do the temperature correction models work in the real world?

- Look at Nitrate fit error
- Compare to CANYONB estimate for nitrate



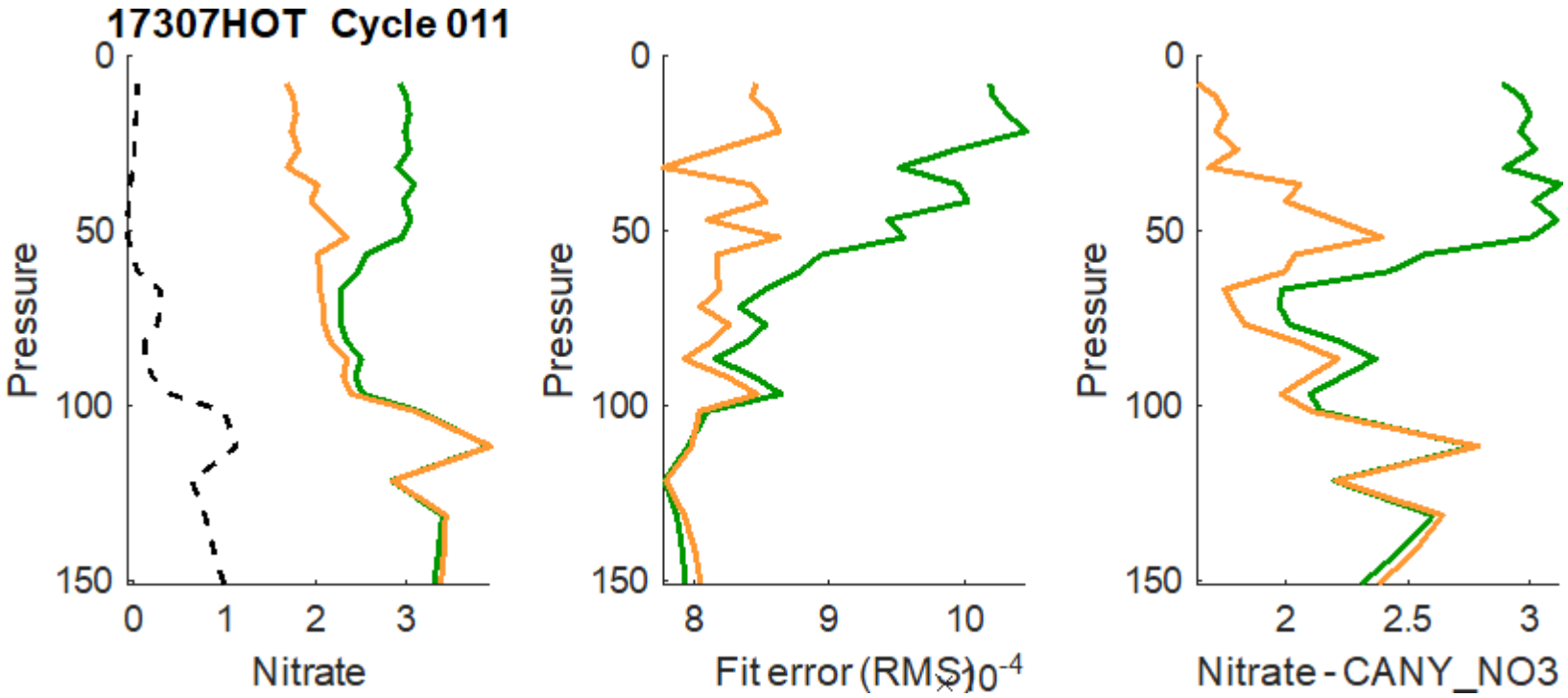
New method:

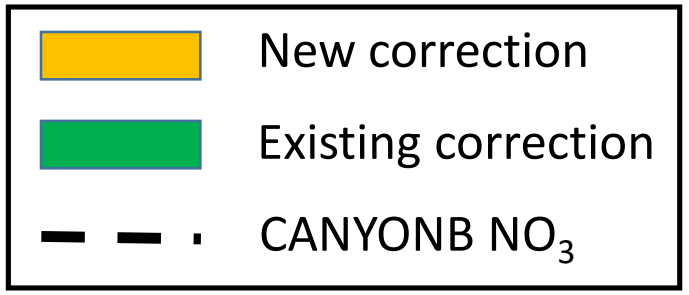
- Smaller fit error
- Less bias from CANYON B

Proposed new ε_{SW} Temperature Correction

How well do the temperature correction models work in the real world?

Same plot just zooming in on surface waters

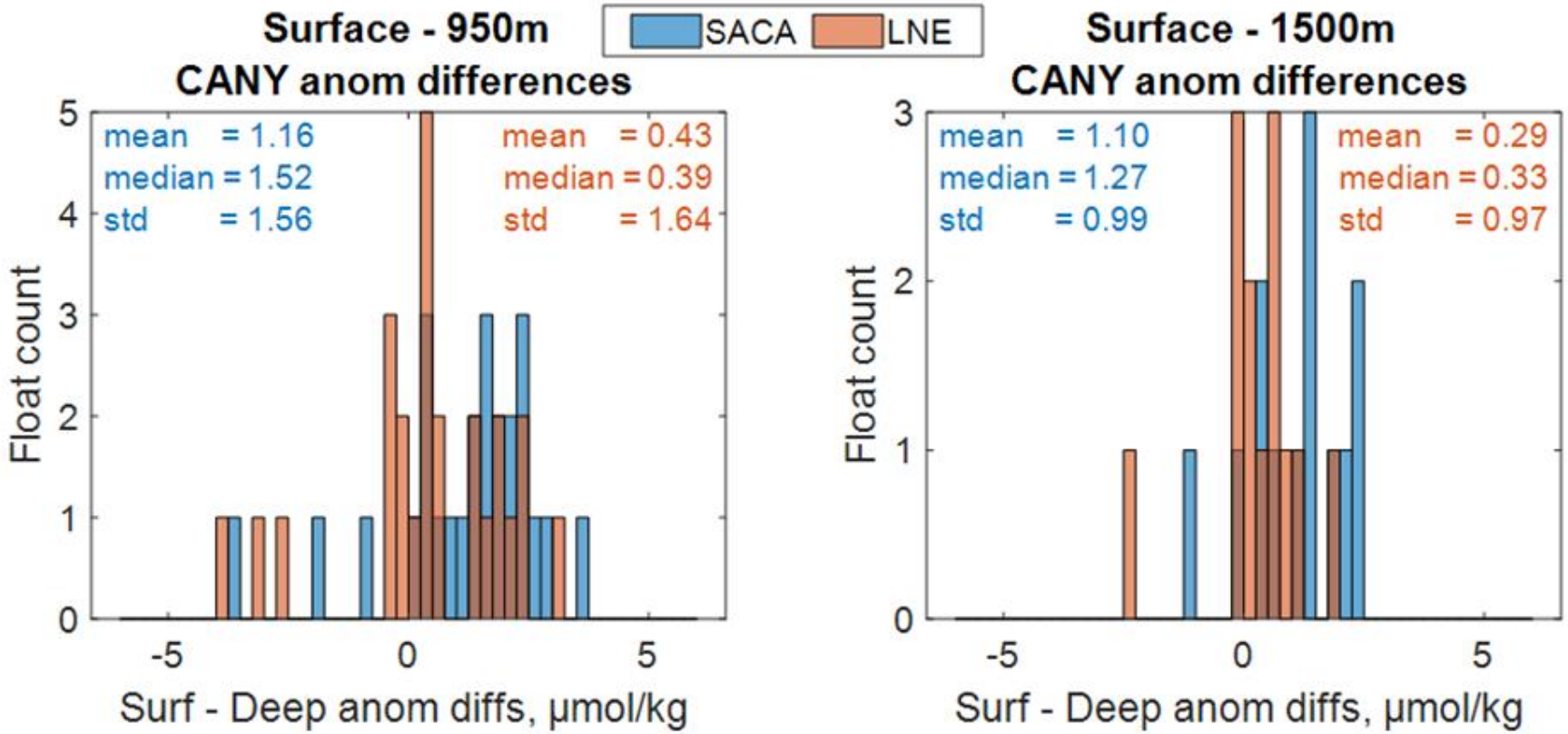




- Anomalous surface increase in nitrate disappears
- Fit error reduced

Assess a bunch of floats – Surface waters > 24C where NO3 should be zero

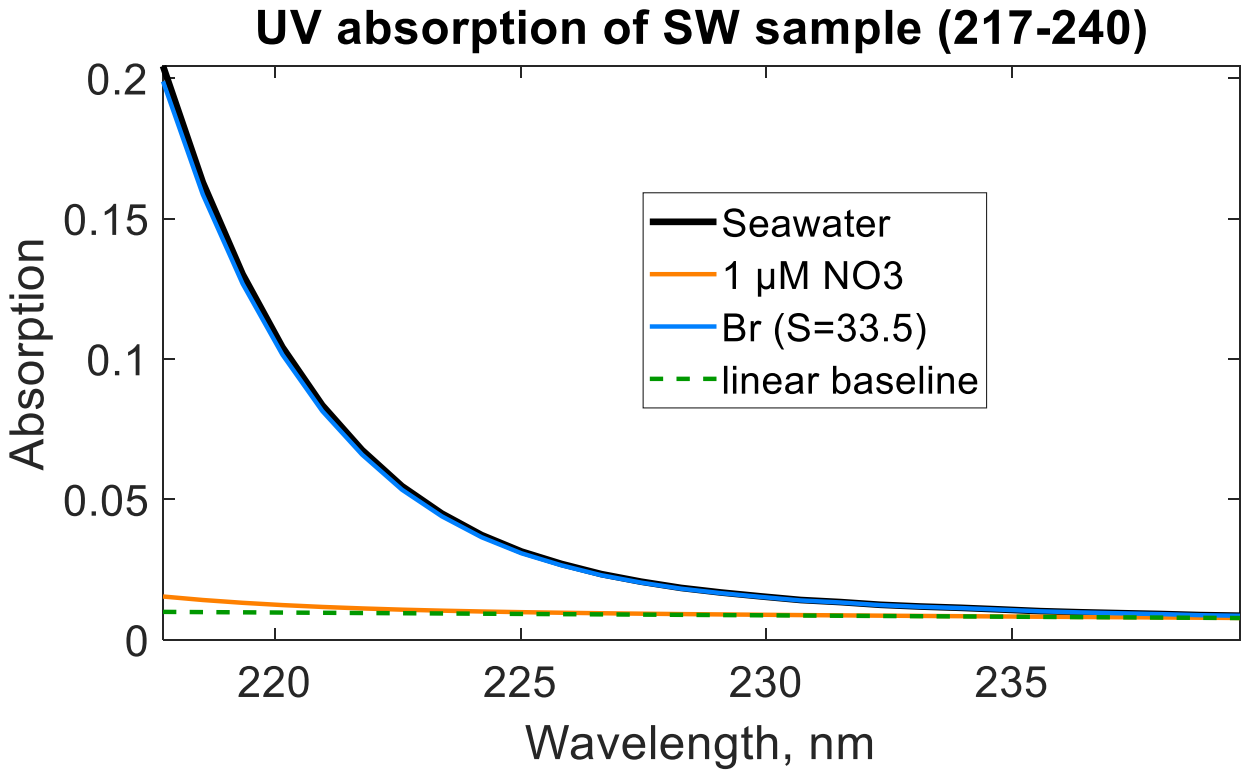
- Correct to CANYONB at depth & look at surface anomaly (ideally zero)
- New correction (LNE) reduces surface bias by ~1 µmol/kg
- New correction (LNE) reduces standard deviation by ~50%



Caveat #2

1 µm/kg is a small is a very small absorbance signal!

- Trying to identify a small signal against a large background
- Small errors in lab calibration or sensor response will add error
- We are continually trying to improve calibration & sensor stability



Proposal

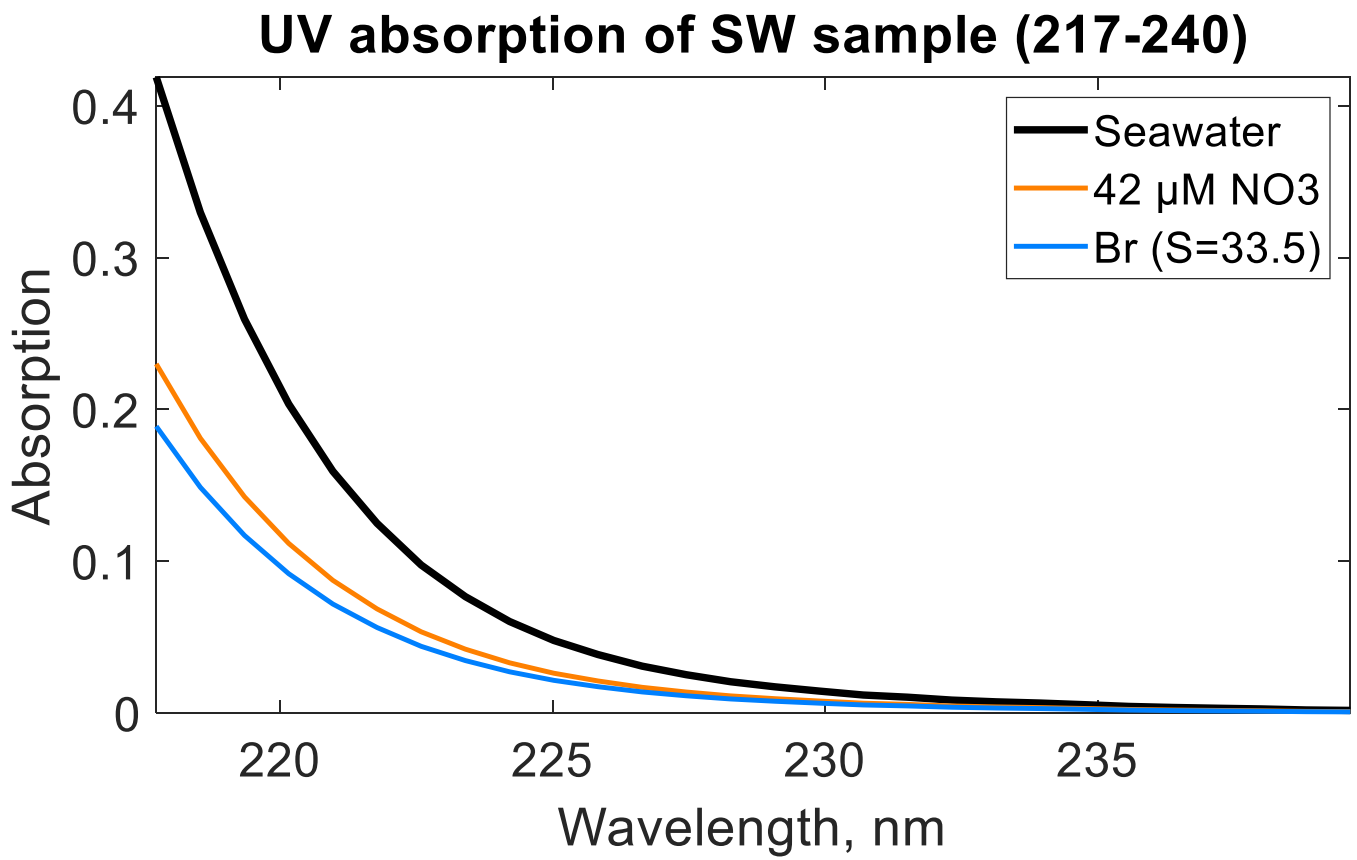
The new temperature correction is an improvement:

- Better fit to lab data
- Reduces warm water nitrate bias
- Reduces nitrate fit error
- Reduced overall bias when compared to CANYONB

New temperature correction should replace existing method

Calculating Nitrate

- Nitrate sensor measures returned light intensity
- Want absorbance (abs = $-\log[I_{seawater} / I_o]$)
- Use Beer's Law to derive concentration: $A(\lambda) = \epsilon(\lambda) \cdot b \cdot c$



$I_{seawater}$ = Sample seawater intensity
I_o = Reference intensity*
$A(\lambda)$ = absorbance at wavelength
$\epsilon(\lambda)$ = wavelength extinction coefficient*
b = path length*
c = concentration

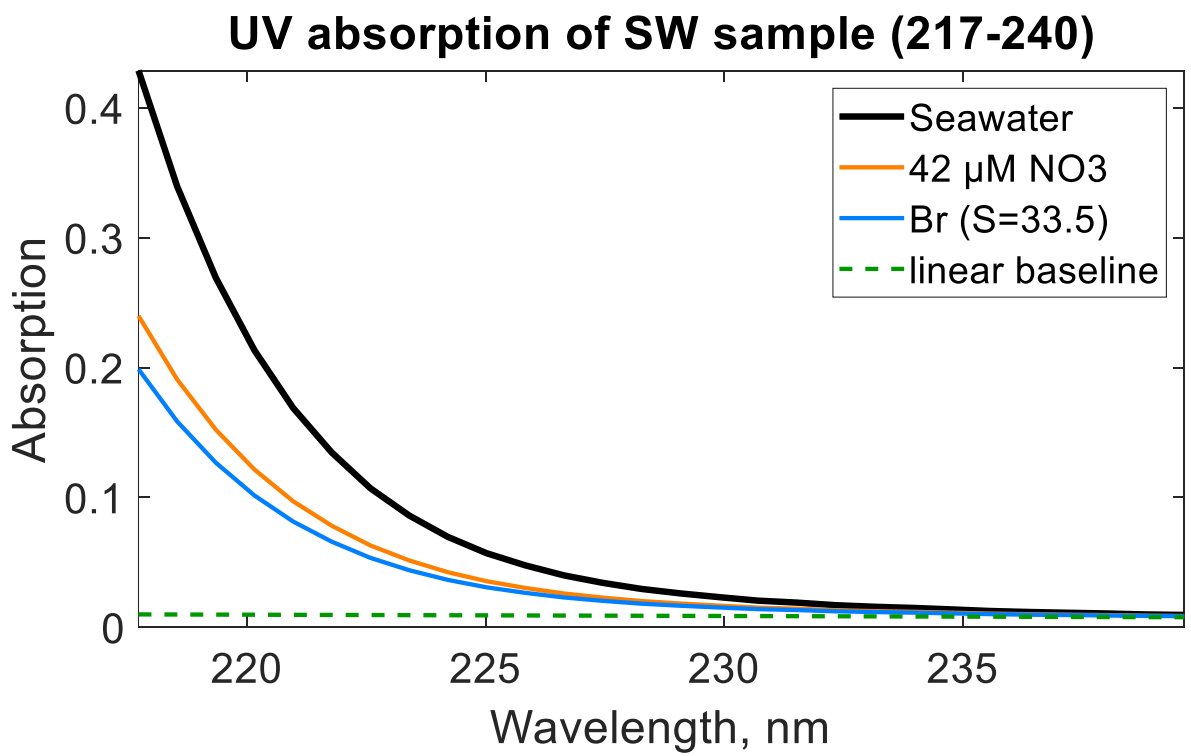
* Determined during lab calibration

Calculating Nitrate

Assume a seawater absorption model

- Salinity is known so remove salinity (bromide) component first
- Solve for Nitrate + linear baseline

abs_{SW}	=	Bromide abs	+	Nitrate abs	+	linear baseline abs
abs_{WL}	=	$\varepsilon_{SW\ WL}$ x Salinity	+	$\varepsilon_{nitrate\ WL}$ x [NO3]	+	linear baseline abs_{WL}
abs_{N+BL}	=		+	$\varepsilon_{nitrate\ WL}$ x [NO3]	+	linear baseline abs_{WL}



- Ɛ's are determined in the lab (Carole!)
- Baseline accounts for fouling, change in light intensity …
- ε_{SW} is temperature dependent!

Current ε_{SW} Temperature Correction

Sakamoto et al. (2009)

LIMNOLOGY
and
OCEANOGRAPHY: METHODS

Limnol. Oceanogr.: Methods 7, 2009, 132–143
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Improved algorithm for the computation of nitrate concentrations in seawater using an in situ ultraviolet spectrophotometer

Carole M. Sakamoto, Kenneth S. Johnson, Luke J. Coletti*
Monterey Bay Aquarium Research Institute, Moss Landing, CA, 95039 USA

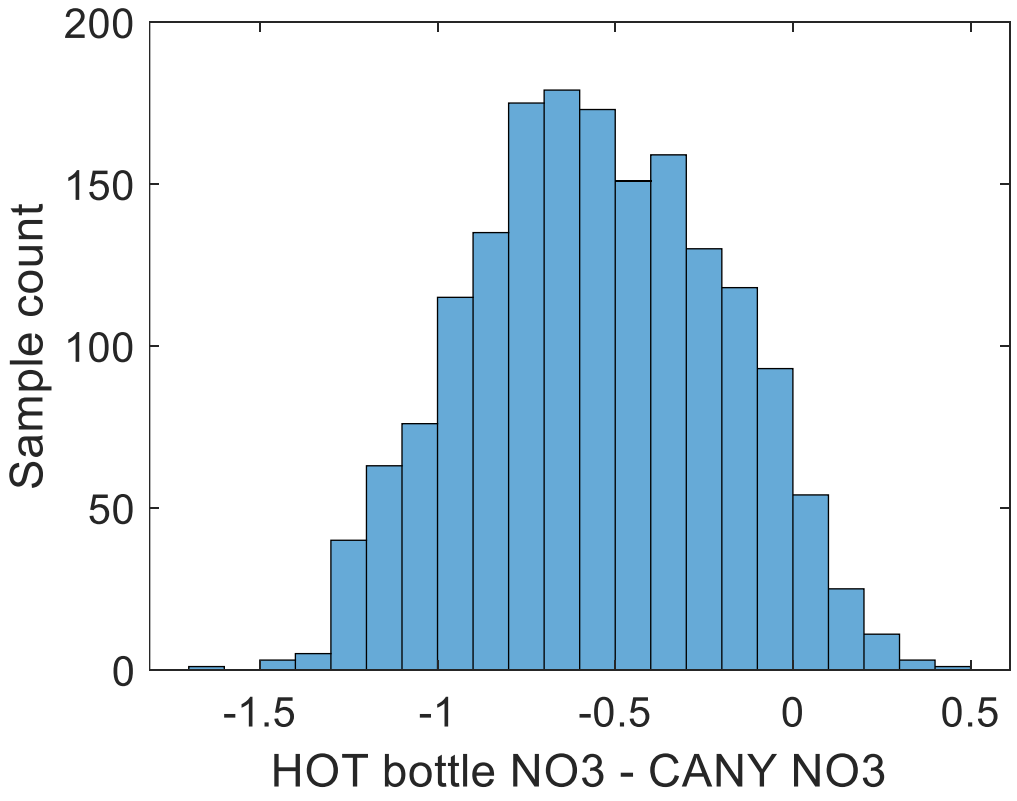
$$ESW_{Tsw} = ESWTc_{al} * \frac{(F+Tsw)}{(F+Tcal)} * exp(D * (WL - 210) * (Tsw - Tcal)]$$

- ESW_{Tcal} * GAIN
- May not adequately correct ESW for really warm (or cold) waters (tropics)
- Published back in 2009 with limited experimental data
- Carole Sakamoto has generated many more data sets with improved T control

Caveat #1

How accurate is deep CANYONB nitrate estimate near Hawaii?

- Grab 30 years of HOT bottle Nitrate data > 1000m and compare to CANYONB estimate (~1700 samples)



- CANYONB appears to be biased high by ~0.5 µm/kg
- This would reduce float bias by ~0.5 µm/kg
- **This gets us pretty close to sensor accuracy!**